

O 29: Organic/bio Molecules on Metal Surfaces III

Time: Tuesday 10:30–13:15

Location: H38

O 29.1 Tue 10:30 H38

Optically and thermally induced reactions of an azobenzene derivative on Bi(111) — ●CHRISTOPHER BRONNER¹, BEATE PRIEWISCH², KAROLA RÜCK-BRAUN², and PETRA TEGEDER^{1,3} — ¹Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany — ²Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 115, 10623 Berlin, Germany — ³Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

Molecular switches which undergo photo-induced isomerization reactions are considered promising building blocks in the development of nanotechnological devices such as data storage, molecular electronics or functionalized surfaces. Generally, such systems are envisioned to be mounted at surfaces or interfaces of solids. However, the majority of such molecules lose their switching functionality when adsorbed directly on a (metal) surface, which is usually attributed to electronic coupling and/or steric hindrance. Controlled tuning of the coupling strength in these adsorbate/substrate systems is therefore considered crucial to restore functionality.

We found that di-meta-cyano-azobenzene (DMC) adsorbed on a semi-metallic bismuth substrate undergoes a photo-induced trans-cis isomerization reaction both in the first layer and the multilayer, while the photo-induced back-reaction is not observed. In addition, we found a thermally activated reaction of the cis isomer.

O 29.2 Tue 10:45 H38

The effect of molecular coverage and molecular vibrations on the adsorption geometry of azobenzene on Ag(111) — ●GIUSEPPE MERCURIO^{1,2}, REINHARD MAURER³, WEI LIU⁴, SEBASTIAN HAGEN⁵, FELIX LEYSSNER⁵, JÖRG MEYER³, ALEXANDRE TKATCHENKO⁴, PETRA TEGEDER⁵, SERGEY SOUBATCH^{1,2}, KARSTEN REUTER³, and FRANK STEFAN TAUTZ^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ²Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology — ³Department Chemie, TU München, Germany — ⁴Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ⁵Freie Universität Berlin, Fachbereich Physik, Berlin, Germany

Experimentally determined adsorption geometries of molecular switches are essential both for understanding their functionality and for benchmarking *ab initio* calculations. We investigate a prototypical molecular switch, i.e. azobenzene (AB), on the Ag(111) surface by means of the normal incidence x-ray standing wave (NIXSW) technique and dispersion-corrected density-functional theory (DFT) calculations. We find that the inclusion of non-local many-body screening in the DFT+vdW^{surf} scheme [1] improves the description of AB. Coverage-dependent calculations reveal the most stable AB packing on Ag(111). The best agreement with NIXSW data is obtained if the additional effect of molecular anharmonic vibrations on the energetically most favorable AB adsorption geometry is taken into account.

[1] V. Ruiz et al. Phys. Rev. Lett. 108, 146103 (2012).

O 29.3 Tue 11:00 H38

Computationally efficient excited state properties of hybrid organic/inorganic systems: dynamics and spectroscopy with Delta Self-Consistent-Field Density Functional Theory (Δ SCF-DFT) — ●REINHARD J. MAURER and KARSTEN REUTER — Technische Universität München, Lichtenbergstrasse 4, 85748 Garching, Germany

Understanding photon- or electron-induced changes in functional molecules adsorbed on well defined substrates forms the basis for rational molecular device design. Predictive-quality *ab initio* modelling of such surface-mounted devices has to be able to supply spectroscopic properties, not just accurately, but also in a computationally efficient manner. Current methods lack either the one or the other property. In this context, we present an approach further extending recent developments in Δ -Self-Consistent-Field Density-Functional-Theory (Δ SCF-DFT) [1].

We illustrate the rationale behind our approach and its performance for organic molecules adsorbed at metal surfaces. The method yields a topologically correct description of excited state potential energy surfaces and an accurate simulation of spectroscopic properties, such as photoemission or photoadsorption. Although a prior knowledge of

the corresponding gas-phase properties of the adsorbate and cautious benchmarking are prerequisites to reliable results, the method can be readily applied to a variety of systems. [1] Gavnholt *et. al.*, PRB **78**, 075441 (2008).

O 29.4 Tue 11:15 H38

Dynamics of charging and bond formation of adsorbates on an ultrathin, insulating film supported by a metal substrate: A density functional study based on the perfect conductor model — ●IVAN SCIVETTI and MATS PERSSON — Surface Science Research Centre, the University of Liverpool, Liverpool L69 3BX, UK

The ability to characterise and manipulate single atoms and molecules on ultrathin, insulating films by scanning tunnelling probe techniques has opened up a new frontier in atomic scale science. A most interesting aspect of these systems is the decoupling of the electronic states of the adsorbates from the metal substrate, which still allows for characterisation and manipulation by tunnelling electrons.

The description of the electronic and geometric structure and the dynamics of these systems exhibiting multiple charge states is very challenging for theory. Density Functional Theory (DFT) calculations are in many cases prohibitive because of the size of these systems and the delocalization error in current exchange-correlation functionals. In this work, we present a new simplified DFT scheme in which the metallic support is replaced by a perfect conductor. This scheme circumvents the limitations of standard DFT and allows us to treat various charge states of adsorbates, together with a considerable reduction of the computational effort. In particular, we are able to carry out *ab-initio* molecular dynamics on an excited (charged) state potential energy surface. We will show some interesting applications of this scheme to different charge states of metal adatoms and the dynamics of reversible bond formation in a metallo-organic molecule.

O 29.5 Tue 11:30 H38

Energetics of azobenzenes on noble metal surfaces — ●MICHAEL SCHULZE¹, REINHARD MAURER², CHRISTOPHER BRONNER¹, KARSTEN REUTER², and PETRA TEGEDER^{1,3} — ¹Freie Universität Berlin, Fachbereich Physik — ²TU München, Theoretische Chemie — ³Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut

Temperature programmed desorption measurements and density-functional theory (DFT) calculations have been employed, to investigate the adsorption properties, in particular the binding energies, of azobenzenes on noble metal surfaces. The studied systems are the unsubstituted azobenzene and tetra-tert-butyl-azobenzene (TBA) on Au(111) and Ag(111), respectively. The only photoisomerizing system out of the four, TBA/Au(111), has been found to be the one with the strongest binding energy. These findings are explained by the larger bending angle of the molecule and the energetic overlap and hence a hybridization of the highest occupied molecular orbital (HOMO) of TBA with the Au(111) d-bands, which has also been proposed in order to elucidate the excitation mechanism in the photoisomerization [1].

[1] Ch.Bronner, M. Schulze et al 2012 New J. Phys. 14 043023

O 29.6 Tue 11:45 H38

Photo-switching of diluted azobenzene-based SAMs on Au(111) — ●THOMAS MOLDT¹, DANIEL BRETE¹, DANIEL PRZYREMBEL¹, JOEL R. GOLDMAN², RAFAL KLAJN², CORNELIUS GAHL¹, and MARTIN WEINELT¹ — ¹Freie Universität Berlin, Department of Physics, Arnimallee 14, 14195 Berlin — ²Weizmann Institute of Science, Department of Organic Chemistry, 76100 Rehovot, Israel

Photoisomerization of azobenzene within densely packed self-assembled monolayers (SAMs) of azobenzene-terminated alkanethiols is strongly suppressed.[1,2]. This is attributed to steric hindering [2] and/or excitonic coupling [3] among the chromophores. In this work we examine SAMs of 11-[(4-phenylazo)phenoxy]-undecane-1-thiol diluted with dodecane-1-thiol prepared by co-adsorption from solution. By differential reflectance spectroscopy (DRS) we demonstrate that the molecules self-assemble at the Au(111) surface whereby the azobenzene concentration is adjustable through the relative concentrations in solution. The azobenzene chromophores form aggregates with the excitonic shift of the S_2 absorption band decreasing with dilution. In addition near-edge X-ray absorption fine structure spectroscopy (NEXAFS) re-

veals changes of the orientation of the azobenzene photoswitch in the pure and mixed SAMs. In contrast to the pure azobenzene SAM, the mixed SAMs can be optically switched with high quantum efficiency.

- [1] Evans et al., *Langmuir*, 1998, **14**, 6436-6440
 [2] Wang et al., *J. Electroanal. Chem.*, 1997, **438**, 213-219
 [3] Gahl et al., *J. Am. Chem. Soc.*, 2010, **132**, 1831-1838

O 29.7 Tue 12:00 H38

On-Surface Polymerization of 1,4-Diethynylbenzene on Cu(111) — ●JOHANNA EICHHORN^{1,2}, WOLFGANG M. HECKL^{1,2}, and MARKUS LACKINGER^{1,2} — ¹Department of Physics & TUM School of Education, Tech. Univ. Munich, 80799 Munich, Germany — ²Deutsches Museum, 80538 Munich, Germany

The last decade has witnessed a growing interest in the use of organic materials in light-emitting diodes, and optoelectronic devices. In this context, the conjugated polymer poly(phenylene butadiynylene) has shown promising properties like photo-, and electroluminescence.[1] A previous study already reported that 1,4-diethynylbenzene (DEB) can be polymerized into PPB strands within Cu²⁺ functionalized mesoporous materials.[2] For a more facile preparation, we study polymerization of DEB on catalytically active Cu(111) surfaces by means of ultra-high vacuum scanning tunneling microscopy.

Upon adsorption at room temperature, DEB self-assembles into a densely packed structure controlled by weak hydrogen bonds (C-H...triple bond). Subsequent thermal annealing results in drastic structural changes, where wormlike chains containing Y-shaped trimers, cross-linked tetramers and dumbbell shaped hexamers were observed. The thermal stability of these surface-supported structures extends up to 450°C, thereby proofing covalent bond formation. The observed topology of the covalent networks can only be explained by at least two different coupling schemes: di- and trimerization.

- [1] X. Zhan, et al., *Adv. Mater.*, 2000, **12**, 51-53.
 [2] V. S.-Y. Lin, et al., *J. Am. Chem. Soc.*, 2002, **124**, 9040-9041.

O 29.8 Tue 12:15 H38

From physisorption to chemisorption: tuning the interaction of cyclooctatetraene with noble metal surfaces — ●MARTIN CALLEN¹, HASMIK HARUTYUNYAN², TOBIAS ALLMERS², NICOLAE ATODIRESEI¹, VASILE CACIUC¹, DANIEL WEGNER², and STEFAN BLÜGEL¹ — ¹Peter Grünberg Institut (PGI-1) and Institute for Advanced Simulation (IAS-1), Forschungszentrum Jülich and JARA, 52425 Jülich, Germany — ²Physikalisches Institut and Center for Nanotechnology (CeNTech) Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

Embedding specifically designed organic molecules into molecular devices or connecting them to an electronic circuit is a technological relevant aspect of molecular electronics. Recently designing molecular switches as one class of possible applications either by redox reactions or by conformational changes has been pursued. In a combined STM and DFT study we have investigated cyclooctatetraene (COT) adsorbed on different noble metal substrates as a possible candidate for a conformational switch. The role of charged states which change the conformation of COT in the gas phase is taken by the different strength of hybridization between the COT molecule and the surface. Long range dispersion interactions have been taken into account via a semi-empirical approach [1] and the non-local xc-functional vdW-DF [2] as implemented in a recent version of the JuNoLo code [3].

- [1] S. Grimme *et al.*, *J. Chem. Phys.* **132**, 154104 (2010)
 [2] M. Dion *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004)
 [3] M. Callen *et al.*, *Phys. Rev. B* **86**, 085439 (2012)

O 29.9 Tue 12:30 H38

Adsorption of V-TCNE on Ag(001): results from ab-initio calculations — ●THORSTEN DEILMANN, PETER KRÜGER und MICHAEL ROHLFING — Institut für Festkörpertheorie, Universität Münster, D-48149 Münster, Germany

Organic molecules coupled to transition metal atoms offer interesting physical properties like large magnetic moments. Recently, Wegner et al. [1] have shown that tetracyanoethylen (TCNE) and vanadium on Ag(001) can be induced by STM manipulation to form a strong che-

mical bond. Here, we present a theoretical study on the adsorption of V-TCNE on Ag(001). Optimized structures, adsorption energies, electronic and magnetic properties have been calculated employing density-functional theory. TCNE adsorbs in *on top* position with the nitrogen atoms bound to Ag surface atoms. Due to the interaction with the surface, an electron transfer occurs and the molecule is negatively charged. The calculated density of states, as well as the simulated STS and STM images show good agreement with respective experimental data [1].

Addition of vanadium leads to a spin-polarized system. We find that V atoms adsorb only at the *hollow* position on Ag(001). In the energetically most favored structure of V-TCNE, two nitrogen atoms are bound to a vanadium atom. Close to the Fermi level, the local density of states shows a dominant V induced peak that is distinctly broadened due to the molecule-substrate interaction.

- [1] D. Wegner et al., *Phys. Rev. Lett.* **103**, 087205 (2009)

O 29.10 Tue 12:45 H38

Trimesic acid-assisted self-assembly of oligoethynylene-thiophene macrocycles: A donor-acceptor rectifier bilayer — ●JOSE D. COJAL¹, MASAHIKO IYODA², and JÜRGEN P. RABE¹ — ¹Department of Physics, Humboldt-Universität zu Berlin, Berlin, Germany — ²Department of Chemistry, Tokyo Metropolitan University, Tokyo, Japan

Fully conjugated π -expanded macrocyclic oligothiophenes [1] have attracted considerable interest due to their structural and optoelectronic properties. They have been envisaged for photovoltaic applications, host-guest systems and as building blocks of supramolecular nanostructures. Here, a self-assembled monolayer of trimesic acid (TMA) at the interface between its heptanoic acid solution and highly oriented pyrolytic graphite (HOPG) provided a way to template the 2D self-assembly of oligoethynylene-thiophene macrocycles. The so-formed bilayer was confirmed using STM tomography [2], i.e. discrete bias set-point imaging of each layer. Scanning Tunneling Spectroscopy of the macrocycle layer allowed us to determine the HOMO-LUMO gap of the bilayer and the position of the combined frontier orbitals. The I-V characteristics revealed an underneath TMA layer with acceptor (A) characteristics and an upper donor (D) macrocycle layer, forming a D-A rectifier bilayer.

- [1] K. Nakao, M. Nishimura, T. Tamachi, Y. Kuwatani, H. Miyasaka, T. Nishinaga and M. Iyoda, *J. Am. Chem. Soc.* **128** (2006) 16740
 [2] C. Seifert, D. Skuridina, X. Dou, K. Müllen, N. Severin and J. P. Rabe, *Phys. Rev. B* **80** (2009) 245429

O 29.11 Tue 13:00 H38

Investigation of Mn₁₂ single molecule magnets on surfaces deposited by means of electrospray ionization — ●PHILIPP ERLER¹, STEFAN AMBRUS², SEBASTIAN HÖLL¹, SAMUEL BOUVRON¹, ULRICH GROTH², ELIZABETA CAVAR¹, and MIKHAIL FONIN¹ — ¹Fachbereich Physik, Universität Konstanz, 78457 Konstanz — ²Fachbereich Chemie, Universität Konstanz, 78457 Konstanz

Single molecule magnets (SMMs), like Mn₁₂-acetate, have attracted significant interest during the past decades due to their unique magnetic properties like hysteresis of pure molecular origin and the possibility to observe quantum tunneling of magnetization. This material class allows for basic studies on quantum effects of magnetism on the molecular scale and is furthermore a promising candidate for preliminary studies aiming at ultrahigh density data storage devices or quantum computing applications. However, progress in this field is hindered by the difficulty of depositing intact SMMs on surfaces.

Here we present a study of Mn₁₂-acetate molecules deposited on different noble metal surfaces by means of electrospray ionization in ultra high vacuum. In contrast to wet chemical preparation procedures, this method offers the advantages of a high sample quality, full control over the surface coverage and a free choice of the substrate and the molecular ligand shell. We studied the structural and electronic properties of sub-monolayers of Mn₁₂ molecules using low temperature scanning tunneling microscopy and spectroscopy (STM/STS). Molecular islands, chain like structures as well as individual clusters were investigated.