

O 40: Organic Molecules on Inorganic Substrates III: Electronic, Optical and other Properties

Time: Tuesday 10:30–13:00

Location: REC C 213

O 40.1 Tue 10:30 REC C 213

Reaction dynamics simulation of an interface between Trecresyl phosphate and Iron oxide by a hybrid quantum and classical method — ●NAOKI UEMURA¹, YOSUKE HARADA^{2,3}, and SHUJI OGATA¹ — ¹Nagoya Institute of Technology, Nagoya, Japan — ²Idemitsu Kosan Co. Ltd., Chiba, Japan — ³ADMAT, Ibaraki, Japan

The understanding of reaction mechanics at the heterogeneous interface, e.g. organic-inorganic interfaces, is of fundamental importance for physics and industries. Trecresyl phosphate molecule (TCP) has been widely used for various industrial applications such as anti-wear additives. However the detailed mechanism of decomposition of TCP on metal and metal oxide under high pressure and high temperature has still been discussed [1, 2]. Our large-scale molecular dynamics simulations by the hybrid quantum and classical method based on DFT [3] indicated breaking P-O bonds of TCP near the surface.

This work was funded by New Energy and Industrial Technology Development Organization of Japan (NEDO) Grant (P16010).

[1] E. Osei-Agyemang et al., Tribol. Lett. 66, 48 (2018).

[2] B. Guan et al., Lubr. Sci. 28, 257 (2016).

[3] N. Ohba et al., Comp. Phys. Comm. 183, 1664 (2012).

O 40.2 Tue 10:45 REC C 213

Energy levels and charge distribution within dipolar molecules on MoS₂/Au(111) — ●SERGEY TRISHIN¹, DANIELA ROLF¹, CHRISTIAN LOTZE¹, JOHANNA RICHTER¹, PHILIPP RIETSCH², SIEGFRIED EIGLER², and KATHARINA J. FRANKE¹ — ¹Fachbereich Physik, Freie Universität Berlin — ²Institut für Chemie und Biochemie, Freie Universität Berlin

Molecules consisting of a donor and an acceptor moiety can exhibit large intrinsic dipole moments. Upon deposition on a metal surface, the dipole may be effectively screened and the charge distribution altered due to hybridization with substrate electronic states. Therefore, the inclusion of a thin band-gapped material can help to preserve gas-phase-like electronic properties. We study Ethyl-Diaminodicyanoquinone molecules on a Au(111) surface and on single-layer molybdenum disulfide (MoS₂) on Au(111) with scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM). By mapping the local contact potential difference (LCPD) over the molecules we show that the intrinsic dipole moment of the molecules is partially preserved upon adsorption on both the bare Au(111) surface and MoS₂. On Au(111), the molecular resonances show an apparent shift in energy within individual molecules. The high energy resolution on molecules adsorbed on MoS₂ allows us to conclude that the apparent shift is due to several resonances of varying intensity, arising from vibronic states. DFT calculations of the molecule in gas phase help to identify certain vibrations of the molecule from their signature in the tunneling spectra.

O 40.3 Tue 11:00 REC C 213

Electronic structure of a donor-acceptor molecule adsorbed on a Pt substrate — ●NARENDRA P. ARASU and HECTOR VAZQUEZ — Institute of Physics of the Czech Academy of Sciences, Cukrovarnicka 10, Prague 6, Czech Republic

Donor-bridge-acceptor molecules exhibit excellent intramolecular charge transfer properties and have a vast potential in optoelectronic applications. In this work, a Donor-bridge-acceptor molecule composed of carbazol and phenalenon derivatives is studied on a platinum substrate using Density Functional Theory (DFT) calculations and low-temperature Scanning Tunneling Microscopy (STM) experiments. Simulations include van der Waals interactions between the molecule and the substrate. After a screening of many interface geometries, two stable adsorption configurations can be identified, and a comparison of these structures is made with experimental STM Images. The donor-acceptor character and its changes upon adsorption are analyzed through the effect of binding and structural changes on the electronic properties. Calculations disentangle the different contributions from the donor, acceptor and bridge units of the molecule. Simulations of the molecular interface thus rationalize the STM experiments and provide an understanding of the role of the platinum-molecule interaction.

O 40.4 Tue 11:15 REC C 213

Hybridization of the NTCDA/Ag(111) interface state with

molecular orbitals — ●LUKAS ESCHMANN, PETER KRÜGER, and MICHAEL ROHLFING — Institut für Festkörperteorie, Westfälische-Wilhelms Universität Münster, 48151 Münster, Germany

At the internal interfaces between adsorbed π -conjugated organic molecules and metallic substrates, two-dimensional, highly dispersive interface states (IS) appear. These states are mainly attributed to the Shockley surface state of the metal that is shifted up in energy and is scattered by an adsorbate induced scattering potential.

We employ density-functional theory (DFT) to analyze the dispersion of the IS between a monolayer of 1,4,5,8-naphthalene-tetracarboxylic acid dianhydride (NTCDA) and the Ag(111) surface. Complemented with a projection technique which maps the interface electronic structure onto the original Ag(111) Shockley state, the DFT calculations enable us to analyze the dispersion of the NTCDA/Ag(111) IS and its interactions with the molecular orbitals. We transfer the ab-initio data into a model Hamiltonian which allows us a deeper understanding of the interaction with the molecular orbitals.

Our analysis shows that interaction with molecular orbitals causes crucial changes in the dispersion of the IS and our model explains the recently both experimentally and theoretically observed pronounced anisotropy of the IS at NTCDA/Ag(111) [1].

[1]L. Eschmann, et al. , Phys. Rev. B 100, 125155 (2019).

O 40.5 Tue 11:30 REC C 213

Corrections to DFT energy level alignment of single molecule junctions using projected orbitals — ●ENRIQUE MONTES and HECTOR VAZQUEZ — Institute of Physics, Czech Academy of Sciences, Cukrovarnicka 10, Prague 16200, Czech Republic

The calculation of the electronic and transport properties of metal/molecule junctions is of paramount importance in many fields of molecular nanoscience. DFT struggles to accurately predict the energy level alignment between the frontier molecular orbitals and the Fermi level of the metal. Several approaches have been proposed to calculate the energy level alignment of metal/molecule interfaces beyond DFT, among them the DFT+ Σ method [1] stands out as it reduces computational cost while maintaining good accuracy. Here, we develop a new method to correct the DFT-based energy level alignment of molecular junctions. We start by projecting the orbitals of the molecular subspace onto the full junction space. The projection coefficients are used to average parameters from DFT+ Σ framework (gas phase and polarization). At variance with previous approaches we introduce the correction in the total junction Hamiltonian, i.e., operator is defined in junction space. Using this methodology we are able to correct the complete electronic structure. We have implemented this method in the DFT SIESTA code [2] because it describes electrons in a localized basis set, allowing for an unambiguous clustering of the system. We will show results for typical metal/molecule/metal junctions. [1] S. Quek, et al. Nano Lett. 7, 3477 (2007). [2] J. M. Soler, et al. J. Phys. Cond. Matt. 14, 2745 (2002).

O 40.6 Tue 11:45 REC C 213

Supramolecular networks assembled on superconducting Pb surfaces — ●CARL DRECHSEL¹, PHILIPP D'ASTOLFO¹, XUNSHAN LIU², SHI-XIA LIU², SILVIO DECURTINS², RÉMY PAWLAK¹, and ERNST MEYER¹ — ¹Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland — ²Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

Due to their vast potential for functionalities, molecular assemblies at surfaces have attracted a certain interest in surface Physics. Recent experiments have shown the feasibility to create metal-organic nanochains with special catalytic properties [1], or to activate selected molecules for the use as molecular quantum cellular automata [2]. On superconductors, these molecules create ground states, formed by a balance between Kondo screening and superconducting pair-breaking interactions [3].

Here, we investigate the structural and electronic properties of self-assembled layers of 3-TBQP (3,6,14,17-tetrabromodibenzo[a,c]-dibenzo[5,6:7,8]-quinoxalino-[2,3-i]phenazine) on the superconducting Pb(111) surface. The layers are characterized at 4 K by scanning tun-

neling microscopy (STM) and atomic force microscopy (AFM) with CO-terminated tips. Our results show a fundamental step in developing functional supramolecular networks at supra-conductors [4].

[1] Krull, C. et al.; Nat Commun 9, 3211 (2018) - [2] Kocic, N. et al.; Nano Lett. 19, 5, 2750-2757 (2019) - [3] Franke, K.J. et al.; Science 332, 940 (2011) - [4] Drechsel, C. et al.; submitted

O 40.7 Tue 12:00 REC C 213

Organic alkali salt layer formation as surface decoupling strategy in metal organic thin films: K and TCNQ on Ag(111)

— ●BILLAL SOHAIL¹, LUKE ROCHFORD¹, PHIL BLOWEY^{1,3}, PHIL WOODRUFF², GIOVANNI COSTANTINI¹, and REINHARD J. MAURER¹ — ¹Department of Chemistry, University of Warwick, UK — ²Department of Physics, University of Warwick, UK — ³Department of Chemistry, University of Leeds, UK

A detailed characterisation of structure and electronic properties at metal-organic interfaces is crucial for the design of novel molecular electronics devices such as organic photovoltaics (OPVs) and organic field effect transistors (OFETs). In these devices, strong donors such as alkaliatoms and acceptor molecules, such as TCNQ (7,7,8,8-tetracyanoquinodimethane), are often added to organic electronics devices to tune the charge injection properties at the metal-organic interface. We present a joint computational and experimental study to examine the intricate coupling of geometry and electronic structure for TCNQ coadsorbed with potassium atoms on a Ag(111) surface. By combining dispersion-inclusive Density-Functional Theory calculations, x-ray standing wave (XSW), LEED, and STM measurements, we find that K and TCNQ form a strongly interacting organic salt. This stands in contrast to TCNQ on Ag(111), which forms strongly surface-bound adlayers containing silver adatoms. We identify the energetic driving force for organic salt formation and discuss the intricate competition between donor, acceptor, and metal surface.

O 40.8 Tue 12:15 REC C 213

Kekulene synthesised on copper surfaces: Orientation and electronic properties

— ●ANJA HAAGS^{1,2}, QITANG FAN⁵, XI-AOSHENG YANG^{1,2}, LARISSA EGGER³, HANS KIRSCHNER⁴, TIM NAUMANN⁵, SIMON WERNER⁵, JÖRG SUNDERMEYER⁵, FRANÇOIS C. BOCQUET^{1,2}, GEORG KOLLER³, ALEXANDER GOTTWALD⁴, MATHIAS RICHTER⁴, MICHAEL G. RAMSEY³, PETER PUSCHNIG³, SERGUEI SOUBATCH^{1,2}, F. STEFAN TAUTZ^{1,2}, and MICHAEL GOTTFRIED⁵ — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — ²Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany — ³Institute of Physics, University of Graz, NAWI Graz, 8010 Graz, Austria — ⁴Physikalisch-Technische Bundesanstalt (PTB), 10587 Berlin, Germany — ⁵Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany

The polycyclic aromatic molecule kekulene was synthesised on the copper (111) and (110) surfaces from a molecular precursor using a surface-assisted reaction. Scanning tunneling microscopy showed compact well-ordered monolayers of kekulene proving a high reaction yield. To address electronic properties of kekulene, we carried out momentum-space imaging photoelectron spectroscopy experiments. The photoemission intensity distributions of particular molecular states are compared to density functional theory calculations of free kekulene using

the plane wave final state approximation. It allows us to prove the chemical nature of the reaction product and to elucidate its orientation and electronic structure on both copper surfaces.

O 40.9 Tue 12:30 REC C 213

Molecular Topology and Surface Chemical Bond of Aromatic Ring Systems

— ●LUKAS RUPPENTHAL, BENEDIKT P. KLEIN, JAN HERRITSCH, STEFAN R. KACHEL, and J. MICHAEL GOTTFRIED — Fachbereich Chemie, Philipps-Universität Marburg, Germany

Metal/organic interfaces formed at the contacts between metal electrodes and organic semiconductors have a large impact on the performance of organic-electronic devices. The detailed understanding of their chemical, electronic and geometric structure is therefore important for the further technological development. Many common organic semiconductors contain π -electron systems with alternant topologies, whereas non-alternant alternatives have only recently found increasing attention due to their unusual electronic properties. Here, we compare naphthalene as an alternant aromatic molecule with azulene as its non-alternant isomer, both on Cu(111), using PES, NEXAFS, TPD, STM, and LEED. With the same approach, we compare the larger aromatic compounds pyrene and its isomer dicyclopenta[*ef,kl*]heptalene (azupyrene), which is also important as a model for the Stone-Wales defects in graphene. In both cases, we find that the non-alternant isomer forms a stronger bond to the metal surface than its alternant counterpart. The increased interaction of the non-alternant isomers is related to their reduced HOMO-LUMO gap, which brings the LUMO energetically close to the Fermi energy of the metal, causing stronger hybridization with electronic states of the metal surfaces. The resulting effects on the electronic and geometric structure will be discussed on the basis of DFT calculations.

O 40.10 Tue 12:45 REC C 213

Adsorption and Electronic Properties of Azaacenes on Au (111)

— ●MOHSEN AJDARI¹, FRIEDRICH MAASS¹, MATTHIAS MÜLLER², HILMAR REISS², MARVIN HOFFMANN³, UWE H. F. BUNZ², ANDREAS DREUW³, and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut — ²Organisch-Chemisches Institut — ³Interdisziplinäres Zentrum für Wissenschaftliches Rechnen, Ruprecht-Karls-Universität Heidelberg

Azaacenes are organic electron-transporting semiconductors that belong to N-heteropolycyclic aromatic compounds, which are promising candidates for a variety of (opto) electronic applications such as field effect transistors. In these molecules, introduction of nitrogen in their aromatic backbone in its pyridine form decreases the energy of both HOMO and LUMO, resulting in an improved stability due to an increased ionization potential and electron affinity of organic semiconductor.

In this study, we investigated the adsorption and electronic properties of azaacenes as a function of coverage on Au (111) by employing temperature-programmed desorption (TPD), vibrational and electronic high-resolution electron energy loss spectroscopy (HREELS) in combination with quantum-chemical theory to gain detailed insights into their adsorption geometry and electronic structure on Au(111) which is of great importance for optimizing and improving a device performance.