Chapter 6

Conclusion

6.1 Summary of the results

This thesis presents a detailed analysis of the IR spectra of PAH variants and discusses the possible astrophysical implications. Variants of PAHs in terms of size, charge, functional groups, etc., have been considered. DFT calculations have been employed to determine the IR emission features of PAHs which are further compared with observations in order to test any correlations present. The important results obtained in this thesis are summarized below:

1. In chapter 2, we have proposed deuteronated PAH ($DPAH^+$) molecules as a potential carrier of the 4.4 and 4.65 μm mid-infrared emission bands that have been observationally detected towards the Orion and M17 regions [5, 6]. Similar features have also been observed towards a few H II regions in the Milky Way by Doney et al. [168]. The vibrational spectra of $DPAH^+$ have been compared with those of the corresponding neutral, cationic, deuterated and protonated forms and it is found that $DPAH^+$ molecules show a weak feature near 4.65 μm that arises due to the stretching of the aliphatic C-D bond. Deuterated PAHs have been previously reported as carriers for such features [5]. Preferred conditions of ionization of PAHs in the ISM indicates the possibility of the formation of $DPAH^+$ molecules. These molecules can potentially be an efficient

reservoir of interstellar deuterium and their existence in the ISM is supported by a 'Deuterium Depletion Model' [15]. Comparison of band positions of DPAH$^+$s shows reasonable agreement with the observations [5, 6]. With increasing size of DPAH$^+$, the aliphatic C-D$_{\text{stretching}}$ approaches the observed position of 4.65 μm. This study also reports a $[\text{D/H}]_{\text{sc}}$ that is decreasing with the increasing size of DPAH$^+$s. It is noted that large DPAH$^+$ molecules (number of C atoms ∼50) match the D/H ratio that has been estimated from observations by *ISO* [5]. This ratio offers prospects to study the deuterium abundance and depletion in the ISM.

2. Taking into consideration the deuterium depletion on to interstellar PAHs, possible forms of deuterium containing ovalene ($C_{32}H_{14}$) variants are studied in chapter 3. An emission model has been used in this chapter for a direct comparison with the observed mid-infrared emission spectra. Similar to previously suggested DPAH$^+$ (chapter 2); deuterated ovalene, cationic deuterated ovalene, deuteronated ovalene and deuterated-deuteronated ovalene also show good agreement with the observed positions of 4.4 and 4.65 μm mid-infrared emission bands. On comparing the $[\text{D/H}]_{\text{sc}}$ obtained for the sample molecules in chapter 2 and chapter 3, deuteronated ovalene and deuteronated circumcoronene agree with the *ISO* observations of Peeters et al. [5]. *AKARI* observations propose comparatively large PAHs (number of C atoms ∼100) with low deuterium content.

3. In chapter 4, we have considered PAHs with aliphatic components to study their infrared characteristics. The aliphatic components can exist in the form of functional groups like, -H (hydrogenated), -CH_3 (methyl), -CH_2-CH_3 (ethyl), -CH=CH_2 (vinyl), etc., in PAHs. These type of molecules might be abundantly present in benign environments of the ISM where the strength of the UV rays is not sufficient enough to completely destroy them. The stretching of the aliphatic C-H band appears at 3.5 μm and as the aliphatic C-H chain in the functional group increases, the feature is blueshifted to 3.4 μm with the appearance of additional sub features forming a

plateau. The 3.4 μm is a well known UIR feature observed towards diffuse ISM, protoplanetary nebulae, reflection nebulae, etc. Many a times, a broad plateau accompanies the 3.4 μm with sub components particularly at 3.46, 3.51 and 3.56 μm [205, 194]. PAHs with aliphatic functional groups may explain the observed extended plateau around 3.4 μm. On substituting one of the H atoms in the functional group with D, another important feature near 4.6 μm arises due to the aliphatic C-$D_{\mathrm{stretching}}$. This provides theoretical explanation for the observed feature at 4.65 μm by *ISO* and *AKARI* [5, 6]. The $[D/H]_{sc}$ computed for the sample molecules however are comparatively large and suggest that consideration of aliphatic components attached to large size PAHs might produce a $[D/H]_{sc}$ that agrees well with the observed D/H ratio.

4. Formation of ionized PAHs (anions and cations) is favourable in the extreme conditions of the ISM. Besides in their pure form, PAHs are also likely to exist in substituted forms; for example, PAHs with functional groups, dehydrogenated PAHs, etc. In chapter 5, vibrational characteristics of an alternative form of PAH, dehydrogenated PAH anion is studied. Spectroscopic features unique to dehydrogenated PAH anions are highlighted. The results suggest that dehydrogenated PAH anions might be significantly contributing to the 3.3 μm region. In the course of successive dehydrogenation, a duo C-H unit gets converted to solo C-H unit, the stretching of which produces a 3.4 μm. The observed 3.4 μm is however usually attributed to arise from aliphatic units in PAHs as described in chapter 4. Other important features obtained for dehydrogenated PAH anions are 5.2 and 5.8 μm due to the stretching of the free C-C/C-C-C units and a broad plateau in the 20-30 μm region due to C-C-C in-plane modes. The plateau becomes significant with increasing size. These spectral characteristics may be used for their possible identification in the ISM.

In broader context, the results demonstrated in the thesis indicate that a few PAH variants are prospective candidate carriers for some of the observed UIR features, if not all. These molecules agree well with some of the observed UIRs in terms of both positions and intensities. Based on this theoretical study, sample PAHs might be selected for sophisticated laboratory experiments which is a requisite in order to firmly assign carriers for the observed UIRs.

6.2 Future Prospects

The current scenario of research in interstellar PAHs has opened up new prospects. With the advancement in experimental and theoretical methodology and high resolution space observations, it is likely that PAH identification in the ISM is possible in the coming future. In continuation of the current work, we would like to explore the following issues in future:

1. In the observational search of deuterated PAHs in some sources, the spectral signatures at 4.4 and 4.65 μm are detected with much weaker intensity which makes it difficult to investigate deuterated PAHs from these lines with high certainty. In such a scenario, any profile variation, if present is desired which may act as an alternative method to estimate the abundance of deuterated PAHs in the ISM. In order to investigate any such existing profile variation in detail, we have obtained SUBARU/COMICS data of sources that have high deuterium content. The sources include NGC1333-IRAS4A (young stellar object), G75.893+0.343 (HII region) and MWC1080 (Herbig Be/Ae star). This observation was part of our existing collaboration with Dr. Itsuki Sakon, University of Tokyo. Analysis of these data give insights to deuterium abundance in the ISM and its depletion on to PAHs.

2. The recent detection of fullerenes [9, 10] indicate the possible presence of five-member ring PAHs which might be an intermediate product in the formation process of fullerene from a PAH molecule. The study of infrared characteristics of five-member ring PAHs can be interesting to seek any observational spectral evidence of these molecules in the ISM.

3. Recently, an aromatic molecule with nitrile group (-C≡N), i.e., Benzonitrile has been proposed to be present in the molecular cloud TMC-1 [33]. We plan to carry out theoretical DFT calculations for nitrogen-included PAHs, for example Polycyclic Aromatic Nitrogen Heterocycle (PANH), PAH with nitrile group (-C≡N) and amine group to study their infrared spectral properties in relation to the observed UIR bands.

4. In the present day research, people seek to understand the origin of building blocks of life; a popular research termed as 'Astrobiology'. PAH molecules might also contain a prebiotic component which may transform into a prebiotic molecule as a course of some interstellar chemical processes. PAH identification may act as an input to understand the formation/destruction mechanism of the prebiotic molecules and how life may have been created from these molecules.

6.2.1 Alternative applications of PAHs

Not only is the study of PAHs important in molecular astrophysics, but also in environmental science and optoelectronics. PAHs are found in form of soot or tar deposits on earth. They are formed in the combustion of carbonaceous fuels and are found in auto exhaust, cigarette smoke, candle soot and burned food items, etc. Environmental PAHs are regarded as highly carcinogenic and its impact on our environment has been extensively studied [237]. Menzie et al. [237] measured concentrations of carcinogenic PAHs in food items and also in environmental media. This information is very helpful for applications in health sciences. PAHs in the environment are subjected to various chemical and photochemical processes some of which result in degradation to less toxic products, while others result in formation of compounds, such as nitrosubstituted PAHs, which exhibit greater carcinogenicity. In that scenario, it is crucial to know the chemistry pathways of environmental PAHs and their effects in our surrounding environment. DFT can be useful to know the reaction mechanism of environmental PAHs. In order to remove these environmental pollutants, several different remediation technologies have been discussed recently [238].

Graphene has been an attractive area of research in optoelectronics due to its rich optical and electronic properties [239] and are widely used in making optoelectronics and semiconducting devices. The optical properties of graphene afford multiple functions of signal emitting, transmitting, modulating, etc. It is a sheet of a one-atom-thick layer of carbon atoms that might be an alternate form of PAH molecule. Different forms of PAHs including dehydrogenated PAHs have been used to develop high quality large area Graphene [240]. Because of the usefulness of graphene, study of optoelectronic property of PAHs by DFT in relation to graphene attracts researchers.