

Chapter 3

The Interstellar Deuterated and Deuteronated PAHs II

3.1 Introduction

In the previous chapter, the infra red characteristics of deuteronated PAHs (DPAH⁺s) in relation to UIR bands have been discussed. It is highly possible that interstellar deuterium (D) exists in the form of PAD or DPAH⁺ which show characteristic bands at 4.4 and 4.65 μm due to aromatic/aliphatic C-D stretching. This also addresses the problem of missing deuterium in the interstellar gas and proposes a D/H ratio in PAHs and offers an explanation to the present value of D/H in the interstellar gas. However, the depletion of D in interstellar PAHs may not be confined to PAD or DPAH⁺ only. Instead, due to the chemical reactions occurring in the ISM, variants of deuterium containing PAHs are expected in the ISM which show similar spectral features as that of deuterated PAHs. The study of deuterium containing PAH variants is crucial as it elaborates on the possibility of wide family of PAHs as UIR carriers instead of a few selected PAHs. In this chapter, possible variants of deuterium-containing PAHs have been studied to determine the expected vibrational transitions and to compare with observational data. A D/H ratio may be estimated from the molecules which might help to select samples for further expensive laboratory study. The findings of this chapter are published in

Buragohain et al. [157].

3.2 Molecules studied

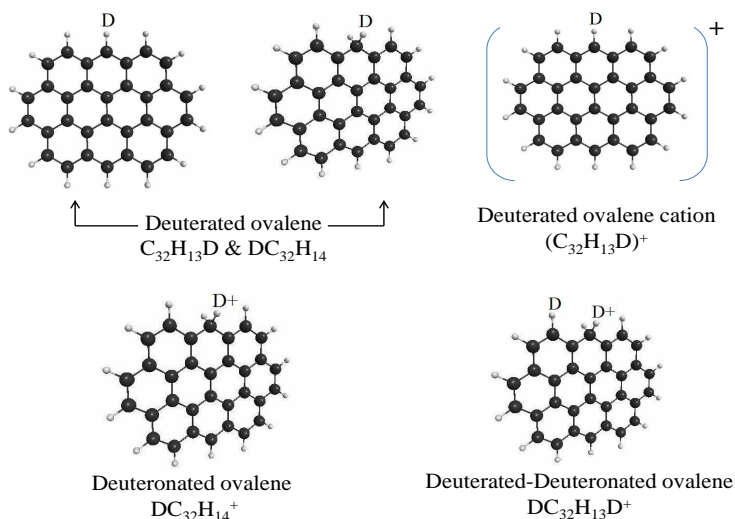


Figure 3.1: Examples of deuterium-containing ovalene variants

The formation of PAD and DPAH⁺ is discussed in the previous chapter. In the testing conditions of the ISM, molecules mostly exist in their ionized forms. In a similar manner, a PAD molecule may also get ionized to form PAD⁺ on being exposed to UV radiation. For simplicity, a single PAH, i.e., ovalene (C₃₂H₁₄) in various forms with deuterium is considered for our study. Figure 3.1 depicts some of the sample molecules that are studied in this chapter. This work includes DFT study of i) Deuterated ovalene (aromatic), ii) Deuterated ovalene (aliphatic), iii) Deuterated ovalene cation iv) Deuterated ovalene, v) Deuterated-Deuterated ovalene. An ovalene molecule has four unique sites of deuteration and the result includes all the isomers of the sample molecule. DFT in combination with B3LYP/6-311G** has been used to optimize the molecular structure of PAHs. Frequencies and intensities of vibrational transitions have been computed using the optimized geometry at the same level of calculation. The calculated intensities are used as input to an emission model which

is employed in this chapter in order to obtain the emission spectra of PAHs. Emission model is important for a direct comparison with the observed spectra. However, the overall spectra remains same as the absorption spectra with a slight increase in the emitted energy that leads to an overestimation of D/H ratio by tens of per cent. The same emission model is used by Cook and Saykally [120], Pech et al. [167] and Pathak and Rastogi [166] and described in the next section. The data presented here were produced using the QChem quantum chemistry suite of programs [14]. The vibrational modes of the molecule are identified using graphical software available for computational chemistry packages.

3.3 Emission Model

The calculated intensities are used as input to an emission model which is exclusively employed in this chapter in order to obtain the emission spectra of PAHs. Emission model is important for a direct comparison with the observed spectra. However, we find that the overall spectral characteristics remain same with a slight increase in the emitted energy that leads to an overestimation of D/H ratio by tens of per cent. Similar emission models have been used by Cook and Saykally [120], Pech et al. [167] and Pathak and Rastogi [166]. The emission model uses black body radiation generated by a source having effective temperature of 40,000 K. The PAH molecule absorbs this radiation of frequency ν with a cut off at 13.6 eV following their respective absorption cross-section (σ_ν). The photon absorption rate, R_{abs} is defined by

$$R_{\text{abs}} = \int_0^{13.6} \frac{B_\nu \sigma_\nu}{h\nu} d\nu \quad (1)$$

Where, B_ν is the Planck constant. The excited PAH after absorbing photons of frequency ν attains a peak temperature T_p which is a function of heat capacity of the molecule and is obtained by

$$U(T) = \sum_{i=1}^n \frac{hc \omega_i}{\exp(hc \omega_i/kT) - 1} \quad (2)$$

Where, i is the characteristic vibrational mode of the PAH molecule that appears at characteristic frequency ω_i (in cm^{-1}) and n is the total number of vibrational modes present in that molecule ($3N-6$, where N is degree of freedom). The molecule then cools down following a cascade transitions from levels $v \rightarrow v - 1$ emitting IR photons corresponding to their vibrational modes. The emission photon flux ϕ_i of the i^{th} vibrational mode is given as

$$\phi_i = A_i^{1,0} \times [\exp(hc \omega_i/kT) - 1]^{-1} \quad (3)$$

Where, $A_i^{1,0}$ is the the Einstein coefficient and is obtained from the absorption intensity, S_i (in km/mole) of the i^{th} vibrational mode by the following relation

$$A_i^{1,0} = (1.2512 \times 10^{-7}) \omega_i^2 S_i \quad (4)$$

For a fall in internal energy by ΔU that corresponds to a fall in temperature by 1 K at each T , the emitted energy E_i of the photons in the i^{th} mode is given by

$$\Delta E_i(T) = \frac{\phi_i \times \omega_i}{\sum_{i=1}^n \phi_i \times \omega_i} \times \Delta U(T) \quad (5)$$

The fractional energy E_i is integrated over the cooling range from the peak temperature T_p to a temperature of 50 K, below which the energy emitted by the photons is negligible. These IR photons are added up to generate the emission spectrum. The emitted energy (relative) and frequency (scaled) thus obtained from emission model is used to plot a Gaussian profile of FWHM 30 cm^{-1} . Relative intensities ($\text{Int}_{\text{rel}}^1$) are obtained by taking the ratio of all intensities to the maximum intensity near 3060 cm^{-1} for neutral ovalenes. Similarly, for cations, we divide all the intensities by maximum intensity that appears near 1600 cm^{-1} for normalization. Several unresolved bands might add up resulting some band intensity to cross unity. Considering the emission model with a lower black body effective temperature of say 30,000 K, we find no difference

¹ $\text{Int}_{\text{rel}} = \frac{\text{absolute intensity}}{\text{maximum absolute intensity}}$

in the PAH emission spectrum except that the emitted energy is slightly reduced.

3.4 Results and Discussion

Neutral and cationic Ovalene

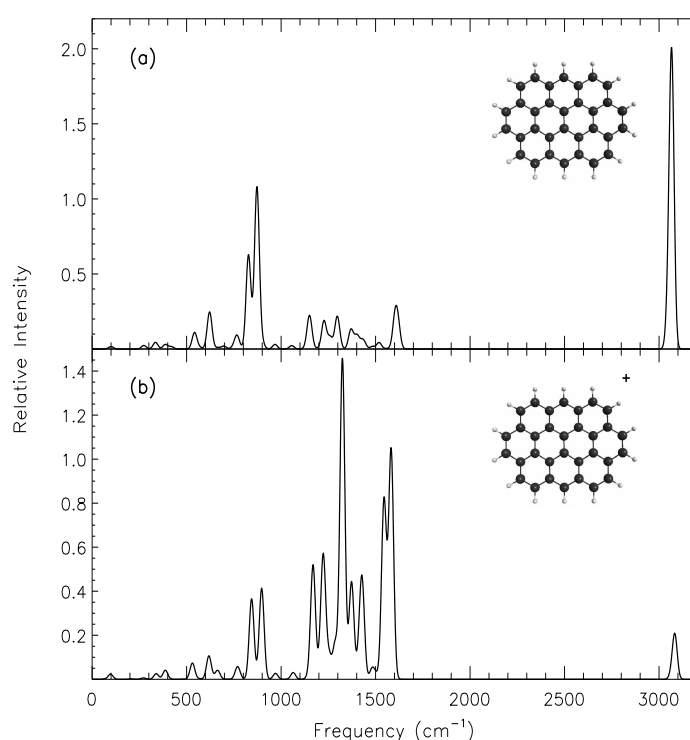


Figure 3.2: Theoretical emission spectra of (a) neutral ovalene (C₃₂H₁₄), (b) ovalene cation (C₃₂H₁₄⁺)

The theoretically computed emission spectra of neutral ovalene (C₃₂H₁₄) and cationic ovalene (C₃₂H₁₄⁺) are presented in Figure 3.2. Neutral ovalene shows strong lines at $\sim 800 - 900 \text{ cm}^{-1}$ ($\sim 13 - 11 \mu\text{m}$) and $\sim 3050 \text{ cm}^{-1}$ ($\sim 3.3 \mu\text{m}$) due to C-H oop and C-H stretching vibrational modes, respectively (Figure 3.2a). Weak features at $\sim 1000 - 1600 \text{ cm}^{-1}$ ($\sim 10 - 6 \mu\text{m}$) are characteristics of C-H in-plane bending and C-C stretching vibrational modes. These features are inherent to all neutral PAH

molecules. Likewise, any form of cationic PAH molecule shows a greater number of features in the $\sim 1000 - 1600 \text{ cm}^{-1}$ ($\sim 10 - 6 \text{ }\mu\text{m}$) region as shown in Figure 3.2b. The region below $\sim 1000 \text{ cm}^{-1}$ is attributed to C-H oop modes. Unlike neutral PAHs, all cationic PAHs show a weak feature at 3080 cm^{-1} , $\sim 3.3 \text{ }\mu\text{m}$ due to C-H stretching vibrational modes. These are the standard features expected from any neutral and ionized PAH molecule. The wavelengths² (in μm) and relative intensities of all the vibrational bands that are present in the sample molecules studied in this chapter are tabulated in the Appendix A.

Deuterated Ovalene

A deuterium atom can attach to the periphery of a neutral PAH molecule either in an aromatic or aliphatic site that leads to the formation of a deuterated PAH molecule (PAD or $\text{D}_n\text{-PAH}$) [5]. Figure 3.3 shows the emission spectra of deuterated ovalene, both aromatic³ and aliphatic⁴ ($\text{C}_{32}\text{H}_{13}\text{D}$ and $\text{DC}_{32}\text{H}_{14}$). Ovalene has four unique sites of deuteration which give four isomers of deuterated ovalene, both aromatic and aliphatic. In Figure 3.3, the emission spectra of all the isomers of deuterated ovalene are also presented.

Both aromatic and aliphatic deuterated ovalene along with its isomers show usual features similar to those present in neutral ovalene. Substitution of D reduces the symmetry of ovalene that activates the modes that were IR-inactive in neutral ovalene [186]. In deuterated ovalenes, weak C-D oop ($\sim 600 - 700 \text{ cm}^{-1}$, $\sim 16 - 14 \text{ }\mu\text{m}$) and C-D in-plane modes ($\sim 860 - 900 \text{ cm}^{-1}$, $\sim 11 \text{ }\mu\text{m}$) appear due to the presence of D in the structure. These modes are red shifted compared to the analogous C-H modes due to the heavier deuterium. Figure 3.3 (a-d) are representatives of the same molecule, i.e., aromatic deuterated ovalene, but differ only in the addition site of D. In Figure 3.3 (a-d), a unique feature

²For converting cm^{-1} to μm , $\frac{10,000}{\text{cm}^{-1}}$ is a simple conversion formula.

³D replacing H atom so that the resulting C-D bond remains aromatic in nature

⁴addition of an extra D to neutral ovalene so that the resulting C-D bond remains aliphatic in nature

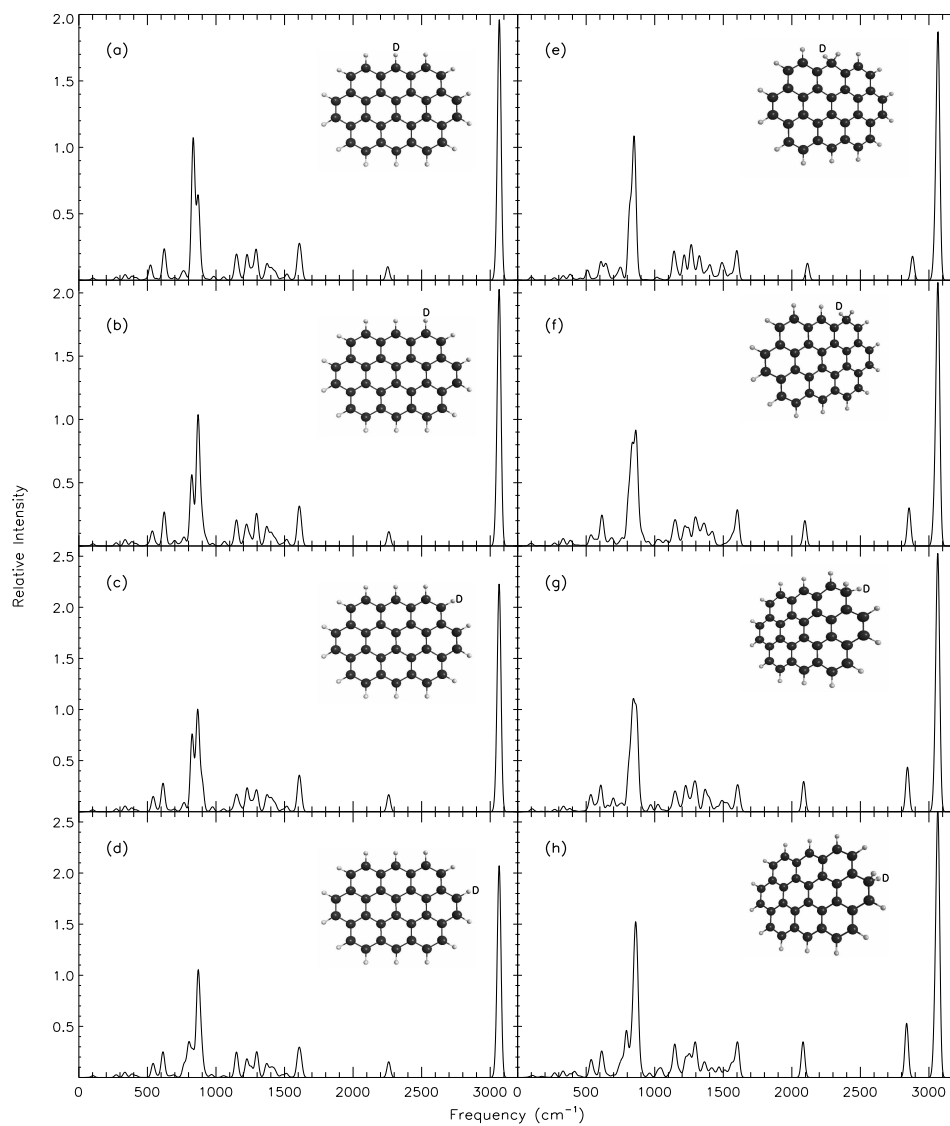


Figure 3.3: Theoretical spectra of (a) deuterated ovalene (aromatic, $\text{C}_{32}\text{H}_{13}\text{D}$), (b) isomer 1 of $\text{C}_{32}\text{H}_{13}\text{D}$, (c) isomer 2 of $\text{C}_{32}\text{H}_{13}\text{D}$, (d) isomer 3 of $\text{C}_{32}\text{H}_{13}\text{D}$, (e) deuterated ovalene (aliphatic, $\text{DC}_{32}\text{H}_{14}$), (f) isomer 1 of $\text{DC}_{32}\text{H}_{14}$, (g) isomer 2 of $\text{DC}_{32}\text{H}_{14}$, (h) isomer 3 of $\text{DC}_{32}\text{H}_{14}$

appears at $\sim 2260 \text{ cm}^{-1}$, $4.4 \text{ }\mu\text{m}$ ⁵ ($\text{Int}_{\text{rel(em)}} 0.13$ ⁶) which is characteristic of C-D stretching in $\text{C}_{32}\text{H}_{13}\text{D}$. This feature is analogous to the strong C-H stretching modes at $\sim 3.3 \text{ }\mu\text{m}$. In the case of $\text{DC}_{32}\text{H}_{14}$ and its isomers, as shown in Figure 3.3 (e-h), addition of an extra deuterium atom does not affect the spectrum much except in the $4-5 \text{ }\mu\text{m}$ region. Addition of deuterium to a neutral ovalene molecule breaks the aromatic nature at the site where D is added. Stretching of the C-D and C-H aliphatic bonds in $\text{DC}_{32}\text{H}_{14}$ gives distinct features at $\sim 2095 \text{ cm}^{-1}$, $4.8 \text{ }\mu\text{m}$ ($\text{Int}_{\text{rel(em)}} 0.24$) and 2880.31 cm^{-1} , $3.5 \text{ }\mu\text{m}$ ($\text{Int}_{\text{rel(em)}} 0.36$) respectively. Table 3.1 lists intensities and positions of C-D stretching transitions for all the deuterated ovalenes (both aromatic and aliphatic) along with its isomers. The positions and intensities of $4.4 \text{ }\mu\text{m}$ (aromatic C-D stretching) and $4.7/4.8 \text{ }\mu\text{m}$ (aliphatic C-D stretching) feature are partially affected by the position of D. A maximum variation in the position of the C-D stretching band for various isomers of deuterated Ovalene is of 8 cm^{-1} for aromatic deuterated ovalene and 32 cm^{-1} for aliphatic deuterated ovalene. Similarly, $\text{Int}_{\text{rel(em)}}$ also varies among the isomers, however no uniform pattern is observed (Figure 3.3).

Deuterated Ovalene cation and Deuterated Ovalene

All the isomers of cationic forms of deuterated ovalene ($\text{C}_{32}\text{H}_{13}\text{D}^+$) show many more features compared to their neutral counterparts; particularly in the region $\sim 1000-1600 \text{ cm}^{-1}$, $\sim 10-6 \text{ }\mu\text{m}$ as shown in Figure 3.4 (a-d). This region is dominated by C-H in-plane and C-C stretching vibrational modes. The bands are similar to that of ovalene cation, $\text{C}_{32}\text{H}_{14}^+$ (Figure 3.2b). The effect of deuterium is not present in this region. The region below $\sim 1000 \text{ cm}^{-1}$ is attributed to C-H oop modes, which is again free from any significant D-associated modes. In Figure 3.4 (a-d), a weak feature at $\sim 2272 \text{ cm}^{-1}$, $4.4 \text{ }\mu\text{m}$ ($\text{Int}_{\text{rel(em)}} 0.03$) is attributed to the aromatic C-D stretching mode in $\text{C}_{32}\text{H}_{13}\text{D}^+$. The $2000-3000 \text{ cm}^{-1}$ ($5-3 \text{ }\mu\text{m}$) region is magnified to highlight the weak features. Unlike the neutral

⁵wavenumbers are averaged among the isomers of the same molecule

⁶Relative intensity from emission model, average is taken for the same molecule including its isomers

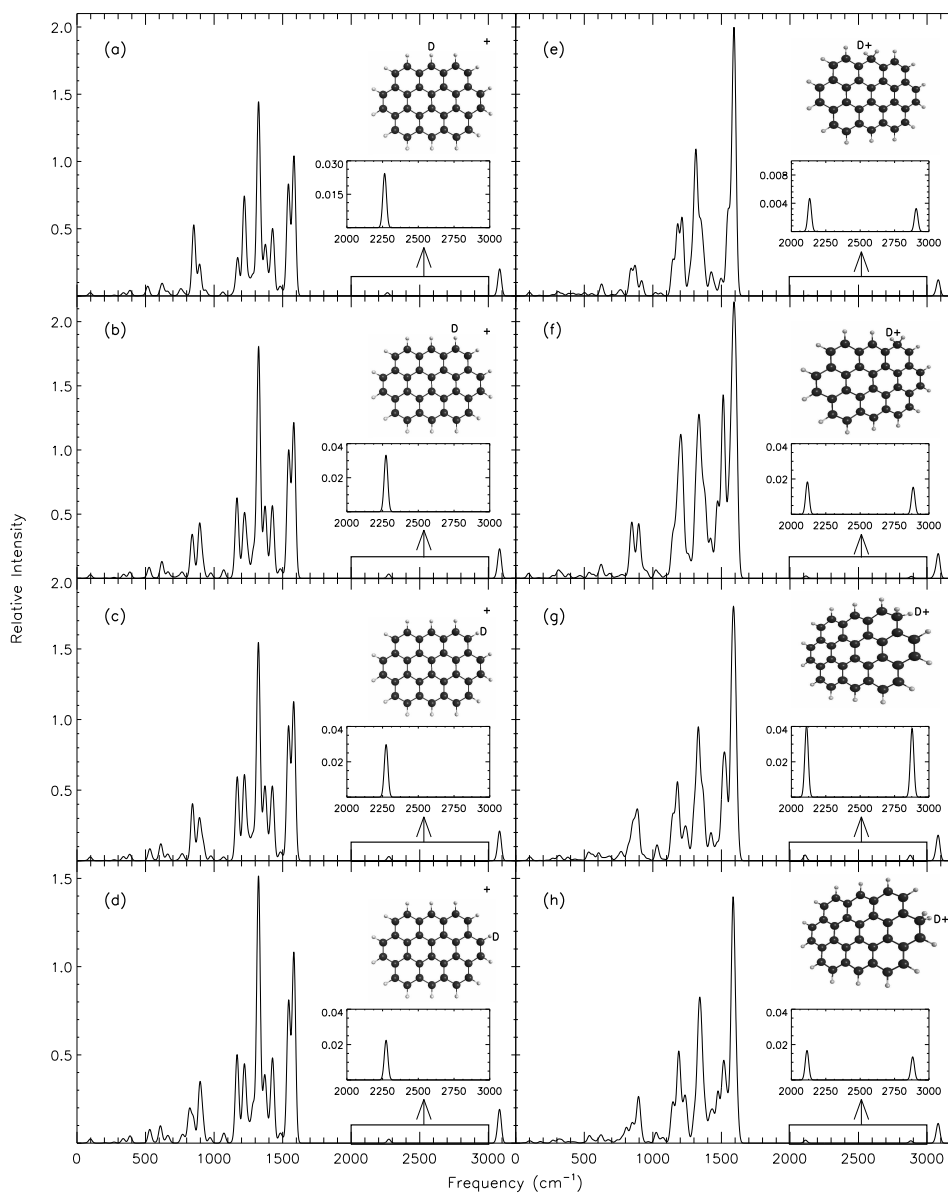


Figure 3.4: Theoretical spectra of (a) deuterated ovalene cation, ($C_{32}H_{13}D^+$), (b) isomer 1 of $C_{32}H_{13}D^+$, (c) isomer 2 of $C_{32}H_{13}D^+$, (d) isomer 3 of $C_{32}H_{13}D^+$, (e) deuterated ovalene, ($DC_{32}H_{14}^+$), (f) isomer 1 of $DC_{32}H_{14}^+$, (g) isomer 2 of $DC_{32}H_{14}^+$, (h) isomer 3 of $DC_{32}H_{14}^+$

counterparts of deuterated ovalene, cationic deuterated ovalenes show a weak feature at 3080 cm^{-1} , $\sim 3.3\text{ }\mu\text{m}$. The position of the $4.4\text{ }\mu\text{m}$ band is not much affected by the position of D in solo and duo site with a maximum difference of 11 cm^{-1} . Similarly, $\text{Int}_{\text{rel}(\text{em})}$ does not vary much as can be seen in Table 3.1.

A new form of PAH candidate carrier of mid infrared emission bands; deuterated PAH (DPAH⁺) has been discussed in the previous chapter and also by Buragohain et al. [156]. Structurally, a deuterated PAH is a PAH with a deuteron added to its periphery. Formation of these PAHs is favorable in the ionized ISM. Its closed shell electronic structure makes a deuterated PAH molecule chemically less reactive than the corresponding PAH cation which is an open shell structure. However, photostability does not change much between similar open shell and closed shell species. Theoretical IR spectra of deuterated ovalene ($\text{DC}_{32}\text{H}_{14}^+$) and its isomers are presented in Figure 3.4 (e-h). Addition of a deuteron (D^+) to a neutral PAH at different positions reduces the symmetry and a rich IR spectrum, particularly in the region $\sim 1000 - 1600\text{ cm}^{-1}$, $\sim 10 - 6\text{ }\mu\text{m}$ is noted. A number of features in this region are contributed by C-H in-plane and C-C stretching modes. However, a new D-associated feature is observed at 1212.41 cm^{-1} , $8.3\text{ }\mu\text{m}$ ($\text{Int}_{\text{rel}(\text{em})}$ 0.41), which arises due to a combination of D – C – H oop, C-H in-plane and C-C stretching vibrations. Prominent features with $\text{Int}_{\text{rel}(\text{em})}$ between 0.1 and 0.2 due to C-H oop modes are present in the $\sim 800 - 900\text{ cm}^{-1}$, $\sim 13 - 11\text{ }\mu\text{m}$ region. This region is not affected by any significant D-associated modes. A pure D-associated mode appears at $\sim 2118\text{ cm}^{-1}$, i.e., $4.7\text{ }\mu\text{m}$ with a very low $\text{Int}_{\text{rel}(\text{em})}$ of 0.02. This feature is attributed to the stretching of the aliphatic C-D bond in $\text{DC}_{32}\text{H}_{14}^+$. Stretching of aliphatic and aromatic C-H bonds give rise to weak features at $\sim 2887\text{ cm}^{-1}$ ($3.5\text{ }\mu\text{m}$) and $\sim 3080\text{ cm}^{-1}$ ($3.3\text{ }\mu\text{m}$), respectively. In Figure 3.4, the $2000 - 3000\text{ cm}^{-1}$ region is zoomed in to show the weak features. Isomers of $\text{DC}_{32}\text{H}_{14}^+$ show a variation in the position of the $4.7\text{ }\mu\text{m}$ with a maximum variation of 23 cm^{-1} . Intensities remain almost the same irrespective of the structural difference of $\text{DC}_{32}\text{H}_{14}^+$.

DovaleneD⁺

DovaleneD⁺ (DC₃₂H₁₃D⁺) carries two types of C-D bonds, aromatic at the addition site of D and aliphatic at the addition site of D⁺. The computed IR spectra of DovaleneD⁺ and its isomer are shown in Fig-

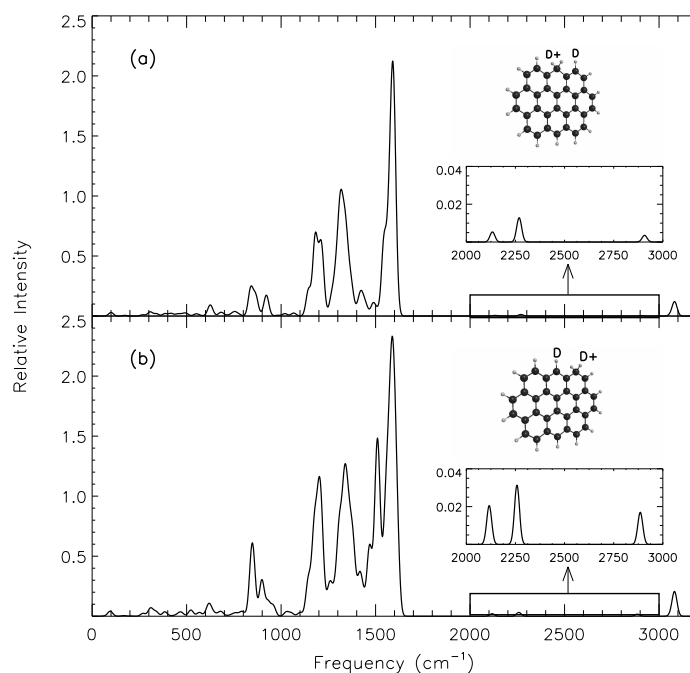


Figure 3.5: Theoretical spectra of DovaleneD⁺ (DC₃₂H₁₃D⁺) and its isomer

ure 3.5 (a,b). Several isomers for DovaleneD⁺ are possible, though only two are randomly chosen. The structure of DovaleneD⁺ is a combination of deuterated ovalene (aromatic) and deuterated ovalene and shows similar characteristic vibrational modes that are present in deuterated ovalene (aromatic) and deuterated ovalene. The spectrum (Figure 3.5) is dominated by rich C-H in-plane and C-C stretching modes that appear in the $\sim 1000 - 1600 \text{ cm}^{-1}$, $\sim 10 - 6 \mu\text{m}$ region. C-H oop modes are comparatively weak and are distributed in the $\sim 600 - 900 \text{ cm}^{-1}$, $\sim 16 - 11 \mu\text{m}$ region. The presence of deuteriums in DovaleneD⁺ causes new features to appear in the $\sim 600 - 1600 \text{ cm}^{-1}$, $\sim 16 - 6 \mu\text{m}$ region. The most significant features (above relative intensity 0.05) are C-D in-plane and D-C-H oop. The former is analogous to the C-H in-plane mode, but

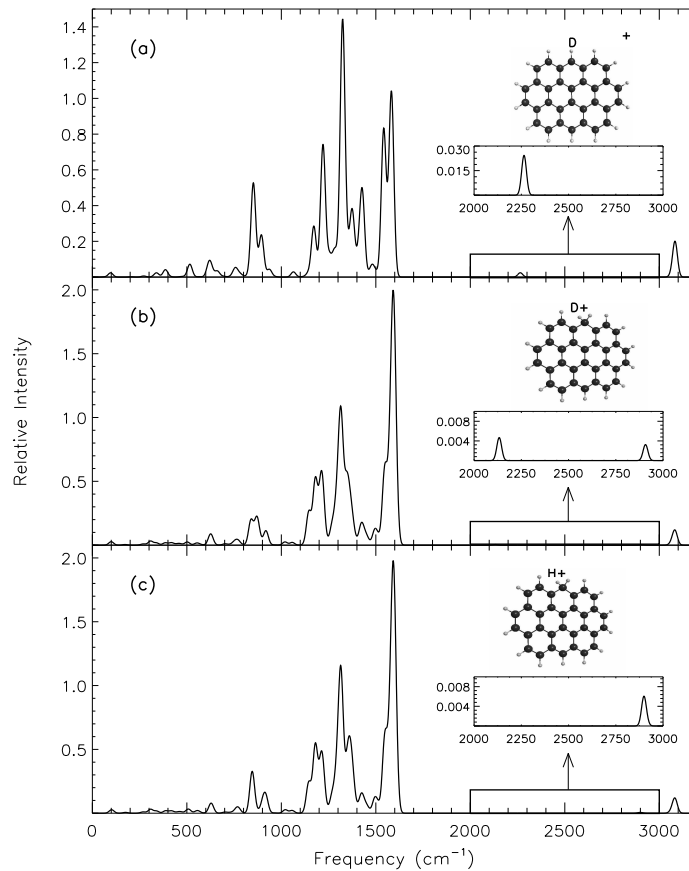


Figure 3.6: Theoretical spectra of (a) deuterated ovalene cation, (C₃₂H₁₃D⁺), (b) deuterated ovalene, (DC₃₂H₁₄⁺) and protonated ovalene (HC₃₂H₁₄⁺)

is redshifted due to the heavier mass of D and blended with the C-H oop modes. This feature appears at ~ 860 cm⁻¹ (11.6 μ m, Int_{rel(em)} 0.08) in DovaleneD⁺ and at ~ 850 cm⁻¹ (11.8 μ m, Int_{rel(em)} 0.15) in its isomer. The latter (D–C–H oop) appears at ~ 1212 cm⁻¹ (8.3 μ m, Int_{rel} 0.42) in DovaleneD⁺ and at ~ 1200 cm⁻¹ (8.3 μ m, Int_{rel} 0.66) in its isomer. These features are however not pure and are mixed with the C-H in-plane and the C-C stretching modes. Pure contributions of D atoms in DovaleneD⁺ are observed at ~ 2133 cm⁻¹ (4.7 μ m, Int_{rel} 0.005) and at ~ 2269 cm⁻¹ (4.4 μ m, Int_{rel} 0.01). These two features arise due to the stretching of aliphatic C-D and aromatic C-D bonds respectively and are extremely weak compared to C–C stretching modes.

The stretching of the aliphatic C-H bond gives rise to a very weak feature at $\sim 2907 \text{ cm}^{-1}$ ($3.4 \text{ }\mu\text{m}$, $\text{Int}_{\text{rel}} 0.004$). In the isomer counterpart (Figure 3.5b), stretching of aliphatic C-D, aromatic C-D and aliphatic C-H bonds are seen at $\sim 2117 \text{ cm}^{-1}$ ($4.7 \text{ }\mu\text{m}$), $\sim 2258 \text{ cm}^{-1}$ ($4.4 \text{ }\mu\text{m}$) and $\sim 2885 \text{ cm}^{-1}$ ($3.5 \text{ }\mu\text{m}$) with $\text{Int}_{\text{rel}} 0.02$, 0.03 and 0.02 respectively. The region of $2000\text{--}3000 \text{ cm}^{-1}$ is zoomed-in as shown in Figure 3.5, to highlight the weak features at $4.7, 4.4$ & $3.5 \text{ }\mu\text{m}$. As expected, another weak but distinct feature appears at $\sim 3080 \text{ cm}^{-1}$ ($3.3 \text{ }\mu\text{m}$) which is due to aromatic C-H stretching vibrational modes and is inherent in all cationic PAHs.

DovaleneD⁺ has a possibility of several isomers and a slight variation is present in the aliphatic and aromatic C-D stretching bands depending on the position of substitution/addition of the D atom. This leads to the broadening of the C-D stretching band if contribution from all the isomers is considered.

Figure 3.6 compares the spectra of deuterated ovalene cation with that of deuterated ovalene and protonated ovalene ($\text{HC}_{32}\text{H}_{14}^+$). A similarity is that all these are in ionized form. A protonated PAH is a PAH with a proton added to its periphery and is structurally identical to a deuterated PAH. We have considered protonation only at one position and compared with respective counterparts of deuterated ovalene cation and deuterated ovalene. The emission spectrum of protonated ovalene shows similar features that are present in deuterated ovalene. An exception is the appearance of a weak feature at $\sim 2900 \text{ cm}^{-1}$ ($3.5 \text{ }\mu\text{m}$, $\text{Int}_{\text{rel}} 0.006$) due to symmetric H-C-H stretching at the addition site. Its associated antisymmetric H-C-H stretching appears at $\sim 2915 \text{ cm}^{-1}$ ($3.4 \text{ }\mu\text{m}$) with very low relative intensity.

3.5 Astrophysical Implications

PAHs with incorporated deuterium might be crucial as they might provide an explanation for the missing primordial D which could not be

Table 3.1: Intensities and positions of the C – D stretching mode in deuterium-containing PAH variants

PAH	Frequency (cm^{-1})	Wavelength (μm)	Absolute intensity (km/mole)	$\text{Int}_{\text{rel(abs)}}^a$	$\text{Int}_{\text{rel(em)}}^b$
Deuterated ovalene ^c	2253	4.44	9.816	0.08	0.10
Deuterated ovalene ^c (isomer 1)	2261	4.42	10.118	0.08	0.11
Deuterated ovalene ^c (isomer 2)	2260	4.42	13.424	0.12	0.17
Deuterated ovalene ^c (isomer 3)	2260	4.42	13.297	0.11	0.15
Deuterated ovalene ^d	2114	4.73	11.681	0.09	0.13
Deuterated ovalene ^d (isomer 1)	2095	4.77	15.748	0.14	0.2
Deuterated ovalene ^d (isomer 2)	2086	4.79	19.360	0.2	0.29
Deuterated ovalene ^d (isomer 3)	2082	4.80	21.566	0.24	0.35
Deuterated ovalene ^c cation	2264	4.42	5.166	0.03	0.02
Deuterated ovalene ^c cation (isomer 1)	2274	4.40	5.887	0.04	0.03
Deuterated ovalene ^c cation (isomer 2)	2275	4.40	5.641	0.03	0.03
Deuterated ovalene ^c cation (isomer 3)	2274	4.40	4.782	0.02	0.02
Deuterated ovalene ^d	2133	4.69	1.434	0.005	0.005
Deuterated ovalene ^d (isomer 1)	2117	4.72	3.561	0.02	0.02
Deuterated ovalene ^d (isomer 2)	2110	4.74	8.755	0.04	0.04
Deuterated ovalene ^d (isomer 3)	2114	4.73	5.699	0.02	0.02
DovaleneD ^{+c,d}	2269	4.41	3.616	0.01	0.01
	2133	4.69	1.460	0.006	0.005
DovaleneD ^{+c,d} (isomer)	2258	4.43	5.673	0.04	0.03
	2117	4.73	3.609	0.02	0.02

For structures of various isomers of deuterium containing PAHs, please refer to Figure 3.3, Figure 3.4 and Figure 3.5

$\text{Int}_{\text{rel(abs)}}$ is directly calculated from absorption data obtained from DFT calculation and $\text{Int}_{\text{rel(em)}}$ is calculated from the emission model. $\text{Int}_{\text{rel(em)}}$ shows an average increase of $\sim 35\%$ from $\text{Int}_{\text{rel(abs)}}$.

^aRelative intensity (Int_{rel}) from absorption

^bRelative intensity (Int_{rel}) from emission model

^cC-D bond is aromatic in nature

^dC-D bond is aliphatic in nature

solely answered by astration⁷. The current value of D/H has been estimated to be ~ 7 ppm to ~ 22 ppm [175, 176, 174, 177] along various lines of sight, whereas the primordial D/H ratio is suggested as ~ 26 ppm [172, 173, 174]. Draine [15] has proposed that the problem of reduced D/H ratio can be explained if some of the primordial Ds are considered to be depleted in interstellar dust. Among all forms of interstellar dusts, some might be depleted onto PAHs which may produce a deuterated PAH molecule. Draine [15] also proposed a D/H ratio of ~ 0.3 in PAHs which is in accordance with the present estimated ratio of D/H in interstellar gas. In the previous chapter, the depletion of D in PAHs forming alternatives is discussed which is limited to only PADs or DPAH⁺s, however presence of other variants of deuterium containing PAHs is also possible in the ISM. For observational search of such deuterium or other deuterium-containing PAH variants in the ISM, spectral observations of these molecules are desired.

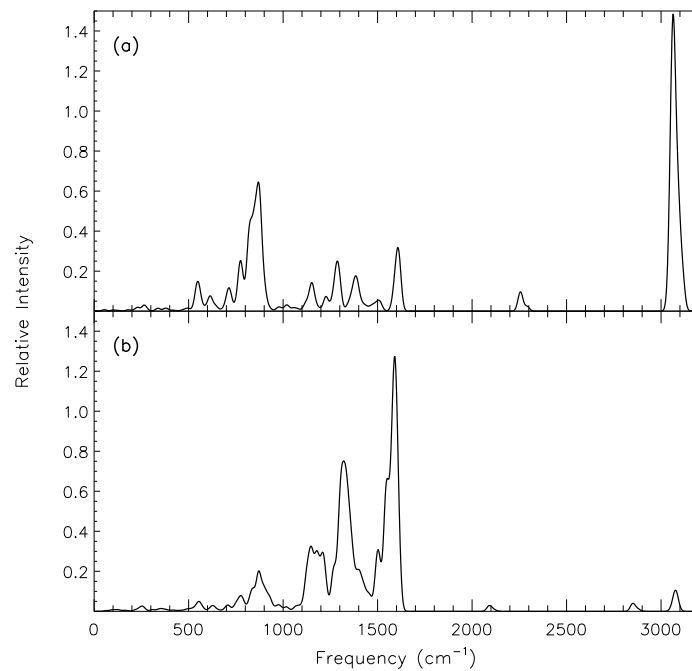


Figure 3.7: co-added emissions from (a) Deuterated PAHs (PADs) , (b) Deuterated PAHs (DPAH⁺)

⁷conversion of D into other heavy elements due to nuclear fusion in stellar interiors

In this chapter, we have considered deuterium-containing PAH variants for theoretical spectroscopic study. All frequencies corresponding to D-associated modes in deuterium-containing PAHs may not be used to compare with observations due to their low intensity. Another important fact is that C-D in-plane and oop modes merge with other usual modes that are present in a pure PAH. Such features are inappropriate to distinguish any interstellar deuterium-containing PAH. An exception is the C-D stretching mode ($4 - 5 \mu\text{m}$) that uniquely may help to identify a PAH candidate with deuterium. The previous section emphasizes that all kinds of deuterium-containing PAH variants show unique features in the $4 - 5 \mu\text{m}$ region. This region has not been identified with any significant lines apart from the lines ($4.4 \mu\text{m}$ and $4.7 \mu\text{m}$) expected from deuterium-containing PAHs as seen in the emission spectra of PAHs. However, there is a possibility of overtones and combination bands occurring at a similar position [78]. Stretching of aromatic and aliphatic C-D bonds in a deuterium-containing PAH causes two features to appear at $\sim 4.4 \mu\text{m}$ and $\sim 4.7 \mu\text{m}$ respectively. Figure 3.7 shows the composite emission spectra of DPAH⁺ and PADs by considering small to large PAHs. The percentage of PAHs are so chosen in view of the fact that large PAHs have more tendency to survive against the UV radiation while small size PAHs are easily prone to destruction in the ISM. The high abundance of large PAHs in comparison to small PAHs in the ISM are also justified by their relatively low D/H ratio that agrees with observations. In the composite spectra, the $\sim 4.4 \mu\text{m}$ ($\sim 2270\text{cm}^{-1}$) from the aromatic PADs and the $\sim 4.7 \mu\text{m}$ ($\sim 2105\text{cm}^{-1}$) from the partially aliphatic DPAH⁺s are clearly seen. Remaining characteristics are similar as described in the previous sections. Table 3.1 describes the position and intensities of the corresponding C – D stretching modes in our sample molecules. The intensity of these features depends on the percentage of deuteration and also on the position of D in the isomers. The same features ($4 - 5 \mu\text{m}$ region) have been observationally detected by Peeters et al. [5] at $\sim 4.4 \mu\text{m}$ and $\sim 4.65 \mu\text{m}$ towards the Orion bar and M17. The observed features are assigned to C-D stretching vibrational modes in PADs or D_nPAHs. *AKARI* also observed a small area of overlapping region as that of Peeters et

al. [5], and only detected some excess emissions at these wavelengths [6]. Bands at $\sim 4.4 \mu\text{m}$ and $\sim 4.65 \mu\text{m}$ are analogous to bands at $\sim 3.3 \mu\text{m}$ (aromatic C-H stretching) and $\sim 3.5 \mu\text{m}$ (aliphatic C-H stretching) respectively. The $4-5 \mu\text{m}$ region is pure in D characteristic vibrational modes and may be used to determine the D/H ratio. Both the observations made by *ISO* and *AKARI* [5, 6] estimated a D/H ratio by taking the ratio of band intensities at $\sim 4-5 \mu\text{m}$ to $\sim 3-4 \mu\text{m}$. Peeters et al. [5] proposed D/H ratios of 0.17 ± 0.03 in the Orion bar and 0.36 ± 0.08 in M17. Onaka et al. [6] suggested a comparatively low value of D/H (0.03) and proposed low deuteration limited to large PAHs. It is implicitly assumed that a molecule can have more than one D [5, 6]. Thus, emission per C–D bond was considered in observations [5, 6]. This work proposes a $[\text{D}/\text{H}]_{\text{int}}$ that is calculated by taking the ratio of integrated band intensities due to C-D stretching to that of C-H stretching from the emission model. Deuterated ovalene, deuterated ovalene cation and deuterated ovalene carry only one D atom, whereas DovaleneD⁺ has two D atoms. To make a comparative study, a $[\text{D}/\text{H}]_{\text{abs}}$ is computed which is nothing but $[\text{D}/\text{H}]_{\text{int}}$ (intensity of C-D stretch/intensity of C-H stretch) per number of D atoms. Table 3.2 describes the theoretical $[\text{D}/\text{H}]_{\text{abs}}$ ratios obtained from deuterium-containing ovalene variants. Since intensity is sensitive to the position in which D is substituted and/or added, $[\text{D}/\text{H}]_{\text{abs}}$ shows variation from one isomer to another isomer in all considered PAHs. Such variation is salient for deuterated ovalene. The calculated $[\text{D}/\text{H}]_{\text{abs}}$ values for deuterated ovalenes are small compared to *ISO* observation and close to *AKARI* observation. On the contrary, for deuterated ovalene cations, $[\text{D}/\text{H}]_{\text{abs}}$ values are in close proximity to *ISO* observations. However, nothing concrete can be deduced by considering a single form of PAH. The observed value of D/H that varies from 3% to 30% [5, 6] indicates a mixture of deuterated PAHs, if present in the ISM. In our recent study [156], a $[\text{D}/\text{H}]_{\text{sc}}$ ratio has been derived for a set of different molecules which is comparable to observation made by *ISO* and *AKARI*. The $[\text{D}/\text{H}]_{\text{sc}}$ ratio is simply $[\text{D}/\text{H}]_{\text{int}}/[\text{D}/\text{H}]_{\text{num}}$ ⁸. In our present work, we have made similar calculations for ionized forms of

⁸ $[\text{D}/\text{H}]_{\text{num}} = \frac{\text{no. of D atoms}}{\text{no. of H atoms}}$

Table 3.2: Theoretically computed D/H ratios in deuterium-containing ovalene variants

PAHs	no of D atoms, n	$[D/H]_{\text{int}}^e$
Deuterated ovalene (aromatic)	1	0.05
Deuterated ovalene isomer 1 (aromatic)	1	0.07
Deuterated ovalene isomer 2 (aromatic)	1	0.05
Deuterated ovalene isomer 3 (aromatic)	1	0.07
Deuterated ovalene (aliphatic)	1	0.06
Deuterated ovalene isomer 1 (aliphatic)	1	0.07
Deuterated ovalene isomer 2 (aliphatic)	1	0.09
Deuterated ovalene isomer 3 (aliphatic)	1	0.1
Deuterated ovalene cation	1	0.11
Deuterated ovalene cation isomer 1	1	0.13
Deuterated ovalene cation isomer 2	1	0.13
Deuterated ovalene cation isomer 3	1	0.12
Deuterated ovalene	1	0.04
Deuterated ovalene isomer 1	1	0.08
Deuterated ovalene isomer 2	1	0.17
Deuterated ovalene isomer 3	1	0.12
DovaleneD ⁺	2	0.14 (0.07) ^f
DovaleneD ⁺ isomer	2	0.22 (0.11) ^f

$[D/H]_{\text{abs}}$ is equal to $[D/H]_{\text{int}}$ for all molecules except for DovaleneD⁺ and its isomer as the no. of D atom is one in deuterated ovalene, deuterated ovalene cation and deuterated ovalene. DovaleneD⁺ and its isomer consist of two D atoms and thereby give a different $[D/H]_{\text{abs}}$ from $[D/H]_{\text{int}}$.

^e $[D/H]_{\text{int}}$ =intensity of C – D stretch/intensity of C – H stretch from the emission model

$$^f[D/H]_{\text{abs}} = \frac{[D/H]_{\text{int}}}{n}$$

Table 3.3: $[D/H]_{sc}$ ratios calculated for DPAH⁺

DPAH ⁺	$[D/H]_{sc}^g$
Deuterated pyrene ^h	5.00
Deuterated perylene ^h	3.39
Deuterated coronene ^h	2.71
DcorD ⁺ ^h	1.43
Deuterated ovalene cation ⁱ	1.38
Deuterated ovalene cation isomer 1 ⁱ	1.63
Deuterated ovalene cation isomer 2 ⁱ	1.63
Deuterated ovalene cation isomer 3 ⁱ	1.50
Deuterated ovalene ⁱ	0.57
Deuterated ovalene isomer 1 ⁱ	1.14
Deuterated ovalene isomer 2 ⁱ	2.43
Deuterated ovalene isomer 3 ⁱ	1.71
DovaleneD ⁺ ⁱ	0.93
DovaleneD ⁺ isomer ⁱ	1.47
Deuterated circumcoronene ^h	0.13

$$^g[D/H]_{sc} = \frac{[D/H]_{int}}{[D/H]_{num}}$$

^hBuragohain et al. [156]

ⁱBuragohain et al. [157]

deuterated ovalene as ionization of molecules is likely to occur in the ISM. This has been compared with our previous results [156]. Table 3.3 lists the $[D/H]_{sc}$ ratios from our previous as well as present results. The molecules are chosen in terms of increasing size. If the observed D/H ratio is lower than the calculated $[D/H]_{sc}$ ratio, it suggests a mixture of pure, deuterated, deuterated and/or other substituted PAH molecules.

D/H ratios provided by Peeters et al. [5] and Onaka et al. [6] may be used to estimate the size of the deuterium-containing PAH variants in the ISM by comparing with the theoretically obtained D/H ratio. Our results from previous work [156] and the present chapter suggest a $[D/H]_{sc}$ ratio (Table 3.3) that is large compared to the Peeters et al. [5] and Onaka et al. [6] observations except for deuterated ovalene and deuterated circumcoronene. The three isomers of deuterated ovalene show a larger value of $[D/H]_{sc}$. With increasing size, the $[D/H]_{sc}$ ratio tends to decrease (Figure 3.8). For a particular molecule, addition of more than one deuterium may or may not lead to an increase in the

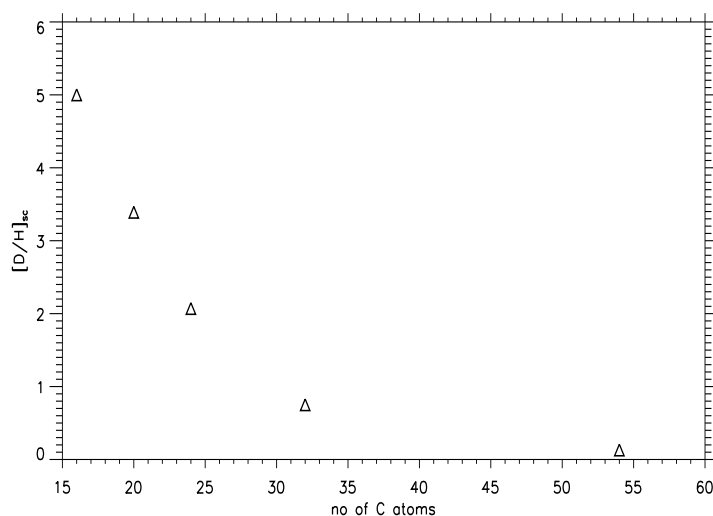


Figure 3.8: $[D/H]_{sc}$ ratio with increasing size, no of C atoms is directly proportional to size of PAH molecule

$[D/H]_{sc}$ ratio. $[D/H]_{sc}$ ratios for deuterated ovalene and deuterated circumcoronene are in close proximity to the D/H ratio observed by Peeters et al. [5] and hence may be considered as feasible carriers for bands at 4–5 μm . $[D/H]_{sc}$ ratios suggested by our work do not match with *AKARI* observation. It is suggested that PAH molecules close to 100 carbon atoms may match the observed D/H ratio by *AKARI*.

Doney et al. [168] observed H II regions in the Milky Way in near infrared in order to estimate the amount of deuterium in PAHs. They did not detect emission from deuterated PAHs towards all the sources and concluded that the deuteration of PAHs is not common. Doney et al. [168] calculated emission spectrum for molecule with aliphatic group attached to the PAH structure and calculated a D/H ratio in the range of 0.01–0.06 by taking the intensity ratio of 3.3 and 4.75 μm band. Our approach is different from Doney et al. [168] and the $[D/H]_{int}$ ratio is calculated by taking the ratio of integrated band intensities of both aromatic and aliphatic C-D stretching to integrated band intensities of both aromatic and aliphatic C-H stretching for our sample molecules. The calculated $[D/H]_{int}$ in our work for solo deuteration is in the range of 0.04–0.17. The molecules with an aliphatic side group however are feasible only in benign environments and may be destroyed in a harsh

interstellar environment such as fully evolved planetary nebulae or H II regions [139].

3.6 Conclusion

Deuterium-containing PAH variants have been studied theoretically in relation to mid-infrared emission bands. This chapter suggests PAH molecules with deuterium content as potential candidate carriers for some of the observed UIR features in the ISM on basis of the band positions. This is obtained by comparing the theoretically computed spectra of deuterium-containing PAHs with the available observational spectra that shows good agreement for some of the observed mid-infrared emission bands. PAHs with a D or D⁺ give features in the 4 – 5 μm region which arises purely due to the stretching of the C-D bond and hence may be considered responsible for observed bands at 4.4 μm and 4.65 μm by *ISO* and *AKARI*. To gain further support, the $[\text{D}/\text{H}]_{\text{sc}}$ ratio for ovalene with D is estimated. On comparing this ratio from the present and previous chapters with observations, it is realized that deuterated ovalene and deuterated circumcoronene agree with the observations of Peeters et al. [5]. *AKARI* observations propose comparatively large PAHs (no. of C atoms ~ 100) with low deuterium content. PAHs with a suitable $[\text{D}/\text{H}]_{\text{sc}}$ may be arranged accordingly for much more expensive laboratory experiments which are of utmost importance for assignment of carriers. The study of deuterium-containing PAHs is essential in order to measure D/H that will give insight into the history of star formation. This study can further be progressed to estimate HD/H₂ ratio in interstellar gas. For reliable analysis, more experimental and observational evidence of interstellar deuterium is needed.

