



Contents lists available at ScienceDirect

# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

## Vibrational spectroscopic study of vinyl substituted polycyclic aromatic hydrocarbons



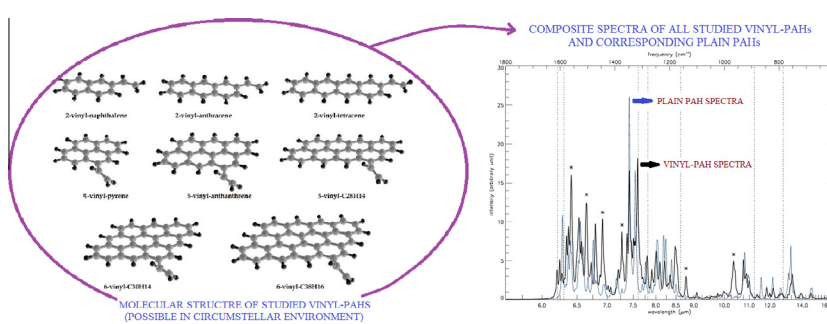
Anju Maurya, Shantanu Rastogi\*

Department of Physics, D.D.U. Gorakhpur University, Gorakhpur 273009, India

### HIGHLIGHTS

- Vibrational spectra of neutral and ionized vinyl-PAHs are reported.
- The possibility of vinyl-PAHs in interstellar medium is analyzed.
- Composite spectral model show new features that match some observed astrophysical bands.
- Data suitable for emission models along proto planetary nebulae type cool objects.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 9 March 2015

Received in revised form 19 June 2015

Accepted 22 June 2015

Available online 23 June 2015

#### Keywords:

PAH  
Aromatic infrared bands  
Interstellar molecules  
DFT calculations  
Astrochemistry

### ABSTRACT

The mid infrared emission features observed in various astrophysical sources are attributed to polycyclic aromatic hydrocarbon (PAH) molecules. The models of emission spectra from a collection of PAHs show uncertainty in matching the 6.2  $\mu\text{m}$  feature. This indicates the need to consider a larger variety of PAHs and PAH derivatives. Chemical pathways towards formation of PAHs in the astrophysical environments involve vinyl substituted PAHs as intermediate products. Vibrational spectroscopic study of vinyl-PAHs is reported in the present work. The vinyl group is substituted at similar positions in eight different PAHs. The obtained optimized structures show that vinyl substitution at 2 position in acenes gives planar geometry, while all other vinyl-PAHs are non-planar. Infrared spectra is simulated for neutrals as well as for cations. The results are compared with the spectra of corresponding plain PAHs and analyzed for possible match with astrophysical observations. New features, due to vinyl group in the composite spectra, identified at 6.64, 6.92, 7.27, 8.77 and 10.35  $\mu\text{m}$  fall close to some sub features of the observed emission spectra. The paper provides data that may be used in the emission models particularly along proto planetary nebulae type cool objects.

© 2015 Elsevier B.V. All rights reserved.

### 1. Introduction

The astrophysical observations of infrared emission features at 3.3, 6.2, 7.7, 8.6, 11.2 and 12.7  $\mu\text{m}$  (3030, 1610, 1300, 1160, 890 and 790  $\text{cm}^{-1}$ ) are attributed to vibrational transitions in polycyclic aromatic hydrocarbon (PAH) molecules [1–4]. These

aromatic infrared bands (AIBs) are ubiquitously observed in a variety of astrophysical objects from star forming regions to late type stars and even in external galaxies [5–10]. It is assumed that the AIBs are composite emission from a population of PAHs in the interstellar medium (ISM).

The variation in the profile of these emission features correlates with object type indicating different PAH types and populations in different regions [9–12]. Emission modeling using quantum chemical data for a large set of PAHs shows good match for the complex

\* Corresponding author.

E-mail address: [shantanu\\_r@hotmail.com](mailto:shantanu_r@hotmail.com) (S. Rastogi).

7.7  $\mu\text{m}$  AIB from different sources [12]. The study points towards possible presence of large PAHs in benign regions around planetary nebulae and small to medium sized PAHs in harsh UV-dominated star-forming regions. Despite the general similarity of AIBs to PAH vibrational spectrum and some feature correlations, the simultaneous matching of all AIBs has not been possible. Especially in the case of 6.2  $\mu\text{m}$  AIB, assigned to aromatic C—C stretching vibration, the spectral models show that the closest bands fall short by 30–40  $\text{cm}^{-1}$ . This suggests that the emission models considering only plain PAHs are not sufficient and other forms of PAHs need to be considered, including derivatives, in emission models. Studies on substituted PAHs, hydrogenated ones, and PAHs with nitrogen heterocycles have been reported with none or partial success [13–15]. Experimental studies on soot formation and amorphous thin films have shown the relevance of PAHs with polyacetylenic side groups [16]. Such side group if present may contribute to the 6.2  $\mu\text{m}$  feature. These side groups have CC double bonds that are stronger than ring aromatic bonds, which may shift the corresponding C—C stretch mode closer to 6.2  $\mu\text{m}$  AIB.

Various molecular species with vinyl group have already been detected in different astrophysical environments. The detection of vinyl cyanide in Sgr B2, provided the first evidence for the presence of the reactive vinyl radical in space [17]. Later ethylene was detected in the circumstellar gas surrounding the super-giant IRC+10216 [18]. Other detected molecules containing the vinyl group include: vinyl alcohol [19] and propenal [20] toward the star-forming region Sgr B2(N), and propylene (or propene) toward the dark cloud TMC-1 [21]. The presence of vinyl unit in astrophysical environments indicate the possibility of PAHs with vinyl side groups. The chemical pathway towards the formation of PAHs in circumstellar environments require vinyl derivatives as intermediate products [22–24]. This makes the study of vinyl-PAHs important for a better understanding of the AIBs.

Our earlier studies on unsubstituted plain PAHs [25–27] show that the vibrational spectra of elongated molecules, where number of rings along the length are more than those along the width, gave a better match for the 6.2  $\mu\text{m}$  feature. Hence in the present work vinyl derivative of these elongated PAH molecules have been chosen. The molecules studied are single-row vinyl-PAHs: 2-vinyl-naphthalene, 2-vinyl-anthracene and 2-vinyl-tetracene and multi-row vinyl-PAHs: 5-vinyl-pyrene, 5-vinyl-anthanthrene, 5-vinyl-C<sub>28</sub>H<sub>14</sub>, 6-vinyl-C<sub>30</sub>H<sub>14</sub> and 6-vinyl-C<sub>38</sub>H<sub>16</sub>.

Study on 2-vinyl-anthracene and 9-vinyl-anthracene [28] indicates the suitability of 6-31G basis set for planar and 6-31G(d) basis set for non planar vinyl derivatives. But the DFT-B3LYP/4-31G level of theory also gave good enough results for a qualitative spectral analysis of these molecules. The rms error in frequency matching is <12  $\text{cm}^{-1}$  and intensity match is also good [28]. Therefore, in the absence of experimental infrared information, the less time consuming method using DFT-B3LYP functionals in conjunction with 4-31G basis set is used for structural optimization and vibrational calculations. This is also the level of theory applied on plain PAHs [25–27] so a comparison of vinyl derivatives with their corresponding plain PAHs becomes feasible. All calculations are performed using the GAMESS ab-initio programme [29]. As molecules in the ISM are mostly ionized, both neutral and ionized forms of above vinyl-PAHs are studied.

## 2. Optimized structures

The optimized structures of all the chosen vinyl-PAHs are shown in Fig. 1. The substitution of vinyl group at position 2 in single-row PAHs gives planar structure i.e. both aromatic and vinyl units are nearly in the same plane. The vinyl substitution in

multi-row PAHs give non-planar structure, with the vinyl moiety being out of the plane of the aromatic unit. The non-planarity is due to strong steric interaction between H atoms [28]. The vinyl moiety is out-of-plane by nearly 40° in all these molecules. Table 1 shows the value of this torsion angle for both neutrals and cations. Ionization of the molecules reduces the torsion angle, but this change gets smaller with increase in size of the molecule. In neutral pyrene the vinyl unit is out-of-plane by 36° while in the cation the angle reduces to 23°. This change is smaller in 5-vinyl-anthanthrene and there is no change in larger molecules.

The energies of the corresponding optimized structures for both neutrals and cations are also given in Table 1. The variation of optimization energy with number of C atom in aromatic unit of vinyl-PAHs for both neutrals and cations is shown in Fig. 2, wherein energies of corresponding plain PAHs are also plotted for comparison. The optimized energy reduces linearly with the size of vinyl-PAH, exactly in the same manner as in plain PAHs for both neutrals and cations. The energy change from plain to substituted PAH is independent of the vinyl group being in-plane or out-of-plane with the aromatic unit.

## 3. Vibrational spectra

The vibrational modes and infrared intensities of these molecules are calculated to study the frequency and intensity shifts on substitution of vinyl side group and with size of the PAH. The calculated frequencies are usually overestimated and need to be scaled down. The scaling factor depends not only on the frequency but also on the level of theory [28,30–32]. In the absence of experimental results the scaling factor of similar molecules may be transferred and so they are taken from [28]. The scaling factor for the C—H stretch range frequencies around 3000  $\text{cm}^{-1}$  is different from that used for lower frequency modes [28]. For single-row vinyl-PAHs (2-vinyl-naphthalene, 2-vinyl-anthracene and 2-vinyl-tetracene), that have a nearly planar structure, the scaling factor of planar 2-vinyl-anthracene is taken. The vibrational frequencies in 400–1700  $\text{cm}^{-1}$  range are scaled by 0.9528 and the C—H stretch frequencies are scaled by 0.9519. Non-planar multi-row species (5-vinyl-pyrene, 5-vinyl-anthanthrene, 5-vinyl-C<sub>28</sub>H<sub>14</sub>, 6-vinyl-C<sub>30</sub>H<sub>14</sub> and 6-vinyl-C<sub>38</sub>H<sub>16</sub>) are scaled by 0.9540 in 400–1700  $\text{cm}^{-1}$  range and 0.9567 scaling factor is used for the C—H stretch range as in non-planar 9-vinyl-anthracene. The intensities of the calculated vibrational frequencies are scaled relative to the intensity of the most intense band. The calculated vibrational frequencies and corresponding intensities for each molecule and its cation are provided in Supplementary material tables, where only modes having relative intensity  $\geq 0.05$  are shown. The vibrational spectra of vinyl-PAHs are simulated using Lorentzian profile with 5  $\text{cm}^{-1}$  FWHM for each calculated mode. The modes closer than 5  $\text{cm}^{-1}$  collocate together resulting in a single broad peak which may be shifted by a few wavenumbers from the corresponding values given in the Tables. The spectra of neutral vinyl-PAHs are dominated by C—H stretch and C—H out-of-plane bend modes, whereas, 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 and the C—H stretch mode intensity is reduced, just as in the case of plain PAHs [25,26,30]. The features in the two frequency regions with different scaling factors are discussed separately.

### 3.1. The 400–1700 $\text{cm}^{-1}$ spectral region

The computed vibrational spectra of vinyl-PAHs are shown in Figs. 3, 5 and 7 for neutrals and in Figs. 4, 6 and 8 for cations. For comparison the infrared spectra of corresponding plain PAHs are

Download English Version:

<https://daneshyari.com/en/article/1230045>

Download Persian Version:

<https://daneshyari.com/article/1230045>

[Daneshyari.com](https://daneshyari.com)