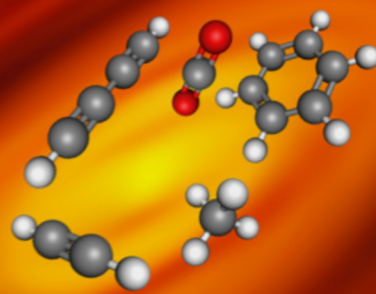
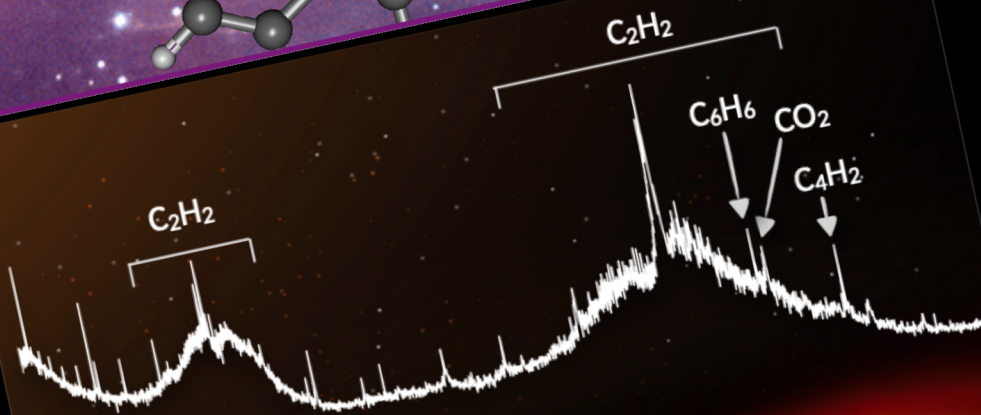
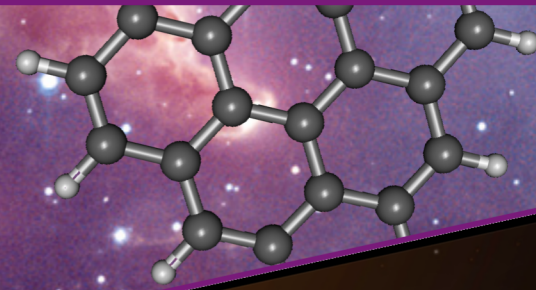


# AstropAH

A Newsletter on Astronomical PAHs

Issue 98 • May 2023



**A rich hydrocarbon chemistry in  
the inner disk of a low-mass star**

Credits: ALMA, PI B.



# Editorial

**Dear Colleagues,**

Welcome to AstroPAH #98!

This month, Prof. Shubhadip Chakraborty from the GITAM University, in India, prepared a delightful *In Focus* on how he is "Exploring the Molecular Universe".

The Abstract Section also explores this Molecular Universe in different environments – low-mass stars (our cover!), PDRs, and asteroids – and with models, calculations, mixtures, physical and chemical conditions, and experiments!

Follow us on [Facebook](#) and [Instagram](#). If you wish to contact us or send contributions for a future AstroPAH, use our [email](#). We welcome your suggestions!

We hope you enjoy reading our newsletter, and we thank you for your contributions and interest in AstroPAH!

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**Next issue: 22 June 2023.  
Submission deadline: 9 June 2023.**

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## PAH Picture of the Month

The MIRI spectrum of J160532 and an artist impression of the disk. The emission lines of gas-phase benzene, diacetylene and carbon dioxide can be seen as narrow peaks in the spectrum. Acetylene ( $C_2H_2$ ) is so abundant in the gas-phase that it gives broad bumps in the spectrum. Interestingly, there is no or little water in the disk.

**Credits:** LMA/MPIA/JWST/MIRI/[Tabone et al.](#)

## Exploring the Molecular Universe

by Shubhadip Chakraborty

### Introduction

The Universe is dusty, icy and chemically rich. Till now, more than 290 molecules have been identified in the interstellar medium (ISM), starting from 2 and all the way up to 70 atoms. Most of these molecules have been identified with the help of millimeter wave spectroscopy coupled with radio observations, and a few have been identified using ultraviolet or infrared astronomy. Interestingly, among all identified molecules, the aromatic molecules have drawn the attention of the scientific community to a great extent. The reason behind this is straightforward. The life-bearing molecules, like deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), are all made up of various aromatic molecules. Undoubtedly the formation and destruction of these molecules under the condition of the ISM is a very interesting area of research. Here I briefly discuss the two projects I have worked on during my first and second postdoctoral tenure in Toulouse and Rennes, respectively.

- The experimental and theoretical IR spectroscopy of cosmic PAHs in order to model their emission profiles in various astronomical objects
- Shock induced dissociation of C<sub>60</sub>

Finally, I will conclude with my current ongoing activities in the Department of Chemistry, GITAM University Bengaluru, India

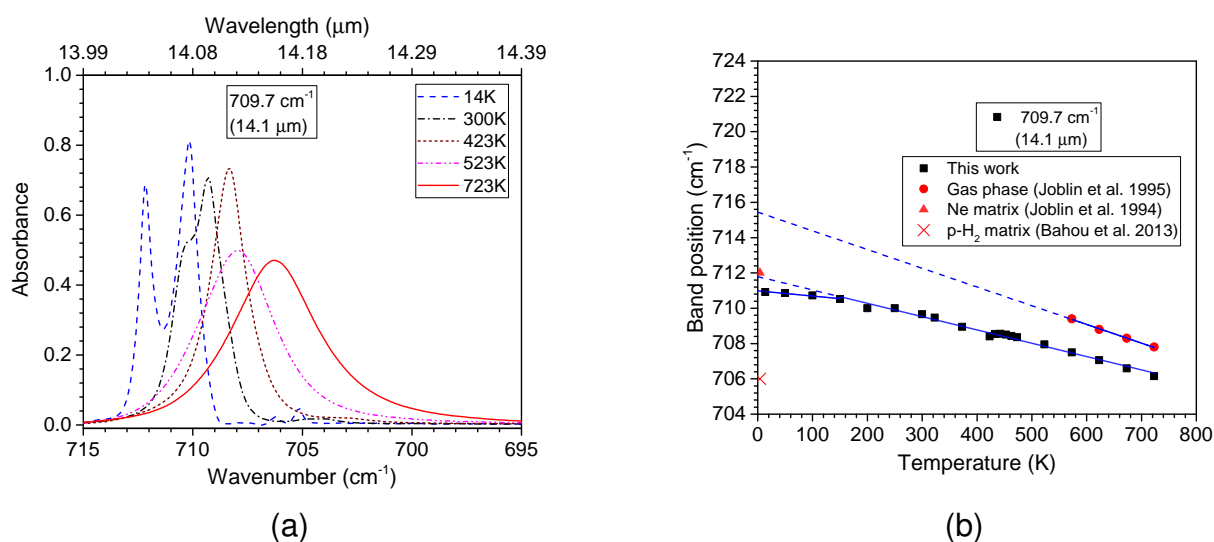
### Physics and Chemistry of Cosmic PAHs

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of organic molecules containing several fused benzene rings in a honeycomb fashion. It has been proposed that ~10-20% of the cosmic carbon is locked in PAHs. They are omnipresent throughout the universe as many astronomical objects glow at 3.3, 6.2, 7.7, 8.6, 11.6 and 12.7  $\mu\text{m}$ , commonly known as aromatic infrared bands (AIBs). Although their presence was first speculated back in the mid-'70s through several broad mid-infrared (MIR) emission features, [Sellgren \(1984\)](#) was the first to propose that large PAHs are likely to be carriers of these mid-infrared emission features. This proposition was further supported by the work of [Leger and Puget \(1984\)](#) and [Allamandola et al. \(1989\)](#). Since then, a large volume of research activities have been carried out for a better understanding of the PAH hypothesis. After 35 years

of dedicated research, very recently, several small PAHs have been conclusively identified unexpectedly in a large amount in the cold region of the Taurus molecular cloud with the aid of rotational spectroscopy coupled to radio observations (McGuire et al., 2021; Cernicharo et al., 2021). The AIBs are believed to originate from the infrared fluorescence of thermally excited large gas-phase PAHs (50-100 carbon atoms), triggered by the absorption of energetic UV-Vis photons (Leger et al., 1989). Their bandwidths span up to several tens of  $\text{cm}^{-1}$  (Verstraete et al., 2001) and are strongly affected by the vibrational anharmonicity (Joblin et al., 1995; Pech et al., 2002; Lemmens et al., 2019). Modelling the AIBs is a long-term goal of the astronomers (Pech et al., 2002; Mulas et al., 2006; Mackie et al., 2021) for a detailed understanding of the physics of PAH emission in the ISM. However, to model the PAH emission bands, one needs to consider the position, width and intensity of the bands at various temperatures. This calls for the variable temperature infrared spectroscopy of PAHs (Bernard et al., 1989; Blanco et al., 1990; Joblin et al., 1995). Joblin et al. (1995) have recorded the IR spectra of naphthalene, pyrene, coronene and ovalene in the gas phase and found that the position of the IR bands moves towards red and the bandwidth increases with temperature. By fitting the band positions and widths with a linear equation, they derived empirical anharmonicity factors required for astronomical modelling. Unfortunately, due to experimental complexity, high-quality gas-phase IR spectral data of PAHs are still scarce.

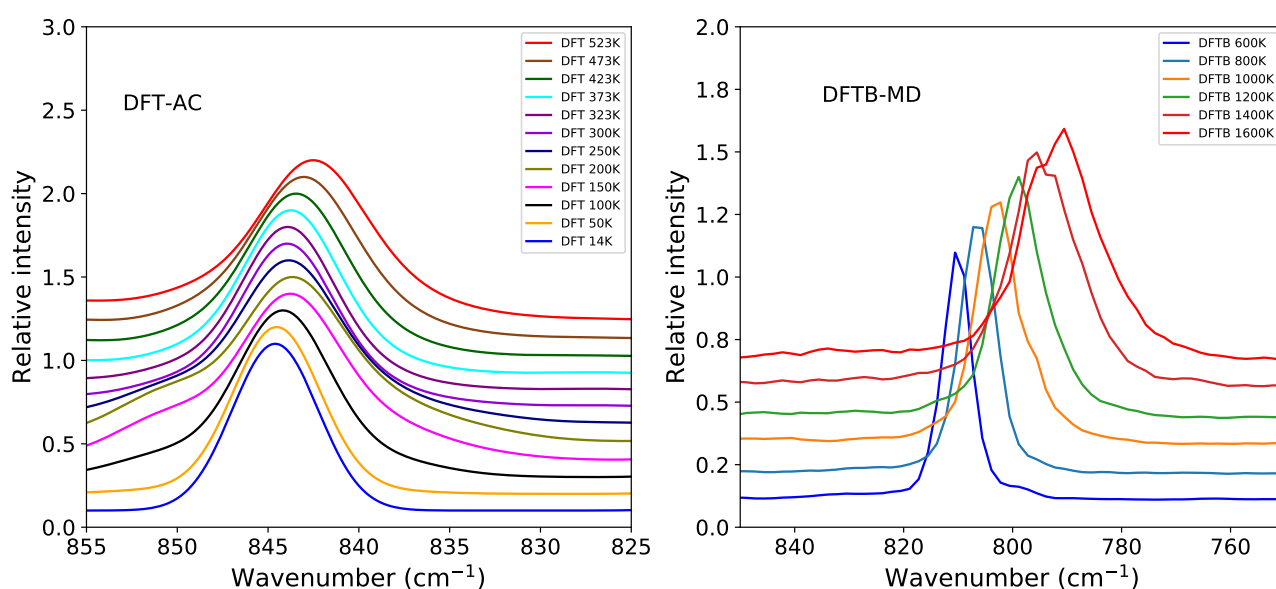
During my postdoctoral tenure in Toulouse, I developed an alternative approach to the gas-phase measurement. I recorded the IR spectrum of medium and large PAHs and  $\text{C}_{60}$  in the solid phase at various temperatures. The derived anharmonicity parameters were compared with some available gas-phase data. Initially, to start with, I have recorded the IR spectrum of solid pyrene embedded in solid KBr from 14 to 723 K (Chakraborty et al., 2019) and the derived anharmonicity factors were found to have a very good match with the gas-phase data recorded by (Joblin et al., 1995). In the Figure1 (a) I have shown the variation of the  $14.1 \mu\text{m}$  band of pyrene. The positions were estimated using a multi-component fitting algorithm and are presented in Figure1 (b).

In parallel, I have computed the IR spectra of pyrene using the AnharmoniCaOs (Mulas et al., 2018) and deMonNano package (Joalland et al., 2010; Simon et al., 2011) and compared the theoretical data with the experimental findings (Chakraborty et al., 2021). In Figure 2, I have presented the variation of band profiles with temperature calculated using the AnharmoniCaOs and deMonNano package. The AnharmoniCaOs package has been developed in collaboration between Cagliari, Toulouse and Orsay. It works in the framework of the VanVleck perturbation theory. The anharmonic spectrum is calculated as a function of excitation energy (or temperature, via a Laplace transformation), including fundamentals and overtones, combinations, and difference bands. This exhaustive calculation helps us to investigate the integrity of the details of the IR band features of hot PAHs with significant accuracy. However, extending this calculation for larger PAHs at higher temperatures becomes relatively expensive because of the high computational cost. Therefore, I have used classical molecular dynamics (MD) simulations using the deMonNano package to investigate the IR band features of large PAHs at very high temperatures. The idea of this work was to use the AnharmoniCaOs package to simulate the band profiles in the low-temperature region and deMonNano for the high-temperature region and combine them smoothly. We showed that the two methods could be used to improve the modelling going from the cheapest and less accurate method, DFTB, to a more expensive and fully quantum treatment method like AnharmoniCaOs.



**Figure 1** – Evolution of the (a) band profiles and (b) positions with temperature for fundamental transitions of pyrene in KBr pellets (black squares). Band positions (in  $\text{cm}^{-1}$  and  $\mu\text{m}$ ) at 300 K are mentioned in the top right corner of each panel. The calculated linear fits in the low and high temperature ranges are shown by blue lines. Also shown with red marks are published data both at high temperature in the gas-phase Joblin et al. (1995) and at very low temperature (3-4 K) either in Ne (Joblin et al., 1994) or  $p\text{-H}_2$  matrices (Bahou et al., 2013).

Experimental data have also been gathered on  $\text{C}_{60}$  and a few PAHs larger than pyrene. The anharmonicity parameters deduced from these measurements will help model PAH spectra in relation to James Webb’s observations.

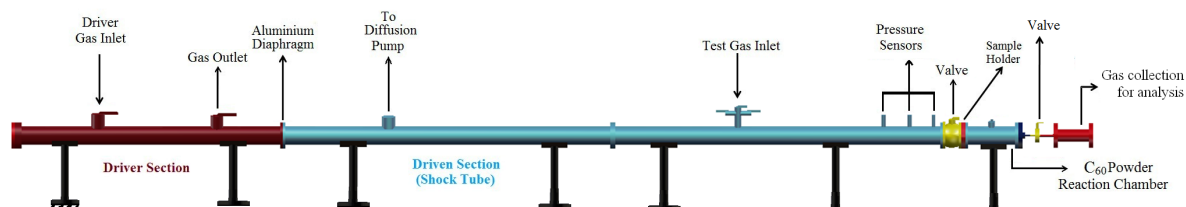


**Figure 2** – Temperature evolution of the highest intensity band of pyrene at  $844.4 \text{ cm}^{-1}$  simulated using DFT-AC and DFTB-MD. Intensities are given in arbitrary units, normalised to unit peak intensity, to emphasize the evolution of the spectral profile.

## Shock Induced Dissociation of C<sub>60</sub> Fullerene

Interstellar dust plays a crucial role in altering the chemical and dynamical behaviour of the ISM. Dust is believed to form predominantly in the ISM at the end of life of low mass stars during their asymptotic giant branch (AGB) phase, supernovae explosions etc. After formation, they get processed under the influence of shock waves, cosmic radiation, UV radiation etc. During my postdoctoral tenure in Rennes, I studied interstellar dust analogues' evolution using pressure-driven shock waves. The application of shock wave research is versatile, starting from defence, medicine, material science etc. However, the application of shock wave in laboratory astrochemistry is a relatively new area of research. In the ISM, shock waves are generated during the star birth (jets/bipolar flows) (Gusdorf et al., 2015), the life of stars (stellar winds) (Ioka et al., 2019) and their death (supernova/supernova remnant), and impacts the chemical evolution of interstellar dust.

The typical velocity of shock waves in the ISM range from 1 to a few tens of thousands of km s<sup>-1</sup>. However, during the formation of early-type stars, the typical velocity of the shock waves ranges  $\leq 10$  km s<sup>-1</sup> (Rudnitskij, 1997). With this idea, I have studied the evolution of C<sub>60</sub> Fullerene with a low-velocity shock wave with a typical shock velocity of 5-6 km s<sup>-1</sup>. Fullerene is an allotrope of carbon which was discovered by serendipity during the laser ablation of graphite (Kroto et al., 1985) aimed to study the formation of long-chain carbon compounds in the circumstellar shell of dying stars. The presence of C<sub>60</sub> and C<sub>70</sub> in the ISM was first speculated by Sellgren et al. (2007) in NGC 7023 reflection nebula. Later on, Cami et al. (2010) and Sellgren et al. (2010) have conclusively identified C<sub>60</sub> and C<sub>70</sub> in Tc1 planetary nebula and the NGC 7023 and NGC 2023 reflection nebulae, respectively through their mid-infrared emission features. It is generally believed that C<sub>60</sub> forms in the ISM during the outflows of AGB stars, but Berné and Tielens (2012) have reported that C<sub>60</sub> can also form in the cold environment of the ISM illuminated by strong UV radiation.



**Figure 3** – Experimental set up to study the shock evolution of interstellar dust analogues. The length of entire tube is 8 meter and divided into two sections, driver section (in brown) and driven section (in cyan).

The research group in Rennes has previously studied the shock evolution of C<sub>60</sub> in the presence of H<sub>2</sub> using the experimental set-up as shown in Figure 3 (Biennier et al., 2017). The major advantage of a shock tube is that by changing the experimental conditions, one can obtain the reflected shock temperature up to 6000 K for 1-2 ms. The details of the experimental set-up can be found in Biennier et al. (2017). In this work, the authors have analyzed the post-shock residue using various analytical tools like infrared microscopy, Raman micro-spectroscopy, X-ray diffraction analysis, scanning electron microscopy (SEM) and tunnelling electron microscopy (TEM). The post-shock gas was collected and was analyzed using gas-chromatography mass spectrometry and cavity-ring-down spectroscopy. The authors found the formation of various gaseous hydrogenated aliphatic compounds.

The analysis also revealed that the fast thermal processing of C<sub>60</sub> with H<sub>2</sub> over 800 to 3400K leads to the formation of amorphous carbons. IR microscopic study reveals the formation of compounds containing aliphatic CH stretching groups.

Recently, we have studied the shock evolution of C<sub>60</sub> in an *in situ* manner. A miniature visible spectrometer was connected with the shock tube as shown in the Figure 3. The emitted light was collected during the shock wave interaction with C<sub>60</sub>. The well-known C<sub>2</sub> Swan bands were observed. High-level quantum chemical calculations were performed to simulate the observed C<sub>2</sub> bands. The details of the analysis are a subject of a dedicated to-be-submitted article on spectroscopy and dynamics of shock evolution of C<sub>60</sub> (Chakraborty et al., 2023).

## Current activities

Very recently I was offered a teaching position in the Department of Chemistry, GITAM university, Bengaluru, India. Currently, I am mostly involved in teaching physical chemistry for the bachelors and masters students of the engineering school and science. Apart from teaching I sometime visit the nearby schools and motivate the high school students to read science, take them for night sky watching etc. At the same time, I am investigating solutions to continue research in astrochemistry.



**Dr. Shubhadip Chakraborty** is an assistant professor in the Department of Chemistry, GITAM University, Bengaluru, India since September 2022.

He finished his doctoral studies from the Indian Institute of Science, Bengaluru, India in 2016 under the supervision of Prof. P. K. Das. His fascination about astrochemistry started while working as a postdoc with Dr. Christine Joblin from IRAP, Toulouse. Later on, in 2019 he started his second postdoc with Dr. Ludovic Biennier and Prof. Robert Georges from the IPR, Université de Rennes in the domain of laboratory astrochemistry. He is also a science collaborator of an early release science proposal of the James Webb Space Telescope.

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# Abstracts

## Polycyclic Aromatic Hydrocarbon emission model in photodissociation regions II: Application of the emission model to PAHs and C<sub>60</sub>

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We present a charge distribution-based emission model that calculates the infrared spectrum of fullerenes (C<sub>60</sub>). Analysis of the modelled spectrum of C<sub>60</sub> in various charge states shows that the relative intensity of the features in the 5-10 μm versus 15-20 μm can be used to probe the C<sub>60</sub> charge state in interstellar spectra. We further used our model to simulate emission from polycyclic aromatic hydrocarbons (PAHs) and C<sub>60</sub> at five positions in the cavity of reflection nebula NGC 7023. Specifically, we modelled the 6.2/11.2 band ratio for circumcoronene and circumcircumcoronene and the 7.0/19.0 band ratio for C<sub>60</sub> as a function of the ionization parameter  $\gamma$ . A comparison of the model results with the observed band ratios shows that the  $\gamma$  values in the cavity do not vary significantly, suggesting that the emission in the cavity does not originate from locations at the projected distances. Furthermore, we find that the C<sub>60</sub> derived  $\gamma$  values are lower than the PAH-derived values by an order of magnitude. We discuss likely scenarios for this discrepancy. In one scenario, we attribute the differences in the derived  $\gamma$  values to the uncertainties in the electron recombination rates of PAHs and C<sub>60</sub>. In the other scenario, we suggest that PAHs and C<sub>60</sub> are not co-spatial resulting in different  $\gamma$  values from their respective models. We highlight that experiments to determine necessary rates will be required in validating either one of the scenarios.

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<https://arxiv.org/abs/2304.11230>

<https://doi.org/10.1093/mnras/stad1180>

# Structures and stabilities of PAH clusters solvated by water aggregates: the case of the pyrene dimer

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Whereas clusters made of polycyclic aromatic hydrocarbon and water monomers are relevant objects in both atmospheric and astrophysical science, little is known about their energetic and structural properties. In this work, we perform global explorations of the potential energy landscapes of neutral clusters made of two pyrene units and one to ten water molecules using a Density-Functional based Tight-Binding (DFTB) potential followed by local optimisations at the Density-Functional Theory level. We discuss the binding energies with respect to various dissociation channels. It shows that cohesion energies of the water clusters interacting with a pyrene dimer is larger than that of the pure water clusters, reaching for the largest clusters an asymptotic limit similar to that of pure water clusters and that, while the hexamer and octamer can be considered as magic numbers for isolated water clusters, it is not the case anymore when they are interacting with a pyrene dimer. Ionisation potentials are also computed making use of the Configuration Interaction extension of DFTB and we show that in cations, the charge is mostly carried by the pyrene molecules.

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# A rich hydrocarbon chemistry and high C to O ratio in the inner disk around a very low-mass star

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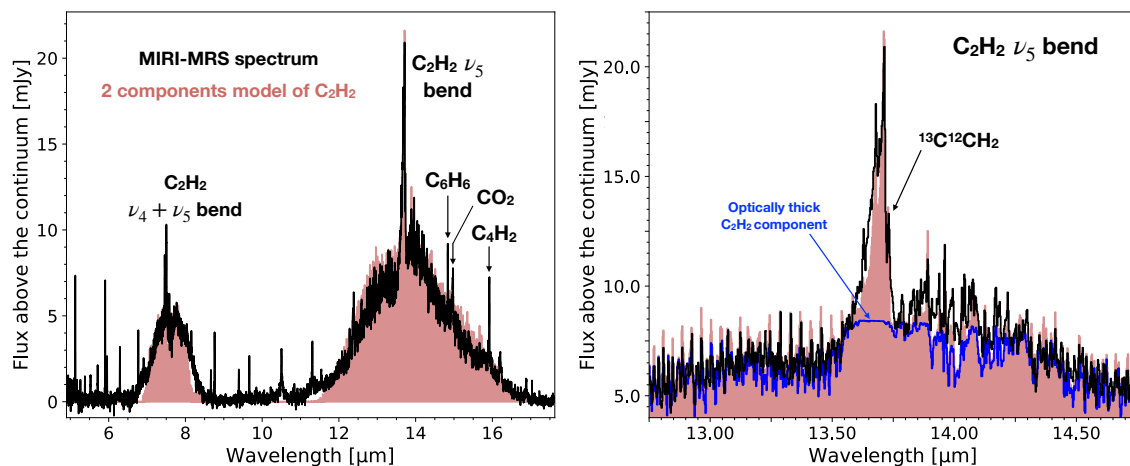
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Carbon is an essential element for life but how much can be delivered to young planets is still an open question. The chemical characterization of planet-forming disks is a crucial step in our understanding of the diversity and habitability of exoplanets. Very low-mass stars ( $<0.2 M_{\odot}$ ) are interesting targets because they host a rich population of terrestrial planets. Here we present the JWST detection of abundant hydrocarbons in the disk of a very low-mass star obtained as part of the MIRI mid-Infrared Disk Survey (MINDS). In addition to very strong

and broad emission from  $C_2H_2$  and its  $^{13}C^{12}CH_2$  isotopologue,  $C_4H_2$ , benzene, and possibly  $CH_4$  are identified, but water, PAH and silicate features are weak or absent (see Figure 1). The lack of small silicate grains implies that we can look deep down into this disk. These detections testify to an active warm hydrocarbon chemistry with a high C/O ratio in the inner 0.1 au of this disk, perhaps due to destruction of carbonaceous grains. The exceptionally high  $C_2H_2/CO_2$  and  $C_2H_2/H_2O$  column density ratios suggest that oxygen is locked up in icy pebbles and planetesimals outside the water iceline. This, in turn, will have significant consequences for the composition of forming exoplanet.



**Figure 4** – The JWST-MIRI spectrum of the disk around the very low-mass star J160532 showing prominent emission from gas-phase hydrocarbons (from Tabone et al. 2023, Nat. Astron.)

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# Influence of hydrothermal asteroidal conditions on the molecular structure and isotopic compositions of polycyclic aromatic hydrocarbons

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A variety of polycyclic aromatic hydrocarbons (PAHs) are reported in carbonaceous chondrites (CCs) and in the interstellar medium (ISM). Although PAHs in CCs are not as large as those detected in the ISM, their carbon isotope composition is interpreted as pinpointing an interstellar origin. In contrast, their hydrogen isotope composition can be related to the extent of secondary processes, as is the proportion of alkylated PAHs within CCs. Here, we experimentally investigate the molecular and isotopic evolution of PAHs under simulated asteroidal hydrothermal conditions at 150 °C. Results show that PAHs are chemically stable under these conditions whatever their size, i.e. no destruction, conjugation nor alkylation occurs, even in the presence of other reactive organic molecules. Plus, PAHs retain their carbon isotope compositions even in the presence of another carbon-rich reservoir, either organic or inorganic. On the other hand, their hydrogen isotope composition is modified through exchange with water. Of note, as shown by additional experiments, the presence of smectites, abundant in CCs, impacts the relative abundances of extractable PAHs, saponite trapping more efficiently the larger PAHs. Altogether, results of the present experiments show that PAHs of CCs can be used as tracers of both pre-accretion and secondary processes.

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# Size distribution of polycyclic aromatic hydrocarbons in space: an old new light on the 11.2/3.3 $\mu\text{m}$ intensity ratio

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The intensity ratio of the 11.2/3.3  $\mu\text{m}$  emission bands is considered to be a reliable tracer of the size distribution of polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM). This paper describes the validation of the calculated intrinsic infrared (IR) spectra of PAHs that underlie the interpretation of the observed ratio. The comparison of harmonic calculations from the NASA Ames PAH IR spectroscopic database to gas-phase experimental absorption IR spectra reveals a consistent underestimation of the 11.2/3.3  $\mu\text{m}$  intensity ratio by 34%. IR spectra based on higher level anharmonic calculations, on the other hand, are in very good agreement with the experiments. While there are indications that the 11.2/3.3  $\mu\text{m}$  ratio increases systematically for PAHs in the relevant size range when using a larger basis set, it is unfortunately not yet possible to reliably calculate anharmonic spectra for large PAHs. Based on these considerations, we have adjusted the intrinsic ratio of these modes and incorporated this in an interstellar PAH emission model. This corrected model implies that typical PAH sizes in reflection nebulae such as NGC 7023 — previously inferred to be in the range of 50 to 70 carbon atoms per PAH — are actually in the range of 40 to 55 carbon atoms. The higher limit of this range is close to the size of the C<sub>60</sub> fullerene (also detected in reflection nebulae), which would be in line with the hypothesis that, under appropriate conditions, large PAHs are converted into the more stable fullerenes in the ISM.

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# Coevolution of the interstellar chemistry: Gas-phase laboratory formation of hydrogenated fullerene-PAH clusters

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Fullerene molecules are affected and constrained by different interstellar environmental factors, such as UV radiation, atoms, and other coexisting molecules. To understand the coevolution of the interstellar fullerene chemistry, by tracking the accretion processes on fullerene cations, we present an investigation of the chemical reactivity of fullerene ( $C_{60}$ ) cations and smaller fullerene ( $C_{54/56/58}$ ) cations with hydrogen and  $C_{14}H_{10}$  in the gas phase. Experiments are performed using a quadrupole ion trap in combination with time-of-flight mass spectrometry. The experimental results show hydrogenated fullerene- $C_{14}H_{10}$  cluster cations (i.e.,  $[H_n C_{60}(C_{14}H_{10})_m]^+$  and  $[H_n C_{54/56/58}(C_{14}H_{10})_m]^+$ ) are efficiently formed through ion-molecule collision reaction. H-atoms are more likely to accumulate on the surface of fullerenes than  $C_{14}H_{10}$ ; not only does hydrogen more easily form a covalent bond, the later accreted hydrogen will also expel the already accreted  $C_{14}H_{10}$ . Through theoretical calculations, we obtain the structure of newly formed clusters (e.g.,  $[HC_{60}(C_{14}H_{10})]^+$  and  $[HC_{58}(C_{14}H_{10})]^+$ ) and the binding energies of their reaction pathways, together with IR spectra. The bonding ability plays a decisive role in the ternary cluster formation processes, and the existence of occupation and expulsion competitive reaction channels in the accretion processes on fullerene surfaces is confirmed. As part of the coevolution of the interstellar chemistry, the occupation and expulsion reaction modes should be considered when fullerenes further react with H-atoms and PAHs. As a result, the molecular structures of hydrogen/fullerene/PAH clusters are diverse, and hydrogenated-fullerene-related clusters (e.g., hydrogenated fullerenes or hydrogenated fullerenes-PAHs) have a higher distribution than nonhydrogenated-fullerene-related clusters (e.g., fullerenes or fullerenes-PAHs) in the interstellar environment.

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