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Polycyclic aromatic hydrocarbons in interstellar medium

Shantanu Rastogi*
Physics Department, D.D.U. Gorakhpur University, Gorakhpur 273 009, India

Abstract. Polycyclic Aromatic Hydrocarbons (PAHs) are an important component of the Interstellar Medium (ISM). They are being used as probes for understanding of process and conditions of different astrophysical environments. The understanding of their IR spectra and its variations with PAH size and ionization state is useful in characterizing the ISM. Spectral features of model graphene sheets and also that of smaller PAH molecules are reported. The variation of intensity with charge state of the molecule shows that cations give a better correlation with observations. The relationship between changes in charge distribution with intensity changes upon ionization has been probed.

Keywords : PAH, Aromatic Infrared Bands, Interstellar Medium

1. Introduction

The infrared emission bands at 3030, 1613, 1299, 1163, 893 and 787 cm^{-1} (3.3, 6.2, 7.7, 8.6, 11.2 and 12.7 μm), observed in a variety of astrophysical objects, were first reported by Gillett et al., (1973). Initially termed as Unidentified Infrared (UIR) bands, these features were identified to be emissions from small grains of Polycyclic Aromatic Hydrocarbons (PAHs) by Leger and Puget (1984) and Allamandola et al., (1985). These Aromatic Infrared bands (AIBs) appear in diverse sources: planetary nebulae, reflection nebulae, photo-dissociation regions, transition objects, H II regions, novae, the galactic disk, and even extragalactic sources such as irregular, starburst and ultra-luminous galaxies (First Infrared Space Observatory (ISO) results 1996) indicating widespread presence of PAHs in the ISM.

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*e-mail: shantanu_r@hotmail.com

PAHs efficiently absorb the background UV radiation to reach excited states up to 1000 K. Inter-system crossings and redistribution of energy over available vibrational modes result in IR emissions. In a population of emitters, each unique signature blends into a composite spectrum representative of the whole family. This makes identification of a specific PAH difficult. PAHs co-evolve with the surrounding ISM causing structural and charge state variations. This in turn leads to source to source variations in the intensity and width of AIBs. Modeling of a composite spectra using combination of several neutral and ionized PAHs to fit the observed spectra has shown that more cations are present in harsh environments of star forming regions while a mixture of neutrals and cations in benign environments of Proto planetary-nebula (Allamandola et al., 1999).

Large scale distribution of PAHs in the ISM point towards explanation of other astrophysical problems. PAHs seem to be partially responsible for the UV extinction bump at 217 *nm* (Clayton et al., 2003) and are also considered to be strong candidates for the carriers of Diffuse Interstellar Bands (DIBs) (Tielens and Snow 1995) which are emission features superimposed on the interstellar extinction curve.

2. Laboratory techniques

The PAH hypothesis follows from comparisons of the observed spectra with laboratory spectra of PAH molecules. While infrared bands reflect only on the Aromatic nature of the source molecules, electronic bands are molecule specific. Matching of PAH electronic transition with a DIB shall not only solve the DIB carrier mystery but also lead to identification of specific PAH present in the ISM. To make meaningful comparisons laboratory spectra must be taken in conditions close to interstellar i.e. isolated molecules at low temperatures. Matrix isolation study, in which PAH molecule is trapped and condensed in an inert gas matrix to mimic isolation, shows that PAH cations absorb in visible and near IR region and a close correlation with several DIBs is proposed (Salama et al., 1999).

A useful method is Cavity ring down spectroscopy (CRDS) (O'Keefe et al., 1990). It is a direct gas phase absorption technique which simulates the low density ISM conditions and there are no matrix interaction shifts. The pulse from a tunable laser is injected into a cavity consisting of mirrors of very high reflectivity and photons exiting from one end are detected after every pass (Fig. 1). First the decay of output intensity is measured in an empty cavity and then in cavity with sample. The difference in the ring-down times gives absorbance. The lower the sample concentration the lesser will be the absorption per pass and thus results in a more accurate measurement of ring-down time and absorbance. High reflectivity of cavity mirrors lead to long path lengths ($\sim$ 10 Km) and high resolution. This basic setup is used to study UV spectra of neutral Pyrene (Rouillé et al., 2004). For the study of PAH cations, the PAH under study must be injected through a discharge for ionization (Sukhorukov et al., 2004).

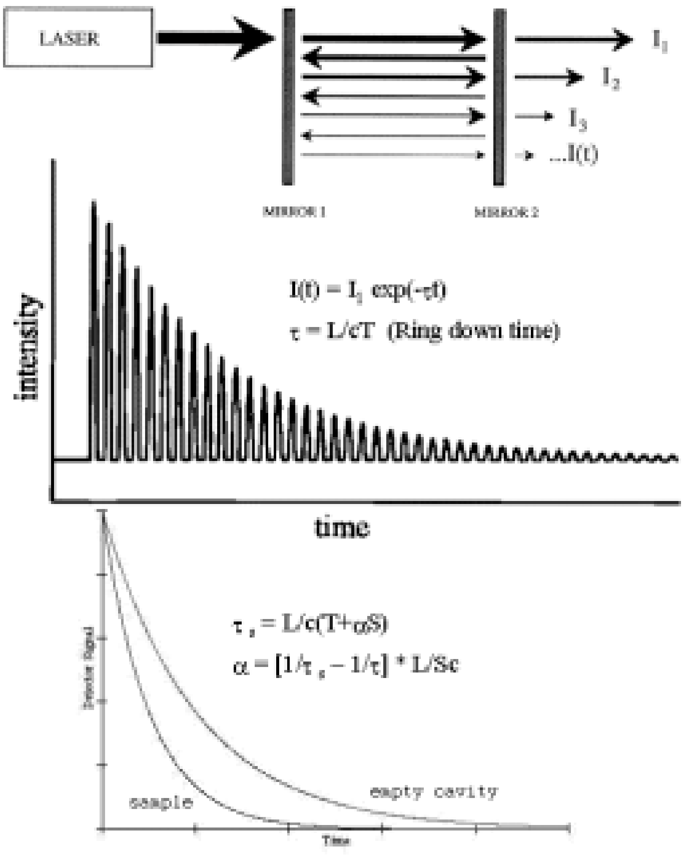

Figure 1. Cavity Ring down spectroscopy scheme.

3. Theoretical studies

3.1 Graphene sheet models

PAHs are extremely stable and up to 96 Carbon atoms can have planar structure. Normal vibrational analysis is performed for infinitely long graphene sheet models (Fig. 2) to unravel the features of its oligomers (finite length basic units). The polymeric calculation method (Rastogi and Gupta 1995) give dispersion curves and their slope is used to get the density of states. For the model sheets (Fig. 3) the density of state peaks, which are observable modes, correspond well with AIBs. The broad 7.7 μm (1300 cm^{-1}) AIB feature assigned to (C-C) stretch mode resolves to 1320 & 1280 cm^{-1}. The density of state regions peaks at 1345 & 1253 cm^{-1} (model-1 & 2) and at 1335, 1310 & 1265 cm^{-1}

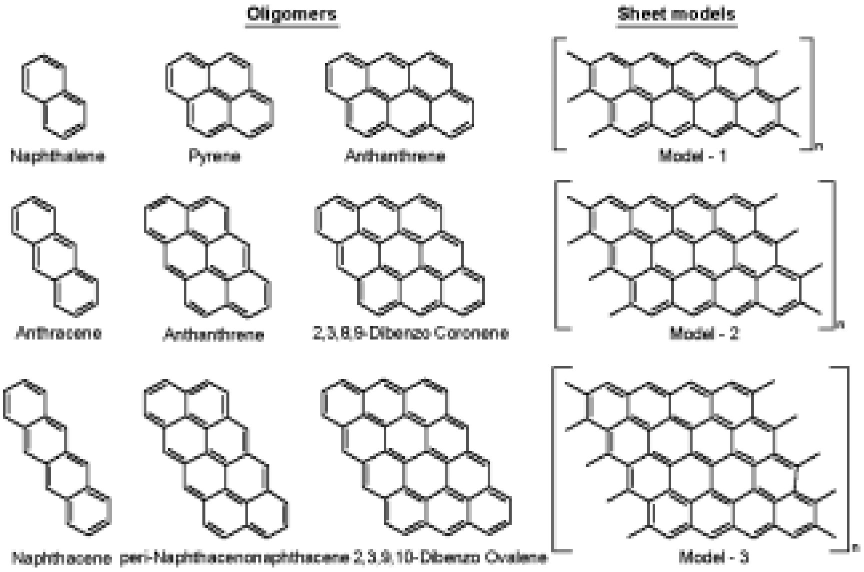

Figure 2. Graphene infinite sheet models.

(model-3). This mode couples with (C-H) in plane bend and appears at very different positions ranging from 1260 - 1330 cm^{-1} in different molecular forms. The width and complexity of this feature increases with size of PAH, as in model-3.

To study stochastic heating of small grains in the ISM vibrational spectra is approximated using information of graphite and smaller molecules. Heat capacity obtained from density of state information of model sheets provides exact vibrational data. Besides density of states IR spectra also depend on the symmetry and selection rules. So study of specific PAHs is also essential.

3.2 Small molecules ab-initio study

PAHs in space are expected to be larger than the ones available or feasible for experimental studies. Theoretical quantum chemical calculations can provide IR spectral information for such systems. The authors have performed ab-initio calculations using General Atomic and Molecular Electronic Structure System (GAMESS) program (Schmidt et al., 1993). The B3LYP Density Functional Theory (DFT) is used in conjunction with 431G-basis set expansion. The prominent features in the spectra of neutral PAHs are due to (C-H) stretch and (C-H) wag motions, while for PAH cations (C-C) stretch and (C-H) in plane modes are the most intense. This is evident in the examples shown in Fig. 4. The AIBs

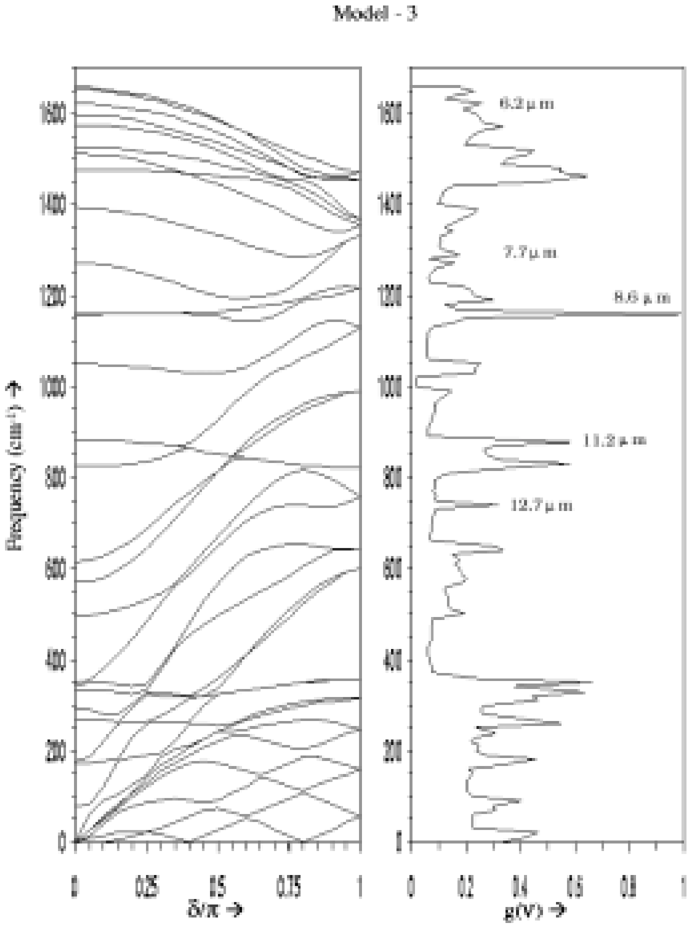

Figure 3. Dispersion Curves and density of states for model-3.

correlate better with cations than neutrals showing that significant number of PAHs in ISM should be in ionized state.

The effects of ionization on the IR spectra is correlated with the atomic charge distribution to elucidate the underlying cause of the variations induced by charging. Change in charge on C atoms results in increase in intensity of 1200 - 1600 cm^{-1} modes and the (C-H) stretch intensity depends on partial charge on the peripheral H atom. Both are clearly demonstrated for Naphthalene anion, neutral and cation in Fig. 5. The charge

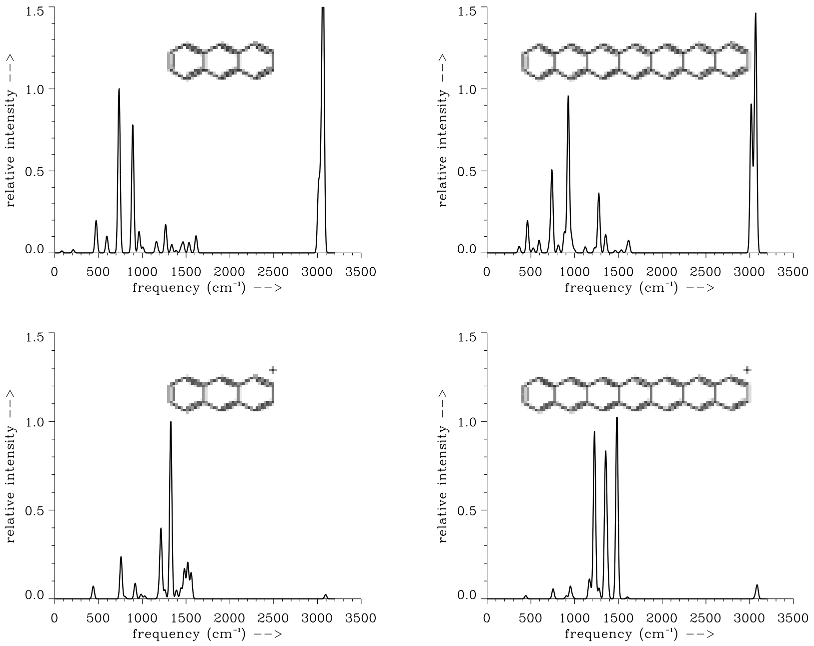

Figure 4. Computed spectra in neutral and cationic forms of Anthracene & Heptacene.

on H atoms is least positive (0.04) in anion, becomes more positive in neutral (0.13) and cation (0.21) while absolute intensity of (C-H) stretch mode follows a reverse trend.

Study of spectral variation with PAH size and charge state (Pathak and Rastogi 2005) show that for linear catacondensed PAHs both frequency and intensity shifts do not correlate well with observations. Thus large non-linear and pericondensed PAHs seem more likely to be present in the ISM.

4. Astrophysical applications

The IR spectral information of PAHs is proving useful in understanding AIBs and probing conditions within Astrophysical objects. There are distinct PAH populations and therefore distinct AIB features for star forming regions and circumstellar shells of late type stars (Peeters et al., 2004 and references therein). The 6.2 μm band profile points to pure Carbon PAH populations in post AGB stars, Planetary-nebulae (PNe) and isolated Herbig AeBe stars while presence of substituted or complexed PAHs is indicated in HII regions, Reflection Nebulae, non-isolated Herbig AeBe stars and galaxies. The

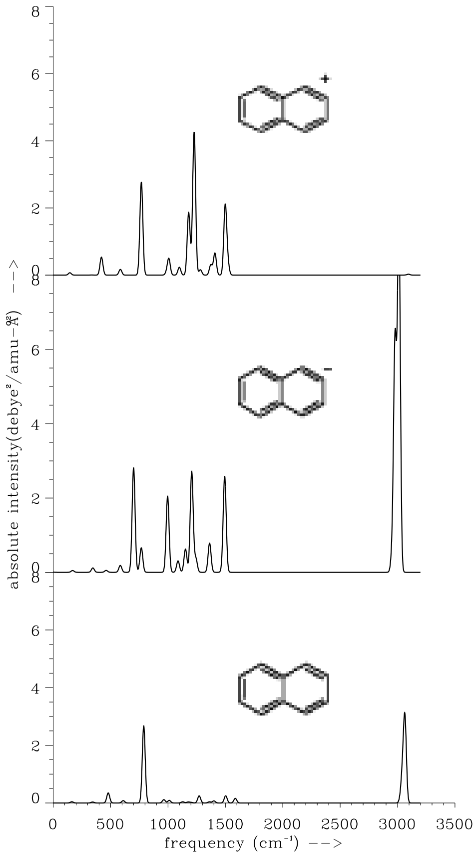

Figure 5. Computed spectra of Naphthalene neutral, anion and cation.

7.7 μm complex appears with a dominant 7.6 or a 7.8 - 8.0 μm component. The 7.6 μm component is associated with HII regions and the 7.8 μm with PNe. Ratio of AIB features remain generally uniform in Galaxies. Using the 7.7 μm line to continuum ratio as AIB strength, a good way to distinguish AGNs and starbursts was proposed by Peeters et al., 2002. Study of 11.2 μm feature in Carbon stars (Hony et al., 2001) shows that before the PNe stage begins population of species is in favour of C-O molecules. As the PNe stage develops PAHs excitation progresses and dominate the spectrum. PAH - AIB understanding is now a useful tracer of chemical evolution and a probe for astrophysical environments.

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