



Spitzer's perspective of polycyclic aromatic hydrocarbons in galaxies

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Polycyclic aromatic hydrocarbon (PAH) molecules are abundant and widespread throughout the Universe, as revealed by their distinctive set of emission bands at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 μm , which are characteristic of their vibrational modes. They are ubiquitously seen in a wide variety of astrophysical regions, ranging from planet-forming disks around young stars to the interstellar medium of the Milky Way and other galaxies out to high redshifts at $z \gtrsim 4$. PAHs profoundly influence the thermal budget and chemistry of the interstellar medium by dominating the photoelectric heating of the gas and controlling the ionization balance. Here I review the current state of knowledge of the astrophysics of PAHs, focusing on their observational characteristics obtained from the Spitzer Space Telescope and their diagnostic power for probing the local physical and chemical conditions and processes. Special attention is paid to the spectral properties of PAHs and their variations revealed by the Infrared Spectrograph onboard Spitzer across a much broader range of extragalactic environments (for example, distant galaxies, early-type galaxies, galactic halos, active galactic nuclei and low-metallicity galaxies) than was previously possible with the Infrared Space Observatory or any other telescope facilities. Also highlighted is the relation between the PAH abundance and the galaxy metallicity established for the first time by Spitzer.

In the early 1970s, a new chapter in astrochemistry was opened by Gillett et al.¹ who, on the basis of ground observations, detected three prominent emission bands peaking at 8.6, 11.3 and 12.7 μm in the 8–14 μm spectra of two planetary nebulae, NGC 7027 and BD+30°3639. Two years later, Merrill et al.² reported the detection of a broad emission band at 3.3 μm , again in NGC 7027. Also around that time, airborne observations became possible. This led to the detection of two additional, ground-inaccessible intense emission bands at 6.2 and 7.7 μm in NGC 7027³ and M82, an external galaxy⁴, with the Kuiper Airborne Observatory (KAO). Subsequently, all these features at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 μm were found to be widespread throughout the Universe and closely related to form a family, exhibiting an overall similar spectral profile among the different sources (Fig. 1).

Although the exact nature of the carriers of these features remains unknown—because of this, they are collectively known as the ‘unidentified’ infrared emission (UIE) features—the hypothesis of polycyclic aromatic hydrocarbon (PAH) molecules as the carriers^{5,6} has gained widespread acceptance and extreme popularity. The PAH model attributes the UIE bands to the vibrational modes of PAHs composed of fused benzene rings of several tens to several hundreds of carbon atoms, with the 3.3 μm band assigned to C–H stretching modes, the 6.2 and 7.7 μm bands to C–C stretching modes, the 8.6 μm band to C–H in-plane bending modes, and the 11.3 and 12.7 μm bands to C–H out-of-plane (CH_{oop}) bending modes. The relative strengths of these bands depend not only on the size, structure and charging of the PAH molecule but also on the local physical conditions^{7–10}.

It is now well recognized that PAHs are an essential component of the interstellar medium (ISM) and play an important role in many aspects of astrophysics. They account for $\lesssim 15\%$ of the interstellar carbon^{9–13} and their emission accounts for up to 20% of the total infrared power of the Milky Way and star-forming galaxies^{14,15}. Therefore by implication, they must be an important absorber of starlight^{16–18} and are possibly related to or even responsible for

some of the longstanding unexplained interstellar phenomena (for example, the 2,175 Å extinction bump^{9,16,19}, the diffuse interstellar bands²⁰, the blue and extended red photoluminescence emission²¹ and the ‘anomalous microwave emission’^{22,23}). PAHs profoundly influence the thermal budget and chemistry of the ISM. They dominate the heating of the gas in the diffuse ISM as well as the surface layers of protoplanetary disks by providing photoelectrons^{24–26}. As an important sink for electrons, PAHs dominate the ionization balance in molecular clouds and hence they influence the ion–molecule chemistry and the ambipolar diffusion process that sets the stage for star formation²⁷.

In this Review, I provide an overview of the current state of knowledge of the astrophysics of PAHs, with details on their observational characteristics obtained from the Spitzer Space Telescope. Special attention is also paid to their diagnostic capabilities to probe the local physical and chemical conditions as well as their reactions to different environments. We focus on Spitzer results, but the science case often builds on pioneering observations performed before Spitzer with ground-based, airborne and space telescopes, in particular, the Infrared Space Observatory (ISO). We discuss the properties of PAHs in the context of both Spitzer observations and observations obtained with previous and other contemporary telescope facilities.

PAHs in the pre-Spitzer era

Over the intervening 30 years between the first detection of PAHs in 1973¹ and the launch of Spitzer in 2003, numerous ground-based, airborne and spaceborne observations have substantially promoted or even revolutionized our understanding of PAHs in astrophysics. These observations have established that PAHs are a ubiquitous and abundant component of a wide variety of astrophysical regions, ranging from planetary nebulae, protoplanetary nebulae, reflection nebulae, H II regions, the galactic infrared cirrus and protoplanetary disks around Herbig Ae/Be stars to the ISM of both normal and active nearby galaxies^{15,28}. Most notably, Sellgren et al.²⁹ showed

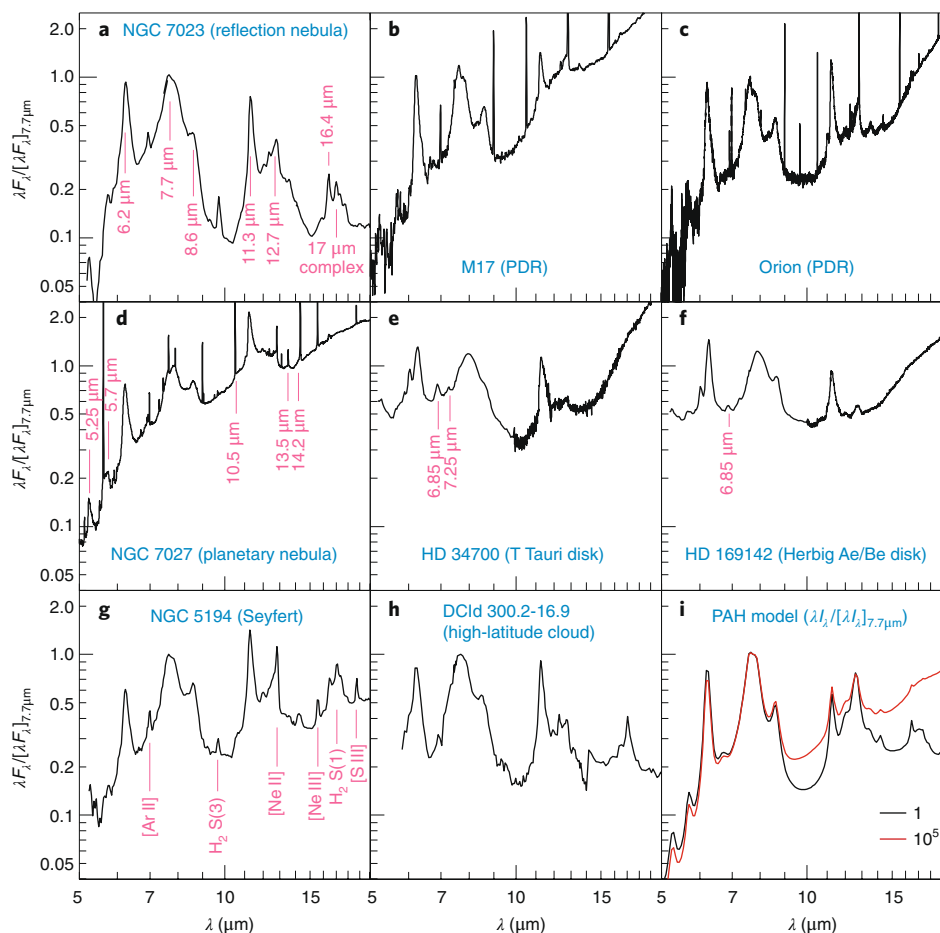


Fig. 1 | Observed and model-predicted 5–20 μm PAH spectra. **a**, Reflection nebula NGC 7023⁵⁶. **b**, M17 photodissociation region (PDR)¹⁷¹. **c**, Orion Bar PDR¹⁷². **d**, Planetary nebula NGC 7027¹⁷³. **e**, T Tauri disk HD 34700¹⁷⁴. **f**, Herbig Ae/Be disk HD 169142¹⁷⁵. **g**, Seyfert grand-design spiral galaxy NGC 5194¹⁴. **h**, Translucent high-galactic-latitude cloud DCld 300.2-16.9¹⁷⁶. **i**, Model emission calculated for PAHs illuminated by the local interstellar radiation field¹⁷⁷ (that is, $U = 1$; black line) or a much more intense radiation field (that is, $U = 10^5$; red line)¹⁰. The major PAH bands are labelled in **a**. Some of the weak, secondary PAH bands (superimposed by sharp gas lines) are labelled in **d**. The 6.85 and 7.25 μm aliphatic C–H deformation bands are labelled in **e** and **f** for protoplanetary disks. The sharp gaseous emission lines are labelled in **g**. F_λ is the observed flux at wavelength λ . U is the starlight intensity measured in the unit of the local interstellar radiation field¹⁷⁷. I_λ is the model emission intensity¹⁰.

that in three reflection nebulae (NGC 7023, NGC 2023 and NGC 2068) the 3.3 μm feature profile shows very little variation with distance from the central star, revealing the emission mechanism of the PAH bands as due to the infrared fluorescence from molecule-sized species vibrationally excited by individual ultraviolet/visible photons^{7,30,31}.

Owing in large part to the fact that the 3 μm region and the 8–14 μm region are accessible to ground-based telescopes, in the 1980s and 1990s, the C–H stretching bands at 3.3 μm and the CH_{oop} bending bands at 11.3 μm were the subject of extensive scrutiny. Careful observations revealed a great deal about the detailed spectral and spatial structures of the emission bands in these regions. The C–H stretch near 3 μm exhibits a rich spectrum: the dominant 3.3 μm feature is usually accompanied by a weaker feature at 3.4 μm along with an underlying plateau extending out to ~ 3.6 μm . In some objects, a series of weaker features at 3.46, 3.51 and 3.56 μm are also seen superimposed on the plateau, showing a tendency to decrease in strength with increasing wavelength^{32–34}. Similarly, the 11.3 μm band is also generally accompanied by a second distinct, but weaker, feature near 12.7 μm . Weaker features are also often present near 11.0, 11.5, 12.0 and 13.5 μm (ref. ³⁵), arising from the CH_{oop} bending vibrations of PAHs.

In the 1970s and 1980s, the 6.2 and 7.7 μm bands were only accessible from the KAO. KAO observations had already revealed substantial variations in the PAH feature profiles among different types of sources. Typically, harsh environments, such as planetary nebulae, reflection nebulae and H II regions, in which the dust has been heavily processed, show ‘normal’-looking PAH spectra. The 7.7 and 8.6 μm bands of these sources are well separated. In contrast, some benign protoplanetary nebulae, in which the dust is relatively fresh, exhibit a broad 8 μm complex³⁶. The CH_{oop} bending bands of these heavily processed sources also differ from that of less processed sources: while the former exhibit a prominent 11.3 μm band and a weaker but distinct 12.7 μm band, the latter tend to show only a broad complex at ~ 12 μm . In addition, these less processed sources often have a much stronger 3.4 μm band (which is often comparable to or even stronger than the 3.3 μm band). Finally, KAO observations also showed that the 7.7 μm band may be composed of at least two variable components³⁷.

ISO provided the first opportunity to obtain complete infrared spectra from 2.4 to 197 μm unobscured by telluric absorption. Spanning a wavelength range of 2.4 to 45 μm , the Short Wavelength Spectrometer (SWS) onboard ISO was well suited to surveying the PAH emission and obtaining a census of the PAH bands³⁸. A new

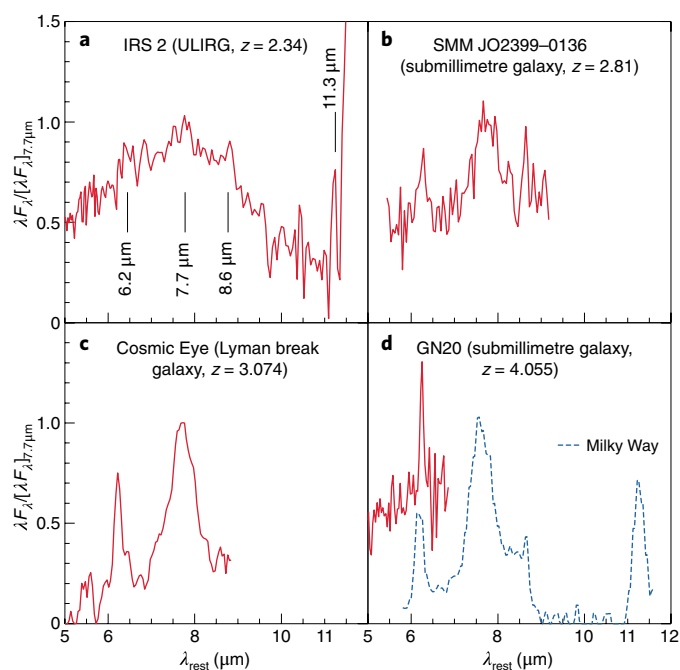


Fig. 2 | Spitzer/IRS rest-frame spectra of galaxies at high redshifts. a, ULIRG IRS 2 ($z = 2.34$)⁷¹. **b,** Submillimetre galaxy SMM J02399–0136 ($z = 2.81$)⁷². **c,** Lyman break galaxy Cosmic Eye ($z = 3.074$)⁷³. **d,** Submillimetre galaxy GN20 ($z = 4.055$)⁷⁴. Also shown in **d** is the ISOPHOT spectrum of the Galactic diffuse ISM (blue dashed line)⁴³. The rest-frame wavelength is labelled as λ_{rest} .

PAH band at 16.4 μm was discovered in the ISO/SWS spectra of various sources³⁹. Also, the aromatic C–H and C–C bands at 3.3 and 6.2 μm were seen in absorption in the ISO/SWS spectra of heavily obscured local sources as well as sources toward the Galactic Centre^{40,41}. The superb spectral resolving power of ISO/SWS found that many of the prominent bands show satellite bands or break up into subfeatures³⁸. Moreover, the ISO/SWS observations have revealed systematic variations in the profiles and relative intensities of the PAH bands from source to source and spatially within sources³⁸. Primarily on the basis of the variations of the 7.7 μm band seen in the ISO/SWS spectra, Peeters et al.⁴² classified the PAH sources into three classes. Furthermore, the 5.8–11.6 μm ISOPHOT low-resolution spectrophotometer PHT-S onboard ISO for the first time detected the 6.2, 7.7, 8.6 and 11.3 μm PAH bands in the diffuse emission of the Galactic Disk⁴³. Although the starlight intensity in the Galactic Disk is substantially lower than that of typical reflection nebulae and planetary nebulae by a factor of ~ 100 –1,000, the profiles and relative intensities of the PAH bands are closely similar to the ‘normal’-looking PAH spectra of reflection nebulae and planetary nebulae (Fig. 2d). At about the same time, the advent of the Japanese Infrared Telescope in Space also detected the 3.3–11.3 μm PAH bands in the diffuse emission near the galactic plane^{44,45}.

The Spitzer legacy of PAH astrophysics

Owing to its up to a factor of 100 better sensitivity than ISO/SWS, Spitzer allowed the extension of mid-infrared spectroscopy and imaging into new regimes that ISO could not probe. The Infrared Spectrograph (IRS) onboard Spitzer was capable of detecting PAH emission in objects that were too faint for ISO (for example, the PAH emission at 6–9 μm of protoplanetary disks around T Tauri stars, which had previously escaped detection by ISO⁴⁶, was unambiguously detected by Spitzer/IRS^{47–49}; Fig. 1e). Spitzer was able to probe PAHs in much larger samples spanning much wider varieties

of astrophysical environments. Therefore, the systematic trends and characteristics of PAHs as well as the exploitation of the PAH bands as diagnostics of the physical and chemical conditions and processes could be determined in an unbiased manner. Also, the high sensitivity of Spitzer/IRS enabled unprecedented PAH spectral mapping of both galactic and extragalactic sources^{50–54}. Complemented with observations by, for example, ISO and the Japanese AKARI infrared satellite, Spitzer made lasting contributions and substantially expanded our knowledge about the physical and chemical properties of PAHs and their important role in astrophysics.

The Spitzer inventory of PAH spectra. Compared with ISO/SWS, the main limitations of Spitzer/IRS were its relatively lower spectral resolution and narrower wavelength coverage. The spectral resolution of Spitzer/IRS in the 5–10 μm wavelength range was lower than that of ISO/SWS by more than an order of magnitude. Also, operating at 5–38 μm , Spitzer/IRS unfortunately missed the PAH C–H stretch at 3.3 μm . Nevertheless, despite its limited spectroscopic capabilities, Spitzer/IRS pioneered both in discovering new PAH bands and in showcasing the richness and complexity of the PAH spectra, particularly at wavelengths longward of ~ 10 μm . The Spitzer/IRS spectroscopy of the star-forming ring in the spiral galaxy NGC 7331 unambiguously revealed, for the first time, a strong, broad emission feature centred at 17.1 μm , with a width of ~ 0.96 μm and an intensity three times as strong as the 16.4 μm feature or nearly half as strong as the ubiquitous 11.3 μm band⁵⁵. As illustrated in Fig. 1a,g, this prominent feature is widely seen in the Spitzer/IRS spectra of both galactic and extragalactic sources^{14,56}. The presence of this feature had been hinted by the ISO/SWS spectra of galactic sources^{57,58}. In addition, Werner et al.⁵⁶ reported the discovery of new PAH features at 15.8 and 17.4 μm in the Spitzer/IRS spectra of NGC 7023, together with a new feature at 18.9 μm , whose carrier was later identified as C_{60} (refs. ^{59,60}). The 16.4, 17.1 and 17.4 μm PAH features, resulting from in-plane and out-of-plane ring bending modes of the carbon skeleton, constitute the so-called 17 μm complex. As the strongest PAH band longward of 12 μm , the 17 μm complex is dominated by the broad 17.1 μm band, with the distinct flanking subfeatures at 16.4 and 17.4 μm contributing only $\sim 20\%$ of the total power in the complex¹⁴.

Spitzer/IRS observations reinforced the richness of the PAH spectra. Together with ISO/SWS observations, Spitzer/IRS observations revealed that, apart from the major bands at 6.2, 7.7, 8.6, 11.3 and 12.7 μm that dominate the mid-infrared emission spectra of many objects, there are also weaker, secondary features at 5.25, 5.7, 6.0, 6.7, 8.3, 10.5, 11.0, 12.0, 13.6, 14.2, 15.8, 16.4, 17.4 and 17.8 μm as well as underlying broad continuum emission plateaus^{14,15,38}. The CH_{oop} bending bands at wavelengths longward of ~ 10 μm are of particular interest. They are characteristic of the edge structure of PAHs and occur at different wavelengths, depending on the number of neighbouring hydrogen atoms on one aromatic ring: for neutral PAHs, the isolated CH_{oop} band (solo CH) occurs at ~ 11.3 μm , doubly adjacent CH (duet CH) at ~ 12.0 μm , triply adjacent CH (trio CH) at ~ 12.7 μm and quadruply adjacent CH at ~ 13.6 μm (refs. ^{61,62}). Hudgins and Allamandola⁶³ experimentally showed that the aromatic CH_{oop} bending wavelengths are substantially blueshifted upon ionization.

In the 6–9 μm wavelength range, Spitzer/IRS observations found that the 7.7 μm band of some carbon-rich post-asymptotic giant branch (post-AGB) stars in the Large Magellanic Cloud (LMC)⁶⁴ and Small Magellanic Cloud⁶⁵ exhibits more pronounced profile variations than previously revealed by ISO/SWS observations for galactic sources. While the profile variations of the 7.7 μm band seen in the ISO/SWS spectra were employed as a spectral classification scheme⁴², the Spitzer/IRS observations led to further classifications of the PAH spectra^{64,65}. Moreover, the subtle variations in the peak wavelength of the 6.2 μm emission band, commonly attributed

to polycyclic aromatic nitrogen heterocycles—PAHs with one or more nitrogen atoms substituted into their carbon skeleton⁶⁶—were recently seen in the Spitzer/IRS spectra of starburst galaxies⁶⁷.

Two-dimensional spectral and photometric mapping of PAH emission with Spitzer. While ISOCAM, the camera onboard ISO, had an imaging capability with its narrow-band filters that cover the major PAH bands, its observation was quite limited because of its sensitivity. Owing to the much higher sensitivity of Spitzer/IRS, two-dimensional spectral mapping observations of PAH emission became possible. Spitzer/IRS provided for the first time substantial data that allow us to study the spatial distribution of PAH emission and quantitatively investigate the spatial variations of the PAH size, structure and ionization and their responses to changing environments^{52–54}. Berné et al.⁶⁸ applied the so-called blind component separation method to analyse the Spitzer/IRS two-dimensional spectral mapping data of several galactic objects. They showed that the observed PAH emission can be decomposed into three components, respectively arising from neutral PAHs, ionized PAHs and PAH clusters or very small grains. The spatial distributions of these components provide useful information on their photochemical evolution and the local physical conditions. The viability of this method depends on how applicable the adopted template emission spectra of neutral PAHs, ionized PAHs and PAH clusters are to various astrophysical regions whose PAH emission spectra are diverse.

The 8 μm broadband imaging photometer of the Infrared Array Camera (IRAC) onboard Spitzer also provided a unique opportunity to explore the spatial distribution of PAHs both in extended galactic sources and in spatially resolved external galaxies, as the IRAC 8 μm emission is dominated by the 6.2, 7.7 and 8.6 μm bands of PAHs. The 8 μm Spitzer/IRAC mapping of the M17 H II region clearly revealed the paucity of PAH emission in H II regions, indicating the destruction of PAHs by extreme ultraviolet photons within H II regions⁶⁹.

PAHs in the early Universe. Although distant galaxies are too faint to be subject to direct ISO/SWS spectroscopy, Elbaz et al.⁷⁰ found that the rest-frame 5–25 μm spectral energy distributions of a sample of 16 distant luminous infrared galaxies (LIRGs) at redshifts $z \approx 0.1$ –1.2, constructed from the 15 μm photometry of ISOCAM and the 24 μm photometry of the Multiband Imaging Photometer (MIPS) onboard Spitzer, indicated the presence of the 7.7 μm PAH band in more than half of the sample. However, as illustrated in Fig. 2, Spitzer provided the first spectroscopic evidence for the presence of PAHs in distant galaxies. Yan et al.⁷¹ reported clear detection of multiple PAH emission bands in the Spitzer/IRS spectra of ultraluminous infrared galaxies (ULIRGs) at $z \approx 2$. Lutz et al.⁷² also detected the PAH emission bands in the Spitzer/IRS spectra of two luminous submillimetre galaxies at $z \approx 2.8$. Also, the 6.2 and 7.7 μm bands of PAHs were clearly seen in the Spitzer/IRS spectrum of the Cosmic Eye, a strongly lensed, star-forming Lyman break galaxy at $z = 3.074$ (ref. ⁷³). As shown in Fig. 2, the PAH spectra of both the Cosmic Eye and the submillimetre galaxies of Lutz et al.⁷² are ‘normal’-looking, exhibiting close similarity to that of the galactic diffuse ISM⁴³. More recently, the 6.2 μm PAH band was detected in the Spitzer/IRS spectrum of the $z = 4.055$ submillimetre galaxy GN20, one of the intrinsically brightest submillimetre galaxies known⁷⁴, indicating that complex aromatic organic molecules were already prevalent in the young Universe, only ~ 1.5 Gyr after the Big Bang. As PAHs play an important role in prebiotic chemistry, which may ultimately lead to the development of organic life, the detection of PAHs in the early Universe has important astrobiological implications^{75,76}.

Because the PAH features are so prevalent and intense in distant galaxies as indicated by Spitzer/IRS observations, in the future era of the James Webb Space Telescope (JWST) and the Space Infrared

Telescope for Cosmology and Astrophysics (SPICA), they might be used as redshift indicators. The integrated luminosity from the PAH features at 6.2, 7.7 and 11.3 μm has been shown to correlate linearly with the star formation rate (SFR) as measured by the extinction-corrected H α luminosity for 105 galaxies of infrared luminosities $\sim 10^9$ – $10^{12} L_{\odot}$ at $0 < z < 0.4$ (ref. ⁷⁷). The luminosity of the individual 6.2, 7.7 and 11.3 μm PAH bands has also been shown to correlate well with the infrared luminosity for both local starburst galaxies and high-redshift submillimetre galaxies, including GN20^{74,78}. These correlations suggest that PAH emission could also be used as an accurate, quantitative measure of the SFR (but also see refs. ^{79,80}) across cosmic time up to high redshifts to study the star formation history of the Universe. While the Mid-Infrared Instrument onboard JWST, which covers the wavelength range of 5 to 28 μm , will limit the detection of the 6.2 μm PAH band to $z \lesssim 3$, the SPICA Far Infrared Instrument, operating at 35–230 μm , will enable the detection of PAHs in the very first galaxies in the Universe⁸¹.

PAHs in early-type galaxies. For a long time, early-type galaxies (that is, E and S0 galaxies) were thought to be essentially devoid of interstellar matter. The detection of PAHs in elliptical galaxies with Spitzer/IRS for the first time by Kaneda et al.^{82,83} demonstrated that, adding to the earlier detection of hot gas and cold dust, elliptical galaxies contain a considerable amount of interstellar matter. Vega et al.⁸⁴ also reported the detection of PAH emission in the Spitzer/IRS spectra of S0 galaxies. As illustrated in Fig. 3, the PAH spectra of early-type galaxies exhibit a strong enhancement at the 11.3 μm band and substantial suppression at the 7.7 μm band^{82–84}. The peculiar 11.3/7.7 band ratios seen in elliptical (and S0) galaxies indicate that the PAH size distribution is skewed towards appreciably larger molecules. In the hostile environments of elliptical galaxies (containing hot gas of temperature $\sim 10^7$ K), small PAHs can be easily destroyed through sputtering by plasma ions. This calls into question the origin of PAHs (and more generally, dust and gas) in ellipticals: are they from internal processes such as mass loss of red giants, or from mergers with spirals or small dust-rich irregular galaxies, or alternatively, could they be made in dense gas in a disk that has cooled out of the hot ISM? Kaneda et al.⁸³ found that the 11.3 μm PAH emission of elliptical galaxies correlates well with the dust continuum emission at 35 μm , whereas it does not correlate with the stellar photospheric emission at 6 μm . Therefore, they suggested that PAHs in elliptical galaxies are mostly of interstellar origin rather than of stellar origin. However, it is also possible that, as long as the quantities of PAHs and dust are both proportional to the amount of interstellar material in these elliptical galaxies, it does not matter where PAHs were formed and one expects the dust continuum emission to correlate with PAH emission. The lack of correlation between starlight and PAH emission could also be explainable if the excitation of PAHs in elliptical galaxies is dominated by electronic collisions instead of stellar photons. In any case, the detection of PAHs in early-type galaxies provides useful constraints on the evolution of the ISM in the harsh environments of these galaxies.

PAHs in galaxy halos. Irwin and Madden⁸⁵ analysed the ISOCAM maps of NGC 5907, an edge-on galaxy with a low SFR of $\sim 1.2 M_{\odot} \text{ yr}^{-1}$, in four narrow bands centred at 6.8, 7.7, 9.6 and 11.3 μm . They found that the infrared emission seen in these bands extends as far as 6.5 kpc from the plane. As the ISOCAM narrow-band photometry at 6.8, 7.7, 9.6 and 11.3 μm traces PAH emission, they suggested that PAHs are present in the halo of NGC 5907.

Engelbracht et al.⁸⁶ obtained the Spitzer/IRAC images of the archetypal starburst, superwind galaxy M82 in which the central starburst drives a galactic outflow or superwind perpendicular to the galaxy plane. As shown in Fig. 4, the IRAC 8 μm emission, generally attributed to PAHs, extends at least 6 kpc from the plane and is seen all around the galaxy, well beyond the cone defined by the

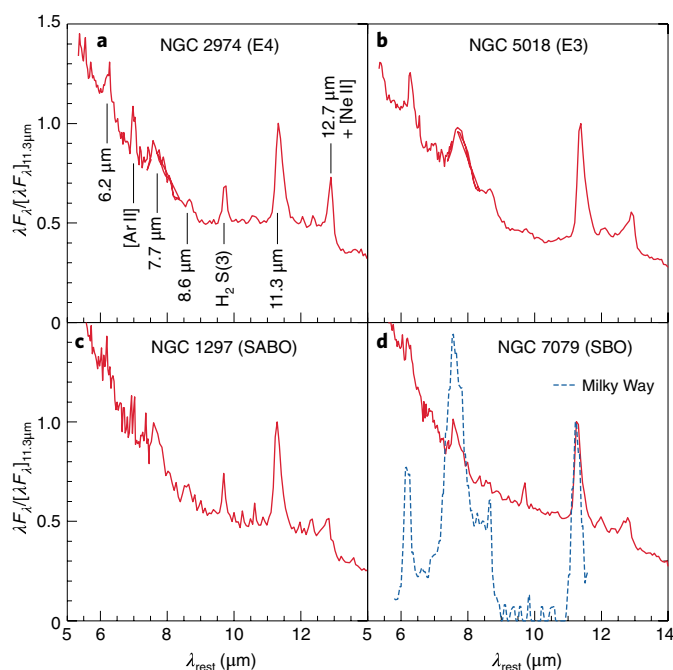


Fig. 3 | Spitzer/IRS spectra of early-type galaxies. **a**, Elliptical galaxy NGC 2974 of type E4 in Hubble's classification scheme⁸³. **b**, E3 elliptical galaxy NGC 5018⁸³. **c**, SAB0 lenticular galaxy NGC 1297⁸⁴. **d**, SBO barred lenticular galaxy NGC 7079⁸⁴. In **a**, both the PAH bands and the gaseous lines are labelled, where the 12.7 μm band is blended with [Ne II]. Also shown in **d** is the ISOPHOT spectrum of the galactic diffuse ISM (blue dashed line)⁴³. Compared with the galactic diffuse ISM of which the 6.2, 7.7 and 8.6 μm bands prevail, the PAH spectra of early-type galaxies are dominated by the 11.3 μm band.

superwind. Engelbracht et al.⁸⁶ also obtained the Spitzer/IRS spectra for M82 and clearly detected the 16.4 and 17.1 μm bands of PAHs in its superwind region.

Beirão et al.⁸⁷ mapped the superwind/halo region of M82 with Spitzer/IRS and obtained spatially resolved PAH spectra. They found that the interband ratios of the 6.2, 7.7 and 11.3 μm features vary by more than a factor of five across the superwind region. As illustrated in Fig. 4, the intensities of the 11.3, 12.7 and 17.1 μm bands relative to the 6.2, 7.7 and 8.6 μm bands are stronger in both the north and south superwinds than in the centre, suggesting that the PAH molecules in the superwind are somewhat larger, probably resulting from preferential destruction of smaller PAHs in the harsh superwind by X-rays and/or shocks.

With AKARI, Yamagishi et al.⁸⁸ obtained the spatially resolved 2.5–4.5 μm near-infrared spectra of M82 and detected the 3.3 μm PAH emission as well as the 3.4 μm emission complex both in the centre and in the superwind, with the intensity ratio of the 3.4 μm complex to the 3.3 μm feature appreciably increasing with distance from the plane. As shown in Fig. 4, in the centre, the 3.4 μm feature is much weaker than the 3.3 μm feature; in contrast, in the superwind, the 3.4 μm feature supercedes the 3.3 μm feature and dominates the near-infrared spectra. While the 3.3 μm emission arises from the aromatic C–H stretch, the 3.4 μm complex is commonly attributed to the aliphatic side chains attached as functional groups to the aromatic skeleton of PAHs^{32–34}, although superhydrogenated PAHs (that is, PAHs whose edges contain excess hydrogen atoms), of which the extra hydrogen atom converts the originally aromatic ring into an aliphatic ring^{89–93}, and the anharmonicity of the aromatic C–H stretch^{94,95} could also be responsible for the 3.4 μm feature. The intensity ratio of the 3.4 μm aliphatic band to the 3.3 μm

aromatic band is often used to derive the aliphatic fraction (that is, the fraction of carbon atoms in aliphatic form) of PAHs^{96–98}. It is puzzling that the PAH aliphatic fraction is considerably higher in the superwind than in the centre. One would imagine that in the harsh superwind environment, PAHs would be easily stripped off any aliphatic sidegroups. For PAHs with an appreciable aliphatic fraction, the 6.85 and 7.25 μm aliphatic C–H deformation bands⁹⁹ would show up (for example, see Fig. 1e). However, a close inspection of Fig. 4 reveals no evidence for these two bands in the Spitzer/IRS spectra of M82, neither in the centre nor in the superwind. It is also puzzling how small PAHs of ~20–30 carbon atoms, which emit at 3.3 μm (ref. ¹⁰), could survive in the superwind. Yamagishi et al.⁸⁸ suggested that they are produced in situ by shattering of large grains. Alternatively, they may be protected in clumps¹⁰⁰.

Finally, the Spitzer/IRS observations of the Galactic Bulge also detected PAHs in a local galactic wind environment¹⁰¹. The presence of PAHs in the diffuse ionized halo of NGC 891, an edge-on spiral, was also spectroscopically revealed by Spitzer/IRS through the observations of the PAH bands at 11.3, 12.7 and 16.4 μm (ref. ¹⁰²). The detection of PAHs in galaxy halos or superwinds provides valuable insight into not only the destruction and survival of PAHs in hostile environments but also the mechanism for transporting PAHs from the plane to the halo through supernova explosion, stellar winds and radiation pressure.

PAHs in galaxy mergers. Galaxy mergers, occurring when two (or more) galaxies collide, could trigger starbursts and lead to the formation of tidal tails stretching $\gtrsim 100$ kpc from the site of the collision¹⁰³. Higdon et al.¹⁰⁴ obtained the Spitzer/IRS spectra of two faint tidal dwarf galaxies, NGC 5291 N and NGC 5291 S, and detected PAH emission bands at 6.2, 7.7, 8.6, 11.3, 12.7 and 16.4 μm , which are remarkably similar to those of normal star-forming galaxies. In contrast, Haan et al.¹⁰⁵ mapped the PAH bands with Spitzer/IRS in eight major merger systems of the Toomre sequence and found that the spatially resolved 6.2/7.7 and 11.3/7.7 interband ratios are often too large to be explainable by the canonical PAH model⁸. Murata et al.¹⁰⁶ examined the relationship of the PAH emission spectra obtained with AKARI with galaxy merger in 55 star-forming galaxies at $z < 0.2$. They found that PAHs are relatively underabundant in merger galaxies than non-merger galaxies and suggested that PAHs are partly destroyed by the intense ultraviolet radiation and large-scale shocks during merging processes of galaxies. On the basis of Spitzer/IRS and AKARI data, Onaka et al.¹⁰⁷ detected PAH emission and found that small grains are deficient in the tidal tails of two galaxy mergers, NGC 2782 (Arp 215) and NGC 7727 (Arp 222). They suggested that PAHs are formed from the fragmentation of small grains during merger events.

PAHs in active galactic nuclei. In the harsh environment around active galactic nuclei (AGNs)—rich in extreme ultraviolet and soft X-ray photons—PAHs would be destroyed and PAH emission is not expected to be present^{108,109}, as first noticed by Roche et al.¹¹⁰ in the ground-based mid-infrared spectra of the nuclear regions of active galaxies. Genzel et al.¹¹¹ proposed to use the strength of the 7.7 μm PAH feature as a discriminator of starburst and AGN activity in ULIRGs, with an aim to determine whether an ULIRG is powered by recently formed massive stars or by a central AGN. However, PAH emission was reportedly detected within $\gtrsim 10$ pc of AGNs, suggesting that PAHs could survive in close proximity to AGNs and be excited by photons from AGNs^{112,113}. On the basis of the Spitzer/IRS spectra of 91 Seyfert galaxies, Tommasin et al.¹¹⁴ also found that, going from AGN-dominated to starburst-dominated objects, the 11.3 μm PAH feature remains almost constant in flux, although its equivalent width increases. They argued that PAHs could survive in the highly ionized medium of AGNs, while the PAH feature appears weaker in the most powerful ones because it is masked by

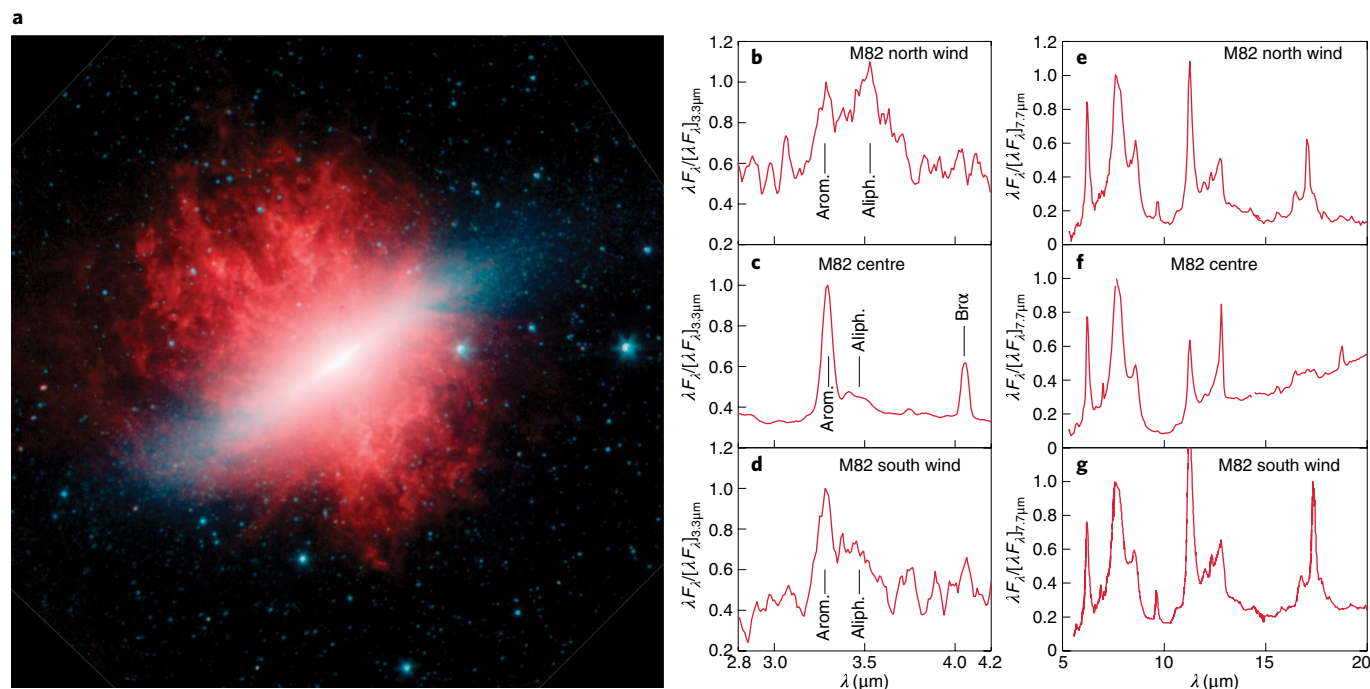


Fig. 4 | PAHs in the superwind of M82. **a**, The galaxy is shown as the diffuse bar of blue light. The Spitzer/IRAC 8 μm emission, dominated by PAHs, is shown in red. The superwind, emanating from the central starburst region, is evident in the 8 μm emission. The PAH emission is seen all around the galaxy, well beyond the cone defined by the superwind. **b–g**, The AKARI and Spitzer/IRS spectra of the north wind (**b,e**), the centre (**c,f**) and the south wind (**d,g**) of M82^{87,88}. While the AKARI spectra illustrate the near-infrared C–H stretches (**b–d**), the Spitzer/IRS spectra show the mid-infrared C–C stretches, C–H bending and C–C–C skeleton bending modes (**e–g**). Most notably, while in the centre the 3.3 μm aromatic (Arom.) C–H band is much stronger than the 3.4 μm aliphatic (Aliph.) C–H band (**c**), in the wind the aliphatic band is so pronounced that it even dwarfs the aromatic band (**b,d**). The intensities of the 11.3, 12.7 and 17.1 μm bands relative to the 6–9 μm bands are stronger in the wind (**e,g**) than in the centre (**g**). Panel **a** adapted with permission from ref. ⁸⁶, AAS.

the strong underlying AGN continuum (see their Fig. 14). In contrast, AKARI and Spitzer/IRS observations have shown that PAHs could be destroyed by the intense, hard radiation in starburst galaxies and in the H II regions within star-forming galaxies^{113,116}. Therefore, caution should be taken when using the PAH emission as a star-formation tracer within a kiloparsec around AGNs or for intense starbursts.

Nevertheless, numerous observations of Seyferts and galaxies that contain low-ionization nuclear emission-line regions with Spitzer/IRS have clearly shown that the PAH emission significantly weakens in AGN-hosting galaxy nuclei and the PAH spectra differ considerably from those of star-forming galaxies. More specifically, the PAH bands at 6.2, 7.7 and 8.6 μm of Seyferts and galaxies that contain low-ionization nuclear emission-line regions are often substantially suppressed relative to the 11.3 μm band^{14,117–119}. These trends have been interpreted as the preferential destruction of small PAHs by the hard radiation field of AGNs.

As demonstrated in Fig. 5, the relative strengths of the PAH bands provide powerful diagnostics of the physical and chemical properties of the PAH molecules (for example, their sizes, charging and structural characteristics). Both laboratory measurements and quantum-chemical computations have shown that the 3.3 and 11.3 μm features arise primarily from neutral PAHs, while the 6.2, 7.7 and 8.6 μm features are dominated by the emission of ionized PAHs^{28,120,121}. Meanwhile, whether a PAH molecule will be ionized or neutral is controlled by the starlight intensity, electron density and gas temperature^{24,25}. Therefore, the band ratios involving the neutrals and ions, such as the 7.7/11.3 ratio, are useful tools for probing the charging of the emitting molecules and hence for probing the local physical conditions^{8,122}.

By comparing the observed PAH interband ratios with the model expectations for neutral and ionized PAHs, one could determine the PAH size and ionization fraction (that is, the probability of finding a PAH molecule in a non-zero charge state)^{8,122}. However, as shown in Fig. 5, Diamond-Stanic and Rieke¹¹⁸ found that the 11.3/7.7 ratios of a number of Seyferts lie beyond the range of model predictions, even for completely neutral PAHs. While large 11.3/7.7 ratios could be produced by large neutral PAHs, they would be expected to have small 6.2/7.7 ratios, inconsistent with the observations. This is because, for a given ionization, larger PAHs tend to emit more at longer wavelengths (that is, larger 11.3/7.7 ratios and smaller 6.2/7.7 ratios)⁸. The discrepancy between the observed and model-predicted 11.3/7.7 ratios cannot be resolved by nitrogen-containing PAHs. Upon insertion of a nitrogen atom, the 6.2 and 7.7 μm C–C stretches and the 8.6 μm C–H in-plane bending of both neutral and cationic PAHs exhibit a twofold increase in intensity^{123,124}. Therefore, nitrogen-containing PAHs would produce even lower 11.3/7.7 ratios. We suggest that these extreme 11.3/7.7 ratios could arise from catacondensed PAHs with an open, irregular structure. Catacondensed PAHs have more hydrogen atoms (on a per-carbon-atom basis) than compact, pericondensed PAHs (for example, coronene, ovalene, circumcoronene)^{54,62} and hence their emission spectra would have a higher 11.3/7.7 ratio. While the model tracks shown in Fig. 5 for ionized and neutral PAHs at varying sizes were calculated from pericondensed PAHs⁸, heavy processing in the nuclear regions of active galaxies may cause PAHs to have an open, irregular structure and thus a higher 11.3/7.7 ratio. Alternatively, the extreme 11.3/7.7 ratios could result from an inappropriate subtraction of the continuum emission underlying the PAH bands.

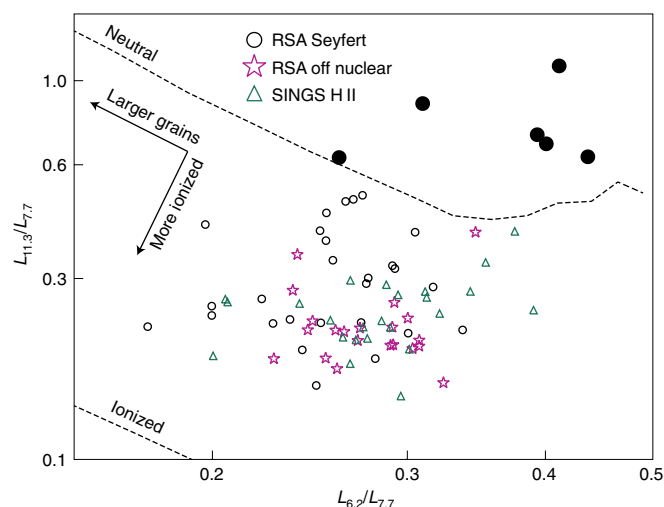


Fig. 5 | Relative strengths of the 6.2, 7.7 and 11.3 μm PAH features. PAH relative feature strengths are shown for Seyfert nuclei (open or filled circles), off-nuclear regions (stars) and H II galaxies (triangles). $L_{6.2}$, $L_{7.7}$ and $L_{11.3}$ are respectively the power emitted from the 6.2, 7.7 and 11.3 μm PAH features. The Seyfert galaxies are from the *Revised Shapley-Ames Catalog of Bright Galaxies* (RSA). The dashed lines correspond to predictions of Draine and Li⁸ for completely neutral and completely ionized PAHs with their sizes increasing from right to left; the permitted region of the diagram is bounded by these two lines. The Seyferts highlighted as filled circles all lie beyond the range of model predictions, even for completely neutral molecules. It is likely that heavy processing causes PAHs to have an open, irregular structure and hence a higher H/C ratio and consequently a higher 11.3/7.7 ratio. Figure adapted with permission from ref. ¹¹⁸, AAS.

PAHs in low-metallicity galaxies. The deficiency or lack of PAHs in low-metallicity galaxies was recognized in the pre-Spitzer era. The $\sim 5\text{--}16\text{ }\mu\text{m}$ mid-infrared spectrum of SBS 0335–052, a blue compact dwarf galaxy with an extremely low metallicity of $Z/Z_{\odot} \approx 1/41$, obtained by Thuan et al.¹²⁵ with the circular variable filter facility of ISOCAM, shows no evidence of PAHs, as later confirmed by the Spitzer/IRS observations¹²⁶. Madden et al.¹²⁷ performed a more systematic investigation of the ISOCAM circular variable filter mid-infrared spectra of a large number of metal-poor dwarf galaxies and found that the PAH features are substantially suppressed. The advent of Spitzer not only confirmed the paucity of PAH emission in low-metallicity environments but also, more importantly, established a trend of decreasing PAH emission with metallicity and a threshold in metallicity below which the PAH abundance drops drastically. The Spitzer/IRS spectra of a large number of metal-poor blue compact dwarf galaxies with metallicities $Z/Z_{\odot} \approx 0.02\text{--}0.6$ show much weaker PAH features than typical starburst galaxies, with a substantial weakening at $Z/Z_{\odot} \lesssim 0.2$ or $12 + \log(\text{O}/\text{H}) \approx 7.9$ (refs. ^{128,129}). Engelbracht et al.¹³⁰ examined the IRAC 8 μm and MIPS 24 μm emission of 34 galaxies spanning two decades in metallicity. They found that $f_{\nu}(8\text{ }\mu\text{m})/f_{\nu}(24\text{ }\mu\text{m})$ —the ratio of the 8 μm emission to the 24 μm emission—drops abruptly from ~ 0.7 for galaxies with $Z/Z_{\odot} > 1/3$ to ~ 0.08 for galaxies with $Z/Z_{\odot} < 1/5\text{--}1/3$. They attributed this drop to a sharp decrease in the 7.7 μm PAH feature at a threshold metallicity of $12 + \log(\text{O}/\text{H}) \approx 8.2$. By modelling the PAH and dust infrared emission of 61 galaxies from the Spitzer Infrared Nearby Galaxies Survey (SINGS), Draine et al.¹³¹ also found that the PAH abundance shows a sharp change around a threshold in metallicity of $12 + \log(\text{O}/\text{H}) \approx 8.1$ (Fig. 6), corresponding to $Z/Z_{\odot} \lesssim 0.23$ if we take $Z/Z_{\odot} = 1$ for $12 + \log(\text{O}/\text{H}) = 8.73$ (ref. ¹³²).

With Spitzer/IRS, Gordon et al.¹³³ investigated the spatially resolved PAH features in the face-on spiral galaxy M101 which has

one of the largest metallicity gradients. They found that the variation of the strengths of the PAH features correlates better with the radiation field hardness than metallicity. On the contrary, Wu et al.¹³⁴ found that the PAH emission of 29 faint dwarf galaxies as traced by the Spitzer/IRAC [3.6]–[8] colour appears to depend more directly on metallicity than radiation hardness.

The exact reason for the deficiency or lack of PAHs in low-metallicity galaxies is not clear. It is generally interpreted as more rapid destruction of PAHs by the more intense and harder ultraviolet radiation (as indicated by the fine-structure line ratio of $[\text{Ne III}]/[\text{Ne II}]$) in an ISM with reduced shielding by dust. Low-metallicity environments lack sufficient dust grains to shield PAHs from photodissociation by ultraviolet radiation, by analogy with the mechanism commonly invoked to explain the deficit of CO emission in low-metallicity galaxies⁸⁰. It could also be due to more effective destruction of PAHs by thermal sputtering in shock-heated gas that cools more slowly because of the reduced metallicity. The reduced PAH abundance in these galaxies might also be due to a deficiency of PAH-producing carbon stars and carbon-rich planetary nebulae, or a suppressed formation and growth of PAHs in the ISM with low gas-phase carbon abundances¹³¹. Seok et al.¹³⁵ related the PAH–metallicity dependence to the formation mechanism of PAHs in the ISM. They suggested that interstellar PAHs are formed from the shattering of carbonaceous dust grains in interstellar turbulence. On the basis of an exploration of the evolution of PAH abundance on a galaxy-evolution timescale, they found that the formation of PAHs becomes accelerated above certain metallicity where shattering becomes efficient.

The dearth of PAHs in low-metallicity galaxies, if they are truly young, could also result from a delayed production of PAHs by low-mass stars, that is, PAH-producing carbon stars have not yet evolved off the Main Sequence¹³⁶. This scenario is supported by the metallicity dependence of the 7.7 μm PAH emission of 476 distant galaxies spanning a wide range in metallicity at redshifts $1.37 \lesssim z \lesssim 2.61$. The PAH emission (relative to the total infrared emission) is indeed substantially lower in the youngest quartile of the sample with an age of $\lesssim 500\text{ Myr}$ (ref. ¹³⁷). However, on the basis of a Spitzer/IRAC 8 μm imaging survey of 15 local group dwarf galaxies, Jackson et al.¹³⁸ found that, although these galaxies are all deficient in PAH emission, they have formed the bulk of their stars more than 2 Gyr ago. Therefore, they argued that the paucity of PAH emission in dwarf galaxies is unlikely due to the shortage of AGB stars.

PAHs in supernova remnants. The PAH spectra of supernova remnants (SNRs) and their implied PAH sizes contain useful information on the shock processing of PAHs. With Spitzer/IRS, Tappe et al.¹³⁹ performed spectroscopic observations of N132D, a young SNR with an age of $\sim 2,500\text{ yr}$ in the LMC. They reported the detection in N132D of a weak PAH feature at 11.3 μm and a prominent, broad hump at 15–20 μm attributed to the C–C–C skeleton bending modes of large PAHs of $\sim 4,000$ carbon atoms. This was the first-ever detection of PAHs in an SNR. The lack of PAH features at 6–9 μm and the large ratio of the 15–20 μm emission to the 11.3 μm emission indicate that small PAHs could have been rapidly destroyed in the supernova blast wave via thermal sputtering and only larger ones have survived in the shocked environment.

In contrast, with AKARI and Spitzer/IRS, Seok et al.¹⁴⁰ detected the 3.3, 6.2, 7.7 and 11.3 μm PAH features in N49, a middle-aged SNR ($\sim 6,600\text{ yr}$) in the LMC, and found that the 6.2/11.3 and 7.7/11.3 band ratios imply a predominance of small PAHs. They suggested that, unlike N132D, the PAHs in N49 are possibly associated with the ambient molecular cloud (with which N49 is interacting) where small PAHs could survive from the shock¹⁰⁰.

The detection of PAH emission in galactic SNRs has also been reported with Spitzer/IRS¹⁴¹. Their $\sim 5\text{--}14\text{ }\mu\text{m}$ PAH spectra closely resemble that of galactic photodissociated regions (PDRs) and

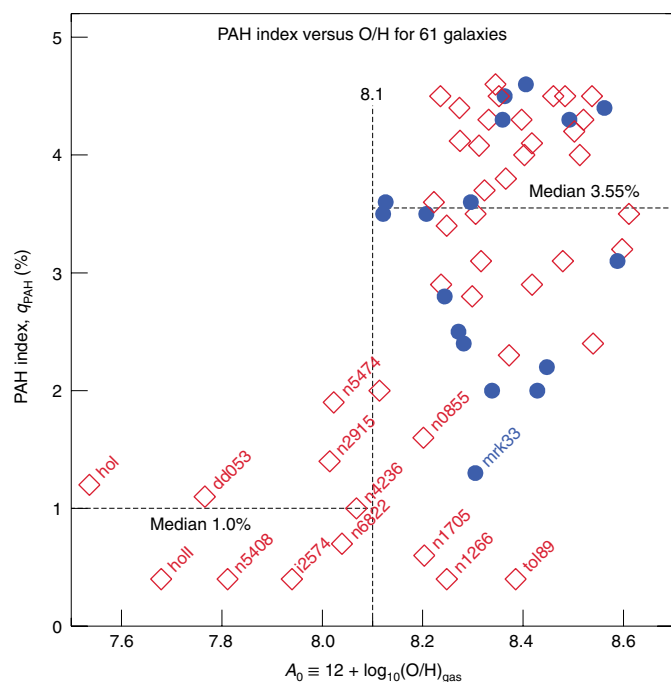


Fig. 6 | PAH abundance versus galaxy metallicity. The galaxy metallicity $A_0 = 12 + \log_{10}(\text{O}/\text{H})$ is measured by the gas-phase oxygen abundance (relative to H). The PAH abundance is measured by the mass fraction of dust in PAHs, with an uncertainty of $\sim 0.1\%$. Low-metallicity galaxies are always deficient in PAHs. Filled circles are for galaxies with submillimetre data; diamonds are for galaxies lacking submillimetre data. Figure adapted with permission from ref. ¹³¹, AAS.

star-forming galaxies, but considerably differ from that of N132D in the LMC. Andersen et al.¹⁴¹ attributed the spectral difference between galactic SNRs and N132D to their different environments. While many of these galactic SNRs are in a dense molecular cloud environment with a slow shock, N132D, in a less dense environment, has a strong shock that has effectively destroyed small PAHs.

Concluding remarks

Spitzer has provided a wealth of spectral and imaging data on the characteristics and spatial distributions of PAHs in a wide variety of astrophysical regions and considerably expanded the field of PAH astrophysics, especially the extragalactic world up to $z \gtrsim 4$ (Box 1). The PAH model has been successful in explaining the overall spectral profiles and the band patterns observed in various regions in terms of a mixture of neutral and charged PAHs of different sizes^{8,9,120}. However, longstanding open questions remain, with some of which arising from Spitzer observations (Box 2).

Spitzer/IRS observations of harsh environments such as AGN-hosting Seyfert galaxies¹¹⁸ and galaxy mergers¹⁰⁵ find extreme 11.3/7.7 band ratios that lie beyond the range of model predictions, even for completely neutral PAHs⁸. Future experimental measurements, quantum chemical computations and theoretical modelling of large catacondensed PAHs with an open, irregular structure will be useful to test the PAH model. Andrews et al.¹⁴² suggested that the interstellar PAH family may be dominated by 'grandPAHs', large and hence stable molecules that can survive the harsh conditions of the ISM. However, it is difficult for 'grandPAHs' to reconcile with these extreme 11.3/7.7 band ratios (Fig. 5).

Another challenge to the PAH model is that, so far, no specific PAH molecule has been identified in the interstellar or circumstellar space¹⁴³. Laboratory measurements have shown that individual small PAH molecules (with $\lesssim 25$ carbon atoms) have strong and

narrow absorption features in the ultraviolet¹⁴⁴. Attempts to search for these features were made with the Space Telescope Imaging Spectrograph onboard the Hubble Space Telescope¹⁴⁵. However, no such absorption features were seen. We argue that it is natural to expect a large number of distinct PAH species to be present in the ISM, and no single ultraviolet band may be strong enough to be identified. The strong interstellar 2,175 Å extinction feature is likely to be a blend of π - π^* absorption bands from the entire population of PAHs^{9,16–19}. Furthermore, internal conversion may lead to extreme broadening of the ultraviolet absorption bands in larger PAHs, which may account for absence of recognizable ultraviolet absorption features other than the 2,175 Å bump. Therefore, the lack of identification of any specific PAH is not a fatal problem for the PAH model, at least at this time. As we develop a better knowledge of the gas-phase spectroscopy of larger PAHs, this may change. If the diffuse interstellar bands are electronic transitions of PAHs, they hold great promise for identifying specific PAH molecules, as the electronic transitions are more characteristic of a specific PAH molecule than the mid-infrared C-H and C-C vibrational bands, while the latter are mostly representative of functional groups and thus do not allow one to fingerprint individual PAH molecules.

It remains unclear where and how interstellar PAHs are formed. Suggested sources for interstellar PAHs include the formation in the ISM through gas-phase ion-molecule reactions, or through shattering of hydrogenated amorphous carbon dust by grain-grain collisions in interstellar shocks. Also suggested is the formation of PAHs in carbon star outflows followed by subsequent injection into the ISM. Nevertheless, the PAH emission bands are rarely seen in the mid-infrared spectra of carbon stars. To our knowledge, only three carbon stars—TU Tau^{146–148}, UV Aur¹⁴⁷ and HD 100764¹⁴⁹—are known to exhibit PAH emission. It has been suggested that PAHs are present in all carbon stars but they are simply not excited sufficiently to emit at mid-infrared due to lack of ultraviolet photons, noting that both TU Tau and UV Aur have a hot companion that emits ultraviolet photons^{146–148}. However, it has been shown that the excitation of PAHs do not need very energetic photons, instead, visible and near-infrared photons are able to excite PAHs to temperatures high enough to emit the mid-infrared bands^{150,151}, in agreement with the detection of PAH emission in regions lacking ultraviolet photons, including vdB 133, a reflection nebula illuminated by a F5 Iab star of effective temperature $T_e \approx 6,800$ K (ref. ¹⁵²), HD 100764, a carbon-rich red giant of $T_e \approx 4,850$ K (ref. ¹⁴⁹) and HD 233517, an oxygen-rich red giant of $T_e \approx 4,475$ K (ref. ¹⁵³). The distribution of PAHs in the Small Magellanic Cloud, derived from the Spitzer/IRAC photometric mapping data, does not follow that of carbon-rich AGB stars, instead, it correlates with molecular gas as traced by CO (ref. ¹⁵⁴). This suggests that PAHs may be forming in molecular clouds. In contrast, the distribution of PAHs in the LMC, also derived from the Spitzer/IRAC mapping data, is enhanced both in molecular clouds and in the stellar bar, which hosts the highest concentration of AGB stars¹⁵⁵. The association of PAH emission with the stellar bar in the LMC was considered as evidence for carbon-rich AGB stars as a PAH source. However, we argue that, if PAHs are formed from the fragmentation of carbonaceous dust grains that were condensed in AGB stars and subsequently injected into the ISM, one would also expect the distribution of PAHs to be enhanced in the stellar bar. With the Faint Object Infrared Camera onboard the Stratospheric Observatory for Infrared Astronomy (SOFIA), the mid-infrared imaging observations of NGC 7027, a planetary nebula of age $\sim 1,000$ yr, suggested rapid PAH formation along the outflow via grain-grain collisions in the post-shock environment of the dense photodissociation region and molecular envelope¹⁵⁶. With the upcoming JWST, smaller spatial scales can be probed; spectral mapping in the PAH bands of the outflows of carbon-rich AGB stars and planetary nebulae will be valuable for exploring the origin and evolution of PAHs.

Box 1 | Major contributions to PAH astrophysics made by Spitzer observations

- Spitzer/IRS observations have provided a complete and unbiased spectroscopic census of the PAH emission bands in the wavelength range of $\sim 5\text{--}20\ \mu\text{m}$, including the discovery of a prominent emission feature centered at $17.1\ \mu\text{m}$ whose intensity is three times as strong as the $16.4\ \mu\text{m}$ feature or nearly half as strong as the $11.3\ \mu\text{m}$ band (Fig. 1a,c)⁵⁵.
- Spitzer/IRS observations have detected PAH emission in external galaxies out to high redshifts $z \gtrsim 4$, indicating the prevalence of complex aromatic organic molecules in the young Universe, only ~ 1.5 Gyr after the Big Bang⁷⁴.
- With its high sensitivity, Spitzer has been able to probe PAH emission in much larger samples spanning much wider varieties of astrophysical regions than ever before, including such hostile environments as AGNs^{117–119}, elliptical galaxies⁸², galactic outflows or superwinds^{86,87,102}, galaxy mergers¹⁰⁴, low-metallicity galaxies^{126,128–131} and supernova remnants^{139–141}. In these harsh environments, the PAH spectra are often substantially suppressed in the 6.2 , 7.7 and $8.6\ \mu\text{m}$ bands and enhanced in the $11.3\ \mu\text{m}$ band. The $6\text{--}9\ \mu\text{m}$ PAH emission of protoplanetary disks around T Tauri stars has also been detected, for the first time, by Spitzer/IRS^{47–49}.
- The high sensitivity of Spitzer/IRS has enabled unprecedented PAH spectral mapping of both galactic and extragalactic sources, providing valuable information on the spatial variations of the PAH characteristics (for example, size, charge, structure) and their responses to the changing environments^{50–54}.
- Spitzer observations firmly established the PAH–metallicity relation for galaxies spanning over two decades in metallicity and revealed a metallicity threshold of $12 + \log(\text{O}/\text{H}) \approx 8.1$, below which the PAH abundance drops drastically^{128–131}.

The emission continuum underlying the discrete PAH features is pervasive¹⁵⁷ and its nature remains unclear¹⁵⁸. It is noteworthy that the reliability of PAH emission as an effective SFR indicator relies on the appropriate subtraction of the underlying continuum for which no consensus has yet been reached^{14,159–162}. The observed band ratios (for example, the extreme $11.3/7.7$ ratios seen in hostile environments) used to derive the PAH size, charge and structure and the local physical and chemical conditions also depend on how the continuum is defined and subtracted. The continuum emission was posited to be related to the anharmonicity of highly vibrationally excited PAHs⁷, some specific PAH species (for example, tubular PAHs) with a zero bandgap¹⁰, or energetically processed PAHs¹⁶³. Kwok and Zhang¹⁴³ proposed that organic nanoparticles with a mixed aromatic–aliphatic structure could be responsible for both the PAH emission bands and the underlying continuum. However, the $3.3\ \mu\text{m}$ emission feature and the underlying continuum emission at $\sim 2\ \mu\text{m}$ in NGC 2023, a reflection nebula, are spatially separated, suggesting that the $3.3\ \mu\text{m}$ feature and the underlying continuum do not share the same carrier¹⁶⁴. Future spatially resolved observations with JWST and SPICA that can map the two components will provide insight into their physical separations and chemical carriers.

Compared with Spitzer, JWST will have more than an order of magnitude increase in sensitivity and spatial resolution as well as a broader wavelength coverage in the near-infrared. While the $3.3\ \mu\text{m}$ C–H stretch and the accompanying satellite features at $3.4\text{--}3.6\ \mu\text{m}$ are beyond the wavelength range of Spitzer/IRS, it is expected that JWST, with its Near InfraRed Spectrograph (NIRSpec) operating at $0.6\text{--}5.0\ \mu\text{m}$, will be able to scrutinize these bands to study the chemical structures (for example, methylation, superhydrogenation

Box 2 | Puzzling questions about PAHs raised partly from Spitzer observations

- No exact identification of the UIE band carriers has been made yet¹⁴³. No specific PAH molecule has been identified in the interstellar or circumstellar space.
- Are interstellar PAHs made in the ISM or condensed in carbon star outflows and subsequently injected into the ISM?
- How do PAHs quantitatively reveal the local physical and chemical conditions and respond to intense, extreme ultraviolet and X-ray photons and shocks? How would the chemical structure (for example, catacondensed versus pericondensed, aliphaticity versus aromaticity, dehydrogenation versus superhydrogenation) of PAHs be affected by photo- and shock processing? How do the extreme $11.3/7.7$ band ratios seen in the Spitzer/IRS spectra of AGNs (Fig. 5) and other harsh environments reflect the size, charging and structure of PAHs and the processing they have experienced?
- How accurate are PAHs as an SFR indicator? While PAHs are seen in regions within as close as $\gtrsim 10\ \text{pc}$ of AGNs^{112,113}, Spitzer/IRS observations have shown that PAHs can be destroyed by intense starbursts^{115,116}. Also, PAH emission does not necessarily trace exclusively young stars as PAHs can also be excited by visible photons^{150–152}.
- What is the nature of the continuum underlying the discrete PAH bands? What is the most appropriate way to subtract the continuum to measure the PAH emission (which is crucial for accurately determining the SFRs and the PAH band ratios)?
- Are PAHs related to other unexplained interstellar phenomena (for example, the $2,175\ \text{\AA}$ extinction bump, the diffuse interstellar bands, the blue and extended red photoluminescence emission, and the ‘anomalous microwave emission’), other interstellar carbon species (for example, C_{60} , carbon chains, and possibly graphene and carbon nanotubes)^{178–181}, and the chemical complexity of the Universe including the formation of molecular hydrogen and their role as a viable sink of interstellar deuterium¹⁶⁷?
- How do PAHs evolve from the ISM to prestellar nebulae, protoplanetary disks, comets and meteorites? Why are PAHs not seen in embedded protostars, the early phases of star formation? Why are PAHs generally smaller in meteorites¹⁸² and T Tauri disks⁴⁹ than in the ISM?

and anharmonicity) of the smallest PAHs and their environmental dependence. Moreover, JWST/NIRSpec will be ideal for searching for the overtone band at $\sim 1.6\text{--}1.8\ \mu\text{m}$ of the $3.3\ \mu\text{m}$ feature of small PAHs, providing valuable insights into the PAH fluorescence process^{165,166}. Furthermore, the C–D stretch at $\sim 4.4\ \mu\text{m}$ of deuterated PAHs will be of particular interest. PAHs could be a major reservoir of deuterium in the ISM. PAHs of intermediate size (with $\lesssim 100$ carbon atoms) are expected to become deuterium enriched in the ISM through the selective loss of hydrogen during photodissociation events¹⁶⁷. While ISO/SWS and AKARI observations have reported the tentative detection of the C–D bands at 4.4 and $4.65\ \mu\text{m}$ in the Orion Bar and M17 PDRs^{168,169} and H II regions¹⁷⁰, the unique high sensitivity of JWST/NIRSpec will place the detection of deuterated PAHs on firm ground and enable far more detailed band analysis than previously possible.

The high-sensitivity and high-spatial-resolution capabilities of JWST and SPICA will open up an infrared window unexplored by Spitzer and unmatched by ISO observations. With JWST and SPICA aided by laboratory studies, quantum chemical computations and theoretical modelling, the future of PAH astrophysics will be even more promising.

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Competing interests

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Additional information

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