Chemistry and photophysics of polycyclic aromatic hydrocarbons in the interstellar medium
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Astronomy is the study of stars, but in this day and age astronomy deals with a far wider selection of celestial objects than stars alone. For example, about 15% of the visible mass of the Milky Way is made up of interstellar gas instead of stars. This gas is part of the interstellar medium (ISM) and it is very diverse in both temperature and density. Temperatures can be as low as 10 K or as high as $10^7$ K. The number density shows an even greater variety, ranging from $10^{-4}$ atoms cm$^{-3}$ to $10^6$ atoms cm$^{-3}$, a difference of 10 orders of magnitude (Tielens, 2005; Ferrière, 2001).

These different conditions correspond to different environments, and these are recognized as different phases. Generally, the ISM is divided into three phases, the Cold Neutral Medium (CNM), the Warm Neutral and Ionized Medium (WNM/WIM), and the Hot Ionized Medium (HIM) (Tielens, 2005, Table 1.1). In the CNM, gas temperatures are typically less than 100 K and number densities hover around $10^2 - 10^4$ atoms cm$^{-3}$. The HIM is the exact opposite, with temperatures up to $10^7$ K and number densities as low as $10^{-4}$ atoms cm$^{-3}$. The Warm Medium falls somewhere in between, with temperatures of several 1000 K and number densities in the range of 0.2 - 0.5 atoms cm$^{-3}$.

In addition to these phases there are molecular clouds, which are cold ($T = 10 - 20$ K), dense clouds of gas and dust from which stars are born. The number densities of these clouds can be as high as $10^6$ atoms cm$^{-3}$, or approximately the same order of magnitude as the best man-made vacuum, which is more than 15 orders of magnitude lower than the atmospheric pressure.
Most of this interstellar gas is in the form of hydrogen atoms, by mass approximately 75% (Spitzer, 1978). Consisting of just a proton and an electron, it is the simplest atom possible, and it is widely observed through its 21-cm line resulting from hyperfine transitions within its ground state (Oort et al., 1958). It is the fusion of these hydrogen atoms into bigger ones that provides the nuclear energy for the light emitted by the stars. Outside our Galaxy, hydrogen is also the main constituent of intergalactic gas.

Two hydrogen atoms can also recombine to form the smallest possible molecule: H\textsubscript{2}. The importance of this molecule can hardly be overstated as it plays a key role in a wide variety of processes. For example, cooling agents are an important contributor to star formation, as they allow the gas in a cloud to cool down and collapse further into a star. In the present days, these cooling agents consist of atoms heavier than hydrogen and helium. For example, an important cooling agent for star formation is CO, consisting of a carbon atom and an oxygen atom (Larson, 2003). However, in the early universe these cooling agents were unavailable, with the exception of H\textsubscript{2} which can radiate energy away through a quadrupole rotational transition. The presence of H\textsubscript{2} is thus an important factor in the formation of the very first stars in the early universe, when other cooling agents had not been produced yet (Glover, 2005).

Moreover, in the present-day universe, the formation of H\textsubscript{2} opens a vast world of chemical pathways through reactions with other elements. Reactions with oxygen and carbon atoms lead to the formation of water, CO, CO\textsubscript{2} and more complex molecules (Watson, 1973). Incorporating nitrogen atoms into the chemical network will lead to the formation of amino acids, which may ultimately lead to the formation of life (Bernstein et al., 2002; Elsila et al., 2007). It will thus come as no surprise that the formation of H\textsubscript{2} in space has earned a copious amount of studies in both the past and present.

### 1.1 The Formation of H\textsubscript{2} in Space

Despite the abundance of hydrogen atoms, it is very difficult to form molecular hydrogen in interstellar space. The collision between two H atoms will only lead to the formation of H\textsubscript{2} if one of the H atoms is in an excited electronic state (Latter & Black, 1991). This is not very likely to happen, as the energy difference between the ground state and the first excited electronic state is 10.2 eV, which corresponds to an excitation
1.1. The Formation of $H_2$ in Space

temperature of $1.2 \cdot 10^5$ K. This is too large to allow a sufficiently large population of electronically excited hydrogen atoms to exist in most of the ISM. If both $H$ atoms are in the electronic ground state a third body is necessary to dissipate some of the reaction energy, but at the typical number densities and temperatures of the ISM ($n_H < 10^6$ cm$^{-3}$, $T < 100$ K) three-body collisions are too rare to support the observed rates of $H_2$ formation (Palla et al., 1983).

There are several gas phase routes available that can alleviate this problem, as described in equations (1.1) and (1.2). The first one uses an electron as a third body for the carrying away of excess energy, whereas in pathway (1.2) a proton is used (Glover, 2003):

\[
\text{H} + e^- \rightarrow \text{H}^- + h\nu; \quad (1.1a)
\]

\[
\text{H}^- + \text{H} \rightarrow \text{H}_2 + e^-; \quad (1.1b)
\]

\[
\text{H}^+ + \text{H} \rightarrow \text{H}_2^+ + h\nu; \quad (1.2a)
\]

\[
\text{H}_2^+ + \text{H} \rightarrow \text{H}_2 + \text{H}^+. \quad (1.2b)
\]

However, these gas-phase routes to molecular hydrogen are very slow, and cannot reproduce the rates of $H_2$ formation that are observed in the ISM. The typical rate of $H_2$ formation derived from observations is found to be approximately $3 \cdot 10^{-17}$ cm$^{-3}$ s$^{-1}$ (Jura, 1974), whereas the rate of $H_2$ formation by electron catalysis falls at least one order of magnitude short under interstellar conditions (Launay et al., 1991; Cazaux & Spaans, 2004). A solution for this difference between predicted and observed rates is found in the presence of dust in our universe (Gould & Salpeter, 1963). Recent calculations by Cazaux & Spaans (2009) find that even at metallicities as low as $10^{-3}$ of the solar metallicity, $H_2$ formation on dust grains dominates the other formation mechanisms by at least an order of magnitude.

This dust is visible as the dark dust lanes in our own Galaxy and other galaxies. Consisting mainly of silicates or amorphous carbon, these dust grains are typically between 0.005 and 0.25 μm in diameter (Mathis et al., 1977; Weingartner & Draine, 2001a). Atoms and molecules stuck to the grain surface are much more likely to interact with one another than if they were in the gas phase, making dust grains ideal catalysts for all sorts of chemical reactions. Moreover, the dust grain can act as a third
Chapter 1. Introduction

body that dissipates some of the reaction energy. As such, dust grains are considered to be the main driver behind the formation of H\textsubscript{2} in the ISM (Gould & Salpeter, 1963; Cazaux & Tielens, 2002).

To enable dust grain catalysis, H atoms must be able to stick to the grain surface, which is possible through either a Van der Waals interaction or a chemical bond. Binding through the Van der Waals interaction is called physisorption and this results in a relatively weak bond (Pirronello et al., 1997, 1999; Perry & Price, 2003; Bergeron et al., 2008). As a result, physisorbed H atoms can move around on the grain surface at low temperatures. The bonding through a chemical (covalent) bond is called chemisorption and is much stronger than physisorption, and chemisorbed H atoms therefore cannot easily move around on the grain surface (Zecho et al., 2002; Hornekær et al., 2006; Mennella, 2006; Rougeau et al., 2006; Bachellerie et al., 2007).

For the catalysis of H\textsubscript{2} formation by dust grains there are two possible mechanisms. In the Langmuir-Hinshelwood (LH) mechanism, a physisorbed H atom is moving around on the grain surface and encounters a second H atom that is either physisorbed or chemisorbed. These two H atoms can then recombine and form a hydrogen molecule, as is shown in the left panel of Figure 1.1. Part of the reaction energy can be converted into kinetic energy, launching 60 - 70% of the newly formed molecules into the gas phase (Katz et al., 1999). The rest of the energy is partly used to excite the H\textsubscript{2} molecule and partly absorbed by the dust grain, which prevents the molecule from being dissociated (Morisset et al., 2003, 2004).

In the Eley-Rideal (ER) mechanism only one H atom is adsorbed onto the dust grain surface, through either chemisorption or physisorption. A second H atom arrives directly from the gas phase and interacts with the first H atom, forming a hydrogen molecule, as depicted in the right panel of Figure 1.1.

The reaction mechanisms mentioned above require H atoms to be adsorbed onto the dust grain surface. Chemisorbed atoms have a high binding energy with the surface and only evaporate when the dust grain temperature exceeds more than a few 100 K, but physisorbed H atoms typically evaporate into the gas phase when the grain temperature exceeds 20 K (Hollenbach & Salpeter, 1971; Cazaux & Tielens, 2004; Cazaux & Spaans, 2002). If the dust grain temperature is too high for the physisorption of H atoms, only the chemisorbed H atoms remain on the dust grain surface. This renders the formation of H\textsubscript{2} through Langmuir-Hinshelwood
impossible, but the Eley-Rideal mechanism remains feasible, though only through chemisorbed H atoms. The capacity of dust grains to form H$_2$ is then reduced by more than an order of magnitude (Habart et al., 2004; Cazaux & Spaans, 2009).

Examples of astronomical environments with dust grains that are too warm for H$_2$ formation are photodissociation regions (PDRs), where a nearby massive star produces enough radiation that its photons dominate the chemical and physical processes (Tielens & Hollenbach, 1985; Hollenbach et al., 1991; Hollenbach & Tielens, 1999; Meijerink & Spaans, 2005; Spaans & Meijerink, 2005). These regions consist of ionized hydrogen gas at the outside closest to the star. As the radiation field is attenuated with increasing column density, there is a transition from ionized to neutral hydrogen gas around a column density of $N$(H) = 10$^{20}$ cm$^{-2}$. At even higher column densities ($N$(H) > 10$^{21}$ cm$^{-2}$) there is a transition from atomic to molecular species, as is shown in Figure 1.2. In these environments the temperatures are high enough ($T_{dust} = 30 - 70$ K (Hollenbach & Tielens, 1999)) to render the formation of H$_2$ through dust grain catalysis insignificant.

Despite the hostile environment, observations show that H$_2$ formation is still happening in these regions, with formation rates as high as 10$^{-16}$ cm$^{-3}$ s$^{-1}$, similar to much colder environments (Habart et al., 2004; Allers et al., 2005). This cannot be explained by dust grain catalysis alone and there are several hypotheses to facilitate the formation of H$_2$ in PDRs.

One of the mechanisms proposed is through the photolysis of hydrogenated amorphous carbons (HACs). These are dust grains consisting of amorphous carbons, and they are estimated to lock up anywhere between
2.6% and 35% of the cosmic carbon abundance (Sandford et al., 1991). Being constantly exposed to hydrogen atoms in the ISM, the amorphous carbon will be hydrogenated and form HACs. Photolysis of these HACs by exposure to UV photons leads to the formation of H$_2$ at a rate sufficient to reproduce the interstellar rates of H$_2$ formation (Alata et al., 2014; Martín-Doménech et al., 2016).

However, in 2000 Joblin et al. (2000) find a correlation between the rate of H$_2$ formation and the intensity of certain infrared emission bands in PDRs. These emission bands are linked to the presence of polycyclic aromatic hydrocarbons (PAHs), large carbon molecules that consist of multiple fused benzene rings.

Because of this correlation, and the inability of dust grains to facilitate the observed rates of H$_2$ formation, PAHs have been proposed as a catalyst for H$_2$ formation. Although the exact mechanism behind the catalysis of H$_2$ formation by PAHs has been unclear for a long time, their anticipated catalysing properties have been included in different theoretical models for PDRs in different ways. Some models consider PAHs as the lower end of the dust grain size distribution (Le Petit et al., 2006), whereas other models
explicitly incorporate chemical reactions involving PAHs (Le Page et al., 2009; Montillaud et al., 2013). For now these explicit chemical networks unfortunately do not do justice to the complex chemistry that PAHs can exhibit. For example, a single, generic, PAH molecule is used in the network, whereas in astrophysical environments there is a large variety in PAH sizes and shapes (Allamandola et al., 1999). Moreover, these models use only a few hydrogenation states for the PAHs, where there are much more states possible. To be able to fully understand the PAH-catalyzed formation mechanism, a more thorough understanding of the physics and chemistry of PAHs is necessary.

### 1.2 Polycyclic Aromatic Hydrocarbons and Their Appearance in the ISM

Interstellar gas clouds are known to exhibit multiple infrared emission features, with the major features located at 3.3, 6.2, 7.7, 8.6, 11.2, 12.7, and 16.4 μm (see Figure 1.3). These emission features take the form of bands, and their central wavelengths are consistent among different observed celestial sources. The origin of these emission bands remained unknown for a long time, and therefore these features have long been known as the Unidentified Infrared Bands.

Duley & Williams (1981) observe that the photon energies of these bands correspond to the energy difference between vibrational states of aromatic C-C and C-H bonds. Allamandola et al. (1985) compare the Raman spectrum of PAH-rich soot from car exhaust fumes with an infrared emission spectrum from the Orion bar in the 5 to 10 μm region. A close resemblance is found between the infrared spectra of soot particles and the interstellar emission features. Since the aromatic compounds in soot are mainly PAHs and related molecules, PAHs were proposed to be the origin of these features, which are now known as the Aromatic Infrared Bands (AIBs).

The presence of PAHs and the astrophysical applications are comprehensively discussed in Allamandola et al. (1989) and Tielens (2008). With a diameter of a few Angström, PAHs can be considered to be either large molecules or very small dust grains. As the small-size tail of the dust grain size distribution, PAHs claim approximately 20% of the cosmic carbon abundance (Joblin et al., 1992) and they contribute up to half of the available dust grain surface area (Weingartner & Draine, 2001a,b).
1.2.1 Molecular structure of PAHs

PAHs are large carbon-based molecules where the carbon atoms are arranged in a honeycomb-like hexagonal pattern. These molecules are quite ubiquitous on Earth, where they are a by-product of combustion processes (soot particles), or serve industrial and household applications.

For example, naphthalene ($C_{10}H_8$) is the smallest PAH with merely two aromatic rings (see left panel of Fig. 1.4), but it has known widespread use as an insecticide in mothballs and is still widely used as a precursor to other chemical compounds. The largest conceivable arrangement of benzene rings is graphene, a monolayer of the graphite known from the lead in pencils. Although technically not considered to be a PAH, it has been studied as the material of the future due to its remarkable strength and electronic properties (Allen et al., 2009, and references therein).

The properties of a PAH molecule are rooted in its elementary building blocks, the carbon atom. A single carbon atom contains six electrons, which are distributed over several atomic orbitals, which are in increasing orbital energy: 1s, 2s, and 2p. The electronic configuration of a single carbon atom is written as $1s^22s^22p^2$, where the superscripts refer to the number of electrons in each electronic subshell. The ground term of a carbon atom is a triplet $P$, i.e. $^3P$, and is determined by the two electrons in the partially filled 2p subshell, which can contain up to 6 electrons.

In molecules, a carbon atom is not isolated, and its electronic structure may be slightly adjusted to achieve optimal bonding. This adjustment of the electronic structure is known as hybridization. In carbon hybridization one of the 2s electrons is promoted to a 2p orbital. In this way in principle...
1.2. PAHs in the ISM

Figure 1.5 – False-color image of Barnard 30, close to Orion’s head, taken by NASA’s Spitzer Space Telescope. Blue denotes the 4.5 \( \mu \text{m} \) emission, 8.0 \( \mu \text{m} \) is coloured green, and the 24 \( \mu \text{m} \) emission is red. The green 8.0 \( \mu \text{m} \) emission comes from PAHs. Figure courtesy of NASA.

![Figure 1.5](image)

Figure 1.6 – The hybridization of one 2s orbital and three 2p orbitals leads to the formation of four different \( \text{sp}^3 \) atomic orbitals, oriented in a tetrahedral shape. Figure courtesy of UC Davis.

![Figure 1.6](image)

four unpaired electrons are available to form molecular bonds. Linear combinations of the four 2s, 2p\( _x \), 2p\( _y \), and 2p\( _z \) orbitals form the final carbon hybrid orbitals that determine carbon bonding in molecules.

For example, in the lightest carbon-bearing molecule, methane (CH\(_4\)), the 2s and all three 2p orbitals hybridize into four so-called \( \text{sp}^3 \) orbitals. These \( \text{sp}^3 \) orbitals are oriented in a tetrahedral shape at a 109.5° angle with respect to each other, as is shown in Figure 1.6. Each orbital can then overlap with an orbital from one of the H atoms to form a \( \sigma \) bond. This is the general shape every carbon atom with four single bonds takes.

However, other hybridizations are also possible, such as the \( \text{sp}^2 \) hybridization, where two 2p orbitals combine with the 2s orbital. The resulting three \( \text{sp}^2 \) orbitals lie in a plane and at a 120° angle with respect
The hybridization of one 2s orbital and two 2p orbitals leads to the formation of three different \( sp^2 \) atomic orbitals, oriented in a triangular plane. The remaining p-orbital (not shown) protrudes perpendicularly from this triangular plane. Figure courtesy of UC Davis.

The left panel shows how two s-orbitals form a \( \sigma \) bond, the right panel shows a \( \pi \) bond. Figure courtesy of UC Davis.

to each other, as shown in Figure 1.7. The remaining 2p orbital protrudes perpendicularly from this plane. If two \( sp^2 \) hybridized carbon atoms lie next to each other, two of their \( sp^2 \) orbitals will overlap to form a \( \sigma \) bond, as is shown in Figure 1.8. Moreover, their out-of-plane 2p orbitals will overlap as well and form an additional \( \pi \) bond, which reinforces the bonding between the two atoms. The combination of these two bonds is called a double carbon bond.

It is also possible to create large carbonaceous molecular networks out of \( sp^2 \) carbon atoms. The p orbitals of adjacent \( sp^2 \) atoms overlap, creating a conjugated \( \pi \) system and electrons can be delocalized throughout the entire system. Following Hückel’s rule, a conjugated \( \pi \) system is extra stable if it is ring-shaped and it consists of \( 4n + 2 \) carbon atoms. In that case, the ring is referred to as an aromatic ring.

Consisting of six \( sp^2 \) carbon atoms (\( n = 1 \)), the benzene ring is the smallest possible aromatic ring. Its hexagonal shape allows for the easy fusion of multiple rings into a single honeycomb-shaped molecule (see Figure 1.4), called a polycyclic aromatic hydrocarbon, or PAH in short. These fused benzene rings constitute a large delocalized \( \pi \) system, that stabilizes the planar shape of the molecule.
Due to their aromaticity, PAHs are very stable and can therefore withstand the constant exposure to UV radiation in interstellar space. This is one of the reasons why they are the prime candidates as carriers of the Aromatic Infrared Bands.

1.2.2 Observational Evidence for PAHs in the ISM

Before the AIBs can be definitely assigned to PAHs, there has to be a unique identification, i.e. a certain emission feature that corresponds uniquely to a single molecule that is part of the PAH family. This has proven to be rather difficult, and the problem lies in the band nature of the emission combined with the large similarity between PAHs. A single PAH does typically not emit in lines, but in broader bands. If this PAH molecule is altered slightly, e.g. by rearranging the aromatic rings or adding an extra benzene ring, the peak wavelength of the emission bands will change slightly in their wavelength. Therefore, different PAHs will have a lot of overlap in their IR emission spectra. Given the fact that PAHs interact frequently with their surroundings, an astronomical source of IR emission will most likely contain a population of PAHs instead of a collection of identical PAHs, and thus it will be almost impossible to identify a single PAH in an interstellar spectrum.

However, closely related to PAHs is the C$_{60}$ molecule, also known as buckminsterfullerene, or more colloquially, the bucky ball. It consists of multiple fused 5- and 6-membered rings, arranged in such a way that they form a sphere, not unlike a football, as is shown in Figure 1.9. This molecule has been discovered in close conjunction with PAHs and its formation process has been linked to the presence of PAHs as well (Zhen et al., 2015, and references therein). C$_{60}$ exhibits a few unique infrared emission features, and in 2010 this molecule has been identified in interstellar spectra of a young planetary nebula (Cami et al., 2010). Moreover, the C$_{60}^+$ cation has been confirmed as the carrier of two diffuse interstellar bands (Campbell et al., 2015).

As mentioned above, observations do not provide direct proof for the existence of PAHs in the ISM. There are no direct detections, but there is a lot of circumstantial evidence.

First, the building blocks of PAHs are carbon and hydrogen atoms. Hydrogen is the most abundant element in the universe, but carbon is a lot rarer with approximately 300 carbon atoms for every million hydrogen atoms (Snow & Witt, 1995). Despite this low number, it is the fourth
most abundant element after hydrogen, helium, and oxygen. The large carbon abundance provides a strong argument for the PAH hypothesis, as an omnipresent unknown emitter is more likely to consist of abundant species than of something much rarer.

Second, the fact that we observe the AIBs as bands instead of lines lends credibility to a large population of similar but not identical emitters. The infrared emission that we observe is due to a change in the vibrational state of the molecule emitting the radiation. The wavelength of this radiation depends on the energy levels of the vibrational modes in which the transition is happening. If the energy difference between the vibrational states varies slightly due to a chemical modification, the emitted radiation will also have a slightly different wavelength. In this manner, a population of PAHs, all similar but different from each other, produces emission bands instead of emission lines. Unfortunately, these bands make it difficult to attribute emission features to a single PAH molecule, as stated above.

Third, the aromatic backbone of a PAH provides an inherent stability that makes it difficult to destroy the carbon skeleton of a PAH. The aromatic bonds between the carbon atoms are very strong compared to other covalent chemical bonds, so more energy is required to break these bonds. Moreover, a PAH contains a large number of atoms and thus has a large number of vibrational degrees of freedom. The energy deposited in a molecule by the absorption of a photon is redistributed over all these

Figure 1.9 – The image on the left show the buckminsterfullerene molecule, and on the right it is compared with a football.
degrees of freedom. The higher the number of degrees of freedom, the lower the average energy per degree of freedom, which in turn decreases the probability of bond breaking. In the case of bond breaking, absorption of a UV or X-ray photon mainly leads to the loss of one or more H atoms, leaving the carbon skeleton intact (Allain et al., 1996a; Reitsma et al., 2015). The interaction with energetic ions similar to cosmic rays can lead to the fragmentation of the PAH, but even then it is still not the most dominant process (Reitsma et al., 2012). It is this stability that makes it an ideal candidate to survive the harsh interstellar conditions, where it is constantly bombarded by intense UV radiation and cosmic rays.

Last but not least, the presence of PAHs can also be inferred from the heating budget. For example, ionization of a molecule upon photoabsorption results in the ejection of an electron with a considerable energy. This electron will subsequently thermalize with the surrounding medium, resulting in heating of the surrounding gas. The contribution of PAHs to the total heating function can be calculated and compared to observations, as is done by Bakes & Tielens (1994) who find that their calculations match the astronomical observations very well.

1.2.3 Observations

The presence of PAHs in space has been inferred from infrared spectroscopic observations. With the exception of fullerenes (see section 1.2.2), there has not been a unique identification of a single PAH. Therefore, all astronomical observations on PAHs only concern populations of PAHs.

Despite the lack of unique identifications of a PAH molecule, it is possible to derive a wealth of information from the existing observations. These observations are most commonly in the form of infrared spectra, and there are several techniques to derive useful information from these spectra.

One way to analyze the IR spectra is by comparing the relative intensity of the PAH emission features. For example, there is the 3.3 micron aromatic stretch emission band, which originates in the aromatic C-H bond at the edge of PAHs. However, an aliphatic C-H bond will emit in the 3.4 micron band (Pendleton & Allamandola, 2002). Comparing the aliphatic and aromatic emission bands, it is possible to study the amount of aromatic and aliphatic carbon. With this method, Li & Draine (2012) have determined an upper limit to the aliphatic fraction of PAHs, which is about 15%.

In addition to the relative intensities, there is more information hidden in the emission features. Both the peak wavelength, where the band emits
the most radiation, and the shape of the band give more insight in the condition of the PAHs emitting them. A study by Peeters et al. (2002) provides a good overview on the behaviour of the different emission bands between 6 and 9 $\mu$m. Another study by van Diedenhoven et al. (2004) expands on this and gives a detailed analysis of the PAH profiles between 3 and 12 $\mu$m.

A prime example is the 6.2 $\mu$m feature, of which the peak wavelength varies from source to source. This feature is due to the CC stretch vibrational transition, and its peak wavelength is influenced by the molecular size, the symmetry of the molecule, and the heterogeneity. In the limiting case of pure graphene, the CC stretch band has a peak wavelength slightly longer than 6.3 $\mu$m, whereas for smaller PAHs this band has a peak emission somewhere between 6.3 and 6.2 $\mu$m. Using this, it is possible to get a general idea about the size of the PAHs in an astronomical object.

Additionally, a PAH can contain a heteroatom, where one of the carbon atoms is replaced by a nitrogen or oxygen atom. Due to the different electronegativity and mass of these atoms, their introduction induces a strong breaking of the molecular symmetry. These changes of the molecular structure are visible as a wavelength shift of the different vibrational transitions. Calculations by Hudgins et al. (2005) show that the introduction of a nitrogen atom will lead to a shift of the 6.2 $\mu$m peak to shorter wavelengths. Their calculations also show that this effect increases with an increasing number of nitrogen substitutions.

Applying the analysis methods described above it is thus possible to get a general idea about the size and symmetry of the PAHs present, as well as the amount of heteroatoms present in the molecules. Hudgins et al. (2005) derive that approximately 1 - 2% of all cosmic nitrogen is locked up in PAHs. A study by Boersma et al. (2013) of the PDR of NGC 7023 finds that larger PAHs ($N_C > 50$) contribute to the majority of the PAH emission close to the central star, whereas this is split more evenly at 60 arcseconds away from the exciting star. Boersma et al. (2013) warn that their results may be skewed due to a lack of irregular large PAHs in the spectral database used to obtain this result.

As is shown in Allamandola et al. (1999) and Rapacioli et al. (2005), neutral PAHs and ionized PAHs have different emission spectra. The charge state has very little influence on the peak wavelengths of the emission bands, but the relative intensities change dramatically. Neutral PAHs emit a large fraction of their radiation in the 10 - 16 $\mu$m region, whereas
ionized PAHs have most of their emission in the 6 - 10 \( \mu m \) wavelength regime (Allamandola et al. 1999), as is shown in Figure 1.10. This makes it possible to extract a PAH charge distribution from the IR spectra, as is done in Rapacioli et al. (2005), Berné et al. (2009), and Boersma et al. (2013). They find that in PDRs ionized PAHs are to be found closer to the central than neutral PAHs, which can be explained by the decrease in ionizing UV radiation farther away from the star.

In addition to information about the presence of hetero atoms and the charge state, an IR spectrum also contains information regarding the edge structure of a PAH. Hydrogen atoms around the edge are classified as being part of a solo, duo, trio, or quartet configuration, as is shown in the left panel of Figure 1.11. In the case of a solo H atom, there is only a single H-bearing carbon atom without any H-bearing neighbours. For a duo configuration, there are two adjacent C atoms that both bear a hydrogen atom, whereas for a trio configuration there are three such C atoms in a row. The quartet configuration consists of four consecutive C atoms that all bear an H atom.

The C-H bending modes associated with these peripheral H atoms emit at different wavelengths (see Fig 1.11 right panel), and thus it is possible to determine the relative amount of each configuration, which provides...
Figure 1.11 – The left panel shows the different configurations of H atoms in a single PAH. Solo, duo, trio, and quartet configurations are indicated by the numbers 1, 2, 3, and 4 respectively. The right panel shows the wavelength regions where each configuration emits its radiation. These regions differ depending on the charge state of the PAH. Figure taken from Hony et al. (2001).

information about the edge structure of PAHs. A high amount of solo configurations (approximately 70%, Hony et al., 2001) is indicative of a straight edge, whereas duo and trio configurations signify the presence of corners in the molecule. Hony et al. (2001) have used the above method to study the edges of PAHs in different astronomical sources, and they find that the PAH edge structure varies from source to source on a continuous scale, where solo configurations contribute to anywhere between 40 and 70% of the total PAH edge. A high amount of solo and duo configurations is indicative of compact PAHs, whereas trio and quartet configurations are present in non-compact PAHs. Although compact PAHs have a higher photostability than non-compact ones, it has not been possible to establish an intrinsic source property that drives the variation in edge structure from Hony et al. (2001).

1.3 Atomic, Molecular, and Photonic Interactions on PAHs

Because PAHs are a good candidate to solve multiple questions in astronomy, they have been studied extensively. To better understand how PAHs are able to survive the harsh conditions of the interstellar
environment, they have been subjected to radiation in a wide range of wavelengths. Experiments involving exposure to infrared photons up to UV and even soft X-ray photons provide a good insight into how PAHs process this radiation.

Additionally, PAHs have been exposed to collisions with a wide range of atoms, ions, and molecules at various energies. These experiments do not only study the fragmentation of the PAH molecule, but also the chemical reactions involving both collision partners. We discuss the interactions between PAHs and other collision partners in section 1.3.1, and the reaction of PAHs to photons is discussed in section 1.3.2.

### 1.3.1 PAH Chemistry

PAHs have been proposed as a catalyst for the formation of $\text{H}_2$, a process which involves the PAH reacting with hydrogen atoms. As a result, the reactions of PAHs with hydrogen atoms have been studied extensively in both theory and experiment.

The theoretical calculations are mostly done using density functional theory (DFT), which is a technique with which one can calculate, among other things, molecular orbitals, electron densities and energies, and reaction barriers. Some of the earliest calculations are performed by Bauschlicher (1998) on very small systems that contain one or two aromatic rings. Developments in computing power allowed for the study of larger systems, up to and including coronene. These calculations find that hydrogen atoms can react with PAHs to form so-called superhydrogenated PAHs. In superhydrogenation, a carbon atom changes its hybridization from $\text{sp}^2$ to $\text{sp}^3$ to allow for the extra bond with an H atom. However, this change in hybridization also induces a local change in geometry, where the carbon atom moves out of the molecular plane. The stress this causes in the molecule results in an energy barrier that must be overcome to allow superhydrogenation (Rauls & Hornekær, 2008).

The calculations by Bauschlicher (1998) have also found a route to the formation of $\text{H}_2$ that involves superhydrogenated PAHs. In this Eley-Rideal-type mechanism an H atom approaches from the gas phase and interacts with one of the hydrogen atoms on a superhydrogenated site, leading to the formation of $\text{H}_2$ and restoring the carbon atom in its original aromatic configuration. The number density of PAHs with respect to the number of hydrogen nuclei is estimated at $3 \cdot 10^{-7}$ (Tielens, 2008), whereas estimates for the abundance of dust grains vary between $4 \cdot 10^{-13}$ and $2 \cdot 10^{-9}$.
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(Tielens, 2005). This difference of several orders of magnitude means that the mechanism to form H\textsubscript{2} through PAH catalysis might be very important in clouds where dust grain H\textsubscript{2} formation is not feasible.

Apart from theoretical studies, there has also been an important experimental effort at understanding PAHs and their interaction with hydrogen atoms. These laboratory studies typically concern PAHs no larger than coronene (C\textsubscript{24}H\textsubscript{12}), although recently experiments have been performed that involve hexabenzocoronene (C\textsubscript{42}H\textsubscript{18}), such as those by Zhen et al. (2015). For proper study, PAHs will have to be in the gas phase at some point during the experiment, and for larger PAHs the temperatures required for this are too high for the PAH to remain intact.

One of the first experiments to study the reactivity between PAHs and H\textsubscript{2} atoms has been done by exposing a film of a solid PAH to a beam of atomic hydrogen. The surface is then slowly heated and the evaporating molecules analyzed with a quadrupole mass spectrometer. With these experiments it is found that exposure to hydrogen atoms leads to superhydrogenation of PAHs (Thrower et al., 2012). Simultaneous analysis with IR spectroscopy finds an increase in the aliphatic C-H stretch mode along with a decrease of the aromatic C-H stretch, indicating that the PAH loses its aromaticity and has aliphatic CH\textsubscript{2} groups (Mennella et al., 2012). Additionally, Thrower et al. (2012) have exposed PAHs to deuterium instead of hydrogen atoms, and this yields results that can only be explained if the original peripheral H atoms are replaced by deuterium in the process. A reversal of this result has also been observed if the exposure to D was followed by exposure to H atoms, i.e. the peripheral D atoms were in their turn exchanged with hydrogen atoms. This points clearly in the direction of abstraction, where a gas-phase H atom reacts with the H atom from a CH\textsubscript{2} group, resulting in the formation of H\textsubscript{2}. Although the production of H\textsubscript{2} has not been directly observed, it is the most likely explanation.

1.3.2 Photoprocessing of PAHs

To understand how PAHs process the sometimes intense interstellar radiation fields, numerous experiments have exposed PAHs to photons. These studies have been done in a wide range of photon energies, but, with the exception of X-rays and cosmic rays, only photon energies lower than 13.6 eV are relevant to the ISM. A photon in this energy range can promote an electron to a higher energy state, and if the photon energy is sufficient it can even remove the electron from the molecule entirely. Both
processes lead to the deposition of energy into the molecule, but the amount of excitation energy depends on whether ionization has taken place.

Verstraete et al. (1990) have measured the ionization yield as a function of photon energy for several PAHs of different sizes. They find that especially for larger PAHs the ionization yield increases linearly from the ionization onset energy upwards and reaches unity at 10 eV above the ionization onset energy. Smaller PAHs exhibit some peaks in the ionization yield before reaching a yield of 1, but these disappear with increasing PAH size. A more recent study by Zhen et al. (2016) has also derived ionization yields for the second photoionization, where a photon removes an electron from an already ionized molecule.

Szczepanski et al. (2011) have investigated the fragmentation patterns of small PAHs after absorption of multiple infrared photons, and find that H₂ loss is the dominant fragmentation channel after IR excitation. Other studies have investigated the fragmentation of PAHs upon photoabsorption of a UV photon. Jochims et al. (1994) have exposed a variety of PAHs, ranging in size from benzene (C₆H₆) to coronene (C₂₄H₁₂) and determined appearance potentials for the the loss of one H atom, two H atoms, and a C₂H₂ group. Ekern et al. (1997) have irradiated both neutral and cationic coronene with a xenon arc lamp and find that coronene may lose H atoms all the way down to full dehydrogenation. Furthermore, there is the study by Zhen et al. (2016), where different PAHs are compared in terms of their respective ionization and fragmentation fractions upon photoabsorption through photon energies ranging from 7 to 20 eV. One of the largest PAHs currently used in a laboratory experiment is hexabenzocoronene (C₄₂H₁₈, Zhen et al., 2014). Kokkin et al. (2008) have established an optical excitation spectrum of hexabenzocoronene.

In addition to laboratory experiments there have been theoretical efforts to understand the photophysics of PAHs. Allain et al. (1996a) calculate the branching ratios for the different photoprocesses of a multitude of PAHs with photon energies between 0 and 13.6 eV. They find that for these photon energies, H loss is the dominant photodissociation mechanism, followed by H₂ loss. Loss of an acetyl group only plays a minor role. These results are corroborated by the experimental results from Ling & Lifshitz (1998), who perform time-resolved photoabsorption mass spectrometry on anthracene and phenanthrene radical cations.
1.4 Modeling of PAHs in the ISM

The presence of PAHs in the ISM, and their influence on it, warrants their incorporation into astrophysical and astrochemical models. These models entail both the influence of PAHs on their environment, and the influence of the environment on the PAH molecules.

For example, there is an interplay between the radiation field and the presence of H atoms, where the H atoms will hydrogenate a PAH, but simultaneously it is dehydrogenated by the impinging radiation field. The intensity of the radiation field and the number density of H atoms will then compete in the establishment of the dominant hydrogenation state of a PAH.

The probability of losing one or more H atoms depends on both the size and the structure of the PAH molecule. Larger PAHs have more vibrational modes to redistribute excitation energy, decreasing the probability of dissociation after excitation. Studies by Montillaud et al. (2013) and Le Page et al. (2001) have led to the general consensus that in radiation-rich environments, PAHs are dehydrogenated at the outside of these clouds. Further inside these clouds, the radiation field is extinguished enough for PAHs to remain in their regular hydrogenation state. The exact profile of how hydrogenation states vary with column density does depend on the properties of the PAH molecule, most particularly the size. A larger PAH has more modes to dissipate any excitation energy, and is therefore less likely to lose H atoms upon photoabsorption. Thus, larger PAHs will regain their regular hydrogenation state at lower column density than their smaller counterparts (Montillaud et al., 2013).

A similar mechanism applies to the ionization state of PAHs, where photoionization is competing with electron recombination (Cox & Spaans, 2006; Ruiterkamp et al., 2005). This results in an ionization balance, where part of the PAHs are ionized and others are neutral. In radiation-rich environments PAHs are typically ionized, and as the radiation field diminishes with increasing column density, the ionization balance shifts towards neutral PAH molecules. In the most shielded regions this can even lead to the formation of PAH anions.

When it comes to the influence of PAHs on the environment, there are multiple effects. First there is the spectral influence, in the way the PAHs modify the spectral signature of their environment, e.g. the AIB emission features. Second, there is the heating of the gas by PAHs, similar to how dust grains heat their environment. Electrons from photo-
ionization processes dissipate their energy into the medium, effectively heating the gas. Based on known parameters for photo-ionization and absorption, the contribution of PAHs to the total heating rate is calculated. Bakes & Tielens (1994) conclude that up to half of the total photoelectric heating is provided by species with less than 1500 C atoms, such as PAHs.

The degree of ionization of PAHs also influences the ionization balance of other species in clouds, as PAH cations can lower the electron abundance through recombination reactions. There is also the possibility of the attachment of an electron to a neutral PAH, creating a PAH anion. These PAH anions can then react with positively charged species, leading to the neutralization and possible dissociation of these species (Wakelam & Herbst, 2008).

Lastly, there is the formation of H$_2$ by PAHs. Currently it is widely accepted that PAHs catalyse the formation of H$_2$, but there is little uniformity in how this catalysis should be treated. This diversity in treatment is largely due to a lack of understanding of the exact mechanism behind the formation of H$_2$ by PAHs. Therefore, some models treat PAHs as a lower-end extension of the dust grain-size distribution, enhancing the cross section available for H$_2$ formation through dust grain catalysis. Other models treat the reactions between PAHs and H atoms in a more explicit manner, but only take into account H$_2$ formation through the catalytic abstraction of an H atom by a gas-phase H atom. Furthermore, these models are typically limited to only a few hydrogenation states, which does not reflect the diversity of PAHs present in the ISM.

1.5 Contents of this Thesis

Currently it is still unclear what the exact mechanism is for the formation of H$_2$ through PAHs in interstellar conditions. This thesis is a joint experimental and computational approach to investigate the mechanism behind this catalysis. The experiments described in chapters 3 through 5 are performed with a tandem mass spectrometer that is specifically developed to study large molecules, such as proteins and DNA strands. This setup is described in detail in chapter 2.

The first experiment in this study is the exposure of coronene cations to hydrogen atoms, which yields valuable information about the addition of H atoms to PAH cations. We find that every second addition of a hydrogen atom to a coronene cation is subject to a thermal barrier. Moreover, the
height of the first two barriers has been established from the experimental
results, as is discussed in chapter 3. Furthermore, these barriers exist up
until full hydrogenation of the molecule. From the experimental results we
also find that coronene cations with an additional 5, 11, or 17 H atoms
are more stable than other hydrogenation states. As such, these states
dominate the mass spectra. These states are referred to as magic numbers
and are discussed in chapter 4.

To study the photostability of superhydrogenated PAHs, we have
exposed coronene cations to vacuum UV (VUV) radiation, and the results
are discussed in chapter 5. Exposure to VUV photons is done for
both regularly hydrogenated coronene and superhydrogenated coronene to
investigate the differences. As a result, we find that for superhydrogenated
coronene cations there is no ionization without loss of the excess H atom.
For regular coronene cations, direct ionization dominates and loss processes
only have a minor contribution.

The outcomes of these experiments are subsequently applied in a model
of a photodissociation region (PDR), where we study the influence of PAHs
on the H₂ formation rate. In this model we implement the barriers found
in chapter 3 and we apply photodesorption of H₂ from PAH molecules as
a pathway to form molecular hydrogen. We also study the hydrogenation
state of PAHs at different depths in these PDRs. We find that within a
certain parameter space of number density and radiation field, PAHs have
a large influence on the structure of the cloud through their H₂ forming
capabilities. This H₂ formation happens mostly through photodesorption
from dehydrogenated PAHs, as is discussed in chapter 6.