SOOT PARTICLES SURFACE ANALYSIS: FROM LABORATORY EXPERIMENTS TO FIELD CAMPAIGNS

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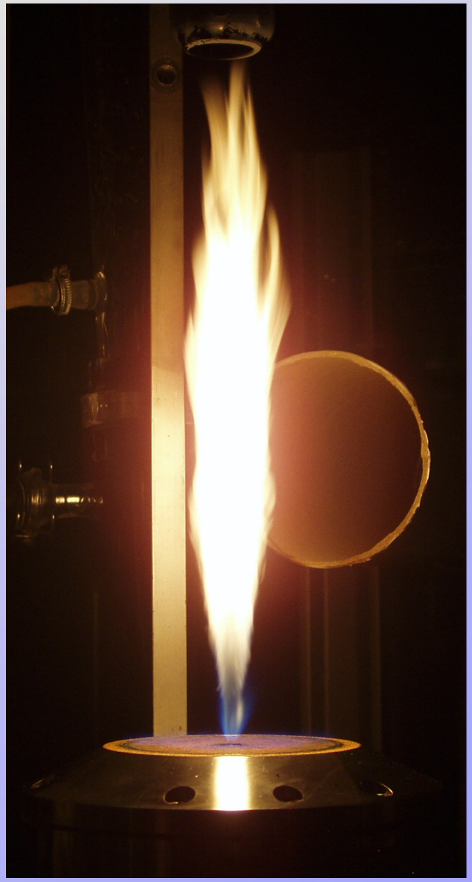
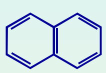
Subject and Motivation



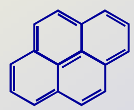
Soot: carbon particles resulting from incomplete combustion processes

PAHs : compounds containing two or more aromatic rings, playing a fundamental role in soot inception

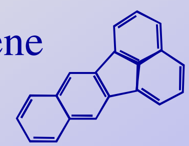
Naphthalene $C_{10}H_8$



Pyrene $C_{16}H_{10}$



Benzo(k)Fluoranthene $C_{20}H_{12}$



PAHs are adsorbed onto the soot matrix

The analysis of soot surface composition provides key information on:

- soot formation mechanism(s)
- health and atmospheric impact depending on the fuel nature and combustion stage

Subject and Motivation


www.20minutes.fr N°510 VENDREDI 7 MAI 2004

Des milliers de morts, l'air de rien

La pollution de l'air serait responsable de 4876 décès chaque année selon l'Agence française de sécurité sanitaire environnementale. Le rapport pointe les particules des gaz d'échappement. P.5

Human health concerns

carcinogenic potential of PAHs adsorbed on soot particles

Atmospheric issues

soot particles as nucleation sites for cirrus clouds formation

➢ health and atmospheric impact depending on the fuel nature and combustion stage

Experimental Technique:

Laser Desorption /Laser Ionization /ToF Mass Spectrometry

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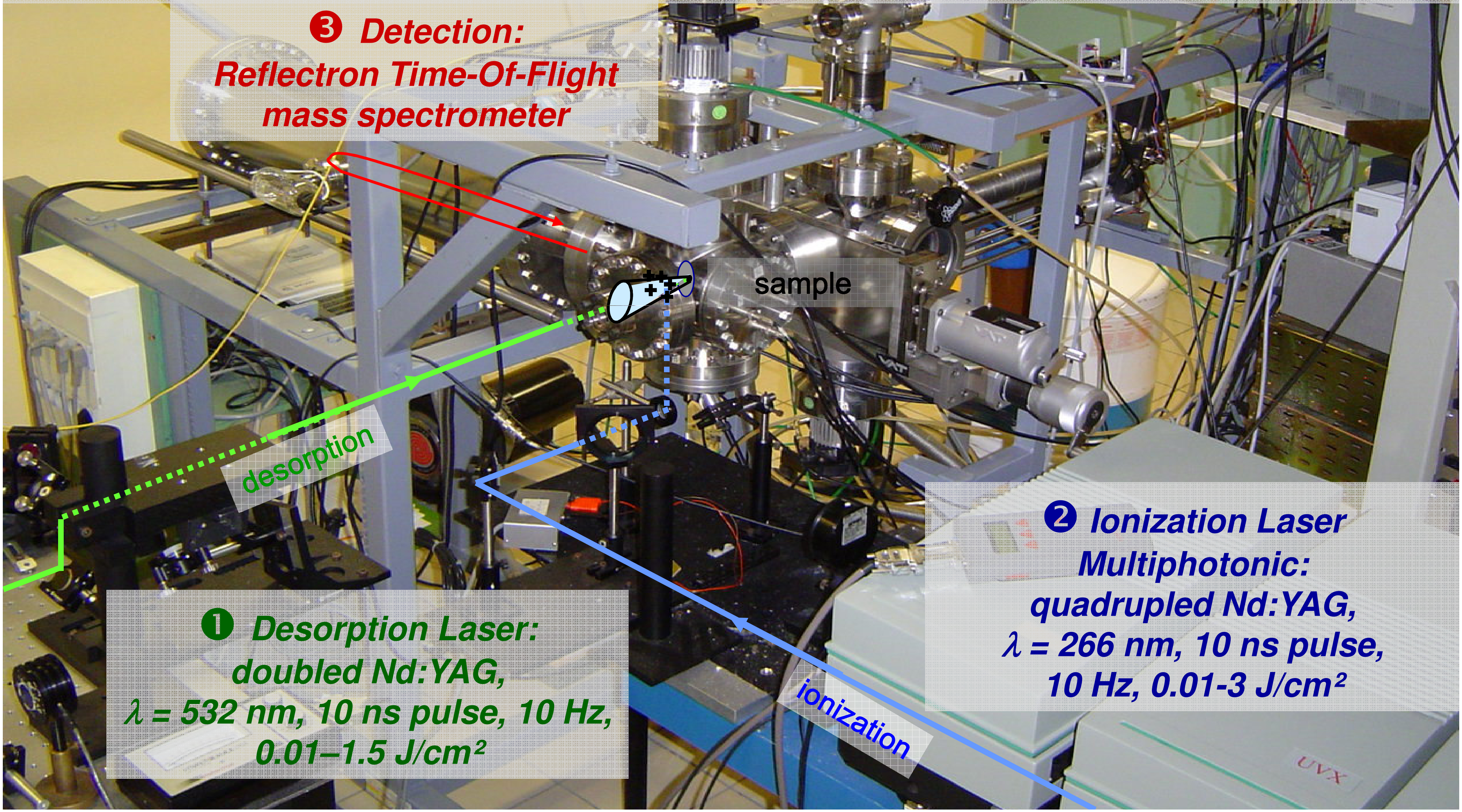
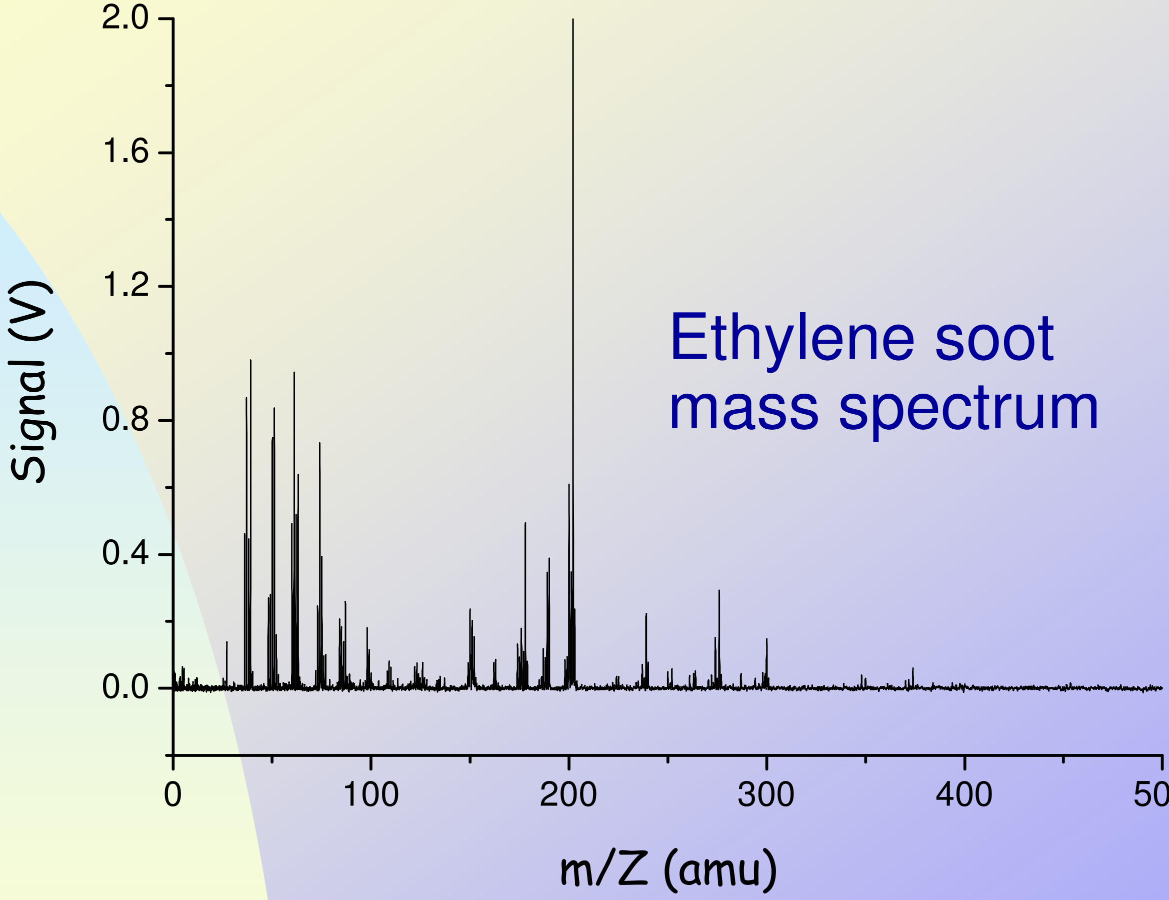


What's Real?



which peaks are representative of the adorbed phase only ?

which ones correspond to by-products of the desorption/ionization processes (fragmentation, destruction of the soot matrix...) ?

How can we minimize these signals ?

3-Step Strategy

1-Thorough characterization of the desorption and ionization processes on pure PAH samples

2-Study of "synthetic" soot samples (PAHs adsorbed on black carbon)

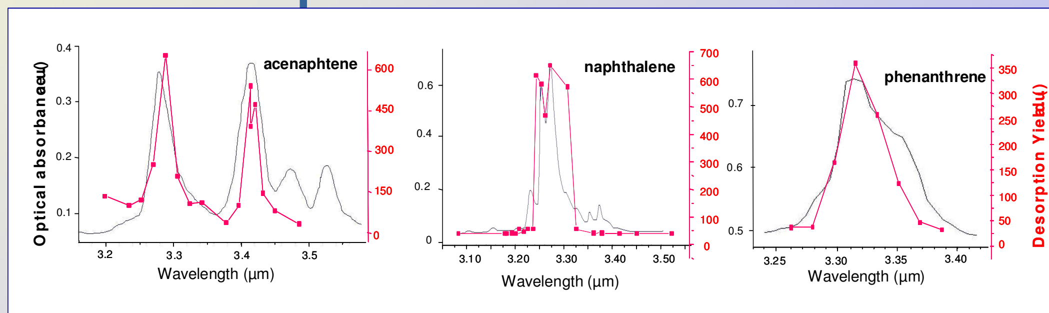
3-Analysis of collected soot

Natural Soot
Synthetic Soot

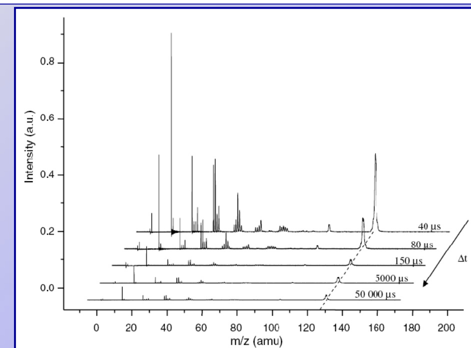
1-Characterization of the desorption and ionization processes on pure PAH samples

exhaustive parametric study on various parameters:

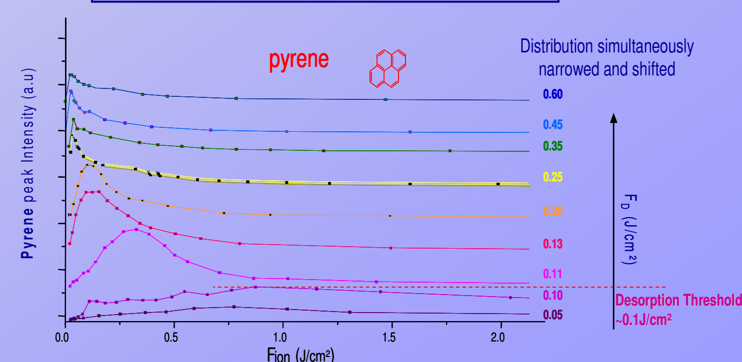
Laser wavelength λ:
⇒ Influence of the optical absorption coefficient on the desorption yield



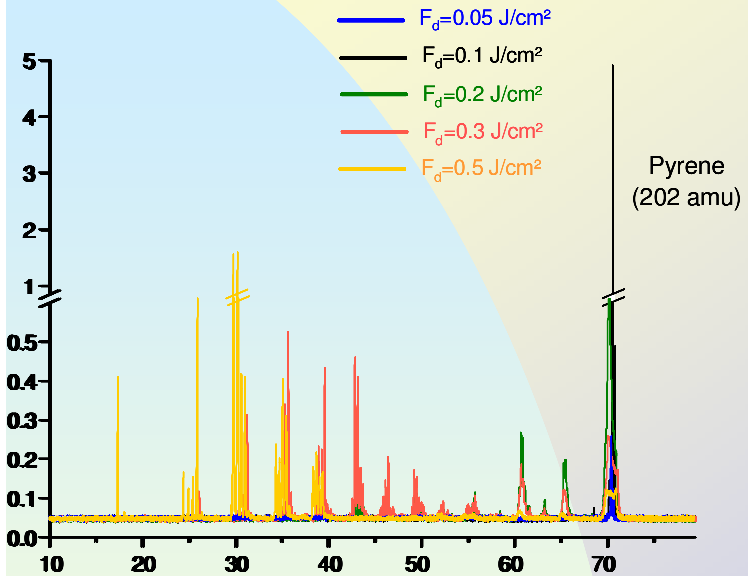
Delay Δt between desorption and ionization laser pulses:
⇒ Dynamic of the species present in the plume



Laser desorption and ionization fluences F_d & F_{ion}
⇒ Fragmentation issue ; Relationship between desorption and ionization processes

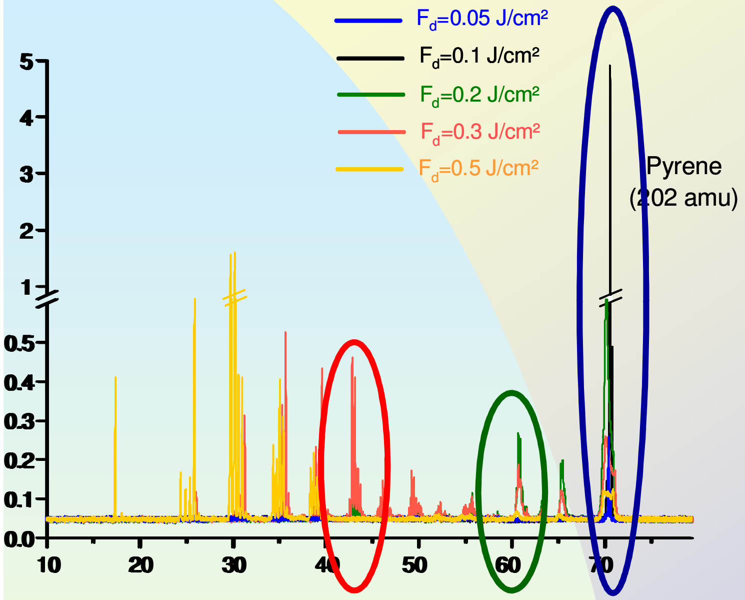


1-Characterization of the desorption and ionization processes on pure PAH samples

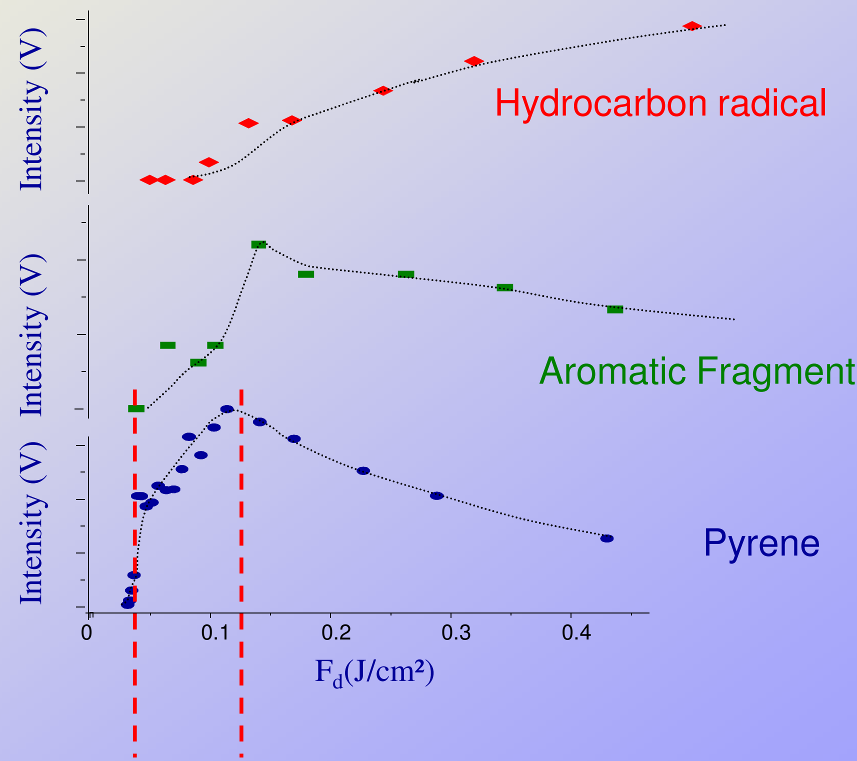


Evolution ot the Spectra with Fluence:

1-Characterization of the desorption and ionization processes on pure PAH samples



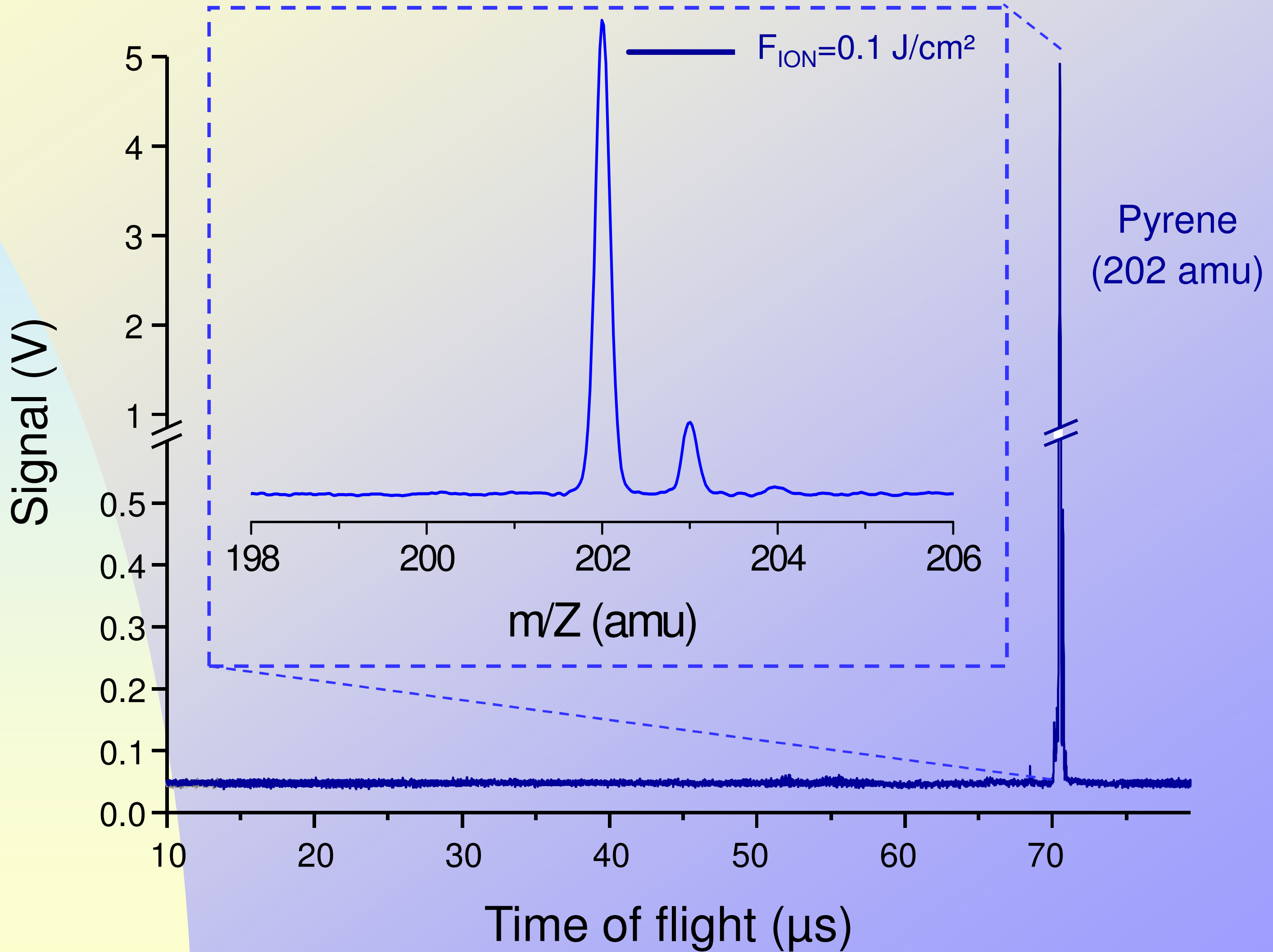
Evolution ot the Spectra with Fluence :
Fragments yields vs laser pulse energy



Range of efficiency between the desorption threshold and emergence of the first fragments

Intensity of the PAH signal ⇔ Competition between ejection and fragmentation through an increase of the internal energy of the desorbed species

1-Characterization of the desorption and ionization processes on pure PAH samples



2-Study of synthetic soot samples

Standard procedure

- Prepare a mother solution having a known PAHs concentration
- Treat the solution with a known amount of black carbon
- Eliminate the solvent (DCM)
- Press the carbon with PAHs so adsorbed

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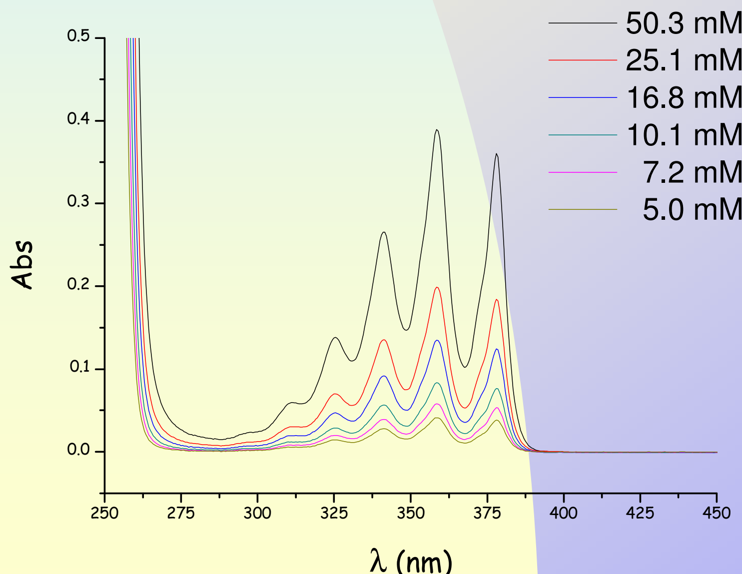
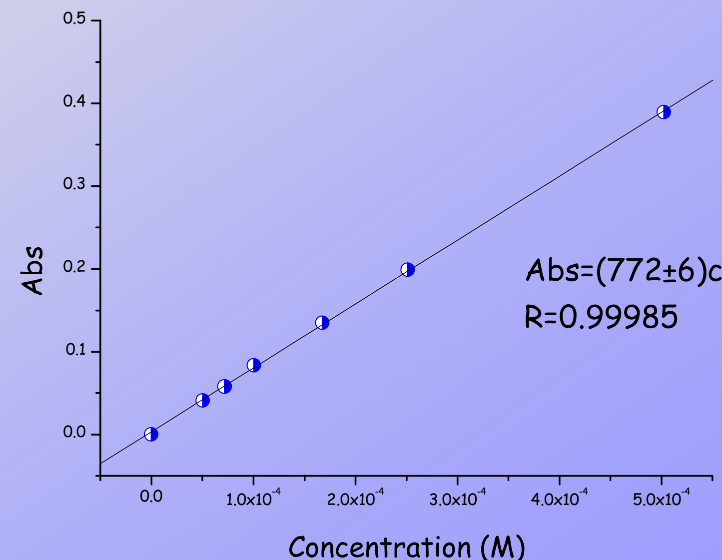
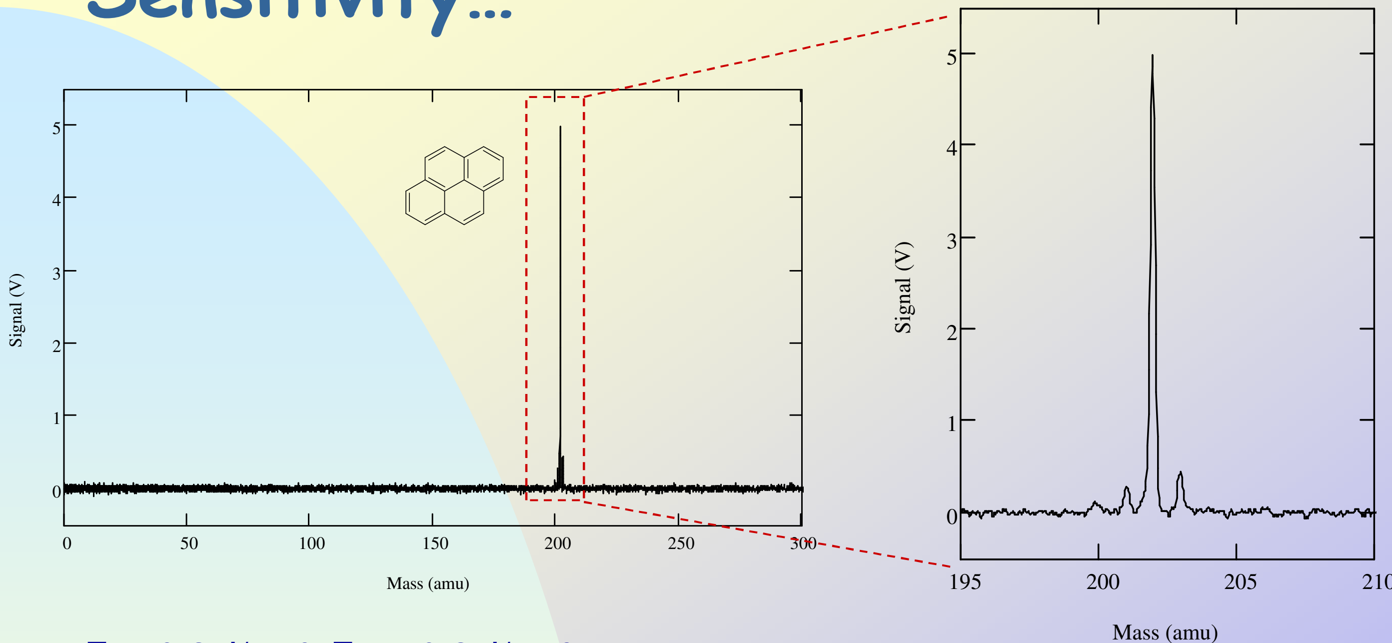
⇒ PAHs concentration in synthetic soot





Quantitative approach … calibration ... standard samples

Sensitivity…



F_D= 0.2 J/cm², F_{ion}= 0.2 J/cm²

Pyrene concentration: 5 .10^{-6} mol/g

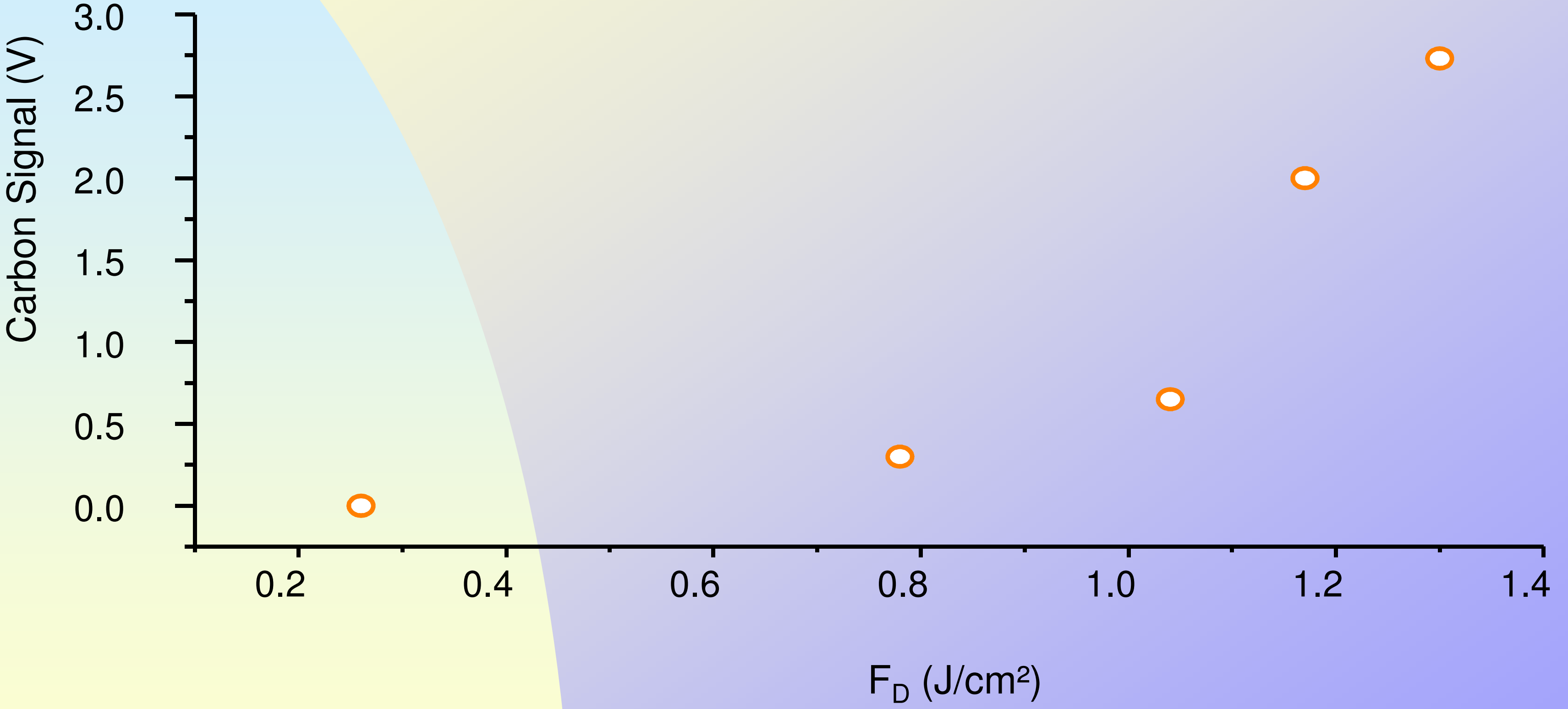
Signal extinction after 20 laser shots

Sensitivity better than 1 fmol/ laser shot for pyrene

Desorption issue in synthetic soot

ejected molecules are representative of the adsorbed phase or come from the destruction of the soot matrix ?

Pure black carbon
F_{ion}=2.5 J/cm² (to ensure the detection of ^{12}C)



Desorption issue in synthetic soot

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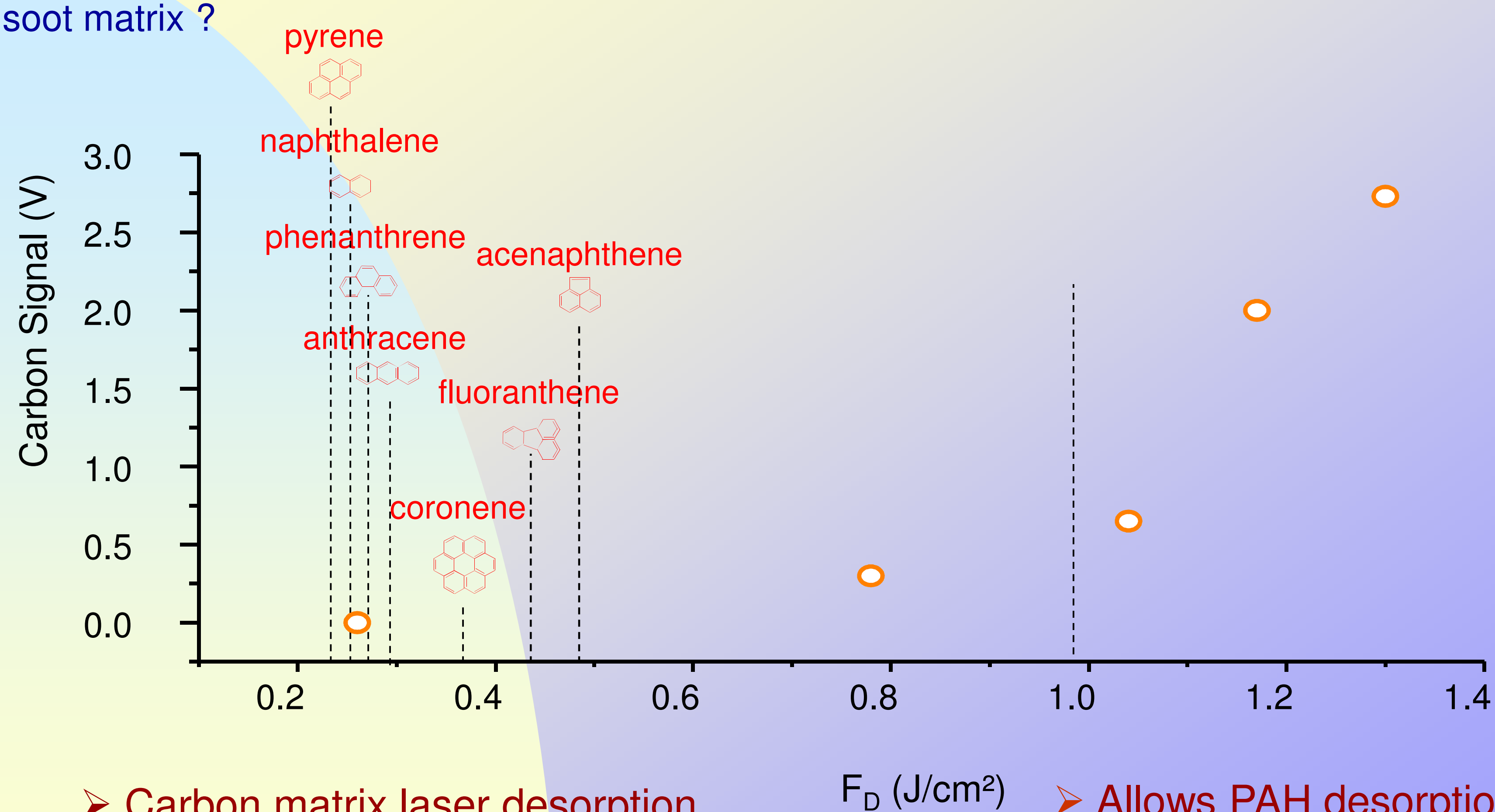


- ➢ Carbon matrix laser desorption threshold **higher** than PAH ones
- ➢ Allows PAH desorption without affecting the soot matrix ("smooth desorption process")

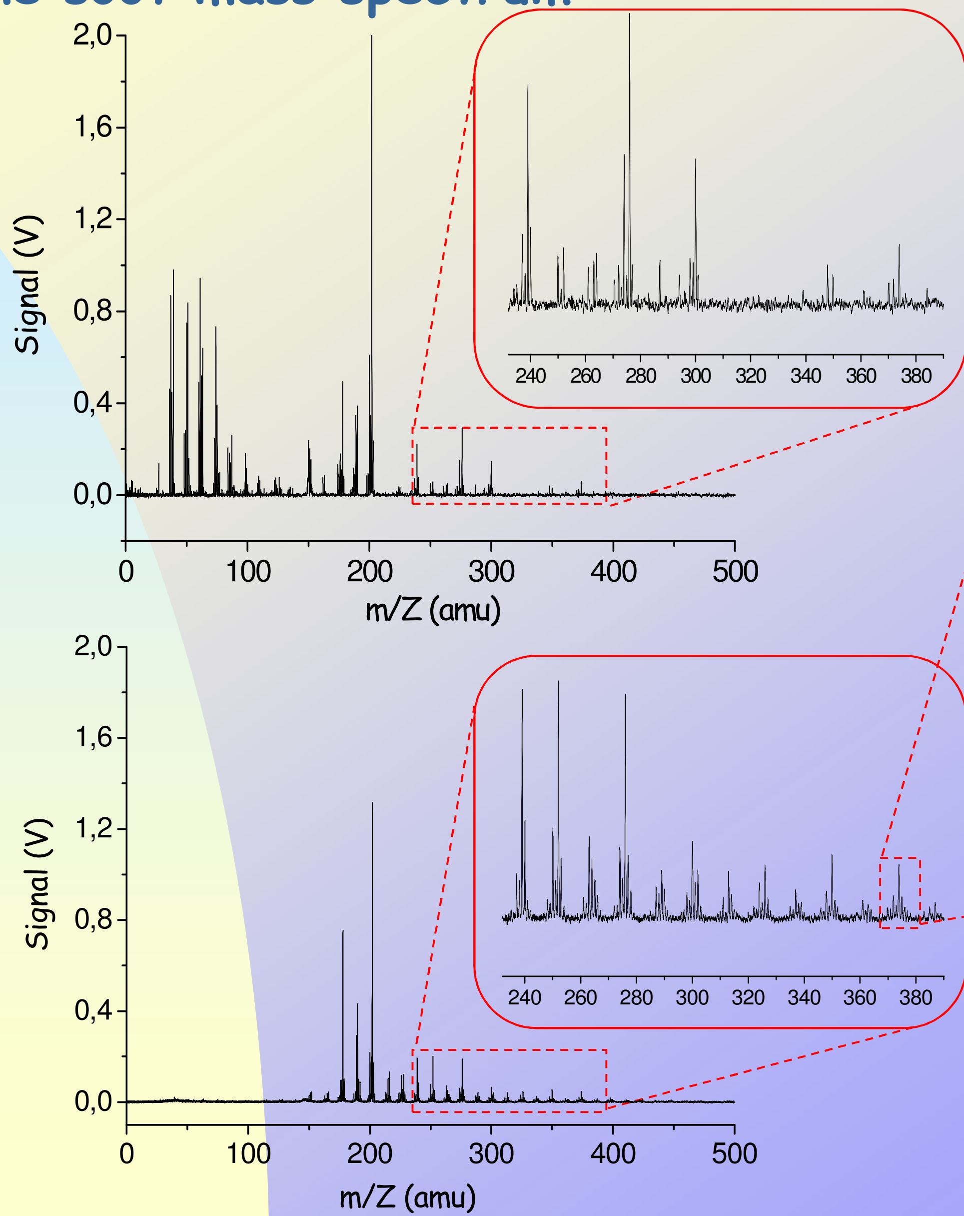
Mihesan, Ziskind, Therssen, Desgroux, Focsa, *J. Phys.: Condens. Matter*, **20**, 025221 (2008)

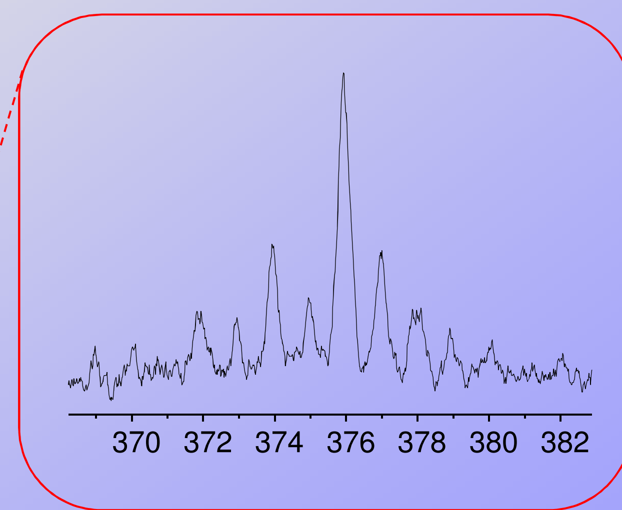
3-Analysis of collected soot

result: ethylene soot mass spectrum

Before optimization

After optimization





✓Mass detected up to 500 amu

3-Analysis of collected soot

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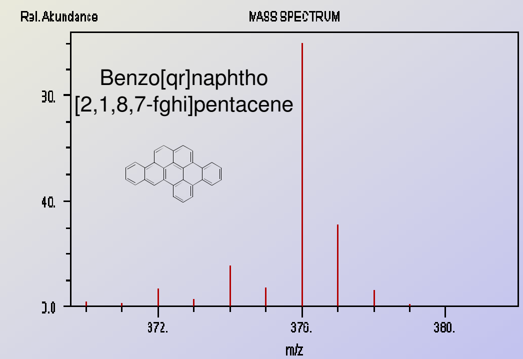
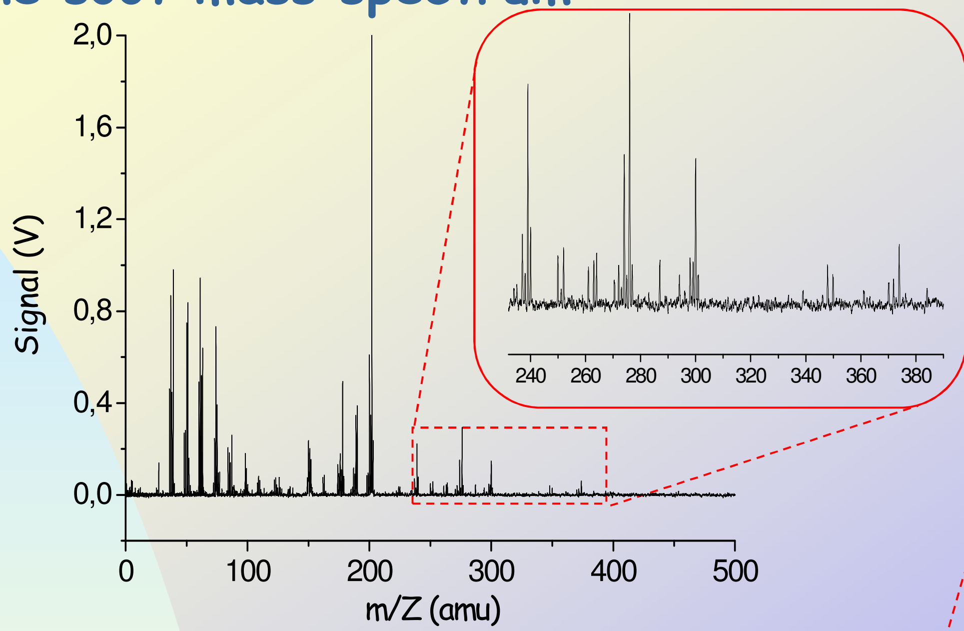
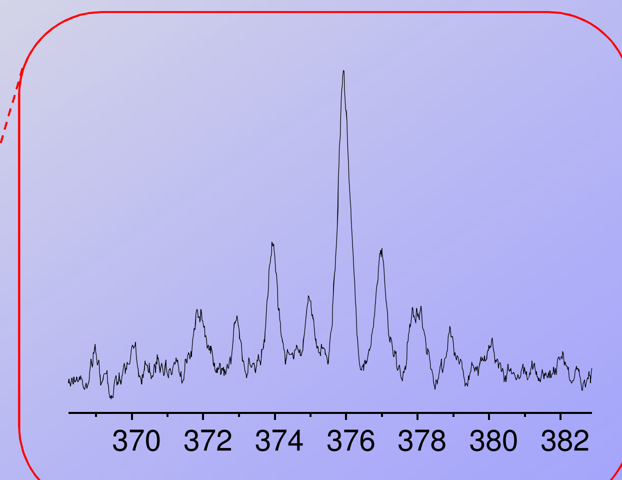
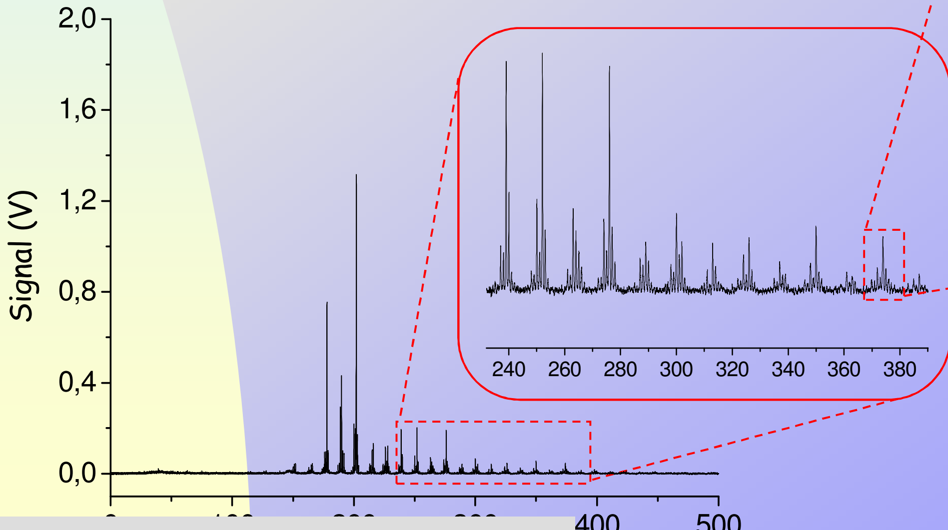


Before optimization





After optimization



C \ H	6	8	10	12	14	16
8	102[1]					
10	126[3]	**128**[1,2,3]				
12		152[1,2]				
14			**178**[1,2,3]			
16			**202**[2,3]			
18			226[3]			
20						
22				276[3]		
24				300[3]		
26				324[3]	326[3]	
28				348[3]	350[3]	
30				372[3]	374[3]	
32				396[3]	398[3]	400[3]
34				420[3]	422[3]	424[3]

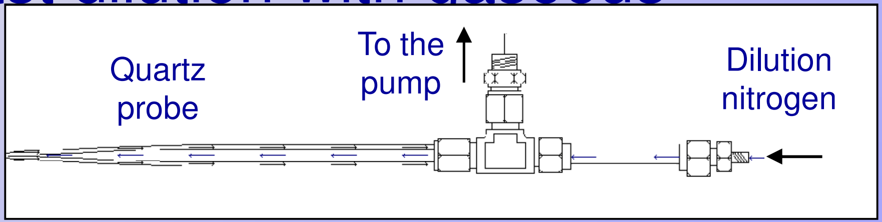
S.E. Stein, A. Fahr, J. Phys. Chem. A 89 (1985) 3714

R.A. Dobbins, R.A. Flechter, H.C. Chang, Combust. Flame 115 (1998) 285

Analysis of soot collected in flame

Soot Sampling

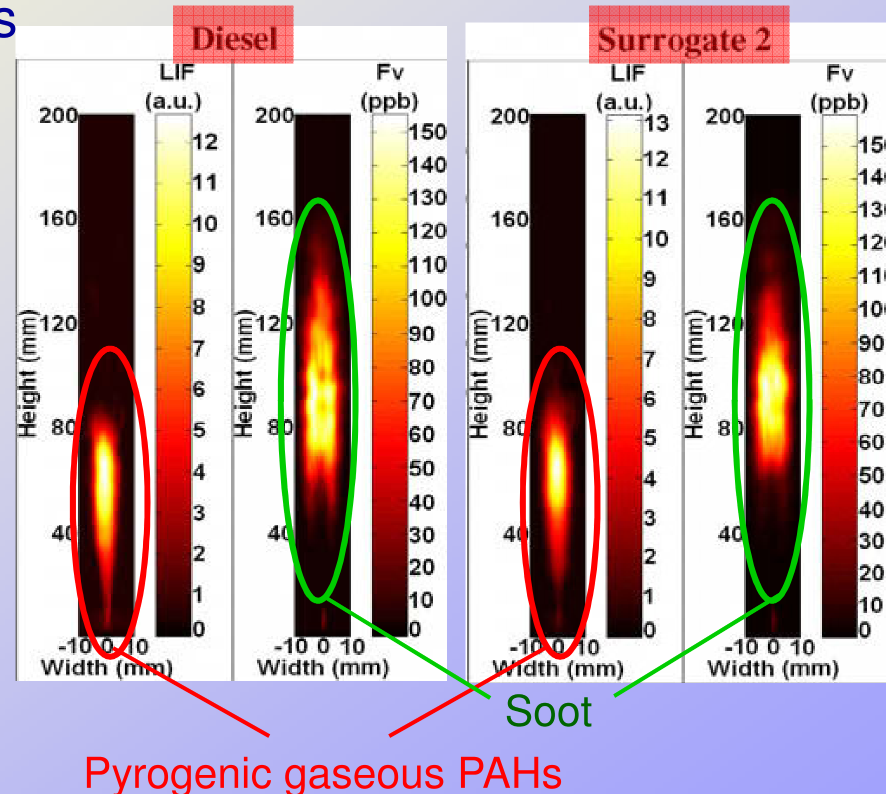
- In our experimental work LDI TOF-MS is an *ex-situ* technique
  - Soot must be ***sampled*** from flames
- Soot is collected through a double-wall quartz probe, which allows (1) local sampling and (2) fast dilution with gaseous nitrogen, needed to minimize:
  - Combustion gas condensation
  - Chemical reactions



- Soot is deposed on the surface of a porous Borosilicate glass filter, suitable for the mass analysis

Fuel influence

- Purpose: test the ability of Diesel surrogates to reproduce the soot formation process occurring during the combustion of a commercial Diesel.
- surrogates:
  - 70% n-decane + 30% α-methylnaphthalene
  - 80% n-decane + 20% α-methylnaphthalene
- Similar physical/optical soot properties



mappings obtained respectively by Laser-Induced Incandescence (LII) at 1064 nm and Laser-Induced Fluorescence at 532 nm

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  - 80% n-decane + 20% α-methylnaphthalene
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BUT Very different adsorbed phase PAH content

the fuel composition strongly influences the adsorbed phase of the soot particles

- *Petrogenic PAHs present in Diesel*
- *how they influence the Pyrogenic PAHs formation ?*

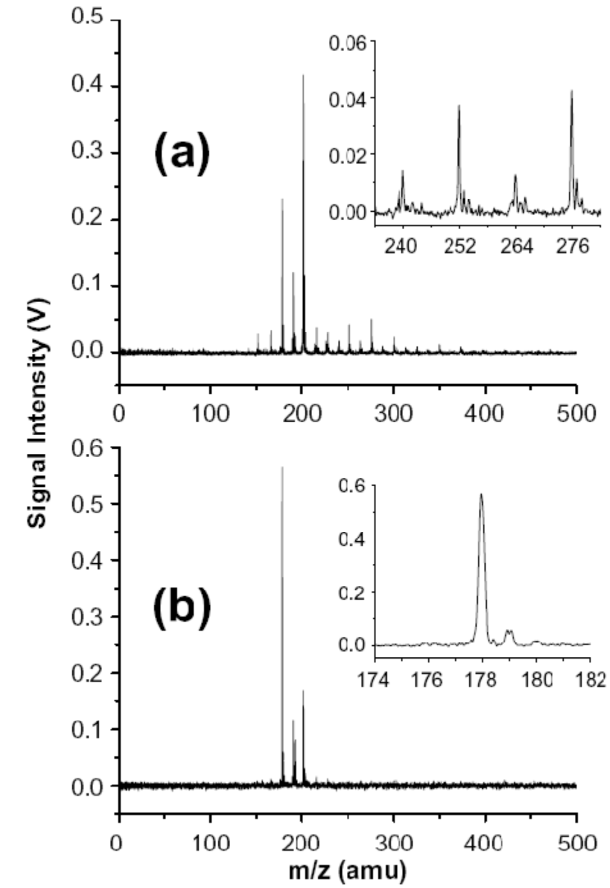


Fig. 5. Five shots averaged mass spectra of PAHs desorbed from soot (desorption fluence 0.26 J/cm^2, ionisation fluence 1.3×10^{-3} J/cm^2). (a) Diesel soot, full range and zoom on heaviest masses in the inset; (b) surrogate soot, full range and zoom on 178 amu peak.

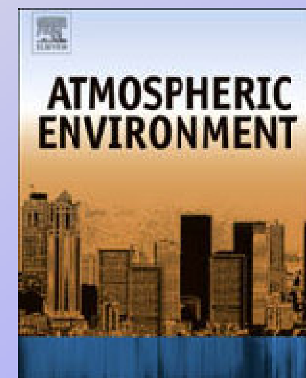
Proc. Combust. Inst. 32 (2009) 737

Analysis of soot collected in field campaigns

EU project QUANTIFY

ATMOSPHERIC SOOT NETWORK (www.asn.u-bordeaux.fr)

Characterisation of particulate matter and gaseous emissions from a large ship diesel engine



Atmospheric Environment 43 (2009) 2632

June 2007,

Celtic Sea, English Channel, North Sea

Technical parameters of the ship.

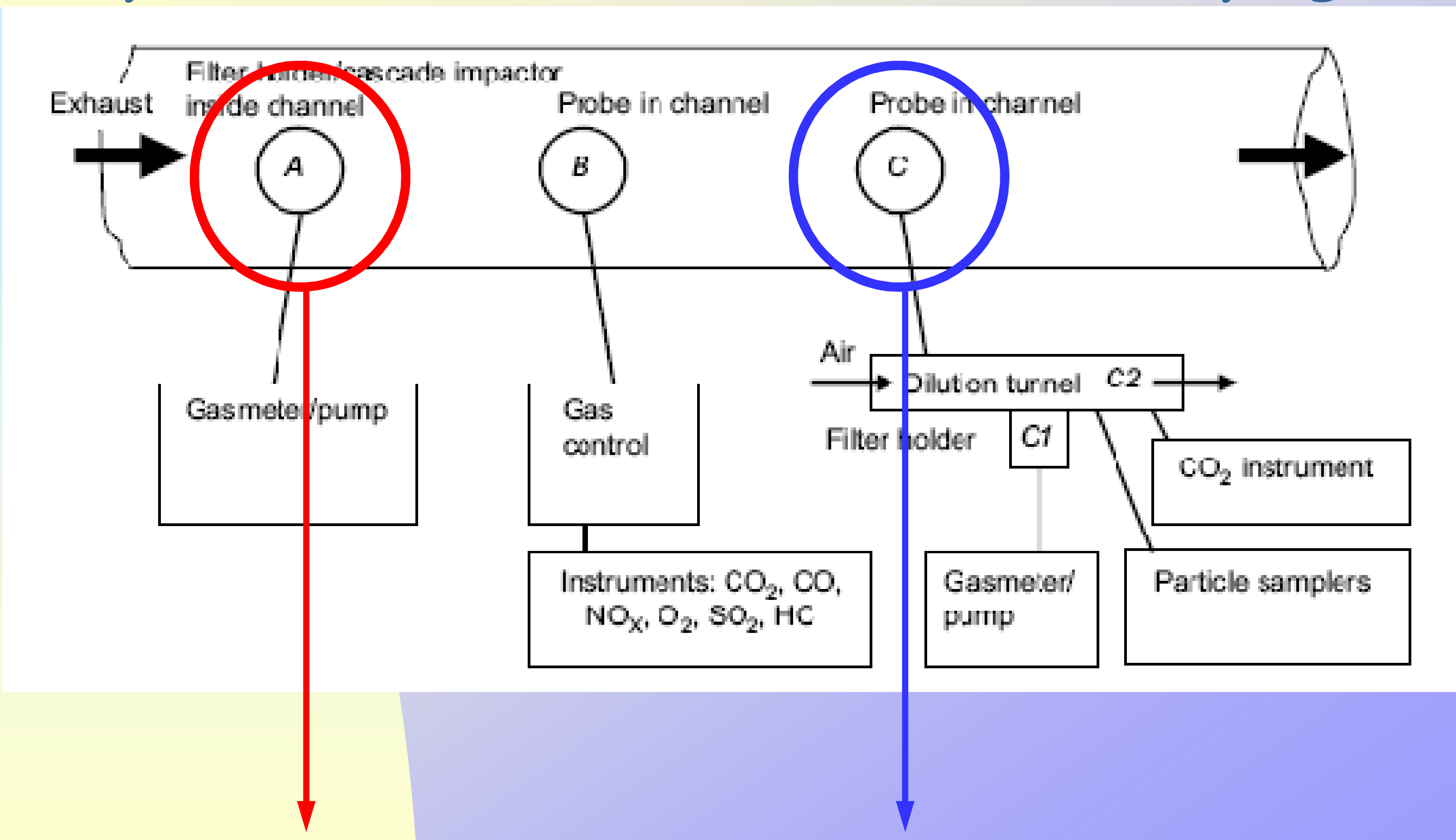
Gross tonnage	58 438
Net tonnage	21 660
Main diesel engine	
Kincaid B&W 6L90 GBE	20 200 kW, 97 rpm[a]
Thrusters	2 × 1398 kW
Full sea speed	17.5 knots (32.4 km h^{-1})
Fuel consumption at sea	HFO[b] 3.2–3.4 m^3 h^{-1}

[a] rpm: rotations per minute.
[b] HFO: Heavy-Fraction Oil (residual oil).

Technical parameters of the ship and ship engine operation specific for the measurement campaign. The exhaust flow is given at normalized conditions (273.14 K, 1013.25 hPa)

Date	14/6/2007
Brake power load, %	84
Brake power, main engine, MW	17.0
Speed, km h^{-1}	31.5
Calculated fuel consumption, kg h^{-1}	3263
Calculated fuel consumption, g kWh^{-1}	194
Exhaust temperature after the engine, °C	330
Exhaust temperature at the funnel top, °C	263–266
Exhaust flow, main engine, Nm^3 h^{-1}	110 000
Exhaust flow speed, m s^{-1}	25

Analysis of soot collected in field campaigns

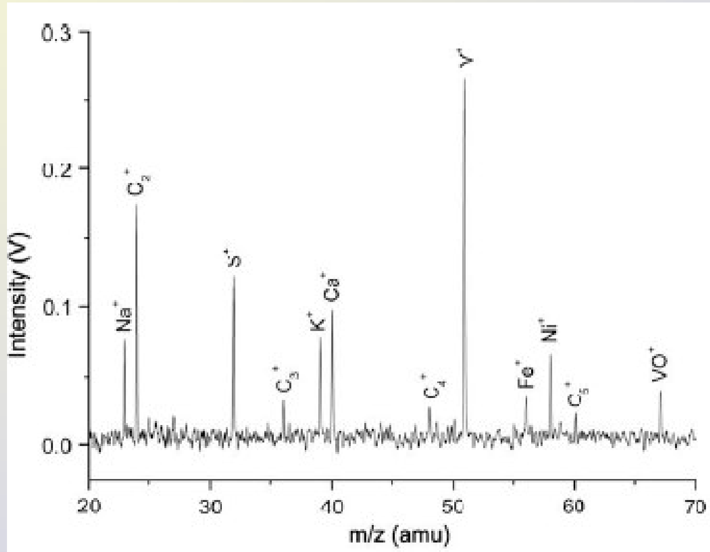


Hot exhaust

Cooled, diluted exhaust

Analysis of soot collected in field campaigns

L2MS



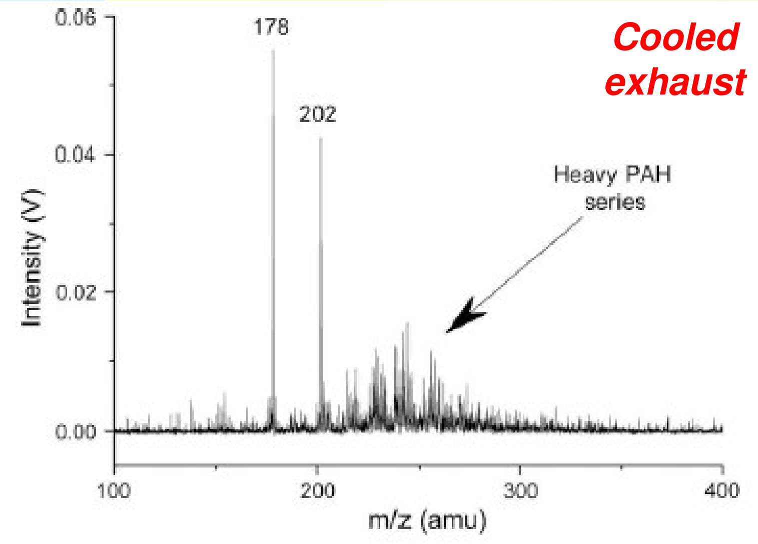
Presence of transition and alkali metal in the samples

In agreement with the fuel composition

Fuel characteristics of the HFO used by the ship: Analysis A1 was performed on routine basis after the fuel purchase on behalf of the ship owner, analysis A2 was performed on fuel sample taken directly from the engine during the campaign. Hyphened cell means that the parameter was not investigated by the analysis.

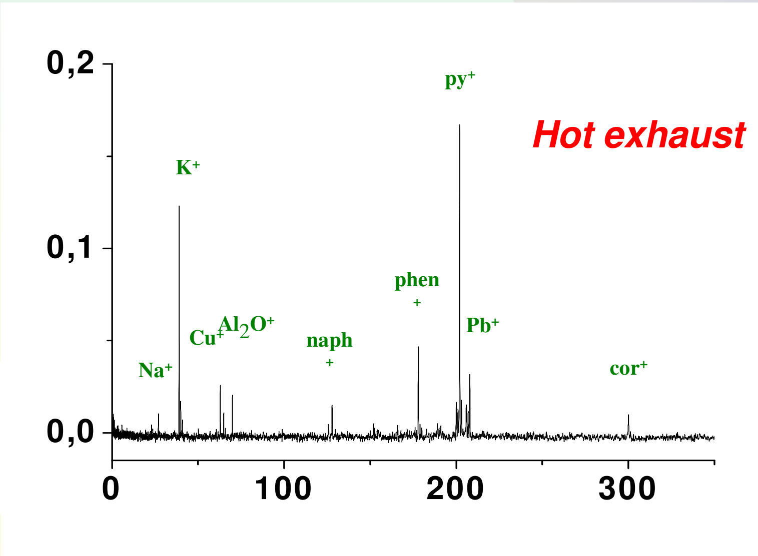
Tested Results	Units	A1	A2
Density at 15 °C	kg m^{-3}	985	987.5
Viscosity at 50 °C	$mm^2 s^{-1}$	373.2	421
Water	% vol.	<0.1	–
Micro-carbon residue	% mass	13	–
Sulphur (S)	% mass	1.97	1.9
Carbon (C)	% mass	–	86.5
Hydrogen (H)	% mass	–	10.6
Nitrogen (N)	% mass	–	0.34
Oxygen (O)	% mass	–	0.7
Total sediment potential	% mass	0.01	–
Ash	% mass	0.03	–
Vanadium (V)	mg kg^{-1}	107	–
Sodium (Na)	mg kg^{-1}	17	–
Aluminium (Al)	mg kg^{-1}	3	–
Silicon (Si)	mg kg^{-1}	5	–
Iron (Fe)	mg kg^{-1}	13	–
Nickel (Ni)	mg kg^{-1}	35	–
Calcium (Ca)	mg kg^{-1}	3	–
Magnesium (Mg)	mg kg^{-1}	<1	–
Lead (Pb)	mg kg^{-1}	<1	–
Zinc (Zn)	mg kg^{-1}	<1	–
Phosphorus (P)	mg kg^{-1}	<1	–
Potassium (K)	mg kg^{-1}	1	–
Flash Point	°C	>70	–
Heating value at const. press.	MJ kg^{-1}	–	40.34
Heating value at const. vol.	MJ kg^{-1}	–	42.59

Analysis of soot collected in field campaigns



L2MS

In agreement with GC analysis of carbonaceous aerosols collecting during summertime in Arctic Ocean, Xie et al, J GEOPHYS RES 112, (2006) D02306



Scarce presence of PAHs in the hot zone:

-different condensation conditions in relation to different volatilities

- consistent with the higher organic content detected by evolved gas analysis (EGA) in the cooled diluted exhaust, compared to the hot zone.

Conclusions & perspectives

Parametric characterization of the laser desorption and ionization processes in the fluence domain

adsorbed phase addressed exclusively

sensitivity, selectivity, no fragmentation

Still work to do:

no C_xH_y = no aliphatics, no fragments or lack of ionization efficiency? (3-photon vs 2-photon)

SOOT ANALYSIS

Systematic measurements … different fuels … combustion stage

Basic soot growth mechanisms … low pressure flames

Field campaigns … december 2009

Acknowledgments

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V. Tishkova

IVL Göteborg

J. Moldanova

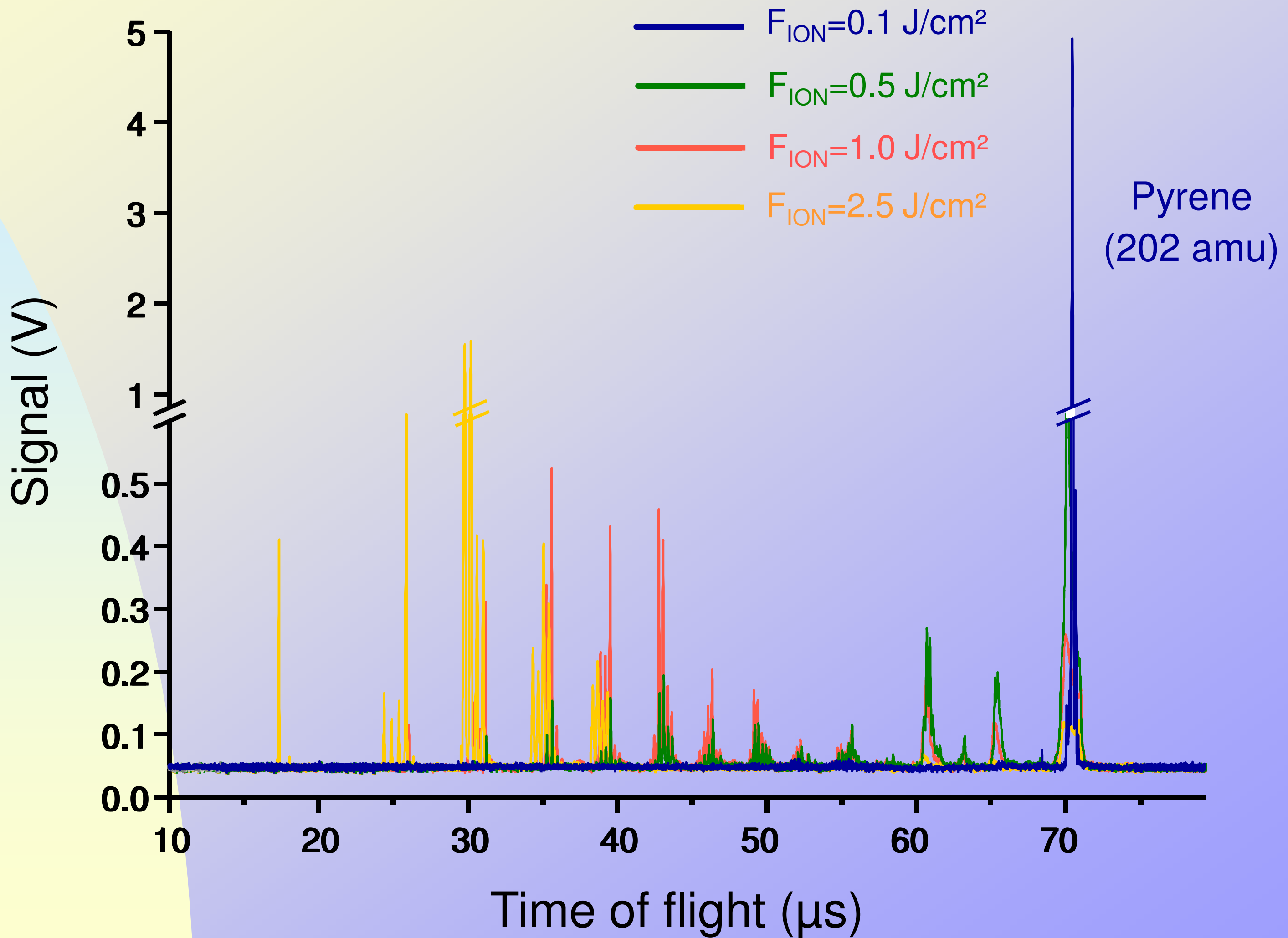
E. Fridell

NSERC Ottawa

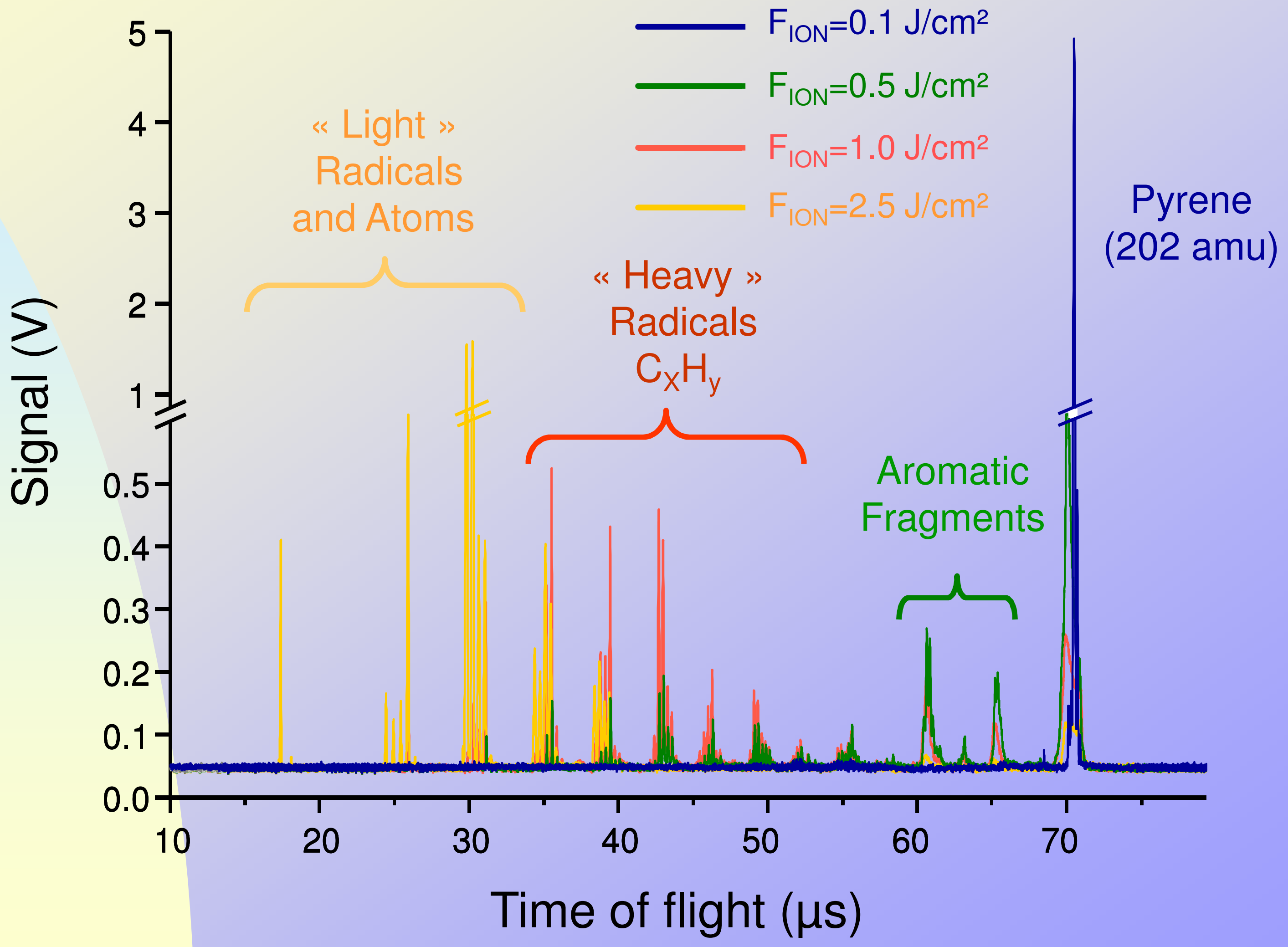
K. Thomson

Thank You !!!

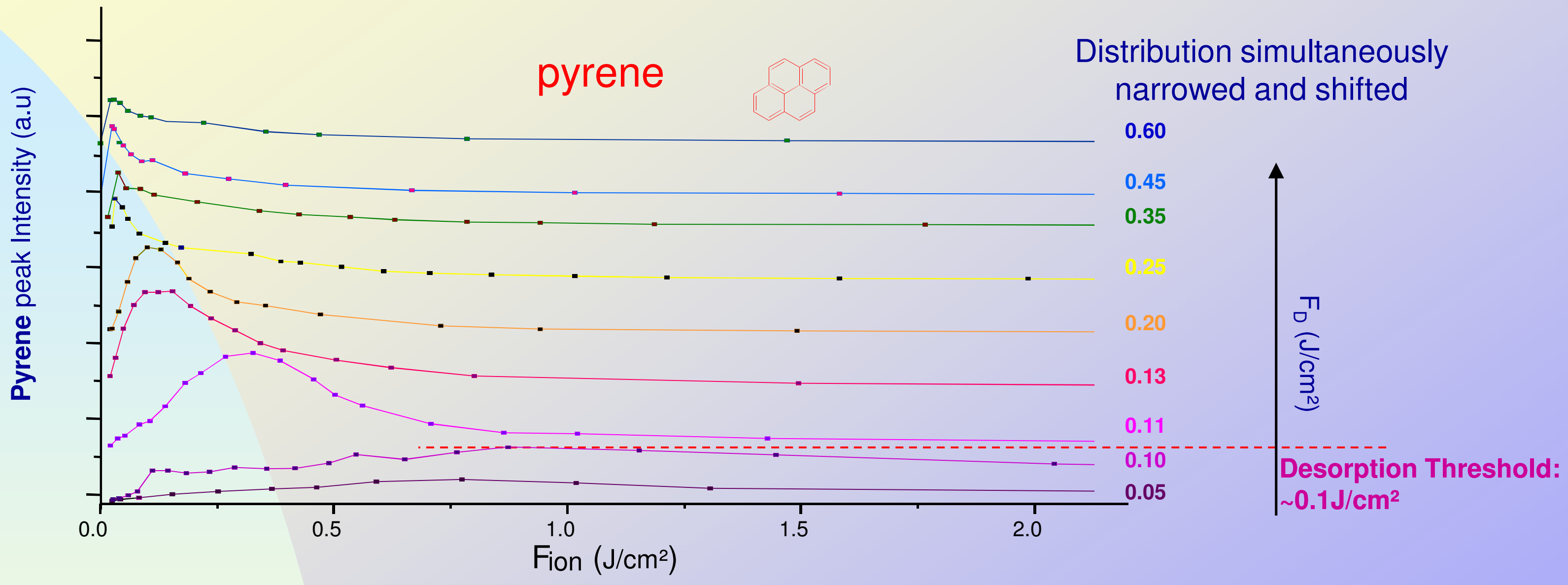
Evolution of the Spectra with Fluence



Evolution of the Spectra with Fluence



Evolution of the Spectra with Fluence

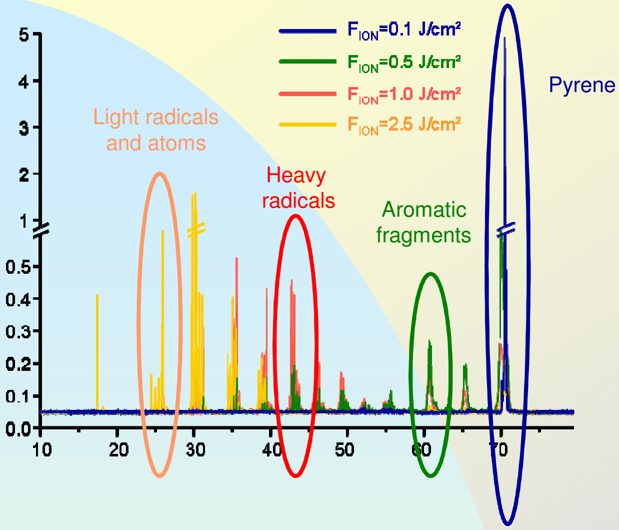


- the increase of internal energy E_{int} acquired at the desorption level :

  - leads to an easier ionization(i.e. at lower Fion)
  - promotes fragmentation at high Fd (together with in-plume collision)

Faccinetto, Thomson, Ziskind, Focsa, *Appl. Phys. A*, **92**, 969 (2008)

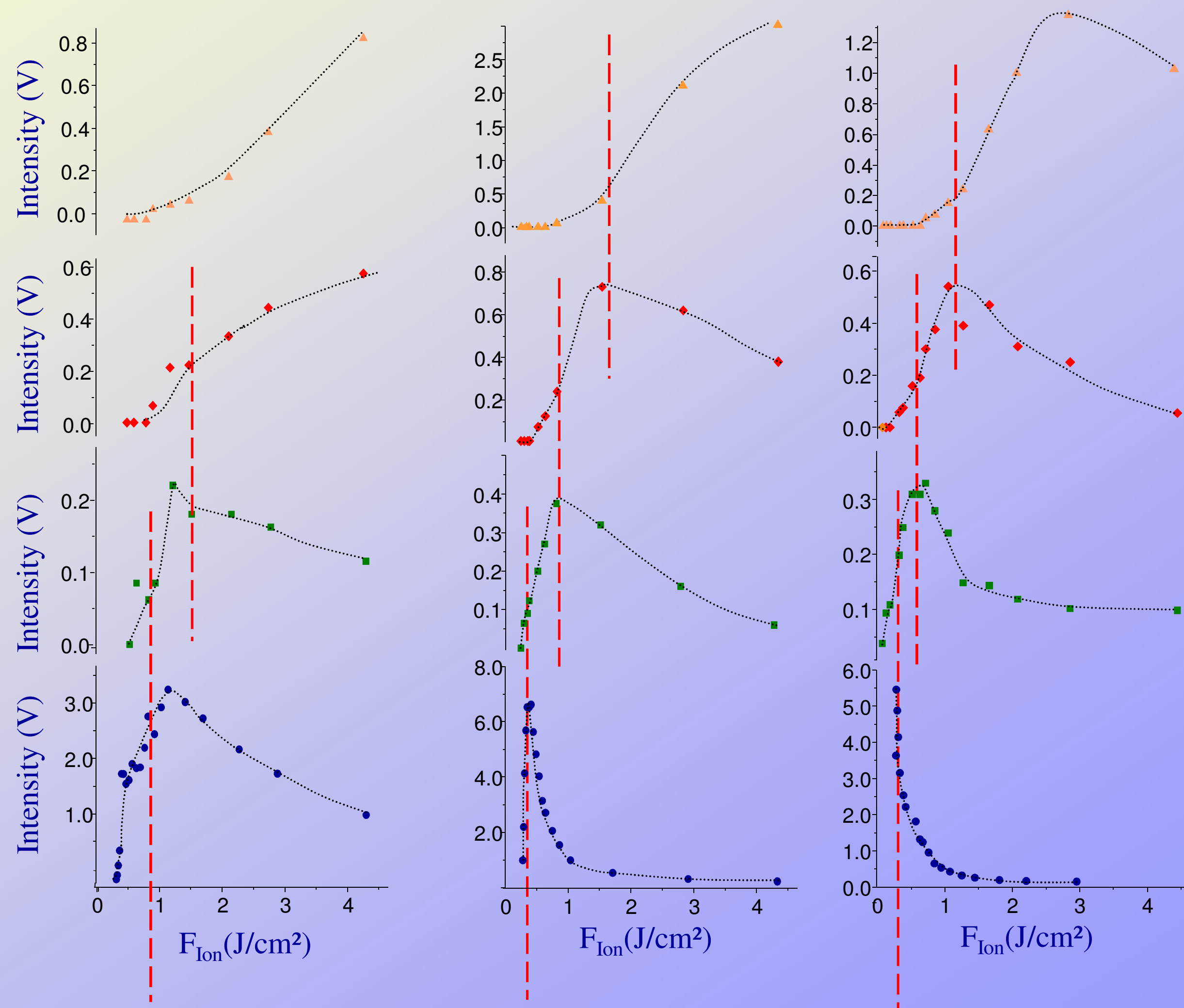
Evolution of the Spectra with Fluence



- Role of the internal energy increase in the progressive dissociation of all the various species involved
- Specific fragmentation pathway of the PAH (ladder switching model, U. Boesl, *J. Phys. Chem.* **95**, 2949 (1991)):

  -Multiphoton absorption interrupted by dissociation channels to fragment ions.

  -Absorption within these fragment ions continues until the next dissociation channels "switch over" to a smaller fragment ion

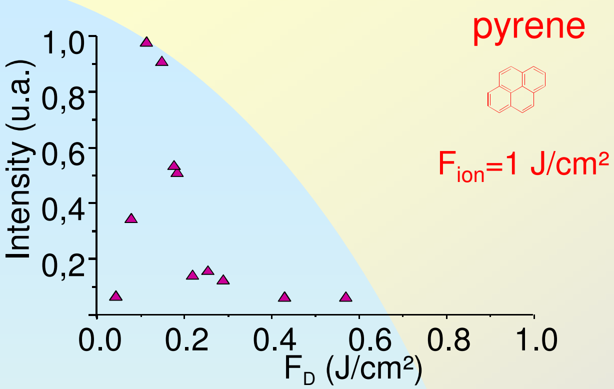


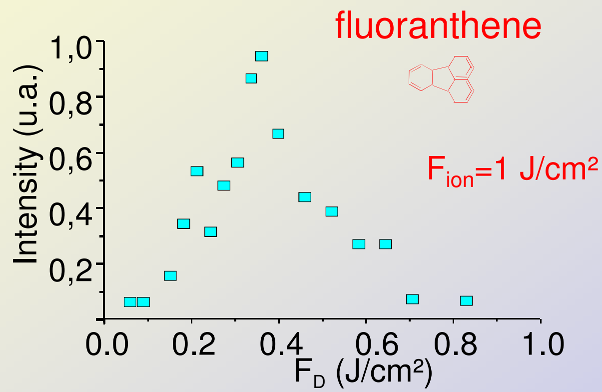
F_D = 0.1 J/cm²

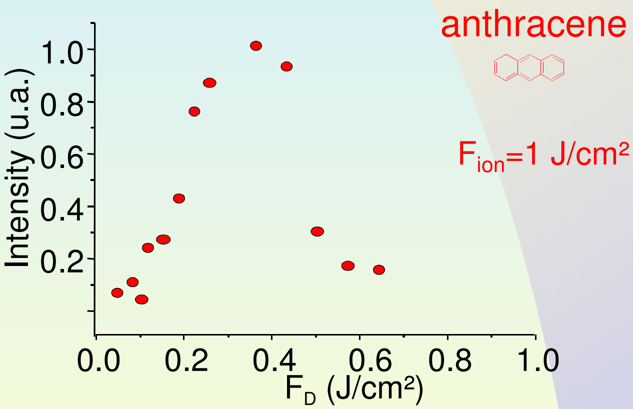
F_D = 0.2 J/cm²

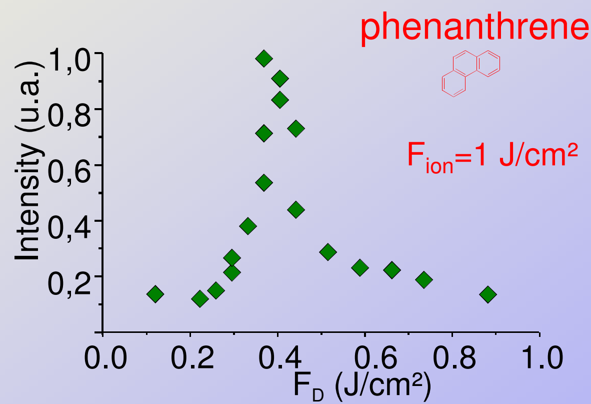
F_D = 0.3 J/cm²

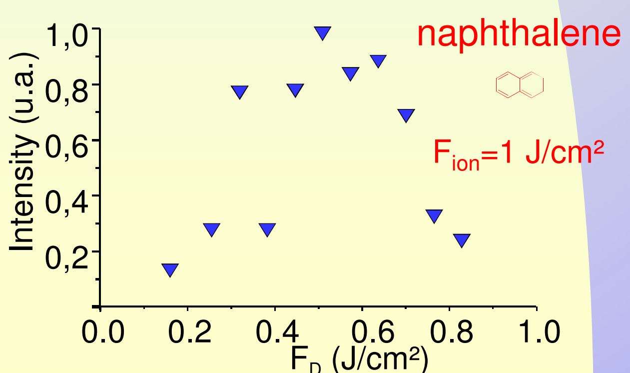
Evolution of the Spectra with Fluence

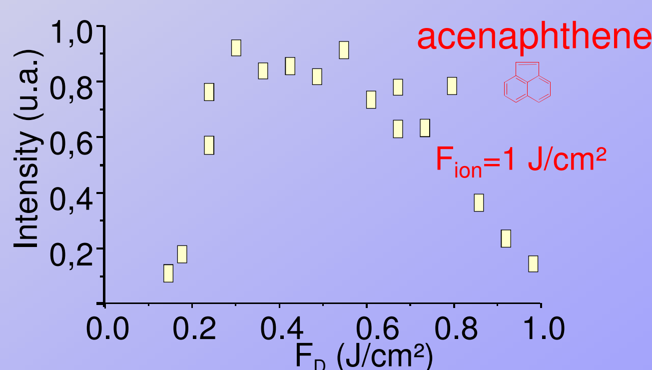








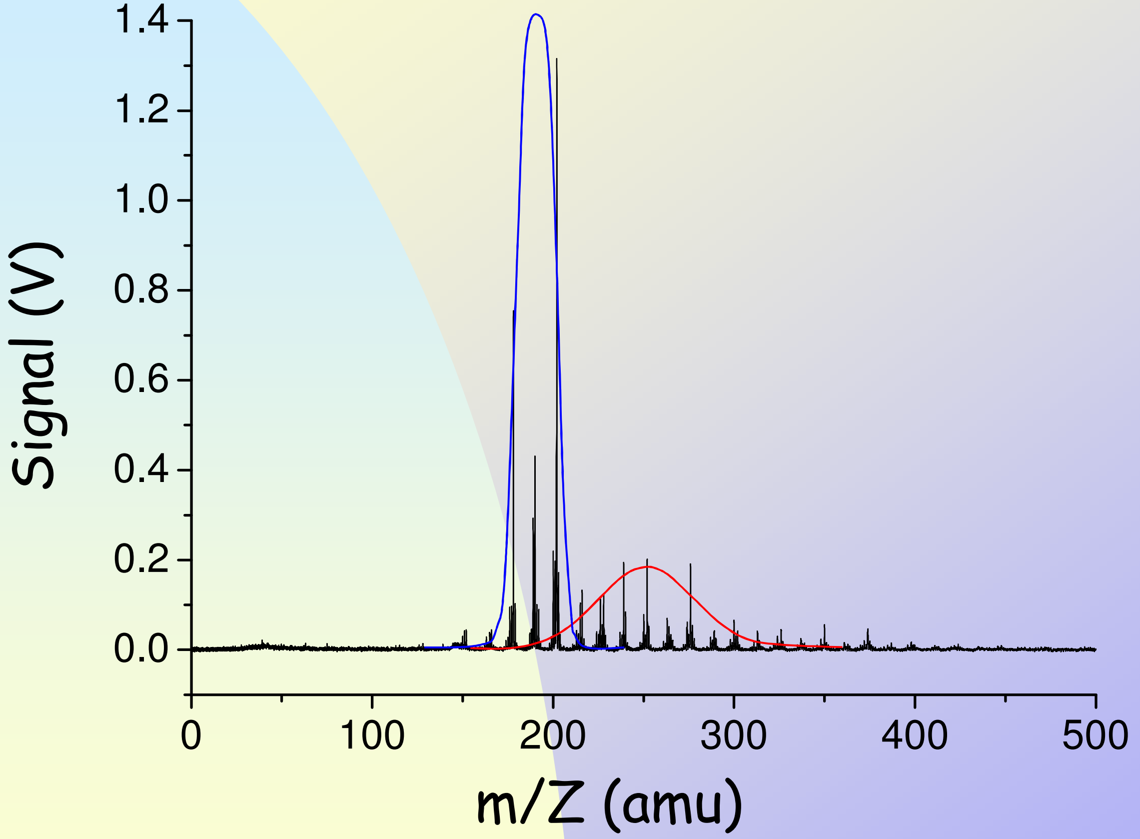




- Specific behavior of different PAHs with respect to the desorption and ionization processes (and to the coupling between them)
- Possible selective desorption method ?

C. Mihesan et al, *J. Phys.: Condens. Matter*, **20**, 025221 (2008)

Ethylene soot mass spectrum

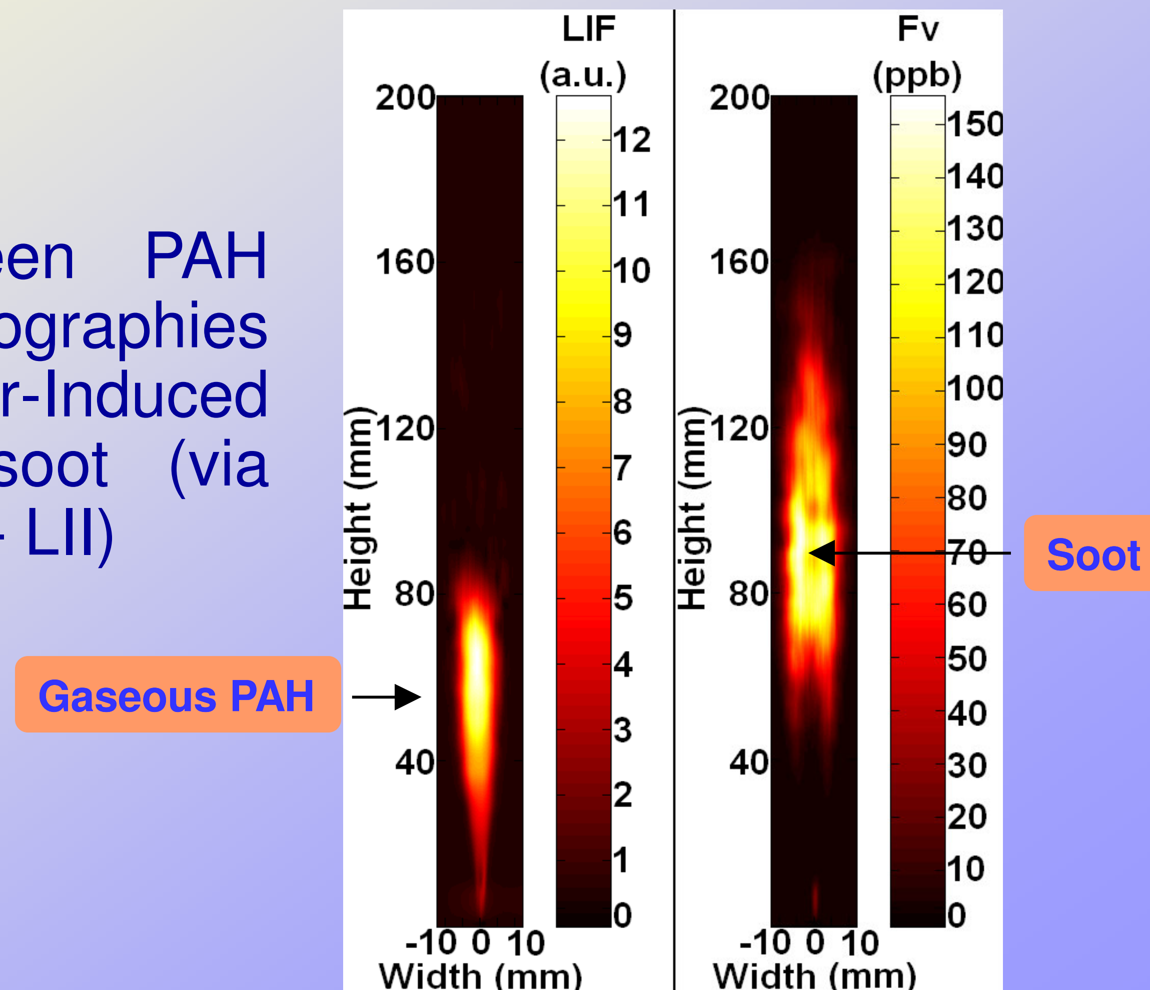


- Very regular mass sequence
  - One peak each 12 amu (C) or sometimes 14 amu (CH_2)
  - Mass detected up to 500 amu
- Identified masses are consistent with high temperature stable PAH
- Peak intensity ratios are constant
- Two different behaviours, « light » and « heavy » masses

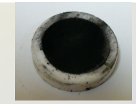
Future work

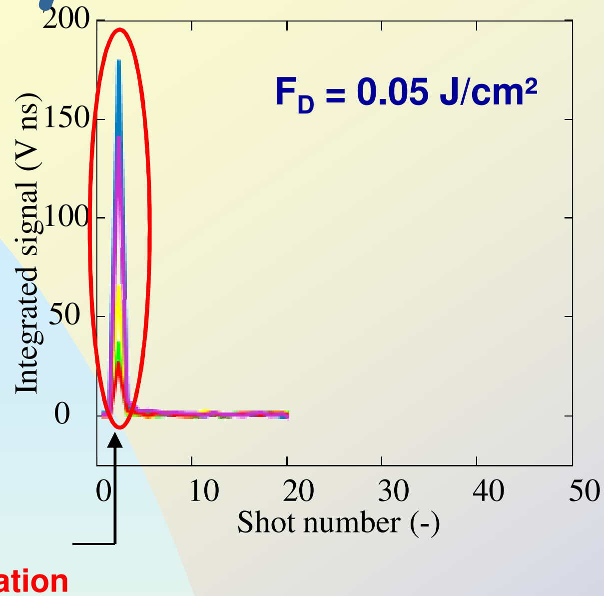
- Find an experimental procedure to completely avoid gas condensation

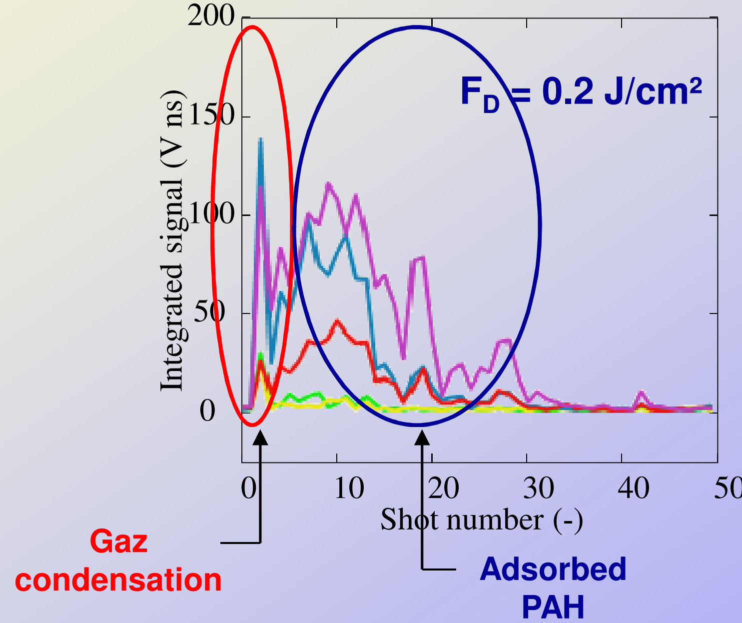
- Find a correlation between PAH adsorbed on soot and the cartographies obtained for PAH (via Laser-Induced Fluorescence - LIF)) and soot (via Laser-Induced Incandescence - LII)



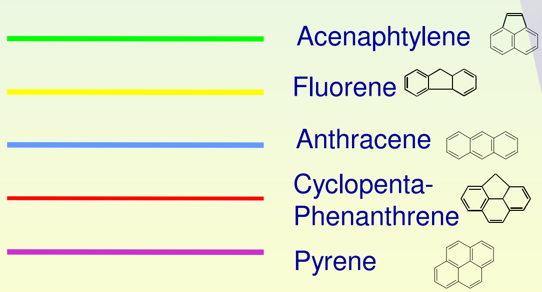
Shot by shot

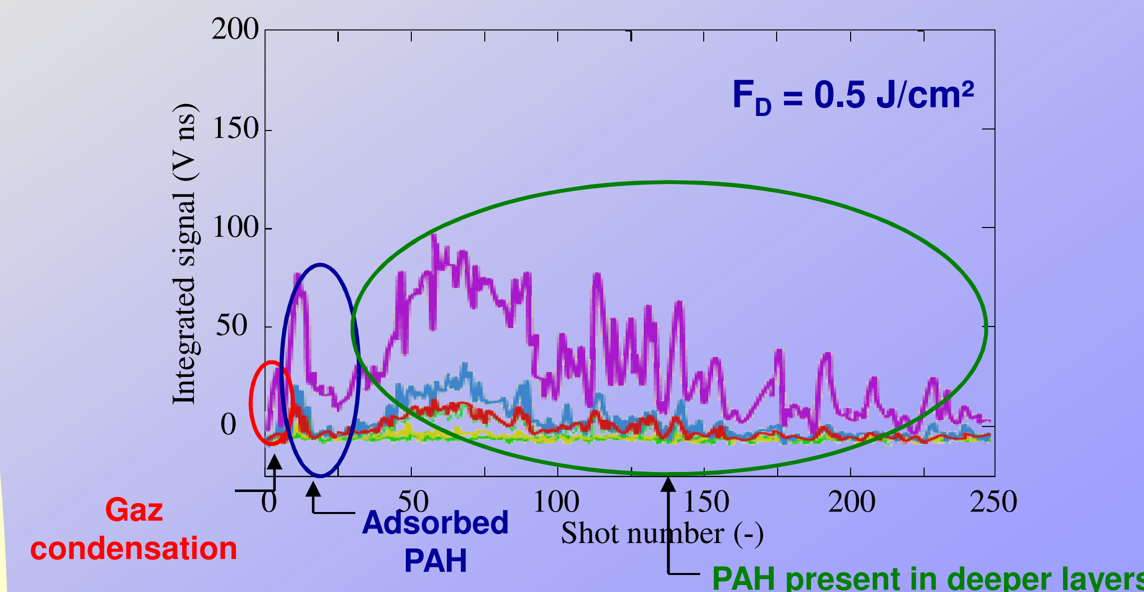






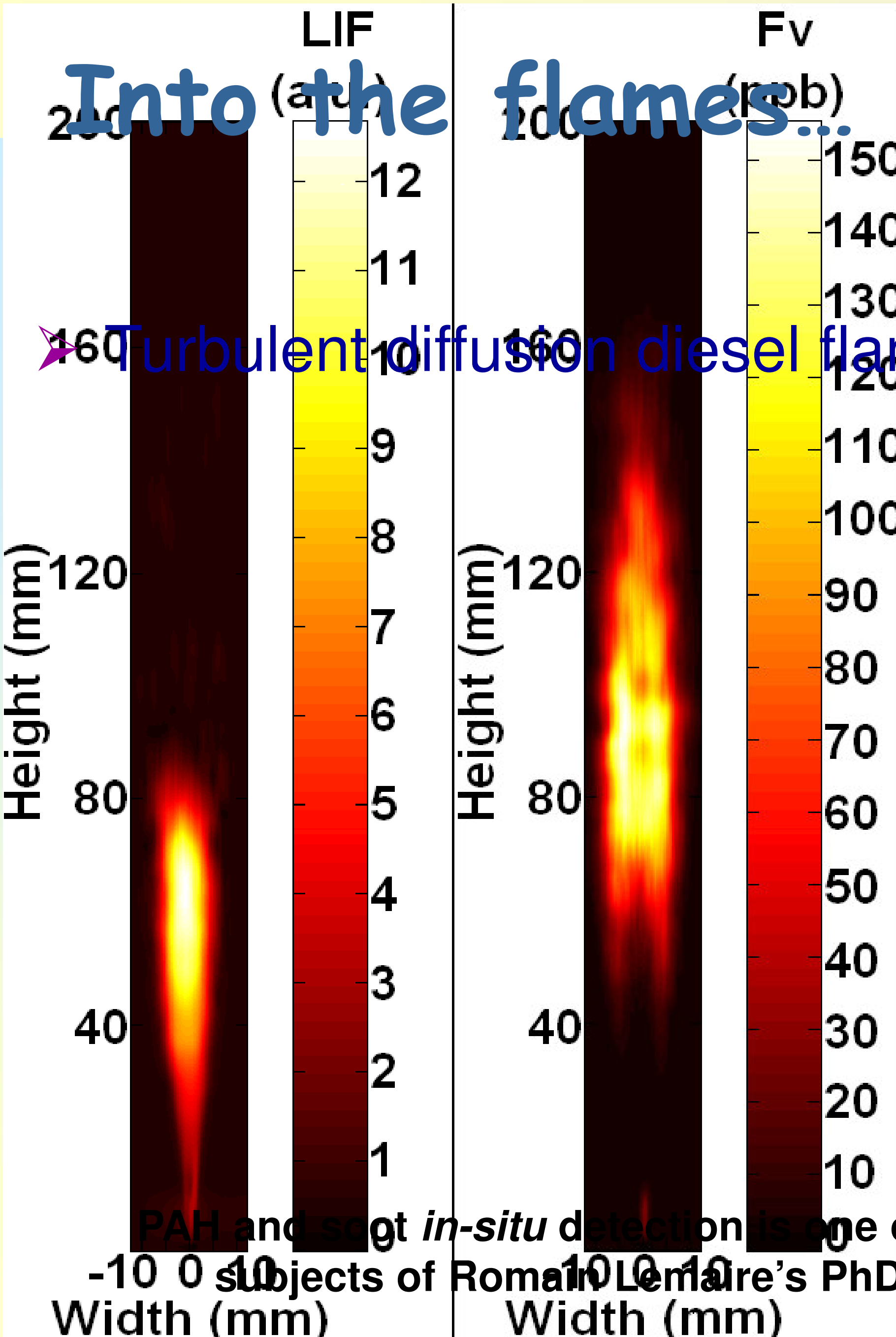
Mass (amu)

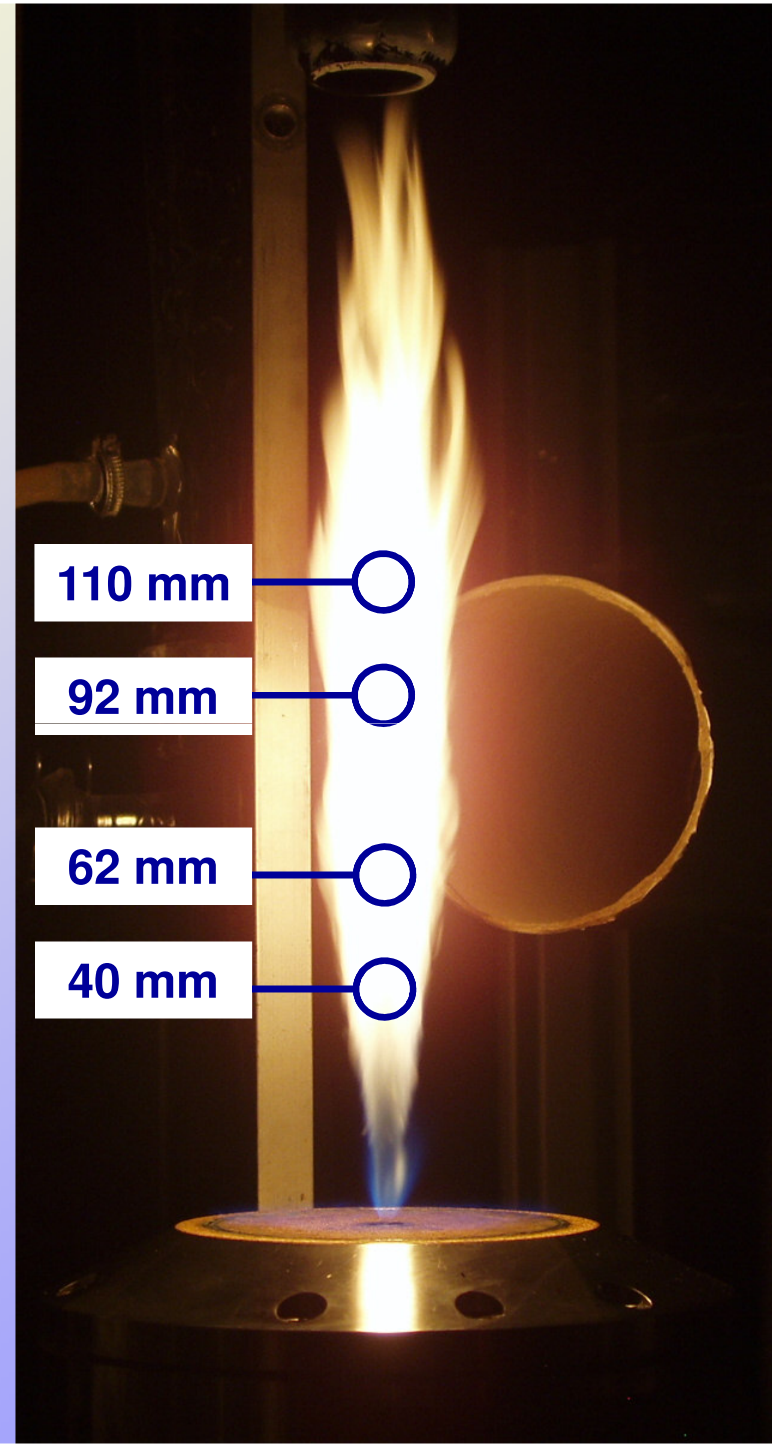




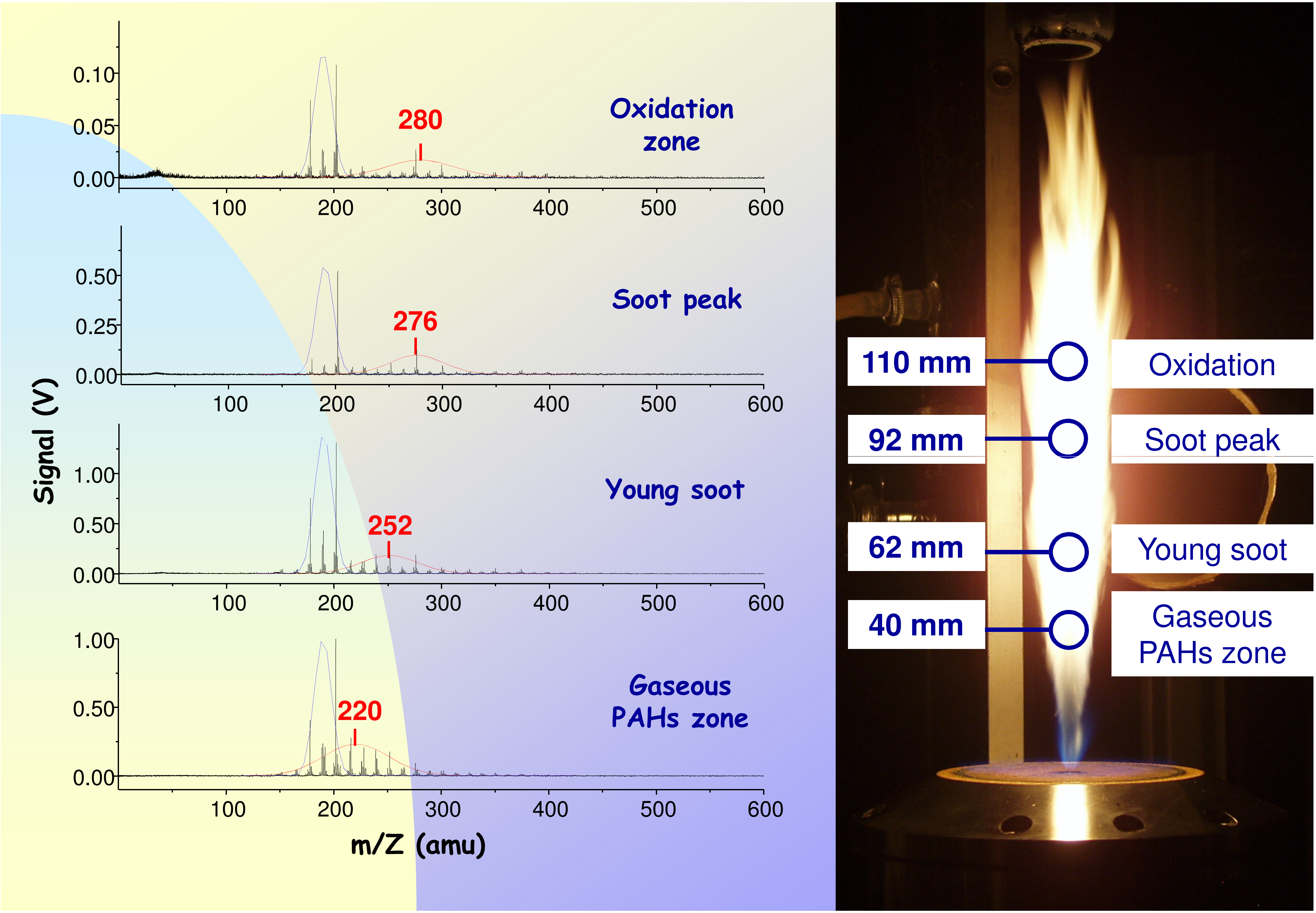
Into the flames…

- Turbulent diffusion diesel flame





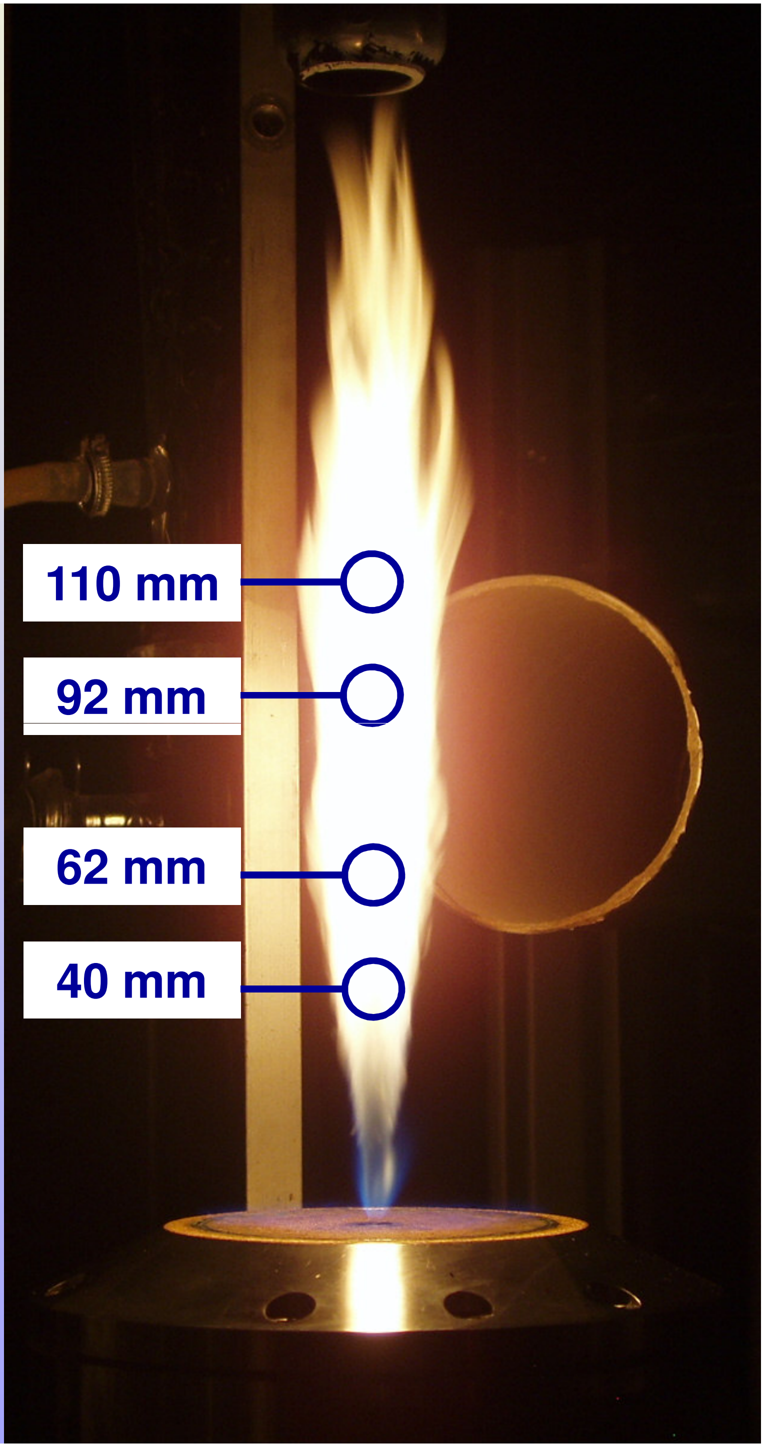
PAH and soot *in-situ* detection is one of the main subjects of Romain Lemaire's PhD thesis



Signal (V)
0.10
0.05
0.00
100
200
300
400
500
600
280
Oxidation zone
0.50
0.25
0.00
276
Soot peak
1.00
0.50
0.00
252
Young soot
1.00
0.50
0.00
220
Gaseous PAHs zone
m/Z (amu)
110 mm
Oxidation
92 mm
Soot peak
62 mm
Young soot
40 mm
Gaseous PAHs zone

Into the flames…

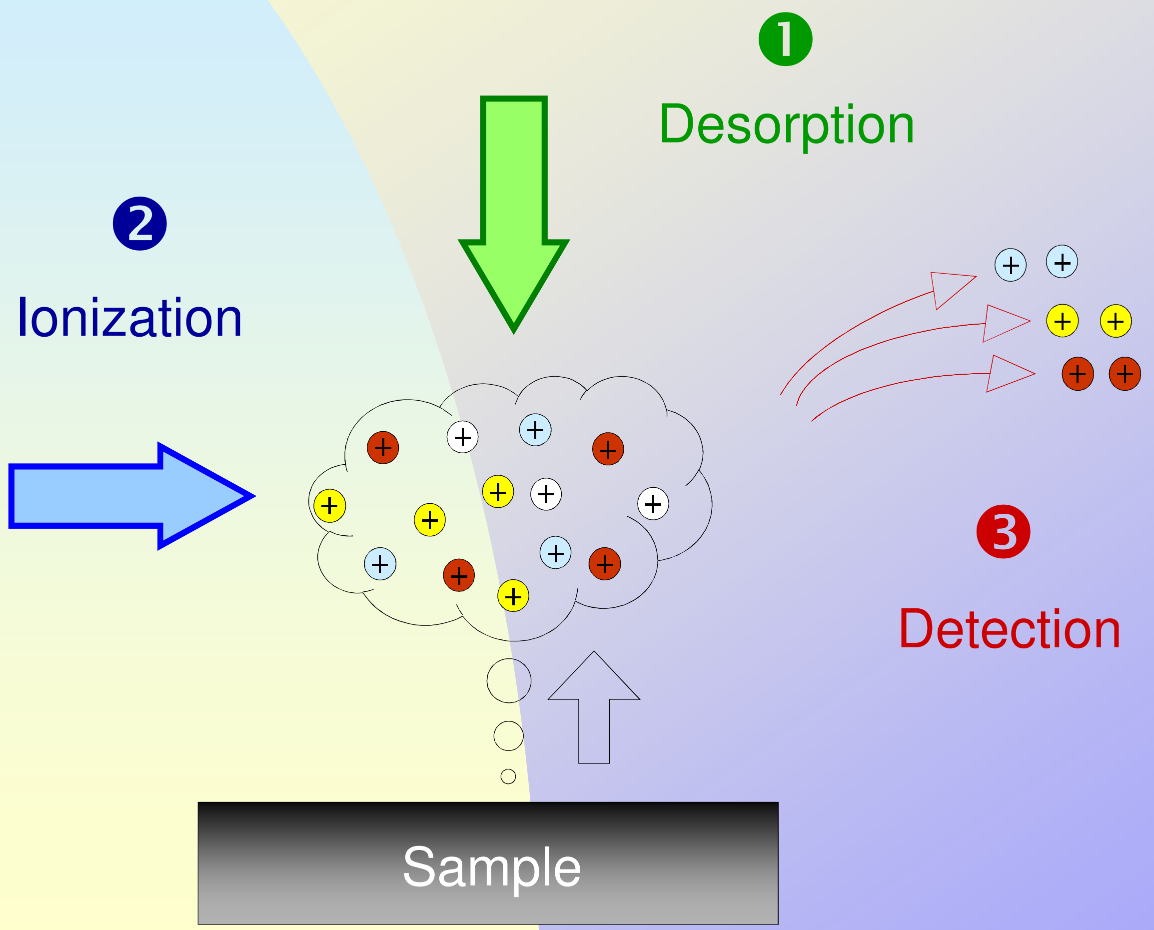
- Turbulent diffusion diesel flame
- Various different heights have been chosen:
  - Only gases before the sooting region (PAH have been condensed on activated carbon)
  - Young soot region
  - Maximum of soot volume fraction F_v
  - Beginning of the oxidation region



PAH and soot *in-situ* detection is one of the main subjects of Romain Lemaire's PhD thesis

Experimental Technique:

Laser Desorption /Laser Ionization /ToF Mass Spectrometry

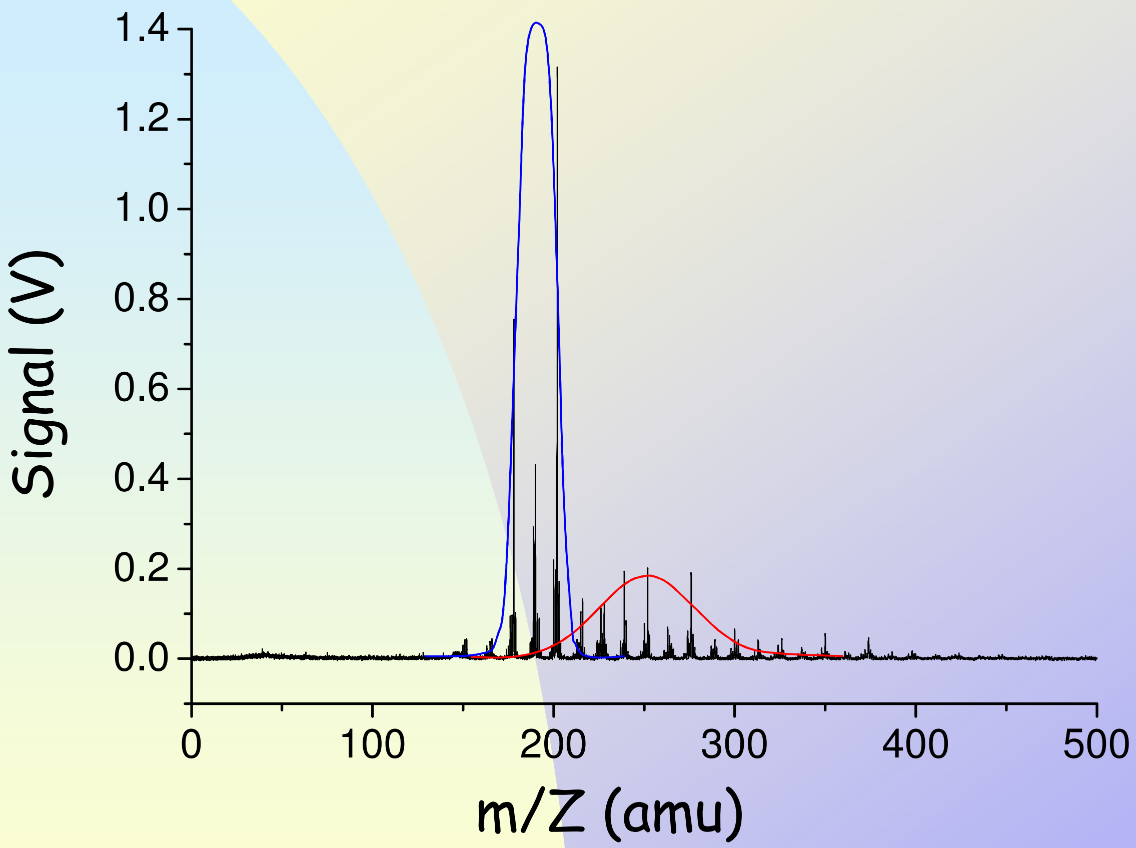


❶ *Desorption Laser:*
doubled Nd:YAG,
λ = 532 nm, 10 ns pulse, 10 Hz,
0.01–1.5 J/cm²

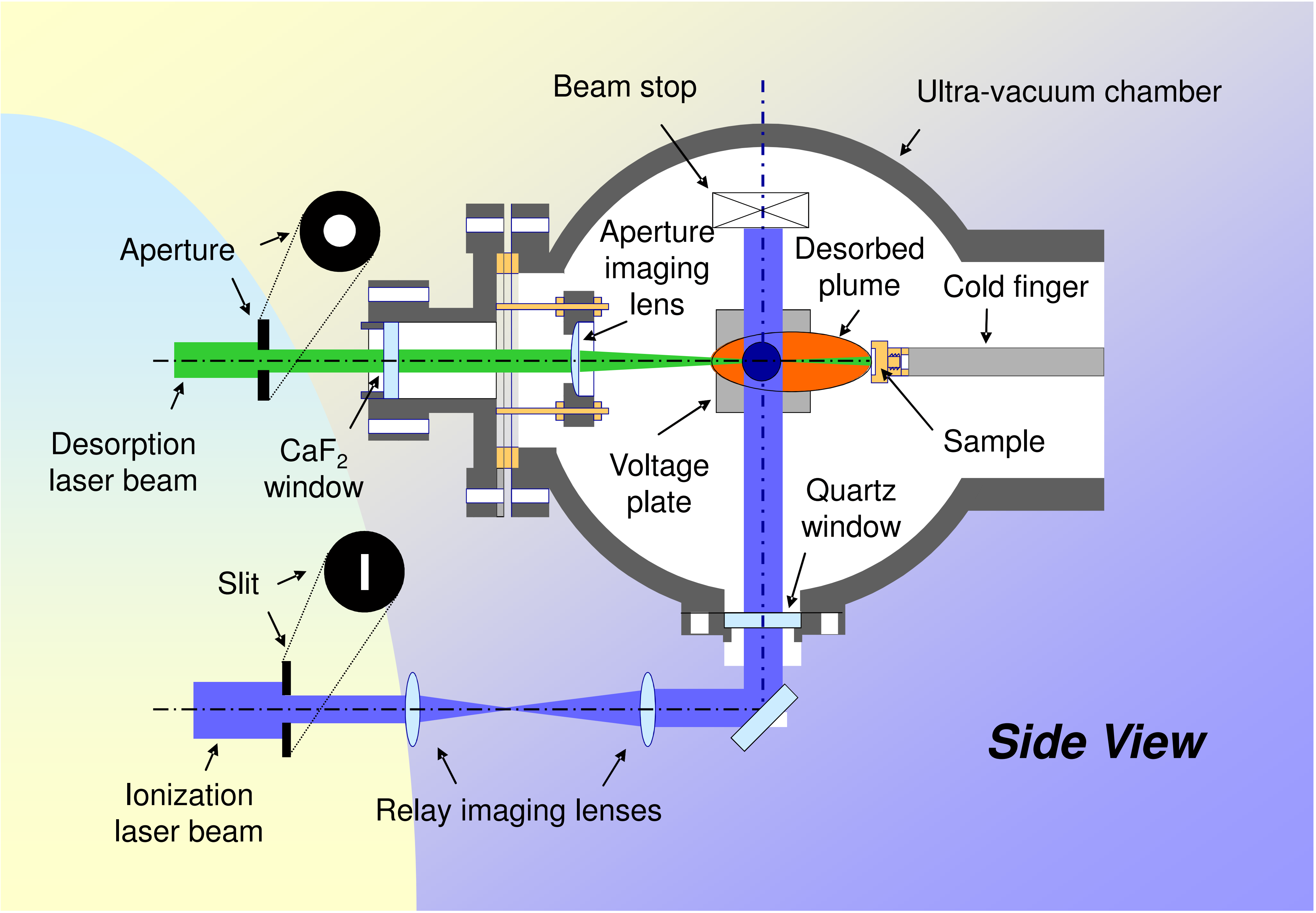
❷ *Ionization Laser*
Multiphotonic:
quadrupled Nd:YAG,
λ = 266 nm, 10 ns pulse,
10 Hz, 0.01-3 J/cm²

❸ *Detection:*
Time-Of-Flight mass
spectrometer

Ethylene soot mass spectrum



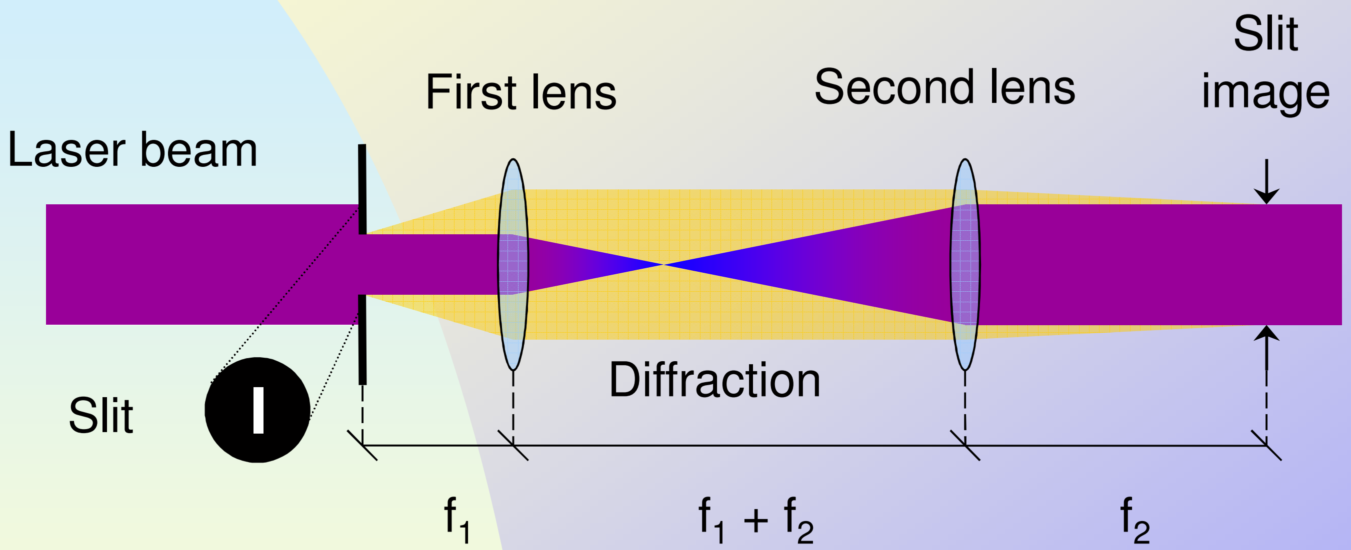
- Very regular mass sequence
  - One peak each 12 amu (C) or sometimes 14 amu (CH_2)
  - Mass detected up to 500 amu
- Identified masses are consistent with high temperature stable PAH
- Peak intensity ratios are constant
- Two different behaviours, « light » and « heavy » masses

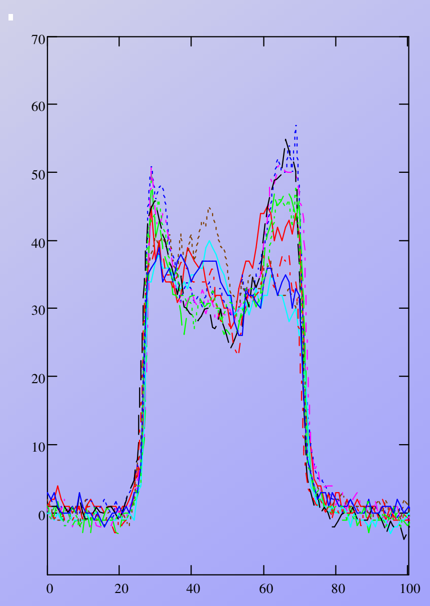


Beam stop
Ultra-vacuum chamber
Aperture
Aperture imaging lens
Desorbed plume
Cold finger
Desorption laser beam
CaF_2 window
Voltage plate
Sample
Quartz window
Slit
Ionization laser beam
Relay imaging lenses
Side View

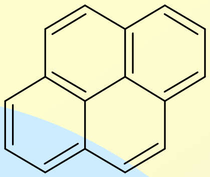
Setup Optimization

Beam imaging configuration allowing a « quasi top-hat » beam profile

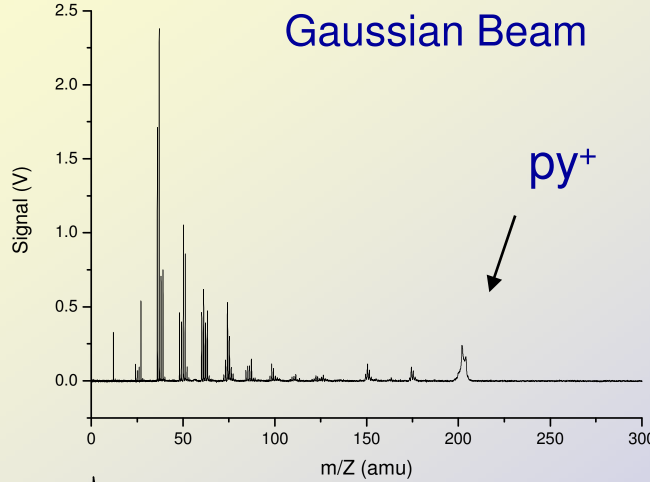


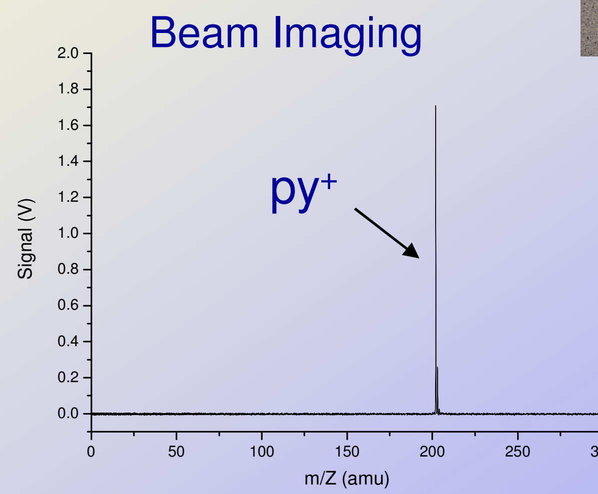


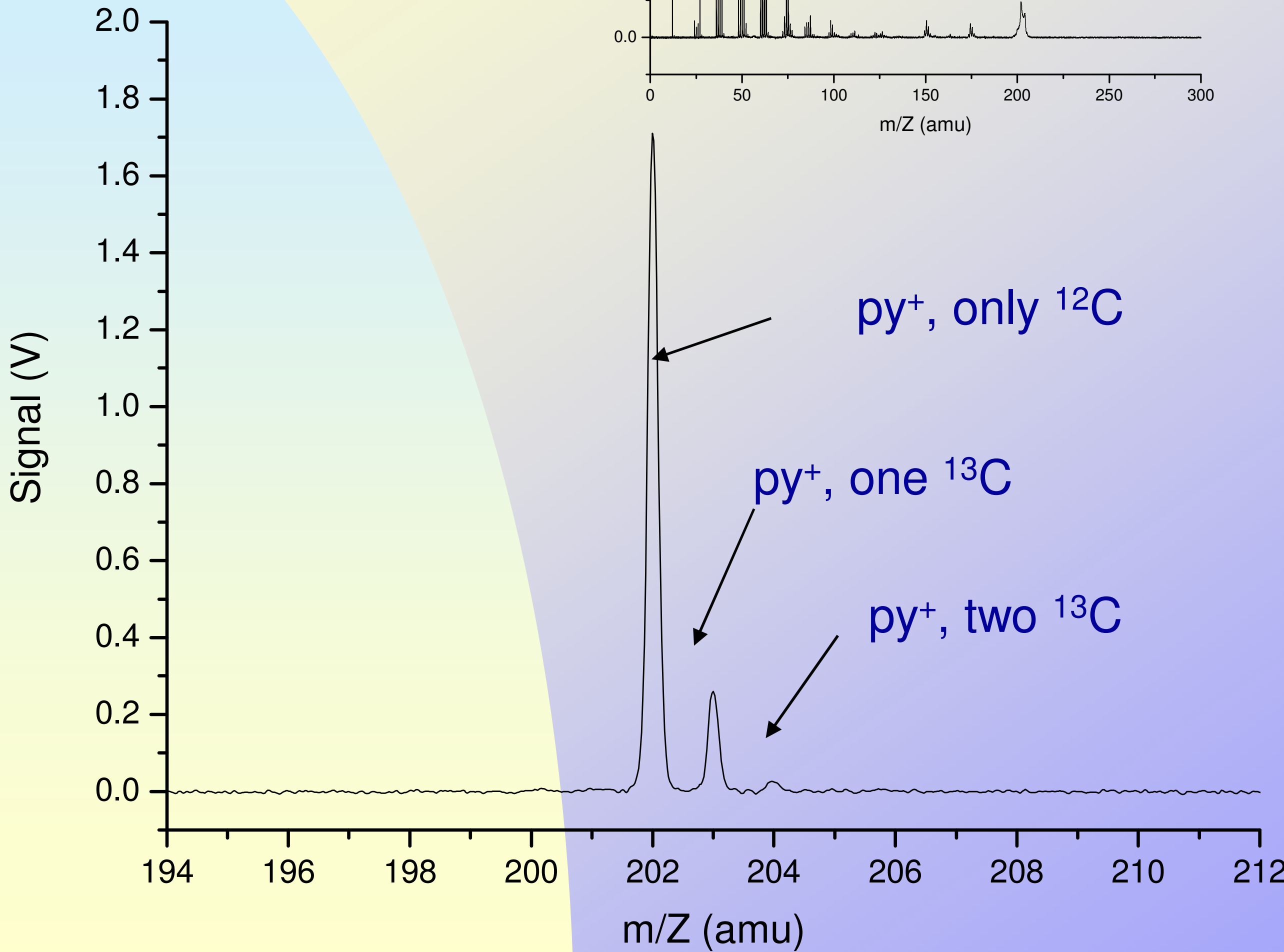
- increase ionization probe volume to increase sensitivity
- with increased sensitivity, lower ionization fluence
- Homogeneous beam over the entire ionization volume for a perfect control of the fluence



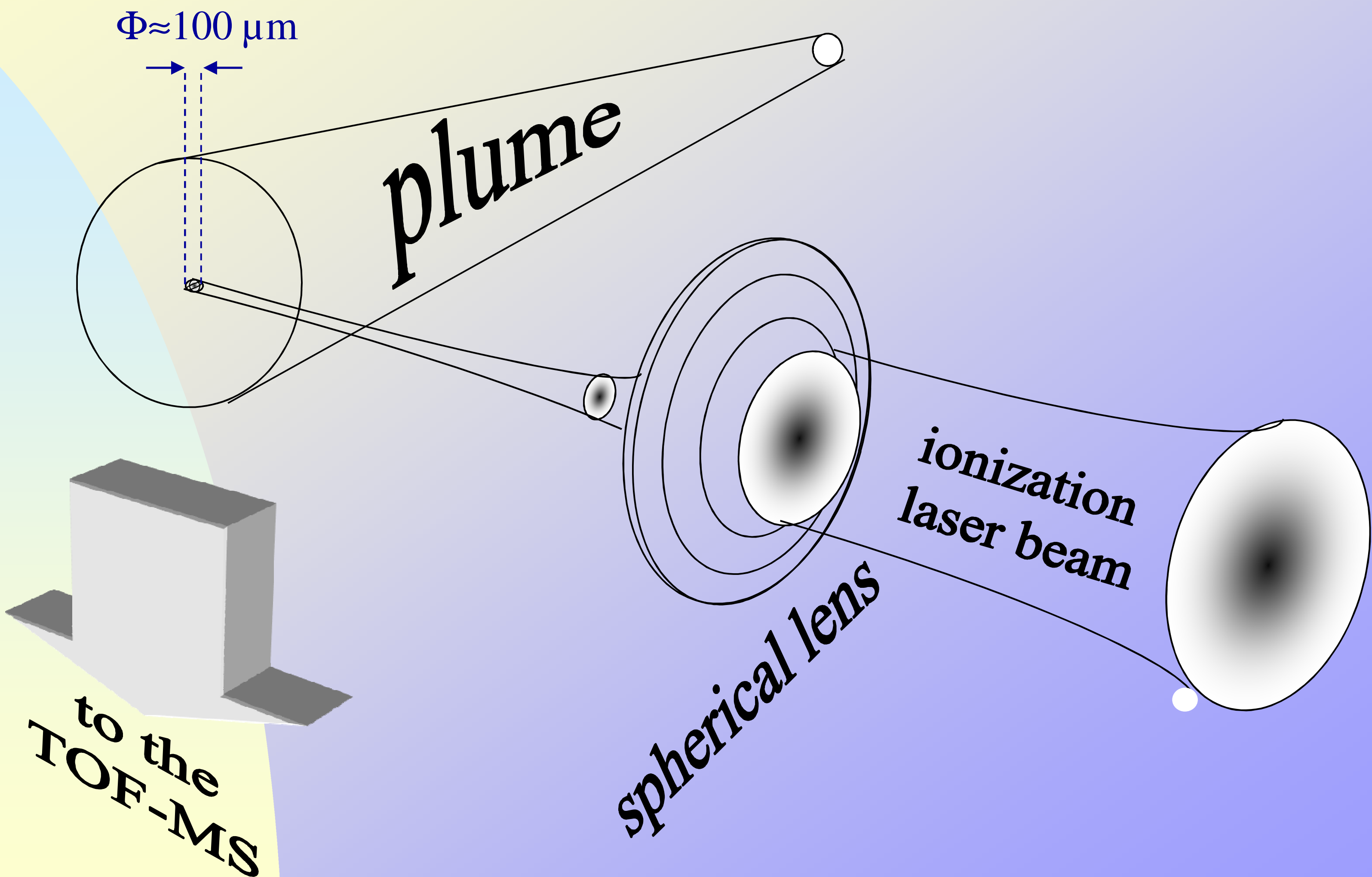
Pyrene
(202 amu)



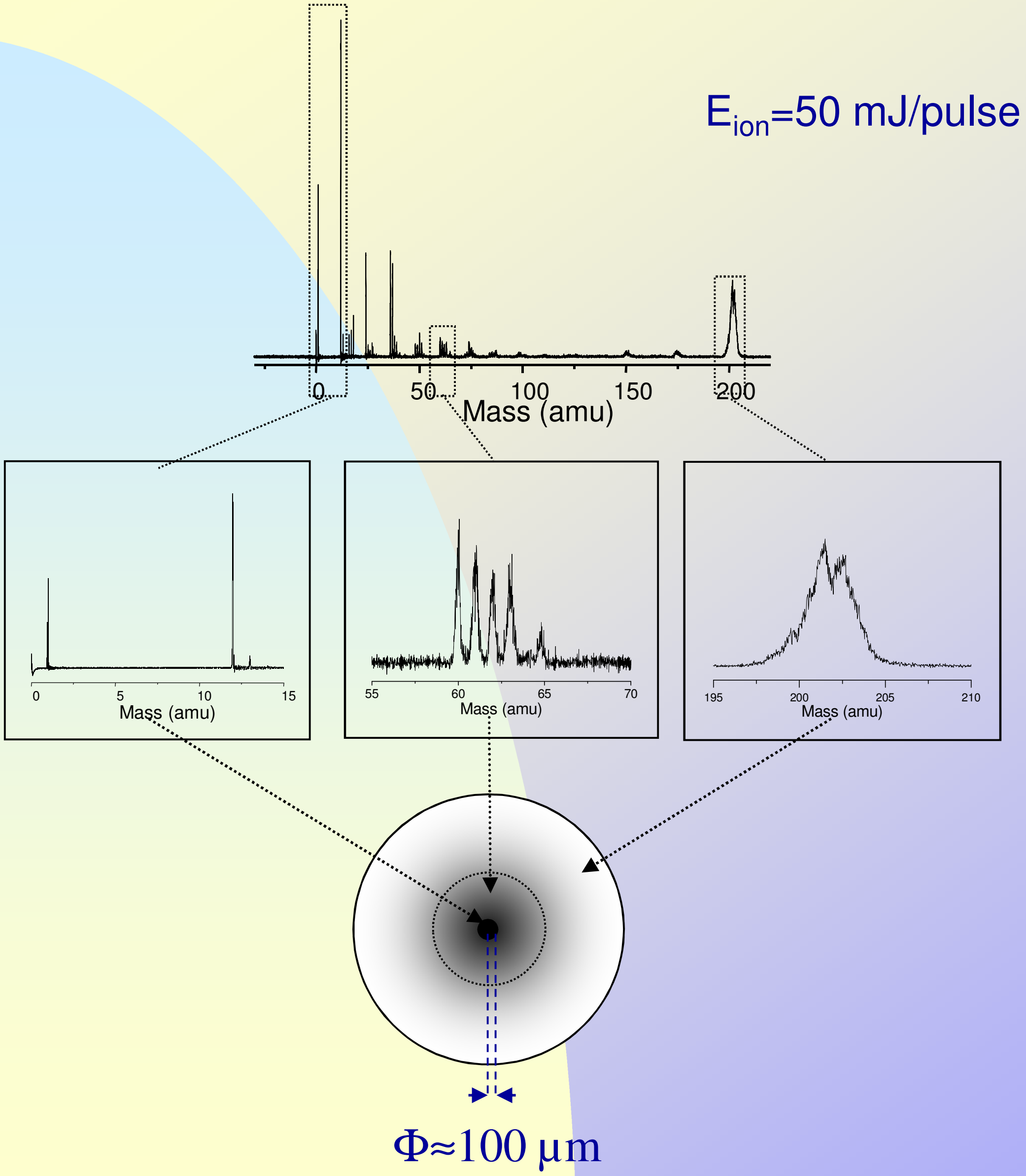


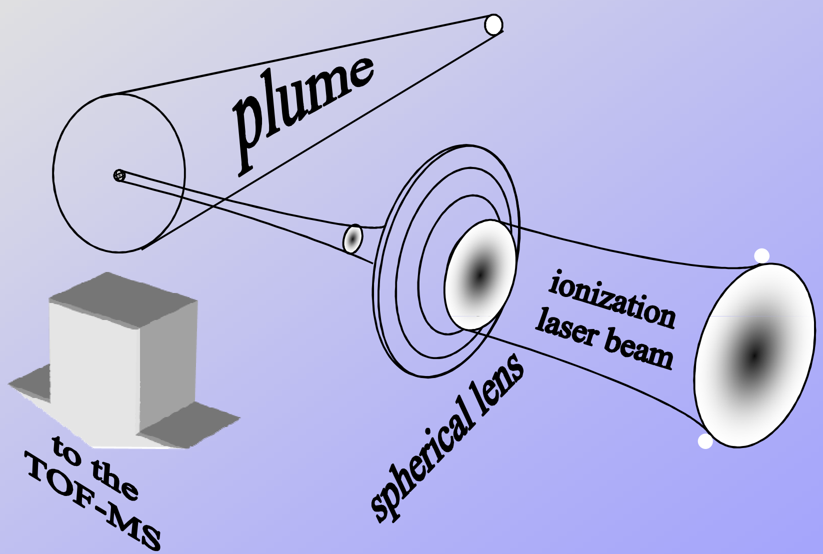


What about the ionization laser ?

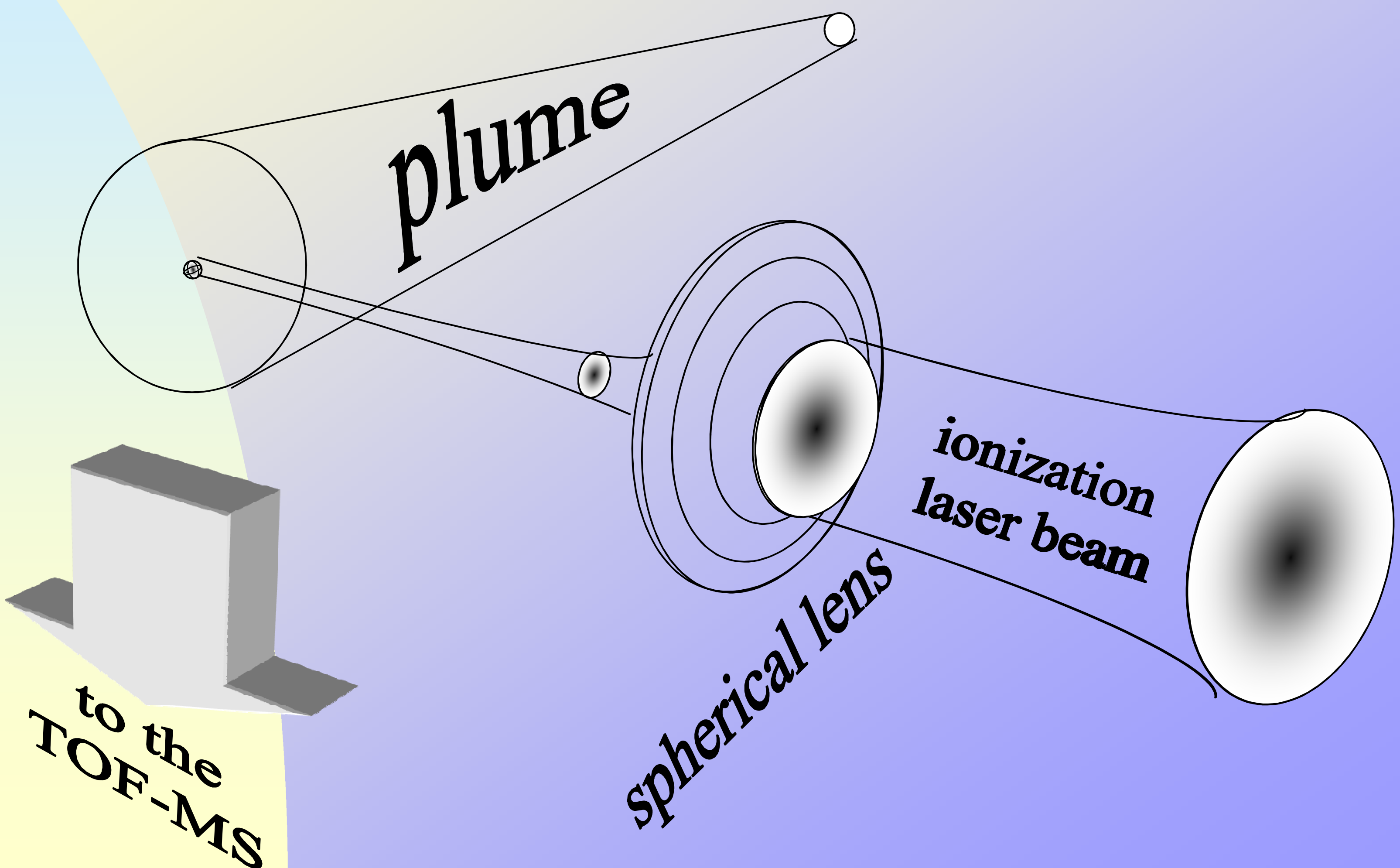


What about the ionization laser ?





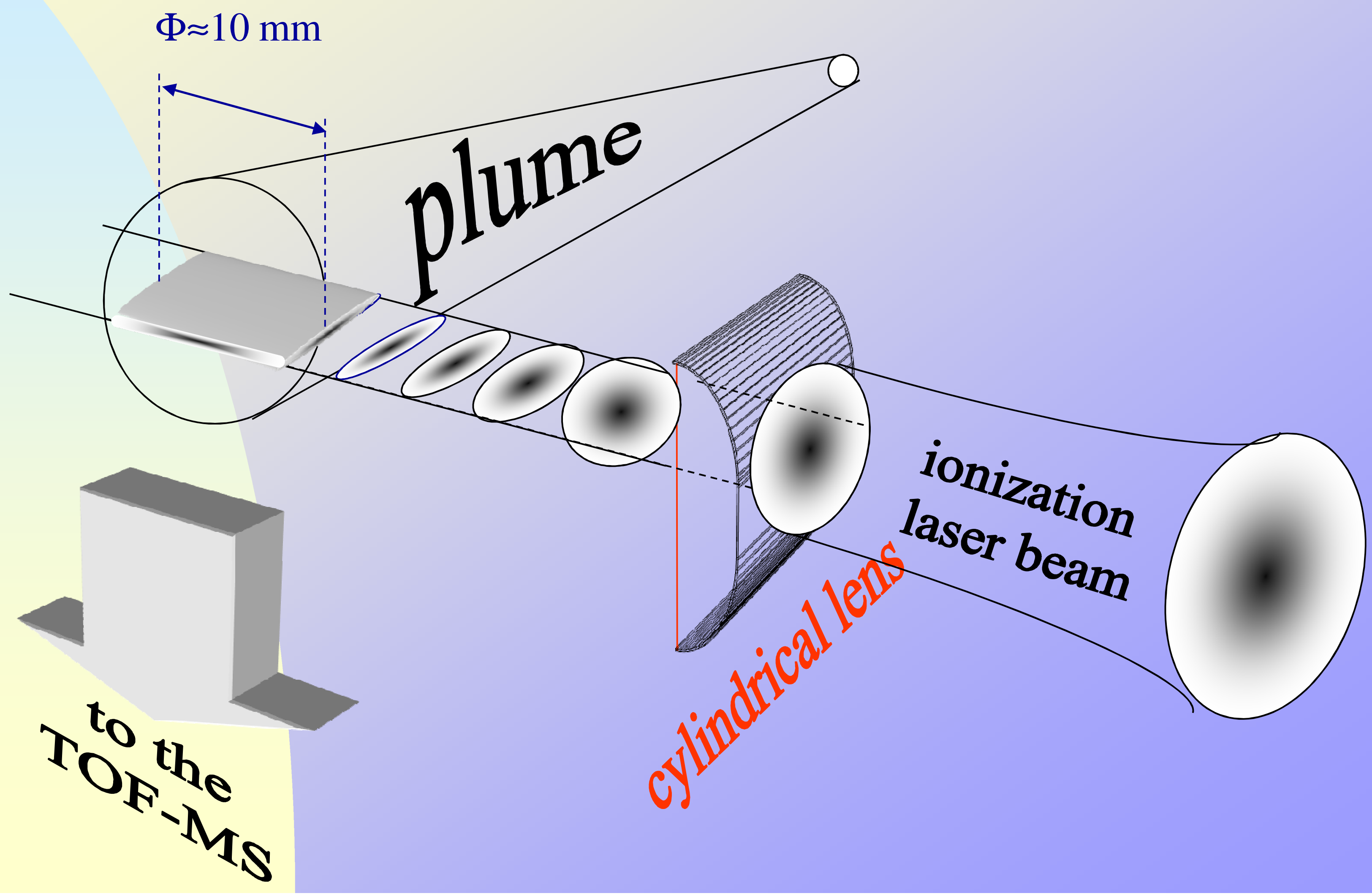
New Geometry



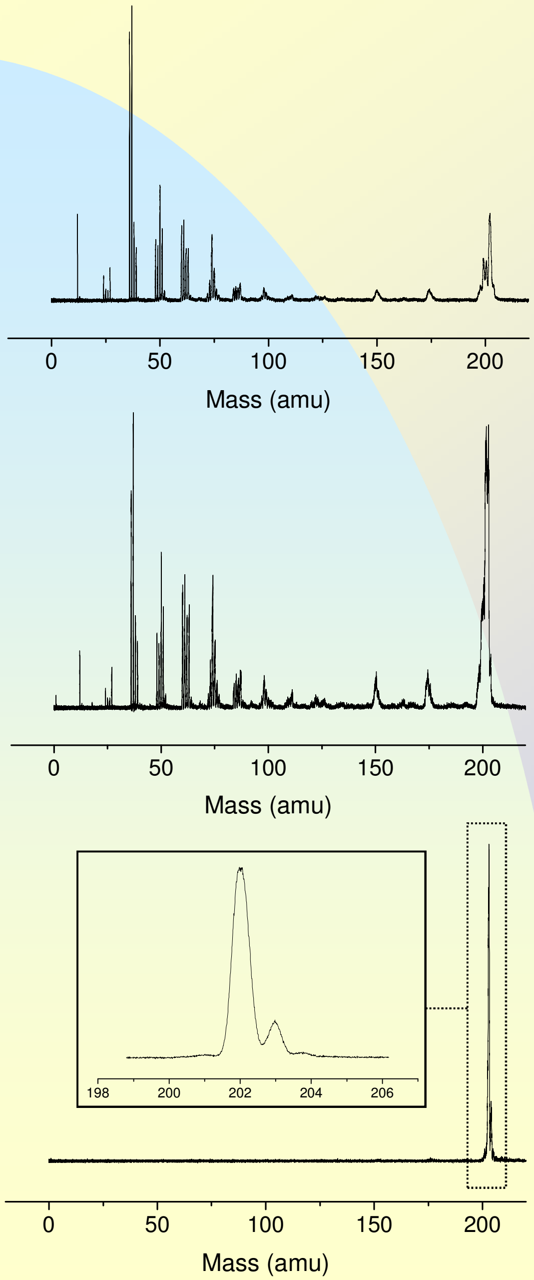
New Geometry

=> laser sheet

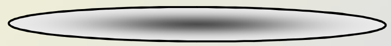
=> higher ionization volume (x10^3)



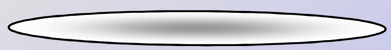
Fragmentation : Ionization intensity influence



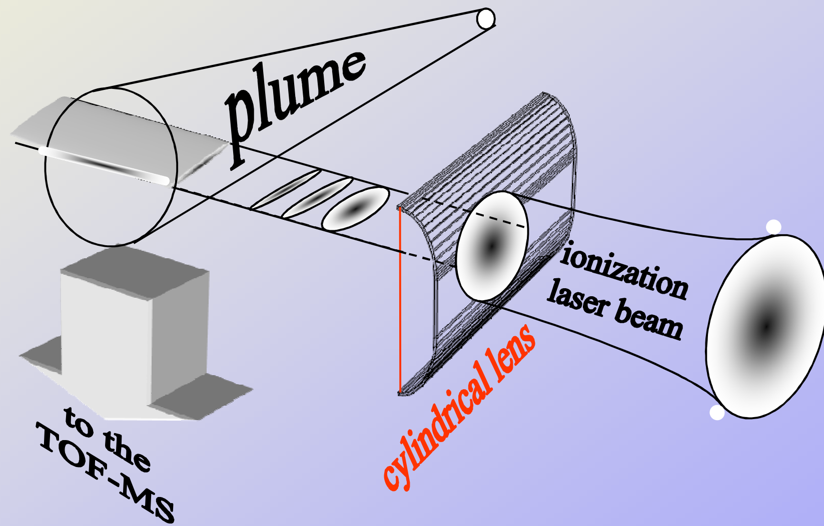
E_{ion}=50 mJ/pulse



E_{ion}= 35 mJ/pulse



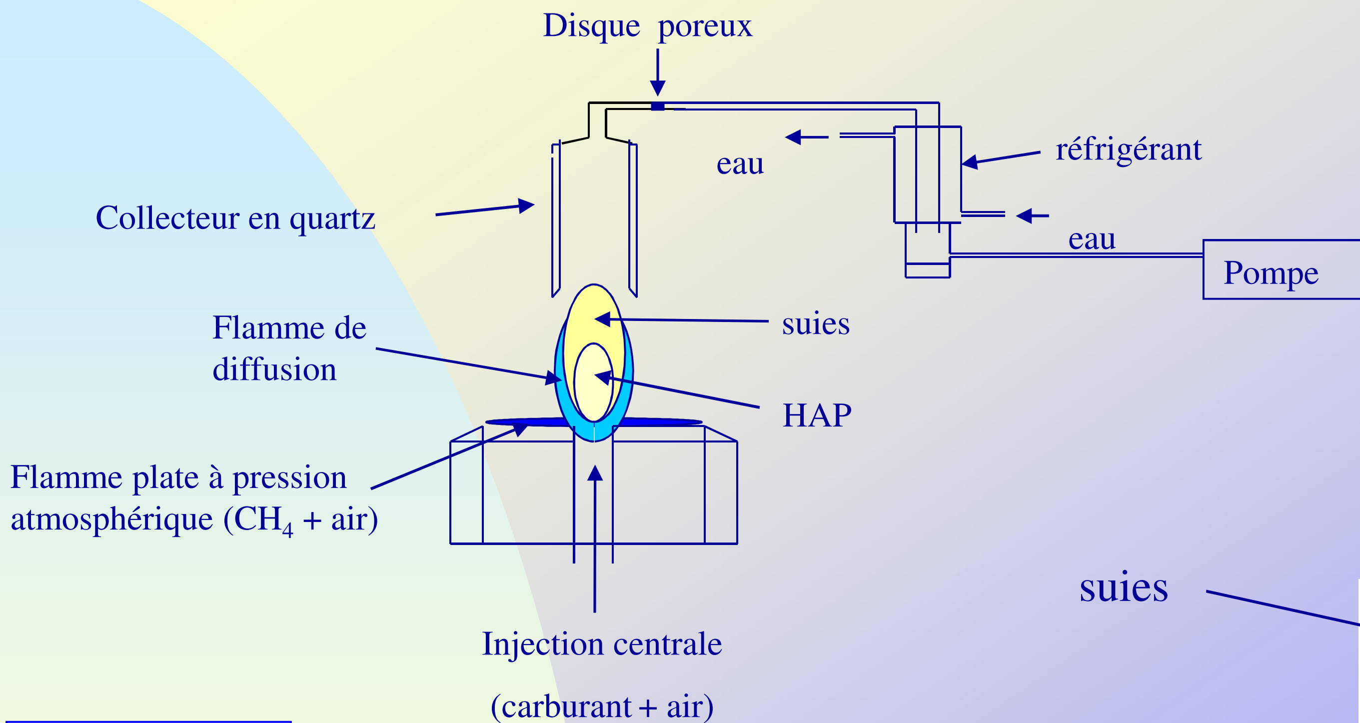
E_{ion}= 5 mJ/pulse

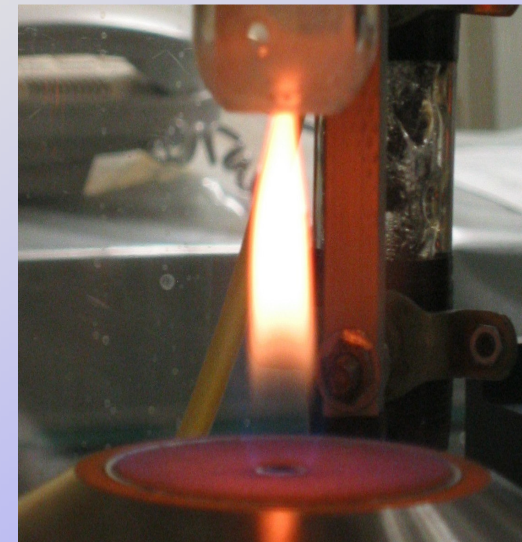


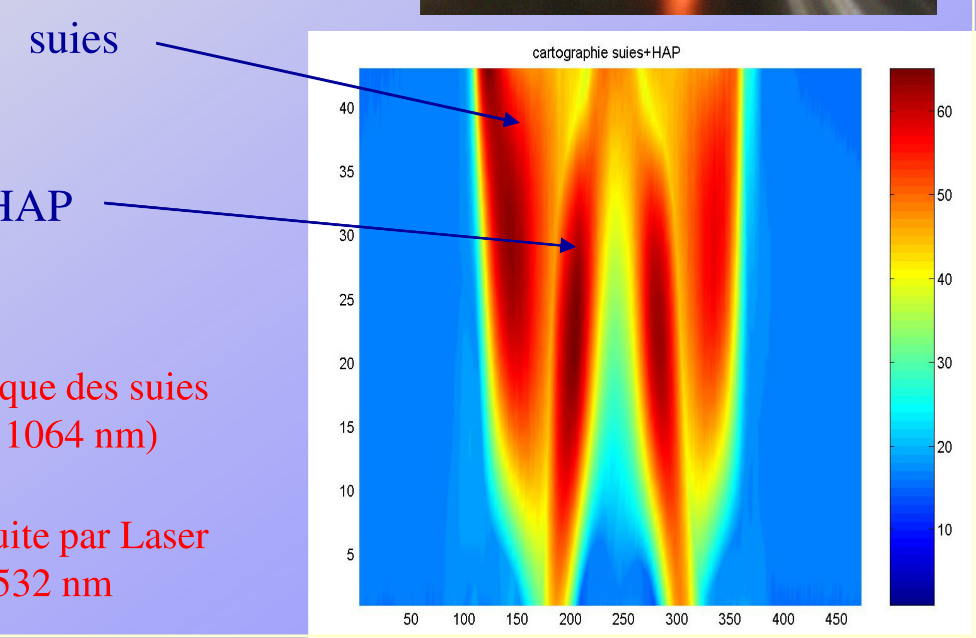
Thomson et al.,
Appl. Surf. Sci., in press

Diagnostics laser:

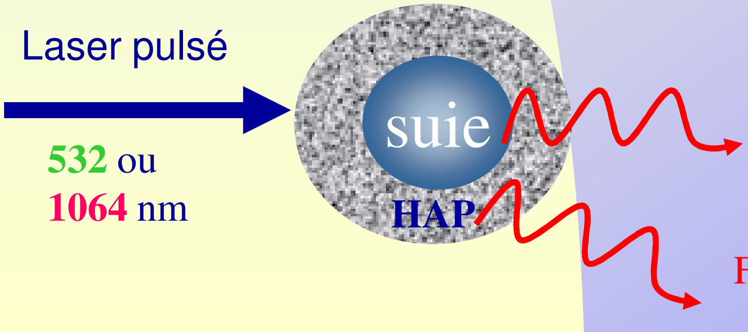
- phase gaz: LII / LIF
- phase adsorbée: désorption laser / spectrométrie de masse





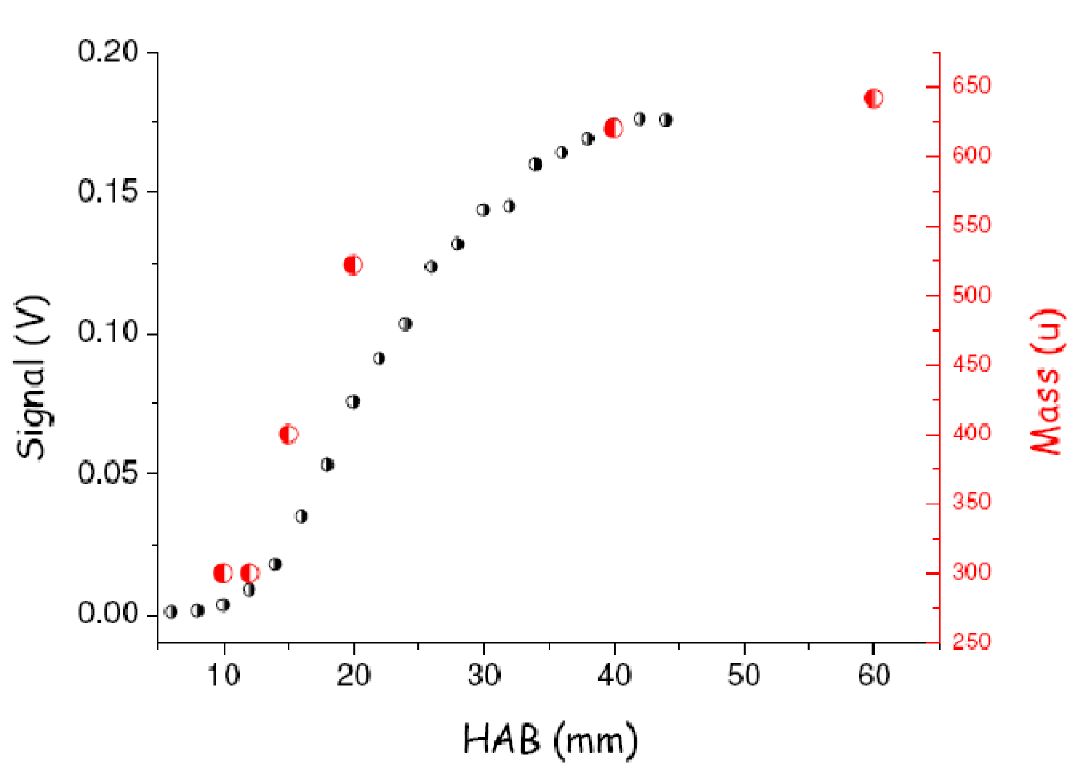


LII / LIF



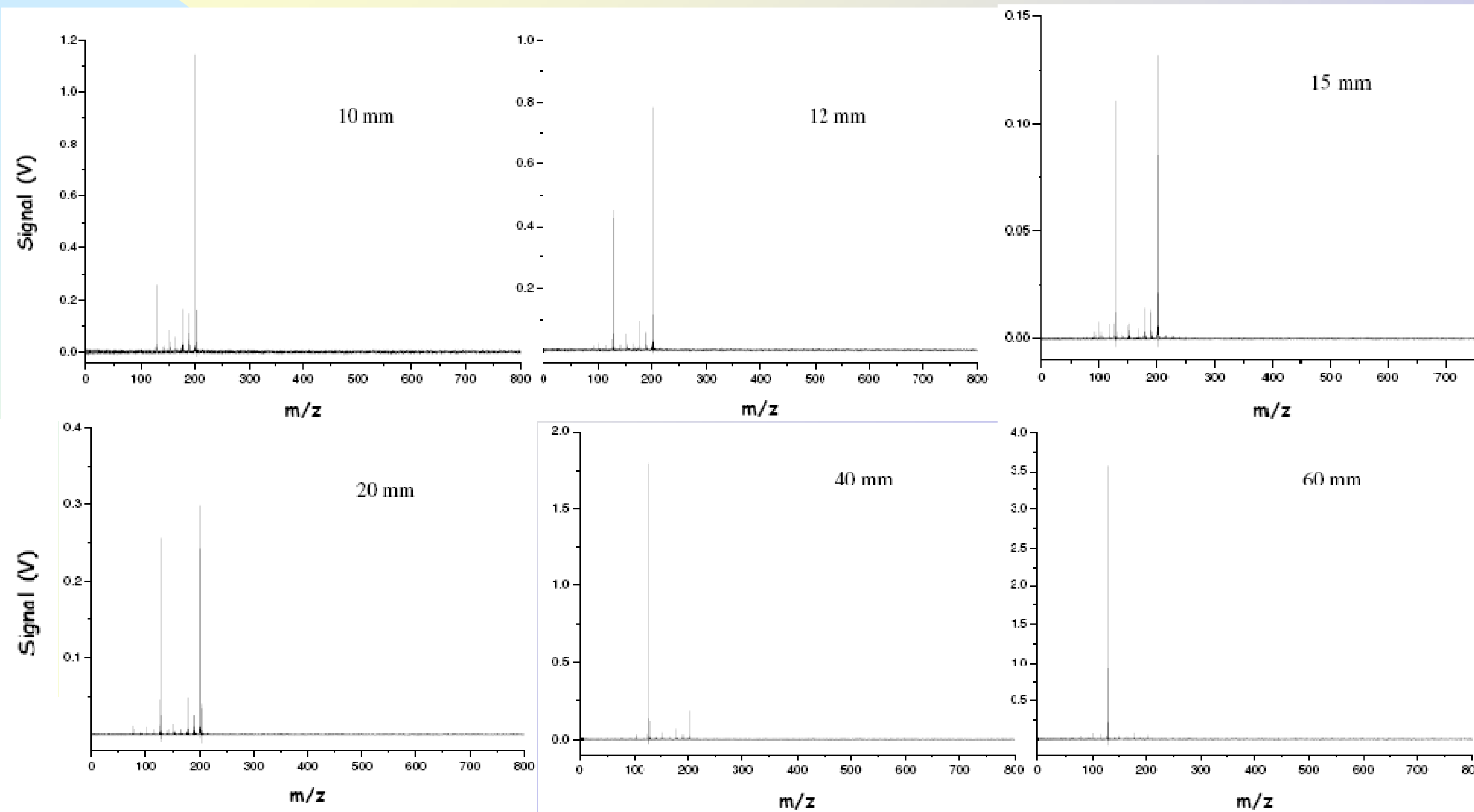
Back to basics …
…low pressure methane flame

$CH_4 : O_2 : N_2 = 0.462 : 0.398 : 0.140$ 200 torr



Heaviest detected mass versus HAB (red dots) compared with the LII soot profile (black dots)

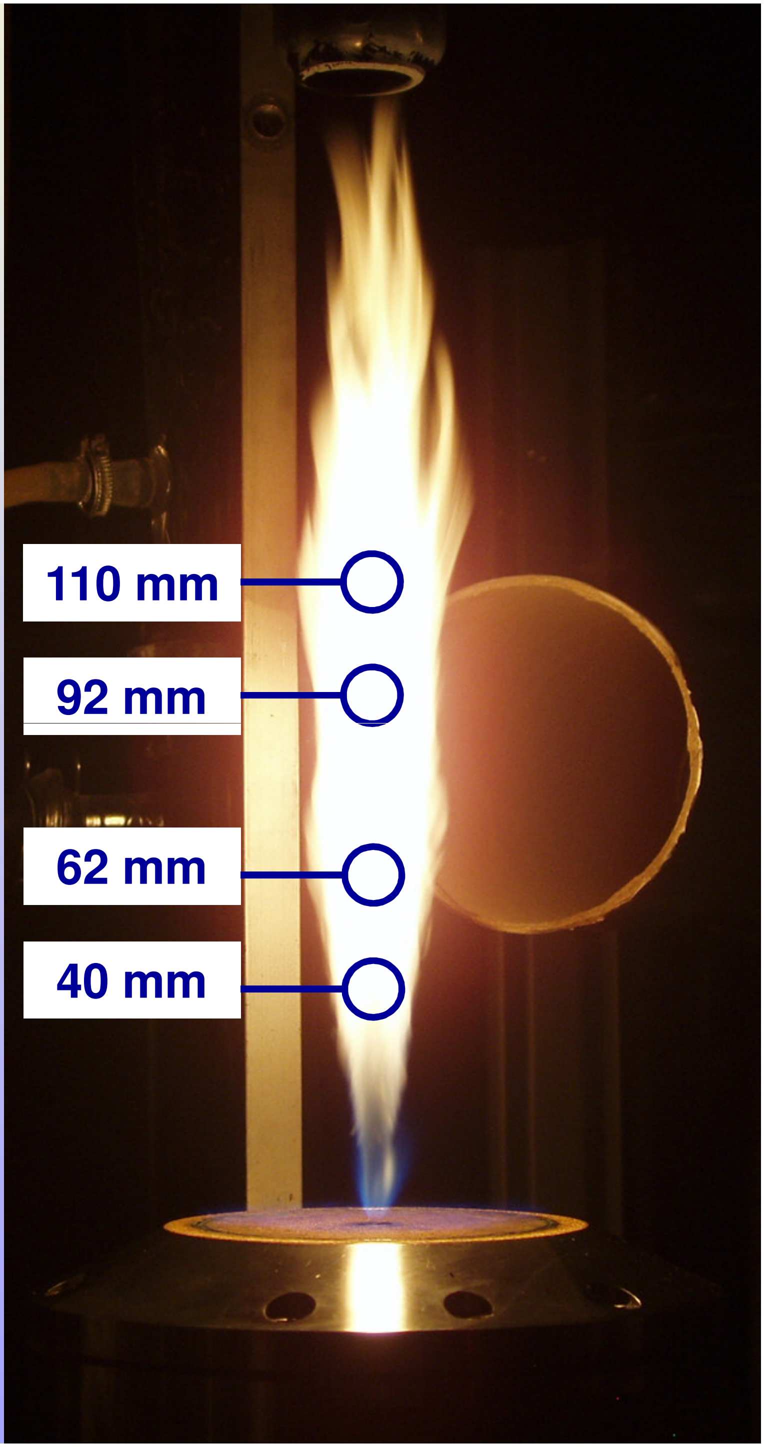
Back to basics …
…low pressure methane flame



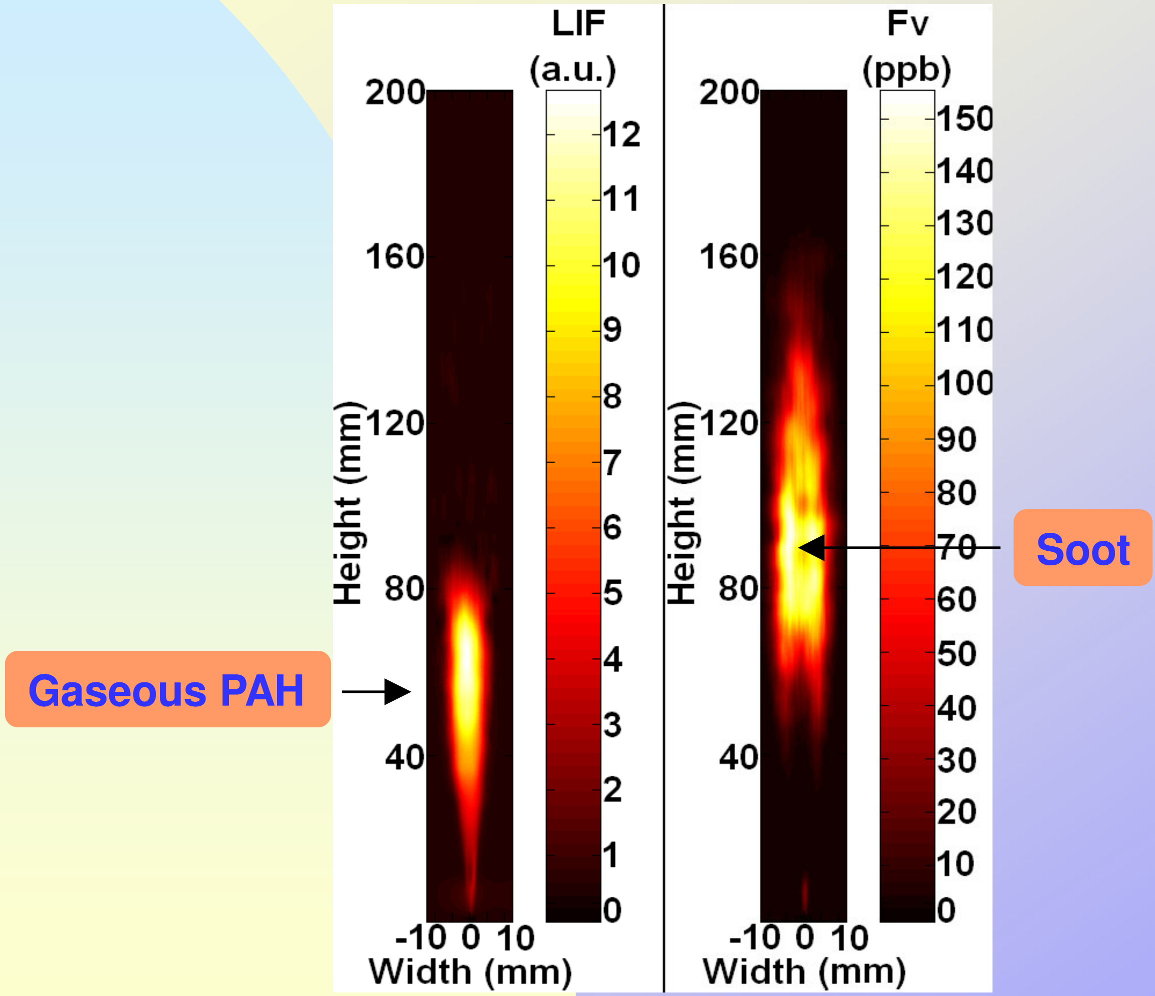
Gas phase: highest mass = 202 … pyrene as elementary brick for subsequent PAH growth on soot surface (heterogeneous mechanism) ???

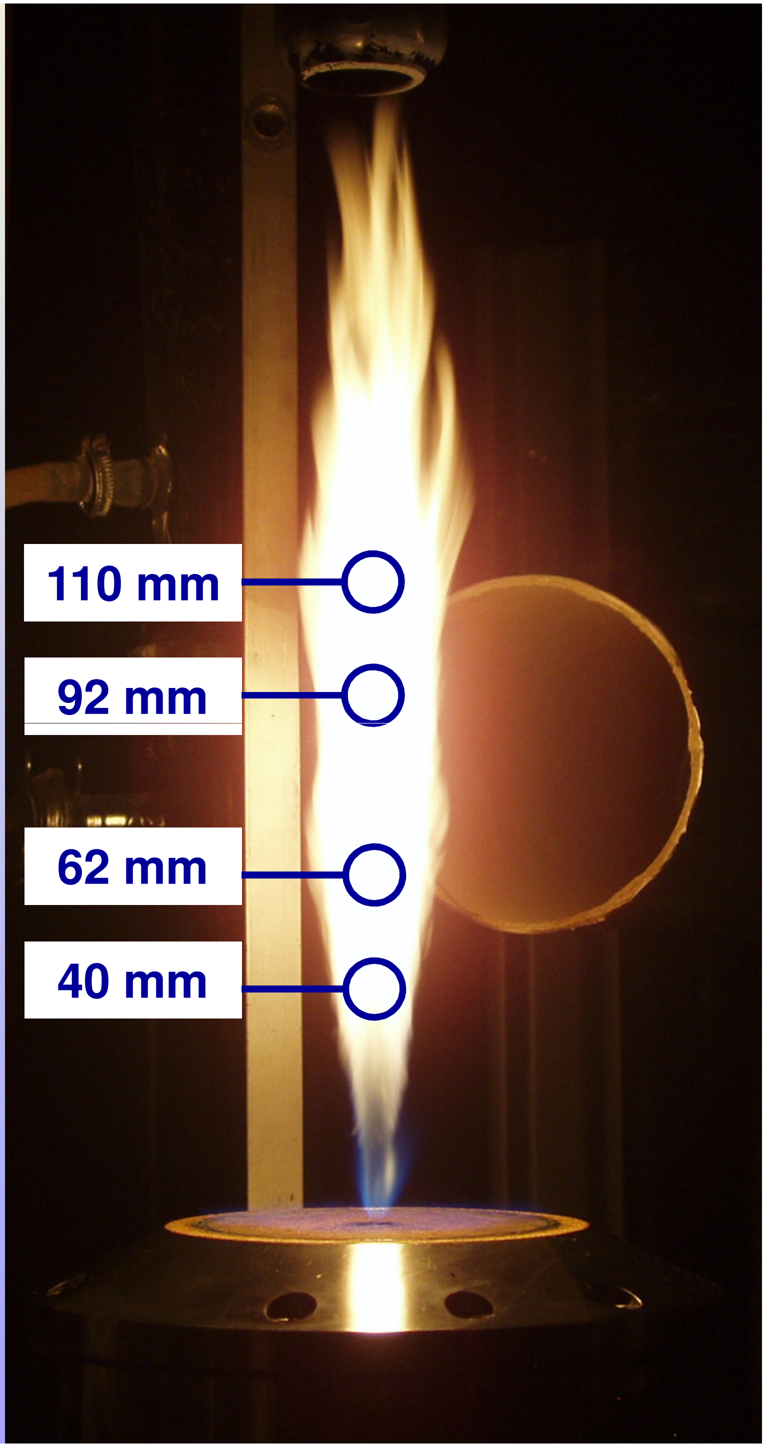
Into the flames…

- Turbulent diffusion diesel flame
- Various different heights have been chosen:
  - Only gases before the sooting region (PAHs have been condensed on activated carbon)
  - Young soot region
  - Maximum of soot volume fraction F_v
  - Beginning of the oxidation region



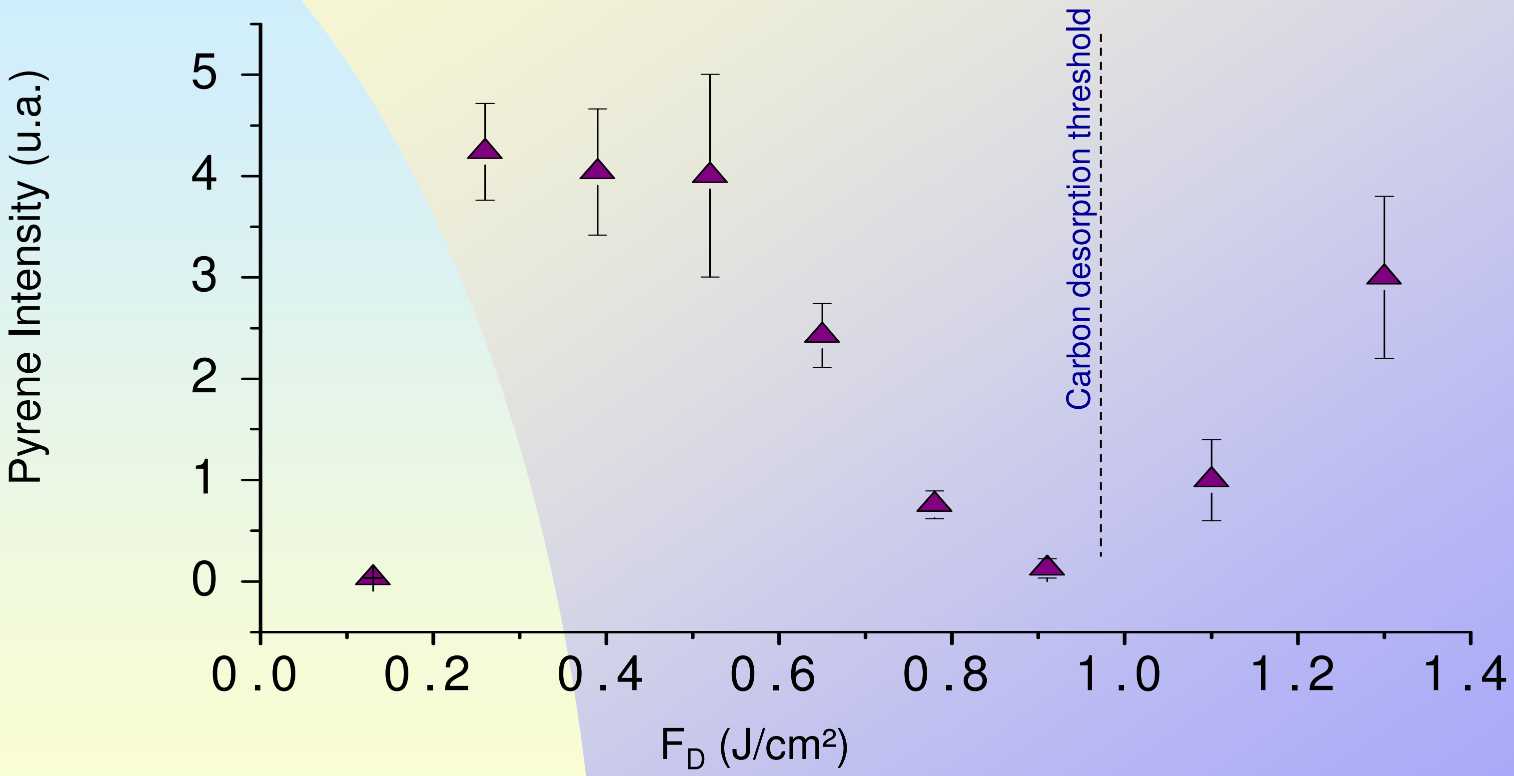
Into the flames…





Lemaire, Faccinetto, Therssen, Ziskind, Focsa, Desgroux,
Proc. Combust. Inst. 32, 737 (2009)

Desorption issue in synthetic soot

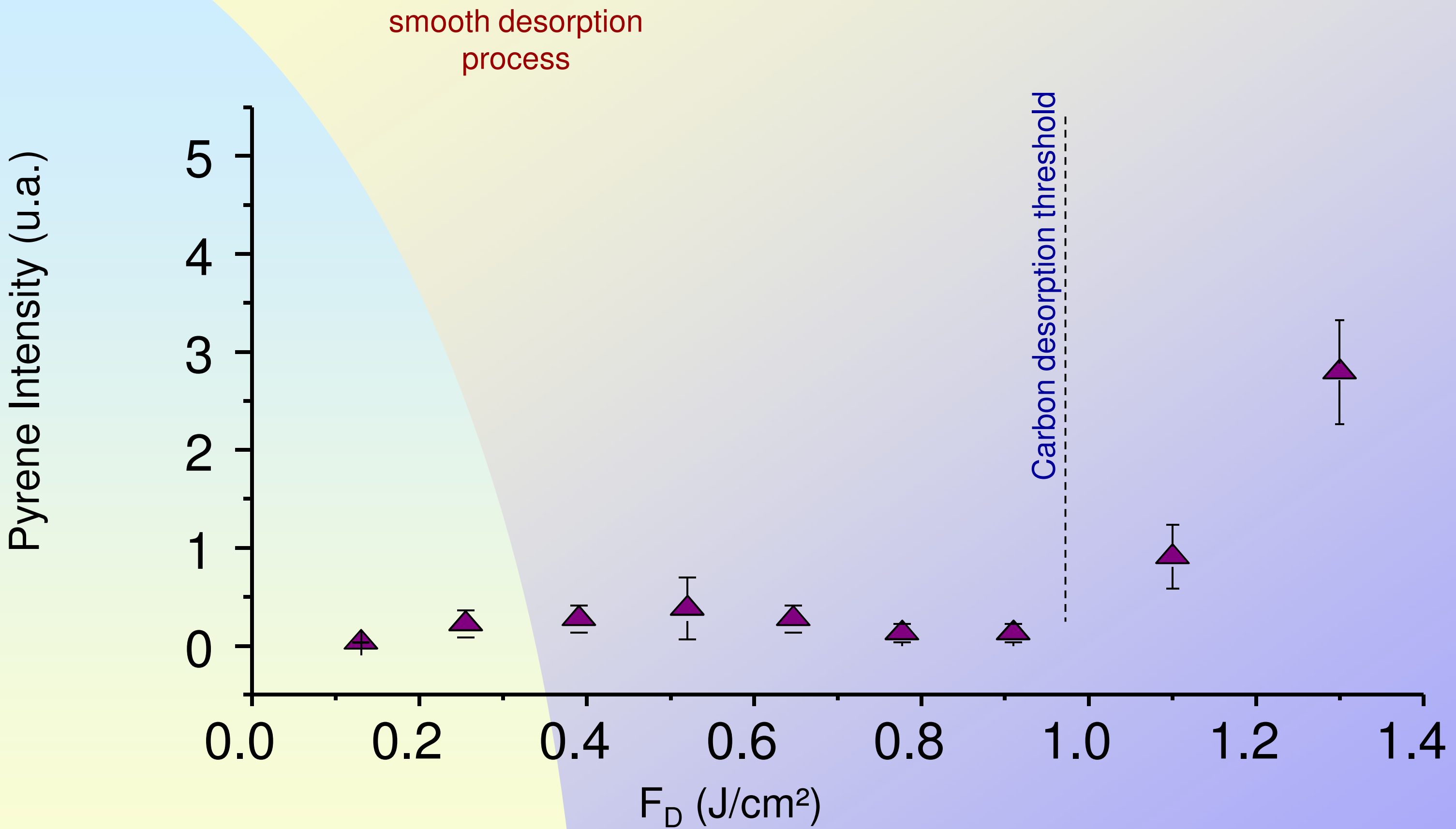


F_{ion}= 0.2 J/cm²

pyrene

Concentration: 5 .10^{-6} mol/g

Desorption issue in synthetic soot



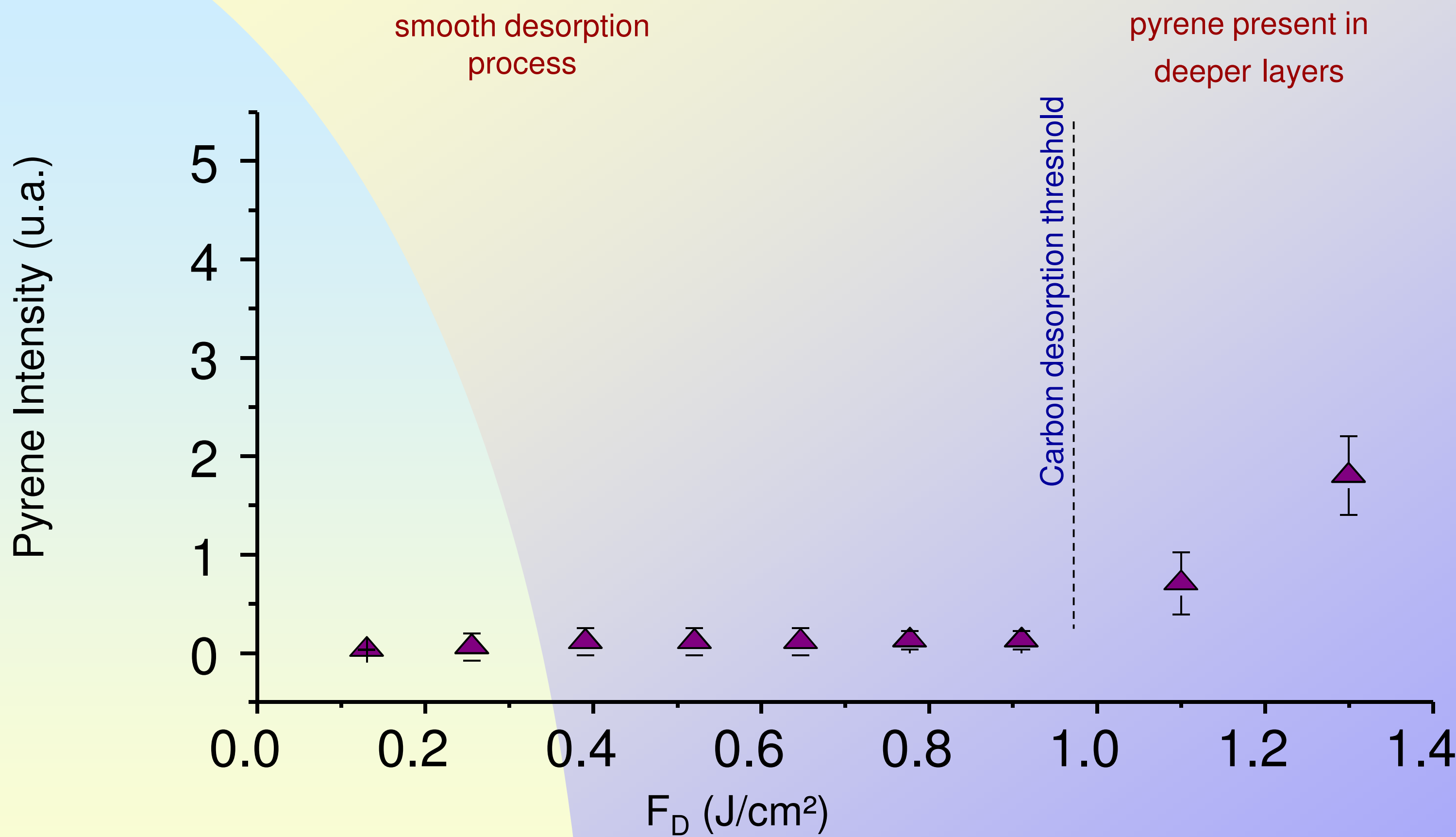
After about 10 laser shots

F_{ion}= 0.2 J/cm²

pyrene

Concentration: 5 .10^{-6} mol/g

Desorption issue in synthetic soot



After about 1000 laser shots

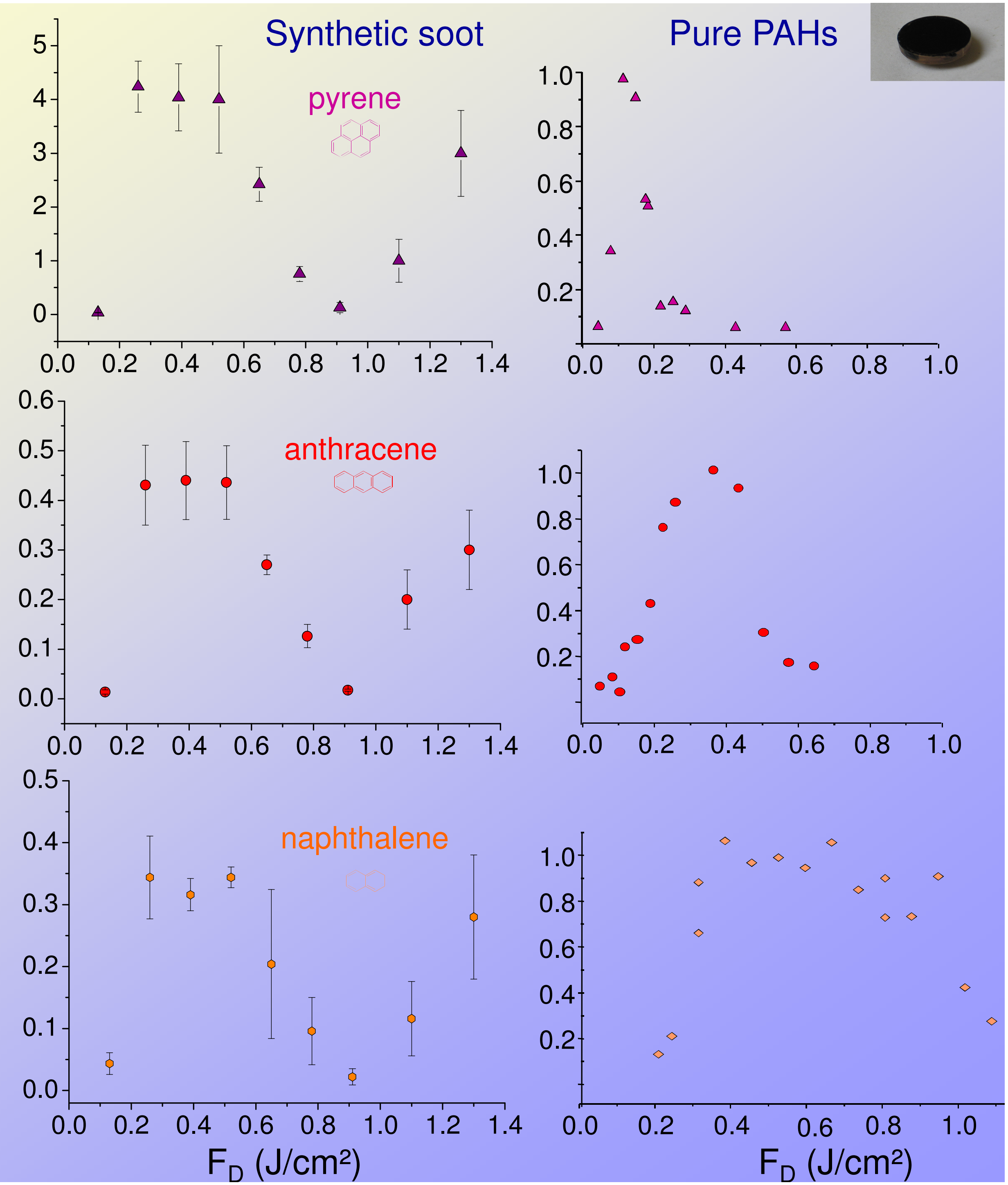
F_{ion}= 0.2 J/cm²

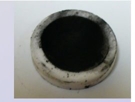
pyrene

Concentration: 5 .10^{-6} mol/g

Desorption issue

- Loss of selectivity
- Facilitates analysis of spectra





Analysis of soot collected in field campaigns

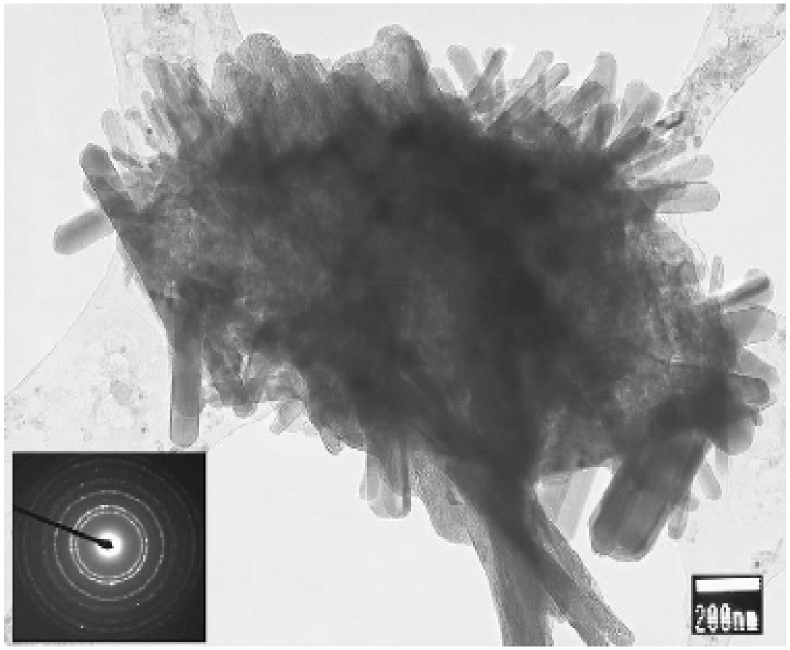


Fig. 11. Mineral/ash particle in the diluted exhaust sample and its SAED pattern.

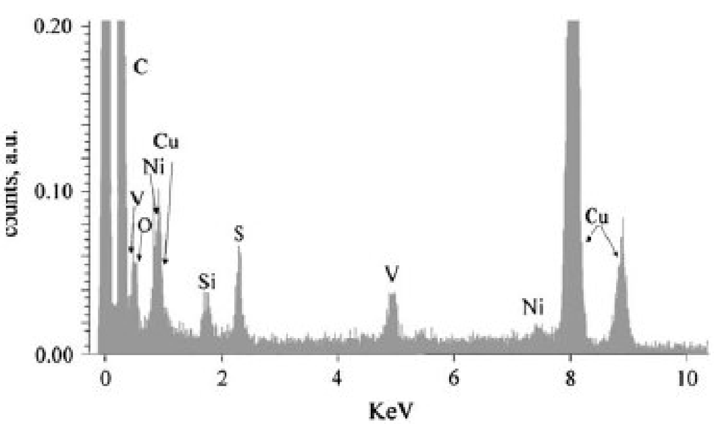
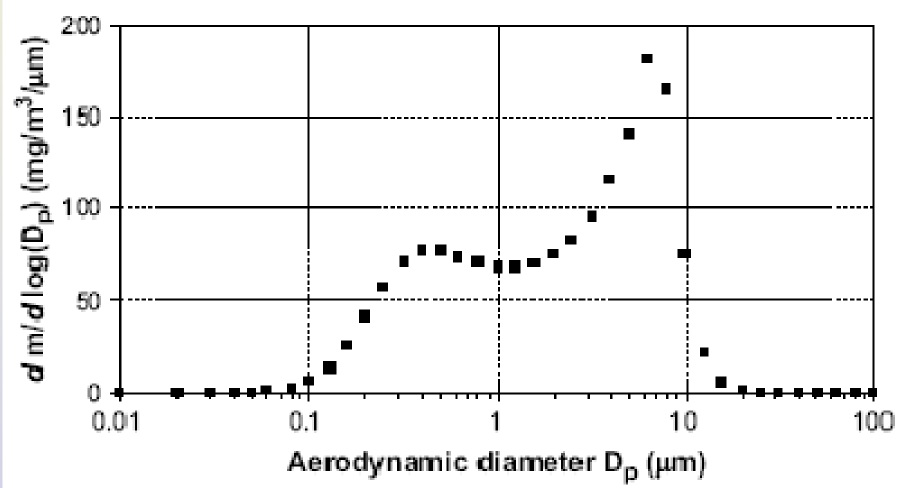


Fig. 8. EDS spectrum of hot-exhaust soot particles presented in Fig. 7.

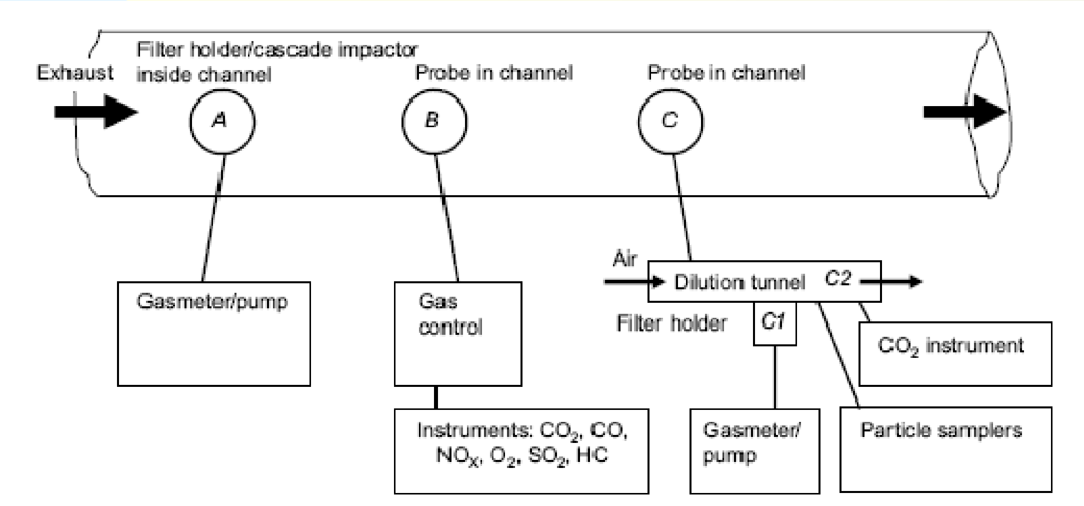


Elemental content obtained from EDS analyses (in weight %) of different types of particles in the hot and the cooled diluted exhaust. Content of each particle type was obtained by one time measurement of an individual particle or aggregate presented by the corresponding figure.

Element	Soot-type particles, Fig. 7	Char particle, Fig. 9	Char–mineral particle, Fig. 10	Mineral/ash particle, Fig. 11	OC-type particles, Fig. 12
C	94.4	93.1	53.5	11.1	79.9
O	0.7	n.d.	3.8	5.7	5.1
S	0.3	2.1	7.5	4.9	3.6
V	2.7	3.8	17.6	30.7	11.2
Ni	1.8	0.9	8.6	20.9	n.d.
Si	0.1	n.d.	n.d.	n.d.	0.2
Ca	n.d.	0.1	9.0	26.7	n.d.

n.d. – not detected.

Analysis of soot collected in field campaigns



List of samples taken for the PM analyses.

Sample name	Description of sample	Analyses
FH	Quarts filter in hot exhaust	PM mass, EGA
FC	Quarts, glassfiber or Teflon filter in cooled, diluted exhaust	PM mass, EGA
MH	Cu microgrids and amorphous-carbon holey film holders in hot exhaust	TEM, EDS, SAED
MC	Cu microgrids and amorphous-carbon holey film holders in cooled, diluted exhaust	TEM, EDS, SAED
LH	Borosilicate porous glass filter in hot exhaust	L2MS
LC	Borosilicate porous glass filter in cooled, diluted exhaust	L2MS

Emission factors EF, emission rates Er and concentrations C in exhaust from the main diesel engine operating under conditions as listed in Table 2 (84% power load) and using the HFO with composition given in Table 3. Concentrations are given at normalized conditions (273.14 K, 1013.25 hPa).

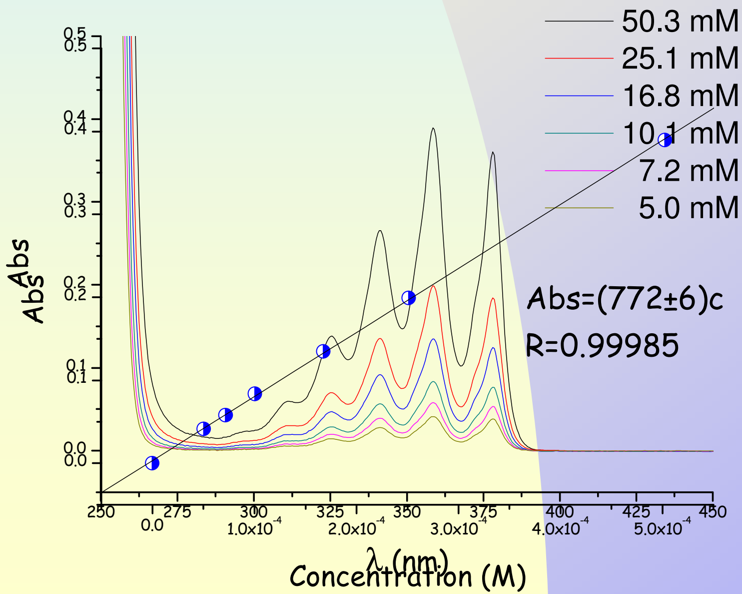
Exhaust component	EF, $g\ kWh^{-1}$	EF, $g\ (kg\ fuel)^{-1}$	Er, $kg\ h^{-1}$	C, $g\ Nm^{-3}$
NO_x	14.22	73.4	241.7	2.20
CO_2	667	3441	11 339	103.1
CO	0.42	2.17	7.1	0.065
HC	0.07	0.36	1.2	0.011
O_2	1270	6553	21 590	196.3
SO_2	7.62	39.32	129.5	1.18
SO_3	0.11	0.57	1.9	0.017
Benzene	0.012	0.06	0.21	0.002
PM	0.29	1.49	4.86	0.044
PM[a]	1.03	5.31	17.43	0.158
OC[a]	0.30	1.58	5.15	0.047
EC[b]	0.02	0.13	0.42	0.004
Ash[b]	0.19	0.98	3.19	0.029
Sulphate[a]	0.15	0.76	2.47	0.022

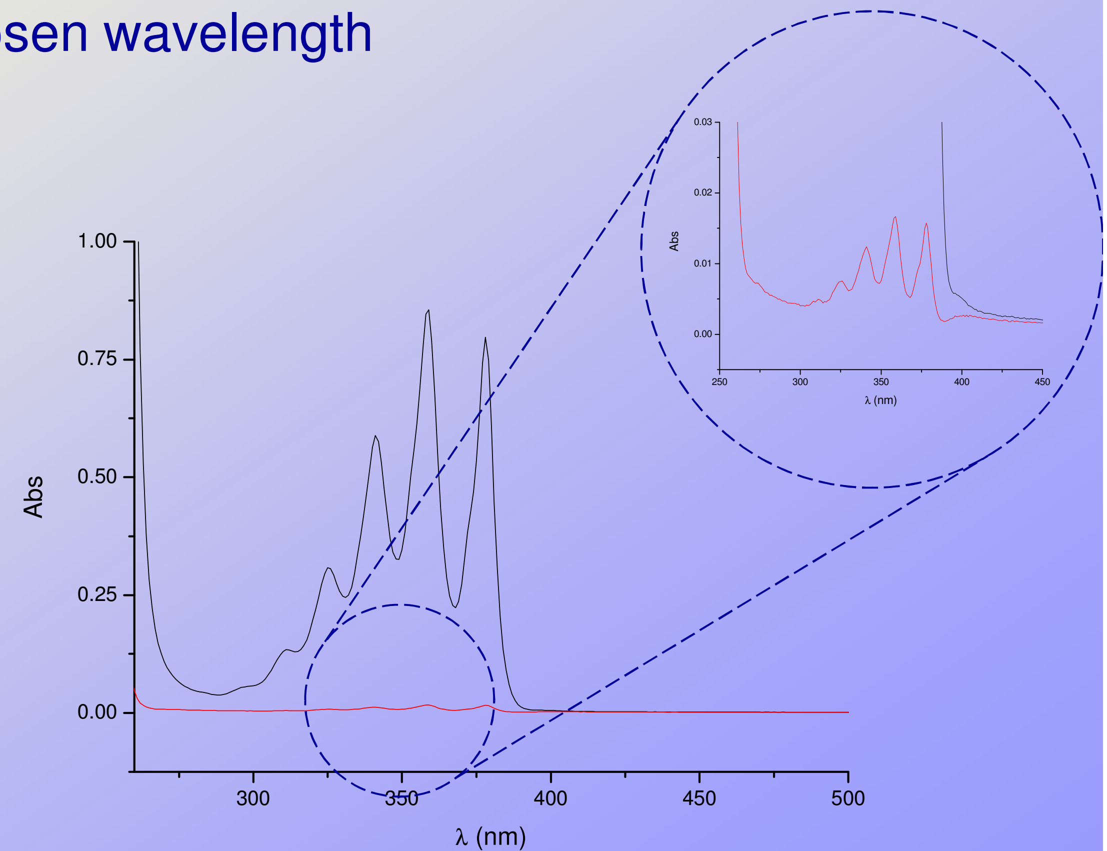
[a] After cooling in the dilution system.
[b] Average hot exhaust and diluted exhaust.

Complementary gas phase / particulate matter analyses

PAHs concentration in synthetic soot

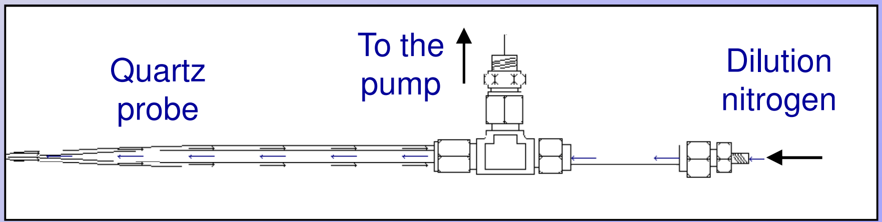
- PAHs' amount in carbon calculated as a difference, using Lambert-Beer's law to measure the exhaust solution concentration:
  - Build a calibration curve for each PAH
  - Read the absorbance at the chosen wavelength





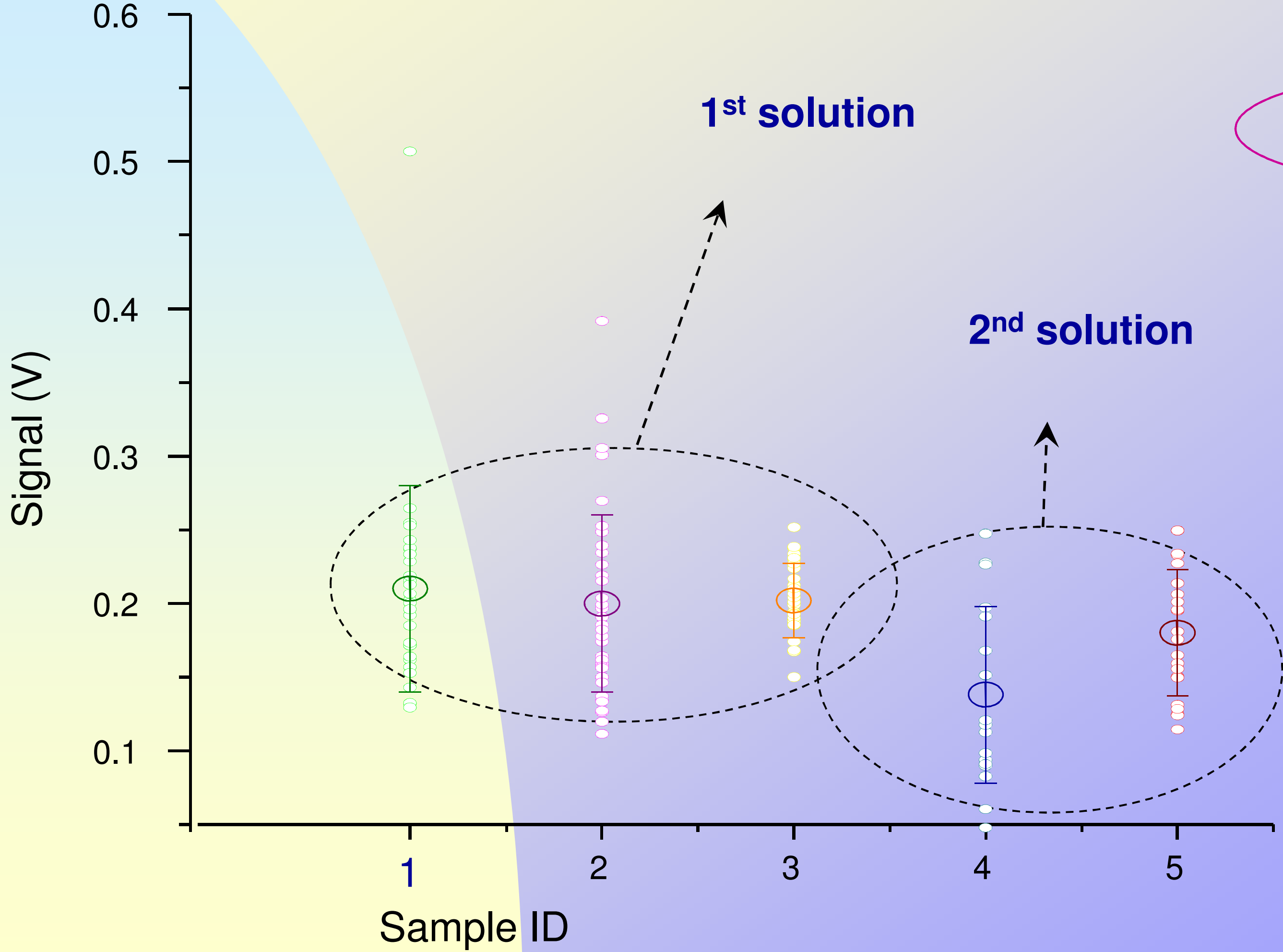
Soot Sampling

- In our experimental work LDI TOF-MS is an *ex-situ* technique
  - Soot must be ***sampled*** from flames
- Soot is collected through a double-wall quartz probe, which allows (1) local sampling and (2) fast dilution with gaseous nitrogen, needed to minimize:
  - Combustion gas condensation
  - Chemical reactions



- Soot is deposed on the surface of a porous Borosilicate glass filter, suitable for the mass analysis

...Reproducibility



$\Delta V / V \sim 30\%$