

O 49: Metal substrates: Adsorption of organic / bio molecules VI

Time: Wednesday 15:00–17:15

Location: PHY C213

O 49.1 Wed 15:00 PHY C213

Investigation of the CuPc/PTCDA interface on Ag(111) — ●BENJAMIN STADTMÜLLER, INGO KRÖGER, CHRISTOPH KLEIMANN, TAMOKI SUEYOSHI, SERGEY SUBACH, and CHRISTIAN KUMPF — Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany and JARA-Fundamentals of Future Information Technology

One crucial issue for improving organic electronics is the understanding of interfaces between different functional materials. While recently interfaces between metal contacts (i.e., noble metal surfaces) and active organic layers were investigated intensively, only few studies so far focused on the interface between different organic materials. In this context we investigated the adsorption of copper-II-phthalocyanine (CuPc) on a closed monolayer of perylene-tetracarboxylic acid dianhydride (PTCDA) on Ag(111). Using high resolution low energy electron diffraction (SPA-LEED) we could show that at room temperature the CuPc molecules form a diluted, disordered layer, similar to the case of direct adsorption on Ag(111). Upon cooling ($<-150^{\circ}\text{C}$) or increasing coverage (close to one monolayer) phase transitions to ordered structures occur. These ordered phases are compared with the adsorption of CuPc on Ag(111) in first and second layer. Furthermore, UV photoemission experiments are reported, which allow to reveal the electronic properties of the interfaces. The experiments nicely demonstrate the strong impact of structure and composition of the first adsorbate layer (which is in direct contact to the Ag surface) on the properties of the second molecular layer.

O 49.2 Wed 15:15 PHY C213

Charge transfer from a metal to a strong electron acceptor molecule through an organic spacer-layer — ●PATRICK AMSALEM¹, JENS NIEDERHAUSEN¹, JOHANNES FRISCH¹, ANDREAS WILKE¹, BENJAMIN BRÖKER¹, ANTJE VOLLMER², RALPH RIEGER³, KLAUS MÜLLEN³, JÜRGEN P. RABE¹, and NORBERT KOCH¹ — ¹Humboldt-Universität zu Berlin, Institut für Physik, Brook-Taylor-Str. 6, 12489 Berlin, Germany — ²HZB-BESSY II, Albert-Einstein-Str. 15., 12489 Berlin, Germany — ³Max Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

We investigate the possibility for electrons to tunnel from a metal surface to a strong electron acceptor molecule through an inert organic layer used as spacer. We report photoemission measurements performed on one monolayer (ML) hexaaza-triphenylene-hexacarbonitrile (HATCN) deposited under ultrahigh vacuum conditions on Ag(111) precoated with 1ML tris(8-hydroxyquinoline)aluminium (Alq3). The valence spectra reveal a density of states (DOS) in the vicinity of the Fermi-level which is attributed to the filling of the HATCN lowest unoccupied molecular orbital derived state, resulting from a charge transfer from the Ag(111). Indications that this DOS is located at the very surface are given by the intensity variations of the molecular level valence features as a function of the emission angle. These variations match well with the expected signal attenuation in photoemission, allowing to conclude that the low-energy DOS arises from HATCN molecules located at the very surface. Work function changes are set in relation to the observed charge transfer.

O 49.3 Wed 15:30 PHY C213

Elucidating the adsorption mechanism of isophorone on the Pd(111) surface — ●WEI LIU, ADITYA SAVARA, WIEBKE LUDWIG, SWETLANA SCHAUERMANN, XINGUO REN, ALEXANDRE TKATCHENKO, HANS-JOACHIM FREUND, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG

We present a joint theoretical and experimental study of the structural, vibrational, and chemical properties of isophorone ($\text{C}_9\text{H}_{14}\text{O}$) on the Pd(111) surface. Experimental vibrational spectroscopy and temperature-programmed desorption data indicate that both the pure isophorone and dehydrogenated moieties coexist on the surface below 400 K. To elucidate the underlying adsorption and dehydrogenation processes, we carried out density-functional theory (DFT) calculations with and without accounting for the long-range van der Waals (vdW) interactions. The PBE+vdW method [1] significantly changes the potential energy surface compared to the standard PBE, altering both the height and the tilt angle of the molecule with respect to the surface. We identify the reaction pathway from the weakly chemisorbed $\text{C}_9\text{H}_{14}\text{O}$ gas-phase reactant to the strongly chemisorbed dehydrogenated prod-

ucts, both by a direct elimination of hydrogen atoms closest to the Pd(111) surface and by *ab initio* molecular dynamics simulations. The coexistence of different isophorone moieties on the Pd(111) surface is attributed to an interplay of covalent and van der Waals bonding, along with zero point motion, and kinetic effects.

[1] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009).

O 49.4 Wed 15:45 PHY C213

Conformations of tetra(phenyl)porphyrine on Au(111): identification by experiment and theory — ●FELIX HANKE¹, JOHANNES MIELKE², LEONHARD GRILL², and MATS PERSSON¹ — ¹University of Liverpool, Liverpool, UK — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

The on-surface synthesis of covalently coupled networks of tetra(phenyl)-porphyrines (TPP) on Au(111) [1] is a significant step toward custom-designed molecular structures. This is particularly useful as single TPP molecules adsorbed on Au(111) and imaged with a scanning tunneling microscope show several distinct configurations, which could be used for information storage. Here we present a combined density functional (DFT) and scanning tunneling microscopy study to elucidate the nature of the observed conformers. They differ in the internal structure of the porphyrin core which can be either flat or buckled. We further assess the importance of accounting for dispersion interactions in the adsorbate-surface coupling by comparing DFT results using the van der Waals density functional (vdw-DF) [2] and the PW91 functional. While the vdw-DF is found to significantly alter both adsorption height and binding energy of TPP, it hardly affects either its internal geometry or the electronic structure, suggesting that TPP is largely decoupled from the substrate.

[1] L. Grill *et al.*, Nature Nanotech., 2 687 (2007). [2] J. Klimeš is acknowledged for his implementation of the vdw-DF density functional.

O 49.5 Wed 16:00 PHY C213

Electronic Decoupling in Monolayer and Multilayer: Fe-Phthalocyanine on Ag(111) — ●THIRUVANCHERIL GOPAKUMAR¹, THOMAS BRUMME², JÖRG KRÖGER¹, CORMAC TOHER², GIOVANNI CUNIBERTI², and RICHARD BERNDT¹ — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany — ²Institute for Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, D-01069 Dresden, Germany

Electronic properties of Fe-phthalocyanine (FePc) molecules in ultrathin films on Ag(111) have been investigated by scanning tunneling spectroscopy and density functional calculations. Single FePc molecules show a broad signature of Fe *d* orbitals. However, in a two-dimensional ordered superstructure spectroscopic contributions from individual d_{z^2} and d_{xz}/d_{yz} orbitals are resolved. Calculations suggest that an increased molecule-surface distance in the superstructure and a change of the Ag(111) surface electronic structure cause the spectral changes, which are consistent with a partial electronic decoupling of the molecules from the substrate. A progressive evolution towards a gap around the Fermi level is observed for molecules atop the first and second molecular layer.

Financial support by the Deutsche Forschungsgemeinschaft through SFB 677 is acknowledged.

O 49.6 Wed 16:15 PHY C213

Phase separation of cobalt- and 2H-tetraphenylporphyrin on Cu(111): A Scanning Tunneling Microscopy Study — ●STEFANIE GLÄSSEL, ELISABETH ZILLNER, FLORIAN BUCHNER, MICHAEL RÖCKERT, MICHAEL STARK, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058

The understanding of the adsorption behavior of large organic molecules on surfaces is a prerequisite to utilize their functional properties either in single-molecule devices or in self-assembled supramolecular architectures. In this regard the discrimination of the corresponding molecule-molecule and molecule-substrate interactions are in the center of our scanning tunneling microscopy (STM) study at

room temperature. While tetraphenylporphyrins (TPP) are known to form ordered square phases and intermix well on Ag(111) [1], on Cu(111) the separation of CoTPP and 2HTPP is observed [2]. This can be explained by the domination of attractive T-type interactions between adjacent CoTPP molecules and the domination of site specific molecule-substrate interactions for 2HTPP on Cu(111); the observed behavior can conclusively be interpreted as due to a coordinative bond between the iminic nitrogens and copper surface atoms.

This work has been funded by the DFG through Sonderforschungsbereich 583.

[1] F. Buchner et al., Phys. Chem. Chem. Phys., 2010, 12, 13082-13090. [2] F. Buchner et al., submitted

O 49.7 Wed 16:30 PHY C213

The adsorption geometry and bonding properties of PTCDA on Ag(110) — ●OLIVER BAUER¹, GIUSEPPE MERCURIO², SERGEY SUBACH², BENJAMIN FIEDLER¹, CHRISTOPH H. SCHMITZ¹, FRANK STEFAN TAUTZ², and MORITZ SOKOLOWSKI¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Bonn — ²Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, und JARA-Fundamentals of Future Information Technology

The vertical bonding distance of an adsorbate to the underlying surface can be regarded as a quantity related to the strength and the chemisorptive character of the bond. The Normal-Incidence X-ray Standing Wave (NIXSW) technique has recently been used to determine the bonding distance of perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) on (111) coinage metal surfaces [1]. In addition, we have investigated the adsorption geometry of PTCDA in the monolayer regime on the more open Ag(110) surface: We find a bonding distance of the perylene core to the substrate which is significantly smaller than the sum of the vdW radii of both Ag and C, indicating a strong chemical interaction. Furthermore, the PTCDA molecule adsorbs in an arc-like geometry with the O atoms being even closer to the surface than the perylene core. This hints at strong local, covalent Ag-O intercalations. The experimental results are discussed in the framework of the Newns-Anderson model and the recent finding, that for coinage metal (111) surfaces the adsorption height of PTCDA correlates with the work function of the bare substrate [1]. Supported by the DFG and the ESRF. [1] a.o. A. Hauschild et al., PRB 81 (2010) 125432.

O 49.8 Wed 16:45 PHY C213

Experimental & theoretical study of a perylene derivative on Cu(111): insight into the bonding mechanism — ●MIHAELA ENACHE¹, JONAS BJÖRK², MANFRED MATENA³, JORGE LOBO-CHECA³, LUTZ GADE⁴, THOMAS JUNG⁵, MATS PERSSON², and MEIKE STÖHR¹ — ¹University of Groningen, Netherlands — ²University of Liverpool, UK — ³University of Basel, Switzerland

— ⁴University of Heidelberg, Germany — ⁵Paul-Scherrer-Institute, Switzerland

By utilizing the concepts of supramolecular chemistry, remarkable results for molecular self-assembly on surfaces have been presented. The outcome of the self-assembly process is known to be affected by the fine tuning of different parameters which have a direct influence on the interplay between intermolecular and molecule-substrate interactions. In our case we studied the influence of temperature by annealing the sample. STM investigations of a perylene derivative (TAPP) deposited on Cu(111) held at -100°C showed that the molecules do not form an ordered arrangement. Annealing at room temperature results in the formation of a herringbone arrangement while the molecules interact with each other via vdW forces. After annealing at 150°C, a metal coordinated rectangular network is obtained which is commensurate to the substrate [1]. By performing XSW measurements, the vertical adsorption geometry for both phases of TAPP on Cu(111) was determined and such insight into the interplay between intermolecular and molecule-substrate interaction is gained. The findings are supported by DFT calculations. [1] Matena et al., Chem. Eur. J., 16, 2079 (2010)

O 49.9 Wed 17:00 PHY C213

Assembly and manipulation of rotatable cerium-porphyrinato sandwich complexes on a surface — ●SARANYAN VIJAYARAGHAVAN¹, DAVID ECIJA¹, WILLI AUWÄRTER¹, KNUD SEUFERT¹, FELIX BISCHOFF¹, KENTARO TASHIRO², and JOHANNES V. BARTH¹ — ¹Physik Department, E20 Technische Universität München, Garching, Germany — ²National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

The characterization and engineering of molecular nanostructures on surfaces is of great interest, especially the development of metal-directed assembly protocols with suitable linkers and metal atoms combined on well-defined surfaces. Porphyrin molecules are ideal building blocks for these surface anchored nanostructures. Particularly interesting are tetrapyrrole-derived sandwich compounds comprising rare-earth metal centres. Here we report a novel route to synthesize such Bis(porphyrinato)cerium double-deckers (Ce(TPP)₂) and Tris(porphyrinato) cerium triple-deckers (Ce₂(TPP)₃) directly on a Ag(111) surface under UHV conditions by exposing a porphyrin precursor layer to a beam of Ce atoms. The double and triple-decker compounds are studied by scanning tunneling microscopy (STM) topographic measurements, including a comparison with Ce(TPP)₂ layers generated by molecular beam epitaxy. Moreover, we address the motion of double- and triple-decker moieties in specific environments: the top porphyrin of each molecular species can be rotated by STM manipulation. Such complexes can have important applications like single molecule magnets or field effect transistors.