



Study of substituted polycyclic aromatic hydrocarbons of astrophysical relevance

Shantanu Rastogi, Anju Maurya and Rashmi Singh

Department of Physics, DDU Gorakhpur University
Gorakhpur – 273 009, India

The ubiquitous mid-infrared emission features, prominently obtained at 3030, 1613, 1299, 1163, 893 and 787 cm^{-1} (3.3, 6.2, 7.7, 8.6, 11.2 and 12.7 μm) generally match the vibrational modes of aromatic hydrocarbons. The composite spectra of mixtures of polycyclic aromatic hydrocarbon (PAH) molecules have been shown to match well with the observational features. Closer inspection and source to source variations in peak positions and line shapes however, create complications. Various size and ionization states of PAHs need to be considered and this can vary for different sources. Thus the study of infrared spectra of PAHs gains significance for not only understanding the composition of the spectral source but also for giving insight into the physical and chemical evolution of the source. Studies show that more ionized and midsized PAHs seem possible in hot star forming regions and larger PAHs in benign regions of late type stars. Further, there is problem in simultaneous fitting of all the bands, originating along a definite sightline, by the same set of PAHs. In particular, for the 6.2 μm feature, most of the plain PAH combinations do not give a good fit. In order to address this issue and to understand other spectral properties, substituted PAHs are studied. PAHs having vinyl or phenyl as side group attachments are considered and their infrared spectra reported. Various PAHs are considered with the side group substitution at different positions. The spectral variations are studied and the possibility of including small compact substituted PAHs to improve models is discussed. © Anita Publications. All rights reserved.

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1 Introduction

The mid-infrared emission features, prominently obtained at 3030, 1613, 1299, 1163, 893 and 787 cm^{-1} (3.3, 6.2, 7.7, 8.6, 11.2 and 12.7 μm), are observed ubiquitously along different astrophysical objects [1 - 4]. These features are obtained along planetary nebulae, reflection nebulae, transition objects, novae, the galactic disk, and even in external galaxies [5]. Initially, when no source could be attributed to these emission bands, they were termed as unidentified infrared bands (UIB). Among several possibilities carbonaceous grains were considered but the high feature-to-continuum ratio indicated a molecular rather than solid-state origin. Early thermal emission model showed that very small grains ($\sim 10 \text{ \AA}$) undergoing thermal fluctuations could explain the 3.3 μm feature [6]. Similar model could be applied to large molecules and considering that these features usually appear together and correspond to vibrational transitions in aromatic moieties pointed to the fact that stable polycyclic aromatic hydrocarbon (PAH) molecules must be the source of these infrared bands [7, 8]. PAHs are fused benzene rings, some representative structures are shown in the first column of Fig 1. They have large absorption cross section for ultraviolet radiation and small heat capacity. The infrared emission from such large molecules is attributed to a process where a PAH first absorbs an ultraviolet photon and is electronically excited. In the sparse, near vacuum and collision-less, interstellar medium (ISM), this is followed by an inter-system crossing and/or internal conversion, to bring the PAH to a high vibrationally excited state in the ground electronic level. From this high vibration state the hot molecule cascades down, one level at a time, to reach the ground state by emitting infrared radiations in each step. These emissions in the cooling down process are referred to as infrared fluorescence and is now recognized as the PAH hypothesis [5, 9, 10]. Over the years, satellite observations, first from IRAS, then ISO and SPITZER, along with laboratory experiments and theoretical considerations of the PAH hypothesis, have all led to a better understanding of the physical and chemical compositions of various astrophysical sources. Very useful insights into the possible nature of PAHs and their evolution in different environments are obtained.

Corresponding author :

e-mail: shantanu_r@hotmail.com (Shantanu Rastogi)

Right from the beginning of the PAH hypothesis it was understood that identification of any specific PAH by matching the mid-infrared bands was not possible as the observed bands are generic vibrational modes in aromatic molecules. Thus the observations suggest the presence of families of PAH molecules and the bands are now often referred to as the aromatic infrared bands (AIBs). For specific identification electronic or radio observations are necessary. Being symmetric molecular systems they do not have permanent dipole moment, so seeing PAHs in the radio frequencies for rotational transitions is also not possible. Despite these hurdles, comparisons of the observed astrophysical spectra with models of composite spectrum from groups of PAHs has led to improved understanding of the conditions in the ISM and also regarding PAH formation and evolution.

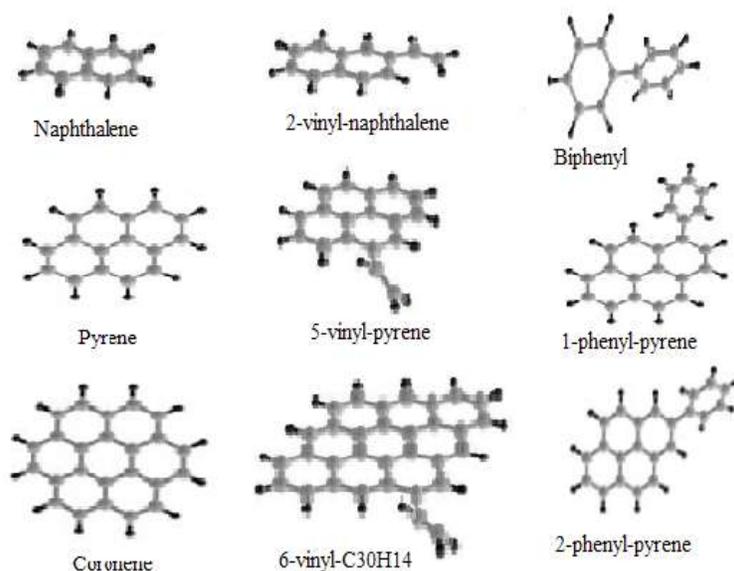


Fig 1. PAH molecules: plain PAHs, vinyl-PAHs and phenyl-PAHs in different columns

Observations of AIB intensity variations between sources and also variations in relative intensities among AIBs have been found to be well correlated with object types. These variations could be due to different background excitation energies provided by different objects and also due to the difference in the molecular species that can survive in corresponding environment. A classification scheme for AIB types related to their peak positions, intensity and width has been developed [11,12] and linked to the type of astrophysical source. This has made observation of AIBs a diagnostic to understand source object type. The frequency range about 10 - 13 μm consists of C-H out-of-plane solo, duo, trio and quarto vibrations that depend on the number of hydrogen atoms in the peripheral rings [13]. Observations thus give indications of the possible peripheral structure of PAHs in the ISM. This and the intensity ratio of various bands indicate the size of possible PAHs [5].

Most of the astrophysical objects show strong features in the 6 - 8 μm spectral region, while laboratory infrared spectra of PAHs have weak features in this range. PAH ions however have strong features in the 6 - 8 μm range and very weak 3.3 μm feature. This fact and the energetics of the AIB sources, point to the possibility of PAHs in the ISM to be mostly in ionized state. Modelling spectra to fit the observations with laboratory spectra [14] and several computational studies [15 - 22] indicate more ionized species in harsh UV environments and a mixture of neutral and ionized PAHs in benign circumstellar shells of late type stars. Specific source modelling of the complex 7.7 μm feature with composite computed spectra of plain PAHs pointed towards the presence of large PAHs in benign regions around planetary nebulae and small to medium

sized PAHs in harsh UV-dominated star-forming regions [23]. The computed infrared spectra of PAHs have also been used to directly fit astronomical spectra for determination of PAH abundances [24].

Despite these successes the simultaneous fitting of all AIBs, originating from a specific source, has not been possible. Match is not obtained especially for the 6.2 μm AIB, assigned to aromatic C-C stretching vibration, which falls short by 30 - 40 cm^{-1} in most molecules [23]. This implies that the plain PAHs alone are not sufficient to fully explain the AIBs. More data on PAHs with substitutions, side groups and in different states of hydrogenation is required. Quantum chemical computations have proved useful in predicting infrared spectrum of species that may not always be available in laboratory [15 - 22]. Therefore, PAHs with suitable side groups can be studied using the density functional theory (DFT). Study is performed on different PAHs having vinyl and phenyl side group attachments. Specific molecules reported in the present communication are shown in second and third columns of Fig 1. Infrared spectral properties of these molecules are studied for variations due to substitution at different positions and also to assess their suitability for incorporation in astrophysical emission band models.

2 The vinyl and phenyl PAHs

PAHs are highly stable and may form in space either by "bottom-up" gas phase chemical growth starting with acetylene [25] or by top-down fragmentation of carbonaceous grains [26]. In the former process PAHs with vinyl side group appear as intermediate products. The C=C bond in the side group may scale up the vibrational mode closest to the 6.2 μm AIB. Few molecules with vinyl group have been detected in ISM [27], which augurs the possibility of vinyl-PAHs. Upon defragmentation from carbonaceous grains or even in some growth processes there is possibility of a ring hanging out as a phenyl group in a PAH. Although molecules with phenyl group have not been confirmed in the ISM but benzene itself has been detected in CRL618 [28].

The optimized structures of the vinyl-PAHs under consideration are obtained using DFT (B3LYP/4-31G) [29]. The vinyl-PAHs are so chosen as to represent single, double and triple rows of rings. The structural variation upon substitution of vinyl group and the suitable level of theory required for computations is discussed in the study on vinyl-anthracenes [30]. In single-row PAHs vinyl substitution at position 2, as in 2-vinyl-naphthalene, leaves the molecule planar i.e. both aromatic and vinyl units are nearly in the same plane. The vinyl substitution at any other position in single row and at all positions in multi-row PAHs give non-planar structure. In all such cases the vinyl moiety is out of the plane of the aromatic unit by about 40°. The non-planarity is due to strong steric interaction between H atoms [30].

In the phenyl-PAHs the phenyl moiety is out of plane with respect to the parent PAH in all molecules. In Fig 2 the variation of energy with the torsion angle is shown, clearly defining the minima at torsion angle of about 40° for biphenyl and for substitution at position 2. In 1-phenyl-pyrene though the minima is around 55° but the curve is nearly flat for higher torsion angles. In biphenyl and 2-phenyl-pyrene there is placement symmetry with respect to the aromatic hydrogens, while in 1-phenyl-pyrene there are different steric hindrances for the hydrogen atoms.

The value of the side group torsion angle with respect to the parent plain PAH, for both neutrals and cations of vinyl- and phenyl-PAHs, is shown in Table 1. Upon ionization, in both PAH derivatives, the torsion angle reduces. This could be due to the change in charge distribution on peripheral hydrogens. In vinyl-C₃₀H₁₄ though, due to the large size of the molecule, upon ionization there is very little variation in the charge distribution, and so there is no change in the torsion angle. Table 1 also provides the optimized energies for both neutrals and cations. There is one electron less in the cations, but now the molecules are no longer closed shell systems, so the energy of cations is higher than that of the neutrals. Interestingly the difference in energies upon ionization is nearly 0.25 kcal/mol for all the molecules irrespective of the PAH and substituent side group. This emphasises that the energy change is mainly attributed to the electrons going from closed shell to open shell systems upon ionization.

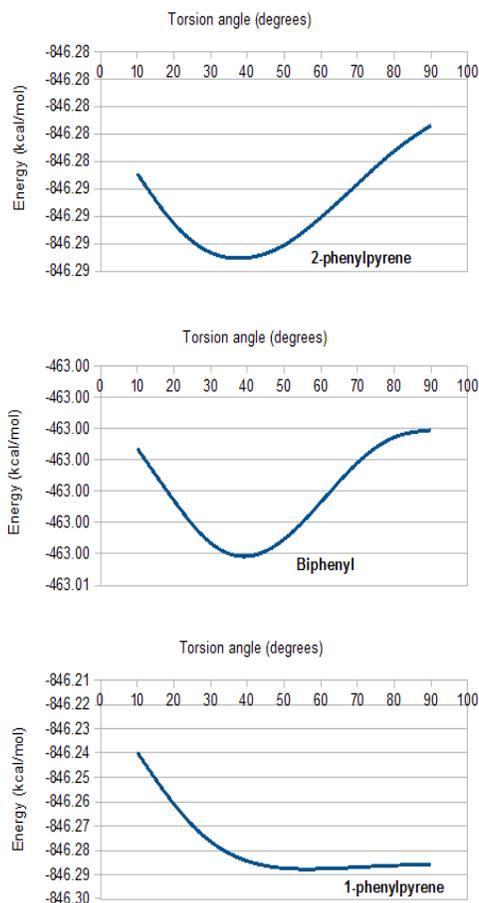


Fig 2. Variation of optimized energy with torsion angle of the phenyl moiety from the PAH plane

Table 1. Optimized energies and torsion angles for the substituted side groups

Molecule	Optimized Energy (kcal/mol)		Torsion angle (°) for vinyl/phenyl group	
	neutral	cation	neutral	cation
2-vinyl-naphthalene	-462.3956121	-462.1289288	01.40	00.60
5-vinyl-pyrene	-691.8299506	-691.5850652	36.00	23.10
6-vinyl-C30H14	-1226.781981	-1226.573023	41.20	41.20
Biphenyl	-463.0040821	-462.7266937	39.09	19.69
1-phenyl-pyrene	-846.2877170	-846.0481901	54.93	46.65
2-phenyl-pyrene	-846.2910842	-846.0439777	38.12	36.44

3 Vibrational spectra

The vibrational spectra are computed for each molecule and its cation in the optimized geometry. In most of the quantum chemical calculations obtained vibrational frequencies are overestimated and must

be scaled down for proper comparison with experimental spectra. The scaling factor depends not only on the frequency but also on the level of theory used [17, 30]. Comparison with experimental data [30] showed very little deviation in frequencies and intensities even at small 4-31G basis set level of calculation. In the absence of experimental results this level of basis set has been considered suitable [17 - 21]. The scaling factor of similar molecules may be transferred and, therefore, the scaling factors derived by Maurya *et al* [30] for 2- and 9-vinyl-anthracene are used in this report. The scaling factor for the C-H stretch range frequencies around 3000 cm^{-1} is different from that used for lower frequency modes [30]. For 2-vinyl-naphthalene that has a nearly planar structure, the scaling factors of planar 2-vinyl-anthracene are taken. For all other vinyl- and phenyl-PAHs the scaling factors of 9-vinyl-anthracene, with out-of-plane side group, are used. The intensities of the calculated vibrational frequencies are scaled relative to the intensity of the most intense band. The infrared spectra are simulated using Lorentzian profile with 5 cm^{-1} full width at half maximum (FWHM) for each calculated mode. The modes that fall closer than 5 cm^{-1} simply collocate together resulting in a feature broader than 5 cm^{-1} .

3.1 Vinyl-PAHs

The spectra of neutral vinyl-PAHs are dominated by C-H stretch and C-H out-of-plane bend modes. While in cations the intensity of C-H in-plane bend and C-C stretch modes ($1150 - 1600\text{ cm}^{-1}$) are increased by an order of magnitude along with reduction in the C-H stretch mode intensity. This is similar to the variations seen in plain PAHs [17 - 21]. The spectra of neutrals and cations of 2-vinyl-naphthalene, 5-vinyl-pyrene and 6-vinyl-C₃₀H₁₄ are presented in Figs 3(a), 3(b) and 3(c), respectively only in the low frequency range from $1700 - 400\text{ cm}^{-1}$. The vertical dotted lines represent positions corresponding to AIBs and in the lower panels spectra of corresponding plain PAHs are shown for comparison. Several features of the plain PAH continue to dominate in vinyl-PAHs but there are a number of additional modes both due to the lowering of symmetry and due to motions in the vinyl moiety.

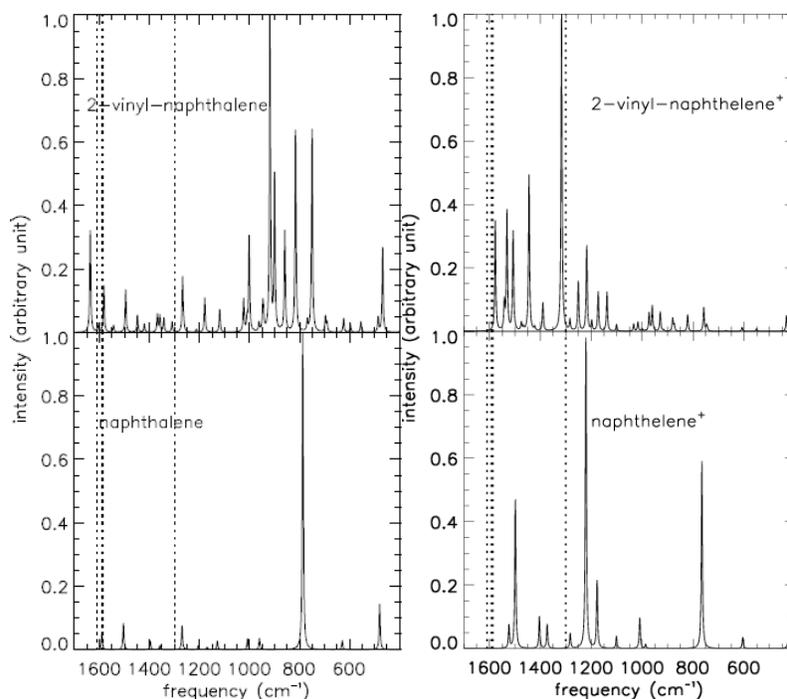


Fig 3(a). Simulated spectra for 2-vinyl-naphthalene neutral and cation in the $400 - 1700\text{ cm}^{-1}$ range; naphthalene in the lower panel shown for comparison.

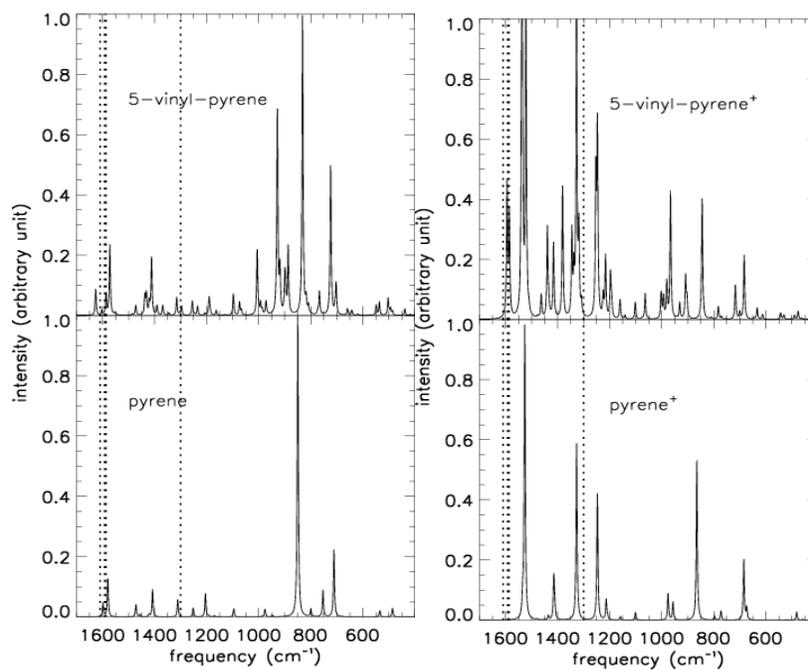


Fig 3(b). Simulated spectra for 5-vinyl-pyrene neutral and cation in the 400 - 1700 cm^{-1} range; pyrene in the lower panel shown for comparison.

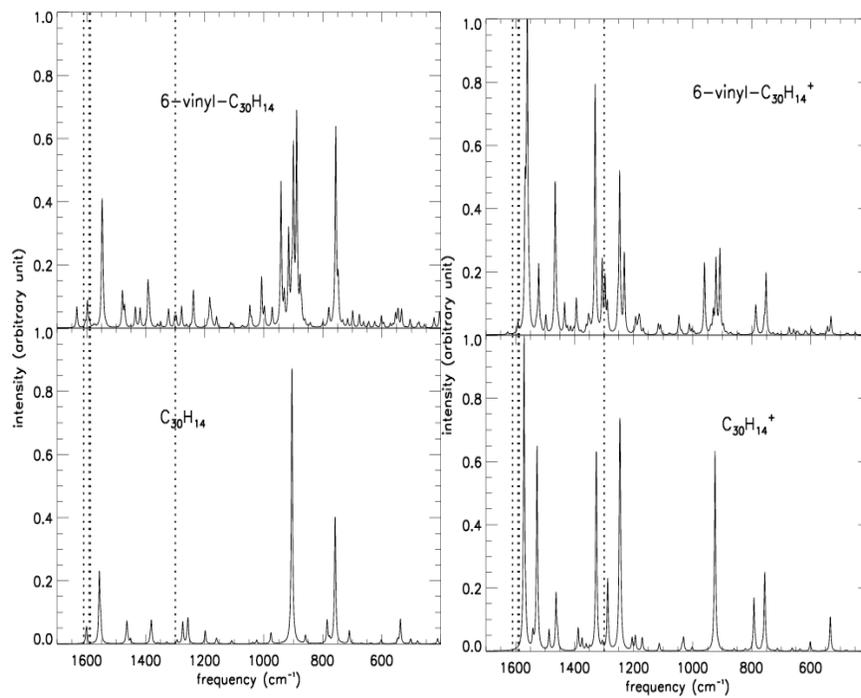


Fig 3(c). Simulated spectra for 6-vinyl-C₃₀H₁₄ neutral and cation in the 400 - 1700 cm^{-1} range; plain C₃₀H₁₄ in the lower panel shown for comparison.

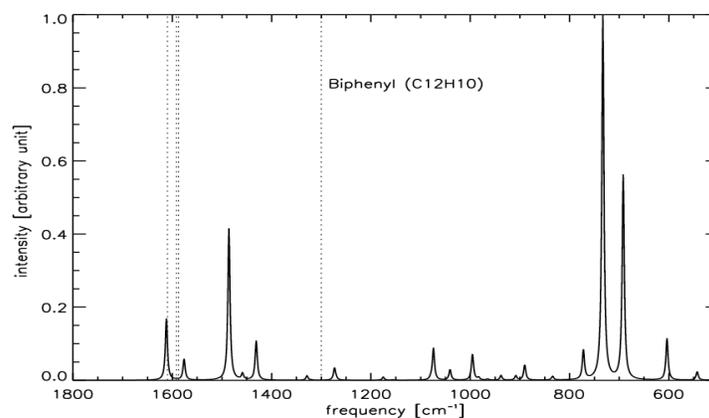
In plain naphthalene there are two quarto groups of hydrogen which give rise to one strong peak. In 2-vinyl-naphthalene the vinyl group is substituted replacing one of the quarto group hydrogen. This disturbs the symmetry and two strong quarto C-H out-of-plane modes appear at 750 and 816 cm^{-1} . The strongest peak in 2-vinyl-naphthalene is the CH_2 wag mode at 918 cm^{-1} . In the cations there are several modes getting active in the 1600 - 1000 cm^{-1} region (Fig 3(a)). In 5-vinyl-pyrene the highest mode at 832 cm^{-1} is due to aromatic C-H out-of-plane vibrations of duo and trio hydrogens, similar to the feature present in plain pyrene. Another medium intensity peak at 724 cm^{-1} is due to similar aromatic C-H out-of-plane motion as in the parent PAH, but the relative intensity is enhanced. The CH_2 wag motion in the vinyl group gives rise to a new intense feature at 930 cm^{-1} . Upon ionization besides other modes an interesting intense feature appears at 1594 cm^{-1} , very close to the AIB at 6.2 μm (Fig 3(b)). In the large triple ring row 6-vinyl-C₃₀H₁₄ molecule the vinyl addition does not cause much change in the main features of the plain PAH (Fig 3(c)).

In neutral vinyl-PAHs there are several intense peaks due to the C-H stretching vibrations, around 3000 cm^{-1} , as in neutral plain PAHs. Upon ionization the drastic suppression of intensity of these modes in vinyl-PAHs is also similar to that in plain PAH cations. Some additional peaks due to the vinyl unit appear in the spectra e.g. the asymmetric vinyl CH_2 stretch mode $\sim 3100 \text{ cm}^{-1}$, is the highest frequency in the spectra of all vinyl-PAHs. The symmetric vinyl CH_2 stretch and the vinyl C-H stretch vibrations are other new modes in this frequency range. There is hardly any mixing of the vibrations of different types of C-H bonds with each other or with the aromatic modes.

3.2 Phenyl-PAHs

The simplest aromatic molecule benzene and the corresponding biphenyl are not exactly PAH but are important as these constitute the simplest forms for bottom-up growth process. Benzene has been discovered along with polyacetylenic chains C_4H_2 and C_6H_2 in the proto-planetary nebula CRL618 [28]. Such objects have already been identified to be possible organic refractory locations and suitable for bottom-up PAH growth [25]. Combustion pyrolysis of hydrocarbons demonstrates the formation of polyphenyls, viz. biphenyl, terphenyls and triphenylene [31, 32], in conditions that are very similar to those around carbon rich circumstellar shells. Study on polyphenyls in the astrophysical context has been attempted earlier [33]. Naturally some features appear to be common with PAHs, but few bands have been identified as typical of polyphenyls [33].

The choice of molecules under study is not polyphenyls but pyrene, the small compact PAH, with phenyl side group at different positions. For completeness and comparison biphenyl is also studied. The infrared spectra of neutral biphenyl and positively charged biphenyl obtained in the present work are shown in Fig 4(a). The obtained frequencies compare well with the earlier reported data [33, 34].



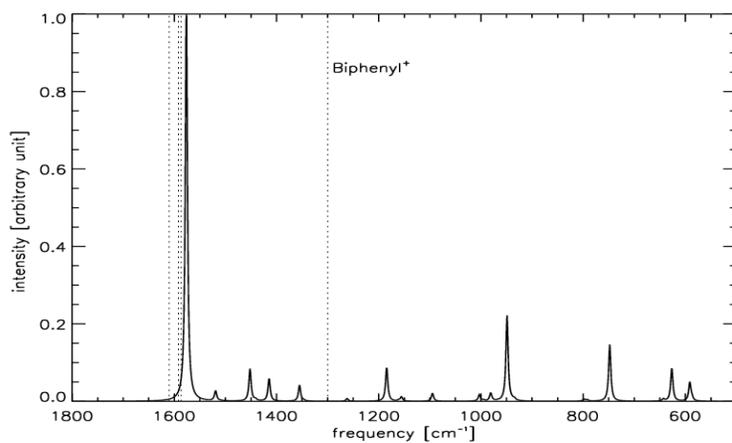


Fig 4(a). Spectra in 1800 – 500 cm⁻¹ range, of neutral biphenyl (upper panel) and its cation (lower panel)

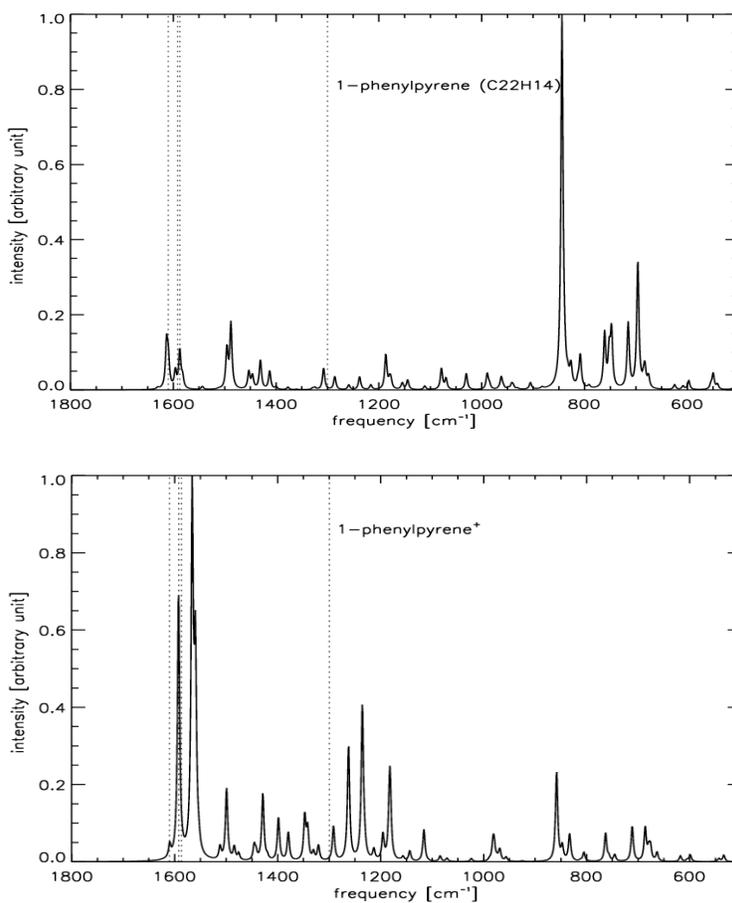


Fig 4(b). Spectra in 1800 – 500 cm⁻¹ range, of neutral 1-phenylpyrene (upper panel) and its cation (lower panel)

The C-H stretching and C-H out-of-plane vibrations appear to be the most intense bands in neutral biphenyl. There are also intense bands at 1612 and 1486 cm^{-1} due to C-C stretch and C-H in-plane bend vibrations. In the cation there is drastic change in the intensity pattern; (i) The C-C stretch mode becomes strong and (ii) the C-H stretch modes become too weak. In neutrals there are two strong C-H out-of-plane modes (733 and 692 cm^{-1}), while in the cations only one mode appears at 748 cm^{-1} . The most intense mode in the cation at 1576 cm^{-1} falls close to the class 'C' AIB at 6.3 μm . In both the neutral and the cation no features appear that can correspond to the 7.7 μm AIB.

Two configurations of phenyl-pyrene are studied to observe any changes in spectral features due to the different substitution position of the phenyl group. It has already been pointed out that in 2-phenyl-pyrene there is symmetric placement of the side group with respect to the neighbouring H atoms, and a clear minima at torsion angle 39° is obtained (Table 1). The 2-phenyl-pyrene configuration is also the more stable (lower energy) and hence the more likely form to exist in the ISM. The spectra of 1-phenyl-pyrene, neutral and cation, are shown in Fig 4(b) and those of 2-phenyl-pyrene, neutral and cation, are shown in Fig 4(c).

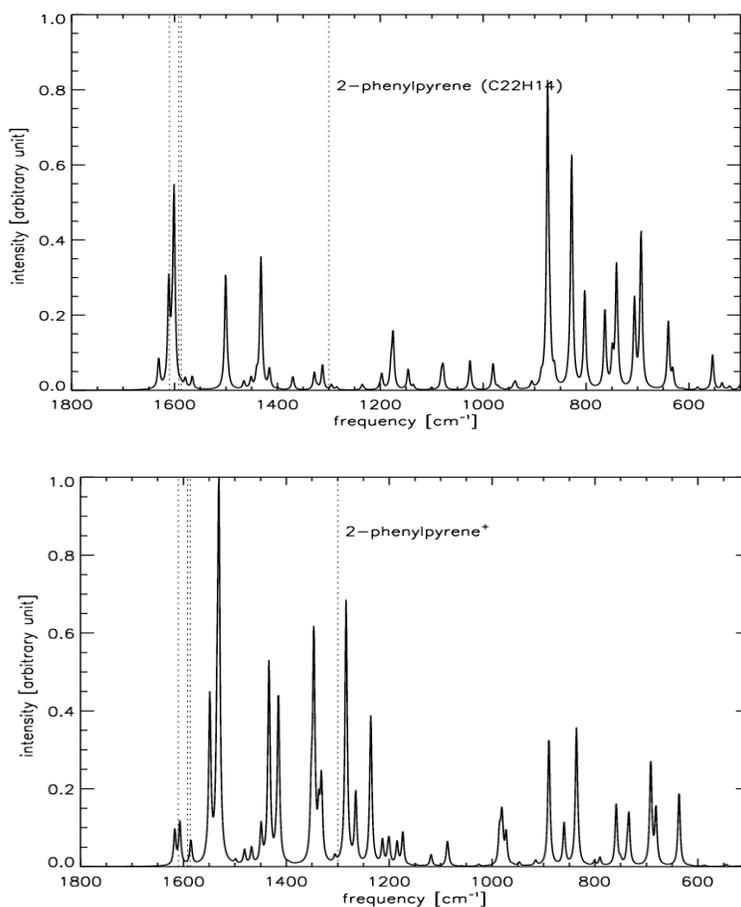


Fig 4(c). Spectra in 1800 – 500 cm^{-1} range, of neutral 2-phenylpyrene (upper panel) and its cation (lower panel)

The spectrum of neutral 1-phenyl-pyrene is typical with strong C-H out-of-plane modes and relatively weak C-C stretch and C-H in-plane bend modes. In the cation several features related to C-C stretch and C-H

in-plane bending vibrations in the 1600 - 1100 cm^{-1} range gain significant intensity. The strongest peak at 1566 cm^{-1} is on the red side of the 6.2 μm AIB, as in most plain PAHs. Other intense band at 1592 cm^{-1} falls close to the class 'C' AIB. Unlike biphenyl some bands, though not matching perfectly, do show up close to the 7.7 μm feature. 2-phenyl-pyrene is more interesting and shows a very rich spectrum, in both neutral and cation (Fig 4(c)). In the neutral, besides several C-H out-of-plane modes between 900 - 700 cm^{-1} , there is a significantly strong peak at 1601 cm^{-1} in the relevant 6.2 μm region. Upon ionization although several bands gain intensity in the 1600 - 1200 cm^{-1} range, the bands close to 1600 cm^{-1} become weak. There are significant peaks that can contribute to the 7.7 μm AIB.

In the higher frequency region of 3000 cm^{-1} , the C-H stretch modes appear with strong intensity only in neutrals. In cations the intensity of these modes is negligible. The number of features in this range depends on the number of hydrogen atoms in the molecule, i.e. 10 in biphenyl and 14 in phenyl-pyrenes. Since all C-H bonds are similar all modes fall very close to each other. A Lorentzian profile model, with FWHM of 5 cm^{-1} , gives a merged band shape where modes collocate together to give the broad profile shown in Fig 5. The profiles are very similar with a few peaks in all three molecules. There is though a small outlier in the spectrum of 1-phenyl-pyrene at 3110 cm^{-1} . This is a higher frequency mode and is due to the vibration of the hindered H atom, at pyrene position 10. In 2-phenyl-pyrene the hydrogen atoms are symmetrically placed with respect to the phenyl group and there is no such mode. The C-H stretch features in plain PAHs also have similar profiles [19-21].

4 Astrophysical aspects

The main focus of the present work is to study the modes appearing near 6.2 μm . These modes are related to C-C stretch vibrations and fall several wavenumbers short of the corresponding AIB in most of the plain PAHs. The intention is to study whether substitution of hydrogen by a vinyl and phenyl group brings this mode any closer to the 6.2 μm feature. On addition of the vinyl group to naphthalene and to pyrene there is a slight increase in the frequency of this mode, but this could be fortuitous as the mode in the larger molecule, 6-vinyl-C30H14, decreases in frequency. The frequency increase in pyrene due to vinyl substitution brings the C-C stretch mode at 1586 cm^{-1} , giving good match to the 'C' type AIB feature [11]. There appears to be a strong feature in cations around 1505 cm^{-1} (6.6 μm), which falls close to an observed 6.66 μm sub-feature along IRAS 18434-0242 [35] and in H2 and seyfert 2 galaxies [36]. This feature is also present in the corresponding plain PAH but is extremely intense in 5-vinyl-pyrene cation. These objects have hot environments and also show a weak feature near 10.5 μm (952 cm^{-1}) that may be fulfilled by the peak at 966 cm^{-1} in 5-vinyl-pyrene.

In biphenyl cation although there is no peak near the 7.7 μm band, but there is an intense peak at 1576 cm^{-1} (6.34 μm) close to the 'C' type AIB [11]. The spectrum of 2-phenyl-pyrene is of astrophysical interest as there is a strong feature peaking at 1601 cm^{-1} (6.25 μm) in the neutral molecule itself. In both the neutral and the cation of 2-phenyl-pyrene there are strong features around 1440 cm^{-1} (~6.9 μm), which is observed in proto planetary nebulae [37] and in cool objects [38].

Although there is no clear indication of either vinyl or phenyl substituted PAHs yet small compact PAHs like pyrene could be used in models to improve fitting. Both 5-vinyl-pyrene and 2-phenyl-pyrene appear to be suitable for incorporation in modelling sightlines towards objects showing 'C' type 6.2 μm AIB. Such objects are mostly cool benign regions of planetary nebulae where bottom-up chemical growth is expected [25], and where substituted PAHs could be intermediaries.

The spectra of large substituted PAHs are dominated by the features of the corresponding plain PAH. This would make it difficult to decipher them in the ISM spectra. Emission models along specific objects may include few small substituted PAHs along with large and medium sized plain PAHs.

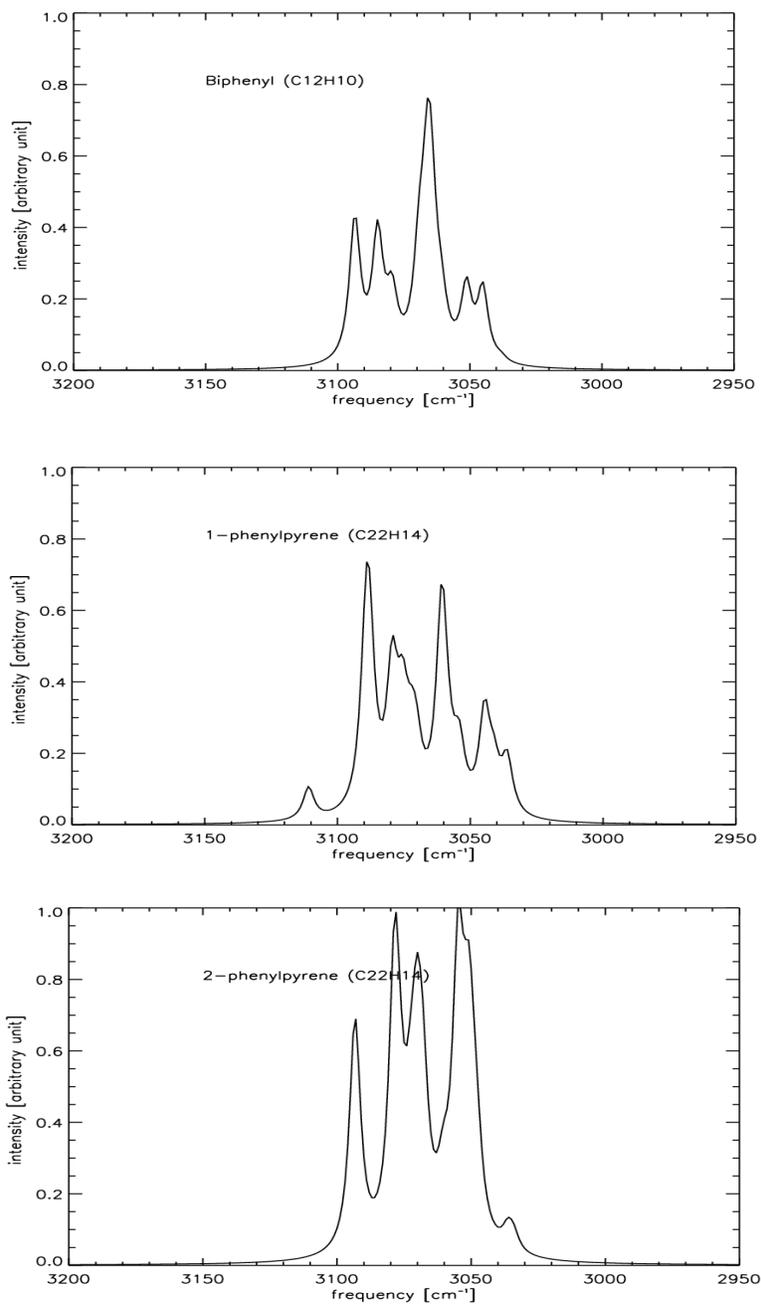


Fig 5. The spectra of neutral phenyl-PAHs in the C-H stretch vibration range. Considering 5 cm^{-1} FWHM several modes collocate together to give the broad profile.

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