

O 15: Metal Substrates II: Adsorption and Reactivity

Time: Monday 15:00–17:30

Location: Kunsthalle

O 15.1 Mon 15:00 Kunsthalle

Photon-Induced Processes at the Bromobenzene/Cu(111) interface — ●JOHN THOMAS¹, ISHITA KEMENY^{1,2}, CORD BERTRAM^{1,3}, MANUEL LIGGES¹, KARINA MORGENSTERN³, and UWE BOVENSIEPEN¹ — ¹Fakultät für Physik, Universität Duisburg-Essen — ²Stanford PULSE Institute, SLAC National Accelerator Laboratory — ³Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum

Bromine-substituted organic molecules are extensively used as precursors in on-surface synthesis where the molecules are activated through thermal dissociation. Hence, these synthesis processes are limited by the desorption temperature of the molecules of interest. If the desorption temperature is in the range of the dissociation temperature, photoinduced dissociation is an attractive alternative to activate these precursors. We present a systematic study of photo-induced processes in bromobenzene on Cu(111) from sub-monolayer to multilayer coverages and address structure and dissociation dynamics. Scanning tunneling microscopy delivers structural information in the regime below 0.5 monolayers where the molecules adsorb parallel to the surface. We observe the decomposition of molecular clusters and dissociation of molecules under ultraviolet photon irradiation at temperatures below 11 K. Using two-photon photoemission spectroscopy we monitor the activation of molecules through the work function change upon photo excitation and identify coverage-dependent electron attachment and dissociation processes.

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O 15.2 Mon 15:15 Kunsthalle

Inducing the Controlled Rotation of Single o-MeO-DMBI Molecules Anchored to Au(111) — ●FRANK EISENHUT^{1,2}, JÖRG MEYER^{1,2}, TIM KÜHNE^{1,2}, JORGE MONSALVE^{1,2}, JUSTUS KRÜGER^{1,2}, ROBIN OHMANN^{1,2}, GIANAURELIO CUNIBERTI^{1,2,3}, and FRANCESCA MORESCO^{1,2} — ¹Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — ²Institute for Materials Science, TU Dresden, 01062 Dresden, Germany — ³Dresden Center for Computational Materials Science (DCMS), TU Dresden, 01062 Dresden, Germany

A key step towards building single molecule machines is to control the rotation of molecules and nanostructures step by step on a surface. Here, we used the tunneling electrons coming from the tip of a scanning tunneling microscope to achieve the controlled directed rotation of complex o-MeO-DMBI molecules. We studied the adsorption of single o-MeO-DMBI molecules on Au(111) by scanning tunneling microscopy at low temperature and observed by lateral manipulation experiments that the molecules chemisorb on the surface and are anchored on Au(111) with an oxygen-gold bond via their methoxy group. Driven by inelastic tunneling electrons, o-MeO-DMBI molecules can controllably rotate, stepwise and unidirectional, either clockwise or counterclockwise depending on their enantiomeric form. Furthermore, we investigated the temperature-induced rotation of the molecules.

O 15.3 Mon 15:30 Kunsthalle

Following the products of a single intramolecular bond dissociation on surface — ●DONATO CIVITA, GRANT JAMES SIMPSON, and LEONHARD GRILL — Department of Physical Chemistry, University of Graz, Austria

Manipulation of molecules adsorbed at surfaces is very appealing to control and understand fundamental chemical processes. Chemical reactions can be triggered in single molecules by using a scanning tunneling microscope (STM). Specifically, chemical bonds within molecules can be cleaved [1], the resulting fragments can be pulled across the surface by lateral manipulation with the STM tip and even new bonds can be formed [2]. In this work, we study the dissociation of a single Br atom from a dibromoterfluorene (DBTF) molecule adsorbed on a Ag(111) surface. Experiments were done by applying voltage pulses with the STM tip on a single molecule at low temperatures (7 K). By imaging the single molecule before and after such a manipulation and, in addition, studying the current signal during the voltage pulse, we obtain insight into the process. Many dissociation experiments were recorded for different molecular isomers and different lateral locations of the voltage pulse over the molecule. A statistical analysis of the results reveals details about the dynamics of the dissociation, in par-

ticular the fate of the reaction products.

[1] B. C. Stipe, M. A. Rezaei, W. Ho, S. Gao, M. Persson, and B. I. Lundqvist, Phys. Rev. Lett. 78, 4410 (1997)

[2] K. Anggara, L. Leung, M. J. Timm, Z. Hu and J. C. Polanyi, Science Advances, EAAU2821 (2018)

O 15.4 Mon 15:45 Kunsthalle

Surface Chemical Bond of Alternant and Non-Alternant Aromatic Molecules: Influence of the Metal Surface — ●BENEDIKT P. KLEIN¹, LUKAS RUPPENTHAL¹, MARKUS FRANKE², STEFAN R. KACHEL¹, FRANÇOIS C. BOCQUET², RALF TONNER¹, CHRISTIAN KUMPF², REINHARD J. MAURER³, and J. MICHAEL GOTTFRIED¹ — ¹Fachbereich Chemie, Philipps-Universität Marburg, Germany — ²Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ³Department of Chemistry, University of Warwick, United Kingdom

Metal/organic interfaces have a large impact on the performance of organic-electronic devices. The understanding of their chemical, electronic and geometric structure is therefore of great importance. Up to now, aromatic systems with alternant topology, such as pentacene, have been studied almost exclusively. To address this neglect of the non-alternant topology, we investigated the adsorption of the non-alternant molecule azulene and its alternant counterpart naphthalene on the (111) surfaces of Cu, Ag and Pt, using a variety of methods including NEXAFS, PES, TPD, and NIXSW. To provide detailed insight into the surface chemical bond, we used complementary periodic DFT calculations including the deconvolution of DOS and NEXAFS simulations in the molecular orbital contributions. Our results show that the non-alternant molecule binds slightly stronger on Ag, where both molecules are physisorbed, and on Pt, where both are chemisorbed. On the Cu surface the difference is largest with the non-alternant molecule chemisorbed in contrast to the physisorbed alternant molecule.

O 15.5 Mon 16:00 Kunsthalle

Properties of Adsorbed Solvent Molecules: Adsorption Strength and Structure of CCl₃ on Ag(111) — ●MARVIN QUACK and KARINA MORGENSTERN — Chair of Physical Chemistry I, Ruhr-University of Bochum, Germany

Characterizing the adsorption processes of solvent molecules on metal surfaces and the fundamental understanding of surface-adsorbate interactions play an important role, as for example in electrochemical cells or solid state catalysts. In order to understand the process of adsorption of solvent molecules, we investigated chloroform (CCl₃) supported on a Ag(111) single crystal surface by means of temperature programmed desorption (TPD) and low-temperature scanning tunneling microscopy (LT-STM) in ultra high vacuum. The TPD spectra reveal the desorption of molecular chloroform below 180 K, indicating a physisorbed species. The STM results show the formation of a (2x2) superstructure at coverages lower than 1 ML of CCl₃. At higher coverage, we observe the growth of 1D-crystallites in the second layer following the high symmetry directions of the substrate. Further STM results and a model for the adsorption will be presented in this talk.

O 15.6 Mon 16:15 Kunsthalle

Kinetic control of reaction products in porphine oligomerization on Au(111) — KNUD SEUFERT^{1,3}, ●SIMON JAEKEL¹, LEONHARD GRILL¹, FIONA MCBRIDE², BARELD WIT², SHAMSAL HAQ², RASMITA RAVAL², PAOLO POLI², and MATS PERSSON² — ¹Institut für Chemie, Universität Graz — ²Dept. of Chemistry, University of Liverpool — ³Fakultät für Physik, TU München

Nanostructures built from porphyrins have shown much promise in diverse applications such as light harvesting, optoelectronics, gas sensing and molecular electronics [1,2,3]. Investigating these nanostructures on metallic surfaces allows investigations of the electronic properties of individual nanostructures [3]. It has been shown that such nanostructures can be synthesized on surfaces through homocoupling of porphyrin molecules at the macrocycle[4,5]. The resulting oligomers are of particular interest as they are fully conjugated and the reaction leaves no side products on the surface.

Here, we report scanning tunneling microscopy results for porphine coupling on Au(111). The binding motifs of the reaction products are shown to be not only determined by energetic stability, but also by

the reaction kinetics. Therefore, the final structure and hence electronic properties of the oligomers can be tuned via different reaction pathways while using the same monomers.

[1]Lin et al. *Science* 1994, 264, 1105 [2]Nguyen et al. *Phys. Rev. B* 2008, 77, 195307 [3] Kuang et al. *J. Am. Chem. Soc* 2016, 138, 11140 [4] Wiengarten et al. *J. Am. Chem. Soc.* 2014, 136, 9346 [5]Xiang et al *ACS Nano* 2018, 12, 1203

O 15.7 Mon 16:30 Kunsthalle

Frequency modulation atomic force microscopy and scanning tunneling microscopy study of CO on Pt(111) — ●OLIVER GRETZ, FRANZ J. GIESSIBL, and ALFRED J. WEYMOUTH — Universität Regensburg, Regensburg, Deutschland

Small molecules, like CO, have a higher binding energy to platinum than to other metals like copper. When comparing CO on Pt(111) to CO on Cu(111), the frustrated translational mode is 2 meV (about 50%) higher and individual CO molecules appear in low-bias STM images as protrusions instead of as depressions. In this talk we present our AFM/STM studies of CO on Pt(111). Previously, CO on Cu(111) has been used to image the apex of an AFM tip (CO-Front atom Identification - COFI). As the lateral stiffness of adsorbed CO scales by the square of the energy of the frustrated translational mode, we expect less aberrations due to CO bending than on Cu(111). We performed COFI measurements with CO on Pt(111). In addition, we performed manipulation experiments and measured the lateral force to move a CO molecule from one adsorption site to another.

O 15.8 Mon 16:45 Kunsthalle

Energy Dissipation Mechanisms for CO+O Association on Ru(0001) on Femtosecond Timeframes — ●MANUEL J. KOLB^{1,2,3}, FRANK ABILD-PEDERSEN^{1,2}, and LARS G.M. PETERSSON³ — ¹SLAC National Laboratory, Stanford, USA — ²Stanford University, Stanford, USA — ³Alba Nova, Stockholm University, Stockholm, Sweden

Recent work in our group[1] on CO+O association taking place on the Ru(0001) surface revealed that the reaction pathway exhibits two independent transition states, with the first of these being rate-determining. However, in contrast to conventional expectations, a significant population was observed in the low-energy region spanned by the two transition states. Here, we present a theoretical investigation into possible energy dissipation mechanisms which account for this increased occupation: Firstly, the energy loss due to electronic friction along the pathway. Secondly, we investigate the energy transfer to and from the individual vibrational degrees of freedom of the CO-O complex to the substrate and its influence on the individual reaction energy barriers.

[1]Henrik Öström et al., *Science*, 2015, 347, 6225, pp 978-982

O 15.9 Mon 17:00 Kunsthalle

The role of the surface in the atomic oxidation of supported Coronene films — JÜRGEN WEIPPERT, VINCENT GEWIESE, SEYITHAN ULAS, DMITRY STRELNIKOV, ●ARTUR BÖTTCHER, and MANFRED M. KAPPES — Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany

Atomic oxidation of Coronene films grown on HOPG results in the formation of various surface species, $C_mH_nO_k$, which subsequently can be desorbed as intact nm-sized graphene oxides, nano-GOs. Coronene films were grown at room temperature by low-energy cluster ion beam deposition (LECBD, $C_{24}H_{12}^+$) and oxidized by exposing them to a beam of near-thermal atomic oxygen. The XPS-based analysis indicated that the oxidation of the $C_{24}H_{12}$ films proceeds predominantly via the formation of epoxides, ethers, and quinones. The mass spectrometric analysis of the subliming species revealed a strong dependency on the film thickness. The sublimation of thick oxidized Coronene films proceeds predominantly via the emission of rim-epoxides $C_{24}H_{12}O_n$ ($n \leq 7$) [1]. The sublimation from oxidized thin films, $\Theta \leq 2$, exhibits lactones $C_{23}H_{10}O_2$ and dilactones $C_{22}H_8O_4$. The sublimation from Coronene monolayers deposited on a pre-oxidized basal plane is also dominated by the aforementioned oxides.

[1] J. Weippert, et al. *JPC C* 2018, DOI: 10.1021/acs.jpcc.8b01655

O 15.10 Mon 17:15 Kunsthalle

Solvent Induced Growth Polymorphs of 1,3-Dithia Derivatives of Ferrocene on HOPG — ●THIRUVANCHERIL G. GOPAKUMAR¹, PRITHWIDIP SAHA¹, VINITHRA GURUNARAYANAN¹, VLADIMIR V. KOROLKOV², PREMA G. VASUDEV³, RAMESH RAMAPANICKER¹, and PETER H. BETON² — ¹Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India — ²School of Physics and Astronomy, The University of Nottingham, Nottingham NG7 2RD, United Kingdom — ³Molecular and Structural Biology Department, CSIR-Central Institute of Medicinal & Aromatic Plants, Lucknow UP-226015, India

Ferrocene (Fc) and its derivatives have attracted interest in electronic applications[1] due to its tunable of electronic properties. In this work we have studies the microscopic structure of ultra-thin films of two 1,3-dithia derivatives of Ferrocene (Fc) on the basal plane of highly oriented pyrolytic graphite (HOPG) using AFM and STM at ambient conditions. Films are prepared by drop-casting Fcs dissolved in different solvents. Upon deposition of Fcs from methanol and DCM, two types of molecular growth polymorphs are observed. When Fcs are deposited from ethanol, acetone, DMF and toluene, one of the growth polymorphs is exclusively observed. The formation of growth polymorphs are understood using the boiling point of solvents and the solubility of Fcs in solvents.[2] Solvents with high boiling point prompts the formation of energetically favorable growth.

[1] N.Nerngchamnonng et al. *Nat. Nanotechnol.* 2013, 8, 113. [2] P. Saha et al. *J. Phys. Chem. C*, 2018, 122, 19067.