Destroy, create, transform and sublimate: laboratory dissociation studies on polycyclic aromatic hydrocarbons and analogues
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Introduction

When one glazes at the night sky with the naked eye, only stars and darkness can be seen. From this observation one could easily think that space is mostly vast nothingness with an occasional star. However, this is far from the truth. The region between stars, so-called interstellar medium (ISM), is filled with neutral and ionized gas clouds, and icy grains/dust, all containing a variety of atoms and molecules. ~ 99 % of the ISM mass is made up of gas, while only ~ 1 % is made up from dust and grains (Casasola *et al.* 2020). How the first stars and interstellar objects formed after the big bang, is still one of the biggest questions in science to date. However, their life cycles are fairly well understood (van Dishoeck 2004; Tielens 2013, and references therein). Ignoring the birth of the first stars, the evolution of all the gas and dust in the ISM can be viewed as a cyclic process, depicted in Fig. 1.1. The life cycle of the ISM is initiated with a star releasing its material into space, either through stellar winds or explosive events ("stellar ejecta" in Fig. 1.1). The ejected material forms a diffuse cloud, which further evolves into a molecular cloud, due to chemical events and gravitational influences. These interstellar objects are able to cycle between each other. At

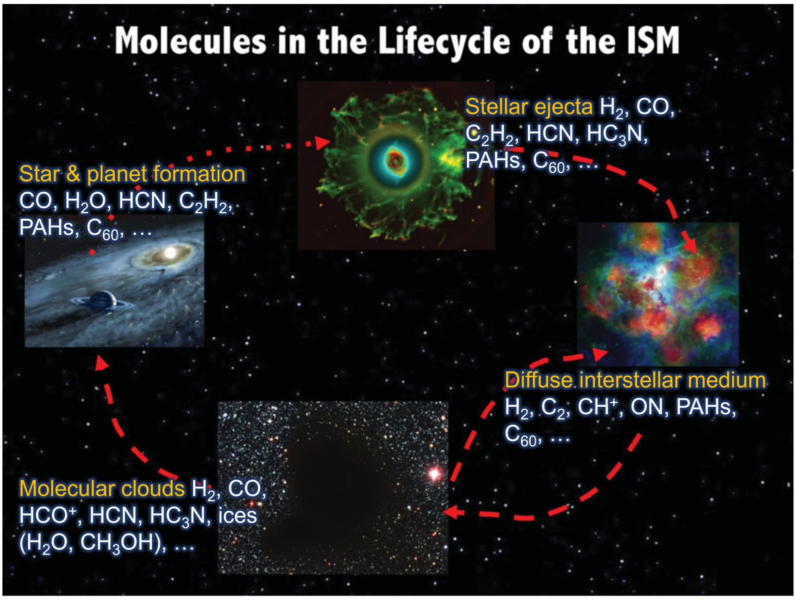
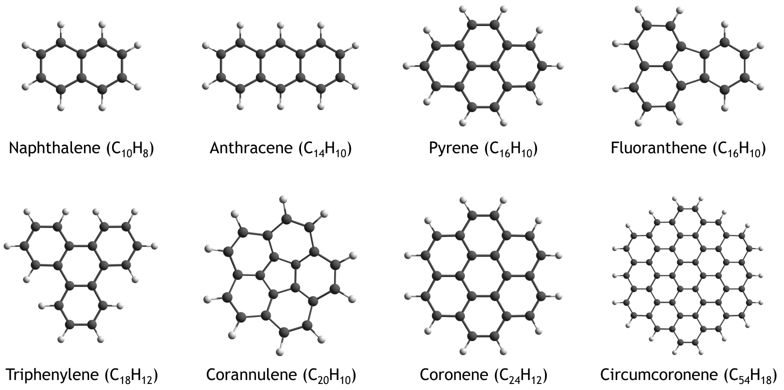


Figure 1.1: Illustration of the lifecycle of the ISM with examples of molecules detected in the interstellar objects. The presence of various molecules in the stellar states enables their characterization and enhances our understanding of their specific chemical properties. Figure adapted from Tielens (2013).



Naphthalene ($C_{10}H_8$) Anthracene ($C_{14}H_{10}$) Pyrene ($C_{16}H_{10}$) Fluoranthene ($C_{16}H_{10}$)

Triphenylene ($C_{18}H_{12}$) Corannulene ($C_{20}H_{10}$) Coronene ($C_{24}H_{12}$) Circumcoronene ($C_{54}H_{18}$)

Figure 1.2: Example of PAH molecules with various sizes and geometries. Although, hexagonal, honeycomb-like structures are iconic to PAHs, some geometries can also contain five-membered rings.

some point, a molecular cloud will become gravitationally unstable and the gas and dust inside will accumulate and start to form new stars and accompanying planetary systems. After the central star dies, it will release its material into the ISM, starting the cycle from the beginning again. Generally, this cycle takes billions of years. Each stage in the life cycle of the ISM is represented by a unique collection of atoms and molecules in various charge states that can be found towards the interstellar object.

For a long time, the universe was thought to be barren and molecules were not expected to be present. That changed with the detection of the first interstellar molecule, methylidyne $CH^{\bullet}$, in 1937 by Swings & Rosenfeld (1937), through its electronic transition at 430.3 nm. Since then the rate at which molecules were detected has steadily gone up and to date, more than 320 molecules are detected in the ISM, and new species are being detected almost every other month.

The detected molecules vary greatly in size, ranging from very small ones like H_2 to ones that are much larger such as C_{60} and C_{70} fullerenes (McGuire 2022). Nearly all detected interstellar molecules contain carbon and hydrogen atoms, underscoring the fundamental role of carbon and hydrogen chemistry in the molecular inventory of the ISM. Carbon being a foundational component, originates from its ability to form complex and stable bonds and molecules. These species can influence (chemical) processes ranging from star formation to the synthesis of organic compounds, potentially the ones responsible for life.

One of the largest and most stable family of – carbon and hydrogen containing – molecules thought to be present in the ISM is classified as:

Polycyclic Aromatic Hydrocarbons (PAHs).

This group of molecules is characterized by their honeycomb-like arrangement of carbon rings with hydrogen atoms bound at the periphery, examples of PAHs are shown in Fig. 1.2. The unique structure of PAHs arises from the bonding characteristics of carbon atoms, which are able to form hybrid orbitals. These hybrid orbitals result from the mixing of individual atomic orbitals, which will later create covalent bonds. Specifically, carbon can mix $2s$ and $2p$ orbitals, leading to the formation of sp^3, sp^2

and *sp* hybridized orbitals. When bonding these can form four, three and two σ bonds, respectively. The remaining electrons of the sp^2 and *sp* hybridization are then to form one or two π bonds, respectively. The formation of these bonds eventually leads to the geometry of carbonaceous species. The aromatic, honeycomb-like structure of PAHs originates from the sp^2 hybridization of the carbon atoms, which is also the responsible hybridization of carbon nanotubes and fullerenes, the latter being already detected in space (Cami *et al.* 2010). Although, sp^2 hybridization does not only lead towards honeycomb-like structures, as five- and seven-membered rings can also be incorporated into a PAH structure, see Fig. 1.2. sp^3 and *sp* hybridization is found in other detected molecules, such as methane (CH_4) and acetylene (C_2H_2).

Astrochemistry encompasses a large variety of problems and questions about the ISM, stars, planets and other celestial objects. Although these problems and questions can be quite diverse, they can all be condensed into four main problems/questions that are being studied in the field of astrochemistry:

- What is the chemical inventory of (newly formed) stars, planets and interstellar objects?
- What role do atoms and molecules play in key processes in the universe, such as temperature regulation and ionization?
- How can molecules be used to probe physical conditions, and trace chemical and physical processes?
- Are molecules in the ISM related to the chemical inventory on earth and other terrestrial planets?

An important part of answering these questions is studying how molecules are formed and destroyed in the harsh conditions of the ISM. And although many studies on this topic were already conducted, we are far from completely understanding the chemical processes that happen in the ISM, and moreover the entire universe.

The aim of this thesis is to increase our understanding and knowledge of the photoprocessing of aromatics, in particular PAHs and their nitrogen bearing analogues, which are ubiquitous species in the ISM, and its relation with the chemical processes in the ISM. The focus will lie on the identification of stable fragmentation products following photodissociation of aromatics and their further chemical processing, as well as the infrared (IR) characterization of nitrogenated PAH analogues. The remainder of the introduction will provide the necessary context for the works presented in this thesis.

1.1 Presence of PAHs in space

PAHs are identified through their mid-infrared (mid-IR) emission features at 3.3, 6.2, 7.7, 8.6, 11.2 and 12.7 μm that are observed towards many diverse astronomical sources in the ISM, such as HII regions, and planetary and reflection nebulae (Tielens 2008; Chown *et al.* 2024). Some example spectra are presented in Fig. 1.3. Especially sources where strong ultraviolet (UV) radiation is present, show intense mid-IR PAH emission features. The fact that these features are observed in such a variety of sources suggests that PAHs play a crucial role in an object's (chemical) evolution and that, regardless of an object's physical conditions or lifespan, PAHs consistently form and persist.

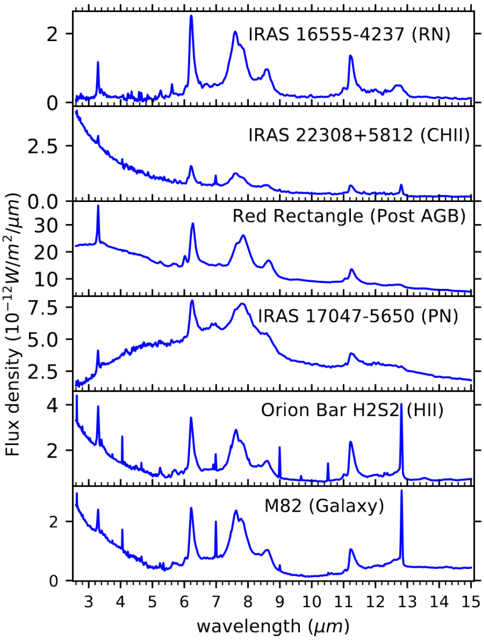


Figure 1.3: Collection of the Infrared Space Observatory (ISO) Short Wavelength Spectrometer (SWS) observational spectra of a variety of astronomical objects. Reoccurring PAH mid-IR emission features can be seen in the spectra, most obviously around 3.3, 6.2, 7.7, 8.6 and 11.2 μm. Figure from Foschino *et al.* (2019).

Moreover, from observations it is estimated that about 15 % of all elemental carbon in the ISM is contained within PAHs (Allamandola *et al.* 1989), thus emphasizing their (chemical) interstellar role and ubiquity.

Due to their relevance in the ISM, PAHs not only become chemically important, but also physically. Differences between observed mid-IR spectra can give information on the charge, size and shape of the PAHs, as well as their degree of photoprocessing. These can all be effected by the local conditions of an interstellar object, such as temperature and density. Thus, the spectral characteristics of PAH mid-IR emission spectra can be used to study the physical conditions of interstellar objects where PAHs are thought to be present (Tielens 2008).

1.1.1 The aromatic infrared bands

In the '70s and '80s, observational IR studies resulted in the detection of a series of emission bands with prominent intensities around 3.3, 3.4, 6.2, 7.7, 8.6, 11.3 (Dwek *et al.* 1980, and references therein) and 12 μm (Aumann *et al.* 1984). Although astronomers knew these bands had to be molecular in origin, a satisfactory identification was yet to be made. Hence, these features became known as the Unidentified Infrared bands (UIBs). Soon after the detection of the UIBs, methane (CH_4) in the mantles of grains was suggested as one of the carriers (Allamandola & Norman 1978), making early links between hydro-carbons and the observed emission features. A second potential source was suggested to be the emission of carbonaceous grains that

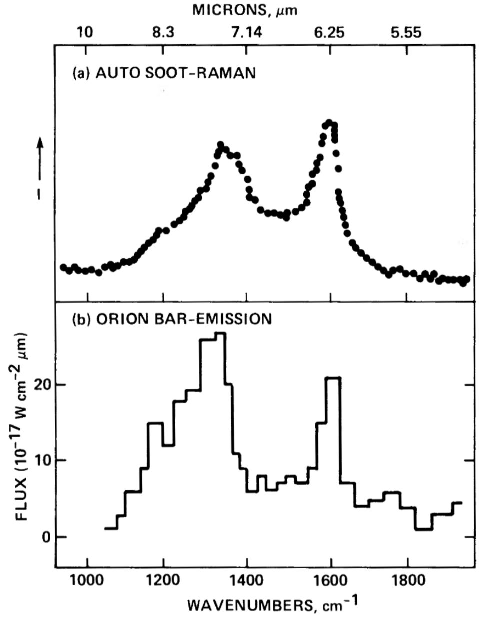


Figure 1.4: Comparison of an experimental Raman spectrum of soot coming from car exhaust fumes (a, Rosen & Novakov 1978) to the observed mid-IR spectra from the Orion bar reflection nebula in the 5 to 10 μm range (b, Bregman *et al.* 1983). Figure from (Allamandola *et al.* 1985).

were stochastically heated (~ 1000 K) by the absorption of UV photons (Leger & Puget 1984). However, this hypothesis would only work for grain sizes that resemble molecules with ~ 50 atoms. Thus, the grains could effectively be considered to be big molecules.

PAHs are suitable candidates to match both the size and the carbonaceous characteristics of these grains. With this in mind, Allamandola *et al.* (1985) compared the observed mid-IR spectra from the Orion bar reflection nebula to an experimental Raman spectrum of soot coming from car exhaust fumes, shown in Fig. 1.4, which is known to contain PAHs, hydrocarbons and other graphitic material, originating from incomplete combustion processes (Rosen & Novakov 1978). Since this identification, a tremendous number of studies have been done on the (chemical) link between PAHs and the ISM and its IR emission features. More and more evidence was gathered and PAHs being carriers of the UIBs bands became set in stone. Due to this, the mid-IR emission bands were no longer unidentified and over time their name changed to:

Aromatic Infrared Bands (AIBs).

IR emission and absorption generally probes the vibrational modes of a molecule, and this is no different for PAHs. The interstellar radiation field bombards particles and matter in space with far-UV photons. When a photon is absorbed by a PAH, it will be excited to a higher electronic state, at which the PAH rapidly (~ 10^{-9} s) distributes the energy, through internal conversion and intramolecular vibrational distribution, into its vibrational modes. The vibrationally excited PAH subsequently

Table 1.1: Common vibrational modes of PAHs associated with their IR emission features (Tielens 2008).

PAH emission feature (μm)	Vibrational mode
3.3	CH stretching
6.2	CC stretching (+ CH in-plane bending)
7.7	CC stretching (+ CH in-plane bending)
8.6	CC stretching (+ CH in-plane bending)
11.2	CH out-of-plane bending
12.7	CH out-of-plane bending

releases its vibrational energy by emitting IR photons while cascading down its energetic ladder to the ground state (Allamandola *et al.* 1989). This process links the intensity of the AIBs to the local UV radiation field. The wavelength of the emitted IR photons is indicative of the specific vibrational modes that were excited. Table 1.1 presents the most common PAH vibrational mode associated with their IR emission feature. Differences in PAH geometry, such as isomers and added functional groups, will (slightly) affect the exact position of its IR emission features and their intensities. Moreover, the charge of a PAH has a significant influence on the intensity of its mid-IR emission spectrum, and a lesser influence of the band positions, as illustrated in Fig. 1.5. The harsh UV radiation in the ISM does not only pump PAHs vibrationally, but can also ionize them due to their low ionization potentials (7 to 10 eV), thus making it likely that a large part of the PAHs in the ISM are positively charged (cationic, Allamandola *et al.* 1985). This statement has been strengthened by the AIBs showing features that can be confidently linked to cationic PAHs (Peeters *et al.* 2002).

Since the AIBs were linked to PAHs, many studies have revealed in what way charge, size, shape and degree of photoprocessing of the PAHs can affect the band positions and intensities of the AIB features, therefore increasing our knowledge and insight on these topics. However, unfortunately the AIBs are more characteristic of specific atomic bond vibrations than of particular molecules. As a result, no PAH has yet been individually identified through its mid-IR emission spectrum.

1.1.2 Current detections of aromatic molecules

Although IR emission is yet to result in the identification of a PAH, aromatic fullerenes C_{60} and C_{70} were detected by comparing their IR emission spectra to the IR emission from planetary nebula Tc 1, recorded with the Infrared Spectrograph (IRS) on board the Spitzer Space Telescope (Cami *et al.* 2010). Furthermore, IR absorption resulted in the first detection of an aromatic molecule in 2001, when benzene (C_6H_6) was identified through ISO observations of its IR ν_4 vibrational mode at 14.84 μm towards protoplanetary nebula CRL 618 (Cernicharo *et al.* 2001).

With the difficulty of detecting aromatic molecules in the IR, the focus of astronomers shifted to radio astronomy. However, this requires the to be detected molecule to have a permanent dipole moment. The first aromatic molecule identified via radio astronomy was polar benzonitrile (C_6H_5CN), towards Taurus Molecular Cloud (TMC-1), in 2018 (McGuire *et al.* 2018). In 2021, benzonitrile was also found in molecular clouds Serpens 1A, Serpens 1B, Serpens 2 and MC27/L1521F (Burkhardt

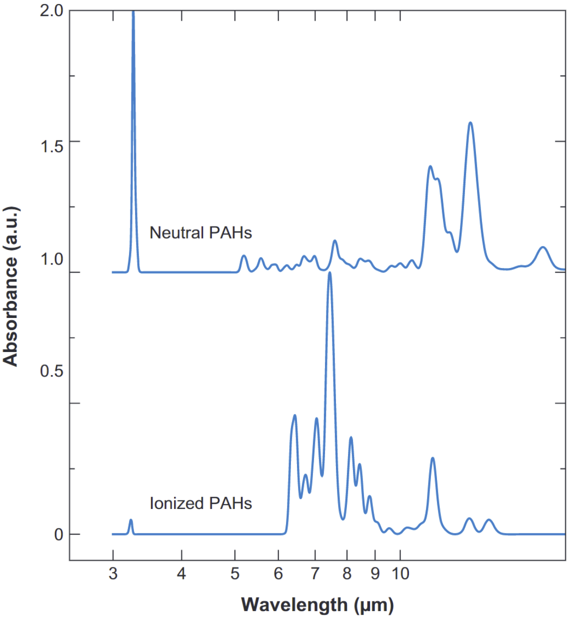


Figure 1.5: Comparison of PAH absorption spectra in different charge states: neutral PAHs (top) and their corresponding cationic forms (bottom). Figure from Tielens (2008).

et al. 2021a). This indicates that aromatic chemistry is not exclusive to just TMC-1, but is common in the ISM, supporting what was also indicated by the AIBs. Benzonitrile is thought to be a tracer of benzene, as it potentially forms via the barrierless radical–neutral reaction: (Cooke *et al.* 2020)

$$CN^{\bullet} + C_6H_6 \longrightarrow C_6H_5CN + H^{\bullet}. \tag{1.1}$$

This reaction implies that benzene may also be present in those molecular clouds. In that same year the first polycyclic aromatic molecules 1- and 2-cyanonaphthalene ($C_{10}H_7CN$, McGuire *et al.* 2021), which are CN functionalized PAHs, and pure polycyclic aromatic molecule indene (C_9H_8, Burkhardt *et al.* 2021b) were also discovered in TMC-1. More recently, the list of discovered CN functionalized PAHs was expanded, by the detection of 1-, 2- and 4-cyanopyrene ($C_{16}H_9CN$) in TMC-1 (Wenzel *et al.* 2024, 2025). Fig. 1.6 shows the geometries of all currently detected interstellar, aromatic molecules.

The unusual geometries of the radio astronomy detected aromatics, lead to the uneven distribution of electrons over the molecule. This creates a difference in local charge density, resulting in the dipole moment that eventually lead to their detection. Generally pure, fully aromatic PAHs have a very symmetric geometry and can therefore not be detected by radio astronomy. While the currently detected polycyclic aromatic molecules share structural similarities with PAHs, they do not meet the criteria to be classified as (pure) PAHs. Nevertheless, their similarity to PAHs is very convincing evidence for the presence of pure, fully aromatic PAHs in the ISM. It has even been suggested (McGuire *et al.* 2021) that these CN functionalized PAHs can form from a reaction similar to (1.1), making the detection of these species indirect detections of PAHs.

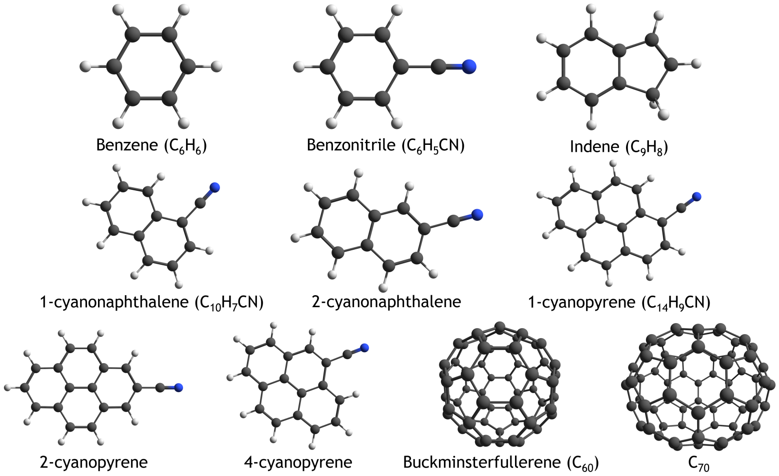


Figure 1.6: Detected aromatic molecules on the day of writing this thesis. (Cami *et al.* 2010; Cernicharo *et al.* 2001; McGuire *et al.* 2021; Burkhardt *et al.* 2021a; Wenzel *et al.* 2024, 2025).

1.1.3 PAH contribution to other cosmic environments

The presence of PAHs in the ISM is well established by the extensive amounts of convincing evidence. The ubiquity of PAHs raises the question of whether traces of PAHs can be found on other astronomical objects that are (currently) not directly tied to the ISM.

One place to look for aromatics is the atmosphere of Saturn's largest moon: Titan. Its dense atmosphere is filled with N_2 and CH_4, and is highly photochemically active (Heintz & Bich 2009). Benzene has already been detected in Titan's atmosphere (Coustenis *et al.* 2007) and experimental data has shown a possibility for benzonitrile to be present as well (Khare *et al.* 1981), hinting towards the existence of more aromatic species. The results of several experimental and computational studies are in favor of PAHs being formed in Titan's atmosphere (Sagan *et al.* 1993; López-Puertas *et al.* 2013; Landera & Mebel 2010; Zhao *et al.* 2018), although a direct identification of a PAH is yet to be made.

Instead of looking for cosmic objects, we can wait for them to reach earth as meteorites, in particular carbonaceous chondrites. As the name already states, these meteorites, as old as our solar system itself, contain a considerable amount of carbon. Investigation of the molecular constituents of carbonaceous chondrites, led to the detection of PAHs (Lecasble *et al.* 2022; Kalpana *et al.* 2021), providing further evidence for the ubiquity of PAHs.

Diffuse interstellar bands (DIBs) are absorption features seen towards diffuse objects in the ISM. So far more than 500 DIBs are observed, but only a handful have been identified to originate from $C_{60}{}^{+}$ (Campbell *et al.* 2015), which also happens to be the only DIB carrier found so far. The abundance and stability of PAHs in the ISM makes them, and their analogues, ideal candidates for other spectroscopic observations, such as the DIBs. Therefore, PAHs, and potential photodissociation fragments, have been considered as potential DIB carriers (Snow 2001; Salama & Ehrenfreund 2013).

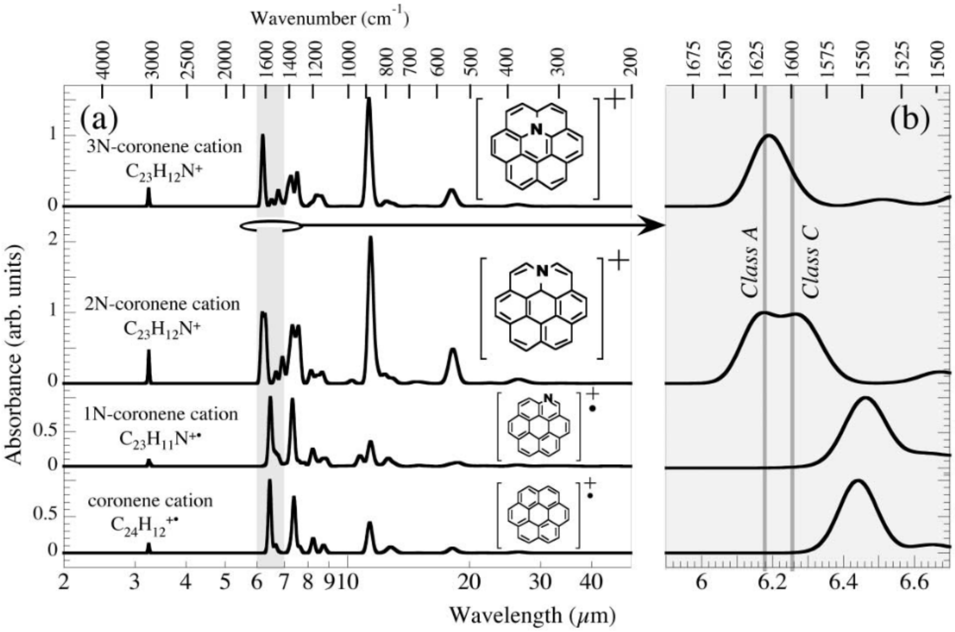


Figure 1.7: Calculated IR spectra of three N-substituted coronene cations compared to that of the parent (unsubstituted) hydrocarbon. (b) shows a zoom-in of the 5.9 to 6.7 μm region from (a). The vertical grey lines in (b) depict the position of the 6.2 μm feature of class A and C mid-IR emission from the ISM. Figure from Hudgins *et al.* (2005).

1.2 The AIB mismatch

When comparing theoretical and experimental PAH IR spectra to observation of the AIBs, a mismatch is often noticed for the 6.2 μm AIB band. A comparison of the mid-IR spectrum a coronene cation to the 6.2 μm AIB feature is presented in Fig. 1.7. Most studies on the mid-IR emission spectra of PAHs present a red-shifted 6.2 μm band, likely originating from CC stretching, towards $\sim 6.3 - 6.4$ μm. While PAHs are generally considered to be AIB carriers and match the other AIB bands, it seems not all of them are able to represent the 6.2 μm band. However, asymmetric and relatively big PAH cations have vibrational modes within the $6.20 - 6.25$ μm region. Highly symmetric and slightly asymmetric PAH cations show contribution to the 6.25–6.30 μm region and elongated shaped PAH cations have bands at > 6.3 μm (Ricca *et al.* 2021). So, pure PAH cations are able to represent the 6.2 μm when subjected to geometrical constraints.

1.2.1 Nitrogen atom inclusion in PAHs

Another route one can take in matching the 6.2 μm AIB band is the substitution of hetero atoms inside of the carbon skeleton of PAHs. Silicon, oxygen and nitrogen are potential atoms for substitution due to their interstellar abundance, valence electron structure and electro-negativity, with respect to carbon atoms. Si and O substitution does not lead to the required shift in band position and, moreover, can distort the

PAH structure such that its existence becomes unlikely. Nitrogen substitution, on the other hand, can result in the required spectral shift and is easily incorporated in the PAH carbon skeleton (Hudgins *et al.* 2005; Ricca *et al.* 2021). The substituted PAHs are generally called:

Polycyclic Aromatic Nitrogen Heterocycles (PANHs)[1].

These PANHs can be divided into two classes: the endo-PANHs and the exo-PANHs. Endo-PANHs have a nitrogen atom substituted *inside* of their carbon skeleton, for an example see the top two cations in Fig. 1.7, by replacing a single carbon atom. In a neutral charge state, these molecules are radical species and therefore difficult the handle under atmospheric conditions, hence no experimental research has been done on these type of molecules so far. In a cationic state, endo-PANHs are closed-shell species, making them very stable. The (computed) mid-IR emission spectra of endo-PANHs cations match the 6.2 μm AIB band very well, thus making them potential AIB carriers (Hudgins *et al.* 2005; Ricca *et al.* 2021). Therefore, cationic endo-PANHs could be present in the ISM and, from observations, an upper limit for the fraction of cationic endo-PANH emission contributing to the astronomically observed 6.2 μm band was estimated to be about 12% (Ricca *et al.* 2021).

Exo-PANHs have a nitrogen atom substituted on the *periphery* of the carbon skeleton, effectively substituting a CH group, for an example see the second cation from the bottom in Fig. 1.7. Due to nitrogen being isoelectronic with CH, it can be incorporated easily in the skeleton without changing too much of the molecular properties. So, in a neutral form these molecules are closed-shell species and can be easily handled. As such, several experiments have already been conducted on these species (Alvaro Galué *et al.* 2010; Bouwman *et al.* 2015; de Haas *et al.* 2017; Subramani *et al.* 2023). Exo-PANH cations have remarkably similar IR emission spectra compared to their pure PAH cation parent (Hudgins *et al.* 2005; Ricca *et al.* 2021), see the bottom two spectra in Fig. 1.7. So, cationic exo-PANHs are not likely to match the 6.2 μm AIB band. However, since their IR spectra are so alike, (cationic) PAHs cannot be considered the only AIB carriers. And with the same arguments that PAHs were thought to be responsible for the AIBS, i.e. their matching IR spectra, exo-PANH cations should be considered as AIB carriers as well. Moreover, exo-PANH cations are radical species and the nitrogen atom proton affinity allows for a potential binding site for hydrogen, which is extremely abundant in the ISM. A reaction with hydrogen would create a protonated exo-PANH, which is a closed-shell species. Interestingly enough, the mid-IR emission of protonated exo-PANHs does match the 6.2 μm AIB band, making it a potential AIB carrier as well.

1.3 Processing PA(N)Hs in the ISM

Carbonaceous species present in the ISM did not appear out of nowhere and must have been formed through chemical and physical processes. Generally, these processes can be separated into bottom-up and top-down. The first involves the formation of molecules out of smaller ones, for instance via gas-phase reactions or reactivity in ice layers on dust grains. The latter describes smaller molecules formed out of big ones,

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[1] When a topic covers both PAHs and PANHs, they are collectively abbreviated as: PA(N)Hs.

most likely following photodissociation. This pathway is normally linked to PA(N)Hs, as those are the biggest molecular species thought to be present in the ISM.

1.3.1 Formation of PA(N)Hs in space

PA(N)Hs are thought to have their origin in carbon-rich asymptotic giant branch (AGB) stars and their outflows (Latter 1991; Johnson 2019). Unfortunately, there is limited direct evidence supporting the presence of PA(N)Hs in the outflows of carbon-rich AGB stars. Generally, these types of stars are relatively low in temperature. This diminishes the UV radiation of the star, subsequently reducing the number of UV pumped PA(N)Hs that are able to emit mid-IR photons. Therefore, (strong) mid-IR PA(N)H features are yet to be observed towards these stars. Sloan *et al.* (2007) did detect PA(N)H IR emission features in the disk around carbon-rich star HD 100764. The presence of PA(N)Hs in hotter and brighter objects in the next stage of AGB star evolution, such as planetary nebula and post-AGB carbon-rich stars, is also demonstrated (Cerrigone *et al.* 2009). The detection of PA(N)H features in the IR spectra of these objects provides indirect evidence that these molecules may have been present or form during the AGB phase.

The formation of PA(N)Hs is thought to be analogous to soot formation in combustion processes on earth (Frenklach & Feigelson 1989; Allamandola *et al.* 1989; Cherchneff *et al.* 1992). CO and acetylene (C_2H_2) primarily lock up the carbon in the outflow of carbon-rich AGB stars and since CO is highly stable, most of the PA(N)H formation will start with acetylene or an (radical) analogue. The trickiest step in the creation of PA(N)Hs is the first (benzene) ring formation. Several pathways towards the formation of benzene are proposed (Frenklach *et al.* 1984; Jursic & Zdravkovski 1995; Lindstedt & Skevis 1996; Woods *et al.* 2002; Miller & Klippenstein 2003; Zhang *et al.* 2010; Wang & Ding 2021), but the topic is still subject of debate and intensively researched. For PANHs the formation of pyridine (C_5H_5N) could very well be a first step in their creation process. However, our understanding on the formation mechanisms of pyridine is lacking and only few studies are done on the topic (Chen *et al.* 2024).

After first ring formation, the potential ring growth mechanisms become far better understood. These mechanisms include hydrogen abstraction carbon/acetylene addition (HACA), Diels-Alder reactions, hydrogen abstraction vinyl acetylene (C_4H_4) addition (HAVA), phenyl (C_6H_5) addition-dehydrocyclization (PAC), methylidyne (CH) addition-cyclization-aromatization (MACA) and reaction of the ring with radicals, such as methyl ($CH_3{}^\bullet$), the ethynyl radical ($C_2H^\bullet$), the vinyl radical ($C_2H_3{}^\bullet$) and the propargyl radical ($C_3H_3{}^\bullet$, Reizer *et al.* 2022; Kaiser & Hansen 2021, and references therein). These mechanisms have different kinetic barriers and are therefore favored under different interstellar conditions. For instance, HACA and PAC typically require high temperatures – conditions found in the circumstellar envelopes of carbon-rich AGB stars – due to their relatively high reaction barriers. Whereas HAVA and MACA mechanisms can proceed at lower temperatures, such as those found in molecular clouds and hydrocarbon rich atmospheres of planets and moons, as their reactions include lower energetic barriers or are even barrierless (Kaiser & Hansen 2021). Figure 1.8 provides an overview of several formation pathways, which fall under the HACA, HAVA, PAC, and MACA mechanisms, from the phenyl radical and toluene to PAHs containing up to six fused rings. The HACA mechanism has been experimen-

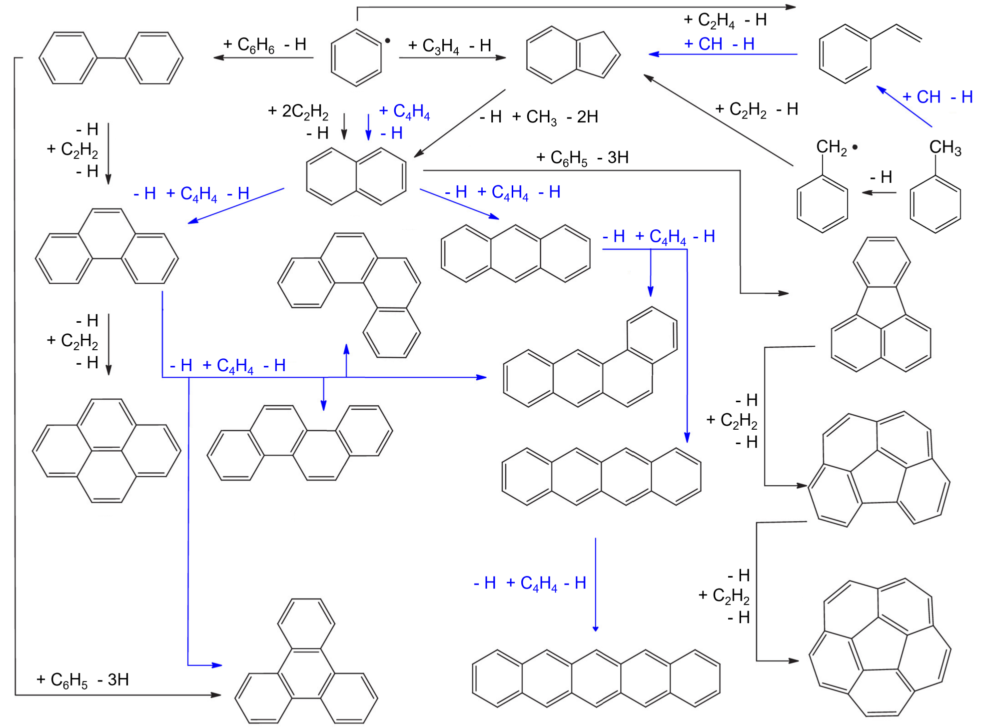

Figure 1.8: Overview of several formation pathways starting from the phenyl radical and toluene, and leading to PAHs with up to six rings. The blue pathways represent barrierless reactions. Figure adapted from Kaiser & Hansen (2021).

tally demonstrated as a potential pathway for the formation of PANHs when starting from a pyridine cation (Rap *et al.* 2022).

After formation, the PA(N)Hs are dispersed into the ISM via stellar winds (Boersma *et al.* 2006). When in the ISM, PA(N)Hs could coagulate to form dust grains and potentially become incorporated in the ices on those grains (Tielens 2008; Bouwman *et al.* 2010, 2011a,b), or they can be further processed via gas-phase reactions and/or photodissociation.

1.3.2 Photodissociation of PA(N)Hs

The PA(N)Hs in the ISM are subject to its harsh conditions, such as intense UV radiation fields. Not only can the absorption of a UV photon by a PA(N)H lead to vibrational excitation or ionization, it can also lead to photodissociation if the energy is sufficient. One common place of dissociation in the ISM is, conveniently named, a photodissociation region (PDR). These regions are mostly filled with neutral molecular and atomic hydrogen, and UV radiation is the main driver of the energy balance and chemical conditions (Wolfire *et al.* 2022). The photon energies within this regions are limited to less than 13.6 eV (the ionization potential (IP) of atomic hydrogen), as the PDR is surrounded by atomic hydrogen, which will absorb any photon with a higher

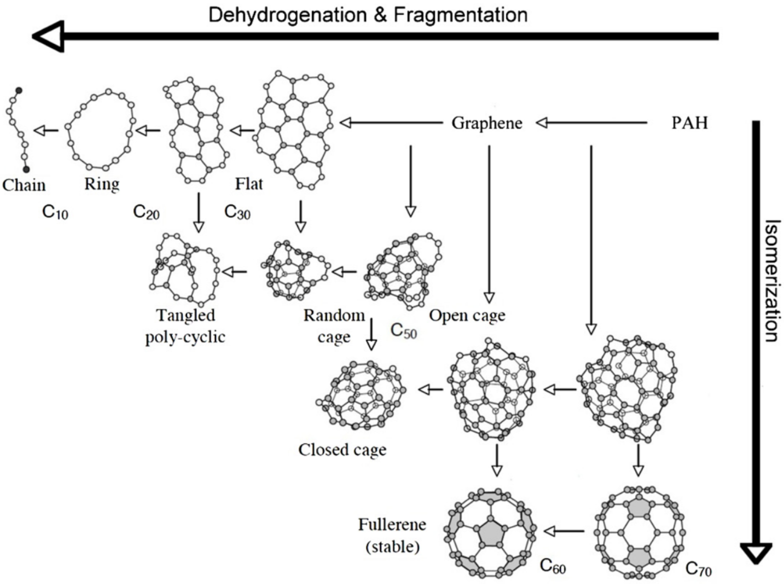

Figure 1.9: Overview of the dissociation pathways of PAHs in the ISM, showing a combination of dehydrogenation and fragmentation (right to left) and isomerization (top to bottom). Figure from Berné & Tielens (2012).

energy and ionize. These HII regions can be found between any UV radiative object and a PDR. The IP of the smallest PAH, naphthalene, is about 8.15 eV, and the IP of PAHs decreases with increasing PAH size (Kuroda 1964). Therefore, PAHs – and likely PANHs as well due to them being isoelectric – are mostly cations in these regions. When a UV photon is absorbed by a PA(N)H cation, it distributes the energy over its vibrational modes of freedom. Instead of IR emission however, it is also possible for the PA(N)H to reduce its energy by expelling a fragment. Due to the energy being in the many vibrational modes, several bonds can be broken, resulting in a variety of potential fragments. Experimentally it is shown that initially, only hydrogen, whether atomic and/or molecular, is lost and as energy increases fragments containing carbon are lost as well (Zhen *et al.* 2014a,b; Hrodmarsson *et al.* 2023; Panchagnula *et al.* 2020; Bouwman *et al.* 2016; Castellanos, P. *et al.* 2018; West *et al.* 2019, 2014a,b; Trinquier *et al.* 2017; Holm *et al.* 2011; Ekern *et al.* 1998). Moreover, the photodissociation fragments seem to be highly similar for PAHs of different sizes and symmetries.

Several observational studies have given evidence for the dissociation of PAHs in PDRs. For instance, small hydrocarbon chains and rings, such as C_2H, C_3H_2, C_3H^+ and C_4H, are detected towards the PDR at the edge of the Horse Head nebula, B 33 (Pety *et al.* 2005; Guzmán *et al.* 2015; Cuadrado *et al.* 2015). Specifically, these molecules were detected in regions with high UV photon flux and the available bottom-up models failed to replicate their presence. This suggests that these small hydrocarbons could originate from the dissociation of PAHs. Furthermore, in interstellar object NGC 7023, the abundance of the C_{60} fullerenes gradually increases the closer one observes towards the nearby UV radiating star of the PDR, at the expense of the PAH abundance. This is highly indicative of PAHs photodissociation, eventually resulting in fullerenes (Berné & Tielens 2012). Fig. 1.9 shows a summary of the expected dissociation fragments of PAHs in the ISM and their potential pathways (Berné & Tielens 2012). This shows a top-down chemistry approach for both fullerenes and carbon chains and rings, both of which are already detected in the ISM (McGuire 2022), although the link between PA(N)H dissociation and carbon chains and rings is yet to be clearly demonstrated.

The dissociation of PA(N)Hs is generally accepted to be the end of their lifecycle (Andrews *et al.* 2015; Peeters *et al.* 2017), and eventually all PA(N)Hs no matter their size will dissociate to photostable fragments. Possibly, albeit being photostable, some of these fragments can be fed into the start of a bottom-up pathway and react with nearby gas-phase molecules. Potentially, this can result in the reaction with hetero atoms such as nitrogen and oxygen, forming more complex species such as amino acids, a group of molecules known to be essential to life.

1.4 Thesis contents

Although various molecules have already been discovered in space and many endeavors are done, and planned, to determine their origins and hierarchy in the cosmic chemical evolution, we are still at the early stages of understanding the chemical inventory and progression of space. Observations have shown PAHs, and their analogues, to be key components within the molecular universe, and especially the containment of hetero atoms, in particular nitrogen, in PAHs is gaining considerable attention. This thesis will focus on the photoprocessing of PAHs, their nitrogen containing analogues and the reactivity of the resulting dissociation fragments, with the ultimate goal to increase our insight and knowledge on the chemical role that PA(N)Hs play in space, especially the interstellar medium.

The research done in this thesis emerges from the utilization of different experimental systems, a range of wavelengths probing the photoprocessing of PA(N)Hs and various computational simulations for comparison to the experimental data. **Chapter 2** starts off by describing the i^2PEPICO endstation at the Paul Scherrer Institute (PSI), which is a system that allows for the measurement of threshold photoelectron spectra and the dissociative photoionization of gas-phase species with tuneable VUV synchrotron radiation from the Swiss Light Source (SLS). Next, a description is given on the inner workings of Paul-type quadrupole ion trap (QIT) mass spectrometers, as this type of mass spectrometer is mainly used for experiments throughout this thesis, albeit at different wavelengths. The QIT user station of Free-Electron Lasers for Infrared eXperiments (FELIX) lab can used to study the mid-IR spectra of ions by utilizing the InfraRed Multiple Photon Dissociation (IRMPD) technique, of which a description will be given. The final experimental setup that is described is the Instrument for the Photoprocessing of PAHs (i-PoP), an in-house QIT in the Laboratory for Astrophysics (LfA) in Leiden that allows for the study of the photodissociation pathways of ionic PA(N)Hs. Lastly, the computational methods used to calculate simulations is presented.

Chapter 3 presents the threshold photoelectron spectrum and the dissociative photoionization of benzonitrile (C_6H_5CN), a molecule already detected in the ISM and suggested to be a precursor species in the bottom-up formation of PA(N)Hs in the ISM, acquired using the i^2PEPICO endstation and SLS VUV beamline at PSI. From these experiments in combination with Franck-Condon and DFT calculations the adiabatic ionization energies of the ground and two excited states of benzonitrile are determined and seven lowest energy dissociative photoionization channels of benzonitrile are found, of which three proceed without a reverse barrier. The pathways and resulting (ionic) fragments are put into astrochemical context and association reactions of benzonitrile$^{\bullet+}$ are suggested by traversing the pathways without a reverse barrier in the opposite direction.

PANHs are suggested to be potential carriers of the AIBs. However, experimental IR data on PANHs is limited, and studies addressing nitrogen-bearing PAHs often focus on species with a single nitrogen atom in their aromatic structure. In order to expand on the spectroscopic investigation of PANHs, **CHAPTER 4** presents the gas-phase mid-IR spectra, measured on the QIT user station at FELIX, of 1,5,9-triazacoronene$^{\bullet+}$ (**TAC**$^{\bullet+}$, $C_{21}H_9N_3{}^{\bullet+}$), a threefold nitrogenated congener of coronene$^{\bullet+}$ ($C_{24}H_{12}{}^{\bullet+}$), its protonated derivative **TACH**$^+$ ($C_{21}H_{10}N_3{}^+$) and the product that forms when water adds to dehydrogenated **TAC**$^{\bullet+}$ **[TAC−H+H$_2$O]**$^+$ ($C_{21}H_{10}N_3O^+$). The mid-IR spectra are compared to vibrational modes calculated at the B3LYP/6-311++G(d,p) level a theory and a possible geometry for **[TAC−H+H$_2$O]**$^+$ is presented. The mid-IR spectra of **TAC**$^{\bullet+}$ and coronene$^{\bullet+}$ are compared and deemed remarkably similar. It is shown, by putting the mid-IR spectra of **TAC**$^{\bullet+}$ and **TACH**$^+$ into astronomical context, that **TAC**$^{\bullet+}$ and **TACH**$^+$ could both be potential AIB carriers.

As **CHAPTER 4** provides experimental evidence for the presence of PANHs in the ISM, it becomes vital to know how PANHs are further photoprocessed and if that is any different compared to pure carbon PAHs. **CHAPTER 5** continues the investigation of **TAC**$^{\bullet+}$ by presenting its photodissociation fragments after 630 nm irradiation using the i-PoP system. Fragmentation of **TAC**$^{\bullet+}$ is initiated by up to three HCN losses often in combination with H- or H_2 losses. The resulting (low mass) fragments are similar to coronene$^{\bullet+}$, although nitrogen atom inclusion in the **TAC**$^{\bullet+}$ photodissociation fragments is also observed. This links PANHs, through top-down formation, to (di)cyanopolyynes, which are detected species in the ISM. The potential of (di)cyanopolyynes to be suitable tracers of the degree of nitrogen incorporation in interstellar PAHs is suggested.

CHAPTER 6 proceeds with the photoprocessing of PA(N)Hs by presenting the reactivity of coronene$^{\bullet+}$ dissociation fragments with water. To study this, a resonant ejection technique is revived from the past and applied to i-PoP in order to find the chemical link between reactants and reaction products. Several fragments are found to react with water and some reaction products stabilized by the loss of atomic hydrogen or CO. Differences in reactivity are explained by the geometry (cyclic vs. linear) of the reactants. The reactivity of the coronene$^{\bullet+}$ dissociation fragments, which are similar for many other PA(N)Hs, highlights the important role that PA(N)Hs, their analogues and dissociation fragments play in the chemical evolution of the ISM.

Finally, **CHAPTER 7** presents the infrared pre-dissociation (IRPD) spectrum of doubly dehydrogenated naphthalene radical cations ($C_{10}H_6{}^{\bullet+}$), measured using the cryogenic 22-pole ion trap system FELion at FELIX. By comparing the experimental IRPD spectrum with computed anharmonic IR spectra of various isomers, nine isomers candidates were identified that match a substantial part of the experimental spectrum. These isomers fall into four distinct molecular groups: ethynylpentalenes, tri-cyclics, azulenes and benzofulvene(s). However, no single isomer could be conclusively assigned to the experimental spectrum. Notably, all identified isomers contain at least one five-membered carbon ring, indicating that H_2 loss from naphthalene radical cations can lead to a variety of different isomers in unique molecular groups. Moreover, this H_2 loss channel could be a potential mechanism for the top-down formation of ions containing five-membered carbon rings.

1.5 Future perspectives

The James Webb Space Telescope (JWST) provides unprecedented sensitivity and resolution in the infrared spectrum, allowing for detailed studies of AIBs. Chown *et al.* (2024) have already presented beautiful IR spectra from JWST and, moreover, have shown the details and subtleties captured in the spectra. These advances allow for improved characterization of band profile shapes and their sub-components, thus facilitating a better way of PAH identification, e.g. determining the presence of methyl groups, heteroatom substitution and (de)hydrogenation. Such capabilities substantially improve the ability to probe the chemical diversity of the ISM. However, it is important to acknowledge the difficulties in achieving individual PA(N)H identifications based on IR observations from the ISM. The diversity and overlapping spectral features of potential carriers means that definitive identification is currently far from reach, or perhaps even impossible. This emphasizes the need for complementary experimental and computational studies and further improvements in instrumentation and theoretical modeling.

With the recent detections of "PAHs" in TMC-1 it becomes inevitable that more detections will follow soon. As our observational capabilities advance, particularly with instruments like JWST and advanced radio telescopes, it is likely that the size and complexity of the identified PA(N)Hs will increase, potentially uncovering larger and more diverse molecular species. These detections are not only crucial for elucidating the chemical role of PA(N)Hs in the ISM, but they also provide compelling insights into the origin and evolutionary pathways of these molecules.

This thesis and other works (Hudgins *et al.* 2005; Ricca *et al.* 2021; Alvaro Galué *et al.* 2010) show that the inclusion of hetero atoms in PAHs should not be omitted in the study of IR emission features. Besides endo-PANHs and protonated exo-PANHs being excellent candidates for the 6.2 μm feature, therefore enforcing their presence in the ISM, regular exo-PANHs have similar IR spectra to pure PAHs and, furthermore, their dissociation provides a well defined link between them and already detected molecules. To improve our ability to place PANHs in the chemical chains of the ISM, more experimental and computational studies should be done on these intriguing species. IRMPD studies, for instance, can provide details about unique spectral fingerprints of PANHs that were previously unknown. This may enable determination of PAH nitrogenation towards an interstellar object from an IR spectrum alone.

The reactivity of pure carbon chains has been studied in the past (McElvany *et al.* 1987; McElvany 1988; Parent & McElvany 1989; Raksit & Bohme 1983), but never directly linked to PAHs and their dissociation products. In this thesis it is shown that the dissociation of PAHs is not the end of their story, as their fragments are highly reactive with water. **CHAPTER 5** shows a high reactivity of $\mathbf{TAC}^{\bullet +}$ with water, but also briefly touches on the reactivity with C_2H_2. This potentially indicates that PANH and PAH fragments can react with any small molecule in the vicinity. This broadens the chemical role of PA(N)Hs in the ISM, as they now become suppliers for molecules partaking in bottom-up formation. The i-PoP system has already proven itself in its capabilities to find reactions of PAH fragments with water. The next logical step would be to study various reactions of the fragments with, for example, C_2H_2, CO and HCN, which can be administered to the ion trap without major modifications to the system. With the study of these reactions, and of course the reaction products as well, the overall chemical knowledge of the ISM will be expanded. And, with the addition of astronomical observations, could lead to accurate modeling of PA(N)H chemistry in the ISM.