15th International Conference on Vibrations at Surfaces

Donostia-San Sebastián, Spain

June 22-26, 2015

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Preface

The 15th International Conference on Vibrations at Surfaces (VAS15) brings together experienced and young researchers as well as students working in surface vibrational spectroscopy, surface dynamics and in the development of new techniques for the understanding of the vibrational properties of surfaces and interfaces which are relevant to the fields of physics, chemistry, biology and engineering.

The conference is the 15th edition of a series of meetings: Jülich (1978), Namur (1980), Asilomar (1982), Bowness on Windermere (1985), Eibsee (1987), Shelter Island (1990), Santa Margherita (1993), Birmingham (1996), Hayama (1998), Saint Malo (1301), Bar Harbor (1304), Erice (1307), Orlando (2010), and Kobe (2012).

VAS15 consists of 24 invited talks and 68 contributed papers, including 28 oral presentations. It will take place in the historical *Palacio de Miramar*, built as a vacation resort for Maria Christina of Austria who ruled Spain in the end of the 19th century. It is located on a small hilltop overlooking the beautiful bay of San Sebastián.

We hope that you will enjoy the scientific program and the charming atmosphere in the city with its range of pleasant offers for visitors and locals.

Thomas Frederiksen
Chair, VAS15
Donostia International Physics Center

VAS15 overview map

Venue

- ★ Palacio de Miramar
- Kutxa Andia Hall

Hotels & residences

- A Hotel Husa Europa
- B Hotel Zenit San Sebastián
- C Hotel San Sebastian
- D Hotel Silken Amara Plaza
- E Hotel Palacio de Aiete
- F Manuel Agud Querol
- G Olarain
- H NH San Sebastian Aranzazu
- I Barceló Costa Vasca
- J Hotel Maria Cristina

Transportation

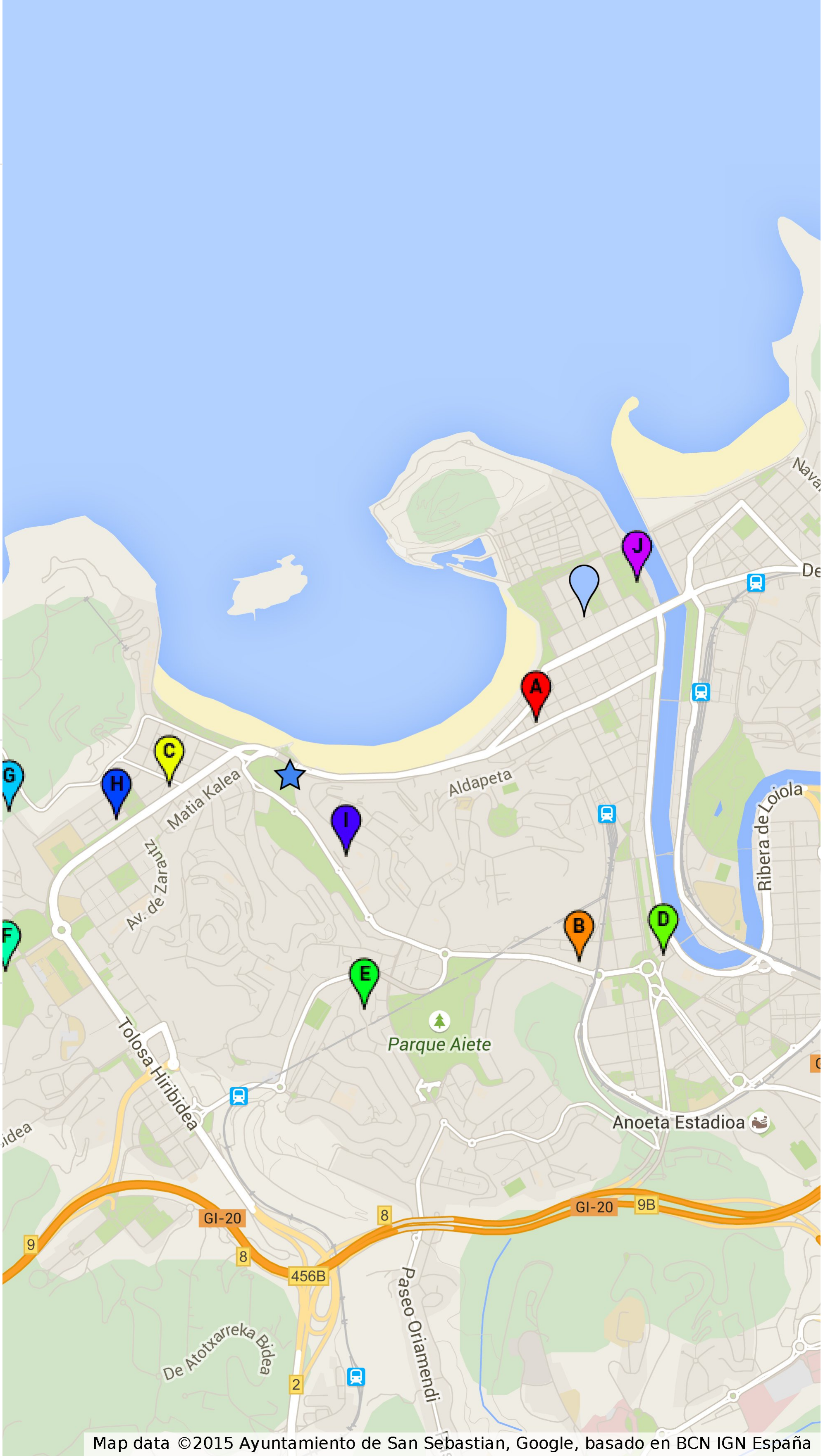
Tourism & sightseeing

Lunch places

Pintxo bars

Dinner places

Walking directions to venue



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Program

Approx. times	Monday June 22	Tuesday June 23	Wednesday June 24	Thursday June 25	Friday June 26
09-11	Registration	Transport in electronic devices	E-ph coupling in novel 2D materials (I)	Adsorbate and interface dynamics	Thermal transport, friction, and dissipation
11-13	Registration	Surface diffusion and migration	E-ph coupling in novel 2D materials (II)	STM-IETS and beyond	Catalysis and single-molecule chemistry
13-15	**Opening 14:30**	Lunch break	Posters B	Lunch break	Poster awards and **Closing**
15-17	Surface scattering and chemistry	Chemistry and growth of graphene	Afternoon off	Molecular films and 2D materials	Departure
17-19	Solid-liquid interfaces	Electron-phonon coupling in graphene		Tip-enhanced vibrational spectroscopies	
19-21	Reception	Posters A	Polanyi public lecture		
21-23				Conference dinner 20:30	

Monday June 22

09:00-14:30 Registration

14:30-14:40 Opening session

T. Frederiksen, *San Sebastian, Spain*

Mo1: Surface scattering and chemistry

Chair: **U. Höfer**, *Marburg, Germany*

14:40-15:10	**R. D. Beck**, *Lausanne, Switzerland* Probing the role of vibrations in dissociative chemisorption by state resolved molecular beam/surface experiments
15:10-15:40	**A. Wodtke**, *Göttingen, Germany* Toward a dynamical understanding of chemistry at metal surfaces
15:40-16:00	**O. Galparsoro**, *San Sebastián, Spain & Talence, France* Role of the vibrational energy to enhance the dissociative adsorption of N_2 on metal surfaces
16:00-16:20	**J. R. Manson**, *Clemson, USA* Hyperthermal atom scattering from surfaces

16:20-17:00 Coffee break

Mo2: Solid-liquid interfaces

Chair: **W. E. Ernst**, *Graz, Austria*

17:00-17:30	**E. H. G. Backus**, *Mainz, Germany* Liquid flow along a solid surface reversibly alters interfacial chemistry
17:30-18:00	**R. K. Campen**, *Berlin, Germany* From UHV to the solid/liquid interface: Water adsorption, surface reconstruction and dynamics on α-Al_2O_3
18:00-18:20	**T. Sugimoto**, *Kyoto, Japan* Spontaneous ferroelectric ordering of strongly correlated protons in crystalline ice films on Pt(111)
18:20-18:40	**A. Tamtögl**, *Cambridge, UK* The motion of water on a hydrophobic surface

19:00-21:00 Welcome reception

Tuesday June 23

Tu1: Transport in electronic devices

Chair: **D. Sanchez-Portal**, *San Sebastián, Spain*

09:00-09:30	**K. Hannewald**, *Berlin, Germany* Polaron transport in organic crystals: theory and modelling
09:30-10:00	**M. Reed**, *New Haven, USA* IETS of single molecule transistors
10:00-10:20	**H. Okuyama**, *Kyoto, Japan* Environmental control of single-molecule conductance
10:20-10:40	**S. Wang**, *Dübendorf, Switzerland* Electronic and vibronic properties of atomically precise bilayer graphene nanoribbons

10:40-11:20 Coffee break

Tu2: Surface diffusion and migration

Chair: **J. Manson**, *Clemson, USA*

11:20-11:50	**J. Ellis**, *Cambridge, UK* The use of atom-surface band structures as a framework for considering quantum effects in surface diffusion
11:50-12:20	**H. Hedgeland**, *London, UK* Surface diffusion of aromatics through van der Waals landscapes and beyond
12:20-12:40	**W. E. Ernst**, *Graz, Austria* Investigation of surface structure and diffusion dynamics of hydrogen adsorbed on Sb(111)
12:40-13:00	**R. Martinez-Casado**, *Madrid, Spain* Diffraction of helium on MgO(100) calculated from first-principles

13:00-15:30 Lunch break

Tu3: Chemistry and growth of graphene

Chair: **H. Hedgeland**, *London, UK*

15:30-16:00	**M.-L. Bocquet**, *Paris, France* Cycloaddition of metal-supported graphene interfaces: a first principles investigation
16:00-16:20	**A. I. Shkrebtii**, *Toronto, Canada* Vibrations, optics and bonding in graphene based heterosystems functionalised with hydrogen
16:20-16:40	**D. Farías**, *Madrid, Spain* Helium diffraction from graphene grown by chemical vapor deposition on copper catalysts

16:40-17:20 Coffee break

Tu4: Electron-phonon coupling in graphene

Chair: **W. Widdra**, *Halle, Germany*

17:20-17:50	**J. W. Wells**, *Trondheim, Norway* Electron phonon mediated transitions in 2D materials; towards a designer superconductor?
17:50-18:10	**S. Tanaka**, *Osaka, Japan* Momentum-resolved direct-observation of the electron-phonon scattering for graphite and graphene by using ARPES and HREELS
18:10-18:30	**V. De Renzi**, *Modena, Italy* Terahertz optical modes of supported graphene bilayer
18:30-18:50	**D. Stradi**, *Lyngby, Denmark* Nanostructured phonons in epitaxial graphene on ruthenium surfaces

19:00-21:30 Poster session A

Wednesday June 24

We1: E-ph coupling in novel 2D materials (I)

Chair: **P. Saalfrank**, *Potsdam, Germany*

09:00-09:30	**M. El-Batanouny**, *Boston, USA* Measuring, interpreting, and translating electron quasiparticle – phonon interactions on the surfaces of the topological insulators
09:30-10:00	**S. O. Valenzuela**, *Barcelona, Spain* Inelastic electronic transport in single-layer graphene and at the surface of topological insulator Bi_2Se_3
10:00-10:20	**F. O. Schumann**, *Halle, Germany* Surface phonons of $BaTiO_3$(001) and $BaTiO_3$ ultrathin films on Pt(001) and Au(001)
10:20-10:40	**M. Herzog**, *Berlin, Germany* Coherent phonon dynamics across the phase transition of quasi-1D Ta_2NiSe_5

Coffee break

We2: E-ph coupling in novel 2D materials (II)

Chair: **J. Wells**, *Trondheim, Norway*

11:20-11:50	**I. Y. Sklyadneva**, *San Sebastián, Spain & Tomsk, Russia* Electron-phonon scattering at surfaces and in ultrathin superconducting films: the effect of spin-orbit coupling
11:50-12:20	**M. Calandra**, *Paris, France* Universal increase in the superconducting critical temperature of two-dimensional semiconductors at low doping by the electron-electron interaction
12:20-12:40	**R. Arafune**, *Tsukuba, Japan* Importance of momentum resolved electron-phonon coupling in analysis of inelastic tunneling and photoemission spectroscopy
12:40-13:00	**I. Errea**, *San Sebastián, Spain* Calculation of strongly anharmonic phonons in transition metal dichalcogenides

13:00-15:30 Poster session B

19:30-20:30 Public lecture:

How Discoveries Are Made and Why It Matters
John C. Polanyi, Nobel Laureate in Chemistry
Kutxa Andia Hall

Thursday June 25

Th1: Adsorbate and interface dynamics

Chair: **P. Jelínek**, *Prague, Czech Republic*

09:00-09:30	**N. Lorente**, *San Sebastián, Spain* Imaging molecular motions with scanning tunnelling microscopy
09:30-10:00	**J. C. Polanyi**, *Toronto, Canada* The role of vibration in surface-migration
10:00-10:20	**T. Kumagai**, *Berlin, Germany* Local impact on intramolecular H-atom transfer studied by STM and nc-AFM
10:20-10:40	**K. Ishioka**, *Tsukuba, Japan* Plasmon-phonon dynamics at GaP/Si(001) interfaces

10:40-11:20 Coffee break

Th2: STM-IETS and beyond

Chair: **M. Alducin**, *San Sebastián, Spain*

11:20-11:50	**Y. Jiang**, *Beijing, China* Probing nuclear quantum effects in water with scanning tunneling microscopy and spectroscopy
11:50-12:20	**J. Repp**, *Regensburg, Germany* Symmetry dependence of vibration-assisted tunneling
12:20-12:40	**F. Schwartz**, *Ilmenau, Germany* Electronic and vibrational states of single Tin-Phthalocyanine molecules – a numerical STM study
12:40-13:00	**P. Jelínek**, *Prague, Czech Republic* The origin of high-resolution IETS-STM images of organic molecules with functionalized tips

13:00-15:30 Lunch break

Th3: Molecular films and 2D materials

Chair: **D. Farías**, *Madrid, Spain*

15:30-16:00	**P. Jakob**, *Marburg, Germany* Infrared-spectroscopy applied to ultrathin molecular films
16:00-16:20	**J. Weber**, *Essen, Germany* Temperature induced conformational disorder in organic monolayers
16:20-16:40	**P. Senet**, *Dijon, France* Protein dynamics and function from a physicist point of view

16:40-17:20 Coffee break

Th4: Tip-enhanced vibrational spectroscopies

Chair: **J. I. Pascual**, *San Sebastián, Spain*

17:20-17:50	**R. P. Van Duyne**, *Evanston, USA* Tip-enhanced Raman spectroscopy
17:50-18:20	**Z. Dong**, *Hefei, China* Sub-nm resolved single-molecule Raman spectromicroscopy
18.20-18:40	**K. F. Domke**, *Mainz, Germany* A novel tool to investigate electrified interfaces on the nanoscale: EC-TERS
18:40-19:00	**I. I. Rzeźnicka**, *Tohoku, Japan* Determination of molecular orientation in monolayers adsorbed on metals using STM-based TERS

20:30-23:00 Conference dinner

Location: Cofradía Vasca de Gastronomía, Parte Vieja (Old Town).

Friday June 26

Fr1: Thermal transport, friction, and dissipation

Chair: **M. Kawai**, *Tokyo, Japan*

09:30-10:00	**D. Donadio**, *San Sebastián, Spain* How surfaces dictate thermal transport in low-dimensional semiconductors
10:00-10:20	**P. Focquet**, *Grenoble, France* A classical collision model for surface friction tested by neutron scattering
10:20-10:40	**P. Saalfrank**, *Potsdam, Germany* Cold or hot: Metal substrate electrons will always couple to adsorbate vibrations

10:40-11:20 Coffee break

Fr2: Catalysis and single-molecule chemistry

Chair: **A. Mugarza**, *Barcelona, Spain*

11:20-11:50	**M. V. Ganduglia-Pirovano**, *Madrid, Spain* Vibrational spectroscopy in catalysis: The power of synergy between theory and experiment
11:50-12:20	**Y. Kim**, *Tokyo, Japan* Single-molecule chemistry and spectroscopy on the ultrathin insulating films
12:20-12:40	**M. Smerieri**, *Genova, Italy* Characterisation of monolayer MgO films on Ag(100)
12:40-13:00	**M. Foster**, *Boston, USA* Surface chemistry of metal oxide nanoparticles

13:00-14:00 Closing session and poster prizes

T. Frederiksen, *San Sebastian, Spain*
G. Benedek, *Milan, Italy*

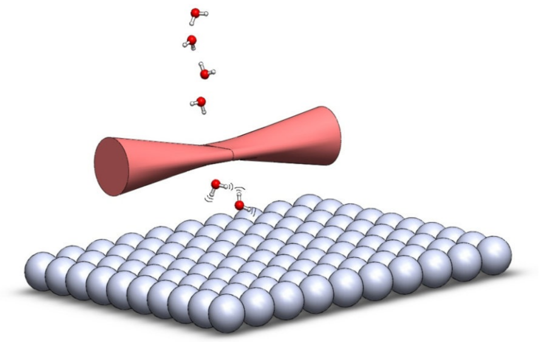
Mo1: Surface scattering and chemistry

INVITED TALK

Probing the role of vibrations in dissociative chemisorption by state resolved molecular beam/surface experiments

P. M. Hundt, M. E. Van Reijzen, H. J. Chadwick, and R. D. Beck

Surface Dynamics Group, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland



We present recent results from our laboratory on quantum state resolved reactivity measurements for the dissociative chemisorption of methane and water and their deuterated isotopologues on Ni and Pt surfaces [1-5]. Both dissociation reactions play an important role in the steam reforming process used to convert methane and water into a mixture of hydrogen and carbon monoxide by heterogeneous catalysis. Using state-selective reactant preparation by infrared pumping in a molecular beam, we prepare the surface incident methane and water molecules in specific ro-vibrational quantum states and measure the state-resolved reactivity on a single crystal surface using surface analytical techniques such Auger electron spectroscopy, King & Wells beam reflectivity, and reflection absorption infrared spectroscopy of the surface bound reaction products. We also probe the quantum state distribution of the non-reactively scattered molecules by combining infrared laser tagging with bolometric detection. The results of our measurements provide evidence for mode- and bond-specificity as well as steric effects, which shows that direct chemisorption reactions of both methane and water cannot be described by statistical rate theory but require dynamical treatments including all internal vibrational and rotational degrees of freedom of the dissociating molecule. The detailed reactivity data obtained in our measurements serves as stringent test for the development of a predictive understanding of these industrially important gas/surface using first principles theory [1,4-6].

[1] P. M. Hundt, B. Jiang, M. E. Van Reijzen, H. Guo, and R. D. Beck, Science **344**, 504 (2014)
[2] P. M. Hundt, M. E. Van Reijzen, H. Ueta, and R. D. Beck, J. Phys. Chem. Lett. **5**, 1963 (2014)
[3] H. J. Chadwick, P. M. Hundt, M. E. Van Reijzen, B. Yoder and R. D. Beck, J. Chem. Phys. **140**, 34321 (2014)
[4] F. Nattino et al., J. Phys. Chem. Lett. **5**, 1294 (2014)
[5] H. Ueta, L. Chen, R. D. Beck, I. Colon-Diaz, and B. Jackson, Phys. Chem. Chem. Phys. **15**, 20526 (2013)
[6] B. Jackson and S. Nave, J. Chem. Phys. Lett. **138**, 174705 (2013)

INVITED TALK

Toward a dynamical understanding of chemistry at metal surfaces

A. Wodtke[1,2]

[1]Georg-August University, Göttingen, Germany
[2]Max Planck Institute for Biophysical Chemistry, Göttingen, Germany

One of our most fundamental scientific challenges is to develop predictive theories of chemistry rigorously grounded in the laws of physics. In 1929, Dirac identified the problem famously in a comment about the importance of quantum mechanics to chemistry… *"The underlying physical laws necessary for the mathematical theory of… …the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."* Despite electrifying advances in computational power, Dirac is still right. The theory of chemistry requires approximate methods for practical computations.

For the theory of surface chemistry, three central approximations are made, involving the use of: 1) classical mechanics for describing nuclear motion, 2) density functionals for calculating electronic states and 3) the Born-Oppenheimer approximation to separate electronic and nuclear degrees of freedom.

The growing importance of computational surface chemistry motivates us to design rigorous experimental tests of these assumptions. Many fundamental questions arise. Can we trust the Born-Oppenheimer approximation for calculating potential energy surfaces for reactions at metal surfaces? Can we characterize and overcome the weaknesses of density functional theory, for example by developing new wave-function based methods for the solid-state? For all of these reasons, it is important to carefully design experimental tests of the capabilities of modern computational surface chemistry.

Using modern molecular beams methods in state-to-state scattering experiments, we obtain a wealth of observational data characterizing the interactions of molecules with metal surfaces. Emphasizing quantitative comparison to first principles theories, we find that energy conversion can occur by unexpected mechanisms, where the electronically adiabatic approximation separating the time scales of electronic and nuclear motion is found to be invalid. The simplicity of the systems under study provides opportunities for developing new theories that go beyond the Born-Oppenheimer approximation. One important outcome of this is the realization that Born-Oppenheimer breakdown can be induced by simple electron transfer events that are common in surface chemistry.

CONTRIBUTED TALK

Role of the vibrational energy to enhance the dissociative adsorption of N_2 on metal surfaces

<u>O. Galparsoro</u>[1,2], I. Goikoetxea[3,5], J. I. Juaristi[1,4], and M. Alducin[1,3]

[1]Donostia International Physics Center, 20018 San Sebastián, Spain
[2]Univ. Bordeaux and CNRS, ISM, UMR5255, F-33400, Talence, France
[3]Centro de Física de Materiales (CSIC-UPV/EHU), 20018 San Sebastián, Spain
[4]Dep. Física de Materiales, Apartado 1072, 20080 San Sebastián, Spain
[5]Humboldt Universität zu Berlin, Institut für Chemie, Unter den Linden 6, D-10009 Berlin, Germany

The dissociation of N_2 on metal surfaces is usually the rate limiting step in the synthesis of many important compounds (ammonia, nitric acid, organic nitrates...) that are produced in chemical industry. In this theoretical study we investigate the efficiency of the vibrational energy to increase the dissociative adsorption of N_2 on the Fe(110) and the W(110) surfaces. As shown in Refs. [1] and [2] for the non-vibrationally excited N_2, dissociation, which is activated in both cases, is dominated by the energy barriers that appear when the molecule is close to the surface in the former [Fe(110)] and far from it in the latter [W(110)].

Here, we perform multidimensional molecular dynamics simulations on precalculated ab-initio potential energy surfaces to calculate the dissociative sticking probability as a function of the initial translational and vibrational energy of the molecule. Based on low dimensional schemes (see Fig.1), it has been thought that the vibrational energy would be efficient to promote dissociation in late barrier systems such as N_2/Fe(110), but inefficient in early barrier systems such as N_2/W(110). Our results show that though the vibrational energy is more efficient in the former, it is still efficient in the early barrier N_2/W(110) system. The reason is that the vibrational energy not only allows to overcoming late barriers, but also can open new dissociation paths with lower early barriers than those found for N_2 in the vibrational ground state. In particular, we observe that the new dissociation paths on the N_2/W(110) system are actually dominated by late barriers. Therefore, there is no contradiction between our results and the original Polanyi's rules developed for gas-phase collisions [3].

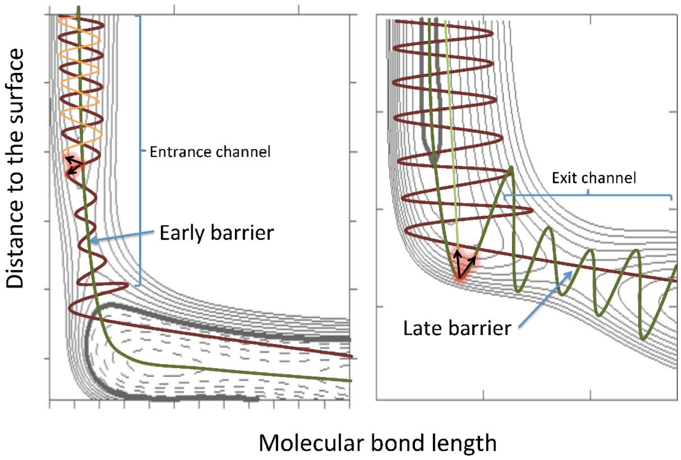


Figure 1: Examples of 2D cuts of early barrier and late barrier systems. The brown (green) line corresponds to the dissociating process of a molecule with (without) vibrational energy in the 2D simplified model.

[1] G. A. Bocan, R. Díez Muiño, M. Alducin, H. F. Busnengo, and A. Salin, J. Chem. Phys. **128**, 154704 (2008)
[2] I. Goikoetxea, M. Alducin, R. Díez Muiño, and J. I. Juaristi, Phys. Chem. Chem. Phys. **14**, 7471 (2012)
[3] J. C. Polanyi and W. H. Wong, J. Chem. Phys. **51**, 1439 (1969)

CONTRIBUTED TALK

Hyperthermal atom scattering from surfaces

J. R. Manson[1] **and W. W. Hayes**[2]

[1]*Department of Physics and Astronomy, Clemson University, Clemson, SC 29634, USA*
[2]*Physical Sciences Department, Greenville Technical College, Greenville, SC 29606, USA*

There have been a number of recent experiments reporting measurements of angular distributions of hyperthermal rare gas atoms scattering from metal and insulator surfaces. The experiments for scattering from metal surfaces usually show broad peaks whose most probable final angles are either sub-specular or supra-specular depending on initial conditions. The scattering from insulators can show rainbow features caused by the corrugations of the surface. The authors have developed a semiclassical theory for atomic scattering that includes the effects of surface corrugation [1, 2]. When extended to the classical limit of large projectile masses, high incident energies and large surface temperatures this theory is capable of explaining heavy rare gas scattering even in cases where rainbow features due to large surface corrugations are present. Examples will be shown for Ne, Ar and Xe scattering from Ru(0001), graphene covered Ru(0001), and LiF(001). The comparisons of theory with the available experiments suggest the following predictions for further experimental measurements. First, the comparisons of rare gas scattering from Ru(0001) and single-layer graphene covered Ru(0001) suggest that Os(0001) and graphene covered Os(0001) should be highly reflective to rare gas scattering. These results further suggest that Os and graphene covered Os should be highly reflective even under quantum mechanical conditions such as for scattering of He atoms with incident energies in the meV range. Second, the study of heavy rare gas scattering from metal surfaces predicts that the most probable final angle of the observed angular distributions will be sub-specular at low incident energies and will smoothly shift to larger final angles and eventually become supra-specular with increasing incident energy. This implies that, for a given system of projectile atom and metal surface, there will be an incident "recovery" energy at which the most probable final angle of the observed angular distribution will appear at the specular position.

[1] W. W. Hayes and J. R. Manson, Phys. Rev. Lett. **109**, 063203 (2012)
[2] W. W. Hayes and J. R. Manson, Phys. Rev. B **89**, 045406 (2014)

Mo2: Solid-liquid interfaces

INVITED TALK

Liquid flow along a solid surface reversibly alters interfacial chemistry

E. H. G. Backus[1], **D. Lis**[2], **J. Hunger**[1], **S. H. Parekh**[1], **and M. Bonn**[1]

[1]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
[2]Physics Department, University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium

Water in contact with a solid surface is often in motion - e.g. water in riverbeds, rain drops falling on the ground, and pouring water in a glass. The influence of this motion on the structure of water at the interface is unclear. By using sum-frequency generation spectroscopy with an infrared and visible laser beam we can obtain the vibrational spectrum of the interfacial water molecules. We show by combining this technique with microfluidics that the interfacial structure is very sensitive to the motion of the liquid. Flow results in a reversible change of the surface charge and thus an alignment of the water molecules present at the interface. We observe this effect for calcium fluoride and silicondioxide interfaces at various pH. To obtain the same effect under static conditions, the pH of the bulk solutions has to be changed by up to 2 pH units. Moreover, we show that flow can invert the orientation of water molecules at the interface [1].

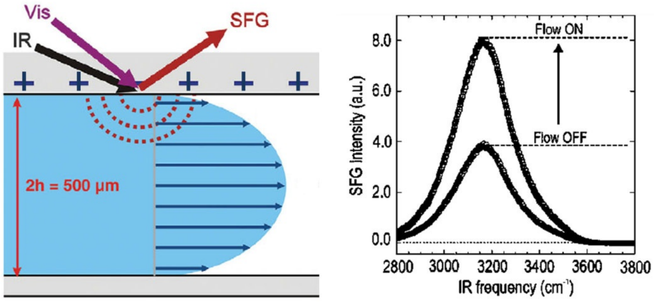


Figure 1: experimental geometry (left) and SFG spectra with the flow on and off for water at pH=3 underneath a CaF_2 window (right).

[1] D. Lis et al., Science **344**, 1138 (2014)

INVITED TALK

From UHV to the solid/liquid interface: Water adsorption, surface reconstruction and dynamics on α-Al_2O_3

R. K. Campen

Fritz Haber Institute of the Max Planck Society, Berlin, Germany

α-Al_2O_3 surfaces exposed to water are ubiquitous in applications and a useful model for alumino-silicate surface/water interactions omnipresent in the environment. Despite this ubiquity, gaining a molecular level understanding of water interaction even with the crystallographically simplest α-Al_2O_3(0001) surface has proven challenging. Here we begin with the well defined α-Al_2O_3(0001) in ultra high vacuum and add controlled amounts water culminating in the solid/liquid interface. We characterize this system principally using time-averaged and ultrafast time-resolved vibrational sum frequency (VSF) spectroscopy in combination with a variety of electronic structure calculations. VSF spectroscopy is all-optical and interface specific by its symmetry selection rules and thus allows us to probe the spectral response of interfacial water, through its OH stretch, and surface Al-O vibrations (i.e. surface phonons) over 10^{10} range in water chemical potentials. This combination of sample preparation and characterization has allowed a series of novel insights: (a) we have experimentally probed the (heretofore only theoretically predicted) unimolecular water dissociative adsorption pathways and shown their relative thermal stabilities [1], (b) we have quantified the effect of water adsorption on surface structure by tracking the surface phonon spectral response as a function of water chemical potential providing new experimental observables for the characterization of partially reconstructed oxide surfaces [2] and (c) we have shown that the α-Al_2O_3(0001)/liquid water interface is, at circumneutral pH, hydrophobic: that the first layer of adsorbed water does not donate hydrogen bonds to bulk liquid.

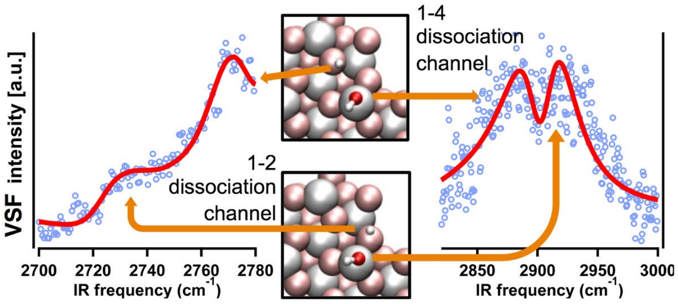


Figure 1: Summary showing the measured spectra of the two theoretically predicted unimolecular water dissociation pathways on the α-Al_2O_3(0001) surface in UHV.

[1] H. Kirsch et al., J. Phys. Chem. C **118**(25), 13623-13630 (2014)
[2] Y. Tong et al., J. Chem. Phys. **142**(5), 054704 (2015)

CONTRIBUTED TALK

Spontaneous ferroelectric ordering of strongly correlated protons in crystalline ice films on Pt(111)

T. Sugimoto, N. Aiga, Y. Otsuki, K. Watanabe, and Y. Matsumoto

Department of Chemistry, Graduate School of Science, Kyoto University, Japan

Protons in ice are strongly correlated due to the ice rules [1]. The kinetic barrier of the synchronized proton motion at low temperature is so high that transition of bulk ice from the ordinary paraelectric state (proton disordered ice-I) to the ferroelectric state (proton ordered ice-XI) is practically prohibited without catalysts that promote proton transfer [2].

On the basis of the vibrational sum frequency generation (VSFG) spectroscopy [3], we report here substantial and extremely high-T_c ordering of strongly correlated protons in crystalline-ice films deposition on Pt(111). Heterodyne-detected VSFG (HD-VSFG) spectra revealed significant orientation preference of first-layer water molecules pointing toward substrate (H-down configuration) and the subsequent progressive propagation of the net-H-down orientation during multilayer deposition process (Fig.1a). The polarized ice film also showed a reversible and second-order like gradual thermal depolarization/repolarization during heating/recooling process with unexpectedly high critical temperature of T_c~180 K (Fig. 1b), proton dynamics of which is completely different from that in proton-ordered bulk ice-XI; irreversible and 1st-order depolarization to proton-disordered ice-I at T_c~72 K [2]. The emergent ordering is dominated by short range constraint of ice rules and their partial breaking due to the screening of polarization charges through the electron transfer at ice/Pt(111) heterointerface followed by the rearrangement of mobile protons.

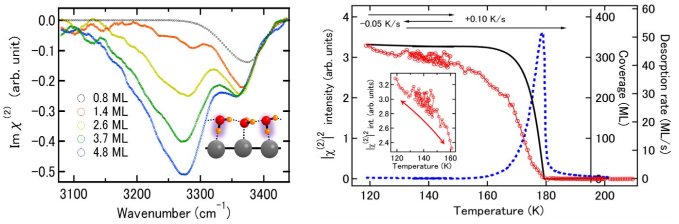


Figure 1. (a) HD-VSFG (Imx$^{(2)}$) spectra of OH-stretch band for HDO crystalline ice film deposited on Pt(111) at 140 K. (b) Simultaneous measurements of VSFG spectra and temperature programmed desorption (TPD). Red circle with red solid line, blue dotted line, and black solid line are VSFG, desorption rate (QMS-mass 19), and coverage, respectively, at each temperature for 330 ML crystalline-HDO-ice film.

[1] L. Pauling, J. Am. Chem. Soc. **57**, 2680-2684 (1935)
[2] Y. Tajima, T. Matsuo, and H. Suga, Nature **299**, 810 (1982)
[3] Y. R. Shen, Annu. Rev. Phys. Chem. **64**, 129 (2013)

CONTRIBUTED TALK

The motion of water on a hydrophobic surface

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We have prepared a system where we can follow the diffusion of water molecules on a picosecond timescale. While the desire to understand the behaviour of water at the nanoscale led to numerous experimental and theoretical studies [1,2], little is known when it comes to the dynamics of water from an experimental point of view [3,4].

By using helium-3 spin-echo spectroscopy [5] we are able to determine the motion of water on the system graphene/Ni(111). The hydrophobic nature of the substrate allows to measure the diffusion of water within a small temperature window (115 - 130 K) by applying an overpressure of water and hence maintaining a dynamic adsorption/desorption equilibrium.

The molecular dynamics extracted from spin-echo measurements shows thermally activated diffusion with a jump mechanism and an activation energy of 60 meV (see figure 2). The dependence upon the momentum transfer clearly shows jumps on a lattice where the preferred adsorption site of H_2O is in the middle of the carbon hexagons (see figure 1). While this is in agreement with density functional theory (DFT) calculations, the energy landscape obtained from DFT is rather flat and cannot explain the experimentally determined activation energy. Furthermore, a characteristic rise at small momentum transfers indicates that interactions between the individual water molecules play a mayor role in the diffusion of water on graphene.

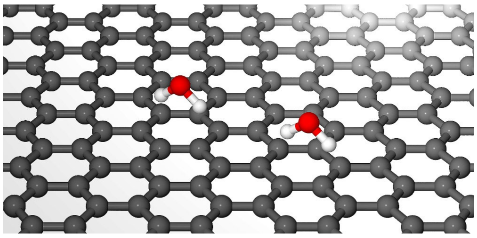

Figure 1: Graphical representation of two water molecules adsorbed on graphene. The preferred adsorption site is in the middle of the hexagon formed by the carbon atoms.

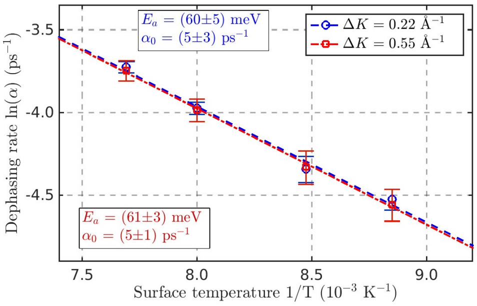

Figure 2: Arrhenius plot for the diffusion of water molecules on graphene/Ni(111) showing an activated process with an activation energy of 60 meV.

[1] A. Hodgson et al., Surf. Sci. Rep. **64**, 381 (2009)
[2] J. Carrasco et al., Nat. Mater. Sci. **11**, 667 (2012)
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Tu1: Transport in electronic devices

INVITED TALK

Polaron transport in organic crystals: theory and modelling

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The charge-carrier mobility of organic semiconductors is a fundamental material property and one of the central quantities for the optimization of device performance in, e.g., organic transistors and organic/hybrid solar cells. In order to investigate the intrinsic fundamental (i.e., not device-specific) charge-transport phenomena in organic solids, molecular crystals are ideal candidates because of their high degree of structural order. Nonetheless, even for such ultrapure organic crystals, the theoretical and numerical description of the charge transport is a highly nontrivial task due to the strong coupling between the electronic and vibronic degrees of freedom.

In this talk, I will present a theory for charge transport in organic crystals which generalizes Holstein's small polaron model to polarons of arbitrary size and allows to calculate the carrier mobilities using ab-initio techniques (density-functional theory). The generalized mobility expression includes both the coherent band transport as well as the thermally induced hopping on equal footing. As a prototypical example, the theory is applied to herringbone-stacked crystals where the temperature dependence of the mobilities is simulated and compared to experimental data. Finally, the mobility anisotropy is analyzed by a novel 3D visualization technique for the relevant transport channels.

[1] K. Hannewald et al., Phys. Rev. B **69**, 075211 & 075212 (2004)
[2] K. Hannewald and P.A. Bobbert, Appl. Phys. Lett. **85**, 1535 (2004)
[3] F. Ortmann, F. Bechstedt, and K. Hannewald, Phys. Rev. B **79**, 235206 (2009)
[4] F. Ortmann, F. Bechstedt, and K. Hannewald, New J. Phys. **12**, 023011 (2010)
[5] F. Ortmann, F. Bechstedt, and K. Hannewald, Phys. Stat. Sol. B **248**, 511 (2011)
[6] D. Nabok, C. Draxl, and K. Hannewald, Acc. Chem. Res. **47**, 3225 (2014)

INVITED TALK

IETS of single molecule transistors

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Electron devices containing molecules as the active region have been an lively area of research over the last few years. In molecular-scale devices, a longstanding challenge has been to create a true three-terminal device; e.g., one that operates by modifying the internal energy structure of the molecule, analogous to conventional FETs. Here we report [1] the observation of such a solid-state molecular device, in which transport current is directly modulated by an external gate voltage. We have realized a molecular transistor made from the prototype molecular junction benzene dithiol (BDT), and have used a combination of spectroscopies to determine the internal energetic structure of the molecular junction, and demonstrate coherent transport [2,3]. Resonance-enhanced coupling to the nearest molecular orbital is revealed by inelastic electron tunneling spectroscopy (IETS), demonstrating for the first time direct molecular orbital gating in a molecular electronic device [1].

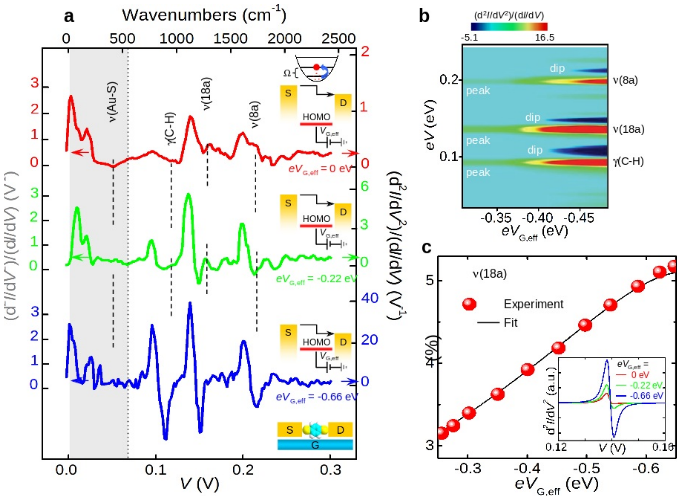

Figure 1: (a) Gate dependent IETS (4.2K) of a BDT transistor. The left-hand y axis corresponds to the grey shaded region, and the various right-hand y axes (with different scales) correspond to spectra in the non-shaded region. (b) Two dimensional color map of the gated IET spectra. (c) Persson-Baratoff resonantly enhanced IETS model of the v(18a) mode.

[1] H. Song et al., Nature **462**, 1039 (2009)
[2] H. Song et al., J. Appl. Phys. **109**, 102419 (2011)
[3] H. Song et al., J. Phys. Chem. C. **114**, 20431 (2010)

CONTRIBUTED TALK

Environmental control of single-molecule conductance

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Electrical properties of single molecules have attracted much attention due to their potential use as basic components of electronics in the limits of miniaturization. To this end, significant experimental efforts have been devoted to make molecular junctions and probe their electrical properties. To precisely measure the conductance through a molecule, reliable connections of the metal probes to the molecule must be made. With scanning tunneling microscope (STM) junctions, one can bridge a 'target' molecule between the tip and substrate and reliably study the conductance through single molecules [1, 2]. Another characteristic of STM is that individual atoms and molecules can be manipulated on the surface with atomic-scale precision, which was used to investigate and control the interaction between them. To make good use of these advantages in the contact regime, it is important to preserve an identical tip-molecule contact geometry during repeated junction formation, which then enables one to compare the conductance through a single molecule on the surface in different arrangements and orientations of neighboring molecules.

Here we present such a non-destructive contact that uses a phenyl ring to reversibly connect the molecule to the tip electrode. In a prior work [3], we studied the adsorption of a phenoxy molecule on Cu(110) and found that it is bonded to the surface via an oxygen atom in a nearly flat configuration. When the STM tip is gradually approached to such a flat-lying phenoxy molecule on the surface at one point the molecule flips up and makes contact to the tip apex while remaining anchored to the Cu surface via the oxygen atom, thus forming a molecular junction between the two electrodes. Because the tip-phenyl interaction is relatively weak (π-bonding) as compared to that between molecule and substrate (covalent bonding), retraction of the tip causes cleavage at the same tip-phenyl interface, releasing the molecule to the original position on the surface without any perturbation of the tip apex. Thus, repeated switching of a phenoxy junction is feasible with this setup. This enables us to investigate the molecular conductance with unprecedented precision and to compare the conductance of a junction in different prearranged environments to reveal the impact of surrounding molecules.

[1] N. Neel et al., Phys. Rev. Lett. **98**, 065502 (2007)
[2] W. Haiss et al., Nature Mater. **5**, 995 (2006)
[3] Y. Kitaguchi et al., J. Chem. Phys. **139**, 044708 (2013)

CONTRIBUTED TALK

Electronic and vibronic properties of atomically precise bilayer graphene nanoribbons

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Graphene nanoribbons (GNRs), by quantum confinement and edge effects, exhibit exceptional electronic properties such as tunable band gaps and magnetic edge states. Here, we focus on armchair GNRs of width N=7 (7-AGNR) as grown on Au(111) via bottom-up method [1,2]. In order to electronically decouple ribbons from the metallic growth substrate, post-growth transfer of the ribbons to insulating substrates is typically needed. In this work, we establish a STM manipulation routine, which allows transferring ribbons with length from 3 nm to 10 nm *in situ* onto various nanostructures such as NaCl islands or other ribbons where the later results in the formation of atomically precise bilayer nanoribbon structures (Fig. 1a).

Scanning tunneling spectroscopy is used to investigate the electronic and vibronic properties of bilayer ribbons. Our well-controlled experimental measurements of 7-aGNRs on top of another ribbon unambiguously resolved magnetic end states at the zigzag termini. Interestingly, we found that the two respective ends of the ribbon exhibit different spectroscopic features, where one end shows an energy splitting of magnetic end states of 0.5 eV and the other end a splitting of 1.3 eV. Besides the main features of magnetic end states, we observed equally-spaced satellite peaks beyond the main peak which is associated with the vibrations of ribbon ends due to inelastic tunneling process. In order to further elucidate our experimental observations, we have performed both, tight-binding and DFT calculations. For the periodic bilayer, on-top and Bernal-type stacking were compared. Bernal-type stacking is more favorable by 140 meV per armchair unit cell and corresponds to a stacking distance of 3.40 Å, which results in two ends with different adsorption configurations, and further affects the energy splitting of magnetic end states. However, both, tight binding and DFT calculations predict a difference of only 50 meV between the magnetic end state splitting at the respective ends, which is significantly smaller than the experimentally observed 800 meV. The reasons behind this discrepancy will be discussed in view of the role of charge doping of GNRs. Furthermore, we will discuss the electronic structure of GNRs that have been decoupled from the metal substrate by STM-based manipulation onto NaCl islands.

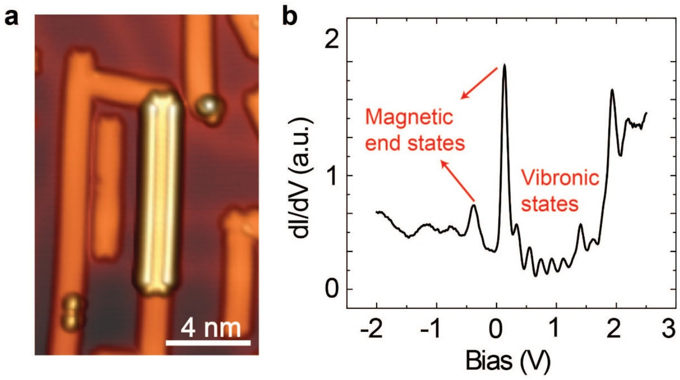

Figure 1: a: STM topography image of a (7, 40) GNR transferred onto another ribbon through STM manipulation (U_{sample} = -1.0 V, I = 100 pA). b: differential conductance spectrum taken at one end of the upper ribbon showing satellite vibronic peaks.

[1] J. Cai et al., Nature **466**, 470 (2010)
[2] H. Söde et al., Physical Review B **91**, 045429 (2015)

Tu2: Surface diffusion and migration

INVITED TALK

The use of atom-surface band structures as a framework for considering quantum effects in surface diffusion

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We have used the helium spin echo (HeSE) technique to study the temperature dependence of H and D diffusion on the Cu(111), Pt(111) [1], Ru(0001) [2], and Ni(111) surfaces, finding both activated and tunnelling diffusion regimes. The quantum states occupied by the H/D atoms are central to any discussion of surface dynamics, so we have calculated the band structures of the H/D atoms moving in a 3D atom/surface potential derived from DFT calculations. These band structures are then used within a transition state theory formalism to calculate temperature dependent diffusion rate. Good agreement is found both with the adatom vibrational frequencies measured with EELS [3-6] and with the rate of diffusion in the 'activated' regime for all of the substrates indicating that the adatom-surface energy correlation time must be comparable with the time taken for the moving adatoms to complete a jump. However, the simulations significantly underestimate the diffusion rates in the tunnelling regime. We show that even in the tunnelling regime the band structures can be used as a basis for a discussion of the observed diffusion rates.

It is widely assumed that quantum effects are essentially limited to hydrogen diffusion. We present HeSE data that shows that during jumps on the Ni(111) surface, CO moves ballistically with an effective mass some 200 times larger than its actual mass. An empirical 2D CO-surface potential energy surface is constructed from the measured CO adsorption site energy differences and from the activation barrier to lateral diffusion. The calculated band structure of the CO centre of mass motion predicts an increase in effective mass for the diffusion CO that is comparable with the experimentally measured value. It is likely that the 3-fold increase in effective mass for methane diffusion on Pt(111) observed with ToF-quasi elastic helium scattering has a similar cause [7]. The observation of such a large effective mass for a relatively massive molecule suggests that quantum effects can have a significant effect on the diffusion of relatively massive ad-species and will sometimes need to be included in attempts at first principles predictions of diffusion rates.

[1] A. P. Jardine et. al., Phys. Rev. Lett. **105**, 136101 (2010)
[2] E. M. McIntosh et. al., J. Phys. Chem. Lett. **4**, 1565 (2013)
[3] E. M. McCash et. al., Surf. Sci. **215**, 363 (1989); C. L. A. Lamont et. al., Chem. Phys. Lett. **243**, 429 (1995); G. Lee and W.E. Plummer Surf. Sci. **498**, 229 (2002)
[4] S. C. Badescu et. al. Phys. Rev. Lett. **88**, 136101 (2002)
[5] K. L. Kostove et.al., Surf.Sci. **560**, 130 (2004)
[6] W. Ho et. al., J. Vac. Sci. and Technol **17**, 134 (1980)
[7] A. P. Graham, J. Ellis, and J.P. Toennies, unpublished work

INVITED TALK

Surface diffusion of aromatics through van der Waals landscapes and beyond

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[6]Institut Laue-Langevin, CS 20156, 38042 Grenoble Cedex 9, France
[7]Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey 08854, USA
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Beginning with the simple aromatic system of benzene molecules adsorbed on a graphite surface [1], we utilise a combination of helium spin-echo spectroscopy (HeSE) and density functional theory (DFT) to explore the surface motion of a number of cyclic molecules with conjugated bonding [2-4]. We establish accurately the surface energy landscapes that could template the molecules' self-assembly and give insight into the dominant modes of motion along the diffusion pathways.

The weakly physisorbed system of benzene/Cu(001) shows bonding dominated by the van der Waals interactions that have previously been difficult to estimate with density functional calculations. Here we couple experimental surface dynamical data with molecular dynamics simulations to allow comparison with van der Waals DFT. Additionally, we gain an increased understanding of the effect of the molecular modes of motion on the density of states at the transition state and subsequent molecular friction and surface dynamics.

As we develop our understanding of aromatic systems, of particular interest are the series of five-membered rings: cyclopentadienyl (C_5H_5), pyrrole and thiophene where, by substituting one of the ring atoms, we influence charge transfer [2] and the effect of the contribution of the molecules' vibrational states to the resultant motion [3]. The dynamic friction in these systems is discussed in terms of the rate of energy transfer between the adsorbed molecules and the substrate and we consider the mechanisms associated with the molecular degrees of freedom that could lead to the high values seen in experiment [5].

Our most recent measurements extend to aromatic polycyclic and macrocyclic compounds. These larger molecules raise new questions for the refinement of the established models of diffusion familiar within the surface dynamics and neutron scattering communities.

[1] Nature Physics **5**, 561-4 (2009)
[2] Phys Rev Lett **106**, 186101 (2011); J Phys Chem C **115**, 16134-1 (2011); Phys Rev B **89**, 121405(R) (2014)
[3] Angw Chem Int Ed **52**, 5085-8 (2013)
[4] J Phys Chem Lett **4**, 1953-8 (2013)
[5] J Chem Phys **138**, 194710 (2013)

CONTRIBUTED TALK

Investigation of surface structure and diffusion dynamics of hydrogen adsorbed on Sb(111)

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As one of the essential components in the class of topological insulators [1] (TI), the semimetal antimony (Sb) and its surfaces has received growing attention by experimental groups throughout the last years. Despite experimental advances in ultra-high-vacuum (UHV) technologies, experimental studies on pure material surfaces may still suffer from the ever-present hydrogen background in vacuum chambers. Moreover, thin layers of hydrogen are more or less invisible to electron scattering methods. Since adsorbed hydrogen atoms on the surface may alter the electronic response of the material, detecting the presence of hydrogen on the surface of a TI is of major importance.

Helium atom scattering (HAS) provides a completely surface sensitive method of materials characterization and can thus provide information on the structure and electronic properties of the very first layer of the sample material [2,3,4].

HAS experiments were performed on cold Sb(111) surfaces without and with coverage of hydrogen molecules or atoms. While the presence of H_2 did not alter the surface diffraction spectrum compared to an uncovered surface, atomic hydrogen coverage resulted in a complete loss of diffraction peaks at low surface temperature. By raising the temperature, the diffraction pattern was regained. However, heating up to a temperature of 500 K was required in order to obtain the clean surface spectrum.

HAS experimental data of the surface temperature dependent diffraction patterns of ordered hydrogen on Sb(111) as well as a determination of its diffusion energy barrier will be presented.

[1] H. Zhang et al., Nature Physics **5**,438-442 (2009)
[2] M. Mayrhofer-R. et al., J. Phys. Condens. Matter **25**, 395002 (2013)
[3] M. Mayrhofer-R. et al., Phys. Rev. B **88**, 205425 (2013)
[4] P. Kraus et al., Phys. Rev. B **87**, 245433 (2013)

CONTRIBUTED TALK

Diffraction of helium on MgO(100) calculated from first-principles

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Interactions between molecules and crystalline surfaces are of great fundamental and technological interest and extensively studied both experimentally and theoretically. The scattering of He atom beams on crystal surfaces has the potential to be an important technique for determining the atomistic structure and dynamics of surfaces. The He beam scatters from only the outermost surface layers unlike X-ray diffraction and it neither damages or charges the surface unlike electron diffraction and microscopy. During the last two decades its usefulness has been demonstrated in the determination of numerous surface structures. The quantitative interpretation of He-diffraction is, however, limited as the He–surface interaction potential is not known accurately. In our most recent works[1,2], we simulate the diffraction peak intensities of He beams scattered on the MgO(100) surface from first principles. Achieving the required accuracy in first-principles calculations is very challenging indeed. We describe a first principles protocol able to achieve very high accuracy for reasonable computational cost. This method is based on periodic local second-order Moller–Plesset perturbation theory where systematic corrections for basis set truncation and for high-order electronic correlation are introduced using coupled cluster calculations on finite model systems mimicking the target system. For the He–MgO system the requirements with respect to the level of theory are very high; it turns out that contributions from connected quadruple excitations are non-negligible. By using this protocol, it is possible to reach the accuracy in the He–MgO potential that is required to predict the observed He diffraction peak intensities.

[1] R. Martinez-Casado et al, Phys. Chem. Chem. Phys. **16**, 21106 (2014)
[2] R. Martinez-Casado et al, Phys. Rev. B **89**, 1098 (2014)

Tu3: Chemistry and growth of graphene

INVITED TALK

Cycloaddition of metal-supported graphene interfaces: a first principles investigation

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[2] Current address: Laboratoire Pasteur, ENS, Paris, France

Chemistry is playing a vital role in the realization of graphene applications. The chemical formation of covalent carbon-carbon bonds involving the graphene layer potentially allows the generation of insulating and semiconducting regions, crucial for electronic devices. In particular, covalent functionalization of graphene by aromatics via Diels-Alder (DA) reactions is emerging as a facile way to achieve these goals.

The cycloaddition reactions of iron porphine with graphene epitaxed to a series of lattice-matched and lattice-mismatched metal surfaces have been investigated by using dispersion-corrected density functional theory (DFT) calculations. Our calculations evidence the non-classic cycloaddition with 3π units from graphene on specific hollow C -top C -hollow C registry areas. The feasibility of the cycloaddition depends on the nature of the metal below graphene : Ir is the most reactive metal while Re is less reactive and Cu almost inactive. [1]

We also propose that iron phthalocyanine reacts similarly with graphene on Ir, causing the STM disappearance of one of the four molecular lobes. [2] Our results provide a fertile playground to the community of chemists working on the functionalization of graphene-related substrates.

[1] M. Lattelais and M.-L. Bocquet, J. Chem. Phys. C, in press 2015.
[2] S. J. Altenburg, M. Lattelais, B. Wang, M.-L. Bocquet and R. Berndt, submitted 2015.

CONTRIBUTED TALK

Vibrations, optics and bonding in graphene based heterosystems functionalised with hydrogen

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Vibrational spectroscopy is among the main tools for the non-invasive characterisation of confined systems (see, e.g., [1]). Thus, it is important to theoretically decode the experimental phonon spectra in terms of microscopic structure of 2D materials, and their electron and bonding properties by extracting their vibrational signatures. We demonstrate the application of such a theoretical approach to characterise electron structure and bonding modification in functionalized graphene and graphene-like-systems (GLSs), which contain bilayers and trilayers. Important requirements for the microelectronic application of such heterosystems (e.g., in 2D p-n junctions) include (i) opening of the electron band gap, (ii) possibility of gap tuning, (iii) creating strongly bonded GLS multilayers and /or depositing the atomically thin monolayers on various substrates. Despite the unique properties of graphene, one challenge is that it is a gapless material. On the other hand, the band gaps of completely hydrogenated graphene (called graphane) or one-atom thick boron nitride (BN) film, both having band gap near to 5 eV, are representative of insulators rather than semiconductors. Importantly, however, the gap can be opened and adjusted by demand, as we have recently demonstrated: the partial graphene hydrogenation [2] opens the band gap, which can be tuned in the wide range by varying H content. This theoretical prediction was confirmed experimentally [1]. A challenge to creating a stable bilayer and trilayer GLS or depositing GLS films on a substrate for device applications is the weakness of van der Waals interlayer bonding in graphene and GLS. Therefore a stronger, preferably covalent, interaction between the layers and / or substrate is desirable.

We discuss here the concept of 2D electron band engineering of GLS functionalized materials that simultaneously satisfies all the above requirements (i) - (iii) and demonstrate non-invasive characterisation of created 2D heterosystems by vibrational and optical methods. In our computer simulations the first principles Quantum Espresso code [3] was used for structure optimization, molecular dynamics (MD), calculation of phonon spectra and optical response. First, we considered atomic structure of graphene multilayers and / or alternating graphene films with semiconducting BN or silicon carbide (SiC) analogue of graphene, functionalized with low dose of hydrogen added on both sides. We previously proved that the one atom-thick SiC nano-layer is thermally stable and can be produced experimentally. Such partial hydrogenation on top and bottom of a 2D sandwich of two or three one-atom thick films not only passivates the outer dangling bonds, but also leads to the formation of covalent bonds between the layers, initially connected by weak van der Waals forces. Secondly, finite temperature MD was used to investigate the thermal stability of the 2D heterosystems of interest and to extract the phonon spectra using the velocity discrete correlation function. Finally electron band structure and optical response of the 2D heterosystems were studied. Submonolayer hydrogenation of the outer surfaces of the multilayer systems, which induces interlayer covalent bonding, opens a controlled gap in otherwise gapless graphene. Structural, vibrational, electronic and optical properties of the various systems of interest were calculated and compared. The formalism developed opens the possibility to experimentally control and characterise properties of graphene based multilayer systems.

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CONTRIBUTED TALK

Helium diffraction from graphene grown by chemical vapor deposition on copper catalysts

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In this work we use Helium atom scattering (HAS) as a sensitive probe of the crystallinity of graphene grown by chemical vapor deposition (CVD) on Cu, and as a probe of its interactions with its substrate. The high sensitivity of HAS to surface defects [1] precluded its use with current available graphene/Cu foils. Our current results have been obtained using graphene/Cu(111) grown on sapphire samples and graphene grown on a peeled-off epitaxial Cu(111) foil using a recently developed scheme [2]. We have measured the structure and the acoustic phonon modes of CVD graphene grown on these two samples. The observation of high reflectivities and clear diffraction peaks demonstrates the presence of high-quality graphene, with both long-range order and a very low density of defects over a surface area of the order of 1mm^2. The shape of elastic and quasi-elastic scattering features proves that, surprisingly, graphene grown on a peeled-off epitaxial Cu(111) foil exhibits a much higher crystallinity than the one grown on Cu(111)/Al_2O_3 samples. The graphene lattice parameter was found to remain constant in the temperature range between 110-500 K, which proves that graphene is decoupled from the Cu substrate. A parabolic dispersion phonon branch has been measured along ΓM, as expected for the acoustic ZA mode in free-standing graphene.

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Tu4: Electron-phonon coupling in graphene

INVITED TALK

Electron phonon mediated transitions in 2D materials; towards a designer superconductor?

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Electron-phonon coupling in conductors is largely responsible for electrical resistance, and is a major cause of power dissipation. On the other hand, exceptionally strong electron-phonon coupling is a prerequisite for traditional superconductivity. Thus, adequate control of the electron-phonon interaction could facilitate the conversion of lossy conductors into lossless superconductors.

To be more specific, strong changes in the electron-phonon interaction can be created by a sudden change in the electron density of states (eDOS). Traditionally, this involves the sudden change in eDOS which is found at the Fermi level - but we have demonstrated that other eDOS changes also cause a strong modification of the electron-phonon interaction. This is especially clear in graphene-like materials, where the eDOS change at the sigma band maximum is very much stronger that that at the Fermi level. Through calculational support, we believe that sufficiently strong doping could allow such materials to support a sigma-band superconducting phase to exist.

Additionally, whilst electron scattering between orthogonal bands is forbidden, we have shown that such scattering exists in graphene-like materials when mediated by a phonon interaction (which temporarily breaks the orthogonality). The temporary lattice distortion facilitates scattering between sigma and pi bands in graphene, and also contributes to a total increase in the electron-phonon interaction. With sufficient doping, this interaction would contribute to an unusually high superconducting transition temperature.

Here, I will present our recent experimental work, alongside simulations and recent calculations. I will show that exceptionally strong electron-phonon coupling exists in the sigma-band of graphene, and that phonon mediation transitions between the pi and sigma bands are also observable. Finally, I will speculate on the possible existence of a superconducting phase in 2D graphene-like materials, and describe our ongoing efforts to realise this experimentally.

CONTRIBUTED TALK

Momentum-resolved direct-observation of the electron-phonon scattering for graphite and graphene by using ARPES and HREELS

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The electron-phonon coupling (EPC) is one of the key issues in the solid/surface state physics. Recently, we proposed a new experimental method which enables us to probe the electron-phonon scattering in HOPG graphite with resolving the momentum and energy of both the electron and the phonon by using the angle-resolved photoelectron spectroscopy (ARPES)[1]. Here, we report recent progresses in the investigation using this method on the single-crystalline graphite and the epitaxial single layer graphene on SiC. When the photon energy is tuned to the excitation to a specific final state, an indirect transition accompanying the electron-phonon scattering can be probed directly by the ARPES[1]. The scattering geometry is shown in Fig.1(a) when the electron emission along the Γ-K line of the graphite is measured, and examples of the ARPES spectra are shown in Fig.1(b). The step-like structures near the binding energy of 150meV are due to the Fermi-edge of the electron, originally located at the K and K' points, scattered into points along the Γ-K line. The energy shift from the Fermi level is ascribed to the energy conservation law in the scattering process and the energy position of the step matches the phonon energy. The momentum conservation law enables us to determine the phonon momentum (except the ambiguity in two lines, K'-Γ and K-M-K'), thus the phonon dispersion can be derived from the experiments as shown in Fig. 1(c) along with the calculation. Only the transverse optical (TO) phonons obtained with the GW-calculation agree the experiments. This indicates that the TO-phonon has much greater efficiency to scatter the electron than the LA or LO phonon in this condition. It should be noted that this phenomenon has a strong photon-energy-dependence. In fact, when a different final state is chosen by changing the photon energy to 7eV, we observe the scattering not by the TO but by the phonons of the interlayer vibration (ZA and ZO modes). In the case of the graphene on SiC, meanwhile, the scattering by the TO phonons is also observed at the photon energy of 10.8eV, but no scattering by ZA or ZO phonons are observed at any photon energies. We will discuss the physical origin of this difference between the graphite and graphene. We also report the high-resolution electron energy loss spectroscopy (HREELS) study for probing the electron-phonon scattering between specific unoccupied bands by tuning the angle and energy of the electron.

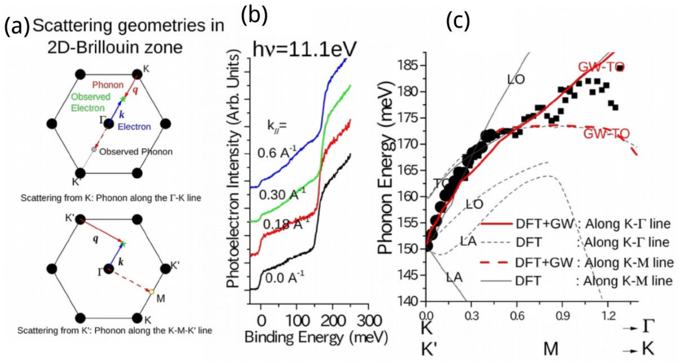

Figure 1: (a): Schematic geometry for measuring the phonon dispersion in EPC on single-crystalline graphite, (b): the ARPES spectra near the Fermi level along the Γ-K line, (c): the phonon dispersion obtained by the experiments (dots) compared with calculation (solid and dotted lines).

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CONTRIBUTED TALK

Terahertz optical modes of supported graphene bilayer

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The peculiar and promising thermal properties of graphene are strongly influenced by interactions with the substrate, presence of defects and lattice distortions. At low temperature, thermal capacity and conduction are mainly related to the properties, i.e. dispersion and density of states, of the acustic modes. The ability to tune these modes can therefore open the way to a fine control on the thermal properties of graphene-based systems, through the so-called phonon engineering [1]. Moreover, ultra-low frequency vibrations could have interesting applications such as the design of novel electromechanical nanoresonators operating in the THz range [2].

In this work, we investigate by HREELS the vibrational properties of a graphene bilayer, grown on the Ru(1000) surface (BLG@Ru) [3], unraveling the details of phonon dispersions in the THz region.

As shown in the inset of Fig. 1 a typical HREEL spectrum is built by several peaks, observed in both loss and gain sides. Spectra are fitted with a sum of gain-loss Voigt doublets, thus allowing a precise determination of the peak energy. In Fig.1 the dispersion curves are shown and compared with the theoretical dispersion of the freestanding bilayer of graphene (BLG) [4]. In the BLG case, the ZA branch splits, giving origin to the optical mode ZO', i.e. a breathing mode of the two layers [4,5]. Moreover, the TA and LA modes are expected to give origin to an optical ultra-low frequency shear mode [6,7]. In the case of BLG@Ru, we observe three optical modes, which near the Γ point are located at 4.7 (38), 8.2 (66) and 12.5 (101) meV (cm^{-1}), respectively. Interestingly, these modes survive also at higher momentum, displaying little dispersion. These findings can be rationalized taking into account the role of the mismatch-induced layer corrugation on the phonon dispersions. In particular, the coexistence of nano-regions characterized by different interlayer distances could explain both the splitting of the optical branches and their partial localization.

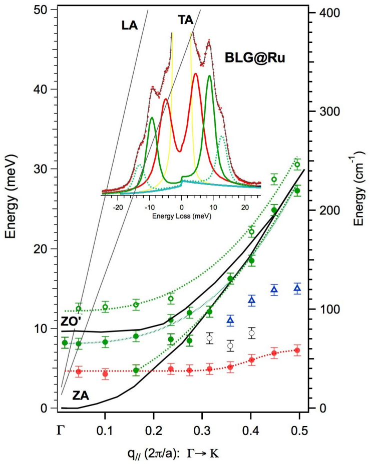

Figure 1: Phonon dispersion curves of BLG@Ru (open and filled symbols). The dotted lines are guidelines for the eyes. The solid-line black curves represents the free BLG dispersions [4]. In the inset, a typical HREELS spectrum is displayed, together with the fitting curves.

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CONTRIBUTED TALK

Nanostructured phonons in epitaxial graphene on ruthenium surfaces

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The growth of epitaxial graphene on lattice-mismatched metallic substrates has emerged as a well-established method to achieve high quality and ultra-perfect nanostructured graphene samples [1]. By varying the nature of the metallic substrate, atomic-scale control can be exerted on the graphene-metal interaction and on the resulting properties of the supported graphene layer, as demonstrated by the observation of periodic deformations in the graphene morphology [2] as well as of highly confined electronic states appearing in the proximity of the Fermi level and well above it [3,4]. Nevertheless, the impact of such modulations on the vibrational properties of these systems has been explored to a much lesser extent [5,6]. Here, we characterize the phonons of the moiré superstructure formed by epitaxial monolayer graphene on Ru(0001) by large-scale frozen phonons density functional theory simulations to evaluate the lattice vibrations and the associated electron-phonon couplings [7,8]. We find that, as a consequence of the adsorption on the Ru(0001) surface, the vibrational properties of the graphene layer are strongly modified with respect to the freestanding counterpart, due to the appearance of, e.g., highly confined phonons appearing in the regions of the graphene/Ru(0001) moiré in which the graphene is more detached from the metallic substrate, as shown in Figure 1.

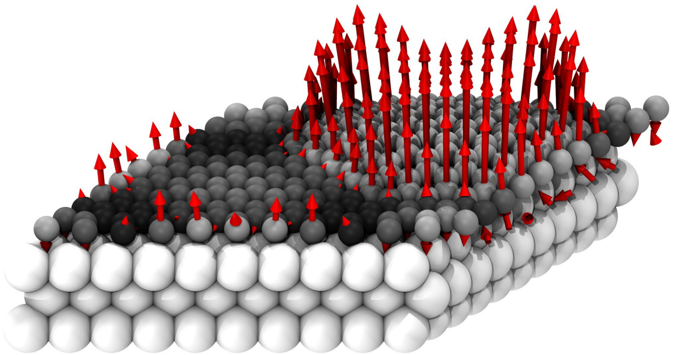

Figure 1: Highly confined phonon in epitaxial graphene on Ru(0001).

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Posters A

POSTER

Surface Structure and Acoustic Phonon Dynamics of graphene on Ni(111)

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The structure and acoustic phonon modes of graphene grown on Ni(111) have been measured by helium atom scattering (HAS). The data are discussed in comparison with earlier HREELS measurements [1,2]. The HAS diffraction spectra reveal that the graphene layer has a three-fold symmetry. The He-specular reflectivity at low temperatures is very high (~20% of incident beam) with a FWHM = 0.07°, which is the limit of our apparatus resolution. This makes this system an excellent candidate to be used as a mirror for He-microscopy. Thermal attenuation measurements give information on the Debye-Waller factor, which were compared to results reported for graphene/Ru(0001) and HOPG. The acoustic phonon modes were determined by time-of-flight measurements. The HAS data are consistent with previous HREELS measurements, and reveal more information on the nature of the graphene-Ni(111) interaction. Surprisingly, the Rayleigh mode observed for graphene/Ni(111) is almost identical to the one measured on clean Ni(111). Our data suggest what appears to be an anomaly in the ZA mode in the middle of the Brillouin zone, as well as a pronounced asymmetry of the ZA mode along both GM and GK directions.

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POSTER

Is the van der Waals interaction relevant to the dissociative dynamics of N_2 on W(110)?

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Using ab initio molecular dynamics (AIMD) calculations we investigate the role of the van der Waals interaction in the dissociative adsorption of N_2 on W(110) [1]. Hitherto, existing classical dynamics calculations performed on six-dimensional potential energy surfaces based on density functional theory (DFT) and semi-local exchange-correlation functionals were unable to fully describe the dependence of the initial sticking coefficient on the molecular beam incidence conditions as found in experiments. N_2 dissociation on W(110) was shown to be very sensitive not only to close molecule-surface distances, but also to the large distances region where the van der Waals interaction, not included in semilocal-DFT, should dominate. In this work, we perform a systematic study on the dissociative adsorption using a selected representation of existing non-local functionals that include the van der Waals interaction. Starting with a pure static analysis of the potential energy surfaces, we find that the original vdW-DF [2] and vdW-DF2 [3] functionals provide a rather good description of the experimental observations regarding the adsorption well and the balance between desorption and dissociation of the chemisorbed N_2. In contrast, the optimized vdW-functionals proposed in Refs. [4,5] share the limitations of the (semi-local) PW91 potential energy surface for this system, i.e., an excessively deep adsorption well from which the dissociation path compared with the desorption one is energetically favored. Unexpectedly, the results of the AIMD performed at different incidence conditions are not as satisfactory as the preliminary static analysis suggested. We have to conclude that none of the used vdW-functionals seem to provide altogether an adequate description of the N_2/W(110) interaction at short and large distances.

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POSTER

Diffusion of H_2O on a NaCl(100)

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The motion of D_2O monomers is investigated on a NaCl(100) bilayer on Ag(111) between 42.3 and 52.3 K by scanning tunneling microscopy and density functional theory [1]. In previous work, we did investigate the diffusion mechanism of H_2O on NaCl(100) at low coverage. For that we determined the energy barriers associated with different hopping mechanisms, classified as translations and reorientations of the water molecule. The combination of these hopping mechanisms leads to net movement of the molecule along the surface with relatively low energetic cost, compared with bare parallel translation of the water molecule [2]. In the recent work the mechanism of the motion is identified by comparison of the experimental results to theoretical calculations. Via low temperature adsorption site determination in connection with density functional theory, we reveal an influence of the metallic support onto the intermediate state of the diffusive motion.

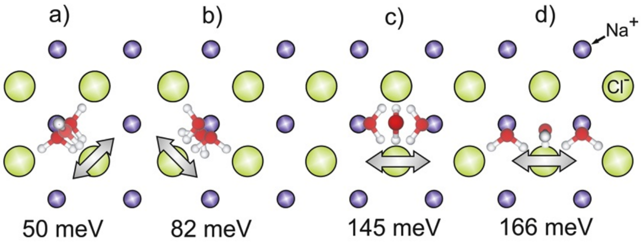

Figure 1: Top view of diffusion processes, (a) OH-flip, (b) parallel rotation, (c) O-flip, (d) higher O-flip. Small blue circles correspond to Na^+, large green circles correspond to Cl^-, red circles correspond to O atoms, and white circles correspond to H atoms.

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POSTER

Structural and dynamical properties of methylated Ge(111) surface

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Germanium has recently attracted a renewed interest for application in electronic devices due to its superior carrier mobility with respect to silicon and the need to substitute in ultrascaled architectures high-k dielectrics for silicon oxide, which is so far the major reason for using Si instead of Ge. A complete and ordered passivisation of the germanium surface by organic adlayers has recently been achieved [1] enlarging the possible technological applications of this material. The vibrational features of methyl-terminated germanium surfaces impact the thermal properties and the ability of the surface to accommodate energy. By combining helium atom scattering spectroscopy (HAS) with density functional perturbation theory (DFPT) we investigated the surface structure and phonon dispersion relations for the CH3 passivated Ge(111)(1×1) surface. This study allows for a characterization of the interactions between the low energy vibrations of the adsorbate and the lattice waves of the underlying substrate, as well as of the interactions between neighboring methyl groups, across the entire momentum-resolved vibrational energy spectrum. As a comparison we also performed DFPT calculations on the CD3-Ge(111)-(1×1) and H-Ge(111)(1×1) surfaces and the hydrogenated and methylated germanium single layer (germanane and methylated germanane).

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POSTER

Adsorption site dependence of vibrational excitations of molecular hydrogen

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Transition-metal phtalocyanines are a well-known class of molecules used as model to study the interaction between metal surfaces and metal-organic compounds [1][2]. These kind of metal-organic complexes present a wide range of properties and functionalities which depend on the coordination of their central metal ion, such as magnetism or the adsorption of small gas molecules [3].

In this work we study Chlorinated Manganese Phtalocyanine (Cl-MnPc) molecules deposited on a Ag (111) substrate. We explore the adsorption characteristics of this system by means of a combined Low Temperature Scanning Tunneling and Atomic Force Microscope. After deposition on a room temperature substrate, a fraction of (dechlorinated) MnPc molecules coexist with Cl-MnPc on the surface. Moreover, Cl-MnPc can be controllably dechlorinated after the evaporation process. We find that both molecules are a preferential site of adsorption for molecular Hydrogen, which is known to present a bistable vibrationally mediated behavior depending on its different adsorption configurations [4]. Inelastic tunneling of electrons from a STM can excite such bistability which induces a fingerprint close to zero-bias on differential conductance measurements. Additionally, force spectra reveal differences on the electrostatic forces exerted between the tip and the molecule when the tunneling electrons trigger such hydrogen fluctuations. We find that these fingerprints are strongly modified by the presence or absence of Chlorine atoms in the phtalocyanine molecules.

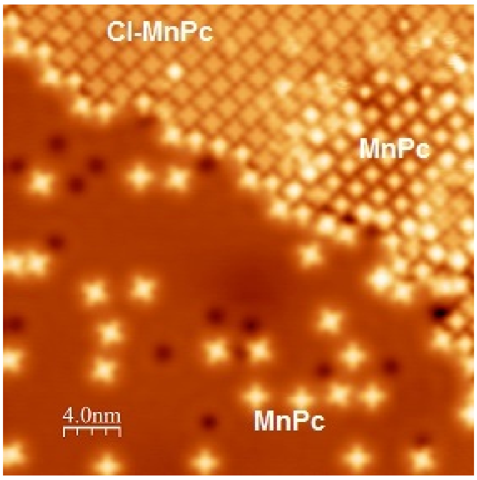

Figure 1: STM image of a self assembled island of Cl-MnPc. MnPcs coexist both in the island and in the Ag (111) surface.

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POSTER

Raman characterization of cove-shape graphene nanoribbons: a first principles study

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Graphene nanoribbons (GNRs), defined as nanometer-wide strips of graphene, are attracting increasing attention as highly promising candidates for nano- and opto-electronics. This interest has been boosted by the possibility to achieve ultra-narrow and structurally well-defined GNRs by bottom-up techniques, where the precise structural pattern is dictated by molecular precursors. While atomically precise GNRs on a metallic substrate can now be produced by advanced and well-established techniques [1], liquid-phase processable GNRs with atomically precise edges have been only recently obtained by solution-mediated methods [2]. Such systems are characterized by cove-shape morphology, where a C ring periodically decorates the zigzag edge. In addition, the solubility is provided by functionalizing the edges with long alkyl chains. These systems show peculiar Raman spectra [2], above all in the low-energy region, which cannot be easily interpreted in light of the previous studies on ideal armchair- and zigzag-edged GNRs [3].

Here we present an ab-initio investigation [4] of the vibrational properties and Raman spectra of such novel structures. We find that both the edge geometry and the functional groups influence the Radial-Like Breathing Mode (RLBM), which is significantly redshited with respect to the case of the zigzag backbone, in agreement with experimental observations [2]. The cove-shape morphology of the edge is instead mainly responsible for the activation of the D peak, which is not present in purely zigzag GNRs [3].

[1] Cai et al., Nature Materials **9**, 611-612 (2010)
[2] Narita et al., Nat. Chem. **6**, 126-132 (2014); ACS Nano **8**, 11622 (2014)
[3] Gillen et al., PRB **80**, 155814 (2009); PRB **81**, 205426 (2010) and references therein
[4] Giannozzi et al., J. Phys. Cond. Matt. **21**, 395502 (2009)

POSTER

Strong electron-phonon coupling in the σ-band of graphene

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We present a first-principles study of the electron-phonon (e-ph) coupling strength in free-standing graphene. We analyze it in terms of the dimensionless mass enhancement parameter λ, resolved in terms of final-state electron energy for a photohole created in either a σ- or a π-band, using the SIESTA code [1] in combination with a finite-difference scheme for the e-ph coupling [2,3]. Our calculations show that λ_σ is significantly greater than λ_π. Near the top of the σ valence band we obtain $\lambda_\sigma \approx 0.8$ in agreement with recent angle-resolved photoemission spectroscopy (ARPES) experiments [4].

As proposed in the experimental work, we confirm that the longitudinal optical phonons provide the most essential contribution to the exceptionally large λ_σ value. However, we also find an important contribution to λ_σ and λ_π from the interband scattering $\pi \rightarrow \sigma$ and $\sigma \rightarrow \pi$, respectively, mediated by the out-of-plane phonons. Finally, we also explore the role of strain which turns out to diminish the interband scattering.

[1] J. M. Soler et al., J. Phys.: Condens. Matter **14**, 2745 (2002)
[2] https://sourceforge.net/projects/inelastica
[3] T. Frederiksen et al., Phys. Rev. B **75**, 205413 (2007)
[4] F. Mazzola et al., Phys. Rev. Lett. **111**, 216806 (2013)

POSTER

Effect of metallic electrodes on opening mechanism of Diarylethene molecule: non-adiabatic molecular dynamics study

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We investigated opening mechanism of a Diarylethene molecule in gas phase or sandwiched between two gold electrodes as consequence of an electron excitation from HOMO to LUMO. We used non-adiabatic molecular dynamics with electronic transitions [1,2] implemented within Fireball code [3]. The simulations reveal quenching of the opening mechanism when the molecule is placed between metallic electrodes. This effect is mainly driven by de-excitation process from localized molecular state to metallic states of electrodes.

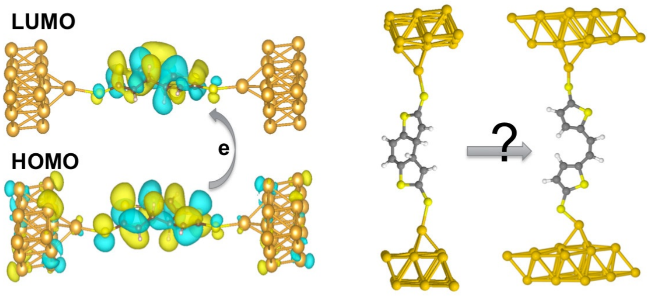

Figure 1: Schematic representation of opening mechanism of Diarylethene molecule after electronic excitation from HOMO to LUMO.

[1] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990)
[2] V. Zobač et al., J. Phys. Condens. Matter. **27**, 175002 (2015)
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POSTER

Tip-enhanced Raman spectroscopy of graphene nanoribbon on Au(111)

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Tip Enhanced Raman Spectroscopy (TERS) is currently one of the most powerful probe techniques available and could be used to study reactions on surfaces at the single molecule level [1]. TERS combines two very well developed techniques scanning probe microscopy (SPM), used to image single molecules on surfaces, and surface enhanced Raman spectroscopy (SERS), used to characterize vibrational spectra also of single molecules on surfaces [2,3]. TERS could therefore provide unique and heretofore unprecedented insight on the adsorbate reactions o at the single-molecule level, e.g., image a molecule while it evolves from reactant to product at well defined surface sites and as well as monitoring vibrational spectra to provide bond specific information about the reaction.

We present the results of tip-enhanced Raman spectroscopy of graphene nanoribbons (GNRs) fabricated on Au(111) by on-surface polymerization technique under ultra-high vacuum conditions [4]. The 0.74 nm wide armchair GNRs are directly observed by scanning tunneling microscopy at room temperature (Fig. 1) and the characteristic vibration modes of GNRs appear in both, the far- and near-field (tip-enhanced) Raman spectra. (Fig. 2) The Raman scattering is enhanced by up to 4 × 10^5 in the near-field, while a strong intensity fluctuation (blinking) frequently emerges in the time series of the near-field spectra. From the STM observation of a stable adsorption structure of GNRs under the laser illumination and statistical analysis of the intensity fluctuation we attribute the origin predominantly to thermal fluctuations of the effective radius of the Au tip apex that induces the localized plasmonic field. The intensity distribution is qualitatively reproduced with a simple theoretical model in which the tip apex is approximated by ideal metal sphere.

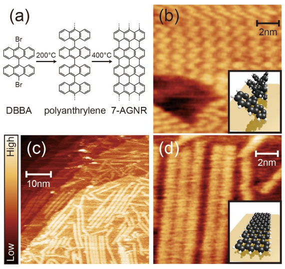

Fig. 1. Preparation of GNR on Au(111).

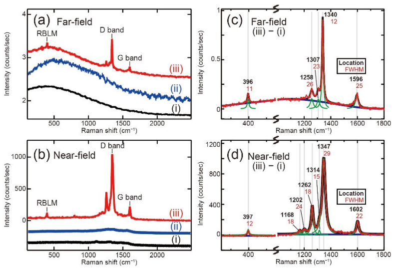

Fig. 2. Far- and near field Raman spectra of GNR on Au(111).

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[3] J. M. Klingsporn et al., J. Am. Chem. Soc. **136**, 3881 (2014)
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POSTER

Femtosecond laser driven molecular dynamics on surfaces: O_2 on Ag(110)

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We present a model for simulating the six dimensional dynamics of an adsorbed molecule on a metal surface which is driven by a ultrashort (~100 fs) laser pulse. Both electron and phonon mediated processes are considered. As an example system we use O_2 on the Ag(110) surface. This system is interesting because it features several adsorption wells, which can then show different dynamical behaviors depending on the three possible outcomes of the simulations: desorption of the molecule, dissociation of the molecule or molecule staying adsorbed in the adsorption well. We simulate the dynamics of the molecule by a classical Langevin model. The interaction of the surface and the molecule is described by a six dimensional potential energy surface which has been recently developed on the basis of semi-local density functional theory [1]. The effect of the laser pulse on the metal surface is described by the two temperature model (2TM), which consists in solving two coupled differential equations for the electron and phonon temperatures. Laser heating of the surface and phonon mediated processes enter the dynamics by setting the surface temperature at every time step in the *Generalized Langevin Oscillator* model (GLO) model to the phonon temperature calculated from the 2TM. The action of laser heated surface electrons on the molecule is modeled by friction and random forces exerted on the molecule. These random and frictional forces are linked via the *fluctuation-dissipation theorem*, and the variance of the random forces is proportional to the electronic temperature obtained from the 2TM. The corresponding friction coefficient is calculated in the basis of the local density friction approximation [2]. In fact, the model is similar to the one used in Ref. [3], but extended to incorporate phonons within the GLO. The dynamics calculations show that for O_2 on Ag(110) inclusion of phonons is important, and that depending on the electronic density in which the molecule is embedded, it can significantly either enhance or reduce desorption probabilities.

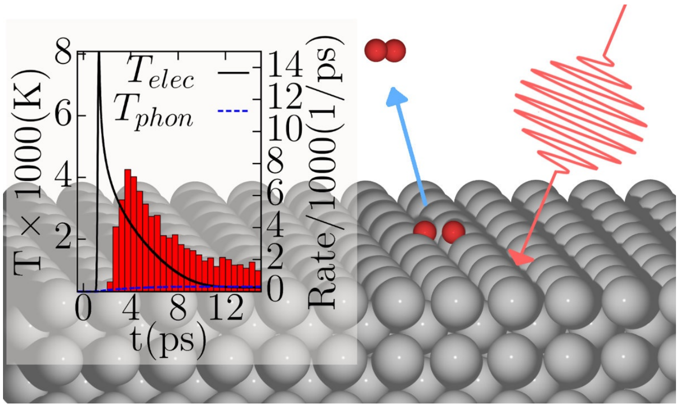

Figure 1: Schematic illustration of the studied problem. In the inset we show electron and phonon temperatures of the surface and the desorption rate.

[1] I. Lončarić et al., Phys. Chem. Chem. Phys. (2015)
[2] J. I. Juaristi et al., Phys. Rev. Lett. **100**, 116102 (2008)
[3] G. Füchsel et al., Phys. Chem. Chem. Phys. **13**, 8659 (2011)

POSTER

The mass correction factor λ of conducting surfaces directly determined from the Helium atom scattering Debye-Waller exponent

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An atom at thermal energy scattered by a conducting surface can exchange energy with the phonon gas of the solid through the oscillations of the electron gas density produced at the surface by the vibrational displacements of the atomic cores. Thus the inelastic atom scattering intensity where a phonon is excited was shown to be approximately proportional to the electron-phonon coupling strength (mass correction factor) for that specific phonon (mode-λ), which enables a mode-λ spectroscopy for the determination of the individual phonon contributions to the mass correction factor. Applying the standard approximations of electron-phonon coupling theory for metals to the distorted wave Born approximation for the atom scattering from the surface potential leads to expressions which relate the elastic and inelastic scattering intensities, as well as the Debye-Waller factor, to the well known mass correction factor of superconductivity theory. This treatment, besides reproducing the previously obtained result that the intensities for single phonon inelastic peaks in the scattered spectra are proportional to the respective mass correction components, leads to a useful result for the Debye-Waller factor $W(T)$. The intensities of elastic diffraction peaks are proportional to $\exp[-2W(T)]$ and their logarithmic temperature dependence is a linear function of the absolute temperature with a slope roughly proportional to the total mass-correction factor λ. As a first application an analysis is presented of such temperature dependence for grapheme on different substrates. The relative size of λ is shown to nicely correlated with that of Kohn anomalies eventually observed in the dispersion curves of the optical branches. The dependence of the elastic and inelastic scattering, and that of the Debye-Waller factor, on the mass correction factor shows that measurements of elastic and inelastic spectra of atomic scattering are capable of revealing detailed information about the electron-phonon coupling mechanism in the surface electron density.

POSTER

Inelastic disordered transport applied to graphene nanoribbons with hydroxyl impurities

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[2]Departamento de Física - UFSC, Brazil
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With the trend toward decreasing the dimensions of electronic devices, the interaction between electrons and ionic vibrations plays an important role in electronic transport. The electron-phonon coupling can cause the loss of the electron's phase coherence, the opening of new conductance channels and the suppression of purely elastic ones. From the technological viewpoint phonons might restrict the efficiency of electronic devices by energy dissipation, causing heating, power loss and instability.

Computer simulations can be an important tool for predicting and helping the design of new devices. However, another important feature of realistic electronic devices that should be taken into account is the fact that these devices most often can reach the 100 nm length scale with a large number of randomly distributed defects. This "disorder" can lead to a fundamentally new transport regime, namely the Anderson localization regime. Therefore, in order to perform quantitatively meaningful simulations of realistic devices, the method used should be able to consider tens of thousands of atoms with randomly positioned defects which, by means of *ab initio* methods, is not an easy task. Also, the combination of disordered systems with electron-phonon interaction might explain open questions such as the nature of conductivity in polymers.

In this work we present a method that allows one to compute the transport properties of realistic electronic devices with the two named features: large number of randomly distributed defects together with realistic electron-phonon interaction. Our method combines the accuracy and functionality of *ab initio* Density Functional Theory to determine the electronic structure with a recursive Green's functions formalism. We considered the case with weak and localized electron-phonon coupling strength. Approximating the contact broadening and the non-interacting retarded Green's functions as energy independent matrices, the current and power expressions can be expanded to second order in the electron-phonon couplings and the integration over energy performed analytically, the so-called Lowest Order Approximation [1,2]. We present results showing the effects produced by considering the electron-phonon interactions in toy models and in graphene nanoribbons with joint attachment of hydroxyl group.

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POSTER

Monitoring the interaction of CO with graphene supported metal nanoparticles by vibrational spectroscopy

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Small metal nanoparticles dispersed on porous substrates have gained increasing interest in surface science because of their widespread applications, especially in heterogeneous catalysis. It was previously shown that nanoparticles grown through UHV vapor deposition of material form ordered arrays on graphene substrates using the moiré of graphene/Ir(111) as a template. The size of these nanoparticles can be carefully controlled with diameters smaller than 2 nm on graphene/Ir(111) by the amount of deposited material. [1,2]

In this contribution we report so far the first describing vibrational spectroscopic studies on Ir, Pt and Au metal-covered graphene/Ir(111) substrate using CO as probe and/or reactant to monitor the frequency of C-O binding to the metal surface. The ultrahigh vacuum IR spectroscopy (UHV-IRRAS) apparatus allowed us to record high-quality IR data and turned out to be a powerful tool to investigate well-arranged metal/graphene/Ir(111) system. Deposition of metal nanoparticles onto the graphene/Ir(111) results in different vibrational C-O bands, while CO does not adsorb on pure graphene/Ir(111) surface. The adsorption, stability and sintering of metal clusters on graphene/Ir(111) are further investigated with respect to the position and intensity of the C-O stretching band. It is found that the small clusters are unstable upon CO adsorption and sintered after binding to CO molecules, which weakens the bonding of the nanoparticles to the graphene. This leads to weaken and consequently a red shift of the C-O stretching vibration band in IR spectra. [3]

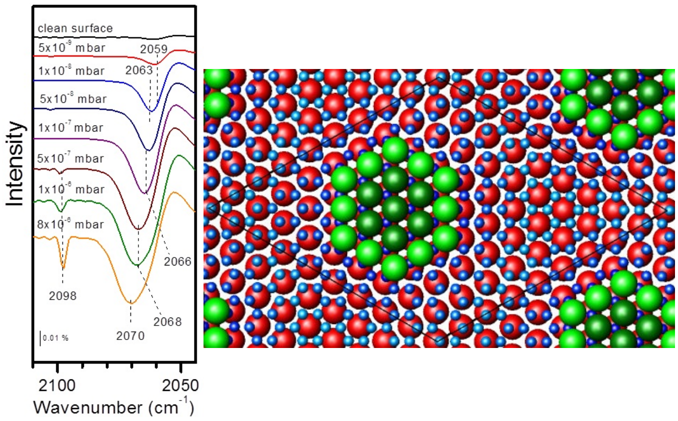

Figure 1: (left) UHV-IRRAS of CO adsorption on graphene supported Ir nanoparticles at 195 K; (right) cluster model for 0.2 ML Ir nanoparticles on Graphene/Ir(111) substrate.

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POSTER

Metal organic complexes induce surface nanostripes

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The actual demand of increasingly smaller devices drives the endeavors to explore new methods to miniaturize the designs. Thus, developments to produce ordered nanostructured surfaces are stimulating fields. In this context, a novedous molecular/substrate interaction mechanism that derives in a unique adsorbate induced surface reconstruction is presented. In particular we show how metalated phthalocyanines can promote the formation of regular arrays of Cu nanoribbons on its (110) surface [1].

At variance with the conventional changes of metal reconstructions upon molecular adsorption observed so far, the presented faceting is found to involve a massive reorganization of Cu adatoms. The energy gain of the final system comes not only from the preferential adsorption position of phthalocyanines on the copper surface, but also from their interaction with the surrounded adatoms. By combining experimental (Scanning Tunneling Microcopy) and theoretical surface science techniques we demonstrate that indeed the mechanism behind the massive surface reshaping involves a molecular mediated uni-directional blocking of diffusing surface adatoms (Figure 1A). Optimization of the organization involves extra adatoms trapped between molecules (Figure 1B).

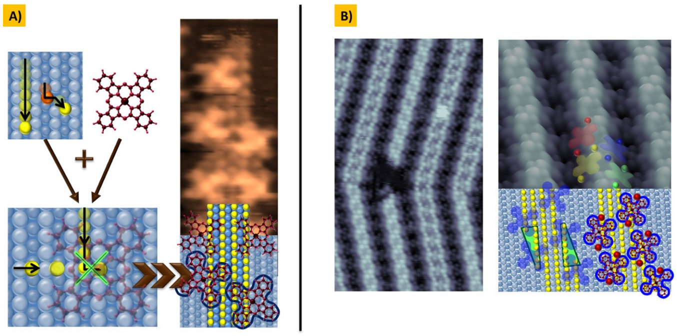

Figure 1: A) Scheme of the adatom diffusion mechanisms and of the blocking to form the ribbons surrounded by tilted molecules. B) STM image of the well-organized Cu nanostripes surrounded by the molecules.

[1] M. Abadía, R. González-Moreno, A. Sarasola, G. Otero-Irurueta, A. Verdini, L. Floreano, A. Garcia-Lekue, C. Rogero, J. Phys. Chem. C **118**, 29704-29712 (2014)

POSTER

Electron-hole transport over surfaces or interfaces in Si, SiC and GaAs based β-voltaic systems

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The idea of betavoltaic energy converters, the low-power long-lifetime energy sources that use beta-electrons in conjunction with *p-n* junctions or Schottky diodes, was proposed a long time ago [1]. But only recently did it begin attracting both experimental and theoretical attention due to the variety of possible applications in hostile or inaccessible environments (see, e.g., [2-5]). The physics of carrier transport through the surfaces and interfaces of the generated electron-hole pairs can be explained in terms of a complex interplay between the surface and bulk related processes, scattering dynamics and recombinations. In this presentation we offer a theoretical formalism to model the role of surfaces or interfaces in generated carrier transport and determine the system's maximum attainable conversion efficiency η_{lim}, which sets an exact target for experimental research. Although our formalism of carrier transport is essentially based on the similarity of betavoltaic and photovoltaic processes [6], several important differences must be properly included in the description of the physical processes of the electron-hole transport in the beta-voltaics systems.

The efficiency of a betavoltaic converter is a product of three terms: $\eta = \eta_\beta \cdot \eta_c \cdot \eta_s$. Here $\eta_\beta = N_\beta / N_0$ is the ratio of the beta-flux N_β, reaching the semiconductor surface to the total flux N_0 emitted by the beta-source; η_c is the coupling efficiency, depending on the electron reflection from the semiconductor surface and proportional to a collection efficiency of electron-hole pairs Q; finally, η_s is the semiconductor efficiency, similar to that of photovoltaic conversion efficiency. While the bidirectional betavoltaic system design allows getting η_β close to unity, the second and third terms in the efficiency can be optimised: they depend on the surface and interface associated mechanisms of carriers' transfer, surface recombination, diffusion and appearance of the so-called "dead layer". (The dead layer is the region close to the beta-electron source surface, where the generations of the electron-hole pairs by energetic beta-electrons can be neglected, and its extent depends on the initial beta-electron energy). The realistic experimentally achieved parameters of the betavoltaic systems were included in the analytical formalism developed. The calculated efficiencies indicate a limit to the maximum possible performance of the betavoltaic systems, e.g., η = 8% for tritium based ^{3}H/GaAs system. While being comparable to experimentally achieved efficiencies, our results demonstrate that there is still sufficient room for efficiency increase using optimised materials parameters and the system design.

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POSTER

Enhanced chemical reactivity of pristine graphene strongly interacting with a substrate: chemisorbed CO on graphene/Ni(111)

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Graphene (G) s usually considered a chemically inert material. Theoretical studies of CO adsorption on free standing graphene predict indeed quite low adsorption energies (< 0.1 eV). In spite of that, pioneering work has recently demonstrated that it can be effectively used in gas sensing applications [1,2] while applications in chemistry have been envisaged, too [3-5]. However, to the best of our knowledge, functionalization of G layers was achieved so far only using reactive species, as aryl radicals or atomic hydrogen, or by adsorption at defect sites. When using less reactive environments/adsorbates only physisorption [1,4] was detected at regular graphene sites.

Here we show by Vibrational Spectroscopy and Scanning Tunnelling Microscopy that non dissociative chemisorption of CO occurs at cold, pristine graphene grown on Ni(111). The CO adlayer remains stable up to 125 K, while some coverage survives flashes to 225 K. This unexpected result is qualitatively explained by the modification of the density of states close to the Fermi energy induced by the relatively strong graphene-substrate interaction. The value of the adsorption energy allows to estimate an equilibrium coverage of the order of 0.1 ML at 10 mbar pressure, thus paving the way to the use of graphene as a catalytically active support under realistic conditions.

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POSTER

Theory of rotational inelastic electron tunneling for physisorbed H_2

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[3]*Institute of Industrial Science, The University of Tokyo, Japan*

A quantum rotor of molecular H_2 retains its rotational motion in a physisorbed state [1]. Rotational and vibrational spectroscopy at the single molecule level has been recently observed for *para*-H_2 (J: 0→2, Fig. 1a) weakly physisorbed on surfaces [2,3]. Despite the remarkable progress of inelastic electron tunneling (IET) spectroscopy technique with scanning tunneling microscope (STM), mechanism of IET mediated by rotational excitation of H_2 remains to be clarified.

Here we propose a new microscopic IET model based on the resonant coupling [4] through rotation-electron interactions between the STM-tip, physisorbed H_2, and a metal surface (Fig. 1b,c). In this model, an electron with σ symmetry in the tip tunnels into the $2p\sigma_u$ or $1s\sigma_g$ state of H_2 through virtual negative or positive ion formation, respectively. In this formalism, the anisotropic term of the electron transfer t and the weak hybridization U induce the rotational excitation of H_2, which leads to a rotational selection rule of $\Delta J=+2$, $\Delta J_z=0$.

With this model, we analyzed the observed rotational spectrum in the IET spectra of H_2 physisorbed on Au(110) [2]. Potential anisotropy derived from the peak shift is in good agreement with our DFT calculation showing that rotational symmetry of H_2 in the nanocavity between the STM-tip and Au(110) is significantly broken.

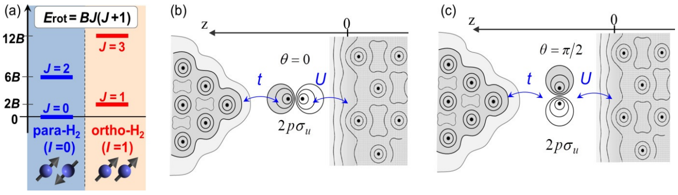

Figure 1. (a) Rotational energy diagram of nuclear spin isomers of para-H_2 and ortho-H_2 [1]. (b) Schematic diagram of molecular-axis angle (Θ) dependent transfer matrix elements t between STM-tip and H_2, and weak hybridization interaction U between H_2 and substrate through the $2p\sigma_u$ orbital of virtual H_2^- state for Θ=0 and (c) Θ=π/2 configuration.

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[2] S. Li et al., Phys. Rev. Lett. **111**, 146102 (2013)
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POSTER

Proposal of a new scattering mechanism in the electron energy loss spectroscopy: A case study in graphite

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High-resolution electron energy loss spectroscopy (HREELS) has been widely employed for investigating not only the vibration of the adsorbates but also the phonon dispersion of the solid surface [1]. Three mechanisms are known so far for the inelastic scattering of the electron; dipole scattering, impact scattering, and negative-ion resonance scattering. Here we propose a new electron scattering mechanism based on the HREELS experiments concerning the phonon in graphite.

Figure 1 shows the HREELS spectra of the HOPG graphite for various primary energies of the incident electron at room temperature. The incident angle was 48˚ from the surface normal and the detection angle was chosen so as to probe the phonon of the constant momentum (0.34 A^{-1}) for all the primary energies. Intensities are normalized by the elastic peak intensity. Two peaks are observed at 7 and 15 meV, which are attributed to the interlayer ZA and ZA' modes of graphite by comparing a series of angle-resolved spectra (not shown here) to the phonon dispersions in previous literatures, on both sides of the elastic peak. Peaks at the negative (gain) and positive (loss) energies correspond to the absorption and emission of phonons, respectively. In figure 2, the intensities of the two peaks are plotted as functions of the primary energy. The two modes of phonon clearly show resonance-like behavior in different manners to each other. They cannot be explained by the dipole or impact scattering mechanisms, and a new mechanism for the probing of the phonon, analogous to the resonance scattering for the molecular vibration, is required. In the proposed mechanism, the electron is trapped in the unoccupied band when the energy and momentum match with it, and the electron-phonon interaction may provide the scattering of the electron into another unoccupied band. The efficiency of the scattering should depend on the characters of both the phonon and electron bands, thus the intensity of the phonon in the HREELS spectra may strongly depend on the phonon mode and the primary energy. Note that the obtained ratios in intensity between the emission and absorption of phonons are nearly constant all though the primary energies [Fig. 2], and they (1.5 and 1.9 for 7 and 15 meV phonons, respectively) approximately agree with theoretical values (1.3 and 1.8 at 300 K) derived by a formula as $[1+n(\omega,T)]/n(\omega,T)$, where $n(\omega,T)$ is the occupation number of the phonon obeying the Bose-Einstein distribution. This fact strongly suggests that the observing phenomenon is not due to any experimental errors.

The HREELS spectroscopy involving this mechanism may provide information about the matrix element of the electron-phonon interaction at the surface with resolving both the energy and momentum. Therefore this may lead to a deeper understanding of many interesting and important phenomena at the surface, e.g., surface superconductivity, where the electron-phonon interaction plays a crucial role.

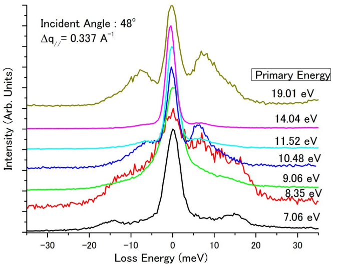

Figure 1: HREELS spectra of HOPG graphite at various primary energies.

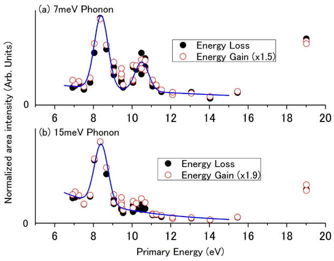

Figure 2: Primary-energy-dependence of the intensities of the two phonon modes normalized for the elastic peak.

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POSTER

Surface vibrations of Strontium Ruthenates

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Ternary perovskite oxides provide a rich playground for materials science and applications in new emerging fields. For the latter applications in all oxide devices, conductive oxide layers are required for the charge transport, which are often realized by thin films of the perovskite $SrRuO_3$(001). The family of strontium ruthenates, which include the so-called Ruddlesden-Popper series $Sr_{n+1}Ru_nO_{3n+1}$ as well as doped variants, shows conductive and in many cases superconductive properties at low temperatures.

Here we present a high-resolution electron energy loss spectroscopy (HREELS) study for the (001) surfaces of $SrTiO_3$, $SrRuO_3$, $Sr_3Ru_2O_7$, $Sr_2Ru_1O_4$, as well as $Sr_2Ru_{0.8}Ti_{0.2}O_4$. These ternary oxides are characterized by three dipole-active phonon polaritons and their combination losses, whereas for the doped ruthenate $Sr_2Ru_{0.8}Ti_{0.2}O_4$ the vibration of the doping Ti can be identified additionally. For selected cases, the surface loss function will be compared with infrared absorption data for bulk samples. For the insulator $SrTiO_3$ we observe strong phonon polaritons, whereas the excitations in the conductive strontium ruthenates exhibits significant damping as shown in Fig. 1. A pronounced deviation from a symmetric loss function is found for the surface of $Sr_2Ru_1O_4$, which is known to be superconducting at low temperatures. Here the high-energy phonon exhibits a broad Fano-like line shape, which is discussed in terms of a prominent electron-phonon coupling.

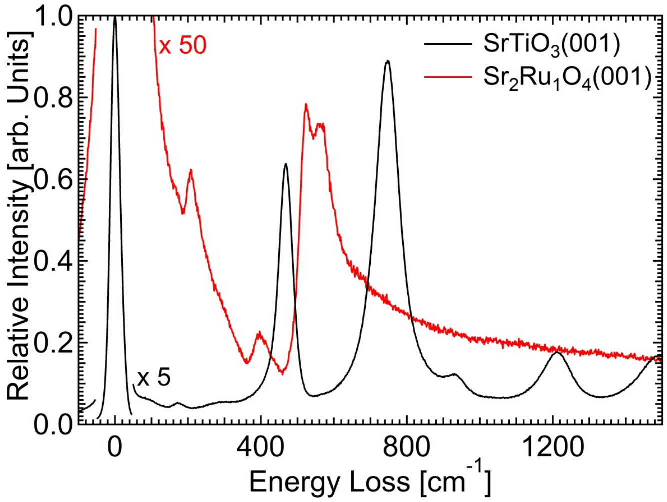

Figure 1: HREEL spectra for $SrTiO_3$(001) and $Sr_2Ru_1O_4$(001) in specular-scattering geometry in red and black, respectively, E_0 = 4 eV.

We1: E-ph coupling in novel 2D materials (I)

INVITED TALK

Measuring, interpreting, and translating electron quasiparticle – phonon interactions on the surfaces of the topological insulators

M. El-Batanouny

Boston University, USA

I will present a comprehensive study of the interaction of Dirac fermion quasiparticles (DFQs) and phonons on the surfaces of the strong topological insulators Bi2Se3 and Bi2Te3. Inelastic helium atom surface scattering (HASS) spectroscopy was used to measure the surface phonon dispersion of these materials along the two high-symmetry directions of the surface Brillouin zone (SBZ). Two anomalies shared by both of these materials are manifest in the experimental data. First, the absence of surface Rayleigh acoustic waves, which points to significantly weak coupling between the DFQs and the surface acoustic phonon modes. Second, both materials exhibit low-lying surface optical phonon branch with vertical shear polarization; which starts at the SBZ center and disperses to lower energy with increasing wave vector along both high-symmetry directions of the SBZ. This downward trend terminates in a V-shaped minimum at a wave vector corresponding to 2kF for each material, after which the dispersion resumes its upward trend. This phenomenon constitutes a strong Kohn anomaly arising from strong interaction of this surface phonon mode with the DFQs.

To quantify the coupling between the low-lying optical phonon branch that couples strongly to the DFQs a phenomenological model was constructed based on the random phase approximation. Fitting the theoretical model to the experimental data allowed for the extraction of the matrix elements of the coupling Hamiltonian and the modifications to the surface phonon propagator encoded in the phonon self energy. This allowed, for the first time, calculation of phonon mode-specific DFQ-phonon coupling $\lambda_v(q)$ from experimental data. Moreover, an averaged coupling parameter was determined for both materials yielding $\lambda^{Te} \cong 2$ and $\lambda^{Se} \cong 0.7$. These values are significantly higher than those of typical metals.

In an effort to connect electron-phonon coupling obtained from experimentally measured surface phonon dispersions with their counterparts obtained from photoemission spectroscopies, we developed a method based on the Matsubara Green's function formalism. A DFQ Matsubara function was constructed. It contained DFQ-phonon interactions manifest in the matrix elements obtained from the RPA model fitting to the optical phonon branch, as well as the phonon Matsubara function. A computational process was then developed that allowed the scenario of translating the electron-phonon interaction from the phonon perspective to the DFQ perspective. This scenario involved the calculation of the real and imaginary parts of the DFQ self energy and, subsequently, DFQ spectral function and the density of states. A direct comparison with photoemission and scanning tunneling spectroscopies results was then possible. The features present in the spectral function were quite valuable in setting the requisite energy resolution for reliable determination of the electron-phonon coupling, and in evaluating different methodologies for determining λ from experimental data pertaining to the DFQs. It is also worth noting that extracting λ from the calculated spectral functions yields results identical to those obtained from HASS, proving the self-consistency of the approach.

INVITED TALK

Inelastic electronic transport in single-layer graphene and at the surface of topological insulator Bi_2Se_3

J. F. Sierra[1], M. V. Costache[1], I. Neumann[1,2], S. Roche[1,3], and S. O. Valenzuela[1,3]

[1]ICN2 - Institut Catala de Nanociencia i Nanotecnologia, Campus UAB, Bellaterra, 08193 Barcelona, Spain
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[3]ICREA - Institució Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain

Understanding of the heating, energy flow and relaxation of two-dimensional Dirac carriers in graphene and topological insulators is essential for the design of electronic devices based on these materials. Elastic scattering by disorder imposes a limit to the conductivity at low temperatures; nevertheless, as disorder is reduced, the limit at finite temperatures will be ultimately set by the intrinsic electron-phonon (e-ph) coupling. In this talk, I will discuss our current understanding about the e-ph coupling in graphene and in the Bi_2Se_3 family of materials. In particular, I will describe recent results on electric-field and temperature-dependent transport measurements in exfoliated thin Bi_2Se_3 crystals [1] and on the generation of thermoelectric voltages due to hot electrons in graphene [2]. In contrast to conventional metals with large Fermi surfaces, 2D Dirac electrons are largely decoupled from acoustic phonons leading to relatively low electron-lattice cooling rates. Temperature and bias dependent measurements reveal the presence of specific optical phonon modes that dominate the electronic response, with similar phenomenology in graphene and Bi_2Se_3. However, the large difference in the energy of the relevant modes (200 meV and 8 meV, respectively) results in dramatically different bias and temperature dependent transport characteristics. While in Bi_2Se_3 the resistivity changes strongly even at low temperatures (<100 K), reflecting inelastic scattering due to the thermal activation of optical phonons, the restriction of the acoustic phonons that can scatter off electrons in graphene leads to very long cooling times and unconventional high-order cooling pathways assisted by disorder in the same temperature range.

Acknowledgements: This work is supported by the European Research Council (ERC Grant Agreement No. 308023 SPINBOUND), and MINECO (MAT2013-146785-P, SEV-2013-0295).

[1] M. V. Costache, I. Neumann, J. F. Sierra, V. Marinova, M. M. Gospodinov, S. Roche, and S. O. Valenzuela, Phys. Rev Lett. **112**, 086601 (2014)
[2] J. F. Sierra, I. Neumann, M. V. Costache, and S. O. Valenzuela, submitted

CONTRIBUTED TALK

Surface phonons of $BaTiO_3$(001) and $BaTiO_3$ ultrathin films on Pt(001) and Au(001)

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Phonons and their softening are key elements for the understanding of the long-range coupling in ferroelectric and multiferroic materials that causes, e.g., the paraelectric to ferroelectric phase transition. In thin films, these ferroelectric properties are often controlled by strain from the underlying substrate or the heterostructures environment.

Here we study the surface phonons of $BaTiO_3$(001) ultrathin films in comparison to $BaTiO_3$ single-crystals by high-resolution electron energy loss spectroscopy (HREELS). In all cases, the HREELS spectra are dominated by three well-developed phonon peaks at about 220, 460, and 660 cm^{-1}. Calculations of the full loss spectra within a semi-classical approach allow to identify the modes as the three A(TO)-derived surface phonon-polaritons (Fuchs-Kliewer modes). In comparison to the single crystal, the surface phonons for the thin films on Pt(001) and on Au(001) are shifted due to the lattice misfit of +2% and -2% for the two different substrates, respectively. Additionally, the surface phonons show a thickness-dependent red shift due to a dielectric coupling to the metallic substrate. Calculations for the $BaTiO_3$(001) thin films which include the response of the substrate can explain the observed shifts.

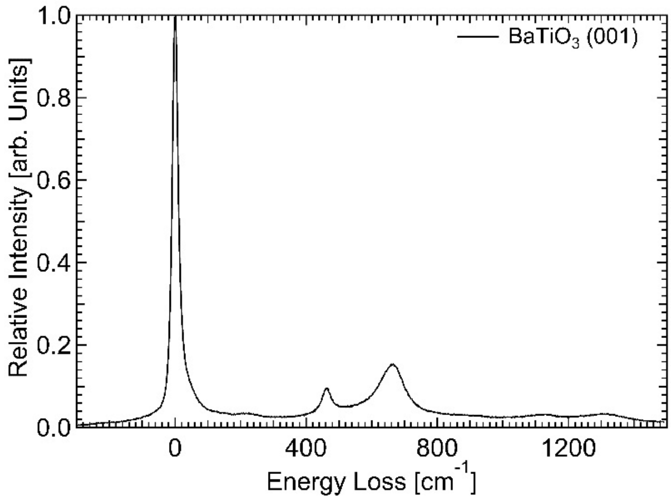

Figure 1: HREELS spectra of a $BaTiO_3$ single-crystal.

CONTRIBUTED TALK

Coherent phonon dynamics across the phase transition of quasi-1D Ta_2NiSe_5

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[2]*University of Zurich, Zurich, Switzerland*

The ternary chalcogenide Ta_2NiSe_5 (TNS) is a layered compound loosely stacked by van-der-Waals interaction [1]. Within each layer Ni single chains and Ta double chains form a quasi-1D structure giving rise to strongly anisotropic behaviour as seen e.g. in electrical conductivity [1]. TNS undergoes a metal-semiconductor transition below 550 K and an additional electronic phase transition from a semiconductor to an excitonic insulator (EI) at T_C = 328 K which stabilizes the band gap to $E_G \approx$ 300 meV [2]. The latter transition is accompanied by a structural distortion from orthorhombic to monoclinic symmetry [1,2].

In order to reveal the microscopic mechanism of the complex phase transitions in TNS we employ optical pump-probe spectroscopy. After laser-pulse excitation into a non-equilibrium state using $h\nu_{pump}$ = 1.55 eV, the infrared reflectivity at $h\nu_{probe} \approx E_G$ is monitored on a femtosecond to few-picosecond timescale. Fig. 1 shows a typical transient reflectivity change after excitation of the monoclinic/EI phase (T = 120 K). The signal shows an incoherent response due to hot-carrier creation and relaxation which is superimposed by damped oscillations due to coherent phonons. A Fourier analysis reveals four phonon modes (inset in Fig. 1), the 4 THz mode being present only below T_C. These findings are confirmed by temperature-dependent Raman spectroscopy. An excitation density-dependence at different temperatures reveals a saturation of both the coherent and incoherent response at a fluence $F_{sat}(T)$ suggesting a saturated pump pulse absorption. As T_C is approached $F_{sat}(T)$ decreases which is interpreted as an increasingly fulfilled resonance condition for the pump pulses. In contrast to the other modes the lifetime of the 4 THz phonon drops from 3 to 1 ps (Fig. 2) also saturating at $F_{sat}(T)$. In conclusion, the first coherent and incoherent phonon spectroscopy experiments on TNS identify a 4 THz phonon mode characteristic of the monoclinic phase which is strongly coupled to the photocarrier density. This work has been done in collaboration with T. Mizokawa, N. Katayama, M. Nohara, and H. Takagi.

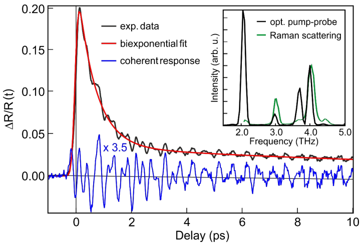

Fig. 1: Relative reflectivity change of TNS at 120 K after 1.55 eV excitation with 0.3 mJ/cm^2 probed by 0.3 eV laser pulses. Inset: FFT spectrum of the coherent component in comparison with Raman spectrum ($h\nu_{probe}$ = 532 nm).

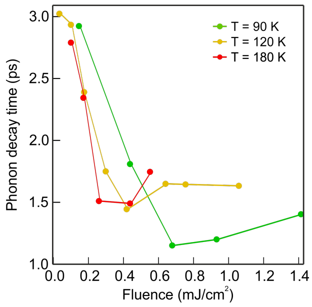

Fig. 2: Dependence of 4 THz phonon lifetime on excitation fluence at different temperatures.

[1] Di Salvo et al., J. Less-Common Met. **116**, 51 (1986)
[2] Wakisaka et al., Phys. Rev. Lett. **103**, 026402 (2009); Seki et al., Phys. Rev B **90**, 155116 (2014)

We2: E-ph coupling in novel 2D materials (II)

INVITED TALK

Electron-phonon scattering at surfaces and in ultrathin superconducting films: the effect of spin-orbit coupling

I. Y. Sklyadneva[1,2], R. Heid[3], K. P. Bohnen[3], and E. V. Chulkov[2,4]

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[2]Tomsk State University Tomsk, Russian Federation
[3]Karlsruher Institut fur Technologie, Karlsruhe, Germany
[4]Departamento de Física de Materiales, UPV/EHU, Basque Country, Spain

Electron-phonon (e-ph) interaction stands out as one of the fundamental many-body processes which play an important role in many phenomena, from electrical conductivity to electronic heat capacity and BCS-type superconductivity. To obtain a deeper insight into the e-ph interaction, it is necessary to study both the electron momentum averaged coupling strength and the electron-lattice dynamics for specific electronic states such as surface states or quantum-well states in ultrathin overlayers where the electronic density of states exhibits strong confinement effects. The electron scattering induced by lattice vibrations at clean bismuth and lead (111) surfaces as well as in quantum-well states of ultrathin superconducting lead films is presented to clarify (i) the role of spin-orbit coupling (SOC) in the e-ph interaction including the case of strong spin-orbit split surface electronic states of bismuth; and (ii) the lattice dynamics in layed Bi-based compounds.

The bismuth (111) surface shows unique properties in relation to the electron spin. Bismuth is a semi-metal but the lack of symmetry in the surface area, leads to a fully 2D metallic surface electron gas, which is almost completely spin polarized due to the spin-orbit interaction. Bi surfaces therefore provide the opportunity to study the e-ph interaction for a nearly 2D electronic system with strong spin-orbit splitting. The e-ph coupling in ultrathin lead films shows that the mass enhancement parameter is strongly underestimated in scalar relativistic calculations regardless of the film thickness. Both a sizable SOC-induced softening of the film phonon spectra and the SOC-mediated increase in the electron-phonon coupling matrix elements account for a large enhancement of the electron-phonon coupling strength.

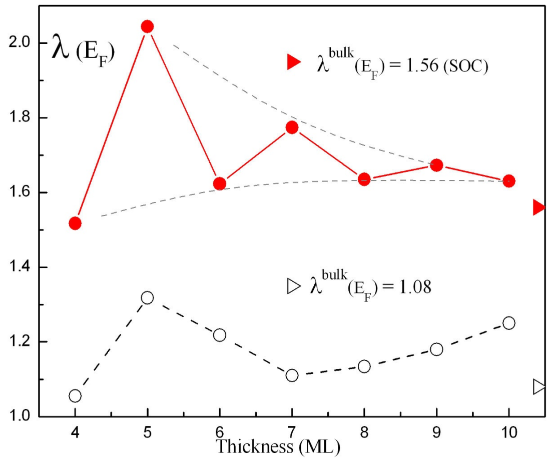

Figure 1: Mass enhancement parameter at the Fermi level of lead films as a function of film thickness.

INVITED TALK

Universal increase in the superconducting critical temperature of two-dimensional semiconductors at low doping by the electron-electron interaction

M. Calandra, P. Zoccante, and F. Mauri

CNRS and Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Université P. et M. Curie, Paris, France

In two-dimensional multivalley semiconductors, at low doping, even a moderate electron-electron interaction enhances the response to any perturbation inducing a valley polarization. If the valley polarization is due to the electron-phonon coupling, the electron-electron interaction results in an enhancement of the superconducting critical temperature. By performing first-principles calculations beyond density functional theory, we prove that this effect accounts for the unconventional doping dependence of the superconducting transition temperature (Tc) and of the magnetic susceptibility measured in Li_xZrNCl. Finally, we discuss what are the conditions for a maximal Tc enhancement in weakly doped two-dimensional semiconductors.

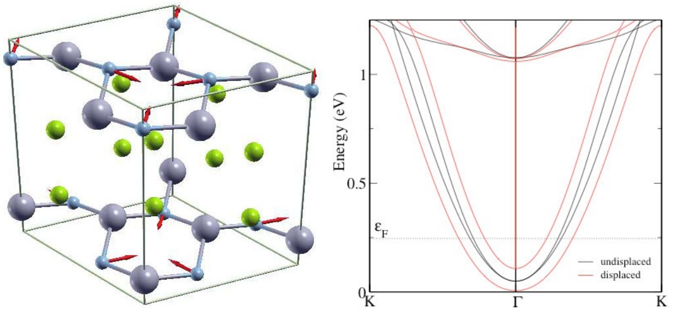

Figure 1: (left) Phonon displacement of the 59 meV mode at K in a √3 × √3 bilayer supercell. The effect of the distortion on the electronic structure is shown on the right.

[1] M. Calandra, P. Zoccante, and F. Mauri, Phys. Rev. Lett. **114**, 077001 (2015)

CONTRIBUTED TALK

Importance of momentum resolved electron-phonon coupling in analysis of inelastic tunneling and photoemission spectroscopy

R. Arafune[1], E. Minamitani[2], N. Tsukahara[3], S. Watanabe[2], M. Kawai[3], and N. Takagi[3]

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[3]Department of Advanced Materials Science, the University of Tokyo, Japan

Electron phonon coupling (EPC) plays a crucial role in determining the range of the electronic thermal diffusion for the femtosecond laser pulse excitation, forming the charge density waves, cooper-pair creation in superconductivity, etc. The EPC has been mostly analyzed through the momentum-averaged description such as the Eliashberg function. While such rather simplified description has successfully served a basis for intuitive understanding the above phenomena, it is often not sufficient to analyze the low-dimensional system and high-resolved experimental data.

In this study, we found that calculating the momentum resolved EPC is requisite for analysis of both the inelastic tunneling spectroscopy with STM (STM-IETS) [1] and inelastic photoemission spectroscopy (IEPES) [2], which are surface vibrational spectroscopic tools based on the inelastic process of the electron at the solid surfaces. The spectrum of the STM-IETS experiments for the Cu(110) surfaces shows a peak at 6 meV, while that of the IEPES for the same surface shows a step structure arising from the phonon excitation at 14.7 meV. The momentum resolved EPC that is described by the matrix element of the interband transition of the electron with transferring the energy and momentum to the phonon can be evaluated from *ab-initio* calculations. While the above characteristic energy does not appear in the phonon density of states straightforwardly, the density functional perturbation theory calculations show the strong peak at around 6.2 meV in the EPC spectrum for the electron near the Fermi level at the Γ point and at 14.5 meV for the electron just above the vacuum level at the *Y* point. Although the elementary processes of the inelastic tunneling and photoemission are different, the momentum resolved EPC calculations effectively work for describing the selectivity of the phonon excitation from among many possible phonon modes in both inelastic processes.

[1] R. Arafune et al., in preparation
[2] E. Minamitani et al., Phys. Rev. B **88**, 224301 (2013)

CONTRIBUTED TALK

Calculation of strongly anharmonic phonons in transition metal dichalcogenides

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[2]CNRS, UPMC, IMPMC, Paris, France

Many transition metal dichalcogenides (TMDs) crystallize in the bulk with layered structures that can be exfoliated down to a monolayer [1]. Both in the bulk and the monolayer, TMDs show a large variaty of remarkable physical phenomena, including superconductivity and the formation of charge-density waves (CDWs) [2]. Therefore, calculating from first-principles their electronic and vibrational properties becomes crucial to characterize and understand these phenomena.

In many TMDs the standard harmonic approximation for calculating vibrational properties breaks down as it predicts that the experimentally observed structures have imaginary phonon modes and, thus, should be dynamically unstable. This is particularly remarkable in TMDs that undergo a CDW transition. Interestingly, the instabilities are larger in the monolayer than in the bulk [3].

The fact that the CDW transition is driven by the softening with temperature of a phonon mode [4] indicates that anharmonic effects play a crucial role in many TMDs. Here we present fully first-principles calculations of anharmonic phonon spectra in NbSe2, a prototypical TMD with a CDW, making use of our recently developed stochastic self-consistent harmonic approximation (SSCHA) [5,6]. The SSCHA is a variational method valid to calculate vibrational properties in strongly anharmonic crystals. We show that with the SSCHA we can understand the dynamical stability of NbSe2, calculate the transition temperature of the CDW, and understand the superconducting mechanism.

[1] K. S. Novoselov et al., Proc. Natl. Acad. Sci. USA **102**, 10451 (2005).
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[5] I. Errea et al., Phys. Rev. Lett. **111**, 177002 (2013)
[6] I. Errea et al., Phys. Rev. B **89**, 064302 (2014)

Posters B

POSTER

Acoustic surface plasmons and phonon-plasmon coupling in Cu(111) from inelastic He-atom scattering

G. Benedek[1-3], **E. V. Chulkov**[2], **V. M. Silkin**[2], **P. M. Echenique**[2], **J. P. Toennies**[3], **and G. Zhang**[3]

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Inelastic Helium atom scattering (HAS) spectroscopy from a conducting surface can excite surface and subsurface phonons only via the phonon-induced modulation of the surface charge density, thus providing a direct measurement mode-selected electron-phonon coupling strength (mode-lambda spectroscopy) [1,2]. The recent discovery of acoustic surface plasmons (ASP) at metal surfaces associated with shallow surface electronic states [3,4] raises the natural question whether HAS spectroscopy can directly detect ASPs. A new analysis of the inelastic HAS spectra from the (111) surface of copper reveals a series of sharp inelastic features whose dispersion can be ascribed to that expected for ASPs in the extreme acoustic limit. In the THz domain the ASPs dispersion curves cross the surface-projected bulk phonon density and the dispersion curves of optical surface phonons. The ASP-phonon coupling leads to avoided crossing with the optical surface phonon branches and to peculiar Fano shapes of the ASP peaks due to the overlap of the ASP dispersion curve with the surface-projected bulk phonon continuum.

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[3] V. M. Silkin, J. M. Pitarke, E. V. Chulkov, and P. M. Echenique, Phys. Rev. B **72** 115435 (2005)
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POSTER

Modelling of STM-induced diffusion of hydrogen interstitials in the Pd(111) near-surface region

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[1]Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco UPV/EHU, Apdo. 1072, 20080 Donostia-San Sebastián, Spain
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STM experiments have shown that it is possible to manipulate buried [1] and adsorbed [2] H on Pd(111) to produce nanopatterned surface structures of PdHx composition. Although the experimental observations point to occupation of the subsurface sites (Oss), the actual distribution of H in the manipulated regions is unknown. The factors determining the diffusion of H are: inelastic collisions with STM electrons, H-H interactions, and tip effects in the form of electrostatic fields. We have studied these three factors first at a static level, by DFT evaluations of the potential energy surface (PES) of a H interstitial at the surface region [3], and then at a dynamical level. In the latter, we use a new quantum-mechanical model of the non-adiabatic coupling (NAC) between the H vibrational states with their metallic embedding electron density, which accounts for the electronic structure details of the Pd Fermi surface [4]. The static study rules out significant electrostatic effects for typical STM bias voltages, $V < 2$ V, but shows that H precoverage strongly modifies the PES around the Oss site (see Figure). Surface, S, sites are energetically favoured by 280-340 meV and resurfacing is likely whenever empty S sites are available, with barriers < 200 meV. The NAC model for H transfer rates evidences this strong preference for resurfacing of buried interstitials for voltages and tunnelling intensities up to $V = 1$ V and I = 1 nA, respectively. It also shows that at saturation Oss sites are also depopulated towards deeper sites. Most importantly, at long times (~100 ns) the system behaves *quasi-thermally*, and the site population dynamics can be described in terms of effective equilibrium constants.

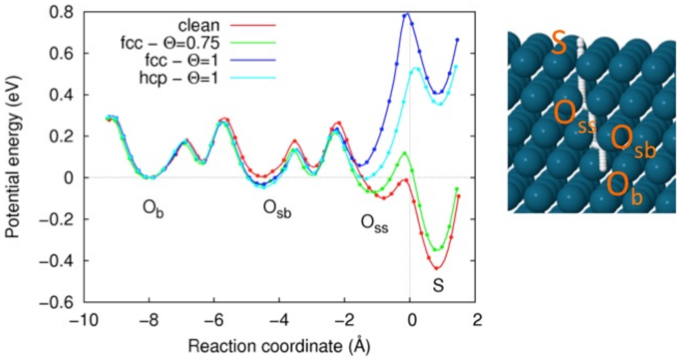

Figure 1: One-dimensional PES for H in the near-surface region of Pd(111) for surface site coverages Θ= 0-1.

[1] E. C. H. Sykes et al, PNAS **102**, 17907 (2005)
[2] T. Mitsui et al, Angew. Chem. Int. Ed. **46**, 5757 (2007)
[3] M. Blanco-Rey and J. C. Tremblay, J. Chem. Phys. **142**, 154704 (2015)
[4] J. C. Tremblay and M. Blanco-Rey, Phys. Chem. Chem. Phys. (in press)

POSTER

Direct observation of photoinduced intramolecular H-atom transfer within a single porphycene molecule on a Cu(111) surface

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Photoinduced H-atom (proton) transfer is of vital importance in several chemical reactions and elementary steps of biological processes [1]. Microscopic understanding of its dynamics will contribute to a precise control of the related processes and functions. In order to examine the fundamental mechanism, the intramolecular H-atom transfer reaction (tautomerization) is one of the interesting model systems. More recently, also tautomerization has gained considerable attention in nanoscale science and technology, because it represents one of the most promising mechanisms for molecular switches, which are an essential component of molecular scale devices.

Here we report the direct observation of photoinduced tautomerization within a single porphycene molecule on a Cu(111) surface using a combination of low-temperature scanning tunneling microscopy and laser excitation, ranging from the UV to the NIR spectral region. Porphycene molecules adsorb on the surface as monomers (without aggregating to clusters at low coverage), and the trans tautomer is observed as the thermodynamically stable state (Fig. 1a). However, laser irradiation can convert the trans tautomer to the metastable cis state unidirectionally (Fig. 1b), while heating the substrate transitions the molecule back to the trans tautomer. We quantified the tautomerization cross-section to be ~10^{-19} cm^2. Furthermore, the wavelength dependence reveals a clear resonance feature in the visible regime as well as a linear increase in cross-section in the UV (Fig. 2). We will discuss the excitation mechanism regarding different contributions; one of which is the direct molecular absorption while the other is a hot-electron (generated in the surface) mediated process. Our approach provides a novel insight into photoinduced adsorbate reactions at the single molecule level.

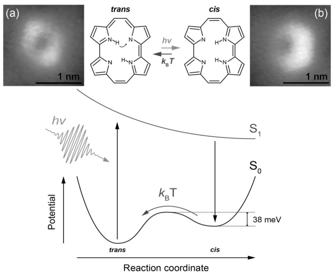

Figure 1: Schematic of photoinduced trans to cis transition of a porphycene molecule on Cu(111).

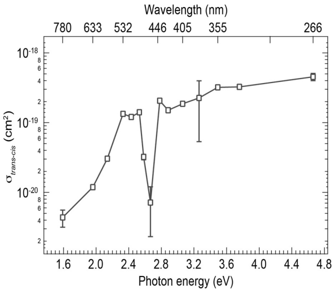

Figure 2: Wavelength dependence of the tautomerization cross-section of a porphycene molecule on Cu(111).

[1] J. T. Hynes et al., Hydrogen-Transfer Reactions (Wiley-VCH, Weinheim, 2007)

Theorical study of NO adsorption on Cu(110) and O(2×1)/Cu(110) surfaces

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Previous work showed the preferred tilted adsorption of Carbon monoxide (CO) on O(2×1)/Cu(110) surface [1]. As a consequence of the tilting, the dipole attraction between CO molecules resulted in the formation of one-dimensional molecular rows along the [110] direction. Recent scanning tunneling microscope (STM) experiments on nitric oxide (NO) adsorption on Cu(110) reveal also two possible orientations, vertical or tilted, depending on temperature [2].

In this work we studied the interaction between NO molecules on Cu(110) and O(2×1)/Cu(110) using Density Functional Theory (DFT). Our results shows that NO interacts strongly with the Cu(110) surface, losing its spin polarization at all coverages. The dimer configuration is favored on a confronted tilted geometry (figure 1) along the [110]. On O(2×1)/Cu(110) surface NO adsorbs between CuO rows, in a way that N atoms produce a spontaneous pulling of the row Cu atoms. In this case, vertical and tilted adsorption along the [001] direction are energetically degenerate and the NO molecule show a spin polarization of 1/2 μB. In spite of the low energetic cost to tilt the molecule, we do not find any evidence that the formation of dimers or molecular rows are favored on the O(2×1)/Cu(110) surface [3].

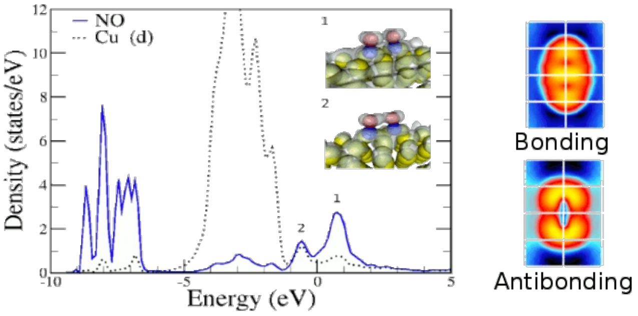

Figure 1: PDOS representation. NO dimer on Cu(110) along the [110] direction. Interaction between 2π molecular orbitals around the Fermi level.*

[1] M. Feng, P. Cabrera-Sanfelix, C. Lin, A. Arnau, D. Sánchez-Portal, J. Zhao, P. M. Echenique and H. Petek, ACS Nano. **5**, 8877-8883 (2011)
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[3] A. X. Brión-Ríos, D. Sánchez-Portal, P. Cabrera-Sanfelix, Phys. Chem. Chem. Phys., submitted

POSTER

Surface lattice dynamics of Cs

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Recent studies of inelastic Helium atom scattering (HAS) from metal surfaces have shown that HAS intensities are determined by electron-phonon (e-p) interaction, i.e., by the surface charge oscillations produced by atomic vibrations. As a consequence HAS has the ability to reveal sub-surface vibrational modes, as deep as the e-p interaction range (quantum-sonar effect) [1]. In this respect it is natural to investigate the case of simple metal (alkali) surfaces, where the surface electron density appears perfectly flat to thermal He atom scattering as expected for highly delocalized electronis states, but electron-phonon interaction is not particularly strong. HAS experiments from 20 ML Cs / Pt(111) show the expected Rayleigh wave (RW) dispersion curve for Cs and the anomalous surface longitudinal resonance, which is normally localized, towards the zone boundary, on subsurface layers and is therefore excited via surface e-p interaction, An theoretical analysis based on density functional perturbation theory (DFPT) calculations is presented.

[1] G. Benedek, M. Bernasconi, K.-P. Bohnen, D. Campi, E. V. Chulkov, P. M. Echenique, R. Heid, I. Yu. Sklyadneva, and J. P. Toennies, Phys. Chem. Chem. Phys. **16**, 7159-7172 (2014)

POSTER

Accounting for van der Waals forces in DFT-based calculations of He and Ne diffraction from metal surfaces

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Motivated by recent experimental studies about He, Ne and Ar diffraction from a Ru(0001) surface [1], where the last two cases display anticorrugation effects, i.e. corrugation inversion, and by the possibility of using van der Waals (vdW) DFT functionals which allow one to simulate accurately the mentioned experiments, we have studied these systems from a theoretical point of view, aiming to determine the role of vdW interactions on the anticorrugation phenomena observed in the mentioned diffraction processes. To achieve this task, we built the 3D potential energy surfaces (PESs) based on periodic DFT calculations performed by means of the Vienna ab initio simulation package (VASP) [2].

We tested different vdW functionals during these calculations in order to simulate the dispersion forces. Finally, the diffraction spectra are being computed using both classical and quantum dynamics simulations. Although diffraction is a 'pure' quantum phenomenon and quantum dynamics is, in principle, unavoidable to study our system, a classical analysis based on parallel momentum binning [3] has already been revealed as a very useful tool to mimic and analyze diffraction spectra [4,5].

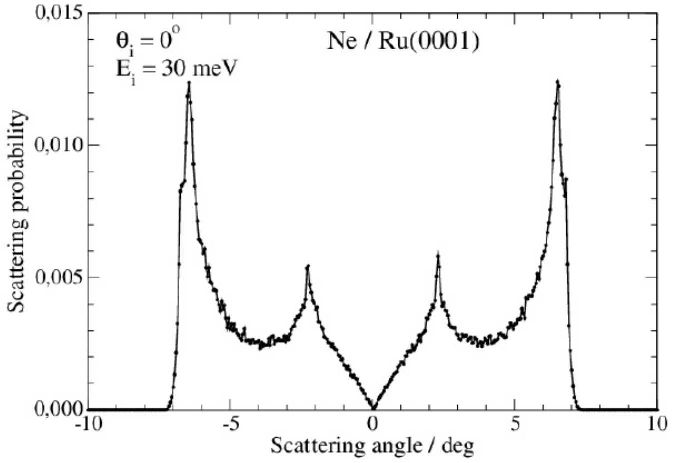

Figure 1: Scattering probability of Ne over Ru(0001) at normal incidence. The scattering distribution presents a classical rainbow, which is proportional to the surface corrugation and will therefore determine the diffraction distribution.

[1] M. Minniti et al, J.Phys. Condens. Matter **24**, 354002 (2012)
[2] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993)
[3] C. Ray and J. Bowman, J. Chem. Phys. **63**, 5231 (1975)
[4] D. Farías et al, Phys. Rev. Lett. **93**, 24104 (2004)
[5] C. Díaz et al, J. Phys. Chem. C **116**, 13671 (2012)

POSTER

The butterfly effect – modelling STM imaging on Si/Ge(001):H

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[1]Centro de Física de Materiales CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain
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Dangling bond arrays on Si/Ge(001):H substrates can be patterned with atomic precision very rapidly and exhibit complex and rich physics making them interesting from both technological and fundamental physics perspectives [1,2]. But the complex behavior makes Scanning Tunneling Microscopy (STM) imaging difficult to interpret. In particular, an interesting symmetric empty-state image, the "butterfly", has so far eluded precise explanation.

We propose a simple model to explain the "butterfly" - that (1) the electron-phonon coupling is strong enough to quickly sample several degenerate microscopic states and that (2) the transition rate out of a specific microscopic state is proportional to the STM current in that state. This model reproduces experimental STM images very well for both Si and Ge. Furthermore, based on our model, we propose a method to actively switch these microscopic states with high selectivity.

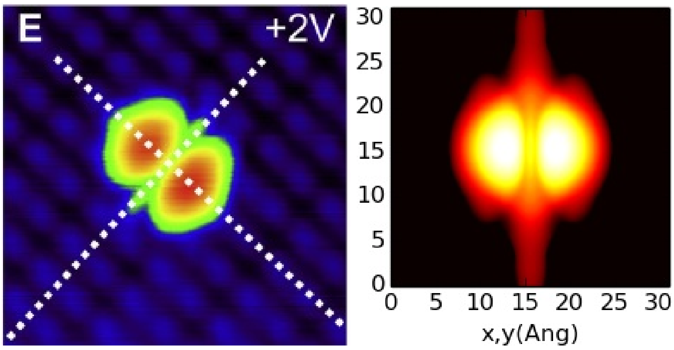

Figure 1: Empty-state image of a nearest-neighbor pair of dangling bonds on the Si(001):H surface (left, reproduced from [2]) and simulated image based on our proposed model (right).

[1] R. A. Wolkow et al., Field-Coupled Nanocomputing, Springer (2014)
[2] M. Kolmer et al., Appl. Surf. Science **288**, 83 (2014)

POSTER

Vibrational properties of TiO-Pc/PTCDA heterolayers on Ag(111)

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Organic molecular heterostructures formed by the combination of titanyl phthalocyanine (TiO-Pc) bilayer with 3,4,9,10-Perylentetracarboxylic dianhydride (PTCDA) layers grown on Ag(111) surfaces are investigated using infrared absorption spectroscopy (IRAS). In order to study the thermal stability of the organic interface, the behaviour of characteristic vibrational modes of both TiO-Pc and PTCDA layers is analysed. Only for temperatures above 450 K indications of intermixing or degradation of the underlying PTCDA/Ag(111) layers are detected, as it is shown in Fig.1. Key for the thermal stability of this heterostructure is the TiO-Pc bilayer, which displays a characteristic "up-down" molecular arrangement that optimizes the dipole-dipole interaction within the bilayer. Additional thermal desorption spectroscopy measurements of TiO-Pc bilayers grown on Ag(111) underline the exceptional thermal stability of this system, which requires temperatures above 500 K to desorb from the Ag(111) surface. Moreover, the coverage dependency of TiO-Pc on Ag(111) was investigated, showing a clearly defined transition between the monolayer and the bilayer regime characterized by distinctly different vibrational modes associated by both regimes. The surface structure of the TiO-Pc layers grown on Ag(111) was also analysed by SPA-LEED. Three different phases that depend on coverage are found in the monolayer regime. First, a 2D-gas phase for low coverage ($\Theta < 0.7$ ML), later a commensurate $(4\sqrt{3}\times7)$rect phase at 0.8 - 0.9 ML, and finally, a point-on-line phase when the coverage approaches saturation.

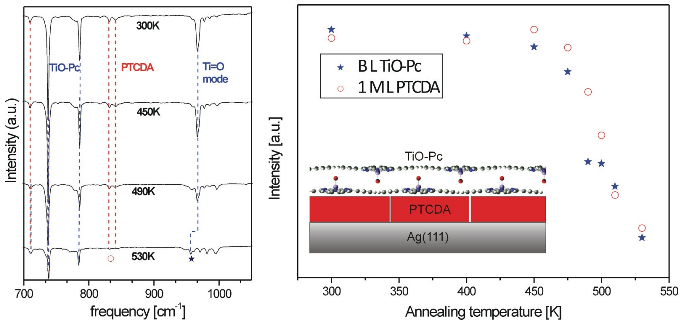

Fig.1: Left panel: Vibrational spectra of TiO-Pc (blue lines) and PTCDA (red lines) layers grown as heterostructure on Ag(111) recorded after annealing (and recooling to 80 K) to increasingly higher temperatures. Right panel: The temperature dependence of two characteristic vibrational modes of TiO-Pc (stars) and PTCDA (circles) is displayed. Only for temperatures above 470 K a continuous decreasing of the intensity signal is observed, which indicates degradation of the layers, i.e. intermixing or desorption.

POSTER

Molecular dehydrogenation reactions on surfaces

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It is a well-know experimental issue that residual H is abundant in a seemingly ideal UHV environment [1], which can have a significant effect on STM and XPS measurements. For example, additional XPS peaks are often observed when evaporating organic molecules on a surface [2]. Although such features are commonly attributed to the splitting of the molecular levels originated by the symmetry-breaking of the system upon deposition on the substrate [3], they might also be induced by the presence of residual H and the consequent hydrogenation of the evaporated molecules.

In this work, we combine density functional theory (DFT) and X-ray photoelectron spectroscopy (XPS) to study the adsorption of ZnPc molecules on Cu(110). Firstly, our calculations demonstrate that the double peak observed in the XPS experiments is not a final-state effect, i.e. is not due to splitting of the LUMO level. Rather, the reaction of the ZnPc molecules with extra H atoms in the chamber gives rise to H3ZnPc molecules, which having two inequivalent N atoms produce a double peak in the XPS spectra. Subsequently, we investigate the thermal evolution of the system and we conclude that the evolution of the XPS peaks upon annealing is related to the dehydrogenation of the H3ZnPc molecules following a two-step process.

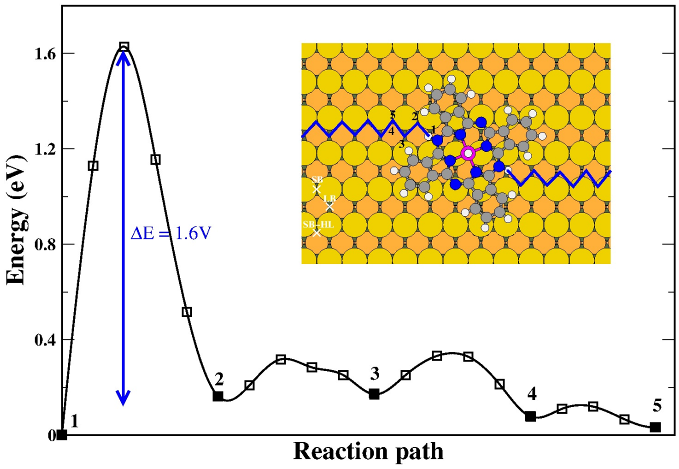

Figure: Energetics along the diffusion path of H atoms on Cu(110) in the vicinity of a HZnPc molecule.

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[2] A. Garcia-Lekue et al., J. Phys. Chem C **116**, 15378 (2012)
[3] P. Borghetti et al., ACS Nano **8**, 12786 (2014)

POSTER

Ab-initio analysis of the vibrational dynamics at the Tl/Si(111) surface

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In this work we present an analysis of the surface lattice dynamics at the Tl/Si(111) surface. We also study the impact in the vibrational spectrum of taking into account relativistic effects. In this sense, we identify several interesting surface vibrational modes of very low energy. We also explore the Gottlieb polynomials method in order to simulate semi-infinite crystals from slab calculations.

POSTER

Activation of water and CO_2 on Fe_3O_4 (111) thin films studied by molecular beam and IRAS

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Conversion of CO_2 into fuels and other value-added chemicals is a currently hot topic addressed by obvious environmental and economic motivations discussed everywhere [1]. However, CO_2 displays the most oxidized state of carbon which makes it rather inert to chemical transformations, thermodynamically highly unfavorable. On the other hand, the use of water as hydrogen resource (instead of hydrogen) for CO_2 reduction/hydrogenation would be the most ideal process which still remains extremely challenging though. Despite advances in this area [2], further fundamental research needs to be addressed to understand the interaction and behavior of water with catalyst substrates, especially metal-oxide surfaces, in order to rationally design heterogeneous catalytic processes involving water either as a hydrogen source or reaction promoter. Thus, we will present here a fundamental study of the interaction of CO_2 and water with the surface of a model Fe_3O_4 (111) thin film supported on Pt (111) single crystal, using molecular beams technology, *in-situ* infrared reflection absorption spectroscopy (IRAS) and temperature-programmed-desorption (TPD). IRAS results display evidence of dissociative adsorption of water on Fe_3O_4 (111), as previously reported in a photoelectron spectroscopy study [3]. Formation of hydroxyl species from water dissociation on Fe_3O_4 (111) surface was confirmed in our study by using D_2O and isotopically labeled oxygen either in the heavy water molecule ($D_2{}^{18}O$) or in the magnetite film ($Fe_3{}^{18}O_4$). Thus, no changes were detected for two typically observed vibrational bands related to O-D species when the corresponding iron oxide substrate was grown using $^{18}O_2$. In contrast, a shift of both vibrational bands to lower energies was observed when exposing regular Fe_3O_4 to $D_2{}^{18}O$ molecular beam. This observation strongly suggests that these O-D vibrational bands originate not from two individual OD groups, formed from dissociation of a single water molecule, but from a complex between an OD-group and molecular water. Theoretical calculations carried out by J. Sauer et al (HU Berlin) on dissociative adsorption of water on Fe_3O_4(111) reproduce very well both the positions and the isotopic shifts of the OD vibrational bands and with this support formation of a OD-D_2O complex.

Adsorption and chemical transformations of CO_2 were spectroscopically investigated as a function of surface temperature and CO_2 surface coverage in the temperature range 120-280 K. These changes in the spectroscopic signatures can be clearly related to strong interaction, activation and transformation of CO_2 on Fe_3O_4 (111). In order to assign and better understand the evolving IR vibrational bands related to these newly formed chemical species, experiments with isotopically labelled $13CO_2$ and $C^{18}O_2$ as well as CO_2 adsorption on isotopically labeled (O^{18}) iron oxide were carried out. Evolution and spectroscopical assignment of surface species formed will be discussed.

[1] K. M. K. Yu et al., ChemSusChem **1**, 893 (2008)
[2] C. Graves et al., Ren. Sus. E. Rev. **15**, 1 (2015)
[3] Y. Joseph et al., Chem. Phys. Lett. **314**, 195 (1999)

POSTER

Surface strain improves molecular adsorption but hampers dissociation for N_2 on the Fe/W(110) surface

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We compare the adsorption dynamics of N_2 on the unstrained Fe(110) and on a 10% expanded Fe monolayer grown on W(110) by performing classical molecular dynamics simulations that use potential energy surfaces calculated with density functional theory [1]. Our results allow us to understand the experimental observations of Homann et al. [2] showing that the inertness of Fe(110) towards N_2 adsorption disappears on Fe/W(110). In agreement with the reported ARUPS spectra, we also illustrate why N_2 adsorbs vertical to the surface though the hollow-parallel adsorption well is energetically more favorable. Surprisingly, we also find that while surface strain favors the molecular adsorption of N_2 it seems, on the contrary, to impede the dissociative adsorption. This unexpected observation of a combined molecular adsorption improvement and dissociative adsorption reduction highly contrasts with the common notion that associates surface strain with an overall increase or reduction of all kind of adsorption events. We attribute the present unusual behavior to the excessive stretching of the Fe monolayer that hampers the efficiency of the N–Fe interaction in triggering dissociation. Probably, our finding is not specific of N_2 on Fe/W(110) as the central condition of a large tensile stretching can be achieved with many heteroepitaxial surfaces.

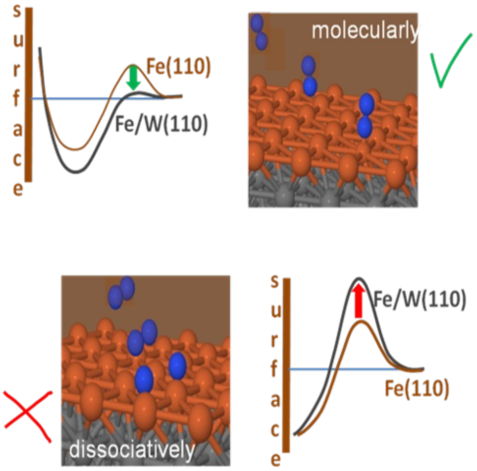

Figure 1: Strain favours molecular adsorption, but hampers dissociation for N_2 on Fe/W(110).

[1] I. Goikoetxea, J.I. Juaristi, R. Díez Muiño, and M. Alducin, Phys. Rev. Lett. **113**, 066103 (2014)
[2] K. Homann, H. Kuhlenbeck, and H.-J. Freund, Surf. Sci. **327**, 216 (1995)

POSTER

Measuring the Sb(111)-phonon dispersion using HAS: Evidence for an extremely low-lying acoustic plasmon mode

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As one of the essential components in the recently discovered group of topological insulators [1], the semimetal antimony (Sb) is an attractive candidate for studying the properties of its surface. Quite recently the surface phonon dispersion curve of Sb(111) as well as the influences of electron-phonon interactions were calculated using density functional perturbation theory [2]. However, there has been a shortage of experimental data for comparison and verification of the models used. Hence, for a comprehensive understanding of topological insulators, measurements on antimony are long overdue.

As a surface sensitive technique, Helium Atom Scattering (HAS) allows investigating elastic as well as inelastic phenomena associated with structure and dynamics of the electronic corrugation slightly above the Sb(111) surface [3,4,5].

Recent inelastic HAS measurements on Sb(111) revealed not only the expected surface phonon dispersion, but also multiple unexpected branches, one of which can be assigned to a low-lying acoustic plasmon mode while the other, lying completely below the Rayleigh curve of the phonon dispersion with a maximum energy at the K-point below 3 meV, can not be assigned to any known feature up to now.

The electronic similarity of Sb(111) with a single graphene layer, both containing two distinguishable groups of three Dirac cones in a hexagonal arrangement suggests that this low lying mode is indeed an additional intervalley plasmon mode such as has been observed in graphene [6].

HAS experimental data including the complete surface phonon dispersion as well as the isolated low plasmon mode will be presented.

[1] H. Zhang et al., Nature Physics **5**, 438-442 (2009)
[2] D. Campi et al., Phys. Rev. B. **86**, 075446 (2012)
[3] M. Mayrhofer-R. et al., J. Phys. Condens. Matter **25**, 395002 (2013)
[4] M. Mayrhofer-R. et al., Phys. Rev. B **88**, 205425 (2013)
[5] P. Kraus et al., Phys. Rev. B **87**, 245433 (2013)
[6] T. Tudorovski et al., Phys. Rev. B **82** 073411 (2010)

POSTER

Hot-carrier induced intramolecular H-atom transfer reaction studied by scanning tunneling microscopy

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Intramolecular H-atom transfer reaction, i.e. tautomerization, is an important molecular process in chemistry and biology. Recent study using low-temperature scanning tunneling microscopy (LT-STM) has opened a unique opportunity to examine tautomerization within a single molecule on surfaces [1-3].

We will present a hot-carrier induced tautomerization within a single porphycene molecule (a structural isomer of porphine) on a Cu(111) surface using LT-STM. The porphycene molecule adsorb on the surface as a monomer (Fig. 1a) in a *trans* tautomer (Fig. 1c,d). It was found that the *trans* tautomer is the thermodynamically stable species, while a voltage pulse of the STM can induce the unidirectional conversion from the *trans* to metastable *cis* configuration (see Fig. 1e,f). The *trans*→*cis* tautomerization is induced through vibrational excitation via the inelastic electron tunneling process. Additionally, as shown in Fig. 1b, the tautomerization occurs in nonlocal fashion, with a spatial range of up to ~100 nm from the STM tip position. The metastable *cis* molecules can be switched back to the *trans* tautomer by heating the surface. From detailed analyses of the nonlocal tautomerization behavior, we conclude that the process is induced by hot-carriers generated in the surface. These results provide a microscopic insight into local carrier dynamics, and their role in the adsorbate reactions.

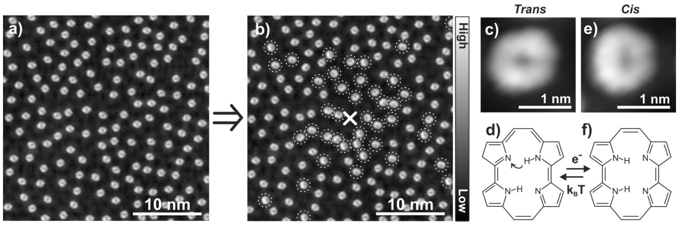

Figure 1: a) and b) STM images of porphycene molecules on Cu(111) at 5 K (I_t = 50 pA; V_{sample} = 50 mV). a) The porphycene molecules show the thermodynamically stable trans state. b) Same area after a voltage pulse of -2 V for 10 ms was applied at the center of the image (indicated by the white cross). Some of the molecules are converted to the cis configuration as indicated by the dashed circles. c) and e) Enlarged STM images of a single porphycene molecule in the trans d) and cis f) tautomer, respectively.

[1] P. Liljeroth et al., Science **317**, 1203 (2007)
[2] W. Auwärter et al., Nature Nanotech. **7**, 41 (2011)
[3] T. Kumagai et al., Nature Chem. **6**, 41 (2014)

POSTER

Exploring the electron induced phonon linewidths of N_2 on the Fe(110) surface: AIMDEF vs. DFPT

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To properly describe gas/surface dynamics it is crucial to understand the non-adiabatic effects that come from the energy exchange between the ionic degrees of freedom of the adsorbates and the electronic continuum of the surface. One way to account for this electron-hole (e-h) pairs excitation is to incorporate an electronic friction term into the classical equations of motion within the local density friction approximation (LDFA) [1]. *Ab initio* molecular dynamics (AIMD) together with this approximation (AIMDEF) [2] constitutes a very useful tool to explore the vibrational relaxation of an adsorbate on a metal surface. Using this method we calculated the e-h pair induced linewidths, Γ, of N_2 vibrating on top (Fig. 1a) and hollow (Fig. 1b) sites of a Fe(110) frozen surface. To make a comparative study we also performed density functional based perturbation theory (DFPT) calculations within the quasi-static limit (i.e. the limit of small vibrational frequencies) [3]. Although we get different values for the two methods, they both agree that phonon linewidth for internal stretch mode of N_2 on the hollow site is larger than on the top site.

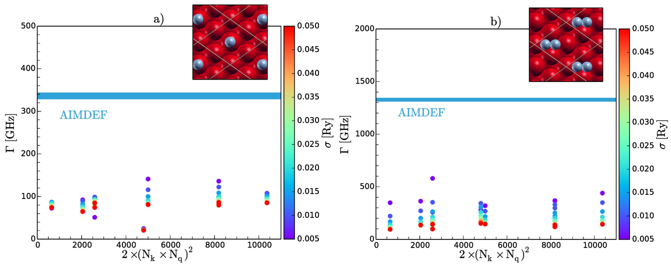

Figure 1: Phonon linewidths, Γ, of the internal stretch mode when N_2 is adsorbed vertically on the top (a) and horizontally on the hollow (b) sites of Fe(110). The abscissas represent the number of electronic transitions across the Fermi level considered in different samplings of the surface Brillouin zone and σ represents the broadening parameter of the initial and final state energies used in DFPT method.

[1] J. I. Juaristi et al., Phys. Rev. Lett. **100**, 116102 (2008)
[2] M. Blanco-Rey et al., Phys. Rev. Lett. **112**, 103203 (2014)
[3] B. Hellsing and M. Persson, Phys. Scr. **29**, 360 (1984)

POSTER

Surface Dynamics of the Wetting Layer and of 2 to 4 Lead Monolayers on Cu(111)

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The growth of Pb ultra-thin films on Cu(111) has been long studied in connection with electronic band-structure quantum-size effects and for the transition from the low-temperature layer-by-layer Frank-van-der-Merwe to the high-temperature Stranski-Kastanov growth regime at room T. At low temperature the formation of a wetting layer (1 monolayer (ML)), an instability of the 2 ML film and a regular layer-by-layer growth for more than 2 ML are observed; the 2 ML film was shown to be stabilized by alloying Pb with 20% Tl [3]. In this work we present a theoretical study of the dynamics of the wetting layer as well as for 2 ML $Pb_{0.8}Tl_{0.2}$, 3 ML and 4 ML Pb on Cu(111) in the 4×4 commensurate phase, for which detailed inelastic Helium atom scattering (HAS) spectra have been measured. The present calculations is based on the embedded atom (EA) method. Besides leading to a detailed interpretation of the HAS experimental data, the present results integrate a previous density-functional perturbation theory (DFPT) study for 3 to 7 ML Pb on a rigid substrate [1,2] with an analysis of the role plaid by the substrate dynamics at the smallest thicknesses, which is quite relevant despite the large mass and stiffness differences between Pb and Cu. Also the different thermal expansion of the film with respect to the substrate is shown to cause appreciable anomalies in the temperature and thickness dependence of the phonon dispersion curves.

Research partially was supported by grant (No. 8.1.05.2015) from "The Tomsk State University Academic D. I. Mendeleev Fund Program" and by grant RFBR (No. 15-02-02717-a).

[1] I. Yu. Sklyadneva, G. Benedek, E. V. Chulkov, P. M. Echenique, R. Heid, K.-P. Bohnen and J. P. Toennies, Phys. Rev. Lett. **107**, 095502 (2011)
[2] G. Benedek, M. Bernasconi, K.-P. Bohnen, D. Campi, E. V. Chulkov, P. M. Echenique, R. Heid, I. Yu. Sklyadneva and J. P. Toennies, Phys. Chem. Chem. Phys. **16**, 7159 (2014)
[3] J. Braun, J. P. Toennies, Surf. Sci. **368**, 226 (1996)

POSTER

Asymmetrical tunneling spectroscopy of close-spaced dangling-bond pairs on Si(001):H

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We present a combined experimental and theoretical study of the electronic properties of close-spaced dangling-bond (DB) pairs on a hydrogen-passivated Si(001):H p-doped surface. Two types of DB pairs are considered, called "cross" and "line" structures.

Our scanning tunneling spectroscopy (STS) data show that, although the spectra taken over different DBs in each pair exhibit a remarkable resemblance, they appear shifted by a constant energy that depends on the DB-pair type. This spontaneous asymmetry persists after repeated STS measurements. By comparison with density functional theory (DFT) calculations, we demonstrate that the magnitude of this shift and the relative position of the STS peaks can be explained by distinct charge states for each DB in the pair, and how these charge states are modified by the presence of the scanning tunneling microscopy (STM) tip and the applied bias. Our results indicate that, using the STM tip, it is possible to control the charge state of individual DBs in complex structures, even if they are in close proximity. This is observation might have important consequences for the design of electronic circuits and logic gates based on DBs at silicon surfaces.

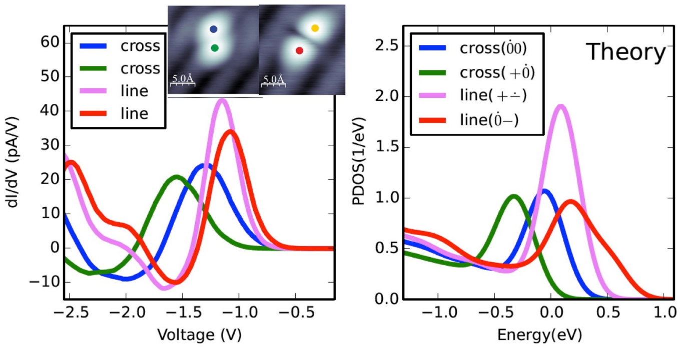

Figure 1: Left panel: STS spectra of different DBs on different types of DB-pairs (STM images in the insets). Right panel: calculated PDOS for each type of pair assuming that transition to a neutral charge-state takes place when a positively-charged DB is imagined with a sufficiently negative bias (energies relative to the valence band top of the Si(001):H).

POSTER

High resolution electron energy loss spectroscopy of Pd- and Pt-phthalocyanine on Ag(111)

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We investigated the geometrical and the vibrational properties of Pd- and Pt-Phthalocyanine on Ag(111) by Low Energy Electron Diffraction (LEED) and by High Resolution Electron Energy Loss Spectroscopy (HREELS). The LEED patterns show that the molecules grow highly ordered on the surface. The HREELS spectrum is dominated by vibrational modes with symmetry A_{2u}, that producing an out-of-plane variation in the dipole moment, indicates a flat geometry adsorption. The asymmetric vibrational losses, between 1000 and 1500 cm^{-1} indicates the presence of an interfacial dynamical charge transfer molecule-substrate, more predominant in the case of Pd molecules. We also studied the systems after molecular hydrogen exposure observing no drastically changes in the behavior with the central metal type.

POSTER

Correlation of temperature dependent vibrations, structure and optical response of Si(100) surface from first principles

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Vibrational and optical spectroscopy combined with theoretical modeling is the tools of choice to accurately and non-invasively characterise various surface processes *in-situ*. Because Si(100) is one of the most fundamentally and technologically important semiconductor surfaces, its microscopic understanding is needed to enhance microelectronics device performance. A connection between dynamics and c(4×2) / p(2×2) reconstructions of the clean Si(100) surface at room temperature conditions with apparent (2×1) phase was established two decades ago through molecular dynamics (MD) simulations [1]. Surface vibrational spectra have also been calculated [1-2] and confirmed experimentally (see [3] and refs. therein). However, due to dimer flipping at Si(100), the dynamical processes at the surface are highly anharmonic. This phenomenon has not sufficiently been addressed theoretically. In addition to being responsible for c(4×2) → (2×1) order-disorder transition near room temperature, the anharmonicity of surface vibrations substantially influences high temperature behaviour of Si(100) [4-5]). Temperature induced modification of the Si(100) optical response [6] clearly indicates the strong contribution of the dimer vibrational anharmonicity to atomic structure, electron bands and optical transitions between them.

Here we combine the formalisms of [1] and [2] to calculate temperature-dependent vibrational spectra of the clean Si(100) surface, and then calculate its temperature dependent reflectance anisotropy (RAS). When modeling surface vibrations, two different first principles techniques are used: (i) highly accurate density-functional perturbation theory (DFPT) [2] that, however, is inherently harmonic; and (ii) postprocessing of temperature dependent MD trajectories through the Fourier transform of the velocity discrete correlation function. The second method includes anharmonicity implicitly, which is evident from our calculated spectra. To extract the vibrational density of states (VDOS), finite temperature Car-Parrinello Molecular Dynamics (CPMD) runs were carried out in a wide temperature range from 250K to 1000K to provide temperature-dependent atomic structural input. When calculating the optical response at nonzero temperature, the vibrational anharmonicity was included through averaging for several representative temperature-perturbed atomic configurations (snapshots). Agreement with experimental results [6] is demonstrated, including a temperature-induced shift of both surface and bulk optical peak to lower energy and broadening, while the temperature induced effects are more pronounced for the surface atoms than for the Si bulk atoms. This conclusion is even better illustrated when the layer-by-layer formalism uses to efficiently decouple the bulk and surface contributions to temperature dependent both vibrational and optical responses.

[1] A. I. Shkrebtii, R. Di Felice, C. M. Bertoni and R. Del Sole, Phys. Rev. B RC **51**, 11201 (1995)
[2] J. Fritsch and P. Pavone, Surf Sci **344**, 159 (1995)
[3] M. Eremtchenko, F. S. Tautz, R. Öttking, J. A. Schaefer, Surf Sci **600**, 3446 (2006)
[4] L. Gavioli, M. G. Betti and C. Mariani, Phys. Rev. Lett. **77**, 3869 (1996)
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[6] A. I. Shkrebtii, J. Heron, J. L. Cabellos, et al., MRS Online Proceedings Library **1370**, 1039 (2011)

POSTER

Probing deep interface electron-phonon interaction in Bi_2Te_3/GaAs with Brillouin scattering

M. Wiesner[1,2], A. Trzaskowska[1], B. Mroz[1,2], S. Charpentier[3], S. Wang[3], Y. Song[3], F. Lombardi[3], P. Lucignano[4], G. Benedek[5,6], D. Campi[5], M. Bernasconi[5], F. Guinea[7], and A. Tagliacozzo[8,4,9]

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[2]The NanoBioMedical Centre, Adam Mickiewicz University, Umultowska 85, PL61614 Poznan, Poland
[3]Department of Microtechnology and Nanoscience, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
[4]CNR-SPIN, Monte S. Angelo-Via Cintia, I-80126, Napoli, Italy
[5]Dipartimento di Scienza dei Materiali, Universitá di Milano-Bicocca, Via Cozzi 55, 20125 Milano, Italy
[6]Donostia International Physics Centre (DIPC), University of the Basque Country (UPV-EHU) Paseo Manuel de Lardizábal 4, 20018 Donostia/San Sebastian, Spain
[7]Instituto de Ciencia de Materiales de Madrid (CSIC), Sor Juana Inés de la Cruz 3, Madrid 28049, Spain
[8]Dipartimento di Fisica, Universitá di Napoli Federico II, Via Cintia, I-80126 Napoli, Italy
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Brillouin light scattering from Rayleigh and Sezawa waves in 50-to-80 nm thick Bi_2Te_3 films on GaAs reveals Kohn anomalies for penetration lengths matching the interface space-charge region. Besides demonstrating important electron-phonon coupling effects in the GHz frequency domain, the experiment shows that information on deep interface fermions can be obtained by tuning the penetration of optically-generated surface phonons, as in a sort of quantum sonar. Density functional perturbation theory (DFPT) calculations for the most probable interface structure, modeled by one quintuple Bi_2Te_3 on a GaAs(001) substrate passivated by an additional Te wetting layer, allow to elucidate the structure of the space charge and to explain the source of the interface electron-phonon coupling and of the observed anomalies.

Th1: Adsorbate and interface dynamics

INVITED TALK

Imaging molecular motions with scanning tunnelling microscopy

J. Schaffert[1], M.C. Cottin[1], A. Sonntag[1], H. Karacuban[1], C. A. Bobisch[1], N. Lorente[2], J.-P. Gauyacq[3], and R. Möller[1]

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The scanning tunneling microscopy (STM) has a time resolution longer than typical molecular motion times. However, the molecular dynamics induced by the tunnelling electrons can nevertheless be probed by the STM. When it involves continuous transitions between several conformations, the real time characterization of the telegraph noise in the tunnelling current is a powerful tool to study STM-induced dynamics. We studied the case of individual copper phthalocyanine molecules on Cu(111) surfaces. The hopping rate between potential minima, the noise amplitude and the relative occupation of the involved states can be measured as a function of the tunnelling parameters, providing spatially resolved maps [1]. In contrast to standard STM, this technique gives access to transiently populated states revealing an electron-driven hindered rotation between the equilibrium and two metastablepositions of an individually adsorbed molecule [1,2]. A DFT based description of the adsorbed molecule reveals the adsorption properties of the molecule with a metastable state corresponding to a rotation of 7° of the molecule from equilibrium. A sudden approximation approach then allows the *ab-initio* treatment of the observed electron-induced transitions.

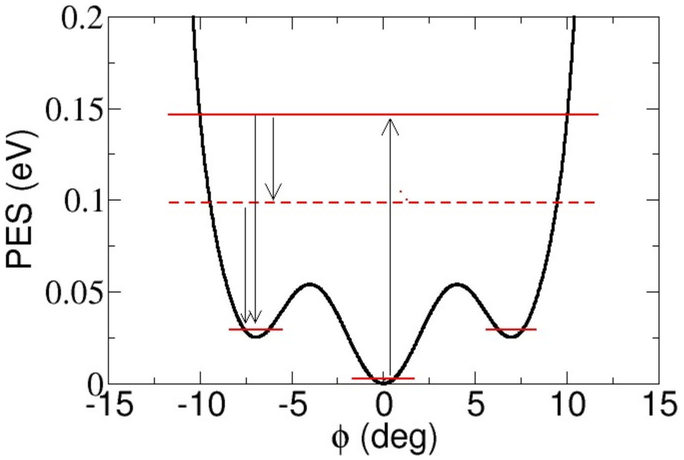

Figure 1: Potential energy surface of a copper phthalocyanine molecule with respect to the rotational angle of the molecule with respect to the Cu(111) surface. The molecule has two local and one global potential minima, and electrons can induce fluctuations among the three wells.

[1] J. Schaffert et al., Nat. Mat. **12**, 223 (2013); Rev. of Scientific Instruments **84**, 043702 (2013)
[2] J. Schaffert et al., Phys. Rev. B **88**, 075410 (2013)

INVITED TALK

The role of vibration in surface-migration

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The motion of adsorbate molecules across surfaces is fundamental to self-assembly, material growth, and heterogeneous catalysis. Scanning Tunneling Microscopy (STM) has shown electron-induced long-range surface-migration of chemisorbed ethylene, benzene and related molecules, moving in directed fashion across Si(100) by distances averaging ~50 Å, and as great as 200 Å [K.R. Harikumar et al. Nature Chem. **3**, 341 (2011); J. Phys. Chem. C **115**, 22409 (2011)]. This motion was ascribed to the effect of a sudden repulsion operating between the adsorbate and the surface. Dynamical studies have not previously been made. They are presented here.

For ethylene at Si(100) we postulate that the energy of the electron (~2.9 eV) has been converted to repulsion. The repulsion is found to excite bending vibration of CH2 in the ethylene which, in subsequent V-T (vibration-to translation) energy-transfer, gives sufficient velocity of the ethylene centre-of-mass to break its two carbon-surface bonds. The resultant motion is that of ethylene arcing upwards in a ballistic trajectory to peak heights ~ 7 Å, thereby carrying the molecule tens of Angstroms perpendicular to the Si(100) dimer-rows --the direction of migration observed. Such 'cannon-ball' behaviour has been postulated previously. Here we compute its molecular dynamics for the first time under the influence of initial repulsion and subsequent van der Waals attraction.

These dynamics indicate that ballistic flight accounts for migration over substantial distances, but are insufficient to explain the observation of migration over the full range of distances. Long-range travel is due instead to a succession of such ballistic events, linked by elastic or super-elastic bounces at the silicon surface. The super-elasticity derives from further V-T vibrational energy-transfer in the course of the bounce [S.Y. Guo, PhD Thesis, U. of Toronto, 2015].

Additionally these calculations predict ballistic migration of neutral halogen atoms, coming from the electron-induced reaction of chemisorbed halides at Cu(110), a system under study here. In this case the downward acceleration returning the ballistic trajectory to the surface is due to long-range chemical attraction operating up to 8 Å above the surface.

Finally, in recent work some of us [A. Chatterjee et al., J. Phys. Chem. C **118**, 25525 (2014); experiment and theory] have found surface migration occurring in the chemisorbed diradical carbene (CH2) on Cu(110) by a characteristic 'walking' along the copper rows, due to rocking vibration.

Surface migration would appear to be a field on the move.

CONTRIBUTED TALK

Local impact on intramolecular H-atom transfer studied by STM and nc-AFM

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Intramolecular H-atom transfer (tautomerization) is an important process in chemistry and biology, which is also regarded as a test bed to study H-bond dynamics. More recently, tautomerization has gained more attention in nanoscale science and technology because it resembles a molecular switch. For applications of molecule-based devices, it is of fundamental importance to understand the molecular process at the single molecule level because the local surroundings of a molecule have a significant impact on the process in condensed phases. We have studied H-bond dynamics within model systems on a metal surface using low-temperature scanning tunneling microscopy (LT-STM), which provided a microscopic insight into the dynamics including quantum effect such as tunneling and zero-point energy [1,2].

We will present the study of tautomerization within a single porphycene molecule on Cu(110) (Fig. 1) using a combination of LT-STM and non-contact atomic force microscopy (nc-AFM). Tautomerization is induced by vibrational excitation via inelastic electron tunneling in the STM, and its behavior can be precisely controlled by changing the surroundings of a molecule in a controlled manner [3]; i.e., either by placing Cu adatoms close to a single molecule, or by flipping a molecular orientation in a neighboring molecule in one-dimensional oligomers of porphycene. To obtain a better understanding of the perturbation to tautomerization, the tip-molecule interaction was investigated during the process by using force spectroscopy with nc-AFM (Fig. 2). The force curve was measured during the approaching (black curve) over the inner H atoms (indicated by the black star in Fig. 1b), and tautomerization occurs when the interaction becomes repulsive (indicated by the arrow). The curve during the retraction (gray curve) shows a different interaction because the tip interacts with N atoms after switching. These results provide a novel microscopic insight into impact from the local surroundings, leading to accurate control of molecular processes.

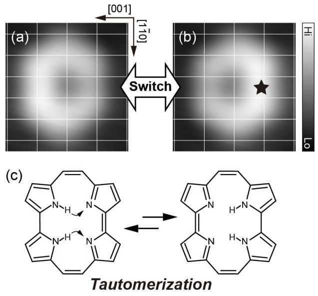

Fig. 1 (a)-(b) STM image of a single porphycene molecule on Cu(110) at 5 K. The switching corresponds to the cis-cis tautomerization.

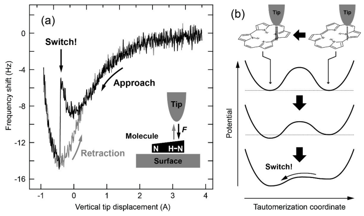

Fig. 2 (a) Force curve during the tip approach (black) and retraction (gray). (b) Schematics of tip-induced tautomerization process through the potential distortion.

[1] T. Kumagai et al. Phys. Rev. Lett. **100**, 166101 (2008).; T. Kumagai et al. Nature Materials **11**, 167 (2012)
[2] T. Kumagai, "Visualization of Hydrogen-Bond Dynamics", Springer (2012).; T. Kumagai, Prog. Surf. Sci. **90**, 239 (2015)
[3] T. Kumagai et al. Phys. Rev. Lett. **111**, 246101 (2013).; T. Kumagai et al. Nature Chemistry **6**, 41 (2014)

CONTRIBUTED TALK

Plasmon-phonon dynamics at GaP/Si(001) interfaces

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Charge carriers in impurity-doped semiconductors can behave collectively as a plasma oscillation. In polar semiconductors the plasma couples with the lattice polarization of the longitudinal optical (LO) phonons, resulting in LO phonon-plasmon coupled (LOPC) modes. The LOPC modes in III-V semiconductors can also be observed as coherent oscillations in the time domain. Monitoring the coherent LOPC mode by means of pump-probe reflectivity measurements can give a good measure of the chemically doped and photoexcited carriers, since the frequency and the dephasing rate depends crucially on the carrier type and density. Here we evaluate the charged carriers at the buried interface of GaP/Si(001) by means of coherent phonon spectroscopy. Lattice-matched GaP layers free from dislocations, staking faults or twins can be grown on exact Si(001) substrate by metal organic vapour phase epitaxy (MOVPE) [1]. Anti phase domains (APDs) are still unavoidable, however, and their boundaries consisting of the "wrong" bonds are expected to affect the interfacial electronic states crucially. Figure 1 compares the FT spectra of the anisotropic reflectivity changes of GaP/Si(001) samples with and without anti-phase domains (APDs). The GaP/Si sample without APDs (II) features oscillations due to the optical phonon of Si substrate at 15.6 THz and the LO phonon of GaP at 12 THz. The GaP/Si sample with APDs (I), by contrast, exhibits a prominent broad peak appears, whose frequency downshifts with increasing pump density. Similar mode was observed also for *n*-type GaAs(001) and assigned as the coherent LO phonon coupled with photoexcited multicomponent plasma [2]. The efficient generation of coherent LOPC mode for the interface sample with APDs indicates the presence of the surface built-in electric field, like for *n*-doped GaAs, in spite that the GaP film is nominally undoped. Our observation suggests that the boundaries of APDs act as donors.

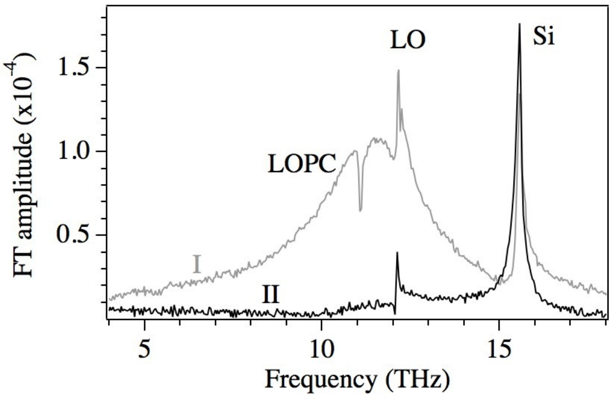

Figure 1: FT spectra of anisotropic reflectivity changes of GaP/Si(001) samples with APDs (I) and without APDs (II) pumped at different pump densities.

[1] A. Beyer et al., J. Appl. Phys. **111**, 083534 (2012)
[2] A. K. Basak et al., Phys. Rev. B **91**, 125201 (2015)

Th2: STM-IETS and beyond

INVITED TALK

Probing nuclear quantum effects in water with scanning tunneling microscopy and spectroscopy

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Quantum behaviors of protons in terms of tunneling and zero-point motion have significant effects on water properties, structure, and dynamics even at room and at higher temperature. In spite of tremendous theoretical and experimental efforts, accurate and quantitative description of the nuclear quantum effects (NQEs) in water is still challenging, due to the difficulty of accessing the internal degrees of freedom of water molecules. Using a low-temperature scanning tunneling microscope (STM), we are able to resolve in real space the internal structure, that is, the O-H directionality, of individual water molecules adsorbed on a solid surface [1,2]. The key steps are decoupling electronically the water from the metal substrate by inserting an insulating NaCl layer and gating the molecular density of states of water around the Fermi level via tip-water coupling. These techniques allow us not only to directly visualize the many-body quantum tunneling of protons within the H-bonded network [3], but also to quantify the impact of quantum fluctuation on the strength of hydrogen bonds by resonantly enhanced inelastic electron tunneling spectroscopy (IETS) [4]. Our work opens up the possibility of exploring the quantum nature of hydrogen bonds at single-bond limit.

[1] J. Guo, X. Z. Meng, J. Chen, J. B. Peng, J. M. Sheng, X. Z. Li, L. M. Xu, J. R. Shi, E. G. Wang*, Y. Jiang*, "Real-space imaging of interfacial water with submolecular resolution", Nature Materials **13**, 184 (2014)
[2] J. Chen, J. Guo, X. Z. Meng, J. B. Peng, J. M. Sheng, L. M. Xu, Y. Jiang*, X. Z. Li*, E. G. Wang, "An unconventional bilayer ice structure on a NaCl(001) film", Nature Communications **5**, 4056 (2014)
[3] X. Meng, J. Guo, J. Peng, J. Chen, Z. Wang, J. R. Shi, X. Z. Li, E. G. Wang*, Y. Jiang*, "Direct visualization of concerted proton tunnelling in a water nanocluster", Nature Physics **11**, 235 (2015)
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INVITED TALK

Symmetry dependence of vibration-assisted tunneling

J. Repp

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The use of ultra-thin insulating films on metal substrates as a support for individual molecules allows for the almost unperturbed electronic properties of molecules to be studied by means of the scanning tunneling microscopy (STM) as it facilitates an electronic decoupling from the substrate. In this weak coupling regime, the current has to pass a double-barrier tunneling junction, and inelastic excitation of molecules manifests itself as vibronic satellites adjacent to electronic resonances in the differential conductance. Hence, this geometry enables spatially resolved vibronic spectroscopy [1]. In usual STM-based inelastic electron tunneling spectroscopy [2], which is a regime quite different from the above mentioned, it has been realized that the symmetries of electronic wave functions play a crucial role [3].

Here we will discuss vibronic spectroscopy of individual pentacene molecules with sub-molecular resolution in such a double barrier tunneling junction geometry in detail. In this context, we show that the spatial position of the electron injection as well as the local electronic wave function symmetry dramatically affect the electron-vibron coupling. This is in contrast to the usual treatment of electron-vibron coupling in the Franck-Condon picture. We observe that the so-called reorganization energy spatially varies by more than a factor of two [4]. Our finding can be rationalized in a simple model of vibration-assisted tunneling, which has analogies to optical excitations in indirect semiconductors and is not limited to STM experiments only. Finally, our recent effort to establish time-resolved inelastic excitation experiments by combining a pulsed THz laser source with low-temperature STM will briefly be discussed.

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[2] B. C. Stipe, M. A. Rezaei, and W. Ho, Science **280**, 1732 (1998)
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CONTRIBUTED TALK

Electronic and vibrational states of single Tin-Phthalocyanine molecules – a numerical STM study

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[4]*Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Germany*

Tin-Phthalocyanine (SnPc) molecules adsorb in two different stable configurations, the protruding central tin atom pointing towards (SnPc↓) or away from (SnPc↑) the surface. Electronic and vibrational properties of both configurations adsorbed on an ultrathin SnPc buffer film on Ag(111) have been investigated with scanning tunneling microscopy (STM) and density functional calculations, using a numerically very efficient approach based on the Tersoff-Hamann approximation. The characteristic features in spectra of the differential conductance are reproduced by the calculations including the remarkable difference between the two configurations. The first-principles approach going beyond the quasistatic approximation reveals that excitations of various vibrational quanta induce replica of orbital spectroscopic signatures for the configuration with a lower molecule–surface coupling (SnPc↑). Spectra of molecules with a larger coupling to the surface (SnPc↓) can be described by considering elastic tunneling to orbital resonances alone. The applicability of our perturbative approach is discussed regarding a possible breakdown of the Born-Oppenheimer approximation.

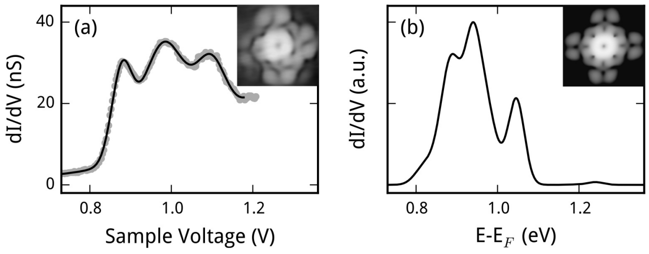

Figure 1: (a) Measured differential conductance (dI/dV) spectrum of SnPc↑ on a SnPc↓ buffer-layer on Ag(111) (gray dots). The full line represents a fit of three Gaussians and an exponential background to the experimental data. The spectrum shows three distinct peaks at 0.88, 0.98 and 1.10 eV. The spectra have been measured atop the center of the molecule. The inset shows the measured constant-current STM image. (b) Calculated dI/dV spectrum for the same configuration including contributions from vibrational excitations due to inelastic tunneling. In agreement with experiment, three peaks are present at 0.88, 0.93 and 1.04 eV, each of them comprising the spectroscopic signature of several molecular vibrational quanta. The purely elastic calculations fail to reproduce the three-peak structure (not shown). The inset shows the calculated constant-current STM image of SnPc↑.

CONTRIBUTED TALK

The origin of high-resolution IETS-STM images of organic molecules with functionalized tips

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Very recently Chang et al. [1] published a novel mechanism of high-resolution imaging of molecules by means of inelastic electron tunneling spectroscopy. But the detailed mechanism of the high-resolution contrast was not clear. Here we will show that our simple mechanical model of high-resolution STM/AFM imaging mechanism [2] can rationalize the underlying IETS imaging mechanism.

Our model unveils a significant particle distortion towards local minima of the interaction potential at close distances, which causes discontinuities in both the frequency shift and the tunneling current. We will show that the bending also affects the hindered translation mode, which gives rise to variation of the characteristic peak of the inelastic tunneling current. Therefore we added on top of the numerical model calculation of the hindered translation mode of molecular probe at each tip position. We assume that variation of the inelastic electron tunneling current is proportional to variation of the hindered translation mode. We calculate the vibrational modes of the particle probe at each point by means of the dynamical matrix. The numerical IETS simulations explain very well the experimental evidence (see Fig. 1).

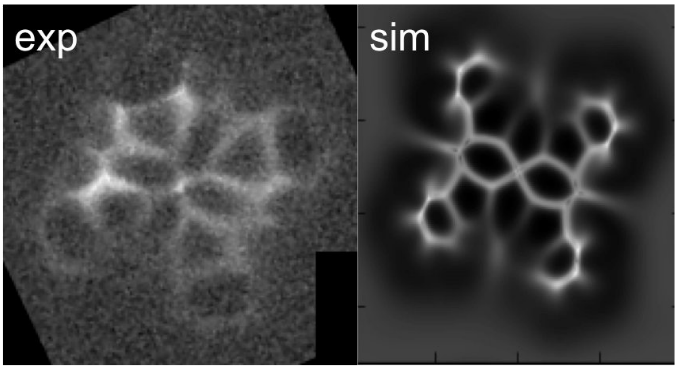

Figure 1: a) Experimental IETS-STM image of cobalt phthalocyanine on Ag(110) [1]; b) corresponding simulated inelastic tunnelling map mapping softening of the hindered translational modes of CO molecule placed on metallic tip [3].

[1] C. I. Chiang et al., Science **344**, 885 (2014)
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[3] P. Hapala et al., Phys. Rev. Lett. **113**, 226101 (2014)

Th3: Molecular films and 2D materials

INVITED TALK

Infrared-spectroscopy applied to ultrathin molecular films

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IR-spectroscopy is commonly referred to as a fingerprint technique to identify molecular species. However, this method can do better! The high spectral resolution and polarization dependence of vibrational modes allows to distinguish between different local environments (→lateral interactions), bonding configurations (→adsorption site and orientation), and phases (monolayer, bilayer, bulk) of large organic molecules with high selectivity. Thereby IR spectroscopy is non-invasive/destructive, obeys strict selection rules, and provides adequate sensitivity to detect even slight differential changes within grown films. Selected examples of various effects and phenomena associated with ultra-thin molecular layers will be presented, demonstrating the excellent quality and potential of infrared spectroscopy in studying such systems. Substantially reduced oscillator strengths (as compared to the popular diatomic adsorbate species studied in the past), in conjunction with more demanding preparation procedures, however, set limits to the widespread use of IRAS to investigate monolayer films and interfaces of large molecular species. Interestingly, for molecular species characterized by a partially filled orbital, e.g. the former LUMO, IR spectra are influenced by interfacial dynamical charge transfer (IDCT) between molecule and metal substrate [1]. By means of line-shape analysis of the associated Fano-type absorption profiles the electron dynamics (electron transfer time) between the molecule and the metal substrate can be estimated [2].

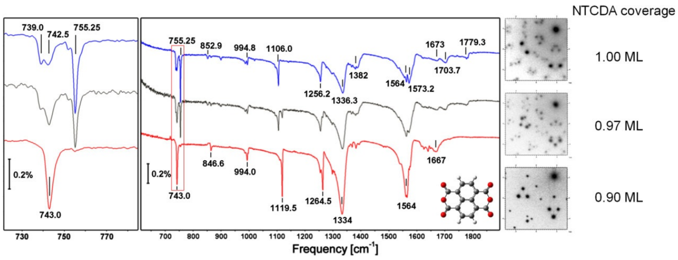

Figure 1: Infrared absorption spectra of typical molecular (mono)layers, the relaxed (bottom) and the compressed (top) NTCDA/Ag(111) phases. On the left, the section of a characteristic out-of-plane vibrational mode has been enlarged; the splitting is due to inequivalent molecules within the overlayer unit cell. On the right, the respective SPA-LEED images are depicted. All spectra have been obtained at T_{sample} = 20K using an instrumental resolution of 1 cm^{-1}. The unusually strong in-plane vibrations (at frequencies above 900 cm^{-1}) are the result of vibrationally induced interfacial dynamical charge transfer between molecule and metal substrate. Asymmetric line shapes arise due to the non-adiabaticity of the electron-vibron coupling.

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[2] D. C. Langreth, Phys. Rev. Lett. **54**, 126-129 (1985)
[3] C. R. Braatz et al., J. Chem. Phys. **136**, 134706 (2012)

CONTRIBUTED TALK

Temperature induced conformational disorder in organic monolayers

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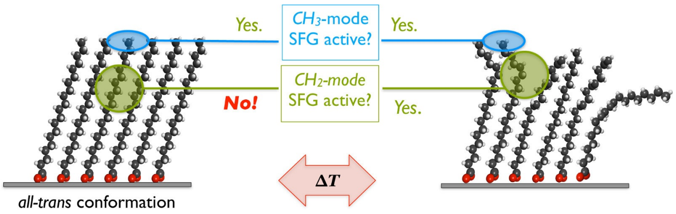
Universität Duisburg-Essen, Fakultät für Chemie, Germany

The conformational order in different organic monolayers is investigated using vibrational sum-frequency generation spectroscopy (VSFS). The symmetric C-H stretching vibrations of both the terminal methyl and the methylene groups are utilized to monitor the chain conformation at various sample temperatures. At room temperature the film is typically well-ordered consisting almost entirely of all-trans configured chains. With increasing temperature a marked increase in the density of gauche-defects is observed before oxidative degeneration starts at Octadecylsiloxane [1] and Ca-arachidate [2] monolayers on glass substrates were studied. Films of various packing densities were prepared using the Langmuir-Blodget preparation technique. The conformational changes are entirely reversible, when heating to no temperature higher than 470 K. It is observed that the ratio of the methyl to methylene modes signal strength behaves like an equilibrium constant characterizing the system. From the temperature dependence of this ratio an apparent enthalpy change for the formation of gauche-defects is obtained. These were determined for systems of increasing packing density. The obtained values are an order of magnitude larger than those of similar gas phase molecules and increase markedly with packing density.

The effect of hydrocarbon chain length is presently studied.



[1] J. Weber et al., J. Phys. Chem. **139**, 244902 (2013)
[2] J. Weber et al., J. Phys. Chem. **141**, 044913 (2014)

CONTRIBUTED TALK

Protein dynamics and function from a physicist point of view

A. Nicolaï[1,2], P. Delarue[1], and P. Senet[1]

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The directions of the largest thermal fluctuations of the structure of a protein in its native state are the directions of its low-frequency modes (below 1 THZ), named acoustical modes by analogy with the acoustical phonons of a material. The acoustical modes of a protein assist its conformational changes and are related to its biological functions. Low-frequency modes are difficult to detect experimentally. A survey of experimental data of low-frequency modes of proteins is presented. Theoretical approaches, based on normal mode analysis, are of first interest to understand the role of the low-frequency modes in proteins [1,2]. In this talk, we present applications of these methods to proteins intimately related to human diseases: ubiquitin and the 70kDa Heat-Shock Protein (Hsp70). The ubiquitin protein is a single domain protein which is a benchmark for biomolecular Nuclear Magnetic Resonance spectroscopy. Present all-atom calculations predict a "boson peak" near 20 cm-1 in the inelastic neutron scattering spectra of this protein. The molecular chaperone Hsp70 is an exemplary model to illustrate the different properties of the low-frequency modes of a multi-domain protein, which occurs in two well distinct structural states (open and closed states). The role of the low-frequency modes in the transition between the two states of Hsp70 is analyzed in detail. It is shown that the low-frequency modes provide an easy means of communication between protein domains separated by a large distance. [1]. Proteins can also subtend nonlinear excitations as we proven for the first time very recently by using molecular dynamics simulations and models from statistical physics [3]. How localized nonlinear excitations are related to the protein structure and sequence will be briefly described [3].

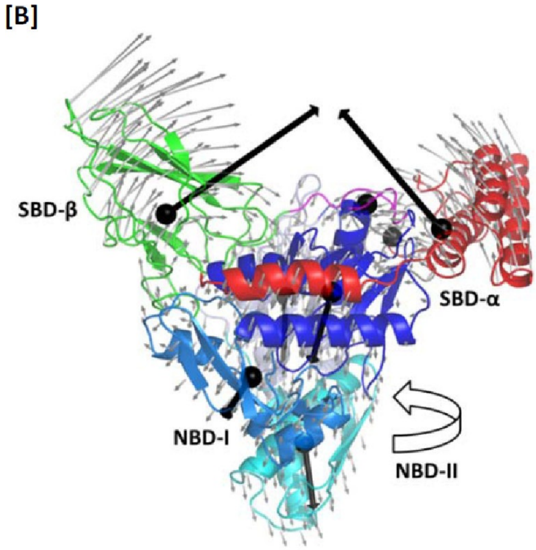

Figure 1: Typical low-frequency mode of the Human HSP70 Chaperone.

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[3] A. Nicolaï, P. Delarue, P. Senet, submitted (2015)

Th4: Tip-enhanced vibrational spectroscopies

INVITED TALK

Tip-enhanced Raman spectroscopy

R. P. Van Duyne

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During the last few years, there has been an explosion of interest and activity in the field of plasmonics. The goal of plasmonics is to control and manipulate light on the nanometer length scale using the properties of the collective electronic excitations in noble metal films or nanoparticles, known as surface plasmons. An improved understanding of the interactions between adsorbed molecules and plasmonic nanostructures (i.e., molecular plasmonics) is having a significant impact in a number of research areas including electrochemistry, surface science, catalysis for energy conversion and storage, the materials science of nanoparticles, biomedical diagnostics, art conservation science, and nanolithography.

I will focus in on three recent advances in tip-enhanced Raman spectroscopy (TERS) which illustrate the power of this nanoscale vibrational spectroscopy. First, new insights into the nature of the relative intensity fluctuations in single molecule tip-enhanced Raman spectroscopy (SMTERS) will be discussed. Second, our current understanding of the adsorbate surface interactions involved in the low temperature (LT), ultrahigh vacuum (UHV) TERS of the Ag tip/Rhodamine 6G (R6G) /Ag(111) system will be described. Finally, an update on our new results in coupling ultrafast lasers with TERS. This last topic illuminates a path forward toward the goal of understanding chemistry at the space-time limit.

INVITED TALK

Sub-nm resolved single-molecule Raman spectromicroscopy

Z. Dong

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To access individual chemical identity of closely packed molecular species at the nanoscale in a reliable and unambiguous way is a scientific challenge but of important practical applications in materials science, biology, and molecular nanotechnology. Molecular vibrations provide a valuable "fingerprint" for this identification. The vibrational spectroscopy based on tip-enhanced Raman scattering (TERS) has opened a path to obtain enhanced vibrational signals thanks to the strong localized plasmonic field at the tip apex. In this talk, I shall demonstrate single-molecule Raman spectroscopic imaging with unprecedented sub-nm spatial resolution, resolving even the inner structure of a single molecule and its configuration on the surface [1]. This is achieved by using a plasmon-enhanced nonlinear TERS technique that invokes a double-resonance process and resultant nonlinear optical effect, thanks to the exquisite control and tuning capability provided by low-temperature ultrahigh-vacuum scanning tunneling microscopy (STM) [2]. I shall also demonstrate the power of this STM-controlled nonlinear TERS technique in distinguishing adjacent but different molecules on surfaces in real space and address the issue of how close and how similar these different molecules can be. These findings should open up new avenues for probing and controlling nanoscale structures, catalysis, photochemistry, and even DNA sequencing, all at the sub-nm and single-molecule scale.

[1] R. Zhang, Y. Zhang, Z. C. Dong*, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang , and J. G. Hou*, Nature **498**, 82-86 (2013)
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CONTRIBUTED TALK

A novel tool to investigate electrified interfaces on the nanoscale: EC-TERS

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A fundamental understanding of molecular processes that take place at electrified solid/liquid interfaces is highly desirable in view of the urgent demand of improved energy conversion or storage schemes. In order to characterize the complex interplay between substrate and adsorbate in the presence of an electrolyte on the nanoscale, we are developing a novel near-field Raman spectroscopy setup that provides local chemical fingerprint and topographic information with nanometer spatial optical resolution and (sub)monolayer sensitivity under well-defined electrochemical conditions (EC-TERS, Fig. 1).

A limited number of TERS studies at solid/liquid interfaces have been reported on optically transparent samples in transmission mode [1]. However, to support accurate potential control of opaque sample electrodes, reflection mode is required where great care has to be taken to ensure efficient light coupling to the tip despite beam aberrations. Our approach compensates aberrations through phase modulation of the laser beam, in this way correcting the focus point at the tip and recovering the Raman signal [2]. Proof-of-concept results show improvements in far-field and near-field Raman signals in water by a factor of 2-3 and thus sufficient signal intensity to conduct potentail-dependent TERS studies. This EC-TERS development paves the way for powerful in situ chemical nano-characterization of a wide range of electrochemical interfaces.

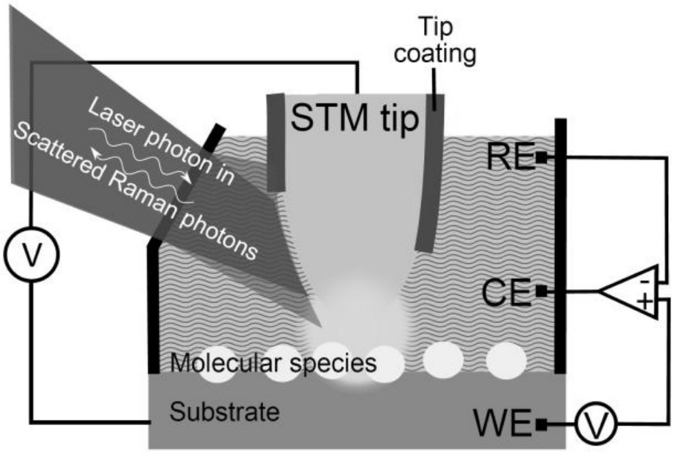

Figure 1: Schematic of EC-TERS setup to study electrified solid/liquid interfaces.

[1] T. Schmid et al., J. Raman Spectrosc. **40**, 1392 (2009); A. Nakata et al. Anal. Sci. **29**, 865 (2013)
[2] B. Gjonai et al., Applied Optics **51**, 8034 (2012)

CONTRIBUTED TALK

Determination of molecular orientation in monolayers adsorbed on metals using STM-based TERS

I. I. Rzeźnicka[1], H. Horino[2], N. Kikkawa[1], S. Sakaguchi[1], A. Morita[1,3], S. Takahashi[4], T. Komeda[4], H. Fukumura[1], T. Yamada[5], and M. Kawai[5,6]

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[3]*Elements Strategy Initiative for Catalysis and Batteries, Kyoto University, Japan*
[4]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan*
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Understanding the orientation of organic molecules in thin films adsorbed on solid surfaces is of fundamental importance for the development of molecular devices such as biosensors or organic displays. Experimental techniques which can provide information on molecular orientation in the adlayers formed on metals have been limited to few techniques requiring an ultra-high vacuum environment, or polarization-dependent infrared studies. The unique feature of the scanning tunneling microscopy-based tip-enhanced Raman spectroscopy (STM-TERS) is its ability to obtain simultaneously molecularly resolved images of the adlayer structure and its vibrational signals [1].

In this talk, I will present our recent results on adsorption of N-heterocycles on metal surfaces using STM-TERS. I will show that information on molecular orientation in the adlayers formed on metals can be derived by comparison of the experimental scattering intensity data and theoretical calculation of Raman tensor elements.

Specifically, we investigated molecular adsorption and orientation of 4,4'-bipyridine (BiPy) and 4,4-bipyridine N,N-dioxide (BiPyO_2) in monolayers formed on Au(111). The results show two adsorption regimes for 4,4'-BiPy. At the initial phase of growth, a physisorbed phase is observed with molecules standing upright and with the molecular longitudinal axis parallel to the surface. At the later stage, molecules form a homogenous monolayer with pits of a single-gold-atom depth. An intense Au-N stretching signal indicated chemisorption of molecules to the metal surface. By comparison of the scattering intensities of TERS vibrational modes with the intensities calculated for three possible molecular orientations an upright molecular orientation with the molecular long axis perpendicular to the surface was concluded.

Adsorption of 4,4'-BiPyO_2 on Au resulted in formation of two-dimensional adlattice with the (6×9) symmetry. Neither Au-O nor Au-N vibrational modes were found for 4,4'-BiPyO_2 adlayer, indicating rather weak interaction with the gold surface. 4,4'-BiPyO_2 was adsorbed in a vertical configuration with the molecular longitudinal axis parallel to the surface.

These results demonstrate that STM-TERS is an effective method for simultaneous imaging and vibrational spectroscopy facilitating identification of the adsorbed layers at nano-scale spatial resolution with monolayer sensitivity [2].

Acknowledgements: This work was partly supported by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (Grant No. 25390001), and 2011 Sunbor Grant from Suntory Foundation for Life Science.

[1] B.S. Yeo et al., Chem. Phys. Lett. **472**, 1 (2009)
[2] I. I. Rzeźnicka et al., Surf. Sci. **617**, 1 (2013)

Fr1: Thermal transport, friction, and dissipation

INVITED TALK

How surfaces dictate thermal transport in low-dimensional semiconductors

D. Donadio[1,2]

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In non metallic solids phonons with frequencies in the Terahertz range are the main heat carriers. Thus, tuning the band structure of phonons and the scattering rates by nanoscale engineering allows one to control energy transport and dissipation. Given the relevant length scales involved in nanoscale heat transport, of the order of tens of nanometers, one cannot always treat the system as a continuum and rely on Fourier's heat equations and the atomistic structure has to be taken into account explicitly.

In this talk we unravel the effect of dimensionality reduction and the prominent role of surface structure and surface resonances in tuning thermal transport in silicon nanostructures, including ultrathin membranes [1,2] and silicon nanowires [3,4]. Large scale molecular dynamics and lattice dynamics simulations provide parameter free recipes to optimize materials for thermoelectric, nanoelectronic and phononic-related applications.

[1] S. Neogi and D. Donadio, The European Physical Journal B **88**, 73 (2015)
[2] S. Neogi, J. Sebastian Reparaz, L. F. C. Pereira, B. Graczykowski, M. R. Wagner, M. Sledzinska, A. Shchepetov, M. Prunnila, J. Ahopelto, C. M. Sotomayor Torres, and D. Donadio, ACS Nano **9**, 3820 (2015)
[3] D. Donadio and G. Galli, Nano Lett. **10**, 847 (2010)
[4] I. Duchemin and D. Donadio, Appl. Phys. Lett. **100**, 223107 (2012)

CONTRIBUTED TALK

A classical collision model for surface friction tested by neutron scattering

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[1]Institut Laue-Langevin, CS 20156, F-38042 Grenoble Cedex 9, France
[2]Cavendish Laboratory, J.J. Thomson Avenue, Cambridge, CB30HE, UK
[3]Instituto de Fisica Fundamental, CSIC, Serrano 123, E-28006 Madrid, Spain
[4]ISIS Facility, Rutherford Appleton Laboratory, Chilton, OX11 0QX, UK

The study of friction and diffusion processes on molecular length scales requires experimental methods that deliver sub-nanometer spatial resolution at nanosecond time resolution as well as a high sensitivity to surface adsorbed species. After decades of research in friction the range of available spectrometers with these characteristics is still too limited. Although, neutron scattering is not a widely used surface science technique because neutrons penetrate deep into matter, neutron spectroscopy is able to cover the space and time domains that are of interest here. In addition, a wide choice of high surface density materials are available now that can serve as substrates for diffusion studies. These materials have the added benefit, that they are widely applied in energy storage, sensing and filtering. Hence, research on these materials has strong potential technical impact. In this presentation, we will show recent progress in friction research using neutron spectroscopy and diffraction.

Our research started with rather small and structurally simple molecules on carbon substrates, such as the aromatic molecule benzene adsorbed on the basal plane surface of graphite(0001) (see Fig. 1) [1,2]. For benzene-graphite(0001) at sub-monolayer coverage, we now established the inter-molecular energy dissipation and the surface friction [2] using a range of neutron time-of-flight spectrometers, neutron spin-echo as well as neutron diffraction. The results led us to a surprisingly simple model: the inter-molecular friction can be quantitatively explained by a model of colliding cogwheels (or rough hard disks) that we had developed on the basis of the long established rough hard sphere model for molecular gases (the equivalent 3D model). The new model explains the collisional friction or viscosity based on universal constants only and makes almost no assumptions about the system. When the molecular density approaches the full monolayer, however, three body and higher order collisions are dominant and the rough hard disk model breaks down.

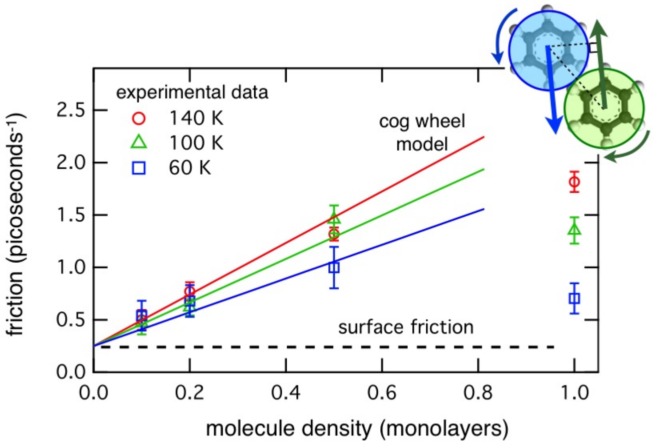

Figure 1: Coverage dependence of the kinetic friction of benzene sub-monolayers on graphite(0001) surfaces.

[1] E. Bahn et al., Physical Chemistry Chemical Physics **16**, 22116 (2014)
[2] I. Calvo-Almazan, E. Bahn et al., Carbon **79**, 183 (2014)

CONTRIBUTED TALK

Cold or hot: Metal substrate electrons will always couple to adsorbate vibrations

P. Saalfrank[1], J. I. Juaristi[2], M. Alducin[2], R. Díez Muiño[2], G. Füchsel[1,3], and G. Floß[1]

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In recent years, a paradigm change began to take shape in experimental and theoretical surface science when it was realized that non-adiabatic effects, i.e., the coupling of electrons of a metal surface, say, to adsorbate degrees of freedom may have a decisive influence on their nuclear dynamics. In this contribution we present first-principles' based dynamical simulations and theory, demonstrating that indeed 'cold' and sometimes even more so, 'hot' electrons play a pronounced role during dynamical gas-surface encounters. In fact, non-adiabaticity seems the rule rather than the exception, certainly in the cases shown here.

In a first example, using the recently developed Ab Initio Molecular Dynamics with Electronic Friction (AIMDEF) method we show that vibrational relaxation of H atoms on metal (Pb) films is entirely dominated by (cold) electron-hole pairs. Phonon motion can nevertheless have some surprising impact, and so do Quantum Size Effects (QSE) which emerge with varying layer thickness [1]. Classical or open-system density matrix dynamics and generalized electronic friction models reveal the importance of 'cold' electrons during reactive and non-reactive molecule-metal surface scattering, as will be demonstrated for H2 near Ru(0001) and NO near Ag(111) [2]. Finally, 'hot' electrons created by femtosecond laser pulses play the music during photoreactions of adsorbates (diffusion, (associative) desorption), for systems like H2:Ru(0001) and CO:Ru (0001) [3].

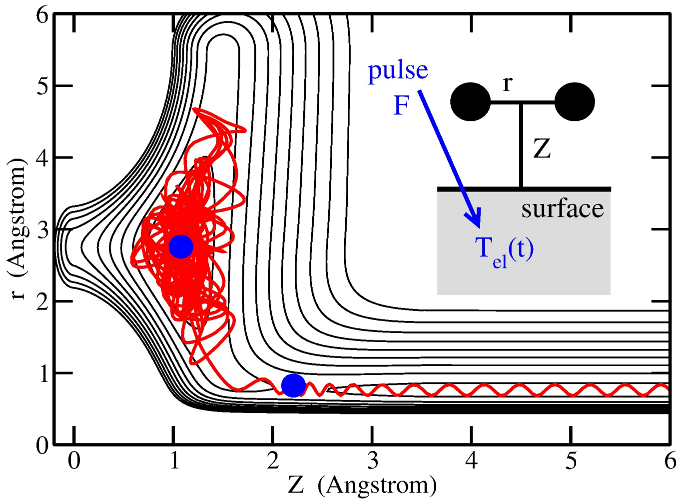

Figure 1: Example Langevin trajectory for hot-electron induced desorption of H2 from Ru(0001) [3].

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Fr2: Catalysis and single-molecule chemistry

INVITED TALK

Vibrational spectroscopy in catalysis: The power of synergy between theory and experiment

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The complexity of real (powder) catalysts hinders the fundamental understanding of their structure, which is essential to establish the relationship between structure and reactivity. Moreover, the possibility of understanding the mechanism of catalytic reactions depends very much on the chances of isolating intermediates in the study of each step in the catalytic cycle. Understanding catalyst structure and reaction mechanism can be obtained by a reductionist approach consisting in creating and evaluating experimental and theoretical model catalysts that mimic the real ones in their complexity. The feasibility of such an approach to date is undoubtedly due to recent advancements in characterization techniques and theoretical methods. In-situ vibrational spectroscopy offers a very powerful experimental tool box, allowing investigation of catalysts surfaces at the molecular level and reaction intermediates on both real and model catalysts than can help bridge the gap between them. Yet, the interpretation of vibrational spectra is far from trivial and the synergy between theory and experiment is essential to it.

In this talk we will demonstrate the capabilities of vibrational spectroscopy analysis for obtaining structure-reactivity relationships and molecular level insight about catalytic reaction intermediates. Specifically, we will discuss the example of an important class of catalysts formed when one metal oxide is deposited on a second metal oxide such as VO_x/CeO_2 - a very active catalyst for oxidative dehydrogenation (ODH) reactions. We will show how a combination of scanning tunneling microscopy (STM), photoelectron spectroscopy (PES), infrared reflection absorption spectroscopy (IRAS), and density functional theory (DFT) calculations, enables the elucidation of the surface functional groups existing on the catalyst surface [1]. The relation between structure and reactivity for ODH reactions will be briefly discussed [2].

A second example deals with the elucidation of the nature of the formate (HCOO) species upon methanol (CH_3OH) decomposition on a CeO_2 support; such species have been proposed as intermediates in the production of hydrogen by the water-gas shift ($CO+H_2O \rightarrow CO_2+H_2$) and methanol steam reforming ($CH_3OH+H_2O \rightarrow CO_2+3H_2$) reactions over CeO_2-based catalysts. We will analyze the structure, stability and vibrational properties of various types of formate species on a model $CeO_2(111)$ surface in equilibrium with a realistic environment containing CH_3OH , H_2O and O_2, using DFT and statistical thermodynamics. We combine this analysis with transmission infrared spectroscopy during the temperature-programmed CH_3OH decomposition reaction on a real CeO_2 support. In doing this we are able to explain the nature of the observed formate species while bridging the above-mentioned gap. Hydroxyl groups are found to be crucial for the species stabilization.

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INVITED TALK

Single-molecule chemistry and spectroscopy on the ultrathin insulating films

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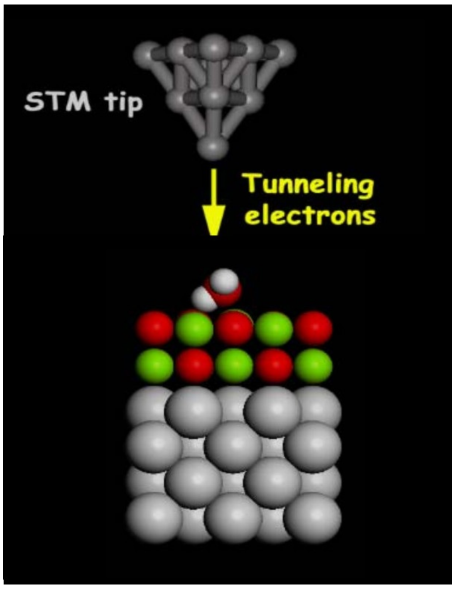
The study of single molecules provides deep insights into bonding nature and underlying quantum mechanics concerning about controlling chemical reaction. The scanning tunneling microscope (STM) is a versatile and powerful tool for investigating and controlling chemistry of individual molecules on the solid surfaces. The coupling of tunneling electrons to the electronic and vibrational states of the target molecule allows us to realize mode-selective and state-selective chemistry of the individual molecules as well as to understand how the electron energy can transport leading to carious surface processes.



Ultrathin insulating films grown on metal substrate has been a subject of great interest for investigation of individual adsorbate atoms and molecules by the STM, because of electronic decoupling between the adsorbate and supporting metal surface under an STM junction. In this talk, I will address two main issues with our experimental and theoretical efforts on investigating interaction of electrons with a single molecule on the ultrathin insulating films. The first part is assigned to the control of chemical reactivity by tuning interface between the insulating film and metal substrate. The chemical reactivity of a water molecule on an ultrathin MgO film supported by the Ag(100) substrate depends greatly on film thickness and be enhanced compared to that achieved with their bulk counterpart [1]. The change of chemical reactivity of ultrathin MgO film depending on the film thickness can be explained by the strengthening of the interaction between the oxide and metal interface layers [2]. Our results clearly show that such structural imperfections at the interface can improve the chemical reactivity of the MgO film supported by an Ag substrate [3]. The second part focuses on the single-molecule luminescence with an STM [4]. Optical properties of a single metal-free phthalocyanine (H_2Pc) molecule on the 2-ML thick NaCl film supported by Ag(111) have been also studied by scanning tunneling luminescence spectroscopy. I will discuss about the single molecule reaction of an H_2Pc molecule with tunneling electrons and accompanied optical property changes in a single-molecule luminescence spectra.

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[4] H. Imada, K. Miwa, J. Jung, T. K. Tomoko, and Y. Kim, to be submitted

CONTRIBUTED TALK

Characterisation of monolayer MgO films on Ag(100)

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The ability to engineer nearly perfect ultrathin oxide layers, up to the limit of monolayer thickness, is a key issue for nano-technological applications in fields as catalysis, corrosion protection, micro- and nano-electronics, sensoristics, spintronics, drug delivery, etc. [1]. We faced the difficult and important case of ultrathin MgO films on Ag(100), for which no extended and well-ordered layers could so far be produced in the monolayer limit. The stoichiometric and morphological characteristics of MgO monolayers were shown to depend critically on growth parameters as temperature (T_g) [2], O_2 partial pressure and Mg evaporation rate [3] during reactive deposition. However, contrasting data are present in literature with respect both to the optimal T_g [2,4] and to the island morphology and orientation [5,6].

Recently we demonstrated [7] that the final morphology of monolayer MgO/Ag(100) films depends not only on the usual growth parameters but also on after-growth treatments - in particular on the cooling rate after growth – which control so far neglected thermodynamics constrains. We succeeded thus in tuning the shape of the oxide films from irregular, nm-sized, monolayer thick islands, to slightly larger, perfectly squared bilayer islands, to extended monolayers limited apparently only by substrate steps. In my talk I will present these new results and I will revise previous finding by our group in light of the new information available.

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CONTRIBUTED TALK

Surface chemistry of metal oxide nanoparticles

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Understanding the surface chemistry of nanoparticles is vital to many fields, including clean energy production and storage, heterogeneous catalysis, materials chemistry, and environmental remediation. Nanoparticles are significantly more reactive than larger substrates due to their increased surface to volume ratio; however, the structural and electronic effects of nanoparticles do not necessarily mimic the macroscopic properties of the bulk material. Nanoparticles can be very difficult to characterize and it is challenging to elucidate their role as substrates in the reactions they are facilitating.

This project describes recent work focused on the surface chemistry of metal oxide nanoparticles, such as TiO_2, ZnO, and ZrO_2, commonly used in catalytic systems. In heterogeneous catalysis, these metal oxides are often used as a support medium for the catalyst and serve as an initial adsorption site for the molecules of interest. In photocatalytic systems, light induced reactions take place at the interface between the nanoparticle and an adsorbed sensitizing molecule. There are two primary classes of photocatalytic reactions: an adsorbate is excited by the light and interacts with the substrate, or the substrate is excited by the light and transfers an electron to the molecule. In both types of catalysis, it is the reaction of the adsorbate with the nanoparticle that truly drives the entire system. To maximize these catalytic processes, a better understanding of the interactions between the nanoparticles and the adsorbate is needed.

Unfortunately, using traditional surface science techniques to understand these reactions can be complicated. Traditionally in surface science, an investigator uses a well-defined substrate (single crystal, atomically smooth) in a controlled system (UHV, cryogenically cooled) to investigate reactions between the surface and an adsorbate of interest, thus isolating the interactions to be studied. However, studying the surface interactions on nanoparticles can be quite difficult due to the "materials gap", where the material used is not well-defined or characterized, and the "pressure gap", where the substrates are exposed to ambient conditions and reactions are performed either under high vacuum conditions or in the liquid phase.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is well suited for analyzing the surface reactions on metal oxide nanoparticles. These particles are mostly transparent to the infrared and the multi-bounce nature of the diffuse reflectance helps to increase the signal from these low coverage reactions. Atomic Force Microscopy (AFM) is useful to monitor changes in nanoparticle morphology over the course of complex reactions. Confocal Raman Spectroscopy allows for the determination of structural variability, especially in the case of TiO_2 which has different Raman spectra for the rutile and anatase phases. Together all of these tools have been used to monitor reactions and analyze product formation between the nanoparticles, both commercially available and synthesized, and a variety of probe molecules, such as acetic acid, formic acid, water and methanol, under different exposure conditions.

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