Aromatic nanoparticle Visible-UV bands : laboratory electronic spectra toward the idenfication of the bump and DIBs carriers

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Interstellar matter and light extinction

Image of the horsehead nebulea in the IR domain, Hubble WFC3/NIR (April 2013)

Interstellar matter

Solid and gas phase

↓

From small free radicals (< nm) to µm solid grains

↓

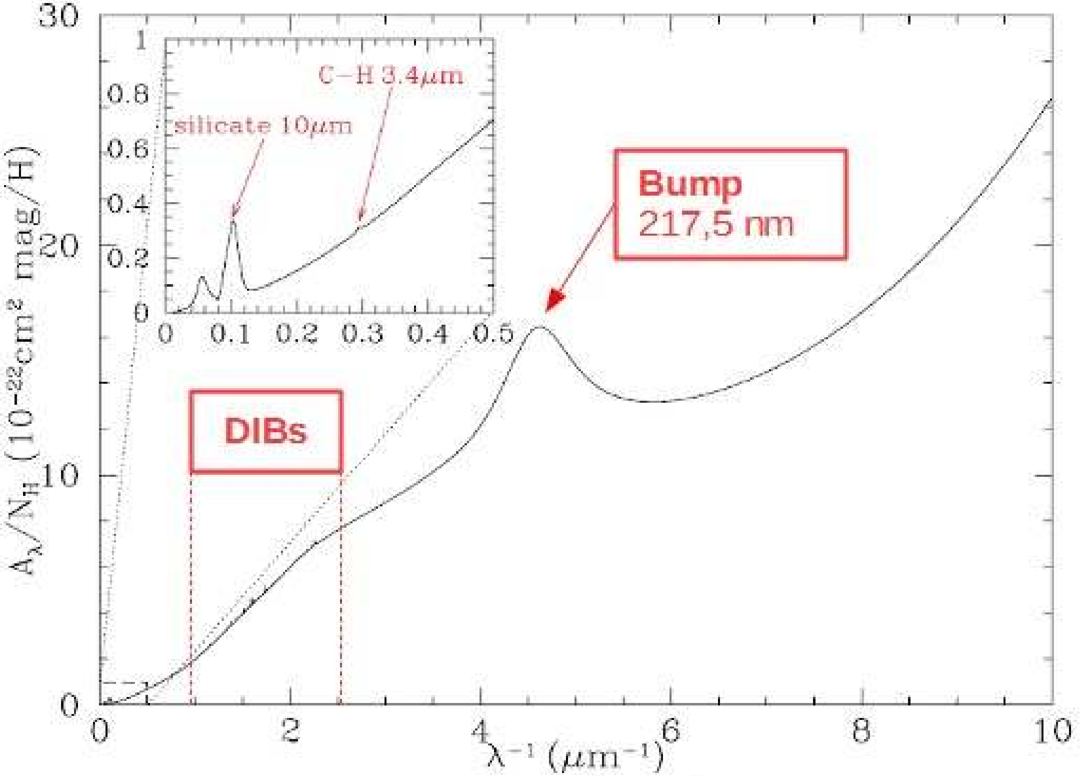
Absorbs light coming from stars

Interstellar matter and light extinction

Bump

$\pi \rightarrow \pi^*$ transition feature from carbonaecous materials

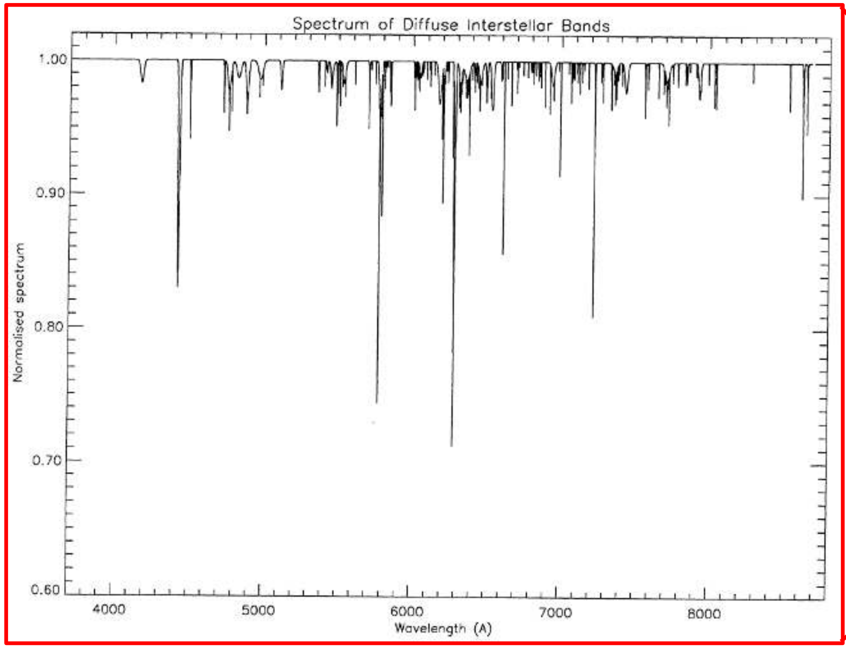
Graphite, graphene, aromatic molecules...



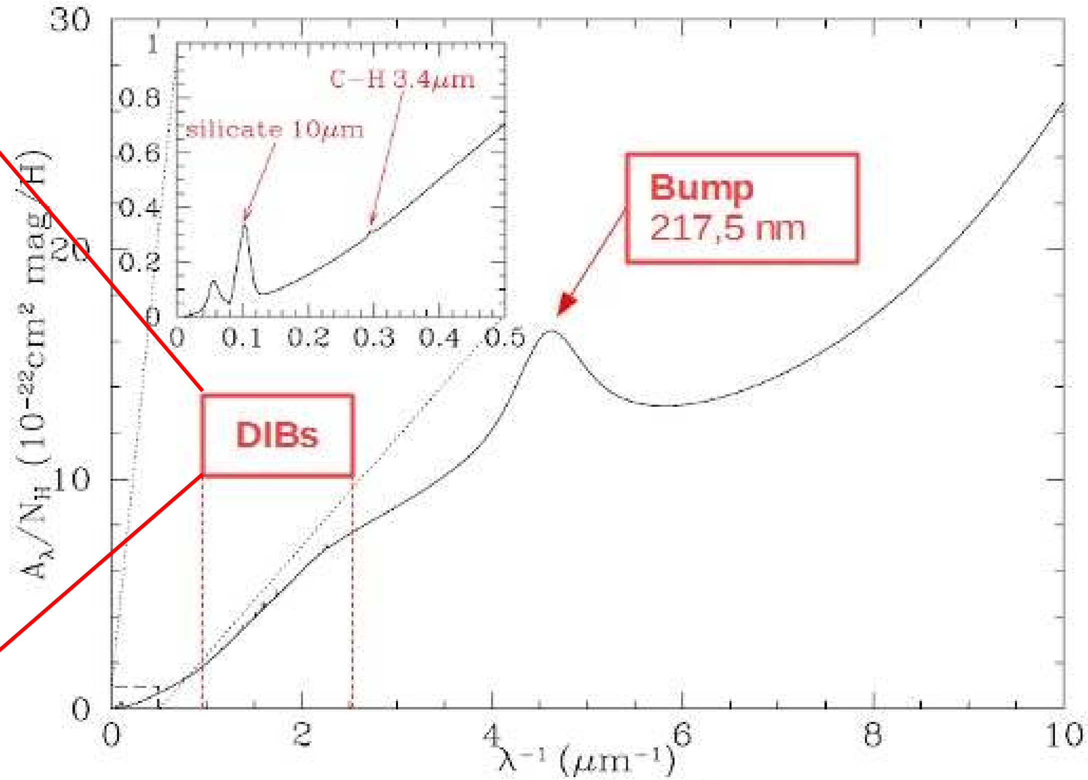
Average extinction curve of the diffuse interstellar medium, A_λ: extinction coefficient (Draine, 2009)

Interstellar matter and light extinction

(Jennisken & Desert, 1994)



Diffuse Interstellar Bands (DIBs)



Average extinction curve of the diffuse interstellar medium,
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Precise determination of interstellar molecular species

Identify physico-chimical processes and understand evolution mecanisms operating inside the interstellar medium

Interstellar matter and light extinction

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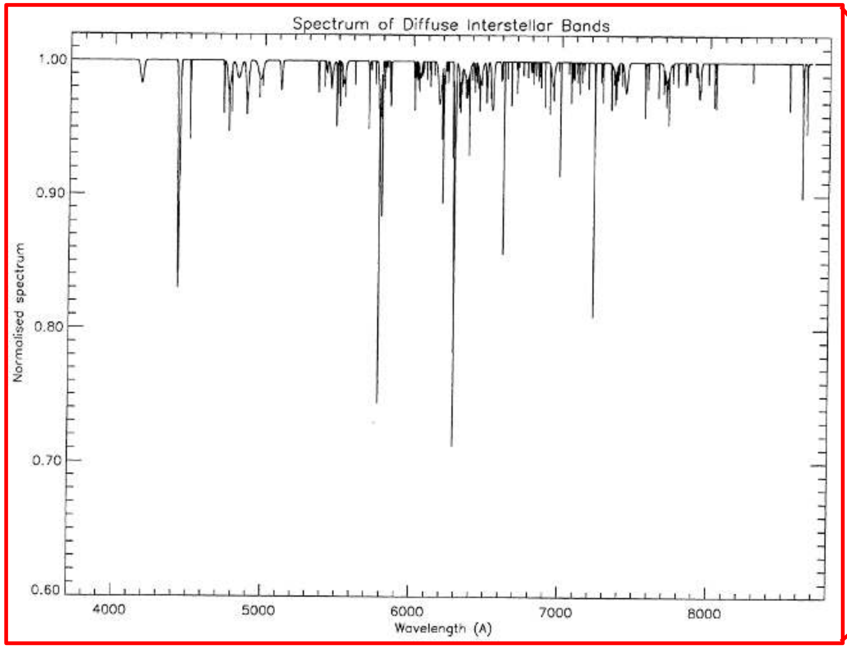

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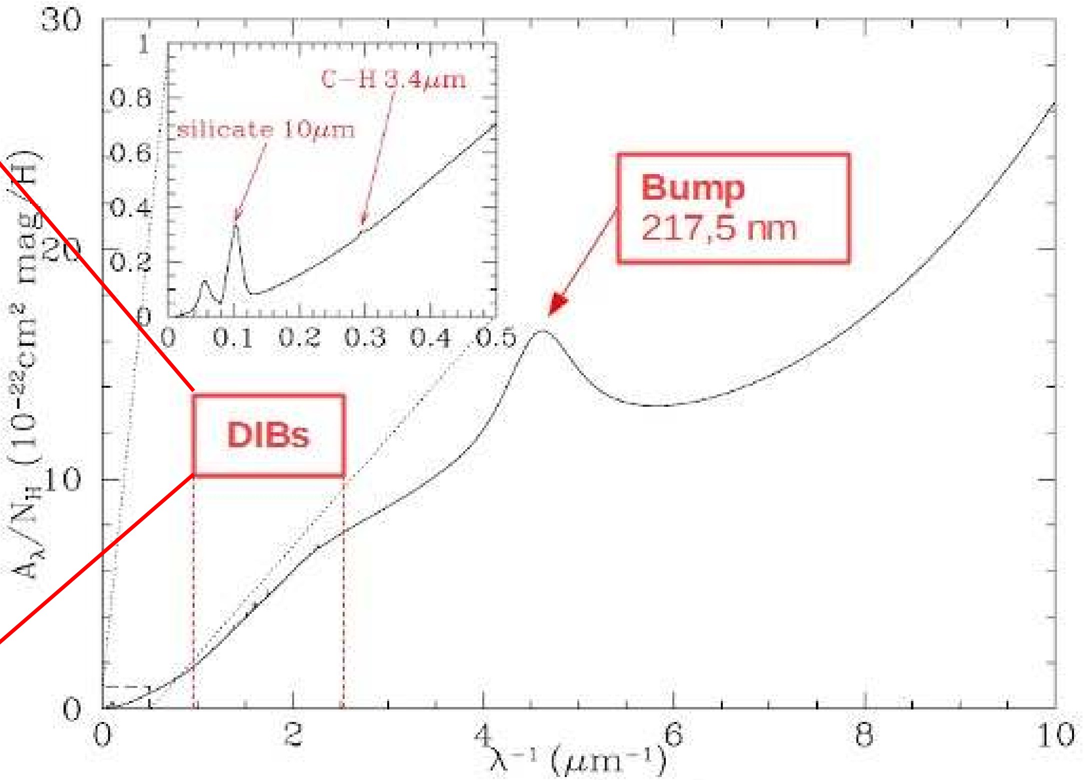

Average extinction curve of the diffuse interstellar medium, A_λ: extinction coefficient (Draine, 2009)

Tough identification !

Precise determination of interstellar molecular species

Identify physico-chemical processes and understand evolution mecanisms operating inside the interstellar medium

Interstellar matter and light extinction

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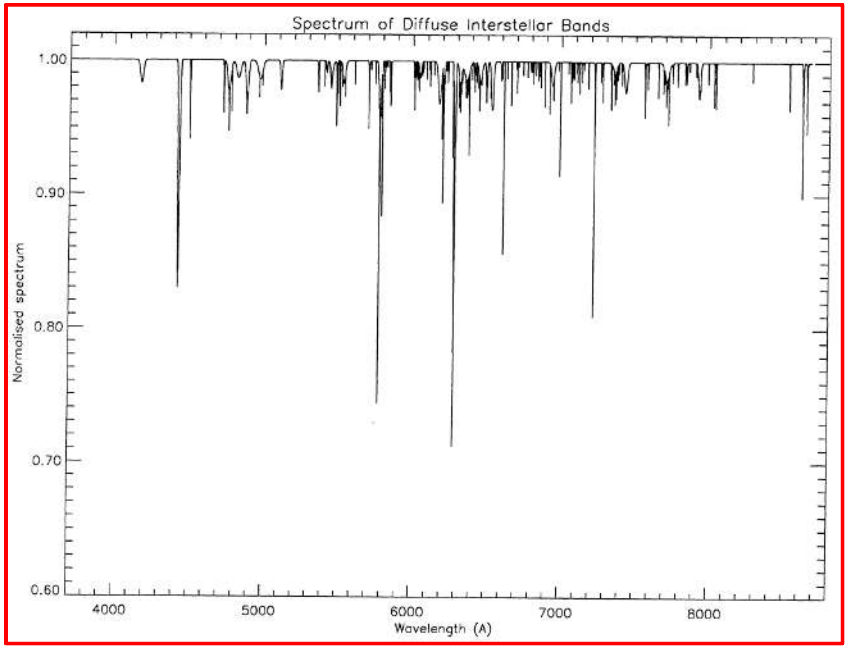


Diffuse Interstellar Bands (DIBs)

Tough identification !

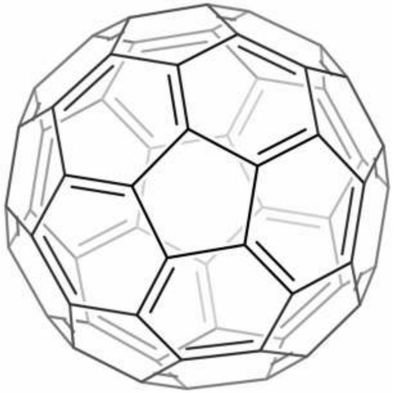
Precise determination of interstellar molecular species

Heger 1922
Observation of the first diffuse bands

Merrill 1934
Interstellar origin of DIBs deduced

Since, more than 400 DIBs observed (L. M. Hobbs, 2009)

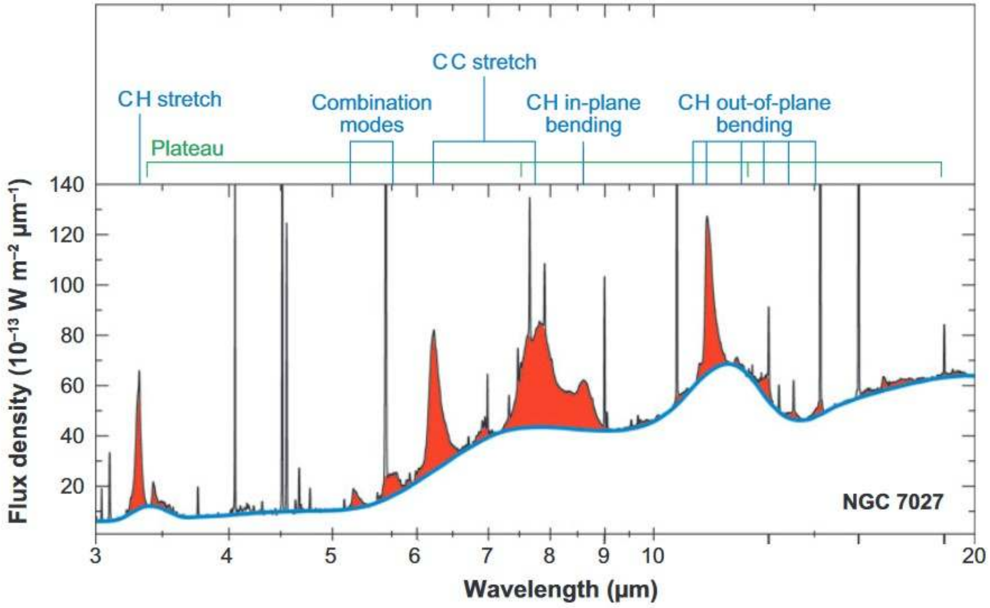
Campbell 2015
First molecule identified as carrier of 5 DIBs : fullerene cation C_{60}^{+}



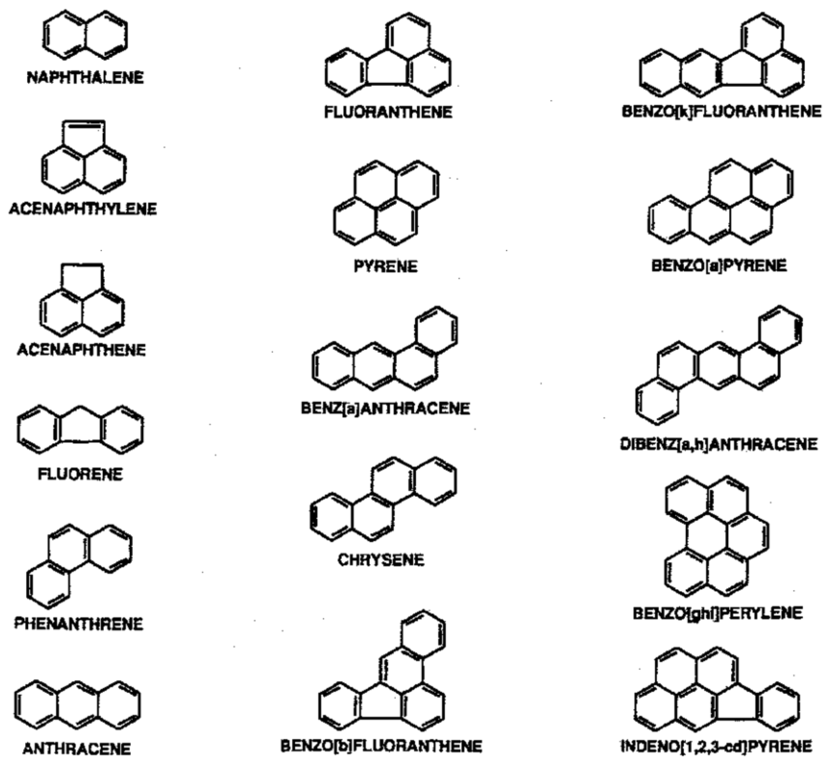
Which molecules could contribute to the DIBs and bump features ?

PAH hypothesis

Infrared emission of the planetary nebulae NGC 7027 (Tielens, 2008)



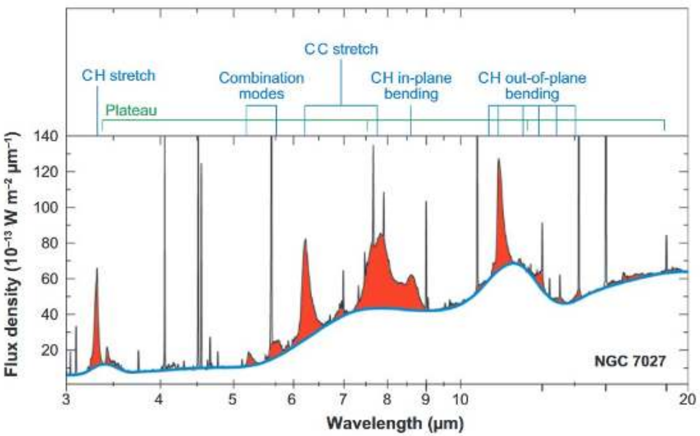
Polycyclic Aromatic Hydrocarbons (PAHs)



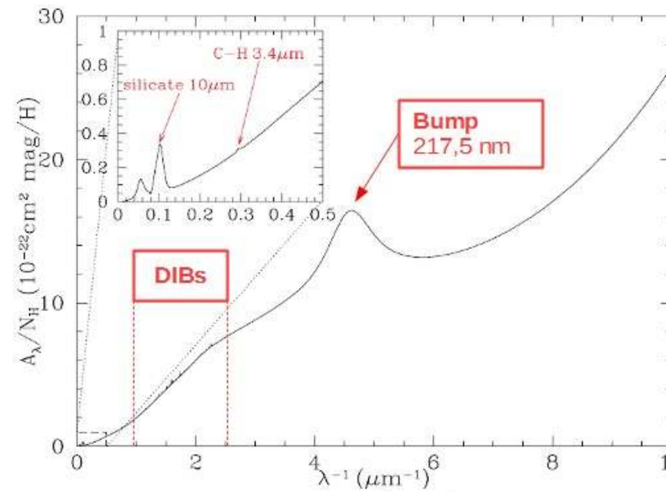
Problem

Spectral signatures of small PAHs do not match with astrophysical observations

PAH hypothesis



Infrared emission



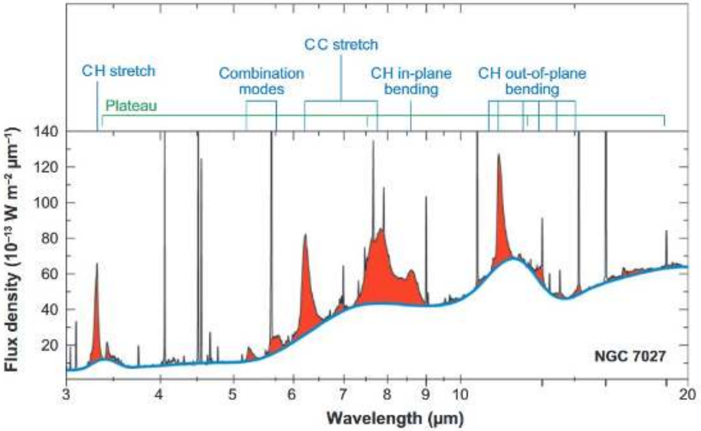
Bump feature

High probability of large PAH (100–200 carbon atoms) inside the interstellar medium

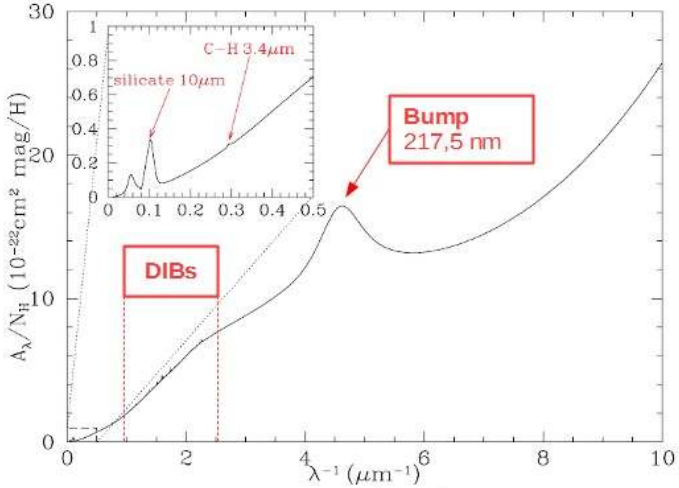
Fullerene C_{60}^{+} : DIBs Carrier

DIBs carriers ?

PAH hypothesis



Infrared emission



Bump feature

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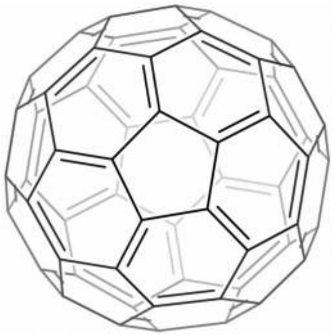

Fullerene C_{60}^{+} : DIBs Carrier

Critical lack of spectroscopic data for large PAHs

DIBs carriers ?

PAH hypothesis

Large PAHs spectroscopic data missing :
<u>3 major reasons</u>

Cold & idolated environnement required

No conventionnal synthesis

Spectra analysis complex

PAH hypothesis

Large PAHs spectroscopic data missing :
3 major reasons

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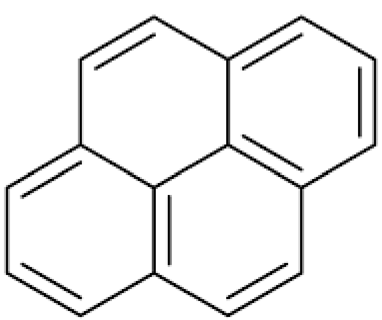
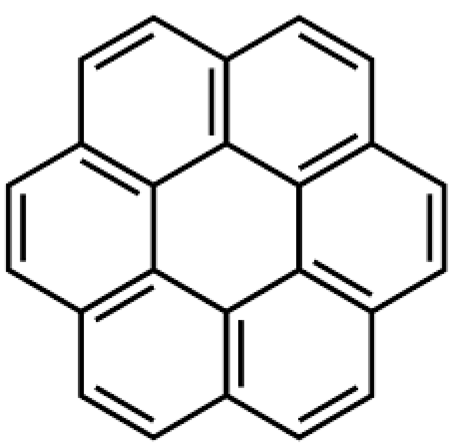
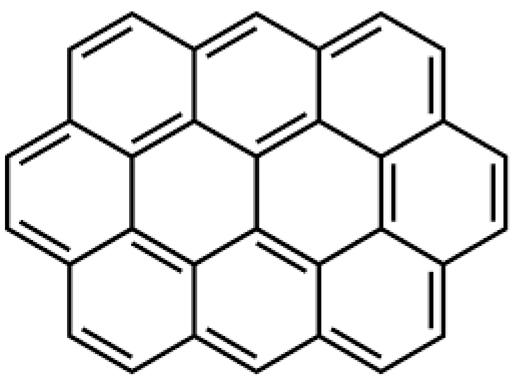
Size



Pyrene



Coronene

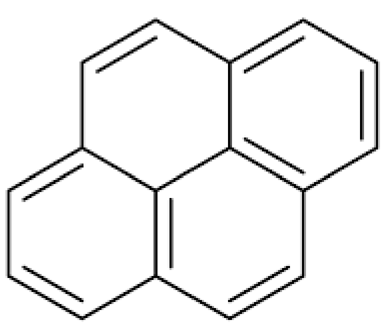


Ovalene

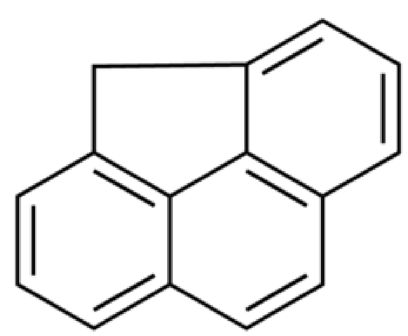
PAH hypothesis

Large PAHs spectroscopic data missing :
<u>3 major reasons</u>

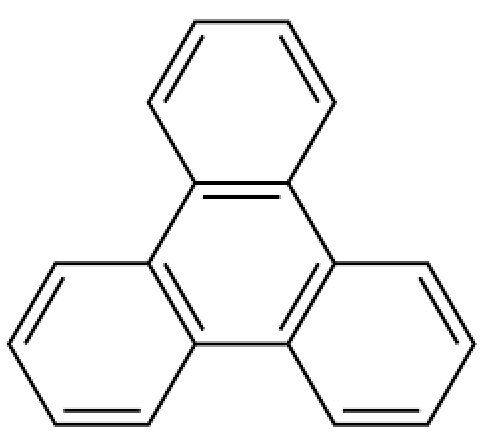
- **Cold & idolated environnement required**
- **No conventionnal synthesis**
- **Spectra analysis complex**
  - Size
  - Structure



Pyrene



Cyclopenta[d,e,f]phenanthrene

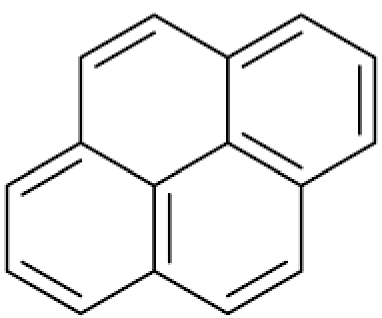


Tryphenylene

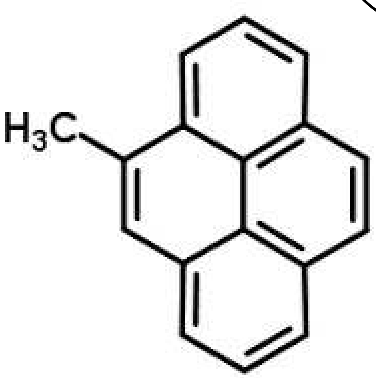
PAH hypothesis

Large PAHs spectroscopic data missing :
<u>3 major reasons</u>

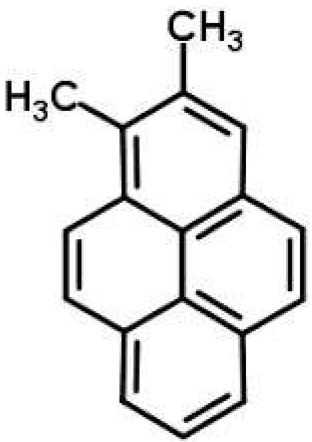
- **Cold & idolated environnement required**
- **No conventionnal synthesis**
- **Spectra analysis complex**
  - Size
  - Form
  - Functional Group



Pyrene



methylpyrene

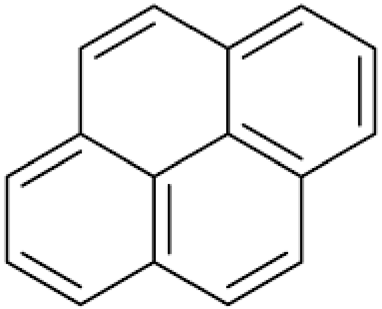


dimethylpyrene

PAH hypothesis

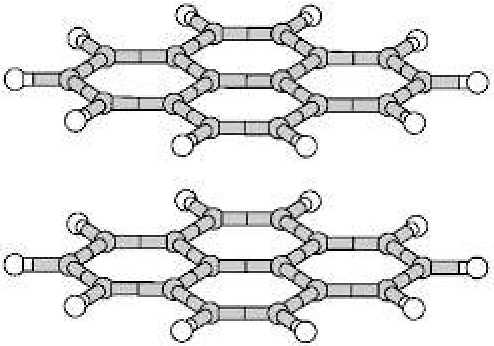
Large PAHs spectroscopic data missing :
3 major reasons

- **Cold & idolated environnement mandatory**
- **No conventionnal synthesis**
- **Spectra analysis complex**
  - Size
  - Form
  - Functional Group
  - Oligomer



Monomer

Pyrene



Dimer

PAH hypothesis

Large PAHs spectroscopic data missing :
<u>3 major reasons</u>

- **Cold & idolated environnement mandatory**
- **No conventionnal synthesis**
- **Spectra analysis complex**
  - Size
  - Form
  - Functional Group
  - Oligomer

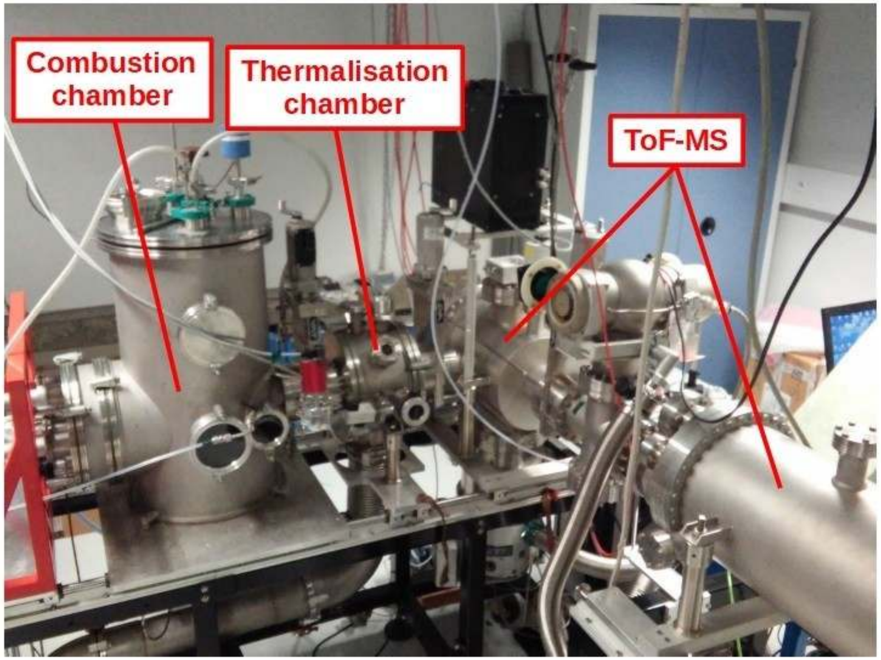
All these factors impact the PAHs elctronic transitions

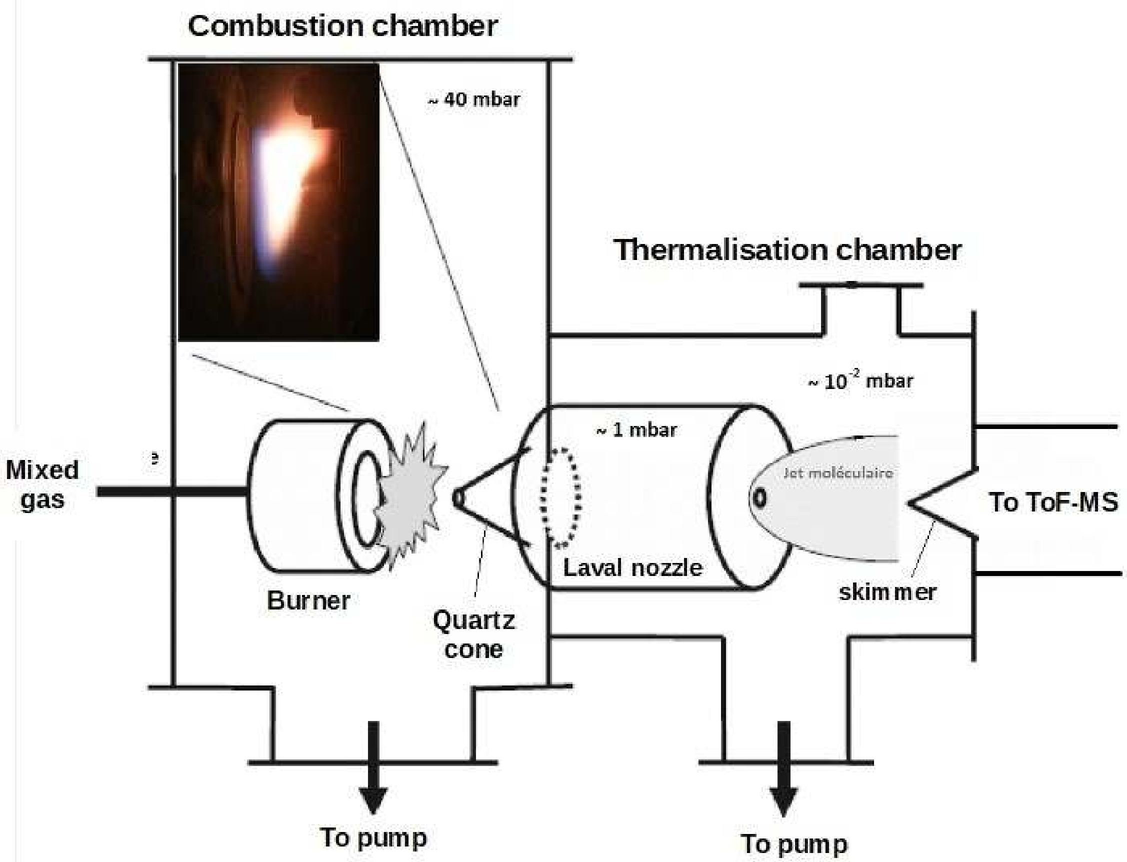
How can we overtake these problems ?

Experimental set-up

Nanograins

- Combustion chamber
- Thermalisation chamber
- REMPI spectroscopy (laser + ToF-MS)





Experimental set-up

Combustion chamber

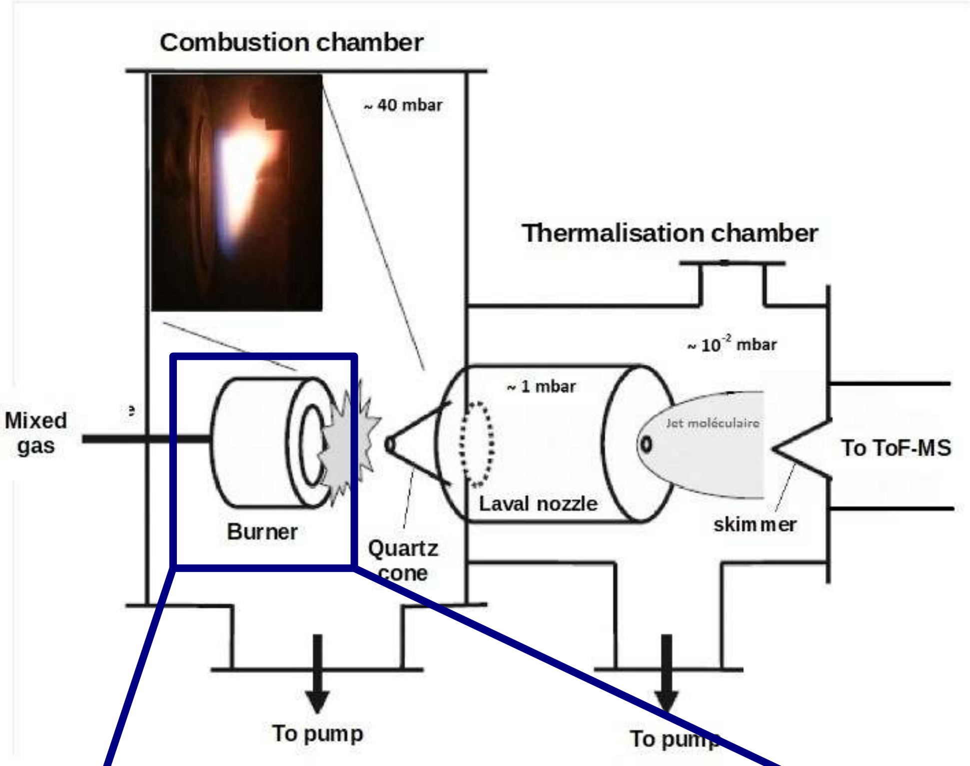
Controled
low pressure flame

Allows all sizes PAHs
production

Lean flame

Rich flame

Two different flame characteristics

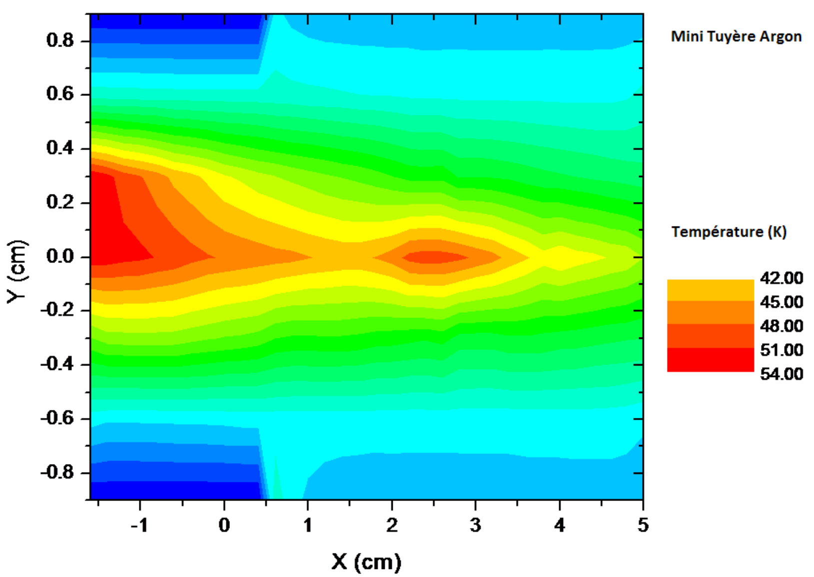


Experimental set-up

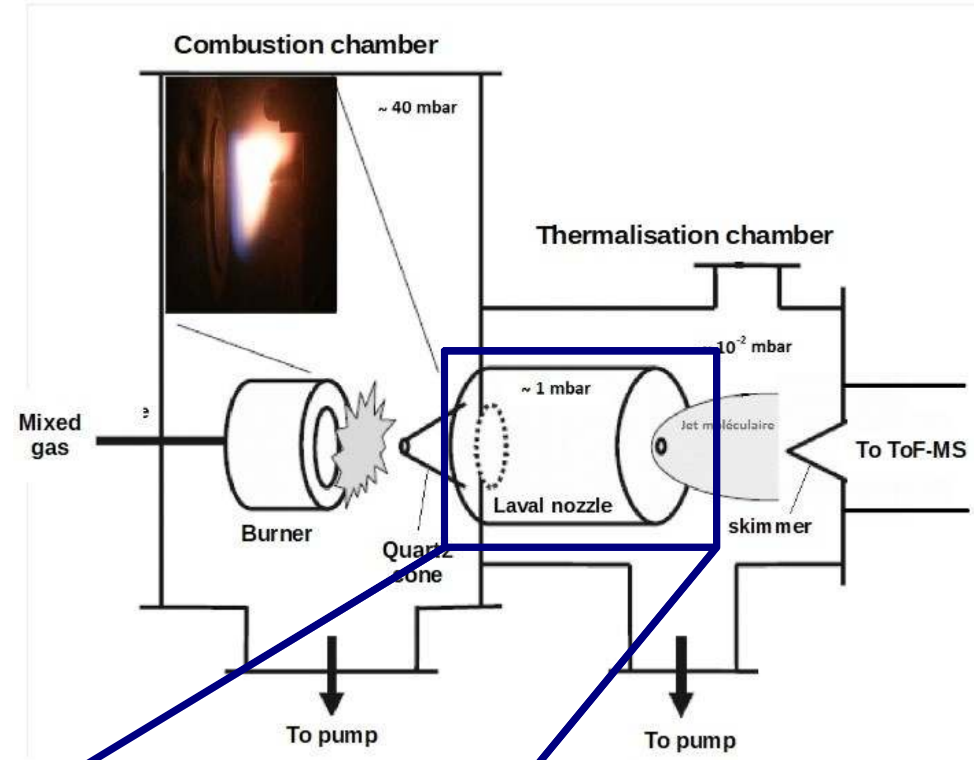
Thermalisation chamber

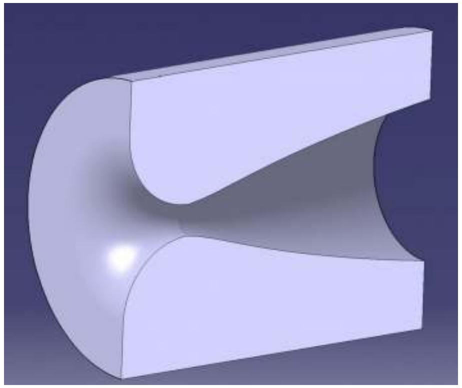
Create a supersonic molecular beam thank to a Laval nozzle

Allows cold and isolated PAHs as in the interstellar medium



Molecular beam temperature vs position at the nozzle exit. The nozzle and X axis are the same one





Laval nozzle (crosssection view)

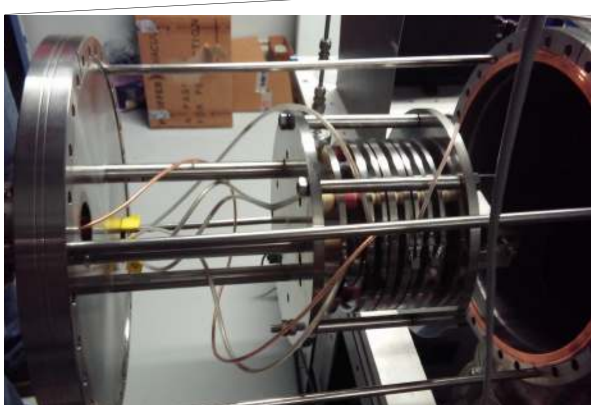
Experimental set-up

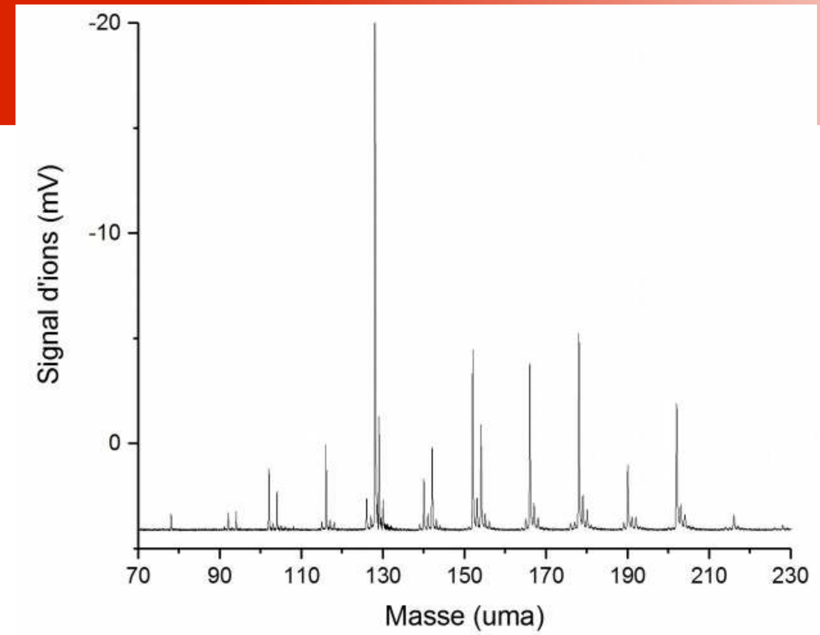
REMPI
(ToF-MS + laser OPO)

Molecules ionization

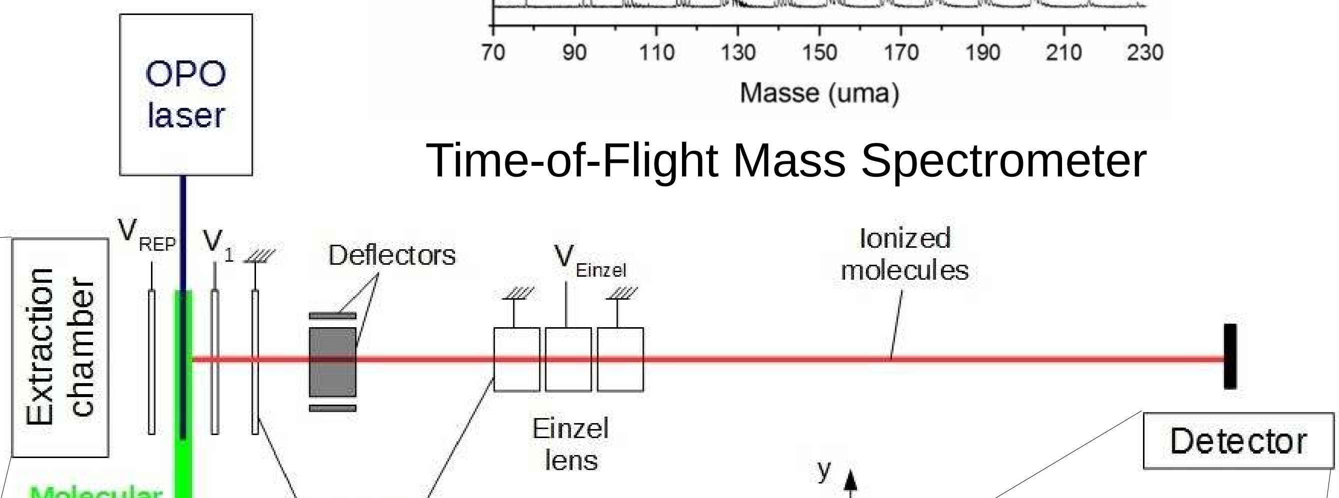
▼

Molecules time arrival on detector depend of their masses





Time-of-Flight Mass Spectrometer



$$M \propto t_{drift}^2$$

t_{drift} : arrival time on the detector
M : molecule mass

Experimental set-up

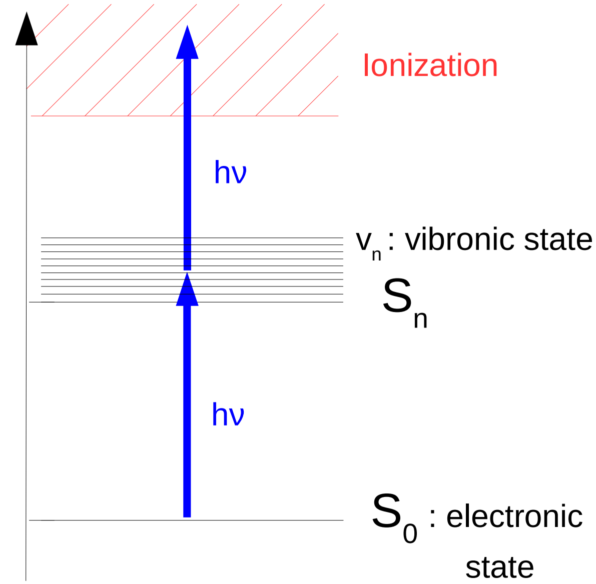
REMPI
(ToF-MS + laser OPO)

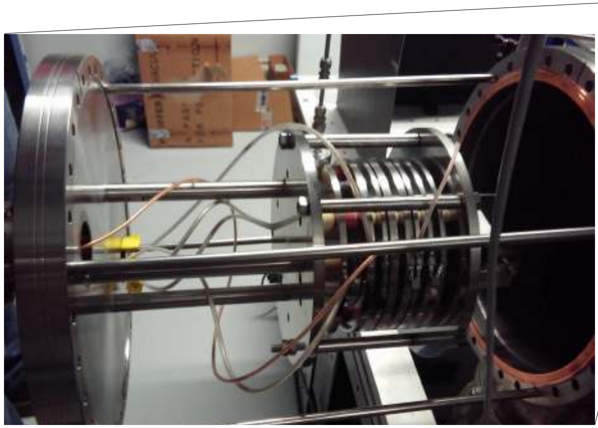
Allows determination of electonic molecular transitions

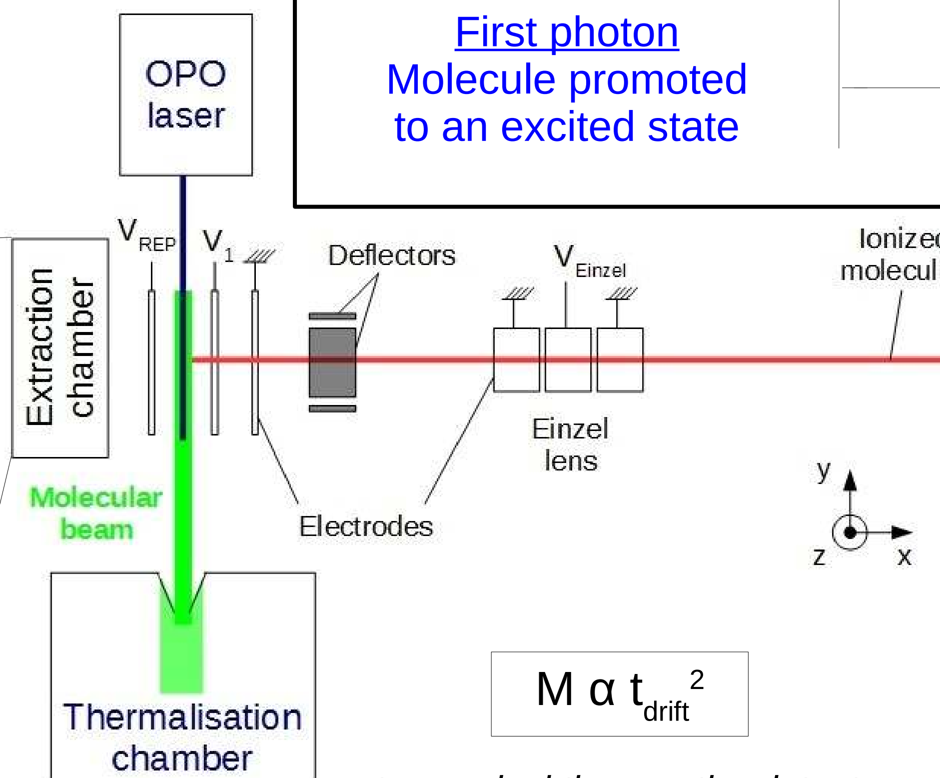
Resonance-Enhanced MultiPhoton Ionization (REMPI)

Second photon
Molecule ionized

First photon
Molecule promoted to an excited state







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t_{drift} : arrival time on the detector
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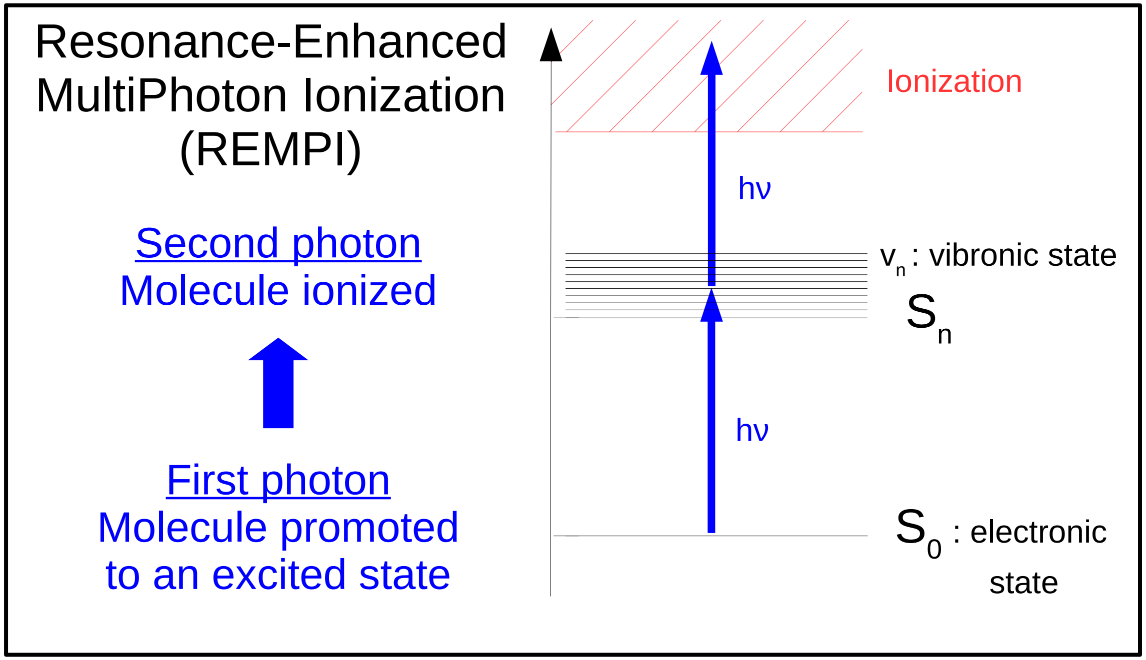
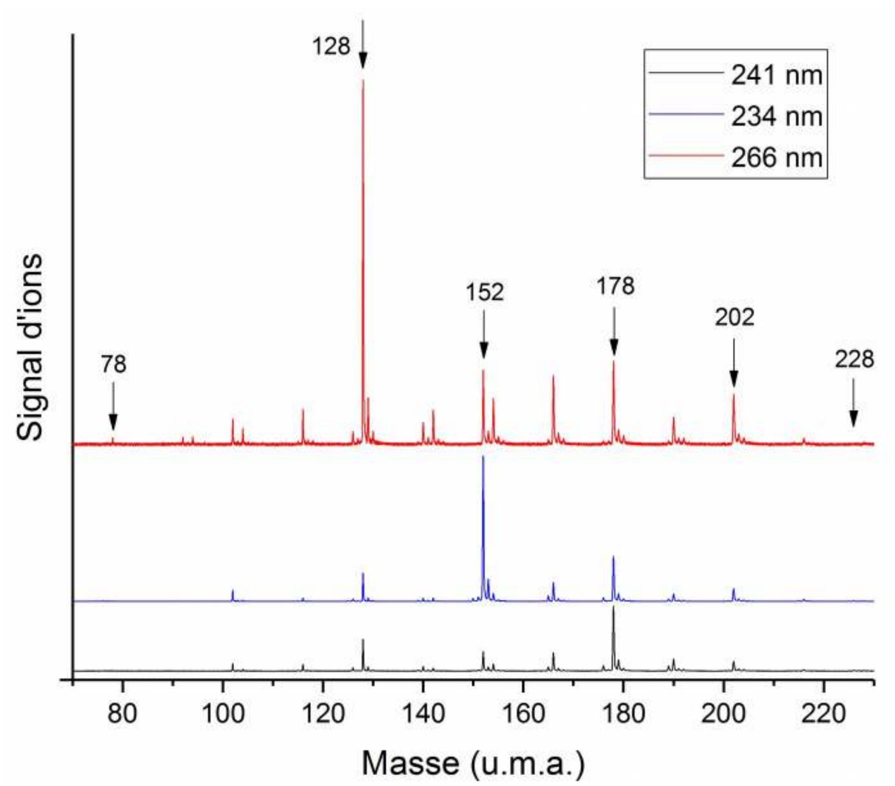
PAHs spectroscopy

REMPI
(ToF-MS + laser OPO)

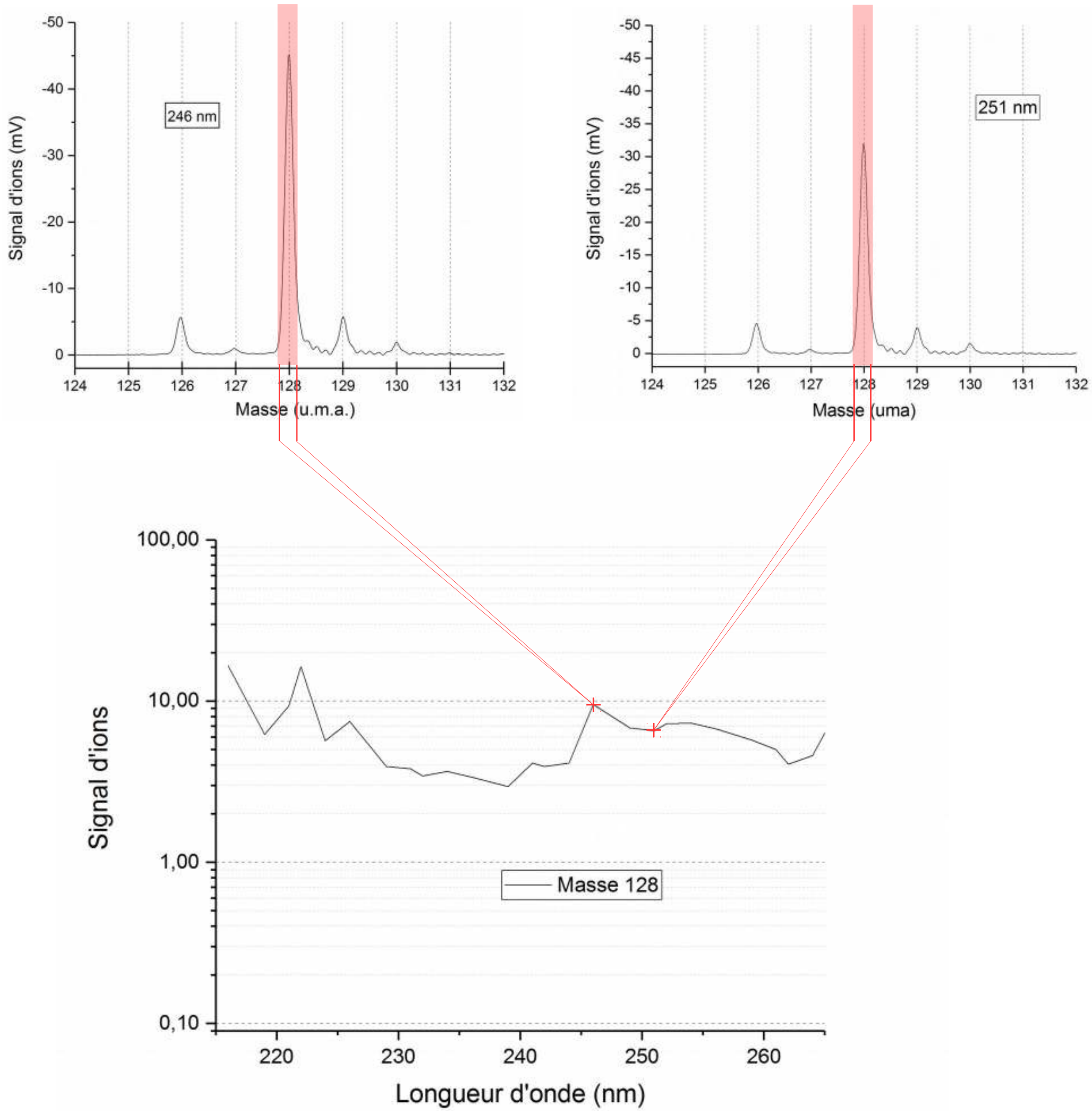




REMPI spectroscopy

Allows determination of transition profiles for each mass

PAHs spectroscopy



REMPI spectra construction

ToF-MS spectrum :
Average over 6000 laser shots

ToF-MS acquisition time :
1 min/spectrum

Time between each acquisition :
2 mins

Spectral step :
2 nm

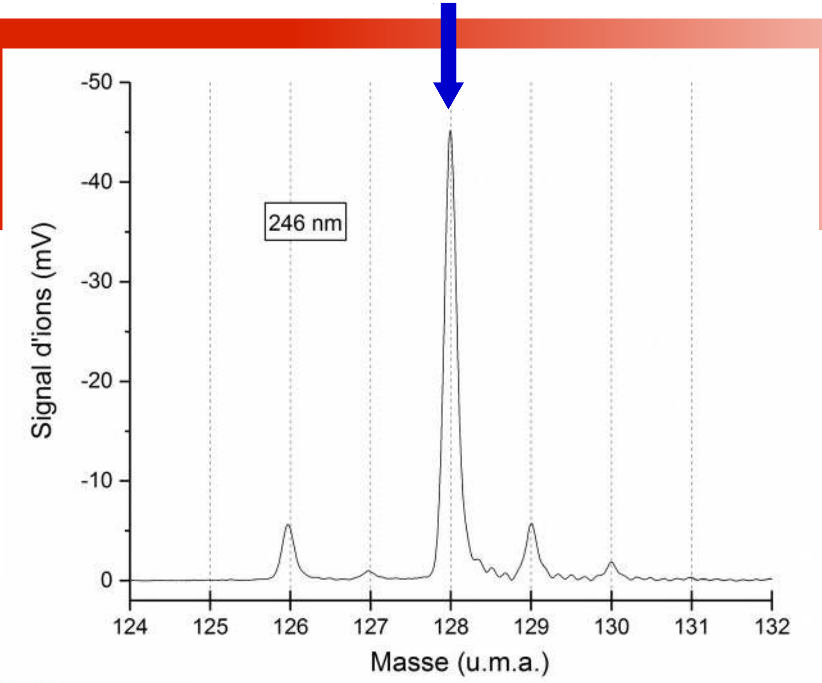
Total time for REMPI spectra acquisition : ~3h

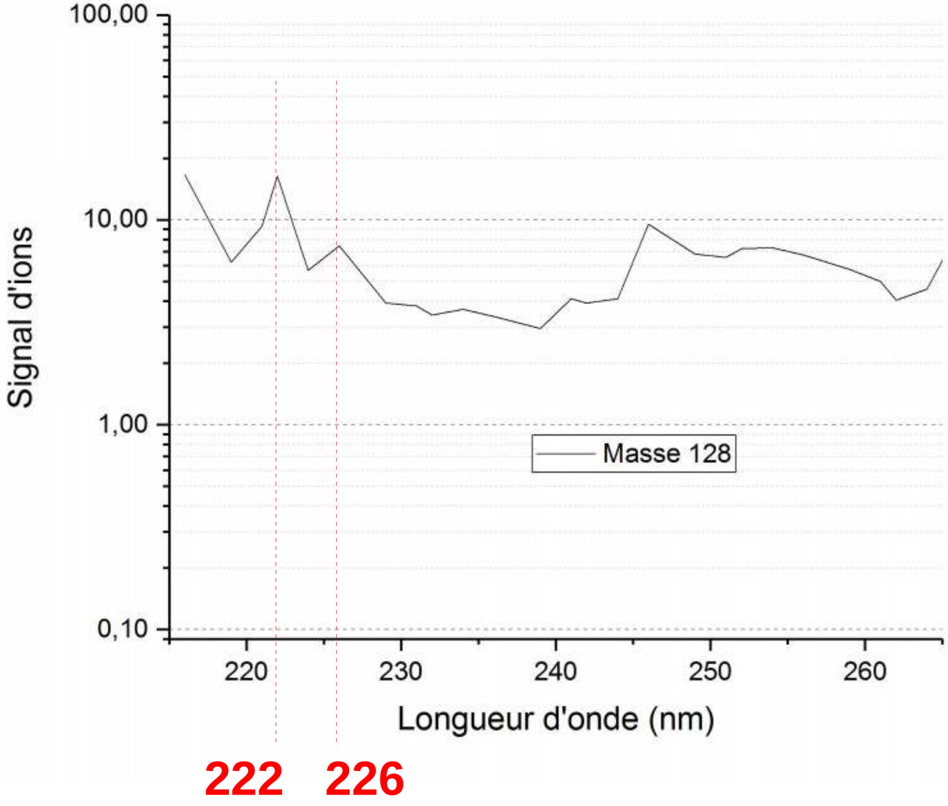
What informations can we extract from REMPI spectrum ?

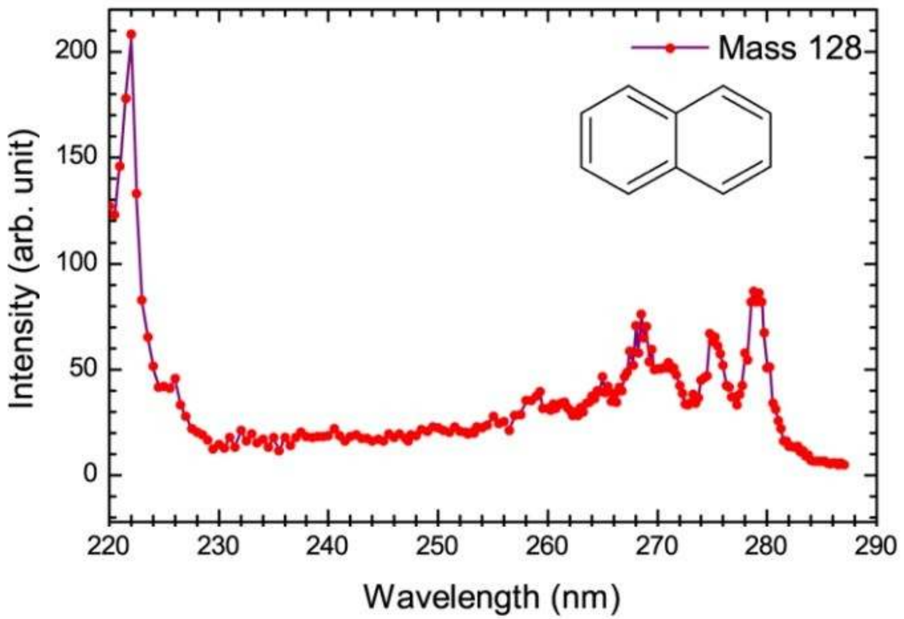
REMPI spectra analysis

2 bands at
222 nm & 226 nm

Bands and mass correspond
to the naphtalene molecule



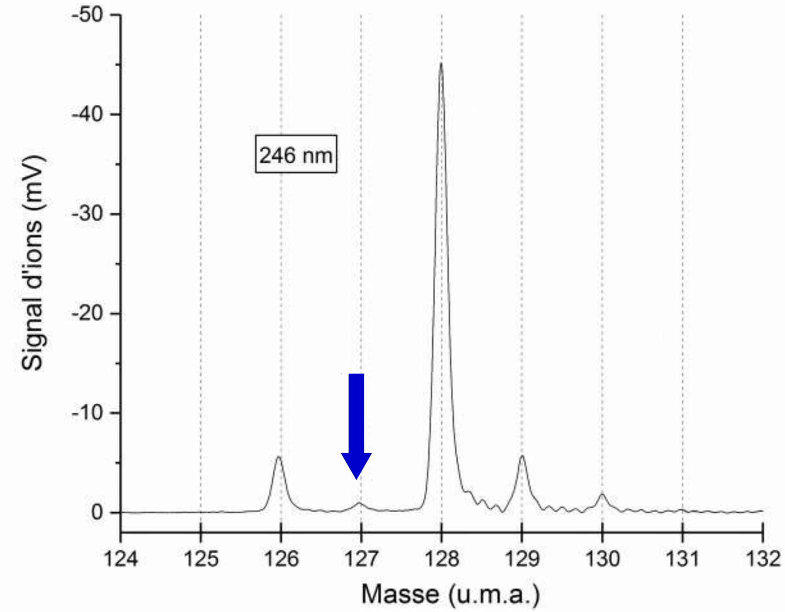


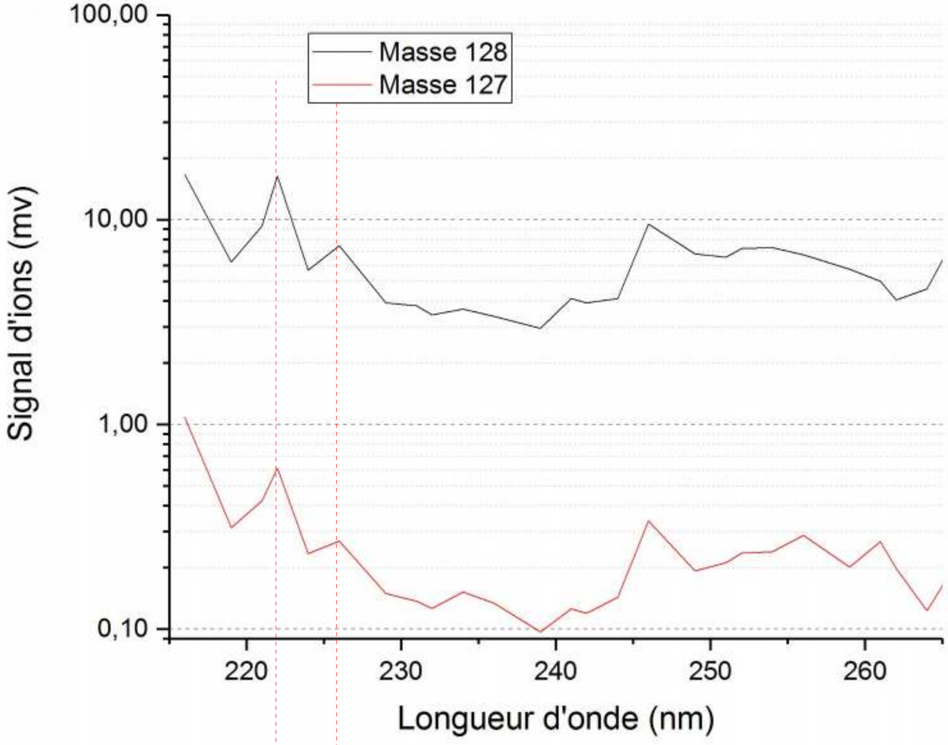


Naphtalene REMPI Spectrum at 300 K (Carpentier, 2013)

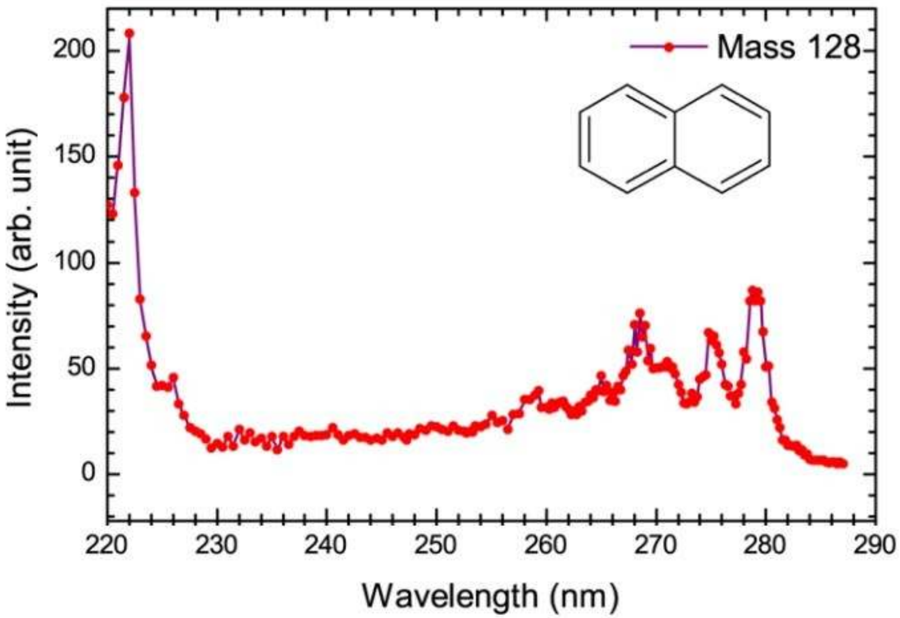
REMPI spectra analysis

Similar REMPI spectrum ▶ Same molecule ▶ Hydrogen fragmentation on the naphtalene molecule





222 **226**



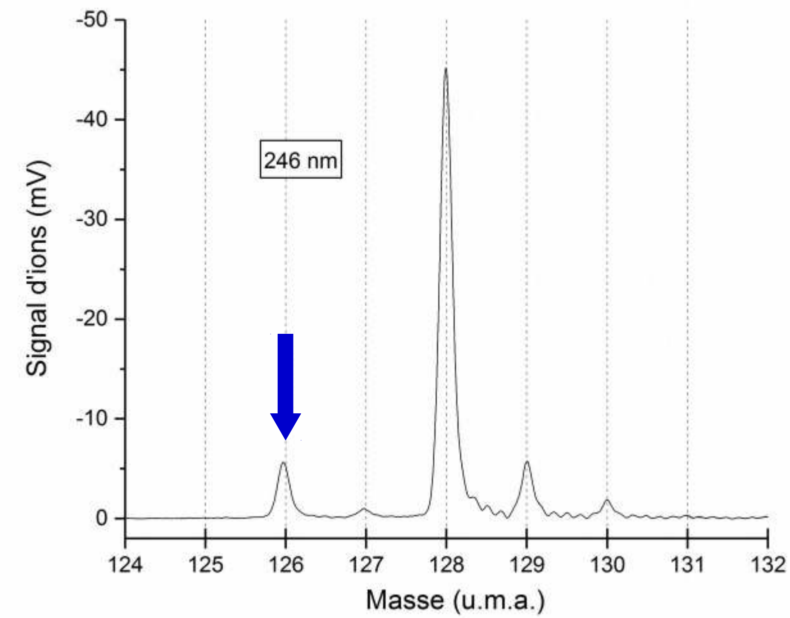
Naphtalene REMPI Spectrum at 300 K (Carpentier, 2013)

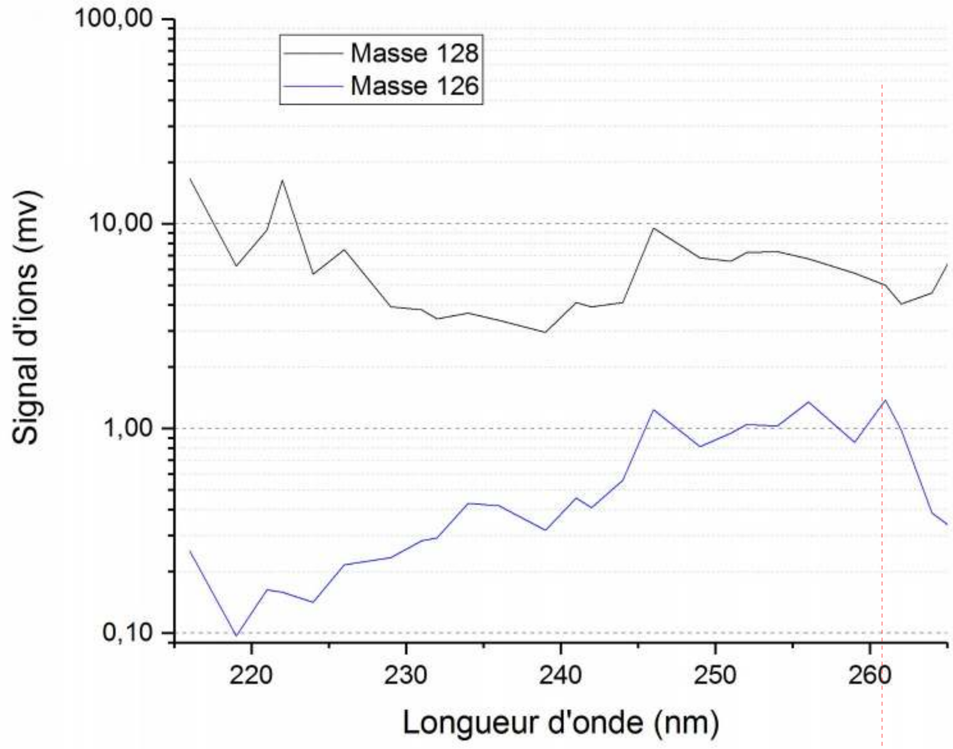
REMPI spectra analysis

Different REMPI spectra between masses 128 uma et 126 uma

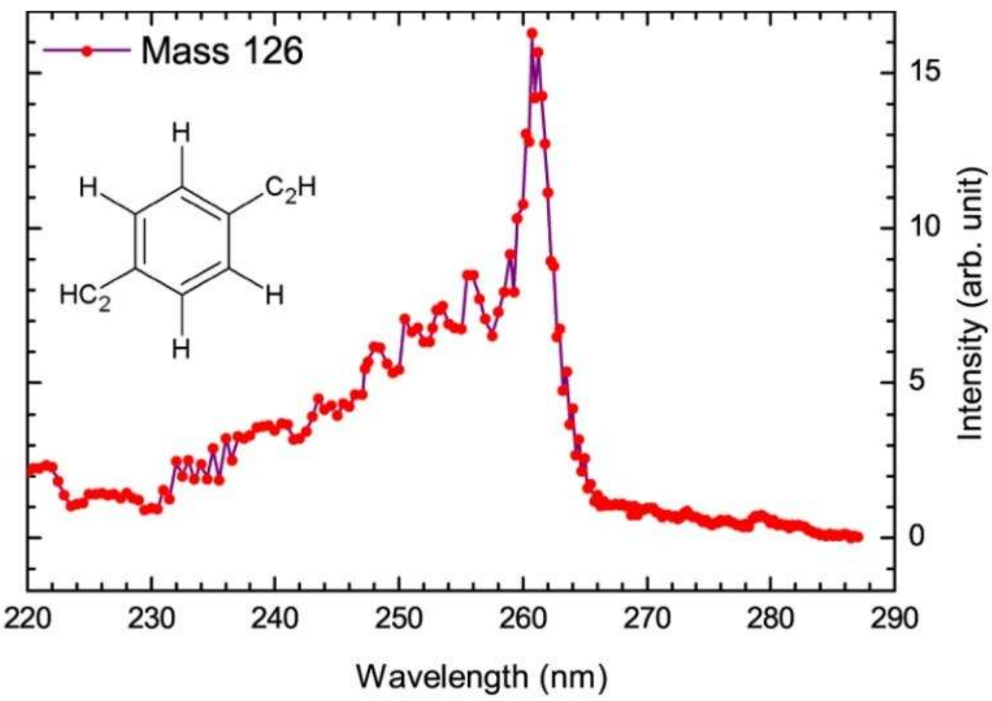
Band at 261 nm
Rempi profile
Mass = 126 uma

P-diethynylbenzene molecule



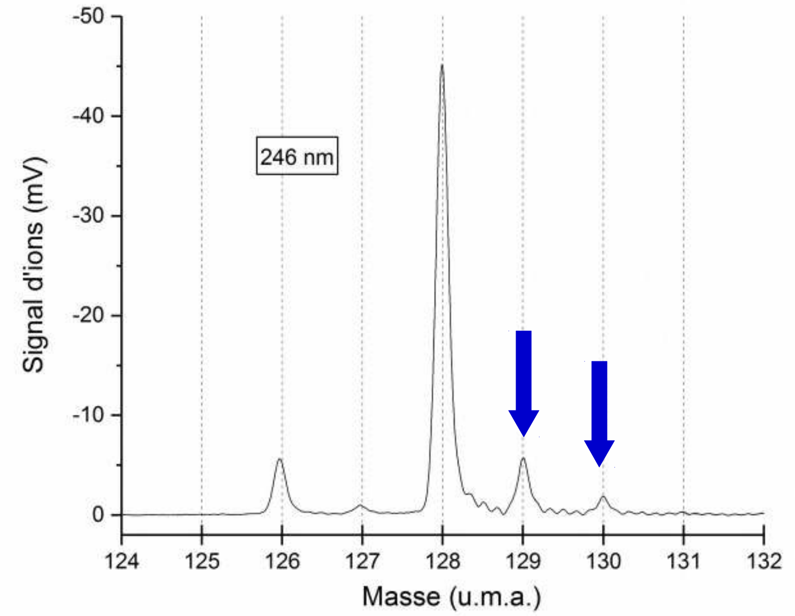


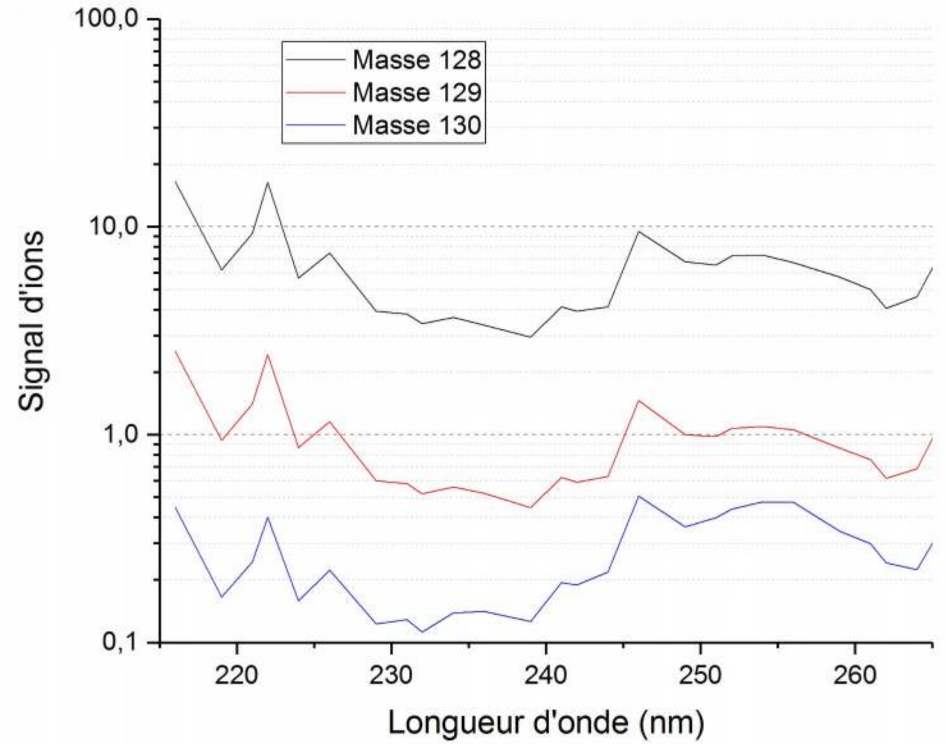
261



p-diethynylbenzene REMPI spectrum at 300 K (Carpentier, 2013)

REMPI spectra analysis





Same REMPI profile

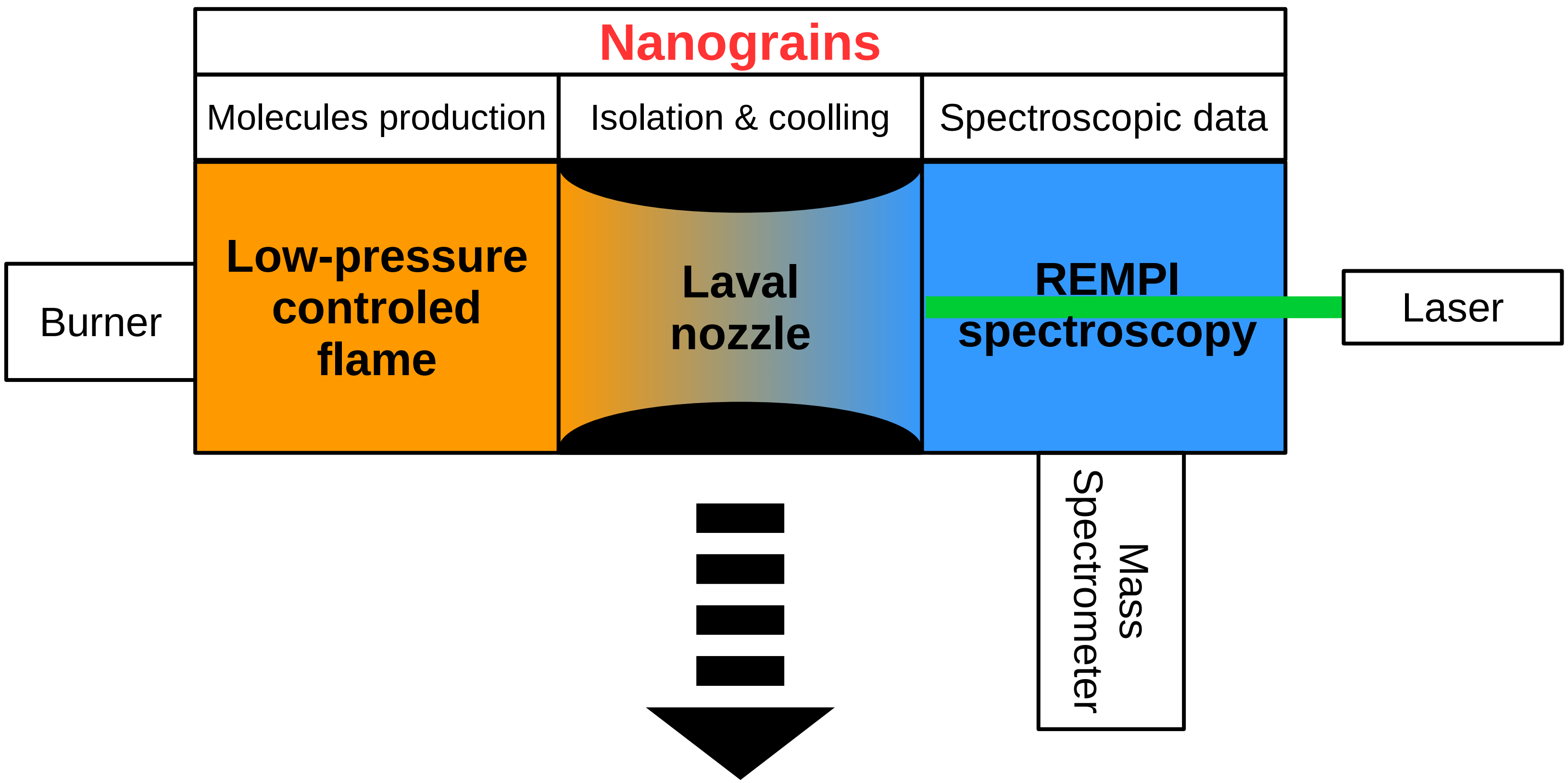
Same molecule

Contribution of carbon isotope ^{13}C for the naphtalene molecule

Conclusion

Spectroscopy of large PAHs molecules still difficult
3 reasons

No conventional way for synthesis
Spectroscopy have to be done in an isolated and cold environment
Spectra analysis complex



Determination of new DIBs and bump carriers !

Conclusion

Thank you for your attention !

SYSTEMAE group
a.k.a. The C-team