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

Action number: CA20129

Grantee name: Lorenzo AVALDI

Details of the STSM

Title: **Pathways of peptide bond formation and degradation in cyclic dipeptides studied by ion collision experiments**

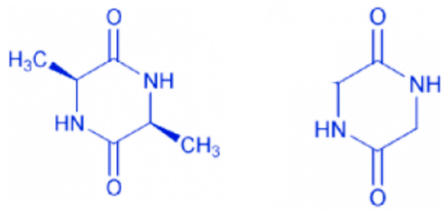
Start and end date: 4/9/2022 to 10/9/2022

Description of the work carried out during the STSM

Description of the activities carried out during the STSM. Any deviations from the initial working plan shall also be described in this section.

(max. 500 words)

During the five days of the STSM ion induced fragmentation of cyclo-Ala-Ala, cyclo-Gly-Gly dipeptide molecules (Figure 1) and their homogeneous clusters have been studied at the COLIMACON end station of the ARIBE facility in Caen.



cyclo-(Ala-Ala) cyclo-(Gly-Gly)

These samples represent a subset of the samples mentioned in the application. This is due the time needed to collect a sufficient statistics in the ion-ion coincidence experiments and for changing target. The latter action implies the cleaning of the sources and about 12 hours to reach the operational vacuum condition. The two samples are commercially available and have already been characterised by photoionisation experiments (J. Phys. Chem. Lett. 12 (2021) 7379, Phys. Chem. Chem. Phys. 24 (2022) 5855). Being powders at room temperature, the molecules require an oven to be desorbed. However they are very stable and robust against thermal decomposition, as proved by the experiments performed at the CNR-ISM laboratories in Rome. They have been chosen because they have been both studied in recent photoelectron-photoion (PEPICO) experiments (J. Phys. Chem. Lett. 12 (2021) 7379, Phys. Chem. Chem. Phys. 24 (2022) 5855) at Elettra.

[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.

An incident beam of 16 KeV H^+ ions has been chosen as projectile, because protons provide the largest contribution to the radiation in space in particular in the solar wind.
The experiments performed are summarised in figures 2-4. In these experiments we exploited the unique characteristic of the COLIMACON set-up that allows to mount two difference sources (one for the molecules and one for the clusters) in the two arms of the set-up. This provision allows to switch from molecules to clusters without breaking vacuum and therefore optimizes the time devoted to the experiment. In figure 2 the mass spectra of the cyclo-Ala-Ala and cyclo-Gly-Gly dipeptide molecules are shown. The spectra have been collected at a temperature of 90 and 150°C for cyclo-Ala-Ala and cyclo Gly-Gly, respectively. A study as a function of heating temperature has confirmed the stability of cyclo-Ala-Ala up to 150°C.

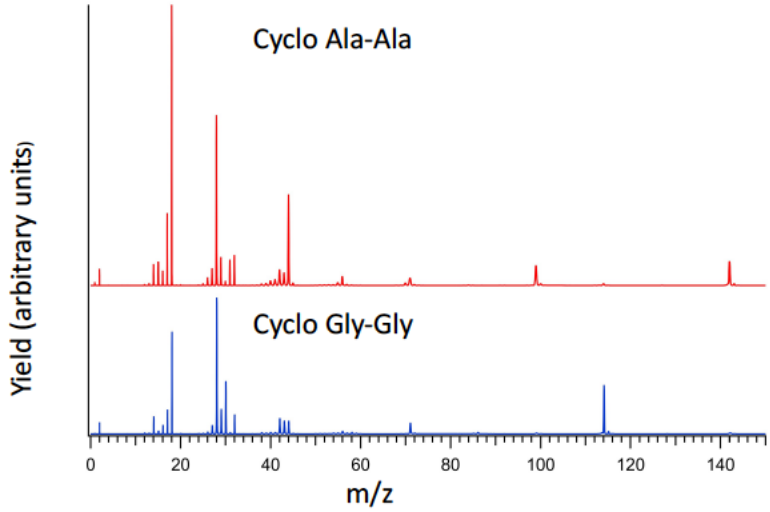


Figure 2 : Mass spectra of the cyclo-Ala-Ala (top) and cyclo-Gly-Gly (bottom) molecules.

In figure 3 the mass spectra of the cyclo-Ala-Ala (a) and cyclo-Gly-Gly (b) dipeptide clusters are shown. The spectra have been collected at a temperature of 140 and 190°C cyclo-Ala-Ala and cyclo Gly-Gly cluster, respectively.

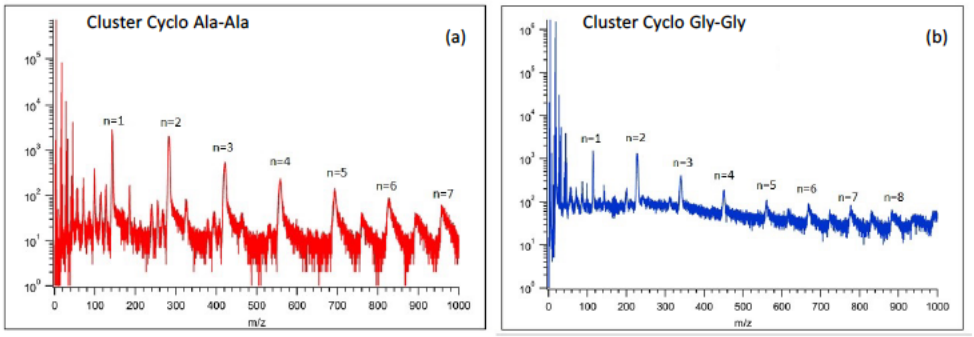


Figure 3 : Mass spectra of the cyclo-Ala-Ala (a) cyclo Gly-Gly (b) clusters.

The interaction of a low energy proton with a molecule or a cluster can lead to the formation of doubly/multiply charged ions. A suitable method to characterize the process is to detect two charged fragments in time coincidence. Such an experiment is possible in the time-of-flight spectrometer of the Colimacon end-station by detecting multiple stop events. This type of experiments implies long acquisition time, because they are run with a low incident flux in order to avoid that random events completely mask the true ones. Due to the limited beamtime available, coincidence experiments have been performed only on cyclo-Ala-Ala molecules and clusters. The results are shown in the 2d maps of figure 4(a) and (b).

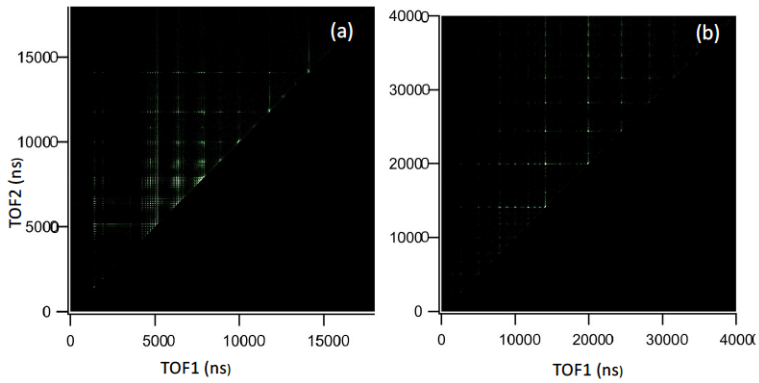


Figure 4. Ion-Ion coincidence maps in the case of cyclo-Ala-Ala molecules (a) and clusters (b)

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

Description and assessment of whether the STSM achieved its planned goals and expected outcomes, including specific contribution to Action objective and deliverables, or publications resulting from the STSM. Agreed plans for future follow-up collaborations shall also be described in this section.

The activities of this STSM fit in the program of the Rome group to investigate the processes of peptide bond formation and degradation in the environment provided by homogeneous and hydrated clusters of aminoacids and cyclic dipeptides. Intramolecular reactions of neighbouring chemical groups are very 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 the crossed beam experiments performed at the ARIBE facility during the STSM.

A detailed analysis of the results has been undertaken and will take some time, but from a fast and preliminary analysis some observations can be made.

The proton induced mass spectra of cyclo-Ala-Ala and cyclo-Gly-Gly dipeptides in figures 2(a,b) show some similarities as well differences with the mass spectra acquired at Elettra. All the features present in the 60 eV photon induced mass spectra are observed also in ion collision. The relative intensity of the features is different and some extra features in the proton collision spectra are observed. This may be due to several differences of the proton collision with respect to the photoionisation process, including the broad energy distribution of the energy transfer, 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 further proved by the results of the ion-ion coincidence experiments shown in figure 4.

In the mass spectra of the cyclo-Ala-Ala and cyclo-Gly-Gly dipeptide clusters (Figure 3), clusters up to n=7 have been observed in the case of cyclo-Ala-Ala and up to n=8 in the case of cyclo-Gly-Gly. In these spectra the same pattern is observed between clusters with n and n+1 dipeptide molecules and well match some fragments observed in the dipeptide molecule. These features can be assigned either to the cluster with n+1 molecules which has lost a fragment or a covalently bond fragment to the cluster with n molecules. The correct assignment can be achieved only by the calculation of the minimum energy structure. These calculations will be performed by the Madrid group that already studied the potential energy surfaces of cyclo-Ala-Ala and cyclo Gly-Gly dipeptides (J. Phys. Chem. Lett. 12 (2021) 7379, Phys. Chem. Chem. Phys. 24 (2022) 5855).

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) the experiments will be continued in 2023 and 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