Electronic spectroscopy of trapped PAH photofragments

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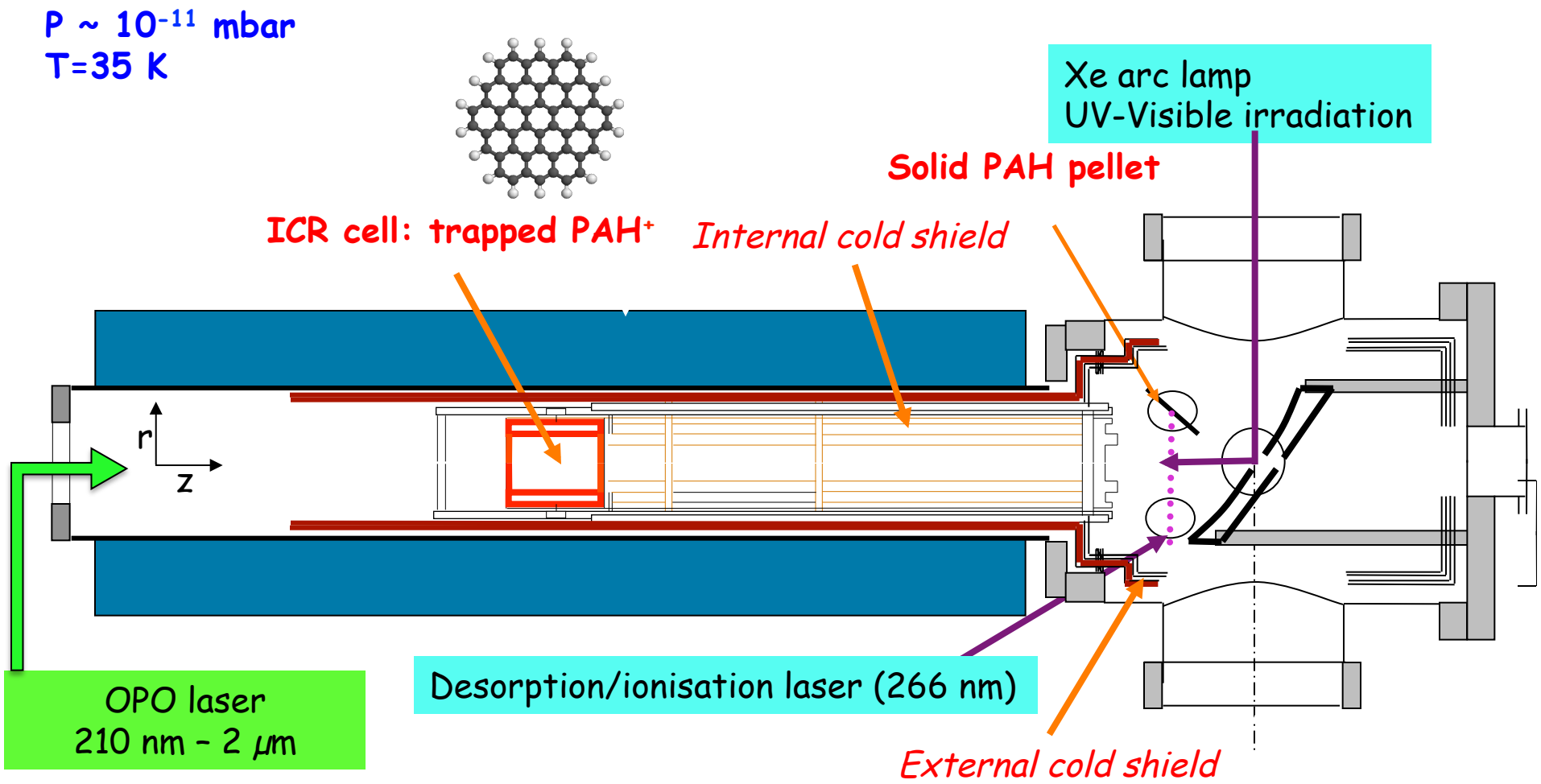
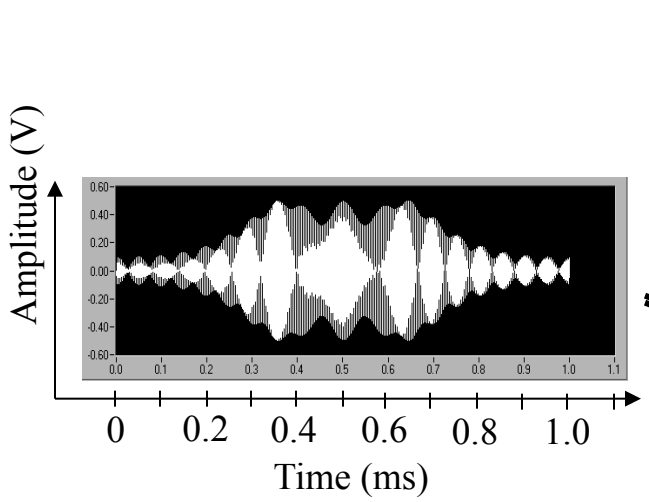
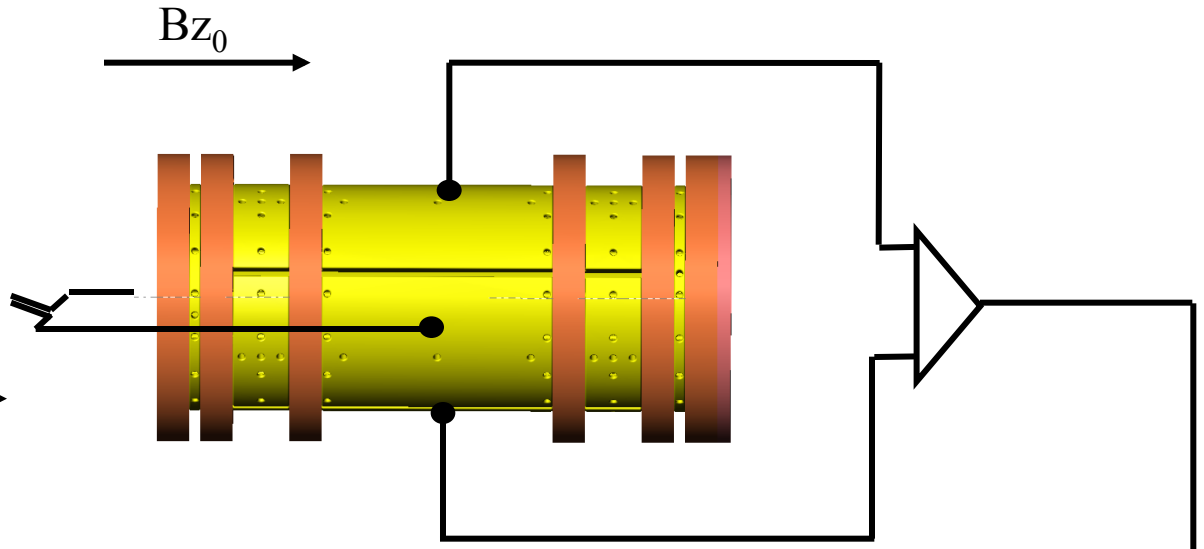
The PIRENEA set-up for astrochemistry



Same cold ICR cell to prepare the ions and detect them

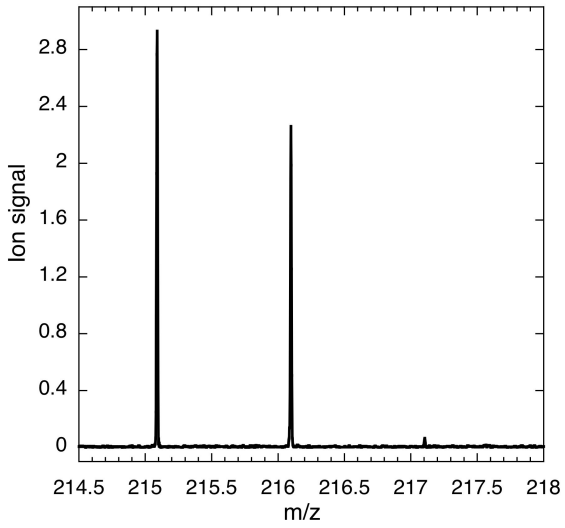




Long trapping time → cooling: radiative + He buffer gas (~10^{-7} mbar)

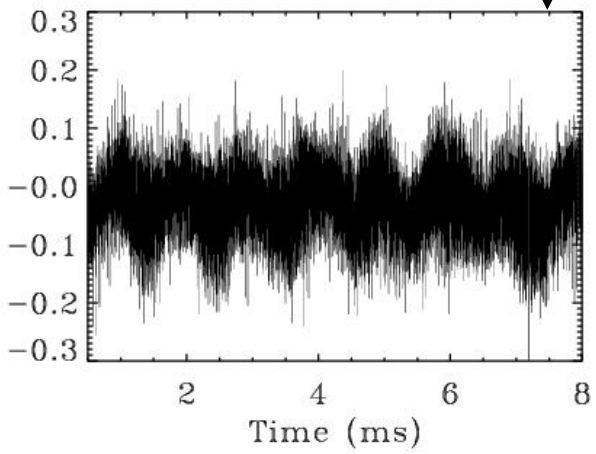
Isolation of fragment of interest

Record FT mass spectrum



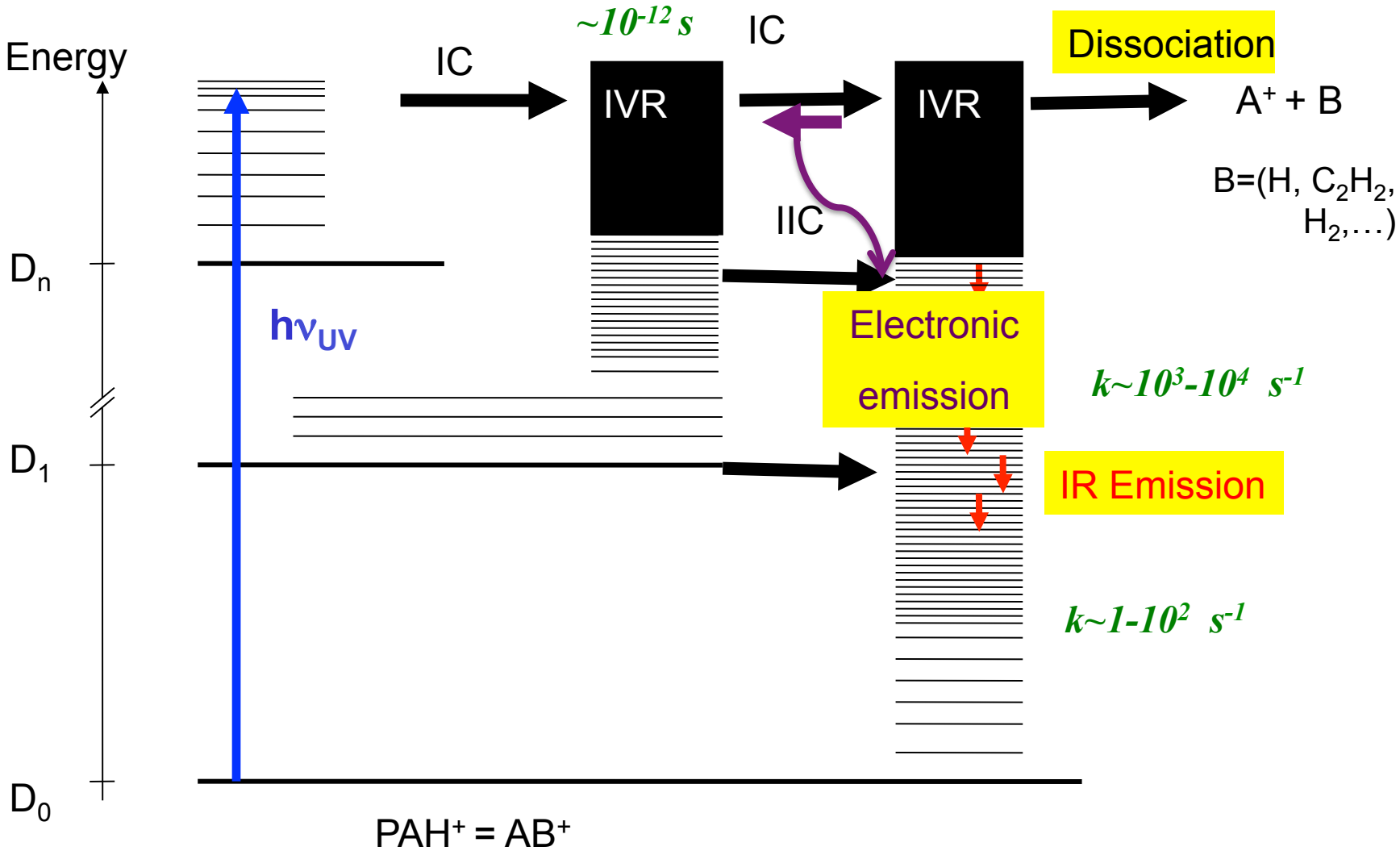
FT

$\nu_c = qB/2\pi m$

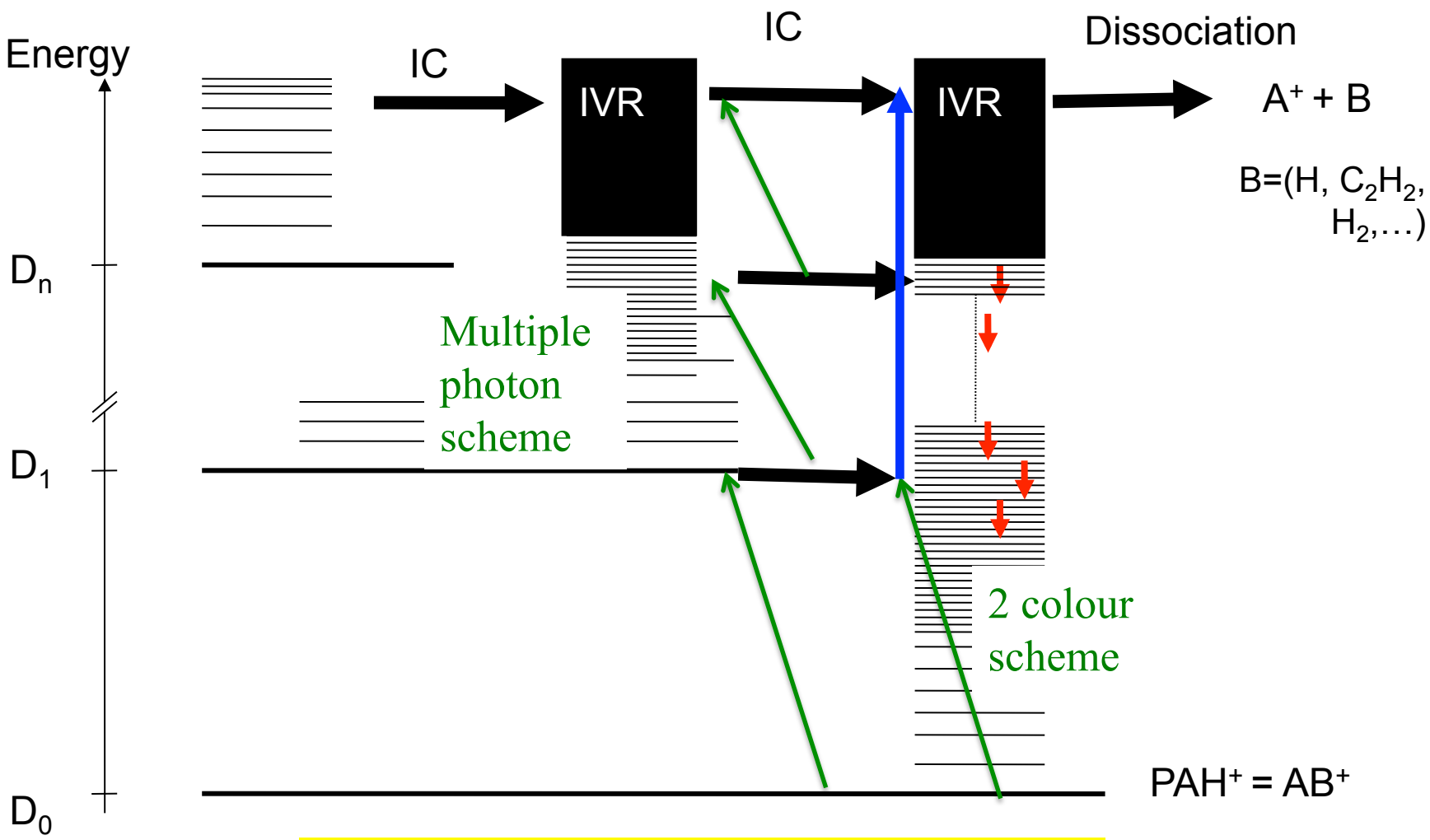


FTICR-MS: non- destructive, very high mass resolution (>10^4), sensitivity, selectivity

Photophysics of an isolated PAH

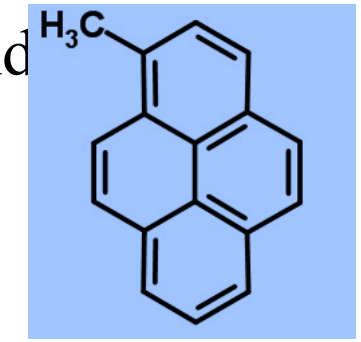


Electronic spectroscopy of a trapped PAH

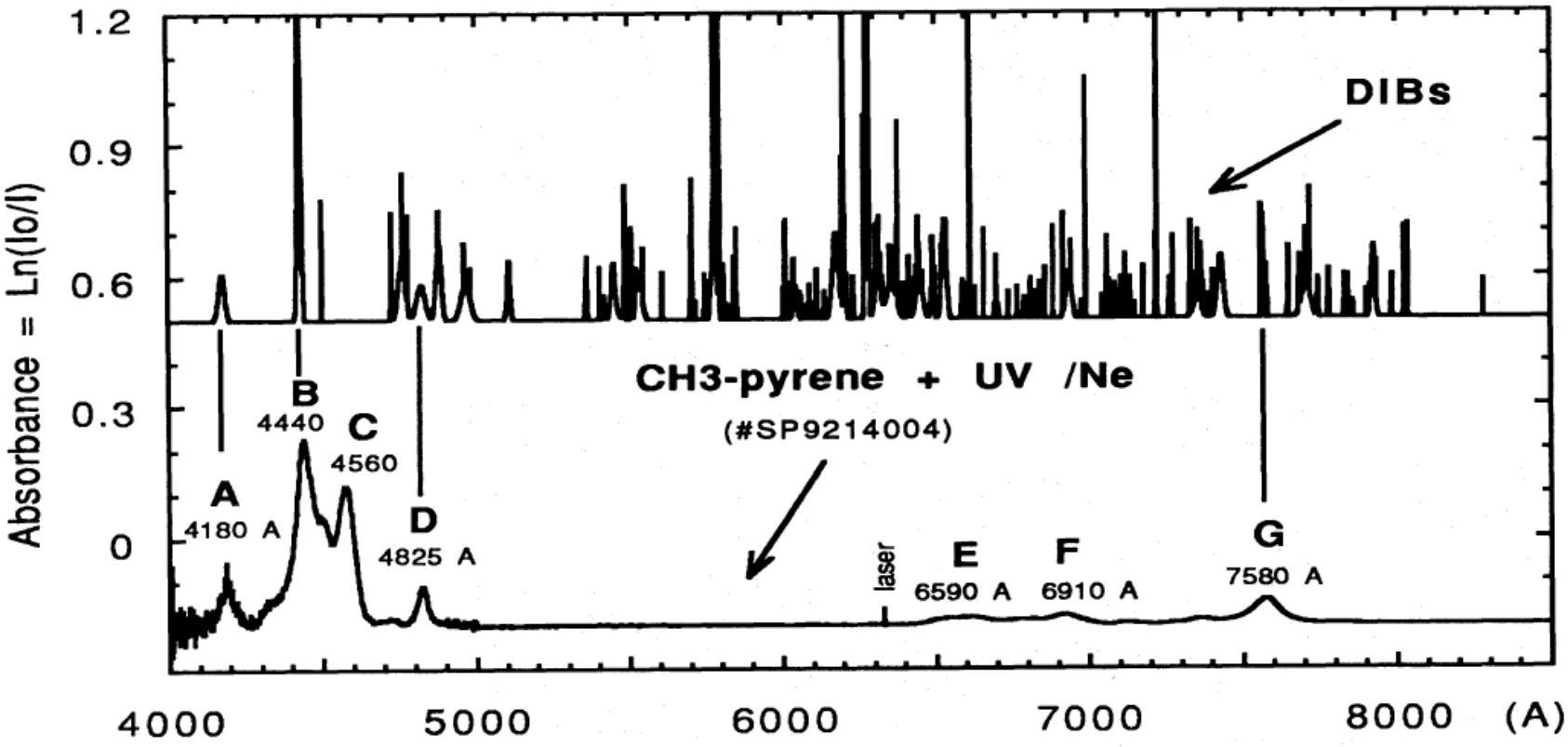


OPO (n photons) vs OPO (1 photon) + UV

A possible candidate for the main diffuse interstellar band one photoproduct of 1-Methylpyrene ?



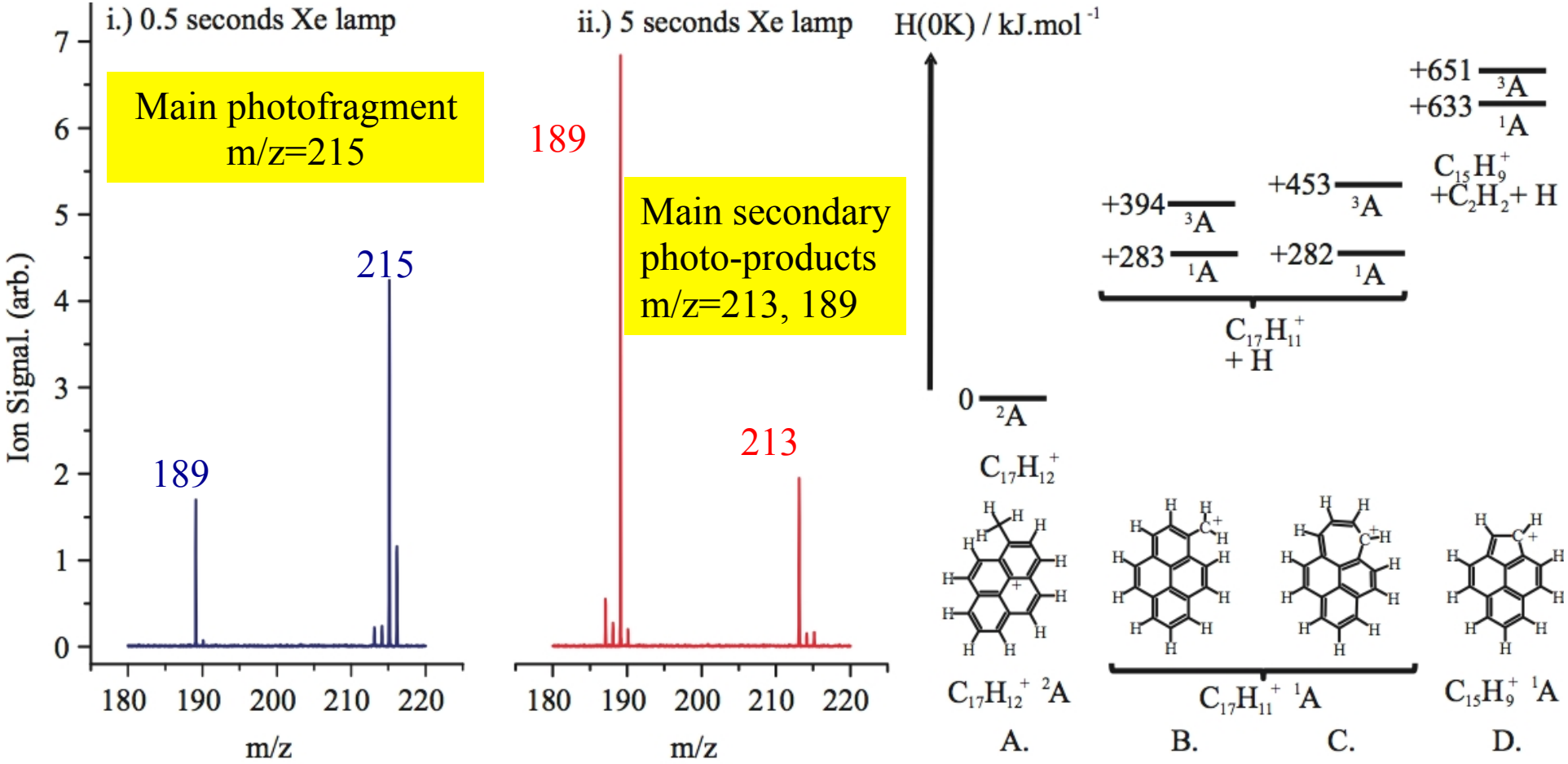
Main DIB at 4430 Å



1- Methylene pyrene + UV (Ly α) → photo product, possible carrier for indicated DIBs from matrix spectra.

Léger A., D'Hendecourt L., & Défourneau D. (1995), A&A 293, L53

1-Methylpyrene cation (m/z=216) fragmentation in PIRENEA



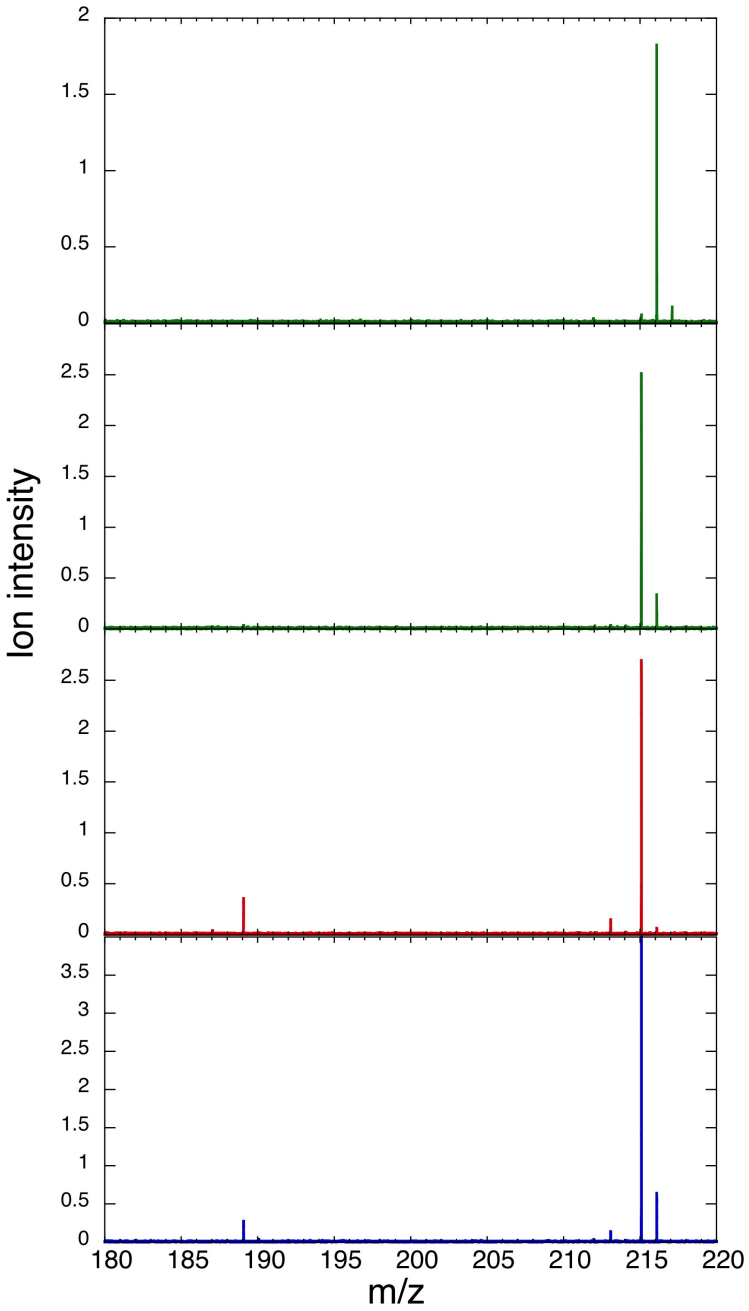
→ First investigation of the spectroscopy of m/z=215; possible presence of the 2 isomers

→ Need a 2 colour scheme

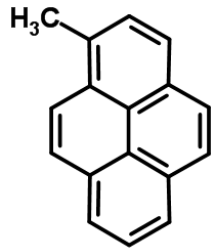
Kokkin et al. 2012, ISMS (67th meeting)

Kokkin et al. 2013, DIB conference. IAU Symp 297, 286

New experiments: spectroscopy of m/z=215 in the UV



Isolation of parent m/z=216

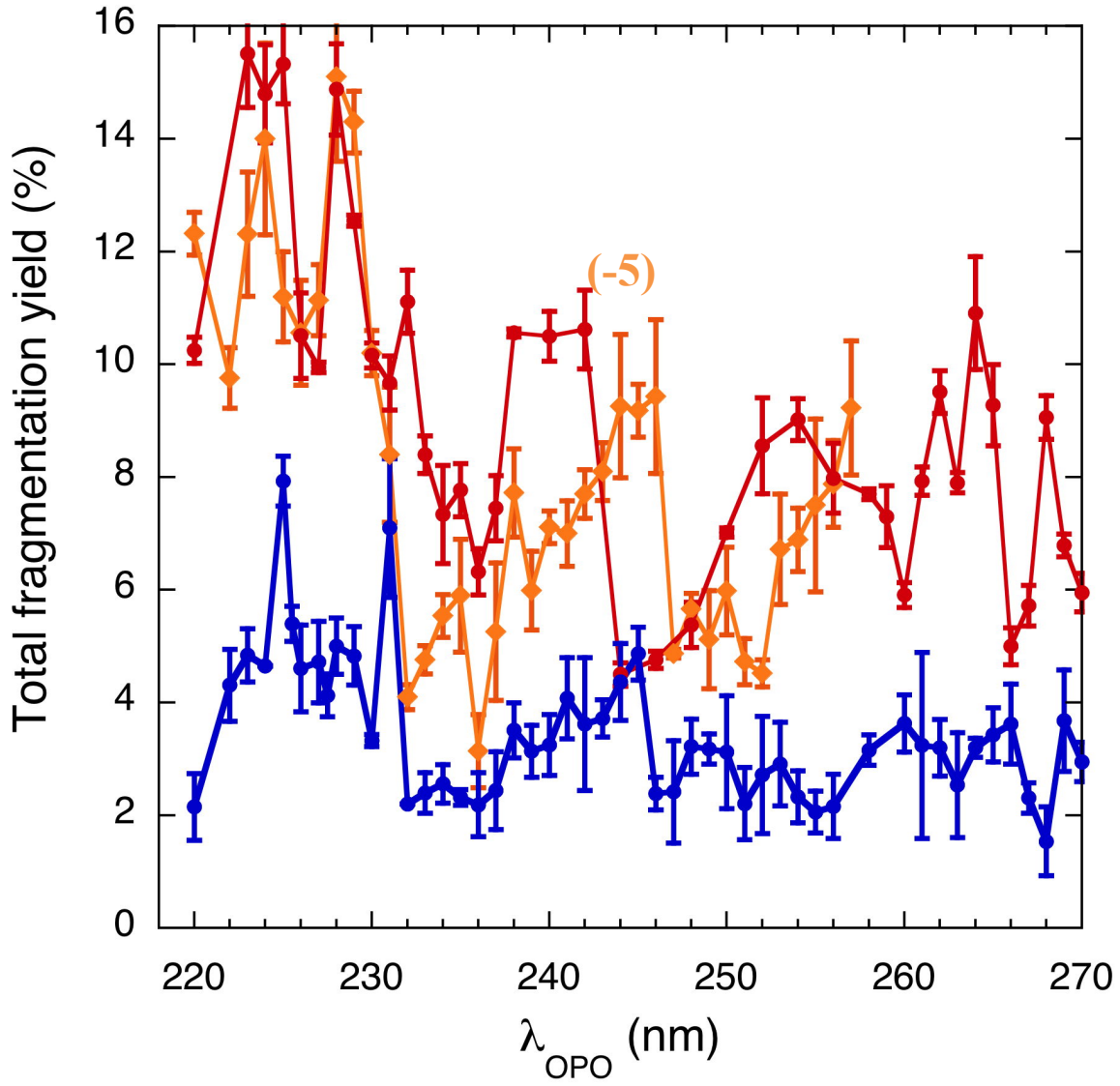


Production of fragment m/z=215 (Xe lamp)

Irradiation with OPO@225nm (5s; 10Hz; 0.4 mJ)

2 colour experiments: OPO@225nm + 266 nm (20 shots; 1 Hz)

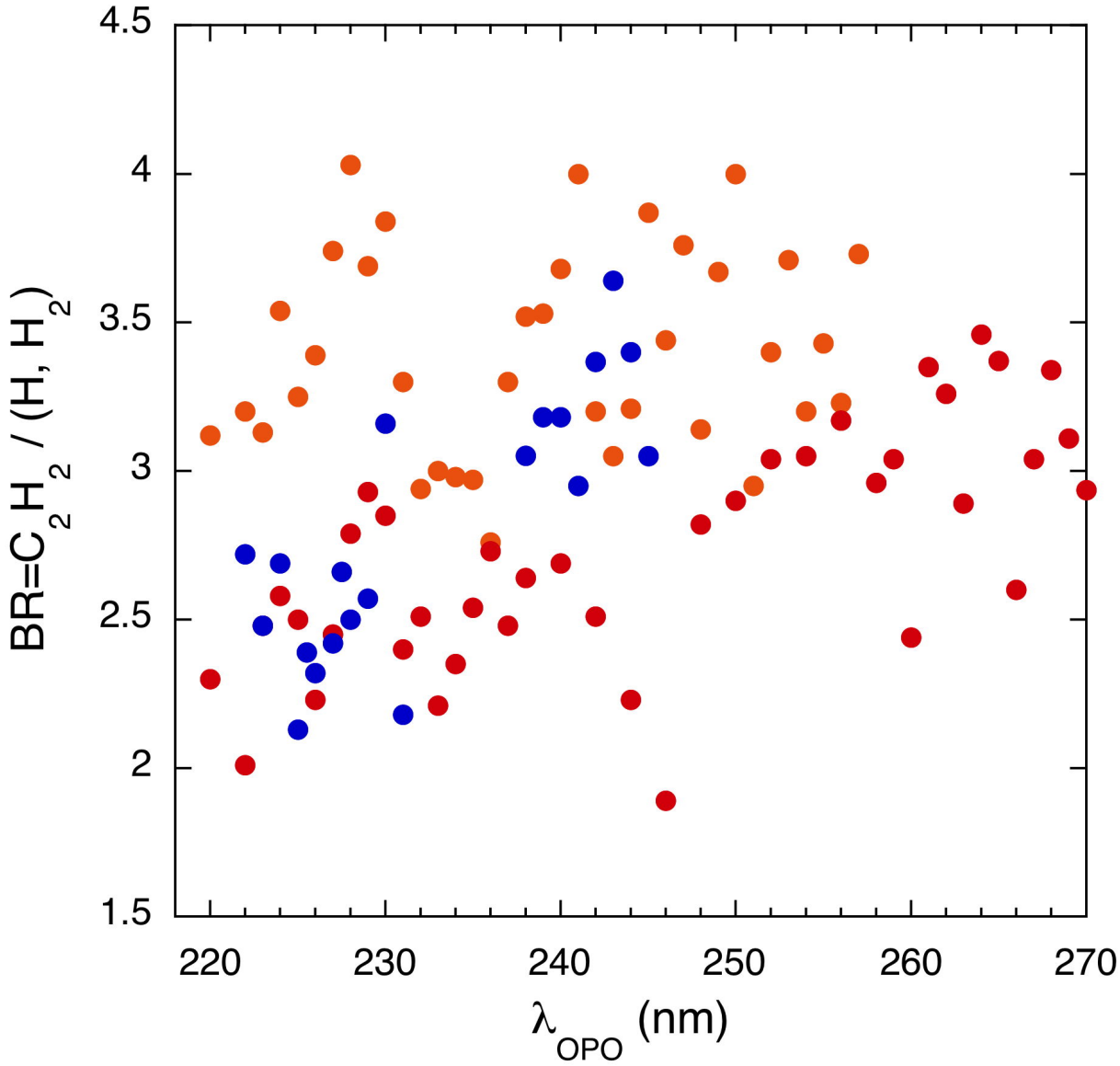
Spectroscopy of m/z=215 ($C_{17}H_{11}^{+}$) in the UV. Preliminary results



OPO only

2 colours (OPO+266nm):
Q_{frag}(266nm only)=1.5%

Spectroscopy of m/z=215 ($C_{17}H_{11}^{+}$) in the UV



Large variations of BR
m/z=189 / m/z=213+214

Very first conclusions

A lot of variations in the dissociation spectra and branching ratio (C_2H_2/(H,$\mathbf{H_2}$)

Variation of the photon excitation:

- OPO in the UV: complicated response curve + fluctuations from shot to shot –corrected at best using a variable filter (~0.4 mJ over the range [220-340 nm]) + average over 20 shots. Does not explain the variations of the BR.
- OPO only at 10 Hz. Dissociation is due to heating following absorption several shots (Frag/e in 130 ms)
- 2 colour scheme (OPO + 266 nm): no dissociation with OPO only – low dissociation with 266 nm; other= 2 colour events.

Relaxation: the delay was not found to be crucial in the range ~30 ns- 1µs as long as 266 nm is after the OPO

Very first conclusions

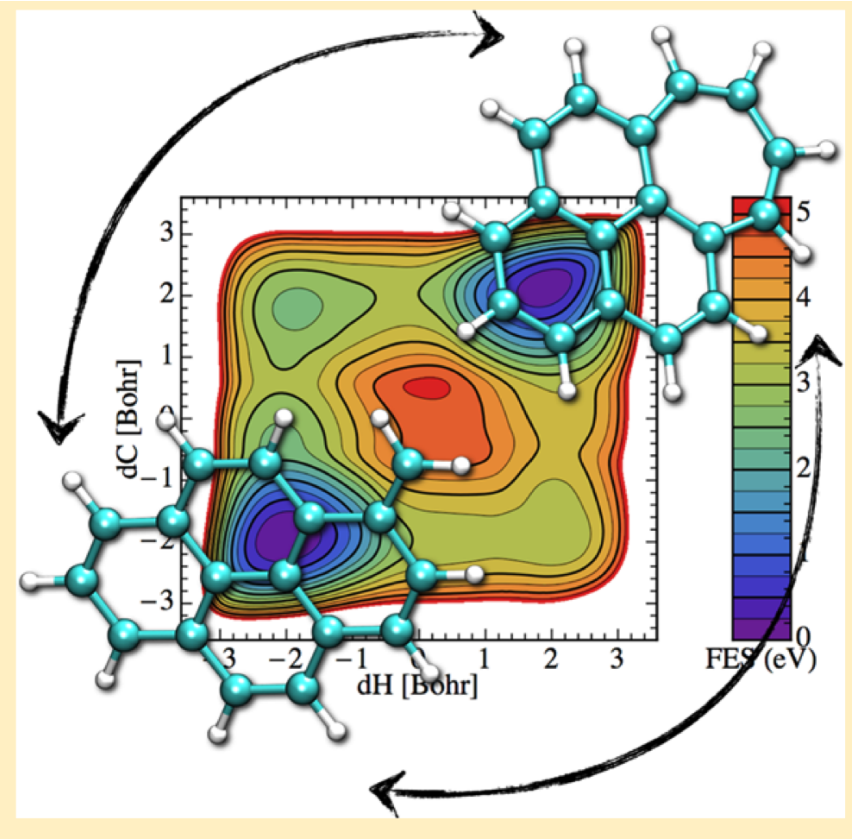
A lot of variations in the dissociation spectra and branching ratio (C_2H_2/(H,$\mathbf{H_2}$)

Variation of the ion populations:

- Variations of the spectrum and BR provide evidence for a contribution of both Isomer 1 and Isomer 2
- Isomer 1 has low BR=C_2H_2/(H,H_2) (<1) and Isomer 2 has high BR (>4) ?

  (BR=0.9 for dissociation by multiple photon absorption in the same pulse @266nm)
- Isomer 1 absorbs more efficiently at 266 nm than Isomer 2
- Isomer 2 absorbs more efficiently at [220-250 nm] than Isomer 1
- Effect of the formation process? Tests by changing the formation procedure (softer irradiation) but difficult to conclude.
- Effect of the excitation scheme? One isomer responds better to the OPO [220-250 nm], the other to 266 nm → challenges the 2 colour scheme.

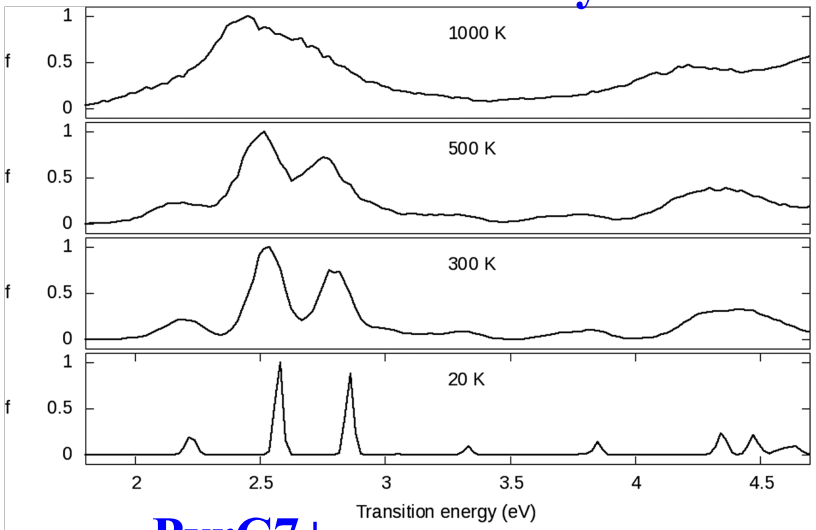
The two isomers of 1-Methylpyrene cation photofragments



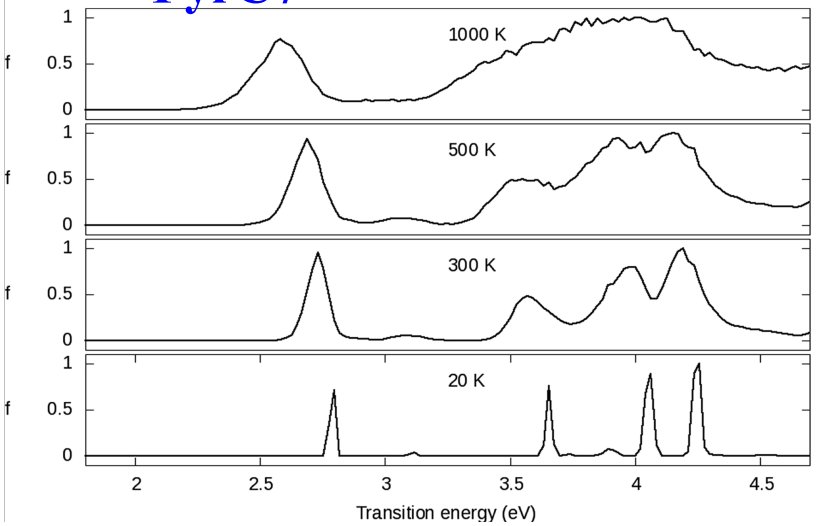
Rapacioli et al., 2015, J. Phys. Chem. A 119, 12845

→ The two isomers are involved in our experiments

PyrCH2+



PyrC7+



620 nm 410 nm 275 nm

Preliminary conclusions and perspectives

A very complicated case but a strong motivation for theoreticians

- Difficulty to quantify the contribution of both isomers. BR seems to be the best tracer.
- Further support from theory (BR,…) to rationalise the results

Advantages and disadvantages of cold ICR cell

- Easy production and selection *in situ* of the photofragments
- Efficiency of the cooling of the ions? Cryogenic environment + low-pressure He gas.
- Investigate band profiles in the visible part (~440 nm) using the 2 colour scheme