

		Marie Skłodowska-Curie Actions Second call for COFUND PhD fellowships
Employer	University Paris-Saclay	
Doctoral School	EDOM	
Domain	EDOM (Waves and Matter)	
Supervision		
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PHD THESIS PROJECT PAHIS - Pathways to Aromatic Hydrocarbons in Interstellar Space		
Summary / Abstract		
This PhD project investigates how small aromatic molecules form in the interstellar medium, key precursors to polycyclic aromatic hydrocarbons (PAHs). It focuses on the $C_5H_7^+$ ion, an intermediate leading to the five-membered ring hydrocarbon C_5H_6, a crucial missing link in indene and related PAHs. The candidate will study ion-molecule reactions of small hydrocarbon cations using the iSELECTION setup at ISMO, combining ion mobility, mass spectrometry, kinetic measurements, and laser spectroscopy. Complementary experiments will be conducted in Prague, where reaction products can be investigated by ion mobility directly within the trap. Results will be fed into astrochemical models to evaluate their relevance in space. By linking laboratory experiments with astrochemical modeling, this interdisciplinary project bridges molecular physics, kinetics, spectroscopy, and astronomy, advancing our understanding of the formation and evolution of carbon-based molecules in the interstellar medium. Principal 3i dimension: international. Keywords • Photochemistry • Atomic, molecular and plasma physics • Laboratory astrochemistry • Mass spectrometry • Ion mobility spectrometry		

PAHIS - Pathways to Aromatic Hydrocarbons in Interstellar Space

Key Objectives

The key objectives of the PhD project Pathways to Aromatic Hydrocarbons in Interstellar Space (PAHIS) are:

- Investigate how the first aromatic molecules form from simple hydrocarbons under interstellar conditions
- Identify and characterize the key ion–molecule reactions leading to crucial intermediates
- Use advanced ion mobility, mass spectrometry, and spectroscopy in France and the Czech Republic to study reaction mechanisms and molecular structures
- Integrate experimental results into astrochemical models to assess the formation and evolution of carbonaceous molecules in space
- Bridge laboratory studies with astronomical observations to improve understanding of the origins and growth of interstellar carbon-based matter

Project

Context and state-of-the-art of Scientific Research project

Ion–molecule reactions are fundamental drivers of chemical complexity in space, shaping the formation of molecules from simple species to complex organic compounds. Accurate astrochemical models rely critically on precise knowledge of reaction rates and the branching ratios of products. Traditionally, these reactions have been studied primarily using mass spectrometry, which discriminates ions based on their mass-to-charge ratio. While effective for identifying molecular formulas, this approach is blind to isomeric effects - molecules with identical masses but different structures. Such isomeric effects are increasingly recognized as playing a key role in the formation and reactivity of aromatic species in astrophysical environments [1].

To address this limitation, we propose to employ a unique experimental setup at ISMO capable of mass- and isomer-selected ion–neutral reactions, combining ion trapping, mass spectrometry, and ultraviolet photodissociation spectroscopy to probe the structures of both reactants and products. This approach allows the direct characterization of molecular structures during and after reactions, rather than relying solely on mass-based identification. This capability is particularly innovative, as it integrates structure elucidation and reaction dynamics within a single experimental platform, enabling insights into subtle isomer-specific reactivity patterns that have so far remained inaccessible.

While a similar goal will be pursued in Prague, the methodology differs significantly. There, no laser spectroscopy will be employed, and isomer selection will occur only within the trap using ion mobility spectrometry, not prior to ion loading. Our approach, in contrast, allows pre-selection of isomeric reactants and in situ spectroscopic probing of products. The complementarity between the two setups will enable meaningful comparison and help identify the most suitable approach depending on the targeted systems. By combining high structural specificity with reaction monitoring, this project introduces a novel strategy to study astrochemical reactions and promises to unveil previously hidden chemical processes driving molecular complexity in space.

Description

Polycyclic aromatic hydrocarbons (PAHs) are believed to account for a significant fraction of the carbon budget in the interstellar medium (ISM). Recent detections of cyano-substituted PAHs—such as cyanopyrene and cyanocoronene—as well as pure aromatic hydrocarbons like indene in dense molecular clouds raise important questions about their formation mechanisms in the ISM. From a bottom-up perspective, the processes leading to the formation of the first aromatic ring species, such as C_6H_6 and C_5H_6 , from small hydrocarbons remain under debate. These molecules are considered cornerstone species in ISM chemistry, serving as building blocks for larger interstellar aromatic compounds. In particular, understanding the formation of the five-membered ring C_5H_6 is crucial, as it represents a missing link in the reaction pathways leading to indene and other PAHs containing pentagonal rings. Like $C_6H_7^+$, which is known to efficiently form benzene via dissociative recombination with electrons, $C_5H_7^+$ is expected to undergo analogous reactions leading to the formation of C_5H_6 . The most straightforward pathway for producing $C_5H_7^+$ appears to be the reaction between $C_5H_5^+$ and H_2 , given that molecular hydrogen is by far the most abundant species in dense clouds. However, our preliminary calculations indicate that this reaction presents an activation barrier. Consequently, alternative formation routes involving more complex carbonaceous reactants should be considered to rationalize the presence of $C_5H_7^+$ in such environments.

The aim of this thesis is to investigate the formation of $C_5H_7^+$ via ion-molecule reactions involving small hydrocarbon cations, selected based on their mass and isomeric structure. Additionally, the structure of the reaction products will be spectroscopically characterized, allowing for complete control over the studied reactions in terms of both the mass and shape of reactants and products.

To address these questions, a modified version of the iSELECTION setup [2] will be employed. This instrument combines ion mobility spectrometry (for shape selection), mass spectrometry (for mass selection), and kinetic studies. Ion generation will be carried out using laser photodissociation/ionization of PAHs.

As part of this PhD project, the candidate will investigate the kinetics and spectroscopy of ion-molecule reactions. The work will primarily involve recording kinetic profiles using the iSELECTION setup at ISMO (Université Paris-Saclay) and performing ultraviolet photodissociation spectroscopy on the reaction products to gain insight into their structure. A significant part of the project will also be carried out in collaboration with J. Jašík in Prague, where a similar ion trap apparatus is operated. There, the candidate will contribute to experiments employing advanced electronics for ion mobility measurements, enabling shape selection directly within the trap [3]. This approach will allow structural studies by ion mobility to be extended not only to the reactive ions but also to the reaction products.

The expected results are reaction rates and branching ratios that will be integrated into astrochemical models, primarily using the Nautilus code in collaboration with J.-C. Loison (ISM, Bordeaux), similar to the work we did for $C_6H_6^+$ [1]. This effort will involve direct collaboration with astronomers and may lead to proposals for new astronomical observations inspired by the laboratory findings.

Preliminary results already obtained at the SOLEIL synchrotron with the CERISE instrument, combined with quantum chemical calculations, have provided us with a set of reactions that we plan to investigate experimentally during the first year. Throughout this period, we will maintain continuous interaction with astrochemical modelers to refine our goals on the fly. In the second year, we aim to repeat experiments where the spectroscopic identification of reaction products proved challenging, using ion mobility spectrometry in Prague. By the end of year two, we expect to have established a well-defined chemical

network capable of reproducing the abundances of the five-membered ring species detected in space, and start to extend the network toward the formation of the second aromatic ring in interstellar PAHs.

Bibliography

We have recent paper accepted in Nature astronomy (dot of the ArXiv given) that describes the importance of isomers in spac chemistry

[1] Evidence for Phenylum Reactivity under Interstellar Relevant Conditions', J.-C. Loison, C. Rossi, N. Solem, R. Thissen, C. Romanzin, C. Alcaraz, U. Jacovella, Nat. Astron. accepted doi: 10.48550/arXiv.2506.13290

A joint publication describes the first part of the iSELECTION setup and a paper describing the spectroscopy part is been written

[2] iSELECTION: An Instrument to Study the Kinetics of Isomer-Selected Gas-Phase Ion-Molecule Reactions, C. Rossi, A. P. Rasmussen, B. Gans, J. Jašík, Jan Žabka, M. Albaret, H. Bauduin, C. Charrière, J.-P. Dugal, J. Guigand, C. Le Bris, U. Jacovella, Chem. Methods (2025) doi: 10.1002/cmt.202500013

The methodology employed to perform the ion mobility spectrometry within the trap is based on the following paper

[3] High-resolution separation of bioisomers using ion cloud profiling, X. Zhou, Z. Wang, J. Fan, Z. Ouyang, Nat. Commun. (2023) doi: 10.1038/s41467-023-37281-7

Facilities and quality of research environment available for the researcher

The experimental setups in France and the Czech Republic are fully operational and already producing data. The plan is to integrate a new ion trap developed by J. Jasik, which is already available at ISMO, with its electronics built in the Czech Republic. Both setups can be operated with minimal running costs, which are covered by grants secured by both research groups. These funds not only cover the operational expenses but also support the PhD student's participation in at least two international conferences per year, as well as attendance at COST meetings (NanoSpace, PLANETS).

3i Dimension - international

Description and expected outcomes

The supervisors of this project—Ugo Jacovella at ISMO, and Juraj. Jašík at the Heyrovský Institute of Physical Chemistry—have launched an international collaboration supported by the European COST Action NanoSpace (2024—) and the PHC Barrande (2025—2026). A memorandum of understanding has been established between, the two institutions in 2022. The complementary experimental setups and skills of both group, along with their shared objective of improving the understanding of the chemical growth in the ISM led to this partnership. Initiated in 2022, the collaboration quickly yielded success with the construction of the iSELECTION setup and the publication of a joint paper in Chemistry Method about isomer-selected ion molecules reactivity (the central part of this PhD project) and one publication in preparation about the recording of electronic spectra of isomer-selected ions in the context of the Diffuse Interstellar bands (part of another PhD project).

Approximate timeline of internships / external stays corresponding to the 3i dimension

- **Year 1 (October 2026 – September 2027)**

Based at ISMO, with a two-week stay in Prague (financed via PHC or COST)

- **Year 2 (October 2027 – September 2028)**

Based in Prague, with a two-week stay at ISMO (financed via PHC or COST)

- **Year 3 (October 2028 – September 2029)**

Based at ISMO

Profile of PhD fellow

PhD studies and research work require curiosity, creativity, rigour, teamwork, and organisational skills. A minimum B2 level of English is mandatory. The below criteria are specific to the thesis project.

pre-requisite	Background in molecular physics or physical chemistry or astrochemistry
pre-requisite	Hold a MSc in Physics, Physical Chemistry, Chemistry, or related fields
pre-requisite	Experience in mass spectrometry, ion mobility, or laser spectroscopy
advantageous	Knowledge of kinetics and instrumentation
advantageous	Data acquisition using Python

Ethics issues in the project as per Horizon Europe Ethics Self-assessment

Section 1. Human embryonic stem cells (hESCs) and human embryos (hEs)			No
Section 2. Humans	No	Section 3. Human cells and tissues	No
Section 4. Personal data	No	Section 5. Animals	No
Section 6. Third Countries	No	Section 7. Environment, health and safety	Yes
Section 8. Artificial Intelligence	Yes	Section 9. Other ethics issues	No
Section 10. Crosscutting issue: potential misuse of results			No

7. Environment, health and safety

All French labs are required to have health and safety procedures in place, which takes into account the use of high-energy light sources such as lasers of class 3 and above, and the use of hazardous / toxic chemical and biological products. The institution and the laboratory comply with the highest safety requirements and PhD fellows have mandatory health and safety training, with additional training if required.

8. Artificial intelligence

The use of machine learning and artificial intelligence is used to fit data and analyse results. This is typically used to improve fits and complex models with multiple parameters. The data in question is related to physical experiments and is not human data.

Artificial Intelligence is not developed during this project and is thus not impacted by the AI Act.