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

Action number: **CA20129**

Grantee name: **Laura Carlini**

Details of the STSM

Title: Peptide bond formation and degradation in linear and cyclo dipeptides under swift ion irradiation

Start and end date: 02/05/2023to 13/05/2023

Description of the work carried out during the STSM

The purpose of the present STSM was to irradiate films of aminoacids and linear (*l*-) and cyclic (*c*-) dipeptides with a fast ion beam of C^{4+}, and measure infrared (IR) spectra at regular, increasing, amounts of radiation dose delivered to the samples. These IR spectra carry information of the stability of the pristine molecules under irradiation and of the formation of new species.

The activity of this STSM has been divided in two parts.

03/05/2023 - 06/05/2023. During the first days of the STMS I deposited films of aminoacids and dipeptides onto ZnSe substrates by drop-casting procedure, optimizing the conditions to obtain homogeneous films of thickness between 0.5-1.0 µm. Different tests have been carried out on solubility and deposition procedure to obtain suitable films of samples to be irradiated. The films have been characterized off-line by transmission IR spectroscopy at room temperature (RT) and compared with literature data and our previous measurements on the pristine sample in powder. No evidences of degradation have been detected (see Figure 1).

[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.

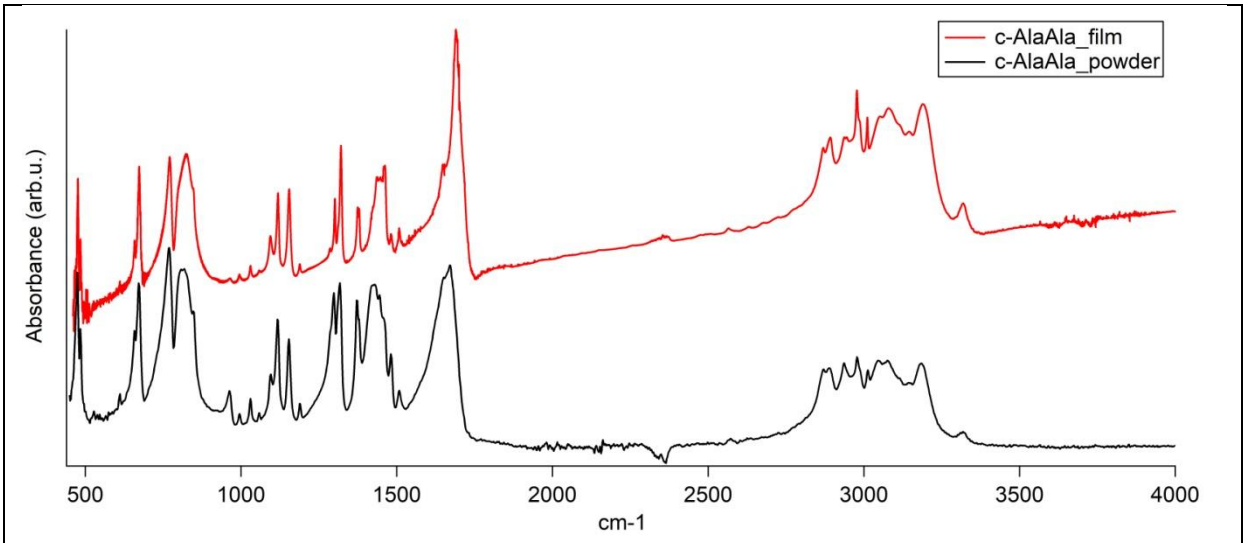

Figure 1. *Comparison between IR spectra of c-AlaAla deposited by drop-casting onto ZnSe window (red curve) and pristine c-AlaAla in powder (black curve).*

After a careful characterization, the films of Ala, *c*-AlaAla, *l*-AlaAla, *c*-GlyGly, *l*-GlyPhe, *c*-GlyPhe, *l*-PheAla have been selected for the ion beam irradiation. Other samples originally planned (Gly, *l*-GlyAla, *c*-GlyAla and *l*-GlyGly) could not be prepared with sufficient uniformity and quality, probably due to poor solubility and/or interaction with the ZnSe windows needed for the IR irradiation. An image of the film of *l*-AlaAla is reported in Figure 2.

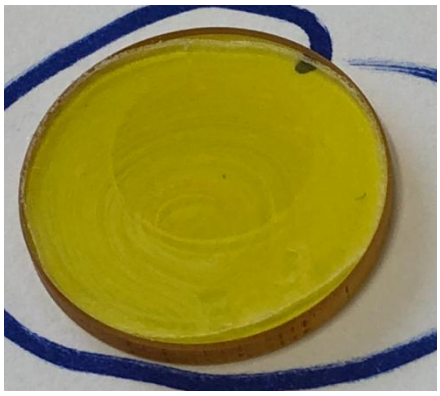

Figure 2.

Photo of the film of l-AlaAla deposited by drop-casting on a ZnSe window. The deposition was obtained drop casting a solution of 30 mg of sample in 100 ml (1 : 1 = water : ethanol).

The inner ring shows the area of ion beam irradiation.

Each sample deposition was tested off-line by IR before being inserted under vacuum for ion beam irradiation.

07/05/2023 - 12/05/2023. We performed ion beam irradiation experiments on the films using the IGLIAS set-up at the IRRSUD beamline. For each sample, we irradiated the film with $^{12}C^{4+}$ ions of 0.98 MeV/u and measured IR spectra at several well-defined doses, up to an ion beam fluence of $2x10^{13}$ ions/cm^2 with an average flux of $2x10^9$ ions x second/cm^2 integrated over 5 minutes. Figure 3 reports an example of such type of measurements for *c*-AlaAla. The spectra clearly show the evolution of the main features, which in general decrease in intensity, and show broadenings and shifts due to the decomposition of the pristine sample and the overlapping signal due to new species being created.

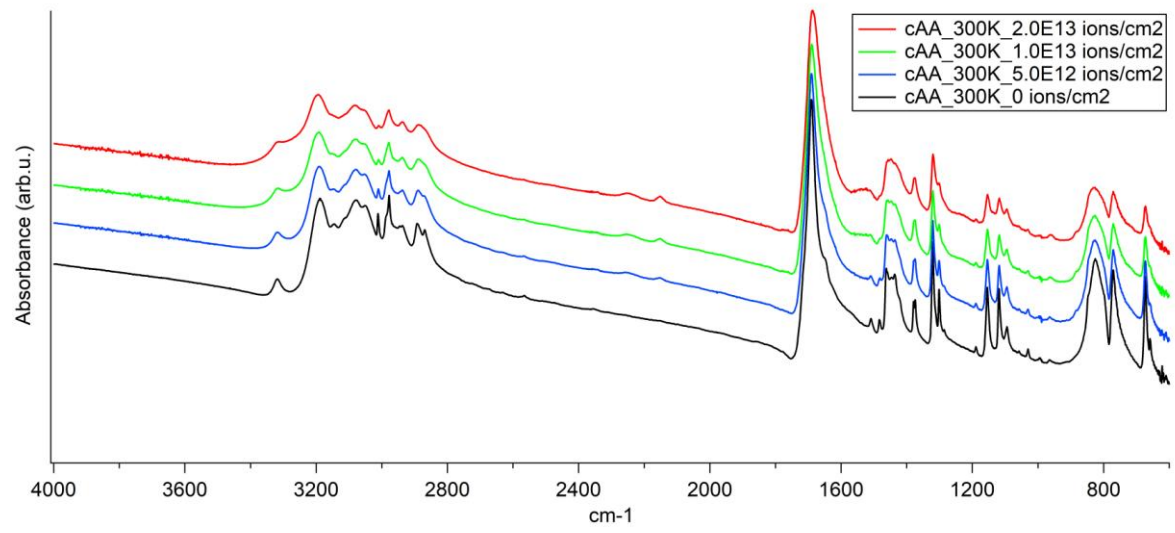

Figure 3. *Some IR spectra of c-AlaAla film irradiated at room temperature (300 K) are reported with their respective values of radiation dose. Spectra are displaced in the vertical axis.*

The main aims of this experiment were to

i) verify the release of important prebiotic species like CO_2, CO, HCN, HNCO. In most cases, it is difficult to disentangle newly formed species if their typical IR fingerprints fall in a region already crowded with many features. However, some newly formed species having typical IR fingerprint in a previously 'flat' region allow for more clear identification. This is the case for example for the features at about 2100 - 2400 cm^{-1} in Figure 3. A theoretical investigation, currently running, will support assignment of these species.

For the case of *l*- and *c*-AlaAla, the samples were also irradiated at temperatures of 80 K and 10 K, in order to mimic realistic conditions in solar system and deep space, respectively. Interestingly, volatile species are more efficiently trapped into the film measured at low temperature (see Figure 4).

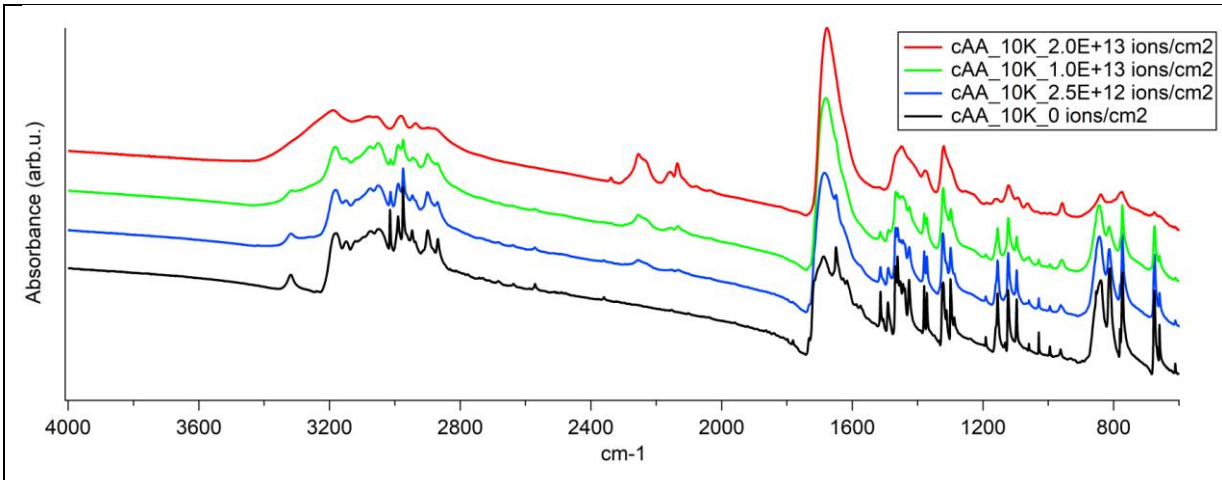

Figure 4. *Some IR spectra of c-AlaAla film irradiated at a temperature of 10 K are reported with their respective values of radiation dose. Spectra are displaced in the vertical axis.*

ii) search for experimental evidence of the theoretically predicted mechanism of reactivity; in particular the formation of cationic oxazolidinone and neutral aziridine. Preliminary calculations by theoreticians in our team predicted the signal of oxazolidinone and aziridine in the region of the C=O stretching to be significantly blue shifted with respect to CO containing fragments of linear structure. These distinctive frequencies have not been clearly observed at first sight, but further analysis will be done.

iii) search for direct experimental evidence of cyclization of linear dipeptides. Linear and cyclic structure of dipeptides have distinct features in the IR spectra due to the diketopiperazine ring. Thermal cyclization was already indirectly observed in *l*-PheAla [1]. The present experiments, that consider two sets of linear and cyclic dipeptides (AlaAla and GlyPhe) will allow investigating mechanisms of cyclization induced by ion irradiation.

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

This STSM was very successful. The measured samples will allow to explore the role of i) linear and cyclic structure, ii) different aminoacids, iii) dose irradiation and iv) temperature in survival strategies (cyclization of linear dipeptides, radioresistance, reactivity) and polimerization mechanisms in these highly interesting and intriguing species along the path of evolution of life.

These outputs, in agreement with some of the main objectives of the CA20129 MultIChem, may help to answer fundamental questions on irradiation-driven processes on very intriguing classes of bio-molecules (*l*- and *c*-dipeptides) and investigate potential mechanisms that can lead to their survival in harsh astrochemical conditions and eventually promote the self-assembling of aminoacids into peptides.

The follow-up activities involve detailed analysis of the data collected during the beamtime in collaboration with the IRRSUD scientific staff and our theoretician colleagues in Madrid and Rome. The careful comparison between experimental and theoretical IR spectra will allow to identify the formation of the structures mentioned previously (such as oxazolidinone and aziridine intermediates and CO_2, CO, HCN, HNCO species) and investigate the changes observed between the spectra at room temperature and at 80 and 10 K.

I thankfully acknowledge the MultIChem Cost Action support for this work.

References

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[3] Jacopo Chiarinelli, Dario Barreiro-Lage, Paola Bolognesi, Robert Richter, Henning Zettergren, Mark H. Stockett, Sergio Daz-Tendero, Lorenzo Avaldi, Phys. Chem. Chem. Phys., 2022, 24, 5855-5867.

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