IR Spectral variations in PAHs substituted with multi-vinyl and acetylenic side groups

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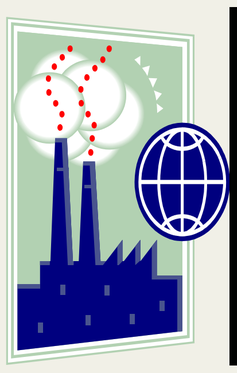
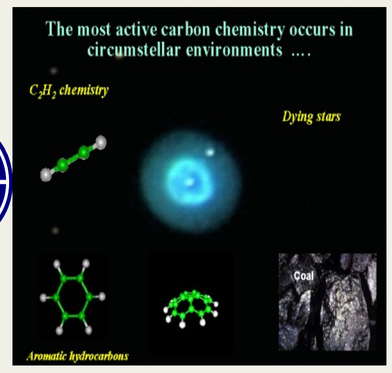
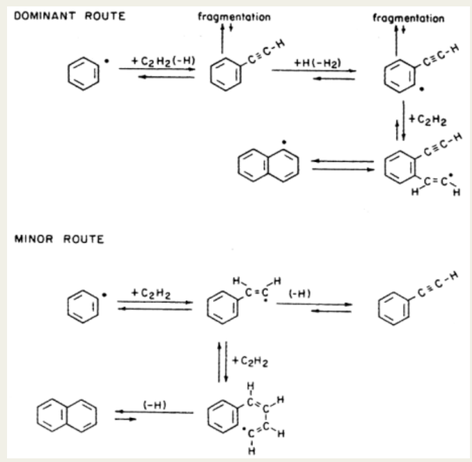
Introduction

Infrared emission bands observed from diverse astrophysical objects at 3.3, 6.2, 7.7, 8.6, 11.2, 12.7 & 16.4 μm are assigned to the vibrational bands of Polycyclic Aromatic Hydrocarbon (PAH) molecules. The variations in the profile of these emission features between sources ranging from star forming regions to late type stars and even extra galactic sources point towards the presence of different populations of PAHs in different objects. The features are well correlated among objects and based on emission models are also correlated to a good extent to PAH size and ionization states (Pathak & Rastogi 2008). Still simultaneous fit for all the features is not yet achieved. The growth and evolution of PAH forms is also not clearly understood. Most of the vibrational studies are confined to planar PAHs without side groups, while reaction intermediaries and fractured species are likely to be with side groups. A composite spectrum of different size groups of PAHs gives a good match for the '7.7' μm complex but the 6.2 μm feature is underestimated in position. Vinyl substituted PAHs are considered as possible intermediary (Hu, Alkhesho & Duley 2006) and the C=C in the side group may enhance the stretch mode closer to the 6.2 μm feature. So a study of the vibrational modes of various vinyl and acetylenic substituted PAHs has been made. The vibrational spectra is obtained by quantum chemical calculations using DFT/B3LYP in conjugation with suitable basis. Shifting of modes due to position of substitution and length of the side group is analyzed.

Growth of PAH forms in various environments & Two pronounced pathways of the formation of PAH molecules in circumstellar envelope of AGB stars.
Dominant route (Frenklach et al. 1984),
Minor route (Bittner & Howard 1981)







Quantum chemical calculation :

PAHs possibly present in the ISM are difficult to synthesize and thus it is difficult to obtain their experimental spectra. Quantum Chemical calculations can provide the much needed IR information.

- Density Functional Theory DFT-B3LYP functional with 4-31G basis is applied for IR absorption data. The **Gamess** package is used.
- The obtained absorption spectra from the Quantum Chemical calculation is used as input for the emission modeling.
- The used scaling factor is 0.9534

Molecules	Optimization Energy (neutral/cation)	Dihedral Angle (Degree)
5-vinyl-anthanthrene	-921.2598849 -921.0342287	C35,C27,C6,C5 138.9
6-vinyl-anthanthrene	-921.2572095 -921.0347395	C35,C28,C8,C7 57.8
5,3-vinyl-anthanthrene	-998.5059400 ----	C35,C27,C6,C7 -145.o C39,C25,C3,C4 43.1
5,7-vinyl-anthanthrene	-998.5079630 ----	C35,C27,C6,C7 -141.o C39,C29,C10,C11 -32.1
5,11-vinyl-anthanthrene	-998.5077674 -998.2843325	C35,C31,C8,C7 140.8 C36,C32,C12,C10 140.8

Emission Modelling :

We use thermal emission model in which the average energy of the individual vibrational modes is assumed to be small compared to total energy U(T) of the exited PAH specie.

- The vibrational modes of PAH molecules assumed as simple harmonic oscillators.
- The total internal energy of the molecule having 'm' normal modes at temperature T is U(T).

$$U(T) = \sum_{i=1}^{m} \frac{h c \omega_i}{\exp(hc\,\omega_i / kT) - 1}$$

Assumed background radiation field temperature is $T_* = 40{,}000$ K

Rate of photon absorption

$$R_{abs} = B_\nu \sigma_\nu / h\nu$$

- Emission photon flux ϕ_i for the i^{th} mode is given as

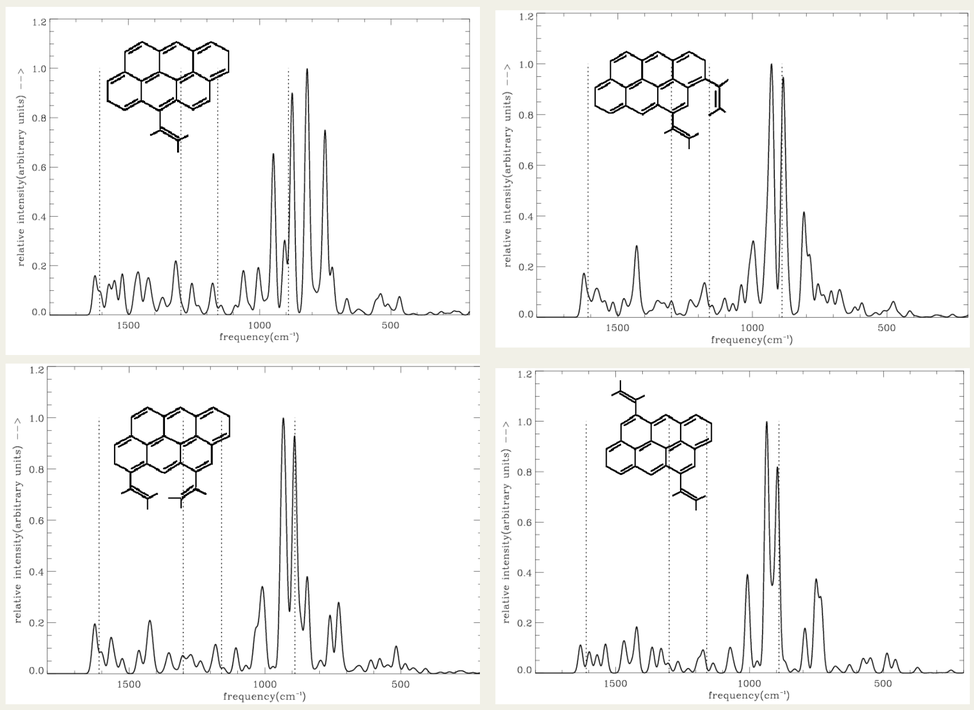
$$\phi_i = A_i^{1,0} \times [\exp(hc\,\omega_i/kT) - 1]^{-1}$$

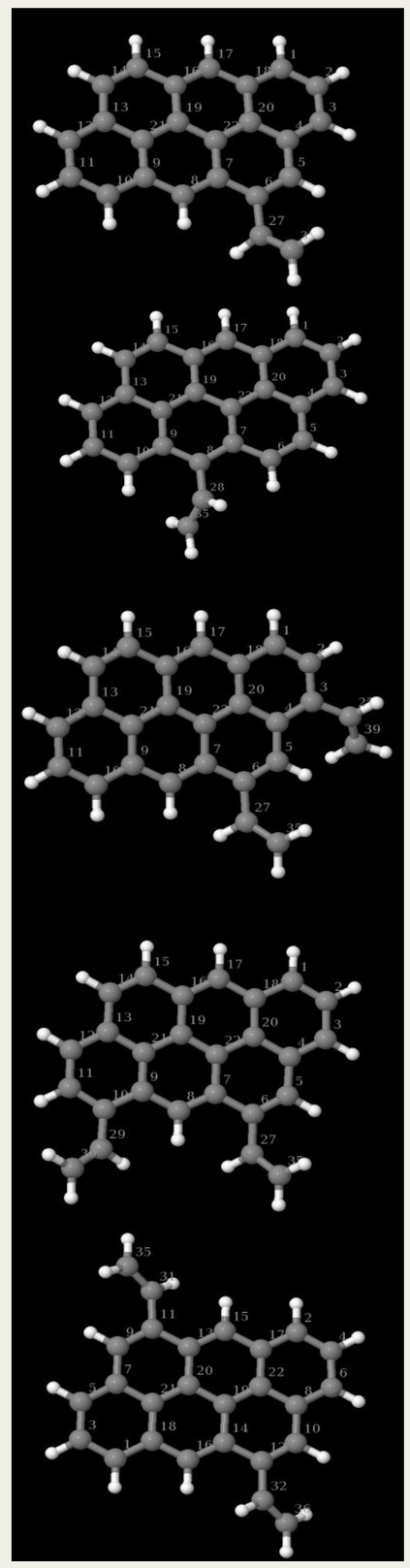
- For a fall in internal energy by dU, the fractional energy emitted in the i^{th} mode is:

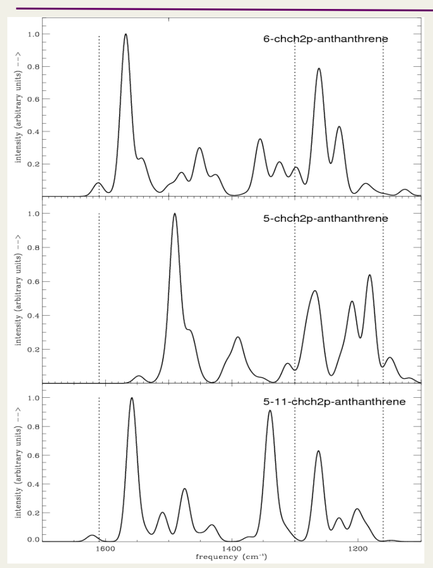
$$\Delta E_i(T) = \frac{\phi_i \times \omega_i}{\sum_{i=1}^{m} \phi_i \times \omega_i} \times \Delta U(T)$$

- The fractional energy E_i is integrated over the cooling range from T_p to a temperature of 50 K below which the energy emitted is negligible.

Emission spectra of the neutral of each molecule using thermal emission model in the 1800 – 200 cm^{-1} range, FWHM 20 cm^{-1}

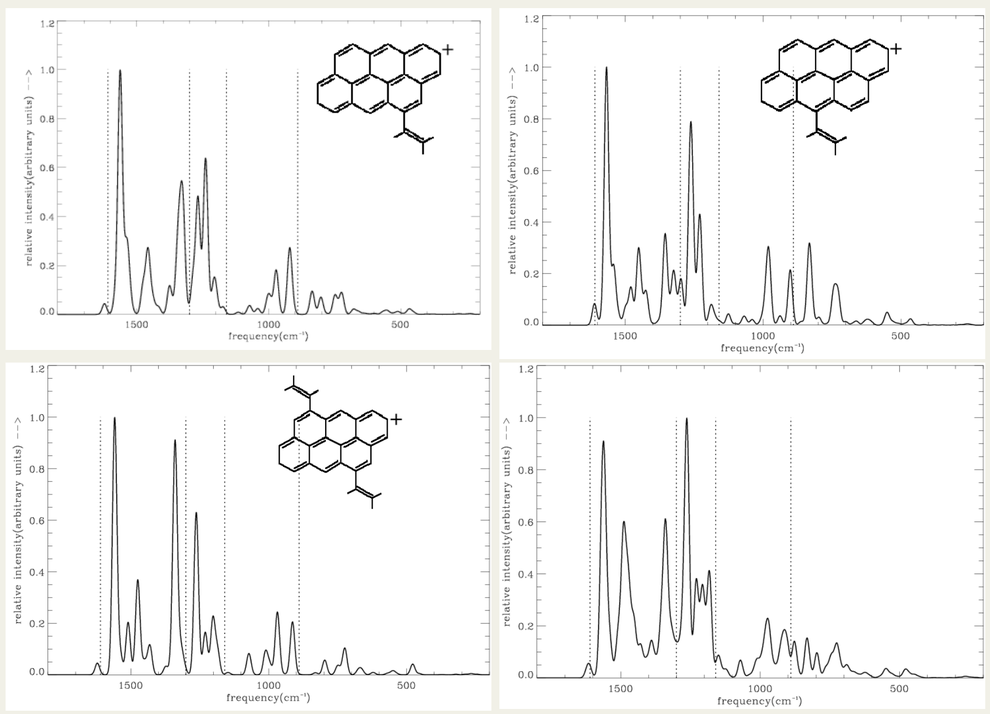






Enlarged emission spectra of cations for 6.2 & 7.7μm feature.
Substitution at solo position gives more shift towards 6.2 μm feature than terminal vinyl.
Vinyl at terminal position gives better position match for 7.7 μm complex.

Emission spectra of the cation of each molecule using thermal emission model and their composite emission spectra taking each one in equal proportion in the 1800 – 200 cm^{-1} range, , FWHM 20 cm^{-1}



Conclusion :

- **The IR spectra of PAHs with vinyl and Di-vinyl side-groups at different position is studied. The variation in the position of C-C stretch feature reveals the possibility of the presence of PAHs with vinyl side-group at different position in different environment.**
- **Matching the complete spectrum of specific object with a model can indicate regarding the type of PAHs present & about the chemical and physical property of the object.**
- **A better understanding of PAH formation and evolution in different astrophysical environments is envisaged.**

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