

O 44: Focussed session: Functional molecules at surfaces II

Time: Wednesday 10:30–13:30

Location: A 053

Topical Talk

O 44.1 Wed 10:30 A 053

Scanning Tunneling Spectroscopy and Atomic Force Microscopy of Functional Molecules on Thin Insulating Films

— ●JASCHA REPP — Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany

Ultrathin insulating films on metal substrates facilitate the use of the scanning tunneling microscope (STM) to study the electronic properties of single atoms and molecules, which are electronically decoupled from the metallic substrate. The ionic relaxations in a polar insulator lead to a charge bistability of some adsorbed atoms and molecules. It is shown that control over the charge-state of individual molecules in such systems can be obtained by choosing a substrate system with an appropriate work function. The distribution of the additional charge is studied using difference images. These images show marked intra-molecular contrast. In addition, we investigated $C_{20}S_2H_{12}$ molecules adsorbed on ultrathin layers of NaCl using a combined low-temperature scanning tunneling and atomic force microscope. These non-planar molecules exist in two stable conformations. By means of excitations from inelastic tunneling electrons we can switch between both conformations. We present atomic force microscopy (AFM) measurements with sub-molecular resolution directly revealing the conformational changes. From AFM data and taking the chirality of the molecules into account, we could unambiguously determine the pathway of the conformational change. Hence, the AFM channel reveals additional information that is truly complementary to the STM data set.

Topical Talk

O 44.2 Wed 11:00 A 053

Conductance switching and quantum interference in molecular junctions — ●SENSE JAN VAN DER MOLEN — Kamerlingh Onnes Laboratorium, Leiden University, Leiden, The Netherlands

A fascinating prospect in nanoscience is to externally manipulate the conductance of molecular junctions. For this, an impressive set of (switchable) molecules has been synthesized in organic chemistry. However, once contacted, switchable molecules may easily lose their functionality, e.g. due to quenching of molecular excitations. Surprisingly, the opposite is possible too: junctions containing passive molecules may become switchable. I will give examples from our research, with a special focus on (arrays) of molecular junctions containing light-sensitive diarylethene molecules. The conductance properties of these devices can be switched reversibly by illumination, although the on/off ratio is limited. Next, I will deviate a bit from molecular switching and focus on the quantum aspects of charge transport through organic molecules. In some cross-conjugated molecules, destructive interference of electron waves can take place, leading to a dramatically low conductance. I will present experimental evidence for destructive quantum interference in (anthraquinone-based) molecular junctions. Remarkably, the large energy level spacing allows this interference phenomenon to be observed at room temperature, unlike the traditional case of Aharonov-Bohm rings. By turning quantum interference on and off, switchable molecular junctions with very high on/off ratios are anticipated shortly.

O 44.3 Wed 11:30 A 053

Direct observation of molecular switching at and close to room temperature by scanning tunneling microscopy —

●STEFANIE DITZE, FLORIAN BUCHNER, 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

An ultimate goal of nanotechnology is the usage of individual molecules as functional entities. One important example is the application of switchable molecular building blocks in information storage. Herein, we report the observation of a supramolecular ordered phase of 2H-5,10,15,20-Tetrakis(3,5-di-tert-butyl)-phenylporphyrin (2HT-TBPP) on Cu(111) by scanning tunneling microscopy (STM) in ultra-high vacuum around room temperature (RT). In this phase, the 2HT-TBPP molecules are arranged in alternating rows with intrinsically different intramolecular conformations, i.e. a concave and a convex appearance in STM. Interestingly, it was found that individual 2HT-TBPP molecules spontaneously switch between these two conformations at RT. Detailed analysis of the temperature dependence of the

switching behavior allows to extract the activation energies and the prefactors for the molecular switching process. In addition, we demonstrate tip-induced switching of individual molecules at 200 K.

This work has been funded by the Deutsche Forschungsgemeinschaft (DFG) through Sonderforschungsbereich 583.

O 44.4 Wed 11:45 A 053

Thermally induced switching of azobenzene at coinage metal surfaces? A DFT perspective — ●REINHARD J. MAURER and KARSTEN REUTER — TU München

Stimulating a controlled isomerization of functional molecules stabilized at a solid surface is a central step en route to a future molecular nanotechnology. Central questions particularly at metal substrates concern the detailed excitation mechanism and in how much established gas-phase isomerization pathways are modified by the presence of the surface. Building the basis for a detailed understanding of photo-induced isomerization we use dispersion-corrected density-functional theory to investigate the thermal switching of the prototypical molecular switch azobenzene at Au(111). For this we compute energy profiles for isomerization mechanisms predominantly discussed in gas-phase and analyze the electronic structure along the way. We find that the interaction with the surface selectively favors the rotational against the inversion pathway, and thereby reverses the ordering established in gas-phase or solution. Extending our calculations to Ag(111) surfaces as well as to tetra-tert-butyl-azobenzene (TBA) we specifically target the role of the substrate d-band and the influence of functional groups.

O 44.5 Wed 12:00 A 053

Photoswitching of Molecular Platform Adlayers — ●ULRICH JUNG¹, SONJA KUHN¹, MATHIAS MÜLLER¹, SANDRA ULRICH², JENS KUBITSCHKE², RAINER HERGES² und OLAF MAGNUSSEN¹ — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Leibnizstr. 19, 24118 Kiel, Germany — ²Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 4, 24098 Kiel, Germany

We have recently introduced a novel approach for preparation of adlayers with freestanding functional groups on metal surfaces based on customizable molecular platforms and characterized the structure of these adlayers by scanning tunneling microscopy [1,2,3] and various spectroscopies [4]. The adlayers were found to exhibit a high degree of order with the functionalities oriented in a defined way with respect to the surface and precisely controllable vertical and lateral distances.

Here, we will focus on photoswitching properties of platform adlayers exhibiting azobenzene functionalities. Generally, photoswitching is preserved upon formation of such adlayers, the according reactions follow first-order kinetics with high quantum efficiencies of $\approx 10^{-4}$. In addition, thermal backswitching is found to proceed several orders of magnitude faster in the adlayers than in solution, which can be attributed to pronounced electronic coupling of the azobenzene functionalities with the metal substrate.

[1] Baisch et al., J. Am. Chem. Soc. (2009), 131, 442, [2] Kuhn et al. PCCP (2010), 12, 4481, [3] Kuhn et al, Chem. Commun. (2011), 47, 8880, [4] Jung et al., Langmuir (2011), 27, 5899

O 44.6 Wed 12:15 A 053

Manipulation and spectroscopy of individual phthalocyanine molecules on InAs(111)A with a low-temperature scanning tunneling microscope — ●CHRISTOPHE NACCI¹, KIYOSHI KANISAWA², and STEFAN FÖLSCH¹ — ¹Paul Drude Institute for Solid State Electronics, Berlin (Germany) — ²NTT Basic Research Laboratories, NTT Corporation, Atsugi (Japan)

Phthalocyanine (Pc) is a promising class of organic molecules to develop functionality concepts based on hybrid organic-semiconductor systems. We report a low-temperature scanning tunneling microscopy (STM) study of single naphthalocyanine (NPc) and tin phthalocyanine (SnPc) molecules adsorbed on the InAs(111)A surface. InAs(111)A is In-terminated and characterized by completely saturated dangling bonds due to its (2x2) In-vacancy reconstruction. We found that NPc is in a physisorbed state, preserving the electronic molecular structure to a large extent. This indicates that the molecule is only weakly coupled to the InAs(111)A template. The non-planar SnPc adsorbs

in two different configurations with the central Sn atom either above or below the molecular plane (SnPc_{up} and SnPc_{down}). We achieved the reversible switching between the two conformers by means of STM tip-induced excitation. It is revealed that SnPc_{up} is characterized by a weaker surface bonding compared to SnPc_{down} . This enables to reposition SnPc_{up} by STM-based lateral manipulation, whereas this is not possible for SnPc_{down} . The reversible switching can thus be utilized to either move the molecule or to pin it down to the surface. We acknowledge support by the Deutsche Forschungsgemeinschaft (SFB658).

O 44.7 Wed 12:30 A 053

First-principles study of redox-molecular switch above a polar thinfilm: a van der Waals + U description — ●JOHN SHARP, FELIX HANKE, and MATS PERSSON — University of Liverpool, Liverpool, UK

A redox-type molecular switch functions by coupling the charging and discharging of a molecule to an obvious change in conformation. Such a switch was recently demonstrated experimentally, by investigating the molecule bis-dibenzoylmethanato-copper(II) ($\text{Cu}(\text{dbm})_2$) adsorbed on an ultra-thin insulating layer above a Cu substrate[1]. Here we aim to understand the molecular adsorption and switching properties using a first principles density functional approach to investigate the electronic structure of the complex. This investigation is challenging due to the van der Waals dominated adsorption and the presence of highly-correlated *d*-electrons in $\text{Cu}(\text{dbm})_2$. Here we use a van der Waals density functional [2] and a 'GGA+U' term to properly address these issues. Crystal field splitting of the *d*-orbitals underlies the conformational change that occurs upon charging, and the magnitude of the splitting is affected by the value of 'U' used. The experimentally observed changes in conformation upon charging the adsorbate are only reproduced with a self-consistently determined value of U. Moreover without inclusion of the U term a spontaneous charging of the adsorbate is observed even for the experimentally neutral configuration. Finally, we present scanning tunnelling microscopy simulations and compare the results with the experimentally available data.

[1] PRL **106** 216103 (2011); [2] PRB **83** 195131 (2011)

O 44.8 Wed 12:45 A 053

Quantum chemical calculations and open-system density matrix simulations for arrays of molecular switches on surfaces — GEREON FLOSS, MANUEL UTECHT, ●TILLMANN KLAMROTH, and PETER SAALFRANK — Theoretische Chemie, Universität Potsdam, Germany

In this work different models are investigated to describe the absorption spectra and excitonic coupling in self-assembled monolayers of azobenzenes, on the (TD-) B3LYP/6-31G* level of theory [1]. The calculated blue shifts in optical absorption spectra account for the experimental observations made for azobenzene/gold SAMs, and hint to the fact that they can indeed be responsible for reduced switching probability in densely packed self-assembled structures [2].

Furthermore, using a quite general open-system density matrix model, we demonstrate that nevertheless controlled and complete switching should be possible in arrays of molecular switches on sur-

faces by analytical and optimal control pulses and the concept of "laser distillation" [3]. The parameters for this dynamics model are chosen to roughly resemble the all-trans \rightarrow all-cis isomerization of an array of azobenzene molecules on a surface.

[1] M. Utecht, T. Klamroth, P. Saalfrank, Phys. Chem. Chem. Phys. **13**, 21608 (2011).

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

[3] G. Floß, T. Klamroth, P. Saalfrank, Phys. Rev. B **83**, 104301 (2011).

O 44.9 Wed 13:00 A 053

Role of the electronic structure of adsorbate/substrate complexes on the photoisomerization ability — ●MICHAEL SCHULZE, CHRISTOPHER BRONNER, SEBASTIAN HAGEN, and PETRA TEGEDER — Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin

We use two-photon photoemission to study two molecular photo-switches at the Au(111) surface, namely azobenzene and its derivative tetra-tert-butyl-azobenzene (TBA). Electronic states at the substrate-adsorbate interface are found to be a sensitive probe for the isomerization state of TBA while azobenzene loses its switching ability at the surface. We partly attribute the latter to a shift of the highest occupied molecular orbital (HOMO) with respect to the gold d-bands which quenches the hole transfer involved in the switching mechanism of TBA.

O 44.10 Wed 13:15 A 053

Adsorption height of benzene and azobenzene on Ag(111) and Cu(111) — ●MARTIN WILLENBOCKEL¹, GIUSEPPE MERCURIO¹, ERIK R. MCNELLIS², CHRISTOPHER BRONNER³, BENJAMIN STADTMÜLLER¹, STEPHAN MEYER³, ERWAN VARENE³, MICHAEL SCHULZE³, ISABEL MARTIN³, SEBASTIAN HAGEN³, FELIX LEYSSNER³, JÖRG MEYER², SERGUEI SOUBATCH¹, MARTIN WOLF^{2,3}, KARSTEN REUTER⁴, PETRA TEGEDER³, and F. STEFAN TAUTZ¹ — ¹Peter Grünberg Institut 3, Forschungszentrum Jülich and JARA, Jülich, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ³Fachbereich Physik, Freie Universität Berlin, Berlin, Germany — ⁴Technische Universität München, Garching, Germany

Research focused on the interactions at organic/metal interfaces revealed that weak long-range van-der-Waals (vdW) forces play a significant role in the bonding mechanism. However, a clear experimental gauge is needed to judge to which extent the vdW interactions influence the adsorption strength. For molecules at surfaces the height of adsorption is known to satisfy this need.

Here we report the normal-incidence x-ray standing waves data on the adsorption height of the classical aromatic molecule benzene on Ag(111) and Cu(111) surfaces. In these systems the contribution of vdW interactions to the bonding is meant to be dominant. To identify the effect of additional chemical interaction channels, we furthermore studied the adsorption of azobenzene, a molecule containing two benzene rings linked by a diazo-bridge. Achieved experimental results are compared to density functional theory calculations.