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EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Meeting of the XLIC Working Group 2

WG2 Expert Meeting on Biomolecules

27-30 April 2015, Fruška gora, Serbia

Institute of Physics Belgrade
University of Belgrade

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WG2 Expert Meeting on Biomolecules is organized in the framework of the COST Action CM1204 ('XUV/X-ray Light and fast Ions for ultrafast Chemistry', XLIC). The project aims to better understand, to monitor and to control the complex ultrafast electronic and nuclear dynamics that occur in medium-sized and large molecules. Furthermore, new control strategies of reactions and a new generation of ultrafast spectroscopies combining attosecond temporal and sub-Angstrom spatial resolutions will be developed.

The WG2 Expert Meeting on Biomolecules will take place in Fruška gora (Serbia) from April 27th to April 30th, 2015. This meeting brings together experts from different disciplines (physics, chemistry), experiments and theory to discuss aspects on photon, ion and electron interaction with biomolecules, as well as properties of biomolecules, stability of highly excited and highly charged biological molecules in the gas phase and their reactivity.

We hope that this meeting will initiate new projects and collaborations, inspire new scientific achievements and help promotion of young researchers. We would like to thank the members of the Scientific Committee and Local Organizing Committee for their collaboration and the excellent work.

Paola Bolognesi and AleksandarMilosavljević
The Meeting Chairs

Practical information

Conference Program

The Conference program includes Invited Lectures (*20 min + 10 min for discussion*) and poster presentations. Your file should be handed over to the operator well in advance of your talk. Poster session will be organized on Tuesday 28th April 2015 afternoon but posters can be installed on the first day of the meeting.

WIFI

CePTOR congress center offers free Wi-Fi.

Social program

Excursion will be organized on Wednesday 29th April 2015 afternoon.
Conference dinner will be held on Wednesday 29th April 2015 at 20:00.

Transfer from the conference site

Transport of participants from the conference site to the Belgrade airport will be organized on 30th of April. Several departures will be arranged. Further questions concearning the transfer should be addressed to mice@panacomp.net.

About COST

COST-European Cooperation in Science and Technology is an intergovernmental framework aimed at facilitating the collaboration and networking of scientists and researchers at European level. It was established in 1971 by 19 member countries and currently includes 35 member countries across Europe, and Israel as a cooperating state.

COST funds pan-European, bottom-up networks of scientists and researchers across all science and technology fields. These networks, called 'COST Actions', promote international coordination of nationally-funded research. By fostering the networking of researchers at an international level, COST enables break-through scientific developments leading to new concepts and products, thereby contributing to strengthening Europe's research and innovation capacities.

COST's mission focuses in particular on:

- Building capacity by connecting high quality scientific communities throughout Europe and worldwide;
- Providing networking opportunities for early career investigators;
- Increasing the impact of research on policy makers, regulatory bodies and national decision makers as well as the private sector.

Through its inclusiveness, COST supports the integration of research communities, leverages national research investments and addresses issues of global relevance. Every year thousands of European scientists benefit from being involved in COST Actions, allowing the pooling of national research funding to achieve common goals.

As a precursor of advanced multidisciplinary research, COST anticipates and complements the activities of EU Framework Programmes, constituting a "bridge" towards the scientific communities of emerging countries. In particular, COST Actions are also open to participation by non-European scientists coming from neighbor countries (for example Albania, Algeria, Armenia, Azerbaijan, Belarus, Egypt, Georgia, Jordan, Lebanon, Libya, Moldova, Montenegro, Morocco, the Palestinian Authority, Russia, Syria, Tunisia and Ukraine) and from a number of international partner countries.

COST's budget for networking activities has traditionally been provided by successive EU RTD Framework Programmes. COST is currently executed by the European Science Foundation (ESF) through the COST Office on a mandate by the European Commission, and the framework is governed by a Committee of Senior Officials (CSO) representing all its 35 member countries. More information about COST is available at www.cost.eu.

Committee

Meeting chairs

Aleksandar Milosavljević *(Institute of Physics Belgrade, University of Belgrade, Serbia)*

Paola Bolognesi *(CNR-Istituto di Struttura della Materia, Roma, Italy)*

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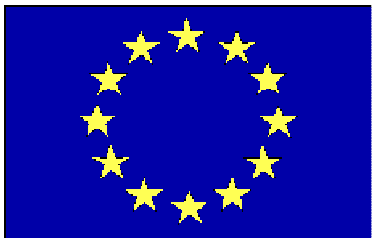

COST is supported by the EU Framework Programme Horizon 2020

Program

PROGRAM SCHEDULE

COST XLIC WG2 Expert meeting on biomolecules

27-30 April 2015, CePTOR congress center, National park Fruška gora, Serbia

(Invited Lectures: 20 min + 10 min for discussion)

Monday 27th April 2015	
17:00-18:30	Registration
18:20-18:30	**Welcome to participants**
	***Session 1**, Chair: Manuel Alcami*
18:30-19:00	*Local control theory using TDDFT-based nonadiabatic dynamics* **Ivano Tavernelli,** EPFL, Switzerland
19:00-19:30	*Shedding light on molecular excited states with novel EUV sources* **Marcello Coreno,** CNR-ISM, Italy
19:30-20:00	*Obvious and nonobvious dissociation pathways of N-substituted glycine ions* **Jaroslaw Kočišek,** CIMAP - GANIL, France
20:00-21:30	Dinner
Tuesday 28th April 2015	
07:00-09:00	Breakfast
	***Session 2**, Chair: Aleksandar Milosavljević*
09:00-09:30	*Ion and photon interactions with superhydrogenated PAHs* **Thomas Schlathölter,** University of Groningen, The Netherlands
09:30-10:00	*Gas-phase spectroscopy of ferric heme nitrosyl cations* **Jean Wyer,** Aarhus University, Denmark
10:00-10:30	*DFT and TD-DFT of nanosolvated biomolecules* **Viktor Cerovski,** University of Belgrade, Serbia
10:30-11:00	Coffee break 1
	***Session 3**, Chair: Alicja Domaracka*
11:00-11:30	*On the role of fluoro-substituted nucleosides for radiosensitization in tumor radiation therapy* **Janina Kopyra,** Siedle University, Poland
11:30-12:00	*Low energy electron interactions with cyclic azines* **Jimena Gorfinkiel,** The Open University, UK
12:00-12:30	*Electron induced dissociation of biomolecules* **Andreas Mauracher,** University of Innsbruck, Austria
12:30-13:00	*Electron impact fragmentation of thymine and cytosine: partial ionization cross sections for positive fragments* **Peter van der Burgt,** National University of Ireland, Ireland
13:00-15:00	Lunch
	***Session 4**, Chair: Steen Broendsted Nielsen*
15:00-15:30	*Studies of biomolecules at the DESIREE facility* **Nathalie de Ruette,** Stockholm University, Sweden
15:30-16:00	*VUV photoionization study of gas phase biomolecules using aerosol thermodesorption* **Héloïse Dossmann,** Universite Pierre et Marie Curie, France
16:00-16:30	*Energy resolved photoelectron-ion-ion coincidence studies of DNA building blocks and amino acids* **Eero Itälä,** University of Turku, Finland

16:30-17:00	Coffee break 2
17:00-18:00	*Round table discussions 1*
18:00-20:00	***Poster session***
20:00-21:30	Dinner
Wednesday 29th April 2015	
07:00-09:00	Breakfast
	***Session 5**, Chair: Thomas Schlathölter*
09:00-09:30	*Fragmentation of halopyrimidines and halouraciles by photoionization and ion impact* **Lorenzo Avaldi,** CNR, Italy
09:30-10:00	*UV and electron induced dynamics in biomolecules and clusters* **Samuel Eden,** The Open University, UK
10:00-10:30	*Plasma interaction with biomolecules* **Nevena Puač,** University of Belgrade, Serbia
10:30-11:00	Coffee break 3
	***Session 6**, Chair: Paola Bolognesi*
11:00-11:30	*Ultrafast non-reactive deactivation induced by excited state hole transfer from retinal chromophore to counterion* **Nadja Došlić,** Rudjer Boškovic Institute, Croatia
11:30-12:00	*Pure electron dynamics in biomolecules initiated by XUV attosecond pulses* **Andrea Trabattoni,** Politecnico di Milano, Italy
12:00-12:30	*Ultrafast electron dynamics in amino acids initiated by attosecond pulses* **Alicia Palacios,** Universidad Autónoma de Madrid, Spain
12:30-13:00	*Photo-induced ultrafast nuclear dynamics in (deeply) core-excited molecules* **Oksana Travnikova,** CNRS, France
13:00-15:00	Lunch
15:00-19:30	***Excursion***
20:00-22:00	**Dinner**
Thursday 30th April 2015	
07:00-09:00	Breakfast (***Departure to Belgrade airport***)
09:00-09:15	**Closing remarks**
09:15-11:00	*Round table discussions 2*
11:00-11:30	Coffee break 4 (***Departure to Belgrade airport***)
11:30-13:00	*Round table discussions 3*
13:00	***Departure to Belgrade airport***

List of posters

List of posters

P-01 *Semiclassical model for strong-field ionization with quantum interference and multielectron polarization effects*
N. I. Shvetsov-Shilovski, L. B. Madsen, Esa Räsänen, J. Burgdörfer and K. Tőkési

P-02 *Calculations of ionization probabilities for sodium in strong laser fields*
A. Bunjac, D. B. Popović, N. Simonović

P-03 *Unusual hydrogen and hydroxyl migration in the fragmentation of excited doubly-positively-charged amino acids in the gas phase*
S. Díaz-Tendero, D. G. Piekarski, M. Alcamí, F. Martín, S. Maclot, R. Delaunay, A. Domaracka, P. Rousseau, L. Adoui and B.A. Huber

P-04 *Charge and energy flows in ionised thymidine*
S. Maclot, R. Delaunay, D. G. Piekarski, A. Domaracka, B. A. Huber, L. Adoui, F. Martín, M. Alcamí, L. Avaldi, P. Bolognesi, S. Díaz-Tendero and P. Rousseau

P-05 *Collision induced dissociation of biomolecular cations*
L. Giacomozzi, N. de Ruette, M. Gatchell, M. H. Stockett, H. T. Schmidt, H. Cederquist and H. Zettergren

P-06 *Synchrotron photoionization spectroscopy of free organic molecules*
Cesare Grazioli, Marcello Coreno, Monica de Simone, Antti Kivimäki, Barbara Ressel, Teng Zhang, Johann Lüder, Ieva Bidermane, Carla Puglia, Barbara Brena, Alessandra Ciavardini, Susanna Piccirillo, Eleonora Polo, Roberta Totani and Luca Lozzi

P-07 *VUV action spectroscopy of bare and hydrated protonated leucine-enkephalin peptide*
M. Lj. Ranković, V. Cerovski, F. Canon, L. Nahon, A. Giuliani and A. R. Milosavljević

P-08 *Gas-phase X-ray action spectroscopy of protonated nanosolvated substance P peptide around O K-edge*
I. Bačić, M. Lj. Ranković, F. Canon, V. Cerovski, C. Nicolas, A. Giuliani and A. R. Milosavljević

P-09 *Investigation of the ultrafast excited state dynamics of ortho-nitrophenol by photoemission spectroscopy*
E. Bodo, B. Bučar, C. Callegari, A. Ciavardini, M. Coreno, G. De Ninno, F. Frassetto, D. Gauthier, D. Golob, D. Gornik, B. Gospodarič, C. Grazioli, A. Kivimaki, M. Merhar, P. Miotti, M. Pezzella, S. Piccirillo, A. Podboršek, L. Poletto, E. Polo, C. Puglia, P. Rebernik Ribic, B. Ressel, M. de Simone and C. Spezzani

Invited Lectures

Notes

Local control theory using TDDFT-based nonadiabatic dynamics

Basile Curchod[1], Thomas Penfold[2], Ivano Tavernelli[3]

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In the mixed quantum-classical description of molecular systems, only the quantum character of the electronic degrees of freedom is considered while the nuclear motion is treated at a classical level. In the adiabatic case, this picture corresponds to the Born-Oppenheimer limit where the nuclei move as point charges on the potential energy surface (PES) associated with a given electronic state. Despite the success of this approximation, many physical and chemical processes do not fall into the regime where nuclei and electrons can be considered decoupled. In particular, most photoreactions pass through regions of the PES in which electron-nuclear quantum interference effects are sizeable and often crucial to the dynamics.
For a reliable description of the photochemical reactions occurring in the excited states, we have recently developed a trajectory-based nonadiabatic molecular dynamics scheme that describes the nuclear wavepacket as an ensemble of particles following classical trajectories on PESs derived from time-dependent density functional theory (TDDFT) [1,2]. The method is based on Tully's fewest switches trajectories surface hopping (TSH) in which the nonadiabatic coupling elements [2] between the different potential energy surfaces are computed on-the-fly as a functional of the ground state and linear response electron densities [3].
In this talk, I will briefly outline the theoretical fundamentals of this approach together with an extension that allows for the direct coupling of the dynamics to an external electromagnetic field [4]. In particular, I will describe the coupling of TDDFT-based nonadiabatic dynamics with local control theory for pulse shaping [5]. The method is applied to the study the photo-induced intra-molecular proton transfer dynamics in an organic molecule (4-hydroxyacrydine). This study highlights the strengths of local control theory for the design of pulses that can trigger chemical reactions associated with the population of a given molecular excited state. In addition, the analysis of the generated pulses reveals significant details that can help shed new light on the photophysics and photochemistry of complex molecular systems.

REFERENCES

[1] Tapavicza E., Tavernelli I., Rothlisberger U., Phys. Rev. Lett., 98 , (2007) 023001.
[2] Tavernelli I.; Tapavicza E.; Rothlisberger U., J. Chem. Phys ., 130, (2009) 124107 .
Tavernelli I., Curchod B.F.E., Rothlisberger U., J. Chem. Phys ., 131 , (2009) 196101.
[3] Curchod B.F.E., Tavernelli I., Rothlisberger U, Phys. Chem. Chem. Phys., 13, (2011) 3231.
[4] Tavernelli I., Curchod B.F.E., Rothlisberger U., Phys . Rev. A , 81 , (2010) 052508.
[5] Curchod B.F.E, Penfold T.J., Rothlisberger U, Tavernelli I., Phys. Rev. A, 84, (2011), 042507.

Notes

Shedding light on molecular excited states with novel EUV sources

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The study of the electronic structure of matter routinely profits from advances in laser and synchrotron radiation instrumentation. At the Elettra synchrotron radiation laboratory (Trieste, I) the Gas Phase beamline [1, 2] currently enables thorough studies of the energetics of isolated system by means of photoionization techniques and inner-shell-electron photoionization, even with low-density targets such as molecular vapours [3] or clusters [4]. More recently the interest of the physical chemistry-chemical physics community has been captured by the opportunity of exploring the temporal dynamics of isolated systems by means of novel EUV light sources. Two new beamlines capable of delivering ultrafast EUV photon pulses have recently been commissioned in the framework of the FERMI Free Electron Laser (FEL) project: the Low Density Matter beamline at FERMI [5, 6] and CITIUS [7, 8], a state-of-the-art fs-VUV source, based on laser High Harmonic Generation on rare gases.
I will outline research opportunities opened in the field of atomic and molecular physics by these novel ultrafast light sources. On the one side advanced atomic physics experimental methods are used for characterization and commissioning of the sources [7, 9-11], on the other side molecular excited states dynamics is probed in gas phase molecular targets of increasing complexity (molecules of biological interest, metal-containing organics, clusters,...).

REFERENCES

[1] K.C. Prince et al. J. Synch. Rad. 5, 565 (1998).
[2] http://www.elettra.eu/elettra-beamlines/gasphase.html
[3] M. Coreno et al. Dalton Trans. 43, 5134 (2014).
[4] T. Mazza, M. Devetta, P. Milani, G. Bongiorno, M. Coreno and P. Piseri, New J. Phys. 13, 023009 (2011).
[5] V. Lyamayev et al. J. Phys. B 46, 164007 (2013).
[6] http://www.elettra.eu/lightsources/fermi/fermi-beamlines/ldm/ldmhome-page.html
[7] C. Grazioli et al. Rev. Sci. Instr. 85, 23104 (2014).
[8] http://www.citius-lab.eu/index.html
[9] E. Allaria et al. New J. Phys. 14, 113009 (2012).
[10] E. Allaria et al. Phys. Rev. X 4, 41040 (2014).
[11] P. Finetti et al. Proceedings of SPIE 9210, 92100K (2014).

Notes

Obvious and nonobvious dissociation pathways of N-substituted glycine ions

Jaroslav Kocisek[1], Rudy Delaunay[1], Bernd A. Huber[1], Patrick Rousseau[1], Lamri Adoui[1], Sergio Díaz Tendero[2], Dariusz Grzegorz Piekarski[2], Manuel Alcamí[2], Fernando Martín[2,3,4] Alicja Domaracka[1] and Janina Kopyra[5]

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[3]*Instituto Madrileno de Estudios Avanzados en Nanociencias (IMDEA-Nanociencia), Cantoblanco, 28049 Madrid, Spain*
[4]Condensed Matter Physics Center (IFIMAC), Universidad Autonoma de Madrid, 28049 Madrid, Spain
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Interactions of slow ions with N-substituted glycines are investigated in the context of astrobiology and ion beam cancer therapy. Isolated molecules of N-methylglycine, N,N-dimethylglycine, N-acetylglycine and their clusters are collided with slow 48keV O^{6+} ions. The ions are produced in the ARIBE facility in Caen and the products of the interaction are analyzed by the means of the coincidence mass spectrometer COLIMACON [1].
The methyl substituted glycine ions exhibit fragmentation which is analogous to that of glycine [2]. The mass spectrum in the gas phase is dominated by the signal of fragment ions formed by the neutral carboxyl group loss and subsequent fragmentation. Fragmentation of ionized clusters is reduced due to the protecting role of the environment [3]. Additionally, effective intermolecular proton transfer occurs within the cluster environment which results in the formation of protonated clusters cations. These cations fragment via novel reaction pathways which are again analogous to that of amino acids [4].
In contrast to the methyl substituted glycines, N-acetylglycine cation in the gas phase fragments primarily by the dissociation of the bond between nitrogen and substituent - the peptide bond. Such fragmentation, typical for peptides, is caused by charge delocalization over the peptide bond. N - acetylglycine also forms metastable parent ions which fragment exclusively by neutral water release. These metastable ions were assigned to the diol tautomer of N - acetylglycine. The stabilization of the parent ion by tautomerization to the diol form is analogous to the glycine molecule. However, quantum chemical calculations uncover different mechanism of tautomerization. The effect of the environment which we mimic by the clusters is analogous to that occurring in the amino acids. Yet, we observed also effective multistep intermolecular reactions caused by the high mobility of hydrogen atoms and protons within the cluster environment.
In the talk, we will consider obvious fragmentation of the N- substituted glycines which is analogous to the glycine molecule and novel - nonobvious dissociation channels observed for N - acetylglycine. We will show also that careful combination of theory and experiment can unveil nonobvious reaction pathways of otherways obvious reaction channels.

Acknowledgements: Financial support from INCa-ITMO (N° PC201307) within the Programme Plan Cancer 2009-2013 (Inserm) and from the XLIC COST action (CM1204) is gratefully acknowledged.

REFERENCES

[1] M. Capron et al., Chem. Eur. J. 18 9321 (2012).
[2] S. Maclot et al., The European Physical Journal D 68, 149 (2014).
[3] S. Maclot et al. ChemPhysChem 12, 930 (2011).
[4] J.-C. Poully et al. Physical Chemistry Chemical Physics, submitted 2015

Notes

Ion and photon interaction with superhydrogenated PAHs

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Gas-phase PAH interactions with energetic photons and ions are the subject of intense study, on one hand because of the relevance of such processes in astrophysical environments [1] and on the other hand because of the opportunities of PAH photoionization as a tool for analytical chemistry [2]. In the astrophysical context, superhydrogenation of PAHs is of great relevance, as it might influence PAH lifetime in the harsh astrophysical environments and contribute to the H_2 balance. On the other hand, graphene hydrogenation is known to cause electronic and structural changes, for instance allowing for opening up the graphene band gap in a tunable fashion and the investigation of similar processes in PAHs might yield deeper insights into the underlying physics.

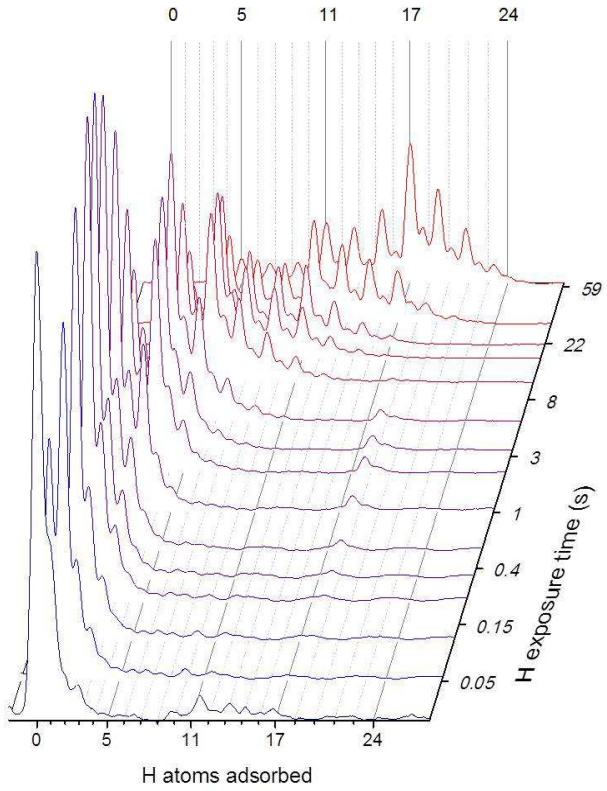

Fig.1. Hydrogen superhydrogenation of coronene as a function of H exposure time

We have studied superhydrogenation of trapped gas-phase coronene cations [3] and the dehydrogenation of these systems upon photoionization [4] as well as the response of PAH cations upon impact of energetic ions and photons [4,5]. Superhydrogenation was achieved by exposure of RF-trapped coronene cations to a thermal atomic H beam. Variation of H exposure time from 50 ms to 80 s allowed for production of $C_{24}H_{13}^+$ to $C_{24}H_{35}^+$ from $C_{24}H_{12}^+$ (i.e. addition of 1-23 H atoms) and for determination of the respective adsorption barriers. The observed magic numbers, i.e. superhydrogenation states of particular stability, and the observed hydrogenation dynamics are in good agreement with preferred binding sites and chemisorption barriers as determined by means of density functional theory (DFT).

We found that $C_{24}H_{12}^+$ superhydrogenation stabilizes the molecule with respect to photofragmentation upon soft X-ray absorption. Quantification of photon induced H "evaporation" from superhydrogenated PAHs even allows for determination of the deposited energy.

REFERENCES

[1] H.-W. Jochims, H. Baumgärtel, S. Leach, Astrophys. J. 512 500 (1999)
[2] F. Qui, Proc. Comb. Inst. 34 33 (2013)
[3] L. Boschman *et al.*, Astrophys. J. Lett. 761 (2012) L33
[4] G. Reitsma *et al.*, Phys. Rev. Lett **113** (2014) 053002
[5] G. Reitsma *et al.*, J. Phys. B 45 (2012) 215201; G. Reitsma *et al.*, J. Phys. B 46 (2013) 245201

Notes

Title Gas-phase spectroscopy of ferric heme nitrosyl cations

Jean Ann Wyer

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The electronic structure of a biochromophore (*i.e.* light absorber) is strongly perturbed by its surrounding environment, *e.g.* water or amino acid residues within protein pockets or crevices. To reveal the intrinsic electronic properties, it is therefore necessary to study isolated molecules *in vacuo*. Many biochromophores are ionic in their natural environment, which renders experiments complicated as it is not possible to produce enough absorbing species for traditional light transmission spectroscopy. In Aarhus we have developed state-of-the-art apparatus to record gas-phase absorption spectra of macromolecular ions. The technique is based on the combination of an electrospray ion source, a multipole ion trap for pre-storage, an electrostatic ion storage ring, and pulsed tuneable lasers and relies on measurements of the delayed dissociation of photoexcited ions (action spectroscopy). In this talk I will present some recent results for porphyrin and metalloporphyrin ions. Porphyrin containing proteins are ubiquitous in nature and are responsible for key biological processes, such as photosynthesis, oxygen transport and storage, and sensing. One important target system is heme which is a porphyrin with an iron atom located in the centre bound to four ring nitrogens. It colours blood red and is located in hydrophobic pockets of heme proteins with minimal access to water. We gradually build up the microenvironment of the heme to elucidate the impact of single molecules on the heme electronic structure. Such information is important in bioanalytical spectroscopy and for monitoring conformational changes and dynamics. Our latest results which show how nitric oxide (NO) perturbs the absorption bands will be presented. Interactions with NO are particularly interesting as heme-NO proteins play a key role in many physiological functions, for example blood clotting and vasodilation upon the bite of blood-sucking insects. Finally, our spectra provide a natural testing ground for future quantum chemical theories and methods.

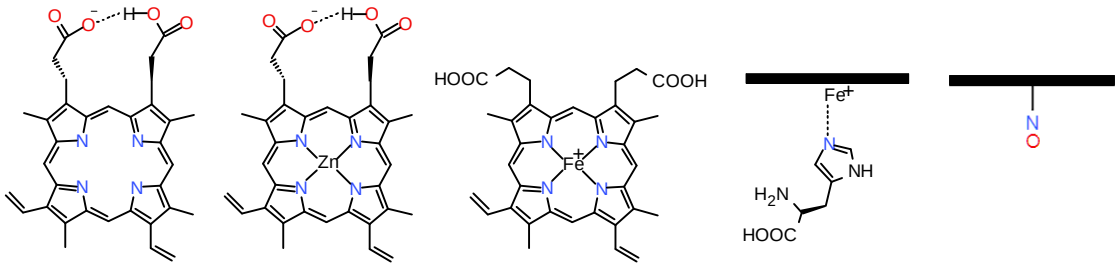

Fig.1. Protoporphyrin IX anion (PP^-), zinc-PP^-, $heme^+$, $heme^+$(His) and $heme^+$(NO).

REFERENCES

[1] M. K. Lykkegaard, A. Ehlerding, P. Hvelplund, U. Kadhane, M.-B.S. Kirketerp, S. Brøndsted Nielsen, S. Panja, J. A. Wyer and H. Zettergren, J. Am. Chem. Soc. 130, 11856 (2008).
[2] M. K. Lykkegaard, H. Zettergren, M.-B. S. Kirketerp, A. Ehlerding, J. A. Wyer, U. Kadhane and S. Brøndsted Nielsen, J. Phys. Chem. A 113, 1440 (2009).
[3] J. A. Wyer and S. Brøndsted Nielsen, J. Chem. Phys. 133, 084306 (2010).
[4] K. Støchkel, J. A. Wyer, M.-B. S. Kirketerp and S. Brøndsted Nielsen, J. Am. Soc. Mass Spectrom. 21, 1884-1888 (2010).
[5] J. A. Wyer, C. S. Jensen and S. Brøndsted Nielsen, Int. J. Mass Spectrom. 308, 126-132 (2011).
[6] J. A. Wyer and S. Brøndsted Nielsen, Angew. Chem. Int. Ed. 51, 10256-10260 (2012).
[7] J. A. Wyer, A. V. Jørgensen, B. M. Pedersen and S. Brøndsted Nielsen, Chem. Phys. Chem. 14, 4109-4113 (2013).

Notes

Density functional theory study of nanosolvated biomolecules

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Nanosolvation of biomolecule(s) with a small number of water molecules can produce large changes in geometric and electronic structure of the complex. Challenges of theoretical description of (non)hydrated biomolecules are addressed by way of going from Adenine to Adenosine to Adenosinemonophosphate (AMP), demonstrating the importance of noncovalent interactions in the case of AMP, as well as discussing the role of a single water molecule through its impact on geometry and absorption properties of the complex in the light of recent experimental findings [1]. Effects of nanosolvation on stability of biomolecular dimers studied within DFT is considered next following experimental findings of Ref [2].

Acknowledgements: This work is done in collaboration with Aleksandar Milosavljević, Alexandre Guilliani, Loren Nahon, Francis Cannon.

REFERENCES

[1] A. Milosavljević, V. Cerovski, F. Canon, M. Ranković, N. Škoro, L. Nahon and A. Giuliani, J. of Phys. Chem. Lett. 11, 1994 (2014).
[2] A. Milosavljević, V. Cerovski, F. Canon, L. Nahon and A. Giuliani, Ang. Chem.-Int. Ed. 52, 7286 (2013).

Notes

On the role of fluoro-substituted nucleosides for radiosensitization in tumor radiation therapy

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The interactions of low energy electrons (LEEs) with biologically relevant molecules have attracted considerable attention in the last decade. It has been mainly motivated by the discovery that LEEs can cause damage to DNA [1]. Paradoxically these genotoxic effect is highly desirable for therapies that combine the synergetic application of radiation and chemical agents with sensitizing properties. As first halouracils have been suggested as potential radiosensitizers [2]. One proposed mechanism involves thermalised or pre-hydrated electrons that cause the dissociation of the halosubstituted nucleobases leading to the formation of the uracil-yl radicals, which then become precursors for DNA damage.
Here we study dissociative electron attachment to another group of potential radiosensitizers namely various fluoro-substituted nucleosides. In particular, we probe the competing pathways of electron attachment to either the nucleobase subunit or the sugar unit by studying DEA to the nucleoside 2'-deoxycytidine (dCyt) and compare the DEA spectra with those obtained from 2'-deoxy-5-fluorocytidine (dFCyt) and 2',2'-difluorocytidine (Gem) (Fig. 1). Our comparative study demonstrates how the reaction pathways can be shifted by fluorination, thus opening up the possibility to control the reaction dynamics by rational chemical design. Furthermore, we demonstrate for the first time an enhanced reactivity of Gem towards LEEs, which might contribute to its radiosensitizing properties [3].

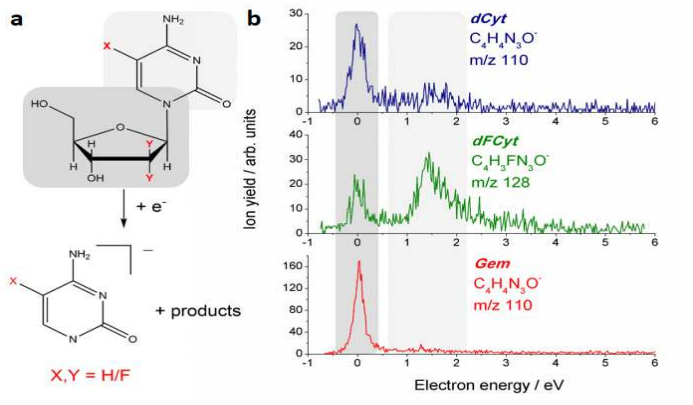

Fig.1. Corresponding ion yield curves and the reaction scheme of the electron induced N-glycosidic bond cleavage in the molecules *dCyt* (X, Y = H), *Gem* (X = H, Y = F) and *dFCyt* (X = F, Y = H) with the excess charge remaining on the nucleobase [3].

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REFERENCES

[1] B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels and L. Sanche, Science, 287, 1658 (2000).
[2] L. Ling and J. F. Ward, Radiat. Res., 121, 76 (1990).
[3] J. Kopyra, A. Keller, I. Bald, RSC Adv., 4, 6825 (2014).

Notes

Low energy interactions with cyclic azines

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Low-energy electrons (E<20eV), produced in great quantities when radiation interacts with biological material, are known to damage DNA. For almost two decades, the interaction of electrons with DNA strands and DNA constituents has been studied, mainly experimentally [1]: the focus has been on dissociative electron attachment (DEA), the main process that leads to DNA damage at low energies. From the theoretical point of view DEA is a highly complex process to describe: both the initial formation of a temporary negative ion (TNI) and the nuclear dynamics that follow require the use of sophisticated methods and significant computational resources. Theoretical work has therefore concentrated on studying the formation of TNIs, and looked at model molecules as well as DNA bases and nucleosides.

Over the last few years we have performed calculations, using the R-matrix method [2], for electron scattering from diazines ($C_4N_2H_4$) [3] and pyridine (C_5NH_5) [4] to gain insight into TNI formation in pyrimidinic DNA bases. The calculations revealed the presence of a number of TNIs, some of which can be directly linked to features in the DEA spectra. However, DNA in the cell is surrounded by water molecules. Therefore, studying how solvation affects TNI formation (and the subsequent break-up) is crucial to the understanding of electron-induced DNA break-up. For this reason we have recently concentrated in modelling the effected of hydration in TNI formation. We have recently performed R-matrix calculations for the pyridine-water dimer; preliminary results indicate that low-lying resonances shift downwards in energy (see Figure 1).

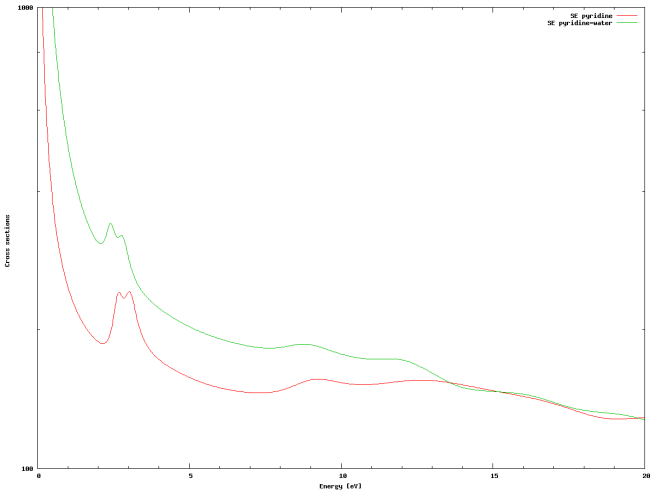

Fig.1. Low energy integral elastic cross section for electron scattering from pyridine (red line) and pyridine-water (green line) calculated at static-exchange level.

REFERENCES

[1] I. Baccarelli, I. Bald, F. A. Gianturco, E. Illenberger and J. Kopyra, Phys. Rep. 508, 1 (2011).

[2] P. Burke, *R-matrix theory of Atomic Collisions* (Springer Series on Atomic, Optical, and Plasma Physics), 2011.

[3] Z. Mašín and J. D. Gorfinkiel, J. Chem. Phys. 135, 144308 (2011); Z. Mašín et al, J. Chem. Phys. 136, 144310 (2012); Z. Mašín and J. D. Gorfinkiel, submitted to J. Chem. Phys.

[4] A. Sieradzka, F. Blanco, M. C. Fuss, Z. Mašín, J. D. Gorfinkiel and G. García, JCPA, 2014, 118, 33, 6657-6663.

Notes

Electron induced dissociation of biomolecules

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The interaction of high-energy radiation with living tissue leads to a range of structural and chemical modifications that can affect the biological function [1]. These modifications are induced via intermediate species, which include excited atoms and molecules, radicals, ions and secondary electrons. The energy distribution of the secondary electrons lies essentially below 100 eV with the most probable energy around 9-10 eV [2]. In electron irradiation experiments with plasmid DNA it was observed that low energy electrons can induce single-strand breaks and double-strand breaks [3]. This finding increased the interest in electron attachment processes to biomolecules in the gas phase. In dissociative electron attachment a transient negative ion is formed which decays by dissociation into a fragment anion and one or more neutral fragments.
Here, recent experiments on the low energy electron attachment to various sized biomolecules are summarized. Severe fragmentation of biomolecules is often observed for electron energies above 3-4 eV. At low electron energies abundant formation of the dehydrogenated parent anion occurs. This hydrogen loss turns out to be highly bond and site selective, i.e. by setting the electron energy to a certain resonance a specific bond in the molecule is cleaved. In addition, the influence of the environment, i.e. the fact whether they are embedded in a more realistic environment, i.e. surrounded by similar molecules in a cluster system or solvated in a given number of water molecules, is discussed.

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REFERENCES

[1] G. G. Cómez-Tejedor and M. C. Fuss, *Radiation Damage in Biomolecular Systems*, pp 3-43 (Springer Science + Business Media B. V., Dordrecht Heidelberg London New York, 2012).
[2] S. M. Pimblott and J. A. LaVerne, Rad. Phys. Chem. 76, 1244 (2007).
[3] B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels and L. Sanche, Science 287, 1658 (2000).

Notes

Electron impact fragmentation of thymine and cytosine: partial ionization cross sections for positive fragments

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Using computer-controlled data acquisition we have measured mass spectra of positive ions for electron impact on thymine [1] and cytosine [2], with electron energies up to 100 eV in 0.5 eV steps. An effusive beam of thymine or cytosine is generated using a resistively heated oven and is collimated using a skimmer. The molecular beam is crossed with a pulsed electron beam and positive ions are extracted into a reflectron time-of-flight mass spectrometer.
Ion yield curves for most fragment ions have been determined by fitting groups of peaks in the mass spectra with sequences of normalized Gaussians. Partial ionization cross sections have been obtained by normalizing the sum of the yield curves to the average of calculated total ionization cross sections. Appearance energies have been determined for most fragment ions. The results will be presented and will be compared with other fragmentation studies involving electron and photon impact, e.g. [3 - 5].
For a number of fragment ions, the ion yields rise very rapidly just above threshold $\propto (E - E_0)^p$ with powers $p \geq 2$. We attribute this to several onsets very close to each other due to the presence of parallel fragmentation pathways with similar appearance energies.
Second onset energies have been determined for a number of fragment ions with energy differences between the first and second onsets of 2 eV and higher. We conclude that there must be distinctly different fragmentation processes producing these fragments.
For thymine successively higher appearance energies are observed for successively smaller fragments in a group (e.g. 53-52-51 u, 40-39-38-37 u), consistent with successive loss of single H atoms.
Several groups of cytosine fragments (83-84 u, 67-69 u, and 41-44 u) have ion yield curves with very similar shapes above 35 or 40 eV. We attribute these constant yield ratios to H atom rearrangements (tautomerization) immediately preceding the fragmentation, but the presence of tautomers in the molecular beam might also contribute to this.
The appearance energies exclude some fragmentations proposed in the literature. For thymine, 83 u and 55 u have the same appearance energy, so loss of HNCO loss followed by CO loss does not occur near threshold. For cytosine, 95 u has a 3.7 ± 1.0 eV higher appearance energy than 68 u, so NH_2 loss followed by HCN loss does not occur.

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REFERENCES

[1] P. J. M. van der Burgt, F. Mahon, G. Barrett and M. L. Gradziel, Eur. Phys. J. D 68, 151 (2014).
[2] P. J. M. van der Burgt, Eur. Phys. J. D 68, 135 (2014).
[3] M. Imhoff, Z. Deng and M. A. Huels, Int. J. Mass Spectr. 245, 68 (2005).
[4] H.-W. Jochims, M. Schwell, H. Baumgärtel and S. Leach, Chem. Phys. 314, 263 (2005).
[5] O. Plekan, V. Feyer, R. Richter, M. Coreno, M. de Simone and K. C. Prince, Chem. Phys. 334, 53 (2007).

Notes

Studies of biomolecules at the DESIREE facility

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The Double Electrostatic Ion Ring Experiment (DESIREE) was developed at Stockholm University (SU) to study interactions between cations and anions at low and well-defined internal temperatures and centre-of-mass collision energies down to about 10 K and 10 meV, respectively [1,2]. Different ion sources can be used to inject ions into the rings. One of them is an ElectroSpray Ionization (ESI) source developed at SU. This source allows to produce heavy molecules including Polycyclic Aromatic Hydrocarbons (PAH) and biomolecules.
The ESI source is currently used to study Collision Induced Dissociation (CID) between PAH ions or biomolecules and noble gas atoms. These experiments, particularly in the 100 eV energy regime, may elucidate the role of such collisions in the formation of large molecules in interstellar environments (for PAHs) [3] or possible pathway to DNA damage caused by radiation interaction. We are interested, in particular, in non-statistical fragmentation processes, like single carbon knockout [4,5,6]. This gives highly reactive fragments which are not formed in statistical fragmentation processes, where the internal energy is redistributed among all degrees of freedom before the decay. The knockout mechanism could be important for any molecular system, including biomolecules, with center-of-mass collision energies around 100 eV.
Here we will report our preliminary results on CID of biomolecules presenting C and N rings in an energy range from 10 to 100 eV in the center-of-mass. Figure 1 shows the mass spectra of the protonated nucleotide Adenosine 5'-monophosphate (AMP) after collision with He at an energy of 100 eV in the center-of-mass. We are also investigating other systems, like porphyrins, to determine if non-statistical processes are present in biomolecules.

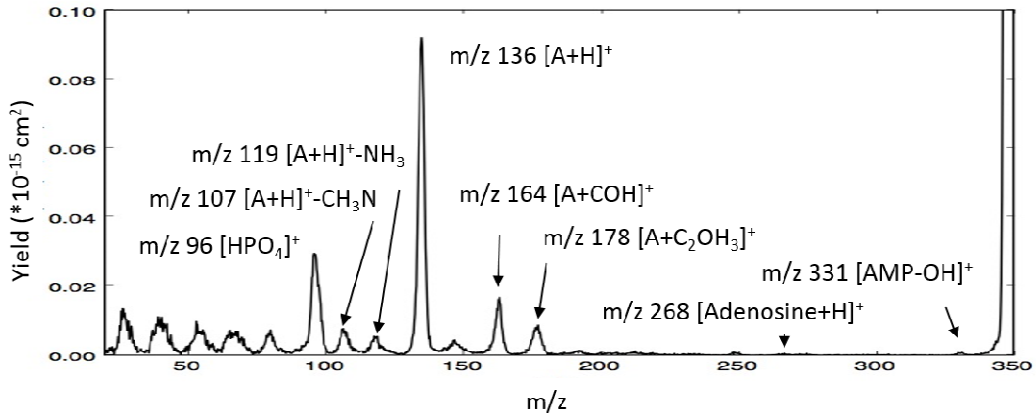

Fig.1. CID mass spectra of protonated AMP in collision with He at an energy of 100 eV in the center-of-mass.

REFERENCES

[1] H. T. Schmidt et al, Rev. Sci. Instrum. 84 055115 (2013).
[2] R. D. Thomas et al, Rev. Sci. Instrum. 82 065112 (2011).
[3] T.Chen et al, J. Chem. Phys. 140(22) 224306 (2014).
[4] M. H. Stockett et al, Phys. Rev. A. 89 032701 (2014).
[5] M. H. Stockett et al, Phys. Chem. Chem Phys. 16 21980 (2014).
[6] M.Gatchell et al, Int. J. Mass Spectrom. 365-366(0) 260-265 (2014).

Notes

VUV photoionization study of gas phase biomolecules using aerosol thermodesorption

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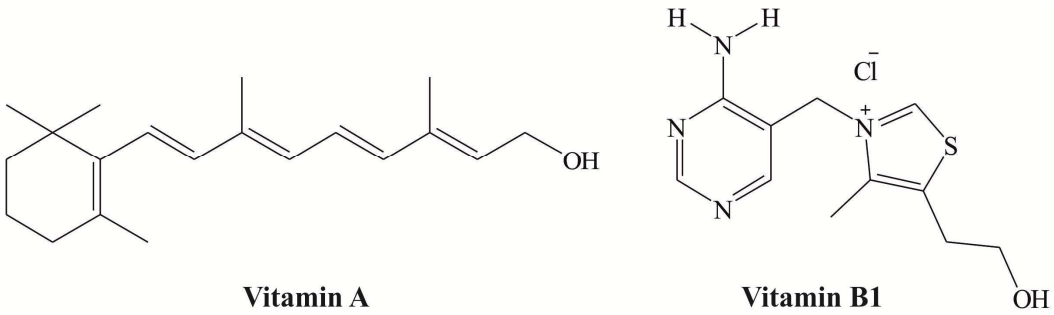
Gas phase studies of biomolecules provide a complementary alternative to the direct, condensed phase approach [1]. The intrinsic physico-chemical properties of these isolated systems might help understand their in-vivo biological functions within a bottom-top or pyramidal logic. Such studies are nevertheless very difficult to initiate because biomolecules are generally thermally fragile and their vaporization using classical methods often leads to their degradation. As a consequence of this experimental challenge, there is a dramatic lack of fundamental electronic properties for many important biomolecules such as ionization energies, electron affinities, etc... In this project, we have taken advantage of a recently developed system to bring intact *neutral* thermolabile vitamins into the gas phase using aerosol thermodesorption. We have then studied the vacuum ultraviolet (VUV) spectroscopy of vitamin A (retinol) and B1 (thiamine) (Scheme 1), which are typical systems to illustrate the difficulty of collecting data on biomolecules in the gas phase.
The threshold photoelectron spectrum of vitamin A will be presented as well as its interpretation by means of molecular orbitals transitions. The ion yields for vitamin B1 and its fragments showing their relative abundance according to the photon energy will also be shown, from which ionization and fragment appearance energies are extracted. *Ab initio* calculations have also been performed in order to interpret the experimental results and will also be presented.



Scheme 1. Structure of Vitamins A and B1

Acknowledgements: the general staff of SOLEIL for smoothly running the facility and Jean-François Gil (DESIRS) for the technical support on the SAPHIRS setup; Alexandre Giuliani (SOLEIL) for helpful discussions; Etienne Derat (UPMC) for introducing us to the ORCA software, for all his tips and advices and for giving access to calculation cluster.

REFERENCES

[1] J. P. Schermann, *Spectroscopy and Modeling of Biomolecular Building Blocks* (2008).

Notes

Energy resolved photoelectron-ion-ion coincidence studies of DNA building blocks and amino acids

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Soft X-ray absorption induced fragmentation of several DNA building blocks and amino acids (see **Figure 1**) into pairs of momentum correlated cations is studied using electron energy resolved PhotoElectron-PhotoIon-PhotoIon Coincidence (PEPIPICO) technique. Also the effect of chemical environment on fragmentation has been studied on a very basic level, by combining thymine and deoxy-d-ribose and uracil and d-ribose into thymidine and uridine respectively.

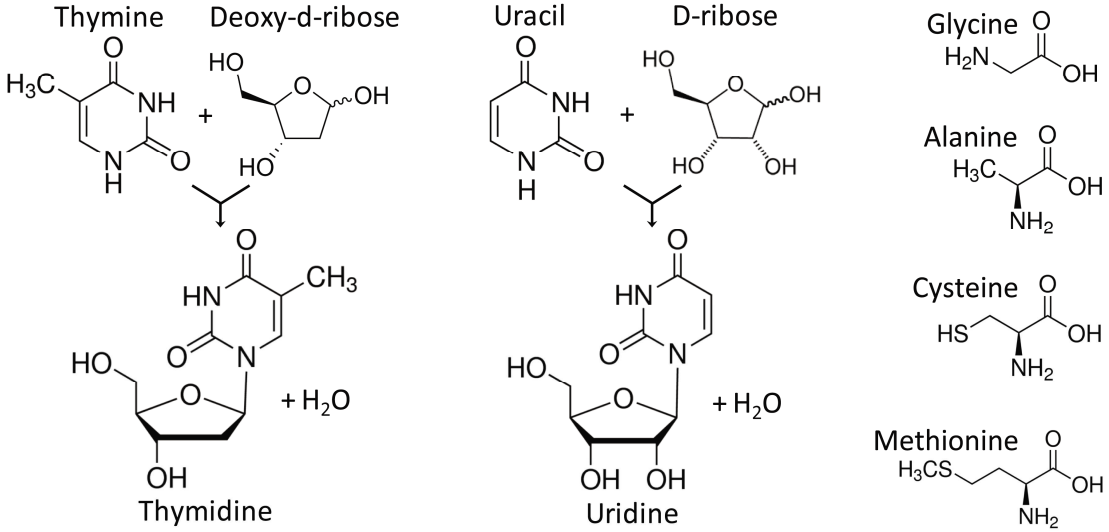

Figure 1. Skeletal formulas of the studied samples.

Thymine and uracil fragment via essentially the same bond cleavages as do d-ribose and deoxy-d-ribose [1-3]. The combination of a base and a sugar does not result into new bond cleavage sites, but can alter the probability of a specific bond cleavage significantly. In thymidine, most of the coincident cations originate purely from the base or the sugar part, whereas in uridine it is more common for one fragment to originate from the base and the other from the sugar [4].
In amino acids, the governing fragmentation channel produces $HNCH^+$ and $COOH^+$ coincident fragments [5-7]. In the case of glycine, where the side chain is substituted by a hydrogen, a two-body process is also very common. As the side chain becomes longer, the probability for two-body process decreases to a point where it is no longer detected. This is the case *e.g.* with methionine.

REFERENCES

[1] E. Itälä *et. al.* J. Chem. Phys. 133, 154316 (2010).
[2] E. Itälä *et. al.* Int. J. Mass Spectrom. 306, 82 (2011).
[3] D. T. Ha *et. al.* Phys. Rev. A, 84, 033419 (2011).
[4] E. Itälä *et. al.* J. Phys. B 46, 215102 (2013).
[5] E. Itälä *et. al.* J. Chem. Phys. 40, 234305 (2014).
[6] D. T. Ha *et. al.* J. Phys. Chem. A. 118, 1374 (2013) .
[7] J. Laksman *et. al.* J. Phys. Chem. B. 118, 11688 (2014) .

Notes

Fragmentation of halopyrimidines and halouraciles by photoionization and ion impact

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In recent years we have focused our interest in processes induced in isolated molecules by soft X-ray and ion beams. By photon ionization the site and state of the energy deposition are well defined and the following chain of processes are characterized by coincidence techniques. In the fragmentation induced by low energy ions, the effects of the increasing complexity of the target and the role played by the 'environment' on the properties of the single molecule are addressed.
In the presentation two examples will be discussed. The first one is the photofragmentation of 2Cl-pyrimidine following inner shell excitation or direct valence ionization studied via electron-ion coincidence techniques. The experiments have been performed at the Gasphase photoemission beamline at Elettra, Trieste (Italy). The results show that the resonant Auger process following inner shell excitation selectively populates the final states of the singly charged ion and the site and state selected fragmentation patterns appear to depend only on the final state of the singly charged ion. The comparison with state selected photofragmentation after valence ionization confirms the role of the cationic state in the type of fragments produced.
In the second example the fragmentation of 5Br-uracil isolated molecules, homogeneous clusters and hydrated clusters by C^{4+} ions has been studied. The experiments have been performed at the ARIBE beamline of the GANIL facility,Caen (France). The observation of series of hydrated fragments provides the experimental evidence that a few water molecules attached to the 5Br-uracil can induce a tautomerisation process. This process can lead to mutagenesis and therefore to a different pairing in the DNA bases and can explain the radiosensitizing effect of compounds bases on 5Br-uracil.

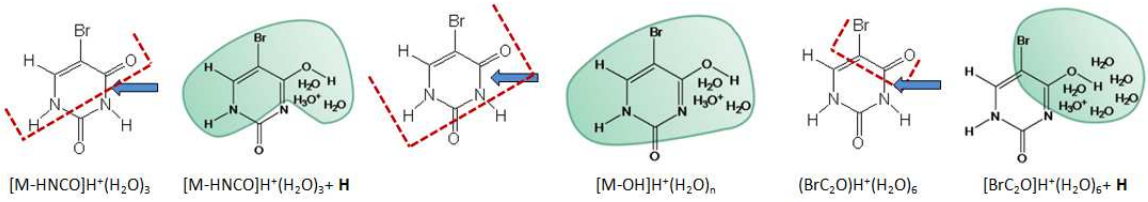

Fig.1. Schematic of the main fragments whose hydrated series are observed and assigned in the mass spectrum of hydrated clusters of 5Br-uracil. The blue arrows indicate the suggested site of hydration and the red dashed lines surround the charged (detected) fragment; M indicates the parent ion.The proposed tautomerisation processes mediated through the presence of a sufficient number of water moleculesis also shown.

Notes

UV and electron induced dynamics in biomolecules and clusters

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Radiation induced processes in biomolecules have been investigated intensively recently, notably in order to better understand the fundamental processes that can initiate DNA lesions [1]. While studies of isolated molecules generally provide the clearest data interpretations, equivalent measurements on hydrogen-bonded complexes enable closer analogies to be drawn with biological environments where different unimolecular or intermolecular reactive pathways can be significant. By comparing fragment ion production by electron impact ionization (EII) and UV multi-photon ionization (MPI) of isolated and clustered nucleobases, we have obtained the first experimental evidence supporting ring opening at the crossing seam of the S_2 and S_1 electronic excited states of uracil [2]. Clustering with water suppresses this channel, indicating a new mechanism by which the hydrogen-bonded environment stabilizes the molecule with respect to radiation damage. Fig. 1 gives examples of recent measurements probing metastable dissociation pathways of excited nucleobase ions. The photon energy thresholds for metastable HNCO loss upon uracil and thymine MPI are traced to the level of vibrational excitation in the S_1 electronic excited states. This channel suppressed in hydrated uracil clusters, most likely due to efficient dissipation of vibrational energy from intra- to intermolecular modes. We will also report on the development of experiments to analyze low energy electron interactions with selected neutral isomers and clusters.

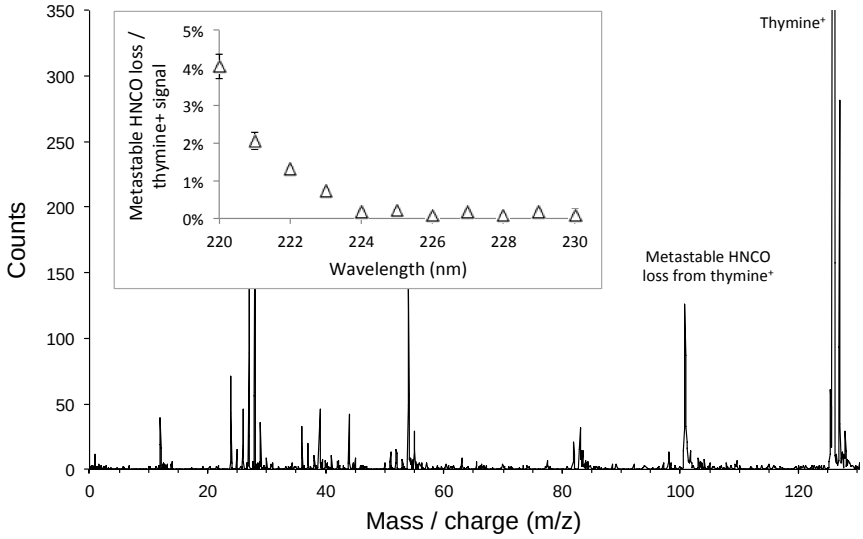

Fig.1. MPI (220 nm, average fluence 8×10^9 Wcm^{-2}) mass spectrum of gas-phase thymine. The insert shows the wavelength threshold for metastable HNCO loss.

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REFERENCES

[1] Middleton et al. Annu. Rev. Phys. Chem. 60, 217 (2009).
[2] Barc et al. J. Chem. Phys. 139, 244311 (2013).

Notes

Plasma interaction with biological tissue

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The interaction of the electrons, ions and radicals on biomolecules and, in general, samples of biological origin is the topic that is of scientific interest in various fields. It is well known that plasma generates reactive oxygen species (ROS) and reactive nitrogen species (RNS) that strongly affect metabolism of living cells. One of the open issues is to correlate external plasma products (electrons, ions, RNS, ROS, photons, strong fields etc.) with the immediate internal response which triggers or induces effects in the living cell. The expansion of the field of plasma medicine and its demand for in-vivo treatments resulted in fast development of various plasma devices that operate at atmospheric pressure. One of the sources that meets all the requirements needed for treatment of biological material is plasma needle. Previously, we have used this device for sterilization of planctonic samples of bacteria, MRSA biofilm, for improved differentiation of human periodontal stem cells into osteogenic line and for treatment of plant meristematic cells. Apart from the general effect of sterilization, improved differentiation or proliferation we have investigated possible mechanisms that can be responsible for those effects. For that purpose we have studied the kinetics of enzymes which are typical indicators of the identity of reactive species from the plasma created environment that can trigger signal transduction in the cell and ensure cell activity.

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Notes

Ultrafast non-reactive deactivation induced by excited state hole transfer from retinal chromophore to counterion

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The photocycle of microbial rhodopsins begins with the ultrafast all-*trans* to 13-*cis* isomerization of the protonated Schiff base of retinal (SBR^+).The photoisomerization of all-*trans* SBR^+ occurs regiospecifically around the C_{13}=C_{14} double bond. In the archetypical bacteriorhodopsin (bR) the reaction takes place on a sub-picosecond timescale with an efficiency approaching 65%. In solution, the performance of the reaction is drastically reduced.[1]
In this talk we will present the cooperative mechanism by which ultrafast, site-specific activation of the all-*trans* protonated Schiff base of retinal (SBR^+) takes place. We show that the same mechanism is responsible for the loss of efficiency and lack of bond-specificity in the SBR^+ photoisomerization in solution. The pump-probe measurements demonstrate the sensitivity of the all-*trans* SBR^+ excited-state dynamics on the electrostatic interaction with the surrounding counterions. Using large scale non-adiabatic dynamics simulations of the chromophore-counterion pairs we show that the relaxation processes that set in after photo-excitation involve as a decisive step a formation of an inter-molecular charge transfer state *via* hole translocation from the retinal backbone to the counterion. In solution this leads to dissociation of the chromophore-counterion pair and abortion of the photoisomerization. By impeding the dissociation, selective activation of the biologically active C_{13}=C_{14} bond is achieved within ~300 fs. Altogether we prove that the optically dark inter-molecular charge-transfer state is the chemically active state in the all-trans to 13-*cis* SBR^+ photoisomerization.

REFERENCES

[1] J. K. Lanyi, Annu. Rev. Physiol 66, 665 (2004).

Notes

Sub-4.5-fs purely electron dynamics in Phenylalanine initiated by attosecond pulses

A. Trabattoni[1], D. Ayuso[2], L. Belshaw[3], S. De Camillis[3], S. Anumula[1], F. Frassetto[4], L. Poletto[4], A. Palacios[2], P. Decleva[5], J. B. Greenwood[3], F. Martín [2,6], F. Calegari [7], M. Nisoli [1,7]

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Purely electron dynamics in large molecules are expected to be at the origin of many biological phenomena. Attosecond pulses provide a unique tool to initiate and observe ultrafast charge migration in complex molecular systems, that is expected to occur on a temporal scale between hundreds of attoseconds up to few femtoseconds, preceding any nuclear rearrangement [1].
In this work we present the first experimental demonstration of charge migration in the amino acid phenylalanine. The molecules were photoionized by sub-300-as isolated attosecond pulses and probed by 4-fs VIS/NIR probe pulses. The molecular fragments were collected in a mass spectrometer, and the time-dependent mass spectrum was investigated as a function of the pump-probe delay. The signal coming from the doubly charged immonium ion (m/q =60) presents an ultrafast dynamics (inset in Fig 1a) [2], with a clear yield oscillation on the decaying slope (Fig. 1a). The oscillation has a time periodicity of 4.3 fs, which is shorter than the vibrational response of the molecule [3]. A sliding-window Fourier-transform analysis was also performed (see Fig. 1b).

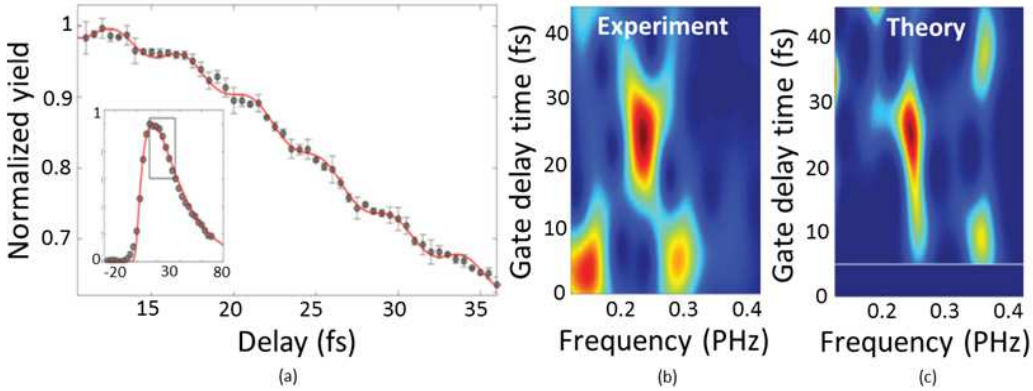

Fig.1. a) Oscillatory dynamics on the decaying slope of the delay-dependent yield of immonium dication (reported in the inset in a 100-fs delay range). b) Sliding-window Fourier-transform of the experimental data. c) Sliding-window Fourier-transform of the numerical result.

Theoretical calculations were performed by using a standard time-dependent density matrix formalism, in order to describe the hole dynamics induced by an attosecond pulse similar to that used in the experiment. Fig 1c reports the numerical result for the hole density evolution integrated on the amine site of the molecule. The results of the simulations clearly show the production of an ultrafast electron dynamics, characterized by oscillation frequencies in good agreement with the experimental results.

REFERENCES

[1] F. Remacle, R. D. Levine, Proc. Natl. Acad. Sci. U.S.A. 103, 6793–6798 (2006).
[2] L. Belshaw et al., J. Phys. Chem. Lett. 3, 3751–3754 (2012).
[3] F. Calegari et al, Science 346, 336-339 (2014).

Notes

Ultrafast electron dynamics in amino acids initiated by attosecond pulses

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The development of attosecond technology has enabled the real-time observation of electron motion in atoms, molecules and condensed matter [1]. In the case of large biological systems, such as amino acids, sudden ionization from a molecular orbital may trigger an ultrafast electronic response which is solely driven by electron correlation, as predicted in various theoretical works [2,3]. However, due to the large bandwidth of attosecond pulses employed in state-of-the-art experiments, electrons are usually removed not from one but from many orbitals, thus leading to a coherent superposition of ionic states. This phenomenon has been recently observed in the amino acid phenylalanine in a two-color pump probe experiment [4], where the production of ionic fragments was measured as a function of the time delay between the two pulses and charge fluctuations manifested as sub-4.5 fs oscillations in the quantum yield of a specific doubly charged fragment. The experimental observations are supported by an accurate description to the ionization process. Our theoretical work in phenylalanine [2] will be summarized, and our latest results in glycine and tryptophan will be presented. Our long-term goal is to perform a systematic study including larger aminoacids such as tryptophan.

We have performed a theoretical study of the field-free evolution of the electronic wave packet generated in amino acids (glycine, phenylalanine and tryptophan) upon the interaction with attosecond pulses. The ionization amplitudes have been quantitatively determined for all open channels using the static-exchange DFT method [5] developed by Decleva and collaborators, which makes use of the Kohn-Sham DFT to describe molecular bound states and of the Galerkin approach to evaluate continuum wave functions in the field of the corresponding Kohn-Sham density. The evolution of the electronic wave packet has then been described by using a standard time-dependent density matrix formalism. The results of the numerical simulations clearly show the production of an ultrafast electronic response occurring in a sub-femtosecond time scale and are in good agreement with the recent experimental observations [4]. We notice that, in contrast with previous work, most valence and inner-valence electrons are efficiently ionized and therefore the observed dynamics is that of a delocalized hole. We have further analyzed the role of the emitted electron in the hole migration mechanism and observed that even faster charge fluctuations (faster than the experimental resolution) might arise as a consequence of the interplay between the ground and continuum states.

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REFERENCES

[1] F. Krausz and M. Ivanov, Rev. Mod. Phys. 81, 162 (2009).
[2] L. S. Cederbaum and J. Zobeley, Chem. Phys. Chem. 307, 205 (1999).
[3] F. Remacle and R. D. Levine, Proc. Natl. Acad. Sci. USA 103, 6793 (2006).
[4] F. Calegari et al., Science 346, 6207 (2014).
[5] M. Stener et al, Chem. Phys. Lett. 351, 469 (2002).

Notes

Photo-induced ultrafast nuclear dynamics in (deeply) core-excited molecules

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Absorption of an X-ray photon by a molecule may lead to the excitation of a localised core electron to a specific unoccupied valence orbital if the energy of the photon matches exactly the difference between the involved core and valence electronic levels. The created core-hole states are highly unstable and eventually decay on a very short timescale emitting a photon (radiative decay) or a so-called *Auger* electron (non-radiative or *Auger* decay).

Soft X-ray absorption leads to creation of K(1*s*) core-holes for the 2nd row elements such as C, O, N, *etc*; L(2*s*, 2*p*) core-holes for the 3rd row elements such as S, Cl; and M(3*d*) holes for the 4th row elements as e.g. Br, and so on. Their lifetime is typically ranging between 3 to 8 femtoseconds (fs). [1] It is well known that for these core-excited states electronic relaxation may compete with nuclear dynamics and so-called *ultrafast dissociation* (UFD) may occur within the lifetime of core-hole states. For example, UFD was observed for Cl $2p\rightarrow\sigma^*$ and Br $3d\rightarrow\sigma^*$ core electron excitations in HCl, CH_3Cl, HBr and O $1s\rightarrow 4a_1$, S $2p\rightarrow 6a_1$ core-excited states of H_2O and H_2S, respectively [1,2]. In larger molecules, dissociation pathways are observed to deviate from the two-body dissociation coordinate due to the internal motion of light linkages, which alters dissociation rates and may yield heavy fragments on very short time scales. The UFD process was observed in *e.g.* dichlroethylenes [2] and 1-bromo-2-chloroethane ($Br\text{-}CH_2\text{-}CH_2\text{-}Cl$) [3], where the low-reduced-mass rotation of C_xH_y-moiety allows the C−Cl or C−Br bond breakage within the lifetime of the Cl2*p* or Br3*d* core-excited states (~ 7 fs).

Hard X-ray photons (>1 keV) may reach deeper-lying core electrons. The lifetime (τ) of deep-core-hole states is very short – of the order of 1 fs or below. Nevertheless, the signature of nuclear dynamics was detected for Cl $1s\rightarrow\sigma^*$ (τ ~1 fs) core-excited states of HCl [4] and even on a sub-femtosecond timescale (τ ~200 attoseconds) for CH_3I [5]. The electronic relaxation dynamics of deep-core-hole states is very rich. At variance with that, the very short lifetimes of these states do not allow for extensive nuclear dynamics to take place before electronic relaxation occurs. However, the dominant channels of the 1st step relaxation processes (both radiative and *Auger* decays) lead to intermediate states that bear 1 or ***2*** holes in *core*-electron shells. The latter ones can be created by direct soft X-ray absorption and can undergo ultrafast dissociation within the *core*-hole lifetime (see above). The former *double core*-hole states are yet exotic and can be also created as so-called "super"-satellites of direct double core-hole ionization [6]. Very recent theoretical studies show that the energy gradients of the $core^{-2}val^{1}$ states can be large and even considerably larger compared to the $core^{-1}val^{1}$ states [6]. Therefore, nuclear dynamics is correspondingly faster in $core^{-2}val^{1}$ "super"-satellites. Consequently, creation of deep core holes leads to extensive nuclear dynamics on a few femtosecond timescale despite the very short (≤1 fs) lifetime of such states.

A mechanism of UFD via internal rotation on example of 1-bromo-2-chloroethane will be discussed and examples of ultrafast dynamics in deep-core excited states will be presented.

REFERENCES

[1] P. Morin et al. J. Electron Spectrosc. Relat. Phenom. 185, 259 (2012).
[2] D. Céolin et al. J. Electron Spectrosc. Relat. Phenom. 184, 24 (2011).
[3] O. Travnikova et al. J. Phys. Chem. Lett. 4, 2361 (2013).
[4] M. Simon et al. Phys. Rev. A 73, 020706(R) (2006).
[5] T. Marchenko et al. J. Chem. Phys. 134, 144308 (2011).
[6] S. Carniato et al. J. Chem. Phys. 142, 014307 (2015).

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Semiclassical model for strong-field ionization with quantum interference and multielectron polarization effects

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Semiclassical models applying a classical description of the electron after it has been promoted into the continuum by the laser field are widely used in strong-field physics. Until recently semiclassical models were not able to describe quantum interference. A new approach developed in Ref. [1] allows to include interference effects into trajectory-based simulations of above-threshold ionization (ATI). Within this approach each classical trajectory is associated with a certain phase.
Here we present a modified version of this semiclassical model for the ATI with inclusion of the Stark-shift of the initial state, the Coulomb potential, and the polarization induced dipole potential capable to describe quantum interference. To this end, we combine the semiclassical model developed in Ref. [2] with the approach described in Ref. [1]. Our model is used to investigate the role of the multielectron polarization effects in the formation of the interference structure in momentum distributions of photoelectrons. Since the multielectron potential affects both the exit point at the tunnel and the electron dynamics in the continuum [3], a pronounced imprint of the polarization effects in the interference patterns is expected. Our results will provide a necessary benchmark for the analysis of experimental data.
An example for momentum distribution of the ATI electrons calculated within our new model is shown in figure 1.

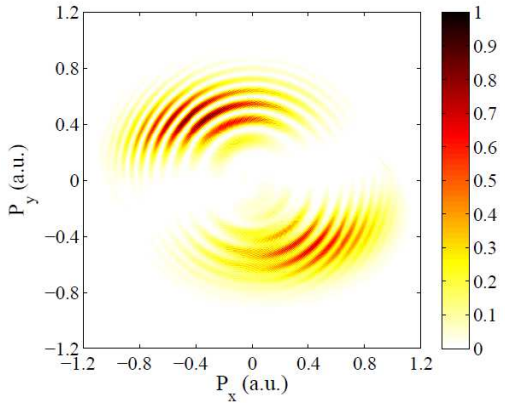

Fig.1. Photoelectron momentum distribution for the ionization of a hydrogen atom by a Ti:sapphire laser pulse (λ = 800 nm) with a duration of n_p = 6 cycles, peak intensity of 2.0×10^{14} W/cm^2, and ellipticity = 0.5 calculated within the semiclassical model.

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REFERENCES

[1] M. Li, J.-W. Geng, H. Liu et al. Phys. Rev. Lett. 112, 113002 (2014).
[2] A. N. Pfeiffer, C. Cirelli, M. Smolarski, D. Dimitrovski, M. Abu-samha, L. B. Madsen and U. Keller, Nat. Phys. 8**,** 76 (2012).
[3] N. I. Shvetsov-Shilovski, D. Dimitrovski and L. B. Madsen, Phys. Rev. A 85, 023428 (2012).

Notes

Calculations of ionization probabilities for sodium in strong laser fields

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Ionization probabilities for sodium atom in strong laser fields are calculated for different ratios between the frequency and the field strength, covering both the quasistatic (tunneling/over-the-barrier) and the multiphoton ionization regimes. The probabilities are determined numerically using the wave-packet propagation technique [1] and the single electron model for alkali-metal atoms, where the valence electron moves in an effective core potential and the external field [2]. In the quasistatic regime (high-field-intensity/low-frequency) the ionization rate (probability per unit time) is obtained from the autocorrelation function, which is the overlap between the initial (here the ground) state $\psi(0)$ and the corresponding state $\psi(t)$ at a later time $t \geq 0$. The calculated values for the lowest state energies and ionization rates as functions of the field strength are in good agreement with the results obtained recently using other methods [2]. Additionally, the transition time from $t = 0$, when the external field is switched on, until the decaying (resonant) state becomes quasistationary (exponential decay) is estimated and the form of the final wave function is determined. The field ionization of sodium in the multiphoton regime (low-field-intensity/high-frequency) is studied for a linearly polarized laser pulse with the intensity profile of the electric field component $F \sin^2(\pi t/T_p)$ and the pulse duration T_p of a few femtoseconds. The ionization probability $P_{\text{ion}}(t)$ is determined by calculating the occupation probabilities $P_n(t)$ for each eigenstate of the valence electron as $P_{\text{ion}}(t) = 1 - \sum_n P_n(t)$ [3]. An example for the calculated probabilities as functions of time is shown in Fig. 1.

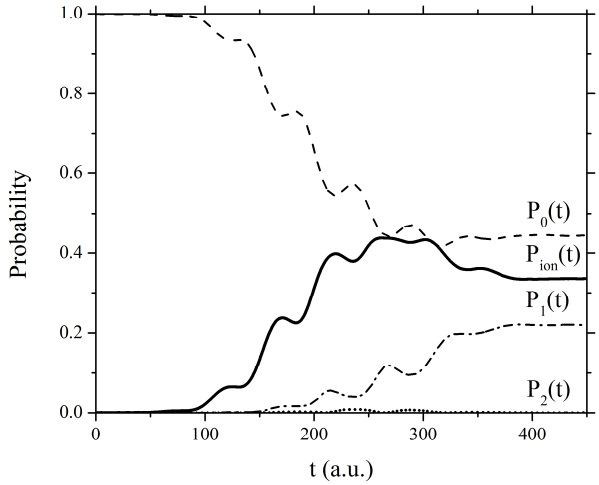

Fig.1. The occupation probabilities for the lowest three states as well as the related ionization probability for the sodium atom irradiated by the laser pulse of the wavelength λ = 760 nm, duration T_p = 10 fs (413.4 a.u.) and the peak intensity $1.72 \cdot 10^{12}$ W/cm^2 (F = 0.007 a.u.).

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REFERENCES

[1] M. D. Feit and J. A. Fleck, Jr., J. Chem. Phys 78, 301 (1983).
[2] M. Z. Milošević and N. S. Simonović, Phys. Rev. A 91, 023424 (2015).
[3] F. Grossmann, *Theoretical Femtosecond Physics*, p. 106, (Springer, Berlin, 2008).

Notes

Unusual hydrogen and hydroxyl migration in the fragmentation of excited doubly-positively-charged amino acids in the gas phase

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Hadron therapy is radiation therapy using strongly interacting particles [1]. A better depth dose profile of the energetic ion beam (Bragg peak) has proven its superiority over gamma radiation for killing cancer cells selectively [2]. With the advent of these ion-beam cancer treatments [3,4], the interaction of biomolecules with ionizing particles (X- rays, electrons, ions) in the gas phase has become a fundamental technique to investigate the radiation damage of biological tissues at the molecular level [5-7]. In biological tissues the damages produced in the biomolecules are not only caused directly by the particle-matter collision but also by radicals and secondary particles created after the fragmentation of different chemical species along the ionization path [8,9]. This underlines the importance of a proper description of the fragmentation mechanisms after electron removal. Thus, studying the behavior of the amino acids after interaction with highly charged ions gives valuable information for the hadron-therapy treatment based on ion beams.

In this communication we present recent results on fragmentation of small lineal amino acids, doubly-positively charged in the gas phase, $NH_2-(CH_2)_n-COOH$: n=1 glycine [10]; n=2 β−alanine [11] and n=3 γ−aminobutyric acid GABA [12]. Experimentally, we obtain the data in the gas phase for neutral molecules in collisions with low-energy highly charged ions. State-of-the-art multi-coincidence detection mass spectrometric techniques are used to determine the charge state of the molecule before fragmentation. The experimental data are analyzed by means of quantum chemistry calculations. In particular, ab initio molecular dynamics simulations of the excited and charged species provide valuable information on the fragmentation mechanisms; further exploration of the potential energy surfaces with the density functional theory calculations allows us to obtain energetic and structural information on the most populated dissociation channels.

Our results [10-12] have shown that in com-petition with the expected Coulomb explosion, the doubly positively charged lineal amino acids present several de-excitation mechanisms. In particular, hydrogen migration and hydroxyl group migration that appear in the femtosecond timescale and lead to unusual fragmentation products.

REFERENCES

[1] Petti and Lennox, Hadronic Radio-therapy, Ann. Rev. Nuclear & Particle Science, 44, 154 (1994).
[2] H. Kaur et al. AIP Conf. Proc. 205, 1530 (2013).
[3] D. Schardt et al. Rev. Mod. Phys. 82 383 (2010).
[4] M. Durante and J. S. Loeffler, Nat. Rev. Clin. Oncol. 7, 37 (2010).
[5] P.Swiderek, Angew. Chem. Int. Ed. 45, 4056 (2006).
[6] B.Boudaïffa et al. Science 287 1658 (2000).
[7] M.H. Holzscheiter et al. Radiother.Oncol. 105 1 (2012).
[8] L. Sanche, Eur. Phys. J. D 35, 367 (2005).
[9] C. V. Parast et al. Biochemistry 34, 2393 (1995).
[10] S. Maclot et al. J.Phys.Chem.Lett. 4, 3903 (2013).
[11] D.G. Piekarski et al. submitted (2015).
[12] M. Capron et al. Chem. Eur. J. 18 9321 (2012).

Notes

Charge and energy flows in ionised thymidine

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We present a study of the ionisation/fragmentation of the thymidine molecule, a nucleoside, in the gas phase. We are coupling photoionisation and ion collisions experiments with quantum chemistry calculations in order to draw a complete picture of the charge and energy transfers in the singly ionised thymidine.
Using the photoelectron-photoion coincidence (PEPICO) method [1], the fragmentation dynamics is investigated as a function of the electronic excitation energy. Particularly, the comparison of the PEPICO mass spectrum with the calculated orbitals shows the strong dependence of the charge localisation with the excited orbitals. From the comparison of the state-selected mass spectra with the calculated energy associated with the different fragmentation pathways for the ground state, we suggest that the electronic state correlates to the nearest fragmentation channel already opened and that the coupling between the electronic excitation and the vibrational one is highly efficient.
Moreover, we propose a method to evaluate the energy transferred into the system by ion collision using a fitting procedure of the ion-impact mass spectrum with the different PEPICO mass spectra. The obtained excitation energy distribution corresponds to the one expected [2].

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REFERENCES

[1] P. Bolognesi, P. O’Keeffe, and L. Avaldi, *Soft X-ray Interaction with Organic Molecules of Biological Interest*, chapter 10 in *Radiation Damage in Biomolecular Systems*, G.G. Gómez-Tejedor and M.C. Fuss (eds.), (Springer, Dordrecht Heidelberg London New York, 2012).
[2] S. Maclot et al., J. Phys. Chem. Lett. 4, 3903 (2013).

Notes

Collision induced dissociation of biomolecular cations

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We have studied collisions between molecular ions and noble gas atoms using a Collision Induced Dissociation (CID) type setup, which is a part of the DESIREE facility [1] [2] at Stockholm University. Briefly, this setup consists of an electrospray ionization source followed by a quadrupole mass filter and a collision gas cell. After the collisions, the fragment ions are analyzed by two pairs of electrostatic detectors and recorded with a position-sensitive microchannel plate detector (see Fig. 1).
We have recently used this setup to measure absolute cross sections for knocking out single carbon atoms in collision between Polycyclic Aromatic Hydrocarbons (PAHs) ions and noble gas atoms [3] [4] [5]. This gives highly reactive fragments which are not formed in statistical fragmentation processes and may be key intermediate steps for the formations of larger molecules in, e.g., the interstellar medium [6]. The knockout mechanism is expected to be important for any molecular system with a center of mass collision energy around 100 eV and down to the threshold energy for the process. Here we report our first CID experiments on biomolecules (Adenosine 5'-monophosphate, Adenine and Adenosine) at a center of mass energy of about 100 eV.

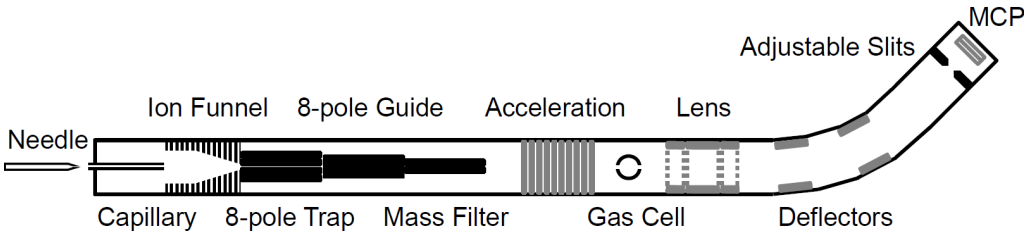

Fig.1. The Collision Induced Dissociation (CID) setup at Stockholm University

REFERENCES

[1] H. T. Schmidt et al, Rev. Sci. Instrum. 84, 055115 (2013).
[2] R. D. Thomas et al, Rev. Sci. Instrum. 82, 065112 (2011).
[3] M. H. Stockett et al, Phys. Rev. A. 89, 032701 (2014).
[4] M. H. Stockett et al, Phys. Chem. Chem Phys. 16, 21980 (2014).
[5] M.Gatchell et al, Int. J. Mass Spectrom. 365-366(0), 260-265 (2014).
[6] T.Chen et al, J. Chem. Phys. 140(22), 224306 (2014).

Notes

Synchrotron photoionization spectroscopy of free organic molecules

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Photon flux and energy resolution achievable at undulator beamlines, such as the Gas Phase beamline at the Elettra storage ring (Trieste, Italy) [1], enable studies of the energy dependence of photoionization processes over a large energy range. It is then possible to address the specific effects that follow selective excitations of inner-shell electrons. However, this kind of measurements often suffers from an intrinsic low signal level attainable from rarefied low-vapor-pressure targets such as biomolecules [2].
We will present recent results where photoionization techniques have been applied to gas phase molecular targets of increasing complexity [3-4]. Our present study addresses biphenylene, pteridine and metal-containing phthalocyanines. These highly conjugated organic molecules are all characterized by a rich photochemistry, which also makes them particularly interesting for pharmacological purposes. Our synchrotron radiation experiments provide insights into their electronic structures, whose detailed knowledge is of great value when planning further investigations on their excited states at novel ultrafast light sources. By comparison with the results of Density Functional Theory (DFT) calculations, we could identify the characteristic contributions of chemically non-equivalent carbon atoms in the x-ray photoelectron spectra as well as in the core hole absorption spectra of these molecules, and to correctly assign them.

REFERENCES

[1] K. C. Prince et al. J. Synchr. Rad. 5, 565 (1998); http://www.eletra.trieste.it/elettra-beamlines/gasphase.html
[2] V. Feyer, O. Plekan, R. Richter, M. Coreno, M. de Simone, K. C. Prince, A. B. Trofimov, I. L. Zayteseva and J. Schirmer, J. Phys. Chem. A 144, 10270 (2010); O. Plekan, V. Feyer, R. Richter, M. Coreno, M. de Simone, K. C. Prince and V. Carravetta, Journal of Physical Chemistry A 111, 10998 (2007).
[3] J. Lüder et al. J. Chem. Physics, 142, 74305C (2015).
[4] I. Bidermane et al. Phys. Status Solid B, 1-7 (2015); Iulia E. Brumboiu et al. J. Phys. Chem. A 118, 927 (2014).

Notes

VUV action spectroscopy of bare and hydrated protonated leucine-enkephalin peptide

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Leucin-enkephalin (Leu-enk) is a model peptide system consisting of 5 amino acids, with a sequence Tyr-Gly-Gly-Phe-Leu and has been intensively investigated previously [1-3] (and references therein). Here, we report a study on VUV photodissociation of gas-phase protonated (Leu-enk) peptide, both bare and hydrated with one water molecule, in the photon energy range from 5.5 to 9.0 eV. By recording photon activation tandem mass spectra at different photon energies, we could measure the photofragment ion yields for a number of selected fragments of Leu-enk and thus record the action spectroscopy of isolated precursors. The experiment has been performed by coupling a linear quadrupole ion trap mass spectrometer (LTQ XL) to the VUV DESIRS beamline [4] of the SOLEIL synchrotron facility (France). The front side of the LTQ mass spectrometer was equipped with an electrospray ionization (ESI) source, whereas the photon beam was introduced from the back side. A detailed description of the experimental setup can be found in the previous references [5,6]. Additionally, we have performed density functional theory (DFT) and time-dependent DFT calculations in order to investigate their structures and absorption bands.

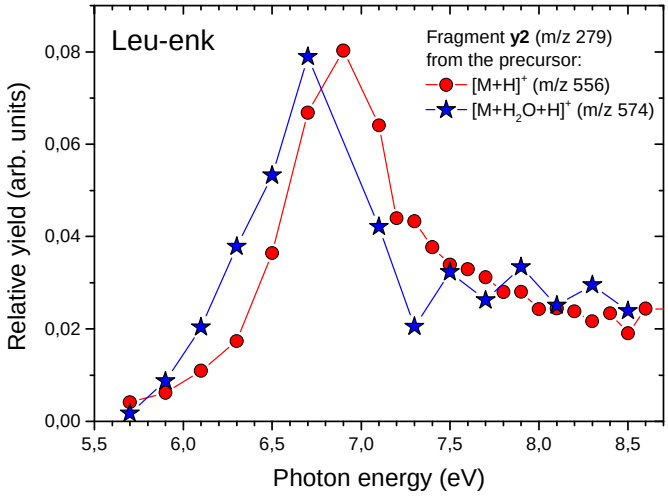

Fig.1. Photodissociation yields of y_2 fragment from $[Leu\text{-}enk+H]^+$ (circles) and $[Leu\text{-}enk+H_2O+H]^+$ (stars) precursors.

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REFERENCES

[1] S. Bari et al., J. Chem. Phys. 134, 024314 (2011).
[2] A.R. Milosavljević et al., Angew. Chem. Int. Ed. 52, 7286 (2013).
[3] A. R. Milosavljević et al., Eur. Phys. J. D 68 (2014).
[4] L. Nahon et al., J. Synchrotron Radiat. 19, 508 (2012).
[5] A.R. Milosavljević et al, Phys. Chem. Chem. Phys. 13, 15432 (2011).
[6] A.R. Milosavljević et al., J. Synchrotron Radiat. 19, 174 (2012).

Notes

Gas-phase X-ray action spectroscopy of protonated nanosolvated substance P peptide around O K-edge

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We report preliminary results from unprecedented near edge X-ray absorption fine structure action spectroscopy of a gas-phase nanosolvated peptide ion. Doubly protonated substance P (Arg-Pro-Lys-Pro-Gln-Gln-Phe-Phe-Gly-Leu-Met-NH2) cations have been isolated in a linear ion trap and submitted to soft X-ray synchrotron radiation by means of coupling a commercial quadrupole ion trap mass spectrometer (Thermo Finningan LTQ XL) to the PLEIADES beamline at the SOLEIL synchrotron radiation facility (France) [1]. X-ray activation tandem mass spectra have been recorded for different photon energies, scanned over C, N and O K-edge ionization thresholds.

Figure 1 shows the photofragment ions yield corresponding to a total water loss (a normalized integral yield of all fragments corresponding to the loss of one or more water molecules) from the doubly protonated substance P cation nanosolvated with 11 water molecules $[M+2H+11H_2O]^{2+}$ upon soft X-ray irradiation. We observed that a resonant excitation of an O 1s electron to an unoccupied molecular orbital, following by a resonant Auger decay, induces an increased water detachment from the precursor.

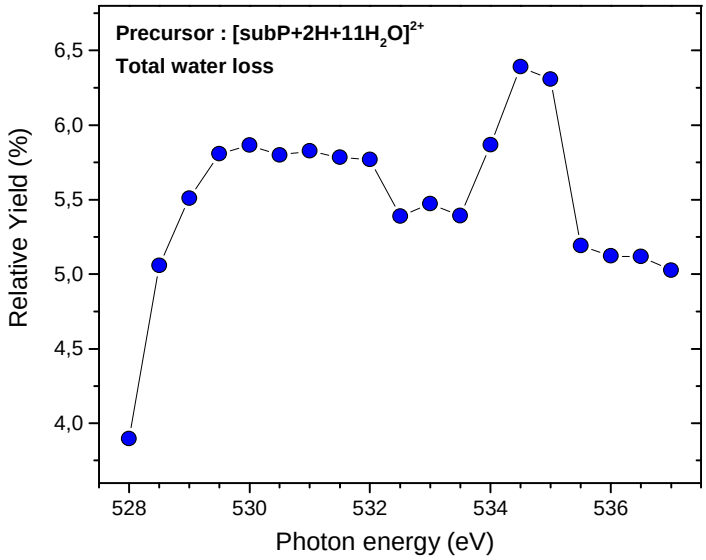

Fig.1. Photofragment ions yield that corresponds to a range m/z 674-766 (an integral yield of all fragments corresponding to the loss of one or more water molecules) from a doubly protonated nanosolvated substance P cation precursor $[M+2H+11H_2O]^{2+}$ (m/z 773.5).

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REFERENCES

[1] A. R. Milosavljević et al., J. Phys. Chem. Letters 3, 1191 (2012).

Notes

Investigation of the ultrafast excited state dynamics of ortho-nitrophenol by photoemission spectroscopy

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Nitroaromatic compounds have recently received much attention, on account of their relevant impact on the environment and human health and for the reason that they have many applications as photochemical reagents as well as photoswitches and photolabile protecting groups [1]. A characteristic feature of nitroaromatics is the efficient photogeneration of highly reactive triplet states, nitric oxide and other radicals, which has recently made them potential candidates for photodynamic therapy [2]. Addition of a nitro group to aromatic hydrocarbons is known to shorten the lifetime of excited electronic states and indeed the gas phase UV absorption spectrum of nitroaromatics often appears broad and almost featureless, indicating ultrafast processes in the excited states.

Our present study focuses on the study of the ultrafast dynamics of the excited states of ortho-nitrophenol (ONP) by ultrafast time-resolved photoelectron spectroscopy (TRPES). This methodology, besides several advantages [3], is particularly suited for the study of ultrafast non-adiabatic processes and spin–orbit coupling in isolated polyatomic molecules.

Measurements were performed with the CITIUS ultrafast VUV source [4], a state-of-the-art fs-laser facility for time resolved photoemission and pump-probe spectroscopies based on laser high-order harmonic generation in gas, which was recently assembled and commissioned thanks to the support of the "Italian-Slovenian Cross-border Cooperation Program 2007-2013". In particular, we employed an ultrafast uv laser pulse to prepare the ONP molecule in an electronically excited state and we followed the dynamics of the molecule by time delayed photoionization with a high-order harmonic (HHG) pulse at 23.2 eV.

The results are interpreted in the light of quantum chemical calculations. Ultrafast relaxation pathways were identified, involving both internal conversions and intersystem crossing. The photochemistry of the process was also recognized by the presence of signals due to reaction products.

REFERENCES

[1] P. Kovacic and R. Somanathan, Journal of Applied Toxicology, 34, 810 (2014); A. P. Pelliccioli and J. Wirz, Photochem. Photobiol. Sci. 1, 441 (2002); J. Henzl, M. Mehlhorn and K. Morgenstern, Nanotechnology 18, 495502 (2007); G. C. R. Ellis-Davis, Nat. Methods 4, 619 (2007).
[2] K. Fukuhara, M. Kurihara, N. Miyata, J. Am. Chem. Soc. 123, 8662 (2001); T. Suzuki et al. J. Am. Chem. Soc. 127, 11720 (2005); S. Diring et al. Nature Communications 4, 2684 (2013).
[3] A. Stolow, Annu. Rev. Phys. Chem. 54, 89 (2003).
[4] C. Grazioli et al. Rev. Sci. Instr. 85, 23104 (2014).

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COST XLIC WG2 meeting

	MONDAY 27. 4. 2015.	TUESDAY 28. 4. 2015.	WEDNESDAY 29. 4. 2015.	THURSDAY 30. 4. 2015.
7:00		Breakfast	Breakfast	Breakfast & Departure
9:00		Schlathölter	Avaldi	Closing remarks
9:30		Wyer	Eden	RTD2
10:00		Cerovski	Puač	
10:30		CB1	CB3	
11:00		Kopyra	Došlić	CB4 & Departure
11:30		Gorfinkiel	Trabattoni	RTD3
12:00		Mauracher	Palacios	
12:30		van der Burgt	Travnikova	
13:00		LB	LB	LB
15:00		de Ruette	EXCURSION	DEPARTURE
15:30		Dossmann		
16:00		Itälä		
16:30		CB2		
17:00	REGISTRATION & Welcome to participants	RTD1		
18:00		PS		
18:30	Tavernelli			
19:00	Coreno			
19:30	Kočišek			
20:00	Dinner	Dinner	Dinner	

Invited Lecture
RTD - Round table discussions
PS - Poster Sesion

CB - Coffee Break
LB - Lunch Break