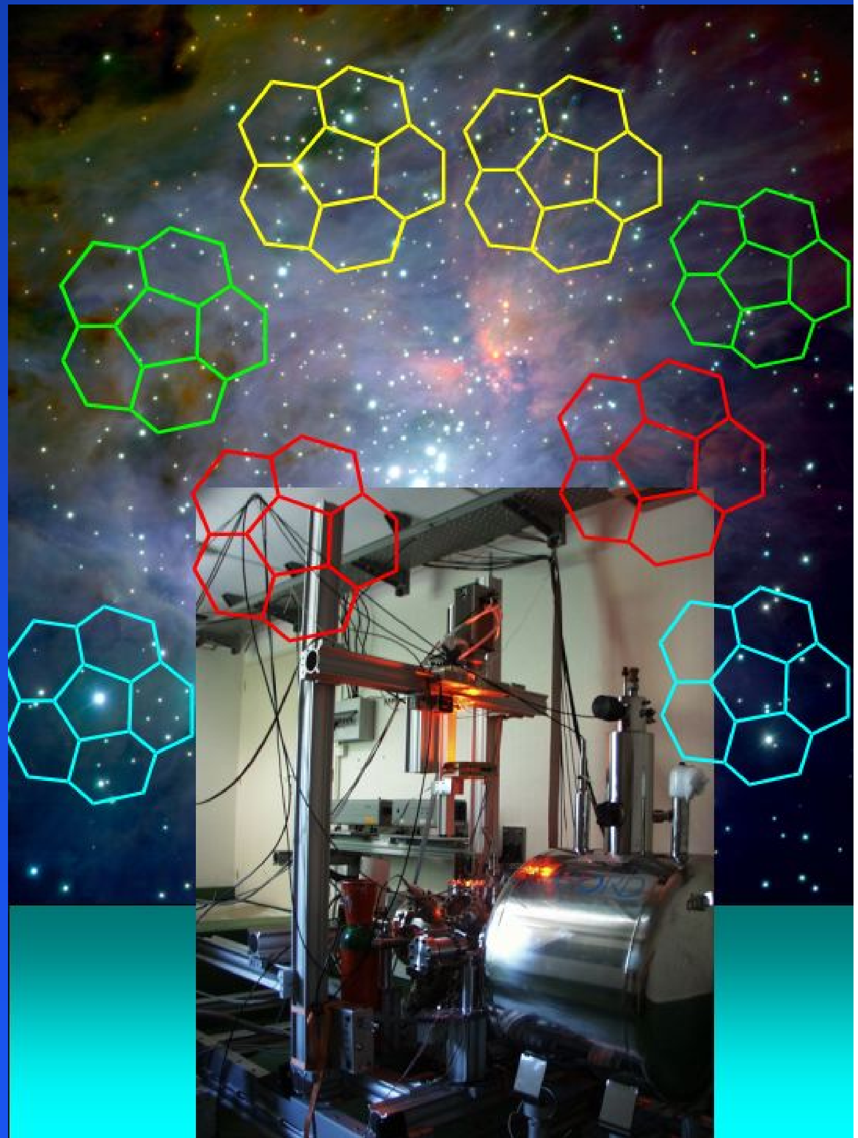
Chemistry of interstellar PAH candidates : from space to the laboratory



Christine Joblin

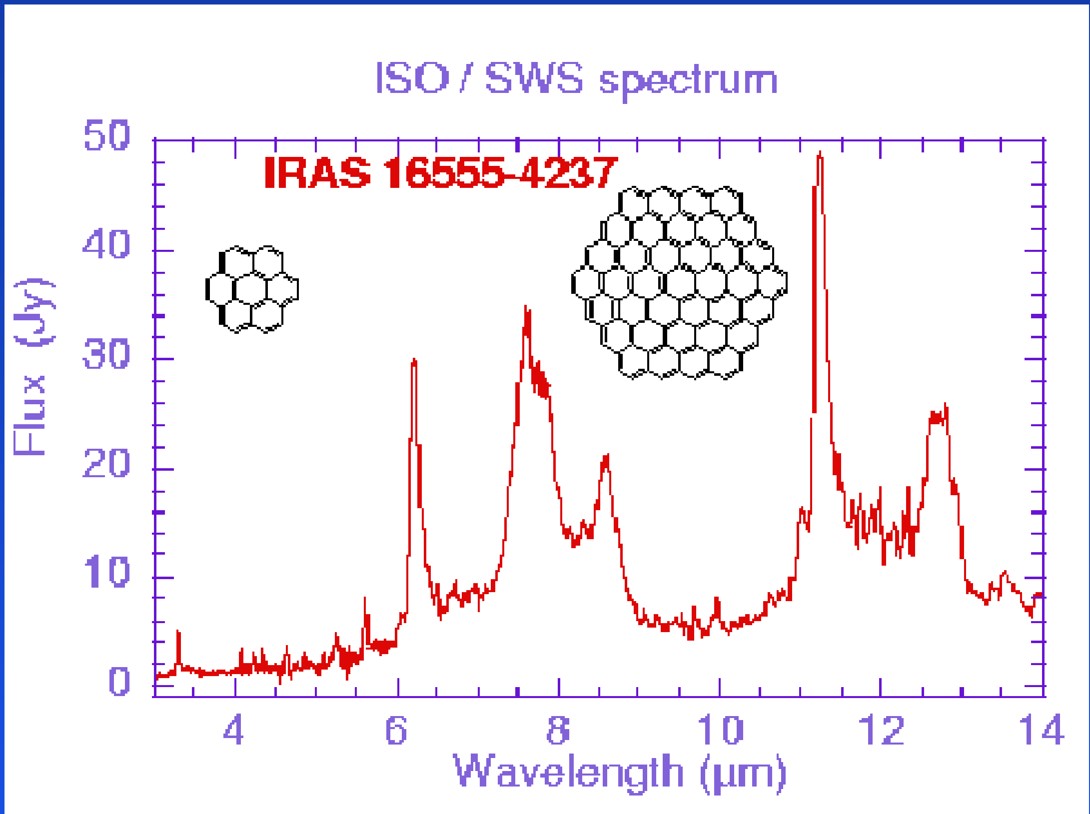
Centre d'Etude Spatiale des Rayonnements
CNRS/UPS
Toulouse -F

ALMA meeting - molecular complexity
8-11 May 2006

Outline

- I- The astronomical context
  - ✓ Aromatic IR bands (AIBs) / PAH model
  - ✓ Emission mechanism / physical conditions
- II- The PIRENEA set-up
  - ✓ Photodissociation of PAHs
  - ✓ Reactivity with molecules: H_2, H_2O, CH_3OH
  - ✓ Perspectives: $[PAH_n]^+$, $[PAH_nFe_m]^+$

Aromatic IR bands / polycyclic aromatic hydrocarbons (PAH)



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

- Stochastic heating

N~50 ; T~1000 K

Sellgren (1984), ApJ 277, 623

- Candidates: PAH molecules

Léger & Puget 1984, A&A 137, L5
Allamandola et al. 1985, ApJ 290, L25

- 10 à 20% of total carbon

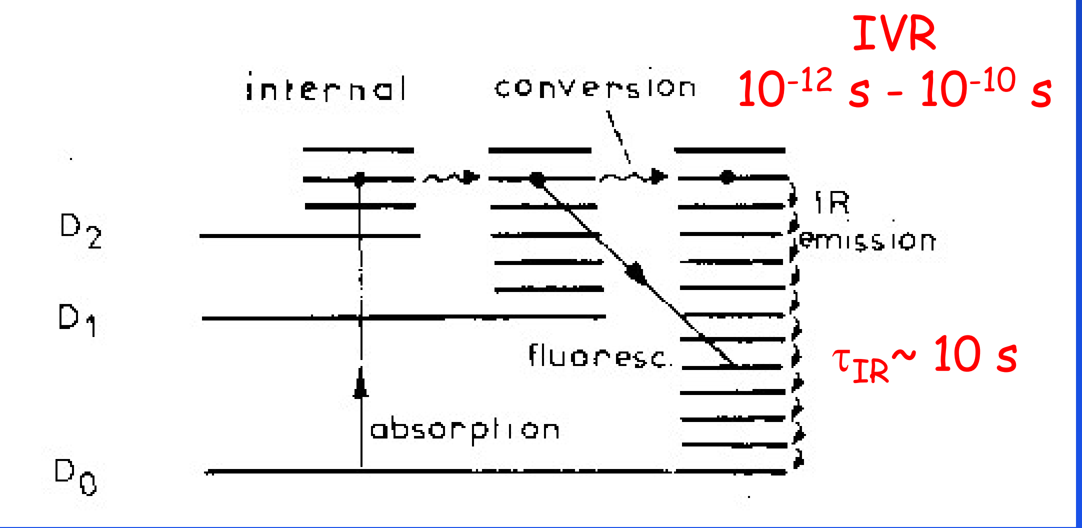
$X \sim 5\ 10^{-5}$

→ $X_{PAH} \sim 10^{-6}$ (N~50 C)

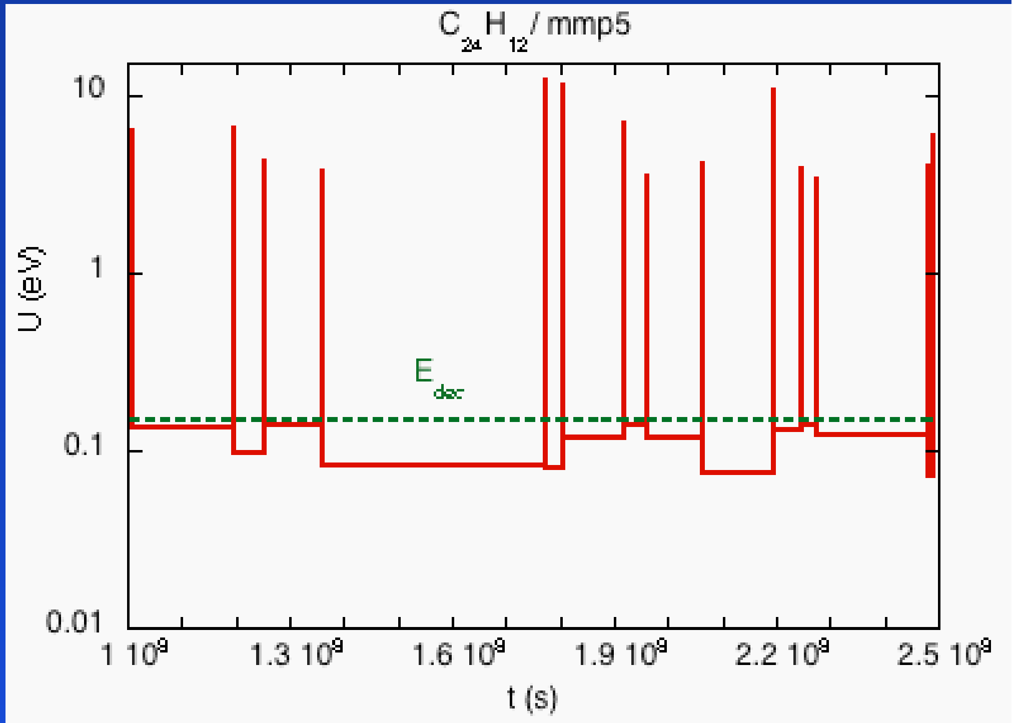
Photophysics of an isolated PAH / IR emission

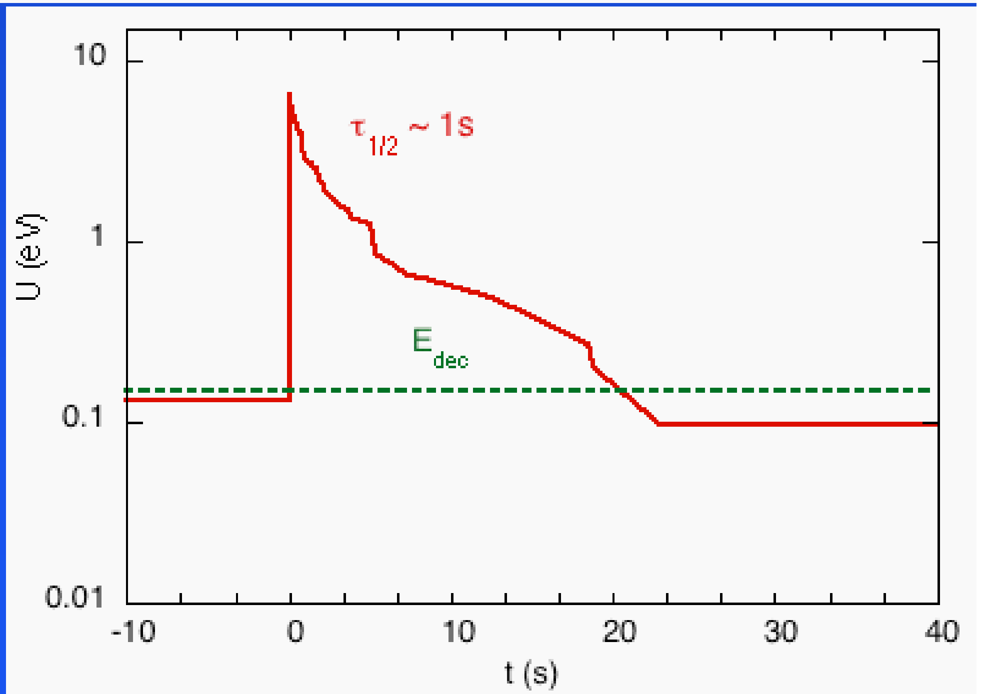
-The ISRF at 5 kpc from GC (mmp5)
Go=3.5 (Go = 1 for 10^8 photons cm^{-2} s^{-1})
⇒ few UV photons per year

Reflection nebula:
Go=10^3 ⇒ few UV photons per day



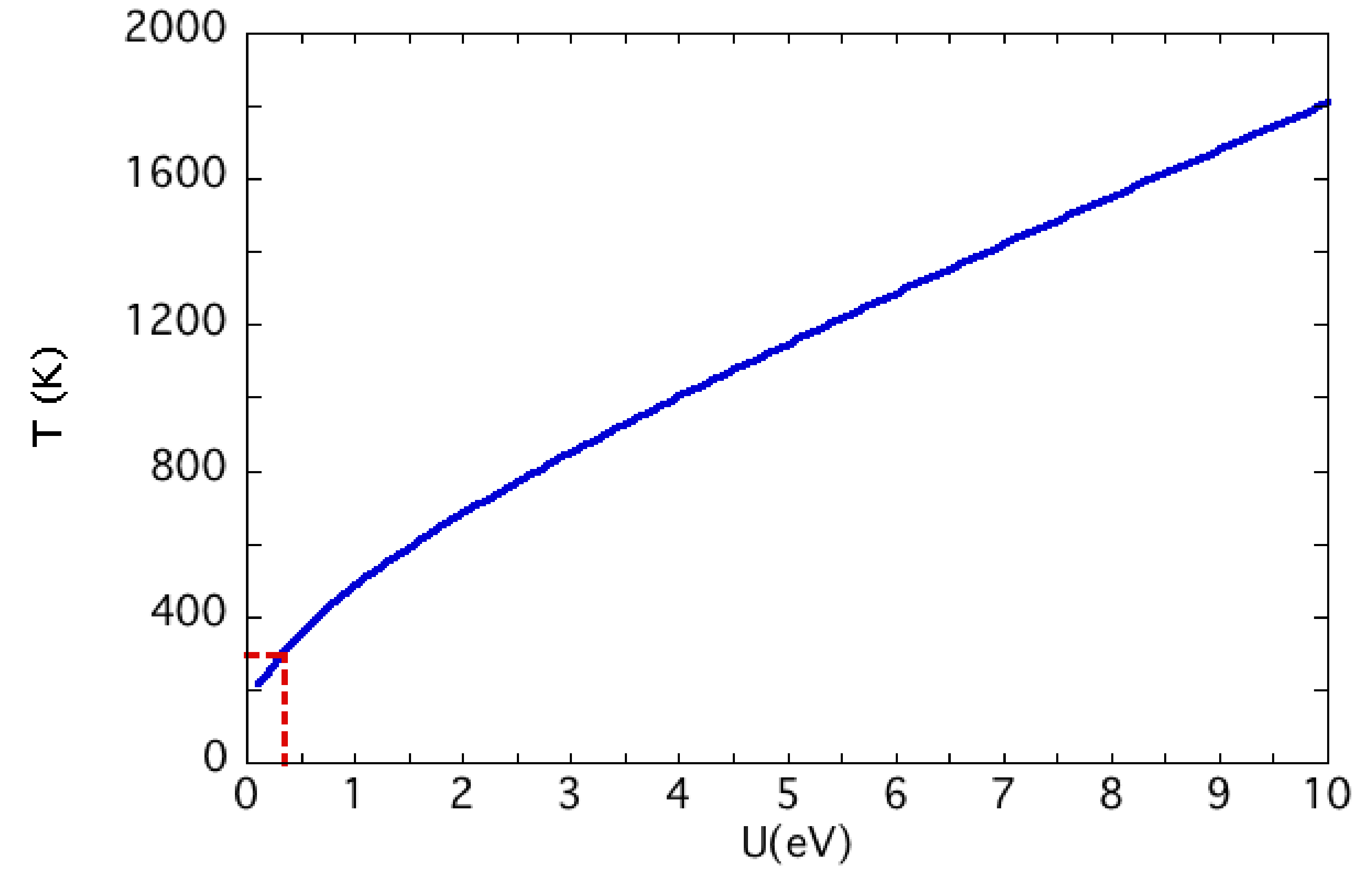
Léger et al. (1989), A&A 216, 148





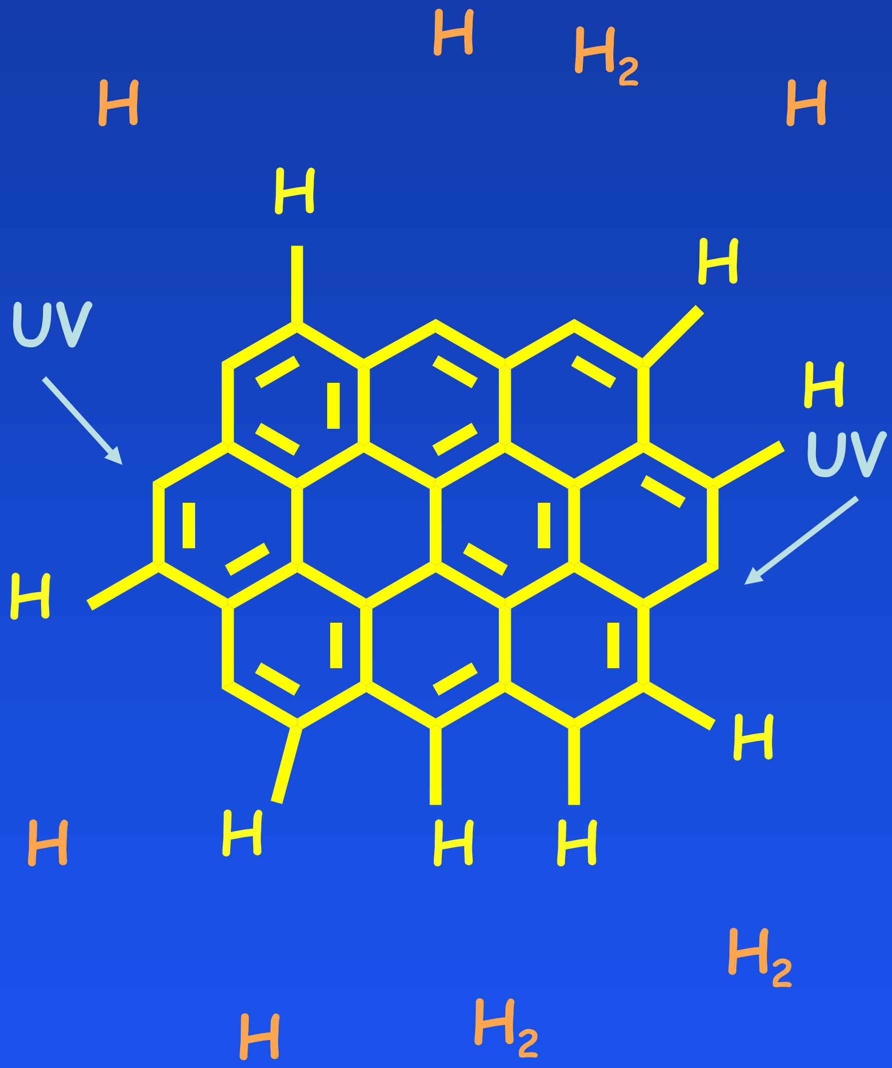
Joblin et al. (2002), Mol. Phys. 100(22), 3595; Mulas et al. (2006), A&A

Internal energy / temperature $C_{24}H_{12}^+$



$C_{24}H_{12}^+$ @ T=300 K $\Leftrightarrow$ U=0.34 eV

Laboratory approach
Photophysical and chemical evolution of interstellar PAHs



Long timescales + cold background

1- Photodissociation in competition with IR cooling (near threshold) fragments: H, H_2, C_nH_m ?

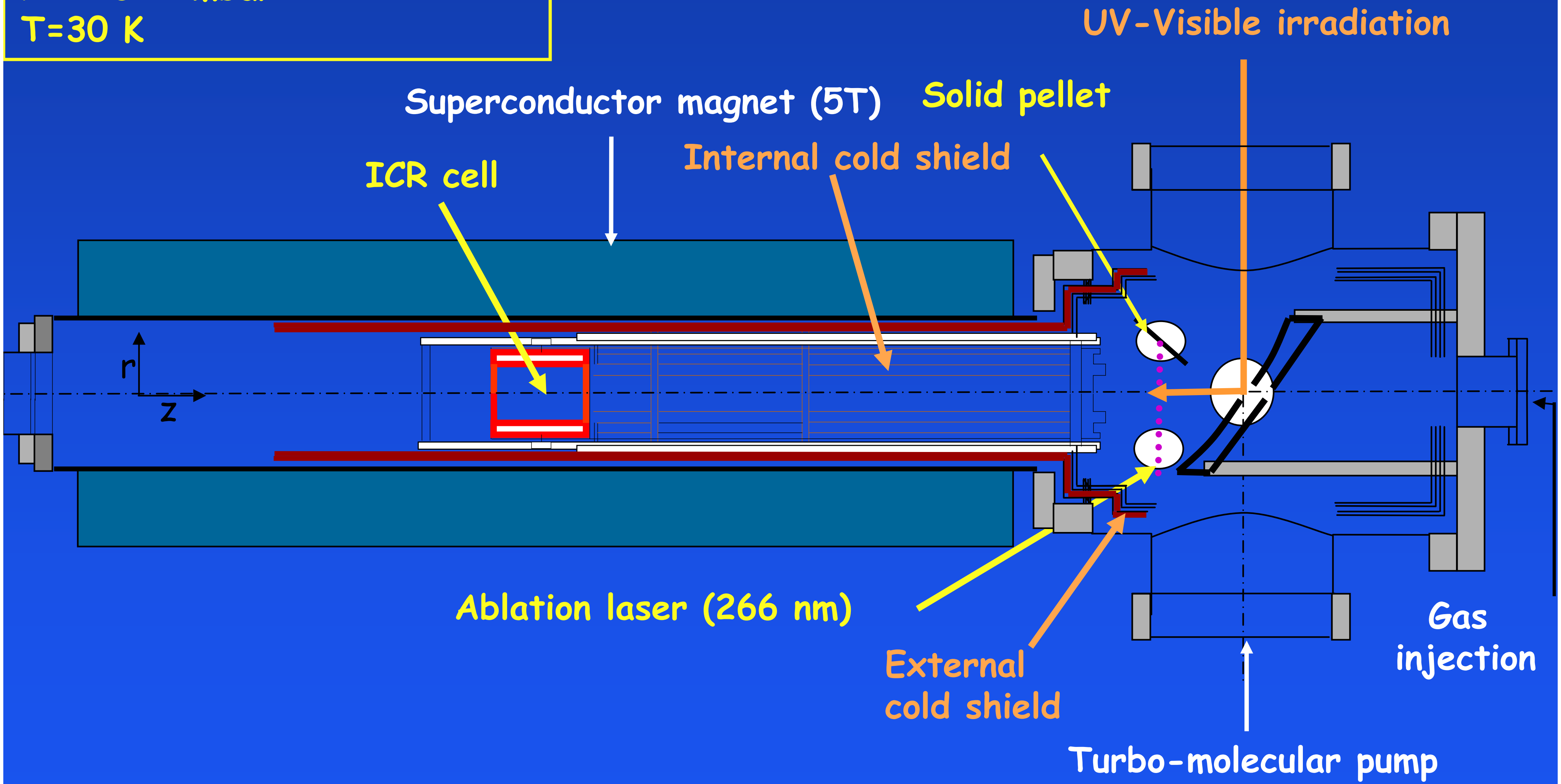
2- Reactivity - *radiative association* with H, H_2, O, C, H, H_2O, C_2H_2, CH_4, CH_3OH, NH_3 , … , PAH, ….

➔ Studies in ion traps (ex. ICR cell)

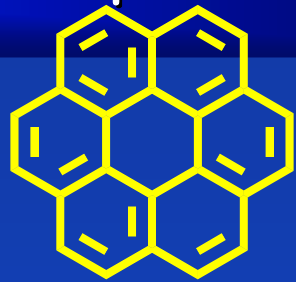
The PIRENEA set-up

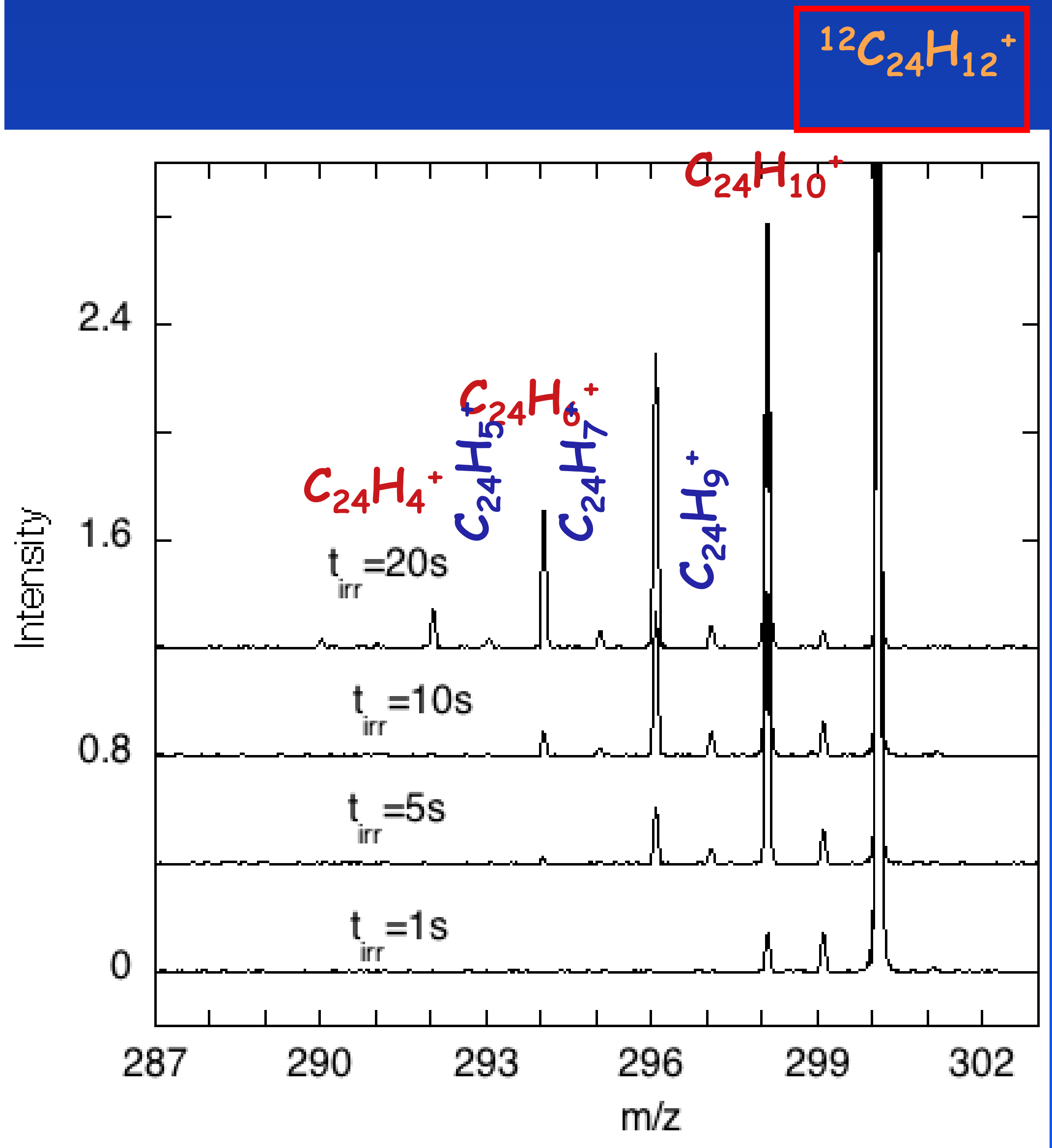
C. Joblin, M. Armengaud, P. Frabel, C. Pech, P. Boissel

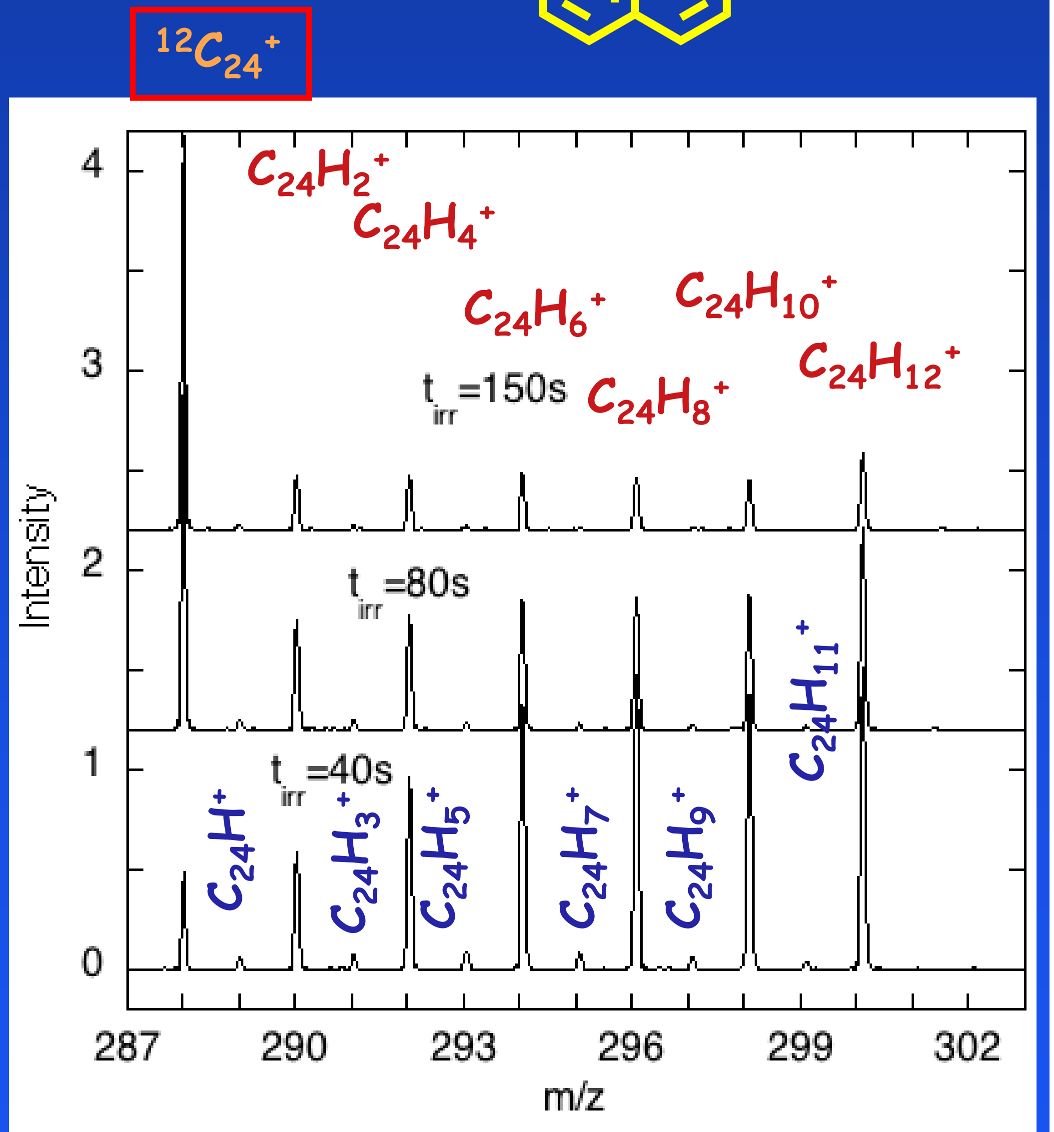
New performances (March 05)
P ~ 10^{-11} mbar
T=30 K



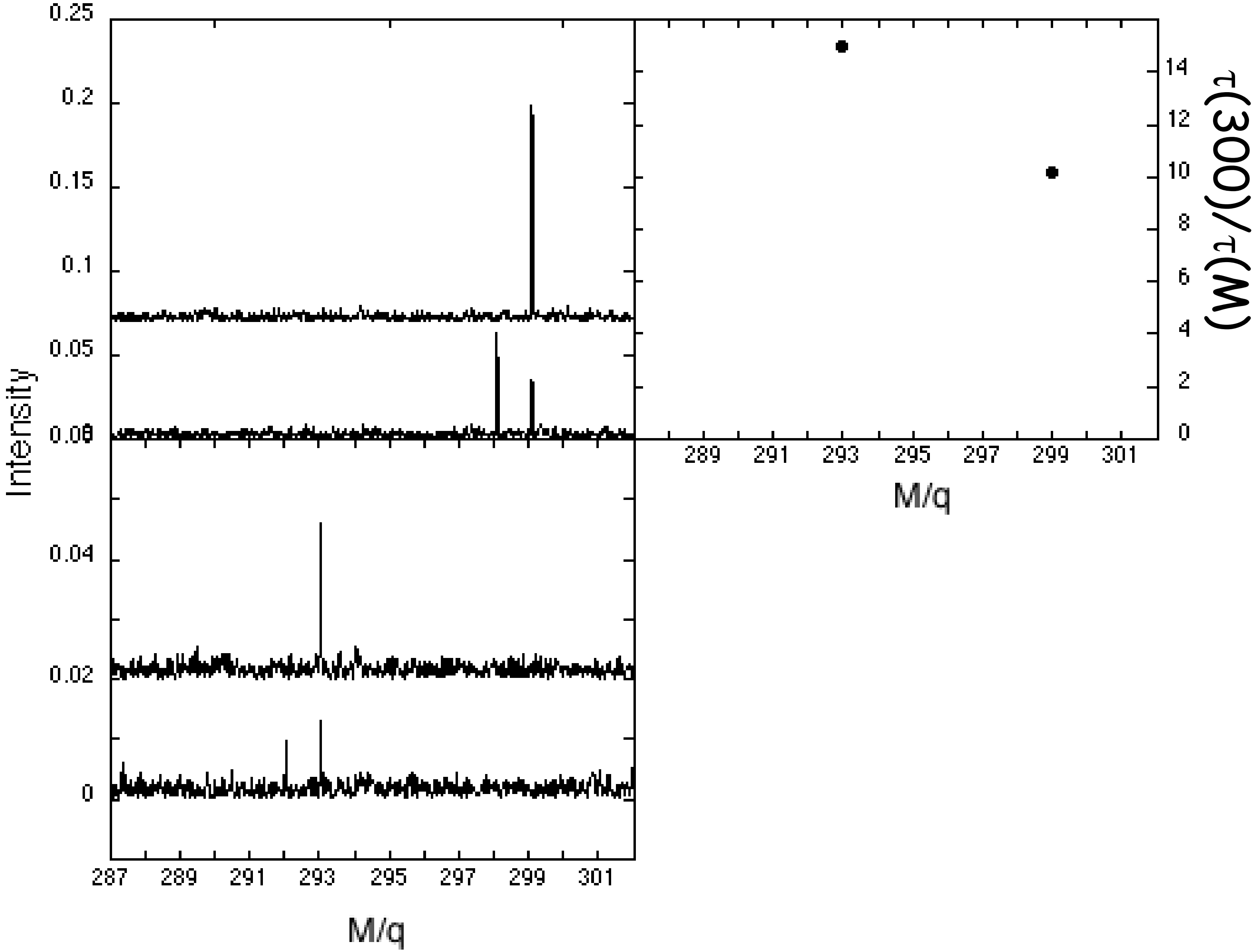
Photodissociation de $^{12}C_{24}H_p^+$ / Xe lamp







Photodissociation of $^{12}C_{24}H_{2p+1}^{+}$



Model of photodissociation of $C_{24}H_n^+$ in PIRENEA

- Exact stochastic method

Gillespie 1976, J. Comp. Phys. 22, 403; Barker 1983, Chem. Phys. 77, 301

Inputs : (a)- UV-vis absorption rate, IR emission rate

$$k^{UV\text{-}vis} = \sigma_{UV\text{-}vis} F_{UV\text{-}vis} \qquad k_i^{IR,v} = A_i^{v,\, v\text{-}1}\, p_i^v$$

$$p_i^v = \rho^*(U - vh\nu_i) \,/\, \rho\,(U) \qquad E > E_{dec}\ \text{(IVR)}$$

(b)-fragmentation rate(-H,-H_2)

Forst 1972, JPC 76, 342

$$k_d = A_d \frac{\rho(U - E_d)}{\rho(U)} H(U - E_d)$$

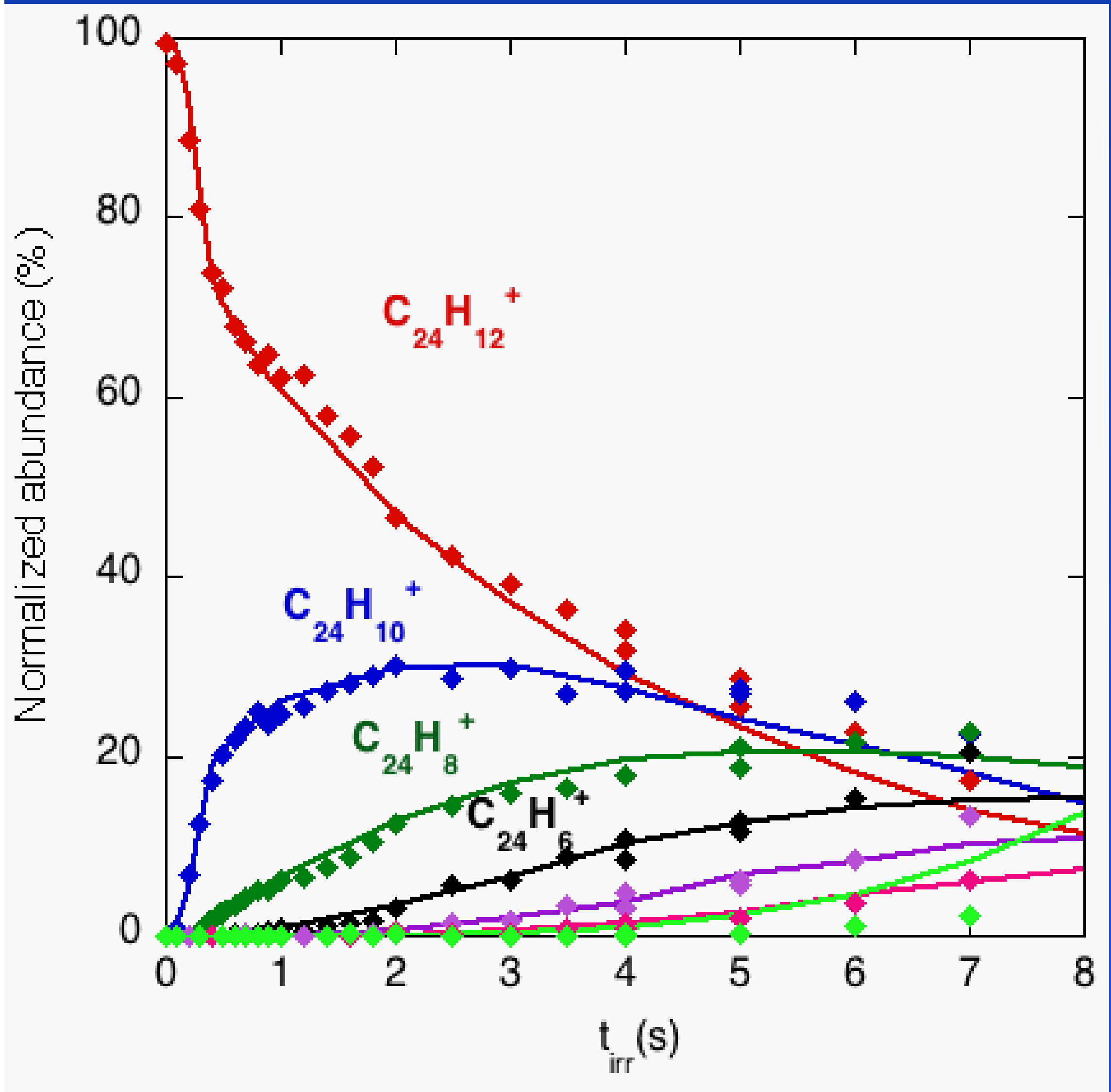
A_{d_Hduo}, E_{d_Hduo}, A_{d_Hsolo}, E_{d_Hsolo}, A_{d_H2}, E_{d_H2}

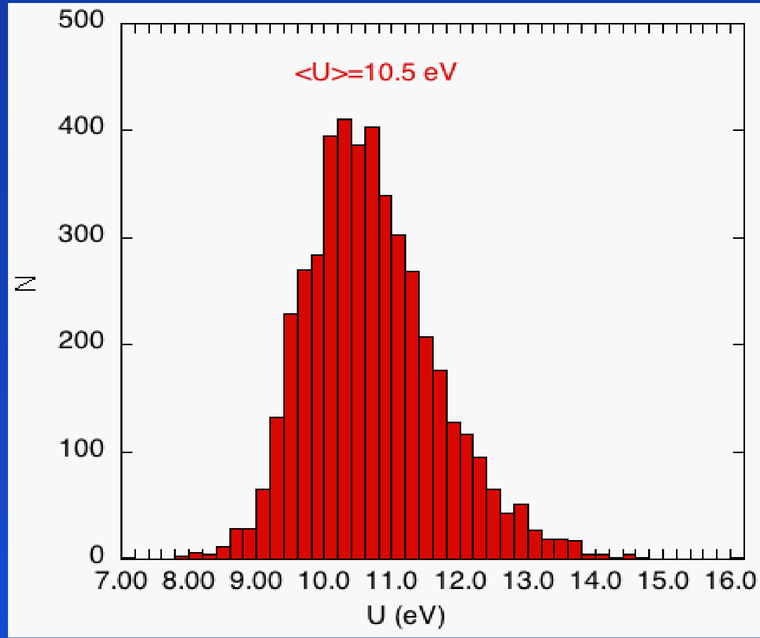
(c)-density of states :

Stein & Rabinovitch 1973, J. Chem. Phys.58, 2438

Photodissociation kinetics of $^{12}C_{24}H_{12}^{+}$/ Xe lamp

$$k_d = A_d \frac{\rho(U - E_d)}{\rho(U)} H(U - E_d)$$





$\langle E_{diss} (C_{24}H_{2p}{}^{+}) \rangle = 10.5$ eV

$\langle E_{diss} (C_{24}H_{2p+1}{}^{+}) \rangle = 5.7$ eV

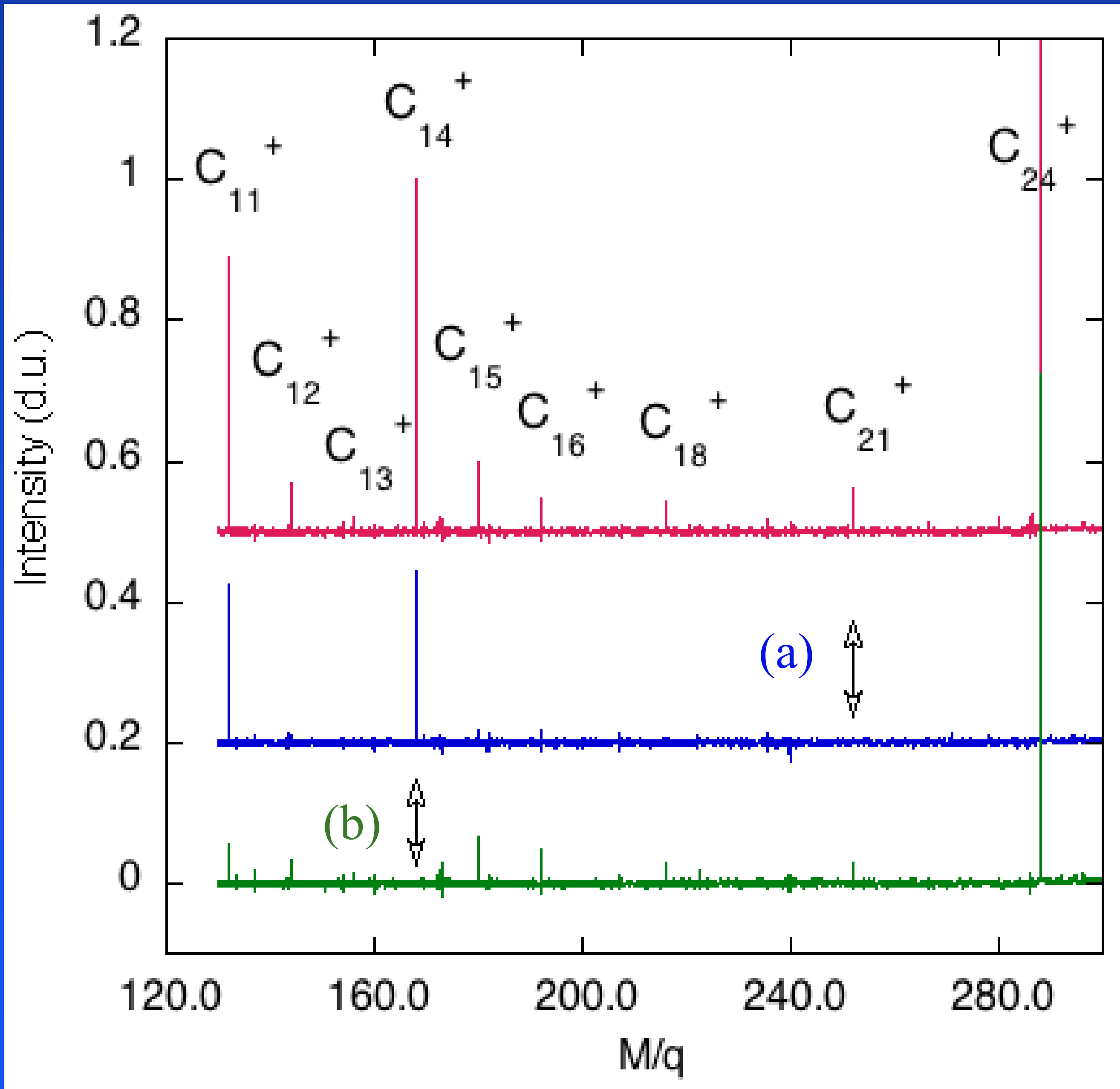
$E_{d\_Heven} = 4.48$ eV / $C_{14}H_{10}^{+}$

Ho et al. 1995, JACS 117, 6504

$E_{d\_Hodd} = 3.2$ eV / $C_{24}H_{2p+1}{}^{+}$

Joblin et al. 2006

Photodissociation of C_n^+



(a)

$C_{24}^+ \rightarrow C_{21}^+ + C_3$
$C_{21}^+ \rightarrow C_{18}^+ + C_3$
$C_{18}^+ \rightarrow C_{15}^+ + C_3$
$C_{15}^+ \rightarrow C_{12}^+ + C_3$

(b)

$C_{24}^+ \rightarrow C_{14}^+ + C_{10}$
$C_{14}^+ \rightarrow C_{11}^+ + C_3$

Astrophysical implications

- Effect of UV photons:

$C_{24}H_{12}^{+} \rightarrow C_{24}^{+} \rightarrow C_{n}^{+}$ ($n \leq 21$)

- Need to study the competition with H recombination

$C_{16}H_{9}^{+} + H_2$ no reaction

Le Page et al. 1999, IJMS 185, 949

$C_{24}H_{p}^{+} + H_2$ ($1 \leq p \leq 11$) no reaction (PIRENEA)

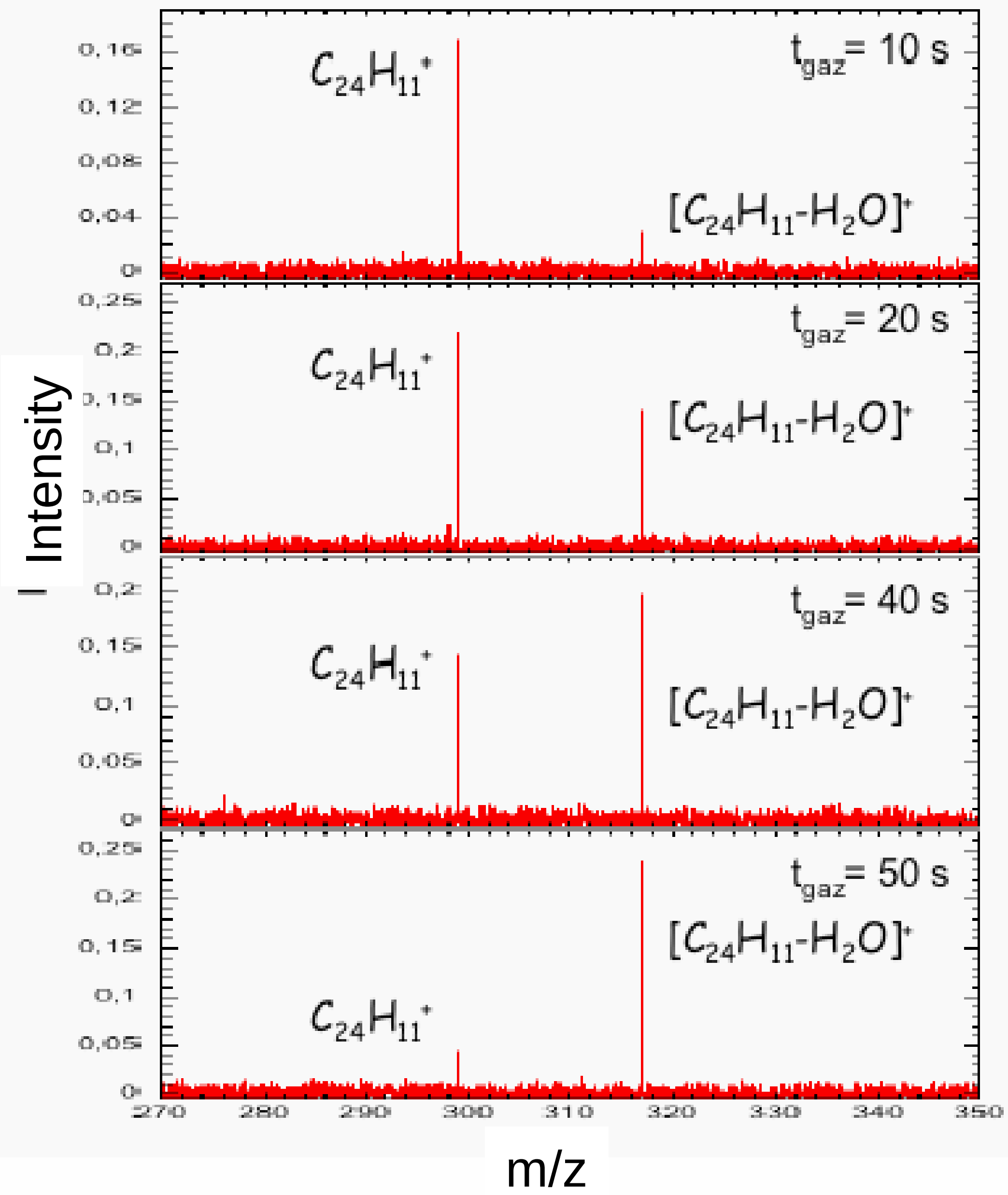
Reactivity with H

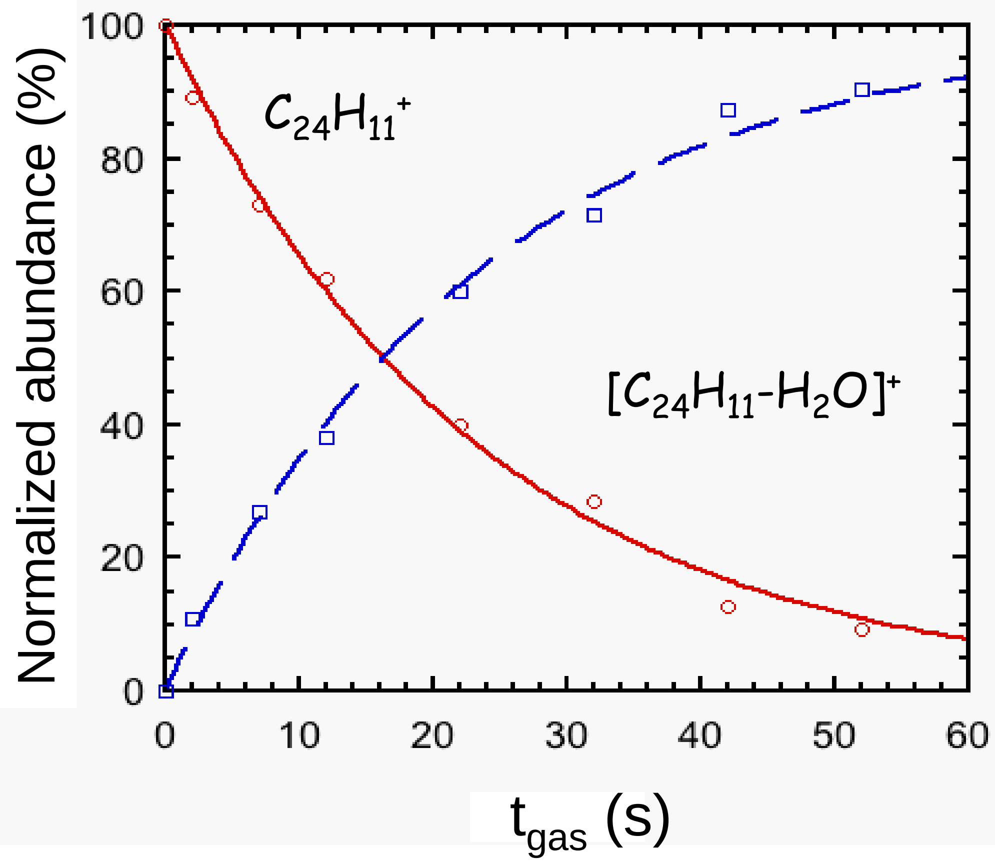
			k (cm^3/s)
$C_{16}H_{11}^{+}$	H	c-$C_{16}H_{12}^{+}$	$\sim 3 \times 10^{-12}$
$C_{16}H_{10}^{+}$	H	$C_{16}H_{11}^{+}$ (1.0)	1.4×10^{-10}
$C_{16}H_{9}^{+}$	H	$C_{16}H_{10}^{+}$ (1.0)	$\sim 1.6 \times 10^{-10}$

Ex: model by *Le Page et al. 2003, ApJ 584, 316*

- $N_c < 20$ - small PAHs are destroyed
- $N_c = \{20, 30\}$ - fully dehydrogenated ⇒ carbon clusters C_n^{+}
- larger N_c - fully hydrogenated / surhydrogenated

Reactivity $C_{24}H_{11}^+ + H_2O$





P_{H2O}=3 10^{-8} mbar

100*exp(-0.0414*t)

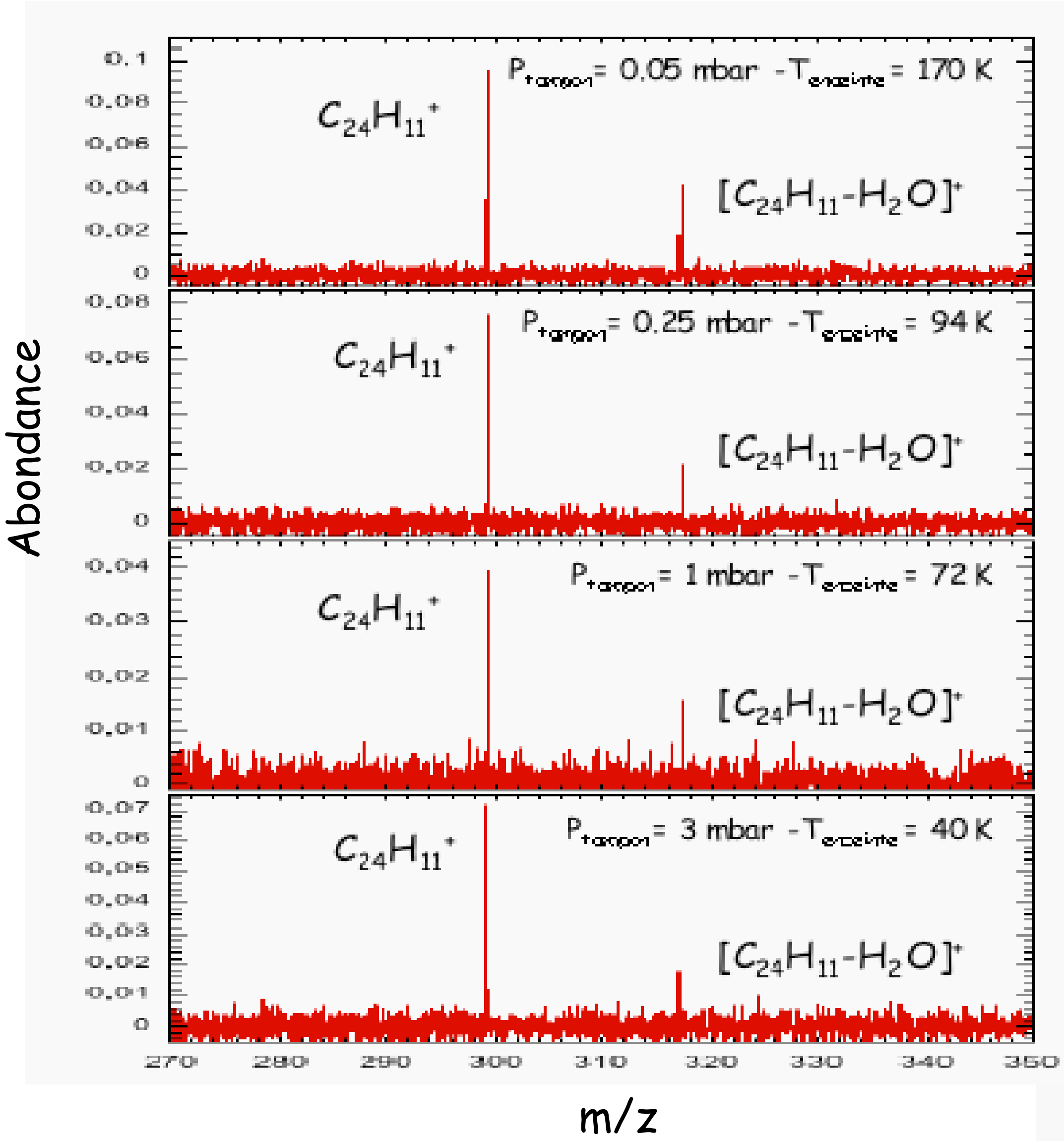
k_{299}= 5.7 ± 0.4 10^{-11} mol^{-1}cm^3 s^{-1}

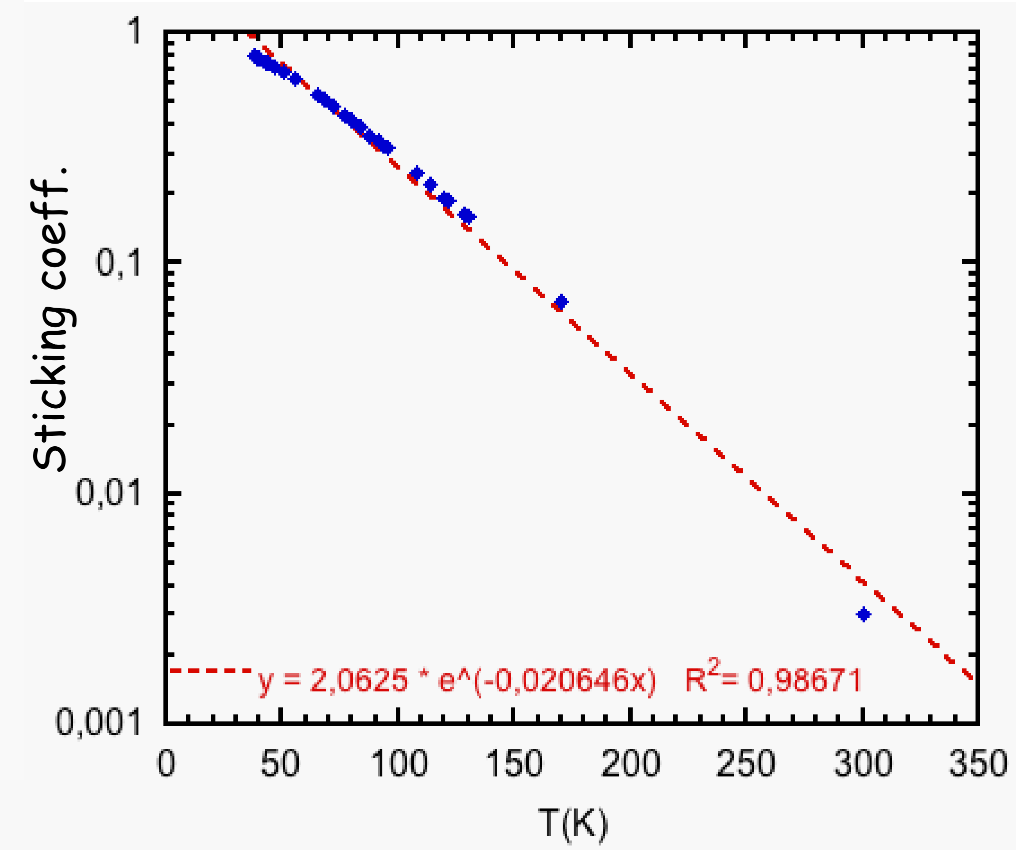
= 2.1 10^{-11} mol^{-1}cm^3 s^{-1}

Keheyan et al. 2001, CPL 340, 405

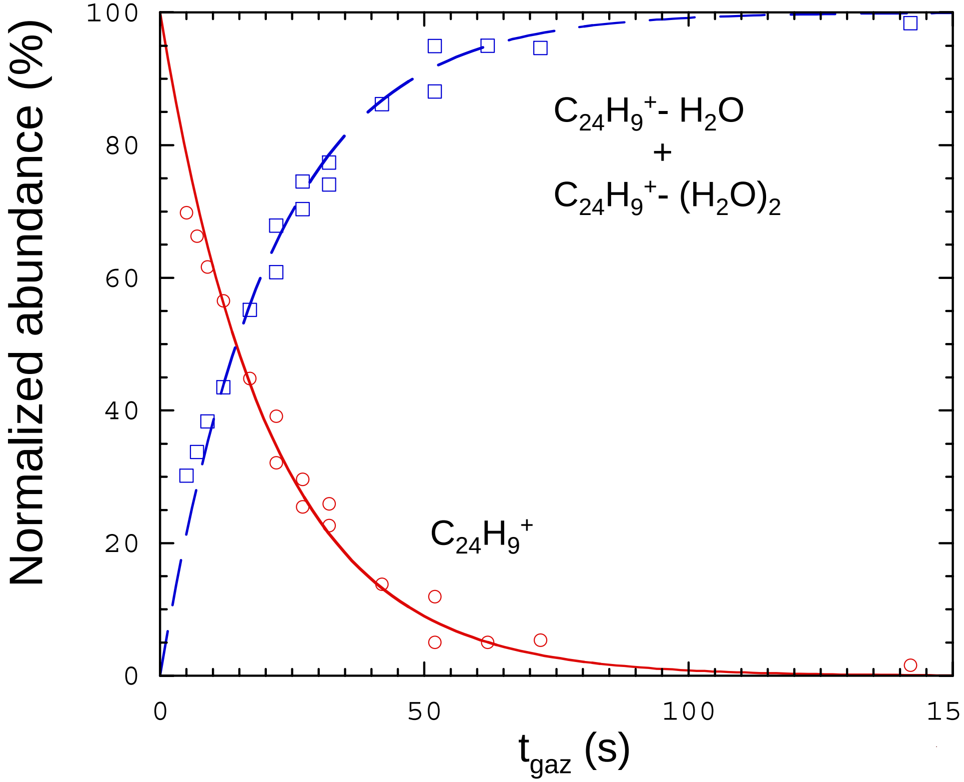
$$
(1)\begin{cases}
\dfrac{dN_g(t)}{dt} = \dfrac{\overbrace{P_1 C}^{S}}{kT_1} - \dfrac{\overbrace{D}^{k_p}}{V_e} N_g(t) - k_{acc} N_g(t) + k_{evap} N_s(t) \\[2ex]
\dfrac{dN_s(t)}{dt} = k_{acc} N_g(t) - k_{evap} N_s(t)
\end{cases}
$$

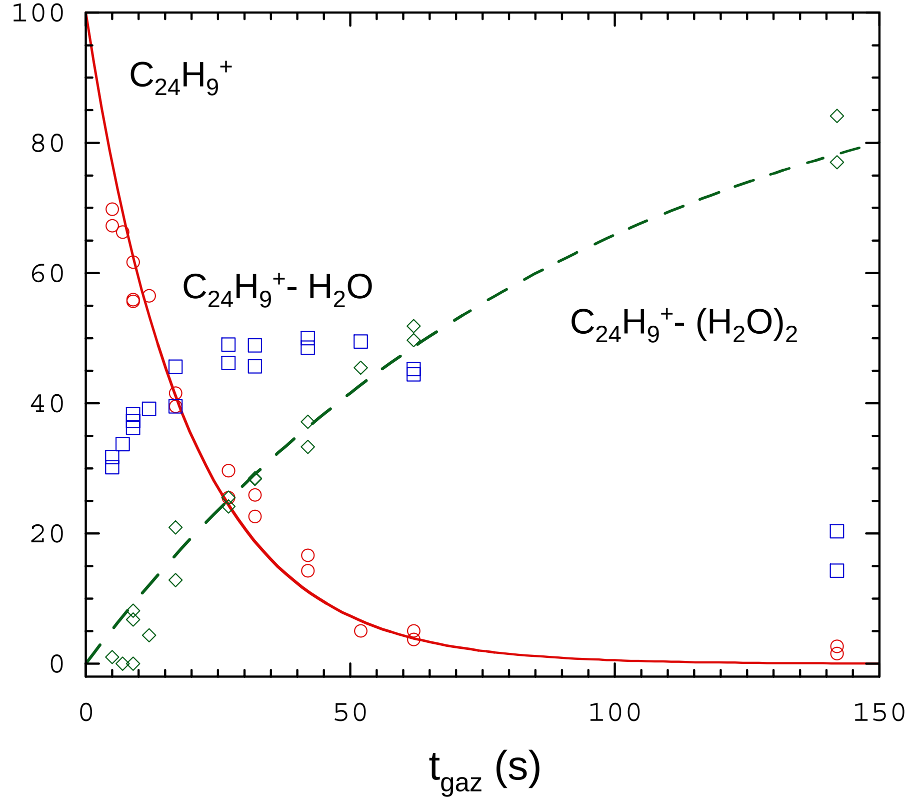
$$
k_{acc} = \varepsilon(T_s)\frac{\upsilon}{l} \qquad k_{evap} = \gamma_0 \exp\left[-E_D / T_s\right]
$$

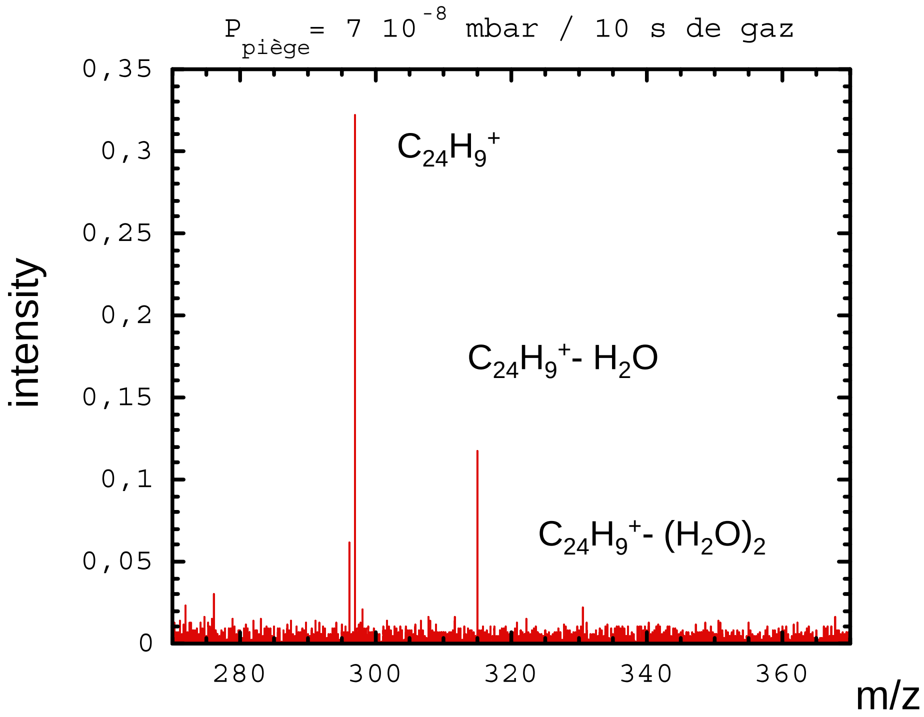




$\Rightarrow k_{299}=5.7 \pm 0.4\ 10^{-11}\ mol^{-1}cm^{3}s^{-1}$ independent of T (PAH) ?

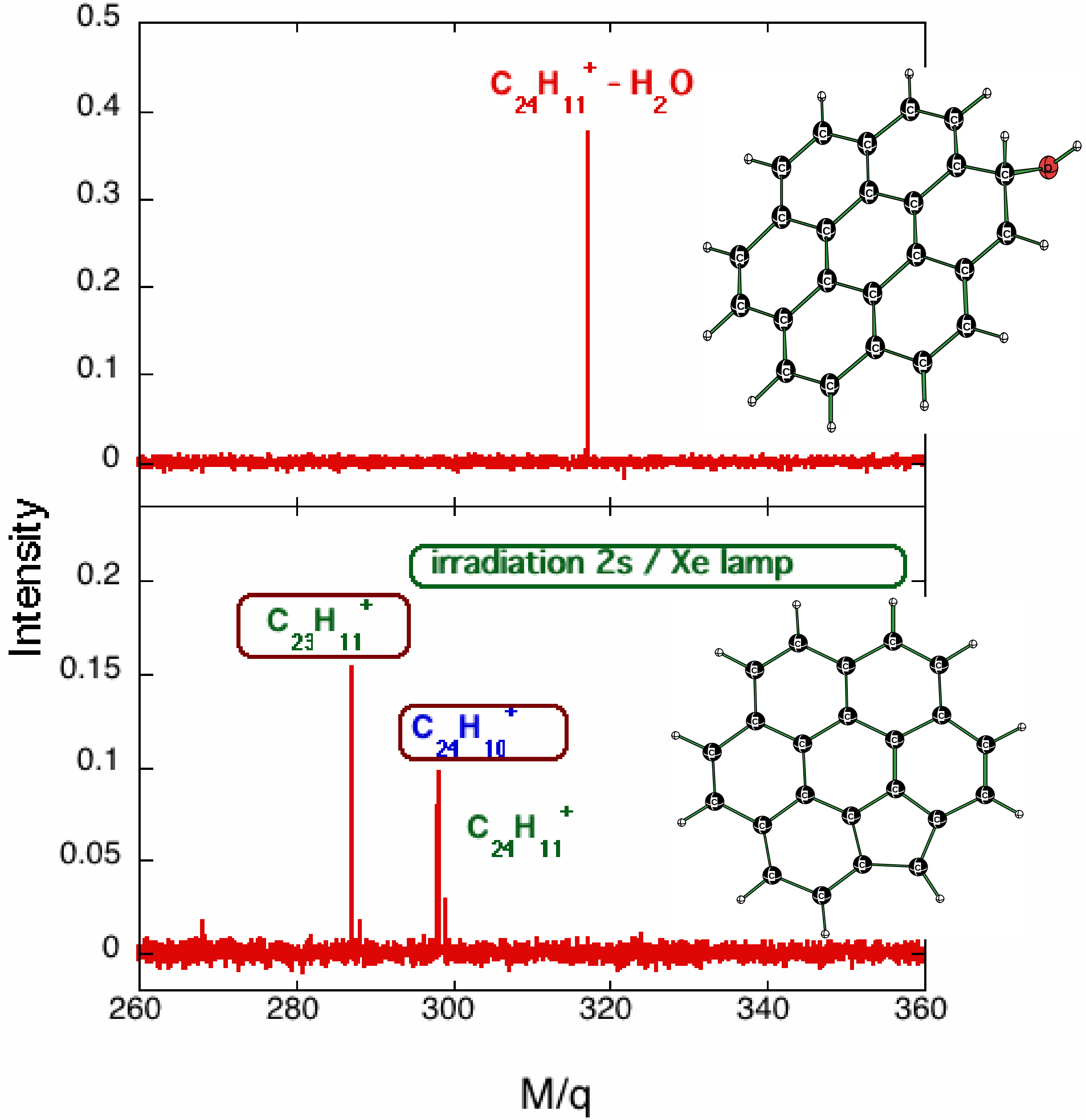






P_{H2O}=7 10^{-8} mbar

Photodissociation : $\{C_{24}H_{11}H_2O\}^+$



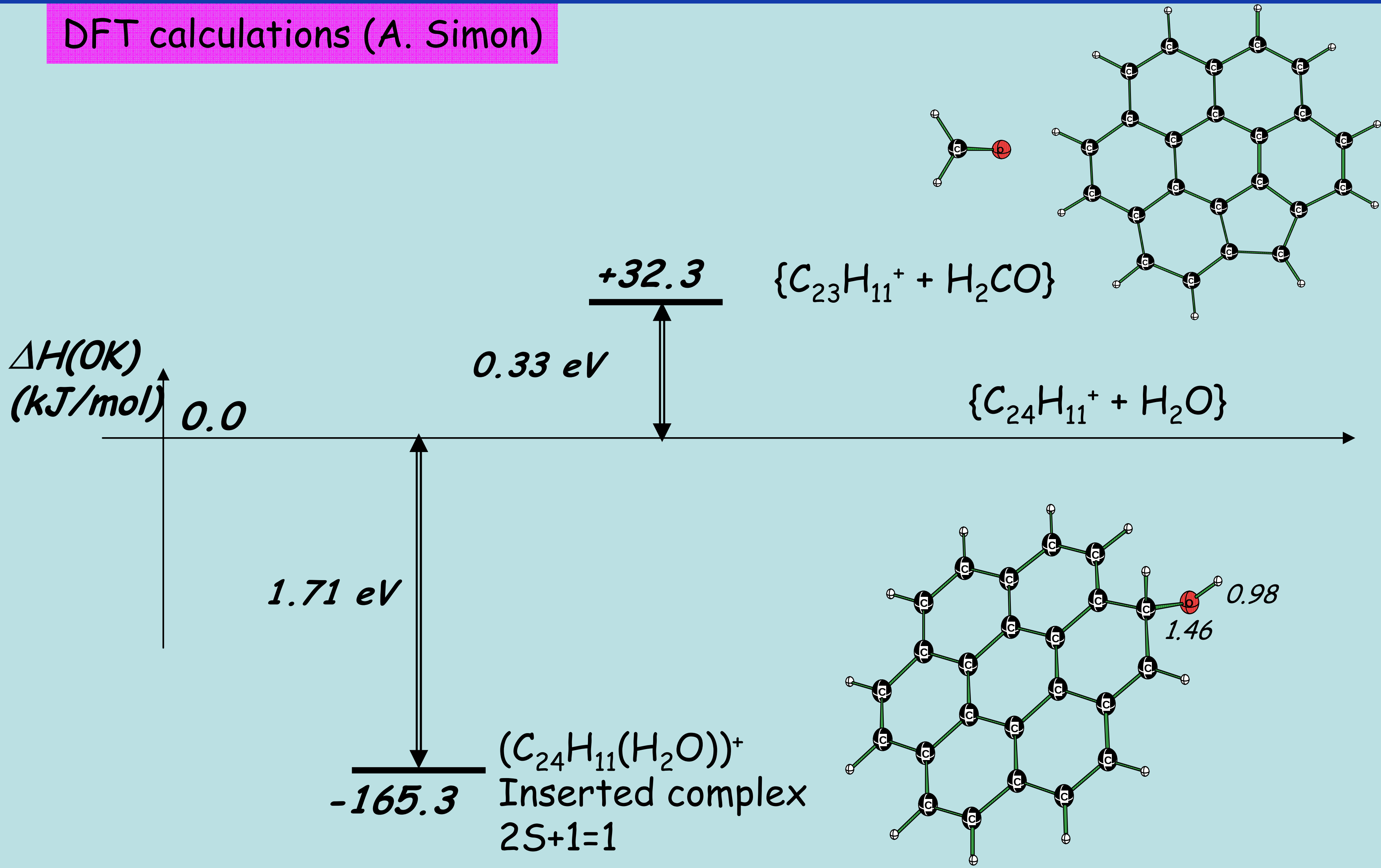
$\{C_{24}H_{11}H_2O\}^+ + h\nu$

$\rightarrow C_{24}H_{11}^+ + H_2O$

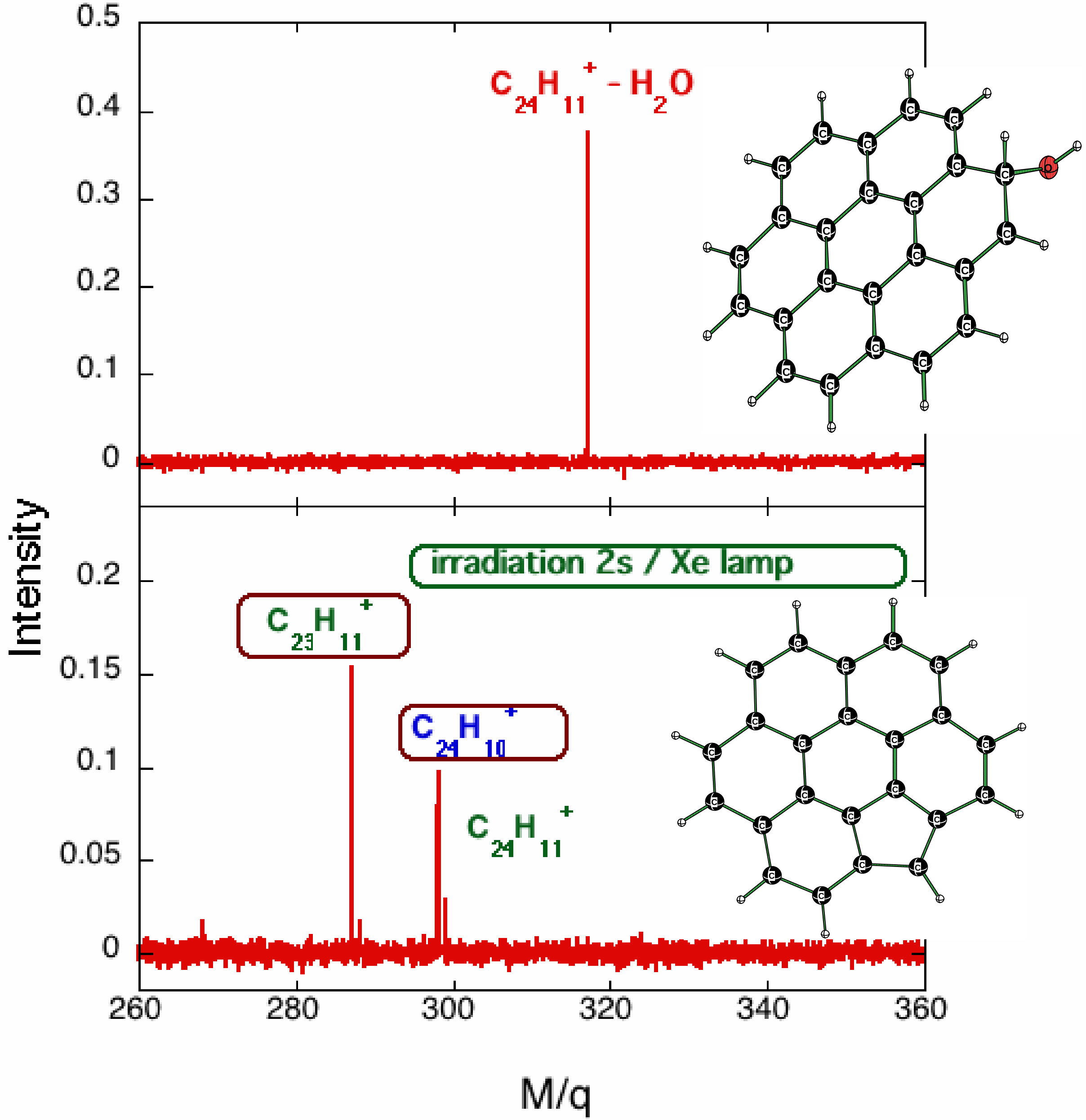
$\rightarrow C_{23}H_{11}^+ + H_2CO$

Theory / thermochemistry : $C_{24}H_{11}^{+} + H_2O$

DFT calculations (A. Simon)



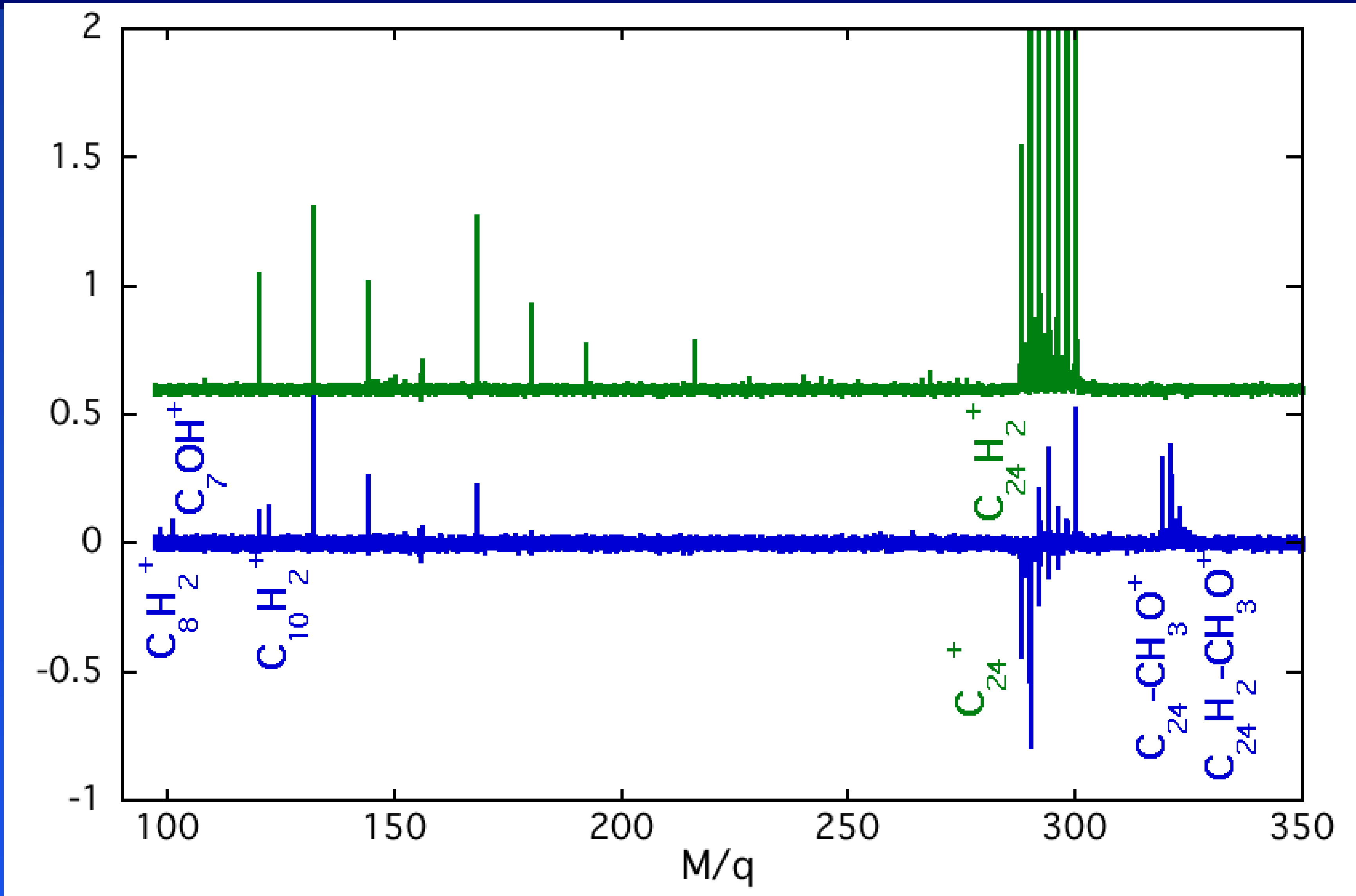
Photodissociation : $\{C_{24}H_{11}H_2O\}^+$



→ formation of molecules by PAH / dust

→ new PAH species produced by chemistry & photons

Reactivity of PAHs/ C-clusters with CH_3OH (preliminary)



$C_{24}^{+} + CH_3OH \rightarrow \{C_{24}CH_3O\}^{+} + H$

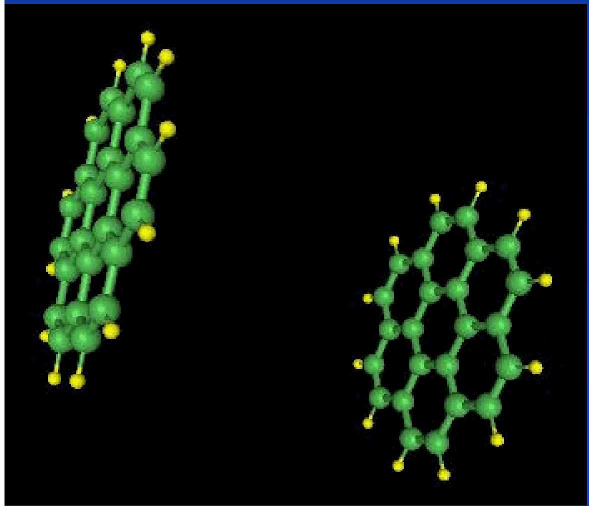
$C_{24}H_2^{+} + CH_3OH \rightarrow C_{24}H\text{-}CH_3O^{+} + H$

$C_8^{+} + CH_3OH \rightarrow C_8H_2^{+} + H_2CO$??

$C_{10}^{+} + CH_3OH \rightarrow C_{10}H_2^{+} + H_2CO$??

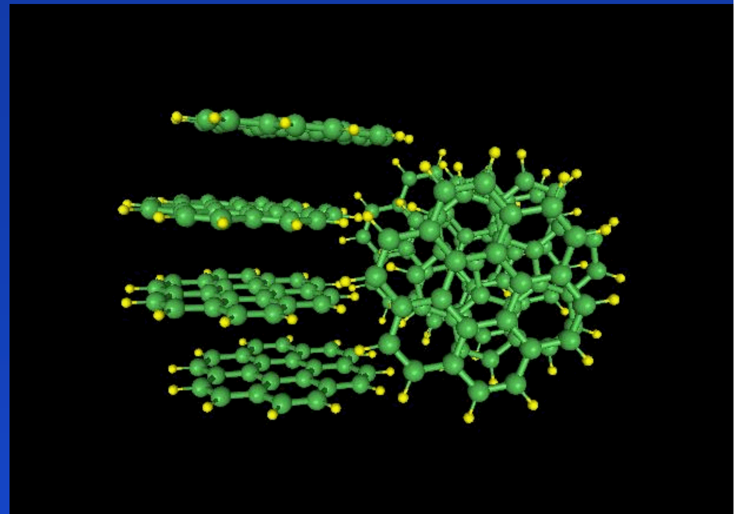
$(C_8H_2^{+}, C_7OH) \rightarrow \{C_{14}CH_3O\}^{+}$

Structure, formation and stability of $(PAH)_n$ and PAH-Fe clusters



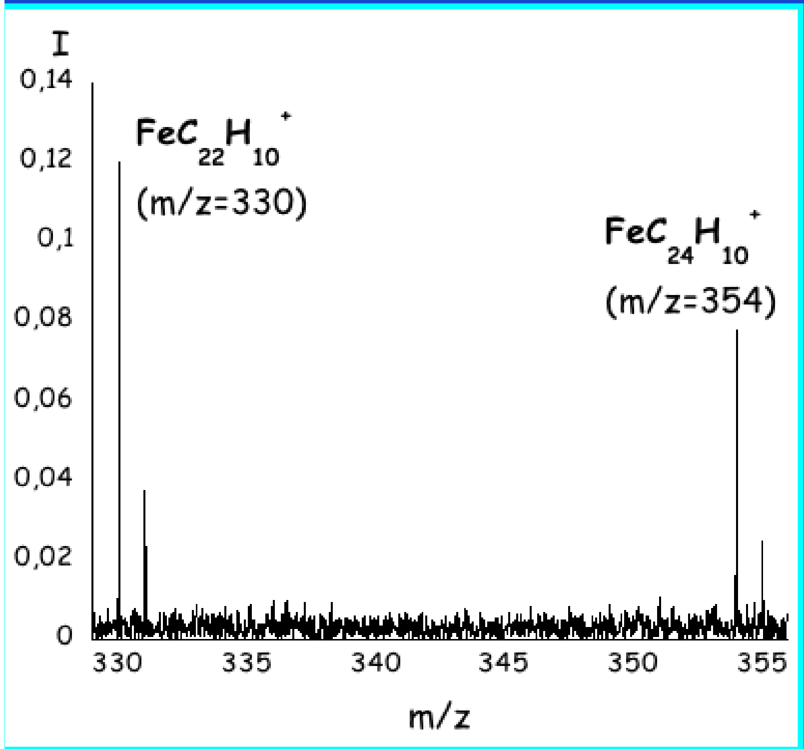
- *Rapacioli, Calvo, Spiegelman, Joblin, Wales, 2005, J.Phys. Chem. A, 109, 2487*

- *Rapacioli, Calvo, Joblin et al. 2006, A&A, soumis*

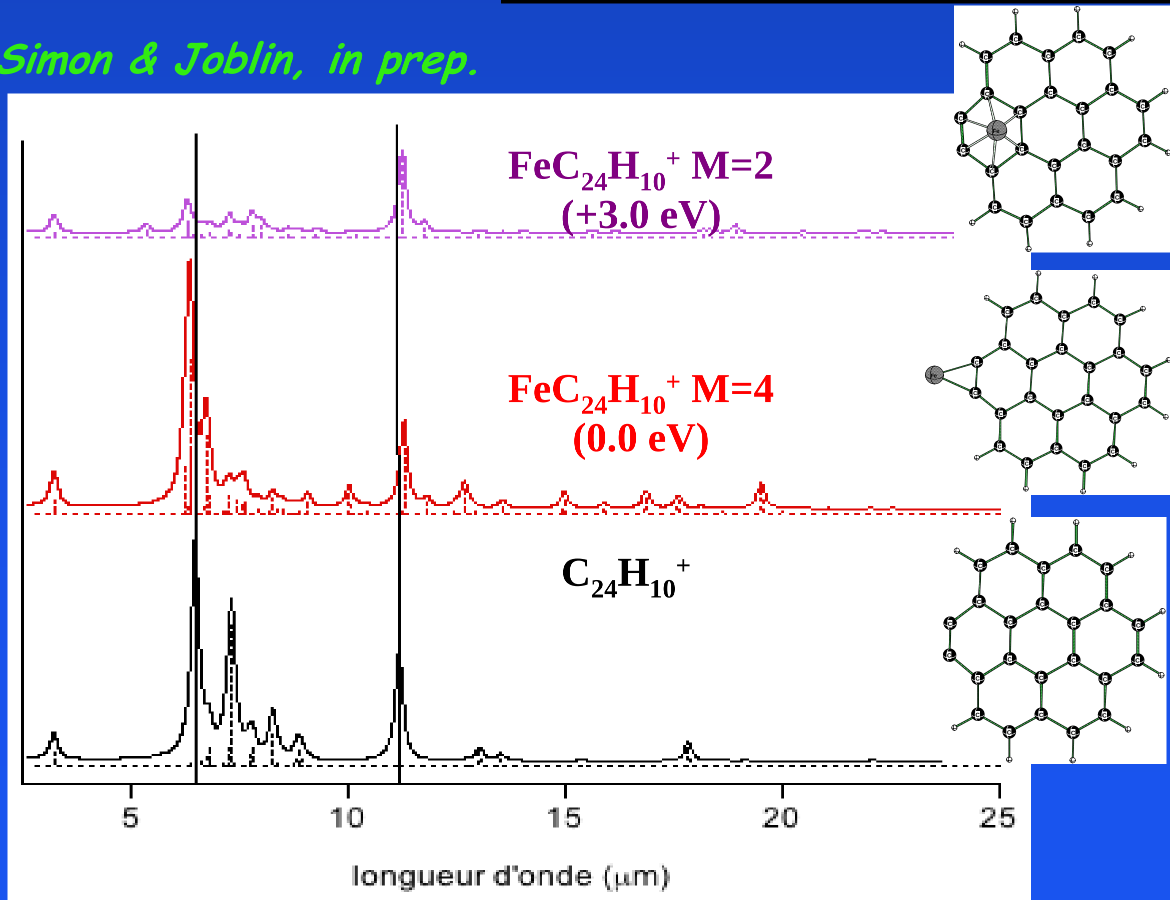


$(C_{24}H_{12})_8$

$E_{PAH\text{-}PAH_{n-1}} \sim 1$ eV



Simon & Joblin, in prep.



Thanks

Collaborators

A. Simon (CESR)

N. Bruneleau (PhD student, CESR)

D. Toublanc (CESR)

P. Boissel (LCP-Orsay),

Technical team of PIRENEA: M. Armengaud, P. Frabel, L. Noguès

Financial support

- ✓ CNRS / Programme National Physique et Chimie du Milieu Interstellaire
- ✓ Région Midi-Pyrénées
- ✓ FP6 Molecular Universe