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

Action number: CA20129

Grantee name: Or Licht

Details of the STSM

Title: Search for Chiral Effects in Peptide Bond Formation of Mixed Amino Acid Clusters

Start and end date: 20/05/2024 to 27/05/2024

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 Short-Term Scientific Mission (STSM) at the DESIRS beamline in the SOLEIL synchrotron, we focused on investigating the chiral effects in peptide bond formation (PBF) within mixed amino acid clusters. Our primary objective was to explore whether there is a chiral preference in intra-cluster bond formation (ICBF) between different amino acid dimers, specifically looking at combinations of serine (Ser), threonine (Thr), and valine (Val).

Our experimental setup involved the production of protonated amino acid dimers via electrospray ionization. These dimers were then mass-selected and subjected to UV irradiation within the range of 7-14 eV. The resulting photo-induced dissociation (PID) spectra were recorded, with particular attention to fragments indicative of ICBF. The MS^3 technique was employed to verify that these fragments originated from ICBF.

We initially expanded our previous studies on protonated serine dimers by including mixed dimers such as Ser-Thr and Ser-Val. For each combination, we studied three enantiomers: LL, LD, and DL. In addition, we examined the corresponding dipeptides to compare fragmentation patterns and confirm peptide bond formation.

[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.

During the beamtime, we also initiated studies on dimers of L-cysteine with L/D-serine and L/D-threonine. Regular meetings with the theory group facilitated discussions on conformer optimization and electronic excitation studies, aiming to correlate theoretical predictions with our experimental data.

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.

(max. 500 words)

Our primary achievements during the STSM include the identification of chiral effects in peptide bond formation within mixed amino acid clusters. Notably, we observed significant differences in fragmentation patterns between L-L and L/D-D/L dimers in the Ser-Thr combination. As expected, D-L and L-D dimers produced symmetric fragments, consistent with their symmetric nature. As opposed to the L/D-D/L In the case of L-L we have indicated a high yield of a fragment that corresponds to the loss of a water molecule, suggesting peptide bond formation.

Comparative analysis with the corresponding dipeptide fragmentation revealed similar behavior as a function of photon energy, reinforcing the occurrence of peptide bond formation.

Further, our studies on L-cysteine with L/D-serine and L/D-threonine dimers showed substantial differences between L-L and L-D fragments, particularly peptide bond-related fragments for the L-L Cys-Thr dimers. However, these findings necessitate further investigation and experimentation with corresponding dipeptides for comprehensive understanding.

The combination of experimental and theoretical results will further advance our understanding of photon irradiation effects on amino acid clusters, and the observation of chiral preference in bond formation within mixed amino acid dimers aligns with WG1's objectives to explore and understand the selectivity in photo-induced chemical processes. This work provides new insights into how chirality influences chemical reactions in molecular clusters. The experimental findings, supported by theoretical simulations, offer mechanistic insights into peptide bond formation in protonated dimers. This knowledge is crucial for understanding the pathways leading to the formation of complex organic molecules, contributing to the broader objective of unraveling the origins of homochirality in biological systems.

Moving forward, our collaboration with the theory group will continue, focusing on optimizing conformers of threonine and valine and performing electronic excitation studies. These efforts aim to match theoretical models with our experimental results, enhancing the understanding of chiral effects in peptide bond formation. As both data analysis and theoretical work will be done, we expect to publish papers regarding our results, both for the chiral preference, and the peptide bond formations.

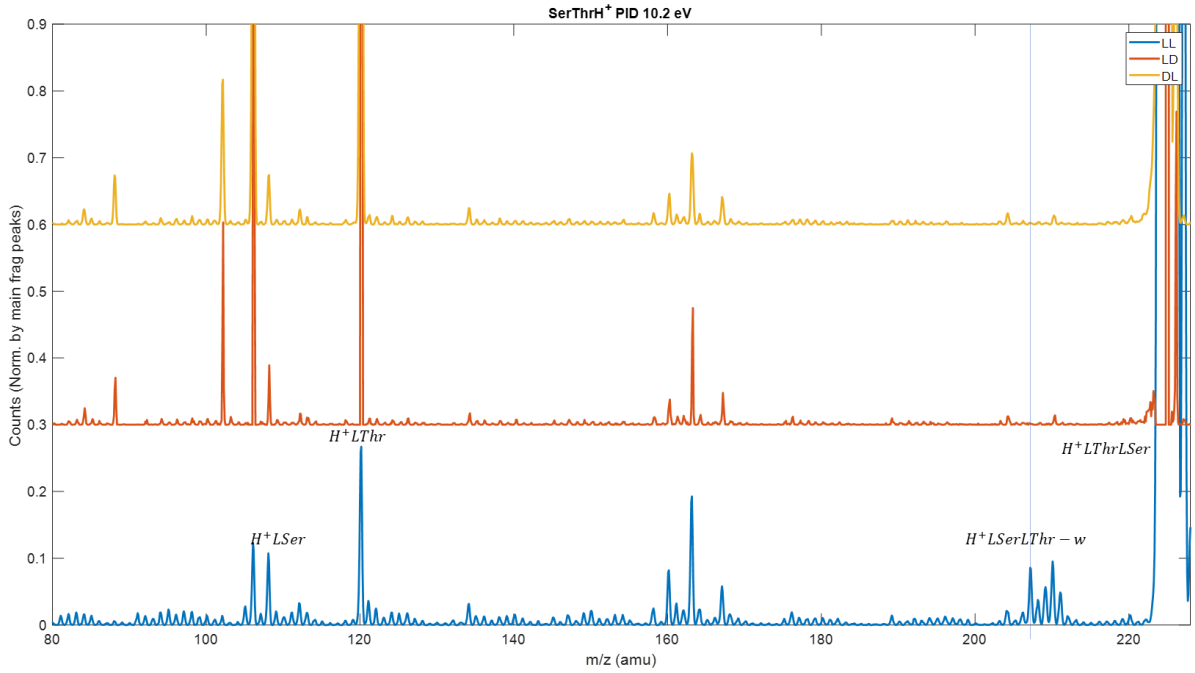

Figure 1- Preliminary comparison between the different dimers of the protonated Serine-Threonine following photon-induced dissociation (ϵ_ph=10.2eV). For the case of L-L (bottom) we see clear indications of fragments which are not seen in both L-D (middle) and D-L (top) dimers.