AstroPAH

A Newsletter on Astronomical PAHs

Issue 102 • October 2023

Asteroid Bennu

Editorial

Dear Colleagues,

It has been 10 years since we started AstroPAH. A delightful journey following the progress of the research on PAHs in space. A progress you, researchers, made it happen. So the congratulations on this AstroPAH anniversary go to you, who produced the Science! And also so goes my thank you for all the contributions you shared on the AstroPAH pages throughout these 10 years.

Producing this newsletter for 10 years was a delightful experience also thanks to the great people that composed its editorial board since the beginning. I have been extremely lucky to know and work with them. They volunteer their time, expertise and professionalism while sharing their love for Science on these pages. They are amazing professionals and wonderful people. Thank you Annemieke, Ale, Ella, Elisabetta, Xander, Amanda, David, Helgi, Sandra, Kelvin, Dona, Ameek, Rijutha, and Julianna!

I am looking forward to the next years of discoveries!

Isabel Aleman

Next issue: 23 November 2023.
Submission deadline: 10 November 2023.

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PAH Picture of the Month

In 2019, NASA's OSIRIS-REx spacecraft captured this picture of the asteroid Bennu ejecting particles from its surface. The same spacecraft has recently collected a sample of Bennu in which scientists have found evidence of both carbon and water. More information can be found here.

Credits: NASA/Goddard/University of Arizona/Lockheed Martin. The image is available here.

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In Focus

An Interview with
Rijutha Jaganathan

Dr. Rijutha Jaganathan completed her doctoral research in 2020 in Professor Liv Hornekær's group at Aarhus University, Denmark under the Horizon2020 Marie Skłodowska-Curie ITN EUROPAH in the field of laboratory astrophysics. Until August 2023, she was a postdoctoral researcher at the Center for Interstellar Catalysis (InterCat). She is passionate about science communication and currently works as a science consultant for a school in India.

How did you get into PAH-related research?

While looking for astrochemistry-related PhD positions in Europe, I came across the advertisement for a laboratory astrophysics project at Aarhus University. It seemed like a great combination of astronomy and laboratory work and I applied for it. I joined the Surface Dynamics group in September 2017 wherein I used surface science techniques to study the interaction of a variety of polycyclic aromatic hydrocarbons (PAHs) with hydrogen atoms leading to small molecule formation. I was especially interested in the effect of the shape, functionalisation and size of the PAHs on their interaction with H-atoms. After my PhD, I joined the Centre for Interstellar Catalysis (InterCat) as a postdoc. While there, I studied PAHs from the perspective of their potential role in the formation of prebiotic molecules.

What are you working on right now?

I am currently working for a school in Bangalore, India, as a science consultant. My role is to introduce and sustain hands-on activities into the science education program. The school caters to children from low-income homes who have almost no exposure to science kits, online science resources or visits to the local science centres. I am hoping to share with them the joy of doing science.

Which open question in Laboratory Astrophysics would you like to see answered in the near future?

I am looking forward to work that will investigate the role of PAHs in setting the stage for the molecular building blocks of life to form in space.

Can you tell us about your experience as an Early Stage Researcher for the EUROPAH network?

Being a part of the EUROPAH ITN opened up collaborations with other research groups from across Europe organically. In addition to a theory collaboration with Prof. Xander Tielens' group at Leiden University, I spent some time at the FELIX Laboratory with Prof. Jos Oomens' group obtaining gas phase IR spectra of the PAHs I had studied at Aarhus. It was also wonderful to share the journey with other ESRs from different parts of the world. I deeply treasure the friendships I made in the network.

Can you tell us about your latest paper on PAHs?

My latest publication is in-fact a collaboration brought out by the EUROPAH ITN! With Rocco Martinazzo's group, we studied the interaction of a curved polycyclic aromatic hydrocarbon (PAH), corannulene ($C_{20}H_{10}$), with H-atoms leading to the formation of highly superhydrogenated species. In particular, we determined the H-atom addition sequence to a monolayer of corannulene deposited on a graphite surface in order to understand the effect of curvature on the interaction of PAHs with H-atoms. We also investigated why superhydrogenated corannulene species with a certain number of additional H-atoms are more stable than the others. You can read the paper Leccese et al. (2023) clicking here

What was the most important advice somebody gave you?

That it is the journey and not the destination that matters.

How do you balance your professional and personal life?

I am still on the path of finding a balance between the two. It helps that I am no longer in academia. There are days on which work takes priority and some others on which personal life takes priority. I am learning to not feel guilty about either.

Can you tell us about your experience working in the editorial team of AstroPAH?

It is great team that is welcoming, encouraging and full of optimism. There is a sense of camaraderie that helps ease the stress when putting together each newsletter while also having a full-time job.

Where would you like to see AstroPAH in the next five years?

I would like to see AstroPAH be the ‘go-to’ newsletter for all things Astro-PAH – abstracts, jobs, conferences, fellowships, etc. It would be nice if it could use modern platforms to be a more interactive space for early career researchers, other scientists looking to step into Astro-PAH research and senior Astro-PAH researchers.

Gas-Phase Preparation of Azulene ($C_{10}H_8$) and Naphthalene ($C_{10}H_8$) via the Reaction of the Resonantly Stabilized Fulvenallenyl ($C_7H_5^\bullet$) and Propargyl ($C_3H_3^\bullet$) Radicals

Wang Li[1], **Jiuzhong Yang**[1], **Long Zhao**[1,2], **David Couch**[3], **Myrsini San Marchi**[3], **Nils Hansen**[3], **Alexander N. Morozov**[4], **Alexander M. Mebel**[4], **and Ralf I. Kaiser**[5]

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Synthetic routes to the 10π Hückel aromatic azulene ($C_{10}H_8$) molecule, the simplest polycyclic aromatic hydrocarbon carrying an adjacent five- and seven-membered ring, have been of fundamental importance due to the role of azulene — a structural isomer of naphthalene — as an essential molecular building block of saddle-shaped carbonaceous nanostructures such as curved nanographenes and nanoribbons. Here, we report on the very first gas phase preparation of azulene by probing the gas-phase reaction between two resonantly stabilized radicals, fulvenallenyl ($C_7H_5^\bullet$) and propargyl ($C_3H_3^\bullet$), in a molecular beam through isomer-resolved vacuum ultraviolet photoionization mass spectrometry. Augmented by electronic structure calculations, the novel Fulvenallenyl Addition Cyclization Aromatization (FACA) reaction mechanism affords a versatile concept for introducing the azulene moiety into polycyclic aromatic systems thus facilitating an understanding of barrierless molecular mass growth processes of saddle-shaped aromatics and eventually carbonaceous nanoparticles (soot, interstellar grains) in our universe.

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https://pubs.rsc.org/en/content/articlehtml/2023/sc/d3sc03231k

Gas-Phase Formation of the Resonantly Stabilized 1-Indenyl ($C_9H_7^\bullet$) Radical in the Interstellar Medium

Zhenghai Yang[1], **Galiya R. Galimova**[2], **Chao He**[1], **Shane J. Goettl**[1], **Dababrata Paul**[1], **Wenchao Lu**[3], **Musahid Ahmed**[3], **Alexander M. Mebel**[2], **Xiaohu Li**[4,5], **and Ralf I. Kaiser**[1]

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The 1-indenyl ($C_9H_7^\bullet$) radical — a prototype aromatic and resonantly stabilized free radical (RSFR) carrying a six- and a five-membered ring — has emerged as a fundamental molecular building block of non-planar polycyclic aromatic hydrocarbons (PAHs) and carbonaceous nanostructures in deep space and combustion systems. However, the underlying formation mechanisms have remained elusive. Here, we reveal an unconventional low-temperature gas-phase formation of 1-indenyl via barrierless ring annulation involving reactions of atomic carbon ($C(^3P)$) with styrene ($C_6H_5C_2H_3$) and propargyl ($C_3H_3^\bullet$) with phenyl ($C_6H_5^\bullet$). Macroscopic environments like molecular clouds act as natural low-temperature laboratories, where rapid molecular mass growth to 1-indenyl and subsequently complex PAHs involving vinyl side-chained aromatics and aryl radicals can occur. These reactions may account for the formation of PAHs and their derivatives in the interstellar medium and carbonaceous chondrites and could close the gap of timescales of their production and destruction in our carbonaceous universe.

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https://www.science.org/doi/full/10.1126/sciadv.adi5060

Anharmonic IR absorption spectra of the prototypical interstellar PAHs phenanthrene, pyrene, and pentacene in their neutral and cation states

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The combination band and overtone transitions of cationic polycyclic aromatic hydrocarbons (PAHs) in the 2000 – 2900 cm^{-1} (5-3.5 µm) region are implicated as carriers of the 'quasi-continuum' observed in the near-infrared (IR) emission spectra of astronomical objects showing the PAH features. In neutral PAHs, the largest intensity absorption features are concentrated in the 700 – 900 cm^{-1} (14 – 11 µm) range, corresponding to the CH out-of-plane bending motions. Following ionization, this intensity shifts to the 1000 – 1600 cm^{-1} (10 – 6 µm) range, C=C stretches and CH in-plane bends, due to delocalization of the positive charge across the entire aromatic system. Anharmonicity is required in order to accurately characterize/compute the IR absorption spectrum of PAHs, indicated herein by the ability to directly assign high-resolution experimental absorption spectra of neutral and cationic phenanthrene, pyrene, and pentacene. The differences in the neutral and cation spectra support that neutral PAHs are the source of the strong 3.3 and 11.2 µm astronomical PAH features, while the very strong, broad features in the 6 – 10 µm region as well as the 'quasi-continuum' from 3.5 – 5 µm are dominated by PAH cations. This study reinforces the requirement for the continued inclusion of anharmonicity in the IR absorption and emission spectra of PAHs as advancements in methodology make larger and more complex systems computationally accessible. This is particularly pertinent to the interpretation of the high-fidelity data returned by the James Webb Space Telescope (JWST).

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Anharmonicity and deuteration in the IR absorption and emission spectrum of phenylacetylene

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Anharmonic cascade emission simulations, herein evinced by full reproduction and deep insights into recent emission spectroscopy experiments of phenylacetylene, are integral to the future successful analysis of JWST observational spectra. Experimental infrared absorption experiments conducted in this study reveal a complex spectrum dominated by quantum effects that are uncovered by anharmonic computational analysis. From this work, it becomes clear that phenylacetylene exhibits strong resonance coupling between fundamental and two-quanta combination modes as well as giving indication for coupling with higher-order, three-quanta combination bands. This study benchmarks the development of advanced computational methods that will be extended to larger systems of astronomical relevance and those including isotopic substitution and side group functionalization with groups such as acetylene. The astrophysical implications of these results, including the potential for detection of acetylenic C–H stretches in space, are discussed in the vein of the impact polycyclic aromatic hydrocarbons have on astronomical infrared emission bands.

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Accurate Prediction of Adiabatic Ionization Energies for PAHs and Substituted Analogues

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The accurate calculation of adiabatic ionization energies (AIEs) for polycyclic aromatic hydrocarbons (PAHs) and their substituted analogues is essential for understanding their electronic properties, reactivity, stability, and environmental/health implications. This study demonstrates that the M06-2X density functional theory method excels in predicting the AIEs of polycyclic aromatic hydrocarbons and related molecules, rivaling the (R)CCSD(T)-F12 method in terms of accuracy. These findings suggest that M06-2X, coupled with an appropriate basis set, represents a reliable and efficient method for studying polycyclic aromatic hydrocarbons and related molecules, aligning well with the experimental techniques. The set of molecules examined in this work encompasses numerous polycyclic aromatic hydrocarbons from *m/z* 67 up to *m/z* 1,176, containing heteroatoms that may be found in biofuels or nucleic acid bases, making the results highly relevant for photoionization experiments and mass spectrometry. For coronene-derivative molecular species with the $C_{6n^2}H_{6n}$ chemical formula, we give an expression to predict their AIEs (AIE (n) = 4.359 + 4.8743n$^{-0.72057}$, in eV) upon extending the π-aromatic cloud until reaching graphene. In the long term, the application of this method is anticipated to contribute to a deeper understanding of the relationships between PAHs and graphene, guiding research in materials science and electronic applications and serving as a valuable tool for validating theoretical calculation methods.

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Evolution of Fullerenes in Circumstellar Envelopes by Carbon Condensation

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Fullerenes, including C_{60} and C_{70}, have been detected in various astronomical environments. Understanding how their structures evolve over time is essential for gaining insights into their life cycle and making further observations. To address this, we conducted reactive molecular dynamics simulations to investigate the evolution of fullerenes in the circumstellar envelopes surrounding carbon-rich asymptotic giant branch stars. Our simulations employed a bottom-up chemistry scheme, wherein fullerenes grow by absorbing and condensing small carbon-based molecules (see Fig.1). The results revealed the formation of different structures through heterogeneous reactions based on hydrogen concentration, leading to the emergence of onion-like nanostructures or single-layer fullerenes. To examine the impact of these structural changes on the infrared emission characteristics of fullerenes, we performed quantum chemical calculations. The results indicate that as fullerenes grow larger, additional emission features are introduced in the infrared spectrum. Moreover, two-layered fullerenes show noticeable blue-shift or weakening effects on the bands associated with out-of-plane vibration modes.

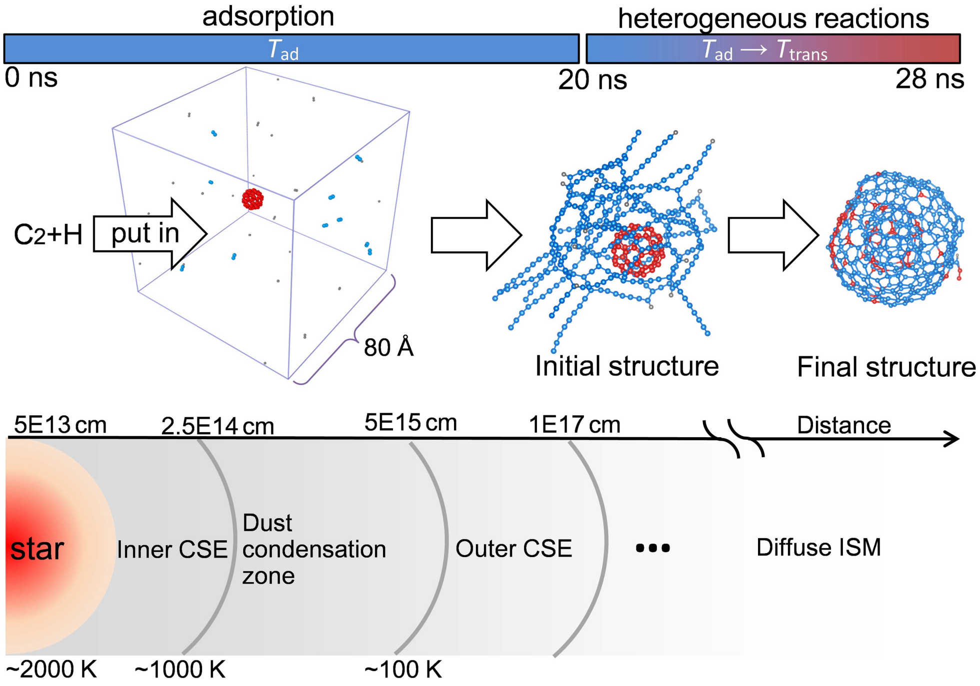

Figure 1 *– Schematics for the simulated evolution of C_{60} via adsorption reactions.*

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https://doi.org/10.1093/mnras/stad2754

Announcements

PhD positions

Molecular Physics / Physical Chemistry Laboratory Astrophysics

Advertised by Otto Dopfer

A fully funded PhD position (3 years) from DFG (German Science Foundation) is available in the laser molecular spectroscopy group of Otto Dopfer at the Berlin Institute of Technology (TU Berlin), Germany.

The funded project involves the IR and electronic characterization of diamondoid cations and their derivatives and clusters using laser spectroscopic, mass spectrometric, and quantum chemical methods. The laboratory astrochemistry work is strongly related to the problem of the diffuse interstellar bands (DIBs), the unidentified/aromatic IR emission bands (UIR/AIB) and hydrocarbon chemistry in water ices.

Available equipment on our laboratory astrochemistry group includes a variety of pulsed and tuneable IR and UV lasers, several ion sources and cryogenic rf-traps, as well as several types of tandem mass spectrometers.

Previous papers of the group in this field include:

- Angew. Chem. Int. Ed. 51, 4925-4929 (2012) DOI: 10.1002/anie.201108937
- Astrophys. J. Lett. 900, L20 (2020), DOI: 10.3847/2041-8213/abafbd
- Astrophys. J. 940, 104 (2022), DOI: 10.3847/1538-4357/ac9733
- Phys. Chem. Chem. Phys. 25, 13593-13610 (2023), DOI: 10.1039/D3CP01514A
- Phys. Chem. Chem. Phys. 25, 5529-5549 (2023), DOI: 10.1039/d2cp04556g
- J. Phys. Chem. Lett. 13, 449-454 (2022), DOI: 10.1021/acs.jpclett.1c03948

Qualified candidates hold a MSc in Physics, Physical Chemistry, or related fields, with focus on experimental work. Experience in one or more of the following fields is not mandatory but highly advantageous:

1. laser spectroscopy, mass spectrometry, ion sources and traps, cluster science
2. vacuum, optics, data acquisition, construction of apparatus
3. writing of publications and reports
4. strong communication and presentation skills

Interested candidates are encouraged to send their application (in a single pdf file) to Prof. Otto Dopfer (dopfer@physik.tu-berlin.de), including a cover letter, a CV, previous certificates (BSc and MSc), a statement of qualifications relevant for the position (max. 1 page), a statement of research interests (max. 1 page) as well as names and complete addresses of two persons willing to provide reference letters.

Evaluation of the applications will begin at October 20 (2023) and will continue until the position is filled. The desired starting date is as soon as possible but this is negotiable to some extent.

Berlin is an international city and offers an exciting scientific and cultural environment.

Deadline: 20 October 2023

E-mail for contact: dopfer@physik.tu-berlin.de

Webpage: https://www.tu.berlin/en/lmsu

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