Surface chemical analysis of soot aerosols by Two-step Laser Mass Spectrometry: Improvements of sensitivity and selectivity

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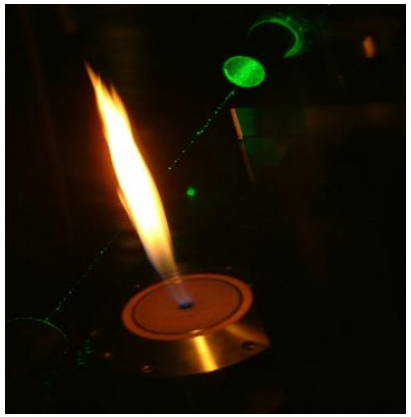
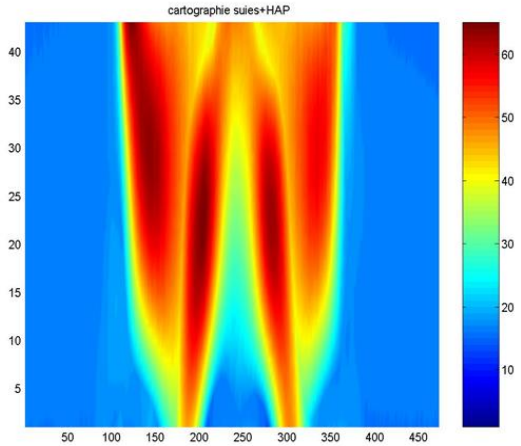
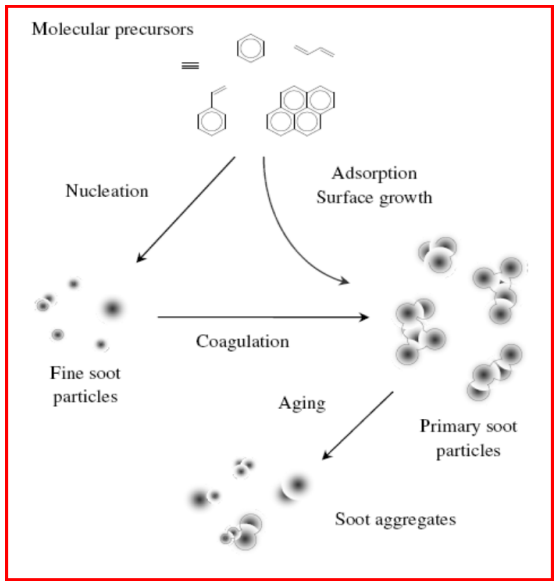
Introduction – soot: residue of the combustion

COMBUSTION MECHANISMS



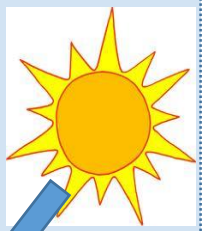




HEALTH EFFECTS

carcinogenic potential

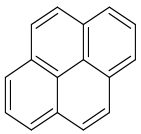
CLIMATE EFFECTS

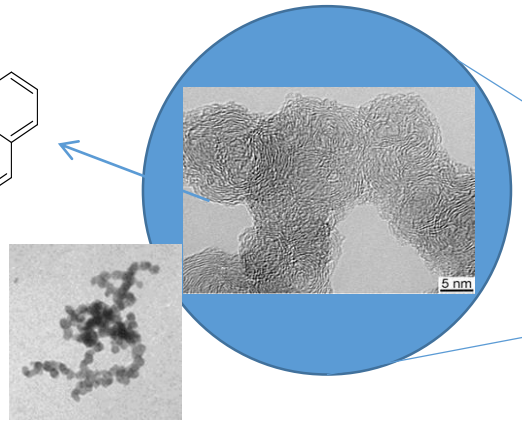


direct effects: radiation extinction

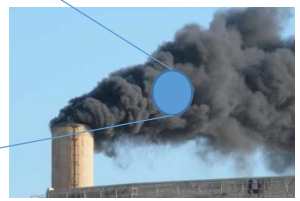
indirect effects: cloud formation

PAHs and other compounds adsorbed on the soot matrix



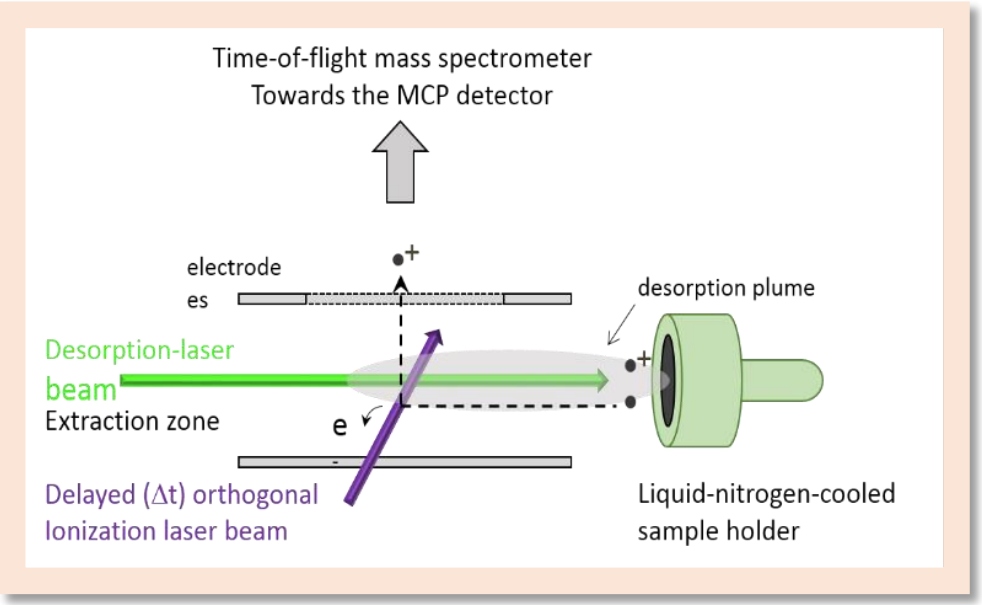


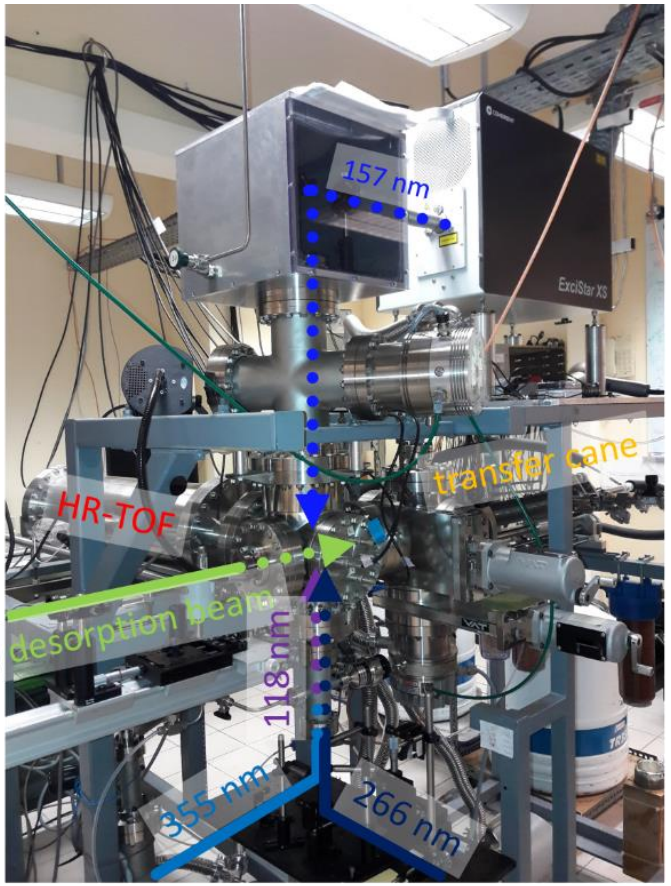
Environmental pollution



Experimental techniques

Laser Desorption / Laser Ionization / Time-of-Flight Mass Spectrometry ⟹ L2MS





❶ *Laser Desorption (LD) :*

- Nd:YAG (2ω, 4ω), 10 ns, 10 Hz, **E_{max}= 10 mJ/pulse**

❷ *Laser Ionization (LI) :*

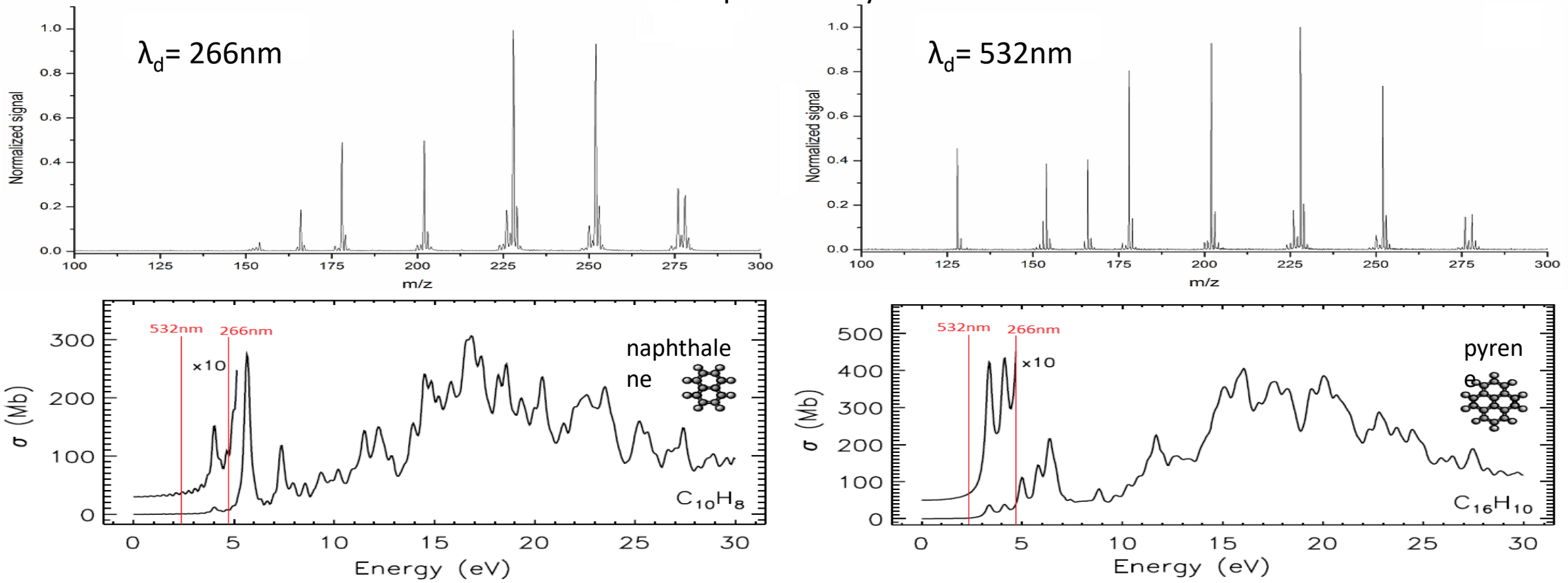
- ***4^{th} harmonic Nd:YAG, λ= 266 nm, 10 ns, 10 Hz, E_{max}= 100 mJ/pulse***
- ***F_2 laser, 157 nm (7.9 eV) - NEW***
- ***118 nm (10.5 eV) source (9th harmonic Nd:YAG) - SPI***

❸ *Detection :*

Reflectron Time-of-Flight Mass Spectrometer (ReTOF-MS) m/Δm ~1000

Effect of the desorption wavelength

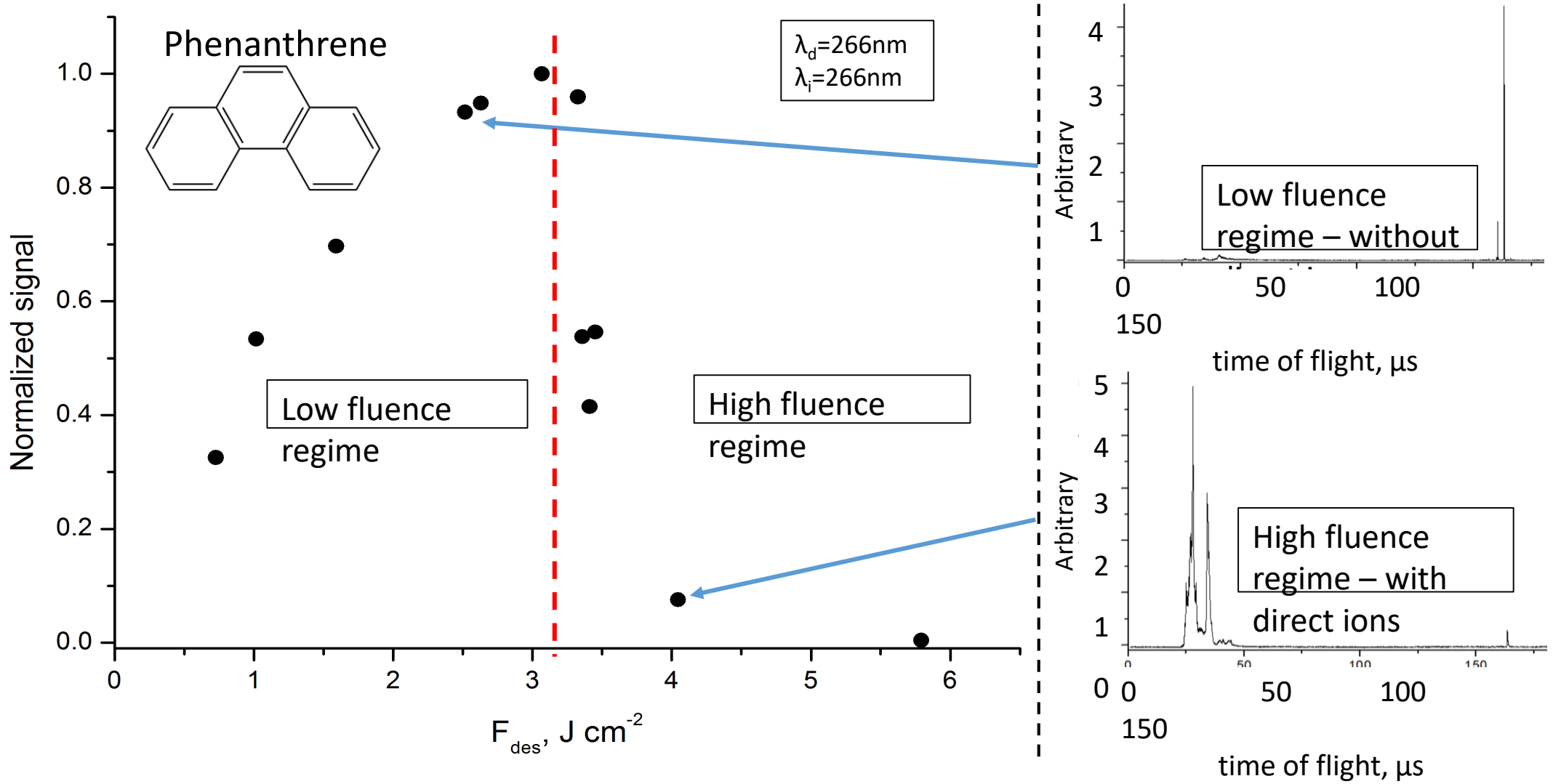
Mass spectra of synthetic soot



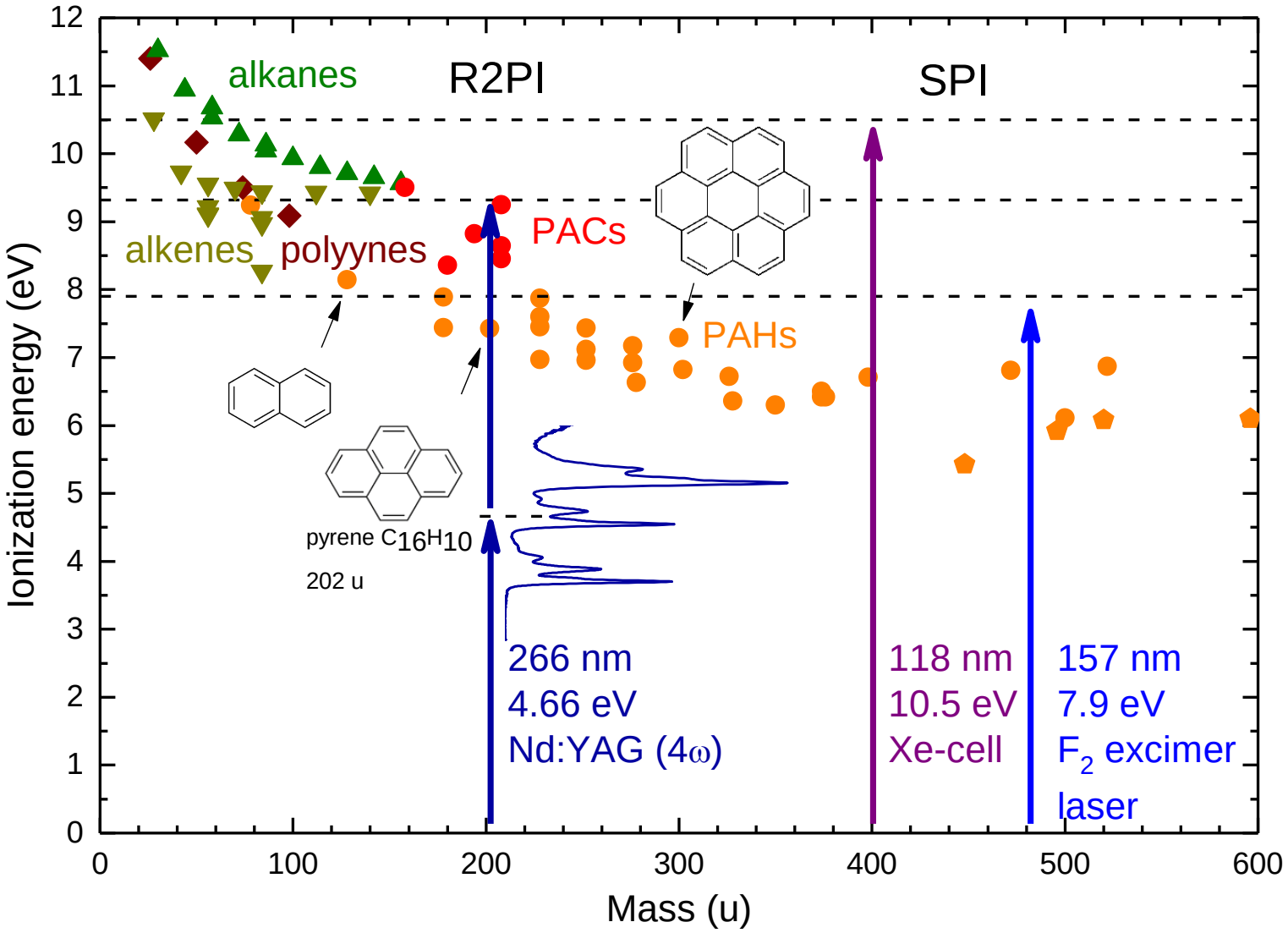
Units on Y axis of the bottom figures are megabarns (1 Mb = $10^{-18}cm^2$)

Desorption wavelength changes the peak distribution in the mass spectrum

Desorption step - Effect of the fluence



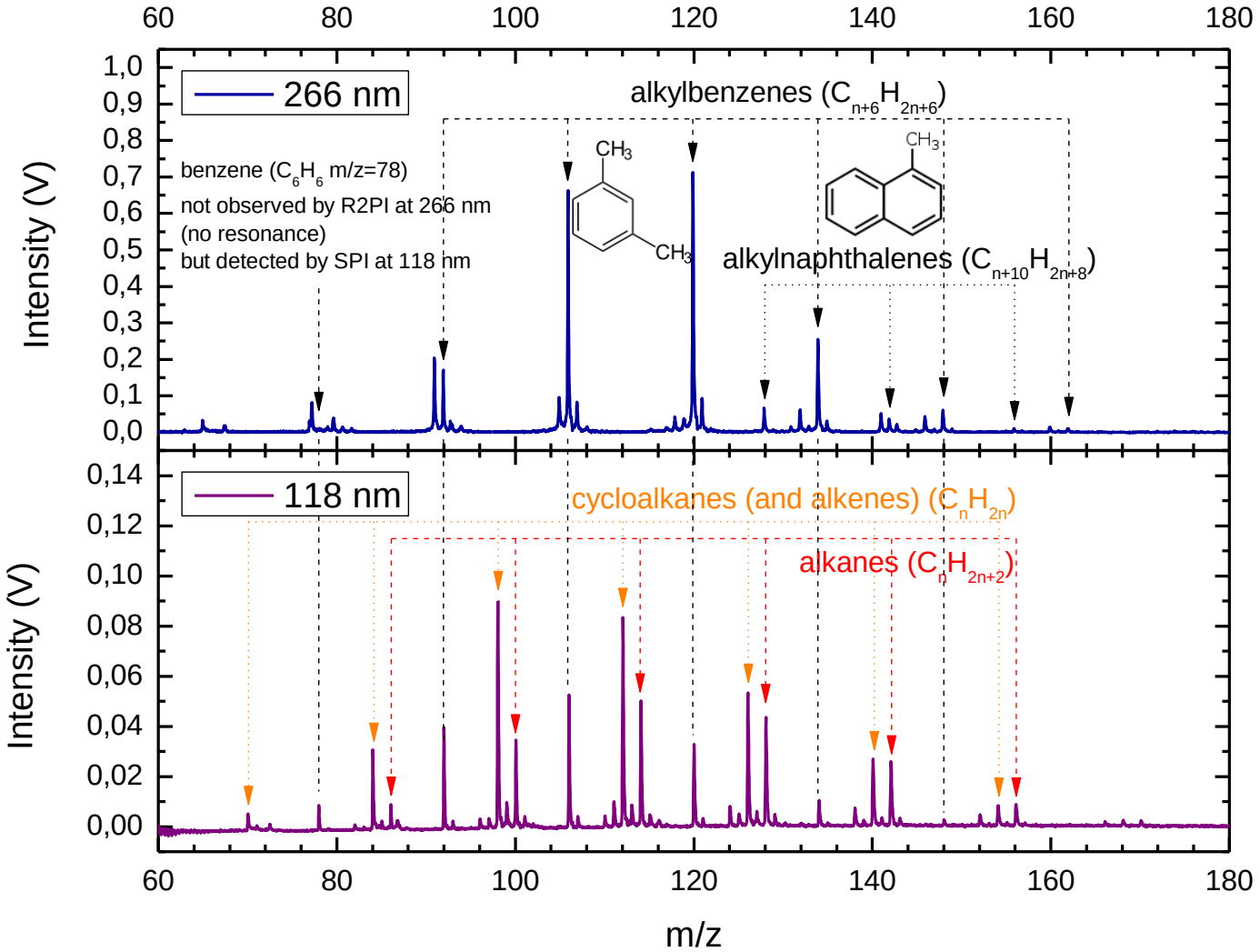
Experimental technique – ionization schemes

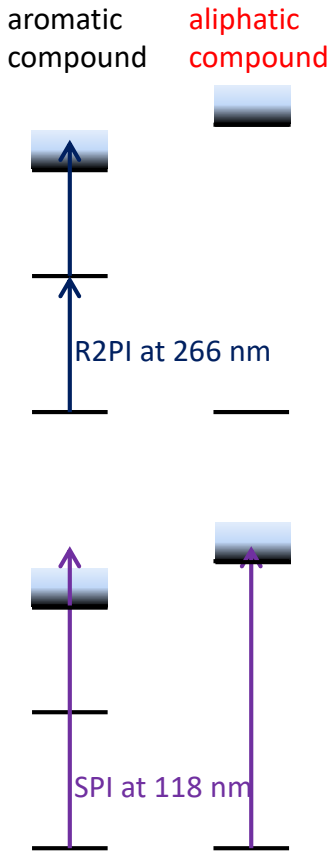


- Controlled fragmentation
- Ultra-sensitive to PAHs
- Selective (laser ionization)

complementary ionization schemes allow the detection of various adsorbed species

L2MS: improvement of the selectivity



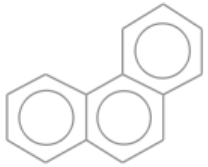


Analysis of a complex mixture: kerosene Jet A1 vapor

- Aliphatic compounds : alkanes and cycloalkanes , alkenes
- Aromatic compounds : alkylbenzenes and alkylnaphtalenes

distinction between aromatic and aliphatic compounds

L2MS: improvement of the selectivity



phenanthrene

isomers
m/z 178

anthracene

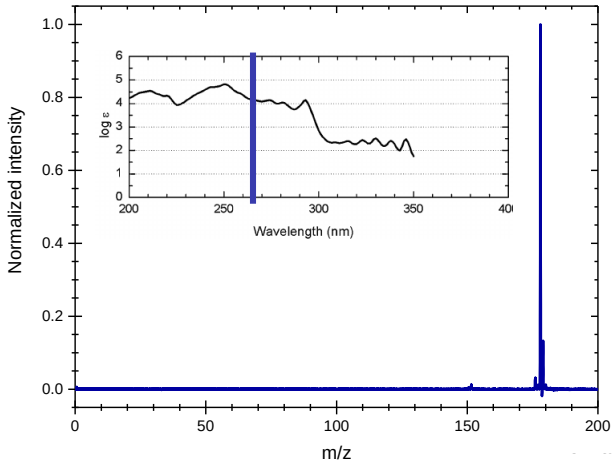
Name	Mass, g mol^{-1}	IE, eV	γ(157nm)
Anthracene	178.078	7.439	0.0498
Phenanthrene	178.078	7.891	0.0007

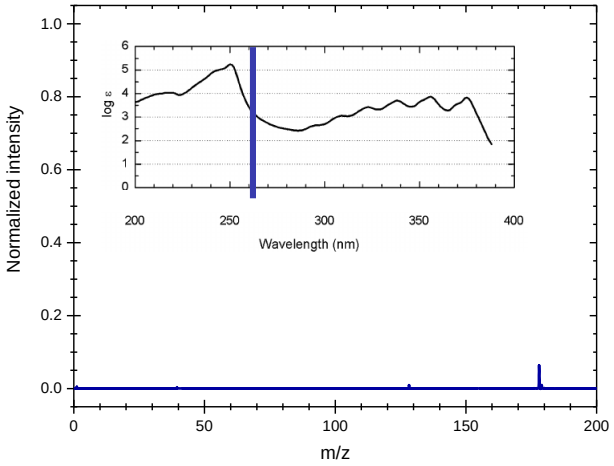
IE- ionization potential, γ(157nm) – ionization quantum yield at 157 nm

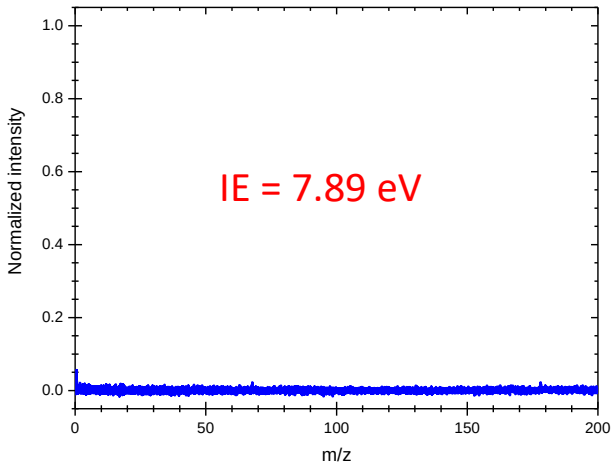
266 nm
(4.66 eV)

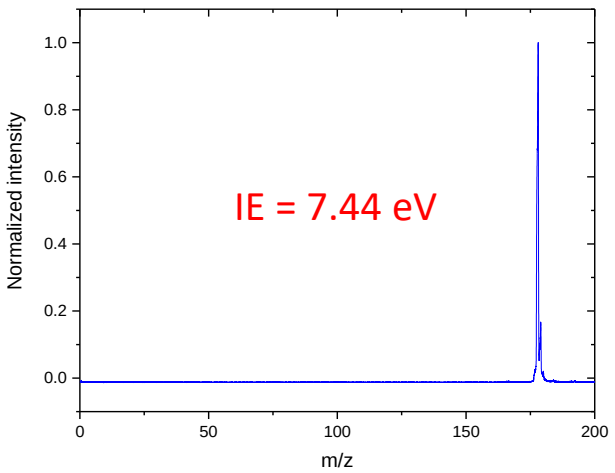
ionization wavelengths

157 nm
(7.9 eV)

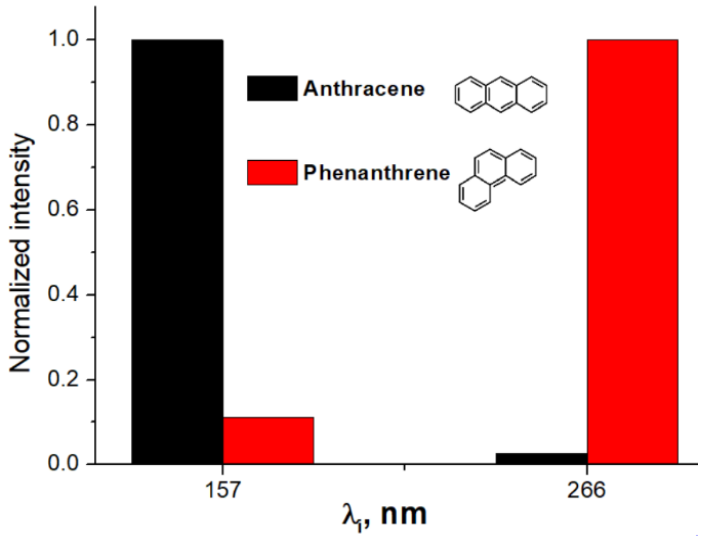




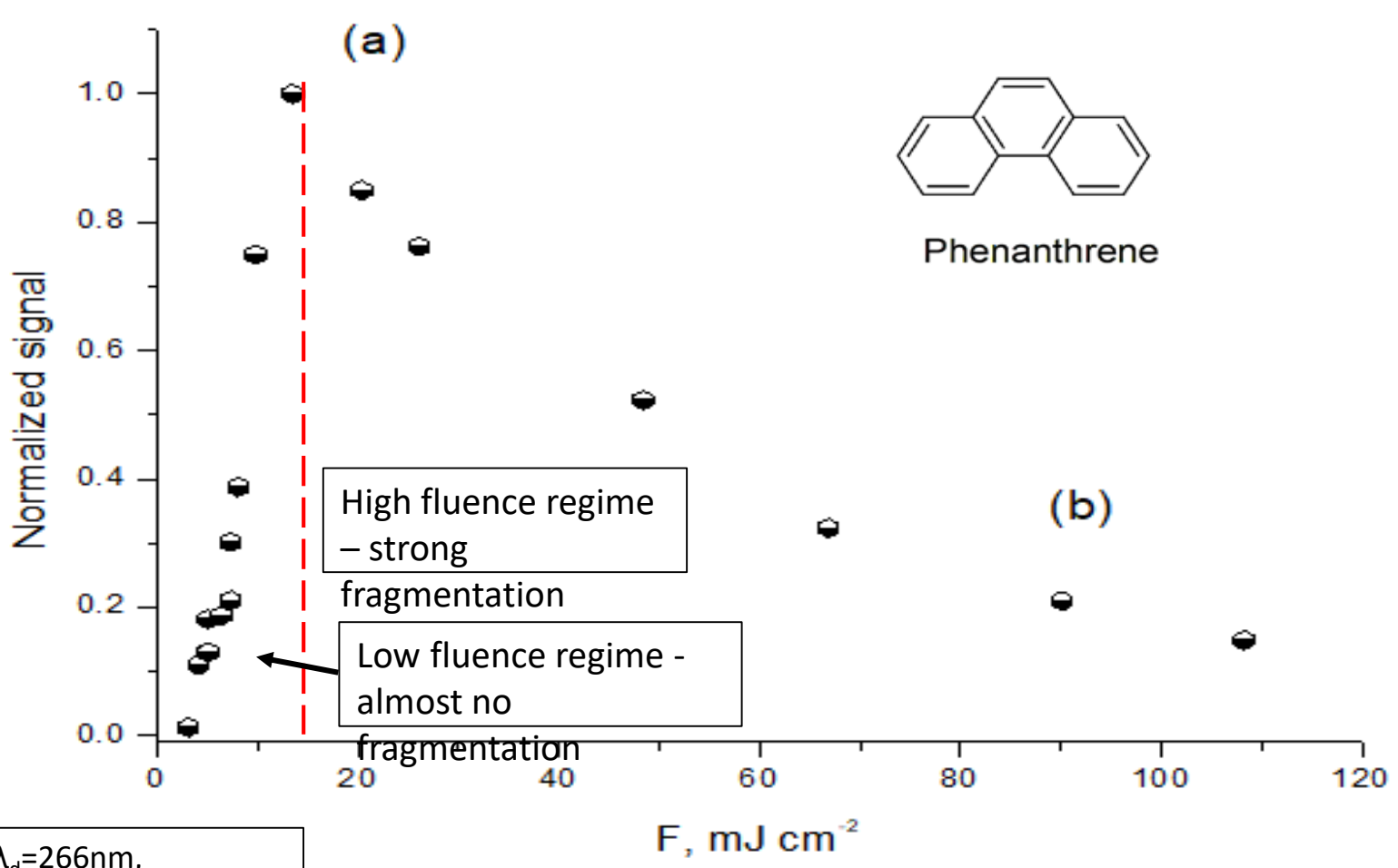


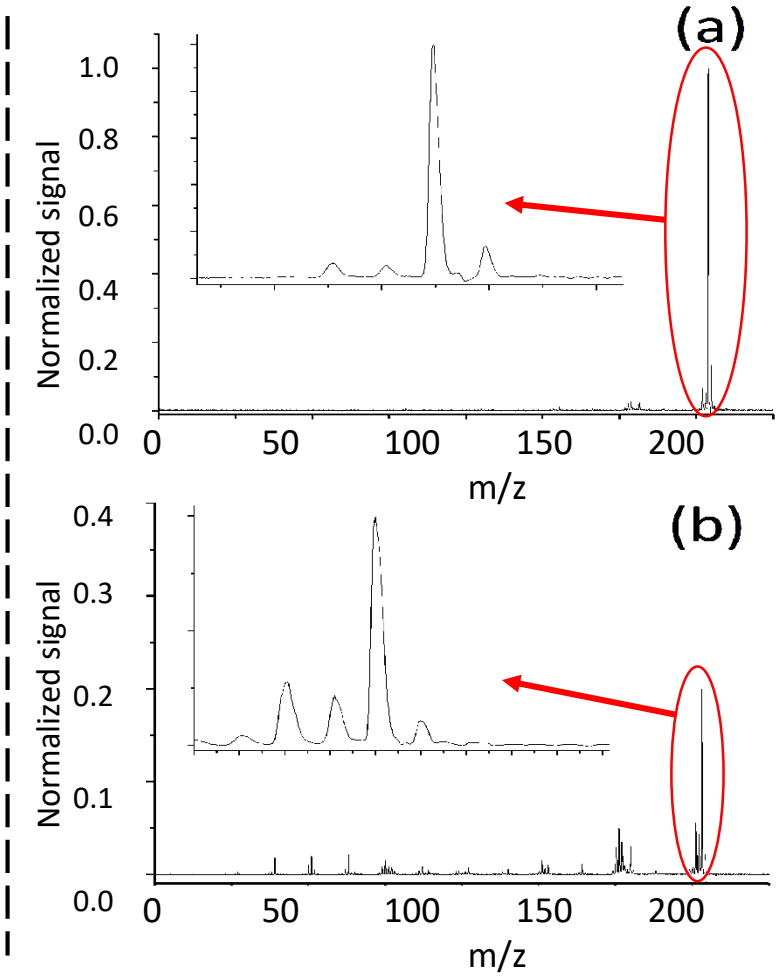


distinction between some isomers



Photoionization of PAHs





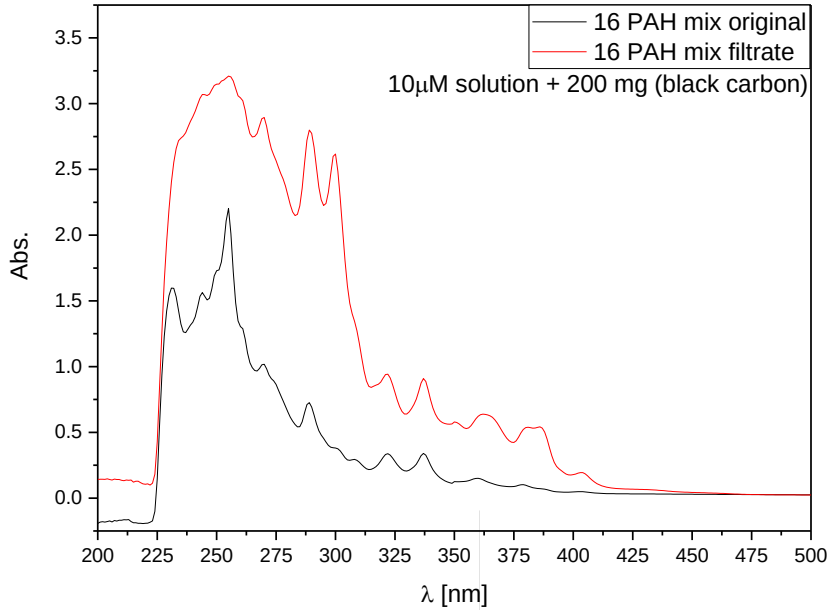
λ_d=266nm,
λ_i=266nm

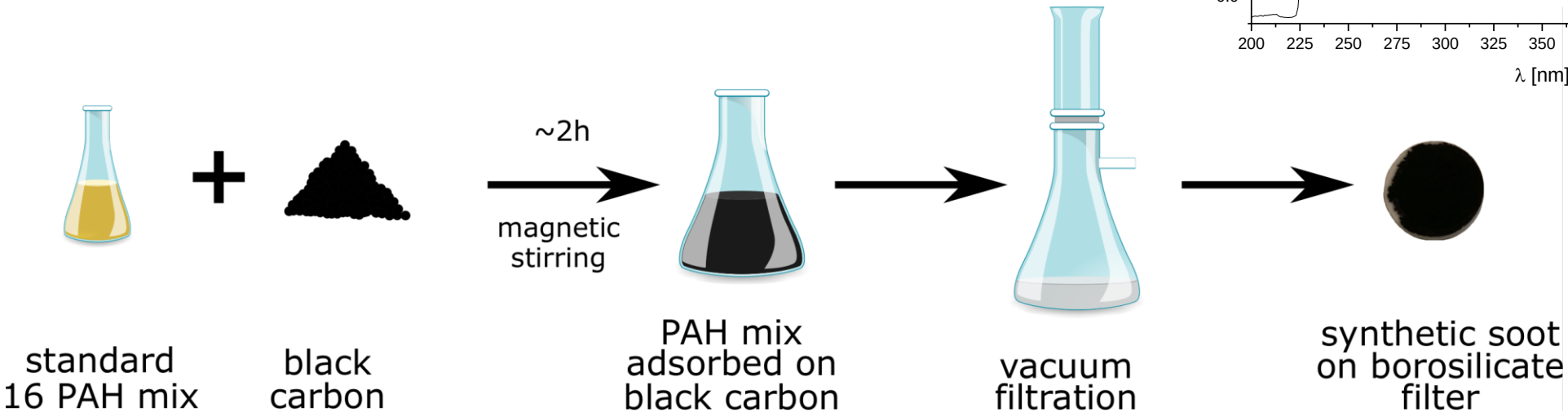
Optimal signal was the one resulting in a highest signal, while causing no fragmentation

Synthetic soot – PAHs adsorbed on carbon

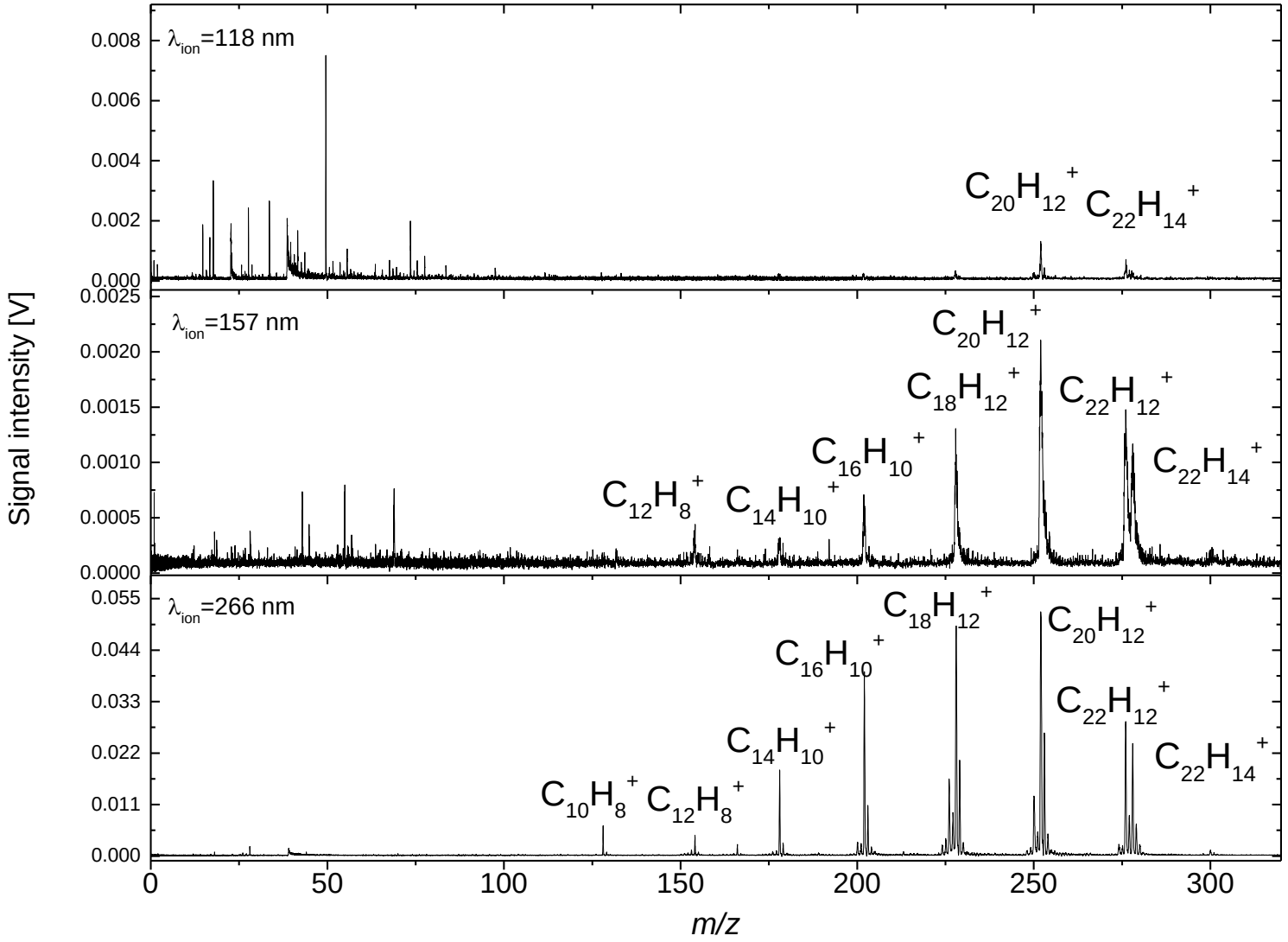
Standard procedure

- Prepare a stock solution having a known PAH concentration
- Treat the solution with a known amount of activated carbon
- Eliminate the solvent (DCM)
- Deposit the carbon with PAHs so adsorbed





Synthetic soot – detection sensitivity



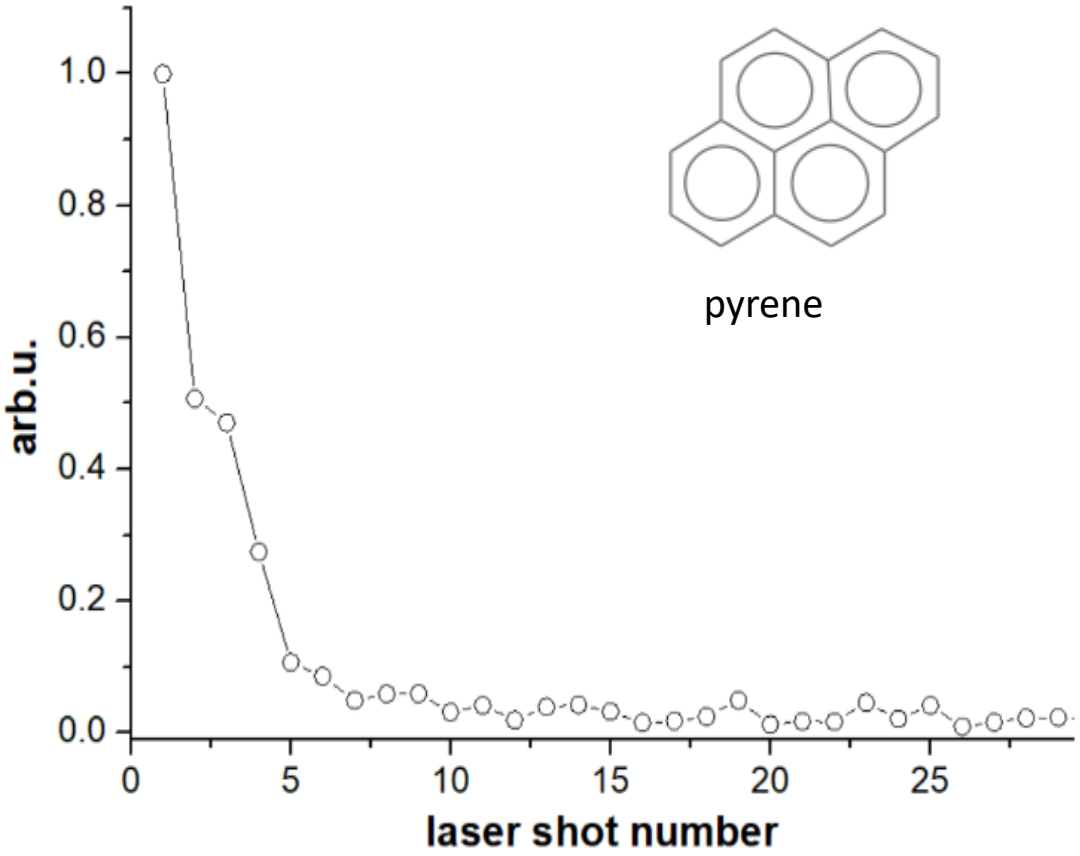
0.01mM stock solution
+
200mg black carbon

vacuum filtration

3.4µmol/g
surface concentration

118 nm – less suitable for PAHs than 157 and 266 nm

Sensitivity improvements



pyrene

limit of detection (LOD) for pyrene

$$n_{\mathrm{LOD}} = n_{\mathrm{tot}} \frac{S_{\mathrm{LOD}}}{S_{\mathrm{tot}}}$$

S_{LOD} : signal recorded at limit of detection (5th laser pulse - SNR~3)

S_{tot} : the total integrated signal

$$n_{\mathrm{tot}} = \frac{A_{\mathrm{irr}}}{A_{\mathrm{SSA}}} c_0$$

A_{irr} : irradiated area

A_{SSA} : sample surface area

c_0: PAH deposited quantity

$\Rightarrow$ $n_{\mathrm{LOD}} \sim 80$ amol / laser pulse

$\Rightarrow$ towards semi-quantitative analysis (Faccinetto *et al.* 2011)

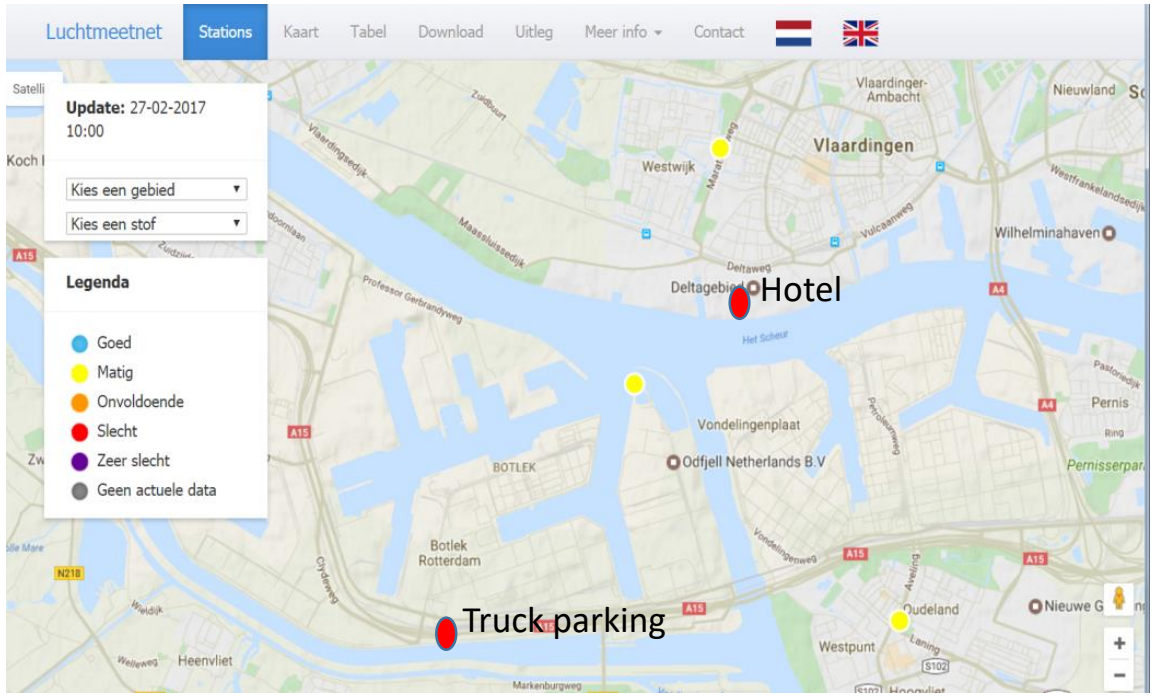
L2MS decay curve of the pyrene mass peak ➡ **surface analysis**

Air quality field samples

INRA – Institute National de la Recherche Agronomique → **Air quality impact of biogenic and anthropogenic VOC**

2 locations for continuous measurements of ambient air:

- Truck parking located south of the Botlek part of Rotterdam harbor
- Parking lot at the Delta Hotel in Vlaardingen



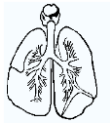
VOC Atmospheric Consequences

Chemistry
(source and sinks, local or long transport)

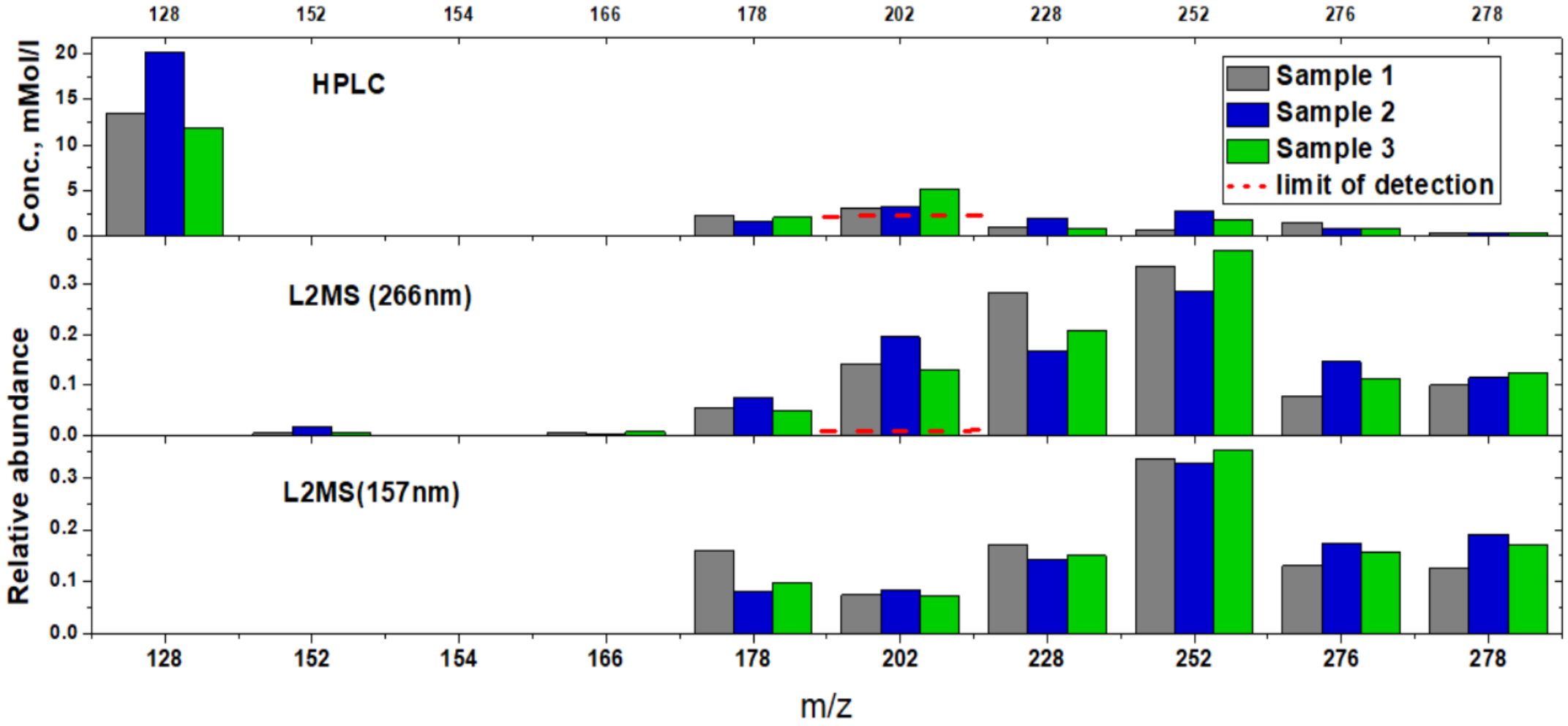
Climate

(light scattering & absorption, effect on clouds)

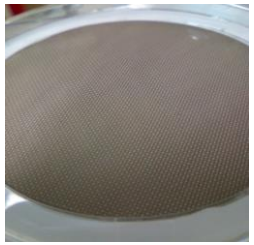
Health
(asthma, mortality, lung cancer …)



Air quality field samples sample analysis



BIOTOX field samples



Exhaust particles deposited on quartz paper filters

Diesel IVECO Tector engine

- Fuel
  - Diesel (B0)
  - Diesel+30% biodiesel (B30)
  - Biodiesel (B100)
- Running cycle
  - 1500rpm 30% load
  - Hot WHTC

Popovicheva *et al.*, accepted

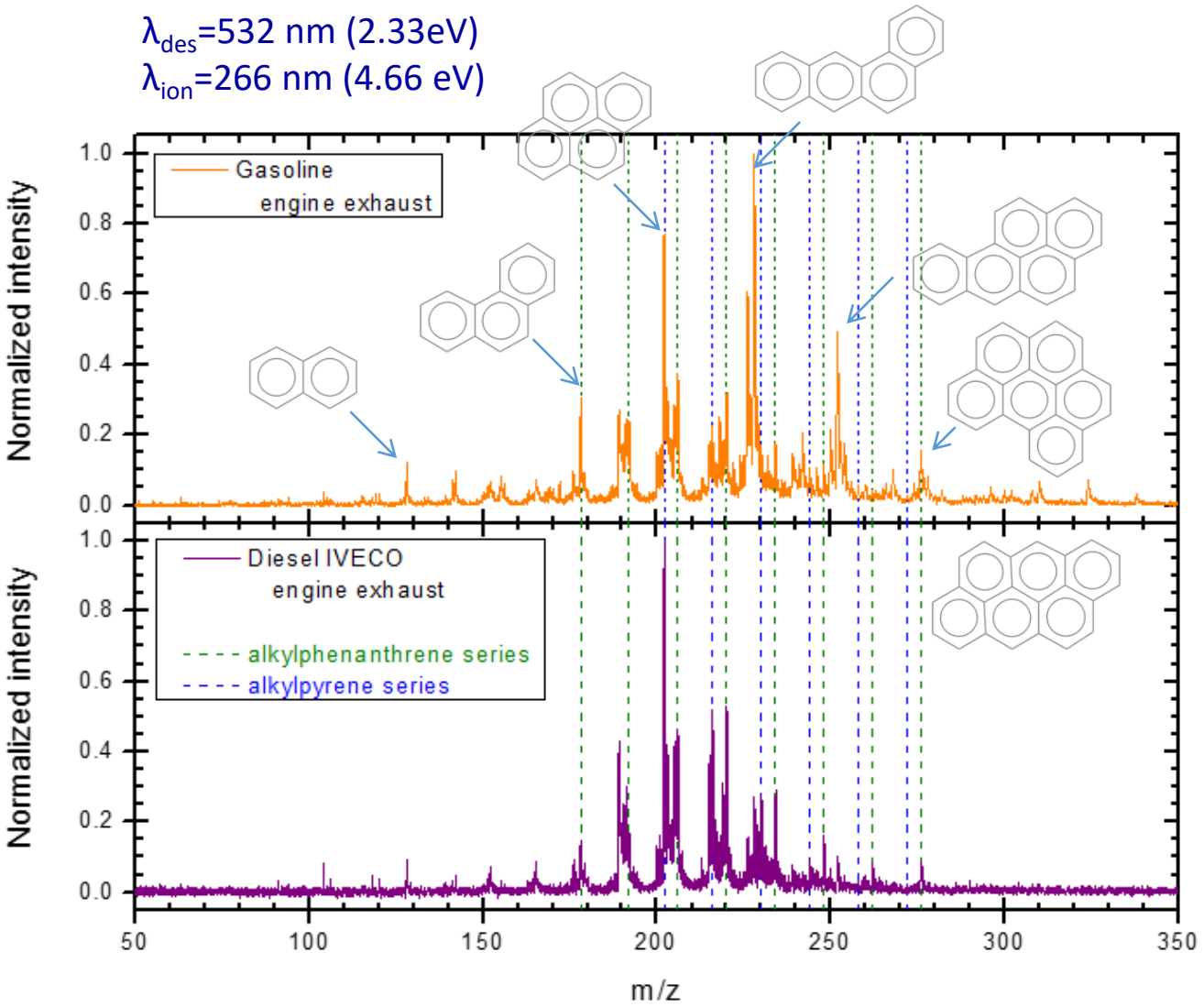
Gasoline Ford Focus car - DISI

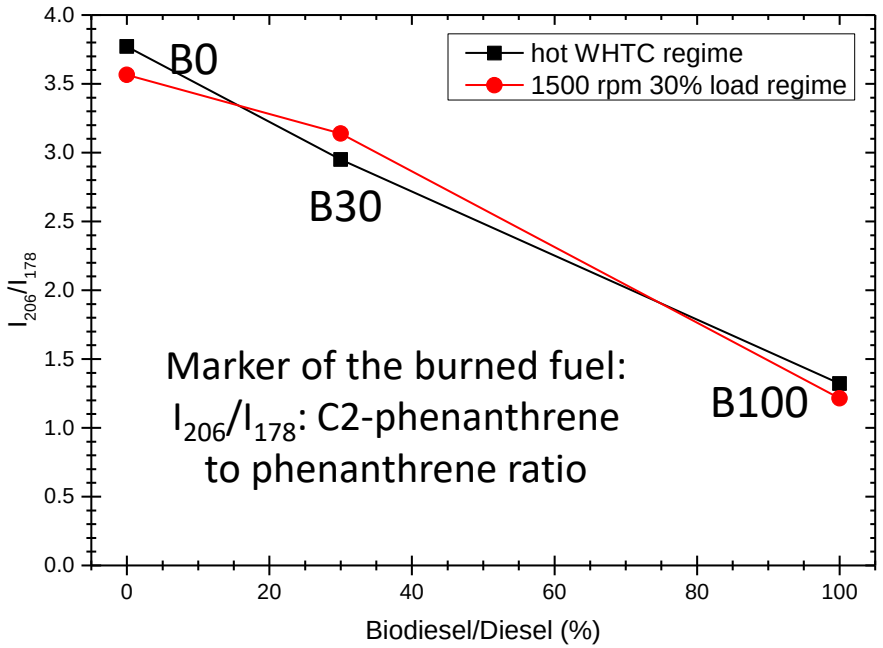
- Fuel
  - Gasoline (G)
  - Gasoline+15% ethanol (G15%E)
  - Gasoline+ 25 % n-butanol (G25%nB)
- Running cycle
  - Artemis urban
  - Artemis rural
  - Artemis130

Article in preparation

BIOTOX: 266 nm L2MS results

λ_{des}=532 nm (2.33eV)
λ_{ion}=266 nm (4.66 eV)





PAH and alkyl-PAH distributions characteristic for the used fuel

Conclusions

- L2MS – a suitable platform for surface analysis
- High sensitivity – up to ~80 attomol/laser pulse
- High selectivity and versatility through complementary ionization schemes
  - new ionization wavelength (157 nm) and new desorption (266 nm) – more possibilities for detection
- Analysis of laboratory standards and field samples
  - Soot from engines or laboratory burners
  - Air quality measurements
  - Laboratory synthesized samples

Thank you for the attention!