Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: CA20129

Grantee name: Paola Bolognesi

Details of the STSM

Title: Pathways of peptide bond formation and degradation in cyclic dipeptides

Start and end date: 04/09/2022 to 10/09/2022

Description of the work carried out during the STSM

The purpose of this STSM was to perform experiments to investigate the process of peptide bond formation and degradation on cyclic dipeptides in the environment provided by homogeneous and hydrated clusters of cyclic dipeptides. The cyclic-Alanine-Alanine molecule, cAA, and cyclic-Glycine-Glicine, cGG, were widely investigated and characterized by photoionization experiments performed at Elettra. In those experiments, supported by quantum chemical calculations, the cAA sample for example was proposed as a molecule of potential interest for the survival of the bimolecular species as well as an intermediated for the polymerization of aminoacids. These models were based on theoretical studies of the reactivity among fragmentation product of cAA.

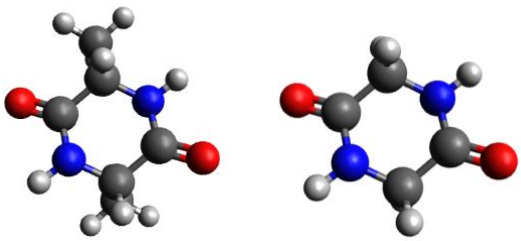

***Figure 1**: The cAA ($C_6H_{10}N_2$, m = 142 Da) and cGG ($C_4H_6N_2$, m = 114 Da) samples.*

Even though the COLIMACON setup is equipped with two independent oven sources to study isolated molecules and clusters, the cleaning and refilling of the ovens with a new sample takes about 12 hours to reach again working condition. Furthermore, the time needed to collect a sufficient statistics in the ion-ion coincidence maps and for changing between isolated molecule and cluster (that still implies turning off one oven, and heating up the other one) did not allow to study more than two species in the given 5 days of the beamtime.

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

As projectile, we selected an incident beam H^+ ions at 16 keV, as representative of the largest contribution to the radiation in solar wind.
The experimental results are summarised in figures 2-4. Figure 2 shows the mass spectra of the cAA and cGG collected at a temperature of 90 and 150°C, respectively.

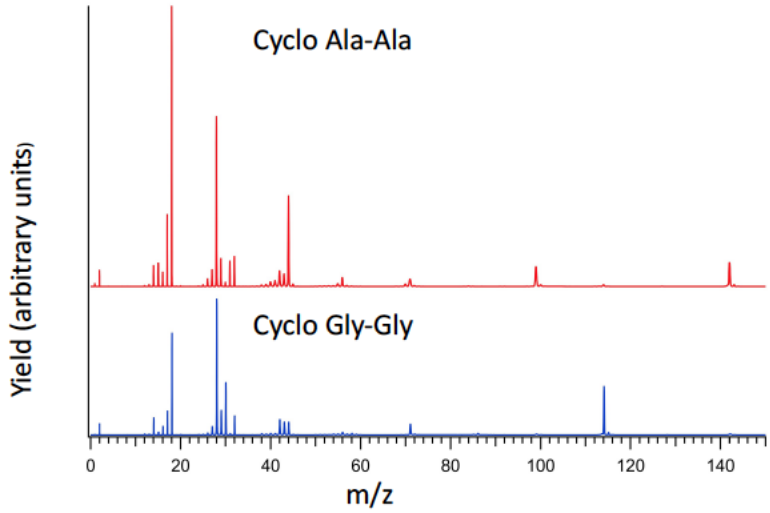

***Figure 2**. The mass spectra of the cAA (top) and cGG (bottom).*

Figure 3 reports the mass spectra of cAA (left) and cGG (right) clusters collected at 140 and 190°C, respectively. The thermal stability at these higher temperatures needed for the cluster experiments was tested on the isolated molecule measurement.

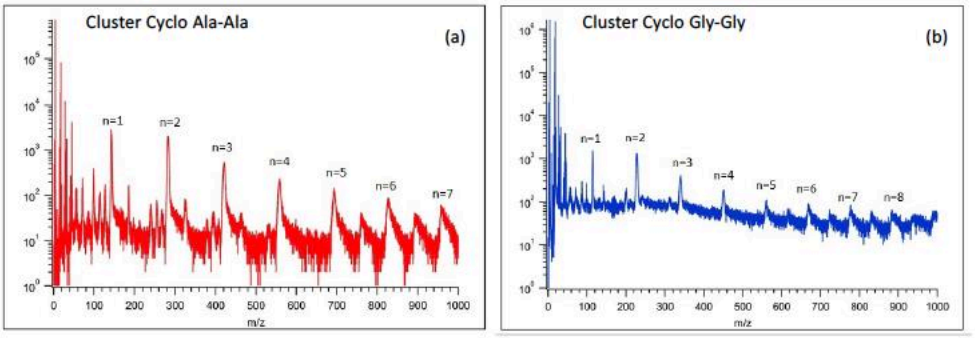

***Figure 3.** The mass spectra of the cAA (left) and cGG (rigth) clusters.*

The interaction with low energy protons can lead, both in the isolated molecules and in the cluster, to the formation of doubly/multiply charged ions, which can be clearly observed with ion-ion coincidence measurements, based on the multi-hit capability of the detector in the time-of-fligth of the COLIMACON set-up. These experiments imply long acquisition times, because they require low incident flux in order to minimise random events that could hide true ones. Due to the limited beamtime available, coincidence experiments have been performed only on cAA isolated molecule and cAA, cGG clusters. The results are shown in the 2D maps of figures 4.

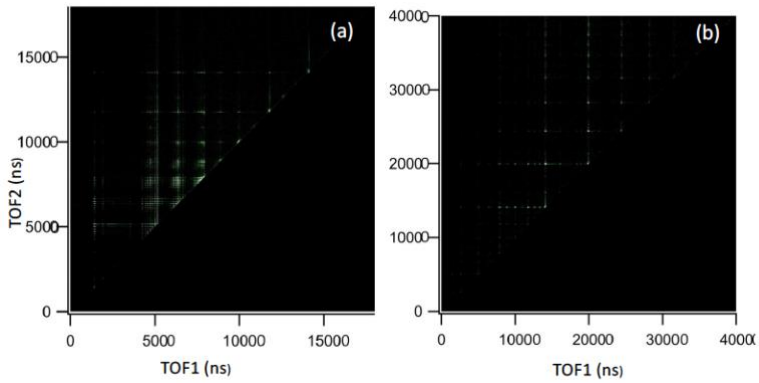

Figure 4. *Ion-Ion coincidence maps for cAA (left) and cGG (rigth).*

Description of the STSM main achievements and planned follow-up activities

The activities of this STSM fit in the program of the Rome group to investigate processes of peptide bond formation and degradation in the environment provided by homogeneous and hydrated clusters of cyclic dipeptides. Intramolecular reactions of neighboring chemical groups may provide efficient opportunities for peptide formation as well as degradation. These molecular rearrangements can be triggered by activating agents, like chemical precursors, or by energetic processes due to particles interactions, like in ion collisions. It is this latter aspect that has been the object of experiments performed at the ARIBE facility during the STSM.

A analysis of the results has been undertaken and will take some time. As a general observations, it can noticed how the proton induced mass spectra of cAA and cGG (figures 2) show similarities as well differences with respect to the mass spectra acquired at Elettra. All the features present in the photon induced mass spectra are observed also in ion collision. However, the relative intensity is different and additional fragments are present in the proton collision spectra. This may be explained by the differences between ion collision and photoionization in the energy transfer to the target, including the broader energy distribution, the knock out process and the significant contribution from the double ionization of the target, that can alter the intensity ratio of some fragments and give rise to features not observed in the photon spectrum. The production of doubly charged ions is clearly proved by the results of the ion-ion coincidence experiments (figure 4).

In the mass spectra of clusters of the cAA and cGG (figure 3), clusters up to n=7 and n=8 units, respectively, are measured. In these spectra the same pattern is observed between clusters with n and n+1 monomers, and these features well match some fragments observed in the isolated molecule. These features can be assigned either to a cluster with n+1 molecules which has lost a fragment or a covalently bond fragment to n molecules. The correct assignment will be attempted by the calculation of the minimum energy structure that will be performed by the Madrid group that already studied the potential energy surfaces of cAA and cGG (1,2).

The future work will involve:

1) the detailed analysis of the present data performed in collaboration between the Rome and Caen experimental groups, while the interpretation of the data will rely on the simulation done in Madrid
2) experiments to be continued in 2023. To the purpose other five days of beamtime have been already allocated. This will allow to complete the investigation of the remaining molecules of the set indicated in the application and, if the time will allow, to study the effect of hydration

REFERENCES

[1] J. Phys. Chem. Lett. 12 (2021) 7379; [2] Phys. Chem. Chem. Phys. 24 (2022) 5855