

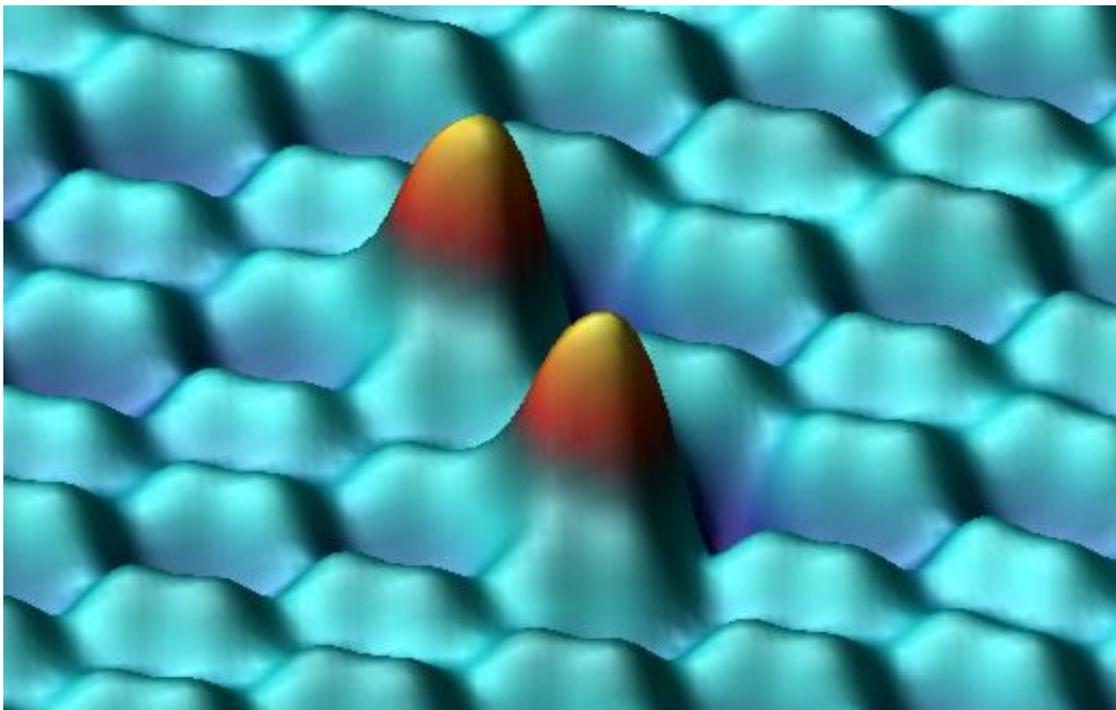
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"Elementary Processes in Molecular Switches at Surfaces"

**International Workshop on
Molecular Switching at Surfaces**

23. September – 26. September 2007

Seehotel Zeuthen



Book of Abstracts

International Workshop on Molecular Switching at Surfaces

23. September – 26. September 2007, Seehotel Zeuthen

Scientific program

Sunday, September 23

15:00 – 18:30 Arrival

19:00 – 20:30 Dinner

Monday, September 24

Morning session I (Chair: M. Wolf)

9:30 – 10:10 **Matt Comstock** (*University of California at Berkeley, USA*),
Reversible Photomechanical Switching of Individual Engineered Molecules at a Metal Surface

10:10 – 10:40 **Karsten Reuter** (*Fritz-Haber-Institut, Berlin*),
Stabilizing a Molecular Switch at Solid Surfaces: A Density-Functional Theory Study of Azobenzene at Cu(111), Ag(111), and Au(111)

10:40 – 11:10 Coffee break

Morning session II (Chair: N. Pascual)

11:10 – 11:50 **Klaus Kern** (*MPI für Festkörperforschung, Stuttgart*),
Building and Addressing Molecular Architectures at Surfaces

11:50 – 12:20 **Jürgen P. Rabe** (*Humboldt Universität zu Berlin*),
Self-Assembly and Molecular Switching of Functionalized Nanographenes at Solid-Liquid Interface

12:20 – 14:20 Lunch break

Afternoon session I (Chair: L. Grill)

14:20 – 15:00 **Gérald Dujardin** (*Université Paris-Sud, Orsay*),
Electronic Control of Single Molecule Dynamics on Silicon Surfaces

15:00 – 15:30 **Nacho Pascual** (*Freie Universität Berlin*),
Switchable Molecules on Metal Surfaces: Conformation, Spectroscopy, and Manipulation Using STM

15:30 – 16:00 **Peter Saalfrank** (*Universität Potsdam*),
Molecular Switches at Surfaces: From Structure to Dynamics

16:00 – 16:30 Coffee break

Afternoon session II (Chair: M. Weinelt)

- 16:30 – 17:10 **Wolfgang Zinth** (*Ludwig-Maximilians-Universität München*),
Folding and Unfolding of a Light-Triggered β -Hairpin Model Peptide
- 17:10 – 17:50 **Rainer Herges** (*Christian-Albrechts-Universität zu Kiel*),
Function by Switching: Pumping, Sensing, Directed Motion and other Engineering Tasks at the Molecular Level
- 18:00 – 19:30 Dinner
- 19:30 – 21:00 Poster session

Tuesday, September 25

Morning session I (Chair: E. Gross)

- 9:00 – 9:40 **Jan M. van Ruitenbeek** (*University of Leiden, NL*),
Simple Molecules as Benchmark Systems for Molecular Electronics
- 9:40 – 10:20 **Max Di Ventra** (*University of California, San Diego, USA*),
Transport in Molecules: Hydrodynamics, Turbulence, and Local Electron Heating
- 10:20 – 10:50 Coffee break

Morning session II (Chair: P. Saalfrank)

- 10:50 – 11:30 **Elke Scheer** (*Universität Konstanz*),
Influence of Laser Light onto the Conductance of Atomic-Size Contacts
- 11:30 – 12:00 **Felix von Oppen** (*Freie Universität Berlin*),
Vibrational non-equilibrium in single molecule transistors
- 12:00 – 13:30 Lunch break

Afternoon session I (Chair: K. Reuter)

- 13:30 – 14:10 **Giovanni Cuniberti** (*Technische Universität Dresden*),
Tuning the Conductance of a Molecular Switch
- 14:10 – 14:40 **Hardy Gross** (*Freie Universität Berlin*),
Time-Dependent Quantum Transport: Electron Pumping, Transients and the Role of Bound States
- 15:00 – 17:00 Boat tour + coffee on Lake Zeuthen

Afternoon session II (Chair: S. Hecht)

- 17:20 – 18:00 **Sense Jan van der Molen** (*University of Leiden, NL*),
*Switching of Diarylethenes on Gold:
Aiming for Functionality and Robustness*
- 18:00 – 18:30 **Leonhard Grill** (*Freie Universität Berlin*),
*Isomerization of Single Azobenzene Derivatives
with a Low Temperature STM*
- 18:30 – 19:00 **Petra Tegeder** (*Freie Universität Berlin*)
*Reversible switching of tetra-tert-butyl-azobenzene on a Au(111) surface
induced by light and thermal activation*
- 19:00 – 20:30 Dinner
- 20:30 – More discussions...

Wednesday, September 26

Morning session I (Chair: A. Grohmann)

- 9:00 – 9:40 **Stefan Tautz** (*Forschungszentrum Jülich*),
*Bonding, structure and function of highly-ordered molecular
adsorbate layers on metal surfaces*
- 9:40 – 10:20 **Wolfgang Kuch** (*Freie Universität Berlin*),
Paramagnetic Molecules on Magnetic and Non-Magnetic Substrates
- 10:20 – 10:40 Coffee break

Morning session II (Chair: J. P. Rabe)

- 10:40 – 11:20 **Andreas Terfort** (*Universität Hamburg*),
*Self-Assembled Monolayers: Principles for Order & Possibilities for
Switching*
- 11:20 – 11:50 **Cornelius Gahl** (*Max-Born-Institut Berlin*),
Self-assembled Monolayers of Azobenzene-Alkanethiols on Gold
- 11:50 – 12:20 **Rainer Haag** (*Freie Universität Berlin*),
*Synthesis of molecular switches as building blocks
for functional surfaces*
- 12:20 – 13:30 Lunch break
- 14:00 – Departure...

Monday Morning, September 24

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- 9:30 – 10:10 **Matt Comstock** (*University of California at Berkeley, USA*),
Reversible Photomechanical Switching of Individual Engineered Molecules at a Metal Surface
- 10:10 – 10:40 **Karsten Reuter** (*Fritz-Haber-Institut, Berlin*),
Stabilizing a Molecular Switch at Solid Surfaces: A Density-Functional Theory Study of Azobenzene at Cu(111), Ag(111), and Au(111)
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- 11:10 – 11:50 **Klaus Kern** (*MPI für Festkörperforschung, Stuttgart*),
Building and Addressing Molecular Architectures at Surfaces
- 11:50 – 12:20 **Jürgen P. Rabe** (*Humboldt Universität zu Berlin*),
Self-Assembly and Molecular Switching of Functionalized Nanographenes at Solid-Liquid Interfaces

Reversible Photomechanical Switching of Individual Engineered Molecules at a Metal Surface

Matthew J. Comstock^{1,3}, Niv Levy^{1,3}, Armen Kirakosian^{1,3}, Jongweon Cho^{1,3}, Luis Berbil-Bautista^{1,3}, Frank Lauterwasser^{2,3}, Jessica H. Harvey^{2,3}, David A. Strubbe^{1,3}, Jean M.J. Fréchet^{2,3}, Dirk Trauner^{2,3}, Steven G. Louie^{1,3}, and Michael F. Crommie^{1,3}

¹*Department of Physics, UC Berkeley, Berkeley, California 94720-730, USA*

²*Department of Chemistry, UC Berkeley, Berkeley, California 94720-1460, USA*

³*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

We have observed reversible light-induced mechanical switching for individual organic molecules bound to a metal surface. Scanning tunneling microscopy (STM) was used to image the features of individual functionalized azobenzene molecules on Au(111) before and after reversibly cycling their mechanical structure between *trans* and *cis* states using light. Azobenzene molecules were engineered to increase their surface photomechanical activity by attaching varying numbers of tert-butyl (TB) ligands ("legs") to the azobenzene phenyl rings. STM images show that increasing the number of TB legs "lifts" the azobenzene molecules from the substrate, thereby increasing molecular photomechanical activity by decreasing molecule-surface coupling. STM observations of molecular photoswitching during prolonged exposures to light allow us to directly determine both the forward (*trans*-to-*cis*) and reverse (*cis*-to-*trans*) photoswitching cross-sections for UV and blue light. We find strong deviation of surface-based molecular switching rates compared to solution-based switching rates, as well as pronounced switching dependence on local surface microstructure surrounding the molecules.

Stabilizing a Molecular Switch at Solid Surfaces: A Density-Functional Theory Study of Azobenzene at Cu(111), Ag(111), and Au(111)

Karsten Reuter

Fritz Haber Institut der Max Planck Gesellschaft, Berlin (Germany)

We perform a density-functional theory trend study for the prototypical cis-trans conformational switch azobenzene adsorbed at noble metal surfaces. As a necessary prerequisite for an atomic-scale understanding of the switching function, we focus on a detailed structural and electronic characterization of the stable (or meta-stable, long-lived) molecular states. Treating electronic exchange and correlation (xc) at the generalized gradient approximation (GGA) level, we obtain an essentially zero net binding of both conformational isomers at Ag(111) and Au(111). This is significantly different at Cu(111), where the bonding particularly of the cis isomer is strong enough to even reverse the gas phase energetic order of the two isomers. We are able to rationalize these findings as a competition between covalent bonding of the central azo (-N=N-) bridge and the surface interaction of the two closed-shell phenyl (-C₆H₅) rings. Deficiencies in the description of either of these interactions at the GGA level will therefore crucially affect the deduced energetic order of the (meta)stable adsorption modes. This concerns notably Van der Waals contributions to the interaction of the -C₆H₅ moiety with the noble metal surface. To obtain a first estimate of the role of these contributions we focus on benzene as a model for this moiety and employ the recently introduced local xc correction method [1] to compute the binding at the Hartree-Fock plus Møller-Plesset perturbation theory (HF-MP2) level.

[1] Q.-M. Hu, K. Reuter, and M. Scheffler, *Phys. Rev. Lett.* 98, 176103 (2007).

Building and Addressing Molecular Architectures at Surfaces

Klaus Kern

*Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart
and Institut de Physique des Nanostructures, EPFL, CH-1015 Lausanne
klaus.kern@fkf.mpg.de*

Supramolecular nanostructuring at surfaces bears unique potential, particularly when designed molecular species are employed, whose structure can be adapted to specific needs. Using noncovalent interactions as hydrogen bonding, ionic bonding and metal-ligand interactions, molecular building blocks can be rationally combined into desired functional architectures at well defined surfaces. The potential functionalities comprise molecular magnetism, novel heterogenous catalysis, selective host-guest interactions and new concepts of nanoscale mechanics.

In the present talk I will demonstrate how the remarkable progress in controlling atomic and molecular interactions at surfaces has provided the unique ability to engineer supramolecular architectures of well-defined size, shape, composition and functionality. Scanning tunneling microscopy is the characterization method of choice. It not only allows us to image molecules adsorbed at surfaces with unprecedented resolution but also to follow supramolecular self-assembly and chemical complex formation in real space and time and to probe the physical and chemical properties of the molecular architectures on the atomic level.

Self-Assembly and Molecular Switching of Functionalized Nanographenes at Solid-Liquid Interfaces

M. Ai, S. Gröper, N. Severin, J.P. Rabe
Institut für Physik, Humboldt Universität zu Berlin
Newtonstr. 15, 12489 Berlin

Conjugated molecules, and particularly polycyclic aromatic hydrocarbons or "nanographenes" with various sizes, symmetries, and substitution types including donors, acceptors and azobenzene, have been self-assembled at the interface between an organic solution and the basal plane of graphite (HOPG). Scanning tunneling microscopy and spectroscopy (STM/STS) were used to investigate both structure and electronic properties of single molecules *in-situ* in a well defined molecular environment [1-8]. A hexabenzocoronene (HBC)-derivative with one azobenzene sidegroup attached via a rigid spacer exhibits highly ordered monolayers of the trans-compound at the interface with a solution in 1,3,5-trichlorobenzene. Upon illumination *in-situ* with UV-light this monolayer disorders, possibly due to a trans-cis isomerization, which may be used to switch a single molecule transistor [9]. Optical absorption and fluorescence spectroscopy in solution reveals a strong dependence of the switching on the solvent. Experiments are under way to vary the molecular environment of the azobenzene in the monolayer by forming mixed monolayers and varying the spacer between the HBC and the azobenzene.

- [1] F. Jäckel, M.D. Watson, K. Müllen, J.P. Rabe, *Phys. Rev. B* 73, 045423 (2006)
- [2] P. Samorí, A. Fechtenkötter, E. Reuther, M.D. Watson, N. Severin, K. Müllen, J.P. Rabe, *Adv. Mater.* 18, 1317 (2006)
- [3] X. Feng, J. Wu, M. Ai, W. Pisula, L. Zhi, J.P. Rabe, K. Müllen, *Angew. Chem. Int. Ed.* 46, 3033 (2007)
- [4] T. Böhme, C.D. Simpson, K. Müllen, J.P. Rabe, *Chem. Eur. J.* in press.
- [5] R.S. Stoll, N. Severin, J.P. Rabe, S. Hecht, *Adv. Mater.* 18, 1271 (2006)
- [6] S. Duhm, H. Glowatzki, J.P. Rabe and N. Koch, R. L. Johnson, *Appl. Phys. Lett.* 88, 203109 (2006)
- [7] H. Glowatzki, S. Duhm, K.-F. Braun, J.P. Rabe, N. Koch, *Phys. Rev. B* in press.
- [8] F. Jäckel, J.P. Rabe, in: *Scanning Probe Microscopies Beyond Imaging*, edited by: P. Samorí, Wiley, 2006, pp. 36-51.
- [9] F. Jäckel, M.D. Watson, K. Müllen, J.P. Rabe, *Phys. Rev. Lett.* 92, 188303 (2004)

Monday Afternoon, September 24

Afternoon session I (Chair: L. Grill)

- 14:20 – 15:00 **Gérald Dujardin** (*Université Paris-Sud, Orsay*),
Electronic Control of Single Molecule Dynamics on Silicon Surfaces
- 15:00 – 15:30 **Nacho Pascual** (*Freie Universität Berlin*),
*Switchable Molecules on Metal Surfaces:
Conformation, Spectroscopy, and Manipulation Using STM*
- 15:30 – 16:00 **Peter Saalfrank** (*Universität Potsdam*),
Molecular Switches at Surfaces: From Structure to Dynamics
- 16:00 – 16:30 Coffee break

Afternoon session II (Chair: M. Weinelt)

- 16:30 – 17:10 **Wolfgang Zinth** (*Ludwig-Maximilians-Universität München*),
Folding and Unfolding of a Light-Triggered β -Hairpin Model Peptide
- 17:10 – 17:50 **Rainer Herges** (*Christian-Albrechts-Universität zu Kiel*),
*Function by Switching: Pumping, Sensing, Directed Motion and other
Engineering Tasks at the Molecular Level*

Electronic Control of Single Molecule Dynamics on Silicon Surfaces

G. Dujardin, D. Riedel, M. Lastapis, M. Cranney, M. Martin and G. Comtet
Laboratoire de Photophysique Moléculaire
Bât. 210, Université Paris-Sud
91405, Orsay (France)

Molecular devices (e.g. switches) on silicon surfaces are of particular interest for integrating molecular functions into nanoelectronics. We have investigated the fundamental processes for powering and controlling with precision the operation of individual bistable and multistable molecules (biphenyl and hexaphenyl) on Si(100). By using a low temperature (5K) scanning tunneling microscope (STM) as a picometer-size source of electrons, electronic excitation can be localized at different positions inside the molecule. This localization enables to precisely control the dynamics of the molecule [1,2]. Furthermore, we have shown that the electronically induced dynamics of the molecule can be modified in a controlled manner either by manipulating a neighbour atom [3] or by changing the type of doping (n or p) of the Si(100) surface [4].

- [1] M. Lastapis, M. Martin, D. Riedel, L. Hellner, G. Comtet and G. Dujardin, *Science* 308, 1000 (2005)
- [2] M. Cranney, D. Riedel, M. Martin and G. Dujardin, in preparation
- [3] M. Martin, M. Lastapis, D. Riedel, G. Dujardin, M. Mamatkulov, L. Stauffer and P. Sonnet, *Phys. Rev. Lett.* 97, 216103 (2006)
- [4] M. Lastapis, M. Martin, D. Riedel and G. Dujardin, in preparation

Switchable Molecules on Metal Surfaces: Conformation, Spectroscopy, and Manipulation Using STM

Nils Henningsen, Gunnar Schulze, Isabel Fernandez Torrente,
Katharina J. Franke, Nacho Pascual
*Institut für Experimentalphysik, Freie Universität Berlin
Arnimallee 14, 14195 Berlin, Germany*

Scanning probe microscopies provide unprecedented access to fundamental information about the dynamics of molecular excitations through a combination of local spectroscopy and manipulation of single molecules. The use of tunnelling electrons to induce local excitations is one of the most fascinating approaches to investigate phenomena at the atomic scale, providing a very complete picture on the processes mediating the manipulation of matter. Here, I will present several results on electron spectroscopy and manipulation of the structure of model molecular systems on metal surfaces.

Electronic excitations of molecules on surfaces exhibit a ubiquitous short life-time due to the finite electronic coupling of molecular resonances with substrate electronic states. Hence, after electron scattering the successful pathways leading to changes in the molecules arises from a competition of various internal and external mechanisms. In our experimental work we intend to shed some light on what properties of the molecule/surface interacting system can favour or hinder STM induced molecular transformations. Our work deals with several types of molecular switches: azobenzene derivatives and spiropyrane. We succeeded to induce reversible switching on a metal surface, although in most cases the mechanism of molecular transformation is found to be mediated by a mixture of electron excitations, electric field and tip-forces.

In the second part of my talk I will present results on electron transport through molecular structures. Self-assembly of C_{60} together with a functionalised adamantane based hydrocarbon (TPA) leads to stable nanostructures, in which the properties of C_{60} are significantly modified compared to the adsorption on the clean substrate. Due to its concave carbon skeleton TPA form an inclusion complex with the curved conjugated carbon cage of C_{60} . Using scanning tunnelling microscopy and spectroscopy, and density functional theory we find that three TPAs lock a C_{60} into a particular orientation and lift it from the surface, reducing its electronic coupling with the surface. This leads to a sharp resonance fingerprint in the transport spectra.

Molecular Switches at Surfaces: From Structure to Dynamics

Peter Saalfrank, Tillmann Klamroth, Karl Zenichowski, Jadranka Dokić
Institut für Chemie, Universität Potsdam, D-14476 Potsdam-Golm

In this contribution, the structure and dynamics of molecular switches at surfaces is investigated by quantum mechanical modelling. All switches considered are of a generalized, e.g. multidimensional, double-minimum type which describes conformational changes of the adsorbed species. The switching can be triggered by various driving forces, e.g. by temperature, charge carriers, a static electric field, or by light.

In the first part of the presentation the electronic and geometric structure of molecular switches, with and without explicit inclusion of a solid surface and/or electric field effects, is addressed with the help of quantum chemical methods. In particular we emphasize substituted azobenzenes, which are treated as free neutral or charged species, and which can undergo cis-trans or other isomerizations, for example by transient electron attachment enforced with an STM tip. Other, more symmetric, double-minimum situations are found for COD:Si(100) (COD=cylco-octadien) and H:Si(100), respectively, for which the silicon substrate has been explicitly included by cluster models.

For the last system, a hydrogen atom can be reversibly switched by an STM from one Si atom of a Si dimer, to the neighbouring one. We present preliminary calculations for the nuclear dynamics of the switching process, which account for various excitation and relaxation channels.

Folding and Unfolding of a Light-Triggered β -Hairpin Model Peptide

W. Zinth, T.E. Schrader, W.J. Schreier, F.O. Koller
*Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München,
Oettingenstraße 67, 80538 München*

Light triggered model peptides, where the introduction of a molecular switch into the backbone of an amino acid chain opens the possibility to induce structural changes at a well-defined moment, have become an important tool for the investigation of protein folding. The defined timing of the molecular changes allows to follow the conformational dynamics by structure sensitive IR techniques on ultrashort timescales. In the past we have investigated linear and cyclic azobenzene peptides and have shown that the strongly driven configurational changes occur on a time scale of a view picoseconds. In the present paper we focus on a β -hairpin model peptide where the peptide structure can be switched by illumination between a β -hairpin-like structure and a less ordered structure, which resembles a hydrophobic cluster. For the folding of the hairpin we isomerise the azobenzene from trans to cis. Here one observes strong initial absorption changes, which are finished on the 10 ps timescale. However, the IR spectrum reached even at 1 ns does not resemble the stationary difference spectrum. It is only on the timescale of 30 μ s that the folding process is completed. On the other hand, the unfolding of the β -hairpin is an ultrafast process: chromophore driven ultrafast (\cong 1 ps) are followed by slower \cong 100ps rearrangements before the unfolding reaction is essentially completed with a 700 ps process.

The investigations on the light triggered β -hairpin structure have shown that folding and unfolding reactions may occur on completely different timescales. While both types of reactions comprise ultrafast picosecond processes, it is only in the unfolding reaction that the process is finished ultrafast on the sub-nanosecond time domain.

Function by Switching: Pumping, Sensing, Directed Motion and other Engineering Tasks at the Molecular Level

Rainer Herges
Christian-Albrechts-Universität zu Kiel

Three months ago scientists from chemistry, physics and material science of the university of Kiel started a new SFB titled "Function by Switching" (SFB 677). There is plenty of overlap between the Berlin SFB 658 and our SFB 677, such as molecular and supramolecular surface physics, organic synthesis, supramolecular design etc. To provide a basis for the exchange of information or potential collaboration I will first give a general overview of topics and goals of our SFB and then go into more detail of our subprojects that are related to the design and synthesis of molecular and supramolecular functional systems.

Tuesday Morning, September 25

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- 9:00 – 9:40 **Jan M. van Ruitenbeek** (*University of Leiden, NL*),
Simple Molecules as Benchmark Systems for Molecular Electronics
- 9:40 – 10:20 **Max Di Ventra** (*University of California, San Diego, USA*),
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- 10:50 – 11:30 **Elke Scheer** (*Universität Konstanz*),
*Influence of Laser Light onto the Conductance
of Atomic-Size Contacts*
- 11:30 – 12:00 **Felix von Oppen** (*Freie Universität Berlin*),
Vibrational non-equilibrium in single molecule transistors

Simple Molecules as Benchmark Systems for Molecular Electronics

Jan M. van Ruitenbeek
University of Leiden

Over the past decade several techniques have been developed aimed at contacting individual organic molecules with metal leads. Although there has been some success, the experiments often cannot be interpreted uniquely. This is not surprising since nearly all the information needs to be deduced from the current and voltage only. There are frequently disagreements between experiments by different groups and between experiments and theory. This motivated us to concentrate on simple molecular systems that can be characterized in more detail and that may provide benchmarks for computations.

Our most studied system is dihydrogen, H_2 , contacted between Pt leads. We use break junction techniques at low temperatures. This allows us to obtain a lot of statistics over many contacts. The molecular junction can be characterized through conductance, the number of conduction channels, and –most significantly– the vibration modes. The vibration modes are seen through point contact spectroscopy (dI/dV). For hydrogen three vibration modes have been observed, their shift upon isotope substitution (D_2 and HD) was obtained, and their dependence on stretching of the contact was measured.

Several model calculations have appeared that may explain these results. They can be grouped into two proposed configurations: one having the hydrogen molecule aligned with the axis of the contact and the other having it perpendicular. In order to distinguish between the calculations we performed shot noise measurements. These demonstrate unequivocally that the current is carried by a single channel. These results agree very well with calculations by K. Thygesen and K.W. Jacobsen (Lyngby), but disagree with other approaches. Clearly, the study of these simple systems may serve to improve the methods.

The experiments are being extended towards other molecules, including CO, CO_2 , H_2O , benzene, and others, and first results will be reported.

Transport in Molecules: Hydrodynamics, Turbulence, and Local Electron Heating

M. Di Ventra

University of California, San Diego

Transport in molecular junctions is usually described as a scattering problem. This picture, however, says nothing about the dynamical onset of steady states, their microscopic nature, or their dependence on initial conditions.[1] In order to address these issues, I will first describe the dynamical many-particle state via an effective quantum hydrodynamic theory [2]. This approach allows us to predict a series of novel phenomena like turbulence of the electron liquid [2], local electron heating in atomic and molecular junctions [3], and the effect of electron viscosity on resistance [4]. I will provide both analytical results and numerical examples of first-principles electron dynamics in nanostructures using the above approach. I will also discuss experimental tests of our predictions. Work supported in part by NSF and DOE.

- [1] N. Bushong, N. Sai and M. Di Ventra, "Approach to steady-state transport in nanoscale systems" *Nano Letters*, 5 2569 (2005); M. Di Ventra and T.N. Todorov, "Transport in nanoscale systems: the microcanonical vs grand-canonical picture", *J. Phys. Cond. Matt.* 16, 8025 (2004).
- [2] R. D'Agosta and M. Di Ventra, "Hydrodynamic approach to transport and turbulence in nanoscale conductors", *J. Phys. Cond. Matt.* 18, 11059 (2006).
- [3] R. D'Agosta, N. Sai and M. Di Ventra, "Local electron heating in nanoscale conductors", *Nano Letters* 6, 2935 (2006) .
- [4] N. Sai, M. Zwolak, G. Vignale and M. Di Ventra, "Dynamical corrections to the DFT-LDA electron conductance in nanoscale systems", *Phys. Rev. Lett.* 94, 186810 (2005).

Influence of Laser Light onto the Conductance of Atomic-Size Contacts

E. Scheer

Fachbereich Physik, University of Konstanz, D-78457 Konstanz, Germany

In this presentation we report on the influence of laser irradiation onto the electrical conductance of gold nanocontacts established with the mechanically controllable breakjunction technique. We concentrate on the study of reversible conductance changes which can be as high as 200%. We investigate the dependence on the initial conductance of the contacts, and on the wavelength, the intensity and the position of the laser spot with respect to the sample. Under most conditions an enhancement of the conductance is observed. Several physical mechanisms which might contribute to the observed effect including thermal expansion, rectification, plasmon excitation and photon-assisted transport are discussed, among which the two latter ones are most likely the dominating ones.

Vibrational non-equilibrium in single molecule transistors

Felix von Oppen
Freie Universität Berlin

The applied current in a single-molecule transistor can drive the molecular vibrations out of thermal equilibrium, which makes this system an interesting testbed for out-of-equilibrium quantum transport. Vibrational non-equilibrium has immediate consequences for the rate of current-driven conformational switching and may also induce interesting new transport phenomena such as avalanche transport in the Franck-Condon-blockade regime [1,2]. An experimental probe of current-induced vibrational non-equilibrium is provided by vibrational absorption sidebands [3] in the Coulomb-blockade regime of transport through single-molecule junctions. Corresponding experiments on suspended carbon nanotubes yielded remarkably long vibrational relaxation times of the order of 10ns. In this talk, we analyze vibrational absorption sidebands theoretically [2,4]. Our analysis reveals that experiment significantly overestimated the vibrational relaxation time and suggests improved measurement schemes which should make future experiments on vibrational absorption sidebands very informative.

[1] J. Koch, F. von Oppen, PRL 94, 206804 (2005); J. Koch, M.E. Raikh, F. von Oppen, PRL 95, 056801 (2005).

[2] J. Koch, F. von Oppen, A. Andreev, PRB 74, 205438 (2006).

[3] B.J. LeRoy, S.G. Lemay, G. Kong, C. Dekker, Nature 432, 371 (2004); B.J. LeRoy, PRB 72, 075413 (2005).

[4] M. Lueffe, J. Koch, and F. von Oppen, unpublished (2007).

Tuesday Afternoon, September 25

Afternoon session I (Chair: K. Reuter)

- 13:30 – 14:10 **Giovanni Cuniberti** (*Technische Universität Dresden*),
Tuning the Conductance of a Molecular Switch
- 14:10 – 14:40 **Hardy Gross** (*Freie Universität Berlin*),
*Time-Dependent Quantum Transport: Electron Pumping, Transients
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15:00 – 17:00 Boat tour

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*Switching of Diarylethenes on Gold:
Aiming for Functionality and Robustness*
- 18:00 – 18:30 **Leonhard Grill** (*Freie Universität Berlin*),
*Isomerization of Single Azobenzene Derivatives
with a Low Temperature STM*
- 18:30 – 19:00 **Petra Tegeder** (*Freie Universität Berlin*)
*Reversible switching of tetra-tert-butyl-azobenzene on a Au(111) surface
induced by light and thermal activation*

Tuning the Conductance of a Molecular Switch

M. del Valle, R. Gutiérrez-Laliga, C. Tejedor, and G. Cuniberti
Universidad Autónoma de Madrid, TU-Dresden

One key element to realize nanoscale electronics is the ability to manipulate in a controlled way the conductance of single molecules. Azobenzene, which undergoes a trans-cis isomerization transition upon irradiation, offers the possibility to realize a conformational, light-driven molecular switch. It is thus crucial to clarify the electrical transport characteristics of this molecule. Here, we investigate theoretically charge transport in a system consisting of carbon nanotubes (CNTs) acting as electrodes which are bridged by cis/trans azobenzene. In clear contrast to Au-electrodes, CNTs can act as true nanoscale electrodes, inducing a strong chirality-dependent renormalization of electronic states near the Fermi level. The low energy conduction properties may thus be dramatically modified by changing the molecule-CNT contact topology and/or the tubes chirality. We propose some possible experimental ways to realize a controlled electrical switching with CNT electrodes.

- [1] M. del Valle, R. Gutiérrez-Laliga, C. Tejedor, and G. Cuniberti, *Nature Nanotechnology* **2**, 176 (2007); [arXiv:0705.0527v1](https://arxiv.org/abs/0705.0527v1)

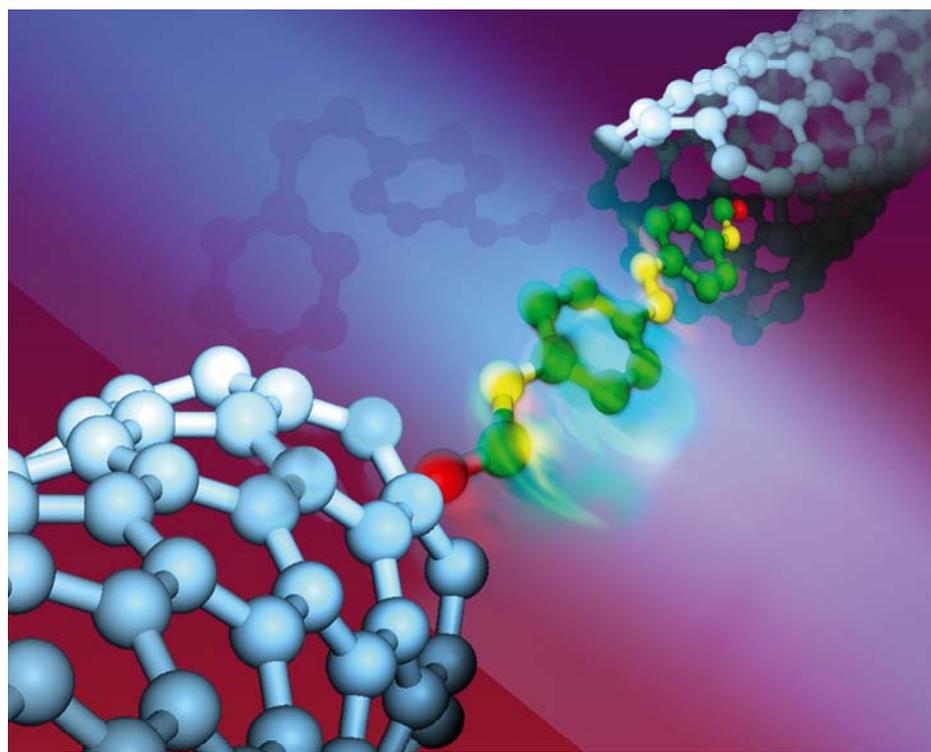


Figure caption: Schematic view of the unimolecular switching device.

Time-Dependent Quantum Transport: Electron Pumping, Transients and the Role of Bound States

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We present a description of transport based on the time evolution of the non-interacting time-dependent Schrödinger equation and develop a numerical algorithm for the time propagation which is suited for implementation of time-dependent density functional theory. The algorithm is used to study time-dependent transport phenomena such as electron pumping, transients and the role of bound states. In electron pumps a pump current is produced between two unbiased electrodes by applying a periodic bias to a gate electrode. The presence of at least two bound states in the biased electrode-device-electrode system, leads to current oscillations which remain undamped in the long-time limit. We investigate the dependence of the time-dependent current on the history of the applied bias or gate voltage and on the initial state.

Switching of Diarylethenes on Gold: Aiming for Functionality and Robustness

Sense Jan van der Molen

Universität Basel, Rijksuniversiteit Groningen, present address: Leiden University

In this talk, I deal with two questions in molecular electronics:

a) How to transfer a functionality of a molecule into a working device?

b) How to make robust devices?

A pivotal example of a functional molecule is a switch. In particular, we investigate photochromically switchable diarylethenes. In solution, these molecules can be reversibly transformed from a conjugated, 'on' state to a cross-conjugated, 'off' state, by using light of the proper wave lengths ('on' to 'off': $\lambda \approx 550$ nm; vice versa: $\lambda \approx 330$ nm). Our first efforts concentrated on thiophene-substituted diarylethene switches connected to gold electrodes by Au-S bonds. However, in a series of experiments, we found that the metallic contact has a profound influence on the properties of these molecules. Once connected to gold, the molecule can switch from conjugated to cross-conjugated, but it cannot switch back. We attribute this effect to the strong coupling of the cross-conjugated molecule to the gold. By chemically modifying the molecule such that it couples more weakly to the gold electrodes, a reversibly switching system is obtained. We demonstrate this using STM and UV-Vis spectroscopy.

An answer to the question of robustness is to use defect-tolerant structures. For this, we utilize 2D-networks of gold nanoparticles, which can be connected by conjugated molecules. The devices consist of many single (or few) molecular junctions and are stable for days at room temperature. By incorporating diarylethene switches in these two-dimensional networks, we aim for devices that combine functionality with robustness. Our first results in this direction are very promising.

Isomerization of Single Azobenzene Derivatives with a Low Temperature STM

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The azobenzene molecule represents an interesting example of a molecular switch as it undergoes a reversible transformation between two stable states, associated with different physical/chemical properties. The two different conformations are a nearly planar trans- and a non-planar, three-dimensional cis-form.

In the present work, the reversible trans-cis isomerization of single azobenzene derivatives adsorbed on a Au(111) surface is studied by scanning tunneling microscopy (STM) at 5 K. The molecule is equipped with four tert-butyl groups, which increase the distance between the azobenzene core and the metallic surface. These substituents decouple the molecule from the substrate and facilitate the formation of highly ordered islands. The exact molecular orientation and configuration is extracted from the STM images. By applying voltage pulses with the STM tip, the isomerization of single molecules from the trans- to the cis-state and vice versa is realized [1]. It turns out that only molecules adsorbed in islands can switch, while single molecules appear to be too mobile. The switching process is characterized by changing the relevant parameters, i.e. the tip height and the bias voltage. Furthermore, isomerization of the molecules by illumination with laser light or by annealing of the sample will be presented.

- [1] M. Alemani, F. Moresco, M. V. Peters, S. Hecht, K.-H. Rieder, and L. Grill
J. Am. Chem. Soc. 128, 14446 (2006)

Reversible switching of tetra-*tert*-butyl-azobenzene on a Au(111) surface induced by light and thermal activation

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14195 Berlin (Germany)*

Molecular switches, like azobenzenes in direct contact with metal substrates, are promising systems for possible applications in molecular electronics and functional surfaces, due to their ability to undergo reversible photo-induced conformational changes (*trans/cis*-isomerization) [1-3]. Whereas the switching behaviour of azobenzene and its derivatives in the liquid phase is well studied, it is an open question how the switching properties change when these molecules interact with a metal surface. For understanding and controlling of switching processes, a detailed knowledge about electronic and geometrical structure of the molecules in contact with metal substrates is essential.

We have shown that 3,3',5,5'-tetra-*tert*-butyl-azobenzene (TBA) on Au(111) can be switched bidirectional by UV-light and thermal activation [4,5]. The switching process resulted in reversible changes in the electronic [4] and vibrational structure [5] of TBA on Au(111) investigated with two-photon photoemission (2PPE) and high-resolution energy loss spectroscopy (HREELS), respectively. Based on wavelength dependent measurements we propose that the optically-induced conformational change (*trans*- to *cis*-isomerization) of the adsorbed molecules is not caused by direct intramolecular excitation as in the liquid phase but rather by an indirect mechanism, i.e., *via* attachment of excited electrons to the molecules, creating a transient molecular anions. The thermal barrier for the *cis*- to *trans*-isomerization elucidated from temperature dependent measurements is found to be around 250 meV [6].

- [1] M.R Bryce, M.C. Petty, D. Bloor, *Molecular electronics*; Oxford University Press: New York, 1995.
- [2] B.L. Feringa, *Molecular Switches*; Wiley-VCH: Weinheim, 2001.
- [3] H. Rau, in *Photochromism - Molecules and Systems*, edited by H. Dürr and H. Bouas-Laurent, Elsevier: Amsterdam, 2003.
- [4] S. Hagen, F. Leyssner, D. Nandi, M. Wolf, and P. Tegeder, *Chem. Phys. Lett.* **444**, 85 (2007).
- [5] L. Óvári, M. Wolf, and P. Tegeder, *J. Phys. Chem. C*, in press, 2007.
- [6] S. Hagen, D. Nandi, P. Kate, M. Wolf, and P. Tegeder, in preparation.

Wednesday Morning, September 26th

Morning session I (Chair: A. Grohmann)

- 9:00 – 9:40 **Stefan Tautz** (*Forschungszentrum Jülich*),
Bonding, structure and function of highly-ordered molecular adsorbate layers on metal surfaces
- 9:40 – 10:20 **Wolfgang Kuch** (*Freie Universität Berlin*),
Paramagnetic Molecules on Magnetic and Non-Magnetic Substrates
- 10:20 – 10:40 Coffee break
- Morning session II (Chair: J. P. Rabe)
- 10:40 – 11:20 **Andreas Terfort** (*Universität Hamburg*),
Self-Assembled Monolayers: Principles for Order & Possibilities for Switching
- 11:20 – 11:50 **Cornelius Gahl** (*Max-Born-Institut Berlin*),
Self-assembled Monolayers of Azobenzene-Alkanethiols on Gold
- 11:50 – 12:20 **Rainer Haag** (*Freie Universität Berlin*),
Synthesis of molecular switches as building blocks for functional surfaces
- 12:20 – 13:30 Lunch break
- 14:00 – Departure...

Bonding, structure and function of highly-ordered molecular adsorbate layers on metal surfaces

R. Temirov, O. Neucheva, A. Lassise, S. Soubatch, F.S. Tautz
Jacobs University Bremen, Forschungszentrum Jülich

During recent years, molecular adsorbate layers on solid surfaces have moved into the focus, because they form the basis of hybrid materials which offer application potential in electronics, sensorics and heterogeneous catalysis. Although some applications are close to being marketed commercially (e.g. organic light emitting displays), many fundamental properties of molecular materials and their interfaces are still the subject of active research.

For semiconducting π -conjugated organic materials, techniques of organic molecular beam deposition have been developed to such an extent that the controlled and reproducible preparation of highly ordered ultra-thin molecular layers on a range of inorganic substrates has become possible, thereby making these films accessible to the sensitive spectroscopies and microscopies of UHV-based surface science. Apart from the adsorption process itself, the intrinsic properties of organic semiconductors as well as their modification by the presence of the interface can thus be studied with precision.

In the present contribution, we will focus on the aspects of *bonding*, *structure* and *function* of organic semiconductors on metal surfaces. In particular, the dynamic properties of these interfaces are stressed. In detail, the following issues will be discussed:

(1) The *bonding* of π -conjugated molecules often involves a chemical as well as a physical contribution. Using the model molecule of PTCDA on noble metal surfaces as an example, the particular properties of such a bond are discussed, with special emphasis on the structure of the adsorbate. (2) In addition to the molecule-substrate bonding, the intermolecular interaction has an important influence on the *structural* evolution of the interface. Depending on the molecule, these interaction can be attractive or repulsive, yielding very different phase behaviour. This will be illustrated by a comparison between PTCDA and tetracene on Ag(111). (3) In organic and molecular electronics, the organic-metal contact is of prime importance for charge injection and charge transport – the prime *function* of organic semiconductors. On highly ordered organic monolayers on a metallic substrate, charge transport across the interface and through the molecule can be investigated under structurally well-defined conditions. We will illustrate this with two examples, (a) the inelastic tunneling transport through an adsorbed molecule and (b) the charge transport through a single-molecular wire, contacted covalently with an STM tip [1].

[1] cond-mat/0612036v2

Paramagnetic Molecules on Magnetic and Non-Magnetic Substrates

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Many six-coordinate iron(II) complexes with an Fe-N₆ core show spin-crossover (SCO) behavior. Depending on temperature, pressure, or optical excitation, these complexes can switch between two magnetic states, for which the *d* electrons either align such that their spins add up (high spin) or compensate partly (low spin). Here we report on X-ray absorption (XAS) measurements of thin layers of Fe(II) 2,6-bis(pyrazol-1-yl)pyridine SCO complexes deposited from solution on gold metal surfaces. By means of angle-dependent x-ray absorption spectroscopy (XAS) at the C and N *K* edges we determine the alignment of the molecules on the surface, whereas their spin state is determined by comparing the Fe-*L*_{3,2} spectra to measurements on bulk samples. We provide also evidence for thiocyanate-terminated ligands to form well-ordered self-assembled monolayers on Au(111). Molecules of the type R-SCN are thus viable alternatives for thiols R-SH.

Paramagnetic Fe porphyrin molecules are promising candidates for applications in molecular nano-electronics. A fundamental understanding of the interaction of these molecules with ferromagnetic substrates is essential to realize future functional devices. The magnetic properties of such molecules adsorbed on ferromagnetic epitaxial Ni and Co films on Cu(001) were studied by XAS and x-ray magnetic circular dichroism (XMCD). Angle-dependent XAS spectra reveal that for coverages below one monolayer the porphyrin molecules lie flat on the surface. Ferromagnetic coupling of the Fe atom to the Ni and Co films is evidenced by XMCD. Comparing to results of density functional theory calculations we conclude that a 90° superexchange interaction between the metal ion across the neighboring nitrogen atoms to the substrate is responsible for this coupling. From the temperature dependence of the Fe XMCD signal, a different coupling strength is observed for the two magnetic substrates, being weaker in the case of Ni.

Self-Assembled Monolayers: Principles for Order & Possibilities for Switching

Andreas Terfort
Universität Hamburg

An inherent property of self-assembled monolayers (SAMs) is the ordered arrangement of (organic) molecules onto surfaces. Since the early days of their discovery, it has been claimed that these surface layers exhibit extraordinary long range order, in particular for the system of thiolates on gold. It turns out that just now, well after 20 years, we start to understand how to reliably make monolayers which are almost defect free and show sufficient order to permit the use of these highly versatile layers e.g. in microelectronics. The first part of this talk will show what principles permit the manufacture of highly ordered SAMs.

In the second part I want to present some results on switchable SAMs in particular in conjunction with wettability. The use of electrochemistry permits fast and reversible switching processes with much less effort than e.g. photochemical systems.

Self-assembled monolayers of azobenzene-alkanethiols on gold

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and Martin Weinelt^{1,2}

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Azobenzene is one of the most intensively studied photochromic molecular switches. Linked to a gold surface via alkanethiols the molecules can form well oriented self-assembled monolayers (SAM). X-ray absorption spectroscopy reveals that the π -conjugated system of the chromophore is aligned almost perpendicular to the surface. While the azobenzene entity is sufficiently decoupled from the metal substrate by the alkane chain, lateral interactions between neighboring molecules within the SAM strongly influence properties and functionality of the optical switch. For well-ordered SAMs the optical absorption spectrum significantly differs from that in solution and no photo-isomerization is observed. This photoinactive form seems also to be formed in thin films on quartz substrates. Furthermore a thin film grown from the photochemically generated *cis*-configuration can be transformed via the *trans* into the light-insensitive configuration by illumination or thermally. Introducing defects into the SAM, e.g., by X-ray beam damage or by roughness of the underlying Au film can restore the original absorption spectrum of the molecules in solution and activate the photochromic molecular switch.

**Synthesis of molecular switches as building blocks
for functional surfaces**

Rainer Haag

Institut für Chemie, *Freie Universität Berlin*

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Switching processes on metal surfaces investigated by scanning tunnelling microscopy

Nils Henningsen, Gunnar Schulze, Isabel Fernandez Torrente, Katharina J. Franke, Nacho Pascual, Sofia Selvanathan, Leonhard Grill

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Scanning probe microscopy (STM) provides unprecedented access to fundamental information about molecular dynamics and excitations through a combination of local spectroscopy and manipulation of single molecules. In this poster we will review our last results on the following systems:

- Electronically and thermally induced rotation of a phenyl ring of di-metacyano azobenzene (DMC) on gold surfaces: An intramolecular conformational change consisting of a rotation of a phenyl ring can be detected when an azobenzene molecule is functionalised on meta sites. This change can be induced either with tunnelling electrons, through an anionic transient state, or by temperature. The latter is found to be an effective pathway mediating the molecular recognition of molecules during the thermally induced assembly of ordered molecular films.

- The isomerization behaviour of various azobenzene derivatives on gold surfaces: Molecules with different substituents attached to an azobenzene core, synthesized by the group of Prof. Stefan Hecht, are studied by means of their adsorption properties. Both the position of the substituents at the phenyl rings and their chemical properties, changing the intermolecular interaction, have been modified. It turns out that the capability of the molecules to be isomerised is strongly influenced by the substituents.

STM-Tip-Induced Bistability of Single 1,5 Cyclooctadiene Molecules on the Si(100) Surface

Christophe Nacci, Jérôme Lagoute, Xi Liu, Stefan Fölsch
Paul Drude Institute for Solid-State Electronics, Hausvogteiplatz 5-7, 10117 Berlin, Germany

The adsorption and tip-induced switching of single 1,5 cyclooctadiene molecules (COD) on the Si(100) surface was studied by low-temperature STM. COD (C₈H₁₂) is a cyclic alkene with two opposite C=C double bonds and a twisted boat ground state configuration. In our experiment, 0.1 L COD was dosed at room temperature followed by sample cooling to 7 K. We observe two different molecular adsorption structures which are identified as (i) the so-called upright structure implying that only one of the two C=C bonds is involved in the reaction with the dimerized Si(100) surface, and (ii) the bridge structure with both C=C bonds reacting with two adjacent Si dimers. The latter occurs as the predominant structure, in line with the predictions of previous density functional calculations [Cho *et al.*, Phys. Rev. B **64**, 241306 (2001)]. Time-dependent measurements of the tunnel current with the tip positioned over the molecule in the bridge structure reveal a telegraph noise signal, i.e. fluctuations between two levels of current with the same population probability. Higher bias and smaller tip-to-sample distance (and therefore higher current) result in an increased switching rate suggesting that the fluctuations are due to an inelastic single-electron excitation process. We interpret this fluctuation as a dynamic switching between two degenerate conformations of the adsorbed molecule which can be triggered and controlled by the vertical charge transport. First measurements on COD adsorbed in the upright structure, on the other hand, reveal a telegraph noise response of significantly enhanced quantum yield and with a lifted degeneracy in the population probability.

Probing Molecular Switches at Surfaces with Localized Optical Fields

M. Breusing, T. Elsässer
Max-Born-Institut Berlin

Optical studies on molecular switches in solution have been successfully performed for several years. For technological applications, such as reversible optical data storage, surface attached films of such molecules are of particular interest.

Scattering type scanning near field optical microscopy (s-SNOM) allows for an optical probing of surfaces with a spatial resolution on the nanometer scale, making use of the strongly enhanced field at the apex of an ultra sharp metallic tip. Using this technique, one can observe and modify small amounts of substances, even up to single molecule sensitivity as recently shown in our group [1]. In order to investigate small numbers of switching molecules, we have constructed a versatile s-SNOM with enhanced performance for measurements on molecular switches. This new set-up is based on an inverted optical microscope with a high numerical aperture, thus improving the detection efficiency compared to prior measurements.

With this set-up, we made measurements on fulgimide molecules, which do a ring opening/closing isomerization under green/ultraviolet illumination. Samples were prepared by spincoating on glass substrates. Far-field absorption measurements of films with a concentration in the range of a monolayer exhibit reversible switching. However, a tendency to form molecular clusters often results in inhomogeneous layers. For nano-sized clusters of fulgimide prepared by vapor deposition followed by annealing, a reversible switching has also been reported [2].

In order to reach the single molecule level, the formation of clusters has to be avoided. Therefore, we work in cooperation with Project B6 on self assembled monolayers (SAM) of such fulgimides on silicon. These structures are analysed by the use of infrared spectroscopy and scanning probe microscopy techniques, aiming at well-ordered monolayers for s-SNOM investigations.

- [1] Neacsu et al., *Scanning-probe Raman spectroscopy with single-molecule sensitivity*, Physical Review B 73, 193406, 2006
- [2] Rath et al., *Scanning near-field optical microscopy investigations on local optical switching of self-organized photochromic nanostructures*, Journal of Luminescence, 2001, 94-95, 157-161

Self-Assembled Monolayers of Molecular Switches – Azobenzene Carrying Alkanethiols on Gold

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Self-assembled monolayers of azobenzene – alkanethiols adsorbed on gold and their potential as a molecular switch have been investigated by X-ray absorption, X-ray and VUV photoemission spectroscopy. The molecules are well oriented at 100 K and the azobenzene entity is sufficiently decoupled from the substrate by the alkane chain. The occupied frontier orbitals of non-bonding n and of π character are identified by angle-resolved photoemission and autoionization spectroscopy at the N1s and C1s absorption edges. Their energetics and oscillator strengths are substantially modified by a CF₃ substituent attached to the azobenzene entity. We present first evidence for optical-induced trans-cis isomerization.

Adsorption Studies of Different Azobenzene Molecules on Cu(001) and Au(111)

M. Piantek, M. Bernien, J. Miguel, W. Kuch
Institut für Experimentalphysik. Freie Universität Berlin

Azobenzene molecules can exist in two different conformational states, as a trans-isomer with a coplanar geometry or as a cis-isomer with tilted benzene moieties. The molecules can be switched between these two conformations by light irradiation, by electric field, or by temperature. This photochromic behavior can be used to trigger the physical properties of the molecules and make them suitable for applications like data storage, for which they have to be deposited on a metallic substrate. We have studied the adsorption of dimetacyano-azobenzene (DMC), dimetacarboxymethyl-azobenzene (CMA) and tetra-tert-butyl-azobenzene (TBA) on Au(111) and Cu(001). Mono- and multilayers of molecules were evaporated under ultra high vacuum conditions directly on the single crystal substrate in order to investigate the intermolecular interactions, as well as the interaction between the molecule and the surface.

From the angular dependence of the near edge X-ray absorption fine structure (NEXAFS), we can study the adsorption geometry. On Au(111) all the three derivatives show the same planar conformation as for the trans isomer, and they are adsorbed flat on the surface. From X-ray photoemission spectroscopy (XPS) of a DMC monolayer on Au(111), we obtained the same spectra as from the multilayer. Thus we conclude that there are no additional bonds formed between the molecule and the metallic surface.

The situation changes drastically if the substrate is Cu(001). In this case, the DMC and CMA molecules present an out-of-plane geometry with respect to the substrate. From the angular dependence of the π^* resonances in the N *K* edge NEXAFS, we derived that, in the case of DMC, the benzonitrile moieties are tilted out of the molecular plane. Similar results were obtained for the N and O *K*-edge NEXAFS of CMA layers. We have also observed a change in the shape of the N 1s XPS spectrum of the DMC monolayer which can be explained by an additional bond to the surface.

Structural and Optical Investigation of Thin Photochromic Spiropyran Films

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Photochromic molecules are reversibly switchable molecules that can be both, addressed and read out using light. Possible applications are optical memory devices and smart materials [1]. We have investigated 6-nitro derivatives of spiropyran, which in addition to their photochromism exhibit a strong change in the dipole moment upon switching. Thin films of these molecules have been prepared using thermal evaporation under ultrahigh vacuum conditions on different substrates as e.g., quartz, MgO(100), and LiNbO₃. Stoichiometry, surface quality and stability of the films were investigated using Auger Electron Spectroscopy. In addition, first STM results for the LiNbO₃ substrates are presented. The photochromism of the films has been studied using optical absorption spectroscopy in the UV-VIS range. Reversible switching by light irradiation between the spiropyran and the merocyanine state was observed. Steady-state transmission spectra of 5 to 40 nm thin films on quartz and MgO(100) will be shown for the spiropyran ground state as well as the metastable merocyanine state and compared to spiropyran molecules in solution [2]. Furthermore, the switching kinetics on a time scale of seconds will be presented and discussed [3].

- [1] G. Berkovic, V. Krongauz, and V. Weiss, *Chem. Rev.* **100**, 1741-1753 (2000)
- [2] A. Chibisov and H. Görner, *J. Phys. Chem. A*, **101**, 4305 (1997)
- [3] M. Karcher, C. Rüdert, C. Elsässer, and P. Fumagalli, *J. Appl. Phys.*, accepted

Iron(II) Spin Crossover Complexes for Self-Assembled Monolayers on Gold Surfaces

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Six-coordinate iron(II) coordination compounds, most of which have an Fe-N₆ coordination core, have long been known to show reversible spin crossover (SCO) between the diamagnetic low spin and the paramagnetic high spin state. In spite of a wealth of such complexes there are no examples where such compounds have been used to form self-assembled monolayers (SAMs) on gold surfaces. Established experiments are based on Langmuir-Blodgett techniques or the embedding of SCO ensembles in polymer matrices.

Switchable units on surfaces have been a fascinating subject due to their potential applications in information storage and optical devices[1].

In order to put such SAMs on gold surfaces we are employing SCO compounds with bis-tridentate donor set, such as those recently reported by Halcrow et al.[2], and equip them with suitable anchoring groups.

We report first coating experiments on gold surfaces using our modified ligands and complexes and their detailed spectroscopic and magnetic investigations using XAS, STM and XPS.

- [1] (a) Respondek, I.; Bressel, L.; Saalfrank, P.; Kämpf, H.; Grohmann, A. *Chem. Phys.* **2007**, *submitted*.
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(e) Kahn, O.; Jay, C. *Science* **1998**, *279*, 44.

- [2] Halcrow, M. A. *Coord. Chem. Rev.* **2005**, *249*, 2880.

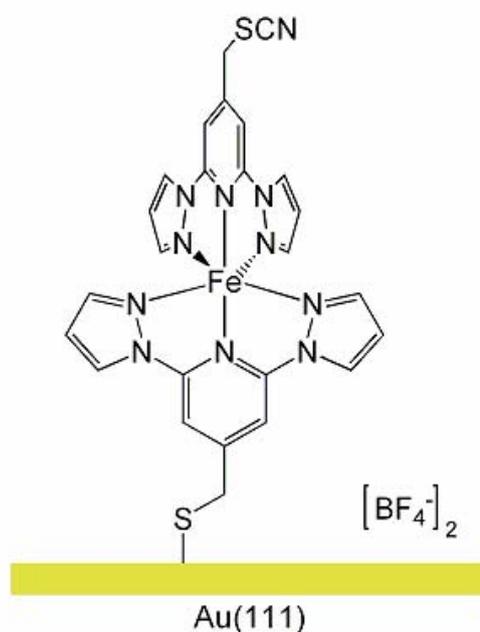


Fig. 1: Iron(II)-Complex, bound to a gold surface

Photoswitches for Molecular Switching Devices

Karola Rück-Braun

Institut für Chemie, TU-Berlin

The aim of this project is the development and investigation of photochromic units consisting of a photoswitch (azobenzenes: *cis/trans* isomerization, fulgimides: electrocyclic ring opening / ring closure reactions), a linker or rigid spacer unit and suitable anchoring or end groups for the immobilization on the respective surface.

The main focus is on the covalent attachment of photochromic units on hydrogen terminated silicon surfaces [H-Si(111)] as well as the connection of photoswitchable molecules on functionalized monolayers on Si(111). The chemical coupling methods have to be adjusted to the reactivity of the respective photoswitch-linker-molecule and the silicon surface.

Designing Molecular Switches: From *cis-trans* Isomerization on Metal Surfaces Towards More Complex Systems

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Photochromism has been intensely investigated in solution and in polymeric materials, largely motivated by its potential use in optical data storage. While this relates to bulk property changes, in principle, the large structural or electronic changes associated for example with the *cis-trans* isomerisation of azobenzenes or the spiropyran-merocyanine ring opening/closing equilibrium can be used to affect properties of individual molecules and have successfully been exploited to create photoresponsive molecular devices [1-3]. However, only recently several reports on reversible switching at the single molecule level on solid substrate surfaces have appeared [4-7].

Here, we present our ongoing efforts to synthesize azobenzene as well as stilbene photochromes for systematic investigations of STM-tip induced *cis-trans* isomerization, performed in a fruitful collaboration with the group of Dr. Leonhard Grill (Project A1) [6]. Structural modifications have been realized by bulky substitution of the four equivalent 3,3',5,5'-positions and by introduction of electron-donating and/or -withdrawing groups in the 4 and/or 4' position(s). The molecules have been photoisomerized in solution and subsequently been investigated on metal surfaces using STM (UHV, LT) with regards to their self-assembly and switching characteristics. In addition to establishing fundamental structure-switching relationships, we have actively been pursuing to increase molecular complexity by breaking the symmetry of the molecules, introducing self-assembling motifs, and increase the number of switching unit in the molecules. These more complex molecular systems will allow for investigation of potential cooperativity effects between and within the molecules and should aid the design of first single molecule devices, as in the case of spiropyran-porphyrin dyads currently synthesized for a collaboration with Prof. Jürgen P. Rabe (project A3). The poster will focus on synthetic chemistry and present selected physical highlights, also featured on the collaborators' posters.

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Substituted Azobenzene Molecules as Molecular Switches: Quantum Chemical Investigations

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We report quantum chemical calculations, mostly based on density functional theory, in order to propose a dynamical model for the rotation of a single phenyl ring of the particular azobenzene derivate: di-meta-cyanoazobenzene (DMC) [1]. The motivation comes from a recently performed STM experiment (Scanning Tunneling Microscope) on the DMC/Au(111) where the rotation was induced [2] between two distinct *trans* isomers (3,3'-and 3.5'-DMC) at the surface corresponding to two different alignments of the functional groups (CN). Calculating PES (Potential Energy Surfaces) for the free azobenzene, as a neutral and a negatively charged molecule, we propose a dynamical model for the ring-rotation pathways, which include the electric field in the STM junction to effectively couple electronic excitation with intramolecular rotation [2]. The scenario of a negative ion-resonance mechanism for the switching process is supported by our quantum chemical calculations.

It has been shown before that azobenzenes undergo *cis/trans* isomerization on noble metal surfaces using STM [3,4,5]. In some cases, a thermal back switching from *cis* to *trans* was observed. We therefore also present several different azobenzene derivates as possible candidates for the switching process as well as the effect of the type, amount and position of the substituents on the phenyl rings of azobenzene on the isomerization *cis-trans* barriers.

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Accurate Description of the Bonding of C₆H₆ at Noble Metal Surfaces, Using a Local Exchange-Correlation Correction Scheme

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The adsorption of benzene (C₆H₆) at the close-packed Cu(111) surface is a much studied model system for the interaction of larger π -conjugated molecules with solid surfaces [1]. At first glance a rather simple system, the suspected predominantly van der Waals type bonding at the extended metal surface poses a severe challenge for accurate first-principles calculations. Density-functional theory (DFT) with present-day local and semi-local exchange correlation (xc) functionals is uncertain to properly account for this type of bonding, while the system sizes required to correctly grasp the metallic band structure quickly become computationally intractable with correlated wave function techniques. We overcome these limitations with a recently introduced “local xc correction” scheme [2], correcting the deficiencies in the adsorption energetics from present-day DFT xc functionals with hybrid functional and Møller-Plesset perturbation theory calculations. Building on the obtained binding energy curves at the different levels of theory we attempt a discussion of the various contributions to the bonding at the noble metal surface.

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