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Shining Light on PAHs in Space

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Theoretical Framework

"If we have made this our task, then there is no more rational procedure than the method of trial and error — of conjecture and refutation: of boldly proposing theories; of trying our best to show that these are erroneous; and of accepting them tentatively if our critical efforts are unsuccessful."

– Karl Popper

Polycyclic aromatic hydrocarbons (PAHs) are now widely accepted to be the carriers of what were once called the Unidentified InfraRed (UIR) bands; emission bands observed in the mid-infrared spectra of a diverse type of astronomical sources subjected to stellar radiation. These molecules are thought to contain a significant amount of carbon (about 15% of the elemental carbon), which places them as the most abundant class of organic compounds in space. As such, they are an important part of the machinery that absorbs high-energy starlight and re-emits it at lower energies, contributing to the heating of the surrounding gas, and playing a crucial role in the ionization balance of interstellar clouds. Interestingly enough, these molecules have even been suggested as building blocks of life as we know it on Earth, as they can be a catalyst agent in the formation of RNA nucleobases, among other functions relevant to the development of organic matter. In this first chapter, we will set the theoretical framework of what this thesis is about. This thesis is particularly important for the research field of PAHs, as it integrates what we currently know from both, laboratory experiments and theoretical quantum calculations, and puts it all in an astronomical context. The questions we intend to answer in this thesis are the following: how much of the current knowledge we have on PAHs actually applies in the interstellar medium? What is the link between their specific molecular properties and the astrophysical conditions under which they emit? And how does this determine their role in space? Starting from how the PAH hypothesis was proposed almost simultaneously by independent scientific teams around the world, to the still pending questions in the field, we will explain where in this storyline, the research projects presented here come into play.

1.1. First is First: What are PAHs?

As their name specifies, *polycyclic aromatic hydrocarbons* (PAHs) refer to a family of planar organic molecules made out of carbon and hydrogen atoms (hence *hydrocarbons*), structured in multiple closed carbon rings (hence *polycyclic*), with the hydrogen atoms attached to the periphery, and whose main characteristic is to be extremely stable due to the ability of the electrons in the π orbitals to delocalize (hence *aromatic*; see Figure 1.1).

These molecules exist in our daily lives, as they are formed whenever and wherever carbon-based materials are burned (e.g., any combustion of fossil fuels, wooden fireplaces, even tobacco smoke). They are currently thoroughly studied in all branches of natural science, as they are considered to be extremely toxic and carcinogenic for terrestrial life. It is paradoxical then, that such dangerous compounds could be ubiquitous in space, and might have a crucial role in the evolution of our universe, and with it, of life as we know it.

In the following pages, we will first describe how their presence in space was inferred, and how the 'PAH hypothesis' was formulated (§1.2). In §1.3 to §1.5 a review will be given on what we know about interstellar PAHs, how they emit, and what PAH properties can be derived from astronomical observations. The concept of 'photodissociation regions' will be introduced (§1.4), as these are the regions where we focus our attention to, in order to study and model PAH emission. Other proposed carriers of the UIR bands will be briefly mentioned in §1.6. Sections 1.7 and 1.8 will then focus on the current state of the field regarding the subjects that are relevant for this thesis. At last, the outline of this thesis will be presented, stating the key questions that are explored in each chapter (§1.9).

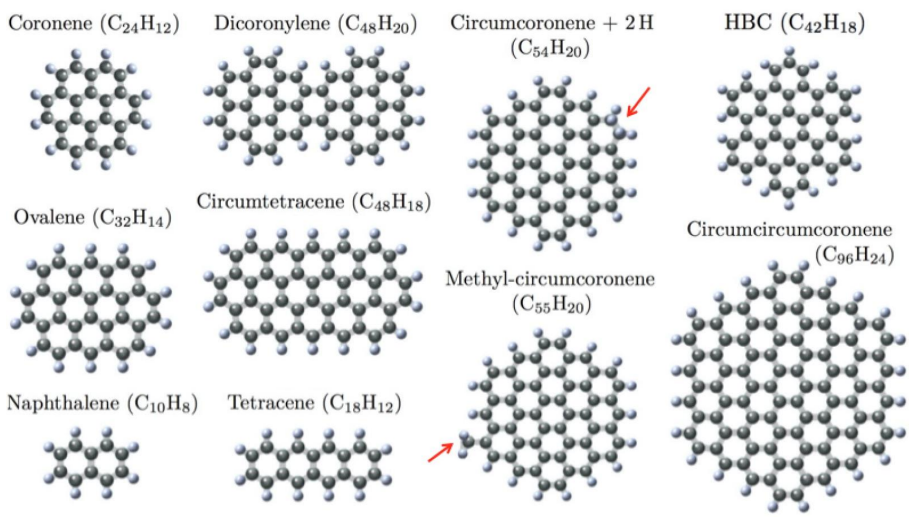

Figure 1.1: Examples of polycyclic aromatic hydrocarbons. Carbon atoms are depicted in grey, while hydrogen atoms are depicted in white. The molecule $C_{54}H_{20}$ corresponds to the circumcoronene molecule ($C_{54}H_{18}$) plus 2 additional hydrogen atoms (that lie perpendicular to the plane of the carbon core; indicated in red), turning each aromatic C-H bond into two aliphatic bonds. Such type of molecule is also referred to as a *superhydrogenated* PAH. The molecule $C_{55}H_{20}$ corresponds to circumcoronene plus a methyl group (–CH_3) attached to one of the edge C atoms (indicated in red). This type of PAH is also called a *methylated* PAH.

1.2. A Little Bit of History...

Before the 1950–1960s little was known about how astronomical objects (other than the Sun and the Moon) emitted at mid-infrared wavelengths. Even though infrared emission had been discovered at the beginning of the XIX century —thanks to the research performed by William Herschel— no major breakthroughs on the field of infrared (beyond-our-solar-system) astronomy had been achieved. It was not until the 1960s that infrared astronomy would make a huge leap into becoming what it is today. With the expected constant advent of technology, new telescopes and instruments opened a new spectral window to the rather 'cool' universe, which would naturally provide more questions than answers to the contemporary knowledge of astronomers.

The observation of astronomical objects at mid-infrared wavelengths (3–13 μm) was pioneered in the 1970s. Little by little astronomers tried to understand the interaction between dust and starlight in different environments. Of particular interest was the discovery of broad bands in the emitted spectra of interstellar material. Gillett et al. (1973) detected very strong and broad emission in the mid-infrared spectrum of two planetary nebulae, BD+30°3639 and NGC7027 (see also Gillett, Low & Stein 1967). The emission was broad but due to the instrumental spectral resolution, it was too soon to deduce whether there was a single feature, the blend of more than one feature, or just continuum emission. As time passed by, astronomers realized that a set of bands at 3.3, 6.2, 7.7, 8.6 and 11.3 μm was observed in the spectra of different planetary nebulae, H II regions, stellar objects, and even extragalactic sources (e.g., Grasdalen & Joyce 1976; Russell et al. 1977; Tokunaga & Young 1980; Aitken 1981; Sellgren 1981; Bregman et al. 1983). These bands became known as the Unidentified InfraRed (UIR) bands (see Figure 1.2).

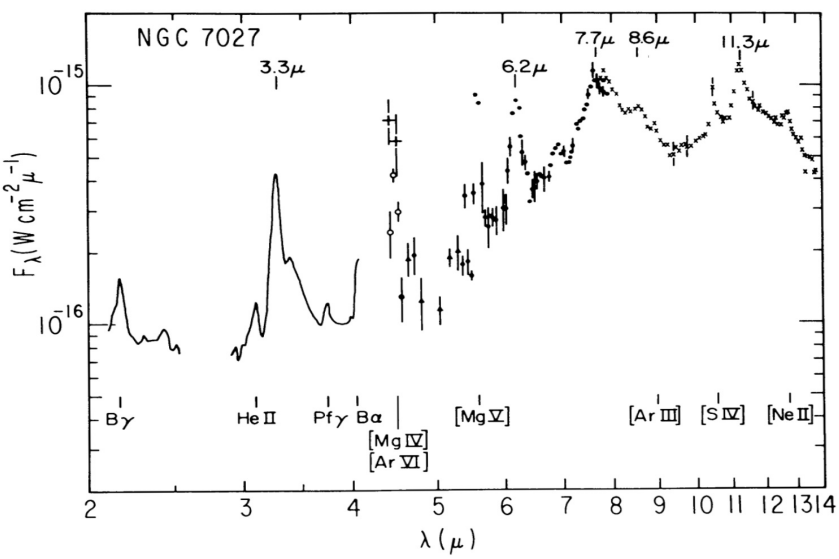

Figure 1.2: Mid-IR spectrum of the planetary nebula NGC7027. The 2–14 μm spectrum has been taken from Russell et al. (1977). The spectrum gathers spectrophotometric data taken with the Kuiper Airborne Observatory (KAO) and with the University of Minnesota 1.5 m telescope on Mount Lemmon. This spectrum became the canonical one as it showed all the UIR bands known in the late 1970s.

Soon astronomers realized that the UIR bands appeared only in regions exposed to UV radiation. It was suggested then, that the excitation mechanism had to do with the absorption of UV photons. Two mechanisms of excitation were proposed: infrared fluorescence of molecules frozen on grain mantles (Allamandola et al. 1979), and equilibrium thermal emission of small (~ 100 Å) grains (Dwek et al. 1980).

The work of Kris Sellgren in the early 80s gave further clues to this *long-standing mystery* (Sellgren et al. 1983, Sellgren 1984). By studying the 3.3 μm emission of reflection nebulae, Sellgren and coworkers inferred that the continuum emission would have to come from dust grains heated to ~ 1000 K; a temperature way too high to be accounted for by equilibrium thermal emission from dust grains. They also noticed that even though the intensity of the continuum emission decreased with distance to the star, the derived temperature remained constant. Thus, it was suggested that the emission should come from the transient heating of very small dust grains of about 5 Å in size. The carriers had to be molecules with a heat capacity small enough, so that they could be rapidly heated to very high temperatures after UV photon absorption (Sellgren 1984).

1.3. PAH Hypothesis

The mystery of identifying the carriers and the excitation mechanism that produced the UIR bands was partially solved with the publication of Léger & Puget (1984), who simultaneously with Allamandola et al. (1985) first proposed polycyclic aromatic hydrocarbons as the carriers of the bands.

Léger & Puget worked based on the premise of transient heating proposed by Sellgren (1984). The presence of PAHs in the interstellar medium (ISM) had already been suggested in the earlier work of Donn (1968), based on his analysis on interstellar extinction curves. Also, Duley & Williams (1981) proposed that the 3.3 and 11.3 μm bands were due to C-H aromatic bonds. Léger & Puget then proposed *planar aromatic carbonaceous molecules* as the carriers of the UIR bands: PAHs were the perfect candidate that had a heat capacity small enough to reach the expected high temperatures, without being internally destroyed or destroyed by sublimation, giving rise to an emission which would be independent from the distance to the star.

For its part, Allamandola and co-workers at NASA Ames Research Center showed that the infrared spectrum of a mixture of PAHs displayed features similar to the UIR bands (see left panels of Figure 1.3), as derived from a direct comparison between the Raman spectrum of automobile soot, and the 5–10 μm spectrum of the Orion bar. They also modelled the IR fluorescence from a small PAH, chrysene ($C_{18}H_{12}$), formally stating the excitation mechanism that we now accept to be the one producing the bands.

It would take almost a decade for the PAH hypothesis to be widely accepted among the ISM community though (see Donn et al. 1989). Since the excitation mechanism was IR fluorescence after UV absorption, to become formally accepted, the presence of PAHs in space was expected to leave a trace in both parts of the spectrum. In other words, electronic transitions in the UV spectrum had to match the vibrational transitions observed in the infrared.

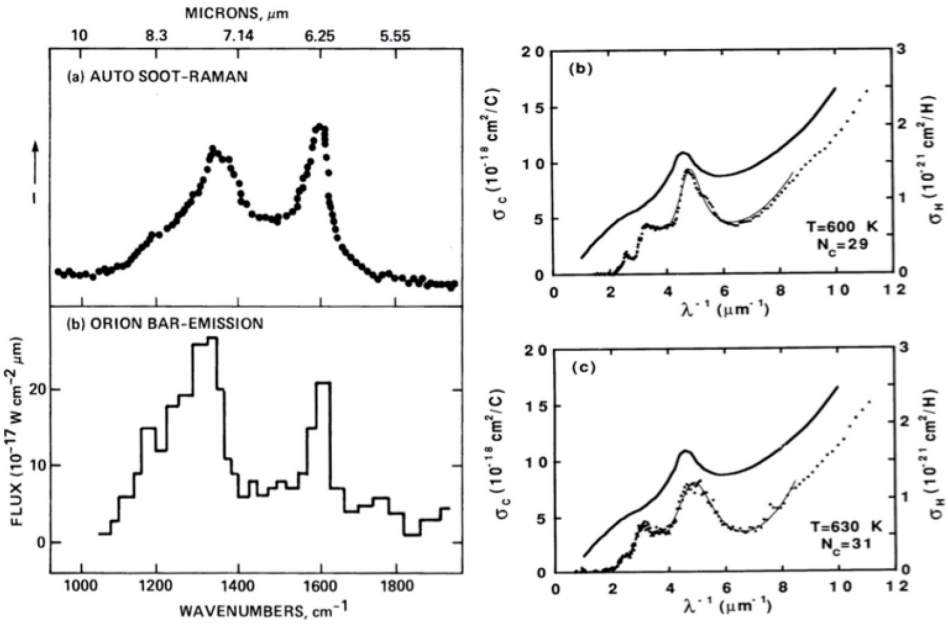

Figure 1.3: *Left panels:* Comparison of the IR Raman spectrum of automobile soot (*top panel*) and the IR spectrum of the Orion Bar (*bottom panel*). This figure has been taken from Allamandola et al. (1985). *Right panels:* Comparison of the absorption cross section of PAH mixtures per carbon atom (*dotted curve*) and the mean interstellar extinction curve derived by Savage & Mathis (1979) (*solid line*). This figure has been taken from Joblin et al. (1992).

Léger et al. (1989) discussed the PAH hypothesis regarding extinction curves, and showed that the UV absorption trace matched closely the overall shape of the UV absorption cross-section of PAHs: PAHs have a feature close to the 2175 Å bump and have the far-UV rise characteristic in interstellar extinction curves (see seminal works of Fitzpatrick & Massa 1986, 1988, 1990; see also Fitzpatrick & Massa 2005, 2007, 2009; Joblin et al. 1992; Li & Draine 2001; Salama 2007; Mulas et al. 2011; see also right panels of Figure 1.3). Accordingly, PAHs would also be proposed as responsible for the so-called Diffuse Interstellar Bands (DIBs; Léger & d'Hendecourt 1985): mysterious narrow features seen in the visible spectral region of the interstellar extinction curves towards background stars (e.g., Merrill 1934; Herbig 1975, 1995; Hobbs et al. 2010).

Subsequently, the PAH hypothesis was refined as different PAHs were being continuously detected in meteorite samples (e.g., Tingle et al. 1991; Kovalenko et al. 1992; Clemett et al. 1992, 1993; De Vries et al. 1993; McKay et al. 1996; Becker et al. 1997; Plows et al. 2003); and more experimental (e.g., Cook et al. 1993; Joblin et al. 1994, 1995), and theoretical spectra of PAH species (e.g., Langhoff 1996; Bauschlicher & Bakes 2000, Hudgins & Allamandola 2004; Mattioda et al. 2005) were obtained, compared and benchmarked. Also, astronomical observations of the PAH bands flourished thanks to the novel spectrometers and spectral imaging capabilities on board the Infrared Space Observatory (ISO), and the Spitzer Space Telescope. These facilities allowed for systematic studies on the mid-infrared emission of astronomical objects (e.g., Hony et al. 2001; Peeters et al. 2002; van Diedenhoven et al. 2004; Rapacioli et al. 2005; Berné et al. 2007; Sellgren et al. 2007; Smith et al.

2007; Galliano et al. 2008; Boersma et al. 2010; Boersma et al. 2014), and have provided (and are still providing) relevant information to test further the PAH hypothesis.

Nowadays we can summarize the PAH hypothesis as follows: the UIR bands we observe in the mid-infrared spectra of regions of dust and gas subjected to UV radiation, come from free-flying PAHs which get rapidly heated by absorbing (visible and) UV photons from their surroundings (Figure 1.4). Each absorption is followed by rapid non-radiative intramolecular processes, e.g., the respective timescales for internal conversion and intersystem crossing are of $\sim 10^{-12}$ s and 10^{-9} s respectively. These processes relax each molecule to its electronic ground state, but leave it vibrationally excited. As PAHs relax further, they emit IR radiation from their vibrational C-C and C-H modes giving rise to the UIR bands (Figure 1.4). The bands we observe then belong to a mixture of PAHs present in the ISM, and not to an individual species.

Interstellar PAHs are expected to have intermediate-to-large sizes (i.e., above 50 carbon atoms), since smaller species are expected to be rapidly destroyed in intense UV fields. The fractional PAH abundance has been estimated to be of about 10^{-7} for intermediate-to-large species (Habart et al. 2004; Tielens 2008). Due to their relatively low ionization potentials ($\sim$ 4–7 eV), they are expected to be mostly in neutral and positively ionized states. Depending on the radiation field under which they emit, they can get ionized, photodissociate, recombine with electrons, react with surrounding atoms through collisions, etc. Therefore, their emission spectra will depend on the radiation field to which they are subjected to, the emission process, and their molecular properties as determined from their photo-chemical evolution. It is precisely this symbiosis what we tackle in this thesis, and we do so by studying PAH emission in the photodissociation regions around stars.

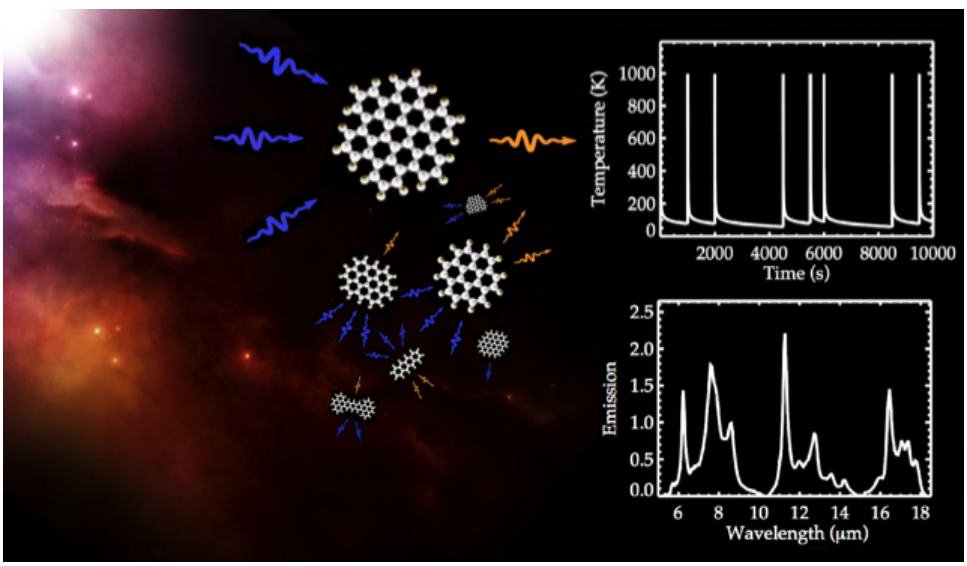

Figure 1.4: Schematic representation of the emission of PAHs in clouds under the influence of UV stellar radiation. When exposed to UV radiation (depicted in purple) PAHs get rapidly heated to high temperatures, and relax through their respective vibrational modes, emitting energy in the IR (orange) giving rise to the emission features also known as UIR bands.

1.4. Photodissociation Regions

Photodissociation regions (PDRs) are the best astronomical laboratories to study PAH emission. They are the UV illuminated surfaces of molecular clouds, where the PAH emission is found to be the strongest (see Figure 1.5). These are regions where the (photo) chemistry is driven by the incident UV radiation that hits the cloud (Hollenbach & Tielens 1999). The physical conditions in a PDR depend then on the intensity of the UV field and the total density. The incident UV radiation is primarily absorbed by PAHs and dust grains, which then re-emit it as IR radiation. PAHs contribute to the heating of the gas in the cloud through the photoelectric effect. Far UV pumping of H_2 is also an important heating mechanism at the edge of the cloud. The gas cools via fine structure lines, mainly [CII] 158 μm and [OI] 63 μm. Deeper in the clouds ion-neutral chemistry is driven by cosmic ray ionization. Observationally then PDRs are bright in PAH emission, far-IR atomic fine structure lines, pure rotational lines of H_2 and (low-J) CO; UV pumped ro-vibrational transitions of H_2, and mid/far-IR continuum emission associated with warm dust.

Figure 1.6 shows the mid-IR spectra of the PDRs in the Orion bar and NGC 7027. Aside from atomic and H_2 emission lines, we see the PAH bands very clearly. PAHs as aromatic hydrocarbons have very well known vibrations associated to their structure: the 3.3 μm band corresponds to the relaxation of aromatic C-H stretching modes; the 5 μm region is due to combination modes; the 6.2 μm band corresponds to aromatic C-C stretching modes;

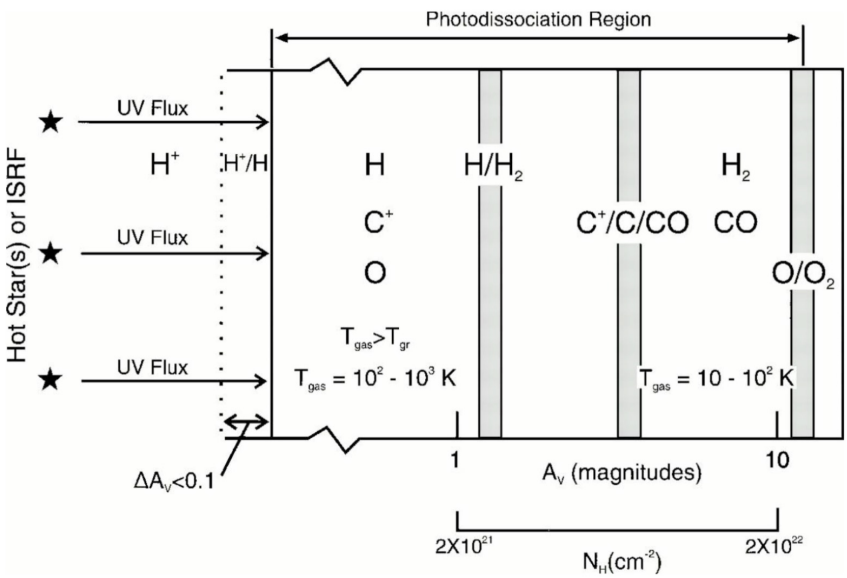

Figure 1.5: Structure of a prototypical PDR. At the surface of the cloud, UV stellar radiation (< 13.6 eV) keeps the atomic material mostly ionized. The conversion from neutral hydrogen to molecular hydrogen H_2 occurs deeper into the cloud. Going into the PDR, the material goes from being mostly atomic into a molecular regime (conversion from CII to CI to CO). The gas temperature decreases as the extinction A_V increases, reaching similar values to the dust temperature.

the 7.7 μm band comes from C-C stretching modes and C-H in-plane bending modes; the 8–9 μm region corresponds to C-H in-plane wagging modes; the 11–15 μm region on the other hand appears to be more sensitive to the edge structure of PAHs, where the 11.3 and 12.6 μm bands correspond to C-H out of plane bending modes of peripheral rings with 1 and 3 hydrogen atoms respectively (e.g., Allamandola et al. 1989; see Tielens 2008 for a more updated review).

Throughout this past decade, Spitzer observations have allowed the detection of other spectral features at 15.9, 16.4, 17.0, 17.4 and 17.8 μm, which have also been ascribed to PAHs (Moutou et al. 2000; Sellgren et al. 2007). These bands have been associated to PAH edge structure, bending motions of the carbon core, and size (Boersma et al. 2010; Ricca et al. 2010, 2012; Peeters et al. 2012). However no clear consensus has been reached yet, as some of the features have also been linked to fullerenes (i.e., molecules of only carbon in the form of a hollow sphere; Sellgren et al. 2010; Bernard-Salas et al. 2012).

Together with the PAH bands, the mid-infrared spectra of PDRs also show broader emission underneath the bands, e.g., below the 3 μm complex, at ~6–9 μm, 11–15 μm and 15–20 μm (e.g., van Kerckhoven et al. 2000; Sellgren et al. 2007). These broad features are referred to as the *plateaus*. Currently, there is a debate on the origin of this emission: plateaus may be considered as the blending of the 'tails' of PAH bands (implying a PAH origin; see Bregman et al. 1989; Sellgren et al. 2007; Galliano et al. 2008), or they may arise from a different carrier that somehow co-exists with PAHs (Boersma et al. 2010; Bernard-Salas et al. 2012; García Hernández et al. 2012; Peeters et al. 2017).

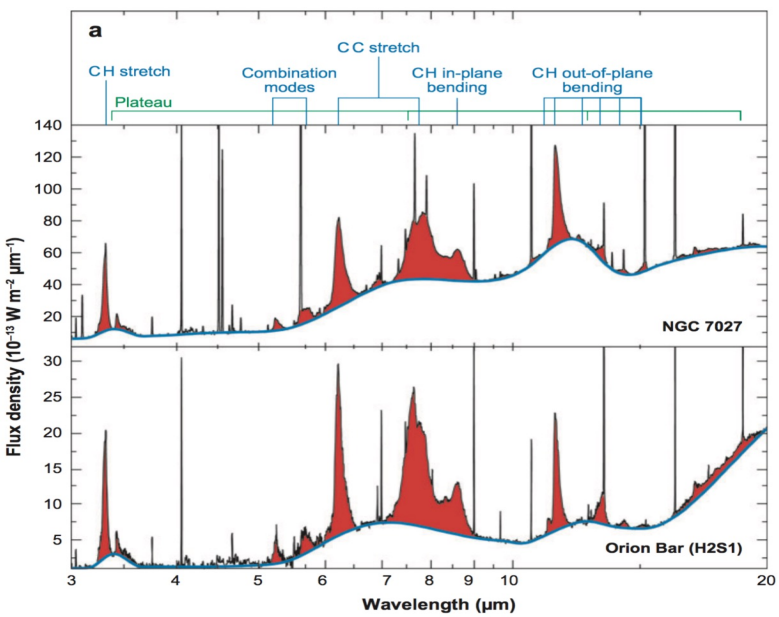

Figure 1.6: The mid-infrared spectra of the PDRs in the Orion Bar and in NGC 7027. This figure has been taken from Tielens (2008) (adapted from Peeters et al. 2002). The top panel indicates the vibrational modes of PAHs.

1.5. PAHs Through The Observation of PDRs

Spectral mapping of PDRs, as well as spectral comparison of large samples of sources, provide a powerful tool to study the characteristics of interstellar PAHs. Techniques like principal component analysis (Rapacioli et al. 2005) and blind-signal separation (Berné et al. 2007; Rosenberg et al. 2011), have been applied to analyze the mid-infrared spectrum of different PDRs, where the observed emission is decomposed into independent components. By jointly studying the spatial distribution of such components, together with the analysis of the vibrational spectra of PAHs, some links can be made between the general properties of the emitting PAH population and the relative strength of some PAH bands (see also Pilleri et al. 2012, 2015).

In order to exemplify this, in the following paragraphs we present the relations that (through both theory and experiments) have been found to arise with PAH a) charge, b) composition, c) size and d) edge-structure (Figures 1.7 and 1.8). Based on these relations and the observation of PDRs, astronomers have been able to characterize the population of emitting PAHs. The upcoming discussion is based on the PAH IR spectra as seen in *absorption*, so keep in mind that in order to compare both, these spectra and the observations *directly*, an emission model has to be applied to the intrinsic PAH spectra.

1.5.1. Charge

When comparing the IR spectra of a given PAH in different charge states (see top panel of Figure 1.7), we notice the C-C modes are intrinsically stronger in cationic species, while C-H modes are stronger in neutral species (e.g., Langhoff 1996; Allamandola et al. 1999; Bauschlicher et al. 2008). Correspondingly, the ratio between the 6.2 and 11.3 μm bands has been linked to the ionization conditions in the astronomical environments under which PAHs emit, and its ratio is currently used as a measure of the level of ionization of PAHs (Hony et al. 2001; Peeters et al. 2002; Bregman & Temi 2005; Galliano et al. 2008; Berné et al. 2007; Boersma et al. 2013; Boersma et al. 2016). This in turn has important effects on the heating of the gas in a PDR, as the photoelectric effect on PAHs is less efficient in positively ionized species (Tielens 2005).

1.5.2. Composition-Hydrogenation

After UV absorption a PAH can also dissociate and fragment depending on how much energy is absorbed, and on how such energy is distributed within the available decay channels of the molecule. The bottom panel of Figure 1.7 shows how the spectra of a small compact PAH such as coronene ($C_{24}H_{12}$) varies with variable hydrogen content. We see that the PAH with 1 hydrogen atom per peripheral carbon atom (i.e., $C_{24}H_{12}$) has intrinsically strong C-H modes compared to the carbon cluster analogue C_{24} which is, as expected, devoid of C-H stretches. Once there are aliphatic groups attached to the molecule (e.g., 2 hydrogen atoms per peripheral carbon atom, $C_{24}H_{24}$) we see that new features arise, especially in the 3 μm region. However, as also PAHs with methyl (-CH_3) groups attached show additional bands at similar wavelengths (see more in Chapter 3 of this thesis), this spectral region is still rather puzzling to explain in astronomical observations.

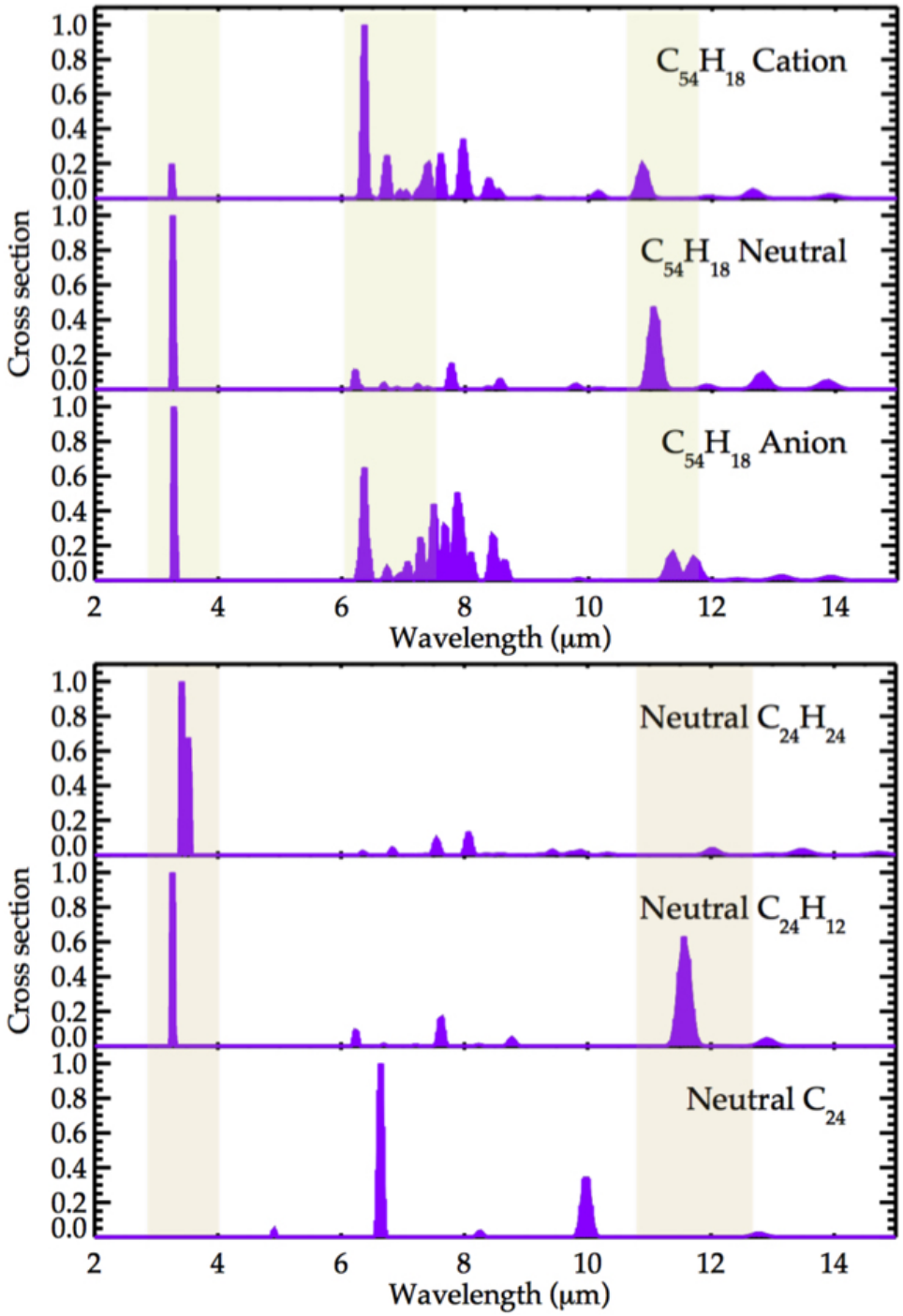

Figure 1.7: Comparison of IR cross sections of PAHs showing how charge state and hydrogenation level affect their intrinsic modes. All spectra have been retrieved from the NASA Ames PAH IR Spectroscopic Database, which contains hundreds of theoretical spectra of different PAHs (further insight on this database will be found in Chapter 2). All IR cross sections have been normalized to the peak intensity of its most prominent feature.

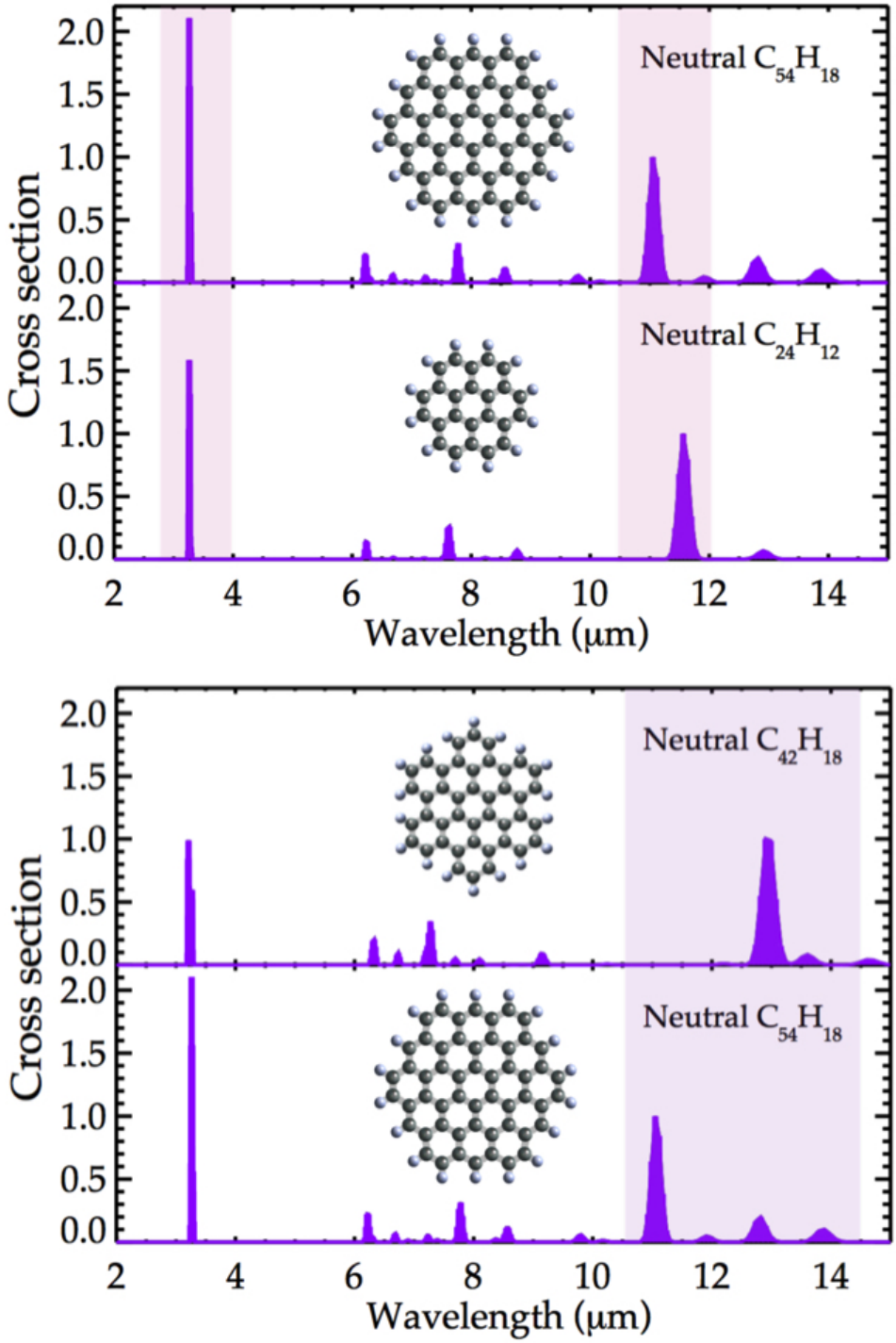

Figure 1.8: Comparison of IR cross sections of PAHs showing how size (i.e., number of carbon atoms) and edge-structure affect their intrinsic modes. Unlike Figure 1.7, the normalization is based on the peak of the most intense feature at long wavelengths ($> 10\,\mu$m).

Aside the hydrogenation level of PAHs, these molecules can also have other elements and/or functional groups, which modify their transitions (Hudgins, Bauschlicher & Allamandola 2005; Bauschlicher et al. 2008). For example, nitrogenated PAHs (also called PAHNs) have been invoked to explain shifts of the 6.2 μm band observed in some astronomical environments (Peeters et al. 2002), which otherwise cannot be explained by 'normal' (i.e., only hydrogen atoms aside carbon) PAHs (Hudgins, Bauschlicher & Allamandola 2005).

1.5.3. Size

Differences in PAH size (i.e., number of carbon atoms) also affect their IR cross sections. The top panel of Figure 1.8 shows an example comparing PAHs of increasing size from 24 to 54 carbon atoms. Even though the edge-structure is slightly modified, we see a variation in the relative strength of the 3.3 and 11.3 μm features (Allamandola et al. 1989; Ricca et al. 2012; see also Chapter 3). In *emission*, small PAHs can excite more easily the 3 μm region, as they get more heated than the larger molecules, and therefore we expect the 3.3/11.3 ratio to decrease with increasing PAH size within a given charge state (see Chapter 3). Recently, this ratio was used as an indicator of the PAH size distribution in the reflection nebulae NGC 7023 using new data from the Stratospheric Observatory For Infrared Astronomy, SOFIA (Croiset et al. 2016). However caution must be taken when using the 3.3/11.3 as a tracer of PAH size, as other aspects of PAHs can affect this ratio as well (see more in Chapter 3). Also the 3 μm region is very sensitive to how the PAH emission spectra is modelled, as it can be highly affected by anharmonicities and combination modes; something theoretical calculations are currently investigating (Mackie et al. 2015; Maltseva et al. 2016; Candian & Mackie 2017). More insights will also come up in time as the James Webb Space Telescope (JWST) will provide spectroscopic observations of the 3 μm region, a spectral region not covered by Spitzer data.

1.5.4. Edge-Structure

Lastly, as we mentioned before, the 11–15 μm region is more sensitive towards the molecular structure of PAHs (e.g., Hony et al. 2001; Bauschlicher et al. 2008). The bottom panel of Figure 1.8 shows that in molecules with more edge-structure (e.g., $C_{42}H_{18}$), bands in the long-wavelength region become intrinsically stronger (Boersma et al. 2010). In fact we see that the 11.3 μm band disappears as no solo-rings (i.e., peripheral rings that can only attach 1 hydrogen atom) are present in $C_{42}H_{18}$ (see also the top panel of Figure 1.8, where increasing the size of the molecule adds solo-rings to the edges). This supports the motion that most interstellar PAHs must be compact, as the 11.3 μm band is almost always present in the IR spectra of astronomical objects. The bands at 12.6, 13.5 and 14.0 μm then have been ascribed to different edge-structures, and the 12.6/11.3 ratio has been used as a tracer of molecular structure of PAHs in astronomical sources (Bauschlicher et al. 2008; Tielens 2008; Candian, Sarre & Tielens 2014).

1.6. Other Carriers

Even though the PAH hypothesis is relatively well-established among the community, other carriers have been proposed as well (although these have not been extensively explored as PAHs have). These are mainly amorphous solids with a mix of aromatic/aliphatic compounds, among which there is the hydrogenated amorphous carbon HAC (Jones et

al. 1990; Buss et al. 1990; Gadallah et al. 2012), quenched carbonaceous composites (QCC; Sakata et al. 1987, 1990), soot (Hu & Duley 2008), coal or kerogen (Papoular et al. 1989), and more recently, Mixed Aromatic/Aliphatic Organic Nanoparticles (MAONs; Kwok & Zhang 2011, 2013). Most of these propose that the UIR bands arise from the excitation of small thermally-isolated aromatic units within or attached to the bulk materials.

The proposal of such carriers is mainly based on two arguments: the missing link to the UV spectral region (see Salama 2007 and Pino et al. 2011 for reviews on the electronic spectra of PAHs and the DIBs discussion), and the missing individual identification of PAHs (Ali-Haïmoud 2013). However both subjects are challenging as experiments are technique-limited (Pino et al. 2011), and astronomical observations rely either on *i*) the far-IR spectral region where carbon-skeleton modes are intrinsically weak, or may be simply hampered by the strong continuum from larger dust grains, or *ii*) rely on rotational spectroscopy, which is limited to PAHs with a dipole moment (e.g., bowl-shaped, PAHNs, among others).

1.7. Current State of the Field

In the following paragraphs we will first give an overview of the contemporary research performed on PAHs, focusing the attention on the topics relevant for this thesis.

1.7.1. Infrared Spectra of PAHs

Laboratory and theoretical studies have altogether allowed a better assessment of the bands and PAH emission process (see Oomens et al. 2003 and 2006 for reviews on experiments, and see Pauzat 2011 and Candian & Mackie 2017 for reviews on theoretical calculations). Nowadays, hundreds of intrinsic IR PAH (theoretical and experimental) spectra are available to the community, and databases such as the NASA Ames PAH IR Spectroscopic Database[1] (Bauschlicher et al. 2010; Boersma et al. 2014) and the Cagliari PAH Database[2] (Malloci et al. 2007) currently offer an opportunity to study PAH emission in a systematic manner, and even compare it to space observations. Such resources are now starting to be used to analyze astronomical spectra (Cami 2011; Rosenberg et al. 2011; Boersma et al. 2014; Andrews et al. 2015, Chapter 2). Care must be taken though, as the previously mentioned databases are not complete (i.e., do not have all PAH classes well-represented), and thus a good handling of their biases and caveats is mandatory before interpreting the results.

The feedback between theoretical computations and laboratory studies is relevant when analyzing PAH properties. Laboratory studies in gas-phase are currently limited to mostly small (less than 50 carbon atoms) cationic and radical species (e.g., Joblin et al. 1994, 1995; Oomens et al. 2000, 2003, 2006; Bakker et al. 2011). While the bulk of the experimental spectra of (cationic) PAHs was obtained through matrix isolation spectroscopy throughout the 90s and early 2000s (see Joblin et al. 1994 for an analysis on possible matrix effects), at present the leading technique in the field is the infrared multiphoton dissociation spectroscopy (IRMPD) using a free electron laser (Oomens et al. 2000; Lorenz et al. 2007). This technique gives the IR spectra of gas-phase PAHs, however it has been mostly used for small cationic species (Oomens et al. 2006). Even though positively ionized species are indeed

[1] http:www.astrochem.org/pahdb
[2] http://astrochemistry.oa-cagliari.inaf.it/database/

important —as they are expected to be the dominant population in warm ionizing regions— neutral species are also relevant and experimental studies are unfortunately scarce (Cook et al. 1996, 1998; Piest et al. 2001; Mattioda et al. 2009). The other limitation regarding PAH size is also given by the commercial unavailability of pure PAHs with more than 42 carbon atoms, which forces most experiments to be performed on smaller species.

For its part, quantum chemistry calculations within the framework of Density Functional Theory (DFT), while extensively used to predict spectral properties of PAHs, still have some issues. Most calculations have been performed on small species, since larger systems are computationally demanding. Symmetry breaking artifacts in open-shell molecules are still problematic, as they produce abnormally large intensities and a significant shift of the bands (Pauzat 2011; Bauschlicher 2016). Theoretical calculations require experiments for benchmarking non-standard systems (e.g., partially hydrogenated PAHs; Ricca et al. 2011; Bauschlicher & Ricca 2013). Also more experiments are required to find the proper scale factors to bring the theoretical harmonic frequencies into agreement with the experiments[3].

1.7.2. Emission Model

In order to compare theoretical (absorption) spectra of PAHs to astronomical spectra, a model of the emission process has to be assumed (Schutte et al. 1993; Cook & Saykally 1998; Pech et al. 2002; Mulas et al. 2006). Such a model requires PAH molecular properties like the UV absorption cross-section, and the IR vibrational transitions. Putting aside the fact that the UV absorption cross-sections have been calculated only for few small species (up to the size of circumovalene $C_{66}H_{20}$) and are limited in accuracy to ± 0.3 eV (Malloci et al. 2007), some important assumptions have to be made. Several parameters need to be assumed since they are not well understood by theorists, such as the profile, width and shift of the bands (Pech et al. 2002; Joblin et al. 1995). The profile and width of the bands reflect intra/inter-mode anharmonicities coupled with the non-radiative vibrational redistribution process of the absorbed energy (e.g., Pech et al. 2002). The shift of the bands also arises from anharmonic effects throughout the emission process. Joblin et al. (1995) is still the only experimental evaluation of the shift induced on vibrational modes as a function of internal energy, performed on a handful of neutral PAHs. On the other hand, theoretical studies are now flourishing on the subject of anharmonicities, and we expect lots of interesting results in the upcoming future (Calvo et al. 2011; Mackie et al. 2015; Maltseva et al. 2016).

1.7.3. Photochemistry of PAHs

Other still pending issues involve not only finding a viable route of formation of PAHs in the envelopes of asymptotic giant branch stars (Latter 1991; Frenklach & Feigelson 1989; Cherchneff, Barker & Tielens 1992; Sloan et al. 2007; Lau et al. 2016), but also the photochemistry that guides their evolution (Jochims et al. 1994; Le Page et al. 2001; 2003; Bakes et al. 2001; Montillaud et al. 2013; Berné et al. 2015). Focusing on the latter, the photochemistry of PAHs is extremely important to better assess the role of PAHs in the ISM. Based on theoretical and experimental results, astrophysical models can be applied to interpret the spectral variations observed within astronomical objects.

[3] http://cccbdb.nist.gov/vibscalejust.asp

Ionization of PAHs has been extensively investigated since the 90s, in terms of both photoionization yields, and the calculation of ionization potentials and electron affinities for some PAH molecules (e.g., Verstraete et al. 1990; Jochims et al. 1996, 1997; Duncan et al. 1999; Malloci et al. 2007). Hydrogen, carbon and acetylene losses are currently under investigation, as well as isomerization of PAHs (Stockett et al. 2015; Zhen et al. 2015; Bouwman et al. 2016). Regarding kinetic parameters, the time-dependent mass spectrometry experiments on small cations performed by Ling and co-workers in the 90s (e.g., Ling et al. 1995) are still unique in their field, and unfortunately similar experiments have still not been carried out on larger species. What it is now mostly studied instead, is the energetic competition between ionization and photodissociation in PAHs (e.g., mass spectrometry experiments; see Reitsma et al. 2014; Zhen et al. 2014, 2015). PAHs appear to lose their hydrogens in pairs independently of their edge structure (work in progress at Sackler Laboratory). Exposure of PAH cations to synchrotron radiation of 8–40 eV, suggests PAHs of different sizes (24–42 carbon atoms) undergo different relaxation channels after photon absorption; with small PAHs being rapidly destroyed, while larger species go through several ionization steps before starting to lose any hydrogen atom (Zhen et al. 2014, 2015).

Few models then have been developed in order to incorporate the studied photochemistry into an astronomical context. Most of the kinetic models consider either generic properties for the PAHs (Allain et al. 1996; Le Page et al. 2001, 2003), and/or limit their analysis to the study of the abundance of PAH species (i.e., Montillaud et al. 2013). The astrophysical modelling of the PAH emission obtained from using specific molecular properties was first performed by Bakes et al. (2001), who focused only on the charge distribution of the species and its effect on the emitted spectra. Chapter 3 of this book constitutes the first attempt to model PAH emission from specific molecules under realistic astrophysical conditions, using the properties specific to each molecule.

1.8. In This Thesis

We have seen the PAH field evolves from the constant interaction between experimentalists, theorists, modellers and observers. While laboratory research and quantum chemical calculations together set up the molecular properties of PAH species, astronomers on the other hand, retrieve as much information as possible from the space observations. Nowadays, the PAH field is advanced enough to start implementing all these results into astronomical models, in order to study PAHs from a molecular groundwork. In this regard, the research projects presented in this thesis do precisely that. They constitute a first attempt to gather the vast current knowledge available on specific PAH molecules (not using generic properties), and put it in an astrophysical context, and with it, target some of the key subjects of the field such as: the existence of the so-called *grandPAHs* in space (§1.8.1); the role of PAHs in the formation of H_2 in PDRs (§1.8.2); the abundance of *superhydrogenated* PAHs and their contribution as a carrier of the 3.4 μm band observed in PDRs (§1.8.3); and the deuterium fractionation in PAHs, and their consequent role in explaining the observed deuterium abundance in the local ISM (§1.8.4).

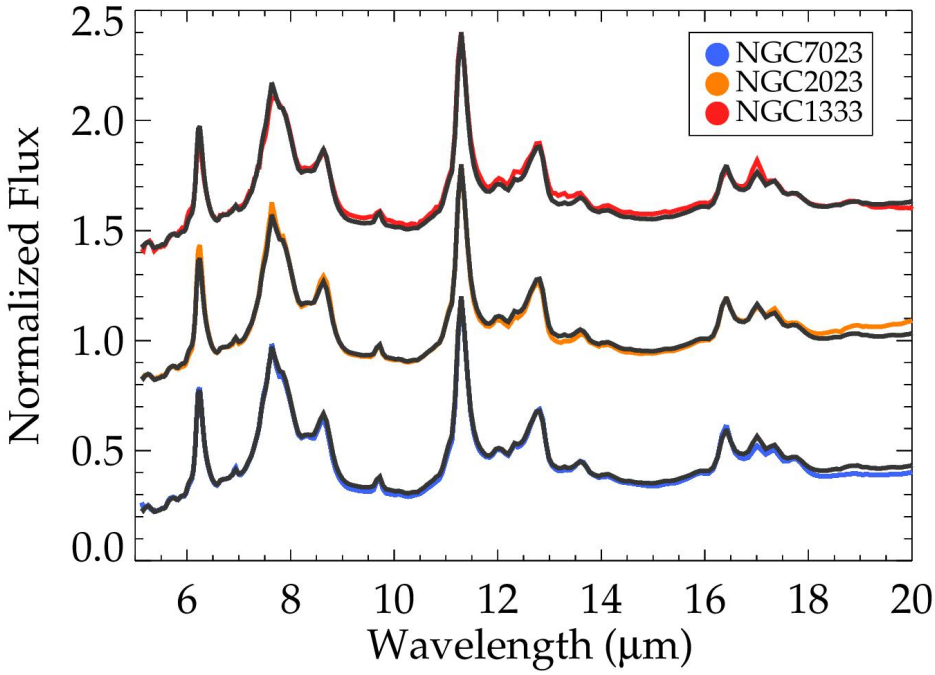

Figure 1.9: Comparison of the spectra taken at the brightest mid-IR spot of three different nebulae: NGC 7023, NGC 2023 and NGC 1333. The spectra have been taken with the InfraRed Spectrograph (IRS) on board the Spitzer Space Telescope. All spectra have been normalized to the peak intensity of the 11.3 μm band. The average of the three normalized spectra is plotted in black. As clear from the Figure, despite the infinite possibility of PAH mixtures in the ISM, the mid-IR spectra at the brightest spots of different PDRs is remarkably similar (Werner et al. 2004, 2009). This has led the community to wonder about the possibility of having a unique mixture of the most stable PAHs emitting at these 'extreme' spots. Chapter 2 of this thesis is the first attempt to explore the grandPAH hypothesis by using the available PAH spectra of the NASA Ames PAH IR Spectroscopic Database.

1.8.1. The GrandPAHs

Tielens (2013) first formally proposed the concept of *grandPAHs*, as a set of the most stable PAH species that are able to survive the harsh conditions of the ISM. The idea of having a sort-of unique mixture of PAHs emitting in the most extreme regions of the ISM, was motivated by the relatively similar PAH emission detected in different interstellar sources, specially at 15–20 μm which is the region expected to trace the more specific structure of PAHs (Boersma et al. 2010, Ricca et al 2010; see Figure 1.9). Since their proposition, the concept of grandPAHs has been mentioned in some works (e.g., Ali-Haïmoud 2014; Peeters et al. 2017). However it has not been explored in any way. Chapter 2 constitutes the first attempt to do this. Given the current availability of PAH spectra thanks to the NASA Ames PAH IR Spectroscopic Database, we have now an actual tool to explore how feasible it is to have grandPAHs in space. If present, their relevance would be extremely helpful in simplifying the picture for the scientific community, as only a handful of species would be important to understand what happens with the carbonaceous material in PDRs.

1.8.2. Formation of H_2 in Clouds

Molecular hydrogen is the most abundant molecule in space. It plays an important role in the thermal balance and chemistry of the ISM. However, the formation of molecular hydrogen in interstellar clouds has been puzzling astronomers since the early 70s. As molecular hydrogen cannot be formed effectively in gas-phase reactions (Gould & Salpeter 1963; Duley & Williams 1984), it has long been suggested that molecular hydrogen can instead be formed through surface reactions on dust grains (Hollenbach & Salpeter 1970, 1971). The main formation mechanism proposed, considered that a hydrogen atom could first be adsorbed on a dust grain, diffuse throughout its surface, eventually interact with another hydrogen atom, and form an H_2 molecule, which would be desorbed into space. Following this scenario, assuming an efficiency formation of H_2 close to unity, can lead to a rate of $\sim 10^{-17}$ cm^3/s, in agreement with the observed estimates for diffuse clouds (Jura 1975). However later observations of PDRs led to rates a factor of 10 higher, which could not be explained by such mechanism (Habart et al. 2003, 2004). Throughout the years, theoretical and experimental studies of H_2 formation on dust grains have shown that different mechanisms work at different dust temperatures (Duley 1996; Pirronello et al. 1997, 1999; Katz et al. 1999; Cazaux & Tielens 2002, 2004; Cuppen & Herbst 2005; Le Petit et al. 2009; Le Bourlot et al. 2012; Bron et al. 2014). Langmuir-Hinshelwood reactions —where two physisorbed mobile hydrogen atoms interact on the surface, and desorb as H_2— appears to be efficient only at grain temperatures below 20 K (Pirronello et al. 1997, 1999). Eley-Rideal reactions on the other hand —where a free hydrogen atom interacts with an already chemisorbed hydrogen atom, and desorb as H_2— has been found to be efficient at much higher temperatures (e.g., Duley 1996, Le Bourlot et al. 2012). PAHs have been invoked to be effective at temperatures where larger dust grains are not (Le Bourlot et al. 2012; Bron et al. 2014). Indeed correlations between H_2 and PAH emission in PDRs have been observed (e.g., Habart et al. 2003, 2004). More recently, experiments on the bombardment of PAHs with deuterium atoms have shown that H_2 can be formed through Eley-Rideal abstraction processes (Thrower et al. 2011; Mennella et al. 2012; see Figure 1.10). Theoretical calculations also support these results (Rauls & Hornæker 2008). In Chapter 3 we will address this issue from the PAH perspective using a kinetic model. This will naturally allow an analysis on the formation of H_2 on PAHs, as derived from the resulting abundance distribution of 3 specific PAH molecules of different (astrophysically-relevant) sizes.

1.8.3. Superhydrogenated PAHs and The 3.4 μm Carrier

Among the observed PAH bands in the mid-IR spectra towards PDRs, aside the main band at 3.3 μm there are weak features that appear in the 3 μm region at 3.4, 3.47, 3.51 and 3.56 μm (see Figure 1.11; Joblin et al. 1996; Pilleri et al. 2015). Their carrier is still unknown (Joblin et al. 1996; Onaka et al. 2014; Pilleri et al. 2015). These could be hot bands of the 3.3 μm mode (Barker et al. 1987), the C-H stretching modes of aliphatic side groups attached to PAHs such as methyl functional groups (Duley & Williams 1981; Li & Draine 2012; Yang et al. 2013, 2016; Sadjadi et al. 2015), or they could be due to PAHs with extra hydrogens (i.e., *superhydrogenated* species; Bernstein et al. 1996; Sandford et al. 2013). The question mark on the carrier of the 3.4 μm band is a recurrent topic in the field. As the knowledge on the photochemistry of PAHs increases, the physics behind superhydrogenated species can be better understood. In Chapter 3 we will study the hydrogenation of specific PAHs with different sizes, and therefore we will naturally tackle the question whether superhydrogenated species can be the solely carriers of the 3.4 μm band.

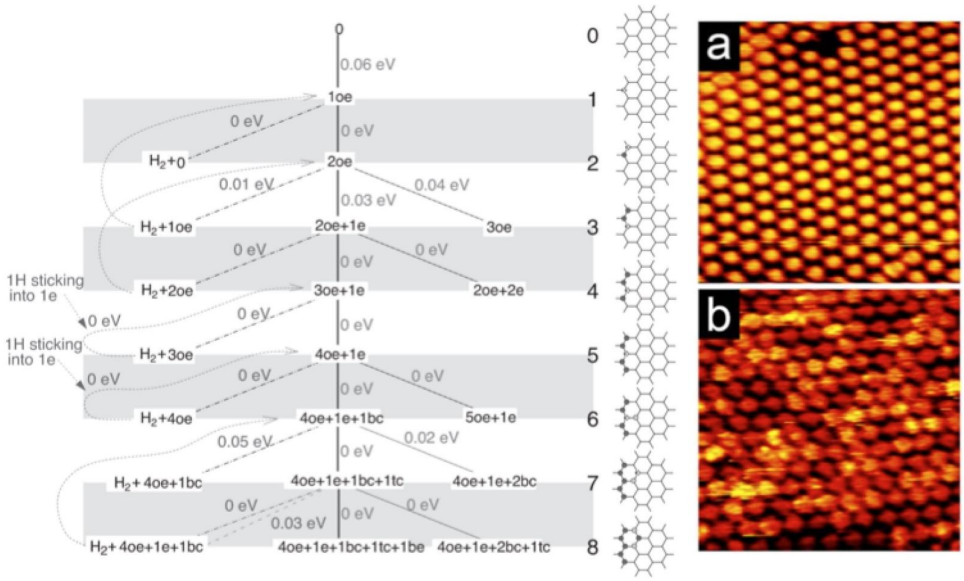

Figure 1.10: Theoretical and experimental results on the formation of H_2 in PAHs. The figures have been taken from Thrower et al. (2011). The right panels correspond to scanning tunneling microscopic images of a monolayer of coronene molecules before (a) and after (b) deuterium bombardment. The left panel shows the DFT calculations on the H_2 formation on coronene presented in Rauls & Hornæker (2008). The central line shows the most energetically favourable route of hydrogenation and H_2 abstraction. For example: starting from the top to bottom, the first hydrogen is attached to an outer edge (oe) of the coronene molecule with a reaction barrier of 0.06 eV; the addition of a second H atom is barrier-less for the adjacent outer edge position; abstraction of H_2 from these positions are essentially barrier-less (there is only a 0.01 eV barrier for the abstraction of one of the two extra H atoms). In general we see that once 1 H atom is added, the following additions require very small barriers (if any). The abstractions of H_2 are also mostly barrier-less processes.

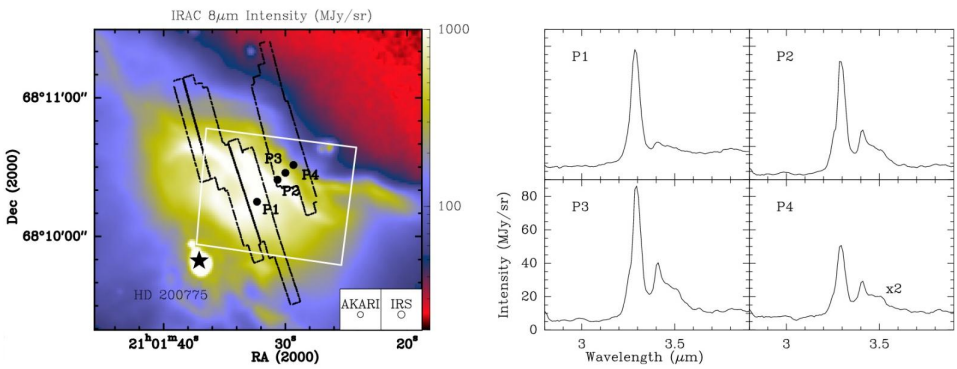

Figure 1.11: Observations of the 3 μm complex from the north-western PDR of NGC 7023. The spectra have been taken with the AKARI satellite. This figure has been taken from Pilleri et al. (2015).

1.8.4. Deuterium Fractionation in the Local ISM

The abundance of deuterium relative to hydrogen (D/H) is an important value that helps constrain the baryonic content in the Universe, since its evolution with cosmic time is expected to steadily decrease as deuterium is heavily processed in stars (Mazzitelli & Moretti 1980; Linsky et al. 2006; Linsky 2010; Tosi et al. 2010). Recent estimates of the primordial (D/H) ratio have led to values of $\sim 2.5\times10^{-5}$ (Srianand et al. 2010; Coc et al. 2015; Cooke & Pettini 2016). For its part, the local (D/H) ratio shows a wide range of values between $0.5–2.2\times10^{-5}$ in the galactic disk, with a value of 1.6×10^{-5} within the Local Bubble (Wood et al. 2004; Linsky et al. 2006; Linsky 2010; see Figure 1.12). This variation in the local ISM is very confusing as it cannot be explained by current models of chemical galactic evolution. In order to explain such variation, infall of unprocessed gas in the galaxy and deuterium depletion onto dust grains have been proposed (Jura 1982; Draine 2004; Prochaska et al. 2005; Romano et al. 2006; Linsky et al. 2006). The latter is strongly supported as correlations between the gas-phase (D/H) ratio and the depletion of refractory metals have been found in different lines-of-sight (Linsky et al. 2006). PAHs then, as an important part of the dust population, have been proposed as important reservoirs of deuterium in space (Tielens 1997; Millar et al. 2000; Draine 2006). Evidence for the presence of deuterated PAHs is motivated by the detection of bands in the 4 μm spectral region of PDRs (Peeters et al. 2004; Onaka et al. 2014; Doney et al. 2016), which is where C-D stretching modes are expected to be found. Indeed, the IR spectra of few deuterated PAHs show bands at wavelengths coinciding with the observations (Hudgins et al. 2004; Buragohain et al. 2015, 2016). Also the energy difference between C-H and C-D bonds is expected to favour deuteration of PAHs. We address this issue in Chapter 4 within the kinetic model presented in Chapter 3, in order to explore how the (D/H) in PAHs varies with astrophysical conditions.

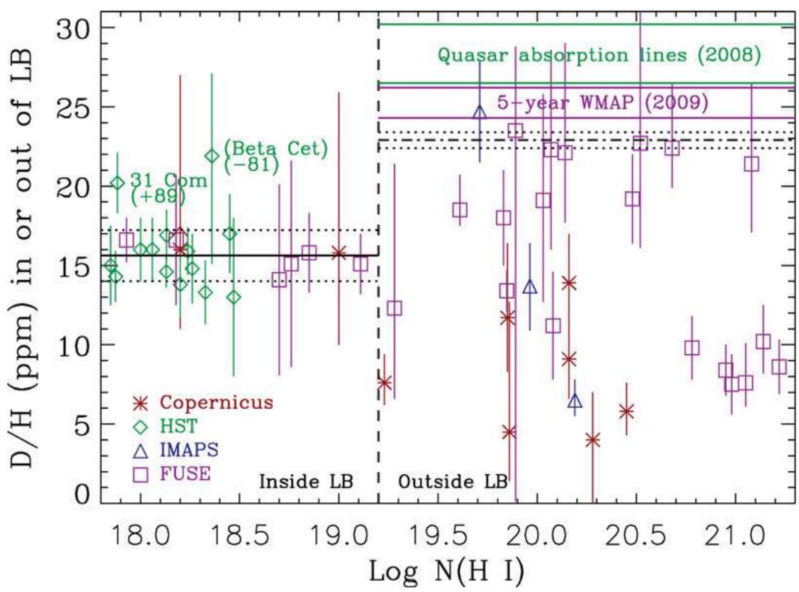

Figure 1.12: Measurements of the (D/H) ratio within and outside the Local Bubble (LB). The upper right corner shows the range of cosmic (D/H) values as derived from quasar absorption lines and from the cosmic microwave background signal. This figure has been taken from Linsky (2010).

1.9. Outline of This Thesis

Chapter 2 As previously mentioned, in this chapter we explore the existence of grandPAHs in the ISM. We do this by using the available data on different PAH species compiled in the NASA Ames PAH IR Spectroscopic Database. The motivation arises from the analysis of the mid-IR spectra of three well-studied nebulae: NGC 7023, NGC 2023 and NGC 1333. The spectra correspond to the brightest spots of PAH emission within the respective PDRs (see Figure 1.9). The PAH emission looks strikingly similar even though these are different lines-of-sight, there are different physical conditions, and all objects present large variations of the PAH emission within themselves. Having all this in mind, the question of whether there could be remarkably similar PAH mixtures emitting at these spots naturally arises. In this way, we call upon the concept of *grandPAHs* proposed in Tielens (2013): a set of the most stable PAH species that are able to survive the intense processing in the ISM, and as such, dominates the PAH population in space. We tackle this proposition for the first time ever, and we also do it in a novelty way by using the available IR spectra of hundreds of PAHs compiled in the NASA Ames PAH IR Spectroscopic Database mentioned earlier. In fact, this is the first work that has made use of this database to fit the observations modelling consistently the emission spectrum of each PAH considering the radiation field under which they emit. In this way, we point out and deal with the uncertainties involved in modelling the PAH emission process, keeping also in mind the caveats when fitting astronomical spectra using a database like the NASA Ames one (see also Boersma et al. 2013).

Chapter 3 There are different techniques by which the properties of PAHs can be linked to astrophysical conditions. Usually this is done using as a start point the space observations. In Chapter 3 we go the other way around, linking the astrophysical conditions to PAH properties but starting from the PAHs themselves. In this project we take 3 individual PAH molecules of astrophysically-relevant PAH sizes (24, 54 and 96 carbon atoms), and we model their emission under PDR-like physical conditions, using their specific properties as derived from theory and experiments. The 3 PAHs are expected to be very stable species due to their compact structure. In the model we take into account the most relevant photo/chemical reactions, using the latest data available for each molecule. This work constitutes then the first astronomical kinetic model built to analyze the PAH emission from specific molecules, considering their resulting ionization and hydrogenation distributions. Together with this, we also address the role of PAHs in the formation of molecular hydrogen in PDRs, and the abundance of superhydrogenated species (and together with that, the discussion on the carrier of the 3.4 μm band: can PAHs with extra hydrogen atoms be the carriers of the observed 3.4 μm band?).

Chapter 4 Using the kinetic model from Chapter 3, here we address the key question of whether the deuterium abundance in PAHs can contribute to the deuterium fractionation problem observed in the local ISM. We aim to answer the specific questions of how sensitive the (D/H) ratio in PAHs is relative to astrophysical conditions, and together with that, elucidate in which way PAHs can contribute to the deuterium fractionation problem mentioned in section 1.8.4. This is the first time that these questions are approached considering specific PAH properties. We consider this to be a first modelling attempt, and we encourage further studies as more experimental and theoretical research on the reactivity of deuterated PAHs come along.

Chapter 5 At last, all previous chapters have considered PDRs as the best laboratories to study PAH emission, as these are regions driven by UV radiation, where the material transitions from the more diffuse ionized medium close to the star, to the molecular domain. This chapter will focus on the famous pair of nebulae IC63-IC59 in the vicinity of the star γCas. We perform a global characterization of both nebulae from an observational perspective, using not only Spitzer and Herschel data, but also high-resolution velocity maps from SOFIA. Our aim here is to study the PDRs associated to these clouds, and derive the physical conditions under which PAHs emit.

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