

O 18: Organic/bio Molecules on Metal Surfaces II

Time: Monday 16:00–19:00

Location: H38

O 18.1 Mon 16:00 H38

Towards a Quantitatively Reliable Modeling of Large Organic Molecules Adsorbing on Metal Surfaces — ●DAVID ALEXANDER EGGER¹, YULI HUANG², ELISABETH WRUSS¹, VICTOR GONZALO RUIZ³, ALEXANDRE TKATCHENKO³, SATOSHI KERA², and EGBERT ZOJER¹ — ¹Institute of Solid State Physics, Graz University of Technology. — ²Graduate School of Advanced Integration Science, Chiba University. — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft.

At interfaces in metal-organic hetero-structures a variety of often difficult to quantify interactions such as charge-transfer, polarization, Pauli pushback and van der Waals (vdW) attraction occurs. Such interactions make the identification of the responsible interfacial binding mechanism particularly difficult. We here model a variety of prototypical metal-organic heterostructures including mono- and double-layers of Cu-phthalocyanine (CuPc), a double-layer of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and CuPc, and non-planar phthalocyanine layers adsorbing on noble-metal surfaces. Using recently developed theoretical tools to properly account for vdW interactions, we achieve remarkable agreement with experiments. Beyond that, we provide atomistic insight into the various processes responsible for the formation of these nanostructures and underline the comparatively large contribution of vdW interactions to the overall binding energies of these systems.

O 18.2 Mon 16:15 H38

Orbital ordering for PTCDA on Ag surfaces — ●MARTIN WILLENBOCKEL^{1,2}, BENJAMIN STADTMÜLLER^{1,2}, KATHRIN SCHÖNAUER^{1,2}, FRANCOIS C. BOCQUET^{1,2}, DANIEL LÜFTNER³, EVA M. REINISCH³, THOMAS ULES³, GEORG KOLLER³, CHRISTIAN KUMPF^{1,2}, SERGUEI SOUBATCH^{1,2}, PETER PUSCHNIG³, MICHAEL G. RAMSEY³, and F. STEFAN TAUTZ^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — ²Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany — ³Institut für Physik, Karl-Franzens-Universität Graz, 8010 Graz, Austria

The energy alignment of electronic levels for molecules adsorbed on noble metal surfaces was investigated extensively. However, the research was focused mainly on the frontier orbitals located close to the Fermi level, namely the LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital).

We report a study of PTCDA (3,4,9,10-perylene-tetracarboxylic-dianhydride) adsorbed on the low index Ag surfaces Ag(100), Ag(111) and Ag(110) where the fine structure of the "HOMO-1" resonance was investigated by angle resolved photoemission spectroscopy. Using the orbital tomography approach we found that this resonance consists of 4 close located molecular orbitals [1,2]. The energy ordering of the orbitals is independent from the Ag surface and the molecular superstructure.

[1] P. Puschnig et al., *Phys. Rev. B* **84** 235427 (2011). [2] P. Puschnig et al., *Science* **326** 702 (2009).

O 18.3 Mon 16:30 H38

Orbital tomography: Deconvoluting photoemission spectra of organic molecules — ●SERGEY SOUBATCH¹, MARTIN WILLENBOCKEL¹, BENJAMIN STADTMÜLLER¹, KATHRIN SCHÖNAUER¹, EVA REINISCH², THOMAS ULES², DANIEL LÜFTNER², MARKUS OSTLER³, GEORG KOLLER², PETER PUSCHNIG², CHRISTIAN KUMPF¹, MIKE RAMSEY², and STEFAN TAUTZ¹ — ¹Peter Grünberg Institut (PGI-3), JARA, Forschungszentrum Jülich, Germany — ²Institute of Physics, Karl-Franzens University Graz, Austria — ³Lehrstuhl für Technische Physik, Universität Erlangen-Nürnberg, Germany

The valence bands of organic molecules consist of closely spaced electronic levels, which is often challenging for both theory and spectroscopic experiment. We propose a tomographic method that employs the energy and momentum dependence of photoemission of adsorbed molecules to deconvolute corresponding valence band into individual orbitals beyond the limits of energy resolution.

Photoemission experiments on different ordered monolayer phases of perylene-tetracarboxylic-dianhydride (PTCDA) molecule on low index Ag surfaces were performed at BESSYII storage ring using toroidal electron energy analyzer. For the phases containing molecules non-equivalent either from intermolecular environment or substrate reg-

istry point of view, method provides access to electronic properties of either molecule separately. This enables detailed description of site- and orientation-specific bonding of organic molecules at metals, and in so doing, delivers stringent tests for the development of ab-initio electronic structure theory.

O 18.4 Mon 16:45 H38

Spatial distribution of molecular orbitals from angle-resolved photoemission — ●DANIEL LÜFTNER¹, THOMAS ULES¹, EVA MARIA REINISCH¹, GEORG KOLLER¹, SERGEY SOUBATCH², F. STEFAN TAUTZ², MICHAEL G. RAMSEY¹, and PETER PUSCHNIG¹ — ¹Institut für Physik, Karl-Franzens-Universität Graz, Austria — ²Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany

The frontier electronic orbitals of molecules are the prime determinants of the respective compounds' chemical, electronic, and optical properties. Several experimental methods have enabled imaging of molecular orbitals under certain conditions. As has been shown in a number of recent publications, angle-resolved photoemission (ARPES) intensity maps of organic molecular layers are related to the Fourier transform of the initial state molecular orbital. However, the missing phase information impedes the back-transformation of the momentum maps of the orbital into real space. Here, we show how the absent phase information can be retrieved by applying an unbiased, iterative procedure which takes the experimental ARPES maps as input and only assumes spatial confinement of the orbital. Thereby we obtain real-space images of several molecular orbitals for two prototypical pi-conjugated molecules: the LUMO, HOMO, and HOMO-1 of pentacene, and the LUMO and HOMO of PTCDA. Our technique further emphasizes the capabilities of ARPES looking at spatial distributions of wave functions of adsorbed molecules thereby complementing data obtained from scanning probe methods.

O 18.5 Mon 17:00 H38

Measuring the electron correlation energy between organic molecules and metal surfaces — ●CHRISTIAN WAGNER^{1,2}, NORMAN FOURNIER^{1,2}, VICTOR G. RUIZ³, ALEXANDRE TKATCHENKO³, F. STEFAN TAUTZ^{1,2}, and RUSLAN TEMIROV^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — ²JARA-Fundamentals of Future Information Technology — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195, Berlin, Germany

Van der Waals forces have to be considered in any quantitatively correct picture of molecular adsorption. Experimental determination of the energy related to long-range correlation effects is, however, difficult. A measured binding energy is always the result of many contributions, including chemical interactions and Pauli repulsion. Here, we present a measurement of single-molecule adsorption potentials as a function of molecule-surface separation using a frequency modulated atomic force microscope[1,2]. We decompose the different contributions to the potential by their different decay lengths. By investigating molecules with a naphthalene, perylene and terrylene core respectively (NTCDA, PTCDA, TTCDA) on Au(111), we study the dependency of the correlation energy on the size of the aromatic system. We compare the experimentally obtained adsorption potentials to DFT+van der Waals calculations which include dielectric screening within the metal[3].

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

[2] C. Wagner et al., *Phys. Rev. Lett.* **109**, 076102 (2012)

[3] V. G. Ruiz et al., *Phys. Rev. Lett.* **108**, 146103 (2012)

O 18.6 Mon 17:15 H38

DFTD Calculations on STHM with Xe and CO — ●UWE FRIEDEL and AXEL GROSS — Theoretical Chemistry, University of Ulm, Germany

The Scanning Tunneling Hydrogen Microscope (STHM) [1] can resolve intramolecular structures of adsorbed molecules and even produce intermolecular contrast along lines of expected hydrogen bondings. The method does not only work with hydrogen, which gave the method the name, but also with other molecules and noble gas atoms. This talk will present results of dispersion corrected DFT calculations (DFT-D3) with a model tip decorated with a Xe-atom and a CO-molecule.

[1] C. Weiss et al., *J. Am. Chem. Soc.* **132**, 11864 (2010)

O 18.7 Mon 17:30 H38

Single-atom substitution to control the nature of bonding of olympicene on Cu(111) — ●WEI LIU¹, BRUNO SCHULER², NIKOLAJ MOLL², LEO GROSS², and ALEXANDRE TKATCHENKO¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²IBM Research – Zurich, 8803 Rüschlikon, Switzerland

The olympicene molecule, consisting of 5 aromatic rings, has been recently synthesized and visualized by atomic force microscopy (AFM) on the Cu(111) surface [1]. Here we show that the substitution of a single atom in the olympicene molecule switches the nature of adsorption from physisorption (olympicene @ Cu), to an intermediate state (olympicene-derived ketone @ Cu), then to strong chemisorption (olympicene radical @ Cu). First-principles calculations using the PBE+vdW^{surf} method (density-functional theory with screened van der Waals (vdW) interactions [2]), allow us to achieve insights into the stability and electronic structure of complex organic/metal interfaces, and lead to quantitative agreement with atomic force spectroscopy.

[1] <http://www-03.ibm.com/press/uk/en/pressrelease/37869.wss>.

[2] V. Ruiz *et al.*, PRL **108**, 146103 (2012).

O 18.8 Mon 17:45 H38

Benchmark database of equilibrium geometries and adsorption energies of hybrid organic/metal systems — ●JAVIER CAMARILLO CISNEROS, WEI LIU, VICTOR G. RUIZ, NICOLA FERRI, MATTHIAS SCHEFFLER, and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der Max Planck Gesellschaft

The adsorption of molecules at transition metal surfaces is important for fundamental and applied surface science studies. Extensive experimental work has been focused on organic/metal interfaces, however, a reliable database that provides accurate binding structures and energetics is still missing. By carefully contrasting a large number of experiments (e.g., normal incidence x-ray standing wave, microcalorimetry, and temperature-programmed desorption), here we create a database that includes more than 20 prototypical adsorption systems, ranging from noble-gas Xe to small/large organic molecules (benzene, naphthalene, C₆₀, PTCDA, etc.) on different metal surfaces. We further study all these interfaces using the PBE+vdW^{surf} method (density functional theory with screened van der Waals (vdW) interactions [1]), and show that this method yields an agreement of 0.1 Å in equilibrium geometries and 0.1 eV in adsorption energies with state-of-the-art experiments. We assess the quantitative role of vdW interactions for both weakly and strongly adsorbed systems, and show that the constructed database can be used to benchmark the performance of vdW-inclusive first-principles approaches. [1] Ruiz *et al.*, PRL (2012). [2] Liu *et al.*, PRB (2012).

O 18.9 Mon 18:00 H38

Adsorption and thermal polymerization of pentacene on Ir(100) — ●PASCAL FERSTL, LISA LAUTNER, LUTZ HAMMER, and M. ALEXANDER SCHNEIDER — LS f. Festkörperphysik, FAU Erlangen-Nürnberg, Germany

Pentacene molecules were deposited at various temperatures on both the unreconstructed and the quasi-hexagonally reconstructed surface phases of Ir(100) and subsequently thermally processed. On both surfaces the molecules adsorb flat lying, they are immobile at room temperature, but apparently intact. On the fourfold symmetric 1x1 phase there is basically only one particular binding configuration for the molecules, which is either along the [011] or the [0 $\bar{1}$ 1] direction and they randomly assume one of these two (symmetry-equivalent) orientations without any tendency to form ordered domains.

On the one-dimensionally corrugated (5x1) phase the pentacene species deposited at room temperature show three different binding configurations: along the rows of the reconstruction, or inclined by 30° or 90°. Increasing the deposition temperature to above 100°C the adsorption site within the troughs of the reconstruction becomes more and more dominant. For deposition (or annealing) temperatures above 360°C the molecules successively decompose towards a surface carbide. At intermediate temperatures, however, one-dimensional head-to-tail polymerization is found leading to molecular chains of at least double or triple length, which are not observed on the (1x1) phase. This indicates that the substrate reconstruction acts as a template for the molecular reaction scheme at the surface.

O 18.10 Mon 18:15 H38

Nanoscale Control of Molecular Conformation via Tuned Coupling to a Substrate — ●HASMİK HARUTYUNYAN¹, MARTIN CALLEN², TOBIAS ALLMERS¹, VASILE CACIUC², STEFAN BLÜGEL², NICOLAE ATODIRESEI², and DANIEL WEGNER¹ — ¹Westfälische Wilhelms-Universität Münster Wilhelm-Klemm-Str. 10, 48149 Münster, Deutschland — ²Peter Grünberg Institut (PGI-1) and Institute for Advanced Simulation (IAS-1) Forschungszentrum Jülich and JARA 52425 Jülich, Deutschland

In recent years the adsorption of organic molecules on noble-metal has shown large interest. Here, it is important to understand the electronic interaction between a gas-phase molecules and the surface, which leads to hybridization and can induce charge transfer. We have investigated the conformation of cyclooctatetraene (COT) on different noble metals by means of low-temperature scanning tunneling microscopy combined with density functional theory. Highly resolved STM images in conjunction with STM simulations enable the unambiguous identification of molecular conformations. The results show, that COT can be stabilized in different conformations by varying its coupling to the noble-metal surface. We find weak physisorption and the tube conformation on Au(111), as know for the gas-phase molecule. On Ag(100) and Cu(100) COT is chemisorbed and planar, as known for charged gas-phase molecules. The conformation of COT can even be manipulated on Au(111) by utilizing nanoscale variations of the molecule-surface interaction. This mechanical and electronic control makes COT an interesting candidate for versatile molecular switches.

O 18.11 Mon 18:30 H38

First Principles Simulations of the Adsorption of Aromatic Molecules on Metallic Surfaces — ●RENGİN PEKÖZ, KAREN JOHNSTON, and DAVIDE DONADIO — Max Planck Institute for Polymer Research, Mainz, Germany

Several technologies and applications involve the interaction of aromatic molecules with metal substrates, including organic electronics (OLED, OPV), sensors, and surface-supported fabrication of graphene. It is, therefore, crucial to study the nature of such interactions on model systems to unravel general trends.

Using a fully non-local vdW density functional (vdW-DF) [1,2] we have studied the adsorption of halogenated benzene, which are simple prototypes for larger and more complex molecules, on stepped and flat Au and Pt surfaces. The effects of various parameters, such as the size of the precursors and type of halogen atoms, on the adsorption properties have also been investigated. Moreover, the calculated potential energy curves revealing both chemisorbed and physisorbed wells, all of which are separated by activation barriers, will be discussed. Specifically for several different adsorption sites of dichlorobenzene, the energies, and equilibrium geometries have been computed, and electron density analysis has been performed using both conventional generalized gradient approximation (GGA) and vdW-DF [3].

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

[2] A. Gulans *et al.*, Phys. Rev. B **79**, 201105 (2009).

[3] R. Peköz *et al.*, J. Phys. Chem. C **116**, 20409 (2012).

O 18.12 Mon 18:45 H38

Investigations of PEEB adsorbed on metallic surfaces — ●L. LOKAMANI, CORMAC TOHER, JOERG MEYER, ANJA NICKEL, ROBIN OHMANN, FRANCESCA MORESCO, and GIANAURELIO CUNIBERTI — Institute for Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, 01062 Dresden, Germany

The electronic and tunable optical properties exhibited by p-phenylene-ethynyls make them excellent candidates for single molecule electronics. A family of derivatives with different electronic properties can be created by adding various functionalized side groups, which effect the conductance properties of the phenylene-ethynylene backbone. These derivatives with different electronic properties can be utilized to implement novel logic functions in nano circuits.

Here we present the results of a combined theoretical and experimental investigation of the adsorption characteristics, electronic structure and bonding geometry of single 1,4-bis(phenylethynyl)-2,5bis(ethoxy)benzene (PEEB) molecules on the Au(111) surface. DFT calculations of the DOS and adsorption geometry were found to be in qualitative agreement with low temperature STM images and STS measurements. The strength of the bonding interaction to the substrate was also calculated.