

O 22: Poster Session: Organic Molecules on Inorganic Substrates I

Time: Monday 18:00–20:00

Location: P2/EG

O 22.1 Mon 18:00 P2/EG

Charge-state lifetimes of single molecules on ultrathin insulating films — ●KATHARINA KAISER^{1,3}, LEONARD-ALEXANDER LIESKE¹, JASCHA REPP², and LEO GROSS¹ — ¹IBM Research - Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland — ²Department of Physics, University of Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany — ³Present address: Institut de Physique et de Chimie des Matériaux de Strasbourg, Département Surfaces et Interfaces, 23 Rue du Loess, BP 43, 67034 Strasbourg, France

In scanning tunneling microscopy (STM) experiments of molecules on insulating films, tunneling through molecular resonances goes along with transiently charging the molecule. The transition back to its charge ground state by tunneling through the insulating film crucially determines the charging dynamics of the system and with this is essential for understanding, e.g., excited state formation and luminescence quenching in electroluminescence experiments. The two quantities describing these processes are the average charging and discharging time, the latter being the lifetime of the charged state, and they are accessible in STM: By approaching the tip to the molecule at resonant tunnel conditions up to a regime where charge transport is limited by tunneling through the NaCl film the saturation of the tunnel current, which is a direct measure of the molecule's charge state lifetime and thus provides a means to study charge and exciton dynamics, can be measured. We report on the charge state lifetimes of individual molecules adsorbed on NaCl films of different thicknesses on Cu(111) and Au(111), and provide insights into the role of the substrate and the spacer layer.

O 22.2 Mon 18:00 P2/EG

Theoretical Investigation of Tetracene-Adsorption on Cu(111)-Substrate — ●FLORIAN ALEXANDER PFEIFFER, JOHANNES BILK, and SIMONE SANNA — Institut für Theoretische Physik, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 16, Gießen, 35392, Hesse, Germany

Due to possible catalytic effects of a substrate, chemical reactions can occur within much smaller timescales on metal surfaces than in solutions. Ullman-coupling of Br-substituents to organic molecules, important to biology, chemistry and medicine, might profit of such catalytic effects. Little is known about this reaction on metallic substrates. Theoretical modelling is crucial for understanding the underlying processes. A first step towards such investigation is the first-principle modelling of tetracene-adsorption on Cu(111). Calculation of adsorption geometry and energy as well as charge transfer between molecule and surface is done utilizing density functional theory (DFT). Our calculations show that dispersion forces (van der Waals corrections) need to be taken into account for adsorption modelling. Adsorption energy and geometry as well as charge transfer suggest physisorption of tetracene at Cu(111). The Tersoff-Hamann-approximation allows for simulating STM-images using the DFT-calculated charge density. The STM-images show p_z orbitals of the benzene rings.

O 22.3 Mon 18:00 P2/EG

Effects of oxygen functionalization on the molecule-substrate coupling — ●JONAS BRANDHOFF, FELIX OTTO, MAXIMILIAN SCHAAL, ROMAN FORKER, and TORSTEN FRITZ — Institute of Solid State Physics, Friedrich Schiller University Jena, Helmoltzweg 5, 07743 Jena, Germany

5,7,12,14-Pentacenetetrone (P4O) is a polycyclic aromatic hydrocarbon which shows promising electronic properties for batteries. Unlike pentacene the π -system is not delocalized over the entire molecule. P4O shows a strong interaction with metal substrates up to a point where the π -system delocalization reemerges partially over the entire molecule. To understand this phenomenon of metallic organic bonding and charge-transfer, as well as the needed interaction strength for enabling a delocalized π -system over the entire molecule, different substrate-P4O systems were investigated. On the one hand, Cu(111) was chosen as a metallic substrate which shows a strong interaction and charge-transfer. On the other hand, the semi-metallic substrate of epitaxial graphene (EG) on SiC(0001) was selected, showing no charge transfer. As an intermediate system, Pt(111) as a noble metal was investigated. Furthermore hexagonal boron-nitride (h-BN) was used to decouple P4O from the Pt(111) substrate. The change in the structure of the adsorbate film was analyzed using STM and LEED. XPS and

UPS measurements gain further insights into the electronic properties. Photoemission orbital tomography (POT) was used to characterize the energetic positions of the frontier orbitals.

O 22.4 Mon 18:00 P2/EG

Vectorial Electron Spin Filtering by an All-Chiral Metal-Molecule Heterostructure — ●CHETANA BADALA VISWANATHA¹, JOHANNES STÖCKL¹, BENITO ARNOLDI¹, SEBASTIAN BECKER^{1,2}, MARTIN AESCHLIMANN¹, and BENJAMIN STADTMÜLLER^{1,3} — ¹Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schrödinger-Straße 46, 67663 Kaiserslautern, Germany — ²Department of Chemistry, University of Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern, Germany — ³Institute of Physics, Johannes Gutenberg University Mainz, Staudingerweg 7, 55128 Mainz, Germany

Chiral-induced spin selective transmission (CISS) has predominantly been explored in structurally helical molecules on surfaces, where the spin selectivity only affects the spin polarization of the electrons along their direction of propagation. Here, we demonstrate[1] a spin-selective electron transmission for a point-chiral molecule 3-Methylcyclohexanone (3-MCHO) adsorbed on the chiral Cu(643) surface. Using spin- and momentum-resolved photoelectron spectroscopy, we detect a spin-dependent electron transmission through a single layer of 3-MCHO molecules that depends on all three components of the electrons' spin. The findings are attributed to the enantiomer-specific adsorption configuration on the surface. This opens the intriguing opportunity to selectively tune CISS by the enantiospecific molecule-surface interaction in all-chiral heterostructures.

[1] J. Phys. Chem. Lett. 2022, 13, 26, 6244-6249.

O 22.5 Mon 18:00 P2/EG

Electronic properties of bi- and peri-tetracene on Cu(111) studied by density functional theory — ●NINA KAINBACHER¹, MAREN KLEIN^{2,3}, JOHN B. BAUER³, HOLGER BETTINGER³, HEIKO PEISERT², and PETER PUSCHNIG¹ — ¹Institute of Physics, NAWI Graz, University of Graz, Austria — ²Institute of Physical and Theoretical Chemistry, University of Tübingen, Germany — ³Institute of Organic Chemistry, University of Tübingen, Germany

Zigzag edged nanographenes with two rows of fused linear acenes, called n-periacenes, have gained increasing attention in the area of organic electronics due to their interesting electronic properties. However, the synthesis is challenging because of their chemical instability. Here we show that a well-ordered monolayer of peritetracene, an n-periacene with four benzene rings in a row, can be produced by depositing the precursor 1,1'-bitetracene on Cu(111) and a subsequent heat treatment. The as-deposited and the annealed films are investigated by STM and UPS and by electronic structure calculations within DFT using a repeated slab approach. We determine the optimal adsorption sites by using damped molecular dynamics and empirical dispersion corrections according to Grimme. We then analyze the electronic structure of the organic/metal interfaces, in particular we focus on the (local) density of states and charge rearrangements upon interface formation which is decisive for the energy level alignment and work function changes. Our results clarify that the interaction of peritetracene with the Cu(111) substrate leads to a charge transfer into the LUMO which is consistent with the experimental observations.

O 22.6 Mon 18:00 P2/EG

Decoupling of vanadyl-naphthalocyanine from a metal substrate by monolayer MoS₂ — ●J. RIKA SIMON, GAËL REECHT, CHRISTIAN LOTZE, and KATHARINA J. FRANKE — Fachbereich Physik, Freie Universität Berlin, Germany

Phthalocyanines with metal centres are well known for their relative stability on surfaces and are of interest because of the spin they can carry in their metal centres. On metal surfaces, the molecular electronic states are often hybridised with the metal underneath, making it difficult to observe fine details in the electronic structure and inelastic excitations. Using monolayers of semiconducting transition-metal dichalcogenides (TMDCs) as a decoupling layer on top of metal surfaces is a well-established way to allow access to highly resolved dI/dV spectra. Here, we use scanning tunnelling microscopy (STM) to probe the properties of vanadyl-naphthalocyanine (VONc)

on MoS₂/Au(111). We observe VONc with molecular centres appearing with different apparent heights, which can be interpreted as different configurations of the central oxygen atom sitting on top or below the molecular macrocycle, as observed previously on the closely related molecule vanadyl-phthalocyanine (VOPc) [1,2]. Additionally, we see sharp molecular states in the semiconducting band gap, which are affected by the perturbation potential of the tip [3], causing them to shift in energy across the VONc molecules.

[1] L. Malavolti et al., *Nano Lett.* 18, 7955 – 7961 (2018)

[2] K. Kaiser et al., *ACS Nano* 13, 6947 – 6954 (2019)

[3] N. Krane et al., *PRB* 100, 035410 (2019)

O 22.7 Mon 18:00 P2/EG

Electronic properties of organic/transition metal dichalcogenide heterostructures — •HIBIKI ORIO^{1,2}, MAXIMILIAN ÜNZELMANN^{1,2}, KIANA BAUMGÄRTNER^{1,2}, CHRISTIAN METZGER^{1,2}, MARKUS SCHOLZ³, KAI ROSSNAGEL^{3,4}, and FRIEDRICH REINERT^{1,2} — ¹Experimentelle Physik VII, Universität Würzburg, Würzburg, Germany — ²Würzburg-Dresden Cluster of Excellence ct.qmat, Würzburg Dresden, Germany — ³Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ⁴KiNSIS, Universität Kiel, Kiel, Germany

Adsorption of organic molecules on transition metal dichalcogenides (TMDCs) can modify the electronic properties of both the organic layer as well as the substrate [1]. Here, we investigate the electronic structure of copper phthalocyanine (CuPc) grown on the TMDC TiSe₂ using angle-resolved and X-ray photoelectron spectroscopy. We find that the binding energy of the highest occupied molecular orbital increases gradually from 310 to 430 meV upon 4 hours of X-ray radiation. On this poster, we will discuss the origin of this phenomenon.

[1] Y. L. Huang et al., *Chem. Soc. Rev.*, 2018, 47, 3241

O 22.8 Mon 18:00 P2/EG

Ligand Size Controls Surface Chemical Bond: Cobalt Porphyrin versus Cobalt Corrole on the Ag(111) Surface — •CONG GUO, GRIGORI PASKO, JAN HERRITSCH, and J. MICHAEL GOTTFRIED — Fachbereich Chemie, Philipps-Universität Marburg

The development of novel functional materials based on biologically relevant molecules such as cobalamins, also referred to as vitamin B₁₂, is an important research topic. In particular, cobalt tetrapyrrole complexes which are related to cobalamins are often-used and well-understood model systems. Due to the structural complexity of

the ligands, their interaction and bonding at interfaces is still poorly understood. Using XPS, we compare here a cobalt(II) porphyrin with a related cobalt(III) corrole. The latter exhibits a smaller ring size and acts as a trianionic ligand. In the multilayer, the Co 2p signal of the porphyrin shows the typical appearance of a paramagnetic Co²⁺ center. The corresponding Co 2p signal of the corrole has a similar shape indicating the presence of unpaired electrons in the Co 3d sub-shell. In the monolayer on Ag(111), both complexes are subject to an interfacial charge transfer from the substrate, as can be seen by the Co 2p signals. Thus, the singly occupied orbitals at the cobalt center are accepting electron density from the substrate. However, the N 1s signal and the valence photoemission spectra indicate that the corrole interacts much stronger with the substrate which is confirmed by periodic DFT calculations. Our study reveals that the two adsorbed complexes differ substantially in their overall interaction with the Ag surface, even though cobalt has a similar electronic state in both cases.

O 22.9 Mon 18:00 P2/EG

Charge Transfer on a 2D Insulator: Influence of the Molecular Functionalization — •MAXIMILIAN SCHAAL, JONAS BRANDHOFF, FELIX OTTO, ROMAN FORKER, and TORSTEN FRITZ — Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany

2D materials like hexagonal boron nitride (h-BN) are widely used as interlayer to decouple organic molecules from metallic surfaces. Despite the large band gap of 2D h-BN of ≈ 6 eV, there are also indications for a possible charge transfer into organic molecules. This raises the question: What is the reason for the charge transfer on this 2D insulator?

To address this question, we systematically studied the influence of the molecular functionalization on the lateral structure as well as on the charge transfer on 2D h-BN grown by chemical vapor deposition on Ni(111). Therefore, we compare the structural and electronic properties of pentacene (Pen) monolayers with the oxo-derivatives 6,13-pentacenequinone (P2O) and 5,7,12,14-pentacenetetrone (P4O) by using low energy electron diffraction (LEED), differential reflectance spectroscopy (DRS), X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) as well as photoemission orbital tomography (POT). For P4O on h-BN/Ni(111) we observed a charge transfer while Pen and P2O remain neutral. This will be discussed in terms of energy-level alignment in these 2D organic/inorganic heterostructures.