Chapter 2

The Interstellar Deuterated and Deuteronated PAHs I

2.1 Introduction

Lately, the advancement in telescopes and observational astronomy has helped the detection of UIR bands towards plenty of new sources in the ISM of our Galaxy and external galaxies. Space missions with sophisticated instrumentation, for e.g., *IRS* on board the *Spitzer*, *SWS* on board the *ISO*, *Infrared Camera (IRC)* on board the *AKARI*, *Wide-field Infrared Survey Explorer (WISE)*, etc., have obtained high quality mid infrared spectra of astrophysical sources that reveal evidences favouring the widespread presence of its carriers. Apart from the major UIR bands, several minor bands have also been detected. A few such bands are observed at 3.4 μm, 3.5 μm, 4.4 μm, 4.65 μm, 18.9 μm, 21 μm, etc. With increasing number of UIR band detections in different interstellar environments, the identification of its carriers is of utmost importance. Though the overall spectra of the UIR bands resemble that of a regular PAH molecule, profile variations observed in the bands, the detection of minor bands, etc., suggest the existence of a slightly altered PAH as well. Many a times, a functional group for example -CH$_3$, -OH, -C$\equiv$N in a PAH may also be responsible for the variation in the band position and band intensity.

Of all the substituted PAHs that have been studied so far to probe

the nature of UIR carriers, a major form is deuterated PAH (PAD) which is simply a PAH with one its peripheral H atoms being substituted by its isotope deuterium (D) without affecting the carbon skeleton. Like PAHs, PADs are also aromatic in nature. Another form of deuterated PAHs is the addition of D atoms to a PAH molecule such that at the sites of addition, the aromatic bond changes to aliphatic resulting in the formation of a D_n-PAH (where n may take values from 1 onwards depending on the number of C-H bonds). Recently, PADs and D_n-PAHs have been studied extensively both experimentally and theoretically in relation to the UIR bands [140, 149]. This is because PADs/D_n-PAHs show distinct features unlike other PAHs at 4.4 and 4.65 μm that have been observationally detected towards Orion Nebula and M17 by *ISO* [5]. Similar bands have also been observed by *AKARI* [6, 168], though with much weaker intensity. The *ISO* and *AKARI* observations of these features are shown in Figure 2.1 and 2.2 respectively. Both the telescopes observed the same sources, however due to small aperture size, *AKARI* covered only an overlapping region observed by *ISO*. These emission bands are characteristics of aromatic/aliphatic C-D stretching modes in PADs and D_n-PAH respectively [5]. The 4.4 and 4.65 μm bands provide a good prospect for observational searches for PADs/D_n-PAHs as they do not overlap with any other PAH features and are a pure C-D contribution [149].

The existence of PADs/D_n-PAHs in the ISM is justified by the Deuterium (D) detection in the ISM established by the higher Lyman lines seen in *Far Ultraviolet Spectroscopic Explorer (FUSE)* spectra [155]. Interstellar PAHs may become deuterium enriched by exchange of D from D_2O ice when exposed to UV radiation [169]. According to a 'Deuterium Depletion model', Interstellar PAHs are proposed to be a major reservoir for D which may explain the present D/H ratio in the ISM [15]. The interstellar D/H ratio has a primordial value $\sim$26 ppm [170, 171, 172, 173, 174] that has been reduced to the present value spanning from $\sim$7 ppm to $\sim$22 ppm from one sight line to another [175, 176, 174]. Linsky et al. [177] discussed a variation in D/H ratios along various lines of sight in the Milky Way and beyond. Usually such reduction is expected to result from astration; a process that con-
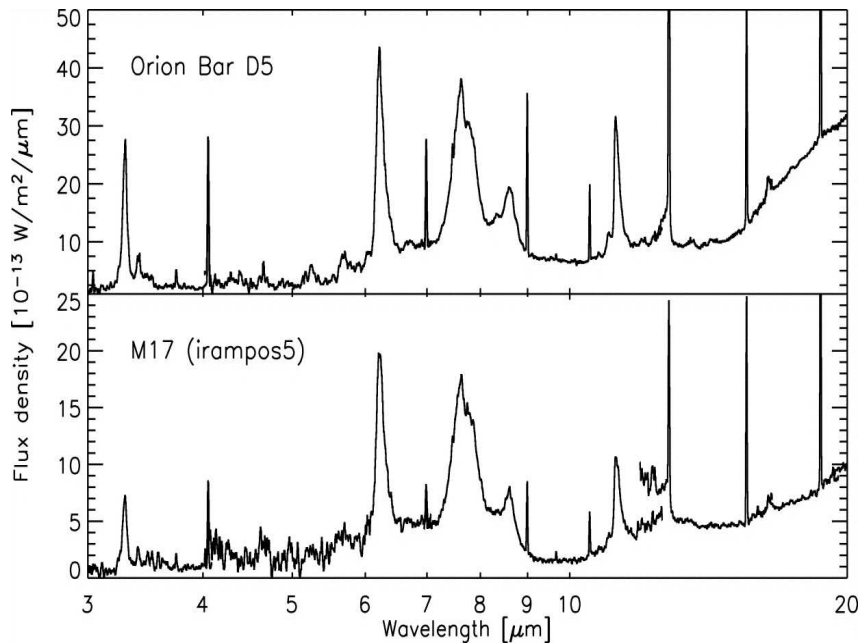
Figure 2.1: The 3-20 μm *ISO SWS* spectra of the Orion Bar and M17 (Figure 1, [5]). The figure has been reproduced after obtaining permission from Els Peeters.

verts lighter elements to heavier elements due to nuclear fusion reactions in stellar interiors. However, Draine [15] suggested that the lower value of the D/H ratio compared to the primordial value is not attributed to astration and instead is a result of depletion of D onto dust particles. Draine [15] further suggested that of all the interstellar dust grains incorporating deuterium, some may be in PAHs that may result in the formation of deuterated PAHs. According to the 'Deuterium depletion model', Draine [15] even proposed a D/H ratio of $\sim$0.3 in PAHs.

In the ISM, several chemical processes for example: ionization, recombination, dissociation, etc., occur simultaneously which result in the distortion of the PAH molecule and/or transformation into other forms. In similar ways, a deuterated PAH may also be altered into a slightly different form. One such form is deuteronated PAHs (DPAH$^+$)[1] which are studied and discussed by Buragohain et al. [156]. DPAH$^+$ molecules might be crucial in an astrophysical context because their closed-shell electronic structure makes them stable enough to survive the extreme inter-

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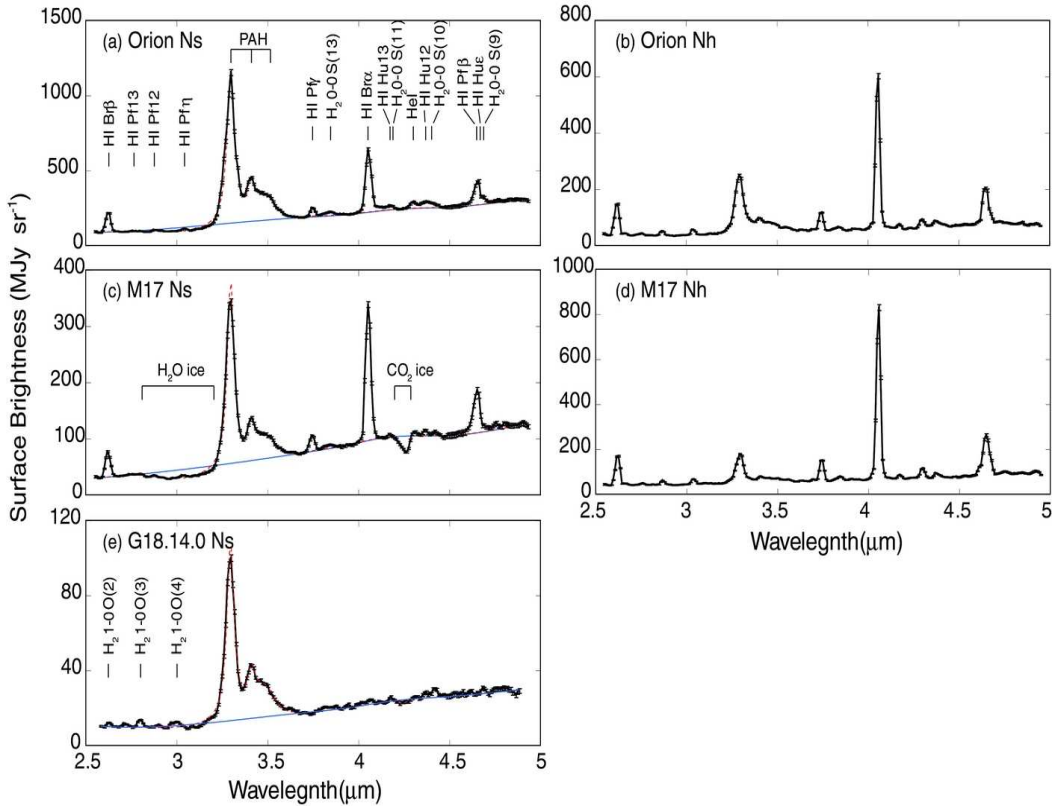[1]deuteronated PAHs are PAHs to which a deuteron is added - the equivalent of protonated PAHs for a proton.

Figure 2.2: The 2.5-5 μm *AKARI IRC* spectra of the (a)-(b) Orion Bar at two different slit positions, (c)-(d) M17 at two different slit positions, (e) G18.14.0 (Figure 2, [6]). The figure has been reproduced after obtaining permission from Takashi Onaka.

stellar environment. In this chapter, theoretical vibrational calculations of DPAH$^+$ as probable carriers of UIR bands are reported. A comparison is also made with the observed UIR features. The findings of this chapter are published in Buragohain et al. [156].

## 2.2 Probable DPAH$^+$ formation mechanisms in the ISM

Deuterium is considered to be one of the lightest elements formed after the Big Bang and in the chemical evolution of the Universe, it is converted to heavier elements by nuclear fusion inside stars. This explains the present lower value of D/H ($\sim$7ppm to $\sim$22 ppm); [175, 176, 174] compared to the primordial value ($\sim$26 ppm) [170, 171, 172, 173, 174].

However, Draine [15] argued that it is highly possible that some primordial deuterium is depleted in interstellar dust, particularly in PAHs that may result in the formation of PADs/D$_n$-PAH. These may be formed in the ISM by the following chemical processes:

i) gas-phase ion-molecule reactions in low temperature environments [178],

ii) gas-grain reactions [179, 180, 178],

iii) photodissociation of carbonaceous dust grains [181, 78] and

iv) exchange of deuterium in D$_2$O ice with one of the peripheral hydrogen atoms of an interstellar PAH when exposed to UV radiation [182].

The abundance of D in the ISM indicates the possible formation of another deuterium containing PAH molecule, DPAH$^+$. Formation of DPAH$^+$ molecules may result from a number of interstellar processes. These include:

(i) Addition of D to PAH radical cations:

$$PAH^+ + D \rightarrow DPAH^+$$
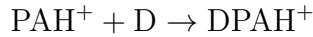
Le Page et al. [106], Snow et al. [107] and Le Page et al. [183] discussed the reaction of PAH cations with atomic and molecular hydrogen to form protonated PAHs (HPAH$^+$) that might emerge as a potential carriers of DIBs [105]. Larger PAH cations tend to associate efficiently with atomic H to form HPAH$^+$ in interstellar environments [184]. In a similar way, deuterium atoms may also react with PAH cations to form deuteronated PAHs.

(ii) Addition of D$^+$, produced by direct ionization and charge-transfer reaction, to a neutral PAH to form DPAH$^+$:

$$H^+ + D \rightleftharpoons D^+ + H \ (charge-transfer \ reaction)$$

$$D^+ + PAH \rightarrow DPAH^+ + h\nu$$
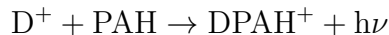
(iii) Low temperature ion-molecule reaction followed by deuterium fractionation: at temperatures below 50 K, deuterium fractionation is significant [39]. Interstellar deuterium mostly exists in the form of HD. Fractionation of HD by exchange reaction with H$_3^+$ occurs efficiently in low
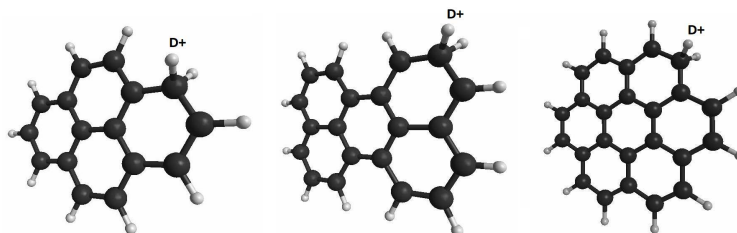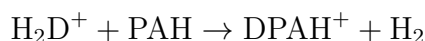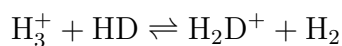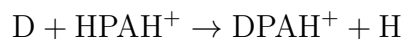
Figure 2.3: Sample molecules studied

temperature dense interstellar clouds, to form deuterated molecular ions H_2D^+ [39]. H_2D^+ has a low deuteron affinity [185] and can transfer D^+ to PAH to form $DPAH^+$.

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2$$

$$H_2D^+ + PAH \rightarrow DPAH^+ + H_2$$

(iv) D may merely replace the hydrogen at the protonation site in $HPAH^+$ without altering the network to form $DPAH^+$

$$D + HPAH^+ \rightarrow DPAH^+ + H$$

Due to the higher mass of deuterium in $DPAH^+$, such interstellar species are expected to give spectral modes (associated with D) towards longer wavelengths compared to their neutral or protonated counterparts.

2.3   Molecules studied

In this chapter, three deuteronated PAHs; deuteronated pyrene ($DC_{16}H_{10}^+$), deuteronated perylene ($DC_{20}H_{12}^+$) and deuteronated coronene ($DC_{24}H_{12}^+$) along with their isomers are studied. The figures of the sample molecules are shown in Figure 2.3. DFT with B3LYP/6-311G** is used to calculate the harmonic frequencies and intensities of vibrational modes of PAHs. Scaling factors are used to reduce the overestimated computed frequencies as described in the Chapter 1. In case of deuterium-containing PAHs,

since we do not have laboratory data for aliphatic deuterium-containing PAHs, a scaling factor of 0.965 corresponding to C-H stretching is used for C-D stretching. The shift in frequencies of aliphatic bonds needs experimental support and may have some uncertainty. The scaled frequencies and relative intensities are used to generate the infrared spectra of sample PAHs with Gaussian line shapes of FWHM 30 cm^{-1}. The data presented here were produced using GAMESS quantum chemistry suite of programs [13]. See Appendix A for tables (frequency and relative intensity) which are not included in the main context.

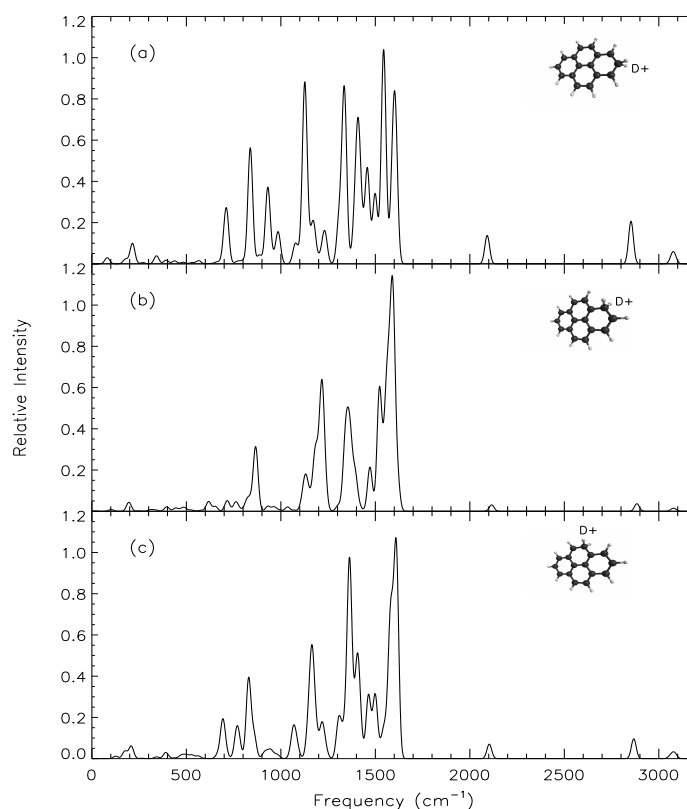## 2.4 Results and Discussion

2.4.1 Deuteronated pyrene

Figure 2.4: Theoretical spectra of (a) $DC_{16}H_{10}^{+}$, (b) Isomer 1 of $DC_{16}H_{10}^{+}$, (c) Isomer 2 of $DC_{16}H_{10}^{+}$

Figure 2.4 shows the theoretical spectra of deuteronated pyrene

($DC_{16}H_{10}^+$) and its isomers. Each isomer shows a unique spectrum. Deuteronated pyrene with C_{2v} symmetry (Figure 2.4a) shows pronounced transitions particularly in the 825-1600 cm^{-1} (12.12-6.25 μm) range compared to its isomers with C_s symmetry (Figure 2.4b and Figure 2.4c). Most of the bands are characteristic of C-H out-of-plane (oop), C-H in-plane, C-C stretching and C-H stretching modes. However, some new features arise due to the contribution of deuterium. These include C-D in-plane, H-C-D oop and C-D stretching particularly. The C-D in-plane modes are distributed in the $\sim 700 - 870$ cm^{-1} (14-11 μm) range with varying relative intensities (Int$_{rel}$[2]) between 0.05 to 0.4. This is the same region where C-H oop occurs in unsubstituted PAHs. The H-C-D oop modes are relatively strong and present in the narrow range of 1125-1185 cm^{-1} (8.4-8.9 μm). The C-D in-plane and H-C-D oop modes are found to be blended with other fundamental modes. An aliphatic C-D stretching mode of noticeable intensity appears at 2092 cm^{-1} (4.78 μm) in Figure 2.4a. Similar but faint feature appears for the other two isomers at 2116 cm^{-1} (4.73 μm) and 2103 cm^{-1} (4.76 μm) (Figure 2.4b and Figure 2.4c respectively). Absolute intensities for the C-D stretching modes are 18.128 km/mole, 8.132 km/mole and 11.682 km/mole respectively for the three isomers.

The C-D stretching mode at 4.78 μm does not overlap with any other PAH vibration mode and appears as a new feature. There is also an aliphatic C-H bond in deuteronated pyrene at the addition site of deuteron. A spectral band near ~ 2850 cm^{-1} (3.5 μm) is attributed to aliphatic C-H stretching, while those near ~ 3060 cm^{-1} (3.3 μm) are due to aromatic C-H stretching. The characteristic modes including the D-associated modes for deuteronated pyrene and its isomers are presented in Table 2.1, Table 2.2 and Table 2.3 respectively. Int$_{rel}$ above 0.05 are listed.

DFT calculations have been carried out on neutral pyrene, cationic pyrene, deuterated pyrene and protonated pyrene to compare the spectra with deuteronated pyrene. Figure 2.5 shows comparison of these spectra with that of deuteronated pyrene. Deuteronated pyrene is transitionally

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[2]Int$_{rel}$=$\dfrac{\text{absolute intensity}}{\text{maximum absolute intensity}}$
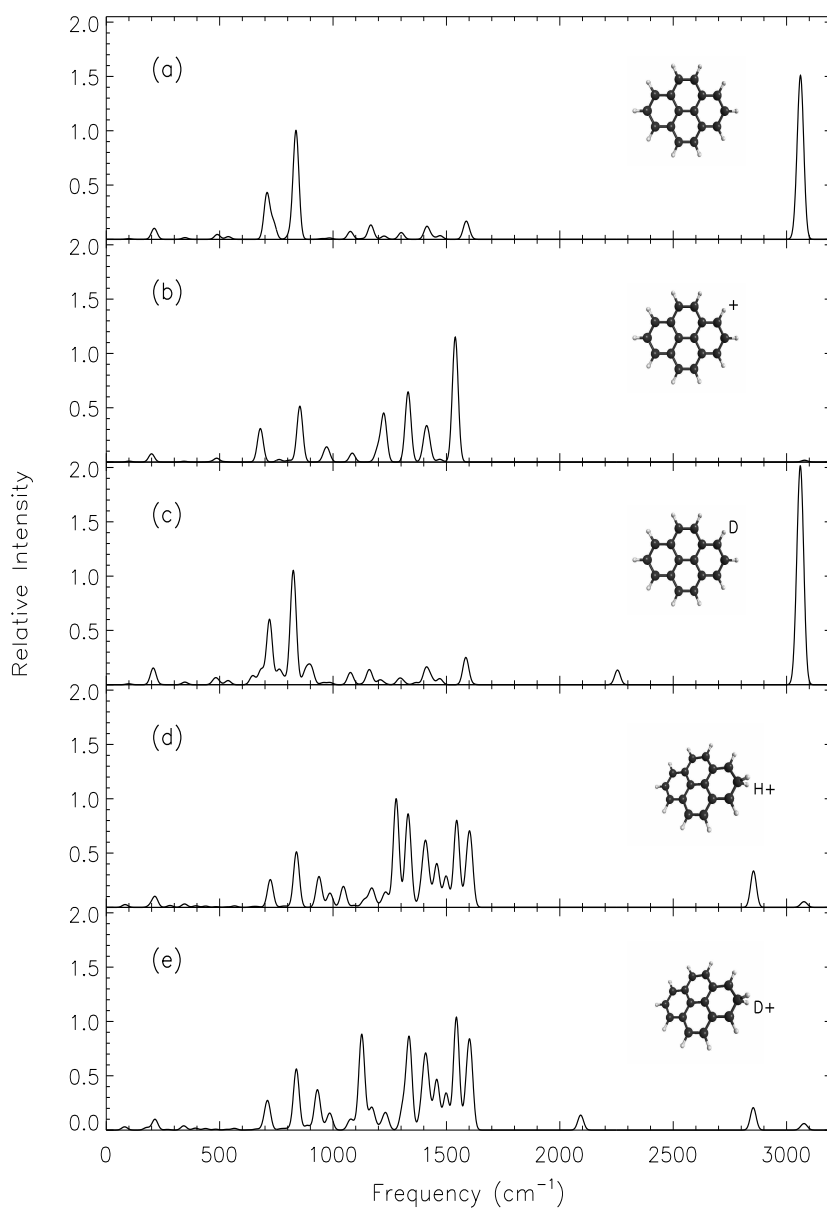
Figure 2.5: Theoretical spectra of (a) Neutral pyrene, (b) Pyrene cation, (c) Deuterated pyrene, (d) Protonated pyrene and (e) Deuteronated Pyrene

Table 2.1: Theoretical spectral data for Deuteronated pyrene

DPAH$^+$	Frequency (cm^{-1})	Wavelength (μm)	Relative Intensity	Mode
	700	14.29	0.05	C-D in plane + C-C-C in plane
	712	14.04	0.24	C-H oop
	838	11.93	0.56	C-H oop
	928	10.77	0.2	C-H oop
	934	10.71	0.18	C-H oop
	985	10.15	0.15	C-C-C in plane
	1076	9.30	0.08	C-H in plane
	1126	8.87	0.86	H-C-D oop + C-H in plane
	1173	8.53	0.18	C-H in plane
	1235	8.10	0.1	C-H in plane + C-C stretching
	1308	7.65	0.2	C-C stretching
Deuteronated	1330	7.52	0.07	C-H in plane + C-C stretching
Pyrene	1336	7.48	0.78	C-C stretching
	1389	7.2	0.15	C-H in plane + C-C stretching
	1408	7.1	0.54	C-C stretching
	1410	7.09	0.05	C-H in plane + C-C stretching
	1425	7.02	0.16	C-H in plane + C-C stretching
	1457	6.86	0.46	C-H in plane + C-C stretching
	1499	6.67	0.34	C-H in plane + C-C stretching
	1544	6.48	1	C-H in plane + C-C stretching
	1591	6.29	0.28	C-C stretching
	1605	6.23	0.66	C-C stretching
	2092	4.78	0.14	C-D stretching
	2853	3.51	0.21	C-H stretching (aliphatic)

active in the $\sim 900 - 1600$ cm^{-1} (11-6 μm) range (Figure 2.5e). This is reasonably similar to protonated pyrene with a variation in intensity (Figure 2.5d). Compared to protonated pyrene, the intensities of the C-H in plane and C-C stretching modes for deuteronated pyrene are increased by a factor of $\sim$1.2. Deuteronated pyrene being structurally similar to protonated pyrene shares similar vibrational modes. However, due to the larger mass of deuterium, all D-associated modes in deuteronated pyrene are red-shifted compared to the protonated form; the H-C-D oop mode shifts from 1278 cm^{-1} (7.82 μm) to 1126 cm^{-1} (8.87 μm) compared to its protonated counterpart. This particular mode at 8.87 μm is distinct (Figure 2.5e) and does not appear in any other form of pyrene. Another striking difference is the presence of a mode at 2092 cm^{-1} (4.78 μm) (Figure 2.5e) in deuteronated pyrene which is assigned to C-D stretching. On comparing with its protonated counterpart, it seems that the Int$_{rel}$ 0.3 of the H $-$ C $-$ H symmetric stretching mode at 2854 cm^{-1} (3.5 μm)

Table 2.2: Theoretical spectral data for Deuteronated pyrene isomer 1

DPAH$^+$	Frequency (cm^{-1})	Wavelength (μm)	Relative Intensity	Mode
	866	11.54	0.31	H-C-D in plane + C-H oop
	1115	8.97	0.05	C-H in plane + C-C-C in plane
	1131	8.84	0.14	C-H in plane
	1149	8.71	0.05	C-H in plane
	1176	8.5	0.1	H-C-D oop + C-H in plane
	1185	8.44	0.19	H-C-D oop + C-H in plane
	1213	8.24	0.22	C-H in plane + C-C stretching
Deuteronated	1218	8.21	0.37	C-H in plane + C-C stretching
Pyrene	1233	8.11	0.11	C-H in plane + C-C stretching
(isomer1)	1336	7.49	0.13	C-H in plane + C-C stretching
	1347	7.42	0.29	C-C stretching
	1366	7.32	0.33	C-C stretching
	1392	7.18	0.16	C-C stretching
	1471	6.8	0.21	C-C stretching
	1522	6.57	0.59	C-C stretching
	1554	6.44	0.33	C-C stretching
	1569	6.37	0.47	C-C stretching
	1592	6.28	1	C-C stretching
	1616	6.19	0.16	C-C stretching

in protonated pyrene is divided between the C-D stretching mode (Int$_{rel}$ 0.14) at 2092 cm^{-1} (4.78 μm) and the aliphatic C-H stretching mode (Int$_{rel}$ 0.21) at 2853 cm^{-1} (3.5 μm) for deuteronated pyrene. Cationic pyrene also shows significant transitions in the 900-1600 cm^{-1} (11-6 μm) region (Figure 2.5b), but there are fewer modes compared to protonated and deuteronated pyrene. This may be due to reduction in the symmetry for deuteronated pyrene. Neutral pyrene and deuterated pyrene show weak features in this region and the C-H stretching mode at 3050 cm^{-1} (3.3 μm) dominates with high intensity (Figure 2.5a and Figure 2.5c). For cationic, protonated and deuteronated pyrene, there are weak bands in the 3.3 μm region. As for deuteronated pyrene, the C-D stretching mode also exists for deuterated pyrene (Figure 2.5c), but is shifted to shorter wavelength and appears at 2254 cm^{-1} (4.44 μm).

2.4.2 Deuteronated perylene

Deuteronated perylene ($DC_{20}H_{12}^+$) has three isomers and the spectra are presented in Figure 2.6. All the isomers have C$_s$ symmetry and contain

Table 2.3: Theoretical spectral data for Deuteronated pyrene isomer 2

DPAH$^+$	Frequency (cm^{-1})	Wavelength (μm)	Relative Intensity	Mode
	692	14.45	0.16	C-H oop
	764	13.08	0.08	C-D in plane + C-C-C in plane + C-H oop
	829	12.06	0.39	C-D in plane +C-H oop
	858	11.65	0.11	C-D in plane + C-H oop
	1067	9.37	0.13	C-H in plane
	1083	9.23	0.05	C-H in plane
	1145	8.74	0.12	C-H in plane
	1163	8.6	0.4	H-C-D oop + C-H in plane
	1171	8.54	0.1	H-C-D oop + C-H in plane
	1187	8.43	0.1	C-H in plane
	1217	8.22	0.11	C-H in plane
Deuteronated	1219	8.21	0.05	C-H in plane + C-C stretching
Pyrene	1305	7.66	0.16	C-H in plane + C-C stretching
(isomer2)	1320	7.58	0.08	C-H in plane + C-C stretching
	1341	7.46	0.12	C-H in plane + C-C stretching
	1363	7.33	0.94	C-H in plane + C-C stretching
	1389	7.2	0.09	C-H in plane + C-C stretching
	1407	7.11	0.43	C-H in plane + C-C stretching
	1424	7.02	0.07	C-H in plane + C-C stretching
	1464	6.83	0.31	C-H in plane + C-C stretching
	1499	6.67	0.31	C-C stretching
	1533	6.52	0.05	C-C stretching
	1550	6.45	0.12	C-C stretching
	1578	6.34	0.48	C-C stretching
	1587	6.3	0.25	C-C stretching
	1611	6.21	1	C-C stretching
	2103	4.76	0.07	C-D stretching
	2867	3.49	0.1	C-H stretching (aliphatic)

D-contributing features along with the other usual PAH bands. C-D in-plane features are present between $730-870$ cm^{-1} (13.7-11.5 μm) and H-C-D oop in the $1120-1212$ cm^{-1} (8.9-8.3 μm) range. The C-D stretching mode appears at 2087 cm^{-1} (4.79 μm) (Figure 2.6a) and is not distinct in the other two isomers (Figure 2.6b & Figure 2.6c). Absolute intensities for the C-D stretching mode for the three isomers of deuteronated perylene are 14.073 km/mole, 5.004 km/mole and 4.582 km/mole respectively. Bands near ~ 2850 cm^{-1} (3.5 μm) and ~ 3060 cm^{-1} (3.3 μm) account for aliphatic C-H stretching and aromatic C-H stretching of deuteronated perylene, respectively. Spectral data for significant modes including D-contributing modes with relative intensities above 0.05 are presented in Table 2.4, Table 2.5 and Table 2.6 respectively.

A comparison of the theoretical spectrum of deuteronated perylene with its neutral, cation, deuterated and protonated forms is shown in
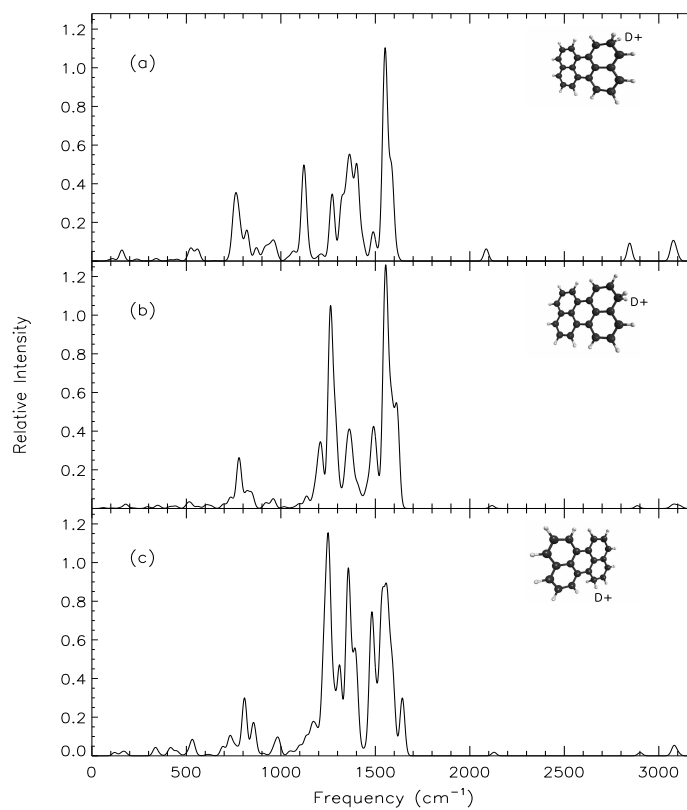
Figure 2.6: Theoretical spectra of (a) $DC_{20}H_{12}^+$, (b) Isomer 1 of $DC_{20}H_{12}^+$, (c) Isomer 2 of $DC_{20}H_{12}^+$

Figure 2.7. Deuteronated and protonated perylene participate in similar types of vibrational modes with increasing number of transitions in the $900 - 1600$ cm^{-1} (11-6 μm) range compared to their neutral counterparts (perylene and deuterated perylene). Despite the fact that most of the modes are similar in this region, they do vary in intensity. However, variation in intensity is not uniform. Protonated and deuteronated perylene show maximum intensity for C-C stretch vibration close to 1550 cm^{-1} (6.45 μm) (Figure 2.7d & Figure 2.7e). For deuterated perylene, H-C-D oop occurs at 1120 cm^{-1} (8.93 μm) and 1130 cm^{-1} (8.85 μm) mixing with the C-H in plane modes (Figure 2.7e). Other forms of perylene do not show any significant intensity modes near this wavenumber. Deuterated and deuteronated perylene show new features at 2291 cm^{-1} (4.36 μm) and 2087 cm^{-1} (4.79 μm), respectively (Figure 2.7c & Figure 2.7e). These two transitions arise due to aromatic (deuterated pery-
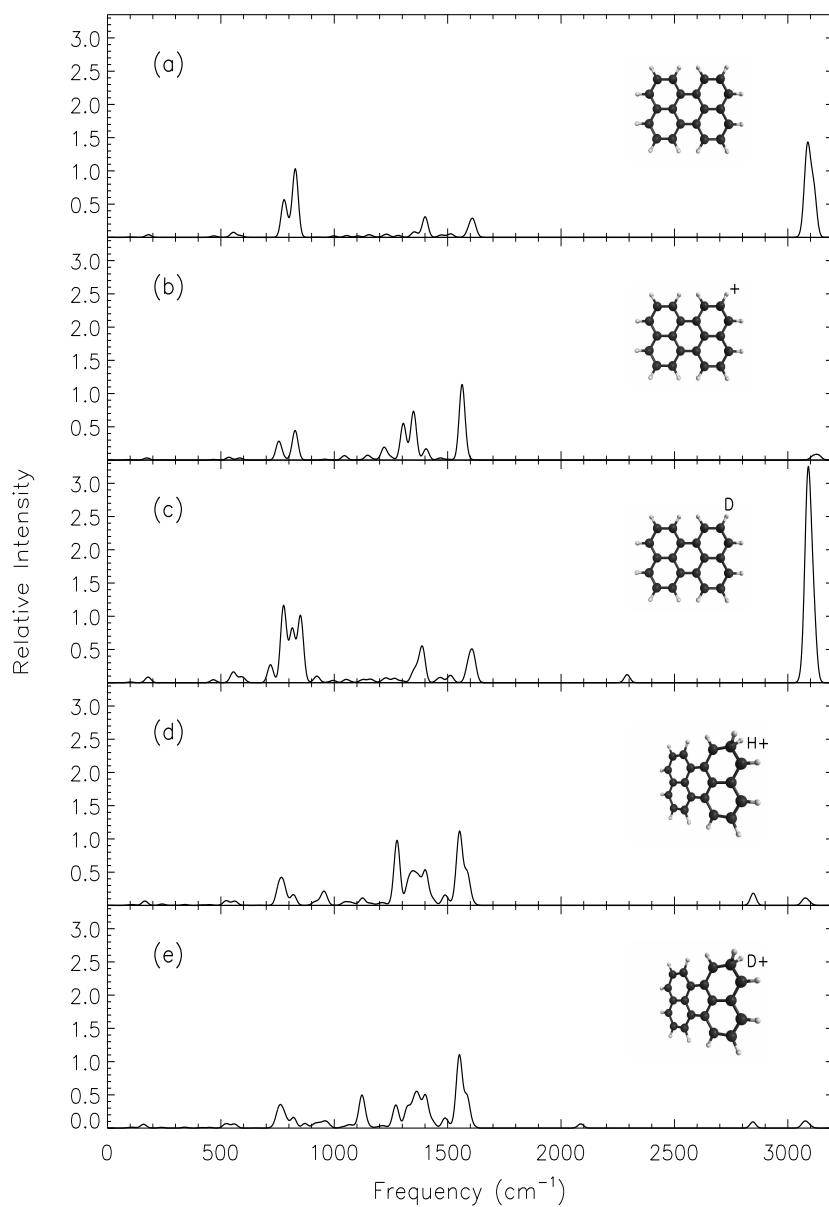
Figure 2.7: Theoretical spectra of (a) Neutral perylene, (b) Perylene cation, (c) Deuterated perylene, (d) Protonated perylene and (e) Deuteronated Perylene

Table 2.4: Theoretical spectral data for Deuteronated perylene

DPAH$^+$	Frequency (cm^{-1})	Wavelength (μm)	Relative Intensity	Mode
	747	13.39	0.05	C-C-C in plane
	755	13.25	0.18	C-D in plane + C-H oop
	770	12.98	0.18	H-C-D in plane + C-H oop
	786	12.73	0.06	H-C-D in plane + C-H oop
	821	12.18	0.16	C-H oop
	870	11.49	0.07	H-C-D in plane + C-H oop
	937	10.67	0.05	C-H oop
	958	10.44	0.08	C-C stretching
	1120	8.93	0.39	H-C-D oop + C-H in plane
	1130	8.85	0.12	H-C-D oop + C-H in plane
	1264	7.91	0.12	C-H in plane + C-C stretching
	1275	7.85	0.25	C-H in plane + C-C stretching
Deuteronated	1321	7.57	0.27	C-H in plane + C-C stretching
Perylene	1344	7.44	0.13	C-H in plane + C-C stretching
	1350	7.41	0.06	C-C stretching
	1358	7.36	0.25	C-H in plane + C-C stretching
	1373	7.28	0.32	C-H in plane + C-C stretching
	1402	7.13	0.46	C-H in plane + C-C stretching
	1422	7.03	0.05	C-H in plane + C-C stretching
	1435	6.97	0.07	C-H in plane + C-C stretching
	1487	6.72	0.14	C-H in plane + C-C stretching
	1552	6.44	1	C-C stretching
	1576	6.35	0.06	C-C stretching
	1585	6.31	0.21	C-C stretching
	1588	6.30	0.2	C-C stretching
	1588	6.30	0.2	C-C stretching
	2087	4.79	0.06	C-D stretching
	2846	3.51	0.09	C-H stretching (aliphatic)

lene) and aliphatic (deuteronated perylene) C-D stretching respectively. All forms of perylene show bands near 3050 cm^{-1} (3.3 μm) with varying intensities which is attributed to aromatic C-H stretching. Neutral forms of perylene (perylene and deuterated perylene) show strong intensities at this wavenumber, while cationic, protonated and deuteronated perylene have weak features in this region. The presence of an aliphatic C-H bond in protonated and deuteronated perylene produces features at 2848 cm^{-1} (3.5 μm) and 2846 cm^{-1} (3.5 μm) due to stretching of the C-H bond. It is remarked that the intensity of aliphatic $H-C-H$ stretching mode (0.15) in protonated perylene is distributed among intensities of aliphatic C-D stretching (0.06) and aliphatic C-H stretching (0.09) in deuteronated perylene.

Table 2.5: Theoretical spectral data for Deuteronated perylene isomer 1

DPAH$^+$	Frequency (cm^{-1})	Wavelength (μm)	Relative Intensity	Mode
	732	13.66	0.05	C-H oop
	778	12.86	0.23	C-D in plane + C-H oop
	819	12.20	0.08	C-H oop
	846	11.82	0.07	C-D in plane + C-H oop + C-C-C in plane
	958	10.44	0.05	C-C-C in plane
	1135	8.81	0.05	C-H in plane
	1175	8.51	0.06	C-H in plane
	1197	8.35	0.1	H-C-D oop + C-H in plane
	1212	8.25	0.22	H-C-D oop + C-H in plane
	1219	8.21	0.05	C-H in plane + C-C stretching
	1262	7.92	1	C-H in plane + C-C stretching
Deuteronated	1289	7.76	0.4	C-C stretching
Perylene	1311	7.63	0.05	C-H in plane + C-C stretching
isomer1	1346	7.43	0.16	C-H in plane + C-C stretching
	1358	7.36	0.1	C-H in plane + C-C stretching
	1363	7.34	0.14	C-H in plane + C-C stretching
	1377	7.26	0.19	C-H in plane + C-C stretching
	1403	7.13	0.1	C-H in plane + C-C stretching
	1459	6.85	0.1	C-H in plane + C-C stretching
	1486	6.73	0.33	C-H in plane + C-C stretching
	1504	6.65	0.21	C-C stretching
	1547	6.46	0.53	C-C stretching
	1558	6.42	0.71	C-C stretching
	1562	6.4	0.1	C-C stretching
	1585	6.31	0.44	C-C stretching
	1596	6.27	0.07	C-C stretching
	1615	6.19	0.49	C-C stretching

2.4.3 Deuteronated coronene

Coronene has only one unique site of deuteronation. Figure 2.8e shows the theoretically predicted spectrum for deuteronated coronene. The C-D in-plane modes are distributed in the $823 - 871$ cm^{-1} ($12.15 - 11.5$ μm) region, the H-C-D oop mode is present at 1181 cm^{-1} (8.47 μm) and a weak C-D stretching mode appears at 2110 cm^{-1} (4.74 μm). Absolute intensity and Int$_{rel}$ for the C-D stretching mode are 7.328 km/mole and 0.04 respectively. The spectral data above Int$_{rel}$ 0.05 are listed in Table 2.7.

Figure 2.8 also shows the comparison of deuteronated coronene with its neutral, cation, deuterated and protonated forms. For deuteronated and protonated coronene, spectral modes in $\sim 1352 - 1612$ cm^{-1} ($7.4 - 6.2$ μm) region follow a similar pattern with variation in intensity. Intensities for deuteronated coronene are increased by an average factor of ~ 1.4 com-
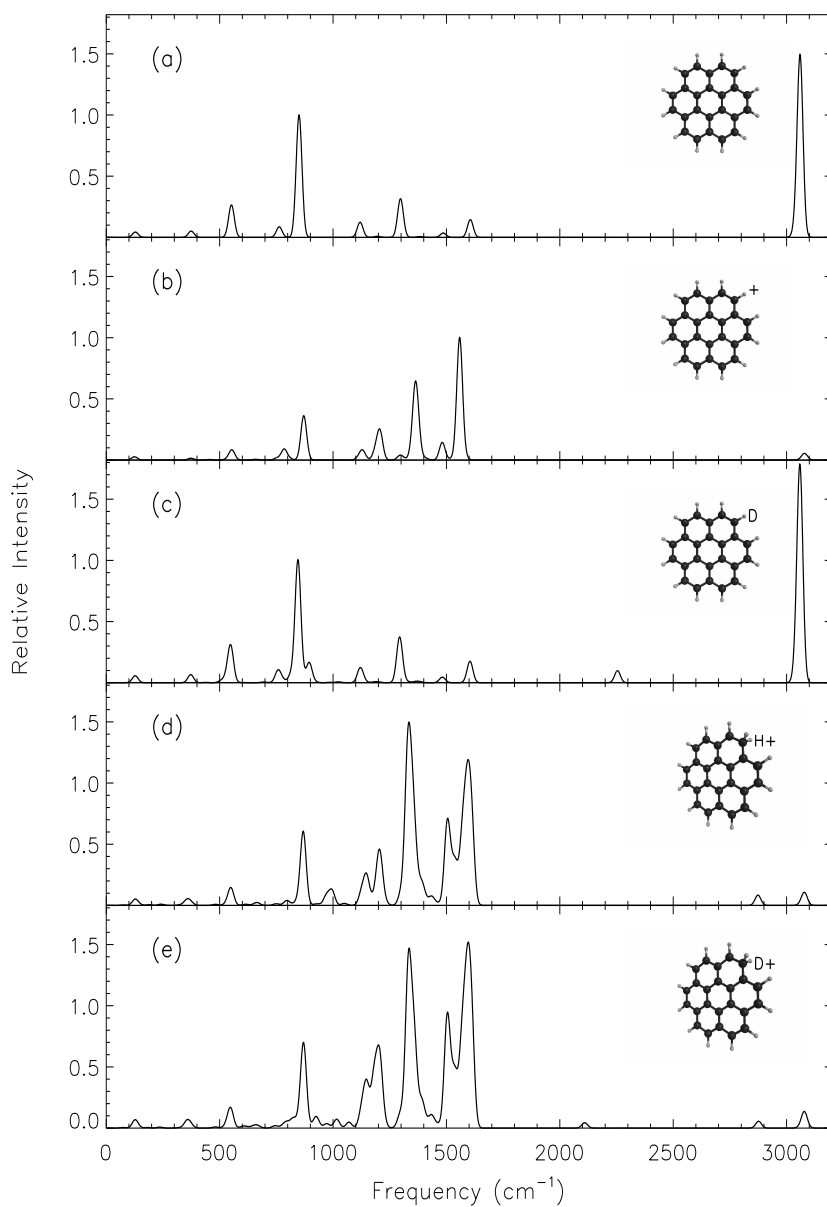
Figure 2.8: Theoretical spectra of (a) Neutral coronene, (b) Coronene cation, (c) Deuterated coronene, (d) Protonated coronene and (e) Deuteronated coronene

Table 2.6: Theoretical spectral data for Deuteronated perylene isomer 2

DPAH$^+$	Frequency (cm^{-1})	Wavelength (μm)	Relative Intensity	Mode
	693	14.44	0.05	C-H oop
	730	13.7	0.1	C-D in plane + C-H oop
	807	12.39	0.28	C-H oop
	853	11.73	0.13	C-D in plane + C-H oop + C-C-C in plane
	863	11.59	0.05	C-D in plane + C-H oop + C-C-C in plane
	986	10.15	0.06	C-H oop
	1131	8.84	0.07	C-H in plane
	1165	8.59	0.13	C-H in plane
	1188	8.42	0.08	C-H in plane
	1221	8.19	0.07	C-H in plane + C-C stretching
	1231	8.12	0.45	C-H in plane
	1252	7.99	1	C-H in plane + C-C stretching
Deuteronated	1280	7.81	0.28	C-H in plane + C-C stretching
Perylene	1311	7.63	0.45	C-H in plane + C-C stretching
isomer2	1350	7.41	0.21	C-C stretching
	1358	7.37	0.71	C-H in plane + C-C stretching
	1368	7.31	0.07	C-H in plane + C-C stretching
	1384	7.22	0.14	C-H in plane + C-C stretching
	1396	7.17	0.4	C-H in plane + C-C stretching
	1410	7.09	0.06	C-H in plane + C-C stretching
	1480	6.76	0.69	C-H in plane + C-C stretching
	1504	6.65	0.24	C-C stretching
	1534	6.52	0.73	C-C stretching
	1560	6.41	0.06	C-C stretching
	1561	6.41	0.67	C-C stretching
	1584	6.31	0.33	C-C stretching
	1597	6.26	0.18	C-C stretching
	1643	6.09	0.3	C-C stretching

pared to its protonated form in this region. The maximum intensity for both appears nearly at same position at 1330 cm^{-1} (7.52 μm), but the corresponding modes are different. For deuteronated coronene, the peak intensity arises due to the combination of C-H in-plane and C-C stretch modes, whereas, for protonated coronene, it is due to the combination of $H - C - H$ oop and C-C stretch modes. The H-C-D oop mode is prominent at 1181 cm^{-1} (8.47 μm) for deuteronated coronene (Figure 2.8e). The C-D stretching vibrational mode for deuterated and deuteronated coronene appear near a featureless region at 2254 cm^{-1} (4.44 μm) and 2110 cm^{-1} (4.74 μm) respectively (Figure 2.8c & Figure 2.8e). These two modes are weak in intensity. Cationic coronene (Figure 2.8b) shows a greater number of transitions in the C-H in plane and C-C stretching region (900-1600 cm^{-1}) compared to its neutral forms (coronene and deuterated coronene, Figure 2.8a and Figure 2.8c respectively). Protonation and deuteronation further increases the number of transitions in this

Table 2.7: Theoretical spectral data for Deuteronated coronene

DPAH$^+$	Frequency (cm^{-1})	Wavelength (μm)	Relative Intensity	Mode
	823	12.15	0.07	C-D in plane + C-H oop
	863	11.59	0.15	C-D in plane + C-H oop
	871	11.48	0.6	C-D in plane + C-H oop
	927	10.79	0.08	C-H oop
	1016	9.84	0.07	C-H in plane
	1070	9.35	0.05	C-H in plane
	1125	8.89	0.11	C-H in plane
	1143	8.75	0.06	C-H in plane
	1147	8.72	0.07	C-H in plane
	1150	8.7	0.21	C-H in plane
	1181	8.47	0.34	H-C-D oop + C-H in plane
	1194	8.37	0.09	C-H in plane
	1204	8.31	0.31	C-H in plane + C-C stretching
	1208	8.28	0.18	C-H in plane + C-C stretching
Deuteronated	1216	8.22	0.05	C-H in plane + C-C stretching
Coronene	1293	7.73	0.06	C-H in plane + C-C stretching
	1304	7.67	0.07	C-H in plane + C-C stretching
	1331	7.51	1	C-H in plane + C-C stretching
	1334	7.49	0.3	C-H in plane + C-C stretching
	1352	7.4	0.4	C-H in plane + C-C stretching
	1361	7.35	0.4	C-H in plane + C-C stretching
	1383	7.23	0.07	C-H in plane + C-C stretching
	1392	7.18	0.11	C-H in plane + C-C stretching
	1398	7.15	0.06	C-H in plane + C-C stretching
	1435	6.97	0.06	C-H in plane + C-C stretching
	1499	6.67	0.08	C-H in plane + C-C stretching
	1503	6.65	0.8	C-C stretching
	1520	6.58	0.2	C-C stretching
	1539	6.5	0.4	C-C stretching
	1569	6.38	0.6	C-C stretching
	1585	6.31	0.44	C-C stretching
	1594	6.27	0.6	C-C stretching
	1600	6.25	0.24	C-C stretching
	1611	6.21	0.7	C-C stretching
	2876	3.48	0.06	C-H stretching (aliphatic)

region (Figure 2.8d and Figure 2.8e respectively). Cationic, protonated and deuteronated forms of coronene show faint features at 3050 cm^{-1} (3.3 μm) unlike the neutral counterparts.

From the data presented in Table 2.1-2.7, it is deduced that the C-D in-plane and H-C-D oop modes overlap the regions corresponding to C-H oop and C-H in-plane modes, respectively. The C-D stretching modes do not overlap with any other mode and are identified easily. For all three molecules along with their isomers (discussed above), C-D in plane modes are found to be distributed in the range $\sim 700 - 870$ cm^{-1} ($14 - 11$ μm) with a range of intensities. The H-C-D oop modes appear in the narrow range $\sim 1120 - 1212$ cm^{-1} ($8.9 - 8.3$ μm). A less intense feature is seen at
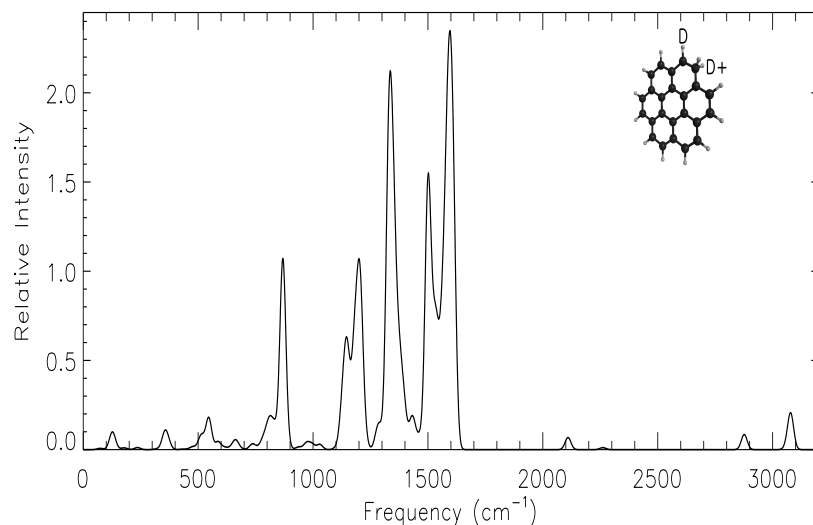
Figure 2.9: Theoretical spectrum of deuterated-deuteronated coronene (DcorD$^+$)

$\sim$ 2105 cm^{-1} (4.75 μm) which arises due to the C-D stretching mode of DPAH$^+$. Symmetrical deuteronated pyrene (C$_{2v}$) shows a greater number of transitions compared to deuteronated perylene (C$_s$) and deuteronated coronene (C$_s$).

2.4.4 Theoretical spectra for deuterated-deuteronated coronene and deuteronated circumcoronene

Figure 2.9 shows the calculated spectrum of deuterated-deuteronated coronene (DcorD$^+$). In DcorD$^+$, a deuterium atom replaces a hydrogen atom to form a C-D bond and a deuteron (D$^+$) is added to a C-H site of the neutral coronene (C$_{24}$H$_{12}$). The resulting DcorD$^+$ molecule thus carries two types of C-D bond, 'aromatic' at the addition site of D and aliphatic at the addition site of D$^+$. The spectrum is very similar to that of deuteronated coronene except for a variation in intensity in the $\sim$ 1318 $-$ 1570 cm^{-1} (7.6 $-$ 6.4 μm) region. There are weak bands at 2110 cm^{-1} (4.7 μm), 2261 cm^{-1} (4.4 μm) and 2876 cm^{-1} (3.5 μm) with Int$_{rel}$ of 0.07, 0.01 and 0.08 respectively. Absolute intensities for these particular bands are 7.4811 km/mole, 1.2101 km/mole and 9.3345 km/mole respectively. The 4.4 μm feature is barely visible in the spec-
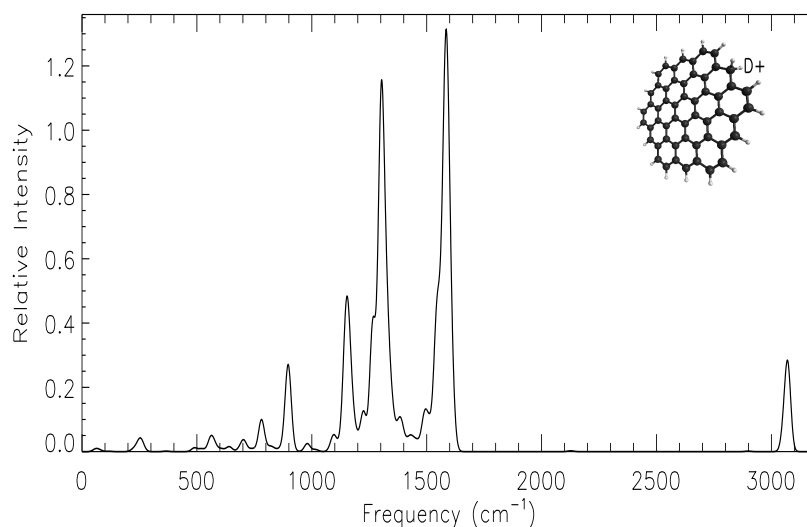
Figure 2.10: Theoretical spectrum of deuteronated circumcoronene

trum. As discussed earlier, these transitions are characteristic of aliphatic C-D stretching, aromatic C-D stretching and aliphatic C-H stretching, respectively.

DFT calculations were also performed on a large-sized DPAH$^+$, i.e. deuteronated circumcoronene (DC$_{54}$H$_{18}^+$), to investigate the effect of PAH size on the intensity and position of the C-D stretching mode. As shown in Figure 2.10, the C-D stretching mode at ~ 2127 cm^{-1} (4.7 μm) for deuteronated circumcoronene is too weak to be visible. The absolute intensity and Int$_{rel}$ for this mode are 1.3165 km/mole and 0.003, respectively.

With increase in size of DPAH$^+$, the absolute and relative intensities of the C-D stretching transitions and the [D/H]$_{num}$ ratio (number of D atoms/number of H atoms) decrease (Table 2.8). DcorD$^+$ has two D atoms unlike other DPAH$^+$s considered and hence has a higher [D/H]$_{num}$ ratio of 0.18. Another point to note is that as the size of the DPAH$^+$ increases, the band corresponding to the aliphatic C-D stretching mode shifts towards shorter wavelengths and closer to the observed astronomical band position of 4.65 μm. The absolute intensity, Int$_{rel}$ and the position of the aliphatic C-D stretching mode for deuteronated pyrene, deuteronated perylene, deuteronated coronene, DcorD$^+$ and deuteronated

Table 2.8: Intensities and positions of aliphatic C-D stretching mode in DPAH$^+$s

DPAH$^+$	Frequency (cm^{-1})	Wavelength (μm)	Absolute Intensity (km/mole)	Relative Intensity	[D/H]$_{num}$[a]	[D/H]$_{int}$[b]	[D/H]$_{sc}$[c]
Deuteronated Pyrene	2092	4.78	18.1282	0.138	0.10	0.500	5.00
Deuteronated Perylene	2087	4.79	14.0726	0.063	0.08	0.271	3.39
Deuteronated Coronene	2110	4.74	7.3279	0.044	0.08	0.217	2.71
DcorD$^+$	2110	4.74	7.4811	0.068	0.18	0.258	1.43
Deuteronated Circumcoronene	2127	4.70	1.3165	0.003	0.06	0.008	0.13

[a] [D/H]$_{num}$ =no of D atoms/no of H atoms
[b] [D/H]$_{int}$ =intensity of C-D stretch/intensity of C-H stretch
[c] [D/H]$_{sc}$ $=\frac{[D/H]_{int}}{[D/H]_{num}}$

circumcoronene are compared in Table 2.8. [D/H]$_{int}$ ratio has been determined by taking the ratio of the intensities of the C-D stretch bands to the intensities of the C-H stretch bands as obtained from the calculations. There is no correlation present between [D/H]$_{int}$ and [D/H]$_{num}$. Having the same [D/H]$_{num}$ ratio, deuteronated perylene and deuteronated coronene give [D/H]$_{int}$ ratios of nearly same magnitude. DcorD$^+$ having two D atoms shows a higher [D/H]$_{int}$ ratio of 0.26 compared to that of deuteronated coronene (one D atom). An exception is deuteronated circumcoronene for which the [D/H]$_{int}$ ratio is lower by an order of magnitude compared to [D/H]$_{num}$ ratio. [D/H]$_{int}$ ratio is dependent on the size of PAHs and percentage of deuteronation. Hence, for a comparative analysis, we compute [D/H]$_{sc}$ which is [D/H]$_{int}$ per [D/H]$_{num}$ (Table 2.8). [D/H]$_{sc}$ is found to be decreasing with increase in size of the molecule.

2.5   DPAH$^+$ molecules as carriers of UIR emission features

From the discussion above, it is established that deuterium containing PAHs (PADs/D$_n$-PAHs and DPAH$^+$s) show features in the $4 - 5$ μm region. This is the same region where spectral contribution of deuterated PAHs have been discussed by Peeters et al. [5] and more recently by Onaka et al. [6]. Peeters et al. [5] reported the detection of PAD/D$_n$-PAH

features at 4.4 μm and 4.65 μm towards the Orion Nebula and M17 with the use of *SWS* on board *ISO*. Onaka et al. [6] using *AKARI* observed an overlapping region but did not confirm the detection and suggested the presence of similar bands with much weaker intensity. Moreover, Onaka et al. [6] did not look at the excess around 4.75 μm region. The observations of Peeters et al. [5] covered a larger area of Orion and M17 compared to the observations of Onaka et al. [6] owing to the large aperture of the *SWS* ($20'' \times 14''$) on-board the *ISO* compared to the *IRC* (Ns $-0'.8 \times 5''$ and Nh $-1' \times 3''$) on *AKARI*. The detections of the 4.4 and 4.65 μm bands reported by Peeters et al. [5] have large uncertainties and are at a level of 4.4 σ and 1.9 σ respectively in M17 and Orion. Stretching of the C-D aromatic and C-D aliphatic bonds in PADs and D_n-PAHs produce bands close to 4.4 μm and 4.65 μm respectively. These bands are analogous to the 3.3 and 3.5 μm bands which arise due to aromatic and aliphatic C-H stretching respectively. From their observations, Peeters et al. [5] calculated the D/H ratio (0.17 ± 0.03 towards the Orion bar and 0.36 ± 0.08 towards M17) by taking the ratio of the sum of intensities for bands in the $4-5$ μm (C-D stretching) region to the analogous sum near 3.3 μm band (C-H stretching). However, Onaka et al. [6] estimated a significantly smaller D/H value of 0.03 which is an order of magnitude smaller than the value proposed by Peeters et al. [5]; which points to the fact that if Ds are depleted onto PAHs, they might be accommodated in large PAHs [6].

The 4-5 μm region is featureless for PAHs without deuterium. The position of the C-D stretch (aromatic and aliphatic) in PADs/D_n-PAHs and DPAH$^+$s are close to the observed positions of 4.4 and 4.65 μm emission bands. The 4.65 μm band in DPAH$^+$ is accompanied by a transition at 3.5 μm corresponding to the aliphatic C-H stretch. Thus, a condition for DPAH$^+$s to be present in the ISM is that the bands at 4.65 μm and 3.5 μm should be observed together in the emission spectra of an astronomical source. In the emission spectra of Orion nebula and M17 [5], these two bands have indeed been detected which is an indicative of the presence of DPAH$^+$ molecules. In the M17 spectra, Peeters et al. [5] have reported the detection of only the 4.65 μm band at 4.4 σ

level (the detection of the 4.4 μm feature towards Orion is with much higher uncertainty). This is a tentative yet strong evidence in support of the presence of deuteronated-PAHs and/or aliphatic deuterated-PAHs. The presence of an aliphatic C-D bond results in a band at 4.65 μm rather than the 4.4 μm feature which arises due to an aromatic C-D stretch vibration. The aliphatic bond also results in features near 3.5 μm that may indicate the presence of aliphatic C-H bonds in neutral and ionized (protonated) PAHs.

In this work we have focused on comparing the band position of DPAH$^+$ molecules with observations rather than correlating the intensity of the bands. Therefore, we have not taken into account the effect of excitation of the bands and their intensity. However, for a direct comparison with the observed spectra, the excitation mechanisms have to be considered. The C-D stretch bands being at lower wavenumbers are easily excited compared to the C-H stretch bands, thus, care has to be taken while comparing the theoretical and the observed D/H ratios. Onaka et al. [6] calculated the emission intensity considering the effect of excitation based on a PAH emission model by Mori et al. [76] and found that the smaller cross-section of the C-D stretch bands is compensated by its easier excitation compared to C-H stretch vibrations. They reported that excitation does not affect the result significantly but an overestimation of D/H ratio by tens of percent is present. We have computed [D/H]$_{sc}$ for DPAH$^+$ molecules, which is nothing but the ratio of C-D stretch and C-H stretch bands per [D/H]$_{num}$.

The observational [D/H] values are estimated by assuming that the band strength per bond is constant for the C-H and C-D bonds. This assumption may not hold for the C-D bond. These values are compared to the theoretically calculated [D/H] values of specific molecules. The [D/H]$_{sc}$ values for deuteronated pyrene, deuteronated perylene, deuteronated coronene and DcorD$^+$ do not fall in the range of the D/H value given by observations [5, 6]. With increase in the size of DPAH$^+$s, the [D/H]$_{sc}$ value tends to decrease. Large PAHs have a tendency to be ionized in the ISM which may subsequently add a deuterium to form DPAH$^+$. Therefore, in such interstellar regions, the formation of

DPAH$^+$s may be preferred over PADs/D$_n$-PAHs. The D/H ratios proposed by Peeters et al. [5] and Onaka et al. [6] may be used to estimate the size of PADs/D$_n$-PAHs or DPAH$^+$s in the ISM. From this work, deuteronated circumcoronene shows a [D/H]$_{sc}$ value close to Peeters et al. [5] observation. For the smaller deuteronated PAHs, the [D/H]$_{sc}$ values are higher by about an order of magnitude. It is noted that DPAH$^+$ molecules of the size of circumcoronene (54 carbon atoms) and larger satisfy the D/H ratio as observed by Peeters et al. [5] and Onaka et al. [6]. This points to the fact the DPAH$^+$ molecules if present may have 50 or more carbon atoms.

Following the observed band ratio as found by Onaka et al. [6], the DPAH$^+$ molecules present in the ISM should be large. If this assumption is strictly followed, only large DPAH$^+$ molecules with low values of [D/H]$_{num}$ will exist in the ISM and these will not be able to account for the inferred depletion of deuterium [15]. The expected D/H without depletion is around 20 parts per million (ppm) and the minimum observed ratio is about 7 ppm. If this difference is attributed solely to the depletion of D onto PAHs then the necessary concentration of D/H (value of [D/H]$_{num}$) in PAHs would be 0.3. This points to the fact that large PAHs that match the D/H value estimated from observed band ratios will have lower elemental D/H values and therefore, will not match the depletion model values of Draine [15]. This discrepancy warrants for an extensive observational programme for the search of DPAH$^+$ and PAD molecules in the ISM. Theoretical and experimental spectroscopic studies are further needed to complement the observations. A refined depletion model of D on PAHs may thus be obtained based on the results of observations and spectroscopic studies.

2.6   Conclusion

Interstellar PAHs may have significant deuterium content with a D/H ratio as high as 0.3 [15]. In this context, we have calculated the vibrational spectra of deuteronated PAHs and have compared them with those of the corresponding neutral, cationic, deuterated and protonated forms. The

theoretical spectral data provides strong evidences in support of DPAH$^+$ molecules to be part of the interstellar PAH family and these may be responsible for some of the observed IR features. For example, DPAH$^+$ molecules show vibrational transitions in the same region ($4-5$ μm) at which *ISO* [5] and *AKARI* [6] reported the detection of two mid-infrared emission bands. In particular, the generally featureless region of $4-5$ μm of pure PAHs may be dominated by features due to C-D bond vibrations in DPAH$^+$s or deuterated PAHs. Stretching of the aliphatic C-D bond gives a distinct transition near 4.7 μm. This warrants for a look at the excess around 4.7 μm region in astronomical sources.

Our calculations of deuteronated circumcoronene yield a D/H ([D/H]$_{\rm sc}$) value that is similar to ones obtained by Peeters et al. [5]. Large DPAH$^+$s will have even small D/H values that might be in accordance with the proposed value of Onaka et al. [6]. A higher deuterium fraction has been observed in M17 [5] with lower uncertainty which only shows the 4.65 μm band (the aliphatic deuterium bond) and not the 4.4 μm band (the aromatic deuterium bond). This clearly points to the dominance of deuteronated-PAHs compared to deuterated-PAHs in such regions.

This study may also be used as input to deuterium depletion models and also for estimating the HD/H$_2$ ratio in interstellar gas. However for a more conclusive analysis, extensive observations followed by laboratory experiments are desired. Revisiting some of the *ISO*, *AKARI* and *SPITZER* data focusing on PAD and DPAH$^+$ systems may provide further insights. Upcoming *James Webb Space Telescope* may supplement this study by the addition of high quality data.