



AstropAH

A Newsletter on Astronomical PAHs

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Ring Nebula



Editorial

Dear Colleagues,

Welcome to our new AstroPAH volume! We hope all of you are healthy and doing well!

Our cover of the month is the famous Ring Nebula as captured in unprecedented detail by the JWST NIRCam instrument. The main shell of this planetary nebula shows a thin ring of emission from PAHs.

We are also pleased to share with you our In Focus written by Amit Pathak from Banaras Hindu University, India, on "Interstellar PAHs in the Age of JWST and ALMA: insights from computational chemistry."

As always, our abstracts provide insight on some of the latest published PAH research. This month, the abstracts detail studies on He-tagged C_{60} anions, hydrogenated amorphous carbon grains, benzonitrile, and nitrile-substituted naphthalene and benzene. Please continue to contribute your abstracts to AstroPAH for us to highlight them every month!

If you are on Instagram, be sure to check out our next [PAH of the Month!](#)

We hope you enjoy reading our newsletter, and we thank you for your dedication and interest in AstroPAH! Please continue sending us your contributions, and if you wish to contact us for a future In Focus or other ideas, feel free to use our [email](#).

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**Next issue: 18 April 2024.
Submission deadline: 5 April 2024.**

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PAH Picture of the Month

This month's cover presents the Ring Nebula, captured in unprecedented detail by the NIRCam on the JWST. The main shell of this beautiful planetary nebula, located relatively close to us, exhibits a thin ring of emission from polycyclic aromatic hydrocarbons.

Credits: Ring nebula image: ESA/Webb, NASA, CSA, M. Barlow (UCL), N. Cox (ACRI-ST), R. Wesson (Cardiff University). The image is available [here](#).

Interstellar PAHs in the Age of *JWST* and *ALMA* Insights from Computational Chemistry

by Amit Pathak

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are large organic molecules, extending the size range of interstellar dust particles into the molecular domain. All the defining characteristics of a PAH conveniently reside within its chemical name. Polycyclic indicates that the carbon atoms in PAHs form structures with multiple interconnected rings, consisting of more than two adjacent rings. Aromatic refers to the delocalization of electrons throughout the ring, leading to stability, and hydrocarbon is a type of organic compound made up entirely of hydrogen and carbon. From an astronomical standpoint, PAHs refer to a broader category including PAHs having other element in their structure (e.g., nitrogen or oxygen), PAHs with different side-groups (e.g., CH_3 or CN), superhydrogenated PAHs, dehydrogenated PAHs, PAH clusters, etc (e.g., [Tielens, 2008](#)). The presence of PAHs is prominently indicated by the mid-IR emission spectra (*aka Aromatic Infrared Bands; AIBs*) of several astronomical environments, including protoplanetary disks, HII regions, reflection nebulae, planetary nebulae, young stellar objects, post-asymptotic giant branch (AGB) objects, the interstellar medium (ISM) of galaxies, as well as in the galactic nuclei ([Tielens, 2008](#); [Chown et al., 2023](#)).

The *James Webb Space Telescope (JWST)* possesses unparalleled spatial resolution, allowing it to effectively resolve the complex, blended spectral signatures of PAHs within the near- and mid-IR wavelength range. As illustrated in **Figure 1**, the AIBs or PAH bands consist of a set of broad emission features strongly present at 3.3, 6.2, 7.7, 8.6, 11.2, 12.7, and 16.4 μm , attributed to the fundamental bands arising from stretching and bending vibrational motion of C–H and C=C bonds in PAHs. There are also a plethora of weaker features in the AIB spectrum at ~ 3.4 , ~ 3.5 , ~ 5.25 , ~ 5.75 , 6.02, ~ 6.6 , 6.94, ~ 8.2 , ~ 10.95 , 11.00, 12.0, 13.5, 13.95, 14.21, and 16.43 μm , some of which exhibiting intensities comparable to the major ones, that have not yet been assigned ([Chown et al., 2023](#)). Accurately assigning these additional features necessitates precise infrared spectroscopy on various PAHs and their clusters, accounting for anharmonicity, and including combination bands, overtones, and Fermi resonances in their spectra. For instance, PAHs with aliphatic C–H stretch are crucial for understanding features around ~ 3.4 and ~ 3.5 μm . Moreover, investigating combination bands and overtones associated with C–H stretching and C–H

out-of-plane bending modes is necessary for comprehending bands in the 1–3 μm and 5–6 μm regions, respectively. In addition to vibrational emission, the rotational emission originating from PAHs is a strong candidate as a source for the dust-correlated anomalous microwave emission (AME) occurring in the 10–60 GHz wavelength range (Kogut et al., 1996). This includes the identification of polar PAHs in the centimeter-wavelength range, as demonstrated by the recent detection of nitrogen-containing PAHs (PANHs) in TMC-1, a cold, dark molecular cloud (McGuire et al., 2021). To understand the structural and dynamic features of molecular systems, rotational and vibrational spectroscopy play a central role as their noninvasive nature allows to reveal diverse physicochemical characteristics.

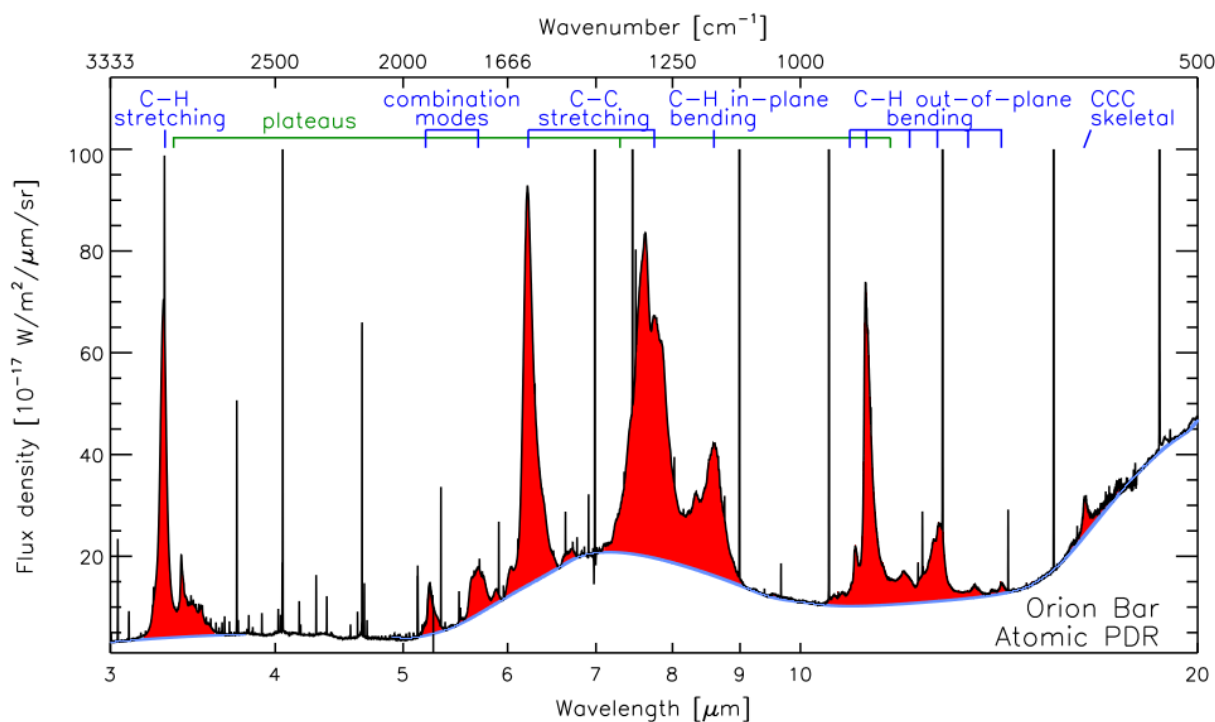


Figure 1 – JWST view of the AIB spectrum of the Orion Bar.
(Figure from Chown et al., 2023)

2. Formation of PAHs

Considering the chemical aspect, PAHs the formation and growth mechanisms of PAHs in AGB envelopes have been investigated theoretically by Frenklach & Feigelson (1989), Frenklach & Wang (1991), and Cherchneff et al. (1992). The mechanisms involved in transforming C_2H_2 into large PAH molecules and, ultimately, soot are similar to those found in the pyrolysis of hydrocarbon molecules, known as the hydrogen abstraction and acetylene or carbon addition (HACA). This mechanism involves a two-step process characterized by the iterative sequence of hydrogen abstraction, activating the aromatic molecule, followed by the subsequent addition of acetylene (C_2H_2) to the radical site formed during the hydrogen abstraction step (Figure 2). The initial conceptual framework was introduced to explain the formation of pyrene from benzene. It was specifically devised to elucidate the ongoing growth of PAHs in flames fueled by C_2 hydrocarbons like ethane, ethylene, and acetylene (Frenklach & Wang, 1991).

Over the past few decades, the HACA mechanism has garnered increasing attention, emerging as a central focus in understanding PAH growth processes (Reizer et al., 2022).

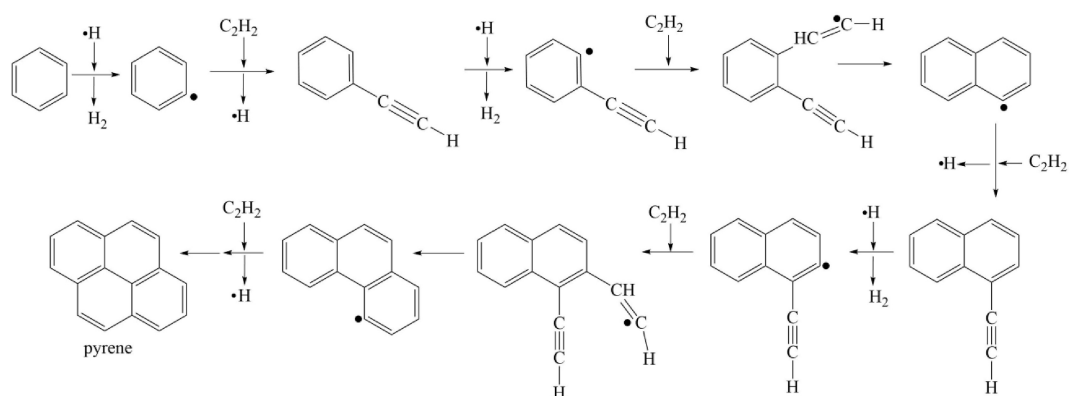


Figure 2 – The hydrogen abstraction and acetylene or carbon addition (HACA) reaction. (Figure from Reizer et al., 2022)

A noteworthy observation about HACA is its role in expediting the formation of benzenoid PAHs, thus contributing to the surface growth of soot mass through acetylene addition. The intrinsic feature of HACA lies in its advantageous and critical alignment between reaction reversibility and kinetic driving force (Frenklach, 2002).

3. Emission Mechanism of PAHs in Space

3.1. Vibrational

In the vastness of interstellar space, PAHs showcase a unique behavior when emitting the vibrational spectra, distinctly different from their counterparts on Earth. The fundamental distinction arises from the density of the surroundings. On Earth, high gas densities result in frequent collisions between molecules, ensuring a uniform temperature for the PAHs. Additionally, energy exchanges with the environment maintain a stable temperature without significant fluctuations. Consequently, laboratory measurements of PAH spectra yield a fixed temperature spectrum due to these controlled conditions. Contrastingly, interstellar space experiences low densities, leading to infrequent collisions among molecules. PAHs in this environment lack thermal equilibrium, allowing them to adopt varying temperatures from neighboring molecules. Energy fluctuations occur stochastically, with short bursts of energy, notably in the form of UV photons. As shown in **Figure 3**, when a PAH absorbs a UV photon, it becomes electronically excited, returning to the ground state through non-adiabatic effects, reaching highly excited (high-temperature) vibrational states. In the next few seconds, the PAH cools down by emitting IR photons before absorbing another UV photon, initiating the process again. This dynamic cycle, known as an infrared cascade, results in the observed IR spectrum (Allamandola et al., 1989).

3.2. Pure Rotational

The pure rotational emission of PAHs are contingent upon their permanent electric dipole moment, μ . PAHs that exhibit symmetry, are neutral, and fully hydrogenated typically possess a μ value close to zero. Due to this, the most important tool to identify a molecule in space, *i.e.*, rotational spectroscopy has not been successful for PAHs. Subsequently,

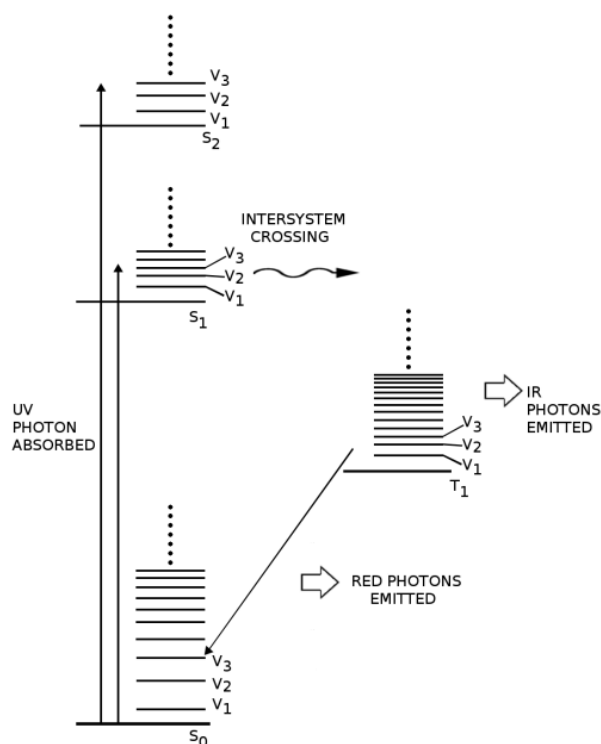


Figure 3 – The energy levels of a neutral PAH, outlining the potential radiative and non-radiative excitation and relaxation pathways.
(Figure from [Allamandola et al., 1989](#))

planar PAHs can develop a permanent dipole moment if they incorporate impurities, primarily through substitution or the presence of different side groups. Among these, nitrogen-containing PAHs or polycyclic aromatic nitrogen heterocycles (PANHs) stand out as prominent and suitable candidates for radio astronomical searches ([Hudgins et al., 2005](#); [Ali-Haïmoud, 2014](#)), particularly with the recent identification of certain PANHs in the TMC-1 ([McGuire et al., 2021](#)). Due to the Boltzmann distribution and the low temperatures prevalent in molecular clouds, PAHs' rotational excited states become populated in the temperature range of 10–100 K and subsequently undergo decay through spontaneous emission. As a result, the molecular cloud's spectrum in the radiofrequency and microwave regions exhibits distinct and sharp lines corresponding to rotational transitions. Rotational transitions are a consequence of the rotation of the dipole due to interaction with the electromagnetic field within the microwave region of the spectrum.

4. The Role of Computational Chemistry: A Temporal Overview

In the quest to understand the intricate spectra of interstellar PAHs, the ideal scenario would involve meticulous laboratory measurements of all relevant PAHs right here on Earth. However, this endeavor is practically impossible, mainly due to the staggering scale of potential PAH species and their low volatility. To address this, computational chemistry plays a crucial role. Experimental data validate and improve theoretical models, enabling the study of a wide range of PAHs and derivatives under diverse conditions.

In the 1980s, computational chemistry methods were well-developed but limited to small molecules (3–4 atoms). Faced with the complexity of larger PAHs (several tens of atoms) and the need for precise determination of their IR frequencies, intensities, and other spectroscopic constants, quantum chemists had to adapt to the computing capabilities of the time. Initial calculations were done at the Hartree-Fock (HF) level, followed by the adoption of Density Functional Theory (DFT), which remains the primary theoretical framework for treating PAHs, even those with over a hundred atoms (see [Pauzat \(2011\)](#) for a review). In HF theory, electrons are considered independent and the correlation among them is neglected. To incorporate correlation effects, various methods can be employed. In post-HF theories, like MP2 (Moller Plesset 2nd order), correlation effects are introduced by combining the ground state wavefunction with excited configurations, specifically doubly excited ones. In DFT, electron correlation is explicitly addressed through a correlation functional, allowing calculations to be confined to the ground state only.

In theoretical rotational and vibrational spectroscopy, the rigid rotor-harmonic oscillator (RR-HO) approximation, foundational for these techniques and their separability, proves inadequate for quantitative purposes. To address this, models incorporating semirigidity and anharmonicity are necessary. Second-order vibrational perturbation theory (VPT2) is widely regarded as the preferred method for extending beyond RR-HO at reasonable costs ([Barone & Puzzarini, 2023](#)).

4.1. Vibrational Spectroscopy

Calculations for the vibrational spectra of PAHs are frequently carried out using Density Functional Theory with the B3LYP functional, paired with small basis sets like 4–31G or 6–311G++(d,p). This has resulted in the creation of extensive online databases containing theoretical IR spectra for various PAHs ([Boersma et al., 2014](#); [Mallocci et al., 2007](#)). Vibrational IR intensities were approximated using the double harmonic approach. To align calculated harmonic frequencies with matrix-isolation experimental features, a scaling factor was employed. While this initial approach has met with some success in roughly reproducing the overall IR spectrum of specific individual PAHs, notable issues arise when comparing it with high-resolution experiments. Particularly, the C–H stretching region's IR features are inadequately modeled through the harmonic level analysis. This deficiency is likely attributed to phenomena such as overtones, combination bands, and Fermi resonance, not captured in the harmonic-level description, as shown in **Figure 4** ([Mackie et al., 2015](#)). To account for these complex interactions and anharmonic effects, it is necessary to include terms up to the fourth power of the displacement from equilibrium positions. This can be achieved through the calculation of Quartic Force Fields (QFFs) using a VPT2 approach. Despite its success with semirigid molecules, VPT2 encounters challenges in vibrational spectroscopy due to resonances, presenting difficulties in identification and accurate description. Systematically identifying and correcting true resonances is crucial, and the resonance conditions depend on electronic structure calculations and coupling between potentially resonant states. A promising approach involves combining perturbative and variational models, with the generalized (G)VPT2 model providing high accuracy and cost-effectiveness for both energies and transition moments, including a systematic treatment of Fermi and Darling-Dennison resonances, as explained in [Mackie et al. \(2015\)](#)

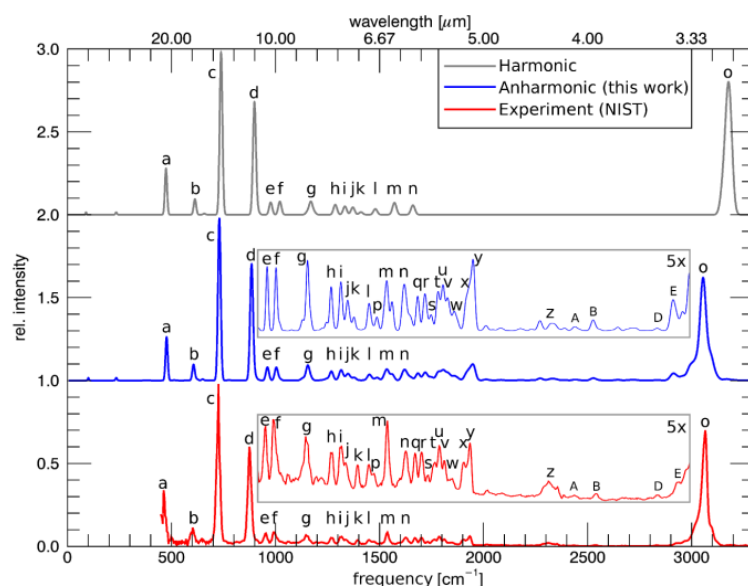


Figure 4 – Absorption vibrational spectra of naphthalene ($C_{10}H_8$) using harmonic (top), anharmonic (middle) and experimental methods (bottom).
(Figure from Mackie et al., 2015)

4.1.1. Emission Spectra

The recent development in constructing computationally obtained absorption spectra into emission spectra marks the final step towards directly comparing theoretical models with the observed PAH emission bands. Two types of emission models have been proposed.

The thermal emission model explains the infrared cooling of PAHs through transitions from one vibrational level to the previous level in an emission cascade. This model calculates the emission in a specific vibrational mode by treating the PAH as a heat bath at the temperature (T) corresponding to the average energy (E) of the molecule. Cook & Saykally (1998), Pech et al. (2002) and Pathak's group (Pathak & Rastogi, 2008; Buragohain et al., 2018, 2020; Vats et al., 2022) utilized this model, incorporating photophysical data and DFT-B3LYP calculations, respectively. **Figure 5** compares the mid-IR emission spectra of the Orion bar with endoskeletal N- $C_{54}H_{18}$ (where N is present inside the PAH structure) and with $NH_2C_{54}H_{18}$ (with N at the periphery bonded with two H atoms). The Orion bar spectra has almost equally strong 6.2 and 11.2 μm bands with a very strong 7.7 μm band. **Figure 5** shows that neutral endoskeletal N-containing PAHs have the strong 6.2 and 11.2 μm band together. Thus, if they contribute significantly to the observed PAH bands, then there should be some N-rich astronomical regions where the 6.2 to 11.2 μm band ratio may not always be a direct indicator of the ionization degree of PAHs.

In contrast, Mulas and colleagues chose a micro-canonical formalism, preserving energy conservation between emissions. Although more challenging to implement than the thermal formalism, this option is more rigorous. The authors employed a Monte Carlo technique on quantum chemical calculations, extending a prior model of photophysics to incorporate rotational and anharmonic band structures, using molecular parameters calculated by DFT (Mulas et al., 2006).

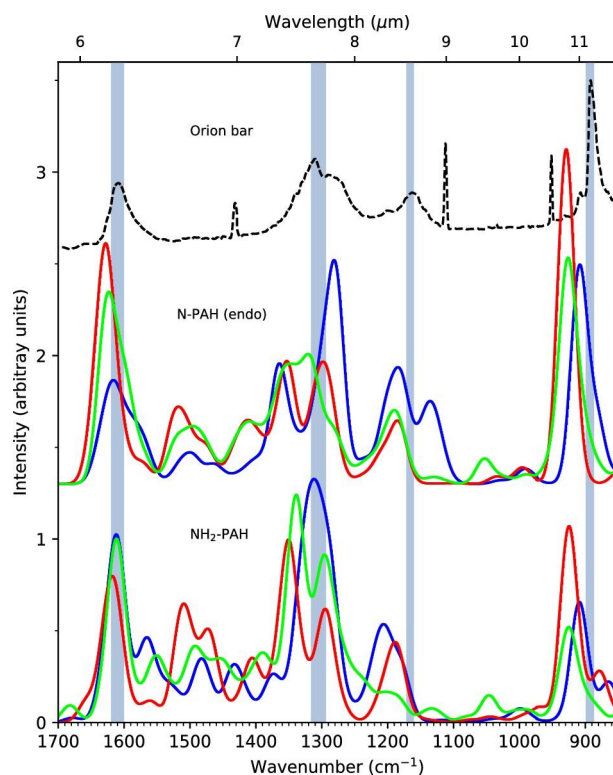


Figure 5 – Theoretical emission spectra of two nitrogen-substituted variants for circumcoronene ($C_{54}H_{18}$) in neutral (blue), cation (red) and protonated (green). The dashed line represents the spectra of the Orion bar taken from Sloan et al. (2003). The shaded vertical region spans the range of the observed position of the 6.2, 7.7 and 8.6 μm bands (Peeters et al., 2002) and the 11.2 μm band (van Diedenhoven et al., 2004). (Figure from Vats et al., 2022)

4.2. Pure Rotational Spectroscopy

Earlier computations regarding rotational spectroscopic parameters of interstellar molecules relied on the *ab-initio* Self-Consistent Field (SCF) methods (Ha & Nguyen, 1982). The essential spectroscopic parameters needed to simulate the rotational spectrum of a polar PAH include its accurate rotational and centrifugal distortion constants. Additionally, in certain instances, magnetic and/or electric interactions may arise, giving rise to the hyperfine structure observed in the rotational spectrum (Gordy & Cook, 1970). According to VPT2 approach, the determination of rotational constants in the vibrational ground state (B_0^i) requires the computation of B_e^i ; equilibrium rotational constant related to the i th inertial axis ($i = a, b, c$), and ΔB_{vib}^i ; vibrational correction term that involves computation of vibration-rotation interaction constants using anharmonic force field calculations (Barone & Puzzarini, 2023). For PAHs, the prevailing approach was to utilize B3LYP and MP2 computations with medium-sized basis sets having inherent errors ($\sim 0.5\%$), which does not permit an unbiased analyses without experimental data. For example, in **Figure 6**, a rotational transition of 1-cyanonaphthalene present around 13,480 MHz shows relative error of 0.07%, reflecting an uncertainty of 70 MHz for a line at 100 GHz. Although this level of precision is appropriate for guiding experiments, it falls far short of the requirements for astronomical searches. Additionally, in contrast to vibrational spectroscopy, rotational spectroscopy lacks systematic effects that can be easily addressed through a scaling factor.

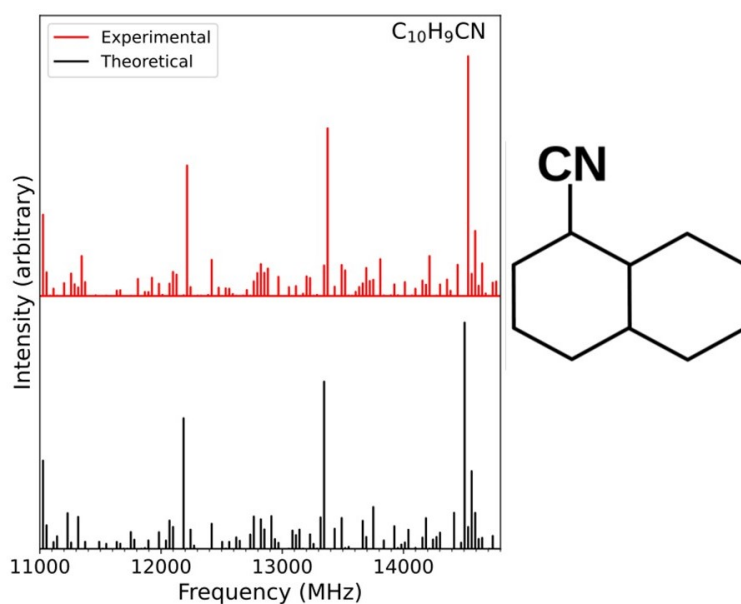


Figure 6 – Pure rotational spectra of 1-cyanonaphthalene ($C_{10}H_9C$) with B3LYP/6-311+G(d, p) at 300 K. (Figure from Vats & Pathak, 2022)

Achieving high accuracy in determining equilibrium structures, which significantly influences the vibrational ground-state rotational constant (constituting approximately 99% of it), requires consideration of basis-set and electron-correlation effects. This can be achieved by utilizing quantum-chemical composite schemes that individually address the different contributions such as Lego Brick (Ye et al., 2022) and PCS/Bonds (Barone & Lazzari, 2023) approaches. The former approach based on coupled-cluster techniques operates under the assumption that a molecular system can be seen as comprised of smaller fragments, each possessing a highly precise equilibrium structure. Within this framework, the template molecule (TM) approach is utilized to accommodate alterations that occur when transitioning from an isolated fragment to the molecular system under consideration. The linear regression model is then applied to rectify the connections between distinct fragments. For example, in this model, 1-cyanonaphthalene is seen to be formed by only two fragments– benzene and benzonitrile, having a significant accuracy for equilibrium rotational constants with mean absolute error (MAE) with respect to experiment being 0.08%. Despite this success, the use of numerous parameters remains unsatisfactory, and suitable fragments are not always readily available, which can be addressed through the recent Pisa composite scheme (PCS). This scheme enhances the accuracy of existing approaches for medium-sized molecules by nearly an order of magnitude, all without a notable increase in computational cost. This is particularly notable when core-valence correlation is considered, which significantly improves the computations of equilibrium structures. Using this model, the MAE for 1-cyanonaphthalene is $\sim 0.01\%$.

5. Electronic Spectroscopy

PAHs could also potentially account for the optical diffuse interstellar absorption bands (Salama et al., 1996, 2011). Typically, stable closed-shell neutral PAH molecules exhibit their most prominent electronic transitions in the UV or near-UV spectral range. A significant emphasis has been placed on radical PAH cations resulting from single electron removal, as these tend to have transitions within the visible spectrum. Time-Dependent-DFT (TD-

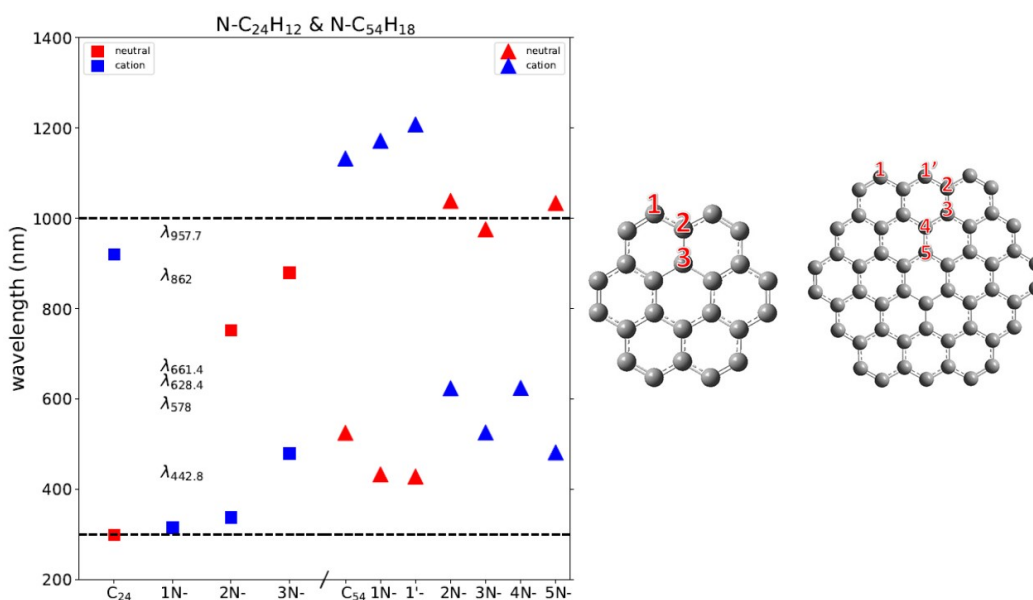


Figure 7 – Strongest transitions of *N*-substituted coronene and circumcoronene. The squares and triangles represent coronenes (red) and circumcoronenes (blue), respectively. The observed range for the most common DIBs fall within the dashed lines. The wavelengths of notable DIBs are also provided. (Figure from Shukla et al., 2022)

DFT) method is extensively used to compute excited electronic states of medium to large molecules, demonstrating an accuracy agreement within ± 0.3 eV in comparison to experiments (Hirata et al., 1999). TD-DFT offers a valuable indication of the general region where electronic transitions are anticipated, providing guidance for laboratory experiments (Pathak & Sarre, 2008). For instance, Figure 7 underscores the significance of PANH neutrals and cations in comprehensively studying DIBs, emphasizing the necessity for extensive experimentation on these molecular species (Shukla et al., 2022). TD-DFT computations, combined with Frank-Condon-Herzberg-Teller calculations, can effectively replicate the overall experimental pattern of excited states in PAHs (Stockett et al., 2023).

6. Future Prospects

The future of computational chemistry holds great promise in advancing our understanding of interstellar PAHs. Innovations in vibrational spectroscopy, focusing on overcoming anharmonic challenges through QFFs and GVPT2, are poised to refine theoretical predictions. In rotational spectroscopy, quantum-chemical composite schemes like the Lego Brick and PCS/Bonds approaches, demonstrate significant potential for achieving unbiased analyses with unparalleled precision. For electronic spectroscopy, the integration of TD-DFT computations with Frank-Condon-Herzberg-Teller calculations provides a robust platform for reproducing experimental patterns. In essence, the trajectory of computational chemistry in unraveling the mysteries of interstellar PAHs is marked by continuous refinement and innovation, offering a bright future for unraveling the complexities of the cosmic landscape.



Prof. Amit Pathak is a Professor at the Department of Physics, Institute of Science, Banaras Hindu University (BHU), India. His research focuses on understanding the properties of interstellar dust and interstellar Polycyclic Aromatic Hydrocarbon (PAH) molecules both theoretically and observationally through spectroscopy.

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Abstracts

Spectroscopy of helium-tagged C_{60} anions

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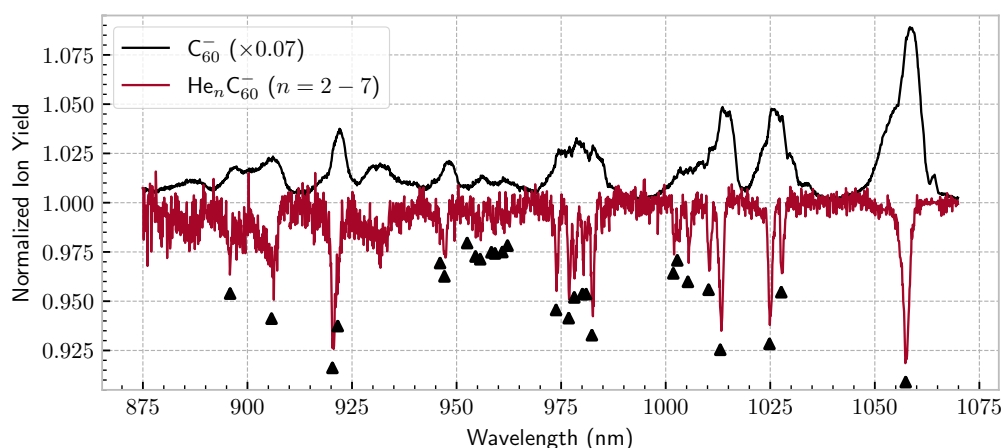
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We present measurements of the electronic absorption spectrum of He-tagged buckminsterfullerene anions, C_{60}^- . Using a new technique that allows for the efficient tagging of complex molecular anions with He, we achieve atomically resolved action spectra that provides an accurate determination of the gas phase absorption spectrum in the near-infrared regime. In total we identify 27 absorption bands between 895 and 1057 nm.



Overview spectra of He-tagged C_{60} anions in the range from 875 to 1075 nm as measured by the increase in yield of bare C_{60}^- ions (black) or the depletion of loosely bound $He_n C_{60}^-$, $n = 2 - 7$, complexes (red). Band positions and relative yields in the depletion spectrum are indicated by black arrowheads.

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Hydrogenated amorphous carbon grains as an alternative carrier of the 9–13 μm plateau feature in the fullerene planetary nebula Tc 1

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Fullerenes have been observed in several astronomical objects since the discovery of C_{60} in the mid-infrared (mid-IR) spectrum of the planetary nebula (PN) Tc 1. It has been suggested that the carriers of the broad unidentified infrared (UIR) plateau features, such as the 9–13 μm emission feature (12 μm hereafter), may be related to the formation of fullerenes. In particular, their carriers have been suggested to be mixed aromatic or aliphatic hydrocarbons such as hydrogenated amorphous carbon (HAC-like hereafter) grains. For this study, we modeled the mid-IR emission of the C_{60} -PN Tc 1 with a photoionization code, including for the first time the laboratory optical constants (n and k indices) of HAC-like dust at 300 K. Interestingly, we find that the broad 12 μm plateau feature in Tc 1 is well reproduced by using a distribution of canonical HAC grains, while at the same time they provide an important fraction of the IR dust continuum emission and are consistent with the other UIR features observed (e.g., the broad 6–9 μm plateau feature). This finding suggests that HAC-like grains may be possible carriers of the 12 μm plateau feature, being likely related to the fullerene formation mechanism in PNe. More laboratory experiments, to obtain the optical constants of HAC-like dust with several structures or a composition at different physical conditions, are strongly encouraged – that is, in order to extend this pilot study to more fullerene PNe, and to unveil the details of fullerene formation and of the potential carriers of the elusive UIR plateau features.

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Ionic fragmentation products of benzonitrile as important intermediates in the growth of polycyclic aromatic hydrocarbons

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In various astronomical environments such as the interstellar medium or (exo)planetary atmospheres, an interplay of bottom-up growth and top-down destruction processes of (polycyclic) aromatic hydrocarbons (PAHs) takes place. To get more insight into the interplay of both processes, we disentangle the fragmentation and formation processes that take place upon dissociative ionization of benzonitrile. We build on previous spectroscopic detections of the ionic fragmentation products of benzonitrile and use these as reactants for low-temperature bottom-up ion–molecule reactions with acetylene. By combining kinetics and infrared action spectroscopy, we reveal exothermic pathways to various (polycyclic) aromatic molecules, including the pentalene and phenylacetylene radical cations. We determine the reaction rate coefficients and unambiguously assign the structures of the reaction products. The data is supplemented by potential energy surface calculations and the analysis of non-covalent interactions. This study shows the unexpected formation of a linked four- and six-membered ring structure (phenylcyclobutadiene radical cation) with molecular formula $C_{10}H_8^+$, and not the commonly observed isomer naphthalene⁺. All observed reactions proceed via radiative association processes and are relevant for the chemistry in (cold) astrochemical environments.

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Photoionization of Nitrile-substituted Naphthalene and Benzene: Cation Spectroscopy, Photostability, and Implications for Photoelectric Gas Heating

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We investigate the vacuum ultraviolet (VUV) photodynamics of gas phase 1- and 2-cyanonaphthalene and cyanobenzene, recently detected in the Taurus molecular cloud, by combining synchrotron radiation and a double imaging electron/ion coincidence setup. The high-resolution threshold photoelectron spectra (TPES) of all three molecules are obtained experimentally from which the adiabatic ionization energies are reported with very high accuracy, particularly for 2-cyanonaphthalene, for which no data exist at this level of precision. Theoretical calculations are performed to compare with the TPES for the ground electronic state of the cations. Furthermore, the different features observed in the extended TPES have been assigned to the different molecular orbitals with the help of the outer valence Green's function calculations. The present experiments also shed light on the kinetic energy distribution of the photoelectrons as a function of the incident photon energy, to describe their contribution to the photoelectric heating effect in the interstellar medium. In this context, we show how kinetic energy distributions can be obtained from our data for any given photon energy, such as the omnipresent Ly α line, or any given interstellar radiation field (ISRF). In addition, from the total ion yields, we estimate the photorates for a few ISRFs. Finally, we discuss the photodissociation of the two cyanonaphthalenes, quoting the activation energies of the dissociation channels with the help of Rice-Ramsperger-Kassel-Marcus modeling. It is observed that CN substitution does not cause any appreciable change to the VUV dissociative photoionization relaxation channel.

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