

Abstract

Over the last three decades, study of the Unidentified Infrared (UIR) emission bands in the Interstellar Medium (ISM) has emerged as one of the acclaimed topics of research in molecular Astrophysics and Astrochemistry. These bands, also known as Aromatic Infrared Bands (AIBs) are broad emission features with major bands at 3.3, 6.2, 7.7, 8.6, 11.2 and 12.7 μm that are frequently observed towards a diverse source of astrophysical objects [2]. Since its first discovery, a quest for its carrier has led to a trail of ongoing research. According to the PAH-UIR hypothesis that was first proposed by Léger and Puget[7] and by Allamandola et al. [8], these features arise as a result of fluorescence of polycyclic aromatic hydrocarbon (PAH) molecules on being irradiated by UV photons in the ISM. PAHs are widely distributed free flying gas phase molecules in the ISM that constitute a major fraction of the total interstellar dust and account for about 5-10 % of interstellar carbon in the ISM [2]. Apart from being proposed carriers of the mid-IR bands, PAHs have other roles towards physical and chemical characteristics of the ISM, say heating of the ISM and charge balance inside the molecular clouds [2]. Other interstellar phenomenon, like Diffuse Interstellar Bands (DIBs), Extended Red Emission, UV bump at 217.5 nm etc. are also proposed to arise due to the presence of PAHs in the ISM. According to a recent study, for cosmic fullerenes [9, 10] which are recently detected in the ISM with observational evidence, PAHs are proposed as a key component towards their formation [11].

Chapter 1 presents an introduction to the thesis title, objectives and methodology that is used for this research. Despite the wide acceptance of PAH-UIR hypothesis, though the elementary structure of the UIR carrier is similar to a PAH molecule, the exact composition, size and nature of the carrier is still not known. The profile variation in the UIR bands

in terms of position, width, intensity indicate a variation in the observed astrophysical environment and also the carriers present in it. Several laboratory and theoretical approaches have been undertaken which is further compared with observations in order to distinguish carriers for the respective bands. Current research indicates a widely distributed family of PAH molecules rather than a single form that can explain some of the observed bands if not all. With increasing number of detections of UIR bands towards various astrophysical sources, it is crucial to understand the characteristics of its carriers. In this thesis, we propose the study of spectral characteristics of PAH molecules and its variants in order to investigate the forms of UIR carriers. The formation and abundance of interstellar PAHs are also discussed. The research is carried out using Density Functional Theory (DFT) method that is highly recommended to study the spectral properties of molecules of different size groups and different forms [12, and references therein]. Software programs, **GAMESS** [13] and **QChem** [14] have been used to perform the computational calculation in this research.

In **chapter 2**, we introduce a new form of interstellar PAH molecule; deuterated PAH (DPAH⁺) that might be a potential carrier of the recently detected 4.4 and 4.65 μm mid infrared emission bands. DPAH⁺ produces characteristics bands at 4.4 and 4.65 μm due to aromatic and aliphatic C-D stretching respectively. The presence of DPAH⁺ in the ISM is supported by a ‘Deuterium Depletion Model’ by Draine [15]. DFT has been applied to compute the infrared spectra of DPAH⁺ of different size groups. The theoretically obtained spectra of DPAH⁺s is compared with their respective neutral, ionized and protonated forms. A D/H ratio is also measured from the sample molecules to compare with observations. The comparison indicates that large DPAH⁺s give a D/H ratio which shows better agreement with observations compared to small size DPAH⁺s.

Chapter 3 presents a follow-up of chapter 2. In continuation to the

work presented in chapter 2, we extend the sample to other possible variants of deuterium containing PAHs. An emission model is employed for a direct comparison with the observed emission spectra. The results comprise of emission spectra of the sample molecules that show the 4.4 and 4.65 μm similar to that obtained in Chapter 2. We calculate a D/H ratio of the sample molecules which is compared with the previous results and observations. The results indicate a decrease in the estimated ratio of D/H with increasing size.

Some interstellar PAHs are identified to carry an aliphatic component that gives rise to 3.4 μm feature near the aromatic 3.3 μm feature. The 3.3 and 3.4 μm features are characteristics of stretching of an aromatic and aliphatic C-H bond in a PAH molecule. In **chapter 4**, we consider PAH molecules with aliphatic side groups to see any spectral similarities with the observed UIR features. This chapter reports DFT calculations of PAHs with -H, -CH₃, -CH₂-CH₃, -CH=CH₂ to determine the expected region of emission features. We also include a deuterium (D) component in the aliphatic side group to see any possible consequences. We present a detailed analysis of the IR spectra of these molecules and discuss the possible astrophysical implications.

Depending upon the local physical environment, interstellar PAHs may even exist in ionized forms rather than being in its neutral form. Formation of ionized PAHs (anions and cations) is favourable in the extreme conditions of the ISM. The recent detections of cosmic fullerenes [9, 10] supports the presence of another important and possible form of PAH; a dehydrogenated PAH. As a consequence of the interstellar chemical processes, modified forms of highly suggested PAHs are always possible. One such form is a dehydrogenated PAH anion molecule. **Chapter 5** presents DFT calculations on dehydrogenated PAH anions to explore the infrared emission spectra of these molecules and discuss any possible contribution towards the observed IR features in the ISM. The results suggest

that dehydrogenated PAH anions might be significantly contributing to the 3.3 μm region. Spectroscopic features unique to dehydrogenated PAH anions are highlighted that may be used for their possible identification in the ISM. A comparison has also been made to see the size effect on spectra of these PAHs.

Chapter 6 summarizes the results discussed in the previous chapters. The thesis draws a conclusion that rather than a single PAH form, PAHs of different size groups, different charge states along with PAHs with different functional groups can explain some of the observed major/minor bands, if not all. The proposed molecules can be equally important similar to the previously suggested candidate carriers. This study can be used to select sample molecules for sophisticated experimental studies which will help to list potential candidate carriers of UIR bands. One important outcome of the thesis is the newly introduced Deuteronated PAHs (DPAH⁺s) which may give explanation of the present lower value of D/H in the interstellar gas. However, to estimate the deuterium abundance in the ISM from PAHs, we seek more observational study of sources that are rich with deuterium content. In continuation to the current research, in chapter 6, we also report a *SUBARU* spectra of young stellar objects and HII regions that have been identified with interstellar deuterium in it. This observation was part of our existing collaboration with Dr. Itsuki Sakon, University of Tokyo. The analysis is still in process and will be discussed in detail in future.