

O 49: Poster Session - Organic Molecules on Inorganic Substrates: Electronic, Optical and Other

Time: Tuesday 18:15–20:00

Location: P2/EG

O 49.1 Tue 18:15 P2/EG

Sum frequency spectroscopy of *o*-, *m*- and *p*-Methylbenzylphosphonic acid on α -aluminium oxide — ●TIM LÄMMERZAHN, MATTHIAS LINKE, DAMIAN FIRLA, and ECKART HASSELBRINK — Universität Duisburg-Essen, Essen, Germany

Self-assembled molecular monolayers (SAMs) are applied to engineer surface properties in a defined way which makes SAMs interesting for numerous applications. While there have been many studies on prominent SAMs e.g. thiols on gold, the existing knowledge on phosphonic acid (PA) SAMs still lacks behind. A very prominent substrate for PA SAMs is aluminum oxide, due to its use in a wide range of research applications like organic field-effect sensors and in different fields of industry e.g. aerospace. The surface sensitive vibrational sum frequency spectroscopy (vSFS) is well suited for the characterization of such surfaces. To this note we studied different isomers of methylbenzylphosphonic acid (MBPA) via vSFS in the spectral range of the C-H vibrations. We were able to show that due to the selection rules for sum frequency generation, different bands are observed for the three possible substitution patterns of MBPA in the spectral range of the aromatic C-H vibrations. When comparing the spectra in the spectral region of aliphatic C-H vibrations, a clear difference between the isomers can be shown. This study provides interesting insights into the orientation of different constitutional isomers on the surface.

O 49.2 Tue 18:15 P2/EG

Single-molecule vibrational progression on two-dimensional materials — ●ALEXANDER MEHLER¹, NICOLAS NÉEL¹, JOHANNES HALLE¹, MARIE-LAURE BOCQUET², and JÖRG KRÖGER¹ — ¹Institut für Physik, Technische Universität Ilmenau, Ilmenau, Germany — ²École normale supérieure, PSL University, Sorbonne Université, CNRS, France

Probing genuine molecular properties even after adsorption on a surface requires the efficient reduction of the molecule-surface hybridization. Two-dimensional materials, such as graphene, hexagonal Boron Nitride (hBN) and stackings thereof, are promising buffer layers to this end. Scanning tunneling microscopy and spectroscopy at low temperature is used to explore molecular orbitals and vibrational quanta of the hydrocarbon molecule DBP (Dibenzotetraphenylperiflanthen) on graphene and hBN with submolecular resolution. Independent of the metal substrate, Ir(111), Pt(111) and Ru(0001), vibrational progression in both DBP frontier orbitals is observed for graphene and hBN, albeit with different numbers of vibrational quanta involved. Density functional calculations unveil that symmetry matching of electronic and vibrational excitations supports the observation of vibrational progression. The lifetime of the vibronic levels can be tuned by the molecular environment of a single DBP as well as by using different kinds and numbers of buffer layers.

O 49.3 Tue 18:15 P2/EG

Site selective adsorption and spin state locking of the spin crossover complex Fe(phen)2(NCS)2 on Au(111) — SUMIT BENIWAL¹, ●SUCHETANA SARKAR², FELIX BAIER², PETER A. DOWBEN¹, and AXEL ENDERS^{1,2} — ¹Department of Physics, Universität Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany — ²Department of Physics and Astronomy, University of Nebraska Lincoln, Lincoln, NE 68588, USA

The iron (II) spin crossover complex, Fe(1,10-phenanthroline)2(NCS)2, dubbed Fe-phen, has been studied with scanning tunnelling microscopy under ultra-high vacuum after adsorption on the "herringbone" reconstructed surface of Au (111) for sub-monolayer coverages. The Fe-phen molecules attach, through their NCS-groups, to the Au atoms of the fcc domains of the reconstructed surface only, thereby lifting the herringbone reconstruction. The molecules stack to form 1D chains, which run along the Au [110] directions. Neighboring Fe-phen molecules are separated by approximately 2.65 nm, corresponding to 9 atomic spacings in this direction. The molecular axis, defined by the two phen groups, is aligned perpendicular to the chain axis, along the Au [221] direction, thereby bridging over 5 atomic spacings, in this direction. Experimental evidence suggests that the molecular spins are locked in a mixed state in the sub-monolayer regime at temperatures between 100 K and 300 K. These results further the understanding of how in-

terfaces could be leveraged to manipulate the spin state and the spin crossover in SCO complexes and demonstrate an avenue for the structural patterning of functional molecular films.

O 49.4 Tue 18:15 P2/EG

Decoupled or not decoupled? Investigation of charged organic molecules on a 2D insulator — ●MAXIMILIAN SCHAAL, ILIYAN KARADZHOV, MARCO GRUENEWALD, FELIX OTTO, ROMAN FÖRCKER, and TORSTEN FRITZ — Friedrich Schiller University Jena, Institute of Solid State Physics, Helmholtzweg 5, 07743 Jena

In the last years 2D materials have attracted much interest in fundamental research and practical applications because of their unique physical properties. One representative of the 2D materials is hexagonal boron nitride (h-BN), which is an insulator with a band gap of ≈ 6 eV [1]. h-BN is widely used as interlayer to decouple molecules from metallic surfaces [1]. This leads us to the question: Is one monolayer h-BN really efficient for decoupling PTCDA from the Ni(111) surface?

In this work we observed a charge transfer by differential reflectance spectroscopy (DRS) during the growth of PTCDA. The lateral structure was investigated in real as well as in reciprocal space by scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED), respectively. Furthermore, the core states as well as the valence electron band structure was investigated by x-ray and angle resolved ultraviolet photoelectron spectroscopy (XPS and ARUPS), respectively. In the end we will discuss the origin of the charge transfer.

[1] W. Auwärter, Surf. Sci. Rep. **74**, 1-95 (2018).

O 49.5 Tue 18:15 P2/EG

DMEP-Ovalene as Precursor-Molecule for Nanographene on H:Si(100) — ●ALEXANDER KÖLKER, LEONID SHUPLETSOV, TAKASHI KUMAGAI, MARTIN WOLF und MATTHIAS KOCH — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Electrically contacting single molecules is one of the biggest challenges in nanotechnology. Sophisticated techniques emerged such as break junction [1] and scanning probe microscopy (SPM) [2,3]. However, interpreting the electrical signal without knowledge of the precise chemical composition of the junction is difficult.

We have developed a SPM sample architecture with integrated sub-surface electrodes in Si(001) for multi-terminal conductance measurements to fabricate robust molecular nano-circuits. To place molecules with highest precision between prior fabricated electrodes we will employ STM hydrogen lithography which enables the creation of reactive adsorption sites on the passivated silicon surface.

A first promising candidate to study is nanographene which localized electronic edge states are expected to be energetically located in the silicon band gap region.

Here we report a detailed structural and electronic characterization of adsorption conformations of Dimethylphenyl-Ovalene (DMEP) on H:Si(001) as function of annealing temperature. STM and STS experiments at 4 K are supported by simulations for a free molecule in gas phase.

O 49.6 Tue 18:15 P2/EG

Adsorption and Electronic Properties of N-Heteropolycycles on Metal Surfaces — ●FELIX LANDWEHR¹, MOHSEN AJDARI¹, MARVIN HOFFMANN², HILMAR REISS³, HENDRIK HOFFMANN³, UWE H. F. BUNZ³, ANDREAS DREUW², and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ²Interdisziplinäres Zentrum für Wissenschaftliches Rechnen, Ruprecht-Karls-Universität Heidelberg — ³Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg

Introduction of nitrogen atoms into the π -electron backbone of polycyclic hydrocarbons lowers the energy of the frontier orbitals and accordingly increases the electron affinity, while the optical gap remains almost constant. Thus, N-heteropolycycles possess a higher stability compared to the corresponding polyaromatic hydrocarbons.

Due to the increased electron affinity, aromatic N-heteropolycyclic compounds are n-type semiconductors and thus promising candidates for applications in field effect transistors. However, a detailed under-

standing of the adsorption and electronic properties of these molecules at interfaces and in thin films is needed to optimize the devices performance.

In this contribution, we used temperature-programmed desorption, electronic and vibrational high-resolution electron loss spectroscopy, as well as scanning tunneling microscopy/spectroscopy to elucidate the adsorption and electronic properties of N-heteropolycycles adsorbed on Au(111).

O 49.7 Tue 18:15 P2/EG

Application of multi-photon PEEM to a biological system: Geobacter sulfurreducens — •FRANZ NIKLAS KNOOP¹, HILKE SOPHIE WICHMANN², GERHARD LILIENKAMP¹, and WINFRIED DAUM¹ — ¹IEPT TU Clausthal — ²IÖNC TU Braunschweig

Excitation of the molecular Soret transition of porphyrins by short tunable laser pulses has made possible multi-photon photoelectron emission microscopy (nP-PEEM) studies of porphyrin thin films and nanoplasmonic porphyrin hybrid systems with high molecular sensitivity [1]. More recently, we have also applied this method to films of the protein cytochrome c whose chromophoric group is a porphyrin. In this contribution we report on nP-PEEM results for a biological system, *Geobacter sulfurreducens* which is a promising candidate for microbial fuel cells. This bacterium as well as its extracellular matrix is rich of cytochrome c which is probed in our PEEM experiments using appropriate laser wavelengths. While films of porphyrin molecules such as MgTPP are very stable against irradiation with 100 fs laser pulses, photoemission from cytochrome c films as well as from *Geobacter sulfurreducens* shows substantial intensity and spectral changes upon laser irradiation. Our experiments point to thermal effects because moderate heating of the sample also increases the photoemission intensity from *Geobacter sulfurreducens*. We present and discuss Soret-resonant single-wavelength and laser-spectroscopic PEEM results obtained from single bacteria and bacteria films.

[1] K. Stallberg, G. Lilienkamp, W. Daum, J. Phys. Chem. C 121, 13833 (2017)

O 49.8 Tue 18:15 P2/EG

First Principles Studies of Electrical Conductance and Thermopower Properties of π -Conjugated Organometallic Complexes in Single Molecule Junctions — •JANNIS JUNG¹, TATSUHIKO OHTO², HIROKAZU TADA², and DOREEN MOLLENHAUER¹ — ¹Institute of Physical Chemistry, Justus Liebig University, Giessen, Germany — ²Division of Frontier Material Science, Osaka University, Osaka, Japan

Single molecule junctions, consisting of a molecule connecting two bulk material electrodes, have a long history of research, which focuses on their electrical properties and uses in electronics. In particular, molecular junctions containing organometallic complexes showed high Seebeck coefficients and low thermal conductance, making them a promising thermoelectric material.

Here, the influence of the binding nature between a complex and differently structured gold surfaces as well as the influence of large side chains of the ligands to the electron transmission was investigated by density functional theory calculations using the Non-Equilibrium Green's Function (NEGF) method. Therefore, we studied junctions containing transition metal (Ru and Pt) complexes with highly π -conjugated ligands binding to different surface contacts. We showed a

shift of the conductive (HOMO) orbitals towards the Fermi energy, effectively increasing the Seebeck Coefficient. Furthermore, intramolecular dispersion interactions can lead to a decrease of the electric conductance.

O 49.9 Tue 18:15 P2/EG

Surface spectroscopy of functionalized Si(001) surfaces — •STEFANO MAZZEI, VALÉRIE VÉNIARD, and CHRISTINE GIORGETTI — Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA/DRF/IRAMIS, Institut Polytechnique de Paris

Understanding the mechanism of interaction between amino acids and peptides with surfaces opens new perspectives. Adsorption of DNA molecules on semiconducting surfaces is evoked for the design of biosensors or the production of bio-materials. The possibility to functionalize surfaces with bio-molecules, to create organized structures up to nanometers' distances depends on our capability to understand precisely the mechanisms which govern the deposition of molecular films onto different kinds of surfaces. For these reasons, this kind of systems have been intensively studied during last decades .

We present in this poster the results obtained for the Si(001) surface functionalized with two different molecules, the Thymine and the Uracil. The electronic structure has been obtained with a DFT approach, using Abinit . Using DP, which allows the calculation of the dielectric response of materials in the TDDFT framework, we computed several surface-related linear spectroscopy quantities (Reflectance Anisotropy Spectrum, adsorbance anisotropy...), that are compared with previous studies. Finally, the code 2Light, which has been recently extended to the case of surfaces, has been used to study the Second Harmonic Generation of the Si(001) functionalized with nucleobases, including local field effects.

O 49.10 Tue 18:15 P2/EG

Molecular chain formation at surfaces: PEEB/Au(111) - A High-throughput Study — •LOKAMANI LOKAMANI^{1,2}, JEFFREY KELLING³, JÖRG MEYER¹, ANJA NICKEL¹, ROBIN OHMANN¹, GIANAURELIO CUNIBERTI¹, JANNIC WOLF⁴, THOMAS HUHN⁴, PETER ZAHN², FRANCESCA MORESCO¹, and SIBYLLE GEMMING^{2,5} — ¹Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, Germany — ²Institute of Ion Beam Physics and Materials Research, HZDR, Germany — ³Department of Information Services and Computing, HZDR, Germany — ⁴Department of Chemistry, Uni Konstanz, Germany — ⁵Institute of Physics, TU Chemnitz, Germany

The geometrical and electronic structure of 4-bis(phenylethynyl)-2,5-bis(ethoxy)benzene (PEEB) molecules adsorbed on the Au(111) is investigated by LT-STM and STS in conjunction with DFT based simulations. Due to low corrugation of the Au(111) surface, PEEB molecules can form quasi interlocked lateral patterns, as observed in experiments. We employ DFTB+ based high-throughput calculations including dispersion corrections via Lennard-Jones potential to evaluate an energy function, which incorporates the adsorption energy of single PEEB molecules on the metal surface and the interaction energy of a pair of PEEB molecules. Our calculations indicate, that the PEEB molecule is physisorbed on Au(111), with negligible distortion in geometry and moderate charge transfer of +0.14e. Furthermore, depending on coverage density specific types of pattern are preferred, which can be exploited to form 1D-molecular-wires on Au(111).