

O 8: Metal Substrates: Adsorption of Organic/Bio Molecules I

Time: Monday 12:00–14:45

Location: MA 041

O 8.1 Mon 12:00 MA 041

Surface stress and its consequences: In-situ study of PTCDA induced faceting of vicinal Ag(111) — ●FLORIAN POLLINGER¹, PAVO VRDOLJAK¹, ZHEN TIAN², DIRK SANDER², STEFAN SCHMITT¹, CHRISTIAN KUMPF¹, ACHIM SCHÖLL¹, JÜRGEN KIRSCHNER², and EBERHARD UMBACH^{1,3} — ¹Universität Würzburg, Experimentelle Physik II, 97074 Würzburg — ²Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle — ³Forschungszentrum Karlsruhe, 76021 Karlsruhe

Adsorption of organic molecules on vicinal metal surfaces is known to promote faceting and self-organized ordering on mesoscopic scales. The adsorption of PTCDA on vicinal Ag(111) surfaces leads to grating-like structures after annealing [1]. The system PTCDA/Ag(10 8 7) was investigated using two complementary techniques: An optical cantilever bending technique sensitive to changes in surface stress and spot-profile analysis low energy electron diffraction (SPA-LEED) to monitor the development of the interface structure during faceting. The data was compared to the related, non-faceting system PTCDA on Ag(111). Overall, we find a surface stress change of 0.7 N/m due to the PTCDA-induced faceting, whereas the adsorption of PTCDA without faceting induces a change of 0.4 N/m. Moreover, the data allows an explicit and unambiguous correlation of the surface stress change to the structural and morphological evolution of the interface during the adsorption of the PTCDA adlayer. In conclusion, the results provide experimental evidence for significant surface stress induced by an organic adsorbate and for its importance for faceting and long-range ordering at metal-organic interfaces. [1] X. Ma et al., APL 84, 4038 (2004)

O 8.2 Mon 12:15 MA 041

Island formation and diffusion of PTCDA on Ag(100) surface — ●JULIAN IKONOMOV, OLIVER BAUER, and MORITZ SOKOLOWSKI — Institut für Physikalische und Theoretische Chemie, Universität Bonn

Perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) forms a $c(8 \times 8)$ ordered structure with a high symmetry on Ag(100). For submonolayers the attractive interactions between the molecules lead to two-dimensional islands with a quadratic equilibrium shape. The ordered PTCDA islands are in equilibrium with a disordered two-dimensional gas-like phase, consisting of highly mobile molecules. The dynamic behavior of this system was studied by variable temperature scanning tunneling microscopy. At room temperature, the islands were found to grow preferentially at the lower side of substrate steps, while at lower sample temperature, they grow on the terraces. At temperatures of about 680 K, a phase transition to a fully disordered phase was observed. The island decay and the diffusion of the PTCDA molecules were quantitatively investigated in order to obtain surface related energies and the diffusion parameters. Funded by the DFG SFB 624.

O 8.3 Mon 12:30 MA 041

Low temperature phases of NTCDA and PTCDA monolayers on Ag(111) — ●TIM LAUGKS, JOHANNES ZIROFF, and FRIEDRICH REINERT — University of Würzburg, Experimental Physics II, 97074 Würzburg, Germany

The organic semiconductor molecule 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA) and 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) exhibit phase transitions and variances in the electronic structure for both samples at low temperatures and for low temperatures during the film preparation. These problems are subject of current research because the interface geometry is decisive for the growth mode of organic molecules and the electronic properties of the interface. To improve our understanding of these systems we prepare NTCDA/PTCDA monolayers on Ag(111) at substrate temperatures down to 100 K and monitor their properties in a range from room temperature systematically down to 10 K. We investigate the electronic structure at the various temperature dependant phases, discussing the photoemission parameters of the HOMO and the former LUMO features. These parameters (i.e. binding energy and width) show a significant variation across the phase transitions and therewith we suggest a model for the interactions between molecule and substrate.

O 8.4 Mon 12:45 MA 041

Tuning the interaction at an organo-metallic interface: PTCDA on epitaxial Ag on Au(111) — ●JOHANNES ZIROFF,

FRANK FORSTER, and FRIEDRICH REINERT — Universität Würzburg, Experimentelle Physik II, 97074 Würzburg

PTCDA (3,4,9,10-perylene-tetracarboxylic acid dianhydride) monolayers on Au(111) and Ag(111) are widely used model systems in the field of organo-metallic interfaces, featuring the basic adsorption types of physisorption and chemisorption respectively. By the growth of epitaxial layers of Ag on Au(111), the electronic states of the substrate can be modified (depending on the thickness of the Ag film) to become more and more "silver-like", up to the point where they resemble the (111) surface of bulk silver. This process includes the formation of quantum well states with well characterised charge distribution and electronic properties. Therefore, this system enables experiments in which we control the substrates physical properties in small discrete steps, meanwhile tuning the molecular bonding from van der Waals to covalent.

We will show angle-resolved photoemission spectra of PTCDA monolayers on Ag films of various thicknesses on Au(111), focusing on the valence band and its electronic features, namely the Shockley surface state, higher molecular orbitals (HOMO, HOMO-1) and the so-called former LUMO. We will comment on correlations between the substrates distinctive electronic features and the appropriate interface structure, thus fathoming their role in the bonding mechanism and the formation of new valence electronic states.

O 8.5 Mon 13:00 MA 041

Investigation of unoccupied electronic states in PTCDA/Ag(111) — ●SÖNKE SACHS¹, CHRISTIAN SCHWALB², MANUEL MARKS², STEFAN KRAUSE¹, ACHIM SCHÖLL¹, EBERHARD UMBACH^{1,3}, and ULRICH HÖFER² — ¹Universität Würzburg, Experimentelle Physik II, Am Hubland, 97074 Würzburg — ²Universität Marburg, Fachbereich Physik, Renthof 5, 35032 Marburg — ³Forschungszentrum Karlsruhe, 76021 Karlsruhe

Energetics, momentum and time evolution of electronic states in organic semiconductors and at their interfaces are fundamental properties that strongly determine the performance in electronic applications. All of these properties can be explored with two-photon photoelectron (2PPE) spectroscopy for occupied and in particular for unoccupied electronic states.

In the archetypal system perylene-tetracarboxylic-dianhydride (PTCDA) on single crystal Ag(111) surfaces considerable differences between the electronic states of chemisorbed monolayer films and multilayer films are eminent. These differences, which are due to the altered chemical environment of PTCDA- and as well Ag-derived states in the vicinity of the interface, can be tracked with 2PPE. A new unoccupied interface state at the Ag/PTCDA interface with a free-electron like dispersion and comparatively short lifetime is detected that influences the charge injection characteristics considerably. The results of the 2PPE spectroscopy are compared to the results of complementary spectroscopies like UPS, IPES, and STS.

O 8.6 Mon 13:15 MA 041

Single molecule transport measurements in a well controlled contact geometry — ●RUSLAN TEMIROV¹, ADAM LASSISE², OLGA NEUCHEVA¹, FRITHJOF ANDERS³, MICHAEL ROHLFING⁴, BO SONG⁵, FLORIAN PUMP⁵, GIANAURELIO CUNIBERTI⁵, and STEFAN TAUTZ¹ — ¹Forschungszentrum Jülich — ²Jacobs University — ³Universität Bremen — ⁴Universität Osnabrück — ⁵Technische Universität Dresden

Transport properties of single molecules are presently in the focus of intense research. The reliability of experimental transport studies is, however, often hindered by difficulties in controlling contacts to the measured molecule on atomic level. Here we present single molecule transport experiments made on PTCDA/Ag(111) and PTCDA/Au(111) epitaxial interfaces which achieve a very high degree of control over the contacts [1]. Although the presented transport experiments were conducted in the LT STM, the limitation of the two-terminal STM geometry has been overcome by using a mechanical gating effect induced by the retraction of the STM tip [1]. Due to the high degree of control and the rich tunability achieved in the presented experiments, the obtained experimental data are fit for the comparison with the theory on ab-initio level. First results of such theoretical analysis will be discussed.

[1] R. Temirov, A. Lassise, F. Anders, S. Tautz. cond-mat/0612036

O 8.7 Mon 13:30 MA 041

Local control of the conductivity of single atoms and molecule probed by scanning tunneling microscopy and spectroscopy — ●LUCIA VITALI¹, ROBIN OHMANN¹, SEBASTIAN STEPANOW², and KLAUS KERN¹ — ¹MPI for Solid State Research, Stuttgart — ²ICREA, Barcelona

The implementation of molecule-based electronics is a pressing challenge of nanotechnology. The realization of such a circuit is still facing challenges such as the contact of the molecule to the electrodes. In order to clarify this, we studied the conductivity through single atoms and more complex molecular systems. Here, we present an experimental study of the electronic transport through single Co atoms and 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA) molecules adsorbed on Cu(111) studied by local probe spectroscopy at low temperatures. Morphology and electronic structure of atoms and molecules, obtained by conventional scanning tunneling microscopy/spectroscopy, are combined with transport properties measurements extracted from point contact spectroscopy. For Co single atoms the transport properties are modulated by the Kondo screening. The Kondo temperatures observed in tunneling and in point contact regime are comparable. A general model to explain our experimental evidence is proposed. For the PVBA molecules, the transport properties are strongly affected by the molecule-metal adsorption orientation. This deepens our understanding of the role of the molecular arrangement in the nano-junction and in molecular electronic transport, and addresses the determining role of the molecule-metal contacts.

O 8.8 Mon 13:45 MA 041

Electron transport across single phthalocyanide (Pc) molecules — ●FLORIAN WITT¹, ALBERT TAKACS^{1,2}, TIMOFEY BALASHOV¹, and WULF WULFHEKEL^{1,2} — ¹Physikalisches Institut, Universität Karlsruhe, Wolfgang-Gaede Strasse 1, 76131 Karlsruhe, Germany — ²CFN-DFG Centrum für Funktionelle Nanostrukturen

Recently molecular electronics is discussed as a future replacement of semiconductor electronics. A detailed knowledge of the electronic properties of the molecules i.e. the HOMO-LUMO gap, the density of states and the conductance is necessary. Scanning Tunneling Microscopy (STM) in combination with Scanning Tunneling Spectroscopy (STS) has become one of the most important methods for studying these molecular properties. We present results on single molecule contact measurements obtained with STM at 4K. A small amount of H₂Pc and CoPc molecules was evaporated on clean Cu(111) and Co/Cu(111). By laterally positioning the STM tip over isolated molecules and approaching the tip towards the molecules we measured the conductance as function of distance. Initially, an exponential increase was observed reflecting electron tunneling. Below a critical distance both H₂Pc and CoPc molecules have a tendency to lift from the surface and jump to contact with the tip. After the jump, the conductance only weakly varies with the distance. On Cu(111) typical conductances of 0.1 G₀ were found while on Co/Cu(111) the conductance is higher by a factor of 3. STS measurements in the tunneling regime revealed strong vibrational modes located on the organic side groups of Pc which are most likely responsible for the jump to contact.

O 8.9 Mon 14:00 MA 041

Low dimensional electronic structure of a metal/organic interface — ●ISABEL FERNÁNDEZ TORRENTE¹, NORA GONZÁLEZ LAKUNZA², KATHARINA JENNIFER FRANKE¹, NICOLÁS LORENTE³, ANDRÉS ARNAU², and JOSÉ IGNACIO PASCUAL¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Germany — ²Unidad de Física de Materiales, Centro Mixto CSIC-UPV/EHU, San Sebastián, Spain — ³Institut de Ciències de Materials de Barcelona-CSIC, Barcelona, Spain

The TTF-TCNQ charge donor-acceptor complex is a prototypical organic metal. In bulk, it crystallizes in a monoclinic structure built

up from parallel stacks of TTF and TCNQ, showing anisotropic conduction along the molecular rows. Our aim is to study the interface of a TTF-TCNQ organic film with a metal. By means of Low Temperature Scanning Tunneling Microscopy and Spectroscopy (LT-STM and STS) we characterise the structure and electronic properties of sub-monolayer films of TTF-TCNQ grown on Au(111). Both molecular species adsorb with a planar configuration. Nevertheless there is a strong donor-acceptor recognition and TTF and TCNQ self-assemble in alternating one-dimensional rows. This arrangement modifies strongly the electronic properties of the molecular entities and the surface state inducing the formation of a resonance with one-dimensional nature delocalised along the TCNQ rows. Ab-initio calculations explain the origin of the detected resonances by a strong modification of the surface state of the underlying metal upon hybridisation with TTF on the mixed TTF-TCNQ phase.

O 8.10 Mon 14:15 MA 041

Electron-phonon coupling in C₆₀ as revealed by scanning tunneling spectroscopy — ●KATHARINA J. FRANKE¹, THOMAS FREDERIKSEN², SERGIO MONTURET³, GUNNAR SCHULZE¹, ANDRÉS ARNAU², NICOLÁS LORENTE⁴, and JOSÉ IGNACIO PASCUAL¹ — ¹Freie Universität Berlin, Berlin, Germany — ²Donostia International Physics Center, Donostia, Spain — ³Universite Paul Sabatier, Toulouse, France — ⁴Centro de Investigaciones en Nanociencia y Nanotecnología, Bellaterra, Spain

Electron-phonon coupling is of major importance for charge transport through single molecule tunneling junctions. In most experimental implementations of molecular junctions the electronic coupling of the molecular orbitals with substrate states leads to a significant broadening, thus obscuring electron-phonon coupling effects. Here, we investigate the electronic structure of single C₆₀ molecules adsorbed on top of a self-assembled pattern of alternating tetraphenyladamantane and C₆₀. Scanning tunnelling spectroscopy reveals that these molecules exhibit properties similar to the free molecule, such as a large gap of 3.7 eV and a narrow LUMO resonance of only ≈60 meV line width. The LUMO resonance is followed by a broad weaker peak at about 240 meV higher energy. By density functional calculations including the Jahn-Teller effect, we show that this broad feature is induced by a complex coupling of the C₆₀ vibrational eigenmodes with the LUMO resonance.

O 8.11 Mon 14:30 MA 041

Electronic and Vibrational Properties of C_{e2}@C₈₀ Metallofullerenes — ●BERT VOIGTLÄNDER¹, ANNA STRÓZECKA¹, JOSEF MYSLIVEČEK^{1,2}, KALIAPPAN MUTHUKUMAR³, and J. ANDREAS LARSSON³ — ¹Institute of Bio- and Nanosystems (IBN 3), and cni - Center of Nanoelectronic Systems for Information Technology, Research Centre Jülich, 52425 Jülich, Germany — ²Department of Surface and Plasma Physics, Charles University in Prague — ³Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland

The electron transport properties of the fullerenes have been investigated by the study of the properties of single-molecule STM junctions over an endohedral metallofullerene C_{e2}@C₈₀ on Cu(111). In comparison to single-molecule STM junctions over C₆₀ molecules the controlled contacts to the metallofullerene show an order-of-magnitude lower conductivity. We ascribe this effect to the encapsulation of metal ions inside the fullerene cage. The STM based inelastic vibrational spectroscopy on C_{e2}@C₈₀ shows, apart from features related to the cage phonons also a low frequency mode at 9 meV. Based on theoretical calculations of the vibrational structure of the molecule, the feature can be assigned to the movement of Ce-Ce unit. The electronic spectroscopic measurements on C_{e2}@C₈₀ molecules reveal an unusually high increase in the differential conductance of this molecule at low bias voltages. The experiments indicate that the effect is related to the excitation of highly efficient vibrational modes and not to e.g. to a Kondo resonance that represents another common zero-bias anomaly.