

# Soot Inception and Growth

What do we know, and where do we go from here?



# Stages of Particle Evolution During Combustion

*Rxns of small radicals and hydrocarbons*

*Molecular growth; Soot-precursor formation*

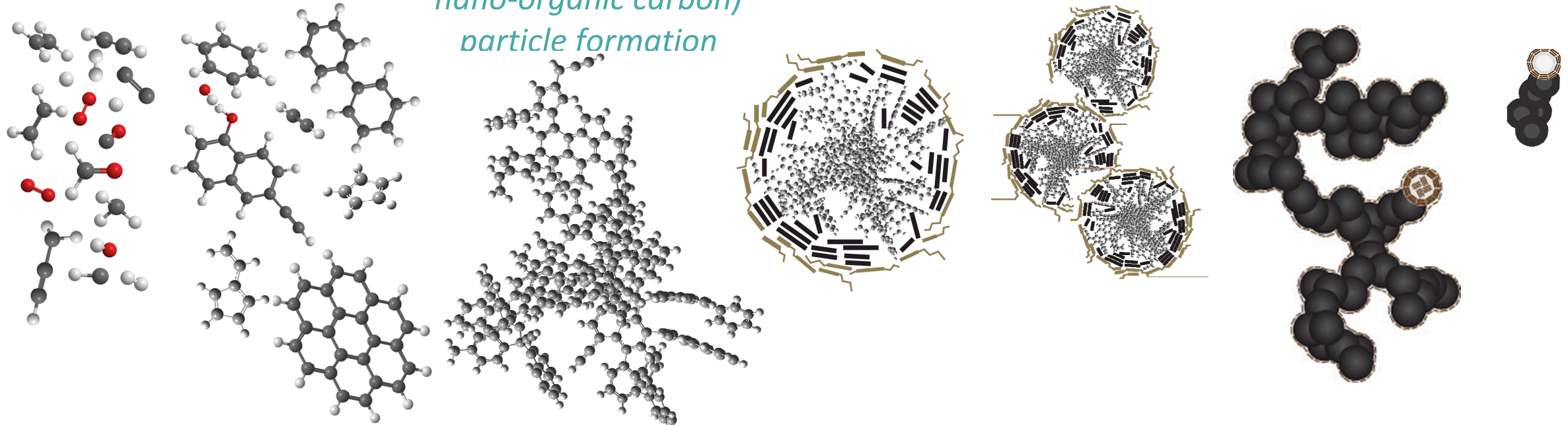
*Soot inception; Incipient soot (nascent soot, nano-organic carbon) particle formation*

*Coalescence, surface growth, graphitization*

*Agglomeration*

*Surface growth, aggregation, graphitization*

*Particle oxidation*



1-2

1.5-2.5

C/H increases

10-20

1.3

Density increases

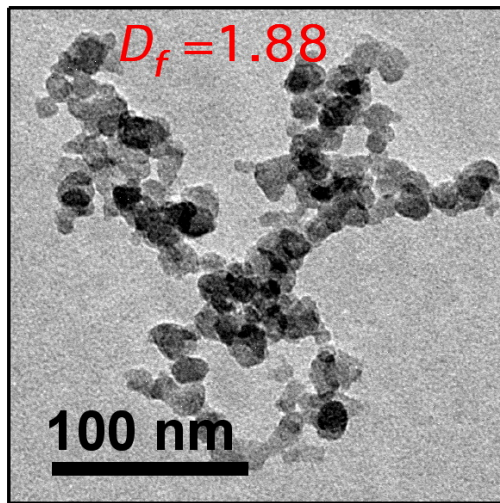
1.8-1.9

Long-range order increases

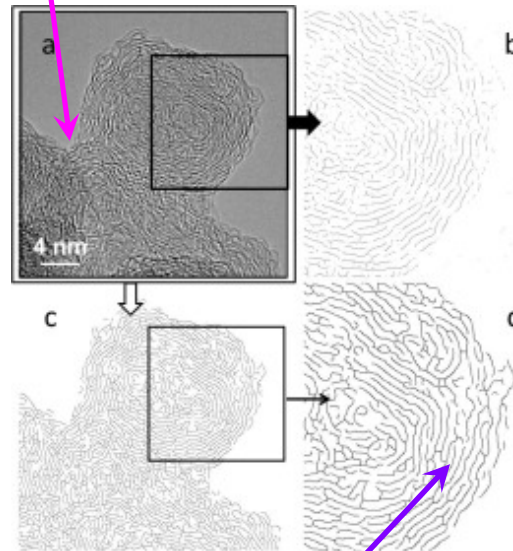
# Characteristics of Mature-Soot Particles

## *The Product*

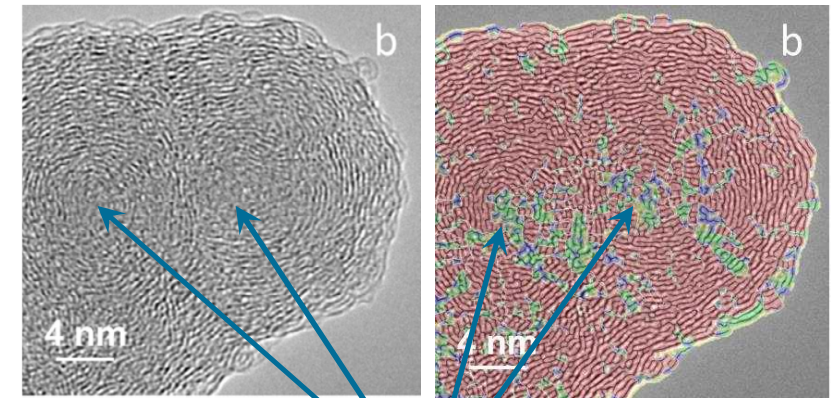
Graphitic overlayers hold aggregate together



Bambha, Dansson, Schrader, Michelsen 2013



Turbostratic graphitic layers or crystallites aligned parallel to the primary-particle surface



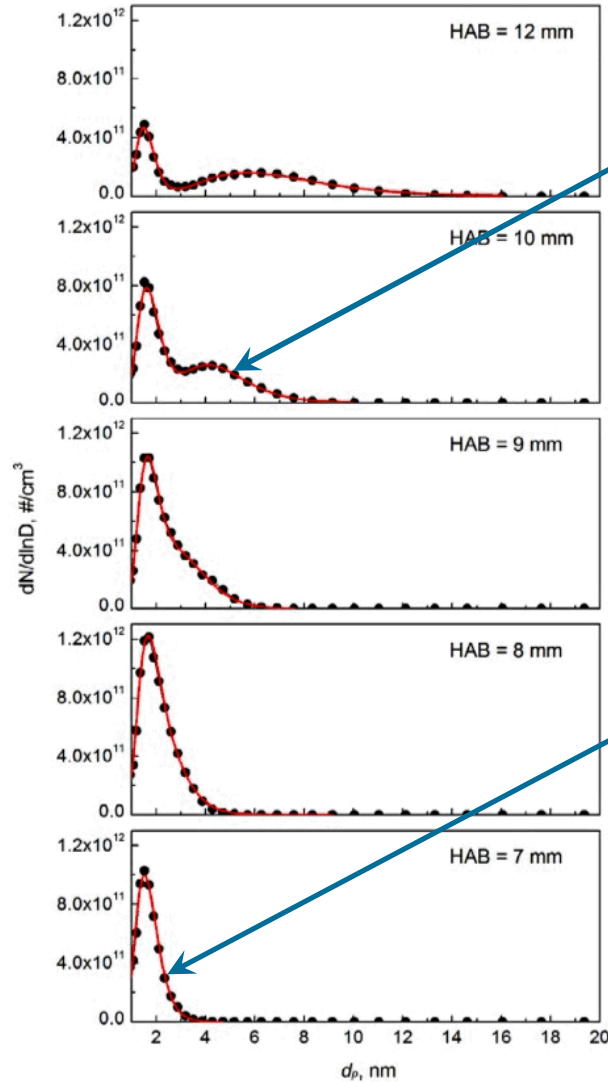
Disordered foci or growth centers, 1-4 nm in diameter

Apicella, Pré, Alfè, Ciajolo, Gargiulo, Russo, Tregrossi, Deldique, Rouzaud 2015

# Characteristics of Incipient Particles

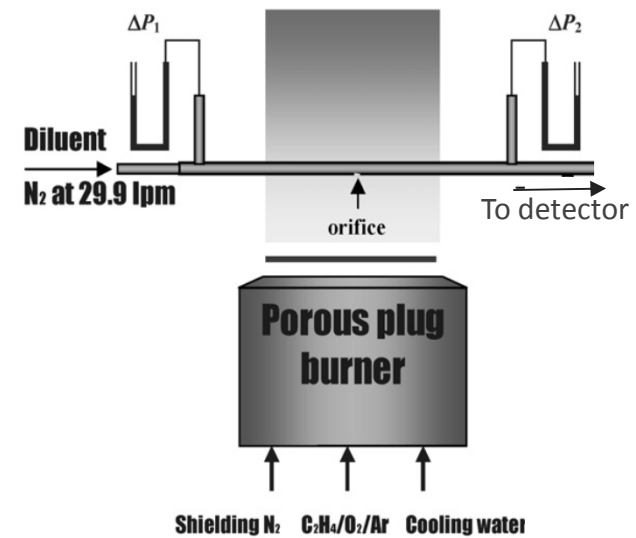
## *Incipient-Particle Size*

Premixed ethylene/air, C/O=0.67,  $\Phi=2.03$



Second mode grows in  
at larger HABs

Incipient-particle size  
< 3 nm

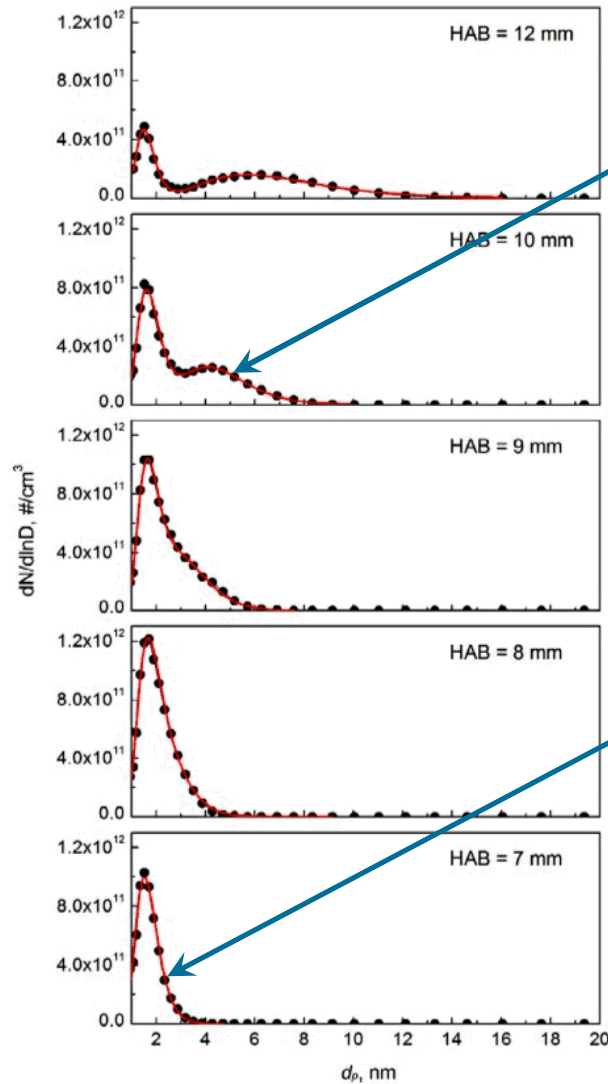


Abid, Heinz, Tolmachoff, Phares, Campbell, Wang 2008

# Characteristics of Incipient Particles

## Incipient-Particle Size

Premixed ethylene/air, C/O=0.67,  $\Phi=2.03$

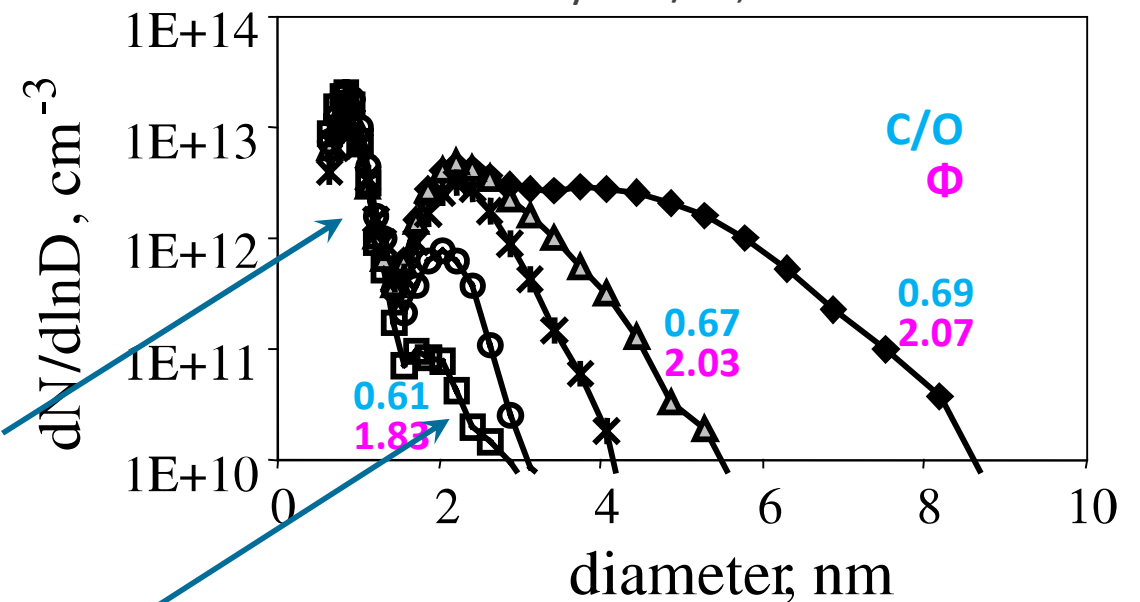


Second mode grows in at larger HABs

Incipient-particle size < 3 nm

Second mode disappears at lower C/O

Premixed ethylene/air, HAB=10 mm



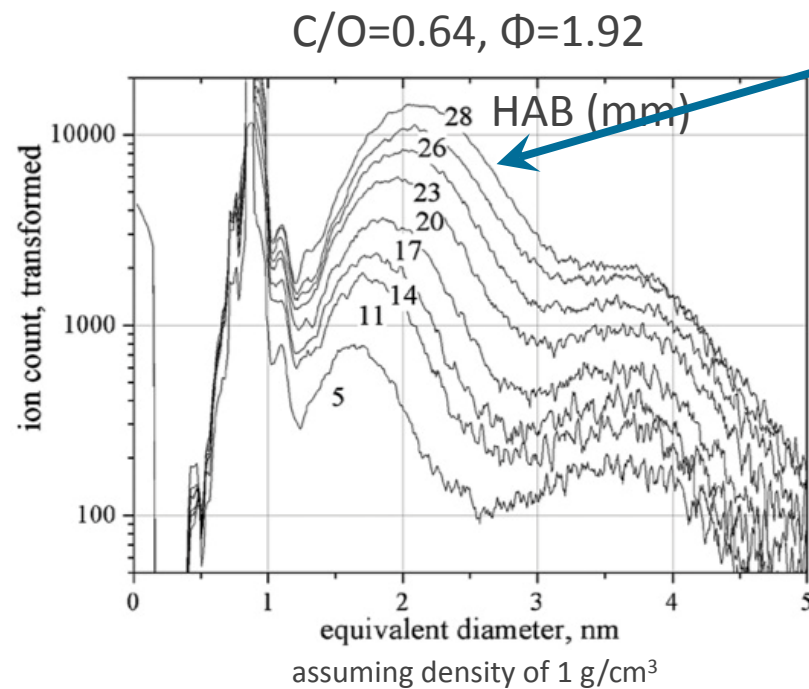
Sgro, De Filippo, Lanzaolo, D'Alessio 2007

# Characteristics of Incipient Particles

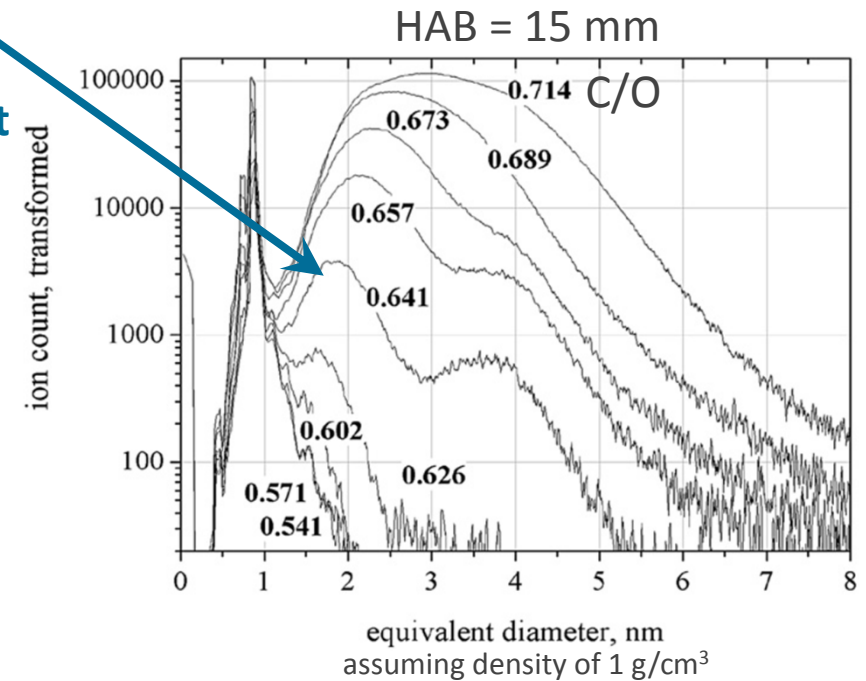
## *Incipient-Particle Size*

Photoionization mass spectrometry

Premixed ethylene/air



Appears to be growth mode required for soot formation



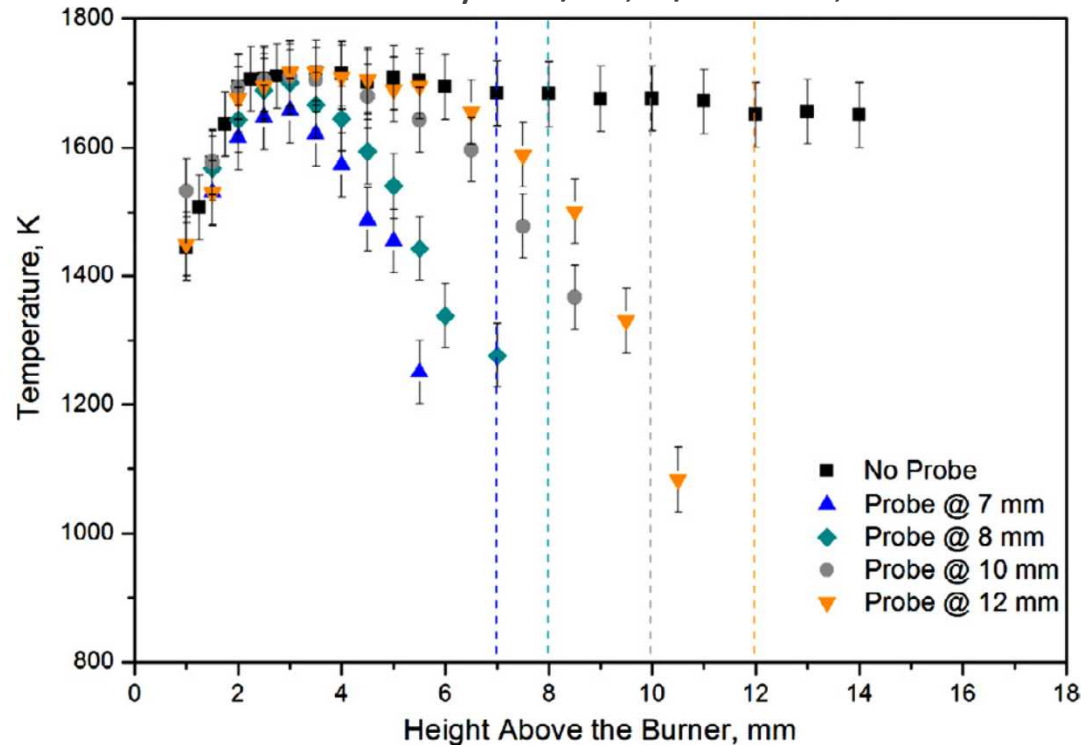
Grotheer, Hoffmann, Wolf, Kanjarkar, Wahl, Aigner 2009

# Characteristics of Incipient Particles

## Extractive Sampling

Rapid-dilution tube sampling probe

Premixed ethylene/air, C/O=0.67,  $\Phi=2.03$



Commodo, De Falco, Bruno, Borriello, D'Anna 2015

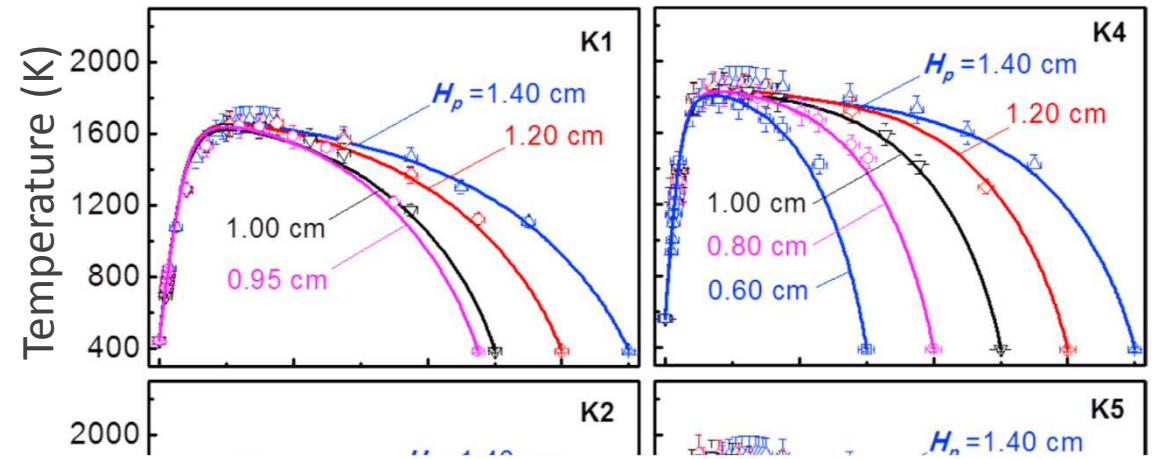
Burner-stabilized stagnation flame

Premixed ethylene/air

C/O=0.60,  $\Phi=1.8$

$V_{gas}=6.0$  cm/s

$V_{gas}=8.5$  cm/s



Gu, Lin, Camacho, Lin, Shao, Li, Gu, Guan, Huang, Wang 2016

# Characteristics of Incipient Particles

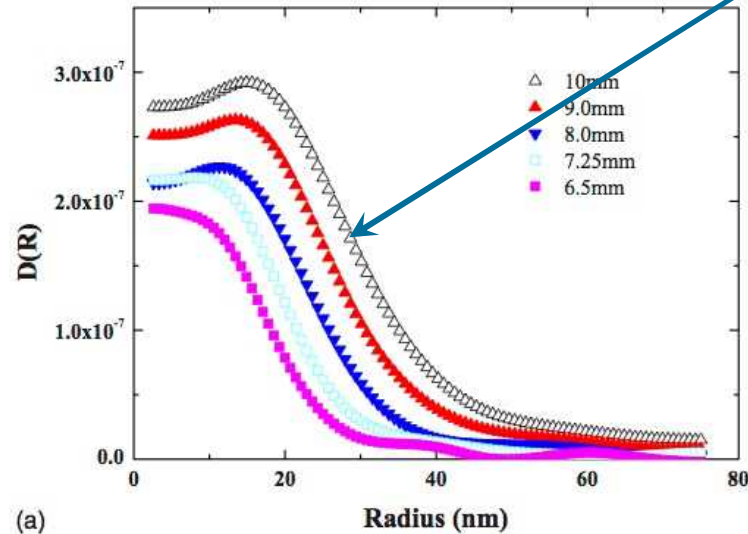
## *Incipient-Particle Size*

Ethylene co-flow diffusion flame

Small-angle X-ray scattering

HAB=10 mm

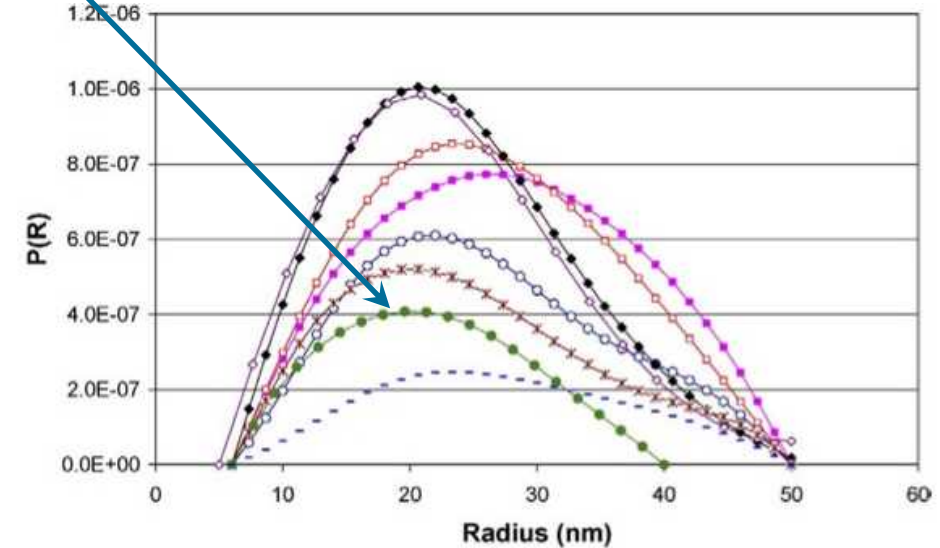
Small-angle neutron scattering



(a)

Radius (nm)

Mitchell, di Stasio, Le Garrec, Florescu-Mitchell,  
Narayanan, Sztucki 2009



Mitchell, Le Garrec, Florescu-Mitchell, di Stasio 2006

- Differences may be due to
  - Neutron beam much larger than SAXS beam
  - Neutron beam sampled larger particles on flame edge
  - Range of scattering angles different for 2 experiments
  - SAXS background subtraction complicated

# What do we know about incipient particles?

They have C/H ratios of  $\sim 1.5-2.5$ .

They are  $< \sim 3-4$  nm in diameter.

They may form at C/O as low as 0.6.

They form at lower HABs and C/O ratios than a second (larger) mode ( $> \sim 4-6$  nm).

They appear to be the source of the larger mode at high C/O.



# Characteristics of Incipient Particles

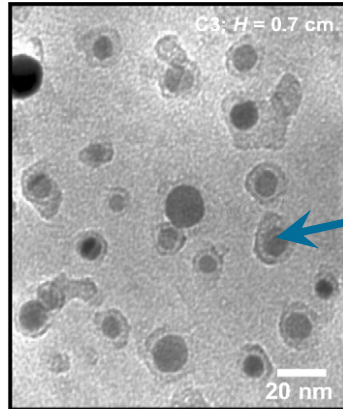
## *Incipient-Particle Consistency and Shape*

Premixed ethylene/O<sub>2</sub>/Ar, C/O=0.69, Φ=2.07

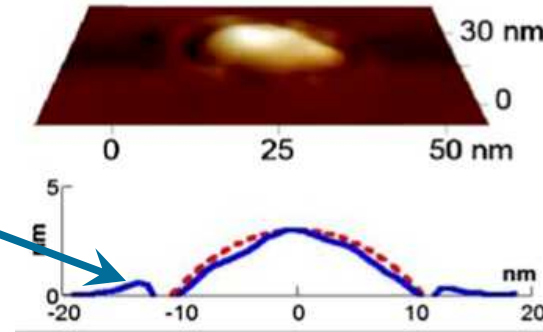
Transmission electron microscopy (TEM)

Atomic force microscopy (AFM)

Helium ion microscopy (HeIM)

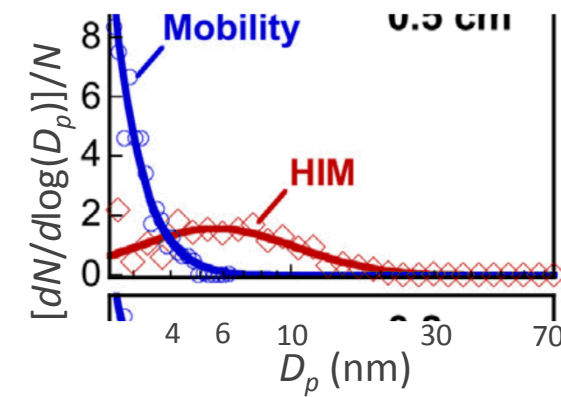
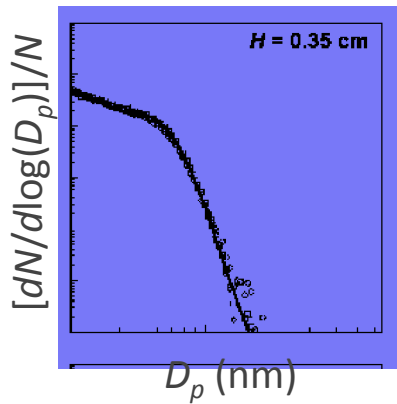
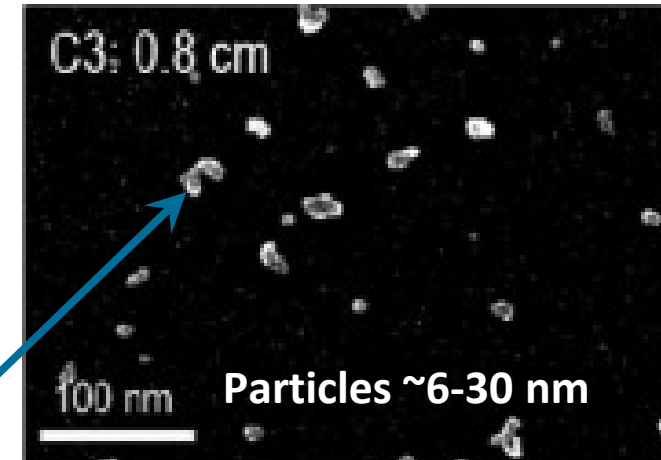


Halo suggests spreading and fluidity



Particles of both modes appear spherical

Some particles in the larger mode may not be spherical



Abid, Heinz, Tolmachoff, Phares, Campbell, Wang 2008

Schenk, Lieb, Vieker, Beyer, Gölzhäuser, Wang, Kohse-Höinghaus 2015

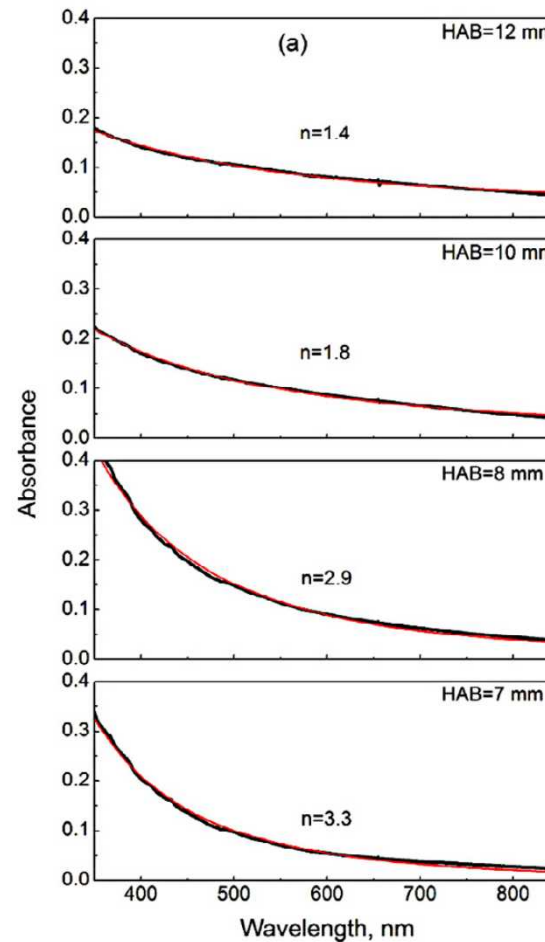
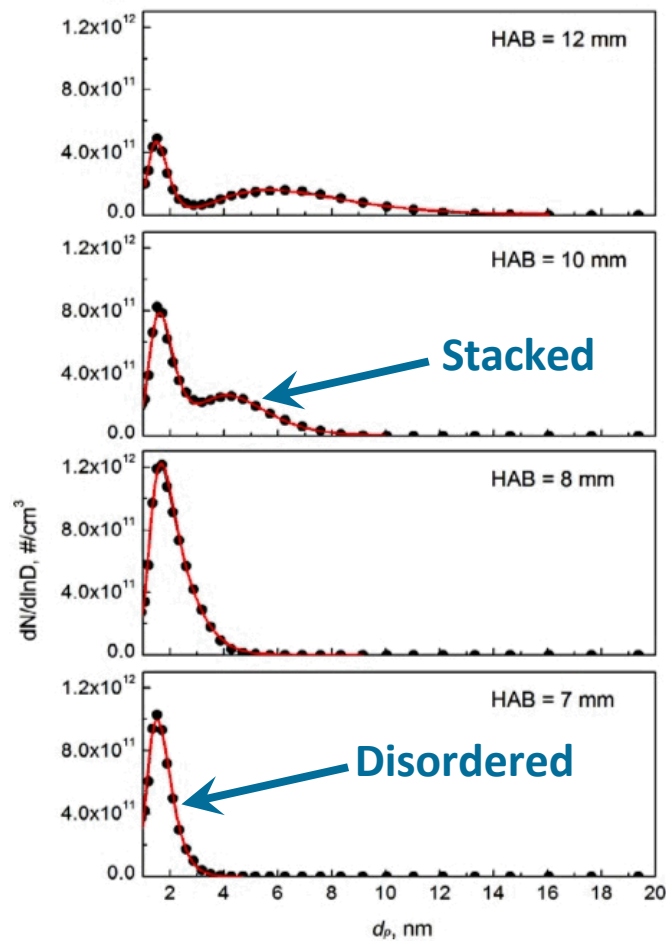
# Characteristics of Incipient Particles

## *Incipient-Particle Optical Properties*

Premixed ethylene/air, C/O=0.67,  $\Phi=2.03$

Ångström exponent

Optical band gap



1.4

0.5 eV

1.8

0.8 eV

2.9

1.4 eV

3.3

1.6 eV

↑  
Increasing maturity – long-range order  
Increasing conjugation length, stacking

Commodo, De Falco, Bruno, Borriello, D'Anna 2015



# Characteristics of Incipient Particles

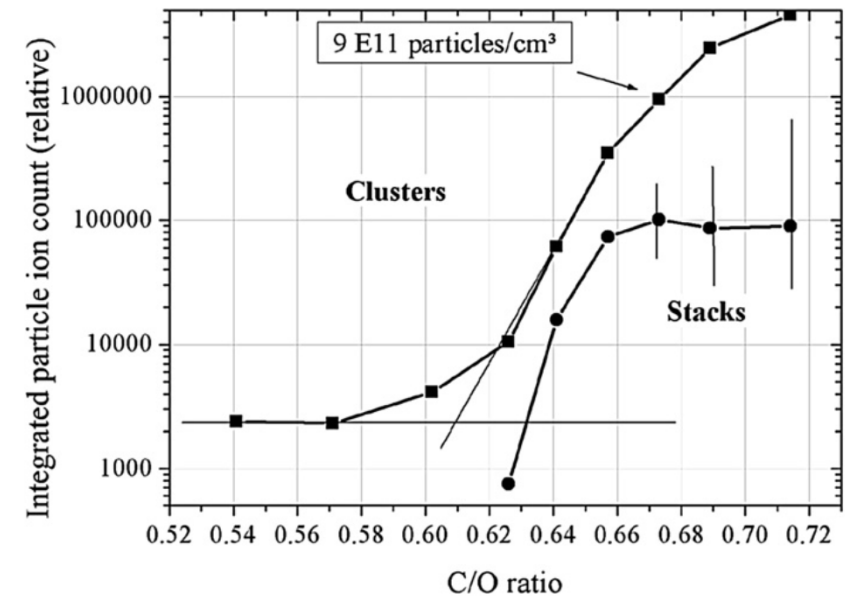
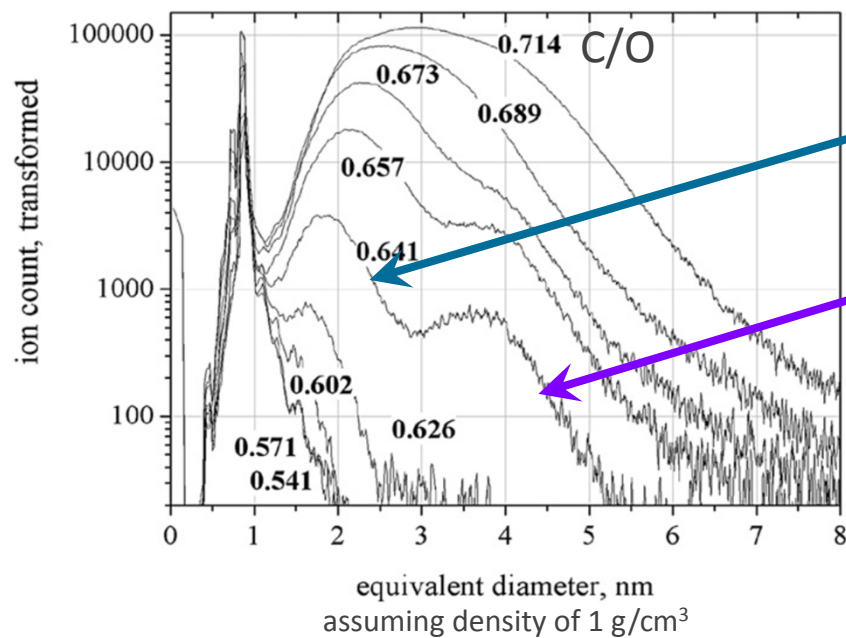
## *Incipient-Particle Optical Properties*

Photoionization mass spectrometry  
 Premixed ethylene/air, HAB=15 mm

**Photoionization  
 at 193 nm, 6.3 eV**

**2 photons  
 Disordered clusters**

**1 photon  
 Stacked large PAHs**



Grotheer, Hoffmann, Wolf, Kanjarkar, Wahl, Aigner 2009

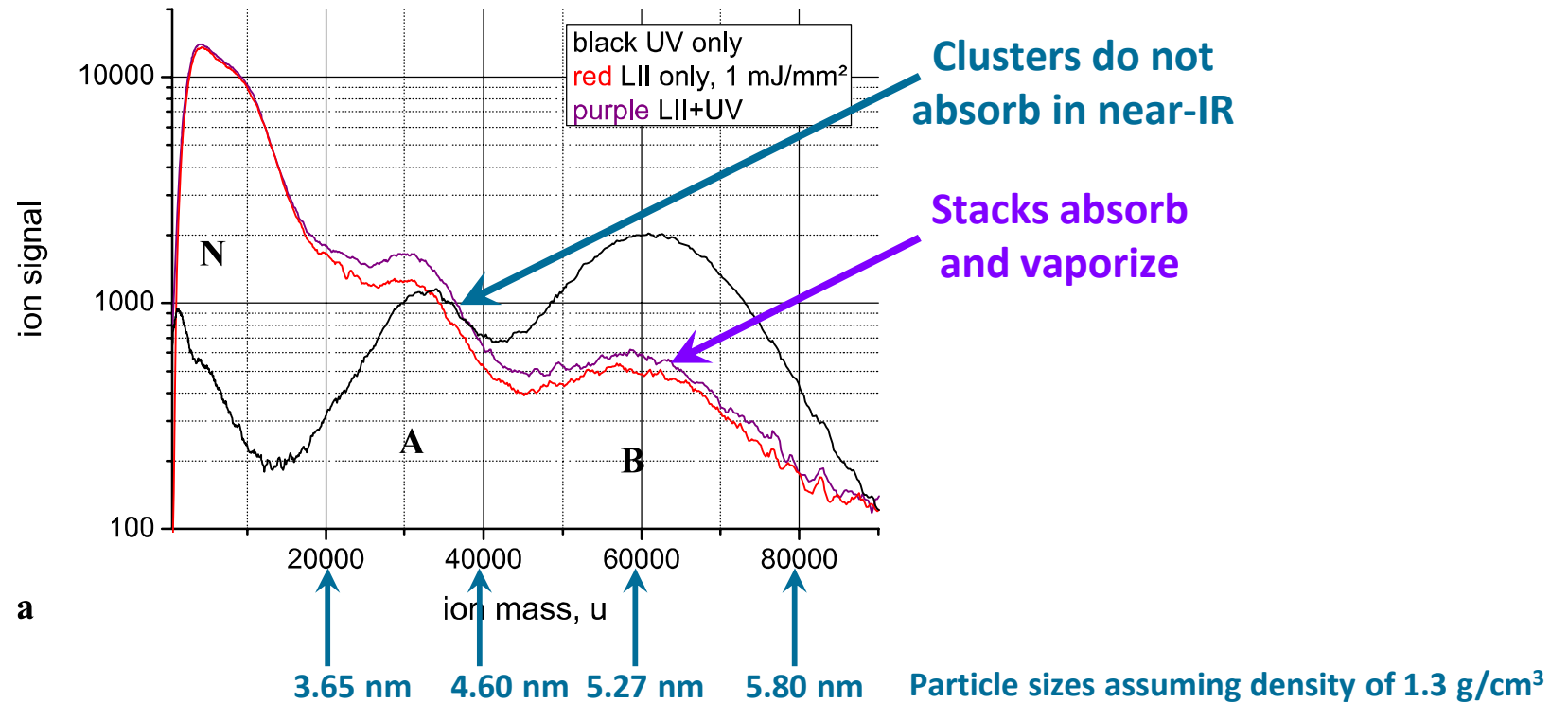


# Characteristics of Incipient Particles

## *Incipient-Particle Optical Properties*

Photoionization mass spectrometry

Irradiation at 1064 nm



Grotheer, Wolf, Hoffmann 2011

# What do we know about incipient particles?

They have C/H ratios of  $\sim 1.5-2.5$ .

They are  $< \sim 3-4$  nm in diameter.

They may form at C/O as low as 0.6.

They form at lower HABs and C/O ratios than a second (larger) mode ( $> \sim 4-6$  nm).

They appear to be the source of the larger mode at high C/O.

They appear spherical and fluid.

They absorb in the UV but weakly at longer wavelengths.

Their photoionization threshold is  $> 6.3$  eV.

They have disordered fine structure.

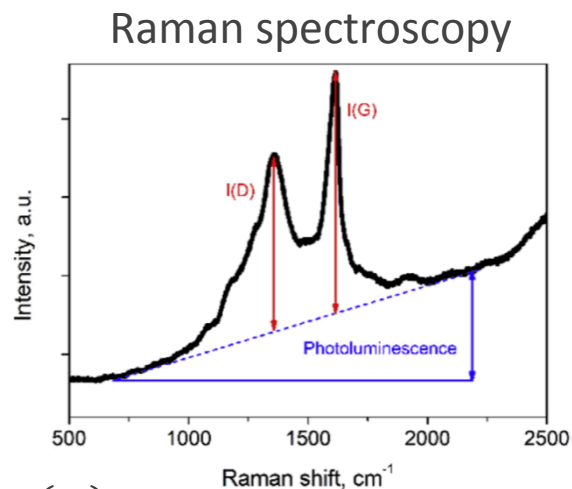
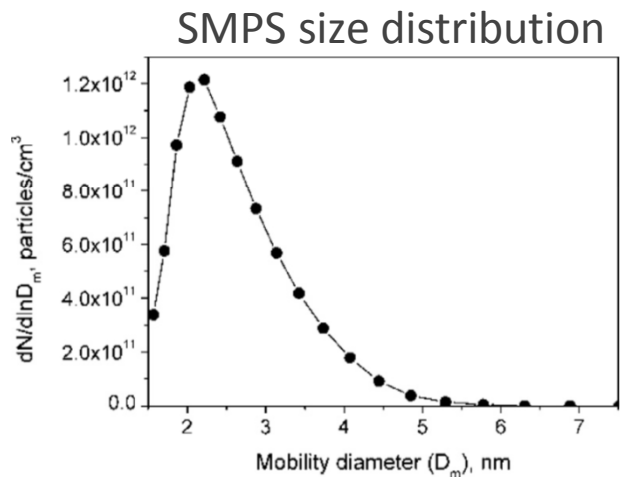


# Characteristics of Incipient Particles

## *Incipient-Particle Composition*

Premixed ethylene/air, C/O=0.67,  $\Phi=2.03$ , HAB=8 mm

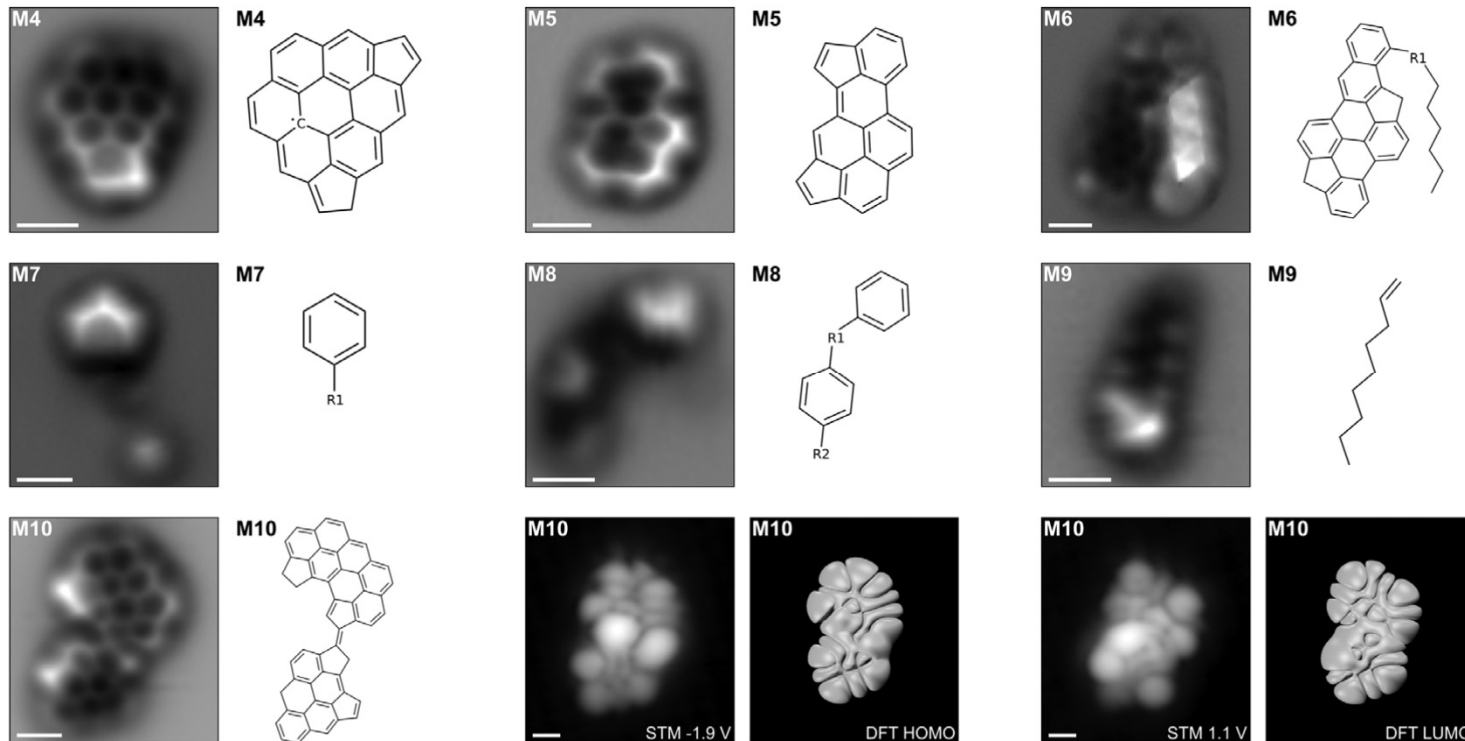
Atomic Force Microscopy (AFM)/Scanning Tunneling Microscopy (STM)



$$\frac{I(D)}{I(G)} \longrightarrow L_a = 1.1 \text{ nm}$$

$$\frac{m_{PL}}{I(G)} \longrightarrow C/H = 2.3$$

Schulz, Commodo, Kaiser, De Falco, Minutolo, Meyer, D'Anna, Gross 2018  
Combustion Symposium talk 4C01

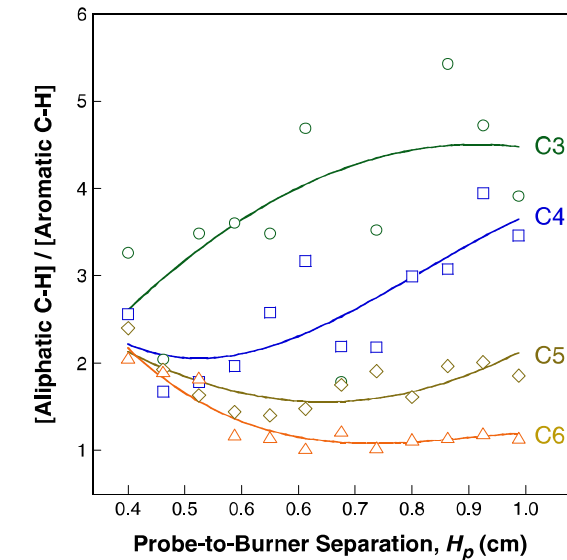
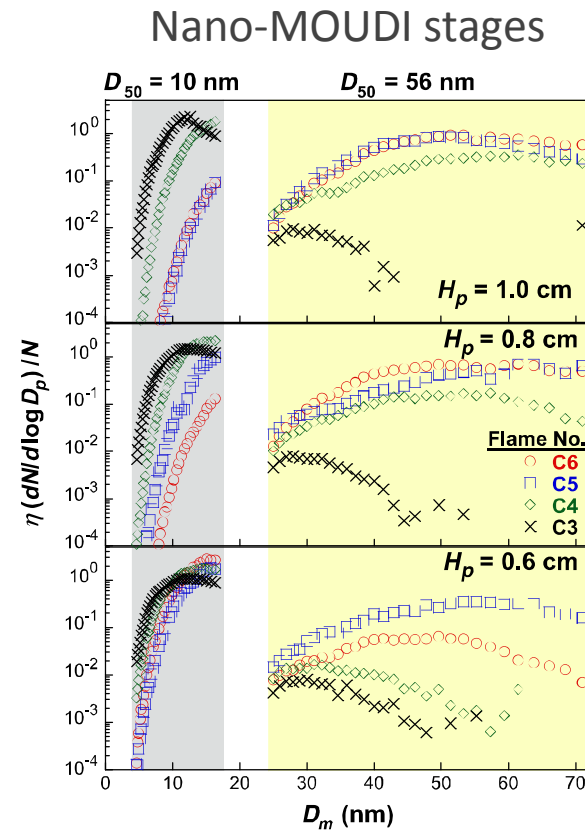
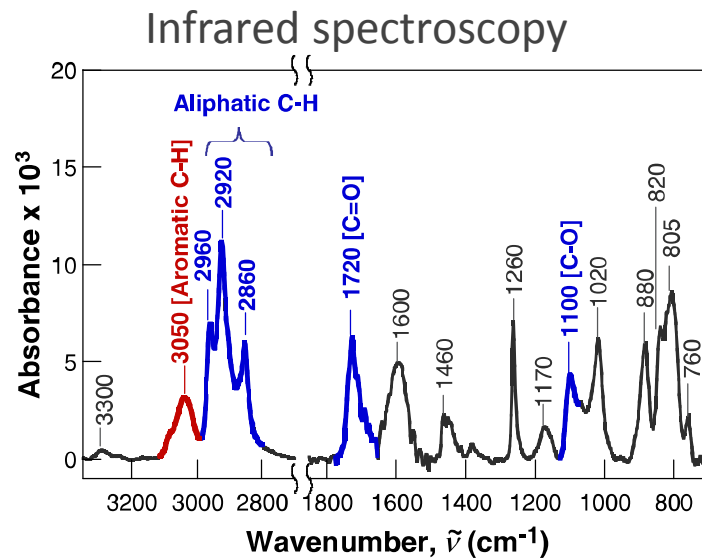


**Significant abundance of 5-membered rings and aliphatic groups**

# Characteristics of Incipient Particles

## *Incipient-Particle Composition*

Premixed ethylene/O<sub>2</sub>/Ar, C/O=0.69,  $\Phi=2.07$



Particles have high aliphatic content

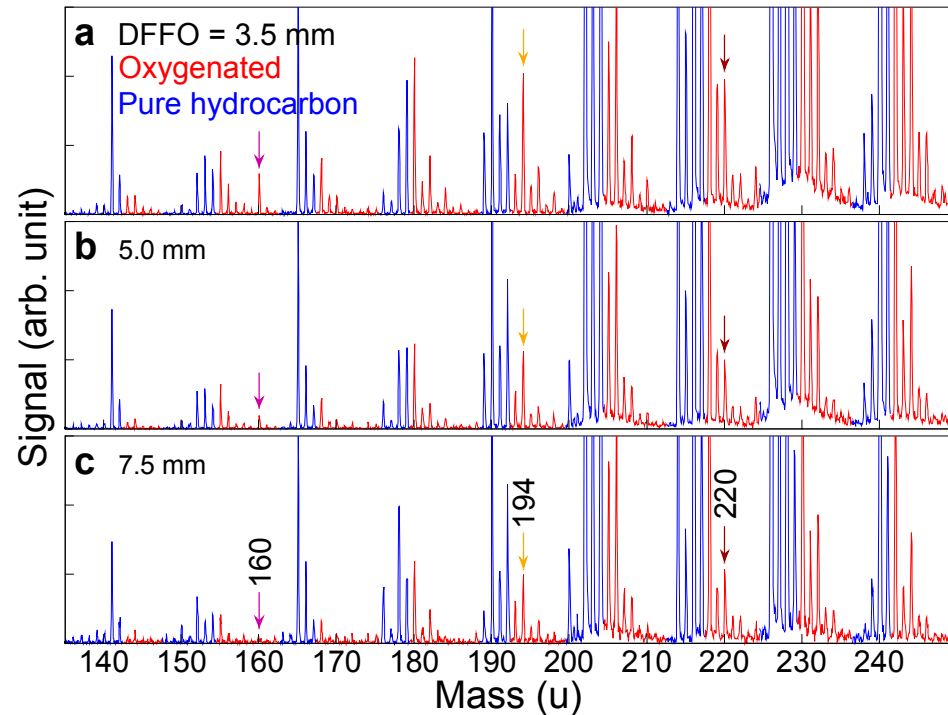
Oxygenated species also present

Cain, Camacho, Phares, Wang, Laskin 2011

# Characteristics of Incipient Particles

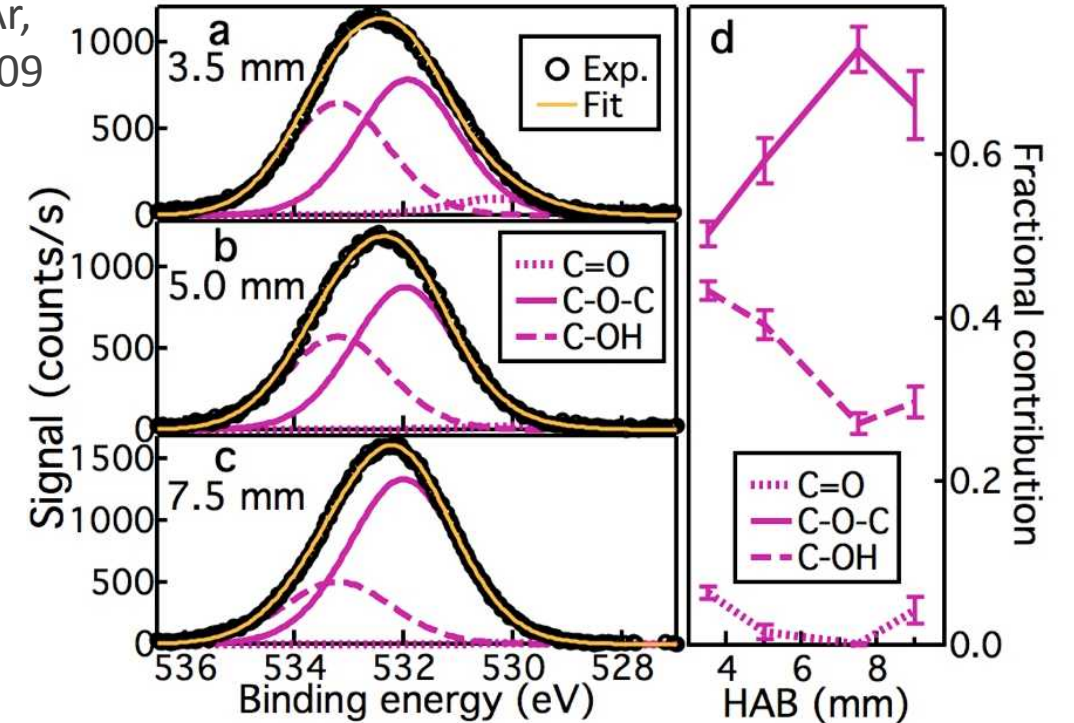
## Incipient-Particle Composition

Aerosol mass spectrometry (AMS)

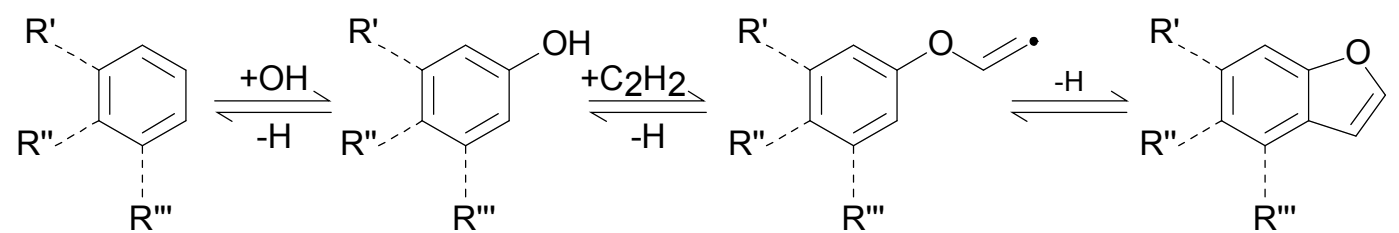
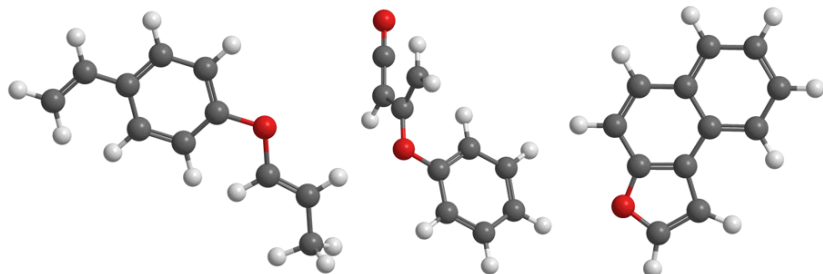


Premixed  
ethylene/O<sub>2</sub>/Ar,  
C/O=0.7,  $\Phi=2.09$

X-ray photoelectron spectroscopy (XPS)



Johansson, Dillstrom, Monti, El Gabaly, Campbell, Schrader, Popolan-Vaida, Richards-Henderson, Wilson, Violi, Michelsen 2016

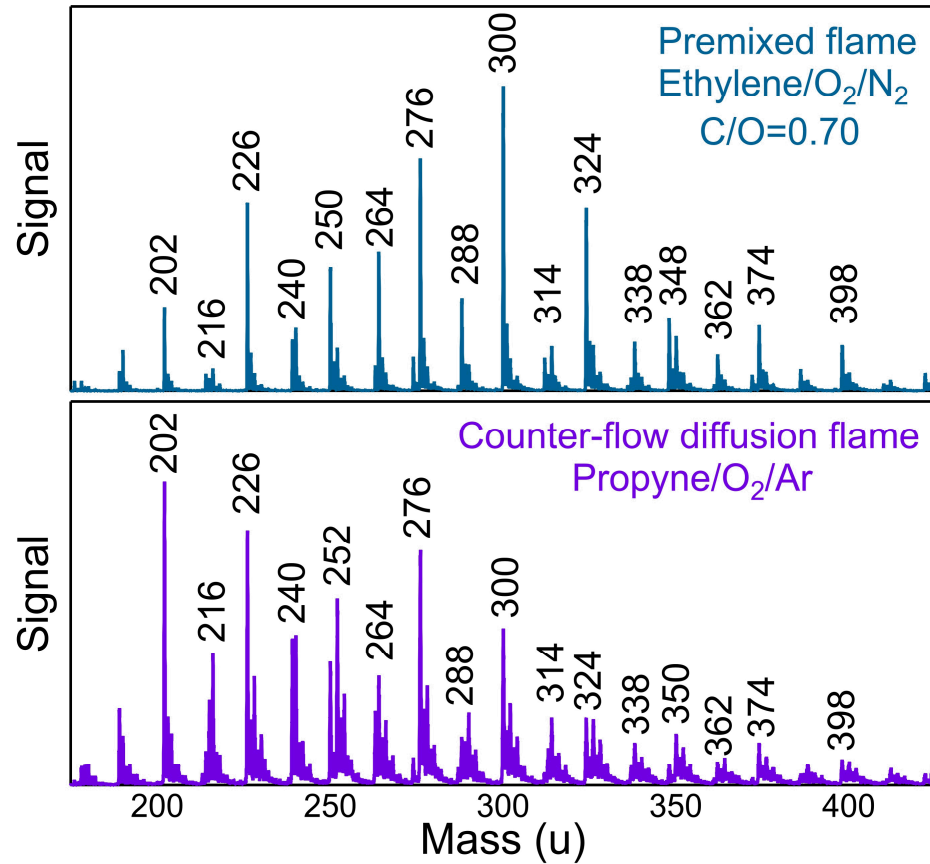


# Characteristics of Incipient Particles

## *Incipient-Particle Composition*

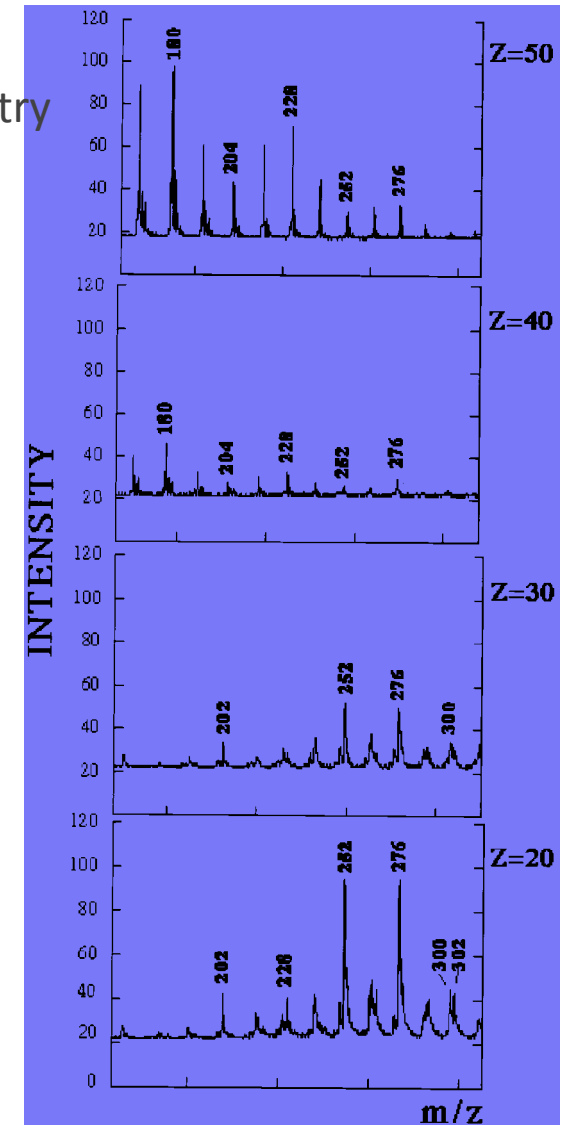
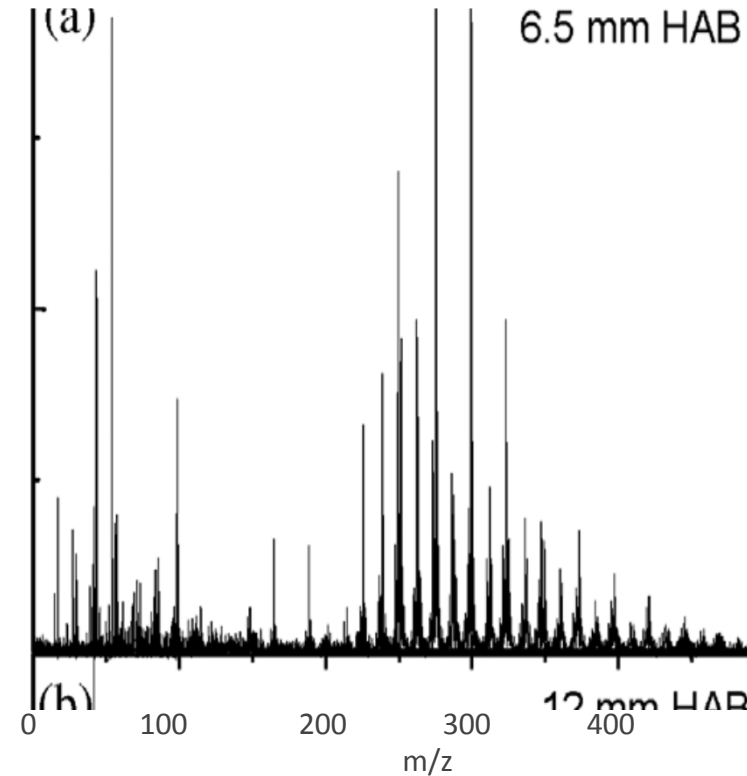
Laser microprobe mass spectrometry  
Coflow diffusion flame

Aerosol mass spectrometry



Photoionization Aerosol Mass Spectrometry

PIAMS mass spectrum of incipient soot using 1064-nm laser desorption, 118-nm photoionization  
Premixed ethylene/O<sub>2</sub>/Ar flame



Öktem, Tolocka, Zhao, Wang, Johnston 2005

Dobbins, Fletcher, Chang 1998



# Characteristics of Incipient Particles

## *Incipient-Particle Composition*

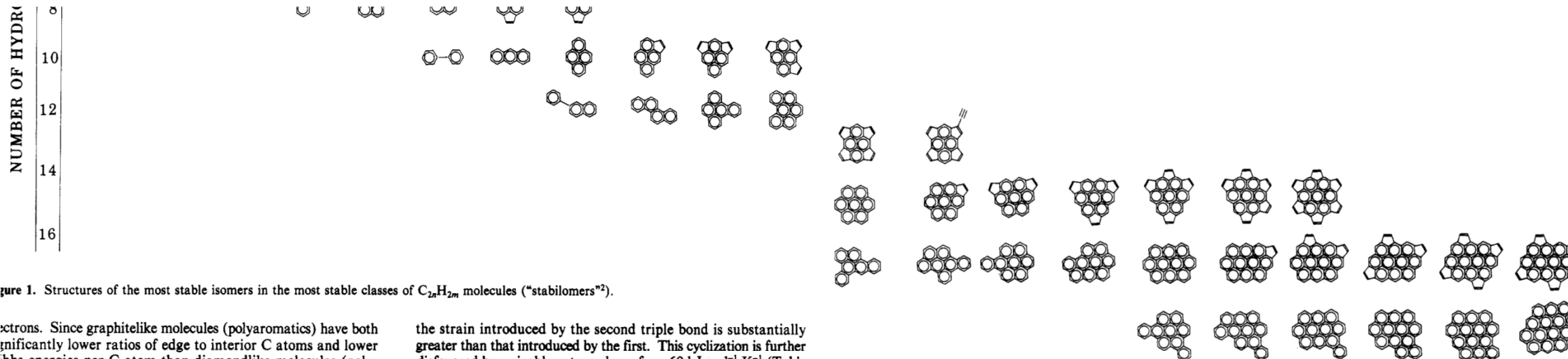


Figure 1. Structures of the most stable isomers in the most stable classes of  $C_{2n}H_{2m}$  molecules ("stabilomers"<sup>2</sup>).

atoms. Since graphitelike molecules (polyaromatics) have both significantly lower ratios of edge to interior C atoms and lower Gibbs energies per C atom than diamondlike molecules (polyamantanes) of comparable C number, the former molecules would always be more stable than the latter at high temperatures. However, the relative contribution of edge atoms to overall thermodynamic stability will decrease with increasing size.

$C_{2n}H_2$ . The most stable classes of moderately sized  $C_{2n}H_2$  molecules are expected to be the polyacetylenes. These are the most stable classes of molecules examined: only one polyacetylene

the strain introduced by the second triple bond is substantially greater than that introduced by the first. This cyclization is further disfavored by a sizable entropy loss of  $\sim -60 \text{ kJ mol}^{-1} \text{ K}^{-1}$  (Table I).

Very large, highly condensed polyaromatic  $C_{2n}H_2$  species, like  $C_{96}H_2$  (2800 K). Clearly, in the temperature range of interest in this work,  $n$  must be quite large before graphitelike molecules become more stable than polyacetylenes. On the other hand, regardless of approximations for stabilities of edge C atoms, polyaromatic molecules larger than  $C_{54}H_2$  are certain to be more stable than polyacetylenes up to at least 1800 K.

$C_{2n}H_4$ . The most stable  $C_{2n}H_4$  molecules are acyclic and contain one double bond and  $n - 1$  triple bonds. Symmetry numbers of

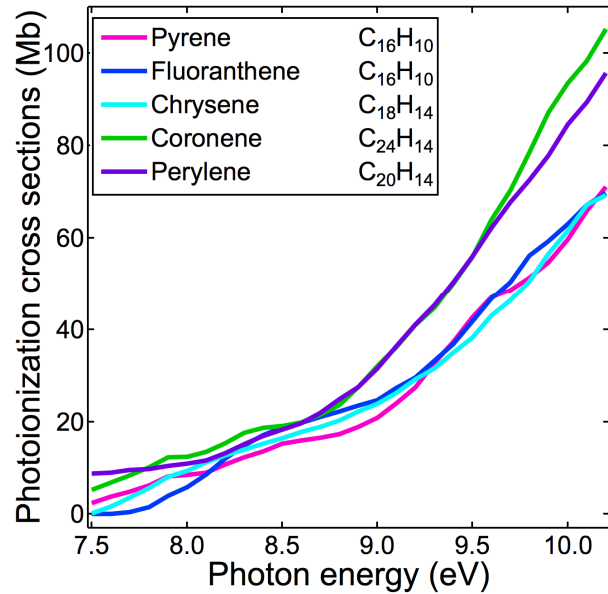
have the same stability near 2700 K, or 400 K lower than the polyacetylene of equal stability for individual molecules.

In view of its estimated  $120 \text{ kJ mol}^{-1}$  higher heat of formation (ignoring any antiaromaticity) and its lower entropy, benzene is always far less stable than ethynylbenzene. The same argument applies to 1,3,5-cyclooctatriene-7-yne, whose heat of formation is  $\sim 170 \text{ kJ mol}^{-1}$  greater than that of ethynylbenzene even when assuming no ring strain.

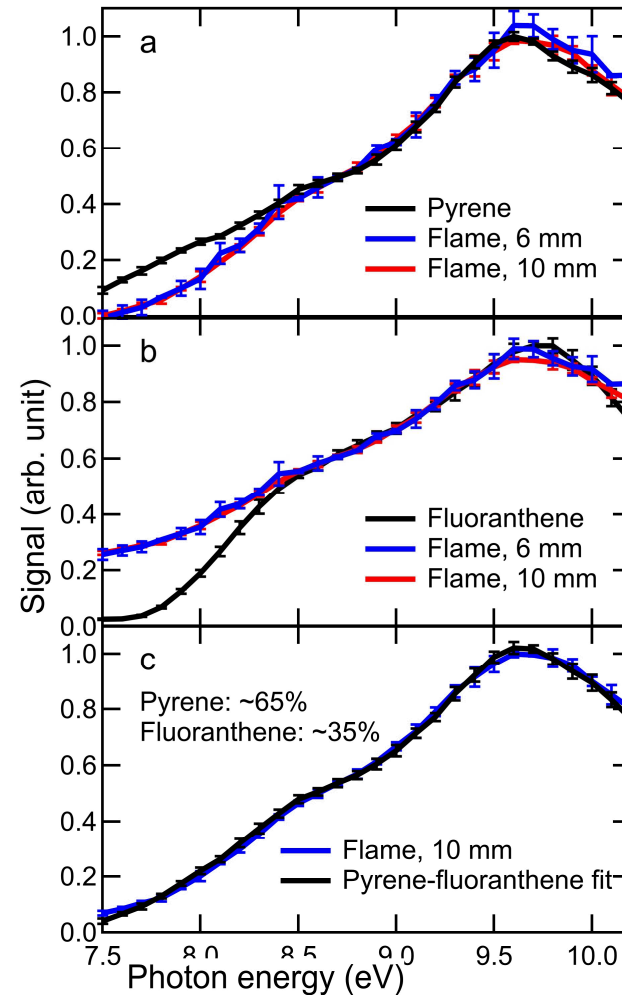
# Characteristics of Incipient Particles

## *Incipient-Particle Composition*

Premixed ethylene/O<sub>2</sub>/N<sub>2</sub>, C/O=0.70,  $\Phi=2.09$



**Masses that look like stabilomers are not always stabilomers**



Johansson, Campbell, Elvati, Schrader, Zádor,  
Richards-Henderson, Wilson, Violi, Michelsen 2017

Johansson, Zádor, Elvati, Campbell, Schrader,  
Richards-Henderson, Wilson, Violi, Michelsen 2017

# What do we know about incipient particles?

They have C/H ratios of  $\sim 1.5-2.5$ .

They are  $< \sim 3-4$  nm in diameter.

They may form at C/O as low as 0.6.

They form at lower HABs and C/O ratios than a second (larger) mode ( $> \sim 4-6$  nm).

They appear to be the source of the larger mode at high C/O.

They appear spherical and fluid.

They absorb in the UV but weakly at longer wavelengths.

Their photoionization threshold is  $> 6.3$  eV.

They have disordered fine structure.

They have significant abundances of aliphatic and oxygenated groups.

They have significant abundances of 5-membered rings.

Their precursor masses are consistent between flames, fuels.

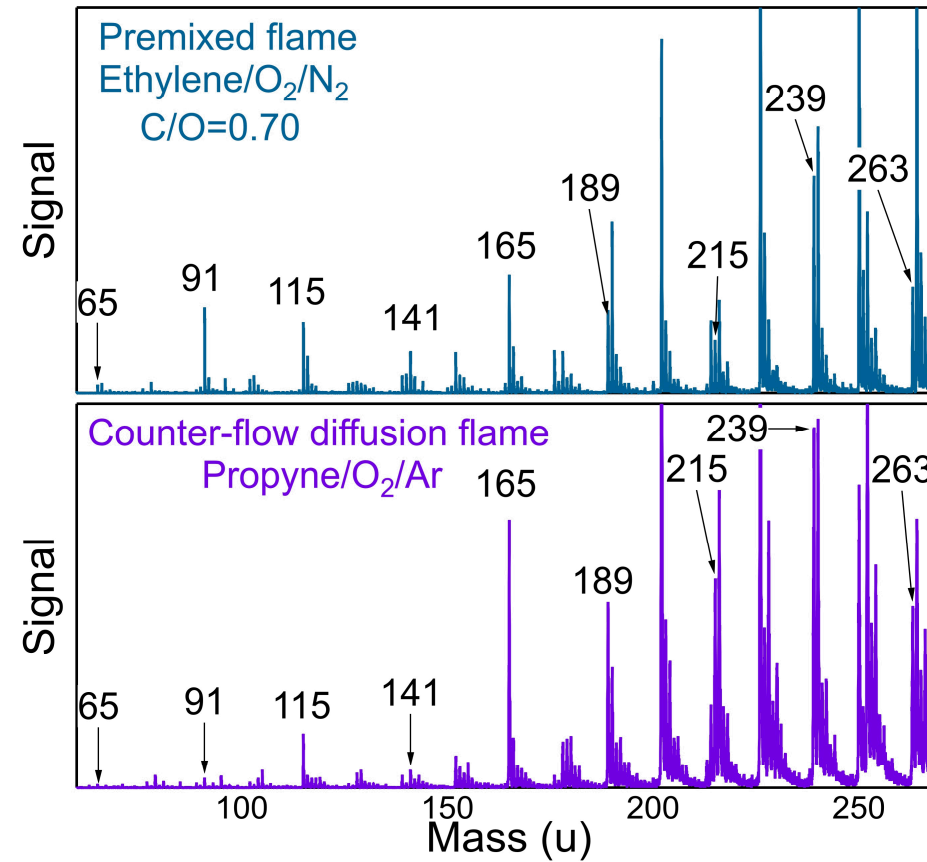
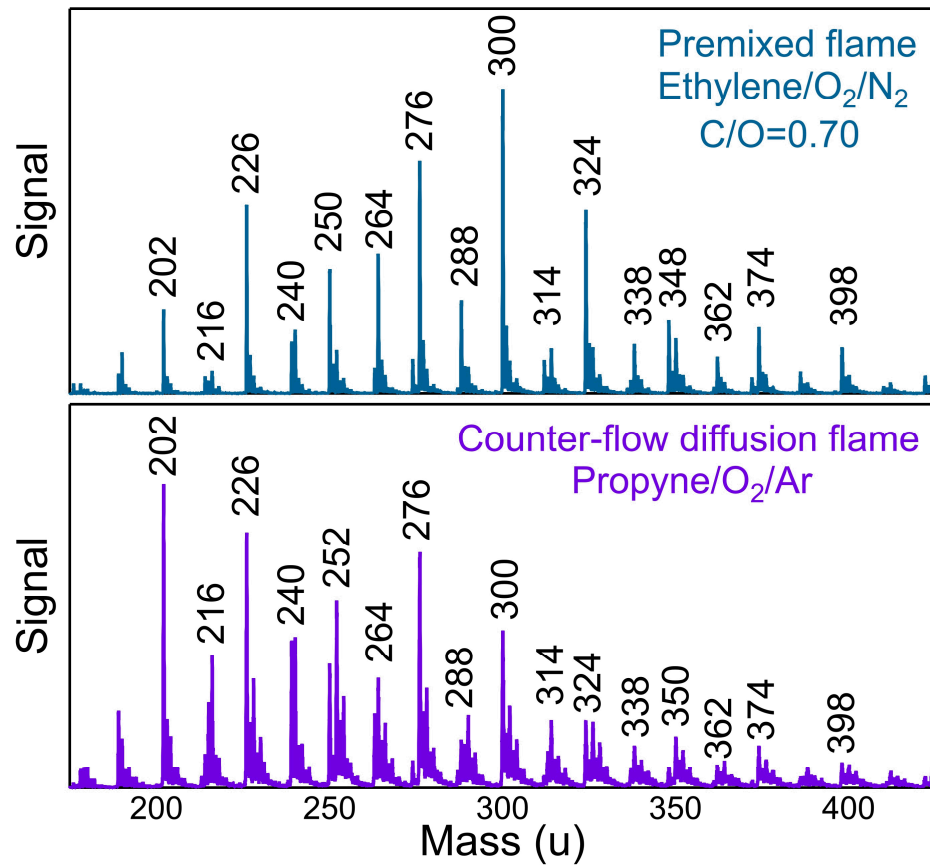
Their precursors may not be the most thermodynamically stable isomers.



# Characteristics of Incipient Particles

## *Incipient-Particle Composition*

Aerosol mass spectrometry



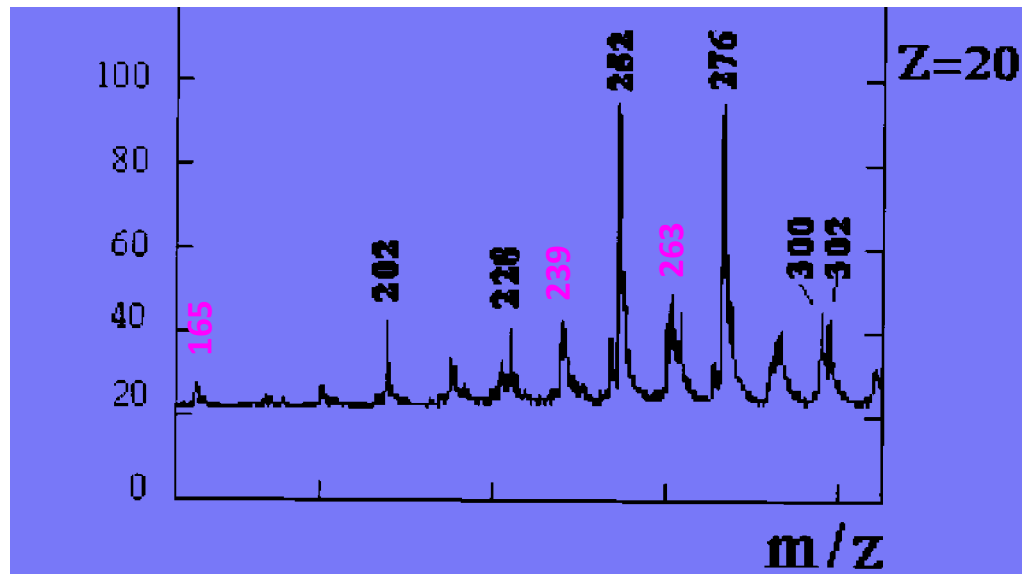
Johansson, Head-Gordon, Schrader, Wilson, Michelsen,  
in press

# Characteristics of Incipient Particles

## *Incipient-Particle Composition*

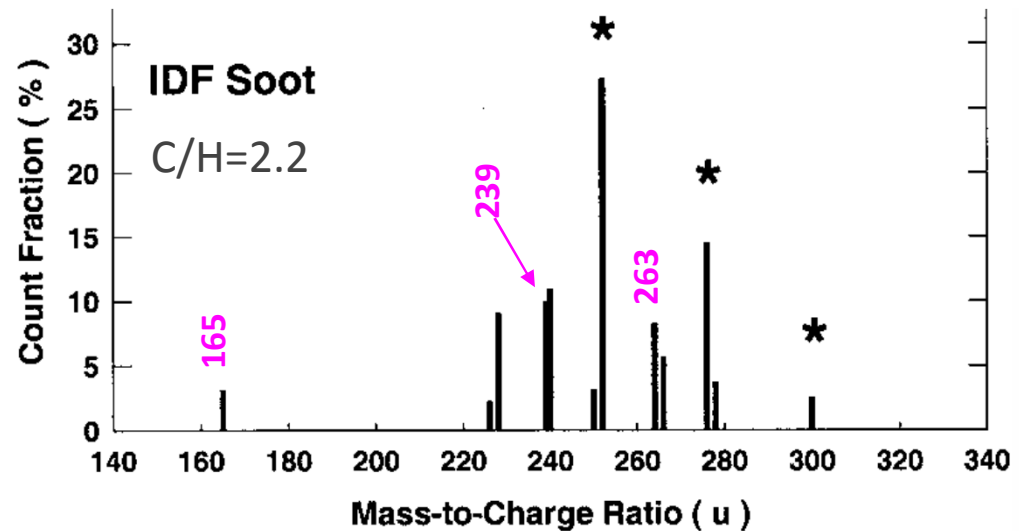
Laser microprobe mass spectrometry

Ethylene/air co-flow diffusion flame



Dobbins, Fletcher, Chang 1998

Ethylene/air inverse diffusion flame



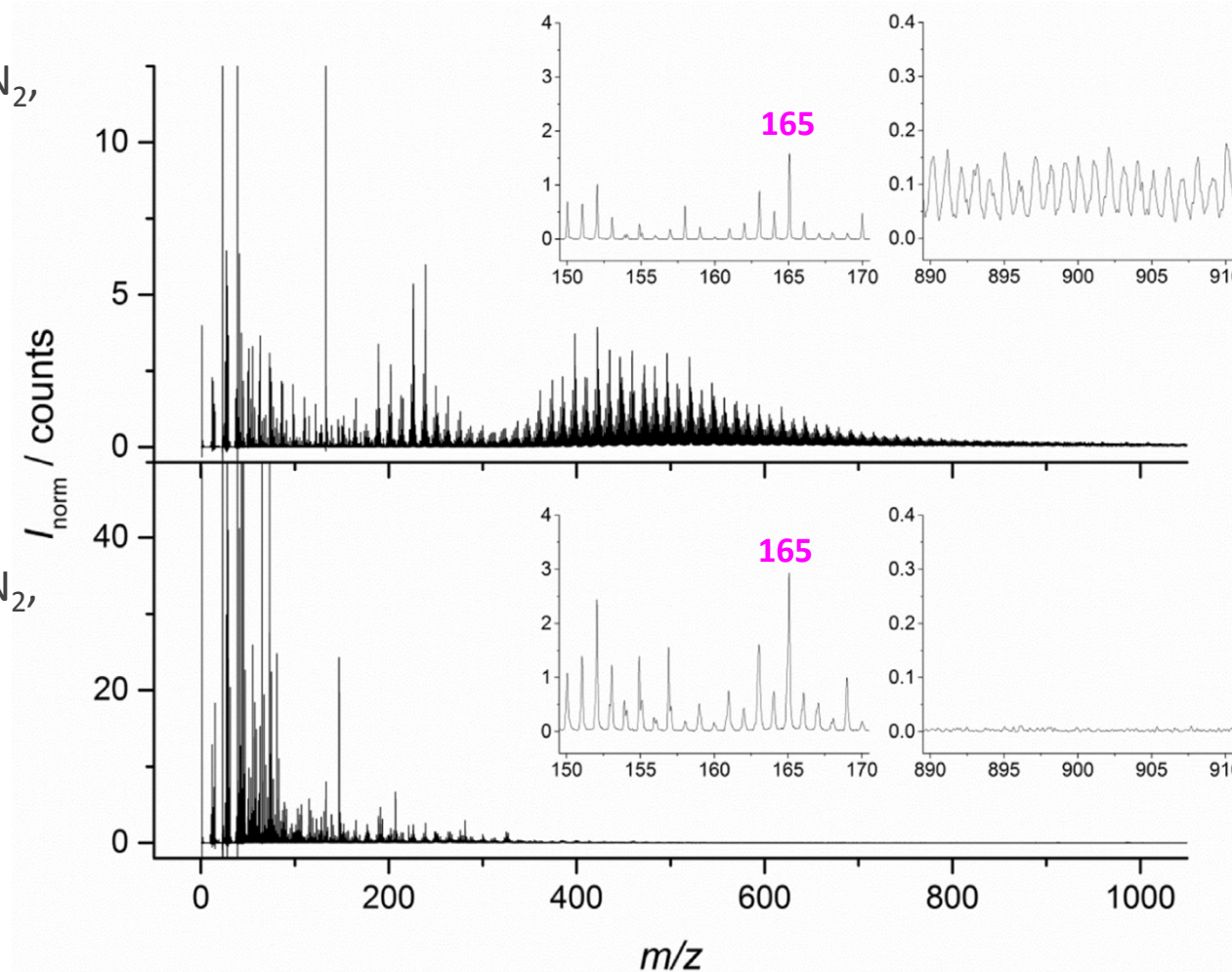
Blevins, Fletcher, Benner, Steel, Mulholland 2002

# Characteristics of Incipient Particles

## *Incipient-Particle Composition*

Time of flight secondary ion mass spectrometry

Low pressure (200 Torr)  
Premixed methane/O<sub>2</sub>/N<sub>2</sub>,  
C/O=0.49,  $\Phi$ =1.95



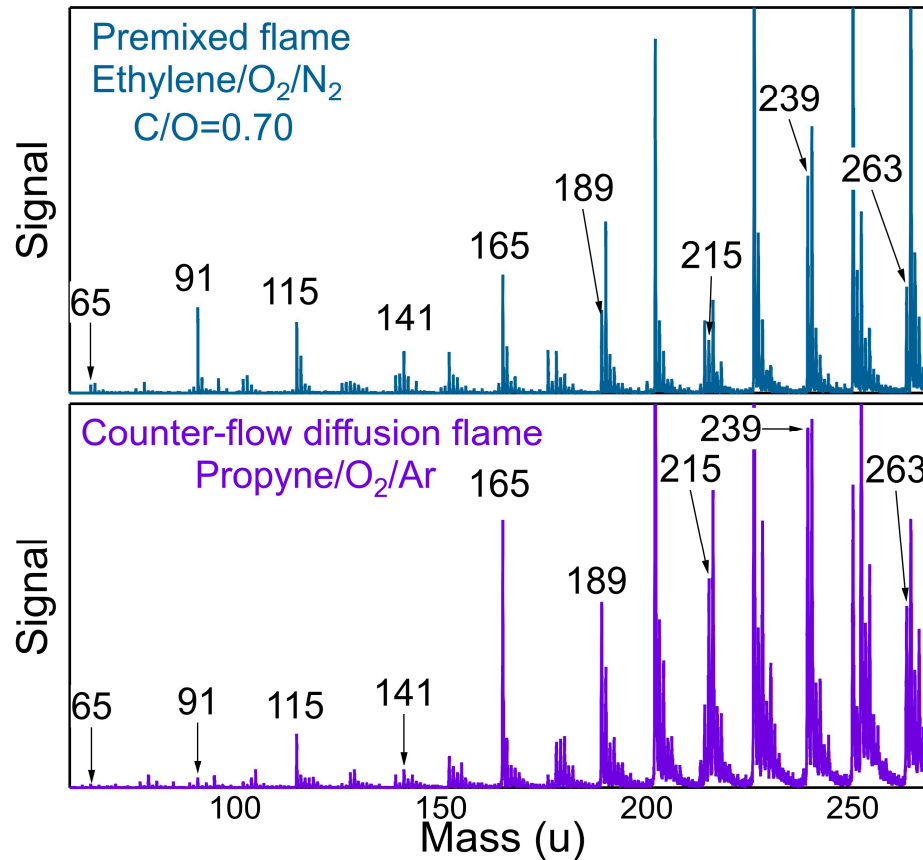
Low pressure (200 Torr)  
Premixed methane/O<sub>2</sub>/N<sub>2</sub>,  
C/O=0.58,  $\Phi$ =2.32

Desgroux, Faccinnetto, Mercier, Mouton, Karkar, El Bakali 2017

# Characteristics of Incipient Particles

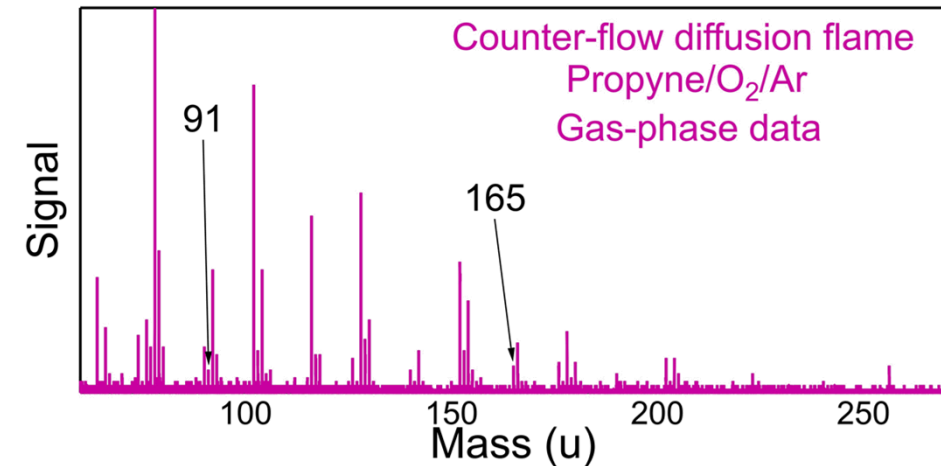
## *Incipient-Particle Composition*

Aerosol mass spectrometry



Johansson, Head-Gordon, Schrader, Wilson, Michelsen,  
in press

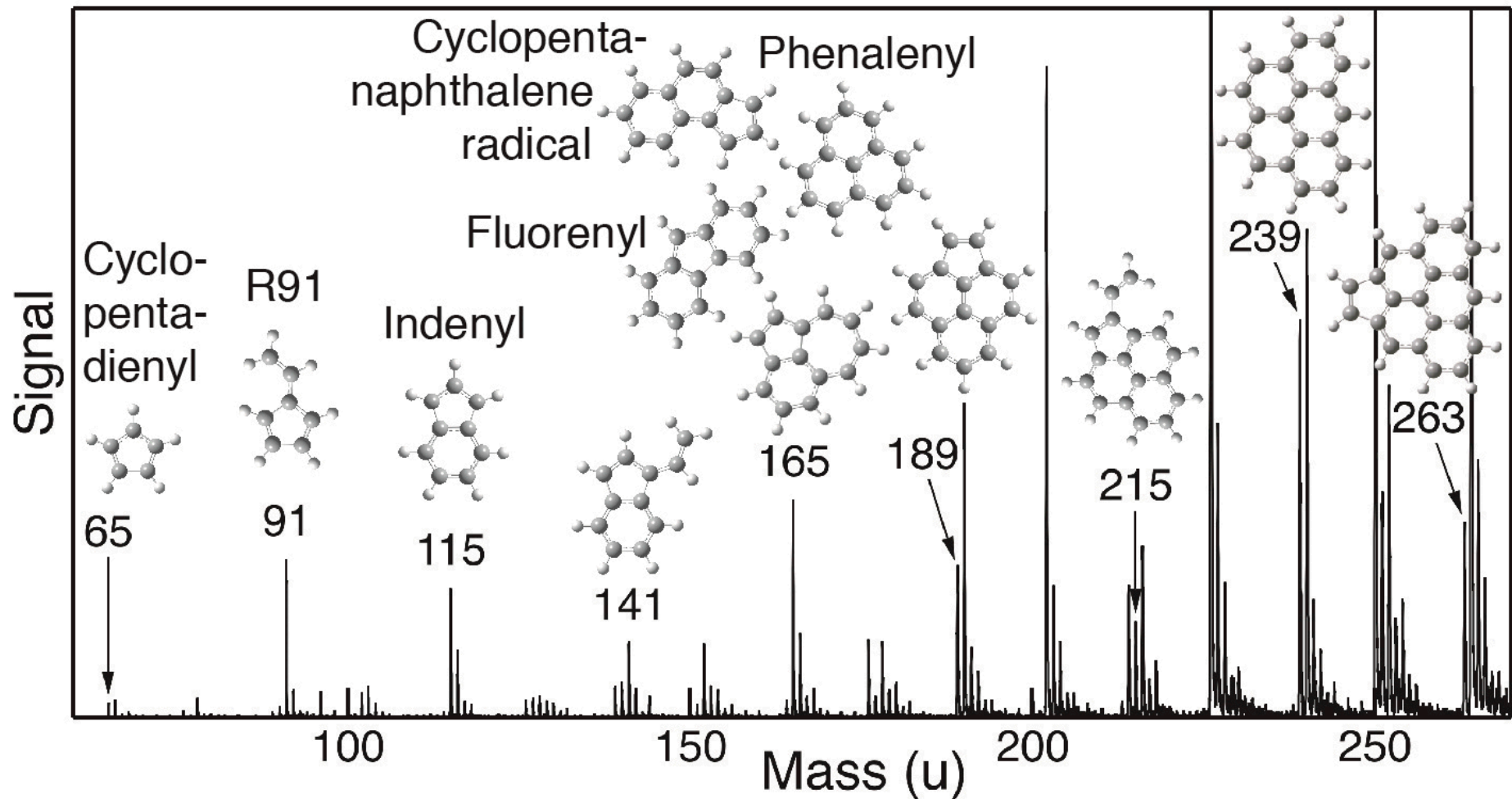
Molecular beam mass spectrometry



Courtesy of Nils Hansen and Kai Moshhammer

# Characteristics of Incipient Particles

## *Incipient-Particle Composition*

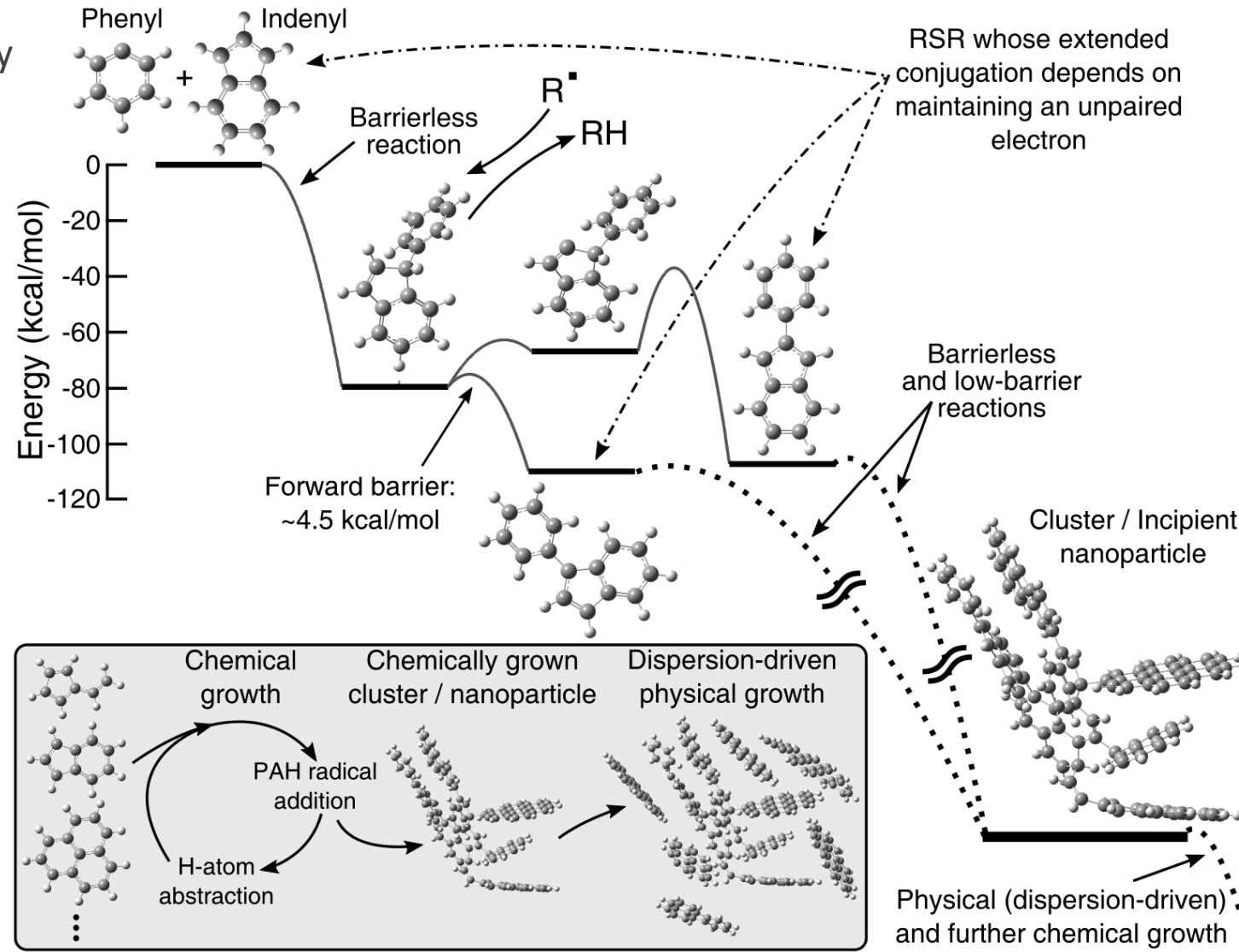


Johansson, Head-Gordon, Schrader, Wilson, Michelsen, in press



# Particle Inception by Radical Chain Reactions

Clustering of Hydrocarbons by Radical Chain Reactions (CHRCR)



# What do we know about incipient particles?

They have C/H ratios of  $\sim 1.5-2.5$ .

They are  $< \sim 3-4$  nm in diameter.

They may form at C/O as low as 0.6.

They form at lower HABs and C/O ratios than a second (larger) mode ( $> \sim 4-6$  nm).

They appear to be the source of the larger mode at high C/O.

They appear spherical and fluid.

They absorb in the UV but weakly at longer wavelengths.

Their photoionization threshold is  $> 6.3$  eV.

They have disordered fine structure.

They have significant abundances of aliphatic and oxygenated groups.

They have significant abundances of 5-membered rings.

Their precursor masses are consistent between flames, fuels.

Their precursors may not be the most thermodynamically stable isomers.

Resonantly stabilized radicals may drive inception.



Olof Johansson

Paul Schrader

Martin Head-Gordon

Kevin Wilson

**THE DREAM IS REAL.**

FROM THE DIRECTOR OF THE DARK KNIGHT

# INCEPTION

**COMING SOON**

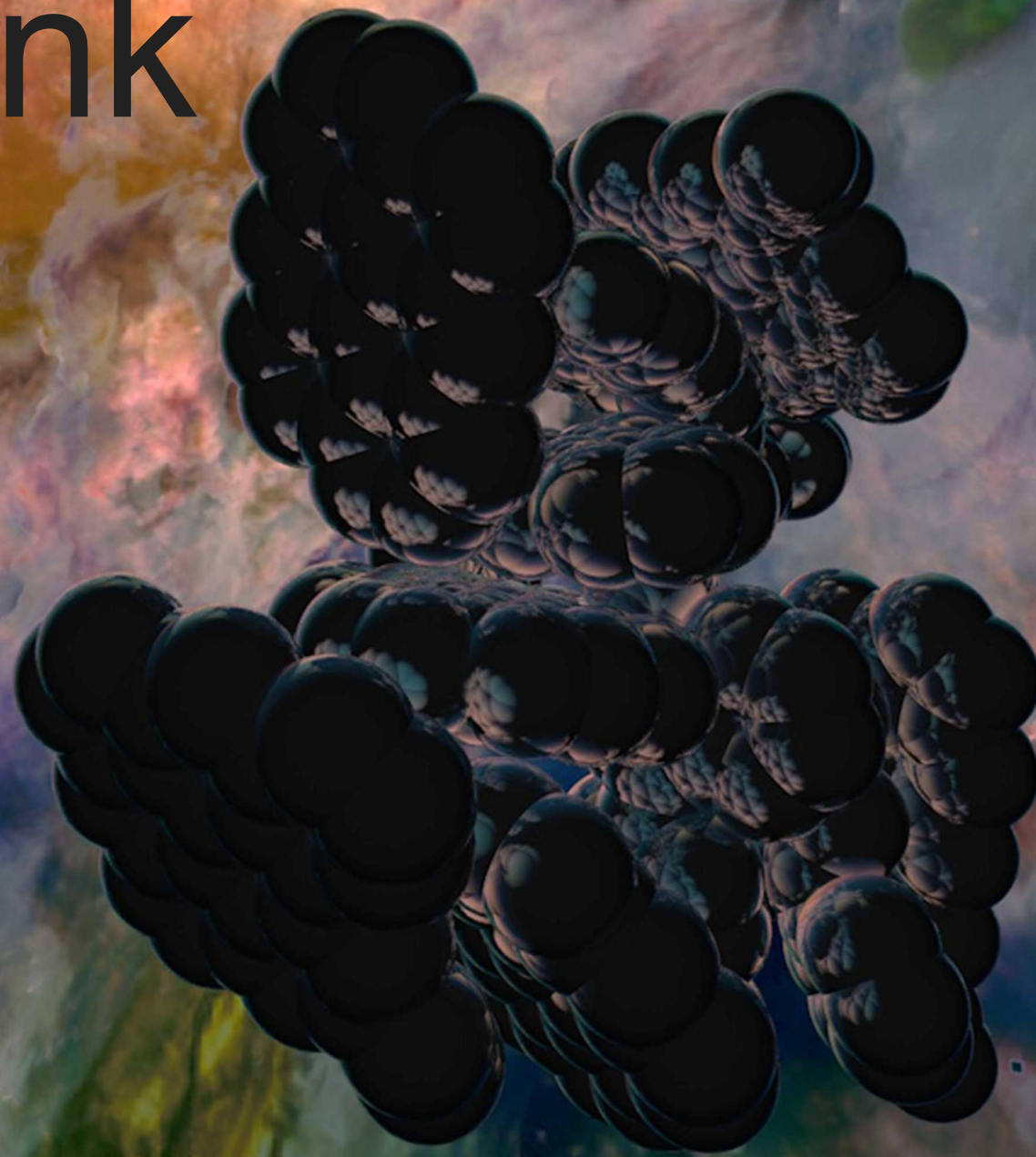
[www.inceptionmovie.co.uk](http://www.inceptionmovie.co.uk)

LEGENDARY

ENTERTAINMENT

WARNER BROS. PICTURES

Thank  
you



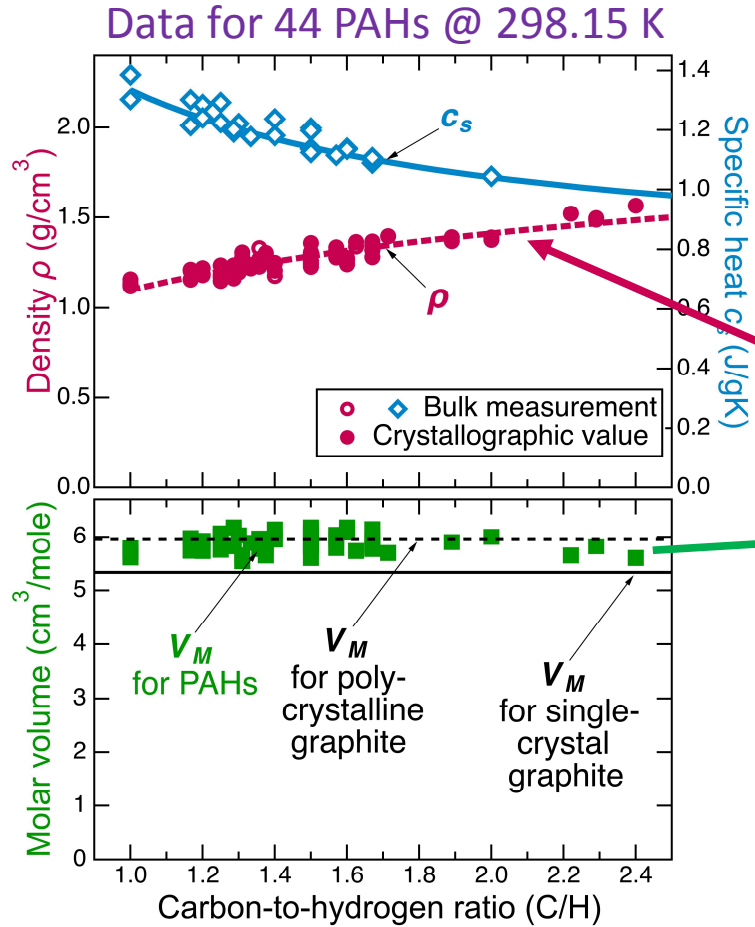


# Density, Specific Heat, and Their Product

*Dependence on Soot-Maturity Level and Temperature*

# Density, Specific Heat, and Their Product

## Dependence on Soot-Maturity Level



Assuming that

Incipient soot is composed of precursor PAHs

Incipient soot has C/H ratios of ~1.5-2.5

Maturing means losing H, becoming more graphitic

How do we predict density and specific heat?

The density is

$$\rho = W/V_M$$

Approx. constant

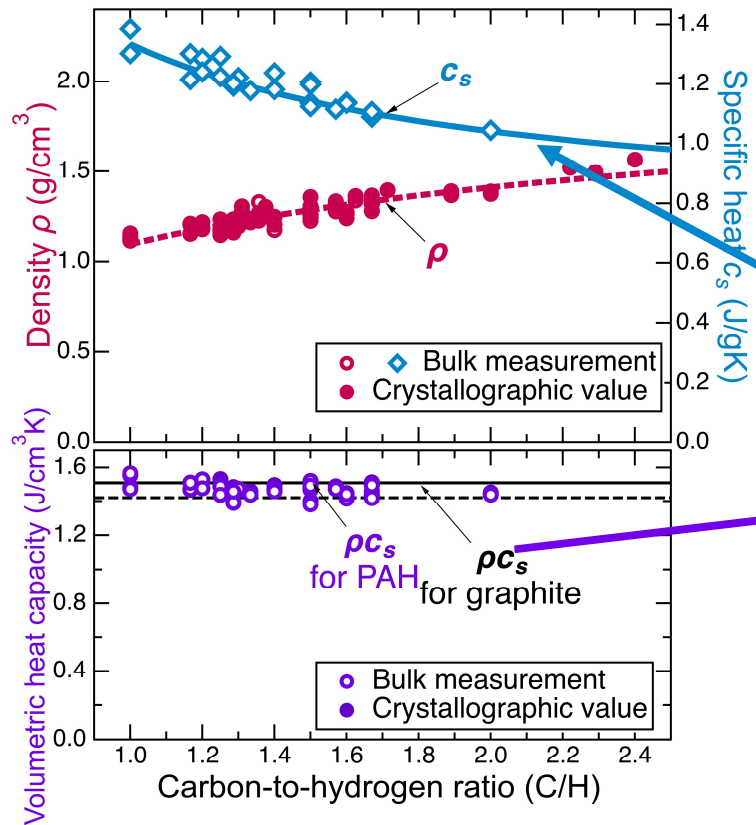
where molecular weight can be given as

$$W = \frac{w_C \frac{C}{H} + w_H}{\frac{C}{H} + 1}$$

# Density, Specific Heat, and Their Product

## Dependence on Soot-Maturity Level

Data for 44 PAHs @ 298.15 K



Assuming that

Incipient soot is composed of precursor PAHs

Incipient soot has C/H ratios of ~1.5-2.5

Maturing means losing H, becoming more graphitic

How do we predict density and specific heat?

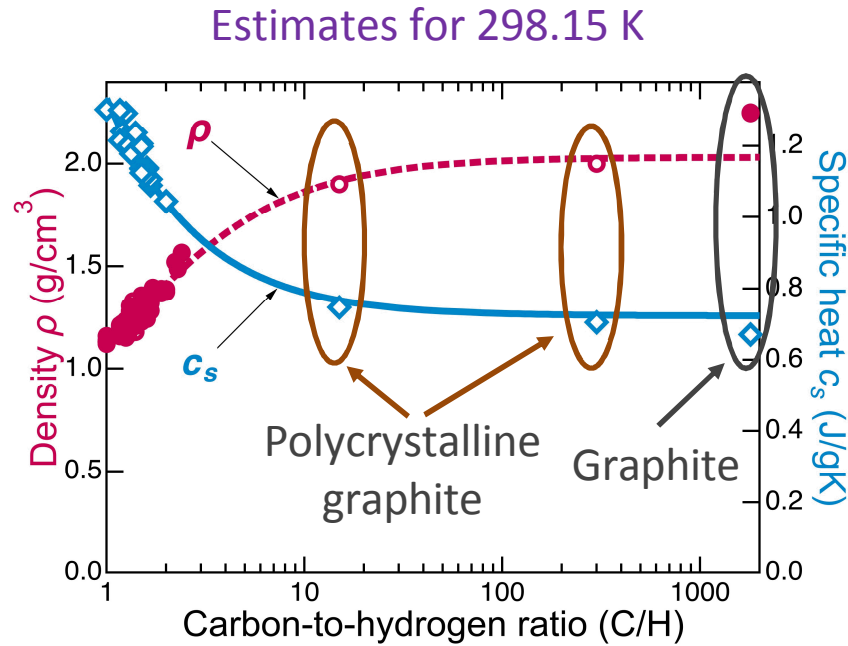
The specific heat is

$$c_s = \overline{\rho c_s} / \rho$$

Approx. constant

# Density, Specific Heat, and Their Product

## *Dependence on Soot-Maturity Level*



The density is

$$\rho = W/V_M$$

where molecular weight can be given as

$$W = \frac{w_C \frac{C}{H} + w_H}{\frac{C}{H} + 1}$$

The specific heat is

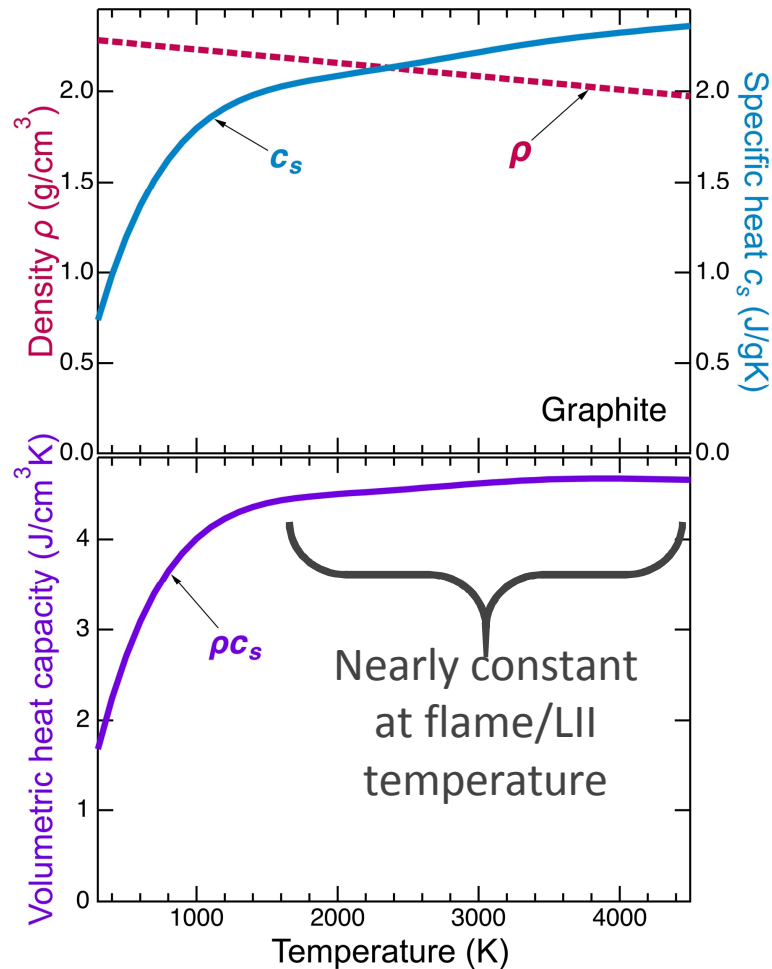
$$c_s = \overline{\rho c_s} / \rho$$

where  $\overline{\rho c_s}$  is constant

**Simple equations estimate  $\rho$  and  $c_s$   
as a function of C/H ratio**

# Density, Specific Heat, and Their Product

## *Temperature Dependence: High-Temperature Conditions*



At high T,  $\rho c_s$  is almost independent of T

At high T,  $\rho c_s$  is almost independent of material  
*Law of Dulong & Petit*

At high T,

$$\rho c_s = 3R/V_M$$

$R$  is the universal gas constant

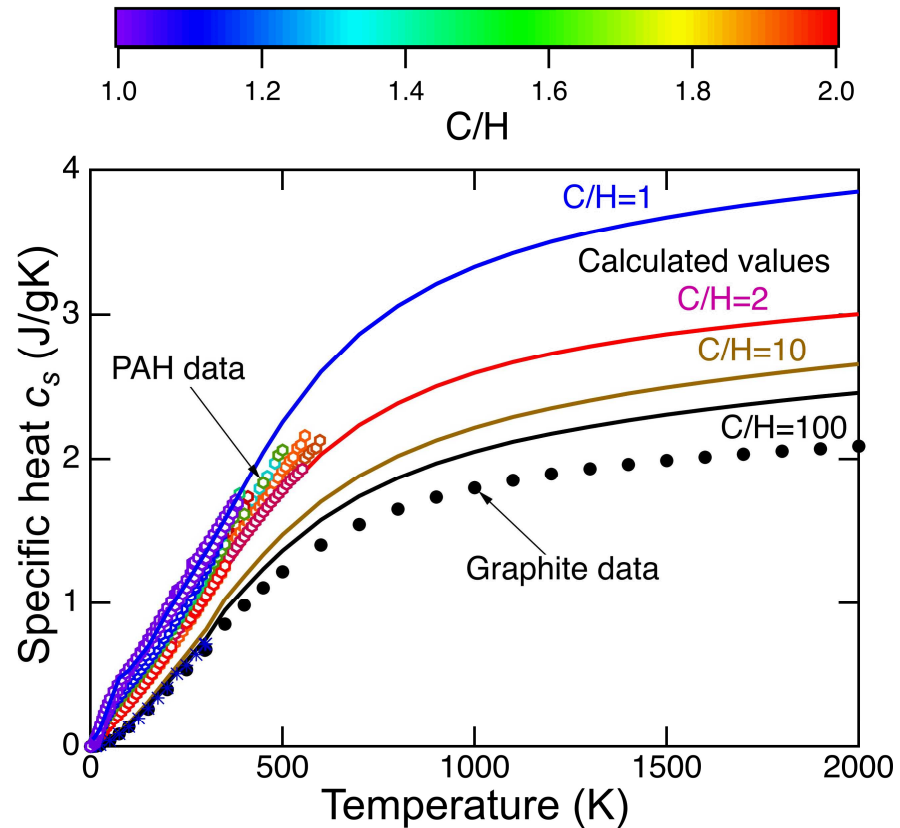
$V_M$  is the molar volume (cm<sup>3</sup>/mole)

$V_M$  is almost independent of material  
esp for materials with the same elements

For more, see Johansson *et al.* AST **51**, 1333-1344 (2017)

# Specific Heat

## *Temperature and Maturity-Level Dependence*



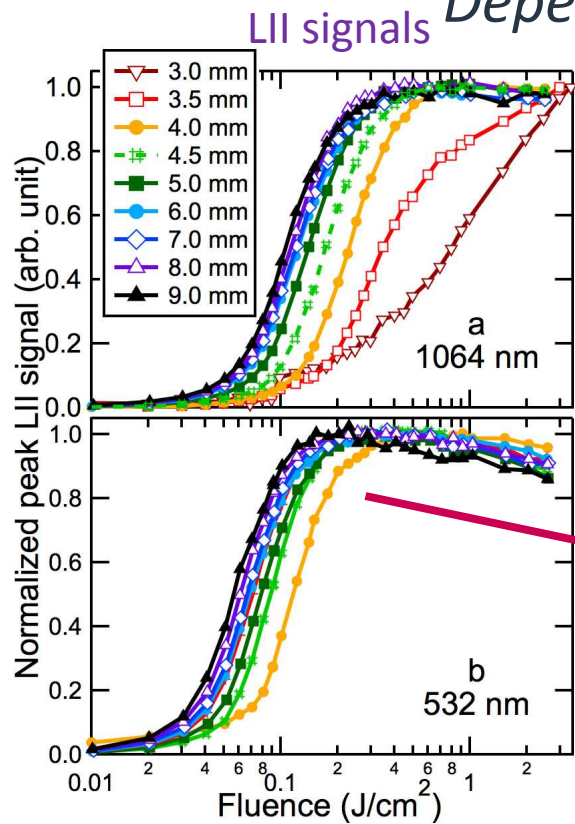
Once we have  $c_s$  as a function of C/H and T, we can use  $\rho c_s$  for graphite to derive  $\rho$  as a function of C/H and T.

# Particle Growth and Evolution

*Evidence for Surface Growth by Hydrocarbon Adsorption and Surface Oxidation*

# Absorption magnitude, $\lambda$ -dependence

Dependence on soot-maturity level



LII signals

Wavelength dependence

$$\left[ \frac{F(\lambda_1)}{F(\lambda_2)} \right]_{S_{max}} = \frac{\sigma_{abs}(\lambda_2)}{\sigma_{abs}(\lambda_1)} = \left( \frac{\lambda_1}{\lambda_2} \right)^\xi = \frac{\lambda_1 E(m, \lambda_2)}{\lambda_2 E(m, \lambda_1)}$$

Desgroux, Therssen, and coworkers

$$\sigma_{abs} = \frac{\pi^2 d^3}{\lambda} E(m, \lambda) = \frac{\pi d^3 \beta}{6 \lambda^\xi}$$

Magnitude (circled  $\beta$ )  
Wavelength dependence (circled  $\lambda^\xi$ )

Magnitude

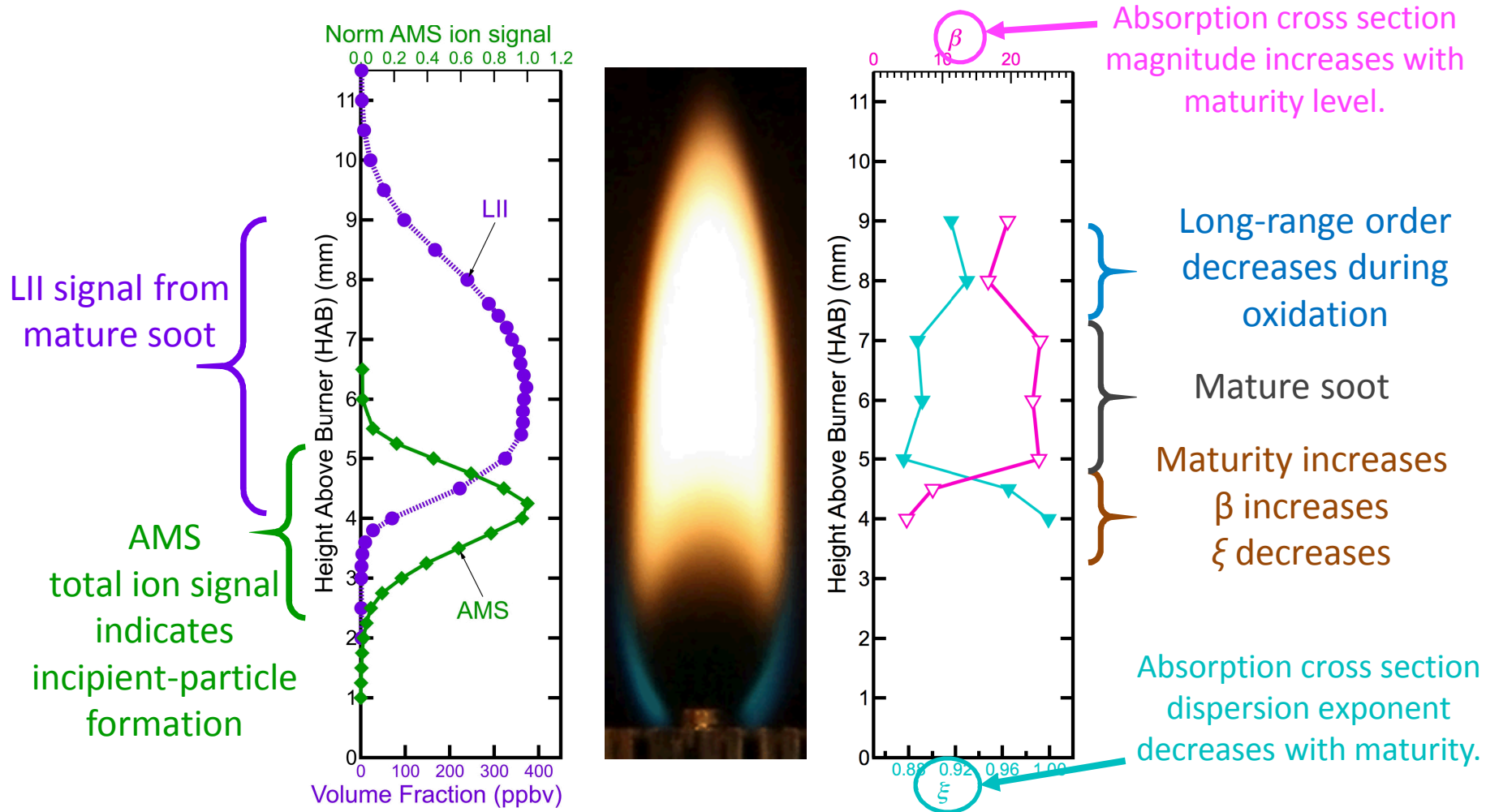
$$\beta = \frac{\rho c_s (T_{max} - T_0) \lambda^\xi}{F(\lambda)}$$

High-T graphite value

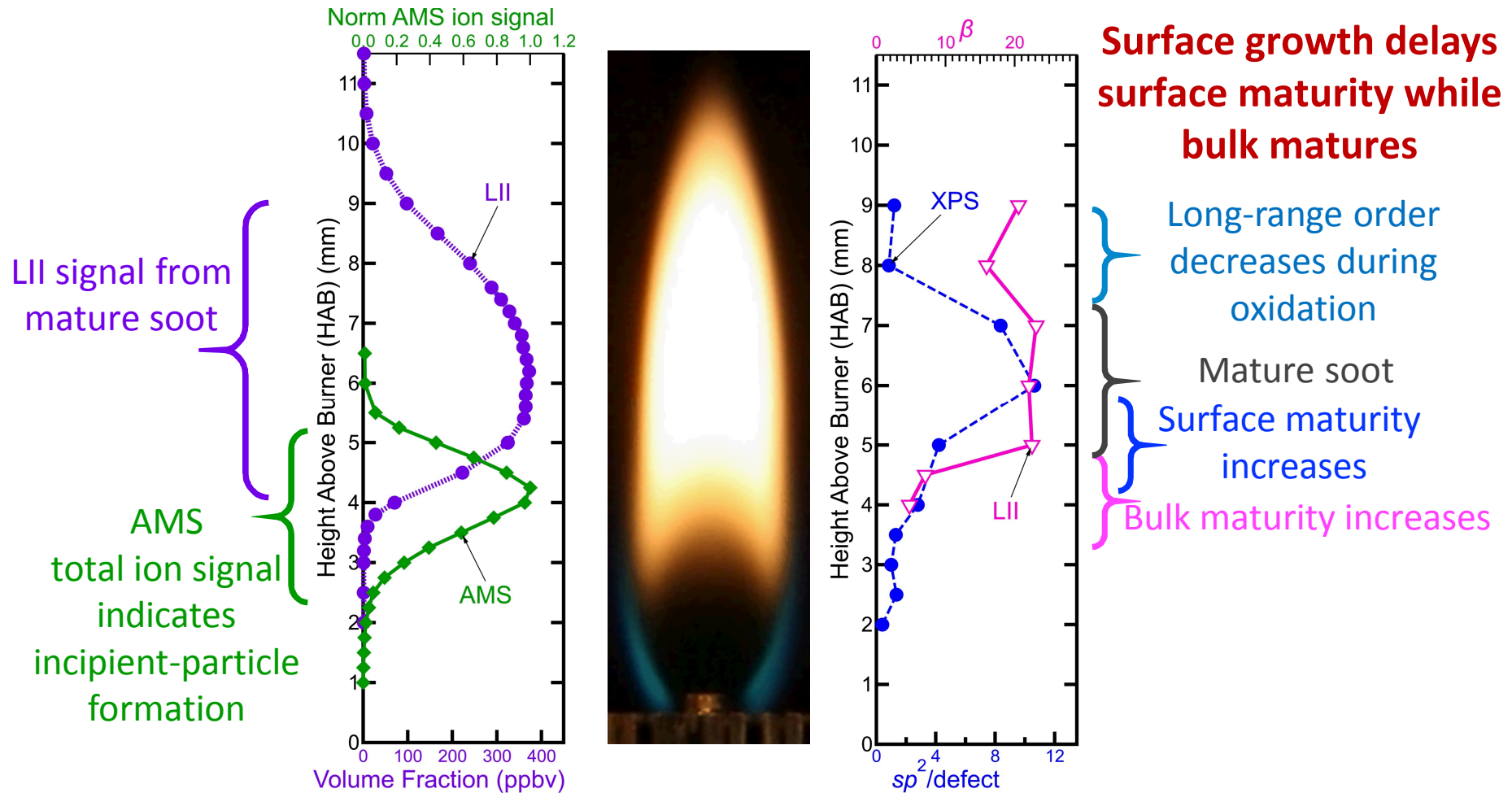
Measured

**LII fluence curves can give wavelength dependence and magnitude of absorption cross section**

# Precursors, Incipient Particle Formation, and Bulk Particle-Maturity Level



# Surface-Sensitive XPS Indicates Surface Growth by Hydrocarbon Adsorption and Oxidation at Surface

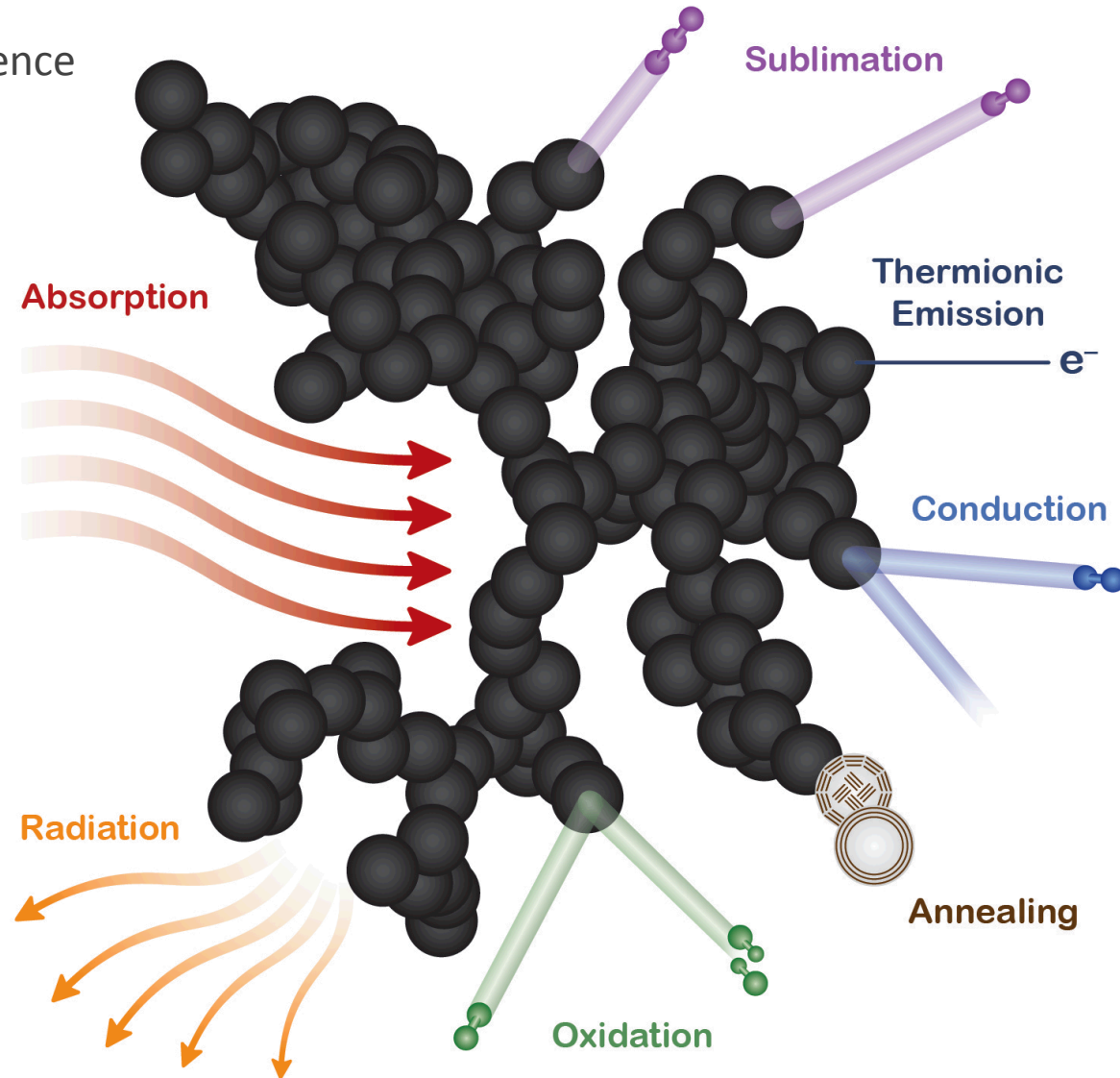


For more, see Johansson *et al.* AST **51**, 1333-1344 (2017)

# Soot Particle Growth and Evolution

## *Diagnostics for Maturity Level*

Laser-Induced Incandescence  
(LII)

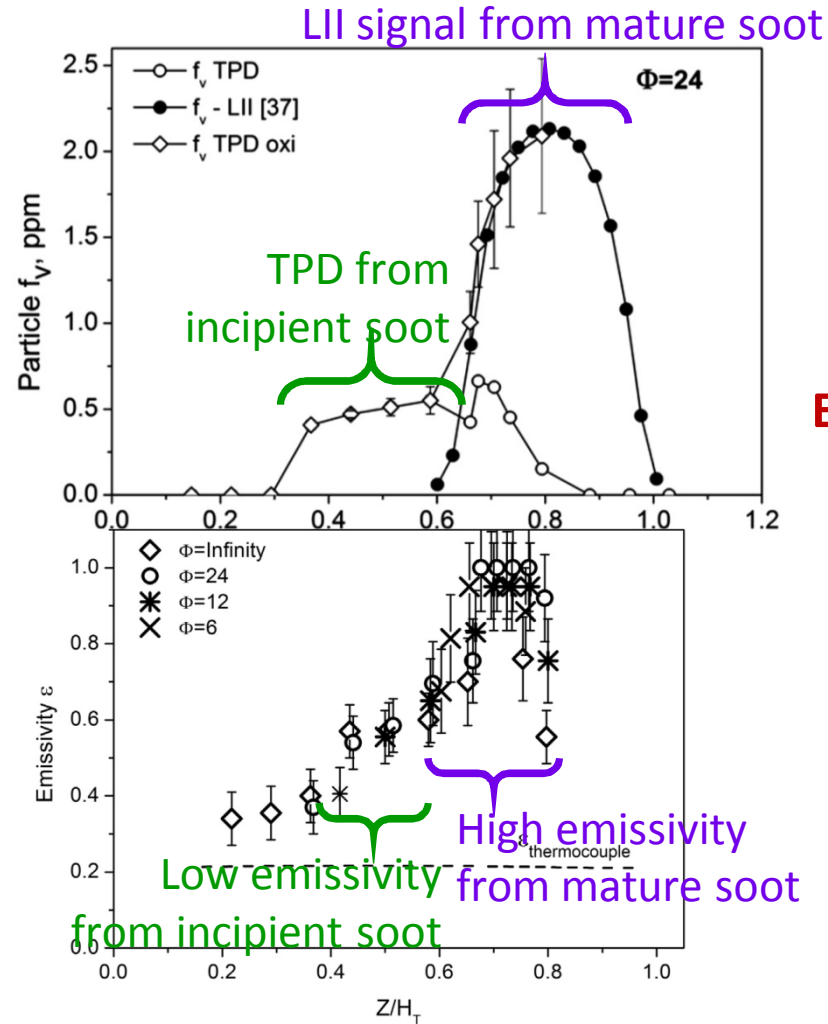


# Soot Particle Growth and Evolution

Thermophoretic Particle Densitometry (TPD): Particle volume fraction and emissivity

Laser-Induced Incandescence (LII): Mature-soot volume fraction

Partially premixed ethylene co-flow diffusion flame



Incipient particles observed by TPD but not by LII;

Emissivity increases with maturity

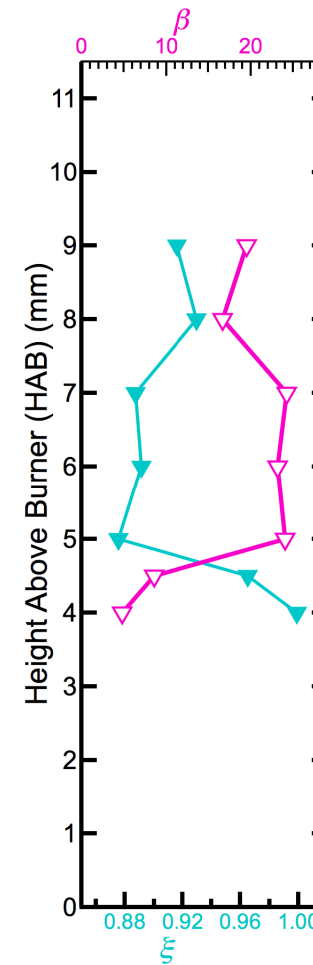
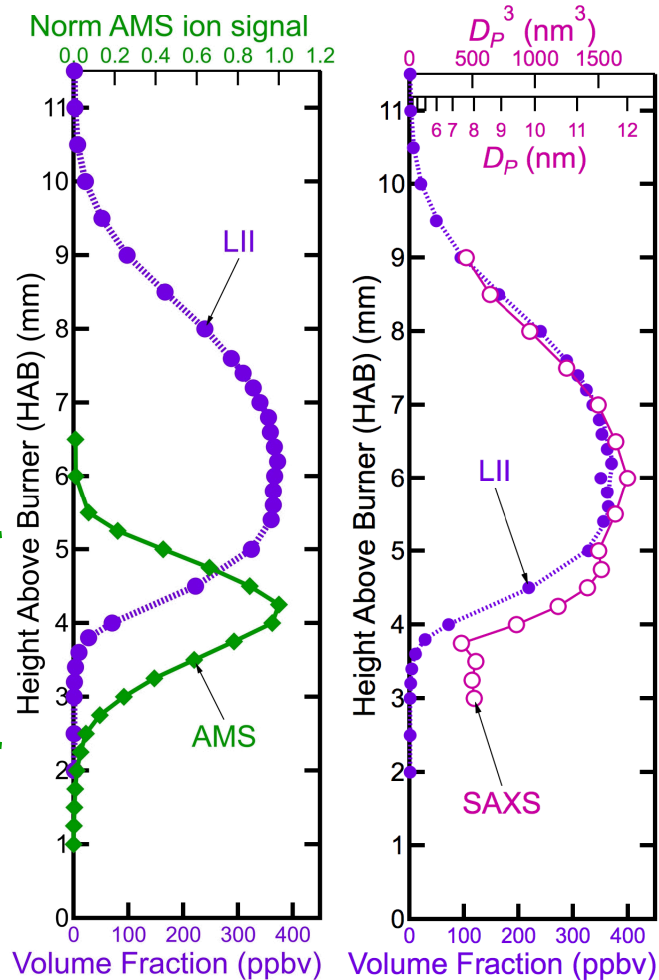
# Soot Particle Growth and Evolution

## Diagnostics for Maturity Level

Incipient particles  
not seen by LII

LII signal from  
mature soot

AMS  
total ion signal  
indicates  
incipient-particle  
formation



Long-range order  
decreases during  
oxidation

Mature soot

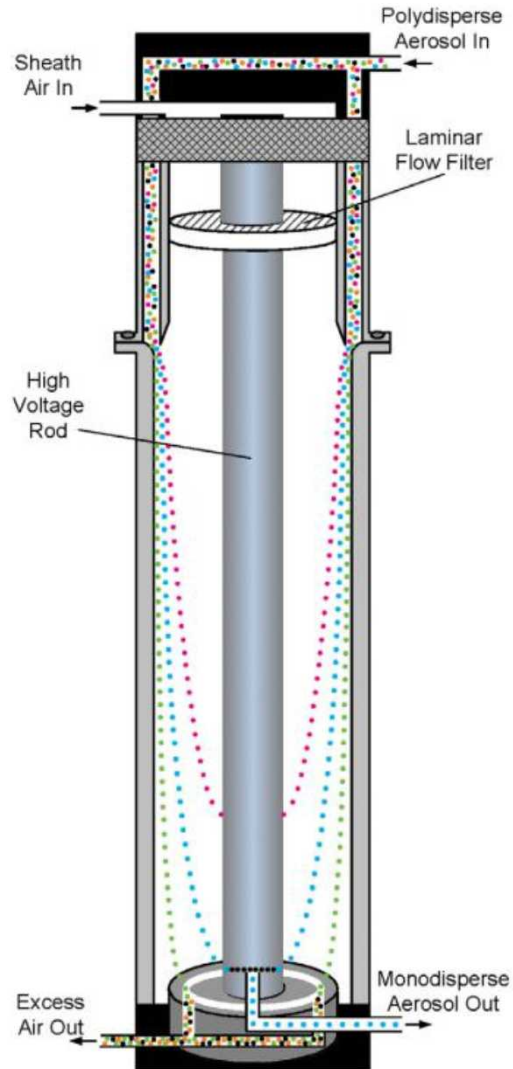
Maturity increases  
 $\beta$  increases  
 $\xi$  decreases

Johansson, El Gabaly, Schrader, Campbell, Michelsen 2017

# Characteristics of Incipient Particles

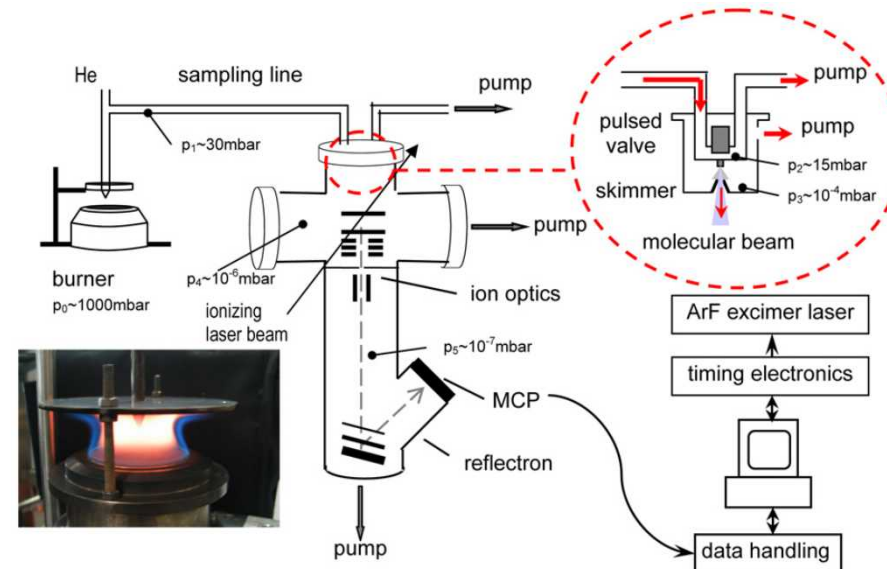
## *Diagnostics for Size Distribution*

Scanning mobility particle sizer



www.TSI.com

Photoionization mass spectrometry



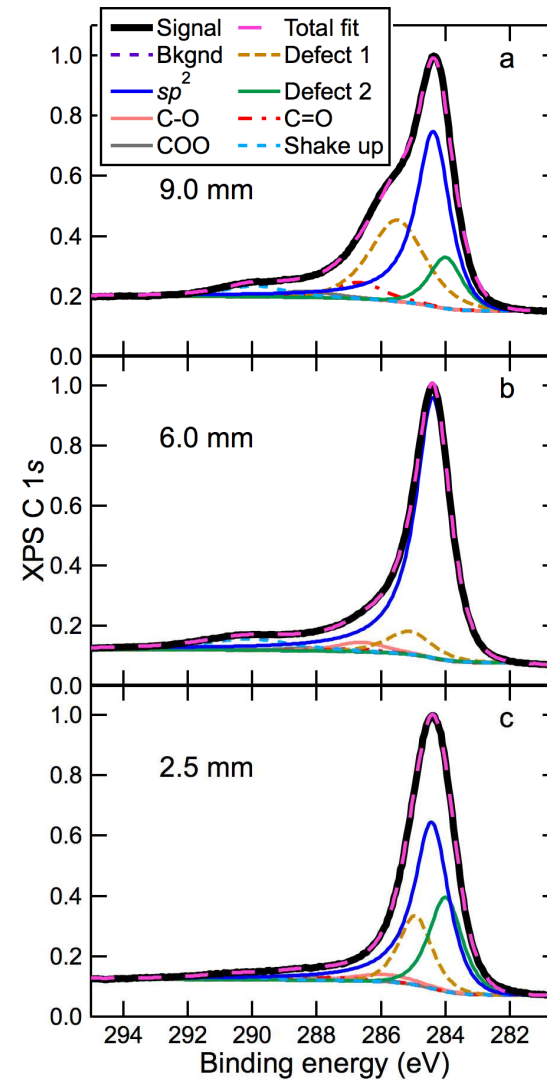
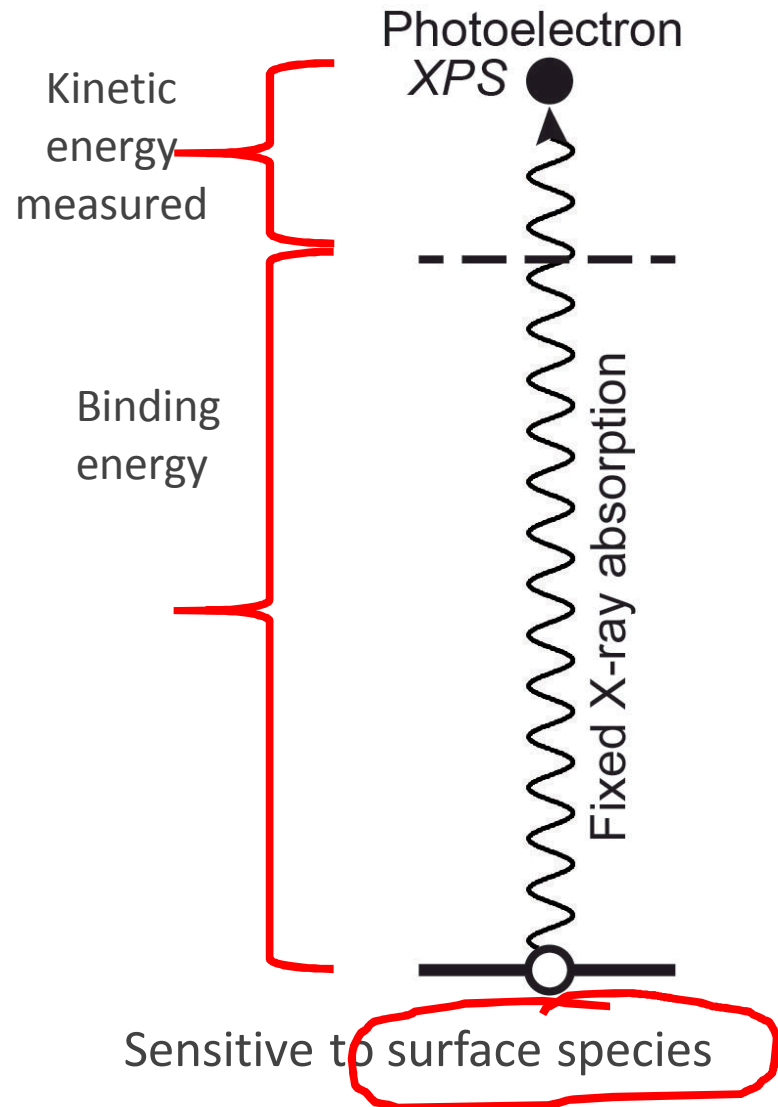
Grotheer, Hoffmann, Wolf, Kanjarkar, Wahl, Aigner 2009



# Characteristics of Incipient Particles

## *Diagnostics for Composition*

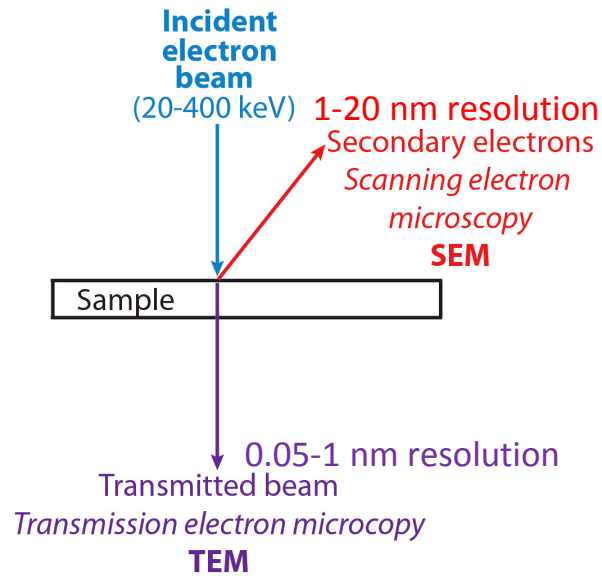
X-ray Photoelectron Spectroscopy (XPS)



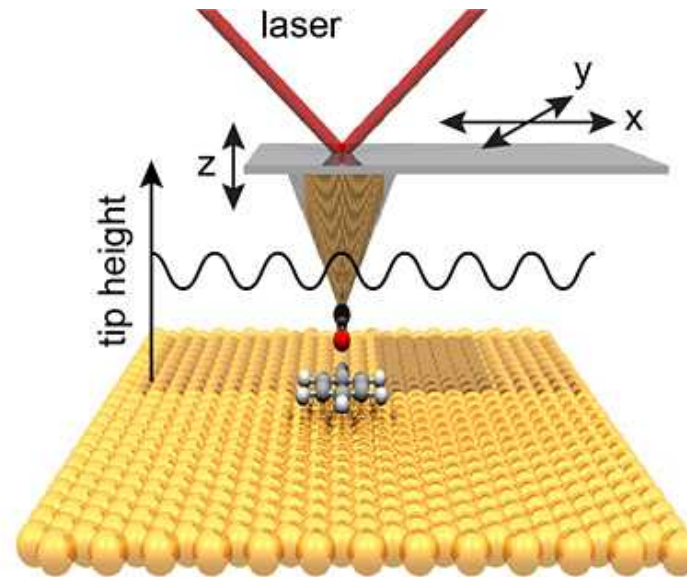
# Characteristics of Incipient Particles

## *Diagnostics for Size and Shape*

### Electron microscopy

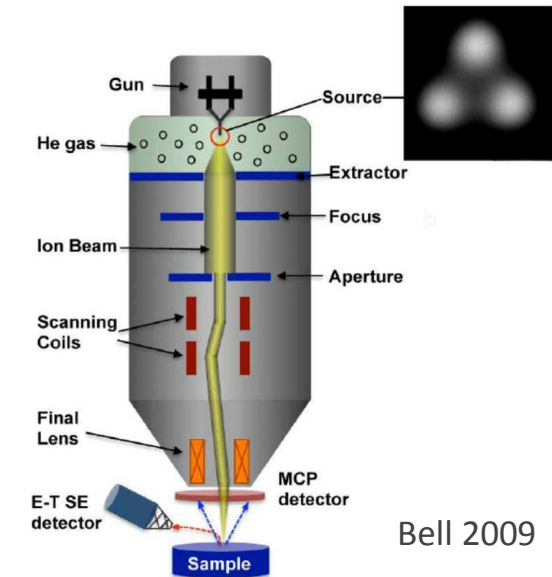


### Atomic force microscopy



News.Berkeley.edu 2013

### Helium ion microscopy

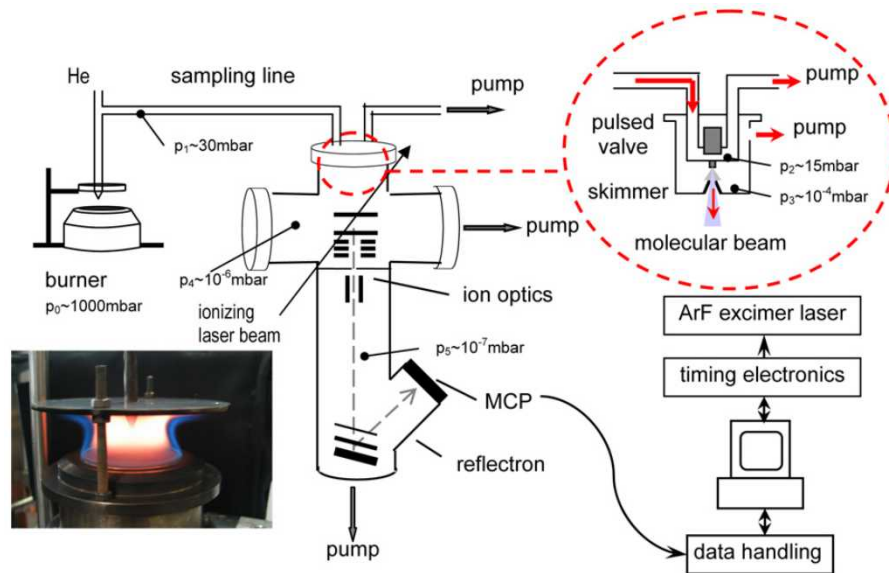


Bell 2009

# Characteristics of Incipient Particles

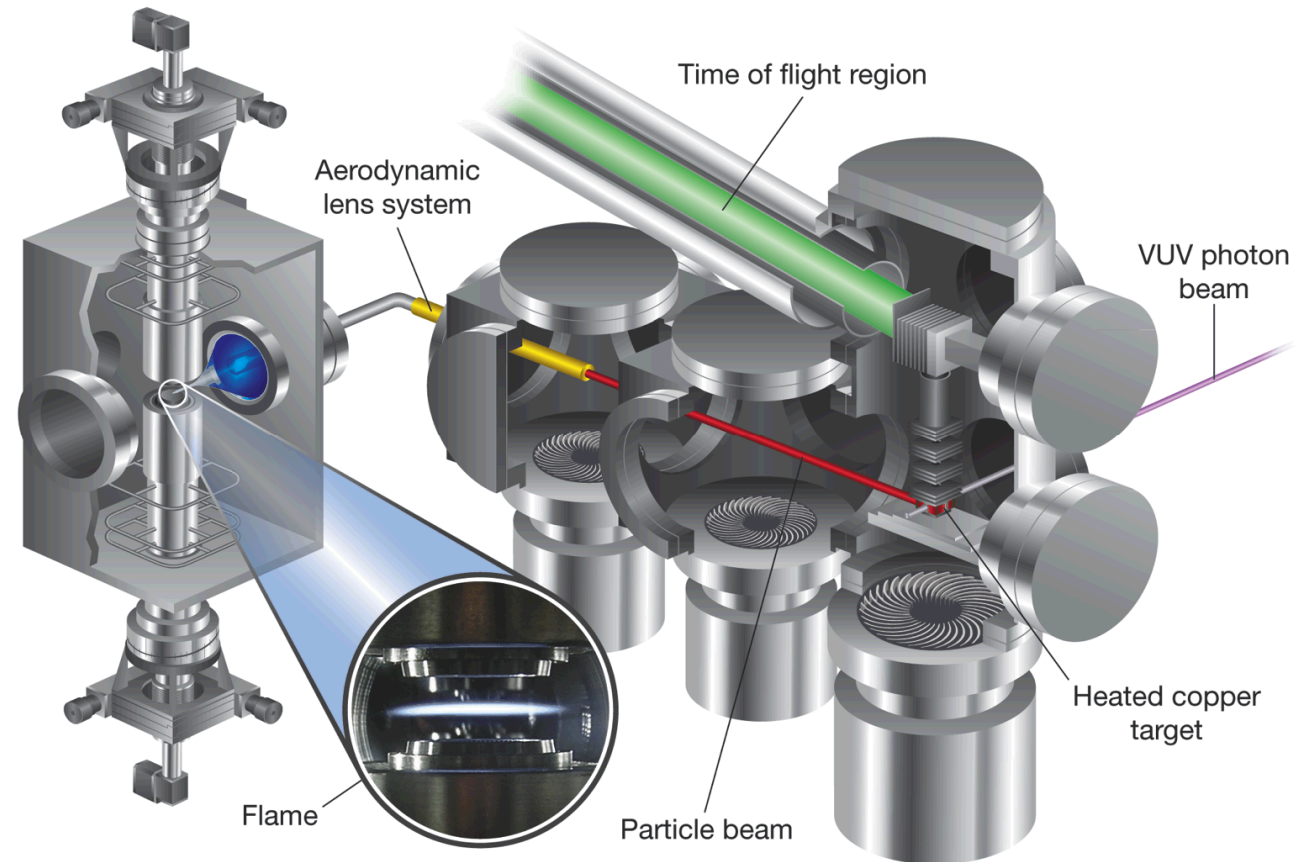
## *Diagnostics for Composition*

### Photoionization mass spectrometry



Grotheer, Hoffmann, Wolf, Kanjarkar, Wahl, Aigner 2009

### Aerosol mass spectrometry



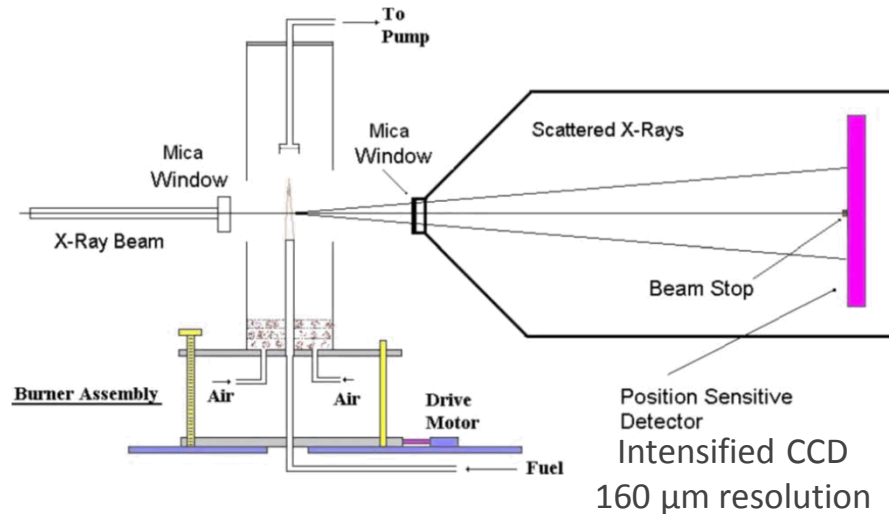
Skeen, Michelsen, Wilson, Popolan, Violi, Hansen 2016

# Characteristics of Incipient Particles

## *Incipient-Particle Size*

Small-angle X-ray scattering

*Scattering of X-rays by electron cloud*

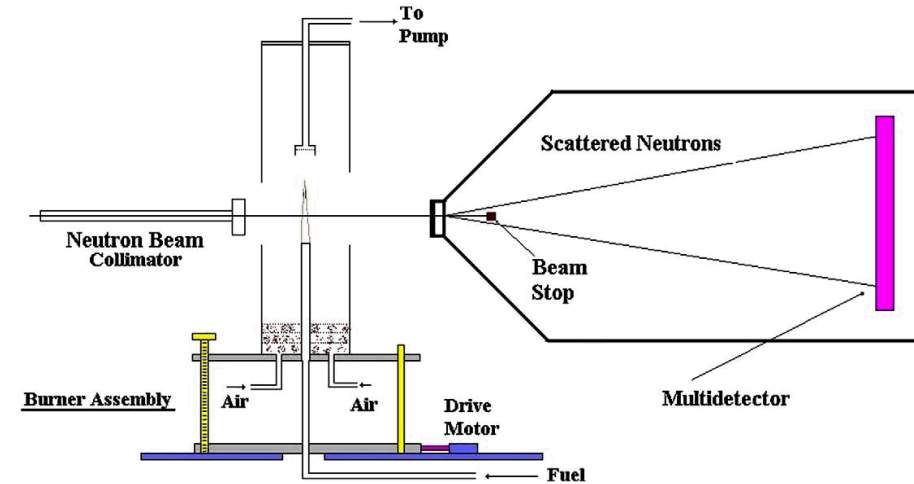


Mitchell, di Stasio, Le Garrec, Florescu-Mitchell,  
Narayanan, Sztucki 2009

- Advantages of SAXS over SANS
  - Better spatial resolution
  - Higher intensity and sensitivity

Small-angle neutron scattering

*Scattering of neutrons by nuclei  
or electron magnetic moment*



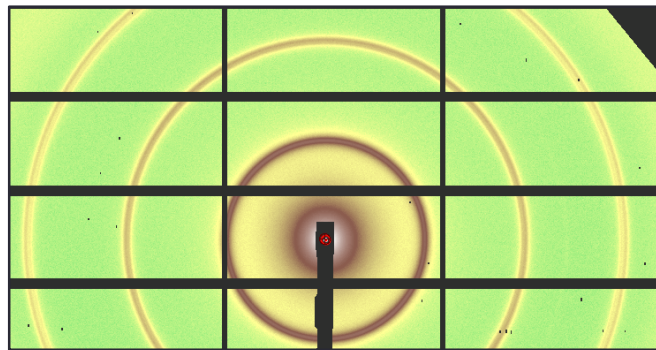
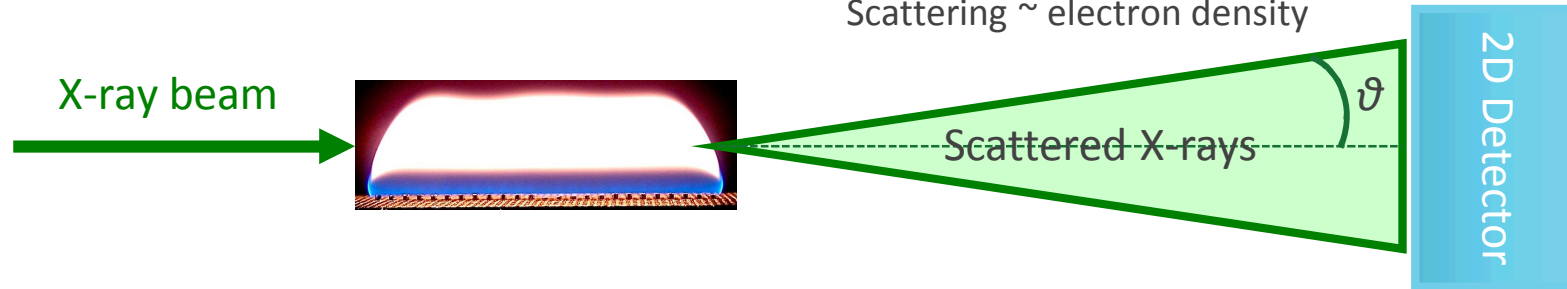
Mitchell, Le Garrec, Florescu-Mitchell, di Stasio 2006

- Advantages of SANS over SAXS
  - Better discrimination against background
  - Lower absorption
  - Better penetration into dense samples
  - Less tendency to ionize/damage samples
  - Potential of isotopic labeling (deuterium)

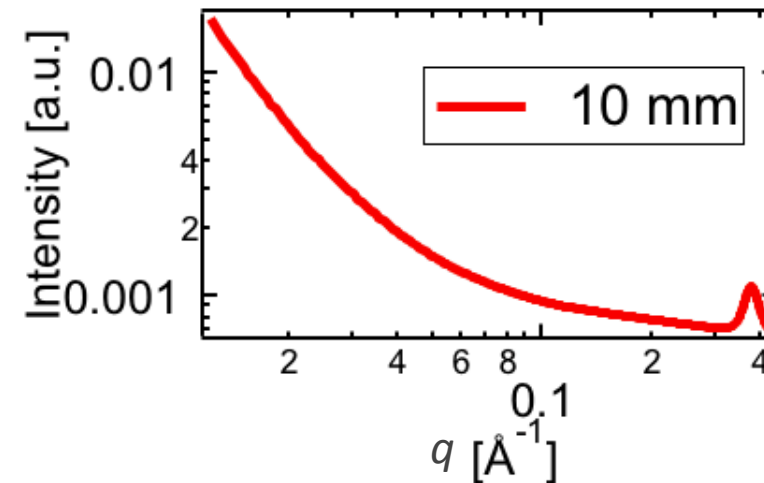
# Characteristics of Incipient Particles

## *Diagnostics for Size Distribution*

Small-angle X-ray scattering (SAXS)  
Scattering  $\sim$  electron density



Random orientations  $\rightarrow$  isotropic scattering



Momentum transfer parameter

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

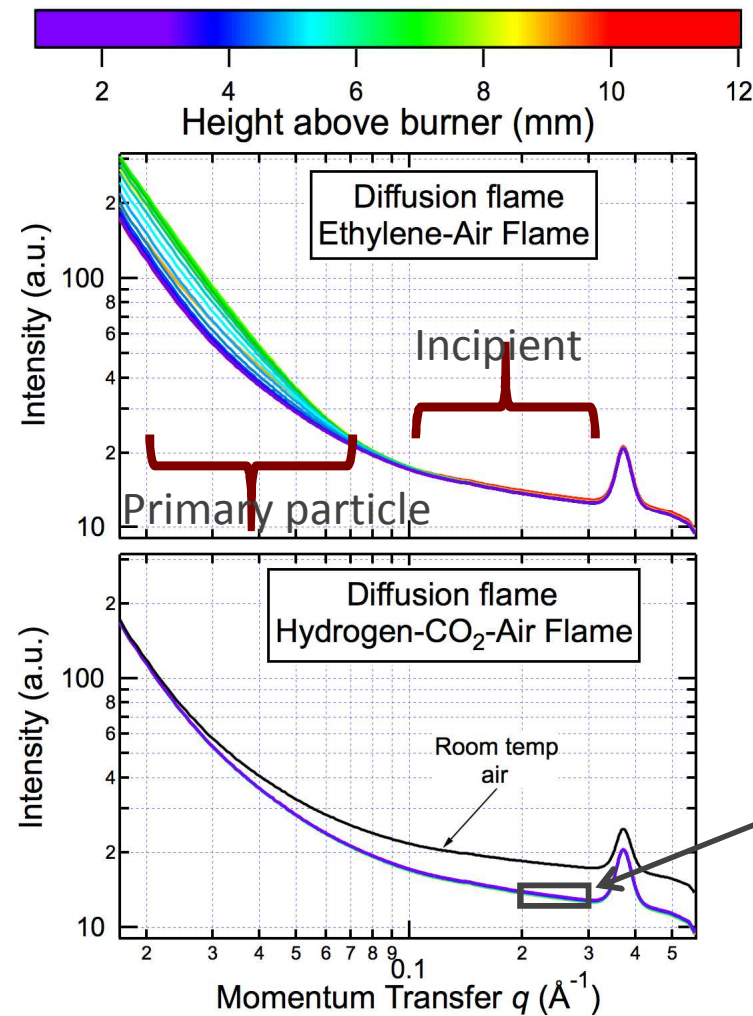
$$L = \frac{2\pi}{q}$$

# Characteristics of Incipient Particles

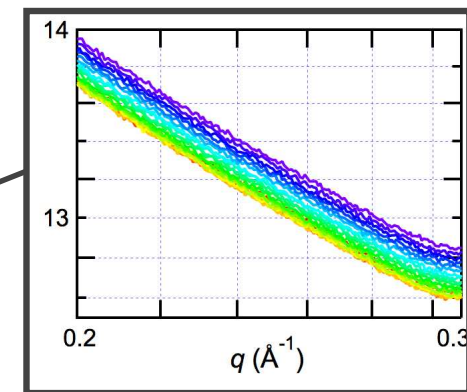
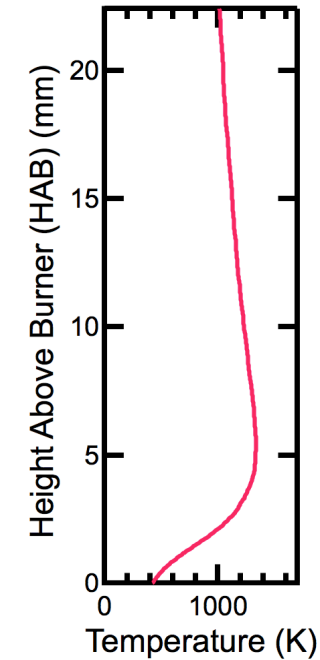
## *Diagnostics for Size Distribution*

Small-angle X-ray scattering (SAXS)

$$L = \frac{2\pi}{q}$$

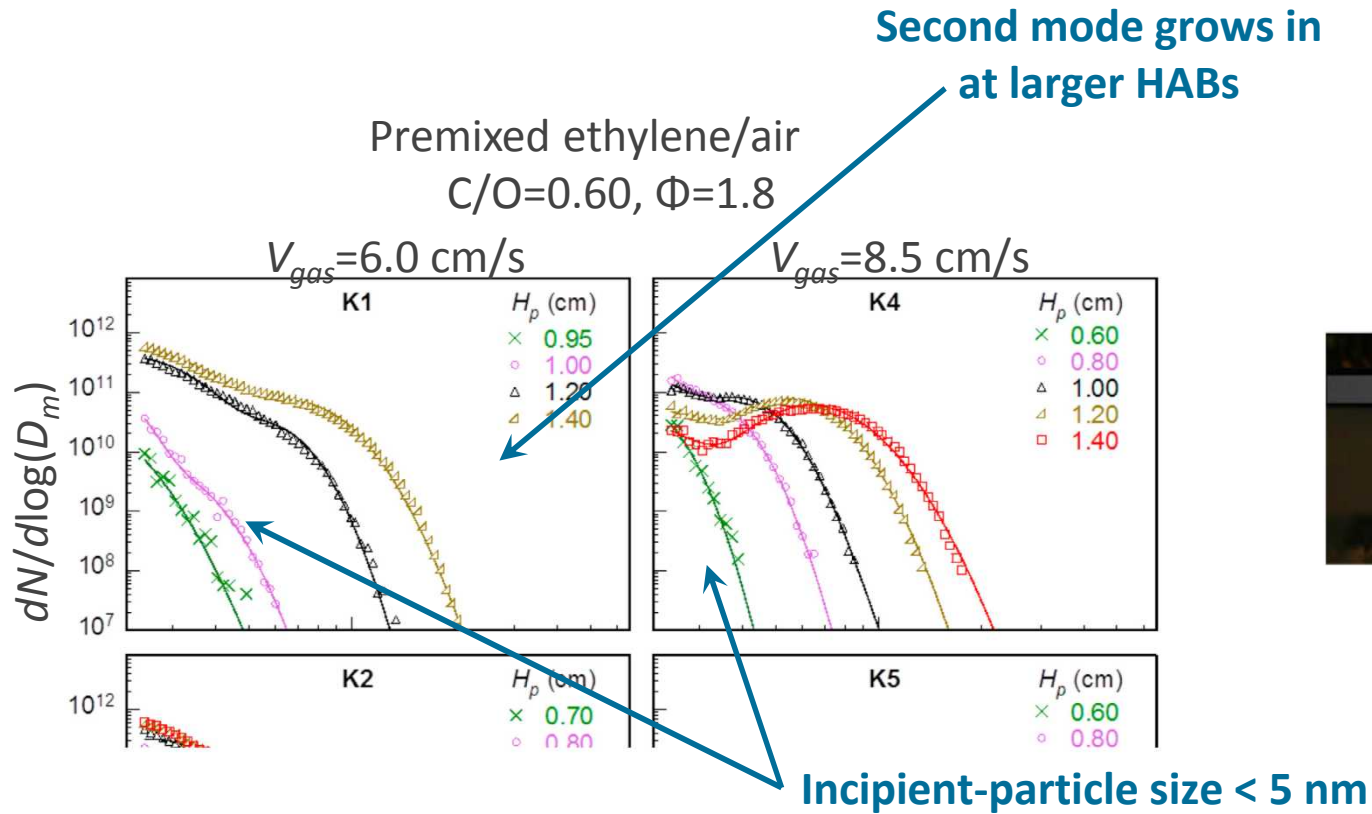


Hydrogen-flame temperature



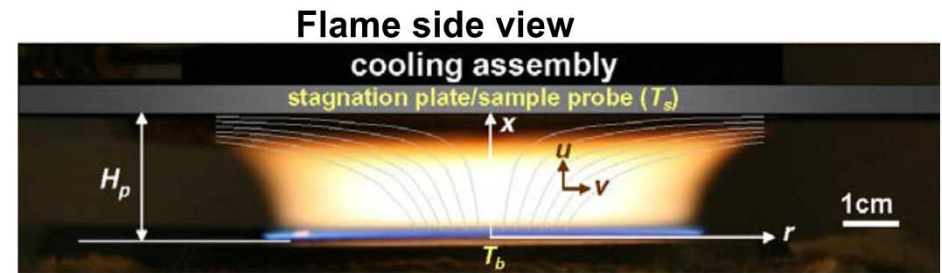
# Characteristics of Incipient Particles

## *Incipient-Particle Size*



Gu, Lin, Camacho, Lin, Shao, Li, Gu, Guan, Huang, Wang 2016

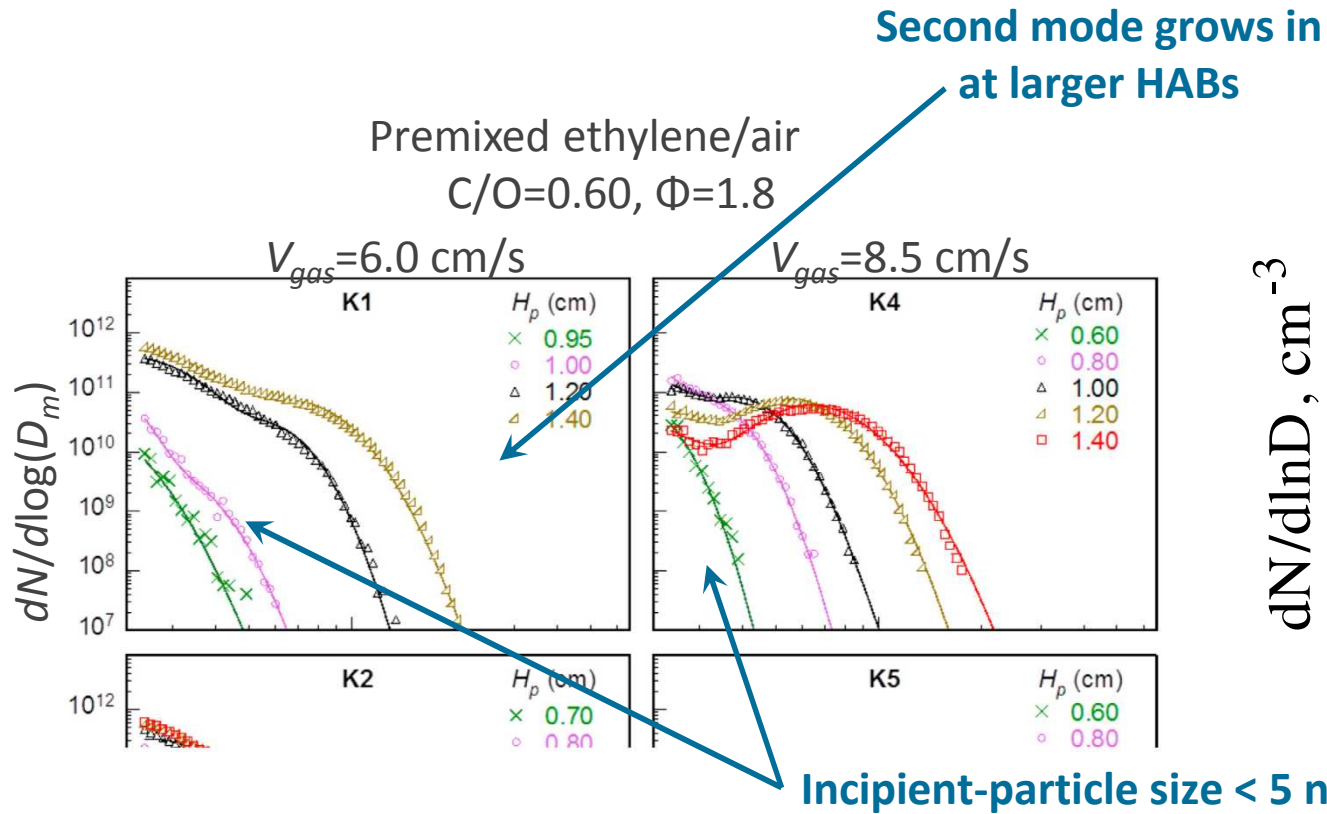
Burner-stabilized stagnation flame



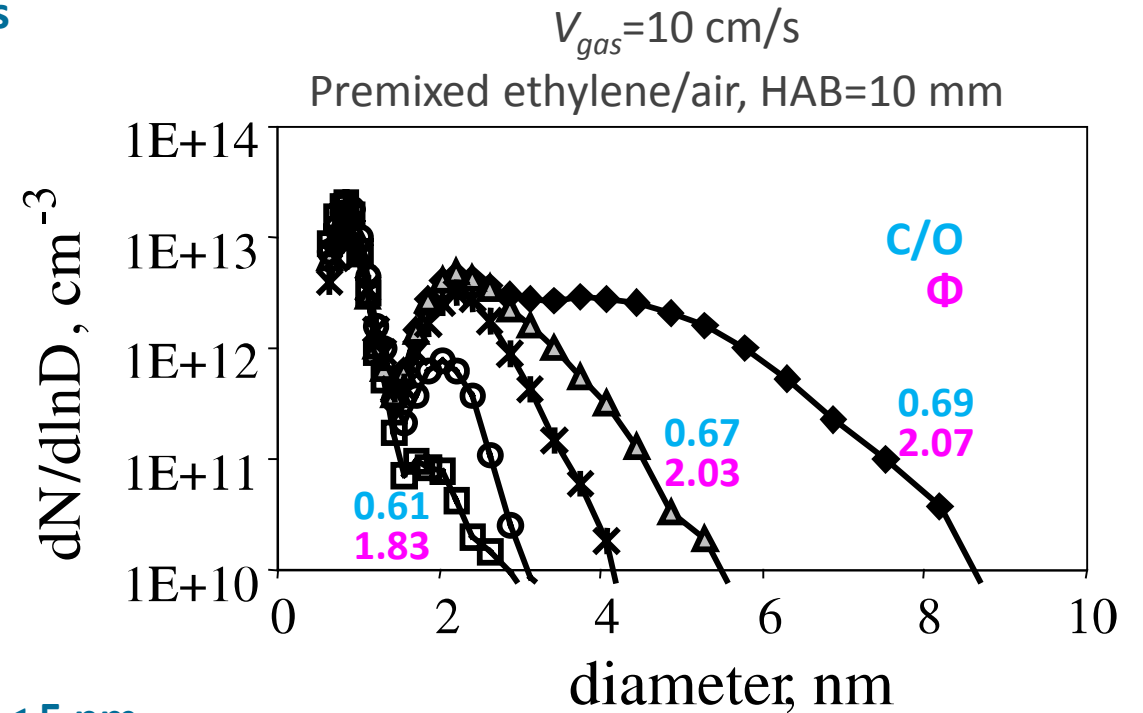
Abid, Camacho, Sheen, Wang 2009

# Characteristics of Incipient Particles

## *Incipient-Particle Size*



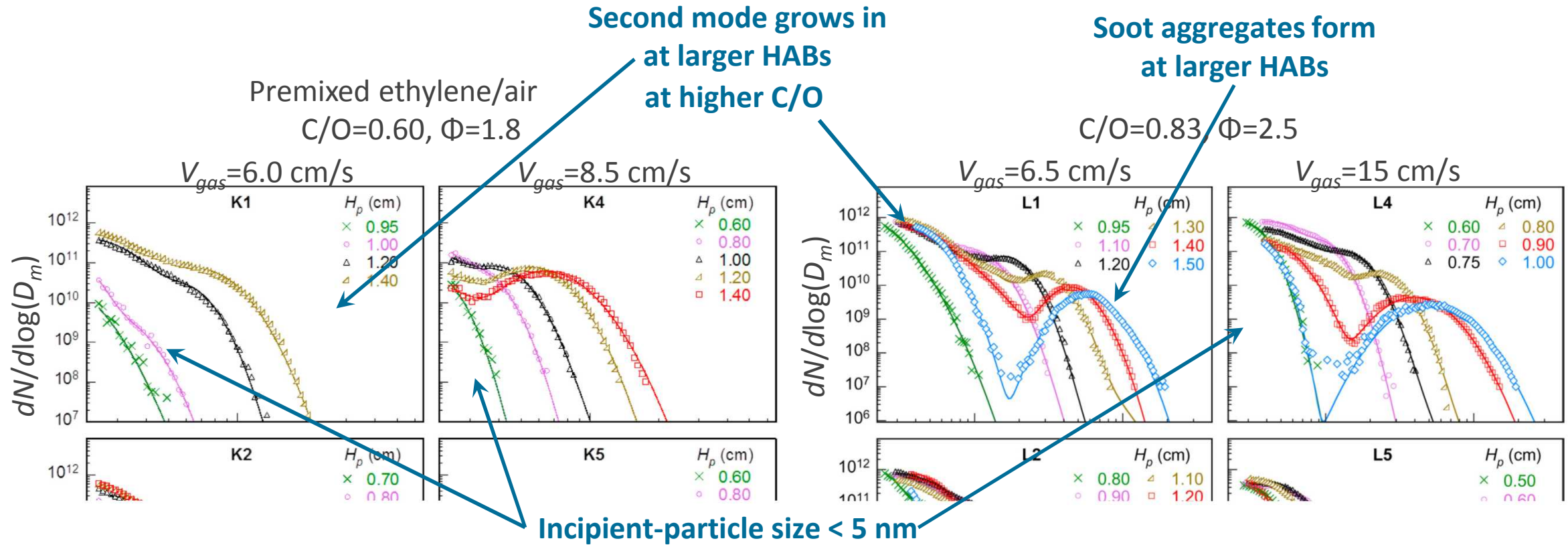
Gu, Lin, Camacho, Lin, Shao, Li, Gu, Guan, Huang, Wang 2016



Sgro, De Filippo, Lanzaolo, D'Alessio 2007

# Characteristics of Incipient Particles

## *Incipient-Particle Size*



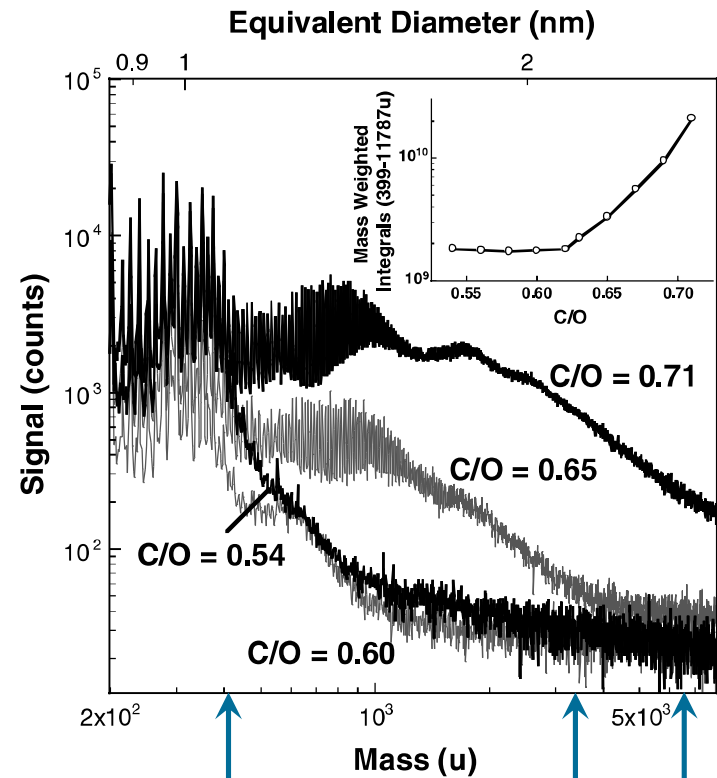
Gu, Lin, Camacho, Lin, Shao, Li, Gu, Guan, Huang, Wang 2016

# Characteristics of Incipient Particles

## *Incipient-Particle Size*

Photoionization mass spectrometry

Premixed ethylene/air



Particle sizes assuming density of 1.3 g/cm<sup>3</sup>

1 nm

2 nm 2.5 nm

Thierley, Grotheer, Aigner, Yang, Abid, Zhao, Wang 2007