Chapter 1

Interstellar Polycyclic Aromatic Hydrocarbon molecules

1.1   The Interstellar Medium

In the Universe, in between the stars lies an enormous, limitless and ten-uous region, which is popularly termed as the Interstellar Medium (ISM). The ISM was initially thought to be completely empty, however there is indeed presence of matter in the form of gas and dust that is diffused between the stellar systems [16, 17]. In order to realize how vast and dense is the ISM, one should first know the distribution of stars. The Universe consists of a huge number of stars that collectively reside in a gravitationally bound region, known as Galaxy. Figure 1.1 shows the image of a galaxy (NGC 6503) taken by *Hubble Space Telescope (HST)*. Our Sun is an ordinary star of the Galaxy known as the Milky Way. Initially, it was thought that our Galaxy, i.e. the Milky Way was the entire Universe. However, the fact is that the Universe consists of an enormously large number of galaxies and the number has increased to nearly 2 trillion in the observable Universe according to a recent survey [18]. An average galaxy like Milky Way contains around 10^{11} stars. Our Sun is located in the plane of the Milky Way at about 2/3 of the Galactic radius from the Galactic center. The Milky Way has a disk of diameter $\sim$100,000 light years with thickness of about 6,000 light
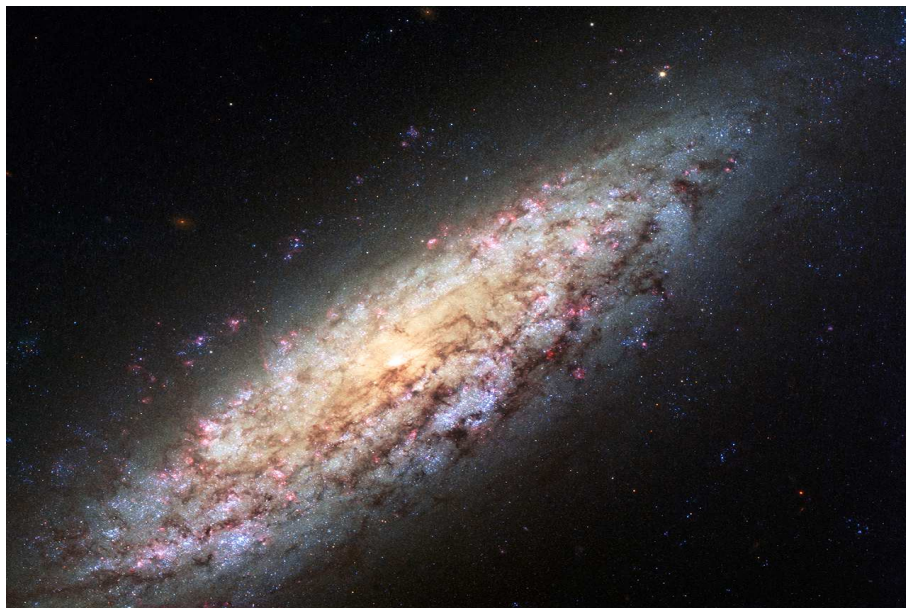
Figure 1.1: Photograph of NGC 6503, Image credit: NASA, ESA, D. Calzetti (University of Massachusetts), H. Ford (Johns Hopkins University), and the Hubble Heritage (STScI/AURA)-ESA/Hubble Collaboration

years. In the Milky Way, on an average stars are at a distance of about 10 light years from their nearest neighbouring star [16]. In between the stars exists the ISM spanning a huge volume of the Galaxy. Distances between two neighbouring galaxies are even greater than the dimension of the Galaxy itself. Considering the fact about the large number of galaxies in the Universe and the distances between them, one should now be able to imagine the enormous Universe and also the size of ISM distributed in it. The ISM has very low densities and is mainly covered by Interstellar gas (99%) and Interstellar dust (1%). The interstellar gas can exist in the form of atoms, molecules as well as charged particles (ions and electrons). By mass, nearly 75% of it is in the form of hydrogen (H) and 25% in the form of helium (He) and only a small fraction consisting of heavier elements. The interstellar dust consists of small irregular particles of sizes smaller than micron. These are mainly composed of silicates, ice and carbon compounds.

Based upon the the density, temperature and the type of species present in a particular region, the ISM is classified into various categories [2]. The most dense region of the ISM is molecular cloud where

the H exists in the form of molecules. The temperature (T) of this region is $\sim$10-20 K and density (n) is 10^2-10^6 particles per cm^3. The least dense region is the hot ionized medium with H as ions and T $\sim 10^6$ K, n $\sim$0.0065 particles per cm^3 [19]. There are intermediate phases, for example: Cold Neutral Medium, Warm Neutral Medium, Warm Ionized Medium, H II regions, etc., that are characterized by decreasing value of densities and increasing value of temperatures respectively. In comparison to our surrounding environment, the density of the ISM is so low that even the artificial vacuum created in a terrestrial laboratory is much greater in comparison to the densest region of the ISM.

The material in the ISM has a significant role towards the formation of structures in the Universe. It is the cloud of gas and dust, known as nebula from which stars are formed. Figure 1.2 shows the *HST* image of pillars of creation which is a thick region of gas and dust in the Egg nebula. Within this cloud, matter collapses together under gravity to initiate the formation of stars. The star ages through different stages of its life and finally it dies. A low mass star usually forms a white dwarf towards the end of its life with its outer shell of gas and dust being expelled back to the ISM in the form of planetary nebulae. Massive stars die with a supernova explosion and the core becomes either a neutron star or a black hole. During the explosion, a tremendous amount of matter including gas, dust and heavy elements are thrown back to the ISM at an incredible velocity and with high temperatures. Through this cycle, matter is replenished in the ISM to make the Universe chemically rich. Supernovae are the basic sources of heavy elements in the ISM. Figure 1.3 illustrates the life cycle of matter in the ISM.

1.1.1   The Interstellar Molecules

The ISM is home to a wide range of molecules that have been formed through interstellar chemical processes. Depending upon the physical condition of the medium, various forms ranging from neutral to ionized, simple to complex, small to large molecules have been proposed to exist in various astrophysical environments. Till date, around 200 molecular species
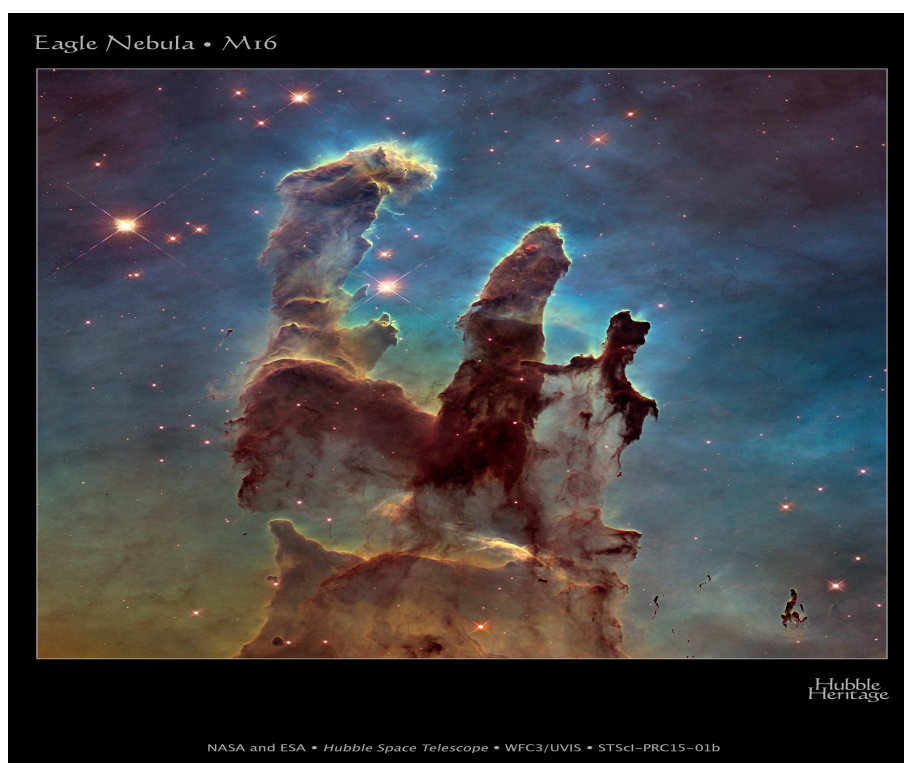
Figure 1.2: *HST* image of Egg Nebula, Credits: NASA, ESA and the Hubble Heritage Team (STScI/AURA)
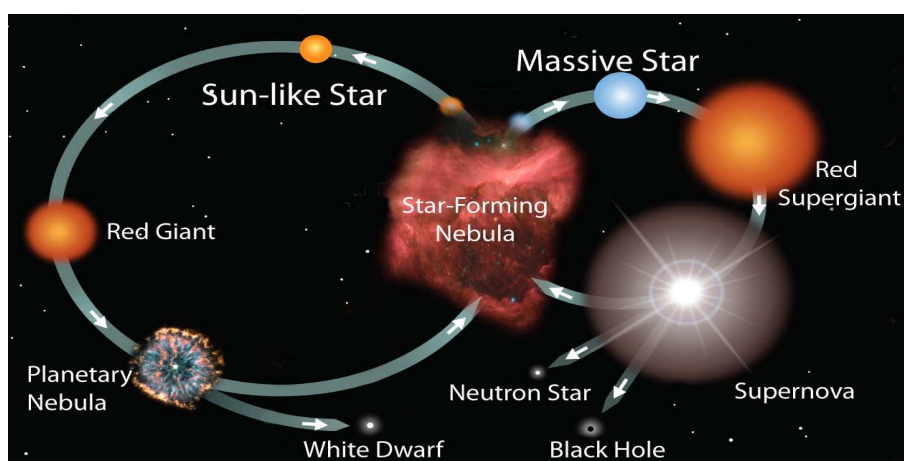

Figure 1.3: A cartoon illustration of the cycle of matter in the ISM, Credits: NASA and the Night Sky Network

have been identified with observational evidence, detected through absorption/emission lines. The molecules have been recognized mainly by observing their rotational features. The most abundant form is molecular hydrogen (H_2) which was first identified by Carruthers [20] through the detection of strong H_2 absorption bands in ξ Persei. Other important forms include NH_3 [21], H_2O [22], CO [23, 24], CH_3OH [25], HCO^+ [26], HCN [27], C_2H_2 [28], H_3^+ [29], C_6H_6 [30], C_6H^- [31], C_4H^- [32], C_{60}^+ [9], c-C_6H_5CN [33], etc. The complete list of the detected molecules in the ISM may be found at http://www.astrochymist.org/. The interstellar molecules mostly exist in cool astrophysical environments, for example dense interstellar clouds, diffuse molecular clouds, planetary nebulae, etc., in which they can survive the moderately intense radiation field and the temperature. In hot environments, for example H II regions, photodissociation regions (PDR), H atoms are ionized and also larger molecules are either destroyed or preferentially exist in ionized form as a result of the intense ultraviolet (UV) radiation.

The interstellar chemical processes that are responsible for the formation of interstellar molecules mainly include i) Gas Phase Reactions and ii) Grain Surface Chemistry. Interstellar chemistry begins with the formation of gas and dust grains in the outflows of giant stars. In the gas phase reactions, interstellar gas in form of atoms, molecules and ions can form new molecules through any of the following processes

i) Photoionization: UV photons from nearby stars can lead to photoionization of the already existing interstellar molecules to form new species [34, 35, 36]. For molecular clouds, the ionization potentials of the UV photons is I < 13.6 eV. Hence, molecules with ionization threshold < 13 eV can be photoionized with a reaction rate of about 10^{-11}-10^{-9} s^{-1} [17].

$$AB + h\nu \rightarrow AB^+ + e^-$$
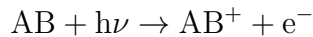
ii) Photodissociation: The absorption of background UV photons can excite the molecule which further can be broken down into fragments, a process known as photodissociation [34, 35, 36]. The photodissociation

rate is in the range of 10^{-11}-10^{-9} s^{-1} [17].

$$AB + h\nu \rightarrow AB^* \rightarrow A + B$$

iii) Neutral–Neutral reaction: New species can be formed through the collisions of neutral molecules provided that the molecules have little or no energy barriers. These reactions are exothermic and mostly occur in circumstellar envelope around star and in dark clouds [37, 38]. The reaction rate co-efficient is of the order of $\sim 10^{-10}$ cm^{3}s^{-1} [17].

$$A + B \rightarrow C + D$$
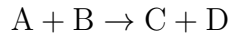
iv) Ion-Molecule reaction: Ion-molecule reactions can readily occur at a low temperature in dense interstellar clouds [39]. The rate coefficients of ion-molecule reactions are relatively large, $\sim 2 \times 10^{-9}$ cm^{3}s^{-1} [17].

$$A^+ + B \rightarrow C^+ + D$$
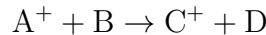
v) Radiative Association: These type of reactions allow the growth of species from smaller fragments. Herbst et al. [40] proposed that the interstellar CH_2^+ molecules are formed through radiative association of C^+ and H_2 in diffuse and dense interstellar clouds at 90 K with rate co-efficient $\sim 10^{-14}$ cm^{3}s^{-1}.

$$A + B \rightarrow AB + h\nu$$

$$\text{or} \ \ A^+ + B \rightarrow AB^+ + h\nu$$
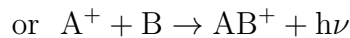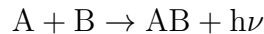
Gas-phase species in the ISM condense to form grains with icy mantles by physical adsorption or chemical adsorption. The interstellar dust grains so formed provide a surface on which accreted species can react to form new molecules (Grain-Surface Chemistry). The grains also shield the species from the stellar radiation which prohibits the photo destruction of the species. One of the most abundant molecule in the ISM is H_2 for which gas phase reactions does not account for its efficient formation [41, 42]. It is proposed that H_2 is efficiently formed on icy surfaces of grains on which the physisorbed or chemisorbed H atoms dif-

fuse across the surface to react and then finally an H_2 molecule desorbs [43, 44, 42, 45]. Apart from H_2, studies show that grain surface reactions are possible pathways of formation for complex organics as well [46, 47]. These organics also include some molecules of biochemical interest that may explain the origin of life [48, 49].

1.1.2   The Polycyclic Aromatic Hydrocarbon Molecules in the ISM

Carbon is one of the key elements formed in the stellar interior and is ejected in the ISM during supernova explosion [3]. The most active carbon chemistry occurs in circumstellar envelopes to form carbon bearing molecules in the ISM [50]. One such form of carbonaceous grain are Polycyclic Aromatic Hydrocarbon (PAH) molecules. These are free flying gas phase molecules in the ISM and are composed of fused aromatic benzene rings (Figure 1.4). Each PAH is of few angstrom size and contains around 20 or more C atoms. These are intermediate between the small molecules (number of atoms, N $\sim$10) and the conventional dust grains (N $\sim$10^5) [51]. Due to the delocalization of electrons in the aromatic structure, PAHs are highly stable against the harsh condition of the ISM. The formation of interstellar PAHs is not clearly understood yet. Carbon rich Asymptotic Giant Branch (AGB) stars are proposed as one of the main sources to produce these molecules in the ISM. Aliphatic or non-aromatic hydrocarbons have already been identified in the circumstellar envelopes of carbon-rich AGB stars [30]. UV photoprocessing of the hydrocarbon bonds in these molecules leads to the formation of aromatic molecules which may then initiate to produce PAH structures [52]. The PAHs so formed are ejected back to the ISM by stellar winds.

There are several other theories that have been proposed to explain the formation of interstellar PAHs. Frenklach and Feigelson proposed that in the outer envelope of carbon rich stars, formation of PAHs in the ISM is initiated through conversion of an already existing linear molecule, say, C_2H_2 into cyclic structure to form the first aromatic ring [53]. The aromatic rings then proceed through analogous reactions to form PAHs.
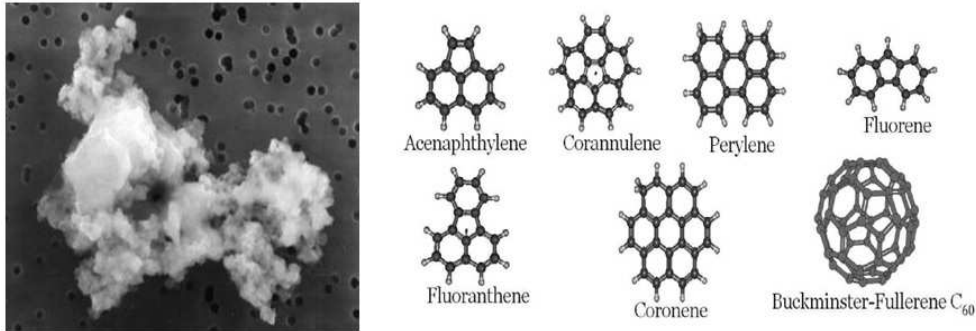
Figure 1.4: Left image: interplanetary dust, Credits: NASA; Right image: sample of PAH molecules

These reactions are predicted to occur at temperature around $900-1100$ K [53]. Tielens et al. [54] and Jones et al. [55] proposed grain-grain collisions induced by interstellar shocks as one of the possible pathways of PAH formation. During collisions, large grains break down into small fragments of size corresponding to the PAH size. Other formation methods include accretion of C^+ ions in the diffuse ISM [51] and gas phase, ion-molecule reactions in dense interstellar clouds [56], photoprocessing of interstellar dust mantles [57], etc.

The importance of PAHs in the ISM is manifold. PAHs account for about 5-10% of cosmic carbon depleted from the gaseous phase [2]. They act as radiative coolants of the ISM and also take major part in heating most of the gas in the PDR through the photoelectric effect [58, 59]. Another crucial role of interstellar PAHs is to balance the charge inside molecular clouds [60, 61, 58, 5]. Being a reservoir for heavy elements, interstellar PAHs also allow to measure the metallicity in different regions of the ISM. Apart from these, PAHs are held responsible for several spectral phenomena that are ubiquitously observed towards a variety of astrophysical objects. These phenomena will be discussed in detail in the next section.

1.2   Evidence of interstellar PAHs in the ISM

The main evidence for existence of interstellar molecules including PAHs is examined through spectroscopy. PAHs are usually non-polar except a

few like corranulene and do not show rotational spectroscopy. They are best probed through infrared spectroscopy that results from the transitions between vibrational levels of the excited molecule. The interplay of interstellar radiation with interstellar PAHs produces spectral features across the electromagnetic spectrum in the ISM that present its observational evidence in various astrophysical environments. Some of them are midinfrared emission bands popularly known as Unidentified Infrared (UIR) bands, UV absorption bump at 217.5 nm, extended red emission, 3.4 μm absorption feature, diffuse interstellar bands, etc.

1.2.1 The mid-infrared emission bands

In recent years, the detection of unidentified infrared (UIR) emission bands, particularly at 3.3, 6.2, 7.7, 8.6, 11.2, 12.7 and 16.4 μm towards many astronomical objects in the interstellar medium (ISM) has opened up new prospects in observational, laboratory and theoretical molecular astrophysics. These bands were first detected by Gillett et al. [62] as broad emission features together with line as well as continuum radiation towards three planetary nebulae NGC 7027, BD+30°3639 and NGC 6572. *Short Wavelength Spectrometer (SWS)* on board the *Infrared Space Observatory (ISO)* and *Infrared Spectrograph (IRS)* on board the *Spitzer* observations have revealed that these features are ubiquitous in the ISM [63, 64]. With the progress in observational astronomy, these features have further been observed towards a variety of astronomical objects including H II regions, reflection nebulae, planetary nebulae, PDR, AGB objects, active star forming regions, young stellar objects, diffuse medium, etc. [65, 66, 67, 68, 69, 70, 1, 71, 72, 73]. These features are also observed in external galaxies of varying metallicity [74, 75, 76]. Apart from strong UIR band emission, there are weak broad features distributed in the emission plateaux in the $\sim 3 - 20$ μm range [2]. Figure 1.5 shows the mid-infrared emission bands of the PDR in the Orion bar.

Depending on the physical conditions of the observed environment, source to source variation of the observed IR features is noticed in terms of peak position, width and intensity, however, an overall corre-
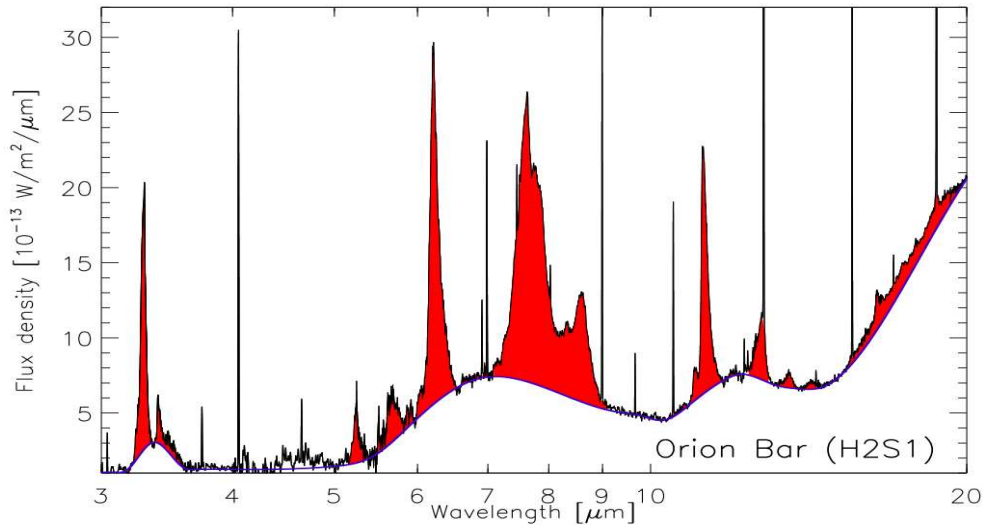
Figure 1.5: mid-infrared emission bands observed towards Orion Bar, Credits: Peeters et al. 2002 [1], Tielens 2008 [2]

lation among the bands is maintained [69, 1, 77, 2, 76]. The spectral variations have been used in classification of the sources in which UIRs have been detected [1].

Increasing number of IR observations indicate that widespread, extremely stable interstellar species are responsible for such features [78]. The search for the origin of these features began with the hypothesis of Duley and Williams [79] that vibrations of chemical functional groups attached to small carbon grains in diffuse ISM might produce emission features at 3.3, 6.2, 7.7, 8.6 and 11.3 μm. In addition, they pointed that -CH$_3$ group attached to the aromatic species can explain the 3.4 μm feature that occurs both in emission and absorption [80] in diffuse clouds. Sellgren [81] proposed transiently heated very small grains (size ∼10Å) like graphites to be the carriers. These graphitic grains resemble the structure of PAH molecules. Later, Léger and Puget [7] and Allamandola et al. [8] independently suggested that the features arise due to the vibrational relaxation of PAH molecules on absorption of background UV photons, giving rise to infrared fluorescence. When a PAH molecule absorbs a background UV photon, it is either ionized or it gets excited to a higher electronic state. These excited PAHs tend to relax through radiation-less processes, including dissociation, internal conversion and in-

tersystem crossing. As a consequence, the molecule comes to its ground electronic state while still in a vibrationally excited state. The molecule emits through IR emission which reverts it back to its ground state. The excess energy is released off through different modes of vibration, giving rise to IR emission features [78, 82]. Having been known the nature of the carrier, the UIR bands are also termed as Aromatic Infrared Bands (AIBs). In this thesis, both the terms are used occasionally to refer to the mid-infrared emission bands.

1.2.2 UV absorption bump at 217.5 nm

In astronomy, the interstellar extinction curve presents the evidence of intervening gas and dust between an observer and an emitting astronomical object that either absorbs or scatters the electromagnetic radiation to cause extinction. The 217.5 nm ($\lambda^{-1} \sim 4.6$ μm^{-1}) bump is the strongest spectroscopic absorption feature on the interstellar extinction curve [83]. The observed sources include diffuse ISM, dense clouds, H II regions, reflection nebulae, etc. Figure 1.6 shows the UV bump at 217.5 nm on the interstellar extinction curve towards different stars. The strength and width of the bump vary with changing environments, but the central wavelength remains consistent irrespective of the sources. Associated is a rise in the far-UV that is independent of the strength of the bump [84].

After almost half the century since its first discovery, there still lies an ambiguity in understanding the nature of the carrier that gives rise to the UV bump. Studies by Duley [85] and Steel and Duley [86] showed that small particles of silicates and Magnesium condensed on to dust or amorphous Mg_2SiO_4 exhibit absorption feature at 217.5 nm that matches the interstellar UV bump. However, studies later proposed that of all the suggested carriers, most of them are structurally related to some form of aromatic carbon. This might be some graphitic grains [83, 87] or PAH molecules [88, 89, 90]. Joblin et al. [88] proposed a mixture of neutral PAH molecules that may contribute to the bump as well the far-UV rise. PAHs in different charge states show spectral properties that
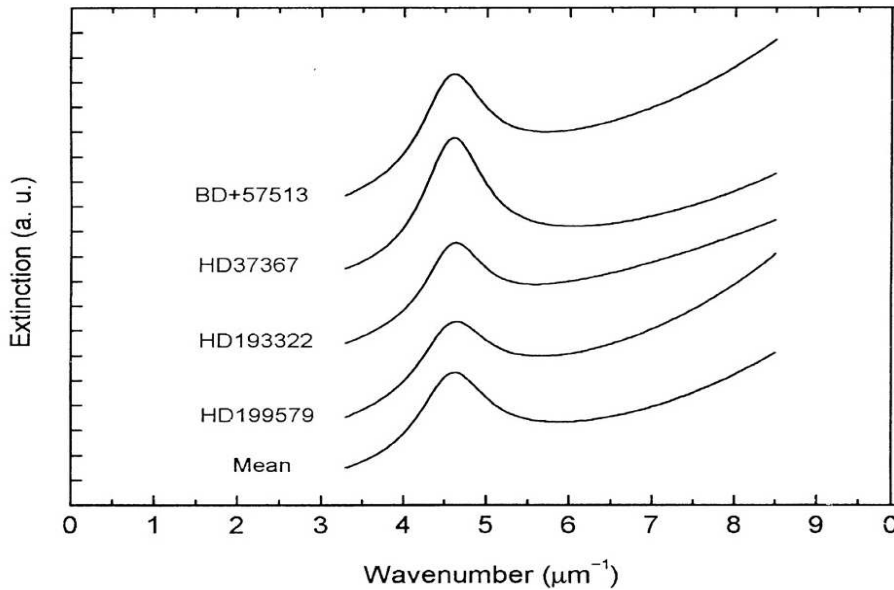
Figure 1.6: Interstellar extinction curves toward different stars probing the diffuse ISM and showing the UV feature at 217.5 nm, Credits: Henning and Salama 1998 [3]

are consistent with the varying relative strengths of the bump and non-linear far-UV rise [91]. Some studies also propose dehydrogenated PAHs which might be formed from carbonaceous grains in shocks as potential candidate carriers for the UV bump [92, 93].

1.2.3 Diffuse Interstellar Bands

Diffuse Interstellar Bands (DIBs) are optical absorption features (Figure 1.7) towards Galactic and extra-Galactic sources, mostly observed in the NUV to the NIR range (4000-13200 Å) [94, 95, 4, 96, 97]. Due to the fact that their strength is proportional to extinction and that their wavelengths are independent of the doppler shift associated with stellar lines, DIBs were recognized to be interstellar in origin [98]. As seen in ultra-high resolution spectroscopic observations, these bands are broad and shallow in comparison to the narrow interstellar atomic lines. DIBs show wide variation in strength and shape and the FWHM value falls nearly between 0.4-40 Å [99, 100]. This variation in profile is however not very strict and the variation is not clear when lines of sights towards many
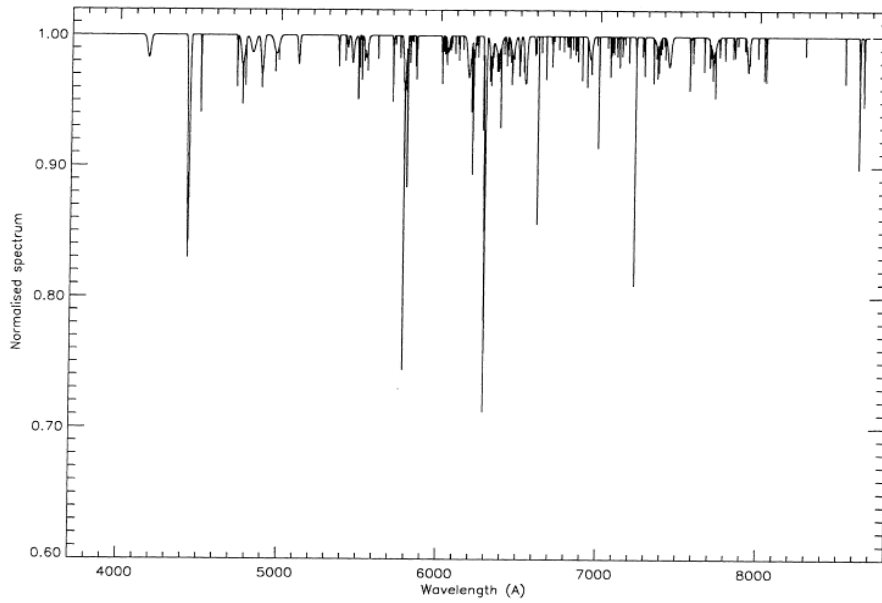
Figure 1.7: The composite spectra of DIBs catalogued in Jenniskens and Desert [4]

clouds are averaged. Some of the strong DIBs are observed at 4430, 5780, 5797, 6284 and 6614 Å [101].

The longest standing problem associated with DIBs is the identification of its carriers. Since its first discovery by Heger [102], around 400 DIBs have been detected so far. However, none of them have been assigned with specific carrier until recently. A recent study confirmed buckminsterfullerene ion (C_{60}^{+}) as carriers for two observed DIBs at 9,577 and 9,632 Å [9, 10]. The DIBs are highly suspected to be arising from large carbon chains and also from PAH molecules due to electronic transitions [96]. Because of its high abundance in the ISM and photostability against the intense radiation field, PAHs are considered as the carriers of DIBs. Considering the fact that small neutral PAHs do not absorb in the visible while ionized PAHs show active transitions in the visible, ionized PAHs are favoured over neutral PAHs as promising carriers of DIBs [103, 104]. Another new form of candidate carrier is a protonated PAH which shows strong absorption features similar to DIBs in the visible region [105]. Protonated PAHs can be formed in interstellar environments by reaction of PAH cations with an atomic H or molecular H_2 [106, 107]. Besides, their closed shell electronic configuration offers higher stability than the respec-

tive parent cation for which they might be treated as potential candidate carriers for DIBs.

1.2.4   Other spectral signatures

There exists two other important spectral phenomena; the 3.4 μm absorption feature and the extended red emission (ERE) for which PAHs are the commonly ascribed carriers. In addition to the 3.4 μm emission line which forms part of the UIR bands, an absorption feature is also seen at 3.4 μm towards several sources located near the Galactic center [108, 109]. The strong consistency of the feature indicates the presence of some common carrier that is widely present in the ISM. This feature is attributed to the C-H stretching fundamental mode of -CH$_2$ or -CH$_3$ functional groups that are attached to amorphous carbons, like PAHs [80, 108, 109, 110]. ERE is another interesting feature that is a broad emission plateau extending nearly between $500-900$ nm and is observed towards planetary nebulae, reflection nebulae, H II regions, diffuse ISM, etc. [111, 112, 113, 114]. The strength of ERE seems to be dependent on the local density of the illuminating radiation field indicating that photoluminescence is the main phenomena associated with ERE [115]. This is induced by suitable carriers on absorption of high energetic background UV photons. Photoluminescence by grains consisting of hydrogenated amorphous carbon (HAC) or coated by HAC mantles was initially proposed as candidate carriers for such features [115, 116]. Based on the fact that molecules are likely to be ionized in sources towards which EREs are observed, Witt et al. [117] proposed dication PAHs as potential carriers for EREs. The electronic energy level structure of PAH dications is consistent with fluorescence in the wavelength band of the ERE [117].

1.3   Laboratory and Theoretical study on PAHs: Implications to PAH-AIB hypothesis

Of all the interstellar spectral phenomena associated with PAHs as carriers, the most widely accepted is the PAH-AIB hypothesis that indicates high abundance of interstellar PAHs. Though the skeletal structure of the AIB carrier resembles to that of a PAH molecule, detection of a single PAH molecule in interstellar space has not been possible and the exact form of PAHs responsible for the bands is not yet definite. The progress in observational astronomy and the launch of several space based telescopes for e.g., *ISO*, *SPITZER*, *AKARI*, etc., have revealed a wealth of new information about the AIBs through observations towards astrophysical objects of varying environments and metallicity [67, 63, 64, 5, 6]. The improved observations signal the presence of a vast interstellar PAH family comprising of pure and substituted PAHs. Different ionization states are also possible depending on the physical condition of the interstellar environment. Both pure and substituted PAHs in different ionization states have been studied theoretically and experimentally for better understanding of the spectroscopy involved. Laboratory studies of PAHs often face constraints due to the complexity of the experiments, the monetary cost involved and the amount of time investment needed. Theoretical study is convenient to perform on a wide range of PAH molecules that vary in size, charge and functional groups attached to it. Based on this theoretical study, specific molecules can be selected for sophisticated laboratory experiments to be performed. A combined laboratory and theoretical study of PAHs is more relevant in order to compare with observational results to identify an accurate form of PAH molecule.

1.3.1   Experimental spectroscopy of PAHs

Experimental study of PAHs is of inevitable importance in order to demonstrate the PAH-UIR hypothesis and provide an evidence for the presence of these molecules in interstellar space. Several PAHs have explicitly been studied experimentally to establish a correlation with the

observed spectra of UIR emission bands and DIBs in particular. Different techniques have been used on different types of PAH molecules in order to reproduce the UIR emission bands. Some of the experiments that have allowed to obtain the IR spectrum of probable PAH candidates include IR absorption spectra of gas phase molecules at high temperatures [118, 119], Single Photon Infrared Emission Spectroscopy (SPIRE) [120], UV Laser Induced Desorption (UV-LID) [121, 122], Infrared Multiphoton Dissociation Spectroscopy (IRMPD) [123, 124, 125, 126] and Infrared absorption spectra of matrix isolated PAHs [127, 128, 129].

The most intense 6.2, 7.7 and 8.6 μm AIBs have been observed towards sources of high density UV radiation where PAHs are likely to exist in ionized form. This gives an edge to the cationic PAHs over the neutral PAHs for sophisticated experimental studies. Hudgins and Sandford [129, 130]; Hudgins et al. [131]; Hudgins and Allamandola [132, 133] have performed a series of Matrix Isolation Spectroscopy (MIS) experiments on neutral and cationic PAHs to obtain the IR absorption spectra. MIS technique is carried out at a low temperature $\approx$ 10 K relevant to interstellar condition of rotationally cold and vibrationally hot PAHs [129]. Spectral data of several PAHs obtained using the MIS techniques are available for free download at the NASA Ames PAH database (http://www.astrochem.org/) [134]. Neutral PAHs show features that fall at frequencies similar to that of the AIBs, however, relative band intensities do not provide a good match. Whereas, PAH cations present an overall good match with the astronomical spectra in terms of intensity as well. Nevertheless, no intense 6.2 μm band has been recorded for neither neutral nor cationic PAHs at the observed position; instead the laboratory 6.2 μm band is red-shifted with respect to the observed band. A few gas phase spectra of neutral and cationic PAHs have also been obtained using SPIRE [122, 120, 135] and IRMPD [136, 137] techniques that agree very well with the available theoretical and MIS data.

Recently, protonated form of PAH (HPAH$^+$) molecules have been experimentally tested as these might be another form of PAH widely present in the ISM [107, 63]. Gas phase infrared spectra of HPAH$^+$ molecules have been recorded using multi-photon dissociation (MPD) spectroscopy

[138] and mass-selected photo dissociation spectroscopy and the messenger atom method [125]. Experimental data points to an intense band close to 6.2 μm band observed AIB. Due to the presence of an aliphatic carbon in HPAH$^+$, aliphatic C-H stretching motions give rise to a feature near 3.5 μm. Observations have shown the presence of weak 3.4 μm and 3.5 μm bands in the spectra of many planetary nebulae, reflection nebulae, and H II regions [139]. No HPAH$^+$ spectrum has been recorded by MIS technique till date. This may be due to difficulty in synthesizing a protonated PAH and trapping it in the matrix. Deuterium containing PAHs (PADs or D$_n$-PAHs) have also been considered for experimental studies using MIS [140]. As expected, due to the larger mass of deuterium in PADs, the characteristic frequencies of C-D modes are shifted to shorter wave numbers compared to the analogous C-H modes.

The complex nature of AIBs cannot be explained by pure PAHs or a single category of PAH alone. There are ambiguous features like the 6.2 μm emission band and several other weak features which cannot be explained by merely varying the molecular size of pure PAHs [141]. The 6.2 μm emission feature is actually a composite of two other bands, one centered at 6.2 μm designated as 'class A' and another centered at 6.3 μm designated as 'class C' band. The composite of 'class A' and 'class C' feature is defined as 'class B' covering an intermediate position [141]. While 'class C' bands are supposed to arise from large PAH cations, the explanation for 'class A' bands needs a completely different type of PAH. Nitrogen, being the fourth most abundant element in the ISM is suspected to form polycyclic aromatic nitrogen heterocycle (PANH) with one or more nitrogen atoms substituted in the aromatic ring structure. MIS technique has been employed on neutral and cationic forms of PANH in order to address the 6.2 μm emission band position [142, 141, 143]. Till date, PANHs are the only PAH type that can account for the 'class A' 6.2 μm band [141]. Gas phase IR spectra of cationized PANH (PANH$^+$) have been obtained using the IRMPD technique [126]. Other than nitrogen, PAHs with neutral and ion complexes of Fe have also been studied experimentally in the astrophysical context [124, 144].

1.3.2   Theoretical spectroscopy of PAHs

In experimental studies, it is extremely difficult to simulate an environment that resembles the ISM. Thus, the experimental spectra may not be directly compared with the observed AIBs. Synthesis of substituted PAHs is another bottle-neck regularly experienced in experimental spectroscopy. Theoretical quantum chemical calculations play a vital role that act as a bridge between laboratory and observational astronomy. Theoretical spectroscopy helps in identifying suitable candidates for laboratory study. Results obtained from the theoretical spectroscopic study of PAHs may be used as inputs for emission simulations for direct comparison with observations. Due to these reasons, theoretical quantum chemical calculations have been widely used to calculate the harmonic frequencies and intensities to address the PAH-AIB hypothesis [145, 140, 146, 147, 148, 149, 150, 151, 152, 105, 153].

Theoretical studies at various levels have been used on several forms of PAHs to compare with experimental and observed spectra. Density functional theory (DFT) has revolutionized the use of quantum chemical calculations to accurately predict the vibrational spectrum of PAHs [145]. Langhoff [145] considered B3LYP functionals along with a range of basis set, viz. 4-31G to 6-311G** to show that the calculated wavenumbers tend to approach the experimental frequencies when a large basis set is used. The results of Langhoff [145] show that a good agreement with experimental and observed spectra is obtained by using the 4-31G basis at a modest computational cost. These results favour the presence of symmetrical PAH cations like coronene as their spectra match better in terms of intensity with the observed bands at 3.3, 6.2, 7.7 and 11.3 μm. Theoretical study has also been applied at different levels say; Self Consistent Field (SCF), second order Møller-Plesset (MP2) by Bauschlicher and Langhoff [146, 154] [66], that clearly indicates that very accurate harmonic frequencies close to experimental frequencies can be obtained using DFT combined with large basis set compared to SCF and MP2.

Hudgins et al. [148] considered another class of PAH cations having a closed shell structure with odd number of carbon atoms and protonated

PAHs for theoretical calculations. Protonated PAHs show a complex spectrum, with distinctive features particularly in the range $1600-1100$ cm^{-1}, compared to their parent radical ions due to the breaking of symmetry. With increasing size of protonated PAHs, the intensity of aromatic C-H stretching tends to increase with a decrease in intensity of aliphatic C-H stretching. However, the overall spectrum is consistent with experimental data concluding that protonated PAHs might be responsible for some of the UIR features.

Deuterium detection in the ISM [155] supports the existence of interstellar deuterium containing PAHs (PADs or D_n-PAHs) which is also being analyzed theoretically [140, 149, 156, 157]. Deuteration affects the complete spectrum and shows unique features in the $4.4-4.6$ μm region which is a featureless zone in pure PAHs. This unique prospect has been utilized to search for interstellar deuterated PAHs in the ISM [5, 6].

Since metal containing PAHs are difficult to synthesize in laboratory, theoretical computational study has been appreciated in order to explain the infrared spectral properties of these molecules. A number of theoretical studies on several metal containing PAHs have been reported. These include nitrogen substituted PAHs [141, 142, 143, 158], oxygen substituted PAHs [141, 159], silicon substituted PAHs [141] and PAHs with Fe and Mg [141, 160, 161, 162]. Hudgins et al. [141] reported that among all the metal containing PAHs, PANH cations can precisely account for the interstellar 6.2 μm emission feature.

1.4 Aim of the thesis

In this thesis, we aim to study PAH variants in order to find correlation with some of the observed UIRs. An ample number of molecules are chosen in terms of feasibility in different regions of the ISM that vary in shape, size and ionization state. Draine [15] proposed depletion of a fraction of cosmic deuterium (D) in PAHs that can account for the missing D in the interstellar gas along various lines of sight. In view of that, deuterium containing PAHs are studied in this thesis. Some PAHs with

aliphatic components are also considered to understand the frequently observed UIR emission plateau at 3.4-3.5 μm. Interstellar molecules usually exist in either fully hydrogenated or fully dehydrogenated and intermediate dehydrogenation state is rare. However, for large molecules it seems still possible. We consider a close member of dehydrogenated PAH family; a dehydrogenated anion for our study and discuss astrophysical implications. The vibrational spectra of PAHs are computed that give the expected region at which the molecules show fundamental vibrational modes with specific intensities. The frequencies and relative intensities of the modes correspond nearly to that of the UIR bands. A variation in the spectral profiles is present depending on the shape, size, ionization state and the functionals groups attached to the PAH molecule. Similar variations are also observed in the UIR bands that helps to identify the associated carriers and to classify sources. In case of possible interstellar existence of these molecules, formation processes are also discussed.

1.4.1   Theoretical methodology applied

DFT is presently the most successful approximation method to derive properties of the molecule, for example: molecular structures, bond-lengths, vibrational frequencies, ionization energies, electric and magnetic properties, reaction paths, etc., based on a determination of the electron density of the molecule [163]. In quantum mechanics, the Schrödinger wave equation describes the behaviour of electrons which determines the properties of the molecule. However, it becomes exponentially difficult to solve Schrödinger equation for many body systems. Hohenberg and Kohn [164] built the foundation of modern Density Functional method by introducing the fact that ground state properties are functionals of the electron density [165]. Unlike the wavefunction, which is not a physical reality but a mathematical construct, electron density is a physical characteristic of all molecules. A 'functional' is a function of a function and the ground state energy is a functional of electron density which is a function of three variables; x, y and z, i.e., the position of the electron. In terms of accuracy, DFT is formally exact as a theory. Its performance in actual applications depends

on the quality of the approximate density functionals employed. According to Hohenberg-Kohn theorem, the ground state energy of a system of electrons can be expressed as a 'functional' of the electron density and this energy shows minimum if the exact density for the ground system is considered. If the form of this functional is known accurately, quantum chemical calculations will give the exact molecular properties. Still the exact form of energy functional is not known. It is necessary to use approximations regarding parts of the functional dealing with kinetic energy and exchange and correlation energies of the system of electrons. Another parameter that affects the accuracy of the DFT calculations is the Basis set. It is the mathematical function to describe the molecular orbitals. More complex the basis set, more defined is the molecular orbital. By choosing higher functional and higher basis set, we are close to the exact solution of the wave equation. However, it takes great amount of computational time. Hence, functionals and basis sets are chosen in such a way that good accuracy of results are obtained in a decent computational time.

For the work presented in this thesis, DFT in combination with a B3LYP functional and a 6-311G** basis set has been used to optimize the molecular structures of PAHs. The optimized geometry is used to obtain the frequencies of various vibrational modes at the same level of theory. Theoretical calculations tend to overestimate the frequency compared to experiments [145]. Hence, scaling of frequencies are required in order to match with the experimental frequencies. The use of a larger basis set, *e.g.* 6-311G**, generally reduces the overestimation compared to smaller basis sets [145]. Use of a larger basis set compared to a smaller one also shows good agreement with experiments. However, the use of a large basis set does not support use of a single scaling factor for all of the vibrational modes [145]. In order to evaluate the mode-dependent scaling factors, calibration calculations were made for selected PAHs, both neutral and ionized. In the absence of sufficient gas phase data of PAHs by SPIRE, IRMPD, etc., we compare the theoretical frequencies with MIS experimental data [132, 133, 129, 130] to compute three different scaling factors for three different sets of fundamental modes. The scaling factors

obtained are 0.974 for the C-H out-of-plane (oop) modes, 0.972 for the C-H in-plane and C-C stretching modes and 0.965 for the C-H stretching modes [156]. While, scaling of frequencies are employed for all forms of PAHs studied in this thesis, scaling of intensities have only been applied for aliphatic PAH molecules and dehydrogenated PAH anions. It is described in detail in chapter 4. Relative intensities (Int_{rel}[1]) are obtained by taking the ratio of all intensities to the maximum intensity for normalization. The computed frequency (in wavenumber) or position (in wavelength) and relative intensity (Int_{rel}) of the lines are used to plot a Gaussian profile with a FWHM of 30 cm^{-1}. The profile width is typical for PAHs emitting in an interstellar environment and depends on vibrational energy redistribution of the molecule [78]. In some cases, a few overlapping bands in a particular region (mostly in the 3 μm region) might add up producing band intensities to exceed unity in the resulting spectra. The computed spectra are then compared with the observed UIR bands to recognize any possible correlation if present.

1.4.2   Emission Model

For a valid and justifiable comparison with the observed UIRs, the theoretically computed absorption spectrum needs to be transformed to an emission spectrum. A model may be used based on the theoretically obtained information as input and an emission spectrum may be generated [166]. In chapter 3, an emission model is indeed used in order to obtain emission spectra of PAHs which can be directly compared with the observed emission features. In the emission model, a PAH molecule is considered in a UV rich interstellar radiation field produced by a source (a star). The PAH molecule absorbs a photon and gets internally excited corresponding to an average temperature of about 1000 K. The absorption of the UV photon depends on the absorption cross section of the particular PAH. The excited PAH then cools down by emitting in a cascade at frequencies corresponding to the vibrational modes of the PAH molecule. The emission model considers thermal approximation that the total en-

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[1]$Int_{rel} = \dfrac{\text{absolute intensity}}{\text{maximum absolute intensity}}$

ergy of the excited PAH molecule is greater than the average energy of an emitting mode [166, 167]. The emitted energy is integrated over the cooling range from 1000 K to 50 K with a decrease in internal energy by a temperature fall of 1 K. The emitted energy is calculated considering the rate of absorption of photons and added up over the whole distribution of photon absorption to produce the emission spectrum. The emission model is described in more detail in chapter 3.

1.5   Organization of the thesis

The thesis is organized as follows:

Chapter 1 gives an introduction to the ISM, interstellar PAHs and their contribution in the ISM. Observational evidence of interstellar PAHs via emission/absorption features have been discussed. we present a brief review on experimental/theoretical spectroscopy on PAHs and its implications towards UIR bands. The theoretical methodology used in this thesis in order to study PAHs as potential carriers of UIR bands is explained towards the end of the chapter 1.

In chapter 2, the infrared spectral characteristics of deuterated and deuteronated PAHs in relation to the observed UIR features have been examined. Possible formation methods of deuterated/deuteronated PAHs in the ISM are explored. Taking into account of recent observations that have measured a D/H ratio in PAHs, we also compute a D/H for the sample molecules and make comparison with the observational D/H value in chapter 2.

Chapter 3 is a follow up of chapter 2 and considers variants of deuterated/deuteronated PAHs that might have great possibility to exist in the ISM. Direct comparison of emission spectra of PAHs with the observed mid-infrared emission bands is more meaningful rather than that with absorption spectra of PAHs. In order to do that, an emission model is employed on sample PAHs to obtain the emission spectra which are further compared with observations. D/H ratio is measured in a similar manner as in chapter 2.

The current research on PAHs as carriers of UIR bands suggest aliphatic PAHs as one of the crucial members of the wide family of interstellar PAHs. In chapter 4, we present the detailed analysis of infrared spectra of PAHs with aliphatic functional groups and discuss their possible correlation with the observed UIRs. More than one aliphatic functional group have been considered for this study. In view of the previous reports on deuterium containing PAHs, we also consider deuterium inclusion in the aliphatic functional groups and examine its effects on the spectral characteristics.

While physical conditions of astrophysical environments in some sources favour PAHs to exist as cations with high abundance, environments in some other sources allow PAHs to occur in anion forms. Chapter 5 considers an alternate form of anionic PAH; a dehydrogenated PAH anion and shows that molecules of this form might be potential candidate carriers for some of the observed UIR bands.

Chapter 6 concludes the thesis with a summary of the results obtained in the previous chapters and a brief discussion on the future prospects of this study.