



# *Recent advances in soot nucleation understanding*

Pascale Desgroux

*with contribution from :*

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Diesel soot has been classified as carcinogenic for humans (Groupe 1) by the International Agency for Research on Cancer since 2012.

Soot particles also contribute to the radiative forcing.

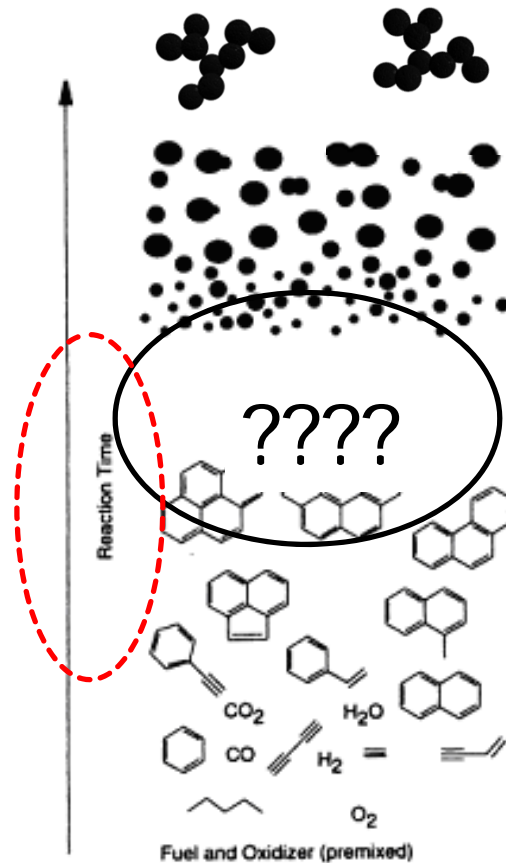
Crucial need to reduce their emission as low as possible in terms of mass but also to pay attention to the smallest soot particles neglected in the current regulations.

# Outline

1. Introduction on soot nucleation
2. Recent advances on identification of gaseous precursors involved in soot formation
3. Recent advances on identification of the smallest soot particles
4. Terminology: what is a nascent or incipient soot?
5. Convenient reactors for studying soot nucleation
6. Recent advances on soot surface analysis
7. From experimental advances to a better understanding of soot nucleation. Impact on soot modelling
8. Perspectives

# 1. Introduction on soot nucleation

# Soot formation: principal steps



HACA mechanism  
Hydrogen abstraction  
acetylene addition  
(Frenklach and Wang)

It is not a spatial representation of soot formation but a **temporal story** of one soot particle whatever is its inception location.

*H. Bockhorn, Soot formation in combustion: mechanism and models. (1994)*

# Nucleation through Smoluchowski equation (Collisional source terms)

## Modelling

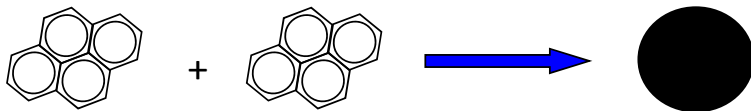


- Equation of Marian Smoluchowski (1916):

$$\frac{dN_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \beta_{j,i-j} N_j N_{i-j} - \sum_{j=1}^{\infty} \beta_{i,j} N_i N_j$$
$$i = 2, \dots, \infty$$

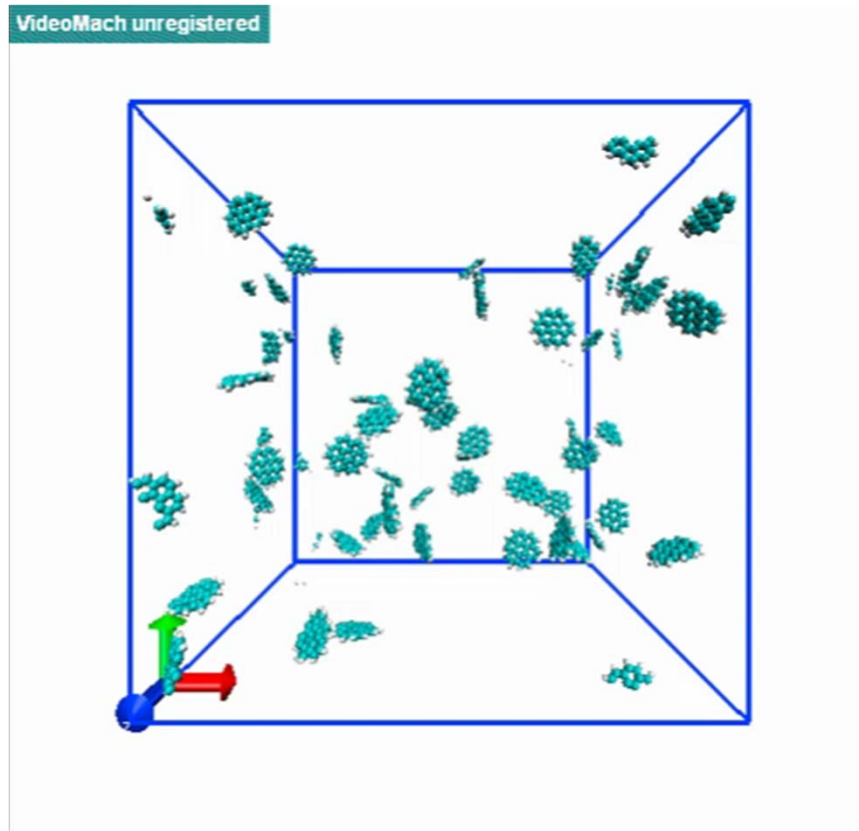
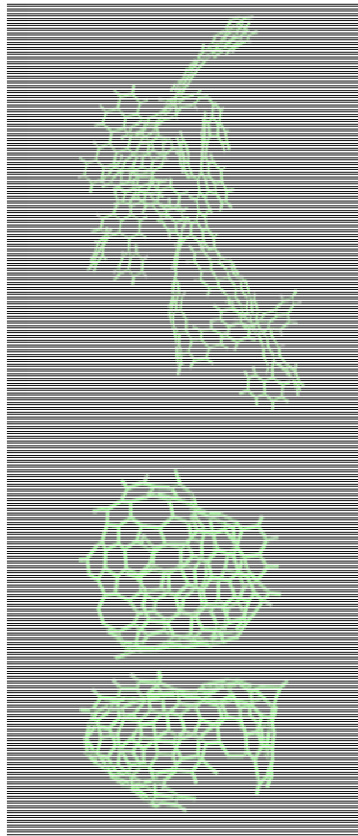
- dynamic of aerosols

- Introduced in the method of moments and sectional method codes
- Nucleation = reaction of coagulation between PAHs that can belong to a large area of PAHs to form the 1st nucleus.

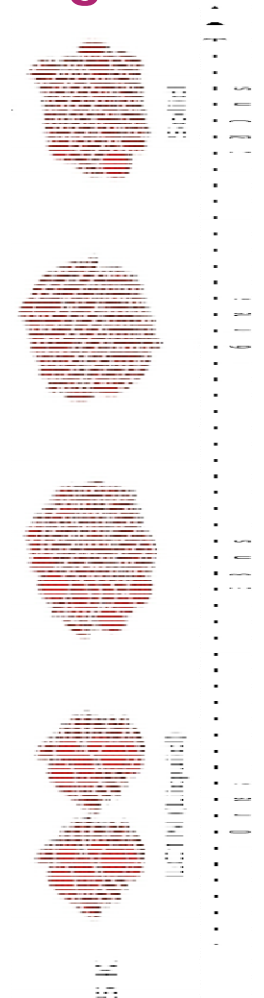


Coalescence of 2 pyrenes ( $C_{16}H_{10}$ )

# Contribution of molecular dynamics for understanding PAH clustering



Size 23 P=0.233	
Size 14 P=0.437	
Size 7 P=0.257	
Size 7 P=0.788	
iso-PAHAP	



Courtesy of Mao, van Duin, Luo

Violi, *J. Phys: Conf. Ser.* (2008)

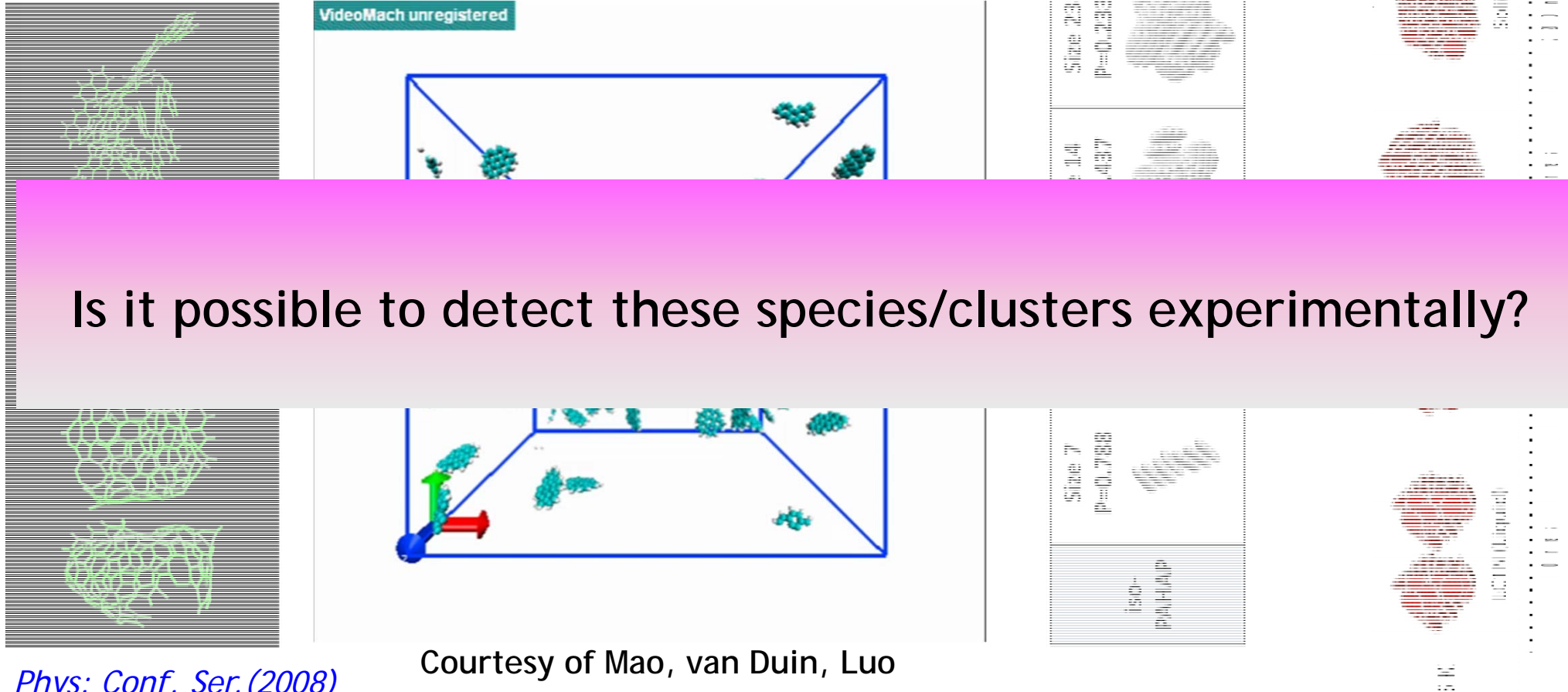
Mao et al., *Carbon* 121, 2017

European Combustion Meeting, Lisboa, 2019, April 14-17th

Pascasio et al.  
*Chm* (2017)

Chen, Kraft et al.  
*Carbon* (2014)

# Contribution of molecular dynamics for understanding PAH clustering



Is it possible to detect these species/clusters experimentally?

Courtesy of Mao, van Duin, Luo

*Violi, J. Phys: Conf. Ser. (2008)*

*Mao et al., Carbon121, 2017*

European Combustion Meeting, Lisboa, 2019, April 14-17th

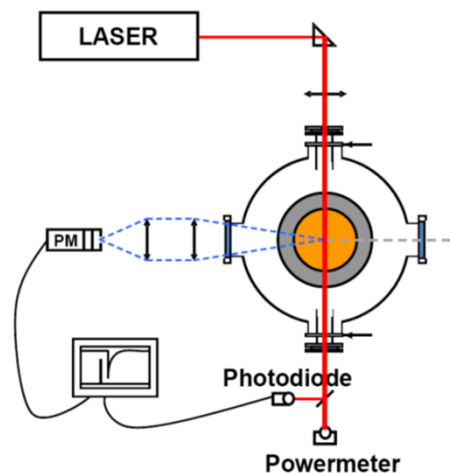
*Pascazio et al. CMB (2017)*

*Chen, Kraft et al. Carbon (2014)*



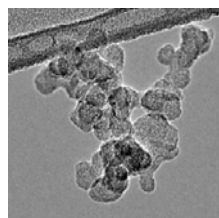
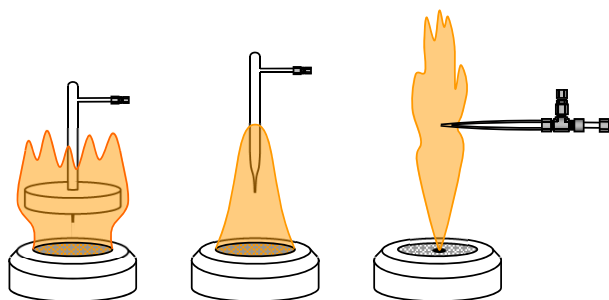
# List of techniques

## ■ IN SITU



- ❖ Laser Induced Fluorescence (LIF) for precursors
- ❖ Laser Induced Incandescence (LII) for soot
- ❖ Extinction
- ❖ Scattering

## ■ EX SITU



## ■ ON LINE

- ❖ Scanning Mobility Particle Sizing (SMPS)
- ❖ Tandem-APPI-Mass Spectrometer
- ❖ Aerosol Mass Spectrometer (AMS)
- ❖ Raman
- ❖ Gas Chromatography (GC)
- ❖ JCLIF
- ❖ SAXS etc

## ■ OFF LINE

- ❖ Time-Of-Flight MS (ToF-SIMS)
- ❖ HRTEM
- ❖ Helium Ion Microscopy (HIM)
- ❖ Atomic Force Microscopy (AFM)
- ❖ Laser Desorption/ionisation/MS
- ❖ Raman, UV-Vis, XPS, Etc

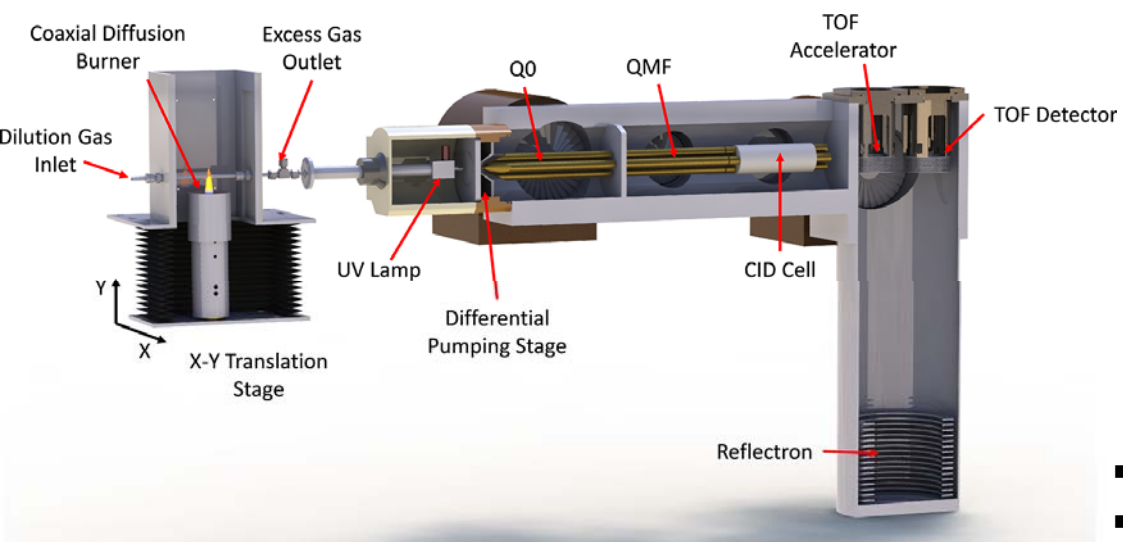
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## 2. Recent advances on identification of gaseous precursors involved in soot formation

2.1 ex situ online APPI-MS

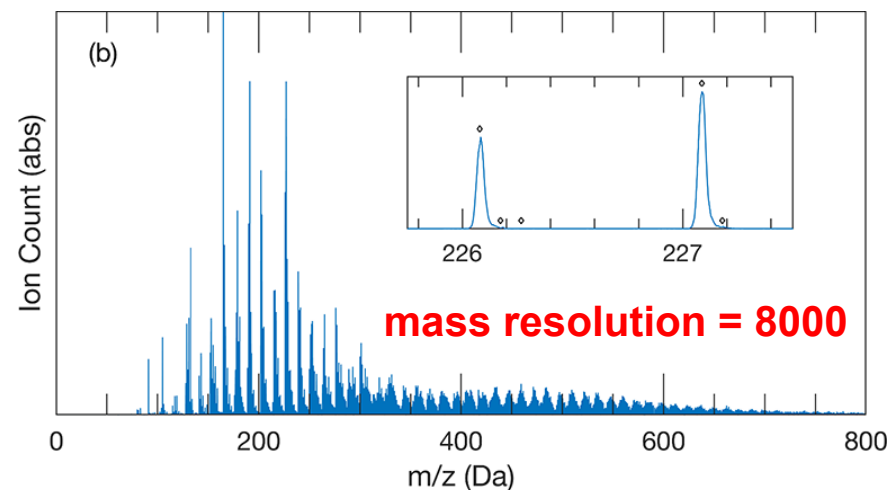
2.2 in situ LIF

## 2.1 Evidence of new chemical structures using online atmosph.sampling high resolution tandem mass spectrometry



Inverse coflow  $C_2H_4$  diffusion flame

*Adamson, Hansen et al. J.Phys.Chem A (2018)*

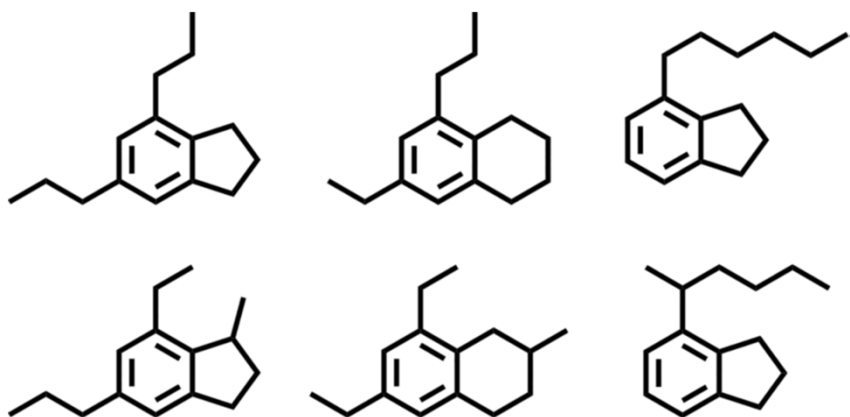


- VUV ionisation
- Tandem-MS
- ion fragmentation in **collision induced dissociation** (CID)

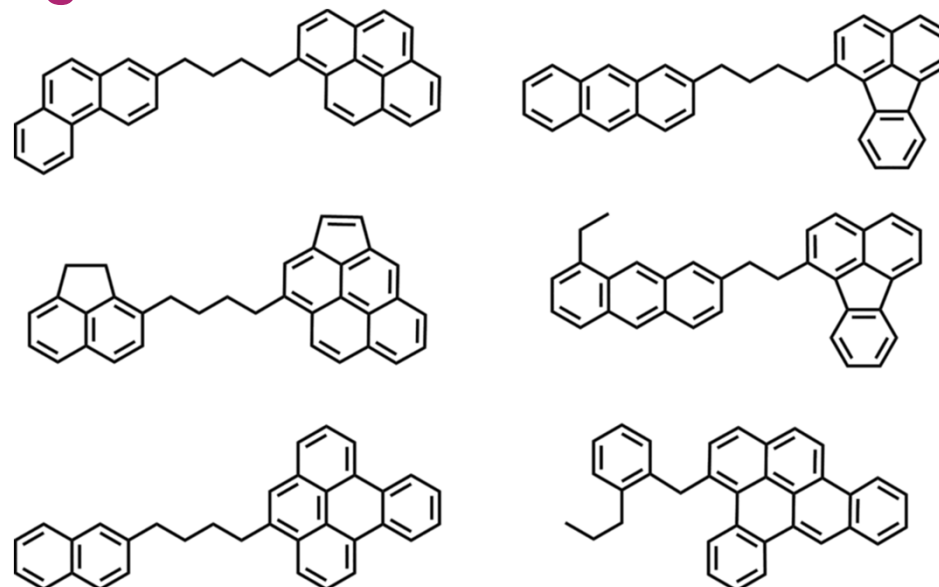
Identification of new structures + repetitive nature of PAH formation chemistry

# Alkylated and aliphatically bridged PAHs

Adamson, Hansen et al. *J.Phys.Chem A* (2018)



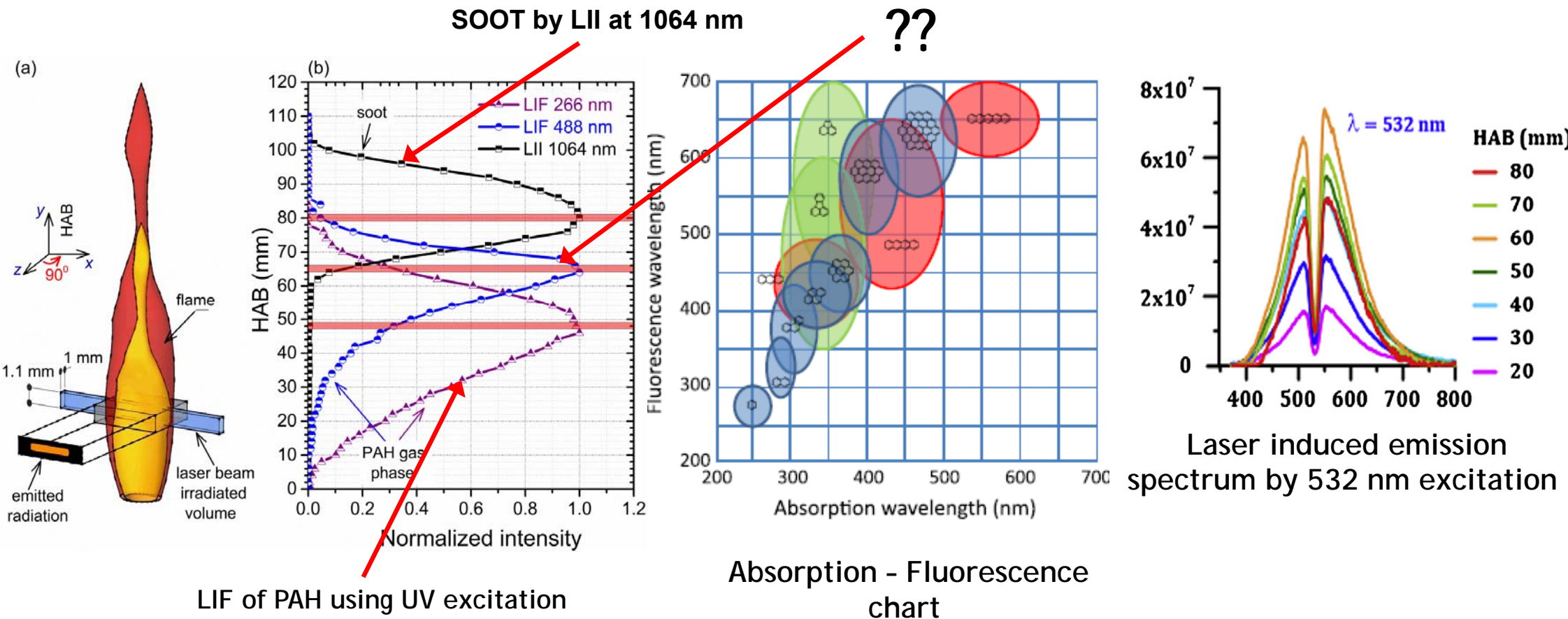
Conceivable  $C_{15}H_{22}$  isomers (202 amu) based on the detection of aliphatic side chains and aromatic structures: **Alkylated- substituted PAHs**



Conceivable  $C_{34}H_{26}$  isomers (434 amu): **aliphatically bridged multicore aromatic hydrocarbons**

Datascience approaches should be developed that automatically explore the available parameter space for reoccurring features in the mass spectra.

## 2.2.a in situ LIF of PAHs and other precursors

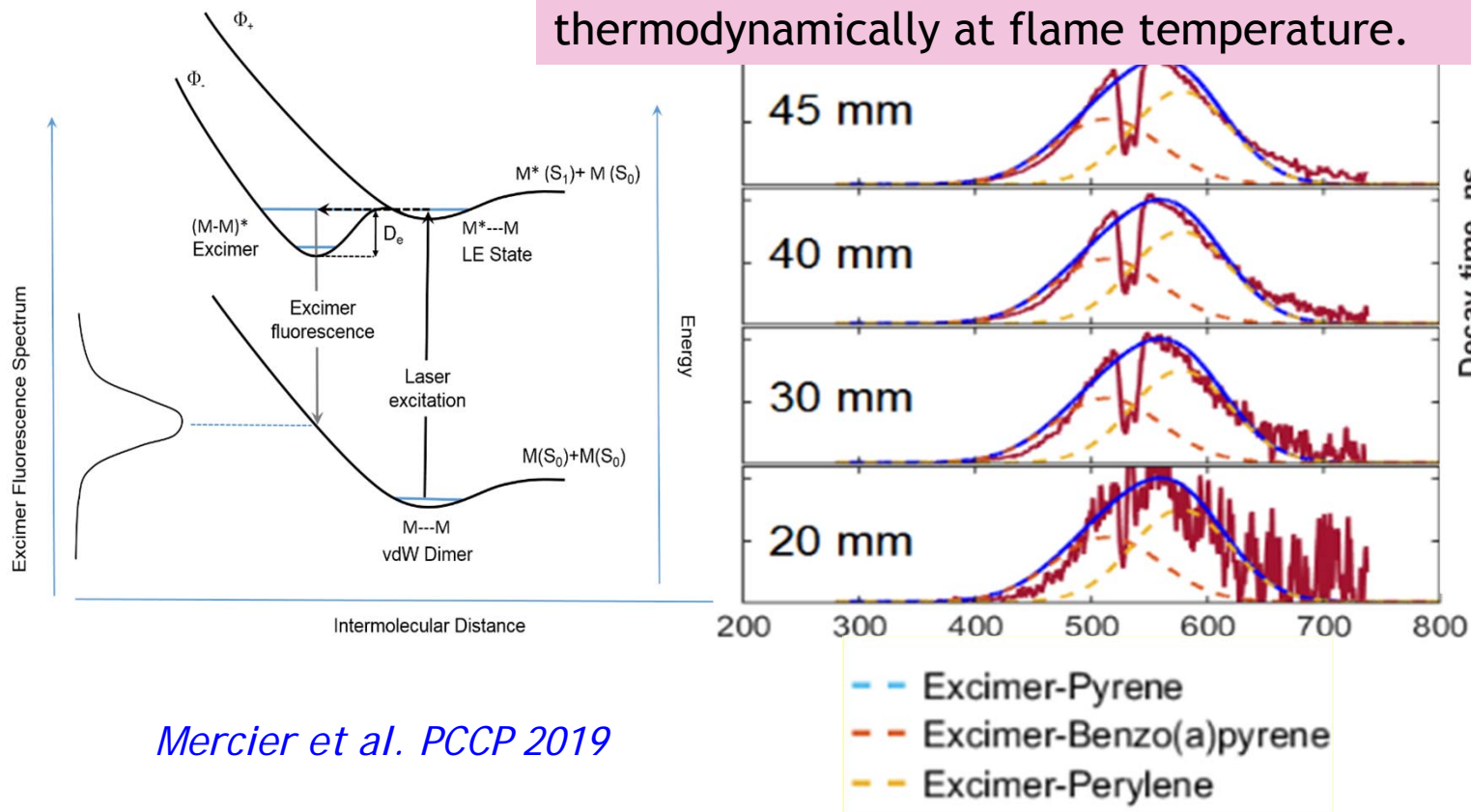


*Irimiea et al., Carbon 2018*

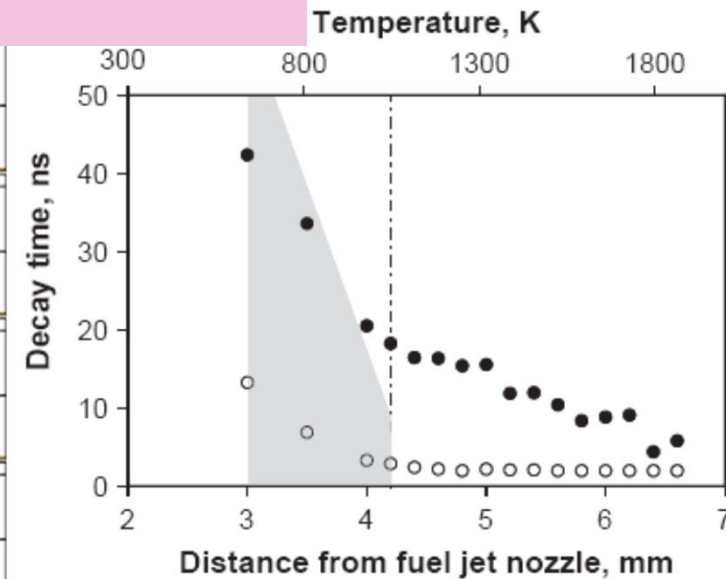
*Bejaoui et al., CnF 2014*

## 2.2.b Evidence of dimers by LIF

Small-size dimers exist before the soot onset despite the fact it is known that dimers are not stable thermodynamically at flame temperature.



Mercier et al. PCCP 2019



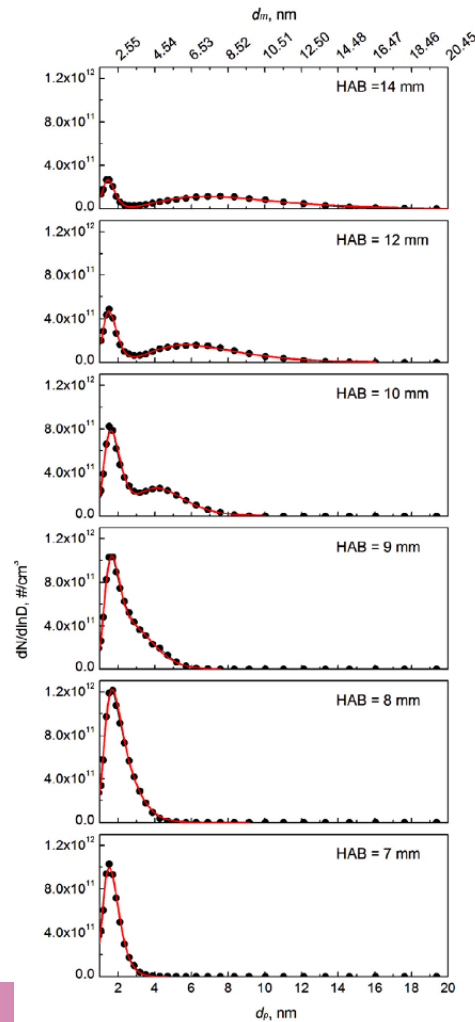
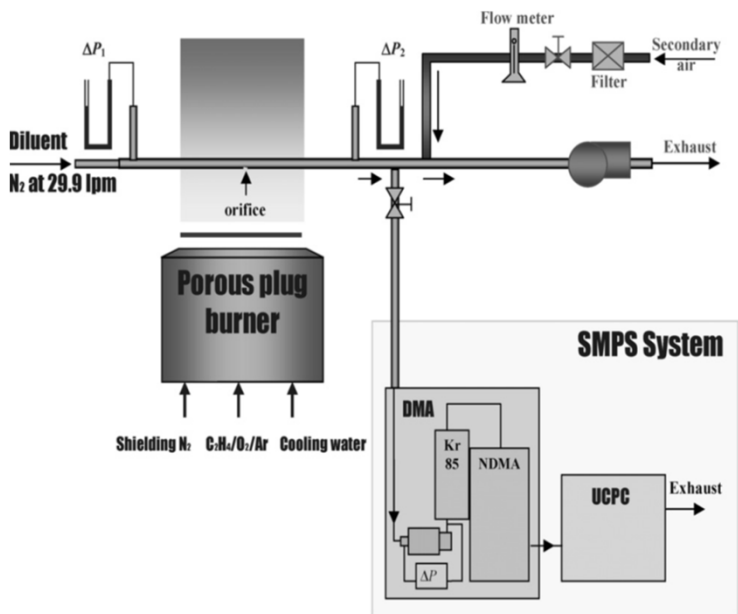
Sirignano et al, CnF 159 (2012)

## 3. Recent advances on identification of the smallest (soot) particles

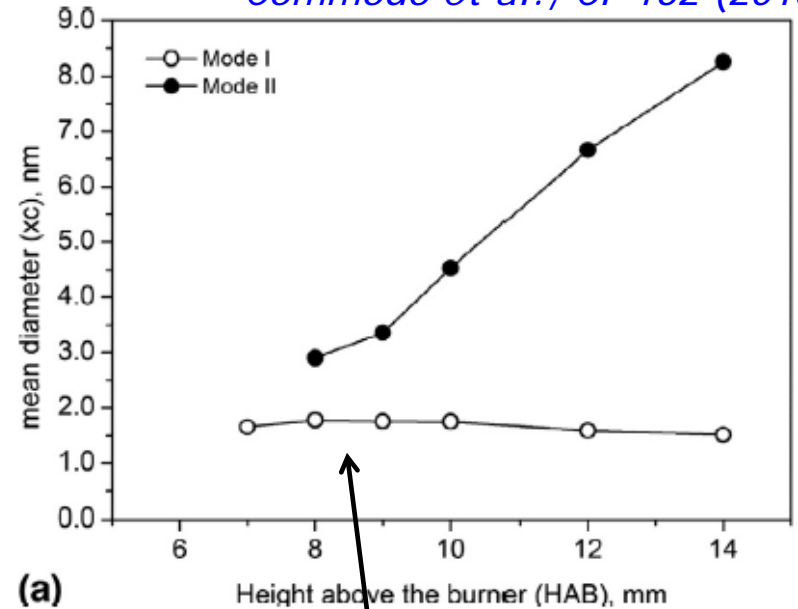
- 3.1 By nano-SMPS
- 3.2 By microscopy
- 3.3 By LII

# 3.1 Highlighting of very small particles by nano-SMPS

Bimodal distribution



Commodo et al., CF 162 (2015)



Nanoparticles of Organic Compounds (NOC)? (transparent particles) - just nucleated carbonaceous particles

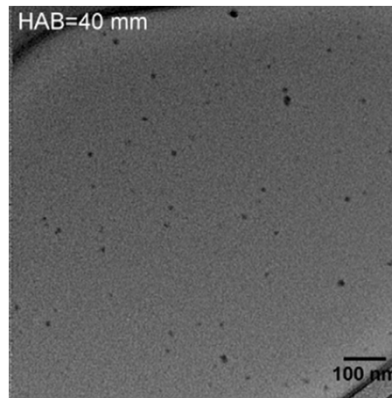
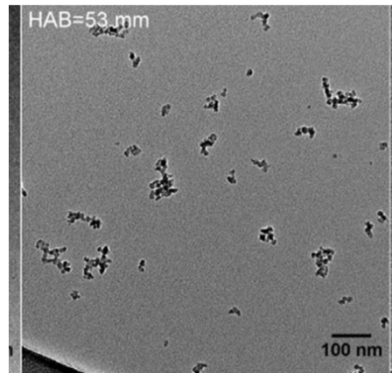
Abid & Wang, PROCI 32(2009)

Tang et al. Tsinghua univ. PROCI 2017

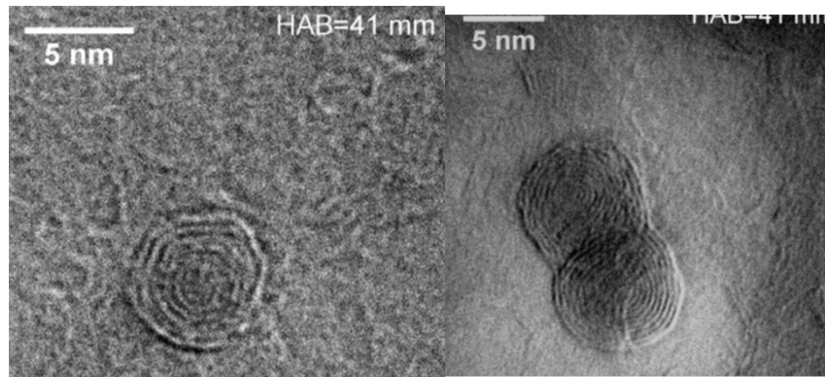


## 3.2 Evidence of very small soot particles by microscopy

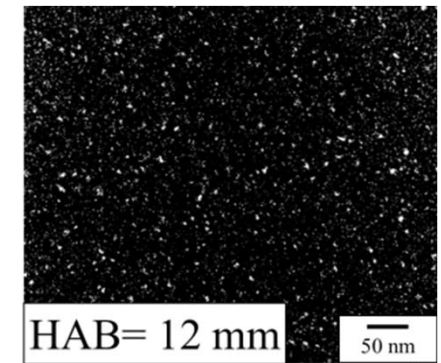
### TEM



HRTEM  
Smallest 4 nm  
(personal comm)



HIM  
Smallest 1 nm  
*Schenk et al. PROCI 2015*



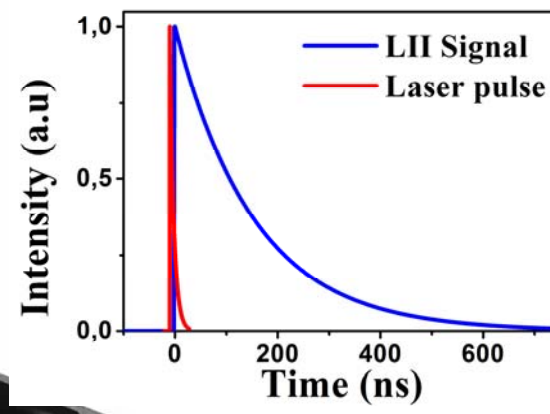
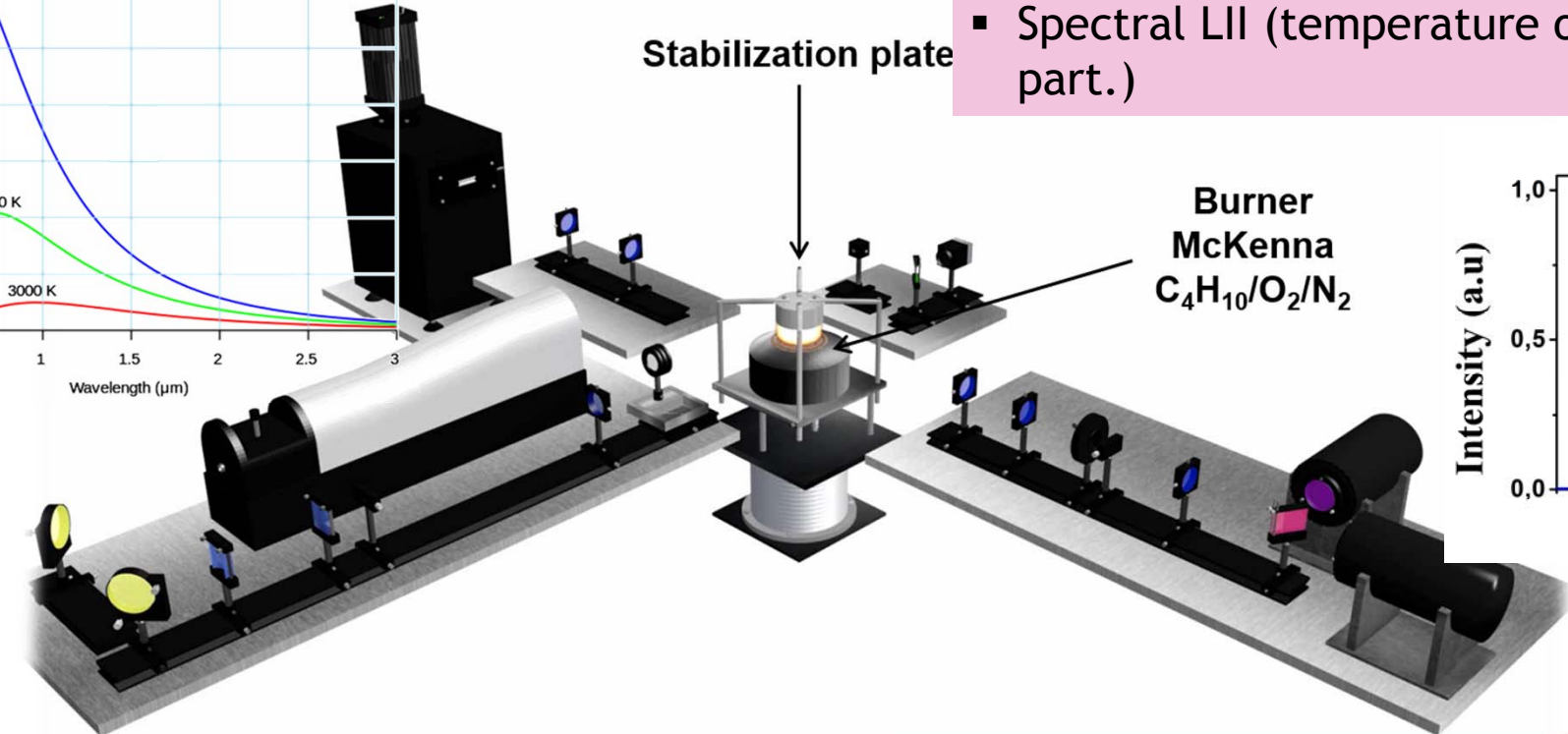
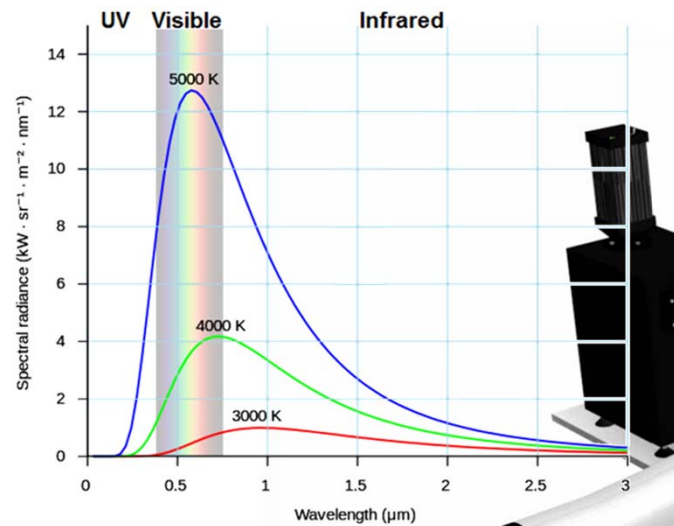
*Moallemi et al., Comb. Flame 188 (2018) - Univ. Alberta*

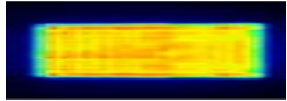
*Lille- Bielefeld (2017)*

### 3.3 Evidence very small soot particles by Laser Induced Incandescence (LII)

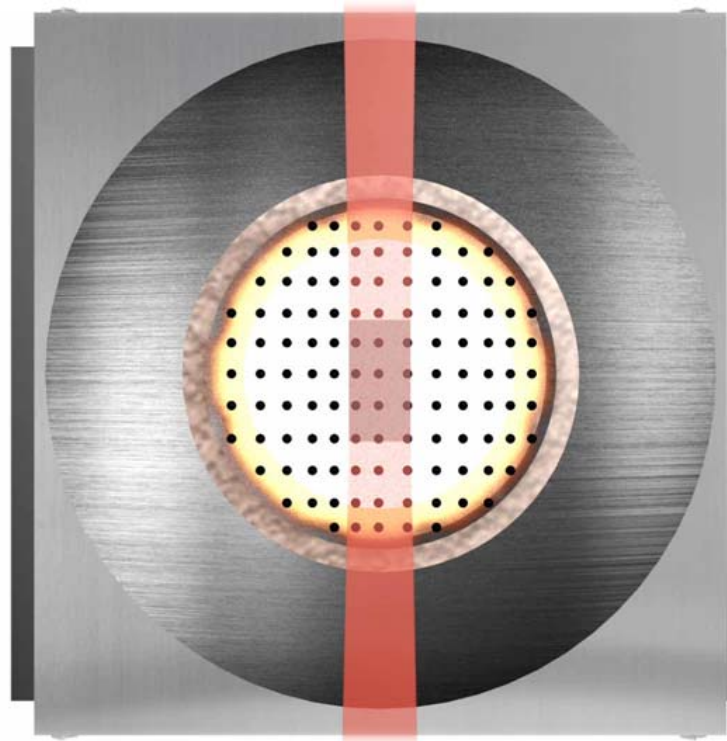
Set-up to detect the smallest size and soot CC

- LII decay time (size)
- LII intensity (Fv)
- Spectral LII (temperature of laser heated soot part.)

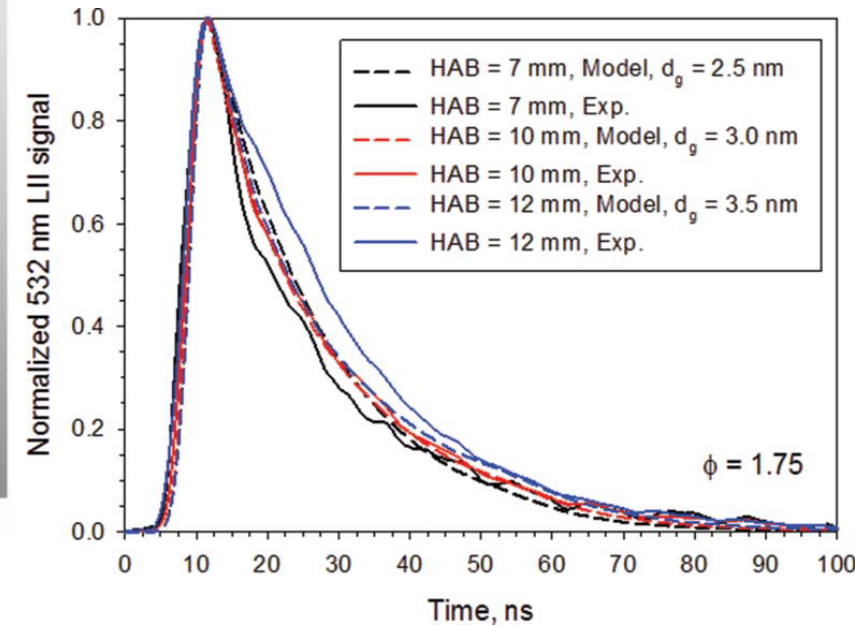




1. Top-hat laser (1064 nm) energy distribution
2. Collection volume: 0.3x5.6x8 mm<sup>3</sup>
3. Shutter rejection of flame emission
4. To have an “ideal” reactor (nucleation flame), exempt of large soot particles



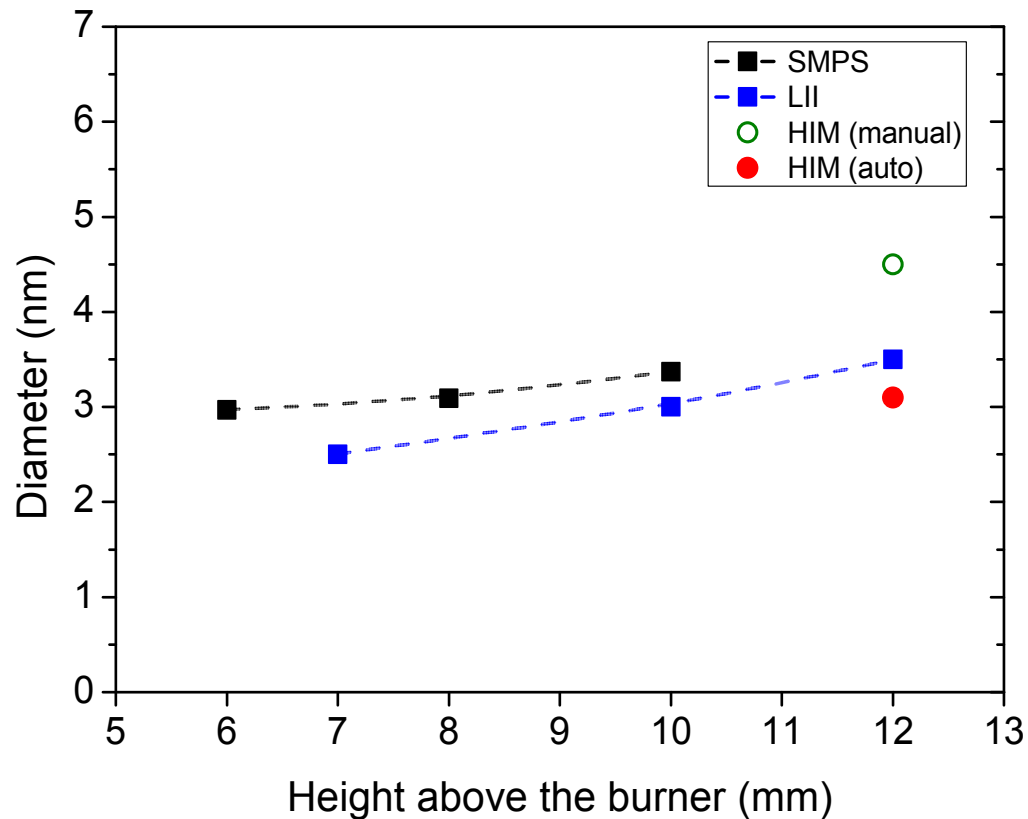
From time-resolved LII modelling, log-normal size distribution peaked at 2.5 ( $\pm 0.5$ ) nm at 7 mm



*Bladh et al., PROCI 2017*

*Betrancourt et al., AST 51 (2017)*

# Comparative determination of the size of the smallest incandescent soot particles by LII/SMPS/HIM

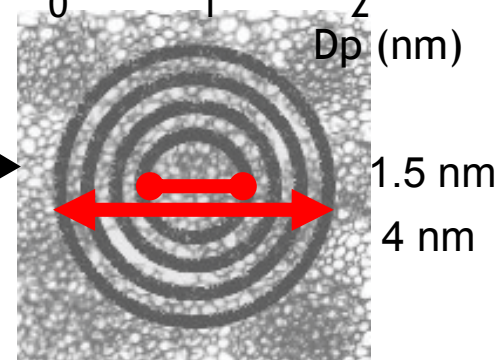
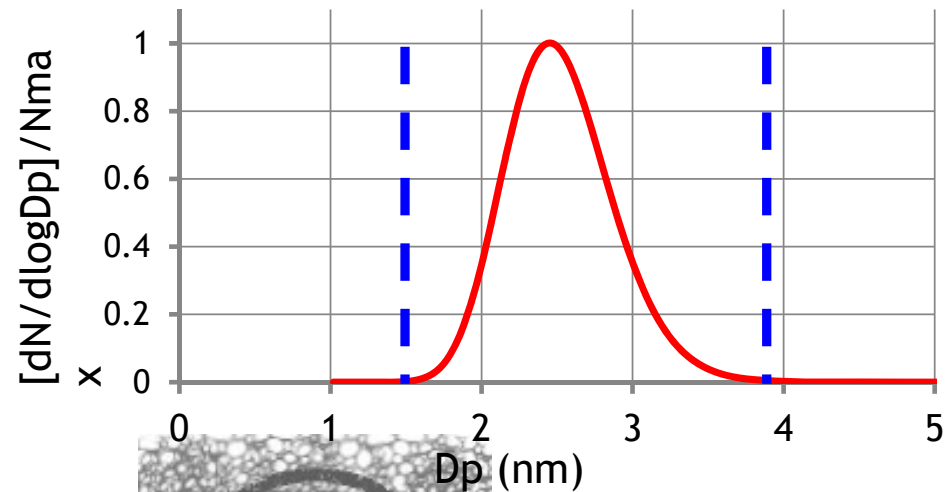
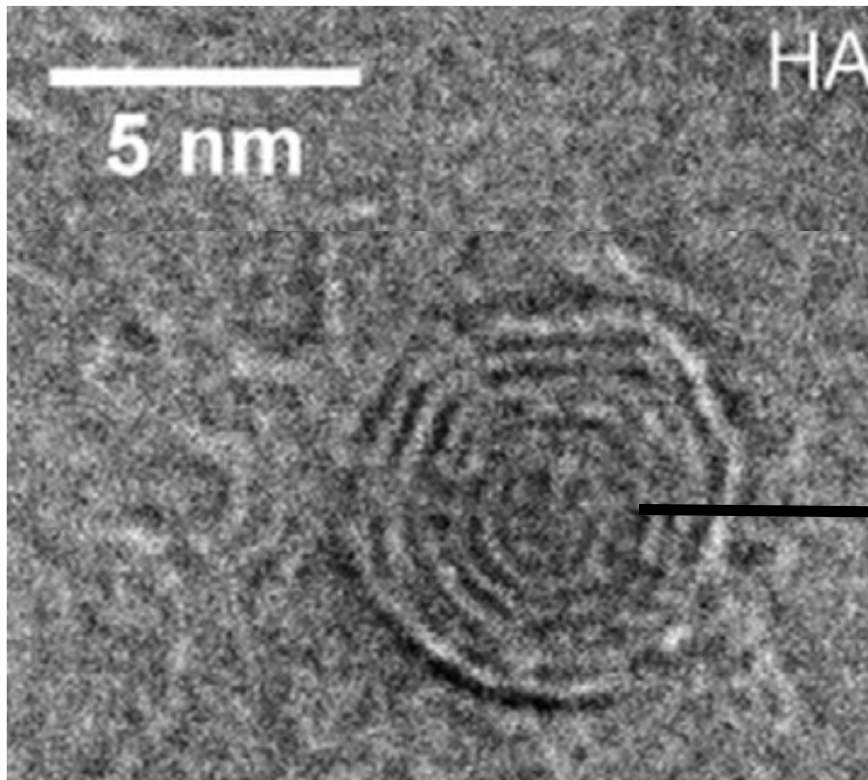


- Very small soot of 1.5- 4 nm have been identified consistently by LII/SMPS/HIM
- They do absorb at 1064 nm and radiate blackbody radiation.

*Betrancourt et al., AST 51 (2017)*

# Why do so small soot particles incandesce upon laser heating?

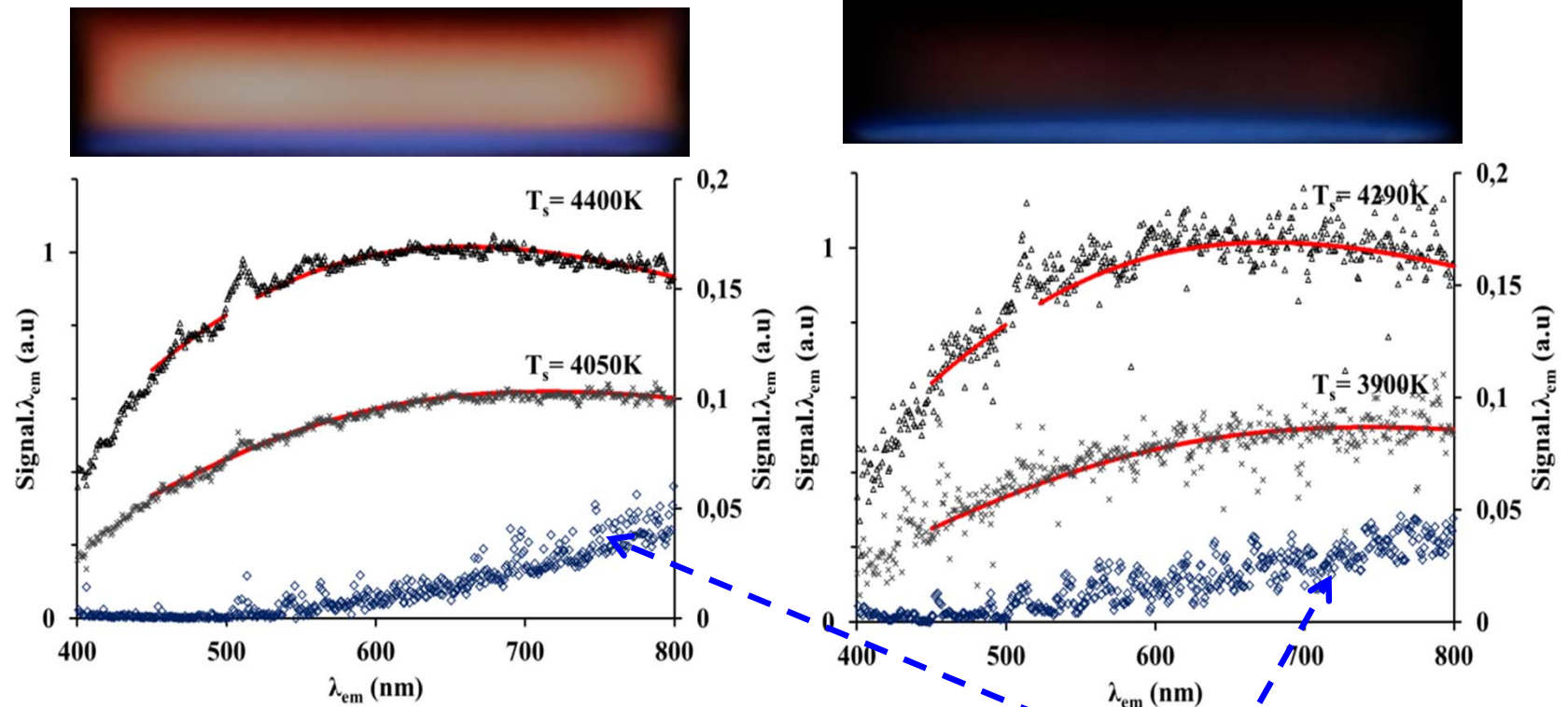
Best size distribution issued from LII modelling



Probably the nascent soot detected by LII are already structured in concentric layers (between 1 and 4 layers)

*Moallemi et al., CnF 188 (2018)*

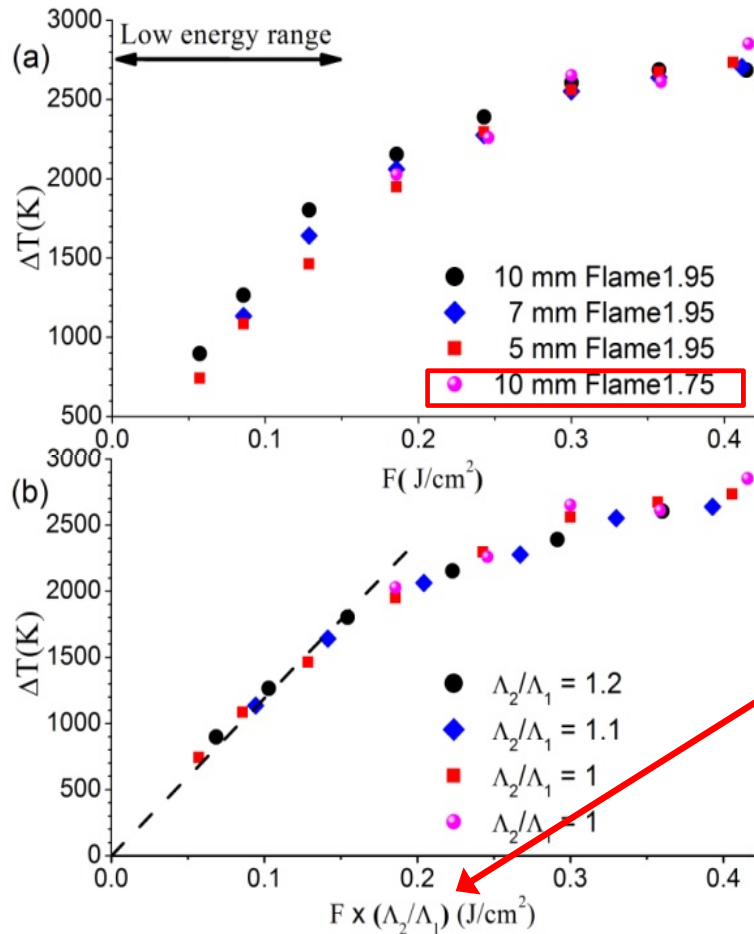
# Comparative behavior of « mature » and « young » soot



$F = 3.5 \text{ mJ/mm}^2$ ;  $F = 2.4 \text{ mJ/mm}^2$ ; blackbody emission ( $F = 0$ )

*Betrancourt et al., AST 51(2017)*

# Comparative behavior of «mature» and «young» soot



$$\Delta T = T(t_p) - T_g = \frac{6\pi}{\lambda_{laser}} \frac{E(m_{\lambda_{laser}})}{\rho_s c_s} \int_0^{t_p} F q(t) dt$$

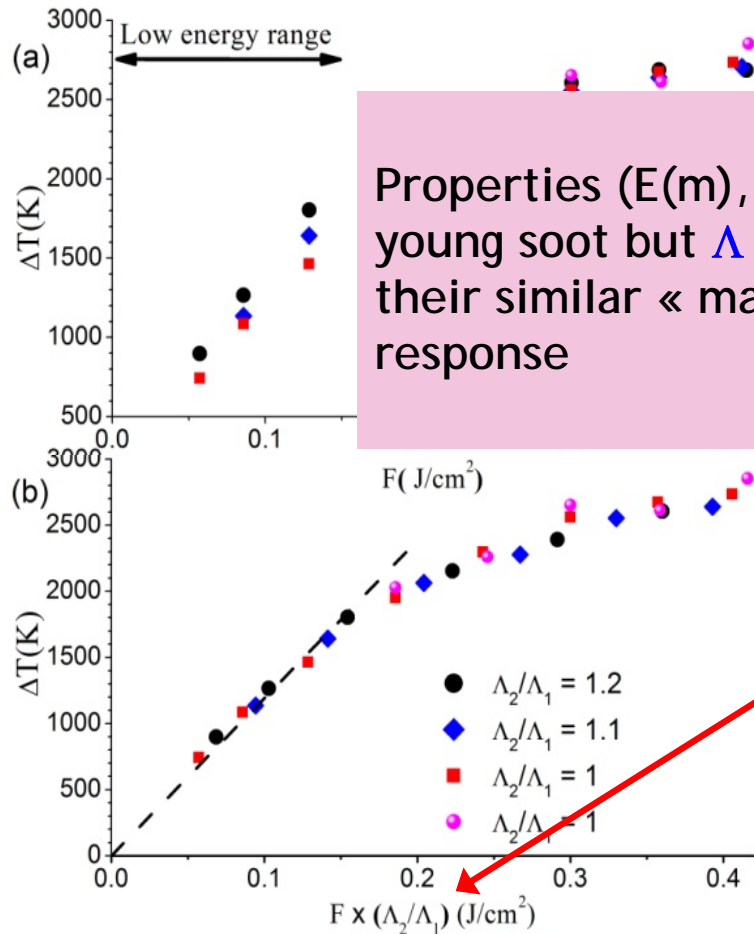
Nucleation flame

Variable change  
 $\Lambda = E(m_{\lambda_{laser}}) / \rho_s c_s$   
 Linear behavior consistent with the theory in the low fluence regime

	$E(m_{1064})$	$\rho_s$
Young	0.25	1.30
Mature	0.41	1.80

Betrancourt et al., Appl.Phys.B(2019)

# Comparative behavior of «mature» and «young» soot



Properties ( $E(m)$ , density) vary between mature and young soot but  $\Lambda$  is nearly constant (20%) explaining their similar « macroscopic » behavior of the LII response

Variable change  
 $\Lambda = E(m_{\lambda_{laser}}) / \rho_s c_s$   
 Linear behavior consistent with the theory in the low fluence regime

	$E(m_{1064})$	$\rho_s$
Young	0.25	1.30
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*Betrancourt et al., Appl.Phys.B(2019)*

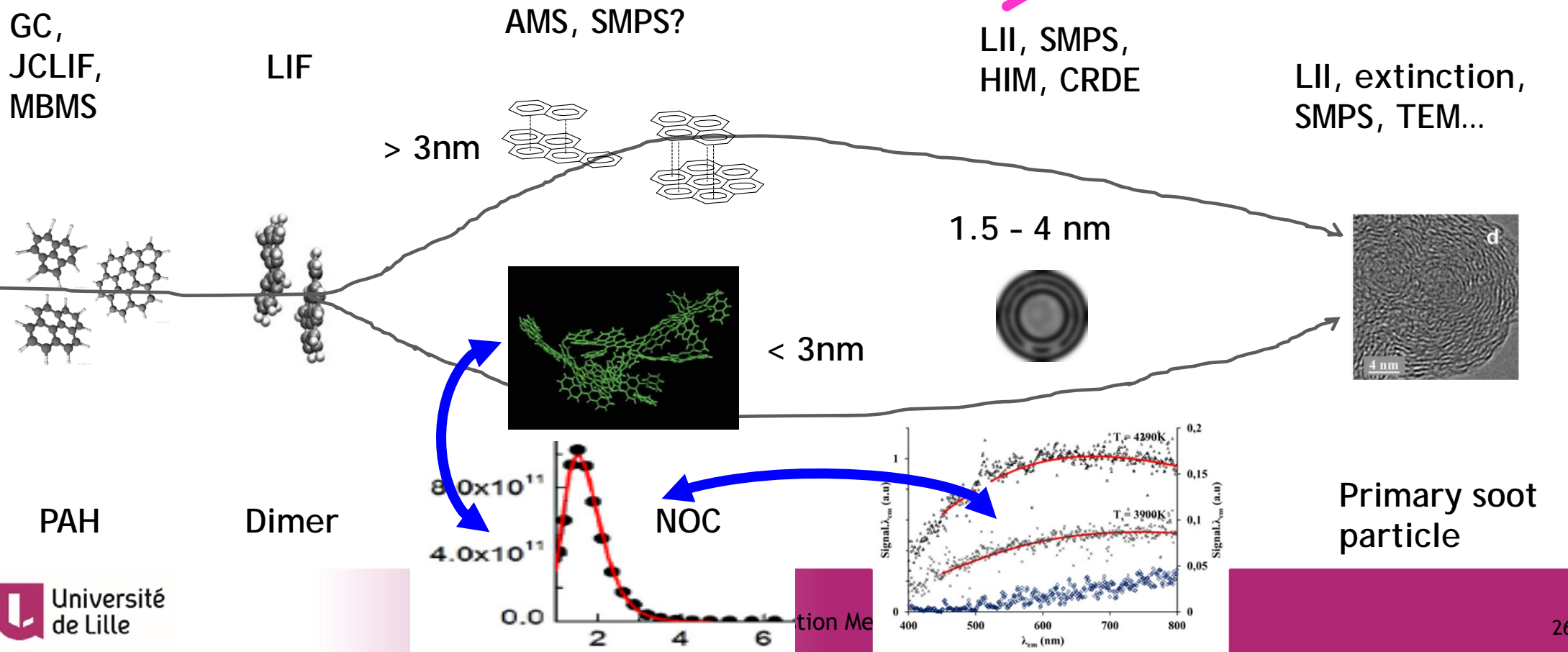


## 4. Terminology: what is a nascent soot, an incipient soot, an incipient particle, a just nucleated (soot) particle, freshly nucleated carbonaceous particles ?

- Calcotte 1981: “**Nucleation**: the **transformation from a molecular system to a particulate system**, which grow faster than they decompose or otherwise disappear by reaction”.
- Sgro, D’Alessio (2009) defined the **soot formation threshold** as “*the C/O value where light absorption in the visible and LII are detected*”.
- Lille (>2013): Soot particles **are able to absorb 1064 nm** radiation and to **radiate spectrally continuous blackbody-type radiation**. We emphasized the existence of soot particles **as small as 1.5 to 4 nm**. These particles are named “**incipient soot**”
- Michelsen, PROCI 2017: “PAH precursors nucleate, react and combine, or grow to form **incipient soot particles**. **Incipient soot particles** are **freshly nucleated particles** with (C/H) ratios in the range of 1.4-2.5. [...] they naturally exist as nanoparticles in the size range of 1-6 nm and are sometimes referred to as **nano-organic carbon (NOC)**. [...] there are at least **two types of incipient particles**.
  - The **first type** (1) absorbs in the UV but is transparent at visible and IR wavelengths, [...] (3) is less than  $\sim 3$  nm in diameter, [...] will be referred to as **disordered incipient (soot) particles**
  - The **second type** (1) absorbs in the visible and IR regions [...] (3) is  $\geq \sim 3$  nm in diameter [...] will be referred to as **stacked incipient (soot) particles**.

First incandescent particle detected by LII + SMPS (1.5 - 4 nm) = incipient soot particles

Incipient (soot) particles (1- 6 nm) - RSRs?



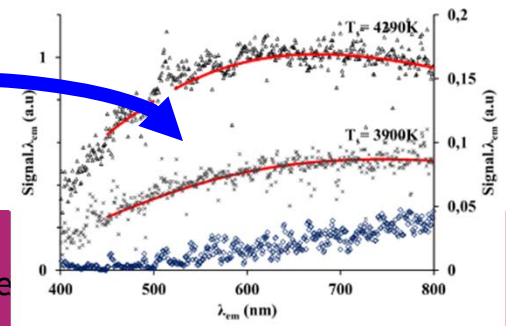
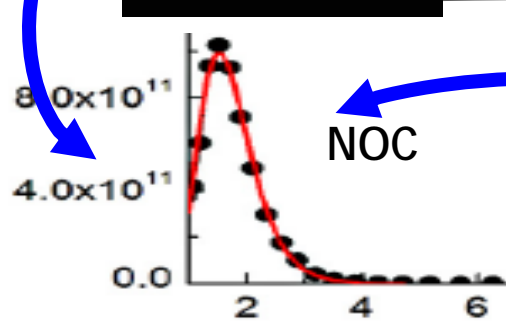
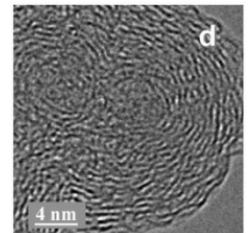
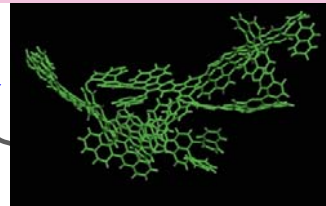
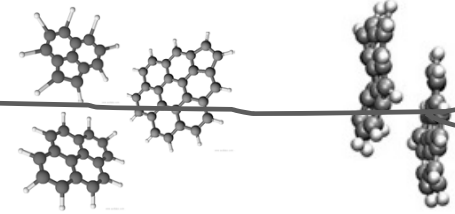
First incandescent particle detected by LII + SMPS (1.5 - 4 nm)  
 = incipient soot particles

Whatever the definition, the most important is how useful is the detected « particle » for understanding the soot nucleation and how it can be inserted as a target to be reproduced by soot modelling

GC,  
JCLIF,  
MBMS

LIF

LII, extinction,  
SMPS, TEM...



# 5. Convenient reactors for studying the soot nucleation

Isolating soot nucleation is a challenging task

5.1 Pyrolysis flow reactors

5.2 Diffusion flames

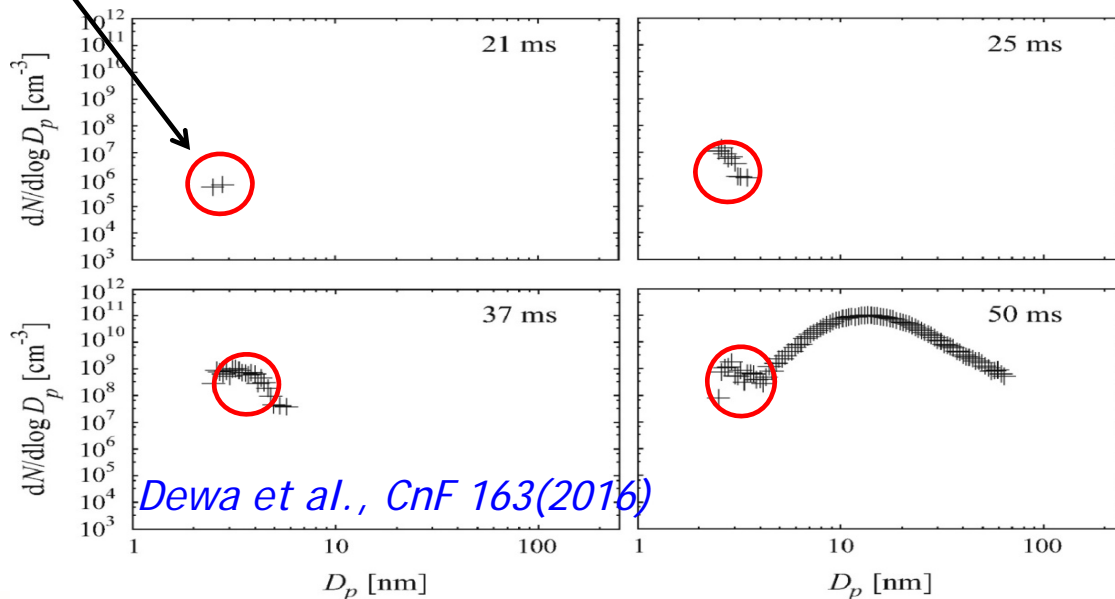
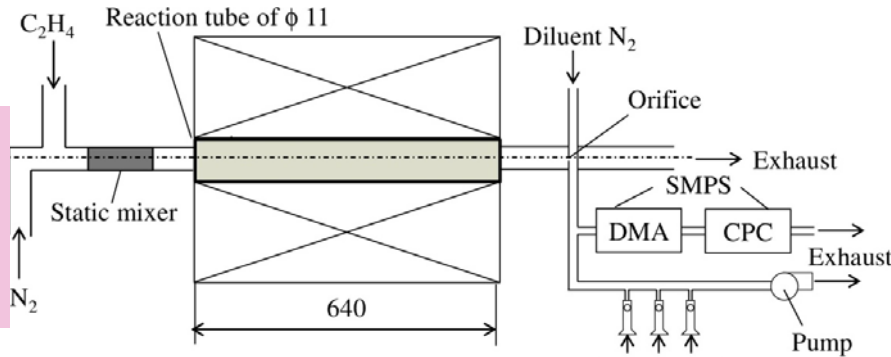
5.3 Premixed stretch-stabilized flat flames

5.4 Nucleation flames

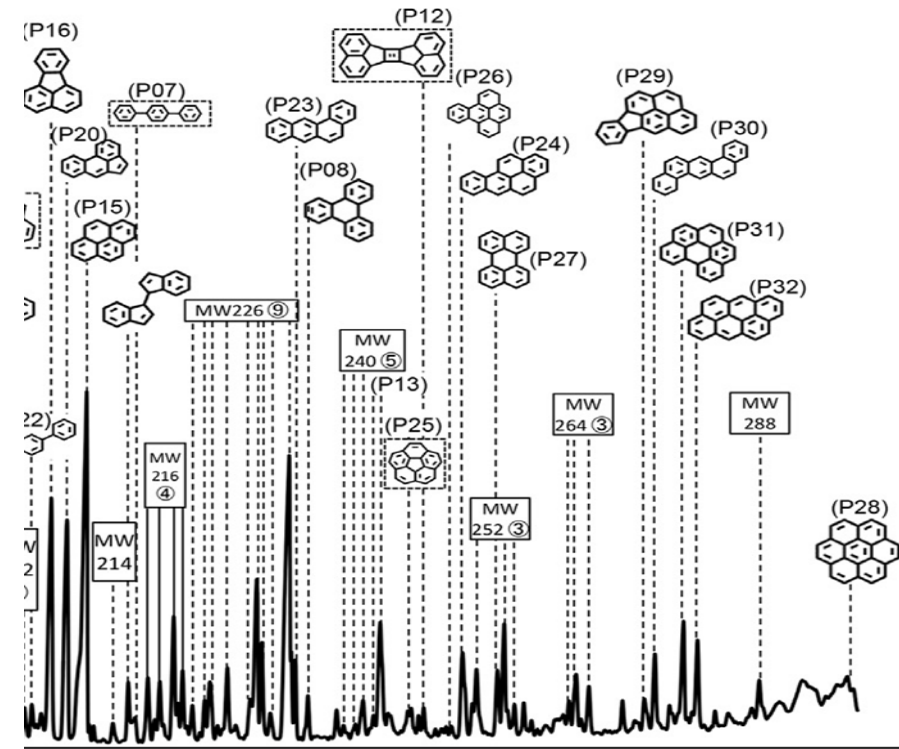
# 5.1 Flow reactor (pyrolysis 1350-1800 K) - Tohoku univ.

*Matsukawa et al., Comb.Flame 167(2016)*

First SMPS signal defines their soot onset

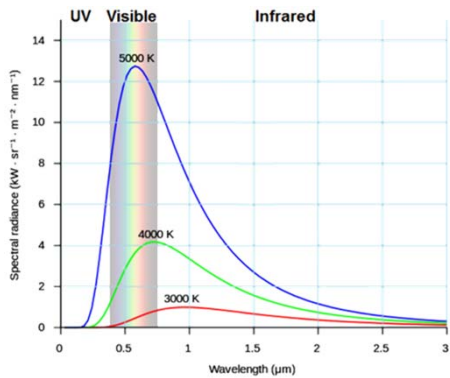


*Dewa et al., CnF 163(2016)*

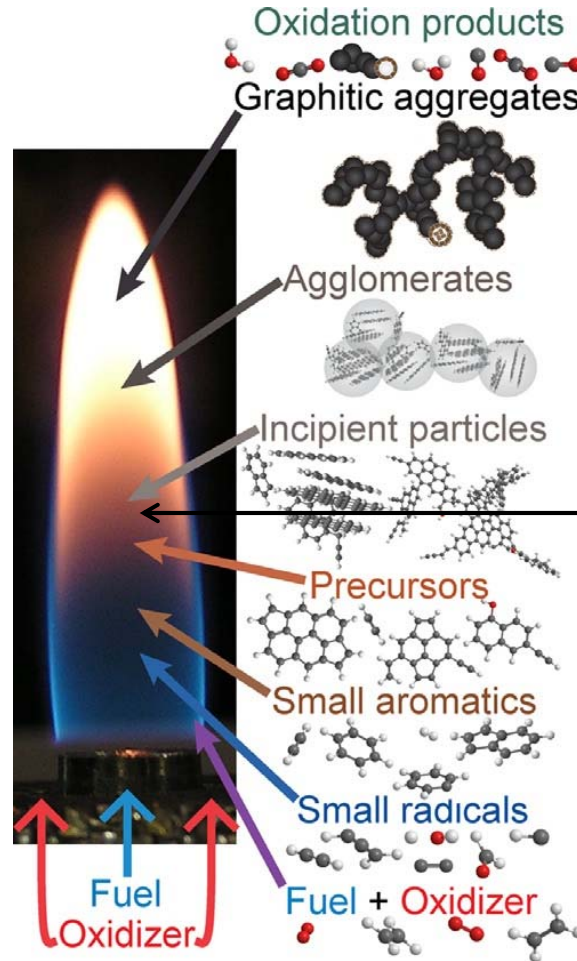


PAH growth pathways are studied around the sooting limit as function of the temperature

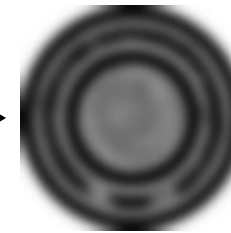
# 5.2 Laminar diffusion flame (coflow or counterflow)



- Toronto
- Kaust
- Naples
- Sydney
- Adelaïde
- SANDIA
- Yale
- etc ...



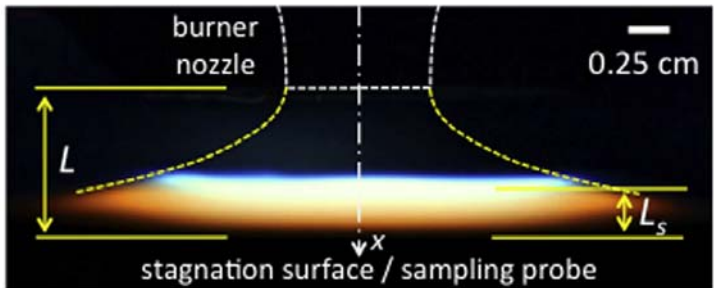
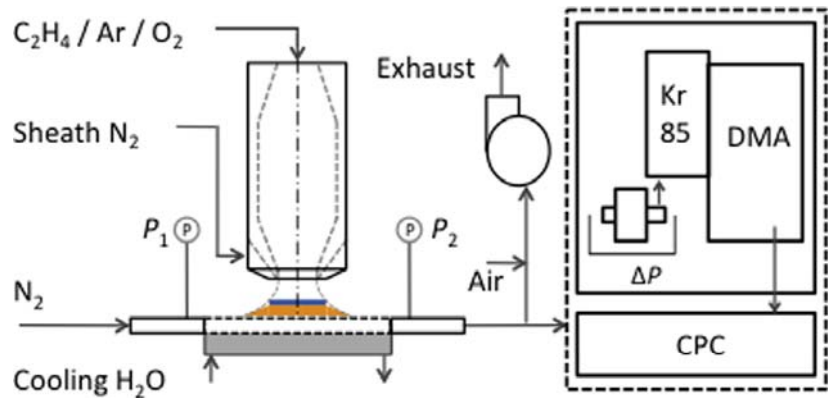
- « Stratification » of the species and soot growth along the flame axis
- Access to in situ and ex situ investigation



Incipient soot particles by LII

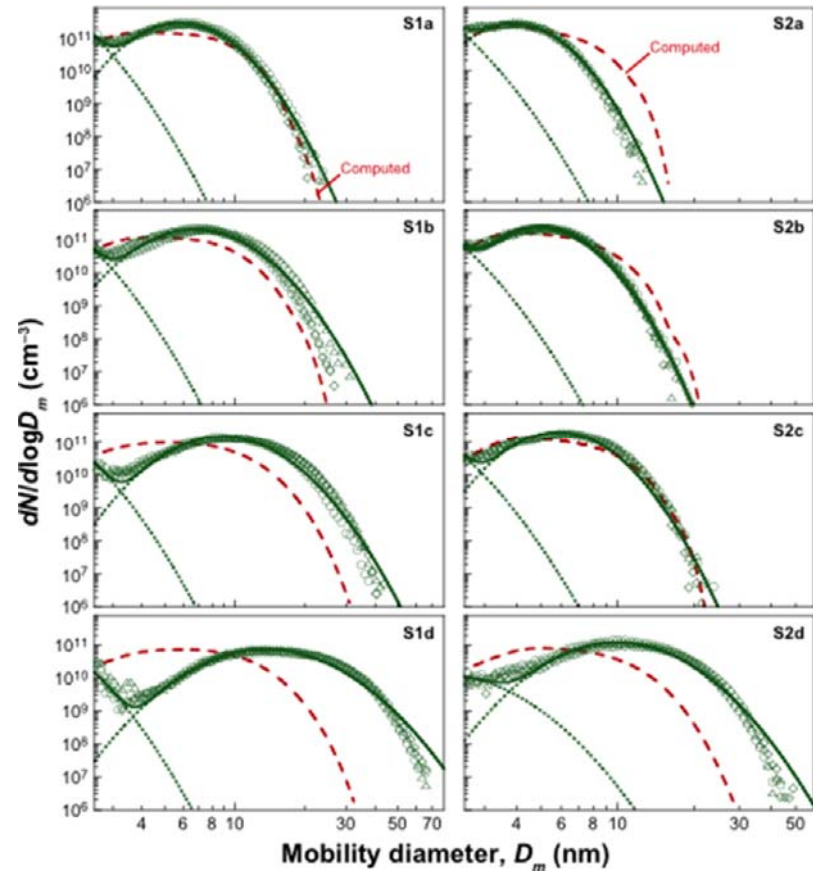
*Michelsen, PROCI 2017*

## 5.3 Premixed stretch-stabilized flat flames (Stanford)



- Aerodynamically shaped nozzle (-> plug flow at burner exit)
- Distance nozzle/stagnation surf constant
- Flame distance is changing by varying the flow rate
- nearly adiabatic

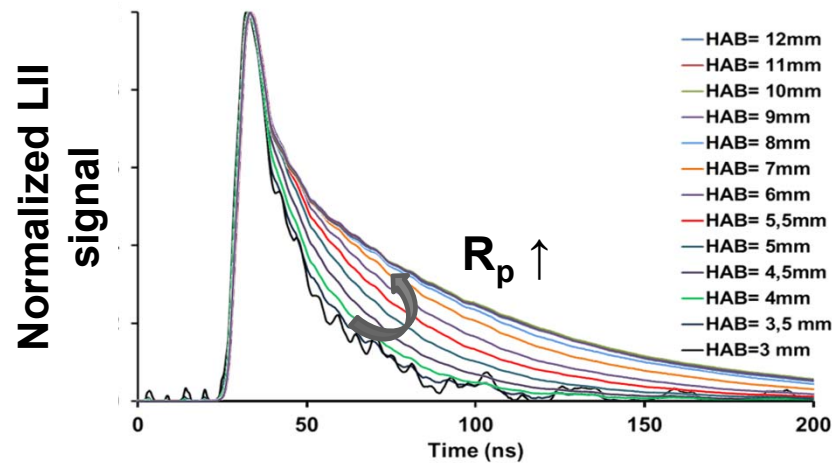
**New burner vs BSSF (burner stabilized stagnation flame)**



*Camacho, Wang et al., PROCI 2017*

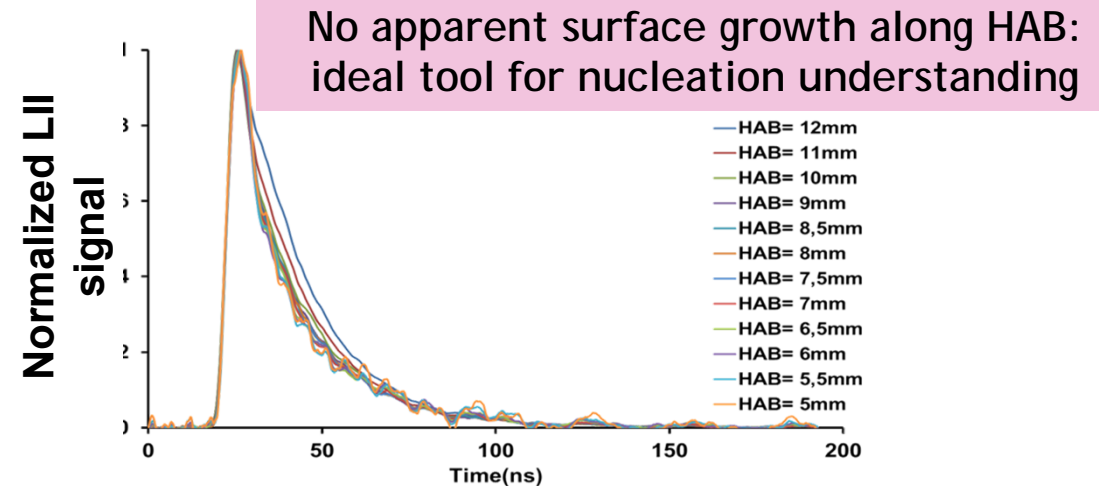
## 5.4 Nucleation flames (Lille)

Standard sooting flame  
n-butane atmospheric pressure  $\Phi = 1,95$



*Mouton et al., Appl.Phys.B 2012*

Nucleation Flame  
n-butane atmospheric pressure  $\Phi = 1,75$



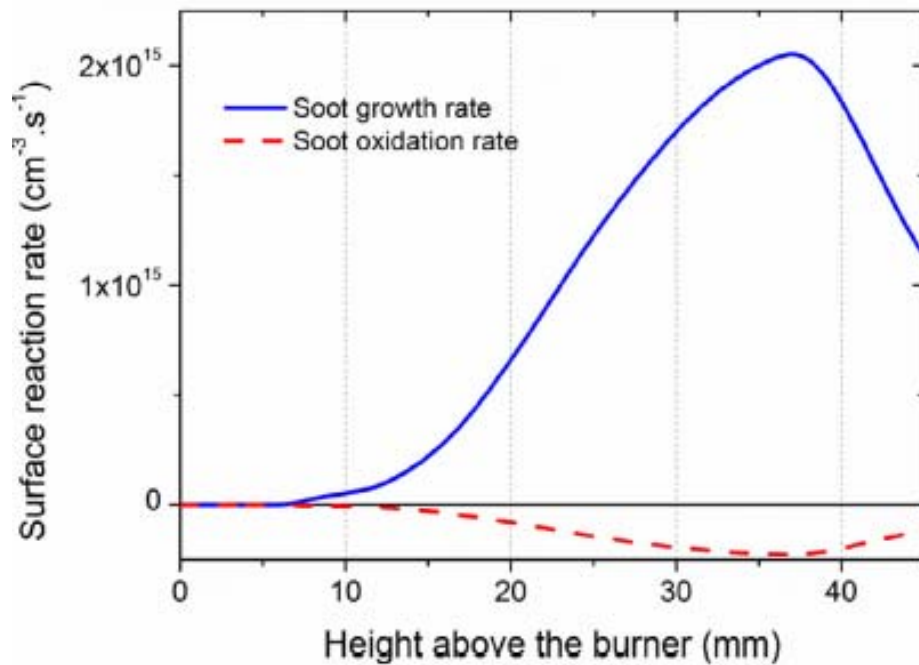
*Bladh et al., PROCI 2017*

*Betrancourt et al., AST 2017*

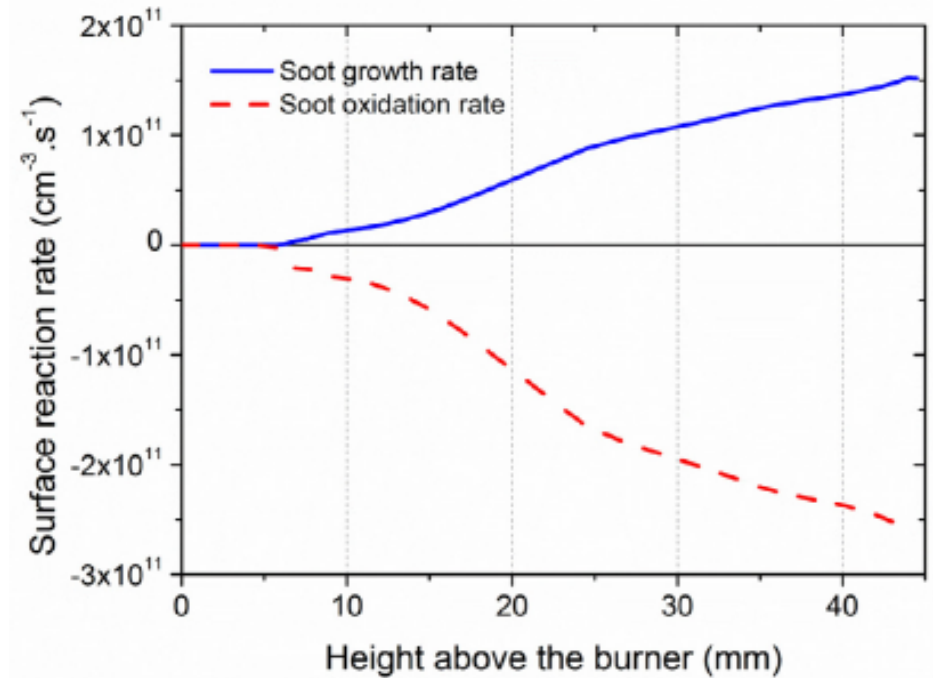


## 5.4 Nucleation flames (part 2)

Standard sooting flame  
Methane low- pressure  $\Phi = 2.32$



Nucleation Flame  
Methane low-pressure  $\Phi = 1,95$



*Desgroux et al., Comb. Flame 184, 2017*

## 6. Soot surface analysis

The chemical composition at soot surface informs on how the soot particle has grown with surface reaction with the gas phase. Soot composition is a « picture » of the gas phase composition at the sampling location.

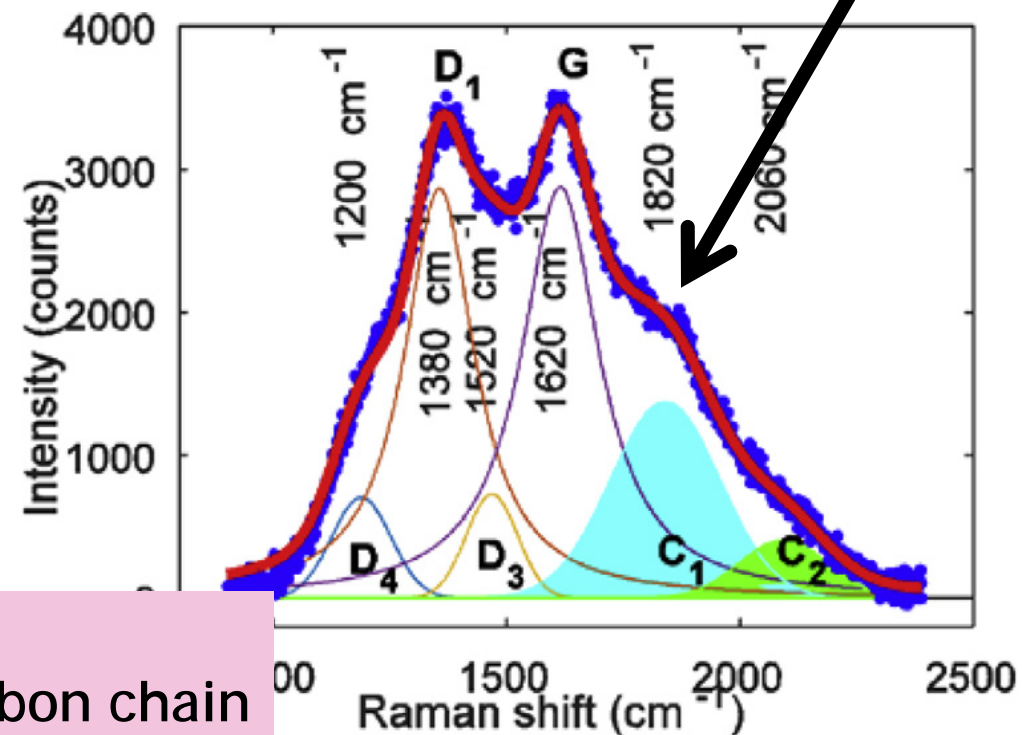
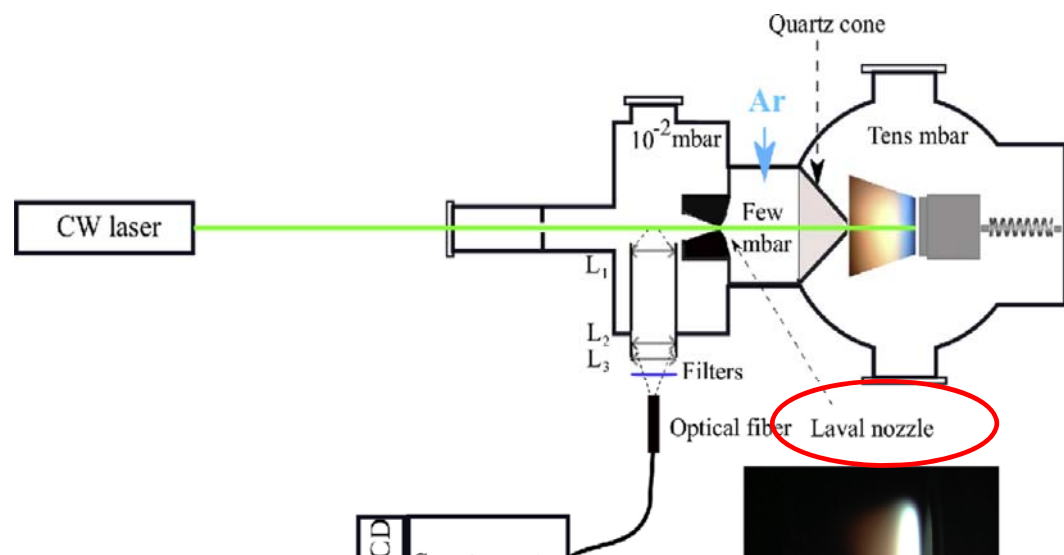
6.1 on line Raman

6.2 Aerosol mass spectrometer

6.3 ToF-SIMS

6.4 AFM

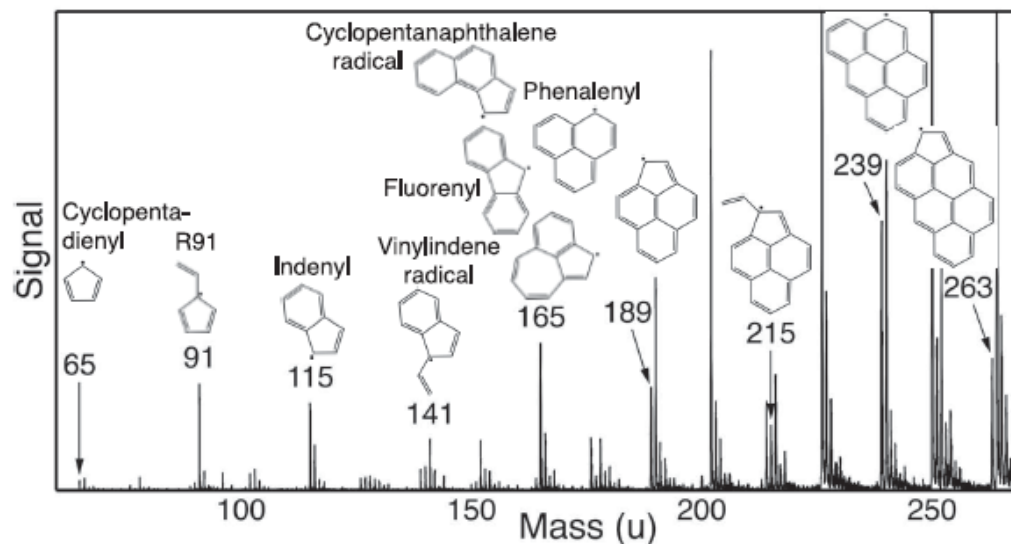
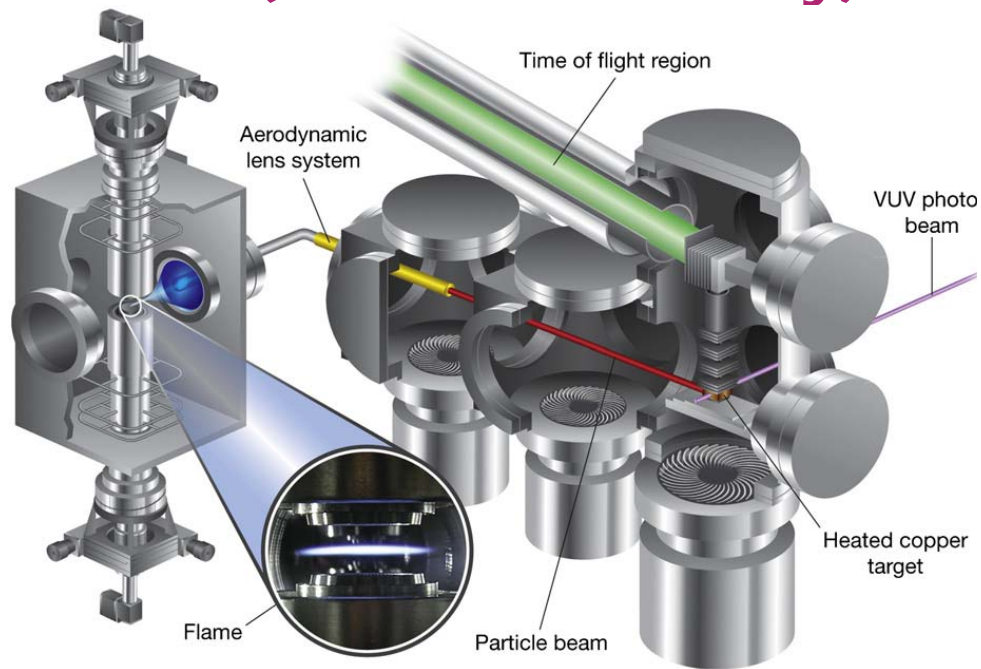
## 6.1 Evidence of aliphatic structures in soot using ONLINE Raman (Paris-Saclay/Lund)



- D3 assigned to sp<sup>2</sup> C
- C1 and C2 peaks is a fingerprint of sp carbon chain
- Promising technique to be further investigated

*Le, Pino, Bengtsson, Lefumeux, PROCI 37, 2019*

## 6.2 Evidence of resonance stabilized hydrocarbon radicals (Sandia/Berkeley) using ON LINE AMS

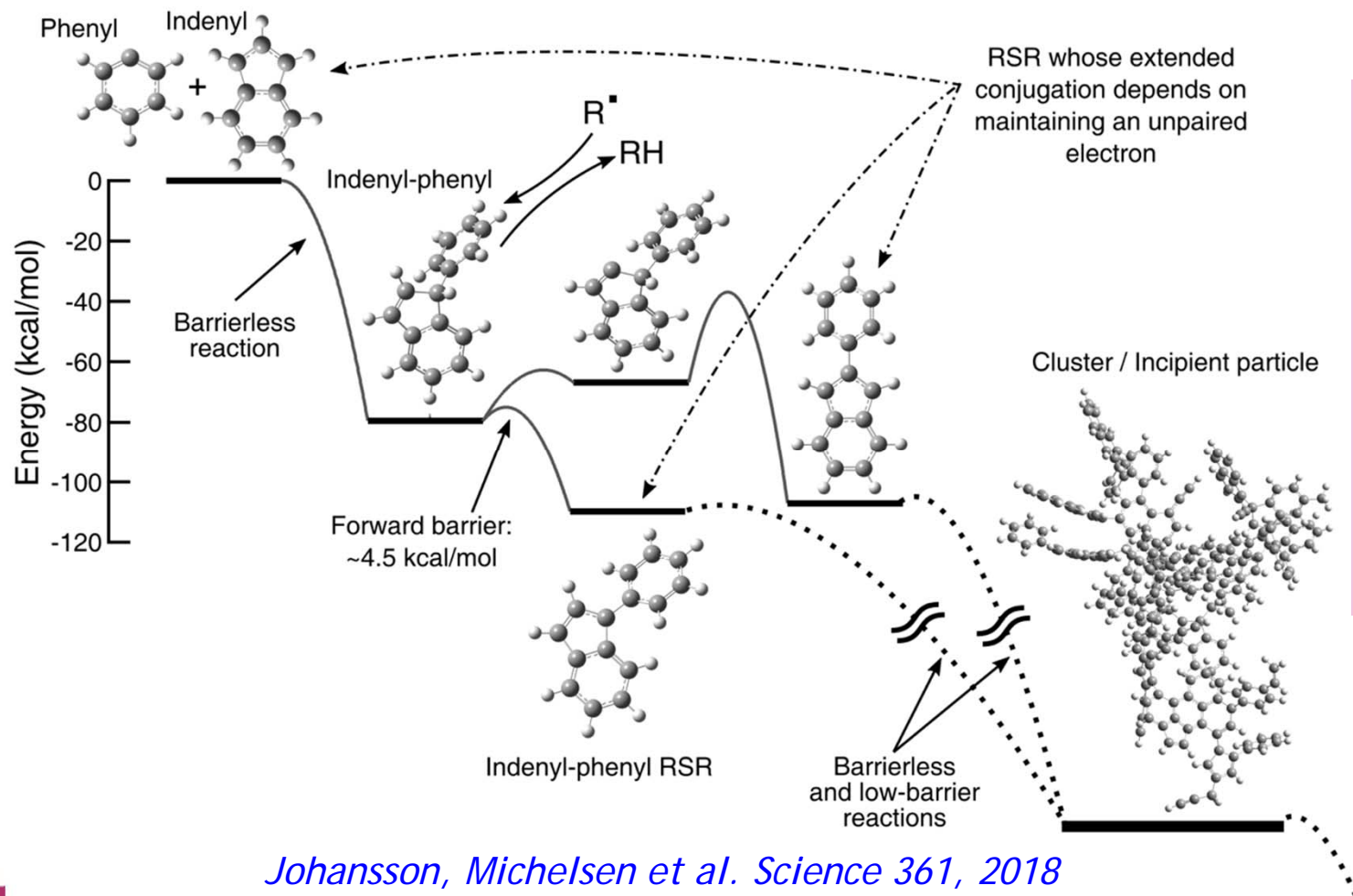


VUV-Aerosol Mass Spectrometer  
Mass resolution = 1500

*Skeen et al., J. Aerosol Sci. 58, 2013*

*Johansson, Michelsen et al. Science 361, 2018*

## 6.2b Evidence of resonance stabilized hydrocarbon radicals



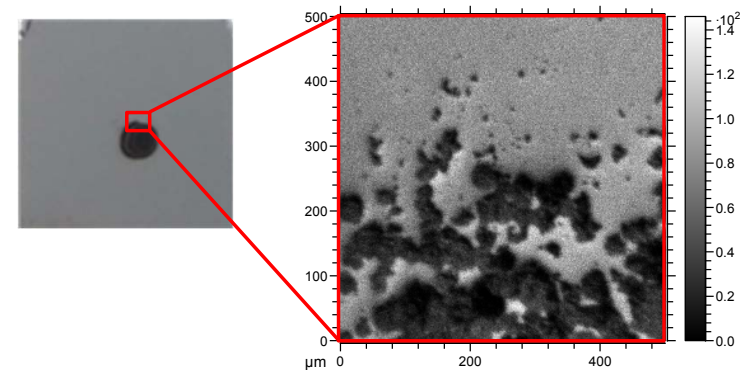
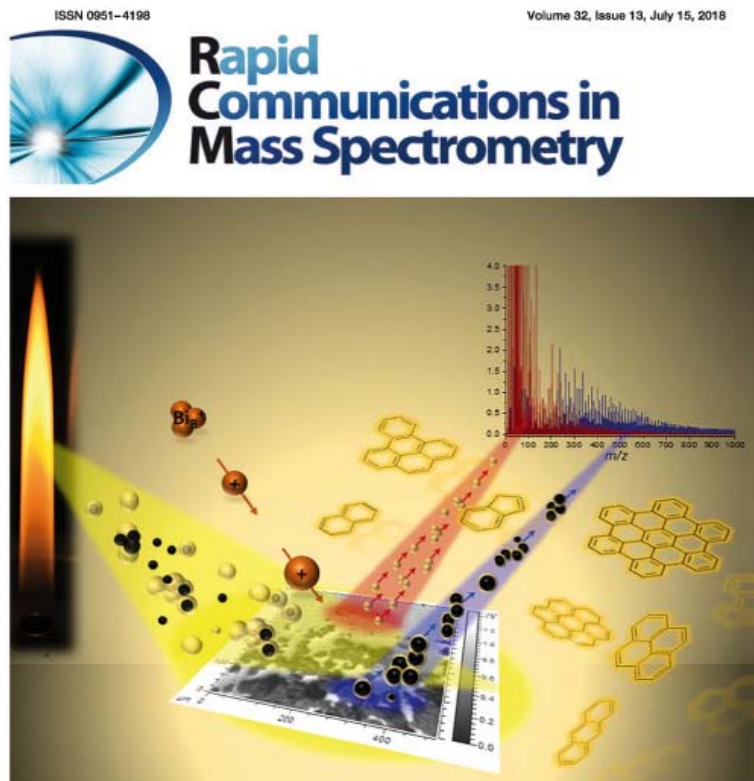
- Evidence of radical driven hydrocarbon clustering mechanism by involving chain reactions of resonance-stabilized radicals (RSR).

- RSR species can form covalent bonds with a variety of HC producing cluster products.

Key mechanistic steps for rapid particle formation

*Johansson, Michelsen et al. Science 361, 2018*

## 6.3 Evidence of structures involved in soot nucleation using Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS)



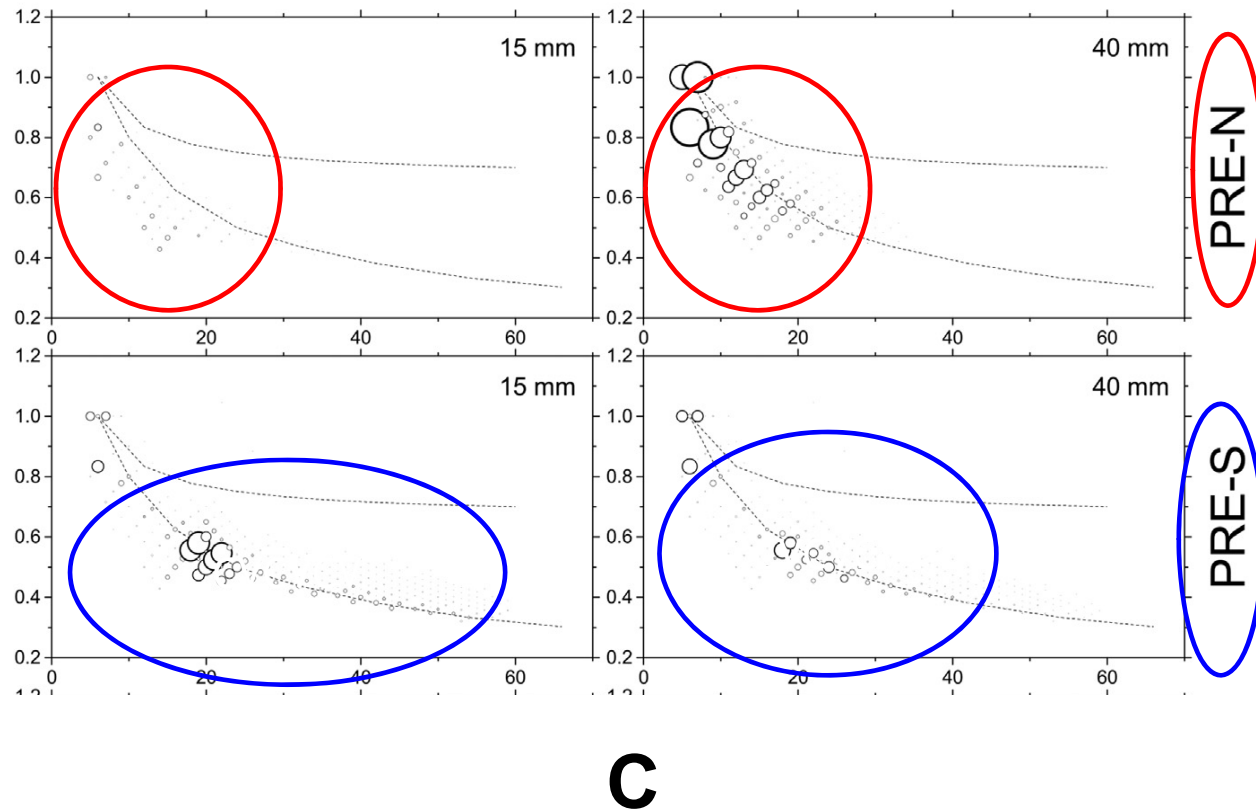
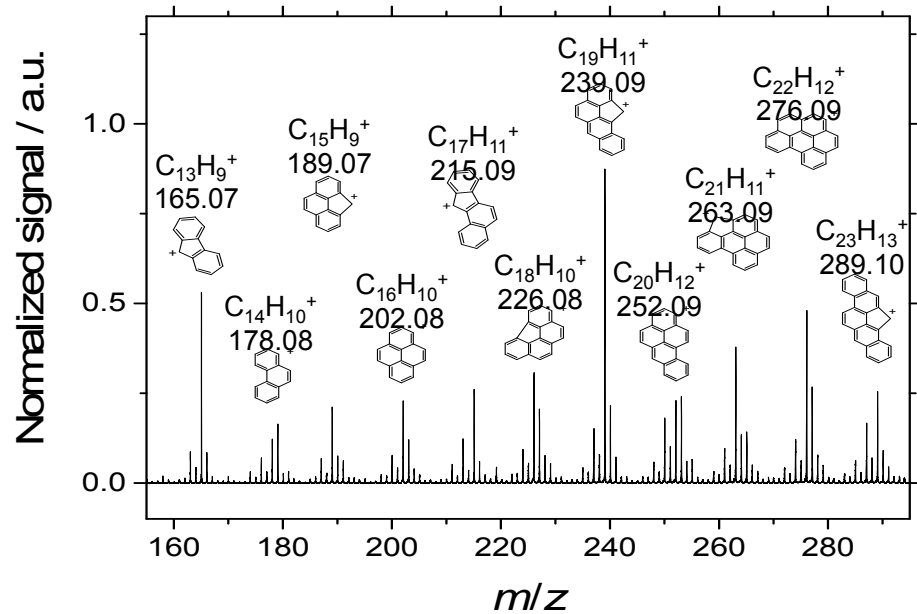
Mathematical analysis of a large number of samples from a large variety of soot particles

- Mass defect analysis
- Principal Component Analysis (PCA)
- Hierarchical Clustering Analysis (HCA)

*Irimiea, Faccinnetto et al. RCM 2018*

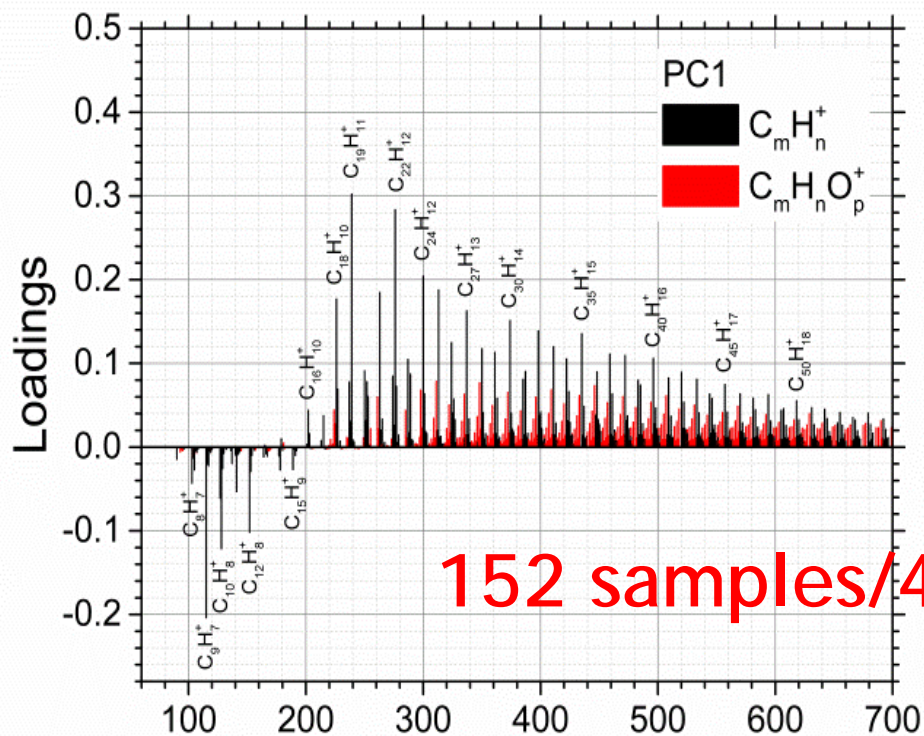
# 6.3b Mass defect analysis $H/C$

Mass resolution = 7000

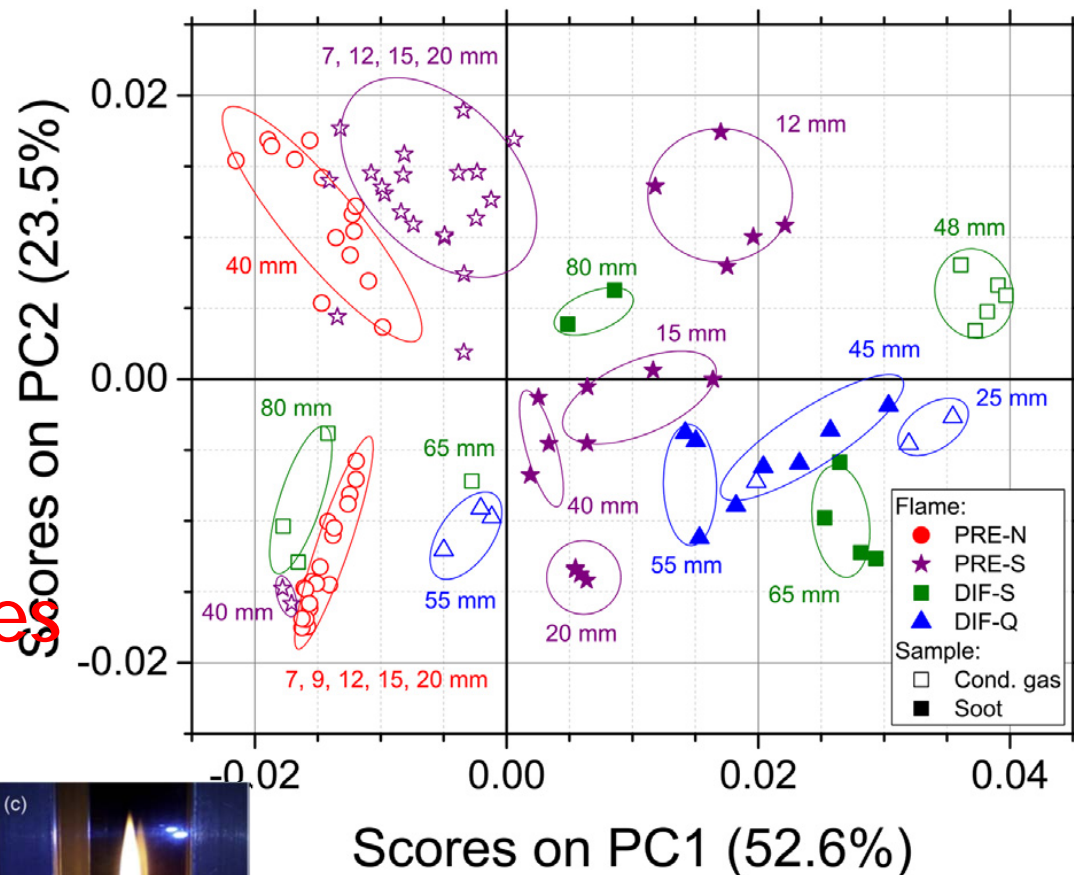


Irimiea, Faccinnetto et al. RCM 2018

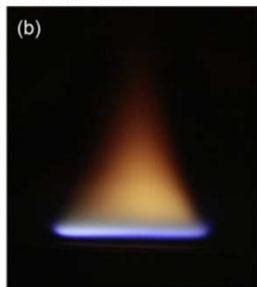
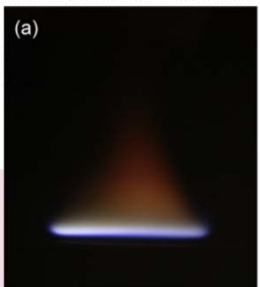
## 6.3c Principal Component Analysis (PCA) and Hierarchical Clustering Analysis (HCA)



152 samples/4 flames



$m/z$



Irimiea, Faccinnetto et al.

RCM 2018

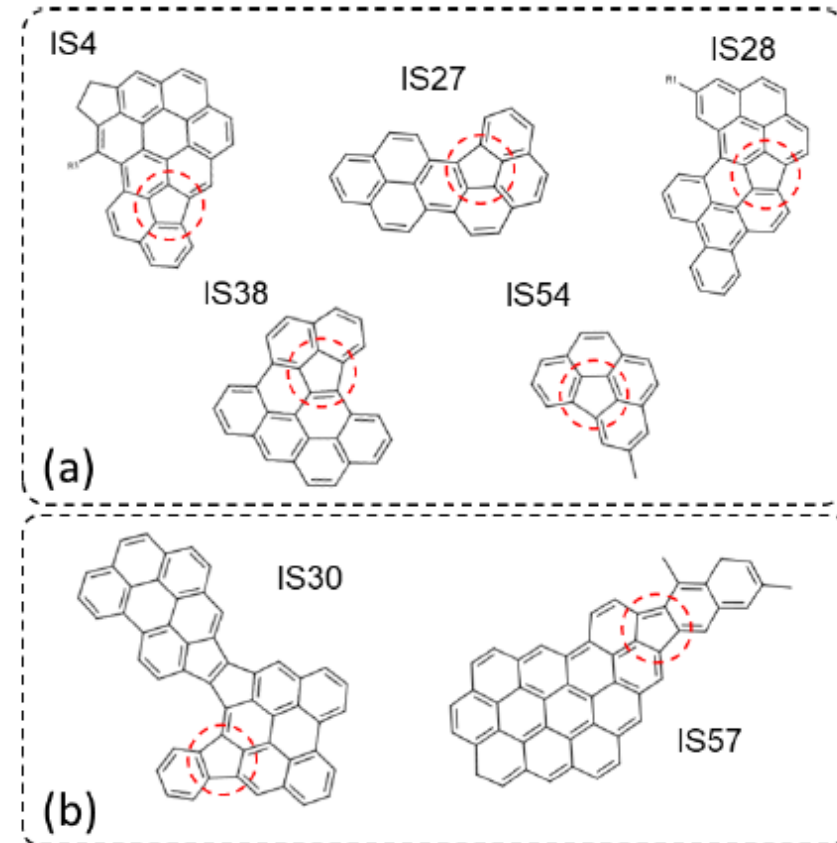
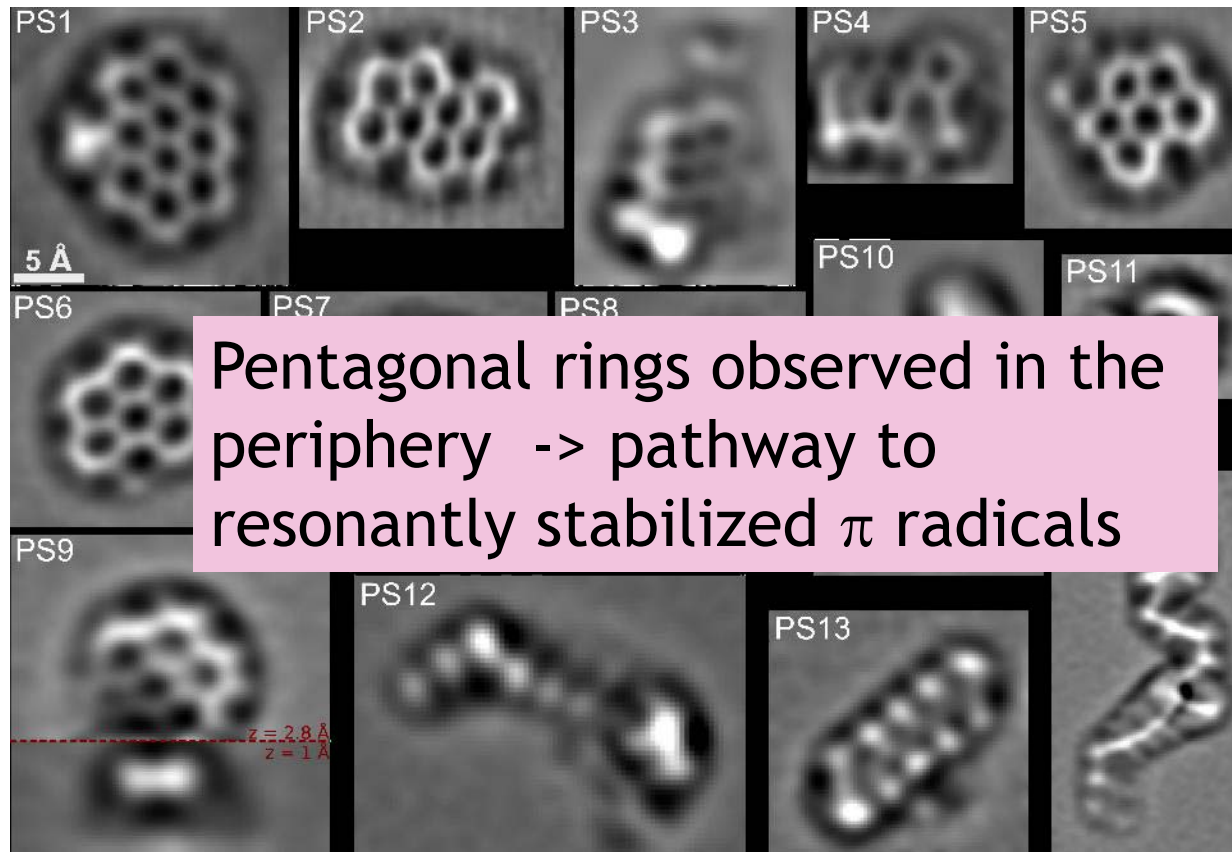
Université de Lille

a, 2019 April 14-17th



# 6.4 Evidence of aliphatic pentagonal rings by Atomic Force Microscopy (AFM)

Schulz, Commodo et al, PROCI38 (2018), Naples + IBM Zurich



Courtesy of M. Commodo, K. Kaiser, G. De Falco, P. Minutolo, F. Schulz, A. D'Anna, L. Gross

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# 7. From experimental advances to a better understanding of soot nucleation. Impact on soot modelling

7.1 Range of species

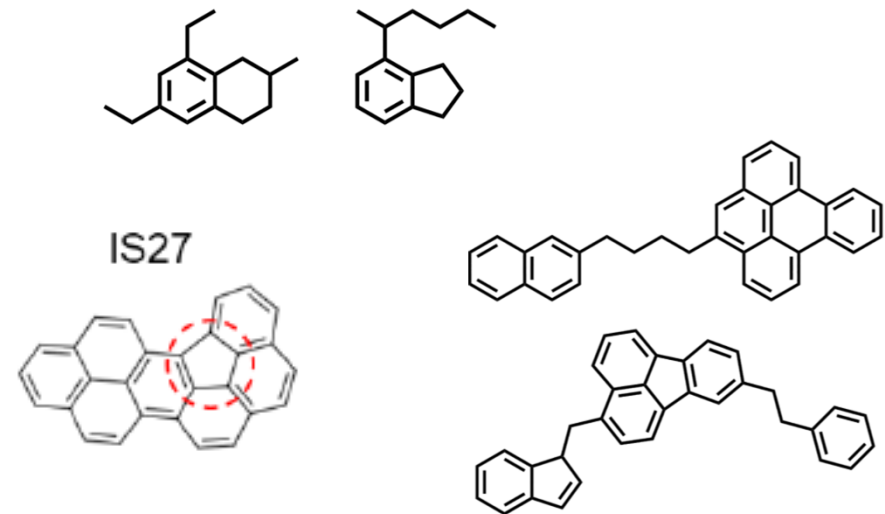
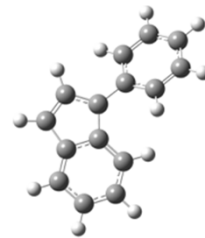
7.2 Range of mass

7.3 Contribution of dimers

7.4 Consequences on soot modelling

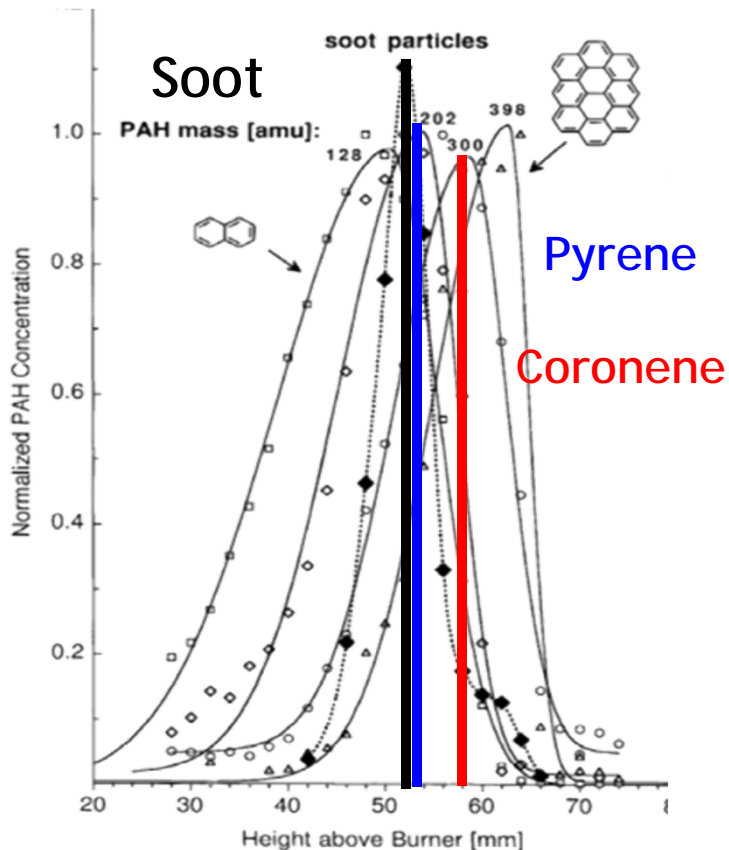
## 7.1 Contribution from recent experiments: Range of species involved in soot nucleation

- Pentacycles
- Aliphatically bridged multi-core PAHs
- Aliphatic substituted PAHs
- resonance-stabilized radicals (RSR)
- Oxygenated PAHs
- etc
  
- DIMERS



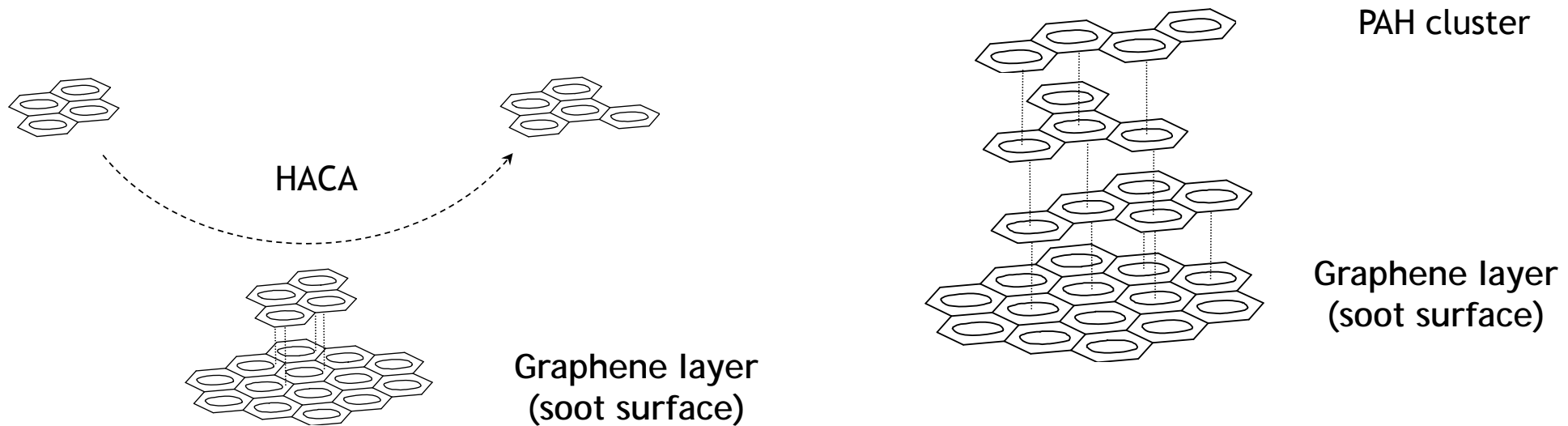
Need to be introduced in the detailed chemical mechanisms

## 7.2 Contribution from recent experiments: Mass range involved in soot nucleation



- *Johansson et al. Science (2018)* explain the rapid growth in PAH mass by Clustering of HC by radical- chain reactions of resonance-stabilized radicals (RSR).
- However the only contribution of small size PAHs was evocated by a few groups on the basis of experimental observations:
  - *Sirignano et al. CnF (2017)* (LIF decay times) « The consistently observed UV-centered LIF spectrum in the measurements suggests that a significant increase in the size of the aromatic island is unlikely, and the mean size of the aromatic island itself is not larger than pyrene”
  - On the basis of PAH profiles obtained by GC, *Mitra et al. CnF (2019)*: PAH larger than A4 are not participating in the formation of young soot
  - On the basis of PC1 (ToFSIMS), *Irimiea et al. Carbon (2018)*: Only small species are contributing to nucleation
  - On the basis of HRTEM (fringe lengths), *Apicella et al., PROCI (2015)*, *Teini et al. CnF (2011)* suggest the limited role for large PAH in soot nucleation

# Role of heterogeneous reactions

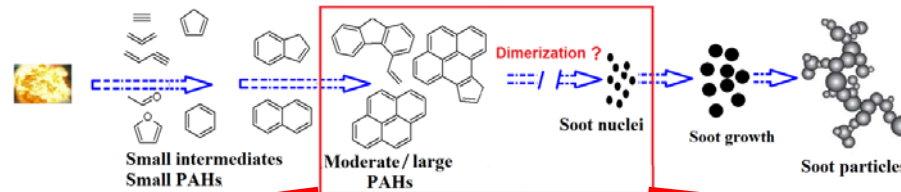


Early soot particles could play an active role in the growth of PAHs, “catalysing” the growth of the graphene-like layer via larger and larger PAHS, or supporting the formation of 3D structures

## 7.3 Contribution of dimers

- Mercier et al. PCCP (2019): reconstruction of LIF spectra in the visible using dimers of small size. Benzopyrene or perylene are good monomer candidates but not exclusively (heterodimers?, stacked PAH clusters or dimers of aliphatically bridged PAHs?)
- It is known that dimers are not thermodynamically stable at flame temperature
- Nucleation may not be controlled by equilibrium but rather the overall kinetics (forward and reverse rate *of dimerization*), for which accounting for **reversibility** is highly important. *Eaves et al., Proc Comb Inst 2017*

# 7.4 Recent advances in soot nucleation modeling



## Soot nucleation process

Irreversible “physical” dimerization of PAHs

Reversible “physical” dimerization of PAHs (RPC) + array of PAHs

Reversible “physical” dimerization followed by irreversible PAH chemical bond to stabilize the dimers

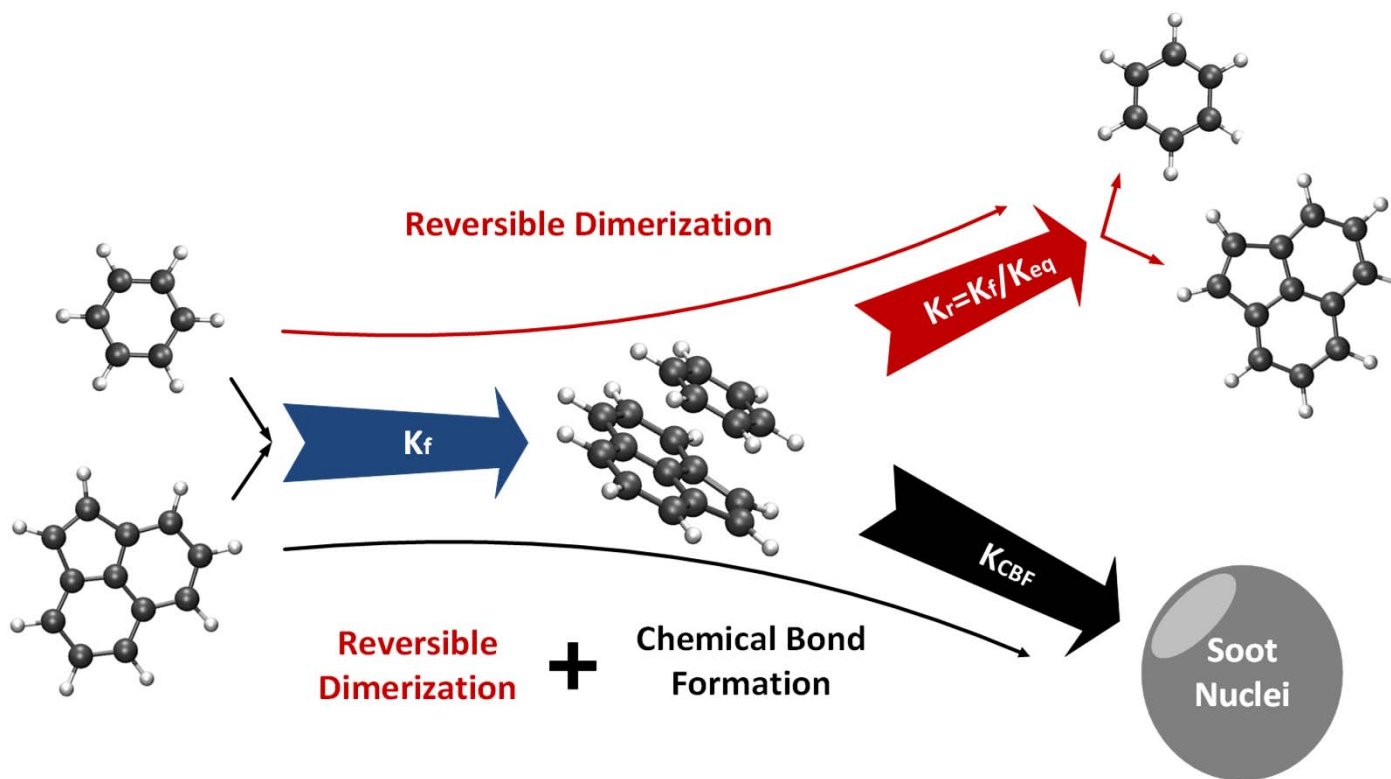
Examples of Refs:  
**Frenklach & Wang**  
 Symp. Int. Combust. 1991

**Miller (1990)**  
**Eaves et al.**  
 PROCI 2015

**Kholghy et al.**  
 PCCP 2018

**D’Anna et al.** [CnF 2001] introduced C-C covalent bonds of PAHs for soot nucleation

# Role of physical and chemical dimerization of PAH



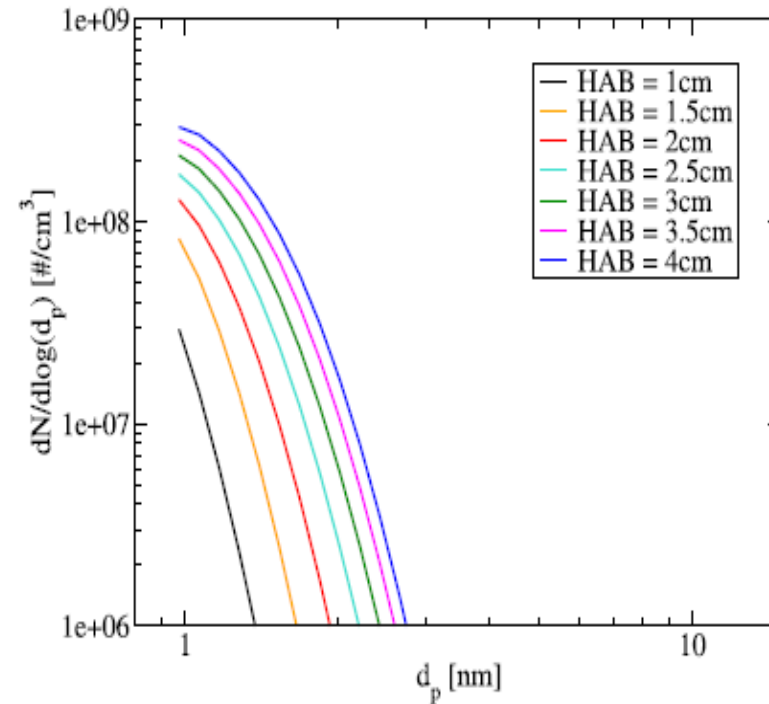
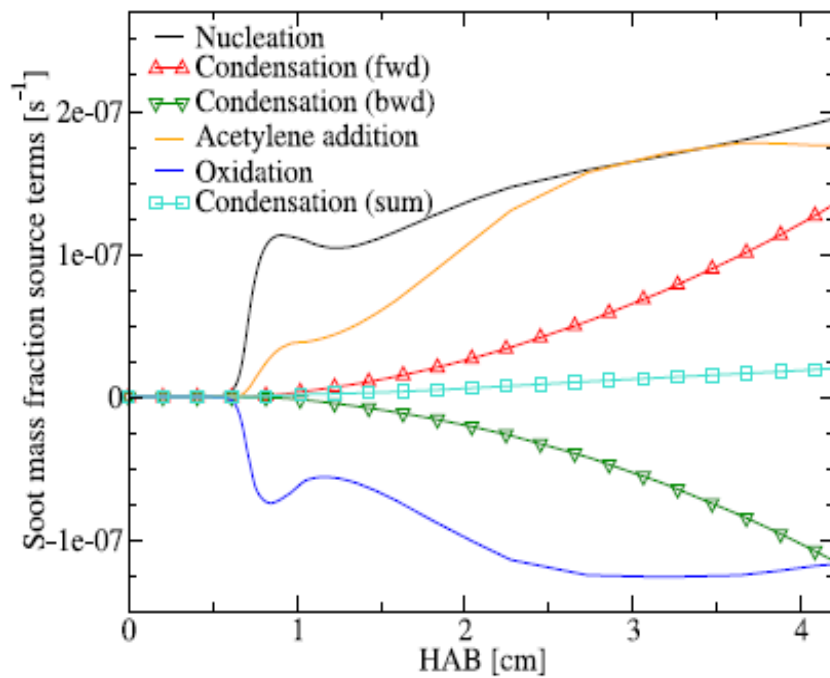
*Courtesy of Khoghly et al.*

*Khoghly , Kelesidis, Pratsinis, PCCP (2018)*



# Nucleation flames: a promising tool for nucleation modelling

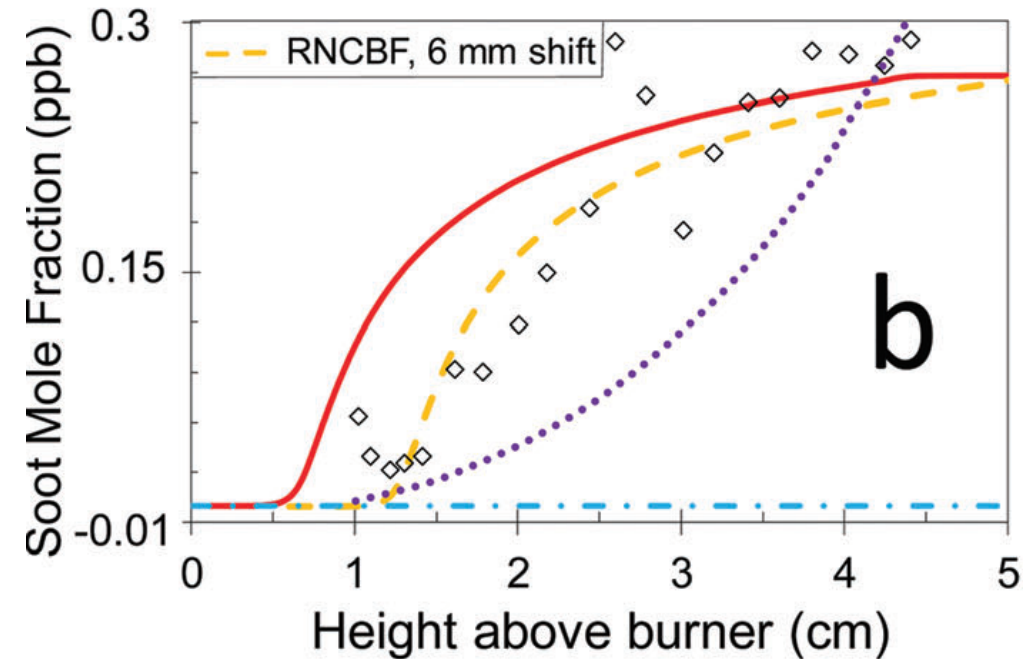
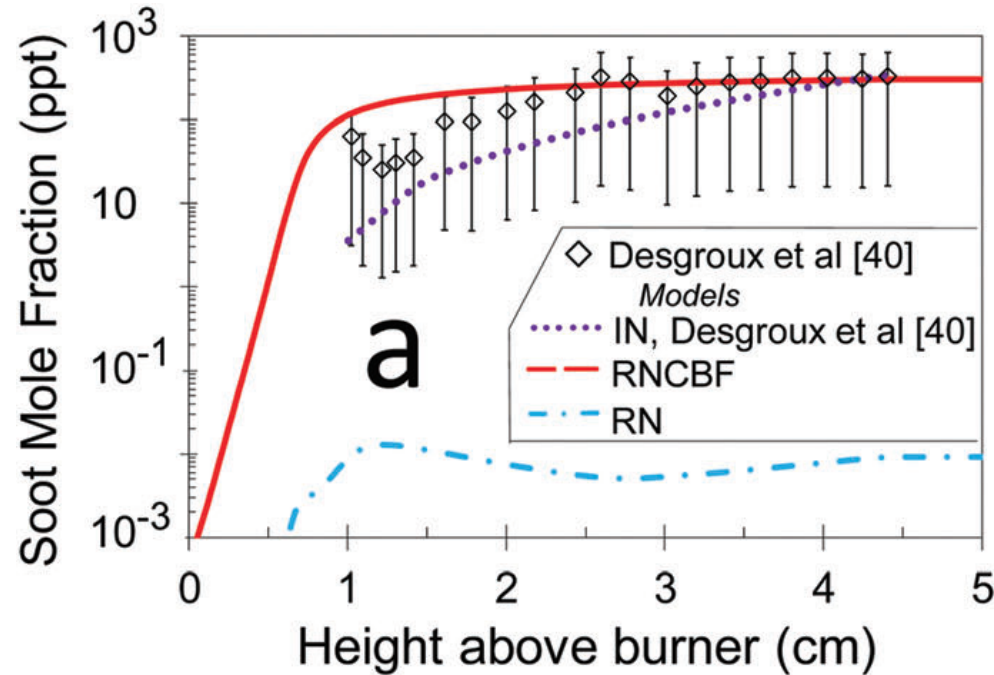
Dampening factor for dimerization and reversibility of PAH condensation



*Aubagnac-Karkar et al. CnF 2018*

# Nucleation flames: a promising tool for nucleation modelling

Khoghly et al., ETH Zurich PCCP (2018)



RN: fully reversible nucleation model  $\text{PAH}_i + \text{PAH}_j = \text{Dimer}_{ij}^*$ ; VdW forces

IN: irreversible nucleation model

RNCBF: rev.nucleation+ PAH chemical bond formation model

Saggese et al., CnF(2015)

