



AstroPAH

A Newsletter on Astronomical PAHs

Issue 114 • December 2024

**Discovery of cyanopyrene
in the TMC-1**



Editorial

Dear Colleagues,

Welcome to our 114th issue, the last AstroPAH of 2024!

The cover of this newsletter is decorated with a cyanopyrene molecular illustration. This molecule was recently discovered in the Taurus Molecular Cloud 1 by Gaby Wenzel and collaborators. To date, it is the largest PAH detected via radio astronomy.

The abstracts of the papers reporting this cyanopyrene discovery, as well as other isomers, are presented in the Abstract section together with studies on PAH emission in galaxies, the evolution of carbon material in the context of AGB stars to planetary nebulae, and spectroscopy of the phenylacetylene cation.

In this month's *In Focus*, our new editor, Dr. Alexander Lemmens, introduces himself and answers some questions.

We would also like to draw your attention to the upcoming *Global Astrochemistry Lecture Series: From the Big Bang to Life*. Registrations close on January 31st 2025. The Series will comprise of 14 lectures and 4 special lectures, and the common theme this year will be on JWST.

Thank you all for all your contributions and keep them coming in the new year!

The AstroPAH editorial board wishes you all a productive and very happy 2025!

The Editorial Team

**Next issue: 20 February 2025.
Submission deadline: 07 February 2025.**

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PAH Picture of the Month

Radio observations with the Green Bank Telescope revealed three isomers of cyanopyrene-1-cyanopyrene, 2-cyanopyrene, and 3-cyanopyrene-a cyano-substituted derivative of the four-ring PAH pyrene, in the TMC-1 molecular cloud. This discovery, led by [Wenzel et al. 2024](#), marks the largest PAH detected via radio astronomy to date. Further details can be found in the abstract section.

Credits: Sophia Dagnello.

In Focus

An interview with **Dr. Alexander Lemmens**

The New Member of the AstroPAH Editorial Team

Sander was born and raised around Maastricht in The Netherlands. He completed his studies at the Radboud University in Nijmegen, with his major in the Molecular and Biophysics group of Anouk Rijs at the free electron laser facility FELIX. During this year (2015), he got involved in PAHs and they stuck. He completed a PhD on PAHs with Wybren Jan Buma and Anouk Rijs in Amsterdam and Nijmegen. In 2022 he crossed the Atlantic to the US and now works at the Lawrence Berkeley National Laboratory, in USA, and brought his PAHs with him. He is driven by curiosity and tries to keep this a priority during his day to day work in the lab, but also outside the lab being outside and seeing all that the world has to offer.



Welcome to AstroPAH, Sander! Tell us first, what inspired you to become a scientist?

I would say that my youth, being exposed to many people, art, science, ideas and perspectives has given me the curiosity to stay in science.

How did you get into PAH-related research?

I approached Anouk Rijs to do a MSc internship with her, because I liked her and her lectures about lasers, FELIX and spectroscopy. A large part of it was also because I was curious to what was going on at FELIX, a large user facility managed by the science faculty.

Can you tell us about your career path, the difficulties you have faced to stay in the field, and what guided your current choice?

I think it is interesting that 'career' and 'scientist' are phrased within the same sentence. I think it is important to distinguish between them. A difficulty arises there, because to be a good scientist may mean not to care (too much) about your career. It is easy to get distracted by things that may help your career, but not help you as a scientist. I realize this becomes

harder as you stay in science longer. In a year or two, my current position will end so I try not to worry or think too much about that.

What is your current research about?

We recently completed a new femtosecond laser-based mass spectrometer that can be used with a variety of sources such as a pyrolysis nozzle. This took us about 1 year. The laser runs at almost 1 MHz and is tunable from the infrared to the UV. It is quite an amazing laser. Using the new set up, I try to extend my experience from the slow(er) infrared spectroscopy to fast UV/VUV experiments. Both time-resolved and spectrally resolved. We also use the Advance Light Source in Berkeley. So far, we have investigated electronic energy transfer ionization processes in PAH-CO₂ complexes and the ultrafast electronic energy decay in the anthracene dimer. The former may be very relevant to astrochemistry, the latter definitely more in the area of physical chemistry.

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

What laboratory experiments or conditions do we need to create to find the origin of some of the DIBs? Because a few have been attributed to molecular species generated in a laboratory, I have the impression that others of these century-old spectroscopic features, discovered not far from where I now work, should also be assignable to laboratory data captured using current techniques.

What was the most important advice somebody gave you?

My mom used to say that I should play with my toes from time to time. Basically not have anything specific to do. I kind of created my own version of this, and it may sound paradoxical but I think it is true: “breaks are the basis of all progress”.

How do you balance your professional and personal life?

Just by going out and having fun. As I said before, I try not to worry about my professional life too much. I noticed that whenever I feel good, I perform better at work too.

What do you do outside of work?

I enjoy many things; being outside, cooking, reading, music. I moved to California because I like surfing, but immersing myself in the cultural melting pot of the Bay Area has me excited most lately.

What does it mean for you to be part of the AstroPAH editorial team?

I have been reading AstroPAH to keep up to date with anything going on in the field and feel honored to be able to contribute.



Abstracts

Detections of interstellar aromatic nitriles 2-cyanopyrene and 4-cyanopyrene in TMC-1

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Polycyclic aromatic hydrocarbons (PAHs) are among the most widespread compounds in the universe, accounting for up to $\sim 25\%$ of all interstellar carbon. Since most unsubstituted PAHs do not possess permanent electric dipole moments, they are invisible to radio astronomy. Constraining their abundances relies on the detection of polar chemical proxies, such as aromatic nitriles. We report the detection of 2- and 4-cyanopyrene, isomers of the recently detected 1-cyanopyrene. We find that these isomers are present in an abundance ratio of $\sim 2:1:2$, which mirrors the number of equivalent sites available for CN addition. We conclude that there is evidence that the cyanopyrene isomers formed by direct CN addition to pyrene under kinetic control in hydrogen-rich gas at 10 K and discuss constraints on the H/CN ratio for PAHs in TMC-1. Our detections of the cyanopyrene isomers suggest that small PAHs like pyrene must either be formed in or transported to the cold interstellar medium, challenging assumptions about the origin and fate of PAHs in space.

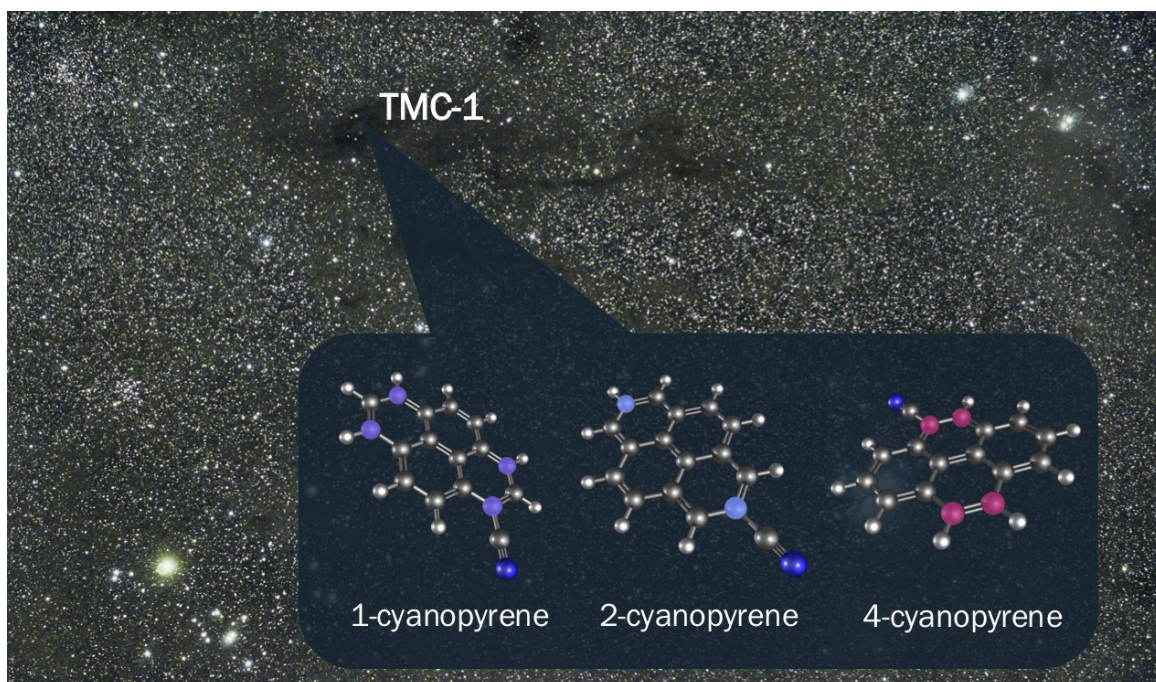


Figure 1 – All three possible cyanopyrene isomers detected in TMC-1. Equivalent carbon sites are marked with colored circles. Credit for the photo of TMC-1: Brett McGuire.

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Nat. Astron., published online 05 November 2024

<https://doi.org/10.1038/s41550-024-02410-9>

Detection of interstellar 1-cyanopyrene: a four-ring polycyclic aromatic hydrocarbon

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Polycyclic aromatic hydrocarbons (PAHs) are organic molecules containing adjacent aromatic rings. Infrared emission bands show that PAHs are abundant in space, but only a few specific PAHs have been detected in the interstellar medium. We detect 1-cyanopyrene, a cyano-substituted derivative of the related four-ring PAH pyrene, in radio observations of the dense cloud TMC-1 using the Green Bank Telescope. The measured column density of 1-cyanopyrene is $\sim 1.52 \times 10^{12} \text{ cm}^{-2}$. We estimate that pyrene itself contains up to 0.1% of the carbon in TMC-1. This abundance indicates that interstellar PAH chemistry favors the production of pyrene. We suggest that some of the carbon supplied to young planetary systems is carried by PAHs that originate in cold molecular clouds.

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Science **386**, 6723, pp. 810–813 (2024)

<https://www.science.org/doi/10.1126/science.adq6391>

Battle of the CH motions: aliphatic vs. aromatic contributions to astronomical PAH emission and exploration of the aliphatic, aromatic, and ethynyl CH stretches

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Strong anharmonic coupling between vibrational states in polycyclic aromatic hydrocarbons (PAH) produces highly mixed vibrational transitions that challenge the current understanding of the nature of the astronomical mid-infrared PAH emission bands. Traditionally, PAH emission bands have been characterized as either aromatic or aliphatic, and this assignment is used to determine the fraction of aliphatic carbon in astronomical sources. In reality, each of the transitions previously utilized for such an attribution is highly mixed with contributions from both aliphatic and aromatic CH motions as well as non-CH motions such as CC stretches. High-resolution gas-phase IR absorption measurements of the spectra of the aromatic molecules indene and 2-ethynyltoluene at the Canadian Light Source combined with high-level anharmonic quantum chemical computations reveal the complex nature of these transitions, implying that the use of these features as a marker for the aliphatic fraction in astronomical sources is not uniquely true or actually predictive. Further, the presence of aliphatic, aromatic, and ethynyl CH groups in 2-ethynyltoluene provides an internally consistent opportunity to simultaneously study the spectroscopy of all three astronomically important groups. Finally, this study makes an explicit connection between fundamental quantum mechanical principles and macroscopic astronomical chemical physics, an important link necessary to untangle the lifecycle of stellar and planetary systems.

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MNRAS, stae2588 (2024)

<https://doi.org/10.1093/mnras/stae2588>

Evolution of carbon particles from the stage of asymptotic giant branch stars to planetary nebulae: observations, experiments, and theory

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We review research into the evolution of carbon particles at stages from the envelopes of asymptotic giant branch stars to planetary nebulae. The evolution of carbon particles is discussed from several standpoints: observational data are summarized; the formation mechanisms and clustering of aromatic molecules are considered; conditions for the formation of carbon particles in the envelopes of stars and for their subsequent evolution in protoplanetary and planetary nebulae are described; results of experiments on creating equivalents of interstellar dust and analyzing their characteristics are presented; and, finally, possible evolutionary scenarios for carbon particles are presented. Particular attention is paid to fullerene molecules, which are important for constructing a comprehensive picture of the evolution. Their presence and nonuniform distribution suggest that, depending on the conditions, the formation of carbon particles can follow two paths: via planar or nonplanar aromatic molecules.

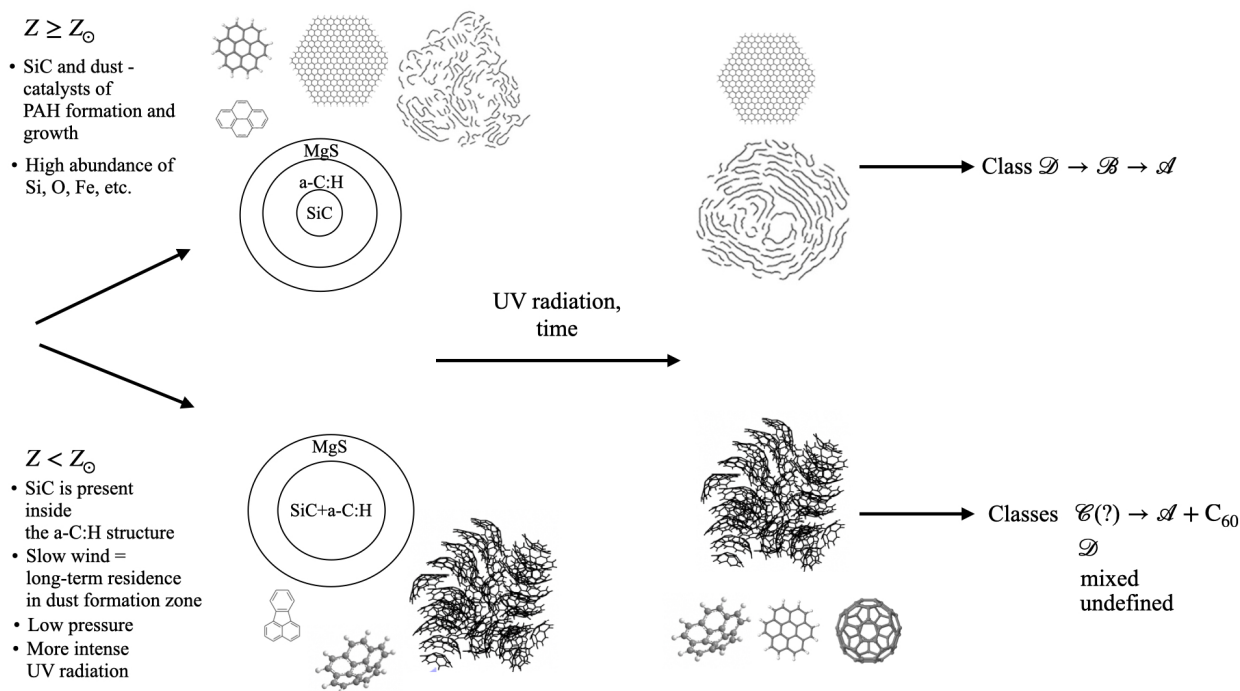


Figure 2 – General scheme of the branching of dust evolution scenarios at different metallicities.

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Physics Uspekhi, **67**, pp. 961–987 (2024)

<https://ufn.ru/en/articles/2024/10/a/>

The stabilization of cyanonaphthalene by fast radiative cooling; Matters Arising

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The description of unimolecular decays is essential for our understanding of the cosmic molecular inventory. In Stockett, M. H. et al., *Nat. Commun.* 14, 395 (2023) the authors report measurements of kinetic energy release distributions of the unimolecular decay and the radiative cooling of cyanonaphthalene, from which the authors reconstruct the ions' decay rate coefficient. The measured kinetic energy distributions is converted to an excitation energy without regard to the significant difference between the measured product temperature and the temperature needed to represent the decay constant with the chosen Arrhenius-like representation. The procedure used leads to a significant error in the estimate of the activation energy, and thereby an exponentially amplified error in the rate constant.

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Nat. Comm., **15**:8442 (2024)

<https://doi.org/10.1038/s41467-024-52695-7>

Ion Spectroscopy in the Context of the Diffuse Interstellar Bands: A Case Study with the Phenylacetylene Cation

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Identification of the molecular carriers of diffuse interstellar bands (DIBs) requires gas phase electronic spectra of suitable candidate structures. Recording the spectra of these in the laboratory is challenging because they include large, carbon-rich molecules, many of which are likely to be ionic. The electronic spectra of ions are often obtained using action spectroscopy methods, which can induce small perturbations to the absorption characteristics and hinder comparison with astronomical observations. In this contribution, the appropriateness of helium-tagging and two-color resonant-enhanced photodissociation spectroscopy as suitable techniques to obtain the requisite laboratory data for comparison to DIBs is explored. As a proof-of-concept, the $\tilde{C}^2B_1 \leftarrow \tilde{X}^2B_1$ electronic transition of the phenylacetylene cation (PA^+ , $C_8H_6^+$), obtained by helium-tagging and two-color photodissociation, is compared to the direct absorption spectrum recorded using cavity ring-down spectroscopy. The results indicate that for DIBs with typical widths of a few  ngstr ms, the wavelengths, bandwidths, and relative intensities from action spectroscopy are obtained with sufficient precision to facilitate accurate comparisons to catalogued DIBs.

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ACS Earth Space Chem., (2024)

<https://doi.org/10.1021/acsearthspacechem.4c00272>

Constraining the link between the 2175Å dust absorption feature and PAHs in Nearby Star-Forming Galaxies using Swift/UVOT and JWST/MIRI

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The 2175 Å bump is a prominent absorption feature at ultraviolet (UV) wavelengths in dust extinction and attenuation curves. Understanding the relative strength of this feature is important for making accurate dust corrections at both low- and high-redshift. This feature is postulated to arise from polycyclic aromatic hydrocarbon (PAH) dust grains; however, the carrier has not been definitively established. We present results on the correlation between the 2175 Å feature and PAH abundances in a spatially-resolved manner for 15 local galaxies in the PHANGS-JWST survey that have NUV and mid-IR imaging data from Swift/UVOT and JWST/MIRI, respectively. We find a moderate positive correlation between the 2175 Å feature strength and PAH abundance, albeit with large intrinsic scatter. However, most of this trend can be attributed to a stronger negative correlation of both quantities with star formation rate (SFR) surface density and specific-SFR (proxies of ionising radiation). The latter trends are consistent with previous findings that both the 2175 Å carrier and PAHs are small grains that are easily destroyed by UV photons, although the proxy for PAH abundance (based on photometry) could also be influenced by dust heating. When controlling for SFR surface density, we find weaker correlations between the 2175 Å feature and PAH abundances, disfavouring a direct link. However, analyses based on spectroscopic (instead of photometric) measurements of the 2175 Å feature and PAH features are required to verify our findings. No significant trends with gas-phase metallicity or galactocentric radii are found for the 2175 Å feature and PAHs, however the metallicity range of our sample is limited. We provide prescriptions for the strength of the 2175 Å feature and PAHs in local massive (metal-rich) galaxies with SFR surface density and specific-SFR, however the former should be used with caution due to the fact that bump strengths measured from Swift/UVOT are expected to be underestimated.

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PASA, accepted (2024)

<https://doi.org/10.48550/arXiv.2412.03690>

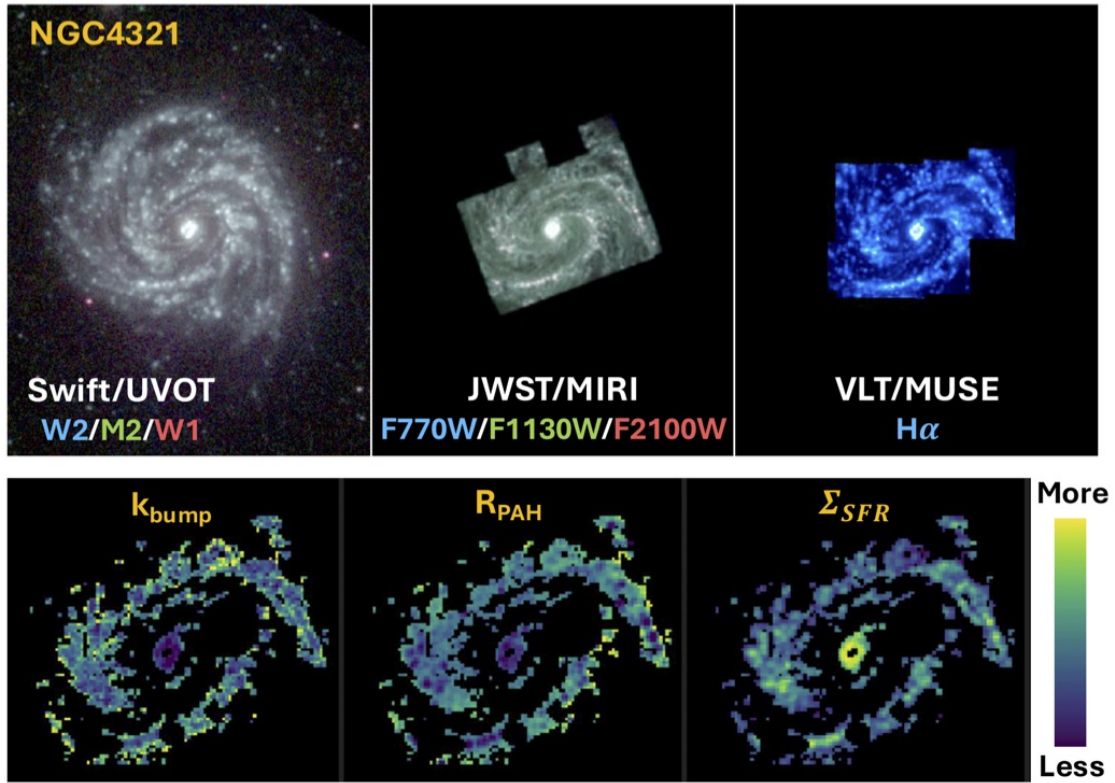


Figure 3 – Top: Gallery of data for NGC 4321. Bottom: Maps of the 2175 Å bump (k_{bump}), PAH abundance (R_{PAH}), and SFR surface density (Σ_{SFR}). There is a slight positive correlation between k_{bump} and R_{PAH} , and a stronger negative correlation of these parameters with Σ_{SFR} .

A sensitivity analysis of the modeling of Polycyclic Aromatic Hydrocarbon emission in galaxies

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We have conducted a sensitivity analysis on the mid-infrared spectral decomposition of galaxies and the modeling of the PAH emission spectrum with the NASA Ames PAH Infrared Spectroscopic Database (PAHdb) to assess the variance on the average galaxy PAH population properties under a grid of different modeling parameters. We find that the SL and SL+LL *Spitzer*-IRS decomposition with PAHFIT provides consistent modeling and recovery of the 5–15 μm PAH emission spectrum. For PAHdb modeling, application of a redshift to the calculated spectra to account for anharmonic effects introduces a 15%–20% variance on the derived parameters, while its absence improves the fits by $\sim 13\%$. The 4.00- α release of PAHdb achieves the complete modeling of the 6–15 μm PAH spectrum, including the full 6.2 μm band, improving the average fitting uncertainty by a factor of 2. The optimal PAHdb modeling configuration requires selection of pure PAHs without applying a redshift to the bands. Although quantitatively the PAHdb-derived parameters change under different modeling configurations or database versions, their variation follows a linear scaling, with previously reported trends remaining qualitatively valid. PAHdb modeling of JWST observations, and JWST observations smoothed and resampled to the *Spitzer*-IRS resolution and dispersion have consistent PAHdb derived parameters. Decomposition with different codes, such as PAHFIT and CAFE, produce PAH emission spectra with noticeable variation in the 11–15 μm region, driving a $\sim 7\%$ difference in the neutral PAH fraction under PAHdb modeling. A new library of galaxy PAH emission templates is delivered to be utilized in galaxy SED modeling.

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Astrophys. J, accepted (2024)

<https://doi.org/10.3847/1538-4357/ad9918>

<https://arxiv.org/pdf/2412.01875>

Not just PAH_{3.3}: Why galaxies turn red in the near-infrared

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We measured the spectral properties of a sample of 20 galaxies at $z \sim 0.35$ selected for having surprisingly red JWST/NIRCAM F200W-F444W colors. Of these, 19 galaxies were observed with JWST/NIRSpec in the PRISM configuration, while the remaining galaxy was observed with the high-resolution gratings. Of the 20 galaxies in our sample, 17 exhibit strong 3.3 μm polycyclic aromatic hydrocarbon (PAH) emission (equivalent width (EW) ($\text{PAH}_{3.3}$) $\geq 0.03 \mu m$). In these galaxies, the strength of the color excess does not depend on environment and correlates with $\text{EW}(\text{PAH}_{3.3})$. Nonetheless, the presence of the $\text{PAH}_{3.3}$ alone cannot fully explain the color excess, as an EW of $\sim 0.1 \mu m$ is able to increase the color of galaxies by only 0.13 mag. A contribution from a hot dust component is required to explain the excess. Both the $\text{PAH}_{3.3}$ EW and flux correlate with the $H\alpha$ EW and flux, suggesting that they are produced by the same mechanism. Five of the galaxies of our sample showing $\text{PAH}_{3.3}$ would be classified as passive based on broadband rest frame colors ((B-V) and/or UVJ diagrams) and are hence “faux passive”. Of these, three galaxies have a significantly lower $\text{EW}(\text{PAH}_{3.3})$ given their color and also have low $\text{EW}(H\alpha)$, and we tentatively conclude that this behavior is due to the presence of an active galactic nucleus. The three galaxies with no $\text{PAH}_{3.3}$ in emission have passive spectra, as do the eight galaxies in our sample with normal F200W-F444W colors. We therefore conclude that the $\text{PAH}_{3.3}$ feature is linked to dust-enshrouded star formation. The dust-corrected star formation rate (SFR) from $\text{PAH}_{3.3}$ is a factor of 3.5 higher than the SFR obtained from $H\alpha$, suggesting that these galaxies are characterized by significant amounts of dust.

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A&A, in press (2024)

<https://doi.org/10.48550/arXiv.2412.07070>



Meetings

Global Astrochemistry Lecture Series (GALS) Astrochemistry: From the Big Bang to Life

Online Spring 2025

Registration: December 1st 2024 - January 31st 2025

<https://www.astrochemistry.de/online-course/>

Our universe is full of molecules, from the simplest – molecular hydrogen – all the way up to the complex molecular structures essential to the chemistry of life on Earth. A large and diverse array of chemical species has been detected not only on planets but in interstellar clouds, in regions of star formation, in protoplanetary disks, and in comets and meteorites within the solar system. But how and when was all this material formed, and how does it evolve over time? How much molecular content is inherited from one stage of star and planet formation to the next? What role does the chemistry of the universe through cosmic time play in the origins of life? A major unanswered question remains whether the molecules essential to life were produced on the early Earth (endogenous origin), or whether they were produced in the parent interstellar medium or planet-forming disk and delivered to Earth via asteroids, comets and their meteoritic remains (exogenous origin).

This lecture course will be devoted to astrochemistry and the exploration of topics related to the chemical origins of life. In 18 lectures from the world-leading experts, we will discuss the history of the early molecular universe starting from the Big Bang; environmental conditions and key physico-chemical processes in space; astronomical observations (from ground to space) of objects of astrochemical interest; chemical models describing astrophysical environments and their reaction networks; key laboratory techniques and approaches for studying astrochemical processes; chemistry in specific environments, such as the interstellar medium, protoplanetary disks, and atmospheres of (exo)planets; exogenous synthesis and delivery of biomolecule precursors; and, finally, evolution of these precursors on the early Earth.

GALS is aimed at providing a broad overview of scientific issues, problems, achievements, and open questions in astrochemistry; and at helping senior undergraduate and postgraduate students as well as early career scientists to expand their interests and develop a firm understanding of this area, sufficient to choose an appropriate direction for their future career. The course is open to students and scientists from all over the world.

GALS is an annual event organized by Robin Garrod (University of Virginia, USA),

Wolf Geppert (Stockholm University, Sweden), Martin McCoustra (Heriot-Watt University, Scotland), and Alexey Potapov (Friedrich Schiller University Jena, Germany). GALS will comprise of two parts: 14 core lectures and 4 special lectures. There will be a new topic for special lectures every year. For the coming semester, we have chosen JWST.

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AstroPAH Newsletter

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Next issue: 20 February 2025

Submission deadline: 07 February 2025