Exploring the Limits of Nanoscience with Scanning Probe Methods

704. WE-Heraeus-Seminar

27 – 31 October 2019
at the Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 704. WE-Heraeus-Seminar:

For nearly forty years the scanning probe methods (SPM) are the dedicated tools to characterize surfaces with atomic-scale accuracy. Besides their intrinsic ability to image matter at the lowest-scale level, scanning probes have been improved and combined with other spectroscopic approaches to provide sensitivity to various types of signals. Nowadays, magnetisms, mechanical and electrostatic forces, optics or time-resolved spectroscopies can be probed down to individual atoms or molecules, and the field of possibilities only seems to grow year after year. Along these experimental developments sophisticated theoretical methodologies have been developed to describe and predict the rich physics encountered in the field of SPM.

The purpose of this workshop is (i) to provide a didactic overview of this very active field of nanoscience, (ii) to expose technological breakthroughs as well as (iii) to provide an ideal opportunity to discuss the most recent scientific discoveries in the field.

Scientific Organizers:

Dr. Thomas Frederiksen	DIPC - Donostia International Physics Center, Spain E-mail: thomas_frederiksen@ehu.eus
Dr. Guillaume Schull	Université de Strasbourg, France E-mail: schull@unistra.fr
Dr. Dimas G. De Oteyza	DIPC - Donostia International Physics Center, Spain E-mail: d_g_oteyza@ehu.eus

Program

Program

Sunday, 27 October 2019

17:00 – 20:00	Registration
18:00	*BUFFET SUPPER and informal get-together*

Monday, 28 October 2019

08:00	*BREAKFAST*	
9:00 – 09:10	Scientific organizers	**Welcome words**
09:10 – 09:55	Jens Wiebe	**STS of spin chains built on superconductors**
09:55 – 10:40	Takashi Kumagai	**Near-field physics and chemistry in plasmonic STM junctions**
10:40 – 11:10	*COFFEE BREAK*	
11:10 – 11:55	Christian Lotze	**Molybdenum Disulfide on Au(111) – growth, electronic structure and outstanding playground for single molecule spectroscopy**
11:55 – 12:40	Pavel Jelínek	**1D organometallic chains: on-surface synthesis and transport properties**
12:40	*LUNCH*	

Program

Monday, 28 October 2019

14:00 – 14:45	Rémi Avriller	**Single-photon emission mediated by single-electron tunneling in plasmonic nanojunctions**
14:45 – 15:30	Emi Minamitani	**Theory of single spin spectroscopy at surfaces: from Kondo singlet to spin-orbit interaction**
15:30 – 16:00	*COFFEE BREAK*	
16:00 – 16:45	Sarah Burke	**Cool chemistry: Watching reaction progression at single-site heterogeneous catalysts**
16:45 – 17:30	Leo Gross	**Molecular synthesis, charge-state control and structure elucidation with AFM**
17:30 – 18:15	**Flash poster presentation**	
18:30	*DINNER*	
20:00	**Poster session 1**	

Program

Tuesday, 29 October 2019

08:00	*BREAKFAST*	
09:00 – 09:45	Jascha Repp	**Actuating and probing a single-molecule switch at femtosecond timescales**
09:45 – 10:30	Volker Deckert	**High resolution tip-enhanced Raman scattering under ambient conditions**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Sebastian Loth	**Ultrafast dynamics of collective charge and spin excitations on surfaces**
11:45 – 12:30	Yousoo Kim	**Single-molecule optical spectroscopy with a photon STM**
12:30 – 12:40	**Conference Photo** (in the front of the lecture hall)	
12:40	*LUNCH*	

Program

Tuesday, 29 October 2019

14:00	**Excursion / free discussions**	
18:00	*DINNER*	
20:00 – 21:00	**After Dinner Highlight session:**	
20:00 – 20:15	Shadi Fatayer	**Molecular structure elucidation with charge-state control**
20:15 – 20:30	Manish Garg	**Attosecond coherent manipulation of electrons in tunneling microscopy**
20:30 – 20:45	Richard Korytár	**Incommensurate oscillations of oligoacene gaps adsorbed on Au(111)**
20:45 – 21:00	Dante Sblendorio	**Quantum state manipulation of single atom magnets using the hyperfine interaction**

Program

Wednesday, 30 October 2019

08:00	*BREAKFAST*	
09:00 – 09:15	Stefan Jorda	**About the Wilhelm and Else-Heraeus-Foundation**
09:15 – 10:00	Richard Berndt	**Probing and controlling molecular spins on surfaces**
10:00 – 10:45	Laurent Limot	**Atomic-scale spin sensing with a single-molecule at the apex of a scanning tunneling microscope**
10:45 – 11:15	*COFFEE BREAK*	
11:15 – 12:00	Marek Kolmer	**Two-probe scanning tunneling microscopy and spectroscopy**
12:00 – 12:45	Amandine Bellec	**Addressing spin-crossover molecules on metallic substrate by voltage pulses and light**
12:45	*LUNCH*	

Program

Wednesday, 30 October 2019

14:00 – 14:45	Ruben Esteban	**Optical coupling with molecules in scanning probe microscopes**
14:45 – 15:30	Aran Garcia-Lekue	**Functional carbon nanostructures: Insights from density functional-theory**
15:30 – 16:00	*COFFEE BREAK*	
16:00 – 16:45	Alexander Riss	**Complex molecular architectures: design and characterization at the atomic scale**
16:45 – 17:30	David Écija	**On-surface synthesis of π- conjugated polymers**
17:30 – 18:15	Christian Wagner	**Scanning quantum dot microscopy**
18:30	*HERAEUS DINNER* *(social event with cold & warm buffet with complimentary drinks)*	
20:00	**Poster session 2**	

Program

Thursday, 31 October 2019

08:00	*BREAKFAST*	
09:00 – 09:45	Christian Ast	**Yu-Shiba-Rusinov states from impurities with a quantum spin**
09:45 – 10:30	Pablo Merino	**Photon statistics measured by scanning tunneling microscopy-induced luminescence on single molecules**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Jingcheng Li	**Engineering the magnetic properties of graphene nanostructures by edge topology**
11:45– 12:30	Martina Corso	**Electronic consequences of chemical doping of graphene nanoribbons**
12:30 – 13:00	Benjamin Heinrich	**Publishing at nature research journals – insights from the other side**
13:00 – 13:15	Scientific organizers	**Final discussion and closing words**
13:15	*LUNCH*	

End of the seminar and departure

Posters

Posters

Soroush Arabi	**3D topological Kondo insulator: Charge screening and neutrality**
Lukas Arnhold	**Expanding holdtime: Measurement capabilities in a cryogen-free low-temperature scanning tunneling microscope**
Susanne Baumann	**The breakdown of the ohmic regime in graphene**
Alejandro Berdonces-Layunta	**Electronic structure of 5-armchair graphene nanoribbons: STM study of their topological end states.**
Nicolaj Betz	**MnNi tips for spin-polarized STM**
Leon Bolat	**The electrostatic potential of atomic chains and clusters imaged quantitatively with scanning quantum dot microscopy**
Ole Bunjes	**Controlling dopant-induced telegraph noise by optical excitation**
Alberto Curcella	**Unveiling the intra-atomic exchange interaction in rare earth adatoms**
Xabier D. de Cerio	**Tuning the electronic properties of nanoporous graphene by Li decoration**
Marco Di Giovannantonio	**On-surface synthesis of antiaromatic, open-shell indenofluorene polymers**
Jiří Doležal	**Exciton control in single-molecule fluorochromes**
Benjamin Doppagne	**Hyper-resolved fluorescence microscopy**

Posters

Andreas Dörr	**Selective on-surface synthesis of oxygen heterocycles on metals**
Robert Drost	**Microwave-assisted tunnelling and self-interference effects in superconducting junctions under fast driving signals**
Qitang Fan	**Non-alternant nanoribbons of graphene allotropes from fusion of polyazulene**
Shadi Fatayer	**Molecular structure elucidation with charge-state control**
Niklas Friedrich	**Inducing magnetism in graphene nanoribbons by substitutional Boron-doping**
Léo Garnier	**Vibron-assisted spin excitation in a magnetically anisotropic molecule**
Abhishek Grewal	**Time-resolved STML investigation of organic molecules with high spin-orbit coupling**
Andreas Heinrich	**Quantum nanoscience: Atoms on surfaces**
Jan Homberg	**YSR-states in manually assembled nanoclusters of phthalocyanine molecules on Pb(100)**
Haonan Huang	**Charge transport between discrete superconducting bound states at the atomic scale**
Felix Huber	**Design of a high-stability miniaturized STM-Head**
Katharina Kaiser	**Combining high-resolution atomic force microscopy with scanning tunneling microscopy induced light emission on single molecules**

Posters

Kensuke Kimura	**Investigation of selective triplet exciton formation in a molecule with an STM**
Marvin Knol	**Discriminating and counting the possible molecular configurations in a prototypical molecular wire junction**
Kira Kolpatzeck	**Structure analysis of ultrathin NaCl-layers on metallic substrates**
Richard Korytár	**Surface-induced bands in atomic and molecular arrays**
Klaus Kuhnke	**Exploring the time evolution of individual molecular systems**
Felix Küster	**Zero energy bound states in the proximity induced topological superconductor system Bi_2Te_3 on Nb(110)**
Benjamin Mallada	**Structural defects on ethynylene-bridged anthracene wires**
Natalia Martín Sabanés	**Development of a photoexcited THz-gated scanning tunneling microscope at FHI**
Mohammed S. G. Mohammed	**Controlling the stereospecific bonding motif of Au-thiolate links and assessment of their catalytic properties**
Amy C. Qu	**Atomic engineering of monolayer graphene: Inducing Kekulé bond order by adatom deposition**
Gaël Reecht	**Vibrational excitation mechanisms in tunneling spectroscopy beyond the Franck-Condon model**
Anna Rosławska	**Dynamics of atomic point contacts studied by STM-induced luminescence**

Posters

Sofia Sanz Wuhl	**N-terminal graphene-based nanostructures for electron quantum optical setups**
Quentin Schaeverbeke	**Single-photon emission mediated by single-electron tunneling in plasmonic nanojunctions**
Paolo Sessi	**Detecting Fermi arcs in chiral topological semimetals by scanning tunneling microscopy**
Shaoxiang Sheng	**Atomically-resolved ultrafast dynamics in 1T-TaS$_2$**
Rika Simon	**The alloy Mn$_{88}$Ni$_{12}$: An intrinsically spin-polarised tip material?**
Anna Sinterhauf	**Substrate induced nanoscale resistance variation in epitaxial graphene resolved by scanning tunneling potentiometry**
Jonas Spethmann	**Complex spin structures in the magnetic monolayer of Mn on Re(0001):**
Oleksandr Stetsovych	**Exploring structural and electronic properties of helical molecules on surfaces**
Martin Švec	**Charge carrier injection electroluminescence with CO functionalized tips on single molecular emitters**
Georg A. Traeger	**Residual thermal signals in shaken pulse pair excitation for optical pump probe STM**
Martina Trahms	**Scanning tunnelling spectroscopy on disordered superconductors**
Sergey Trishin	**Energy levels and charge distribution within dipolar molecules**

Posters

Stefano Trivini	**Interaction of single Ti magnetic impurities with β-Bi$_2$Pd superconductor surface**
Marion A. van Midden	**Scrutinizing the bonding of 2-mercaptobenzimidazole on Cu(111) by STM and DFT**
Werner van Weerdenburg	**Demonstration of single atom ESR and pump-probe with a 30 mK STM setup**
Tao Wang	**Controlling reactions of Bromine substituted terminal alkynes on metal surfaces**
Yuqi Wang	**Study of magnetic molecules on superconductors by STM/AFM**

Abstracts of Talks

(in chronological order)

STS of spin chains built on superconductors

J. Wiebe[1]

[1]*Department of Physics, Hamburg University, Hamburg, Germany*

Chains of magnetic atoms on an s-wave superconducting materials with a large atomic number can exhibit topological superconductivity and may host Majorana bound states at their ends. Most previous experimental work towards the realization of such systems focused on the self-assembly of chains [1,2] where a full control of the atomic composition in the chain is difficult to achieve. In this study, we use superconducting Ta and Re substrates which enable STM-tip induced assembly of chains with a control on the chemical composition and position of each individual atom in the chain [3,4]. We investigate the evolution of the Yu-Shiba-Rusinov states [5] of the building blocks of the chains, the single atoms [6,7], into bands in the two extreme regimes, i.e. the dilute chain and the wire limits. For particular combinations of substrate and adatom species, we find indications for topological superconductivity in the wire limit [4].

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References

[1] S. Nadj-Perge *et al.*, Science **346**, 6209 (2014)
[2] M. Ruby *et al.*, Nano Letters **17**, 4473 (2017)
[3] A. Kamlapure *et al.*, Nature Comm. **9**, 3253 (2018)
[4] H. Kim *et al.*, Science Advances **4**, eaar5251 (2018)
[5] A. V. Balatsky *et al.*, Rev. Mod. Phys. **78**, 373 (2006)
[6] L. Cornils *et al.*, Phys. Rev. Lett. **119**, 197002 (2017)
[7] L. Schneider *et al.*, npj Quantum Materials **4**, 42 (2019)

Near-Field Physics and Chemistry in Plasmonic STM junctions

Takashi Kumagai

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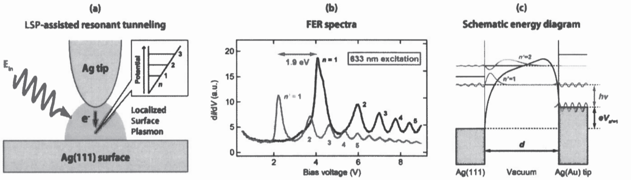
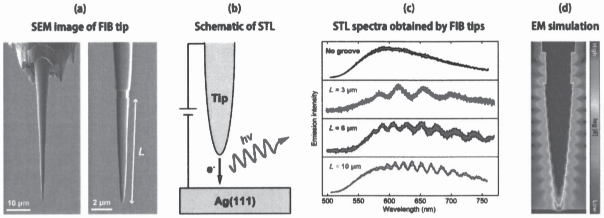
JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

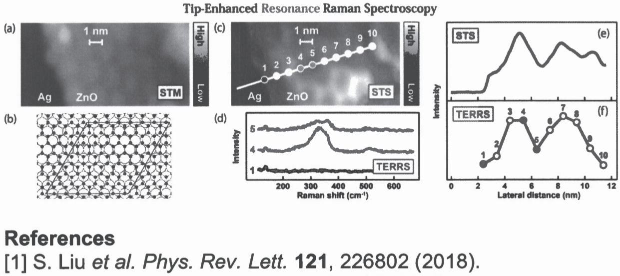
Nanostructures made of coinage metals strongly interact with visible light through excitation of localized surface plasmon resonance, enabling efficient light-harvesting and concentrating light on the nanoscale. Plasmonic nanocavities are of particular interest due to their capability leading to extreme confinement and enhancement of an electromagnetic field, which can largely promote near-field-driven processes. However, the direct observation of local field enhancement and near-field-driven processes in plasmonic nanocavities remains a significant experimental challenge. I will talk about our recent study on near-field physics and chemistry in plasmonic nanocabities using low-temperature photon scannig tunneling microscopy combssined with local optical excitation and detection [1-5].



Plasmon-assisted resonant electron tunneling in the STM junction [1].
(a) Schemaric of the process.
(b) Field emission resonance spectra with and without plasmon excitation in the STM junction.
(c) Schematic energy diagram.



Control of plasmonic resonance in the STM junction [4].
(a) SEM image of an Au tip fabricated by focused ion beam (FIB) milling.
(b) Schematic of STL
(c) STL spectra by FIB tips.
(d) Simulation of plasmonic Fabry–Pérot resonance.



Tip-enhanced „resonance" Raman spectroscopy [5].
(a–b) STM image and schematic of ultrathin ZnO layers on Ag(111).
(c) STS mapping of the conduction band edge of ZnO.
(d) TERRS spectra at different positions.
(e–f) Line scan of STS and TERRS signals.

References

[1] S. Liu *et al. Phys. Rev. Lett.* **121**, 226802 (2018).
[2] H. Böckmann *et al. Nano Lett.* **18**, 152 (2018).
[3] H. Böckmann *et al. J. Phys. Chem. Lett.* **10**, 2068 (2019).
[4] H. Böckmann *et al. Nano Lett.* **19**, 3597 (2019).
[5] S. Liu *et al. Nano Lett.* **19**, 5725 (2019).

Molybdenum Disulfide on Au(111) – growth, electronic structure and outstanding playground for single molecule spectroscopy

Christian Lotze, **Nils Krane, Gaël Reecht, Nils Bogdanoff and Katharina J. Franke**

Freie Universität Berlin, Germany

Single layer molybdenum disulfide (MoS_2) has been of large interest recently, because of features like a direct band gap and a strong spin-splitting of the valence band at the K-point, which make it an interesting material for optoelectronic applications.

We grow MoS_2 epitaxially on a Au(111) surface, adopting a recipe from [1], and investigate its exact structural and electronic properties using combined STM/AFM at low temperatures. Furthermore we get an insight into the band structure of MoS_2 with STM by measuring the decay length κ of the tunneling current, which depends on $\kappa_{\parallel}$. We find a strong spatial dependence of κ, which we ascribe to the Moiré reconstruction of MoS_2 on Au(111) [2,3].

Scanning tunneling spectroscopy (STS) is a tool that allows to address individual molecules in a precisely known surrounding. However, it bears the drawback that it requires a conductive substrate. Deposition of organic molecules on a metal substrate leads to strong hybridization of the electronic states. Preservation of the molecular character requires the inclusion of thin band-gapped materials.

Here, I will show that MoS_2 acts as an effective electronic decoupling layer that exhibits a small electron-phonon coupling strength. Differential conductance spectra of *2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene* (BTTT) molecules exhibit a multitude of sharp characteristic peaks, originating from vibronic states. These vibronic fingerprints of different molecules allow for an identification of different rotamers. DFT calculations of the molecules in gas phase provide all details for an accurate simulation of the vibronic spectra of both investigated rotamers [4].

Moreover, we will make use of the vibronic fingerprints to investigate the influence of the tip potential on the apparently shifted molecular states along the extended molecular backbone of BTTT [5]. Finally, the impact of molecular vibrations on spatial variations of the molecular conductance on BTTT and H_2Pc will be discussed [6].

[1] Signe Sørensen Grønborg, *et al.*, Langmuir, **31**, 35, 9700 (2015)
[2] Krane, *et al.*, Nano Letters, **16**, 5163 (2016)
[3] Krane, *et al.*, Surf. Sci., **678**, 136 (2018)
[4] Krane, *et al.*, ACS Nano, **12**, 11, 11698 (2018)
[5] Krane, *et al.*, Phys. Rev. B, **100**, 035410 (2019)
[6] Reecht, *et al.*, in preparation

1D organometallic chains: on-surface synthesis and transport properties

P. Jelínek[1]

[1]*Institute of Physics CAS, Prague, Czech Republic*

Low dimensional materials offer very interesting material and physical properties due to reduced dimensionality. At present, 2D materials are the focus of attention. However, 1D systems often show far more exotic behavior, such as Tomanaga-Luttinger liquid, Peierls distortion, etc.. In this talk, we will present different classes of 1D molecular chains formed on metallic surfaces by on-surface synthesis, which physical properties were investigated by low temperature UHV scanning probe microscopy supported by theoretical simulations. Namely, we will discuss transport measurements of quasi free-standing molecular wires suspended between metallic probe and sample showing non-trivial transport properties on external stimuli (bias, light). The experimental observation will be rationalized by theoretical simulations.

Single-photon emission mediated by single-electron tunneling in plasmonic nanojunctions

Q. Schaeverbeke[1,2], R. Avriller[1], T. Frederiksen[2,3], and F. Pistolesi[1]

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[2] Donostia International Physics Center (DIPC), E-20018, San Sebastian, Spain
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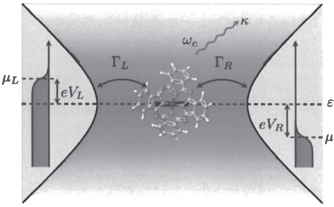

Scanning tunneling microscopy (STM) is a powerful spectroscopic tool to obtain local information about surfaces and molecules at the atomic level. The tunneling current flowing between the STM tip and the substrate is known to contain information about the electronic density of states and vibrational structure [1] of the molecules lying on the substrate.

Interestingly, in the nanoplasmonic cavity formed by the STM tip and the substrate, tunneling currents can also induce single-molecule fluorescence [2]. Recently, the analysis of the emitted fluorescence light was shown to provide useful information about molecular vibrations [3]. The precise understanding of the physical mechanism underlying light-emission and its consequences in STM molecular junctions is still a matter of active research.

In this talk, we investigate theoretically one of such mechanisms for which the electric field of the cavity mode couples with the current-induced charge fluctuations of the molecule, allowing the excitation of the mode [4] (see Fig.). In the experimentally relevant limit of large damping rate κ for the cavity mode and arbitrary coupling strength to a single-electronic level, we find that for bias voltages close to the first inelastic threshold of photon emission, the emitted light displays anti-bunching behavior with vanishing second-order photon correlation function [4]. We find that the current and the intensity of emitted light display Franck-Condon steps at multiples of the cavity frequency ω_c with a width controlled by κ rather than the temperature T. Our theory thus predicts that strong coupling to a single level allows current-driven non-classical light emission [4].

Finally, we open the discussion toward not standard effects for which chemical reactivity of embedded single molecules could be altered, as a result of the interplay between the tunneling current and its strong coupling to the plasmonic mode.

References

[1] Qiu, X. H., Nazin, G. V., & Ho, W., Phys. Rev. Lett., **92**, 206102 (2004).
[2] Berndt, R., Gaisch, R., Gimzewski, J. K., Reihl, B., Schlittler, R. R., Schneider, W. D., & Tschudy, M., Science, **262**(5138), 1425-1427 (1993).
[3] Doppagne, B., Chong, M. C., Lorchat, E., Berciaud, S., Romeo, M., Bulou, H., Boeglin, A, Scheurer, F & Schull, G. (2017), Phys. Rev. Lett., **118**, 127401 (2017).
[4] Schaeverbeke, Q., Avriller, R., Frederiksen, T., & Pistolesi, F., arXiv:1907.11269 (2019).

Theory of single spin spectroscopy at surfaces: from Kondo singlet to spin-orbit interaction

E. Minamitani

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Detection of a single spin at atoms and molecules on surfaces is one of the breakthroughs given by scanning probe microscopy [1,2]. The mechanisms to observe the single spin by tunneling electron can be classified into two types. One is elastic measurement where the differential conductivity reflects the many-body density of states. The other is inelastic measurement where the energy loss of tunneling electron corresponds to the energy difference between spin multiplets. The representative example of the former is the Kondo singlet states, and the latter is the zero-field splitting (ZFS) induced by spin-orbit interaction. In this presentation, I will introduce the theoretical background of measurements of these effects in the single molecules on surfaces and show several examples.

For the Kondo singlet states, I will introduce the results on Fe-phthalocyanine (FePc) on Au(111)[3] and Mn-phthalocyanine (MnPc) on Pb(111)[4]. In FePc/Au(111), the four-fold symmetry of the molecule and Fe d^6 electron configuration result in a novel Kondo effect arising from the combination of the spin and orbital degrees of freedom. In MnPc/Pb(111), the strong π-d interaction mediates indirect Kondo screening and forms a spatially extended Kondo state.

In bulk FePc, the ZFS induces the in-plane magnetic anisotropy and energy gap opens between $S_z=0$ and $S_z=\pm1$. The presence of ZFS in FePc on an insulating surface is confirmed by inelastic electron tunneling spectroscopy by STM [5], but the effect of substrate on ZFS remained unanswered. We combined the ligand-field theory and density functional theory and developed a method to investigate the influence of hybridization of d-electrons and substrate on ZFS[6]. We also revealed the hidden competition between the Kondo effect and ZFS in FePc/Au(111). We found that the strong renormalization of the ZFS by Kondo effect enables to form the Kondo singlet state in this system. With reducing the Kondo coupling, the Kondo singlet formation is hampered by ZFS and phase transition to ZFS dominant state occurs, which is realized by STM experiments [7].

References

[1] A. J. Heinrich et al., Science, 306, 466 (2004)
[2] A. Zhao et al., Science, 309, 1542 (2005)
[3] E. Minamitani et al., Phys. Rev. Lett., 109, 086602 (2012)
[4] E. Minamitani et al., Phys. Rev. B, 92, 079144 (2015)
[5] N. Tsukahara et al., Phys. Rev. Lett., 102, 167203 (2009)
[6] E. Minamitani et al., Phys. Rev. B, 94, 205402 (2016)
[7] R. Hiraoka et al., Nat. Commun., 8, 16012 (2017)

Cool chemistry: watching reaction progression at single-site heterogeneous catalysts

Sarah A. Burke[1]

[1]*Quantum Matter Institute, Department of Physics & Astronomy, Department of Chemistry, University of British Columbia, Vancouver, Canada*

Scanning probe microscopy has long played a role in examining chemical reactions on surfaces. Scanning tunneling microscopy (STM) quickly emerged as a powerful tool for studying heterogeneous catalysts, capturing the often “messy” nature of real surfaces. The ability to spatially correlate electronic states, physical structure and activity towards reactant molecules provided important insights for heterogeneous catalysis. Over the past decade, the ability to image bonds with tip-functionalized noncontact atomic force microscopy (ncAFM) measurements has provided new avenues for tracking surface reactions.

A more recent approach to *controlling* chemistry on surfaces is the use of metal-organic molecules – like those often used in homogenous catalysis – that are anchored to the surface combining benefits of heterogeneous and homogeneous catalysis. In this talk, I will describe how we have used STM, STS, and ncAFM together to characterize and track the reactivity and reaction progression of such single-site heterogenous catalysts. We investigated a Fe-terpyridine system prepared in-situ by self-assembly on Ag(111), exposed to gaseous CO, or ethylene and CO together, and then annealed step-wise at increasing temperatures up to 40K. STM images acquired at 4K before and after dosing or annealing allow us to track both individual sites and populations. Through a combination of STM, STS and ncAFM measurements we identify several species. At low annealing temperatures we see species with CO or ethylene bonded to the Fe atom via a surface-bound intermediate. Above 30K, additional products begin to form at the Fe nodes indicating further reactivity even at these very low temperatures. These results provide a demonstration of self-assembly-based single-site heterogeneous catalysts and the utility of low-temperature SPM-based methods for studying reactivity, while showing that the surface itself plays a role by mediating an initial intermediate.

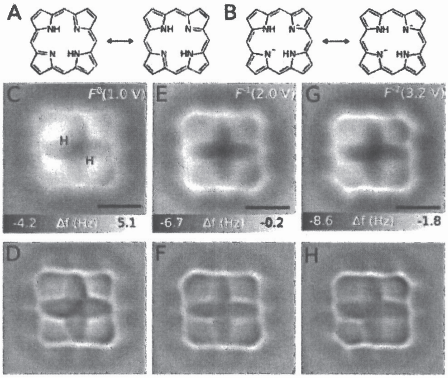
Molecular synthesis, charge-state control and structure elucidation with AFM

S. Fatayer, K. Kaiser, F. Schulz, F. Albrecht, N. Moll, L. Gross

IBM Research – Zurich, 8803 Rüschlikon, Switzerland

Elusive molecules can be created using atomic manipulation with a combined atomic force/scanning tunneling microscope (AFM/STM). Employing high-resolution AFM with functionalized tips provides insights into the reactions performed and geometry, adsorption, aromaticity, and bond-order relations of the molecules created [1,2].

Recently, we showed measured the reorganization energy of a molecule on an insulator [3]. We expanded the toolbox for the synthesis of molecules by atomic manipulation, demonstrating skeletal rearrangements [4] and controlled reactions on insulating substrates by electron attachment and detachment [5]. On insulating substrates, we control molecular charge states and resolve changes of the molecular geometry, adsorption and aromaticity related to its charge state (see Figure) [6].



Structure elucidation with charge-state control: Porphine resonant structures for (**A**) neutral F^0 and (**B**) dianion F^{-2}. AFM CO-tip measurements of porphine on 20 monolayer NaCl on Cu(111) in (**C, D**) neutral, (**E, F**) negative and (**G, H**) doubly negative charge state. The indicated voltage was applied to the sample with respect to the tip. The position of the inner hydrogens indicated in **C** is the same in all three measurements. The bottom row shows Laplace filtered data. Scale bars: 5Å.

References

[1] L. Gross *et al. Angew. Chem Int. Ed.* **57**, 3888 (2018)
[2] K. Kaiser *et al. Science* **365**, 1299 (2019)
[3] S. Fatayer *et al. Nat. Nano.* **13**, 376 (2018)
[4] N. Pavliček *et al. Nat. Chem.* **10**, 853 (2018)
[5] S. Fatayer *et al. Phys. Rev. Lett.* **121**, 226101 (2018)
[6] S. Fatayer *et al. Science* **365** 142 (2019)

Actuating and probing a single-molecule switch at femtosecond timescales

Dominik Peller, Lukas Z. Kastner, Thomas Buchner, Carmen Roelcke, Florian Albrecht, Rupert Huber and Jascha Repp

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Accessing ultra-fast non-equilibrium phenomena is enabled by terahertz (THz) scanning tunneling microscopy [1] (THz-STM) through combining STM with lightwave electronics. In THz-STM, the electric field of a phase-stable single-cycle THz waveform acts as a transient bias voltage across an STM junction. These voltage transients may result in a net current that can be detected by time-integrating electronics. The recent development of this lightwave STM has enabled the combined femtosecond and sub-angstrom resolution in observing matter [2].

We now demonstrate the first combined femtosecond and sub-angstrom access in the control of matter. Ultrafast localized electric fields in lightwave STM enable exerting atom-scale femtosecond forces to selected atoms. By shaping atomic forces on the intrinsic timescale of molecules, coherent atomic motion can now be excited. Utilizing this coherent structural dynamics, we can modulate the quantum transitions of a single-molecule switch by up to 39%. We directly visualize the coherent excitation of the switch in the first femtosecond single-molecule movie [3].

To resolve the impact of coherent control of the single-molecule switch, alongside, we introduce single-shot action spectroscopy in lightwave STM as the first concept resolving individual path-selective reaction events of a single molecule in space and time. With this novel concept, we detect the outcome of every single laser shot and further separate the statistics of the two inverse reaction paths.

Our results open a new chapter in the control and observation of reactions of individual molecules directly on the relevant ultrafast and ultrasmall scales.

References

[1] T. L. Cocker et al., Nature Photon. **7**, 620 (2013)
[2] T. L. Cocker et al., Nature **539**, 263 (2016)
[3] D. Peller et al., under review (2019)

High resolution tip-enhanced Raman scattering under ambient conditions

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High lateral resolution aspects of Raman spectroscopy, specifically of tip-enhanced Raman scattering (TERS) are currently of large interest, as sub molecular resolution has been demonstrated experimentally by several groups. This could particularly to correlate nanoscale material properties with the actual local structure.

Presently, most experiments are done under cryogenic conditions, that allow extremely stable and reproducible conditions. At this time this is an important prerequisite to compare with current theoretical models. Ultimately, however, it is important to move forward towards more “chemically relevant” conditions, where reactions can and will occur. For such applications the temperature range eventually will have to be increased. As a consequence not only dynamic changes due to reactivity can be observed, but also thermal effects regarding the molecules position need to be considered.

We will present high resolution Raman experiments at room temperature conditions that will demonstrate the high-resolution capabilities of near-field Raman spectroscopy and allow to overcome critical aspects like thermal sample diffusion or simple stage drift. Specifically, we will present experimental investigations accompanied with the respective theoretical models regarding the inevitable localised heat deposition that occurs when using plasmonic enhancement, by utilizing simultaneous Stokes/anti-Stokes investigations.

Ultrafast dynamics of collective charge and spin excitations on surfaces

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Spin and charge correlations are particularly pronounced in low-dimensional materials and enable new technologies that harness quantum behavior. Accessing these correlations on their intrinsic length and time scales is an important step towards a microscopic understanding of correlated-electron physics.

We combine scanning tunneling microscopy with pump probe schemes to achieve ultrafast spectroscopy of spin and charge dynamics with atomic spatial resolution. Using electronic pulse generation [1] and optical excitation with THz pulses [2,3] it is possible to achieve time resolution between milliseconds and femtoseconds thereby matching the instrument to the dynamics of the investigated system. At nanosecond time resolution, we can track the spin dynamics of magnetic atoms on surfaces and identify miniscule magnetic interactions between few-atom spin chains [4]. At femtosecond time resolution, we can detect electron dynamics and follow the evolution of collective modes in a correlated-electron state at individual atomic defects.

These experiments access the microscopic dynamics of correlated electrons and highlight pathways to design and control quantum properties of matter at the single atom level.

References

[1] S. Loth, M. Etzkorn, C. P. Lutz, D. M. Eigler, A. J. Heinrich, Science **329**, 1628 (2010).

[2] T. L. Cocker, V. Jelic, M. Gupta, S. J. Molesky, J. A. J. Burgess, G. de los Reyes, L. V. Titova, Y. Y. Tsui, M. R. Freeman, F: A. Hegmann, Nature Photon. **7** 620 (2013).

[3] T. L. Cocker, D. Peller, P. Yu, J. Repp, R. Huber, Nature **539**, 263 (2016).

[3] S. Yan, L. Malavolti, J. A. J. Burgess, S. Loth, Science Adv. **3** e1603137 (2017).

Single-molecule optical spectroscopy with a photon STM

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The study of single molecules provides deep insights into bonding nature and underlying quantum mechanics. The scanning tunneling microscope (STM) is the most powerful tool for investigating and controlling quantum states of a single molecule on solid surfaces. The coupling of tunneling electrons to the electronic and/or vibrational states of the molecule allows us to realize mode-selective and state-selective chemistry as well as spectroscopy of a single molecule. We have focused our recent studies on the excitation and the accompanied energetic processes, such as energy transfer, conversion, and dissipation. Detailed understanding of the molecular excited states is crucial to develop organic energy conversion devices based on opto-electronic/opto-chemical processes. We developed an STM combined with optical systems both for photon detection and for optical illumination to achieve controlled excitation of the molecular quantum states either by tunneling electrons or by localized surface plasmon at the STM junction. In this talk, I will share some recent issues about single-molecule optical spectroscopy investigated by the photon STM. An explanation will be first given about construction of the photon STM by combining with optical systems, which will be followed by the detailed description of development of single-molecule luminescence and absorption spectroscopic techniques with the photon STM. The energy of localized surface plasmon (LSP) generated at the tip apex can be utilized either to measure energy absorption [1] or to control chemical reaction [2] of a single molecule. The single-molecule luminescence spectroscopy was further utilized to detect both fluorescence and phosphorescence signals according to the recombination of singlet and triplet exciton states in a molecule, respectively [3]. I will also discuss how the molecular excitons are generated in a controlled manner at the STM junction and how we visualized the exciton formation/recombination processes playing in the energy transfer between two different molecules on the solid surfaces [4].

References

[1] H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, K. Kimura and Y. Kim, Phys. Rev. Lett. **119**, 013901 (2017)

[2] E. Kazuma, J. Jung, H. Ueba, M. Trenary, Y. Kim, Science **360**, 521 (2018).

[3] K. Kimura, K. Miwa, H. Imada, M. Imai-Imada, S. Kawahara, J. Takeya, M. Kawai, M. Galperin and Y. Kim, Nature **570**, 210 (2019)

[4] H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, K. Kimura and Y. Kim, Nature **538**, 364 (2016).

Molecular structure elucidation with charge-state control

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The charge state of an adsorbed molecule significantly affects its physical as well as its chemical properties, for example, adsorption position, molecular conformation and aromaticity. The proven capabilities of single-electron sensitivity [1,2] and atomic-resolution [3] of atomic force microscopy (AFM) make it an ideal tool to perform charge-state manipulation experiments while atomically resolving the induced changes within the molecule. Here, we present AFM-based results that simultaneously demonstrate both the control in charge-state and the capability of resolving the atomic structure of a single molecule for different molecules [4].

References

[1] L. Gross, et al. Science **324**, 5933 (2009)
[2] S. Fatayer, et al. Nature Nanotechnology **13**, 376 (2018)
[3] L. Gross, et al. Science **325**, 5944 (2009)
[4] S. Fatayer, et al. Science **365**, 6449 (2019)

Attosecond coherent manipulation of electrons in tunneling microscopy

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We demonstrate coherent manipulation of electrons in a tunnel junction of a scanning tunneling microscope, by tuning the carrier-envelope-phase (CEP) of two-cycle long (< 6 fs) optical pulses. We explore two different tunneling regimes at the tunnel junction, photon and field-driven tunneling and demonstrate transition from one to the other regime. Spatially localized and atomically strong electric fields of strength ~ 1V/Å substantially modulate the tunneling barrier on attosecond timescales, hence allowing taming of flow of electrons to either side of the tunnel junction. Capability to tune CEP with precision of less than 0.1π enables manipulation of electron tunneling at timescales of ~ 200 as. The strong atomic confinement of tunneling current induced by laser pulses enables optical-field driven tunneling microscopy. Real-time tracing of decay dynamics of oscillations of quasiparticles (localized-surface plasmon) in a gold nanorod is studied with a nanoscale probe in tunneling contact; enabling concurrently angstrom-scale and sub-fs resolution. We expect our results to enable inducing, tracking, and controlling electronic current at atomic scales and pave the way to petahertz coherent nanoelectronics and microscopy.

Incommensurate oscillations of oligoacene gaps adsorbed on Au(111)

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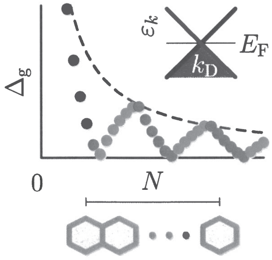
For gas phase oligoacenes, our recent theoretical work suggests a possibility for oscillations of the excitation gaps with the length of the molecule. In view of the recent experimental progress of on-surface synthesis, we employ the density functional theory to investigate here the fate of these oscillations for oligoacenes adsorbed on a Au(111) surface. Since the Coulomb interaction is screened on metallic substrates, correlation effects are weaker and the tendency towards oscillatory behavior is enhanced.



References

1. R. Korytár, D. Xenioti, P. Schmitteckert, M. Alouani, F. Evers, Signature of the Dirac cone in the properties of linear oligoacenes, Nature Communications **5** 5000 (2014)
2. P. Schmitteckert, R. Thomale, R. Korytár and F. Evers, Incommensurate quantum-size oscillations in acene-based molecular wires—Effects of quantum fluctuations, The Journal of Chemical Physics **146**, 092320 (2017)
3. M. J. van Setten, D. Xenioti, M. Alouani, F. Evers, R. Korytár, Incommensurate Quantum Size Oscillations of Oligoacene Wires Adsorbed on Au(111), J. Phys. Chem. C, **123**, 14,8902-8907 (2019)

Quantum State Manipulation of Single Atom Magnets using the Hyperfine Interaction

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The three essential pillars of magnetic data storage devices are readability, writeability, and stability. However, these requirements compete as magnetic domain sizes reach the fundamental limit of single atoms and molecules. The magnetic quantum states of holmium single atom magnets on MgO(100) have proven extremely robust when exposed to high magnetic fields and temperatures up to 35 K [1]. Additionally, reading and writing of the long-lived holmium magnetic states has been demonstrated with spin-polarized scanning tunneling microscope (SP-STM) via tunnel magnetoresistance and current pulses, respectively [2]. The voltage thresholds for magnetization switching and the total magnetic moment determined by these measurements are compatible with pure $J_z = \pm 7$ and $J_z = \pm 8$ ground states. We propose a writing protocol that utilizes the magnetic stray field created by the tip of the scanning tunneling microscope to sweep through avoided level crossings at low magnetic fields. By controlling the magnetic field sweep rate, we demonstrate quantum state control via Landau-Zener tunneling. This protocol also allows us to address the stability of Ho at small magnetic fields, where the ground states become distinguishable. Our observations indicate a total spin ground state of $J_z = \pm 8$. Combined quantum and classical control render Ho a promising qubit candidate.

References

[1] F. Natterer, F. Donati, F. Patthey, and H. Brune. Physical Review Letters, **121**:027201, (2018).
[2] F. Natterer, K. Yang, W. Paul, P. Willke, T. Choi, T. Greber, A. Heinrich, and C. Lutz. Nature, **543**:226, (2017).

Probing and controlling molecular spins on surfaces

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Using low-temperature scanning tunneling microscopy (STM) and synchrotron radiation methods we explore the spin states and the electron transport properties of molecules at single crystal surfaces. The talk will address the selective switching of spin-crossover compounds and unexpected conversions of closed-shell molecules into radicals.In addition to conventional tunneling spectroscopies of the Kondo effect and spin excitatons we also use the shot noise of the current through molecules in contact with the STM tip as a probe of spin effects.

Atomic-scale spin sensing with a single-molecule at the apex of a scanning tunneling microscope

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Recent advances in scanning probe techniques rely on the chemical functionalization of the probe-tip termination with single molecules weakly connected to the metallic apex. Information, otherwise inaccessible with a metallic tip, can be gathered in this way [1]. The success of this approach opens the tantalizing prospect of introducing spin sensitivity through the probe-tip termination by a magnetic molecule. Here, we use a nickelocene-terminated tip (Nc-tip), which offers the possibility of producing spin excitations on the tip apex of a scanning tunneling microscope (STM) [2,3]. We show that when the Nc-tip is a hundred pm away from point contact with a surface-supported object, magnetic effects may be probed through changes in the spin excitation spectrum [4] of nickelocene. We use this detection scheme to determine the exchange field and the spin polarization of the sample with atomic-scale resolution. Our findings demonstrate that the Nc-tip is a powerful probe for investigating surface magnetism with STM, from single magnetic atoms to surfaces as we exemplify in this talk.

References

[1] L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, Science **325**, 1110 (2009)
[2] M. Ormaza *et al.*, Nano Lett. **17**, 1877 (2017)
[3] M. Ormaza *et al.*, Nat. Commun. **8**, 1974 (2017)
[4] A. J. Heinrich *et al.*, Science **306**, 466 (2004)

Two-probe scanning tunneling microscopy and spectroscopy

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In my talk I will describe methodology of two-probe scanning tunneling microscopy and spectroscopy (2P-STM/STS) experiments, in which both STM probes are kept in atomically defined locations with respect to the characterized nanosystems on exact probe-to-probe distances reaching tens of nm [1,2]. Such probe-to-probe lateral positioning precision is combined with pm vertical sensitivity in probe-to-system contacts. These two factors enable realization of 2P-STS, where transport properties can be characterized by macroscopic probes kept in atomically defined tunneling conditions. First, I will show that 2P-STS signal carries information about quasi-ballistic (coherent) transport through one-dimensional π^* states of Ge dimer row wires [2]. Then, I will present application of 2P-STS methodology to probe quantum transport properties in a functional system: graphene nanoribbons (GNRs) epitaxially grown on the sidewalls of silicon carbide (SiC) mesa structures. These GNRs display ballistic transport channels with exceptionally long mean free paths and spin-polarized transport properties as proven by mesoscopic multiprobe transport experiments [3-5]. Interestingly, the nature of the ballistic channels remains an open question. I will show that 2P-STS experiments can give a new insight into quantum origin of these transport properties. Finally, I will discuss perspectives for broader application of multiprobe STM/STS.

References

[1] M. Kolmer et al.,, J. Phys.: Condens. Matter **29(44)**, 444004 (2017)
[2] M. Kolmer et al., Nat. Commun. **10**, 1573 (2019)
[3] J. Baringhaus, Nature **506**, 349–354 (2014)
[4] J. Aprojanz et al., Nat.Commun. **9**, 4426 (2018)
[5] A.L. Miettinen et al., Phys. Rev. B **100**, 045425 (2019)

This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

Addressing spin-crossover molecules on metallic substrate by voltage pulses and light

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Spin-crossover molecules show the unique ability to switch between two spin-states by means of external stimuli such as temperature, light or voltage. If controlled at the molecular scale, such switches would be of great interest for the development of molecular devices in electronics and spintronics. If the behavior of such molecules is well documented in bulk, little is known on their properties at the molecular scale and in direct contact with an electrode. We focus our recent studies on Fe^{II} pyrazolyl borate molecules (FePz) adsorbed on metallic substrates (Au(111) and Cu(111)). Once absorbed on surfaces, FePz molecules self-assembled in array in which both spin states can coexist at low temperature [1-3] while in bulk only the low spin state is stable. Thanks to scanning tunneling microscopy, we followed at the molecular scale the light transition dynamics of the molecules. It appears that in direct contact with the metal the molecules are switched from high spin state to a low spin state on the contrary to the bulk behavior. In addition, we demonstrate the possibility to selectively address single molecules in a 2D molecular array.

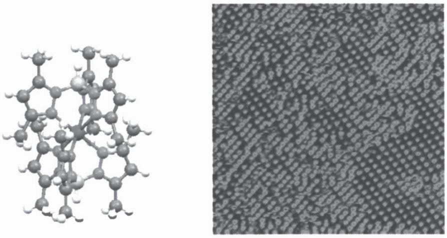

Figure: STM image (50nm x 50 nm) acquired under blue illumination which presents an excited mixed spin-state phase of FePz molecules

References

[1] K. Bairagi et al., Nat. Comm. **7**, 12212 (2016)
[2] K. Bairagi et al., J. Phys. Chem. C **122**, 727 (2018)
[3] C. Fourmental et al., J. Phys. Chem. Lett. **10**, 4103 (2019)

Optical coupling with molecules in Scanning Probe Microscopes

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One of the main limitations of conventional optical systems is that they do not allow to localize the light to the nanoscale, due to the diffraction limit. However, this limitation can be overcome by exciting collective excitations of the free electron of metallic nanostructures that are called localized plasmons. A structure of particular interest consists in the metallic tip of a scanning microscope probe (SPM) over a metallic substrate, as it has been shown that this configuration can lead to very strong plasmonic fields confined down to the subnanometer scale.

In this talk, we first introduce the plasmonic response of SPM configurations [1], and discuss the origins of the field confinement [2] and how it opens the possibility to use SPMs to map the optical properties of molecules with submolecular resolution[3]. We show that the interaction allows to study the vibrational [4,5] and electronic [6,7,8] transitions of the molecules, including dark transitions that are not accessible to standard illumination [3,4].

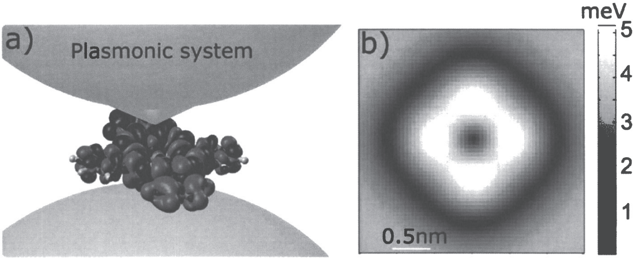

Fig: (a) Sketch of a molecule interacting with a plasmonic system. (b) Map of the optical properties of the molecule as it is scanned by a plasmonic tip. Specifically, the plasmon-molecule coupling strength is displayed

References

[1] R. Esteban et al. Nat. Comm. 3, 825, 2012
[2] M. Barbry et al., Nano Lett., 15, 3410 (2015)
[3] T. Neuman et al., Nano Lett. **18**, 2358 (2018)
[4] F. Benz et al. Science **354**, 726 (2016)
[5] R. Zhang et al., Nature **498**, 82(2013)
[6] Y. Zhang et al. Nature Communications **8**,15225 (2017)
[7] H. Imada et al. Phys. Rev. Lett. **119**, 013901 (2017)
[8] Y. Zhang et al., Nature 531, 623 (2016)

Functional carbon nanostructures: insights from density functional-theory

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Creating covalently bonded carbon nanostructures with atomic precision is now possible by on-surface synthesis methods. These experimental advances have boosted the research attempts to create novel carbon-based structures aimed at their use in nanoelectronic or optoelectronic applications.[1] However, before carbon nanostructures can be used in real devices, an atomic level understanding and control of their properties is required. As such, *ab initio* simulation has developed as an essential partner in the search of optimal carbon based low dimensional systems.

In this talk, I will present some studies of functional carbon-based nanostructures that we have performed in close collaboration with our experimental colleagues.[2-4] Using density-functional theory (DFT), we have investigated the structural, electronic and transport properties of 0D (carbon-based macromolecules), 1D (graphene nanoribbons) and 2D (nanoporous graphene) systems. Special focus has been given to understanding the role of chemical doping and pore formation. Our findings are compared with scanning tunneling microscopy and spectroscopy (STM/STS) data. Depending on the doping mechanisms and conformational details, various effects are observed and explained, such as electron confinement, energy gap modification, or semiconductor-to-metal transition.

References

[1] S. Clair et al., Chem. Rev. **119**, 4717 (2019)
[2] J. Hieulle *et al.*, Nano Letters **18**, 418 (2018)
[3] E. Carbonell-Sanromà *et al.*, J. Phys. Chem. C **122**, 16092 (2018)
[4] C. Moreno *et al.*, Science **360**, 199 (2018)

Complex molecular architectures: design and characterization at the atomic scale

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Technological utilization of molecular materials relies on fabrication of complex device architectures based on organic and inorganic building blocks. Of particular interest are the control of molecular assembly and coupling on non-metal substrates, as well as the use of two-dimensional materials as support or protective layers for the molecules.

We will outline strategies for the atomic-scale characterization of such materials using scanning probe techniques, *i.e.* scanning tunneling microscopy (STM) and atomic force microscopy (AFM). In particular, we will show (i) how functionality of intercalated molecules in metal/molecule/insulator stacks can be investigated (Fig. 1), (ii) how the geometric corrugation of two-dimensional layers can be determined with subatomic precision (Fig. 2), and (iii) how the local molecular response to electrostatic gating can be probed.

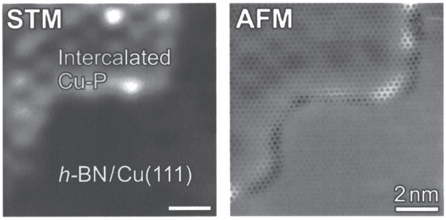

Figure 1. STM (left) and AFM (right) measurements of an island of porphyrins intercalated between Cu(111) and a monolayer of *h*-BN.

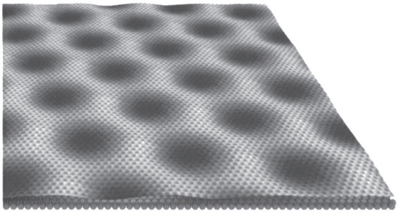

Figure 2. Experimentally determined geometric corrugation of a *h*-BN layer on Cu(111).

References

[1] A. Riss et al., ACS Nano **8**, 5395 (2014)
[2] M. Schwarz et al,: ACS Nano **11**, 9151 (2017)
[3] J. Ducke et al., ACS Nano **12**, 2677 (2018)

On-surface synthesis of π-conjugated polymers

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On-surface synthesis has emerged as a powerful strategy to design unprecedented nanomaterials on surfaces. In this talk, we review our recent findings regarding the formation on Au(111) of π-conjugated one-dimensional polymers featuring ethynylene or cumulene-like bridges. A comprehensive study, based on tight-binding calculations, DFT and nc-AFM simulations, STS and STM/nc-AFM imaging, shows the emergence of specific topological quantum phases, which can be rationalized within the framework of the SSH topological band model and are specifically related to the π-conjugation of the polymer.

Scanning quantum dot microscopy

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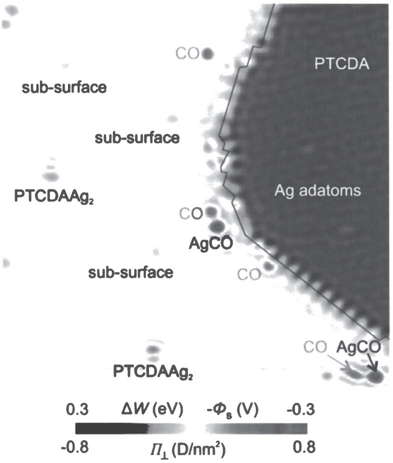

Because materials consist of positive nuclei and negative electrons, electric potentials are omnipresent at the atomic scale. However, due to the long range of the Coulomb interaction, large-scale structures completely outshine small ones. This makes the isolation and quantification of the electric potentials that originate from nanoscale objects such as atoms or molecules very challenging. In my presentation I will give an overview over a recently developed noncontact scanning probe technique which addresses this challenge [1,2,3]. Scanning quantum dot microscopy (SQDM) exploits a quantum dot sensor attached to the SPM tip and the joint electrostatic screening by tip and surface, thus enabling quantitative surface potential imaging across all relevant length scales down to single atoms. We applied this technique to the characterization of a nanostructured surface, thereby extracting work function changes and dipole moments for important reference systems (figure). I will also discuss a formalism in the framework of which SQDM can be understood and interpreted quantitatively based on the classical boundary value problem of electrostatics [4].

References

[1] C. Wagner, M. F. B. Green, P. Leinen, T. Deilmann, P. Krüger, M. Rohlfing, R. Temirov, and F. S. Tautz, Phys. Rev. Lett., **115**, 026101 (2015)

[2] M. F. B. Green, C. Wagner, P. Leinen, T. Deilmann, P. Krüger, M. Rohlfing, F. S. Tautz, and R. Temirov, Jpn. J. Appl. Phys, 55 (2016) 08NA04.

[3] C. Wagner, M. F. B. Green, M. Maiworm, P. Leinen, T. Esat, N. Ferri, N. Friedrich, R. Findeisen, A. Tkatchenko, R. Temirov, and F. S. Tautz, Nat. Mater. DOI 10.1038/s41563-019-0382-8 (2019)

[4] C. Wagner and F. S. Tautz, J. Phys. Cond. Mat. DOI 10.1088/1361-648X/ab2d09 (2019)

Yu-Shiba-Rusinov States from Impurities with a Quantum Spin

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Magnetic impurities in a superconductor give rise to pairs of quasiparticle levels inside the superconducting gap called Yu-Shiba-Rusinov (YSR) states. On or near surfaces, these impurities can be well studied locally by scanning tunneling microscopy (STM). We have studied intrinsic impurities in Vanadium showing a single pair of YSR states at the surface. Several indicators point towards a quantum spin-1/2 impurity, which will be discussed. In addition, we have observed a non-trivial energy dependence of the YSR state as a function of tip-sample distance, similar to findings that have been reported before. We find that the impurity-substrate coupling plays a decisive role in the behaviour of the YSR states at surfaces. We discuss this in the context of a model that extends the existing Green's function description of YSR states and also bridges a gap to related models. Further, picking up a magnetic impurity with the tip allows for tunnelling between single YSR states. This opens up an entirely new perspective for understanding tunnelling between single quasiparticle states, such as lifetime and spin polarization of YSR states as well as interaction with the environment during the tunnelling process.

Photon statistics measured by scanning tunneling microscopy-induced luminescence on single molecules

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Photon correlations permit to distinguish between classical and quantum states of light. There are three types of light sources, coherent, bunched and antibunched.[1] Despite recent advances in understandng photon statistics on nanoscale systems, obtaining correlations from individual quantum emitters (QEs) is difficult as non-classical phenomenology becomes obscured in ensemble measurements. Suppression of photons from adjacent QEs requires spatial or energetical separation between them. By contrast, it is possible to address individual QEs even at high densities if a selective excitation by charge injection is employed. This method allows on to access classes of light sources which could not be investigated otherwise.

In this talk I will give a brief introduction on the experimental observation of photon (anti) bunching from individual molecular systems with atomic resolution. We have merged correlation spectroscopy with scanning tunneling microscopy luminescence (STML). By profiting from STML we can image and identify individual molecular emitters located in the nanocavity formed between a gold tip and surface. By using the tip to inject current with atomic precision we are able to excite plasmons and excitons on individual molecules [2] and demonstrate antibunched single photon emission from C_{60} films [3]. Additionally, we have measured bunched emission from H_2 molecules adsorbed on gold surfaces. [4] By analyzing the photon statistics we conclude that in the first case C_{60} defects acts as QEs and undergo a pure quantum-mechanical emission process whereas in the second case the emission stems from intensity blinking upon H_2 motion in the nanocavity that is fully classical.

References

[1] K. Kuhnke, et al. Chem. Rev. 117, 5174-5222 (2017)
[2] P. Merino et al. Sci. Adv. 4, 8344 (2018)
[3] P. Merino et al. Nat Commun.6, 8461 (2015)
[4] P. Merino et al. Nano Letters 19, 235-241 (2019)

Engineering the magnetic properties of graphene nanostructures by edge topology

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Turning graphene magnetic is a promising challenge to make it an active material for spintronics[1]. Predictions state that graphene structures with specific shapes can spontaneously develop magnetism driven by Coulomb repulsion of π-electrons[2], but its experimental verification is demanding. The strong radical character of this kind of structures makes it extremely hard for both the synthesis and magnetism characterization. Here in this talk, I will show you our latest results on the observation and manipulation of magnetic moments in graphene open-shell nanostructures[3]. The graphene open-shell nanostructures are created on a gold surface through on-surface synthesis route[4]. Using scanning tunneling spectroscopy, we can detect the presence of electron spins localized around certain zigzag sites of the nanostructures and map their localizations. Theoretical simulations picture how electron correlations result in spin-polarized radical states with the experimentally observed spatial distributions. Furthermore, we show that the exchange coupling between localized spins can be engineered by precise controlle over the size and edge topology of the nanostructures.

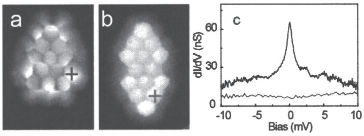

Figure:
a,b constant height current image of two graphene nanostructures (V=2 mV).
c, dI/dV spectra taken on the two structures.

References

[1] Han, W., Kawakami, R. K., et al, *Nat. Nanotechnol.* **9**, 807 (2014).
[2] Yazyev, O. V. *Rep. Prog. Phys.* **73**, 056501 (2010).
[3] Li, J.; Sanz, S.; Corso, M.; Choi, D. J.; Peña, D.; Frederiksen, T.; Pascual, J. I. Nat. Commun. 10, 200 (2019).
[4] L. Talirz; P Ruffieux; R Fasel. Advanced materials 28, 6222 (2016)

Electronic consequences of chemical doping of Graphene Nanoribbons

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Quasi-one-dimensional graphene nanoribbons (GNRs) are a promising new platform for future nanoelectronics applications [1]. Their electronic, optical and magnetic properties, defined by their width and edge topology, can be tuned through the control over their chemical structure. For this purpose, on-surface synthesis allows to fabricate GNRs with atomic precision using customized molecular precursors [2]. We grow chiral [3] and armchair [4,5] graphene nanoribbons, pure and doped, and by means of Scanning Tunneling Spectroscopy measurements and Density Functional Theory calculations we clarify how the chemical modifications on the nanoribbons' morphology affect their electronic properties in terms of dopant type, concentration and position within the ribbon.

We find that substitutional boron atoms within seven armchair GNRs' backbone induce the formation of new bands and bandgap renormalization [4]. Substitutional functional groups at the chiral and armchair ribbons' edges induce doping of the ribbons bands [5] that can be so effective to induce a semiconductor to metal transition.

References

[1] A. Celis et al., J. Phys. D: App. Phys. **49**, 143001 (2016).
[2] L. Tarliz et al., Adv. Mater. **28**, 6222 (2016).
[3] D. G. de Oteyza et al., ACS Nano **10**, 9000 (2016).
[4] E. Carbonel-Sanroma et al., J. Phys. Chem. C **122**, 16092 (2018).
[5] E. Carbonel-Sanroma et al., ACS Nano **11**, 7355 (2017).

Publishing at Nature Research journals – insights from the other side

Benjamin Heinrich

Nature Nanotechnology, London, Shanghai, Berlin

The review and publishing process in a peer-reviewed journal may look like a black box, especially to early career scientists. Using the example of Nature Research journals, I will give some insights in the editorial process; what happens to the manuscript after submission, which stages goes the paper through, how are decisions taken, how do we choose reviewers, and what do we as full-time editors add to manuscripts. Furthermore, I will discuss what we look for in submitted manuscript and what the editorial criteria are for sending a paper out to review. I will also provide an overview over the hierarchy and the relationship among the different Nature-branded journals and the manuscript transfer system.

Abstracts of Posters

(in alphabetical order)

3D Topological Kondo Insulator: Charge Screening and Neutrality

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Topological Kondo insulators (TKIs) are a new class of topological insulators, emerging through the interplay of strong correlations and spin-orbit coupling. In TKIs, the bulk is a narrow band insulator due to the appearance of a localized Kondo resonance near the Fermi level and its hybridization with the conduction band. Additionally, the strong spin-orbit coupling of the localized moments generates a nonlocal hybridization between the local moments and the conduction band, which results in a ground state with nontrivial topology and gapless surface states [1]. In this work, we study TKIs in a slab geometry and address the problems of space charges and screening near the surfaces. The strong Kondo correlations in the 4*f*-orbitals are treated by a layer-dependent slave boson mean field (SBMF) theory, while the Coulomb repulsion in the conduction band is described by Hartree-Fock (HF) approximation. We solve the coupled SBMF+HF theory self-consistently and thereby analyze the existence of topological surface states.

References

[1] M. Dzero et al., Physical Review Letters **104**, 106408 (2010)

Expanding holdtime: Measurement capabilities in a cryogen-free low-temperature Scanning Tunneling Microscope

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Conventional low-T STMs are extremely stable but limited in their continuous operation time to the hold time of the bath cryostat. By use of a Gifford-McMahom cryocooler, the system's hold time can be extended to well beyond one month of continuous measurement. the STM mitigates the introduced vibrations of the cryocooler by a multi-stage decoupling system with external frames and internal spring suspension [1]. The extended hold time allows comprehensive measurements with unprecedented resolution and pushing of parameter spaces not accessible to conventional scanning probe experiments [2].
We use these methods to explore point defects and their effects on the local electronic structure of the excitonic insulator candidate Ta2NiSe5 [3].

References

[1] Zhang, et al., *RSI* **2016**, 87, 063701
[2] Hackley, et al., *RSI* **2014**, 85, 103704
[3] Lu, et al., *Nat. Com.* **2017**, 8, 14408

The breakdown of the ohmic regime in graphene

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We are using scanning nitrogen-vacancy (NV) center magnetic imaging to probe graphene devices. The NV center is a quantum probe that is sensitive to a variety of fields (magnetic, electric, thermal, strain), can achieve nanoscale spatial resolution, is non-invasive, and can operate over a wide range of temperatures; hence it is an ideal tool for studying novel phases of matter that often emerge only below a critical temperature. Here we use a cryogenic scanning NV magnetometer to probe the stray magnetic field of a current running through a single layer graphene device. With this technique we are able to probe different regimes of current flow via their local signatures over a variety of temperatures and observe the breakdown of the ohmic regime.

Electronic structure of 5-armchair graphene nanoribbons:
STM study of their topological end states.

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The properties of graphene nanoribbons (GNRs) vary significantly with their width and edge shape. For those with armchair edges, computational models group the GNRs into three families depending on their width, i.e. with 3n, 3n+1 or 3n-1 C atoms across the ribbon. The lowest bandgaps are displayed by the latter[1].

This work is a detailed study of the narrowest ribbons of this family, namely 5-aGNRs, combining cryogenic (4 K) scanning tunnelling microscopy (STM), spectroscopy (STS) and density function theory (DFT) calculations. The 5-aGNRs were synthesized on Au (111) from dibromoperylene[2] (DBP) and characterized on the metal substrate, as well as on decoupling NaCl monolayers. Correcting misconceptions from previous experimental works, we have determined their band gap and have additionally assessed the dispersion of their bands for the first time. We have also disclosed the presence of in-gap states at both ends (end states) and ascertained their topological origin. Lastly, we have studied the properties of those states as a function of the ribbon length and unambiguously proved their magnetism in sufficiently long 5-aGNRs. Experimental proof for the magnetism and the determination of its originating electronic state is obtained from transport measurements through pristine and appropriately oxidized GNRs in a model two-terminal device structure. That is, the GNRs are contacted on one side by the scanning probe and are then gradually lifted up, resulting in ribbons bridging between the tip and substrate that act as electrodes. As a function of the lifting height the binding energy of the magnetic state is shifted, allowing to probe the system´s conductance across the different occupation regimes described in the Anderson model for magnetic states: empty-, mixed-valence- and Kondo regime.

References

[1] Kharche, N. et al., J. Phys. Chem. Lett. 2016, **7**, 1526−1533 (2016).
[2] Kimouche, A. et al., Nat. Commun. 6, 1–6 (2015).

MnNi Tips for Spin-Polarized STM

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In combination with electron spin resonance, spin polarized STM has shown to be a useful technique. It can reveal spin properties of individual atoms down to hyperfine splitting [1] and spin-spin interactions [2]. ESR STM requires the combination of high frequency electronics, sub-Kelvin temperatures and spin polarized tips in high magnetic fields. We investigate the use of the antiferromagnetic MnNi tips as promising material for permanently spin polarized tips with small magnetic stray fields. The tips have been etched [3] using HCl and characterized with electron beam microscopy. Spin sensitive measurements have been performed on Cobalt islands evaporated on the Au(111) surface.

References

[1] Willke et al., Science 362, 336–339 (2018)
[2] Yang et al., Phys. Rev. Lett. 119, 227206 (2017)
[3] Forrester et al., Rev. Sci. Instrum. 89, 123706 (2018)

The electrostatic potential of atomic chains and clusters imaged quantitatively with scanning quantum dot microscopy

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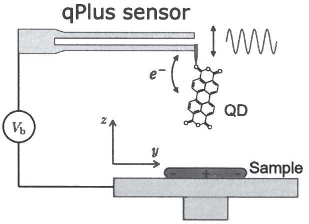

Fig 1. Principle of Scanning Quantum Dot Microscopy (SQDM): The local change in surface potential due to a nanostructure is compensated by adjusting and recording the sample bias. The (molecular) quantum dot acts as a sensor to verify correct compensation.

Fabrication of artificial atomic clusters and chains facilitates the observation and investigation of various quantum effects. The size and geometry of such assemblies influence electrostatic potentials, catalytic efficiency as well as a magnetic response. Here, we investigate the electrostatic properties of differently sized and shaped Ag clusters which have been created on a Ag(111) substrate by atomic manipulation with a scanning probe microscope (SPM). We use scanning quantum dot microscopy (SQDM, Fig. 1) [1,2,3] with a single molecule quantum dot attached to the SPM tip [4] to image the surface potential on atomic chains and compact clusters. Since this potential reflects a dipole density the associated surface dipoles of the individual chains and clusters can be obtained by integration. These dipoles originate from a summation over the Smoluchowski dipoles of individual adatoms in conjunction with depolarization effects. We find that the surface dipole moment per adatom drops rapidly for compact assemblies while it converges to a value of about 0.26 Debye for atoms in a chain. Since the depolarization depends on the number of neighbors, chain ends exhibit larger dipoles. This can be verified in SQDM surface potential images.

References

[1] F. Author, Journal **volume**, page (year)
[2] C. Wagner, et al. Phys. Rev. Lett. **115**, 026101 (2015)
[3] M. Green, et al. Japan. J. Appl. Phys. **55**, 08NA04-7 (2016)
[4] M. Maiworm, et al. American Control Conf. **4360**, (2018)
[5] R. Temirov, et al. Phys. Rev. Lett. **120**, 206801 (2018)

Controlling dopant-induced telegraph noise by optical excitation

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Charging and discharging of single donors in the space charge region (SCR) on GaAs has been found to appear as discrete variations of the tunnel current [1]. Such abrupt changes of the tunnel current between well-defined levels are known as telegraph switching.

In our study, we focused on the temporal evolution of the tunnel current caused by single-electron charging events in a few donor system. We investigated the effect of light-generated free charge carriers induced into the SCR on the telegraph signal. Experimentally, we extended the capabilities of low-temperature scanning tunneling microscopy using near-infrared continuous wave excitation of the tunnel junction. The (110) surface of n-doped GaAs was used as sample system. The variations in the current were accessed by recording current time series at every lateral tip position. In this way, spatial variations of both telegraphic step heights and lifetimes can be characterized with atomic resolution.

We investigated, in the first step, the effect of an adjacent ionized donor on the current variations. In the second step, we investigated the effect of light-induced minority charge carriers on the current's telegraph noise. Using the tunnel current as control parameter, we induced a small, but non-vanishing hole concentration into the SCR [2]. Thereby, the current's telegraph noise was reduced. We suggest that this is due to a homogenization of the surface potential landscape by the photo-generated low-density hole gas, suppressing the effect of single donor charging events on the overall current.

We acknowledge the financial support by the Deutsche Forschungsgemeinschaft (DFG) through the SFB1073 project C4.

References

[1] K. Teichmann et al., Nano Lett. **11**, 3538-3542 (2011)
[2] P. Kloth et al., Nat. Commun. **7**, 10108 (2016)

Unveiling the intra-atomic exchange interaction in rare earth adatoms

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The manipulation of the magnetization of nano objects and single atoms is at the center of an active research as it could pave the way for future spintronic and settle the basis for the realization of high-density magnetic memory devices. Spin-polarized scanning tunneling microscopy (SP-STM) delivers the topographic image and at the same time records the magnetization state of a target nanomagnet. Complementarily, inelastic scanning tunneling spectroscopy (IETS) identifies the exact energies at which tunneling electrons induce magnetic excitations.

Here we use these techniques to investigate the magnetism of rare earth atoms on gr/Ir(111) and gr/Cu, with special focus on Dy. Low temperature IETS shows inelastic excitations in the 30-200 meV range, the exact value being element dependent. We attribute these excitations to the intra-atomic exchange between the magnetic moment of the outer 6s5d and the inner 4f shells. This interpretation is validated by the scaling of the IETS excitations following the $2\ J_{ex}\ S_{6s5d}\ S_{4f}$ equation, where J_{ex} is the intra-atomic exchange energy, S_{6s5d} and S_{4f} are the spin moments of outer and inner shell, respectively. The relatively high energy of the intra-atomic exchange excitations is a consequence of the charge transfer of approximately one electron from the atom outer shells to graphene [1], leading to almost fully polarized outer shells, which corresponds to $S_{6s5d} \sim 1/2$. This high outer shell polarization is confirmed by SP-STM telegraph-noise traces acquired on Dy/gr/Ir(111), one of the two so-far-reported single atom magnets [2], showing a giant contrast up to 60% for parallel vs anti-parallel alignment of tip and atom magnetization.

The intra-atomic exchange energy is a hidden parameter that strongly affects atomic magnetism. These measurements represent the first experimental assessment of the intra-atomic exchange. The values we find are in good agreement with calculated ones [3].

References

[1] M. Pivetta, S. Rusponi, and H. Brune, Phys. Rev. B **98**, 115417 (2018)

[2] R. Baltic, M. Pivetta, F. Donati, C. Wäckerlin, A. Singha, J. Dreiser, S. Rusponi, and H. Brune, Nanolett. **16**, 7610 (2016).

[3] Hong-Shuo Li, Y. P. Li and J. M. D. Coey, J. Phys. Condens. Matter **3**, 7277 (1991)

Tuning the electronic properties of nanoporous graphene by Li decoration

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Recently, the atomically precise synthesis of nanoporous graphene (NPG) was reported [1], an unprecedented 2D graphene based semiconductor that exhibits novel electronic properties. In particular, the presence of a semiconducting gap and 2D electronic anisotropy stand out as promising characteristics for nanoelectronics. Besides, electronic states localized at vacuum pore regions (pore states) open the door to sensing and sieving applications. However, the high energies of such pore states represent an obstacle towards the use of this material in real devices.

In this work, we consider different Li decoration scenarios with the aim of optimizing pore state energies [2]. Our density functional theory (DFT) based calculations predict a significant downshift of pore states, bringing them close to experimentally accessible energy regions. Moreover, we observe the emergence of a Li related nearly free electron (NFE) like band crossing the Fermi level. These results confirm the efficacy of the proposed strategy to tune the electronic properties of NPG, further expanding its functionalities.

References

[1] C. Moreno *et al.*, Science **360**, 199 (2018)
[2] M. Feng *et al.*, Science **320**, 359 (2008)

On-surface synthesis of antiaromatic, open-shell indenofluorene polymers

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The formation of extended low-dimensional molecular nanostructures is a scientific challenge with exciting technological prospects. On-surface synthesis has opened pathways to molecular nanostructures that have been inaccessible so far. Here, we demonstrate the successful use of methyl groups to achieve five-membered rings at specific position of a one-dimensional polymer, which allows for the realization of fully conjugated chains, composed of indenofluorene units. Indenofluorenes are appealing molecules consisting of an array of fused 6-5-6-5-6-membered rings with 20 pi-electrons, which have received increasing attention for their formal anti-aromaticity, open-shell biradical character, and narrow HOMO-LUMO gap. Our surface-assisted approach allows for the unprecedented fabrication of indenofluorenes without the usual protecting groups at reactive sites. Different indenofluorene isomers can be obtained upon careful design of the precursor molecules. We report the on-surface synthesis of polymers made of [1,2-b], [2,1-a] and [2,1-b] indenofluorene isomers, the latter bearing higher radical character. The structure and electronic properties of the obtained indenofluorene polymers have been characterized by STM, nc-AFM, and STS, which are supported by theoretical calculations [1, 2].
The observed reaction steps and products can extend the knowledge of on-surface reactivity of novel, unconventional carbon-based materials, being of general interest for the community. Moreover, the reported synthetic protocol can potentially be extended to other novel molecular nanostructures and eventually to graphene nanoribbons incorporating five-membered rings at desired positions to fine tune their electronic properties.

References

[1] M. Di Giovannantonio *et al.*, J. Am. Chem. Soc. **140**, 3532 (2018)
[2] M. Di Giovannantonio *et al.*, J. Am. Chem. Soc. **141**, 12346 (2019)

Exciton control in single-molecule fluorochromes

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Plasmonic picocavities in highly defined environment of ultrahigh vacuum and cryogenic temperatures represent ideal testbeds for investigation of the photophysical properties of single-molecule photon emitters and to explore fundamental aspects of their luminescence. In this work, we studied two structural analogs with distinct electronic properties using a photon-scanning probe microscope: CuPc and ZnPc molecules adsorbed on NaCl / Ag(111) substrates. For the CuPc, we determine how its exact adsorption configuration and coupling to the substrate affect the S_1 exciton energy and lifetime. For the ZnPc molecule, two competing excitons [1] are mapped in the real-space with submolecular resolution. Both phenomena are discussed in a broader context of ab-initio simulations and additional experimental evidence available from the atomic force and electron tunneling channels of the microscope.

[1] Doppagne B, Chong MC, Bulou H, Boeglin A, Scheurer F, Schull G. Electrofluorochromism at the single-molecule level. Science 2018;361:251–5.

Hyper-resolved fluorescence microscopy.

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In 2016 Zhang *et al.* [1] developed an experimental configuration where Zinc Phthalocyanine molecules, decoupled from a metallic substrate by a thin layer of salt (Fig.1 (a)), can be electrically driven in their excited state by the tunnelling current coming from the tip of a Scanning Tunnelling Microscope to obtain an optical spectrum. Following this approach, we have shown that in such configuration it is possible to obtain optically an effective vibrational signature (Fig. 1 (c)) of the probed molecule [2]. Then, it is possible to obtain, without light excitation, an optical signature of a single molecule together with the spatial resolution offered by the STM. This new kind of fluorescence spectroscopy has allowed us to obtain, for the first time, the vibrational signature of a charged single molecule (Fig.1 (d)), different of the one acquired on the neutral species (Fig. 1 (c)) [3]. Therefore, it is possible to monitor the redox state of a single molecule by a measure of its optical spectrum. Recent results suggest that it may be also possible to use this hyper-resolved fluorescence microscopy to follow the dynamic of a single molecule tautomerization process.

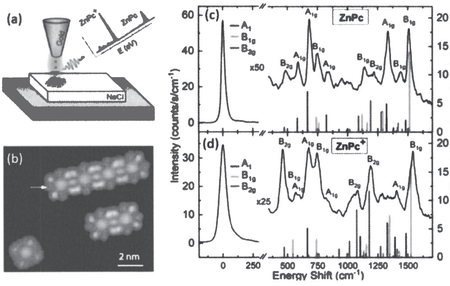

Figure 1 : **Hyper-resolved fluorescence spectroscopy of a zinc phtalocyanine molecule (ZnPc) and its radical cation (ZnPc$^+$).** (a) Sketch of principle. (b) STM image different oligomers of ZnPc molecules. STM-Induced Fluorescence spectra of the neutral molecule (c) and the radical cation (d). The red, black and blue lines represent the calculated Raman mode related to the two species.

References

[1] Zhang, Y. ; Luo, Y. ; Zhang, Y. ; Yu, Y-J. ; Kuang, Y-M. ; Zhang, L. ; Meng, Q-S. ; Luo, Y. ; Yang, J-L. ; Dong, Z-C. ; Hou, J-G. *Nature* **(2016)**, 531, 623.
[2] Doppagne, B. ; Chong, M-C. ; Lorchat, E. ; Berciaud, S. ; Romeo, M. ; Bulou, H. ; Boeglin, A. ; Scheurer, F. ; Schull, G. *Phys. Rev. Lett.* **(2017)**, 118, 127401.
[3] Doppagne, B. ; Chong, M-C. ; Bulou, H. ; Boeglin, A. ; Scheurer, F. ; Schull, G. *Science* **(2018)**, 361, 251-255.

Selective on-surface synthesis of oxygen heterocycles on metals

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Heterocycles containing nitrogen, oxygen, or sulfur atoms are the basic units to incorporate chemical functionalization to carbon scaffolds. For oxygen-based structures, furan[1] and pyran – having five- and six-membered rings, respectively - are the most common ones to explore the properties of oxygen-functionalized heterocarbons. However, their on-surface synthesis via cyclomerization reactions remains elusive so far. Here we present a low-temperature scanning tunneling microscopy study to understand the on-surface synthesis of furan and pyran moieties on metal surfaces from ketone-functionalized precursors. We use CH-activation reactions to fuse two ketone-derivatives in either cis- and trans-configuration selectively. Finally, cyclomerization reactions towards furan and pyran moieties are observed after further annealing. These results are highly unexpected because ketone derivatives are mostly known to convert to cyclic trimers or tetramers in solution-based chemistry. On the surface, however, the strong interaction of the ketones with the metal surface opens up new reaction pathways.

References

[1] L. Liu, H. Klaasen, A. Timmer, H.Y. Gao, D. Barton. H. Mönig, J. Neugebauer, H. Fuchs, A. Studer: *J. Am. Chem. Soc.* **2018**, 140, *18*, 6000-6005

Microwave-assisted tunnelling and self-interference effects in superconducting junctions under fast driving signals

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As the area of application of the scanning tunnelling microscope is pushed towards fast local dynamics, a quantitative understanding of a tunnel junction under the influence of a fast AC driving signal is required, especially at the ultra-low temperatures relevant to spin dynamics and correlated electron states. We subject a superconductor-insulator-superconductor junction under DC bias to a microwave signal from an antenna mounted in situ and examine the response of basic quasi-particle and correlated electron states to this driving signal. Despite their stark differences in origin, quasi-particles, Cooper pairs, and multiple Andreev reflections exhibit a similar reaction to the incident microwave radiation. We show that the current carried by multiple Andreev reflections cannot be understood through an effective multi-charge tunnelling approach, but contains explicit signatures of the reflection events inside the barrier.

References

Non-Alternant Nanoribbons of Graphene Allotropes from Fusion of Polyazulene

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Various two-dimensional (2D) carbon allotropes with non-alternant topologies, such as pentaheptites and phagraphene, have been proposed. Predictions indicate that these metastable carbon polymorphs, which contain odd-numbered rings, possess unusual (opto)electronic properties. However, none of these materials has been achieved experimentally due to synthetic challenges. In this work, by using on-surface synthesis, nanoribbons of the non-alternant graphene allotropes, phagraphene and tetra-penta-hepta(TPH)-graphene have been obtained by dehydrogenative C-C coupling of 2,6-polyazulene chains. These chains were formed in a preceding reaction step via on-surface Ullmann coupling of 2,6-dibromoazulene. Low-temperature scanning probe microscopies with CO-functionalized tip and density functional theory calculations have been used to elucidate their structural properties. The proposed synthesis of non-alternant carbon nanoribbons from the fusion of synthetic line-defects may pave the way for large-area preparation of novel 2D carbon allotropes.

References

[1] Liu, Y.; Wang, G.; Huang, Q.; Guo, L.; Chen, X. Phys. Rev. Lett. **108,** 225505 (2012).
[2] Crespi, V. H.; Benedict, L. X.; Cohen, M. L.; Louie, S. G. Phys. Rev. B **53,** 13303 (1996).
[3] Wang, Z.; Zhou, X. F.; Zhang, X.; Zhu, Q.; Dong, H.; Zhao, M.; Oganov, A. R. *Nano lett.* **15,** 6182 (2015).

Molecular structure elucidation with charge-state control

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The charge state of an adsorbed molecule significantly affects its physical as well as its chemical properties, for example, adsorption position, molecular conformation and aromaticity. The proven capabilities of single-electron sensitivity [1,2] and atomic-resolution [3] of atomic force microscopy (AFM) make it an ideal tool to perform charge-state manipulation experiments while atomically resolving the induced changes within the molecule. Here, we present AFM-based results that simultaneously demonstrate both the control in charge-state and the capability of resolving the atomic structure of a single molecule for different molecules [4].

References

[1] L. Gross, et al. Science **324**, 5933 (2009)
[2] S. Fatayer, et al. Nature Nanotechnology **13**, 376 (2018)
[3] L. Gross, et al. Science **325**, 5944 (2009)
[4] S. Fatayer, et al. Science **365**, 6449 (2019)

Inducing magnetism in graphene nanoribbons by substitutional Boron-doping

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Bottom-up synthesized graphene nanoribbons (GNRs) are a versatile playground for engineering electronic properties of low-dimensional systems to one's desires. Controlled synthesis of magnetic structures is unachieved so far, despite its big potential for spintronics. One of the main obstacles to overcome is the hybridization of the electronic structure of the GNR and the metallic substrate, that is needed for the atomically precise synthesis.

Here, we induce a spin-polarized state in 7-armchair GNRs by substitutional Boron-doping [1]. In the centre position of the GNR, two Carbon atoms are replaced with two Boron atoms. The doped system is investigated by suspending a single GNR between a Au(111) substrate and the tip of a scanning tunnelling microscope. By this, we overcome the problem of hybridization. The spin-polarization manifests itself as a zero-bias Kondo resonance, measured in transport experiments through the suspended GNR. Density functional theory calculations confirm an emerging spin-polarization in the GNR upon detachment of the dopant from the surface.

We also investigated the spin texture induced by the presence of several doping sites within one GNR. DFT reveals that an antiferromagnetic effective interaction between neighbouring sites dominates, altering the net spin-polarization of the ribbon. Our experimental transport results confirm the presence of a non-conventional spin texture in these systems.

References

[1] Carbonell-Sanromà et al., J. Phys. Chem. C, 122, 28 16092-16099 (2018)

Vibron-assisted spin excitation in a magnetically anisotropic molecule

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The control and readout of molecular spin states through the electron current is key for high-density storage. The coupling of electrons with the vibrational modes, or vibrons, of the molecule can, however, modify or even suppress the molecular conductance, thus indirectly impacting spin manipulation.

Here, we use inelastic electron tunneling spectroscopy to promote and detect the excited spin states of a prototypical molecule with magnetic anisotropy. We demonstrate the existence of a vibron-assisted spin excitation spatially displaced off the molecular orbital carrying the spin, that can exceed in energy and in amplitude a simple excitation among spin states. The excitation, which can be quenched by modifying the molecular spin, is explained using first-principles calculations and model calculations that include dynamical correlations. This vibron-assisted spin excitation should be common to molecular systems possessing magnetic anisotropy.

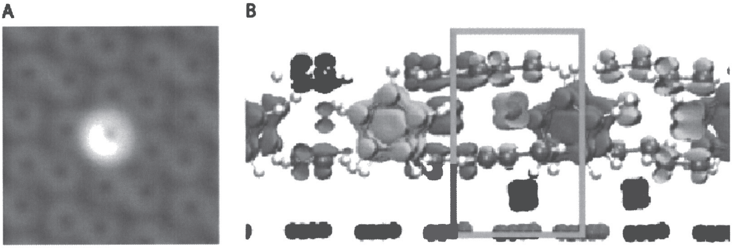

Figure : (A) Stm image of a self-assembled layer of nickelocene and a NiNc complex on Cu(100). The molecular arrangement is sketched in orange. (B) Side view of the spin density map of the paired structure containing two Ni adatoms. Orange rectangles mark the NiNc complex. Yellow: Spin up, red: Spin down.

References

[1] A.J.Heinrich, J.A.Gupta, C.P.Lutz, and D.M.Eigler, Science**306**, 466 (2004).
[2] M. Ormaza et al., Nat. Commun. 8, 1974 (2017)
[3] M. Ormaza et al., Nano Lett. 17, 1877 (2017)

Time-resolved STML investigation of organic molecules with high spin-orbit coupling

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Scanning tunneling microscopy induced luminescence (STML) provides information about optoelectronic properties of single molecular species in unprecedented detail [1]. STML investigation of various technologically significant phenomena, such as intermolecular energy transfer [2], emission from charged species [3], up-conversion electroluminescence (UCEL) [4], and selective exciton formation [5], has improved our understanding of their underlying mechanisms.

We report on the investigation of Platinum phthalocyanine, with the heavy-metal center resulting in high spin-orbit coupling, decoupled from an Au(111) surface by 3ML NaCl. Thanks to the energetically symmetric positioning of the frontier orbitals, we are able to obtain bipolar intrinsic emission. Furthermore, by analyzing the effect of tunneling current on the emission we further explore the observed UCEL.

High spin-orbit coupling in Platinum phthalocyanine makes it a good candidate for investigating inter-system crossing pathways and triplet emission in the visible range. We discuss how time-controlled charge injection may allow us to study such phenomena and share insights on how radiative or non-radiative transitions would manifest themselves in such a measurement.

References

[1] K. Kuhnke, et al., Chem. Rev. **117**, 5174 (2017)
[2] H. Imada, et al., Nature **538**, 364 (2016)
[3] B. Doppagne, et al., Science **361**, 251 (2018)
[4] G. Chen, et al., Phys. Rev. Lett. **122**, 177401 (2019)
[5] K. Kimura, et al., Nature **570**, 210 (2019)

Quantum Nanoscience:
Atoms on Surfaces

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The scanning tunneling microscope is an amazing tool because of its atomic-scale spatial resolution. This can be combined with the use of low temperatures, culminating in precise atom manipulation and spectroscopy with microvolt energy resolution. In this talk we will apply these techniques to the investigation of the quantum spin properties of magnetic atoms sitting on thin insulating films.

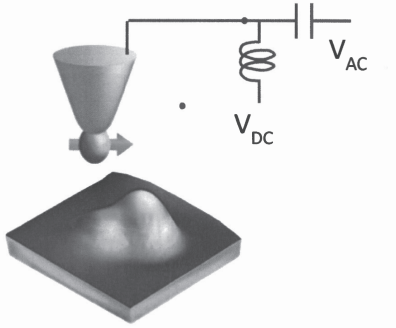

Fig 1. STM image of two Ti atoms on thin MgO film. Superimposed is a model of a spin-polarized STM tip

We will start our exploration with the understanding of the quantum spin states (also called the magnetic states) of these adsorbates. To measure these states, we combined scanning tunneling with x-ray absorption spectroscopy and found amazing agreement of those vastly different techniques (*Science* 2014, *PRL* 2015).

Next, we will investigate the lifetimes of excited states. Surprisingly, we find lifetimes that vary from nanoseconds to hours, a truly amazing consequence of the quantum states of different adsorbates.

Finally, we will explore the superposition of quantum states which is inherent to spin resonance techniques. We recently demonstrated the use of electron spin resonance on single Fe atoms on MgO (Science 2015). This technique combines the power of STM of atomic-scale spectroscopy with the unprecedented energy resolution of spin resonance techniques, which is about 10,000 times better than normal spectroscopy.

YSR-states in manually assembled nanoclusters of phthalocyanine molecules on Pb(100)

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In this LT-STM-study, we show that purely organic nonmagnetic phthalocyanine (H_2Pc) molecules can acquire a net magnetic moment, which manifests itself in a Yu-Shiba-Rusinov state on Pb(100).

We manually assembled clusters of nine molecules and observed that the LUMO of the central H_2Pc becomes partially filled.

We show that this effect depends on the number of neighbour molecules, the cluster orientation, and, in particular, on the positions of the central H atoms of H_2Pc. These positions can be modified to control the LUMO energy of the central molecule and consequently the YSR state.

Furthermore, we compare our experimental data with the results of DFT calculations and predictions from an Anderson impurity model.

The experiments and the theoretical approaches yield consistent results and lead to a fairly detailed understanding of the molecular interactions and the YSR state.

Charge transport between discrete superconducting bound states at the atomic scale

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Tunneling processes between discrete levels have been intensely studied in double quantum dot systems (typically around 100nm), where the level spacing originates from Coulomb charging and can be tuned by gating. To push these observations to the quantum limit of wavefunction localization is challenging not only because it is difficult to gate single atom, but also since the static charging is replaced by dynamical Coulomb blockade at the atomic scale.

One solution is to use the sharp in-gap level (Yu-Shiba-Rusinov states) generated by a single magnetic atom on a superconductor, which does not rely on charging and gating. Using a scanning tunneling microscope with a base temperature of 15mK, we can controllably introduce a YSR state at the apex of the superconducting vanadium tip and study the intrinsic YSR defects on the superconducting V(100) sample. We call these tunneling processes between YSR states Shiba-Shiba tunneling.

Shiba-Shiba tunneling shows features of tunneling between discrete levels, from sharp peak feature in I(V), linear to sublinear transition of peak area with increasing conductance, to complicated interaction with the environment through inelastic processes. The current peak in the linear regime is a direct measurement of the P(E) function. Moreover, the peak area at the linear to sublinear transition is a direct and local measurement of the lifetime, which makes the YSR tip an ideal tool to reliably measure the lifetime of discrete levels on the substrate. With further indication of parity protection as well as intrinsic spin feature, Shiba-Shiba system opens a new field with potential in quantum sensing and computing.

References

[1] L. Yu, Acta Phys. Sin **21**, 75-91 (1965)
[2] H. Shiba. Progress of Theoretical Physics **40**, 435-451 (1968)
[3] A. I. Rusinov, Jetp Letters-Ussr **9**, 85 (1969)

Design of a high-stability miniaturized STM-Head

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Due to unparalleled spatial resolution, extensive spectroscopy capabilities, and the ability to manipulate atoms or molecules on surfaces, the Scanning Tunneling Microscope has become a widely used technique in fields ranging from surface chemistry to magnetic dynamics. State-of-the-art STM setups are typically housed in large cryostats, require proportionally large vacuum chambers, as well as extensively-shielded custom built laboratories to reach the signal-to-noise ratios (SNR) required for cutting edge experiments. However, by miniaturizing the STM-head, the SNR can be significantly improved, due to the favorable scaling of resonant frequency, thermal characteristics, and measurement time. The STM design presented here is optimized to work in noisy environments, and due to the low mass and dimensions can be used in a standard bore cryogenic dewar. The setup is designed for long hold times, as well as for short turn-around modification, allowing for rapid sample preparation and characterization. This design could be used for extended-averaging experiments, as well as being easily added to upgrade existing setups with the powerful capabilities of scanning tunneling microscopy.

Combining high-resolution Atomic Force Microscopy with Scanning Tunneling Microscopy induced light emission on single molecules

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The field of STM induced light emission (STM-LE), especially on single molecules, has grown rapidly in the past 25 years [1, 2] with astounding spatial as well as energetic resolution [3, 4]. Yet, combining structural and optical information on single molecules remains challenging.

We present first results of a combined AFM and STM-LE setup on single vanadyl-phthalocyanine (VOPc) molecules. This setup so far allows for structure determination with atomic resolution by AFM with CO functionalized tips [5] and the possibility to perform controlled atom manipulation conjunct with the investigation of opto-electronic properties by STM-LE.

This work was financially supported by the European Research Council consolidator grant AMSEL.

References

[1] R. Berndt et al. (1993). *Science*, *262*(5138), 1425–1427.
[2] X. Qiu et al. (2003). *Science*, *299*(5606), 542–547.
[3] B. Doppagne et al. (2017). *Phys. Rev. Lett.*, *118*(12), 127401.
[4] A. Yu et al. (2018). *Nano Lett.*, *18*(5), 3076–3080.
[5] Gross et al. (2009). *Science, 325*(5944), 1110–1114.

Investigation of selective triplet exciton formation in a molecule with an STM

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Exciton formation by charge injection is a central physical process in organic light emitting diodes (OLEDs), and more effective exciton formation mechanism has been extensively explored to improve their performance. Especially, effective use of phosphorescence from triplet excitons (T_1) is of a practical importance for developing high-efficiency OLEDs [1,2]. T_1 formation at low voltage without singlet exciton (S_1) formation has been considered and explored as a promising way to reduce the energy consumption of these devices. In this study, we conduct a single-molecule investigation of electroluminescence using a scanning tunnelling microscope (STM) [3-8] and demonstrate a simple way for selective T_1 formation which utilizes a charged state of molecule.

Fig. 1a shows the scanning tunnelling luminescence (STL) spectrum of a 3,4,9,10-perylenetetracarboxylicdianhydride (PTCDA) molecule on NaCl film grown on Ag(111) substrate. The luminescence peaks originated from fluorescence and phosphorescence are observed at 2.45 eV and 1.33 eV, respectively. To investigate the S_1 and T_1 formation mechanism, we examined the voltage dependence of the STL spectra. In Fig. 1b, the intensities of fluorescence and phosphorescence are plotted as a function of sample voltage, clearly showing that selective formation of T_1 without creating S_1 from −2.1 V to −3.3 V. The combination of luminescence and differential conductance measurements reveals that spin-selective electron removal occurs from a negatively charged PTCDA, which is rationalized by the exchange interaction in the charged molecule.

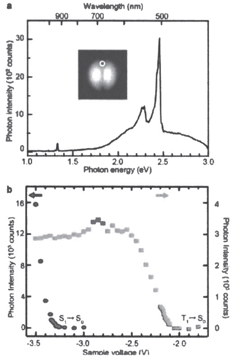

Fig. 1 STL results of PTCDA/NaCl(3ML)/Ag(111)
a. STL spectrum of a PTCDA molecule (V = −3.5 V, I = 50 pA, exposure time t = 60 s). The tip position is shown as a dot in the inset STM image of a PTCDA (4 × 4 nm^2, V = 1.0 V, I = 5 pA).
b. Sample voltage dependence of the intensities of fluorescence (dark gray circles, left-hand vertical axis) and phosphorescence (bright gray squares, right-hand vertical axis).

References

[1] M. A. Baldo *et al., Nature* **395**, 151 (1998). [2] A. Köhler *et al., Mater. Sci. Eng. R Rep.* **66**, 71 (2009). [3] X. H. Qiu *et al., Science* **299**, 542 (2003). [4] Y. Zhang *et al., Nature* **531**, 623 (2016). [5] H. Imada *et al., Nature* **538**, 364 (2016). [6] B. Doppagne *et al., Science* **361**, 251 (2018). [7] K. Miwa *et al., Nano Lett.* **19**, 2803 (2019). [8] K. Kimura *et al., Nature* **570**, 210 (2019)

Discriminating and counting the possible molecular configurations in a prototypical molecular wire junction

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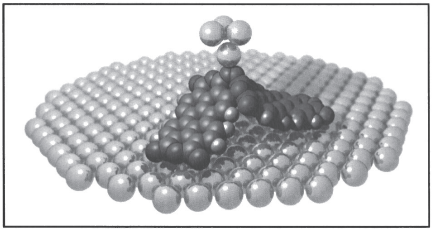

Mechanical manipulation of molecules with a scanning probe microscope (SPM) is a versatile technique to study molecular properties and to create new single-molecular devices [1,2,3]. One example is the exciting research field of quantum transport through single molecules, which is often hampered by the lack of precise control over the molecular junction configuration [4]. Another fascinating challenge is to enable on-surface construction of molecular structures beyond the lateral rearrangement [2].

Here we report molecular manipulation experiments in which a single PTCDA (perylene-tetracarboxylic dianhydride) molecule is suspended between two metal electrodes; a Ag(111) surface and a non-contact AFM/STM tip in a variety of discrete junction configurations (Figure). In a first step, we record frequency shift and conductance fingerprints in a tip-space volume of about 0.1 $Å^3$. In the next step, we randomize the configuration of the molecule in the junction without breaking its bonds to the tip, by dragging the molecule over the surface under well-defined parameters. Returning to the very same tip position allows the comparison of all data-sets. Both steps are repeated hundreds of times to ensure that all possible configuration have been reached. To discriminate and count the observed tip-molecule-surface configurations, we perform a statistical analysis of the fingerprints by taking advantage of an unsupervised machine-learning algorithm. Finally we demonstrate the possibility of selectively preparing individual molecular configurations using specific manipulation trajectories.

Our work is a step towards the complete identification of the so-far unobservable atomic structure of molecular junctions and could be the key to e.g. fully reproducible quantum transport studies on the one hand and 3-D devices of molecular building blocks on the other hand.

References:

[1] C. Wagner et al. Phys. Rev. Lett. 115, 026101 (2015).
[2] T. Esat et al. Nature 558, 573 (2018).
[3] R. Temirov et al. Phys. Rev. Lett. 120, 206801 (2018).
[4] L. Venkataraman et al. Nano Lett. 6(3), 458 (2006).

Structure analysis of ultrathin NaCl-layers on metallic substrates

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The electronic decoupling of single atoms, molecules or clusters from a metallic substrate gains in importance whenever radiative transitions shall be observed. Moreover, for various surface science methods, such as scanning tunneling microscopy, a non-vanishing surface conductivity is necessary. To combine those two requirements ultrathin insulating layers come into play. We have studied the growth of ultrathin NaCl films with various thicknesses on Au(110) by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) at low temperatures (8 K and 80 K). As well-known from previous studies [1] the evaporation of NaCl onto a clean Cu(111) surface at room temperature leads to the growth of rectangular monolayer NaCl islands on top of a continuous NaCl film, which covers the surface partially. The study of evaporated NaCl on Au(110) reveals the growth of NaCl islands of different height. The lowest islands show a (1x4) superstructure and erratic edge geometry, whereas the next layer shows the well-known rectangular island growth. Here we present a first structure model to explain this growth structure.

References

[1] R. Bennewitz, et al., Surf. Sci. 438, 289 (1999).

Surface-induced bands in atomic and molecular arrays

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A single impurity ad-atom coupled to a conduction band is known to induce a resonance or a bound state (outside the band).
Results on a linear chain of orbitals -- applicable to molecular films or ad-atom chains -- are presented in this poster.
It is shown that for a single conduction band, the spectral function consists of a broad absorptive peak and
a cusp singuarity. The cusp is the edge of a band induced in the linear chain by the conduction band.
Conditions on the observability are discussed and possible connection to heavy-fermion physics is concluded [1].

Reference

M. Moro-Lagares, R. Korytár, M. Piantek, R. Robles, N. Lorente, J. I. Pascual, M. R. Ibarra, D. Serrate,
Real space manifestations of coherent screening in atomic scale Kondo lattices, Nature Communications, 10, 2211 (2019)

Exploring the time evolution of individual molecular systems

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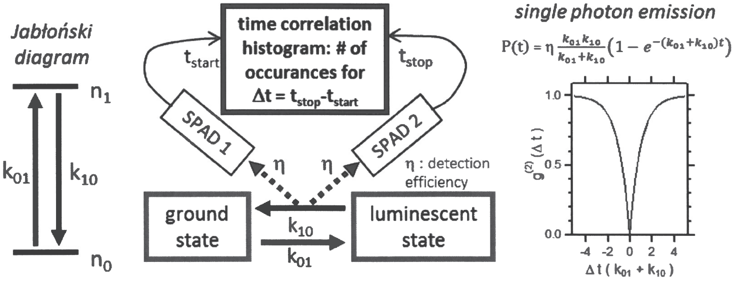
Luminescent quantum systems like molecules and solid-state defects can be prepared in a defined state with an external electronic or electromagnetic excitation. After this initialization, a sequence of quantum mechanical (i.e. stochastic) transitions will govern its time evolution, carrying the system through different internal states each time at a different pace. Averaging over zillions of individual paths allows exploring the details of the internal dynamics. A way to track experimentally the evolution of a luminescent system is Hanbury Brown - Twiss (HBT) photon interferometry. It is based on time-correlated single photon counting (TCSPC) and provides time resolution down to 30 ps. Combining precise local charge injection and local field enhancement at the tip of a scanning tunneling microscope (STM) ensures moreover, the selection and pre-characterization of one individual quantum system even in nm-spaced structures of similar systems.

This conference contribution shall convey some intuition for understanding photon correlations from an evolving quantum system, in which rate equations govern the internal processes. We will show how the internal dynamics appears in the correlation function, and address which additional information we can gain by introducing spectral photon selection. Beginning with the modelling of single photon emission in the most basic system with one ground and one excited state (see figure below), we proceed by including charged intermediate states and address "photon bunching" due to a shelving state as well as two-photon emitters. The analysis of cascaded photon emission will lead to more complex emission sequences for molecular systems in space-, time-, and energy-resolved luminescence.



$$P(t) = \eta \frac{k_{01}k_{10}}{k_{01}+k_{10}}\left(1 - e^{-(k_{01}+k_{10})t}\right)$$

Zero Energy Bound States in the Proximity Induced Topological Superconductor System Bi_2Te_3 on Nb(110)

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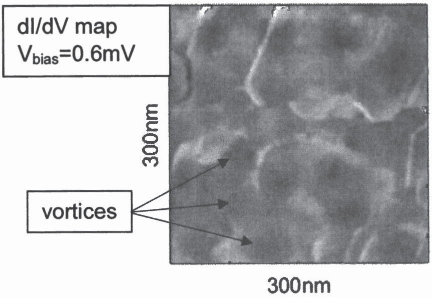
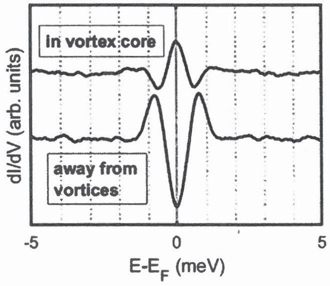
Majorana bound states can be hosted by states on the surface of a strong topological insulator coupled to an ordinary s-wave superconductor and localized inside Abrikosov vortices [1]. This prediction provided the ingredients needed to find topologically protected, robust quantum states suited to form Qbits and motivated experimental research to investigate such structures thoroughly [2,3]. We observed, by measuring differential conductance spectra and maps, zero-energy bound states inside vortices on 5 QL Bi_2Te_3 grown by MBE on Nb(110) to create a proximity induced topological superconductor system. Bi_2Te_3 is a strong topological insulator with a single Dirac cone at the gamma point [4] which was confirmed by ARPES data on our sample. A comparison shows that neither the bare Nb(110) nor a proximity induced Pt film on the Nb(110) substrate exhibit a zero-energy peak in the vortex core or other anomalous features observed on the Bi_2Te_3 film. Therefore we suggest that the observed phenomena of unconventional superconductivity originate from the topological character of the Bi_2Te_3 surface.





References

[1] L. Fu and C. Kane, PRL **100,** 096407 (2008)
[2] J. Xu *et al.*, PRL **112**, 217001 (2014)
[3] Q. He *et al.*, Nat. Commun. **5**, 4247 (2014)
[4] H. Zhang *et al.*, Nat. Phys. **5**, 438-442 (2009)

Structural defects on ethynylene-bridged anthracene wires

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Recently, our group was able to synthesize anthracene-based polymers on metallic surfaces [1]. Such polymers, with a length up to 30 nm, show a well-defined band structure with a band-gap of approximately 1.5 V. However, after the addition of pentagonal defects, we found electronic features at the Fermi level. Pentagons in carbon-based materials are often related to open shell structures and the ability to tailor their magnetic properties [2].

Here we report the addition of structural defects to ethynylene-bridged anthracene polymers wires (4BrAn) on Au (111). These defects are observed as bright features on the chains for low bias voltages in the STM images. The structure of the defects is elucidated using high-resolution non-contact atomic force microscopy. Scanning tunneling spectroscopy recorded on the bright positions of the STM images reveals a zero-bias resonance localized around the structural defect.

References

[1] Sánchez-Grande, A. et al. On-Surface Synthesis of Ethynylene-Bridged Anthracene Polymers. Angewandte Chemie International **Edition 58**, 6559–6563 (2019).
[2] Li, J. et al. Single spin localization and manipulation in graphene open-shell nanostructures. Nature Communications 10, (2019).

Development of a photoexcited THz-gated Scanning Tunneling Microscope at FHI

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THz-gated Scanning Tunneling Microscopy (THz-STM) uniquely combines sub-molecular spatial with femtosecond temporal resolution, as impressively demonstrated in 2016 by T. Cocker and Co-workers [1]. Combined with optical photoexcitation, THz-STM provides a powerful platform to study the local atomically-resolved dynamics of photoexcited nanostructures and surfaces, giving access to a broad variety of spatio-temporal phenomena relevant in surface science. In this regard, complementing the wide variety of time-resolved surface science techniques available in the department of physical chemistry at FHI, we developed an ultrahigh-vacuum STM system optimized for broadband excitation from the visible through the THz spectral range using two motorized parabolic mirrors integrated on the STM platform, employing a broadband spintronic emitter [2] as single-cycle THz source to gate the tunneling junction.

Optimal operation of the THz-STM requires exact knowledge and control of the THz near-field in the STM junction. As this can deviate significantly from its corresponding far-field waveform measured by electro-optic sampling, we characterized the THz near-field directly in the time-domain via THz-induced modulation of photoemission from the tip [3] at distances down to few nanometers. We find pronounced spectral filtering due to frequency-dependent spatial overlap of the point-like STM tip inside the THz focus, and only little tip-dependence of the near-field waveform. We further identify variations of the waveform's shape and polarity by variation of the STE excitation conditions, allowing for precise THz near-field control in the STM junction. As a first step towards probing femtosecond photocarrier dynamics on the nanoscale, we observe temporal broadening of the sampled near-field waveform in a metal-HOPG junction, potentially caused by photoelectron propagation in the tunneling junction or long-lived charge carriers inside tip and sample, respectively.

References

[1] T.L. Cocker, Nature **539**, 263–267 (2016)
[2] T. Seifert, Nature Photonics **10**, 483–488 (2016)
[3] S. Yoshida, ACS Photonics **6**, 1356–1364 (2019)

Controlling the stereospecific bonding motif of Au-thiolate links and assessment of their catalytic properties

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Organosulfur compounds at the interface of noble metals have long been proved to be extremely versatile systems. In this work we explore the formation of gold-thiolate-based organometallic structures from 1,4-bis(4-mercaptophenyl) benzene (BMB) deposited on Au(111) surface. By controlling the on-surface reaction conditions we can selectively choose the resulting structures to be either arrays of cyclic Au_3BMB_3 units or linearly stacked $\mathrm{poly}-[-\mathrm{S}-\mathrm{Au}-\mathrm{S}-\mathrm{BMB}-]_n$ nanowires, although the former turn out to be the thermodynamically favored products[1]. Most interestingly, co-deposition of alkyne-functionalized pyrene derivatives on this system reveals the catalytic activity of the R-S-Au-S-R vertices on alkyne coupling reactions. In the frame of "on-surface synthesis", we thus demonstrate a multistep approach in which first the surface-supported formation of a catalyst takes place, which is then used to control the resultant products of subsequent reactions.

References

[1] L. Colazzo, M. S. G. Mohammed, A. Gallardo, Z. M. Abd El-Fattah, J. A. Pomposo, P. Jelínek and D. G. de Oteyza, Nanoscale 2019, DOI: 10.1039/c9nr04383g

Atomic engineering of monolayer graphene: Inducing Kekulé bond order by adatom deposition

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The Kekulé distortion (KD) periodically modifies the carbon-carbon bonds in graphene, resulting in a $\sqrt{3} \times \sqrt{3}$ R30° superstructure and symmetry breaking between three previously equivalent hexagonal plaquettes. Previous scanning tunnelling microscopy (STM) experiments have shown that such a distortion can produce charge density modulations corresponding to the superstructure [1]. Here, we induce a KD phase in monolayer graphene by low-flux deposition of a small number of lithium adatoms. Using angle-resolved photoemission spectroscopy (ARPES), we observe backfolding of the Dirac cones to Γ, as well as a gap opening ($2\Delta = 0.22 \pm 0.02$ eV) at the Dirac point. Low-energy electron diffraction (LEED) measurements also show the appearance of peaks corresponding to the new periodicity. Finally, we discuss the real-space behaviour of the adatoms by comparing STM data with predictions by a Monte Carlo toy model.

References

[1] C. Gutiérrez, Nature Physics **12**, 950–958 (2016)

Vibrational excitation mechanisms in tunneling spectroscopy beyond the Franck-Condon model.

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Since two decades, scanning tunneling spectroscopy (STS) is used to study molecular vibrations. That can be done with inelastic tunneling spectroscopy (IETS) or vibronic spectroscopy, *i.e.* vibrations associated to electronic excitation coupled to a molecular orbital. In the last cases, experimental results were generally explained within the Franck-Condon picture, which treats vibronic excitations within the Born-Oppenheimer approximation and derives the excitation probabilities from an overlap integral of initial and final state. However this model, cannot justify any spatial dependence of vibronic excitations.
Pavliček et al. [1] have recently explained these spatial variations of vibronic excitations by the coupling of wave functions of different symmetry in the tip and molecule. Apart from symmetry arguments, a clear demonstration of selection rules in terms of vibrational modes of the molecule could not be derived because the experimental energy resolution was insufficient for the identification of the involved mode.

Here we study with low temperature STM, large organic molecules (thiophene derivative and phthalocyanine) on single layer MoS_2 on Au(111). The van der Waals layer acts as an efficient decoupling layer from the metal substrate and provides exceptional energy resolution of a few meV [2-3], which give access to the rich vibronic signature of the investigated molecules. To explain the complete excitation model, spatially and energetically, we show that the Franck-Condon picture has to be combined with a vibration-assisted process, which perturbs the molecular wave functions, and therefore its overlap with the tip wave function.

Using DFT calculations of the molecule in gas phase, our simple model reproduces the experimental spectra at arbitrary position of the STM tip over the molecule in great detail.

References

[1] N. Pavliček *et al.*, Phys. Rev. Lett. **110**, 136101 (2013)
[2] N. Krane *et al.*, ACS Nano **12**, 11698 (2018)
[3] G. Reecht *et al.*, ACS Nano **13**, 7031 (2019)

Dynamics of atomic point contacts studied by STM-induced luminescence

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The plasmonic enhancement occurring at the nanoscale can be used to perform spectroscopic measurements at the scale of individual molecules employing, for instance, surface-enhanced Raman spectroscopy (SERS) or tip-enhanced Raman spectroscopy (TERS). A common issue in such measurements is the blinking of the recorded light intensity, occurring on the scale of seconds and minutes, which can be attributed to fluctuations in the plasmonic enhancement or configuration of the molecule in the nanocavity formed between the adjacent nanoparticles (as in SERS) or the tip and the surface (as in TERS). Atomically precise plasmonic junctions can be routinely addressed using the tip of a scanning tunneling microscope (STM) approaching a single adatom on a surface down to the contact regime. Such junctions emit light due to the excitation of surface plasmons and are known to exhibit overbias emission, i. e. emit light with energy higher than the applied energy level difference. In this poster, we present a study on such overbias emission in an Au-Au contact and show how to utilize the time-resolution of STM-induced luminescence (STML) to follow the fluctuations of the luminescence intensity in real time. In this way, we show that STML is an ideal tool to probe the plasmonic enhancement and relate its variation to the dynamics of atomic arrangements in the vicinity of the junction. These rearrangements may be responsible for the blinking in plasmon-enhanced Raman spectroscopies.

N-terminal Graphene-based Nanostructures for Electron Quantum Optical Setups

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Graphene exhibits many exceptional mechanical and electronic properties that make it attractive for the fabrication of electronic devices at the nanoscale [1], but its gapless spectrum is a major obstacle for carbon-based electronic applications, since the absence of an electronic gap makes it a poor candidate to build logic electronic devices, e.g. field-effect transistor [2]. A gap can be however induced in different ways, among others, via lateral quantum confinement of the electrons, e.g., as it occurs in one-dimensional (1D) graphene nanoribbons (GNRs). On the other hand these GNRs can be produced [3] and manipulated [4, 5] with atomistic precision.

Here we analyze the effect of placing two GNRs one on top of the other interacting via the van-der-Waals interaction (4-terminal device). Previous work based on DFT and Non-equilibrium Green's functions (NEGF) formalism [6] showed that electrons injected from one terminal can be split into two outgoing waves with a tunable ratio that strongly depends on the intersection angle between the ribbons. In this work we complement this by adopting a simple and numerically efficient tight-binding description that captures the essential physics [7]. In addition to the intersection angle, the precise stacking of the device results in a powerful tool to control the direction and intensity of the electron beam. Here we study the electron transport properties in terms of the Scattering matrix, which can be easily computed in the NEGF formalism by means of the generalized Fisher-Lee relations [8], of the different highly-symmetric configurations of crossed GNRs of varying width and edge chiralities, and their possible applications for electron quantum optical setups [9, 10].

References

[1] A. H. Castro Neto, et al., *Rev. Mod. Phys.*, **81**, 109–162 (2009)
[2] F. Schwierz, *Nat Nano*, **5**, 487–496, (2010).
[3] J. Cai, et al., *Nature,* **466,** 470-479 (2010).
[4] M. Koch, et al., *Nat Nano*, **7**, 713–717 (2012).
[5] S. Kawai, et al., *Science*, **351**, 6276, 957–961 (2016).
[6] P. Brandimarte, et al., *The Journal of chemical Physics,* **146,** 092318 (2017).
[7] N. R. Papior, sisl: v0.9.2, https://github.com/zerothi/sisl/
[8] D. S. Fisher and P. A. Lee, *Phys. Rev B,* **23**, 6851 (1981).
[9] Y. Ji, et al., *Nature,* **422**, 415 (2003).
[10] P. Roulleau, et al., *Phys. Rev. B,* **76**, 161309 (2007).

Single-photon emission mediated by single-electron tunneling in plasmonic nanojunctions

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Scanning tunnelling microscopy (STM) experiments have shown single-molecule fluorescence induced by tunneling currents in the nanoplasmonic cavity formed by the STM tip and the substrate [1, 4]. The electric field of the cavity mode couples with the current-induced charge fluctuations of the molecule, allowing the excitation of the mode [2]. We investigate theoretically this system for large damping and find the emitted light displays anti-bunching behavior with vanishing second-order photon correlation function for a single electronic level. At the same time, the current and the intensity of emitted light display Franck–Condon steps [3] at multiples of the cavity frequency ω_c with a width controlled by κ rather than the temperature T.

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[1] Richard Berndt, James K. Gimzewski, and Peter Johansson. Inelastic tunneling excitation of tip-induced plasmon modes on noble-metal surfaces. *Phys. Rev. Lett.*, 67(27):3796–3799, December 1991.

[2] A. Cottet, T. Kontos, and B. Douçot. Electron-photon coupling in mesoscopic quantum electrodynamics. *Phys. Rev. B*, 91:205417, May 2015.

[3] J Koch and F von Oppen. Franck–Condon blockade and giant Fano factors in transport through single molecules. *Phys. Rev. Lett.*, 94(20):206804, 2005.

[4] Christopher C Leon, Olle Gunnarsson, Dimas G de Oteyza, Anna Rosławska, Pablo Merino, Abhishek Grewal, Klaus Kuhnke, and Klaus Kern. Single photon emission from a plasmonic light source driven by a local field-induced coulomb blockade. *arXiv preprint arXiv:1909.08117*, 2019.

Detecting Fermi arcs in chiral topological semimetals by scanning tunneling microscopy

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Topological semimetals with a chiral crystal structure are expected to display numerous exotic physical phenomena, including long Fermi arcs surface states spanning a large fraction of the Brillouin zone. We used high-resolution scanning tunneling microscopy and spectroscopy to explore the properties of these new class of materials. We map the quasiparticle interference patterns at both occupied and unoccupied states and compare the data to the predictions of density functional theory. Our results reveal a rich pletora of different scattering channels, which can be directly linked to a strongly energy dependent evolution of both the shape and the length of the Fermi arcs.

Atomically-resolved ultrafast dynamics in 1T-TaS_2

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Electron-phonon and electron-electron interaction play important roles in strongly correlated systems. The layered 1T-TaS2, as a model system, presents rich electronic properties, which go through a series of charge-density wave (CDW) phases into a Mott insulating ground state as the temperature decreases.[1] By combining THz pump-probe spectroscopy and low-temperature scanning tunnelling microscopy (STM), new phases in 1T-TaS2 were created and the ultrafast electron dynamics could be studied at the atomic scale. It was found that the pump-probe spectra vary strongly on the scale of one unit cell of the CDW. The results shed new light onto the microscopic dynamics of electron motion in the different phases.

References

[1] Sipos, B., et al. Nature Materials **7,** 960-965 (2008).

The alloy $Mn_{88}Ni_{12}$: An Intrinsically Spin-Polarised Tip Material?

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Spin-polarised tips are necessary for the realisation of electron-spin resonance (ESR) in a scanning tunnelling microscope (STM). These tips are typically obtained by transferring a few magnetic atoms to the tip apex and controlling their magnetisation by an external magnetic field [1]. Recently, Forrester et. al. have suggested $Mn_{88}Ni_{12}$ as an alternative tip material because of its intrinsic magnetic properties [2]. Moreover, it has been shown very recently by Willke et. al. that the magnetic field created by a spin-polarised tip is sufficient to perform single-atom ESR [3]. Combining both would allow for ESR-setups without the need for an external magnetic field.

We fabricate a $Mn_{88}Ni_{12}$ tip and investigate its properties using different model systems to study their spin-polarisation: Co nano-islands on Cu(111), and Fe(III)-octaethylporphyrin (FeOEP) on Au(111) and on Pb(111). Since the Co islands exhibit two different out-of-plane spin orientations, the oppositely magnetised Co islands should show contrasting scanning tunnelling spectroscopy (STS) signals when measured with a spin-polarised tip. We did not observe these kind of differences between islands, despite attempting to change the polarisation of the tip with voltage pulses. The other model system relies on changes in inelastic tunnelling via spin-excitations through the presence of a spin-polarised current. The STS signal should become asymmetric when going to higher currents, yet we still observe symmetric spin-excitations when close to contact with the $Mn_{88}Ni_{12}$ tip.

Our experimental results therefore do not yield unambiguous observation of spin-polarisation. The discrepancy of the results of our measurement techniques to those utilised by Forrester et. al. could be due to differences in preparation and treatment of the tip prior to the measurements, requiring a detailed analysis of the tip fabrication.

References

[1] M. Bode, *Reports on Progress in Physics* **66**, 523–582 (2003).

[2] P. R. Forrester, T. Bilgeri, F. Patthey, H. Brune, F. D. Natterer, *Review of Scientific Instruments* **89**, 123706 (2018).

[3] P. Willke *et al.*, *arXiv e-prints*, arXiv: `1908.11061 [cond-mat.mes-hall]` (2019).

Substrate induced nanoscale resistance variation in epitaxial graphene resolved by scanning tunneling potentiometry

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Scanning Tunneling Potentiometry (STP) is a powerful tool for the investigation of local transport properties as it measures the electrochemical potential of a sample with the spatial resolution of a scanning tunneling microscope [1]. Since STP is a surface sensitive technique, it is particularly useful to investigate charge transport in two-dimensional materials providing a comprehensive picture of the local transport properties. Among the growing class of two-dimensional materials graphene still reveals the most remarkable transport properties. Here, we quantitatively investigate the local transport properties of graphene prepared by polymer assisted sublimation growth (PASG) [2] using STP. PASG graphene is characterized by a spatially homogeneous current density, which allows to analyze variations in the local electrochemical potential with high precision. We examine the local sheet resistance in great detail and find a significant variation of up to 270% at low temperatures. In addition, we identify a correlation of the sheet resistance with the stacking sequence of the 6H-SiC substrate as well as with the distance between the graphene sheet and the substrate. Our results experimentally quantify the strong impact of the graphene-substrate interaction on graphene's local transport properties.

Financial support of the Deutsche Forschungsgemeinschaft (DFG) through project We 1889/13-1 is gratefully acknowledged.

References

[1] P. Muralt and D. Pohl, Appl. Phys. Lett. **48** (8), 514-516 (1986)
[2] D. Momeni Pakdehi et al., ACS Appl. Mater. Interfaces **10**, 6039-6045 (2018)

Complex spin structures in the magnetic monolayer of Mn on Re(0001):

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We report the first experimental observation of two distinct spin textures: the row-wise antiferromagnetic state (RW-AFM) and the so-called 3Q state [1]. Both magnetic states were measured on the monolayer of Mn on a Re(0001) single crystal using spin-polarized scanning tunneling microscopy. The fcc-stacked Mn exhibits a RW-AFM with three symmetry-equivalent rotational domains, separated by characteristic phase boundaries. The 3Q state was observed in the hcp-stacked Mn. It is a non-collinear state that has a hexagonal symmetry with 4 atoms in the magnetic unit cell and an angle of 109.4° between neighboring spins. It can be constructed by a linear combination of three RW-AFM spin spirals. In ultra-thin films complex spin textures are stabilized either by frustrated Heisenberg exchange, Dzyaloshinskii-Moriya interactions, or higher-order exchange interactions. However, only the latter are able to lift the energetic degeneracy between RW-AFM and 3Q state. Therefore in this system higher-order interactions must play a crucial role for the preference of a specific spin structure in a given stacking.

References

[1] Ph. Kurz, *et al.*, Phys. Rev.Lett., **86**:1106-1109, Feb 2001.

Exploring structural and electronic properties of helical molecules on surfaces

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Molecules with helical structure fascinate chemists for many years due to their nonplanar structure, which introduces inherently chirality and exhibits interesting optical and electronic properties. Here, I will show two different studies of helicene molecules on metal surfaces to explore: i) their mechanical response to an external field and ii) electronic transport through molecules of different chirality. In the first case, I will show simultaneous tunneling current and force measurements through helicene molecules deposited on Ag(111) surface. These measurements together with the support of DFT calculations reveals strong piezoelectric effect on a single molecule on metal surface [1]. In the second case, I will show short summary of experimental results on electronic transport measurements on single helical molecules of different chirality. In principle, as electrons move along the chiral molecule they should generate a magnetic field that should split its spin state (Chiral induced spin selectivity effect [2]). This should result in a change of conductivity between the molecules of different chirality measured in spin-polarized scanning tunneling spectroscopy. Here, two data sets of transport measurements will be shown: i) with spin-resolved tip on double layer Fe/W(110) and with spin-averaged tip on Co islands of different magnetization states on Cu(111) surface. The measured conductivity in our experiments, however, did not depend on the chirality of the molecules suggesting electron tunneling through the molecules rather moving across the molecule backbone.

References

[1] O. Stetsovych et al, JACS 10.1021/jacs.7b08729 (2017)
[2] R. Naaman, David H. Waldeck, J. Phys. Chem. Lett 10.1021/jz300793y (2012)

Charge carrier injection electroluminescence with CO functionalized tips on single molecular emitters

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We investigate electroluminescence of single molecular emitters on NaCl on Ag(111) and Au(111) with submolecular resolution in a low-temperature scanning probe microscope with tunneling current, atomic force and light detection capabilities. Role of the tip state is studied in the photon maps of a prototypical emitter, zinc phthalocyanine (ZnPc), using metal and CO-metal tips. CO-functionalization is found to have a dramatic impact on the resolution and contrast of the photon maps due to the localized overlap of the p-orbitals on the tip with the molecular orbitals of the emitter. The possibility of using the same CO-functionalized tip for tip-enhanced photon detection and high resolution atomic force is demonstrated. We study the electroluminescence of ZnPc, induced by charge carrier injection at sufficiently high bias voltages. We propose that the distinct level alignment of the ZnPc frontier orbital with the Au(111) and Ag(111) Fermi levels governs the primary excitation mechanisms as the injection of electrons and holes from the tip into the molecule, respectively. These findings put forward the importance of the tip status in the photon maps and contribute to a better understanding of the photophysics of organic molecules on surfaces. [1]

References

[1] J. Doležal, P. Merino, J. Redondo, L. Ondič, A. Cahlík, M. Švec, arXiv:1909.10934 [cond-mat.mes-hall]

Residual Thermal Signals in Shaken Pulse Pair Excitation for Optical Pump Probe STM

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Combining Scanning Tunneling Microscope (STM) and optical excitation by a laser has been tried since the early 1990s. Disentangling thermal effects due to heating of the tip from optically induced dynamics of the sample has always been a major issue. Shaken Pulse Pair Excitation (SPPX) is an advanced pump probe technique, which allows for optical pump probe with Lock-In detection and constant average power, to eliminate any thermal contributions to the signal. Nevertheless Kloth et al.[1] found thermal contributions of up to 10% of the SPPX-signal. In this study we investigated the origin of the residual thermal signal. A fixed lens near the junction and remote controlled mirror outside of the STM allow us to precisely focus a laser on the STM tip. By using an electro optical modulator in combination with an arbitrary waveform generator, we are able to create laser excitations from continuous wave excitation down to the nanosecond regime. We find that, despite constant average power, the thermal residuum can be traced back to low-frequency contributions in the excitation pattern.

References

[1] Kloth et al., Rev. Sci. Instr. **87**, 123702 (2016);

Scanning tunnelling spectroscopy on disordered superconductors

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In some materials superconductivity co-exists with a certain amount of disorder. Known since the 1960s, the true microscopic nature of disordered superconductors remains unknown [1,2]. These systems have mainly been investigated in transport experiments which average over the macroscopic sample area. More recently, scanning tunnelling microscopy/spectroscopy (STM/STS) has been employed to investigate the local properties of the superconducting phase. The measurements revealed large spatial fluctuations of the superconducting gap, indicating a local modification of the ground-state. Ongoing research is aimed at understanding these features as well as finding evidence for other theoretical predictions, *e.g.* localized preformed Cooper pairs [3-6].

Here, we will present preliminary results of high resolution STM measurements enabled by utilizing superconducting tips. Low temperature transport measurements are performed on the same samples to complement these results. In particular, we study thin films of amorphous InO and polycrystalline NbN as well as a 400 nm TiN sample. We observe local gap variations on the nanometer length scale and resolve a number of in-gap states showing high fluctuations both in energy and spatial distribution. These in-gap states can partly be attributed to local fluctuations of the superconducting order parameter by relating their spatial position to topographic features.

References

[1] P. W. Anderson, J. Phys. Chem. Solids **11**, 26-30 (1959).
[2] M. Ma and P. Lee, Phys. Rev. B **32**, 5658 (1985).
[3] B. Sacépé *et al.*, Phys. Rev. Lett. **101**, 157006 (2008).
[4] B. Sacépé *et al.*, Nat. Phys. **7**, 239-244 (2011).
[5] C. Carbillet *et al.*, Phys. Rev. B **93**, 144509 (2016).
[6] T. Dubouchet *et al.*, Nat. Phys. **15**, 233-236 (2019).

Energy levels and charge distribution within dipolar molecules

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Molecules consisting of a donor and an acceptor moiety can exhibit large intrinsic dipole moments. Upon deposition on a metal surface, the dipole may be effectively screened and the charge distribution altered due to hybridization with substrate electronic states. Therefore, the inclusion of a thin band-gapped material can help to preserve gas-phase-like electronic properties. We study Ethyl-Diaminodicyanoquinone molecules on a Au(111) surface and on single-layer molybdenum disulfide (MoS_2) on Au(111) with scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM). By mapping the local contact potential difference (LCPD) over the molecules we show that the intrinsic dipole moment of the molecules is partially preserved upon adsorption on both the bare Au(111) surface and MoS_2. On Au(111), the molecular resonances show an apparent shift in energy within individual molecules. The high energy resolution on molecules adsorbed on MoS_2 allows us to assign that the apparent shift is indeed due to several resonances of varying intensity, arising from vibronic states. DFT calculations of the molecule in gas phase help to identify certain vibrations of the molecule from their signature in the tunneling spectra.

Interaction of single Ti magnetic impurities with β-Bi_2Pd superconductor surface

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In the last decade a lot of work has been addressed to study properties of magnetic atom chains on top of superconductors. The main motivation is that they provide a promising way to realize a topological superconductor bounded by Majorana zero energy edge states.[1] In this work we study the Yu-Shiba-Rusinov (YSR) intragap states of Ti atoms magnetic impurities on the s-wave superconductor β-Bi2Pd, by means of low temperature scanning tunneling microscopy (LTSTM) at 1.2K. The low temperature and a superconducting tip allow us to have a resolution in conductance (proportional to the density of states) down to 100 μeV. In this way, we can resolve the intra-gap states called Yu-Shiba-Rusinov (YSR).[2] A free Ti atom has electronic configuration $[Ar]4s^2 3d^2$, with each electron in the d shell carrying spin ½. We measure that this give rise to two Yu-Shiba-Rusinov (YSR) scattering channels split due to the crystal field anisotropy on the surface.[3] The YSR states are very sensitive to the adsorption site, we observe that Ti adsorb in mainly two different places on the square lattice of top-most Bi atoms, showing YSR states only in one of the two. It is also known that the anisotropy of the Fermi surface of the superconductor enhances the observation of a scattering pattern that reflects the symmetry of the host lattice,[3] squared in case of β-Bi2Pd. We measured these patterns mapping the density of states at the energy of the YSR peaks. With this system is possible to manipulate the Ti atoms horizontally, moving them on the surface, and vertically, picking up a magnetic atom on the tip apex. The first allows to potentially form atomic structures on the surface and the latter to do STS using YSR states as a high-sensitive probe of substrate YSR excitations.

References

[1] Alicea, J. *Rep. Prog. Phys.* **75**, 076501 (2012).

[2] Heinrich, B. W., Pascual, J. I. & Franke, K. J., *Prog. Surf. Sci.* **93**, 1–19 (2018)

[3] Ruby, M. et. al. *Phys. Rev. Lett.* **117**, 186801 (2016).

Scrutinizing the bonding of 2-mercaptobenzimidazole on Cu(111) by STM and DFT

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Although organic corrosion inhibitors such as 2-mercaptobenzimidazole are widely used to protect the surface of copper, their bonding mechanism on the atomic scale remains elusive. DFT calculations have shown that different bonding configurations have comparable energies when considering the binding of a single molecule to the surface. In the case of larger coverages, which are common in real-life applications, various inter-molecular interactions have to be considered as well, further complicating calculations.

To determine which interactions are most significant for the bonding and self-assembly of 2-mercaptobenzimidazole on the surface of Cu(111) we prepared samples in ultrahigh vacuum and imaged them using STM. Varying the evaporation rate and time allowed us to prepare samples with different coverages. The substrate temperature during deposition limits the energy the molecules have available to self-assemble, allowing us to gain insight in the energetics of the leading interactions. Surprisingly the molecules formed ordered self-assembled structures even when depositing on samples cooled to approximately 50 K, which opposes the idea that strong binding to specific sites on the surface is crucial for corrosion prevention. The large variety of obtained self-assembled structures at different deposition parameters suggests, that the energy scales of competing interactions must be similar.

Based on STM images of the structures we proposed different binding models that were confirmed using DFT simulations. This allows us to gain insight in the bonding mechanism and energetics of 2-mercaptobenzimidazole on Cu(111) possibly enabling development of better organic corrosion inhibitors in the future

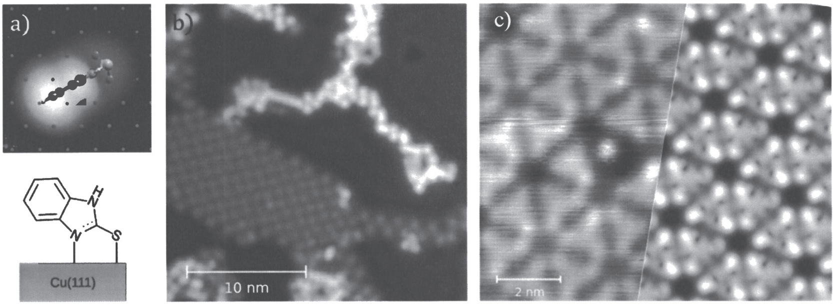

Figure 1: a) The top part represents the optimal binding of 2-mercaptobenzimidazole on Cu(111) according to DFT calculations together with a simulated STM image in the background. In the bottom panel the same model is presented schematically. b) Ordered self-assembled structured that form at ≈ 90 K. c) Comparison of a STM (left) and DFT simulated image (right) of a structure obtained after annealing to ≈ 450 K.

Demonstration of single atom ESR and pump-probe with a 30 mK STM setup

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The recent advances in electron spin resonance (ESR) with STM have allowed the detection of low-energy spin excitations with neV energy resolution [1]. Furthermore, all-electrical pump-probe schemes have pushed the limits of timescales accessible with an STM into the nanosecond regime [2, 3]. These methods combined, pulsed-ESR, hold promise for performing quantum computations with spins with long coherence times [4].
Although the energy resolution of the ESR measurement is not restricted by temperature, a lower measurement temperature does allow a richer playground of quantum phenomena to apply these methods on.

Here, we demonstrate the implementation of ESR and all-electrical pump-probe on a 30 mK STM [6]. By measuring the transmission of rf voltages and doing pulse shape analysis, we characterize the time-domain performance of our setup. We extract the magnetic moments of Fe and hydrogenated Ti on MgO/Ag(100) from the linear progression of the ESR resonance in field-sweep and frequency-sweep mode. With pump-probe schemes [5], we also reproduce comparable lifetimes for Fe on MgO/Ag(100) [3] and show how these are affected by an externally applied in-plane and out-of-plane magnetic field.

References

[1] S. Baumann et al., Science **350**, 417-420 (2015)
[2] S. Loth et al., Science **329**, 1628-1630 (2010)
[3] W. Paul et al., Nature Physics **13**, 403-407 (2017)
[4] G. Wolfowicz et al., Nat. Nano. **8**, 561-564 (2013)
[5] F. Natterer, ArXiv. 1902.05609 (2019)
[6] H. v. Allwörden et al., RSI **89** (2018)

Controlling Reactions of Bromine Substituted Terminal Alkynes on Metal Surfaces

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How to control pathways of ultra-high vacuum (UHV) based on-surface reactions has been an important but challenging topic. With the interplay of STM, nc-AFM, SRPES, and DFT calculations, kinetic strategies for steering the reactions of Bromine substituted terminal alkynes on surfaces are shown here.

(1) The formation of graphdiyne vs. graphyne nanowires from 1,1’-biphenyl-4-bromo-4’-ethynyl (BPBE) on Ag(111) has been successfully controlled, by using distinct kinetic strategies.[1] When depositing BPBE on Ag(111) held at a relatively low temperature of 360 K, only low-barrier Glaser coupling can be activated, leading to the formation of conjugated diyne type dimer. These conjugated diynes connect with each other via C−Ag−C bonds. Further annealing the sample to 460 K gives rise to the generation of covalent graphdiyne nanowires. In contrast, high-barrier Sonogashira coupling occupies the dominant position when BPBE are deposited on a hot Ag(111) surface of 700 K and covalent graphyne nanowires can be formed. Because of the strong desorption of molecules from Ag(111) at high surface temperatures, only the molecular chains can stay stably on the surface; the one-by-one growth mechanism of chains under low monomer concentration at surfaces makes the Sonogashira coupling dominating.

(2) The reaction selectivity of a kind of chiral terminal alkyne on Ag(111) has been studied.[2] Using precursor molecules with different substituents, the reaction pathways have been successfully controlled under appropriate kinetic parameters. The homochiral molecules are covalently connected via intermolecular Glaser coupling. In sharp contrast, the cross-coupling reaction pathway between two heterochiral molecules (one of them involving intramolecular Bergman cyclization) also takes place. It is revealed that the single-molecule Bergman cyclization followed by the formation of H-type product from heterochiral molecules is the kinetically favorable pathway for the reactions of free molecules. However, the template effect of the organometallic chain could enhance the Glaser coupling from homochiral molecules.

References

[1] T. Wang, *et al.* J. Am. Chem. Soc. **140**, 13421-13428 (2018)
[2] T. Wang, *et al. Nat. Commun.* **10**, 4122 (2019)

Study of magnetic molecules on superconductors by STM/AFM

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The exchange coupling between magnetic impurities and a superconducting substrate leads to Yu-Shiba-Rusinov (YSR) states within the superconducting gap. Recent work has shown the continuous shift of the YSR state energy, which has a quantitative relationship to the impurity-substrate exchange coupling, as a particular function of the tip-sample distance of the scanning tunneling microscope (STM)[1-2]. Due to the weak bonding between the adsorbed magnetic molecules and the substrate, the attractive force exerted by the tip on the molecule has an effect on the molecule-substrate coupling, which influences the YSR states. Using simultaneously STM and atomic force microscope (AFM), we demonstrate how this force modifies the local YSR states, including the dynamical process of the quantum phase transition between screened and unscreened impurity spin.

References

[1] S. Kezilebieke & P. Liljeroth et al., Nano Lett, **18**, 2311-2315 (2018)
[2] L. Farinacci & K. J. Franke et al., Phys. Rev. Lett. **121**, 196803 (2018)