

O 34: Metal Substrates: Adsorption of Organic/Bio Molecules II

Time: Tuesday 13:45–16:30

Location: MA 043

O 34.1 Tue 13:45 MA 043

Conformations vs. Interaction energy: adsorption of flexible (bio)molecules on inorganic substrates — ●LUCA M. GHIRINGHELLI and LUIGI DELLE SITE — Max-Planck-Institute for Polymer Research, Ackermannweg 10, D 55021 Mainz, Germany

We present a first principle density functional study of phenylalanine interacting with three different classes of surfaces, namely a purely repulsive hard-wall, mildly interacting close packed surfaces of group 11 metals (Cu(111), Ag(111), and Au(111)), and strongly interacting close packed surfaces of group 10 metals (Ni(111), Pd(111), and Pt(111)). In particular, we characterize, by changing the substrate, the passage from the statistical behavior of a flexible molecule in the presence of the topological confinement of a hard-wall to a purely chemical behavior where the molecule, highly deformed compared to the free state, strongly binds to the surface and statistical conformations play no more a role. Such a comparative study allows to characterize some of the key aspects of the adsorption process for a prototype of flexible amino acids on experimentally and technologically relevant metal surfaces.

O 34.2 Tue 14:00 MA 043

Spectroscopic mapping of chirality at the molecular level: PVBA on Cu(111) — ●ROBIN OHMANN, LUCIA VITALI, and KLAUS KERN — Max-Planck-Institute for Solid State Research, Stuttgart, Germany

Chirality is a fundamental aspect of molecular biology and biochemistry, and is of central importance in pharmaceuticals, yet directly imaging chirality of molecules proves to be challenging. Here, we present a combined scanning tunneling microscopy (STM) and spectroscopy (STS) study of 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA) adsorbed on a Cu(111)-surface. The molecules, deposited in ultra high vacuum (UHV) via molecular beam epitaxy, have been measured at low temperature (6 K). Single PVBA molecules (monomers), which become chiral upon adsorption on the surface, dimers and linear as well as triangular ensembles consisting of more than two molecules are observed. The contribution of different molecular orbitals to the local density of states has been measured for monomers and dimers by acquiring conductance maps. This allows directly visualizing the chirality of the adsorbed molecules. In the case of dimers we found homochiral and heterochiral species, which show respectively point-symmetric and mirror-symmetric spectroscopic features. Furthermore the interaction of monomers and dimers with the surface, as revealed by the scattering of the standing waves, will be discussed.

O 34.3 Tue 14:15 MA 043

Entropy driven stabilization of oligopyridine mono- and multilayer phases on HOPG - a thermal desorption study — ●MICHAEL ROOS, HARRY E. HOSTER, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University

As shown in recent STM investigations, bis(terpyridine)derivates (BTP) form highly ordered hydrogen bonded networks on HOPG at both the solid/liquid [1] and the solid/gas [2,3] interface. In this study, we systematically investigate and compare the thermal desorption behavior for varying initial coverages of BTP molecules. We can clearly distinguish between two peaks corresponding to the mono- and multilayer regime. Surprisingly, the activation energies for desorption are about equal for both phases. Therefore, the different stabilities of mono- and multilayers must be associated with large differences in the preexponential factors, which are $\nu = 1 \cdot 10^{24} \text{ s}^{-1}$ for the zero order-like desorption from the multilayer and $\nu = 1 \cdot 10^{18} \text{ s}^{-1}$ for the submonolayer regime. In this coverage range, we find a repulsion-dominated desorption behaviour, indicated by a pronounced down-shift of the onset of desorption, which is in contradiction to the expected attractive influence of the increasing number of C-H...N bonds. The thermal desorption results can be explained in terms of transition state theory, keeping in mind the large moment of inertia of the BTP molecules.

1. C. Meier et al., J Phys Chem B 109, 21015 (2005).
2. H. E. Hoster et al., Langmuir 23, 11570 (2007).
3. A. Breitruck et al., Surf Sci 601, 4200 (2007).

O 34.4 Tue 14:30 MA 043

Analysis of structural and electronic properties of complex

molecular phases: Tetracene on Ag(111) — ●SERGEY SOUBATCH, RUSLAN TEMIROV, and STEFAN TAUTZ — Forschungszentrum Jülich, Jülich, Germany

Formation and properties of disordered and ordered phases of tetracene on Ag(111) surface have been studied using LT-STM. At submonolayer coverage, tetracene forms a disordered phase due to repulsive interactions between flat-lying molecules on the metal surface. As the coverage rises, the tetracene phase starts to order. This process is driven by a balancing of intermolecular repulsion, attraction between molecules and the substrate, and competition between the positional and rotational entropy. Two long range ordered phases can appear at the surface. The alpha-phase represents a compact monolayer of flat-lying molecules, those electronic properties are strongly affected by interaction with the metal. It is revealed by significant shift of LUMO level registered by differential conductance spectroscopy. The beta-phase has more complex structure including interfacial layer and additional layer and molecular chains on top. Whilst the molecules in more planar configuration at the interface are strongly coupled to metallic electron states of the substrate, the molecules tilted out of the metal surface and/or separated from the metal by interfacial layer are found to be decoupled. For such molecules strong effect of local environment and intermolecular interaction on the energy of LUMO level is observed. The structural model for complex tetracene beta-phase has been proposed.

O 34.5 Tue 14:45 MA 043

The Influence of Alkanespacers on the Structure of Biphenyl-alkanethiol SAMs on Au(111) Surfaces — ●MICHEL KAZEMPOOR and GERHARD PIRUG — Institut für Bio- und Nanosysteme (IBN3) and Center of Nanoelectronic Systems; Forschungszentrum Jülich GmbH, D-52425 Jülich

We prepared self assembled monolayers of ω -(4'-methylbiphenyl-4-yl)-alkanethiols (BPn, n = number of CH₂ units) on Au(111) surfaces and analyzed the unit cell size by means of Low Energy Electron Diffraction (LEED). The structural dependency on the number of CH₂ units (n = 2 - 6) in the alkane chain has been studied systematically. The samples were prepared in a separate preparation chamber by gas phase deposition and subsequently transferred into the UHV analysis chamber. The formation of ordered phases after annealing for at least 12 h to temperatures between 298 K and 410 K was studied. All investigated molecules show commensurate structures on the Au(111) surface which are at variance to unit cells derived from repeating units seen by STM. The odd numbered molecules (BP3 and BP5) show the same ordered ($2\sqrt{3} \times \sqrt{91}$) structure. In comparison the even numbered BPn molecules exhibit different phases clearly distinguished by their LEED patterns. While BP2 and BP6 show only one, but not the same dominant structure, BP4 forms three temperature dependent phases. Structure models will be presented based on the unit cells determined by LEED and the molecular packing seen by STM. Different unit cell sizes imply that the stress between the Au-S interface and the biphenyl overlayer is compensated within the alkane spacer.

O 34.6 Tue 15:00 MA 043

Why a 'decoupled' switch doesn't switch. Self-assembled monolayers of Azobenzene on gold — ●ROLAND SCHMIDT¹, DANIEL BRETE^{1,2}, WOLFGANG FREYER¹, CORNELIUS GAHL¹, and MARTIN WEINELT^{1,2} — ¹Max-Born-Institut, Max-Born-Straße 2A, 12489 Berlin — ²FU-Berlin, Arnimallee 14, 14195 Berlin

We have investigated well oriented, self-assembled monolayers of alkanethiols on gold, functionalized by the molecular switch azobenzene ($HS - (CH_2)_n - O - C_6H_4 - N_2 - C_6H_4 - CF_3$, n = 3, 6, 10). Using X-ray absorption spectroscopy the tilt angle between the backbone of the azobenzene group and the surface normal was shown to be $\sim 15^\circ$, with only slight dependence on the length of the alkane chain n. The evaluation of autoionization spectra of the $N1s^{-1}\pi^{*+1}$ state in terms of the core-hole-clock approach gave a charge-transfer time τ_{CT} of the LUMO of several 10 fs. Also τ_{CT} showed no significant dependence on the length of the alkane chain n. Hence the switches are significantly decoupled from the substrate. However, a strong quenching of the SAM's $\pi - \pi^*$ -excitation is observed in UV-Vis spectroscopy, pointing out that lateral interactions among the azobenzene chromophores in the crystal-like layer dominate both the charge transfer and the

geometrical structure of the SAM. This is supported by the energy dependence of τ_{CT} that is atypical for tunnelling into the substrate. We suppose that the ultrafast delocalization of the S_2 excitation causes the observed inefficiency of photochemical switching of alkanethiol based SAMs.

O 34.7 Tue 15:15 MA 043

Molecular Switches at Solid Surfaces: A DFT Study of Azobenzene on Coinage Metals — ●ERIK MCNELLIS, ABBAS DEGHAN BAGHI, and KARSTEN REUTER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin (Germany)

Following the rapidly advancing miniaturization in microelectronics and sensing, molecules that may be switched between defined conformational states are envisioned as fundamental storage and logic units in a future “molecular nanotechnology”. Considering contacting and defined integration into a larger framework, it is more precisely the molecular function when the molecule is stabilized at a solid surface that is of key interest. A necessary prerequisite for an atomic-scale understanding of this function of the adsorbed switch is a detailed structural and electronic characterization of the stable (or meta-stable, long-lived) molecular states. For this, we use density-functional theory and study the prototypical cis-trans isomer azobenzene ($C_6H_5-N=N-C_6H_5$) at coinage metal surfaces. Treating electronic exchange and correlation (xc) at the generalized gradient approximation (GGA) level, we obtain an essentially zero net binding of both conformational isomers at Ag(111) and Au(111). This is significantly different at Cu(111), where the bonding particularly of the cis isomer is strong enough to even reverse the gas phase energetic order of the two isomers. We are able to rationalize these findings as a competition between the covalent bonding of the central azo ($-N=N-$) bridge to the substrate on the one side, and the surface interaction of the two closed-shell phenyl ($-C_6H_5$) rings on the other side.

O 34.8 Tue 15:30 MA 043

The role of surface-molecule interaction in the isomerisation of Azobenzene molecules — ●NILS HENNINGSEN¹, RICCARDO RURALI², KATHARINA J. FRANKE¹, ISABEL FERNANDEZ TORRENTE¹, GUNNAR SCHULZE¹, BEATE PRIEWISCH³, KAROLA RÜCK-BRAUN³, and NACHO PASCUAL¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Germany — ²Departament d'Enginyeria Electrònica, Universitat Autònoma de Barcelona, Spain — ³Institut für Chemie, Technische Universität Berlin, Germany

Azobenzene is a prototype molecular switch in the gas phase and in solution. Upon adsorption on a surface, the switching properties are largely influenced. By means of scanning tunnelling microscopy (STM) and density functional theory (DFT) we investigate the switching behaviour of an azobenzene derivative (DMC: di-metacyano-Azobenzene) on several noble metal surfaces, Au(111), Ag(100) and Cu(100). STM reveals that, after vacuum deposition, DMC adsorbs exclusively as trans-isomers. By applying voltage pulses with the STM tip, we are able to induce a conformational change into the cis-configuration on Ag(100) and on Cu(100). DFT calculations show that the stabilization of the cis isomers is mediated by a strong hybridization of the azo-group with the substrate. We argue that the larger the hybridization with the substrate the more stable is the cis configuration. This causes that the cis isomer is very stable on Cu(100), while the reversible switching into the trans state is possible on Ag. On Au(111) almost no hybridization is present thus we observe that only the trans molecules is a stable state on the surface.

O 34.9 Tue 15:45 MA 043

Adsorption studies of azobenzene molecules on Cu(001) and Au(111) — ●MARTEN PIANTEK, MATTHIAS BERNIEN, JORGE MIGUEL,

and WOLFGANG KUCH — Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14145 Berlin

Mono- and multilayers of Dimetacyano-azobenzene (DMC) have been evaporated under ultra high vacuum conditions on Au(111) and Cu(001) substrates in order to investigate the influence of the substrate on their physical properties. The electronic properties as well as the adsorption geometry of the molecules were studied by angle-dependent near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. DMC molecules adsorb in their planar trans conformation flat on the Au(111) surface. X-ray photoemission spectroscopy (XPS) of the monolayer on Au(111) yielded the same spectra as for the multilayer. Thus we conclude that there are no additional chemical bonds formed between the molecule and the metallic surface. On Cu(100) the molecules in the first monolayer present an out-of-plane geometry with respect to the substrate. From the change in the π^* resonances at the N K-edge NEXAFS we conclude that a molecular nitrogen π -bond breaks, while the angular dependence of NEXAFS shows that the benzonitrile moieties are tilted out of the molecular plane. The XPS N1s peaks of a monolayer of DMC on Cu(001) are shifted compared to those of the multilayer sample, due to an additional bond formation to the substrate.

O 34.10 Tue 16:00 MA 043

Reversible switching of tetra-*tert*-butylazobenzene on Au(111): A vibrational analysis — ●LÁSZLÓ ÓVÁRI^{1,2}, MARTIN WOLF¹, and PETRA TEGEDER¹ — ¹Fachbereich Physik, Freie Universität Berlin — ²Reaction Kinetics Research Laboratory, Chemical Research Center of HAS, Szeged, Hungary

High resolution electron energy loss spectroscopy (HREELS) is employed to analyze reversible changes in the geometrical structure of the molecular switch 3,3',5,5'-tetra-*tert*-butylazobenzene (TBA) adsorbed on Au(111), which are induced by UV-light and thermal activation. TBA was chosen because the four lateral *tert*-butyl-groups act as “spacer-legs” to increase the separation between the surface and the azobenzene π -system, and therefore leading to a reduced electronic coupling. From angular dependent measurements, *viz.* specular and off-specular scattering geometry, it could be proved that TBA adsorbs in the planar trans configuration in the submonolayer regime. UV-light exposure at 355 nm (3.5 eV) leads to pronounced changes in the vibrational structure of the TBA molecules in direct contact with the Au(111) surface, which we assign to a trans to cis isomerization. The reverse process, that is, the cis to trans isomerization, can be stimulated by thermal activation. An intensity decrease of vibrational modes as a function of photon dose allows calculation of an effective cross section of $\sigma \approx 2 * 10^{-21} \text{ cm}^2$ for the trans to cis isomerization.

O 34.11 Tue 16:15 MA 043

Switching of Spiropyran molecules on a Au(111) surface — ●GUNNAR SCHULZE, MICHAEL KARCHER, KATHARINA FRANKE, CHRISTOPH RÜDT, PAUL FUMAGALLI, and JOSE IGNACIO PASCUAL — Inst. für Experimentalphysik, Freie Universität Berlin, Berlin, Germany

The photon and electron mediated conversion of the molecule 3-methyl-6-nitro-spiropyran (SP) into its merocyanine isomer were investigated on a Au(111) surface by means of low temperature scanning tunnelling microscopy (STM) and by photo-absorption spectroscopy. STM resolves that the structure of SP molecular assemblies strongly depend on parameters like temperature and molecular density. The electronic properties of SP molecules on a metal surface, as obtained by scanning tunnelling spectroscopy (STS) and by photo-absorption spectroscopy, were compared to the electronic properties in solution. The alignment of these molecular states is specially important when inducing the SP to MC conversion.