

O 62: Poster Session V: Organic molecules on inorganic substrates: electronic, optical and other properties I

Time: Wednesday 10:30–12:30

Location: P

O 62.1 Wed 10:30 P

Plasmon-driven motion of an individual molecule — ●TZU-CHAO HUNG, BRIAN KIRALY, JULIAN STRIK, ALEXANDER KHAJETOORIAN, and DANIEL WEGNER — Institute for Molecules and Materials, Nijmegen, The Netherlands

Combining scanning tunneling microscopy (STM) and spectroscopy (STS) with STM-induced light emission, we demonstrate that nanocavity plasmons injected a few nanometers away from a molecule can induce molecular motion. For this, we studied the rapid shuttling motion of zinc phthalocyanine molecules adsorbed on ultrathin NaCl films. Single-molecule luminescence spectra from molecules anchored to a step edge were compared with isolated molecules adsorbed on the free surface. We found that the azimuthal modulation of the Lamb shift is almost two times larger compared to isolated molecules. A remotely induced rapid shuttling motion of isolated molecules by plasmon-exciton coupling can explain the difference. Plasmon-induced molecular motion may open an interesting playground to bridge the nanoscopic and mesoscopic world by combining molecular machines with nanoplasmonics to control directed motion of single molecules without the need for a local probe.

O 62.2 Wed 10:30 P

Application of laser PEEM to a biological system: Geobacter sulfurreducens — ●FRANZ NIKLAS KNOOP, GERHARD LILIENKAMP, and WINFRIED DAUM — Institute of Energy Research and Physical Technologies, TU Clausthal, Leibnizstraße 4, 38678 Clausthal-Zellerfeld, Germany

Recently, multi-photon photoelectron emission microscopy (nP-PEEM) was successfully applied to the spectromicroscopy of porphyrin thin films and exciton-plasmon coupling in nanoplasmonic-porphyrin hybrid systems by tuning the laser wavelength for multi-photon excitation in resonance with the molecular $S_0 \rightarrow S_2$ transition (Soret band) [1]. Here, we report on our laser-PEEM study of a biological system, the bacterium *Geobacter sulfurreducens*. This anaerobic bacterium features membrane-associated and extracellular cytochromes containing iron porphyrins. In contrast to porphyrin films of ZnTPP or MgTPP, near-Soret excitation of photoelectrons from *Geobacter sulfurreducens* results in pronounced dependencies of the photoemission on irradiation time indicating laser-induced, irreversible changes of the bacteria. An initial decrease of the photoemission can be related to an irreversible photo-induced oxidation of the cytochromes while a strong increase for longer periods of irradiation is shown to be caused by thermal effects. PEEM excitation spectra of the exposed bacteria also show the degenerative effect of the exciting laser pulses.

[1] K. Stallberg, G. Lilienkamp, W. Daum, *J. Phys. Chem. C* **121**, 13833 (2017).

O 62.3 Wed 10:30 P

First-principles simulation of core-level spectroscopy to reveal the nature of chemical bonding at metal-organic interfaces — ●SAMUEL J. HALL, BENEDIKT P. KLEIN, and REINHARD J. MAURER — Department of Chemistry, University of Warwick, Coventry, United Kingdom

X-ray photo-emission spectroscopy XPS and near-edge adsorption fine structure spectroscopy (NEXAFS) experiments are routinely used to characterise the chemical environment and the valence electronic structure of organic materials and metal-organic interfaces. In the past, certain spectral changes upon adsorption of molecules to surfaces have been connected to changes in chemical bonding and charge distribution, however complex overlapping spectra of multiple species often complicate such an interpretation. Through the use of Density Functional Theory (DFT) calculations, we study two molecular isomers, azulene and naphthalene, adsorbed on three different metal(111) surfaces. These six systems fall into three distinct regimes of molecule-metal chemical bonding. Our core-level spectroscopy simulations connect the changes seen in the spectra with different levels of chemical bonding and decompose these signatures into initial core state and final valence state contributions. We analyse the effect of charge transfer, electronic hybridisation and dispersion effects, all with the aim to provide new insights to experimental spectral analysis.

O 62.4 Wed 10:30 P

Benchmarking ab-initio methods to predict non-adiabatic charge transfer at metal-organic interfaces — ●DANIEL CORKEN, NICHOLAS D.M. HINE, and REINHARD J. MAURER — University of Warwick, Coventry, United Kingdom

State-resolved molecular beam scattering experiments have shown that small molecules scattering from metal surfaces exhibit non-adiabatic behaviour whereby charge is dynamically transferred from the metal to the molecule, creating a transient anion. Understanding chemical dynamics of molecule-metal systems is essential for designing the next generation of heterogeneous catalysts. Such dynamical non-adiabatic charge-transfer is not captured by ground state Density Functional Theory or classical dynamics and the explicit anionic excited-state and coupling constants between states need to be described. Metal-organic interfaces feature a continuum of electronic states rendering conventional excited state methods prohibitively expensive. Here we assess three approximate and computationally efficient methods to predict excited states at metal surfaces: The use of an applied electric field, constrained DFT, and the linear-expansion-Delta-Self-Consistent-Field method. For the prototypical system of CO on Au(111), we compare the methods based on how accurately they predict excited-state energy landscapes and their computational efficiency and numerical robustness, with the aim to identify an excited state method to perform non-adiabatic dynamics simulations for charge transfer systems in the future.

O 62.5 Wed 10:30 P

How molecular composition affects molecular double bond switching at metal surfaces: Azobenzene vs. Benzalaniline vs. Stilbene on Ag(111) — ●MARTIN LEA¹, DAVID A. DUNCAN², and REINHARD J. MAURER¹ — ¹University of Warwick, Coventry, United Kingdom, CV4 7AL — ²Diamond Light Source, Didcot, United Kingdom, OX11 0DE.

Photoswitches are a class of organic molecules which have shown prevalence within the field of nanotechnology; the ability to reversibly convert between two geometric states as a response to light absorption has shown prospects for molecular-based electronics applications, transistors, and storage devices. Integration of such organic molecules in devices requires adsorption upon a metal surface, which often leads to quenching of the molecules switching ability. Adsorption of the prominent photoswitch azobenzene upon metallic substrates has shown that the switching behavior observed in both gas and solution phases does not translate to the interface, as the surface modifies the energy landscape. In this work we explore whether this same deactivation effect is consistent with other similar molecular switch architectures. Using dispersion-corrected density functional theory, we explore the consequences of metal adsorption for a series of homologous molecules with central double bonds of varying composition: azobenzene, benzalaniline and stilbene. We compare minimum energy paths and electronic structure characteristics to unveil how molecular architecture can affect switching capabilities at surfaces.

O 62.6 Wed 10:30 P

Application of periodic energy decomposition analysis to metallic systems — ●JAN-NICLAS LUY¹, BENEDIKT P. KLEIN², J. MICHAEL GOTTFRIED², and RALF TONNER¹ — ¹Fakultät für Chemie und Mineralogie, Universität Leipzig, Germany — ²Fachbereich 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 aromatics dispersion dominates on Cu(111), orbital interactions can be identified in non-alternant cases. With the more reactive Pt(111) surface, both types 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 62.7 Wed 10:30 P

Imaging Charge Localization in a Conjugated Oligophenylene — ●LAERTE PATERA^{1,2}, FABIAN QUECK¹, and JASCHA REPP¹ — ¹Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany — ²Department of Chemistry, Technical University of Munich, 85748 Garching, Germany

Polaron formation in conjugated polymers has a major impact on their optical and electronic properties. In polyphenylenes, the molecular conformation is determined by a delicate interplay between electron delocalization and steric effects. Injection of excess charges is expected to increase the degree of conjugation, leading to structural distortions of the chain. Here we investigated at the single-molecule level the role of an excess charge in an individual oligophenylene deposited on sodium chloride films. By combining sub-molecular-resolved atomic force microscopy with redox-state-selective orbital imaging, we characterize both structural and electronical changes occurring upon hole injection. While the neutral molecule exhibits a delocalized frontier orbital, for the cationic radical the excess charge is observed to localize, inducing a partial planarization of the molecule. These results provide direct evidence for self trapping of the excess charge in oligophenylenes, shedding light on the interplay of charge localization and structural distortion.

O 62.8 Wed 10:30 P

Controlling long-distance motion of single molecules on Ag(111) — ●DONATO CIVITA, GRANT J. SIMPSON, and LEONHARD GRILL — Institute of Chemistry, University of Graz, Austria

The motion of single molecules adsorbed on solid surfaces is of fun-

damental importance in various fields as heterogeneous catalysis, film growth processes, and on-surface polymerization. However, the motion of adsorbed molecules is usually a diffusive process with random changes in the direction of motion, and thus limited control. Here, we show how the motion of single di-bromo-ter-fluorene molecules on a Ag(111) surface can be controlled over distances of more than 100 nm with picometric precision [1]. The molecule moves strictly in one dimension across the surface, driven by an interplay of van der Waals and electrostatic interactions, which are used to repel and attract the molecule. The large spatial extension of the motion, and its astonishing confinement allow the direct measurement of the molecular speed, and to realize a sender-receiver experiment where a single molecule is transferred between two independent STM tips. These results suggest how a single molecule may be aimed toward a stationary target to study chemical reactions in relation to momentum and orientation of the reagent.

[1] D. Civita, M. Kolmer, G. J. Simpson, A.-P. Li, S. Hecht, L. Grill, Control of long-distance motion of single molecules on a surface, *Science*, Vol. 370, Issue 6519, pp. 957-960 (2020).

O 62.9 Wed 10:30 P

Controlled Manipulation of Single Molecules on an Ag(111) Surface — ●JULIA LANZ, DONATO CIVITA, and LEONHARD GRILL — Single Molecule Chemistry, Institute of Chemistry, University of Graz

Thermal motion of molecules at surfaces is a stochastic process which makes it complicated to control the molecular trajectory. Here, we have used scanning tunneling microscopy under ultrahigh vacuum conditions to manipulate individual molecules to move controllably across a flat Ag(111) surface, kept at low temperatures of about 7 K. The controlled motion of single molecules gives deeper understanding of the relation between molecular motion and the chemical as well as geometrical properties of the molecules and the surface. Vertical manipulation provides insight into the dependence of molecular motion on conformational changes. Upon lateral manipulation the molecules follow the STM tip in a precise fashion. This occurs preferably in pairs, which will be discussed in view of intermolecular interaction.