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The hidden life of cosmic carbon

Infrared fingerprint spectroscopy and fragmentation chemistry of gas-phase polycyclic aromatic hydrocarbons

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Chapter 1

Introduction

1.1 Chemistry in Space

1.1.1 Space is not empty

People tend to think of space as a vast, empty void. This is not so surprising, considering how low the number densities in outer space are. In the interstellar medium (ISM), the space between solar systems, densities vary between 10^6 and 10^{-4} molecules per cm^3 , while what we consider a high vacuum on Earth contains about 10^{10} molecules per cm^3 . Even at these low densities, a wealth of different, interesting processes happen, due to the long timescales, harsh radiation and the immense sizes of the involved environments. Interstellar molecular clouds can vary in size from a radius of less than a light year [1] to more than 600 light years [2], meaning that starlight originating from the inside of such an astronomical object passes through a large amount of matter before it reaches our telescopes. An example of how the passage of light through such an object affects our observations, is shown in Fig. 1.1.¹ It displays a very small cloud (Barnard 68), only a quarter of a light year in radius. This cloud still contains enough dust to block all visible light attempting to pass through. Due to its vicinity to Earth, there are no stars between us and the cloud. When it is observed in the infrared (IR), the stars behind the cloud become detectable because they heat the dust and cause it to emit black-body radiation in the IR regime. By observing space at different parts of the electromagnetic spectrum, the properties of the dust itself can be explored. A smaller dust grain has a lower heat capacity, so it produces black-body radiation at a shorter wavelength. The grains on the outside of the cloud are exposed to more UV star light, and will likely have fragmented partially. This makes them smaller than those at the center, allowing them to begin emitting at $0.90 \mu\text{m}$, while the center is still obscured. The gravity of the cloud and the cold environment at the core promotes clustering to larger grains, which is reflected through the gradual decrease in opacity at longer wavelengths.

¹Image credit to the European Southern Observatory (ESO).
<https://www.eso.org/public/images/eso9934b/>

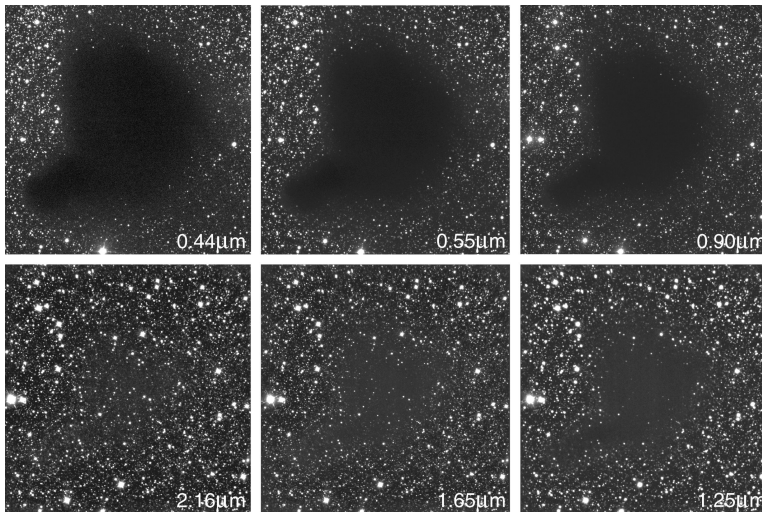


FIGURE 1.1: Observations of the dark molecular cloud Barnard 68 at various wavelengths, showing how the extinction of the light reduces with increasing wavelength (clockwise). Visible light (blue at $0.44 \mu\text{m}$, and green/yellow at $0.55 \mu\text{m}$) is blocked for the most part. Starting from the near-infrared at $0.90 \mu\text{m}$, the edges begin to blur, and then for the three bottom frames, an increasing number of stars becomes visible as the wavelength increases. Image credit in footnote.

1.1.2 On the origin of matter

Molecular clouds form both the nursery and cemetery for stars in our galaxy, but they are not the only chemically relevant part of the interstellar medium. Most matter in stars does not exist in a molecular form, but as a plasma. In our galaxy, the Milky Way, gas and dust accounts for 8×10^9 solar masses (M_{\odot}), while stars account for $10^{11} M_{\odot}$ [3].

To understand the life cycle of matter in a galaxy, it is important to understand where this matter comes from, and what its composition is. H is the most abundant element in the Universe by orders of magnitude, followed by He-4 [4]. Right after the Big Bang, only three other nuclei were formed, D (H-2), He-3 and a relatively very small amount of Li-3. All other elements are the result of stellar nucleosynthesis processes, where one or more nuclei merge into a heavier nucleus, releasing an abundance of energy in the form of photons in the process. The fusion of hydrogen and deuterium is exothermic, and primarily produces He-4. Oxygen, and at a lower abundances carbon and then nitrogen, are formed through less efficient processes at the end of a star's life [5]. Even though these elements are orders of magnitude less abundant than H and He, their ability to form several bonds creates a far richer chemistry than H and He on their own. As it is on Earth, organic chemistry is central to the chemistry in space [6, 7]; as evidenced by the fact that most of the detected interstellar compounds contain carbon [8].

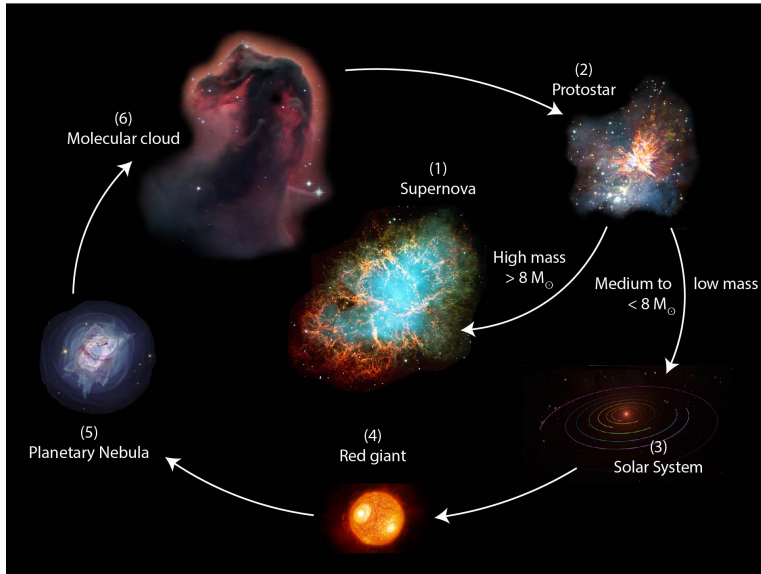


FIGURE 1.2: A graphical depiction of the life cycle of stars and clouds inside a galaxy. These objects are not to scale. Image credit in footnote.

Most stars and objects in the Universe right now are of the second or third generation, meaning that they are made up of matter that has already been cycled through one or more stellar lifetimes [9]. In Fig. 1.2,² a simple diagram of the cycle of matter in a galaxy is given. In the center of this diagram (1) is a massive star, typically larger than eight solar masses ($> 8M_{\odot}$). These stars lead a relatively short life, ending in a supernova (SN) explosion. These explosions produce a large component of the (far) ultraviolet (FUV) radiation field in the ISM, the pressure needed to form the heaviest elements, and shock waves that induce density changes in surrounding clouds [10]. The ripples in the density of molecular clouds lead to the formation of clumps, and later pre-stellar cores [7], depicted in stage (2). Sudden strong gravitational collapse will trigger fusion reactions, which create an outward radiative pressure [11]. As the core shrinks, it begins to spin faster, and a disk of matter is formed around it, which can be detected from its extinction (*i.e.* extreme absorption) properties, using the principles introduced around Fig. 1.1. The process of spinning and collapsing of these protoplanetary disks drives the formation of clumps of

²(1) Crab Nebula, image credit to ESO. (2) Possible protostar explosion in the Orion Nebula, image credit ALMA (ESO/NAOJ/NRAO), J. Bally/H. Drass et al. (3) Visualization of TRAPPIST-1 and its seven planets, image credit to NASA/JPL-Caltech (4) Artist's impression of Antares, image credit to ESO/M. Kornmesser (5) Planetary nebula NGC 7027, image credit to ESA, NASA Hubble, by J. Kastner (RIT) (6) Horsehead nebula, image credit to SPECULOOS Team/E. Jehin/ESO

dust and grains, which can evolve into planetesimals, and later planets [12]. Smaller stars of less than eight solar masses ($< 8M_{\odot}$) lead longer, and less violent lives, ending up in the outer cycle of this diagram. This low-mass star continues to exist in a rather steady state, spending 90% of its life fusing hydrogen into helium, as depicted by stage (3) in Fig. 1.2 [11]. The lives of most of these stars end as red giants, which begin to expel their outer shells through solar winds once they run out of hydrogen and helium as fuel for their nuclear fusion, shown in stage (4). In this process, they lose a large amount of their mass, and produce C, N and O in less efficient nucleosynthesis processes [13]. This expelled gas forms a dusty circumstellar shell (CS), which is rich in silicates and oxides (sand) for O-rich giants, and rich in carbonaceous clusters (soot) for C-rich giants [14]. Various kinds of organic molecules are also present in these ejecta [15]. Typically, the giant produces bursts of intense FUV radiation, ionizing the gas on the inside of the CS. The continued radiative pressure and stellar winds push the shell further away, eventually creating a planetary nebula (PNe, 5). The resulting PNæ are often made up of ionized molecular and atomic gas, as the giant becomes a white dwarf. The next stage in the life cycle, is the return of this matter into the ISM. The PNe falls apart into a diffuse cloud, which mixes with material from other systems. Gravitational forces pull several of these clouds together, forming molecular clouds, which end up becoming stellar nurseries again, coming full circle at stage (6). The insides of these clouds are shielded from radiation, and can become very cold (10–20 K). The gas is mostly neutral, will often freeze out, and accumulate further on grains. Isotopic ratios are heavily influenced by the cold chemistry in molecular clouds, because differences in bonding energy that would seem negligible at room temperature become very significant at 10 K [16]. The ratios between different nucleic isotopes (H/D, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$) are an excellent tracer for specific chemical processes in the interstellar medium [17–21], and can even be used to trace back the origins of meteorites that land on Earth [22–24]. Considering that the D/H ratio of our oceans far exceeds the primordial ratio and that of the giant planets in our Solar System, it has also been hypothesized that the water on Earth is of cometary origin [25, 26].

1.1.3 Detecting molecules

Detecting interstellar compounds, especially molecules, is far from trivial. The theory of molecules was first put forward in the second half of the 19th century, but only in 1937 the first molecule was found in space — CH [27]. Before that time, only atomic compounds such as H and He could be detected. The principle behind the astronomical detection of many molecules is shown in Fig. 1.3.³ Light originating from a star passes first through a layer of hot gas first, the circumstellar medium (CSM), giving rise to broad absorption lines as shown on the left side of the figure. When this light passes through a large, cold cloud, the chemical composition of the cloud is reflected through the narrow, cold absorption lines in the spectrum.

³Image credit to Fraknoi & Wolff [11], Fig. 20.4.

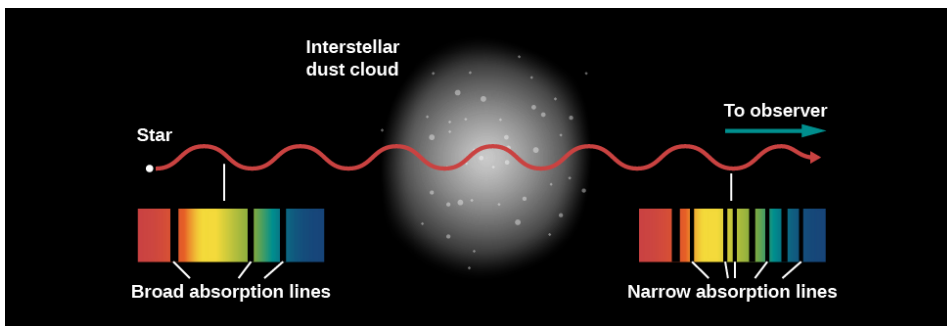


FIGURE 1.3: A cloud of cold dust and gas is present in the line of sight between the observer and a star. The star's own spectrum exhibits broad, hot absorption lines caused by the CSM, whereas the cold cloud only filters narrow lines out of this spectrum, making it easy to distinguish between their respective origins [11]. Image credit in footnote.

To find out which line belongs to which compound requires laboratory studies on Earth. The laboratory study of visible emissions from plasmas of various molecules (called a glowing arc, analogous to neon discharge lights) provided a great wealth of lines that could be assigned to optical lines in astronomical observations [28]. The detection of polyatomic and many more diatomic molecules had to wait until the 1960s, when the concurrent advent of radio- and microwave astronomy, and the development of masers and lasers for laboratory study led to a boom in the detection of new interstellar molecules [15]. Currently, at least 210 molecules have been confirmed in the ISM and CSM [8]. Table 1.1 lists the molecules included in the Cologne Database.

Most molecules in space contain less than 13 atoms, with diatomics and triatomics, and then organic molecules dominating the list. There are three main causes for the relative dominance of small molecules. Firstly, there is a certain bias in the available detection methods towards smaller molecules, considering their detection by radio- or optical astronomy, and their identification by both experiment and theory is easier. Most laboratory methods are more easily applied to smaller molecules because there are fewer degrees of freedom, and thus spectroscopically fewer levels to distribute available populations over. This greatly simplifies the unequivocal assignment of astronomically observed lines to one molecular species. These degrees of freedom are likewise limited in highly symmetric species, such as the large, astronomically-detected molecules C_{60} , C_{60}^+ , and C_{70} [29, 30]. Secondly, there are fewer steps to take for the formation of smaller species, creating a bias in their favor. As a third reason, fragile molecules are readily destroyed due to the intense (F)UV fields, which are present in most environments, except the insides of cold molecular clouds. This means that molecules found in space need to be continually produced, or able to survive those harsh conditions. The three large, symmetric species mentioned before have shown to be able to survive these harsh conditions. They derive their stability from their large, cage-like aromatic structure [31]. However, the gap in size between $c-C_6H_5CN$

(the smallest aromatic molecule in space) and C_{60} is so large that there needs to be a range of species of intermediate size as well in the interstellar medium. Clues for their presence are found in the infrared part of the electromagnetic spectrum.

1.1.4 Finding PAHs

Even though infrared signatures are commonly used to distinguish between chemical compounds on Earth, it was not possible to do infrared astronomy until the mid 1970s. Atmospheric H_2O and CO_2 block most infrared lines, while thermal background radiation makes it difficult to see faint objects in the sky. These two aspects posed a great challenge to observers. Airborne and space observatories changed this, as physicists developed new methods that astronomers at first considered to be of little use [33]. Broad, but resolved emission features were observed around 8.6 and 11.2 μm in three PNæ [34], and later new bands were found at 3.3, 6.2 and 7.7 μm in two reflection nebulae [35]. The carriers of these bands went unidentified for nearly a decade, leading to them being referred to as the Unidentified InfraRed (UIR) bands.

Many types of grains were proposed as carriers, but Sellgren [36] found in 1984 that the particles responsible for this radiation would need to be relatively small, with a limited heat capacity. In the same year, Leger and Puget [37] compared the spectrum of a reflection nebula to the emission spectrum of coronene, $C_{24}H_{12}$, and concluded that the two spectra showed a remarkably good match. Building on that hypothesis, the groundbreaking work of Allamandola *et al.* [38] showed one year later how the Raman spectrum of soot from car exhausts matched the emissions from the Orion Belt. This made it evident that the UIRs were produced by a large group of aromatic compounds, that would have to be present in myriad astronomical objects. The observed MIR bands are indicative of C–C stretching and C–H bending modes in aromatic species, correlating particularly well with known spectra of Polycyclic Aromatic Hydrocarbons (PAHs). The UIRs are thus presently referred to as the Aromatic Infrared Bands (AIBs). The AIB spectra recorded from three different objects, the center of the HII (ionized hydrogen) type galaxy NGC 4536, the planetary nebula NGC 7027, and a photodissociation region (PDR) in the Orion Bar, are shown in Fig. 1.4,⁴ exhibiting the same typical aromatic C–C and C–H vibrations characteristic of PAH species. Small spectral shifts and differences in band intensity ratios indicate that dissimilar PAH populations exist in these various environments.

1.2 PAHs in the interstellar radiation field

To understand the role that PAHs play in the ISM, the nature of the radiation field needs to be understood as well. Throughout the life cycle of matter in a galaxy, the radiation emitted or absorbed by the different forms of matter, varies widely in both intensity and

⁴Image credit to Els Peeters [32] who also supplied the high-resolution figure. Used with permission from Cambridge University Press.

1.2. PAHs in the interstellar radiation field

TABLE 1.1: Size-sorted molecules detected in the interstellar medium and in circumstellar shells, up to the year 2019. [8]

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms
H ₂	C ₃	c-C ₃ H	C ₅	C ₅ H	C ₆ H	CH ₃ C ₃ N
AlF	C ₂ H	l-C ₃ H	C ₄ H	l-H ₂ C ₄	CH ₂ CHCN	HC(O)OCH ₃
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄	CH ₃ C ₂ H	CH ₃ COOH
C ₂	C ₂ S	C ₃ O	l-C ₃ H ₂	CH ₃ CN	HC ₃ N	C ₇ H
CH	CH ₂	C ₃ S	c-C ₃ H ₂	CH ₃ NC	CH ₃ CHO	C ₆ H ₂
CH ⁺	HCN	C ₂ H ₂	H ₂ CCN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO
CN	HCO	NH ₃	CH ₄	CH ₃ SH	c-C ₂ H ₄ O	l-HC ₆ H
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	H ₂ CCHOH	CH ₂ CHCHO
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO	C ₆ H ⁻	CH ₂ CCHCN
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO	CH ₃ NCO	H ₂ NCH ₂ CN
SiC	H ₂ O	HNCS	H ₂ CNH	C ₅ N	HC ₅ O	CH ₃ CHNH
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O	l-HC ₄ H	HOCH ₂ CN	CH ₃ SiH ₃
KCl	HNC	H ₂ CO	H ₂ NCN	l-HC ₄ N		H ₂ NC(O)NH ₂
NH	HNO	H ₂ CN	HNC ₃	c-H ₂ C ₃ O		
NO	MgCN	H ₂ CS	SiH	H ₂ CCNH		
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺	C ₅ N ⁻		
NaCl	N ₂ H ⁺	c-SiC ₃	C ₄ H ⁻	HNCHCN		
OH	N ₂ O	CH ₃	HC(O)CN	SiH ₃ CN		
PN	NaCN	C ₃ N ⁻	HNCNH	C ₅ S		
SO	OCS	PH ₃	CH ₃ O	MgC ₄ H		
SO ⁺	SO ₂	HCNO	NH ₄ ⁺			
SiN	c-SiC ₂	HOCN	H ₂ NCO ⁺			
SiO	CO ₂	HSCN	NCCNH ⁺			
SiS	NH ₂	H ₂ O ₂	CH ₃ Cl			
CS	H ₃ ⁺	C ₃ H ⁺	MgC ₃ N			
HF	SiCN	HMgNC				
HD	AlNC	HCCO				
FeO	SiNC	CNCN				
O ₂	HCP	HONO				
CF ⁺	CCP	MgC ₂ H				
SiH	AlOH					
PO	H ₂ O ⁺	9 atoms	10 atoms	11 atoms	12 atoms	>13 atoms
AlO	H ₂ Cl ⁺	CH ₃ C ₄ H	CH ₃ C ₅ N	HC ₉ N	c-C ₆ H ₆	C ₆₀
OH ⁺	KCN	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	CH ₃ C ₆ H	n-C ₃ H ₇ CN	C ₇₀
CN ⁻	FeCN	(CH ₃) ₂ O	(CH ₂ OH) ₂	C ₂ H ₅ OCHO	i-C ₃ H ₇ CN	C ₆₀ ⁺
SH ⁺	HO ₂	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO	CH ₃ OC(O)CH ₃	C ₂ H ₅ OCH ₃	c-C ₆ H ₅ CN
SH	TiO ₂	HC ₇ N	CH ₃ CHCH ₂ O			
HCl ⁺	C ₂ N	C ₈ H	CH ₃ OCH ₂ OH			
TiO	Si ₂ C	CH ₃ C(O)NH ₂				
ArH ⁺	HS ₂	C ₈ H ⁻				
N ₂	HCS	C ₃ H ₆				
NO ⁺	HSC	CH ₃ CH ₂ SH				
NS ⁺	NCO	CH ₃ NHCHO				
HeH ⁺	CaNC	HC ₇ O				

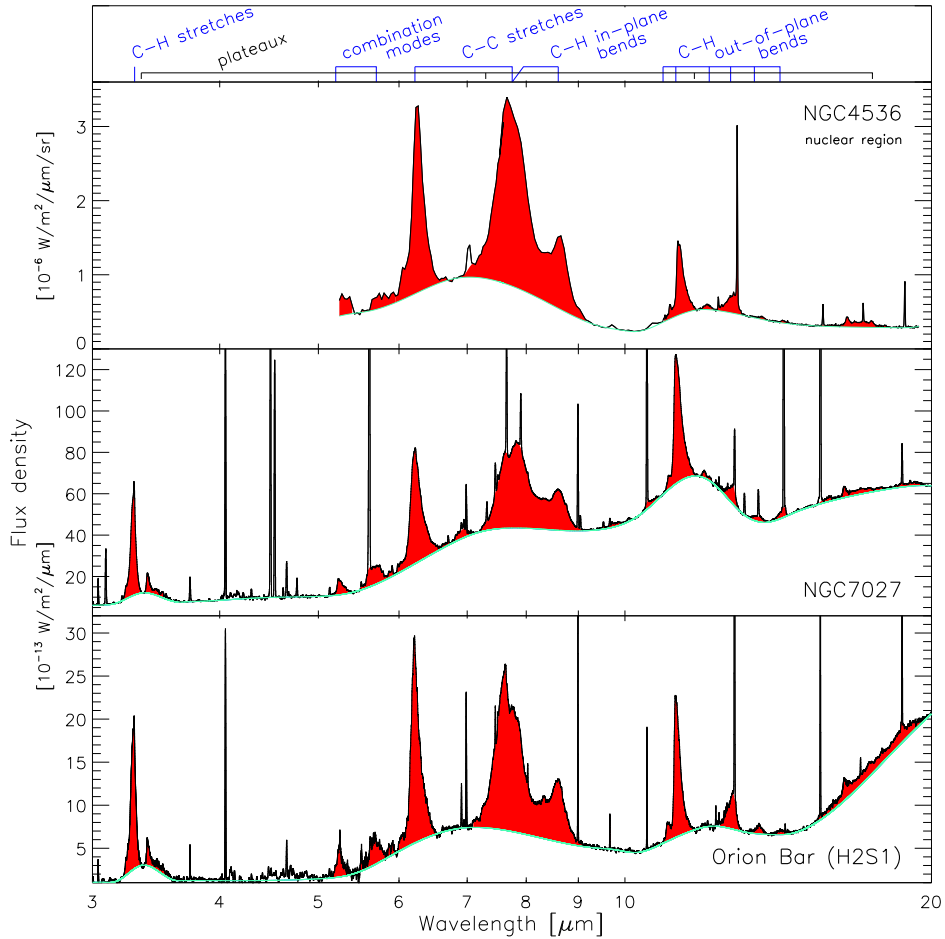


FIGURE 1.4: Astronomically observed mid-infrared spectra for three different objects, each displaying the characteristic vibrational modes of PAHs. All three spectra are highly similar, but show significant spectral variations pointing to differing PAH populations [32]. Image credit in footnote.

1.2. PAHs in the interstellar radiation field

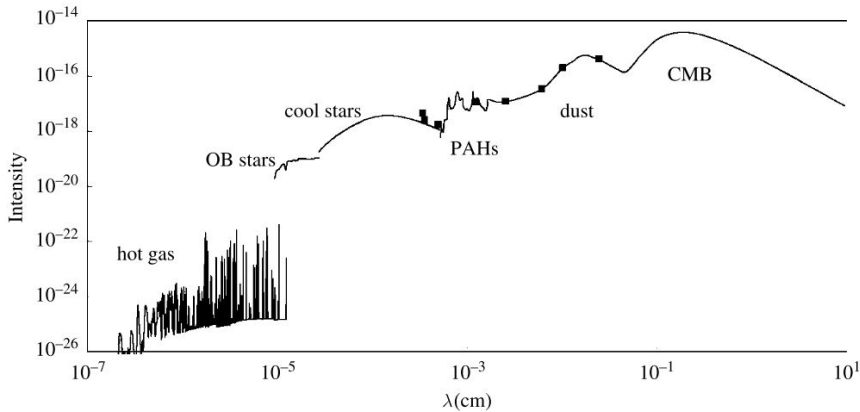


FIGURE 1.5: Mean intensity in $\text{erg}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{Hz}^{-1}\cdot\text{sr}^{-1}$ of the interstellar radiation field in our solar neighborhood. The curve comprises a collection of different observations: hot gas, OB stars (highly luminous blue giants), older stars, large molecules (PAHs), dust, and the cosmic microwave background [7]. Image credit in footnote.

wavelength, as is shown in Fig. 1.5.⁵ Massive (young) stars account for most of the radiation produced at the shortest wavelengths. Small quantities of hydrogen gas that are efficiently ionized, also re-emit in this region, giving rise to the forest of X-ray lines shown by the leftmost curve. The abrupt cut-off of this part is caused by the Lyman limit (912 Å), above which the ionization of hydrogen goes directly into the continuum. The OB stars, as they are labeled in the figure, are relatively rare, but emit very strongly in the (F)UV. Cooler stars are responsible for most of the visible radiation field. The radiation field evolves into relatively broad IR emission lines, which, as we know, are caused by the UV excitation of PAHs. Even though the interstellar radiation field in the UV and visible range is intense, carbonaceous materials (*i.e.* PAHs and dust) extinguish a large part of this radiation [39]. The largest extinction feature in the UV (217.5 nm, not visible on this scale) can be attributed for at least $\frac{2}{3}$ of the total extinction to absorption by PAHs [40–42]. The re-emission of this absorbed light is in turn responsible for a large part of the discrete IR lines (PAHs) and the sub-mm continuum (dust). As is shown in the middle of Fig. 1.5, the PAH and dust curves rise above UV/VIS emissions in terms of mean intensity. Beyond these wavelengths, the Cosmic Microwave Background (CMB) is found, which represents the residual energy emitted after the recombination of matter right after the formation of the Universe.

As was hinted at in the previous section, Sellgren [36] found that the carriers of the UIRs would have to be able to reach temperatures as high as ~ 1000 K to be able to emit

⁵Sources for these individual spectra are indicated in Tielens [7], page 12, from where the figure was taken, with permission from Cambridge University Press.

in the mid-infrared (MIR), and dust would not be able to become that hot. PAHs are able to reach such temperatures when absorbing a UV photon. They can also efficiently release this energy through infrared emission [43]. An isolated PAH that absorbs a UV photon is excited to an electronically-excited state, after which the molecule undergoes rapid internal conversion to a highly vibrationally excited electronic ground state. The vibrational energy is dispersed over many vibrational states through intramolecular vibrational redistribution. Due to the low pressure in the ISM, there is ample time for infrared emission to occur from all of these different occupied vibrational states. When the excitation energy is high enough, the PAH may also lose an electron or a hydrogen atom, while the fused hexagonal system remains intact. The band positions in the emission spectra of these partly dehydrogenated or ionized molecules remain very similar, although small spectral shifts may occur and the corresponding intensity ratios will differ [7, 43, 44]. The high aromaticity of hydrocarbons in space is a consequence of this hostile environment filled with high-energy radiation. The percentage of carbon that is present in aliphatic, rather than aromatic form, seems to be quite limited (<15%) [45, 46]. So, even though the AIBs also reveal some aliphatic features, the dominant character of the hydrocarbon species responsible for these emissions is aromatic.

In spite of all of the research that has been done on PAHs, not a single PAH molecule has been unambiguously identified in the ISM up to this point. Considering that the C–C and C–H modes that make up the spectra in Fig. 1.4 are present in all PAH molecules, none of them are diagnostic to one specific species of PAHs [47]. The band positions are however weakly dependent on the size and structure of the molecules and as mentioned before, the intensity ratios can vary as well. The spectra from different astronomical objects reveal this varying spectral behavior, which has been attributed to populations of PAHs with different sizes and charge states. A typical example is shown in Fig. 1.6.⁶ Composite spectra of PAHs of different charge states needed for assignment of astronomical spectra such as in Fig. 1.6a, are primarily derived from theoretical surveys. Similarly, theoretical work has led to the proposition that the size of interstellar PAHs is between 30 and 150 carbon atoms, depending on the environment in which they are found [37, 48–51].

Molecule-specific spectral signatures may be found in FIR region. As many PAHs do not possess a dipole moment, radio discovery is not possible. However, FIR spectroscopy can reveal low-intensity vibrational modes that are more strongly dependent on the size and the structure of the PAH molecule [54–57]. This field of PAH research is relatively unexplored, both due to the large dust background that makes it difficult to observe clear PAH signatures (see Figs. 1.4 and 1.5), and the difficulty in recording laboratory spectra of FIR modes. This is both due to the limited availability of suitable table-top light sources and the low oscillator strength associated with these molecular modes.

⁶Taken from Tielens [47], with permission from Annual Reviews

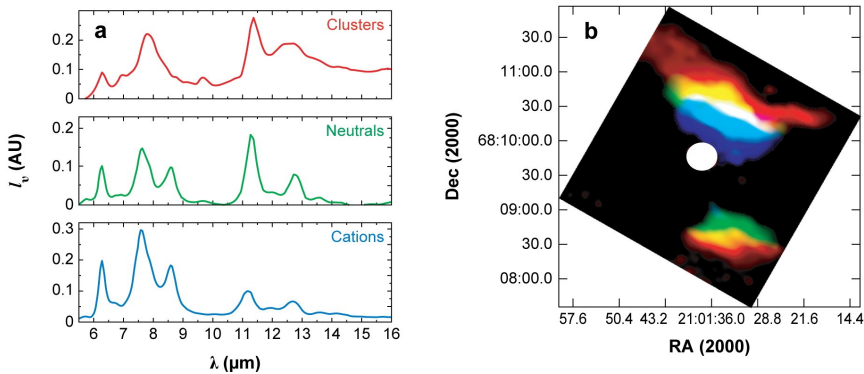


FIGURE 1.6: (a) Spectra recorded for three different sections of the reflection nebula NGC 7023. Each spectrum was normalized by its integrated intensity [52]. (b) A spatial map of the same nebula, showing the distribution of the different types of PAHs around the central star, using the same color code. Red and green combine to yellow [47, 53]. Image credit in footnote.

1.3 PAHs in interstellar chemistry

PAHs contain up to 20% of all cosmic carbon [43, 58], making them undeniably an important part of the chemical network in the ISM. A clear example how PAH spectra change under the influence of their environment is given in Fig. 1.6. The right panel shows how the IR spectrum of the gas in a reflection nebula is composed of different PAH spectral components, which are plotted in the three curves in the left panel. The PAHs closest to the hot, young star in the center are mostly ionized. Moving away from the star, they are neutral, and further away, they are increasingly clustered [47].

This allows AIBs to be used as a direct probe of the stellar formation rate throughout the Universe [59–62]. PAHs that were originally produced in the carbonaceous outflows of a dying star are eventually returned to the ISM, and gathered in molecular clouds, as described by Fig. 1.2. When a star is born in such a cloud it begins to illuminate the surrounding gas. The PAHs in the cloud that were formed in the stellar outflows of previous cycles are excited once again, and start emitting AIBs.

The detection of PAHs in meteors [22, 63, 64] and comets [65] reveal a possible key role of PAHs in the formation of planets around new stars. In the next stage of a solar system’s life (stage (3) in Fig. 1.2), PAHs are hypothesized to cluster, and form larger and larger grains that will maintain their orbit around the star and eventually ‘snowball’ into a planet. However, to form a planetesimal, the Van der Waals forces between the PAHs in the clusters need to be strong enough to survive the nascent star’s shock waves. Biennier *et al.* [66] found that the forces between pyrene molecules in a cluster were insufficient, but considering that pyrene only contains fourteen carbon atoms, it is very small for an interstellar PAH.

Although it is clear that larger PAHs are found in more energetic radiation fields than the smaller ones, there is a large uncertainty around the exact sizes and the formation of PAHs [67]. In possibly the most popular theory, PAHs are proposed to be a by-product of dust formation, produced in a top-down mechanism where the edges of graphitic dust are exposed to FUV radiation and the deformed rims are hydrogenated to form PAHs [51, 68, 69]. It has also been suggested that PAHs can be formed through a combination of different bottom-up mechanisms, in which small organic molecules react with one another to form large PAHs. These mechanisms have been validated through the study of sooty flames [70–74], but it is unclear to what extent this applies to inter- or circumstellar chemistry.

PAHs are important in various chemical processes, affecting ionization, molecular, and isotopic balances in the ISM, particularly in relation to the ratio of atomic versus molecular hydrogen. In cold parts of the ISM, most hydrogen is present in molecular form, but it has been known since the 1940s [75] that the simple $\text{H} + \text{H} \longrightarrow \text{H}_2 + h\nu$ reaction is far too slow to account for all H_2 present [76, 77]. Many studies point towards dust and icy grains as catalysts, although some suggest PAHs can act as catalysts too, allowing H_2 to be formed over a larger temperature range [78–84].

Due to their ability to maintain an intact carbon backbone through both severe dehydrogenation and superhydrogenation conditions [80, 81, 85–90], PAHs could play the role of H_2 formation catalyst in various environments, from PDRs [80, 81, 86], to the cold centers of molecular clouds [84, 91]. Recent work has revealed a possible role for PAHs with edges containing bays or coves, in which the hydrogen atoms are sterically hindered and more likely to shift to other carbon atoms, breaking the aromaticity [92]. Such processes allow H_2 to be stripped off at increased rates. The exact role of PAHs and the mechanisms underlying these reactive networks is complicated, and is still under investigation.

The influence of temperature on hydrogen catalysis also opens the door to exaggerated isotopic differences. Deuterated PAHs (D-PAHs) have been speculated to be the reason for unexplained deficits in the deuterium background [17–19, 43, 93]. D-PAHs have been shown to exist in the ISM through the observation of C–D vibrational bands at $4.40 \mu\text{m}$ and at $4.63/4.75 \mu\text{m}$ [16, 94–98], but the underlying mechanism and the possible influence on the interstellar D/H ratio is still unknown. The detection of C–D bands is strongly correlated with the strong aliphatic C–H stretch bands [95, 98], which suggest a shielded environment where hydrogenated PAHs can exist. Further research, including an experimental perspective on the reaction mechanisms is strongly needed.

1.4 Infrared spectroscopy for astrochemistry

PAH astrochemistry would not have been possible if it were not for the spectroscopic data that is available for many of the candidate species [99]. Advances in astrochemistry are hinged on the close collaboration of observational astronomers, theoretical chemists and laboratory physical chemists. The large number of AIB candidate species, and their size, necessitates the use of theoretical chemistry methods. These theoretical spectra need to be

validated through experiments. Laboratory astrochemists, in turn, often need theoretical calculations to identify experimental results and to be able to extrapolate these results to astronomical contexts. This back-and-forth leads to a constant improvement of the available methods, and the development of new observational tools leads to big leaps forward with every new telescope launch.

The spectroscopy of PAHs and related molecules of (partly) aromatic nature can be roughly divided into four major spectral regions. The UV/visible relating to electronic spectroscopy, the MIR relating to the AIBs and the local vibrational modes, the FIR relating to the skeleton vibrational modes, and the microwave/radio range related to rotational transitions. Many studies have tried to link PAHs to visible absorption lines observed in the ISM - the Diffuse Interstellar Bands (DIBs) [100–104]. To this date, the fullerene C_{60}^+ is the only polyaromatic molecule to be matched [30] to the DIBs. PAHs have been linked to MIR emissions and, as mentioned before, reveal information on size ranges, structure, and PAH classes (such as ions, clusters, and those containing aliphatic carbons or nitrogen hetero atoms). These MIR emissions can therefore give boundary conditions for interstellar PAH populations and their evolution. Rotational spectroscopy is not feasible for most PAHs as they possess a zero or negligible dipole moment.

Laboratory studies on the spectroscopy of astronomically-relevant PAHs are challenging, but necessary. Considering that the computational cost associated with theoretical work on increasingly large PAHs puts tight constraints on the level of theory that can be used, experimental benchmarking is of the utmost importance. However, for these experiments to be of use, the employed methods either need to reproduce astronomical conditions, and record the findings precisely, or deviations from the astronomical context and the induced changes in the spectrum need to be known. For several spectroscopic methods, the involatile and photostable nature of astronomically-sized PAHs forms a substantial hurdle, especially for measurements in MIR and FIR.

The most traditional type of laboratory spectroscopy is direct absorption spectroscopy. Light with a known wavelength λ and intensity I_0 is passed through a medium with an optical path length l , and either a known density/concentration n or a known absorption cross section $\sigma(\lambda)$. In order to be able to observe attenuation of the light, n needs to be high enough, which is done by increasing the concentration in a liquid or the pressure in a gas. This type of spectroscopy is practical and viable in many occasions, but much less so as a model for interstellar environments.

The lack of density in the gas phase can be compensated by placing the dilute gas sample in a reflective cavity, allowing the laser light to make many passages through the medium, amounting to an l of several kilometers in a method known as cavity ring-down spectroscopy (CRDS) [105, 106]. However, CRDS's sensitivity is inhibited by high backgrounds due to stray light, and difficulties with distinguishing spectra of different molecules present in the sample. The background problem was amended, and the resolution greatly improved by the introduction of mode-locked laser techniques and improved cavity quality in the methods NICE-OHMS (noise-immune cavity-enhanced optical heterodyne molecular spectroscopy) [107] and later a second modulation mode to correct

for Doppler broadening in NICE-OHVMS (noise-immune cavity-enhanced optical heterodyne velocity modulation spectroscopy) [108]. These methods have been used to record infrared spectra with resolutions comparable to microwave spectra for small, astrochemical molecules such as H_3^+ [109], of even complex systems of hydrocarbon plasmas [110].

However, all these methods require a pristine cavity and lasers which can be mode-locked to these cavities, making this a difficult experiment to run over large wavelength ranges. Furthermore, mirrors that allow for the required precision in resonance are not available for FIR frequencies, rendering this method impractical for surveys of the mid- to far-infrared. For PAHs specifically, their tendency to lose H in ionization processes and the impurities frequently encountered in commercially obtained samples introduce significant complications, making CRDS a relatively unpopular method for PAH spectroscopy [111], although it is used for UV spectroscopy in an effort to find the PAHs responsible for DIBs [104].

Most of the early work in laboratory PAH astrochemistry has been done using matrix isolation spectroscopy (MIS) [112–115]. In this method, the molecule of interest is brought into the gas phase, and sputtered onto a cold substrate together with an inert gas, such as para-hydrogen, argon or krypton [116, 117], which isolates the molecule and brings it down to a vibrational and rotational ground state. The IR spectrum is then obtained through Fourier Transform IR (FTIR) spectroscopy [118]. This method is less sensitive than CRDS, but measurements can be performed over a much broader spectral range, and the end result is still an absolute absorption spectrum. Although the cold spectra obtained through MIS give narrow bandwidths, the matrix itself imposes a relatively unknown variable on the band positions and intensities, and is therefore not an analogous environment for interstellar, gas-phase PAHs [119, 120].

Gas-phase action spectroscopy provides a means to measure low-density samples of truly isolated molecules or ions with zero to almost-zero background. Ionization (neutrals), electron detachment (anions), or fragmentation (cations) are induced by laser light, which changes the molecular composition of the gas sample or beam. The actively-induced change in molecular composition allows detection of absorptions on a single-event sensitivity level, thanks to mass spectrometry techniques such as time-of-flight or Fourier transform ion cyclotron resonance. The increase or decrease in the flow of particles can be plotted as a wavelength-dependent spectrum.

A rather common technique takes advantage of the weak Van der Waals interaction that can be established between a cold cation and a rare gas atom. Breaking this bond requires less than the energy contained in a MIR photon. This photon is resonantly absorbed by the cold molecule, and the heat causes the cation to lose the rare gas atom. This loss is then detected through mass spectrometry as a function of the wavelength. Infrared photon dissociation (IR-PD) requires cold molecules, and thus produces very narrow lines [121–123]. When the tag is very small compared to the ion of interest, the measurements can be very accurate, as was shown by the measurement of the high-resolution visible spectrum of $\text{C}_{60}^+ - \text{He}$ [30, 109]. However, the rare-gas tag can lead to hard-to-predict shifts in the spectra, which need to be taken into account, much like the shifts observed in MIS.

Furthermore, the Van der Waals bond is often only a few hundred wavenumbers, meaning that IR-PD cannot be used for measurement in the FIR.

The method of choice to record spectra of bare, cationic PAHs is InfraRed Multiple Photon Dissociation (IRMPD) spectroscopy. Highly intense infrared light is used to induce successive absorption of photons by the ion, thereby enabling to reach energy levels at which dissociation can occur [124]. At least $2 \text{ eV}/16000 \text{ cm}^{-1}$ of energy is needed to break a C–H bond, which means that absorption of at least five IR photons of $0.4 \text{ eV}/3300 \text{ cm}^{-1}$ is needed. The required high photon densities can only be achieved with free-electron lasers (FELs) [125]. IRMPD spectroscopy using FELs has been proven to be an indispensable method to record IR spectra of cationic PAHs with high sensitivity over a large range of frequencies [126–130]. Furthermore, IRMPD spectroscopy can be used to measure FIR spectra of PAHs, whereas rare-gas tagged IR-PD in that wavelength range is quite difficult to do [131]. It should also be remarked that action spectroscopy based on reaching photodissociation is also not just a means to an end, since the fragmentation patterns that arise after photo-excitation (*i.e.* differences in $\text{C}_2\text{H}_2/\text{H}_2$ -loss or H/D-loss, the subsequent formation of pentagonal structures) can provide unique insights in the fragmentation chemistry as for instance relevant in the UV photolysis of PAHs occurring in space [132–134].

1.5 Scope of this thesis

IRMPD is the cornerstone of this thesis. It has allowed the study of photochemical processes key for understanding the evolution of PAHs in space. Equally important, it has allowed for spectroscopic studies with unprecedented detail that cover large frequency ranges and that shed light on the MIR and FIR spectral features observed in astronomical studies. The research presented in this thesis covers key characteristics of small model systems for interstellar PAHs: fragmentation propensities, isomerization pathways, and infrared signatures.

The physics and chemistry associated with the spectroscopic, mass spectrometric and theoretical methods are treated in detail in Chapter 2. Chapter 3 contains the first, detailed presentation of the unique FELICE FT-ICR apparatus, on which the work for Chapters 5, 6, and 7 has been performed. Chapter 3 also provides a detailed description of the deuteration procedure developed to produce the molecules studied in Chapter 4.

Chapter 4 explores the role photochemical reactions PAHs have in causing variations in the cosmic deuterium abundance. By studying the UV and IR-induced elimination of H and D from D-containing anthracene and phenanthrene, we investigate photochemical processes underlying deuteration in the ISM. The experimental data are key to validate and advance astronomical models that use Density Functional Theory (DFT) calculations to provide estimates of the interstellar abundances of deuterium-containing PAHs.

Chapter 5 presents the first infrared spectra recorded for bare, gas-phase phenylium (C_6H_5^+). The role of phenylium in the formation of PAHs in both combustion flames and

stellar outflows has been studied in detailed laboratory and theoretical studies, but little is known about its own fragmentation pathways, nor has its spectrum been recorded in the fingerprint region. The spectrum recorded here is used to validate previous assignments of its ground-state spin configuration and to benchmark high-level anharmonic DFT calculations. We present DFT calculations detailing the isomerization pathways phenylium goes through before fragmentation, and compare this to our observed fragmentation after IRMPD.

In Chapter 6 we present the gas-phase infrared spectra of three cationic PAHs — phenanthrene, pyrene and perylene — in the 6–95 μm (1700–105 cm^{-1}) range. The intracavity setup of the Free-Electron Laser for Intra-Cavity Experiments (FELICE) allows the recording of IR multiple photon dissociation (IRMPD) spectra of strongly-bound PAHs using low-energy photons below 18 μm (555 cm^{-1}), and thereby the study of the molecule-specific, low-lying skeleton modes of PAHs, for which investigations so far needed to rely on models. The experiments described in the Chapter are the first ones to explore the complete available wavelength range of the FELICE FT-ICR and its available power attenuation methods. Anharmonic DFT spectra were calculated for pyrene and perylene in order to assess the need for anharmonic calculations in the FIR, and to explain anomalous low-intensity modes. We use our experimental data to validate trends that were found for the propagation of certain skeletal modes into the FIR for increasingly large PAHs of the same shape. Depending on the interstellar environment, such trends are quite useful for the future identification of modes belonging to specific PAH molecules in astronomical FIR spectra.

Lastly, in Chapter 7 we present the first infrared spectrum of a truly irregular PAH, dibenzo[a,l]pyrene ($\text{C}_{24}\text{H}_{14}^+$), in the 6–40 μm (250–1650 cm^{-1}) range. This molecule is asymmetric and non-planar, which means that every vibrational mode can in principle be IR-active. Furthermore, the molecule possesses nearly all possible edge geometries, making its infrared spectrum a rich testing ground for many pre-conceived notions on how PAH spectra are composed. The IRMPD spectrum is compared to harmonic DFT calculations to interpret the observed modes. We also explore the role of the cove region in this molecule's photostability, and explore the possibility of similar molecules being present in the ISM.