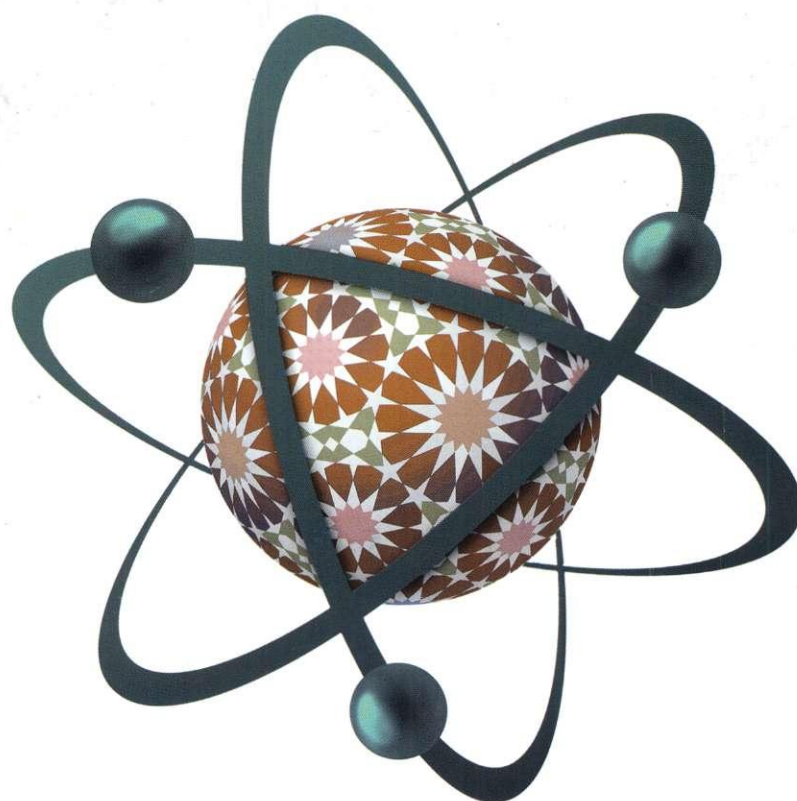# ICPEAC 2015

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PR

WEDNESDAY

Probing DNA radiation damage by DNA nanotechnology

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Synopsis Absolute cross sections for DNA strand breaks induced by low-energy electrons (< 20 eV) and photons (< 10 eV) can be determined by using DNA origami nanostructures and analysis by atomic force microscopy. In this way electron and photon induced processes are studied in oligonucleotides of defined sequence. The DNA strand breakage depends on the nucleotide sequence with A containing sequences being the most sensitive ones. By using synchrotron VUV radiation we have determined the quantum yield for strand breakage for a range of photon energies and different DNA sequences.

DNA radiation damage is either due to the direct interaction of radiation with DNA or due to the indirect effect of secondary particles such as low-energy electrons [1]. The most important type of DNA radiation damage is strand breakage, which can lead to cell death, mutations and cancer. The DNA strand breakage is dependent on the nucleotide sequence [2]. We have developed an approach to determine absolute cross sections for radiation induced strand breakage in specific oligonucleotide target strands to study this sequence dependence [2-4]. The target strands are immobilized on DNA origami nanostructures, which serve as a platform to organize the target strands, and irradiated and non-irradiated samples are analyzed by atomic force microscopy (AFM) [5]. The main advantages of the technique are (i) a rather simple determination of absolute cross section for strand breakage at specific irradiation conditions, (ii) the analysis and comparison of multiple sequences at the same time, and (iii) the analysis of rather complex higher-order structures [6].

We have applied the DNA origami technique to DNA strand breaks induced by low-energy electrons (10 and 18 eV) [2-4], and vacuum UV photons (5 – 9 eV). Results from both experiments will be presented and discussed.

In experiments using low-energy electrons we find a clear dependence of strand break cross sections on the nucleotide sequence. Among the sequences TT(XTX)₃TT (X = A; G, C) the adenine (A) containing sequence has the highest cross section for strand breakage. The work is now extended to higher-order DNA structures such as guanine (G) quadruplexes [6].
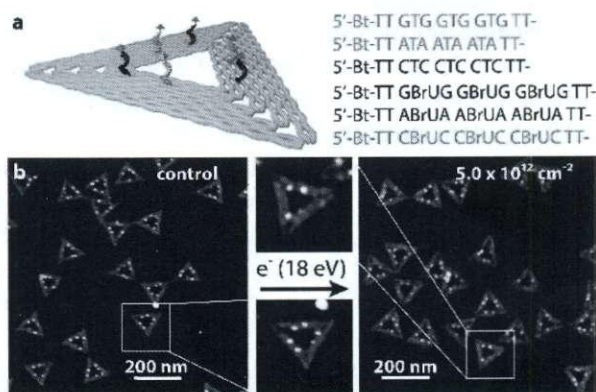

Figure 1. a) Scheme showing DNA target strands protruding from the DNA origami platform. b) The target strand positions can be distinguished in AFM images. On the left a typical AFM image of non-irradiated DNA origami samples carrying TT(GTG)₃TT and TT(GBrUG)₃TT oligonucleotides is shown. On the right, a typical AFM image after irradiation with 18 eV electrons is shown.

UV photons are able to directly induce DNA strand breaks. We have carried out experiments using synchrotron radiation in the energy range 5 – 9 eV to determine the strand break and absorption cross sections for a range of oligonucleotide sequences and photon energies. We observed a clear energy and moderate sequence dependence of UV-induced strand breakage, which becomes more pronounced at higher energies.

References

[1] I. Baccarelli *et al* 2011 *Phys. Rep.* **508** 1.
[2] A. Keller *et al* 2014 *Sci. Rep.* **4** 7391.
[3] A. Keller *et al* 2012 *ACS Nano* **6** 4302.
[4] A. Keller *et al* 2013 *New J. Phys.* **15** 083045.
[5] I. Bald *et al* 2014 *Molecules* **19** 13803.
[6] L. Olejko *et al* 2015 *Angew. Chem. Int. Ed.* **54** 673.

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Transport processes for electrons and positrons in gases and soft-condensed matter: Basic phenomenology and applications

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Synopsis An understanding of electron and positron transport in gases and soft-condensed matter under non-equilibrium conditions finds applications in many areas, from low-temperature plasmas, to positron emission tomography, radiation damage and particle detectors in high-energy physics. In this work we will highlight how the fundamental kinetic theory for solving the Boltzmann equation and fluid equation models are presently being adapted to study the various types of non-equilibrium plasma discharges and positron-based technologies.

The transport theory of electrons and positrons in gases and soft-condensed matter is of interest both as a problem in basic physics and for its potential for application to modern technology. For electrons, these applications range from low-temperature plasmas to particle detectors in high energy physics and to understanding radiation damage in biological matter. For positron based systems, the emission of back-to-back gamma rays resulting from annihilation of a positron and an electron is a fundamental process used as a tool in many areas, ranging from fundamental atomic and molecular physics, particle and astrophysics, to diagnostics in biological and material sciences.

In this work we explore analytical framework and numerical techniques for a multi term solution of Boltzmann's equation [1], for both electrons and positrons in gases and soft-condensed matter, and associated fluid equation models [2,3]. Together with the basic elements of our Monte Carlo method, the particular attention will be placed upon the rescaling procedures for compensation of electrons for losses under conditions when transport is greatly affected by electron attachment in strong electronegative gases.

For electrons, we will highlight recent advancements in the determination of the high-order transport coefficients in both atomic and molecular gases. Then we will discuss the elementary physical processes of electrons in the mixtures of gases used to model planetary atmospheric discharges. In particular, we will present the results of our theoretical calculations for expected heights of occurrence of sprites above lightning discharges in atmospheres of planets in our Solar system.

As an example of fluid equation models, we will discuss the recently developed high order fluid model for streamer discharges [3]. The balance equations for electron density, average electron velocity, average electron energy and average electron energy flux have been obtained as velocity moments of Boltzmann's equation and are coupled to the Poisson equation for the space charge electric field. Starting from the cross sections for electron scattering, it will be shown how the corresponding transport data required as input in fluid model should be calculated under conditions when the local field approximation is not applicable. We will illustrate the non-local effects in the profiles of the mean energy behind the streamer front and emphasize the significance of the energy flux balance equation in modeling. Numerical examples include the streamers in N_2 and noble gases.

In the last segment of this talk we will discuss the interaction of primary positrons, and their secondary electrons, with water vapor and its mixture with methane using complete sets of cross sections having bio-medical applications in mind [4]. We will also highlight recent advancements in the testing/validation of complete cross section sets for electrons in biologically relevant molecules, including water vapor and tetrahydrofuran [5].

References

[1] S. Dujko *et al* 2010 *Phys. Rev. E* **81** 056403
[2] R.D. White *et al* 2009 *J. Phys.D: Appl. Phys.* **42** 194001
[3] S. Dujko *et al* 2013 *J. Phys.D: Appl. Phys.* **46** 475202
[4] S. Marjanović *et al* 2015 Plasma Sources Sci. Technol. **24** 025016
[5] White *et al* 2014 *Eur. Phys. J. D* **68** 125

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ESI-Mass spectroscopy of proteins and large biomolecules

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Synopsis We present

Gas phase spectroscopy offers the unique advantage of accessing intrinsic properties in the absence of solvent, and ultimately provides a mean to test theoretical methods. Such an approach is desirable for biological molecules, but this class of compound represents a specific case among the possible targets. Most of biomolecules are fragile and difficult to place in the gas phase intact [1]. In spite of recent developments in vaporization means [2], the collection of potential targets remains limited to small molecules or biopolymers building blocs. The so-called modern ionization technique, such as electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) have demonstrated their potential to place large biomolecules and even complex and fragile assemblies intact in the gas phase, but under ionized form. This last specificity is especially interesting for biomolecules, as a large proportion of these species are ionic in their natural environment in solution. Indeed, nucleic acids are found in anionic form, as well as fatty acids and most of the proteins are basic or acids [3]. However, direct absorption spectroscopy of ions is not trivial and has been reported hitherto only in particular arrangements [4]. Action spectroscopy offers a mean to circumvent the difficulties of measuring the attenuation of photon beams through dilute ion clouds. Hence, mass spectrometry based action spectroscopy provides unprecedented control over the target, such as the ability to control the isotopic content and

elemental composition, the temperature [5], and the molecular shape in combination with ion mobility [6].

Action spectroscopy of polypeptides has been probed using synchrotron radiation in the VUV and soft X-ray ranges. The targets are produced by ESI, stored and irradiated in the photon energy range on interest in an ion trap [7]. The products of the irradiation are monitored by measuring the mass spectrum after photon excitation. This method is sensitive to any changes of the mass to charge ratio of the precursor ion of interest, thereby allowing photoionization, photodetachment and photofragmentation to be detected. All the other decays are hidden to the technique.

References

[1] F. Gaie-Levrel *et al* 2011 *Phys. Chem. Chem. Phys.* **13** 7024
[2] K.R. Wilson *et al* 2006 *J. Phys. Chem. A* **116** 2106
[3] B. Ganisl *et al* 2011 *Eur. J. Mass Spectrom.* **17** 333
[4] A. Terasaki *et al.* 2007 *J. Chem. Phys.* **127** 231101
[5] T.R. Rizzo *et al* 2009 *Int. Rev. Phys. Chem.* **28** 481
[6] G. Papadopoulos *et al* 2012 *J. Am. Soc. Mass Spectrom.* **23** 1173
[7] A.R. Milosavljević *et al* 2012 *J. Synchrotron Radiat.* **19** 174

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TUESDAY

SR

Photodissociation of protonated Leucine-Enkephalin peptide in the VUV range

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Synopsis We present results of VUV action spectroscopy of gas-phase protonated Leucin-Enkephalin peptide. The experiment has been performed by coupling a linear quadrupole ion trap with a synchrotron radiation VUV beamline.

Recent development of experimental methods that use electrospray ion source (ESI) to bring macromolecules into gas phase and collect the ions in an ion trap, which is coupled to bright synchrotron radiation sources, has allowed the investigation of large biopolymers (proteins and nucleotides) under well-defined conditions. These studies can provide more detailed insight into fundamental properties of biopolymers and their interaction with high energy photons.

We present the results of VUV photon action spectroscopy of Leucin-Enkephalin (Leu-Enk) peptide in 5-15 eV energy domain. This peptide has been studied with wide range of spectrometry techniques and has become a standard biomolecular target [1].

The experiment has been performed at the beamline DESIRS [2] of the synchrotron radiation facility SOLEIL near Paris, France. More details about the experimental setup can be found in recent publications [3, 4]. Briefly, precursor ions [Leu-Enk+H]$^+$ were produced by ESI and injected into the ion trap from the front side. Ions were irradiated with monochromatized VUV photon beam, during 500 ms from the back side of the ion trap. After irradiation all ion fragment species were ejected from the ion trap and tandem mass spectra (MS^2) as a function of the photon energies were recorded. Leu-Enk molecules were provided from Sigma Aldrich and dissolved in water/acetonitrile at 10 μM.

Photodissociation ion yields were extracted from the MS^2 and normalized to the total ion current and the photon flux. The ion yields show spectroscopic structure allowing the studying of absorption-like bands of the peptide.

Figure 1 shows the relative ion yield of one of the backbone fragments. The present experimental results are in good agreement with our time dependent density functional theory (TD DFT) calculations.
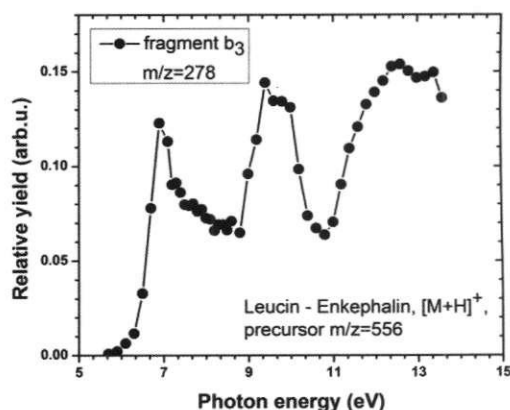

Figure 1. Relative ion yield of fragment b$_3$ from the photodissociation of precursor [Leu-Enk+H]$^+$.

References

[1] S. Bari et al 2011, J. Chem. Phys. 18 **134**, 024314.
[2] L. Nahon et al 2012, J. Sync. Rad. **19**, 508 – 520.
[3] A. Milosavljević et al 2011, Phys. Chem. Chem. Phys. **13**, 15432–15436.
[4] A. Milosavljević et al 2012, J. Sync. Rad. **19**, 174.

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TUESDAY