Book of Abstracts

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Gas-phase linear and cyclic dipeptides: a study of peptide bond formation and decomposition

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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 mechanism are observed.

We have undertaken a study of the peptide bond formation and degradation on the simplest peptides, the cyclic (*c*) and linear (*ℓ*) dipeptides in the gas phase, by photoionisation and ion collision experiments. In the poster, preliminary results on the study of *c*- and *ℓ*- GlyGly, AlaAla, GlyPhe, GlyAla and of *ℓ*-PheAla by mass spectrometry and PEPICO experiments are presented. These measurements show that the most important fragmentation channel is the loss of the OCHN (43 amu) moiety, with the resulting charge fragments at m/z 99 and 85 in c-AlaAla and c-GlyAla, respectively. The lighter fragments at m/z 44 (c-AlaAla) and 30 (c-GlyAla) become important for binding energies >12 eV and are likely related to sequential rearrangement and secondary fragmentation of larger fragments.

The mass spectra of the *ℓ*- species show a common pattern of fragmentation, dominated by m/z peaks attributable to the cyclic structure. The parent ion and fragments attributable to the *ℓ*-species, if present at all, diminishing with time.

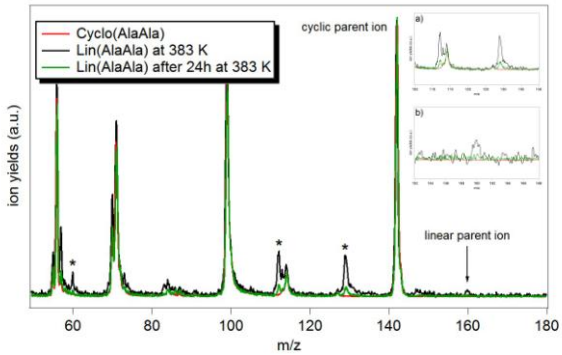

Figure 1. *The mass spectra of ℓ-(black curve) and c-(red curve) AlaAla at photon energy 21.22 eV. The ℓ-AlaAla spectrum (green curve) after 24h at the same sublimation temperature clearly shows the disappearance of the parent ion and associated fragments (indicated by the *). Insets a) and b) show the m/z ranges 105-140 and 152-168, respectively.*

These observations may suggest that cyclisation occurs at some stage of the experimental procedure [1,2,3], driven either by the temperature in the condensed phase or the 'electrostatic forces' in the unstable zwitterion produced in the sublimation or the fast rearrangement of the highly reactive cation following ionisation. In the *ℓ*-AlaAla molecule, for example, a careful characterisation of the mass spectrum as a function of the temperature (Figure 1) suggests a temperature induced cyclisation in the condensed phase, prior to sublimation. This hypothesis, in the case of *ℓ*-PheAla molecule has been confirmed by IR measurements of the sample before and after sublimation (Figure 2).

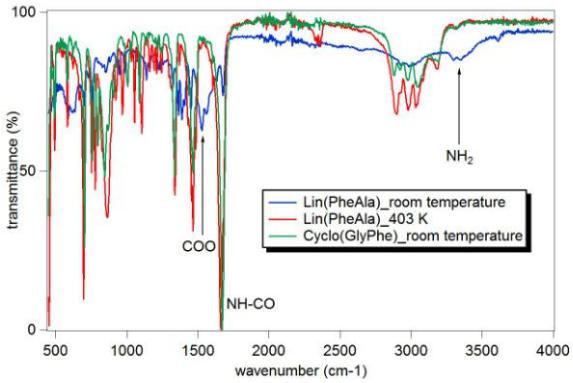

Figure 2. *Comparison of the ℓ-PheAla and c-GlyPhe IR spectra. The IR spectrum of ℓ-PheAla at 403 K shows evidences of cyclisation: the high intensity of the NH-CO signal and the disappearance of the NH2 and COO signals.*

Different samples, however, have shown different behaviours, suggesting that a complex and not easily predictable chemistry occurs. This sets a limit of feasibility for the study in the gas phase of polypeptides by thermal evaporation.

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