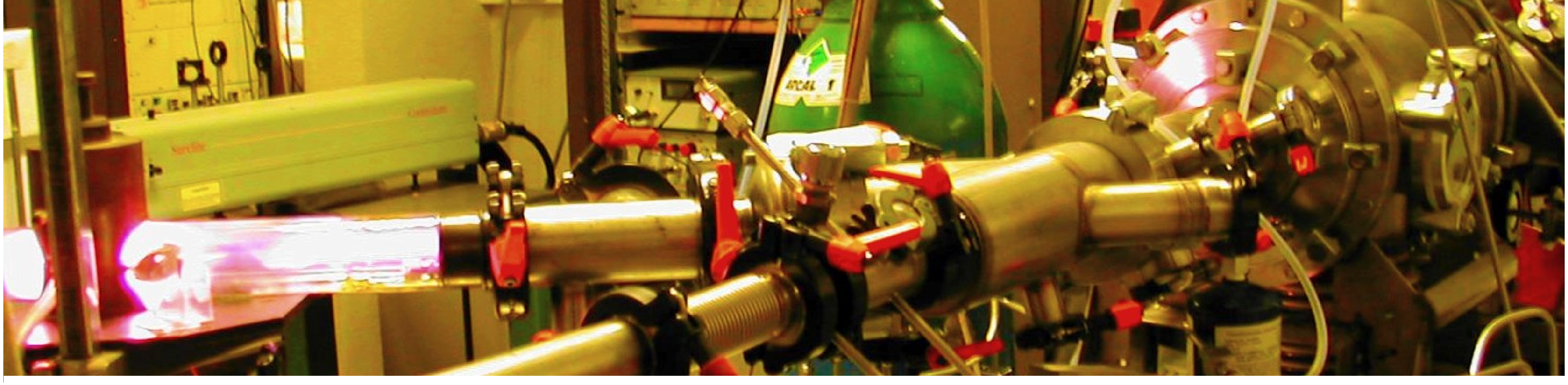
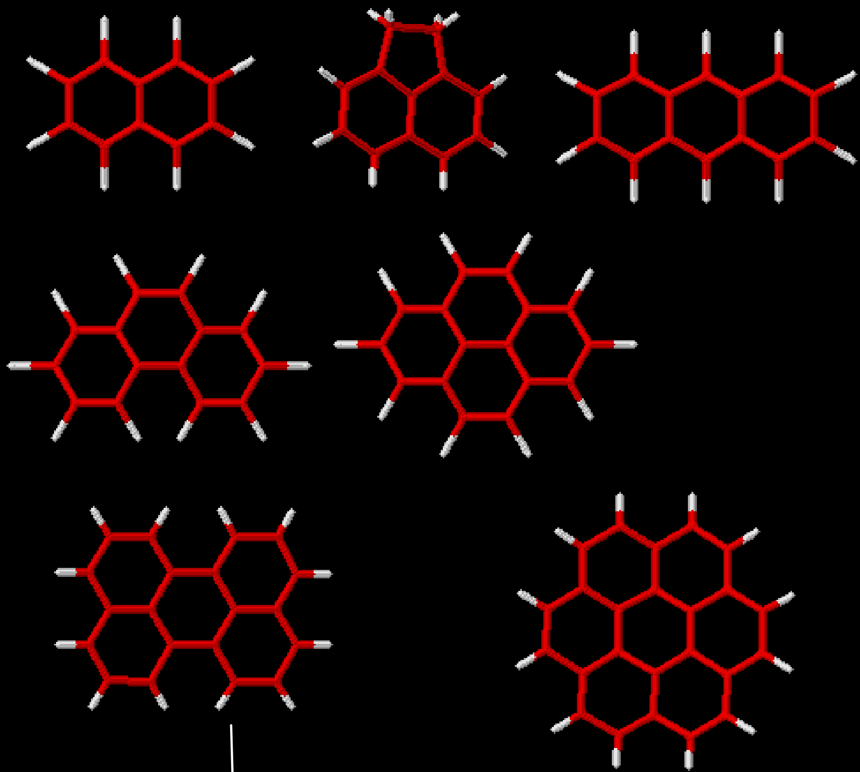


Recent results on recombination of PAH cations with electrons

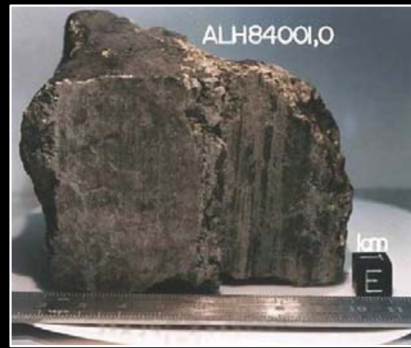
Ludovic Biennier

Laboratoire PALMS CNRS

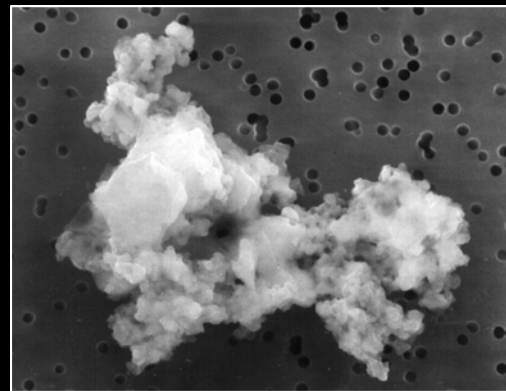
Polycyclic Aromatic Hydrocarbons



Combustion



Meteorites



IDPs

ISM

Planetary atmospheres?

Current (but recent) consensus: PAHs are ubiquitous

- Mid infrared emission features (at 3.28, 6.3, 7.7, 8.6, 11.3, 12.7 μm) observed in a variety of environments such as H II regions, post AGB stars, planetary nebulae, diffuse ISM… are attributed to PAH molecules

- PAHs are the building blocks of carbon IS dust

- Up to 10-20% of C could be locked up in PAHs

- But their chemistry is poorly known

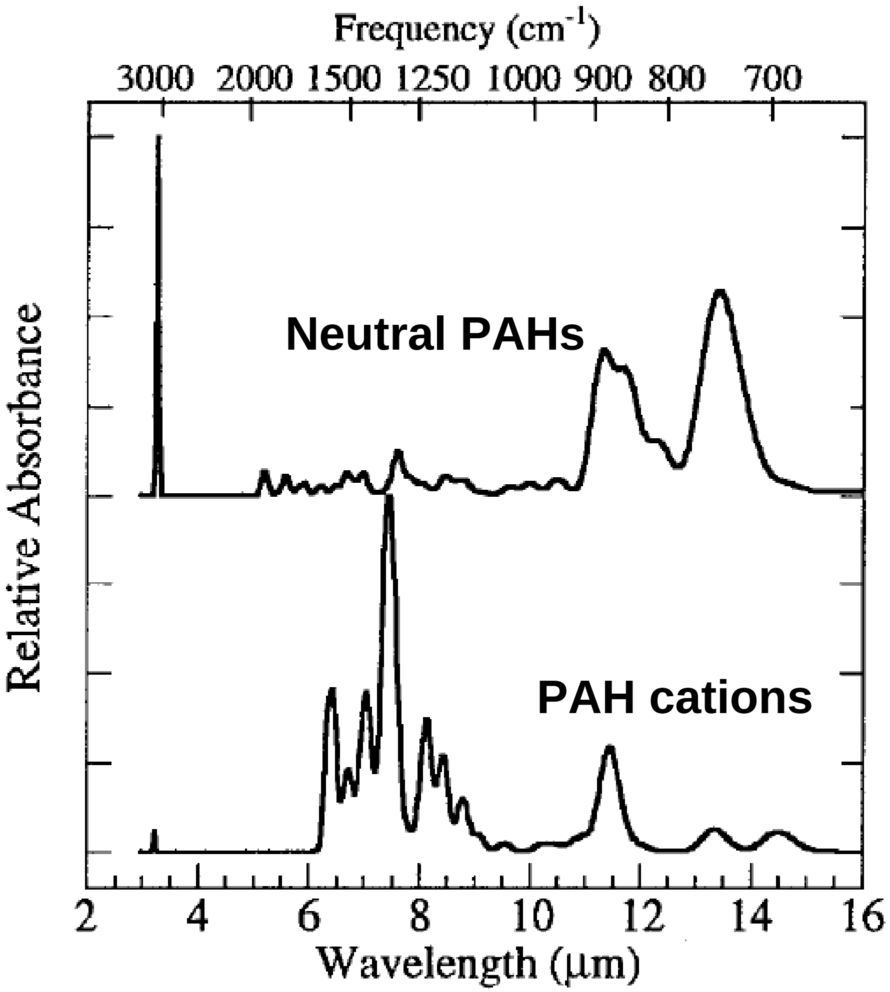
  How are PAHs formed and destroyed?

  What is their role in the formation of carbon dust particles

  How are they processed in space (may explain why no specific identification)?

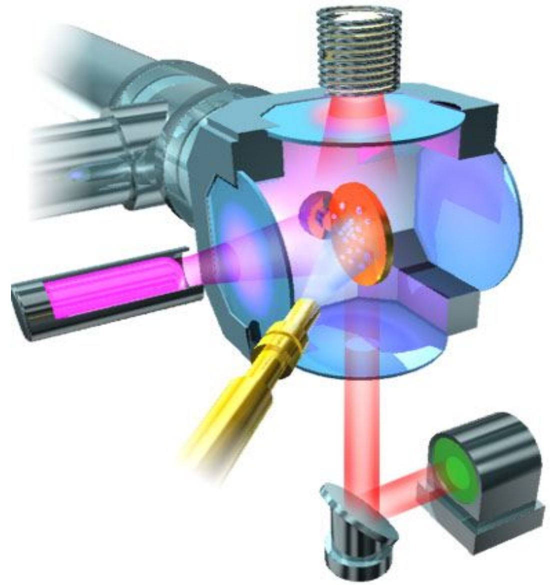
  What is their charge state?

Low temperature Mid-IR spectroscopy of PAH analogs



Allamandola, ApJ 1999

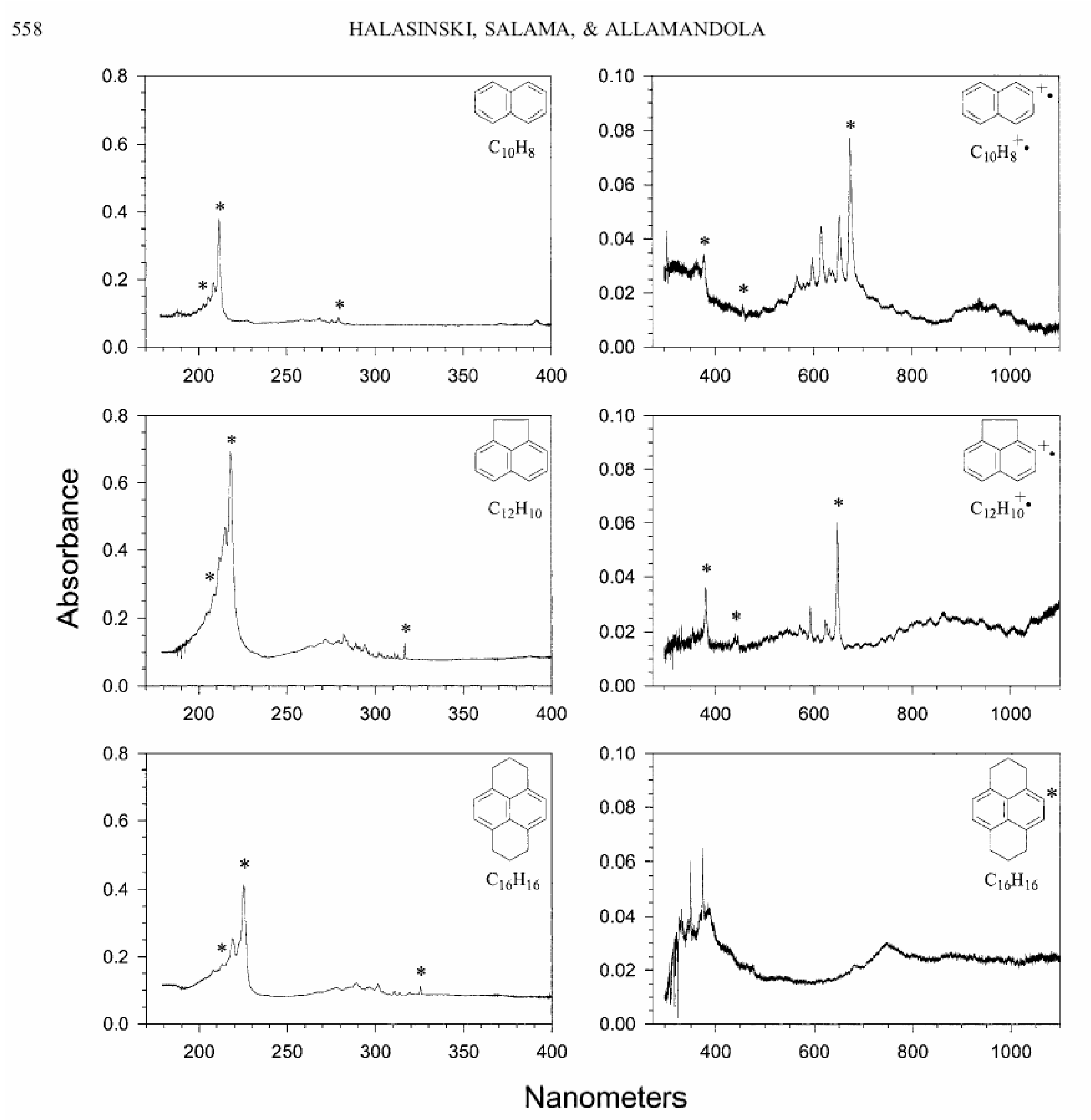
Absorption spectroscopy of PAH molecules trapped in Ne matrices



From Bernstein et al., Scientific American (1999)

→ The relative intensities of the bands depend on the PAH charge state

Laboratory low temperature UV – visible spectroscopy



- The spectra of the PAH cations are shifted towards the NIR compared to the neutrals
- Multi-wavelength lab approach to assess the possible contribution of the PAHs to the Diffuse Interstellar Bands

200+ Diffuse Interstellar Bands. Zero identification

- DIBs: Absorption bands seen in the NUV to NIR spectral range in lines of sight crossing diffuse clouds

- Small PAH cations and large neutral PAHs have been proposed as DIB carriers

Processes governing the PAH charge state

Include:

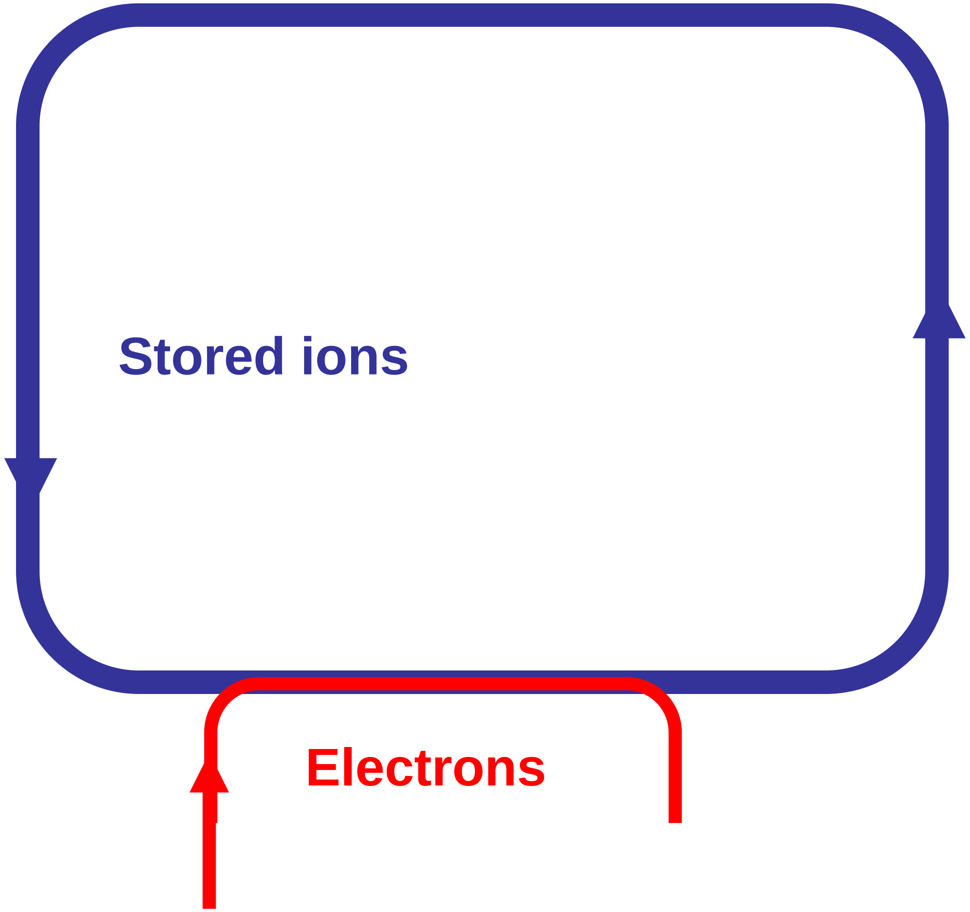
- photo-ionization (diffuse clouds)
- electron attachment (dense clouds)
- photo-detachment
- electron-ion recombination (main neutralization channel)

But

laboratory data are severely lacking (PAHs are difficult to handle)

Laboratory approaches

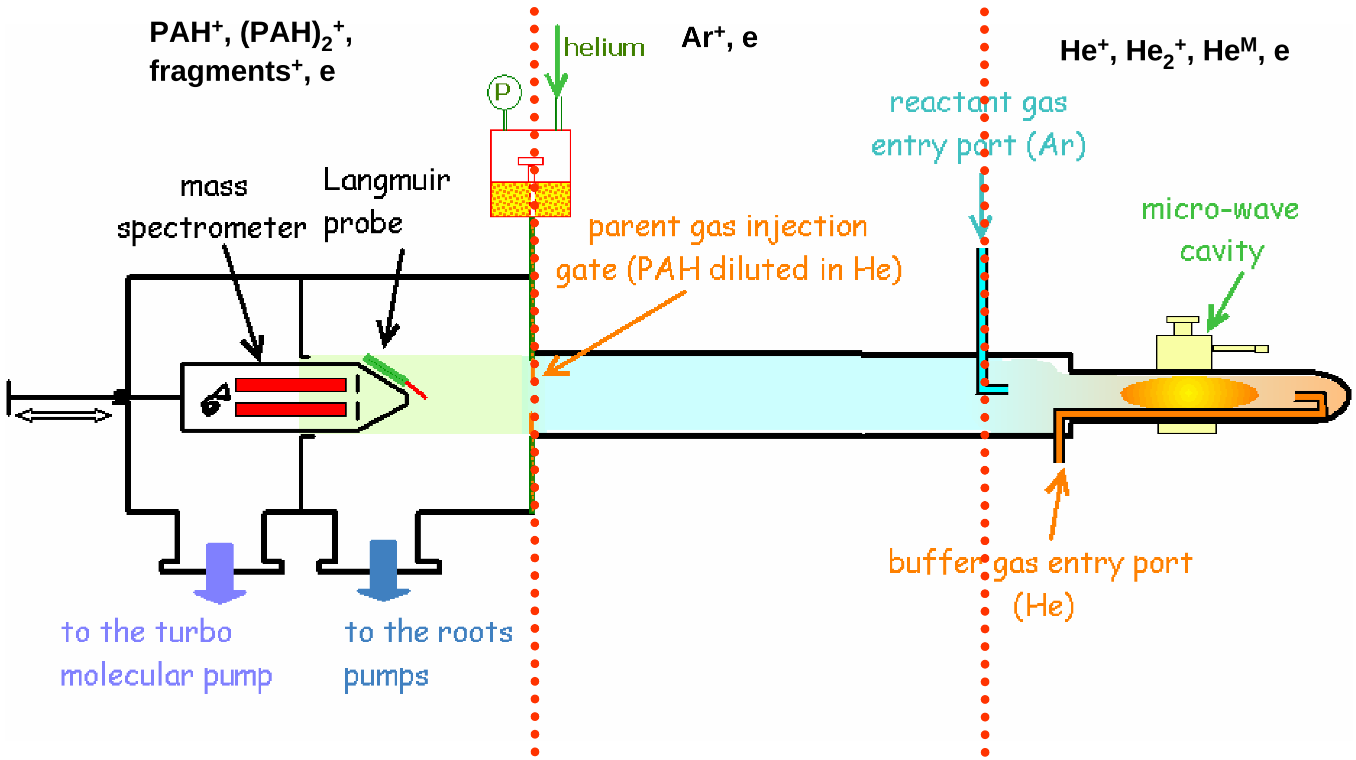
- Merged beams with storage rings



Heavy ions: challenge to merge high energy ion beam with electron beam propagating at the same speed

Swarm experiments: flowing afterglow

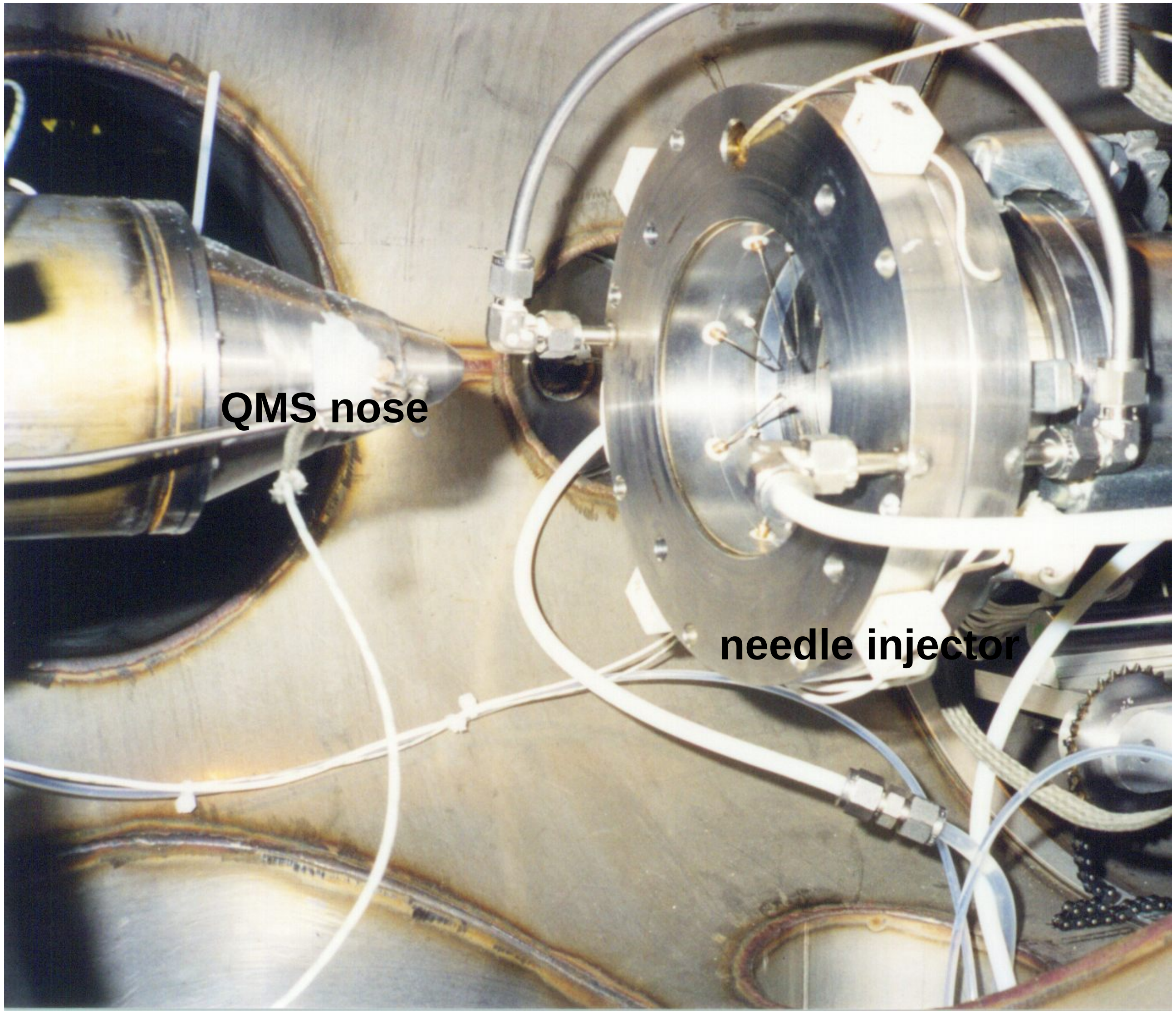
• Flowing afterglow reactors have been used extensively to study dissociative recombination of volatile ions at room temperature



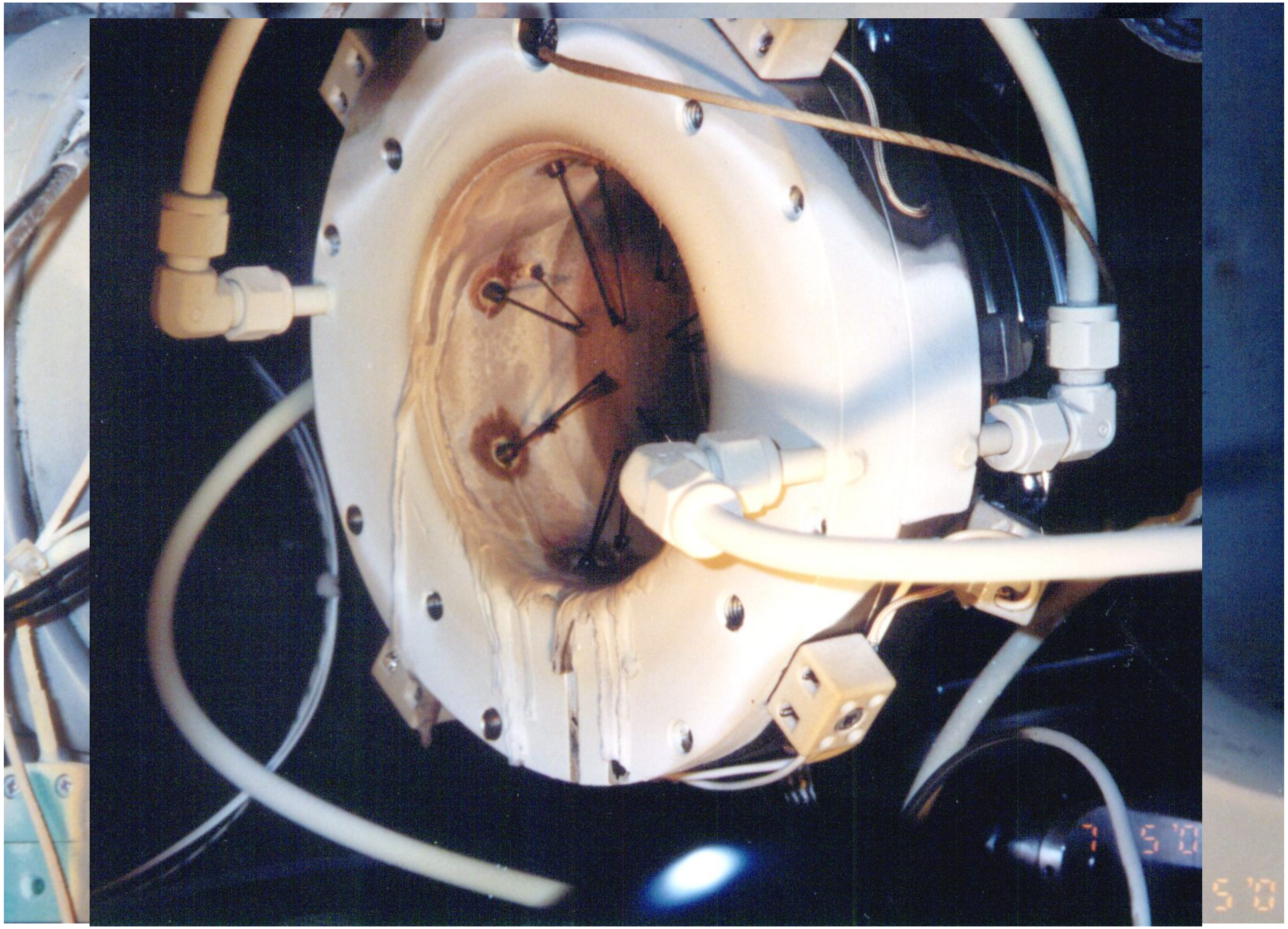
Problem:

low yield of PAH ion production by charge exchange (PAH + Ar^+ → PAH^+ + Ar)

the apparatus before experiment…….



…….and after.



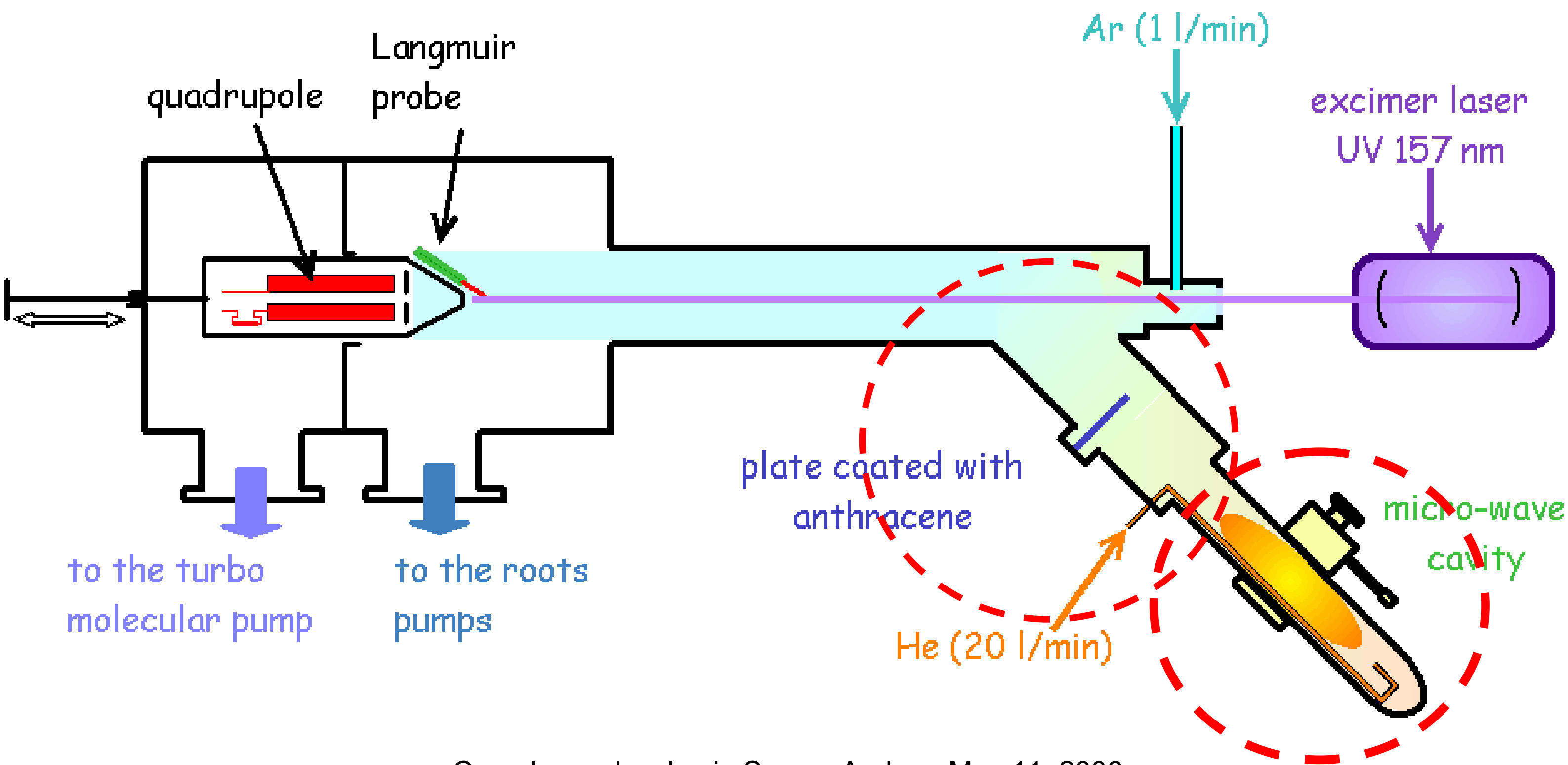
• Severe problems of condensation onto the walls of the chamber

Recent evolution: from the FALP-MS to the FℓAPI

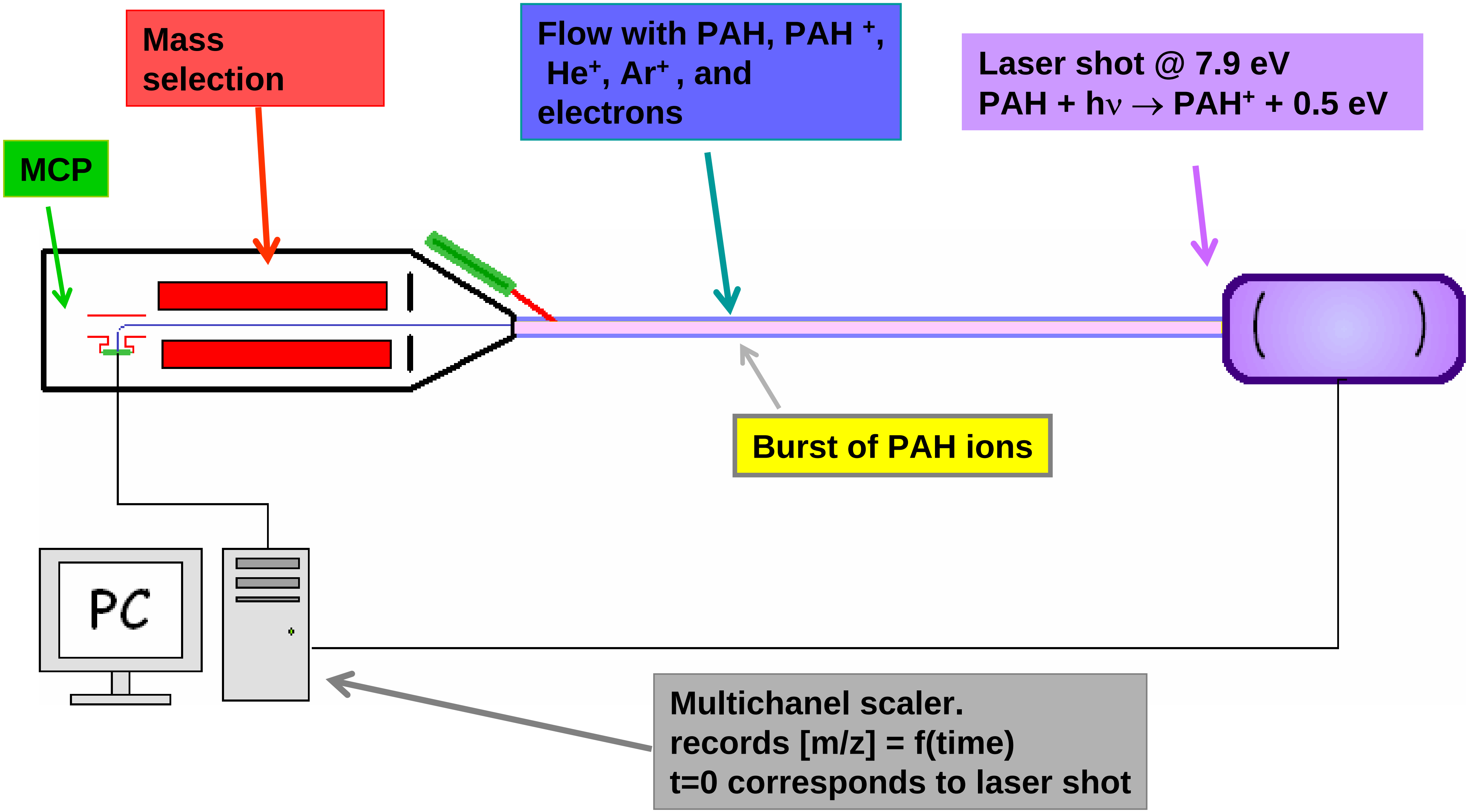
• PAHs coated on a plate are evaporated in the chamber

•The plasma provides the thermalized electrons

• PAH ions are generated efficiently by one photon photoionization of PAH vapors



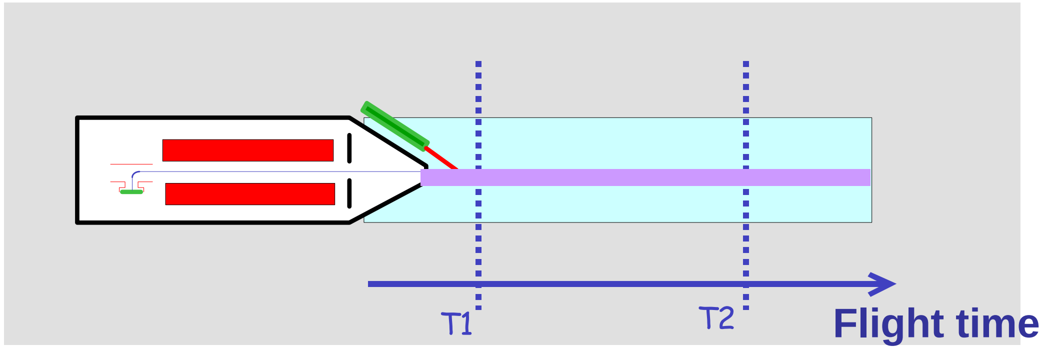
Principle

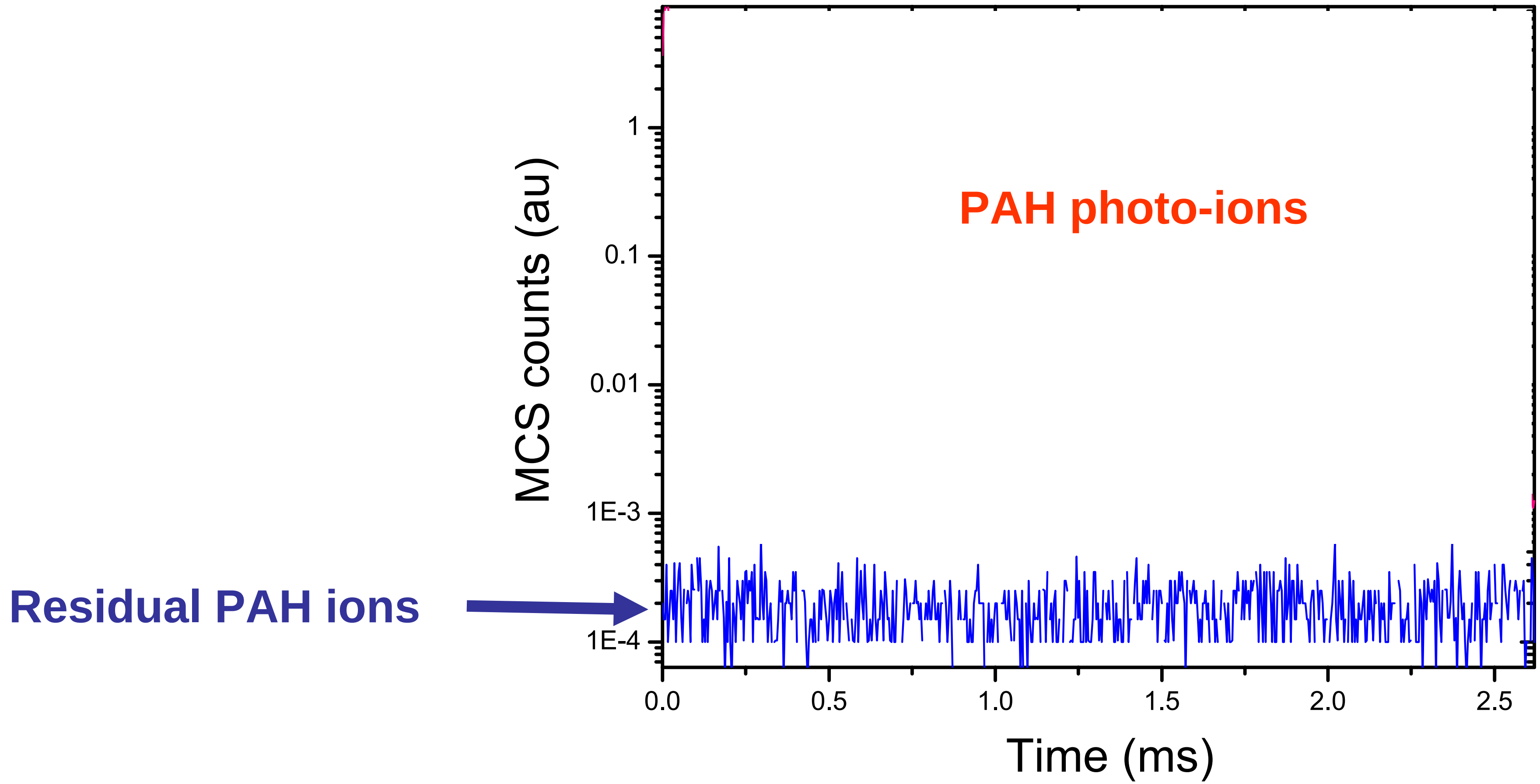


Mass selection
Flow with PAH, PAH +, He+, Ar+ , and electrons
Laser shot @ 7.9 eV
PAH + hν → PAH+ + 0.5 eV
MCP
Burst of PAH ions
PC
Multichanel scaler.
records [m/z] = f(time)
t=0 corresponds to laser shot

Time profile of the PAH ion population

•Step 1: Measuring PAH(t)

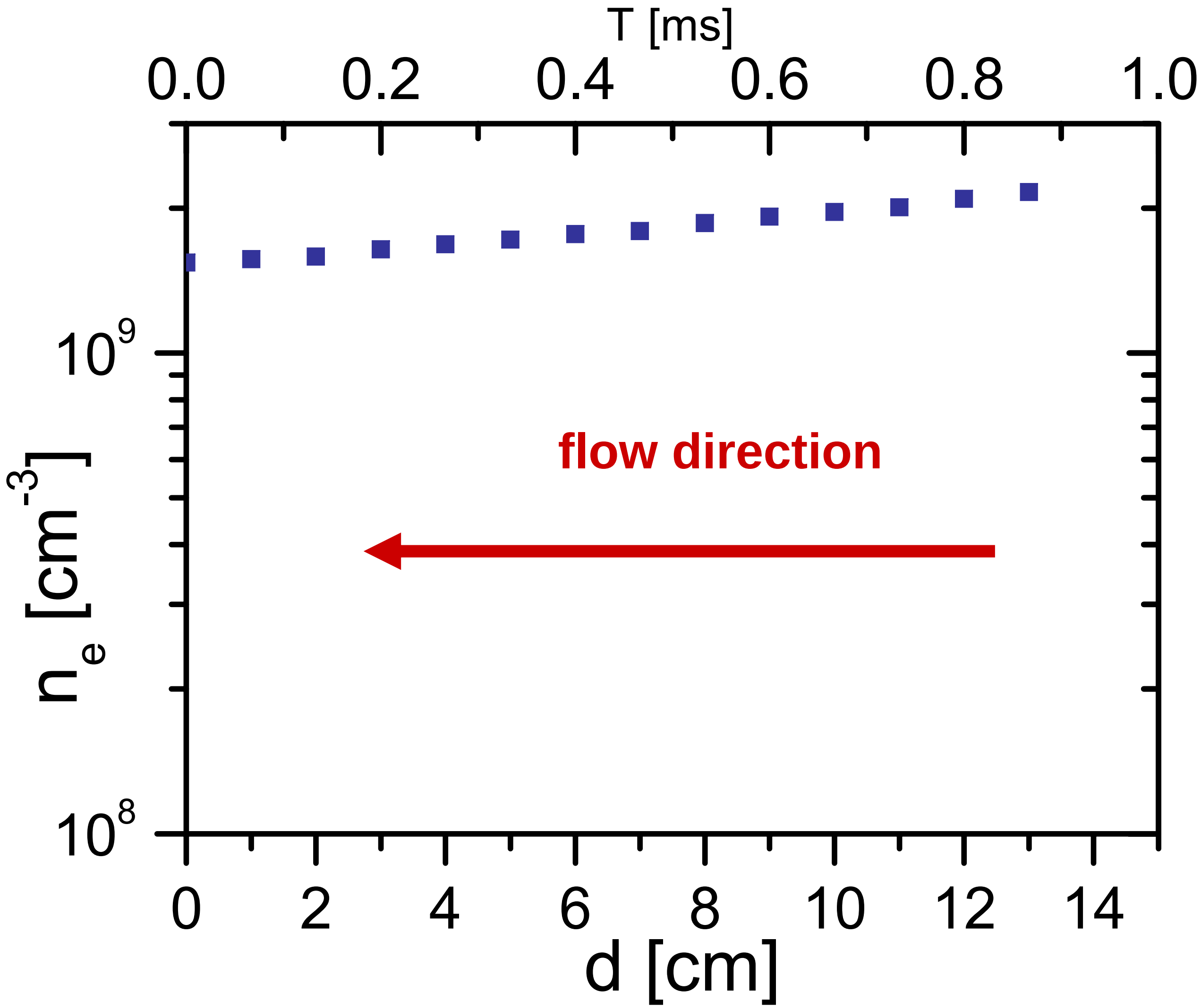




Electron density LP measurements

•Step 2: Measuring $n_e(z)$

• Notice that the electron density should be maintained in excess



Chemistry in the afterglow

- PAH ion generation

$$Ar^{+} + PAH \xrightarrow{k_f} PAH^{+} + Ar$$

$$PAH \; + h\nu \longrightarrow PAH^{+} + e$$

- Possible reactions in the chamber:

  - dimer formation $\quad PAH^{+} + PAH \xrightarrow{k_{\dim}} (PAH)_2^{+}$
  - dimer recombination $\quad (PAH)_2^{+} + e \xrightarrow{\alpha_2} products$
  - electronic attachment $\quad PAH + e \xrightarrow{\beta} PAH^{-}$
  - cation recombination $\quad PAH^{+} + e \xrightarrow{\alpha_1} products$

The information retrieval journey

The rate of destruction of PAH ions is given by:

Loss by diffusion

$$\frac{d[PAH^+]}{dt} = -\alpha[PAH^+][e]_d - k_{dim}[PAH^+][PAH] - \frac{D_a}{\Lambda^2}[PAH^+]$$

$$= -\alpha[PAH^+][e]_d - K[PAH^+]$$

… which can be written after integration

$$\ln\frac{[PAH^+](t_1)}{[PAH^+](t_2)} = -\alpha\int_{t_2}^{t_1}[e](d)dt - K(t_1 - t_2)$$

[PAH⁺](t) measured with QMS

Electron number density [e] Measured with mobile Langmuir probe. [e] >> [PAH⁺]

Choice of identical t1 and t2 for different [e] → constant term

Afterglow composition

Before laser shot:

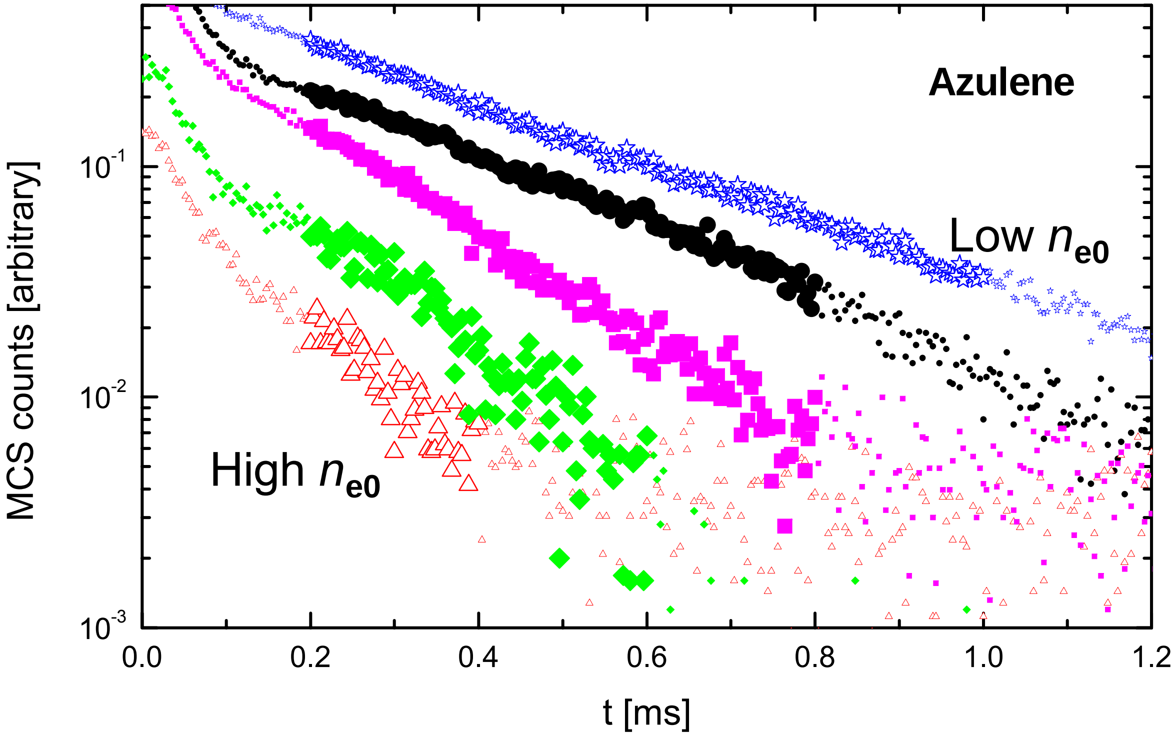
	[He]	[Ar]	[PAH]	$[He^+]+[Ar^+] \cong [e^-]$	$[PAH^+]$
Order of magnitude ($cm^3\ s^{-1}$)	2.6×10^{16}	10^{15}	$<5 \times 10^{10}$	3×10^8 to 5×10^9	10^6 to 5×10^7

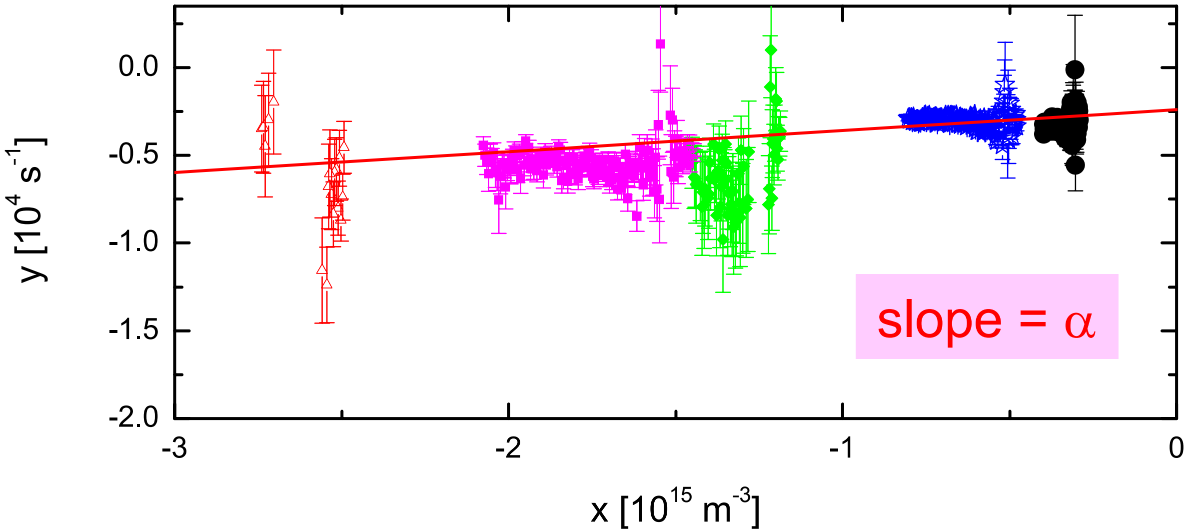
After laser shot:

$[e^-]$ returns to steady state

Excess of $[PAH^+]$

Time evolution of the [PAH$^+$] population for variable n_{e0}





- Azulene, $C_{10}H_8$, mass 128,~2x10^4 laser shots

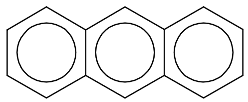
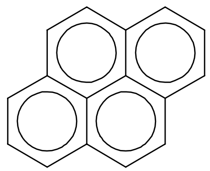
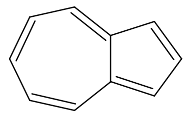
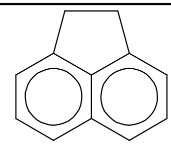
- From a set of PAH ion population time profiles & electron density measurements, we can plot *y* vs *x* with

$$y \equiv \frac{\ln\left(\frac{[A^+(t_1)]}{[A^+(t_2)]}\right)}{t_2 - t_1}$$

and

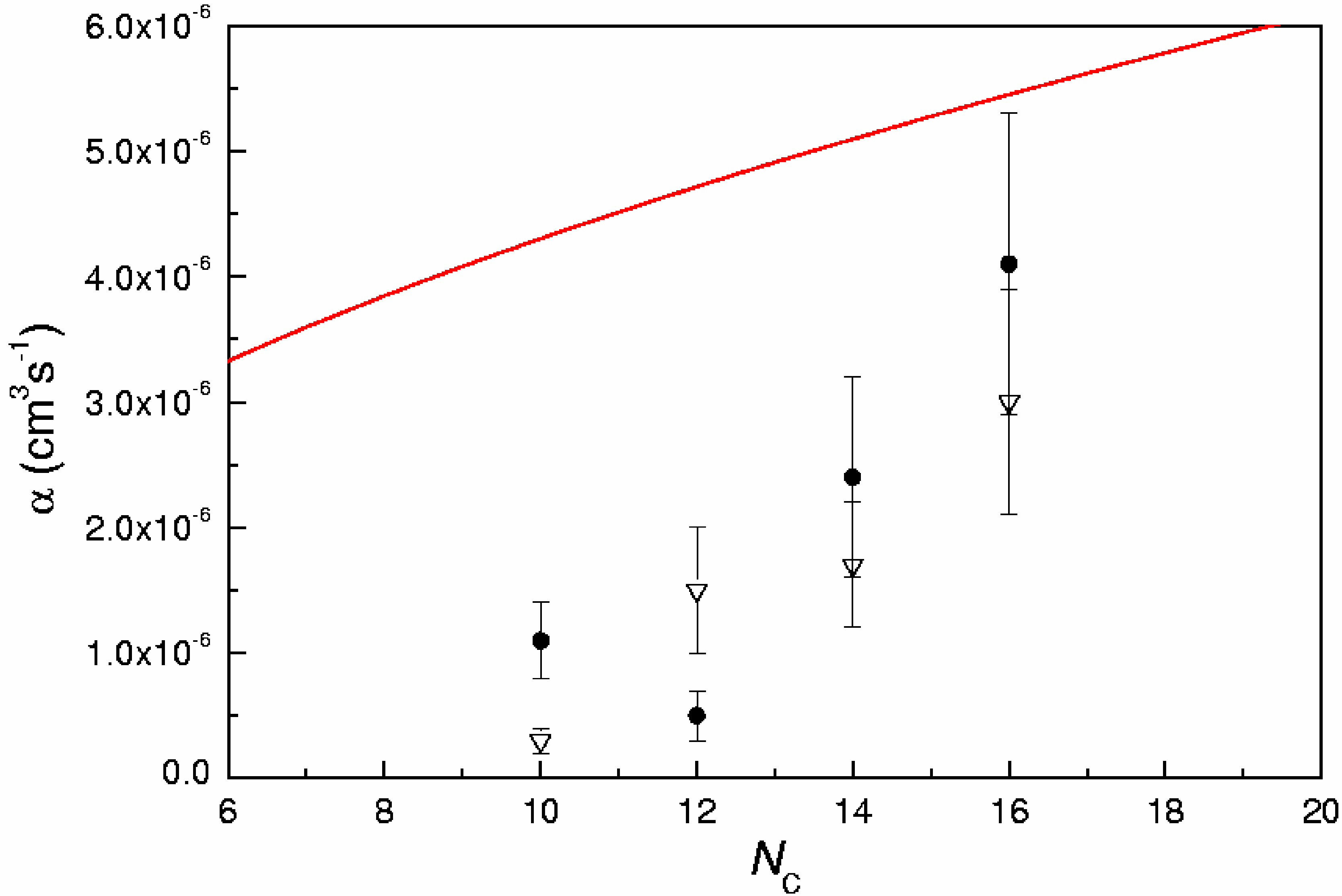
$$x \equiv -\frac{1}{v}\frac{\int_{z_1}^{z_2} n_e(z)dz}{t_2 - t_1}$$

Experimental results

Name	Anthracene ($C_{14}H_{10}$)	Pyrene ($C_{16}H_{10}$)	Azulene ($C_{10}H_8$)	Acenaphthene ($C_{12}H_{10}$)
Structure				
Mass (amu)	178.23	202.25	128.17	152.19
IP_z (eV)	7.42	7.41	7.43	7.78
p_υ (mbar)	2.7×10^{-5}	7.6×10^{-6}	1.8×10^{-2}	4.0×10^{-3}
σ_{PI} (Å^2)	0.14	0.16	0.10	0.12
k_{rec} (10^{-6} cm^3/s)	**2.4 ± 0.8**	**4.1 ± 1.2**	**1.1 ± 0.3**	**0.5 ± 0.2**

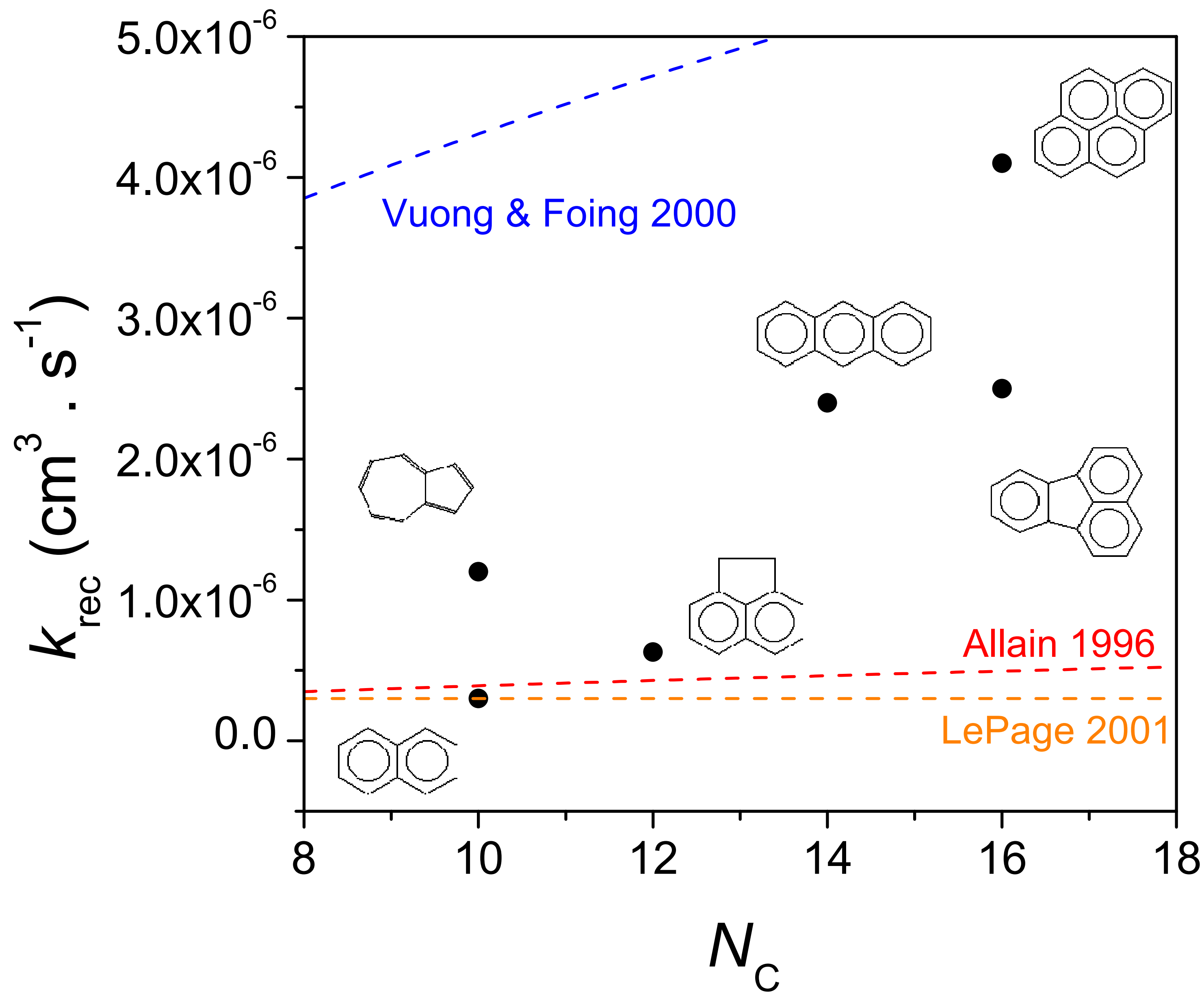
- Experimental recombination rates at T=300K are high

Trends with size

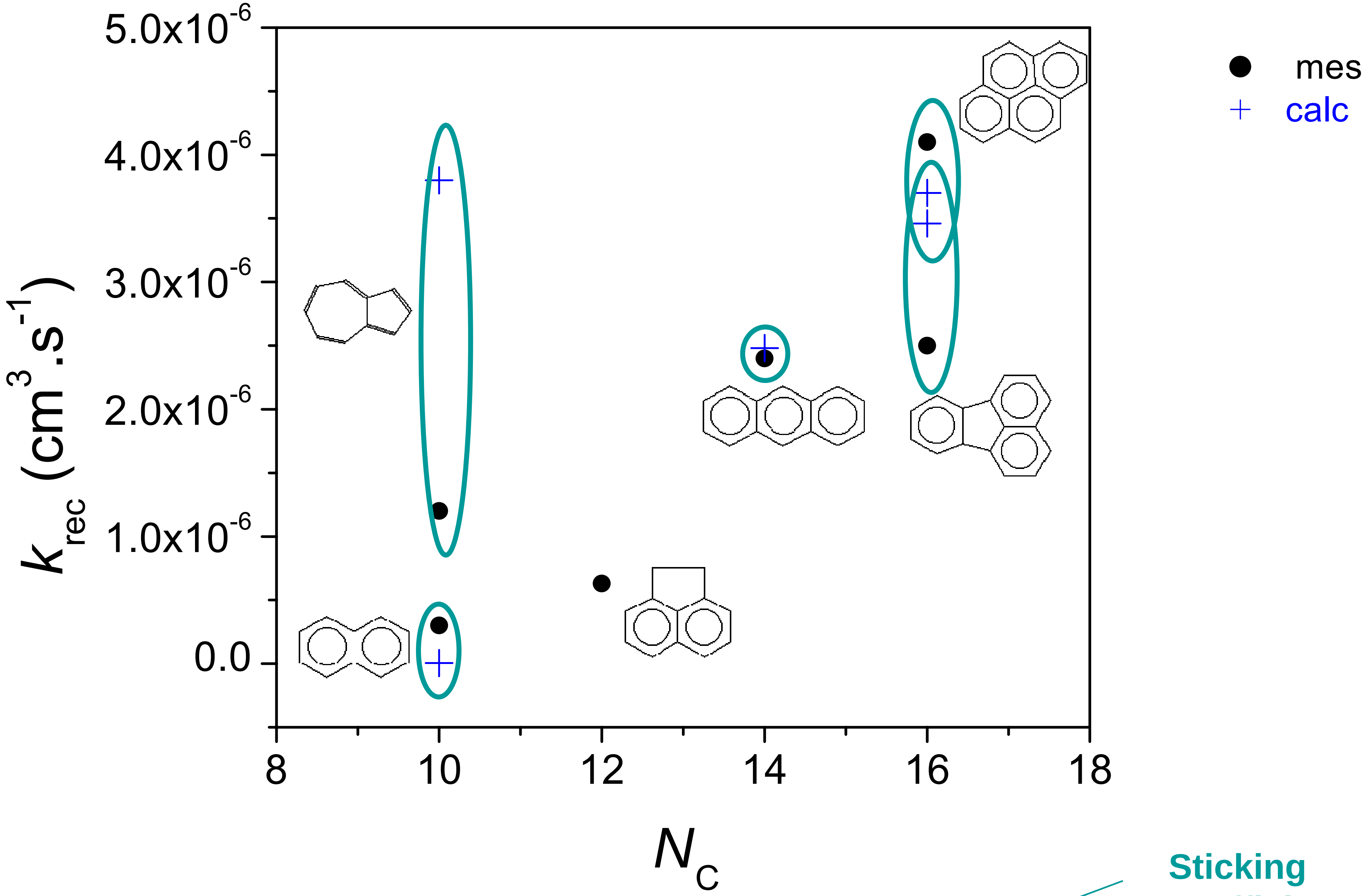


- Spitzer limit with sticking coefficient of 1

Comparison with models



Comparison with models (cont'd)

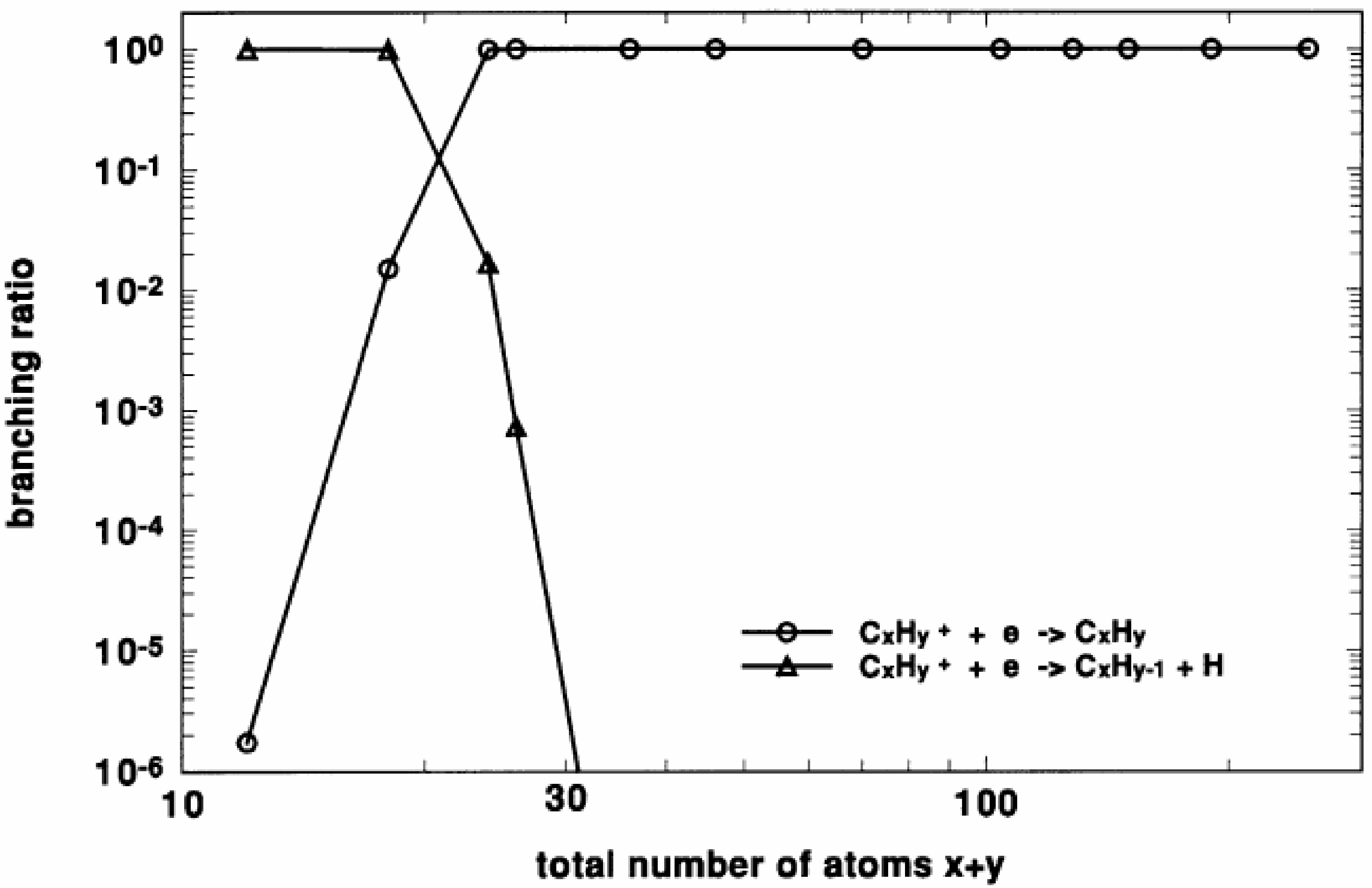


$$k_{rec} = C \cdot N_C^{1/2}\, T^{-1/2}\, s(e)$$

Sticking coefficient *f*(EA)

(Ruiterkamp 2005)

Nature of the products



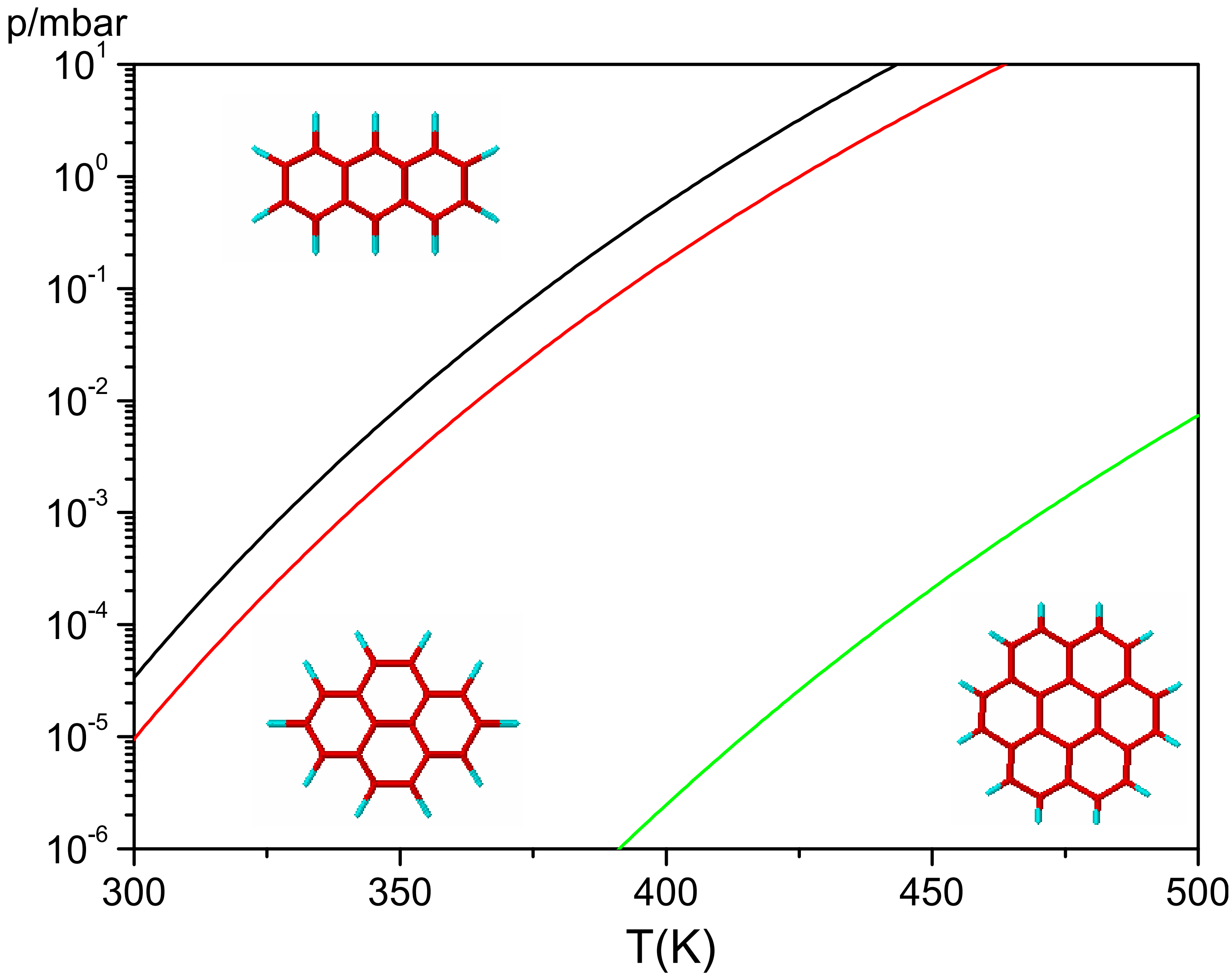
• Recombination is expected to be non dissociative for PAH cations larger than Pyrene

(Le Page 2001)

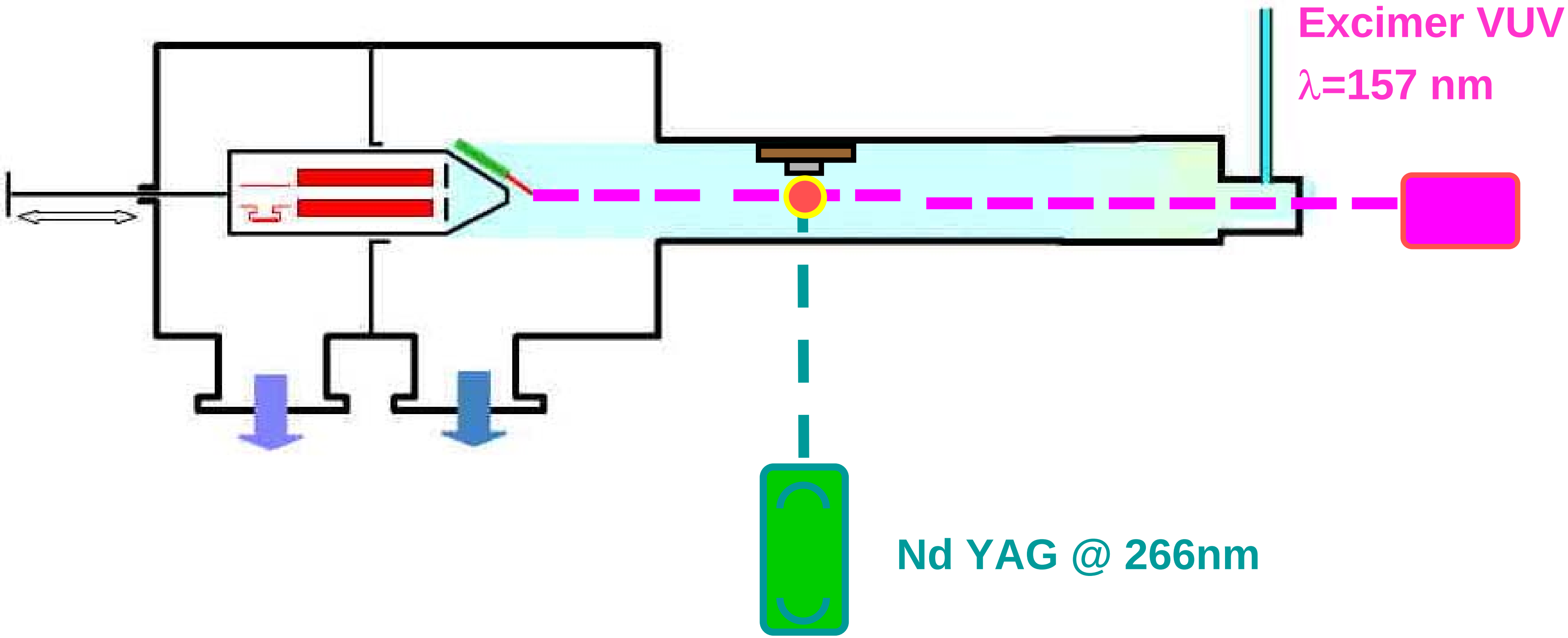
Suitable candidates are ?

- This experiment can be used for any PAH^+
  - whose neutral parent has a vertical ionization potential lower than 7.9 eV
  - even if electron attachment occurs
  - with a molecular mass lower than 1000 amu
  - but the vapor pressure must be high enough
- Small quantities of parent neutral are required.
  - The price becomes less important.

Investigations limited by the PAH vapor pressure

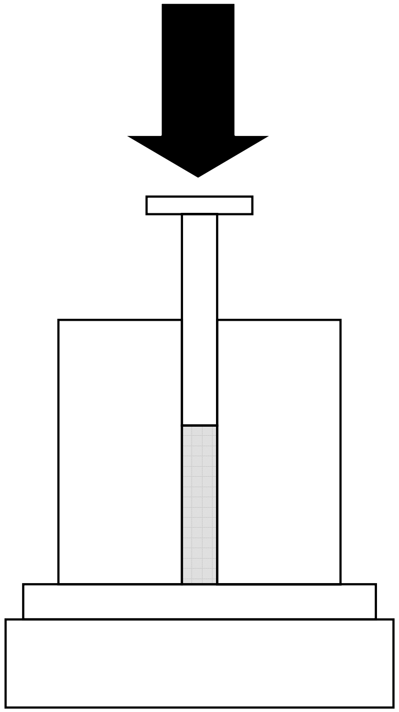


Exploring new ways for producing PAH ions

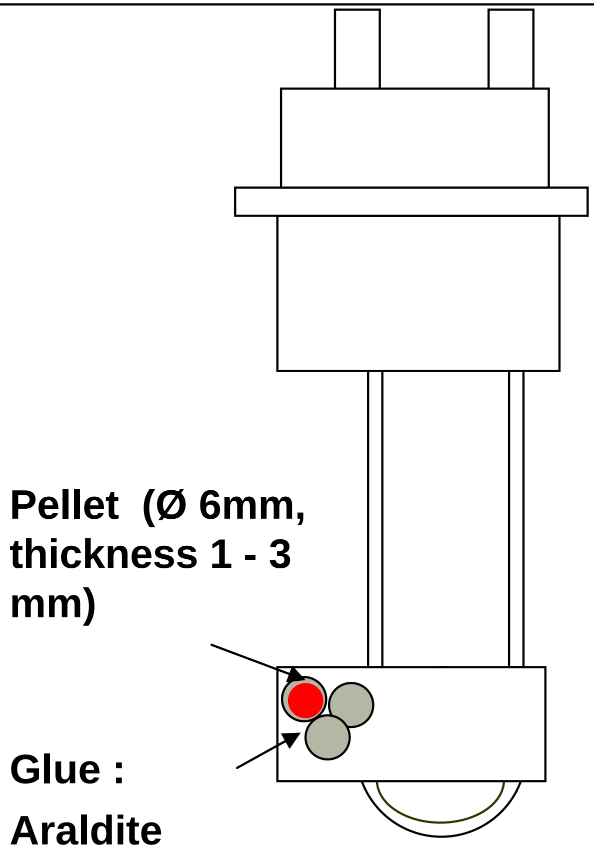


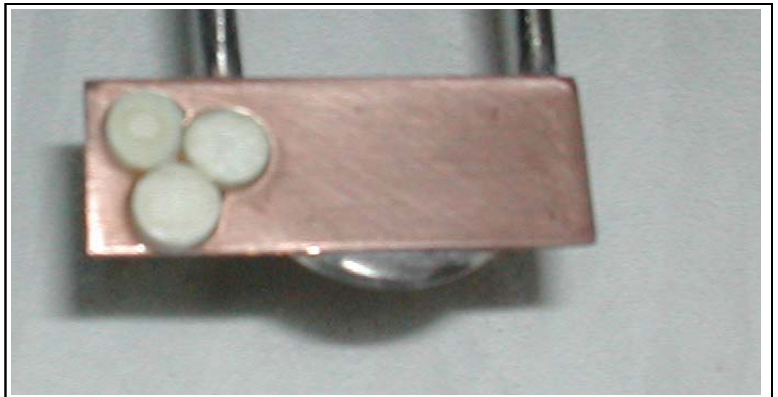
•No plasma: photoelectrons only

Preparation of the sample

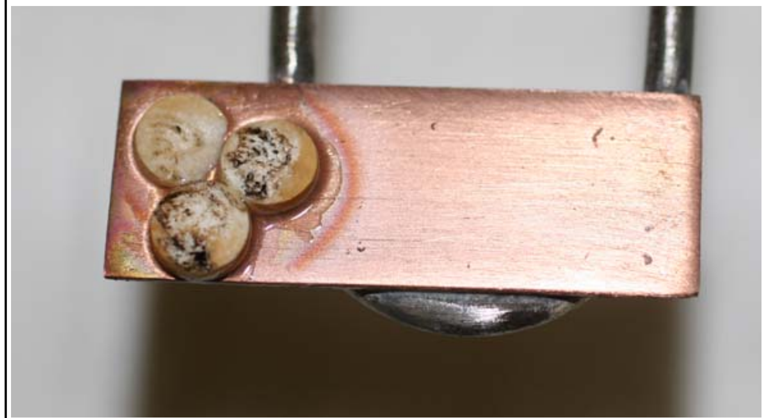


Sample preparation



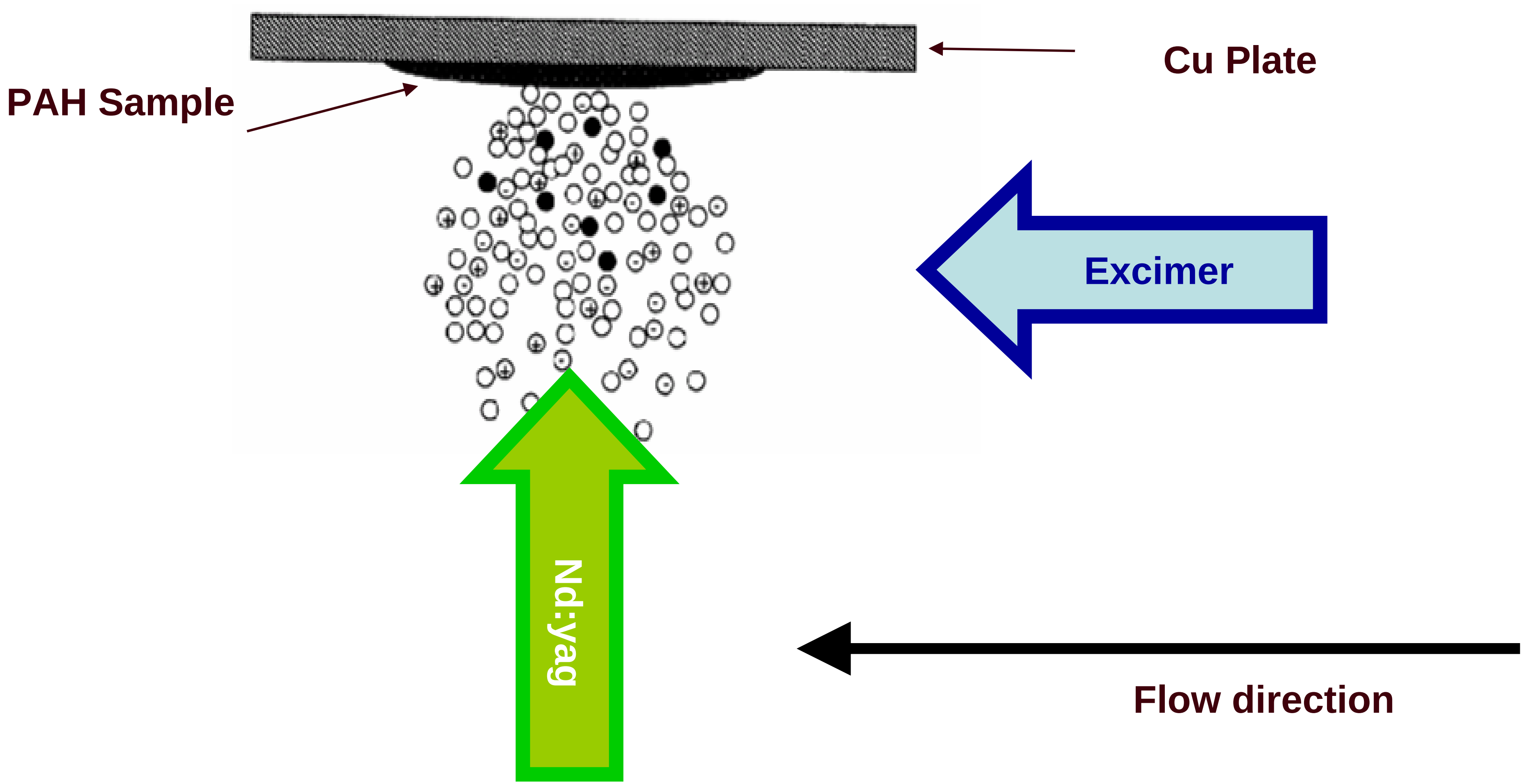


Before exposure



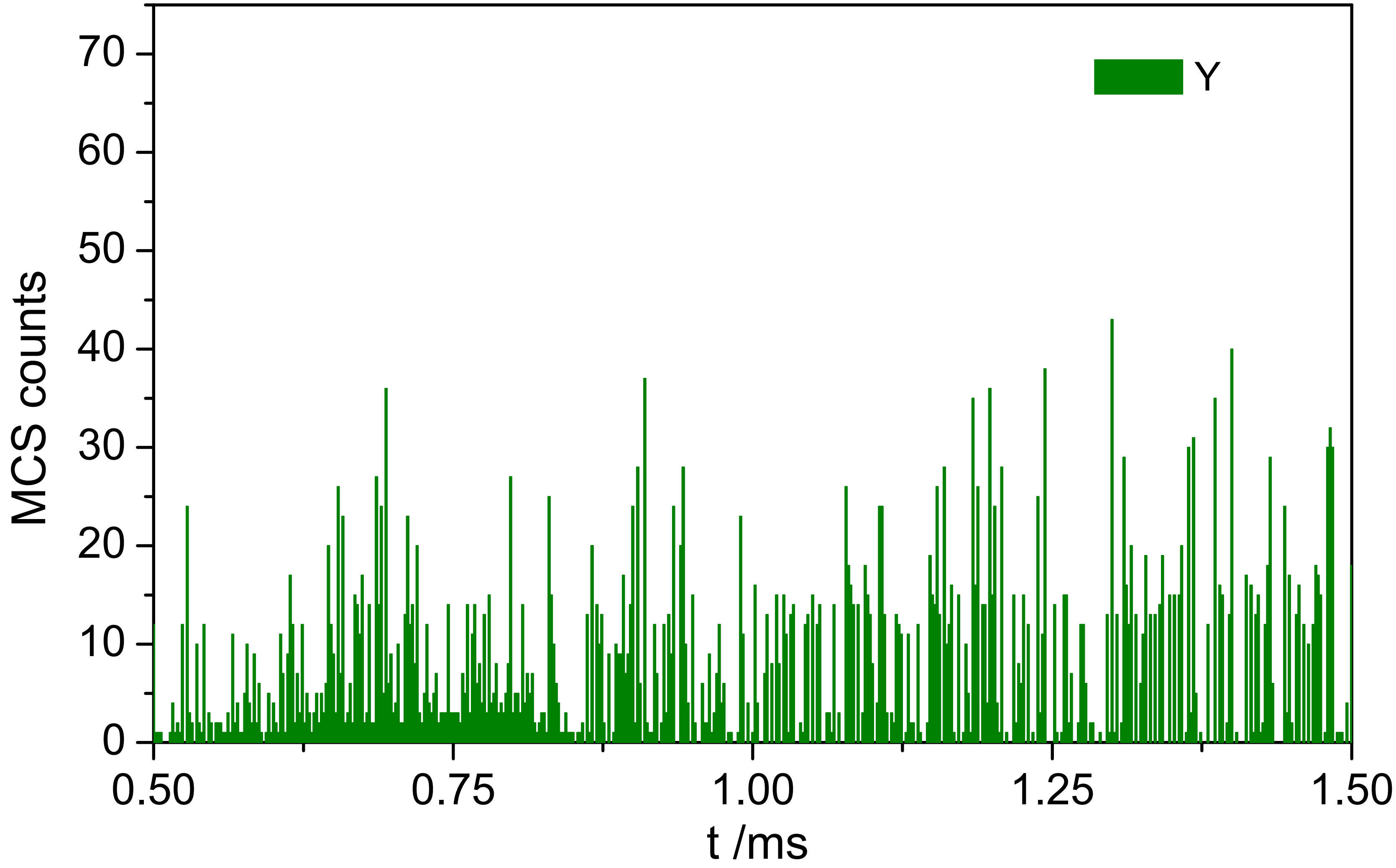
After exposure

Laser desorption / laser ionization



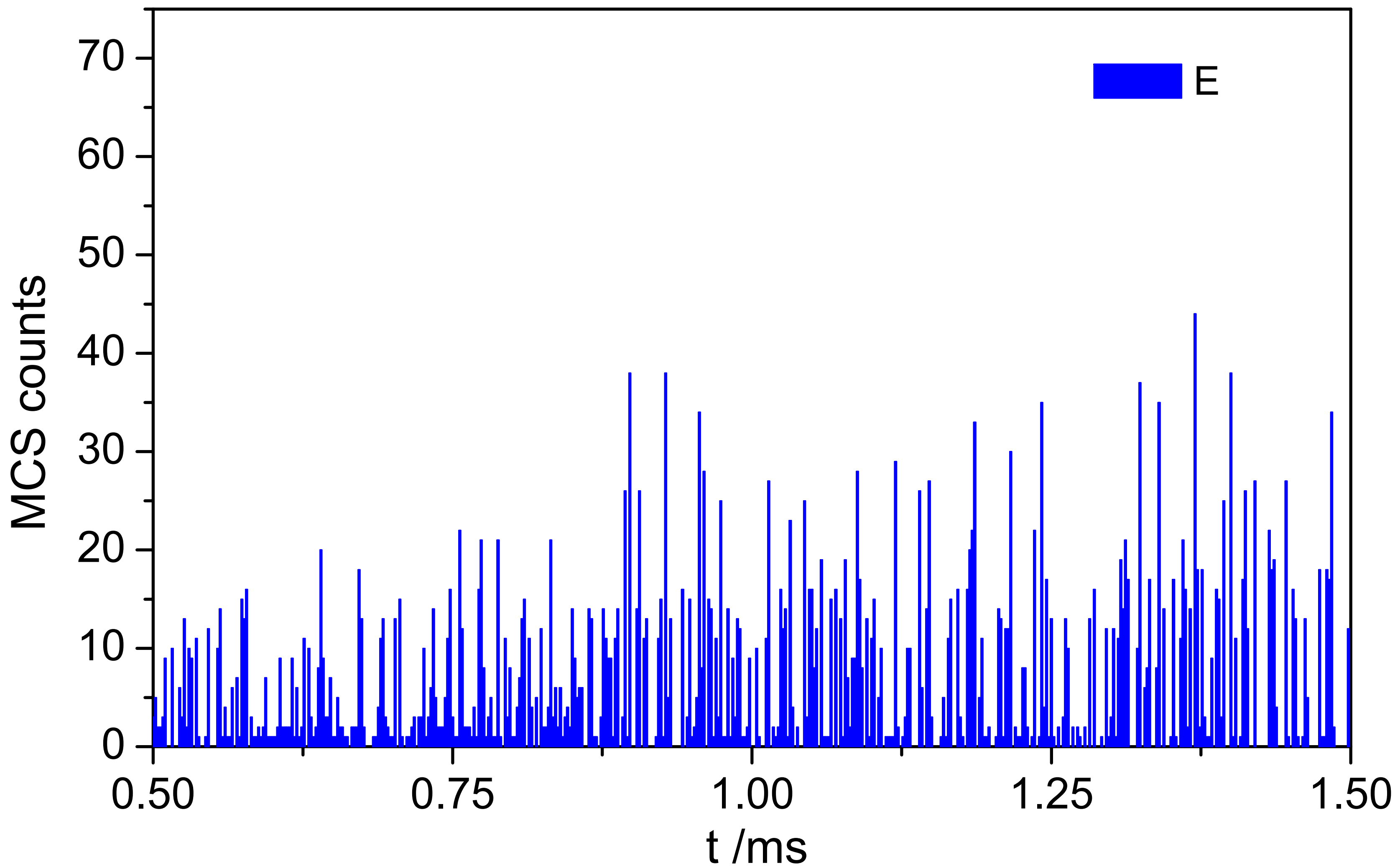
→ photo-generation of an ion/electron packet

Evidence of a two steps mechanism: L²DI



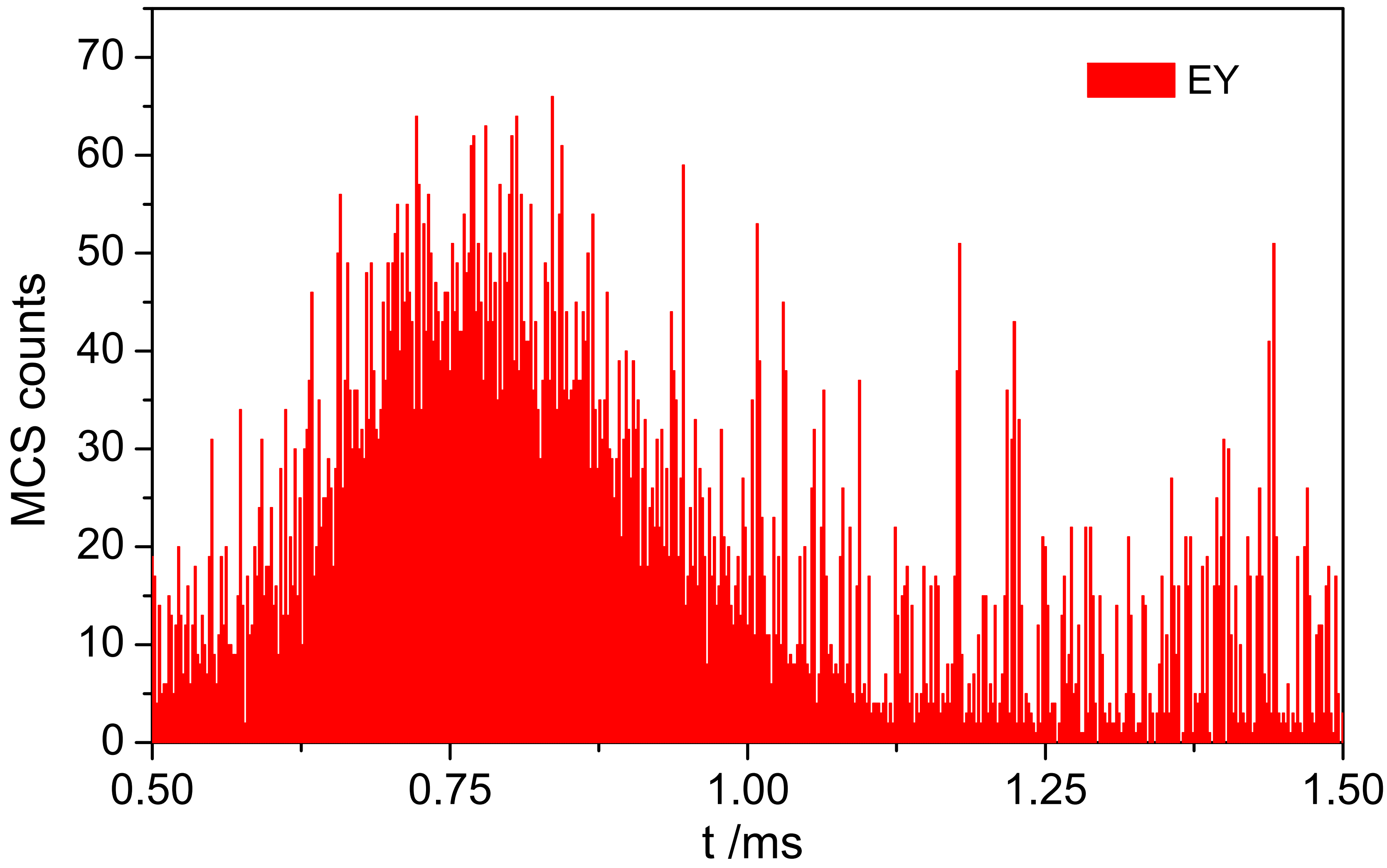
[178+] signal with laser desorption only (NdYAG @ 266nm)

Evidence of a two steps mechanism: L²DI



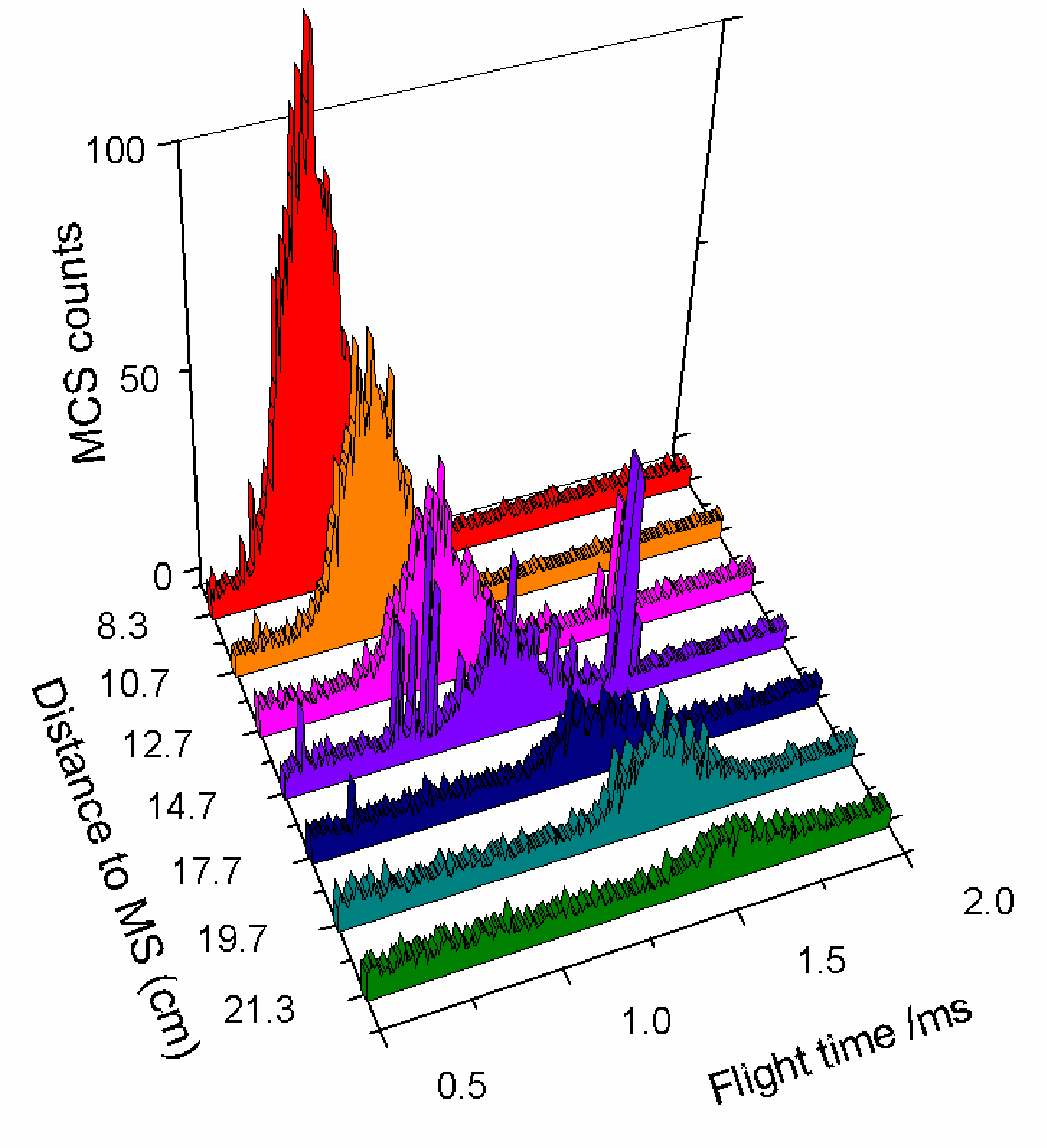
[178+] signal with laser ionization (F2 @ 157 nm)

Evidence of a two steps mechanism: L^2DI



[178+] signal with laser desorption /laser ionization

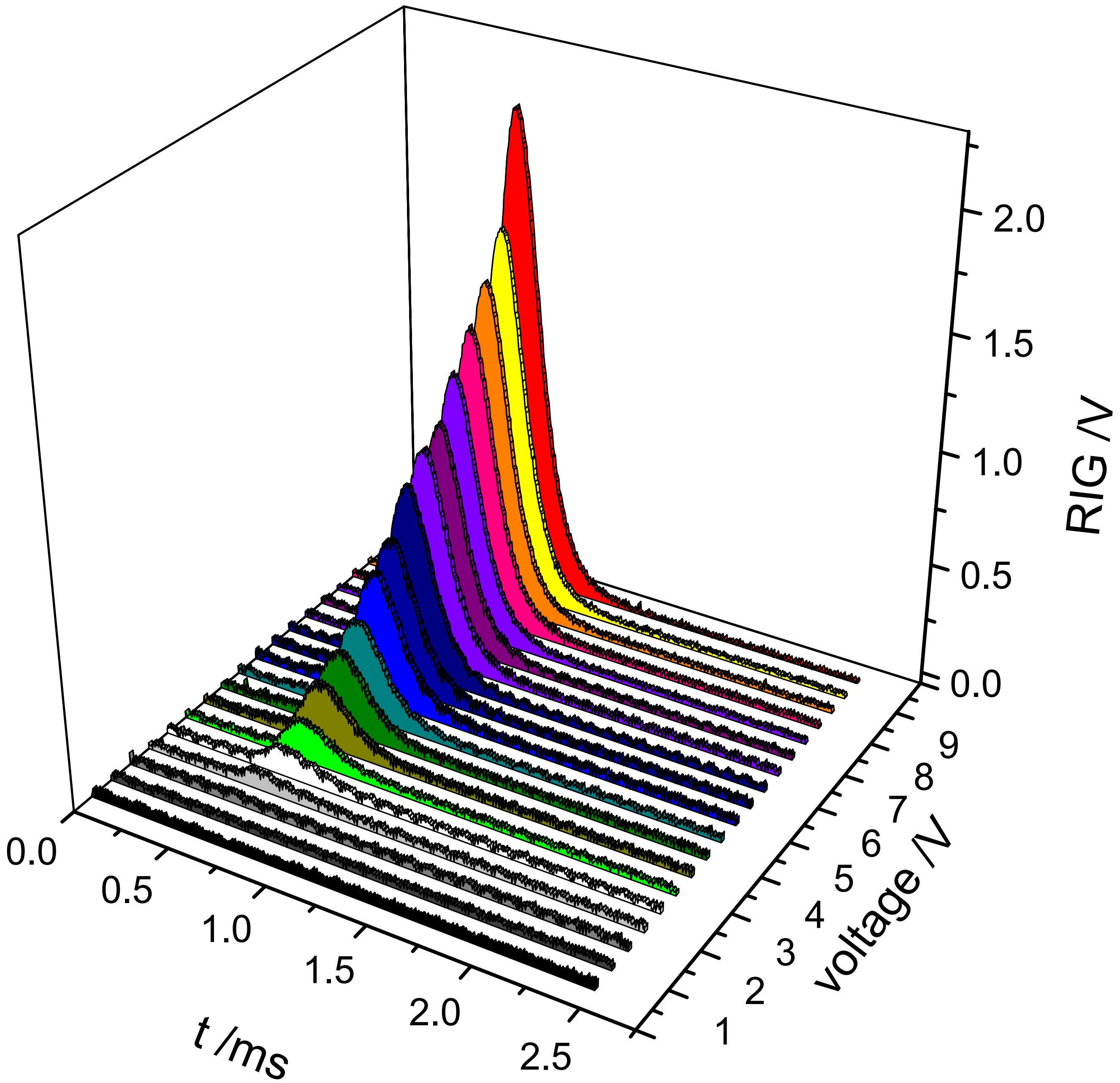
Ion packet time of flight



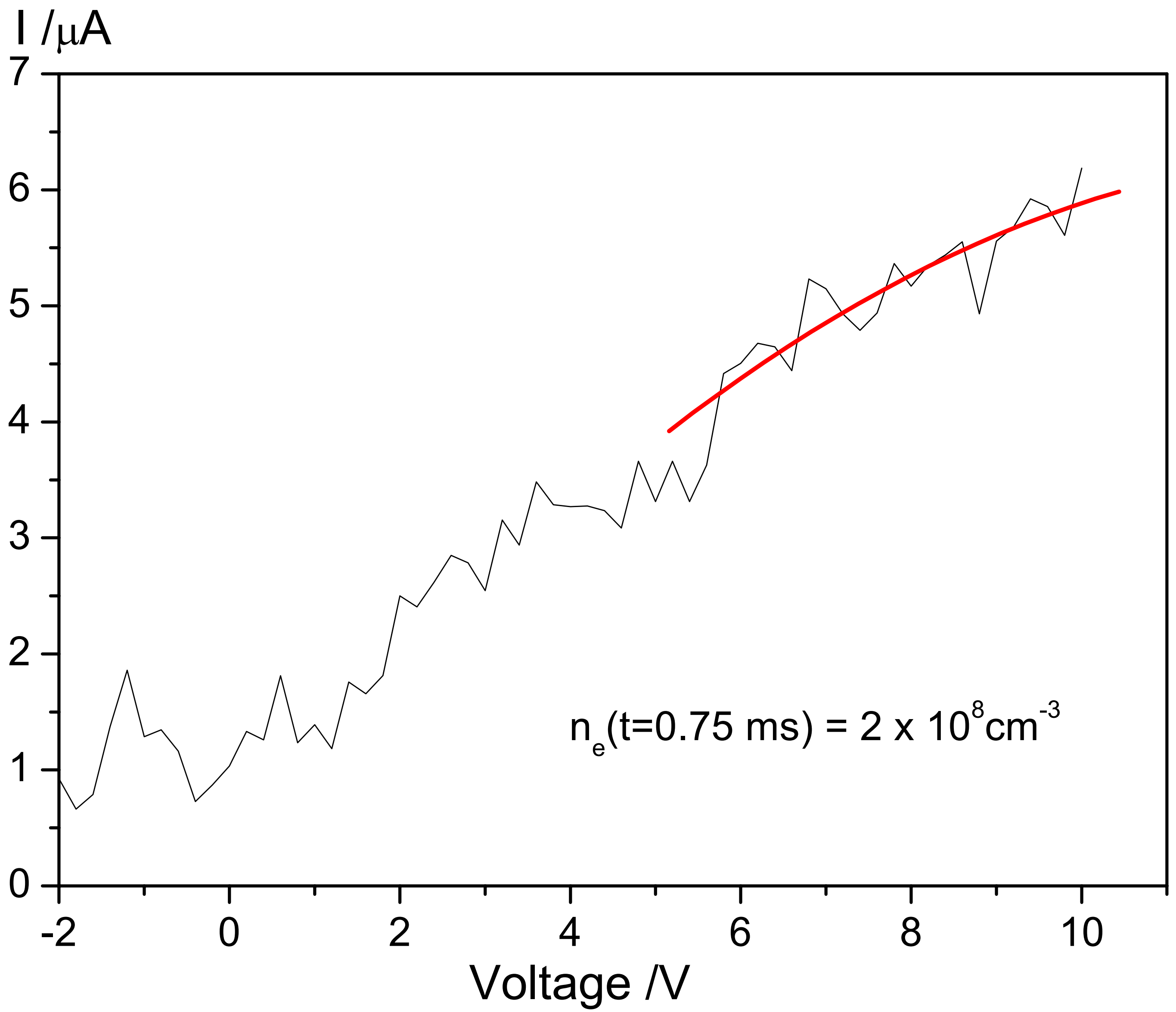
- [178$^+$] ion packet population strongly decrease with flight time
- Causes: diffusion and recombination with electrons

Time resolved Langmuir probe measurements

- Measurements of photoelectrons performed at a fixed distance from the probe
- Absence of afterglow → only photo-electrons
- Slice gives IV characteristic for given time *t*

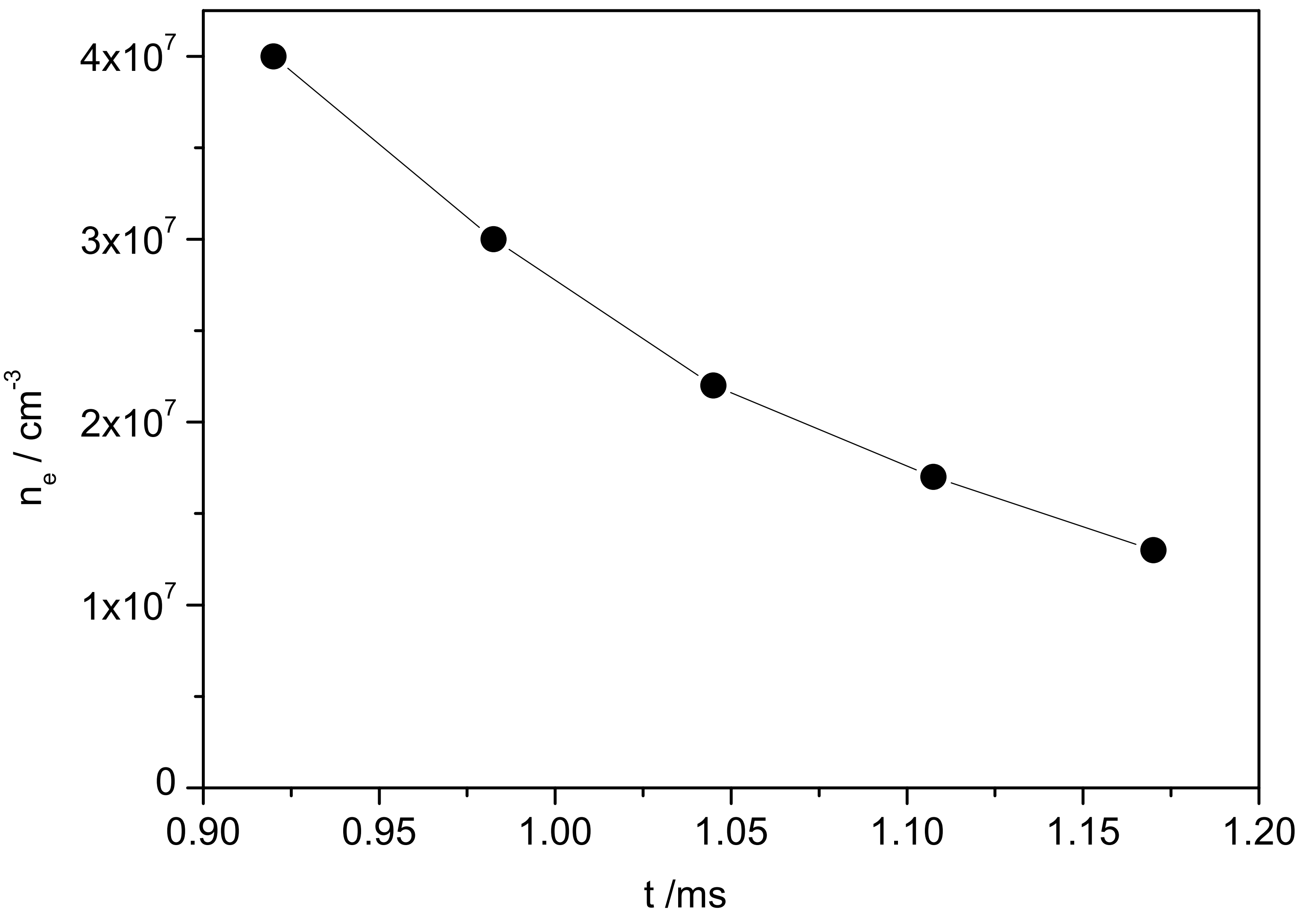


IV characteristic at t=0.75 ms and fixed z



Electron number density derived from the IV characteristic and the probe geometry

Electron number density vs. flight time



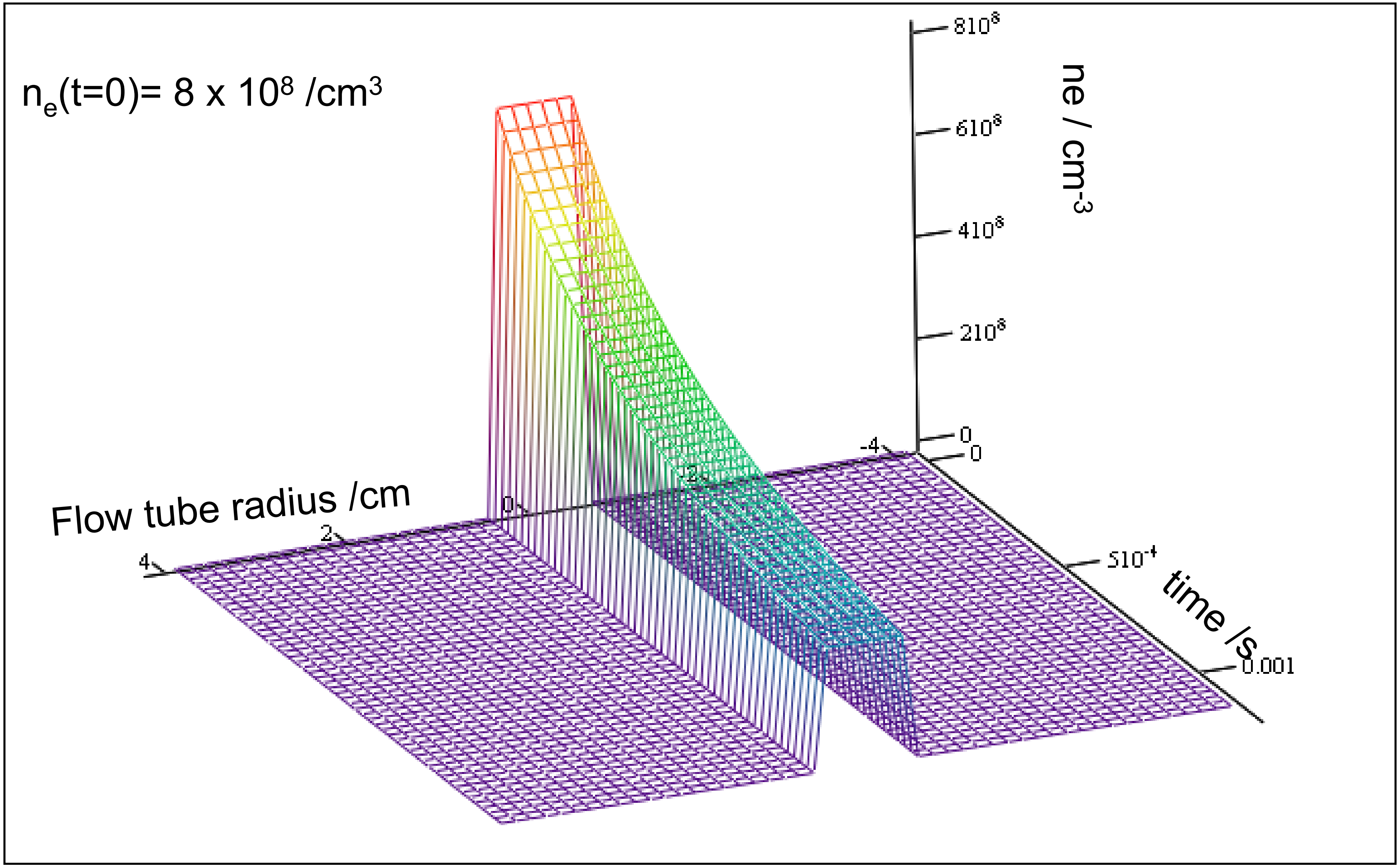
Information retrieval journey

$$\frac{\partial n_e}{\partial t} = D\nabla n_e - \alpha \times n_e \times PAH^+$$

In absence of other ions: $n_e \approx PAH^+$

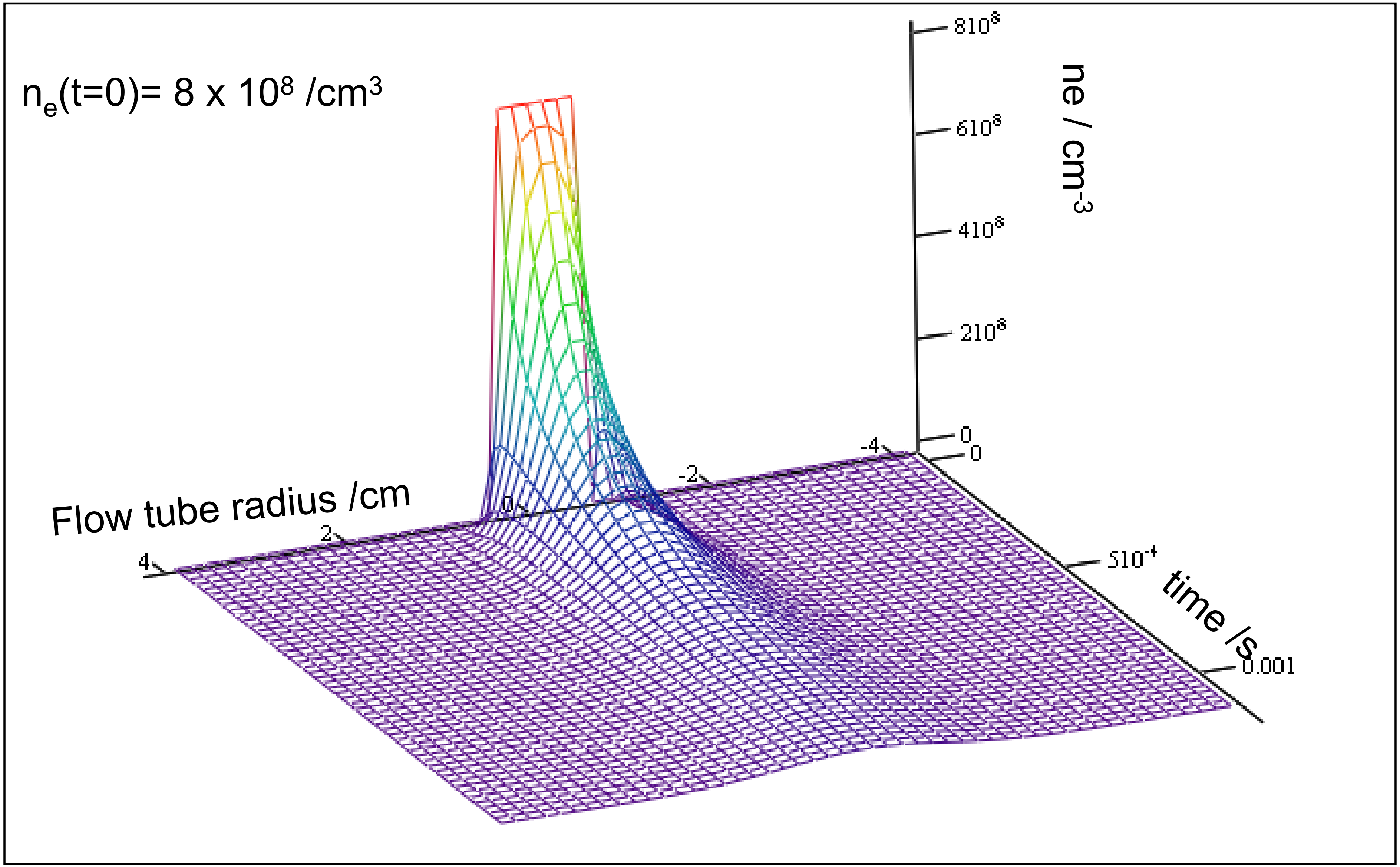
$$\Rightarrow \quad \frac{\partial n_e}{\partial t} = -\alpha \times n_e^2 + D\nabla n_e$$

Numerical simulation (no diffusion)



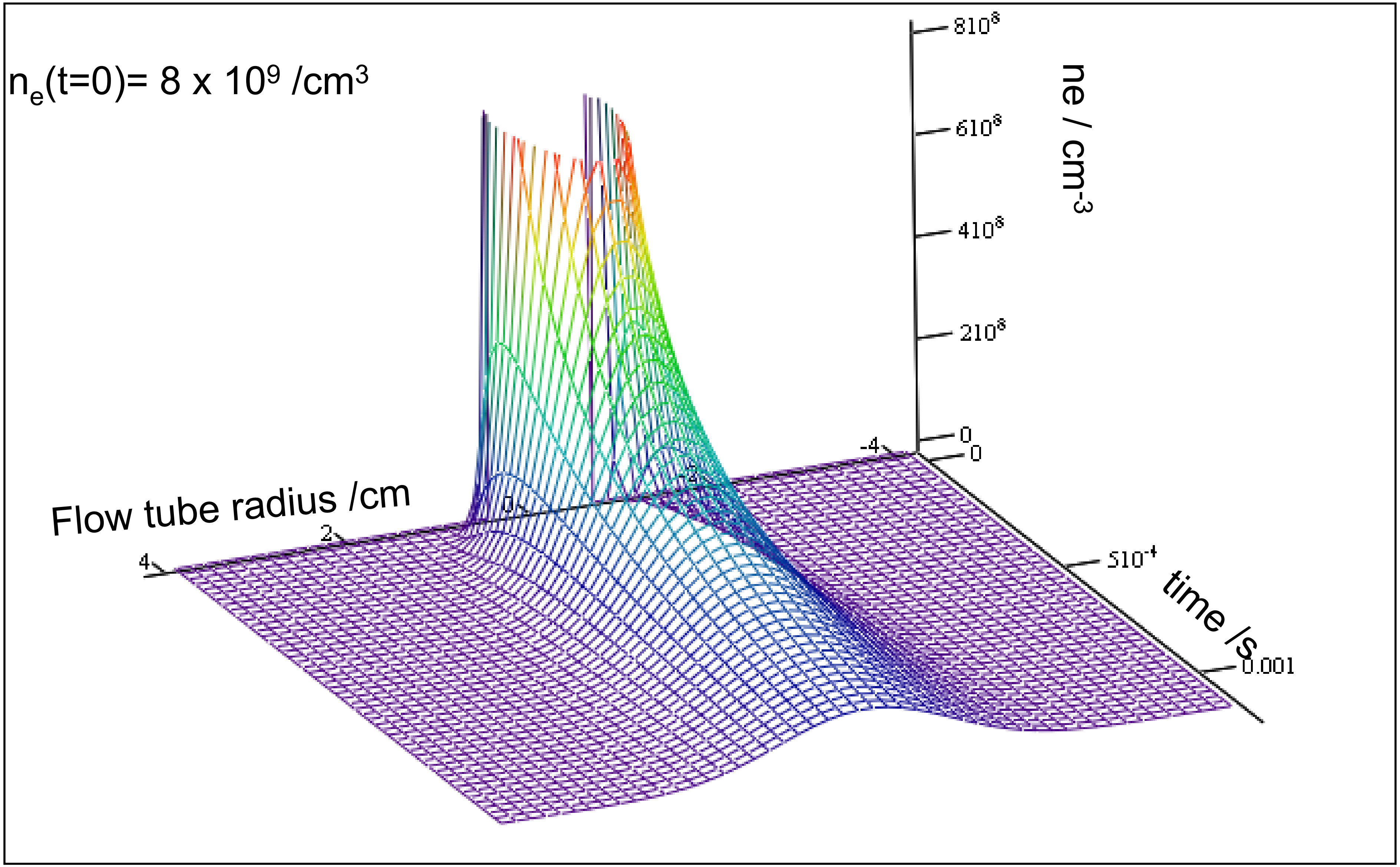
Y

Numerical simulation (incl. diffusion)



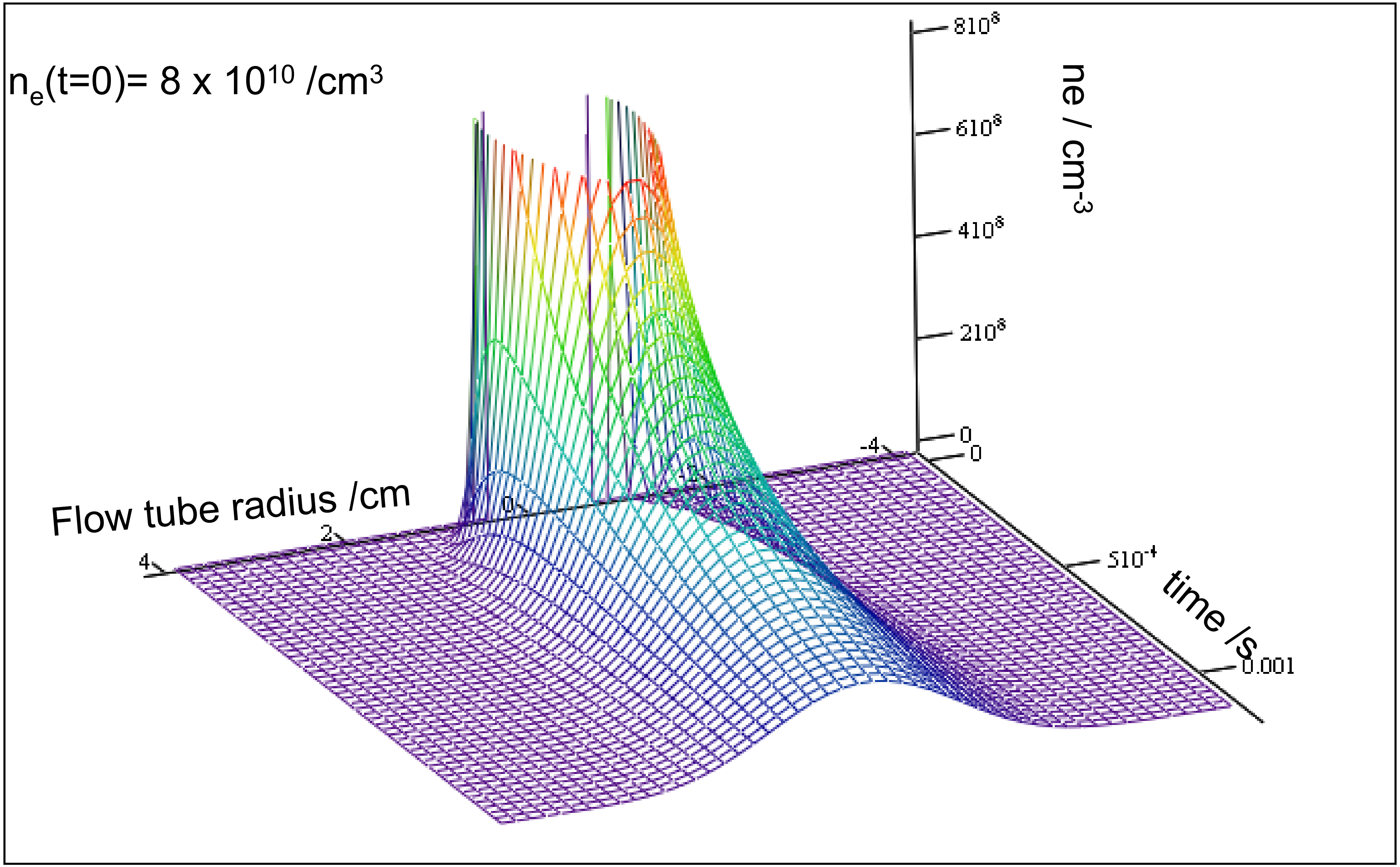
Y

Numerical simulation



Y

Numerical simulation



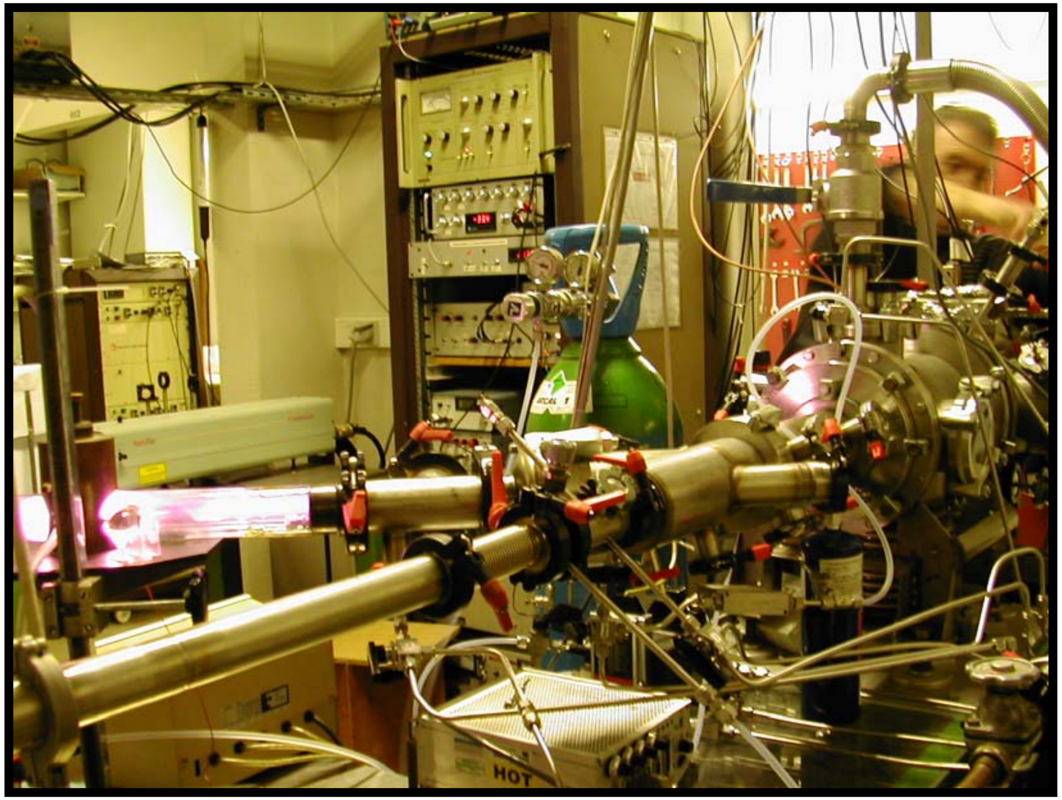
Y

Conclusions

- L2DI production of PAH ions is under test. We are now working on robust methods to extract the recombination rate from the electron density time profile

- This study reveals high PAH^{+} - e^{-} recombination rates that tend to increase with size

- Open questions :
  - nature of the products
  - temperature dependence



Acknowledgments

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- Mohamed Ali Al-Sayed (L2DI measurements)
- Christiane Rebrion-Rowe
- Daniel Travers (time resolved LP)

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