

O 89: Inorganic/Organic Interfaces: Molecular Switches

Time: Thursday 15:00–18:30

Location: MA 043

O 89.1 Thu 15:00 MA 043

Electronic and Thermal Fluctuations of Functional Molecules on Metals — REINHARD MAURER^{1,2}, WEI LIU³, IGOR POLTAVSKY³, THOMAS STECHER², HARALD OBERHOFER², ALEXANDRE TKATCHENKO³, and KARSTEN REUTER² — ¹Yale University, New Haven, USA — ²Technische Universität München, Germany — ³Fritz-Haber Institut der Max-Planck-Gesellschaft, Berlin, Germany

The prevailing working hypothesis in vacuum surface science is that finite-temperature effects do not significantly alter the equilibrium properties of molecules adsorbed to surfaces. In this work, we show this not to be the case for the adsorption geometry, energetics, and desorption temperature of the molecular switch Azobenzene on Ag(111). Comparing to X-ray standing wave measurements and temperature programmed desorption experiments, we find strong discrepancies to static Density-Functional Theory calculations. We overcome these through anharmonic corrections and explicit *ab initio* molecular dynamics simulations of the free energy of desorption to account for the thermal fluctuations. Additionally, inclusion of many-body dispersion effects accounts for the electronic fluctuations that govern the interaction strength. With respect to both, our calculations show that more modest, prevalent approaches fail to capture the sizable entropy of desorption and therewith the correct desorption temperature. An accurate description of adsorbate interactions and entropies of adsorption in functional hybrid metallic-organic systems thus necessitates a full account of the inherent anharmonicity of adsorbate and substrate, in addition to an accurate description of dispersion interactions.

O 89.2 Thu 15:15 MA 043

Excited-State Properties of Azobenzene Self-Assembled Monolayers from Many-Body Perturbation Theory — CATERINA COCCHI and CLAUDIA DRAXL — Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Self-assembled monolayers (SAMs) of azobenzene-functionalized alkanethiols on gold exhibit remarkable intermolecular interactions in the excited state [1]. Excitonic coupling plays a crucial role in quenching the *trans/cis* photo-isomerization in the SAMs, compared to single molecules. We perform an in-depth first-principles study of the excited-state properties of the chromophore SAMs. In the framework of density-functional and many-body perturbation theory, as implemented in the all-electron full-potential code exciting [2], we investigate optical and core-level excitations of azobenzene SAMs, functionalized with different end groups. By analyzing the character of the electron-hole pairs, systematically going from the constituent molecules to SAMs of increasing density, we identify the fingerprints of the backbone structures and those of the functional groups. Our results represent an important step forward to interpret available experiments [1], and to gain insight into the microscopic mechanisms that rule excited-state isomerization in these materials. [1] C. Gahl et al. J. Am. Chem. Soc. 132, 1838 (2010). [2] A. Gulans et al. J. Phys.: Condens. Matter 26, 363202 (2014).

O 89.3 Thu 15:30 MA 043

Azobenzene based self-assembled monolayers as a means to control the work function — SWEN SCHUSTER¹, MUSAMMIR KHAN¹, PIOTR CYGANIK², ANDREAS TERFORT³, and MICHAEL ZHARNIKOV¹ — ¹Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — ²Smoluchowski Institute of Physics, Jagiellonian University, 30-059 Krakow, Poland — ³Institute for Inorganic and Analytical Chemistry, Frankfurt University, 60438 Frankfurt, Germany

Controlled adjustment of the work function of surfaces and interfaces by external stimuli is a challenging task. In this context we designed novel photoresponsive, azobenzene-based self-assembled monolayers (SAMs) bearing dipolar functional groups, even though the first experiments were performed on the non-substituted films. To monitor and partly relax the steric constraints upon the photoisomerization we introduced an aliphatic linker of variable parity between the azobenzene unit and the head group, relying on the odd-even effect in the monomolecular assembly. The variation of the packing density was found to be ca. 10% only, which appeared to be insufficient to avoid the steric constraints to the necessary extent. Consequently, photoinduced variation of the work function did not exceed 50 meV, indepen-

dent of the parity of the aliphatic linker. To improve the photoresponsive properties, the azobenzene-based moieties were diluted with other, short molecules to create sufficient space for isomerization. A clear improvement of the photoisomerization behavior was found, correlated with both the extent of the dilution and the identity of the short molecules.

O 89.4 Thu 15:45 MA 043

Probing the Photostationary State of Photochromic SAMs by Two-Photon Photoemission Spectroscopy — WIBKE BRON-SCH, DANIEL PRZYREMBEL, CORNELIUS GAHL, and MARTIN WEINELT — Freie Universität, Berlin, Deutschland

In densely packed monolayers of azobenzene derivatives, *trans-cis* photoisomerization is strongly suppressed due to electronic and steric interaction among the chromophores [1]. Mixing and thus diluting an azobenzene derivative with an alkanethiol of appropriate chain length allows tuning the free volume around the chromophores in the SAM and thereby controlling their interactions. We investigate optical switching in SAMs of azobenzene-decorated undecane thiol diluted with dodecanethiol on Au(111) by means of two-photon photoemission (2PPE) spectroscopy. Along with changes in the electronic structure, we observe a pronounced isomerization-induced shift of the work function up to 250 meV. In order to tune the photostationary state between predominantly *trans* and *cis* we vary the intensity ratio of femtosecond UV pulses and a 450 nm continuous-wave laser.

[1] C. Gahl, R. Schmidt, D. Brete, E. R. McNellis, W. Freyer, R. Carley, K. Reuter, and M. Weinelt, J. Am. Chem. Soc. 132, 1831 (2010).

O 89.5 Thu 16:00 MA 043

Applications of the non-adiabatic molecular dynamics to diarylethene molecule: based light-induced switches — VLADIMIR ZOBAC¹, PROKOP HAPALA¹, ENRIQUE ABAD², JOSE ORTEGA², JAMES LEWIS³, and PAVEL JELINEK¹ — ¹Institute of Physics, Academy of Sciences of the Czech Republic — ²Departamento de Física Teórica de la Materia Condensada and Condensed Matter Physics Center Universidad Autónoma de Madrid — ³Department of Physics, West Virginia University

The light-induced molecular processes are frequently studied in various experiments using. One of the most spread methodology allowing to theoretically describe the dynamics of these photochemical processes is non-adiabatic molecular dynamics (NAMD) [1]. Recently, we have implemented the calculation of the non-adiabatic coupling vector, which is the main quantity in NAMD [2]. The NAMD implementation in DFT Fireball code [3] allows to study large systems with more than 100 atoms. We will present the ring closing and opening mechanism of diarylethene based molecules. Most of the statical or dynamical studies were done for this smaller type of molecules on the different level of the accuracy [4]. All of them were performed for the gas phase of the molecule. Here we extend this simulations on the molecules embedded between the gold electrodes in comparison with gas phase simulations. [1] J. C. Tully, J. Chem. Phys. 93, 1061 (1990) [2] E. Abad, et al, J. Chem. Phys., vol. 138, p. 154106, (2013) [3] J.P. Lewis et al, Phys. Stat. Sol. B, 248, 1989 (2011) [4] B. C. Arruda, R. J. Sension, Phys. Chem. Chem. Phys., 4439-4455 (2014)

O 89.6 Thu 16:15 MA 043

Reversible long range surface state mediated switching of pentacene derivatives — VERENA SCHENDEL¹, BOGDANA BORCA¹, IVAN PENTEGOV¹, ULRIKE KRAFT¹, HAGEN KLAUK¹, PETER WAHL^{1,2}, UTA SCHLICKUM¹, and KLAUS KERN^{1,3} — ¹Max-Planck Institute for Solid State Research, D-70569 Stuttgart — ²School of Physics and Astronomy, University of St. Andrews, Scotland, KY 16 9SS, United Kingdom — ³Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Molecular switches represent an essential building block for molecular electronics exhibiting two or more distinct stable states associated with different chemical/physical properties which are reversibly accessible. Therefore they constitute promising candidates for information storage. We report the use of low temperature scanning tunneling microscope (STM) to image and electronically induce reversible conformational changes of the pentacene derivate antracenedithiophene (ADT).

ADT adsorbs as statistically distributed monomers on a Cu(111) surface adopting a cis or trans configuration. The conformational switch of an entire array of single molecules is induced by injecting hot electrons from the tip directly into the bare Cu(111) substrate. The (111) faces of noble metals exhibit surface state electrons that have a free electron-like character. Due to the long inelastic mean free path of hot carriers in the surface state switching is enabled over distances on the order of 100 nm. The remote switching process is found to be isomer-selective. We demonstrate a switching process that is fully reversible, isomer selective as well as remotely controlled.

O 89.7 Thu 16:30 MA 043

Self-assembly and thermally induced conformational changes of Ni(II)-meso-tetrakis (4-tert-butylphenyl) benzoporphyrin on Cu(111) studied by STM — •MICHAEL LEPPER, MICHAEL STARK, LIANG ZHANG, STEFANIE DITZE, 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

A detailed scanning tunneling microscopy study of the self-assembly and thermally induced conformational changes of Ni(II)-meso-tetrakis (4-tert-butylphenyl) benzoporphyrin (Ni-TTBPP) on Cu(111) will be presented. The coverage-dependent adsorption behavior at room temperature reveals that Ni-TTBPP molecules can easily diffuse on the surface and self-assemble into islands with square order and a certain registry to the substrate. The role of molecule-molecule and molecule-substrate interactions for the formation of the well-ordered supramolecular structure will be discussed. Interestingly, upon moderate heating two successive, irreversible intramolecular conformational changes are observed. This is explained comprehensively by a thermally induced dehydrogenative, intramolecular aryl-aryl coupling reaction. In addition this intramolecular structural change is coverage dependent, exhibiting a lower rate at higher initial coverage. This modification and the overall adsorption behavior of Ni-TTBPP on Cu(111) will be discussed and compared to the very different behavior of the similar Ni(II)-tetraphenylbenzoporphyrin on the same substrate.

O 89.8 Thu 16:45 MA 043

Measuring forces on a single molecule in an STM junction — •LUKAS GERHARD¹, KEVIN EDELMANN¹, JAN HOMBERG¹, MARCIN LINDNER¹, MICHAL VALASEK¹, MARCEL MAYOR^{1,2}, WULF WULFHEKEL^{1,3}, and MAYA LUKAS¹ — ¹Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen — ²Department of Chemistry, University of Basel, CH-4056 Basel — ³Physikalisches Institut, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe

The possibility to incorporate molecular groups into carrier platforms allows to isolate functional units from a metallic substrate. Here we present a low-temperature STM study of spirobifluorene platforms with a benzonitrile head group deposited on a Au(111) surface [1]. We show by systematic variation of the tunneling parameters that the dipole moment of the benzonitrile allows us to exert forces on the molecule by applying electric fields in the STM junction. In this way we are able to form and brake a well defined contact between tip and molecule depending on the applied bias voltage. This switching between ON and OFF states of the conductance is highly reproducible and deterministic. Tuning the electrically applied force such that ON and OFF state are close in energy we observe thermally induced random switching which allows to deduce the energy difference between the two states. We measure this energy difference as a function of the distance between tip and sample and hence derive the force that is needed to pull apart the molecular junction. [1] M. Valášek et al., JOC 2014 79 (16), 7342-7357

O 89.9 Thu 17:00 MA 043

Conformational switching of single tetraphenylmethane molecules on Au(111) studied by STM — •JAN HOMBERG¹, KEVIN EDELMANN¹, MARCIN LINDNER¹, MICHAL VALASEK¹, LUKAS GERHARD¹, MARCEL MAYOR^{1,2}, and WULF WULFHEKEL^{1,3} — ¹Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe — ²Department of Chemistry, University of Basel, CH-4056 Basel — ³Physikalisches Institut, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe

One of the main challenges in the field of molecular electronics is still the coupling of the molecules to a metallic electrode or substrate. To decouple functional units from the substrate, we follow the idea of tripodal carrier molecules. As a core structure we used tetraphenyl-

methane with sulfhydryl groups for anchoring. Various derivatives with varying head groups were deposited onto a Au(111) surface via spraying from solution and investigated by low temperature STM. Certain molecules can be switched by the STM tip between different stable conformations. Furthermore we report on the morphology and electronic properties of single molecules on the surface.

O 89.10 Thu 17:15 MA 043

Switching Orientation of adsorbed Molecules: Reverse Domino on a Metal Surface — •TANER ESAT^{1,2}, CAROLIN R. BRAATZ³, CHRISTIAN WAGNER^{1,2}, RUSLAN TEMIROV^{1,2}, F. STEFAN TAUTZ^{1,2}, and PETER JAKOB³ — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ²JARA-Fundamentals of Future Information Technology — ³Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität Marburg, 35032 Marburg, Germany

In a two-pronged approach, using infrared absorption spectroscopy and scanning tunneling microscopy, a thus far unknown monolayer phase of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA) on Ag(111), characterized by an all perpendicular orientation of the planar molecules has been identified. This conclusion is based on a quantitative analysis of characteristic vibrational modes with specific polarizations, as well as STM images of the standing NTCDA molecules. Formation of the vertically standing NTCDA phase requires second layer NTCDA to squeeze into empty spaces between relaxed monolayer NTCDA molecules. This process causes initially parallel oriented NTCDA to likewise adopt the inclined adsorption geometry. The new phase shows a pronounced tendency to form 1D rows or narrow islands. We suggest that extra NTCDA preferentially transforms into the upright configuration next to existing islands, i.e. the transformation process proceeds in a directed and recurrent manner (reversed domino effect). We also present revised structure models for the relaxed and the compressed NTCDA/Ag(111) monolayer phases.

O 89.11 Thu 17:30 MA 043

Intramolecular Dipole of Merocyanine Probed by Local Contact Potential Difference Measurements — •NILS KRANE¹, CHRISTIAN LOTZE¹, XIANWEN CHEN¹, JOSÉ IGNACIO PASCUAL^{1,2,3}, and KATHARINA FRANKE¹ — ¹Freie Universität Berlin, Berlin, Germany — ²CIC nanoGUNE, San Sebastián, Spain — ³Ikerbasque, Basque Foundation for Science, Bilbao, Spain

In gas phase and solution 1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran can be switched reversibly by light and temperature to its merocyanine form. This form has been shown to exhibit an intramolecular dipole [1]. When adsorbed on a metal surface the switching back to the spiropyran form is inhibited [2]. Charge redistribution and screening may considerably alter the expected dipole behavior of the merocyanine form. Utilizing combined low-temperature scanning tunneling microscopy and dynamic atomic force microscopy, we characterize the adsorption of merocyanine on Au(111). The intramolecular charge distribution is measured by the local contact potential difference (LCPD) [3]. The vertical and lateral distribution of the LCPD hints at the persistence of an intramolecular dipole.

[1] Lapienis-Grochowska *et al.*, JCS, Far.Trans. **2** 1979, 75, 312

[2] Marten Piantek *et al.*, J. Am. Chem. Soc. 2009, **131**, 12729

[3] Mohn *et al.*, Nature Nanotechnology 2012, **7**, 227-231

O 89.12 Thu 17:45 MA 043

Force and conductance in a single molecule switch: SnPc on Ag(111) — NUALA CAFFREY¹, KRISTOF BUCHMANN², NADINE HAUPTMANN², CESAR LAZO¹, •PAOLO FERRIANI¹, STEFAN HEINZE¹, and RICHARD BERNDT² — ¹Institut für Theoretische Physik und Astrophysik, Christian-Albrecht-Universität zu Kiel, D-24098 Kiel, Germany — ²Institut für Experimentelle und Angewandte Physik, Christian-Albrecht-Universität zu Kiel, D-24098 Kiel, Germany

Transport in molecular electronic devices is ultimately determined by the properties of the interface between the metallic electrodes and the organic molecule. To understand the interface properties, the relation between structure and conductance needs to be assessed. The combined use of scanning tunneling and atomic force microscopy is an ideal technique as it allows to simultaneously measure interaction forces and conductance between a tip and an adsorbed molecule. Here, we apply it to study Sn-Phthalocyanine (Pc) on Ag(111). This molecule has a shuttle-cock shape and on a surface can acquire one of two possible conformations – either with the central metal atom pointing away from or towards the surface. We have performed conductance and

force measurements on both molecular configurations as a function of tip-sample distance. First-principles calculations of the force and conductance curves agree well with the experiment. We find a non-trivial distance-dependence of the force curves which is explained based on the competition of forces acting on different atoms in the molecule.

O 89.13 Thu 18:00 MA 043

Direct observation of intramolecular H-atom transfer reaction by scanning tunneling microscopy — ●JANINA LADENTHIN¹, LEONHARD GRILL^{1,2}, JACEK WALUK³, and TAKASHI KUMAGAI¹ — ¹Department of Physical Chemistry, Fritz-Haber Institute of the Max-Planck Society, Faradayweg 4-6, 14195 Berlin, Germany. — ²Department of Physical Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria. — ³Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw 01-224, Poland.

Intramolecular H-atom transfer reaction, i.e. tautomerization, is an important molecular process in chemistry and biology. More recently tautomerization in free-base phthalocyanine [1] and porphyrin derivatives [2,3] was directly observed and controlled by low-temperature STM. We have studied tautomerization within a single porphycene molecule, which is a structural isomer of porphine but there exist H-bonding interaction in the cavity, adsorbed on Cu(111) by low-temperature STM. After the deposition of porphycene molecule onto the surface at room temperature the adsorption structure and dynamics were investigated at 5 K. The molecules show the thermodynamically favorable trans configuration. A voltage pulse of the STM can induce the unidirectional conversion from the trans to cis configuration, interestingly, which occurs non-locally and the spatial range of the reaction reaches up to ~100 nm from the STM tip position.

[1] P. Liljeroth, J. Repp, G. Meyer, *Science* 317, 1203 (2007). [2] W.

Auwärter et al. *Nature Nanotech.* 7, 41 (2011). [3] T. Kumagai et al. *Nature Chem.* 6, 41 (2014).

O 89.14 Thu 18:15 MA 043

A supramolecular motor at work: Rotation and translation of single atoms — ROBIN OHMANN^{1,2}, ●ANJA NICKEL^{1,2}, JÖRG MEYER^{1,2}, JORGE ECHEVERRIA³, MARICARMEN GRISOLIA³, CHRISTIAN JOACHIM³, GIANAURELIO CUNIBERTI^{1,2}, and FRANCESCA MORESCO^{1,2} — ¹Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, 01062 Dresden, Germany — ²Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — ³GNS & MANA Satellite, CEMES, CNRS, 29 rue J. Marvig, 31055 Toulouse Cedex, France

Molecular motors perform rotational and translational movements or undergo conformational changes converting chemical or electrical energy into mechanical energy. Their size can range from large motor proteins to small nanocars or single molecules. While motor proteins are known to transport large intracellular objects, the displacement of a load at the atomic scale by a molecular motor has not been realized so far. Here, we have bound the smallest possible load - a single atom - to a supramolecular motor and, by feeding it with tunneling electrons, we have triggered the motor to move the atom. As a supramolecular motor we use a windmill-shaped supramolecular structure composed of four 4-Acetylbiphenyl molecules which self-assemble on a Au(111) surface. We controllably load the supramolecular motor with single Au adatoms and, by applying voltage pulses with the tip of a STM, we induce the rotation or translation of the motor, thus performing a minute work at the atomic scale, which is enough for the supramolecular motor to move the load.