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

Action number: CA21126

Grantee name: Sergio MATO DOMINGUEZ

Details of the STSM

Title: Spectroscopic and Fragmentation Studies of Interstellar PAHs: Probing the Formation, Dissociation, and Reaction Pathways of Fluoranthene Cations

Start and end date: 18/03/2025 to 30/05/2025

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)

Grantee enters max 500 word summary here.

During the allocated beamtime at the FELIX (Free Electron Laser for Infrared eXperiments) facility in the Netherlands, we performed IR action spectroscopy experiments using the FELion cryogenic ion trap instrument. The main objective was to characterize the vibrational signatures of fluoranthene cations (m/z 202) and their dissociation products, specifically the H_n-loss and C_2H_n-loss fragments.

The target ions were generated via electron impact ionization of neutral fluoranthene vapor. The generated ions will be mass-selected by a first mass-filter and guided into the 22-pole ion trap, where a He-Ne gas mixture cools them to ~6.5 K. Ternary collisions lead to van der Waals complexes between the ions and Ne atoms. Pre-dissociation spectra were acquired by monitoring the depletion signal resulting from the loss of the Ne tag upon IR absorption from FELIX. The irradiated ions were then extracted from the trap by mass-selecting the parent using a second quadrupole mass selector and counted by a Daly detector. In addition, mass spectra in the m/z 0–230 range were recorded at various electron impact energies (10–45 eV) to study the fragmentation pathways of fluoranthene and to optimize ion production.

Due to the limited resolution of the second quadrupole mass filter at high masses, it was not possible to distinguish between the parent ion (m/z 202) and the H-loss fragment (m/z 201), as both yielded identical IR spectra. Furthermore, only two of the three scheduled FEL beamtime shifts could be carried out due to unforeseen technical issues during the campaign. Consequently, it was not possible to obtain a high-

[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.

quality IRPD spectrum of the C_2H_2-loss fragment (m/z 176), which had been included in the initial work plan.

To support spectral interpretation, several quantum chemical calculations were carried out using different levels of theory, including B3LYP, B2PLYP, and BP86 functionals, in combination with Grimme's empirical dispersion corrections and basis sets such as 6-311++G(d,p) and def2-VP(TZ). However, none of these approaches, harmonic neither anharmonic, succeeded in fully reproducing the experimental spectrum of the parent species, likely due to symmetry-breaking effects associated with electronic state mixing. The same phenomenon were note in H2-loss species.

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)

Grantee enters max 500 word summary here.

The STSM successfully achieved its primary objectives by recording infrared pre-dissociation (IRPD) spectra in the 600–1600 cm^{-1} range for the fluoranthene parent ion ($C_{16}H_{10}^+$, m/z 202), its H_2-loss fragment (m/z 200), and a preliminary spectrum of the C_2H_2-loss product (m/z 176). The obtained spectrum of the fluoranthene cation significantly surpasses the resolution of previous measurements (e.g., by Jos Oomens et al.), enabling a more refined analysis of its vibrational structure.

A clear distinction between the IR spectra of fluoranthene and its isomer pyrene was observed, suggesting that isomerization during the ionization process is unlikely under the experimental conditions used. However, noticeable deviations between the experimental and computed spectra suggest the presence of symmetry-breaking effects not captured by the current level of theory. To resolve these discrepancies, we plan a detailed benchmarking study using state-of-the-art quantum chemical methods. Establishing a reliable theoretical description of the parent ion is a prerequisite for interpreting the spectra of its fragments. This theoretical effort will be undertaken in collaboration with Dr. Alessandra Candian (University of Amsterdam), whose expertise in theoretical spectroscopy and PAH chemistry will be instrumental in guiding the methodological development and spectral assignments for both the parent and fragment ions.

The exploration of the fluoranthene fragmentation pathway under varying electron impact energies revealed notable features in the mass spectra, particularly enhanced signals at m/z 175 and 174 within the C_2H_2-loss region (m/z 176). These signals suggest additional dehydrogenation of the m/z 176 species, potentially arising from sequential C_2H_2 loss from partially dehydrogenated parent ions, or from direct C_2H_n elimination from the parent cation (m/z 202). This indicates a complex fragmentation pattern involving multiple steps.

Additionally, in the mass range around m/z 150—tentatively associated with a second C_2H_2-loss channel—we observed a prominent signal at m/z 152. This peak is likely attributable to acenaphthylene ($C_{12}H_8^+$), a thermodynamically stable isomer and a well-known intermediate in the proposed top-down fragmentation scheme of larger PAHs. Its presence supports the hypothesis that fluoranthene undergoes stepwise fragmentation through rearranged, stable intermediates.

Motivated by these findings, we have submitted a new beamtime proposal at the FELIX facility, requesting six shifts dedicated to recording high-resolution IRPD spectra of six selected fluoranthene fragments. These future measurements will provide essential structural information to verify proposed fragmentation pathways and improve theoretical models of PAH processing in astrophysical environments.

Overall, the STSM has made a significant contribution to the objectives of the COST Action, particularly in advancing our understanding of PAH fragmentation mechanisms and providing high-quality experimental benchmarks for theoretical modelling. The collaboration initiated during this STSM will continue with planned joint work on spectral interpretation and publication of the results, strengthening international cooperation in this research area.