Selective excision of biomolecules in electron transfer experiments: current developments

Paulo Limão-Vieira* [1]

* Laboratório de Colisões Atómicas e Moleculares, CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

The influence of functional groups on site-selective dissociation of biomolecules (e.g. pyrimidines, purines and their methylated derivatives) has been probed for the first time in charge transfer experiments through time-of-flight mass spectrometry. The decomposition reaction yielding the dehydrogenated parent anion, $(M\text{-}H)^-$, proceeds not only through the breaking of the (C–H) against (N–H) bonds whereas methylated substitution provides an effective way to hydrogen loss exclusively from key sites.

Electron interactions with isolated biomolecules in the gas phase have been extensively investigated because they can efficiently induce substantial yields of single- and double strand breaks in plasmid DNA at impact energies as low as 15 eV [1]. DNA damage was identified by Leon Sanche's group in Canada as due to the fast decay of transient negative resonances localized on the DNA base constituents [2].

These species, e.g. excited atoms and molecules, radicals, ions, secondary electrons, can cause mutagenic, genotoxic, and other potentially lethal DNA lesions [3], such as base and sugar modifications, base release, single strand breaks, and cluster lesions, which include a combination of two single modifications, double strand breaks and cross-links.

As part of our research programme on negative ion formation in atom-molecule collision experiments to explore the routes by which a transient negative ion decomposes either through direct or even statistical dissociation [4], we have investigated collisional excitation and dissociation processes in biomolecules [5-9] to explore the role of site- and bond-selectivity in pyrimidines [10] and purines [11]; the role of the collision complex and how it influences new fragmentation pathways; and competitive and even concerted fragmentation mechanisms.

In this talk I will present the most recent experimental data on negative ion formation in electron transfer experiments from collisions of neutral potassium atoms with adenine and its derivative, probing the influence of functional groups on the molecular decomposition processes.

References

[1] I. Baccarelli *et al* 2011 *Phys. Rep.* **508** 1.
[2] B. Boudaïffa *et al* 2000 *Science* **287** 1658.
[3] C. von Sonntag 2005 *Free-Radical-Induced DNA Damage and Its Repair. Springer: New York*.
[4] A. Rebelo *et al* 2016 *Eur. Phys. J. D* **70** 130.
[5] D. Almeida *et al* 2011 *Phys. Chem. Chem. Phys.* **13** 15657.
[6] D. Almeida *et al* 2011 *Phys. Chem. Chem. Phys.* **13** 15657.
[7] D. Almeida *et al* 2014 *J. Phys. Chem. A* **118** 6547.
[8] D. Almeida *et al* 2013 *J. Chem. Phys.* **139** 114304.
[9] F. Ferreira da Silva *et al* 2016 *Chem. Phys. Lett.* **662** 19.
[10] D. Almeida *et al* 2013 *Phys. Rev. Lett.* **13** 15657.
[11] T. Cunha *et al* 2016 in preparation.

[1] E-mail: plimaovieira@fct.unl.pt