

Electron Driven Processes at the Molecular Level



19th – 21st October 2011

Prague, Czech Republic

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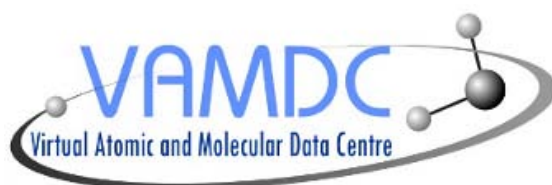


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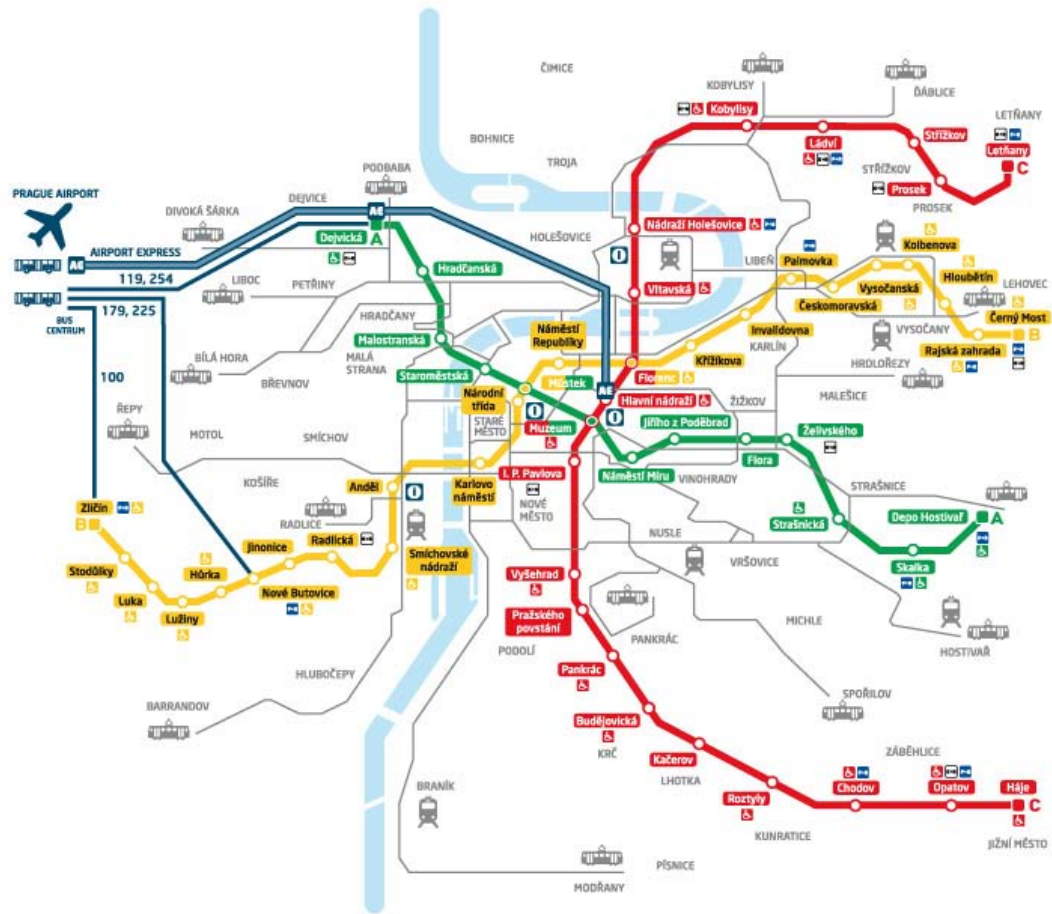
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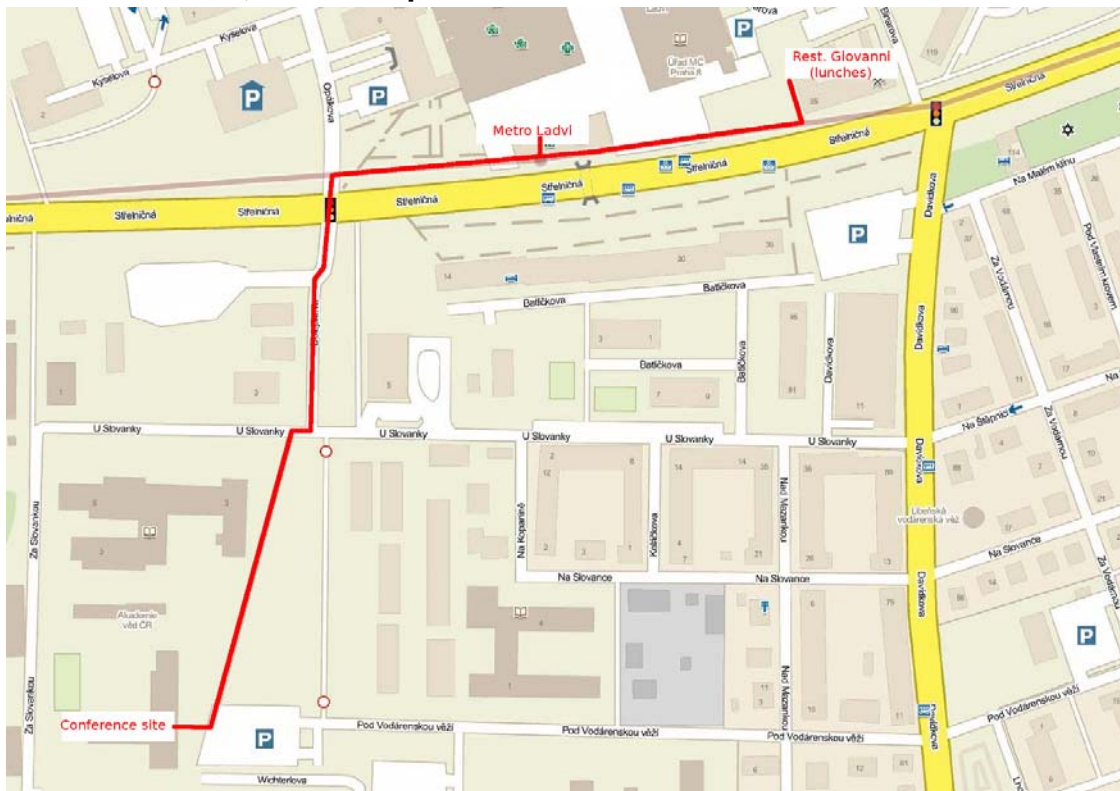
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Prague public transport map



Conference site, metro stop and restaurant Giovanni



Scientific Programme

Tuesday 18th October 2011

| | |
|---------------|-------------------|
| 16:00 – 18:00 | Registration |
| 18:00 – 21:00 | Welcome Reception |

Wednesday 19th October 2011

| Session 1: Introductory overviews | | Chair: Hartmut Hotop |
|---|---|--|
| 08:45 – 09:00 | Opening | |
| 09:00 – 09:40 | What does an experimentalist learn from theoreticians? | Michael Allan (University of Fribourg) |
| 09:40 – 10:10 | Applications of electron scattering | Nigel Mason (The Open University) |
| 10:10 – 10:40 | R-matrix method I | Jimena Gorfinkiel (The Open University) |
| 10:40 – 11:10 | Tea/Coffee break | |
| Session 2: Electron-molecule collisions | | Chair: Franco A. Gianturco |
| 11:10 – 11:40 | R-matrix method II: pseudostates | Jonathan Tennyson (University College London) |
| 11:40 – 12:10 | Nonlocal resonance model as a tool for complete description of inelastic collisions in low-energy electron-molecule and anion-atom collisions | Martin Čížek (Charles University) |
| 12:10 – 12:40 | Towards the nonlocal nuclear dynamics of electron collisions with polyatomics | Karel Houfek (Charles University) |
| 12:40 – 14:00 | Lunch at Restaurant Giovanni | |
| Session 3: Biomolecules and clusters | | Chair: Jonathan Tennyson |
| 14:00 – 14:40 | Experimental studies on electron collisions with biomolecules | Stephan Denifl (University of Innsbruck) |
| 14:40 – 15:10 | A quantum analysis of the response of biological molecules to low-energy-electron impact | Isabella Baccarelli (CASPUR) |
| 15:10 – 15:40 | Ions in Helium droplets | Andreas Mauracher (Uppsala University) |
| 15:40 – 16:10 | Ionization mechanism of atoms and molecules embedded in superfluid helium droplets | Lukas An der Lan (University of Innsbruck) |
| 16:10 – 18:30 | Coffee and posters | |

Thursday 20th October 2011

| | | |
|---|--|---|
| Session 4: Dissociative attachment | | Chair: Michael Allan |
| 09:00 – 09:40 | Electron attachment to small short lived molecules | Thomas Field (Queen's University Belfast) |
| 09:40 – 10:10 | Dissociative electron attachment dynamics in small molecules | Juraj Fedor (Heyrovský Institute) |
| 10:10 – 10:40 | Application of scattering theory to description of anionic formation in interstellar medium and protoplanetary atmospheres | Fabio Carelli (University 'Sapienza') |
| 10:40 – 11:10 | Tea/Coffee break | |
| Session 5: Electron tunneling | | Chair: Nicolás Lorente |
| 11:10 – 11:40 | The strange excitation of vibration in molecular oxygen with tunnelling electrons | Maite Alducin (CSIC) |
| 11:40 – 12:10 | Magnetic transitions induced by tunnelling electrons in individual adsorbates | Frederico D. Novaes (ICMAB Barcelona) |
| 12:10 – 12:40 | Assignment of vibrations in alkane chains using simulations of inelastic electron tunneling | Magnus Paulsson (Linnaeus University) |
| 12:40 – 14:00 | Lunch at Restaurant Giovanni | |
| Session 6: Radiation damage | | Chair: Jimena Gorfinkiel |
| 14:00 – 14:40 | Molecular level assessment of biodamage: multiscale approach | Andrey Solov'yov (Frankfurt Institute for Advanced Studies) |
| 14:40 – 15:10 | Role of secondary electrons in radiation damage by ion beams | Emanuele Scifoni (GSI) |
| 15:10 – 15:40 | Electron relaxation-induced thermo-mechanical effects in biodamage: molecular dynamics simulations | Alexander Yakubovich (Frankfurt Institute for Advanced Studies) |
| 15:40 – 16:00 | Tea/Coffee break | |
| Session 7: Electron dynamics | | Chair: Petr Čářský |
| 16:00 – 16:30 | Fano-ADC approach to the calculation of non-radiative decay rates. | Přemysl Koloreč (Charles University) |
| 16:30 – 17:00 | Interatomic Coulombic electron capture | Kirill Gokhberg (University of Heidelberg) |
| 17:00 – 18:30 | Discussion session: Future developments | |
| 19:00 | Conference dinner at Hotel Troja | |

Friday 21th October 2011

| Session 8: STM | | Chair: Nigel Mason |
|-------------------------------------|---|--|
| 09:00 – 09:40 | The STM as a vibrational and magnetic spectroscopy on the single molecule level | Nicolás Lorente (CIN2 Barcelona) |
| 09:40 – 10:10 | Revealing molecular dynamics through scanning noise microscopy and spectroscopy | Johannes Schaffert (University of Duisburg-Essen) |
| 10:10 – 10:40 | Atomic-scale engineering of electrodes for single molecule contacts | Thomas Frederiksen (DIPC) |
| 10:40 – 11:10 | Tea/Coffee break | |
| Session 9: Electron dynamics | | Chair: Jiří Horáček |
| 11:10 – 11:40 | Electron correlation in adsorbed molecules: the Kondo effect in phthalocyanines on noble metal surfaces | Richard Korytar (CIN2 Barcelona) |
| 11:40 – 12:10 | Ultrafast electron dynamics following ionization of molecular systems | Alexander Kuleff (University of Heidelberg) |
| 12:10 – 12:40 | Dissociative recombination of LiHe ions | Roman Čurík (Heyrovský Institute) |
| 12:40 – 13:00 | Closing and conclusions | |
| 13:00 -- | Lunch at Restaurant Giovanni | |

Talk abstracts

(in order of programme)

What does an experimentalist learn from theoreticians?

Michael Allan

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Discussions with theoreticians have been a tremendous source of enlightenment, understanding and inspiration during my entire career of an experimentalist. The talk will give a somewhat personal retrospective of selected cases where theoreticians provided me with qualitative understanding, with physical pictures which made me understand what is going on in my experiments. The examples will include oscillatory structures in vibrational cross sections in H₂ and hydrogen halides, vibrational Feshbach resonances in HF, dramatic selectivity in the excitation of Fermi-coupled states in CO₂, "dual structures" in NO and N₂.

In the second part of the talk I shall express specific wishes, what would I like to learn from the theoreticians. I will show that from the perspective of an experimentalist there are four families of DEA processes. Listed in order of decreasing energy they are:

- about 5 – 15 eV range, dominated by core-excited resonances, often Feshbach resonances with Rydberg orbital occupation. Predissociation mechanism by repulsive, either core-excited or shape resonances, is essential (prototype is methanol [1])
- about 0-5 eV range, dominated by shape resonances, where symmetry-lowering to bypass an energy barrier is often essential (prototypes are chlorobenzene [2] or acetylene [3])
- dipole and polarizability bound states, resulting in large cross sections near threshold (prototype is HBr [4])
- complex fragmentation, where substantial rearrangement of atoms occurs on parts of the potential surface where the anion is bound, its potential energy surface energetically below that of the neutral (prototype is methyl acetate [5] or formic acid dimer [6])

Each of the four categories will be illustrated with a prototype example. Since the potential surfaces of different types are interconnected, it is essential on the long term that all four types are treated by theory capable of describing them on the same footing. Calculations of molecular dynamics on such surfaces must become a norm.

A close collaboration between experiment and theory is required to approach this goal, where theory is validated by experiments. It is essential that

- the experiment provides data as complete (elastic, vibrational excitation VE, electronic excitation EE, dissociative electron attachment DEA) and quantitative (absolute cross sections) as possible
- theory also provides quantitative cross sections for all four processes. Quantitative theoretical cross sections are particularly scarce for DEA.

In view of the difficulty of the task, effort should focus on relatively small molecules which contain the same motives as biomolecules (functional groups, π -systems, dipole moment).

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- [1] B. C. Ibănescu and M. Allan, *Phys. Chem. Chem. Phys.* **10**, 5232 (2008)
- [2] T. Skalický, C. Chollet, N. Pasquier and M. Allan, *Phys. Chem. Chem. Phys.* **4**, 3583 (2002)
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- [4] J. Fedor, O. May and M. Allan, *Phys. Rev. A* **78**, 032701, (2008)
- [5] Y. Pariat and M. Allan, *Int. J. of Mass Spectr. and Ion Proc.* **103**, 181 (1991)
- [6] M. Allan, *Phys. Rev. Lett.* **98**, 123201, (2007)

Applications of Electron Scattering

From Astrochemistry to Radiotherapy

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Electron induced reactions in both the gaseous and condensed phases initiate and drive many of the basic physical and chemical processes in science and technology with applications from industrial plasmas to radiation damage in living tissue. For example, in contrast to previous hypotheses, collisions of very low energy (sub-ionization) secondary electrons with the components of DNA molecules (or to the water around them) has been shown to be a crucial process in inducing radiation damage in the DNA of living systems. Understanding electron interactions with larger biomolecules is therefore providing new insights to radiation damage and thence the development of new, alternative radiotherapies. In the technological field electron induced reactions underpin most of the multibillion dollar modern semiconductor industry since it is those reactive fragments produced by electron impact of etchant gases that react directly with the silicon substrate. Studies on electron scattering from molecules capable of improving the etch rate of surfaces are leading to development of new (environmentally cleaner) plasma technologies. Electron induced processes are also of extraordinary importance for determination of structure and chemical reactivity of species adsorbed on surfaces. Indeed recently it has been demonstrated that, using STM based technology, discrete electron reactions may be performed at the individual molecular level thus introducing the prospect of designer synthesis on the nanoscale.

The energy region below 10 eV is of particular interest since chemical reactions may be induced by through the formation of low lying transient anions. Such anions arise from the capture of low energy electrons by the parent molecule induced by short range polarization interactions. The subsequent decay of the transient ion leads to both anionic and neutral fragments whose chemical reactivity may be higher than that of the parent molecule. Such a process is known as Dissociative Electron Attachment (DEA) and in many systems a 100 % selectivity with respect to the cleavage of a particular bond can be obtained. This opens interesting prospects for chemical control with wide applications in surface processing and assembly of nanoscale surface structures. It should also be noted that electron induced processes are often directly linked to photon induced processes since photons of sufficient energy excite or liberate electrons from targets which may then drive the local chemistry. Such chemistry may be prevalent in the Interstellar Medium (ISM) where it may allow the synthesis of prebiotic molecules, themselves playing a central role in the origins of life itself!

The R-matrix method I

Jimena Gorfinkiel

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The R-matrix method has proved both popular and flexible for the treatment of low-energy electron (and positron) molecule collisions [1]. Among the processes studied are rotational, vibrational and electronic excitation, dissociative attachment and recombination, anion formation annihilation (in positron scattering), etc. The targets treated, both neutral and charged, range from diatomic molecules of astrophysical interest to biomolecules (e.g. guanine and adenine), molecules relevant to technological plasmas and small molecular clusters.

The R-matrix method is an *ab initio* variational solution to the time-independent Schrödinger equation in which configuration space is partitioned by a sphere [2]. Inside the sphere, accurate quantum chemical techniques produce a 'full' set of eigen-solutions for the system, independent of the scattering energy. The energy-dependent R-matrix is formed on the surface of the sphere from the eigenvalues and surface amplitudes of the inner region solutions. Outside the sphere the target wavefunctions are negligible; exchange and correlation may be neglected and a multipole potential expansion is sufficient to describe the electron-target interaction. In this region the R-matrix is propagated radially and matched to asymptotic scattering solutions: K-matrices are obtained and from them cross sections, temporary negative ions energies, etc.

The UK diatomic and polyatomic R-matrix suites [3], now called **UKRmol**, have recently undergone a complete upgrade. In my talk I will describe the basics of the method and discuss how recent developments are allowing us to treat a new range of targets. Specific examples will be given in the following talk.

References

- [1] Tennyson, J. , *Physics Reports* **491**, 29-76 (2010).
- [2] P G Burke, 'R-matrix Theory of Atomic Collisions', Springer (2011)
- [3] <http://ccpforge.cse.rl.ac.uk/gf/project/ukrmol-in/>, <http://ccpforge.cse.rl.ac.uk/gf/project/ukrmol-out/>

The R-matrix method II: pseudostates

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The R-matrix method has proved both popular and flexible for the treatment of low-energy electron (and positron) molecule collisions [1,2]. However, in common with other methods based on the use of close-coupling expansion, it is difficult to demonstrate convergence of the model with respect to polarisation effects and to extend calculations to intermediate energies, ie ones which span the target ionisation.

In the R-matrix with pseudostates (RMPS) method extra, unphysical states ("pseudostates") are used to represent both physical states of the target used in the expansion and the continuum of target states that lie above the target ionisation limit. RMPS calculations have proved capable of giving fully ab initio treatment of electron-impact ionisation and an excellent representation of the potential. Examples of successful calculations featuring both electron [3] and positron [4] impacts will be given.

However RMPS calculations are computationally very demanding. At present, computational considerations provide the major limit on the application of the RMPS method. Prospects for improving this will be discussed.

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- [1] J. Tennyson, *Physics Reports* **491**, 29-76 (2010).
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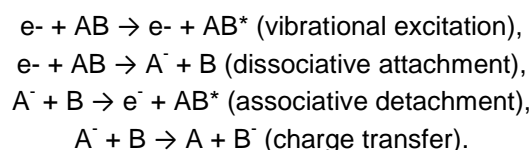
Nonlocal resonance model as a tool for complete description of inelastic collisions in low-energy electron-molecule and anion-atom collisions

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Collisions of low-energy electrons with molecules in the gas phase exhibit several interesting resonance and threshold phenomena that stem from the strong coupling of electron and nuclear degrees of freedom [see for example review of Hotop et al. *Adv.At.Mol.Opt.Phys.* 49 (2003) 85]. The strong coupling is consequence of breaking of the Born-Oppenheimer approximation for the description of the processes. On the other hand the separation of the treatment of the electronic and nuclear degrees of freedom can be achieved by selection of the proper diabatic basis in the electronic Hilbert space. This idea leads to the nonlocal resonance model for the description of the nuclear dynamics[see the review by Domcke: *Phys.Rep.* 208(1991)97].

In this talk, I will review the main ideas of the nonlocal resonance model and show it on the example of the process involving two atomic nuclei



I will write the basic equations for the dynamics and the various cross sections. I will also review various numerical methods used to solve the vibrational dynamics in the nonlocal energy dependent potential. The generalization to the case involving more discrete states and the generalization for more than two atomic nuclei will be briefly mentioned.

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Towards the nonlocal nuclear dynamics of electron collisions with polyatomics

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In the last few decades, the nonlocal theory of the nuclear dynamics of the resonant low-energy electron-molecule collisions [W. Domcke, Phys. Rep. 208, 97 (1991)] has been applied to many diatomic systems and also to some polyatomics, but only when one nuclear degree of freedom plays an important role, thus it is effectively described in a similar way as diatomic system.

In my contribution, I will address problems with solving the equations of the non-local theory for polyatomic molecules and possibilities of overcoming these problems. The equations describing the nuclear dynamics can be reformulated in such a way that the driving equation with the non-local, complex, and energy-dependent (or time-dependent) potential is replaced by the infinite system of coupled differential equations for nuclear wave functions corresponding to the electronic discrete state and continuum states. This system is then reduced to a finite system using some appropriate discretization of the electronic continuum [A. K. Kazansky, J. Phys. B 29, 4709 (1996)].

For systems with two or more nuclear degrees of freedom like H₂O, the resulting system of coupled differential equations with local potentials and couplings could be easier to solve numerically than a single equation with nonlocal potential. We have tested this alternative approach on diatomic molecules. For numerical solution we have applied the FEM and DVR methods together with the exterior complex scaling method [T.N. Rescigno and C.W. McCurdy, Phys. Rev. A 62, 032706 (2000)]. The results have shown that even for relatively small number of the electronic states used for the discretization of the electronic continuum one can get reasonably accurate cross sections for processes of interest. Currently, the first non-local resonance model with two nuclear degrees of freedom, which will capture the main characteristics of e + CO₂ system, is under construction which will be used to test this alternative approach.

Acknowledgments: Support from the Czech Science Foundation (GAČR) by Grant No. 208/10/1281 and by Záměr MSM0021620860 of the Ministry of Education, Youth and Sports of the Czech Republic is gratefully acknowledged.

Experimental studies on electron collisions with biomolecules

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Collisions of low-energy secondary electrons with molecules of cell constituents are expected to be an important process in the radiation damage of living tissue [1]. Electrons are formed in large amounts by the interaction of the primary radiation with cells. Before entering the pre-solvated and finally solvated stage, ballistic electrons with sub-ionization energies may resonantly attach to constituents of the cell and induce severe damage for example in DNA. In the present contribution I will review experimental approaches to investigate damage induced by low energy electrons on the molecular level and discuss advantages but also drawbacks and problems of certain methods used. For example, one rather simple approach is to study electron attachment to isolated (small) biomolecules in the gas phase, which is an excellent method to determine the fundamental properties of the electron attachment process like resonance energies, bond and site selectivity in dissociation, sequential dissociation pathways and so on [2]. So far, the heating of biomolecular samples in an oven was a common method to form efficient molecular beams in the gas phase which, however, can be used only for sufficiently stable molecules. Currently we are testing laser induced acoustic desorption to transfer more complex biomolecules into the gas phase. Another question concerning experiments with isolated molecules is that for example the environment in a cell may lead to a considerable change of fragmentation processes because excess energy deposited by the electron may be transferred in the energy dissipating environment. While studies of processes in the bulk are complex and difficult to interpret, experimental studies with clusters of biomolecules allow a qualitative conclusion on processes occurring in complex cell environments. Results for clusters of amino acids [3,4] and nucleobases [5] formed in helium nanodroplets will be presented.

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A quantum analysis of the response of biological molecules to low-energy-electron impact

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The impact of a high energy radiation on a living cell initiates a complex sequence of processes and reactions. Among the secondary species created by the initial high-energy quanta along the radiation tracks, an important role is played by the large amount of low energy electrons (LEEs) which are produced at initial energies up to some tens of eV and which appear to trigger the crucial reactions relevant to direct damage of DNA [1]. A crucial step towards the molecular dissociation has been identified in the formation of resonant negative ions, where the ballistic electrons are temporarily trapped in the potential field of the molecule.

In gas phase experiments the intrinsic properties of molecules can be probed via a variety of spectroscopic methods and technique using photons and/or particles, often in combination with mass spectrometry. Along that line, the experimental and theoretical study of dissociative electron attachment to the building blocks of DNA revealed indeed that these components are surprisingly sensitive towards low energy electrons. The condensed phase is naturally the more appropriate environment to study the problems relevant to radiation damage. Clearly enough, the quantities which can experimentally be obtained are often composed from different events or identify the final product of a complex reaction sequence which is usually not straightforward to disentangle. The essential point is to ascertain to which extent the properties of a molecule will change when going from the gas phase to the condensed phase.

In the last ten years we started the investigation of electron scattering by molecular targets of biological interest [2] by means of the theoretical procedure developed in Rome for the study of electron/positron-molecule scattering. The method is based on a Single Center Expansion of the bound, scattering and potential functions in a basis of symmetry-adapted angular functions. The delay-matrix formalism revealed to be a powerful tool in the computational detection and characterization of the transient negative ions occurring in the scattering process [3], together with the identification of the mechanism of the dynamical trapping of the electron in the molecular potential field. In order to apply the procedure to large biomolecules, usually exhibiting low or no symmetry properties, and in the perspective to extend the calculations to larger macromolecules, we devoted a significant amount of work to make our suite of codes capable to cope with complex systems. The technological advances introduced in our computational machinery, which included the use of the novel architectures based on graphics accelerators, allowed us to carry out a full analysis of the resonant features in the electron scattering by DNA nucleotides. In the present report we will briefly review our most recent findings and show to which extent we can correlate the results obtained on isolated molecules, i.e., the DNA components, with realistic macromolecules made up of those components, such as the nucleotides. We will also present our progress in the analysis of the interaction of LEEs with some representative radiosensitizers.

References

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Ions in Helium droplets

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The theoretical work presented at the EDPML Meeting 2011 was inspired by different experimental studies carried out by the group of Paul Scheier [1,2]. Although a lot of information can be obtained from the experimental data, some important features cannot be derived, e.g. the arrangement of the Helium atoms around the ions. We will show the characteristic steps to carry out MD simulations capable of describing the weak bonds, which are involved in Helium-Helium interactions.

In the first step of the project the interaction of Helium atoms with small atomic and molecular systems is studied using quantum mechanical electronic structure (*ab initio*) methods. These calculations are performed using different levels of theory and large basis sets – additionally corrected for the basis set superposition error – of different accuracy to determine the level required for a reliable description of small gas phase clusters containing these ions, as well as one to several Helium atoms. The interaction of Helium atoms with ions is very weak and therefore it is essential to use a method that can reliably compute these weak bonds. In the second step the derived level of theory and basis set are used to calculate potential energy surfaces for different systems. The third step is the derivation of an advanced state-of-the-art many-body force-field for the Helium-solvated systems. In the fourth step the functions fitted in step 3 are used in MD simulations of the solvation of the molecules in small liquid Helium droplets.

First, classical MD simulations are performed to acquire a general understanding of how the Helium atoms want to coordinate. Secondly, since the Helium atoms are very light, and the temperatures used in the experiment are very low, quantum mechanical motion (delocalization) of the nuclei is an important effect to incorporate. For this reason, the method of PIMD is used to study the preferred solvation of the molecular ions by Helium. A representative system and the obtained results from the simulations will be presented at the meeting. We compare quantities derived from MD and PIMD, such as radial distribution function but also number of helium atoms in first and second solvation shells, to experimental data to judge the quality of the methods employed in this work.

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[1] S Denifl *et al* 2008 *J. Am. Chem. Soc.* 15/130 5065

[2] A Mauracher *et al* 2009 *Phys. Chem. Chem. Phys.* 37/11 8240

Ionization mechanism of atoms and molecules embedded in superfluid helium droplets

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Superfluid Helium nanodroplets (HND) have been a widely used tool to investigate atomic and molecular complexes at ultralow temperatures. Their properties allow for the creation and investigation of exotic and novel complexes. In this contribution two findings on the properties of the HNDs will be presented.

The first one is the discovery of a novel ionization mechanism in the HNDs. An electronically excited He atom (He*) collides with a singly-charged cation preformed inside the HND and transfers its internal energy which results in the formation of a doubly-charged cation. This mechanism can be attributed to a Penning-like process. This reaction was discovered during our investigations of methyl iodide embedded in HNDs, where the formation of doubly-charged iodine was observed [1].

The second topic will discuss the wetting of alkali clusters deposited on HNDs. A recent theoretical paper by Kresin and Stark [2] predicted the specific cluster size, beyond which the alkali cluster will completely penetrate the HND. We present the first experimental proof of this transition for Sodium [3] and Potassium clusters by comparing appearance energies of clusters with different sizes. Due to the different ionization mechanism, where clusters on the surface are more likely to be ionized through a Penning process and submerged clusters through direct charge transfer, we could confirm the submersion of Na_n clusters with n ≥ 21, which is in remarkably good agreement with the theoretical prediction. For K_n clusters preliminary results will be presented.

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Electron Attachment To Small Short Lived Molecules

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Electron attachment to small reactive molecules, such as CS [1], CF₂ [2], and C₂F₅ [3] has been investigated experimentally and, in the case of CS, with theory. Experimental observations of dissociative electron attachment to these molecules, made with ERIC [4], will be discussed. Where possible these observations will be considered with theory. Challenges for larger molecules may be considered time permitting.

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Dissociative electron attachment dynamics in small molecules

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Scattering of slow electrons on molecules in the gas phase represents a tool to gain insight into the nuclear dynamics of transient negative ions. The dynamical information is achieved via measuring cross sections for individual scattering channels and using isotopic substitutions in molecules – change of the nuclear masses usually leads to change in the dissociation timescales and thus to the shift in competition between dissociation and electron autodetachment. This is then reflected in the change of corresponding cross sections.

Here we are concerned with the dissociative electron attachment (DEA) channel. We present an experimental setup that combines the total ion collection and the time-of-flight quantitative mass spectrometer, so that two independent values are obtained for each cross section [1, 2]. We concentrate on small molecules: either diatomic (hydrogen halides) or small polyatomic (C_2H_2 , C_4H_2 , HCN). In all cases, the deuterated species show considerable decrease in cross section. The amount of this decrease reflects both the width of the involved resonant state and the trajectory of dissociating nuclei. Since the resonant electron scattering is difficult to describe theoretically, our measurements also serve as tests for various theories. As an example, our data confirmed very good performance of the nonlocal resonance model for HBr [1] and lead to construction of an improved model for HCl [3].

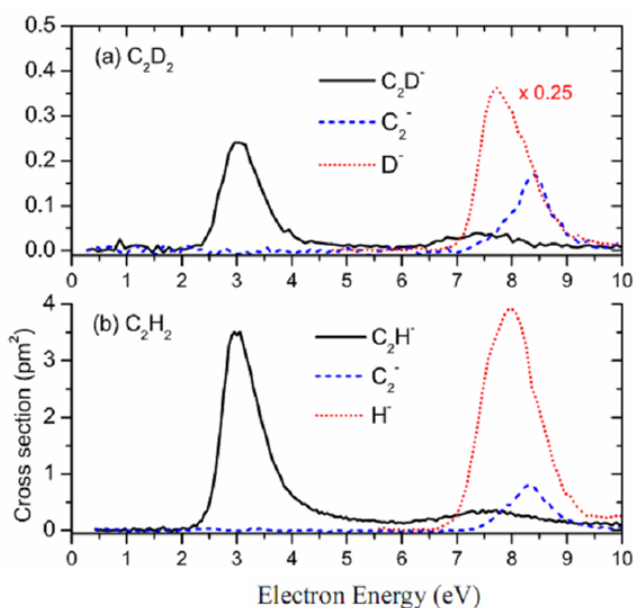


Figure 1. Dissociative electron attachment cross sections for C_2H_2 and C_2D_2 .

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Application of scattering theory to anionic formation in interstellar medium and protoplanetary atmospheres

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Polycyclic aromatic hydrocarbons (PAHs) are large planar aromatic molecules. Due to their marked electronic delocalization they are particularly stable against photodissociation. According to this, free neutral and/or cationic gas-phase PAHs have been surmised to efficiently absorb in the visible and ultraviolet spectral windows, so they have been proposed as potential carriers for at least a subset of the diffuse interstellar bands (DIBs, [1]). They are also thought to efficiently convert the absorbed energy in infrared emission in the so-called unidentified infrared bands (UIBs, [2]), where however the aromatic bands are not seen in C-rich AGB stars while they appear in proto-planetary nebulae (PPN).

Moreover, both medium-size ($N_C < 30$) and large-size PAHs are seen as an intermediate stage between the gas and the dust phases of the interstellar matter, and as such they are currently included in almost all relevant interstellar dust models [3].

Recently, the role of the charge state of PAHs in ultraviolet extinction has also been the object of some theoretical investigations [4]: in this work the authors show how a combination of classical dust particles and mixtures of real PAHs satisfactorily matches the observed interstellar extinction curve (ISEC) where variations of the spectral properties of PAHs in different charge states (thus including the anions) produce changes consistent with the varying relative strengths of both the bump and non-linear far-UV rise features.

Furthermore, according to most astronomers and astrophysicists, it is assumed that PAHs should almost soak up free electrons, if present in the same spatial region, having thus deep repercussions on the chemical evolution of such an astrophysical environment.

In this framework, due to its size, the coronene molecule ($C_{24}H_{12}$) can be viewed as an astrophysically interesting medium-size PAH whose importance can be found when looking at this molecule as one possible link between medium-size and large-size PAHs.

Therefore, its positive electron affinity ($EA = 0.5$ eV) coupled with a large static polarizability, makes this molecule interesting from the point of view of the formation mechanisms of metastable anions as doorways for the ensuing possible stabilization of various negative species. Such an investigation is then made more intriguing by the fact that in our group we have recently analysed the behaviour under low-energy electron collisions with another aromatic (smaller) system, the o-benzyne [5,6], which has a similar EA but possesses also a strong dipole moment.

The detailed search of the possible formation of threshold, metastable anions for the coronene molecule will be therefore discussed under the light of the most recent available experimental data; additionally, our findings [7] about its possible behaviour, at the molecular level, as a deflector of low-energy electrons present in those astrophysical contexts shall be also presented.

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The strange excitation of vibration in molecular oxygen with tunnelling electrons

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Vibrational spectra of single molecules on solid surfaces have become possible by the scanning tunneling microscope (STM) operating in inelastic electron tunneling spectroscopy (IETS) mode. The STM drives a tunneling current through the vacuum gap between a metallic tip and a substrate where molecules can be adsorbed. Under certain conditions, the tunneling electrons can give energy to the molecule and excite a vibrational mode. Varying the tip-substrate voltage, the opening of this new scattering channel is detected in the STM-IETS as an increase in the total electron current just at the energy threshold of the vibration. Interestingly, this picture, i.e., the conductance increase, does not seem to hold for oxygen molecules adsorbed on a silver substrate. Indeed, when the molecules are chemisorbed along the [001] direction on Ag(110) instead of increasing, the current decreases at the vibrational threshold. Furthermore, no evidence of vibrational excitation is instead observed when the molecule is chemisorbed along the [1 $\bar{1}$ 0] direction. These experiments have remained unexplained during years [1].

In this talk, I will present the results of our recent IETS simulations that permit us to solve this long-standing puzzle [2,3]. We will see that when semilocal DFT is corrected by including static intra-atomic correlations (DFT+U), the IETS simulations are in excellent agreement with the experiment. The analysis of the projected density of states shows that intra-atomic correlation leads to the spin splitting of the π_g orbital and the subsequent pinning of one of these orbitals to the Fermi level. This effect is observed on the O₂[001] chemisorption state, but not on the O₂[1 $\bar{1}$ 0] one. The unforeseen consequence of our calculations is that when adsorbed along the [001] direction, O₂ on Ag(110) is a mixed-valent system in which a localized spin polarized orbital is at resonance with the Fermi level.

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Magnetic transitions induced by tunnelling electrons in individual adsorbates

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Recently, several IETS (Inelastic Electron tunneling Spectroscopy) experiments¹⁻⁴ demonstrated the existence of magnetic anisotropy in individual adsorbates, i.e. different energy levels of an adsorbate exist that can be associated to the orientation of the adsorbate spin with respect to its surroundings. They also showed that tunneling electrons were extremely efficient in inducing transitions between these magnetic energy levels. In these cases, transport through the magnetic adsorbates is highly inelastic. This is at variance with the case of molecular vibrational excitation where inelastic transport was much weaker than elastic transport⁵.

We will initially discuss the strong coupling approach developed by Gauyacq and Lorente⁶ for inelastic magnetic transitions induced by electrons tunneling through adsorbates at surfaces. It combines DFT-based studies with a sudden approximation treatment of the magnetic interactions. It is non-perturbative and the transition probabilities are expressed in terms of spin coupling coefficients. In this approach, a global tunneling amplitude is shared between the various magnetic states following spin coupling coefficients, so that inelastic probabilities can be very large and even exceed the elastic one. This approach thus yields quantitative predictions for the strength of the various magnetic excitations in particular with respect to the elastic part of the tunneling current.

We will present results of this approach applied to the case of Fe and Mn single adsorbates on CuN/Cu(111) surfaces⁶ as well as to the case of Fe-Phthalocyanine molecules on CuO/Cu(100)⁷. We will stress how the very large probability for inelastic transport can be accounted for – e.g. in the case of the electron tunneling through the central Fe atom of an adsorbed Fe-Phthalocyanine molecule, the inelastic transport is twice stronger than elastic transport.

Finally, we can mention that this approach can also be used to quantitatively evaluate the lifetime of magnetic excitations at surfaces⁸.

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Assignment of vibrations in alkane chains using simulations of inelastic electron tunneling.

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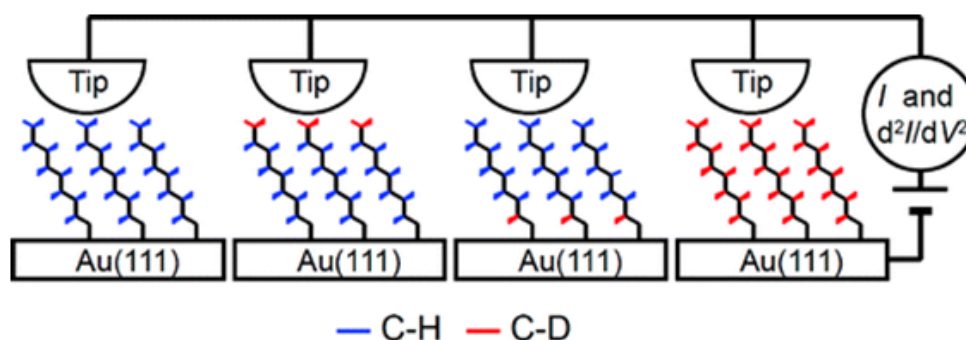
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Inelastic electron tunnelling spectroscopy (IETS) has emerged as an important tool to investigate the structure of molecular junctions. The emission of vibrations by the tunnelling electrons gives a fingerprint allowing the experimentalist to confirm the existence of molecules in the junction. Furthermore, the IETS is in principle sensitive to details of the molecular conformation and binding to metal electrodes which is information vital for the development of molecular electronics.

In this talk I will describe the theoretical method that allows us to calculate the conductance and IETS from density functional theory. The theory gives the selection rules for inelastic scattering and describes heating of the molecular vibrations. Using recent experimental measurements of alkanthiol self-assembled monolayers we have unambiguously determined which molecular vibrations are active in the inelastic electron tunnelling spectroscopy confirming the theoretical predictions. Using selective deuteration of the molecule also allows us to show how the different parts of the molecule contribute to the inelastic signal and provide insights on electron transport through molecules.



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Molecular level assessment of biodamage: multiscale approach

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The multiscale approach to the assessment of radiation damage consequent to irradiation by ions was designed in order to qualitatively and quantitatively describe effects that take place when energetic ions interact with living tissues. A road to the understanding physical aspects of ion-beam cancer therapy (IBCT) on the microscopic level revealed that this problem has many temporal spatial, and energy scales, while the main events leading to the cell death happen on a nanometer scale. This approach has become interdisciplinary since it has addressed the key issues of physical, chemical, and biological sciences related to IBCT. The approach is phenomenon-based and, having started five years ago, passed several milestones making discoveries on different scales. In Refs. [1, 2], the effects of ion stopping in the medium and secondary electron production were addressed. Different aspects of the Bragg peak and energy spectra of secondary electrons were studied and compared to experiments. The transport of secondary electrons was studied in Ref. [3], where the DSB yield due to secondary electrons was estimated. Then the complex DNA damage has been quantified in Ref. [4]. This is one of the most important features of radiation with ions. This type of damage, caused by high concentration of damage agents such as secondary electrons, is the most lethal to the cells, because of difficulties in repairing of severely damaged sites by proteins. This work led us to the development of Ref. [3] and calculation of complex damage in Ref. [5].

Another pathway of DNA damage is related to the local heating in the vicinity of the ion tracks due to the energy deposited by ions. The heat transfer initiated by ions was studied and thermal and pressure spikes were predicted to occur for a very short time after the ion's passage [6]. The investigations of thermo-mechanical effects continued with a study of shock waves caused by the pressure spikes [7]. The predicted forces acting on DNA are strong enough to cause a bond rupture leading to strand breaks.

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Role of secondary electrons in radiation damage by ion beams

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Radiation damage induced by ion beams in biological tissues, on a molecular scale, is an expanding topic of research [1], boosted by outstanding possibilities of application for ion beam cancer therapy [2] and assessment of radiation risk in space exploration [3].

A nanoscopic view of the process has a crucial step in the analysis of the secondary electrons. The key role of secondary electrons produced in the process of ionization, while the energetic ions penetrate the tissue, has been pointed out for a long time, and it is well accepted that a significant part of the resulting damage is related to collisions of these abundant secondary species on the biological target rather than from the direct collision of the primary ion. The details of the production and propagation of such electrons in tissue (water, DNA constituents or nuclear cell proteins) and the related radial dose deposition has a great relevance in the assessment of the quantitative entity of the following damage, such as double strand breaks in DNA sub-units which are lying close-by to the ion track and allowing to derive the relative biological effectiveness.

After reviewing the state of the art in the field, we will present calculations and analysis of electron production and radial dose distribution for energetic carbon ions in liquid water. Our method advances further a recently introduced multi-scale approach [4], which was suggested to explore the effect of damage by keeping into account the different physical effects and scales in play [5,6]. For the electron spectra we introduced a new parametrization based on several effects, including experiments on penetration depth of energetic ions, and also exploited a dielectric response function based approach. For the electron propagation we distinguished between different regions of distance from the track: in the inner region a random walk method is proposed, on its turn with different parameters for the subexcitation region and an intermediate energy one, while in the outer radial distance region another approach based on an energy range formalism is preferred and an overall agreement with experimental results is achieved at all the distances from the track. Calculations of double strand breaks rates obtainable with the present dose calculation result will be also reported and discussed, as well as comparison with other simulations performed with the Monte Carlo track structure code TRAX (7).

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Electron relaxation-induced thermo-mechanical effects in biodamage: molecular dynamics simulations

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A number of different agents cause DNA damage as a consequence of irradiation. These include interactions of a DNA molecule with secondary electrons, holes, produced in the process of ionization, and free radicals. Each of these effects may result in the base damage, single or double strand break in a DNA molecule, or more complex damage, which is a combination of the above lesions.

This work is devoted to a study of the possibility of producing these lesions as a result of a thermomechanical effects caused by ions stopping in tissue. Thermomechanical effects in this case can be described as a dynamical change in temperature and pressure in the medium causing forces that may rupture bonds in DNA molecules [1]. The understanding of such a possibility evolved from the estimates of temperature increase in the medium as a result of ion propagation [2], then from the analysis of thermal and pressure spikes in liquid water [3], and finally from the study of the cylindrical shock wave caused by ions [4-6].

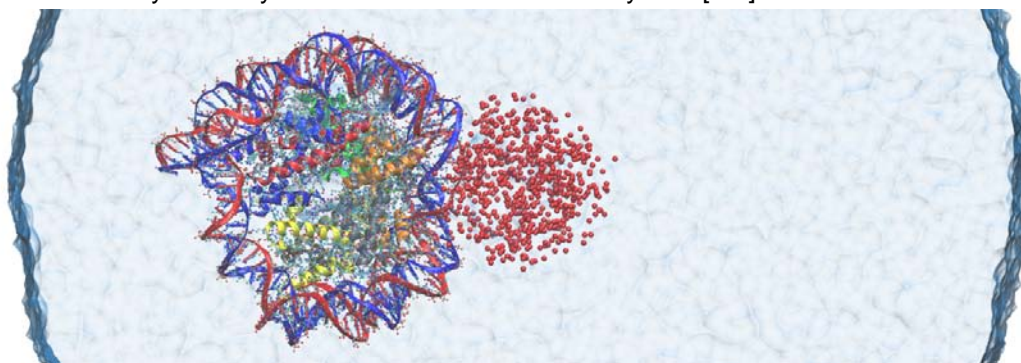


Figure 1. Structure of the nucleosome 150 fs after the carbon ion propagation. Water molecules initially located within 1 nm from the ion's track are shown by spheres. It is seen as substantial distortion of the nucleosome structure caused by the propagation of the shock wave.

We present the results of molecular dynamics (MD) simulation of the temperature spike in the vicinity of a nucleosome, i.e., a DNA fragment wrapped around a histoneprotein complex. This unit presents a particular interest in relation with a so-called complex DNA damage, which is deemed to be lethal to the cell. The results of MD simulations demonstrate that the three dimensional structure of nucleosome experiences noticeable deformations. The propagating shock wave leads to the partial destruction of the DNA secondary structure. We analyze the thermomechanical stresses placed on the covalent bonds of the DNA backbone chain during the shock wave propagation and estimate the probability to induce a thermomechanical breakage of the DNA backbone chain.

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Fano-ADC approach to the calculation of non-radiative decay rates

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Since their theoretical prediction a decade ago [1], inter-atomic Coulombic decay (ICD) and related processes has been in focus of intensive theoretical and experimental research [2]. The remarkable progress in this field has been stimulated both by the fundamental importance of the discovered decay phenomena as well as by the possibility of their practical application, for example in spectroscopy. Recently, ICD was observed also in inner-valence ionized water clusters [3,4], which naturally leads to the question of the relevance of ICD as a source of low-energy electrons for biochemical environment, e.g. in the processes of radiation damage.

The main objective of the theory of inter-atomic decay processes is the reliable calculation of measurable spectra, i.e. those of the kinetic energies carried by the secondary ICD electron and other decay products. To that end, accurate computation of the relevant decay widths as functions of inter-nuclear distances is essential. We will present the Fano-ADC approach [5], which has been established as probably the most effective tool for this task presently available, for singly and doubly ionized [6] as well as excited [7] clusters. One of the critical steps of the method is the partitioning of the ADC configuration space into its bound and continuum subspaces. We will discuss different schemes applicable within the second order ADC approximation and their impact on the quality of the metastable state description.

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Decay of excited electronic states and electron capture in an environment

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Ultrafast non-radiative decay of excited electronic states embedded into an environment by interatomic Coulombic decay or ICD mechanism has been a topic of extensive theoretical and experimental work [1]. In ICD the correlation between electrons located on different species leads to the de-excitation of the original excited state and simultaneous ionisation of the environment. The ICD of neutral dipole-allowed excited states is a particular manifestation of this general phenomenon [2,3] which provides an insight into the importance of ICD in nature, while also offering methodological challenges for a theoretician. While photoexcitation of an electron into a valence or Rydberg orbital of an isolated molecule often leads to a fast nuclear rearrangement such as dissociation or isomerisation, we argue that in the environment this rearrangement can be quenched by ICD. We present an ab initio method for calculating the ICD rates of neutral excited states [4], and use it to demonstrate the quenching of predissociation of CO molecule in CO-Mg_n cluster. We also discuss a phenomenon, whereby free electrons can be captured by an atom or positive atomic ion leading to the simultaneous ionisation of an environment [5]. This phenomenon called interatomic Coulombic electron capture or ICEC is driven like ICD by interatomic electron correlation and can be viewed as "ICD with continuum electrons". We demonstrate the efficiency of this process in an environment compared with photorecombination common in isolated systems.

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The STM as a vibrational and magnetic spectroscopy on the single molecule level.

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The scanning tunneling microscope drives a tiny electron current through the vacuum barrier separating a metallic tip from a solid surface. The solid surface can be nanostructured and can also contain isolated adsorbates such as atoms, molecules or clusters. The vacuum barrier height is typically some 4-eV high, while the tip-substrate bias is rarely above the volt. Hence electrons tunnel from the tip to the substrate. This tunneling electrons are evanescent waves that are exponentially confined, both laterally and vertically, conferring the STM with an enhanced capacity to detect small electronic variations on the substrate's surface. Figures of merit are 0.1 Angstroms in vertical resolution and 0.01 Angstroms in lateral one. By injecting electrons at different biases, the STM also has energy resolution. It can probe the excitations of the substrate and hence become a spectroscopy.

Stipe, Rezaei and Ho [1] showed that by studying the electrical signal, vibrations could be detected. Their first example was the excitation and detection of the C—H stretch mode of single acetylene molecules adsorbed on a Cu surface. Since then, many experiments have been performed and a rich body of theoretical results have emerged. I will highlight the main points of this vibrational spectroscopy.

Heinrich and co-workers [2] extend the previous work to study magnetic excitations on surfaces. Magnetic excitations are strongly system dependent. While a magnetic excitation in an atom easily reaches the eV energy scale, the magnetic excitations of a solid are greatly reduced. This is in part due to the continuum character of the solid, where extended excitations can take place, such as spinwaves (magnons), but it is mainly due to the breaking of the spherical atomic symmetry. Indeed, the atomic spins will not be invariant under rotations, and they will be subjected to the magnetic anisotropy caused by the atom-surface interactions. This magnetic anisotropy is generally very small, and typical excitation energies are within the milli-eV. Hence, new techniques were mastered to render the observation of this small excitations on a surface. I will briefly review the experimental data, and rationalize their findings in terms of a simple spin scattering theory [3].

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Revealing molecular dynamics through scanning noise microscopy and spectroscopy

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Although noise is observed in many experiments, it is rarely used as a source of information. However, valuable information about atomic or molecular motion can be extracted from noisy tunneling current signals. Unfortunately, standard STM is not a useful tool to study dynamics in detail, as it is an intrinsically slow technique. This problem can be solved by Scanning Noise Microscopy, an experiment providing the full real-time characterisation of the random telegraph noise observed in the tunneling current. The hopping rate, the noise amplitude and the relative occupation of the involved states are measured as a function of the tunnelling parameters providing spatially resolved maps. Our data give access to transiently populated states revealing an electron-driven back and forth rotation by a small angle - a so called libration. It takes place between the equilibrium and two metastable positions of an individually adsorbed molecule. The new approach yields a complete picture, ranging from dynamical processes on surfaces to the underlying electronic structure on the single-molecule level. Results for individually adsorbed copper phthalocyanine molecules on Cu(111) together with density functional theory calculations will be presented.

Atomic-scale engineering of electrodes for single-molecule contacts

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The transport of charge through a conducting material depends on the intrinsic ability of the material to conduct current and on the charge injection efficiency at the contacts between the conductor and the electrodes carrying current to and from the material. To explore if this remains valid down to the limit of single-molecule junctions, experiments with atomic-scale control of the junction geometry is required.

Here we present a method for probing the current through a single C₆₀ molecule while changing, one by one, the number of atoms in the electrode that are in contact with the molecule [1]. We show quantitatively that the contact geometry has a strong influence on the conductance. We also find a crossover from a regime in which the conductance is limited by charge injection at the contact to a regime in which the conductance is limited by scattering at the molecule. Thus, the concepts of 'good' and 'bad' contacts, commonly used in macro- and mesoscopic physics, can also be applied at the molecular scale.

To interpret the experimental observations we performed electronic structure calculations for different contacting configurations to a C₆₀ molecule sandwiched between Cu(111) electrodes [1,2]. The calculations reproduce the experimental behavior and explain the crossover from cluster-size limited to molecule limited transport regimes in terms of projected density of states and position of the molecular resonances.

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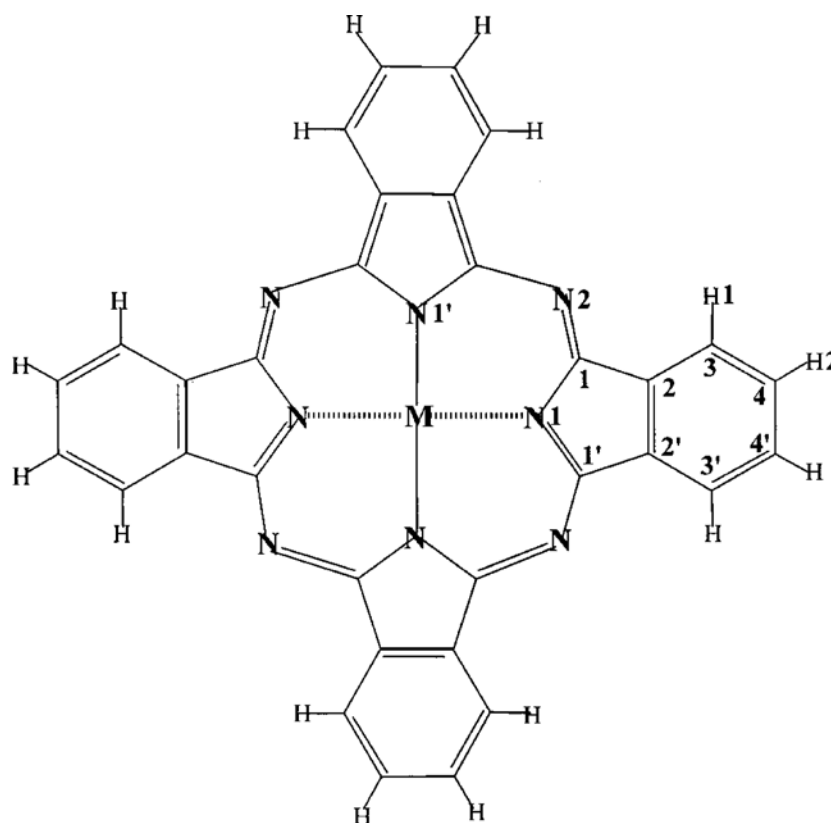
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Electron correlation in adsorbed molecules: the Kondo effect in phthalocyanines on noble metal surfaces

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Organic molecules adsorbed on top of metallic surfaces are systems with significant interplay between itinerant and localized electronic degrees of freedom. Intramolecular Coulomb repulsion induces correlations in the conduction electron scattering, known as Kondo effect. The strongest spectroscopic manifestation of Kondo effect is a sharp resonance pinned to the Fermi level. This picture has been demonstrated recently in a number of STM (Scanning Tunneling Microscope) experiments with organic adsorbates. We have developed a computational approach based on Kohn-Sham density functional calculations that allows to identify molecular orbitals responsible for anomalous Kondo scattering. Molecular and substrate Wannier functions play a key-role in this method, providing a tight-binding representation of the DFT electronic structure. This serves as a starting point for the non-crossing approximation calculation of the molecular orbital spectral function. This method is applied to copper phthalocyanine and nickel phthalocyanine on the surface of silver (100). Guided by experiments, we reveal the fingerprint of molecular spin excitations in the shape of the Kondo resonance.



Ultrafast Electron Dynamics Following Ionization of Molecular Systems

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More than ten years ago it was shown theoretically [1] that after a sudden ionization the electronic many-body effects *alone* can beget rich ultrafast electron dynamics. The positive charge created upon ionization of a molecule can migrate throughout the system on a femtosecond time scale *solely* driven by the electron correlation and electron relaxation. Charge migration triggered by ionization appeared to be a general phenomenon taking place both after inner- [2,3] and outer-valence [4,5] ionization of molecules. Results from *ab initio* calculations on different systems will be presented and the mechanisms underlying the charge migration will be analyzed in terms of simple models. The possibilities for experimental verification of the phenomenon will also be discussed. In particular, it will be shown that the charge migration generates a measurable IR radiation [6]. Moreover, it will be shown that the ultrafast removal of an electron leads to a much stronger UV emission [6]. This emission appears as an ultrafast response of the remaining electrons to the perturbation caused by the sudden ionization and as such is a universal phenomenon to be expected in every multielectron system.

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Dissociative recombination of LiHe ions

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The dissociative recombination (DR) process, in which a colliding electron is captured, results in dissociation and destruction of the molecule. The conventional mechanism characteristic of most species with a high DR rate, which normally involves direct capture into a dissociative resonance potential curve, is absent here. For this reason, this is a prototype for indirect DR that must instead proceed through Rydberg capture pathways. I apply the ab initio multichannel quantum defect theory (MQDT), in combination with a rovibrational frame transformation based on Siegert pseudostates, to treat indirect DR for this fundamental diatomic ion.

Poster abstracts

(in alphabetical order of first author's name)

Electron scattering from krypton: High-resolution electron scattering experiments and B -spline R -matrix calculations

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In a joint experimental and theoretical effort, we carried out a detailed study of elastic scattering and electron impact excitation of the $4p^55s$ states in Kr [1]. The incident electron energy resolution was about 13 meV at a current of about 400 pA. A specially designed magnetic angle changer allowed for measurements up to 180° scattering angle. The calculations were performed in a fully relativistic Dirac B -spline R -matrix (DBSR) framework [2]. We present independently normalized, absolute angle-differential cross sections over the entire angular range ($0^\circ - 180^\circ$) for a number of energies in the near-threshold region, as well as energy scans for selected angles. An example of the latter, for the $5s[3/2]_2$ state measured at 135° , is shown in the Figure. The experimental results are seen to be in very satisfactory agreement with predictions from the DBSR model [2,3].

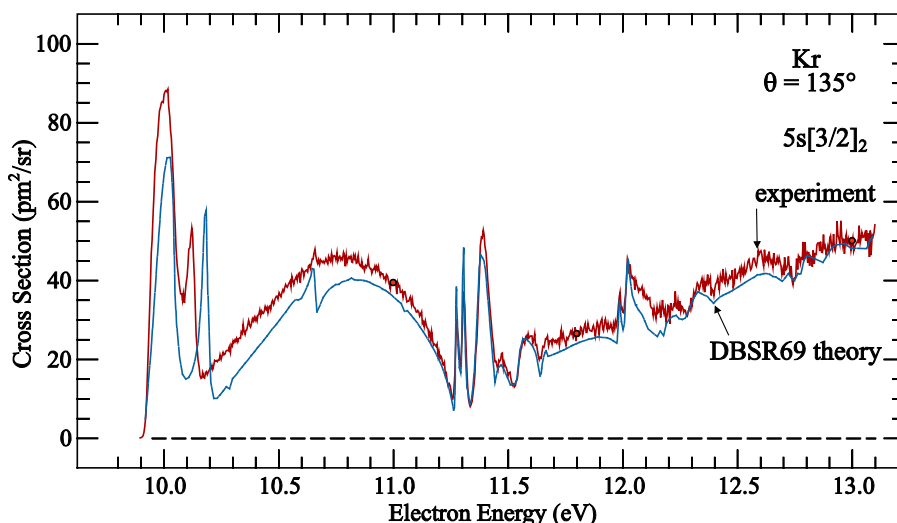


Figure 1. Cross section for electron-impact excitation of Kr.

It should be emphasized that the test is very stringent since we compare the absolute values of the cross sections, *i.e.*, the heights of the curves, *and* the many sharp resonances, their energies, widths and heights in the spectrum. The latter indicate that the branching ratios, with which the individual resonances decay into the accessible final excited states, are also correctly described by the theory. The new data also clearly improve the agreement between experiment and theory relative to our earlier comparison [3] with the experimental data of Phillips [4].

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Dissociative electron attachment to formic acid

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The study of dissociative electron attachment (DEA) to formic acid (HCOOH) was motivated by current interest of theory in the process and by possible role HCOOH could play in the chemistry governing the formation of more complex molecules in the interstellar media. [1]

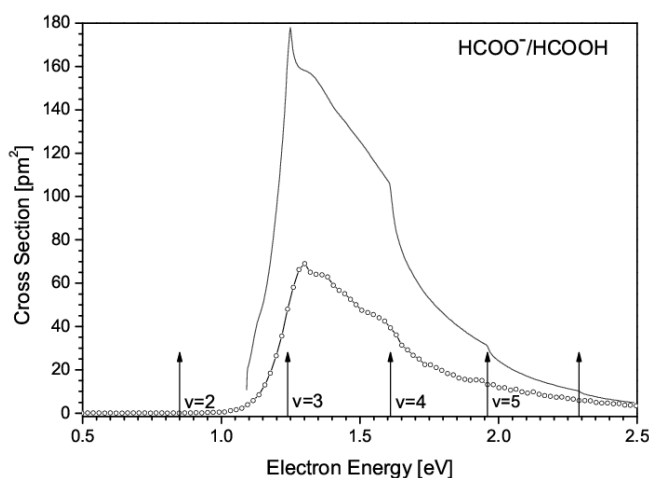


Figure 1. DEA cross section for HCOO⁻/HCOOH; line with circles – experimental data, solid line – theory of Gallup *et al.* [5]; arrows – thresholds for excitations of the O-H stretch vibrational mode.

Four anionic fragments resulting from DEA to HCOOH have been observed: HCOO⁻, OH⁻, O⁻ and H⁻. Corresponding DEA cross sections have been measured with the resolution of approximately 60 meV by standard trochoidal electron monochromator/quadrupole mass spectrometer instrument and subsequently normalized to absolute values from recently constructed time-of-flight/TEM instrument [2]. Similar relative cross sections were reported at lower resolution and lower signal/noise ratio by Pelc *et al.* [3] and in absolute scale by Prabhudesai *et al.* [4]. Cross section of the process



shows unique, step-like structure, that is in agreement with one dimensional R-matrix model of Gallup *et al.* [5], who propose that the rotation of the O-H bond out of plane caused by σ/π coupling is not essential for the description of DEA to the formic acid – contrary to the conclusion of Ref. [6]. Absolute DEA cross sections for production of remaining fragments will be presented at the conference.

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Exploratory work on the use of mixed B-spline and Gaussian atomic basis sets for scattering calculations

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The choice of atomic basis sets is one of the most important aspects of quantum chemistry and scattering calculations as it significantly influences the shape of the target molecule orbitals. It is a common practice in variational ab-initio methods for electron-molecule collisions to use (usually a subset of) the target molecule orbitals for the description of the short-range electron-molecule interaction [1]. It is also necessary to accurately represent in these calculations the unbound (continuum) colliding electron.

In this work we present elementary results on what is an attempt to improve the quality of representation of the continuum within the molecular R-matrix method as implemented in the UK R-matrix codes [2]. The current implementation relies on the use of standard Gaussian-type orbitals (GTOs) for representation of the target molecular orbitals. The continuum is represented by center of mass-centered GTOs, which have the advantage of allowing for analytic evaluation of all (i.e. overlap, kinetic energy, nuclear attraction and electron repulsion) integrals needed for construction of the Hamiltonian matrix of the N+1 electron system. With the recent emergence of high-level R-matrix calculations (e.g. on pyrazine [3] or Li₂ [4]) requiring R-matrix radii well above 15 a.u., the representation of the continuum based on GTOs has reached its limits.

In this work we consider the use of products of center of mass-centered radial B-spline functions (with real spherical harmonics) as a basis for representation of the continuum. These B-spline orbitals have been used routinely in atomic calculations and an extensive literature on this subject exists (see e.g. [5]). Our method is unique in the sense that it tries to combine the atom-centered GTO basis functions *and* molecule centered B-spline orbitals. The goal of this work is to identify and implement the most promising method(s) for solving the problem of the accurate calculation of the integrals involving B-spline orbitals and atom-centered GTOs. We attack this problem by invoking a single-center expansion of the atomic GTOs [6] followed by numerical integration in the radial coordinate. We have already implemented the calculation of the overlap integrals between B-spline orbitals and GTOs and demonstrate on this simple example some of the numerical problems associated with the radial integration, which originate in the appearance of the exponentially diverging Modified Bessel function in the integrand.

Calculation of the remaining integrals will have to rely on accurately converged single-center expansions of the atomic GTOs. This convergence is discussed for water and pyrazine and selected atomic basis sets. We also compare the results of calculations of the radial charge densities of target molecular orbitals using a) the current method based on numerical integration over the angular variables and b) using the single-center expansion of GTOs as discussed above.

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Low-energy electron collisions with pyrimidine and pyridazine

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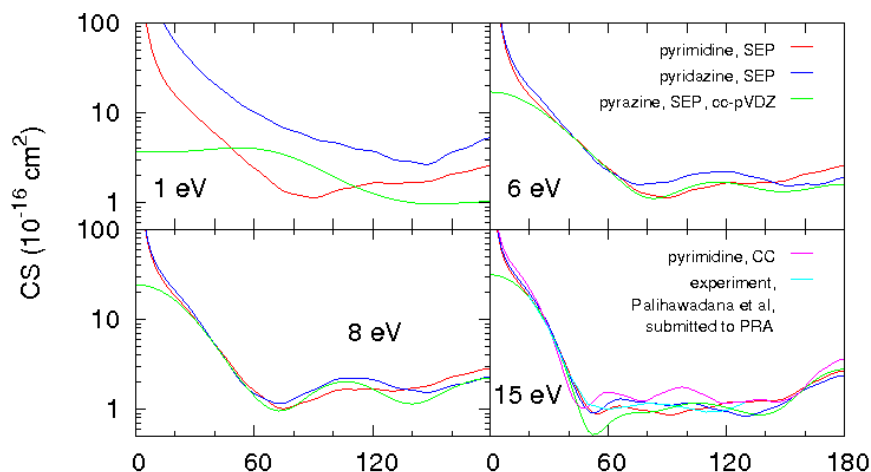
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High-level calculations of electron collisions with molecules modeling pyrimidine nucleobases are useful for complementing our understanding of the experimental evidence for DNA damage induced by low-energy electrons [1]. Inelastic calculations for these processes are still scarce as they pose a significant challenge to both the theory itself and the existing computational tools.

We present *ab-initio* calculations using the R-matrix method on electron collisions with the isomers pyrimidine and pyridazine, carried out at various levels of approximation ranging from Static-Exchange to Close-Coupling. Apart from the three well-known π^* shape resonances [1], we find several higher-lying (above 5 eV) core-excited resonances built on the lowest-lying excited states of the molecule; we also identify the parent states of some of these resonances.

To the best of our knowledge our inelastic calculations, which are based on those performed for pyrazine [3], are the first ones for these molecules. For our Close-Coupling calculations we use target molecular orbitals from state-averaged MC-CASSCF calculations employing the cc-pVDZ basis set. We also plan to explore the use of a diffuse basis set 6-311+G**, which has been found to give better results in calculations with pyrazine.

Unlike pyrazine, where predominantly only triplet excited states contribute to the formation of the third (core-excited shape) π^* resonance [3,4], in pyrimidine and pyridazine excited states of the singlet and triplet spin symmetry lie very close in energy in our calculations and a clear assignment of the parent states is much less clear. A detailed analysis of the configurations included in our scattering models shows the third core-excited shape π^* resonance in pyrimidine to have potential parent states 1B_2 , 3B_2 , 3A_1 . The figure below shows the Differential cross sections for the molecules we studied, including pyrazine. For the molecules pyrimidine and pyridazine we can clearly see the significant enhancement of the cross sections at small scattering angles typical for dipolar molecules. It is also apparent that the cross sections for all three molecules become more similar at higher electron energies.



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Absolute measurements of dissociative electron attachment to $\text{Pt}(\text{PF}_3)_4$

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The interest in electron collisions with $\text{Pt}(\text{PF}_3)_4$ was motivated by new applications of metal-organic compounds, used as precursors in FEBIB, Focused Electron Beam Induced Processing, to produce nano-size devices [1]. $\text{Pt}(\text{PF}_3)_4$ is a volatile platinum compound (with a molar mass of 547 amu) which, in contrast to complexes with carbon-containing ligands, yields carbon free deposits [2].

In order to understand the roles of the various possible decomposition processes, absolute differential cross sections for elastic scattering, and for vibrational and electronic excitation of $\text{Pt}(\text{PF}_3)_4$ were measured [3]. Complementary to this work we carried out a study of dissociative electron attachment (DEA) to $\text{Pt}(\text{PF}_3)_4$. The DEA spectra have been measured with a recently constructed time-of-flight (TOF) mass spectrometer/TEM apparatus [4].

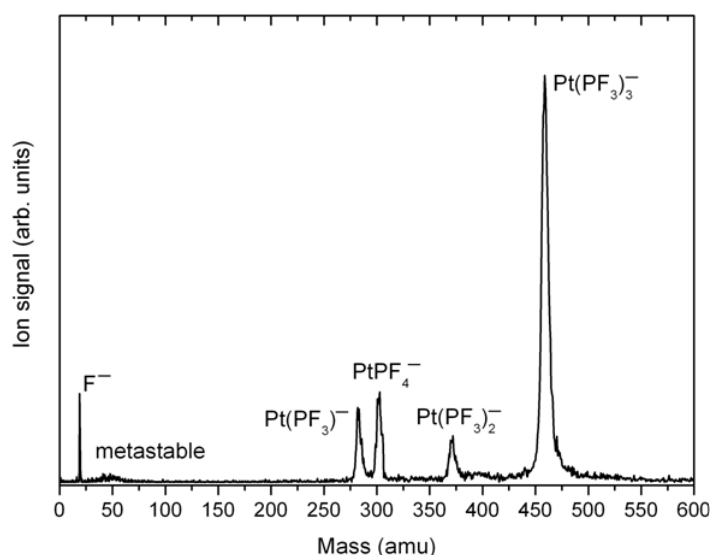


Figure 1. Negative ion TOF mass spectrum following DEA to $\text{Pt}(\text{PF}_3)_4$ (combination of 2, 6 and 10 eV).

Several anionic fragments resulting from DEA to $\text{Pt}(\text{PF}_3)_4$ have been observed: F^- , $\text{Pt}(\text{PF}_3)^-$, PtPF_4^- , $\text{Pt}(\text{PF}_3)_2^-$ and $\text{Pt}(\text{PF}_3)_3^-$. The corresponding DEA spectra reveal two low-lying resonances at 0.52 and 1.8 eV as well as three higher-lying resonances at 5.8 eV, 6.8 eV and 12.0 eV respectively which are in good agreement with the observations made by means of resonant vibrational excitation and electronically excited states characterized by electron energy-loss spectra [3]. The two lower bands are assigned to shape resonances, the three higher-lying bands to Feshbach resonances with Rydberg parent states [3]. We found $\text{Pt}(\text{PF}_3)_3^-$ to be the by far dominant fragment formed in electron attachment to $\text{Pt}(\text{PF}_3)_4$ at low energies (< 2 eV).

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Total cross section measurements for electron scattering from biologically relevant molecules

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The primary ionizing radiation like heavy ions, α -rays and γ -rays during interaction with living matter can produce significant amount of secondary electrons. It is well known that such electrons can induce serious damage to the living cell via direct and resonant interaction [1]. Thus it is essential to study interaction of low energy electrons with building blocks of biologically important tissues and with their simple molecular analogues in different phases.

In our laboratory we conduct systematical measurements of the total cross section (TCS) for electron collisions with polyatomic molecules including many biologically relevant targets [2,3]. In the present study the absolute TCS for electron scattering from isoxazole (C_3H_3NO) molecules have been measured using the electrostatic 127° electron spectrometer [4]. In figure 1 the measured TCS is shown in the vicinity of the main maximum. Detailed discussion on the recent results and comparison with other data will be presented at the Conference.

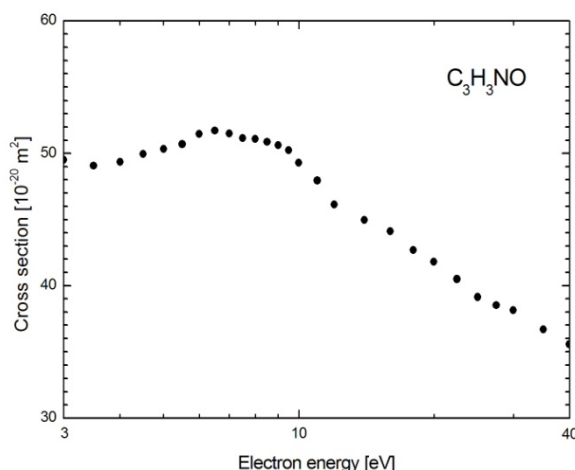


Figure 1. Total cross section for electron scattering from isoxazole molecules.

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Cross section calculations for electron impact ionization and elastic scattering on rhodanine and their derivatives

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Recent interest in electron interaction with rhodanine $C_3H_3NOS_2$ and its derivatives is connected with their potential use in dye-sensitized solar cells [1]. In the present contribution we report the total cross section calculations for the single electron-impact ionization of rhodanine. Elastic cross sections calculations for electron scattering from rhodanine have been also carried out using the independent atom method. The ionization cross section has been derived using the binary-encounter-Bethe (BEB) method [2] for energies between the ionization threshold up to 4 keV. The physical quantities which are necessary in the BEB calculation like electron binding energies and orbital electron kinetic energies have been obtained for the ground state of the geometrically optimized molecule with the Hartree-Fock method using Gaussian code [3] and 6-31G+d basis set. Moreover, to include effect of electron correlations within molecule, the valence orbital energies have been evaluated with OVGF method implemented in Gaussian. In figure 1 the electron-impact ionization cross section of rhodanine molecule by electron impact for energies ranging from the ionization threshold at 9.61 eV up to 4keV is shown. The cross section maximum of $12.98 \times 10^{-20} \text{ m}^2$ is located at 85 eV.

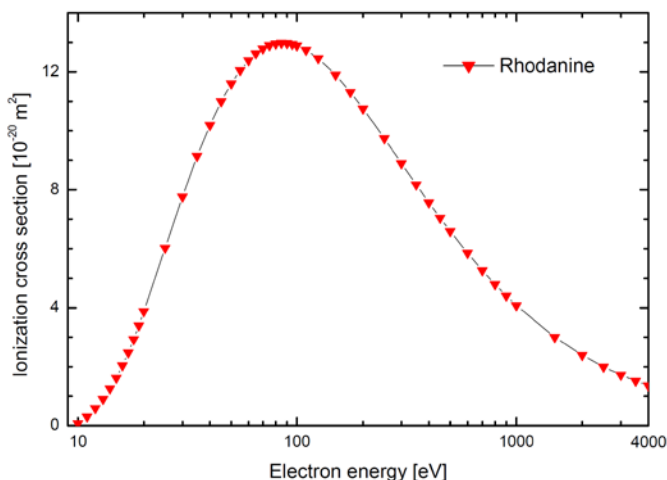


Figure 1. Total cross section for the single electron-impact ionization of rhodanine molecule

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References

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