

Action CM0601



Electron Controlled Chemical Lithography

Wednesday 12th March - Sunday 16th March 2008 Altis Park Hotel, Lisbon, Portugal



http://www.isa.au.dk/meetings/eccl08/index.html

Table of Contents

Introduction	
Programme Thursday Friday Saturday	
Abstracts for talks arranged chronologically Thursday Friday Saturday	13 26 34
List of posters	45
Poster abstracts arranged in alphabetical order of presenting author	48
List of Participants	

Introduction

Dear Colleagues,

Welcome to Lisboa and *ECCL 2008*, the First Annual Meeting of the COST Action CM0601 on 'Electron Controlled Chemical Lithography' (ECCL).

ECCL 2008 permits for the first time to achieve a very privileged forum of sharing and developing our scientific expertises of current electron interaction research with the STM community, where there are exciting and new advances in molecular manipulation by means of electron induced dissociation. Therefore, we are very pleased to gather together these communities.

The COST Action ECCL was aproved by the Committee for Chemistry and Molecular Sciences and Technologies in 2006. The Action which is funded for 4 years was initially ratified by 13 countries and formally launched in May 2007. At the present the number of European countries formally joining the Action has increased to 15. ECCL is divided into 3 Working Groups each of which are devoted to a specific research theme. Combined the Working Groups bring together a variety of complementary experimental and theoretical expertise. WG1 focuses on "Selective bond cleavage by electron induced dissociation", WG2 on "Chemical control by electron-induced molecular fragmentation" and WG3 on "Chemical control using scanning tunnelling microscopy".

ECCL 2008 promises as the launching Annual Meeting to be an exciting and stimulating conference with 32 oral presentations and more than 40 posters providing a very privileged opportunity of scientific discussion on electron interactions and STM research. Contributions from most of Europe's leading groups are presented at this meeting with several plenary talks from senior academic and industrial researchers We are also very pleased by the encouragement to younger researchers to make their progress report presentations. Since we are celebrating 200 years that the Portuguese Royal Family moved to Rio de Janeiro, Brazil in March 7 1808 to set there for 13 years and rule the Empire from the Southern Hemisphere, we are very pleased to have invited a special guest from outside Europe Professor Gerardo Gerson de Souza from the Federal University of Rio de Janeiro to this forum.

Last but not least, we would like to express our gratitude to the local Co-Chairs Maria Raposo and Paulo Ribeiro with whom we initiated this truly challenging and exciting project. We also wish to extend our thanks to Nykola Jones, João Lourenço, Paulo Gomes, Rodrigo Antunes, Paula Correia, Ana Luísa Cruz and Beverley Harker who worked so hard and made this meeting happen.

Oddur Ingólfsson ECCL Chair Paulo Limão-Vieira ECCL 2008 Chair

Lisboa, March 2008

A special tribute to our colleagues

It is a pleasure for me to take this opportunity to recognise the vital role that Professor Jacques Delwiche and Drs Marie-Jeanne Hubin-Franskin and Isobel Walker have played in establishing Europe as an internationally leading centre of molecular physics. All are, by training, chemists and so they were amongst the first to appreciate electron energy loss spectroscopy (EELS) may be used as a methodology for studying molecular spectroscopy. When EELS is combined with the techniques of photoelectron spectroscopy and VUV absorption spectroscopy (using synchrotron radiation) a definitive analysis of the electronic states of molecular systems is produced that covers both Valence and Rydberg states, defines ionisation potentials and explores the coupling of electronic with vibrational and (when resolution allows) rotational degrees of freedom. Together they have authored over 200 papers - many of which remain the definitive study of the electronic state spectroscopy of the chosen molecule Each have also developed other fields of study, for example Isobel has produced some of the pioneering papers on low energy electron attachment that form the basis of much of the work upon which this ECCL programme is built, while Jacques research into thin films and nanoparticles is particularly relevant to our wish to extend electron induced chemistry to surfaces and lithography. Marie Jeanne has extended her molecular studies to the inner shells data which is now used to explore radiation induced damage in complex biomolecules.

It is particularly fitting that we are able to celebrate the achievements of these three leading members of our community together at ECCL since in the last ten years they have worked together often with my own group and that of our local host (Professor Paulo Vieira). Together we have produced a large number of papers (with many more 'pending') and shared many memorable experiences with a wonderful group of students and postdocs etc. Personally I must thank them for teaching me (a physicist) about molecular spectroscopy and Isobel for guiding me is my first days at a synchrotron facility! Not only are they first rating scientists but they are wonderful teachers and loyal and caring friends.

Therefore, on behalf of all your many friends and colleagues in the EU electron and molecular sciences community I convey to you Jacques, Isobel and Marie-Jeanne our heartfelt thanks and very best wishes for the future, hoping that we will have the opportunity to still benefit from your experience and wisdom.

Nigel John Mason

As recalled by Professor Nigel Mason, the contribution to molecular spectroscopy of Marie-Jeanne, Jacques and Isobel is widely acknowledged by the community. But beside their passion for electrons and synchrotron radiation, all three share another common quality. They have formed and educated masses of students, to which I am belonging. I did an undergraduate training under the authority of Marie-Jeanne officially, but practically supervision was shared by Jacques and both have educated me during my first steps in research. It was during this period that I met Isobel and took part to the ritual Thursday cake in the Lab. I was in big trouble with my study of the electronic spectroscopy of ethyl iodide and I found with her an unexpected source of advices and helps. Isobel put me back on the right track and gave me again confidence. It was also this year that all three guided me during my first visit at the Daresbury synchrotron radiation facility. Without any doubt they succeeded, because I am presently working at a synchrotron! At the end of this period, I happily signed again for a PhD position. Marie-Jeanne took care of the scientific directions and Jacques started to teach me his huge technical and experimental knowledge. At the end of the first year, I had the feeling to have

learnt more in this year than during all my previous undergraduate studies. Jacques and Marie-Jeanne taught me, among many other things I cannot list here, the sense experimental rigor and the art of measuring cross sections. They also forgave me when I twisted the gas needle of the electron spectrometer! A few later, I went to Edinburgh for a month to do some measurements in Isobel's laboratory. It was again a period of enriching moments. I am really indebted to them for all these gifts and their generosity. I must admit that I still run to Liège to get their advices on complicated problems.

I know that my personal example is not isolated and that Jacques, Marie-Jeanne and Isobel have educated plenty of students who would say similar things at my place. One can say that they were Schools of chemical physics.

On behalf of these entire students that passed through your hands, I would like to express you the warmest thanks, deepest gratitude for all these things you were so keen on teaching and also our best wishes for the future!

Alexandre Giuliani

As the host for ECCL first annual meeting and on behalf of the local organizing committee, I feel a tremendous responsibility to bring you all into a comfortable and pleasant place. I hope that we've made it. I dare to affirm that today is a very special and deserved occasion to celebrate the scientific careers of our three loyal and trusted friends. Nigel Mason and Alexandre Giuliani have already expressed their very sincere truthfully testimonies for Marie-Jeanne, Isobel Walker and Jacques Delwiche to which I also would like to join with you all. I am very privileged to have known and worked with them over the years and learnt so many interesting things on the electronic state spectroscopy of the molecular world.

I feel very honoured that this particular occasion has brought to the attention of the highest level of our university, here represented by the Dean of the Faculty of Science and Technology of the New University of Lisbon, Prof. Fernando Santana and also the Head of the Scientific Council, Prof. João Crespo.

I take this chance to thank you all that since the first minute we have proposed to embrace this special tribute to our loyal colleagues, I could collect the warmest agreement for this special occasion. Last but not least, I would like to raise my glass and ask you to join on a toast to Marie-Jeanne, Isobel and Jacques.

Paulo Limão-Vieira March 14th 2008

ECCL International Committee

Oddur Ingolfsson, Iceland, Chair Karina Morgenstern, Germany, Vice-Chair Flemming Besenbacher, Denmark Jacques Delwiche, Belgium Gerald Dujardin, France Karl-Heinz Ernst, Switzerland David Field, Denmark Thomas Field, United Kingdom Mieczyslaw Forys, Poland Gustavo Garcia, Spain Armin Golzhauser, Germany Werner Hofer, United Kingdom Marie-Jeanne Hubin-Franskin, Belgium Anne Lafosse, France Paulo Limão-Vieira, Portugal Bratislav Marinkovic, Serbia Stefan Matejcik, Slovakia Nigel Mason, United Kingdom Sveinn Olafsson, Iceland Paulo Ribeiro, Portugal Paul Scheier, Austria Jan Skalny, Slovakia Petra Swiderek, Germany Mariusz Zubek, Poland

ECCL 2008 Local Committee

Paulo Limão-Vieira, Chair Maria Raposo, Vice-Chair Paulo António Ribeiro, Vice-Chair Rodrigo Antunes Paulo Gomes João Lourenço Nykola Jones Paula Correia (local secretary) Ana Luísa Cruz Beverley Harker (secretary)

Programme

All talks will be held in the Sala Atlantico on the 3rd floor of the Altis Park Hotel, Avenida Engenheiro Arantes e Oliveira, 1900-221 Lisboa, Portugal

Thursday 13 th March		
	Session 1	
08:50-09:00	<i>Welcome:</i> The meeting will be opened by the Dean of the Faculty of Science & Technology of the New University of Lisbon Prof. Fernando Santana	
09:00-09:40	Electron Controlled Reactions in Gas Phase and Condensed Phase Molecules	Eugen Illenberger (Freie Universtitaet Berlin, Germany)
09:40-10:00	Theory of inelastic electron-molecule collisions. From gas phase to molecules on surfaces	Martin Čížek (Charles University Prague, Czech Republic)
10:00-10:20	Surface Dynamics study during the manipulation of single molecules on $Si(100)$ -(2x1) at 5K	Damien Riedel (Centre Universitaire de Paris Sud, France)
10:30-11:00	Coffee Break	
11:00-11:20	Cold electron collisions with solids	David Field (University of Aarhus, Denmark)
11:20-11:40	Molecular nanostructures on surfaces formed by organic reactions	Trolle Linderoth (University of Aarhus, Denmark)
11:40-12:00	Selective bond cleavage by low energy electron impact on gas phase nucleobases derivatives	Robert Abouaf (Université Paris Sud Centre d'Orsay, France)
12:00-12:20	Investigation of low-energy electron irradiation-induced changes in organic materials by thermal desorption spectroscopy	Elisabeta Burean (Universität Bremen, Germany)
12:30-14:00	Lunch	
	Session 2	
14:00-14:40	First-Principles Simulation of Mechanically Induced Chemistry	Irmgard Frank (Universität Hannover, Germany)
14:40-15:00	Modelling resonant fragmentation in biosystems upon electron attachment	Isabella Baccarelli (Supercomputing Center CASPUR, Italy)

Thursday 13th March (cont.)

15:00-15:20	Guiding of low-energy electrons through insulating nanocapillaries	Aleksandar Milosavljević (Institute of Physics Belgrade, Serbia)
15:20-15:40	Using electrons to template a dielectric substrate	Geoff Thornton (University College London, UK)
15:45-16:15	Coffee Break	
16:15-16:35	Design of an instrument to identify suitable molecules for ECCL – work in progress	Elias Bjarnason (University of Iceland, Iceland)
16:35-16:55	Thermally Programmed Desorption experiments at very low temperature (10-30K). Desorption and formation of molecular hydrogen on heterogeneous water ice surfaces of different porosity	Lionel Amiaud (Université Paris-Sud/ Orsay, France)
18:00-	Welcome reception and poster session	

Friday 14th March

	Session 3	
08:30-09:10	Magnetic nanostructures probed on the atomic scale	Cyrus Hirjibehedin (London Centre for Nanotechnology, UK)
09:10-09:30	Electron Induced Molecular Reorganization and Switching at Metal Surfaces	Martin Wolf (Freie Universitaet Berlin, Gemany)
09:30-09:50	Laser-Induced Acoustic Desorption Combined With Electron-Attachment Spectroscopy and Quantum Chemical Methodologies as a Means of Studying DNA Strand Breaks	Iwona Dabkowska (University of Gdańsk, Poland)
09:50-10:10	Coffee	
10:10-10:50	On the behaviour of electron attachment cross sections near zero energy	Harmut Hotop (Technical University Kaiserslautern, Germany)
10:50-11:10	Effective cross sections for low-energy electron scattering from monomolecular films of condensed thymidine	Radmila Panajotovic (The Open University, UK)
11:10-11:30	Optical emission spectroscopy of reactive magnetron discharges.	Andre Wemans (Faculdade Ciencias e Tecnologia/UNL, Portugal)
11:30-12:00	Electronic excitation, single and double ionization of molecules of biological interest using fast electrons and synchrotron radiation	Gerardo de Souza (Universidade Federal do Rio de Janeiro, Brazil)
12:00-12:30	Applications of focused electron beam induced chemical reactions	Klaus Edinger (Carl Zeiss - NaWoTec, Germany)

12:30-14:30 Lunch

14:30-	Excursion to Queluz National Palace and the conference dinner, with a special tribute to our colleagues.
	The conference dinner will also be attended by the Dean of the Faculty of Science and Technology, New University of Lisbon, Prof. Fernando Santana and the Head of the Scientific Council, Prof. Joao Crespo

Saturday 15th March

	Session 4	
09:00-09:40	Patterning of surfaces at the 10nm scale and below	Richard Palmer (University of Birmingham, UK)
09:40-10:00	Vibrational excitation of methane by slow electrons revisited: Joint theoretical and experimental study	Roman Čurík (J Hyerovsky Institute of Physical Chemistry, Czech Republic)
10:00-10:40	Scanning Tunneling Microscopy of Adsorbates on Insulating Films: From Manipulation of the Charge State to Imaging of Individual Molecular Orbitals and Bond Formation	Gerhard Meyer (IBM Zurich Research Laboratory, Switzerland)
10:40-11:00	Coffee Break	
11:00-11:20	Current-Induced Conductance Switching of Individual Molecules	Jascha Repp (University of Regensburg, Germany)
11:20-11:40	Atomic Force Microscopy Characterization of Polyelectrolytes Self- Assembly Films Using Dynamic Scaling Concepts	Quirina Ferreira (FCT - UNL, Portugal)
11:40-12:00	Inelastic interactions of electrons with molecules and clusters embedded in superfluid helium droplets	Paul Scheier (Universität Innsbruck, Austria)
12:00-12:20	Absolute electron – molecule cross sections: elastic, vibrational and electronic excitation, and dissociative attachment	Michael Allan (University of Fribourg, Switzerland)
12:30-14:00	Lunch	

Session 5

14:00-14:40	The hunt for single atom deposition	Cornelis W. Hagen (Delft University of Technology, Netherlands)
14:40-15:00	STM-driven molecular switches at surfaces: From structure to dynamics	Peter Saalfrank (Universität Potsdam, Germany)
15:00-15:20	Jahn-Teller effect in C ₆₀ molecules studied with the Scanning Tunneling Microscope	Nicolas Lorente (CISC, Spain)

Saturday 15th March (cont.)

15:20-15:50	Direct quantitative measurement of	Ahmet Oral
	lateral forces at atomic scale using non-	(Sabanci University,
	contact Atomic Force Microscopy (nc-	Turkey)
	AFM)	

- 15:50-16:15 Coffee Break
- 16:15-17:30 General discussion: further input on the "Action Statement"
- 17:30-18:00 Final remarks
- 18:00- Steering committee group meeting

Talk abstracts

Electron Controlled Reactions in Gas Phase and Condensed Phase Molecules

Eugen Illenberger

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The interaction of free electrons with gas phase molecules can generate transient negative ions (TNIs) by resonant electron capture. One of the possible relaxation pathways is the unimolecular decomposition into a thermodynamically stable fragment anion and into one or more neutral fragments. Owing to the fact that the cross section for electron attachment increases with decreasing electron energy, such dissociative electron attachment (DEA) processes can be very effective at low electron energy. In addition, the accommodation of the extra electron often proceeds via localised molecular orbitals of antibonding nature which can result in a completely selective bond cleavage in a polyatomic molecule. Thus, in many large molecules, including biomolecular systems [1,2], low energy electrons can drive selective dissociation processes at cross sections ranging up to 100 Å² and more.

Extended studies in free molecular aggregates and in condensed molecules (molecular nanofilms) have demonstrated that transient negative ions (resonances) known from single gas phase molecules are often preserved when the molecule is coupled to an environment [3]. In this case both the *formation* of the resonance and its *evolution* is affected by the medium. While the energy of a bound resonance is lowered due to the polarisation of the environment by the presence of the excess charge, its reactivity (cleavage of chemical bonds) is generally strongly suppressed due to energy dissipation. There are, however, particular medium effects which can dramatically enhance the reactivity of a negative ion resonance when bound to a medium [4].

We shall present recent results on low energy driven reactions in single molecules in effusive molecular beams, molecular aggregates in supersonic beams [5], and in molecular nanofims prepared under UHV conditions [6]. It is shown the initial selective cleavage of a chemical bond by low energy electrons can trigger remarkably complex chemical reactions in finite systems like homogeneous or heterogeneous clusters but also in molecular nanofilms.

1. I. Baccarelli, F.A. Gianturco, A. Grandi, R. R. Lucchese, N. Sanna, I. Bald, J. Kopyra, and E. Illenberger, J. Am. Chem. Soc. 129 (2007) 6269.

2. C. König, I. Bald, J. Kopyra and E. Illenberger, Phys. Rev. Letters 97 (2006) 018105.

3. J. Langer, R. Balog, S. Gohlke, M. Stano, H. Abdoul-Carime and E. Illenberger, Int. J. Mass Spectrom. 233 (2004) 267 (Review).

4. E. Illenberger, Surf. Sci. 528 (2003) 67.

5. I. Martin, J. Langer, G. Karwasz and E. Illenberger, Int. J. Mass Spectrom. 249/250 (2006) 477.

6. R. Balog and E. Illenberger, Phys. Rev. Letters 91 (2003) 213201.

Theory of inelastic electron-molecule collisions. From gas phase to molecules on surfaces

Martin Čížek

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I will review the success of the nonlocal resonance model to describe accurately the inelastic low-energy electron collisions with diatomic molecules in gas phase and the prediction of the existence of long-lived states of the molecular hydrogen anion. Then I will continue with explanation, how similar theoretical model can also be applied to electron transfer from excited molecule to the semiconductor surface. Finally the model is applied to electron conduction through molecule attached to two metallic surfaces. The focus is on the theory of interaction of the electron with vibrational degrees of freedom. The application to a linear harmonic model coupled to vibrational bath will be shown and transport of current through some simple organic molecules will also be briefly discussed.

Surface Dynamics study during the manipulation of single molecules on Si(100)-(2x1) at 5K

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²Université de Lyon, Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, CNRS, France

Manipulation of single molecules on semiconductors with tunnel electrons of a scanning tunneling microscope (STM) may lead to dissociation, diffusion and/or molecular conformational changes. For reversible manipulation processes the molecular surface dynamic can be studied with a great accuracy.

We have investigated the manipulation of a bistable molecule (biphenyl) adsorbed on a clean Si(100)-(2x1) surface. The very fine localisation of the tunnel electrons that are provided by the STM tip allows the excitation of specific electronic processes inside a single molecule. The molecular surface dynamics is shown to depend on (i) the initial molecular adsorption configuration (ii) the polarity of the surface voltage during the manipulation and (iii) the substrate dopant type (n or p). To achieve a deeper insight into the molecular surface dynamics, this experimental study is combined with the use of the nudge elastic band (NEB) method to provide calculations of molecular reaction pathways on the surface.

Cold electron collisions with solids

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³Department of Physics and Astronomy, Queen's University Belfast, Belfast, BT7 1NN, United Kingdom

⁴Laboratoire Collisions Agrégats Réactivité-IRSAMC, Université Paul Sabatier and CNRS-UMR 5589, 31062 Toulouse Cedex, France

We using our ASTRID synchrotron photoionization source to irradiate solid material with currents of a few hundred femtoamps, with high resolution in the electron beam. Data will be reported down to energies of a few tens of meV.

We will show our latest work on cold electron transmission and charging properties of water ice at 135K and 40K. We find that hexagonal ice at 140K has a charging cross-section for low energy electrons of <0.003 Å² whereas porous ice, formed at 40K, has a charging cross-section as high as 1.75 Å². We also find that the charging cross-section for 40K porous ice is strongly film thickness dependent, achieving the high value mentioned for sub-monolayer coverage.

Data will also be reported showing the very low energy behaviour of transmission through CF_4 with comparison with data for Xe. We will discuss the possible presence of a Ramsauer-Townsend minimum.

Below we show data which illustrates how hexagonal ice at 140K is transparent to low energy electrons up to an energy of 650 meV. The transmission properties of this material are shown to be independent of the film thickness.



Figure 1. Transmitted current through hexagonal ice at 135K showing full transmission for both a thin layer (12 BL) and a thick layer (430 BL) up to 650 meV incident energy

Molecular nanostructures on surfaces formed by organic reactions

Trolle R. Linderoth

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Molecular nanostructures on solid surfaces are central to formation of advanced functional surfaces for a large number of important application areas. The principles of supramolecular chemistry have therefore been applied extensively to molecules adsorbed at surfaces under Ultra-High Vacuum (UHV) conditions, and complex molecular structures formed by selfassembly based on interactions such as Van der Waals forces, dipole-dipole interactions, hydrogen bonding, or metal complexation have been revealed using local-probe Scanning Tunnelling Microscopy (STM). To form structures of increased thermal and chemical stability, covalent interlinking of adsorbed species would be highly desirable, but similar studies into formation of surface nanostructures by covalent synthesis directly on surfaces under UHV conditions are only just now beginning to emerge.

Here we report on the use of a two-component condensation reaction between aldehyde and amine compounds to form surface nanostructures.



A two-dimensional, branched polyimine network formed by condensation polymerisation between trialdehydes and diamines co-adsorbed on the Au(111) surface under ultrahigh vacuum conditions. The bonding pattern is characterised by Scanning Tunneling Microscopy.

The molecules are co-adsorbed on the Au(111) surface under UHV conditions and reaction is induced by thermal activation. Covalent interlinking of the reactants through formation of iminebonds is confirmed by comparison to the STM signature of the reaction product formed *ex-situ* as well as by NEXAFS spectroscopy [1]. Insight into the reaction mechanism under solvent-free conditions is obtained from Density Functional Theory calculations. It is shown that the combination of on-surface synthesis and subsequent self-assembly may lead to unique structures that are not obtained by conventional, direct deposition of similar molecular building blocks [2]. Two-dimensional branched polymeric surface networks are obtained using three-spoke aldehydes and di-amine linkers (see figure) [3]. The networks exhibit pores with 3-10 nm dimension, and it is demonstrated that the network connectivity can be controlled by varying kinetic parameters of the preparation procedure.

[1]: Sigrid Weigelt, Carsten Busse, Christian Bombis, Martin M. Knudsen, Kurt V. Gothelf, Thomas Strunskus, Christof Wöll, Mats Dahlbom, Bjørk Hammer, Erik Lægsgaard, Flemming Besenbacher and Trolle R. Linderoth, *Covalent Interlinking of Aldehydes and Amines on Au(111) under Ultrahigh Vacuum Conditions.* Angewandte Chemie Int. Ed. 46 9227 (2007).

[2]: Sigrid Weigelt, Christian Bombis, Carsten Busse, Martin M. Knudsen, Kurt V. Gothelf, Erik Lægsgaard, Flemming Besenbacher, and Trolle R. Linderoth, Molecular self-assembly from building blocks synthesized on a surface in Ultra-high Vacuum: Kinetic control and topo-chemical reactions, ACS-Nano, Accepted (2008).

[3]: Sigrid Weigelt, Carsten Busse, Christian Bombis, Martin M. Knudsen, Kurt V. Gothelf, Erik Lægsgaard, Flemming Besenbacher, and Trolle R. Linderoth, Surface Synthesis of 2D Branched Polymer Nanostructures, Angewandte Chemie Int. Ed. Accepted (2008).

Selective bond cleavage by low energy electron impact on gas phase nucleobases derivatives

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Bond cleavage of gas phase molecules by low energy electron impact (0-10eV) occurs mainly via dissociative electron attachment (DEA). The first step of this process is the temporary capture of the incident electron, leading to a very short lived metastable anion state ("resonance"), within a rather well defined energy range (generally a few eV or less). One of the decay channels of this resonant state is dissociation, giving a stable anion and one or several neutral fragments. This fragmentation is therefore clearly incident energy selective. Furthermore, the symmetry of the fragments is dependent on the resonant state symmetry, inducing also another selectivity in the fragmentation.

We will present various DEA results concerning the bond cleavage selectivity in some derivatives of uracil, cytosine and adenine nucleobases.

It is well known that the major low energy dissociation processes for these nucleobases lead to a selective ablation of a H atom giving rise to (M-H)⁻ anions at an incident energy of about 1eV. However, the substitution of a H atom in uracil by a halogen atom strongly modifies the nature and the cross section of the dissociation processes (1,2). Besides (M-H)- fragments, many more anions appear with a threshold lowered down to zero energy, and the total dissociation cross section increases by more than 2 orders of magnitude.

We have observed that the substitution of the same H atom in uracil by an NO₂ group leads also to very efficient dissociation processes. $(M-NO_2)^-$ and $(M-H)^-$ anions are observed at zero energy with huge cross sections ($\geq 10^{-18}m^2$). The $(M-H)^-$ cross section versus electron energy presents several features revealing the energy selectivity of the H abstraction site.

Dissociation results in adenine and in some of its derivatives demonstrate a strong selectivity for the formation of (M-H)⁻ anions (3). Other dissociation processes in bromo-cytosine and fluoro-cytosine, will also be presented and discussed.



References

1. S. Denifl, S. Matejcik, B. Gstir, G. Hanel, B.M. Probst, P. Scheier, T.D. Märk, J. Chem. Phys. **118** (2003) 4107

2. R. Abouaf, H. Dunet, Eur. Phys. J. D 35 (2005) 405

3. S. Denifl, P. Sulzer, D. Huber, F. Zappa, M. Probst, T.D. Märk, P. Scheier, N. Injan, J. Limtrakul, R. Abouaf, H. Dunet, Angew. Chem. Int. Ed. **46** (2007) 5238

Investigation of low-energy electron irradiation-induced changes in organic materials by thermal desorption spectroscopy

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Lithographic approaches using electrons, photons, or ions that induce changes and bond breakages in molecular systems are widely used to pattern surfaces and create nanometer-scale complex structures of a great importance in modern electronic industry as well as in other applications. Electron beam techniques have been used for creating structures with sub 100-mn resolution. For instance, the production of nanostructures using self-assembled monolayers as positive and negative resist on surfaces by means of low energy electron beam technique has been reported [1].

The aim of ongoing research is to demonstrate the selectivity of such processes through the proper choice of electron dose and energy at which the lithography process is carried out. Thus, the mechanisms of the underlying electron-induced reactions need to be studied in depth. This includes identification of reaction products following electron irradiation as well as measurement of cross sections for their formation.

The selectivity of low-energy electron-induced fragmentations can be used to create highly reactive species which may further recombine to form more complex molecules [2]. The present work focuses on identification and quantification of such reaction products following bombardment with electrons using thermal desorption spectroscopy (TDS) [3]. The procedure used for this purpose which is based on the comparison of TDS spectra obtained from exposure experiments with those of reference mixtures containing the suspected product in different percentages will be discussed. Equally the measurement of cross sections for the depletion of the initial material and the formation of products will be presented.

- [1] A. Gölzhäuser, W. Geyer, V. Stadler, W. Eck and M. Grunze. J. Vac. Sci. Technol. B 2000, 18, 3414.
- [2] P. Swiderek, C. Jaggle, D. Bankmann, E. Burean J.Phys. Chem. C 2007, 111, 303.
- [3] E. Burean, P. Swiderek, Surf.Sci., in print.

First-Principles Simulation of Mechanically Induced Chemistry

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The simulation of mechanically induced chemical reactions is most fascinating and most difficult for those cases where the reaction mechanism (radicaloid / acid-base / redox etc.) is not known from experiment. Then it is usually not possible to parametrize a force field for the description of the system under investigation. Instead a first-principles approach must be applied where the electronic structure is described on a quantum mechanical basis. The most successful scheme in this context is Car-Parrinello molecular dynamics which uses density functional theory for the electronic structure and Newton dynamics for the nuclei. Naturally, the broad applicability of the approach to almost arbitrary molecular systems is connected with high demands of CPU time and limited simulation times.

The talk presents some recent applications to mechanically induced reactions in polymers under mechanical load demonstrating the factors which determine reaction mechanisms and rupture forces.

Modelling resonant fragmentation in biosystems upon electron attachment.

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Recent years have witnessed a remarkable growth of both experimental and theoretical investigations on the capabilities of low-energy electrons to selectively break molecular bonds. Such a remarkable property shed a new light on the general understanding of complex phenomena, such as the damage to a living tissue under exposure to an ionizing radiation, and it opened the way to the `engineering' use of electrons in the chemical control of processes.

A key point to understand (and act on) such selectivity property lies in the formation of (quantum-mechanical) resonance states due to the temporary electron attachment to the system at specific collision energies. Such states are commonly referred to as Temporary Negative lons (TNIs) and essential information on the possible molecular break-up can be gained from the specific features of the corresponding wavefunctions. The resonant nature of the process also suggests the possibility to control the break-up by tuning the collision energy.

In the last few years we devoted a great amount of effort in the study of electrons as probes of the various DNA building blocks in the gas-phase: one important motivation of such studies resides, as mentioned, on their providing nanoscopic information when real biosystems are exposed to ionizing radiation and can undergo irreversible molecular damage [1]. The quantum mechanical analysis of such processes is a challenging task, due to the size and the generally low symmetry of the system under study and in the perspective of extending the analysis from individual building blocks to larger biological macromolecules.

The nanoscopic mechanism which has reached by now a rather broad consensus in the relevant literature [2,3] involves the initial removal of electrons from the molecular components of the complex network by the impinging radiation. Secondary electrons with initial kinetic energies up to about 20 eV turn out to be indeed the most abundant of the secondary species created by the primary ionizing radiation. The ability of presolvated, free electrons to efficiently induce SSB and DSB effects in super coiled DNA has clearly been shown in several experiments [4].

We will discuss here our computational study of the electron attachment process for selected biosystems. The elastic cross sections and a high-level Breit-Wigner analysis of the resonance structures are presented together with the characterization of the TNIs' wavefunctions [5,6]. The comparison between different methodologies allows us to estimate the reliability of the approximations employed while providing a more complete picture of the process.

[1] I. Baccarelli, F.A. Gianturco, A. Grandi, R.R. Lucchese and N. Sanna, Adv. Quantum Chem. **52**, 189(2007).

[2] B. D. Michael and P. O'Neill, Science 287, 1603 (2000).

[3] B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels and L. Sanche, Science 287, 1658 (2000).

[4] L. Sanche, Eur. Phys. J. D 35, 367 (2005).

[5] A. Grandi, F. A. Gianturco and N. Sanna, Phys. Rev. Lett. 97, 018105 (2006).

[6] I. Baccarelli, F.A. Gianturco, A. Grandi, R.R. Lucchese, N. Sanna, I. Bald, J. Kopyra and E. Illenberger, JACS, **129**, 6269 (2007).

Guiding of low-energy electrons through insulating nanocapillaries

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We report an experimental study of guided transmission of low-energy (≈10–350 eV) electrons through highly ordered Al₂O₃ nanocapillaries with large aspect ratio (diameters of approximately 40, 140 and 250 nm and 15 μm length). The nanochannel array was prepared using selfordering phenomena during a two-step anodization process of a high-purity aluminum foil [1]. Our recent experimental results [2] clearly showed for the first time the existence of the auiding effect for electrons, as found for highly charged ions (HCI) [3]. The guiding of the electron beam was observed for tilt angles up to 12°. As seen for HCI, the guiding efficiency increases with decreasing electron incident energy. However, the transmission efficiency appeared to be significantly lower than observed for HCI (see [2]). Furthermore, the transmission appeared to decrease significantly with decreasing electron energy, so limiting the lowest used incident energies to about 200 eV. The electron guiding has been also investigated more recently for the highly insulating polyethylene teraphthalate (PET) nanocapillaries [4], where authors reported results for the incident electron energies of 500 eV and 1000 eV. The most recently, we have performed experiments using a new improved setup, in order to investigate transmission of electrons through insulating Al₂O₃ nanocapillaries of different diameters at very low energies down to below 10 eV. We were focused on finding a dependence of the transmitted electron signal as a function of the incident electron energy, tilt angle (the angle between the incident electron beam and the nanocapillary axis), charging time and incident current, as well as electron energy loss spectra of transmitted electrons.

The guiding of charged particles through insulating nanocapillaries has been attracting a considerable attention, since Stolterfoht *et al.* [3] reported an unprecedented experiment of transmission of 3 keV Ne⁷⁺ ions through nanocapillaries of PET. Besides the investigation of hollow-atom formation at large distances from the surface, these studies might gain important information about the properties of the inner walls of the capillaries and for possible applications (e.g., manipulation of charged particles on the nanoscale). Using the electrons as projectiles gives new possibilities both for a fundamental understanding of the guiding phenomenon and applications. The interaction of the projectile with the inner walls, the insulator charge-up and discharge processes are expected to be different; also, the low-energy electrons are more affected by the electric field than ions, so representing a more sensitive tool for the characterization of the nanotubes.

References:

- [1] S. Mátéfi-Tempfli, M. Mátéfi-Tempfli, L. Piraux, Z. Juhász, S. Biri, É. Fekete, I. Iván, F. Gáll, B. Sulik, Gy. Víkor, J. Pálinkás, and N. Stolterfoht, Nanotechnology 17, 3915 (2006).
- [2] A. R. Milosavljević, Gy. Víkor, Z. D. Pešić, P. Kolarž, D. Šević, B. P. Marinković, S. Mátéfi-Tempfli, M. Mátéfi-Tempfli, and L. Piraux, Phys. Rev. A 75, 030901(R) (2007).
- [3] N. Stolterfoht, J.-H. Bremer, V. Hoffmann, R. Hellhammer, D. Fink, A. Petrov, and B. Sulik, Phys. Rev. Lett. 88, 133201 (2002).

[4] S. Das, B. S. Dassanayake, M. Winkworth, J. L. Baran, N. Stolterfoht, and J. A. Tanis, Phys. Rev. A **76**, 042716 (2007).

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Using electrons to template a dielectric substrate

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Electron bombardment from a filament as well as voltage pulses from a scanning tunnelling microscope tip have been employed to modify the surface of $TiO_2(110)$. Individual H-atoms are selectively desorbed with electrical pulses of +3 V from the scanning tunnelling microscopy tip, whilst leaving the oxygen vacancies intact. This allows us to distinguish between oxygen vacancies and hydroxyl groups, which have a similar appearance in scanning tunnelling microscopy images. This then allows the oxygen vacancy-promoted dissociation of water and O_2 to be followed with the microscope. Electrical pulses between +5 and +10 V induce local $TiO_2(110)1\times2$ reconstructions centred around the pulse. As for electron bombardment of the surface, relatively low fluxes increase the density of oxygen vacancies whilst higher fluxes lead to the 1×2 and other $1\times n$ reconstructions. Higher energy (70 eV) electron beams cause an apparent cracking of the surface. This can be healed locally using a tip pulse, which seem to give rise to a local heating. Tip pulses can also be used to create small (100 Å diameter) areas of $TiO_2(110)1\times2$ reconstructed surface, which can be returned to a 1x1 termination with an additional tip pulse of a nearby area. These results suggest the possibility of using electron beams to pattern dielectric surfaces for use in nanoelectronics applications.

Design of an instrument to identify suitable molecules for ECCL – work in progress

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Electron controlled chemical lithography (ECCL) is based on the ability of low energy electrons to initiate and effectively drive selective bond cleavage processes in molecular systems. The selectivity is being controlled by the kinetic energy of the electron within the range of few electron-volts or by the choice of functional groups of the target molecule. An example of an ECCL process, is where molecules are linked to a substrate by chemical reactions induced by injecting tunneling electrons from a STM tip, resulting in microscopically patterned surfaces with specific chemical or physical properties.

We present a design of an instrument, soon to be constructed, that serves the purpose of identifying, in an efficient way, suitable molecular targets for use in ECCL. Such candidates need to show high selectivity and high efficiency with regards to bond rupture induced by DEA, and should maintain that selectivity and efficiency when coupled to an environment in clusters, in condensed phase or adsorbed on surfaces.

The instrument design is based on typical crossed electron- and molecular beam electron attachment ionization process combined with TOF-MS [1], with electron-beam energy range of 0 to 20 eV with sub 100 meV resolution. All necessary parameters which affect the mechanism of chemical reactions when low energy electrons interact with molecules are planned to be measurable. Desired features will include the introduction of molecules in different environments: isolated or embedded in homogeneous- or heterogeneous molecular clusters and large low vapor pressure molecules with molecular mass up to 100 kDa.

A laser desorption electron attachment time-of-flight mass spectrometry feature will be included [2], where the molecules of interest may be laser-desorbed in the presence of a high pressure carrier gas and subsequently the analyte/carrier gas mixture is expanded to form a cold molecular beam. The predominantly neutral beam may then be ionized by attachment of low energy electrons. The negatively charged ions, formed upon electron attachment, are mass analyzed with a TOF-MS perpendicular to the molecular beam.

Furthermore, a modification to the TOF-chamber in order to measure the lifetime of ions during their drift, will be presented. The intention is to design the instrument in such a way that the life time with regards to autodetachment and the lifetime with regards to dissociation can be measured and also the part of the electron energy that converts to the molecule-fragment kinetic energy.

[1] Wiley W. C. and McLaren I. H., *Time-of-Flight Mass Spectrometer with Improved Resolution*, Review of Scientific Instruments, 1955, 26, 1150 – 1157

[2] Ingolfsson O. and Wodtke A. M., Laser Desorption Electron Attachment Time-of-Flight Mass Spectrometry: A New Approach to Detection of Involatile Compounds, Journal of American Society for Mass Spectrometry, 2001, 12, 1339 – 1347

Thermally Programmed Desorption experiments at very low temperature (10-30K).

Desorption and formation of molecular hydrogen on heterogeneous water ice surfaces of different porosity

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Thermally Programmed Desorption (TPD) experiments are a quantitative probe of the dynamic of gas-surface interactions. The LERMA (Laboratoire de l'Etude du Rayonnement et de la Matière en Astrophysique, Observatoire de Paris) has developed an experimental setup devoted to studies of surface reactions encountered in the interstellar medium. We have studied the adsorption/desorption process of molecular hydrogen on water ice surfaces at low temperature and the molecular hydrogen formation on these surfaces, a key process for the interstellar medium dynamic.

Experiments: In an ultrahigh vacuum chamber, a water ice sample is deposited on a copper substrate regulated in temperature down to 10 K. It is next exposed to a molecular or atomic deuterium beam. At last, the sample is heated up to 30 K, and the coincident D_2 desorption is measured with a quadrupole mass spectrometer.

Model: We have developed a specific model for the molecular hydrogen desorption. It takes in account some specificities of the system: light species physisorbed and efficient diffusion on a heterogeneous surface prior to desorption. The population of adsorbed molecules is described statistically. TPD from different ice morphologies and for mixed isotopes experiments are reproduced.

TPD experiments are now implemented in LCAM (Laboratoire des Collisions Atomiques et Moléculaires, Orsay) as an additional diagnostic for studying surface reactions induced by electron irradiation in thin ice films condensed on semiconductor, monitored by HREELS and ESD.

Magnetic nanostructures probed on the atomic scale

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Magnetic nanostructures are increasing data storage capacities and are promising candidates for implementations of novel spin-based computation techniques. The relative simplicity and reduced dimensionality of nanoscale magnetic structures also make them attractive model systems for studying fundamental interactions between quantum spins. We used a scanning tunneling microscope (STM) to build individual magnetic nanostructures one atom at a time. By measuring their spin-excitation spectra with inelastic electron tunneling spectroscopy, we determined the orientation and strength of the anisotropies of individual Fe and Mn atoms on copper nitride.

First-principles calculations indicate that the magnetic atoms become incorporated into a polar covalent surface molecular network, making them similar to the building blocks of molecular magnets. In linear chains of up to 10 Mn atoms, we observed excitations of the coupled atomic spins that can change both the total spin and its orientation. The large magnetic anisotropy and strong spin-coupling manifested in these structures, which provide atom-by-atom accessibility via local probes, have the potential to produce atomic-scale magnetic structures that have a stable magnetization at low temperatures.

Electron Induced Molecular Reorganization and Switching at Metal Surfaces

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We discuss the dynamics of electron induced molecular processes in two types of systems, namely (1) solvation in polar adsorbate layers and (2) STM and light induced molecular switching at metals surfaces:

In the first set of experiments we study the ultrafast dynamics of interfacial electron transfer and solvation processes in ice and ammonia layers adsorbed on single crystal metal surfaces by fs-time-resolved two-photon-photoemission (2PPE) spectroscopy. In this process, photoinjection of electrons from the metal into the adsorbate conduction band is followed by ultrafast localization and solvation of the excess electrons. The subsequent energetic stabilization of these solvated electrons due to nuclear rearrangements of the polar molecular environment is accompanied by an increasing degree of localization. In the solvation dynamics in amorphous NH₃ layers on Cu(111) two different species of interfacial electrons are observed, (i) a precursor state (e_P) exhibiting fs transfer times and solvation dynamics and (ii) a solvated electron state (e_S), which envolves on a 1-100 picosecond timescale. It is found that the electron transfer rate of e_S back to the substrate depends exponentially on NH₃ layer thickness, which demonstrates that the electron transfer is mediated by tunnelling through a potential barrier and allows extracting characteristic transmission lengths for different stages of solvation.



Fig.1 a) Schematic potential energy surface for light induced switching of TBA on Au. Thermal activation leads to *cis-trans* isomerization in the ground state. b) Two-photon photoemission spectroscopy of 0.9 ML TBA/Au(111) in *trans*-configuration (dashed line) and after irradiation with h =4.05 eV leading to a photostationary mixture of *cis*-and *trans*-isomers (red line).

The second class of experiments addresses molecular conformational changes (switching) at a metal surface induced by light and tunnelling electrons. 2PPE and HREELS spectroscopy are employed to analyze reversible changes in the electronic and vibrational structure of the molecular switch tetra-*tert*-butyl-azobenzene (TBA) adsorbed on Au(111) induced by UV-light and thermal activation. Cycles of illumination and annealing steps confirm the reversibility of the switching process, which is assigned to a *cis-trans*-isomerization of TBA molecules in direct contact with the metal surface. From the photon energy dependence of the photo-induced isomerization cross section we conclude that the switching process is induced by the transfer of photoexcited holes from the Au *d*-band to the HOMO level of the adsorbed TBA molecule. This mechanism opens the possibility for chemical lithography by appropriate patterning techniques.

Laser-Induced Acoustic Desorption Combined With Electron-Attachment Spectroscopy and Quantum Chemical Methodologies as a Means of Studying DNA Strand Breaks

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The interaction of low energy electrons with biomolecules is vitally important for the molecular mechanisms of radiation damage. The irradiation of a living cell leads to a cascade of ionisation events producing reactive secondary electrons with kinetic energies below 10 eV, as the most abundant species [1]. It was demonstrated that these electrons induce single and double strand breaks in plasmid DNA [2]. The characteristic resonant features in the strand break yields indicate that dissociative electron attachment (DEA) may be the initial step of decomposition.

A new experimental setup is presented here that utilises the combination of electronattachement techniques with laser-induced acoustic desorption (LIAD). LIAD was very recently proven to be the gentliest method of desorption of biomolecules. It was successfully employed to desorb neutral intanct molecules as large as oligonucleatides [3].

In this study we investigated the interaction of low energy electrons with gas-phase thymidine (the whole DNA nucleotide) and ribose-5'-phosphate (RNA sugar-phosphate unit). In both cases we observed new features, which were not previously detected for the isolated DNA bases, sugars, phosphates. For instance, the ion yield curve of [Thymine-H]⁻, generated by N-glycosidic bond cleavage in thymidine exhbit a single maximum around 7 eV, while the corresponding resonance for isolated thymine was observed as a double resonance already at 1.2 eV [4].

Concerning ribose-5-phosphate unit, the attachment of electrons with energies close to zero eV results in the formation of $H_2PO_4^-$ and (Ribose-H)⁻, which are created by a C-O and P-O bond cleavages, respectively. Both reactions represent a strand break in DNA or RNA at very low electron energies.

Calculated kinetic and thermodynamic barriers for the bond cleavages as well as electron affinities of all the involved moieties will also be discussed.

[1] S.M. Pimblott, J.A. LaVerne, Rad. Phys. Chem. 76, 1244 (2007).

[2] B. Boudaiffa, P. Cloutier, D. Hunting, M.A. Huels, L. Sanche, Science 287, 1658 (2000).

[3] R.C. Shea, H.I. Kenttämaa et al., Anal. Chem. 78 (2006) 6133.

[4] S. Ptasinska, S. Denifl, P. Scheier, T. D. Märk, S. Gohlke, and E. Illenberger, Angew. Chem. Int. Ed. **45**, 1893 (2006).

On the behaviour of electron attachment cross sections near zero energy

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Experimental advances involving laser photoelectron sources [1-3] have recently allowed detailed studies of the dynamics for anion formation by low-energy electron attachment to several polyatomic molecules XY, i.e. $e^{-}(E) + XY \rightarrow [XY]^{-} \rightarrow X + Y^{-}$, at (sub)meV resolution down to (sub)meV energies [3-6]. For the first time, investigations of the limiting $(E \rightarrow 0)$ threshold behaviour for the attachment cross section $\sigma(E)$ involving free electrons became possible with the laser photoelectron attachment (LPA) method. According to basic considerations [3,7,8], the energy dependence for capture of a slow electron by a short range potential (including a polarization tail) is dominated by barrier penetration through the centrifugal potential with orbital angular momentum *L*, and the limiting energy dependence of the corresponding partial attachment cross section is given by $\sigma_L(E \rightarrow 0) \propto E^{L-1/2}$ [3,7,8]. This behaviour has been demonstrated for several molecules (such as SF_6 [4,5] and CCl_4 [6]) involving s-wave (L = 0) attachment. For two cases with expected p-wave (L=1) threshold behaviour (F_2, Cl_2) , resulting from the ungerade parity of the attaching ${}^{2}\Sigma_{u}^{+}$ anion resonance state, conflicting observations of an s-wave-type energy dependence [9] were only recently clarified [10,11]. For molecules with a permanent dipole moment, the threshold exponent is modified [3,12]; the s-wave attachment cross section for dipolar molecules is given by $\sigma_{L=0}(E \rightarrow 0) \propto E^{-\kappa}$ with $0.5 < \kappa < 1$, and analytical expressions for the low-energy capture cross section have been reported [3,12].

Using the highly-resolved LPA cross sections, *direct* tests of the quasi-free electron model for Rydberg electron transfer (RET) became possible for the first time [13,14]. According to this model the rate coefficient k_{nl} for the RET process involving highly-excited Rydberg atoms $A^{**}(nl)$, i.e. $A^{**}(nl) + XY \rightarrow A^{+} + X + Y^{-}$, is given by $k_{nl} = \int v \sigma(v) f_{nl}(v) dv$, where $f_{nl}(v)$ denotes the normalized velocity distribution of the Rydberg electron.

At the conference, a survey will be given on the indicated basic aspects as well as on the experimental verifications of s-wave and p-wave electron attachment for selected molecules.

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References

- [1] D. Klar, M.-W. Ruf, H. Hotop, Meas. Sci. Technol. 5 (1994) 1248
- [2] J. Bömmels et al., Rev. Sci- Instrum. **72** (2001) 4098
- [3] H. Hotop, M.-W. Ruf, M. Allan, I. I. Fabrikant, Adv. At. Mol. Opt. Phys. 49 (2003) 85
- [4] D. Klar, M.-W. Ruf, H. Hotop, Australian J. Phys. **45** (1992) 263
- [5] A. Schramm et al., Phys. Rev. Lett. 81 (1998) 778
- [6] D. Klar, M.-W. Ruf, H. Hotop, Int. J. Mass Spectrom. 205 (2001) 93
- [7] E. P. Wigner, Phys. Rev. **73** (1948) 1002
- [8] E. Vogt, G. H. Wannier, Phys. Rev. 95 (1954) 1190
- [9] A. Chutjian, A. Garscadden, J. M. Wadehra, Phys. Rep. **264** (1996) 393
- [10] S. Barsotti, M.-W. Ruf, H. Hotop, Phys. Rev. Lett. 89 (2002) 083201
- [11] M. Braun, M.-W. Ruf, I. I. Fabrikant, H. Hotop, Phys. Rev. Lett. 99 (2007) 253202
- [12] I. I. Fabrikant, H. Hotop, Phys. Rev. A 63 (2001) 022706
- [13] D. Klar, B. Mirbach, H. J. Korsch, M.-W. Ruf, H. Hotop, Z. Phys. D 31 (1994) 235
- [14] F. B. Dunning, J. Phys. B **28** (1995) 1645

Effective cross sections for low-energy electron scattering from monomolecular films of condensed thymidine

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Investigation of the vibrational and electronic excitation of nucleic bases and nucleosides by low-energy electron impact leading to dissociation through formation of temporary negative ions aims at understanding the correlation of nucleic base-sugar moiety conformational coupling and its consequences on the bond cleavage in DNA. The conformation of the 2'-deoxyribose moiety with respect to the base is expected to influence which species are formed upon exposure of nucleosides to ionizing radiation.

Thymidine is one of the most important nucleosides of DNA and an important component of antiviral compounds [1]. In the condensed phase, thymidine's 2'-deoxyribose ring is in the pentose sugar ring form, which is a true conformation of this nucleoside in DNA (Figure 1). From Raman, IR and UV spectroscopic measurements, [2] it is known that thymidine vibrations are dominated by thymine modes. However, virtually all normal modes of thymidine involve some degree of vibrational coupling between the thymine base and the deoxyribose! Most deformation from the sugar moiety is attributed to a CH2 group, while the OH group vibration is represented at the highest energy-loss. The gas-phase experiments on sugar analogs of deoxiribose [3] showed the existence of a resonance at the energy below 1 eV as a result of the dissociative electron attachment. Based on this fact and the earlier result on resonances in DNA [4] and thymine [5], we turned our attention to possible resonances in thymidine cross sections at incident energy below 5 eV. We showed that there is an evident enhancement of the effective cross sections of certain vibrational modes in thymidine for incident electron energies of 1.5 and 2 eV as a possible contribution from deoxyribose. Our results suggest that possible dissociation of thymidine through temporary electron attachment will probably proceed through hydrogen detachment from thymine and dissociation of OH from deoxyribose

In this talk, recent results from low-energy (1.5 - 12 eV) electron scattering from thin molecular films of condensed thymidine will be described and their relevance for strand breaking in DNA will be discussed.

References

- [1] Martin J C 1989 *Nucleotide Analogues as Antiviral Agents; ACS Symp. Ser*, Vol. 401 American Chemical Society, Washington, DC
- [2] Tsuboi M *et al* 1997 *J.Am.Chem.Soc.* 119 2025 and Santamaria *et al* 1999 *J.Comp. Chem.* 20 (5) 511
- [3] Ptasińska S, Candori P, Denifl S, Yoon S, Grill S, Scheier P and Märk T D 2005 *Chem. Phys. Lett.* 409 270-276
- [4] Levesque P L, Michaud M, Sanche L 2003 *Nuc. Instr. Meth. Phys. Res. B* 208 225; Levesque P L, Michaud M, Cho M and Sanche L 2005 *J. Chem. Phys.* 122 224704
- [5] Panajotovic R, Martin F, Cloutier P, Hunting, D, and Sanche L, 2006 Rad.Res. 165 452-459

Optical emission spectroscopy of reactive magnetron discharges.

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The reactive magnetron sputtering is commonly used to produce high resistance thin films, as TiN and TiCN, or with special optical proprieties, like high optical absorption with AIN thin films. In cases where only one gas is present in the discharge atmosphere, the abnormal glow macroscopic characteristics, discharge voltage and current, usually follow the Thornton equation:

$$I_P = k V^n$$

(Eq. 1)

where k and n are constants depending on the cathode and discharge gas. In some cases it has been observed an abrupt change of the values of the constants in Eq. 1 and the characteristic curve $I_P(V)$ is better described by two segments each one with a different Thornton equation.

When one or more different gases are added to the discharge atmosphere, even in very low partial pressures, the curve $I_P(V)$ behaviour changes strongly and stops following the Eq. 1, see Fig. 1,



Fig. 1- $I_P(V)$ for different partial pressures of N₂, at a discharge pressure of 0,7 Pa in a hollow cathode with Ti target.

The macroscopic characteristics of the plasma are the result of the summation of several processes in the gas phase and on the surface of the cathode and anodes. To better understand the changes in the macroscopic characteristics and the dominant processes within the plasma, the optical emission spectroscopy for several partial pressures of N₂ and Ar, with targets of Ti, Al and Cu and in different discharge pressures, has been measured and analysed. The fast current increase in the two $I_P(V)$ with low partial pressure of N₂ is simultaneous to the appearance of strong emission lines of the metal.

Electronic excitation, single and double ionization of molecules of biological interest using fast electrons and synchrotron radiation

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In the last few years, an experimental program has been under development at the Federal University of Rio de Janeiro, oriented towards the study of the electronic excitation and ionization of molecules of biological interest. Basically electron energy-loss spectroscopy and time-of-flight techniques (both using fast electrons and synchrotron radiation) are used to probe excited and ionic states (singly and doubly-charged) of chemical compounds of biological interest. Coincidence electron-ion and electron ion-ion techniques are employed in the study of the fragmentation mechanisms of the ionic species.

The results will be exemplified with recent data, associated with the excitation and ionization of a common anesthetic, halothane (CF₃CHClBr), and a volatile organic compound extensively emitted by plants, isoprene (CH₂(CH₃)CHCH₂).

Applications of focused electron beam induced chemical reactions

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Focused electron beam induced processing is a high resolution nanostructuring technique for local deposition and etching of materials. In analogy to the well established focused ion beam methods, gas assisted etching (GAE) and ion beam induced deposition (IBID) a suitable precursor gas is dispensed through a nozzle in close vicinity to the incident beam. Depending on the precursor chemistry, a reaction is induced by the electrons, leading to either a deposition caused by fragmentation of precursor molecules or to a reaction between the adsorbed molecules and the substrate material, resulting in volatile products and thus etching of the substrate material. Since the reaction is confined to the area exposed by the electron beam, this technique allows high resolution nanostructuring with feature sizes well below 50 nm. Furthermore, since the process is solely chemically induced, unwanted side effects observed for ion beam based processing, such as ion implantation or sputtering are absent.

Although a large number of experimental data on electron beam induced deposition (EBID) and, to a lesser extend, on etching is reported in the literature, many aspects of the involved physical and chemical mechanisms are still poorly understood. This paper will give a brief overview of the current state of research and will illustrate the potential of the technique showing several examples of its applications. In particular, two recent applications in the area of semiconductor fabrication (mask repair and circuit editing) are presented.

Patterning surfaces at the 10nm scale and below

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The patterning of surfaces on the size-scale of individual biological molecules, i.e. 1-10 nm, has implications both for fundamental scientific studies (e.g. of protein-protein interactions) and for applications in biochips and sensors as well as next-generation electronic and photonic devices. I will address a number of methods which can achieve the formation of surface structures on this length scale, ranging from the esoteric (in practical terms), atomic manipulation with electrons from the STM tip, to the more established, electron beam lithography - where more electron-sensitive materials are nevertheless needed for practical pattern production - and the novel, size-selected (ionised) cluster deposition, which is the basis of a new biochip aimed at early stage cancer detection. Common underpinning themes are the issues of precision and uncertainty in the organization of atoms.

1. P.A. Sloan and R.E. Palmer, Nature 434 367 (2005).

2. F. Gibbons, H.M. Zaid, M. Manickam, J.A. Preece, R.E. Palmer and A.P.G. Robinson, Small **3** 2076 (2007).

3. R.E. Palmer, S. Pratontep and H.-G. Boyen, Nature Materials 2 443 (2003).

4. Z.Y. Li, N.P. Young, M. Di Vece, R.E. Palmer, A.L. Bleloch, B.C. Curley, R.L. Johnston, J. Jiang, J. Yuan, Nature 451 46 (2008).

www.nprl.bham.ac.uk

Scanning Tunneling Microscopy of Adsorbates on Insulating Films: From Manipulation of the Charge State to Imaging of Individual Molecular Orbitals and Bond Formation

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Ultrathin insulating films on metal substrates are unique systems to use the scanning tunneling microscope to study the electronic properties of single atoms and molecules, which are electronically decoupled from the metallic substrate. Since the lifetime of the tunneling electrons in adsorbate states is significantly increased, inelastic tunneling processes are strongly enhanced in such double barrier tunneling junctions.

Individual metal atoms on an ultrathin insulating sodium chloride film supported by a copper surface exhibit two (three) different charge states, which are stabilized by the large ionic polarizability of the film. The charge state and associated physical and chemical properties can be controlled by adding or removing a single electron to or from the adatom with a scanning tunneling microscope tip. The simple physical mechanism behind the charge bistability in this case suggests that this is a common phenomenon for adsorbates on polar insulating films. The different charge states can be directly resolved in non-contact AFM by measuring the electrostatic force between the AFM tip and the metal adatom.

In the case of molecules on ultrathin NaCl films the electronic decoupling allows the direct imaging of the unperturbed molecular orbitals, as will be shown in the cases of individual pentacene molecules. Using atomic/molecular manipulation a covalent bond between an individual pentacene molecule and a gold atom can be formed employing inelastic electron tunneling. This bond formation is reversible and different structural isomers can be produced. Direct imaging of the orbital hybridization upon bond formation provides insight into the energetic shifts and occupation of the molecular resonances.

Vibrational excitation of methane by slow electrons revisited: Joint theoretical and experimental study.

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We have calculated and measured differential and integral cross sections for vibrationally inelastic scattering of electrons by methane molecules. Calculations were carried out using Discrete momentum representation (DMR) method. We solved two-channel Lippmann-Schwinger equation in the momentum space. Interaction between the scattered electron and the target molecule is described by exact static-exchange potential. Correlation-polarization forces were included by a simple local DFT potential of Perdew and Zunger 1981 [1]. Calculated cross sections are compared with new experimental data. In the light of the new results we believe that cross sections for stretching modes of methane are higher than referred previously. An example of the calculated and measured EELS spectra is shown in Fig. 1.



FIGURE 1: Computed and measured electron energy-loss spectra for the scattering angle θ =90°. The left panel is for the collision energy E_c = 5 eV and the right panel is for E_c = 10 eV. Vertical bars represent the actual value of the differential cross-section for the particular mode.

References

[1] Perdew J P and Zunger A 1981 Phys. Rev. B 23 5048
Current-Induced Conductance Switching of Individual Molecules

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The bistability in the position of the two hydrogen atoms in the inner cavity of single free-base naphthalocyanine molecules constitutes a two-level system that was manipulated and probed by scanning tunneling microscopy. When adsorbed on an ultrathin insulating film, the molecules can be switched in a controlled fashion between the two states by excitation induced by the inelastic tunneling current. The tautomerization reaction can be probed by resonant tunneling through the molecule and is expressed as considerable changes in the conductivity of the molecule. Since both the injection point of the current (tip position) and the reaction site (inner cavity of the molecule) are confined to the sub-molecular length-scale, the spatial dependence of the switching probability allows one to learn more about electron and/or energy transport within a single molecule. A striking feature apparent in this spatial dependence is that the largest switching rate is achieved when the tip is above the far periphery of the molecule, i.e. >10 Å from the reaction site.

In contrast to previously investigated systems, the present molecular switch is planar, does not involve conformational changes at the periphery of the molecule, and is well-suited for use in self-assembled monolayers. Another advantage is that the symmetry inherent to the system implies that both positions of the switch have the same total energy and do not differ in the binding to the substrate. We also demonstrated a coupling of the switching process so that the charge injection in one molecule induced tautomerization in an adjacent molecule. The well-defined coupling of molecules is a first step to use molecules as building blocks for more complex molecular devices such as logic gates in the future.

Atomic Force Microscopy Characterization of Polyelectrolytes Self-Assembly Films Using Dynamic Scaling Concepts

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Ultrathin polyelectrolyte multilayer (PEMUs) films are promising molecular superstructures for the creation of molecular electronics and photonics. Over the past decades several applications have been addressed, such as, conducting layers light-emitting devices, optical devices, biosensors, membrane separation and biocompatible surfaces. The production of PEMUs is achieved using the so called layer-by-layer technique, which consists of the alternate adsorption from solution of oppositely charged molecules, has been found to be a versatile method for the build-up of ultrathin molecular multilayer with accurate control of thickness, composition and function.

The study of surface morphology of PEMUs is important to understand the film deposition process and for acknowledgement of adsorption model¹. The success of multilayer growth is achieved when it is possible to control the factors that affect morphology. The physical processes involved in polyelectrolytes adsorption determine the film topography and may be affected by pH, salt concentration and the experimental details used in films production. The atomic force microscopy (AFM) technique has been broadly used to imaging and quantitative measurements on PEMUs surfaces. Scaling concepts have been used to quantitatively characterize the morphology of a surface, and that allows applying empirical models to explain particle deposition², such as ballistic deposition, random deposition, the Kardar-Parisi-Zhang model and Villain model. They are based on the self-affine property of particles deposited on the film, reflected by the power law dependence of roughness on the system size. In the early time regime, the roughness is seen to increase as a power law of time and in the long time regime, it goes steady. The use of dynamic scale theory and fractal analysis in the study of distinct growth stages of layer-by-layer (LBL) films as Poly(allylamine hydrochloride) (PAH) and azopolyelecrolyte poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido]-1,2ethanediyl, sodium salt] (PAZO) is reported here. The PEMUs films with a PAZO at the top layer were analyzed by AFM revealed granular morphology was found to follow the Villain model.



Figure 1 – Topographies of PAH/PAZO films with different adsorptions times: a) t = 30 s, b) t = 180 s, c) t = 600 s.

¹ Ferreira, Q.; Gomes, P. J.; Nunes, Y.; Maneira, M.; Ribeiro, P.A.; Raposo, M.; "Atomic force microscope characterization of PAH/PAZO multilayers", Microelectronics Engineering, 84, pp 506-511, (2007)

² Raposo, F.; Ferreira, Q.; Ribeiro, P.A.; "A Guide for Atomic Force Microscopy Analysis of Soft-Condensed Matter" Current Issues on Multidisciplinary Microscopy Research and Education, FORMATEX Microscopy Book Series N.3, Edited for A. Méndez-Vilas (Formatex Research Centre, Badajoz, Spain) and L.Labajos-Broncano (Department of Physics, University of Extremadura, Spain).

Inelastic interactions of electrons with molecules and clusters embedded in superfluid helium droplets

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The inelastic electron interactions (attachment/ionization) with doped helium droplets are studied utilizing a two sector field mass spectrometer. The dopants range from diatomic molecules such as H₂ and I₂ to water, halocarbons, biomolecules and fullerenes. Positive-ion mass spectra are recorded and are compared with results in the gas phase. Moreover, negative-ion mass spectra are recorded at the electron energies where resonances appear. Both the negative and positive mass spectra show that cluster ions are easily formed by embedding molecules in helium droplets. The yield of anions is determined as a function of the electron energy. In several cases we observe a substantial stabilization of complex product ions compared to the gas phase. Solvation of both anions and cations in He is observed in several cases and investigated by means of high resolution mass spectrometry.

So far experiments with pure and mixed doped clusters of atmospheric and biological relevance have been carried out mainly by means of optical spectroscopy (see review [1]). Several electron impact ionization studies of molecules embedded in helium droplets also have been reported [2-5]. In contrast, electron attachment to (doped) helium droplets has been studied only rarely (see review in [6] and [7]). Very recently we have published the first mass spectrometric investigation of negative ions formed via electron attachment to molecules embedded in helium clusters [8]. The molecules chosen for this first study were the nucleobases adenine, thymine and partially methylated or deuterated thymine. The DEA to these molecules in helium droplets (see [8]) exhibits the remarkable site selectivity that we have previously established for these biomolecules in the gas phase [9]. However, core excited resonances that lead to low mass fragments upon electron attachment in the gas phase are almost completely quenched and lead to the formation of dehydrogenated closed shell anions via loss of a neutral H-atom.

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References:

- [1] F. Stienkemeier, and K.K. Lehmann, J. Phys. B: At. Mol. Opt. Phys. 39, R127 (2006)
- [2] M. Lewerenz, B. Schilling and J.P Toennies, J. Chem. Phys. 102, 8191 (1995)
- [3] T. Ruchti, K. Forde, B.E. Callicoatt, H. Ludwigs and K.C. Janda, J. Chem. Phys. 109, 10679 (1998)
- [4] F. Zappa, S. Denifl, I. Mähr, J. Lecointre, F. Rondino, O. Echt, T.D. Märk and P. Scheier, Eur. Phys. J. D 43, 117 (2007)
- [5] S. Yang, S.M. Brereton, M.D. Wheeler and A.M. Ellis, Int. J. Mass Spectr. 253, 79 (2006)
- [6] J.A. Northby, J. Chem. Phys. 115, 10065 (2001)
- [7] M. Farnik and J.P. Toennies, J. Chem. Phys. 118, 4176 (2003)
 [8] S. Denifl, F. Zappa, I. Mähr, J. Lecointre, M. Probst, T.D. Märk and P. Scheier, Phys. Rev. Lett. 97. 043201 (2006)
- [9] S. Ptasinska, S. Denifl, P. Scheier, E. Illenberger and T.D. Märk, Angew. Chem. Int. Ed. 44.6941 (2005)

Absolute electron – molecule cross sections: elastic, vibrational and electronic excitation, and dissociative attachment

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Absolute cross sections for electron – isolated molecule processes are a prerequisite for understanding plasmas, are required for assessing new developments of theory, and are useful as a reference for understanding electron – induced processes on the surfaces and in the bulk.

The two important processes in view of chemical change are dissociative electron attachment (DEA), and electronic excitation, which is generally the primary step in neutral dissociation yielding useful chemically reactive fragments. Our work concentrates on these two aspects.

A new instrument has been constructed to measure total DEA cross sections. It is an essentially standard total ion collection tube. It has been tested on the O^-/O_2 , O^-/N_2O , and O^-/CO_2 processes with results which compare favorably with published data. It has then been applied to halogen hydrides HX, where there is an interest to validate advanced nonlocal resonance theories. It has also been applied to acetylene and diacetylene, which are currently of interest because of the discovery of the C₄H⁻, C₆H⁻, and C₈H⁻ anions in space, but which could also be potentially interesting as precursors for forming grids on surfaces.

Many DEA processes are mediated by Feshbach resonances with temporary occupation of Rydberg-like orbitals, but little is generally known about their detailed mechanism. We gained insight into these processes by a comparative study of many saturated compounds with the alcohol and the ether groups.

Finally, ethene, the prototype of π -electron systems, has been re-measured. In particular, the lowest electronically excited state is convenient for testing theoretical approaches to calculate cross sections for electronic excitation in molecules. The results are about 15% higher than earlier measurements from this laboratory, but still only about 0.6x as large as available calculations. The elastic and vibrational excitation cross sections have also been measured at this occasion, over a large range of scattering angles. The results for the elastic cross sections agree well with the recent results of calculations taking into account the target polarizability.



Fig. 1. Elastic cross section at 180°. Dashed line is a calculation of Winstead *et al.* [1].

Reference

[1] C. Winstead, V. McKoy, and M. H. F. Bettega, Phys. Rev. A 72, 042721 (2005).

The hunt for single atom deposition

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Electron beam induced deposition (EBID) is recently drawing attention as a potential nanofabrication technique. In an increasing number of groups it was demonstrated that nanostructures even down to 1 nm in size can be fabricated using EBID. The principle of EBID (Fig. 1) is that precursor molecules, adsorbed at a substrate surface, are dissociated as a result of the interaction of an incident electron beam with the gas-substrate system. As electron beams can be focused to 0.1 nm in today's state of the art electron microscopes, ultra-high resolution patterning becomes possible. In contrast with low-energy scanning probe based lithography the resolution of high-energy EBID is determined by the secondary electrons rather than the primary electrons.

We performed EBID experiments in an environmental Scanning Transmission Electron Microscope (STEM) at a beam energy of 200 keV, a 0.2 nm probe and $W(CO)_6$ as a precursor gas. Typical precursor gas pressures during the deposition are 10^{-3} Torr, and to reduce contamination from the microscope the substrates are held at an elevated temperature of 100-150 °C. We deposited arrays of nanometer sized dots on various thin membranes (SiN, amorphous carbon, graphite) and discovered differences in mass between dots intended to have equal mass and deviations in position with respect to the intended rectangular grid. To understand these findings we studied the nucleation of the deposits (Fig. 2). We use the STEM in annular dark field (ADF) mode and use the ADF signal to control the deposition such that a preset amount of mass is deposited. The smallest deposits we have made so far have an average volume of 0.4 nm³.



Fig. 1. Cartoon of the EBID principle



Fig. 2. ADF-STEM image of a typical dot deposited on a carbon membrane from $W(CO)_6$ as a precursor. The white square measures 5x5 nm².

STM-driven molecular switches at surfaces: From structure to dynamics

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In this talk, quantum chemical and quantum dynamical methods will be applied to rationalize recent experiments on the switching of molecules at surfaces, driven by Scanning Tunneling Microscopes (STMs).

In particular, we shall study the energetics of substituted azobenzenes, which, when adsorbed on metal surfaces, can be switched by temporary electron attachment from one conformer to another [1,2]. Field effects, as well as substituent effects are discussed in the light of experiments.

A simpler system is H:Si(100), where single H atoms can be STM-switched reversibly back and forth between the dangling bonds of a Si dimer [3]. Quantum dynamical models are developed to study both the "above threshold" [4] and the "below threshold" [5] regimes, for which the bias voltage is above or below the excitation energy to reach a short-lived ion resonance, respectively. In the modelling, vibrational relaxation due to vibration-phonon coupling [6], and also electronic relaxation is accounted for. In the below-threshold regime "ladder climbing" over the barrier takes place, and individual contributions of dipole and resonance mechanisms to the transition rates are estimated.

- [1] N. Hennigsen et al., J. Phys. Chem. C **111**, 14843 (2007).
- [2] G. Füchsel, T. Klamroth, J. Dokic, and P. Saalfrank, J. Phys. Chem. B **110**, 16337 (2006).
- [3] U.J. Quaade et al., Surf. Sci. **415**, L1307 (1998).
- [4] A. Abe, K. Yamashita, and P. Saalfrank, Phys. Rev. B 67, 235411 (2003).
- [5] K. Zenichowski, T. Klamroth, and P. Saalfrank, Appl. Phys. A (submitted).
- [6] I. Andrianov and P. Saalfrank, J. Chem. Phys. **124**, 034710 (2006); Chem. Phys. Lett. **88**, 535 (2007).

Jahn-Teller effect in C₆₀ molecules studied with the Scanning Tunneling Microscope.

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The scanning tunneling microscope (STM) yields local information on molecules at surfaces by plotting contours of constant tunneling current between the STM's tip and the sample. It can also probe different electronic states of the sample by continuously changing the tip-sample bias voltage. Typically, the tip is spatially fixed, and the conductance is recorded at different biases permiting us to collect a scanning tunneling spectrum (STS). The conductance contains information on the sample's electronic states and also on its vibrational properties.

Recently, the local imaging properties of the STM have been used to show a distorted C_{60} on a surface after doping by K atoms [1]. The distorsion is due to a Jahn-Teller effect of the negative ion. However, the electronic spectrum should also contain information on the Jahn-Teller effect. Photoemission experiments have shown the rich electronic behaviour of a negative C_{60} due to the Jahn-Teller effect [2]. I will present some results showing that STS can also give interesting data on the Jahn-Teller effect of the C_{60} anion.

Our theoretical results can be compared with recent experiments in the Pascual group, Freie Universität Berlin, where a C_{60} molecule is studied on top of a molecular layer. This molecular layer reduces the direc C_{60} -substrate coupling, leading to considerably lengthening of the anion lifetime. We show that the recorded STS is indeed related to the electronic structure expected for this Jahn-Teller system, where coupling to the molecular vibrations leads to considerably renormalization of the electronic spectrum. However, the particularities of the non-equilibrium measuring process leads to substantial heating of the C_{60} molecule, modifying the vibronic STS of the C_{60} anion.

References:

- [1] A. Wachowiak et al. Science **310**, 468 (2005).
- [2] O. Gunnarsson et al. Phys. Rev. Lett. 74, 1875 (1995).

Direct quantitative measurement of lateral forces at atomic scale using non-contact Atomic Force Microscopy (nc-AFM)

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Lateral force microscopy has shown its capability to manipulate single atom and molecules laterally, however quantitative measurement of lateral forces that govern the activated or induced movement of atomic or molecular scale objects along surface has still remained a challenge. To investigate this important issue, we specially designed and constructed a nc-AFM, capable of measuring lateral stiffness simultaneously with tunneling current. In our technique a sensitive fiber interferometer is aligned at the side of a home-made tungsten cantilever with typical stiffness of about 150 N/m. To improve the sensitivity, a RF circuit is designed to inject RF current into the laser diode. The frequency and the amplitude of the RF current can be adjusted to optimize the noise reduction. Using this technique a noise level of

~9×10⁻⁵ Å/ \sqrt{Hz} is obtained. The cantilever is dithered in lateral direction respect to the sample with sub-Ångstrom oscillation amplitudes (A₀ =0.25 Å) at a frequency, well below the resonance frequency and the changes in lateral oscillation amplitudes. The amplitude at the tip, which is altered by the tip-surface, is detected from the interferometer output using a lock-in amplifier. We present the performance of our microscope, lateral stiffness and tunnel topography images on Si(111)(7×7) surface (Fig. 1).



Topography image

Lateral Stiffness image

Fig. 1. Topography & Lateral force image of atomic terraces on Si(111)(7×7) surface

List of Posters

- P1 Absolute cross sections for electron scattering by ethene: elastic, vibrational, and electronic excitation Michael Allan
- P2 Cleavage of the ether bond by electron impact: differences between linear ethers and tetrahydrofuran Bogdan Catalin Ibanescu, Olivier May and *Michael Allan*
- P3 Anion TOF detection for electron transfer processes in potassiumnitromethane collision experiments *R. Antunes*, D. Almeida, V. Kokhan, N. J. Mason, M. J. P. Maneira, G. Garcia, P. Limão-Vieira
- P4 Direct and Indirect Processes in collision of ions with biomolecules *M.C. Bacchus-Montabonel*, E. Bene, G.J Halász, Á. Vibók
- P5 Resonant Processes In Substituted Hydrocarbons Induced By Low-Energy Electrons *F. Carelli*, F. Sebastianelli, F.A. Gianturco
- P6 Angular Distributions for Vibrationally Inelastic Nonresonant Scattering of Electrons by Molecules *Petr Čársky*, Roman Čurík, and Josef Michl,
- P7 Development of Biomimetic Membranes to study the effect of DNA targets to create intelligent lesions during cancer therapies *M. Coelho*, P.J. Gomes, C. Lage, P.A. Ribeiro P. Limão-Vieira and M. Raposo
- P8 Absolute cross sections for the dissociative electron attachment to HCl, HBr and their deuterated analogs *Juraj Fedor*, Olivier May and Michael Allan
- P9 Electron attachment to pentafluorinated phenyl isocyanate and phenylacetonitrile H. D. Flosadóttir, I. Bald, S. Ptasinska, I. Dabkowska, O.Ingólfsson, E. Illenberger
- P10 DISCO a UV beamline dedicated to biology and chemistry Alexandre Giuliani, Frank Wien, Matthieu Refregiers
- P11 Carbon nanosheets: Novel two-dimensional nanomaterials and their application in electron microscopy A. Beyer, C.T. Nottbohm, X. Zhang, A. Turchanin, A. Sologubenko, J. Mayer, A. Gölzhäuser
- P12 Carbon lons Interaction with PAH and DNA Cast Films P.J. Gomes, B.W. McCullough, P.A.Ribeiro, N.J.Mason and M. Raposo
- P13 Study of Radiation Effect on DNA LBL Films P.J. Gomes, S.V. Hoffmann, P.A. Ribeiro and M. Raposo
- P14 X-rays Effect on Biomimetic Membranes Studied by Neutron Reflectivity *P.J. Gomes*, M.L. Moraes, R. Köhler, P.A. Ribeiro and M. Raposo
- P15 Radiation Effect at Solid-Liquid Interface N. C Jones, P.J. Gomes, J.P. Afonso, P.A. Ribeiro and M. Raposo

- P16 Effect of UV Radiation on Langmuir Films *P.J. Gomes*, F. Pavinatto, P.A. Ribeiro, O. N. Oliveira Jr. and M. Raposo
- P17 XPS Study on the Influence of Ultra-Violet Radiation Energy on DNA Cast Films

P.J. Gomes, A.M.B. Rego, S.V. Hoffmann, P.A. Ribeiro and M. Raposo

- P18 Electron induced switching of azobenzene derivates on metal surfaces observed by scanning tunneling microscopy *Jörg Henzl*, Heiko Gawronski, Michael Mehlhorn, and Karina Morgenstern
- P19 Resonance-enhanced vibrational excitations of c-C5F8 by high resolution spectroscopies, and ab initio calculations M-J Hubin-Franskin, J Delwiche, A Giuliani, D Duflot, P M Santos, N J Mason and P Limão-Vieira
- P20 Molecular fingerprinting for atmospheric sensing: isoprene high resolution spectroscopic studies J Delwiche, M-J Hubin-Franskin, F N Rodrigues, A M S Ferreira-Rodrigues, N J Mason, G G B de Souza and *P Limão-Vieira*
- P21 Influence of counterions in presence water molecules in layer-by-layer films *J.M.C. Lourenço*, P.J. Gomes, Q.Ferreira, A. M. Botelho do Rego, P.A. Ribeiro and M. Raposo
- P22 Dependence of pH and temperature in the mechanism of photo-induced birefringence in PAZO/PAH layer-by-layer films *C. Madruga*, Q. Ferreira, Paulo J. Gomes, Maria Raposo, P.A. Ribeiro
- P23 Chemical modification of biological surfaces induced by X- rays Sylwia Ptasińska, Agnieszka Stypczyńska and *Nigel J. Mason*
- **P24** Formation of negative ions from leucine and isoleucine molecules P. Shchukin, P. Papp, Š. *Matejčík*
- P25 Absolute dissociative electron attachment cross sections for acetylene and diacetylene. *Olivier May*, Juraj Fedor, Bogdan Catalin Ibanescu, and Michael Allan
- P26 A description of inelastic effects induced by an electronic current by wave packet propagation Serge Monturet
- P27 Controlled Magnetron Sputtering Codeposition of [AI,Ti] Thin Films with accurate Depth Profile Stoichiometry Y. Nunes, A. Wemans, H. P. Marques, J. Faustino, J. Ferreira, O. M. N. Teodoro and M. J. P. Maneira.
- P28 Simulations of electron trajectories for three different electron monochromators and the interaction region combining these with a ToF-MS Benedikt Ómarsson, Elías H. Bjarnason, Oddur Ingólfsson
- P29 Damaging amino acids in the gas phase via transient negative ion formation

Chiara Panosetti, Francesco Sebastianelli, Isabella Baccarelli, Francesco A. Gianturco

- P30 Electron-induced manipulation, vibrational excitation and chemistry of single molecules at surfaces Manfred Parschau, Karl-Heinz Rieder, Hans Josef Hug and Karl-Heinz Ernst
- P31 Impedance base electronic interface for measuring the response of biosensor array *R. Ramos*, C. Ribeiro, P.J. Gomes, P.A.Ribeiro and M. Raposo
- P32 Irradiation of Lipids Solutions with VUV Radiation *M. Raposo*, N. C. Jones, P.A. Ribeiro and P.J. Gomes
- P33 The Role of Water on UV Radiation Damage in Biomimetic Membranes *P.A. Ribeiro*, P.J. Gomes, N.J. Mason and M. Raposo
- P34 STM induced Surface-isomers reactions of trans-stilbene molecules adsorbed on highly doped Si(100)-(2x1) surface at 5K D. Riedel, M. Dubois, Ph. Sonnet, M. Cranney, M. Martin, and G. Dujardin
- P35 Low-energy electron-induced modification of polysaccharides and monomeric sugars *A.Ryzhkova*, U.Jarzak, and P.Swiderek
- P36 First Principles Calculations of Organic Disulfide Molecules: Towards Single Molecule Dissociation in the STM S. Sakulsermsuk, R. L. Johnston and R. E. Palmer
- P37 Negative ion formation and fragmentation upon free electron attachment to amino acids
 E. Reichsöllner, S. Denifl, A. Mauracher, F. Zappa, M. Probst, H.D. Flosadottir, O. Ingolfsson, H. Jónsson, T.D. Märk, and *P. Scheier*
- P38 Ring-Breaking Electron Attachment To Uracil: Following Bond Dissociations Via Evolving Resonances *F. Sebastianelli*, I. Baccarelli, R.R. Lucchese, and F.A. Gianturco
- P39 Reversible isomerization of an azobenzene derivative on Au(111) probed by two-photon photoemission
 S. Hagen, F. Leyssner, P. Kate, M. Wolf, and *P. Tegeder*
- P40 Assessment of surface kinetics and interaction parameters governing gas-assisted focused electron beam induced deposition *I. Utke*, V. Friedli, M. Purrucker, J. Michler
- P41 Rectification behaviour of molecular layers on Si(111) Harold J.W. Zandvliet, Ann-Sofie Hallbäck and Bene Poelsema
- **P42** Autodetachment of energy selected metastable SF₆⁻ anions Karola Graupner and *Thomas A Field*

Poster abstracts

Absolute cross sections for electron scattering by ethene: elastic, vibrational, and electronic excitation

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Absolute cross sections for electron – isolated molecule processes are a prerequisite for understanding plasmas, are required for assessing new developments of theory, and are useful as a reference for understanding electron – induced processes on the surfaces and in the bulk.

The two important processes in view of chemical change are dissociative electron attachment (DEA), and electronic excitation, the latter the primary step in neutral dissociation.

This work on ethene, the prototype of π electron systems, concentrates on electronic excitation, in particular the excitation of the lowest triplet excited state which is convenient for testing theoretical approaches to calculate cross sections for electronic excitation in molecules in general. The present results are about 15% higher than earlier measurements from this laboratory, but are still only about 0.6x as large as available calculations.

Elastic and vibrational excitation cross sections have also been measured at this occasion,



Fig. 1. Elastic cross sections at 45° and 180° . Dashed lines are the calculations of Winstead *et al.* [1], dash-dotted lines those of Trevisan *et al.* [2]. Circles are the the ANU, squares the Sophia data of Panajotovic *et al.* [3].

over a large range of scattering angles. The results for elastic cross sections generally agree well with the recent results of calculations taking into account the target polarizability, as illustrated in Fig. 1.

References

- [1] C. Winstead, V. McKoy and M. H. F. Bettega, Phys. Rev. A 72, 042721 (2005)
- [2] C. S. Trevisan, A. E. Orel and T. N. Rescigno, Phys. Rev. A 68, 062707 (2003)
- [3] R. Panajotovic, M. Kitajima, H. Tanaka, M. Jelisavcic, J. Lower, L. Campbell, M. J. Brunger,

and S. J. Buckman, J. Phys. B: At. Mol. Opt. Phys. 36, 1615 (2003)

Cleavage of the ether bond by electron impact: differences between linear ethers and tetrahydrofuran

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Electron interactions with the cyclic ether tetrahydrofuran (THF) have been studied due to the fact that THF serves as a convenient model for the sugar ring in the DNA backbone in connection with radiation damage [1]. Consequently there are many studies concerning the resonances [2] and fragmentation pattern of THF, both in gas phase [3] and in condensed phase [4].

400

The present work [5] reports DEA spectra of diethylether, dibutylether and THF to understand how the ether bond breaks by electron impact, and what are the differences between cyclic and open-chain ethers. Our results show that the cyclic ether and the open-chain ones yield very different type of fragments in the Feshbach resonance energy region (6 -12 eV) but the primary step is the same in both cases. We propose that the different fragmentation pattern results from the fact that in the case of linear ethers the anion is 'cooled' by depositing part of the excess energy into the kinetic energy of the fragments. In THF, the entire energy is retained by the anion, making it too shortlived to be detected.

A difference in dissociation pattern of ethers and alcohols [6] is also noticed. In the case of alcohols the lowest Feshbach resonance is predissociated by a repulsive resonant state while in the case of ethers no suitable repulsive surface is available. While in the first case, in the 1 - 5 eVregion, the dissociation proceeds without an activation barrier, in the latter case a substantial barrier is found.

PES 200E M = 720 10 9 11 12 13 Ioniz. Energy and Photoelectron Currents (c/s) 60 6.70 8.50 40 Θ M = 43 H_2C 20 0 7.65 600 400 c=c=o 200 M = 410 8.61 Ы 6.88 100 M = 1Η 0 2 6 4 8 10 12 Electron Energy (eV)

9.73

tetrahydrofuran

11.48

Fig. 1. The Hel photoelectron spectrum (top, shown shifted by -4.5 eV) and DEA spectra of THF.

References

[1] D. Antic, L. Parenteau, M. Lepage, and L. Sanche, J. Phys. Chem. B, 1999, 103, 6611.

[2] M. Lepage, S. Letarte, M. Michaud, F. Motte-Tollet, M.-J. Hubin-Franskin, D. Roy, and L. Sanche, J. Chem. Phys., 1998, 109, 5980.

[3] A. Aflatooni, A. M. Scheer, and P. D. Burrow, J. Chem. Phys., 2006, 125, 054301.

[4] C. Jäggle, P. Swiderek, S.-P. Breton, M. Michaud, and L. Sanche, J. Phys. Chem. B, 2006, 110, 12512.

[5] B. C. Ibanescu, O. May, and M. Allan, Phys. Chem. Chem. Phys., 2008, DOI: 10.1039/ b718130b.

[6] B. C. Ibanescu, O. May, A. Monney, and M. Allan, Phys. Chem. Chem. Phys., 2007, 9, 3163.

Anion TOF detection for electron transfer processes in potassium-nitromethane collision experiments

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Nitromethane (CH₃NO₂) has been extensively studied [1-4], due to its importance in the chemistry of the earth's atmosphere and possible biological relevance. However, further investigations of this molecule can be justified by the fact that (i) is a simple nitro-organic compound with typical characteristics of explosives and propellants and (ii) due to it's high dipole moment, it can form dipole-bound as well as valence anions upon the capture of an extra electron [5,6]. The electron transfer (electron harpooning) processes in low energy atommolecule collisions mostly happen at (or very near) the crossing of the covalent (K + AB) and ionic ($K^{+} + AB^{-}$) potential energy surfaces. This crossing is due to the Coulomb component of the potential energy surfaces [7]. The resulting processes can then lead to the formation of both K^{+} and AB, allowing the access to states that are not accessible through free EA experiments [8]. In particular, states with a positive electron affinity can be formed, which makes it possible to study the vibration excitation of the parent neutral molecule. In these experiments, we are making use of a crossed molecular beam configuration, with a neutral beam of potassium atoms, formed in a charge exchange source, crossing an effusive beam of nitromethane. The negative ions formed in the interaction region are extracted with a home-made TOF spectrometer. We are comparing these results with those obtained through similar free electron experiments [9], as a way to further complement the study of the various DEA processes.

References:

- [1] A. Di Domenico and J. L. Franklin, Int. J. Mass Spectrom. Ion Phys., 9 (1972) 171.
- [2] A. Modelli and M. Venuti, Int. J. Mass Spectrom., 205 (2001) 7.
- [3] I. C. Walker, M. A. D. Fluendy, Int. J. Mass Spectrom., 205 (2001) 171.
- [4] W. Sailer, A. Pelc, S. Matejcik, E. Illenberger, P. Scheier and T. D. Märk, J. Chem. Phys., 117 (2002) 7989.
- [5] R. N. Compton, H. S. Carman Jr, C. Desfrancois, H. Abdoul-Carime, J. P. Schermann, J. H. Hendricks, S. A. Lyapustina and K. H. Bowen, J. Chem. Phys., 105 (1996) 3472.
- [6] T Sommerfeld, Phys. Chem. Chem. Phys., 4 (2002) 2511.
- [7] P. Limão-Vieira, A. M. C. Moutinho and J. Los, J. Chem. Phys., 124 (2006) 054306.
- [8] L. G. Christophorou, D. L. Mc Corkle, A. A. Christodoulides in Electron-Molecule Interactions and Their Applications, Vol.2, ed. L G Christophorou, Academic Press Inc., NY, 1984.
- [9] E. Alizadeh, F. Ferreira da Silva, F. Zappa, A. Mauracher, M. Probst, S. Denifl, A. Bacher, T. D. Märk, P. Limão-Vieira, P. Scheier, Int. J. Mass Spectrom., (2008) in press.

Direct and Indirect Processes in collision of ions with biomolecules

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Interaction of ionizing radiation with biological tissue can induce severe damage to DNA [1]. Important damage has been shown [2] to be due to secondary particles - low energy electrons, radicals or singly and multiply charged ions - generated along the track after interaction of the ionizing radiation with the biological medium. In that sense, experiments have been performed recently in order to investigate the action of these secondary particles on biological relevant molecules, in particular, a number of experimental investigations have been devoted to the action of ions on biomolecules, generally at relatively low collisional energies. These secondary ions may be involved either in direct processes involving direct action of ions on biomolecular systems, or indirect processes where action of ions with the medium, generally water, generates OH radicals which could then interact with biomolecules.

As a direct process, we have studied the collision of C^{q^+} ions on uracil, in relation with mass distribution experiments [3]. In such collisions between biomolecule and ions, different processes may be considered: excitation and fragmentation of the biomolecule, ionization of the gaseous target, and also possible charge transfer from the multicharged ion towards the biomolecule. A strong influence of the electronic structure and charge q of the C^{q^+} ion on the ionization and fragmentation processes has been shown experimentally. In order to have a more complete understanding of the different mechanisms and electronic structure of the projectile and target involved in these reactions, we have developed a theoretical study of the charge transfer of the RNA base uracil by C^{q^+} ions by means of *ab-initio* quantum chemistry molecular methods followed by a semiclassical dynamical treatment. The results are in accordance with the experimental measurements and allow a detailed description of the electronic structures. The mechanism involves a strong delocalization of the electrons from the uracil target towards the projectile ion and a strong anisotropic effect has been pointed out, in particular in the case of the C^{4^+} + uracil reaction where the charge transfer process is markedly favoured in the perpendicular geometry [4,5].

In order to have an insight into indirect processes, we develop now a theoretical study of the action of carbon ions on the OH radical. The first approach concerns the C^{2+} + OH charge transfer process. As previously, the system is treated by means of *ab-initio* methods and semiclassical dynamical treatment but with consideration of vibration motion of OH. The molecular treatment involves a great number of states as OH⁺ and C⁺ excited states have to be taken into account simultaneously. The first calculations in the linear approach show an important vibrational effect with a two step mechanism for very constrained geometries of the target.

- 1. C. von Sonntag, in *The Chemical Basis for Radiation Biology* (Taylor and Francis, London) (1987)
- 2. B.D. Michael, P.D. O'Neill, Science 287, 1603 (2000).
- 3. J. de Vries, R. Hoekstra, R. Morgenstern, T. Schlathölter, J. Phys. B 35, 4373 (2002).
- 4. M.C. Bacchus-Montabonel, M. Łabuda, Y.S. Tergiman, J.E. Sienkiewicz, Phys. Rev. A 72, 052706 (2005)
- 5. M.C. Bacchus-Montabonel, Y.S. Tergiman, Phys. Rev. A 74, 054702 (2006)
- 6. E. Bene, Á. Vibók, G.J. Halász, M.C. Bacchus-Montabonel, J. Chem. Phys. (submitted)

Resonant Processes In Substituted Hydrocarbons Induced By Low-Energy Electrons

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Unstable molecules and molecular radicals, such as CS and CF₂, are of great importance for the processes in the plasma gas phase. Moreover, the carbon monosulphyde (improperly described as a radical although it does not have any unpaired electrons in its ground state, $X^{1}\Sigma$) plays a role of first importance both in atmospheric and in molecular astrophysics. Infact, the CS is fundamental in producing atmospheric carbonyl sulfide molecule, O=C=S, that is a source for the stratospheric sulfate aerosol layer which directly influences Earth's climate, since it has been connected to the effect of acid rain. At the same time, the CS is a very abundant species in space: it is found in molecular clouds, circumstellar envelops, planetary nebulae, comets and other galaxies. On the other side, the CF₂ constitutes another example of important highly reactive molecular radical. Its importance is not only based on developing plasma device, since it is an important chemically active product formed in a plasma environment during the etching of wafers. We retain important to emphasize that only a restricted number of publications on low-energy electron collisions with CS [1] and CF₂ [2] exists, especially from an experimental point of view.

In this work we are mainly interested in dissociative electron attachment to both the unstable carbon monosulphyde and the molecular radical difluoromethylene in their electronic ground states, respectively $X^{1}\Sigma$ and $X^{1}A_{1}$. As a consequence, we first start to study the integral elastic cross sections for electron collisions with these two molecules. We find in both cases a peak that corresponds to a shape resonance, which is confirmed when calculating the S-matrix poles at different bond lengths [3]. With this information we are then able to study the resonance energy as a function of bond length while its imaginary part gives us the lifetimes as a function of bond stretching. Finally, we build the electronic wave functions and the electron density maps, always at different bond lengths, for both systems. This is done in order to show on which fragment the incoming electron shall remain bound.



Figure shows, from left to right, carbon monosulphide resonant electron density maps at R_{CS} = 1.10 Å, R_{CS} = 1.55 Å = R_{eq} , R_{CS} = 1.64 Å

References

- [1] K. Graupner, T.A. Field and L. Feketova, New J. of Physics 8 220,314 (2006)
- [2] M.T. Lee, I. Iga, L.E. Machado, L.M. Brescansin, E.A. y Castro and G.L.C. de Souza, *Phys. Rev. A* 74, 052716 (2006)
- [3] F.A. Gianturco, R.R. Lucchese, Int. Rev. Phys. Chem. 15, 429-466 (1996)

Angular Distributions for Vibrationally Inelastic Nonresonant Scattering of Electrons by Molecules

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Polar graphs for differential cross section (dcs) called dcs maps are presented as graphical representation of the angular distribution of vibrationally inelastic electron scattering by polyatomic molecules. The objective of this study was to show that an intuitive understanding of the principal features of these graphs can be obtained from a simple analysis of the normal modes of vibration of the target molecule and plane-wave functions representing the scattering electron [1]. For the 1 \leftarrow 0 vibrational transition the integrand in the amplitude $\langle \chi_1 k_1 | T | \chi_0 k_0 \rangle$ must be totally symmetric for a nonvanishing value of dcs. For qualitative estimates, we may neglect the exchange term. If the harmonic approximation is adopted, the amplitude can be expressed as $\langle k_2|\partial U_{\text{static}}/\partial q_i|k_1\rangle$, where $\partial U_{\text{static}}/\partial q_i$ is the derivative of the electrostatic potential with respect to the *i*-th normal coordinate. The $\partial U_{\text{static}}/\partial q_i$ maps can be easily obtained form standard quantum chemistry software by using the option for electrostatic potential maps. The planewave functions for the incoming and outgoing electrons can be expressed in a partial wave expansion and from all possible $j_2 Y_2 j_1 Y_1$ combinations only those are selected that match $\partial U_{\text{static}}/\partial q_i$ best to satisfy the condition for the product $j_2 Y_2 \partial U_{\text{static}}/\partial q_i$. $j_1 Y_1$ to be totally symmetric. The procedure is illustrated on the bending mode v₂ in the CH₄ molecule. For the case of electron energy of 10 eV and \mathbf{k}_1 fixed parallel to the CH(1) bond the best fit for the $\partial U_{\text{static}}/\partial q_2$ map is provided by pairs of real spherical functions Y_{22}^{s} , Y_{21}^{c} , $Y_{$ show that from these data we can understand why the preferential directions for \mathbf{k}_2 are at about 55 and 235°...



Figures: CH_4 in the coordinate system and dcs map for the bending mode in CH_4 , k_2 is chosen to lie in the C(1)-H-C(2) plane.

Reference:

[1] P. Čársky, R. Čurík. B. Pezler and J. Michl: J. Phys. Chem A 111, 12216 (2007)

Development of Biomimetic Membranes to study the effect of DNA targets to create intelligent lesions during cancer therapies

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lonizing radiation is often used in medical cancer therapy to destroy cancer cells via the induction of a high number of lethal DNA strand-breaks on these cells. To improve the interaction of radiation with cancer cells to make more effective its destruction chemical agents groups with radiossensibilizating properties, i.e., chemical groups which can act as DNA binding drugs and present high cross sections to radiation. These are expected to be able to break the DNA strand at specific zones and to promote damage in malignant cells which are quite active to efficient bind to these radiossensibilizating drugs. This work addresses an approach to study the effect of radiossensibilizating DNA binding agents to be carried out on biomimetic membranes. These membranes produced by layer-by-layer (LbL) technique which consists of the alternate adsorption from solution of opposite charged molecules onto a solid substrate. The first step of these studies, involved the optimization of membrane build-up which consisted of characterizing the kinetics of adsorption in terms of adsorption time, solutions concentration, pH, ionic strength and layer drying process. The membrane layer were made of Deoxyribonucleic acid (DNA) alternated with the polyelectrolyte poly(allylamine hydrochloride) (PAH) and methylene blue as DNA binding radiossensibilizating, which were adsorbed on solid support by the LbL technique. The membrane growth was monitored by visible and infrared spectrophotometry.

Absolute cross sections for the dissociative electron attachment to HCI, HBr and their deuterated analogs

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We present dissociative electron attachment cross-section measurements for HX and DX (X= Cl and Br). We have utilized a trochoidal electron monochromator with a recently constructed total ion collection collision chamber. The chamber can be used in two independent modes of measurement - in the "no ion extraction" mode, the created ions hit the collection sheets due to their large gyroradii; in the "active ion extraction" mode a small electrostatic voltage is applied across the chamber and ions are collected due to the electric field.

Electron attachment to both hydrogen halides leads to the production of X⁻ at low electron energies, below 1 eV, and to the production of H⁻(D⁻) at higher energies, around 7 eV. The experimental cross section for the X⁻ production was compared with the predictions of the nonlocal resonance theory [1]. Whereas the theoretical results agree with our measurements in case of Br⁻/HBr, the model seems to overestimate the cross section for Cl⁻/HCl by approximately a factor of 3. Both HBr and HCl cross sections show a strong isotope effect, however, this effect is much weaker for the H⁻(D⁻) production than for the X⁻ production.

References [1] J. Horáček, M. Čížek, P. Kolorenč and W. Domcke, *Eur. Phys. J. D*, **35**, 225, 2005

Electron attachment to pentafluorinated phenyl isocyanate and phenylacetonitrile

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Electron attachment to the pentafluoro halobenzenes C_6F_5X with X being F, Cl, Br or I was studied in detail the last decade of the past century[1-3]. These studies were conducted on the isolated molecules as well as on hetero- and homogeneous clusters containing these compounds. The motivation behind the studies was the systematic change in key parameters with regard to electron attachment that can be attained as one proceeds from X=F over Cl, Br and I. As one progresses from fluorine over chlorine and bromine to iodine the binding energy $D(C_6F_5-X)$ decreases by more than 2 eV and due to the different σ -acceptor/ π -donor properties of the X substitute the electron affinity of the molecule increases by about 1 eV when proceeding from fluorine to iodine. Also the systematic change in the electron affinity of the halogens is reflected in the energetics of the dissociative electron attachment processes observed with these molecules.

Recently pentafluorobenzonitrile and pentafluoronitrobenzene was measured by J. Langer et al. by the same means as the halogenated pentafluorobenzenes[4]. These compounds were observed to fragment in similar manner as the pentafluorohalobenzenes, but at the same time they show different resonance profiles that can be attributed to the different nature of the X-substituent (CN and NO₂).

Here we continue the study of pentafluorinated phenyls and present preliminary results of the electron attachment to pentafluorophenyl isocyanate (C_6F_5 -NCO) and pentafluorophenyl acetonitrile (C_6F_5 -CH₂CN). The isocyanate gives further insight into the effect of exocyclic π -MO's conjugated to the π system of the phenyl ring. In the acetonitrile, on the other hand, the π orbitals of the CN group are separated from the ring's π system by a CH₂ group.

In this study we focus on the formation of the metastable parent anion and the two competing decay channels involving the rupture of the C_6F_5 -X bond. Scheme 1 shows these channels - the first leading to charge retention on the fragment X, while the second to the formation of the closed shell anion C_6F_5 .



Scheme 1. The two main competing dissociative channels of the metastable parent ion

The relative efficiencies of these processes mainly depend on the electron affinity of the substituent in respect to that of the radical fragment C_6F_5 , whose π electron delocalization and the R-C bond energy. The current results on pentafluorophenyl isocyanate and pentafluorophenyl acetonitrile are compared to the previous measurements on the monosubstituted pentafluorophenyl compounds mentioned above.

Ingolfsson, O. et al (1995). <u>International Journal of Mass Spectrometry</u> **150**: 79-86.
 Ingolfsson, O. et al (1996). <u>International Reviews in Physical Chemistry</u> **15**(1): 133-151.
 Tegeder, P., et al (1996). <u>Zeitschrift Fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics</u> **195**: 217-236.
 Langer, J. et al (2008). Physical Chemistry, Chemical Physics DOI: 10.1039/b714320f

DISCO a UV beamline dedicated to biology and chemistry

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The new synchrotron radiation facility SOLEIL near Paris is a third generation storage ring. Its first beamlines are accessible to users this year. The DISCO beamline is a phase II beamline, which will be available to users in the beginning of 2009.

DISCO, located on a bending magnet, uses the visible to VUV light range of the emission. It will possess three end-stations.

One devoted to confocal microscopy in the visible-UV range exploitable all time. This station will allow tuneable excitation to select wavelength ranges of interest. Hence, spectral confocal imaging will be possible with a broad range of excitations between 180 and 800 nm and true UV spectral and temporal imaging of natural occurring fluorochromes.

The two others endstations will share a monochromator fitted with two low-resolution high fluxes gratings. The first one will deliver photons from 3 to 10 eV devoted to circular dichroism measurements of biological macromolecules in solution. Beamtime will be shared equally with the third endstation devoted to atmospheric pressure experiments. This branchline will deliver photons between 4 and 20 eV at atmospheric pressure, enabling virtually all kind of samples to be irradiated. It will notably be coupled with the atmospheric pressure photoionisation source of a mass spectrometer.

The DISCO beamline and especially the atmospheric pressure branchline should open new possibilities in photochemistry.

Carbon nanosheets: Novel two-dimensional nanomaterials and their application in electron microscopy

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The main goals of molecular nanotechnology are the fabrication, manipulation and application of macro- and supramolecular objects with nanometer dimensions. Here, we employ a combination of molecular self-assembly and electron beam lithography for the building of ultrathin carbon nanosheets. The nanosheets are made by irradiation-induced cross-linking of aromatic self-assembled monolayers and their subsequent release from their substrate [1]. Comparable to graphene, carbon nanosheets are only 1-2 nm thin and thus are among the thinnest two-dimensional extended objects. Carbon Nanosheets can now be made with sizes up to several mm² and they can be transferred onto the surfaces of metals and insulators as well as onto porous or holey objects, such as TEM grids (Fig. a), resulting in ultrathin freestanding films. We found that such freestanding sheets have high mechanical strength and are thermally stable up to 1000K in UHV [2].

A technical application of carbon nanosheets is their use as ultrathin sample supports for transmission electron microscopy (TEM) [3]. We tested their applicability by placing gold nanoparticles onto 1.6 nm thick nanosheets that have been transferred onto TEM grids. The corresponding TEM and STEM images show significant improvements over those made with a conventional (thicker) carbon films. The contrast of Au clusters, as well as of single diffusing gold atoms is much higher on the nanosheet (Fig. 1b) than on any conventional support.

[1] W. Eck, A. Küller, M. Grunze, B. Völkel, A. Gölzhäuser: Free-standing nanosheets from cross-linked biphenyl self-assembled monolayers, Adv. Mat., <u>17</u>, 2583-2587, (2005)

[2] A. Turchanin, M. El-Desawy, A. Gölzhäuser: High thermal stability of cross-linked aromatic self-assembled monolayers: Nanopatterning via selective thermal desorption. Appl. Phys. Lett., <u>90</u>, 053102 (2007)

[3] C. T. Nottbohm, A. Beyer, A. S. Sologubenko, I. Ennen, A. Hütten, H. Rösner, W. Eck, J. Mayer, A. Gölzhäuser: Novel carbon nanosheets as support for ultrahigh resolution structural analysis of nanoparticles. *submitted to Ultramicroscopy.*



Fig.1: a) Scanning electron micrograph of a carbon nanosheet transferred onto a TEM grid. The region covered by the sheet appears darker than the uncovered region in the lower right of the image. The insert shows nanosheet as a grey film covering the openings with a few folds. b) TEM micrographs 0.5 - 3 nm gold clusters deposited onto a 1.5 nm thin carbon nanosheet.

Carbon lons Interaction with PAH and DNA Cast Films

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This work explores the effect of carbon ions beam on DNA containing biomimetic membranes. It is aimed to probe the effect of ion beams on the cell membrane and to predict the damage in a biological within the cell environment which might have consequences to cancer therapy. Mimic of biomembranes can be achieved by using the layer-by-layer technique which allows the creation of modular layered molecular heterostructures and allows investigate the interaction of radiation or particles beam with a well controlled biological systems. For this purpose it is essential in o first stage to investigate the effect on individual components of the biomimetic membranes which are lipid layers DNA water molecule networks and ions. In this work cast films of deoxyribonucleic acid sodium salt of calf thymus (DNA), poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene sulfonate) (PSS) were irradiated with carbon ions beams of different energies. The effect of irradiation was monitored by "in-situ" infrared spectroscopy as a function of time and ions energy. The obtained results are displayed in the infrared spectra in figures below; the ion beam induced an decrease on DNA principal bands, 960 cm⁻¹, 1060 cm⁻¹ and 1097 cm⁻¹ and this ion effect is an accumulative effect, increase with radiation time.



Figure 1: Absorbance spectra for different irradiation times, in the 900 to 1400 cm⁻¹ wavenumber region of a DNA cast film irradiated with beam: **a**) 4 keV C⁺ and **b**) 4 keV C²⁺.

Study of Radiation Effect on DNA LBL Films

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Mimicking biological structures is at the present an important tool to study the biological systems. Particular interest is being paid to artificial membrane development namely for drug delivery systems. The main objective here is to study the effect of Ultra-Violet (UV) radiation on DNA when it is placed in a cell like environment. This objective can be achieved either in vivo in a living cell or in DNA contained in artificial lipid membrane in a well controlled supramolecular structure. This approach allows infer about real damage caused by UV radiation onto in a close to the cell environment with the advantage of being a controlled flat structured with well defined layers. The biomimetic membranes were obtained from alternated adsorption from solution of DNA and the polyelectrolyte poly(allylamine hydrochloride) (PAH) onto solid substrates as a result of prepared by Layer-by-Layer (LbL) technique. The LbL films of [PAH/DNA] were irradiated using vacuum ultraviolet synchrotron radiation at different wavelengths and the effect of radiation dose at 140 nm was investigated. After irradiating the LbL film, the effect of radiation was monitored using infrared spectroscopy. The results revealed that lower wavelengths are a more effective damage and an accumulative effect of radiation damage at 140 nm has been observed. The principal bonds affected by the radiation are phosphate group, -PO₂⁻, (1090 cm⁻¹) and ether group, -C-O, (1060 cm⁻¹) as in can be seen from the spectra of figure below.



Fig. 01: Infrared spectra for [PAH/DNA]_n film: a) Kinetics study; b) Wavelength effect.

X-rays Effect on Biomimetic Membranes Studied by Neutron Reflectivity

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Radiation induced damage within the lipid bilayers of a cell membrane may alter ionic pumps causing to either increased or decreased permeability. This may be due to changes associated with disruptions in the ratio of bound to unbound water. Such changes would result in an impairment of the ability of the cell to maintain metabolic equilibrium and can be dramatic even if the shift in equilibrium is quite small. The most extreme effects may lead to rupture of the cell membrane and thence cell death. Therefore simulating the effects of radiation on biomembranes should be addressed. The main objective of this work was to explore physical and chemical changes within membranes structure when exposed to radiation using neutrons reflectivity technique. This technique was chosen because the neutron beam is usually not destructive due its weak interaction with only with atomic nuclei. Moreover it has already been observed that the neutrons reflectivity is an excellent technique to probe the damage caused in lipid bilayers and cholera toxin by repeated exposure to the X-rays beam. Biological membranes and their interfaces were simulated by preparing sequential lipid layers using a layer-by-layer technique. This technique consists on the alternated adsorption from solution of opposite charge molecules. Layered lipid and DNA structures were obtained via the LBL technique and used as a mimic of cell environment to study the effect of radiation when submitted to X-rays in a controlled environment and at the solid/liquid interface. The effect of X rays in the structure of a deoxyribonucleic acid (DNA) layer deposited onto a precursor film obtained from polymers adsorbed onto a silicon block, was monitored by measuring the neutrons reflectivity curves (fig.1a). In addition structure changes caused by UV radiation in 1,2-dipalmitoyl-sn-glycero-3-[phospho-rac-(1-glycerol)] (Sodium Salt) (DPPG) layers adsorbed onto polymeric precursor were also characterized by neutrons reflectivity measurements (fig. 1b).



Fig.1: Neutrons reflectivity curves measured for: a) DNA and b) DPPG

Radiation Effect at Solid-Liquid Interface

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The studies of the radiation effect at the solid/liquid interface are of central significance in biotechnology and medicine since the radiation is highly incoherently scattered and/or absorbed by the liquid phase. In fact, the high attenuation cross-section of radiation in liquids limits the signal gain from the interface in such a way that the intensity that really reaches the membrane which causes damage to the biological matter is unknown. This implies that it is necessary to know about the amount of radiation that really reaches the membrane and causes damage. In order to simulate the cell environment, biomolecular cast and layer-by-layer films were exposed to VUV radiation at the solid/liquid interface. For this study, several biomimetic membranes were prepared onto calcium fluoride windows, namely: i) deoxyribonucleic acid (DNA) cast films: ii) 1,2-dipalmitoyl-*sn*-glycero-3-[phospho-*rac*-(1-glycerol)] (Sodium Salt) (DPPG) and iii) poly(allylamine hydrochloride (PAH) and DNA layer-by-layer (LbL) films. The radiation effect was studied by infrared spectroscopy, measuring the films spectra before and after irradiation with and without water at the interface. The results reveal that the presence of water has a significant role in the damage of the biomolecules as is shown in figure below which reveals a higher decrease bands intensity for the [PAH/DNA] LbL film irradiated with water.



Fig.01: Infrared spectra of: **a)** [PAH/DNA] LbL on different conditions: not irradiated, irradiated during 30min at 200 nm without and with water.

Effect of UV Radiation on Langmuir Films

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All cells whether bacterial, plant or animal are enclosed by membranes which make up about 80% of the total dry-matter content of animal cells. How cells generate and maintain their internal structures and integrity depends upon how the cell membrane controls the transport of material in and out of the cell. The basic structural components of any cell membrane are lipid bilayers. Lipid bilayers are semi-permeable such that small uncharged molecules can pass more or less freely across the membrane but for charged species and macromolecules such as proteins and DNA the membrane is a major obstacle to diffusion. In contrast to the extensive research on radiation damage on biomolecules only a few studies have been undertaken to probe the effect of radiation on the cell membrane. In this work, the effect of ultraviolet radiation (254 nm) on biomimetic Langmuir membranes of 1,2-Dipalmitoyl-sn-Glycero-3-Phosphocholine (DPPC) deposited onto water surface. The subphase was composed by deoxyribonucleic acid (DNA) aqueous solutions with different concentrations. The presence of DNA in the subphase allows the formation of an adsorbed layer at DPPC layer. The effect of UV radiation on the membrane was monitored by measuring the barrier position as a function of irradiation time maintaining the surface pressure constant at 20 mN/m. When irradiated, a decrease of the distance between barriers was observed followed increase of that distance as shown in figure 1 being this kinetics process dependent of DNA concentration in subphase.



Fig: 01: Stability studies for Langmuir films. a) DPPC on DNA not irradiated compared with DPPC on DNA irradiated at 254 nm. b) DPPC on different concentrations of DNA irradiated at 254 nm.

XPS Study on the Influence of Ultra-Violet Radiation Energy on DNA Cast Films

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The influence of UV radiation energy onto deoxyribonucleic Acid (DNA) cast films was investigated by X-Ray Photoelectron Spectroscopy (XPS). Information about the damage caused by this radiation was monitored by evaluating the relative amount of elements and about the relative amount of determined chemical groups. It is known that UVC (200-280 nm) irradiation is strongly absorbed by intracellular biomolecules inducing DNA damage and mutation. Moreover, structural changes in DNA were considered to be one of the primary consequences of the deleterious effects of UVB (280-320nm) at the cellular level and irradiation with large doses of UVA (320-400nm) may help to bring light about cancer formation induced by UVB irradiation. In previous studies about the effect of ultra-violet (UV) radiation in DNA molecules of cells revealed that the energy of UV radiation was influences the damage extension. In this work, the effect of UV radiation energy onto DNA t films has been addressed. The samples were DNA cast film prepared from aqueous solutions onto silicon substrates. The films were exposed to UV radiation wavelengths between 160 and 340 nm with 1.14x10¹⁵ photons from synchrotron radiation source. The samples composition changes were monitored by XPS. Analysis of XPS spectra allow conclude that the UV energy increase has a systematic effect in the relative number of determined elements and respective bonds. The results showed that as the UV radiation energy increases, a decrease of C-O and C=O bonds relatively to aliphatic carbons, a decrease of the of N bonds relatively to other types of nitrogen bonding, a decrease of nitrogen elements relatively to carbon elements, a decrease of phosphorous groups relatively to carbon and finally a slight decrease followed by an accentuated increase of O=C bonds relatively to O-C bonds.



Fig.1: Ratio between carbon and oxygen atoms bonded by different types of groups after irradiated with 1.14x10¹⁵ photons at different wavelenghts.

Electron induced switching of azobenzene derivates on metal surfaces observed by scanning tunneling microscopy

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Azobenzene molecules ($C_6H_5N=NC_6H_5$) have attracted much attention because of their model character as a molecular switch based on a light-induced reversible *trans-cis* isomerization. The isomerization in gas and fluid phase has been studied for a long time, where different substitutional groups were used to tune the isomerization wavelength. Here we report on our investigations of different azobenzene derivates adsorbed onto single crystal surfaces under UHV conditions. The adsorption of the molecules is characterised by means of low temperature scanning tunneling microscopy and the isomerization reaction is induced with inelastic tunneling electrons.



First, we investigate the adsorption of 4-dimethylaminoazobenzene-4-sulfonic acid (NC2H6- $C_6H_4N=NC_6H_4-SO_3Na^+$) on the Au(111) surface.[1] This derivate adsorbs in both *trans*- and *cis*configuration on the substrate. The cis-configuration largely dominates in contrast to the gas phase where the trans-configuration is energetically preferred. Electron-induced manipulation with electron energies of 900 meV allows to switch the trans- into the cis- configuration while the inverse process is not possible below the fragmentation of the molecule at electron energies of 1000 meV. Second, we describe the adsorption of amino-nitro-azobenzene (NH2- $C_6H_5N=NC_6H_5-NO_2$) on the Au(111) surface.[2] Like in the gas phase, the trans-configuration is the dominant species on the surface. The *cis*-configuration is also present on the surface, but has a slightly modified molecular structure compared to the gas phase. The planar bonding angle between the N-N double bond and the phenyl ring is increased on the substrate, allowing parallel adsorption of the rings without steric repulsion between them. In contrast to the former molecule, the isomerization reaction triggered by inelastic tunneling electrons can be induced in both directions. The treshold energies are 650 meV for the trans- to the cis-configuration and below 640 meV for the reverse process. In addition, the adsorption of amino-nitro-azobenzene at 230 K leads - besides the monomer - to variety of molecular arrangements, including two different types of dimer.[2.3] The parallel dimer consists of two molecules in *cis*-configuration and is stabilized by two hydrogen bonds. The isomerization of the molecules inside the dimer is sterically obstructed, but electron-induced manipulation leads to a reversible change in the hydrogen bonding, i.e. in the relative orientation of the molecules inside the parallel dimer. In contrast the isomerization is possible inside the X-dimer consisting of two molecules lying across each other.[3] We can induce the isomerization of either the upper- or lower-lying molecule with electron energies in the range of 650 meV. Isomerization of the upper-lying molecules forces a small motion of the lower-lying molecule. In this way, we perform mechanical work on the nano-scale.

This study demonstrates that the isomerization of azobenzene molecules is not always quenched while in contact with a metal surface. But the functionality, i.e. the reversible switching behaviour, of the molecule is governed by the appropriate choice of the substitutional groups.

- [1] Henzl, et. al., Chem. Phys. Lett. 435 (2007), p. 278.
- [2] Henzl, et. al., Angew. Chem. Int. Ed. 45 (2006), p. 603.
- [3] Henzl, et. al., Nanotechnology 18 (2007), p. 495502.

Resonance-enhanced vibrational excitations of c-C₅F₈ by high resolution spectroscopies, and *ab initio* calculations

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As part of an international effort to reduce the emission of atmospheric pollutants that may lead to global warming, the Kyoto Protocol and its amendments have been developed to phase out the use of several anthropogenic gases by 2010, these include several species arising from the plasma processing industries. Therefore, in order to meet the requirements of the Kyoto Protocol, industry has been seeking alternative gases that will both operate in current plasma reactors and maintain high performance of current feed gases (e.g. SF₆ and CF₄). Octafluorocyclopentene, c-C₅F₈, is among the fluorocarbons suggested as a candidate to replace the traditional feed gases used in the semiconductor industry to prepare silicon wafers for SiO₂ reactive ion etching [1]. Surface reactions induced by $c-C_5F_8$ plasmas have been studied on silicon dioxide and silicon nitride substrates using an inductively coupled plasma source revealing larger etching selectivity and polymerization than in a more conventional c- C_4F_8 plasma [2]. However, before c- C_5F_8 can be widely adopted it must be shown to have little (or no) environmental impact. The electronic transitions and resonance-enhanced vibrational excitations of octafluorocyclopentene $(c-C_5F_8)$ have been investigated using high resolution photoabsorption spectroscopy in the energy range 6 – 11 eV, electron energy loss (HREELS) in electric dipolar excitation conditions (100 eV incident energy, $\sim 0^{\circ}$ scattering angle) over the 5 – 14 eV energy loss range, He(I) photoelectron spectrum (PES) has also been recorded between 11 and 20 eV, allowing to derive a more precise value of (11.288 ± 0.002) eV for the ground neutral state adiabatic ionisation energy. Ab initio calculations have been performed for helping in the assignment of the spectral bands for both neutral excited states and ionic states [3].

[1] E Vasekova, E A Drage, K M Smith, N J Mason, *J. Quant. Spect. Rad. Transf.*, 102 (2006) 418.

[2] H Motomura, S-I Imai, K Tachibana, Thin Solid Films, 374 (2000) 243.

[3] P Limão-Vieira, D Duflot, A Giuliani, E Vasekova, J M C Lourenço, P M Santos, S V Hoffmann, N J Mason, J Delwiche, and M-J Hubin-Franskin, *J. Phys. Chem. A*, (2008) *in press*.

Molecular fingerprinting for atmospheric sensing: isoprene high resolution spectroscopic studies

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One of the most important goals of modern environmental research is to determine the role of biological activity on our climate. Although industry ejects huge amounts of pollutant gases into our atmosphere these are still minor compared to the incredible amounts of materials arising from flora and fauna. Hence the biosphere plays a key role in regulating the Earth's climate and may be used to mitigate our own industrial emissions. However only recently have we begun to quantify the emissions of VOCs and other biologically produced species and our knowledge of how these effect (and are influenced by) our climate remains poor. In particular the spectroscopy of those molecules emitted by biogenic sources remains largely unquantified. However the importance of biogenic activity in atmospheric chemistry is now increasingly recognized and the subject of considerable research as the role of anthropogenic change compared to natural effects is quantified, so that the next generation of global climate models may couple the atmosphere with the biosphere. The biogenic emissions we are focused upon are VOC emissions found principally in forests, such emissions are the largest single source of VOCs in Portugal and Brazil. Estimation of biogenic emissions is therefore critical to assessing those regional atmospheric chemistry processes causing tropospheric ozone since research has shown that VOC emissions lead to formation of NOx a critical source precursor of tropospheric ozone. The subsequent reaction of ozone with VOCs may then lead to particulate formation leading to the characteristic haze seen over rich deciduous forest. Isoprene is one of the most important nonmethane hydrocarbons in the atmosphere [1] and its gas phase reaction with ozone represents an important atmospheric sink for this alkene.

The photoabsorption cross section of isoprene has been measured in the energy range 10.8 to 3.9 eV. Further experimental studies include angle-resolved electron energy loss spectroscopy at 1 keV impact energy to determine absolute generalized oscillator strengths (GOS) of discrete transitions of isoprene. The He I photoelectron spectrum has been verified in the energy range 8.0 to 17 eV.

[1] C Warnecke et al., J. Atmos. Chem., 167 (2001) 38.

Influence of counterions in presence water molecules in layerby-layer films

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The Layer-by-Layer (LbL) technique has received significant attention over the past ten years mainly because it allows the fabrication of low cost functional molecular heterostructures for organic-based electronic, photonic devices, sensors, drug delivery systems and bio-system mimicking. The LbL technique is based on the alternate adsorption from aqueous solutions of oppositely charged molecules onto solid substrates. It involves rather complex processes and phenomena that are still not fully understood. One of these phenomena concerns the presence of counterions in the LbL films as a result of complete or partial replacement of counterions by oppositely charged polyelectrolytes and the water presence in the films which is a fundamental issue in what concerns to biomimetics. The presence of bond water molecules in laver-by-laver films has been detected in layer-by-layer films by X-rays photoelectron spectroscopy (XPS) as revealed by the XPS spectra of O 1s components. This result also indicates that counterions near the ionic groups are immersed in a water network which is of great relevance as this kind of structured water is often present in bio-systems. In addition, these bonded water molecules are not easily removed from surfaces even in ultra-high vacuum due to water vapour high sticking coefficient. The knowledge of how to control of the amount of water molecules in molecular heterostructures is also a fundamental issue particularly in the development of biomimetic membranes which is the main issue of this work.

Dependence of pH and temperature in the mechanism of photoinduced birefringence in PAZO/PAH layer-by-layer films

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Multilayer thin films of azo-polyelectrolytes can reveal a rich suite of physicochemical properties due to its photoisomerization capabilities in relation the N=N azo group, which makes it appropriate for optical storage devices. In this work Layer-by-layer (LBL) films of the azopolyelectrolyte poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzene sulfonamide]-1,2-ethanediyl, sodium salt] (PAZO) and poly(allylamine hydrochloride) (PAH) have been investigated with respect to its optical storage features in terms of adsorption parameters as function pH, ionic strength and temperature. Optical Storage was achieved by producing birefringence on the film as a result of successive trans-cis-trans isomerization cycles induced by light of adequate wavelength from a linearly polarized laser source. Light promotes the azo-group to go from the lower energy trans conformation to the higher energy cis conformation which tends relax back to the trans conformation and when doing it can be oriented in a direction perpendicular to the light electric field. Birefringence creation dynamics, the writing process, has been shown to be governed by two processes one at short times and another at longer times. The first process has been associated to the azo-group orientation and the second associated with the azo-group orientation which involves the polymeric chain both as a result of successive trans-cis-trans photoizomerization cycles. The second process in what concerns to relaxation presents characteristics times of hours. Other factors such as number of bilayers, polyelectrolyte solutions pH and temperature reveled to influence the birefringence creation/relaxation dynamics. In what concerns with the number of bilayers the birefringence signal for the writing process is dependent of the number of bilayers being slower for samples having more layers. In addition, the chain movements are shown to be the ones that are more contributing for the writing process once more than 70% of the signal is coming from the slow process. The presence of counterions is other factor that affects the birefringence as their presence causes the decrease in free volume around the azo groups which difficult the photoisomerization process. When the polyelectrolytes are totally ionized, which happens for PAH solutions pHs of 4 and PAZO solutions of pH 9.5, a smaller birefringence signal is observed and the dynamics of the writing process is slower. With respect to temperature dependence, the writing process a decrease in the writing signal is observed when temperature increases as a result of chain Characteristic times for both writing and relaxation process showed Arhenius dependence with temperature allowing activation energies determination. The obtained values are consistent with a dynamics governed by electrostatic interactions in the sense that more intense electrostatic interactions are giving rise to higher activation energies for both writing and relaxation ergies are processes. In addition the activation energies are lower when PAH is completely ionized at pH 4.

Chemical modification of biological surfaces induced by X- rays

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In the present work the decomposition of the calf thymus DNA fiber and poly-L-arginine by irradiation with soft X rays (magnesium K α X-ray source) in ultra-high vacuum has been studied by means of X-ray Photoelectron Spectroscopy (XPS). XPS is one of the most powerful methods of surface analysis providing a quantitative elemental analysis of thin films and provides information on the chemical transformation of functional groups. The XPS method is able to characterize the elements and molecules present in the top 20-100 Å of a surface with detection limits as low as nanograms per square centimetre. In our work X-ray photoelectron spectra were measured using a Kratos Model XSAM 800 with dual-anode X-ray source, a hemispherical energy analyzer and a channeltron detector.

The X-ray beam both damages and probes the samples. In most cases, XPS spectra have complicated shapes due to contributions of atoms in several sites. For example high resolution XPS spectra of C 1s region for all DNA nucleobases, i.e. adenine, cytosine, guanine and thymine exhibit a range of features and can be uniquely assigned to specific species in the nucleobases.

To study the effect of X-ray exposure our samples were irradiated over 5 hours and the spectra were recorded every 0.5 hour. A comparative analysis of changes observed in XPS line shapes upon irradiation indicates that DNA and poly-L-arginine molecules may decompose via a number of pathways.

For a DNA molecule, detailed studies of high resolution spectra of C 1s, N 1s, O 1s and P 2p before and after irradiation show several decomposition pathways which lead to base damage and/or strand breaks in a DNA molecule. The decrease in observed peak area for phosphorous and oxygen in the phosphate and C-OH groups respectively, indicates a break in backbone of DNA, while loss of amino and C=O species in studied sample can be attributed to fragmentation of nucleobases.

In the case of poly-L-arginine, changes in the photoelectron spectra after irradiation were also observed. The intensities of photoelectrons ejected from all elements present, i.e. C, O and N decrease during X-ray exposure, mostly due to mass loss in the sample but significant changes in the shape of photoelectron lines were also observed for C 1s, which can be attributed to radiation induced rupture of a peptide bond in the studied molecule.

These results are expected to be relevant for study of 'directly induced' damage of biomolecules by ionizing radiation. However, it is well known that irradiation by high energy photons liberates many secondary particles that can lead to 'indirect' damage, therefore we are also investigating the effect of low-energy electrons on DNA. During the meeting preliminary results concerning this latter topic will be also presented.

Formation of negative ions from leucine and isoleucine molecules

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We report a study of the resonant electron capture by leucine and isoleucine molecules in the gas phase using a crossed electron/molecule beams apparatus (Comenius University, Bratislava) [1]. Leucine and isoleucine belong to subgroup of monoamino-monocarbonic aminoacids (other memebers glycine, alanine, valine), where R is alcylic fragment. Leucine and isoleucine have large alcylic fragments $R=CH_2CH(CH_3)_2$ and $R=CH(CH_3)CH_2CH_3$. These objects are structural isomers and differ from each other in position of one methyl functional group. The present study we contine in the effort to study the electron attachment reactions to the alcylic aminoacids [2,3,4]

The negative ion mass-spectra of leucine and isoleucine at resonant energies are very similar. The resonant electron capture to the compounds leads to the formation of at least eleven fragment anions (130, 115, 114, 113, 112, 84, 82, 74, 45, 26, 17 m/z). These ions are formed in three resonant energy regions at about 1.2, 5.5 and 8 eV. Although the mass spectra have similarity, the effective yields curves of some fragment anions show difference. The most significant difference is observed at low ($E \sim 1.2 \text{ eV}$) and high ($E \sim 8.0 \text{ eV}$) energy resonances. lons 115 and 114 m/z demonstrate different yields in low energy region and 113, 84 and 74 m/z have difference at high energy resonant peak.

The formation of the selected negative ions from leucine and isoleucine molecules is discussed in terms of the rearrangement mechanisms, which strongly depend on molecular conformation. Leucine and isoleucine have different structures, hence different rearrangement processes may occure in these two compounds. The mechanism of the ion formation is discussed on the base of *ab initio* DFT (B3LYP/6-31G*) calculations of the structure and the energies of the products formed in DEA reactions to the studied molecules. The differences in total ions currents in both isomers are small, hence autodetachment processes are approximately the same in leucine and isoleucine. The differences in the efficiencies in the ion yields we tentatively assign to the competition between the fragmentation channels.

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[1] M. Stano, S. Matejcik, J.D. Skalny, T.D. Mark, J. Phys. B 36 (2003) 261

[2] S. Gohlke, A. Rosa, E. Illenberger, F. Brüning, M. Huels, J. Chem. Phys., 116 (2002)10164
[3] S. Ptasinska, S. Denifl, P. Scheier, T.D. Märk, S. Matejcik, Chem. Phys. Lett., 403 (2005) 107
[4] P. Papp, J. Urban, S. Matejčík, O. Ingolfsson, Journal of Chemical Physics 125 (2006) 204301
Absolute dissociative electron attachment cross sections for acetylene and diacetylene.

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Although more than one hundred neutral molecules and cations have been recorded in the interstellar space so far, the first anions were reported only recently. The first identified anion was C_6H^- [1], followed by C_4H^- [2] and C_8H^- [3]. A necessary prerequisite for the assignment of the observed astronomical bands are the laboratory microwave spectra – recorded with negative ions prepared in discharges containing acetylene C_2H_2 and diacetylene C_4H_2 . For addressing the question how the $C_{2n}H^-$ ions are formed, both in laboratory discharges and in space, the knowledge of the cross section for elementary processes in plasmas is necessary. We present the study of dissociative electron attachment to C_2H_2 and C_4H_2 .

We utilized two complementary instruments: (i) a dissociative electron attachment (DEA) spectrometer providing a mass analysis of the created DEA fragments as a function of the incident electron energy and (ii) a newly constructed total ion collection tube providing absolute total DEA cross sections. At low electron energies that are present in the laboratory discharges, both molecules show DEA bands corresponding the production of the (M-1)⁻ molecular anions. In case of acelytlene the C₂H⁻ fragment peaks at 2.95 eV with a cross section of 3.6 pm², in fair agreement with the value of 2.2 0.3 pm2 obtained by Azria and Fiquet-Fayard [4]. In diacetylene C₄H⁻ peaks at 2.5 eV with a cross section of 3.0 pm². At higher electron energies, additional bands are present (see also Abouaf et al. [5]), in this region diacetylene has a considerably higher DEA cross section. The relatively low cross sections at low electron energies are rather surprising with respect to production of negative ions in laboratory discharges and space. However, additional experimental results for mixtures of diacetylene and CO₂ suggest that the ion-molecule charge transfer reactions can play an important role. These reactions can possibly increase the negative ion production in plasmas.

References

- [1] M.C. McCarthy et al., Astrophys. J. 625, L141 (2006)
- [2] J. Cernicharo et al., Astrophys. **476**, L37 (2007)
- [3] S. Brünken et al., Astrophys. J. 664, L43 (2007)
- [4] R. Azria et al., J. Physique 33, 663 (1972)
- [5] R. Abouaf et al., in Proc. 12th Int Conf. On the Physics of Electronic and Atomic Collisions, edited by S. Datz (North-Hollan, Amsterdam), p. 409

A description of inelastic effects induced by an electronic current by wave packet propagation

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Controlled Magnetron Sputtering Codeposition of [AI,Ti] Thin Films with accurate Depth Profile Stoichiometry

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Thin films with a linear gradient depth composition of aluminium and titanium are produced from a bespoke codeposition system, which includes two independent planar magnetron cathodes, one for each metal.

In this work [AI,Ti] films with composition gradient in depth, starting either with pure AI or pure Ti, were deposited on Au substrate at room temperature in a DC magnetron discharge without bias. The plasma parameters, for both custom made cathodes, were determined and the process was real time controlled to obtain, from the plasma, the necessary deposition rates for each metal and to get the desired depth profile composition on the films. The process till now was designed to get a constant gradient for the composition depth profile. The composition gradients where confirmed by Secondary Ion Mass Spectrometry (SIMS), see Figure 1.



Figure 2 - SIMS depth profile results for 500nm, AlTi

The thin film gradient, corresponding to the results of the figure, starts with Ti at bottom and Al at surface. Depth profile was acquired using SIMS, with thickness of 500nm. These films have been grown onto Au foil in Argon atmosphere.

Further analysis will be carried using atomic force microscopy (AFM) to investigate the surface morphology and X-ray photoelectron spectroscopy (XPS) in order to detect possible chemical interactions between the film compounds. Our results validate the coating technique, opening new application possibilities.

Simulations of electron trajectories for three different electron monochromators and the interaction region combining these with a ToF-MS

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Here we present current work on comparing the energy distribution and the current of three different electron monochromator designs by simulations using SIMION 7 [1]. The instruments at large are a Trochoidal Electron Monochromator [2,3] by Stamatovic and Shultz, a Hemispherical Monochromator (Hemispherical deflection analyzer) as suggested by T.J.M. Zouros et al. [4,5] and a hypocycloidal monochromator as suggested by Smialek et al. [6]. An effort is made to compare the relative current and the resolution of the monochromatized electron beam between the three designs.

For each simulated monochromator, different sets of geometries for the electrostatic lens systems are compared. The lens systems are optimized to obtain the best energy distribution using the work of Omer Sise et al. [7] as a point of reference.

The simulations are run under what we believe is close to actual operation conditions. The electrons are flown having their velocities distributed inside a cone of variable angles and the electrons speeds are subjected under normal distribution around a fixed value.

As the intention is to combine the electron monochromator with a Time of Flight Mass Spectrometer (ToF-MS) a design of an ion source chamber; for acceleration of ions right after their interactions with the monochromatized electron beam, is also simulated. The combination of a low energy electron source with a ToF-MS is not trivial as a ToF-MS is conventionally a pulsed high voltage device. Field penetration from the acceleration optics of the ToF-MS may consequently have strong influence on the electron energy and resolution in the interaction region. These simulations are therefore essential for the successful combination of a ToF-MS with a low energy electron gun as the ionization source.

Here we present simulations of ion optics where the effects of the acceleration potential on the monochromatized electron beam is visualized. These simulations are a part of a new spectrometer currently being designed at the University of Iceland.



^[1] www.simion.com

^[2] A. Stamatovich and G. J. Schulz, Rev. Sci. Instrum. 39, 1752 (1968).

^[3] A. Stamatovich and G. J. Schulz, Rev. Sci. Instrum. 41, 423 (1970).

^[4] E.P. Benis, T.J.M. Zouros, J. Electr. Spectr. Rel. Phenom. Vol. 125, Issue 3, (2002) 221-248

^[5] E.P. Benis, T.J.M. Zouros, Nucl. Instrum. Meth. Phys. Res. Sect. A440(2000) 462.

^[6] M. Smialek, B. Mielewska and M. Zubek, Radiation Physics and Chemistry 76 (2007) 599-603

^[7] O. Sise, M. Ulu and M. Dogan, Nucl. Instrum. Methods Phys. Res. A 554 (2005), p. 114

Damaging amino acids in the gas phase via transient negative ion formation

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We performed calculations to investigate some aspects of the radiation damage of biomolecules. We focused on low-energy scattering of secondary electrons by some gas-phase aminoacids in order to reproduce the fragmentation patterns emerged from experiments [1]. Due to the complexity of the systems, we had to employ several approximations, such as elastic scattering, fixed nuclei, ab-initio model potentials [2]. However, our model will be shown to be able to reproduce the behavior of the resonant structures seen experimentally, of which we have found the correct number and positions from the S-matrix poles calculations.



Fig.1: Position and width shift vs R(C-OH) for the A" resonance of glycine.

We also propose a one-dimensional model for the dynamics of intramolecular energy transfer via vibrational excitation of selected bonds (i.e. the ones for which the resonant electron density maps show the presence of nodal planes). The basic idea is that, when the excess resonant electron energy is converted into vibrational energy of the bond which eventually breaks up, one should observe a corresponding shift in the the resonance position and width as that bond is stretched. Since we actually find this kind of behavior (see figure), if our hypothesis were to be correct, we would then be able to identify, for a given resonance, those bonds, the breaking of which directly or indirectly relate to the latter. Details of this interpretation will be provided at the Meeting.

References

[1] G.A. Gallup et al., J.Chem.Phys. **126**, 174301 (2007)

[2] I. Baccarelli et al., Advances in Quantum Chemistry, 190 (2007)

Electron-induced manipulation, vibrational excitation and chemistry of single molecules at surfaces

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Chemistry of single molecules at surfaces with the scanning tunneling microscope (STM) has been performed for more than a decade. The mechanism of molecular excitation by the electrons tunneling between the STM tip and the surface are not entirely understood. We present experiments performed on single molecules of the hydrocarbons propane (C_3H_8) and propene (C_3H_6) on a Cu(211) surface.

Exceeding the threshold energy for exciting C-H vibrations, we observe lateral hopping of C_3H_8 . This can be easily induced by increasing the energy of the tunneling electrons above a value of $eV_s \approx 360$ meV. The result of the excitation of the C-H stretch mode by inelastic tunneling electrons is the translation of the molecule onto a different adsorption site via anharmonic coupling between a C-H stretch mode and a translational mode of C_3H_8 .

Different modes of lateral manipulation of C_3H_6 molecules are presented, including the STMinduced conversion between two distinct chiral states. The switching of chirality involves the flipping of the molecule and therefore the manipulation signal for this process differs significantly from a lateral manipulation signal without flipping. Finally, harsh manipulation conditions create species not observed by plain adsorption of C_3H_6 .

The electron induced microscopic processes in relation to the experimental conditions, like electron energy and current, will be discussed.

Impedance base electronic interface for measuring the response of biosensor array

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The detection of aromatic compounds of agriculture contaminants as herbicides, insecticides and fungicides, is actually of great interest since these compounds are being used in large scale, are accumulating in the environment, namely on aquifers, water supplies and water courses and its presence is pernicious for the environment and human health. In this work one proposes to develop portable prototype based on a lab-on-a-chip sensor for "in situ" detection of agricultural contaminants as herbicides as phenols, insecticides as organophosphates and carbamates and fungicides as phthalimides in water. For this propose, biosensors based on structural mimics of biological membranes by deposition of sequential layers obtained by the laver-by-laver (LbL) technique using common polyelectrolytes, dendrimers, functional polymers and biologic molecules. This technique consists of obtaining thin films by alternate adsorption from aqueous solutions of macromolecules of opposite electrical charge onto a solid substrate. The main advantages of this technique are the possibility of assemble different types of molecules, and consequently different functionalities on the same film, thickness control, formation of films on any shape and type of substrate and the solvent is water not requiring the use of organic solvents. The response of film membrane sensors was obtained by impedance spectroscopy at the solid/liquid interface using the principal components array (PCA) analysis or neural networks technique, successful used in electronic tongue device for classification and quantification of components in solutions. A measuring unit prototype for this purpose has been developed which essentially is an impedance measuring system at an appropriated frequency range. The hardware consists of an electronic unit which is schematized in the figure below that basically determines the complex impedance of each of a biosensors set in a given frequency range by measuring the input and output signal amplitude on each sensor and the respective phase difference.



Figure –Schematization of the electronic interface developed for measuring the impedance as a function of frequency for a biosensor in an array.

Irradiation of Lipids Solutions with VUV Radiation

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Experimental observations in irradiated tissues proved that it cannot be fully explained by a simple DNA rupture model. Biological tissues are composed of intercommunicating cells of one or more types, it is not surprising that non-DNA-directed effects may also be triggered by radiation, as the "bystander effect" and the "abscopal effect", that to date its physical/chemical processes are unknown. In addition, cell damage can be induced on the membrane structure which has the fundamental role of keeping the chemical equilibrium between what is inside from what is outside. Any damage may have dramatic consequences on the cell's viability by altering membrane permeability with the most extreme effects leading to cell membrane rupture and thence cell death. The base structure of cellular membrane is essentially composed by a double lipid layer. The phospholipids are composed by a hydrophobic tail composed by an aliphatic chain and a hydrophilic part designed by head which is basically composed by a phosphate group. This work addresses the study of ultra-violet radiation on lipid vesicles solutions of 1,2-Dipalmitoyl-sn-Glycero-3-[Phospho-rac-(1-glycerol)] (Sodium Salt) (DPPG), 1,2-Dipalmitoyl-sn-Glycero-3-Phosphocholine(DPPC) and 1,2-Dimyristoyl-sn-Glycero-3-Phosphocholine (DMPC) were prepared by extrusion technique. The solutions were irradiated with the same photons dose of different wavelengths vacuum ultra-violet synchrotron radiation and changes were monitored by infrared spectroscopy. The chemical effects monitored by infrared spectroscopy revealed a decrease on C-O bonds, and the decrease ratio is different for different wavelengths, which is indicative of beak in head to tail bounds.



Fig.01: Infrared spectra for DPPG not irradiated and irradiated at different wavelengths during with 1.14x10¹⁵ photons. Spectra reveal a decrease of C-O bonds after irradiation.

The Role of Water on UV Radiation Damage in Biomimetic Membranes

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Experimental results on ultraviolet (UV) irradiation of deoxyribonucleic acid (DNA) in solution and adsorbed on electrophoresis gel obtained by M. Folkard et al [1] showed DNA single-strand (SSB) and double-strand (DSB) breaks formation is improved by the presence of water molecules in the media. This result is of extreme importance to radiation effects in biomolecular systems since water is a fundamental component on life tissue. In this work, the effect of presence of water in UV irradiated biomimetic membranes has been investigated. The biomimetic membranes were obtained by the layer-by-Layer (LbL) technique, alternating DNA layers with the polyelectrolyte poly(allylamine hydrochloride) (PAH) by adsorption from solution at the solid/liquid interface. The amount of water molecules present in the DNA/PAH LbL films was controlled preparing films from different salt concentrations and preparing these films between cushions obtained as well by the LbL technique by alternating PAH with Poly(styrene sulfonate) (PSS). All the obtained films were irradiated and characterized by Vacuum-Ultra-Violet (VÚV) spectrophotometry. The VUV spectra reveal that UV radiation has a strong effect when DNA LbL films were prepared between polymeric cushions, being the major damage observed in the presence of water molecules. This result can be inferred from the spectra of fig.1a and fig.1b.



Fig.1: VUV spectra before and after irradiated biomimetic membrane: **a)** DNA Cast 0M Salt **b)** [PAH/PSS]5/[PAH/DNA]15/[PAH/DNA]15 0.5M in NaCl.

¹ M. Folkard, K.M. Prise, Acta Physica Polonica A, 109(3), 265, 2006

STM induced Surface-isomers reactions of trans-stilbene molecules adsorbed on highly doped Si(100)-(2x1) surface at 5K

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The manipulation of single molecules with particular isomerisation reactions known in the gas phase may lead to specific effects when adsorbed on a surface, especially on semiconductors.

In this context, we have studied the isomerisation of trans-stilbene molecules adsorbed on Si(100)-(2x1) surface at 6K by means of a low temperature scanning tunneling microscope. We observe four different conformations after adsorption: the trans-stilbene (TS), the cis-stilbene (CS), and two respective surface isomers I_1 and I_2 . *stilbene (TS), cis-stilbene (CS), and two respective surface isomers I*₁ and *I*₂. Tight binding calculation method used to simulate STM topographies suggests that the TS and CS molecules are physisorbed. Electronic excitation of individual stilbene molecules is used to activate reversible surface isomerisation by means of tunnel electrons. The surface-isomerisation and the diffusion reactions yields are shown to markedly depend on the initial molecular conformation and on the substrate dopant type (n or p).

Low-energy electron-induced modification of polysaccharides and monomeric sugars

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The radiation treatment of polysaccharides has received considerable interest in recent years because this class of natural materials is abundant and new ways to modify their properties can offer access to a wide range of new applications. For example, radiation-degraded chitosan has been suggested as plant growth promotor /1/, but the same material may also serve as a medium for radiation-induced production of metal nanoparticles /2/. Alternatively, irradiation of polysaccharides can produce cross-linked materials serving as hydrogels /3/. The ability of less soluble polysaccharides to form hydrogels has also been exploited to produce surface structures with reversible swelling properties by spatially selective deposition on patterned electrodes/4/. In this context, radiation processing is also of considerable interest as it could produce the same structures with less production steps if the polysaccharide can be removed completely upon irradiation.

In order to gain more control over the modifications occuring in polysaccharides under the effect of radiation, it is worth exploring new techniques of treatment. Experiments on gaseous saccharide monomers have revealed that these compounds are efficiently decomposed by exposure to electrons with energies as low as 0-13 eV and that the produced fragments can be selected by proper tuning of the electron energy /5,6/. This contribution presents the first results of investigations on the effect of low-energy electrons on thin spincoated polysaccharide layers and on thin films of monomeric sugars produced by vapour phase deposition.

- /1/ L.Hai, T.B.Diep, N.Nagasawa, F.Yoshii, T.Kume, Nucl.Instrum.Methods Phys.Res. B 208, 466 (2003).
- /2/ D.Long, G.Wu, S.Chen, Radiat.Phys.Chem. 76, 1126 (2007).
- /3/ F.Yoshii, L.Zhao, R.A.Wach, N.Nagasawa, H.Mitomo, T.Kume, Nucl.Instrum.Methods Phys.Res. B 208, 320 (2003).
- /4/ L.-Q.Wu, K.Lee, X.Wang, D.S.English, W.Losert, G.F.Payne, Langmuir 21, 3641 (2005).
- /5/ S.Ptasińska, S.Denifl, P.Scheier, T.D.Märk, J.Chem.Phys. 120, 8505 (2004).
- /6/ P.Sulzer, S.Ptasińska, F.Zappa, B.Mielewska, A.R.Milosavljevic, P.Scheier, T.D.Märk, J.Chem.Phys. 125, 044304 (2006).

First Principles Calculations of Organic Disulfide Molecules: Towards Single Molecule Dissociation in the STM

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We are aiming to probe experimentally the dissociation of individual molecules containing the S-S bond in the scanning tunnelling microscope (STM). To support this experimental program we are also conducting energetic and structural calculations of naphthalene 1,8-disulfide and diphenyl disulfide in the gas phase, which we present here. Various charge states of the two molecules have been investigated. The Gaussian03 program was employed in these calculations, using the B3LYP density functional and 6-31G* and 6-31+G* basis sets. For both molecules, the S-S unit plays the most significant role when electrons are attached to or removed from the molecules. We show that the dissociation process in diphenyl disulfide can occur even when zero kinetic energy electrons are attached to the neutral molecule, which is consistent with other recent work [1]. We also consider the adsorption of diphenyl disulfide on the Si(100) surface, exploring butterfly, tight-bridge, twisted and dissociated binding modes using a cluster model of the surface and HF/DFT hybrid calculations. For undissociated diphenyl disulfide adsorption, the tight-bridge configuration is the most stable. However, dissociative adsorption is energetically favoured on this surface.

[1] A. Modelli and D. Jones, J. Phys. Chem. A **110**, 10219 (2006)

Negative ion formation and fragmentation upon free electron attachment to amino acids

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Dissociative attachment of free electrons (DEA) to gas phase amino acids (e.g. glycine, alanine and valine) leads to a variety of fragment anions [1-3]. The decomposition of an excited anion may occur via a direct repulsive state of the transient negative ion (TNI), however, often it requires a substantial rearrangement of the molecular structure of the TNI. The time scale of such processes can extend to several microseconds, which corresponds to the observation time of typical mass spectrometers. Nevertheless almost no attention has been given so far to such secondary processes, i.e. the subsequent (metastable) decay of fragment anions, although they can provide further insight concerning structure, stability and energetics of the anion.

Here we present a combined experimental and theoretical study exploring the decomposition of negatively charged amino acids in two different time regimes: (i) metastable decay reactions of the dehydrogenated valine anion [Val-H]⁻ [5] and (ii) prompt decomposition upon DEA in the sub microsecond time regime. We utilize two different instruments that provide either good electron energy resolution or high mass resolution. Furthermore comparison of the metastable decomposition is made with deprotonated valine formed via MALDI. The present studies demonstrate that different resonances of the anion efficiency curve for one mass can often be assigned to completely different anions (e.g. CN^- and $C_2H_2^-$ formed upon DEA to gylcine [6]).

Like for many other biologically relevant molecules [M-H]⁻ is the most abundant fragment ion formed upon DEA to Valine. By measuring the energy dependence of the metastable and collision induced decay reactions of [Val-H]⁻ into smaller fragment anions selective loss of hydrogen from specific sites from valine as a function of the electron energy is identified.

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References:

- [1] S. Ptasińska, S. Denifl, A. Abedi, P. Scheier and T. D. Märk, Anal. Bional. Chem. 377, 1115 (2003).
- [2] S. Gohlke, A. Rosa, F. Brüning, M. A. Huels, and E. Illenberger, J. Chem. Phys. 116, 10164 (2002).
- [3] P. Papp, J. Urban, S. Matejčík, M. Stano and O. Ingólfsson, J. Chem. Phys. 125, 204301 (2006).
- [4] B. Boudaiffa, P. Cloutier, D. Hunting, M.A. Huels, L. Sanche, Science 287, 1658 (2000).
- [5] H. D. Flosadóttir, S. Denifl, F. Zappa N. Wendt A. Mauracher, H. Jonsson, T. D. Märk, P. Scheier, O. Ingólfsson, Angew. Chem. Int. Ed. 46, 8057-8059 (2007).
- [6] A. Mauracher, S. Denifl, A. Aleem, N. Wendt, F. Zappa, P. Cicman M. Probst, T. D. Märk, P. Scheier, H. D. Flosadottir, O. Ingólfsson, E. Illenberger, Phys. Chem. Chem. Phys. 9, 5680-5685 (2007). [9] S. Ptasińska, S. Denifl, P. Scheier, E. Illenberger and T.D. Märk, Angew. Chem. Int. Ed. 44, 6941 (2005)

Ring-Breaking Electron Attachment To Uracil: Following Bond Dissociations Via Evolving Resonances

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Calculations are carried out at various distinct energies to obtain both elastic cross sections and S-matrix resonance indicators (poles) from a quantum treatment [1] of the electron scattering from gas-phase Uracil. The low-energy region confirms the presence of resonances as revealed by earlier calculations and experiments [2, 3] which are compared with the present findings. They turn out to be little affected by bond deformation, while the Transient Negative Ions (TNIs) associated with resonances in the higher energy region (8 eV) indeed show that ring deformations which allow vibrational redistribution of the excess electron energy into the molecular target strongly affect these shape resonances. They turn out to evolve along different dissociative pathways and to stabilize different fragment anions. The excess electron wavefunctions for such scattering states, once mapped over the molecular space, provide nanoscopic reasons for the selective breaking of different bonds in the ring region. They in turn lead to molecular dissociation and to the formation of a variety of stable anions, in agreement with observations.



Computed A' component and A" component of the elastic (rotationally summed) integral cross sections for gaseous Uracil at its equilibrium geometry.

[1] R.R. Lucchese and F.A. Gianturco, *Int. Rev. Phys. Chem.* **15**, 429 (1996). [2] A.M. Scheer et al., *Phys. Rev. Lett.* **92**, 068102-1 (2004). [2] P. Burrow et al., *J. Chem. Phys.* **124**, 124210 (2006).

[3] P.D. Burrow et al., J. Chem. Phys. 124, 124310 (2006).

Reversible isomerization of an azobenzene derivative on Au(111) probed by two-photon photoemission

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Photochromic molecular switches are a fascinating class of molecules which permit the control of molecular geometry and functional properties with light [1, 2]. Understanding and controlling conformational changes of these molecules in direct contact with metal substrates is the major goal related to the development of functional molecular devices. Azobenzenes are one of the main representatives of molecular switches and are regarded as attractive candidates for applications for instance in molecular electronics, functional surfaces, or data storage [3]. Azobenzene and its derivatives undergo a photochemical interconversion between the *trans*-and *cis*-configuration, which have a different spatial arrangement of the aromatic moieties. While the *trans*-form is nearly planar, the *cis*-isomer is three-dimensional [1, 2].

In this contribution, two-photon photoemission (2PPE) spectroscopy is employed to analyze the photochemically and thermally induced *trans/cis* isomerization of the molecular switch tetra-*tert*-butyl-azobenzene (TBA) adsorbed on a Au(111) surface [4]. The isomerization of TBA is accompanied by significant changes in the electronic structure, namely different energetic positions of the lowest unoccupied molecular orbital (LUMO) of both isomers and the appearance of an unoccupied final state for *cis*-TBA. A quantitative analysis of these effects allows the calculation of cross sections for the reversible isomerization and determination of the ratio between both isomers in the photostationary state, where around 60% of the molecules are switched to *cis*-TBA. Furthermore a pronounced reduction of the activation energy by a factor of four compared to the free molecule is found for the thermally activated *cis* to *trans* isomerization of the surface-adsorbed TBA. This demonstrates that the potential energy landscape of the adsorbed TBA is remarkably different from the liquid phase [5].

In addition, based on wavelength dependent photoemission measurements the excitation mechanism for the photoinduced isomerization has been determined. We propose that the optically-induced conformational change of the adsorbed molecules is not caused by direct intramolecular excitation as in the liquid phase but rather by an indirect mechanism, *viz.* a substrate-mediated process. Thereby photoexcitation of holes in the Au *d*-band, which relax to the top of the *d*-band followed by a hole transfer to the highest occupied molecular orbital (HOMO) of TBA drives the isomerization in the wide photon energy regime between 2.1 and 4.5 eV. In addition, for photon energies above 4.5 eV hot electron transfer from the metal substrate to an unoccupied electronic state of TBA has to be considered [6].

References:

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

Assessment of surface kinetics and interaction parameters governing gas-assisted focused electron beam induced deposition

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Local chemical reactions of surface adsorbed molecules with focused electrons are increasingly used for maskless three dimensional depositions of metals, dielectrics, and polymers at the nanometre scale [1]. Typical precursor molecules comprise metal carbonyls, metal acetylacetonates, metal trifluorophosphines, metal halides, silanes, and organic aromatic or chain structures. The knowledge about electron induced dissociation or polymerization reactions of these molecules in the adsorbed state is rather poor. Furthermore, their adsorption / desorption and surface diffusion behaviour is almost unknown. Nevertheless, pure gold [2], copper [3], cobalt, and SiO₂ [4] deposits could be obtained using a focused electron beam of a scanning electron microscope in the energy range of 5 to 25 keV.

In order to quantify the fundamental processes involved in the electron beam induced deposition process shown in fig. 1 we solved the corresponding rate equation involving the contributions of electron impact dissociation, adsorption, desorption, diffusion, and the molecule and electron impingement rates. Solving this equation numerically for the Gaussian electron distribution allows modelling deposit shapes, see fig. 2. By fitting the deposit shapes grown in variable conditions, parameters like the electron-impact dissociation cross sections, the molecule residence time, the surface diffusion coefficient, the surface coverage, and sticking probability can be quantified. The deduced dissociation cross section represents an "integral" value over all dissociation channels activated by the energy spectrum generated by the impinging beam.



Fig. 1: Sketch of focused electron beam (FEB) induced deposition process.



Fig. 2: AFM of deposits from a focused electron induced (5 keV, FWHM 110 nm, exposure times indicated) using Cu(II)-hexafluoro-acetyl-acetonate (3D inset and continuous lines). Dashed lines represent fits with steady-state solutions of the rate equation. Best fits were obtained with a reaction cross section of 0.09 nm², a residence time of 1 ms, and a surface diffusion coefficient of 4×10^7 cm²/s [5].

- [2] I. Utke, P. Hoffmann, B. Dwir, K. Leifer, et al., J. Vac. Sci. Technol. B 18 (2000) 3168.
- [3] I. Utke, A. Luisier, P. Hoffmann, D. Laub, and P. A. Buffat, Appl. Phys. Lett. 81 (2002) 3245.
- [4] A. Perentes, P. Hoffmann, J. Vac. Sci. Technol. B 25 (2007) 2233.
- [5] I. Utke, V. Friedli, M. Purrucker, J. Michler, J. Vac. Sci. Technol. B 25 (2007) 2219.

^[1] W. F. van Dorp, B. van Someren, C. W. Hagen, P. Kruit, Nanoletters 5 (2005) 1303.

Rectification behaviour of molecular layers on Si(111)

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Since today's electronics industry heavily relies on silicon technology, probably the next step towards molecular based electronics would be hybrid technologies, i.e., the incorporation of functional molecules into silicon-based electronics. Due to their large variation in properties, which can be carefully selected by a proper choice and design the of molecule, such as conductivity, absorption spectrum, chemical affinity, flexibility, size, shape, etc., organic molecules have the potential to enhance silicon technology and modify the interface properties of silicon systems. Here we present reproducible and very strong diode-like behaviour observed for molecular films of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) on n-type Si(111)-7×7 surfaces studied by scanning tunnelling microscopy (STM) and spectroscopy (STS) at 77 K. The mechanism behind the rectification is likely to be related to the asymmetry of the junction containing the molecule or to the electron distribution at the molecule-surface interface.

Autodetachment of energy selected metastable SF₆ anions

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Attachment of close to zero energy electrons to sulphur hexafluoride gives the well know metastable ion SF_6^{-2} ;

 $SF_6 + e^- \rightarrow SF_6^-$

which can loose an electron by autodetachment or fragment in collision free conditions on microsecond timescales;

 $SF_6^{-*} \rightarrow SF_6 + e^ SF_6^{-*} \rightarrow SF_5^{-} + F$

Autodetachment is the dominant deexcitation channel, but it is possible to observe fragmentation of metastable SF6* with mass spectrometry as demonstrated, for example, in a recent investigation of the fragmentation of energy selected metastable sulphur hexafluoride anions [1].

In this poster we present preliminary observations of autodetachment of energy selected SF_6 ions. The electron attachment apparatus ERIC, see [2], which includes a trochoidal electron monochromator and a time-of-flight mass spectrometer was set up for formation of negative ions by low energy electrons and for negative ions to pass through the mass spectrometer, but the detector was set with the normal settings to detect positive ions. Thus negative ions, such as SF_{6} , that reached the detector were not detected, but fast neutrals, such as SF_{6} formed in autodetachment of SF_6 , could be detected. In fact, there was a very low probability of detecting SF_{6}^{-2} ions due to collisions with surfaces generating positive ions near the detector, but this signal is shifted in the time-of-flight mass spectrum with respect to the signal of neutral SF₆, as shown in Figure 1. The neutral SF_6 and SF_6^* anion signals are shown in Figure 2 as a function of electron energy; the neutral SF₆ was formed in the drift region of the time-of-flight mass spectrometer ~ 3 to 6 µs after electron attachment.



[1] K Graupner, T A Field, A Mauracher, P Scheier, A Bacher, S Denifl, F Zappa, and T D Märk, J. Chem. Phys. In press

[2] T. A. Field, A. E. Slattery, D. J. Adams and D. D. Morrison, J. Phys. B: At. Mol. Opt. Phys. 38 (2005) 255

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