O 97: Organic Molecules on Inorganic Substrates: Electronic, Optical and Other Properties II

Time: Friday 10:30–12:30 Location: H6

O 97.1 Fri 10:30 H6

Nanostructuring of organic radicals on hybrid interfaces — •Arkaprava Das, Ewa Malgorzata Nowik-Boltyk, Tobias Junghoefer, and Maria Benedetta Casu — Institute of Physical and Theoretical Chemistry, University of Tübingen, 72076 Tübingen, Germany

Organic radicals are potential candidates for groundbreaking applications like energy storage, quantum computing, and spintronics. In order to investigate the nature of the adsorption of the radical derivative molecules on hybrid surfaces based on polycrystalline Au and native SiO_2, we investigate their electronic structure and morphology. The electronic structure at the interface is investigated by using X-ray photoelectron spectroscopy (XPS) and the morphology is studied with scanning electron microscopy. The substrate-dependent interface interactions have resulted in different nanostructures crucial for device fabrication whereas changes in line shape of core level spectra confer direct evidence of changed electronic properties.

O 97.2 Fri 10:45 H6

Beyond the Koopmans' theorem: Energy-level alignment of PTCDA on BlueP-Au-network on Au(111) — •Maximilian Schaal[1], Felix Otto[1], Marco Gruenewald[1], Roman Forker[1], Keisuke Fukutani[2], Satoshi Kera[2], and Torsten Fritz[1] — [1]Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany — [2]Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Koopmans' theorem is often used to relate the observed spectroscopic features in UP spectra to the orbital energies of molecules calculated by Hartree-Fock calculations. However, this theorem neglects the self-energy (charging energy), which can be as large as 1 eV for molecules in the gas phase [1]. Therefore, the ground state energy levels of the frontier orbitals are not sufficient to describe the energy-level alignment and the initial and final states must be considered [2].

In this study, we present a framework to investigate the energy-level alignment of a monolayer of PTCDA decoupled from the Au(111) surface by a BlueP-Au-network [3]. We have determined the electronic transport and the optical gap using differential reflectance and (low-energy inverse) photoelectron spectroscopy. From these values, we determined the exciton binding energy and the charging energy. Finally, we compared the energy levels of the adsorbed monolayer with measured and calculated quantities of molecules in the gas phase.

[1] Kirchhuebel *et al.*, J. Phys. Chem. C **124** (2020).

[2] Kirchhuebel *et al.*, Phys. Chem. Chem. Phys. **21** (2019).

[3] Gruenewald *et al.*, Phys. Rev. Materials **6** (2022)

O 97.3 Fri 11:00 H6

Disentangling the components of a multireference excited state in an isolated chromophore — Rodrigo Ferreira[1,2], Tomáš Neuman[1], Amandeep Sagwal[1], Jiří Doležal[2], Petr Kahan[1], and •Martin Švec[1,2] — [1]Institute of Physics, Czech Academy of Sciences — [2]Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences

Excited states of open-shell chromophores are commonly multireference in their nature. Distinguishing the components of these superposition states in a single chromophore by experimental means is a challenging task as it would essentially require capturing their orbital occupancies in the excited state. We demonstrate this can be achieved by atomically precise mapping of photon-induced tunneling current under a varying electric field, on a model case of a PTCDA anionic excited state coupled to a plasmonic nanocavity. To simulate the cascade of energy conversions and charge transfer events occurring within the molecule, a set of rate equations is derived from a many-body state scheme using an input from TD-DFT. The resulting bias-dependent tunneling current maps reach a very good agreement with the experimental data, corroborating the validity of the theoretical understanding.

O 97.4 Fri 11:15 H6

Second harmonic spectroscopy of Fe-porphyrin/Cu(001) interfaces — •Newsha Vesalimahmoud, Mahendra Kabbinahithlu, Ping Zhou, Uwe Bovensiepen, and Andrea Eschenlohr — University of Duisburg-Essen, Faculty of Physics and CENIDE, Lotharstr. 1, 47057 Duisburg, Germany

When a molecule interacts with a metal surface, metal-molecule interaction induces a rearrangement of their electronic densities, shifting the molecular orbitals relative to the metal's Fermi level. This study focuses on the FeOEP/Cu(001) interface, using interface-sensitive SHG spectroscopy. We analyze polarization- and wavelength-dependent SHG for varying molecular adsorbate thicknesses on Cu(001) using a fundamental beam in the 500-600 nm range. Polarization-dependent measurements show a higher SHG yield for p-P polarization than s-P SHG, as the intrinsic value of $\left|\chi^{(2)}_{zzz}\right|$ is much larger than $\left|\chi^{(2)}_{zxx}\right|$. As the number of monolayers increases, P-polarized SHG intensity decreases due to reduced nonlinear susceptibility from less polarizable free electrons, while S-polarized SHG shifts from 4-fold to 2-fold symmetry. The SHG spectra show an intensity peak at 2.17 eV due to a one ω resonance in Cu(001). After adsorption of 2, 5, and 8 monolayers (ML) of FeOEP on Cu(001), the spectral dependence remains similar to the Cu(001) surface, except for an enhancement at 2.21 eV for 5ML and 8ML. This enhancement is attributed to the energetic position of the lowest unoccupied molecular orbital (LUMO) at the FeOEP/Cu(001) interface.

O 97.5 Fri 11:30 H6

Probing the Roles of the Substrate Material, Spin Scattering, Temperature and Cooperative Effects in CISS — •Paul V. Möllers[1], Adrian J. Urban[2,3], Bianca C. Baciu[4], Rafael Rodriguez[5], Albert Guijarro[4], Jeanne Crassous[5], Steven De Feyter[3], Hiroshi M. Yamamoto[2], and Helmut Zacharias[1] — [1]Center for Soft Nanoscience (SoN), University of Münster, Busso-Peus-Str. 10, 48149 Münster, Germany — [2]Institute for Molecular Science, Research Center of Integrative Molecular Systems, Division of Functional Molecular Systems, 38 Nishigonaka, Myodaiji Okazaki, Aichi prefecture, 444-8585 Japan — [3]Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven, Celestijnenlaan 200 F, 3001 Leuven, Belgium — [4]Departamento de Química Orgánica, Instituto Universitario de Síntesis Orgánica, Unidad asociada al CSIC, Universidad de Alicante, E-03080, Alicante, Spain — [5]University of Rennes, CNRS, Institut des Sciences Chimiques de Rennes (ISCR), UMR 6226, Rennes, France

Monolayers of heptahelicene ([7]H) and helical tetrapyrrole (TPBT) complexes were adsorbed onto different single-crystalline metal substrates, and the spin polarization of photoelectrons emitted from these surfaces was measured. The substrate material, the temperature and the surface coverage were systematically varied to investigate the roles of the substrate spin–orbit coupling, molecular vibrations, and intermolecular interactions in the generation of the spin polarization. Furthermore, thiolized (chemisorbed) [7]H and all-carbon (physisorbed) [7]H layers were compared.

O 97.6 Fri 11:45 H6

Electrons don't wear bowties: The mechanism of Fermi-level pinning and charge for mixed donor-acceptor layers — •Richard Berger1 and Oliver T. Hofmann — TU Graz, Institute of Solid State Physics

Controlling the work function of metal substrates is critical when optimizing the performance of organic electronic devices. A particular powerful method to obtain such control is by employing a monolayer of strong electron donors or electron acceptors, i.e. so-called Fermi-level pinned systems which form charge-transfer-induced dipoles with the underlying substrate However, while the major advantage of this Fermi-level pinned systems is that the effective work function of the interface is (essentially) independent of the underlying substrate, there are only limited ways to fine-tune it. A more flexible way could be to employ a mixture of electron donors and acceptors. However, for such complex systems the underlying charge-transfer mechanism is less clear. In this work, we elucidate this mechanism using machine-learning augmented density functional theory calculations to predict both the atomistic and the electronic structure of the interface using a mixture of F4TCNQ and paraquat as an example. Counterintuitively, we find that the nominally weaker donor overpowers the stronger acceptor, resulting in a dependence of the work function that is effectively determined by the nominal coverage of the donor. At the same time, we find that multiple geometries are energetically very similar, but result in different work function, affecting the reproducibility of different experimental realizations.

O 97.7 Fri 12:00 H6

Magnetic Coupling in Triangulene Dimers: Impact of Number and Dihedral Angles of para-Biphenyl Linkers — •Marco Lozano[1], Elena Perez-Elvira[2], Qiang Huang[3], Ji Ma[3], Aurelio Gallardo[2], Ana Barragan[2], Alba Garcia-Frutos[2], Koen Lauwaet[2], Jose Gallego[4], Pavel Jelinek[1], David Ecija[2], Diego Soler-Polo[1], and Jose Urgel[2] — [1]Institute of Physics of the Czech Academy of Science, CZ-16253 Praha, Czech Republic — [2]IMDEA Nanoscience, C/ Faraday 9, Campus de Cantoblanco, 28049 Madrid, Spain — [3]Center for Advancing Electronics Dresden (cfaed) & Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01069 Dresden, Germany — [4]Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, Cantoblanco, 28049 Madrid, Spain

Triangulene and its homologues are promising building blocks for high-spin low-dimensional networks with long-range magnetic order. Despite the recent progress in the synthesis and characterization of coupled triangulenes, key parameters such as the number or the dihedral angles of organic linking units remain scarce, making further studies crucial for an essential understanding of their implications. Here, we investigate the synthesis of two triangulene dimers linked by two or one para-biphenyl units on a metal surface in an UHV environment. First-principles calculations and model Hamiltonians reveal how the spin excitation and radicalism depend on the rotation of the para-biphenyl units.

O 97.8 Fri 12:15 H6

Insights into Nonlinear CD-ee Dependence in Tryptophan Thin Films — •Charitini Panagiotopoulou, Changseop Jeong, Ueli Heiz, and Aras Kartouzian — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

Chiral analysis is essential, especially for enantio-separation and -enrichment, with Circular Dichroism (CD) spectroscopy being a fast and straightforward method for studying enantiomeric excess (ee) and its dependence on circular dichroism (CD-ee dependence). While most systems show linear CD-ee dependence, studies reporting non-linear CD-ee behaviour are relatively rare and, thus, more attractive for research. Building on our earliest findings of negative nonlinear CD-ee dependence in polycrystalline BINOL thin films (Liang et al. 2023), we extend this study to a different system: the well-known amino acid responsible for synthesizing important proteins in humans, Tryptophan. We prove our hypothesis that the non-linear CD-ee dependence is not limited to BINOL films and can be applied to biomolecules, and we outline this non-linear dependence with different methods, such as CD spectroscopy, SHG-CD spectroscopy and FTIR study. This behaviour is linked to the structural characteristics of Tryptophan when a series of different enantiomeric excesses are deposited onto thin films via molecular evaporation. This approach paves the way for extensive exploration in the field of biomolecular chirality.