

Chapter 4

The Interstellar PAH molecules with aliphatic side groups

4.1 Introduction

Since the discovery of the UIR bands, a quest for its carrier has led to a trail of ongoing research that has proposed several alternative hypotheses apart from the widely accepted PAH-UIR hypothesis [7, 8, 78] to determine the structure of its carriers. The most popular are HAC (hydrogenated Amorphous Carbon) [187], QCC (Quenched Carbonaceous Composites) [188], coal [189] and MAON model (mixed aromatic/aliphatic organic nanoparticles) [190, 191, 192]. Recently Yang et al. [193, 12, 154] suggested UIR carriers to be predominantly aromatic. However some interstellar PAHs are suggested to carry an aliphatic component that gives rise to the 3.4 μm feature near the aromatic 3.3 μm feature. The 3.4 μm , though weak compared to the 3.3 μm is a well known feature and ubiquitously detected towards several astrophysical sources [194, and references therein]. Initially, the 3.3 μm feature was detected as a broad emission feature [195, 196]. Later, high resolution spectroscopy confirmed that the 3.3 μm emission feature indeed has sub components that form a plateau centered near 3.45 μm and can extend upto 3.6 μm [197]. These bands are particularly observed at 3.40, 3.46, 3.51, and 3.57 μm and are proposed to come either from overtones and combinational bands of the

fundamental C-H vibrational modes or due to the presence of aliphatic functional group in a PAH molecule [198, 199, 200, 201, 202]. For a PAH molecule, the 3.3 and 3.4 μm features are characteristics of stretching of aromatic and aliphatic C-H bonds respectively and are crucial towards the detection of aromatic/aliphatic components in a PAH molecule. Yang et al. [193, 12, 154] even proposed an upper limit of $\sim 2\%$ of aliphatic carbon atoms that might be attached to an aromatic unit of PAH and can account for the observed intensities of the 3.3 and 3.4 μm bands. They used the observed intensities of the 3.3 and 3.4 μm bands and intrinsic strengths of the theoretically computed 3.3 and 3.4 μm bands (on a per unit C-H bond basis) to estimate the aliphatic to aromatic ratio in PAHs. Aliphatic side chain linked to a PAH molecule can be of different forms, for example: hydrogenated, methyl, ethyl or unsaturated alkyl chains. Recently, Maurya and Rastogi [203] discussed the spectral characteristics of PAHs with unsaturated alkyl chains i.e., vinyl substituted PAHs in relation to the UIR emission bands. In the chapters 2 and 3, the depletion of interstellar deuterium (D) into PAHs forming PAD/D_n-PAH and DPAH⁺ is discussed. It is important to consider PAH molecules with aliphatic side groups and include a deuterium (D) component in the aliphatic side group to look for any possible signatures that may relate to the UIR bands. In this chapter, we present a detailed analysis of the IR spectra of these molecules and discuss the possible astrophysical implications. A D/H ratio is also calculated and compared with the previous value of D/H reported in the previous chapters.

4.2 Molecules studied

This work reports DFT calculations on PAHs with -H (hydrogenated), -CH₃ (methyl), -CH₂-CH₃ (ethyl), -CH=CH₂ (vinyl) functional groups to determine the expected region of infrared features due to their characteristic vibrational modes. Their deuterated and deuterated counterparts are also considered for the study. Coronene (C₂₄H₁₂) being a symmetric and compact molecule has greater photostability against UV radiation. Therefore, we have considered coronene molecule with functional groups

attached to it for this study. The structure of the sample molecules studied in this chapter are shown in Figure 4.1. These type of molecules are expected to be present in benign environments of the ISM as they are easily prone to destruction in an intense UV irradiated region.

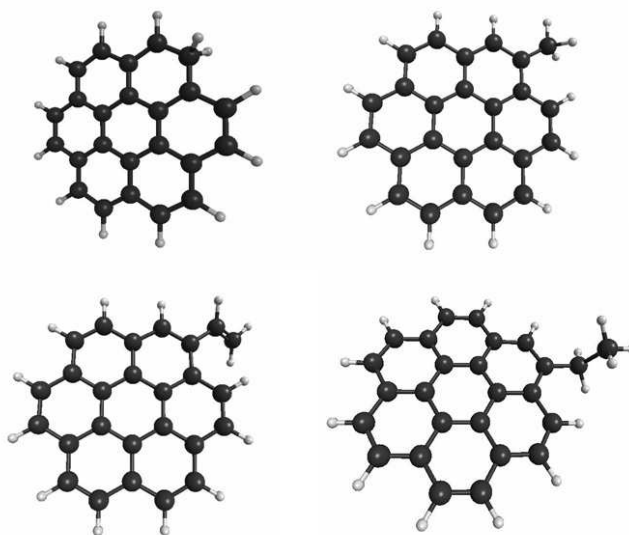


Figure 4.1: Examples of PAH molecules with aliphatic components (H-coronene, coronene-CH₃, coronene-CH=CH₂, coronene-CH₂-CH₃)

For theoretical calculations, similar method as applied in the previous chapters is attempted to obtain the infrared spectra of the molecules. When the relative strengths of the modes obtained from theoretical calculation are compared with those obtained from experiments, the intensity of C-H stretch is found to be much larger as compared to the other modes and an intensity scaling is required. The rest of the modes however, show better matching in terms of band strength when compared with the experimentally obtained spectra. Considering that the second order Møller-Plesset (MP2) perturbation theory with large basis set (for example, MP2/6-311+G(3df, 3pd)) gives quite accurate oscillator strengths compared to B3LYP DFT, Yang et al. [154] have derived a relation for MP2/6-311+G(3df, 3pd) and B3LYP/6-311+G** level of theories to scale the intensities of C-H_{stretch} modes near $\sim 3 \mu\text{m}$ region. There are two important features in this region; $3.3 \mu\text{m}$ and $3.4 \mu\text{m}$ due to the

stretching of aromatic C-H and aliphatic C-H bonds respectively. By using, $A_i \approx 0.6372 A_j$, where A_i and A_j are the intensities of C-H_{stretch} modes computed at the MP2/6-311+G(3df, 3pd) and B3LYP/6-311+G** level, respectively, we can achieve good accuracy for band strength by computing at an inexpensive level [154]. For frequency scaling, same scaling factors are used that are applied in the previous chapters. The scaled intensities and scaled wavelengths are plotted as Gaussian profiles in a similar manner as in the previous chapters.

4.3 Results and Discussion

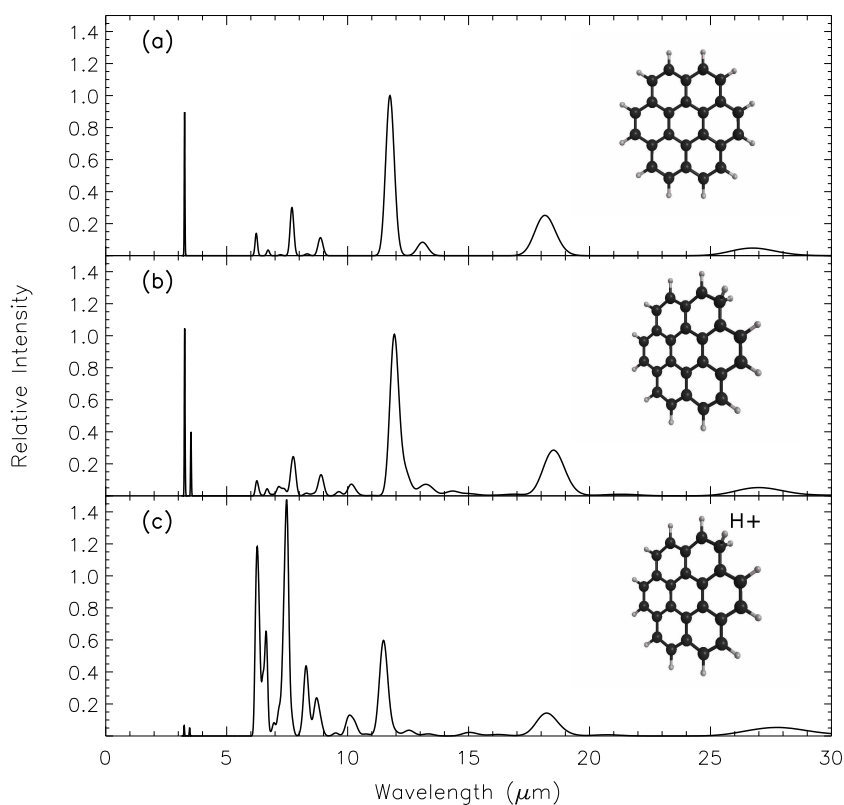


Figure 4.2: Theoretical spectra of (a) neutral coronene (C₂₄H₁₂), (b) hydrogenated coronene (HC₂₄H₁₂), (c) Protonated coronene (HC₂₄H₁₂⁺)

Figure 4.2 shows a comparison of the infrared spectra of coronene,

hydrogenated coronene and its cationic counterpart (protonated coronene). A hydrogenated coronene ($\text{HC}_{24}\text{H}_{12}$) which is partially aliphatic in nature shows almost similar features as that of a pure coronene molecule ($\text{C}_{24}\text{H}_{12}$). This is expected as hydrogenated coronene is simply a coronene molecule with an additional hydrogen attached to it forming an aliphatic C-H bond at the addition site. The $3.3 \mu\text{m}$ feature arises due to aromatic C-H_{stretching}, while $6\text{-}10 \mu\text{m}$ and beyond $10 \mu\text{m}$ regions are mostly dedicated to C-C_{in-plane}/C-C_{stretching} and C-H_{oop} (out of plane) modes respectively. This is true for all forms of PAHs. The main difference appears in the $3.5 \mu\text{m}$ feature which is a composite of two modes; symmetric and antisymmetric stretching of aliphatic C-H bonds with relative intensities (Int_{rel}) of 0.3 and 0.1 respectively. A protonated coronene ($\text{HC}_{24}\text{H}_{12}^+$, Figure 4.2c); like any other ionized form of PAH shows an intensity rise in the $6\text{-}10 \mu\text{m}$ region with a slight decrease in the intensity beyond $10 \mu\text{m}$ and a significantly reduced intensity near the $3 \mu\text{m}$ region. $\text{HC}_{24}\text{H}_{12}^+$ gives rise to a comparatively less intense feature at $3.5 \mu\text{m}$ (Int_{rel} 0.05). Unlike $\text{C}_{24}\text{H}_{12}$, a small plateau near $10 \mu\text{m}$ arises due to C-C-C_{in-plane} mode in case of both $\text{HC}_{24}\text{H}_{12}$ and $\text{HC}_{24}\text{H}_{12}^+$. This might reflect the change in the symmetry of $\text{HC}_{24}\text{H}_{12}$ and $\text{HC}_{24}\text{H}_{12}^+$ from that of $\text{C}_{24}\text{H}_{12}$ after an additional H is attached to $\text{C}_{24}\text{H}_{12}$. The positions (wavelength) and Int_{rel} of the lines that are present in the sample molecules are tabulated in the Appendix A.

The theoretically obtained vibrational spectra of hydrogenated coronene ($\text{HC}_{24}\text{H}_{12}$), methyl-coronene ($\text{C}_{24}\text{H}_{11}\text{-CH}_3$), ethyl-coronene ($\text{C}_{24}\text{H}_{11}\text{-CH}_2\text{-CH}_3$) and vinyl-coronene ($\text{C}_{24}\text{H}_{11}\text{-CH=CH}_2$) along with their deuterated counterparts¹ are presented in Figure 4.3. With the addition of an aliphatic component to the PAH molecule, the symmetry of the system breaks down and the spectrum becomes more and more rich with new features. The lines in the spectrum are the manifestations of the characteristic vibrational modes occurring within a molecule. However, the effect of the presence of an aliphatic component in the molecule is only evident from features near $\sim 3.5 \mu\text{m}$ that arises due to the stretching of the aliphatic C-H bond. Other modes that also include the vibra-

¹H or one of the H atoms in the functional group is substituted with D

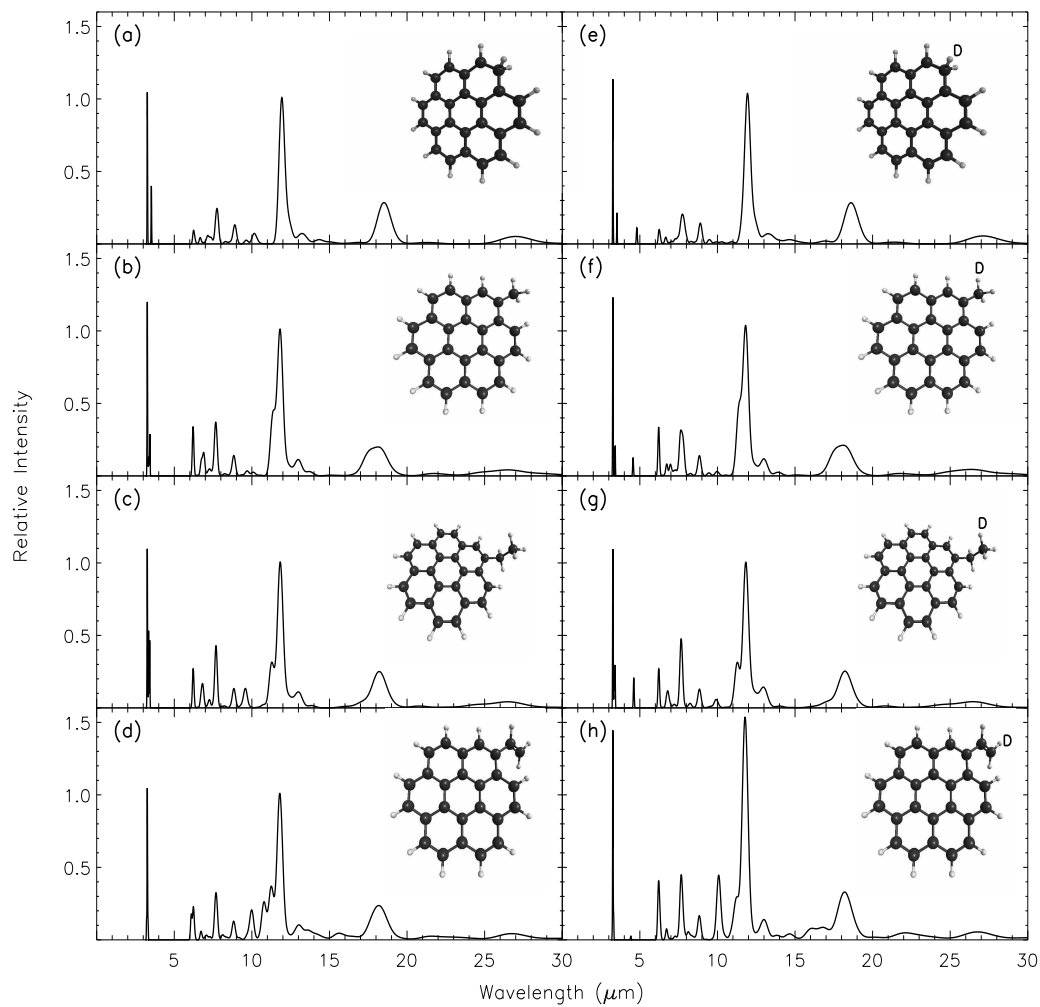


Figure 4.3: Theoretical spectra of (a) $\text{HC}_{24}\text{H}_{12}$, (b) $\text{C}_{24}\text{H}_{11}\text{-CH}_3$, (c) $\text{C}_{24}\text{H}_{11}\text{-CH}_2\text{-CH}_3$, (d) $\text{C}_{24}\text{H}_{11}\text{-CH=CH}_2$, (e) $\text{DC}_{24}\text{H}_{12}$, (f) $\text{C}_{24}\text{H}_{11}\text{-CH}_2\text{D}$, (g) $\text{C}_{24}\text{H}_{11}\text{-CH}_2\text{-CH}_2\text{D}$, (h) $\text{C}_{24}\text{H}_{11}\text{-CH=CHD}$

tions of aliphatic component are too weak to be seen in the spectra. The 3.5 μm is not seen in the case of any other molecule except PAHs with aliphatic C-H bonds. For hydrogenated coronene, this feature distinctly appears at 3.5 μm while for methyl-coronene and ethyl-coronene, the feature is slightly blueshifted to 3.4 μm and extends upto 3.3 μm . For vinyl-coronene, the C-H bonds present in the aliphatic component (-CH=CH₂) however do not show stretching near 3.4 μm and instead fall in the aromatic region, i.e., near 3.3 μm . Similar results were obtained by Yang et al. [12] and Maurya and Rastogi [203] for vinyl-substituted PAHs. Maurya and Rastogi [203] also showed the additional features that arise due to the vibrations of the -CH=CH₂ group in vinyl-substituted PAHs. These include features near 6.2 μm due to vinyl C=C stretch and near 10 μm due to vinyl CH₂ wag and twist motions. Vinyl-substituted coronene in our work also shows peaks at 6.1 μm (1640.76 cm^{-1}) and 10.8 μm (927.20 cm^{-1}) respectively. With increasing size of the functional groups attached to PAH, the number of aliphatic C-H bonds increase, this causes an increase in the integrated intensity of the 3.5/3.4 μm band. The ratio of integrated intensities of 3.3 μm to integrated intensities of 3.5/3.4 μm , i.e., $\frac{\text{Int}_{3.3}}{\text{Int}_{3.5/3.4}}$ decreases with increasing number of aliphatic C-H bonds (~ 2.9 , ~ 2.7 , ~ 1.3 for -H, -CH₃, -CH₂-CH₃ respectively). The deuterated counterparts of the molecules show almost similar features as those of aliphatic PAHs without D, but with an additional feature near 4.6 μm due to the stretching of the aliphatic C-D bond. The 3.5 μm is also present due to the associated aliphatic C-H_{stretching}. For deuterated coronene (DC₂₄H₁₂), the C-D_{stretching} is seen at 4.8 μm (Int_{rel} ~ 0.1) which is shifted to 4.6 μm (Int_{rel} ~ 0.1) with increase in the size of functional group (-CH₂D) attached to the molecule. For -CH₂-CH₂D group, the position of the feature remains same with a slight increase in the Int_{rel} ~ 0.2 . The exception is C₂₄H₁₁-CH=CHD for which the C-D_{stretching} does not appear at 4.6 μm and falls at the aromatic region of C-D stretching, i.e at 4.4 μm (Int_{rel} ~ 0.03). The positions and relative intensities of aliphatic/aromatic C-H_{stretching}/C-D_{stretching} for the sample molecules are presented in Table 4.1. Though, the aliphatic nature of the PAH molecule can only be distinctly seen at ~ 3.5 and ~ 4.6 μm

due to aliphatic C-H_{stretching} and aliphatic C-D_{stretching} respectively, there are some indirect effects due to the inclusion of an aliphatic component to coronene. For example: usually, C₂₄H₁₂ has duo C-H bonds² at its periphery, the out of plane vibrations of which give intense features at $\sim 12 \mu\text{m}$. However, with one of the peripheral H atom being replaced with -CH₃/-CH₂D, -CH₂-CH₃/-CH₂-CH₂D or -CH=CH₂/-CH=CHD group, the H atom near the addition site of these functional groups becomes solo C-H³ unit for which the C-H_{oop} mode appears at $\sim 11.3 \mu\text{m}$. However, this situation is particular for molecules which originally has duo C-H groups, but addition of an aliphatic component like -CH₃ etc. converts it into a solo C-H group.

In testing conditions of the ISM, molecules are likely to be ionized on being illuminated by the UV radiation. In such a case, the ionized forms of the PAH molecules should also be considered for our study. In Figure 4.4, we present the theoretically obtained spectra of the same molecules (as shown in Figure 4.3) in their ionized forms. Ionization results in the removal of an electron from the additional H or D atom which then behaves as a proton (H⁺) or deuteron (D⁺) and the structure resembles the structure of protonated or deuterated PAHs. The structures in Figure 4.4 are therefore representatives of protonated and deuterated PAHs where proton and deuteron have replaced H or one of H atoms in the functional group. Some of these type of molecules are already discussed in the previous chapters. Protonation or deuteration reduces the symmetry of the structure which results in a rich spectrum with more number of features in the protonated/deuterated form compared to that from the conventional form. These new features might arise due to the merging of several fundamental modes producing combinational modes. Like any other ionized PAHs, protonated and deuterated PAHs show dominant features in the 6-10 μm region, with comparatively less intense features in other regions including the 3 μm and 4 μm regions. The (C₂₄H₁₁-CH=CH₂)⁺ despite being ionized however shows comparatively significant aromatic 3.3 μm feature. The aliphatic C-H/C-D stretching modes

²A 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

³A solo C-H group, also referred as on the same ring

Table 4.1: Intensities and positions of the C-H/C-D stretching mode in PAHs with aliphatic components

PAHs	Nature of Mode	μm	Int _{rel}	PAHs	Nature of Mode	μm	Relative Intensity
HC ₂₄ H ₁₂	C-H _{stretching} (arom)	3.26	0.14	DC ₂₄ H ₁₂	C-H _{stretching} (arom)	3.26	0.15
	do	3.26	0.52		do	3.26	0.56
	do	3.26	0.24		do	3.26	0.25
	do	3.26	0.06		do	3.26	0.07
	do	3.28	0.07		do	3.28	0.07
	do	3.29	0.06		do	3.29	0.06
	C-H _{stretching} (aliph)	3.52	0.3		C-H _{stretching} (aliph)	3.52	0.21
do	3.53	0.1	C-D _{stretching} (aliph)	4.81	0.11		
C ₂₄ H ₁₁ -CH ₃	C-H _{stretching} (arom)	3.24	0.14	C ₂₄ H ₁₁ -CH ₂ D	C-H _{stretching} (arom)	3.24	0.15
	do	3.26	0.28		do	3.26	0.29
	do	3.26	0.62		do	3.26	0.65
	do	3.26	0.11		do	3.26	0.12
	do	3.27	0.06		do	3.27	0.06
	do	3.28	0.07		do	3.28	0.07
	do	3.29	0.1		do	3.29	0.09
	C-H _{stretching} (aliph)	3.33	0.12		C-H _{stretching} (aliph)	3.38	0.13
do	3.37	0.13	do	3.41	0.2		
do	3.42	0.29	C-D _{stretching} (aliph)	4.56	0.12		
C ₂₄ H ₁₁ -CH ₂ -CH ₃	C-H _{stretching} (arom)	3.24	0.15	C ₂₄ H ₁₁ -CH ₂ -CH ₂ D	C-H _{stretching} (arom)	3.24	0.15
	do	3.26	0.29		do	3.26	0.29
	do	3.26	0.55		do	3.26	0.55
	do	3.26	0.08		do	3.26	0.07
	do	3.26	0.05		do	3.26	0.06
	do	3.27	0.05		do	3.27	0.05
	do	3.29	0.12		do	3.29	0.12
	C-H _{stretching} (aliph)	3.34	0.2		C-H _{stretching} (aliph)	3.34	0.19
	do	3.35	0.35		do	3.39	0.19
	do	3.41	0.2		do	3.41	0.2
do	3.42	0.28	C-D _{stretching} (aliph)	4.61	0.21		
C ₂₄ H ₁₁ -CH=CH ₂	C-H _{stretching} (aliph)	3.21	0.1	C ₂₄ H ₁₁ -CH=CHD	C-H _{stretching} (arom)	3.22	0.06
	C-H _{stretching} (arom)	3.23	0.07		C-H _{stretching} (aliph)	3.25	0.07
	do	3.26	0.24		C-H _{stretching} (arom)	3.26	0.31
	do	3.26	0.56		do	3.26	0.75
	do	3.26	0.13		do	3.26	0.18
	do	3.27	0.08		do	3.27	0.11
	do	3.28	0.09		do	3.28	0.05
	C-H _{stretching} (aliph)	3.31	0.1		do	3.28	0.12
					C-H _{stretching} (aliph)	3.31	0.16

‘arom’ stands for aromatic

‘aliph’ stands for aliphatic

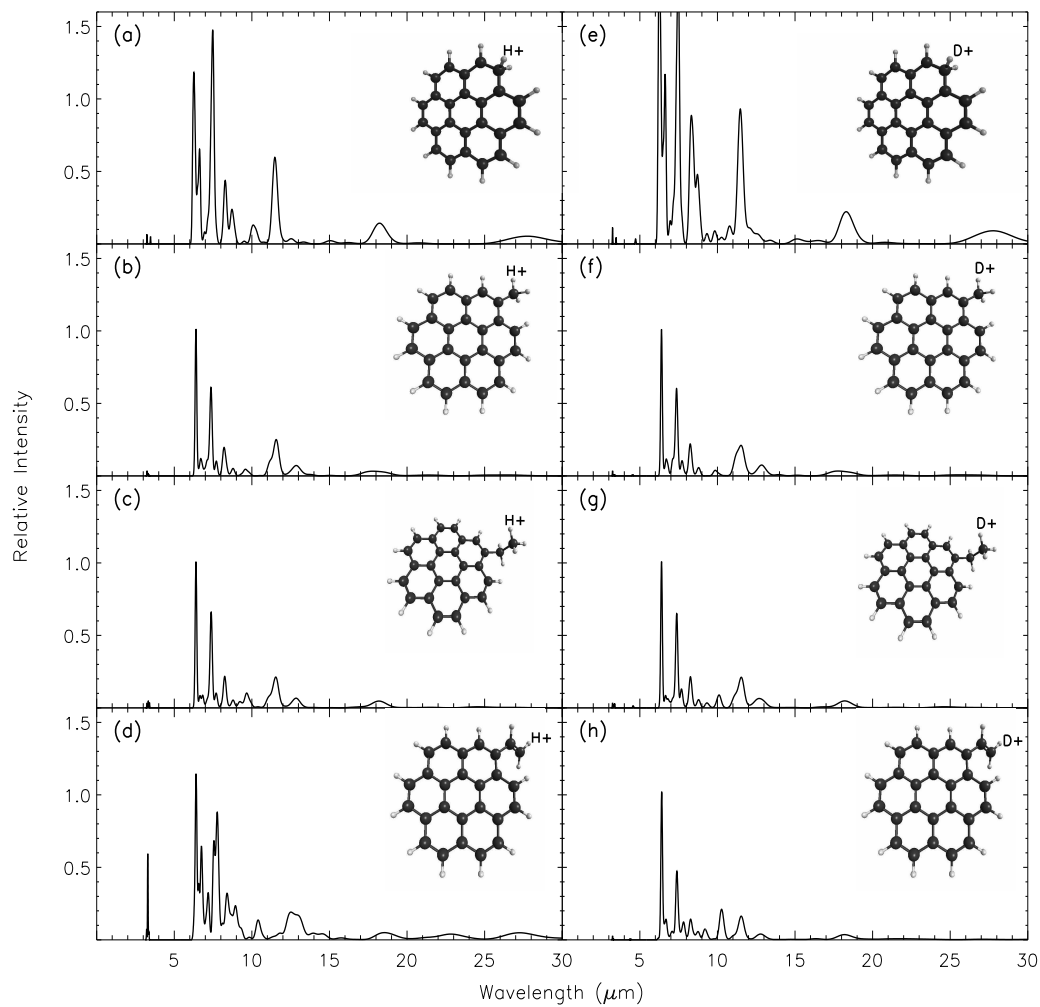


Figure 4.4: Theoretical spectra of (a) $\text{HC}_{24}\text{H}_{12}^+$, (b) $\text{C}_{24}\text{H}_{11}\text{-CH}_3^+$, (c) $\text{C}_{24}\text{H}_{11}\text{-CH}_2\text{-CH}_3^+$, (d) $\text{C}_{24}\text{H}_{11}\text{-CH=CH}_2^+$, (e) $\text{DC}_{24}\text{H}_{12}^+$, (f) $\text{C}_{24}\text{H}_{11}\text{-CH}_2\text{D}^+$, (g) $\text{C}_{24}\text{H}_{11}\text{-CH}_2\text{-CH}_2\text{D}^+$, (h) $\text{C}_{24}\text{H}_{11}\text{-CH=CHD}^+$

for protonated/deuterated forms appear at $3.5 \mu\text{m}$ and $4.6 \mu\text{m}$ respectively and are very weak in these molecules (see the Appendix A). In the previous chapters, though we considered deuterated PAHs (DPAH⁺) for our study, the structures were limited to only those molecules which are initiated by the addition of aliphatic -D component. In this chapter, we consider other deuterated PAHs as well in which deuterium forms the part of the functional group itself. While the aliphatic C-D_{stretching} appears at $4.7 \mu\text{m}$ ($\text{Int}_{\text{rel}} \sim 0.03$) for DC₂₄H₁₂⁺, the same feature is blueshifted with increasing size of the functional groups of which D⁺ forms the part. The feature is seen at $4.5 \mu\text{m}$ ($\text{Int}_{\text{rel}} \sim 0.01$) and $4.6 \mu\text{m}$ ($\text{Int}_{\text{rel}} \sim 0.01$) for C₂₄H₁₁-CH₂D⁺ and C₂₄H₁₁-CH₂-CH₂D⁺ respectively. For deuterated coronene with vinyl-group (C₂₄H₁₁-CH=CHD⁺), the stretching of the C-D bond (which forms the part of the aliphatic component) appears at $4.4 \mu\text{m}$ ($\text{Int}_{\text{rel}} \sim 0.01$), which is commonly seen for aromatic C-D_{stretching} rather than aliphatic C-D_{stretching}. Of all the protonated and deuterated PAHs, DC₂₄H₁₂⁺ shows the maximum number of features as compared to others. The significant features with their band positions and relative intensities for the sample molecules are listed in the Appendix A.

The interstellar D may not essentially be part of the aliphatic side chain in interstellar PAHs (for example: CH₃, CH₂-CH₃, etc.) and instead can be present independently anywhere in the PAH structure. In Figure 4.5, we have shown the infrared spectra of two such possibilities where a deuterium is present in aromatic and aliphatic site of the PAH molecule and does not form part of the methyl (-CH₃) functional group. Their ionized counterparts are also considered that resemble the structures of deuterated PAHs. C₂₄H₁₀D-CH₃ carries the C-D bond at the aromatic site and shows the aromatic C-D_{stretching} at $4.4 \mu\text{m}$, aliphatic C-H_{stretching} (in the -CH₃ group) at $3.4 \mu\text{m}$ and aromatic C-H_{stretching} at $3.3 \mu\text{m}$. In C₂₄H₁₁D-CH₃, the C-D bond is aliphatic in nature and an additional aliphatic C-H bond is present in the addition site of D which is independent of the aliphatic C-H bonds in the -CH₃ functional group. The stretching of the aliphatic C-H bond in the addition site of D is slightly redshifted to $3.5 \mu\text{m}$ compared to aliphatic C-H_{stretching} of the -CH₃ group at $3.4 \mu\text{m}$. A feature at $4.8 \mu\text{m}$ appears in the spectra of

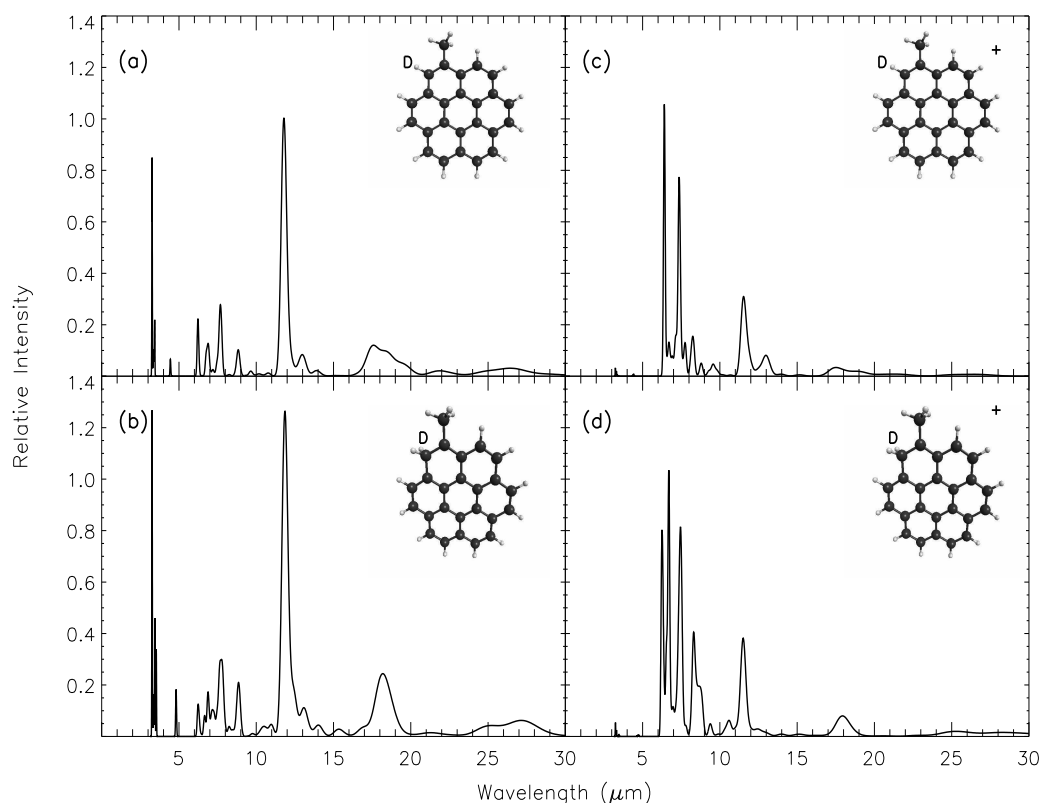


Figure 4.5: Theoretical spectra of (a) $C_{24}H_{10}D-CH_3$, (b) $C_{24}H_{11}D-CH_3$, (c) $C_{24}H_{10}D-CH_3^+$, (d) $C_{24}H_{11}D-CH_3^+$

$C_{24}H_{11}D-CH_3$ due to aliphatic $C-D_{\text{stretching}}$. Ionization of these molecules ($C_{24}H_{10}D-CH_3^+$, $C_{24}H_{11}D-CH_3^+$) considerably reduces the intensities of 3.3, 3.4, 4.4 and 4.8 μm features as shown in Figure 4.5 (c-d). See the Appendix for the positions and Int_{rel} of all the bands occurring in these molecules.

4.4 Astrophysical Implications

It is known that in case of PAHs with aliphatic components, the aromatic 3.3 μm is associated with an additional weak 3.5 μm feature that arises due to the aliphatic $C-H_{\text{stretching}}$. With increasing chain of aliphatic C-H units that are attached to the molecule, the 3.5 μm feature is slightly blueshifted to 3.4 μm with additional sub features appearing to form a

plateau. Also, the integrated intensity of the aliphatic C-H_{stretching} mode increases. For any possible detection of such molecules, these two bands should be observed together. The strength of the 3.5 μm is usually expected to be quite less compared to the 3.3 μm in the observed sources. This is because the aliphatic components if present in a PAH molecule can easily be destroyed compared to its aromatic units by strong UV radiation in the ISM. Joblin et al. [204] identified both 3.29 and 3.4 μm in the spectra of two reflection nebulae; NGC 1333 SVS3 and NGC 2023. The spatially resolved 3 μm spectroscopy at different positions of the reflection nebulae showed that at certain positions, the 3.4 μm band is too intense and the variation in the intensity ratios of 3.29 and 3.4 μm shows a correlation with the photochemical evolution of alkylated PAHs, particularly methylated PAHs [204]. More observations near 3 μm show a weak plateau consisting of minor features particularly at 3.4, 3.46, 3.51 and 3.56 μm near the comparatively stronger 3.3 μm region [194, 197, 201, 202]. Sloan et al. [205] obtained similar features near 3.4 μm in the *IRS* spectra of carbon star (HD 100764) which is proposed as ‘class C’ source according to the classification scheme of Peeters et al. [1]. ‘Class C’ sources are illuminated by comparatively UV-poor radiation fields which may allow the aliphatic side groups in PAHs to survive and hence the appearance of the 3.4 μm plateau is expected in these sources. If we further replace a H atom in the functional group with a D, another important feature near 4.6 μm along with 3.3 and 3.5 μm arises due to the aliphatic C-D_{stretching}. In our previous chapters, the observational detection of 4.65 μm has been discussed by Peeters et al. [5] and Onaka et al. [6]. The ionized forms of the sample molecules resemble the structures of protonated (HPAH⁺) and deuterated PAHs (DPAH⁺) which show very weak aliphatic 3.5 and 4.6 μm features. These features are analogous to the aromatic 3.3 and 4.4 μm features respectively. In chapters 2 and 3, we proposed that large size deuterated PAHs give a $[\text{D}/\text{H}]_{\text{sc}}$ ratio which agrees to the observational value of D/H given by Peeters et al. [5]. In this chapter, apart from DC₂₄H₁₂⁺ which is already studied previously, we consider deuteration (addition of D) and deuteration (addition of D⁺) in the functional groups, for example, -

Table 4.2: $[D/H]_{sc}$ ratios calculated for PADs/DPAH⁺

PADs/DPAH ⁺	$[D/H]_{sc}$
DC ₂₄ H ₁₂	1
C ₂₄ H ₁₁ -CH ₂ D	0.87
C ₂₄ H ₁₁ -CH ₂ -CH ₂ D	1.43
C ₂₄ H ₁₁ -CH=CHD	0.125
DC ₂₄ H ₁₂ ⁺	2.71
C ₂₄ H ₁₁ -CH ₂ D ⁺	1.87
C ₂₄ H ₁₁ -CH ₂ -CH ₂ D ⁺	2.28
C ₂₄ H ₁₁ -CH=CHD ⁺	2.75
C ₂₄ H ₁₀ D-CH ₃	0.625
C ₂₄ H ₁₀ D-CH ₃ ⁺	1.5
C ₂₄ H ₁₁ D-CH ₃	1
C ₂₄ H ₁₁ D-CH ₃ ⁺	1

CH₃, -CH₂-CH₃ and -CH=CH₂. All these molecules are partially aliphatic in nature and the observed 4.65 μm feature by *ISO* [5] is expected to be present in these molecules. We also consider molecules with deuterium at the aromatic site (for example: C₂₄H₁₀D-CH₃ and C₂₄H₁₀D-CH₃⁺) which are expected to show C-D_{stretching} at 4.4 μm . The $[D/H]_{sc}$ ratio calculated for these molecules are listed in Table 4.2. It is found that deuterated PAHs studied in this chapter show a larger value of $[D/H]_{sc}$ compared to observations. However, within the same molecule, $[D/H]_{sc}$ ratio decreases for -CH₂D⁺ and -CH₂-CH₂D⁺ functional groups. In chapter 3, we proposed that deuterated ovalene (DC₃₂H₁₄⁺) and deuterated circumcoronene (DC₅₄H₁₈⁺) give a $[D/H]_{sc}$ ratio close to that obtained from observations. If we consider functional groups of which D⁺ forms a part attached to large size molecules, it might show a smaller value of $[D/H]_{sc}$. Such molecules containing an aliphatic component might also be feasible in the ISM as these will be relatively stable against photo dissociation by UV radiation. The neutral forms, i.e., aliphatic deuterated PAHs give comparatively smaller value. Though, C₂₄H₁₁-CH=CHD gives the smallest $[D/H]_{sc}$ among the sample molecules, C₂₄H₁₁-CH=CHD behaves peculiarly unlike other deuterated PAHs and shows the aliphatic C-H_{stretching} and aliphatic C-D_{stretching} near the aromatic region. C₂₄H₁₀D-CH₃ also shows a comparatively smaller $[D/H]_{sc}$ ratio among the four molecules in which

D does not form part of the functional group and instead is attached to the aromatic/aliphatic site of the PAH molecule.

4.5 Conclusion

The vibrational spectra of PAH molecules with aliphatic components have been studied in this chapter. As expected, a distinct $3.5 \mu\text{m}$ appears due to aliphatic C-H_{stretching} close to the aromatic $3.3 \mu\text{m}$. This feature is important towards the detection of any possible aliphatic component present in a PAH molecule. With increasing number of aliphatic C-H bonds, more features at nearby positions arise which might explain the observed plateau near $3.4\text{-}3.5 \mu\text{m}$. Observations indeed showed the evidence of two emission features at 3.29 and $3.4 \mu\text{m}$ towards astronomical sources [204] and also reported the presence of a weak plateau near $3 \mu\text{m}$ region [194]. The interstellar deuterium (D) may replace H atom at the aliphatic site and form deuterated/deuteronated PAHs. Such molecules show a weak $4.6 \mu\text{m}$ due to aliphatic C-D_{stretching} and might be potential candidate carriers for the recently observed band at $4.6 \mu\text{m}$. However, the molecules studied in this chapter produce a $[\text{D}/\text{H}]_{\text{sc}}$ which is greater than the observed value of D/H towards astrophysical sources. Similar study can be performed for larger PAHs with aliphatic components and with D to determine the $[\text{D}/\text{H}]_{\text{sc}}$. On basis of this calculated value of $[\text{D}/\text{H}]_{\text{sc}}$, molecules can be chosen for further sophisticated laboratory experiments which is required in the identification of the UIR carriers.

