

Milan, Italy, Sept. 19th-21st, 2016



17th Workshop on Dynamical Phenomena at Surfaces

Organizers

Guido FRATESI

Università di Milano, Italy

William ALLISON

University of Cambridge, UK

Giulio CASATI

Università dell'Insubria, Italy

Talat Shahnaz RAHMAN

University of Central Florida, FL, USA

Gian Paolo BRIVIO

Università di Milano-Bicocca, Italy

Local committee

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Elena MOLTENI

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Invited speakers

Alessandro COATI

Synchrotron SOLEIL
France

George MALLIARAS

ENS Mines de Saint Etienne
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Eva RAULS

Universität Paderborn
Germany

Stephan RAUSCHENBACH

Max Planck Institute, Stuttgart
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Alex SHLUGER

University College London
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Ralf TONNER

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Latha VENKATARAMAN

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<http://wdps17.fisica.unimi.it>

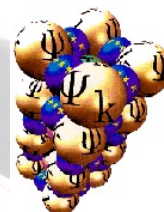
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PHYSICS AND CHEMISTRY OF ADVANCED MATERIALS
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Leonardo da Vinci
(statue by Pietro Magni)



https://commons.wikimedia.org/wiki/File:Milano_collage.jpg



	Monday 19 th		Tuesday 20 th		Wednesday 21 st
08:30	Registration	08:30		08:30	
09:00	Opening	09:00		09:00	
			09:15		09:15
09:30	Session A (Allison) (I) Shluger	09:30	Session D (Brivio) (I) Rauschenbach	09:30	Session G (Alexandrowicz) (I) Malliaras
10:00	Morgenstern	10:00	Einstein	10:00	Carnevali
10:30	Tamtögl	10:30	Vattuone	10:30	Calloni
11:00	Coffee	11:00	Coffee	11:00	Coffee
11:30	Session B (Morgenstern) (I) De Wijn	11:30	Session E (Einstein) (I) Tonner	11:30	Session H (Rahman) (I) Rauls
12:00	Manini	12:00	Scalise	12:00	Alexandrowicz
12:30	Righi	12:30	Lončarić	12:30	Le
	Lunch		Lunch		Closing remarks
14:30	Session C (Fratesi) (I) Venkataraman	14:30	Session F (Zojer) (I) Coati	14:30	
15:00		15:00		15:00	
	Zojer		Floreano		
15:30		15:30		15:30	
	Ravikumar		Molteni		
16:00	Coffee	16:00	Coffee	16:00	
16:30	Poster 1	16:30	Poster 2	16:30	
18:30		18:30		18:30	
19:30	Happy Hour	19:30	Social dinner	19:30	

Monday Sept. 19th

08:30	Registration
09:00	Opening
	Session A: Monday morning Chairman: Allison
09:15	Alexander Shluger (invited) Understanding the adsorption and self-assembly of functional organic molecules on insulating substrates
09:55	Karina Morgenstern Correlated diffusion investigated by low-temperature scanning tunneling microscopy
10:20	Anton Tamtögl Diffusion on a topological insulator surface: H ₂ O on Bi ₂ Te ₃ (111)
10:45	Coffee break
	Session B: Monday morning Chairman: Morgenstern
11:15	Astrid de Wijn (invited) Nanoscale friction under electrochemical control
11:55	Nicola Manini Frictional features in graphene nanoribbons deposited on gold
12:20	Maria Clelia Righi Ab initio investigation of tribochemistry mechanisms in solid and boundary lubrication
12:45	Lunch
	Session C: Monday afternoon Chairman: Fratesi
14:30	Latha Venkataraman (invited) Physics and Chemistry of Single-Molecule Circuits
15:10	Egbert Zojer Collective electrostatics determining photoexcitations and charge transport in self-assembled monolayers
15:35	Abhilash Ravikumar Femtomagnetism in graphene induced by core level excitation of organic adsorbates and the role of electron transfer
16:00	Coffee break
16:30	Poster session (1)
19:00	Happy hour

Tuesday Sept. 20th

	Session D: Tuesday morning Chairman: Brivio
09:15	Stephan Rauschenbach (invited) Electrospray Ion Beam Deposition of Proteins, Peptides, and Sugars: Macromolecular Structure Revealed by STM
09:55	Theodore L. Einstein Transient Mobility Revisited: Impact on Signatures of Island Growth on Surfaces
10:20	Luca Vattuone Observation of the acoustic surface plasmon by inelastic neon scattering
10:45	Coffee break
	Session E: Tuesday morning Chairman: Einstein
11:15	Ralf Tonner (invited) Surface chemistry for organic-inorganic interfaces – a quantum chemical perspective
11:55	Emilio Scalise Probing the interface between semiconducting nanocrystals and molecular metal chalcogenide surface ligands: insights from first principles
12:20	Ivor Lončarić Dynamics of CO interaction with Ru(0001): microscopical elucidation of the results of molecular beam experiments
12:45	Lunch
	Session F: Tuesday afternoon Chairman: Zojer
14:30	Alessandro Coati (invited) Organic molecules/Metallic surfaces structures studied by x-ray scattering
15:10	Luca Floreano Porphyrin Self-Metalation on Rutile TiO ₂ (110)
15:35	Elena Molteni Uracil-like nucleobases on Si(001): effect of molecule adsorption, geometry and chemical substitutions on the electronic and optical properties of the silicon surface
16:00	Coffee break
16:30	Poster session (2)
19:30	Social dinner

Wednesday Sept. 21th

	Session G: Wednesday morning Chairman: Alexandrowicz
09:15	George Malliaras (invited) Interfacing with the Brain using Organic Electronics
09:55	Virginia Carnevali Graphene Moire' structures on Ni(001): atomic-scale investigation
10:20	Alberto Calloni Structure and electronic properties of Zn-tetra-phenyl-porphyrins single- and multi-layers films grown on Fe(001)-p(1×1)O
10:45	Coffee break
	Session H: Wednesday morning Chairman: Rahman
11:15	Eva Rauls (invited) The Interesting Properties of Functionalized Macromolecules on Metal Surfaces
11:55	Gil Alexandrowicz Molecular Beam Spin Echo – Probing Molecule-Surface Interaction with a Molecular Interferometer.
12:20	Duy Le Metal-dipyridyltetrazine chains with single metal coordination site: insights from first principles calculations
12:45	Closing remarks
	Visit to Milan & Departures

Presentation

We are pleased to welcome all participants into the XVII Workshop on Dynamical Phenomena at Surfaces (WDPS-17). We hope that you will be able to enjoy not only stimulating science but also to discover some unexpected features of Milano, which mainly looks like a modern city, but boasts a 25 century history with a lot of important and often hidden monuments.

Coming back to the series of workshops on Dynamical Phenomena at Surfaces, we note that this title has only been introduced recently being the focus of the first workshops only on surface phonons. Tentatively we could talk of a first period in which the outstanding character was Peter Toennies who organized quite a few of these meetings following the first measurements by his Group at Göttingen of surface phonons in insulators and later metals by using a novel Helium atom surface scattering apparatus. The first workshop was entitled Statics and Dynamics of Surfaces and was chaired by Heinz Bilz at Max-Planck-Institut für Festkörperforschung, Stuttgart on 27th September 1983. In that occasion after an experimental talk by Toennies six theoretical contributions including those by Giorgio Benedek and Fritz de Wette were presented. Note that from the very beginning the combination of experimental and theoretical talks has been and is still one of the main assets of this series of workshops.

Already since the 1999 workshop, at that time called Surface Dynamics (organized by V. Celli, A. Kara, T. Raman and J. Skofronik at University of Virginia, Charlottesville, USA), whilst presented phonon studies were still numerous, talks on new topics related to other dynamical phenomena at surfaces were already part of the program such as electron-hole pair energy loss in sticking. The anticorruagating effect of Helium scattering on metals was a central topic at the next workshop at El Escorial in 2001. Since the XIII workshop in Cambridge in 2008 (organized by W. Allison, J. Ellis, and G. Alexandrowicz) these biennial meetings are named Workshop on Dynamical Phenomena at Surfaces (WDPS).

In the last few editions the WDPS has succeeded in gathering scientists with a long tradition in surface vibrations and dynamical processes at surfaces (scattering, sticking, diffusion) with other ones which could contribute to new important topics such as growth, molecule-surface interaction, friction, complexity at surfaces (Leiden, NL 2012) photochemical reactions at surfaces (Madrid 2014). The Milano edition will emphasize research on the properties of hybrid interfaces at the nanometer length scale, which are basic for the foundation of organic electronics and photovoltaics. Still to stress the continuity of this series of workshops with the scientists involved at its very beginning we look forward to hosting two researchers who gave pioneering contributions to the studies of surface phonons, Andrea Levi and Virginio Bortolani. To conclude we expect the XVII WDPS to supply a couple of scientifically exciting days of talks and informal discussion capable to foster new projects and initiatives in surface science and to set up new stimulating editions of WDPS.

This scientific event combines with the X Anniversary of the European Doctorate in Physics and Chemistry of Advanced Materials (PCAM). So in the afternoon of 21st September a European delegate meeting of several Universities will discuss new international initiatives including the EIT-labelled (European Institute of Innovation and Technology) educational program at Master and PhD levels to foster students to become more creative, innovative and entrepreneurs. Finally, Talat Rahman will capture the interest of students and researchers with a talk on her overmastering feeling and devotion to science on 22nd September at 14:30. [*GF and GPB*]

Acknowledgments

We gratefully acknowledge the support by the Physics Department of the University of Milano, the Psi-K network, SAES Getters S.p.A., the European Doctorate in Physics and Chemistry of Advanced Materials (PCAM), the THINFACE Network, and the University of Central Florida. The organizers also wish to thank the University of Milano for hosting the Workshop and for providing logistic support, and Dr. Elena Molteni for helping in the local organization.

Guido Fratesi, Università di Milano, Italy

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Giulio Casati, Università dell'Insubria, Italy

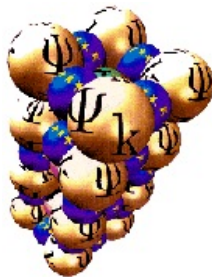
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List of participants

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16. EINSTEIN, Theodore L. – University of Maryland, Maryland (USA)
17. FLOREANO, Luca – CNR-IOM, Trieste (Italy)
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22. LEVI, Andrea – Università degli Studi di Genova, Genova (Italy)
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40. RAUSCHENBACH, Stephan – Max Planck Institute, Stuttgart (Germany)
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42. RIGHI, Maria Clelia – Università di Modena e Reggio Emilia, Modena (Italy)
43. ROSA, Patrizia – Università di Milano, Milano (Italy)
44. SAFDARI, Fatemeh – Sharif University of Technology, Tehran (Iran)
45. SCALISE, Emilio – Max Planck Institut für Eisenforschung, Düsseldorf (Germany)
46. SCHUMANN, Florian – Martin-Luther-Universität Halle, Halle (Germany)
47. SHLUGER, Alex – University College London, London (UK)
48. TAMTÖGL, Anton – Graz University of Technology, Graz (Austria)
49. TONNER, Ralf – Philipps-Universität Marburg, Marburg (Germany)
50. VATTUONE, Luca – Università di Genova and IMEM-CNR, Genova (Italy)
51. VENKATARAMAN, Latha – Columbia University, New York (USA)
52. WARD, David – University of Cambridge, Cambridge (UK)
53. WITKOWSKI, Nadine – Université Pierre et Marie Curie, Paris (France)
54. ZOJER, Egbert – Graz University of Technology, Graz (Austria)

Abstracts of
invited and
oral contributions

Understanding the adsorption and self-assembly of functional organic molecules on insulating substrates

David Z. Gao, Julian Gaberle, Matthew Watkins, Christian Loppacher, Laurent Nony and Alexander L. Shluger

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Understanding the adsorption and self-assembly of functional organic molecules on insulating substrates is of critical importance for many applications, ranging from molecular electronics to lubrication. We will discuss the challenges facing these studies by presenting the results of combined non-contact atomic force microscopy (NC-AFM) experiments and theoretical calculations of the effects of molecular structure and flexibility on the adsorption and self-assembly of organic molecules on KCl. A set of variable molecules were synthesized, deposited onto the KCl (100) surface, and imaged using NC-AFM. A 2-dimensional periodic implementation of quantum mechanics/molecular mechanics (QM/MM) combined with genetic algorithm (GA) techniques was used to produce classical force fields to study the dynamic properties and film structures of these molecules. The accuracy of the van der Waals corrected DFT-D3 was benchmarked using Møller–Plesset perturbation theory calculations. These force fields were used to perform potential of mean force (PMF) calculations of adsorption of individual molecules and extract information on the entropic contributions to adsorption energy. The formation of self-assembled monolayers was studied using both static and molecular dynamics simulations. We demonstrate that the functional groups, the length of the molecular backbone, and the flexibility of these molecules all greatly affect their ability to form defect free self-assembled networks and the morphology of these films.

Correlated diffusion investigated by low-temperature scanning tunneling microscopy

Ch. Zaum and K. Morgenstern

Chair of Physical Chemistry I, Ruhr-Universität Bochum, Germany

As part of reactions, the motion of adparticles on surfaces is a particular active area of research, because a variety of basic physical and chemical processes start with the transport of objects on a surface. For instance in heterogeneous catalysis, the reactants have to diffuse to active sites, at which the actual reaction proceeds. The mobility of the objects frequently limits the overall reaction rate. Atomic diffusion has therefore been studied intensively, however, mostly at dilute coverage. At realistic conditions, adsorbate interactions might alter diffusion rates. Indeed, our time-lapsed studies of CO diffusion on Ag(100) and on Cu(111) in the temperature range below 50 K [1] reveal a multitude of interactions that alter the overall diffusion rate. On Ag(100), the short-range interactions enhance the diffusion rates by orders of magnitude. On Cu(111), long-range interactions as mediated by surface states influence diffusivities [2]. Moreover, we present evidence for a many-body interaction. The effect of the interaction is surprisingly different, if diffusion is induced by fs-laser irradiation [3]. The origins of the different phenomena will be discussed.

[1] Christopher Zaum, Cord Bertram, Kastur M. Meyer auf der Heide, Michael Mehlhorn, Karina Morgenstern
Review of scientific instrumentation 87, 053902 (2016)

[2] Christopher Zaum, Karina Morgenstern, Nano Letters 16 (2016) 3001

[3] Christopher Zaum, Kastur M. Meyer-auf-der-Heide, Michael Mehlhorn, Steve McDonough, William F. Schneider, Karina Morgenstern, Physical Review Letters 114 (2015) 146104

Diffusion on a topological insulator surface: H₂O on Bi₂Te₃(111)

A. Tamtögl^{1,2}, N. Avidor¹, I. Calvo-Almazán¹, P. Townsend¹, D. J. Ward¹, M. Bianchi³, P. Hofmann³, J. Ellis¹, W. Allison¹ and W. E. Ernst²

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Water is ubiquitous in everyday life, yet the simplest mechanisms controlling its molecular motion at a surface have to be revealed by experiment[1-3]. We have studied the diffusion of H₂O on the Bi₂Te₃(111) surface using helium-3 spin-echo spectroscopy[4], a reciprocal-space technique that places tracer and collective diffusion on the same footing. While it is known that water does not react with Bi₂Te₃[5], information about the diffusion of adsorbates on topological insulator surfaces is scarce. Notably, surface diffusion measurements are capable of providing new bench-mark data for energy landscapes on topological insulator surfaces with their peculiar electronic surface effects.

The diffusion of H₂O on in-situ cleaved single crystals of Bi₂Te₃(111) was studied by applying a water overpressure in the temperature range of 135 - 160 K. The molecular dynamics extracted from spin-echo measurements shows thermally activated diffusion with a jump mechanism and an activation energy of 40 meV. The dependence upon the momentum transfer is characteristic for jumps on a hexagonal lattice in accordance with the preferred adsorption site from density functional theory calculations. Furthermore, the measurements indicate that interactions between the individual water molecules play a significant role in the diffusion mechanism of water.

[1] A. Hodgson et al., *Surf. Sci. Rep.* 64, 381 (2009).

[2] S.-C. Heidorn et al. *ACS Nano* 9, 3572 (2015).

[3] J. Carrasco et al., *Nat. Mater. Sci.* 11, 667 (2012).

[4] A. Jardine et al., *Prog. Surf. Sci.* 84, 323 (2009).

[5] L. V. Yashina et al. *ACS nano* 7, 5181 (2013).

Nanoscopic friction under electrochemical control

Astrid de Wijn

University of Stockholm, Sweden

A unique path to control and ultimately manipulate forces between material surfaces is through an applied electric field. Several experimental and theoretical studies of electro chemical interfaces demonstrated that the orientation of polar molecules adsorbed at electrode surfaces is potential dependent. We propose a theoretical model for friction under electrochemical conditions focusing on the interaction of a force microscope tip with adsorbed polar molecules of which the orientation depends on the applied electric field. The dependence of friction force on the electric field is shown to be determined by the interplay of two channels of energy dissipation: (i) the rotation of dipoles and (ii) slips of the tip over potential barriers. We use this model to investigate the effects of molecule anchoring to the surface, and the dispersion in the layer of molecules. The effects of oscillating fields are investigated as well.

[1] Nanoscopic friction under electrochemical control A. S. de Wijn, A. Fasolino, A. Filippov, M. Urbakh, Phys. Rev. Lett. 112, 055502 (2014).

[2] Effects of molecule anchoring and dispersion on nanoscopic friction under electrochemical control A. S. de Wijn, A. Fasolino, A. E. Filippov, and M. Urbakh, J. Phys.: Condens. Matter 28, 105001 (2016).

Frictional features in graphene nanoribbons deposited on gold

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We address the atomistic nature of the longitudinal static friction of graphene nanoribbons (GNRs) deposited on Au (111); the structural and mechanical properties of such graphitic nanostructures have been recently the subject of intense experimental investigation [1-4].

By means of numerical simulations and modeling we show that the bulk of the longitudinal friction originates at the front/tail edges of the ribbons which provide an extra graphene-gold interdigitation. By comparison with an open-boundary Frenkel-Kontorova model we explain the dependence of the total frictional force on the GNR length in terms of the increased compliance of the GNRs edges.

Supporting the experimental data, our model reveals a negligible frictional contribution of the internal “bulk” region of the ribbons. The edges dominate the total friction force which, as a result, does not grow with the GNR length, but rather oscillates around a fairly constant mean value in the 10 pN region, even at very large GNR length.

[1] S. Kawai, A. Benassi, E. Gnecco, H. Söde, R. Pawlak, X. Feng, K. Müllen, D. Passerone, C. A. Pignedoli, P. Ruffieux, R. Fasel, and E. Meyer, *Science* 351, 957 (2016).

[2] P. Ruffieux, S. Wang, Bo Yang, C. Sánchez-Sánchez, J. Liu, T. Dienel, L. Talirz, P. Shinde, C. A. Pignedoli, D. Passerone, T. Dumlaff, X. Feng, K. Müllen, and R. Fasel, *Nature* 531, 489 (2016).

[3] R. M. Jacobberger, B. Kiraly, M. Fortin-Deschenes, P. L. Levesque, K. M. McElhinny, G. J. Brady, R. Rojas Delgado, S. Singha Roy, A. Mannix, M. G. Lagally, P. G. Evans, P. Desjardins, R. Martel, M. C. Hersam, N. P. Guisinger, and M. S. Arnold, *Nature Comm.* 6, 8006 (2015).

[4] S. Kawai, M. Koch, E. Gnecco, A. Sadeghi, R. Pawlak, T. Glatzel, J. Schwarz, S. Goedecker, S. Hecht, A. Baratoff, L. Grill, and E. Meyer, *Proc. Nat. Ac. Soc.* 111, 3968 (2014).

Ab initio investigation of tribochemistry mechanisms in solid and boundary lubrication

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2.Total Research Center Solaize, France

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Tribologically-induced chemical modifications of surfaces interacting with lubricant additives or other molecules present in the environment surrounding the sliding media can substantially change the adhesion and friction of materials in contact, therefore it is highly desirable to understand how they take place. However, tribochemical reactions are difficult to monitor in real-time by experiments, which leaves a gap in the atomistic understanding required for their control.

We investigate the tribochemistry of some of the most common solid lubricants, namely molybdenum disulfide, graphene/graphite and carbon-based films, the performances of which are highly affected by humidity. We apply ab initio molecular dynamics to monitor the chemical reactions involving water molecules activated at the sliding interface. Combining the results of the dynamic simulations with thermodynamic analysis based on static first principles calculations, we elucidate important differences in the tribochemistry of the considered layered materials.[1] We explain the effects of Si dopants in enhancing the hydrophilic character of carbon-based films and discuss its impact on the sliding properties.[2,3]

As second issue, we investigate the tribochemistry of sulfur-, phosphorus-containing additives and graphene at iron interfaces.[4,5,6] The results point at the important role of metal passivation in reducing the adhesion and shear strength of the interface. We generalize the result by establishing a connection between the tribological and the electronic properties of interfaces. This adds a new piece of information for the ultimate understanding of the fundamental nature of frictional forces.

[1] P. Restuccia, G. Levita and M. C. Righi Understanding the tribochemistry of graphene and molybdenum disulfide interacting with water by ab initio molecular dynamics. To be published.

[2] S. Kajita and M. C. Righi Insights into the tribochemistry of silicon-doped carbon based films by ab initio analysis of water/surface interactions, *Tribology Letters*, 61,17 (2016).

[3] S. Kajita and M. C. Righi A fundamental mechanism for carbon-film lubricity identified by means of ab initio molecular dynamics, *Carbon* 103, 193 (2016).

[4] M. C. Righi, S. Loehle', M. I. de Barros Bouchet, D. Philippon and J. M. Martin Trimethyl-phosphite dissociative adsorption on iron by combined first-principle calculations and XPS experiments, *RSC Advances* 5, 101162 (2015).

[5] M. I. de Barros Bouchet, M. C. Righi, D. Philippon, S. Mambingo-Doumbe, T. Le-Mogne, J. M. Martin and A. Bouffet A comparative study on the functionality of S- and P-based lubricant additives by combined first principles and experimental analysis, *RSC Advances* 6, 47753 (2016).

[6] P. Restuccia and M. C. Righi Tribochemistry of graphene on iron and its possible role in lubrication of steel. *Carbon* 106, 118 (2016).

Physics and Chemistry of Single-Molecule Circuits

L. Venkataraman

Department of Applied Physics, Columbia University

The proposal to create molecular analogs of circuit components dates back to the work of Aviram and Ratner from 1974, where they suggested using a single molecule as a diode circuit element in giving birth to the field of molecular electronics. This field has advanced tremendously since then; nanoscale single-molecule devices are now also used as test beds for understanding and controlling electron transfer across metal/organic interfaces. Despite the long-standing interest in creating molecular diodes, their experimental realization has been difficult, with only a handful of studies showing rectification at the single molecule level. In this talk, I will present methods to create single-molecule devices and measured their physical properties, including electronic transport and thermopower. I will then show how their molecular structure as well as the environment around these nanoscale systems can control their electronic characteristics.

Collective electrostatics determining photoexcitations and charge transport in self-assembled monolayers

D. A. Egger^{1,2}, V. Obersteiner¹, T. Taucher¹, I. Hehn¹, A. Kovalchuk³, R. Chiechi³, T. Abu-Hussein⁴, A. Terfort⁴, S. Schuster⁵, M. Zharnikov⁵ and E. Zojer¹

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It has been extensively discussed during the past decade that collective (often also termed cooperative) electrostatic effects arising as a consequence of the regular arrangements of dipoles dominate the electronic properties of self-assembled monolayers.[1,2] They are, for example, responsible for a decoupling of interfacial level alignment from SAM-induced work-function modifications.[3] Recently, it has also been suggested that they can be used to design adsorbate systems with unprecedented properties like interfacial quantum cascades or quantum wells.[4] The present contribution aims at highlighting that such effects also play a crucial role for charge transport and photoionization processes involving SAMs. We show that collective electrostatics results in fundamentally different current-voltage characteristics for SAMs compared to isolated molecules, rendering, for example, the direct comparison between calculations employing periodic boundary conditions and single molecule experiments problematic. For example, collective electrostatics can be responsible for a switching of the transport polarity [5] or can significantly impact the measured transition voltage [6]. It is omnipresent in SAMs-based junctions, as there are always dipole moments present due to the polar docking groups and bonding-induced charge rearrangements [7], but polar groups can also be incorporated next to the docking sites [5,8] or within the backbones [6]. Finally, it will also be described, how collective electrostatic effects shift core level energies (on top of the well-known chemical shifts), an effect often overlooked in literature [9]. This renders x-ray photoelectron spectroscopy as useful tool for probing the electrostatic properties of nanostructures, making it, for example, capable to probe the homogeneity of mixed self-assembled monolayers on a molecular length scale.[10]

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Femtomagnetism in graphene induced by core level excitation of organic adsorbates and the role of electron transfer

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We predict the induction or suppression of magnetism in the valence shell of physisorbed and chemisorbed organic molecules on graphene occurring on the femtosecond time scale as a result of core level excitations and electron transfer at the interface [1]. For physisorbed molecules, where the interaction with graphene is dominated by van der Waals forces and the system is non-magnetic in the ground state, numerical simulations based on density functional theory show that the valence electrons relax towards a spin polarized configuration upon excitation of a core-level electron with the LUMO shifting closer to the Fermi level to accommodate the additional charge and screen the positive core hole. The system is magnetic until the core electron de-excites via one of the several electronic decay channels [2,3]. The magnetism depends on efficient electron transfer from graphene and the corehole lifetime is in the femtosecond (fs) time scale. On the other hand, when graphene is covalently functionalized, the system is magnetic in the ground state showing two spin dependent mid gap states localized around the adsorption site [4]. At variance with the physisorbed case upon core-level excitation, the LUMO of the molecule and the mid gap states of graphene hybridize and the relaxed valence shell is not magnetic anymore.

The influence of a substrate is then considered for charge transfer between molecules and supported graphene. We focus on the resonant charge transfer lifetime of N-1s core excited 1,1' Bipyridine adsorbed on epitaxial graphene/Ni(111). In the ground state, even though the system is magnetic, there is no magnetic moment on the molecule. Upon photoexcitation, our calculations predict that charge transfer may occur bidirectionally to/from the LUMO on a few-fs timescale in good agreement with experimental results [2] and differently from unsupported graphene where no itinerant states are available at the Fermi level.

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Electrospray Ion Beam Deposition of Proteins, Peptides, and Sugars: Macromolecular Structure Revealed by STM

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Measuring and understanding the complexity that arises when synthetic or natural, molecular nanostructures interact with their environment are a current challenge of nanoscale science and technology. High-resolution microscopy methods such as scanning probe microscopy or electron microscopy have the capacity to investigate nanoscale systems with ultimate precision, for which, however, atomic scale precise preparation methods of surface science are a necessity. Often however, ultrahigh vacuum surface science and biological molecules are incompatible. Preparative mass spectrometry (pMS) with soft ionization sources links the world of large, biological molecules and surface science, enabling atomic scale chemical control of molecular deposition in ultrahigh vacuum.

In this talk I explore the application of high-resolution scanning probe microscopy to the characterization of structure and properties of large molecules at surfaces. I briefly introduce the fundamental principles of the combined experiments electrospray ion beam deposition. Examples for the deposition and investigation of single particles, for layer and film growth, and for the investigation of structure, conformation, and electronic properties of individual nonvolatile molecules are presented.

They show that our methodology offers a highly controlled and pure path to high resolution microscopy with unique features of the deposition due to the use of charged polyatomic particles. This new field is an enormous sandbox for researching novel, sequence controlled molecular materials and large, individual molecules.

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Transient Mobility Revisited: Impact on Signatures of Island Growth on Surfaces

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Transient mobility has a long history in the study of accommodation of incident particles. However, its effect of growth exponents has not heretofore been treated. In the study of the case of parahexaphenyl (6P) on sputter-modified mica [1], there were inconsistencies between two standard methods of analyzing island growth: the growth exponent α (island density $\log N \sim \alpha \log F$, for flux F) and the capture-zone distribution (CZD) of the islands. The CZ's are the proximity cells (Voronoi tessellations) of the islands, the areas of which are usually well described by the generalized Wigner distribution (GWD)[2,3]. Specifically, the characteristic exponent of the GWD is simply related to the critical nucleus size i [2,3], which in this case was much smaller than the value deduced from $N(F)$ scaling. In treating transient mobility, we used a rate-equation approach [4]. Two key parameters are the competing times of ballistic monomers decaying into thermalized monomers vs. being captured by an island. There are several other times and energies in the model, with simplifications need on binding and phonon energies to achieve a tractable problem. We obtain an implicit analytic solution and a convenient asymptotic approximation for limiting values of key dimensionless ratios. Our model exhibits non-monotonic crossover of exponents and several intermediate scaling regimes, marked by distinctive values of α and an effective activation energy. One of these, rather than ALA, gives the best fit of the experimental data and a value of i consistent with the CZD analysis. Our approach yields not only the scaling exponent but also the effective bonding energy in an Arrhenius plot. The resulting energies accord well with other assessments of these energies. Applications to other systems and indications of when these effects are likely are discussed.

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Observation of the acoustic surface plasmon by inelastic neon scattering

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The Acoustic Surface Plasmon (ASP), arising from the counter-phase motion of electrons in the Shockley Surface State and in bulk, has been reported so far only by High Resolution Electron Energy Loss Spectroscopy (HREELS). The experiments, performed on Be(0001) [1] Cu(111) [2,3], Au(111) [4,5] and Au(788) [6], confirmed the linear dispersion and evidenced that, in the short wavelength limit, the slope of the ASP dispersion on noble metal surfaces can be markedly smaller than the initially predicted Fermi velocity of the 2D electron gas. HREELS is, however, unable to explore the long wavelength limit because the ASP loss overlaps with the Drude tail. Alternative methods have thus to be sought to explore this very important region extending down to terahertz frequencies which is most promising for applications.

We show here that the ASP can be efficiently excited on Cu(111) by hyperthermal (0.24 eV) Ne beams, obtained by seeding in He. The Time of Flight (ToF) spectra recorded at different polar angles show evidence of energy losses larger than the highest phonon frequency (30 meV) and extending up to 150 meV at small transferred momentum, thus fully compatible with the ASP dispersion on Cu(111) extrapolated from the HREELS data. From the energy width of the observed ASP losses we infer a lower limit to the ASP mean free path of about 25 nm, an information relevant to assess the feasibility of ASP based devices operating in the Terahertz region.

Surprisingly, the intensity of the ASP losses in the Ne ToF spectra is comparable to, and in some cases even larger than, those due to phonon excitations. Our data demonstrate, therefore, that the ASP represents a relevant, and so far not considered, channel for energy dissipation in molecule surface scattering and in adsorption processes.

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Surface chemistry for organic-inorganic interfaces – a quantum chemical perspective

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The interface between a solid inorganic substrate and an ordered adsorbate layer of organic molecules is of continued interest for the experimental and theoretical physics and chemistry community due to their promised application range, e.g. for building chemical sensors. Many fundamental aspects of these interfaces are not yet well understood and concerted efforts of the aforementioned communities are currently being undertaken.

Among the most challenging aspects in this context is the controlled formation of a highly ordered layer of organic molecules covalently bound to the semiconductor surface.[1] The high reactivity of the surface, the need for at best barrier-less adsorption of the organic molecule in the orientation required for further functionalization and the understanding of non-Langmuir behavior of multiple adsorption are some examples here.

Experimental endeavors can help to rationalize some of these aspects but some key quantities, for example reaction barriers and transition state structures, are available only to first principles methods. The talk will highlight aspects of surface chemistry for organic-inorganic interfaces that can be approached by theoretical methods. Special emphasis will be on the successful transfer of concepts from molecular chemistry to surface reactions that can lead to surprising insights in this field.[2]

Examples from our work on surface adsorption, reactivity and chemical bonding[3] of organic molecules with the silicon(001) surface will be used to highlight the strength of the approach.

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Probing the interface between semiconducting nanocrystals and molecular metal chalcogenide surface ligands: insights from first principles

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Colloidal nanocrystals (NCs) are emerging as cost-effective materials offering exciting prospects for solar energy conversion, light emission and electronic applications. Recent experimental advances demonstrate the synthesis of fully inorganic nanocrystal solids from chemical solution processing. The properties of the NC-solids are heavily determined by the NCs surface and their interactions with the host matrix, due to the high surface-to-volume ratio. However, information on the atomistic structure of such composites is hard to obtain, due to the complexity of the synthesis conditions and the unavailability of robust experimental techniques to probe nanointerfaces at the microscopic level. Here we present a systematic theoretical study of the interaction between InAs and InP NCs with Sn_2S_6 ligands. Employing a grand canonical ab initio thermodynamic approach we investigate the relative stability of a multitude of configurations possibly realized at the NC-ligand interface. Our study highlights the importance of different structural details and their strong impact on the resulting composite's properties. We show that to obtain a detailed understanding of experimental data it is necessary to take into account complex interfacial structures beyond simplified NC-ligand model interfaces.

Dynamics of CO interaction with Ru(0001): microscopical elucidation of the results of molecular beam experiments

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A longstanding goal in the field of heterogeneous catalysis is to understand surface reactions on a microscopical level, which would allow for construction of optimal catalysts. In this respect, the interaction of CO with transition metals is one of the most studied examples, both as a simple model system and due to its relevance in the first stage of the Fischer–Tropsch process.

Ruthenium is known to be a very good Fischer–Tropsch catalyst and for this reason the CO/Ru(0001) system has been particularly well studied experimentally. Molecular beam experiments [1,2] have established that at low incidence energies and regardless of surface temperature (in the range of 80–390 K) the sticking probability is close to unity and that it decreases slowly with increasing incidence energy. These results are explained by the existence of a deep chemisorption well. However, the measured scattering angle distributions and the angular dependence of the energy loss are not consistent with such deep chemisorption well.

We will present our recent molecular dynamics simulations on top of a density functional theory based six dimensional potential energy surface [3]. With our calculations we are able to reproduce all experimental observations, and thus give microscopical explanation for them. We will show that the dynamics and the reaction probabilities are dominantly influenced by the initial orientation of the molecule, i.e., whether the O atom or the C atom is closer to the surface. Due to this, scattered molecules, in contrast to adsorbed molecules, explore different regions of the potential energy surface which results in the unexpected scattering angle distributions observed in the molecular beam experiments.

By employing the local density friction approximation [4], we will also quantify for this system, the importance of the energy loss due to excitations of electron-hole pairs compared to the energy loss to phonon excitations.

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Organic molecules/metal interface structures studied by x-ray scattering

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Organic molecules on metallic surfaces constitute nowadays a huge field of studies due to their potential applications in various fields, depending on their properties: semiconductor devices, spintronics... A particular role in the properties of the devices is played by the interfaces between the molecular film and the metal.

Surface x-ray scattering techniques (grazing incidence x-ray diffraction – GIXD- and small angle x-ray scattering – GISAXS- and x-ray reflectivity are powerful tools to study the structural properties of organic/metal interfaces. In this presentation I will show how these x-ray scattering techniques can be used to address the structure and the morphology of these interfaces. Two examples will be shown and commented:

- i. The pentacene (Pn)/copper system, showing long-range ordered molecular arrays when deposited on Cu(110) [1,2]. Ab-initio calculations have confirmed the changes occurring in the electron density [3] and distortions in the molecule and substrate upper layers have been proposed, however, no direct determination of the actual atomic displacements had been attempted. GIXD measurements supported by state-of-the-art DFT calculations [4] could determine the atomic structure of the Pn/Cu(110) interface for coverages at and just below one monolayer.
- ii. Organic molecules can be used as a non-magnetic spacer between two magnetic layers, attracting interest for spintronics applications. Promising results have already been obtained on C60 based spin-valves at room temperature [5] and nano-junction devices at low temperature even present large magneto-resistance value [6]. GIXD, XRR and GISAXS are used to monitor the structure, the morphology and the stability of thin C60 films grown on a Co(0001) substrate. A subsequent Co thin film growth on C60 completes the sample structure Co/C60/Co.

All the experiments were conducted in-situ under ultra high vacuum at the UHV end-station of the SixS (Surfaces and Interfaces x-ray scattering) beamline at Synchrotron SOLEIL.

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Porphyrin Self-Metalation on Rutile TiO₂(110)

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Among dye-sensitized solar cells, porphyrin molecules and titania surfaces are much studied because of the possibility to tune the optical window by a suitable choice of the porphyrin central metal, which can be incorporated post-growth either by metal deposition atop the molecular overlayer [1] or by temperature induced extraction from a metallic substrate.[2]

Recently, the incorporation of deposited Ni atoms in the macrocycle of tetra-phenyl porphyrins (TPP) has been reported also on the TiO₂(110) surface.[3] In addition, the large anisotropy of the rutile TiO₂(110) surface has been shown to drive the ordering of Zn-TPP into compact overlayer domains.[4] In both cases, the optimal metalation and molecular ordering were achieved upon mild annealing to 550 and 420 K, respectively.

Here, we report a combined Synchrotron spectroscopy (XPS, NEXAFS), STM topography and DFT simulation study of the self-metalation of porphyrin molecules deposited on the rutile TiO₂(110) surface. We have recently found that metal-free porphyrins are very reactive on this substrates, so that hydrogen capture by the iminic nitrogen atoms takes place already at room temperature.[5] The incorporation of Ti substrate atoms into TPP is found to start at a substrate temperature as low as ~350 K. The interfacial molecules are found to be fully metalated at 400-450 K, irrespective of the molecular coverage (in the monolayer range). Interestingly, the Ti incorporation drives both conformational and orientational changes in isolated molecules, while no phase symmetry changes are observed for compact domains, likely due to steric limitation. We have observed equivalent annealing temperatures also for the self-metalation of differently functionalized porphyrins, namely octa-ethyl (OEP) and tert-butyl-tetra-phenyl (TBTPP) porphyrins.

In conclusion, the mild annealing, as routinely employed for improving the molecular ordering, makes the Ti self-metalation a process competitive with metalation by deposition, and makes potentially active the metal exchange reaction at the interfacial porphyrin layer.

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Uracil-like nucleobases on Si(001): effect of molecule adsorption, geometry and chemical substitutions on the electronic and optical properties of the silicon surface

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The adsorption of nucleobases on silicon surfaces is relevant both for the possibility of incorporating molecular functionalities within the semiconductor technology[1], and for the role of prebiotic molecules in models of the origin of life[2].

In this work we study the electronic properties of uracil-like nucleobases, thymine (THY), uracil (URA) and 5-fluorouracil (5-FU), adsorbed on the Si(001) surface[3], with first principles methods, based on density functional theory (DFT) with pseudopotentials and plane wave basis set. We investigate both the effects of chemical substitutions and of molecule orientation, finding important changes in band dispersion and energy gaps as a function of molecular tilting with respect to the surface normal.

We then extend our analysis to the study of optical properties[4] of the functionalized silicon surface, focusing on optical absorption and reflectance anisotropy spectra (RAS) and on their dependence on molecule adsorption, chemical substitutions and geometric details of the adsorbate. RAS is in fact a surface sensitive technique[5], which could be successfully used for in-situ, non-destructive surface monitoring. We obtain that the optical response of the Si(001) surface is strongly modified by the presence of the adsorbed molecules. We analyze molecule and substrate contributions to absorption and RAS spectra of the Si(001):X systems (X=THY,URA,5-FU), by considering additional model systems to disentangle the geometric and electronic effects of molecule adsorption. Our results may be of interest for applications in hybrid silicon/biomolecule-based nanodevices.

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Interfacing with the Brain using Organic Electronics

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One of the most important scientific and technological frontiers of our time lies in the interface between electronics and the human brain. Interfacing the most advanced human engineering endeavor with nature's most refined creation promises to help elucidate aspects of the brain's working mechanism and deliver new tools for diagnosis and treatment of a host of pathologies including epilepsy and Parkinson's disease. Current solutions, however, are limited by the materials that are brought in contact with the tissue and transduce signals across the biotic/abiotic interface. The field of organic electronics has made available materials with a unique combination of attractive properties, including mechanical flexibility, mixed ionic/electronic conduction, enhanced biocompatibility, and capability for drug delivery [1]. I will present examples of organic-based devices for recording and stimulation of brain activity, highlighting the connection between materials properties and device performance. I will show that organic electronic materials provide unparalleled opportunities to design devices that improve our understanding of brain physiology and pathology, and can be used to deliver new therapies [2-6].

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Graphene Moire' structures on Ni(001): atomic-scale investigation

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Graphene on Ni(100) forms a variety of Moire' patterns which can be well explained in atomistic models by the mismatch with the substrate, with periodicity depending on the relative angle between the hexagonal graphene and the square surface lattices. Evidence of the different Moire' structures is given by high resolution scanning tunneling microscopy images, that are well reproduced by ab-initio simulations. Beyond providing the detailed atomic-scale structures, the numerical simulations allow a deep local characterization of the chemical bonding between the graphene layer and the support. We also discuss the possible formation beneath the graphene of a surface-confined nickel-carbide in specific regions of the Moire', whose presence is suggested by experimental STM images.

Structure and electronic properties of Zn-tetra-phenyl-porphyrins single- and multi-layers films grown on Fe(001)-p(1x1)O

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Porphyrins have attracted the interest of researchers in different fields: chemistry, biology, physics, material science and technology. This is due to the enormous variations of the molecule reactivity obtained by simply changing the peripheral radical groups and/or the inner metal atom. Thin porphyrin films have been grown on metals, semiconductors or organic-compatible substrates in view of possible applications in scalable organic-based devices (sensors, solar cells, etc.). Unfortunately, the molecule-substrate interaction can significantly perturb the reactivity of the porphyrin and the properties of the hypothetical device. Trying to overcome this limit, thin metal-oxide (MO) layers can tangibly reduce the molecule-substrate interaction. In MO an ordered layer of oxygen atoms passivates the buried metal substrate, decoupling the deposited molecules from the metal bulk. Although MO thin films represent an extremely wide class of compounds, we will focus our attention on the well characterized Fe(001)-p(1x1)O system. From a structural point of view, oxygen atoms reside in the (001) surface hollow sites with a fourfold symmetry, slightly above the Fe surface layer, a structural configuration that could help decoupling the porphyrin from the substrate.

We will show results obtained when a prototypical porphyrin molecule [namely, Zn-tetra-phenyl-(meso) porphyrin (ZnTPP)] is deposited on Fe(001)-p(1x1)O. The structure and electronic properties of the samples are studied by low-energy electron diffraction (LEED) and UV-(inverse) photoemission spectroscopy (PES, IPES), respectively. The results are compared with ZnTPP films grown on Si(111)-(7x7), oxygen-free Fe(001) and Au(001)-(5x20) to evaluate the role of the oxide layer. On Fe(001)-p(1x1)O, ZnTPP molecules form a (5x5) reconstruction when the first monolayer is completed, but PES and IPES still show the characteristic HOMO and LUMO states of the molecule. These results suggest that the ultra-thin oxygen layer significantly reduces the molecule-substrate interaction and increases the porphyrin mobility, allowing the molecules to form an ordered film.

The Interesting Properties of Functionalized Macromolecules on Metal Surfaces

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Macromolecules offer a wide range of possible applications, like e.g. as functional agents in (nano-)medicine, catalysis, sensors or in photovoltaics. Furthermore, once synthesized, they are typically quite easy to manipulate and functionalize in order to prepare the desired property.

Porphyrins belong to this class of molecules, and upon varying them and studying model systems of these molecules in gas phase, as monolayers or as multilayers on a surface or in crystalline phases, we can learn much about the systematics and effects of their functional parts.

Corroles are structurally closely related to porphyrins, they have a lower symmetry and smaller cavities, enabling them to stabilize metal ions in exceptionally high oxidation states. This makes them highly interesting for a variety of applications especially in catalysis.

As one example, I will present our dispersion-corrected density-functional theory (DFT) calculations supported by scanning tunneling microscopy (STM) measurements and X-ray photoelectron spectroscopy (XPS) measurements on the adsorption of the free-base 5,10,15-tris(pentafluorophenyl)corrole on Ag(111) surfaces. We studied both single adsorbed molecules as well as monolayer and multilayer thin films. Single molecules adsorb with its macrocycle tilted with respect to the surface, contrasting the typical saddle-shape conformation of related porphyrin species. The tilted adsorption geometries enable the molecules to aggregate in nontrivial interwoven monolayer structures.

Our novel method to simulate the X-ray photoelectron spectroscopy (XPS) of the 1s edges of C, F, and N in conjunction with simulated STM data and the corresponding measurements nicely confirm the molecular structures concluded from the totalenergy calculations and predict the new molecular chemical states obtained after annealing at elevated temperatures. Strong changes in the symmetry of the adsorbed molecular film are observed. At 330 K, our calculations confirm the experimental observation of a singly deprotonated 2H-C species with a near-to-planar macrocycle tilted approximately 20° with respect to the surface plane. At 430 K, the calculations predict an evidence of a ring-closure reaction between a phenyl ring of the molecule and a pyrrole moiety accompanied by hydrogen and fluorine abstraction. Furthermore, polymerization reactions between adjacent molecules start to happen at these temperatures and are currently under investigation.

Molecular Beam Spin Echo – Probing Molecule-Surface Interaction with a Molecular Interferometer

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In this talk, I will give a brief description of a new type of experiments we recently developed in our group, where we combine the helium spin-echo setup [1], with the ability to magnetically manipulate and spin-select molecules [2]. The resulting experiment follows the different rotational and nuclear spin states before and after scattering from a surface, by measuring the Rabi oscillations of the different states interfering one with another. A unique advantage of this method, is that it contains information about the angular momentum projections and not only the principle quantum numbers. Furthermore, the technique does not rely on specific optical excitations, making it widely applicable for different types of molecules. In the talk I will present our first results for hydrogen molecules scattering from a flat metallic surface.

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Metal-dipyridyltetrazine chains with single metal coordination site: insights from first principles calculations

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Creation, stabilization, characterization and control of single atom transition metal sites on surfaces may lead to significant advancement of the next-generation catalyst. Motivated by the experimental results of Skomski et al.,¹ we have performed density functional theory based calculations of Pt-dipyridyltetrazine complexes on the reconstructed Au(100) surface to find that these complexes form 1-dimensional chains aligned 45° with respect to the Au(100) reconstruction row and with the molecule-molecule distance of 6.93 Å. Bader analysis shows that Pt atoms are cationic with a charge of +0.75. This amount of charge is in accord with that on Pt atoms in PtO, as determined by a similar Bader analysis, and indicating that the oxidation state of the Pt atoms in the above Pt-dipyridyltetrazine network is closer to that of Pt atoms in PtO, which is +2, than in Pt₃O₄ or PtO₃. This result is in excellent agreement with XPS data.¹ In addition, our computational screening of the propensity of several other metal atoms for assembling similar dipyridyltetrazine molecular chains show sufficiently large (from 4.8 eV to 6.9 eV) formation energies which suggest their stability. More importantly, the coordination centers of the dipyridyltetrazine chains constituted by Mo, Cr, Fe or Co atoms bind CO and O₂ strongly, suggesting that these chains are potential candidates for CO oxidation catalyst. Details of reaction pathway (energetic and kinetic) of CO oxidation on the chains will be also presented and discussed.

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Abstracts of
poster contributions

The diffusion of COT on Cu(111) observed in the angstrom-picosecond window

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Recent developments in scattering experiments have allowed motion on a molecular scale to be explored in the pico- to nano- second timescales, using ³He Spin Echo spectroscopy[1,2]. We have applied the method to study the mobility of 1,3,5,7-cyclooctatetraene (COT,C₈H₈) on Cu(111). We have measured the dynamics both at low coverage (isolated molecules) and at a medium coverage of 0.3ML, at temperatures of 200K-450K. The diffusive translational motion of COT proceeds by jump diffusion over a Bravais lattice of preferred adsorption sites, with a short residence time of 2[ps] and a low energy barrier of ~30[meV]. In addition, we see evidence for fast diffusion which we relate to rotational motion, and intermolecular interactions between adsorbates. A weakly dispersive vibrational mode at ~1[meV] is seen over a narrow window of parallel momentum transfer.

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Electronic properties of K doped PTCDA monolayer on Ag(111)

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Alkali metal doped organic semiconductors have been used in numerous interesting applications ranging from superconductivity [1, 2] to hydrogen storage [3]. We hereby investigate the K doping of well-ordered herringbone PTCDA monolayer on Ag(111) by means of theoretical techniques and the results are compared with those of the experiments to identify the structural evolution upon doping and the modified molecule-substrate interaction [4]. The calculations are done with density functional theory (DFT) methods, using pseudopotentials, plane waves and Perdew-Burke-Ernzerhof (PBE) functional on the VASP and Quantum Espresso platforms. The experimental methods employed are: low-temperature scanning tunneling microscopy (LT-STM), scanning tunneling hydrogen microscopy (STHM) [5], low-energy electron diffraction (LEED), differential reflectance spectroscopy (DRS - a variation of absorption spectroscopy) [6] and X-ray standing wave (XSW). Tersoff-Hamann approach was employed to compute the ST[H]M images and time dependent DFT (TDDFT) method as implemented in Yambo [7] was used to simulate the absorption spectra. Two highly ordered and stable doping stages are obtained even without annealing named K2PTCDA and K4PTCDA as per their stoichiometry. The K atoms adsorb in the vicinity of the oxygen atoms of PTCDA in both cases as clearly seen in the STHM images. K interacts and decouples the oxygen atoms from the Ag surface. This changes the adsorption structure from that of the undoped PTCDA on Ag(111) as now the molecular backbone is bend into a small U-shape with the perylene ring closer to the Ag surface than the oxygen atoms. K is oxidized loosing its electrons to PTCDA and Ag thereby reducing the surface work function. Density of states show the LUMO which was at the Fermi level in the case of PTCDA/Ag(111) getting filled and shifting continuously to higher binding energies with K doping. As for the absorption spectra, we observe increasing intensity on the higher energy side of the spectrum with increasing doping levels.

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Atomistic simulation of the formation of NH_3 at the pyrite surface under hydrothermal conditions

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Iron sulfides play an important role in various geochemical and environmental processes. Their oxidation is responsible for acid production in mine wastewater which is of great environmental concern. Moreover, iron-sulfides have been proposed to act as catalysts in the synthesis of prebiotic molecules in hydrothermal vents. This feature is the basis for the so called "iron-sulfur world" scenario for the origin of life which was stimulated by the discovery of complex ecosystems close to the black smokers in the deep ocean [1]. Seawater penetrating through cracks and fissures hundreds of meters deep into the oceanic crust is heated at supercritical condition. In this environment, iron-sulfide minerals are available abundantly providing conditions suitable for prebiotic redox processes. An important constituent of the prebiotic pool of reactants is the most reduced nitrogen compound NH_3 which is a necessary precursor for nitrogen-containing organic molecules.

In this contribution, we report on the simulation of the prebiotic synthesis of ammonia from NO_3^- and NO_2^- at FeS_2 surfaces under hydrothermal conditions [2]. Ab initio metadynamics simulations have successfully uncovered a full reaction path consistent with experimental reaction rates [3]. We have found that the reaction mechanism consists of several stepwise single atom transfers. The kinetic bottleneck of the full process is the reduction of NO_2^- which starts preferably at surface defect sites. The supercritical hydrothermal conditions provide a particularly suitable interface arrangement where surface Fe sites are not covered by water thus providing room for both adsorption and reduction of nitrogen oxides.

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V(V) at carbon-based electrodes: a computational study

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In the last decades we observed a growing interest in energy storage systems based on the redox flow battery (RFB). [1] Among all the RFBs presently under study, the all-vanadium RFB shows good properties such as good electrochemical activity, reversibility, and low maintenance costs. [2] Despite the various advantages, this device presents also some drawbacks. In particular, the slow kinetics of V(V) near the electrode can be an issue. [3, 4] It has been observed that the reaction at the cathode highly depends on the type of electrode: both the intrinsic structure of the surface and the presence of chelating agents can influence the redox rate and the reversibility of the process. For this reason carbon surfaces are commonly subject to both thermal and chemical treatments, [5] whose major effect is the formation of oxygen functional groups on the carbon material. These functional groups have two opposite effects: they are able to facilitate the electron transfer step in the V(V)/V(IV) reaction due to the formation of C-O-V-O intermediates, but if in excess, they can diminish the ET due to an increase in charge transfer resistance. Despite the large number of experimental studies conducted, the correlation between surface treatment and electrochemical activity [6, 7] is still unclear. For instance, some studies [3, 5-7] suggest that these groups are important while others [8] argue that they only play a secondary role and emphasize instead a direct correlation between surface sp² states and the oxidation peak potential. A comprehensive understanding of the factors that influence the kinetics of the reactions is a key step in the design of new and more efficient devices. Unfortunately, at present there is a limited number of studies on the basis steps of the kinetics of the VRFB reactions at the electrodes because more attention has been paid to the applied technologies and device development. Here we propose to study the interaction between the V(V) with the surface passivated with different functional groups by means of ab-initio Molecular Dynamics simulations [9] boosted by Well-Tempered Metadynamics [10]. In particular, we determine the structure and energetics of the V(V) in the five functionalized model systems, differing for the structural and chemical properties of the surface in contact with the solution.

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Biom mineralization and Biom mineralization-Inspired Drug Design: Calcite - Peptide Interactions

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The field of interface chemistry has been heavily focused in recent years on the development of systems that could be used for the controlled introduction and release of active pharmaceutical compounds in the living organisms and tissues. Some of the most interesting systems in this respect, attracting interest from both the pharmaceutical and food industry, are the bioinorganic composites of calcite (calcium carbonate) functionalized by small, biologically active molecules, with the aim of controlled drug delivery [1]. In this respect, we decided to investigate the interactions of calcite with two highly active biomolecules, which are experimentally found to strongly interact with the biomineral [2], in an attempt to uncover the roles of flexibility and chirality in biom mineralization and biom mineralization-inspired drug design.

More precisely, using advanced simulation techniques we characterized the adsorption behavior of two epimeric peptides, namely R- and S-Sal (N-Sal-Gly-S-Asp-R-Asp-S-Asp and N-Sal-Gly-S-Asp-S-Asp-S-Asp respectively, where N-Sal denotes the N-terminal residue which is a salicylic acid derivative), on both the stable (104) and growing (001) surfaces of calcite. This, on one hand, allowed us to analyze the conformational behavior of the adsorbed peptides in detail, while, on the other hand, permitted us to investigate the underlying thermodynamics of the process by calculating free energy profiles of adsorption. We thereby found that even small differences, such as the change in the chirality of only one constituent amino acid, can change the conformational behavior/flexibility of the peptide to an extent significant enough to induce different binding patterns and interactions on mineral surfaces, leading to an overall different adsorption of active biomolecules/peptides.

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CO interaction with Graphene /Ni(111): chemisorption at regular sites and intercalation at vacancies

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Due to its exceptional properties graphene (G) is considered one of the most promising materials for the future. Although its possible use as gas sensor has already been demonstrated [1] the surface chemistry underlying it is still unclear.

We investigated the reactivity of single layer G on different substrates (polycrystalline Cu and Ni(111) single crystal) by High Resolution Electron Energy Loss Spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS) and Low Temperature Scanning Tunneling Microscopy (LT-STM).

Non-dissociative chemisorption of CO occurs at cold, pristine graphene grown on Ni(1 1 1) [2]. The CO adlayer remains stable up to 125 K, with some admolecules surviving flashes to 225 K. This unexpected result is explained qualitatively by the modification of the density of states close to the Fermi energy induced by the relatively strong graphene–substrate interaction. Indeed no adsorption is found under the same conditions for G supported on less interacting substrates, like polycrystalline Cu.

We also investigated [3] the reactivity of defects, created by low energy Ne⁺ ions bombardment.

No vibrational signatures of adsorbed CO is found for G/Cu while they are promptly observed for G/Ni(111). The vibrational frequencies and the ratio of the intensity of single and double coordinated CO molecules indicate that the latters have chemisorbed at the G/Ni(111) interface close to vacancies. The red-shift of the C1s binding energy in XPS proves that, close to vacancies, detachment of the G layer from the substrate occurs.

Therefore, contrary to theoretical predictions [4], the edges of single and di-vacancies are chemically inert for all substrates and intercalation occurs only in presence of a reactive substrate.

If CO is dosed again after annealing the CO pre-exposed defected G at 380 K, less CO adsorbs. Since only traces of oxygen remain after annealing at 450 K, it is reasonable that a Boudouard reaction between two intercalated CO molecules has occurred leading to CO₂ desorption and leaving C atoms which may amend the vacancy. STM inspection of the annealed CO/G/Ni(111) layer confirms a significant change of the surface morphology: after annealing the film. Vacancies induced by sputtering are no longer present and the surface presents ""scars"" indicating that the original surface morphology is not fully recovered [3].

These results suggest that neither pristine G sites nor vacancies can be responsible for the sensing activity of Single Layer free standing G.

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The role of rotational excitation in H₂ diffraction from LiF(001) at grazing incidence conditions

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Grazing incidence fast atom and molecule diffraction (GIFAD and GIFMD) techniques have been extensively used as a surface analyzing tool during the last years [1]. Diffraction at GIFAD and GIFMD conditions is observed thanks to the strong decoupling between the normal and parallel motion, so the diffraction is ruled by the slow normal motion. Molecular diffraction spectra tend to be richer than their atomic counterparts, because of the extra internal degree of freedom, and a detailed theoretical analysis may shed light on the role of rotational excitation in these diffraction processes.

To carry out this study, we have built a 6D PES describing the electronic structure of the H₂/LiF(001) system, by interpolation of a set of DFT energies, which have been calculated using the Vienna ab initio simulation package (VASP) [2]. The interpolation has been performed using a modified version of the corrugation reducing procedure (CRP) [3]. Then, we have used a time-dependent wave-packet propagation method [4] to study the dynamics of the system. In this method, a discrete variable representation (DVR) is used for all degrees of freedom, the wavepacket is propagated using the split-operator (SPO) method [5], and then the scattered wavepacket is analyzed using a scattering amplitude formalism [6].

In order to validate the method used, we have performed dynamics at low incidence energy, which successfully compare with previous experimental and theoretical studies [7,8]. Then, we have extended our analysis to high energy grazing incidence conditions, for which there are previous experimental GIFMD results [9]. These experimental diffraction results strongly depend on the incidence direction, and our results indicate that this difference may be due to the different initial rotational distribution of the molecular beam.

In summary, we have been able to accurately simulate the experimental diffraction patterns of the H₂/LiF(001) system at low and high energy at different incidence directions, and our results allow us to rationalize the role of rotational excitation in the diffraction processes, granting us new insight into the experimental patterns.

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The effects of fluorination and side-chain addition on core-level spectra of anthracene

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The performance of organic electronic devices depends to a significant extent on the interfaces that form in these devices; this makes the investigation of organic-inorganic interfaces a topic of active research. Over the past few decades, X-Ray Photoelectron Spectroscopy (XPS) and Near-Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS) have emerged as standard tools for analyzing organic thin-film structures adsorbed on inorganic surfaces. Simultaneously, the theoretical understanding as well as the ability to simulate and disentangle the experimental features has also been developed. Overall, this makes XPS an effective tool to reveal adsorption-induced changes in the chemical environment of the thin film and NEXAFS to determine its spatial orientation.

In this poster, we present the results from density functional theory calculations of XPS and NEXAFS spectra. We compare the XPS spectra for anthracene and perfluorinated anthracene molecules to determine the chemically-induced core-level shifts that arise due to the fluorination. The analysis of NEXAFS spectra provides additional information on how valence states are affected. Considering the many initial and final states relevant in a NEXAFS process, which is even larger for perfluorinated anthracene, we find a comparison of theoretical and experimental spectra crucial for properly understanding the various spectral features. Last we discuss the consequences of side-chain addition to the molecule (relevant for SAM formation) and highlight its impact on the simulated NEXAFS spectra.

The impact of functional group on the electronic structure of surface coordination center

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While 9, 10 dicyano-anthracene (DCA) forms a coordination network on Cu(111) surface with Cu adatom coordinated by three DCA molecules [1], its isomers, 9,10-diisocyano-anthracene forms, surprisingly, molecular rows on the same surface [2]. To understand the impact of functional groups on the electronic structure of the coordination center, we have carried out density functional theory based calculations of the electronic structure of a set of naphthalene molecules with different functional groups (N, CN, NC, NH₂, COH, COOH) adsorbed on Cu(111), with and without a Cu adatom. Our results show that while the interaction between the naphthalene backbone and the Cu(111) surface is dominated by van der Waals (vdW) forces, in all cases considered the functional group forms a covalent bond with the Cu (ad)atom (on) of the surface. The calculated differential charge redistribution shows that the strongest covalent bond is formed by the NC group, which differs remarkably from that formed by the CN group, while the vdW interaction is very similar in both cases. These results provide insights into the different surface coordination behavior of molecules with above-mentioned functional groups.

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A photoelectron study of BSCF and LSCF perovskites after long term aging at high temperatures and permeation tests

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Among the materials developed as membranes for high temperature oxygen separation (for oxycombustion or coal gasification processes) the nonstoichiometric perovskitic compounds ($\text{ABO}_{3-\delta}$) are very promising due to their high permeation.[1] The Barium (BSCF) and Lanthanum (LSCF) strontium cobalt–ferrite are among the most studied mixed ionic electronic conducting materials having interesting properties as Oxygen Transport Membranes (OTM). [2] Among the two mentioned material families the best compositions results to be $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582), which show remarkable permeation properties and adequate structural stability during heating/cooling between ambient and operating temperatures ($800^\circ\text{C} < T < 950^\circ\text{C}$). [3]

In BSCF samples, the main features of Co 2p and Ba 3d are compatible with both elements in the perovskite phase. After thermal treatment the formation of Co oxides comes out together with the formation barium carbonate and strontium carbonate. This result is compliant with a kinetic decomposition of BSCF membranes, assessing a possible decline in long term permeation performances.

The LSCF membranes do not show any significant change electronic structure compared to the as delivered material. The main achievement obtained by XPS measurements is the accumulation of oxygen ions on both sides. This feature is more evident on the side exposed to the gas flow and is completely removed by the sputtering process. A similar superficial accumulation of oxygen is not evident in the BSCF membrane.

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Modeling the Electronic Properties and Absorption Spectrum of Dye-Sensitized TiO₂

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We investigated the adsorption of prototypical dyes (catechol and isonicotinic acid) on the TiO₂ anatase (101) and rutile (110) surfaces by means of Ab initio molecular dynamics simulations and time-dependent density functional calculations. We found that thermal fluctuation induce changes in the alignment of the molecular levels with the TiO₂ valence band edge. These changes have a significant effect on the absorption spectrum of the anatase (101) surface, whose sensitization can be improved by increasing the hybridization between the adsorbed dye and TiO₂ states. Sensitization effects are instead less relevant for the rutile (110) surface. As an extension towards more realistic materials for applications, we further studied two more complex molecular species, namely PTCDI and PTCDAs, adsorbed on the TiO₂ rutile (110) surface. These molecules have a more pronounced sensitization effect with a substantial red-shift of the first peak of the dye/TiO₂ absorption relative to the free dye.

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Effect of electric fields on transport properties of small molecules in aqueous environments

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It is well established that hydrophobicity of an interface, droplet or a particle can be modulated by an external electric field. However, the provided explanations why these essentially uncharged objects like oil droplets exhibit a directional specific movement in the presence of electric fields remain controversial and continuously challenged. Here we study the static and the dynamic behaviour of a model hydrophobic object (Lennard-Jones particle) in water (SPC/E model), by performing extensive molecular dynamics simulations in the absence and the presence of electric fields using the GROMACS software package. We first combine simulations with the linear response theory to show that shear viscosity of water increases with the strength of the electric field. Furthermore, we identify a novel relaxation process in the water network. We then show that both the diffusion and the friction coefficient of the particle can be calculated independently, which allows us to demonstrate the validity of the Stokes-Einstein relation at the nanometer length scale, subject to clearly identified constraints on the mass and the size of the spherical particle, as well as the size of the system. After establishing a sound simulation protocol, we show that the electric field evokes on an average asymmetric distribution of the water molecules around the Lennard-Jones particle. This acts as a steady state density gradient, inducing a phoretic motion of the hydrophobic object towards the region of higher concentration of water. We interpret our data on a basis of Derjaguin theory for diffusiophoresis which predicts the steady state velocity of a colloidal particle as a function of the first moment of the concentration gradient, the effective hydrodynamic radius of the particle, and the shear viscosity of the solvent. This theoretically predicted driving velocity agrees exceptionally well with the results of the simulations.

Nanoclusters on graphene/Ir(111): insights from ab-initio calculations and experiments

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Fabrication of ordered arrays of metallic nanoclusters (NCs) for catalysis applications is the goal of many efforts. The Moire' pattern of graphene/Ir(111) works as an efficient template to this purpose, in particular for the growth of Pt and Ir based NCs, as predicted by ab-initio calculations and observed for different metal loadings. The chemical and morphological behavior of metallic NCs upon interaction with small molecules of environmental importance such as carbon mono- and dioxide is investigated with atomic-level detail from ultra-high vacuum to near ambient pressure by both spectroscopy and microscopy approaches.

Ab initio calculations give insights into the different nucleation behavior of Pt and Ir with respect to other metals, such as for instance Cu, and predict that even materials that do not form cluster superlattices can be grown promoting their nucleation through a seeding mechanism with another properly chosen metal.

Support from the Italian Ministry of Foreign Affairs and International Cooperation (MAECI), MIUR, and the University of Trieste (Finanziamento di Ateneo per progetti di ricerca scientifica - FRA2015) is acknowledged.

Quantitative modeling of a polyatomic molecule-metal surface reaction

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Reactions at the gas-solid interface are ubiquitous and exploited, for instance, in heterogeneous catalysis [1]. Despite the relevance of the field, an accurate theoretical description and a thorough understanding of even the simplest molecule-metal surface reactions are generally still lacking. We report calculations on the dissociation of methane on metal surfaces [2-4]. This reaction does not only represent a model system for the rate-limiting step of the steam reforming process, but it is also of fundamental interest, as the reactivity of this system depends highly on how energy is distributed over the molecular degrees of freedom [5,6]. We show that *ab initio* molecular dynamics (AIMD) calculations in combination with a semi-empirical density functional return a chemically accurate description of the experimentally measured sticking probability of partially deuterated methane CHD₃ on Ni(111). The analysis of our calculations allows us to obtain insight into the reaction mechanism and to validate the use of dynamical approximations employed in recent high-dimensional quantum dynamics studies [7-9]. Through the AIMD method we can also include surface atom motion into our model. This allows us to simulate surface temperature effects and to perform a detailed (mode-decomposed) analysis of phonon excitations in order to elucidate their role for energy dissipation.

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Dynamics study on dissociative chemisorption of H₂ on Pt(111)

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Recently a novel implementation of the Specific Reaction Parameter (SRP) approach to Density Functional Theory (DFT) was proposed for molecule--metal surface reactions, in which the accuracy of the barrier height could be determined within chemical accuracy (1 kcal/mol ~ 4.2 kJ/mol) using density functional theory at the Generalized Gradient Approximation (GGA) level. The SRP functional was taken as a weighted average of two GGA functionals often used for the description of molecule--surface reactions. In this present work we aim to develop an SRP functional for the weakly activated H₂ + Pt(111) system. Single point DFT calculations have been performed using the Vienna ab initio Simulation Package (VASP) computer software and the corrugation reducing procedure (CRP) method has been used to interpolate the DFT results. We have studied the effects of lattice motion on the interaction of H₂ with the Pt(111) surface using a candidate SRP--DFT XC functional and investigated how the motion of surface atoms effects the dissociation barrier height and the barrier geometry. Furthermore, we present dynamics calculations on the dissociation of H₂ and D₂ on Pt(111) using the candidate SRP--DFT potential energy surface. Molecular beam simulations have been done for normal and off--normal incidence for two different incidence directions of D₂ dissociating on Pt(111) with the quasi--classical trajectory (QCT) method and diffractive scattering of H₂ from the surface has been performed with quantum dynamics using wave packets. The results are compared with available experimental data. Our dynamical calculations treat the motion of H₂ (D₂) in all six degrees of freedom. It is shown that the candidate SRP--DFT XC functional (PBE--vdW--DF) can describe reaction probabilities fairly well but fails in the description of the diffraction probabilities, not only quantitatively but also qualitatively. Our results suggest that the PBE--vdW--DF XC functional may not correctly describe the geometric corrugation of the lowest barrier.

Exploring the electron-induced vibrational linewidths of adsorbates on metal surfaces

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The essential part of describing the energy loss mechanism in gas-metal dynamics is to understand the role of non-adiabatic effects that come from the coupling of the adsorbates ionic degrees of freedom and the electronic continuum of the metal surface. Although these effects have been experimentally known to exist for a long time [1], some parts of the theoretical and computational insight have not achieved the desired depth. For example, it is not completely clear whether the vibrational linewidths of the adsorbates on the metal surfaces obtained in infrared absorption spectroscopy (IRAS) [2] can be explained through classical equations of motion corrected with an electronic friction term [3]. In many-body perturbation theory this problem of vibrational linewidths is well established by means of the dynamical phonon self-energy. Therefore, to understand the problem of the electronic friction term, it would be very helpful to establish the connection between the former and the latter physical quantities.

In our work we explore the non-adiabatic coupling in three different gas-metal systems: the H atom on the Pd(111) surface, the N₂ molecule on Fe(110), and CO on Cu(100). To do so, we employ two different computational methods: on the one side we use ab-initio molecular dynamics with electronic friction (AIMDEF) [4], together with the local density friction approximation (LDFA) [5], while on the other side we use the phonon self-energy due to the electron-phonon coupling based on the density functional theory (DFT). Through the results of our simulations we show how both of the mentioned methods give similar qualitative behaviors, and we further explore to what extent the LDFA friction term quantitatively agrees with the DFT-based phonon self-energy. The crucial part of this exploration is to keep track of the approximations done in both formulations.

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Dissipative quantum dynamics of Eley-Rideal H₂ recombination on graphite

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The molecular hydrogen recombination on graphitic surface has been widely studied in the last decades, mainly because of its importance for the chemistry of the InterStellar Medium (ISM). In fact, H₂ is the most abundant molecule in the universe, but its formation mechanism is not yet fully understood. It is now generally accepted that the reaction occurs

on the graphitic surface of interstellar dust grains [1]. Among the the typical mechanism of gas-surface chemistry, we focused on the Eley-Rideal reaction. This mechanism occurs when one H atom (the so called "targon") is previously adsorbed on the substrate and in thermal equilibrium with it; a second hydrogen atom (called the "incidon"), coming from the gas phase, collides and forms the molecule, which leaves the surface.

Due to the collision between the reactants and the products formation, a large amount of energy is released. Part of the available energy goes in the H₂ excitation, while the remaining part is transferred to the substrate and dissipated through phonons and surface heating. In order to fully understand the process dynamics, it is crucial to exploit a quantum approach and to correctly describe the energy transferred to the substrate. Thus, we developed a new approach in which a system-bath description is adopted and used to investigate the zero temperature quantum dynamics with high dimensional wavepacket calculations [2].

In our simulations the system is composed of three degrees of freedom (DOFs), which are the distances from the graphitic surface of the C atom bonded to the targon (z_c) and of the two involved hydrogen atoms (z_t and z_i); only the collinear geometry as been considered. The system can exchange energy with a bath of independent harmonic oscillators.

The oscillators are chosen and characterized so that they can reproduce the fluctuating-dissipative properties of the environment and its coupling with the system.

We performed quantum dynamical simulations with the Multi Layer Multi Configuration Time Dependent Hartree (ML-MCTDH) method, as well as classical and quasiclassical calculations, in order to study the reaction probability as functions of the incidon collision energy.

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Bifunctional cyclooctyne molecules on Si(001): Investigating their suitability as interface building blocks using DFT

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The creation of organic/semiconductor interfaces is important in extending the application range of semiconductors and in the development of new materials and devices. A possible approach for this is depositing organic molecules onto a silicon surface until the highest possible coverage is reached, and subsequent covalent attachment of further molecules to build up the organic phase layer by layer. Cyclooctyne is a promising candidate for this, as it has been shown to bind strongly to the Si(001) surface and form dense and ordered structures.[1] In order to allow the attachment of the second layer, a functional group has to be introduced at the molecule and furthermore meet the following requirements: Low reactivity and weak interaction with the surface for adsorption selectivity, and easily achievable coupling reactions later on.

We investigate the adsorption dynamics and reactivity of two functionalized cyclooctyne molecules on the Si(001) surface: One featuring an ether side group and another one featuring an ethynyl side group. Since for ethers, reactivity into covalently bound states has been shown to be temperature-controllable,[2,3] the cyclooctyne ether should meet the selectivity requirement, while the ethynyl cyclooctyne promises easily performable click chemistry reactions for the coupling reaction requirement.

Using periodic density functional methods, we present the results for single-molecule adsorption of these two molecules on Si(001). Reaction barriers into the most important bound states are calculated and an estimate of the reactivity at different temperatures is given. Comparing the results, the advantages and disadvantages of using each molecule as an interface building block are furthermore presented and discussed.

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Influence of ordered adsorbates on atomic and molecular diffusion on solid surfaces: the case of oxygen passivated Fe(001)

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The diffusion of atomic and molecular species on solid surfaces is a fundamental phenomenon that drives a large variety of physical and chemical processes. In the field of epitaxial growth, the self-assembly of metallic nanosized clusters on either oxide or metallic substrates is exploited to produce nanopatterned materials in parallel bottom-up approaches [1]. In this frame, adatom diffusion is of paramount importance, since the kinetic constraints typically determine the final morphology of the self-assembled nanostructures. Considering heterogeneous catalysis, adatom diffusion is particularly relevant in cases where spill-over effects operate and the reaction proceeds through different steps, mediated by spatially separated active sites [2]: the atomic diffusivity can therefore tune the rate of the chemical reactions. On the other hand, in catalysts consisting in oxide-supported metal clusters, sintering due to mass transfer induced by atoms detaching from smaller clusters and diffusing to larger ones (Ostwald ripening) often leads to catalyst deactivation.

Various factors affect surface diffusion, such as isotropic strain, mesoscopic relaxations and adatom-adatom long range interactions. Among the factors affecting diffusivity, the presence of foreign species adsorbed on the surface might play an important role. Such species can be either light elements, such as atomic oxygen, or heavy elements, such as Pb and Bi, or graphene.

We will analyze the effects that a single layer of oxygen atoms adsorbed on the Fe(001) surface has on the diffusivity of transition metal atoms and fullerene molecules (C₆₀). Combining Scanning Tunneling Microscopy and Density Functional Theory, we will show that the oxygen overlayer dramatically changes both the interlayer and intralayer diffusivity of atoms deposited on Fe(001) [3,4,5]. In addition, the influence of oxygen on the morphology of C₆₀/Fe(001) will be discussed, showing that C₆₀ follows an hybrid nucleation path in between diffusion-mediated growth and ballistic deposition.

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Density Functional Theory Study of Gas Adsorption on metal-Graphene Surface

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Carbon nanostructures are of great importance in academic research and industry, which can be mentioned to chemical sensors, catalytic processes, pharmaceutical and environmental issues [1,2]. Common point in all of these applications, is the occurrence of adsorption of molecules on these structures [3, 4]. Important carbon nanostructures in this case are mainly nanotubes and graphene. To modify pure graphene, recently, many experimental and theoretical studies have carried out to investigate of metal adsorption on graphene [4]. In this work, the adsorption of CO molecules on pure graphene and on metal adatom on graphene surface has been simulated based on density functional theory (DFT). All calculations were performed by PBE functional and Troullier-Martins pseudopotentials. The geometry of CO adsorbates on the pure graphene surface, is shown in (figure 1). CO molecules are adsorbed from oxygen side on the surface of graphene. The 5×5×1 k-point mesh is selected for optimization of the supercell. As seen in (figure 2), density of states (DOS) for graphene-CO, graphen and CO around the Fermi energy have been moved and very small mixing occurred which implies the physisorption of CO on the bare graphen surface. While, the results have showed that CO adsorption on metal adatom on graphene surface is chemisorption. In order to better representation of CO dynamics on the surface, its internal stretching frequency on the surface was calculated.

Keywords: Adsorption, density functional theory, graphene, metal adatom, CO dynamics

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Vibrational Properties of ultrathin Perovskite Films

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Phonons and their softening are key elements for the phase transitions in ferroelectrics and multiferroics. In thin films, the phonons depend sensitively as well as the phase transition temperatures on the strain within the film. Here we report on high-resolution electron energy loss spectroscopy (HREELS) on the (001) surfaces of BaTiO₃, SrTiO₃, and the Ruddlesden-Popper series of Sr_{n+1}Ru_nO_{3n+1} with n of 1 and 2. HREELS reveals three dipole-active phonon-polariton (Fuchs-Kliwer) modes, which are derived from the known transversal optical bulk phonons. In addition, it will be demonstrated that the complex dielectric function in the energy range from 4 to 1000 meV (30 to 8000 cm⁻¹) can be quantitatively extracted from the experimental loss function.

The full dielectric characterization for (001)-oriented single crystals of BaTiO₃ and SrTiO₃ with different intentional doping levels will be presented. The extracted surface dielectric function will be quantitatively compared with available bulk infrared data and allows the experimental determination of the surface-near doping level in oxides. For ultrathin films of BaTiO₃(001) as grown by MBE or magnetron sputtering on various substrates, HREELS data allow for the first time the determination of the complex dielectric functions of ultrathin oxide films down to single unit cell thicknesses. These data will be discussed with respect of a possible two-dimensional electron gas (2DEG) at the surface, electron-phonon coupling, as well as strain-driven phonon softening.

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A neutral helium atom microscope for high resolution microscopy of delicate surfaces

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Helium atom beams have been exploited in surface science investigations because they can be formed into controllable beams, have immense surface sensitivity and a small enough wavelength for high resolution studies. In the current work I will cover the use of helium beams in the latest instrument in the helium scattering family: A helium atom microscope, that acquired first images recently [2].

Microscopy has been a major enabling technique for the development and understanding of materials from the bottom up. Some of the major insights in the development of modern materials have come from scanning probe, electron and ion microscopies, with advances in resolution and sensitivity enabling new material science. Unfortunately charged beam techniques tend to cause surface damage and scanning probe techniques are limited to relatively flat surfaces and suffer from limited scan speeds.

In 2013, in collaboration with colleagues at the University of Newcastle, NSW some of the first reflective mode images with a neutral helium beam [1,2] were acquired. In comparison with a charged beam microscope, the instrument delivers uniquely surface sensitive images with atomic resolution and critically produces no surface damage. Helium microscopy is suitable for measuring a variety of samples including insulator, semiconductor, explosive, biological and 3D self-assembled materials and being a real space technique does not involve complicated post processing techniques. Since generating the first images, in 2013 academic avenues have turned to investigation of potential contrast mechanisms that the technique affords, while also developing the instrument to increase sensitivity and resolution with the objective of commercially viable instrument in the near future.

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Notes

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