

Chapter 5

The Interstellar Dehydrogenated PAH anions

5.1 Introduction

The mid infrared UIR bands vary in terms of peak position, band width and intensity as a function of the local physical condition of the observed sources [69, 1, 2]. An overall correlation among the bands is consistent across the source environment. The variation possibly arises due to change in the shape, size and ionization state of the PAH molecule which is usually affected by the physical condition of the source environment. In a benign environment, molecules are expected to be present in its neutral forms whereas in a region with intense UV radiations, PAHs are predominantly affected by photoionization resulting into PAH cations [51]. In contrast to this, a comparatively less intense UV irradiated field can leave a PAH negatively charged, or an anion formed by addition of an electron [51]. It is concluded that neutral, cationic as well as anionic PAHs contribute to the emission of some of the infrared bands depending on the interstellar conditions [206, 207]. Emission at 6.2, 7.7 and 8.6 μm are mostly contributed by PAH cations whereas the 3.3 and 11.2 μm bands preferentially arise from neutral PAHs in the ISM [1, 2, 208]. In the previous chapters, the spectral properties of neutral and cationic PAHs in relation to AIB carriers are dis-

cussed. Recent observational evidence for negatively charged molecules in the dense molecular cloud TMC-1 indicates that some of the interstellar PAHs might exist as anions [31]. Several theoretical and experimental studies [209, 210, 211, 212, 213, 214, 215, 216] discuss the role of astrophysical PAH anions and their contribution to heating the ISM, free electron density, recombination processes, etc. Herbst [217] and Herbst and Osamura [218] showed that negative ions are formed through radiative attachment of electrons to neutral species in dense clouds. In a similar way, PAHs may bear a significant fraction of the negative charge which then become the principal carriers of the negative charge in the cold interstellar medium. When an electron is attached to a PAH molecule, the resultant can be a transient negative ion $[\text{PAH}_n^-]^*$ which further can decay into a stable full anion PAH_n^- or to a dehydrogenated PAH anion (PAH_{n-1}^-) through subsequent loss of an H atom [219]. Another possibility for the formation of dehydrogenated PAH anions is that dehydrogenated PAHs have larger electron affinities compared to the parent hydrocarbons as a result of which a dehydrogenated PAH can efficiently accommodate an electron to form dehydrogenated PAH anion in environments like diffuse or circumstellar media [220]. Moreover, Tobita et al. [221] showed the formation of dehydrogenated PAH anion from a PAH molecule and reported that dehydrogenated PAH anions are the only possible fragment anions formed. Thus, any astrophysical model that takes into account interstellar PAH anions should also include its dehydrogenated forms. The dehydrogenation state of PAH molecules in the ISM is further endorsed by the recent detection of fullerenes as carriers for two observed DIBs [9, 10]. It is proposed that cosmic fullerenes may be formed from interstellar PAHs in a top-down or a bottom-up process [222, 223]. In either of the two formation processes initiated by PAHs, dehydrogenated PAHs are an intermediate form [11] which may subsequently be altered into other forms; for example, a dehydrogenated PAH anion through radiative attachment of electrons in dense cloud.

This chapter reports DFT calculations of PAH anions (PAH_n^-) along with dehydrogenated forms (PAH_{n-1}^-) to study their possible spectral characteristics in the infrared in relation to the AIBs. PAH anions are astro-

physically important as these have a stable configuration (in terms of energy) compared to cations and neutrals under interstellar conditions. The size effect on the intensity of vibrational transitions of these PAHs is also studied in this chapter. The findings of this chapter are published in Buragohain et al. [224].

5.2 Molecules studied

In this chapter, we aim to understand the infrared characteristics of PAH anions as they gradually lose H atoms from its periphery and become fully dehydrogenated. Usually, having lost the first H atom from the molecule, it is easier to remove the next H atom and then the C atoms to finally destroy its structure. This highly depends on the size of the PAH molecule. Large size PAHs have less tendency towards dehydrogenation compared to small size PAHs. Therefore, it is important to consider PAH molecules of different size groups for this study. The dehydrogenated anion forms of small to large size PAHs (perylene, coronene, ovalene) has been considered as sample molecules. The methodology for obtaining the spectra and the scaling factors to scale the calculated frequencies and intensities are same as used in the previous chapters. It is important to note here that for some species, several (at least 2) spin-multiplicities are possible (for $C_{24}H_{11}^{-1}$ for instance, singlet and triplet spin states are a priori possible). However, as a preliminary study, we have limited our calculation to molecules with the lowest possible spin-multiplicity. This is because the sample molecules that we have considered exhibit the lowest energy with the lowest possible spin-multiplicity corresponding to the most stable configuration to endure in the interstellar domain [225, 226, 227]. For example, for $C_{24}H_{11}^{-1}$, lowest lying state is a singlet state. We have used QChem (quantum chemistry package) to perform the calculations [14].

5.3 Results and Discussion

5.3.1 Coronene

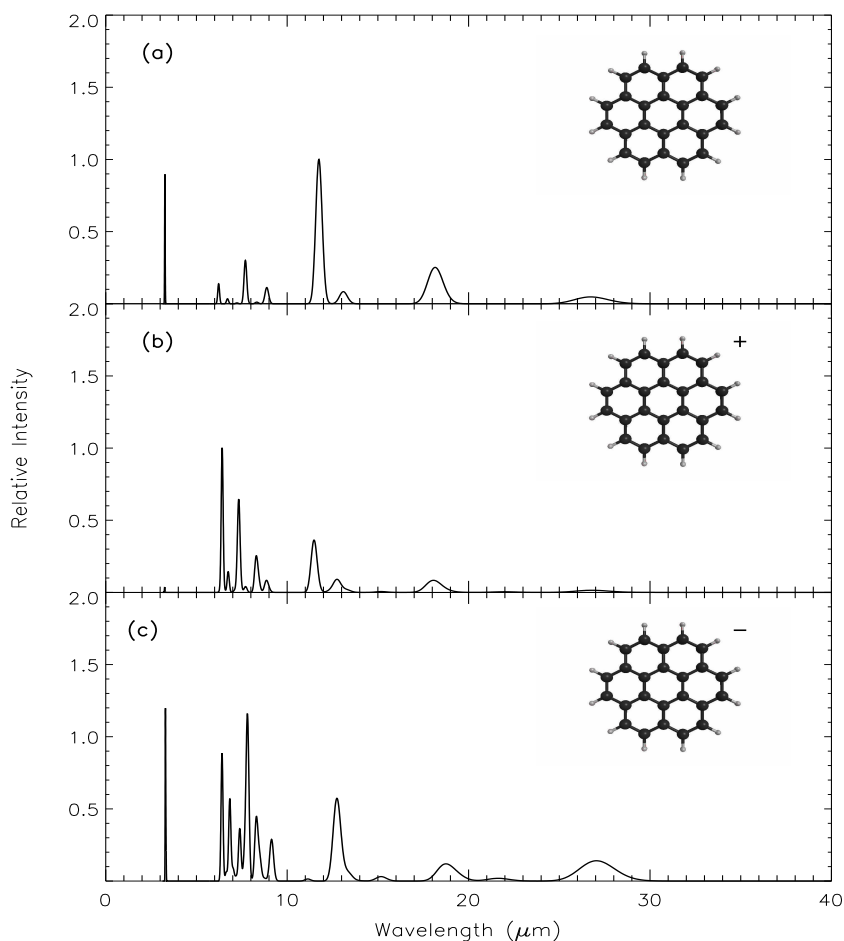


Figure 5.1: Theoretical spectra of (a) neutral coronene ($\text{C}_{24}\text{H}_{12}$), (b) cationic coronene ($\text{C}_{24}\text{H}_{12}^+$), (c) anionic coronene ($\text{C}_{24}\text{H}_{12}^-$)

Coronene ($\text{C}_{24}\text{H}_{12}$) is a mid-sized compact PAH molecule and is a good representative of the interstellar PAH family. For its stable configuration due to the delocalization of the electrons and its compactness, coronene is considered as a good choice for this study. We compare the IR spectra of neutral coronene ($\text{C}_{24}\text{H}_{12}$) with its cationic ($\text{C}_{24}\text{H}_{12}^+$) and anionic ($\text{C}_{24}\text{H}_{12}^-$) forms in Figure 5.1. The features are characteristic of

various vibrational modes present in the respective molecules. Table 5.1 presents the wavelengths corresponding to different modes of coronene in its neutral and ionized forms. While the wavelengths of these bands are less affected by ionization (positive or negative), a distinct variation in the intensity is produced on ionization of the molecule. This is similar to the results discussed in De Frees et al. [228], Langhoff [145] and Pauzat et al. [229]. Intensities of bands in the 6-10 μm regions which are weak in $\text{C}_{24}\text{H}_{12}$ become significantly prominent in $\text{C}_{24}\text{H}_{12}^+$ and $\text{C}_{24}\text{H}_{12}^-$ (Figure 5.1b & Figure 5.1c. The features in the 6-10 μm region are characteristic of the C-C stretch and C-H in-plane bending vibrations of the PAH molecules. The 3.3 μm feature due to the C-H stretch mode is intense for $\text{C}_{24}\text{H}_{12}$ and $\text{C}_{24}\text{H}_{12}^-$ and weak for $\text{C}_{24}\text{H}_{12}^+$. Intensities of all the 3.3 μm features are scaled here (scaling factor ~ 0.6372) [154] and the relative intensity of the 3.3 μm feature in cation is more consistent with the astronomical 3.3 μm band. Previous laboratory and theoretical studies [2, and references therein] reveal that the astronomical 3.3 μm feature is likely to be dominated by the C-H stretch modes in neutral PAH molecules, whereas 5-10 μm region arises due to the C-C stretch and C-H in-plane bending modes in cationic PAH molecules. PAH anions also contribute to the 5-10 μm region and to the 3.3 μm feature which indicates them to be an important constituent of the ISM. Importantly anionic PAHs show a comparatively strong 3.3 μm feature.

The band positions and intensities beyond 15 μm are affected to a lesser extent by ionization, both positive and negative. For example: a feature near 18 μm in neutral and cationic $\text{C}_{24}\text{H}_{12}$ which is a combination mode of C-C-C oop and C-H oop bending is shifted to 18.7 μm for anionic $\text{C}_{24}\text{H}_{12}$. Similarly, a variation in intensity is also observed, particularly for the feature near 28 μm , which is a C-C-C in-plane vibration that distinctly appears in the spectrum of $\text{C}_{24}\text{H}_{12}^-$ unlike its neutral and cationic counterparts. These features in the longer wavelength side are not thoroughly studied.

Dehydrogenated forms of anions have been studied to understand any possible contribution towards the observed AIBs. Peripheral H atoms in a PAH anion molecule ($\text{C}_{24}\text{H}_{12}^{-1}$) have been removed one-by-one to un-

Table 5.1: Theoretical spectral data for neutral, cationic and anionic coronene

| PAH | Frequency (cm^{-1}) | Wavelength (μm) | Relative Intensity | Mode |
|---------------------|-----------------------------------|---------------------------------|-------------------------------------|-------------------------------------|
| Neutral coronene | 3068.32 | 3.3 | 0.43 | C-H stretch |
| | 3067.74 | 3.3 | 0.44 | C-H stretch |
| | 1607.23 | 6.2 | 0.07 | C-C stretch |
| | 1606.67 | 6.2 | 0.07 | C-C stretch |
| | 1300.34 | 7.7 | 0.15 | C-C stretch + C-H in-plane |
| | 1297.93 | 7.7 | 0.15 | C-C stretch + C-H in-plane |
| | 1127.93 | 8.9 | 0.06 | C-H in-plane |
| | 851.15 | 11.7 | 1 | C-H oop bending |
| | 550.9 | 18.2 | 0.25 | C-C-C oop bending + C-H oop bending |
| Coronene cation | 1558.29 | 6.4 | 1 | C-C stretch |
| | 1482.10 | 6.7 | 0.12 | C-C stretch + C-H in-plane |
| | 1377.30 | 7.3 | 0.1 | C-C stretch + C-H in-plane |
| | 1363.26 | 7.3 | 0.58 | C-C stretch + C-H in-plane |
| | 1206.86 | 8.3 | 0.18 | C-C stretch + C-H in-plane |
| | 1206.47 | 8.3 | 0.05 | C-C stretch + C-H in-plane |
| | 1187.09 | 8.4 | 0.07 | C-H in-plane |
| | 1130.89 | 8.8 | 0.07 | C-H in-plane |
| | 870.9 | 11.5 | 0.36 | C-H oop bending |
| | 784.04 | 12.8 | 0.09 | C-C-C in-plane |
| 554.58 | 18 | 0.08 | C-C-C oop bending + C-H oop bending | |
| Coronene anion | 3040.03 | 3.3 | 0.59 | C-H stretch |
| | 3038.47 | 3.3 | 0.57 | C-H stretch |
| | 3013.34 | 3.3 | 0.28 | C-H stretch |
| | 1563.83 | 6.4 | 0.35 | C-C stretch |
| | 1558 | 6.4 | 0.56 | C-C stretch |
| | 1505.7 | 6.6 | 0.06 | C-C stretch |
| | 1473.22 | 6.8 | 0.05 | C-C stretch + C-H in-plane |
| | 1461.75 | 6.8 | 0.54 | C-C stretch + C-H in-plane |
| | 1424.3 | 7 | 0.08 | C-C stretch + C-H in-plane |
| | 1353.75 | 7.4 | 0.36 | C-C stretch + C-H in-plane |
| | 1305.68 | 7.7 | 0.18 | C-C stretch + C-H in-plane |
| | 1286.69 | 7.8 | 0.15 | C-C stretch + C-H in-plane |
| | 1279.13 | 7.8 | 1 | C-C stretch + C-H in-plane |
| | 1206.34 | 8.3 | 0.37 | C-C stretch + C-H in-plane |
| | 1196.79 | 8.4 | 0.08 | C-H in-plane |
| | 1177.63 | 8.5 | 0.14 | C-H in-plane |
| | 1093.85 | 9.1 | 0.29 | C-H in-plane |
| | 785.14 | 12.7 | 0.48 | C-H oop bending |
| 779.28 | 12.8 | 0.07 | C-C-C stretch | |
| 747.96 | 13.4 | 0.05 | C-C-C in-plane | |
| 535.98 | 18.7 | 0.1 | C-C-C oop bending + C-H oop bending | |

Modes with intensity equal to or greater than 0.05 are only listed in the table.

oop stands for out of plane.

intensity of $3.3 \mu\text{m}$ band has been scaled [154].

derstand the effect of dehydrogenation on the spectra as shown in Figure 5.2. Usually, H atoms are removed in a consecutive order, but in absence of a stable configuration, a preferable site for dehydrogenation is considered provided that the energy is minimized. As mentioned earlier, unlike neutrals all anions show rich 6-9 μm spectra which is characteristic of C-C stretch modes on the shorter wavelength side and C-H in-plane bending modes on the longer wavelength side. The intermediate features represent a combination of these modes. As H atoms are removed, the C-C modes gradually become dominant compared to the C-H in-plane modes and eventually for a fully dehydrogenated molecule ($N_{\text{H}}=0$)¹, C-C modes are the only possible modes present in the 5-10 μm region. In fact, for $(\text{C}_{24}\text{H}_n)^{-1}$ with $n=8, 6, 4, 2, 1$ & 0 , the C-C mode gives rise to the most intense band ($\text{Int}_{\text{rel}}\sim 1$)² seen near 5.2 & 6.8 μm . The 5.2 μm band is a unique feature observed for dehydrogenated PAHs only and arises due to the stretching of those C-C bonds that are exposed on removal of associated H atoms. The 5.2 μm band, however, does not appear immediately after dehydrogenation starts and arises only after a certain level of dehydrogenation is attained. In contrary to the predominance of the C-C stretch modes (5-10 μm), a distinct fall in the intensity of the 3.3 μm is found. This is obvious as the 3.3 μm feature is a contribution from the C-H stretch mode. For $(\text{C}_{24})^{-1}$, this feature is absent as expected. Besides this, the intensity of the 3.3 μm band is also affected by the symmetry of the molecule and is usually less for a more symmetric structure. When an odd number of H atoms are removed from the structure, the coronene molecule loses its symmetry by a degree lower compared to the removal of an even number of H atoms. A lower symmetry structure shows a higher intensity of the 3.3 μm feature compared to a more symmetric structure.

Usually, a coronene molecule contains duo C-H groups³ at all sites. Removal of an odd number of H atoms from the periphery leaves one of

¹ N_{H} =number of H atoms in the periphery of a PAH molecule

² $\text{Int}_{\text{rel}} = \frac{\text{absolute intensity}}{\text{maximum absolute intensity}}$

³A duo C-H group, also referred as doubly-adjacent C-H unit, is a group with one neighbouring adjacent C-H units on the same ring

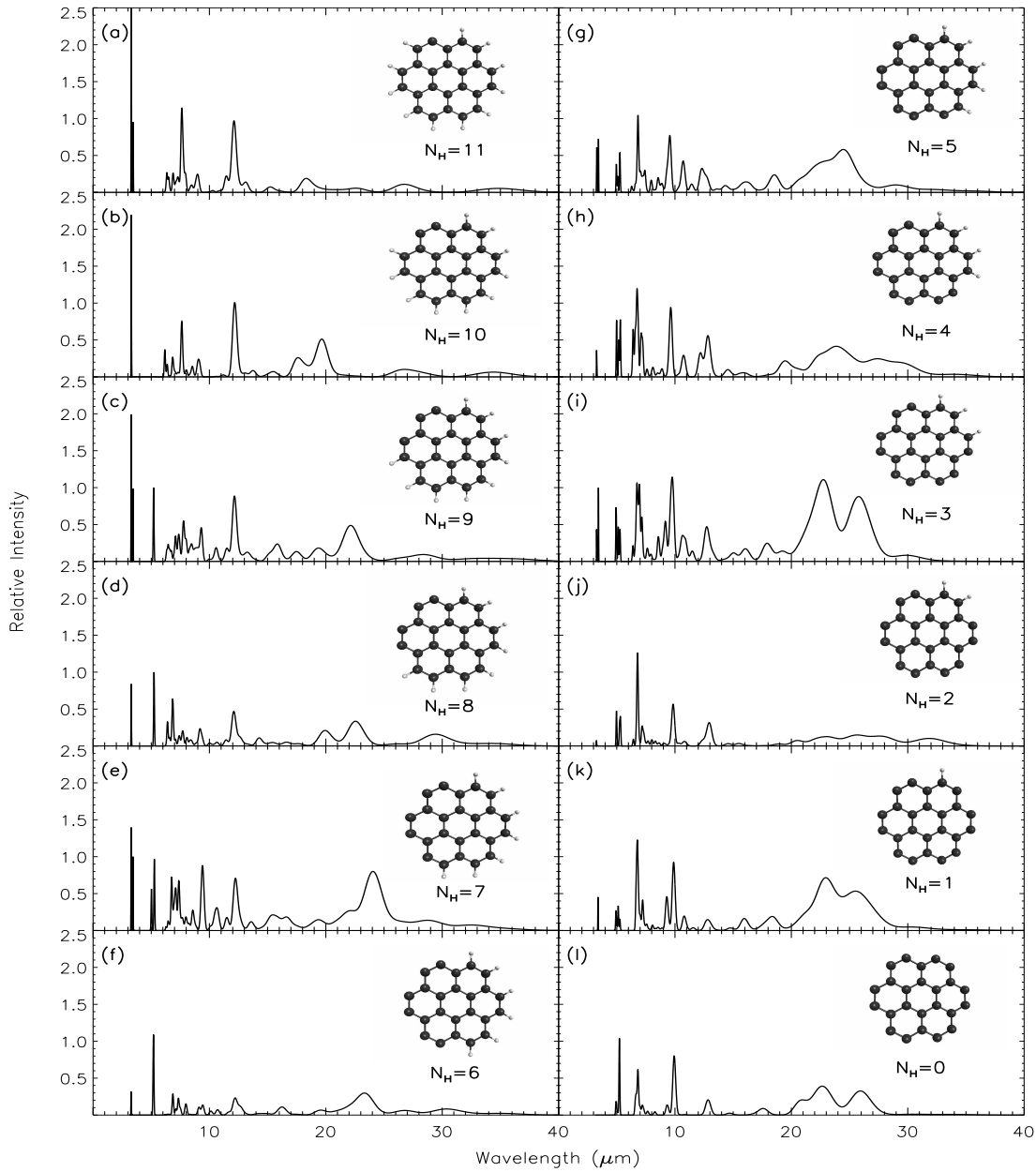


Figure 5.2: Theoretical spectra of (a)-(l) coronene anion ($C_{24}H_{12}^{-1}$) dehydrogenated forms

N_H =number of H atoms in the periphery of a PAH molecule

the associated C-H units to convert into a solo C-H unit⁴ which originally was a duo C-H group. Interestingly, the stretching of such a converted solo C-H produces a 3.4 μm feature. Int_{rel} values for this feature are 0.95, 0.99, 1, 0.72, 1 and 0.45, respectively, for $\text{C}_{24}\text{H}_{11}^-$, $\text{C}_{24}\text{H}_9^-$, $\text{C}_{24}\text{H}_7^-$, $\text{C}_{24}\text{H}_5^-$, $\text{C}_{24}\text{H}_3^-$ and $\text{C}_{24}\text{H}_1^-$. This is surprising as the molecules that originally have a solo C-H group do not exhibit a 3.4 μm band. It should be noted that the astronomical 3.4 μm feature is proposed to be originated from PAH molecules with aliphatic or superhydrogenated side groups due to the aliphatic C-H stretch [12, and references therein].

For coronene molecule containing solo C-H groups after dehydrogenation, an oop bending mode of the solo group is present at $\sim 11.5 \mu\text{m}$. We suspect that significant shift in the bands for a non-adjacent solo C-H unit arises due to the local electronic environment as the negative charge tends to be localized at the adjacent dehydrogenated site. As for the duo C-H groups of dehydrogenated molecules, the oop mode is redshifted and appears at $\sim 12\text{-}13 \mu\text{m}$. The longer wavelength features beyond 13 μm are mostly due to the C-C-C oop and C-C-C in-plane bending modes with a possible contribution from C-H oop modes in a PAH molecule. Anionic coronene ($\text{C}_{24}\text{H}_{12}^{-1}$) shows features in the 20 – 30 μm region mostly due to the C-C-C in-plane modes which become significant as the dehydrogenation increases. These theoretically obtained features are unique and do not appear for any other molecule studied so far.

We also performed similar calculation for a comparatively smaller PAH- Perylene ($\text{C}_{20}\text{H}_{12}$) and a comparatively larger PAH- Ovalene ($\text{C}_{32}\text{H}_{14}$) to investigate any possible spectral variations. Figure 5.3 shows the theoretically obtained IR spectra for a few representatives of dehydrogenated forms of $\text{C}_{20}\text{H}_{12}^{-1}$ and $\text{C}_{32}\text{H}_{14}^{-1}$. The full table of the band positions and intensities of the modes for all the possible forms is given in the Appendix A.

⁴A solo C-H group, also referred as non-adjacent C-H unit, is a group with no neighbouring adjacent C-H units on the same ring

5.3.2 Perylene

The intensity of the 3.3 μm feature decreases with the consecutive dehydrogenation similar to coronene. The C-C stretch modes in the 5-10 μm region are present in the spectra of dehydrogenated perylene anions as can be seen from Figure 5.3 (a-f). While this is expected for all forms of ionized PAHs, a unique features at $\sim 5.8 \mu\text{m}$ is observed for dehydrogenated forms of perylene. This is analogous to the 5.2 μm band observed for dehydrogenated coronene anion. When H atoms are removed from a perylene molecule successively, at a certain instance, one of the benzene ring in the network (apparently C-C-C) is completely free of H atoms. Due to the stretching of that free C-C-C bond in dehydrogenated perylene, a feature at $\sim 5.8 \mu\text{m}$ arises. The wavelengths beyond 10 μm are assigned to the C-H oop and C-C-C oop modes, while features beyond 20 μm arise due to the C-C-C in-plane modes.

5.3.3 Ovalene

Figure 5.3 (g-l) shows spectra of various forms of dehydrogenated ovalene anion. With increasing dehydrogenation, the intensity of the 3.3 μm band decreases. Apart from the other usual features that are common to all PAHs, dehydrogenated ovalene anions show a 5.2 μm band due to a free C-C bond stretch. This is similar to the 5.2 μm feature observed for a dehydrogenated coronene and does not appear for a low degree of dehydrogenation. Another crucial aspect is the increasing number of features with increasing size. Partial dehydrogenation of a comparatively large PAH anion ($\text{C}_{32}\text{H}_{14}^{-1}$) shows more features distributed throughout the 5–30 μm region compared to smaller dehydrogenated PAH anions. Table 5.2 lists the wavelengths together with Int_{rel} values that are present in a partially dehydrogenated (50% dehydrogenation) perylene anion ($\text{C}_{20}\text{H}_6^{-1}$), coronene anion ($\text{C}_{24}\text{H}_6^{-1}$) and ovalene anion ($\text{C}_{32}\text{H}_7^{-1}$) that shows the enhancement of features in number with size.

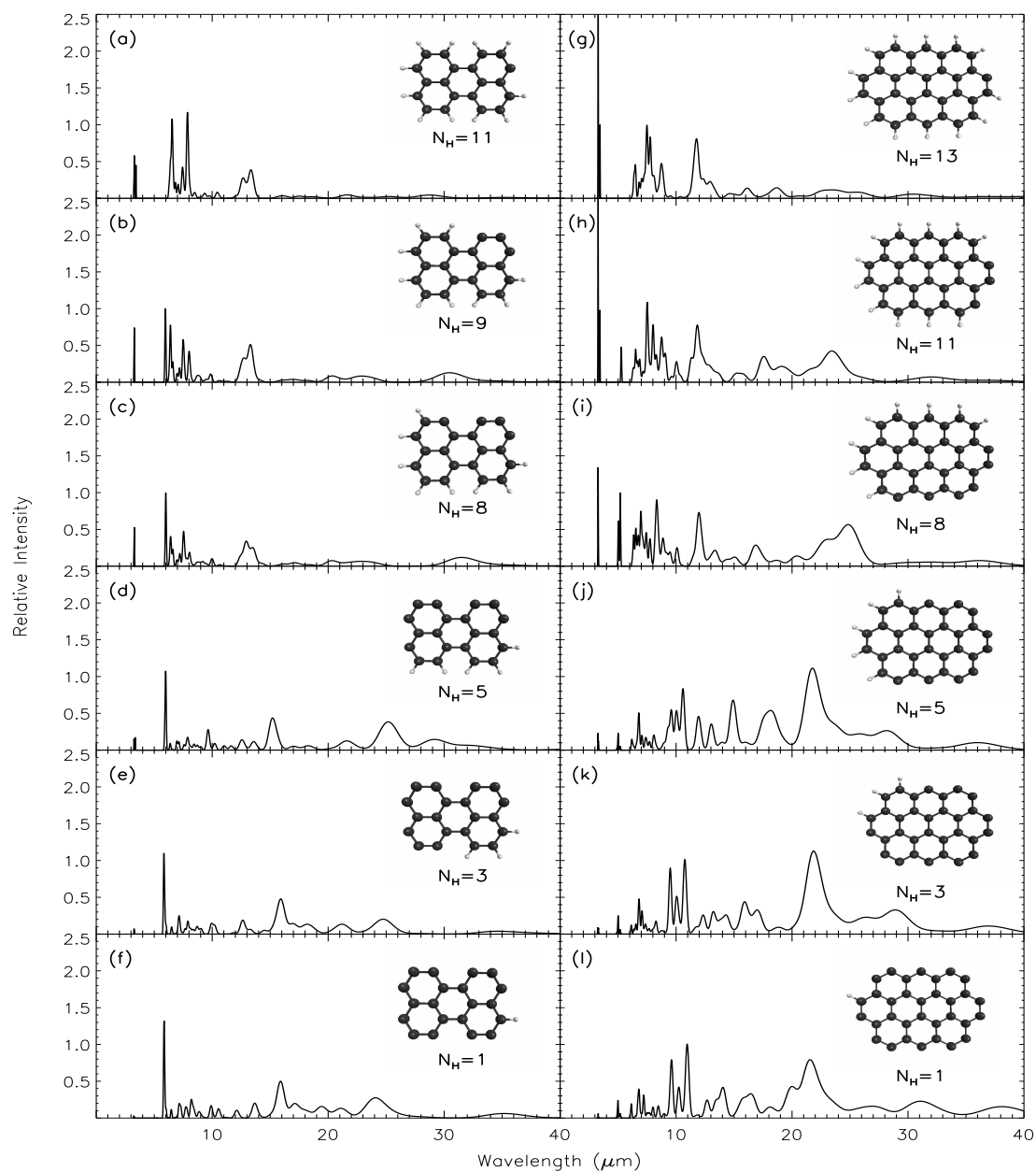


Figure 5.3: Theoretical spectra of dehydrogenated forms of (a)-(f) perylene anion ($C_{20}H_{12}^{-1}$), (g)-(l) ovalene anion ($C_{32}H_{14}^{-1}$)

N_H =number of H atoms in the periphery of a PAH molecule

Table 5.2: Spectral lines in the 5-30 μm region in $\text{C}_{20}\text{H}_6^{-1}$, $\text{C}_{24}\text{H}_6^{-1}$ & $\text{C}_{32}\text{H}_7^{-1}$

| $\text{C}_{20}\text{H}_6^{-1}$ | | $\text{C}_{24}\text{H}_6^{-1}$ | | $\text{C}_{32}\text{H}_7^{-1}$ | | | |
|--------------------------------|--------------------|--------------------------------|--------------------|--------------------------------|--------------------|-----------------------------|--------------------|
| λ (μm) | Int _{rel} | λ (μm) | Int _{rel} | λ (μm) | Int _{rel} | λ (μm) | Int _{rel} |
| 5.9 | 1 | 5.1 | 0.21 | 5 | 0.56 | 9.1 | 0.12 |
| 6.3 | 0.07 | 5.2 | 1 | 5.1 | 0.96 | 9.3 | 0.17 |
| 6.3 | 0.19 | 6.9 | 0.28 | 5.2 | 1 | 9.5 | 0.11 |
| 6.4 | 0.60 | 7.1 | 0.07 | 6.2 | 0.05 | 9.7 | 0.09 |
| 6.7 | 0.06 | 7.3 | 0.21 | 6.3 | 0.22 | 10.1 | 0.23 |
| 7.2 | 0.18 | 7.5 | 0.08 | 6.3 | 0.1 | 11.6 | 0.05 |
| 7.2 | 0.11 | 8 | 0.09 | 6.5 | 0.19 | 11.6 | 0.08 |
| 7.4 | 0.21 | 8 | 0.05 | 6.6 | 0.46 | 11.9 | 0.6 |
| 7.5 | 0.3 | 9.1 | 0.11 | 6.7 | 0.05 | 12.3 | 0.16 |
| 7.5 | 0.14 | 9.4 | 0.13 | 6.8 | 0.09 | 12.3 | 0.06 |
| 7.9 | 0.10 | 10.1 | 0.05 | 6.8 | 0.75 | 12.8 | 0.15 |
| 8.5 | 0.17 | 10.7 | 0.07 | 6.9 | 0.24 | 13.3 | 0.05 |
| 8.7 | 0.14 | 12.2 | 0.22 | 6.9 | 0.73 | 13.3 | 0.08 |
| 8.9 | 0.21 | 12.6 | 0.06 | 7.1 | 0.25 | 14.5 | 0.16 |
| 9.9 | 0.28 | 12.7 | 0.05 | 7.1 | 0.16 | 14.6 | 0.1 |
| 9.9 | 0.06 | 16.3 | 0.09 | 7.3 | 0.12 | 14.6 | 0.06 |
| 12.4 | 0.08 | 19.5 | 0.06 | 7.3 | 0.13 | 15.1 | 0.31 |
| 12.5 | 0.25 | 20.1 | 0.05 | 7.7 | 0.13 | 16.7 | 0.3 |
| 13.2 | 0.35 | 22.1 | 0.09 | 7.8 | 0.1 | 16.9 | 0.1 |
| 16.6 | 0.09 | 23.4 | 0.28 | 7.8 | 0.05 | 17.1 | 0.07 |
| 26.9 | 0.09 | 26.8 | 0.06 | 7.9 | 0.07 | 18.2 | 0.2 |
| 28.4 | 0.08 | 30.3 | 0.08 | 8.2 | 0.07 | 19.9 | 0.09 |
| | | | | 8.2 | 0.82 | 20.3 | 0.05 |
| | | | | 8.4 | 0.24 | 22.6 | 0.21 |
| | | | | 8.5 | 0.07 | 22.7 | 0.54 |
| | | | | 8.7 | 0.05 | 24.1 | 0.09 |
| | | | | 8.9 | 0.21 | 24.4 | 0.09 |
| | | | | 8.9 | 0.07 | 25.0 | 0.46 |
| | | | | | | 26.0 | 0.19 |

The full table of the band positions and intensities of the spectral lines for all the molecules is given in the Appendix A.

5.4 Astrophysical implications

Recent studies by Bauschlicher et al. [206, 207] conclude that PAH neutrals, cations and anions are equally important for some of the observed AIBs, if not all. Particularly, the 3.3 μm feature is attributed to arise from the C-H stretch mode in a neutral PAH whereas the 6.2, 7.7 and 8.6 μm features are inherent to C-C stretch/C-H in-plane modes in a PAH cation [167]. The 11.2 and 12.7 μm features have been attributed to the oop bending modes associated with solo and duo/trio C-H groups respectively in a neutral PAH [230]. In general, PAH cations are proposed

to be promising candidates of AIB carriers in terms of intensities, while neutral PAHs are consistent with the band profiles and peak positions of the bands [167, and references therein]. The ionization (positive/negative) will result in a slight blueshifting of the peak position with a distinct variation in the intensity.

Anionic PAHs have been considered to be the principal carriers of negative charge in diffuse and dense interstellar clouds [231, 232, 2, 233]. Similar to cations, PAH anions may also contribute to the astronomical bands at $7.8 \mu\text{m}$ and $8.6 \mu\text{m}$ [206, 207]. The variation in the intensity of the IR bands is a function of the physical condition of the environment and can be used to probe the abundance of PAH cations/anions in the sources. Our results suggest that PAH anions show spectral characteristics that are in-between PAH neutrals and PAH cations. We also include dehydrogenated forms of PAH anions to understand any possible contribution towards the observed AIBs. PAH anions are formed through radiative attachment of electrons in dense cloud. There is a possible channel for stabilization of PAH anion by releasing a H atom to form dehydrogenated PAH anion [234, 219]. The higher electron affinity of dehydrogenated PAH molecules in comparison to the parent hydrocarbon also indicates the possibility of formation of dehydrogenated PAH anions in the ISM. Le Page et al. [183, 235] reported that intermediate size PAHs (carbon atoms ~ 20 to 30) are prone to extreme dehydrogenation, while small PAHs (fewer than 20 carbon atoms) are destroyed and large PAHs (more than 30 carbon atoms) are mostly hydrogenated/fully hydrogenated under interstellar conditions. Those with dehydrogenation can further be altered into a dehydrogenated PAH anion in dense clouds. Similar to neutral PAHs, anionic PAHs also show a distinct $3.3 \mu\text{m}$ band with a comparatively stronger intensity. From this chapter, $\text{Int}_{\text{rel}(3.3)}$ ⁵ for neutral coronene ($\text{C}_{24}\text{H}_{12}$) is 0.44 and for anionic coronene ($\text{C}_{24}\text{H}_{12}^{-1}$), it is 0.59. $\text{Int}_{\text{rel}(3.3)}$ is large compared to the observations. Tielens [2] pointed out that neutral PAHs can still be considered as potential candidates for the $3.3 \mu\text{m}$ band as long as the relative strength of the C-H versus

⁵Relative intensity of the C-H_{stretch} mode that appears at $3.3 \mu\text{m}$, the highest C-H_{stretch} intensity among all the C-H_{stretch} vibrations is considered.

the C-C modes is comparable to observations. However for the anions, $\text{Int}_{\text{rel}(3.3)}$ is so large that it only becomes comparable to observations when H atoms are removed from the periphery of the molecule. Dehydrogenation may not necessarily result into an immediate decrease in $\text{Int}_{\text{rel}(3.3)}$ as the intensity is also governed by the symmetry of the molecule. PAHs with higher symmetry show a lower value of $\text{Int}_{\text{rel}(3.3)}$ compared to less symmetric structures. As dehydrogenation proceeds, we expect to see a fall in $\text{Int}_{\text{rel}(3.3)}$ and after a certain level of dehydrogenation, it may give an $\text{Int}_{\text{rel}(3.3)}$ which is equivalent to that of neutral and gradually may approach the $\text{Int}_{\text{rel}(3.3)}$ value obtained for a PAH cation. For example, $\text{C}_{24}\text{H}_8^{-1}$ has $\text{Int}_{\text{rel}(3.3)} \sim 0.37$ which is then close to the value obtained for $\text{C}_{24}\text{H}_{12}$. Thus, $\text{C}_{24}\text{H}_8^{-1}$ may be equally important as $\text{C}_{24}\text{H}_{12}$ for the astronomically observed feature at $3.3 \mu\text{m}$. The low symmetry structures of dehydrogenated coronene containing an odd number of H atoms usually show a higher value of $\text{Int}_{\text{rel}(3.3)}$ compared to high symmetric structures with an even number of H atoms as shown in Table 5.3. $\text{C}_{24}\text{H}_2^{-1}$ gives $\text{Int}_{\text{rel}(3.3)} \sim 0.07$ which is close to the $\text{Int}_{\text{rel}(3.3)} \sim 0.02$ obtained for $\text{C}_{24}\text{H}_{12}$ cation. Perylene ($\text{C}_{20}\text{H}_{12}$) also shows similar behaviour and on partial dehydrogenation, $\text{C}_{20}\text{H}_{10}^{-1}$ gives $\text{Int}_{\text{rel}(3.3)} \sim 0.59$ which is close to the $\text{Int}_{\text{rel}(3.3)}$ obtained for $\text{C}_{20}\text{H}_{12}$ ($\text{Int}_{\text{rel}(3.3)} \sim 0.69$). $\text{Int}_{\text{rel}(3.3)}$ for the $\text{C}_{20}\text{H}_{12}$ anion is high (~ 0.93). Increasing dehydrogenation gives a lower value of $\text{Int}_{\text{rel}(3.3)}$ as discussed for coronene. As for ovalene ($\text{C}_{32}\text{H}_{14}$), the situation is somewhat different and $\text{Int}_{\text{rel}(3.3)}$ obtained for its neutral, anionic and cationic forms are 0.83, 0.29, 0.07 respectively. $\text{Int}_{\text{rel}(3.3)}$ increases to 1 when we remove the first H atom from $\text{C}_{32}\text{H}_{14}^{-1}$ (i.e., for $\text{C}_{32}\text{H}_{13}^{-1}$) and it then comes down to a lower value for a $\text{C}_{32}\text{H}_{10}^{-1}$ ($\text{Int}_{\text{rel}(3.3)} \sim 0.37$), $\text{C}_{32}\text{H}_6^{-1}$ ($\text{Int}_{\text{rel}(3.3)} \sim 0.32$) and so on. For $\text{C}_{32}\text{H}_3^{-1}$ and $\text{C}_{32}\text{H}_1^{-1}$, $\text{Int}_{\text{rel}(3.3)}$ is 0.08 and 0.06 respectively which are comparable to observations.

Dehydrogenation also results in prominent features in the $5\text{-}10 \mu\text{m}$ region. The same characteristic is also observed for cationic PAH molecules. A band at $5.2 \mu\text{m}$ is a unique feature present only in highly dehydrogenated PAH anions. This feature may help in identification of dehydrogenated PAH anions in the ISM. Its absence also suggests that the size of PAHs studied here may be only weakly dehydrogenated. Another

Table 5.3: $\text{Int}_{\text{rel}(3.3)}$ obtained for dehydrogenated forms of coronene anion

| dehydrogenated coronene anion | $\text{Int}_{\text{rel}(3.3)}$ |
|-----------------------------------|--------------------------------|
| $\text{C}_{24}\text{H}_{11}^{-1}$ | 0.63 |
| $\text{C}_{24}\text{H}_{10}^{-1}$ | 0.92 |
| $\text{C}_{24}\text{H}_9^{-1}$ | 0.99 |
| $\text{C}_{24}\text{H}_8^{-1}$ | 0.37 |
| $\text{C}_{24}\text{H}_7^{-1}$ | 1 |
| $\text{C}_{24}\text{H}_6^{-1}$ | 0.16 |
| $\text{C}_{24}\text{H}_5^{-1}$ | 0.72 |
| $\text{C}_{24}\text{H}_4^{-1}$ | 0.21 |
| $\text{C}_{24}\text{H}_3^{-1}$ | 1 |
| $\text{C}_{24}\text{H}_2^{-1}$ | 0.07 |
| $\text{C}_{24}\text{H}_1^{-1}$ | 0.45 |

Table 5.4: Energies (absolute and relative) of dehydrogenated PAH anions

| Dehydrogenated PAH anions | E_T^a (in Hartree) | Relative energy ^b |
|--|----------------------|------------------------------|
| Perylene ($\text{C}_{20}\text{H}_{12}^{-1}$) | -769.359 | 1.00020 |
| Coronene ($\text{C}_{24}\text{H}_{12}^{-1}$) | -921.838 | 1.00015 |
| Ovalene ($\text{C}_{32}\text{H}_{14}^{-1}$) | -1227.959 | 1.00012 |

^a E_T , total energy = Electronic energy + Zero point energy

^bRelative energy = $\frac{C_x H_y^{-1}}{C_x H_{y-1}^{-1} + H}$

important characteristic is that with increasing dehydrogenation, a broad plateau in the 20-30 μm region gains intensity mainly due to C-C-C in-plane modes. With increasing size, this feature gains intensity. This region together with the other characteristics mentioned here may be used as a probe to identify any possible dehydrogenated forms of PAH anions in the ISM. $[\text{FePAH}]^+$ complexes also show intense features in the 20-60 μm regions [236], however the assignment of carriers in the far-infrared region is still ambiguous. This calls for new astronomical data in the far-infrared which would help concretize theoretical results.

It is important to note here that interstellar PAHs usually exist either in fully hydrogenated or fully dehydrogenated form and the intermediate hydrogenated/dehydrogenated state is rare [11]. Le Page et al. [183, 235] suggest that partial dehydrogenation may be possible for in-

intermediate size PAHs (carbon atoms ~ 20 to 30). In such a scenario, intermediate dehydrogenation states for $C_{32}H_{14}$ may exist long enough to emit the AIBs. Once all the H atoms are removed, a C atom may be lost subsequently to form a pentagonal ring which will then initiate the formation of fullerenes in the ISM [11]. Dehydrogenation may therefore be considered as an intermediate phase in the formation of fullerenes from PAH molecules. The energies (absolute and relative) of dehydrogenated PAH anions are listed in Table 5.4.

5.5 Summary

Interstellar PAH anions are likely to exist in cold dense regions where a PAH molecule can easily attract an electron to form a PAH anion that shows important characteristic features in IR. This chapter reports the vibrational study of dehydrogenated PAH anions to seek any correlation with the observed AIBs. The theoretical data shows that PAH anions along with their dehydrogenated forms show characteristics that are similar to neutrals and cations. This implies that the astronomically observed bands that are usually assigned to either a neutral or a cationic PAH are also likely to have contributions from dehydrogenated PAH anions provided that the physical conditions support their presence in the ISM.

We summarize the results here:

1. Partially dehydrogenated PAH anions may contribute to the $3.3 \mu\text{m}$ region and the broad intense features in the $5\text{-}10 \mu\text{m}$ region.
2. The $3.3 \mu\text{m}$ feature is immensely strong for a PAH anion. Dehydrogenation of a PAH anion reduces the intensity of the $3.3 \mu\text{m}$ feature which then becomes comparable to its neutral counterpart and is closer to observed intensities of regions where the $3.3 \mu\text{m}$ is intense.
3. During the process of successive dehydrogenation, the molecule passes through a series of changes in its symmetry. The dehydrogenated PAH anion with a higher symmetry produces a less intense $3.3 \mu\text{m}$

band compared to that with a lower symmetry.

4. During the process of dehydrogenation, a duo C-H group in the PAH anion may convert into a solo C-H unit which produces a $3.4 \mu\text{m}$ feature due to the solo C-H stretch vibrations.
5. Unique features at 5.2 and $5.8 \mu\text{m}$ are observed for a dehydrogenated PAH anion that arise due to the stretching of the free C-C/C-C-C units. The $5.2 \mu\text{m}$ band observed in coronene and ovalene may be used to identify dehydrogenated PAH anions. Absence of this feature in observations suggests that such PAHs may be dehydrogenated up to a certain limit.
6. A broad plateau in the $20\text{-}30 \mu\text{m}$ region arises in the spectra of a dehydrogenated PAH anion that becomes more significant with increasing size.

These characteristics can be used as a tool to understand any possible contribution of dehydrogenated PAH anions in the ISM. The calculated energy configuration indicates that before they convert into fully dehydrogenated molecules, a partially dehydrogenated form of PAH anion may be present for a large PAH molecule as it is less susceptible to the loss of H atoms and requires time to remove all the H atoms from its periphery. The spectral characteristics together with stability offers support to the existence of large dehydrogenated PAH anions in the ISM as members of the extended PAH family.

