Revisiting polycyclic aromatic hydrocarbon emission in Photodissociation regions

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Astronomy

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Abstract

The mid-infrared (IR) spectrum of almost all objects in the Universe is dominated by a set of strong emission features characteristic of a class of large organic molecules made of carbon and hydrogen known as polycyclic aromatic hydrocarbons (PAHs). These molecules account for \( \sim 15\% \) of the cosmic carbon and \( \sim 20\% \) of the total IR power of the Milky Way and star-forming galaxies. They are strong absorbers of ultraviolet (UV) photons and release the absorbed energy through vibrational transitions that result in strong IR emission features. PAHs play a critical role in the evolution of the interstellar medium (ISM) as they drive much of the ISM’s heating and ionization balance. As a result, detailed knowledge of the molecular astrophysics of PAHs, including a thorough understanding of their molecular properties and their interactions with the environment in which they reside, is crucial to understand the evolution of the ISM. Although decades of experimental, theoretical, and observational work have helped gain important insights into the behaviour of PAHs in the ISM, our understanding is far from complete. In this thesis, we investigate the astrophysical behaviour of PAHs from both an observational and theoretical standpoint.

Our observational study focuses on identifying the key parameters that drive the PAH behaviour in two well-known Galactic reflection nebulae, NGC 2023 and NGC 7023, using a Principal Component Analysis. We find that the amount of PAH emission, which represents the PAH abundance and excitation, and the PAH charge state are the only two parameters that drive their behaviour in both environments. In our theoretical study, we develop a model that determines the charge distribution of PAHs and uses it to compute the PAH emission spectrum in astrophysical environments. The relative strengths of the PAH emission features predicted by our model in the Orion Bar, NGC 2023, NGC 7023, the Horsehead nebula, and the diffuse ISM compare well to those obtained from observations. Furthermore, the results of our model highlight the necessity of experimentally determined electron-recombination rates of PAHs and the molecular characteristics of PAH anions, both of which are crucial in understanding PAH behaviour but for which the data is scarce to date.

Keywords: Polycyclic Aromatic Hydrocarbons, IR Astronomy, Interstellar medium, Photo-Dissociation Regions, Reflection Nebulae, NGC 2023, NGC 7023, Orion Bar, Horsehead Nebula, Principal Component Analysis, Theoretical emission spectra
Summary for Lay Audience

Molecules are powerful messengers in the Universe, providing us with critical information about physical and chemical processes occurring there. One such important class of molecules are polycyclic aromatic hydrocarbons (PAHs). These molecules, which are made up of carbon and hydrogen, pervade the Universe. They regulate the temperature and the ionization balance of the interstellar gas, which ultimately impacts major astronomical processes, including star formation, planet formation, and galaxy evolution. The specifics of PAH-driven small-scale physical processes are determined by their molecular properties, such as charge, size, and molecular structure. These molecular properties are not well constrained in astronomical environments. It is crucial to bridge this gap in our understanding of astronomical PAH molecules to better comprehend the large astrophysical processes.

The infrared (IR) emission features of PAHs that we observe encode the precise molecular properties of PAHs in a given environment. Much work has been done in the past to deduce these underlying properties of PAHs but we are still a long way from uncovering the whole picture. This thesis contributes to solving this puzzle by investigating PAH molecules from an observational and theoretical perspective. For the observational study, we employ an advanced statistical technique called Principal Component Analysis to analyze the IR emission features of PAHs in two different environments and find that in terms of the molecular properties, the charge state is the major driving factor of the observed PAH emission. In our theoretical study, we develop a model based on the results of the observational study to predict the spectral signatures of these molecules in the Universe. This model serves as a test-bed for our understanding of the astrophysics of PAHs required for the small scale physical processes driven by PAHs, which ultimately drive the large-scale processes occurring in the Universe.
Authorship statement

The following authors contributed to Chapter 2: A. Sidhu, E. Peeters, J. Cami, and C. Knight
AS wrote the code to perform PCA of PAH emission in NGC 2023 with regular input from EP and JC. AS, EP, and JC did the interpretation of the results from PCA. CK prepared spatial map of the radiation field strength from far-infrared continuum emission (Fig. A.3). EP prepared the IRAC [8.0] image of NGC 2023 (Figure 2.1). AS prepared the remaining figures. AS wrote the paper with regular feedback from EP and JC. CK wrote the section on method to determine radiation field strength from far-infrared continuum emission.

The following authors contributed to Chapter 3: A. Sidhu, J. Bazely, E. Peeters, and J. Cami
JB used the code from AS and performed PCA of PAH emission in NGC 7023. AS, JB, EP, and JC did the interpretation of the results from PCA. AS prepared all the figures. AS wrote the paper with regular feedback from EP and JC.

The following authors contributed to Chapter 4: A. Sidhu, A.G.G.M. Tielens, E. Peeters, and J. Cami
AS wrote the code to model PAH charge distribution and emission with regular input from AGGMT, EP, and JC. AS, AGGMT, EP, and JC interpreted the results of the charge distribution and PAH emission predicted by the model. EP obtained the observational data used for the validation of the model. AS prepared all the figures. AS wrote the paper with regular feedback from AGGMT, EP, and JC.
To my grandparents Nirvail Singh and Parkash Kaur, my parents Parminder Singh and Gurmeet Kaur, and my brother Anmol who gave me the wings to fly.
“The truth, however ugly in itself, is always curious and beautiful to seekers after it.” - Agatha Christie
Acknowledgements

I can’t begin to express how grateful I am to my advisors, Els Peeters and Jan Cami. Throughout my PhD, they have provided me with unparalleled knowledge, guidance, and unwavering support. Thank you, Els and Jan, for believing in my abilities and providing me with numerous opportunities to grow as a graduate student.

During my PhD, I had the opportunity to travel to the Netherlands and work with Xander Tielens at the Leiden Observatory. I am incredibly grateful for the opportunity to collaborate with the world’s foremost authority on PAH research. Bedankt, Xander, for being a mentor to me since the last two years of my PhD.

I’d also like to thank my colleagues at Western. Collin, Keegan, Hadi, Arpan, and Alexandros, I really appreciate our conversations. Your company made my time at Western memorable. I would also like to thank Western University for their nurturing and inclusive working environment.

A huge thank you to my family! None of this would have been possible without your unconditional love and support. Mamma, Papa, Daddy, Anmol, and Navdeep Bhabhi your constant encouragement has always kept me going throughout my life. Your values have made me a better person, and thanking you would be an understatement. Thank you to my Canadian family, Ashu, Gugu, Pavan, and Inderpreet, for never making me feel far from home. Words cannot express how grateful I am to each and every one of you.

To my friends, Manmeet, Arjama, and Ronit, your words of upliftment have helped me sail smoothly through my journey. Thank you so much for your precious friendship. Mansimrat, thank you for keeping me motivated and pushing me to do my best. I consider myself fortunate to have you in my life.
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<th>Description</th>
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<tbody>
<tr>
<td>2MASS</td>
<td>The Two Micron All-Sky Survey</td>
</tr>
<tr>
<td>AGB</td>
<td>Asymptotic Giant Branch</td>
</tr>
<tr>
<td>AGN</td>
<td>Active Galactic Nuclei</td>
</tr>
<tr>
<td>AIB</td>
<td>Aromatic Infrared Band</td>
</tr>
<tr>
<td>CI</td>
<td>Confidence Interval</td>
</tr>
<tr>
<td>eVSG</td>
<td>evaporating small grains</td>
</tr>
<tr>
<td>FOV</td>
<td>Field of View</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HACA</td>
<td>Hydrogen Abstraction Carbon Addition</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>IRS</td>
<td>Infrared Spectrograph</td>
</tr>
<tr>
<td>ISM</td>
<td>Interstellar Medium</td>
</tr>
<tr>
<td>ISO</td>
<td>Infrared Space Observatory</td>
</tr>
<tr>
<td>JWST</td>
<td>James Webb Space Telescope</td>
</tr>
<tr>
<td>MIR</td>
<td>Mid-Infrared</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbon</td>
</tr>
<tr>
<td>PANH</td>
<td>Polycyclic Aromatic Nitrogen Heterocycle</td>
</tr>
<tr>
<td>PC</td>
<td>Principal Component</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>PDR</td>
<td>Photodissociation Region</td>
</tr>
<tr>
<td>PDRT</td>
<td>Photodissociation Region Toolbox</td>
</tr>
<tr>
<td>rms</td>
<td>root mean square</td>
</tr>
<tr>
<td>SL</td>
<td>Short Low</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal to Noise Ratio</td>
</tr>
<tr>
<td>SWS</td>
<td>Short Wavelength Spectrometer</td>
</tr>
<tr>
<td>UIR</td>
<td>Unidentified Infrared</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VSG</td>
<td>Very Small Grain</td>
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Chapter 1

Introduction

1.1 The mystery of the Aromatic Infrared Bands and the PAH model

The early 1970s saw the advent of infrared (IR) astronomy, ushering in a new era in molecular astrophysics. While studying the planetary nebulae NGC 7027 and BD+30°3639, Gillett et al. (1973) discovered an emission band at 11.3 \( \mu \)m. Other emission bands at 3.3, 6.2, 7.7, 8.6, and 12.7 \( \mu \)m were soon discovered in a wide variety of objects including H \( \alpha \) regions, planetary nebulae, and reflection nebulae (Gillett et al., 1975; Merrill et al., 1975; Russell et al., 1977a, 1978; Roche et al., 1989). These bands always appeared together and could not be attributed to any of the known atomic or molecular transitions at the time, so they were dubbed the Unidentified Infrared (UIR) bands. Fig. 1.1 shows one of the earliest IR spectra highlighting the broad features known as the UIR bands.

In 1983, an interesting study by Sellgren et al. (1983) provided hints into the carriers of the UIR bands. These authors observed the UIR bands in three reflection nebulae, NGC 7023, NGC 2023, and NGC 2068, and discovered that their strength did not change with distance from the illuminating star. In the wake of this constancy, Sellgren (1984) proposed that small grains (of \(~10\ \text{Å} \text{ in size}) can momentarily get heated to high temperatures \(~1000\text{K}\) after absorption of an ultraviolet (UV) photon, and subsequently cool down by IR emission giving rise to the UIR bands. Duley & Williams (1981) pointed out that the 3.3 and 11.3 \( \mu \)m bands correspond to vibrational modes of aromatic molecules. This prompted Leger & Puget (1984) and Allamandola et al. (1985) to propose that the UIR bands originate from the vibrational modes of Polycyclic Aromatic Hydrocarbon (PAH) molecules, giving rise to the PAH model. PAHs can efficiently absorb UV radiation and, due to their small heat capacity, can get heated to high temperatures and subsequently cool down by IR fluorescence through their vibrational modes. PAHs are now widely recognized as the carriers of the UIR bands, therefore also referred to as the Aromatic Infrared Bands (AIBs) or the PAH bands. Throughout this thesis, we use the terms “AIBs” and “PAH bands” interchangeably. For the sake of completeness, we mention that a number of other carriers, most notably small, partially hydrogenated amorphous carbon grains, have also been proposed as the carriers of the AIBs (Jones et al., 2013). In this thesis, however, we consider PAHs as the carriers of the AIBs.

PAHs have been observed across the Universe from the interstellar medium (ISM) of the...
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2

Milky Way to the ISM of other galaxies with redshift of up to $\sim 4$ (e.g. Verstraete et al., 1996; Peeters et al., 2002b; Brandl et al., 2006; Geers et al., 2006; Armus et al., 2007; Riechers et al., 2014). The astrophysics of PAHs is an active research field with considerable effort going towards identifying the characteristics of the astronomical PAH population and the role these molecules play in the evolution of the ISM. In this chapter, we review the current state of knowledge of PAH astrophysics and the big questions pertaining to these molecules that remain unanswered.

1.2 Polycyclic Aromatic Hydrocarbons

PAHs are a family of planar organic molecules containing two or more benzene ($C_6H_6$) rings fused together, resulting in a honeycomb structure with hydrogen (H) atoms at the periphery of the structure. Fig. 1.2 shows the molecular structure of benzene and some representative PAH molecules. Each carbon (C) atom in a PAH molecule has four valence electrons. Three of these valence electrons are in $sp^2$ hybridized orbitals and form sigma ($\sigma$) bonds with the adjacent C or H atoms resulting in a planar structure. The remaining fourth valence electron is in a p orbital perpendicular to the plane of the molecule defined by the $\sigma$ bonds. These p orbitals of adjacent C atoms overlap to form $\pi$ bonds with a delocalized electron cloud above and below the plane of the molecule, thereby making the PAH molecules aromatic and hence very stable.

In the context of the AIBs, the term “PAHs” refers to a rather broad family of species, including conventional PAHs and some closely related species. Few examples of such species
are fully or partially dehydrogenated PAHs, superhydrogenated PAHs, and chemically modified PAHs in which another element or a side group replaces C or H atom. There are currently two schools of thought regarding the astronomical PAH family: the “grand-PAH” hypothesis and the “multi-PAH” hypothesis. According to the “grand-PAH” hypothesis, AIBs result from a few compact and stable PAHs known as grand-PAHs (Tielens, 2013; Andrews et al., 2015). On the other hand, according to the “multi-PAH” hypothesis, the astronomical PAH family comprises of a mix of all kinds of PAHs (Rosenberg et al., 2014). The determination of the correct hypothesis awaits the identification of the individual PAH molecules in the astronomical PAH family, which have eluded detection in the IR because all PAH molecules exhibit IR bands in the same wavelength range. Using radio observations, however, McGuire et al. (2021), Cernicharo et al. (2021), and Burkhardt et al. (2021) recently reported the detection of a pure PAH molecule, indene (C$_9$H$_8$), and two nitrile-group–functionalized PAHs, 1- and 2-cyanonaphthalene, in the TMC-1 molecular cloud. Small aromatic molecules like benzene and benzonitrile (Cernicharo et al., 2001; McGuire et al., 2018) and PAH-related species like fullerenes (e.g. C$_{60}$ and C$_{70}$; Cami et al., 2010; Sellgren et al., 2010), have also been unequivocally detected in the ISM. The discovery of these molecules lends very strong support to the PAH model, as these species are either building blocks in the PAH formation process or byproducts of the photo-processing of the PAH population in the ISM.

1.2.1 IR Emission from PAHs

PAH molecules emit IR radiation following their excitation through absorption of a UV photon. Fig. 1.3 shows the emission mechanism of PAHs using the energy level diagram of a neutral PAH molecule. A neutral molecule consists of a series of singlet ($S_n$) and triplet ($T_n$) states with $S_0$ as the ground state and the first triplet state $T_1$ lying between $S_0$ and the first
excited singlet state $S_1$. A charged PAH molecule, on the other hand, consists of doublet ($D_n$) and quartet ($Q_n$) states with $D_0$ as the ground state and the first excited quartet state $Q_1$ lying above the first excited doublet state $D_1$. A PAH molecule in its ground state absorbs a UV photon and undergoes a transition to an upper electronic state ($S_1, S_2$ or higher in neutral PAHs; $D_1, D_2$, or higher in charged PAHs). The excited molecule then undergoes a series of radiative and non-radiative transitions. Among the non-radiative transitions, a PAH molecule can undergo internal conversion from a highly excited state to the vibrational manifold of a lower-lying state of the same multiplicity (e.g. from $S_2 \rightarrow$ the vibrational manifold of $S_1$), or the molecule can undergo intersystem crossing from an excited state to the vibrational manifold of a lower-lying state of different multiplicity (e.g. from $S_1 \rightarrow$ the vibrational manifold of $T_1$). Either of these non-radiative transitions leaves the PAH molecule in a highly excited vibrational state. This highly vibrationally excited PAH molecule then de-excites following radiative transitions, namely fluorescence involving a transition from a highly excited electronic state to a lower electronic state of the same multiplicity (e.g. radiative transition from $S_1$ to $S_0$), phosphorescence from a higher excited electronic state to a lower-lying electronic state of different multiplicity (e.g. radiative transition from $T_1$ to $S_0$) and infrared vibrational relaxation through specific vibrational modes. It is this infrared vibrational relaxation process that results in the emission features of PAHs (the AIBs) that we observe in astrophysical environments.

1.3 A detailed look at the AIBs

A typical mid-IR spectrum from 3–20 $\mu$m (see Fig. 1.4) contains a plethora of features such as H i recombination lines, fine structure lines, molecular hydrogen ($H_2$) lines, and dust features. However, it is primarily dominated by strong and broad AIBs at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.7 $\mu$m. Numerous weaker AIBs (at 3.4, 3.5, 5.25, 5.75, 6.0, 6.9, 10.5, 11.0, 12.0, 12.7, 13.5, 14.2, 15.8, 16.4, 17.4, and 17.8 $\mu$m) accompany the main AIBs. These AIBs are perched on the top of broad plateaus ranging from 3.2–3.6, 6–9, 11–14, and 15–19 $\mu$m. Although the
Chapter 1. Introduction

Figure 1.4: An example of mid-IR emission from a typical photodissociation region, the Orion bar, highlighting PAH features perched on top of plateaus and the underlying continuum (Peeters et al., 2004a). The vibrational modes associated with the PAH features are indicated at the top. Figure taken from Peeters et al. (2021). Reprinted with permission from Peeters et al. (2021). Copyright 2021 American Chemical Society.

The exact origin of the plateaus is uncertain, these are generally attributed to clusters of PAHs (Allamandola et al., 1989; Bregman et al., 1989; Tielens, 2008). Furthermore, all these emission features and plateau components are lying on top of a rising continuum. Very small grains (VSGs; nanometer-sized), or hot equilibrium grains are thought to be responsible for this underlying continuum (Sellgren et al., 1985; Bregman et al., 1989; Cesarsky et al., 2000; Berné et al., 2007). In the following sections, we will present a comprehensive review of the spectral characteristics of the AIBs.

1.3.1 Feature assignments

The AIBs arise from various vibrational modes of PAHs, such as stretching and bending vibrations of C-H and C-C bonds (Allamandola et al., 1989). Stretching vibrations are typically associated with changes in bond length in the plane of the molecule, whereas bending vibrations are associated with changes in the bond angle. If a change in the bond angle is confined to the plane of a molecule, the resulting vibration is known as an in-plane bending vibration, whereas a change in the bond angle with respect to the plane of the molecule is known as an
out-of-plane bending vibration. The vibrational modes dependent on nearest neighbour interactions of C and H atoms result in AIBs at wavelengths below 15 µm. The C-H stretching mode gives rise to the 3.3 µm band, the C-C stretching mode to the 6.2 µm band, the C-C stretching mode and C-H in-plane bending mode to the 7.7 µm band, the C-H in-plane bending mode to the 8.6 µm band, the C-H out-of-plane bending modes to the emission features in the 10 - 15 µm region, and combination modes to the weak features in the 5 - 6 µm region. Since the equivalent lengths and angles of C-C and C-H bonds are very similar for all PAH molecules, similar energies are required to excite or relax the vibrational modes associated with these bonds. As a result, the assignments of features below 15 µm are generic for the entire PAH family. On the other hand, the emission features in the wavelengths longer than 15 µm are molecule specific since these features are a result of the in-plane and out-of-plane bending modes of the carbon skeleton and are considered as the fingerprints of a specific PAH molecule. Furthermore, as discussed in section 1.2, the definition of PAHs in the context of AIBs is not strictly confined to aromatic molecules but rather encompasses a broad category of PAH related species. As a result, some of the weak AIBs are assigned to the vibrational modes of such species; for example, the 3.4 µm band is assigned to an aliphatic C-H stretching mode due to a methyl side group attached to a PAH molecule or a superhydrogenated PAH molecule, the 6.0 µm band is assigned to a C-O stretching mode, and the 6.9 µm band is assigned to an aliphatic C-H bending mode (Duley & Williams, 1981; Jourdain de Muizon et al., 1986; Allamandola et al., 1989).

### 1.3.2 Spectral Variations

To first order, all IR PAH emission from individual sources and spatially from within extended sources is very similar, but a closer look reveals the presence of spectral variations in terms of relative band strengths and band profiles (e.g. Joblin et al., 2000; Verstraete et al., 2001; Hony et al., 2001; Peeters et al., 2002b; Bregman & Temi, 2005; Galliano et al., 2008; Peeters et al., 2017; Boersma et al., 2018). Moreover, the intensities of some bands correlate better with each other than the other bands. The subtleties of PAH emission spectra encode the precise molecular characteristics, e.g. charge, size, structure, and chemical composition, of the astronomical PAH population. Combining knowledge of the observed spectral variations and correlations with experimental/theoretical data on PAH characteristics can yield information about the molecular characteristics of the astronomical PAH population, which we discuss in detail in section 1.4. In this section, we will discuss the spectral variations observed in PAH features.

#### Relative intensity variations and correlations

The relative intensities of the PAH bands vary between astronomical sources and within extended sources. The most prominent variations are observed in the intensities of the 6.2, 7.7, 8.6, and 11.0 µm bands in comparison to the intensities of the 3.3 and 11.2 µm bands with the intensities of the former four bands tightly correlating with each other and the latter two bands correlating with each other globally (e.g. Joblin et al., 1996b; Bregman et al., 1989; Hony et al., 2001; Vermeij et al., 2002; Galliano et al., 2008; Peeters et al., 2017). Fig. 1.5 shows these well-known correlations between major PAH bands. Although the intensities of the 3.3
and 11.2 µm bands show correlation with each other, variations in these two band intensities have also been observed (Croiset et al., 2016; Knight et al., 2021a). In the 10–15 µm region, the most prominent variations occur between the intensities of the 11.2 and 12.7 µm bands when comparing the PAH spectra across various environments. Particularly, in evolved stars, the 11.2 µm band emerges as a dominant feature and the 12.7 µm band as a weak feature, whereas in H II regions, both 11.2 and 12.7 µm bands emerge as dominant features. Furthermore, the intensity of the 12.7 µm band has been found to have a good correlation with that of the 6.2, 7.7, and 8.6 µm bands in a wide range of environments (Hony et al., 2001).

Aside from variations in the major bands, variations in the intensities of weak features have also been observed. For example, variations in the relative intensities of a strong 3.3 µm band and a weak 3.4 µm band have been observed band in a handful of sources (Geballe et al., 1985; Joblin et al., 1996a; Sloan et al., 1997; Pilleri et al., 2015). The 7.7 µm band consists of at least two sub-components (at 7.6 and 7.8 µm), the intensities of which vary with respect to one another (e.g. Bregman et al., 1989; Cohen et al., 1989; Verstraete et al., 2001; Peeters et al., 2002b; Bregman & Temi, 2005; Peeters et al., 2017). There are numerous weak features in the 15–20 µm range that vary in relative intensity with respect to one another. In particular, the intensities of the 16.4, 17.4, and 17.8 µm correlates with each other and with the 11.0 and 12.7 µm bands outside the 15–20 µm range. On the other hand, the intensity of the 15.8 µm correlates with the 11.2 µm band and with none of the other bands in the 15–20 µm range (Boersma et al., 2010; Peeters et al., 2012; Shannon et al., 2015).
Profile variations

There are clear variations in the peak positions and profile shapes of the major PAH bands observed in a large number of sources in our Galaxy and neighbouring galaxies such as the Magellanic Clouds. This has led to the classification of PAH profiles into four classes: A, B, C, and D (Peeters et al., 2002b; van Diedenhoven et al., 2004; Matsuura et al., 2014). Fig. 1.6 shows the PAH classification for the 6–9 \(\mu\)m region. The C-C stretching band in class A peaks at 6.2 \(\mu\)m and has an asymmetric profile, whereas this band is rather symmetric for class B, C, and D sources for which the band is shifted to longer and longer wavelengths. The largest profile variations are however seen in the 7-9 \(\mu\)m region. Class A and B sources exhibit traditional PAH features at 7.7 and 8.6 \(\mu\)m which are shifted towards longer wavelengths in Class B compared to Class A. In addition, the relative intensity of the two sub-components of the 7.7 \(\mu\)m band (at 7.6 and 7.8 \(\mu\)m) varies with the 7.6 \(\mu\)m component dominating in class A profiles and the 7.8 \(\mu\)m component dominating in class B profiles. Class C and D, on the other hand, have a single broad feature in the 7-9 \(\mu\)m region which peaks at 8.2 \(\mu\)m in class C profiles and at \(\sim\) 7.7 \(\mu\)m in class D profiles.

These classes are related to the type of object, with ISM-type sources (e.g. \(\text{H} \\Pi\) regions, reflection nebulae, and the diffuse ISM) exhibiting Class A profiles and circumstellar material (e.g. in planetary nebulae, post asymptotic giant branch (AGB) objects, and protoplanetary disks associated with Herbig AeBe stars or T Tauri stars) exhibiting Class B profiles (Peeters et al., 2002b; van Diedenhoven et al., 2004). Classes C and D have been observed in a very small number of AGB objects (Matsuura et al., 2014). Furthermore, except for Class D sources, there appears to be an anti-correlation between the peak position of the bands and the effec-
Figure 1.7: Absorption spectra of a mixture of neutral PAHs in the top panel and ionized (cations) PAHs in the bottom panel (Allamandola et al., 1999). Cationic PAHs exhibit strong spectral features in the 6–9 \( \mu \text{m} \) region, whereas neutral PAHs exhibit strong features at 3.3 and 11.2 \( \mu \text{m} \). Figure taken from Peeters et al. (2002b), reproduced with permission © ESO.

The effective temperature of the central star (Sloan et al., 2007). These observations, which link the PAH Classes to their host environments, imply that PAHs undergo photo-processing in their host environments, altering the composition of the PAH family, which is then reflected in the characteristics of emission we observe.

### 1.4 Information obtained from AIBs

A detailed analysis of the IR PAH emission combined with theoretical and experimental spectroscopy of a large collection of PAH molecules reveals some of the characteristics of the astronomical PAH population. In this section, we will discuss how we obtain information about the PAH characteristics from the AIBs.

#### 1.4.1 Charge State

The charge state of PAHs dominates their IR spectral characteristics. Experimental and theoretical studies have shown that a change in the charge state of PAHs influences the spectral characteristics dramatically. While PAH cations exhibit intrinsically strong C-C modes (6-9 \( \mu \text{m} \) region) and weak C-H modes (3.3 and 11.2 \( \mu \text{m} \) region), this trend is reversed for neutral PAHs (Figure 1.7; Langhoff, 1996; Hudgins & Allamandola, 1999). Though less studied, PAH anions also exhibit strong C-C modes and weak C-H modes. As a consequence, the relative
intensity of the major features due to C-C modes vs the C-H modes is traditionally used to trace the PAH charge state. Intensities of the weak features are also influenced by the charge state of PAHs. In particular, the weak 11.0 \( \mu \text{m} \) (a C-H out-of-plane bending mode) band is intrinsically strong in ionized PAHs as opposed to neutral PAHs. Therefore, the relative intensity of the weak 11.0 \( \mu \text{m} \) band with respect to the strong 11.2 \( \mu \text{m} \) band is also used to trace the charge state of PAHs (Rosenberg et al., 2011). Since the most prominent variations in the observed PAH emission spectra are in the relative intensities of the 6.2, 7.7, 8.6, and 11.0 \( \mu \text{m} \) vs the 3.3 and 11.2 \( \mu \text{m} \) (see section 1.3.2), the PAH charge balance is the key driver of the observed spectral variations and well-established correlations between the main PAH bands (e.g. Joblin et al., 1996b; Sloan et al., 1999; Allamandola et al., 1999; Bregman & Temi, 2005; Compiègne et al., 2007; Galliano et al., 2008; Rosenberg et al., 2011; Peeters et al., 2017).

### 1.4.2 Edge Structure

Features in the 11–14 \( \mu \text{m} \) region reveal information about the edge structure of PAHs. This region harbours two strong features at 11.2 and 12.7 \( \mu \text{m} \) and a couple of weaker features at 11.0, 12.0, 12.7, 13.5, and 14.6 \( \mu \text{m} \). These features are characteristic of the C-H out-of-plane bending modes whose precise peak wavelength depends on the number of adjacent hydrogen atoms at the periphery of the molecule, i.e. on the number of adjacent peripheral C-H bonds (Hudgins & Allamandola, 1999; Hony et al., 2001). Laboratory and theoretical studies show that the 11.0 and 11.2 \( \mu \text{m} \) bands are characteristic of solo C-H mode (1 peripheral C-H bond per cyclic unit), the 12.0 \( \mu \text{m} \) of duo C-H mode (2 adjacent peripheral C-H bonds per cyclic unit), 12.7 \( \mu \text{m} \) of trio C-H mode (3 adjacent peripheral C-H bonds per cyclic unit), 13.5 and 14.2 \( \mu \text{m} \) of quartet C-H modes (4 adjacent peripheral C-H bonds per cyclic unit). Fig. 1.8 shows examples of molecular structures of PAHs with different types of C-H out-of-plane bending modes indicating that the predominance of solo peripheral C-H bonds corresponds to molecules with long straight edges. In contrast, duos, trios, and quartets are associated with corners implying an irregular molecular structure.

Theoretical calculations have also revealed the impact of the molecular structure on other PAH bands. The 16.4 \( \mu \text{m} \) band, in particular, has been found to be strong in PAHs containing pendant rings (Moutou et al., 2000; Van Kerckhoven et al., 2000; Peeters et al., 2004b; Boersma et al., 2010). Moreover, recent studies have revealed that in addition to charge, the features in the 7–9 \( \mu \text{m} \) region are also sensitive to the molecular structure of PAHs, with the 7.6 \( \mu \text{m} \) band being strong in compact PAHs, the 8.2 \( \mu \text{m} \) band in irregular PAHs, and the 8.6 \( \mu \text{m} \) band in large symmetric PAHs (Bauschlicher et al., 2008, 2009; Ricca et al., 2012; Peeters et al., 2017).

### 1.4.3 Size

PAH photo-physics lies at the origin of the influence of PAH size on the emission characteristics. When a UV photon of specific energy is absorbed, a small PAH molecule, which has fewer vibrational modes than a large PAH molecule, obtains a higher average energy per mode than the larger PAH molecule because the absorbed photon energy is redistributed over a smaller number of vibrational modes. As a result, smaller PAH molecules are vibrationally “hotter” and emit more strongly at shorter wavelengths, while larger PAH molecules emit strongly at longer wavelengths. Therefore, the relative intensities of strong PAH features on opposite ends
of the spectra spanning a wide wavelength range will hold information about the size of the emitting species. Taking this into account, the relative intensities of the solo C-H out-of-plane bending mode (at 11.2 µm in neutrals and 11.0 µm in cations) and the C-H stretching mode (at 3.3 µm) are used as a tracer of PAH size (Allamandola et al., 1989; Schutte et al., 1993; Ricca et al., 2012; Maragkoudakis et al., 2020; Knight et al., 2021a). Since both the 3.3 and 11.2 µm features are associated with neutral PAHs, the ratio of 11.2/3.3 is independent of the charge state of PAHs. Theoretical studies by Ricca et al. (2012) and Maragkoudakis et al. (2020) have shown that the relative intensity of these PAH features does, indeed, correlate with the number

Figure 1.8: Molecular structure of some PAH molecules highlighting the number of solo, duo, trio, and quartet C-H out-of-plane bending modes. Figure taken from Hony et al. (2001), reproduced with permission © ESO.
of C atoms ($N_C$) in PAHs (see Fig. 1.9).

### 1.4.4 Chemical Composition

The mid-IR spectra, as shown in Fig. 1.4, are extremely rich in weak PAH features and show significant substructure in various PAH bands. The intensities, peak positions, and profile shape of these PAH features reveal subtle details about the chemical composition of the PAH population and their evolution in astrophysical environments. There is a wealth of literature on the chemical composition of the PAH population. Here, we summarize some widely accepted interpretations of the chemical modification of PAHs derived from these features.

The 3.4 µm band is attributed to the aliphatic C-H stretching mode due to an addition of either a methyl group or an extra H to C-H groups (Duley & Williams, 1981; Jourdain de Muizon et al., 1986; Allamandola et al., 1989). Additional aliphatic bands are detected at 6.9 and 7.2 µm (e.g. Buss et al., 1990; Bouwman et al., 2001; Sloan et al., 2007). Similarly, the 6.0 µm band is linked to a quinone (CO) sidegroup attached to a PAH molecule (Allamandola et al., 1989). A list of wavelengths associated with possible side groups attached to a PAH molecule can be found in Tielens (2008). The weak features at 4.4 and 4.65 µm are assigned to the aromatic and aliphatic C-D stretching modes of deuterated PAHs respectively (Peeters et al., 2004c; Hudgins et al., 2004; Doney et al., 2016). Hetero-atom substitution of a C atom in a PAH molecule, in particular a substitution by N (PANHs), has been put forward as the origin of the class A 6.2 µm emission (Peeters et al., 2002b; Hudgins et al., 2005). The presence of nitrogen in the PAH molecule alters its electron density, causing the IR activity of the C-C stretching mode to systematically shift to shorter wavelengths.

### 1.4.5 PAH Abundance

The measurement of the total flux due to PAH emission combined with the flux due to dust yields information about PAH abundance which is measured in terms of the fraction of carbon,
Chapter 1. Introduction

\( f_C \), locked in PAHs. Since both PAHs and dust compete for the same UV photons, the ratio of their IR fluxes are related to the ratio of the UV flux absorbed by PAHs to that absorbed by dust which in turn when rewritten in terms of the standard dust parameters and measured UV cross-sections of PAHs yields \( f_C \) as follows (Allamandola et al., 1989):

\[
f_C = 1.086 \frac{A_V \kappa_{UV} (1 - \omega_{UV})}{N_H \kappa_{V} \sigma_{UV} A_C} \frac{f_{IR}}{(1 - f_{IR})}
\]

where \( A_V / N_H \) is the dust extinction per H atom, \( \kappa_{UV} / \kappa_{V} \) is UV to visual extinction cross-section of dust, \( \omega_{UV} \) is the dust albedo in UV, \( \sigma_{UV} \) is the UV absorption cross-section of PAHs per C atom, \( A_C \) is the elemental C abundance, and \( f_{IR} \) is the ratio of the flux due to PAH emission to the flux due to dust.

1.5 The lifecycle of astronomical PAHs

The PAH population in space is not static but is continuously evolving. In this section, we discuss two aspects of the lifecycle of these molecules: their formation and subsequent evolution in the ISM.

1.5.1 PAH Formation

Despite the substantial amount of research done in the field of PAHs, their exact formation mechanism is not fully established. There are two main PAH formation pathways: bottom-up processes, where PAHs are formed from smaller hydrocarbon molecules, and top-down processes, where PAHs are formed through fragmentation of large carbonaceous grains. In this section, we briefly summarize both pathways.

**Bottom-up formation**

Bottom-up processing typically occurs in the circumstellar environments of C-rich AGB stars, where the conditions (temperature and density) are favourable for the formation of PAHs from smaller hydrocarbons (Frenklach & Feigelson, 1989; Cherchneff et al., 1992; Buss et al., 1991; Boersma et al., 2006). The first step in this process, which is also a rate-limiting step, is the formation of a benzene ring. There are several reaction pathways that lead to the formation of benzene, all of which involve neutral-neutral reactions with hydrocarbon radicals and small hydrocarbons like acetylene \( C_2H_2 \) (Miller & Melius, 1992; Frenklach et al., 1988; Cole et al., 1984). Following the formation of the first benzene ring, the second step entails the addition of additional rings to form PAH molecules. The Hydrogen Abstraction Carbon Addition (HACA) mechanism proposed by Frenklach et al. (1985) is one of the most studied mechanisms for further ring growth. This involves repeated steps for the formation of radical sites on benzene via hydrogen abstraction and subsequent addition of \( C_2H_2 \) ultimately resulting in the formation of a new aromatic ring. Recently, other mechanisms are proposed for further ring growth such as Hydrogen Abstraction Vinylacetylene Addition, Phenyl Addition–DehydroCyclization, Radical–Radical Reactions, and Methylidyne Addition–Cyclization–Aromatization (Kaiser & Hansen, 2021). Our understanding of the bottom-up processing route for PAH formation,
however, is still rudimentary because the efficiencies of the reactions involved in the relevant astrophysical environments are not well known and other reaction pathways have not been fully explored (Kislov et al., 2013; Kaiser & Hansen, 2021).

Top-down formation

Top-down processing of PAHs occurs primarily in interstellar environments. There are numerous top-down processing routes to PAH formation. In one pathway, the energetic processing of carbonaceous dust grains via grain-grain collisions in interstellar shocks can result in the fragmentation of these dust grains into smaller and smaller PAH molecules (Jones et al., 1996). In the other pathway, proposed by Cesarsky et al. (2000) and Pilleri et al. (2012), PAHs form through the photoprocessing of VSGs by the UV radiation field of stars and shock waves. There is some observational evidence in support of these top-down formation routes. Berné et al. (2007) performed a Blind Signal Separation on PAH emission in reflection nebula NGC 7023 and extracted three distinct signals; two due to PAHs (neutral and ionized) and one due to VSGs. These signals showed different spatial distribution, with ionized PAHs found closest to the star, neutral PAHs slightly farther away from the star, and VSGs deeper into the molecular cloud. The spatial distribution of the signals is evidence of the photoprocessing of VSGs into PAHs due to the increased UV radiation field closer to the star. Moreover, the relative intensity of the weak 3.4 μm band characteristic of an aliphatic C-H stretching mode with respect to the strong 3.3 μm band characteristic of an aromatic C-H stretching mode decreases with the increased intensity of the UV radiation field of the star reflecting the photoprocessing from more aliphatic composition to an aromatic composition (e.g. Geballe et al., 1989; Joblin et al., 1996a; Sloan et al., 1997; Pilleri et al., 2015). VSGs and dust grains are known to have aliphatic components (e.g. Kwok et al., 2001; Goto et al., 2003; Sloan et al., 2007); therefore, the decrease of the 3.3/3.4 ratio is also indirect evidence of the top-down formation scenario.

More recently, Merino et al. (2014) proposed yet another top-down route for PAH formation via hydrogen processing of silicon-carbide (SiC) dust grains in circumstellar environments. These SiC grains are covered with layers of graphite and UV processing followed by interactions with H at high temperatures found in circumstellar environments can cause surface erosion, resulting in the formation of first graphene sheets and then PAHs.

1.5.2 PAH Evolution

PAHs are subjected to physical and chemical processing throughout their life cycle. They can be ionized, undergo structural changes, or be destroyed by stellar UV photons. There is plenty of observational evidence demonstrating the modification of the PAH population in their host environments. For example, variations in the intensities of the ionized (6.2, 7.7, and 8.6 μm) and neutral (3.3 and 11.2 μm) PAH bands in different environments as well as within extended environments shows that the charge state of PAHs changes (e.g. Joblin et al., 1996a; Sloan et al., 1997; Bregman & Temi, 2005; Berné et al., 2007). A decrease in the average size of PAHs with distance from the illuminating star was reported for the reflection nebulae NGC 7023 and NGC 2023 (Fig. 1.10; Croiset et al., 2016; Knight et al., 2021a). The star’s UV field destroys small PAHs, resulting in an increase in average size. The results of these studies demonstrate the ongoing photochemical evolution of PAHs. The photo processing
of PAHs in terms of molecular structure was shown by Hony et al. (2001) by analyzing the features in the 11-14 $\mu$m region in a sample of H ii regions, Young Stellar Objects, and evolved stars. They showed that large, compact PAHs dominate the PAH population in circumstellar environments, in contrast to the interstellar environments where small irregular PAHs dominate the PAH population, thereby highlighting the photoprocessing of PAHs as they evolved in the ISM. Peeters et al. (2017) highlighted a detailed picture of the UV-processing of PAHs in extended environments by analyzing the spatial distribution of PAH emission in NGC 2023. The results of their analysis revealed that at the edge of the molecular cloud, IR emission is dominated by VSGs and PAH clusters. As the distance to the star decreases, VSGs and PAH clusters are dissociated into large PAHs, which are further photo-processed into smaller compact PAHs or ionized PAHs due to increased UV radiation closer to the star.

PAH molecules can also be processed into different species. Berné & Tielens (2012) found that in NGC 7023, closer to the star, the PAH abundance decreases while the C$_{60}$ fullerene abundance increases (see Fig. 1.11). These authors suggested that the decrease in the PAH abundance is due to their photoprocessing into C$_{60}$ fullerene. They hypothesized that PAHs are subjected to photoprocessing by first dehydrogenating and then isomerizing into fullerenes. In cold and dense environments, PAHs can condense onto ice mantles covering the surface of dust grains (Bregman et al., 2000). Further reactions on these ice mantles can subsequently lead to the formation of complex molecules (Bernstein et al., 1999; Gudipati & Allamandola, 2003; Bouwman et al., 2011). Furthermore, high energy photons, cosmic rays, and strong shocks driven into the ISM by supernova explosions can completely or partially destroy PAHs (Jones et al., 1996; Micelotta et al., 2010, 2011).
1.6 The importance of PAHs in astronomy

PAHs are ubiquitous in the Universe, accounting for up to 15% of the cosmic carbon (Allamandola et al., 1989). Moreover, emission from PAHs represents up to 20% of the total IR power of the Milky Way and star-forming galaxies (Madden et al., 2006; Smith et al., 2007). Thus, given their large abundance and ubiquitous nature in space combined with their unique molecular characteristics, PAHs play an important role in a wide range of physical and chemical phenomena occurring in the Universe. In this section, we give an overview of the many roles that PAHs play in the Universe.

1.6.1 PAHs as drivers for interstellar physics and chemistry

We highlight a few important physical and chemical processes in which PAHs play a significant role. First, PAHs regulate the charge balance of the interstellar gas in H\textsc{i} regions, photodissociation regions (PDRs), and molecular clouds. Essentially, PAHs provide an alternative route for electron recombination of atomic and molecular ions through mutual neutralization reactions with PAH anions, thereby influencing the abundance of neutral and charged species in the ISM (Lepp & Dalgarno, 1988; Lepp et al., 1988).

Through the photoelectric effect, PAHs dominate the gas heating in the neutral ISM (D’Hendecourt & Leger, 1987; Lepp & Dalgarno, 1988; Verstraete et al., 1990; Bakes & Tielens, 1994). The absorption of UV photons by PAHs can also result in photo-ionization instead of IR emission. The ejected photo-electrons carry away some of the photon energy as kinetic...
energy which results in the heating of the gas through collisions. Bakes & Tielens (1994) calculated the photoelectric heating of species of various sizes and found that species of size less than 15 Å, consisting of PAHs and PAH clusters, cause approximately half of the gas heating (see Fig. 1.12). PAHs thus play a significant role in the evolution of the neutral ISM. This includes the surface layers of protoplanetary disks and thus the formation of planetary systems, which is a topic of major interest in modern astrophysics. Indeed, the energetic electrons produced upon photoionization of PAHs heat the gas and set the temperature in the surface layer of the disk which drives the far-UV photoevaporation of the gas at a critical planet-forming epoch in the lifetime of disk evolution (e.g. Kamp & Dullemond, 2004; Jonkheid et al., 2004; Gorti & Hollenbach, 2008; Champion et al., 2017).

PAHs also serve as catalysts in the formation of H$_2$ in dense PDRs (Habart et al., 2004; Boschman et al., 2015; Castellanos et al., 2018). There are currently two proposed mechanisms for the formation of H$_2$: the photodesorption and the abstraction mechanism. In the photodesorption mechanism, H$_2$ formation is a relaxation channel for a UV-excited PAH molecule (i.e. PAH fragmentation through H$_2$ loss; Jochims et al., 1994; Allain et al., 1996; Le Page et al., 2001; Boschman et al., 2015; Andrews et al., 2016; Castellanos et al., 2018). Alternatively, in the abstraction mechanism, H$_2$ forms when a gas phase H atom forms a covalent bond with a PAH cation and subsequently abstract an H atom from the PAH molecule to form H$_2$ (Rauls & Hornekaer, 2008; Thrower et al., 2012; Foley et al., 2018; Mennella et al., 2021). Although the precise route for H$_2$ formation via PAHs is still debated, there is agreement on the important role of PAHs in the H$_2$ formation process in dense PDRs.
Finally, photoprocessing of PAHs in the ISM leads to a rich interstellar chemistry. UV photolysis in strong radiation fields (i.e. near stars) leads to dehydrogenated PAHs eventually resulting in either fragmentation of dehydrogenated species to smaller carbon chains or isomerization to cages or fullerenes (e.g. Le Page et al., 2001, 2003; Tielens, 2005; Berné & Tielens, 2012). In addition, processing of PAHs by energetic ions in shocks, supernova remnants, and by cosmic rays leads to fragmentation of PAHs to smaller hydrocarbons and complex organic molecules (e.g. Micelotta et al., 2010, 2011).

1.6.2 PAHs as diagnostic tools

The diagnostic capabilities of PAHs are widely used in extragalactic studies. PAH emission is often used as a tracer of star formation in galaxies, one of the key indicators of galaxy evolution (e.g. Peeters et al., 2004c; Calzetti et al., 2007; Shpley et al., 2016; Maragkoudakis et al., 2018; Calzetti, 2020). Observations of many nearby galaxies have revealed a correlation between the strength of the PAH emission and the IR luminosity (e.g. Pope et al., 2008; Riechers et al., 2014). Essentially, PAHs are most efficiently excited by UV radiation, copiously produced by young massive stars, and remit it in IR thus serving as a dye to trace the star formation activity. However, there are caveats in using PAHs as tracers of star formation. Firstly, the PAH molecules can get excited by UV photons from evolved stellar populations which are not related to the recent star formation thereby over-estimating star formation rate. Secondly,
PAHs can get destroyed by the harsh radiation field of Active Galactic Nuclei (AGN), thereby under-estimating star formation rate in galaxies hosting AGN. Finally, the PAH abundance drastically decreases at very low metallicities complicating quantitative relationships between the PAH emission and the star formation rate (Calzetti, 2020). Nevertheless, PAHs have the potential to probe star formation rate provided the above mentioned caveats are carefully taken into account. A large number of extragalactic studies have also revealed a correlation between PAH emission and CO emission, making them the tracers of molecular gas as well (e.g. Regan et al., 2006; Sandstrom et al., 2010; Cortzen et al., 2019).

The spectral variations observed in PAH bands are a manifestation of changes in the molecular characteristics of PAHs due to changing physical conditions such as the strength of the UV radiation field, gas density, and gas temperature of their host environment. As a result, PAHs are potentially an effective tool for determining the physical conditions of the environments in which they reside. Following this idea, several authors have investigated the potential of PAHs to probe the physical conditions. E.g., Galliano et al. (2008) used few well studied galactic regions to derive an empirical relationship between the PAH charge state (traced by the 6.2/11.2 ratio) and the ratio of the ionization to the recombination rate given by $\gamma = G_0 T_{\text{gas}}^{1/2} n_e$ that sets the PAH charge state (see Fig. 1.13). Here $G_0$ is the intensity of the radiation field in units of the average interstellar radiation field (the Habing field = $1.6 \times 10^{-3}$ erg cm$^{-2}$ s$^{-1}$), $T_{\text{gas}}$ is the gas temperature, and $n_e$ is the electron density. Boersma et al. (2015) derived a slightly different relationship between the 6.2/11.2 and the $G_0 T_{\text{gas}}^{1/2} n_e$ based on their analysis of PAH emission in NGC 7023. Boersma et al. (2015) attributed the differences in the two relationships to the different treatment of the measurement of PAH band fluxes. In a recent study, Stock & Peeters (2017) discovered a link between $G_0$ and the 7.8/7.6 PAH band ratio. PAHs carry immense potential in determining the physical conditions of astrophysical regions. However, the precise relationships between PAH emission and the physical conditions of their host environment are yet to be fully developed (see section 1.7).

1.7 Big Questions

Significant progress has been made in our understanding of the molecular astrophysics of astronomical PAHs owing to the large amount of observational, experimental, and theoretical studies carried out to date and, importantly, to the numerous excellent interdisciplinary collaborations in the field. Nevertheless, several key questions still remain unanswered. Some of the big questions pertaining to this field are discussed in this section.

1. Which specific molecules make up the astronomical PAH family?

Until 2021, one of the most significant challenges to the astronomical PAH model was the lack of an unambiguous detection of a specific PAH molecule. Only recently, in 2021, McGuire et al. (2018), Cernicharo et al. (2021), and Burkhardt et al. (2021) reported the detection of a few small PAH molecules in the molecular cloud of TMC-1 using radio data. The discovery of these molecules is a major breakthrough and a strong argument in favour of the astronomical PAH model. However, the composition of the PAH population in various environments, from molecular clouds such as TMC-1 to more irradiated PDRs, still remains elusive.
2. What are the major factors responsible for variations in the spectral characteristics of the PAH emission?

Based on experimental and theoretical studies, we have been able to relate (some of) the spectral variations in the PAH emission to molecular properties of PAHs. However, we only have a first-order, qualitative understanding of the parameters that are driving the PAH emission characteristics. On the observational front, our progress is hampered by the fact that AIBs result from a PAH population (rather than a single PAH molecule) and the complex interplay of various molecular properties of PAHs complicates the interpretation of the observed PAH emission. On the theoretical front, we lack a comprehensive photochemical evolution model of the PAH population to interpret the astronomical observations which is in part due to the lack of quantitative measurements of PAH characteristics.

3. How can PAH emission spectra be used as a tool to probe local physical conditions?

Despite significant progress in understanding the relationship between PAHs and physical conditions, full diagnostic capabilities of PAHs are yet to be developed. There are several issues that have hampered the progress in this direction. Firstly, while the overall trends between PAH emission and the physical conditions characterized by $\gamma$ are similar, the quantitative relationship between them is not. Secondly, these empirical relationships between PAH emission features and physical conditions are not universal. Some of these relationships hold only in specific environments. Lastly, in most cases, these empirical relationships are derived from physical conditions that are not well constrained.

4. What is the exact formation mechanism of PAHs and how do they evolve in space?

As stated earlier in section 1.5.1, the precise mechanism of PAH formation is not fully understood. Likewise, while we know the various ways with which PAHs can evolve in space, their precise evolutionary scenario is not fully understood. This is due in part to the fact that we have not fully explored the PAH formation pathways experimentally, and in part to the lack of an astrochemical model that can incorporate both bottom-up and top-down formation scenarios. The lack of a comprehensive model is also responsible for our incomplete understanding of the evolution of PAHs, in addition to the lack of our understanding of specific molecular properties of the astronomical PAH population.

1.8 Thesis Outline

In this thesis, we address some of these open questions. In particular, we investigate the major factors responsible for the observed spectral variations in the PAH emission in different environments, and the utilization of PAHs as diagnostic tools of environmental conditions. This requires a thorough understanding of the astrophysical behaviour of PAHs. Against that background, we investigate PAH characteristics in astrophysical environments from an observational and a theoretical standpoint in this thesis.

In Chapters 2 and 3, we present observational studies of the PAH emission in two well studied Galactic reflection nebulae, NGC 2023 and NGC 7023. These studies focus on identifying the key parameters that drive the spectral variations in the PAH emission in response to the varying physical conditions in these environments. We perform a Principal Component
Analysis (PCA) of a set of fluxes of five PAH bands at 6.2, 7.7, 8.6, 11.0, and 11.2 µm. A PCA is a mathematical procedure that transforms a large number of correlated variables in a dataset into a smaller number of new uncorrelated variables called Principal Components (PCs). There are two advantages to using a PCA to analyze PAH emission. One is the ability to extract a set of parameters that best describe the observed PAH emission in a specific region, and the second lies in the ability to quantify the extent to which those parameters contribute to the observed PAH emission. In our studies, we further investigate the resulting Principal Components (PCs) through their correlations with various PAH band fluxes and ratios and by analyzing their spatial distributions in order to assign these PCs to physical parameters.

In Chapter 4, we develop a theoretical model to describe the PAH emission based on how the charge state of PAHs changes in different environments. This model first determines the charge state of a sample of PAHs for the full range of physical conditions present in PDRs (where PAHs reside). Based on the resulting charge balance, the model then calculates the corresponding PAH IR emission spectrum given the proper radiation field which then sets the excitation energy obtained by the PAH molecules. We validate this model against four well-known PDRs: the Orion Bar, NGC 2023, NGC 7023, and the Horsehead nebula and the diffuse ISM. Essentially, we compare the relative strengths of PAH emission features predicted by the model with the observations. In this study, we also investigate the diagnostic potential of the 6.2/11.2 and 3.3/11.2 PAH band ratios traditionally used to determine PAH charge and size.

In Chapter 5, we summarize our results and outline future projects triggered by these investigations.
Chapter 2

A Principal Component Analysis of polycyclic aromatic hydrocarbon emission in NGC 2023

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Published in Monthly Notices of the Royal Astronomical Society
https://ui.adsabs.harvard.edu/abs/2020MNRAS.500..177S/abstract

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2.1 Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a large class of complex organic molecules made of carbon and hydrogen. They are strong absorbers of UV photons and release the absorbed energy mainly through vibrational modes in the mid-infrared (MIR) with dominant emission features at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.3 µm (Sellgren et al., 1983; Leger & Puget, 1984; Allamandola et al., 1985, 1989).

PAHs have been observed in a wide variety of astronomical environments via their characteristic emission features (e.g. Joblin et al., 1996a; Sloan et al., 1999; Smith et al., 2007; Galliano et al., 2008). To first order, the PAH emission spectrum observed in diverse astronomical environments looks similar. However, there are subtle variations in relative intensities, peak positions, and profile shapes of the emission features depending on the environment in which they are observed (e.g. Hony et al., 2001; Peeters et al., 2002a; Galliano et al., 2008). These variations are not only present between the different sources but also spatially within extended sources (e.g. Bregman & Temi, 2005; Peeters et al., 2017; Boersma et al., 2018). Various experimental and theoretical studies suggest that the observed variations in the PAH emission
features are due to the changes in the properties of the PAH population such as the ionization state, size, and molecular structure (e.g. Allamandola et al., 1999; Bauschlicher et al., 2008, 2009; Ricca et al., 2012; Hony et al., 2001; Candian et al., 2014). The most prominent variations are observed in the ratio of 6.2, 7.7, and 8.6 µm bands to the 11.2 µm band, which are attributed to the changes in the ionization state of the PAHs (e.g. Allamandola et al., 1999; Galliano et al., 2008). Other observed variations include (but are not limited to) variations in the relative intensity of the short to long wavelength PAH bands (e.g. 3.3/11.2) associated with changes in the size distribution of the PAHs (e.g. Schutte et al., 1993; Ricca et al., 2012; Croiset et al., 2016; Knight et al., 2021a), and variations in the relative intensity of the 11-14 µm PAH bands associated to the edge structure of the PAHs (e.g. Hony et al., 2001; Bauschlicher et al., 2008, 2009).

The observed changes in the characteristics of the PAH population are a result of the changing physical conditions such as density, strength of the UV radiation field, temperature, and metallicity of their residing environments. This clear dependence of PAHs on their local environment makes them a potential tool to probe the physical conditions. Galliano et al. (2008) and Boersma et al. (2015) used the variations in the ionization state of PAHs to develop a diagnostic tool for tracing the physical conditions. These authors derived an empirical relation between the PAH ionization state (as traced by the 6.2/11.2 band ratio) and the so-called ionisation parameter, \( \gamma = G_0 T^{1/2}/n_e \) where \( G_0 \) is the intensity of the FUV radiation field in units of the average interstellar radiation field (the Habing field = \( 1.6 \times 10^{-3} \text{ erg cm}^{-2} \text{ s}^{-1} \)), \( T \) the gas temperature, and \( n_e \) the electron density. Recently, Pilleri et al. (2012) discovered a strong anti-correlation between \( G_0 \) and the fraction of carbon locked up in evaporating small grains (eVSGs). In addition, Stock & Peeters (2017) reported a relation between \( G_0 \) and the 7.8/7.6 PAH band ratio in Galactic H II regions and reflection nebulae. Although a great deal of work has thus been done to explore the relationships between the PAH variability and the characteristics of their environments, the precise nature of this relationship is not clear yet.

In this work, we use a statistical approach to investigate the variations in the major PAH emission features in the well-known reflection nebula NGC 2023. We perform a Principal Component Analysis (PCA) of a set of fluxes of five major PAH bands at 6.2, 7.7, 8.6, 11.0, and 11.2 µm to obtain the major driving factors of the observed variations in the PAH emission seen in NGC 2023. The paper is organized as follows. We describe the reflection nebula NGC 2023 in Section 2.2. In Section 2.3, we briefly summarize the key elements of a PCA. In Section 2.4, we present the results of our PCA of the PAH fluxes, followed by a discussion of PAH sub-populations in Section 2.5 and the peculiar behaviour of the ionic bands in Section 2.6. Finally, in Section 2.7, we discuss our results in the context of the physical conditions in the reflection nebula.

### 2.2 NGC 2023

NGC 2023 is a bright visual reflection nebula in the Orion constellation at a distance of 403 ± 4 pc (Kounkel et al., 2018). It is illuminated by the young B 1.5V star HD 37903, which carves out a dust-free cavity of \(~0.05\ \text{pc} \) around itself (Witt et al., 1984), and creates a photodissociation region (PDR) beyond that. For our analysis, we focus on the PAH emission observed in the PDR (e.g. Sellgren, 1984; Abergel et al., 2002; Peeters et al., 2012; Shannon et al., 2016;
Figure 2.1: The IRAC [8.0] image of NGC 2023 with the IRS-SL fields of view (FOV) for the north and south regions shown as pink rectangles. The illuminating star HD 37903 is indicated by a black circle. The white circles represent 2MASS point sources, including sources C and D from Sellgren et al. (1983), located inside the SL FOV. In the south FOV, there are four ridges, the southern ridge (S’) at the top of the FOV, the southernmost ridge (S) in the middle of the FOV, the southeastern ridge (SE), and the south-southeastern ridge (SSE). In the north FOV, there are two ridges, the north ridge (N) and the northwestern ridge (NW). Figure is adapted from Peeters et al. (2017).

Boersma et al., 2016; Stock et al., 2016; Peeters et al., 2017; Knight et al., 2021a).

We analyzed the MIR data obtained in the two regions of NGC 2023 (see Fig. 2.1), hereafter referred to as the north and the south field of view (FOV) respectively, with the Infrared Spectrograph (IRS Houck et al., 2004) in the Short-Low (SL) module (Spectral resolution ~ 60-128, pixel scale ~ 1.8”), on board the Spitzer Space Telescope (Werner et al., 2004b) in mapping mode. The observations were centered around RA = 5:41:40.65, Dec = -2:13:47.5 in the north FOV and RA: 5:41:37.63, Dec: -2:16:42.5 in the south FOV. In the north FOV, the SL slit was moved 20 times in direction perpendicular to its long axis in a step size of 1.85” resulting in a data cube with 30×20 pixels. In the south FOV, the SL slit was moved 18 times in direction perpendicular to its long axis in a step size of 3.6” and 3 times in a direction parallel to its long axis in a step size of 26” resulting in a data cube with 58×34 pixels. The observed FOVs encompasses PDR surrounding the illuminating star which has bright ridges referred to as the southern ridge (S’) at the top of the FOV, the southern ridge (S) in the middle of the FOV, the southeastern ridge (SE), and the south-southeastern ridge (SSE) in the south FOV and the north ridge (N) and the northwestern ridge (NW) in the north FOV as defined by Peeters et al.
(2017). The north FOV is characterized by a gas density of \( \sim 10^4 \text{ cm}^{-3} \) (Burton et al., 1998; Steiman-Cameron et al., 1997; Sandell et al., 2015) and a radiation field of \( \sim 10^3 G_0 \) (Burton et al., 1998; Sandell et al., 2015) which are lower as compared to a gas density of \( \sim 10^5 \text{ cm}^{-3} \) (Steiman-Cameron et al., 1997; Sheffer et al., 2011; Sandell et al., 2015) and a radiation field of \( \sim 10^4 G_0 \) (Steiman-Cameron et al., 1997; Sheffer et al., 2011) in the south FOV.

### 2.3 Principal Component Analysis

A Principal Component Analysis (PCA) is a statistical technique for data visualization and dimensionality reduction developed by Pearson (1901) and Hotelling (1933). It transforms a set of correlated variables in a given data set into a new set of uncorrelated variables called the principal components (PCs) using an orthogonal transformation. The PCs are linear combinations of the original variables obtained in such a way that the first principal component has the largest variance and contains as much of the statistical information in the data as possible. Each succeeding component has a variance lesser than the preceding component thereby containing the remaining information in the data set. Thus, the goal of a PCA is to find the key variables that can best describe the data. A PCA can be applied to any dataset and is widely used in astronomy. A comprehensive review of PCA can be found in Abdi & Williams (2010) and Jolliffe & Cadima (2016).

Here, we briefly describe the underlying mathematical formalism of PCA. Consider a set of \( m \) variables \( \{x_i\} \), measured from a set of \( n \) observations in the data set \( X \), an \( n \times m \) matrix. As a first step, the raw data set, \( X \), is standardized such that each variable in the standardized data set, \( Z \), an \( n \times m \) matrix, has a mean of zero and a unit standard deviation. The standardization is done to ensure that all the variables have a comparable scale of measurement so that we get a more meaningful set of PCs. Next, we calculate the covariance matrix, \( C \), an \( m \times m \) matrix, of the standardized dataset \( Z \). The covariance is a measure of the degree to which the two variables are correlated. It is zero for two independent variables and is equal to the variance when we calculate the covariance of a variable with itself. The covariance matrix has a set of \( m \) eigenvectors, \( \{v_1, v_2, \ldots, v_m\} \), given by the linear combination of the standardized variables:

\[
v_i = a_{i,1}z_1 + a_{i,2}z_2 + \ldots + a_{i,m}z_m
\]  

(2.1)

where \( a_{i,j} \) are the coefficients of the eigenvector \( v_i \) and the \( \{z_1, z_2, \ldots, z_m\} \) are the set of original standardized variables. The corresponding set of \( m \) eigenvalues, \( \{\lambda_1, \lambda_2, \ldots, \lambda_m\} \), represents the variance of the eigenvectors (for the derivation, see Jolliffe & Cadima (2016)). Since the key objective of a PCA is to find a set of variables that successively maximizes the variance, the eigenvector corresponding to the largest eigenvalue of \( C \) is called the first PC (\( PC_1 \)), followed by the eigenvector corresponding to the second largest eigenvalue as the second PC (\( PC_2 \)) and so on. Note that the covariance matrix, \( C \), is a symmetric matrix, so the eigenvectors corresponding to different eigenvalues are orthogonal and hence the principal components obtained are independent of each other.

The data set in the reference frame of the PCs can be obtained from the following equation:

\[
Y = AZ^T
\]  

(2.2)
where the transpose of the matrix $Y$ ($Y^T$) is a new data set in the reference frame of the principal components and $A$ is a transformation matrix given by

$$A = \begin{bmatrix}
a_{11} & a_{12} & \cdots & a_{1m} \\
a_{21} & a_{22} & \cdots & a_{2m} \\
\vdots & \vdots & \ddots & \vdots \\
a_{m1} & a_{m2} & \cdots & a_{mm}
\end{bmatrix}$$

where the rows of the matrix correspond to the coefficients of the PCs determined from the eigenvalue decomposition of the covariance matrix $C$, with the first row containing coefficients of $PC_1$, the second row containing coefficients of $PC_2$ and so on.

### 2.4 PCA of PAH band fluxes in NGC 2023

#### 2.4.1 Measurements of PAH bands

To determine the main parameters that drive the variability in the PAH fluxes in NGC 2023, we performed a PCA of the fluxes of five PAH bands at 6.2, 7.7, 8.6, 11.0, and 11.2 $\mu$m observed at each pixel in the north and the south FOVs of the nebula. The flux values of these bands at each pixel are taken from Peeters et al. (2017). We summarize their measurements here. Peeters et al. (2017) applied three different methods to measure the fluxes of the PAH bands. Here we use the band fluxes measured with the spline decomposition method. In this method, they subtracted a local spline continuum from the spectra and obtained the fluxes of the 6.2, 7.7, and 8.6 $\mu$m PAH bands by integrating the continuum subtracted spectra. The flux measurements of the 11.0 and 11.2 $\mu$m bands, however, were done differently because of their blending with each other. To measure these fluxes, Peeters et al. (2017) fitted these bands with two Gaussians peaking at 10.99 and 11.26 $\mu$m with a FWHM of 0.154 and 0.236 $\mu$m respectively. The Gaussian at 10.99 $\mu$m provides the flux of the 11.0 $\mu$m band. To obtain the flux of the 11.2 $\mu$m band, they subtracted the flux of the 11.0 $\mu$m from the integrated flux of the 11.0 and 11.2 $\mu$m bands in the continuum-subtracted spectra (i.e. not using the Gaussian fit for the 11.2 $\mu$m band). Furthermore, the signal-to-noise ratios (SNR) of the PAH bands were estimated using the following expression:

$$SNR = \frac{I_{PAH}}{rms \times \sqrt{N} \times \Delta \lambda}$$

where $I_{PAH}$ is the intensity of a PAH band in units of $Wm^{-2}sr^{-1}$, $rms$ is the root-mean-square estimate of the noise in units of $Wm^{-2}\mu m^{-1}sr^{-1}$, $N$ is the number of spectral wavelength bins in the corresponding PAH band, and $\Delta \lambda$ is the wavelength bin size determined from the spectral resolution. Note that Peeters et al. (2017) take $N$ as the number of data points in the corresponding PAH band. Since the Spitzer IRS data is oversampled by a factor of two, a discrepancy by a factor of $\sqrt{2}$ occurs in the SNR of the PAH band measurements in Peeters et al. (2017) dataset. Various studies show that the plateaus are distinct from the individual PAH bands perched on top of them (e.g. Bregman et al., 1989; Roche et al., 1989; Peeters et al., 2012, 2017). We have used the measurements of PAH bands from Peeters et al. (2017)
that does not include plateaus. Therefore, for any other measurement of PAH bands that does not include plateaus we would expect change in the results smaller than that probed by the dynamic range of PCA.

The 6.2, 7.7, 8.6, and 11.0 \( \mu \text{m} \) bands are strong in charged PAH molecules whereas the 11.2 \( \mu \text{m} \) band is strong in neutral PAH molecules (e.g. Allamandola et al., 1999; Hony et al., 2001; Bauschlicher et al., 2008). In our analysis, we have used only the fluxes of the strongest PAH bands except for 11.0 \( \mu \text{m} \), in order to have good quality measurements. We used the weaker 11.0 \( \mu \text{m} \) band because when normalized to 11.2 \( \mu \text{m} \), it is a better tracer of the ionization state of PAHs than the other ionized PAH bands (e.g. Rosenberg et al., 2011; Peeters et al., 2017). The 11.0 \( \mu \text{m} \) band originates from the out of plane bending modes of solo C-H groups in ionized PAH molecules while the 11.2 \( \mu \text{m} \) originates from the same mode in neutral PAH molecules, thus the ratio 11.0/11.2 traces solely the ionization state of PAHs without any dependency on other parameters such as the size or the structure of molecule (e.g. Hudgins & Allamandola, 1999; Hony et al., 2001; Bauschlicher et al., 2008, 2009). Moreover, for our analysis, we only included pixels where we have a 3\( \sigma \) detection in all five PAH bands considered here and masked the remaining pixels. Following Peeters et al. (2017), we also masked the young stellar objects C and D (Sellgren et al., 1983). Note that we combined the measurements from the north and south FOVs for the PCA analysis discussed in this paper.

We standardized the PAH fluxes of the five bands considered here such that the standardized flux variables have a zero mean and a unit standard deviation

\[
    z_{PAH,i} = \frac{I_{PAH,i} - \langle I_{PAH} \rangle}{\sigma_{PAH}}
\]

where \( I_{PAH,i} \) is the intensity of a PAH band at pixel \( i \), \( \langle I_{PAH} \rangle \) and \( \sigma_{PAH} \) are the mean and standard deviation of the measured fluxes of a given PAH band, and \( z_{PAH,i} \) is the corresponding standardized intensity. Table 2.1 lists the mean \( \langle I_{PAH} \rangle \), and standard deviation \( \sigma_{PAH} \) values of the PAH flux variables in the nebula along with their respective average SNRs. The standardized variables \( (z_{PAH}) \) have comparable magnitudes and are the input variables in our PCA.

---

1Given the different SNR calculations in Peeters et al. (2017), our applied 3\( \sigma \) limit corresponds to a 4.2\( \sigma \) detection.


<table>
<thead>
<tr>
<th>PC</th>
<th>% variance explained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90.94</td>
</tr>
<tr>
<td>2</td>
<td>7.96</td>
</tr>
<tr>
<td>3</td>
<td>0.59</td>
</tr>
<tr>
<td>4</td>
<td>0.44</td>
</tr>
<tr>
<td>5</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 2.2: Fraction of variance explained by the principal components (PCs).

### 2.4.2 Principal Components

Our PCA resulted in five principal components (PCs). These PCs are linear combinations of the standardized flux variables ($z_{PAH}$). We note that the sign of a PC in PCA is arbitrary. Since we will be comparing the PCs (and especially the first two PCs), it makes sense to have them point in the same direction to facilitate interpretation. We thus choose to have the PC$_1$ and PC$_2$ vectors point in the direction of positive $z_{11,2}$ so that larger values of both PC$_1$ and PC$_2$ correspond to larger values of $z_{11,2}$ as well. With that convention, the PCs are determined by the following expressions:

\[
PC_1 = 0.466 z_{6,2} + 0.467 z_{7,7} + 0.453 z_{8,6} \\
+ 0.444 z_{11,0} + 0.403 z_{11,2} \\
PC_2 = 0.106 z_{6,2} - 0.016 z_{7,7} - 0.349 z_{8,6} \\
- 0.469 z_{11,0} + 0.804 z_{11,2} \\
PC_3 = -0.002 z_{6,2} - 0.288 z_{7,7} - 0.582 z_{8,6} \\
+ 0.741 z_{11,0} + 0.174 z_{11,2} \\
PC_4 = 0.461 z_{6,2} + 0.551 z_{7,7} - 0.567 z_{8,6} \\
- 0.141 z_{11,0} - 0.378 z_{11,2} \\
PC_5 = 0.747 z_{6,2} - 0.629 z_{7,7} + 0.115 z_{8,6} \\
- 0.121 z_{11,0} - 0.132 z_{11,2}
\]  
(2.4)

These equations include the directional choice discussed above.

Table 2.2 lists the fraction of the variance explained by the individual PCs. Clearly, the first two PCs combined account for the majority of the variation (~99%) present in the data. Since the last three PCs combined account for only 1% of the variation, we exclude those PCs from further analysis. Thus, in the framework of PCA dimensionality reduction, we can now decompose the standardized flux variables into PC$_1$ and PC$_2$ components:

\[
\begin{align*}
    z_{6,2} &= 0.466 PC_1 + 0.106 PC_2 \\
    z_{7,7} &= 0.467 PC_1 - 0.016 PC_2 \\
    z_{8,6} &= 0.453 PC_1 - 0.349 PC_2 \\
    z_{11,0} &= 0.444 PC_1 - 0.469 PC_2 \\
    z_{11,2} &= 0.403 PC_1 + 0.804 PC_2
\end{align*}
\]  
(2.5)

These equations include the directional choice discussed above.
Fig. 2.2 shows so-called “biplots” obtained from this PCA analysis that show the projection of the standardized original variables \( z_{PAH} \) onto the axes in the new reference frame defined by the PCs. Note that biplots are the visual representation of equation 2.5. The larger the projection of a variable on a PC axis, the better that variable correlates with that PC. These biplots are thus useful tools to get a first idea about what drives variations in the original data set. We note that the projection of all \( z_{PAH} \) on \( PC_1 \) is in the positive direction indicating that \( PC_1 \) represents changes in total PAH flux. The magnitude of the projection of \( PC_1 \) is roughly the same for all the ionized flux variables \( (z_{6.2}, z_{7.7}, z_{8.6}, \text{ and } z_{11.0}) \) but is relatively small for the neutral flux variable \( (z_{11.2}) \). This means that \( PC_1 \) has a slightly higher contribution from the ionized PAH bands than the neutral PAH band. Note also that \( z_{7.7} \) is nearly horizontal in the biplot. Thus, \( PC_1 \) correlates almost perfectly with \( z_{7.7} \), and \( z_{7.7} \) is hardly affected by \( PC_2 \).

Similarly, the projections of \( z_{PAH} \) on \( PC_2 \) provide a hint for the physical interpretation of \( PC_2 \). The projection of \( z_{11.2} \) and \( z_{6.2} \) on \( PC_2 \) is in positive direction although the projection of \( z_{6.2} \) is tiny as compared to that of \( z_{11.2} \) while \( z_{8.6} \) and \( z_{11.0} \) project in the negative direction of \( PC_2 \). The projection of \( z_{7.7} \) is almost zero. Due to a clear distinction in the direction of the projection of \( z_{8.6} \) and \( z_{11.0} \) and \( z_{11.2} \), \( PC_2 \) may be interpreted as a tracer of the ionization state of PAHs. However, in this scenario, the positive projection of \( z_{6.2} \) is very intriguing and needs further investigation. At the same time, it is worth pointing out that the four ionic bands appear grouped in these biplots: \( z_{6.2} \) and \( z_{7.7} \) point in a similar direction, and also \( z_{8.6} \) and \( z_{11.0} \) point in a similar direction, but the two sets are quite distinct from each other. As will discuss later, this is the first evidence that points to a different character for a subset of the ionic bands.
2.4.3 Spectrum of PCs

Since $PC_1$ is a linear combination of PAH fluxes, the eigen vector corresponding to $PC_1$ represents a particular ratio of individual flux values, and thus a characteristic PAH spectrum. In Fig. 2.3, we show the characteristic PAH spectrum of $PC_1$. This spectrum is derived from equation 2.5 by setting $PC_1 = 1$ and $PC_2 = 0$. From the values of the standardized flux variables thus obtained we then extract the actual flux values for the PAH bands by applying an inverse of the standardization operation i.e. adding the mean value of the original flux variables ($\langle I_{PAH} \rangle$) to the product of the standard deviation of the original flux variables ($\sigma_{PAH}$) and the standardized values obtained from equation 2.5 under the condition of $PC_1 = 1$ and $PC_2 = 0$. The spectrum is then constructed by representing each PAH band by a normalized Gaussian profile at its nominal peak position. Since the width of the observed PAH bands varies from one another, we constructed the Gaussians at 6.2, 7.7, 8.6, 11.0, and 11.2 $\mu$m with a standard deviations of 0.08, 0.19, 0.12, 0.07, 0.10 $\mu$m respectively. The 6.2 and 7.7 $\mu$m bands emerge as strong features. The 8.6 and 11.2 $\mu$m bands also have considerable intensities, but significantly lower than those of the 6.2 and 7.7 $\mu$m bands. The 11.0 $\mu$m is the weakest feature because of its weak intrinsic intensity. Theoretical and experimental studies have shown that the spectra of ionized PAH molecules have strong 6.2, 7.7, and 8.6 $\mu$m bands whereas the spectrum of neutral PAH molecules have strong 11.2 $\mu$m band intensity with weak 6.2, 7.7, and 8.6 $\mu$m band intensities (e.g. Allamandola et al., 1999; Peeters et al., 2002a; Bauschlicher et al., 2009). Thus, the characteristic PAH spectrum for $PC_1$ is neither a spectrum typical of solely cations nor solely neutrals but rather that of some mixture of cationic and neutral PAH molecules. The strong contribution from the 6.2, 7.7, and 8.6 $\mu$m bands as compared to the 11.2 $\mu$m in $PC_1$ suggest that $PC_1$ represents PAH emission of a mixture of PAH molecules where ionized PAHs outweigh the neutral PAHs.

In order to test our hypothesis and take into account the fact that the 6.2 and 7.7 $\mu$m bands
Figure 2.4: Eigen spectrum of $PC_1$ in NGC 2023. The eigen spectrum is an artificial spectrum created to visualize the contribution of a given PAH band to $PC_1$ (see text for details).

have large intrinsic intensities that can manifest as strong features in the characteristic spectrum of $PC_1$, we also constructed a spectrum using only the standardized values of the variables and a standard deviation of 0.1 $\mu$m – essentially the “eigen spectrum” corresponding to $PC_1$ – and show it in Fig. 2.4. We note that the eigen spectrum is representative of the eigen vector associated with the PC. In the eigen spectrum of $PC_1$, the 6.2, 7.7, 8.6, and 11.0 $\mu$m bands have similar intensities, with the 11.2 $\mu$m band being slightly weaker. This implies that the 6.2, 7.7, 8.6, and 11.0 $\mu$m bands have larger contribution towards $PC_1$ as compared to the 11.2 $\mu$m band. Hence, our conclusion about $PC_1$ representing PAH emission of a mixture of PAH molecules having more ionized PAHs than the neutrals still holds.

We also derived an eigen spectrum of $PC_2$. Since $PC_2$ represents a first order correction to the PAH fluxes predicted by $PC_1$, we only constructed an eigen spectrum of $PC_2$ from the standardized flux variables so that we can clearly identify the variations in the relative correction intensities of each of the PAH bands. Setting $PC_1 = 0$ and $PC_2 = 1$ in equation 2.5 results in the PAH band intensities corresponding to the eigen spectrum of $PC_2$. We emphasize that since the PAH band intensities thus derived are the intensities of the standardized flux variables (with a mean of 0 and a standard deviation of 1), they can have negative values. The resulting eigen spectrum is illustrated in Fig. 2.5.

The intensities of the 8.6 and 11.0 $\mu$m bands are negative, whereas the 6.2 and 11.2 $\mu$m bands have positive intensities. The 7.7 $\mu$m band has almost no intensity. The fact that the 8.6 and the 11.0 $\mu$m bands behave differently than the 11.2 $\mu$m band suggests that $PC_2$ is dependent on the PAH ionization state. However, the fact that the 6.2 $\mu$m (strong in ionized PAHs) behave similar as the 11.2 $\mu$m PAH band (strong in neutral PAHs) is very surprising. Indeed, although the 6.2, 7.7, and 8.6 $\mu$m bands correlate very well with each other (see Peeters et al., 2017), their relative contribution to $PC_2$ is different with the 6.2 and 7.7 $\mu$m band having opposite contribution with respect to the 8.6 $\mu$m PAH band. This is further addressed in Section 2.6.
Figure 2.5: Eigen spectrum of $PC_2$ in NGC 2023. The eigen spectrum is an artificial spectrum created to visualize the contribution of a given PAH band to $PC_2$ (see text for details).

<table>
<thead>
<tr>
<th>PAH ratio</th>
<th>R-value</th>
<th>95% Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2/11.2</td>
<td>-0.8030</td>
<td>-0.7866 — -0.8184</td>
</tr>
<tr>
<td>7.7/11.2</td>
<td>-0.8217</td>
<td>-0.8066 — -0.8357</td>
</tr>
<tr>
<td>8.6/11.2</td>
<td>-0.8514</td>
<td>-0.8386 — -0.8632</td>
</tr>
<tr>
<td>11.0/11.2</td>
<td>-0.8601</td>
<td>-0.8480 — -0.8714</td>
</tr>
</tbody>
</table>

Table 2.3: 95% Confidence Interval of the correlation coefficient (R-value) of $PC_2$ with PAH ionization ratios.

### 2.4.4 Correlations between PCs and PAH fluxes

To gain further insight into the characteristics of the PCs, we investigated the correlations of $PC_1$ and $PC_2$ with the PAH band fluxes and various PAH band ratios. Fig. 2.6 shows the observed correlations for $PC_1$ with these variables, and lists their Pearson correlation coefficients. Overall, $PC_1$ is well correlated with the individual PAH fluxes and the total PAH flux, albeit with considerable variation in the correlation coefficients. The best correlation is that of $PC_1$ with the total charged PAH flux, i.e. the sum of the fluxes of ionized PAH bands (6.2, 7.7, 8.6, and 11.0 $\mu$m) with correlation coefficient of 0.995. This observation is in line with our previous conclusion of $PC_1$ tracing emission of a mixture of PAH molecules comprising more ionized PAH molecules than neutrals (we also present the spatial distribution of $PC_1$ in Appendix A.1 which reinforces this conclusion). Furthermore, $PC_1$ does not correlate at all with any PAH band ratio. As an example of this, we show the correlation of $PC_1$ with the 6.2/11.2 band ratio.

We also note some “branching” in the correlation plots of $PC_1$, i.e. there appears to be sets of data points that each correspond to slightly different relationships between parameters. The branching is most prominent in the correlation of $PC_1$ with the 11.2 $\mu$m band. Branches are also evident in the correlation of $PC_1$ with the 6.2 $\mu$m band and to some extent with the 11.0...
Figure 2.6: Correlations of $PC_1$ with the 6.2, 7.7, 8.6, 11.0, and 11.2 $\mu$m PAH band fluxes, the charged PAH flux, the total PAH flux, and the 6.2/11.2 ratio in NGC 2023. The Pearson correlation coefficient is shown at the top left corner of each plot. $PC_1$ is a dimensionless quantity representing the largest variance in the data set.

and 8.6 $\mu$m bands as well. We will discuss the origin of these branches in Section 2.5.

Similar to $PC_1$, we also investigated the correlations of $PC_2$ with individual band fluxes and various band ratios (Fig. 2.7). $PC_2$ does not correlate with individual PAH fluxes nor the total PAH flux. Instead, $PC_2$ anti-correlates best with 11.0/11.2, which is a measure of the PAH ionization state. This implies that high $PC_2$ values originate from more neutral regions and low $PC_2$ values originate from more cationic regions (see also the spatial distribution of $PC_2$ in Appendix A.1). $PC_2$ also anti-correlates well with other PAH ratios, the 8.6/11.2, 7.7/11.2, and 6.2/11.2 ratios, but with a decreasing correlation coefficient (ranging from $R^2 : 0.7$ to 0.6) in that order. The 11.0, 8.6, 7.7, and 6.2 $\mu$m bands are all attributed to ionized PAHs, so a ratio of any of these PAH fluxes with the 11.2 $\mu$m band traces the ionization state and thus a decrease in the correlation coefficient for these ionic bands requires further investigation. To test the statistical significance of this decrease in the correlation coefficient, we obtained the 95% confidence intervals (CIs) for each Pearson correlation coefficient (R-value) and checked if there is an overlap between those intervals (Table 2.3). The 95% CI of the correlation coefficient indicates that if we were to repeat our measurements of the PAH bands, we would find that 95% of the time, the correlation coefficient would fall within this interval. The calculated CIs follow the same trend as the correlation coefficients with a slight overlap between the CIs for 6.2/11.2 and 7.7/11.2 as well as for 8.6/11.2 and 11.0/11.2. We note that the CIs for 6.2/11.2 and 7.7/11.2 do not overlap with the CIs for 8.6/11.2 and 11.0/11.2. Thus the drop in the correlation coefficients of the PAH ionization ratios is not merely an anomaly by chance; rather, it hints towards systematically different behaviour of the ionic bands. We discuss this decrease in the correlation coefficient further in Section 2.6. In addition, we find (anti-) correlations of $PC_2$
Figure 2.7: Correlations of $PC_2$ with the 6.2, 7.7, 8.6, 11.0, and 11.2 μm PAH band fluxes, the total PAH flux, and the various PAH band ratios across the south FOV in NGC 2023. The Pearson correlation coefficient is shown in the corner of the each plot. $PC_2$ is a dimensionless quantity representing the second largest variance in the data set.
with the other PAH band ratios which are not as tight as those tracing the charge state of PAHs. $PC_2$ shows a weak correlation with the $7.7/11.0$, $6.2/11.0$, $6.2/8.6$, and $7.7/8.6$ ratios. No (anti-) correlations are found between $PC_2$ and the $8.6/11.0$ nor the $6.2/7.7$ in our dataset.

2.5 Evidence for multiple PAH sub-populations

We now return to the branching observed in the correlations of the PCs with the PAH band fluxes (see Section 2.4.4). This branching is most prominent in the correlation of $PC_1$ with the 11.2 $\mu$m. We show two such branches labelled as $B - 1$ and $B - 4$ in Fig. 2.8. A straight line in this correlation represents a set of data points with a specific relationship between the 11.2 $\mu$m PAH flux and the flux of the mixture of PAH molecules traced by $PC_1$. The existence of these branches, i.e. a few sets of data points that each are characterized by their own 11.2/PAH flux as traced by $PC_1$ ratio, suggests that some of the properties of the underlying PAH populations are very similar within each of the branches, but different across the branches, and hence points towards the presence of distinct PAH sub-populations within the nebula.

In this section, we address the origin of these PAH sub-populations. In order to do so, we color coded the correlations of $PC_1$ with all possible PAH band ratios and checked which ratio sets the branches apart. We found that the 11.0/11.2 produces the cleanest separation of the branches (Fig. 2.8), thereby suggesting that the PAH sub-populations indicated by the branches in the correlation plot of $PC_1$ with the 11.2 $\mu$m are the result of the varying PAH ionization across the nebula. We note that while $PC_2$ has a strong correlation with the 11.0/11.2 PAH ratio, the branches are not the PAH emission variations traced by $PC_2$. Due to the nature of the correlation between $PC_2$ and the 11.0/11.2 PAH ratio, $PC_2$ values show a relatively wide range of values within each of the branches, although the average value of $PC_2$ between the branches is different as well. To illustrate this, we show the dynamic range of $PC_2$ and 11.0/11.2 in two of the branches labelled $B - 1$ and $B - 4$ in Fig. 2.9. Note that the Fig. 2.9 is merely a sub-part of the PC2-11.0/11.2 plot shown in Fig. 2.7. While there are clear differences in ionization (as traced by $PC_2$) within a sub-population, their 11.0/11.2 ratio does not change much, and thus the branches or sub-populations are best characterized based on the 11.0/11.2 PAH ratio rather than $PC_2$.

There is a gradient in the 11.0/11.2 values across the correlation plots of $PC_1$ with the PAH band fluxes. In the $PC_1$-11.2 plot, the high 11.0/11.2 values are at the lower part of the envelope of data points and the low 11.0/11.2 values are at the upper part of the envelope of data points as expected. This trend is reversed for the correlations of $PC_1$ with the 8.6 and 11.0, i.e. the high 11.0/11.2 values are at the upper part and the low 11.0/11.2 values are at the lower part of the envelope of data points. Surprisingly, this trend is not followed in the $PC_1$-6.2 and the 7.7 plot, where there is an increased overlapping of the 11.0/11.2 values.

Since 11.0/11.2 traces the ionization state of PAHs, there is also a gradient of color, as expected, across the y-axis in the correlation plots of $PC_1$ with the 6.2/11.2, 7.7/11.2, and 8.6/11.2 PAH band ratios which are also the tracers of the PAH ionization. In addition, there is also an obvious gradient in the 11.0/11.2 values across the y-axis in the $PC_1$-6.2/8.6, 7.7/8.6, 6.2/11.0, and 7.7/11.0 plots with high 11.0/11.2 values having low y-values and low 11.0/11.2 values having high y-values. In contrast, we do not observe any gradient in the $PC_1$-6.2/7.7 and 8.6/11.0 plots. The presence of the gradient in the 6.2/8.6, 6.2/11.0, 7.7/8.6, and 7.7/11.0 PAH
Figure 2.8: Correlations of $PC_1$ with the PAH band fluxes and the PAH band ratios color coded based on the $11.0/11.2$ ratio to study the origin of the branches, most evident in the $PC_1$ - 11.2 correlation (see Section 2.4.4 for details).
band ratios suggests that there is a distinction between the 6.2, 7.7 $\mu$m bands and the 8.6, 11.0 $\mu$m bands. The absence of any gradient in the 6.2/7.7 and the 8.6/11.0 ratios further suggests that the 6.2 and the 7.7 $\mu$m bands belong to one group of ionic bands and the 8.6 and the 11.0 $\mu$m belong to another. This is further addressed in the next Section.

### 2.6 Peculiar behaviour of the ionic bands

By now, we have encountered several instances that suggest that the ionic bands show different behaviour. First, there was the clear separation of the two sets of bands in the biplots. The characteristic spectrum of $PC_2$ furthermore shows a very peculiar behaviour of the ionic bands where we found that the behaviour of the 6.2 $\mu$m bears some similarity with that of the 11.2 $\mu$m, a neutral PAH band, while the other ionized PAH bands do not show such similarity. This behaviour is also reflected in the correlation of $PC_2$ with the 11.0/11.2, 8.6/11.2, 7.7/11.2, and the 6.2/11.2, where the correlation coefficient decreases in this order, in spite of the 6.2, 7.7, 8.6, and 11.0 $\mu$m bands being attributed to ionized PAHs. Furthermore, the in-depth analysis of the branches seen in the correlations of $PC_1$ and $PC_2$ reveals that the 6.2 and 7.7 $\mu$m bands behave as one group of ionized bands and the 8.6 and 11.0 $\mu$m bands as another group.

The subtle behaviour of the ionic bands has been recognized previously by several authors (e.g. Galliano et al., 2008; Whelan et al., 2013; Stock et al., 2014; Peeters et al., 2017). Numerous studies in the literature show that the correlation between the 6.2 and 7.7 $\mu$m bands is stronger than the correlation between the 6.2 or 7.7 and 8.6 $\mu$m bands (e.g. Vermeij et al., 2002; Galliano et al., 2008; Peeters et al., 2017; Maragkoudakis et al., 2018). Recently, Whelan et al. (2013) and Stock et al. (2014) observed the breakdown between the 6.2 and 7.7 $\mu$m bands in two H II regions in the Small Magellanic Cloud and in the Milky Way respectively. Furthermore, the broad 7.7 $\mu$m band is known to have at least two components at 7.6 and 7.8
\( \mu m \) (e.g. Bregman et al., 1989; Cohen et al., 1989; Verstraete et al., 2001; Peeters et al., 2002a; Bregman & Temi, 2005). Rapacioli et al. (2005) argue that the component at 7.8 \( \mu m \) is due to very small grains (VSGs). More recently, Bouwman et al. (2019) studied the effect of size, symmetry and structure on the infrared spectra of four PAH cations and noted a drastic change in the vibrational modes of 7-9 \( \mu m \) region upon the decrease of the molecular symmetry (see also Bauschlicher et al., 2009).

Peeters et al. (2017) did a detailed analysis of emission in the 7-9 \( \mu m \) region in NGC 2023. They decomposed the spectrum in the 7-9 \( \mu m \) region into four Gaussian components. These authors found that two of the components centered at 7.6 and 8.6 \( \mu m \) correlate with each other and with the 11.0 \( \mu m \) band. These Gaussian components were the main contributors to the traditional 7.7 and 8.6 \( \mu m \) band intensities. The remaining two Gaussian components centered at 7.8 and 8.2 \( \mu m \) correlated with each other and displayed a spatial morphology similar to the 11.2 \( \mu m \) band and the 5-10 and 10-15 \( \mu m \) plateau emission in the south FOV and to the 10-15 \( \mu m \) plateau and the 10.2 \( \mu m \) continuum emission in the North FOV of NGC 2023. Despite the apparent arbitrariness of the decomposition, their results suggested the presence of at least two distinct sub-populations contributing to the emission in the 7-9 \( \mu m \) region. In this scenario, the contribution from the Gaussian component at 7.8 \( \mu m \) to the 7.7 \( \mu m \) complex is at the origin of the distinction observed between the 7.7 and 8.6 \( \mu m \) bands detected by the PCA analysis. Thus, the analysis presented here does not explicitly separate the two different PAH populations as suggested by Peeters et al. (2017) in their decomposition of the 7-9 \( \mu m \) region, rather it provides additional supporting evidence for their existence. Furthermore, our result that the 6.2 and 7.7 \( \mu m \) bands belong to a single group (as opposed to the 8.6/11.0 group), suggests that, similar to the 7.7 \( \mu m \) band, the 6.2 \( \mu m \) band contains contributions of both these two PAH populations responsible for the 7.7 \( \mu m \) band, which Peeters et al. (2017) were unable to extract using their analysis method. This is also supported by the fact that the correlation between the 6.2 and 7.7 \( \mu m \) bands is the strongest (e.g. Peeters et al., 2017).

We further notice that based on the correlations of \( PC_1 \) color-coded with the 11.0/11.2 ratio, the points with low values of 11.0/11.2 populate the regions of high values of 6.2/11.0, 7.7/11.0, 6.2/8.6, and 7.7/8.6. The fact that we see a color distinction in the ratios of these ionic bands due to an ionization ratio (11.0/11.2) itself may suggest that these ratios are further tracing the different ionization states of the PAH molecules. Since high values of 6.2/11.0, 7.7/11.0, 6.2/8.6, and 7.7/8.6 correspond to low values of 11.0/11.2, this then implies that the 6.2 and 7.7 \( \mu m \) bands originate from less ionized PAHs than the 8.6 and 11.0 \( \mu m \) bands. Thus, an alternative interpretation for the distinction between the two groups of the ionized bands is that the 6.2 and 7.7 \( \mu m \) trace singly charged PAH cations and the 8.6 and 11.0 \( \mu m \) trace doubly charged PAH cations. We emphasize that based on previous studies (e.g. Bauschlicher et al., 2009; Peeters et al., 2017; Bouwman et al., 2019; Maragkoudakis et al., 2018, 2020), other PAH properties such as size and molecular structure are known to influence the PAH emission spectrum. Maragkoudakis et al. (2020) have shown that PAH size primarily effect the 3.3 \( \mu m \) band and to a lesser extent the 11.2 \( \mu m \) band indicating that size is likely not the driver of the observed dichotomy between the ionic bands. The effect of molecular structure on these ionic bands in terms of band assignments has been discussed in Peeters et al. (2017). However, we currently can not systematically investigate its role within this context based on the astronomical observations.
2.7 The PCs and the physical conditions

The primary goal of a PCA is to reduce the set of parameters needed to represent a multivariate data set and find the key variables that drive the input data. By performing a PCA of five PAH band fluxes in NGC 2023, we find that only two variables (PCs) are required to explain ~99% of the variance in the PAH emission in NGC 2023. Based on the characteristic spectrum of the PCs and their correlations, we conclude that i) $PC_1$ representing the largest variance represents the PAH emission of an ion dominated PAH mixture, and ii) $PC_2$ constituting the second largest variance has a strong (anti)-correlation with the PAH band ratios, $6.2/11.2$, $7.7/11.2$, $8.6/11.2$, and $11.0/11.2$, tracing the ionization state of the PAHs, and a moderate to weak correlation with the $7.7/11.0$, $6.2/11.0$ and the $6.2/8.6$, $7.7/8.6$ respectively. In this section, we now explore if there is a relation between the PCs and the parameters that describe the physical conditions in the nebula. Note that the key physical parameters that determine the PAH emission characteristics are the strength of the radiation field, the PAH abundance, electron density, and the temperature. We focus here on the radiation field strength distribution.

We note that the spatial morphology of $-PC_2$ resembles that of $G_0$ in the north and south FOVs of NGC 2023 (see Fig. A.2) with $-PC_2$ exhibiting high values in the high $G_0$ regions closer to the star (i.e at the bottom of the north FOV and the top of the south FOV) and vice versa. This similarity highlights the influence of $G_0$ on $PC_2$. Although $PC_1$ also exhibits maxima in the high $G_0$ regions (S’ and SE ridge in south FOV; west of the southern part of the NW ridge), the overall morphology of $PC_1$ and $G_0$ is very different in both FOVs (see Figs. A.1 and A.2). Thus we conclude that, variations in the PAH emission reflected by $PC_2$ are strongly affected by $G_0$, this seems to be less so for $PC_1$. We also compared the spatial distribution of PCs to that of $G_0/n_H$, where $n_H$ is the local hydrogen density. Fleming et al. (2010) presented the map of $G_0/n_H$ estimated from the ionization state of the PAHs for the south FOV. We find no morphological similarity in the maps of PCs and $G_0/n_H$ (see Fig. 6 in Fleming et al., 2010).

In Section 2.4.4, we noted that $PC_2$ correlated well with the ratios of ionic PAH bands, $6.2/8.6$, $7.7/8.6$, $6.2/11.0$, and $7.7/11.0$ (see Figs. 2.7), which reflects the distinction between the two groups of ionic PAH bands. Since $G_0$ affects $PC_2$ values, one could conclude that the distinction between these two groups of ionic bands is driven by $G_0$. This also extends support to our hypothesis that the 8.6 and 11.0 $\mu$m band could be tracing dications as one would expect more doubly charged cations than singly charged cations in high $G_0$ regions corresponding to low $PC_2$ values and hence low values of $6.2/8.6$, $7.7/8.6$, $6.2/11.0$, and $7.7/11.0$ which is indeed the case.

2.8 Conclusion

We have presented a principal component analysis of the fluxes of five major PAH features at $6.2$, $7.7$, $8.6$, $11.0$, and $11.2$ $\mu$m in the south and the north FOV of NGC 2023. We find that only two principal components (PCs) are required to explain 99% of the variance in the fluxes of the five PAH bands considered here. Out of the two components, the first PC ($PC_1$) is the most important component as it carries the majority (91%) of the information about the data.

In order to interpret the characteristics of the PCs, we studied their characteristic PAH spectrum, eigen spectrum, and the correlations with the individual PAH band fluxes and PAH
band ratios. Based on these we concluded that $PC_1$ represents the PAH emission of a mixture of molecules having more ionized PAHs than neutral PAHs and $PC_2$ traces the ionization state of PAH molecules. In addition, the correlations of PCs with PAH band fluxes revealed distinct “branches” which indicated the presence of multiple PAH sub-populations due to varying PAH ionization across the nebula.

Based on the eigen spectrum of $PC_2$ and its correlations with the ionic PAH band ratios, we find that there is a distinction between the ionic PAH bands, with the 6.2 and 7.7 $\mu$m bands and the 8.6 and 11.0 $\mu$m bands belonging to two different groups of ionized bands. We further argue that the 6.2 and 7.7 $\mu$m bands originate from less ionized PAHs than the 8.6 and 11.0 $\mu$m bands and thus the 6.2 and 7.7 $\mu$m bands could be attributed to singly charged PAH cations and the 8.6 and 11.0 $\mu$m bands to doubly charged PAH cations. Furthermore, the comparison of PCs with the physical conditions in the nebula shows that the spatial map of $-PC_2$ is similar to that of $G_0$, and hence we concluded that the $G_0$ drives the distinction observed between the ionic bands.

**Data Availability**

The data underlying this article are available at [https://github.com/Ameek-Sidhu/PCA-NGC2023](https://github.com/Ameek-Sidhu/PCA-NGC2023).

**Acknowledgements**

The authors thank the referee for providing valuable comments which led to the improvement of this paper. EP and JC acknowledge support from an NSERC Discovery Grant.
Chapter 3

A Principal Component Analysis of polycyclic aromatic hydrocarbon emission in NGC 7023

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Submitted to Monthly Notices of the Royal Astronomical Society

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3.1 Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of large organic molecules with carbon atoms arranged in a honeycomb-like structure and hydrogen atoms attached at the edges. These molecules are ubiquitous in the universe and are observed via their characteristic vibrational emission features in the mid-infrared (MIR) at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.7 µm (e.g. Sellgren et al., 1983; Hony et al., 2001; Peeters et al., 2002a; Geers et al., 2006; Smith et al., 2007; Galliano et al., 2008). In addition to the strong features, PAHs exhibit a plethora of weak features at 3.4, 3.5, 5.25, 5.75, 6.0, 6.6, 6.9, 7.2-7.4, 8.2, 10.1, 10.5, 10.8, 11.0, 12.0, 13.5, 14.2, 15.8, 16.4, 16.6, 17.0, 17.4, and 17.8 µm (e.g. Cohen et al., 1985; Geballe et al., 1985; Jourdain de Muizon et al., 1986; Moutou et al., 2000; Peeters et al., 2004c; Werner et al., 2004a). PAHs represent up to 15% of the cosmic carbon (Tielens, 2008), however, the specific PAH molecules comprising the astronomical population is still largely unknown.

Subtle variations in relative intensities and profiles of PAH emission features observed in different environments have been found in the MIR studies of a large number of Galactic and extragalactic sources (e.g. Peeters et al., 2002a; Smith et al., 2007; Sandstrom et al., 2012; Matsuura et al., 2014; Shannon et al., 2016; Peeters et al., 2017). These variations are related to the physical conditions such as gas density, temperature, metallicity, and radiation field strength.
of environments where PAHs reside (Galliano et al., 2008; Pilleri et al., 2012; Boersma et al., 2015; Stock & Peeters, 2017). Comparison of astronomical observations with laboratory and theoretical studies have indicated that changes in physical conditions cause changes in PAH properties such as the ionization state, size, molecular structure, and molecular symmetry, resulting in the variations in PAH emission features (e.g. Hony et al., 2001; Galliano et al., 2008; Bauschlicher et al., 2008, 2009; Ricca et al., 2012; Candian et al., 2014; Boersma et al., 2016; Bouwman et al., 2019).

We analyzed the variability of five PAH emission features (at 6.2, 7.7, 8.6, 11.0, and 11.2 µm) in a Galactic Photodissociation region (PDR), NGC 2023 using a statistical technique called Principal Component Analysis (PCA) and concluded that the amount of PAH emission and the ionization fraction are the two key drivers of the observed PAH variations (Sidhu et al., 2021). Furthermore, the PCA analysis revealed a peculiar behaviour of the PAH features at 6.2, 7.7, 8.6, and 11.0 µm that are usually attributed to ionized PAHs. The features at 6.2 and 7.7 µm were found to form one group of ionic bands, while those at 8.6 and 11.0 µm form another distinct group. We argued that this distinction would arise if the 6.2 and 7.7 µm bands belong to less ionized PAHs, and the 8.6 and 11.0 µm to more ionized PAHs. In this paper, we extend the PCA analysis to another well known galactic PDR, NGC 7023, and compare and contrast the results with the previous study on NGC 2023. We will investigate whether the results obtained for NGC 2023 also hold for NGC 7023.

This paper is organized as follows. In Section 3.2, we describe the source NGC 7023. In Section 3.3 we provide a brief overview of PCA. We present the results of our PCA analysis of PAH emission in NGC 7023 in Section 3.4, followed by a discussion on distinct PAH emission in the PDR and the cavity of NGC 7023 in Section 3.5. We discuss the origin of the subsets of ionic bands in Section 3.6 and compare the results of this study with a previous study on NGC 2023 in Section 3.7. Finally, we present a summary of our results in Section 3.8.

### 3.2 NGC 7023

NGC 7023 is a bright visual reflection nebula 430 pc away from the Earth, and illuminated by HD 200775, a spectroscopic binary (Herbig B3Ve - B5) (van den Ancker et al., 1997a; Witt et al., 2006; Alecian et al., 2013). It is a well-studied reflection nebula owing to its high surface brightness and proximity to the Earth (e.g. Watt et al., 1986; Chokshi et al., 1988; Sellgren et al., 1992; Fuente et al., 1993; Rogers et al., 1995; Lemaire et al., 1996; Gerin et al., 1998; An & Sellgren, 2003; Witt et al., 2006; Joblin et al., 2010; Rosenberg et al., 2011; Berné & Tielens, 2012; Montillaud et al., 2013; Köhler et al., 2014; Boersma et al., 2015; Croiset et al., 2016; Le et al., 2017; Joblin et al., 2018). Observations in the ultraviolet, optical, and at infrared wavelengths show that the central star has carved out a cavity (gas density ~ 100 cm⁻³) in the nebula (Watt et al., 1986; Gerin et al., 1998; Joblin et al., 2010; Berné et al., 2015, see Fig. 3.1). The walls of the cavity are surrounded by PDRs at ~ 42° North West (NW), 55° South West (SW), and 150° East (E) of the central star. These PDRs are made up of diffuse gas, n_H ~ 10³ - 10⁴ cm⁻³, embedded within relatively dense filamentary structures (n_H ~ 10⁵ - 10⁶ cm⁻³) of size ~ 0.004 pc or less (Chokshi et al., 1988; Rogers et al., 1995; Fuente et al., 1996, 1999; Martini et al., 1999; Köhler et al., 2014; Joblin et al., 2018). In this paper, we analyzed the emission from PAHs using the MIR data obtained with the Infrared Spectrograph...
3.3 Principal Component Analysis

A Principal Component Analysis (PCA) is an unsupervised learning technique widely used in astronomy to analyse complex data sets (e.g. Wang et al., 2011; Hurley et al., 2012; Ensor et al., 2017; Sidhu et al., 2021). PCA reduces the dimensionality of a data set by transforming the original set of variables into a new set of variables called the principal components (PCs) in such a way that only the first few PCs contain most of the statistical information about the data set (Pearson, 1901; Hotelling, 1933; Jolliffe & Cadima, 2016). Here, we present a summary of PCA. A comprehensive mathematical formulation of PCA, is given in Sidhu et al. (2021).

To perform PCA, we first standardize the original data set so that each variable has a mean of zero and a standard deviation of one. PCs are then derived from the eigenvector decompo-
Chapter 3. A PCA of PAH emission in NGC 7023

### 3.4 PCA of PAH fluxes in NGC 7023

#### 3.4.1 Measurement of PAH bands

We performed a PCA of the extinction corrected fluxes of the 6.2, 7.7, 8.6, 11.0, and 11.2 µm PAH bands observed at each pixel in the SL FOV of NGC 7023. We obtained the flux measurements of these PAH bands from Stock et al. (2016). Here we briefly summarize their flux measurement strategy. First, they subtracted the continuum from the spectra by computing a spline fit to a set of continuum points at wavelengths of 5.37, 5.46, 5.86, 6.58, 6.92, 8.28, 9.15, 9.40, 9.64, 10.14, 10.33, 10.76, 11.82, 13.18, 13.49, 14.43, and 14.74 µm. Fluxes of the strong bands at 6.2, 7.7, 8.6, and 11.2 µm were then measured by direct integration. Fluxes of the 6.2 and 11.2 µm bands measured this way contained contributions from the weaker 6.0 and 11.0 µm bands, which they accounted for by fitting the Gaussian profiles at 6.0 and 11.0 µm to determine their contribution. The fluxes of 6.0 and 11.0 µm bands thus obtained were then subtracted from the fluxes of 6.2 and 11.2 µm bands measured with direct integration to obtain the final flux of the 6.2 and 11.2 µm bands. They calculated the uncertainties by comparing the integrated feature flux and the rms noise of featureless areas of the continuum between 9.3 and 9.5 µm, 13.3 and 13.5 µm, and 13.7 and 13.9 µm, respectively.

For our PCA analysis, we first masked the pixels where the signal-to-noise ratio (SNR) of fluxes in any of the five bands is less than 3. We also masked the pixels contaminated with diffraction effects from the central star and the two 2MASS point sources in our FOV (see Fig. 3.1). We then standardized the fluxes from the remaining pixels before using them as input variables in our PCA analysis. After the standardization operation, all the input flux variables have a mean of zero and a standard deviation of unity. The standardization is done so that all the input variables in PCA have comparable magnitudes that would result in meaningful PCs as

<table>
<thead>
<tr>
<th>PAH band</th>
<th>( \langle I_{PAH} \rangle ) (x10^{-5})</th>
<th>( \sigma_{PAH} ) (x10^{-6})</th>
<th>( \langle SNR \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2</td>
<td>1.225</td>
<td>5.056</td>
<td>221</td>
</tr>
<tr>
<td>7.7</td>
<td>2.037</td>
<td>8.267</td>
<td>198</td>
</tr>
<tr>
<td>8.6</td>
<td>0.375</td>
<td>1.838</td>
<td>47</td>
</tr>
<tr>
<td>11.0</td>
<td>0.009</td>
<td>0.048</td>
<td>10</td>
</tr>
<tr>
<td>11.2</td>
<td>0.460</td>
<td>2.899</td>
<td>47</td>
</tr>
</tbody>
</table>

Table 3.1: The mean (\( \langle I_{PAH} \rangle \)) and standard deviation (\( \sigma_{PAH} \)) values of the PAH band flux variables along with their respective average SNRs in the SL FOV of NGC 7023. \( \langle I_{PAH} \rangle \) and \( \sigma_{PAH} \) values are in units of Wm^{-2}sr^{-1}.

The position of the covariance matrix of the standardized data set. These eigenvectors then form the PCs, with their relative importance determined by their corresponding eigenvalues. The eigenvector with the largest eigenvalue becomes the first PC and accounts for most of the variance in the data set. Each succeeding PC accounts for less variance than the preceding one. In this way, by transforming from original variables into PCs, we get, in principle, the parameters that drive the variance in the data set.
output. We provide the mean and the standard deviation values of the PAH band flux variables along with their respective average SNRs used in our PCA analysis in Table 3.1.

### 3.4.2 Principal Components

The five PCs, i.e. the unit eigenvectors, that result from our PCA are then given by these equations:

\[
P C_1 = 0.481 z_{6,2} + 0.476 z_{7,7} + 0.474 z_{8,6} \\
+ 0.461 z_{11,0} + 0.322 z_{11,2} \\
P C_2 = 0.117 z_{6,2} - 0.149 z_{7,7} - 0.267 z_{8,6} \\
- 0.316 z_{11,0} + 0.890 z_{11,2} \\
P C_3 = -0.396 z_{6,2} - 0.575 z_{7,7} + 0.184 z_{8,6} \\
+ 0.648 z_{11,0} + 0.241 z_{11,2} \\
P C_4 = -0.699 z_{6,2} + 0.647 z_{7,7} - 0.198 z_{8,6} \\
+ 0.133 z_{11,0} + 0.188 z_{11,2} \\
P C_5 = -0.331 z_{6,2} - 0.039 z_{7,7} + 0.794 z_{8,6} \\
- 0.499 z_{11,0} + 0.097 z_{11,2}
\]

(3.1)

where \([z_{6,2}, z_{7,7}, z_{8,6}, z_{11,0}, z_{11,2}]\) are the standardized flux variables.

The relative importance of these PCs is determined by the amount of variance explained by each PC. Table 3.2 lists the fraction of the variance explained by the PCs obtained from our PCA analysis. Recall that the fraction of variance explained by a PC is the eigenvalue of that PC eigenvector. We note that the first two PCs combined explain \(\sim 98\%\) of the variance in the data, with the first PC explaining the majority of the variance. Therefore, the first two PCs are the primary drivers of the PAH flux variations observed in NGC 7023. If we ignore the three remaining marginal PCs, we can then decompose the standardized flux variables into \(PC_1\) and \(PC_2\) as follows:

\[
\begin{align*}
z_{6,2} &= 0.481 PC_1 + 0.117 PC_2 \\
z_{7,7} &= 0.476 PC_1 - 0.149 PC_2 \\
z_{8,6} &= 0.474 PC_1 - 0.267 PC_2 \\
z_{11,0} &= 0.461 PC_1 - 0.316 PC_2 \\
z_{11,2} &= 0.322 PC_1 + 0.890 PC_2
\end{align*}
\]

(3.2)
In the following sections, we investigate whether we can assign a physical interpretation to $PC_1$ and $PC_2$. For the remainder of our paper, we exclude the last three PCs explaining $\sim 2\%$ of the variance from any further analysis.

### 3.4.3 PCA biplots

To interpret the physical meaning of $PC_1$ and $PC_2$, we begin by constructing biplots that depict the contribution of standardized flux variables to the PCs. Fig. 3.2 shows the biplots obtained from our PCA analysis of PAH emission in NGC 7023 where we show the projection of the standardized flux variables in the reference frame of PCs. These projections are a measure of the correlation between the standardized flux variables and PCs, i.e. the larger the projection of the standardized flux variable on a PC, the larger the correlation of that variable with the PC. All the PAH bands considered here have a positive projection on $PC_1$: the traditional ionized PAH bands (at 6.2, 7.7, 8.6, and 11.0 $\mu$m) have a projection of $\sim 0.5$ and the neutral PAH band (at 11.2 $\mu$m) has a slightly smaller projection of $\sim 0.3$. On the other hand, the projections of PAH bands on $PC_2$ are more diverse. While the 7.7, 8.6, and 11.0 $\mu$m bands have a small negative projection ($\sim -0.1$ – -0.3) on $PC_2$, the 6.2 $\mu$m band exhibits a small positive projection ($\sim 0.1$), and the 11.2 $\mu$m band a large positive projection ($\sim 0.9$) on $PC_2$.

The trends observed in the biplots suggest that $PC_1$ represents the characteristic PAH emission of a mixture of neutral and ionized PAHs. The slight difference in the projections of the ionized and neutral PAH bands on $PC_1$ suggests that the characteristic PAH emission in NGC 7023 has more contribution from ionized PAHs than neutral PAHs. Directions of the PAH band projections on $PC_2$ distinguishes between the neutral and the ionized PAH bands.
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3.4.4 Spatial Maps of PCs

We also studied the spatial distribution of the magnitude of the PC eigenvectors in order to better understand their physical meaning. We emphasize that although the PC eigenvectors given by equations 2.4 have unit magnitude, their magnitude is not unity across the spatial map of the nebula. In Fig. 3.3 we present the spatial maps of $PC_1$ and $PC_2$ overlaid with the contours of the 7.7 and 11.2 $\mu$m PAH intensities. The star is at the bottom right corner of those maps. High $PC_1$ values (yellowish hues) form a ring-shaped structure which is also traced well by the 7.7 $\mu$m PAH band (white contours). The ring-shaped structure was first identified by An & Sellgren (2003) in their intensity map of the 3.29 $\mu$m PAH band. The origin of this ring-shaped structure is still unknown. Intermediate $PC_1$ values (purple hues) form an elongated rectangular patch and belong to regions outside the ring-shaped structure. Low $PC_1$ values (dark) are further present in regions outlining the rectangular patch of intermediate $PC_1$ values, with the neutral band (at 11.2 $\mu$m) exhibiting a positive projection and the ionized bands (at 7.7, 8.6, and 11.0 $\mu$m except at 6.2 $\mu$m) exhibiting a negative projection, thereby indicating that $PC_2$ is related to the ionization state of PAHs. The different behaviour of the 6.2 $\mu$m PAH band compared to the other ionized PAH bands at 7.7, 8.6, and 11.0 $\mu$m is worth mentioning as it depicts the subtle differences between the ionic bands which have traditionally been treated similarly. We address these differences in ionic bands further in Section 3.6.

Figure 3.3: Spatial maps of $PC_1$ (left) and $PC_2$ (right) in the SL FOV of NGC 7023. For reference, the contours of the 7.7, 11.2 $\mu$m PAH intensity, and $PC_2 = -0.1$ are overlaid in white, black, and cyan respectively. Pixels where the SNR of the fluxes in any of the five PAH bands used in PCA is less than 3, and those contaminated with the diffraction effects from the illuminating star and the 2MASS point sources in the FOV are shown in white.
in the lower right and top left corner of the map. We note that the spatial morphology of \( PC_1 \) looks identical to the spatial distribution of total PAH flux (see figure B.1) thereby reinforcing our earlier suggestion that \( PC_1 \) represents the characteristic PAH emission in NGC 7023.

The spatial map of \( PC_2 \) is quite intriguing as it offers insight into the PAH emission characteristics of NGC 7023 beyond the general picture that emerges from the biplots in Section 3.4.3. We note that the high \( PC_2 \) values (\( \gtrsim 1.5 \)) are co-located with the strong 11.2 \( \mu \text{m} \) PAH emission (shown in the black contour map). The 11.2 \( \mu \text{m} \) PAH emission aligns very well with the \( \text{H}_2 \) emission tracing the PDR front (Berné et al., 2009; Croiset et al., 2016). On the other hand, low \( PC_2 \) values (\( \lesssim -0.1 \)) originate from the cavity and intermediate \( PC_2 \) values (\( \sim -0.1 - 1.5 \)) probe the transition from the PDR to the cavity as well as the region behind the PDR ridge, i.e. the top left corner of the map. The ring-shaped structure is not visible in the spatial map of \( PC_2 \) though the lowest \( PC_2 \) values are found slightly offset (to the right, i.e. in the direction of the central star) from the peak of the PAH emission found in the ring-shaped structure and thus not closest to the central star. Thus, the spatial distribution of \( PC_2 \) clearly distinguishes between the cavity and the PDR. In the framework of PCA, \( PC_2 \) is a first-order correction to the characteristic PAH emission traced by \( PC_1 \). Therefore, the differentiation between the cavity and the PDR highlighted by \( PC_2 \) implies that the PAH properties vary between these two regions. Furthermore, since \( PC_2 \) is related to the ionization state of PAHs (see Section 3.4.3), PAHs in the cavity and the PDR seems to differ primarily in their ionization states.

We also compared the spatial maps of the PCs to the spatial maps of the spectral components extracted using PAHTAT, a tool that decomposes the observed spectrum into four components: neutral PAHs, ionised PAHs, PAH clusters, and evaporating very small grains (eVSGs; see e.g. Berné et al., 2007; Pilleri et al., 2012). We find that \( PC_1 \) exhibits a maximum (minimum) in the same regions where the PAHTAT components of the ionized and neutral PAHs exhibit a maximum (minimum). Thus, the spatial morphology of \( PC_1 \) emerges as the spatial morphology of the sum of the neutral and ionized PAH components derived from PAHTAT. Comparison of \( PC_2 \) with the PAHTAT components reveals a striking similarity with the spatial morphology of the inverse of the ionized PAHs. This comparison further strengthens our argument that \( PC_1 \) is related to the PAH emission of a mixture of neutral and ionized PAHs and \( PC_2 \) is related to the PAH charge state.

### 3.4.5 Correlation plots

We further analysed the correlations of PCs with the PAH fluxes and the PAH ratios. Since \( PC_1 \) and \( PC_2 \) jointly account for the majority of the variance in PAH fluxes, we did not analyse the \( PC_1 \) and \( PC_2 \) correlations separately. Instead, we studied the correlations of both PCs together by plotting the correlations of \( PC_1 \) with the PAH fluxes and the PAH ratios and colour-coding the data points with their \( PC_2 \) values (see Fig. 3.4).

First of all, we note that \( PC_1 \) exhibits a linear relationship with the individual PAH fluxes and the total PAH flux (i.e. the sum of the fluxes of PAH bands at 6.2, 7.7, 8.6, 11.0, and 11.2 \( \mu \text{m} \)) but does not correlate with any of the PAH ratios. Moreover, the best correlation of \( PC_1 \) is with the total PAH flux with a correlation coefficient of 0.9851, thus lending support to our arguments in Sections 3.4.3 and 3.4.4 that \( PC_1 \) probes the characteristic PAH emission in NGC 7023.
Figure 3.4: Correlations of $PC_1$ with the PAH fluxes and the PAH ratios, colour-coded with $PC_2$ values. The Pearson correlation coefficient is shown in the corner of the each plot.
Secondly, there are observable branches in the $PC_{1}$-11.2 $\mu$m plot, which are neatly separated by their $PC_{2}$ values. Such branches are also evident in the $PC_{1}$-8.6 and 11.0 $\mu$m plots, although not as cleanly as observed in the $PC_{1}$-11.2 $\mu$m plot. In the branches of $PC_{1}$-11.2 $\mu$m plot, we note that for a given $PC_{1}$ value, low $PC_{2}$ values correspond to low 11.2 $\mu$m fluxes which gradually increases with increasing $PC_{2}$ values. These branches indicate different relationships between $PC_{1}$ and the 11.2 $\mu$m flux in our FOV, implying that the PAH populations leading to these distinct branches are different. Since these branches correspond to different $PC_{2}$ values and the fact that $PC_{2}$ clearly distinguishes between the cavity and the PDR as observed in the spatial map of $PC_{2}$ (see Section 3.4.4), we once again reach the same conclusion that the PAH population in the cavity differs from that in the PDR. Moreover, it is clear that this difference in population is primarily driven by a difference in ionization fraction. Indeed, the data points for which $PC_{2} > -0.1$ belong to the PDR and the transition region, and are characterized by low 6.2/11.2, 7.7/11.2, 8.6/11.2, and 11.0/11.2 PAH ratio, in contrast to the much higher ratios for data points originating from the cavity ($PC_{2}$ values $< -0.1$).

Finally, the correlation plots also illustrate the different character of the ionic bands in the PDR. We observe that the data points originating from the PDR and the regions surrounding it exhibit a broad range of values in the 6.2/8.6, 7.7/8.6, 6.2/11.0, 7.7/11.0, and 8.6/11.0 PAH ratios. The 6.2/7.7 PAH ratio, however, shows only a narrow range of values. This means that while the relative strengths of the 6.2 and 7.7 $\mu$m bands do not change significantly, there is a considerable change in the strengths of the 6.2 and 7.7 $\mu$m bands with respect to the 8.6 and 11.0 $\mu$m bands. Thus, the 6.2 and 7.7 $\mu$m bands form one subset of ionic bands that change together, but that behave differently from the other subset formed by the 8.6 and 11.0 $\mu$m bands. Moreover, there also appears to be a distinction in the behaviour of the 8.6 and 11.0 $\mu$m bands. We address this peculiar behaviour of the ionic bands further in Section 3.6.

### 3.5 Comparing PAH emission in the PDR and the cavity of NGC 7023

The spatial map of $PC_{2}$ and the correlation analysis of PCs in Sections 3.4.4 and 3.4.5 respectively indicated that the PAH population in the cavity differs from the PDR. These results also highlighted the obvious difference between the ionization states of PAHs in the two regions. Furthermore, we discriminate two different subsets of the ionic bands that are evident only in the PDR environment and not in the cavity. In this section, we now further explore the variations in the PAH emission of the cavity and the PDR by performing two independent PCA analyses of the PAH emission in these two regions. We used the spatial map of $PC_{2}$ as the reference point to identify the data points originating from the PDR and the cavity, i.e. we assumed that the regions with $PC_{2} < -0.1$ belong to the cavity and the regions with $PC_{2} > -0.1$ belong to the PDR. We note that the regions with $PC_{2} > -0.1$ also includes the region separating the cavity from the PDR. Since the trends observed in the region separating the cavity and the PDR are similar to those observed in the PDR (Section 3.4.5), we will treat this region identical to the PDR for the remainder of this paper.

The equations of the PCs resulting from the independent PCA analyses of the PDR and the cavity are given in Appendix B.2 and B.3 respectively. The amount of variance explained by
Table 3.3: Fraction of variance explained by PCs obtained from two independent PCA of PAH emission in the PDR and the cavity of NGC 7023. The segregation of the PDR and the cavity is based on the spatial map of $PC_2$ obtained from the PCA analysis of PAH emission of the entire SL FOV of NGC 7023 (see text for details).

<table>
<thead>
<tr>
<th>PC</th>
<th>% variance explained</th>
<th>PDR</th>
<th>Cavity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>91.58</td>
<td>95.98</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.84</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.28</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.19</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

each PC is presented in Table 3.3 and shows that once more, the first two PCs ($PC_1$ and $PC_2$) account for the majority of the variance ($\sim 98\text{-}99\%$) in the PAH emission of both the PDR and the cavity. However, the fraction of the variance explained by individual PCs varies. For instance, $PC_1$ in the PDR accounts for $\sim 91\%$ of the variance in the PAH emission compared to $\sim 96\%$ in the cavity. $PC_2$, on the other hand, accounts for $\sim 7\%$ of the variance in the PDR and only $\sim 3\%$ in the cavity. Nonetheless, similar to the results of PCA on the entire SL FOV (see Section 3.4.2), only two PCs are relevant to explain the variance in PAH emission in both the PDR and the cavity.

### 3.5.1 Biplots in the PDR and the cavity of NGC 7023

We then investigated the characteristics of the new PCs found in the PDR and the cavity by analysing the biplots for the PCs obtained in the two regions (see Fig. 3.5). For both the PDR and the cavity, all PAH bands have similar positive projections on $PC_1$, implying that $PC_1$ represents emission from a mixture of neutral and ionized PAHs. The projections of $PC_2$, on the other hand, are quite distinct between the PDR and the cavity. In the PDR, the projections of 11.0 and 11.2 $\mu m$ PAH bands form the two ends of the spectrum exhibiting the largest negative and positive projection, respectively. The 6.2 and 7.7 $\mu m$ bands have positive projections, with the projection of 6.2 $\mu m$ band being greater than that of 7.7 $\mu m$ band. The 8.6 $\mu m$ PAH band, on the other hand, has a large negative projection although less than that of 11.0 $\mu m$ PAH band. Since $PC_2$ provides a clear distinction between the ionized 11.0 $\mu m$ band and the 11.2 $\mu m$ neutral band, we conclude that $PC_2$ is describing the effect of changes in the charge state in the PDR. Furthermore, we note that the projections of the 6.2 and 7.7 $\mu m$ ionized PAH bands follow the 11.2 $\mu m$ band while the 8.6 $\mu m$ ionized band follow the 11.0 $\mu m$ band, implying that the 6.2 and 7.7 $\mu m$ bands form a subset of ionic bands which behave differently than the 8.6 and 11.0 $\mu m$ bands.

In the cavity on the other hand, the projections of the 11.2 and the 7.7 $\mu m$ PAH bands onto $PC_2$ are on opposite ends. However, the projection of the 11.2 $\mu m$ band is twice as large as the 7.7 $\mu m$ band. The 11.0 $\mu m$ band exhibits a small projection in the direction of the 11.2 $\mu m$ band while the 6.2 and 8.6 $\mu m$ bands exhibit negative projections though less so than the 7.7 $\mu m$ band. Thus, it appears that in the cavity, $PC_2$ is tracing some PAH property other than the ionization state. Interestingly, the positive projections correspond to PAH bands that
Figure 3.5: Biplots of PCA in the PDR (top) and cavity (bottom) of NGC 7023.
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3.5.2 Characteristic PAH emission spectrum in the PDR and the cavity of NGC 7023

In Fig. 3.6 we present the characteristic PAH spectrum of $PC_1$ representing the PAH emission in the PDR and the cavity. We followed the procedure given in Sidhu et al. (2021) to derive the characteristic PAH spectrum of $PC_1$. First, we obtained the standardized fluxes for the PAH bands by substituting $PC_1 = 1$ and $PC_2 = 0$ in Equations B.2 and B.4. To the standardized fluxes thus obtained we then applied the inverse standardization operation, i.e. we added the mean value of the original PAH flux variables in the cavity and the PDR to the product of the standard deviation of the original PAH flux variables and $z_{PAH}$. We find that the 6.2 and 7.7 $\mu$m emerge as strong bands in both the cavity and the PDR and that the 6.2, 7.7 and 8.6 $\mu$m bands are stronger in the cavity than in the PDR. The 11.2 $\mu$m band on the other hand is stronger in the PDR than in the cavity, implying that as we go from the cavity to the PDR, the contribution of neutral PAH molecules to the total PAH emission increases. The 11.0 $\mu$m band is a weak feature in both the cavity and the PDR.
3.5.3 Comparing the PDR to the cavity: summary

The independent PCA analysis of PAH emission in the PDR and the cavity thus establishes the following observations:

1. The PAH population in the PDR is different from that in the cavity.

2. The primary difference in the PAH population in the PDR and the cavity is the ionization fraction: the PAH population in the PDR contains more neutral PAH molecules while that in the cavity contains more ionized PAH molecules.

3. The photochemical evolution of PAHs is different between the PDR and the cavity. Variations in the PDR can be primarily ascribed to changes in the charge state; in the cavity, another molecular property drives much of the variations.

4. The peculiar behaviour of the ionic bands is only seen in the PDR and not in the cavity.

3.6 Subsets of the ionic bands and their behaviour

The results of the PCA using our entire data set showed that the ionic PAH bands form two distinct subsets. The 6.2 and 7.7 \(\mu\)m bands form one subset that behaves differently than the other subset comprised of the 8.6 and 11.0 \(\mu\)m bands. The 8.6 and the 11.0 \(\mu\)m bands furthermore show subtle differences in their behaviour (see Sections 3.4.3 and 3.4.5). This distinction is furthermore only present in the PDR and not in the cavity. Here, we will discuss the possible origin of this behaviour.

In the biplots stemming from the PCA applied to the PDR only (see the top panel of Fig. 3.5), the 6.2 and 7.7 \(\mu\)m bands follow the 11.2 \(\mu\)m whereas the 8.6 and 11.0 \(\mu\)m bands point the other way. This suggests that the 6.2 and 7.7 \(\mu\)m bands may be less ionized than the 8.6 and the 11.0 \(\mu\)m bands. To test this hypothesis, we studied how the ratios of the ionic PAH bands correlate with the 11.0/11.2 ratio, which serves as an indicator of the charge state of PAHs, in the PDR only (Fig. 3.7). It is clear that larger 11.0/11.2 ratios correspond to smaller 6.2/11.0 and 7.7/11.0 ratios, and to a lesser extent also 8.6/11.0 ratios. In contrast, however, there is no relation between the 11.0/11.2 and the 6.2/7.7 PAH ratios. The presence of a relationship between the 6.2/11.0 and 7.7/11.0 on one hand and the 11.0/11.2 on the other hand suggests that 6.2 and 7.7 \(\mu\)m bands probe a different ionization state than the 11.0 \(\mu\)m band. Within this framework, the 6.2 and 7.7 \(\mu\)m bands are thus less ionized than the 8.6 and 11.0 \(\mu\)m PAH bands given that highest values of 11.0/11.2 correspond to lower values of the 6.2/11.0 and 7.7/11.0 ratios.

Alternatively, the two different subsets of the ionic PAH bands could be the result of contributions from larger species such as PAH clusters or very small grains (VSGs) to the PAH bands in the 6-9 \(\mu\)m region. In their analysis of PAH emission in the 7-9 \(\mu\)m region in NGC 2023, Peeters et al. (2017) concluded that there are two distinct subpopulations contributing to the emission in this region. The spatial morphology of one subpopulation bore similarity with the 11.0 \(\mu\)m band and the other with the dust continuum and 5–10 \(\mu\)m PAH plateau. Several studies attribute the emission from plateaus to the PAH clusters or VSGs (e.g. Allamandola et al., 1989; Bregman et al., 1989; Peeters et al., 2017). In this scenario, the subpopulation bearing
similarity with the plateau emission could therefore contain a contribution from larger species such as PAH clusters or VSGs which in turn could be at the origin of the distinct nature of the ionic bands. Since the larger species can not survive in the cavity, they can not contribute to the ionic bands in the 6-9 $\mu$m region resulting in the absence of distinction between the ionic bands in the cavity. In contrast, in the more shielded PDR environments, PAH clusters and VSGs can survive and contribute to the fluxes of PAH features in the 6-9 $\mu$m region. The amount of contribution from larger species to the fluxes of 6.2, 7.7, and 8.6 $\mu$m bands would lead to the different characters of the ionic bands. In this regards, the amount of contribution from larger species to the 6.2 and 7.7 $\mu$m bands would be comparable and more than to the 8.6 $\mu$m band.

Finally, we note that the PAH properties other than charge such as size, molecular structure, and symmetry can also influence the behaviour of the ionic bands. However, based on our current state of knowledge of PAH astrophysics, we cannot systematically analyse the effect of these properties on the distinct behaviour of the ionic bands.

Figure 3.7: Correlations of ionic PAH ratios with the 11.0/11.2 ratio, an indicator of charge state of PAHs, in the PDR of NGC 7023.
One of the goals of this paper is to compare and contrast the results of our PCA of PAH emission in NGC 7023 to a similar study on NGC 2023 (Sidhu et al., 2021) to investigate whether the results obtained pertaining to PAH emission are universal. We carried out the PCA analysis of PAH emission observed in the SL FOVs in both of these environments. While in NGC 7023, we studied one FOV comprising the dust-free cavity created by the exciting star (HD 200775) and the NW PDR; in NGC 2023, we investigated two FOVs north and the south of the exciting star (HD 37903), comprising of the PDRs embedded with bright ridges. These regions represent different physical conditions. In particular, while the NW PDR of NGC 7023 studied in this paper is characterized by a gas density of $10^3 - 10^4 \text{ cm}^{-3}$ (Chokshi et al., 1988; Rogers et al., 1995; Fuente et al., 1996, 1999; Martini et al., 1999; Köhler et al., 2014; Joblin et al., 2018) and a radiation field strength, $2600 \text{ G}_0$ (Chokshi et al., 1988; Rogers et al., 1995; Joblin et al., 2018), the PDR environments studied in NGC 2023 are characterized by a gas density of $10^4 \text{ cm}^{-3}$ (Steiman-Cameron et al., 1997; Burton et al., 1998; Sandell et al., 2015) and a radiation field strength of $10^3 \text{ G}_0$ (Burton et al., 1998; Sandell et al., 2015) in the north FOV, and by a gas density of $10^5 \text{ cm}^{-3}$ (Steiman-Cameron et al., 1997; Sheffer et al., 2011; Sandell et al., 2015) and a radiation field strength of $10^4 \text{ G}_0$ (Steiman-Cameron et al., 1997; Sheffer et al., 2011) in the south FOV. Since the environments studied in NGC 2023 only comprises PDRs, we compared the results of PCA in the PDR of NGC 7023 presented in section 3.5 to the results of NGC 2023.

The key finding is that in both the nebulae, only two PCs are required to explain the variance in the PAH emission in the PDRs. In both studies, the first PC represented the PAH emission of a mixture of PAHs of neutrals and cations, and the second PC probed the ionization state of PAHs. This indicates that in the PDR environment, the amount of PAH emission and the degree of ionization drive the variation of PAH emission. In Fig. 3.8, we compare the characteristic PAH spectrum of $PC_1$ for NGC 2023 and the PDR environment of NGC 7023. We note that the 6.2, 7.7, 8.6, and 11.2 \mu m bands emerge as strong features in both nebulae. However, the relative strength of these features varies between both nebulae. While the strength of the 6.2,
Chapter 3. A PCA of PAH emission in NGC 7023

7.7, and 11.2 µm bands is higher in NGC 7023, the strength of the 8.6 µm band is similar and the strength of the 11.0 µm band is higher in NGC 2023 compared to NGC 7023. This indicates that the PAH population in NGC 2023 may be different from that in NGC 7023. These findings appear to be inconsistent with the grandPAH hypothesis (Andrews et al., 2015), according to which only a few stable PAHs comprise the astronomical PAH family. High spectral resolution data that will be obtained with the James Webb Space Telescope (JWST) would be instrumental in verifying this result.

Furthermore, we identified the different character of the subsets of ionic bands in both environments. In NGC 2023, we found that the 6.2 and 7.7 µm formed one group of ionic bands and the 8.6 and 11.0 µm the other. While the PCA analysis of PAH emission in NGC 7023 confirmed that the 6.2 and 7.7 µm bands indeed behave as one group as opposed to the 8.6 and 11.0 µm bands, we find a further subtle distinction in the behaviour of the 8.6 and 11.0 µm bands. We have discussed various possibilities for the origin of the different subsets of the ionic bands in Section 3.6. The exact reason for this distinction would require high spectral resolution data which will become available with JWST.

3.8 Conclusion

We have presented the results of a PCA of the fluxes of five major PAH bands at 6.2, 7.7, 8.6, 11.0, and 11.2 µm in NGC 7023. The region of NGC 7023 studied in this paper comprises the NW PDR and the dust-free cavity. We find that only two parameters (PCs) are required to explain most of the observed variance (∼ 98%) in the PAH fluxes. The first PC (PC₁), accounting for ∼ 84% of the variance, represents the PAH emission of a mixture of neutral and ionized PAHs and hence the amount of PAH emission. The second PC (PC₂), accounting for ∼ 14% of the variance, probes the ionization state of PAHs across the nebula. Based on the biplots and correlations of PCs with the PAH ratios, we found that there are subsets of the ionic bands with the 6.2 and 7.7 µm bands forming one subset and the 8.6 and 11.0 µm bands the other. The subset comprising the 8.6 and 11.0 µm bands further shows subtle distinctions in their behaviour.

In addition, PCA analysis shows that the PAH emission characteristics are distinct between the cavity and the PDR. The PAH population in these two regions differs mainly in the ionization state of PAHs, with the PDR consisting of a higher fraction of neutral PAHs than the cavity, which contains more contribution from ionized molecules. The cavity and the PDR also differ in terms of the photochemical evolution of PAHs. While ionization drives PAH variations in the PDR, another molecular property, such as e.g. hydrogenation or molecular edge structure, is responsible for PAH variations in the cavity. Furthermore, we find that the subsets of the ionic bands can only be discerned in the PDR and not in the cavity.

We discussed two likely scenarios for the origin of the subsets of the ionic PAH bands. In one scenario, we argue that the 6.2 and 7.7 µm bands are less ionized than the 8.6 and the 11.0 µm bands, thereby resulting in the two distinct subsets of ionic bands. Alternatively, there could be a contribution from VSGs and PAH clusters to the PAH bands in the 6-9 µm region. In this scenario, the amount of contribution from VSGs and PAH clusters to the PAH bands would lead to the distinct behaviour of the ionic bands in the PDRs.

Finally, we compared the PCA results of PAH emission in NGC 7023 to a similar study
conducted previously on NGC 2023. The comparison shows that only two parameters, the amount of PAH emission and the ionization state, drive the variation of PAH emission in PDR-like environments.

**Data Availability**

The data underlying this article will be shared on reasonable request to the corresponding author.

**Acknowledgements**

EP and JC acknowledge support from an NSERC Discovery Grant.
Chapter 4

Revisiting the Polycyclic Aromatic Hydrocarbon emission model in photodissociation regions

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4.1 Introduction

The strong emission features at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.7 µm in a typical mid-infrared (mid-IR) spectrum are characteristic of a family of complex organic molecules known as Polycyclic Aromatic Hydrocarbons (PAHs; Sellgren et al., 1983; Leger & Puget, 1984; Allamandola et al., 1985, 1989). PAH molecules account for \(\sim 15\%\) of the total cosmic carbon (Allamandola et al., 1989) and \(\sim 20\%\) of the total IR power of the Milky Way and star-forming galaxies (Madden et al., 2006; Smith et al., 2007). Emission from PAHs typically originates from photo-dissociation regions (PDRs), where the physics and chemistry of the gas are driven by far-ultraviolet (FUV; 6–13.6 eV) photons (Hollenbach & Tielens, 1997). Gas within a PDR is stratified, with regions of atomic gas found closer to the star and molecular gas further away. The atomic gas consists largely of hydrogen (H) and ionised carbon (C), and the molecular gas of molecular hydrogen (H\(_2\)) and carbon monoxide (CO). PAH emission typically outlines the PDR surface, decreasing into the PDR as the UV radiation field is attenuated.

The physical conditions (radiation field strength \(G_0\), gas density \(n_{\text{gas}}\), and gas temperature \(T_{\text{gas}}\)) within the PDRs regulate the molecular properties of the PAH population such as their
charge, size, and molecular structure (e.g. Hony et al., 2001; Peeters et al., 2002a; Galliano et al., 2008). Several experimental and theoretical studies have shown that changes in the PAH properties affect the spectral characteristics of the PAH population’s emission features. For example, changes in the charge state of PAHs influence the intensity of the 6.2, 7.7, and 8.6 μm features relative to the 11.2 μm feature, changes in the size distribution influence the relative intensity of the 3.3 μm to 11.2 μm feature, and changes in the molecular structure influence the relative intensities of the features in the 11-14 μm region (e.g. Hudgins & Allamandola, 1999; Allamandola et al., 1999; Hony et al., 2001; Peeters et al., 2002a; Bauschlicher et al., 2008, 2009; Ricca et al., 2012; Candian et al., 2014). The PAH emission features observed in PDRs show spectral variations, the most prominent of which are due to changes in the charge state of the PAH population (e.g. Joblin et al., 1996a; Sloan et al., 1999; Allamandola et al., 1999; Bregman & Temi, 2005; Compiègne et al., 2007; Galliano et al., 2008; Rosenberg et al., 2011; Peeters et al., 2017; Sidhu et al., 2021).

Bakes et al. (2001b) presented a PAH emission model that calculates the charge distribution of PAHs and uses these results to determine the PAH emission in astrophysical environments. In this paper, we revisit the emission model adopting recent experimentally or quantum chemically determined PAH characteristics such as the ionization potentials, photo-absorption cross-sections, IR cross-sections, for individual PAHs. The aim of this paper is to demonstrate that the PAH charge distribution can account for the observed spectral characteristics of PAHs by comparing the model results with observations of PDRs exhibiting a wide range of physical conditions. This paper is organized as follows. In Section 4.2, we describe the PAH emission model, which combines the charge distribution, PAH characteristics, and the IR emission from PAHs in a given astrophysical environment. In Section 4.3, we present the results of our model for five different PAH molecules, namely, tetracene (C_{18}H_{12}), pentacene (C_{22}H_{14}), ovalene (C_{32}H_{14}), circumcoronene (C_{54}H_{18}), and circumcircumcoronene (C_{96}H_{24}), over a range of physical conditions. We discuss the application of the model in five different environments, NGC 2023, NGC 7023, the Orion Bar, the Horsehead nebula, and the diffuse interstellar medium (ISM), in Section 4.4. Finally, we provide a summary of this work in Section 4.5.

### 4.2 PAH emission Model

Following Bakes et al. (2001b) we model the PAH emission taking into account the charge distribution of PAHs in astrophysical settings by adopting realistic properties of PAHs measured experimentally or calculated theoretically as available. In this section, we present a comprehensive overview of the three main components of our model: the calculation of the PAH charge distribution, the calculation of IR emission from PAHs, and the PAH characteristics, as well as a strategy for combining these to model PAH emission in astrophysical environments.

#### 4.2.1 The PAH charge distribution model

The charge distribution of molecular species in astronomical environments is set by the balance between the processes of ionization and electron recombination. Bakes & Tielens (1994) developed a model using the principle of ionization equilibrium to determine the charge distri-
bution of PAHs and very small graphitic grains in a variety of physical conditions pertaining to interstellar environments. In this work, we adopt the Bakes & Tielens (1994) model solely for PAHs by using the ionization, electron recombination, and electron attachment rates derived from recent theoretically calculated or experimentally measured molecular characteristics of PAHs. In this section, we describe the framework of our charge distribution model.

In our model, we assume that a PAH molecule in a given charge state, $Z$, can get ionized by absorbing a photon of energy $h\nu$

$$\text{PAH}^Z \xrightarrow{h\nu} \text{PAH}^{Z+1} + e^- \quad (4.1)$$

The ionized PAH can further undergo electron recombination

$$\text{PAH}^{Z+1} + e^- \rightarrow \text{PAH}^Z \quad (4.2)$$

and the neutral PAH ($Z = 0$) can undergo electron attachment

$$\text{PAH} + e^- \rightarrow \text{PAH}^- \quad (4.3)$$

The fraction of PAHs in a given charge state, $f(Z)$, is then determined by considering the ionization balance which yields

$$f(Z) = \frac{k_e(Z+1)}{k_{ion}(Z)} f(Z+1) \quad (4.4)$$

where $k_{ion}(Z)$ and $k_e(Z)$ are the photo-ionization and electron recombination rates of PAH molecule in a charge state $Z$ in units of s$^{-1}$. For $Z = -1$, $k_e(Z+1)$ is the electron attachment rate, $k_{ea}(Z)$.

We determine the charge distribution of PAHs by solving the set of equations given by equation (4.4) for each charge state in conjunction with the normalization condition

$$\sum_{Z=-1}^{Z=N_{max}} f(Z) = 1 \quad (4.5)$$

where $N_{max}$ is the highest charge state accessible to the PAH molecule.

**Photo-ionization rate**

We estimate the photo-ionization rate for a given PAH molecule in a charge state $Z$ using the following expression from Bakes & Tielens (1994):

$$k_{ion}(Z) = \pi W \int_{\nu_{z}}^{\nu_{H}} Y_{ion}(Z,\nu)\sigma_{abs}(Z,\nu)\frac{B_{\nu}(T_{eff})}{h\nu} d\nu \quad (s^{-1}) \quad (4.6)$$
where

\( Y_{\text{ion}}(Z, \nu) \) the ionization yield of a PAH molecule in a charge state \( Z \)

\( \sigma_{\text{abs}}(Z, \nu) \) the photo-absorption cross-section of a PAH molecule in a charge state \( Z \)

Units: \( \text{cm}^2 \)

\( B_{\nu}(T_{\text{eff}}) \) the Planck function for the incident blackbody radiation field at the effective temperature \( T_{\text{eff}} \) of the exciting star

Units: \( \text{erg cm}^{-2} \text{ s}^{-1} \text{ Hz}^{-1} \text{ sr}^{-1} \)

\( W \) the FUV radiation field dilution factor

\( \nu_Z \) the frequency of the photon corresponding to the ionization potential (IP) for a PAH molecule in charge state \( Z \)

Units: Hz

\( \nu_H \) the frequency of the photon corresponding to photon energy of 13.6 eV

Units: Hz

\( h \) the Planck constant i.e. \( 6.6261 \times 10^{-27} \text{ erg s} \)

The Planck function is calculated as

\[
B_{\nu}(T_{\text{eff}}) = \frac{2\hbar \nu^3}{c^2} \frac{1}{e^{\hbar \nu/kT_{\text{eff}}} - 1} \tag{4.7}
\]

where

\( k \) the Boltzmann constant i.e. \( 1.3807 \times 10^{-16} \text{ erg K}^{-1} \)

\( c \) the speed of light i.e. \( 2.99792458 \times 10^{10} \text{ cm s}^{-1} \)

The FUV radiation field dilution factor is calculated as

\[
W = \frac{1.6 \times 10^{-3} G_0}{\sigma T_{\text{eff}}^4 f_{\text{FUV}}} \tag{4.8}
\]

where

\( G_0 \) the FUV radiation field strength in Habing Field

\( 1 \ G_0 = 1.6 \times 10^{-3} \text{ erg cm}^{-2} \text{ s}^{-1} \)

\( \sigma \) the Stefan-Boltzmann constant

\( 5.6704 \times 10^{-5} \text{ erg s}^{-1} \text{ cm}^{-2} \text{ K}^{-4} \)

\( f_{\text{FUV}} \) the fraction of the FUV flux in the radiation field of the star with an effective temperature \( T_{\text{eff}} \)

The fraction of the FUV flux, \( f_{\text{FUV}} \), is further calculated as

\[
f_{\text{FUV}} = \frac{\pi \int_{\nu_6}^{\nu_H} B_{\nu}(T_{\text{eff}})d\nu}{\sigma T_{\text{eff}}^4} \tag{4.9}
\]

where \( \nu_6 \) is the frequency of the photon corresponding to a photon energy of 6 eV. In the calculation of \( W \), we use the fraction of the FUV flux because the ratio of \( G_0 \) and the FUV radiation provides a measure of the radiation field dilution. Since, by definition, \( G_0 \) is the FUV radiation field, we calculate the incident blackbody FUV radiation field by multiplying \( f_{\text{FUV}} \) with \( \sigma T_{\text{eff}}^4 \).
**Electron-recombination rate**

Measurements of electron recombination rates exist only for a few small PAHs. Therefore, we estimate the electron recombination rates theoretically by adopting the following formula proposed by Tielens (2005):

\[
  k_e(Z) = 1.3 \times 10^{-6} Z N_C^{1/2} \left( \frac{300}{T_{\text{gas}}} \right)^{1/2} n_e \quad (s^{-1})
\]

(4.10)

where \( N_C \) is the number of C atoms in a PAH molecule, \( T_{\text{gas}} \) is the gas temperature in K, and \( n_e \) is the electron density in a given environment in units of \( \text{cm}^{-3} \). This expression is based on the collisional rates of an electron’s interaction with an ionized PAH molecule represented by a conductive disk (Bakes & Tielens, 1994). We note that Biennier et al. (2006) compared the experimentally measured electron-recombination rates of small PAHs to theoretically calculated recombination rates (equation 4.10) and found that the electron recombination rates increase with size and approach the theoretical estimate for larger sized PAHs.

**Electron attachment rate**

We adopt the theoretical expression for electron attachment rates derived by Tielens (2005):

\[
  k_{ea}(Z = 0) = 1.3 \times 10^{-7} s_e \ N_C^{1/2} n_e \quad (s^{-1})
\]

(4.11)

where \( s_e \) is the dimensionless sticking coefficient for electron attachment.

**4.2.2 Theoretical calculation of IR emission from PAHs**

In this section, we describe the procedure we use to calculate the IR emission from a PAH molecule with a charge state \( Z \). First, we estimate the average photon energy, \( E_{\text{avg}}(Z) \), that a PAH molecule in a charge state \( Z \) will absorb in a given environment that will lead to the IR emission using the following expression:

\[
  E_{\text{avg}}(Z) = \frac{\int_{0}^{\nu_H} (1 - Y_{\text{ion}}(Z, \nu)) \sigma_{\text{abs}}(Z, \nu) h\nu \frac{B_{\nu}(T_{\text{eff}})}{h\nu} d\nu}{\int_{0}^{\nu_H} (1 - Y_{\text{ion}}(Z, \nu)) \sigma_{\text{abs}}(Z, \nu) \frac{B_{\nu}(T_{\text{eff}})}{h\nu} d\nu}
\]

(4.12)

where \( E_{\text{avg}}(Z) \) is in units of erg. The average photon energy depends on the physical conditions of the environment and the photo-absorption cross-section of the PAH molecule itself. Moreover, for a photon that is absorbed by a PAH molecule, there is always a competition between the process of IR emission and ionization. Therefore, we include a factor of \( 1 - Y_{\text{ion}}(Z, \nu) \) in the calculation of the average photon energy to account for this competition between the IR emission and photo-ionization. The factor \( 1 - Y_{\text{ion}}(Z, \nu) \) is derived from the probability, \( P_{\text{emission}}(Z) \), that a PAH molecule in a charge state \( Z \) will absorb a photon that leads to emission as opposed to ionization:

\[
  P_{\text{emission}}(Z) = \frac{k_{\text{abs}}(Z) - k_{\text{ion}}(Z)}{k_{\text{abs}}(Z)}
\]

(4.13)

where \( k_{\text{abs}}(Z) \) is the photo-absorption rate given by
$k_{\text{abs}}(Z) = \pi W \int_0^{\nu_H} \sigma_{\text{abs}}(Z, \nu) \frac{B_\nu(T_{\text{eff}})}{h\nu} d\nu \hspace{1cm} (s^{-1}) \hspace{1cm} (4.14)$

and $k_{\text{ion}}(Z)$ is the photo-ionization rate for a PAH molecule in a charge state $Z$ in a given environment.

Substituting the expression for $k_{\text{abs}}(Z)$ from equation 4.14 and $k_{\text{ion}}(Z)$ from equation 4.6 in equation 4.13, shows that $P_{\text{emission}}(Z) \propto \bar{1} - Y_{\text{ion}}(Z, \nu)$; $P_{\text{emission}}(Z) = \int_0^{\nu_H} \sigma_{\text{abs}}(Z, \nu)(1 - Y_{\text{ion}}(Z, \nu)) B_\nu(T_{\text{eff}}) h\nu d\nu \hspace{1cm} (4.15)$

Once the molecule absorbs the photon of energy, $E_{\text{avg}}(Z)$, it redistributes the absorbed energy over its various vibrational modes. A molecule with $N$ number of atoms will have $3N - 6$ number of vibrational modes called the fundamental vibrational modes. Out of these $3N - 6$ modes, only a few will be IR active and have intrinsic strengths, $\sigma_\nu$.

Upon absorption of a photon, the temperature of the molecule rises immediately. We calculate the temperature, $T_{\text{max}}$, the molecule will attain upon absorption of a single photon using the following expression from Bakes et al. (2001b):

$E_{\text{avg}}(Z) = \int_2.7K^{T_{\text{max}}} C_v(T, Z) dT \hspace{1cm} (4.16)$

where $C_v(T, Z)$ is the specific heat of a PAH molecule in a charge state $Z$ as a function of the temperature of the molecule in units of erg/K. In our calculation, we assume that initially before the absorption of a photon, the molecule has a temperature of 2.7 K and after the absorption it reaches a temperature $T_{\text{max}}$. Considering each fundamental vibrational mode of a molecule as a harmonic oscillator, we calculate the specific heat of a molecule, $C_v(T, Z)$, as follows (equation 6.33 in Tielens, 2005):

$C_v(T, Z) = k \sum_{i=1}^{3N-6} \left( \frac{h\nu_i, Z}{kT} \right)^2 \frac{exp\left(\frac{h\nu_i, Z}{kT}\right)}{[exp\left(\frac{h\nu_i, Z}{kT}\right) - 1]^2} \hspace{1cm} (4.17)$

Here, the $\nu_i$’s correspond to the frequencies of the fundamental vibrational modes of the PAH with charge $Z$.

In our model, we assume that the energy is quickly distributed over all available vibrational modes – the ergodic approximation. The molecule cools down via emission of IR photons through its IR active vibrational modes. We recognize that the PAH molecule can absorb yet another photon at any time during the cooling process and reach a higher temperature than $T_{\text{max}}$. In other words, we consider the absorption of multiple photons by a PAH molecule before it completely cools down. We account for the effect of the absorption of multiple photons on the temperature of a PAH molecule in a charge state $Z$ and hence on its IR emission, by calculating a temperature distribution function, $G(T, Z)$. For the first photon absorption, $G_1(T, Z)$ is defined as follows assuming that the temperature distribution of a PAH molecule is a Poisson process (see equation 6 in Bakes et al., 2001b):

$G_1(T, Z) = \frac{k_{\text{abs}}(Z)}{dT/dt} \exp[-k_{\text{abs}}(Z)\tau_{\text{min}}(T)] \hspace{1cm} (4.18)$
where

- $k_{\text{abs}}(Z)$ the photo-absorption rate for a PAH molecule in a charge state $Z$
  Units: $\text{s}^{-1}$
- $dT/ dt$ the cooling rate of a PAH molecule
  Units: $\text{K s}^{-1}$
- $\tau_{\text{min}}(T)$ the time taken by the molecule to cool down from maximum temperature reached after one photon absorption, $T_{\text{max}}$, to some temperature $T$
  Units: $\text{s}$

We calculate the rate, $dT/ dt$, at which the molecule cools down following equations 3 and 4 from Bakes et al. (2001b):

$$
\frac{dT}{dt} = \frac{4\pi}{C_{\nu}(T, Z)} \sum_{\nu} \sigma_{\nu,Z} B_{\nu}(T)
$$

emphasizing that in equation 4.19, the summation is taken over IR active vibrational modes only. Here $\sigma_{\nu,Z}$ is the intrinsic intensity of the IR active mode of a PAH molecule in a charge state $Z$ expressed as IR cross-section in units of cm$^2$ Hz. To calculate $\tau_{\text{min}}$, we then use the following expression (see equation 6.31 in Tielens, 2005):

$$
\tau_{\text{min}}(T) = \int_{T}^{T_{\text{max}}} \frac{1}{dT/ dt} dT
$$

For $n$ photon absorptions, we calculate the temperature distribution function, $G_n(T, Z)$, in an iterative fashion as follows:

$$
G_n(T, Z) = \int_{T_{\text{max}}}^{T_{\text{max}}(n)} G_{n-1, T_{n-1} \rightarrow T'}(T_{n-1}, Z) G_{T \rightarrow T'}(T, Z) dT_{n-1}
$$

where $G_{n-1, T_{n-1} \rightarrow T'}(T_{n-1}, Z)$ is the probability of finding a PAH molecule at temperature $T_{n-1}$ after $n - 1$ photon absorptions that can absorb the $n^{\text{th}}$ photon and reach the temperature $T'$ and $G_{T \rightarrow T'}(T, Z)$ is the probability of finding the molecule at temperature $T$ after it began to cool down from the temperature $T'$ it attained after the absorption of the $n^{\text{th}}$ photon. We calculate the temperatures $T'$ using equation 4.16 by replacing the left hand side with $E_{\text{avg}} + E_{T_{n-1}}$, sum of the energy $E_{\text{avg}}$ of a new photon absorbed and the energy $E_{T_{n-1}}$ remaining in a molecule from previous $n - 1$ photon absorptions, and the upper limit of the integral with the temperature $T'$ that the molecule will attain after the $n^{\text{th}}$ photon absorption.

After determining the temperature distribution, $G_n(T, Z)$, for a PAH molecule after absorption of $n$ photons, we calculate the IR emission of a molecule through its IR active vibrational modes as follows:

$$
I_{\nu}(Z) = \sigma_{\nu,Z} \int_{2.7}^{T_{\text{max},n}} B_{\nu}(T) G_n(T, Z) dT
$$

where $T_{\text{max},n}$ is the highest possible temperature that a PAH molecule can attain after $n$ photon absorptions.
4.2.3 Resulting PAH emission in astrophysical environments

In order to model the PAH emission in a given environment, we combine the calculation of the PAH charge distribution described in Section 4.2.1 with the theoretical calculation of IR emission from a PAH molecule described in Section 4.2.2. In other words, we multiply the intensity of each IR active mode of a molecule in a charge state $Z$, obtained from equation 4.22, with the fraction of PAHs having the charge state $Z$, $f(Z)$, obtained from equation 4.4, and sum the product over all the charge states accessible to a PAH molecule in that environment as follows:

$$I_{v_i} = \sum_{Z = -1}^{Z = N_{\text{max}}} f(Z) I_{v_i}(Z)$$  \hspace{1cm} (4.23)

4.2.4 PAH characteristics

In this paper, we study the IR emission from five representative PAHs, namely, tetracene ($C_{18}H_{12}$), pentacene ($C_{22}H_{14}$), ovalene ($C_{32}H_{14}$), circumcoronene ($C_{54}H_{18}$), and circumcircumcoronene ($C_{96}H_{24}$) covering a large range in size. The tetracene and pentacene molecules belong to the acene family, whereas the ovalene, circumcoronene, and circumcircumcoronene belong to the compact/pericondensed PAH family. Fig. 4.1 shows the structure of the PAH molecules studied in this work. We chose compact PAHs in our study due to their potential relevance to the interstellar PAH family. Compact PAHs are highly stable and can withstand harsh conditions in the ISM (Ricca et al., 2012). Their spectra in the 15-20 $\mu$m range are simple in comparison to those of non-compact PAHs, highlighting their potential as candidates for the
interstellar PAH family, which also exhibit relatively constant spectra in this wavelength range (Boersma et al., 2010; Ricca et al., 2012; Andrews et al., 2015). We include acenes in our study as examples of catacondensed and small PAHs with a large number of solo C-H modes. The strong 11.2 µm PAH feature is associated with the out-of-plane bending of solo C-H mode and, due to their zig-zag edges, acenes have a large number of solo Hs thereby making them relevant for the 11.2 µm PAH feature (Hony et al., 2001; Bauschlicher et al., 2008; Candelier & Sarre, 2015). Though not much explored in the context of the ultimate interstellar PAH family, acenes are studied in the context of H₂ formation on PAHs owing to their large reactivity (e.g. Campisi et al., 2020). In this section, we describe the molecular characteristics we adopt to model the IR emission from PAHs.

The PAH emission model takes into account the following molecular characteristics of PAHs: the ionization potential (IP), the ionization yield, the photo-absorption cross-section, the sticking coefficient, and the frequencies and corresponding intensities of the vibrational modes.

**Ionization Potential of PAHs:** The number of charge states that are accessible to a PAH molecule depends on their IP. Since, in this work, we calculate the charge distribution of PAHs in the PDR environments where H ionizing photons are absent, the charge state $Z + 1$ will be accessible to a PAH molecule if its IP(Z) is less than 13.6 eV. Table 4.1 lists the IPs of the PAH molecules considered in this work for charge states with an IP of less than 13.6 eV. We adopt the experimentally measured IP values where available. Where experimental data was unavailable, we adopt the IP values estimated from quantum chemical calculations (Malloci et al., 2007) or a conducting disk formula (Bakes & Tielens, 1994). Based on these IPs, the maximum accessible charge state for tetracene, pentacene, and ovalene is $Z = 2$, for circumcoronene $Z = 3$, and for circumcircumcoronene $Z = 4$.

**Ionization yield:** For the PAH molecules considered in this work, the ionization yields have not been measured experimentally with the exception of the singly charged ($Z = 1$) cation of ovalene (Wenzel et al., 2020). So we employ the semi-empirical relation proposed by Jochims et al. (1996) to estimate the ionization yields:

$$Y_{ion}(Z) \approx \begin{cases} 1, & h\nu \geq IP(Z) + 9.2 \text{ eV} \\ \frac{h\nu - IP(Z)}{9.2}, & h\nu < IP(Z) + 9.2 \text{ eV} \end{cases}$$ (4.24)

We note that Jochims et al. (1996) derived this relationship for ionization yields of neutral

---

Table 4.1: Ionization potential of PAHs in various charge states.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>IP($Z$) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Z = -1$</td>
</tr>
<tr>
<td>Tetracene (C₁₈H₁₂)</td>
<td>1.06 ¹</td>
</tr>
<tr>
<td>Pentacene (C₂₂H₁₄)</td>
<td>1.39 ¹</td>
</tr>
<tr>
<td>Ovalene (C₃₂H₁₄)</td>
<td>1.17 ⁴</td>
</tr>
<tr>
<td>Circumcoronene (C₅₄H₁₈)</td>
<td>1.44 ⁴</td>
</tr>
<tr>
<td>Circumcircumcoronene (C₉₆H₂₄)</td>
<td>3.1 ⁵</td>
</tr>
</tbody>
</table>

¹ Mitsui et al. (2007)  
² Clar et al. (1981)  
³ Tobita et al. (1994)  
⁴ Malloci et al. (2007)  
⁵ Bakes & Tielens (1994)
PAHs only. However, due to the lack of available data and formalisms to calculate ionization yields for higher charge states, we adopt the Jochims et al. (1996) relationship for higher charge states by choosing the appropriate IPs. It is worth pointing out that Wenzel et al. (2020) proposed a relationship to estimate ionization yields of singly charged cations of PAHs with sizes $N_C > 32$. These authors compared their ionization yields of singly charged PAHs to the yields of their neutral counterparts obtained from Jochims et al. (1996). They conclude that equation 4.24 describes well the experimentally measured ionization yields for PAH cations, lending further support for its general use in our analysis.

**Photo-absorption cross-section:** We obtain the data for the photo-absorption cross-sections from the online database of quantum chemically calculated molecular properties of PAH molecules (Malloci et al., 2007)\(^1\). The database holds absorption cross-sections of all the PAH molecules considered in this work except circumcoronene in the anionic ($Z = -1$), neutral ($Z = 0$), and cationic ($Z = 1, Z = 2, \text{ and } Z = 3$) states. We estimate the photo-absorption cross-sections for circumcoronene in the desired charge state from the photo-absorption cross-sections of circumcoronene in a corresponding charge state by scaling it with the number of carbon atoms of circumcoronene, i.e. multiplying the photo-absorption cross-sections of circumcoronene with a factor of $96/54 = 1.8$.

**Sticking coefficient:** The sticking coefficients, $s_e$, approach unity for PAHs with electron affinity $> 1$ eV. None of the PAHs considered in this work have electron affinity, i.e. $\text{IP}(-1)$ below 1 eV, therefore we adopt $s_e = 1$ following Tielens (2005).

**Frequencies and corresponding intensities of the vibrational modes:** We obtain the frequencies corresponding to the fundamental and the IR active vibrational modes, and the intrinsic intensities corresponding to the IR active vibrational modes from the the NASA Ames PAH IR Spectroscopic database (PAHdb, version 3.20; Bauschlicher et al., 2018; Boersma et al., 2014; Bauschlicher et al., 2010; Mattioda et al., 2020) except for the tetracene dication and the pentacene anion for which the database has no data. In Appendix C.1, we provide the UIDs of the molecules in PAHdb. For the tetracene dication and the pentacene anion, we obtain the relevant data from the Malloci et al. (2007) database. In both the databases, the intrinsic intensities of the IR active vibrational modes are expressed in terms of A-value, $A$ (km/mol). The A-value is related to the laboratory measured absorbance (see equation 6 in Mattioda et al. (2020)). For the purpose of our calculation, we convert A-value in the units of cross-section integrated over frequency following Mattioda et al. (2020);

$$\sigma_{\nu_i} = \frac{10^5}{N_A} \times c \times A_i \quad (4.25)$$

where $N_A$ is Avogadro’s number i.e. $6.02 \times 10^{23}$.

### 4.3 Results of the model for PAHs under astrophysical conditions

We use the PAH emission model to investigate the charge distribution and subsequent IR emission characteristics of the five PAHs described in Section 4.2.4 over a range of relevant astro-

\(^1\)https://astrochemistry.oa-cagliari.inaf.it/database/pahs.html
Chapter 4. PAH emission model

\[ \gamma = G_0 \times \sqrt{\frac{T_{\text{gas}}}{n_e}} \text{ (Habings K}^{1/2}\text{ cm}^3) \]

Figure 4.2: Charge distribution of ovalene as a function of the ionization parameter \( \gamma \), for a fixed value of \( G_0 = 2600 \), \( T_{\text{gas}} = 300\text{K} \), and \( T_{\text{eff}} = 17000\text{K} \).

physical conditions. Since PAH charge distribution is set by the so-called ionization parameter, \( \gamma = G_0 \times \sqrt{T_{\text{gas}}/n_e} \), we investigate the model results as a function of \( \gamma \).

4.3.1 Charge distribution

Adopting a fixed value of \( G_0 = 2600 \) in units of the Habing field, \( T_{\text{gas}} = 300 \text{K} \), an electron abundance of \( 1.6 \times 10^{-4} \), and \( 10^3 < n_{\text{gas}} < 10^6 \text{ cm}^{-3} \), we obtain \( \gamma \) values ranging from \( \sim 30 \)– \( 2 \times 10^5 \) Habings \( K^{1/2} \text{ cm}^3 \) for which we calculate the charge distribution of the PAH molecules considered in this work. This range of \( \gamma \) values cover well the variety of the physical conditions prevalent in the PDRs (see Table 4.2). We first use \( T_{\text{eff}} = 17000 \text{ K} \) for the blackbody radiation field, which is a required parameter for determining the photo-ionization rate in the charge distribution model (see Section 4.2.1); we will consider other values later. Fig. 4.2 shows the results of the calculation for ovalene, one of the PAH molecules considered in this work. The results for the remaining PAH molecules are shown in Appendix C.2 (see Fig. C.1). In comparing the results for different PAHs, it should be kept in mind that the charge distribution is controlled by the ionization rate over the recombination rate. This ratio is proportional to the ionization parameter as well as the ratio of the photo-ionization cross section to the electron-PAH interaction cross section. To first order, the former varies as \( N_C \) while the latter varies with \( N_C^{1/2} \). The small differences in ionization potential between the different PAHs have only a small effect given the broad energy dependence of the ionizing flux distribution. Of course, with increasing PAH size, more charge states may become accessible for \( h\nu < 13.6 \text{ eV} \).

We find that with increasing \( \gamma \) values, the dominant charge state shifts from anions through
neutrals to cations. In the case of ovalene, the anions remain the dominant charge state up to \( \gamma \sim 4 \times 10^2 \) after which the neutrals dominate up to \( \gamma \sim 4 \times 10^4 \), beyond which the cationic charge states dominate. We note that for other PAH molecules, the general trend remains the same, but as outlined above, the precise distribution of the charge states varies somewhat with \( N_C \); e.g., as the size of the molecule increases, cations begin to dominate at lower \( \gamma \) values. Likewise, the highest \( \gamma \) value for which anions dominate decreases with increasing size. While there are differences in the precise values of the fraction of charge for individual PAH molecules, the key result that emerges from the calculations is that the anions are the dominant charge state for \( \gamma \) values less than \( \sim 2 \times 10^2 \), the neutrals for \( \gamma \) values in the range \( \sim 10^3 \text{--} 10^4 \), and the cations for \( \gamma \) values greater than \( \sim 5 \times 10^5 \). These results are consistent with the charge distribution results from Bakes et al. (2001b).

We now investigate how the charge distribution would change if we choose values of \( G_0 \), \( T_{\text{gas}} \), and \( n_e \) other than those described above. We find that at a particular \( \gamma \) value, we get the same result for the charge distribution regardless of the values of the individual parameters characterizing it. This is expected since the ratio of the photo-ionization rate and the electron-recombination rate that goes in equation 4.4 is proportional to \( \gamma = G_0 \times \sqrt{T_{\text{gas}}/n_e} \).

We note that, in contrast to the electron recombination rate, the electron attachment rate (equation (4.11)) does not depend on \( T_{\text{gas}} \). In any event, since any \( T_{\text{gas}} \) dependence scales only with \( T_{\text{gas}}^{1/2} \) and the relevant range in \( T_{\text{gas}} \) is rather limited, it has only a small effect on the charge distribution. However, we find that the results of the charge distribution of PAHs are sensitive to the excitation conditions, i.e. the effective temperature, \( T_{\text{eff}} \), of the radiation field (see Fig. C.2). While the overall trend remains the same; that at low values of \( \gamma \), anions dominate, and at high values of \( \gamma \) cations dominate, the precise values of the fraction of each charge at a particular value of \( \gamma \) vary with \( T_{\text{eff}} \).

### 4.3.2 PAH spectra

The effect of the charge state on the intrinsic strengths of the vibrational modes of a PAH molecule has been extensively analyzed previously by several authors (see, e.g. Langhoff, 1996; Hudgins & Allamandola, 1999; Bauschlicher & Bakes, 2000; Bakes et al., 2001b,a). We present the intrinsic spectra of the molecules considered here in Appendix C.4. We encourage the reader to refer to the studies by, e.g. Langhoff (1996); Hudgins & Allamandola (1999); Bauschlicher & Bakes (2000); Bakes et al. (2001b,a) for a detailed discussion on the effects of the charge state on intrinsic spectra. In this section, we discuss the effects of the charge on the spectra of the PAH molecules after we apply the PAH emission model. We emphasize that after applying the emission model, the relative strength of the features will differ from the intrinsic strengths; however, the entire character of a molecular spectrum will not change.

Figs. 4.3-4.7 show the spectra of PAHs considered in this work after the application of the emission model. We calculate the spectra in each charge state for the excitation conditions typical of NGC 7023 (\( G_0 = 2600 \) and \( T_{\text{eff}} = 17000 \) K) following the procedure outlined in section 4.2.2. The average energies absorbed by the PAH molecule corresponding to the excitation conditions for which we calculate the spectra in each charge state are given in Table 4.3. In the calculation of the spectra, we consider three-photon absorptions before the molecule cools down. Essentially, we perform three iterations on the temperature distribution function, \( G(T)dT \), after which our calculated intensities of each vibrational mode converge. Once we
Figure 4.3: Calculated spectra of tetracene (C\textsubscript{18}H\textsubscript{12}) in the anionic, neutral, cationic, and dicationic states at excitation conditions characteristic of NGC 7023 ($G_0 = 2600$ and $T_{\text{eff}} = 17000$K).
Figure 4.4: Calculated spectra of pentacene ($C_{22}H_{14}$) in the anionic, neutral, cationic, and dicationic states at excitation conditions characteristic of NGC 7023 ($G_0 = 2600$ and $T_{\text{eff}} = 17000\text{K}$).
Figure 4.5: Calculated spectra of ovalene ($C_{32}H_{14}$) in the anionic, neutral, cationic, and dicationic states at excitation conditions characteristic of NGC 7023 ($G_0 = 2600$ and $T_{\text{eff}} = 17000\text{K}$).
Figure 4.6: Calculated spectra of circumcoronene (C$_{54}$H$_{18}$) in the anionic, neutral, cationic, dicationic, and tricationic states at excitation conditions characteristic of NGC 7023 ($G_0 = 2600$ and $T_{\text{eff}} = 17000$K).
Figure 4.7: Calculated spectra of circumcircumcoronene (C\textsubscript{96}H\textsubscript{24}) in the anionic, neutral, cationic, dicationic, and tricationic states at excitation conditions characteristic of NGC 7023 (\(G_0 = 2600\) and \(T_{\text{eff}} = 17000\)K).
obtain the strength of each IR active mode, we convolve the intensity of each vibrational mode with a Gaussian profile with a full width at half maximum (FWHM) determined by the spectral resolving power of 200.

The anionic and cationic charge states exhibit the strongest features in the 6–9 \( \mu \text{m} \) region, characteristic of the C-C stretching and C-H in-plane bending modes for all of the PAH molecules considered here, while the neutral charge states exhibit the strongest features in the 10–15 \( \mu \text{m} \) region characteristic of the C-H out of plane bending modes. While there are differences in the relative intensities of the PAH features in the 6–9 \( \mu \text{m} \) region for cationic and anionic charge states, these differences are not as distinct as those that distinguish neutrals from the other charge states. The intensity of the 3.3 \( \mu \text{m} \) feature, on the other hand, appears to differentiate between different charge states. The 3.3 \( \mu \text{m} \) feature is strongest in neutral charge states and weakest in cationic charge states. The intensity of this feature varies between molecules in the anionic charge states, with tetracene exhibiting a strong 3.3 \( \mu \text{m} \) feature compared to the other molecules. However, for a given PAH molecule, the 3.3 \( \mu \text{m} \) feature is always stronger in anions than in cations. As a result, the relative intensity of the 3.3 \( \mu \text{m} \) and 6–9 \( \mu \text{m} \) features may serve as a distinguishing feature between anionic and cationic charge states. Finally, we note that there are few strong features in the region long wards of 15 \( \mu \text{m} \), but we could not identify a systematic trend among the features in this region that can distinguish between different charge states.
The 6.2/11.2 band ratio

Traditionally, the ratio of the 6.2 and 11.2 μm PAH features is used as an indicator of the PAH charge state in astrophysical environments where low values imply neutrals as the dominant charge state and high values imply cations as the dominant charge state (e.g. Peeters et al., 2002b; Berné et al., 2007; Boersma et al., 2018). In light of the results presented in Figs. 4.3-4.7 as discussed above, this interpretation may be unreliable for high values of this ratio. To investigate how the similarity between the features of anions and cations in the 6–9 μm region translate in the interpretation of the 6.2/11.2 band ratio, we analyze this ratio as a function of the ionization parameter γ.

We obtain the spectra of a PAH molecule in all the charge states at the conditions that are typical of NGC 7023. We note that for circumcircumcoronene in charge state Z = 4, there is no available data on the frequencies and the intensities of the vibrational modes, and therefore, we do not include it in our calculation. However, it does not have a significant impact on the results of the PAH ratio because the contribution from the Z = 4 state of circumcircumcoronene for the γ values investigated here is negligible (see Fig. C.1). For the calculation of the 6.2/11.2, we do not convolve the spectra with Gaussian functions. Instead, for each charge state, we extract the intensities corresponding to the C-C modes (6.2 μm) by adding the intensities of all the modes in the 6.1–6.9 μm range, and for C-H modes (11.0+11.2 μm) in the 10.0–12.0 μm range. We note that, although the wavelength range used to calculate the intensities of C-H modes theoretically consists of a couple of weak and strong features, only the features at 11.0 and 11.2 μm bands are observed, with the 11.2 μm PAH band being the dominant band. Therefore, for the remainder of the paper, we will refer to the intensities of the C-H modes as the 11.0+11.2 μm band. This will also serve as a reminder to the reader that the weak 11.0 μm PAH band characteristic of cations is also included in the measurement of the C-H modes. We multiply the extracted intensities of the C-C and C-H modes for a charge state Z of a molecule with its corresponding charge fraction. Finally, we add up the weighted intensities of the C-C and C-H modes for all the charge states of a molecule to obtain the 6.2 and 11.0+11.2 μm band intensities, respectively.

Fig. 4.8 shows the 6.2/(11.0+11.2) band ratio as a function of γ for all the PAH molecules considered in this work. We note that high values of 6.2/(11.0+11.2) can be reached for both low and high values of γ. We recall from section 4.3.1 that anions dominate at low values of γ and cations at high values of γ. Therefore, the high values of 6.2/(11.0+11.2) at low values of γ result from the contribution of anions to the 6.2 μm band, thereby illustrating that observed high values of 6.2/(11.0+11.2) do not always necessarily imply a large fraction of cations. For intermediate γ values, where neutrals dominate, the curve of 6.2/(11.0+11.2) is relatively flat for all molecules exhibiting almost similar values. In contrast, the 6.2/(11.0+11.2) ratio varies for the different molecules at low and high γ values, although there is no systematic trend between the molecules. Finally, we note that compared to compact PAHs, acenes exhibit relatively high 6.2/(11.0+11.2) values at the left end of the curve, where anions dominate. We discuss the implications of this result further in section 4.4.3 where we compare the results of the PAH emission model with observations of PDRs.
Figure 4.9: Ratios of the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ color-coded with $\gamma$ values for the five PAH molecules considered in this work. Except for circumcircumcoronene, there are two values of $3.3/(11.0+11.2)$ for a given value of $6.2/(11.0+11.2)$, one originating from low $\gamma$ values and the other from high $\gamma$ values. See text for details of the calculation of the $6.2/(11.0+11.2)$ and $3.3/(11.0+11.2)$ band ratios.
6.2/(11.0+11.2) vs 3.3/(11.0+11.2)

Given that high values of the 6.2/(11.0+11.2) ratio can arise from both anions and cations, it becomes important to have a tool to distinguish between these two charge states while interpreting astronomical observations. As noted in section 4.3.2, the relative intensities of the features in the 3.3 and 6–9 μm range can be used to distinguish between cations and anions. To investigate this, we analyze plots of the 6.2/(11.0+11.2) vs 3.3/(11.0+11.2) for the PAH molecules considered here. To calculate the 3.3/(11.0+11.2) ratio, we extract the intensity of the 3.3 μm feature by adding up intensities of all the modes in the 3.0–4.0 μm range for each charge state before weighting them with their corresponding charge fraction. We show the resulting plots in fig. 4.9. There are essentially two branches for each molecule, with both branches overlapping in the case of circumcircumcoronene. In one branch, the 3.3/(11.0+11.2) values decrease with increasing 6.2/(11.0+11.2) values. This branch corresponds to γ values > 10^3 where neutrals and cations dominate. However, in the second branch, the 3.3/(11.0+11.2) values increase with increasing 6.2/(11.0+11.2) values for the acenes and ovalene, remain almost constant with increasing 6.2/(11.0+11.2) values for circumcoronene, and decreases with increasing 6.2/(11.0+11.2) values for circumcircumcoronene. The second branch originates from γ values < 10^3 where anions dominate. The 3.3/(11.0+11.2) vs 6.2/(11.0+11.2) plots separate cations from anions in acenes, ovalene, and circumcoronene, but not for circumcircumcoronene. We further note that the slope of the second branch originating from anions not only vary with respect to the molecule considered but also with respect to the excitation conditions (see Fig. C.8). For example, at \( G_0 = 26000 \) and \( T_{\text{eff}} = 40000\text{K} \), the 3.3/(11.0+11.2) values in the second branch decrease with increasing 6.2/(11.0+11.2) values for circumcoronene whereas they remain constant for \( G_0 = 2600 \) and \( T_{\text{eff}} = 17000\text{K} \). Therefore, we conclude that the 3.3/(11.0+11.2) vs 6.2/(11.0+11.2) plots can not be used as a diagnostic tool for astronomical purposes. However, the plots presented here show that corresponding to a single value of 6.2/(11.0+11.2), there are two values of 3.3/(11.0+11.2). This result demonstrates the influence of charge state on 3.3/(11.0+11.2) ratio which is traditionally used to determine the PAH size (e.g. Allamandola et al., 1989; Schutte et al., 1993; Ricca et al., 2012; Croiset et al., 2016; Knight et al., 2021a). It also has implications in interpreting the 3.3/(11.0+11.2) - 6.2/(11.0+11.2) diagnostic plots often used in the literature to determine PAH charge and size (e.g. Draine & Li, 2001; Maragkoudakis et al., 2018, 2020). We discuss this further in Section 4.4.4.

4.4 Application of the model to PDRs

We apply the PAH emission model to the IR observations of four well-studied PDRs and the diffuse ISM that sample various physical conditions.

4.4.1 Environments

In the following sections, we describe the environments and present a relevant discussion on the measurements of physical conditions (\( G_0, n_{\text{gas}}, \) and \( T_{\text{gas}} \)) in these environments. We emphasize that the measurement of the physical conditions strongly depends on the method adopted to
measure these, and as such, there exists a range of values for some of the parameters across the literature. In such cases, we adopt an average value of the parameters over the range present in the literature. To calculate $n_e$ from $n_{\text{gas}}$, we adopt an electron abundance, $X_e$, of $1.6 \times 10^{-4}$ from Sofia et al. (2004) assuming that the $X_e$ is a result of the ionization of C. Table 4.2 presents the physical conditions we adopt, the $\gamma$ values we derive from these, and the $T_{\text{eff}}$ of the radiation field in the environments considered here. For the diffuse ISM, we use the expression provided by Tielens (2005) for the energy dependence of the radiation field.
Table 4.2: Physical conditions in the environments studied in this work.

<table>
<thead>
<tr>
<th>PDR environment</th>
<th>$G_0$ (Habings field)$^a$</th>
<th>$n_{gas}$ (cm$^{-3}$)$^b$</th>
<th>$T_{gas}$ (K)$^c$</th>
<th>$X_e$$^d$</th>
<th>$T_{eff}$ (K)$^e$</th>
<th>$\gamma$</th>
</tr>
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<tbody>
<tr>
<td>NGC 7023</td>
<td>2600</td>
<td>$10^4$</td>
<td>400</td>
<td>$1.6 \times 10^{-4}$</td>
<td>17000</td>
<td>$3.3 \times 10^4$</td>
</tr>
<tr>
<td>NGC 2023</td>
<td>17000</td>
<td>$2.0 \times 10^5$</td>
<td>500</td>
<td>$1.6 \times 10^{-4}$</td>
<td>23000</td>
<td>$1.2 \times 10^4$</td>
</tr>
<tr>
<td>Horsehead Nebula</td>
<td>100</td>
<td>$2.0 \times 10^5$</td>
<td>100</td>
<td>$1.6 \times 10^{-4}$</td>
<td>33000</td>
<td>30</td>
</tr>
<tr>
<td>Orion Bar</td>
<td>26000</td>
<td>$10^5$</td>
<td>500</td>
<td>$1.6 \times 10^{-4}$</td>
<td>40000</td>
<td>$3.6 \times 10^4$</td>
</tr>
<tr>
<td>diffuse ISM</td>
<td>1.7</td>
<td>30</td>
<td>80</td>
<td>$1.6 \times 10^{-4}$</td>
<td></td>
<td>$3.2 \times 10^3$</td>
</tr>
</tbody>
</table>

$^a$ NGC 7023: Chokshi et al. (1988); NGC 2023: Sheffer et al. (2011); Horsehead Nebula: Abergel et al. (2003); Orion Bar: Marconi et al. (1998); diffuse ISM: (Habing, 1968; Draine, 1978)

$^b$ NGC 7023: Chokshi et al. (1988), Joblin et al. (2010), Köhler et al. (2014), Bernard-Salas et al. (2015), Joblin et al. (2018); NGC 2023: Steiman-Cameron et al. (1997), Sheffer et al. (2011); Horsehead Nebula: Habart et al. (2005); Orion Bar: Parmar et al. (1991), Tauber et al. (1994), Young Owl et al. (2000), Bernard-Salas et al. (2012), Joblin et al. (2018); diffuse ISM: (Wolfire et al., 2003)

$^c$ NGC 7023: Fuente et al. (1999), Fleming et al. (2010); NGC 2023: Steiman-Cameron et al. (1997), Sheffer et al. (2011); Horsehead Nebula: Habart et al. (2011); Orion Bar: Allers et al. (2005); diffuse ISM: (Wolfire et al., 2003)

$^d$ Sofia et al. (2004)

$^e$ NGC 7023: (Racine, 1968; Witt & Cottrell, 1980; van den Ancker et al., 1997b); NGC 2023: (Racine, 1968; Mookerjea et al., 2009); Horsehead Nebula: (Edwards, 1976; Abergel et al., 2003); Orion bar: (Kraus et al., 2007)
NGC 7023

NGC 7023 is a reflection nebula illuminated by HD 200775, a spectroscopic binary (Herbig B3Ve - B5; Racine, 1968; Witt & Cottrell, 1980; van den Ancker et al., 1997b). It is situated at a distance of 361 ± 6 pc (Gaia Collaboration et al., 2016, 2018) and is a well-studied reflection nebula due to its high surface brightness and proximity to the Earth. There are three PDRs in NGC 7023 towards the North West (NW), South West (SW), and East of the central star. In this work, we focus on the NW PDR. The structure of NGC 7023 towards the NW PDR is easy to visualize with stratified layers of a cavity carved out by the illuminating star, followed by the almost edge-on PDR at the edges of the cavity. The PDR is made of diffuse gas embedded with filaments of dense gas. In this work, we adopt the values of the physical conditions estimated previously by several authors. We take the estimate of $G_0 = 2600$ in units of Habing Field from Chokshi et al. (1988) who estimated this from the far-infrared (FIR) continuum intensity assuming that the UV radiation from the star is absorbed and reradiated in the IR by the dust. There are several estimates for $n_{\text{gas}}$ in the literature. Using observations of O I (63 µm), C II (158 µm), and low J 12CO and 13CO lines, Chokshi et al. (1988) estimated $n_{\text{gas}} \sim 4 \times 10^3$ cm$^{-3}$ in dense clumps and 500 cm$^{-3}$ outside of the clumps in the NW PDR. Joblin et al. (2010) estimated $n_{\text{gas}} \sim 7 \times 10^3$ cm$^{-3}$ from the Herschel measurements of the C II (158 µm) line alone. Köhler et al. (2014) modelled intermediate- to high-J CO lines in NGC 7023 and estimated $n_{\text{gas}} \sim 5 \times 10^4 - 5 \times 10^6$ cm$^{-3}$ from high-J CO lines and $10^4 - 10^5$ cm$^{-3}$ from low-J CO lines. Bernard-Salas et al. (2015) estimated densities of $1.7 \times 10^4 - 1.8 \times 10^5$ cm$^{-3}$ from the measurements of the O I (145 µm) line. Recently, Joblin et al. (2018) modelled high-J CO lines and estimated $n_{\text{gas}}$ of $4 \times 10^4$ cm$^{-3}$ at the edge of the PDR. These estimates of $n_{\text{gas}}$ range from values as low as 500 cm$^{-3}$ in the diffuse gas to as high as $10^6$ cm$^{-3}$ in the dense filaments. We note that the estimates of $n_{\text{gas}}$ strongly depend on the line being used for the estimation that probe regions of different densities within the PDR. Here, we adopt an average value of $\sim 10^4$ cm$^{-3}$. For $T_{\text{gas}}$, we adopt a value of $\sim 400$ K measured using pure H$_2$ rotational lines by Fuente et al. (1999) based on the Infrared Space Observatory (ISO) observations. This value of $T_{\text{gas}}$ is in agreement with the calculation of $T_{\text{gas}}$ by Fleming et al. (2010) based on the Spitzer observations.

NGC 2023

NGC 2023 is a reflection nebula in the Orion constellation illuminated by B1.5V star HD 37903 (Racine, 1968; Mookerjea et al., 2009). It is at a distance of 403 ± 4 pc from the Earth (Kounkel et al., 2018). The illuminating star has carved out a cavity in the molecular gas, the edges of which form the PDR. In this work, we focus on the bright ridge in the PDR known as the South ridge. We adopt the physical conditions in the ridge from Sheffer et al. (2011). They determined a value of radiation field $\chi = 10^4$ in terms of Draine interstellar radiation field, which translates to a $G_0 = 1.7 \times 10^4$ in terms of the Habing field and $n_{\text{gas}}$ of $2 \times 10^5$ cm$^{-3}$ using pure rotational H$_2$ emission lines. They also measured excitation temperatures, $T_{\text{ex}}$, and found that $T_{\text{ex}}$ ranges from 240–700 K. Since transitions between low-J levels of the pure rotational H$_2$ probe $T_{\text{gas}}$ owing to their low critical densities, we adopt an average $T_{\text{gas}}$ value of $\sim 500$ K. These estimates for the physical conditions are consistent with the estimates obtained using measurements of [O i] (63, 145 µm), [C ii] (158 µm), [Si ii] (35 µm) and CO lines (Steiman-
Horsehead Nebula

The Horsehead nebula is a dark nebula situated due west of NGC 2023 in the Orion constellation. The Horsehead nebula lies at the edge of the L1630 molecular cloud and is illuminated by the O9.5V binary system σ Orionis star (Edwards, 1976; Abergel et al., 2003). The illuminating star and the horsehead nebula are almost in the same plane perpendicular to our line of sight, presenting an almost edge-on view of the PDR. It is also a prototypical example of a low illumination PDR. In this work, we focus on the narrow filament at the edge of the PDR. We adopt a $G_0$ of 100 Habings field from Abergel et al. (2003). These authors estimated $G_0$ based on dilution assuming a distance of ~3.5 pc between σ Orionis and the PDR. We take $n_{\text{gas}} = 2 \times 10^5$ cm$^{-3}$ estimated from the H$_2$ 1-0 S(1) line, low-J CO lines, and dust continuum emission by Habart et al. (2005). Habart et al. (2011) estimated rotational temperatures for low-J pure rotational lines of H$_2$ ranging from 250 – 400 K. However, a quick look at the model parameters in the PhotoDissociation Region Toolbox, an online toolbox to estimate physical conditions from observations (Kaufman et al., 2006; Pound & Wolfire, 2008), shows that at $G_0 = 100$ and $n_{\text{gas}} = 2 \times 10^5$, the $T_{\text{gas}}$ is ~100 K. Therefore, in this work, we adopt a $T_{\text{gas}}$ of 100 K.

Orion Bar

The Orion Bar is a PDR situated in the Orion nebula at a distance of 414 ± 7 pc (Menten et al., 2007). It is illuminated by four stars of type O-B in the trapezium cluster with θ1 Orionis C being the most massive and luminous star (Kraus et al., 2007). It is one of the brightest and the most studied PDR. The Orion Bar lies at the edge of the H ii region created by the star. For this work, we adopt a $G_0$ of 2.6 × 10$^4$ Habings field determined by Marconi et al. (1998) using near-IR observations of an OI fluorescent line. The generally accepted picture of the Orion Bar entails dense clumps of density 10$^6$ cm$^{-3}$ embedded in diffuse gas of density 5 × 10$^4$ cm$^{-3}$. These estimates for the density have been derived consistently by several authors using H$_2$, CO, HCN, and HCO$^+$ observations (Parmar et al., 1991; Tauber et al., 1994; Young Owl et al., 2000; Bernard-Salas et al., 2012; Joblin et al., 2018). In this work, we adopt an average $n_{\text{gas}}$ of 10$^5$ cm$^{-3}$. For $T_{\text{gas}}$, we use the value of 500 K estimated from pure rotational H$_2$ lines by Allers et al. (2005).

Diffuse ISM

In this work, we adopt the physical conditions characteristic of the Cold Neutral Medium. For $G_0$, we take a value of 1.7 in the units of Habing field (Habing, 1968; Draine, 1978). For $n_{\text{gas}}$ and $T_{\text{gas}}$, we take the values estimated by Wolfire et al. (2003). These authors estimated average $n_{\text{gas}}$ and $T_{\text{gas}}$ from detailed modelling of the gas heating rate and the gas-phase abundances of interstellar gas and found average $n_{\text{gas}}$ of ~30 cm$^{-3}$, and $T_{\text{gas}}$ of ~80 K.
Figure 4.10: Charge distribution of the five PAHs considered in this work in NGC 7023, NGC 2023, the Horsehead nebula, the Orion Bar, and the diffuse ISM.
4.4.2 Charge distribution in PDR environments

In Fig. 4.10 we show the charge distribution predicted for the five PAH molecules, \( \text{C}_{18}\text{H}_{12}, \text{C}_{22}\text{H}_{14}, \text{C}_{32}\text{H}_{14}, \text{C}_{54}\text{H}_{18}, \text{and C}_{96}\text{H}_{24} \), by the charge distribution model (see Section 4.2.1) in NGC 7023, NGC 2023, the Horsehead nebula, the Orion Bar, and the diffuse ISM. Here, we briefly summarize the model predictions for each of the environment. In NGC 7023, neutrals emerge as the dominant charge state for the small-sized PAHs (e.g., \( \text{C}_{18}\text{H}_{12}, \text{C}_{22}\text{H}_{14}, \text{C}_{32}\text{H}_{14} \)) and cations for the large-sized PAHs (e.g., \( \text{C}_{96}\text{H}_{24} \)). For the intermediate-sized PAHs (e.g., \( \text{C}_{54}\text{H}_{18} \)), both neutrals and cations have similar charge fractions of roughly 50%. In NGC 2023, the neutrals emerge as the dominant charge state for all the PAHs considered here, though the fraction of neutrals decreases as the size of the PAH molecule increases. The Horsehead nebula presents an interesting case where the dominant charge state is anions for all the PAHs with a minimal decrease in the fraction of anions with increasing size of the PAH molecule. In the Orion Bar, the dominant charge state is cations with singly charged cations as the dominant charge state in small and intermediate-sized PAHs and singly and doubly charged cations as the dominant charge states in large-sized PAHs. Finally, in the diffuse ISM, neutrals are the dominant charge state for small sized PAHs and cations for the large sized PAHs.

4.4.3 Validating the model

In order to test the PAH emission model, we compare the relative intensities of the PAH features, in particular the 6.2/(11.0+11.2) and 3.3/6.2 band ratios, predicted by the model with the observations of the PDRs and the diffuse ISM. In the PDRs, we take the Spitzer Infrared Spectrograph (IRS) Short Low (SL) observations for the 6.2/(11.0+11.2) band ratio, and ISO - Short Wavelength Spectrometer (SWS) observations for the 3.3/6.2 band ratio. For the 6.2/(11.0+11.2) band ratios, we take the flux measurements at the NW PDR of NGC 7023 from Stock et al. (2016), at the South ridge in NGC 2023 from Peeters et al. (2017), at the Horsehead PDR from the Spitzer archive (published previously by Ochsendorf & Tielens (2015)), and the Orion Bar from Knight et al. (2021b). For the 3.3/6.2 band ratio, we take the flux measurements in all the environments from Peeters et al. (2002b); van Diedenhoven et al. (2004). We note that the ISO-SWS apertures are larger than the Spitzer IRS SL apertures and are not centered on the same positions, therefore the observations of 6.2/(11.0+11.2) and 3.3/6.2 are not necessarily at the same location. Moreover, because of the lack of the ISO-SWS observations in the Horsehead nebula, we do not calculate the 3.3/6.2 band ratios from the model for the excitation conditions corresponding to the Horsehead nebula. In the diffuse ISM, we take the observations for the 6.2/(11.0+11.2) and 3.3/6.2 from AROME observations from Giard et al. (1994) and ISO camera (ISOCAM) from Flagey et al. (2006).

To determine the 6.2/(11.0+11.2) and 3.3/6.2 band ratios from the model, we compute the spectra for each charge state of a PAH molecule at the average energy set by \( T_{\text{eff}} \) and the PAH characteristics (see equation 4.12). In Table 4.3, we present the average energy absorbed by a specific PAH molecule in each charge state in the environments considered here. From the calculated spectra, we first determine the strengths of the 3.3, 6.2, and 11.0+11.2 \( \mu \text{m} \) bands in each charge state of a molecule following the procedure described in section 4.3.2 and weight the strengths with the fraction of charge states before adding the band strengths in all the charge states to determine the 3.3, 6.2, and 11.0+11.2 \( \mu \text{m} \) bands for a PAH molecule. Since the charge
Table 4.3: Average energy absorbed by each charge state of PAH molecules considered in this work in NGC 7023, NGC 2023, the Horsehead nebula, the Orion Bar, and the diffuse ISM.

**NGC 7023**

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<tr>
<td>Tetracene</td>
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</tr>
<tr>
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<td>Ovalene</td>
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<tr>
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<td>4.51</td>
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<tr>
<td>Circumcircumcoronene</td>
<td>4.68</td>
</tr>
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**NGC 2023**

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<td>Pentacene</td>
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**Horsehead nebula**

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**Orion Bar**

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<td>Circumcircumcoronene</td>
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**Diffuse ISM**

<table>
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</table>
Figure 4.11: The $6.2/(11.0+11.2)$ band ratio as a function of the ionization parameter $\gamma$. Individual panels correspond to the $6.2/(11.0+11.2)$ ratio determined from the PAH spectra calculated at excitation conditions characteristic for NGC 7023 ($G_0 = 2600$ and $T_{\text{eff}} = 17000K$), NGC 2023 ($G_0 = 17000$ and $T_{\text{eff}} = 23000K$), the Horsehead nebula ($G_0 = 100$ and $T_{\text{eff}} = 33000K$), the Orion Bar ($G_0 = 26000$ and $T_{\text{eff}} = 40000K$), and the diffuse ISM. See text for details about the method of calculation of the $6.2/(11.0+11.2)$ band ratio. The observational data points are also shown in the corresponding panels (black square). The dashed line shows the adopted $\gamma$ value for the environments considered here.
Figure 4.12: The 3.3/6.2 band ratio as a function of the ionization parameter $\gamma$. Individual panels correspond to the 3.3/6.2 ratio determined from the PAH spectra calculated at excitation conditions characteristic for NGC 7023 ($G_0 = 2600$ and $T_{\text{eff}} = 17000$K), NGC 2023 ($G_0 = 17000$ and $T_{\text{eff}} = 23000$K), the Orion Bar ($G_0 = 26000$ and $T_{\text{eff}} = 40000$K), and the diffuse ISM. See text for details about the method of calculation of the 3.3/6.2 band ratio. The observational data points are also shown in the corresponding panels (black square). The dashed line shows the adopted $\gamma$ value for the environments considered here.
distribution is a sensitive function of \( \gamma \), whose value for the PDRs is not strictly constrained (see discussion in section 4.4.1), we calculate the 3.3/6.2 and 6.2/(11.0+11.2) values as a function of \( \gamma \).

Fig. 4.11 shows the predicted values of the 6.2/(11.0+11.2) as a function of \( \gamma \) for the excitation conditions characteristic for NGC 2023, NGC 7023, the Horsehead nebula, the Orion Bar and the diffuse ISM. The corresponding observed values of the 6.2/(11.0+11.2) band ratio are also shown in the figure. For NGC 7023 and NGC 2023, the predicted value of 6.2/(11.0+11.2) ratio for \( \text{C}_{96}\text{H}_{24} \) compares well with the observational value, for the Horsehead nebula, the predicted value for \( \text{C}_{22}\text{H}_{14} \) compares well the observational value. For the Orion Bar and the diffuse ISM, the predicted value for \( \text{C}_{32}\text{H}_{14} \) compares well with the observational value. We emphasize that since the \( \gamma \) of these sources is not strictly constrained, the observational data point can shift in the 6.2/(11.0+11.2) vs \( \gamma \) plane and, as a consequence, the size of the molecule for which there will be a good match between the model prediction and the observation may change. The 6.2/(11.0+11.2) vs \( \gamma \) plots shown here do not predict the size of the PAH molecule but rather shows that the PAH emission model based on the charge distribution can explain the observed PAH emission. Moreover, it shows that compact PAHs, which are considered potential candidates for grandPAHs - a set of few stable PAHs comprising the astronomical PAH population (Andrews et al., 2015) - can effectively produce the observed 6.2/(11.0+11.2) ratios in NGC 7023, NGC 2023, the Orion Bar, and the diffuse ISM. In contrast, in the Horsehead nebula, an acene shows a good comparison with the observed value. Thus, while the grand-PAH hypothesis remains plausible in high illumination PDRs like NGC 7023, NGC 2023, and the Orion Bar, it is not the case in low illumination PDRs like the Horsehead nebula. We emphasize that a good match between the predicted 6.2/(11.0+11.2) for \( \text{C}_{22}\text{H}_{14} \) and the observed value in the Horsehead nebula does not necessarily mean that acenes are present in the PDR environment of Horsehead nebula. It merely shows that either \( \text{C}_{22}\text{H}_{14} \) or a molecule behaving like \( \text{C}_{22}\text{H}_{14} \) (e.g., molecules with a high ratio for the intrinsic strength of the 6.2/(11.0+11.2) bands in anions) is responsible for the observed emission in the Horsehead nebula. Finally, we reiterate that a high value of 6.2/(11.0+11.2) does not always indicate the presence of a large fraction of cations in the astronomical environment. As shown in Fig. 4.11, while the high 6.2/(11.0+11.2) ratio in the Orion Bar is a result of the large fraction of cations, the high 6.2/(11.0+11.2) ratio in the Horsehead nebula is a result of the large fraction of anions.

Fig. 4.12 shows the plots of predicted and observed values of 3.3/6.2 as a function of \( \gamma \) for NGC 7023, NGC 2023, the Orion Bar, and the diffuse ISM. The observed values of NGC 7023 compare well with predicted values for the compact PAHs \( \text{C}_{54}\text{H}_{18} \) and \( \text{C}_{96}\text{H}_{24} \). For the NGC 2023, the observed value shows a good match with \( \text{C}_{96}\text{H}_{24} \), for the Orion bar and the diffuse ISM, it matches with \( \text{C}_{54}\text{H}_{18} \). These results demonstrate that the PAH emission model based on the charge distribution presented here can effectively explain the observed PAH emission. However, as discussed above, a good match between the observed value and model prediction does not predict the precise size of the molecule as the observed value can shift in the plane of the 3.3/6.2 vs \( \gamma \) due to uncertainty in \( \gamma \) in the PDRs and the uncertainty in the electron recombination and attachment cross-sections (c.f., section 4.4.5).
Figure 4.13: The 6.2/(11.0+11.2) vs 3.3/(11.0+11.2) plots of compact PAHs considered in this work over $\gamma$ values ranging from 30 to $2 \times 10^5$. The points of constant $\gamma$ values for each PAH molecule are joined together. In each panel, the high $\gamma$ values are at the right end of the plot and decrease towards the left. Each panel corresponds to the ratios determined from the PAH spectra calculated for different excitation conditions. $T_{\text{eff}} = 17000K$ corresponds to conditions characteristic of NGC 7023, $T_{\text{eff}} = 23000K$ to NGC 2023, and $T_{\text{eff}} = 40000K$ to the Orion bar. The corresponding observational data point is also shown in each panel.
Figure 4.14: A section of the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ plots shown in Fig. 4.13 demonstrating that the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ can be used as a tool to determine the precise $\gamma$ value and PAH size in astrophysical environments if we have a rough estimation of the range of $\gamma$ values.
4.4.4 Revisiting the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ as a diagnostic tool

The $6.2/11.2$ and $3.3/11.2$ band ratios are often employed to determine the charge and the size of the emitting PAH population in astrophysical environments (e.g., Draine & Li, 2001; Croiset et al., 2016; Boersma et al., 2016; Maragkoudakis et al., 2020; Knight et al., 2021a). Furthermore, the $6.2/11.2$ band ratio has been related to the ionization parameter $\gamma$ (e.g., Galliano et al., 2008; Fleming et al., 2010; Boersma et al., 2016; Stock et al., 2016). However, the results of the PAH emission model show that the interpretation of the $6.2/(11.0+11.2)$ ratio is ambiguous in the low and high regimes of $\gamma$. Moreover, we find that for a PAH molecule, two values for the $3.3/(11.0+11.2)$ may correspond to one $6.2/(11.0+11.2)$ value (section 4.3.2); one for high $\gamma$ values and the other for low $\gamma$ values. This adds a layer of complexity to the interpretation of PAH size from observations of the $3.3/11.2$ ratio in astronomical environments. Given these results, we revisit the diagnostic potential of the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ ratios and investigate whether these are reliable indicators of $\gamma$ and the average size of the astronomical PAH population.

We analyze the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ plots for the excitation conditions typical of NGC 7023, NGC 2023, the Orion bar, and the diffuse ISM (see Fig. 4.13). Essentially we plot the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ curves for compact PAHs in the same plane and join the curves for different PAH molecules corresponding to the same $\gamma$ values forming a grid. We note that the grid corresponding to each excitation temperature overlaps for a certain range of $\gamma$ values. We emphasize that this overlapping results from the fact that two values of $3.3/(11.0+11.2)$ corresponds to a single value of $6.2/(11.0+11.2)$.

To understand the diagnostic potential of $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$, we investigate Fig. 4.13 by considering two scenarios. In one scenario, we assume no prior knowledge of the $\gamma$ value of the astrophysical region, whereas, in the other scenario, we assume a rough estimate for the range of $\gamma$. In the first scenario, where we have no idea about the $\gamma$ value, it becomes unfeasible to use these plots as indicators of $\gamma$. For NGC 7023 and NGC 2023, the observed data point is in the region of the grid where there is no overlap, implying a unique solution for $\gamma$ and PAH size. In contrast, for the Orion bar and the diffuse ISM, the observed data point is in the overlapping region of the grid, implying a unique solution for PAH size but not for $\gamma$. As a result, in the first scenario, the $3.3/(11.0+11.2)$ ratio can be used to predict PAH size, but the $6.2/(11.0+11.2)$ ratio cannot be used to predict $\gamma$. However, in the second scenario, where we assume prior knowledge about the range of $\gamma$ values in an astrophysical environment, these diagnostic plots have enormous potential because now we are essentially sampling only a portion of the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ grid, avoiding the grid-overlap problem (see Fig. 4.14). For example, assuming that the $\gamma$ values for NGC 7023, NGC 2023, and the Orion bar range from $10^3$–$10^5$, we show the part of the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ plot from Fig. 4.13 corresponding to this range in Fig. 4.14. From Fig. 4.14 we can now infer that in NGC 7023 the size of the emitting PAH population is $\sim 50$ N$_C$, and the $\gamma$ value is $\sim 7 \times 10^4$, in NGC 2023, size is $\sim 70$ N$_C$ and $\gamma$ is $\sim 3 \times 10^4$, in the Orion Bar, the size is $\sim 80$ N$_C$ and $\gamma$ is $\sim 1.5 \times 10^4$, and in the diffuse ISM, the size is $\sim 70$ N$_C$ and $\gamma$ is $\sim 2 \times 10^3$. We note that the inferred $\gamma$ values differ from the ones we adopt in this work (see Table 4.2) by about a factor of 2. This difference could be due to uncertainty in the $\gamma$ values we adopt (see section 4.4.1) or due to uncertainty in the electron recombination rates that we discuss in section 4.4.5. The key point of this discussion, however, is not to infer the precise values of PAH size and $\gamma$ values
but to illustrate that the 6.2/(11.0+11.2) vs 3.3/(11.0+11.2) grids are only useful if we know an approximate range of $\gamma$ values for the astrophysical environment considered. If we have no prior knowledge of $\gamma$, only the 3.3/(11.0+11.2) can be used to predict the PAH size but the 6.2/(11.0+11.2) cannot predict the $\gamma$ values.

4.4.5 Caveat in the model

When comparing the predicted values of the 6.2/(11.0+11.2) and 3.3/6.2 with the observed values, we find that the exact size of the PAH molecule for which a good match between the observation and the predicted value is obtained can vary due to uncertainty in the $\gamma$ we adopt (see section 4.4.3). In this section, we highlight one more caveat in this comparison. We calculate the band ratios using a model based on the PAH charge distribution, which is determined by the ratio of the photo-ionization and electron recombination/attachment rates. In our model, we use analytical relations involving PAH characteristics to calculate these rates. While the photo-ionization rate calculation involves PAH characteristics, the ionization yield, and absorption cross-sections that have been measured experimentally or calculated theoretically for astrophysically relevant PAHs, the electron recombination and attachment rates calculations involve no such experimentally measured PAH characteristics (see section 4.2.1). This lack of laboratory data on electron recombination and attachment rates results in uncertainty in the charge distribution calculations, which then propagates into calculations of PAH band ratios. Therefore, laboratory experiments to determine electron recombination and attachment rates of astrophysically relevant PAHs are highly desirable.

4.5 Conclusions

We present a PAH emission model that calculates the IR emission from PAHs in PDRs taking into account the PAH charge distribution. Following Bakes et al. (2001b), the model first calculates the charge distribution of PAHs in the PDRs based on the physical conditions, $G_0$, $n_{gas}$, $T_{gas}$, $Xe$. The model then computes the IR emission from a specific PAH molecule by adding the emissions from all relevant charge states and weighing them according to their charge distribution. We model the IR emission from five different PAH molecules, tetracene ($C_{18}H_{12}$), pentacene ($C_{22}H_{14}$), ovalene ($C_{32}H_{14}$), circumcoronene ($C_{54}H_{18}$), and circumcircumcoronene ($C_{96}H_{24}$), adopting their recent experimentally measured or quantum chemically calculated data on PAH characteristics. The selected PAHs span a wide range in physical and chemical properties and are therefore a suitable set of species for the analysis of observations.

We show that anions are the dominant charge state for $\gamma < 2 \times 10^2$, neutrals for $10^3 < \gamma < 10^4$, and cations for $\gamma > 5 \times 10^5$. Based on the analysis of the PAH spectra of the molecules considered in this work in all the charge states, we show that anionic and cationic charge states exhibit similar spectral characteristics with strong features in the 6–9 $\mu$m region and weak features in the 10–15 $\mu$m region. We investigated the implications of this similarity between cationic and anionic charge states on the 6.2/(11.0+11.2) band ratio and discovered that the large contribution from either anions and cations can result in high values of the 6.2/(11.0+11.2) band ratio. We further found that the charge state of PAHs also influences the 3.3/(11.0+11.2) band ratio beyond the well-known dependence on the PAH size.
We also model the PAH emission in five astrophysical environments (NGC 7023, NGC 2023, the Horsehead nebula, the Orion Bar, and the diffuse ISM) for the five PAH molecules considered and show that changes in the charge distribution can account for the observed variations in the IR emission in these environments. We further find that anions, which have previously been overlooked, are the dominant charge carriers in low illumination PDRs such as the Horsehead nebula. In light of the similarity between the spectral characteristics of cations and anions, we revisited the diagnostic potential of the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ plots to determine the $\gamma$ of astrophysical environments and PAH size, respectively. We find that even in the absence of prior knowledge about an approximate value of $\gamma$, the $3.3/(11.0+11.2)$ can be used to infer PAH size, but the $6.2/(11.0+11.2)$ cannot be used to infer $\gamma$. Comparing the model predictions of PAH emission with observations highlights the need for more experiments to determine the electron recombination and attachment cross-sections of astrophysically relevant PAHs as the lack of this experimental data results in an uncertainty in the charge distribution calculation which then propagates into PAH emission calculation.

**Acknowledgements**

AS acknowledges support from the Mitacs Globalink Research Award. EP and JC acknowledge support from an NSERC Discovery Grant.
Chapter 5

Conclusions

In this thesis we investigated the molecular characteristics of polycyclic aromatic hydrocarbons (PAHs) in the pursuit of answering the following key question:

What factors drive the spectral variations observed in the emission features of astronomical PAHs?

The spectral variations in the PAH emission observed across various environments and spatially within extended environments result from changes in the molecular properties of the PAH population which, in turn, are due to changes in the physical conditions of the environment in which they reside (e.g. Hony et al., 2001; Peeters et al., 2002b; Bregman & Temi, 2005; Galliano et al., 2008; Peeters et al., 2017). While we have a qualitative understanding of the main processes responsible for this spectral variability, our understanding is far from complete. A better understanding of the molecular astrophysics of PAHs will enhance our understanding of the factors that influence their spectral variations and interactions with their host environments. This is required in order to develop diagnostic tools to use PAHs as tracers of the local physical conditions across the Universe, a potential powerful tool owing to their dependence on the environmental conditions and high abundance throughout the Universe. Furthermore, it would refine the specifics of the PAH-driven physical processes, such as regulating the ionization balance and the temperature of the interstellar gas, which are essential to comprehend the evolution of the interstellar medium (ISM).

In Chapters 2 and 3 we analyzed the PAH emission from two galactic reflection nebulae NGC 2023 and NGC 7023 employing a statistical technique called Principal Component Analysis (PCA). We performed PCA on the fluxes of five PAH bands at 6.2, 7.7, 8.6, 11.0, and 11.2 $\mu$m. We found that in both reflection nebulae, only two principal components (PCs) are required to explain $\sim 98\%$ of the variance in the PAH fluxes. Comparison of the PCs with PAH fluxes and analysis of their spatial distribution and characteristic PAH spectrum revealed that $PC_1$ represents the total PAH emission of PAH molecules and $PC_2$ represents changes in PAH emission due to changes in the charge state. Moreover, we found that the interpretation of $PC_2$ holds only for photodissociation regions (PDRs). In NGC 7023, the FOV comprises a PDR and a cavity carved out by the central star. While the interpretation of $PC_1$ holds in the cavity, that of $PC_2$ does not. In the cavity, $PC_2$ corresponds to changes in PAH properties other than the charge state, possibly some structural molecular changes. In Chapter 2, we also compared the spatial distribution of PCs to the radiation field strength $G_0$ and found that the spatial
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distribution of \(-PC_2\) compared well with \(G_0\), reinforcing our interpretation of \(PC_2\) relating to the changes in the charge state of PAHs.

These results furthermore revealed a peculiar behaviour of the ionic bands at 6.2, 7.7, 8.6, and 11.0 \(\mu\text{m}\). We found that the 6.2 and 7.7 \(\mu\text{m}\) bands behave as one group and the 8.6 and 11.0 \(\mu\text{m}\) bands as the other. We put forth two scenarios to explain this grouping of the ionic bands. In one scenario, we argue that the 6.2 and 7.7 \(\mu\text{m}\) bands originate from less ionized PAHs than the 8.6 and 11.0 \(\mu\text{m}\) bands, forming two distinct groups. In the alternative scenario, we argue that the contribution from PAH clusters and very small grains (VSGs) to the 6-9 \(\mu\text{m}\) region is probably responsible for the observed distinction between the two groups of ionized bands. Together with earlier studies (e.g. Joblin et al., 1996a; Sloan et al., 1999; Allamandola et al., 1999; Bregman & Temi, 2005; Compiègne et al., 2007; Galliano et al., 2008; Rosenberg et al., 2011; Peeters et al., 2017), the results of the observational studies presented in chapters 2 and 3 quantitatively demonstrated that in terms of the molecular property of PAHs, charge is the major driving factor of the variations observed in the PAH emission.

In chapter 4 we then modelled the PAH emission based on changes in the charge state of PAHs in PDRs following Bakes et al. (2001b). Specifically, we modelled the PAH emission of five astrophysically relevant PAHs, pentacene (\(C_{18}H_{12}\)), tetracene (\(C_{22}H_{14}\)), ovalene (\(C_{32}H_{14}\)), circumcoronene (\(C_{54}H_{18}\)), and circumcircumcoronene (\(C_{96}H_{24}\)), using the wealth of available laboratory and quantum chemically calculated data on PAH characteristics such as the ionization yield, absorption cross-sections, ionization potentials, the frequencies and intrinsic strengths of the vibrational modes.

We calculated the charge distribution and the resulting emission for these five molecules over a range of astrophysical conditions characterized by the ionization parameter \(\gamma = G_0 \times \sqrt{T_{\text{gas}}/n_e}\), where \(G_0\) is the far-ultraviolet (FUV) radiation field strength, \(T_{\text{gas}}\) is the gas temperature and \(n_e\) is the electron density. We found that in the low \(\gamma\) regime (\(\gamma < 2 \times 10^2\)), anions dominate the PAH emission; for intermediate \(\gamma\) values (\(10^3 < \gamma < 10^4\)), neutrals dominate the PAH emission and, in the high \(\gamma\) regime (\(\gamma > 5 \times 10^4\)), cations and dications begin to dominate the PAH emission. Furthermore, we found that the anions and cations exhibit similar spectral characteristics with strong features in the 6–9 \(\mu\text{m}\) region and weak features in the 10–14 \(\mu\text{m}\) region. This similarity between cations and anions resulted in a relationship between the 6.2/(11.0+11.2) and \(\gamma\), where high values of the 6.2/(11.0+11.2) ratio originate at both low and high values of \(\gamma\). While high 6.2/(11.0+11.2) values at high \(\gamma\) values resulted from a large contribution from cationic charge states, the high values at low values of \(\gamma\) resulted from a large contribution from anionic charge states.

We validated the PAH emission model by comparing the 6.2/(11.0+11.2) and 3.3/6.2 band ratios predicted by the model to those observed in NGC 7023, NGC 2023, the Horsehead nebula, the Orion Bar, and the diffuse ISM. We found that the observed values compare well with the predicted values of compact PAHs in NGC 7023, NGC 2023, the Orion Bar, and the diffuse ISM, and with the predicted values of acenes in the Horsehead nebula. We found that while high values of 6.2/(11.0+11.2) observed in the Orion Bar (characterized by \(\gamma\) of \(\sim 3 \times 10^4\)) are a consequence of the large fraction of cations, the high values of the 6.2/(11.0+11.2) in the Horsehead nebula (characterized by \(\gamma\) of \(\sim 30\)) are a consequence of the large fraction of anions.

The model results also revealed a subtle dependence of the 3.3/(11.0+11.2) band ratio on the charge state in addition to the PAH size. For each of the PAH molecules we studied,
we found that the $3.3/(11.0+11.2)$ PAH ratio decreases with increasing $6.2/(11.0+11.2)$ values for the neutral and cation dominated $\gamma$ regions. In the anion dominated $\gamma$ region, the $3.3/(11.0+11.2)$ revealed a more complex picture, where this ratio exhibited a positive correlation with the $6.2/(11.0+11.2)$ values for some molecules and a negative correlation for the others. Moreover, we found that the nature of the correlation between the $3.3/(11.0+11.2)$ and $6.2/(11.0+11.2)$ ratios is also affected by the excitation conditions. In light of these findings, we investigated the diagnostic potential of the $6.2/(11.0+11.2)$ vs $3.3/(11.0+11.2)$ in determining $\gamma$ of astrophysical environments and the average size of the emitting PAH population. We concluded that, when assuming no prior knowledge of $\gamma$ for a given astrophysical region, these diagnostic plots will not yield a unique solution for $\gamma$ although they may yield a unique solution for the average PAH size.

The research presented in this thesis has quantitatively demonstrated that charge is the primary driver of the observed PAH variation. In addition, it has revealed a more complex picture of the charge state of PAHs than previously known. Here we summarize our key conclusions:

1. The ionic bands at 6.2 and 7.7 $\mu$m behave systematically differently from those at 8.6 and 11.0 $\mu$m.

2. The spectral characteristics of PAH anions are similar to PAH cations with strong features in the 6–9 $\mu$m region and weak features in the 10–14 $\mu$m region.

3. Owing to the similar spectral characteristics of PAH anions and cations, a high value of $6.2/(11.0+11.2)$ in an astronomical environment does not always imply presence of large fraction of cations. While high $6.2/(11.0+11.2)$ values at high $\gamma$ values originate from a large fraction of cations, high $6.2/(11.0+11.2)$ values at low $\gamma$ values originate from a large fraction of anions.

4. The $3.3/(11.0+11.2)$ band ratio also exhibits a dependence on charge state in addition to the well-known dependence on PAH size.

5. A variety of charge states of PAHs, other than neutrals and singly ionized cations, may be present in astrophysical environments. For example, in low illumination PDRs, like the Horsehead nebula, anions are likely to be the dominant charge state, whereas, in high illumination PDRs, like the Orion Bar, cations and dications are likely to be the dominant charge state.

### 5.1 Future perspectives

While the research presented in this thesis revealed a more complex picture of the charge state of astrophysical PAHs than was previously known, it also suggests some avenues for future research. In addition, some longstanding puzzles remain in the field (see section 1.7). In this section, we discuss potential future directions to pursue as we stand on the verge of the revolution that the upcoming IR facility, the James Webb Space Telescope (JWST), will bring to the field of PAH astrophysics.

JWST will observe in the 0.6–28 $\mu$m range, where emission from PAHs dominates. Due to its unprecedented spectral resolution ($R \sim 3000$), we will be able to detect weaker features
and disentangle substructures within main PAH features, particularly in the 6–9 µm and 10–14 µm regions, at a spatial scale relevant to the processes responsible for the evolution of the PAH family. JWST will also provide broad wavelength coverage, including the 3.3 µm band and other MIR PAH bands, which will be critical for determining the molecular properties (such as charge, size, and structure) of the PAH population. Furthermore, because of the higher angular resolution of JWST than previous IR facilities, we will be able to study changes in PAH properties over very small spatial scales, shedding light on e.g. PAH photo-processing. Such studies in a large number of sources will also contribute to a much better understanding of the behaviour of these large molecules in response to the varying physical conditions. This, in turn, will enhance our understanding of the molecular physics of PAHs, and will be a step forward in developing templates to use PAHs as tracers of physical conditions.

The results presented in this thesis revealed that the ionic bands have a peculiar nature, with 6.2 and 7.7 µm behaving as one group of bands and 8.6 and 11.0 µm as the other (chapters 2 and 3). Previously, Peeters et al. (2017) demonstrated that ionic bands have distinct spatial morphologies despite showing strong correlations with each other, indicating that these ionic bands originate from different PAH populations. Detailed information about the spectral features that distinguish these two likely distinct PAH populations will be critical in determining the true cause of the ionic band grouping. However, the spectral resolution of the data available so far is insufficient to resolve the features unique to these two PAH populations hidden beneath the broad ionic bands. With the high spectral resolution data of JWST, we will be able to uncover these hidden spectral features and understand the cause of the grouping of the ionic bands.

In order to understand the interaction of PAHs with their environments and their relation to other carbonaceous species such as fullerenes and VSGs, we need to develop a comprehensive model of the photochemical evolution of PAHs. The PAH model that we developed in this thesis focused on the charge state of PAHs through photoionization and electron recombination, and attachment processes. A natural extension of this model would be to include other relevant chemical reactions that these species can undergo, such as charge exchange, photodissociation with carbon or hydrogen loss, and hydrogen-addition reactions. At the same time, we can expect much progress in our understanding from JWST observations that trace changes in PAH emission and in the physical conditions at small spatial scales. One of the caveats of the model we presented in chapter 4 arises from the lack of experimental data on PAH characteristics which introduces uncertainty in the calculations. More laboratory experiments determining electron interaction cross-sections of PAHs, especially anions, will be useful in developing a photochemical evolution model. Such a model will provide valuable insights into the overall evolution of PAHs in the ISM and their interactions with their environments, which will help develop templates for PAHs as tracers of physical conditions. Developing a comprehensive PAH photochemical evolution model of this scope will require collaborative efforts between experimentalists, astronomers, and theorists and will be critical in the era of JWST.
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Appendix A

Additional content for Chapter 2

A.1 Spatial Maps of PCs

It is insightful to create maps of the variations in $PC_1$ and $PC_2$ and compare those to spatial maps of PAH features described in Peeters et al. (2017). Fig. A.1 shows the spatial distribution of $PC_1$ and $PC_2$ in the north and the south FOV. In order to facilitate comparison with the spatial maps of PAH features in Peeters et al. (2017), we show the contours of the 7.7 and 11.2 µm PAH bands at the same intensity levels as chosen by Peeters et al. (2017), i.e. at $1.40, 1.56, 1.70,$ and $1.90 \times 10^{-5} \text{ Wm}^{-2}\text{sr}^{-1}$ and $3.66, 4.64, 5.64,$ and $6.78 \times 10^{-6} \text{ Wm}^{-2}\text{sr}^{-1}$ respectively. Moreover, we annotate the ridges as defined by Peeters et al. (2017) in the two FOVs.

To first order, the spatial morphology of $PC_1$ is very similar to the map of total PAH flux (see Figs. 5 and 6 in Peeters et al., 2017). However, there are subtle differences. In the south FOV, the total PAH emission peaks at S’, SE, SSE, and S ridges with the S’, SE, and SSE ridges being dominated by cations and the S ridge by neutral PAHs (Peeters et al., 2017). $PC_1$ peaks at S’, SE, and SSE ridges but not at the S ridge. In the S ridge, $PC_1$ values are high, but do not exhibit a maximum. In addition, $PC_1$ is strong at the broad, diffuse plateau north and north-west of the S and SSE ridges, where strong emission is also observed from the 8.6 and 11.0 µm PAH emission bands (Peeters et al., 2017). In the north FOV, the total PAH flux peaks on the NW ridge, while $PC_1$, although high in the NW ridge, peaks slightly west of the southern part of the NW ridge, where emission from PAH cations peak. Thus, the spatial morphology of $PC_1$ in two FOVs shows that $PC_1$ peaks in the cation dominated ridges and is high but does not peak in the neutral dominated ridges. This lends further support to our conclusion about $PC_1$ that it represents emission of a mixture of PAH molecules with more ionized PAHs than the neutral PAHs.

$PC_2$ peaks at the S and the SSE ridge in the south FOV. In all regions other than the S, SSE and a part of the S’ ridge, $PC_2$ is negative and seemingly uniform. The spatial morphology of $PC_2$ resembles that of the H$_2$ 9.7 µm S(3) and 12.3 µm S(2) line intensities (see Fig 5 in Peeters et al., 2017). In the north FOV, $PC_2$ peaks at the north part of the NW ridge and has a sub-dominant emission in the center part of the N ridge where its projection connects with the NW ridge. $PC_2$ exhibits a minimum in the regions south of the N and the NW ridge and west of the southern part of the NW ridge, which are closer to the illuminating star. Its spatial morphology seems to fall between that of the 10-15 µm plateau and the 11.2 µm PAH emission. The fact...
Figure A.1: Spatial map of $PC_1$ (left) and $PC_2$ (right) in the north (top) and the south (bottom) FOV of NGC 2023. For reference, the ridges as defined by Peeters et al. (2017) are annotated and the contours of the intensity of the 7.7 and 11.2 $\mu$m PAH bands are shown in white and black respectively. Pixels without $3\sigma$ detection for all five PAH bands and containing the YSOs C and D from Sellgren et al. (1983) are masked from the analysis and are shown in black.
that $PC_2$ exhibits a maximum in the neutral dominated ridges and a minimum in the cation dominated regions reinforces the suggestion that $PC_2$ is a quantity related to the ionization state of the PAHs.

A.2 Methodology: Spatial map of radiation field strength

The intensity of the radiation field, $G_0$, can be determined indirectly from observations of the FIR continuum emission or the $\text{H}_2$ rotation-vibration lines (e.g. Meixner et al., 1992; Black & van Dishoeck, 1987; Draine & Bertoldi, 1996; Burton et al., 1998; Sheffer et al., 2011). It can also be estimated indirectly based on PDR models combined with observations of the FIR cooling lines (e.g. Wolfire et al., 1990; Kaufman et al., 1999; Sandell et al., 2015). These methods, however, are limited in spatial resolution. Alternatively, we can estimate $G_0$ from empirical calibrations where $G_0$ is first estimated from other methods and then calibrated against some suitable dust grain or PAH parameter (e.g. Pilleri et al., 2012; Stock & Peeters, 2017). Here, we obtained the maps of $G_0$ for NGC 2023 using the empirical calibrations of Stock & Peeters (2017) and Pilleri et al. (2012) (hereafter referred to as method 1 and method 2 respectively) and from observations of the FIR continuum emission (referred as method 3 in the remaining of the paper). These three methods are described in detail below.

Method 1: We derived the morphology of radiation field strength ($G_0$) using the empirical relationship established between $G_0$ and the ratio of two subcomponents (7.6 and 7.8) of the 7.7 $\mu$m feature by Stock & Peeters (2017). These subcomponents are two of the four Gaussian components, approximately centered at 7.6, 7.8, 8.2, and 8.6 $\mu$m, used by Peeters et al. (2017) to better fit the features in the 7-9 $\mu$m region. Based on a sample of Galactic H II regions and reflection nebulae, Stock & Peeters (2017) found the following relationship between $G_0$ and the 7.8/7.6 ratio:

$$I_{7.8}/I_{7.6} = (1.70 \pm 0.13) - (0.28 \pm 0.03) \log G_0$$  \hspace{1cm} (A.1)

We note that the south FOV of NGC 2023 was in the sample used by Stock & Peeters (2017) to derive equation A.1. These authors used slightly different values of central wavelength and full width at half maximum than Peeters et al. (2017) to decompose the features in the 7-9 $\mu$m region into the four Gaussian components. Thus, to derive the map of $G_0$ in the south FOV we used the fluxes of the 7.6 and 7.8 $\mu$m bands obtained from the decomposition parameters of Stock & Peeters (2017). The north FOV of NGC 2023 was not part of the sample used by Stock & Peeters (2017). We therefore obtained the fluxes of the 7.6 and 7.8 $\mu$m bands for this FOV using the average decomposition parameters for the reflection nebulae given by Stock & Peeters (2017).

Method 2: The second method used to derive the $G_0$ map is based on another empirical relation reported by Pilleri et al. (2012). These authors found a strong anti-correlation between $G_0$ and the fraction of carbon locked in evaporating Very Small Grains ($f_{eVSG}$). eVSGs are carbonaceous grains having a wide size distribution (Li & Draine, 2001). It is thought that photo-evaporation of these grains by UV photons lead to the formation of free gas-phase PAH molecules and hence the name eVSGs (Cesarsky et al., 2000; Rapacioli et al., 2005; Berné et al., 2007). Based on a sample of PDRs, Pilleri et al. (2012) found the following relation:

$$f_{eVSG} = (-0.23 \pm 0.02) \log G_0 + (1.21 \pm 0.05)$$  \hspace{1cm} (A.2)
which is reliable in the range of $G_0$ from 100 to $5 \times 10^4$.

We obtain $f_{eVSG}$ from the decomposition method PAHTAT, which fits the template spectra of neutral PAHs, ionized PAHs, cluster of PAHs, and eVSGs to the observed spectrum.

**Method 3**: The third method is based on the FIR continuum emission. This estimation of $G_0$ is based on the assumption that all FUV photons are absorbed by dust and re-radiated in the FIR. To measure the FIR flux density, we used the photometric images observed at 70 and 160 μm with the Herschel Photodetector Array Camera and Spectrometer (PACS, Poglitsch et al. (2010), AOR Key: ‘PPhoto-ngc2023-135’) from the Herschel Science Archive. The PACS 70 and 160 μm filters have pixel scales of 3.2” and 6.4” respectively. In order to achieve the same spatial resolution for both maps, we convolved the 70 μm image to the lower resolution 160 μm image using the convolution kernels and procedures from Aniano et al. (2011). Furthermore, these maps are constrained by the 3σ detection limit in the convolved 70 μm and 160 μm images.

The FIR flux density is then estimated by composing a spectral energy distribution (SED) and then fitting a modified blackbody function to the SED of the form

$$I(\lambda, T) = \frac{K}{\lambda^\beta} \times B(\lambda, T)$$  \hspace{1cm} (A.3)

where $K$ is a scaling parameter, $\beta$ is the spectral index, and $B(\lambda, T)$ is the Planck Function as a function of the wavelength ($\lambda$) and the dust temperature ($T$) (e.g. Abergel et al., 2010; Berné & Tielens, 2012; Andrews et al., 2018). To obtain the best fit, we fixed $\beta = 1.8$ and considered $K$ and $T$ to be the free parameters following previous analysis of similar regions (e.g. Berné & Tielens, 2012; Andrews et al., 2018). The FIR flux is subsequently determined by integrating the area underneath the modified blackbody fit.

Subsequently, we determine $G_0$ from this FIR flux measurements following Meixner et al. (1992):

$$G_0 = 4\pi V l^{-1} S^{-1} \tau \lambda_0^\beta \int \lambda^{-\beta} B(\lambda, T) d\lambda$$  \hspace{1cm} (A.4)

where $V$ is the volume of the region, $S$ the surface area of the cloud facing the illuminating star, $l$ the pathlength along the line of sight, and $\tau$ the optical depth at the reference wavelength $\lambda_0$. Assuming a spherical geometry for the cavity of NGC 2023 (e.g. Field et al., 1994), the geometry factor $V l^{-1} S^{-1}$ reduces to 1.0. Thus an estimate for $G_0$ is derived by multiplying the FIR flux calculated from equation A.3 by a factor of $4\pi$ and converting the units to the Habing field. Note that, the $\tau \lambda_0^\beta$ term in equation A.4 is accounted for by the scaling parameter, $K$.

**A.3 Spatial maps of radiation field strength**

Here, we compare the $G_0$ maps obtained from the three methods described in Appendix A.2 with each other in order to have a consistent spatial picture of $G_0$ across the nebula. Figs. A.2 and A.3 shows the resulting spatial distributions of $G_0$ for the north and south FOV based on the three methods. In the south FOV, the absolute values of $G_0$ in units of Habing Field estimated from method 1 and method 3 ranges between $10^3$ and $10^5$, while those estimated from method 2 varies in the range of $10^3$ and $10^5$. We emphasize that the $G_0$ values $> 5 \times 10^4$ obtained with
Figure A.2: Spatial maps of $G_0$ in units of Habing Field derived from empirical calibrations across the north (top row) and the south (bottom row) FOV of NGC 2023. Left panel: $G_0$ derived from its correlation with the 7.8/7.6 PAH ratio given by Stock & Peeters (2017) in the logarithmic color scale. Pixels where the intensity of both 7.6 and 7.8 $\mu$m bands is zero are shown in black in addition to those masked while performing PCA; Middle panel: $G_0$ derived from its (anti)-correlation with eVSGs given by Pilleri et al. (2012) in the logarithmic color scale. Pixels where $f_{\text{eVSG}} = 0$ are shown in black in addition to those masked while performing PCA; Right panel: $-PC_2$ for comparison. Pixels masked while performing PCA are shown in black. For reference, the ridges as defined by Peeters et al. (2017) are annotated for the north and south FOV in left panels. The contours of the intensity of the 7.7 and 11.2 $\mu$m PAH bands are shown in white and black respectively.
method 2 are not reliable (Pilleri et al., 2012). The spatial morphology derived from these three methods is fairly similar in the south FOV with high values of $G_0$ in the upper half of the FOV containing the S’ and the SE ridges and low values in the lower half of the FOV containing the SSE and the S ridges. In the north FOV, the absolute $G_0$ values obtained with method 1 and method 2 range from $10^3$ to $10^5$, whereas those derived from method 3 are of the order of $10^3$. We note that the method 1 of estimating $G_0$ based on the 7.8/7.6 PAH band ratio is highly sensitive to the decomposition parameters of the 7-9 $\mu$m region. Therefore, the high values of $G_0$ in the north FOV obtained with method 1 are a consequence of the chosen decomposition parameters. Thus, we conclude that similar to method 2, the high $G_0$ values from method 1 are also not reliable in this FOV. Nevertheless, the similar spatial morphology of $G_0$ derived from method 1 and method 2 implies that there is a definite variation in $G_0$ across the FOV, with $G_0$ exhibiting a minimum in the upper part of the FOV containing the N and the northern part of the NW ridge, intermediate values in the south of the NW ridge and a maximum in the lower part of the FOV towards the star. However, due to the limitation in the spatial resolution, a similar conclusion about the spatial morphology could not be drawn for the $G_0$ map obtained with method 3. Thus, overall in the south FOV, the three methods of estimating $G_0$ are consistent with each other in terms of spatial distribution and the absolute values except for the high values of $G_0$ in method 2. On the other hand in the north FOV, the absolute $G_0$ values derived from these three methods are not comparable. While the information on spatial morphology of $G_0$ from method 3 could not be obtained, we find that method 1 and method 2 are consistent with each other in this FOV.
Appendix B

Additional content for Chapter 3

B.1 Spatial Map of Total PAH flux

In Fig. B.1, we show the spatial distribution of the total PAH flux, i.e. the sum of the fluxes of PAH bands at 6.2, 7.7, 8.6, 11.0, and 11.2 μm in the SL FOV of NGC 7023.

B.2 PCA of PAH emission in the PDR

We performed an independent PCA of PAH band flux variables observed in the NW PDR of NGC 7023 (see 3.5 for details). Table B.1 lists the mean and standard deviation values of the

<table>
<thead>
<tr>
<th>PAH band</th>
<th>$\langle I_{PAH} \rangle$ (×10^{-5})</th>
<th>$\sigma_{PAH}$ (×10^{-6})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2</td>
<td>1.199</td>
<td>5.458</td>
</tr>
<tr>
<td>7.7</td>
<td>1.820</td>
<td>8.231</td>
</tr>
<tr>
<td>8.6</td>
<td>0.312</td>
<td>1.840</td>
</tr>
<tr>
<td>11.0</td>
<td>0.008</td>
<td>0.048</td>
</tr>
<tr>
<td>11.2</td>
<td>0.647</td>
<td>3.065</td>
</tr>
</tbody>
</table>

Table B.1: The mean ($\langle I_{PAH} \rangle$) and standard deviation ($\sigma_{PAH}$) values of the PAH band flux variables in the PDR of NGC 7023. All values are in units of Wm^{-2}sr^{-1}. 
PAH band flux variables. The PC eigenvectors that result from this PCA are

\begin{align*}
PC_1 &= 0.460 z_{6.2} + 0.459 z_{7.7} + 0.456 z_{8.6} \\
& \hspace{1cm} + 0.433 z_{11.0} + 0.426 z_{11.2} \\
PC_2 &= 0.256 z_{6.2} + 0.051 z_{7.7} - 0.344 z_{8.6} \\
& \hspace{1cm} - 0.614 z_{11.0} + 0.661 z_{11.2} \\
PC_3 &= -0.236 z_{6.2} - 0.696 z_{7.7} + 0.049 z_{8.6} \\
& \hspace{1cm} + 0.401 z_{11.0} + 0.544 z_{11.2} \\
PC_4 &= -0.325 z_{6.2} + 0.442 z_{7.7} - 0.687 z_{8.6} \\
& \hspace{1cm} + 0.451 z_{11.0} + 0.153 z_{11.2} \\
PC_5 &= -0.749 z_{6.2} + 0.327 z_{7.7} + 0.445 z_{8.6} \\
& \hspace{1cm} - 0.266 z_{11.0} + 0.250 z_{11.2}
\end{align*}

We can further decompose the standardized flux variables in the NW PDR of NGC 7023.
Figure B.2: Spatial maps of $PC_1$ (left) and $PC_2$ (right) obtained from the independent PCA analysis of PAH emission in the PDR of NGC 7023. For reference, the contours of the 7.7 and 11.2 $\mu$m PAH intensity are overlaid in cyan and black respectively.

into two most important PCs ($PC_1$ and $PC_2$) as follows

$$z_{6.2} = 0.460\ PC_1 + 0.256\ PC_2$$
$$z_{7.7} = 0.459\ PC_1 + 0.051\ PC_2$$
$$z_{8.6} = 0.456\ PC_1 - 0.344\ PC_2$$
$$z_{11.0} = 0.433\ PC_1 - 0.614\ PC_2$$
$$z_{11.2} = 0.426\ PC_1 + 0.661\ PC_2$$

(B.2)

In Fig. B.2, we present the spatial maps of PCs obtained for this PCA of PAH emission in the PDR.

### B.3 PCA of PAH emission in the cavity

We also performed a PCA of PAH band flux variables in the cavity of NGC 7023. Table B.2 lists the mean and standard deviation values of the variables used in the PCA. The PC eigen-
Figure B.3: Spatial maps of $PC_1$ (left) and $PC_2$ (right) obtained from the independent PCA analysis of PAH emission in the cavity of NGC 7023. For reference, the contours of the 7.7 and 11.2 $\mu m$ PAH intensity are overlaid in cyan and black respectively.

<table>
<thead>
<tr>
<th>PAH band</th>
<th>$\langle I_{PAH} \rangle$ ($\times 10^{-5}$)</th>
<th>$\sigma_{PAH}$ ($\times 10^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2</td>
<td>1.246</td>
<td>4.709</td>
</tr>
<tr>
<td>7.7</td>
<td>2.207</td>
<td>7.890</td>
</tr>
<tr>
<td>8.6</td>
<td>0.424</td>
<td>1.683</td>
</tr>
<tr>
<td>11.0</td>
<td>0.011</td>
<td>0.044</td>
</tr>
<tr>
<td>11.2</td>
<td>0.314</td>
<td>1.668</td>
</tr>
</tbody>
</table>

Table B.2: The mean ($\langle I_{PAH} \rangle$) and standard deviation ($\sigma_{PAH}$) values of the PAH band flux variables in the cavity of NGC 7023. All values are in units of Wm$^{-2}$sr$^{-1}$. 
vectors that result from this PCA are

\[
\begin{align*}
PC_1 &= 0.452 z_{6.2} + 0.446 z_{7.7} + 0.455 z_{8.6} \\
&
+ 0.454 z_{11.0} + 0.429 z_{11.2} \\
PC_2 &= -0.300 z_{6.2} - 0.475 z_{7.7} - 0.124 z_{8.6} \\
&
+ 0.123 z_{11.0} + 0.809 z_{11.2} \\
PC_3 &= 0.039 z_{6.2} + 0.562 z_{7.7} - 0.311 z_{8.6} \\
&
- 0.654 z_{11.0} + 0.397 z_{11.2} \\
PC_4 &= 0.838 z_{6.2} - 0.447 z_{7.7} - 0.237 z_{8.6} \\
&
- 0.197 z_{11.0} + 0.042 z_{11.2} \\
PC_5 &= -0.040 z_{6.2} - 0.244 z_{7.7} + 0.790 z_{8.6} \\
&
- 0.558 z_{11.0} + 0.048 z_{11.2}
\end{align*}
\]

We can decompose the standardized flux variables in the cavity of NGC 7023 into two most important PCs (\(PC_1\) and \(PC_2\)) as follows

\[
\begin{align*}
z_{6.2} &= 0.452 PC_1 - 0.300 PC_2 \\
z_{7.7} &= 0.446 PC_1 - 0.475 PC_2 \\
z_{8.6} &= 0.455 PC_1 - 0.124 PC_2 \\
z_{11.0} &= 0.454 PC_1 + 0.123 PC_2 \\
z_{11.2} &= 0.429 PC_1 + 0.809 PC_2
\end{align*}
\]

In Fig. B.3, we present the spatial maps of PCs obtained for this PCA of PAH emission in the cavity.
Appendix C

Additional content for Chapter 4

C.1 PAH database UIDs

In Table C.1, we present the UIDs of the PAH molecules studied in this work in the PAHdb.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Z = -1</th>
<th>Z = 0</th>
<th>Z = 1</th>
<th>Z = 2</th>
<th>Z = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetracene (C_{18}H_{12})</td>
<td>210</td>
<td>282</td>
<td>283</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Pentacene (C_{22}H_{14})</td>
<td>–</td>
<td>307</td>
<td>308</td>
<td>672</td>
<td></td>
</tr>
<tr>
<td>Ovalene (C_{32}H_{14})</td>
<td>11</td>
<td>4</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Circumcoronene (C_{54}H_{18})</td>
<td>46</td>
<td>37</td>
<td>38</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Circumcircumcoronene (C_{96}H_{24})</td>
<td>114</td>
<td>108</td>
<td>111</td>
<td>112</td>
<td>113</td>
</tr>
</tbody>
</table>

C.2 Charge Distribution

In Fig. C.1, we present the charge distribution of tetracene (C_{18}H_{12}), pentacene (C_{22}H_{14}), circumcoronene (C_{54}H_{18}), and circumcircumcoronene (C_{96}H_{24}), as a function of γ, for a fixed value of G_0=2600, T_{gas} = 300K, and T_{eff} = 17000K.

C.3 Effect of the change in the excitation conditions on the charge distribution of PAHs

In order to investigate the influence of the change in excitation conditions on the charge distribution of PAHs, we modelled the charge distribution at T_{eff} = 17000K and T_{eff} = 40000K for the blackbody radiation field and present the results in Fig. C.2.
Figure C.1: Charge distribution of tetracene, pentacene, circumcoronene, and cirumcircumcoronene as a function of the ionization parameter $\gamma$, for a fixed value of $G_0 = 2600$, $T_{\text{gas}} = 300K$, and $T_{\text{eff}} = 17000K$. 

\[ \gamma = G_0 \times \sqrt{T_{\text{gas}}/n_e} \text{ (Habings K}^{1/2}\text{ cm}^3) \]
Figure C.2: Charge distribution of the five PAHs considered in this work as a function of the ionization parameter $\gamma$ for two different effective temperatures at which we calculate the blackbody radiation field in order to calculate charge distribution (see text for details).
C.4 Intrinsic spectra of PAHs

In Figs. C.3-C.7, show the intrinsic spectra of the PAH molecules for all the charge states. To facilitate the comparison, we have normalized the intrinsic spectra to the maximum intensity in each charge state. The neutrals exhibit strong features at the 3.3 $\mu$m and in the 10-15 $\mu$m range and weak features in the 6-9 $\mu$m range with 3.3 $\mu$m as the strongest feature in all the cases. The anions exhibit strong features at the 3.3 $\mu$m and in the 6-9 $\mu$m range and weak features in the 10-15 $\mu$m range. Similar to anions, the cations also exhibit strong features in the 6–9 $\mu$m region and weak features in the 10-14 $\mu$m region. The features in the 3.3 $\mu$m region, on the other hand are weaker in cations. In fact the intrinsic strength of the 3.3 $\mu$m feature is even less than that of the features in the 10-14 $\mu$m region. Longwards of 15 $\mu$m, the molecules in all the charge states exhibit few weak features with strength of these features in neutrals slightly greater than that in other charge states.

C.5 6.2/(11.0+11.2) vs 3.3/(11.0+11.2)

Fig. C.8, we present the ratios of 6.2/(11.0+11.2) vs 3.3/(11.0+11.2) color coded as a function of $\gamma$ at $T_{\text{eff}} = 40000$ K, demonstrating the effect of the change in the excitation conditions on the slopes of the two branches observed in the plots.
Figure C.3: Intrinsic stick spectra of tetracene (C$_{18}$H$_{12}$) normalized to the maximum intensity in anionic, neutral, cationic, and dicationic charge states.
Figure C.4: Intrinsic stick spectra of pentacene ($C_{22}H_{14}$) normalized to the maximum intensity in anionic, neutral, cationic, and dicationic charge states.
Figure C.5: Intrinsic stick spectra of ovalene ($C_{32}H_{14}$) normalized to the maximum intensity in anionic, neutral, cationic, and dicationic charge states.
Figure C.6: Intrinsic stick spectra of circumcoronene ($\text{C}_{54}\text{H}_{18}$) normalized to the maximum intensity in anionic, neutral, cationic, dicationic, and tricationic charge states.
Figure C.7: Intrinsic stick spectra of circumcircumcoronene (C\textsubscript{96}H\textsubscript{24}) normalized to the maximum intensity in anionic, neutral, cationic, dicationic, and tricationic charge states.
Figure C.8: Ratios of the 6.2/(11.0+11.2) vs 3.3/(11.0+11.2) color coded with $\gamma$ values for the five PAH molecules considered in this work at $G_0 = 2600$ and $T_{\text{eff}} = 40000K$. These plots demonstrate that the slope of the branch corresponding to low $\gamma$ values is sensitive to excitation conditions.
Curriculum Vitae

Ameek Kaur Sidhu

Education:

- **University of Western Ontario, London, ON, Canada, 2021**
  *Ph.D. Astronomy with Collaborative Specialization in Planetary Science and Exploration*
  *Dissertation: “Revisiting polycyclic aromatic hydrocarbon emission in Photodissociation regions”*
  *Advisors: Prof. Els Peeters and Prof. Jan Cami*

- **Panjab University, Chandigarh, India, 2016**
  *M.Sc. (Honour School) Physics*

- **Guru Nanak Dev University, Amritsar, India, 2014**
  *B.Sc. (Honour School) Physics*

Awards:

- **William H. Wehlau Award, 2020**
  *University of Western Ontario, London, ON, Canada*
  *Awarded to graduate students in Astronomy based on a variety of criteria including but not limited to scientific contributions and volunteer work.*

- **Western Science Student Internship Award, 2020**
  *University of Western Ontario, London, ON, Canada*
  *Awarded to graduate students to assist in the development of online educational resources for undergraduate courses during the COVID-19 pandemic.*

- **MITACS, Globalink Research Award, 2019**
  *University of Western Ontario, London, ON, Canada*
  *Awarded to graduate students in Canada to conduct research projects at universities outside of Canada. This award gave me an opportunity to go work with Prof. A.G.G.M. Tielens at Leiden Observatory in the Netherlands.*
• Award of Merit for academic excellence, 2016
  Department of Physics, Panjab University, Chandigarh, India
  Awarded to graduate students that rank the highest amongst their peers academically.

Publications:

   “A Principal Component Analysis of Polycyclic Aromatic Hydrocarbon Emission in NGC 2023”

2. A. Sidhu, J. Bazely, E. Peeters, J. Cami, Submitted to MNRAS
   “A Principal Component Analysis of Polycyclic Aromatic Hydrocarbon Emission in NGC 7023”

Presentations:

• “Molecular evolution of cosmic carbon”, January 30, 2020
  Oral presentation delivered online in collaboration with Partners in Research Canada as a part of Canadian Space Agency’s Junior Astronaut Campaign.

• “Principal Component Analysis of PAH emission in NGC 2023”, September 23, 2019
  Oral presentation delivered at a conference: “PAHRTEA - PAH Research: Theory, Experiments in an Astronomical context”, Nijmegen, the Netherlands

• “Principal Component Analysis of PAH emission in NGC 2023”, September 2-6, 2019
  Poster presentation delivered at a conference: “Celebrating 40 years of Alexander Tie- lens' contribution to Science”, Avignon, France

• “The interstellar medium”, August 17, 2019
  Oral presentation delivered at a public night at Hume Cronyn Observatory, University of Western Ontario, London, ON, Canada

• “The Spitzer Space Telescope - Observing the Universe in the Infrared”, July 6, 2019
  Oral presentation delivered at a public night at Hume Cronyn Observatory, University of Western Ontario, London, ON, Canada

• “Principal Component Analysis of PAH emission in NGC 2023”, June 24-28, 2019
  Poster presentation delivered at a summer school: “PAHs in extreme environments”, Toulouse, France

• “Measuring gas density and radiation field strength in NGC 2023 from PAH emission”, April 12, 2019
  Poster presentation delivered at a conference: “Space day”, University of Western Ontario, London, ON, Canada
• “NASA’s New Horizons mission to Pluto”, August 4, 2018  
  Oral presentation delivered at a public night at Hume Cronyn Observatory, University of Western Ontario, London, ON, Canada

• “Galactic chemical evolution of elements beyond iron”, February 14, 2016  
  Poster presentation delivered at a conference: “10th Chandigarh Science Congress”, Panjab University, Chandigarh, India