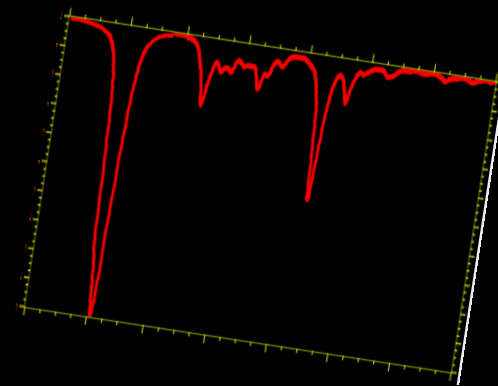
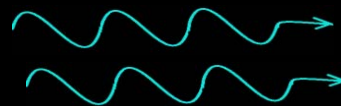


# Vibrational Spectroscopy of PAHs

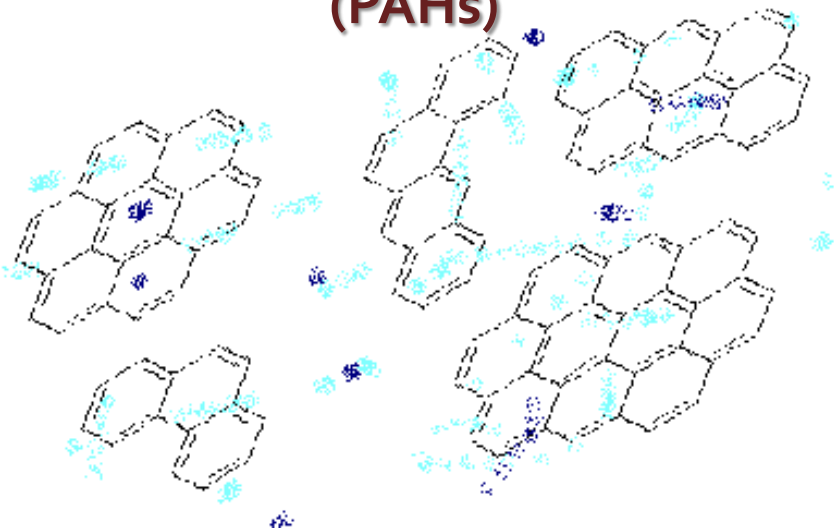


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# Polycyclic Aromatic Hydrocarbons (PAHs)



'Ubiquitous'  
in Space

Detected via IR emission features  
at  
3.3, 6.2, 7.7, 8.6, 11.2 & 12.7  $\mu\text{m}$

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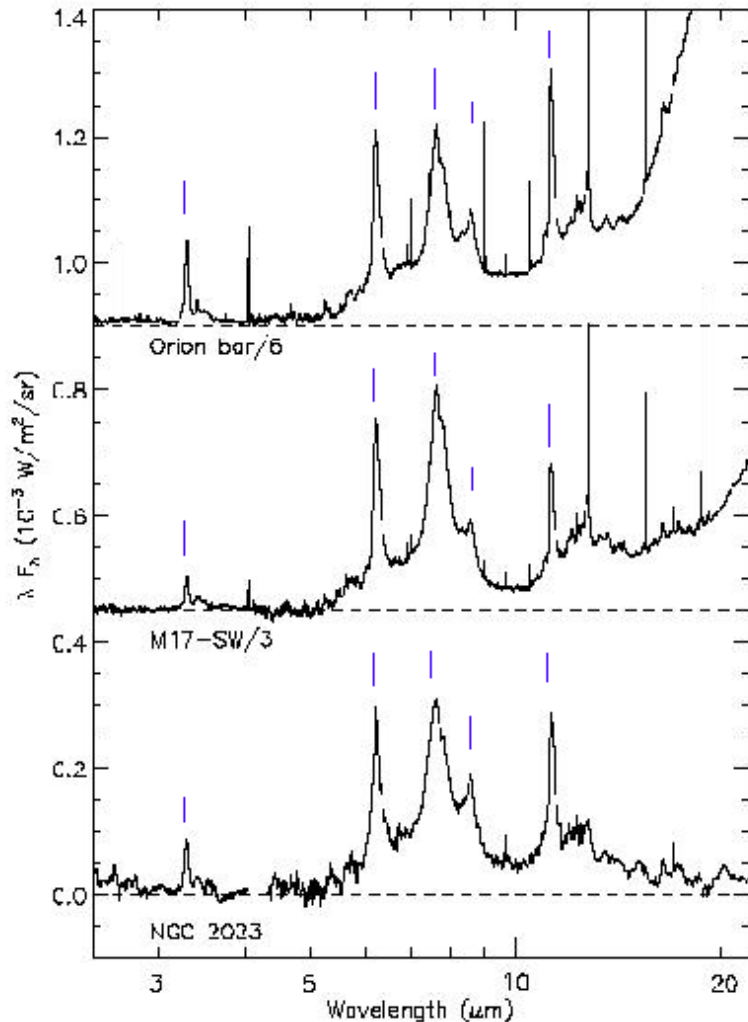


"I'm afraid you have emphysema. Try to avoid sooty chimneys."

- ❖ **Emphysema** is a lung disease; caused by exposure to toxic chemicals and tobacco smoke.

## Infrared emission features –

3030, 1613, 1299, 1163, 893 & 787  $\text{cm}^{-1}$  (3.3, 6.2, 7.7, 8.6, 11.2 & 12.7  $\mu\text{m}$ ).

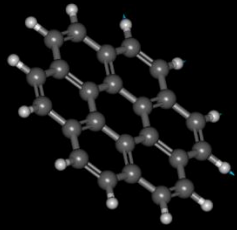


ISO-SWS spectra,  
(First ISO results, 1996, A&A, 315)

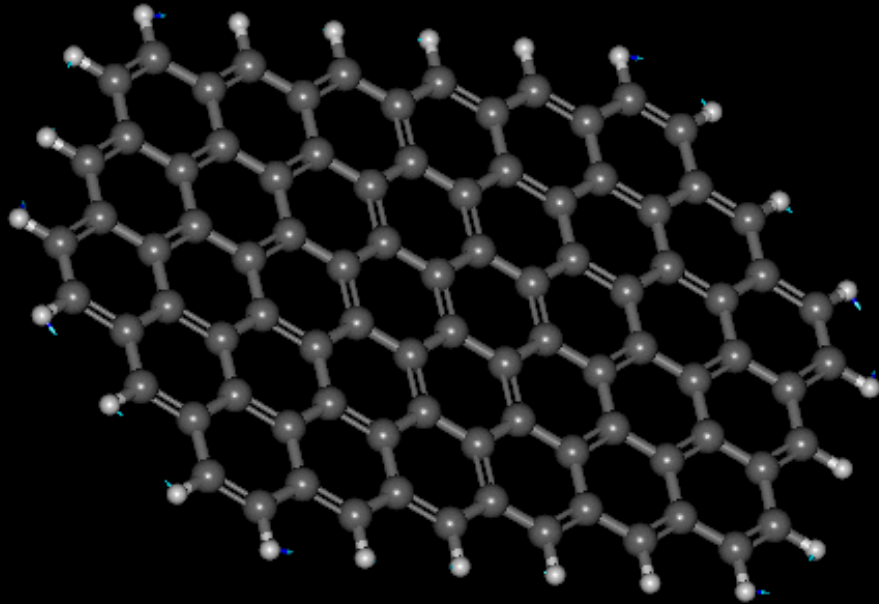
- The features observed in a variety of sources: planetary nebulae, reflection nebulae, transition objects, novae, the galactic disk, and even external galaxies.
- The bands: typical vibrational transitions in Aromatic moieties, indicating widespread presence of PAHs in the ISM.

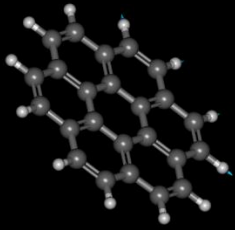


- 3030 cm<sup>-1</sup> – CH stretching vibration



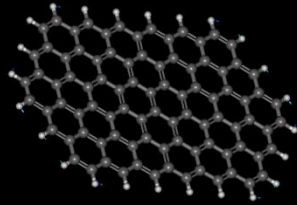
- 3030  $\text{cm}^{-1}$  – CH stretching vibration
- 1600  $\text{cm}^{-1}$  – CC stretching vibration
- 1300 – 1100  $\text{cm}^{-1}$   
– CC stretch + CH bend vibration





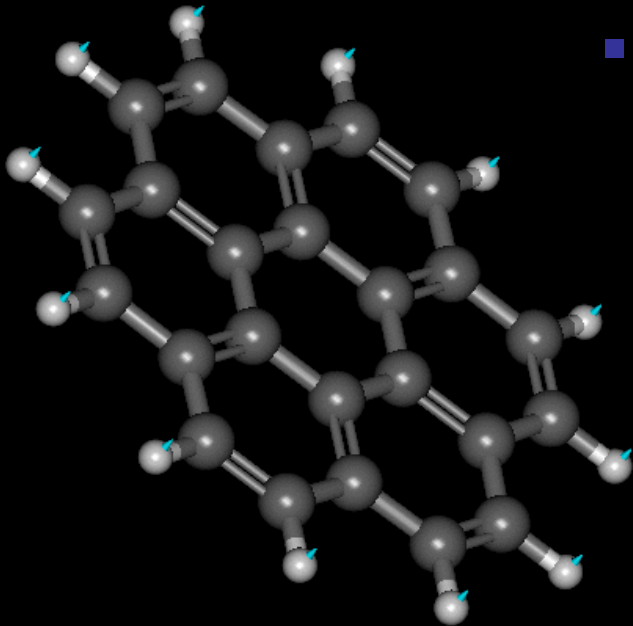
- $3030\text{ cm}^{-1}$  – CH stretching vibration

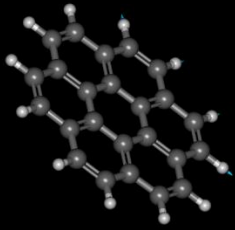
- $1600\text{ cm}^{-1}$  – CC stretching vibration



- $1300 - 1100\text{ cm}^{-1}$   
– CC stretch + CH bend vibration

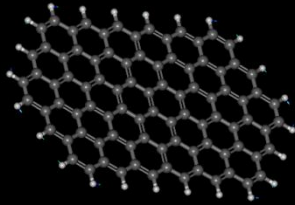
- $\sim 900\text{ cm}^{-1}$  – CH out of plane vibration



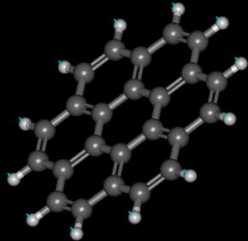


- 3030  $\text{cm}^{-1}$  – CH stretching vibration

- 1600  $\text{cm}^{-1}$  – CC stretching vibration



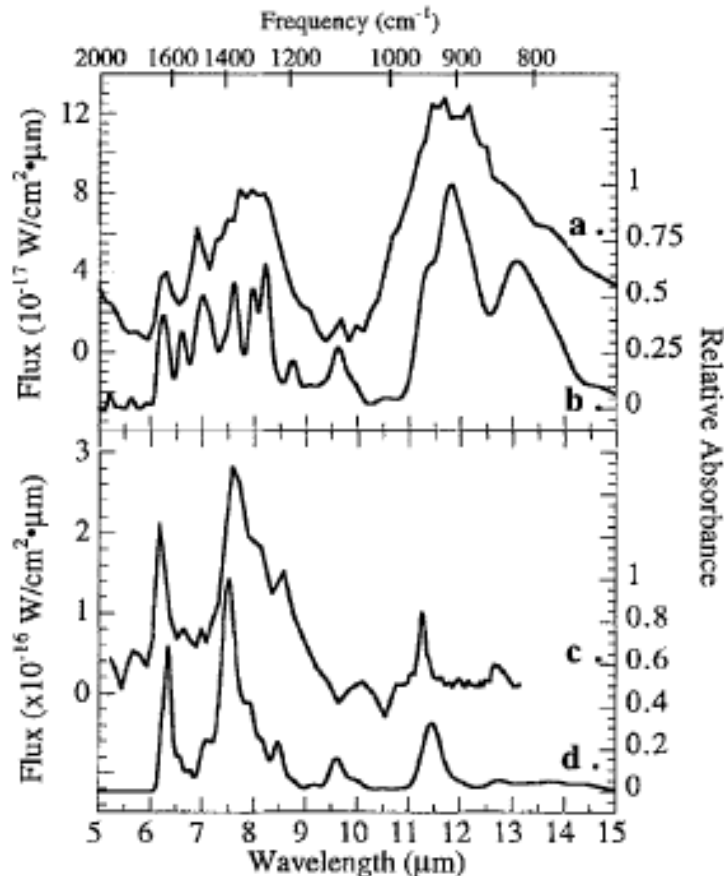
- 1300 – 1100  $\text{cm}^{-1}$   
– CC stretch + CH bend vibration



- ~900  $\text{cm}^{-1}$  – CH out of plane vibration

- All vibrations are typical aromatic characteristics
- No specific molecule identification possible

# The emission features vary from source to source



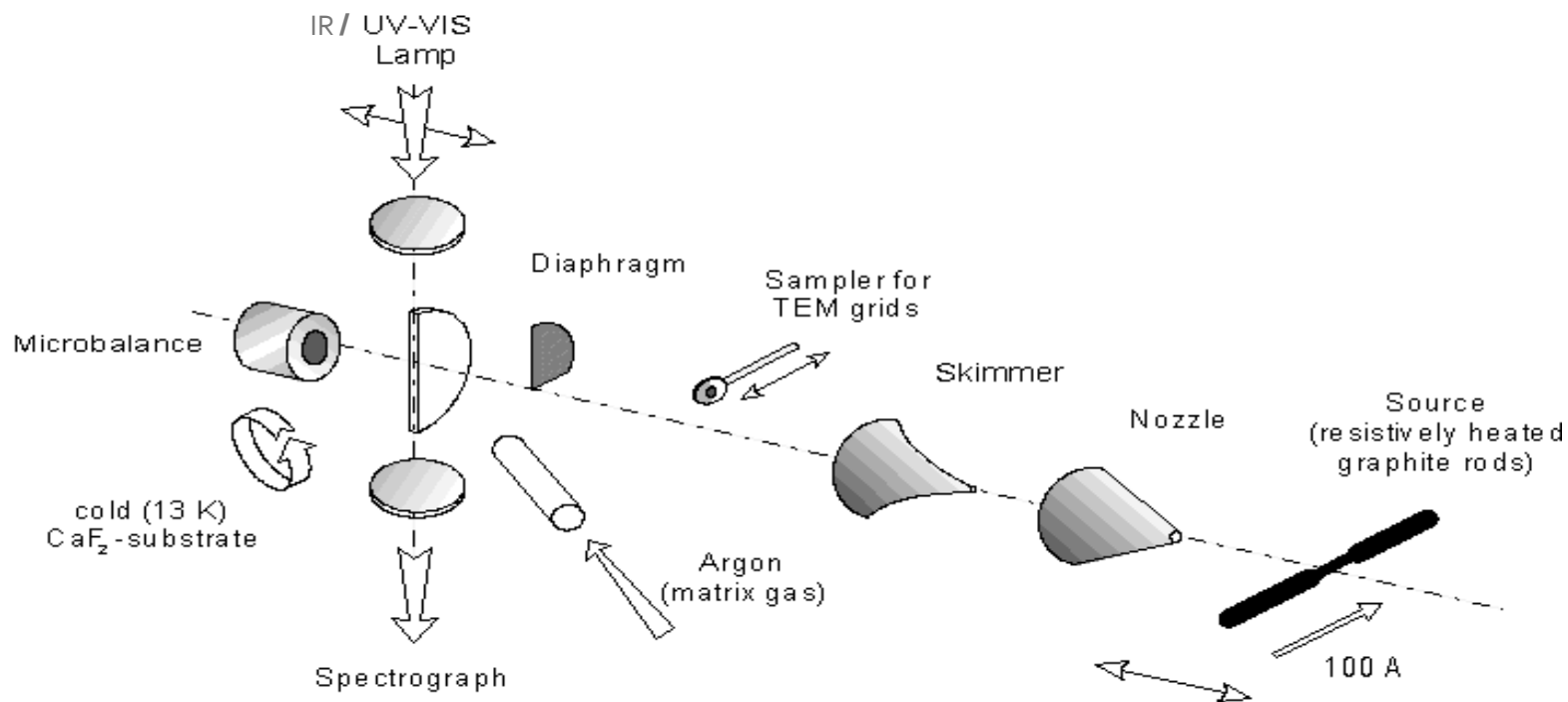
- ❖ In a population of emitters, each unique signature blends into a composite spectrum representative of the whole family.
- ❖ More ionized species in star forming regions and hydrogenated species in dense molecular clouds or outflows of AGB stars.

- a) Emission from IRAS 22272+5435 (a proto PNe)
- b) Absorption from PAH mixture (60% neutral + 40% ionized)
- c) Orion nebula emission spectra
- d) Absorption from a mixture of ionized PAHs only.

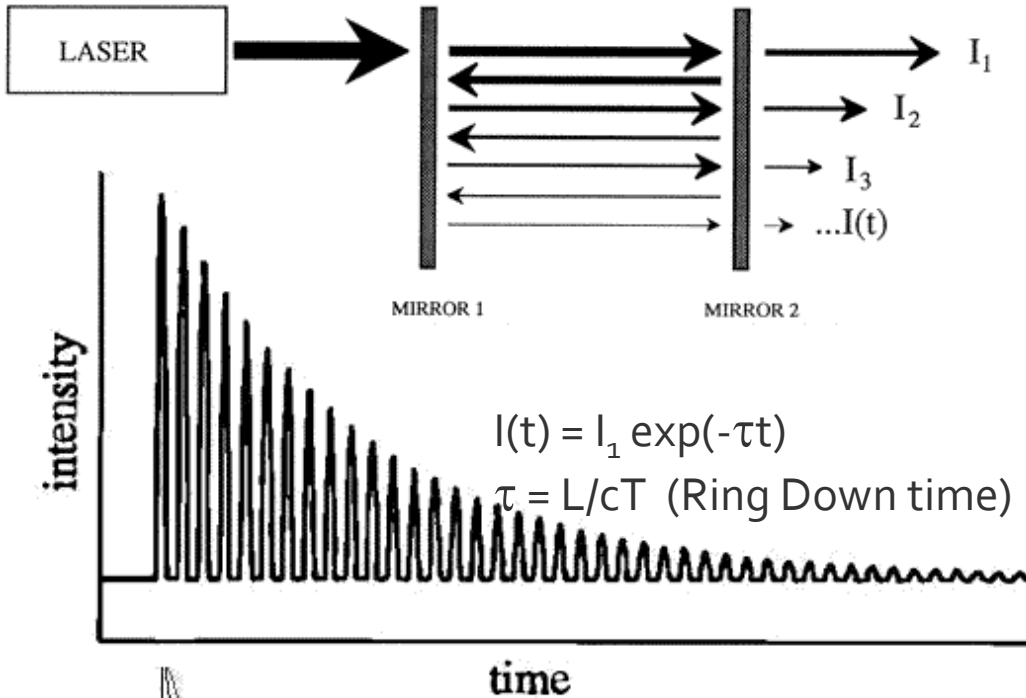
# Laboratory Study of PAH vibrations – Infrared spectroscopy

- ❖ Collision-free low temperature environment of ISM are reproduced in supersonic gas expansions.

## Matrix Isolation Spectroscopy (MIS)

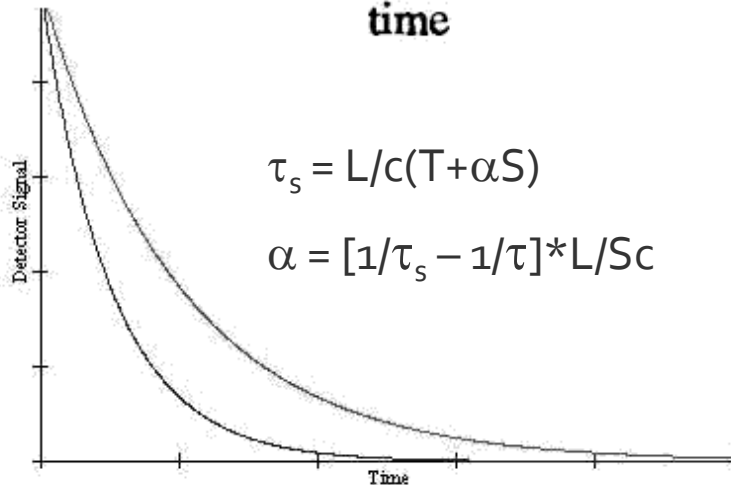


# Cavity Ring Down Spectroscopy (CRDS)



\* Gas phase direct absorption spectra.

\* Low sample concentration  $\rightarrow$  less absorption per pass  $\rightarrow$  accurate measurement of ring-down time.



\* High reflectivity cavity mirrors lead to long path lengths ( $\sim 10$  Km) and high resolution.

\* PAHs injected into the cavity need to be ionized through a discharge.

- Difficult to obtain experimental spectra in ISM conditions
- PAHs possible in the ISM difficult to synthesize

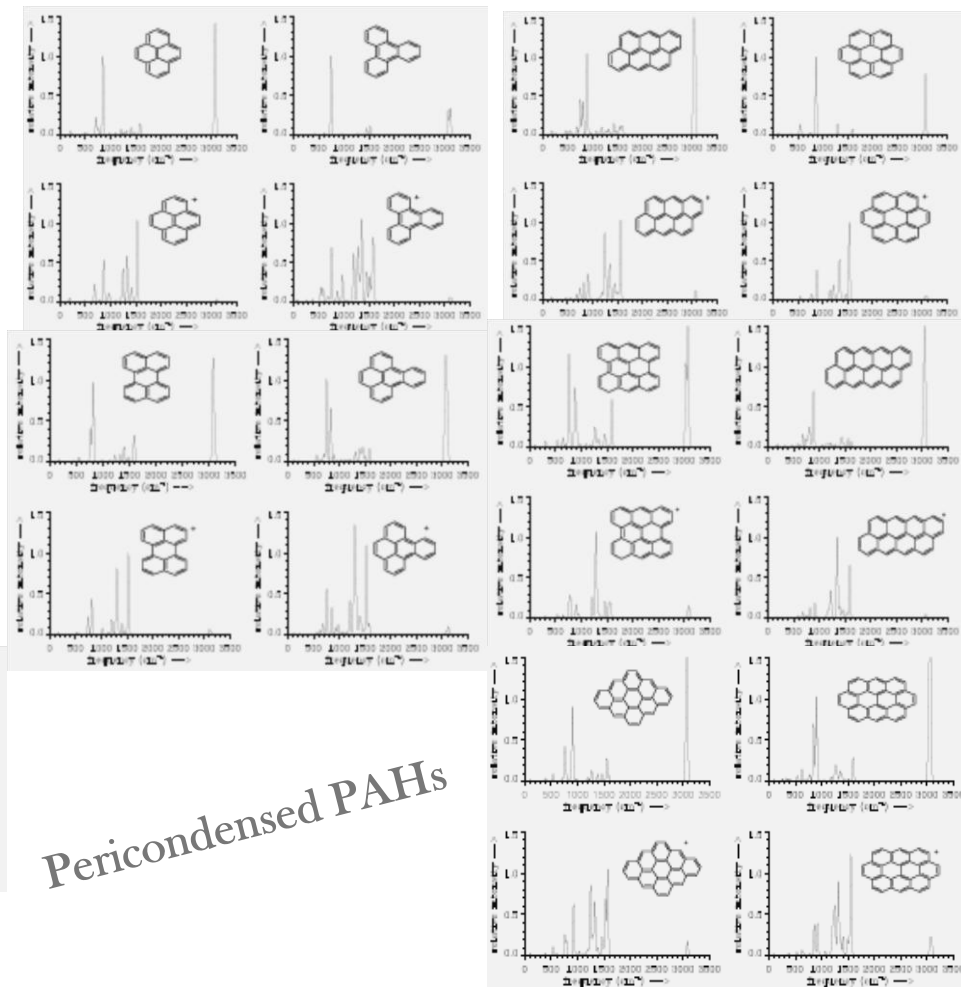
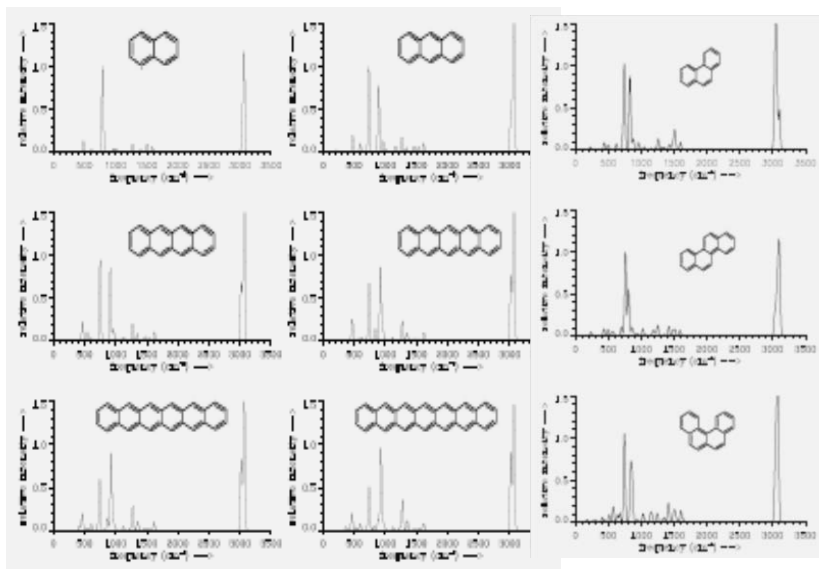
Quantum Chemical calculations provide the missing link.

- Visualize a possible PAH.
- Optimize geometry - obtain normal vibrations.

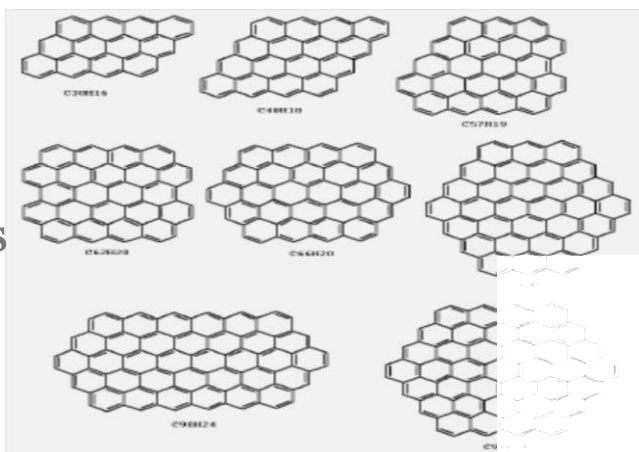
Density Functional Theory (DFT) applied for IR absorption database.

# The Sample database – Plain PAHs DFT - B3LYP/4-31G

## Catacondensed PAHs



38 to 96 C  
atom PAHs

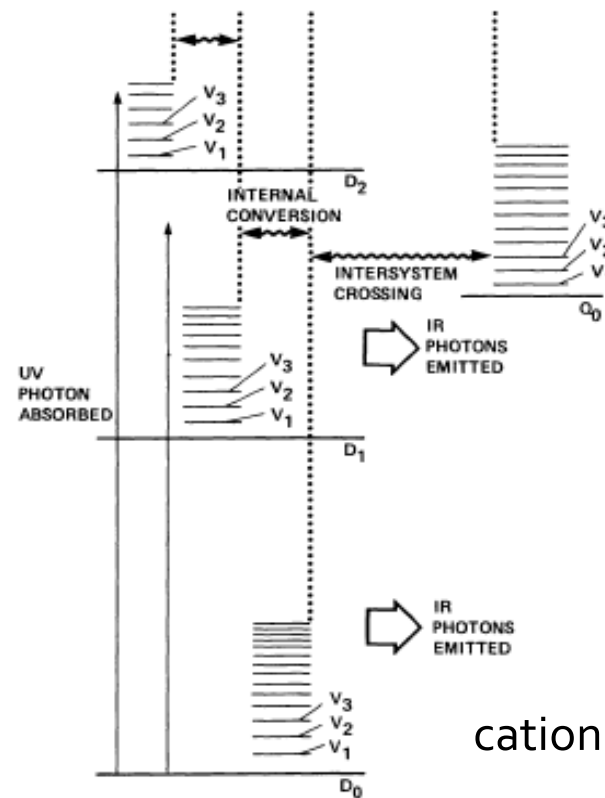
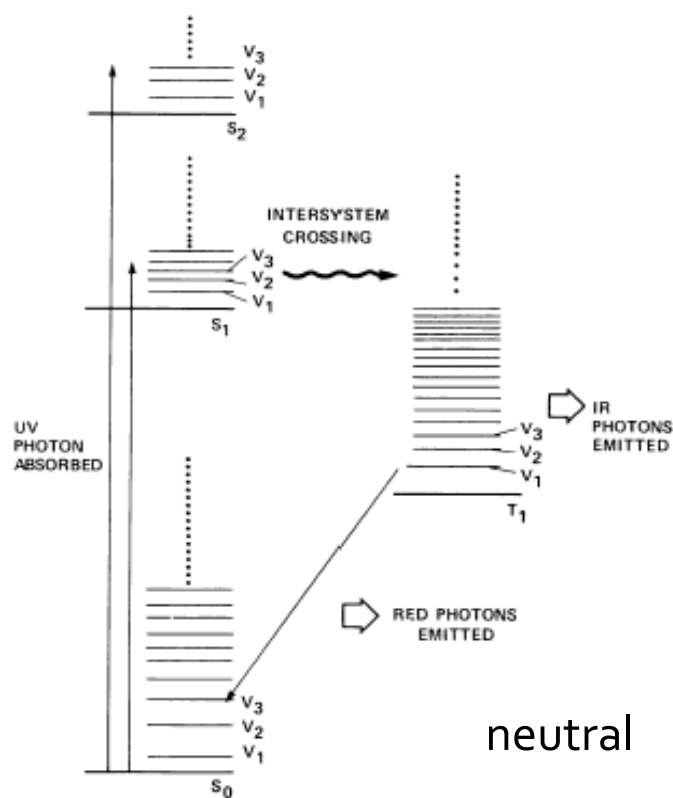


Pericondensed PAHs

# Meaningful comparison with observations require *emission spectra*

## PAH Emission Mechanism

- Absorption of UV 'hv' photon excites the PAH to a peak temperature ~ 1000 K, depending on size and absorption cross section.
- Intersystem crossing / Internal conversion to very high vibrational levels;
- Emission from  $v \rightarrow v-1$  levels in a cascade.



## The Thermal Emission Model

- The thermal approximation for cascade emission model is considered as average energy of individual modes is small compared to the total energy  $U(T)$  of the excited PAH.

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

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

- 'i' is vibrational mode within individual PAH having frequency  $\omega_i$  in  $\text{cm}^{-1}$  and  $m$  is total number of normal modes ( $3N - 6$ ;  $N$  being the number of atoms). Emission photon flux for the  $i^{\text{th}}$  mode is  $\phi_i$ .
- For a fall in internal energy by  $\Delta U$ , the fractional energy emitted in the  $i^{\text{th}}$  mode is given as:

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

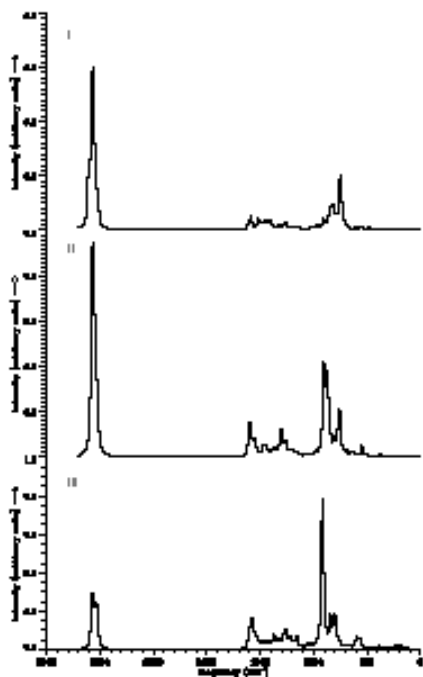
- Fractional energy  $E_i$  is integrated over the cooling range from  $T_p$  to a temperature of 50 K below which the energy emitted is negligible.

# Composite emission spectra

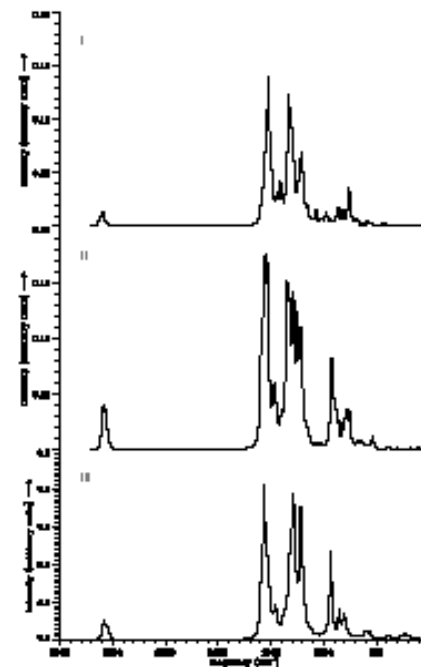
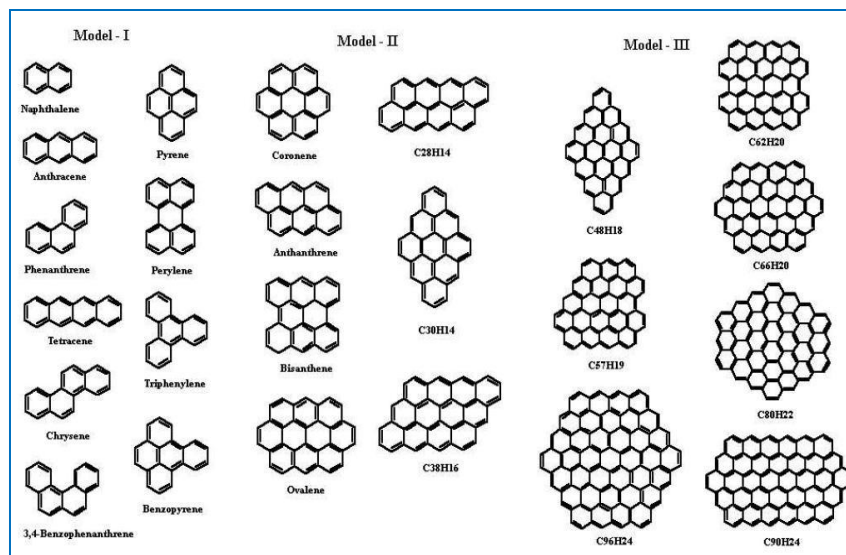
Model I – small PAHs; less than 30 carbon atoms

Model II – medium sized PAHs; 30-50 carbon atoms.

Model III – large PAHs; up to ~100 carbon atoms.

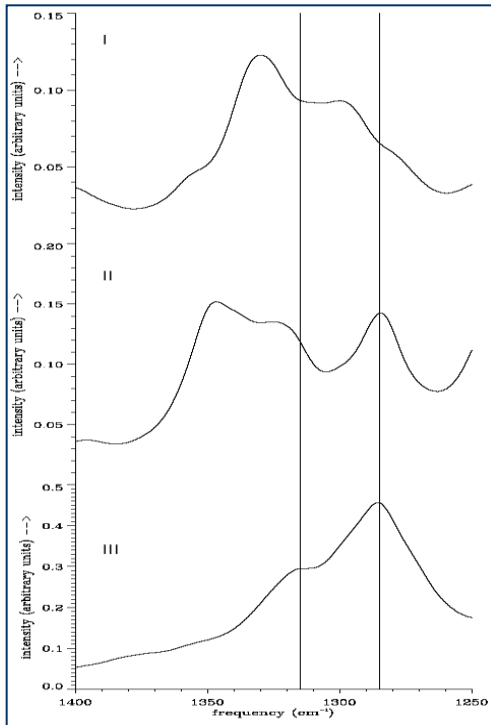


neutrals

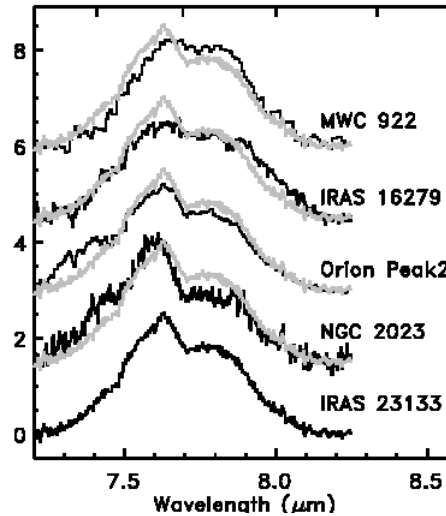


cations

# Enlarged 7.7 $\mu\text{m}$ band

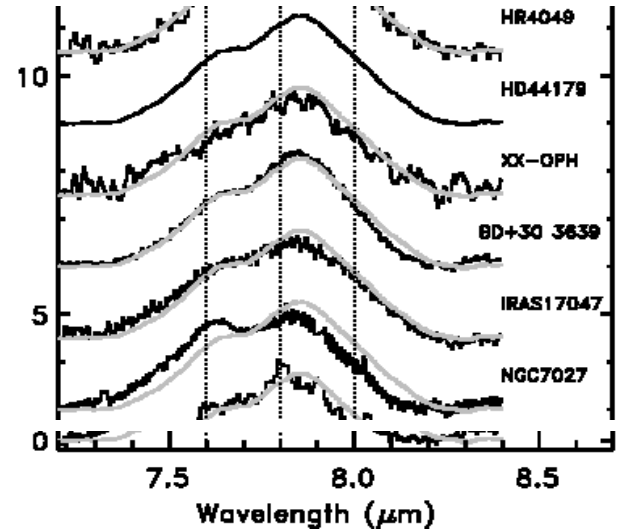


## Observational classifications



Class A'

Strong UV sources

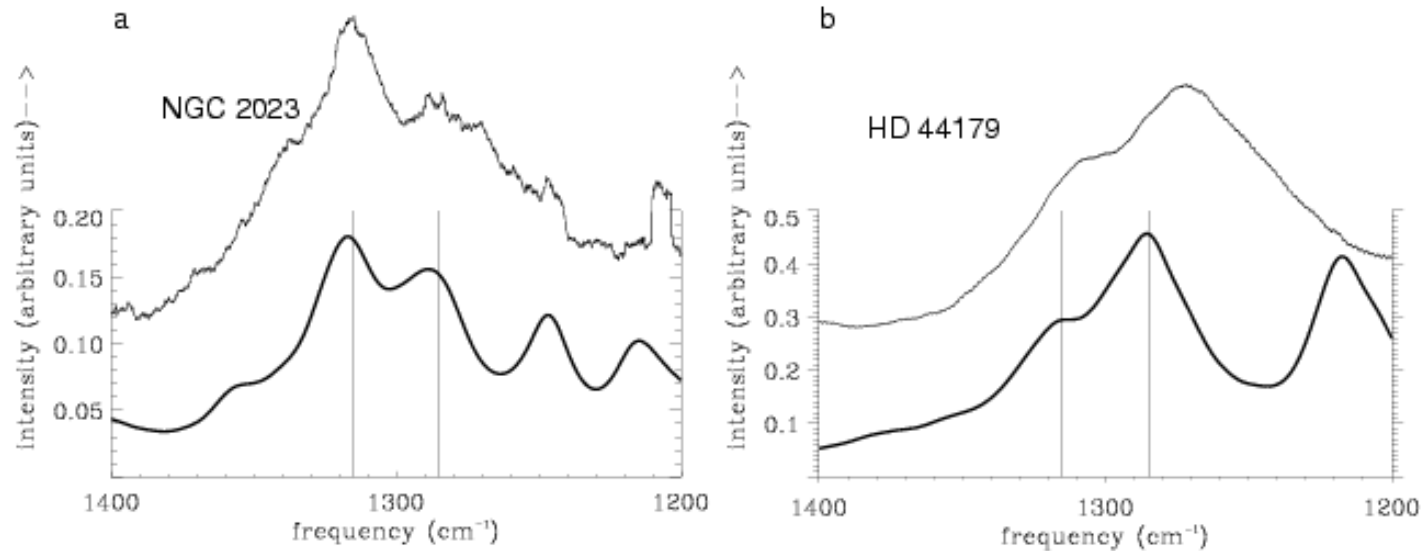


Class B'

Peeters et al., A&A 390, 1089, 2002

- The 7.7  $\mu\text{m}$  Aromatic IR Band has components at 7.6 and 7.8  $\mu\text{m}$ .
- 7.6  $\mu\text{m}$  dominates in UV rich environments with processed PAHs.
- 7.8  $\mu\text{m}$  feature dominates in cooler regions having newly formed PAHs.

## Modeling observations - The “7.7” $\mu\text{m}$ complex

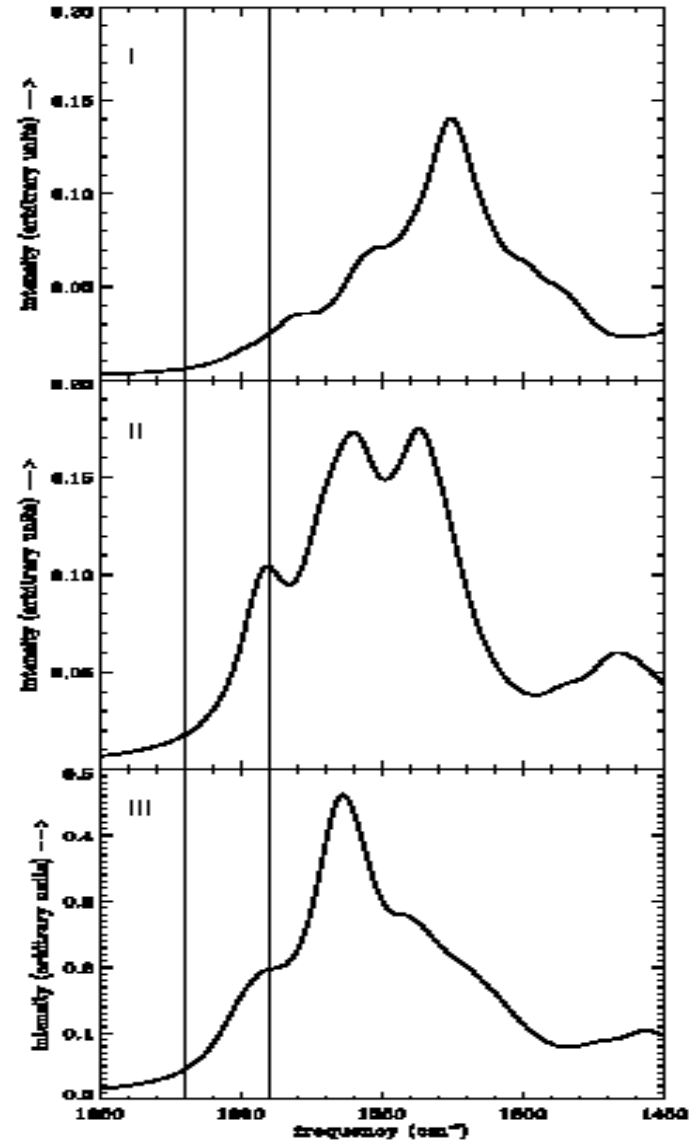


- The 7.6  $\mu\text{m}$  feature dominant in UV rich regions matches the model spectra of medium sized PAH cations (a).
- The 7.8  $\mu\text{m}$  component, observed in benign regions, correlates with the model spectra of large PAH cations (b).

**Large PAHs form in out flows of post-AGB stars that transform to medium sized ones in strong UV sources.**

## Problems...

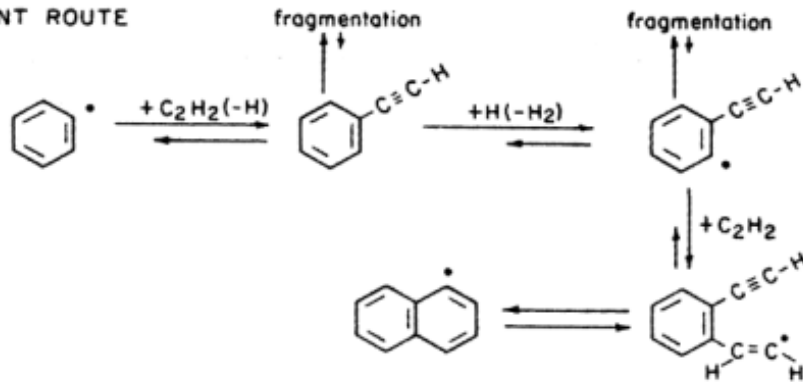
- The models do not satisfactorily match the 6.2  $\mu\text{m}$  feature.
- Most spectra fall short by 30 - 40  $\text{cm}^{-1}$  from this 1610  $\text{cm}^{-1}$  AIB.
- Study of a **wider variety of PAHs** needed to explain all bands simultaneously.



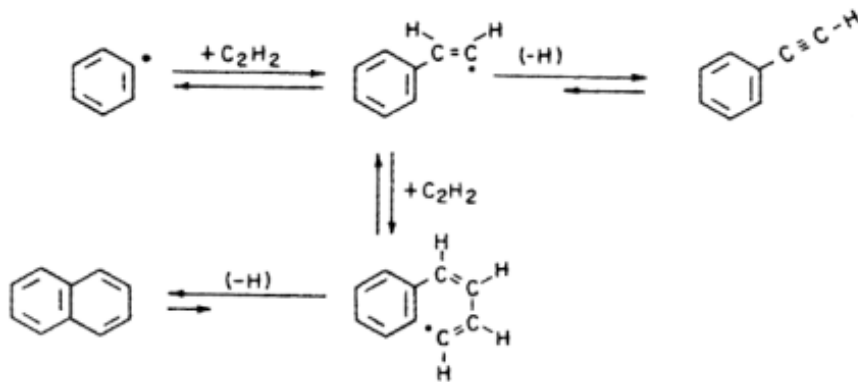
Emission from cations for the three models in the 1450 to 1650  $\text{cm}^{-1}$  region

# Growth of PAHs in the ISM

DOMINANT ROUTE



MINOR ROUTE



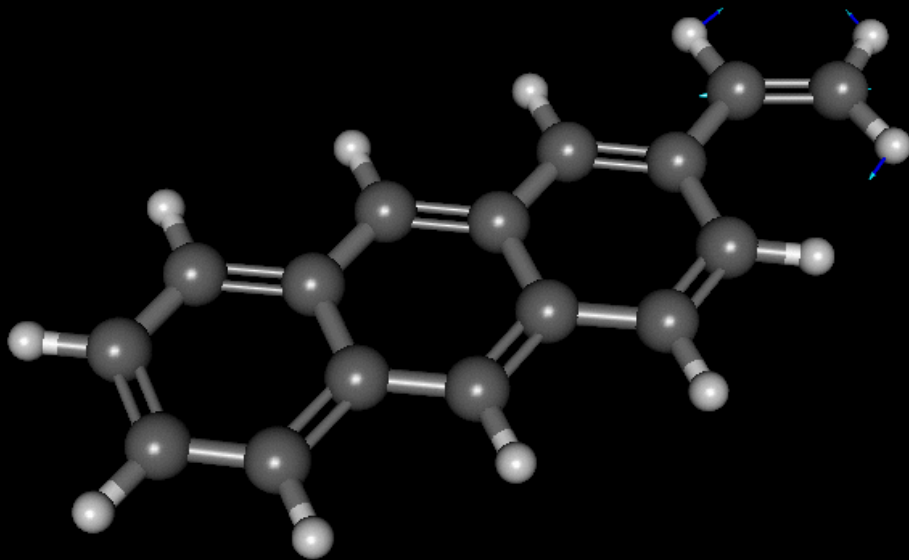
➤ The most favorable pathway is condensation acetylene ( $C_2H_2$ ).

➤ Intermediate products like **acetylene**, **vinyl-radicals**, **poly-acetylene** indicate the possibility of PAHs with side groups.

## PAH with vinyl side groups

The presence of C=C bond in the vinyl side group on PAHs may increase the frequency of vibration of the C – C stretch mode.

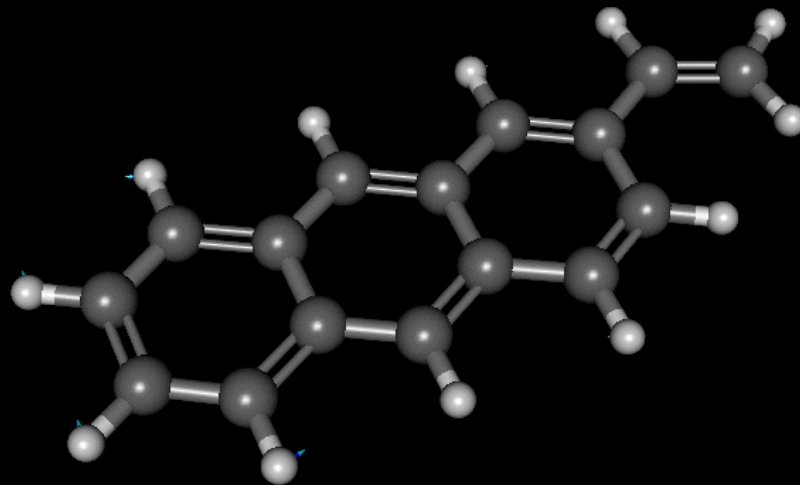
2-vinyl-anthracene;  $1625\text{ cm}^{-1}$  mainly vinyl C=C stretch



## PAH with vinyl side groups

The presence of C=C bond in the vinyl side group on PAHs may increase the frequency of vibration of the C – C stretch mode.

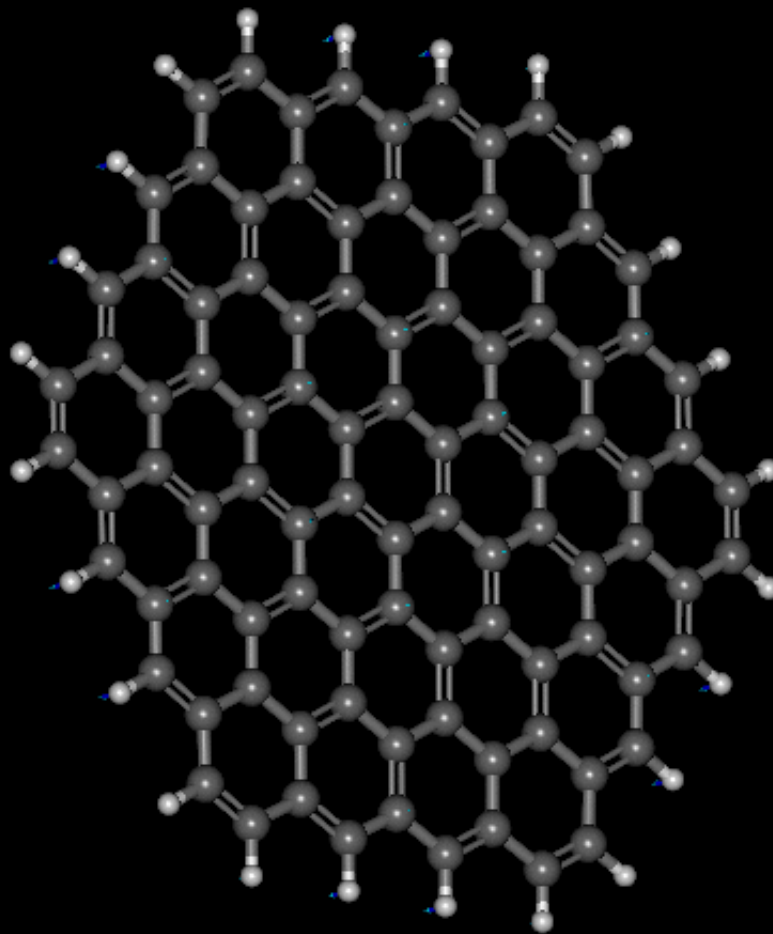
2-vinyl-anthracene;  $1615\text{ cm}^{-1}$  mainly ring C – C stretch





# PAH vibrational signatures in the *Far-infrared*

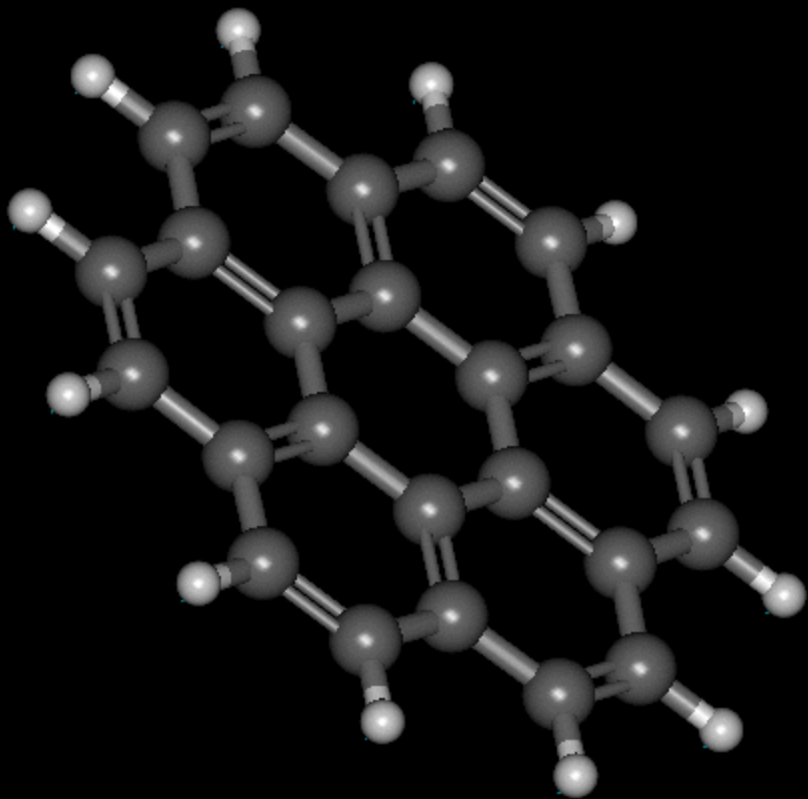
- beyond 20  $\mu\text{m}$  ( $500\text{ cm}^{-1}$ )



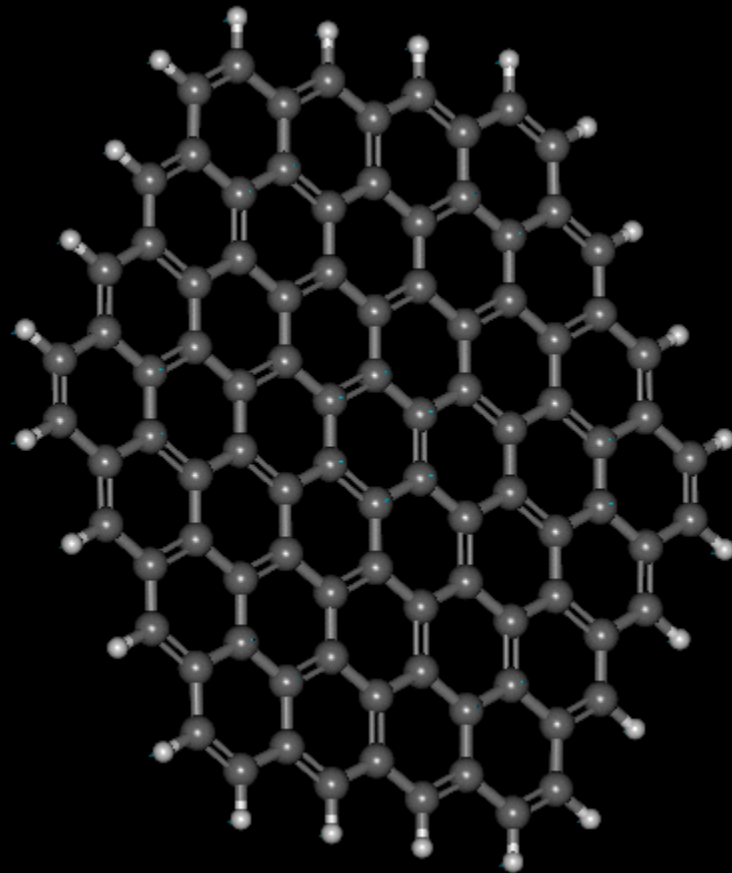
C<sub>96</sub> Jumping jack,  $570\text{ cm}^{-1}$  ( $17.5\ \mu\text{m}$ )

# PAH vibrational signatures in the *Far-infrared*

- beyond 20  $\mu\text{m}$  ( $500\text{ cm}^{-1}$ )



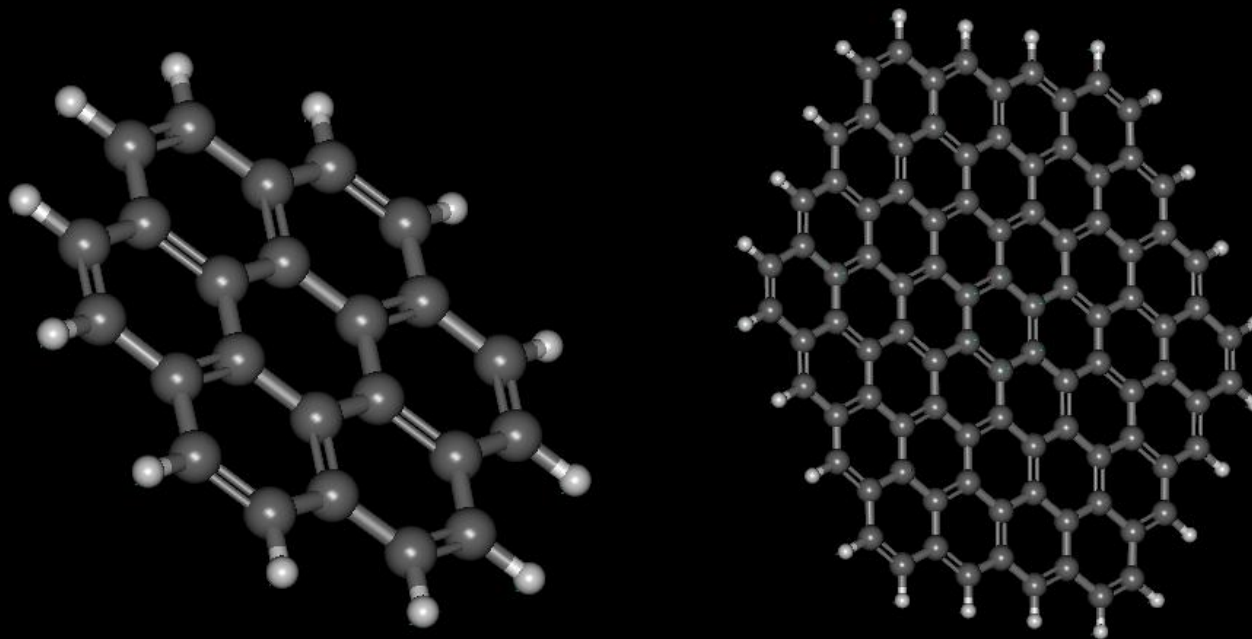
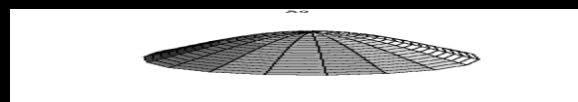
Coronene Drum head,  $118\text{ cm}^{-1}$  ( $84\ \mu\text{m}$ )



C<sub>96</sub> Drum head  $300\text{ cm}^{-1}$  ( $33\ \mu\text{m}$ )

# PAH vibrational signatures in the *Far-infrared*

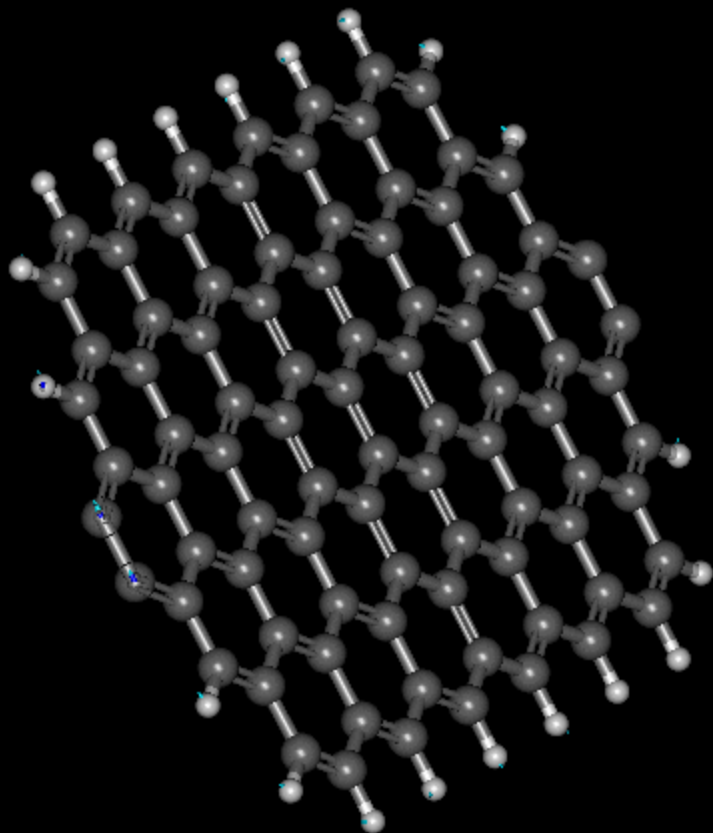
- beyond 20  $\mu\text{m}$  ( $500\text{ cm}^{-1}$ )



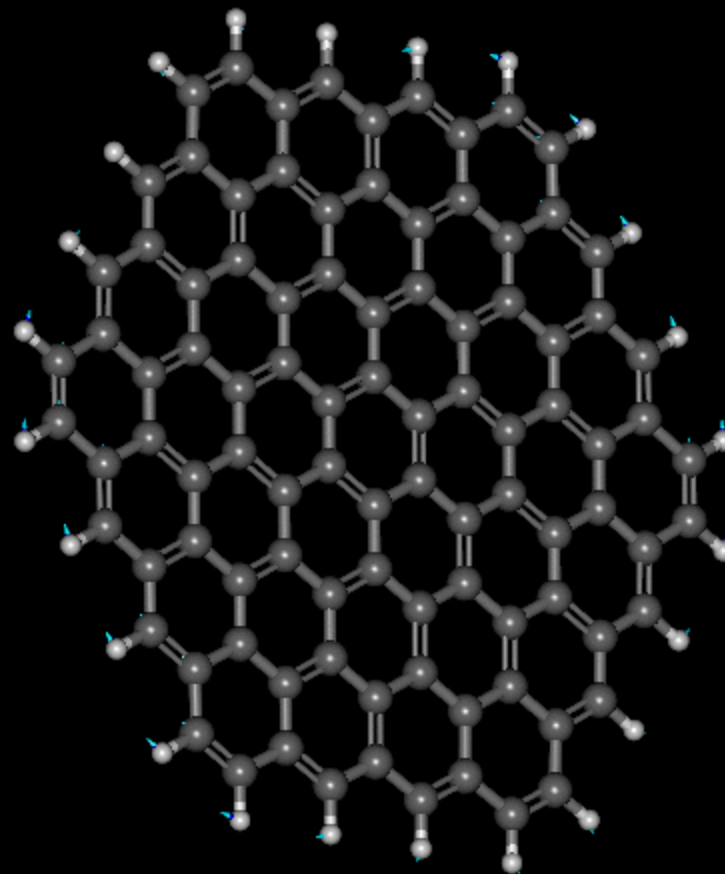
Drum heads – edge not fixed

# PAH vibrational signatures in the *Far-infrared*

- beyond 20  $\mu\text{m}$  ( $500\text{ cm}^{-1}$ )



C<sub>90</sub> Swimming – breast stroke  
130 cm<sup>-1</sup> (77 micron)



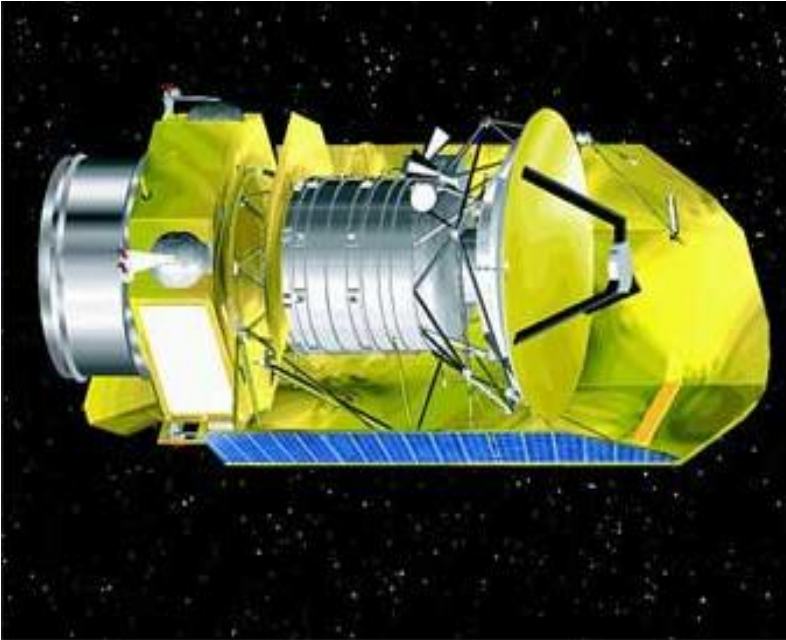
C<sub>96</sub> Swimming – breast stroke  
195 cm<sup>-1</sup> (51 micron)

# Extremely large PAHs $\rightarrow$ Graphene

**Lattice / skeletal motions**

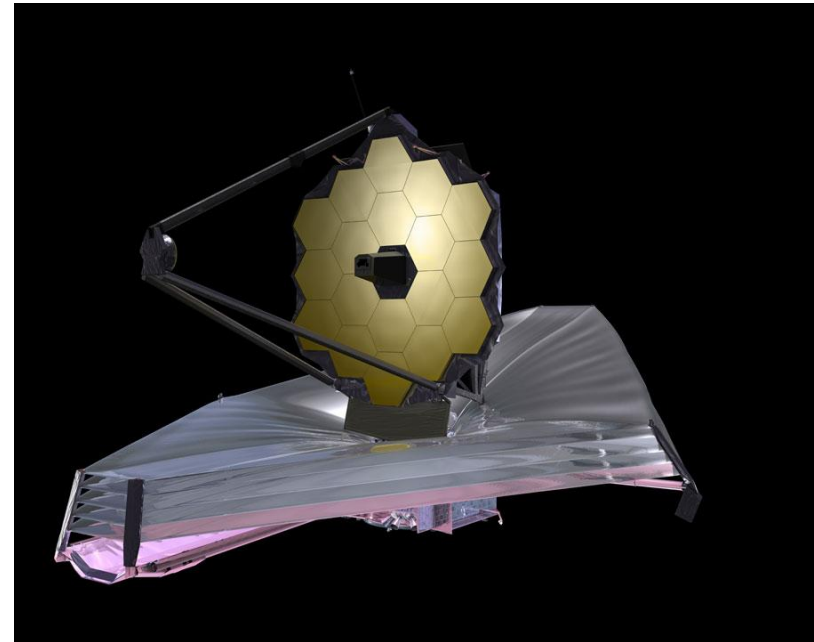


## Herschel Space Telescope



- ❑ 3.5 metre diameter
- ❑ 55 – 672  $\mu\text{m}$  range

## James Webb Space Telescope



- ❑ 6.5 metre diameter
- ❑ 0.6 – 28  $\mu\text{m}$  range