O 15: Organic Molecules on Inorganic Substrates II: Electronic, Optical and other Properties

Time: Monday 15:00–18:00 Location: MA 043

O 15.1 Mon 15:00 MA 043

Investigation of the electronic structure of solvent based multispin bearing metallacrown CuCu4 molecules on a Au(111) surface — •Benedikt Baumann[1], Robert Ranecki[1], Lukas Bolz[1], Ellen Brennfleck[1], Stefan Hornig[1], Yves Kurek[1], Frederik Pütz[1], Philip Schreyer[1], Paul Steuernagel[1], Dominic Stephan[1], Robert Wendels[1], Stefan Lach[1], Eva Rentschler[2], and Christiane Ziegler[1] — [1]RPTU Kaiserslautern - Landau and Research Center OPTIMAS, Erwin-Schrödinger-Str. 56, 67663 Kaiserslautern, Germany — [2]Inst. of Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, Germany

Transition metal complexes with exchange-coupled open-shell metal ions have attracted attention in the last decade. In such systems, spin relaxation time enhancement can provide a route to nanoscale spintronic devices. Because of their mostly low thermal stability, such molecules must be prepared by solvent based methods to investigate the electronic structure on metallic substrates,. We will demonstrate different UHV compatible preparation setups to prepare ultra-thin layers of the solvent based metallacrown complex CuCu4 [1] on a Au(111) surface. Furthermore, we show how a multi-method approach of vibrational spectroscopy and complete photoelectron spectroscopy (X-ray, UV, and inverse photoemission) can be used to demonstrate the integrity of the molecules during the adsorption process as well as the evolution of the electronic structure of this molecule in comparison with theoretical single molecule calculations.

[1] P. Happ et al. Phys. Rev. B 93, 174404 (2016)

O 15.2 Mon 15:15 MA 043

Influence of Core-Substitution on the Electronic Structure of Thiadiazole Derivatives — •Mohsen Ajdari[1], Felix Landwehr[1], Ronja Pappenberger[1], Marvin Hoffmann[2], Hendrik Hoffmann[3], Lukas Ahrens[3], Uwe H. F. Bunz[3], Andreas Dreuw[2], and Petra Tegeder[1] — [1]Physikalisch-Chemisches Institut — [2]Interdisziplinäres Zentrum für Wissenschaftliches Rechnen — [3]Organisch-Chemisches Institut, Universität Heidelberg

Thiadiazole derivatives, such as naphtothiadiazole (NTD) and benzobisthiadiazole (BBT) are of great interest for the use as electron acceptor in (opto)electronic applications.

In this study, vibrational and electronic high-resolution electron energy loss spectroscopy (HREELS) in combination with quantum-chemical calculations are utilized to investigate the influence of core-substitution via halogens or aromatic groups on the adsorption geometry and electronic structure of NTD and its halogenated derivatives (NTD- Cl/Br) as well as phenyl (BBT-Ph) and thiophene (BBT-Th) substituted BBT on Au(111).

Our findings indicate that core-substitution influences the electronic structure of the corresponding molecules by narrowing of the optical gap from 2.6 eV for NTD to 2.4 eV for NTD-Cl/Br, as well as a reduction from 2.2 eV for BBT-Ph to 1.8 eV for BBT-Th. Additionally, the first triplet state energies of NTD at 1.7 eV is reduced to 1.6 eV for NTD-Cl/Br and BBT-Ph at 1.2 eV to 0.7 eV for BBT-Th.

O 15.3 Mon 15:30 MA 043

Interaction between polyatomic molecules on layered surfaces beyond the dipole approximation — •Hsiao-Han Chuang, Ulf Saalmann, and Alexander Eisfeld — Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Str 38, Dresden

For aggregates of molecular monomers above layered surfaces, the dipole approximation breaks down when the distance between monomers and surfaces is less than several nanometers. To overcome this problem, we employ macroscopic quantum electrodynamics and use the complete transition current density of the individual monomers. Within this framework, the resulting Master Equation for the excitonic degrees of freedom of the aggregate is derived. For example, we discuss the case of PTCDA on a KCL surface.

O 15.4 Mon 15:45 MA 043

Non-conductive NaCl films impact the charge configuration in a single molecule — •Moritz Frankerl[1], Laerte Patera[2,3], Thomas Frederiksen[4], Jascha Repp[3], and Andrea Donarini[1] — [1]Institute of Theoretical Physics, University of Regensburg — [2]Institute of Physical Chemistry, University of Innsbruck — [3]Institute of Experimental and Applied Physics, University of Regensburg — [4]Donostia International Physics Center (DIPC), Spain

The utilization of non-conductive NaCl films allows the stabilization of multiple charge states on a single molecule [1]. Consequently, these films enable the observation of electronic transitions between distinct charge states by single-electron alternate-charging scanning tunneling microscopy (AC-STM) [2]. Specifically, when charging a copper-phthalocyanine (CuPc) molecule, the Jahn-Teller (JT) distortion induces a splitting of the degeneracy between the lowest unoccupied molecular orbitals (LUMOs). Notably, the AC-STM measurements reveal a double occupation of the same LUMO upon charging CuPc a second time. We show by DFT calculations complemented by a grouptheoretical analysis how the molecular electron-phonon coupling in gas phase is insufficient to explain this behavior. To address this, we propose a coupling between vibronic modes within the NaCl substrate and charges residing on the molecule. This proposition highlights the significant influence of the NaCl substrate on the electronic configuration of charged molecules, extending beyond charge stabilization. [1] Fatayer S. et al., Nature Nanotechnology 13, 376-380(2018) [2] Patera L.L. et al., Nature 566, 245-248(2019)

O 15.5 Mon 16:00 MA 043

Integer Charge Transfer at an Organic–2D Material Interface: PTCDA on h-BN/Ni(111) — •Maximilian Schaal[1], Anu Baby[2,3], Marco Gruenewald[1], Felix Otto[1], Roman Forker[1], Guido Fratesi[4], and Torsten Fritz[1] — [1]Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany — [2]Department of Materials Science, University of Milano-Bicocca, Via R. Cozzi 55, 20125 Milano, Italy — [3]STMicroelectronics, Via Tolomeo 1, 20010 Cornaredo, Italy — [4]ETSF and Dipartimento di Fisica "Aldo Pontremoli", Università degli Studi di Milano, Via Celoria, 16, 20133 Milano, Italy

Weakly interacting systems such as organic molecules on monolayers of hexagonal boron nitride (h-BN) offer the possibility of integer charge transfer leading to the formation of organic ions. Such systems exhibit unique optical and electronic properties which differ from their neutral counterparts. In this study, we used a joint experimental and theoretical approach to investigate the charge transfer of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) molecules on h-BN/Ni(111) by using *in-situ* differential reflectance spectroscopy (DRS), scanning tunneling spectroscopy (STS) and photoelectron orbital tomography (POT) measurements in combination with density functional theory (DFT) calculations. Our results show that the PTCDA monolayer consists of highly-ordered organic radical anions and neutral molecules. In addition, the occurrence of the integer charge transfer is discussed based on the energy-level alignment.

O 15.6 Mon 16:15 MA 043

Dioxygen ligation and activation at a biomimetic 2D metal organic framework — •Stefania Baronio[1], Michela De Col[1], Davide Bidoggia[1], Danilo Comini[2], Mattia Scardamaglia[3], and Erik Vesselli[1,4] — [1]Physics Department, University of Trieste, Trieste, Italy — [2]II Physics Department, University of Cologne, Cologne, Germany — [3]MAX IV Laboratory, University of Lund, Lund, Sweden — [4]CNR-IOM, Istituto Officina dei Materiali, Trieste, Italy

The investigation of 2D metal organic frameworks at surfaces is a hot topic in surface science due to their potential applications also as single atom catalysts [1]. Our work focuses on the in situ spectroscopic characterization of a bimetallic MnTPyP-Co framework self-assembled on Gr/Ir(111) and structurally similar to previously investigated Fe- and Co-based systems active towards the oxygen evolution and reduction reactions [2,3]. By means of a combined approach exploiting Sum Frequency Generation Spectroscopy and Ambient Pressure XPS, we show how the tetra-coordination of Co ad-atoms by adjacent MnTPyPs affects the overall electronic and vibrational structure of the layer, including the oxidation state of the Mn centers. The bimetallic system is extremely reactive towards O_2: while dioxygen weakly ligates at room temperature and under UHV conditions, at close-to-ambient pressure the molecule undergoes activation and dissociation at the Co sites, and CO oxidation becomes then possible.

[1] W. Auwärter et al., Nat. Chem. 7, 105-120(2015) [2] B. Wurster et al., J. Am. Chem. Soc. 138, 3623-3626(2016) [3] F. Armillotta et

al., ACS Catal. 12, 7950-7959(2022)

O 15.7 Mon 16:30 MA 043

Electronic structure of acenes on an MoS2 monolayer — •Jan-Phillip Topmöller and Michael Rohlfing — Institute of Solid State Theory, University of Münster, Germany

TMDCs show great potential in terms of their applicability in optical electronics. Due to their large surface, molecules can easily bind to the TMDC and affect its electronic properties. Here we investigate acenes as a prototypical class of molecule.

We use DFT (GGA) and DFT-D3 to determine the most stable adsorption position of the smallest acenes like benzene, naphthalene and anthracene on MoS2. Subsequently, we use many body perturbation theory to calculate the electronic structure of the adsorbate system and its individual components (MoS2 and the molecule) in order to investigate the effect of the molecule on the MoS2 electronic and optical spectrum.

O 15.8 Mon 16:45 MA 043

Energy level alignment at organic-transition metal dichalcogenide interfaces — •Hibiki Orio[1], Maximilian Ünzelmann[1], Kiana Baumgärtner[1], Christian Metzger[1], Markus Scholz[2], Kai Rossnagel[2,3], and Friedrich Reinert[1] — [1]Universität Würzburg, Experimentelle Physik VII and Würzburg-Dresden Cluster of Excellence, Würzburg, Germany — [2]Deutsches Elektronen Synchrotron DESY, Hamburg, Germany — [3]IEAP and KiNSIS, CAU Kiel, Kiel, Germany

The hybrid interface between organic molecules and transition metal dichalcogenides (TMDCs) is characterized by weakly binding van der Waals interactions. In such systems, the interfacial energy level alignment is not in equilibrium and can be modified by external perturbations [1]. Here, we investigate the electronic structure of copper phthalocyanine (CuPc) films grown on different layered materials (graphite, TiSe$_2$, and WSe$_2$). Using ultraviolet and x-ray photoelectron spectroscopy, we study in particular the influence of x-ray radiation on the electronic states. We find that the HOMO level is stable in the case of CuPc/graphite, but shifts by 140 meV and 70 meV for TiSe$_2$ and WSe$_2$ substrates, respectively. Changes in film morphology and beam damage are subtle and insufficient to explain these different energy shifts.

[1] D. A. Racke, and O. L. A. Monti, Surf. Sci. **630**, 136 (2014).

O 15.9 Mon 17:00 MA 043

Momentum-sensitive characterization of hybrid states in metal-organic coordination networks — •Simone Mearini[1], Daniel Baranowski[1], Dominik Brandstetter[2], Andreas Windischbacher[2], Iulia Cojocariu[3], Luca Schio[4], Luca Floreano[4], Pierluigi Gargiani[5], Manuel Valvidares[5], Peter Puschnig[2], Vitaliy Feyer[1,6], and Claus M. Schneider[1,6] — [1]Forschungszentrum Jülich, Germany — [2]University of Graz, Austria — [3]University of Trieste, Italy — [4]CNR-IOM, Trieste, Italy — [5]ALBA Synchrotron, Barcelona, Spain — [6]Universität Duisburg-Essen, Germany

The electronic and magnetic properties of metal-organic coordination networks (MOCN) are to a great extent defined by the nature of the metal core and the coordinating organic ligand. To probe the new electronic states emerging due to the metal-organic bond formation, we fabricate MOCNs via co-deposition of transition metals (TMs) and benzene derivatives onto metallic substrates and apply a multi-technique approach supported by theoretical calculations to comprehensively study the local electronic structure of MOCNs. Using ARPES, we observed the appearance of energy-dispersive electronic states, attributed to the interaction between the 3d states of the TM and the ligand π molecular orbitals. This interaction stabilizes specific electronic and spin configurations of the TM ion, as determined by XPS and XMCD experiments. Finally, experimental and theoretical evidences fully support the crucial role held by the choice of the TM in the control of MOCNs properties.

O 15.10 Mon 17:15 MA 043

Imaging single protonated molecules — •Jimin Ham[1], Xu Wu[1], Klaus Kern[1,2], and Kelvin Anggara[1] — [1]MPI for Solid State Research, Stuttgart — [2]Institute de Physique, École Polytechnique Fédérale de Lausanne

Protonation of molecules is one of the most fundamental events in chemistry. Direct study of protonated molecules, however, has remained challenging due to their transient existence, short lifetimes, low abundance, and high reactivities. These characteristics cause studies of protonated molecules to be intractable for ensemble-averaged analytical methods. Here we circumvented these challenges by direct imaging of protonated molecules at single molecule level. We accomplish this by soft landing protonated molecules on surfaces using the Electrospray Ion Beam Deposition (ESIBD) technique, followed by direct imaging using Scanning Tunneling Microscopy (STM). By imaging single protonated molecules, we are able to observe directly the effect of protonation on molecular motions and electronic structures, as well as the structure of proton-catalyzed reaction intermediates. These findings open new avenues to explore proton-mediated chemical effects at the ultimate single molecule level.

O 15.11 Mon 17:30 MA 043

Electronic properties of N-heterocyclic carbenes and olefins on Si(111)$\sqrt{3} \times \sqrt{3}$ R30°-B — •Eva Glomski[1], Milan Kubicki[1], Mowpriya Das[2], Ankita Das[2], Robert Zielinski[1], René Schöder[1], Susi Lindner Franz[1], Mike Thomas Nehring[1], Mario Dähne[1], Frank Glorius[2], and Martin Franz[1] — [1]Technische Universität Berlin, Institut für Festkörperphysik, Berlin, Germany — [2]Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Münster, Germany

Silicon is the most widely used semiconductor material in electronic devices and a modification or functionalization by organic overlayers is a promising approach to enhance their functionality. Recently, N-heterocyclic carbenes (NHCs) and olefins (NHOs) were found to be promising candidates for a modification of silicon surfaces [1,2]. In this work, the adsorption of NHCs and NHOs on the Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-B surface is investigated using synchrotron based high-resolution photoelectron spectroscopy allowing an in-depth study of the binding behavior and the electronic properties of the formed interfaces. Furthermore, the evolution of the band bending is investigated on the basis of Si 2p spectra revealing a different behavior for the studied NHCs and NHOs.

[1] M. Franz et al., Nat. Chem. 13, 828-835 (2021).

[2] M. Das et al., Angew. Chem. Int. Ed. 2023, e202314663.

O 15.12 Mon 17:45 MA 043

Simulating Smart Surfaces for Lithium Ion Batteries — •Fabian Dietrich — Departamento de Ciencias Físicas, Universidad de La Frontera, Temuco, Chile

Self-assembled monolayers (SAM) are a common tool for the functionalization of surfaces. Such surfaces can be used form controlable solid electrolyte interfaces (SEI) on cathode materials for lithium ion batteries. Using photo-switchable organic molecules for the formation of the SAM yields a controlabilty of the surface properties - a so-called smart surface. These smart surfaces are supposed to be used to avoid undesired charge (and with that energy) loss in a fully charged lithium ion battery.

For being used as smart surface, the organic molecules have to fulfill the following requirements: 1.) A photo-switchable moiety with both photoisomers separated by at least 5000 cm^{-1}; 2.) Having polar functional groups for the interaction with the metal oxide surface; 3.) Both photo-isomers can build a stable SAM and 4.) The structural rearrangement upon photo-switching is large enough to influence the Li ion insertion and small enough to keep the SAM stable. For this challenge, we applied density functional theory (DFT) to evaluate different molecules with respect to their aggregation behavior on the previously studied vanadium pentoxide surface and subsequently different diffusion pathways through a SAM of the selected molecules.