

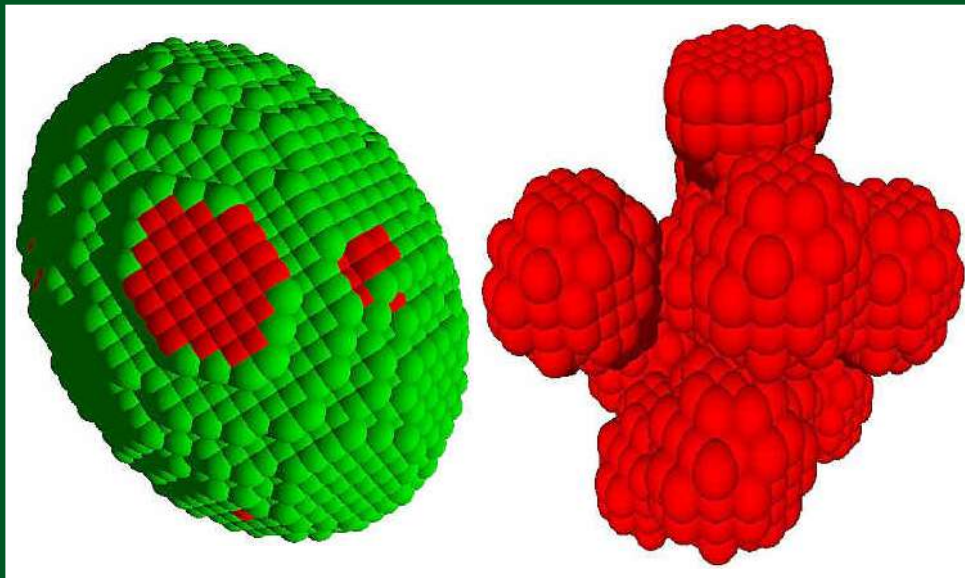
AJP

ISSN : 0971 - 3093

Vol 24, No 8, August, 2015

ASIAN JOURNAL OF PHYSICS

An International Research Journal



ANITA PUBLICATIONS

FF-43, 1st Floor, Mangal Bazar, Laxmi Nagar, Delhi-110 092, India
B O : 2, Pasha Court, Williamsville, New York-14221-1776, USA



ap

Asian Journal of Physics

Available on www.asianjournalofphysics.in

Vol. 24, No 8 (2015) 1127-1142

Spectral properties of astrophysical polycyclic aromatic hydrocarbons

Mridusmita Buragohain and Amit Pathak

Department of Physics, Tezpur University, Tezpur -784 028, India

Polycyclic Aromatic Hydrocarbon (PAH) molecules have been identified as carriers of the interstellar emission features lying in the 3-20 μm wavelength range. Detection of these bands towards several diverse astrophysical sources and an observed variation in intensity ratios has attracted high quality experimental and theoretical analysis of PAHs in order to recognize the precise form(s) present in the interstellar medium of Milky Way and external galaxies. In this short review, several experimental and theoretical studies carried out on probable interstellar PAH candidates have been visited. It is emphasized that a significant fraction of interstellar PAHs might not be pure hydrocarbons and will have a deuterium or metal substitution. Implications to the diffuse interstellar band problem have been cited. © Anita Publications. All rights reserved.

Keywords: Astrochemistry; Interstellar Medium (ISM); Interstellar molecules: Polycyclic Aromatic Hydrocarbons; I R Spectra; Unidentified infrared bands.

1 Introduction

It has been long proposed that polycyclic aromatic hydrocarbon (PAH) molecules; a major component of the interstellar medium (ISM) are widely spread out in the Universe [1, 2]. Their spectroscopic signatures are well established by the detection of 3.3, 6.2, 7.7, 8.6, 11.2 and 12.7 μm bands in the emission spectra of various interstellar objects. After being first discovered by Gillett *et al* [3] towards three planetary nebulae (NGC 7027, BD+30°3639 and NGC 6572), these bands have been extensively observed towards a variety of astronomical objects, viz. H II regions, photodissociation regions, reflection nebulae, planetary nebulae, star forming regions, diffuse interstellar medium, external galaxies, etc. [4-15]. These bands, popularly known as the Unidentified Infrared (UIR) emission bands, are broad emission features with line and continuum radiation distributed through the mid-infrared range of 3–20 μm [4]. Sellgren [16] initially proposed transiently heated small grains by ultraviolet (UV) photons to be producing these bands. Léger & Puget [17] identified these small grains as PAH molecules. Extensive theoretical and experimental studies show that these bands arise due to the vibrational relaxation of a PAH molecule on absorption of a background UV photon [1, 2, 17, 18]. These bands have also been known as the Aromatic Infrared Bands (AIBs) or Aromatic Infrared Emission (AIE) bands because of the aromatic nature of the carrier. The ubiquitous presence and stability of PAHs in the ISM established by the detection of AIBs has led to the hypothesis that electronic transitions in PAHs might also give rise to some of the Diffuse Interstellar Bands (DIBs) [19-21]. DIBs are numerous optical absorption features on the interstellar extinction curve observed towards galactic and extra-galactic sources [22-24]. Despite the fact that PAHs account for the emission features lying in the 3–20 μm range, detection of a single PAH molecule in interstellar space has not been possible and the exact form(s) of PAH(s) responsible for the band(s) is not yet definite. The progress in observational astronomy and the launch of several space based telescopes for e.g., *ISO*, *SPITZER*, *AKARI*, etc. have revealed a wealth of new information about the AIBs through observations towards astrophysical objects of varying environments and metallicity [6, 25-28]. The improved observations signal the presence of a vast interstellar PAH family comprising of pure and substituted PAHs. Besides being carriers for AIBs, PAHs also contribute to the heating of the ISM and the charge balance inside molecular clouds [27, 29-31], that is why the study of PAH formation and chemistry in the ISM is of utmost importance. Both pure and substituted PAHs have been studied theoretically and experimentally for better understanding of the spectroscopy involved. Laboratory studies of PAHs often face constraints due to the complexity of the experiments, the monetary cost involved and the amount of time investment needed especially for the case of substituted PAHs. Theoretical study is convenient to perform

Corresponding author :

e-mail: amitpah@gmail.com (Amit Pathak)

on a wide range of PAH molecules that vary in size, charge and functional groups attached to it. Based on this theoretical study, specific molecules can be selected for sophisticated laboratory experiments to be performed. A combined laboratory and theoretical study of PAHs is more relevant in order to compare with observational results to identify an accurate form of PAH molecule. In this short review, several experimental and theoretical studies carried out on probable interstellar PAH candidates have been visited.

2 Review of experimental spectroscopy of PAHs

Experimental study of PAHs is of inevitable importance in order to demonstrate the PAH-UIR hypothesis and provide an evidence for the presence of these molecules in interstellar space. Several PAHs have explicitly been studied experimentally to establish a correlation with the observed spectra of UIR emission bands and DIBs in particular. Different techniques have been used on different types of PAH molecules in order to reproduce the UIR emission bands. Some of the experiments that have allowed to obtain the IR spectrum of probable PAH candidates include IR absorption spectra of gas phase molecules at high temperatures [32, 33], Single Photon Infrared Emission Spectroscopy (SPIRE) [34], UV Laser Induced Desorption (UV-LID) [35, 36], Infrared Multiphoton Dissociation Spectroscopy (IRMPD) [37-40], and Infrared absorption spectra of matrix isolated PAHs [41-43].

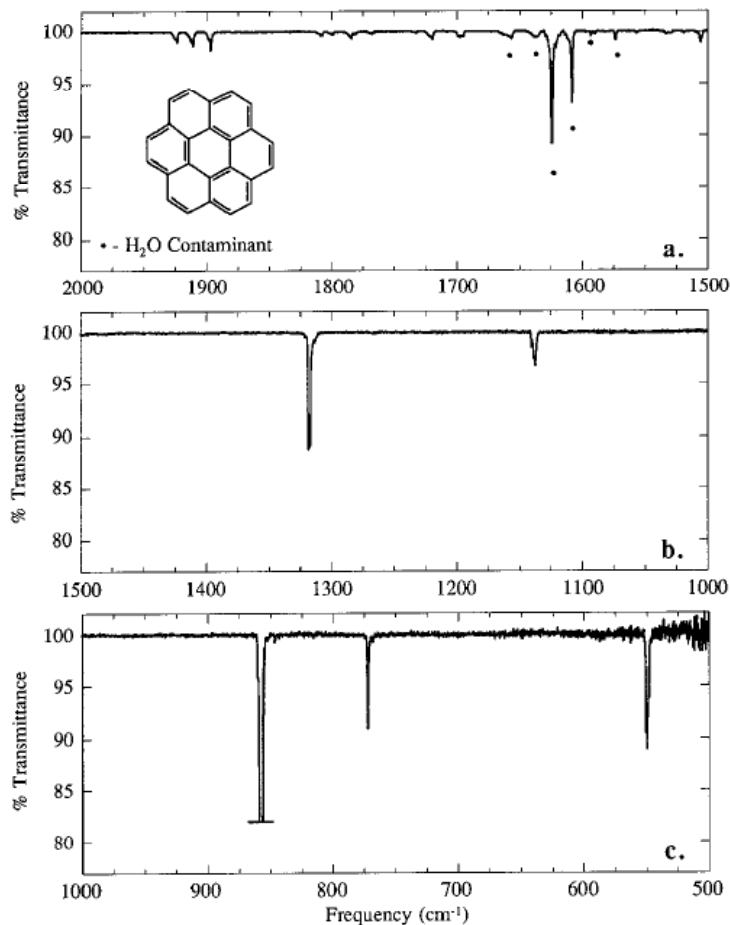


Fig 1. Experimental spectra of matrix isolated coronene in (a) 2000-1500 cm⁻¹, (b) 1500-1000 cm⁻¹, (c) 1000-500 cm⁻¹ ranges [44]

2.1 PAHs: neutrals and cations

The most intense 6.2, 7.7 and 8.6 μm AIBs have been observed towards sources of high density UV radiation where PAHs are likely to exist in ionized form. This gives an edge to the cationic PAHs over the neutral PAHs for sophisticated experimental studies. Hudgins & Sandford [43, 44]; Hudgins *et al* [45]; Hudgins & Allamandola [46, 47] have performed a series of Matrix Isolation Spectroscopy (MIS) experiments on neutral and cationic PAHs to obtain the IR absorption spectra. MIS technique is carried out at a low temperature ≈ 10 K relevant to interstellar condition of rotationally cold and vibrationally hot PAHs [43]. Spectral data of several PAHs obtained using the MIS techniques are available for free download at the NASA Ames PAH database (<http://www.astrochem.org/>) [48]. Neutral PAHs show features that fall at frequencies similar to that of the AIBs, however, relative band intensities do not provide a good match. Whereas, PAH cations present an overall good match with the astronomical spectra in terms of intensity as well. Nevertheless, no intense 6.2 μm band has been recorded for neither neutral nor cationic PAHs at the observed position; instead the laboratory 6.2 μm band is red-shifted with respect to the observed band. A few gas phase spectra of neutral and cationic PAHs have also been obtained using SPIRE [34, 35, 49, 50] and IRMPD [37, 51-54] techniques that agree very well with the available theoretical and MIS data. Experimental spectra for neutral coronene (obtained by the MIS technique) and cationic coronene (obtained by the multi-photon dissociation technique) are shown in Fig 1 (adopted from [44]) and Fig 2 (adopted from [52]), respectively.

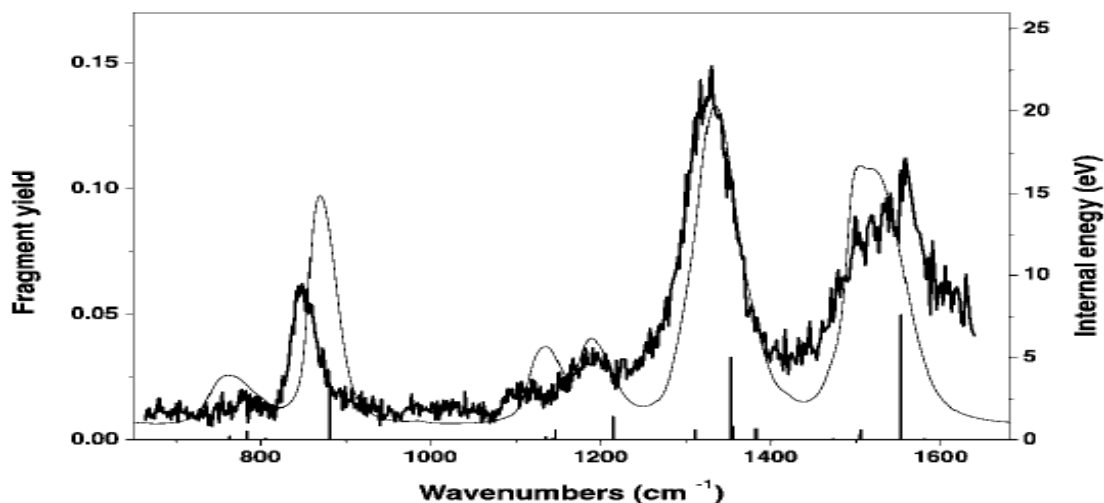


Fig 2. Experimental spectrum of coronene cation with corrections (thick line, left scale), without corrections (thin line, right scale) compared with theoretical spectrum (stick spectrum) [52]

2.2 Protonated and deuterated PAHs

Recently protonated form of PAH (HPAH^+) molecules have been experimentally tested as these might be another form of PAH widely present in the ISM [24, 55]. Gas phase infrared spectra of HPAH^+ molecules have been recorded using multi-photon dissociation (MPD) spectroscopy [56] and mass-selected photo dissociation spectroscopy and the messenger atom method [57]. Experimental data points to an intense band close to 6.2 μm band observed AIB. Due to the presence of an aliphatic carbon in HPAH^+ , aliphatic C-H stretching motions give rise to a feature near 3.5 μm that is not usually present in the AIBs. Some observations have shown the presence of weak 3.4 μm and 3.5 μm bands [58]. Figure 3 (adopted from Knorke *et al* [56]) shows the laboratory gas phase spectrum of protonated coronene using MPD spectroscopy.

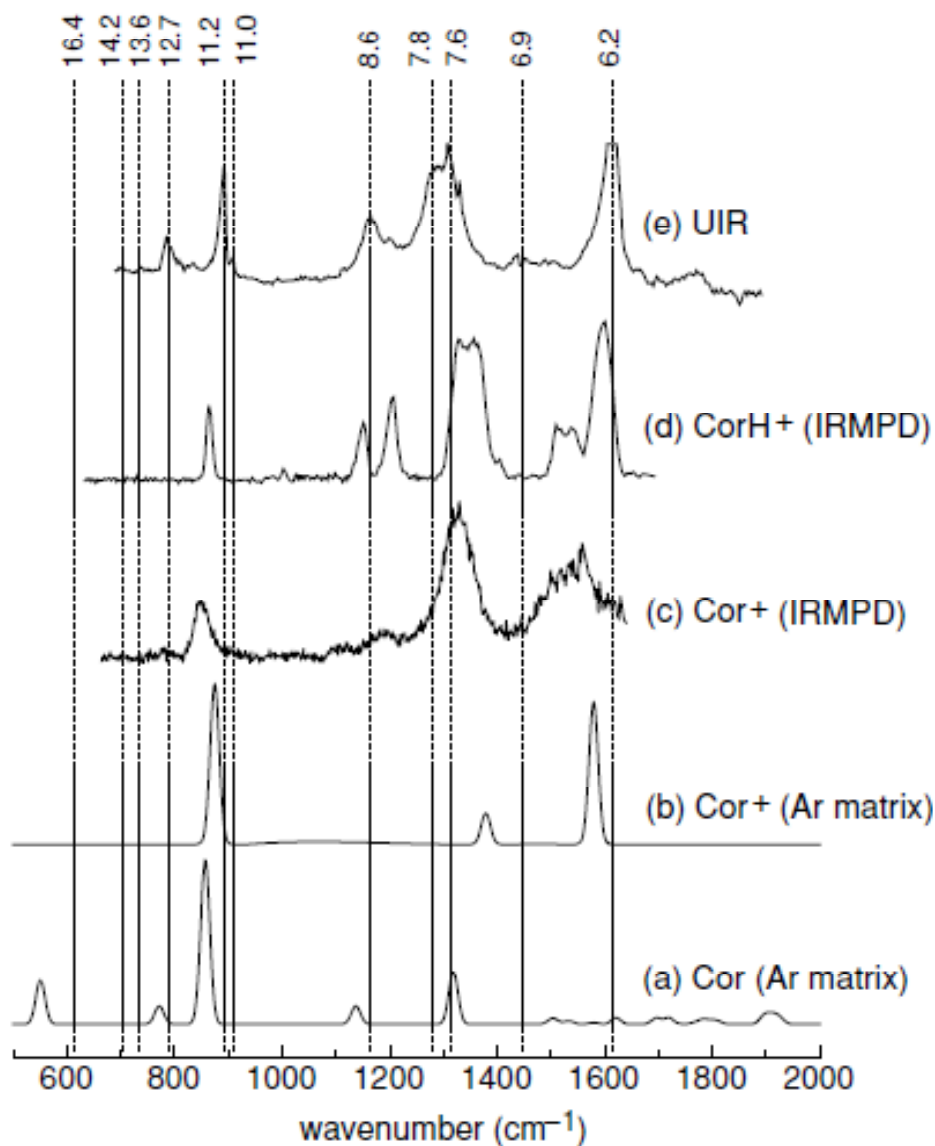


Fig 3. Comparison of experimental IR spectra of coronene, coronene cation and protonated coronene with astronomical UIR spectra observed towards Orion bar. (a) and (b) are obtained using MIS technique. (c) and (d) are obtained using MPD technique [56]

No HPAH⁺ spectrum has been recorded by MIS technique till date. This may be due to difficulty in synthesizing a protonated PAH and trapping it in the matrix. Deuterium containing PAHs (PADs or D_n-PAHs) have also been considered for experimental studies using MIS [59]. As expected, due to the larger mass of deuterium in PADs, the characteristic frequencies of C-D modes are shifted to shorter wave numbers compared to the analogous C-H modes. Laboratory spectrum for perdeuterated naphthalene is shown in Fig 4 (adopted from [59]).

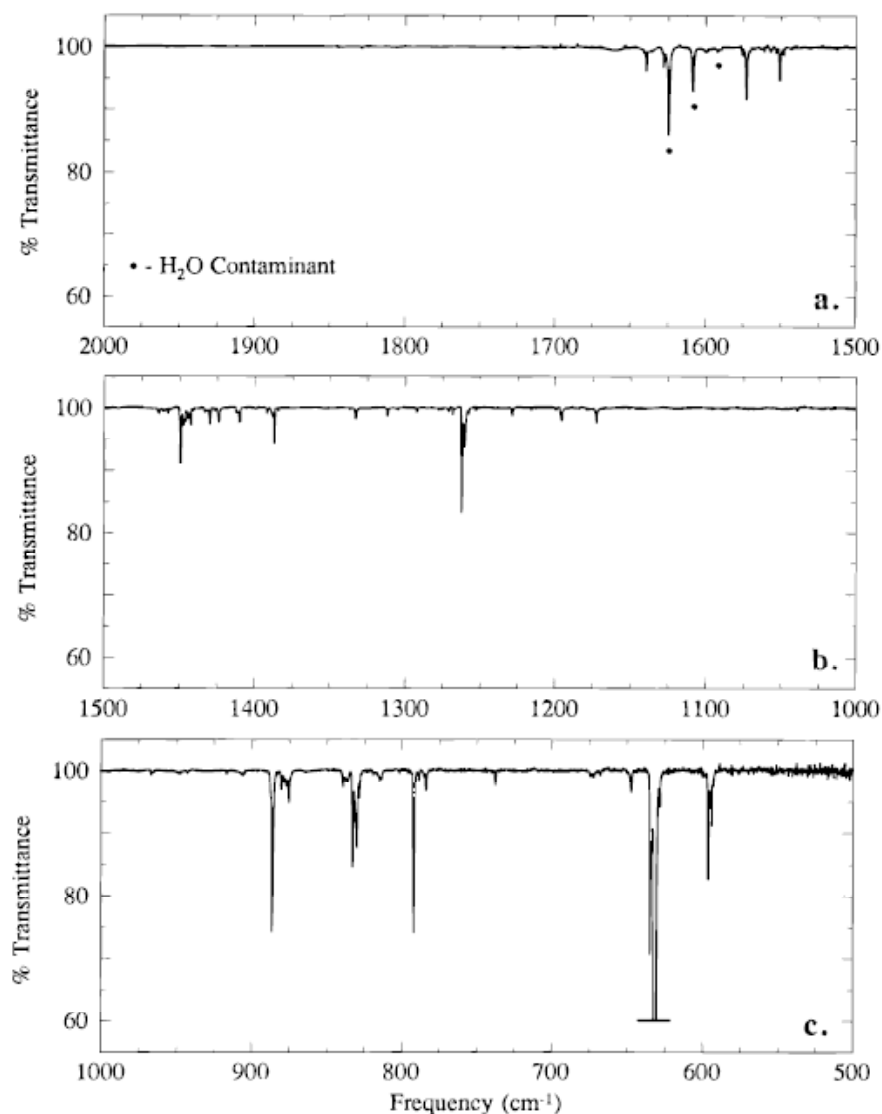


Fig 4. Laboratory spectrum of Matrix isolated perdeuterated naphthalene in the (a) 2000-1500 cm^{-1} , (b) 1500-1000 cm^{-1} , (c) 1000-500 cm^{-1} range [59]

2.3 Nitrogen and other metal containing PAHs

The complex nature of AIBs cannot be explained by pure PAHs or a single category of PAH alone. There are ambiguous features like the 6.2 μm emission band and several other weak features which cannot be explained by merely varying the molecular size of pure PAHs [60]. The 6.2 μm emission feature is actually a composite of two other bands, one centered at 6.2 μm designated as ‘class A’ and another centered at 6.3 μm designated as ‘class C’ bands. The composite of ‘class A’ and ‘class C’ feature is defined as ‘class B’ covering an intermediate position [60]. While ‘class C’ bands are supposed to arise from large PAH cations, the explanation for ‘class A’ bands needs a completely different type of PAH [60]. Nitrogen, being the fourth most abundant element in the ISM is suspected to form polycyclic aromatic nitrogen heterocycle

(PANH) with one or more nitrogen atoms substituted in the aromatic ring structure. MIS technique has been employed on neutral and cationic forms of PANH in order to address the 6.2 μm emission band position [60-62]. Till date, PANHs are the only PAH type that can account for the 'class A' 6.2 μm band [60]. IR absorption spectrum for PANH is shown in Fig 5 (adopted from Mattioda *et al* [61]). Gas phase IR spectra of cationized PANH (PANH^+) have been obtained using the IRMPD technique [40]. Other than nitrogen, PAHs with neutral and ion complexes of Fe have also been studied experimentally in the astrophysical context [39, 63].

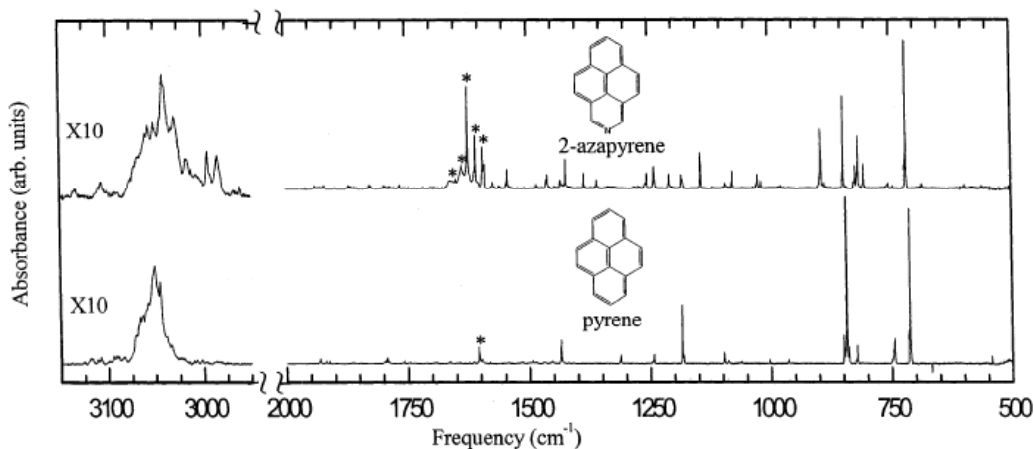


Fig 5. Laboratory spectra of matrix isolated 2-azapyrene and parent pyrene molecule. * indicates the position of the contaminant band [61]

3 Review of theoretical spectroscopy of PAHs

In experimental studies, it is extremely difficult to simulate an environment that resembles the ISM. Thus, the experimental spectra may not be directly compared with the observed AIBs. Synthesis of substituted PAHs is another bottle-neck regularly experienced in experimental spectroscopy. Theoretical quantum chemical calculations play a vital role that act as a bridge between laboratory and observational astronomy. Theoretical spectroscopy helps in identifying suitable candidates for laboratory study. Results obtained from the theoretical spectroscopic study of PAHs may be used as inputs for emission simulations for direct comparison with observations. Due to these reasons, theoretical quantum chemical calculations have been widely used to calculate the harmonic frequencies and intensities to address the PAH-UIR hypothesis [64-72].

3.1 PAHs: neutrals and cations

Theoretical studies at various levels have been used on several forms of PAHs to compare with experimental and observed spectra [64, 66, 67]. See Pauzat [73] for a recent review of the theoretical IR spectroscopy of PAHs. Density functional theory (DFT) has revolutionized the use of quantum chemical calculations to accurately predict the vibrational spectrum of PAHs [64]. Langhoff [64] considered B3LYP functionals along with a range of basis set, viz. 4-31G to 6-311G** to show that the calculated wavenumbers tend to approach the experimental frequencies when a large basis set is used. The results of Langhoff [64] show that a good agreement with experimental and observed spectra is obtained by using 4-31G basis at a modest computational cost. These results favour the presence of symmetrical PAH cations like coronene as their spectra match better in terms of intensity with the observed bands at 3.3, 6.2, 7.7 and 11.3 μm . Figures 6 and 7 (adopted from [64]) present the theoretical IR spectra of coronene and coronene cation. Theoretical study has also been applied at different levels say ; Self Consistent Field (SCF), second order Moller-Plesset

(MP2) by Bauschlicher and Langhoff [66], that clearly indicates that very accurate harmonic frequencies close to experimental frequencies can be obtained using DFT combined with large basis set compared to SCF and MP2.

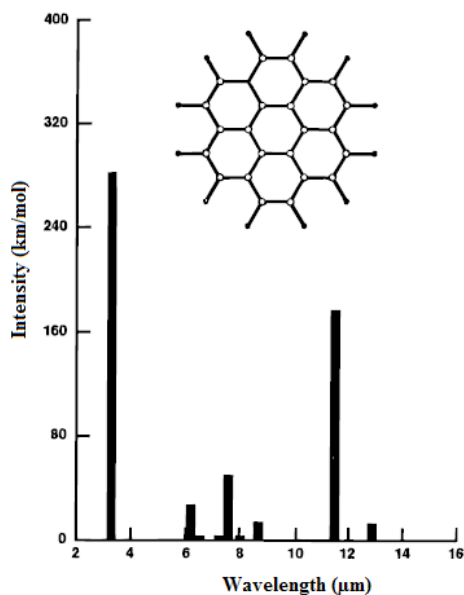


Fig 6. Infrared absorption band intensities of neutral coronene [64]

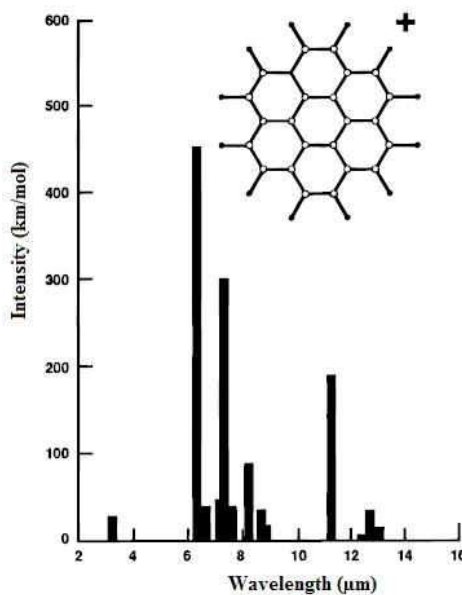


Fig 7. Infrared absorption band intensities of cationic coronene [64]

3.2 Protonated and Deuterated PAHs

Hudgins *et al* [67] considered another class of PAH cations having a closed shell structure with odd number of carbon atoms and protonated PAHs for theoretical calculations. Protonated PAHs show a complex spectrum, with distinctive features particularly in the range 1600–1100 cm^{-1} , compared to their parent radical ions due to the breaking of symmetry, Fig 8, (adopted from [67]). With increasing size of protonated PAHs, the intensity of aromatic C-H stretching tends to increase with a decrease in intensity of aliphatic C-H stretching [67]. However, the overall spectrum is consistent with experimental data concluding that protonated PAHs might be responsible for some of the UIR features.

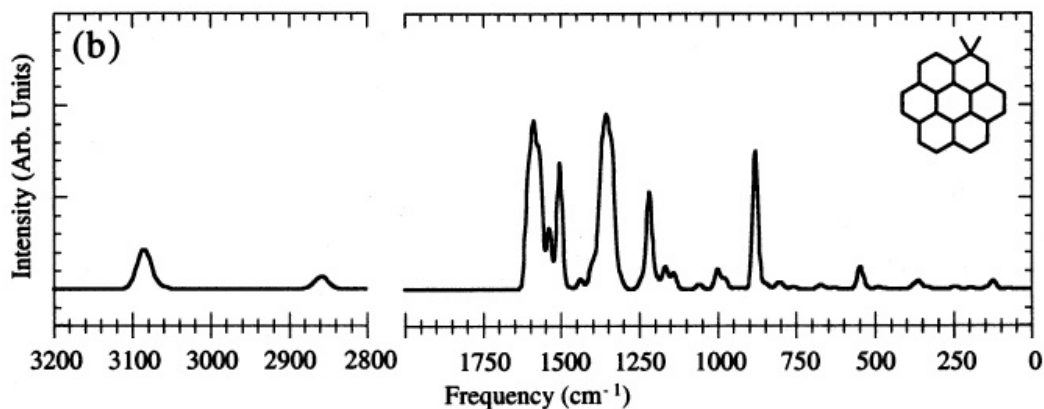


Fig 8. IR spectrum of protonated coronene [67]

Deuterium detection in the ISM [74] supports the existence of interstellar deuterium containing PAHs (PADs or D_n -PAHs) which is also being analyzed theoretically [59, 68]. Deuteration affects the complete spectrum and shows unique features in the 4.4-4.6 μm region which is a featureless zone in pure PAHs [68]. This unique prospect has been utilized to search interstellar deuterated PAHs in the ISM [27, 28]. The spectrum for deuterated PAHs is presented in Fig 9 (adopted from [68]).

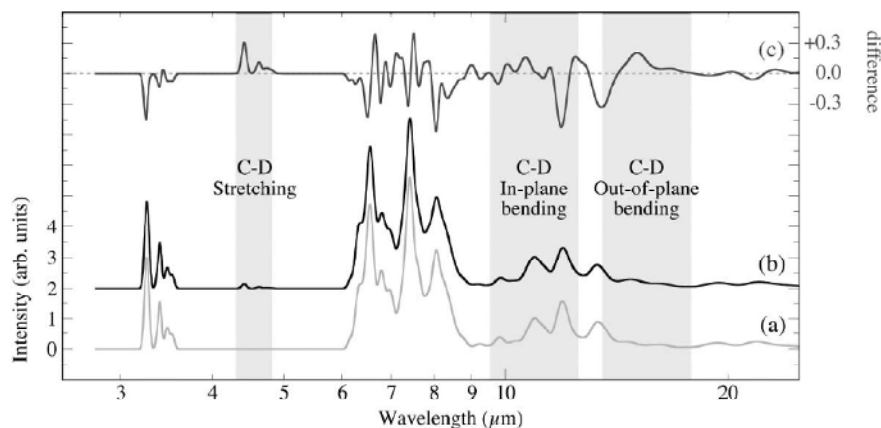


Fig 9. Calculated IR spectra of (a) hydrogenated naphthopyrene, (b) average of all singly deuterated isomers of naphthopyrene and (c) difference between a and b [68]

3.3 Metal containing PAHs

Since metal containing PAHs are difficult to synthesize in laboratory, theoretical computational study has been utilized in order to explain the infrared spectral properties of these molecules. A number of theoretical studies on several metal containing PAHs have been reported. These include nitrogen substituted PAHs [60-62,75], oxygen substituted PAHs [60, 76], silicon substituted PAHs [60], methyl substituted PAHs [77], and PAHs with Fe and Mg [60, 78-80]. Hudgins *et al* [60] reported that among all the metal containing PAHs, PANH cations can precisely account for the interstellar 6.2 μm emission feature. A spectrum of PANH cation is shown in Fig 10 (adopted from Hudgins *et al* 2005, [60]).

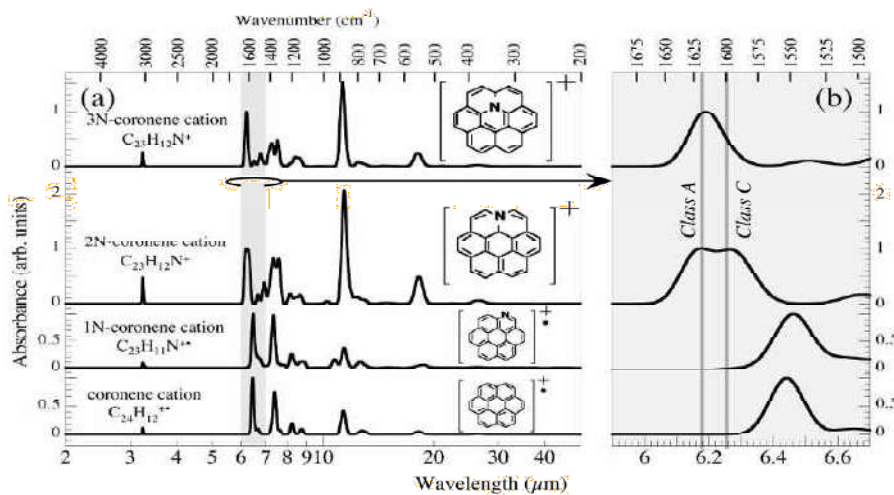


Fig 10. (a) IR spectra of three possible N-substituted coronene cations along with their parent cation in the 2-50 μm range (b) Zoom view of 6 μm region [60]

4 Emission model

For a valid and justifiable comparison with the observed AIBs, the theoretically computed absorption spectrum needs to be transformed to an emission spectrum. A model may be used based on the theoretically obtained information as input and an emission spectrum may be generated [81]. In an emission model, a PAH molecule is considered in a UV rich interstellar radiation field produced by a source (a star). The PAH molecule absorbs a photon and gets internally excited corresponding to an average temperature of about 1000 K. The absorption of the UV photon depends on the absorption cross section of the particular PAH.

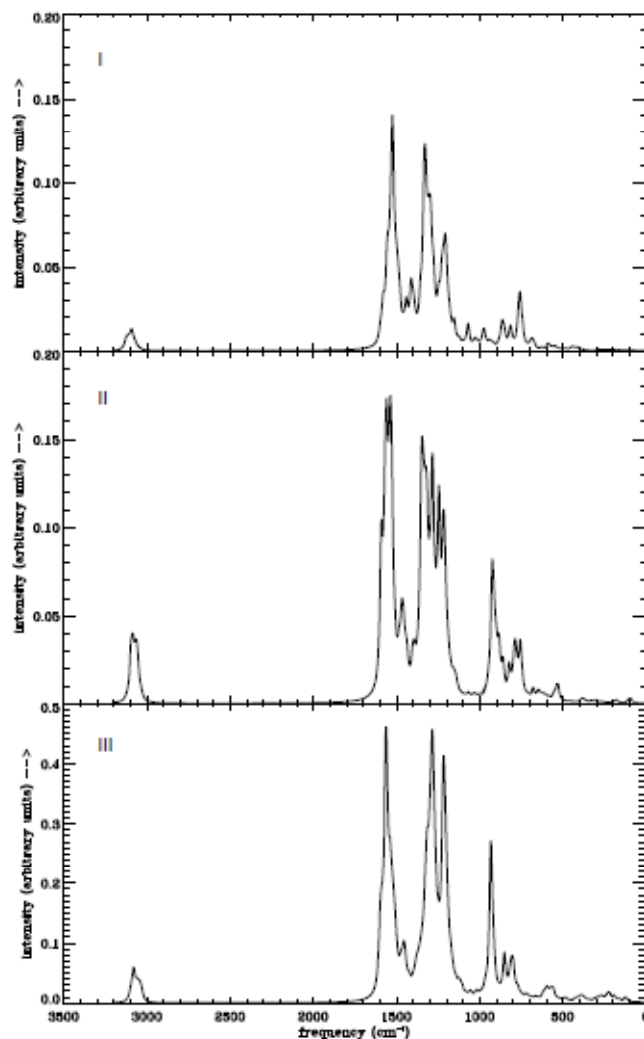


Fig 11. Composite emission spectra of PAH cations (I) less than 20 carbon atoms, (II) 20 to 40 carbon atoms and (III) More than 40 carbon atoms [81]

The excited PAH then cools down by emitting in a cascade at frequencies corresponding to the vibrational modes of the PAH molecule. The emission model considers thermal approximation that the total energy of the excited PAH molecule is greater than the average energy of an emitting mode [34, 81, 82]. The emitted energy is integrated over the cooling range from 1000 K to 50 K with a decrease in internal energy by a

temperature fall of 1 K. The emitted energy is calculated considering the rate of absorption of photons and added up over the whole distribution of photon absorption to produce the emission spectrum. The Emission model is employed on a set of PAHs to correlate with the profile variations of 6.2 and 7.7 μm bands observed towards diverse sources [81, 10]. The 7.7 μm feature is a composite band of two sub components; at 7.6 and 7.8 μm [83, 84, 10]. The 7.6 μm band dominates the emission spectra of UV enriched environments of say H II region, reflection nebulae, star forming regions, etc. and is classified as A' profile. Whereas the 7.8 μm band dominates the emission spectra of generous astrophysical environment where formation of PAHs recently occurred and is classified as B' profile. Similarly 6.2 μm band also consists of two components; at 6.2 and 6.3 μm designated as 'Class A' (Or A') and 'Class C (or C)', respectively and intermediate of these is defined as 'Class B' profile. We have categorized three models according to the number of carbon atoms, small PAHs (model-I, carbon atoms ≤ 20), medium PAHs (model-II, 20 to 40 carbon atoms) and large PAHs (model-III, carbon atoms >40) [81]. Emission spectrum for each PAH is obtained using the above described emission scheme and for each category of PAHs, spectra are co-added to produce a composite spectrum corresponding to each model. Emission models reveal that small and medium sized PAH cations show profiles similar to class A' (7.6 μm) profiles, whereas large PAH cations account for the class B' (7.8 μm) profile [81]. Emission spectra for the three models of PAH cations are shown in Fig 11 ([81]). However, none of the considered models could explain the 6.2 μm band of AIBs [81]. As mentioned earlier this is the motivation to explore greater variety of PAHs and theoretical calculations are useful in converging on the type of species. Vinyl substituted PAHs are one possible class of PAHs for which a suitable level of theory is studied by Maurya *et al* [85]. The study also indicates the possibility to employ the emission scheme and include such PAHs in emission spectra models for generous astrophysical environments, where PAHs might be forming [85].

5 Implications to DIBs

In order to identify specific forms of interstellar PAHs, UV and visible spectroscopy of PAHs is essential, as the IR spectrum provides information about the vibrating bond and is not helpful in identification of the exact molecule. The PAH-DIB connection has added to the relevance of the UV-visible spectroscopy of PAHs. DIBs are absorption features on the interstellar extinction curve observed in the visible part of the electromagnetic spectrum. It is suggested that electronic transitions in PAHs due to absorption of background UV photons may produce interstellar DIBs [19-21]. This enhances experimental and theoretical study of PAH variants to find a correlation of electronic spectra of PAHs with DIBs. Experimental spectra of matrix isolated PAHs [86] and gas phase electronic spectra of PAHs using cavity ring down spectroscopy (CRDS) [87-90] have been reported to study the PAH-DIB connection. The one line summary of the experimental electronic spectroscopy of PAHs is that PAH ions appear to be promising carriers for some of the DIBs. In particular, 1-methylpyrene⁺, carbohydroxypyrene⁺, tetracene⁺, benzo(ghi)perylene⁺, naphthalene⁺ show positive correlation with astronomical spectra of DIBs, whereas coronene⁺, perylene⁺, phenanthrene⁺, pyrene⁺, 4-methylpyrene⁺ can be ruled out as potential candidate carriers for DIBs. Neutral forms of PAHs show profiles identical to the observed spectra of narrow DIBs but these mostly fall in the UV wavelength bands where the identification/search of DIBs is extremely difficult because of the presence of numerous atomic lines. Theoretical studies carried out in reference to DIBs [55, 91-96] match the previous experimental and theoretical calculations and suggest that neutral PAHs along with its anions, cations, dications and protonated forms are attractive DIB carrier candidates. Time-dependant DFT (TDDFT) with a combination of BLYP/6-311G** applied on neutral and protonated forms of PAHs indicate that protonation increases the number of transitions in visible part of the spectrum. Figure 12 shows the absorption spectra of neutral pyrene along with three isomers of protonated pyrene. Neutral pyrene does not show a single transition in the visible range, whereas its protonated counterparts show significant strong transitions in the visible and near UV regions.

Similar characteristics are found for protonated coronene and ovalene [55]. Deuterated forms of PAHs (addition of a deuteron) also display similar profiles as that of protonated forms. This is shown in Fig 13 (adopted from Buragohain *et al* [97]), which makes them prospective diffuse band carrier candidates. The computational results also show that the HOMO-LUMO gap is reduced upon protonation and deuteration of PAHs. Thus less energy is required by the electrons in the excitation process transitions occur towards longer wavelength side as compared to the parent neutrals.

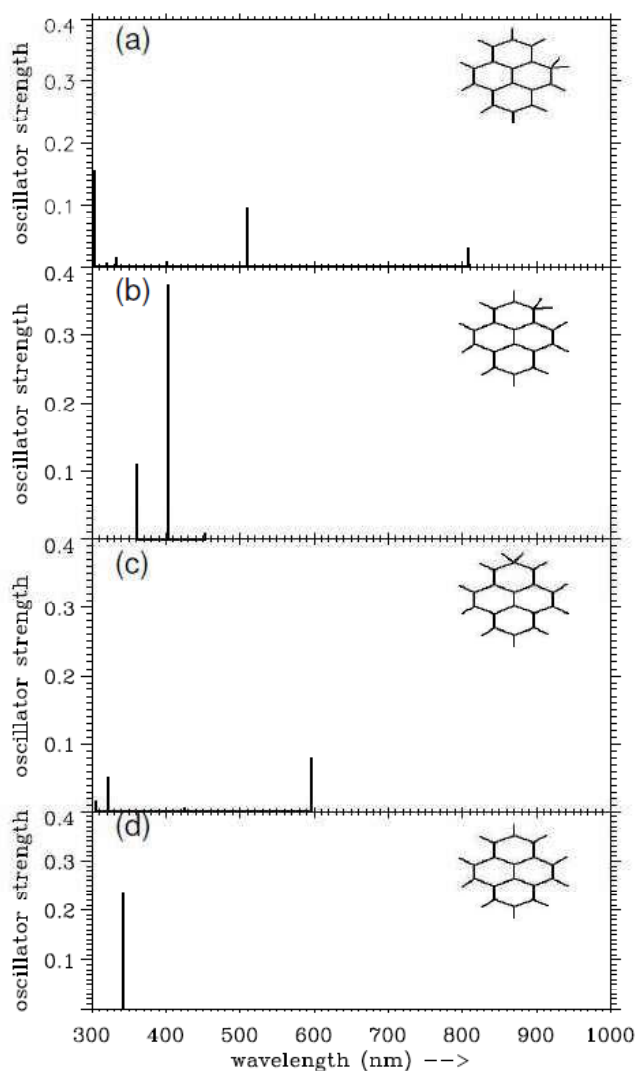


Fig 12. TDDFT absorption spectra of (a)-(c) Protonated pyrene and (d) Neutral pyrene

6 Future course

Despite the fact that PAHs have been established as carriers for AIBs and are an important component of the ISM, identification of an exact form of interstellar PAH molecule has not been successful so far. For a direct identification of the carriers, infrared spectroscopy should be accompanied by UV and

visible spectroscopy. Using infrared spectroscopy, one can only confirm for the possible chemical bonds or groups present in ISM, whereas UV and visible spectroscopy is unique to a specific molecule [90]. In continuation, we intend to perform DFT as well as TDDFT calculations on various PAH variants to obtain the vibrational as well as electronic properties. This will be helpful for the study of vibronic features and line shape comparison with observed DIBs. The use of emission model with an improved set of PAHs will help to compare theoretical spectra directly with the astronomical spectra. Substituted PAHs have received much attention as they may be significant part of the interstellar PAH formation chemistry [98]. In particular, considering deuterated-deuteronated PAHs for the study of bands near 4.4 and 4.65 μm will be interesting as these bands have been detected through IR observations.

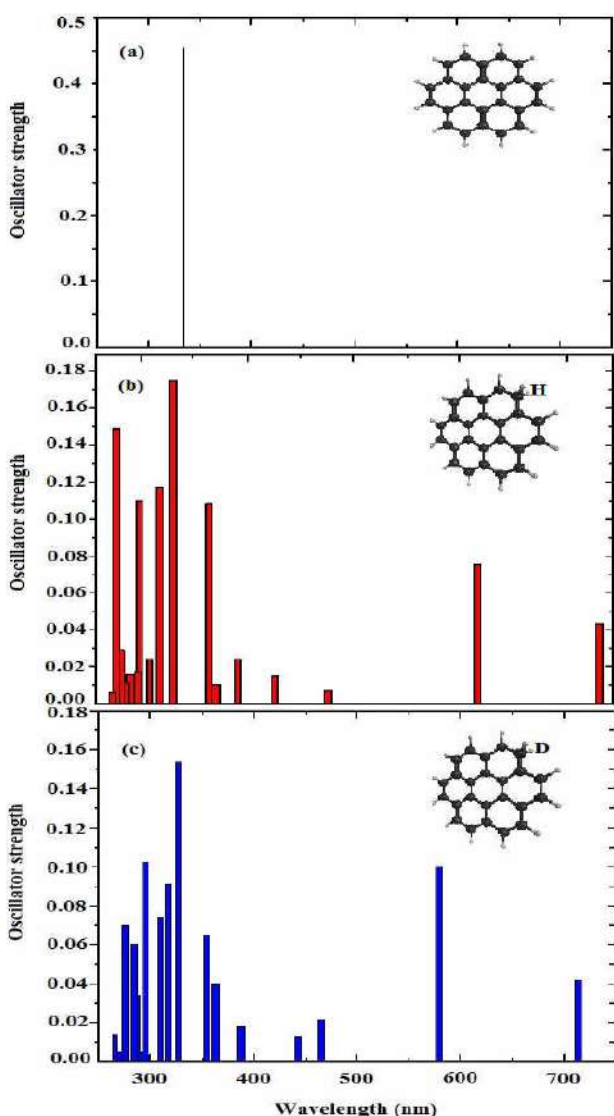


Fig 13. TDDFT absorption spectra for (a) Neutral coronene, (b) Protonated coronene, (c) Deuterated coronene [97]

Three decades after the PAH hypothesis, several searches especially for substituted PAHs and PAHs with a five-member ring (these have permanent dipole moment) have been done using radio astronomy but without any success. With the advancement in experimental and theoretical methodology and high resolution space observations, it is likely that PAH identification is possible in the coming future.

Acknowledgement

MB is a junior research fellow in a SERB – DST FAST TRACK project. A P acknowledges financial support from SERB – DST FAST TRACK and DST – JSPS grants and associateship of the Inter-University Centre for Astronomy and Astrophysics, Pune.

References

1. Allamandola L J, Tielens A G G M, Barker J R, *ApJS*, 71(1989)733-775.
2. Puget J L, Léger A, *ARA & A*, 27(1989)161-198.
3. Gillett F C, Forrest W J, Merrill K M, *ApJ*, 183(1973)87-93.
4. Tielens A G G M, *ARA&A*, 46(2008)289-337.
5. Mattila K, Lemke D, Haikala L K, Laureijs R J, Léger A, Lehtinen K, Leinert C, Mezger P G, *A&A*, 315(1996) L353-L356.
6. Verstraete L, Puget J L, Falgarone E, Drapatz S, Wright C M, Timmermann R, *A&A*, 315(1996)L337-L340.
7. Moutou C, Sellgren K, Verstraete L, Léger A, *A&A*, 347(1999)949-956.
8. Hony S, Van Kerckhoven C, Peeters E, Tielens A G G M, Hudgins D M, Allamandola L J, *A&A*, 370(2001) 1030-1043.
9. Verstraete L, Pech C, Moutou C, Sellgren K, Wright C M, Giard M, Léger A, Timmermann R, Drapatz S, *A&A*, 372(2001)981-997.
10. Peeters E, Hony S, Van Kerckhoven C, Tielens A G G M, Allamandola L J, Hudgins D M, Bauschlicher C W, *A&A*, 390(2002)1089-1113.
11. Abergel A, Bernard J P, Boulanger F, Cesarsky D, Falgarone E, Jones A, Miville-Deschenes M-A, Perault M, Puget J-L, Hultgren M, Kaas A A, Nordh L, Olofsson G, André P, Bontemps S, Casali M M, Cesarsky C J, Copet M E, Davies J, Montmerle T, Persi P, Sibille F, *A&A*, 389(2002)239-251.
12. Acke B, van den Ancker M E, *A&A*, 426(2004)151-170.
13. Regan M W, Thornley M D, Bendo G J, Draine B T, Li A, Dale D A, Engelbracht C W, Kennicutt R C (Jr), Armus L, Calzetti D, Gordon K D, Helou G, Hollenbach D J, Jarrett T H, Kewley L J, Leitherer C, Malhotra S, Meyer M, Misselt K A, Morrison J E, Murphy E J, Muzerolle J R G, Rieke M J, Roussel H, Smith J-D T, Walter F, *ApJS*, 154(2004)204-210.
14. Brandl B R, Bernard-Salas J, Spoon H W W, Devost D, Sloan G C, Guilles C S, Wu Y, Houck J R, Weedman D W, Armus L, Appleton P N, Soifer B T, Charmandaris V, Hao L, Marshall J A, Higdon S J, Herter T L, *ApJ*, 653(2006)1129-1144.
15. Armus L, Charmandaris V, Bernard-Salas J, Spoon H W W, Marshall J A, Higdon S J U, Desai V, Teplitz H I, Hao L, Devost D, Brandl B R, Wu Y, Sloan G C, Soifer B T, Houck J R, Herter T L, *ApJ*, 656(2007)148-167.
16. Sellgren K, *ApJ*, 277(1984)623-633.
17. Léger A, Puget J L, *A&A*, 137(1984)L5-L8.
18. Allamandola L J, Tielens A G G M, Barker J R, *ApJ*, 290(1985)L25-L28.
19. Léger A, d'Hendecourt L, *A&A*, 146(1985)81-85.
20. Crawford M K, Tielens A G G M, Allamandola L J, *ApJ*, 293(1985)L45-L48.

21. Salama F, Bakes E L O, Allamandola L J, Tielens A G G M, *ApJ*, 458(1996)621-636.
22. Herbig G H, *ARA&A*, 33(1995)19-74.
23. Sarre P J, *J Mol Spectrosc*, 238(2006)1-10.
24. Snow T P, Le Page V, Keheyan Y, Bierbaum V M, *Nature*, 391(1998)259-260.
25. Cox P, Kessler M F, The universe as seen by ISO, Proceedings European Space Agency, ESTEC, Noordwijk (Netherlands), 1999.
26. Smith J D T, Draine B T, Dale D A, et al, Moustakas J, Kennicutt R C (Jr), Helou G, Armus L, Roussel H, Sheth K, Bendo G J, Buckalew B A, Calzetti D, Engelbracht C W, Gordon K D, Hollenbach D J, Li A, Malhotra S, Murphy E J, Walter F, *ApJ*, 656(2007)770; doi.org/10.1086/510549
27. Peeters E, Allamandola L J, Bauschlicher C W (Jr), Hudgins D M, Sandford S A, Tielens A G G M, *ApJ*, 604(2004) 252; doi.org/10.1086/381866.
28. Onaka T, Mori T I, Sakon I, Ohsawa R, Kaneda H, Okada Y, Tanaka M, *ApJ*, 780(2014)114; doi.org/10.1088/0004-637X/780/2/114
29. Lepp S, Dalgarno A, *ApJ*, 324(1988)553-556.
30. Verstraete L, Léger A, d'Hendecourt L, Defourneau D, Dutuit O, *A&A*, 237(1990)436-444.
31. Bakes E L O, Tielens A G G M, *ApJ*, 427(1994)822-838.
32. Joblin C, d'Hendecourt L, Léger A, Defourneau D, *A&A*, 281(1994)923-936.
33. Joblin C, Boissel P, Léger A, d'Hendecourt L, Defourneau D, *A&A*, 299(1995)835-846.
34. Cook D J, Saykally R J, *ApJ*, 493(1998)793; doi.org/10.1086/305156.
35. Cook D J, Schlemmer S, Balucani N, Wagner D R, Steiner B, Saykally R J, *Nature*, 380(1996)227-229.
36. Schlemmer S, Cook D J, Harrison J A, Wurfel B, Chapman W, Saykally R J, *Science*, 265(1994)1686-1689.
37. Oomens J, Meijer G, von Helden G, *J Phys Chem A*, 105(2001)8302-8309.
38. Ricks A M, Douberly G E, Duncan M A, *ApJ*, 702(2009)301; doi.org/10.1088/0004-637X/702/1/301.
39. Szczepanski J, Wang H, Vala M, Tielens A G G M, Eyley J R, Oomens J, *ApJ*, 646(2006)666-680.
40. Alvaro Galue H., Piralí O, Oomens J, *A&A*, 517(2010)A15; doi.org/10.1051/0004-6361/201014050
41. Szczepanski J, Vala M, Talbi D, Parisel O, Ellinger Y, *J Chem Phys*, 98(1993)4494;doi.org/10.1063/1.465009.
42. Vala M, Szczepanski J, Puzat F, Parisel O, Talbi D, Ellinger Y, *J Phys Chem*, 98(1994)9187-9196.
43. Hudgins D M, Sandford S A, *J Phys Chem A*, 102(1998)329-343.
44. Hudgins D M, Sandford S A, *J Phys Chem A*, 102(1998)344-352.
45. Hudgins D M, Sandford S A, Allamandola L J, *J Phys Chem A*, 98(1994)4243-4253.
46. Hudgins D M, Allamandola L J, *J Phys Chem A*, 99(1995)3033-3046.
47. Hudgins D M, Allamandola L J, *J Phys Chem A*, 99(1995)8978-8986.
48. Boersma C, Bauschlicher C W (Jr), Ricca A, Mattioda A L, Cami J, Peeters E, de Armas F S, Saborido G P, Hudgins D M, Allamandola L J, *ApJS*, 211(2014)8; doi.org/10.1088/0067-0049/211/1/8
49. Kim H-S, Wagner D R, Saykally R J, *Phys Rev Lett*, 86(2001)5691; doi.org/10.1103/PhysRevLett.86.5691
50. Kim H-S, Saykally R J, *ApJS*, 143(2002)455; doi.org/10.1086/343078.
51. Oomens J, van Roij A J A, Meijer G, von Helden G, *ApJ*, 542(2000)404; doi.org/10.1086/309545.
52. Oomens J, Sartakov B G, Tielens A G G M, Meijer G, von Helden G, *ApJ*, 560(2001)L99; doi.org/10.1086/324170.
53. Oomens J, Tielens A G G M, Sartakov B G, von Helden G, Meijer G, *ApJ*, 591(2003)968; doi.org/10.1086/375515
54. Oomens J, Sartakov B G, Meijer G, von Helden G, *Int J Mass Spectrom*, 254(2006)1-19.

55. Pathak A, Sarre P J, *MNRAS*, 391(2008)L10-L14.
56. Knorke H, Langer J, Oomens J, Dopfer O, *ApJ*, 706(2009)L66. doi.org/10.1088/0004-637X/706/1/L66.
57. Ricks A M, Douberly G E, Duncan M A, *ApJ*, 702(2009)301; doi.org/10.1088/0004-637X/702/1/301.
58. Bernstein M P, Sandford S A, Allamandola L J, *ApJ*, (472)1996 L127; doi.org/10.1086/310376.
59. Bauschlicher C W, Langhoff S R, Sandford S A, Hudgins D M, *J Phys Chem A*, 101(1997)414-2422.
60. Hudgins D M, Bauschlicher C W (Jr), Allamandola L J, *ApJ*, 632(2005)316; doi.org/10.1086/432495.
61. Mattioda A L, Hudgins D M, Bauschlicher C W, Rosi M, Allamandola L J, *J Phys Chem A*, (2003)1486-1498.
62. Mattioda A L, Hudgins D M, Bauschlicher C W, Allamandola L J, *Advances in Space Research*, 36(2005)156-165.
63. Wang Y, Szczepanski J, Vala M, *Chem Phys*, 342(2007)107-118.
64. Langhoff S R, *J Phys Chem*, 100(1996)2819-2841.
65. Langhoff S R, Bauschlicher C W, Hudgins D M, Sandford S A, Allamandola L J, *J Phys Chem A*, 102(1998) 1632-1646.
66. Bauschlicher C W, Langhoff S R, *Spectrochim Acta*, A53(1997)1225-1240.
67. Hudgins D M, Bauschlicher C W (Jr), Allamandola L J, *Spectrochim Acta*, A57(2001)907-930
68. Hudgins D M, Bauschlicher C W (Jr), Sandford S A, *ApJ*, 614(2004)770; doi.org/10.1086/423930.
69. Pathak A, Rastogi S, *Chem Phys*, 313(2005)133-150.
70. Pathak A, Rastogi S, *Chem Phys*, 326(2006)315-328.
71. Pathak A, Rastogi S, *Spectrochim Acta*, 67(2007)898-909.
72. Candian A, Sarre P J, Tielens A G G M, *ApJ*, 791(2014)L10; doi.org/10.1088/2041-8205/791/1/L10
73. Pauzat F, in EAS Publications Series, (eds) Joblin C, Tielens A G G M, 46(2011)75.
74. Hoopes G C, Sembach K R, Hébrard G, Moos H W, Knuth D C, *ApJ*, 586(2003)1094. doi.org/10.1086/367890
75. Bauschlicher C W (Jr), *Chem Phys*, 234(1998)87-94.
76. Bauschlicher C W (Jr), *Chem Phys*, 233(1998)29-34.
77. Bauschlicher C W (Jr), Langhoff S R, *Chem Phys*, 234(1998)79-86.
78. Serra G, Chaudret B, Saillard Y, Le Beuze A, Rabaa H, Ristorcelli I, Klotz A, *A&A*, 260(1992)489-493.
79. Klotz A, Marty P, Boissel P, Serra G, Chaudret B, Daudey J P, *A&A*, 304(1995) 520-530.
80. Simon A, Rapacioli M, Lanza M, Joalland B, Spiegelman F, *Phys Chem Chem Phys*, 13(2011)3359-3374.
81. Pathak A, Rastogi S, *A&A*, 485(2008)735-742.
82. Pech C, Joblin C, Boissel P, *A&A*, 388(2002)639-651.
83. Cohen M, Tielens A G G M, Bregman J D, Witteborn F C, Rank D M, Allamandola L J, Muizon M D, *ApJ*, 341(1989)246-269.
84. Bregman J D, Allamandola L J, Tielens A G G M, Geballe T R, Witteborn F C, *ApJ*, 344(1989)791-798.
85. Maurya A, Rastogi S, Rouillé G, Huisken F, Henning T, *ApJ*, 755(2012)120; doi.org/10.1088/0004-637X/755/2/120.
86. Salama F, Galazutdinov G A, Krelowski J, Allamandola L J, Musaev F A, *ApJ*, 526(1999)265; doi.org/10.1086/307978
87. Biennier L, Salama F, Allamandola L, Scherer J, *J Chem Phys*, 118(2003)7863; doi.org/10.1063/1.1564044
88. Tan X, Salama F, *J Chem Phys*, 122(2005)084318; doi.org/10.1063/1.1851502
89. Tan X, Salama F, *J Chem Phys*, 123(2005)014312; /jcp.aip.org/jcp/copyright.jsp

90. Salama F, Galazutdinov G A, Krelowski J, Biennier L, Beletsky Y, Song I.-O, *ApJ*, 728(2011)154; doi.org/10.1088/0004-637X/728/2/154
91. Weisman J L, Lee T J, Head-Gordon M, *Spectrochim Acta*, 57(2001)931-945.
92. Weisman J L, Lee T J, Salama F, Head-Gordon M, *ApJ*, 587(2003)256; doi.org/10.1086/368103.
93. Mallocci G, Mulas G, Joblin C, *A&A*, 426(2004)105-117.
94. Mallocci G, Joblin C, Mulas G, *Chem Phys*, 332(2007)353-359.
95. Mallocci G, Joblin C, Mulas G, *A&A*, 462(2007)627-635.
96. Mallocci G, Mulas G, Cappellini G, Joblin C, *Chem Phys*, 340(2007)43-58.
97. Buragohain M, Pathak A, Hammonds M, Sarre P J, in American Institute of Physics Conference Series, (eds) Chakrabarti S K, Acharyya K, Das A, 1543(2013)258-264.
98. Rastogi S, Maurya A, Singh R, *Asian J Phys*, 24(2015)1113-1125.

[Received:5.6.2015; accepted: 16.6.2015]