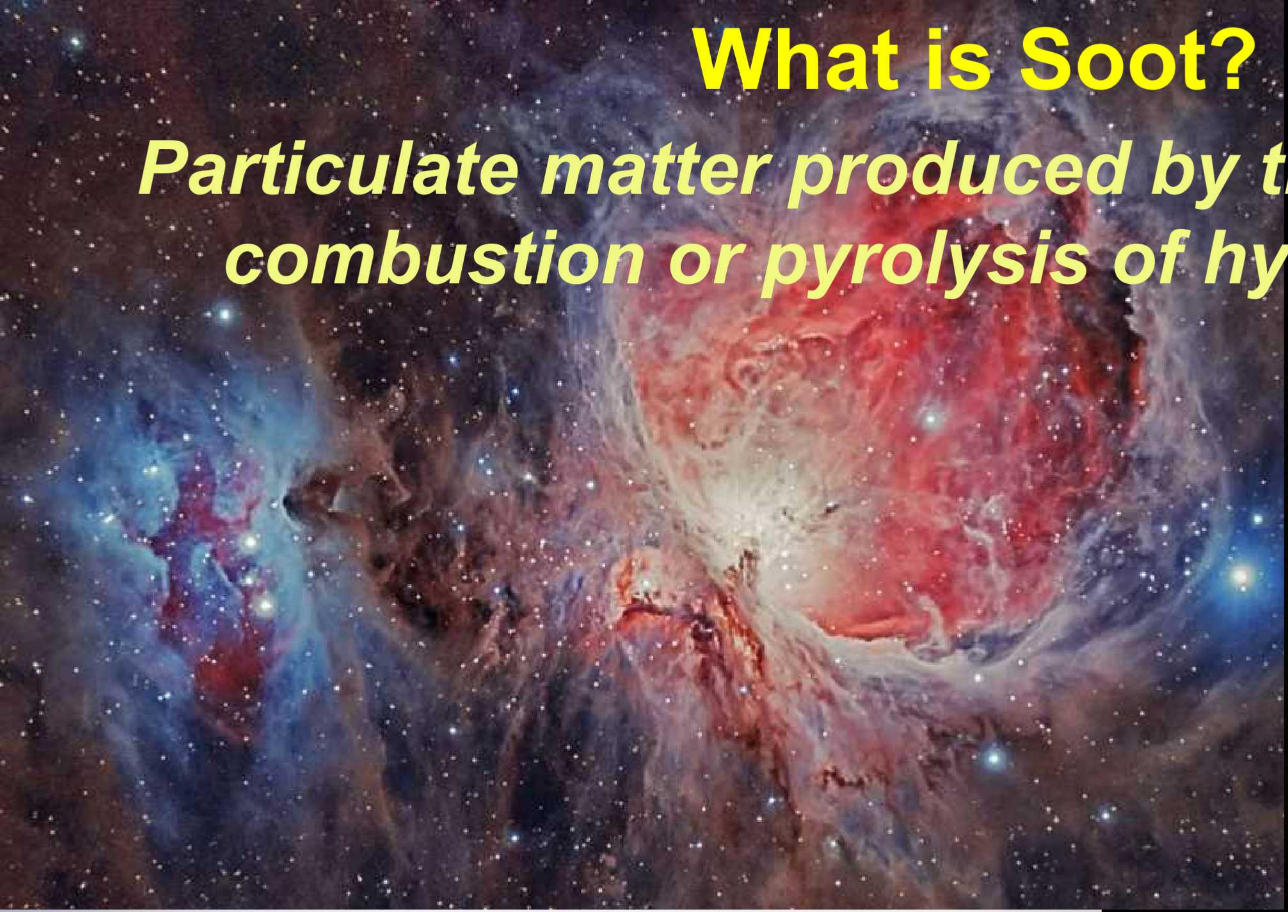
SAND2019-7730C

Using Vacuum Ultraviolet and X-Ray Tools to Solve the Mystery of Soot Formation

What is Soot?

Particulate matter produced by the incomplete combustion or pyrolysis of hydrocarbons



Soot: The Good Side

- Commercial and personal uses

Tattoozza.com

Sally Smith, Art studio, Berkeley, CA

  - Pigment in inks and dyes
  - Filler to reinforce rubber products

  - Radiative heat-transfer medium in boilers and furnaces

Glass furnace
LumaSenseInc.com, 2019

Soot: The Good Side

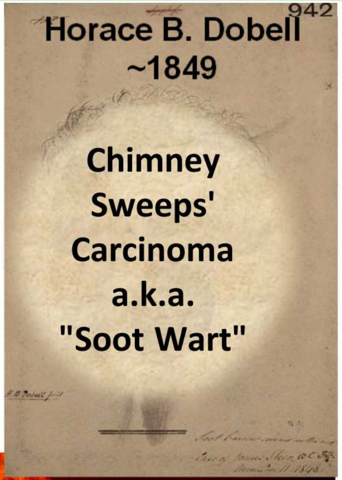
- Positive impact on soil and water

Ultrakulture.com

  - May increase fertility of soils
  - In small amounts, may sequester pollutants in natural water supplies

Soot: The Other Side


Reveal, 2015


942

Horace B. Dobell
~1849

Chimney
Sweeps'
Carcinoma
a.k.a.
"Soot Wart"

- Negative impact on health and safety
  - Increases risk of pulmonary disease
  - Increases risk of cardiovascular disease
  - Provides vector for other toxins and carcinogens
  - Reduces fire safety and control


Camp Fire, Washington Post, 2018

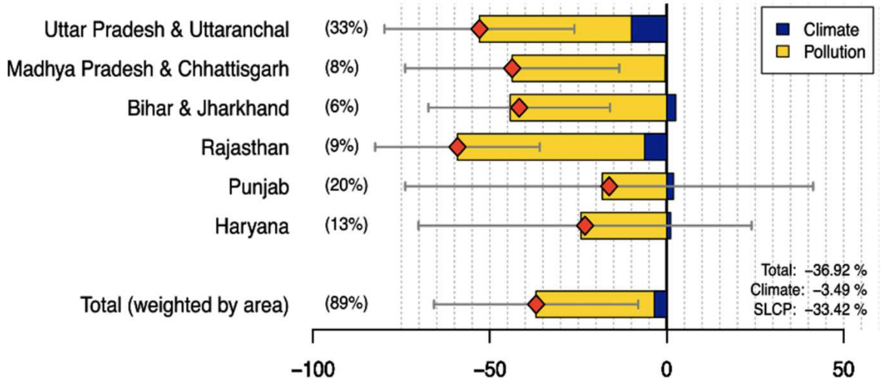
- Negative impact on air quality
  - Decreases indoor air quality
  - Decreases ambient air quality
  - Decreases visibility


Camp Fire, sfbws.com, 2018

Soot: The Other Side

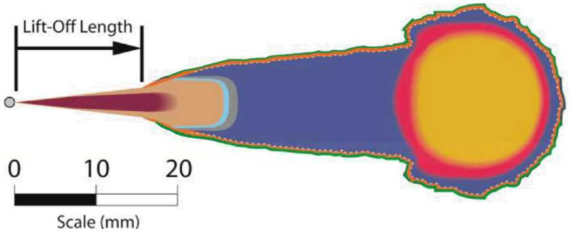
- Negative impact on agriculture
  - Reduces crop yield

Effect of Soot and Ozone on Wheat Crops in India



Percent reduction in crop yield 1980 - 2010
Burney & Ramanathan, 2014

- Negative impact on energy efficiency
  - Reduces combustion efficiency
  - Increases radiative heat losses

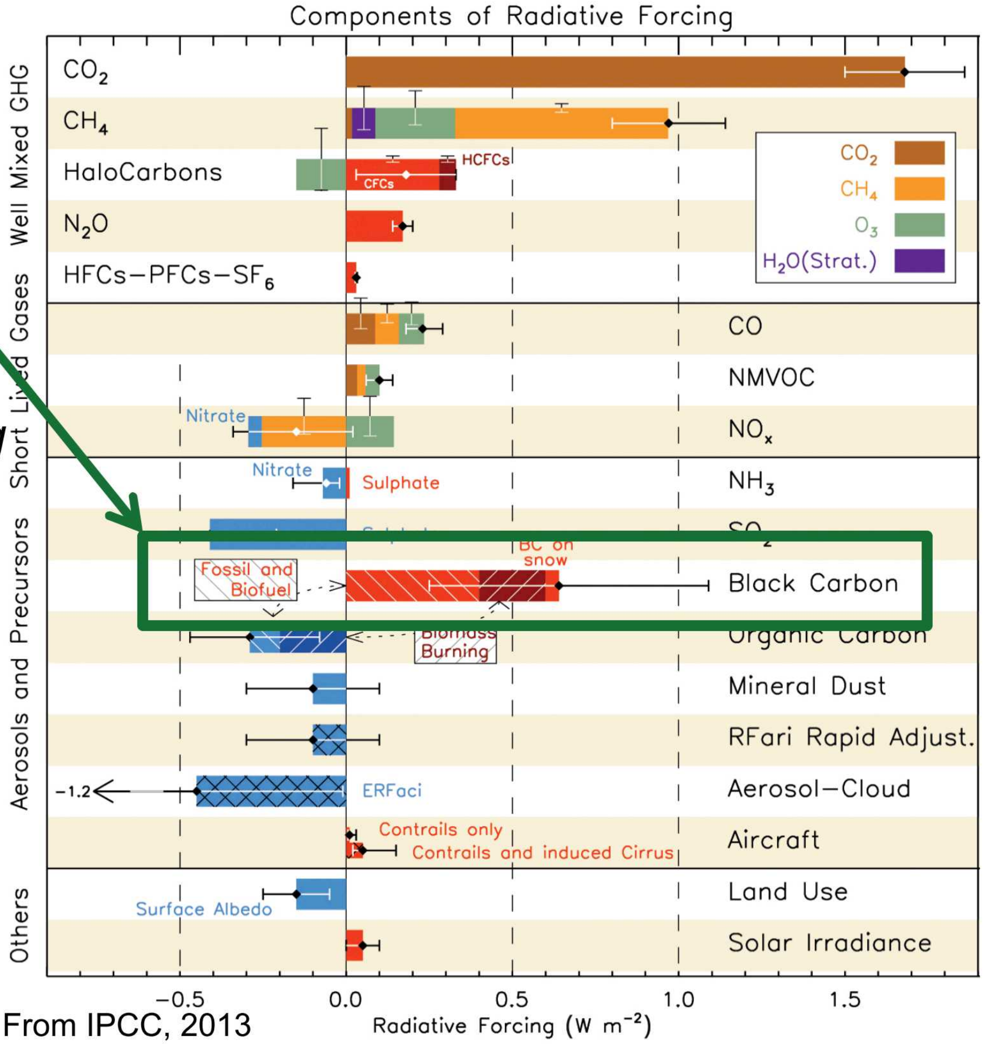


Dec, 1997, O'Connor & Musculus, 2013

- Negative impact on Priuses
  - Increases stress of Prius drivers

Soot: The Other Side

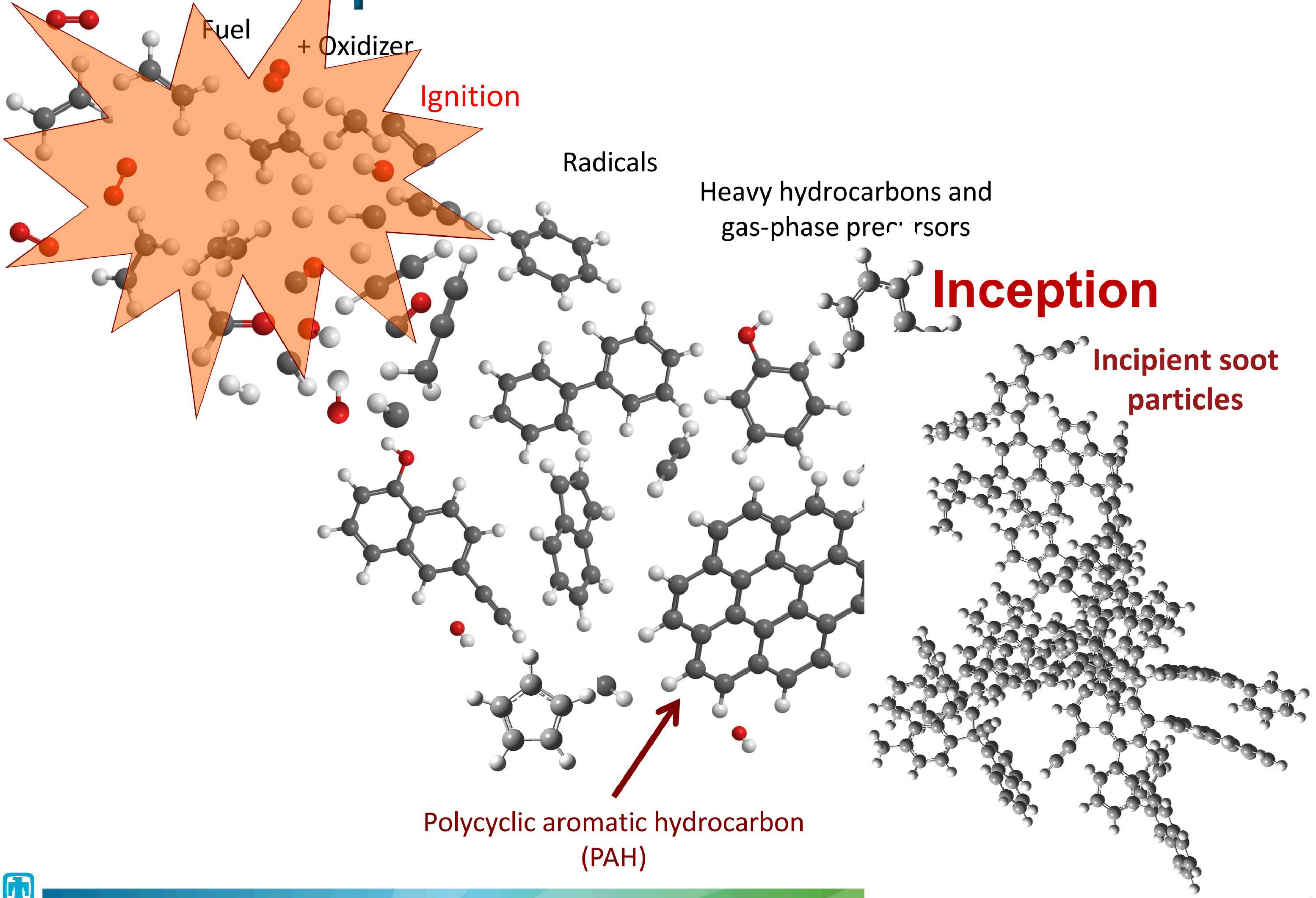
- Negative impact on climate
  - Soot absorbs light – *heating effect*
  - Soot lowers snow reflectivity - *heating*
  - Soot increases glacial melt – *heating*
  - Soot influences clouds – *heating/cooling*



From IPCC, 2013

- Why focus on soot?
  - Short atmospheric lifetime (~1 wk)
  - Near-term climate-change mitigation candidate

Incipient Particle Formation



Fuel

+ Oxidizer

Ignition

Radicals

Heavy hydrocarbons and gas-phase precursors

Inception

Incipient soot particles

Polycyclic aromatic hydrocarbon (PAH)

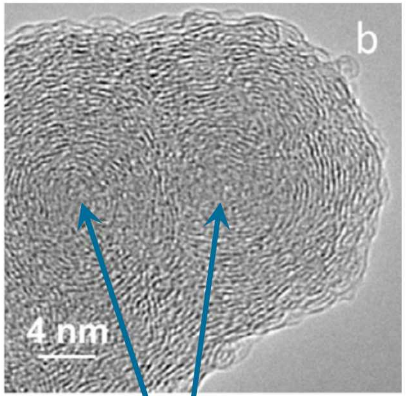
What is Soot?

Mature soot particles – Black carbon

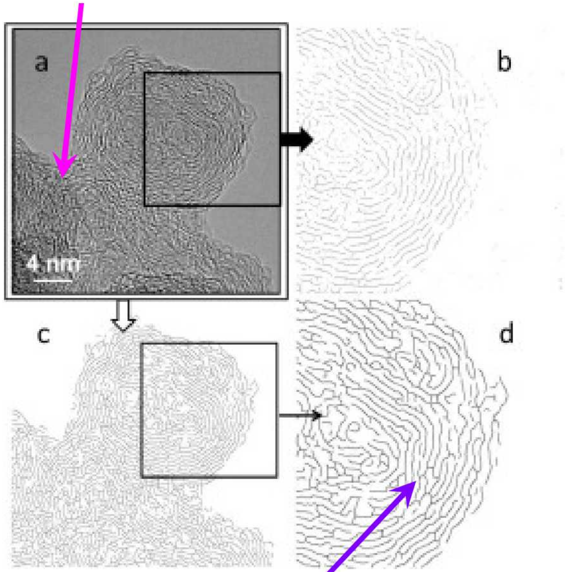
Refractory solid
Absorb strongly of broad wavelength range
C/H ratio of 10-20
Density ~1.8-1.9 g/cm^3

Primary particles: 10-50 nm
Aggregates: 100 to 600 nm

Graphitic overlayers hold aggregate together

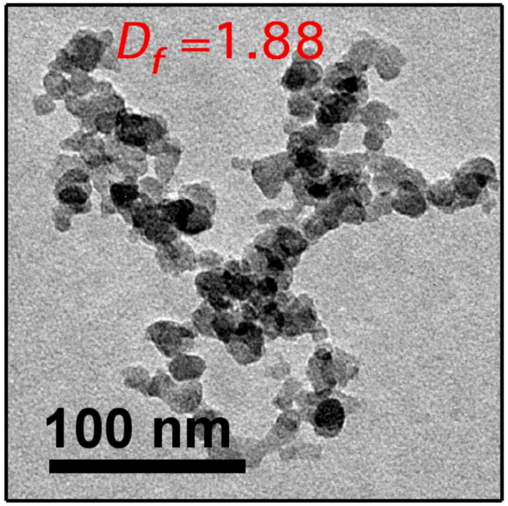


Disordered foci or growth centers, 1-6 nm in diameter



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

Apicella et al., *Proc. Combust. Inst*. 2015



Bambha et al., *Appl. Phys. B* 2013

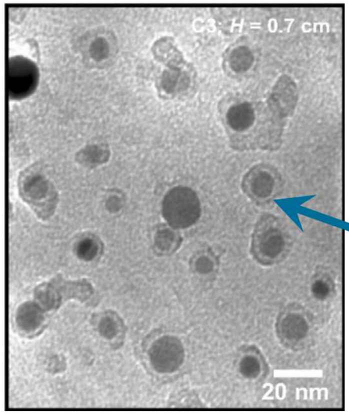
What is Soot?

Incipient soot particles

Incipient particles: 1-6 nm

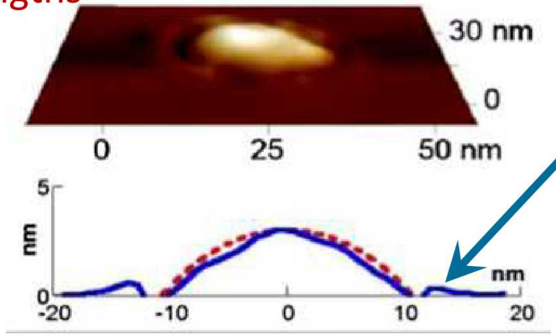
Absorb in UV, weakly at longer wavelengths
C/H ratio of 1.5-2.5
Density ~1.3 g/cm^3

Transmission electron microscopy
(TEM)



Halo suggests spreading and fluidity

Atomic force microscopy
(AFM)



Abid et al., *Combust. Flame* 2008

What is Soot?

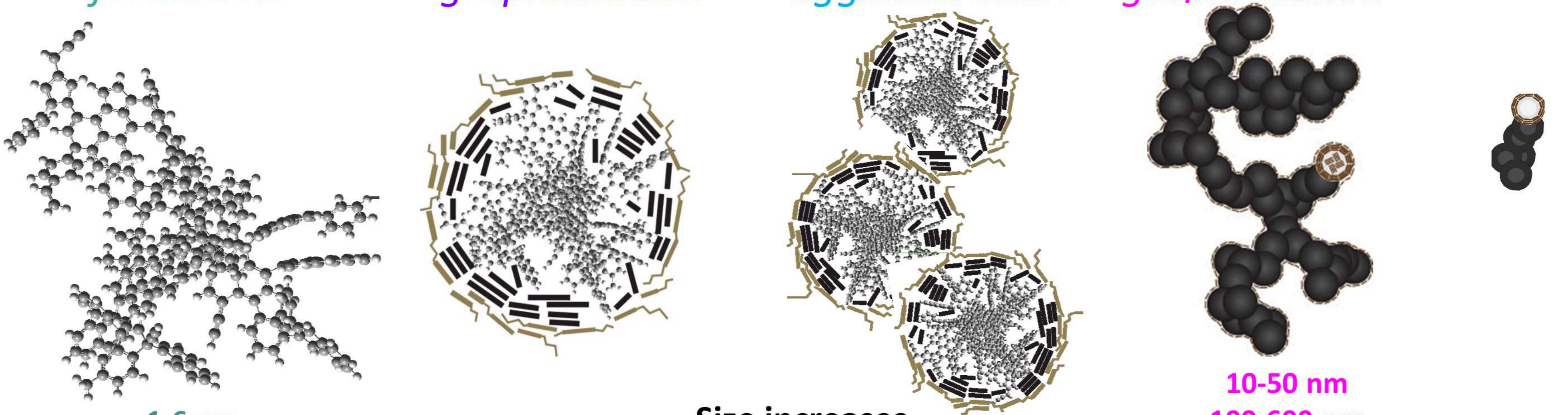
Soot inception; Incipient soot formation

Coalescence, surface growth, graphitization

Primary-particle agglomeration

Surface growth, aggregation, graphitization

Particle oxidation



1-6 nm — **Size increases** — **10-50 nm**
100-600 nm

Morphology changes

Liquid — **Consistency changes** — **Refractory solid**

1.5-2.5 — **C/H increases** — **10-20**

Fine structure changes; long-range order increases

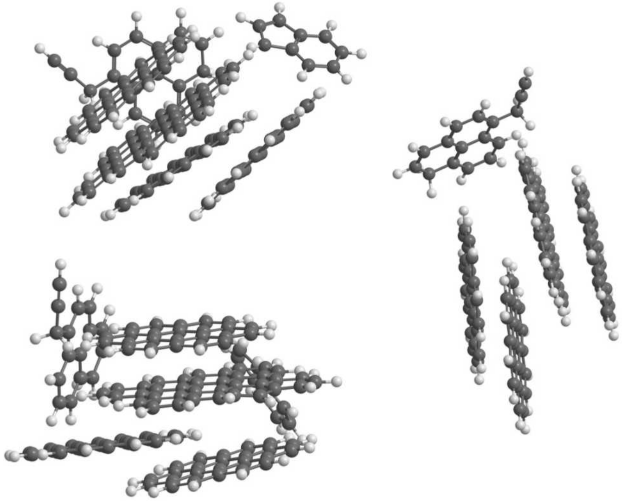
1.3 — **Density increases** — **1.8-1.9**

Surface reactivity decreases

Optical properties change

Proposed Inception Mechanisms

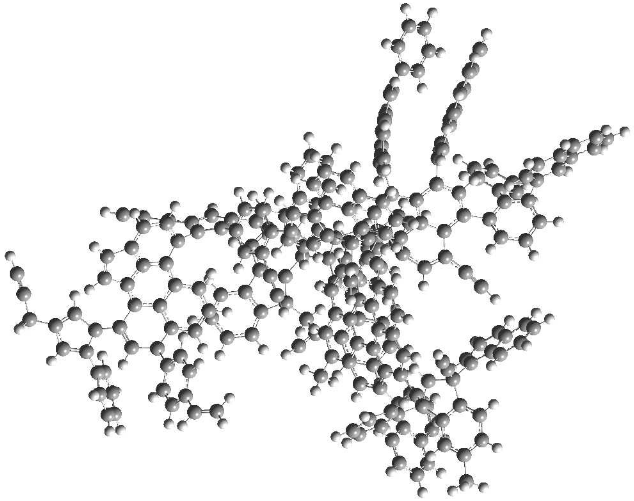
Thermodynamically driven



Nucleation of stable PAH species
Bound by dispersive forces

Species available too small to condense at relevant temperatures (1400-1700K)

Kinetically controlled



Chemical reactions between precursors
Clusters of aliphatic and aromatic content
Covalently bound

Reactions between stable precursors too slow

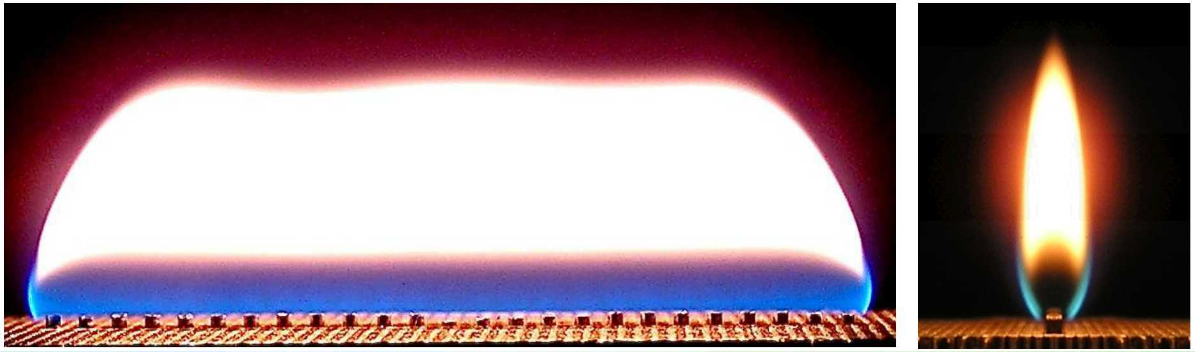
Particle-Inception Studies

Co-flow diffusion flame

Inverse diffusion flame

Counter-flow diffusion flame

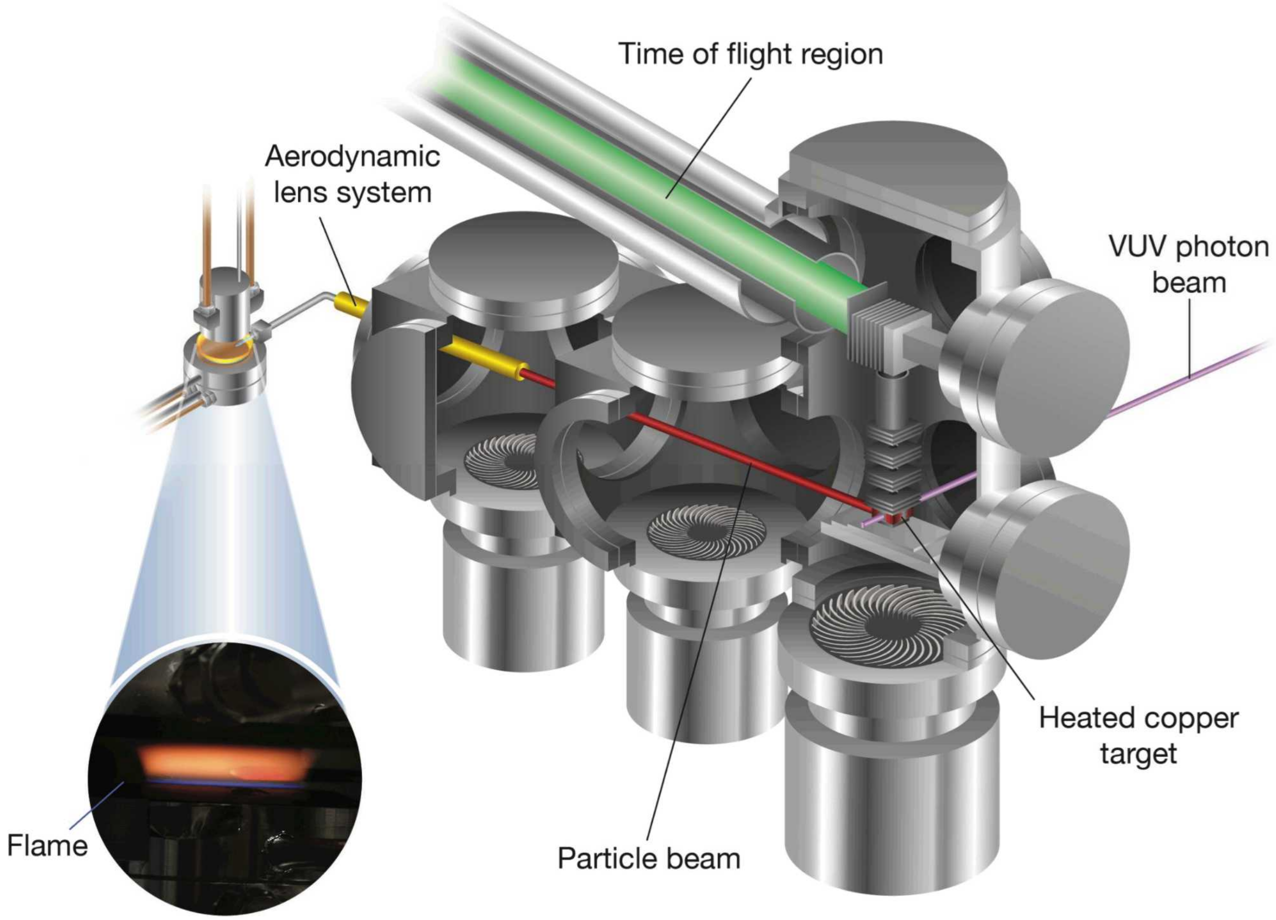
Premixed flame



Partially premixed diffusion flame

Incipient-Particle Composition

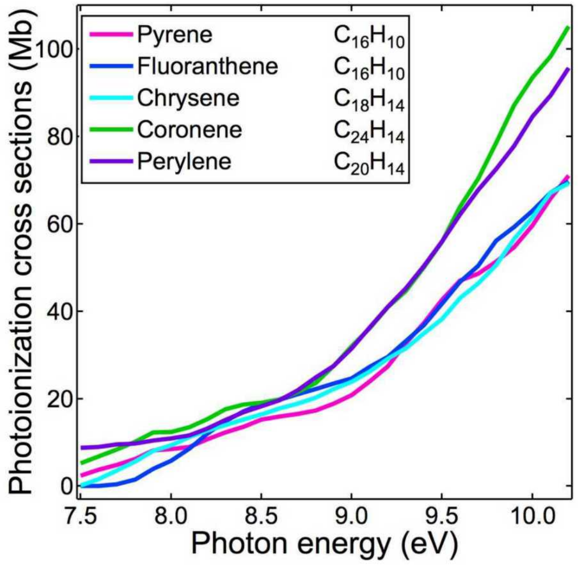
Aerosol Mass Spectrometry using VUV Photoionization (VUV-AMS)
Beamline 9.0.2 at the Advanced Light Source/LBL



Our flame

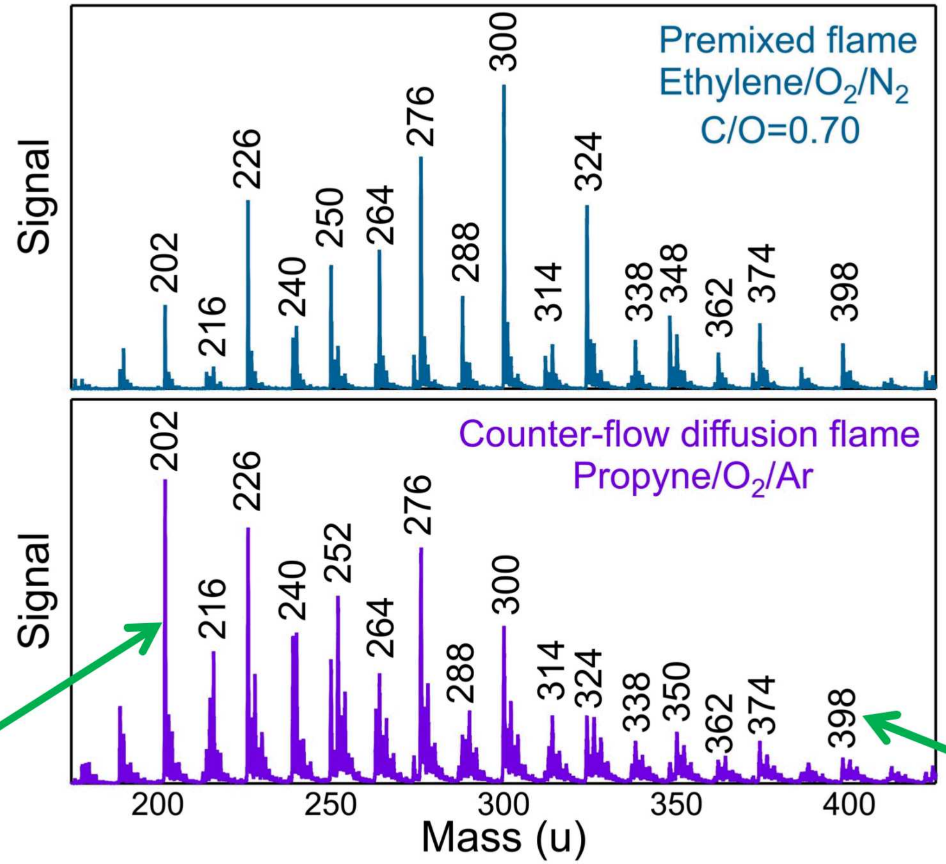
Kevin Wilson's machine at the ALS

Tunable VUV



Incipient-Particle Composition

Aerosol Mass Spectrometry using VUV Photoionization (VUV-AMS)
ALS BL 9.0.2



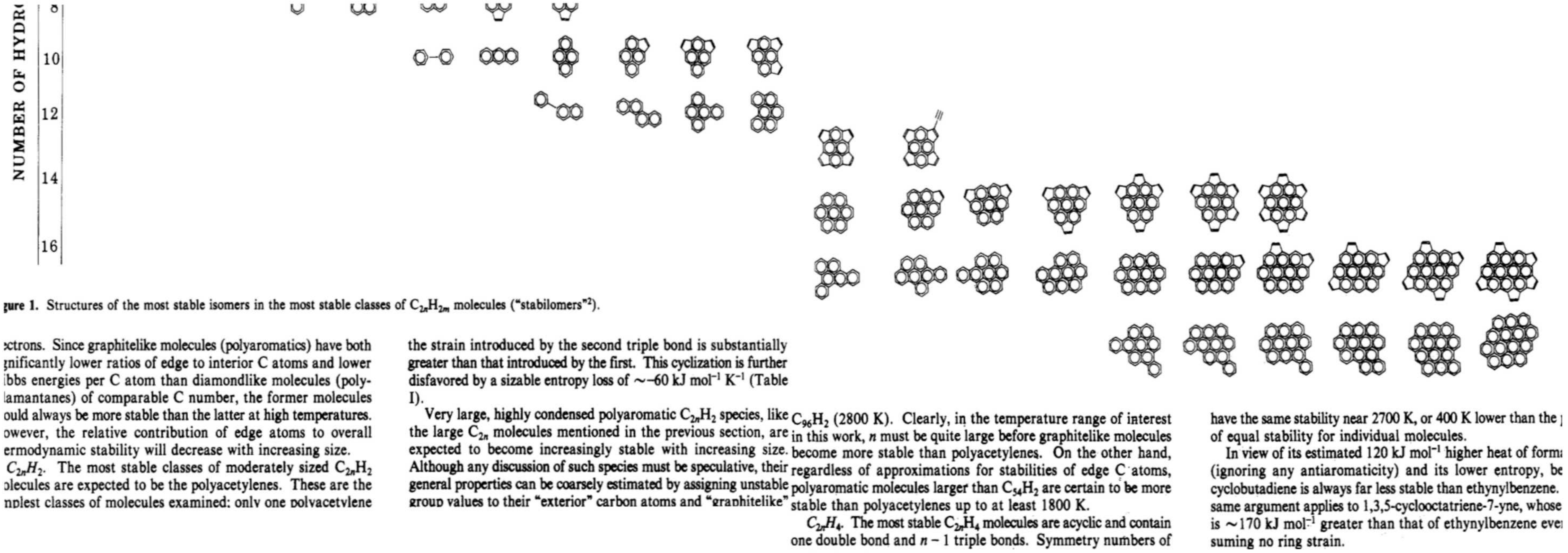
~4-ring PAH

~10-ring PAH

Johansson et al., *Proc. Combust. Inst*. 2017

Incipient-Particle Composition

Stabilomers



ure 1. Structures of the most stable isomers in the most stable classes of $C_{2n}H_{2m}$ molecules ("stabilomers"[2]).

ctrons. Since graphitelike molecules (polyaromatics) have both nificantly lower ratios of edge to interior C atoms and lower bbs energies per C atom than diamondlike molecules (polylamantanes) of comparable C number, the former molecules ould always be more stable than the latter at high temperatures. owever, the relative contribution of edge atoms to overall ermodynamic stability will decrease with increasing size.

$C_{2n}H_2$. The most stable classes of moderately sized $C_{2n}H_2$ olecules are expected to be the polyacetylenes. These are the nplest 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 ~−60 kJ mol^{-1} K^{-1} (Table I).

Very large, highly condensed polyaromatic $C_{2n}H_2$ species, like the large C_{2n} molecules mentioned in the previous section, are expected to become increasingly stable with increasing size. Although any discussion of such species must be speculative, their general properties can be coarsely estimated by assigning unstable group values to their "exterior" carbon atoms and "graphitelike"

$C_{96}H_2$ (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

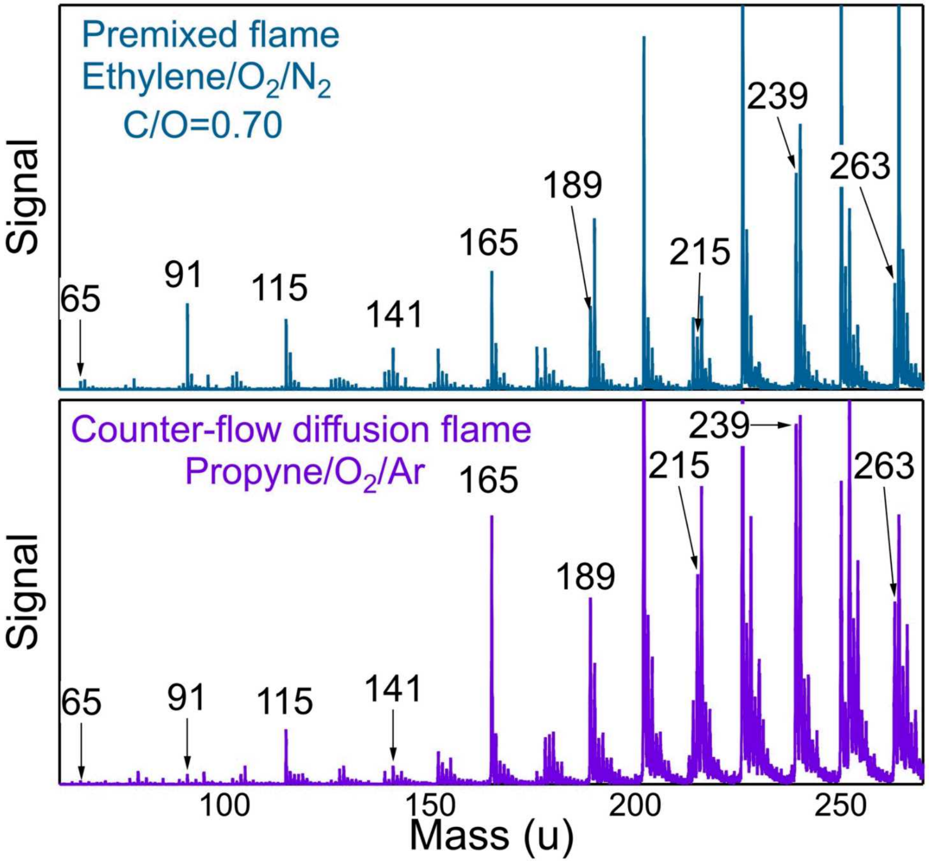
have the same stability near 2700 K, or 400 K lower than the of equal stability for individual molecules.

In view of its estimated 120 kJ mol^{-1} higher heat of form (ignoring any antiaromaticity) and its lower entropy, be cyclobutadiene is always far less stable than ethynylbenzene. same argument applies to 1,3,5-cyclooctatriene-7-yne, whose is ~170 kJ mol^{-1} greater than that of ethynylbenzene eve suming no ring strain.

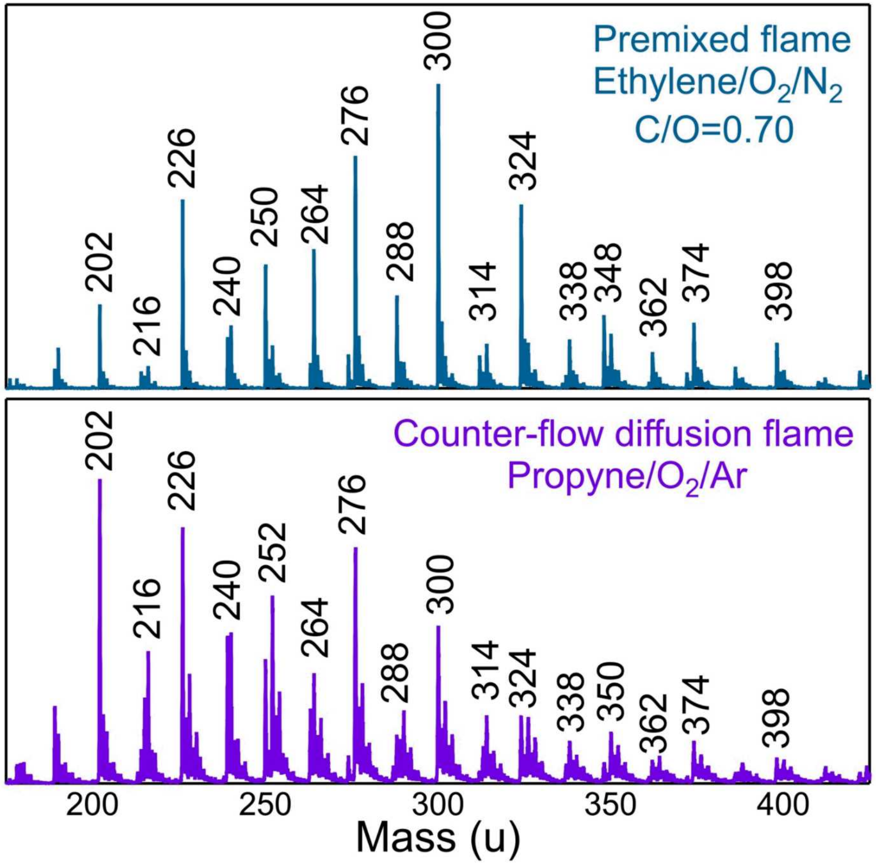
Stein, Fahr 1985

Incipient-Particle Composition

Aerosol Mass Spectrometry using VUV Photoionization (VUV-AMS)
ALS BL 9.0.2



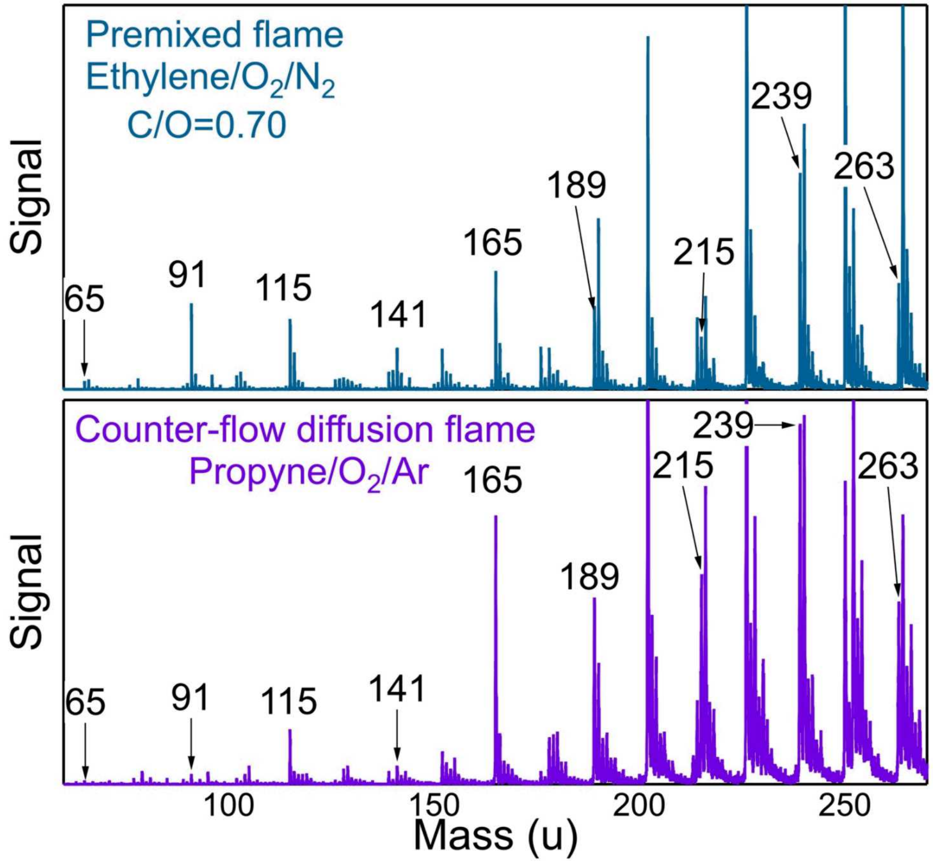
Johansson et al., *Science* 2018



Johansson et al., *Proc. Combust. Inst*. 2017

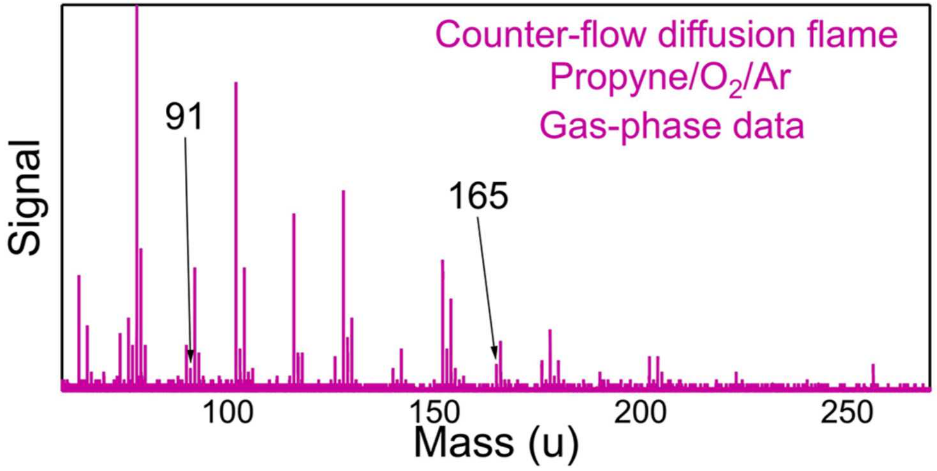
Incipient-Particle Composition

Aerosol mass spectrometry



Johansson et al., *Science* 2018

Gas phase
Molecular beam mass spectrometry

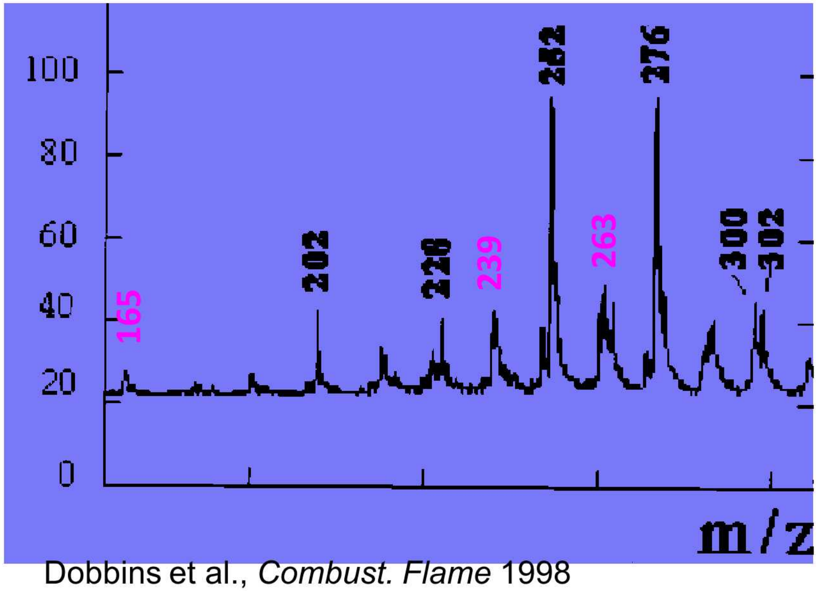


Courtesy of Nils Hansen and Kai Moshammer

Incipient-Particle Composition

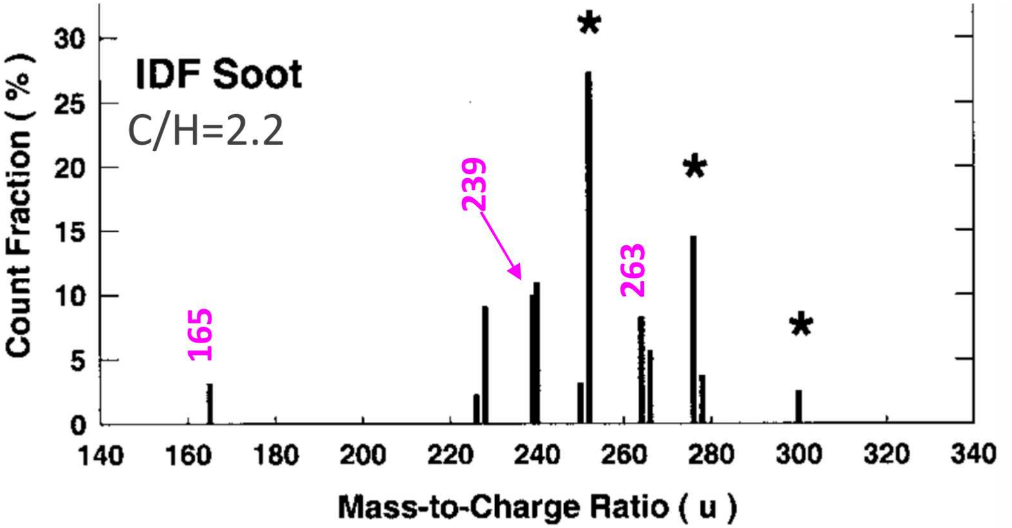
Laser microprobe mass spectrometry

Ethylene/air co-flow diffusion flame



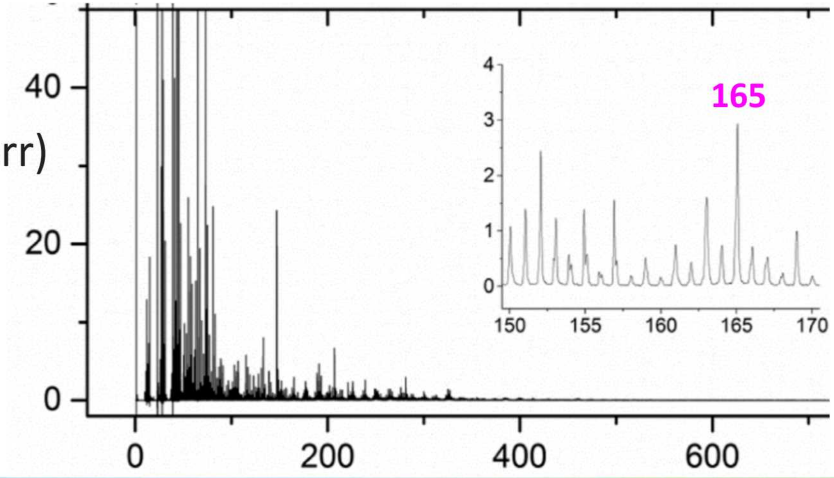
Dobbins et al., *Combust. Flame* 1998

Ethylene/air inverse diffusion flame



Blevins et al., *Proc. Combust. Inst.* 2002

Low pressure (200 Torr)
Premixed $CH_4/O_2/N_2$
C/O=0.58, Φ=2.32

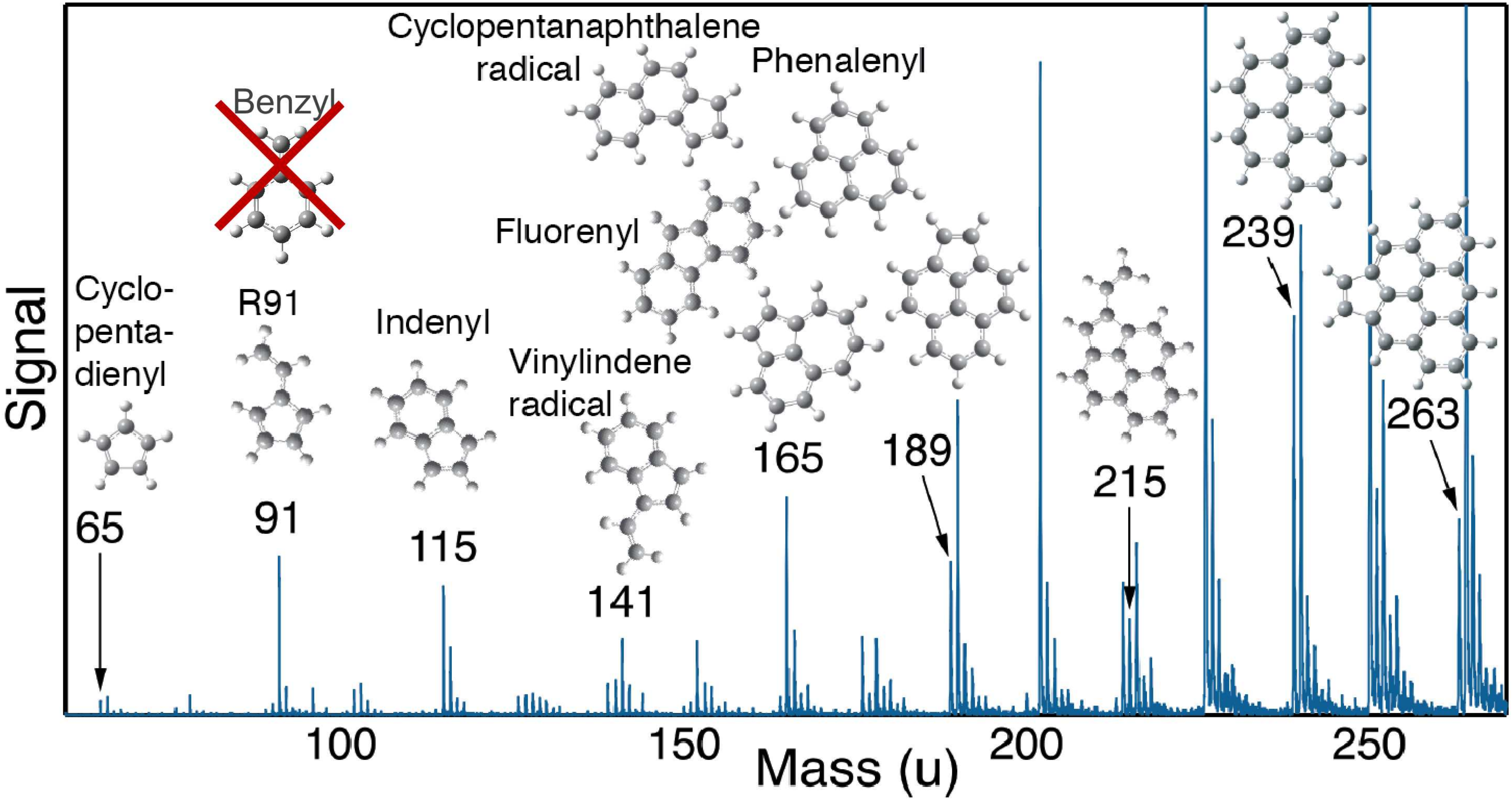


Time of flight secondary ion mass spectrometry

Desgroux et al., *Combust. Flame* 2017

Incipient-Particle Composition

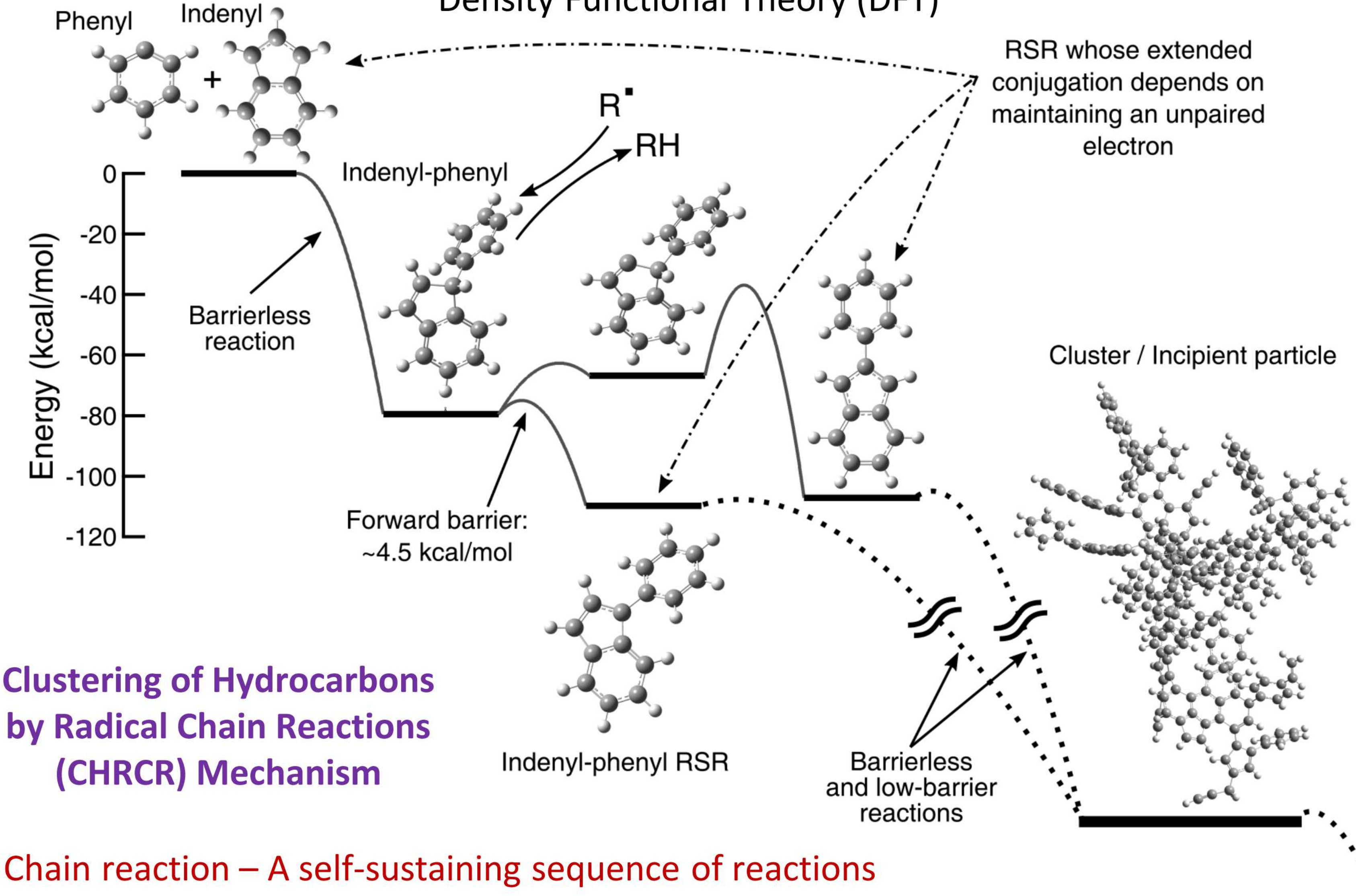
Aerosol Mass Spectrometry using VUV Photoionization (VUV-AMS)
ALS BL 9.0.2



Johansson et al., *Science*, 2018

Possible Soot-Inception Mechanism

Density Functional Theory (DFT)



Clustering of Hydrocarbons by Radical Chain Reactions (CHRCR) Mechanism

Chain reaction – A self-sustaining sequence of reactions

Johansson et al., *Science*, 2018

ωB97X-D functional with aug-cc-pVTZ basis set and ROCBS-QB3 hybrid method

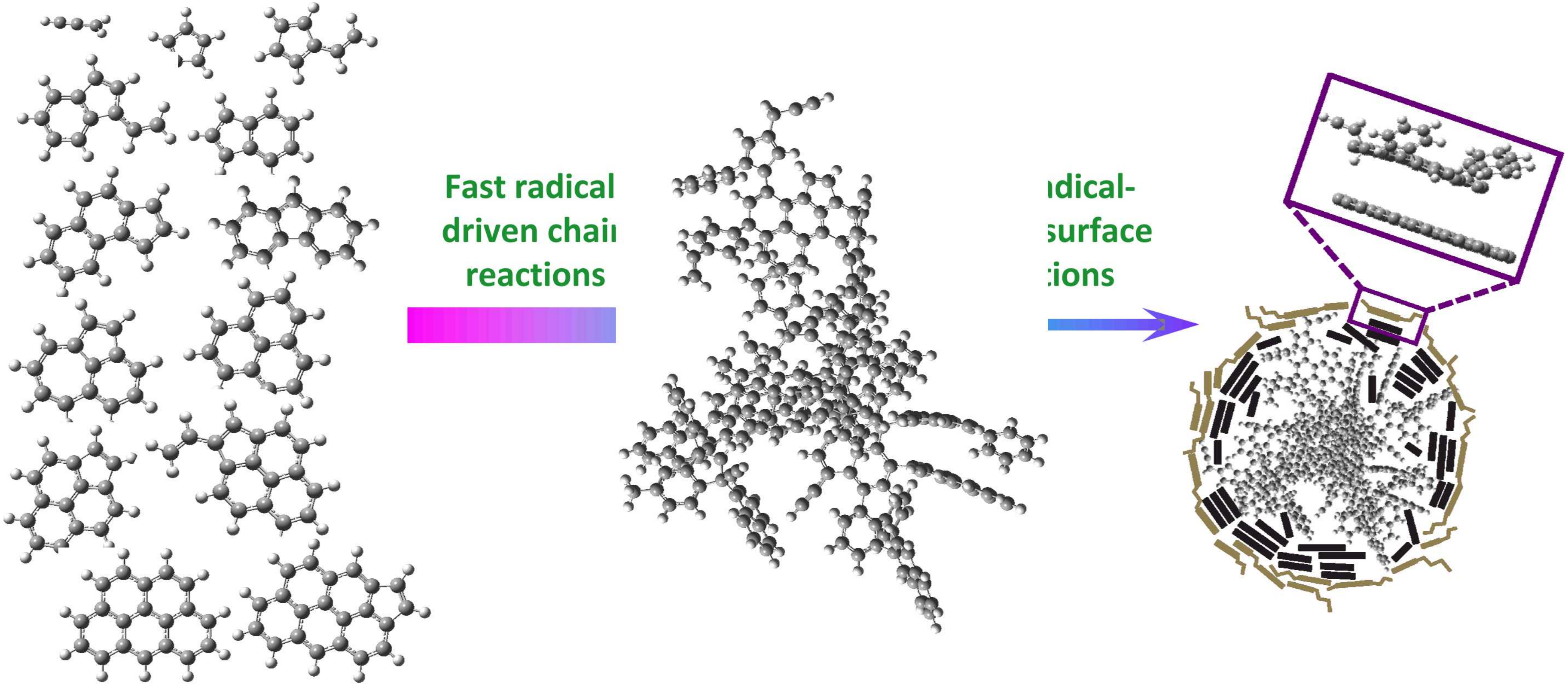
Particle Growth by Radical Chain Reactions

Clustering of Hydrocarbons by Radical Chain Reactions (CHRCR) Mechanism

Resonance-stabilized radicals

Incipient particles
Hydrocarbon clusters

Primary particles
Soot aggregates



Fast radical
driven chai
reactions

ıdical-
surface
:ions

Johansson, Head-Gordon, Schrader, Wilson, and Michelsen,
Science **361**, 997-1000 (2018)

Surface Growth

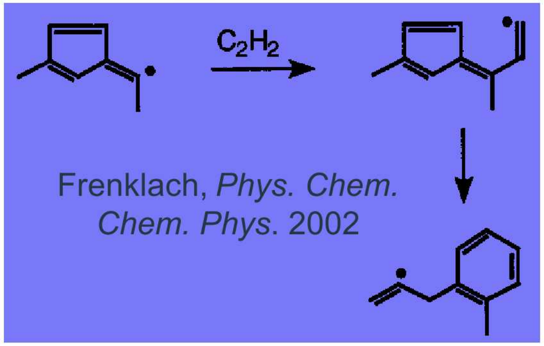
Hypothesized mechanisms for particle growth

Surface reactions at edge sites

Hydrogen abstraction, C_2H_2 addition (HACA)

HACA at edge sites grows graphene layer size
Should increase surface-maturity level

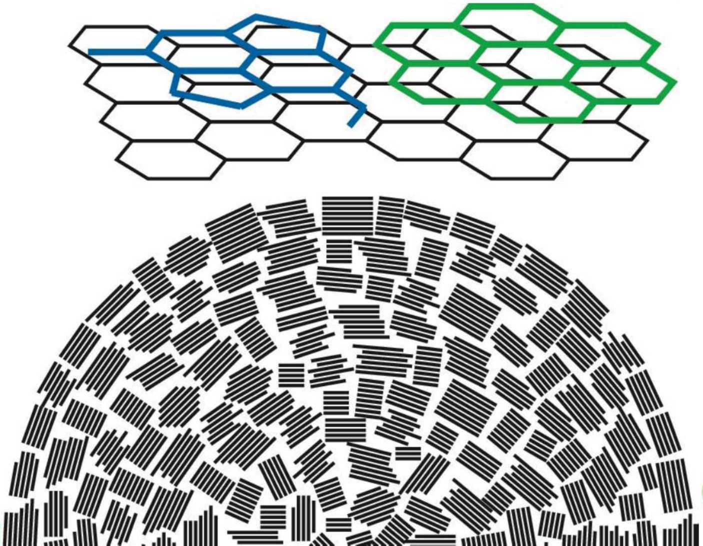
Ring formation



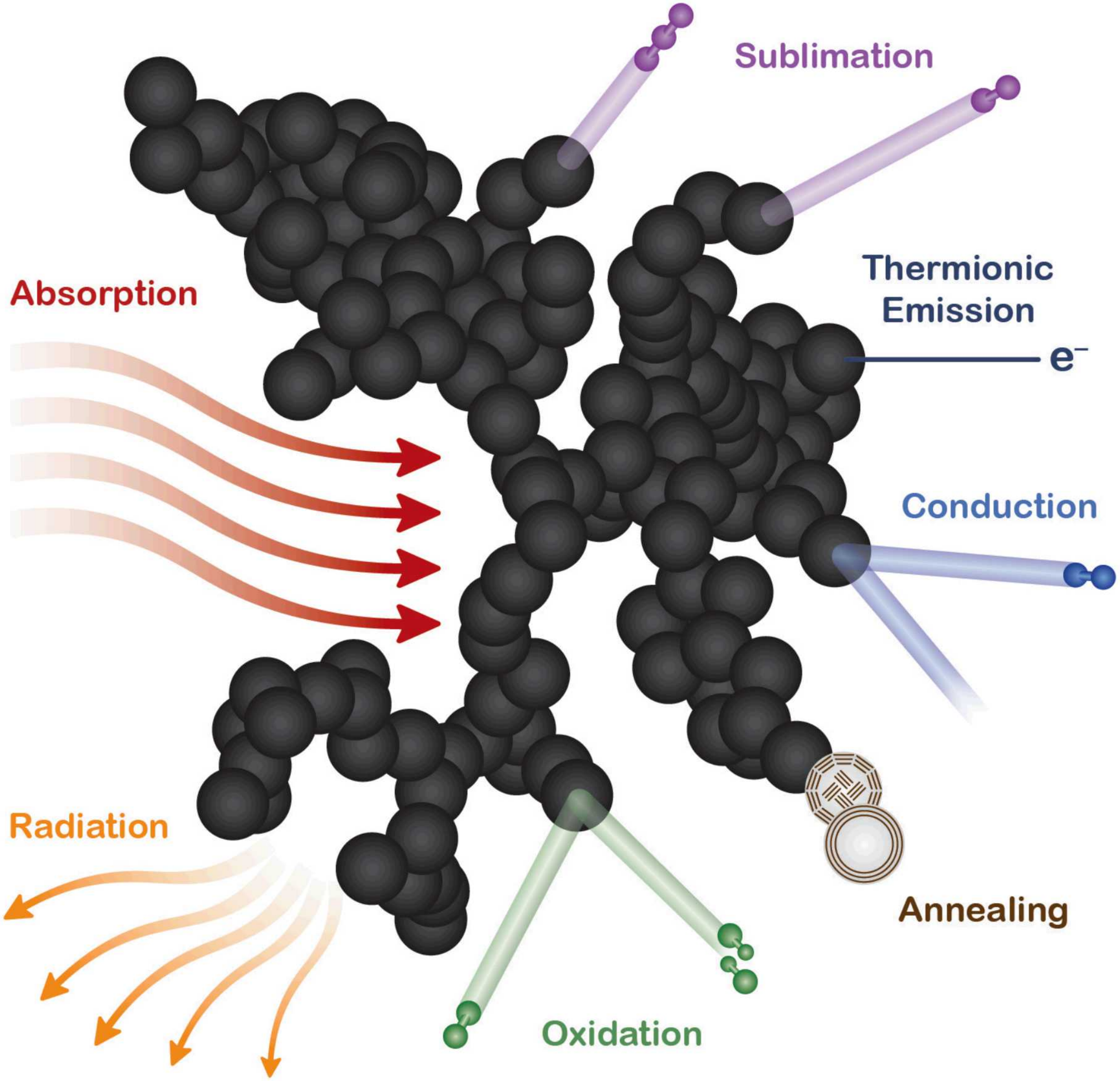
Frenklach, *Phys. Chem. Chem. Phys.* 2002

Surface adsorption of small PAHs (4-10 rings)

Adsorption of 4-10-ring PAHs
Not likely to increase surface-maturity level



Laser-Induced Incandescence

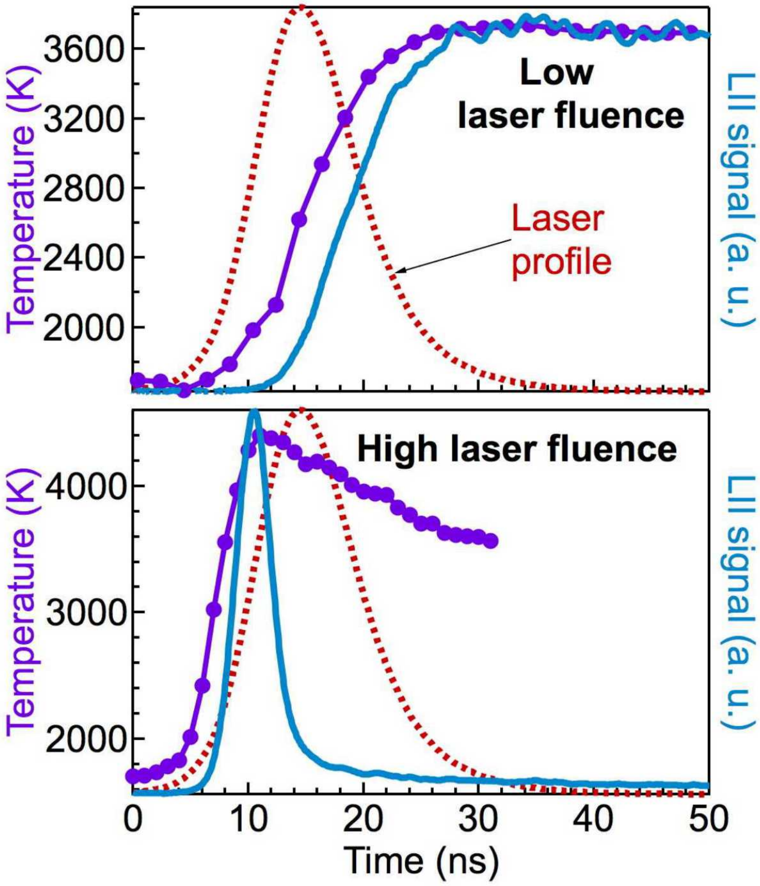


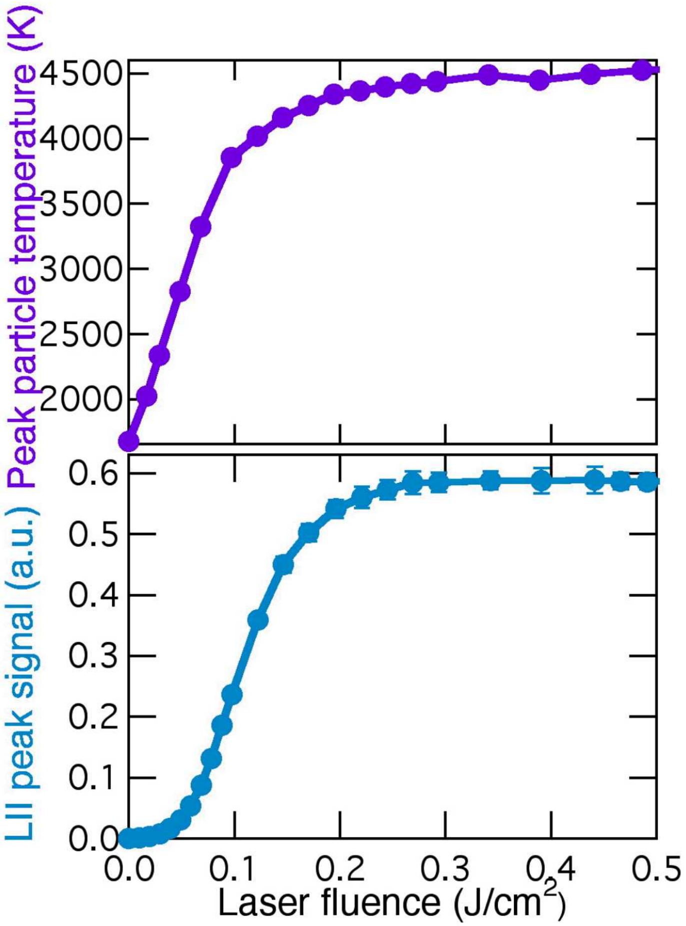
Soot volume fraction
Primary-particle size
Maturity level of bulk?

Michelsen et al., *Prog. Energy Combust. Sci.* 2015

LII for Volume Fraction of Mature Soot

$S_{LII} \propto VT^5$



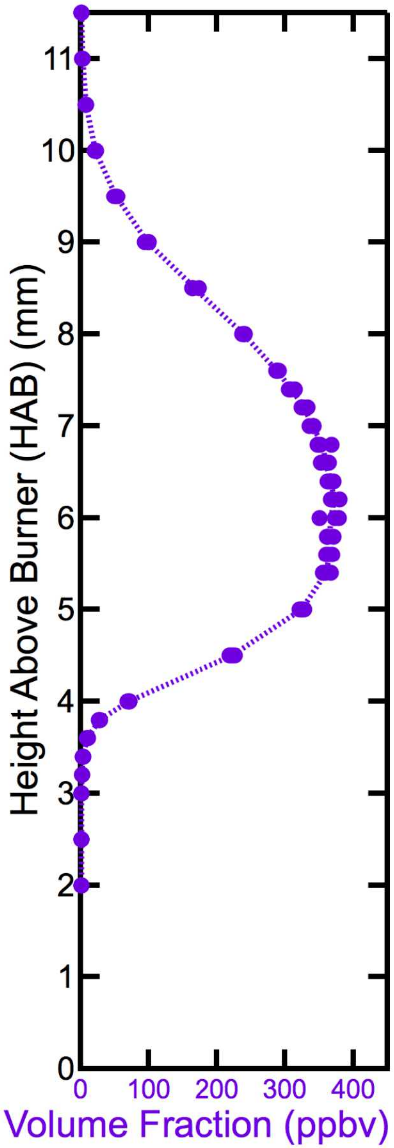


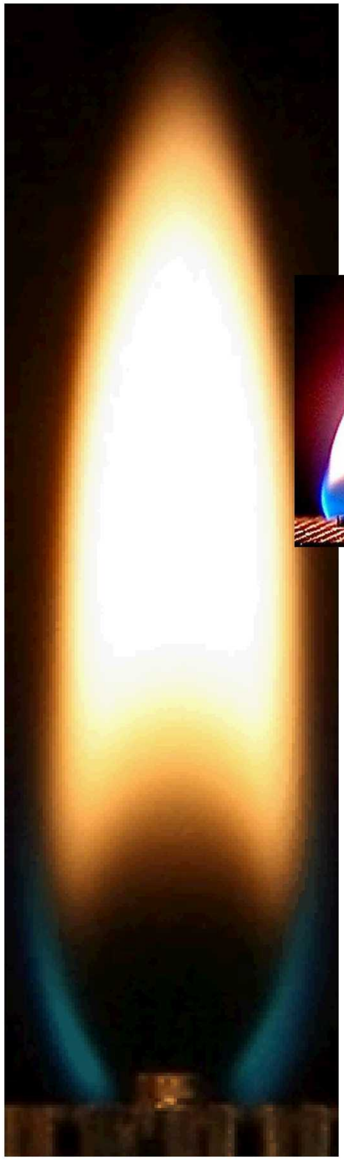
Goulay, Schrader, López-Yglesias, Michelsen, *Appl. Phys. B* 2013

Sensitive and selective for strongly absorbing, refractory particles

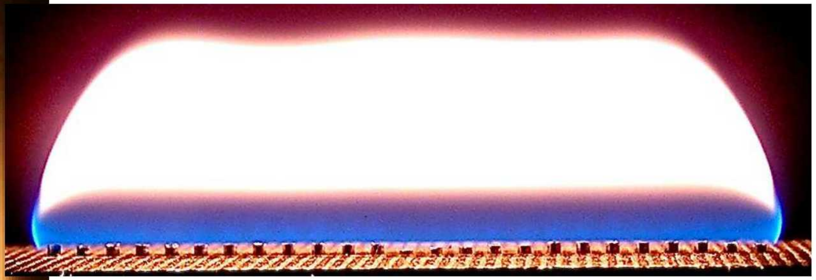
LII for Volume Fraction of Mature Soot

Laser-Induced Incandescence (LII) calibrated with Extinction



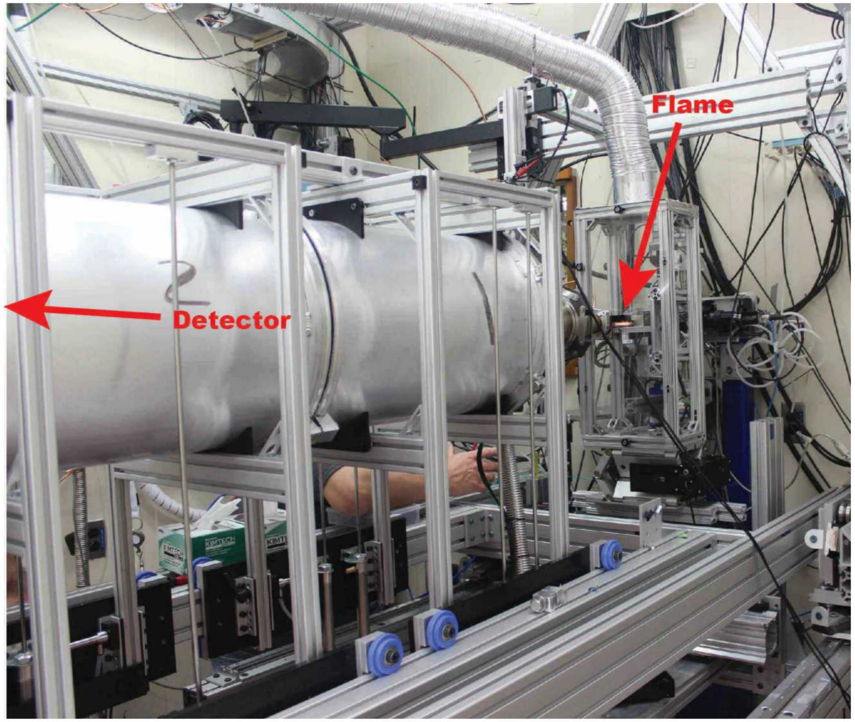


Linear Hencken burner
Diffusion flame



X-Ray Scattering for Primary-Particle Size

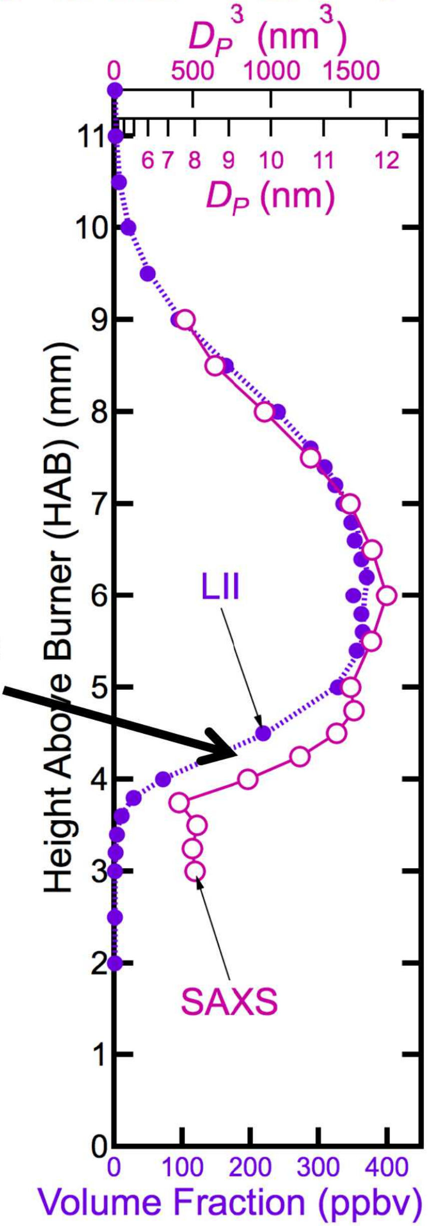
Small-angle X-ray scattering (SAXS)
Beamline 7.33 at the Advanced Light Source/LBL

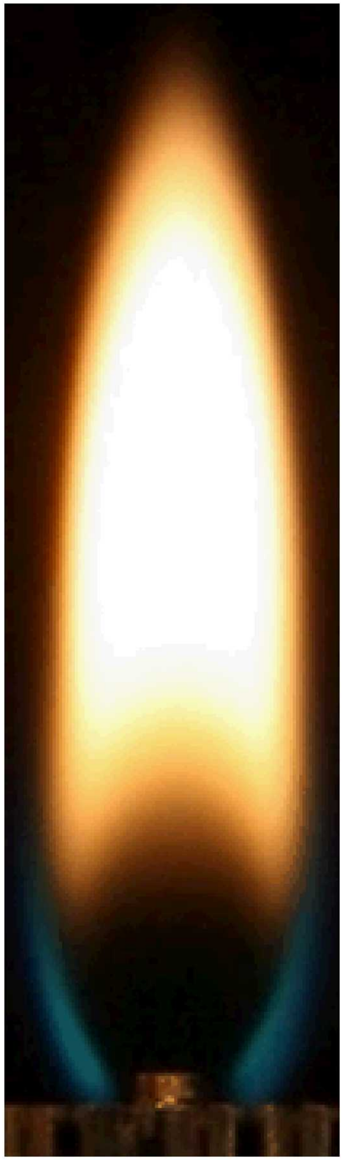


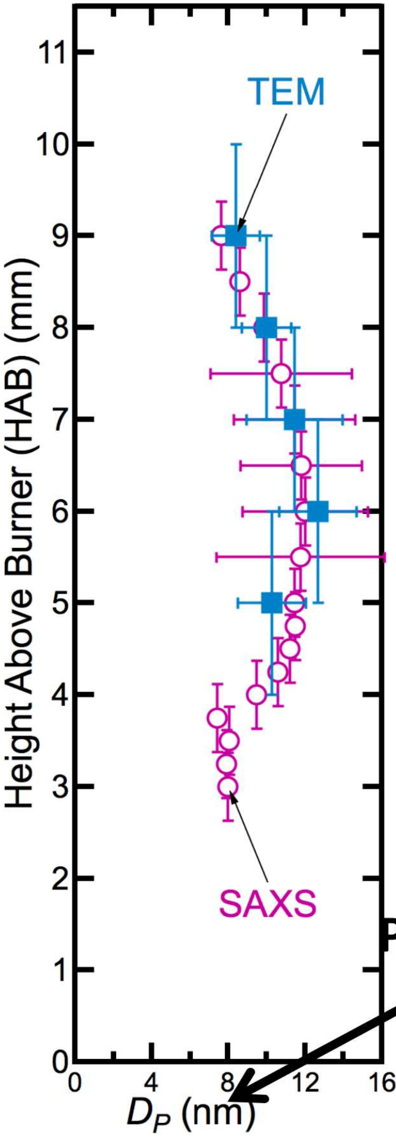
SAXS for Primary-Particle Size

LII and SAXS

Difference may be due to less mature soot particles





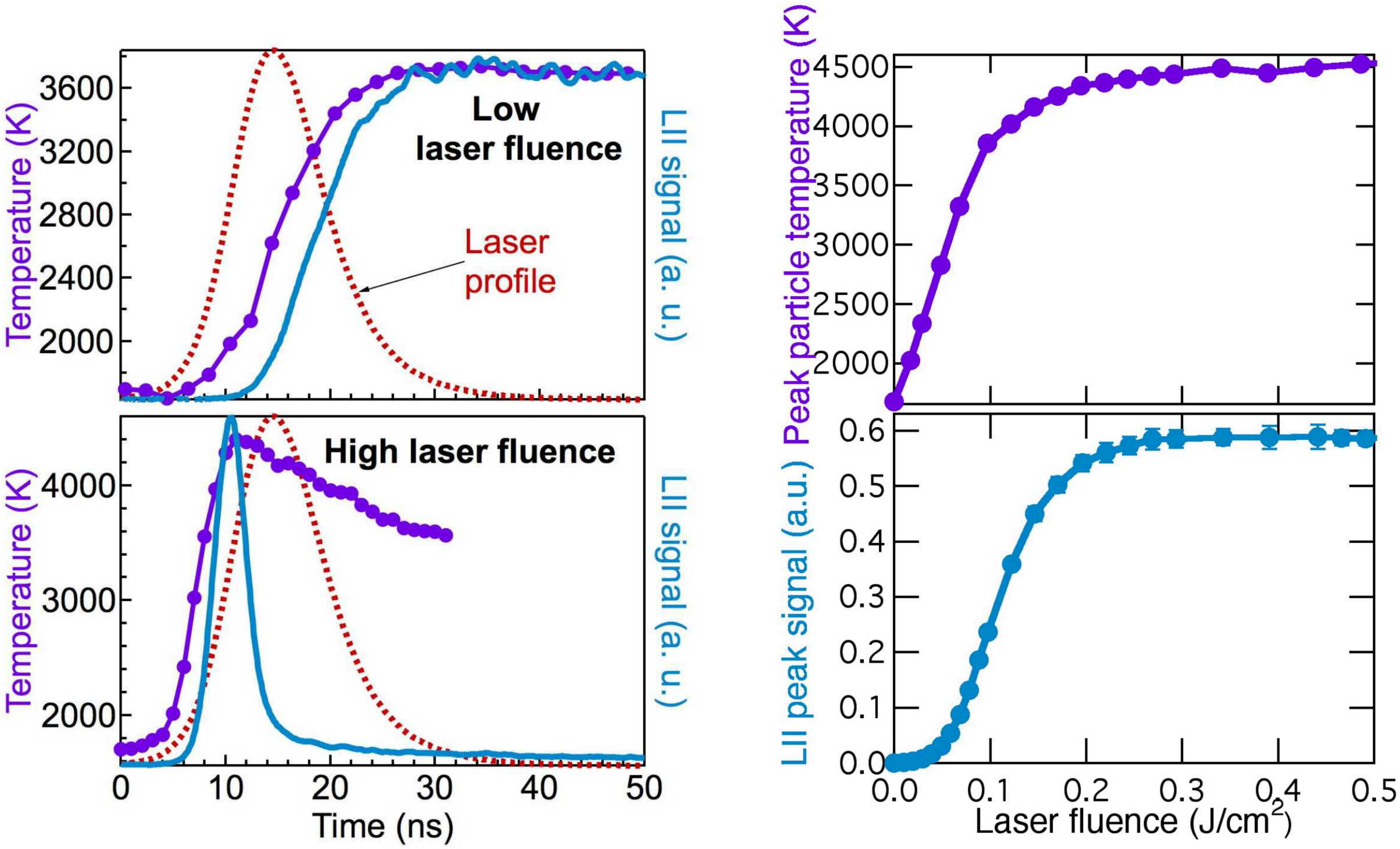


SAXS and TEM

Primary-particle diameter

LII for Absorption Cross Section

$S_{LII} \propto VT^5$



Goulay et al., *Appl. Phys. B* 2013

LII peak signal can be used as a proxy for peak temperature

LII for Absorption Cross Section

$$\sigma_{abs} = \frac{\pi d^3 \beta}{6\lambda^{\xi}}$$

Scaling factor

Dispersion exponent

As soot maturity increases, β increases, but ξ decreases

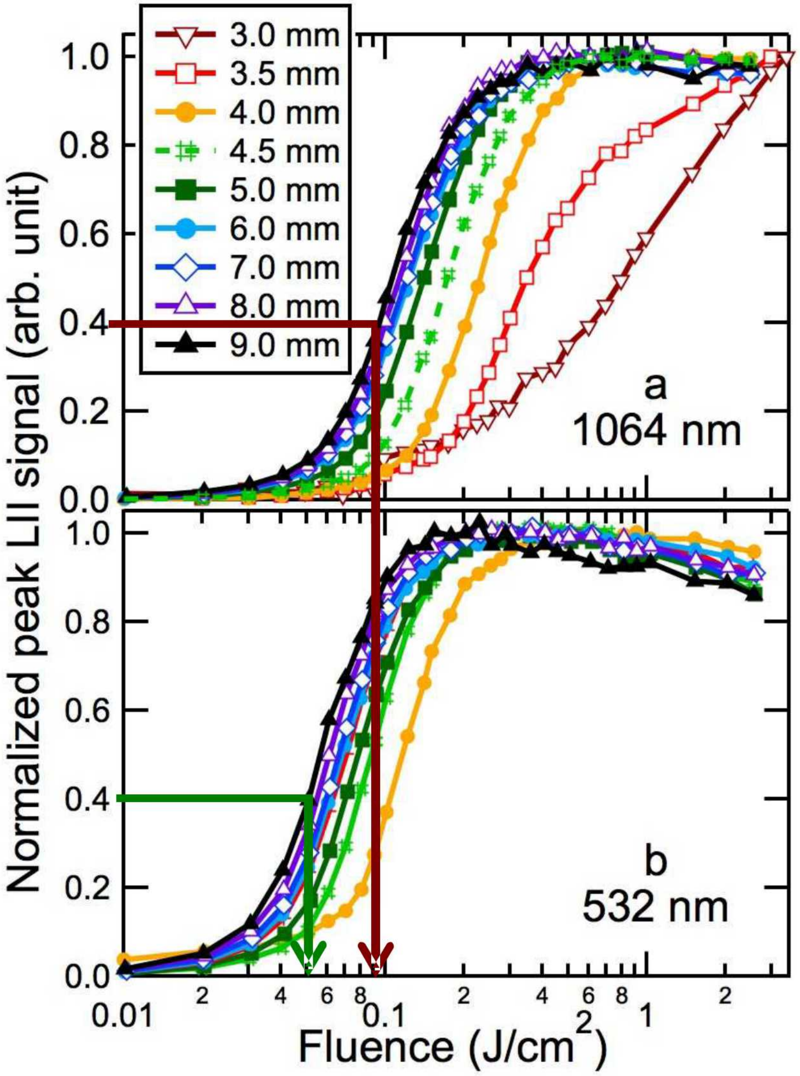
$$\xi = \frac{\ln\left[\frac{\sigma_{abs}(532)}{\sigma_{abs}(1064)}\right]}{\ln 2}$$

$$\frac{\sigma_{abs}(532)}{\sigma_{abs}(1064)} = \frac{F_{1064}(LII_{\max})}{F_{532}(LII_{\max})}$$

López-Yglesias et al., *Appl. Phys. B* 2014

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

Plot and fit slope



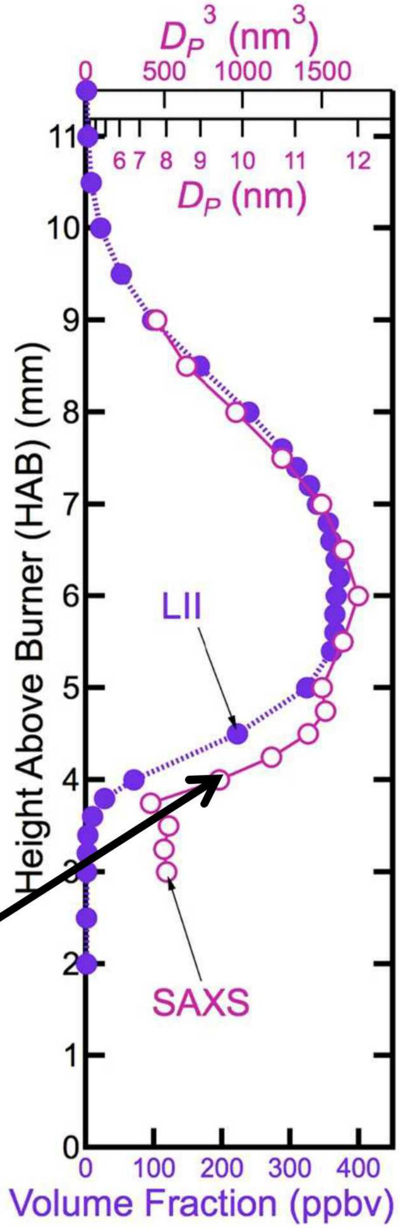
Johansson et al., *Aerosol Sci. Technol.* 2017

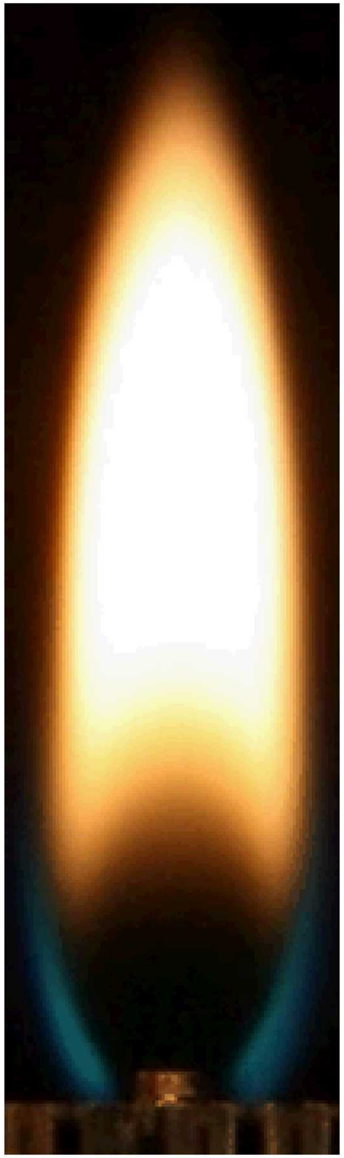
X-Ray Scattering for Primary-Particle Size

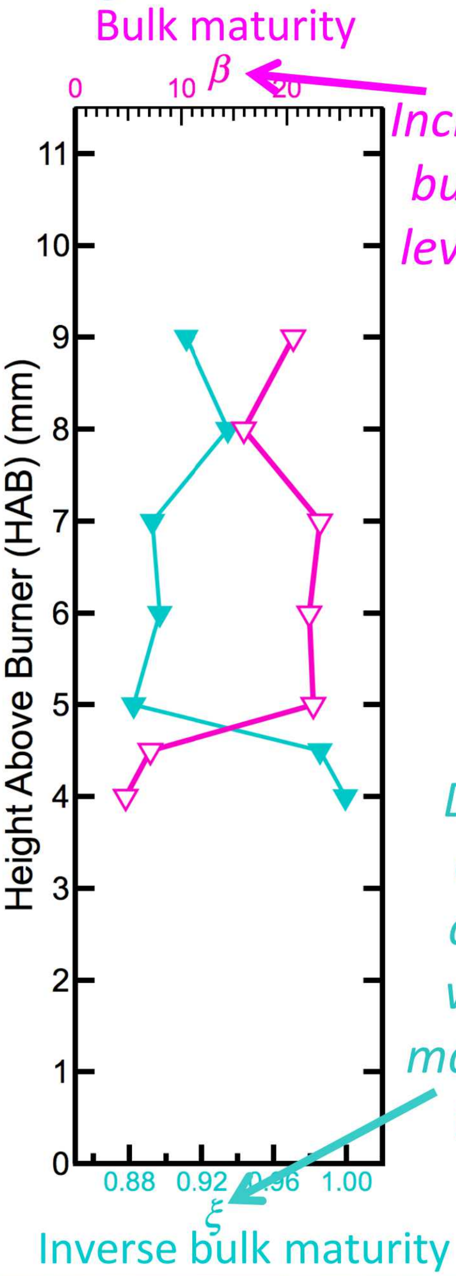
LII

Small-Angle X-Ray Scattering (SAXS)

Difference likely due to less mature soot particles



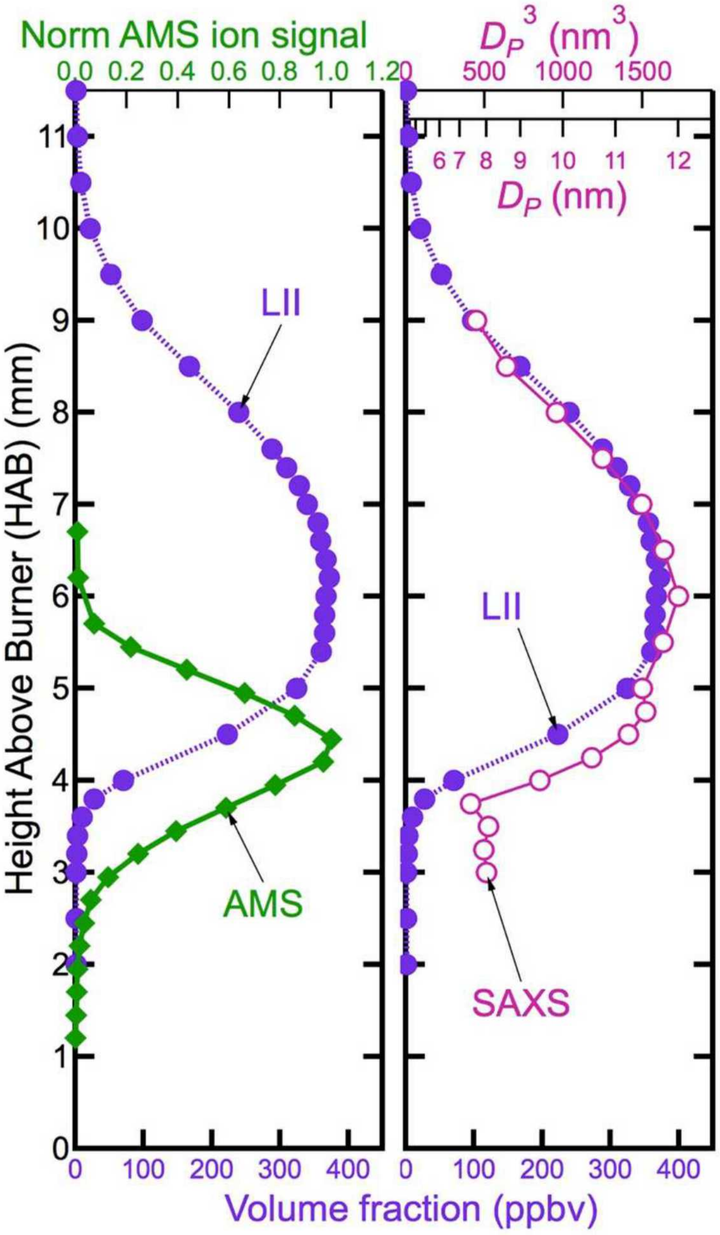


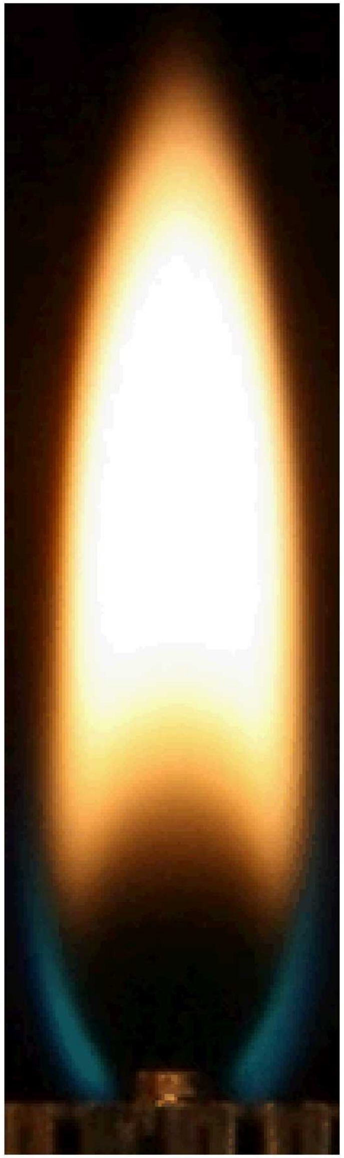


Increases when bulk maturity level increases

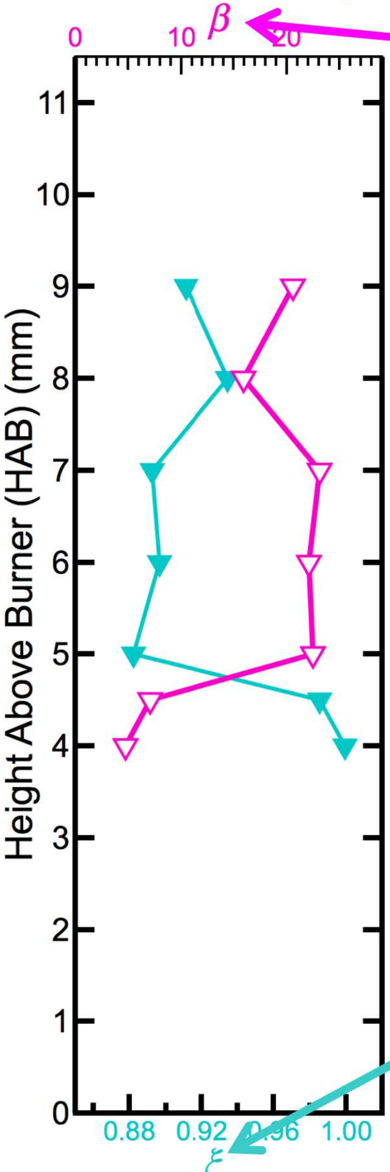
Dispersion exponent decreases when bulk maturity level increases

Aerosol Mass Spectrometry for Precursors





Bulk maturity

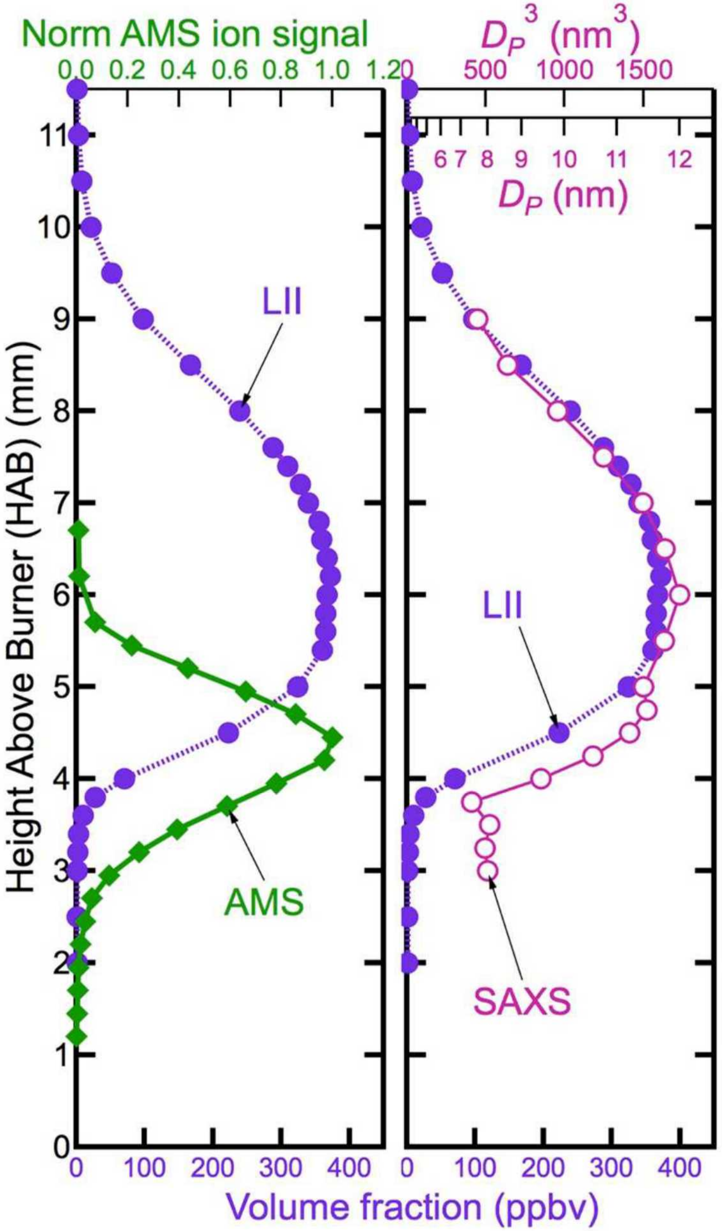


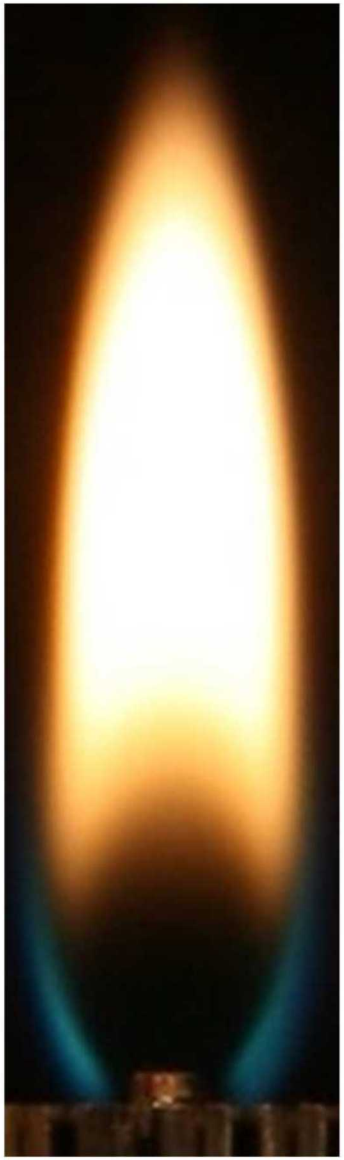
Inverse bulk maturity

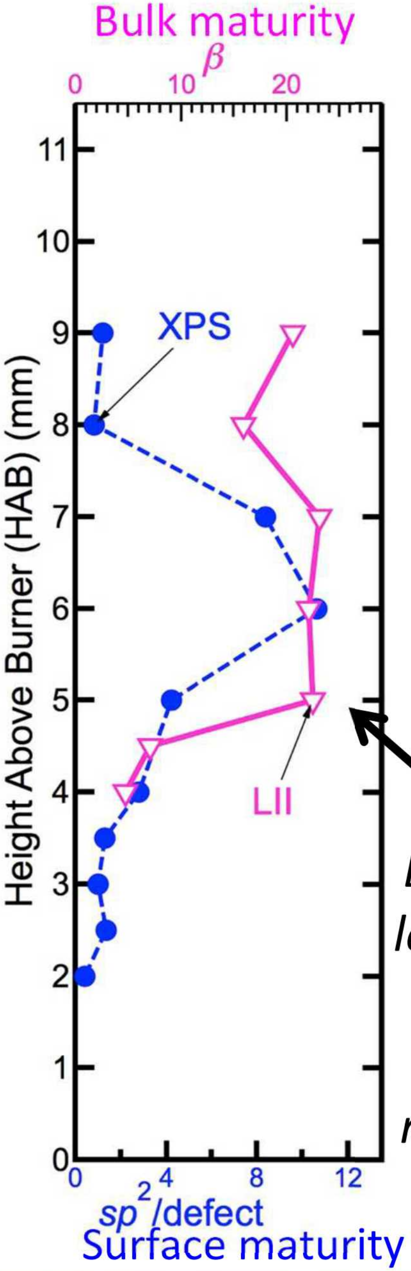
Increases when bulk maturity level increases

Dispersion exponent decreases when bulk maturity level increases

XPS for Surface Maturity







Bulk maturity level increases more rapidly than surface maturity level

Surface Growth

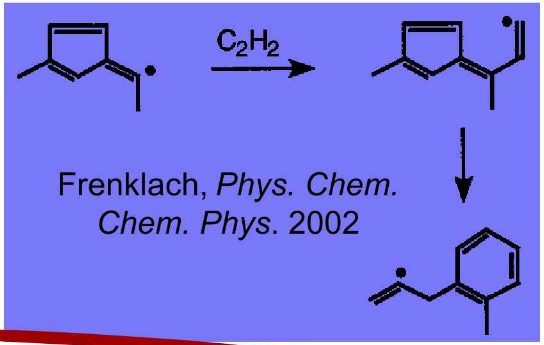
Hypothesized mechanisms for particle growth

Surface reactions at edge sites

Hydrogen abstraction, C_2H_2 addition (HACA)

HACA at edge sites grows graphene layer size
Should increase surface-maturity level

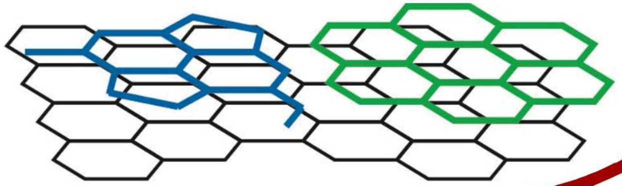
Ring formation

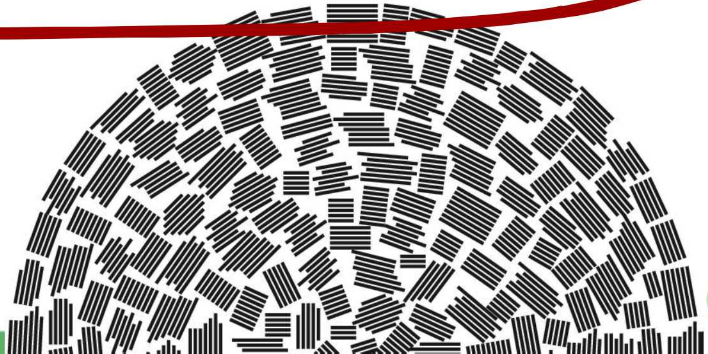


Frenklach, *Phys. Chem. Chem. Phys.* 2002

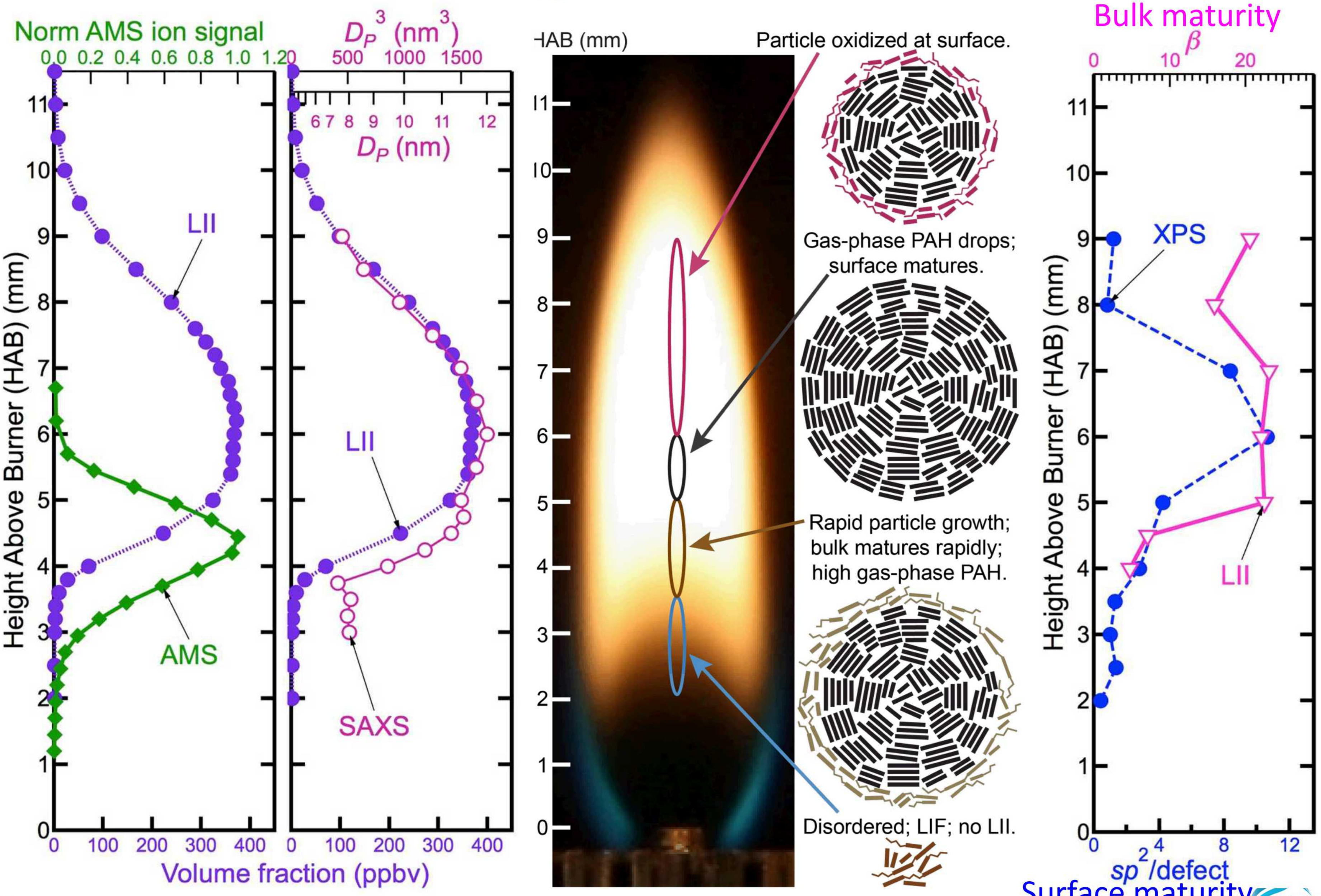
Surface adsorption of small PAHs (4-10 rings)

Adsorption of 4-10-ring PAHs
Not likely to increase surface-maturity level



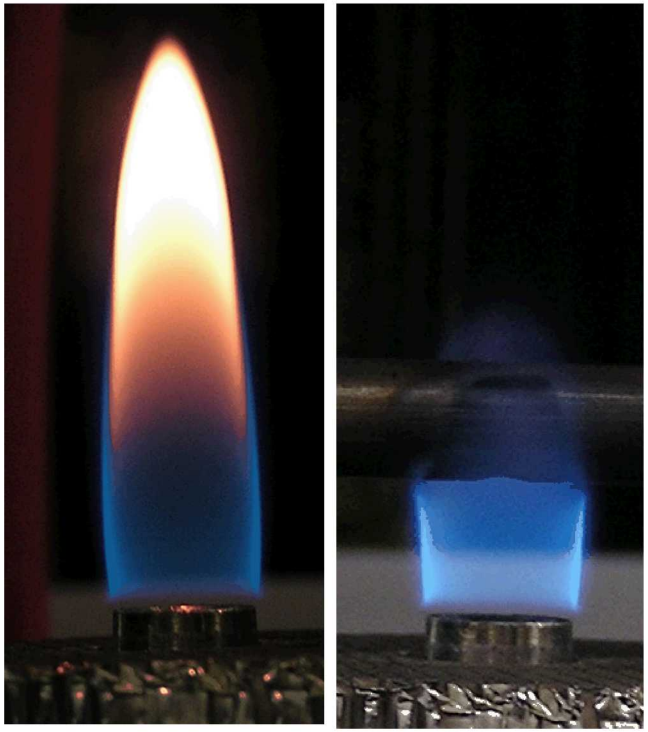


Laser Diagnostics for Soot

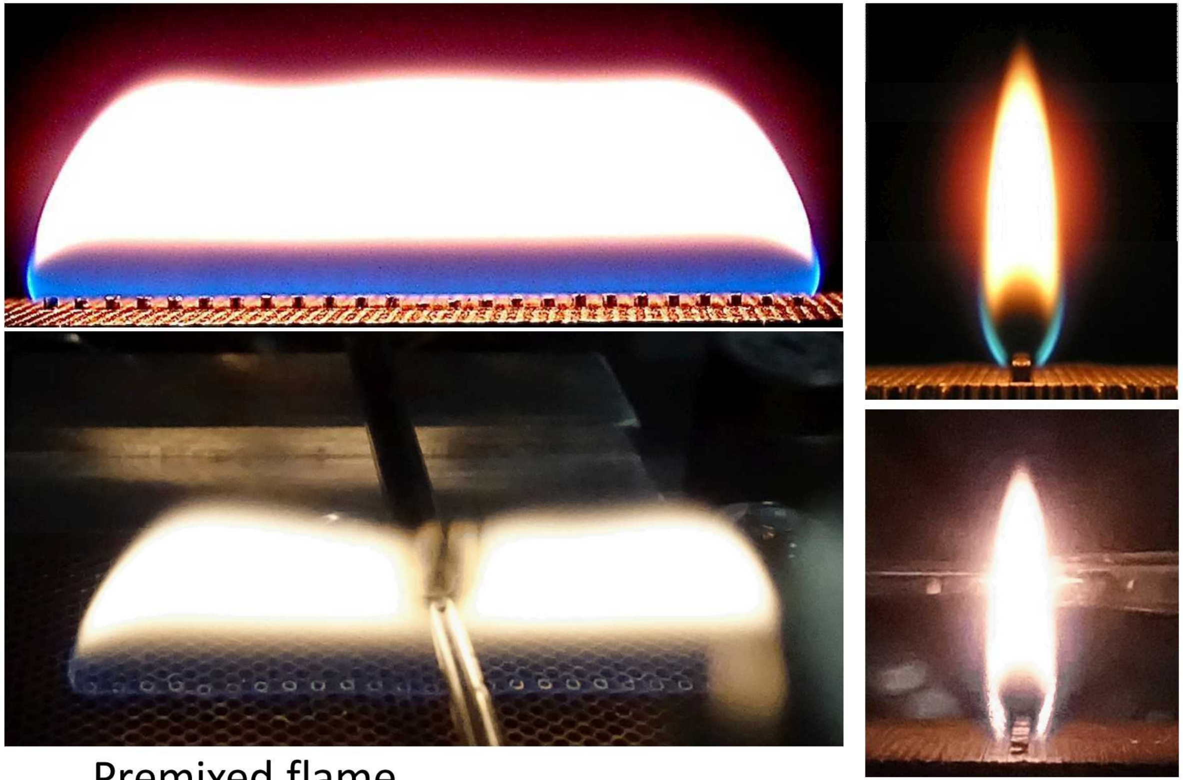


Probe Sampling

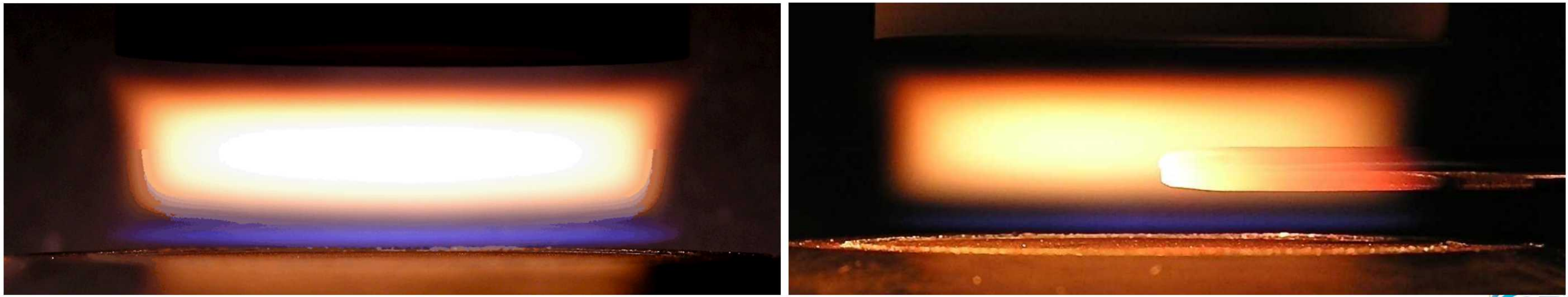
Co-flow diffusion flame



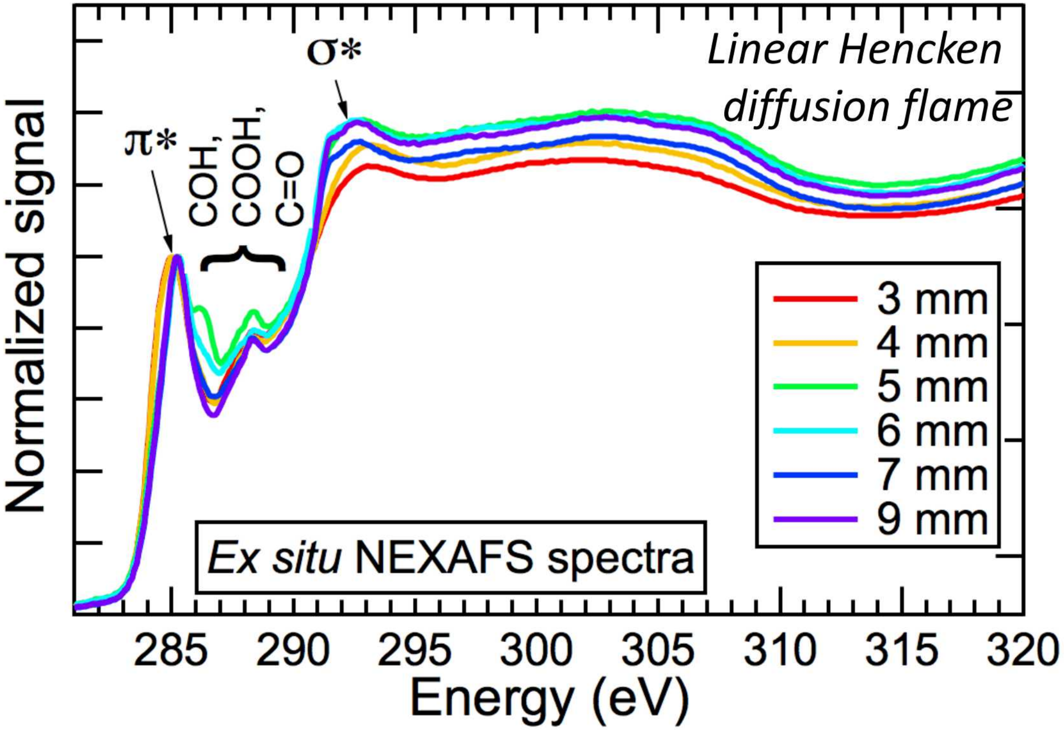
Partially premixed diffusion flame



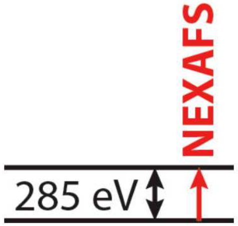
Premixed flame



X-Ray Absorption for Particle Composition

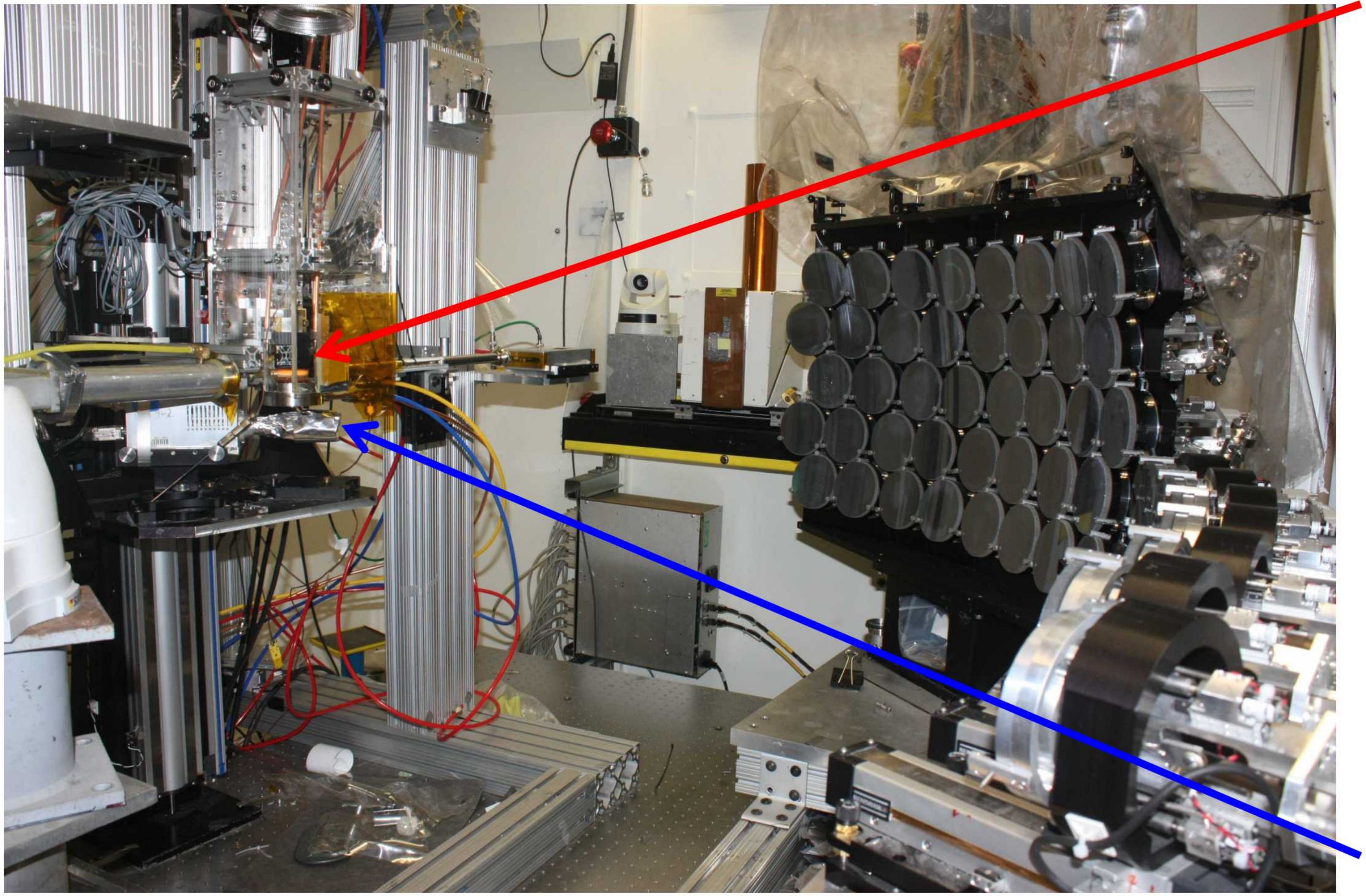


Energy-level diagram



X-Ray Raman Spectroscopy for Composition

XRS setup on Beamline 6-2 at SSRL/SLAC

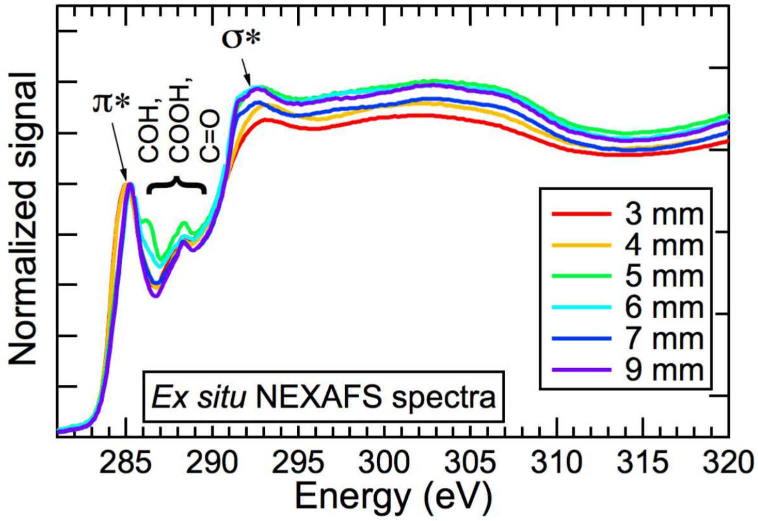


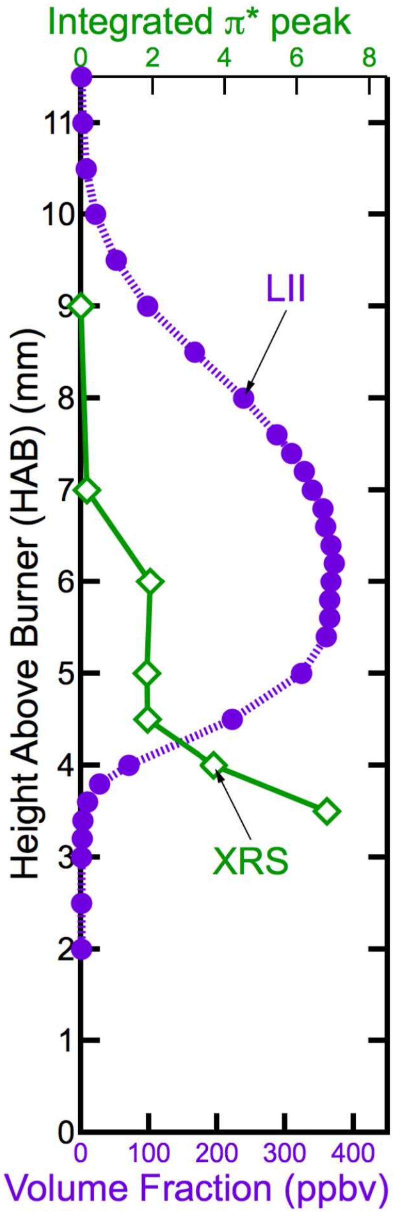
Our flame

Detector

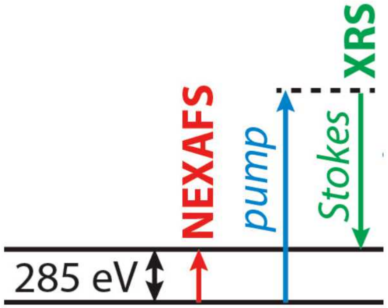
X-Ray Raman Spectroscopy for Composition

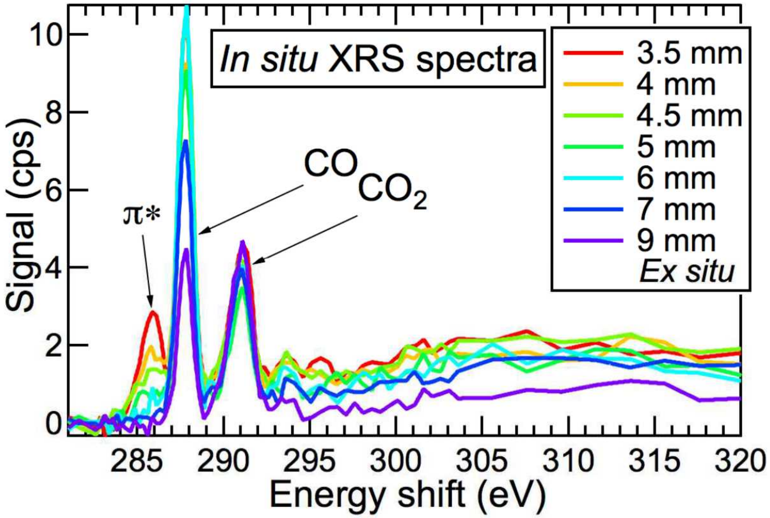
Linear Hencken diffusion flame





Energy-level diagram





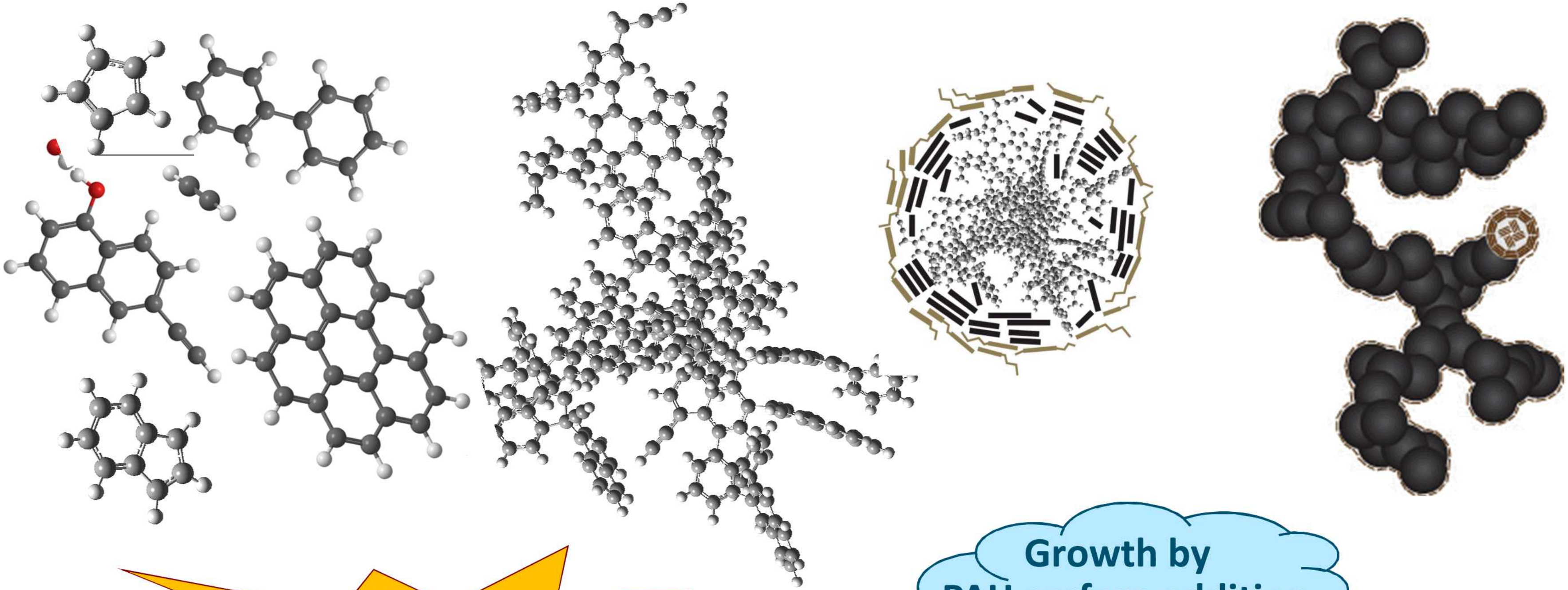
Summary and Conclusions

Molecular growth; Soot-precursor formation

Incipient particle formation

Maturation, surface growth, graphitization

Particle growth, aggregation, graphitization



Inception driven by radical chain rxns

Growth by PAH surface addition

Possibly by radical rxns

The Path Forward

- Need better experimental tools
  - Particle maturity
  - Particle size and morphology
  - Particle composition
  - Precursors and other gas-phase species
  - Temperature
  - Pressure
  - Boundary conditions

***In situ* (probe-free)**

Applicable to non-steady, high-pressure, multi-phase conditions

- Need better computational tools
  - Electronic structure for large, complex species
  - Mechanisms & rate constants for reactions of large, complex species
  - Physics-based chemical sub-models and chemical transport models

Applicable to non-steady, high-pressure, multi-phase conditions

Our Team

Many, Many Thanks to

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Thank you

Happy 4th of July