

O 6: Organic Molecules on Inorganic Substrates I: Electronic, Optical and other Properties

Time: Monday 10:30–13:30

Location: REC C 213

O 6.1 Mon 10:30 REC C 213

Molecular orientation and phase transitions of DHTAP on Cu(110) — ●CLAUDIA LÓPEZ-POSADAS¹, MICHAEL GYÖRÖK¹, ANTONY THOMAS², THOMAS LEONI², OLIVIER SIRI², CONRAD BECKER², and PETER ZEPPENFELD¹ — ¹Institute of Experimental Physics, Johannes Kepler University Linz, Altenberger Str. 69, A-4040 Linz, Austria — ²Aix-Marseille University, CNRS, CINaM, UMR 7325, F-13288 Marseille, France

The structure and orientation of 5,14-dihydro-5,7,12,14-tetraazapentacene (DHTAP) layers deposited on Cu(110) was studied using reflectance difference spectroscopy (RDS), Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED). The evolution of the RDS signal allows to identify the sequential formation of up to three monolayers as well as a phase transition upon completion of the first one. DHTAP molecules in the first monolayer are always lying flat with their long molecular axis aligned parallel to the [-110]-direction of the Cu(110) surface. However, for subsequent layers the orientation critically depends on the deposition temperature T. At T=240K the DHTAP molecules are mostly aligned parallel to the ones in the first layer, whereas at room temperature and above their preferential orientation is along the [001]-direction, i.e., orthogonal to the molecules in the first layer. Finally, the main optical transitions and the orientation of the transition dipole moments of the DHTAP layers were extracted from the RDS spectra and compared with recent theoretical investigations on individual DHTAP molecules.

Invited Talk

O 6.2 Mon 10:45 REC C 213

Excited State Dynamics at Interfaces with Organic Semiconductors — ●PETRA TEGEDER — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Germany

Understanding the dynamics of electronically excited molecular states after optical excitation in organic semiconductors is necessary for improvement and optimization of potential molecule-based devices such as organic photovoltaic cells or organic light emitting diodes. Using femtosecond time-resolved spectroscopies, namely two-photon photoemission (2PPE) and second harmonic generation (SHG) we studied the excited state dynamics at interfaces and within thin films of several organic semiconducting molecules. This includes the singlet fission dynamics in triisopropyl-silylethynyl-pentacene (TIPS-Pn) adsorbed on Au(111). Based on 2PPE measurements we proposed a coherent excitation of the singlet and multiexciton state, both decaying with the same time constant of 160 fs. The triplet state stabilizes on a time scale of 1.6 ps and decays to the ground state. The latter occurs within 620 ps. However, SHG measurements on TIPS-Pn films point towards a non-coherent formation of the singlet and multiexciton state. In well-ordered diindenoperylene (DIP) and perylene alkylidimide (PDIR) films, respectively, and at differently structured DIP/PDIR interfaces we elucidated the exciton and charge transfer dynamics in the femtosecond regime using SHG.

O 6.3 Mon 11:15 REC C 213

Dynamic Momentum Mapping of Excited Molecular Wave Packets — ●KIANA BAUMGÄRTNER¹, MARKUS SCHOLZ², CHRISTIAN METZGER¹, 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, Julius-Maximilians-Universität Würzburg, Germany — ²European XFEL, Germany — ³DESY Hamburg, Germany — ⁴Universität Hamburg, Germany

In the last decade [1], the interpretation of the momentum distribution from static angle-resolved photoemission experiments has improved our understanding of charge transfer processes at the molecule-metal-interface [2], vibronic progression [3] as well as the geometric alignment in these systems [4]. In this contribution I will present our experimental findings on time-resolved orbital mapping of excited molecular states. We conducted pump-probe experiments on pentacene bilayers atop Ag(110) at a free-electron-laser facility with a momentum microscope. Pentacene presents an ideal material system to study not only because of its broad applicability in devices such as OFETs and OLEDs but it is also well characterized by static experiments [4,5] and it has the potential to showcase ultrafast photoinduced processes such as singlet fission.

[1] P. Puschnig et al., *Science* **326**, 702 (2009). [2] G. Zamborlini et al., *Nat. Comm.* **8**, 335 (2017). [3] M. Graus et al., *Phys. Rev. Lett.* **116**, 147601 (2016). [4] M. Grimm et al., *Phys. Rev. B* **98**, 195412 (2018). [5] M. Scholz et al., arXiv:1907.10434.

O 6.4 Mon 11:30 REC C 213

Dodecacene generated on Surface: Re-opening of the Energy Gap — TIM KÜHNE¹, FRANK EISENHUT¹, FÁTIMA GARCIA³, SALETA FERNÁNDEZ³, ENRIQUE GUITIÁN³, DOLORES PÉREZ³, GEORGES TRINQUIER⁵, GIANAURELIO CUNIBERTI², CHRISTIAN JOACHIM⁴, DIEGO PEÑA³, and ●FRANCESCA MORESCO¹ — ¹Center for Advancing Electronics Dresden, TU Dresden, Germany — ²Institute for Materials Science, TU Dresden, Germany — ³Leibniz Institute of Polymer Research, Dresden, Germany — ⁴GNS & MANA Satellite, CEMES, CNRS, Toulouse Cedex, France — ⁵Laboratoire de Chimie et Physique Quantiques, Université Paul-Sabatier, Toulouse Cedex, France

The acene series represents a unique model system to investigate the intriguing electronic properties of extended π electron structures in the one-dimensional limit, which are important for applications in electronics and spintronics and for the fundamental understanding of electronic transport. Here we present the on-surface generation of the longest acene obtained so far: Dodecacene. Scanning tunneling spectroscopy gives access to the energy position and spatial distribution of its electronic states on the Au(111) surface. We observe that, after a progressive closing of the gap and a stabilization to about 1 eV at the length of decacene and undecacene, the energy gap of dodecacene unexpectedly increases to 1.4 eV. Considering the acene series as an exemplary general case, we discuss the evolution with length of the single tunneling resonances in comparison with ionization energy, electronic affinity, and optical gap.

O 6.5 Mon 11:45 REC C 213

Exciton Fission, Fusion, Annihilation and Quantum Beating in Deposited Tetracene Films — KEVIN OLDENBURG, ●INGO BARKE, CHRIS REHHAGEN, STEFAN LOCHBRUNNER, and SYLVIA SPELLER — Institute of Physics, University of Rostock

One technique to overcome the Shockley-Queisser limit in dye-sensitized solar cells is to exploit singlet fission processes, effectively doubling the number of charge carriers per photon. Here we present photoemission electron microscopy (PEEM) data of the excited state dynamics and spatial distribution of tetracene thin films. In order to locally enhance the excitation density, plasmon excitations in mass-selected silver nanoparticles (diameter \approx 10 nm) are used [1]. Signatures of a singlet fission process are visible leading to an efficient population of a triplet state with annihilation governed decay dynamics on the order of ns to μ s, while we observe an intrinsic lifetime exceeding 10 μ s. Complementary fluorescence lifetime microscopy (FLIM) reveals quantum beats in the signal of delayed fluorescence on the time scale of several ns which are attributed to a coherent excitation of a triplet manifold [2]. The coherence time appears to be dependent on the exciton density which is analyzed by changing the excitation power. The characteristic lifetimes obtained by PEEM are consistent with fluorescence data (see also [3]).

[1] K. Oldenburg *et al.*, *J. Phys. Chem. C* **123**, 1379 (2019).

[2] J. Burdett, C.J. Bardeen, *JACS* **134**, 8597 (2012).

[3] G.M. Akselrod *et al.*, *Nat. Commun.* **5**, 3646 (2014).

O 6.6 Mon 12:00 REC C 213

Good Vibrations - Mode Coupling in Fatty Acids — MICHAEL LACKNER, ●MARVIN HILLE, and ECKART HASSELBRINK — University of Duisburg-Essen, Essen, Germany

Internal vibrational energy distribution (IVR) in molecules is fundamental for understanding their chemical reactivity and research in this field has gained a lot of popularity in the past. It is, however, still fair to say that predictive power over the energy flow in vibrationally excited molecules has yet to be obtained. We will present newest findings regarding the energy flow dynamic of a fatty acid Langmuir-Blodgett film on a picosecond scale. Vibrational sum frequency generation (vSFG) spectroscopy allows precise monitoring of resonant vibrations of an adsorbate monolayer. In our setup we use a resonant ps narrow-band IR laser pulse for pumping and a fs broadband IR-visible pulse pair for vSFG probing of the monolayer. Using this pump-probe setup

we observed a very fast (< 2 ps) energy transfer to the other modes when pumping the anti-symmetric methyl or methylene stretch, followed by a longer decay (~ 85 ps) into presumably bending and internal rotational modes.

O 6.7 Mon 12:15 REC C 213

excited states dynamics of unsubstituted terylene, a text book molecule — ●BOUBACAR TANDA BONKANO¹, KOBIN BJÖRN², SERGEY KOVALENKO², STEFAN HECHT², and JULIA STÄHLER¹ — ¹Fritz-Haber Institute of the MPG, Berlin — ²Institut für Chemie, Humboldt Universität zu Berlin

In hybrid solar cells, the separation of the electron-hole pairs after photogeneration is a key aspect of their functionality. This requires, in hybrid inorganic/organic systems, the use of molecules that have excited states with sufficiently long lifetime to allow charge separation. In order to investigate terylene molecules, we performed two types of time-resolved spectroscopy, time-correlated single photon counting (TCSPC) and broadband transient absorption (TA) using a white light continuum probe. The steady state absorption and emission of terylene molecules in solution show mirrored lineshapes displaying a clear vibronic progression. Terylene molecules have their maximum absorption and emission lines at 560 nm (2.21 eV) and 570 nm (2.17 eV) respectively. Both TCSPC and TA consistently show a decay of 3.7 ns for the excited state S_1 . Our results demonstrate that terylene molecules have long-lived excited states, and, therefore could facilitate charge separation process. First measurements of thin terylene films indicate a significant change of absorption properties, possibly resulting from H-aggregate formation.

O 6.8 Mon 12:30 REC C 213

Unbaking a cake: Computational strategies to disentangle core-level spectroscopy signals of chemical interaction at metal-organic interfaces — ●SAMUEL J. HALL and REINHARD J. MAURER — Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom

X-ray photo-emission spectroscopy (XPS) and x-ray absorption, so-called near-edge absorption fine structure spectroscopy (NEXAFS) provide insight into the structure, chemical interaction, and electronic properties of metal-organic interfaces. The interpretation of NEXAFS spectra is challenged by peak broadening, overlapping features and electronic hybridisation between organic and metallic states at the interface. These effects diminish the usefulness of reference spectra and literature values when it comes to peak assignment for complex metal-adsorbed molecules. In this talk, we will present a systematic computational study of the effect of molecule-metal interaction strength and overlayer structure on spectral features in NEXAFS spectroscopy. Using dispersion-inclusive Density Functional Theory and the Transition-Potential method, we have simulated NEXAFS spectra for a benchmark set of various aromatic organic compounds adsorbed on a series of (111) facets of single crystal transition metal surfaces. By decomposing the spectra into initial core state and final valence state contributions, we analyse how weak and strong molecule-metal interaction, charge transfer, and electronic hybridisation and dispersion effects manifest in spectra. On the basis of these findings, we provide suggestions for future interpretation strategies.

O 6.9 Mon 12:45 REC C 213

Manipulation of the noble metal rare earth surface alloy DyAg₂ by adsorption of organic molecules — ●EVA SOPHIA WALTHER¹, JOHANNES SEIDEL¹, DOMINIK JUNGKERN¹, MARKUS FRANKE^{2,3}, AHMED ALHASSANAT⁴, HANS-JOACHIM ELMERS⁴, CHRISTIAN KUMPF^{2,3}, MARTIN AESCHLIMANN¹, and BENJAMIN STADTMÜLLER¹ — ¹Department of Physics and Research Center OPTIMAS, TU Kaiserslautern — ²Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich — ³Jülich-Aachen Research Alliance (JARA) — ⁴Institute of Physics, JGU Mainz

The vast requirement for novel nano-sized information technology de-

vices has triggered the search for functional low dimensional materials with distinct spin order. A particularly interesting case is the contact of molecular complexes and surface alloys, which combines the unique functionality of molecular complexes with the spin order of surface alloys. Here, we focus on Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on the DyAg₂ surface alloy. Alloying the topmost layer of an Ag(111) surface with Dy results in a long range ordered magnetic phase at low sample temperature. Using synchrotron-based photoemission and magnetic circular dichroism experiments we can reveal the manipulation of the electronic and magnetic properties of this surface alloy by adsorption of PTCDA. These changes of the DyAg₂ surface alloy are attributed to the formation of σ -like local bonds between the molecules oxygen end groups and the Dy-alloy atoms.

O 6.10 Mon 13:00 REC C 213

Direct observation of conductive polymer induced inversion layer in n-Si and correlation to solar cell performance — ●RONGBIN WANG^{1,2}, YUSHENG WANG², CHEN WU², TIANSHU ZHAI², JIACHENG YANG², BAOQUAN SUN², STEFFEN DUHM², and NORBERT KOCH^{1,2} — ¹Institut für Physik, Humboldt-Universität zu Berlin, Germany — ²Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, China

Heterojunctions formed by PEDOT:PSS films and n-type silicon were investigated by photoelectron spectroscopy. By diluting the original PEDOT:PSS solution and increasing the spin-coating speed, a series of PEDOT:PSS thin films with nominal thicknesses down to 5 nm were achieved on n-Si substrates. Large shifts of Si 2p core levels upon PEDOT:PSS deposition provide direct evidence that a dopant-free p-n junction, i.e., an inversion layer, is formed within Si. Among the investigated PEDOT:PSS formulations, the largest induced band bending within Si (0.71 eV) is found for PH1000 combined with a wetting agent and the solvent additive dimethyl sulfoxide (DMSO). Without DMSO, the induced band bending is reduced, as is also the case with a PEDOT:PSS (AI4083) formulation with higher PSS content. By comparing PEDOT:PSS/n-Si solar cells with MoOx/n-Si cells, it becomes apparent that a large contact-induced band bending does not necessarily lead to a high Voc. Adequate passivation of the silicon surface to decrease recombination and high conductivity of the covering layer are also needed to achieve high PCE devices. Reference: Wang et al., Adv. Funct. Mater. 2019, 1903440 (doi.org/10.1002/adfm.201903440)

O 6.11 Mon 13:15 REC C 213

Investigation of a Novel Tetrapodal Self-Assembled Monolayer for Orthogonal Orientation — ●VALENTINA ROHNACHER^{1,2}, FRANK S. BENNECKENDORF^{2,3}, SEBASTIAN BECK^{1,2}, JAN FREUDENBERG^{2,3}, WOLFRAM JAEGERMANN^{2,4}, PAOLO SAMORI⁵, MICHAEL ZHARNIKOV⁶, UWE H.F. BUNZ^{2,3}, ANNEMARIE PUCCI^{1,2}, and KLAUS MÜLLEN^{2,7} — ¹KIP, Uni Heidelberg — ²InnovationLab, Heidelberg — ³TU Darmstadt — ⁴OCI, Uni Heidelberg — ⁵CNRS, Uni Strasbourg — ⁶PCI, Uni Heidelberg — ⁷MPIP, Mainz

Conformationally rigid multipodal molecules should control the orientation and packing density of functional head groups upon self-assembly on solid supports. Common tripods frequently fail in this regard, because of inhomogeneous bonding configuration and stochastic orientation. These issues are circumvented by a suitable tetrapodal diazatriptycene (DAT) moiety, bearing four thiol-anchoring group. We performed infrared reflection-absorption spectroscopy (IRRAS) on DAT molecules assembled on gold substrates to probe the orientation. Together with the results of contact angle measurements, STM, NEXAFS and PES, a better understanding about the formation of self-assembled monolayers (SAMs) was achieved. We found out that DAT molecules form well-ordered SAMs on Au(111) substrates, whereby the tetrapodal scaffold enforces a nearly upright orientation of the terminal head group with respect to the substrate. Functionalization by condensation chemistry allows a large variety of functional head groups to be introduced to the tetrapod, paving the path towards advanced surface engineering and sensor fabrication.