

O 86: Poster Session - Organic Molecules on Inorganic Substrates: Electronic, Optical and other Properties II

Time: Wednesday 18:15–20:00

Location: P2/EG

O 86.1 Wed 18:15 P2/EG

STM and DFT study of BF₄ anion migration on a triaza-triangulenium SAM on Au(111) — ●SERGIH SNEGIR¹, YANNICK DAPPE², DMITRO SYSOIEV³, OLIVIER PLUCHERY⁴, THOMAS HUHN¹, and ELKE SCHEER¹ — ¹University of Konstanz, Konstanz, Germany — ²SPEC, CEA, CNRS, University Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France — ³Institute of Organic Chemistry and Biochemistry, Prague, Czech republic — ⁴Institut des Nano-Sciences de Paris (INSP), Sorbonne Universités, CNRS, Paris, France

Chemical coupling of functional molecules with so-called platforms allows the formation of functional Self-Assembled Monolayer (SAM). An example is triaza-triangulenium (TATA), with extended aromatic core, allowing the formation of good electronic contact with the metal surface. Here we present studies on SAMs of TATA-BF₄ molecules on Au(111) by means of Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT). In solution, these molecules exist as ion pairs of TATA⁺ and BF₄⁻. However, under electrochemical deposition on Au(111) [1], on the TATA⁺ cations formed SAMs the BF₄⁻ anions seemingly disappear. Our STM experiments reveal dissociation of the TATA-BF₄ complex. The TATA⁺ remains stable within the SAM while the BF₄⁻ spontaneously migrates through the TATA SAM on the surface. DFT calculations show a reduction of the TATA-BF₄ binding energy after deposition. [1]-S. Kuhn, U. Jung, S. Ulrich, R. Herges and O. Magnussen, *Chemical Communications*, 2011, 47, 8880-8882.

O 86.2 Wed 18:15 P2/EG

Pump-Probe Photoelectron Momentum Microscopy of Molecular Thin Films at a Free-Electron Laser — ●CHRISTIAN METZGER¹, MARKUS SCHOLZ², KIANA BAUMGÄRTNER¹, CHUL-HEE MIN¹, THIAGO R. F. PEIXOTO¹, DMYTRO KUTNYAKHOV³, MICHAEL HEBER³, FEDERICO PRESSACCO⁴, WILFRIED WURTH^{3,4}, ANDERS MADSEN², and FRIEDRICH REINERT¹ — ¹Experimentelle Physik 7, Universität Würzburg, Germany — ²European XFEL, Germany — ³DESY Hamburg, Germany — ⁴Universität Hamburg, Germany

The analysis of the momentum distribution from static angle-resolved photoemission experiments has provided new insights into the electronic interaction at molecule-metal interfaces [1], electron-vibration coupling [2] as well as structural alignment [3] in the last decade [4]. Our pump-probe measurements focus on translating these previous achievements into the time-domain. To this end, we conducted dynamic experiments on pentacene bilayers on top of Ag(110) with a time-of-flight momentum microscope at a free-electron-laser facility [5]. Pentacene is an ideal archetype for this endeavor due to its broad applicability in electronic devices and its well characterized properties in static experiments [6]. Furthermore, it has the potential to showcase a variety of ultrafast photoinduced processes such as singlet fission.

[1] G. Zamborlini et al., *Nat. Comm.* 8, 335 (2017). [2] M. Graus et al., *Phys. Rev. B* 98, 195412 (2018). [3] B. Stadtmüller et al., *EPL* 100, 26008 (2012). [4] P. Puschnig et al., *Science* 326, 702 (2009). [5] M. Scholz et al., arXiv:1907.10434. [6] M. Grimm et al., *Phys. Rev. B* 98, 195412 (2018)

O 86.3 Wed 18:15 P2/EG

Application of periodic energy decomposition analysis to metallic systems — ●JAN-NICLAS LUY, BENEDIKT P. KLEIN, J. MICHAEL GOTTFRIED, and RALF TONNER — Fachbereich Chemie, Philipps Universität Marburg, Germany

The Energy Decomposition Analysis (EDA) is a wavefunction based bonding analysis scheme that enjoys significant popularity in the molecular chemistry community [1]. Recently the method has been extended to surfaces and solids [2] and applied to organic surface chemistry [3]. It was shown that localized, covalent bonds in a periodic system can be interpreted in a similar fashion as their 0D molecular counterparts. Adsorption of organic molecules on transition metal surfaces, however, requires a more nuanced description [4]. In addition to covalent bonds, interactions are often characterized by large charge transfer, polarization and dispersion contributions. While for many alternant hydrocarbons (e.g. naphthalene) dispersion dominates on Cu(111), orbital interactions can be identified in non-alternant cases (azulene). With the more reactive Pt(111) surface,

both naphthalene and azulene form strong chemisorptive bonds that show donor/acceptor and shared-e⁻ character.

[1] M. von Hopffgarten and G. Frenking, *WIREs Comput Mol Sci* **2012**, 2, 43.

[2] M. Raupach, R. Tonner, *J. Chem. Phys.* **2015**, 142, 194105.

[3] L. Pecher, S. Laref, M. Raupach and R. Tonner, *Angew. Chem. Int. Ed.* **2017**, 56, 15150.

[4] B. P. Klein et al., *Phys. Rev. X* **2019**, 9, 011030.

O 86.4 Wed 18:15 P2/EG

Vibron-assisted spin excitation in a magnetically anisotropic molecule — ●GARNIER L.¹, VERLHAC B.¹, BACHELLIER N.¹, ZALDÍVAR J.², RUBIO-VERDÚ C.², ABUFAGER P.³, ORMAZA M.¹, CHOI D.-J.^{4,6}, BOCQUET M.-L.⁵, PASCUAL J.I.^{2,6}, LORENTE N.⁴, and LIMOT L.¹ — ¹Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France — ²CIC nanoGUNE, 20018 Donostia-San Sebastián, Spain — ³Instituto de Física de Rosario, CONICET and Universidad Nacional de Rosario, Av. Pellegrini 250 (2000) Rosario, Argentina — ⁴Centro de Física de Materiales (CFM) & DIPC, 20018 Donostia-San Sebastián, Spain — ⁵PASTEUR, ENS, Sorbonne Universités, CNRS, 75005 Paris, France — ⁶Ikerbasque, Basque Foundation for Science, Bilbao, Spain

The electrical control and readout of molecular spin states is key for high-density storage. Expectations are that electrically-driven spin and vibrational excitations in a molecule should give rise to new conductance features in the presence of magnetic anisotropy, offering alternative routes to study and, ultimately, manipulate molecular magnetism. Here, we use inelastic electron tunneling spectroscopy to promote and detect the excited spin states of a prototypical molecule with magnetic anisotropy. We demonstrate the existence of a vibron-assisted spin excitation that can exceed in energy and in amplitude a simple excitation among spin states. The excitation, which can be quenched by chemical changes in the magnetic molecule, is explained using first-principles calculations and model calculations that include dynamical correlations.

O 86.5 Wed 18:15 P2/EG

Electronic properties of N-substituted pentacene derivatives on Au(111) — ●TANJA SCHMITT¹, JAKOB STEIDEL¹, MARVIN HOFFMANN², HILMAR REISS³, UWE BUNZ³, ANDREAS DREUW², and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ²Interdisziplinäres Zentrum für Wissenschaftliches Rechnen, Universität Heidelberg — ³Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg

N-heteropolycyclic aromatic compounds are promising candidates for n-channel semiconductors. The introduction of nitrogen into the π -electron-backbone of the polycyclic aromatic hydrocarbons stabilizes the frontier orbitals and increases the electron affinity, while the size of the HOMO-LUMO (optical) gap is nearly unaffected.

Thus, the electronic properties of N-functionalised pentacene derivatives were studied using two-photon photoemission (2PPE). With this powerful technique, the energetic positions of occupied, unoccupied and excitonic states were determined. In addition, the dynamics upon optical excitation can be investigated on a femtosecond time scale. Also, angle-resolved 2PPE can be performed in order to study the dispersion of present states.

Crucial properties such as optical and transport gap as well as binding energy was determined and compared to non-substituted pentacene using 2PPE. In addition, state-of-the-art quantum chemical theory was carried out.

O 86.6 Wed 18:15 P2/EG

Dehydrogenation Reactions of O-Heterocyclic LOHC Molecules — ●FELIX HEMAUER, PHILIPP BACHMANN, FABIAN DÜLL, JOHANN STEINHAEUER, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Friedrich-Alexander-Universität, Erlangen, Germany

With the dwindling of fossil fuels and the alarming progression of global warming, the ecological and social demand for cleaner and more sustainable energy sources has never been as high. As renewable sources, such as wind and solar power, give no continuous and constant power

output, hydrogen is a promising candidate for the chemical storage of energy. The concept of Liquid Organic Hydrogen Carriers (LOHCs) avoids unfavorable handling of elemental hydrogen.

Heterocyclic LOHC molecules display advantageous thermodynamic properties regarding their heat of dehydrogenation. Consequently, several N-heterocycles have been successfully investigated, e.g. the indole-based systems and their derivatives.

In order to investigate the feasibility of O-heterocyclic compounds as possible LOHCs, synchrotron radiation-based high resolution X-ray photoelectron spectroscopy and temperature-programmed desorption measurements of furan and benzofuran were performed on Pt(111) under UHV conditions. By applying heating ramps after the adsorption experiment, the respective dehydrogenation and decomposition reactions are monitored via evaluation of the characteristic spectra. This allows for fundamental insights into the reactivity and stability and helps assessing the viability of the compound class as LOHC.

O 86.7 Wed 18:15 P2/EG

How Metrology can improve Photoemission Tomography —

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Photoemission tomography (PT) is a powerful tool to identify the electron orbital structure of mono- and bi-layers of molecules on surfaces. Using angle-resolved photoemission spectroscopy and assuming a basic plane wave as the final state of the photoelectrons, the molecular orbital can generally be represented by a Fourier Transformation of the resulting impulse map. Thus, detailed information on electronic and geometric structures, as well as orbital densities of molecular systems on different surfaces is extracted.

In order to receive accurate relative electron densities of the orbitals, it already has been shown that a normalization to the precise photon flux is essential. In this context, we seek to apply the PT method to experimental datasets for angle-resolved photoemission of atomic photoionization. The resulting impulse distributions will be compared to those, received from analytically calculated hydrogen-like atomic orbitals, in order to show and overcome differences in the electron densities of the orbitals due to the PT method.

O 86.8 Wed 18:15 P2/EG

The geometric and electronic properties of kekulene monolayers on Cu(111) and Cu(110) studied by den-

sity functional theory — •ALEXANDER REICHMANN¹, ANJA HAAGS^{2,3,4}, QITANG FAN⁶, TIM NAUMANN⁶, SIMON WERNER⁶, JÖRG SUNDERMEYER⁶, XIAOSHENG YANG^{2,3,4}, LARISSA EGGER¹, HANS KIRSCHNER⁵, FRANCOIS C. BOCQUET^{2,3}, GEORG KOLLER¹, ALEXANDER GOTTWALD⁵, MATHIAS RICHTER⁵, MICHAEL G. RAMSEY¹, J. MICHAEL GOTTFRIED⁶, SERGUEI SOUBATCH^{2,3}, F. STEFAN TAUTZ^{2,3,4}, and PETER PUSCHNIG¹ — ¹Institute of Physics, University of Graz, Austria — ²Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ³Jülich Aachen Research Alliance (JARA), Germany — ⁴Physics IV A, RWTH Aachen University, Germany — ⁵Physikalisch-Technische Bundesanstalt (PTB), Germany — ⁶Fachbereich Chemie, Philipps-Universität Marburg, Germany

Kekulene is a polycyclic aromatic hydrocarbon made of 12 fused benzene rings which has attracted renewed interest. For instance, its aromaticity is still debated and it may serve as a model for graphene pores. In this contribution, we use density functional theory to study kekulene adsorbed on the (111) and (110) surfaces of copper. We determine kekulene's adsorption height, site and its azimuthal alignment. Based on the relaxed adsorption geometry, we further analyze the electronic structure in detail by computing the molecular orbital projected density of states and by simulating angle-resolved photoemission (ARPES) band and momentum maps. Finally, we compare our results to experimental ARPES data.

O 86.9 Wed 18:15 P2/EG

Structure and Morphology of Tetracene Aggregates on HOPG —

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Exciton formation in tetracene involves fascinating phenomena such as long-range triplet propagation and singlet fission, and fusion [1]. Our aim is to elucidate the spatially resolved population dynamics and energetics of these processes in tetracene nano- and microstructures at surfaces. Here we present scanning probe (AFM, LT-STM) and fluorescence microscopy data on tetracene aggregates on HOPG prepared by *ex-situ* deposition from a solution via drop-casting or immersion, as well as *in-situ* evaporation. For the latter polarization dependent fluorescence reveals highly ordered crystallites, while the structure of *ex-situ* prepared layers in the monolayer regime is more fragile. Since literature about tetracene on HOPG is scarce we compare the results to studies on pentacene on HOPG [2]. Formation of tetracene mono- and multilayers is discussed with regard to lying-down and standing-up molecular configurations, respectively.

[1] Akselrod et al., Nat. Commun. **5** (2014).

[2] Götzen et al., Phys. Rev. B **81** (2010).