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SOCIETÀ ITALIANA LUCE DI SINCROTRONE
ITALIAN SYNCHROTRON RADIATION SOCIETY

MOST@Elettra 2.0 Workshop

Trieste
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POSTER SESSION

- P1:** **Laura Carlini**, CNR– ISM Roma
“Peptide bond formation and decomposition in linear and cyclic dipeptides”
- P2:** **Alessandra Ciavardini**, CERIC – ERIC Trieste
“Peptide bond formation and decomposition in linear and cyclic dipeptides”
- P3:** **Emanuele Coccia**, Università degli studi di Trieste
“Role of coherence in ultrafast spectroscopies on single molecules and nanostructures”
- P4:** **Sergio D’Addato**, Università di Modena e Reggio Emilia e CNR - NANO
“Magnetic and plasmonic metal@oxide, core@shell nanoparticles: a fundamental case study for advanced synchrotron radiation techniques”
- P5:** **Alessandro D’Elia**, Università degli studi di Trieste e CNR - IOM
“XUV investigation of free metal cluster and nanostructured films”
- P6:** **Cesare Grazioli**, CNR – IOM Trieste
“ULLA: end-station for photoionization spectroscopy of free organic molecules”
- P7:** **Ambra Guarnaccio**, CNR – ISM Potenza
“Photoionization and electronic structure of π -conjugated organic molecules for organic photovoltaics”
- P8:** **La Mattina**, EMPA, Dübendorf, Switzerland
“Charge induced structural reconstruction at buried STO/YBCO interface”
- P9:** **Valeria Lanzilotto**, Università di Roma La Sapienza
“XPS micro liquid-jet of melamine in aqueous solution”
- P10:** **Aurora Ponzi**, Institut Ruđer Bošković, Zagreb, Croatia
“Calculation of MFPADs profiles for different excited states of acetylacetone”
- P11:** **Javad Rezvani**, INFN Roma
“Shaping of Synchrotron radiation beams by spherically bent optical devices”
- P12:** **Luca Schio**, Università di Roma La Sapienza e CNR – ISM Trieste
“Photoelectron and nuclear dissociation dynamics of gas phase molecules studied with Synchrotron Radiation”
- P13:** **Andrea Sterzi**, EMPA, Dübendorf, Switzerland
“WO₃ hydrogenation probed by high pressure photoemission”
- P14:** **Daniele Toffoli**, Università degli studi di Trieste
“Development of a CIS/TDDFT B-spline Scattering Code for Molecular Ionization Processes in the Weak and Strong-Field Regimes”
- P15:** **LDM beamline**, Elettra Sincrotrone Trieste
“The Low Density Matter beamline at the FERMI Free Electron Laser”

P1 - Peptide bond formation and decomposition in linear and cyclic dipeptides

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Synopsis The peptide bond formation and decomposition is studied by photoelectron spectroscopy, time-of-flight mass spectrometry and photoelectron-photoion coincidence (PEPICO) spectroscopy in a series of isolated linear and cyclic-dipeptides. Interesting cyclization mechanisms are observed.

It has been proposed that a dynamic chemical process [1,2], which involves the coupling of the condensation of α -aminoacids into peptides with the peptide degradation 'returning' individual aminoacids, may have provided an effective mechanism for reshuffling and building up the complexity of aminoacid sequences preceding the emergence of life. These processes rely on peptide bond formation and cleavage mechanisms, respectively, and can be influenced by the presence of activating agents, chemical precursors or the delivery of energy in a proper environment.

Our group has undertaken a study of the peptide bond formation and degradation on the simplest aminoacids, the cyclic (c) and linear (l) dipeptides in the gas phase, by photoionisation and ion collision experiments. In the poster, we will present preliminary results on the study of c- and l- GlyGly, AlaAla, GlyPhe, GlyAla and of l-PheAla by mass spectrometry and PEPICO experiments.

The mass spectra of the l- species have shown a common pattern of fragmentation, with i) dominance of the m/z peak attributable to the cyclic structure, ii) very strong similarities between the measured mass spectra in l- and c-structure, with the associated observation that iii) parent ion and fragments attributable to the l-species, if present at all, diminish with time until they disappear. All of this suggests that cyclisation phenomena may happen in the l-species at some stage of the experimental procedure, driven by either the temperature in the condensed phase or the 'electrostatic forces' in the unstable zwitterion produced in the sublimation, or due to the fast rearrangement of the highly reactive cation following ionisation.

In the l-AlaAla molecule, for example, a careful characterisation of the mass spectrum (Figure 1) as a function of the temperature as well as the IR spectra of the sample analysed before and after thermal evaporation, consistently indicate a temperature induced cyclisation in the condensed phase, prior to sublimation. Different scenarios may arise in other samples, suggesting that a complex and not easily predictable chemistry occurs already at the stage of simple dipeptides and the limit of feasibility for the study of polypeptides produced in gas phase by thermal vaporation is very rapidly reached. In the framework of the MOlecular Science and Technology (MOST), the implementation of an end-station, which combines an ElectronSpray Ionization Source with electron and ion spectroscopies will allow to make a step forward in the study of peptide chains in their natural conformation, controlling molecular stability, preventing the linear dipeptides cyclization or

decomposition and, eventually, increasing the peptides chain elongation.

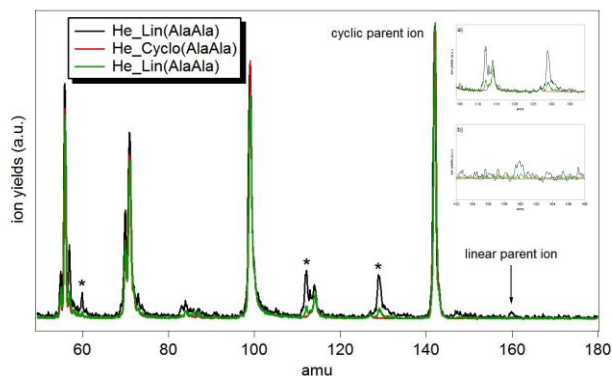


Figure 1. The mass spectra of *l*- and *c*-AlaAla at photon energy 21.22 eV are reported in black and red, respectively. The *l*-AlaAla spectrum collected after 24h at the same sublimation temperature (green) clearly shows the disappearance of the parent ion and associated fragments (indicated by the *). In the inset a) and b) are shown the amu range 105-140 (associated fragments) and 152-168 (parent ion), respectively.

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