

## O 29: Metal substrates: Adsorption of organic / bio molecules II

Time: Tuesday 10:30–13:00

Location: MA 043

O 29.1 Tue 10:30 MA 043

**Adsorption of Dodecahydro-N-Ethylcarbazole and N-Ethylcarbazole on Pd(111) – An XPS study** — ●HANS-JÖRG DRESCHER, STEFAN SCHERNICH, KARIN GOTTERBARM, MAREK SOBOTA, CHRISTIAN PAPP, JÖRG LIBUDA, and HANS-PETER STEINRÜCK — Friedrich-Alexander-Universität Erlangen-Nürnberg

Hydrogen is a promising alternative energy carrier for CO<sub>2</sub>-free vehicle propulsion. Applications are, however, hampered by serious deficiencies of conventional storage at high pressures and cryogenic temperatures. Recently, a promising concept was put forward making use of "Liquid Organic Hydrogen Carriers", which are regenerable chemical hydrogen storage compounds with high capacity. N-ethylcarbazole (NEC) has been identified as a highly attractive candidate, with hydrogen storage being performed through reversible hydrogenation to dodecahydro-N-ethylcarbazole (H<sub>12</sub>-NEC), typically over oxide-supported Pt or Pd catalysts. This contribution covers *in-situ* high-resolution XPS studies identifying the main surface species and reaction intermediates on a Pd(111) surface upon adsorption and heating. The thermal stability of the reactants and intermediates gives valuable information on reaction, decomposition and catalyst deactivation mechanisms and provides better understanding of more complex model catalysts like palladium nanoparticles on an alumina substrate. Financial support by the DFG within the Excellence Cluster *Engineering of Advanced Materials*, the DAAD, BMW, Fonds der Chemischen Industrie and the European Union is gratefully acknowledged.

O 29.2 Tue 10:45 MA 043

**A three-state single molecular junction** — ●YONGFENG WANG<sup>1</sup>, NICOLAS NÉEL<sup>2</sup>, JÖRG KRÖGER<sup>2</sup>, HECTOR VÁZQUEZ<sup>3</sup>, MADS BRANDBYGE<sup>3</sup>, BIN WANG<sup>4</sup>, and RICHARD BERNDT<sup>1</sup> — <sup>1</sup>Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität, D-24098 Kiel, Germany — <sup>2</sup>Institut für Physik, Technische Universität Ilmenau, D-98693 Ilmenau, Germany — <sup>3</sup>DTU Nanotech - Department of Micro and Nanotechnology, NanoDTU, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark — <sup>4</sup>Department of Physics and Astronomy, Vanderbilt University Nashville, TN 37235, USA

Single molecule electronics aims at using individual molecules as electronic components for miniaturizing electric circuits. Molecular switches, diodes, and transistor-like devices have been reported. Passing current through molecules inevitably causes heating which may be detrimental for their functionality. Here, Ag-Sn-Phthalocyanine-Ag junctions are shown to exhibit three conductance states. While the junctions are conductive at low bias, their impedance drastically increases above a critical bias. Two-level fluctuations occur at intermediate bias. These characteristics may be used to protect a nanoscale circuit. Further experiments along with calculations reveal that the self-limiting conductance of junctions is due to reversible changes of the junction geometry. Financial support through SFB 677 is acknowledged.

O 29.3 Tue 11:00 MA 043

**Nucleation in action: BDA on Cu(001) studied by LEEM** — ●DANIEL SCHWARZ, RAOUL VAN GASTEL, HAROLD ZANDVLIET, and BENE POELSEMA — Physics of Interfaces and Nanomaterials, MESA+ Institute for Nanotechnology, University of Twente

The growth and structure of 4,4'-biphenyldicarboxylic-acid (BDA) on Cu(001) at temperatures between 300 K and 400 K was studied by LEEM and  $\mu$ -LEED. BDA is a linear molecule consisting of two phenyl rings with a carboxylic-acid group at opposite ends. During growth on Cu(001) the adsorbed BDA molecules form first a disordered 2D gas phase. Once this phase reaches a sufficiently large density, a crystalline phase nucleates, in which the molecules form a hydrogen-bonded 2D supramolecular network. By a careful analysis of the bright-field image intensity we can measure the density of the 2D gas phase, which is up to 40% of that in the crystalline phase. From the equilibrium densities at different temperatures we can construct the 2D phase diagram and extract the cohesive energy (0.47 eV). During the distinct nucleation period we can observe a fascinating phenomenon: sub-critical nuclei form, grow up to 4000 nm<sup>2</sup> in size and decay with lifetimes of several seconds. These sizes are considerably larger than what is usually seen in epitaxial growth and we explain this observation with the relatively

weak intermolecular interactions.

O 29.4 Tue 11:15 MA 043

**Growth mode of formic acid on Au(111) surfaces** — CHRISTA ELSÄESSER<sup>1,2</sup>, MIRKO MÜLLER<sup>1,2</sup>, CHRISTIAN WAGNER<sup>1,2</sup>, and ●GERHARD PIRUG<sup>1,2</sup> — <sup>1</sup>Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich GmbH, 52425 Jülich — <sup>2</sup>JARA-Fundamentals of Future Information Technology

The adsorption of formic acid (HCOOH) on a Au(111) surface has already been characterized by vibrational spectroscopy and electron diffraction using HREELS and LEED, respectively. The vibrational signature indicates weak chemical substrate interaction of flat lying chains of H-bonded HCOOH molecules<sup>1</sup> well ordered in a  $\begin{pmatrix} 1.9 & -0.3 \\ 1.7 & 2.7 \end{pmatrix}$  surface structure, as shown by LEED. The formation of  $\sqrt{3}$ -chains, as identified in crystalline formic acid and proposed from the pg glide mirror plane symmetry in the LEED pattern could be proven by topographical STM images. The rectangular 6.0 × 6.8 Å<sup>2</sup> unit cell, azimuthally rotated by 8.3° with respect to the [110] substrate direction could be attributed to a line-on-line epitaxial growth mode<sup>2</sup>. This result is generally not expected on a (111)-oriented metal surface. While the intermolecular interaction due to H-bonding within the adsorbed layer results in a bulk-like periodic surface structure, the comparably weak adsorbate substrate interaction leads to its azimuthal alignment.

<sup>1</sup> M. Kazempoor, and G. Pirug, Appl. Phys. A 87, 435-441 (2007)<sup>2</sup> S. C. B. Mannsfeld, K. Leo, and T. Fritz, Phys. Rev. Lett. 94, 056104 (2005)

O 29.5 Tue 11:30 MA 043

**Investigation of Pentacene Submonolayers Adsorbed on Cu(110)-(2×1)O and Cu(110)-c(6×2)O** — ●JOHANNES GALL, MARIELLA DENK, GÜNTHER WEIDLINGER, DANIEL QUETESCHNER, LIDONG SUN, MICHAEL HOHAGE, and PETER ZEPPENFELD — Institut für Experimentalphysik, Johannes Kepler Universität Linz, 4040 Linz, Österreich

We have investigated the sub-monolayer adsorption behavior of pentacene molecules on both the Cu(110)-(2×1)O and the Cu(110)-c(6×2)O surface with RDS (reflectance difference spectroscopy), STM/STS (scanning tunneling microscopy and spectroscopy) and LEED (low energy electron diffraction).

In case of the Cu(110)-(2×1)O surface it was found that pentacene sub-monolayers undergo a temperature-dependent phase transition from a (densely packed) condensed phase at low temperatures to a (dilute) 2D-gas phase at higher temperatures. The characteristics of this phase transition could also be well reproduced by Monte Carlo simulations. From the experiments we were able to derive important adsorption parameters, such as the effective lateral molecule-molecule interaction energy, which also agree with the simulation results.

For the Cu(110)-c(6×2)O surface the situation is quite different: pentacene molecules were not observed to condense into densely packed islands at low temperature. Instead, a low-density frozen 2D-gas phase was observed. We attribute this behavior to a repulsive interaction between adsorbed species. Furthermore, we found strong evidence that those species in the 2D-gas phase actually consist of pentacene dimers.

O 29.6 Tue 11:45 MA 043

**Density-Functional Theory with Screened van der Waals Interactions for the Modeling of Hybrid Inorganic/Organic Systems** — ●VICTOR GONZALO RUIZ<sup>1</sup>, WEI LIU<sup>1</sup>, EGBERT ZOJER<sup>2</sup>, MATTHIAS SCHEFFLER<sup>1</sup>, and ALEXANDRE TKATCHENKO<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG — <sup>2</sup>Institute of Solid State Physics, Graz University of Technology

The electronic properties and the function of hybrid inorganic/organic systems (HIOS) are intimately linked to their geometry, with van der Waals (vdW) interactions playing an essential role for the latter. Here we show that the inclusion of the many-body collective response of the substrate electrons inside the inorganic bulk enables us to reliably predict the HIOS geometries and energies. Specifically, dispersion-corrected density-functional theory (the DFT+vdW approach) [*PRL* **102**, 073005 (2009)], is combined with the Lifshitz-Zaremba-Kohn theory [*PRB* **13**, 2270 (1976)] for the non-local Coulomb screening within the bulk. Our method (DFT+vdW<sup>surf</sup>) includes both image-

plane and interface polarization effects. We show that DFT+vdW<sup>surf</sup> yields geometries in remarkable agreement ( $\approx 0.1 \text{ \AA}$ ) with normal incidence x-ray standing wave measurements for the 3,4,9,10-perylene-tetracarboxylic acid dianhydride ( $C_{24}H_8O_6$ , PTCDA) molecule on Cu(111), Ag(111), and Au(111). Similarly accurate results are obtained for xenon and benzene adsorbed on metal surfaces.

O 29.7 Tue 12:00 MA 043

**Assessing Density-Functional Theory with Screened van der Waals Interactions (DFT+vdW<sup>surf</sup>) for Model Hybrid Inorganic/Organic Systems** — ●NICOLA FERRI, MATTHIAS SCHEFFLER, and ALEXANDRE TKATCHENKO — Theory Department, Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

Hybrid inorganic/organic systems (HIOS) are widely investigated for usage in a variety of devices, e.g., for opto-electronic applications. The interface geometry plays a crucial role in HIOS, and its correct description is a requisite for predicting electronic properties. Here we study two model HIOS: diindenoperylene (DIP,  $C_{32}H_{16}$ ) and  $C_{60}$  on coinage metal surfaces (Cu(111), Ag(111), and Au(111)). These systems are used to test the recently developed PBE+vdW<sup>surf</sup> approach, which accurately treats hybridization and long-range Coulomb screening, and includes interface polarization effects [1]. We show that for both systems (DIP and  $C_{60}$ ), the PBE+vdW<sup>surf</sup> approach yields average equilibrium adsorption positions in excellent agreement (about  $0.1 \text{ \AA}$ ) with experimental data. In the case of DIP, measurements have been performed using X-ray standing wave technique plus X-ray photoelectron spectroscopy (XSW+XPS) [2]. In the case of  $C_{60}$ , STM and LEED results are available [3]. Finally, we assess the role of self-consistency of the vdW energy in the DFT+vdW<sup>surf</sup> method, by adding the potential due to vdW energy to the DFT potential.

[1] V. G. Ruiz *et al.*, submitted to Phys. Rev. Lett. (2011).

[2] C. Bürker *et al.*, [http://ftp.esrf.eu/pub/UserReports/43789\\_A.pdf](http://ftp.esrf.eu/pub/UserReports/43789_A.pdf)

[3] H.L. Li *et al.*, Phys. Rev. Lett. **103**, 056101 (2009).

O 29.8 Tue 12:15 MA 043

**Semi-empirical versus ab-initio non-local correlation effects: Thiophene adsorbed on Cu(111)** — ●MARTIN CALLSEN, NICOLAE ATODIRESEI, VASILE CACIUC, and STEFAN BLÜGEL — Peter Grünberg Institut (PGI-1) and Institute for Advanced Simulation (IAS-1), Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The adsorption mechanism of single thiophene ( $C_4H_4S$ ), 4-thiophene ( $C_{16}H_{10}S_4$ ) and their dimers on the Cu(111) surface has been studied within the framework of density functional theory (DFT). The importance of the long-range dispersion interaction on the molecule-surface adsorption geometry and the corresponding binding energy was investigated by using a first-principles approach [1] implemented in the JuNoLo code [2] which was recently updated with the scheme developed by Román-Pérez and Soler [3,4] as well as semi-empirical methods [5,6]. Interestingly, the physisorption character of the thiophene bonding on Cu(111) suggested by the DFT calculations is changed to weak chemisorption even for the DFT ground-state geometry when a non-local correlation energy functional [1] is used.

[1] M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2004)

[2] P. Lazić *et al.*, Comput. Phys. Commun. **181**, 371 (2010)

[3] G. Román-Pérez, J. M. Soler, Phys. Rev. Lett. **103**, 096102 (2009)

[4] M. Callsen, V. Caciuc, N. Atodiresei, S. Blügel to be published.

[5] S. Grimme, J. Comput. Chem. **27**, 1787 (2006)

[6] S. Grimme *et al.*, J. Chem. Phys. **132**, 154104 (2010)

O 29.9 Tue 12:30 MA 043

**Structure and energetics of benzene adsorbed on transition-metal surfaces: Density-functional theory with screened van der Waals interactions** — ●WEI LIU, VICTOR G. RUIZ-LÓPEZ, GUO-XU ZHANG, XINGUO REN, MATTHIAS SCHEFFLER, and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der MPG

The adsorption of benzene on metal surfaces is an important benchmark system for more complex hybrid inorganic/organic interfaces. Here, the recently developed DFT+vdW<sup>surf</sup> method (density-functional theory including screened van der Waals (vdW) interactions) [1] is used to study the structure and energetics of benzene on transition-metal surfaces (Cu, Ag, Au, Pd, Pt, Rh, and Ir). Benzene adsorbs in a planar configuration at coinage metal surfaces, with almost zero distortion and a flat potential-energy surface. In contrast, benzene is strongly bound to the (111) surface of Pd, Pt, Rh, and Ir, and located at the bridge-30° site. The vdW interactions significantly enhance the binding energy by more than  $0.75 \text{ eV}$  for all metals. The screening of the vdW energy plays a critical role in coinage metals, shortening the equilibrium distance by  $0.2 \text{ \AA}$ , and lowering the binding energy by  $0.25 \text{ eV}$ . The validity of our results is confirmed by comparison with calculations using the random-phase approximation including renormalized single excitations (EX+cRPA+rSE scheme [2]), and the experimental data from temperature-programmed desorption and calorimetry measurements.

[1] V. G. Ruiz-López *et al.*, submitted.

[2] X. Ren *et al.*, Phys. Rev. Lett. **106**, 153003 (2011).

O 29.10 Tue 12:45 MA 043

**DFT Studies on the Adsorption of Alkanethiolates at Coinage Metal Surfaces** — ●PORNTIP SEEMA, JÖRG BEHLER, and DOMINIK MARX — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum

A large number of theoretical and experimental studies has been carried out to determine the structures and the properties of sulfur-containing molecules adsorbed on coinage metal surfaces, but still several questions remain open. We present density-functional theory calculations for the adsorption of alkanethiolates ( $CH_3(CH_2)_nS-$ ) adsorbed on Cu(111), Ag(111) and Au(111). Calculations have been performed for a variety of adsorbate coverages, binding sites and surface models. We find that the sulfur-metal interaction is stronger for Cu(111) than for Ag(111) and Au(111), with an increased binding strength at surface defects. Moreover, the experimentally suggested models consisting of  $c(4 \times 2)$  with Au adatoms,  $(\sqrt{7} \times \sqrt{7})R19.1^\circ$  and pseudo-(100) for Au(111), Ag(111) and Cu(111), respectively, have been studied.