Theoretical spectra of PAHs in modeling astrophysical IR features

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Abstract

The mid infrared emissions known as Unidentified Infrared (UIR) bands are observed ubiquitously in a variety of astrophysical sources and are attributed to emissions from Polycyclic Aromatic Hydrocarbon (PAH) molecules. The observed features result from a composite mix of PAH populations consisting of neutrals, cations, anions and hydrogenated/dehydrogenated species. There are source to source variations in the UIR features indicating the presence of different PAH populations in different Astrophysical regions. An understanding of the IR properties of PAHs can, therefore, lead to an understanding of the astrophysical environments. With this view vibrational characteristics using quantum chemical calculations for a large number of PAH neutrals and cations of different shapes and sizes have been studied. The obtained infrared data is used to model emission spectra of diverse PAH groups and compared with the observed bands. The model spectra presented here points out the presence of different size group of PAHs in different interstellar environments.

Key words: PAH, Interstellar organic molecules, IR spectra, Unidentified Infrared Bands

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1 Introduction

Bands at 3.3, 6.2, 7.7, 8.6, 11.2 and 12.7 μm (3030, 1610, 1300, 1160, 890 and 790 cm^{-1}) and beyond dominate the mid-infrared emissions of diverse astronomical sources ranging from UV-rich HII regions to benign environments of proto-planetary-nebulae (Gillett et al. 1973); (Cohen et al. 1989); (Geballe et al. 1989); (First ISO resutls 1996); (Peeters et al. 2002). These bands are popularly known as the unidentified infrared (UIR) bands and have been attributed to emissions from isolated gas phase polycyclic aromatic hydrocarbon (PAH) molecules likely to be present in the interstellar medium (ISM) (Leger & Puget 1984); (Allamandola et al. 1985); (Puget & Leger 1989); (Allamandola et al. 1989). The emission

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process of a PAH molecule involves the absorption of an energetic photon that heats up the molecule to temperatures of the order of 1000 K. PAH molecules de-excite through internal vibrational redistribution and IR fluorescence with the emission bands corresponding to fundamental modes of vibrations set up within the molecule. Different ISM regions may contain a complex mix of PAH neutrals and cations giving rise to UIR bands (Allamandola et al. 1999). The fractional abundance of cations and neutrals depends on the astrophysical environment which results in source to source variations exhibited in observations.

Experimental and theoretical spectroscopic studies on PAHs strengthen the PAH hypothesis and result in a better perception of the interstellar PAH population (Szczepanski & Vala 1993); (Allamandola et al. 1999); (Cook et al. 1996); (Kim et al. 2001); (Kim & Saykally 2002); (Langhoff 1996); (Bauschlicher & Bakes 2000); (Pathak 2006). These studies emphasize that PAH cations and to a lesser extent neutral PAHs contribute towards the UIR bands. But the size of PAH molecules residing in ISM is unclear and under constant debate. Extrapolating the spacing between 6.2 and 7.7 μm PAH bands obtained from PAH spectroscopy experiments, Hudgins & Allamandola (Hudgins & Allamandola 1999b) have proposed that PAHs with 50–80 carbon atoms dominate the mid-IR emission. Studies testing the photo-physical stability of PAHs (Schutte et al. 1993); (Allain et al. 1996a); (Allain et al. 1996b); (LePage et al. 2003) have pointed to the presence of even larger PAHs depending on the surrounding environment.

In this report we have used the existing IR information of several PAHs including fluoranthenes and their cations (Pathak 2006) to construct emission models for comparison with observed UIR bands. The results lead to a better idea of the PAH population residing in different regions of the ISM.

2 Vibrational calculations and charge distribution

In order to understand the vibrational spectra of PAHs and its variation with the change in size and ionization state of the molecules a detailed theoretical study of several PAHs of varying sizes has been done. The effect of ionization on the charge distribution and its relation to the significant changes occurring in the IR spectra of these PAHs is also studied.

Calculations using density functional theory (DFT) play a vital role to provide the IR information of PAHs for interpretation of observations. GAMESS (Schmidt et al. 1993) ab-initio program has been used to calculate the IR spectra of PAHs and their cations. Optimized geometries of all the molecules were obtained first using B3LYP functionals in conjunction with 4-31G basis expansion. The frequencies and intensity values compare well with the experimental data wherever available. The computed IR emission spectra of each PAH is plotted considering Gaussian peaks with FWHM (Full Width at Half Maximum) to be 30 cm^{-1}. The FWHM depends on the internal vibrational redistribution time of the molecule and 30 cm^{-1} is the typical width for PAHs emitting in conditions similar to those of the ISM (Allamandola et al. 1989).

The spectra of the neutral PAH molecules mainly consists of $C-H$ out of plane bend mode and

$C-H$ stretch modes. On the other hand the spectra of cations is rich in the $C-C$ stretch and $C-H$ in plane bend modes. Upon ionization there are negligible structural changes. To understand the changes in the IR spectra upon ionization of PAHs the corresponding charge changes are reported and discussed (Pathak & Rastogi 2005); (Pathak & Rastogi 2006a); (Pathak & Rastogi 2006b). The charge on the innermost carbon atoms is small in all the neutral species and minor change is present upon ionization. In neutrals the outer carbons carry negative charge and the hydrogens are positively charged. Significant change in charges of these atoms is noticed upon ionization. These charge changes affect the intensities of various modes particularly the $C-H$ stretch vibrations and the $C-C$ stretch modes. The vibrational modes having a very small dipole change in neutral PAHs show large dipole variations upon ionization.

3 Modeling the UIR bands

Exact identification of a single PAH molecule is difficult in IR but comparison with laboratory and theoretical data give information of the possible PAH groups. Profile variations associated with the observed UIR bands in different sources reflect the presence of different PAH groups therein; more cations being estimated 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). Model emission spectra of different size groups of PAHs and their comparison with observations can lead to better understanding of the correlation between astrophysical environment and PAH group therein. The theoretical calculations undertaken (Pathak 2006) have resulted in a database of IR spectra of several PAHs and their cations. This information is utilized to model the interstellar UIR bands.

Simple thermal emission model (Schutte et al. 1993); (Cook & Saykally 1998); (Pech et al. 2002) is used to calculate emission photon flux ϕ_i of the i^{th} mode with frequency $\omega_i\ cm^{-1}$ from a particular PAH:

$$\phi_i = A_i \times [exp(hc\ \omega_i/kT) - 1]^{-1} \tag{1}$$

here T is the temperature equivalent to the internal energy of the molecule. Einstein A coefficient is obtained from absorption intensities S_i (taken in units of Km/mol) using equation (25) in Cook & Saykally (Cook & Saykally 1998):

$$A_i = (1.2512 \times 10^{-7})\ \omega_i^2\ S_i \tag{2}$$

Incorporating cooling of a PAH via transitions in an emission cascade requires fractional energy emitted by i^{th} mode per $1K$ drop in temperature:

$$\Delta E_i = \frac{\phi_i \times \omega_i}{\sum_i \phi_i \times \omega_i} \Delta U \tag{3}$$

where ΔU is the drop in internal energy per $1K$ cooling. Here in the harmonic approximation internal enegry and temperature T are related through the heat capacity of the molecule (Schutte et al. 1993) and given as:

$$U(T) = \sum_i \frac{hc\,\omega_i}{exp(hc\,\omega_i/kT) - 1} \tag{4}$$

Upon absorption of a photon, a PAH is excited to a temperature T_{peak} that depends on its size. Adding ΔE_i through cooling upto $T_{final} = 50$ K gives the emission for a particular mode. For simplifying calculations Cook & Saykally (Cook & Saykally 1998) assume each PAH is excited to the same temperature. The assumption is justified considering not much size variation in the small set of PAHs taken in their study. For the large size variation in our sample we assume a photon of 100,000 cm^{-1} is absorbed by each PAH. The spectra thus, obtained for each PAH can be co-added to derive composite emission spectra for modeling UIR bands.

3.1 Small PAHs

The co-added absorption spectra of catacondensed and pericondensed PAHs have been reported (Pathak & Rastogi 2005); (Pathak & Rastogi 2006a). The cations of both class have intense bands in the 1100 – 1600 cm^{-1} region. Pericondensed PAHs show a better intensity as well as band position match with the interstellar UIR bands.

The $C - H$ out-of-plane bend vibrations give rise to features at 11.2 μm and at higher wavelengths depending on the number of adjacent hydrogen atoms per ring (Hudgins & Allamandola 1999a); (Hony et al. 2001). ISO observations (Hony et al. 2001) conclude that the spectra of planetary nebulae and evolved carbon-rich stars, where PAHs are supposed to be synthesized, have a strong 11.2 μm feature (at 893 cm^{-1}; representing solo wag modes), weak features at 12.7 μm (787 cm^{-1}) and longer wavelengths (arising from trio and quartet hydrogen wag modes). The situation is almost reversed in case of UV-rich environments where the features at 12.7 μm and beyond are as intense as the 11.2 μm band. For correlation with observations, the emission model of small catacondensed and pericondensed PAHs in the range 500–1000 cm^{-1} is presented in Fig. 1. The top two panels are the co-added emission spectra of neutral and cation catacondensed PAHs and the bottom panels are the co-added spectra of neutral and cation pericondensed PAHs. All the four representative spectra are dominated by peaks due to the out-of-plane vibrations of the quartet and trio hydrogens. Upon ionization, a slight blue shift in the peaks is noticed (Fig. 1(a) to 1(b) and Fig. 1(c) to 1(d)). Fig. 1(a), (c) and (d) have intense bands due to the out of plane vibrations of solo hydrogen atoms. These model spectra are similar to observations of UV-rich environments where the 12.7 μm band is as intense as the 11.2 μm band (Hony et al. 2001). Observations of benign environments are dominated by 11.2 μm band which is different from the theoretical model spectra presented here. For better matching with these, a different class of PAHs needs to be considered.

The co-added spectra (Fig. 9 in (Pathak & Rastogi 2006a)) shows that catacondensed PAH cations have three sharp peaks in the 1100 – 1600 cm^{-1} region while the UIR bands have a broad feature near 1300 cm^{-1}. The co-added spectra of pericondensed PAHs show a better match with observations. Fig. 2 shows the comparison of co-added emission model of small catacondensed and pericondensed PAH cations in the range 1200 to 1400 and 1450 to 1650 cm^{-1}. The spectra in the top panels (a & b) are for catacondensed PAHs while the bottom panel (c & d) shows the co-added spectra of pericondensed PAH cations.

Fig. 2(a) and Fig. 2(c) are theoretical representations for the observed 7.7 μm (1300 cm^{-1}) band. The spectra for catacondensed PAHs (Fig. 2(a)) has the band at 1340 cm^{-1} (7.5 μm) which is away from the observed position. The spectra of pericondensed PAH cations (Fig. 2(c)) has this band at 1310 cm^{-1} presenting a better position match with observations. The profile of this theoretical band consists of two components at 1290 and 1320 cm^{-1}. The 1320 cm^{-1} (7.6 μm) component has a slightly higher intensity than the lower frequency component. This profile presents a good match with the UIR band profile of NGC-2023 and other similar objects categorized as A' profile (Peeters et al. 2002); (Pathak & Rastogi 2006a).

Theoretically modeled representative spectra for the 6.2 μm (1610 cm^{-1}) UIR band are presented in Fig. 2(b) and Fig. 2(d). The emission spectra of catacondensed PAH cations (Fig. 2(b)) has the band at around 1500 cm^{-1} while pericondensed PAH cations have the band near 1530 cm^{-1}. The blue-shift of 30 cm^{-1} is coming from medium sized pericondensed PAH constituents for the spectra presented in Fig. 2(d). Still the position match with the 6.2 μm UIR band is very poor which calls for a different sample of pure PAHs or substituted PAHs to be examined for a better representation. It has been previously suggested (Hudgins & Allamandola 1999b) that PAH cations having 50 - 80 C atoms may be the carriers of 1610 cm^{-1} UIR band and features redder to it may be carried by smaller (20 - 40 C atoms) PAHs.

3.2 Large PAHs

It is now widely accepted that PAHs present in the ISM are significantly larger than those studied experimentally (Schutte et al. 1993); (Allain et al. 1996a); (Allain et al. 1996b); (LePage et al. 2003). Theoretical quantum chemical studies provide with the missing IR information of such PAHs (Pathak & Rastogi 2006b). The results indicate that the spectra of large PAHs present a better intensity as well as position match with observations.

The model emission spectra of large (having more than 30 carbons) and small PAHs (having less than 30 carbons) are compared in Fig. 3. The spectra of large neutral PAHs are dominated by the 11.2 μm band matching well the observations of planetary nebulae and evolved carbon-rich stars (Hony et al. 2001). The spectra of small PAHs is distinct from that of large PAHs as features due to out of plane bend vibrations of duo, trio and quartet hydrogens are more intense. The $C - H$ stretch vibrations give rise to an intense feature in the spectra of large PAH cations while small PAHs show weak intensity.

Large neutral PAHs have significantly intense peaks closer to 6.2 and 7.7 μm as compared to small PAHs, though the magnitude of the intensity is not enough to match the UIR band intensities. The theoretical IR spectra of PAH cations show closer position and intensity match for the 6.2 and 7.7 μm UIR bands. It is noted that with increasing cation size, the $C - C$

Table 1
Band positions corresponding to the 7.8 μm (1280 cm^{-1}) and 7.6 μm (1315 cm^{-1}) component of the 7.7 complex UIR feature of the studied large PAHs.[1]

PAHs	7.8 μm AIB	7.6 μm AIB
$C_{38}H_{16}$	1295 (1.19)	1323 (1.24)
$C_{48}H_{18}$	1292 (1.13)	
$C_{57}H_{19}$		1312 (1.26)
$C_{62}H_{20}$	1285 (1.09)	1328 (0.49)
$C_{66}H_{20}$		1304 (0.74)
$C_{80}H_{22}$	1288 (0.64)	
$C_{90}H_{24}$	1284 (1.19)	
$C_{96}H_{24}$	1274 (0.47)	1311 (0.77)

[1] Wavenumbers are in cm^{-1} and relative intensities are given in parentheses.

stretch feature near 1570 cm^{-1} shows regular rise in intensity. A blue shift also accompanies this band with increasing size. As extra rings are added to PAHs, the inner $C-C$ bonds have tighter vibrations shifting their band position to higher wavenumber. The blue shift in large PAHs is not systematic and even not enough to match the 6.2 μm position of the observed UIR band. For most of the studied large PAH cations, this band lies near 1570 cm^{-1} which is away from the 6.2 μm (1610 cm^{-1}) UIR feature. Recent theoretical calculations incorporating nitrogen inside the ring, replacing one or more carbon atoms, proposes to explain the 6.2 μm emission feature (Hudgins et al. 2005).

The 1300 cm^{-1} (7.7 μm) PAH feature in the spectra of large PAH cations present excellent position and intensity correlation with the observations. The 7.7 μm feature is a composite of two sub-features at 7.6 and 7.8 μm as indicated by observations (Peeters et al. 2002); (Peeters et al. 2004); (Bregman et al. 1989); (Bregman & Temi 2005). These sub-features are also present in the theoretical spectra of large PAHs. The two sub-components for most of the studied large PAHs have been identified around 1285 cm^{-1} (7.78 μm) and 1315 cm^{-1} (7.60 μm) as presented in Table 1. The emission in the 1285 cm^{-1} mode dominates in most of the large PAH cations. Rapacioli et al. (Rapacioli et al. 2005) attribute the 7.8 μm sub-feature to very small grains (VSGs) made up of PAH clusters. The significance of large PAHs as portrayed by its stability is further reflected by its better correlation with the UIR bands.

3.3 Fluoranthenes

The introduction of a pentagonal ring within a PAH results in variations in the IR spectra. To explore the possibility of their relation with UIR bands co-added model emission spectra of three fluoranthenes: fluoranthene, benzo(a)fluoranthene and benzo(k)fluoranthene and their cations are presented (Fig. 4). An intense band at 1430 cm^{-1} distinguishes the neutral spectra of fluoranthenes from other PAHs. This band is due to $C-C$ stretch vibrations set up in the five membered ring which is not found in pure PAHs. The $C-H$ stretch mode has maximum intensity and intense bands due to wag of quartet hydrogen atoms and a small peak due to trio hydrogen out of plane vibrations are present in the neutral spectra.

The cation spectra is relatively complex with several peaks coming up due to the in-plane vibrations of hydrogen atoms and $C-C$ stretch vibrations. Intensity of $C-C$ stretch vibrations of the five membered ring increases. The intensity of out-of-plane vibrations of solo hydrogen atoms dominates over wag of trio and quartet hydrogen atoms in the cation spectra. Overall the cation spectra is dominated by the feature at 1330 cm^{-1} due to $C-C$ stretch vibrations of the outer bonds in all the constituent species.

Contribution of neutral fluoranthenes towards UIR bands is restricted to the 12.7 μm band and similar bands at longer wavelengths. Fluoranthene cations may contribute towards the broad complex 7.7 μm feature and 8.6 μm band. The feature corresponding to the 6.2 μm AIB lies at 1560 cm^{-1} in the composite emission spectra of fluoranthene cations.

4 Spectral model

Based on the IR information of small and large compact PAHs, two groups comprising medium sized PAHs (20 – 40 carbons) and large PAHs (> 40 carbons) are taken to produce two model emission spectra. The emission model in the range 1200 to 1400 cm^{-1} is given in Fig. 5. The two parallel lines at 1285 and 1315 cm^{-1} enclose the observed 7.7 μm complex. The lower wavelength component around 1340 cm^{-1} (7.46 μm) dominates the 7.7 μm band in Fig. 5(a) while the higher wavelength sub-feature at 1286 cm^{-1} (7.78 μm) is less intense. Profiles similar to model in Fig. 5(a) have been observed in UV-rich environments of HII regions and reflection nebulae; comparison shown with reflection nebula NGC 2023. These have been classified as A' profiles (Peeters et al. 2002). In Fig. 5(b) the 7.7 μm band is dominated by the higher wavelength sub-component at 1290 cm^{-1} (7.75 μm) with an apparent shoulder at around 1314 cm^{-1} (7.61 μm); comparison shown with post-AGB star HD 44179 that is classified as B' profile (Peeters et al. 2002). This agrees very well with observations of relatively benign astrophysical regions where PAHs are supposed to be synthesized.

The analysis of the two models points towards formation of PAHs in the outflows of carbon rich AGB stars. Spectra of such sources are dominated by the 7.8 μm (1285 cm^{-1}) sub-component (Beintema et al. 1996) matching well with the theoretical representative spectra of large PAHs (Fig. 5(b)). As these PAHs are expelled, harsh interstellar environments process these molecules and may result in transformation of large PAHs to medium sized ones. Medium sized compact PAHs are stable enough to survive in strong UV environments. Spectra in Fig. 5(a) fits well the spectra of such regions involved in processing of PAHs.

5 Conclusions

The obtained infrared data of PAHs is used to model co-added spectra of diverse PAH groups and compared with the observed bands. Variations observed in profiles of the UIR bands are well correlated with different PAH groups in different regions. The spectra of large neutral PAHs are dominated by the solo wag at 11.2 μm matching well the observations of benign regions while the duo, trio and quartet modes at higher wavelengths dominate in UV rich star forming regions as in small and medium sized PAHs. Analysis of the complex 7.7 μm band points to formation of large PAHs in the outflows of carbon rich AGB stars where the 7.8 μm (1285 cm^{-1}) sub-component is dominant. Harsh interstellar processing transforms the large PAHs to stable medium sized ones where the 7.6 μm (1315 cm^{-1}) sub-feature is stronger.

Large and medium sized PAH groups may not be specifically disconnected and some common molecules may be present. The PAHs may also be in different proportions in different regions. The absorption from background radiation field depends on the absorption cross-section of individual PAHs so information of radiation field in UV upto visible together with absorption cross section in this range is needed. Shifts due to anharmonicity and hot bands should also be taken in to account (Pech et al. 2002); (Mulas et al. 2006). The presented composite emission models provide some insight but in an exhaustive emission model of observations from a specific object all these points must be incorporated.

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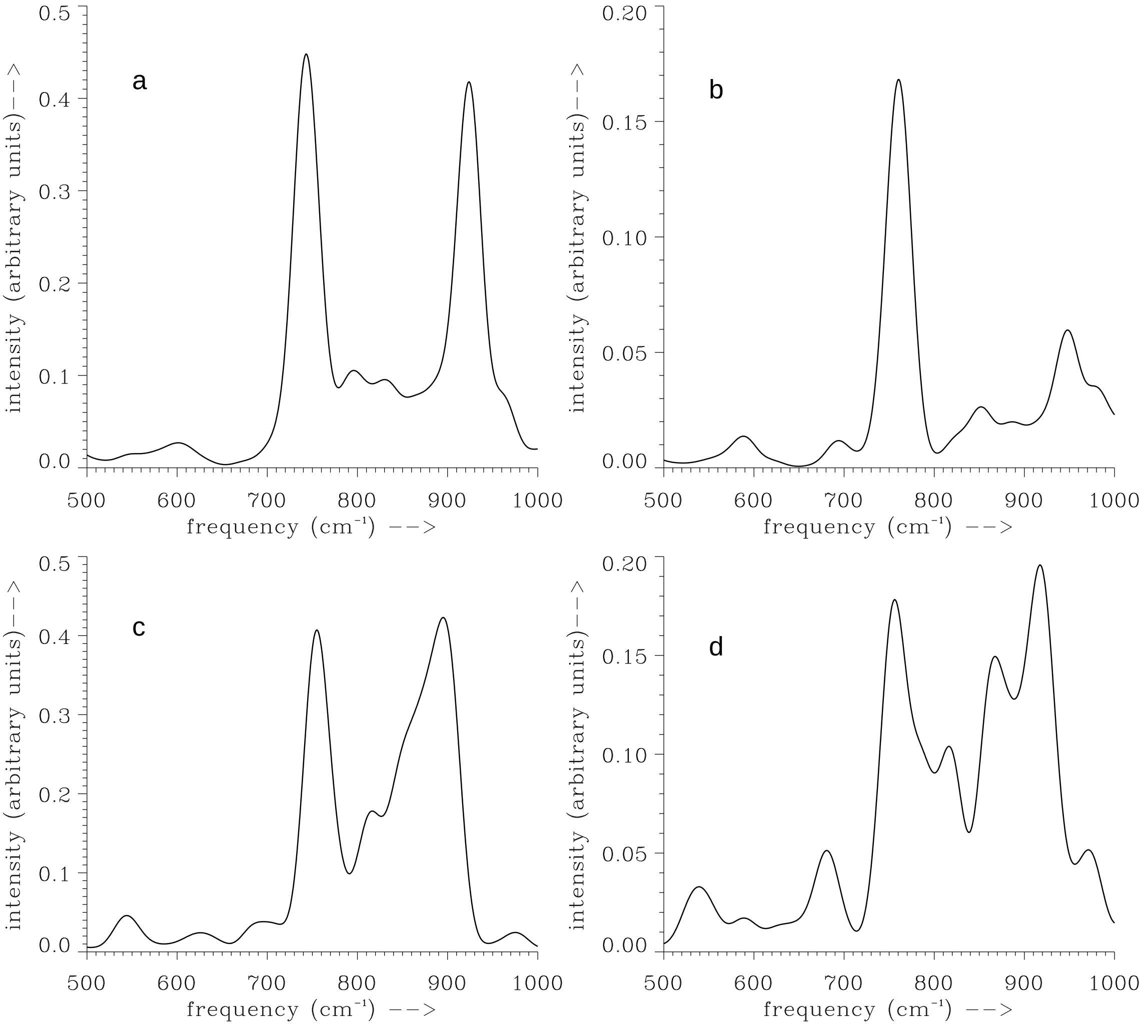

Fig. 1. Co–added emission spectra in the range 500 to 1000 cm^{-1} with equal proportions of: Studied Catacondensed PAH (a) neutrals, (b) cations; Studied Pericondensed PAH (c) neutrals and (d) cations.

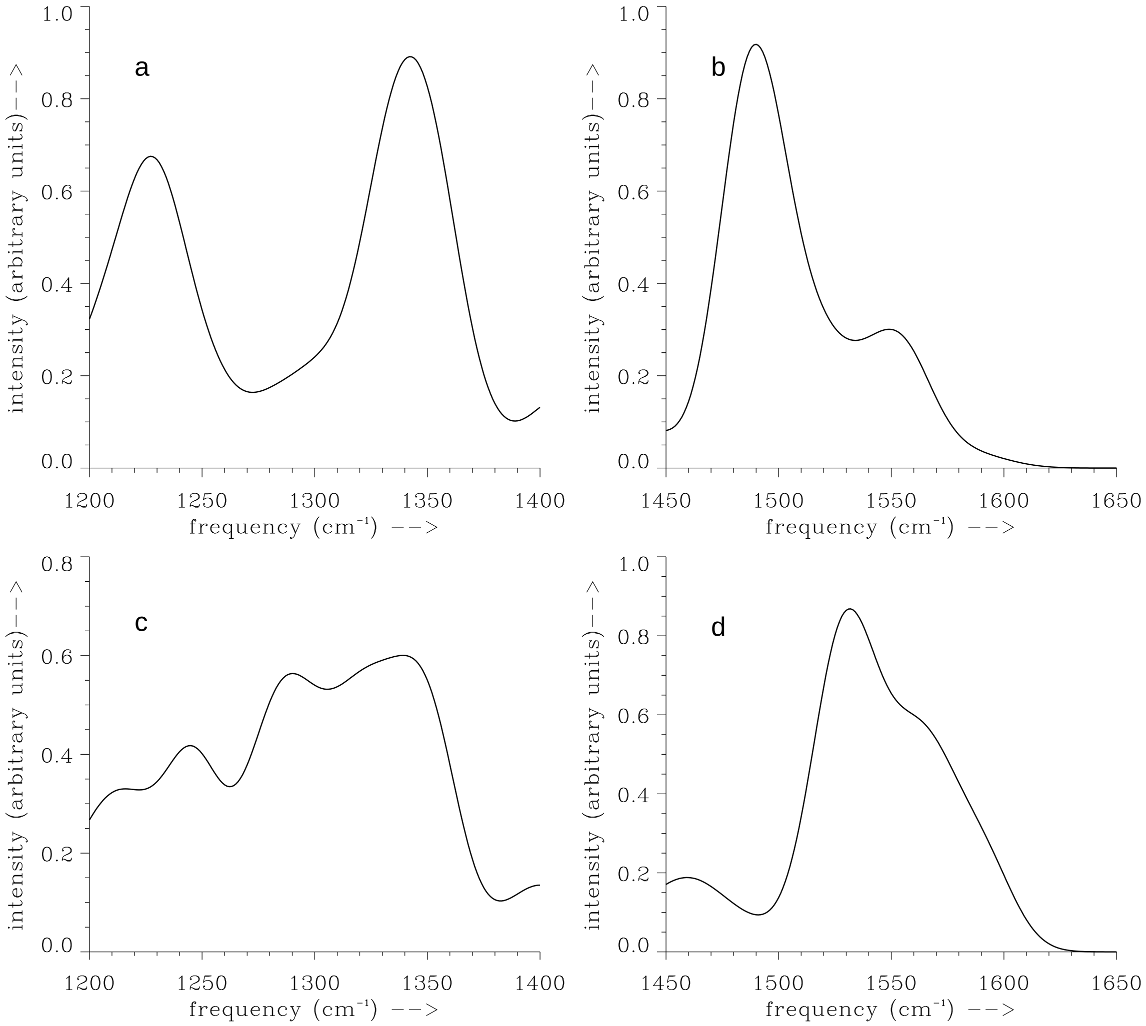

Fig. 2. Co–added emission spectra with equal proportions of: Studied Catacondensed PAH cations (a) 1200 to 1400 cm^{-1}, (b) 1450 to 1650 cm^{-1}; Studied Pericondensed PAH cations (c) 1200 to 1400 cm^{-1} and (d) 1450 to 1650 cm^{-1}.

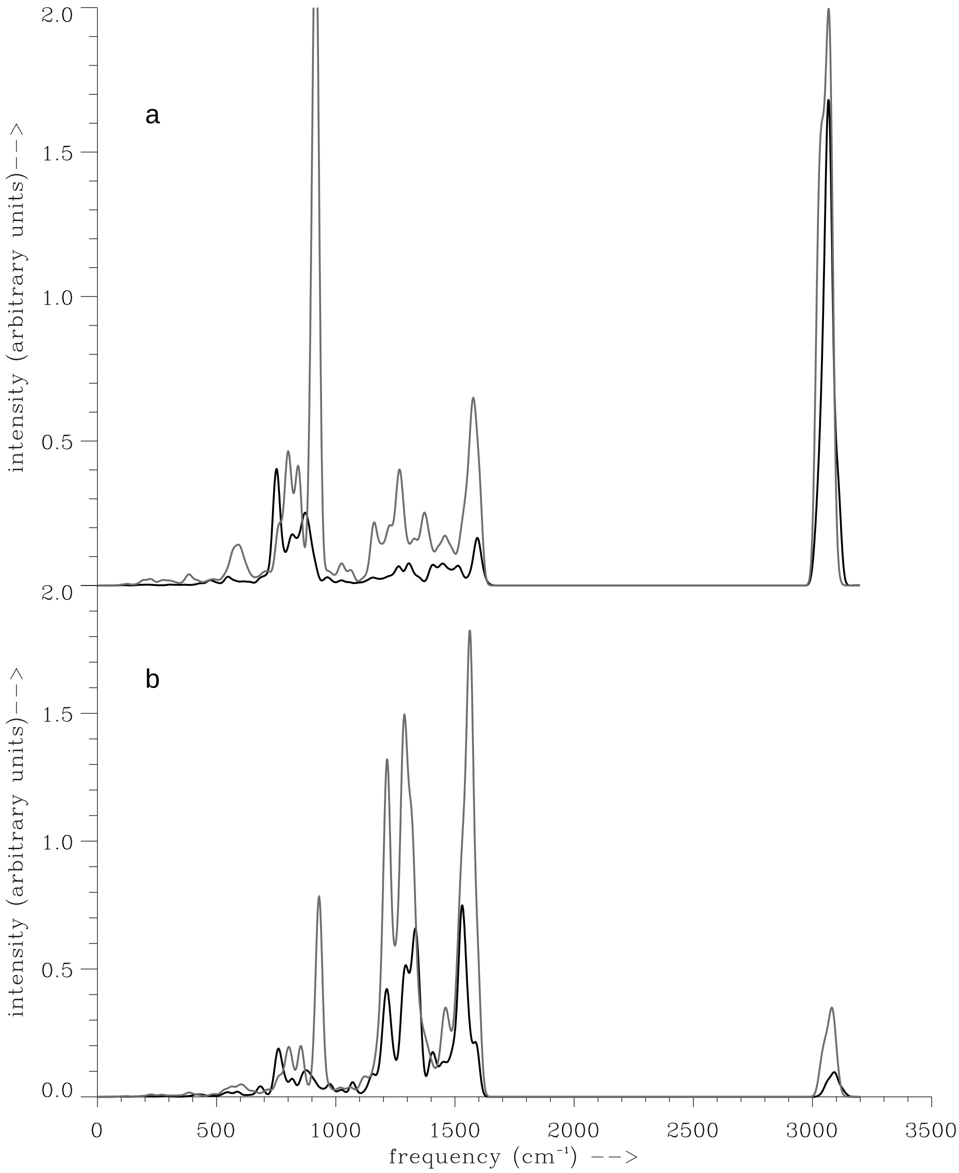

Fig. 3. Comparative emission spectra of PAHs having less than 30 C atoms (black) and more than 30 C atoms (grey) – (a) neutrals and (b) cations

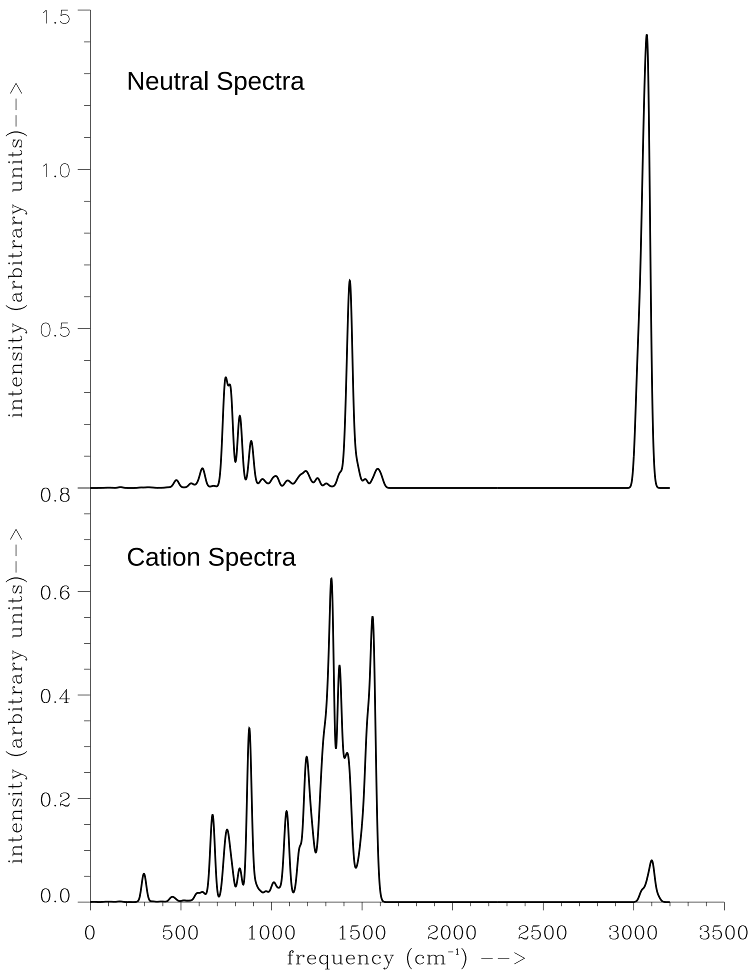

Fig. 4. Co-added emission spectra of fluoranthenes: fluoranthene, benzo(a)fluoranthene and benzo(k)fluoranthene and their cations.

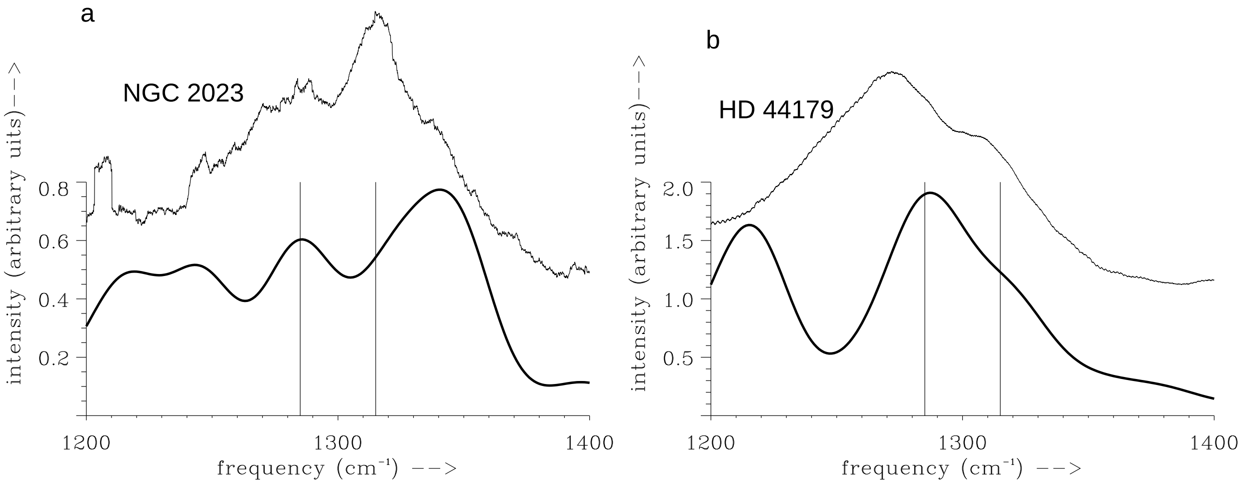

Fig. 5. Model emission spectra in the 1200 to 1400 cm^{-1} region of two PAH groups (a) 20 to 40 C atoms and (b) more than 40 C atoms compared with observed spectra. The 7.7 μm band lies within the two parallel lines.