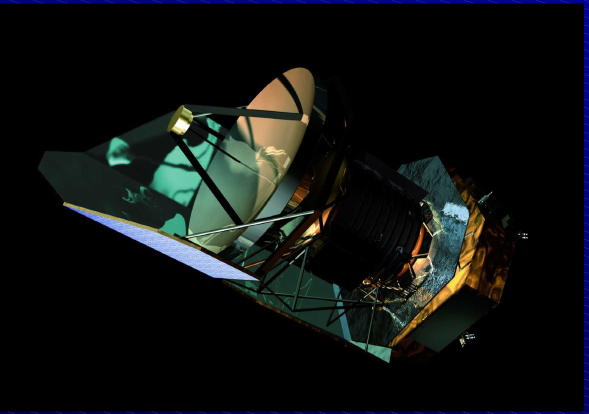
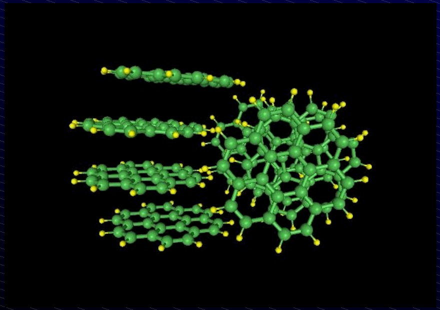
Polycyclic aromatic hydrocarbons, evaporating very small grains and H_2 in photodissociation regions



Christine Joblin

Centre d'Etude Spatiale des Rayonnements

Université de Toulouse – CNRS



"Elementary mechanisms of hydrogen / carbon-surface interactions"

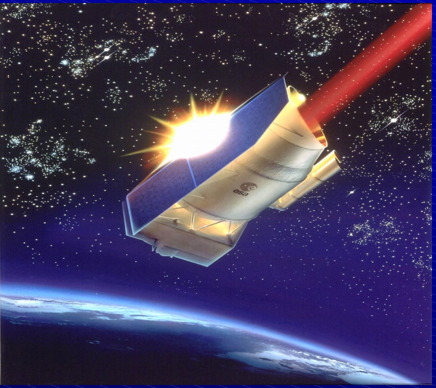
ARCHES workshop

Marseille , 27-28 October 2008

Outline

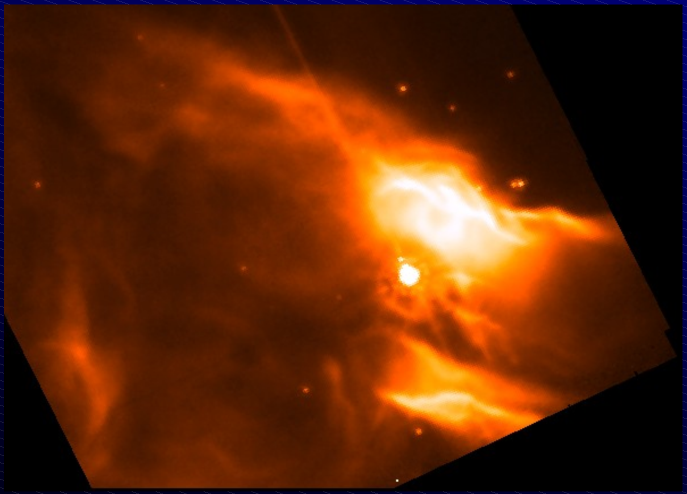
- The Aromatic Infrared Bands (AIBs) – which carriers (PAHs, C-VSGs)?
- Role of the PAHs / C-VSGs in H_2 formation in photodissociation regions
- The laboratory approach

PAHs revealed through the mid-IR emission of PhotoDissociation (UV-irradiated) Regions

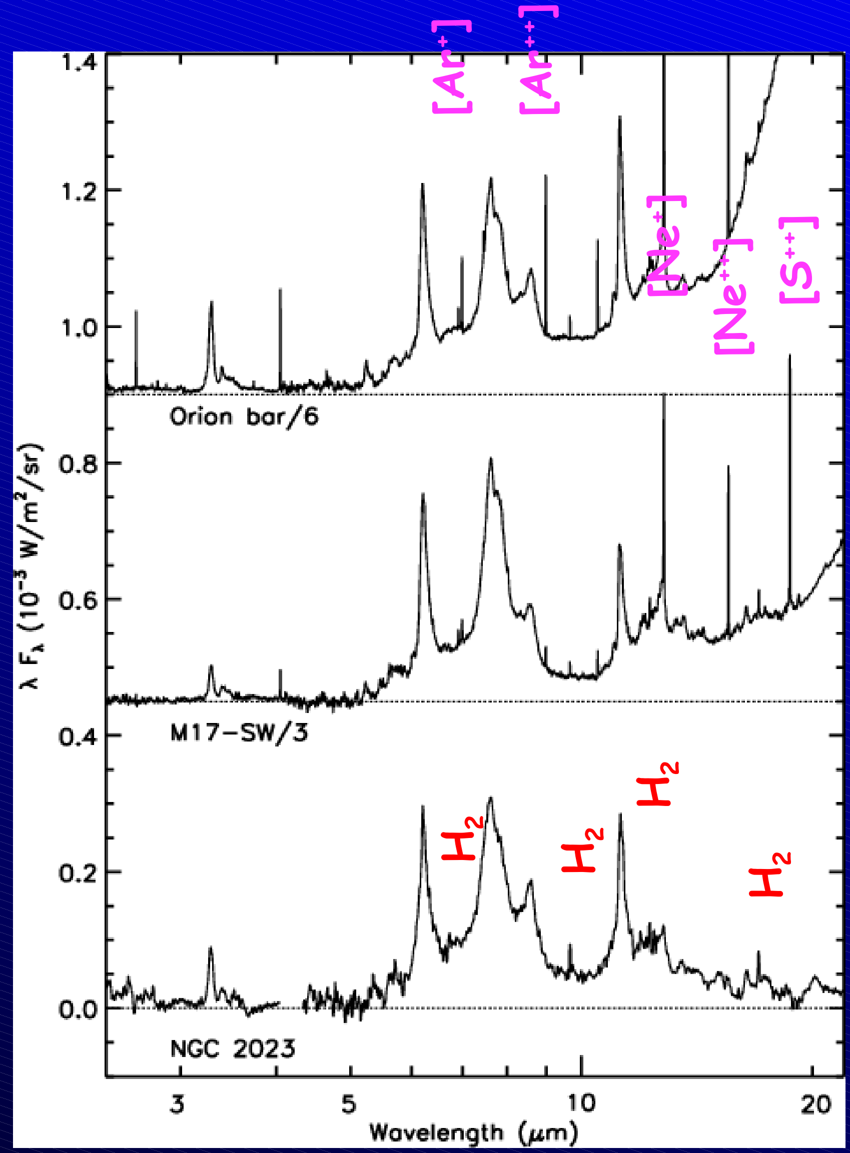


« Infrared Space Observatory »
ESA; 1995-1998

« Spitzer Space Telescope »
NASA; 2003-2009



SST IRAC 8 μm image – NGC 7023
Werner et al. 2004, ApJ Supp 154, 309

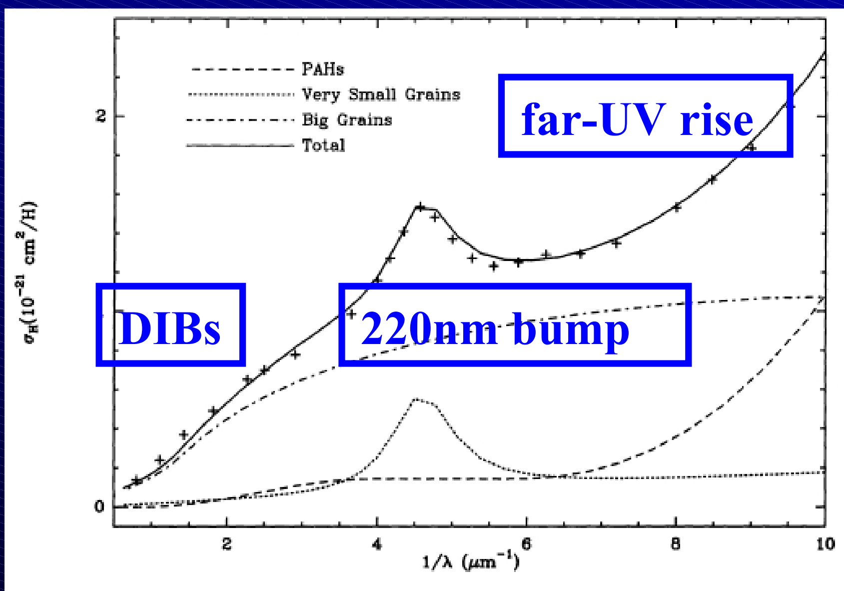


ISO SWS spectra
Vertratete et al. 2001, A&A 372, 981

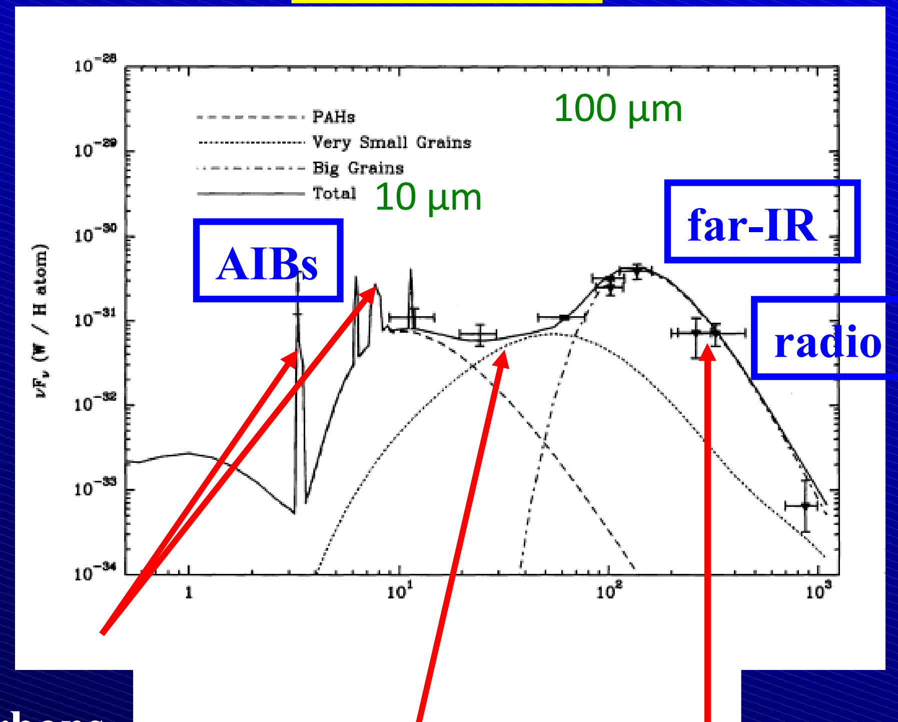
Interstellar dust :
from grains to aromatic molecules

From Désert et al. 1990, A&A 237, 215

UV-visible extinction



IR emission



Polycyclic Aromatic Hydrocarbons
PAH

Very Small Grains
VSG

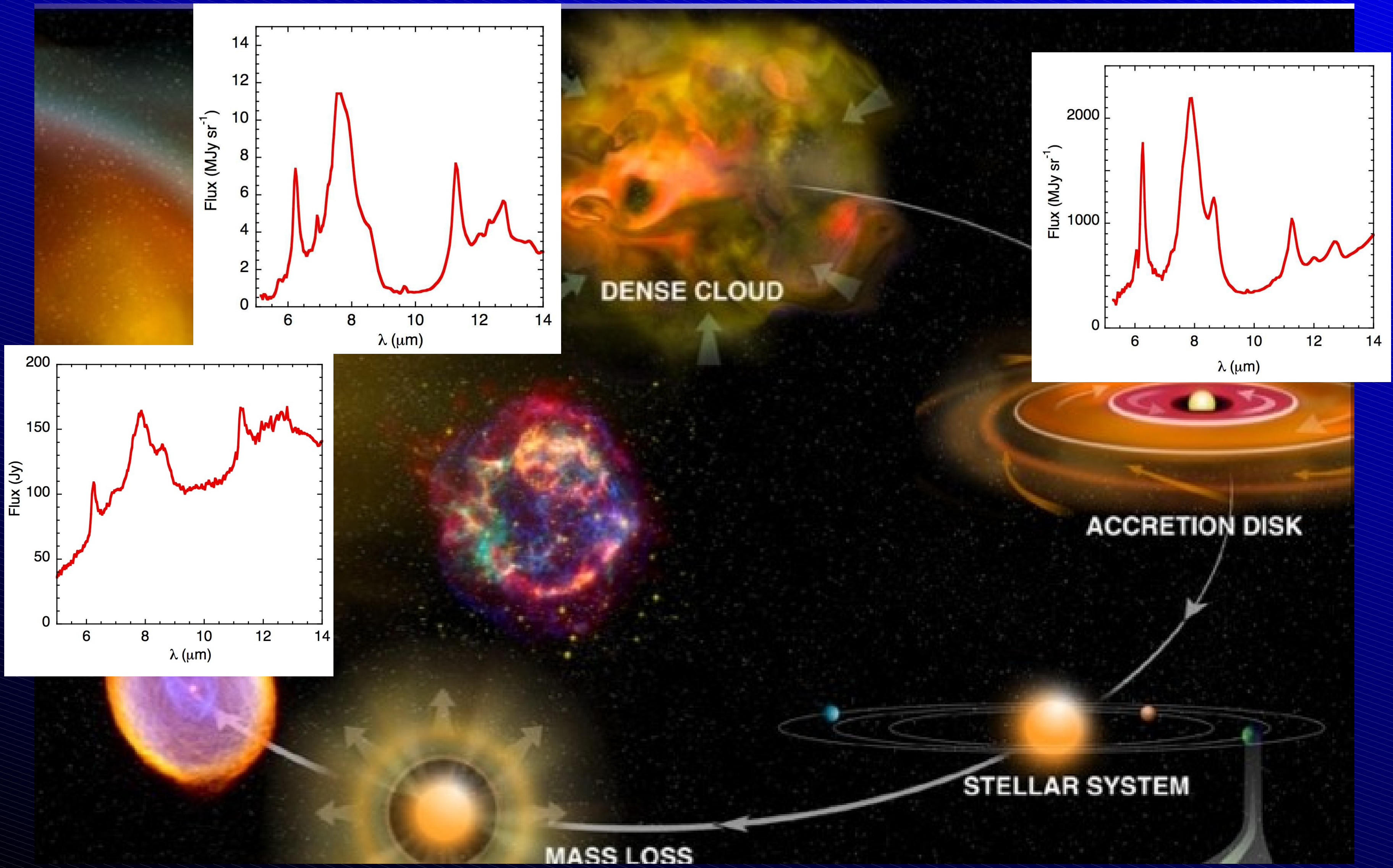
Big Grains
0.1 µm - BG

Nano-objects (1-20 nm)
composition?
C, Si, Fe,….

silicates

PAHs in the dust cycle

What can we learn on PAHs from the analysis of the AIB spectrum?



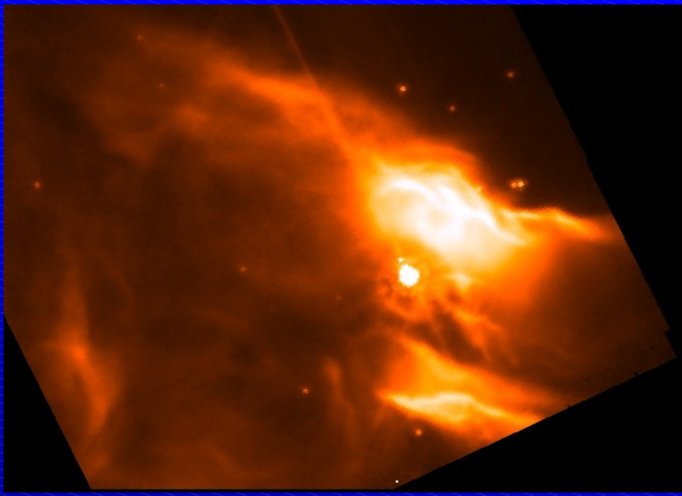
Adapted from http://www.nrao.edu/pr/2006/gbtmolecules/ Bill Saxton, NRAO/AUI/NSF

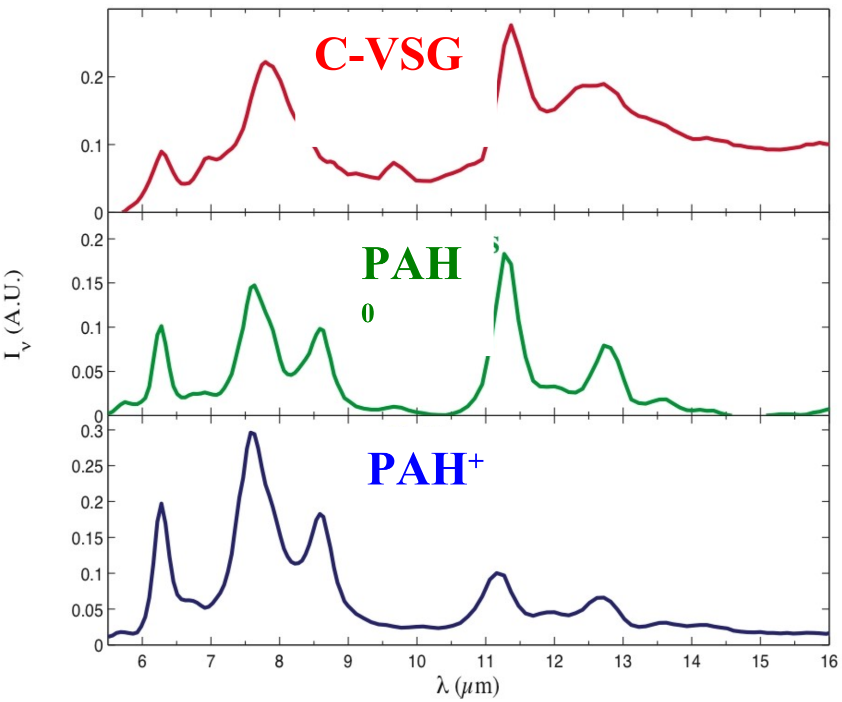
Photoprocessing of AIB carriers

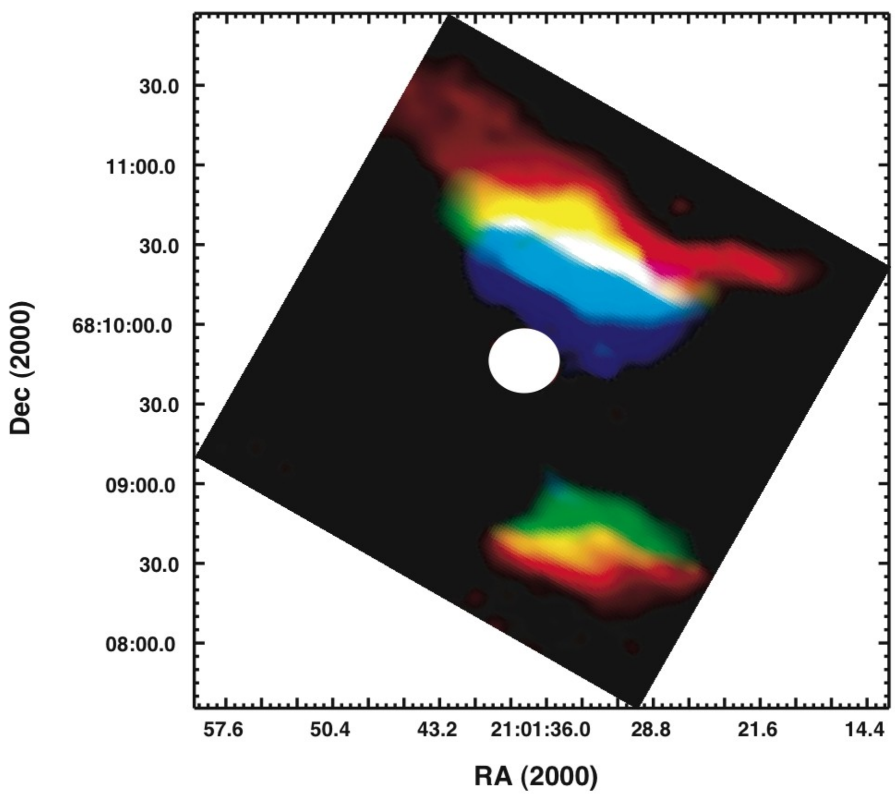
Mild excitation conditions

Ex: NGC 7023 PDR

Rapacioli, Joblin, Boissel, 2005, A&A 429, 193
Tielens 2008, ARA&A, in press







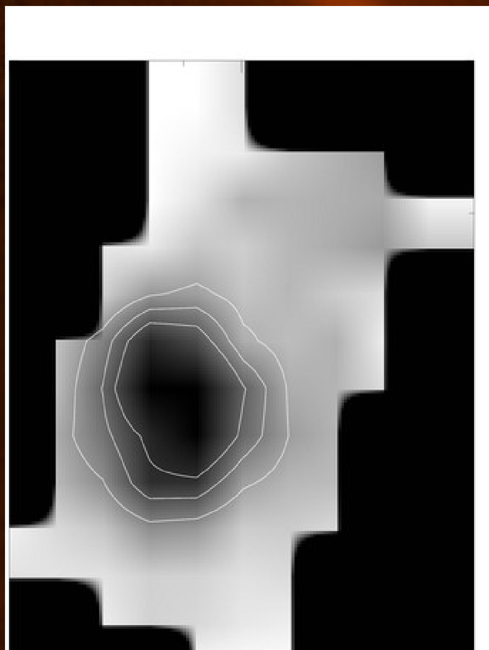
Programme SPECPDR on Spitzer

Berne, Joblin et al. 2007, A&A 469, 575

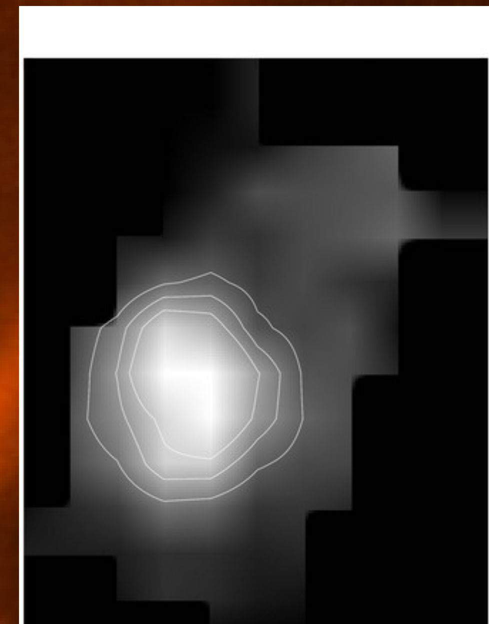
Ced 201

B9.5 V star

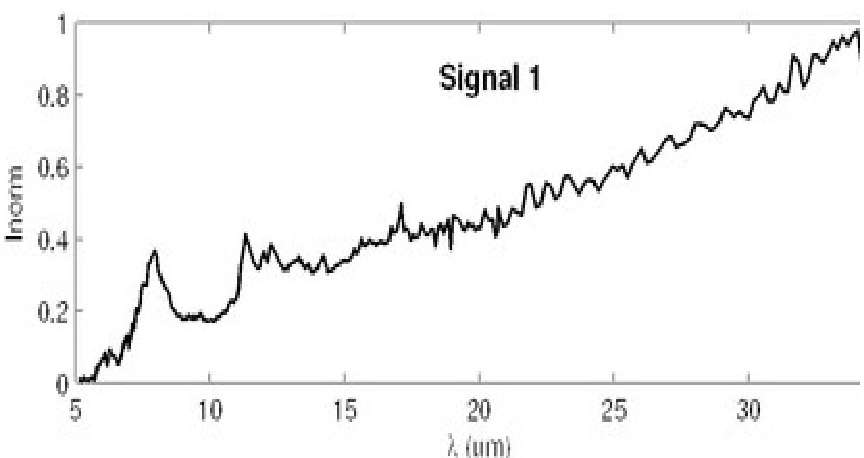
VSG Map



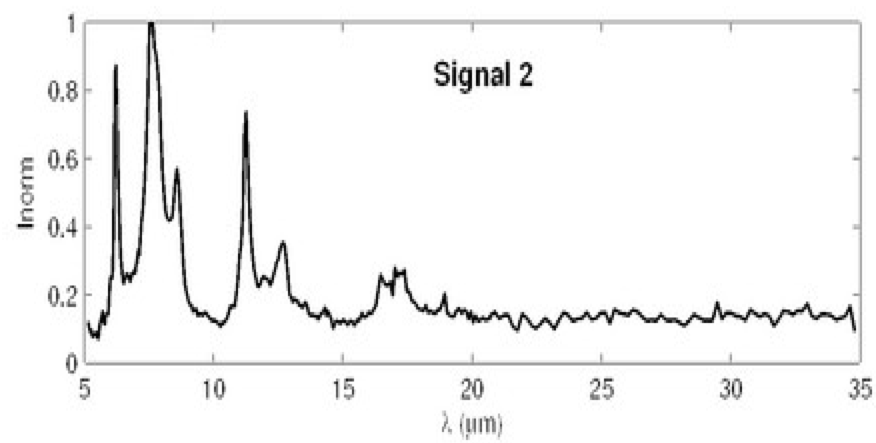
PAH Map



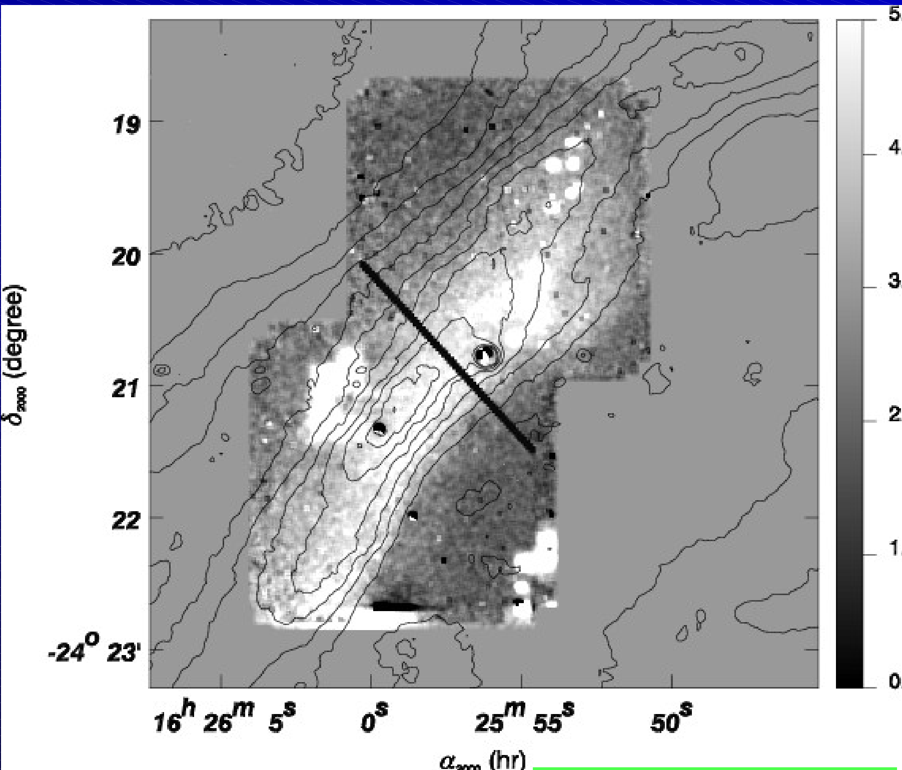
VSG spectrum



PAH spectrum

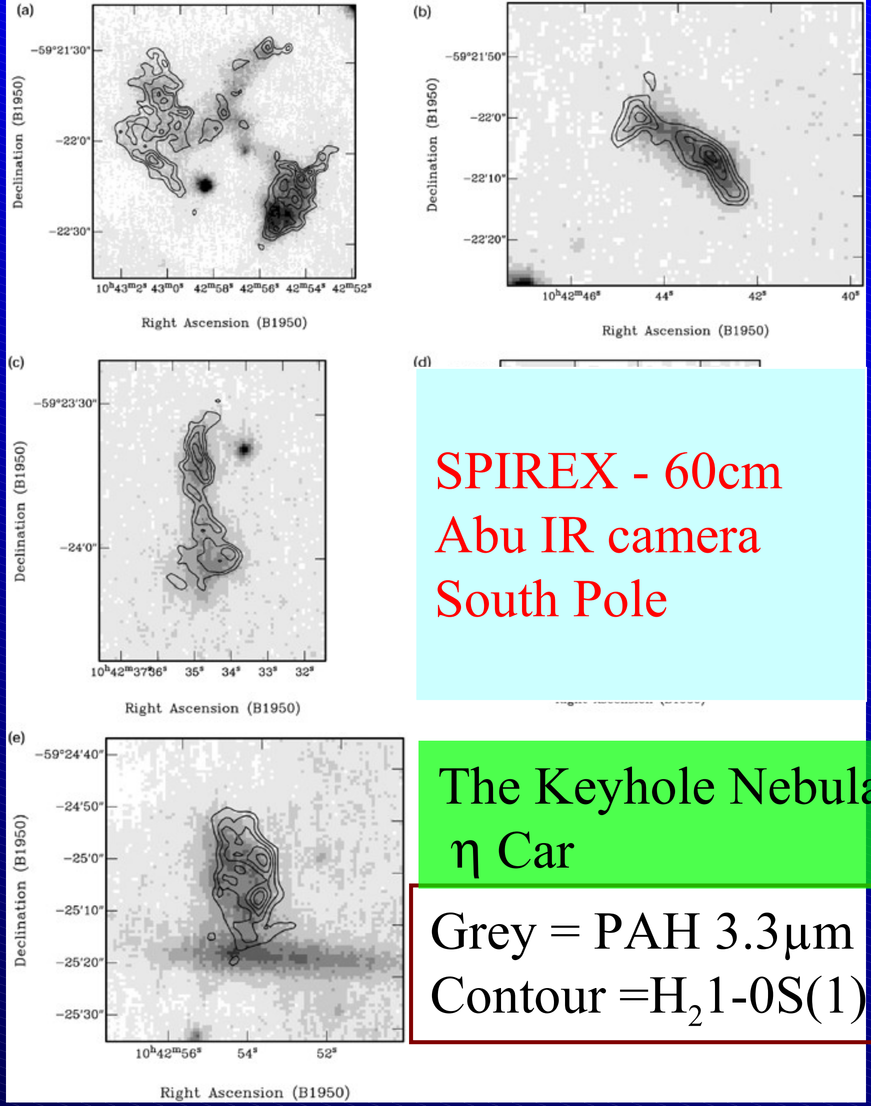


AIB and H_2 emissions



ρ Oph filament

Habart et al., 2003, A&A 397, 623



SPIREX - 60cm
Abu IR camera
South Pole

The Keyhole Nebula
η Car

Grey = PAH 3.3μm
Contour =$H_2$1-0S(1)

Brooks et al. 2000, MNRAS 319, 95

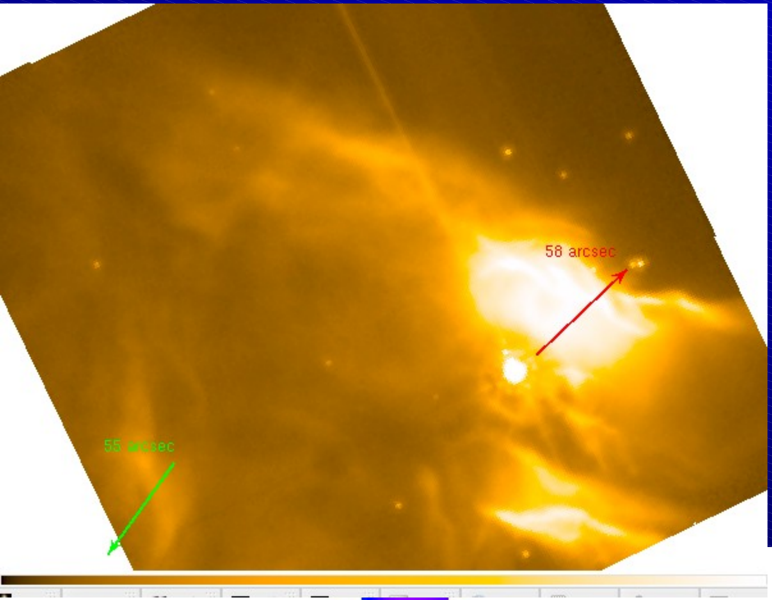
Abundance of H_2 in PDRs + spatial coincidence with the Aromatic Ir Bands

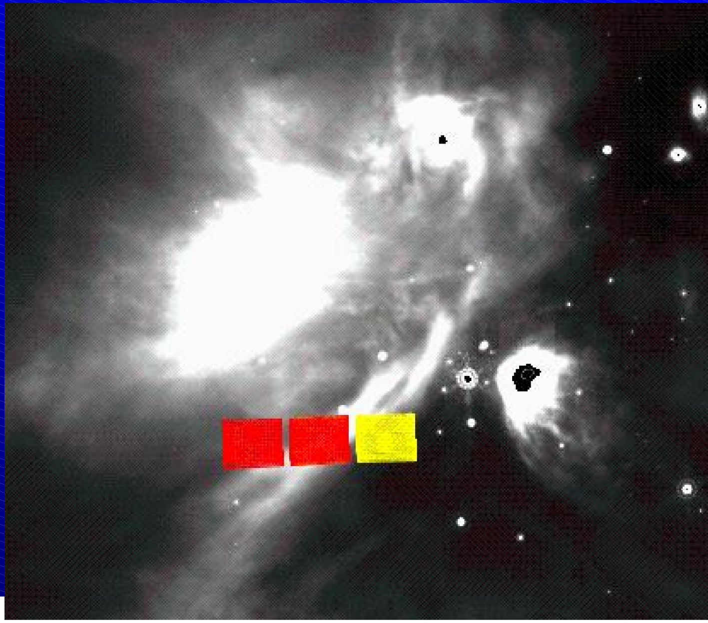
Formation of H_2 in PDRs related to the photophysics/chemistry of PAHs/C-VSGs

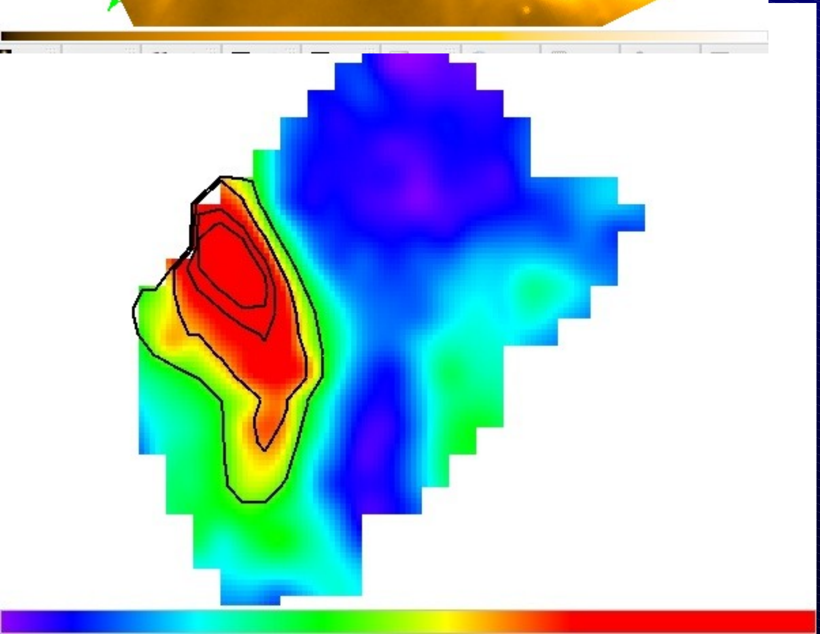
C-VSGs and H_2 emission in PDRs - SPECPDR on Spitzer

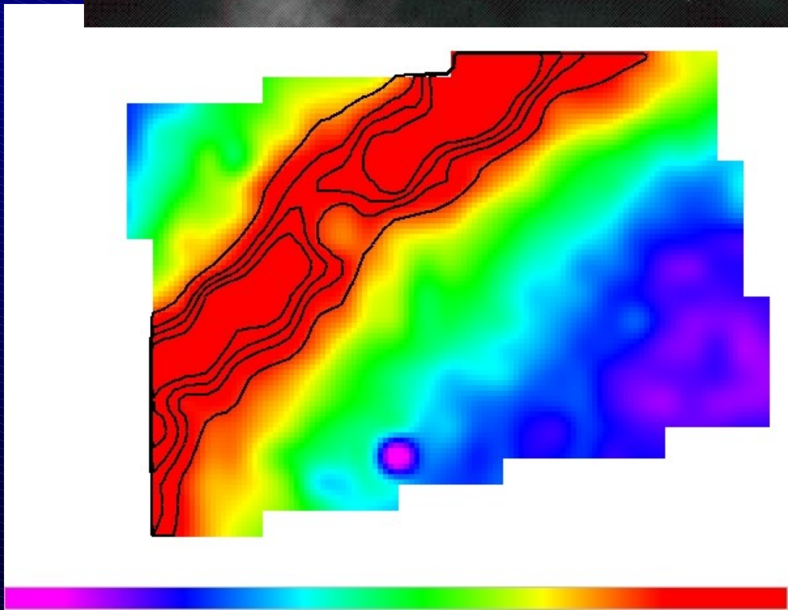
H_2 0-0S(0) @ 28 μm / C-VSGs (contours)

Joblin et al. 2008



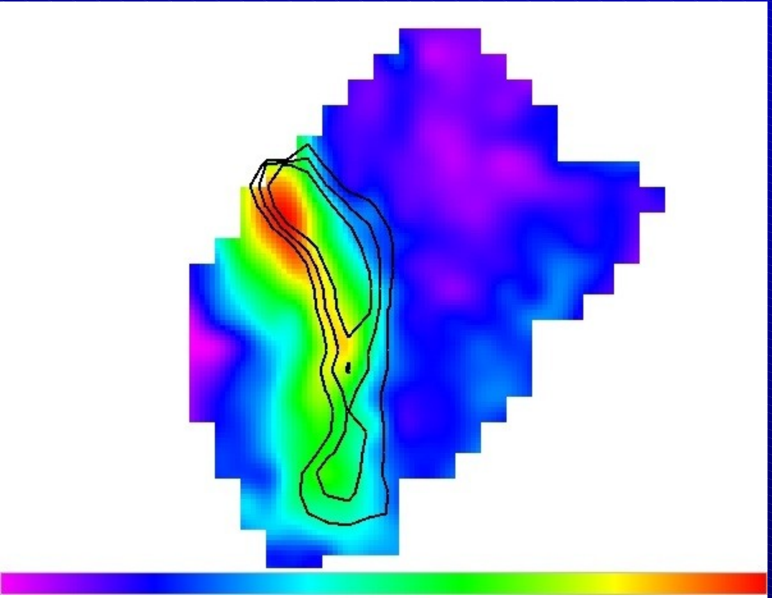


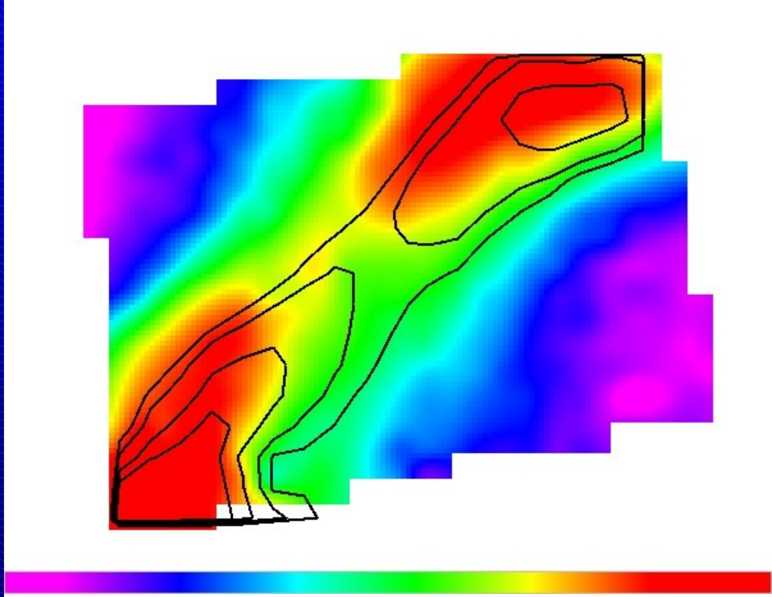


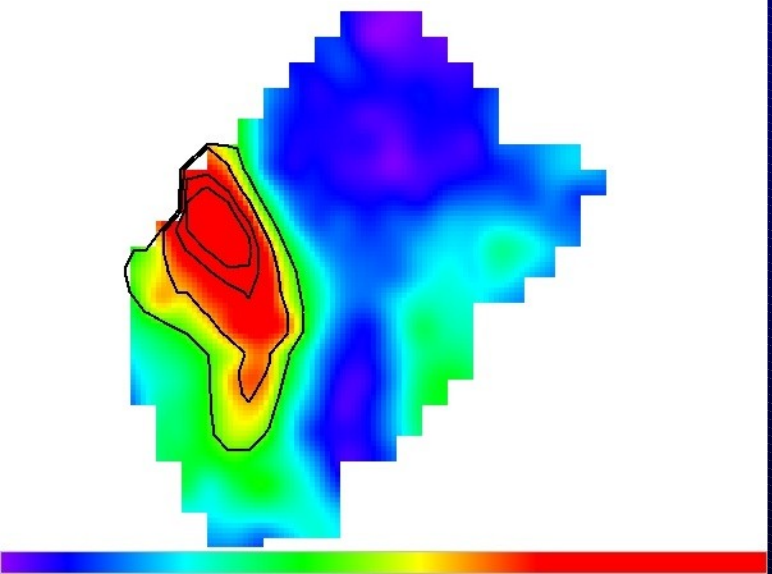


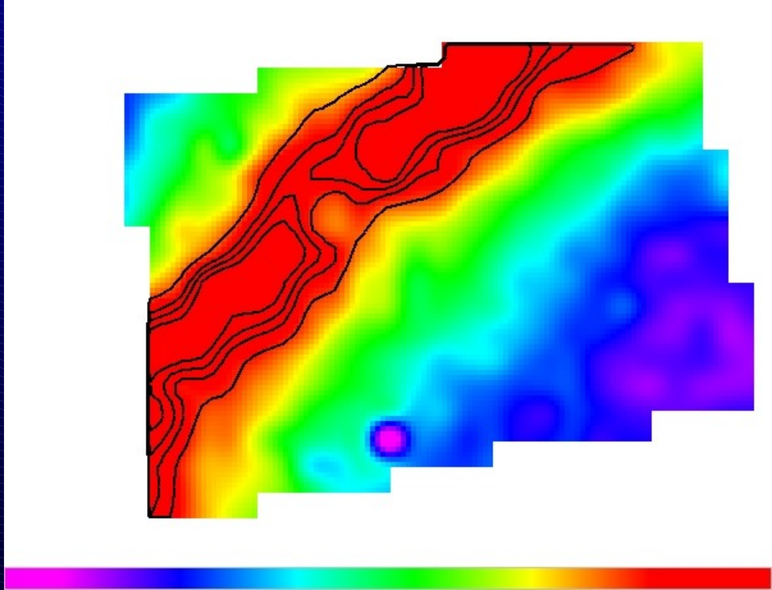
C-VSGs and H_2 emission in PDRs - SPECPDR on Spitzer

H_2 0-0S(3) @ 9.7 μm / PAH emission (contours)









H_2 28 μm

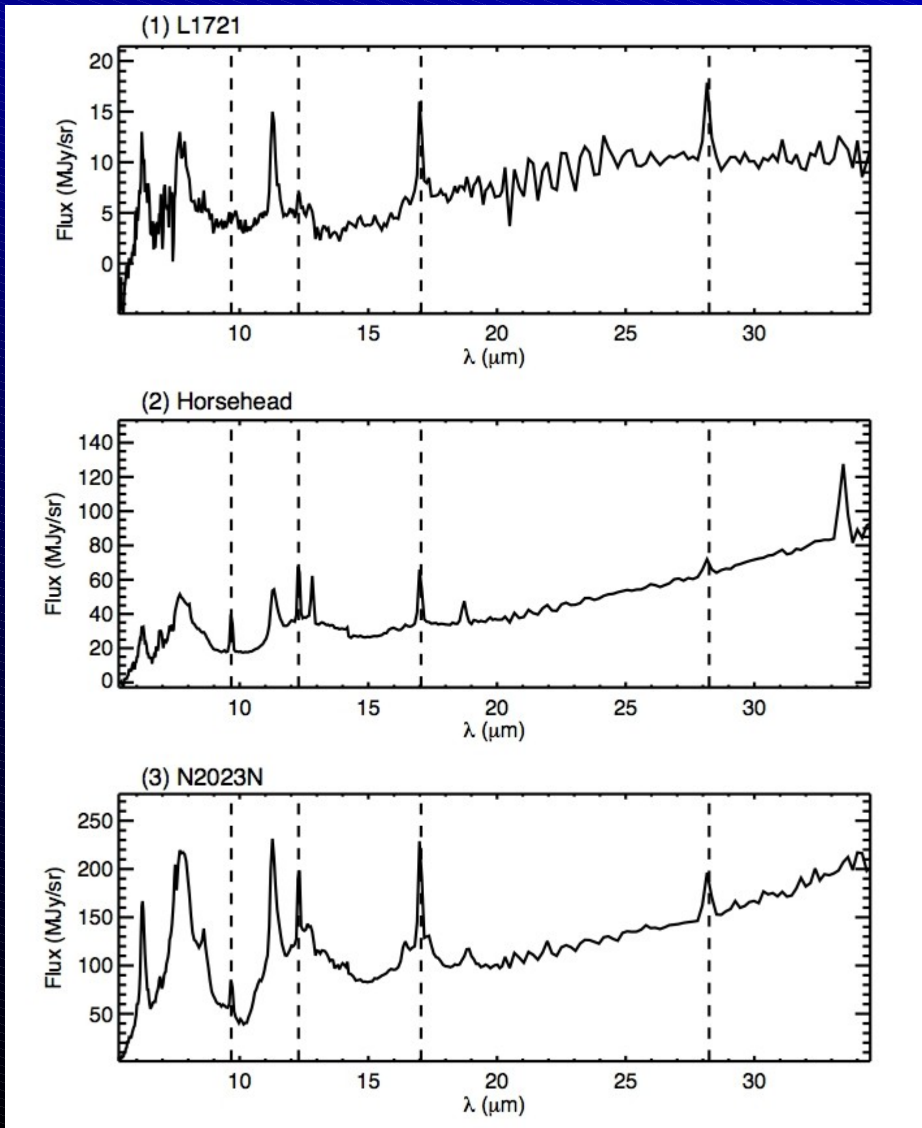
C-VSG emission

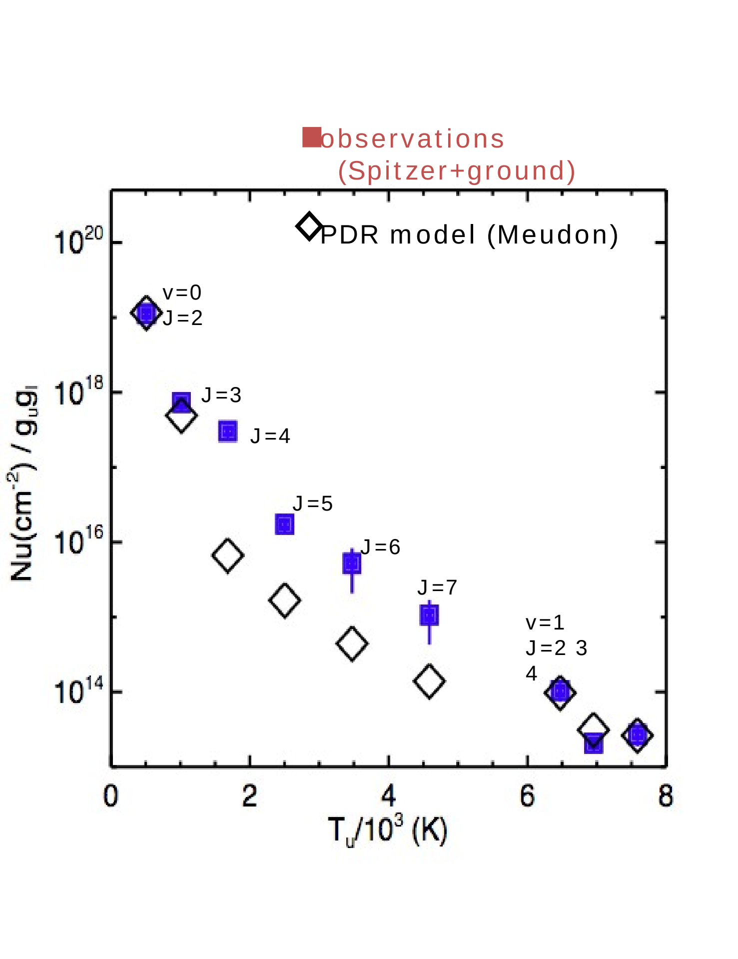
H_2 emission in PDRs

S(3) S(2) 0-0 S(1) 0-0 S(0)

J=5 J=4 v=0 J=3 v=0 J=2

Habart et al. 2007, A&A, subm.





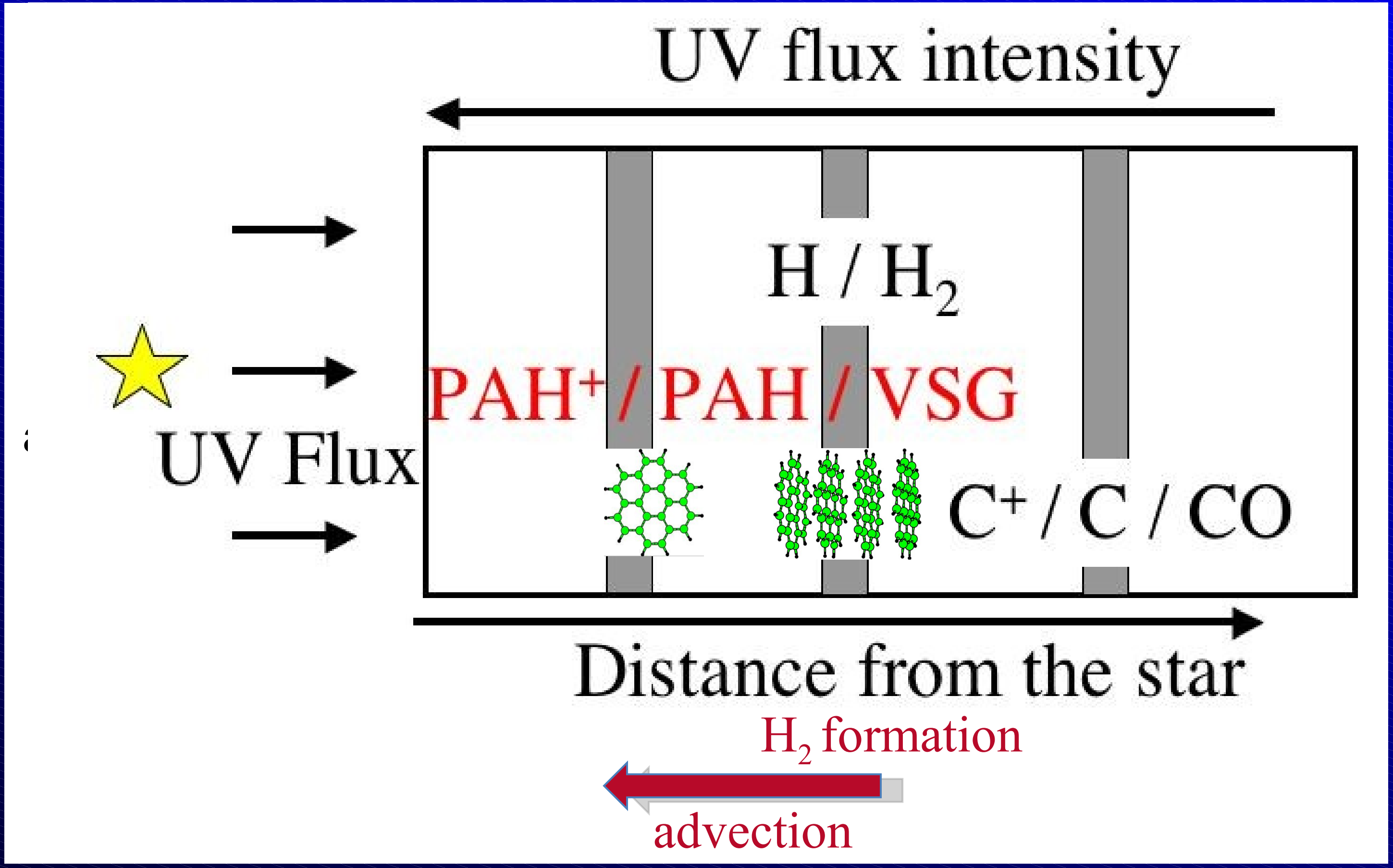
Unexpected rotationally excited H_2 in low/moderate excited PDRs.

Observations of H_2 in PDRs

- PDRs are regions rich in UV photons, where the gas temperature is high and the dust temperature is higher (T_g~50K).
- Need for a high formation rate of H_2 in PDRs - *Habart et al. (2004, A&A)*
- Role of chemisorbed H (reactivity of physisorbed H atoms not efficient enough) – *Cazaux & Tielens (2004, A&A)*
- Excitation : collisions, UV pumping, formation process. Unexpected rotationally excited H_2 concerns a small fraction of excited H_2 (few percents). Role of advection? Formation process?

  Habart et al. (2007, A&A, subm.) – Joblin et al. (2008)

Proposed candidates for "evaporating" VSGs



PAH clusters $[PAH_n]^{+/0}$

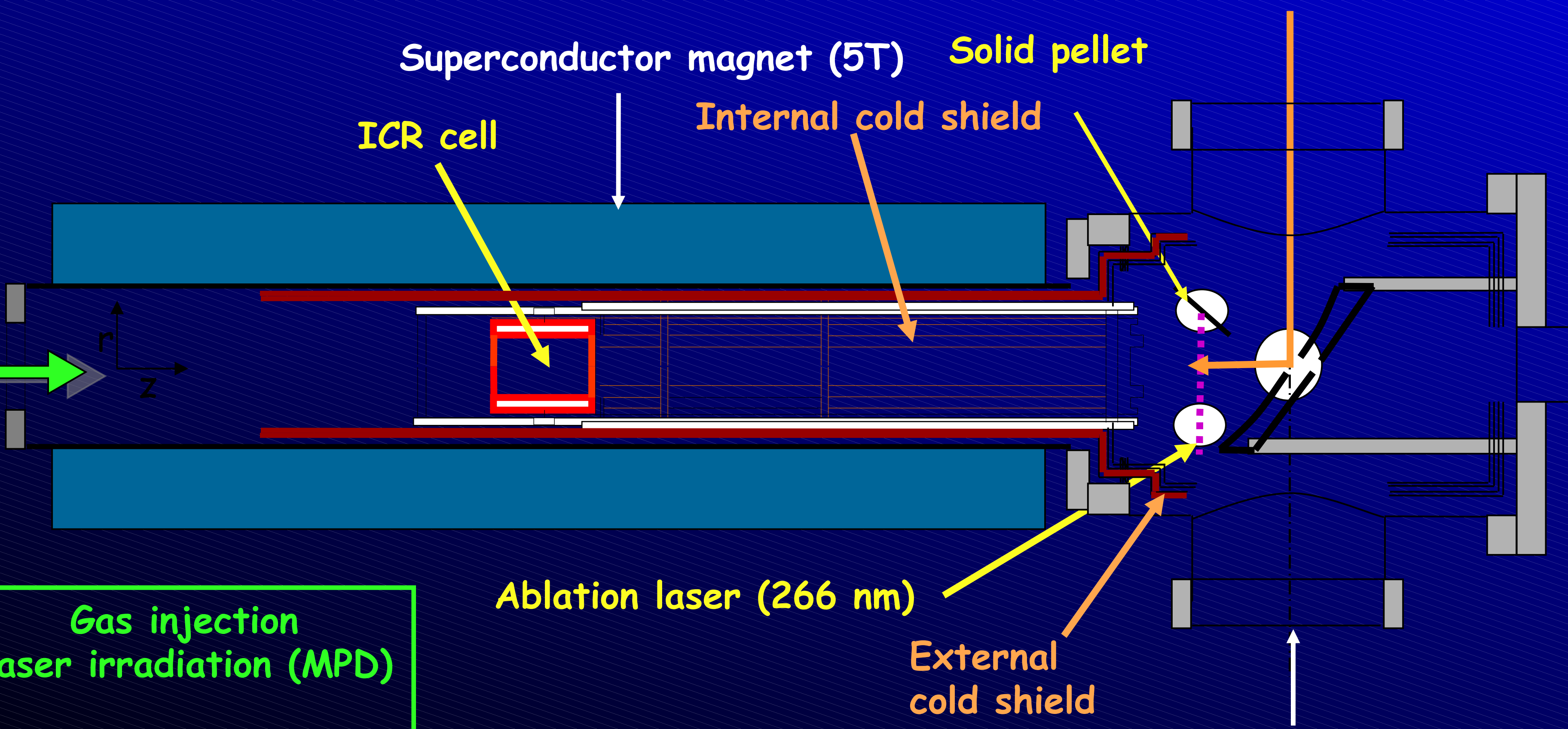
ISOCAM up to 16 µm: N_C~400 atoms ***Rapacioli et al. 2005, A&A 429, 193***

Spitzer up to 35 µm: N_C few 1000 atoms ***Berne et al. 2007, A&A 469, 575***

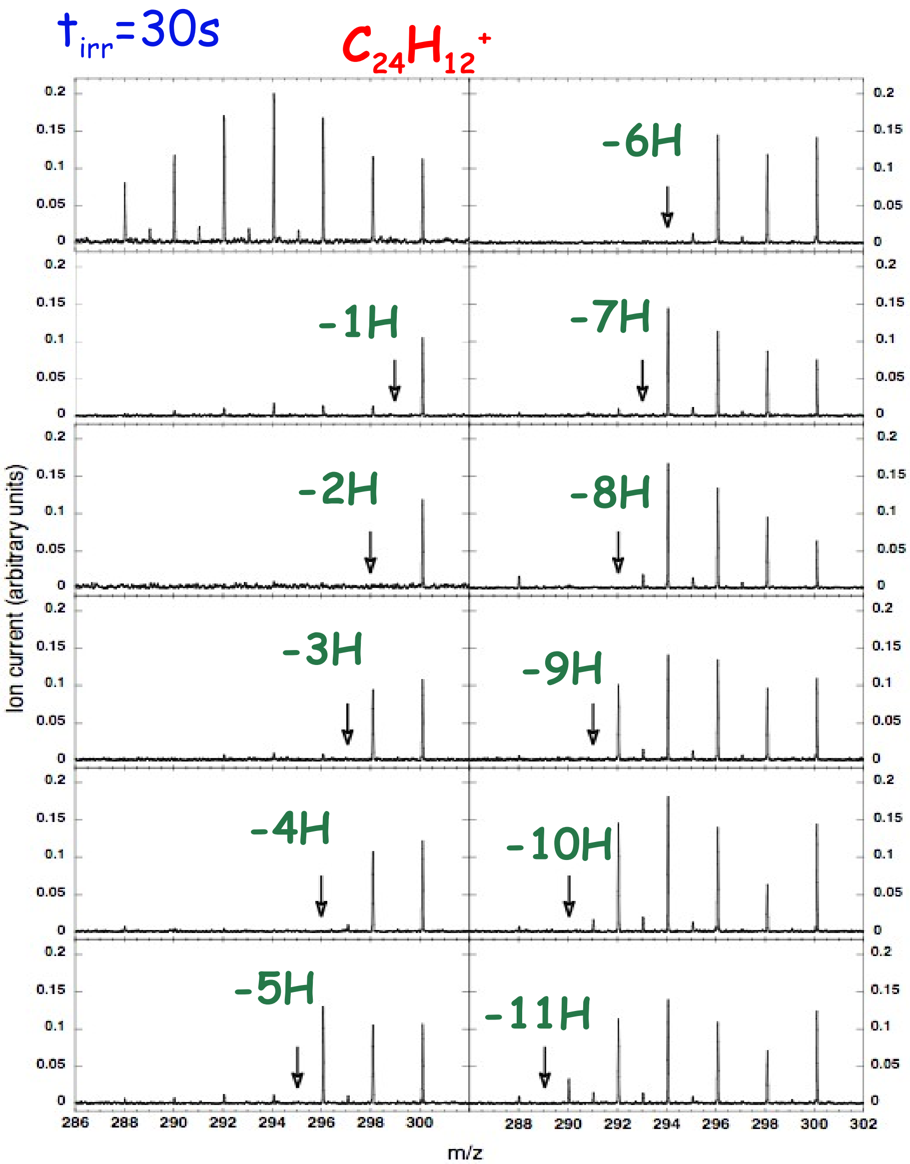
The PIRENEA set-up for astrochemistry FTICR-MS with cold cell

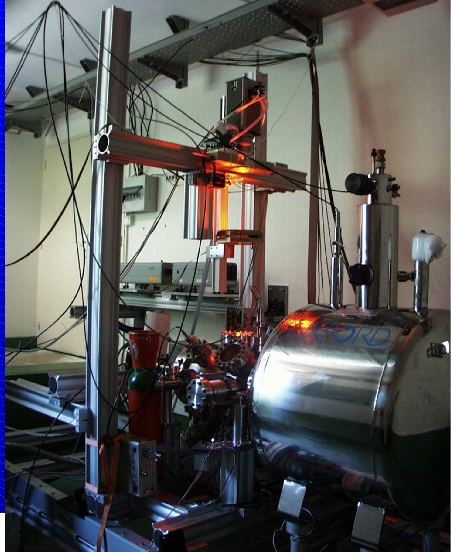
C. Joblin, M. Armengaud, P. Frabel, C. Pech, P. Boissel

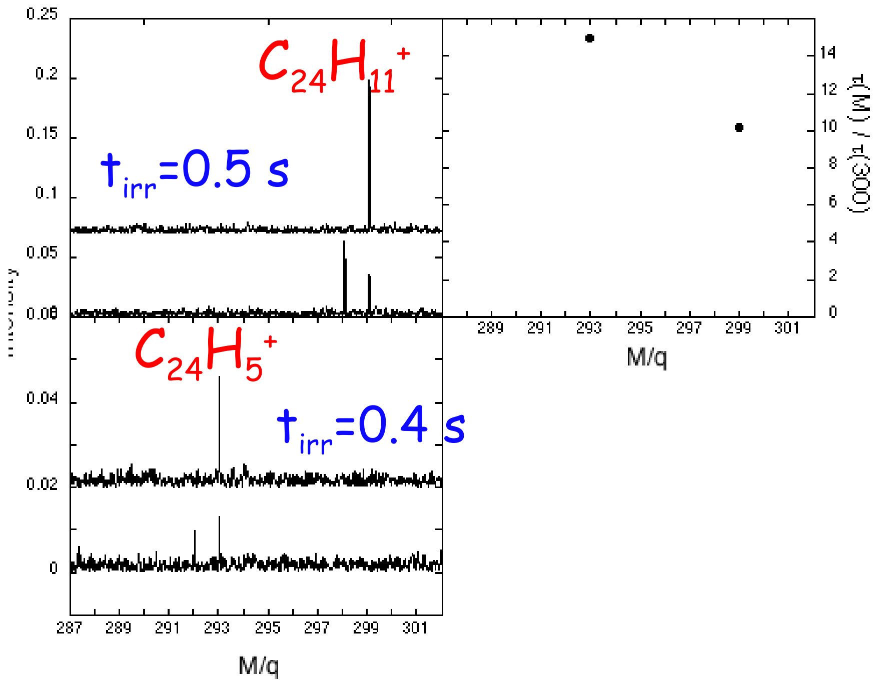
P ~ 10^{-11} mbar
T=35 K



Gas injection
Laser irradiation (MPD)



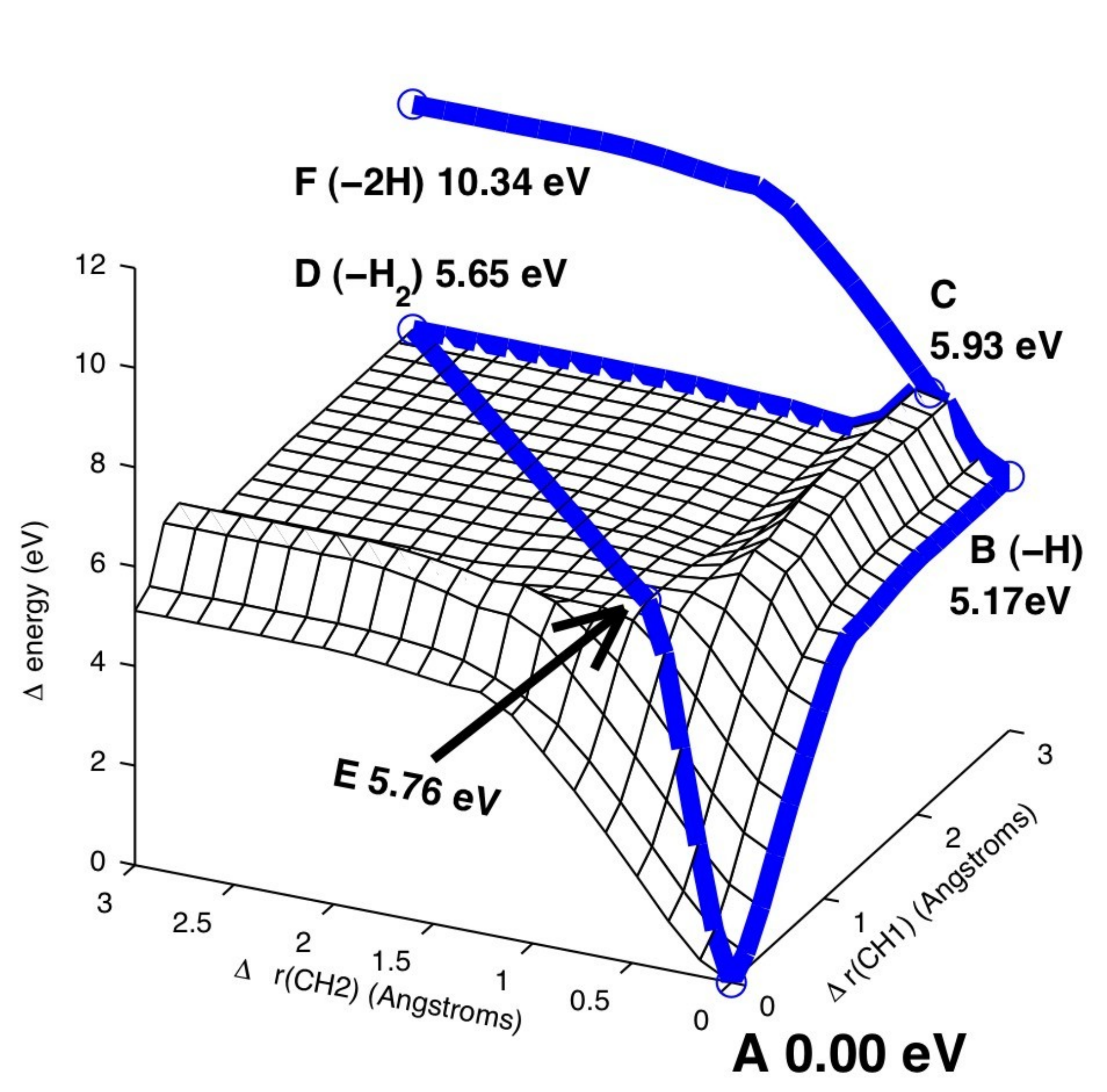


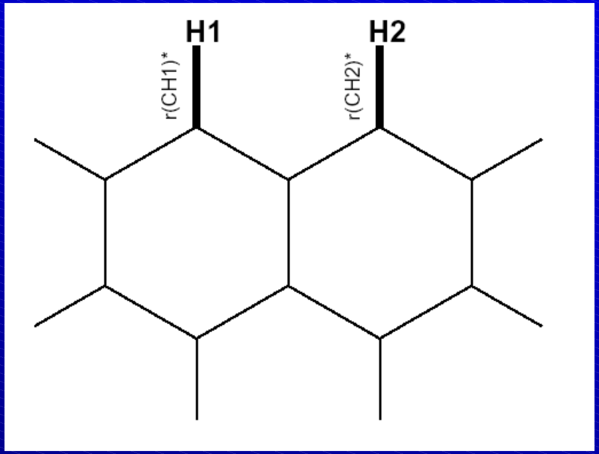


$C_{24}H_{12}^+ \rightarrow C_{24}H_{11}^+ \rightarrow ....C_{24}^+$
by successive H losses

Dissociation kinetics of $C_{24}H_{2p+1}^+$
~10 times faster than $C_{24}H_{2p}^+$

Photodissociation of PAHs / theory





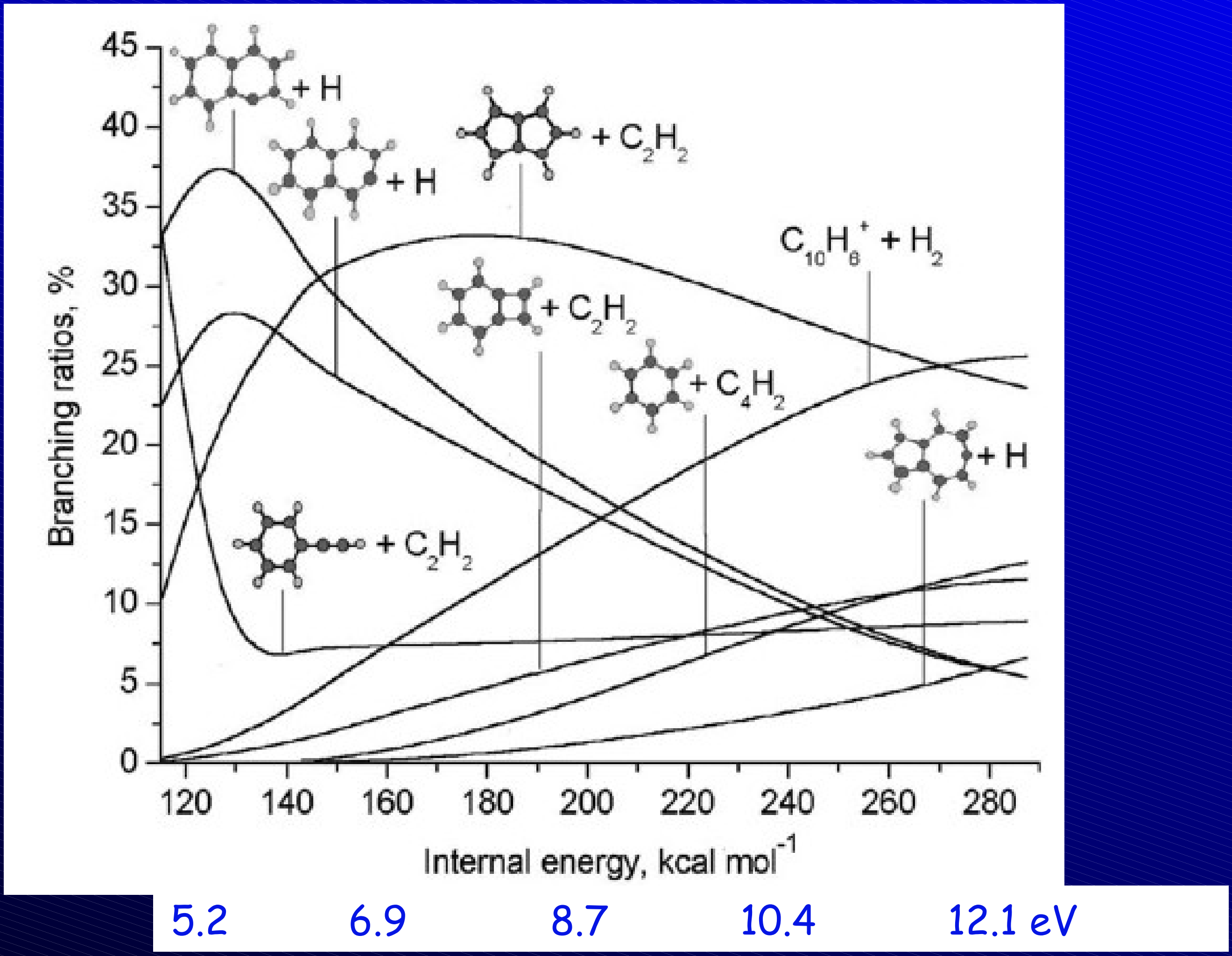
DFT calculations
/ B3LYP/6-31G**

Jolibois et al. 2005, A&A, 444, 629

PST model + DFT
Dissociation rate - E_d=4.8 eV

Pino et al., 2007, J. Phys. Chem. A

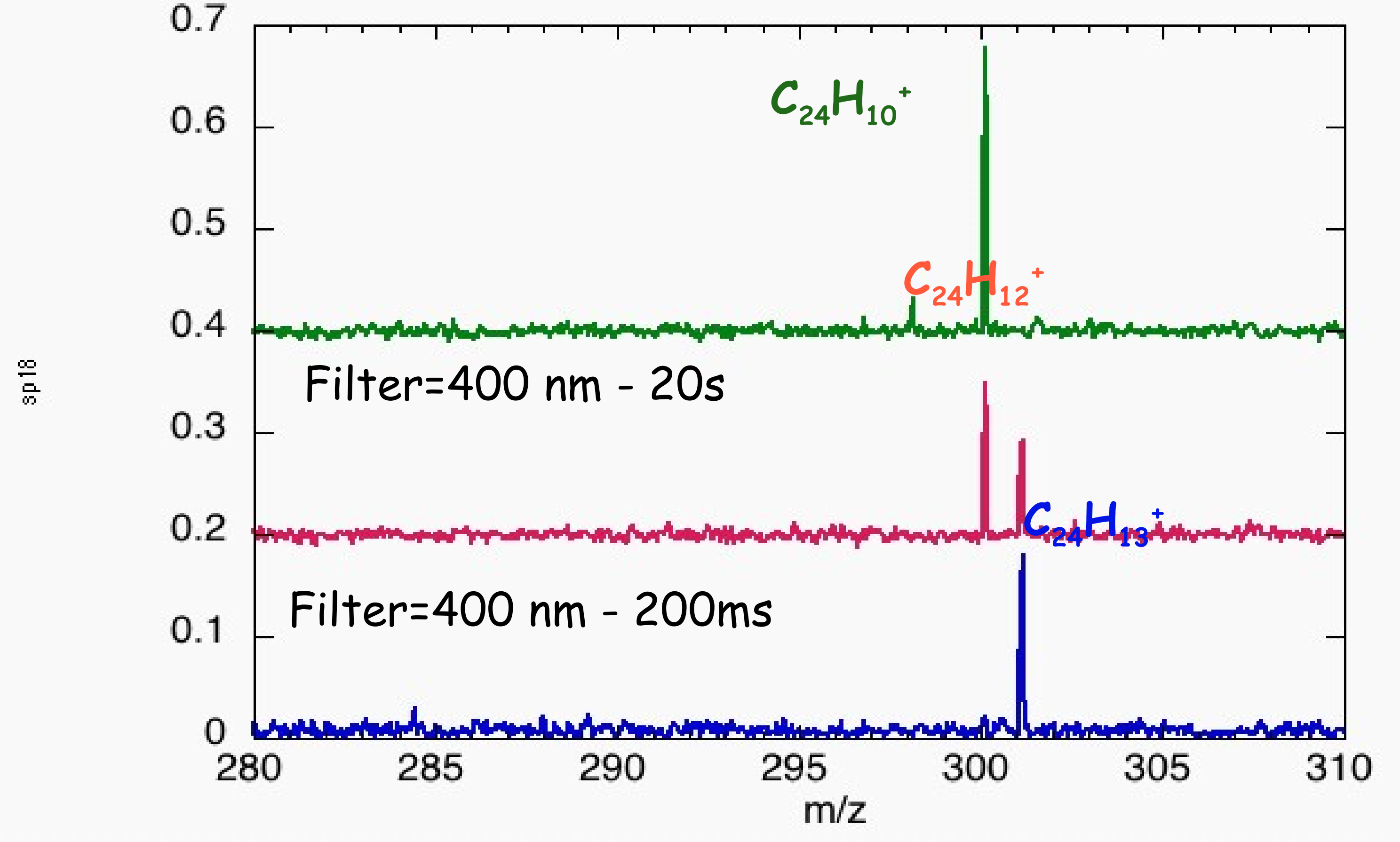
Theoretical study - dissociation of $C_{10}H_8^+$

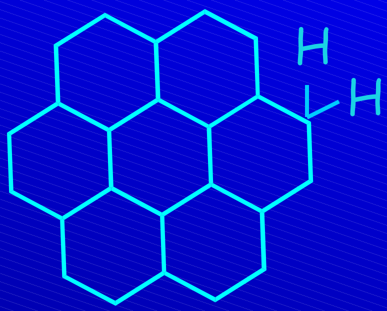


Dyakov et al. 2006, PCCP 8, 1404

In PDRs (hν ≤ 13.6 eV), higher-energy dissociation channels are efficient only for small PAHs

Low-energy dissociation channel of PAHs : -H





$C_{24}H_{11}$-H

E_d=4.5 eV

$C_{16}H_{10}$-H

E_d=1.5 eV

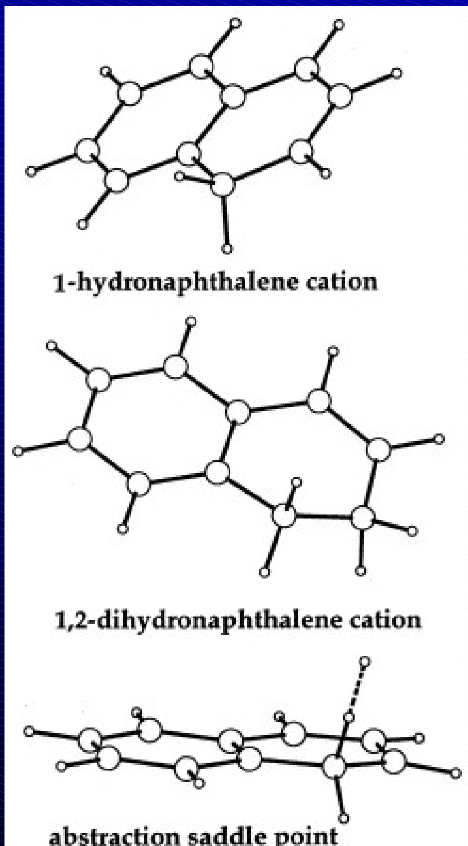
May et al. 2000, PCCP 2, 5089

Still to be studied, irradiation of $[PAH-H]^+$ with H atoms

Bauschlicher 1998, ApJ 509,L125

Formation of H_2 mediated by PAHs

Bauschlicher 1998, ApJ 509, L125



Eley-Rideal abstraction
DFT calculations

New results on $C_{24}H_{12}$
Rauls & Hornekaer 2008, ApJ 679, 531

+ preliminary lab. results
talk L. Hornekaer

Need for molecular dynamics simulations

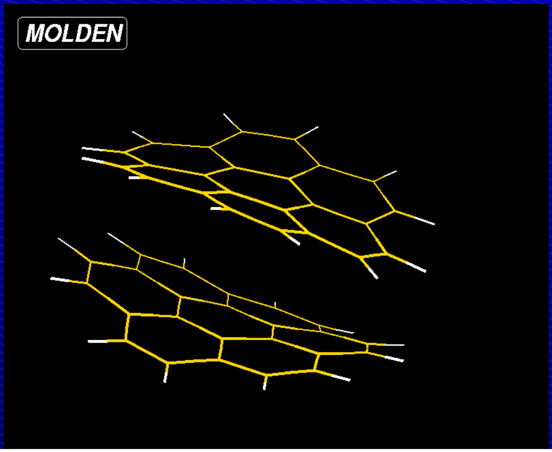
Experimental studies ****soon : installation of an H source on PIRENEA****

TABLE 1
SUMMARY OF THE B3LYP/4-31G RESULTS (IN UNITS OF kcal mol^{-1})

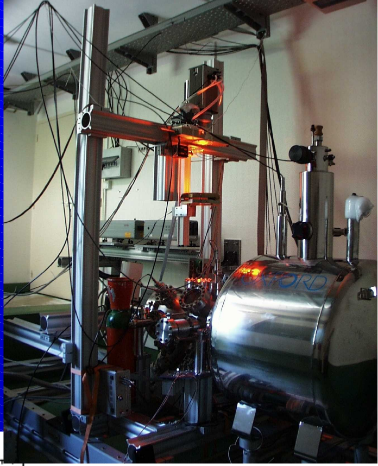
Reaction	Value
Bond Energies	
(*a*) $C_6H_6 \rightarrow C_6H_5 + H$	110.3[a]
(*b*) $C_{10}H_8^+ \rightarrow C_{10}H_7^+ + H$	111.93
(*c*) $C_{10}H_7D^+ \rightarrow C_{10}H_7^+ + D$	113.93
(*d*) $C_{10}H_9^+ \rightarrow C_{10}H_8^+ + H$	62.09
(*e*) $C_{10}H_8D^+ \rightarrow C_{10}H_8^+ + D$	64.00
(*f*) $C_6H_7^+ \rightarrow C_6H_6^+ + H$	75.88
(*g*) $C_{10}H_{10}^+ \rightarrow C_{10}H_9^+ + H$	45.81
(*h*) $H_2 \rightarrow H + H$	103.67[b]
(*i*) $C_{10}H_9 \rightarrow C_{10}H_8 + H$	29.45
(*j*) $C_{10}H_{10} \rightarrow C_{10}H_9 + H$	73.96
Barrier Heights[c]	
(1) $C_{10}H_9^+ + H \rightarrow C_{10}H_8^+ + H_2$	−0.25
(2) $C_{10}H_8D^+ + H \rightarrow C_{10}H_8^+ + HD$	−0.66
(3) $C_{10}H_8D^+ + H \rightarrow C_{10}H_7D^+ + H_2$	−0.20
(4) $C_{10}H_9^+ + D \rightarrow C_{10}H_8^+ + HD$	−0.002
(5) $C_6H_7^+ + H \rightarrow C_6H_6^+ + H_2$	0.52
(6) $C_6H_6D^+ + H \rightarrow C_6H_6^+ + HD$	−0.11
(7) $C_6H_6D^+ + H \rightarrow C_6H_5D^+ + H_2$	0.35
(8) $C_6H_7^+ + D \rightarrow C_6H_6^+ + HD$	0.73

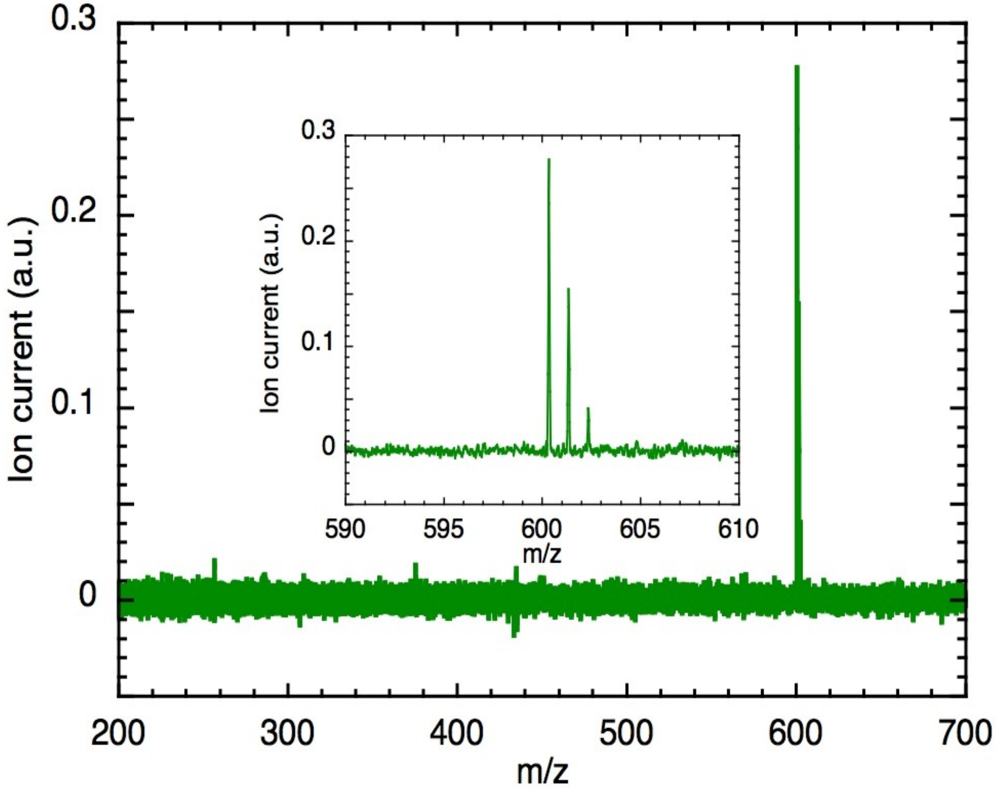
[a] The experimental values are 109.8 (Lias et al. 1988) and 109.4 kcal mol^{-1} (McMillen & Golden 1982).
[b] The experimental value is 103.268 kcal mol^{-1} (Huber & Herzberg 1979).
[c] A negative barrier height indicates that the barrier is below the energy of the reactants.

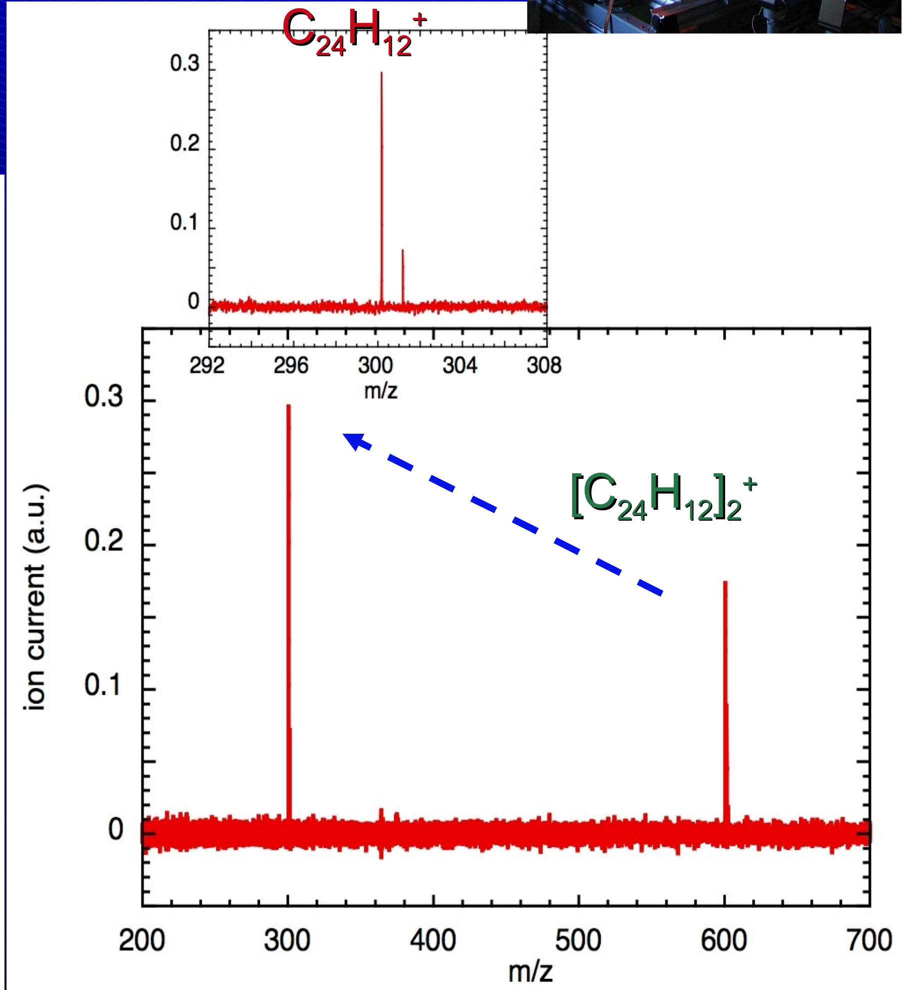
Photodissociation of $[PAH]_n^+$ in PIRENEA



Heating by UV-visible radiation
(multiple photons)







Candidates for evaporating VSGs
Pure $[PAH]_n^+$ vs the depletion of (heavy) elements

- proposal that Fe can easily form complexes with PAH in the 1990s
  Serra et al. 1992, A&A 260, 489

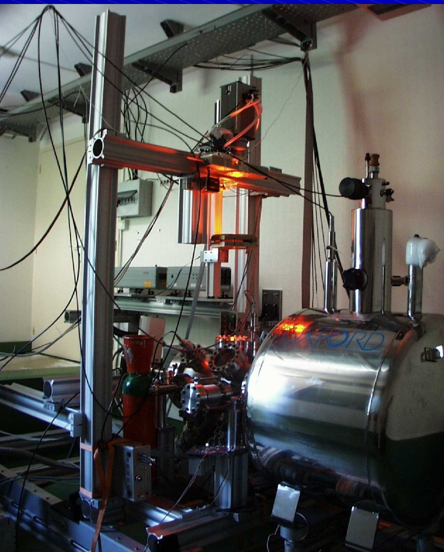
- other "metals" such as Si can be involved *Klotz et al. 1995, A&A 304, 520*

- easy formation of **$[SiPAH]^+$** , **$[FePAH]^+$**, **$[FePAH_2]^+$** by radiative association
  Dunbar et al, 1994, JACS 116, 2466 ; Pozniak & Dunbar 1997, JACS 119, 10439

- signatures of **$[SiPAH]^+$** π complexes in astronomical spectra
  Joalland et al. 2008, A&A

- **$[Fe_xPAH_y]^+$** candidates for evaporating VSGs
  Simon & Joblin 2008, subm.

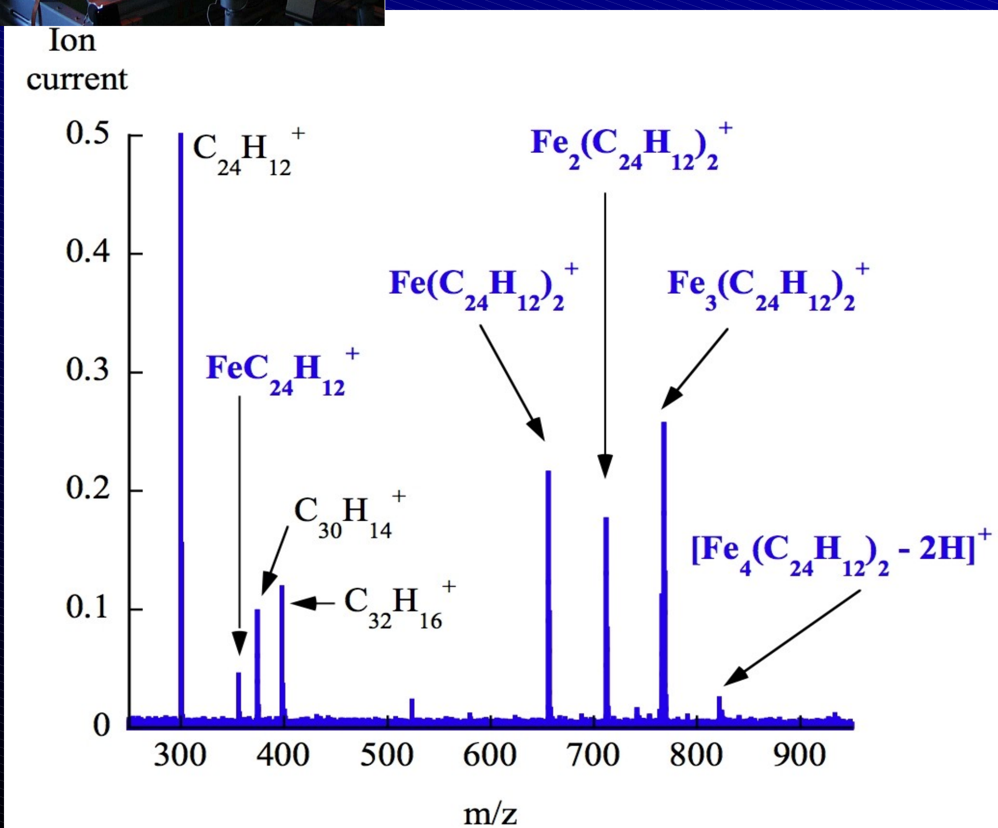
Photodissociation of $[Fe_mPAH_n]^+$
New analogues for evaporating VSGs

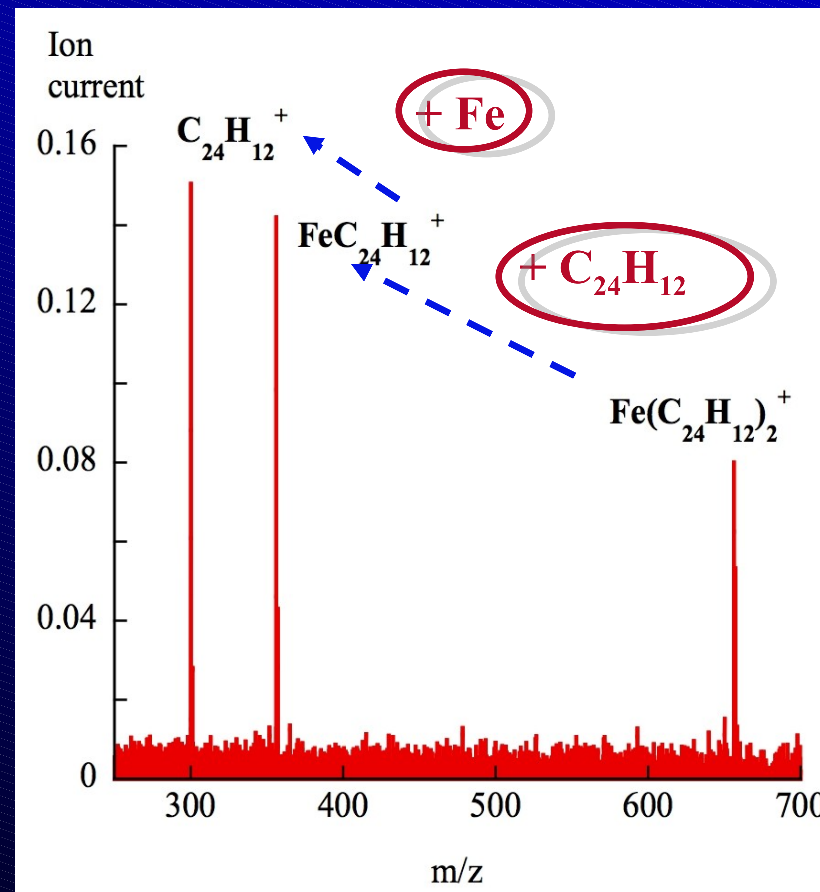


Simon & Joblin, 2008, subm.

- Contrary to Si, Fe can form $[FePAH_2]^+$ complexes
Dunbar et al, 1994, JACS 116, 2466

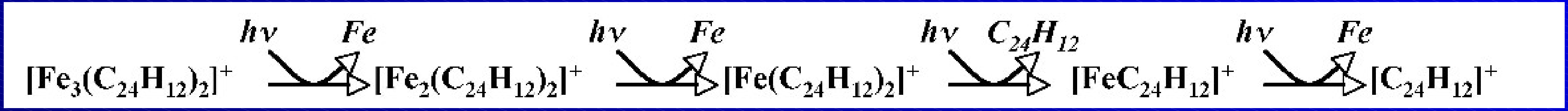
- Formation of $[Fe_xPAH_2]^+$. Heating by UV-visible radiation





Photodissociation of $[Fe_mPAH_n]^+$

Simon & Joblin, 2008, subm.



- $[Fe_x(C_{24}H_{12})_2]^+$ (x=1-3) dissociate by sequential loss of Fe and $C_{24}H_{12}$ units

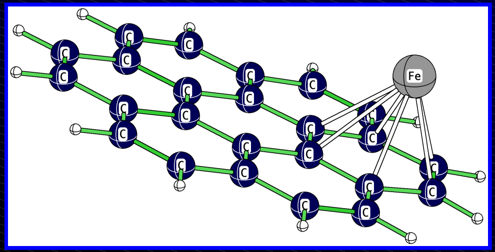
- Gas-phase Fe more tightly bound than Si :

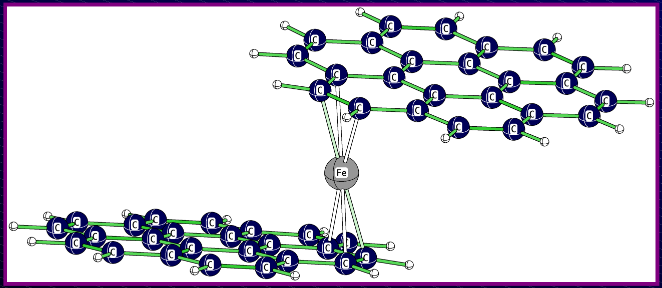
E_b(Fe-PAH)=2.6 eV vs E_b(Si-PAH)=1.5 eV

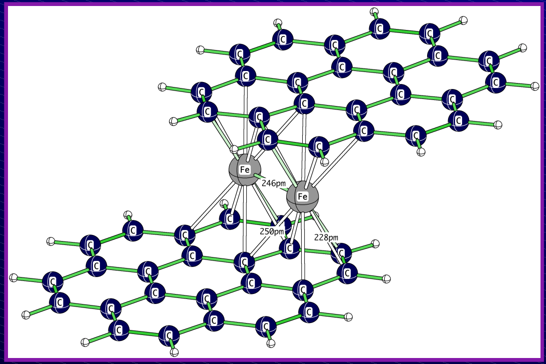
➔ could contribute to the highest depletion of Fe relative to Si in the diffuse ISM

- How much Fe could be included in such grains?

Some destruction in PDRs, more in HII regions. Abundance of Fe released from grain destruction ~5% . Would imply 2 Fe per PAH assuming **[PAH]/[H]=7 10^{-7}**







Current status: PAHs, VSGs and H_2 formation

- Based on observational and laboratory results, free PAHs are not attractive candidates to account for the formation of H_2 in PDRs
  - ***Still some work to do to study if H_2 could be formed by irradiation of hydrogenated PAHs with H atoms (Eley-Rideal abstraction mechanism)***
  - ***Physisorption of H_2 on PAHs***

    E_{phys} of H_2 on PAHs 5.2 kJ mol^{-1} (0.05 eV) – Trans et al. 2002, J. Phys. Chem. B 106, 8689 - This workshop : Ellinger & Pauzat

    3.5 and 7.2 kJ mol^{-1} (0.035-0.07 eV) – Heine et al. 2004, PCCP 6, 980

- Search for candidates for evaporating C-VSGs
  - ***Clusters containing PAH, Si and Fe are candidates for evaporating VSGs***
  - ***New catalytic chemistry (H_2 formation,...)?***
  - ***Trapping possibilities: porosities, active site (Fe) → higher binding energies***

    Ex : organometallic complexes made of fullerenes and transition metals are good candidates for H_2 trapping (max H_2 storage up to 9 wt %)

    Zhao et al. 2005, PRL 94, 155504

Thanks

- A. Simon (CESR), B. Joalland (CESR)
- O. Berne (CESR)
- Technical team of PIRENEA : M. Armengaud, A. Bonnamy, P. Frabel, L. Nogues

- CNRS / Programme National Physique et Chimie du Milieu Interstellaire

Formation H_2 /excitation (Théorie - D. Lemoine- LCAR)

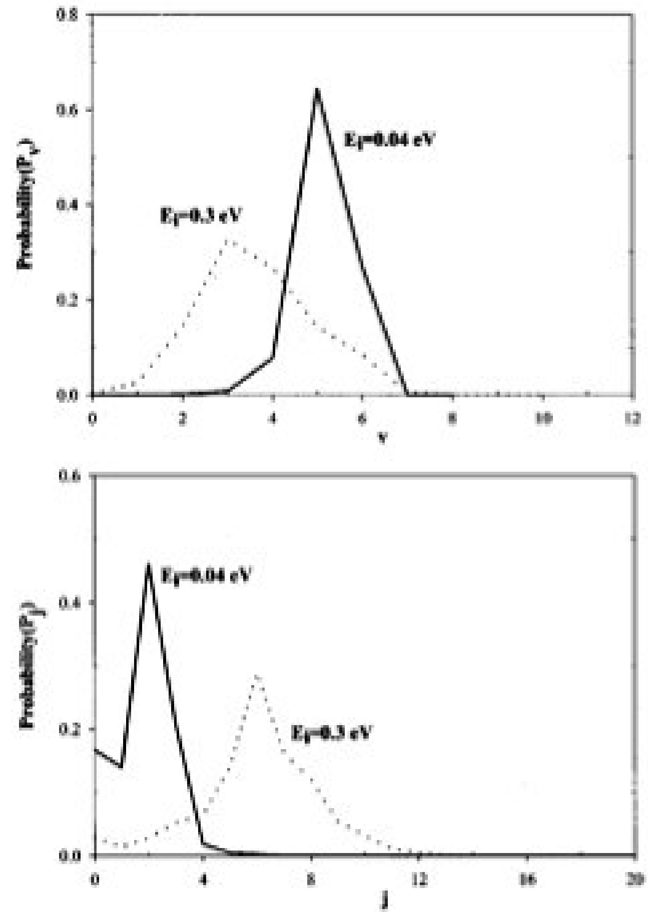


FIG. 7. Product H_2 vibrational (P_v) and rotational (P_j) distributions, for two incident energies, 0.04 eV and 0.3 eV, for the chemisorbed-H, rigid-puckered lattice case.

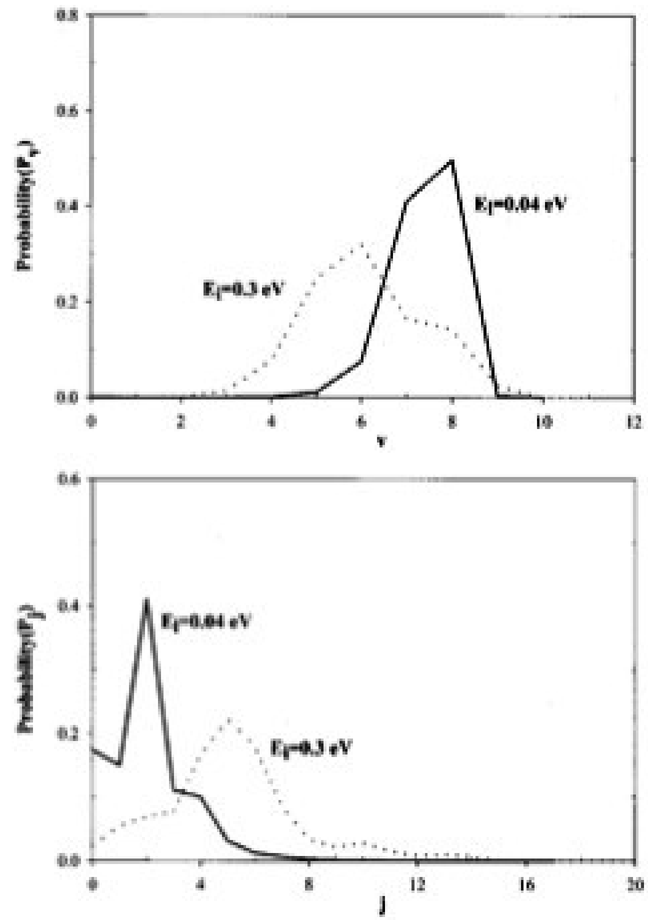


FIG. 9. Same as Fig. 7, but for the chemisorbed-H, relaxed-surface case.

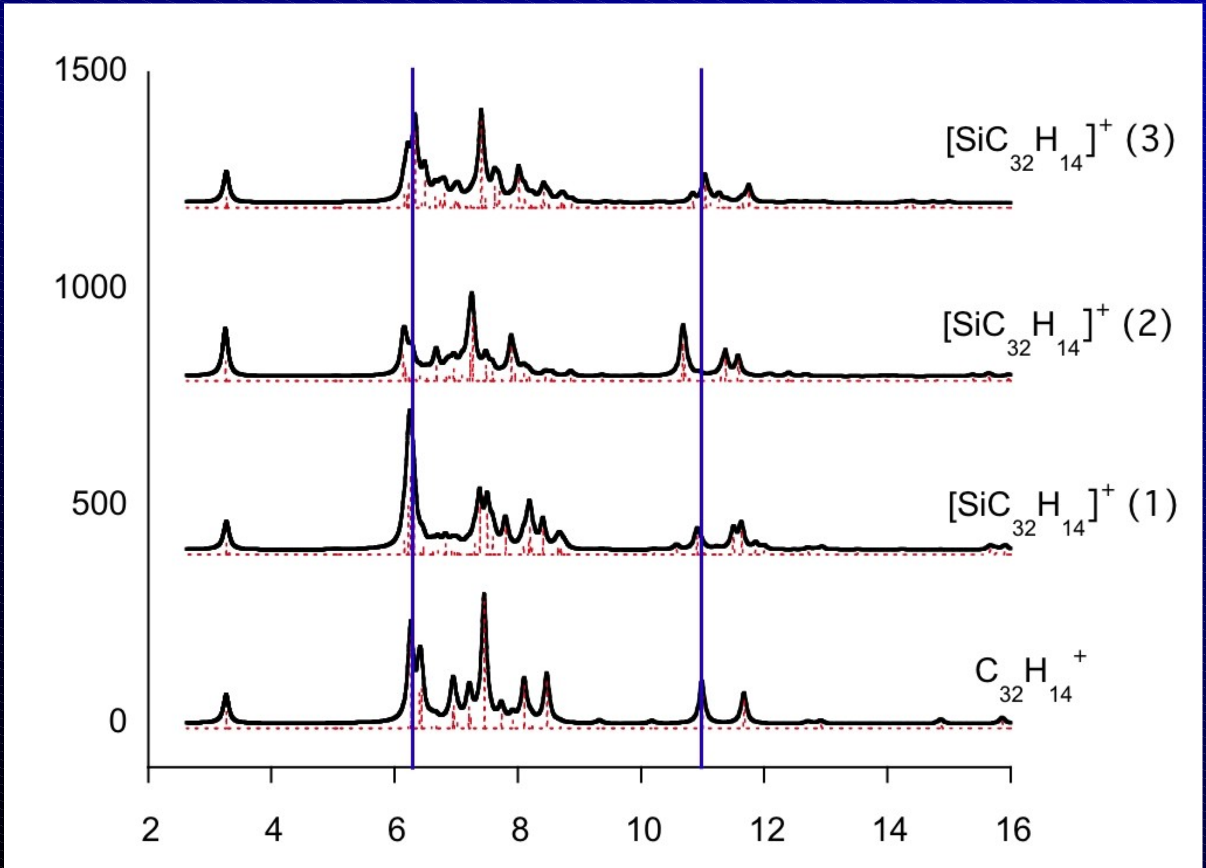
Sha, Jackson, Lemoine, 2002, J. Chem. Phys. 116 (16), 7158

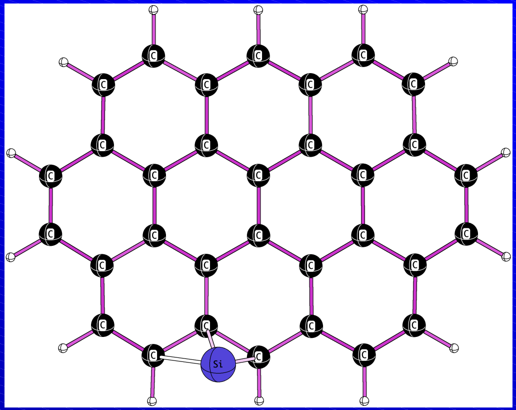
New analogues for interstellar PAHs
Signatures of $[SiPAH]^+$ π-complexes

DFT calculations

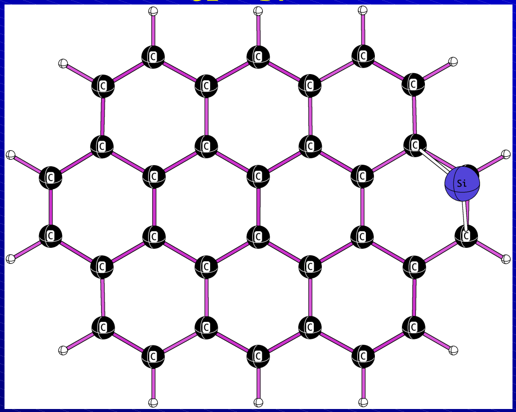
Joalland et al. 2008, A&A, subm.

➔Fingerprints: expected blueshift for the 6.2 and 11.2 μm bands (Δλ~0.2 μm)

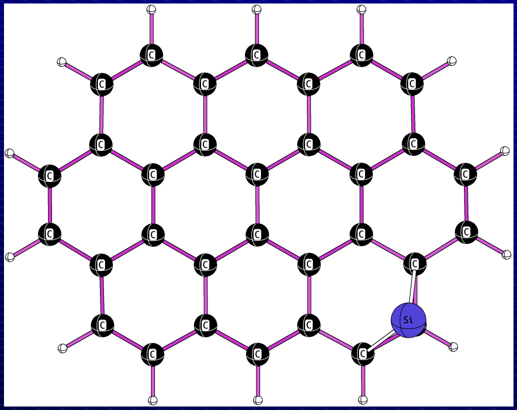




$[SiC_{32}H_{14}]^+$ (1)



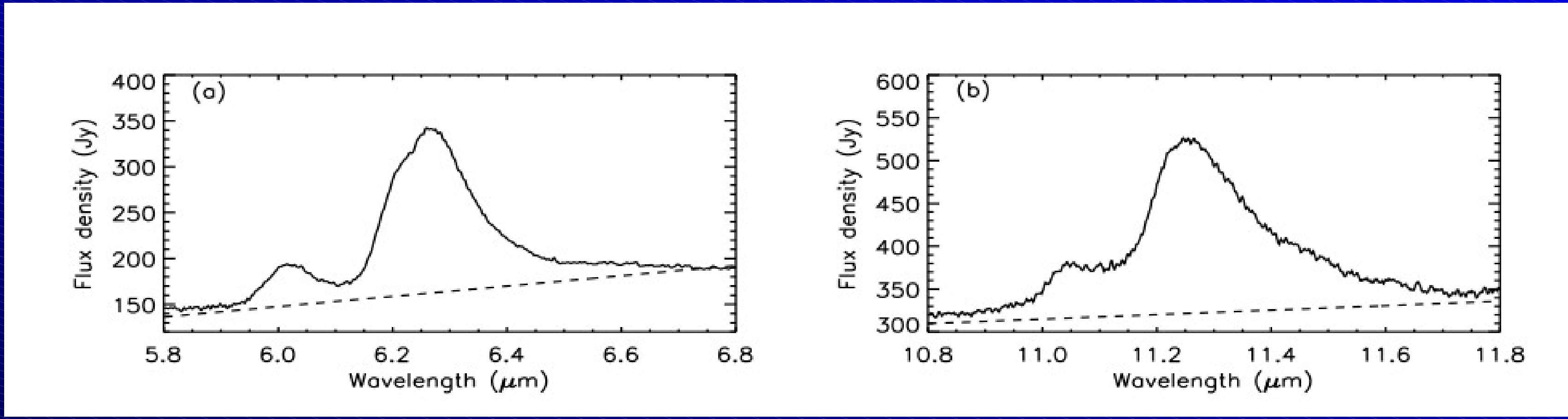
$[SiC_{32}H_{14}]^+$ (2)



$[SiC_{32}H_{14}]^+$ (3)

Signatures of [SiPAH]$^+$ π-complexes

Joalland et al. 2008, A&A, subm.



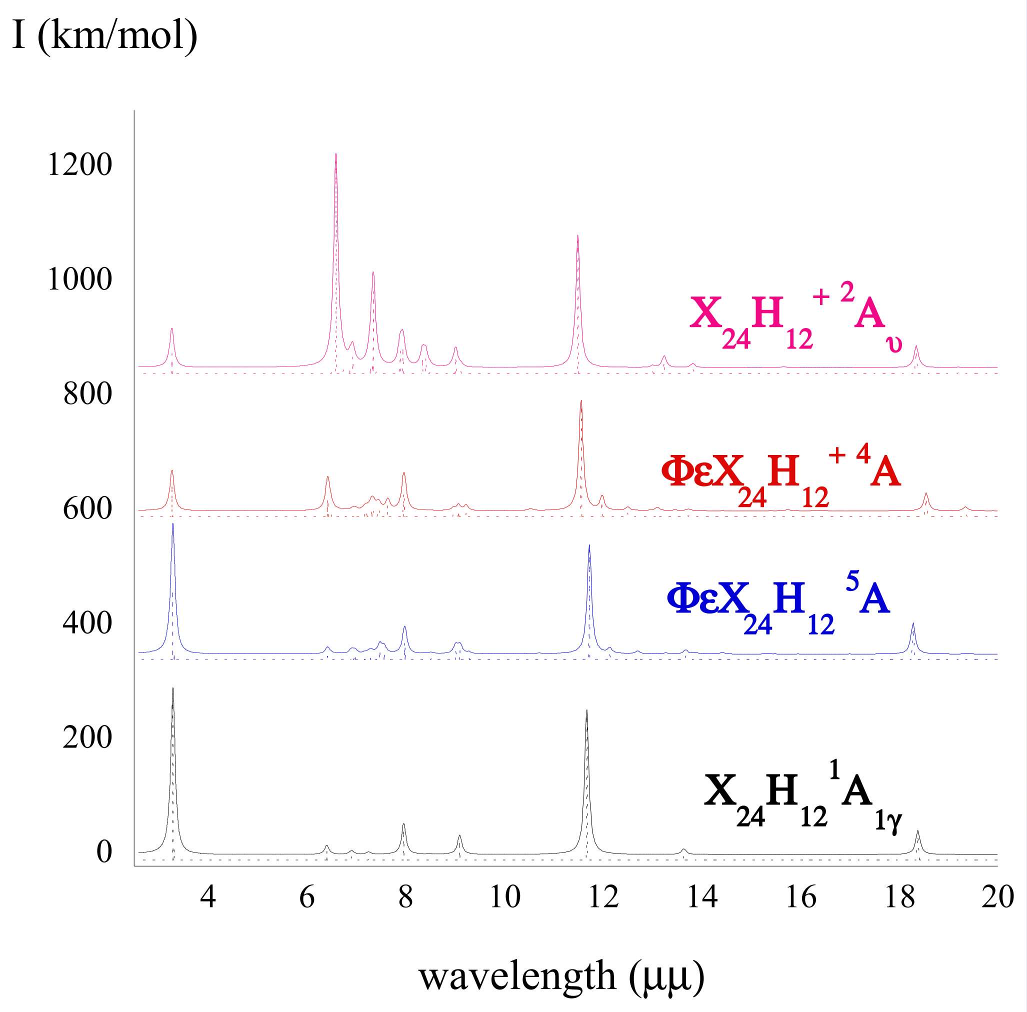
- Proposed signatures for [SiPAH]$^+$: - the 11.0 μm sideband
  - blue wing of the 6.2μm and/or the 6.0 μm sideband

- >10% of the PAH population (based on the IR band ratios at 11μm)
  ➔ >4% of gas-phase Si in the Red Rectangle **[PAH]/[H]=7 10^{-7}**

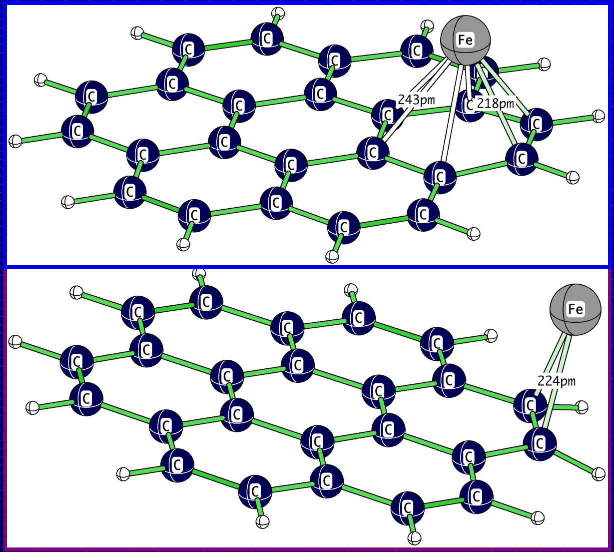
What about Fe ?

Signatures of $[FePAH]^+$ complexes

Simon & Joblin, 2007, JPCA 111, 9745. Simon et al. 2008, JPCA



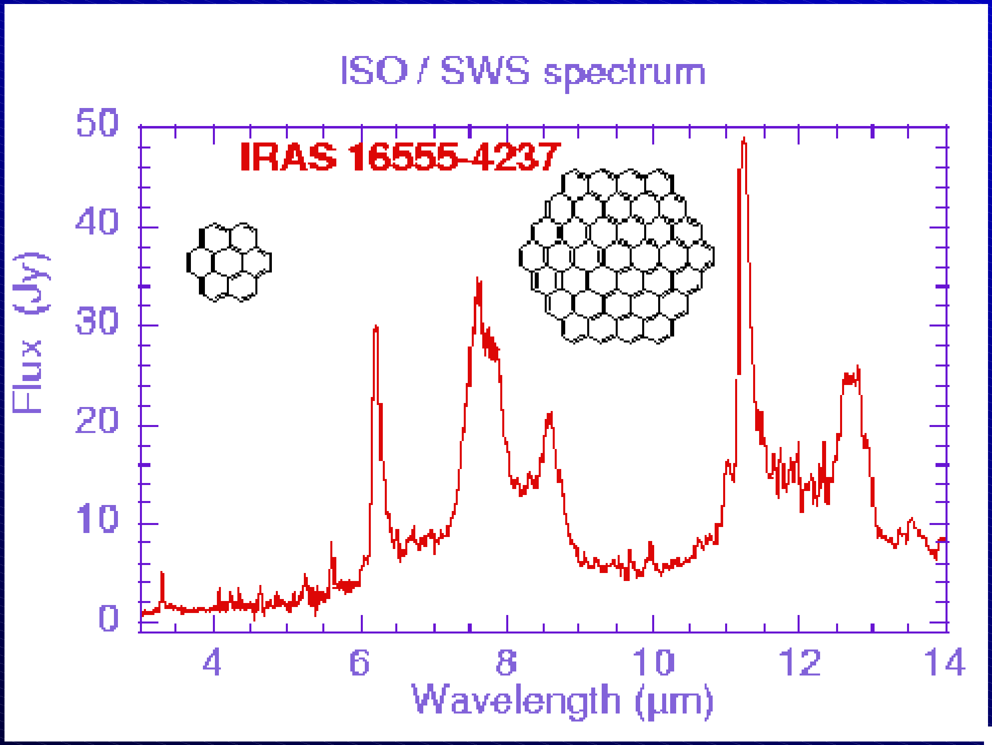
Main effect on PAH^+ spectrum: decrease of the intensities in the [6-10] μm range



IR absorption spectra calculated with DFT at the MPW1PW91/6-31+G(d,p) level of theory

BUT: no obvious signatures to identify $[FePAH]^+$ species

Aromatic IR bands / polycyclic aromatic hydrocarbons (PAH)



- Stochastic heating

N~50 ; T~1000 K

Sellgren (1984), ApJ 277, 623

- Candidates: PAH molecules

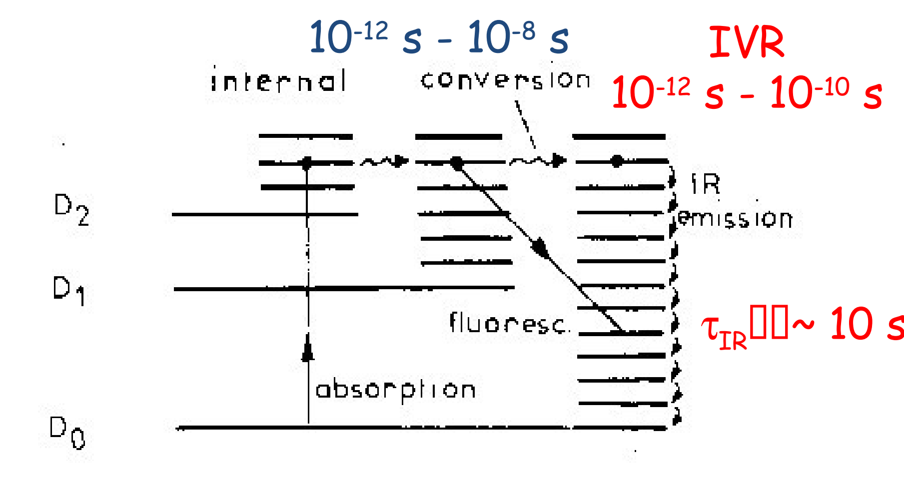
Léger & Puget 1984, A&A 137, L5
Allamandola, Tielens & Barker 1985, ApJ 290, L25

- 10 to 20% of total carbon

X_{PAH}~ 10^{-7} (N_C~50)

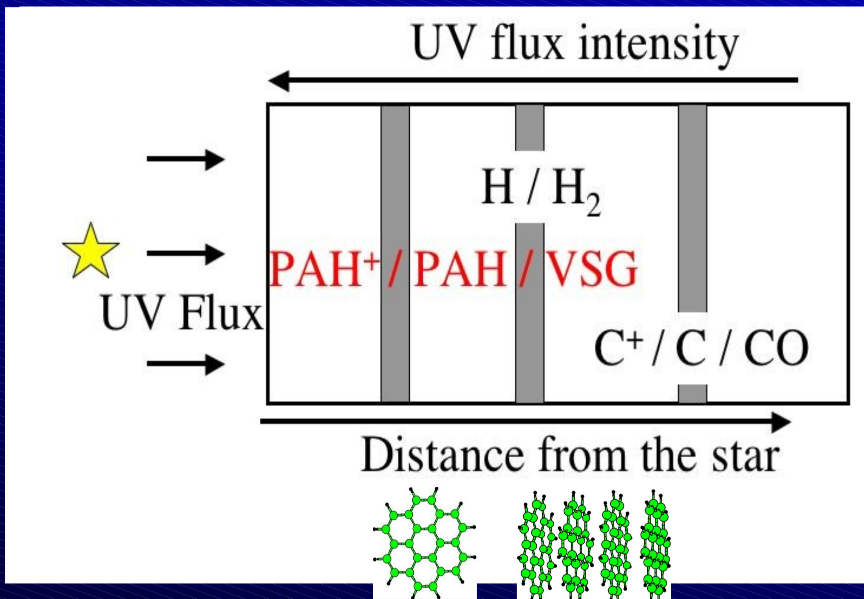
3.3 µm (3050 cm^{-1}); 6.2 µm (1610 cm^{-1});
" 7.7 " µm (1300 cm^{-1}); 8.6 µm (1160 cm^{-1});
11.3 µm (890 cm^{-1}); 12.7 µm (785 cm^{-1})

CH and CC aromatic modes

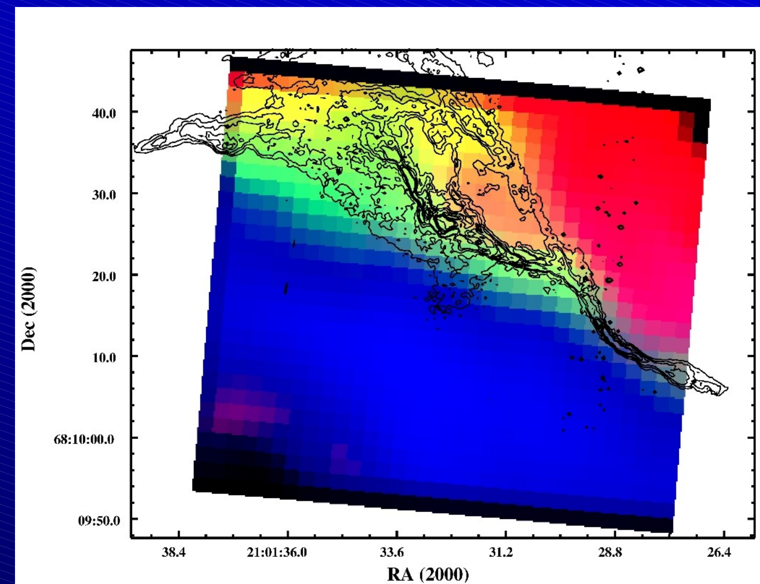


[PAH_n] a model for VSGs

Rapacioli, Joblin, Boissel, 2005, A&A 429, 193



Berné et al., 2008, A&A 479, L41



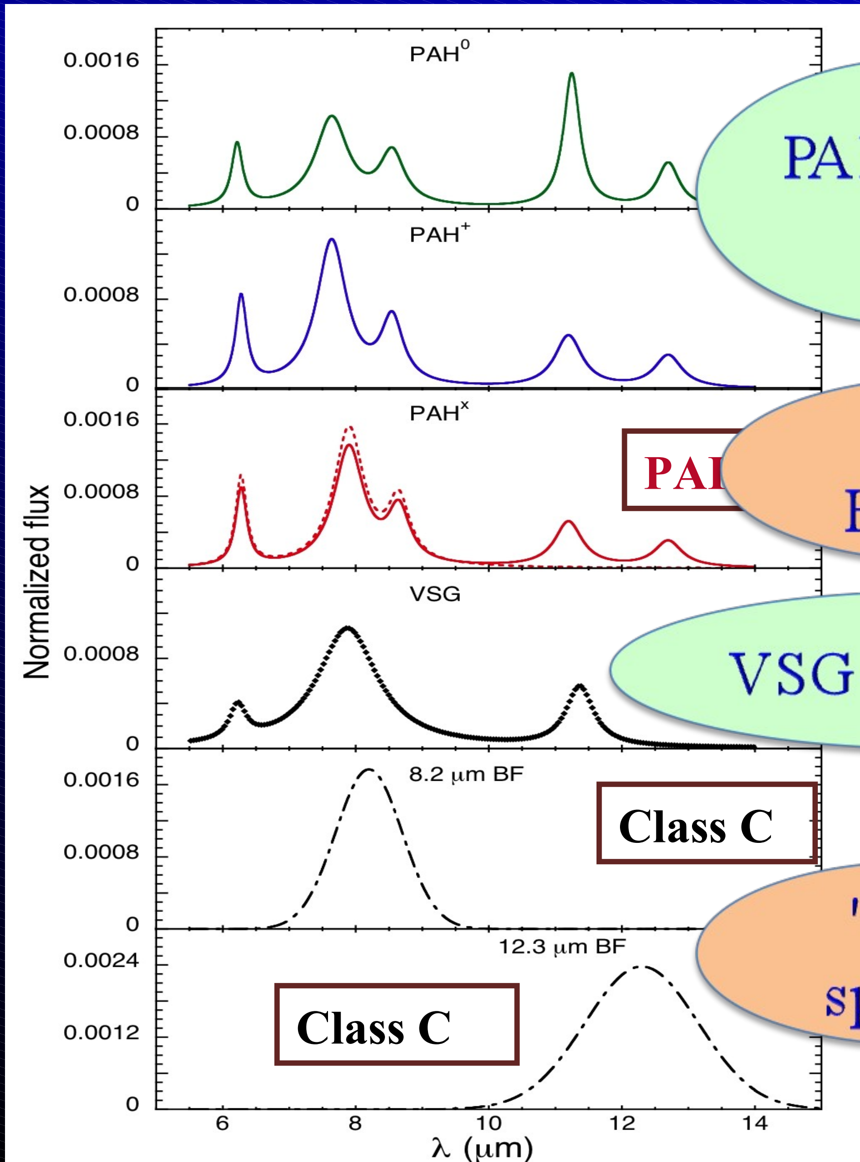
- Spatial correlation between Extended Red Emission (600-800 nm) and the transition VSG/PAH or PAH/VSG

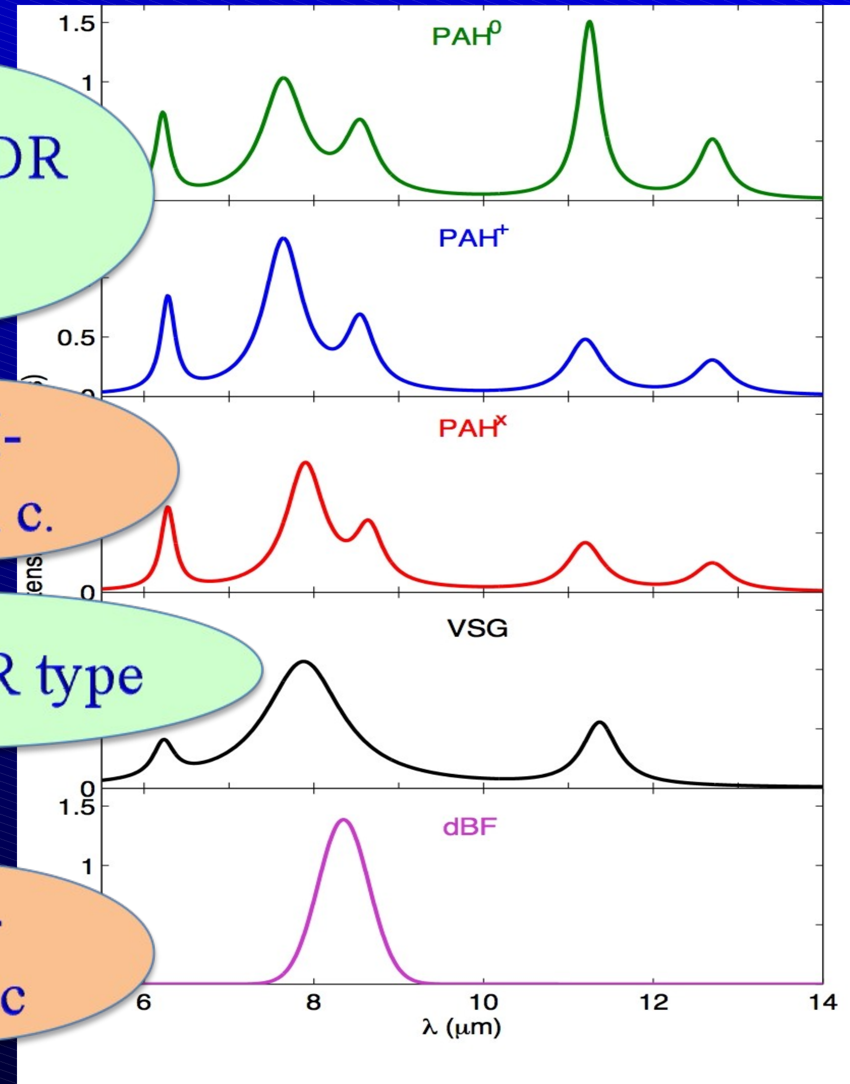
- Spectroscopy : PAH dimers (closed-shell cation dimers) as good candidates for ERE *Rhee et al., 2007, PNAS 104, 5274*

Photoprocessing of AIB carriers – high excitation conditions
Planetary nebulae / Protoplanetary disks

Joblin, Szczerba, Berne, Szyszka, 2008, A&A
http://arxiv.org/abs/0809.1532

Berne et al. 2008, submitted

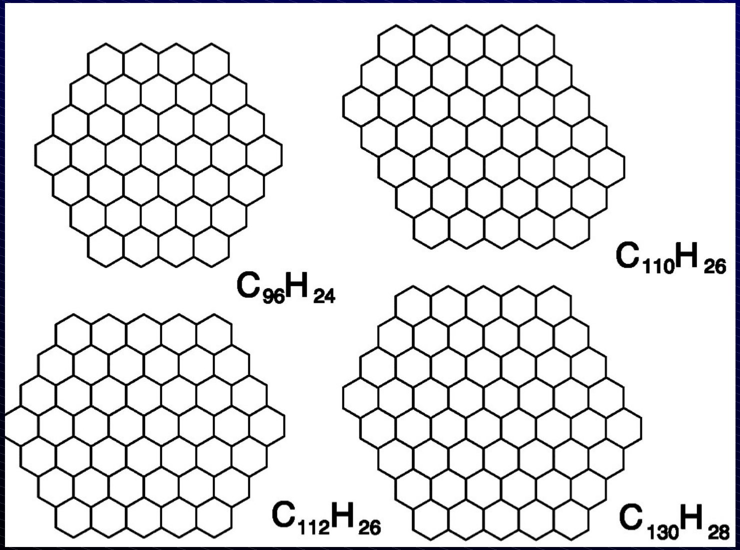


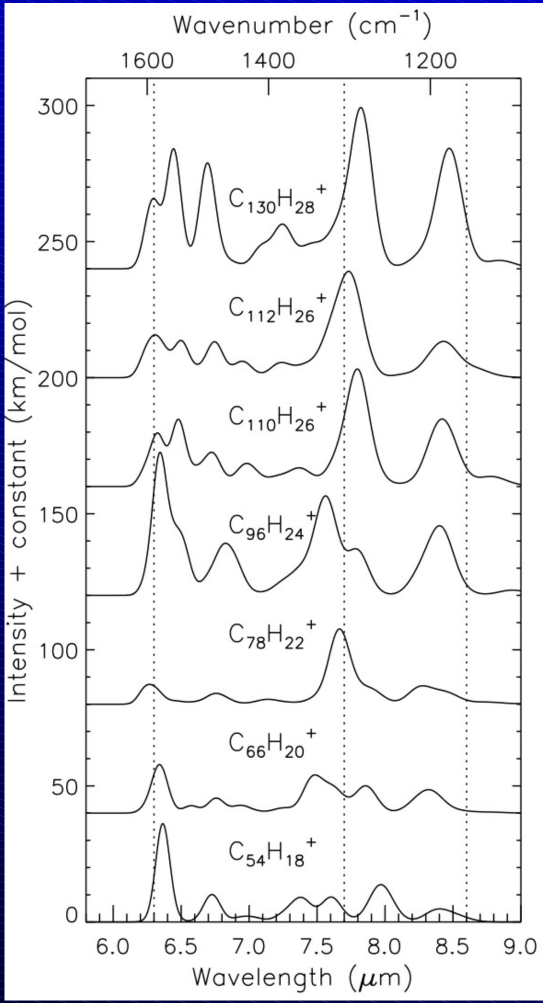


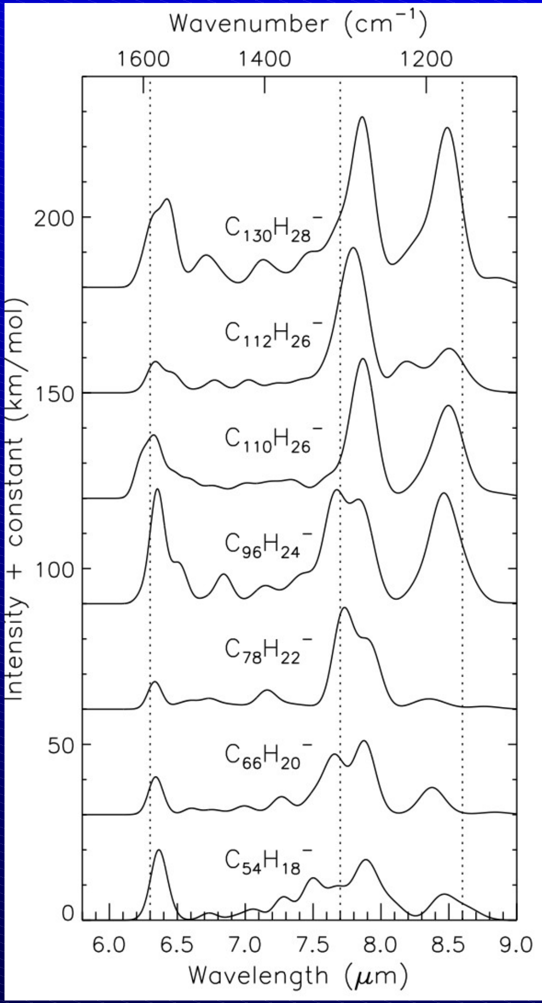
Proposed candidates for PAH^x

- Main spectral feature: 7.6 µm band of PAHs redshifted to 7.9 µm
- IR spectroscopy / DFT calculations ➔ large charged PAHs (cations and anions)

Bauschlicher, Peeters, Allamandola, 2008, ApJ 678, 316)







Formation/ destruction of $[PAH]_n$ clusters in PDRs

Rapacioli, Calvo, Joblin et al. 2006, A&A 460, 519

Formation

$(C_{24}H_{12})_n + C_{24}H_{12} \rightarrow (C_{24}H_{12})_{n+1}$

Molecular dynamics simulations

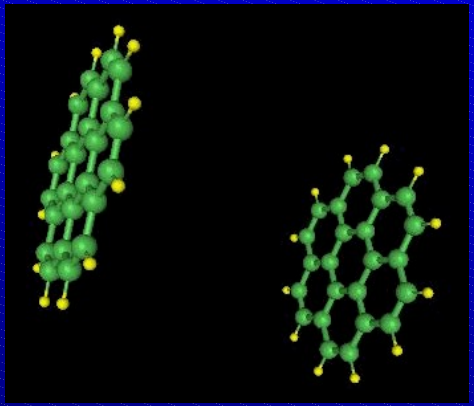


Photo-evaporation

$(C_{24}H_{12})_n + C_{24}H_{12} \leftarrow (C_{24}H_{12})_{n+1}$ hν

$k_{evap}(E_{inter})$

$k_{IR}(E_{intra})$

$(C_{24}H_{12})_{n+1}$

Statistical approach (phase space theory)

Calvo & Parneix, 2003, JPC 120, 6

Rigid molecules ⇒ $k_{evap}(E_{inter})$

Microcanonical approach

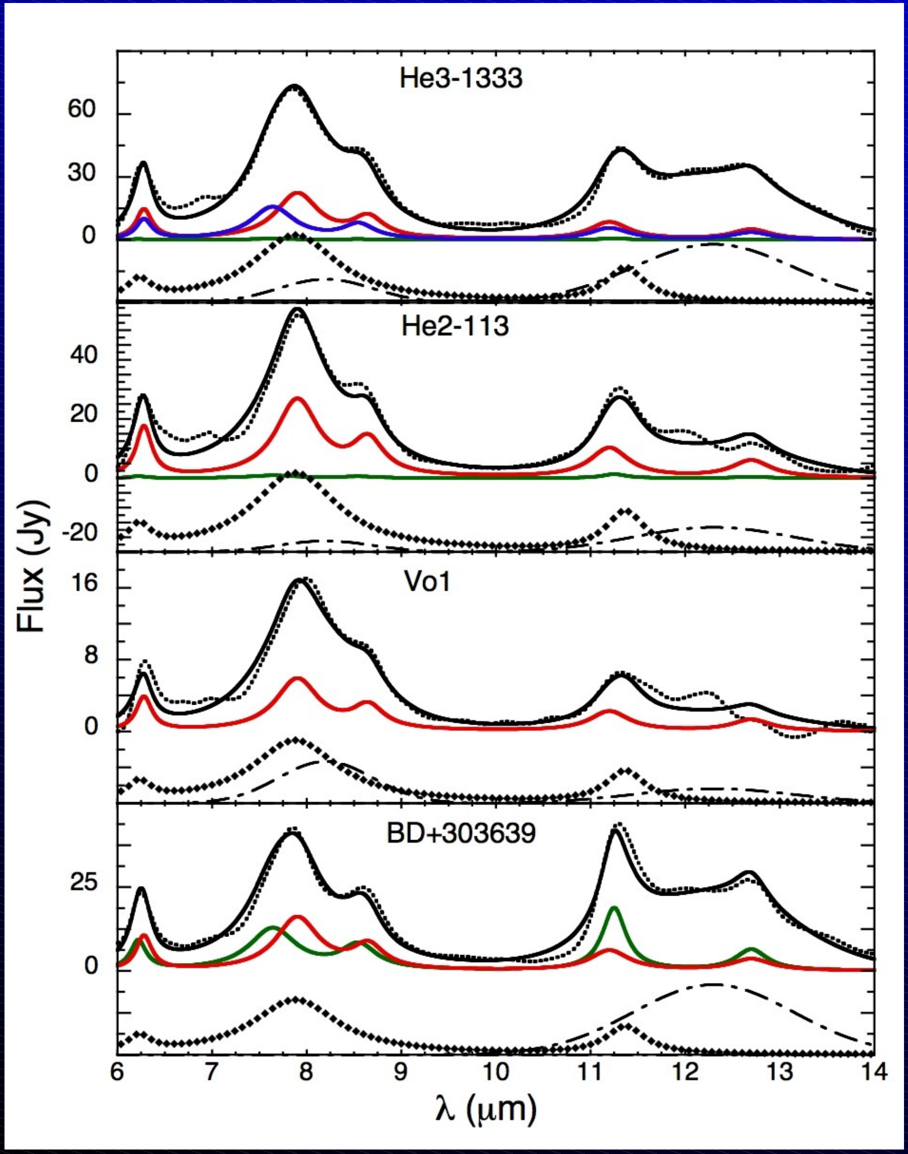
Joblin et al., 2002, Mol. Phys.100 (22), 3595

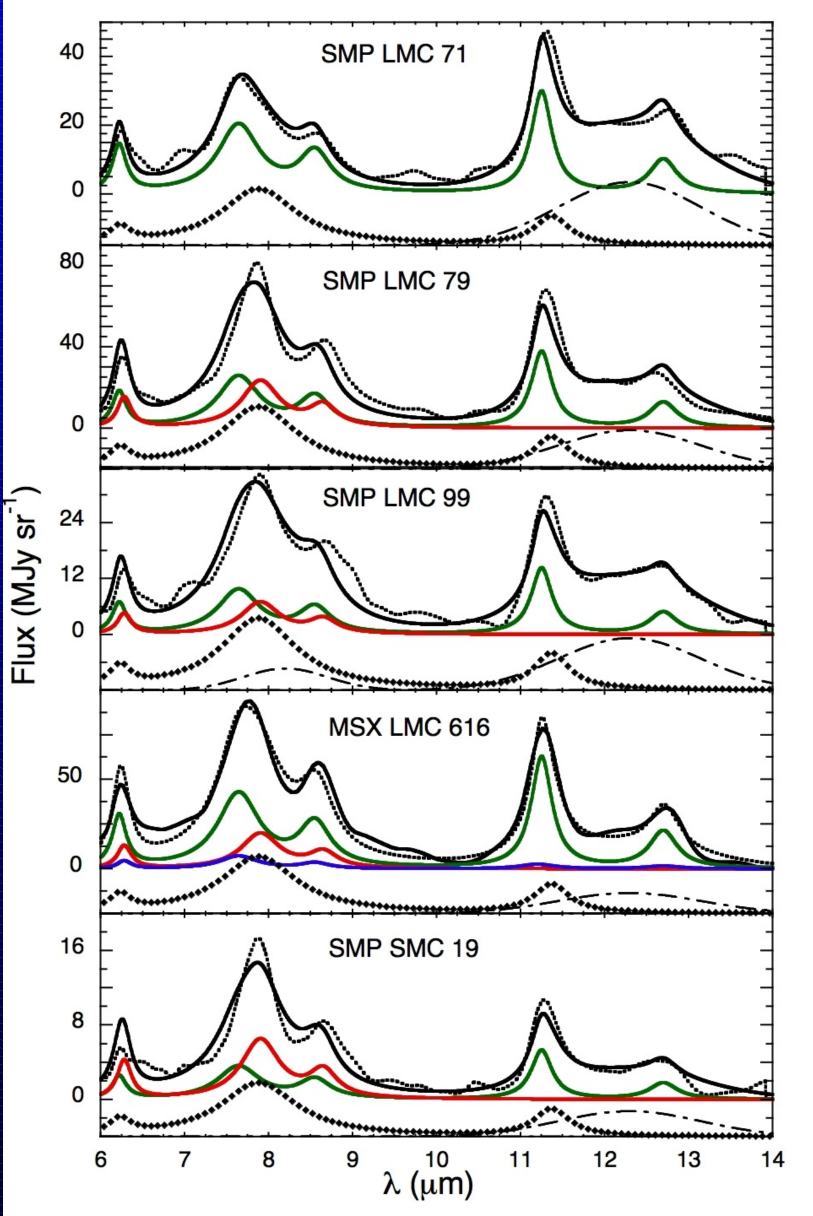
$k_{IR}(E_{intra})$ of isolated molecules

Need for fundamental data

Analysis of the mid-IR spectrum in planetary nebulae

Joblin, Szczerba, Berne, Szyszka, 2008, A&A, in press





Formation/ destruction of $[PAH]_n$ clusters in PDRs

Rapacioli, Calvo, Joblin et al. 2006, A&A, 460, 519

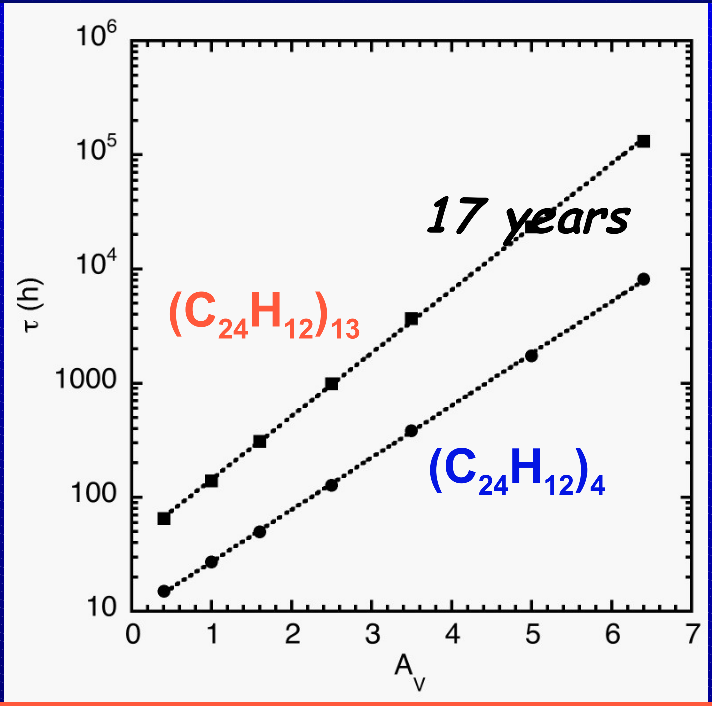
NGC7023 NW (1300 G_0)

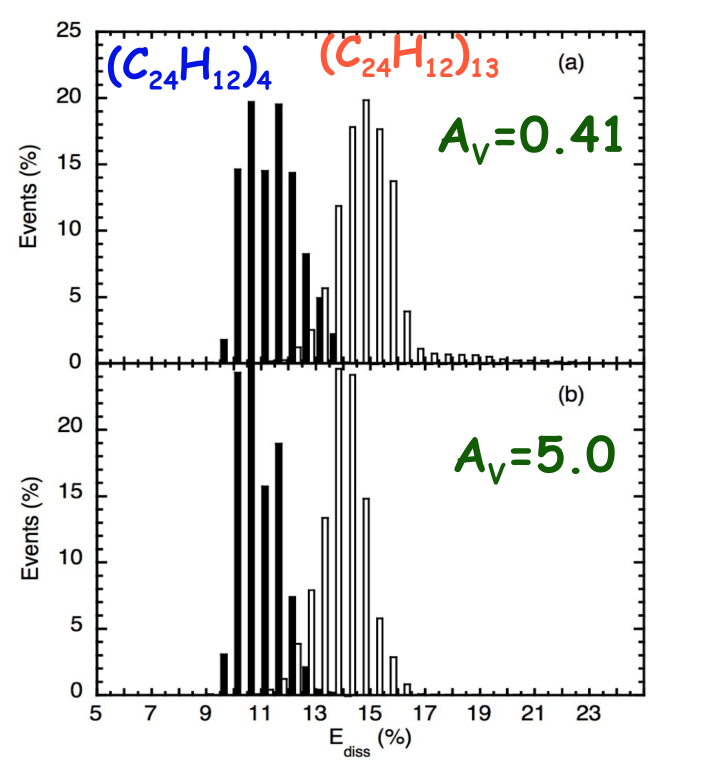
n_H~7 10^3 cm^{-3} ⇒ $\tau_{form.}$~ 10^5 years

τ_{evap} ~ few years for $(C_{24}H_{12})_{13}$

Multiple photon absorption

⇒ Medium-sized PAH clusters cannot survive





⇒ surdensity (clumps) n_H~10^6 cm^{-3}

⇒ larger clusters (larger units, increased stability by charge effect, Fe,…)

$E_{C24H12-(C24H12)_{n-1}}$~ 1 eV

⇒ dynamical process : continuous photo-evaporation of preformed clusters

⇒ NEED for FUNDAMENTAL DATA