



**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

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

M. Lj. Ranković<sup>1</sup>, V. Cerovski<sup>1</sup>, F. Canon<sup>2</sup>, L. Nahon<sup>3</sup>, A. Giuliani<sup>3,4</sup> and A. R. Milosavljević<sup>1</sup>

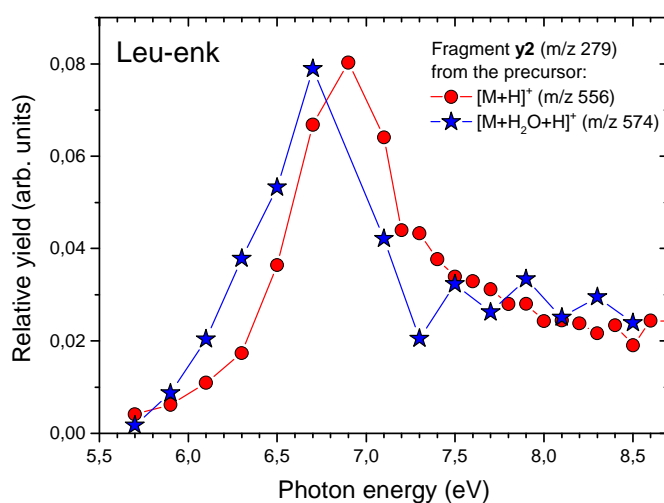
<sup>1</sup> *Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia*

<sup>2</sup> *INRA, UMR1324 Centre des Sciences du Goût et de l'Alimentation, F-21000 Dijon, France*

<sup>3</sup> *SOLEIL, l'Orme des Merisiers, St Aubin, BP48, 91192 Gif sur Yvette Cedex, France*

<sup>4</sup> *INRA, UAR1008, CEPIA, Rue de la Géraudière, BP 71627, 44316 Nantes, France*

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  $[\text{Leu-enk}+\text{H}]^+$  (circles) and  $[\text{Leu-enk}+\text{H}_2\text{O}+\text{H}]^+$  (stars) precursors.

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

I. Bačić<sup>1</sup>, M. Lj. Ranković<sup>1</sup>, F. Canon<sup>2</sup>, V. Cerovski<sup>1</sup>, C. Nicolas<sup>3</sup>, A. Giuliani<sup>3,4</sup> and A. R. Milosavljević<sup>1</sup>

<sup>1</sup> Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

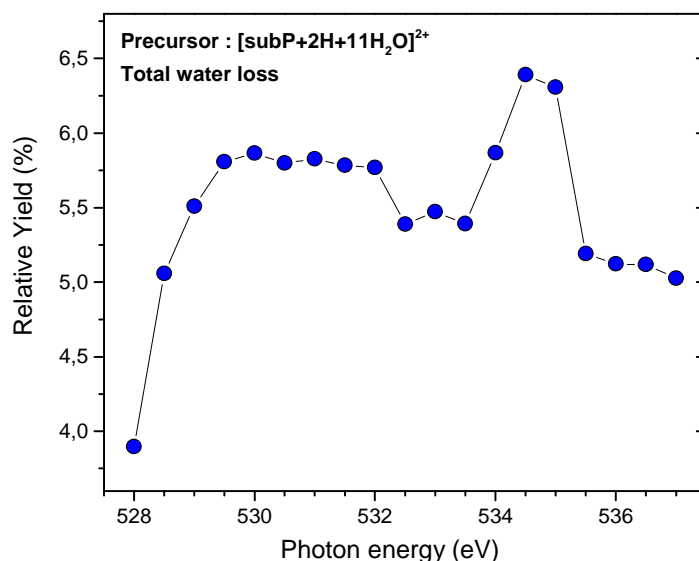
<sup>2</sup> INRA, UMR1324 Centre des Sciences du Goût et de l'Alimentation, F-21000 Dijon, France

<sup>3</sup> SOLEIL, l'Orme des Merisiers, St Aubin, BP48, 91192 Gif sur Yvette Cedex, France

<sup>4</sup> INRA, UAR1008, CEPIA, Rue de la Géraudière, BP 71627, 44316 Nantes, France

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-NH<sub>2</sub>) 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 Finnigan 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).

**Acknowledgements:** Supported by ANR-08-BLAN-0065 (France), MESTD (Serbia) (projects 171020 and 171033) and COST Action XLIC. SOLEIL general staff (project 20140023).

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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 Aleksandar Milosavljević  
The Meeting Chairs*

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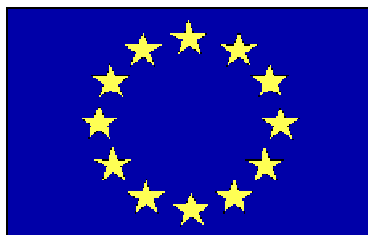
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