

O 68: Focused session: Functional molecules at surfaces III

Time: Thursday 10:30–13:00

Location: A 053

Topical Talk

O 68.1 Thu 10:30 A 053

Frontier Nanoscience: Molecular Superconductors to Molecular Machines — ●SAW WAI HLA — Center for Nanoscale Materials, Argonne National Laboratory, IL 60439, and Department of Physics and Astronomy, Ohio University, Athens, OH 45701, USA.

We combine a variety of scanning tunneling microscope (STM) manipulation schemes with tunneling spectroscopy techniques to image and manipulate properties of molecules on surfaces. This talk will include our recent results and achievements: In molecular spintronics area, orbital Kondo effect of single molecules generated by an interfacial charge transfer process will be discussed. In nanoscale superconductivity area, we will present the smallest molecular superconductor ever studied to date. Here, the finding of superconductivity in just four pairs of (BETS)2-GaCl4 molecules opens the possibility of investigating superconducting phenomena locally. Finally, in molecular nanomachine area, complex rotation mechanisms of Ru based multi-component molecular rotors operated by injecting tunneling electrons from an STM tip will be presented. These experiments are innovative, and are tailored to address several critical issues covering both for fundamental understanding, and for demonstration of novel molecule based nanodevices on materials surfaces.

Topical Talk

O 68.2 Thu 11:00 A 053

Directional motion of a four-wheeled molecule on a metal surface — ●MANFRED PARSCHAU — Empa - Swiss Federal Laboratories for Materials Science and Technology, Nanoscale Materials Science Laboratory, Ueberlandstrasse 129, CH-8600 Dübendorf, Switzerland

Propelling single molecules in a controlled manner along an unmodified surface remains extremely challenging because it requires molecules that can use light, chemical or electrical energy to modulate their interaction with the surface in a way that generates motion. Although controlled movement of molecules along a surface has been reported, the molecules in these examples act as passive elements that either diffuse along a preferential direction with equal probability for forward and backward movement or are dragged by a tip of a scanning tunneling microscope. Here I present a molecule with four functional units that undergo continuous and defined conformational changes upon sequential electronic and vibrational excitation. Scanning tunneling microscopy confirms that activation of the conformational changes of the rotors through inelastic electron tunneling propels the molecule unidirectionally across a Cu(111) surface. The system can be adapted to follow either linear or random surface trajectories or to remain stationary, by tuning the chirality of the individual motor units.

Topical Talk

O 68.3 Thu 11:30 A 053

Charge transfer dynamics in assemblies of functional molecules — ●MICHAEL ZHARNIKOV — Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany

Development of future technologies such as molecular electronics and sustained progress in organic electronics and photovoltaics rely on reliable information about the charge transport (CT) through individual molecular units (or loosely "molecular wires") which serve as important building blocks of a variety of potential devices. In this context, femtosecond CT dynamics in a series of self-assembled monolayers with different backbones, which are prototypes of potential molecule wires, was addressed by resonant Auger electron spectroscopy using the core hole clock approach. The CT pathway was unambiguously defined by resonant excitation of a special marker group attached to the backbone. The length of the backbone was varied to monitor the respective dependence of the CT time. Similar to the static conductance, this dependence can be coarsely described by an exponential function. The respective attenuation factors and CT time associated with the anchoring to the substrate were determined. These factors and characteristic CT times through molecular frameworks are found to depend strongly on the character of the molecular orbital which mediates the CT process. Thus, the efficiency of tunnelling in molecular wires can be significantly affected by controlling the specific orbitals into which charge carriers are injected. This can be a valuable input for theory and an important consideration for molecular electronics devices where improvements in conductance can have significant technological impact.

O 68.4 Thu 12:00 A 053

Electronic and structural properties of azobenzene adsorbed on layered materials — ●ERIC LUDWIG¹, TORBEN JOHANNSEN¹, MICHAEL NABOKA², THOMAS STRUNSKUS³, ALEXEI NEFEDOV², CHRISTOF WÖLL², LUTZ KIPP¹, and KAI ROSSNAGEL¹ — ¹Institut für Experimentelle und Angewandte Physik, Universität Kiel, D-24098 Kiel — ²Institut für Funktionelle Grenzflächen, Karlsruher Institut für Technologie, D-76344 Eggenstein-Leopoldshafen — ³Institut für Materialwissenschaft, Universität Kiel, D-24098 Kiel

Molecular switches with optically tunable properties are often ascribed a high potential in the field of molecular electronics. However, one of the main challenges has not yet been solved, namely to attach a large number of molecules to a solid surface in a way that efficient switching remains possible.

Here, we present a combined direct and inverse photoelectron spectroscopy and NEXAFS study of azobenzene adsorbed on layered transition metal dichalcogenides. Specifically, we have used a metallic and a semiconducting substrate to determine the influence of the substrate electronic structure and a novel sublimation setup to deposit azobenzene non-destructively from sub-monolayer to multilayer coverages.

Our results indicate generally weak substrate-adsorbate interactions, which is reflected, for instance, in Vomer-Weber growth on the semiconducting substrate and almost flat-lying molecules for monolayer coverage. The photoemission and NEXAFS data also show evidence for photoswitching of multilayers on both substrates. This work was supported by the DFG through SFB 677.

O 68.5 Thu 12:15 A 053

First-principles calculations on dependence of electron transport through molecular junctions on the anchoring groups — ●SHIGERU TSUKAMOTO, VASILE CACIUC, NICOLAE ATODIRESEI, and STEFAN BLÜGEL — Peter Grünberg Institut & Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich

Molecular electronics is exciting by the perspective that various types of electric properties are potentially realized only by single molecules with unique electronic structures. In particular, the anchoring groups in a molecular junction, which link a molecule to an electrode, are recognized as an important part to control the electron conductivity.

Here, by means of first-principles calculations we report how the anchoring groups of molecular junctions affect the electron transmissions. The systems used here are M-R-C₆H₄-R-M, where M is a Cu or Au electrode, and R is an anchoring group as R=S, COO, BOO, NOO.

The transport calculations have revealed significant differences in the electron transmissions of the four molecular junctions: The molecular junctions with S and BOO anchoring groups have finite electron transmissions at the Fermi level, and the transmission of the system with the BOO group changes rapidly at the energies above and below the Fermi level. For the molecular junctions with COO and NOO anchoring groups, the electron transmissions at the Fermi level are small but they increase at the energies above and below the Fermi level, respectively. The difference in the electron transmissions obviously originates from the difference in the anchoring groups, and the variation in electric functionality of single molecular junctions is suggested.

O 68.6 Thu 12:30 A 053

Electron Dynamics in Azobenzene SAMs on Gold — ●STEFANIE PAARMANN, CORNELIUS GAHL, and WEINELT MARTIN — Fachbereich Physik, Arnimallee 14, 14195 Berlin

Electronic structure and femtosecond electron dynamics of self-assembled monolayers of azobenzene functionalized alkanethiols on gold have been investigated with time-resolved two-photon photoemission spectroscopy (2PPE). Two excited electronic states at 2.4 and 3.6 eV above E_F are attributed to unoccupied states in the chromophores, which are populated via charge transfer from the metal substrate and exhibit lifetimes in the order of 100 fs. Additional to the ultrafast dynamics we observe a continuous change of the monochromatic 2PPE spectra on the time scale of hours. While at a photon energy of $h\nu=4.2$ eV the SAM is irreversibly modified by the UV illumination, reversible changes attributed to photoisomerization occur at $h\nu=3.6$ eV. The low cross-section of $< 10^{-22}$ cm² is in accordance with earlier experiments where within the experimental error no photoresponse to UV light was observed.

O 68.7 Thu 12:45 A 053

Orbital tomography: Deconvoluting photoemission spectra of organic molecules — ●F. S. TAUTZ¹, P. PUSCHNIG^{2,3}, E.-M. REINISCH², T. ULES², G. KOLLER², S. SOUBATCH¹, M. OSTLER⁴, L. ROMANER³, C. AMBROSCH-DRAXL³, and M. G. RAMSEY² — ¹Peter Grünberg Institut, Forschungszentrum Jülich — ²Institut für Physik, Karl-Franzens Universität Graz — ³Chair of Atomistic Modeling and Design of Materials, Montanuniversität Leoben — ⁴Lehrstuhl für Technische Physik, Universität Erlangen-Nürnberg

We propose a tomographic method which uses the energy and momentum dependence of photoemission from adsorbed molecules to deconvolute valence band spectra into individual orbitals beyond the

limits of energy resolution.

The method allows the purely experimental determination of molecule-projected densities of state (PDOS), to be compared to theoretically calculated PDOS. The method further allows the direct observation of the effects of bonding on individual orbitals, and in so doing, provides stringent tests for the development of ab-initio electronic structure theory.

Photoemission experiments on PTCDA/Ag(110) were performed at BESSYII using a toroidal electron energy analyzer. The valence band of PTCDA was unambiguously disentangled into contributions from six molecular orbitals with a binding energy below 4 eV, four of them within an energy range of only 0.4 eV.