O 56: Metal substrates: Adsorption of organic / bio molecules VI

Time: Wednesday 15:00–17:30 Location: H36

O 56.1 Wed 15:00 H36

Electron induced conformational changes of imine-based molecular switches on a Au(111) surface — •Christian Lotze[1], Ying Luo[2], Rainer Haag[2], and Jose Ignacio Pascual[1] — [1]Inst. f. Experimentalphysik, Freie Universität Berlin — [2]Inst. f. organische Chemie, Freie Universität Berlin

Organic molecules exhibiting controllable reversible transitions between isomeric states on surfaces promise an enormous potential in the field of molecular electronics. The reversible cis-trans isomerization of azobenzene-like molecules is often hindered by a strong interaction of the nitrogen lone-pair electrons of the di-azo bridge (-N=N-) with the substrate. In order to improve the isomerization capabilities, the di-azo bridge is substituted by an imine-group (-N=CH-).

Here, we use low-temperature scanning tunneling microscopy to investigate a sub-monolayer of the newly designed imine-based molecular switch NPCI on a Au(111) surface. Its carboxylic termination mediates the formation of hydrogen-bonded dimers, which align in rows along the herringbone reconstruction. We were able to induce reversible conformational changes with the tunneling electrons from the STM tip and determine its efficiency as a function of electron energy.

O 56.2 Wed 15:15 H36

Optical Isomerization of tetra(*tert*-butyl)azobenzene (TBA) on Gold (111) and Coverage Dependent Conformation of the Corresponding Imine — •Daniel Brete[1], Roland Schmidt[1], Cornelius Gahl[1], Robert Carley[1], Sebastian Hagen[2], Petra Tegeder[2], and Martin Weinelt[1,2] — [1]Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin — [2]Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin

NEXAFS and XPS have been used to investigate optically induced conformational changes of 3,3',5,5'-tetra(*tert*-butyl)azobenzene (TBA) monolayers and the influence of coverage and temperature on the conformation of the analogue imine 3,5-di-*tert*-butylbenzaldehyde-(3,5-di-*tert*-butyl-phenylimine)(TBI) on gold (111) surfaces.

Monolayers of TBA adsorb flat on the surface. Upon illumination with blue light TBA is transformed into a non-planar configuration. This change is thermally reversible. The photoisomerization cross section of TBA is reduced by two orders of magnitude compared to solution suggesting a substrate induced photoisomerization mechanism.

In contrast the monolayer of TBI exhibits a non-planar configuration, while submonolayers obtained by partial desorption exhibit a planar adsorbtion geometry. Both are very similar to the non-planar and planar species of TBA. We conclude that the energy gained by a higher packing density favours the non-planar configuration in the case of TBI.

O 56.3 Wed 15:30 H36

Single enantiomorphism and chiral conflict in 2D crystals — •Christian Roth, Leo Merz, Manfred Parschau, and Karl-Heinz Ernst — Nanoscale Materials Science, Empa, Swiss Federal Laboratories for Materials Testing and Research, Dübendorf, Switzerland

In order to investigate chiral recognition on the molecular level, we investigated the effect of chiral doping of monolayers of tartaric acid (TA), malic acid (MA) and succinic acid (SU) with STM and LEED. We reported earlier that doping achiral SU with a small amount of chiral TA leads to single chirality (sergeants-and-soldiers effect) [1]. Here we present results of cross-contamination experiments of TA and MA. The mixture of left and right handed TA (rac-TA) shows a superposition of the two enantiomorphs in LEED that are observed for the pure enantiomers. Adding one enantiomer of MA to the mixture suppresses formation of the two enantiomorphs. (R)-MA allows thereby only the formation of the structure known for pure (R,R)-TA, while (S)-MA leads to the (S,S)-enantiomorph. Mixing chiral (R,R)-TA into rac-MA leads indeed to single enantiomorphism as well, however, this time the structure is a completely new polymorph that has not been observed for pure MA. Two different mechanisms are proposed for the observed results: an entropy driven effect in the rac-TA / MA experiment and a chiral conflict in the rac-MA / TA case.

References

[1] M. Parschau, S. Romer and K.-H. Ernst 2004 J. Am. Chem. Soc.126 15398

O 56.4 Wed 15:45 H36

The Role of Functional Groups for the Switching Efficiency of Surface-Adsorbed Molecular Switches — •Erik R. McNellis[1] and Karsten Reuter[1,2] — [1]Fritz-Haber-Institut Berlin (Germany) — [2]Technische Universität München (Germany)

Azobenzene (C_6H_5-N=N-C_6H_5) adsorbed at coinage metal surfaces has transformed into an increasingly studied prototype system for a surface-adsorbed molecular switch. With photo-induced switching between the cis and trans configuration suppressed for bare azobenzene, controlled decoupling from the surface through bulky functional groups appears as a promising strategy. In particular, tetra-tert-butyl azobenzene (TBA), in which groups of three butyl (CH_3) groups are added to both meta positions of each phenyl ring, can be efficiently switched at Au(111), albeit not at Ag(111). In order to shed more light on the role of the functional groups and surface electronic structure for the different switching efficiency we perform density-functional theory calculations, accounting for van der Waals interactions on the level of semi-empirical dispersion correction schemes. The thereby obtained structural and vibrational properties of both bare azobenzene and TBA at Ag(111) and Au(111) compare favorably with existing experimental data. In the analysis of the electronic structure we focus on the hybridization of the molecular frontier orbitals with the substrate states, and discuss this in the context of previously published hypotheses concerning the switching mechanism of surface-adsorbed TBA.

O 56.5 Wed 16:00 H36

Reversible photoisomerization of an azobenzene-functionalized self-assembled monolayer probed by sum-frequency generation vibrational spectroscopy — •Felix Leyssner[1], Steffen Wagner[1], Christian Kördel[1], Sebastian Zarwell[2], Karola Rück-Braun[2], Martin Wolf[1], and Petra Tegeder[1] — [1]Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, D-14195 Berlin — [2]Technische Universität Berlin, Institut für Chemie, Strasse des 17. Juni 135, D-10623 Berlin

We studied the reversible photoinduced *trans/cis*-isomerization of an azobenzene-functionalized self-assembled monolayer on a gold substrate using sum-frequency generation (SFG) vibrational spectroscopy. A cyano-group in *para*-position at the outer phenyl-ring is utilized as a marker to directly investigate the molecular orientation and therefore the switching state. The azobenzene unit is connected to a tripodal linker system with an adamantane core. This linker system provides: i) an adequate free volume to prevent steric hindrance and ii) sufficient decoupling from the metallic substrate to enable the isomerization process. Light exposure at a wavelength of 405 nm induces the *trans* → *cis* isomerization whereas illumination at 470 nm leads to the back reaction. The effective cross section for the photoinduced *trans* → *cis* reaction at 405 nm is $\sigma_{eff}(cis) = 4 \pm 1 \times 10^{-18} cm^2$, while for the back reaction (*cis* → *trans*) at 470 nm we obtain $\sigma_{eff}(trans) = 2.5 \pm 0.9 \times 10^{-19} cm^2$. Our study demonstrates that SFG vibrational spectroscopy is a highly suitable technique to analyze the molecular structure of functional surfaces.

O 56.6 Wed 16:15 H36

Structure and energetics of azobenzene on Ag(111) — •Giuseppe Mercurio[1,2], Erik McNellis[3], Isabel Martin[4], Sebastian Hagen[4], Felix Leyssner[4], Sergey Soubatch[1,2], Jörg Meyer[3], Martin Wolf[3,4], Petra Tegeder[4], Frank Stefan Tautz[1,2], and Karsten Reuter[3] — [1]Institut für Bio- und Nanosysteme 3, Forschungszentrum Jülich, 52425 Jülich, Germany — [2]JARA-Fundamentals of Future Information Technology — [3]Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany — [4]Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany

Normal Incidence X-ray Standing Wave (NIXSW) and Temperature Programmed Desorption experiments have been performed in order to determine the adsorption geometry of azobenzene on Ag(111), i.e. to define the following key parameters: vertical adsorption height of N=N bridge, tilt angle of the phenyl rings, and adsorption energy. Experimental results suggest nearly planar adsorption geometry of the azobenzene molecule, with the nitrogen atoms at a height of 3.07 Å. Adsorption energy was found to be 1.08 eV. The determined geometry is in good agreement with the theoretically predicted values (2.98 Å and 3°) obtained by DFT with semi-empirical dispersion corrections, validating therefore this calculation method. Discrepancy between experimental and theoretical adsorption energy was attributed to electronic screening of dispersive interactions at the metallic surface.

O 56.7 Wed 16:30 H36

Studies of azobenzene-containing triazatriangulenium adlayers on Au(111) surfaces — •Ulrich Jung[1], Sonja Kuhn[1], Mathias Müller[1], Olena Filinova[1], Belinda Baisch[1], Jens Kubitschke[2], Rainer Herges[2], and Olaf Magnussen[1] — [1]Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Leibnizstraße 19, 24118 Kiel, Germany — [2]Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 3, 24098 Kiel, Germany

The attachment of molecular functions such as photoswitches to metal surfaces is of major interest in nanotechnology. One of the most frequently studied class of photoswitches are azobenzenes, which exhibit trans-cis isomerism. The typical method to attach azobenzene to surfaces is self-assembly of thiols on Au. However, in such adlayers the photoisomerization is often totally quenched because of steric effects. To overcome the problems of conventional azobenzene adlayers, we were employing a novel approach using customizable triazatriangulenium (TATA) platforms [1]. Here, we will present the structure and photoswitching properties of azobenzene-containing TATA adlayers on Au(111), obtained by structure-sensitive, spectroscopic, and electrochemical methods. Functionalized TATA molecules exhibit a strong tendency to form bilayers. We will demonstrate, that it is possible to suppress bilayer formation and thus to form highly-ordered functionalized TATA monolayers. Furthermore, the photoswitching processes in these adlayers obey first order kinetics with quantum efficiencies of < 10-3. [1] Baisch et al., J. Am. Chem. Soc. (2009), 131, 442

O 56.8 Wed 16:45 H36

Surface mounted molecular rotors with variable functional groups and rotation radii — •Dingyong Zhong[1], Tobias Blömker[2], Katrin Wedeking[2], Lifeng Chi[1], Gerhard Erker[2], and Harald Fuchs[1,3] — [1]Physikalisches Institut, Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany & Center for Nanotechnology (CeNTech), Universität Münster, Heisenbergstr. 11 , 48149 Münster, Germany — [2]Organisch-Chemisches Institut, Universität Münster, Corresstr. 40, 48149 Münster, Germany — [3]Institut für Nanotechnologie, Forschungszentrum Karlsruhe, 76021 Karlsruhe, Germany

A strategy for designing and activating surface-mounted molecular rotors with variable rotation radii and functional groups is proposed and demonstrated. The key point of the strategy is to separate the anchor and the rotating functional group from each other by using a connector of adjustable length. The three independent parts of the molecule are responsible for different functions to support the rotating movement of the molecule as a whole. In this way, one can easily change each part to obtain molecular rotors with different sizes, anchors, and functional rotating groups.

O 56.9 Wed 17:00 H36

Repulsion Between Molecules on a Metal: (Sub-) Monolayers of Hexa-*peri*-hexabenzocoronene on Au(111) — •Christian Wagner[1,3], Daniel Kasemann[1], Roman Forker[1,2], and Torsten Fritz[1,2] — [1]Inst. für Angewandte Photophysik, TU Dresden — [2]Inst. für Festkörperphysik, FSU Jena — [3]Inst. für Bio- und Nanosysteme 3, FZ Jülich, JARA Fundamentals of Future Information Technology

We investigate the growth of hexa-*peri*-hexabenzocoronene (HBC) on Au(111) for monolayer (ML) and sub-ML coverage by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). A transition from a disordered isotropic phase at low coverage to a highly ordered phase with a coverage-dependent lattice constant at higher coverage is found and attributed to a repulsive intermolecular force. To deduce the origin of this repulsion a model is developed, containing the Coulomb and van der Waals interaction between the molecules. The metal substrate is accounted for by the inclusion of mirror charges and a dipole created by the pushback effect, while the van der Waals interaction is modeled on a force field level. The Coulomb repulsion is caused by the partially positively charged hydrogen atoms. The effect can, however, only be explained under the postulate of a screening of the attractive London forces by the metal substrate as a result of the non-additivity of dispersion forces. As the mechanisms described are rather universal they should be able to explain a similar repulsion observed for other hydrocarbons [1,2].

[1] C. Seidel et al., *Phys. Rev. B* **64**, 195418 (2001)

[2] S. Müllegger and A. Winkler, *Surf. Sci.* **600**, 1290 (2006)

O 56.10 Wed 17:15 H36

Nanojoule Calorimetry of Surface Reactions: Cyclohexene on Pt(111) — •Ole Lytken[1,2], Wanda Lew[1], Jonathan J.W. Harris[1], Ebbe K. Vestergaard[1], J. Michael Gottfried[2], and Charles T. Campbell[1] — [1]Department of Chemistry, University of Washington, Seattle, WA, USA — [2]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Erlangen, Germany

Platinum is an excellent hydrogenation/dehydrogenation catalyst. Many hydrocarbons therefore readily dehydrogenate on platinum instead of desorbing. This severely limits the usefulness of traditional desorption based techniques for measuring heats of adsorption, such as temperature programmed desorption (TPD). Cyclohexene on Pt(111) is a typical such system where reaction prevails over desorption. At 100 K cyclohexene adsorbs intact, but with increasing temperature, it dehydrogenates, forming first a partially dehydrogenated 1-cyclohexenyl species, then benzene and eventually graphite. However, unlike TPD, single-crystal microcalorimetry does not rely upon desorption and can therefore directly measure the heats of adsorption and reaction of the wealth of species formed as hydrocarbons adsorb on platinum. We have used microcalorimetry to successfully measure the heat of adsorption of cyclohexene on Pt(111) at 100 - 300 K and determined the heats of formation as a function of coverage of two adsorbed intermediates in the hydrogenation of benzene to cyclohexane, namely cyclohexene and 1-cyclohexenyl.