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

Action number: CA21126

Grantee name: Danial Mohammadi

Details of the STSM

Title: Infrared spectroscopy of C11H8 (m/z 140) ethynyl-indene isomers for astrochemical applications

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)

The STSM was conducted at the HFML-FELIX Laboratory (Radboud University, Nijmegen, The Netherlands) using the BUMA station, which integrates a pulsed electrical discharge source, a supersonic molecular beam apparatus, time-of-flight mass spectrometry, and tunable UV and free-electron laser (FEL) infrared capabilities. The mission aimed to acquire gas-phase IR-UV ion dip spectra of $C_{11}H_8$ isomers (m/z 140) with a focus on ethynyl-substituted indene derivatives and to compare these against density functional theory (DFT) calculations to achieve isomer-specific spectral assignment.

The experimental campaign spanned approximately ten days (March 11-20, 2026) and was organized into two phases.

Phase 1: REMPI Characterization and Beam Optimization (March 11-16, 2026): The molecular beam source was prepared using a 50:50 mixture of bromobenzene (C_6H_5Br) and 1,2-dibromopropane ($C_3H_6Br_2$) as precursors, loaded into a glass reservoir connected to a heatable pulsed valve. Electrical discharge (0.70-0.75 kV) was applied before supersonic expansion to generate radical species and PAH products, including $C_{11}H_8$ at m/z 140. Resonance-enhanced multiphoton ionization (REMPI) wavelength scans were performed in both 1+1 and 1+1′ (Nd:YAG dye laser + ArF excimer) schemes across the 260-279.5 nm and 308-317.5 nm ranges. A broad ionization feature near 264.5 nm (Frequency doubled to 539 nm) was identified for m/z 140 and subsequently used as the fixed UV excitation wavelength for all FELIX-coupled measurements.

[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 Grant Holder Manager to verify the grant documents compliance and proceed with the payment.

Phase 2: FELIX IR-UV Ion Dip Spectroscopy (March 17-20, 2026): Three beamtime shifts were conducted using the FEL2 beam in combination with 1+1′ REMPI ionization at 529 nm:

- Shift 1 (March 17): The diagnostic fingerprint region (730-1600 cm^{-1}) was scanned at 2 cm^{-1} steps with 100 averages per point. A pronounced depletion feature near 1200 cm^{-1}, consistent with the ≡C-H overtone of an ethynyl substituent, was clearly observed. High-quality data were obtained across the 730-1300 cm^{-1} and 1300-1600 cm^{-1} sub-ranges.
- Shift 2 (March 19): The low-frequency out-of-plane C-H bending region (400-800 cm^{-1}) was surveyed, also yielding good signal quality after FELIX power optimization.
- Shift 3 (March 20): This shift targeted the C≡C triple bond stretching region (~2050-2200 cm^{-1}). An internal discharge fault within the FELIX accelerator caused repeated beam interruptions, leaving approximately one hour of usable beamtime. The data acquired in this region are of insufficient quality for reliable spectral assignment. FELIX operations staff acknowledged the disruption and indicated that compensatory beamtime may be provided.

In parallel with the experimental work, DFT calculations were carried out using ORCA 6.1.0 (B3LYP/N07D with D3BJ dispersion correction) for geometry optimization and Semi-anharmonic (NEAIRIR ORCA) vibrational frequency prediction across 47 $C_{11}H_8$ isomers. Anharmonic (VPT2) calculations were additionally performed for the 4-, 5-, and 6-ethynyl-1H-indene isomers using four DFT functionals (B3LYP, B3P86, B971, M062X) and two basis sets (DZ and 6-311++G**). A Pearson Correlation Coefficient (PCC)-based spectral matching algorithm has been developed to enable quantitative, intensity-independent comparison of experimental and theoretical spectra.

The primary deviation from the original working plan was the loss of effective beamtime during Shift 3 due to the FELIX malfunction, which prevented acquisition of reliable spectra in the C≡C stretch region (2050-2200 cm^{-1}). All other planned measurements were completed successfully.

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)

The STSM achieved the majority of its primary scientific objectives. High-quality IR-UV ion dip spectra of $C_{11}H_8$ (m/z 140) were successfully acquired across the 400-1500 cm^{-1} fingerprint region using FEL2 at the BUMA station. This spectral coverage encompasses the out-of-plane C-H bending modes (400-1000 cm^{-1}), in-plane C-H bending and C-C stretching modes (1000-1600 cm^{-1}), and the prominent feature near 1200 cm^{-1} previously attributed to the ≡C-H overtone diagnostic of an ethynyl substituent. These data represent a substantial improvement in signal-to-noise ratio relative to the preliminary spectra from the June 2024 FELIX campaign, where low-quality features at 695, 830, 1200, and 1500 cm^{-1} had only permitted a tentative isomer assignment to 6-ethynyl-1H-indene.

The identification of a REMPI resonance near 264.5 nm (Frequency doubled to 539 nm) for m/z 140, confirmed via both 1+1 and 1+1′ (ArF-assisted) ionization, is a key methodological outcome of this mission. This resonance enables mass-selective, potentially isomer-specific ionization and will serve as the reference UV excitation wavelength for subsequent FELIX campaigns targeting this mass channel.

On the computational side, DFT calculations at the B3LYP/N07D/D3BJ level converged successfully for all 47 $C_{11}H_8$ candidate structures. The five lowest-energy isomers - 2-, 3-, 4-, 5-, and 6-ethynyl-1H-indene (relative energies ≤ 3 kcal mol^{-1}) - are the primary structural candidates for spectral assignment. Anharmonic corrections for the 4-, 5-, and 6-ethynyl isomers shifted key high-frequency bands by −130 to −230 cm^{-1} relative to harmonic predictions, and revealed strongly isomer-specific patterns in the 600-900 cm^{-1} fingerprint region. The 6-ethynyl isomer was found to exhibit the strongest IR intensity in the

C≡C stretching region. The PCC-based spectral matching protocol will provide a systematic and reproducible framework for ranking isomer candidates against the experimental spectrum.

The outstanding primary objective is the acquisition of reliable spectra in the C≡C stretching region (2050-2200 cm^{-1}), which was not achieved due to the FELIX malfunction during Shift 3. This region is structurally diagnostic for ethynyl-substituted PAHs, as the triple bond stretching frequency is sensitive to the position of substitution and provides a critical additional constraint for isomer identification.

Planned follow-up activities:

- Data analysis and isomer assignment: The 400-1500 cm^{-1} spectra will be systematically compared against harmonic and anharmonic calculated spectra using the PCC scoring approach to identify the dominant isomers present in the molecular beam.

- Electronic spectroscopy benchmarking: The experimentally obtained REMPI spectrum will be benchmarked against time-dependent DFT excited-state calculations for candidate isomers, providing an independent spectroscopic dimension to the assignment.

- Compensatory beamtime: A follow-up FELIX shift targeting the 2050-2200 cm^{-1} C≡C stretch region is planned, pending formal confirmation from HFML-FELIX operations.

Publication: All experimental and computational results - including the REMPI characterization, the 400-1500 cm^{-1} IR-UV ion dip spectra, and the multi-isomer DFT dataset - will be compiled and submitted to a peer-reviewed astronomical journal. This work directly supports the goal of providing laboratory reference infrared spectra for interpretation of JWST astronomical observations and radio-astronomical searches for ethynyl-substituted PAHs in environments such as TMC-1.