

## O 75: Metal substrates: Adsorption of organic / bio molecules VIII

Time: Thursday 15:00–17:00

Location: PHY C213

O 75.1 Thu 15:00 PHY C213

**Self-assembled structures of a molecular switch on Ag(111)** — ●KONRAD BOOM<sup>1</sup>, ANDREAS SCHAATE<sup>2</sup>, BORIS UFER<sup>2</sup>, PETER BEHRENS<sup>2</sup>, JÖRG HENZL<sup>1</sup>, and KARINA MORGENSTERN<sup>1</sup> — <sup>1</sup>Leibniz Universität Hannover, Institut für Festkörperphysik, ATMOS, Appelstraße 2, 30167 Hannover — <sup>2</sup>Leibniz Universität Hannover, Institut für Anorganische Chemie, AK Festkörper- und Materialchemie, Callinstrasse 9, 30167 Hannover

Molecular switches are a potential answer to meet future requirements of electronics. We investigated one possible molecule, p-hydroxy-azobenzene, on Ag(111) with a low-temperature STM. A coverage of 0.6 ML was deposited at a sample temperature of 213–233K. With these parameters p-hydroxy-azobenzene self-assembles into islands with varying local densities. In some areas the molecules build regular, symmetric, and reoccurring structures. These structures are classified depending on density and regularity. For special structures the molecules have different apparent heights. In some of the structures, it is possible to induce isomerisation of single molecules. The main requirement for that is enough space around the switching molecule. In this presentation we show the classification of the structures and give some examples for likely bindings in prominent structures. Possible origins of the apparent height difference will be discussed.

O 75.2 Thu 15:15 PHY C213

**Reversible switching of ex-situ surface mounted molecular switches probed by laser-based photoemission.** — ●NILS HEINEMANN<sup>1</sup>, JAN GRUNAU<sup>1</sup>, TILL LEISSNER<sup>1</sup>, SONJA KUHN<sup>1</sup>, DORDANEH ZARGARANI<sup>2</sup>, ULRICH JUNG<sup>1</sup>, OLEKSIY ANDREEV<sup>1</sup>, RAINER HERGES<sup>2</sup>, OLAF MAGNUSSEN<sup>1</sup>, and MICHAEL BAUER<sup>1</sup> — <sup>1</sup>Inst. f. Exp. u. Angew. Phys., Uni Kiel — <sup>2</sup>Inst. f. Org. Chem., Uni Kiel

Molecular electronics hold the potential as boom town of nanotechnology. The controlled manipulation of molecular switches adsorbed on surfaces is a key prerequisite to advance into more sophisticated applications. In this contribution we will present a photoemission study of the molecular switch 3-(4-(4-Hexylphenylazo)-phenoxy)-propan-1-thiol adsorbed on Au(111) single crystal (1/Au).

This molecule undergoes trans-cis isomerisation upon absorption of UV light (365 nm), the back-isomerisation is induced by absorption of blue light (440 nm) or thermal activation. With regard of application, we chose an ex-situ preparation for the experiments, i. e. deposition from solution. The switching behavior of these samples was investigated with photoemission spectroscopy under UHV conditions, using the fourth harmonic laser light of a tuneable 80 MHz fs-laser system.

In our study we were able to follow the reversible switching between the trans- and the cis-isomere of 1/Au, induced by photo-thermal and photo-photo stimulation. The quantitative analysis of our data show that only a minor fraction of the adsorbed molecules undergo a switching indicating the potential relevance of substrate and/or film defects in this process.

O 75.3 Thu 15:30 PHY C213

**Isomerization Dynamics of Adsorbed Molecular Switches: A ΔSCF Density-Functional Theory Study** — ●REINHARD J. MAURER and KARSTEN REUTER — Department Chemie, Technische Universität München

Stabilizing molecules at solid surfaces and switching them reversibly between defined states would be a key component of a future molecular nanotechnology. Adsorption at metal surfaces is of particular interest as it could lead to novel functionality in form of isomerization mechanisms not present in gas-phase or solution. Recent experiments indeed suggest such a photo-induced mechanism for tetra-tert-butyl functionalized azobenzene (TBA) at Au(111) [1], involving electron transfer from the molecule to a photo-excited hole in the metal *d*-band.

Addressing this suggestion with first-principles modeling requires a numerically highly efficient approach to make the calculations of photo-excited molecular motion at the extended surface tractable. To this end we explore a density-functional theory based Delta self-consistent field approach and assess its reliability for a test set of small, related molecules against higher-level theory. Obtaining encouraging results we proceed to a discussion of azobenzene and TBA in excited states corresponding to the suggested hole-mechanism. [1] S. Hagen *et al.*, J. Chem. Phys. **129**, 164102 (2008).

O 75.4 Thu 15:45 PHY C213

**Coverage and temperature driven isomerization of TBI on Au(111)** — ●CORNELIUS GAHL<sup>1</sup>, DANIEL BRETE<sup>1</sup>, ROBERT CARLEY<sup>1</sup>, ROLAND SCHMIDT<sup>1</sup>, ERIK R. MCNELLIS<sup>2</sup>, KARSTEN REUTER<sup>2,3</sup>, PETRA TEGEDER<sup>4</sup>, JOHANNES MIELKE<sup>2</sup>, LEONHARD GRILL<sup>2</sup>, and MARTIN WEINELT<sup>1,4</sup> — <sup>1</sup>Max-Born-Institut, Max-Born-Str. 2a, 12489 Berlin — <sup>2</sup>Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin — <sup>3</sup>Technische Universität München, Lichtenbergstr. 4, 85747 Garching — <sup>4</sup>Freie Universität Berlin, Arnimallee 14, 14195 Berlin

Tetra-*tert*-butyl azobenzene (TBA) is one of the few examples of molecular switches which have been successfully photoisomerized after adsorption on a metal surface. We have now studied the corresponding imine, N-(3,5-di-*tert*-butylbenzylidene)-3,5-di-*tert*-butylaniline, referred to as TBI, by core-level spectroscopy, STM and dispersion corrected DFT. Although isomerization of TBI/Au(111) could not be optically induced, the molecules can run through a complete thermally driven isomerisation cycle. At 210 K TBI adsorbs in *trans*-conformation. Upon annealing to 320 K a bilayer of *trans*-TBI is transformed into a densely packed *cis*-monolayer. Further heating to 420 K results in desorption of half of the molecules leaving a close-packed *trans*-monolayer. Experiment and theory result in a consistent picture of the molecular adsorption geometry for both isomers as well as the lateral layer structures. The isomerization reaction is governed by the activation energy as well as the interplay of adsorption energies (*cis* < *trans*) and maximal monolayer coverage (*cis* > *trans*).

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**Intramolecular proton transfer: surface-confined porphyrins as four-level conductance switches** — ●KNUD SEUFERT, WILI AUWÄRTER, FELIX BISCHOFF, DAVID ÉCIJA, SARANYAN VIJAYARAGHAVAN, and JOHANNES V. BARTH — Physik Department E20, TUM, Germany

Free-base porphyrins accommodate two protons bound at opposing nitrogen positions in the macrocycle. The saddle-shape deformation of 2H-TPP anchored on a Ag(111) surface leads to two different configurations for every molecule, represented by a 90° rotation of the hydrogen pair. By using a low-temperature STM to apply a tunneling current, we induce a proton transfer and thus can switch the 2H-TPP reversibly between these two configurations. Controlled voltage pulses lead to a single or double deprotonation of the macrocycle resulting in 1H-TPP or TPP species. In the first case, the remaining hydrogen has four possible positions that can be clearly identified in high-resolution STM images. Again, a tunneling current applied at a bias voltage above a given threshold induces the transfer of the proton between the different nitrogens. This switching process can be directly monitored by recording I(t) traces. We present a statistical analysis of the proton transfer rate as a function of bias voltage and current. The linear current dependence of the switching events for both the 2H-TPPs and the 1H-TPPs points to a single electron process, where twice as many electrons are necessary for the case of two protons. This is related to a transition state represented by two hydrogens in a cis-like configuration that can relax either into the initial state or the rotated configuration.

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**Switching and electron transport through Sn-Phthalocyanin** — ●YONGFENG WANG<sup>1</sup>, JÖRG KRÖGER<sup>2</sup>, and RICHARD BERNDT<sup>1</sup> — <sup>1</sup>IEAP, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany — <sup>2</sup>Technische Universität Ilmenau, 98684 Ilmenau

SnPc exhibits two configurations (SnPc-up and SnPc-down) upon adsorption on Ag(111). A localized but irreversible conformational switching from up to down state was obtained on the bare Ag(111) surface. From the second layer, local and reversible switching was achieved via resonant electron or hole injection into molecular orbitals.

SnPc molecules adsorbed on Ag(111) were contacted with the tip of a STM. Orders-of-magnitude variations of the single-molecule junction conductance were achieved by controllably dehydrogenating the molecule and by modifying the atomic structure of the surface electrode. Nonequilibrium Green's function calculations reproduce the trend of the conductance and visualize the current flow through the junction, which is guided through molecule-electrode chemical bonds.

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**Molecular switching analyzed with sub-molecular precision: CuPc on Cu(111)** — ●JOHANNES SCHAFFERT<sup>1</sup>, MAREN COTTIN<sup>1</sup>, ANDREAS SONNTAG<sup>1</sup>, HATICE KARACUBAN<sup>1</sup>, NICOLÁS LORENTE<sup>2</sup>, CHRISTIAN BOBISCH<sup>1</sup>, and ROLF MÖLLER<sup>1</sup> — <sup>1</sup>Faculty of Physics, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany — <sup>2</sup>Centro de Investigación en Nanociencia y Nanotecnología, Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

The current fluctuations in Scanning Tunneling Microscopy and Spectroscopy have been analyzed in real time using special analogue electronics. This type of Scanning Action Microscopy technique allows to map topography and switching processes simultaneously. For the Cu-Phthalocyanine (CuPc) molecule on Cu(111), switching between two states is observed. The switching frequency, the switching amplitude and the ratio between the residence times in the observed states can be studied with Angstrom spacial resolution. Spectroscopic data obtained at 7K yields information about the involved electronic states. Based on the experimental data as well as DFT calculations a model will be presented. The CuPc molecule switches between different adsorption configurations, which are attributed to different angles of molecular rotation on the Cu(111) surface.

O 75.8 Thu 16:45 PHY C213

**Electronic Structure of a Spiropyran Derived Molecular Switch in Direct Contact with the Au(111) Surface** — ●CHRISTOPHER BRONNER, GUNNAR SCHULZE, KATHARINA J. FRANKE, JOSÉ IGNACIO PASCUAL, and PETRA TEGEDER — Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany

As nanometer scale phenomena advance into the grasp of technological application, the potential building blocks of molecular electronics and sensorics are studied in detail. Surface-bound molecular switches are of particular interest, since the functionality of the substrate/adsorbate system can be switched by an external stimulus.

We present combined two-photon photoemission (2PPE) and scanning tunneling spectroscopy (STS) investigations of a nitro-spiropyran derivative's occupied and unoccupied electronic states at the Au(111) surface in both its open and closed form. Both forms exhibit significant differences in the electronic structure which allows following a potential ring-opening/closure reaction. Resonant electron tunneling from the STM tip into the LUMO of the adsorbate molecule induced ring-opening, while the corresponding photon driven process via transfer of electrons from the substrate to the adsorbate turned out to be inefficient. The loss of the molecule's functionality is attributed to a strong electronic coupling between adsorbate and metallic substrate and accordingly to short lifetimes of molecular excited states.