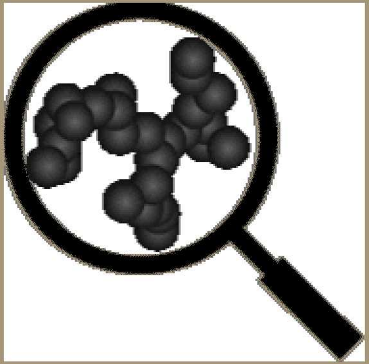
SAND2019-6014PE

Finding the Smoking Gun

Solving the Mystery of Soot Formation



Chemical Dynamics

Ultrafast Chemistry

Advanced Diagnostics

GAS PHASE CHEMICAL PHYSICS

Ultrafast Physics

Chemical Kinetics

Multiphase Chemical Physics

What is soot?

Particulate matter formed during the incomplete combustion or pyrolysis of hydrocarbons

What is Soot?

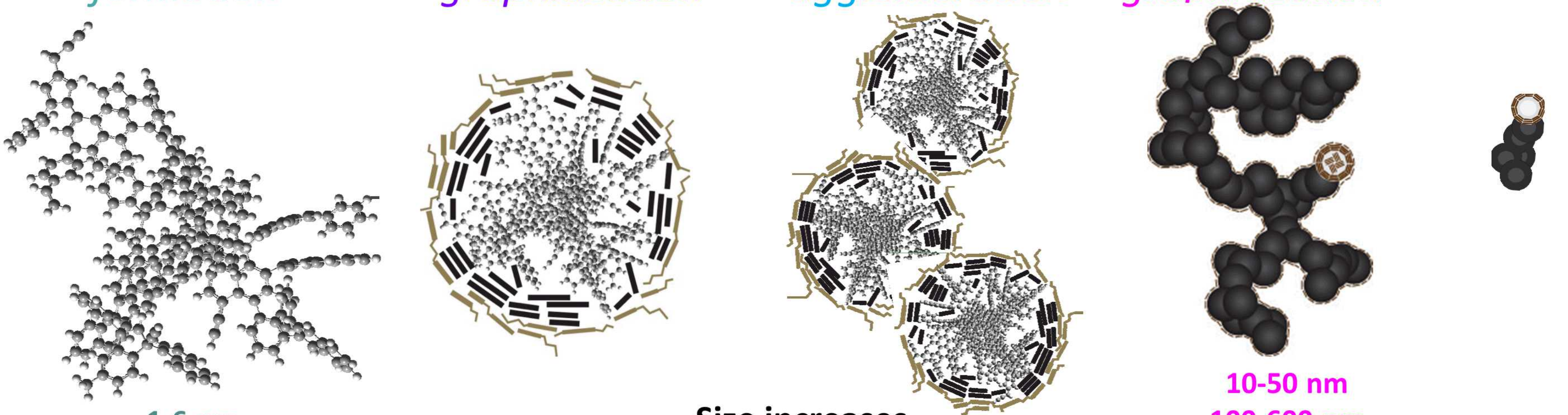
Soot inception; Incipient soot formation

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	

What is Soot?

Soot inception; Incipient soot formation

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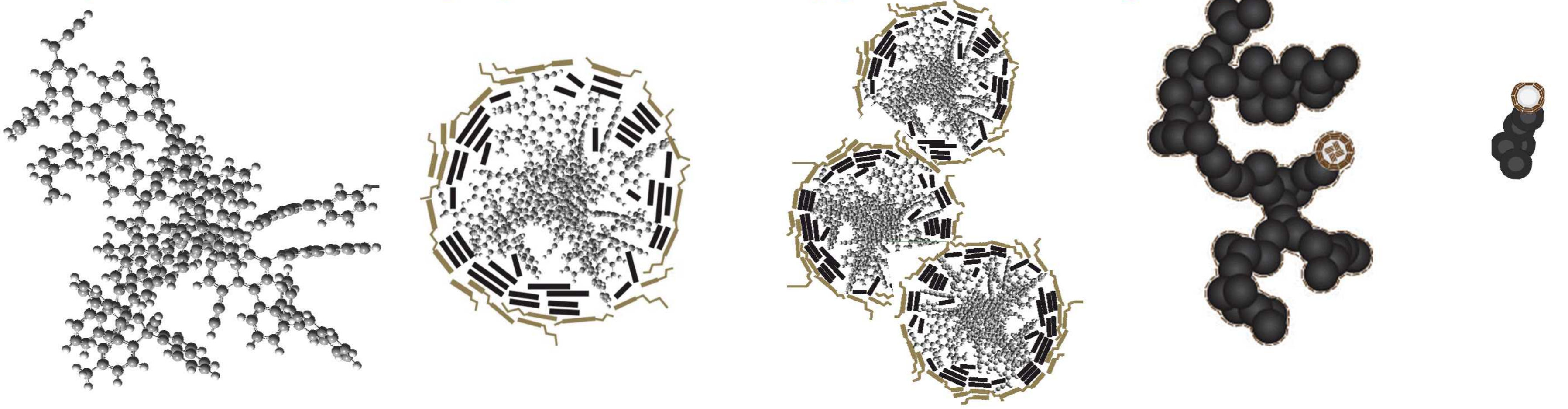


Size

1-4 nm

7-10 nm

20 nm

10-50 nm
100-600 nm

Timescale

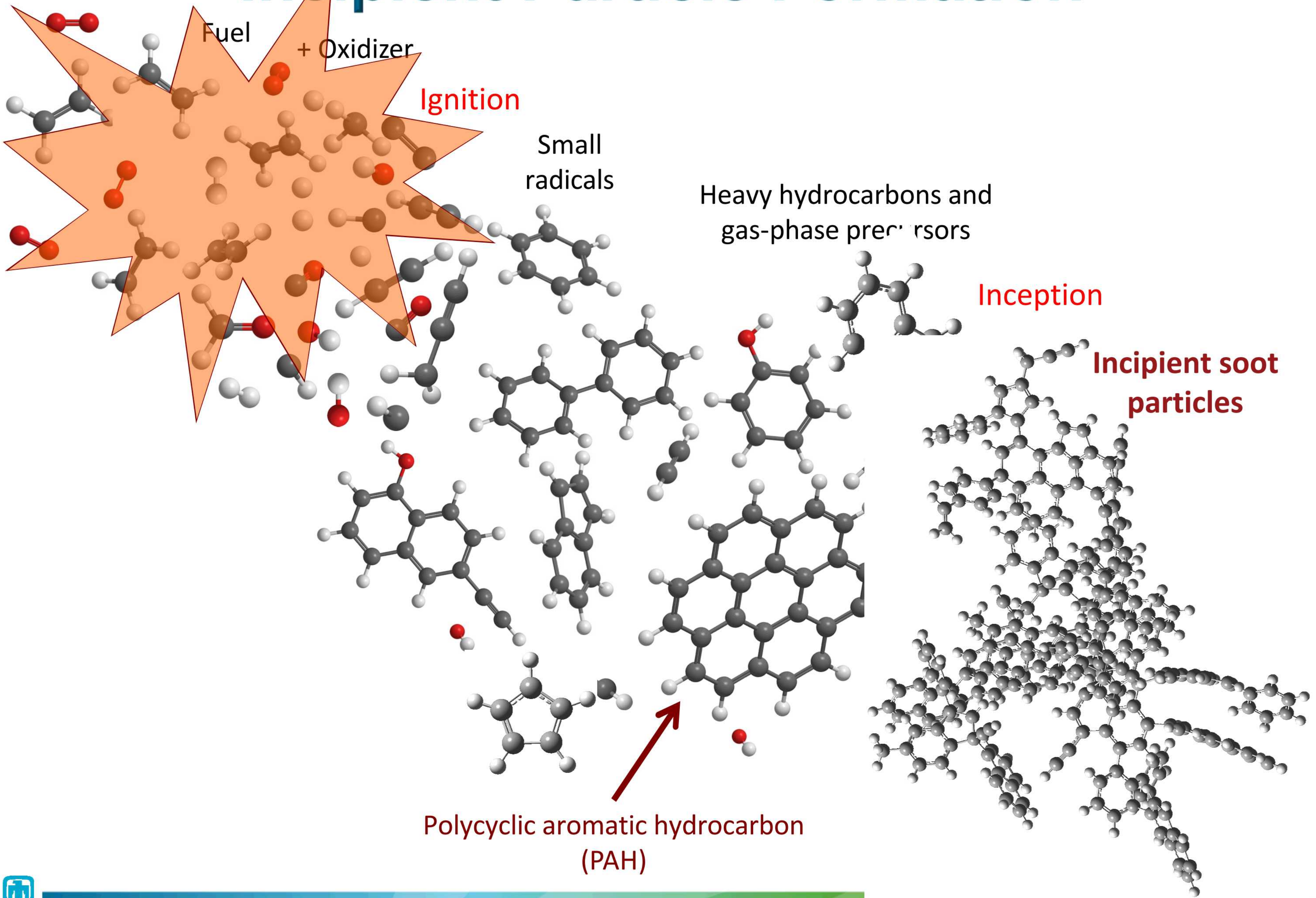
1-3 ms

10 ms

30 ms

50 ms

Incipient Particle Formation



Fuel

+ Oxidizer

Ignition

Small
radicals

Heavy hydrocarbons and
gas-phase precursors

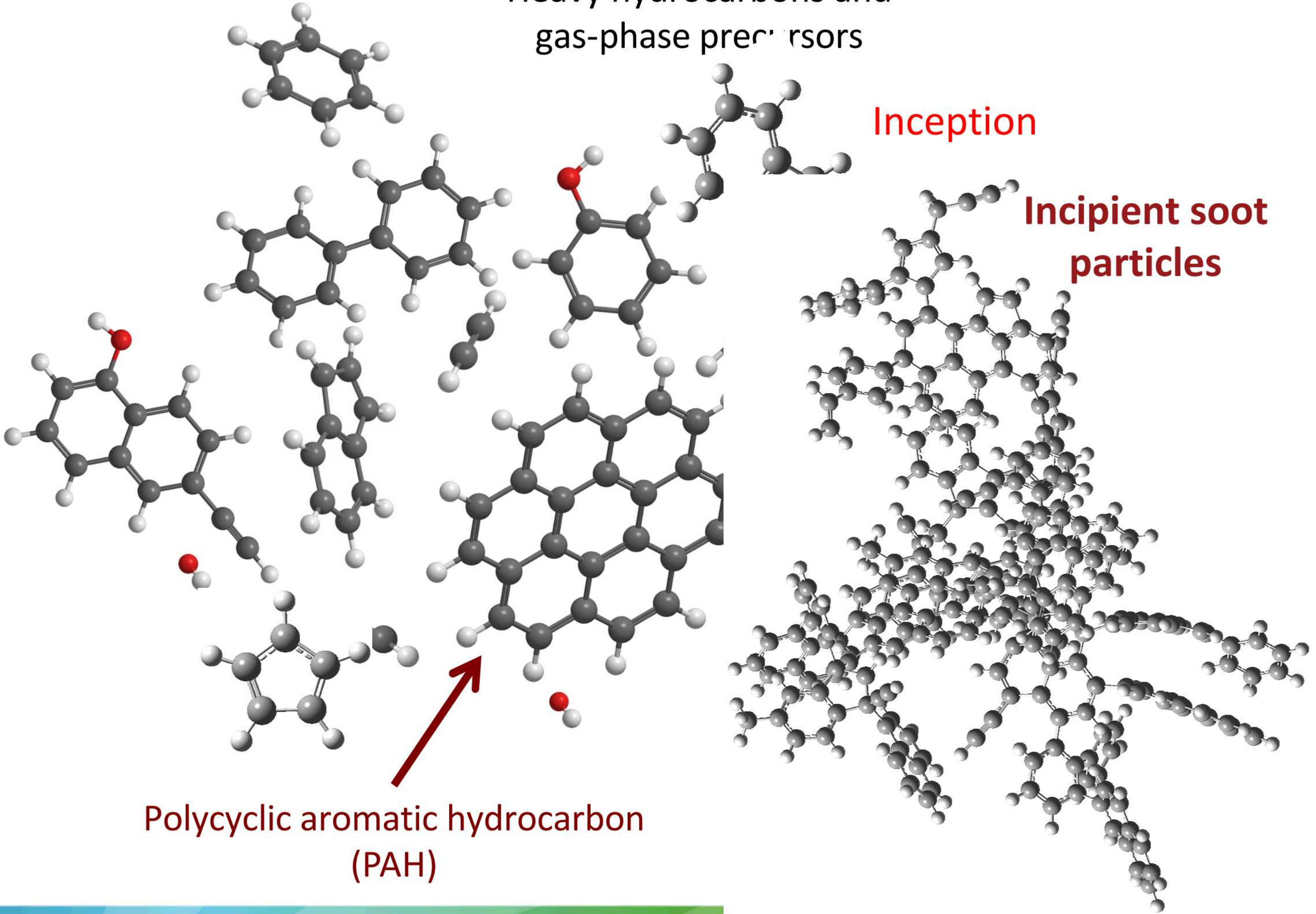
Inception

**Incipient soot
particles**

Polycyclic aromatic hydrocarbon
(PAH)

What is Inception?

The transition from gas-phase species to condensed-phase species



Heavy hydrocarbons and gas-phase precursors

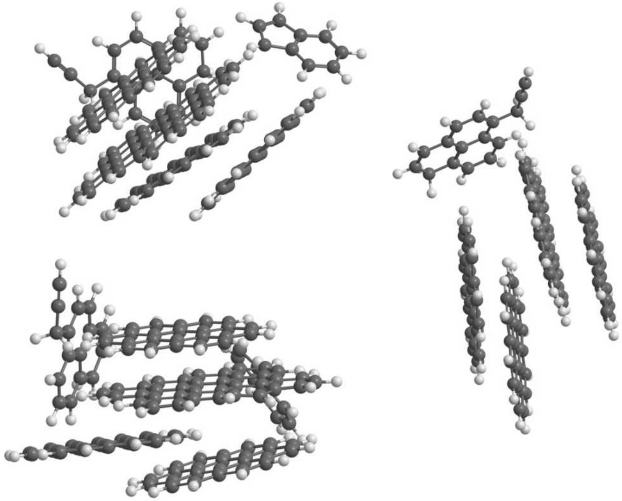
Inception

Incipient soot particles

Polycyclic aromatic hydrocarbon (PAH)

Proposed Inception Mechanisms

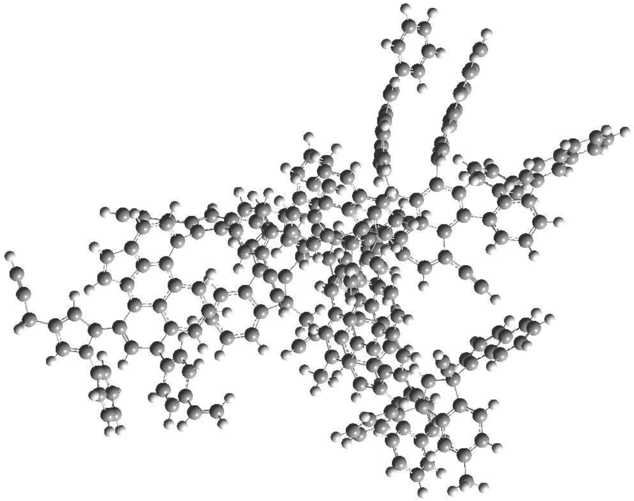
Thermodynamically driven



Nucleation of stable PAH species
Bound by dispersion 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

What is Inception?

The transition from gas-phase species to condensed-phase species

- **Physical characteristics of species change**
  - Spectroscopic properties
  - Thermodynamic properties: density, specific heat capacity
  - Morphology: from 2D to 3D

- **Average growth rate increases**

- **Distribution of growth over population changes**
  - Before inception, growth distributed over many species
  - During inception, growth centered on selected sites (growth centers)

Particle-Inception Studies

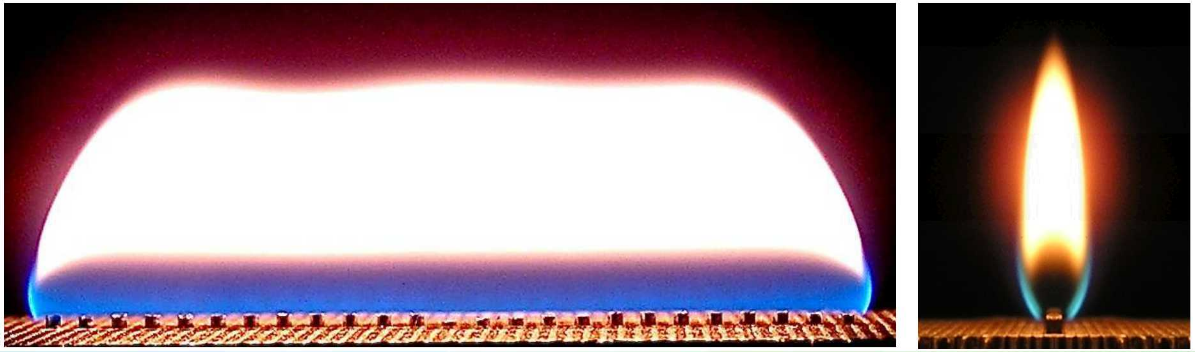
Co-flow diffusion flame

Inverse diffusion flame

Counter-flow diffusion flame

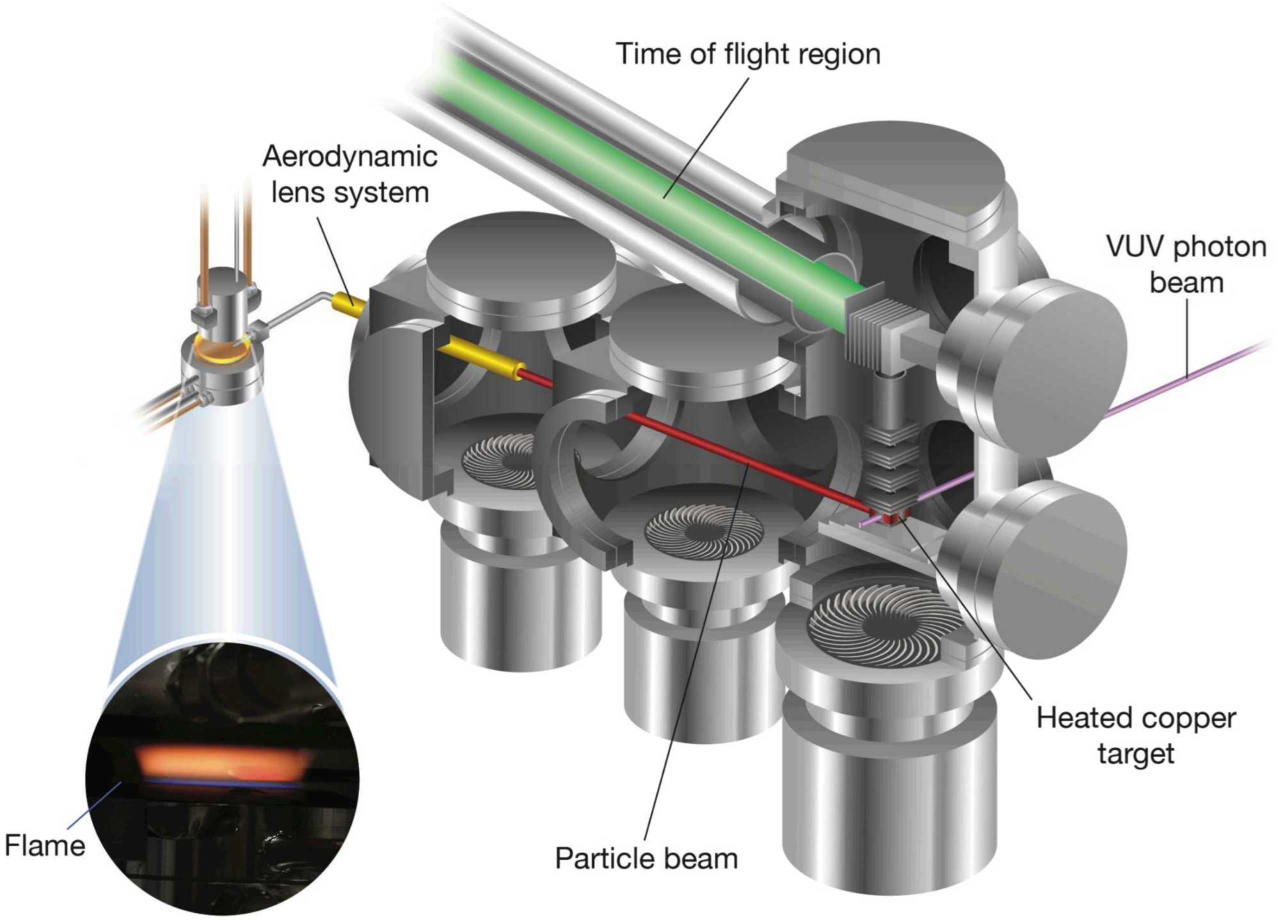
Premixed flame

Partially premixed diffusion flame



Incipient-Particle Composition

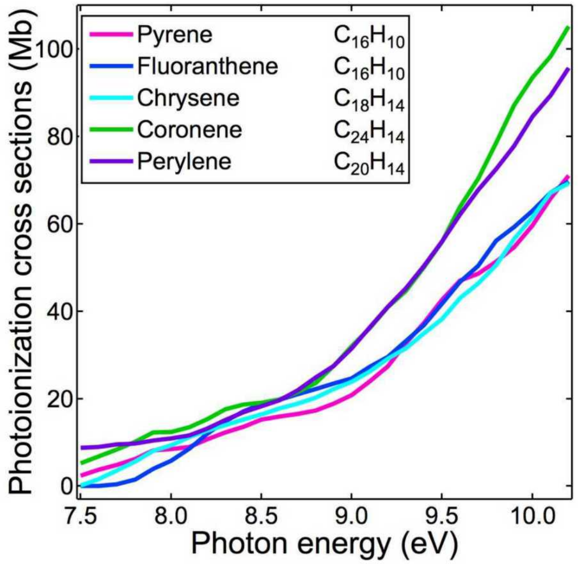
Aerosol Mass Spectrometry using VUV Photoionization (VUV-AMS)
ALS BL 9.0.2



Our flame

Kevin Wilson's machine at the ALS

Tunable VUV



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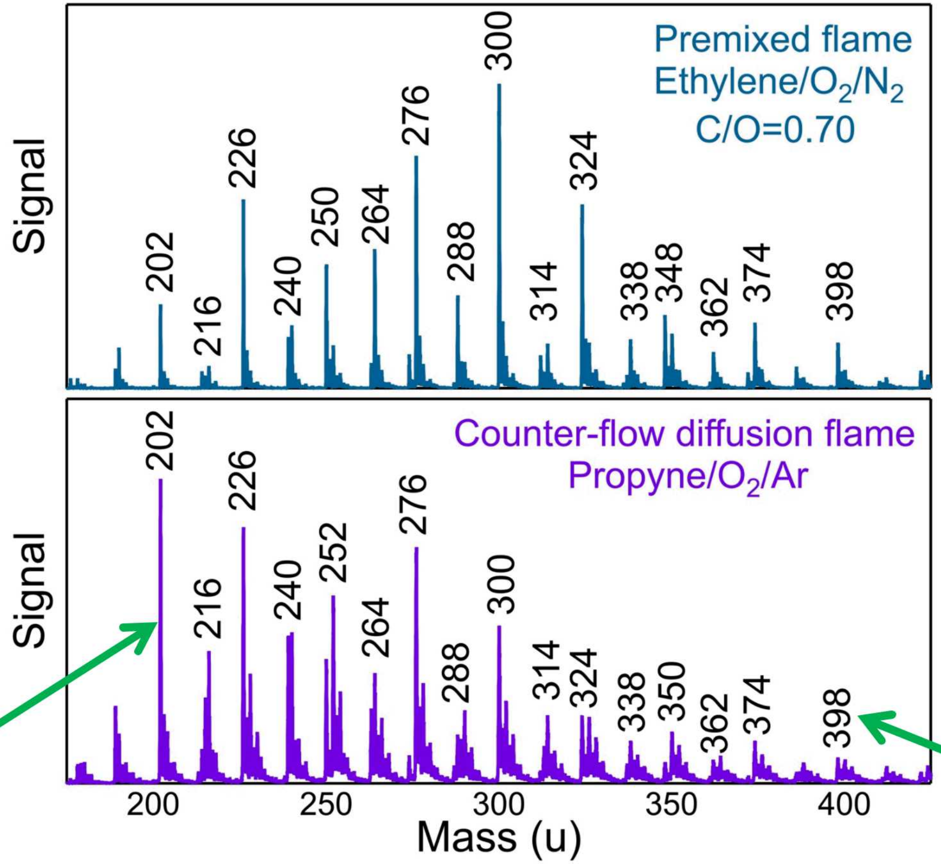


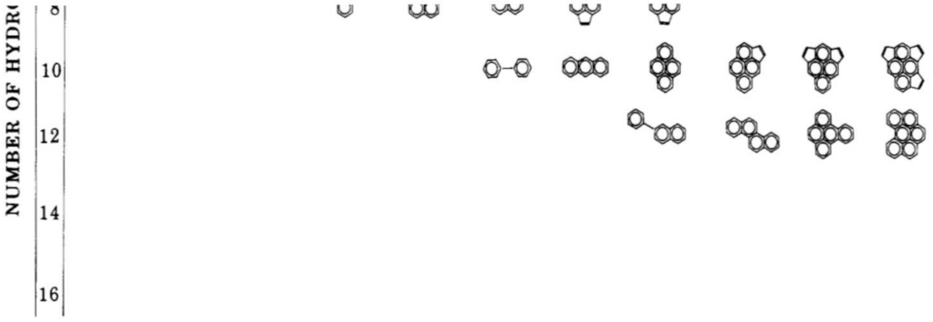
~4-ring PAH

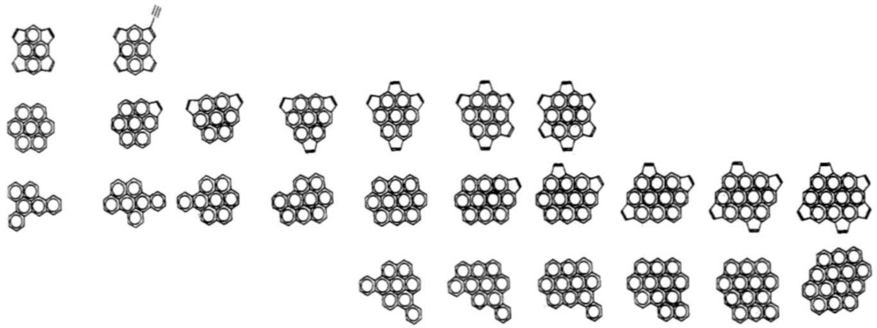
~10-ring PAH

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

Incipient-Particle Composition

Stabilomers





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

ectrons. Since graphitelike molecules (polyaromatics) have both gnificantly lower ratios of edge to interior C atoms and lower ibbs energies per C atom than diamondlike molecules (poly-lamantanes) 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

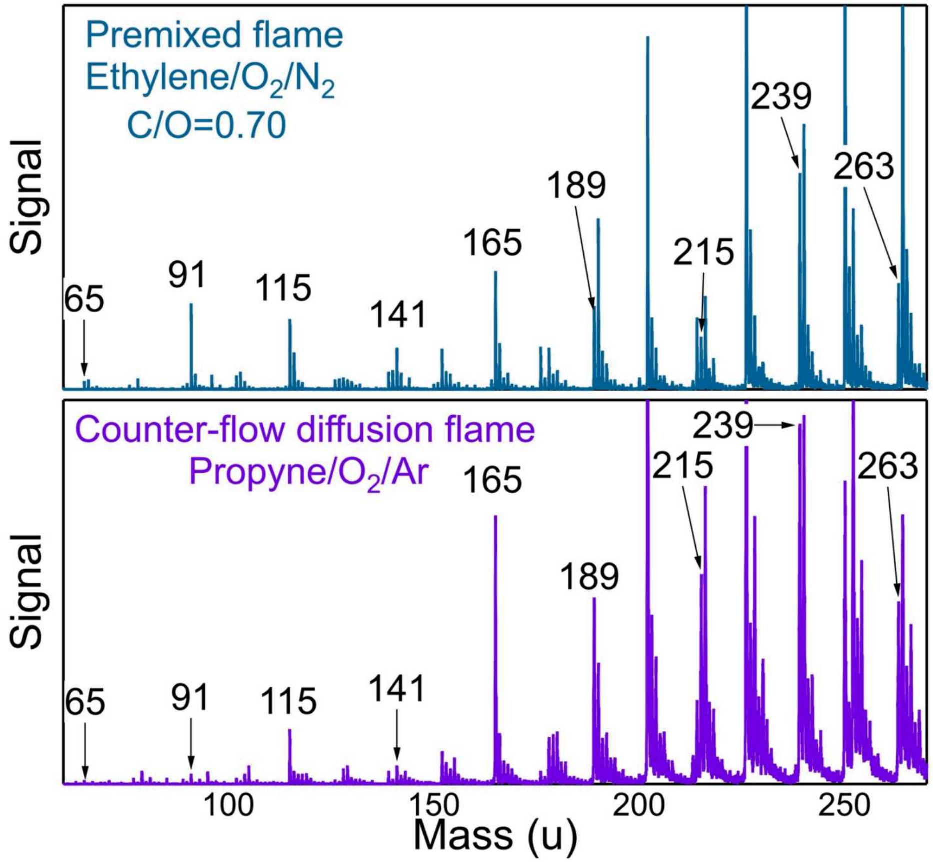
have the same stability near 2700 K, or 400 K lower than the of equal stability for individual molecules.

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.

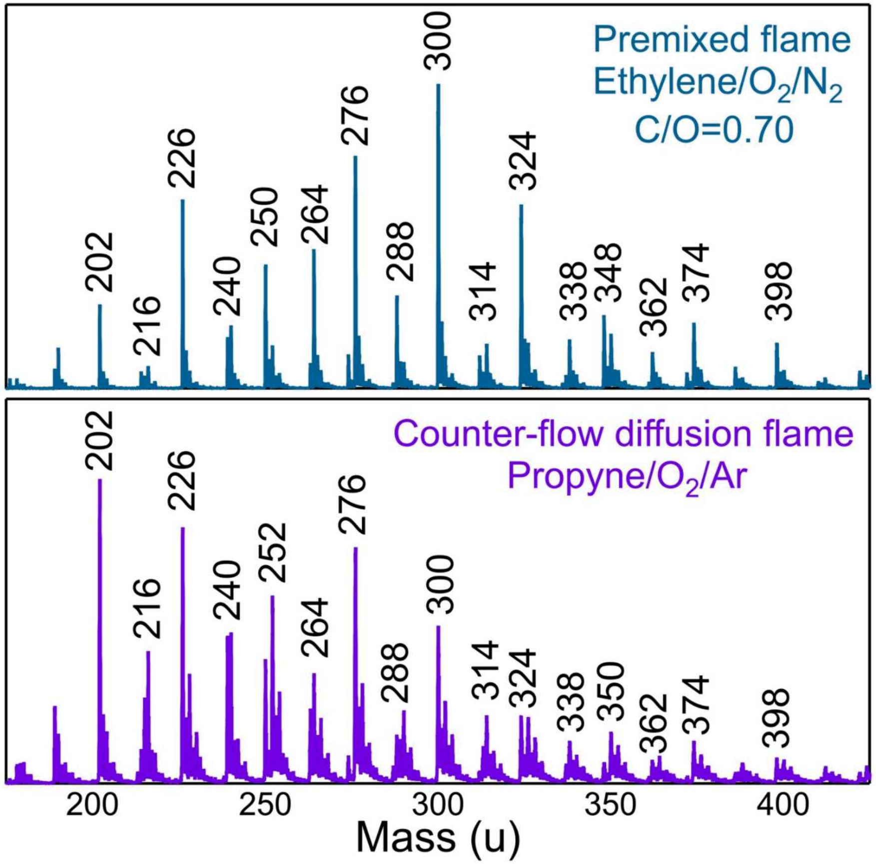
Stein, Fahr 1985

Incipient-Particle Composition

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



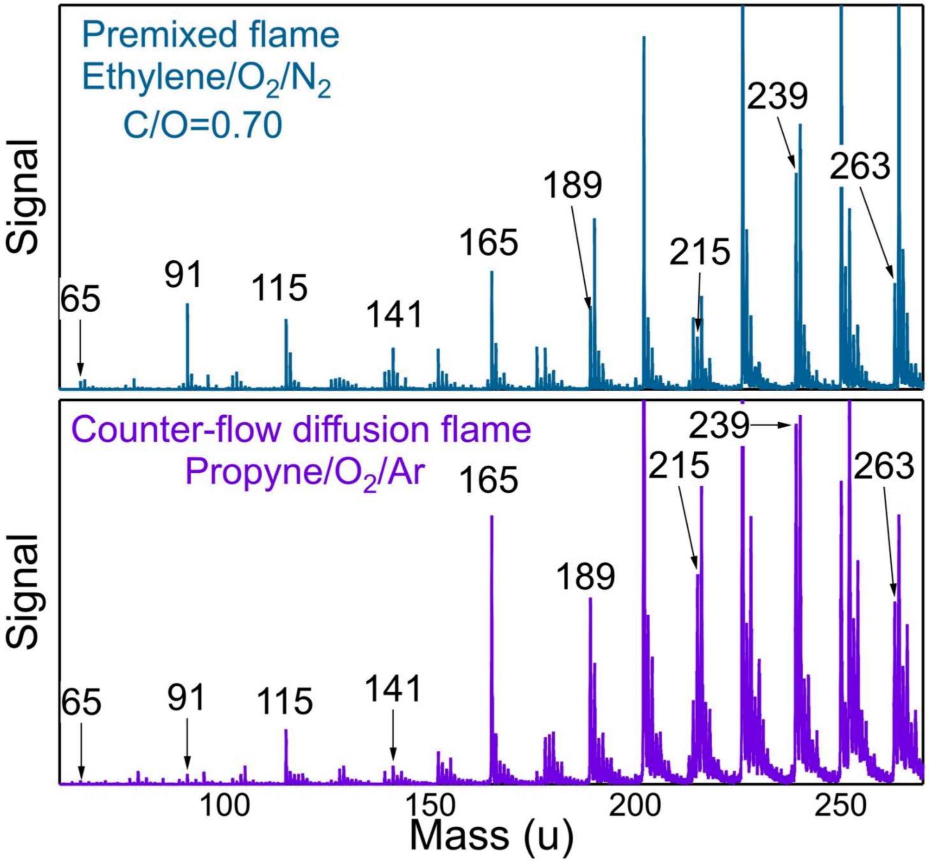
Johansson et al., *Science* 2018



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

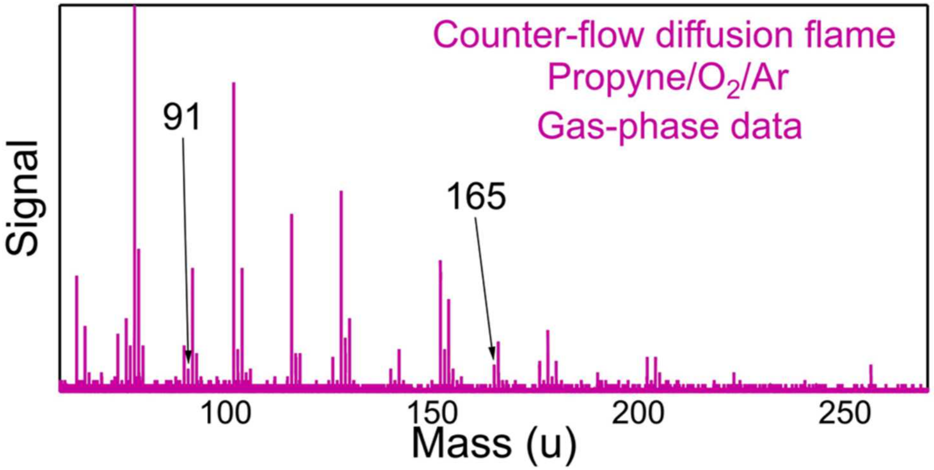
Incipient-Particle Composition

Aerosol mass spectrometry



Johansson et al., *Science* 2018

Gas phase
Molecular beam mass spectrometry

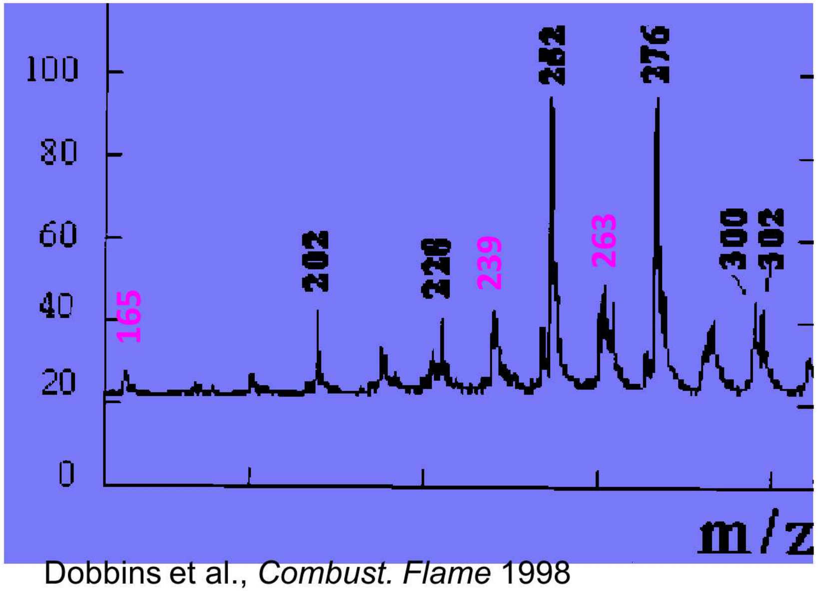


Courtesy of Nils Hansen and Kai Moshammer

Incipient-Particle Composition

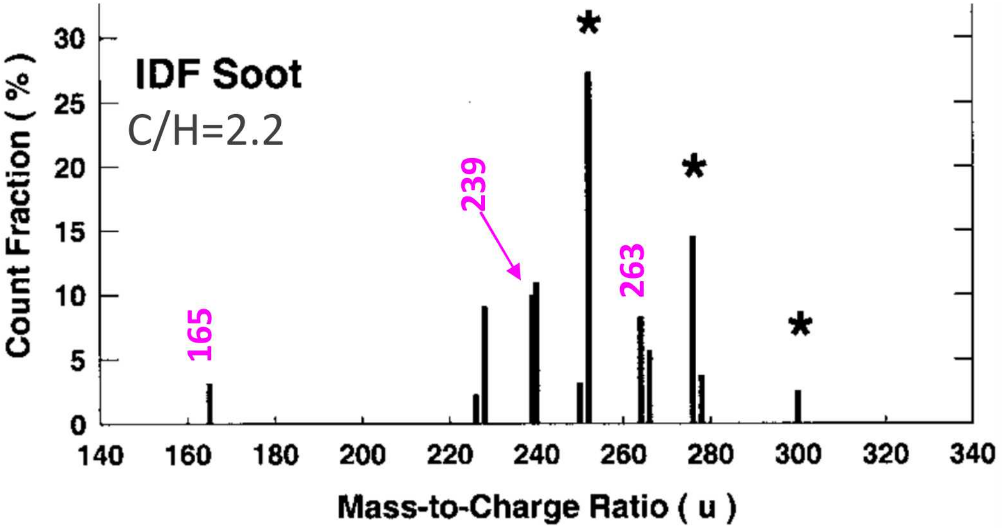
Laser microprobe mass spectrometry

Ethylene/air co-flow diffusion flame



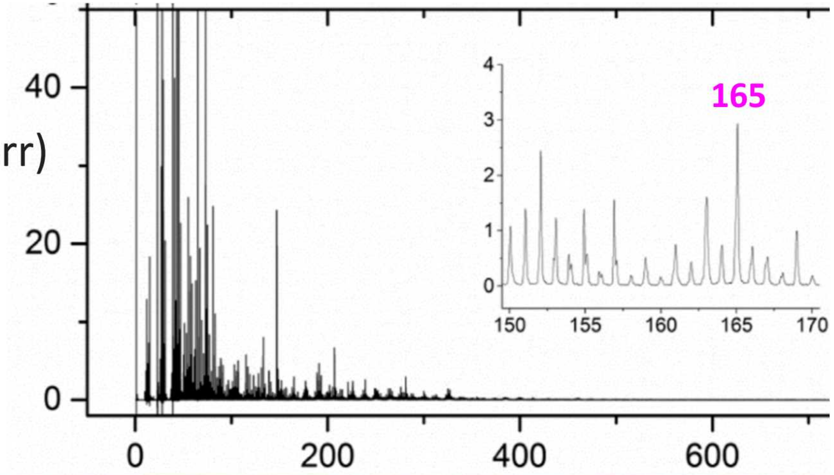
Dobbins et al., *Combust. Flame* 1998

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

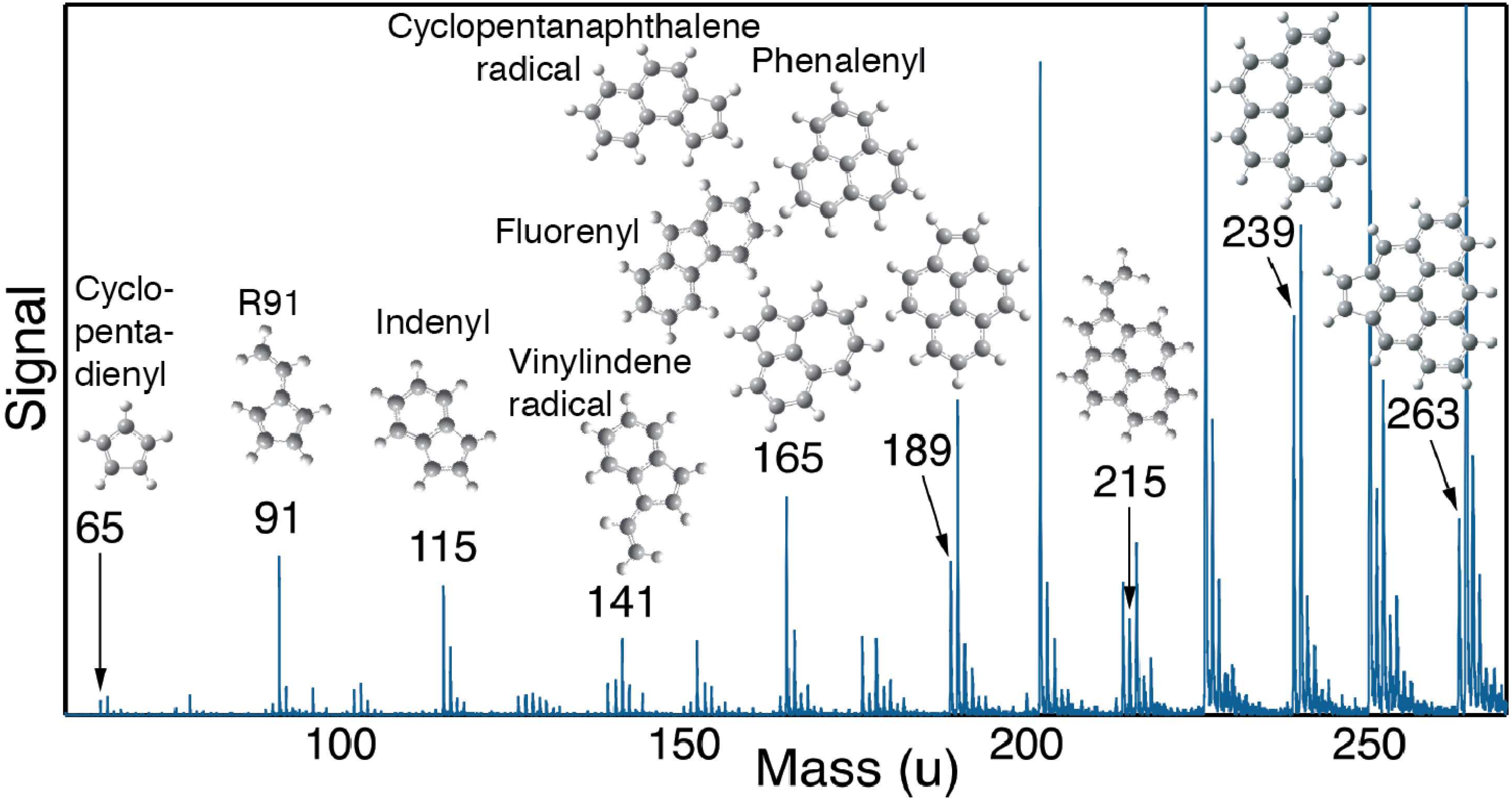


Time of flight secondary ion mass spectrometry

Desgroux et al., *Combust. Flame* 2017

Incipient-Particle Composition

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

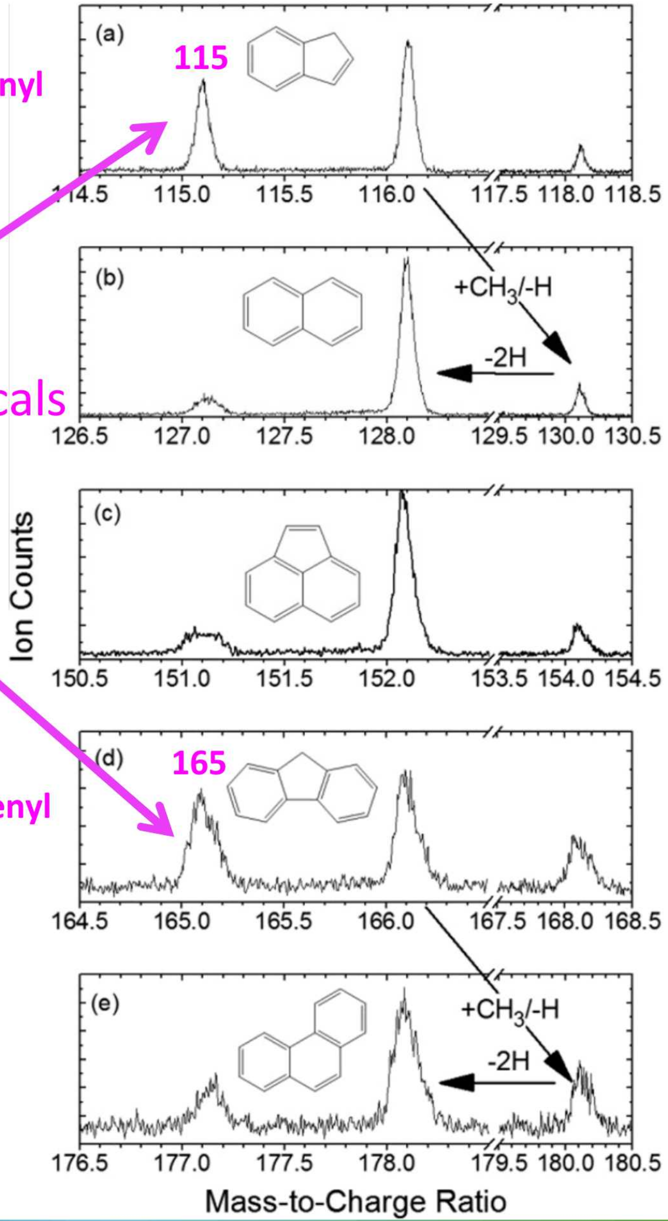


Johansson, Head-Gordon, Schrader, Wilson, Michelsen,
Science, 2018

Other Evidence for RSR Involvement

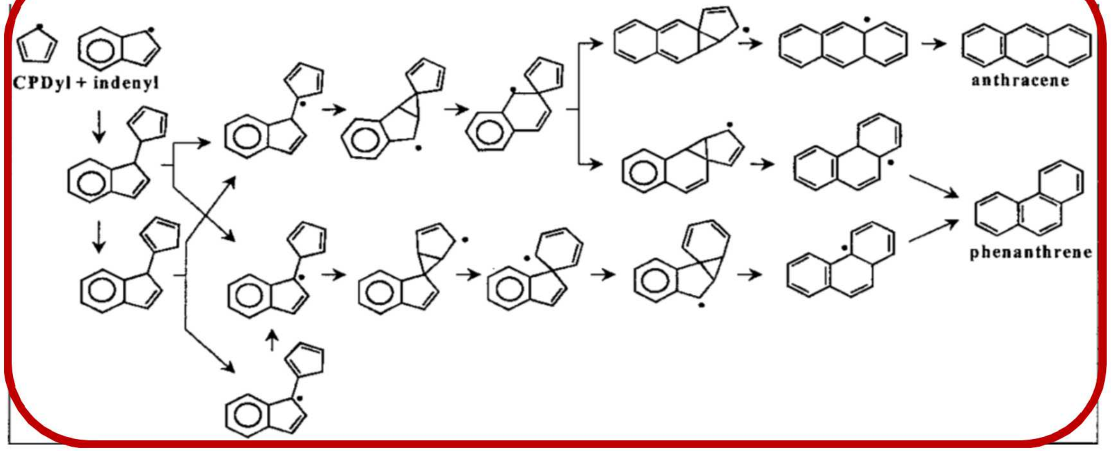
Electron-Impact Molecular Beam Mass Spectrometry (EI-MBMS)

Resonance-stabilized radicals
RSR



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

Role of RSRs in Soot Inception

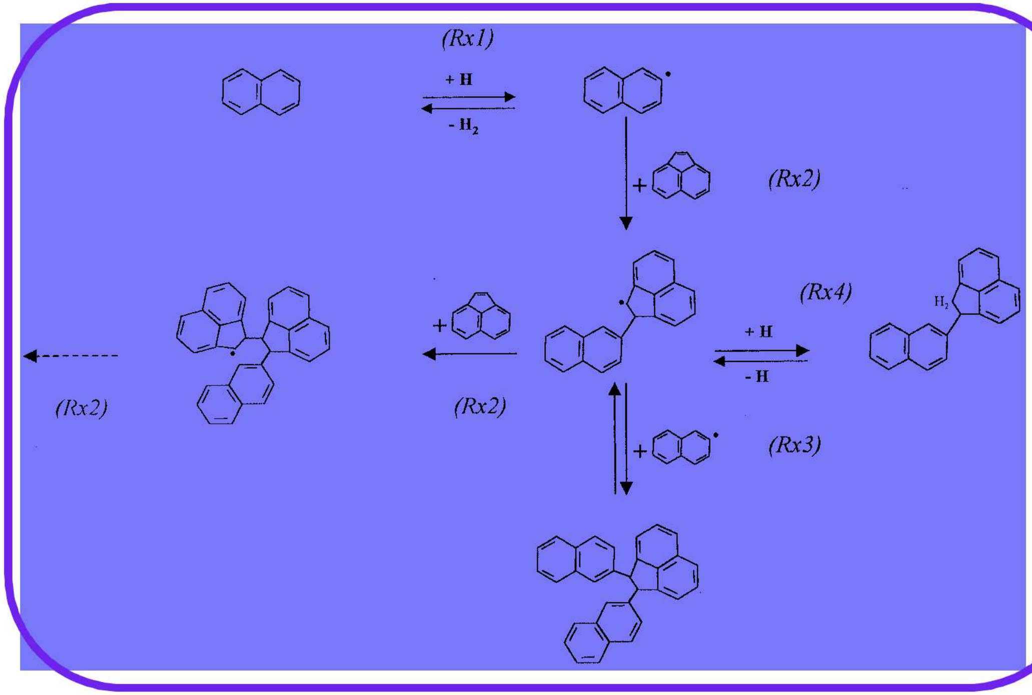


Radical recombination producing larger stabilomers

Mulholland et al., *Proc. Combust. Inst.* 2000

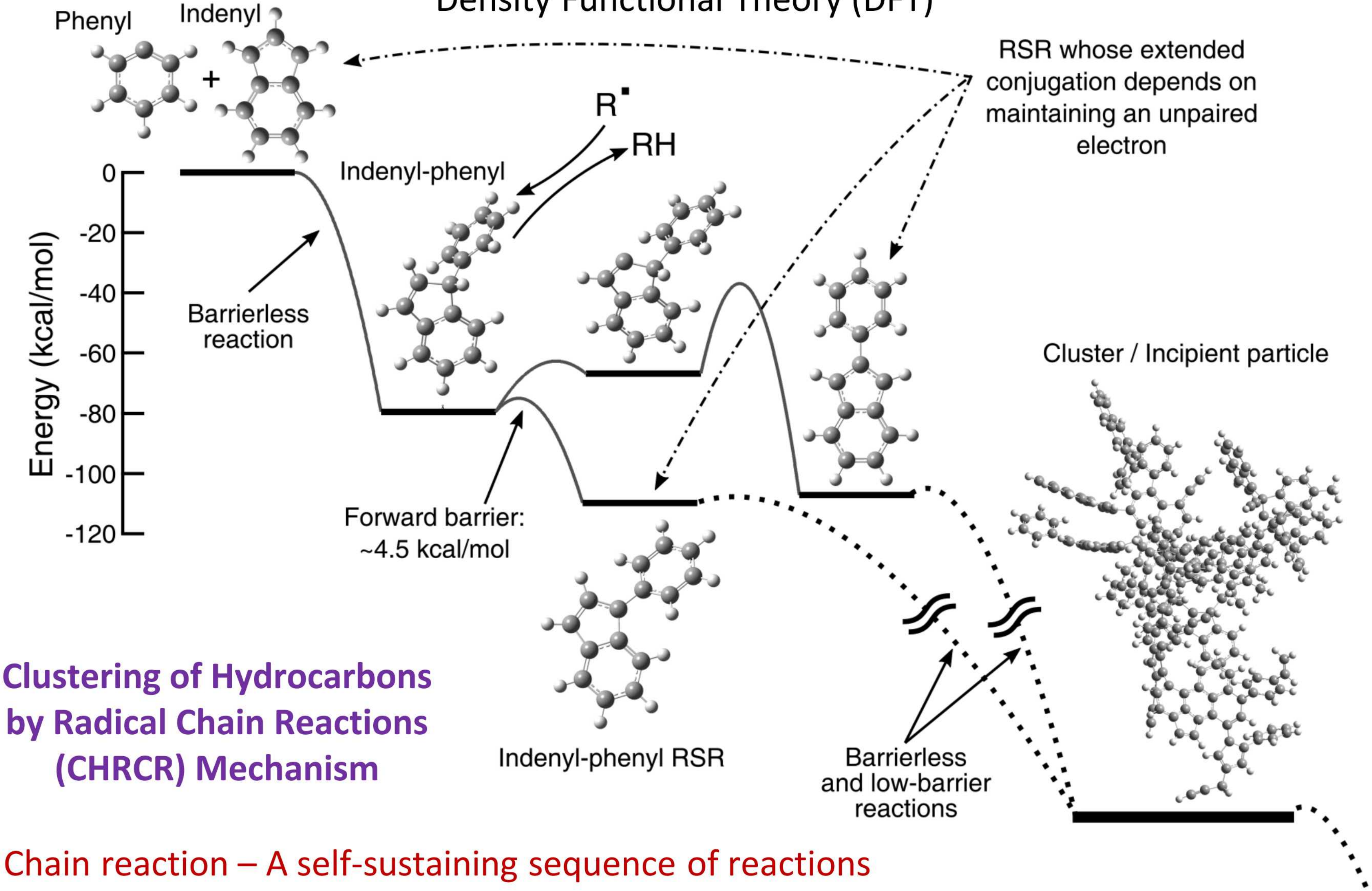
Covalent hydrocarbon clustering via radical addition to acenaphthylene

D'Anna et al., *Combust. Flame* 2001



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

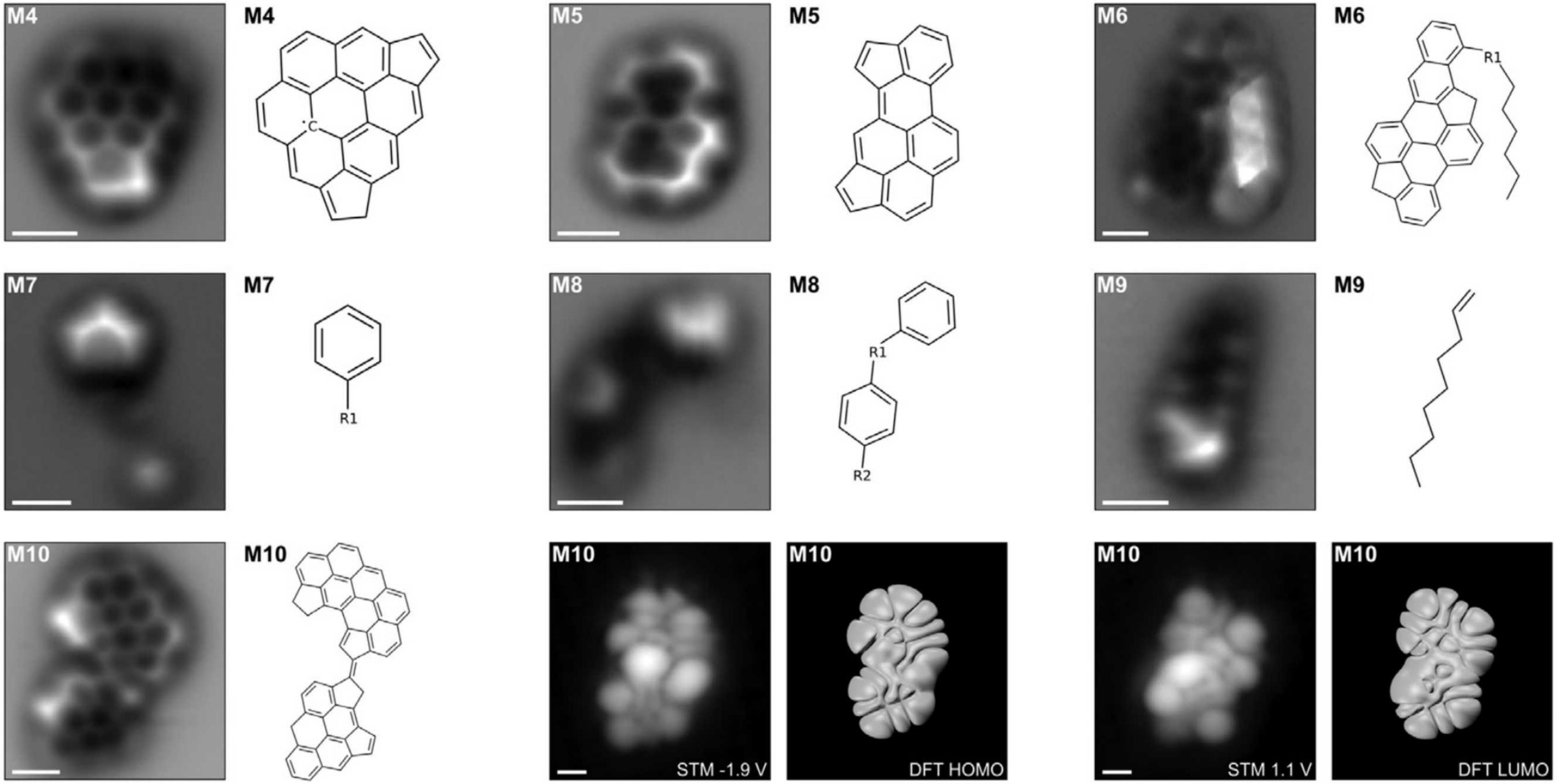
Other Evidence for RSR Involvement

Electron Spin Resonance (ESR)/Electron Paramagnetic Resonance (EPR) Spectroscopy

Homann and Wagner, *Proc. Combust. Inst.* 1967; Vitiello et al., *Combust. Flame* 2019

ESR signal from young soot particles ~100 times larger than from mature soot particles

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



Significant abundance of 5-membered rings and bridged aromatics

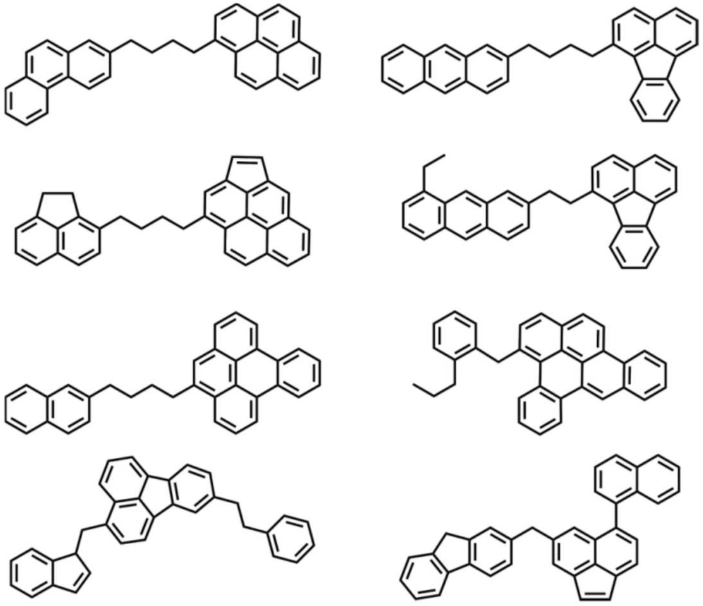
Schulz et al., *Proc. Combust. Inst.*, 2019

Other Evidence for RSR Involvement

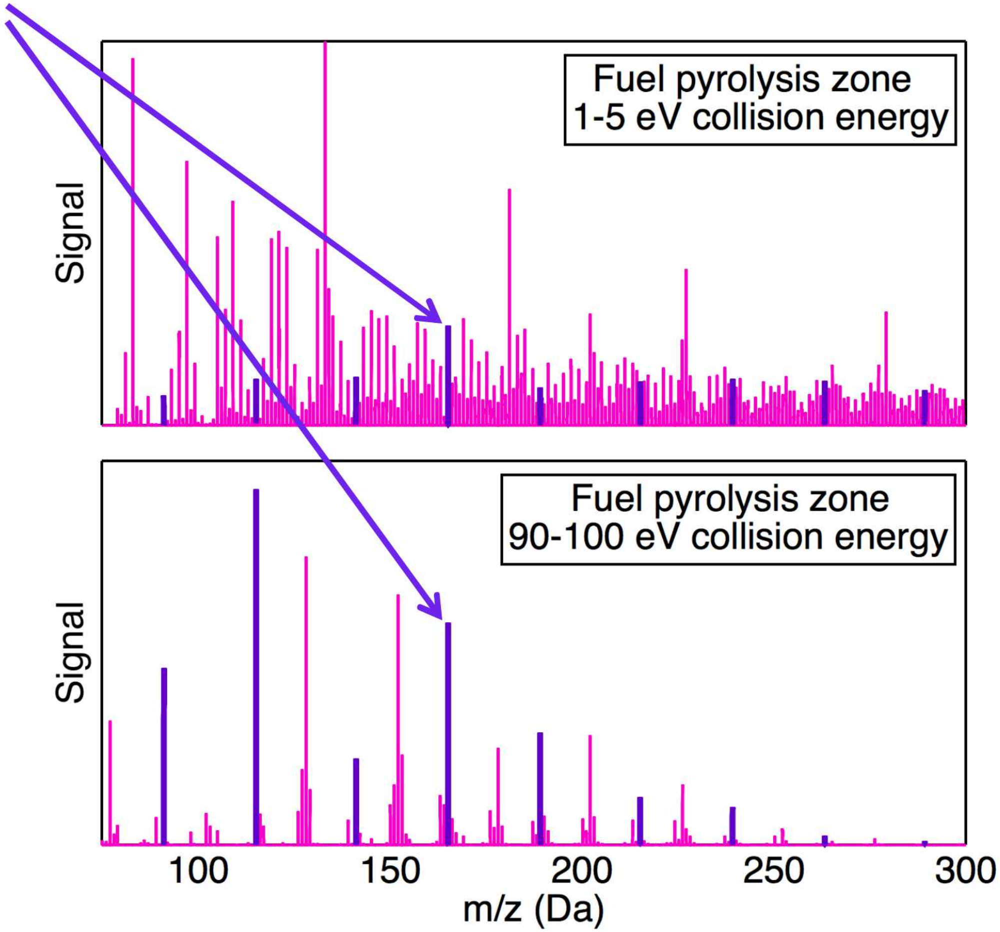
Tandem Mass Spectrometry (MS-MS)

Collision-Induced Dissociation Time-of-Flight Mass spectrometry (CID-TOFMS)

Species consistent with the data



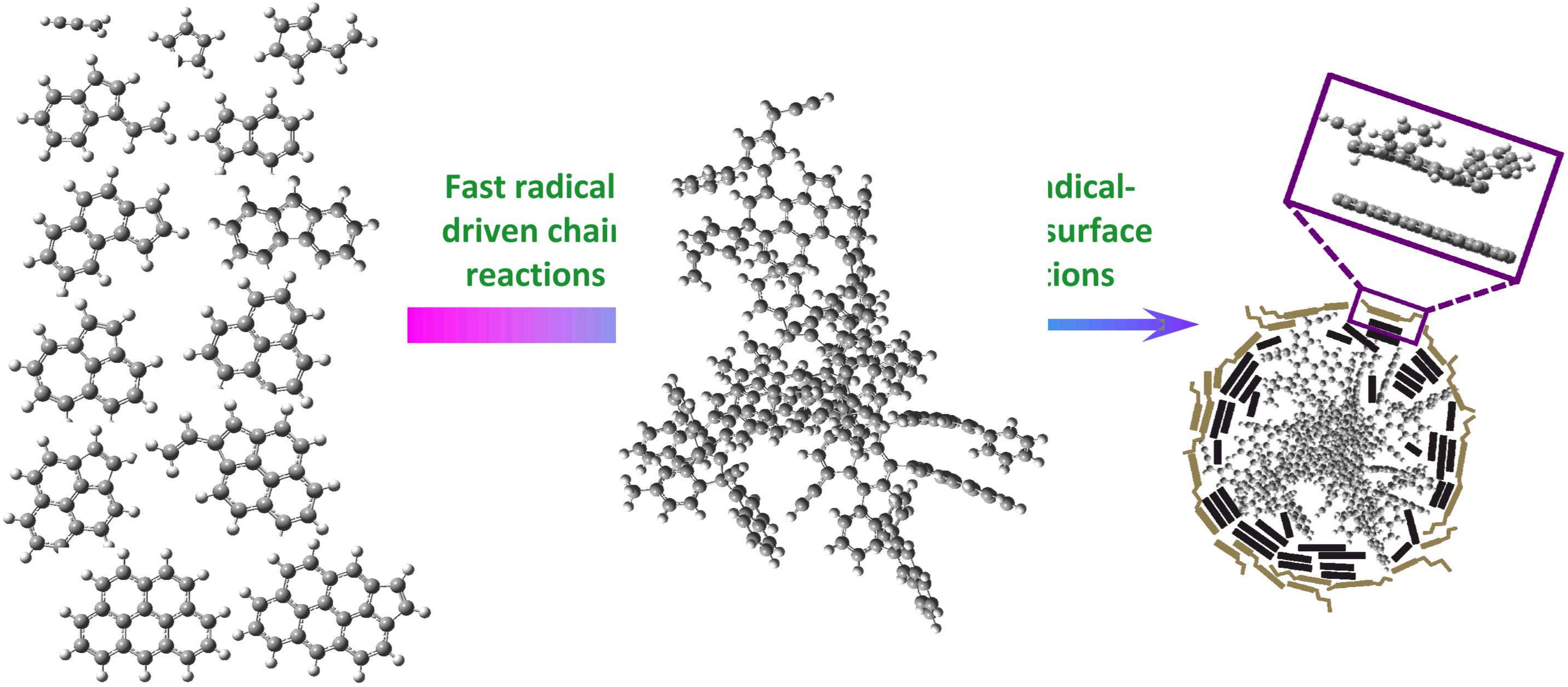
Adamson et al., *J. Phys. Chem.*, 2018



RSRs

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

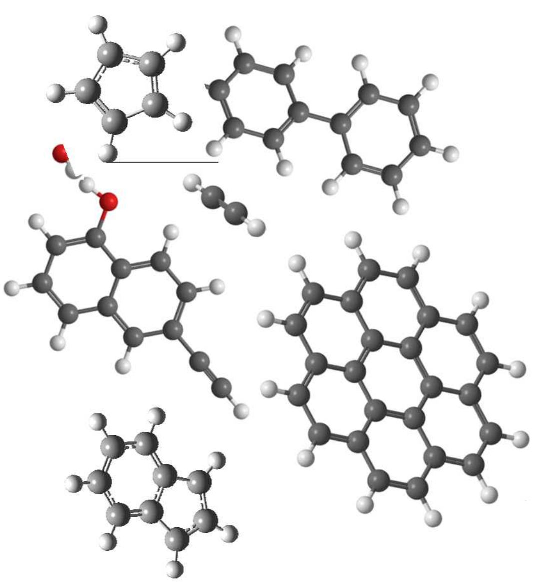
Fast radical
driven chai
reactions

dical-
surface
ions

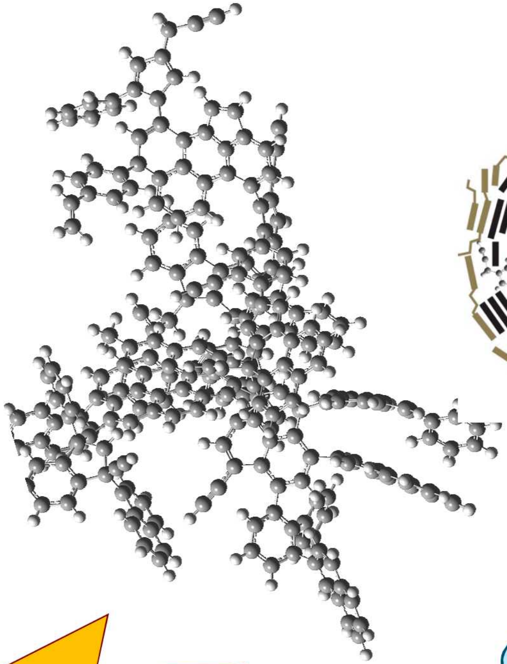
Johansson, Head-Gordon, Schrader, Wilson, Michelsen, *Science*, 2018

Summary and Conclusions

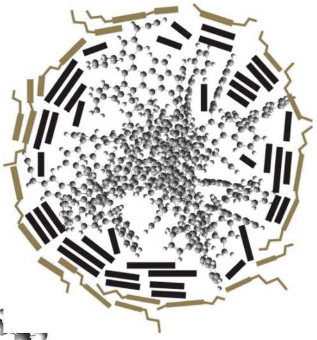
Molecular growth; Soot-precursor formation



Incipient particle formation



Maturation, surface growth, graphitization



Particle growth, aggregation, graphitization

Inception driven by radical chain rxns

Growth by surface addition

Possibly by radical rxns

Future Directions

- **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

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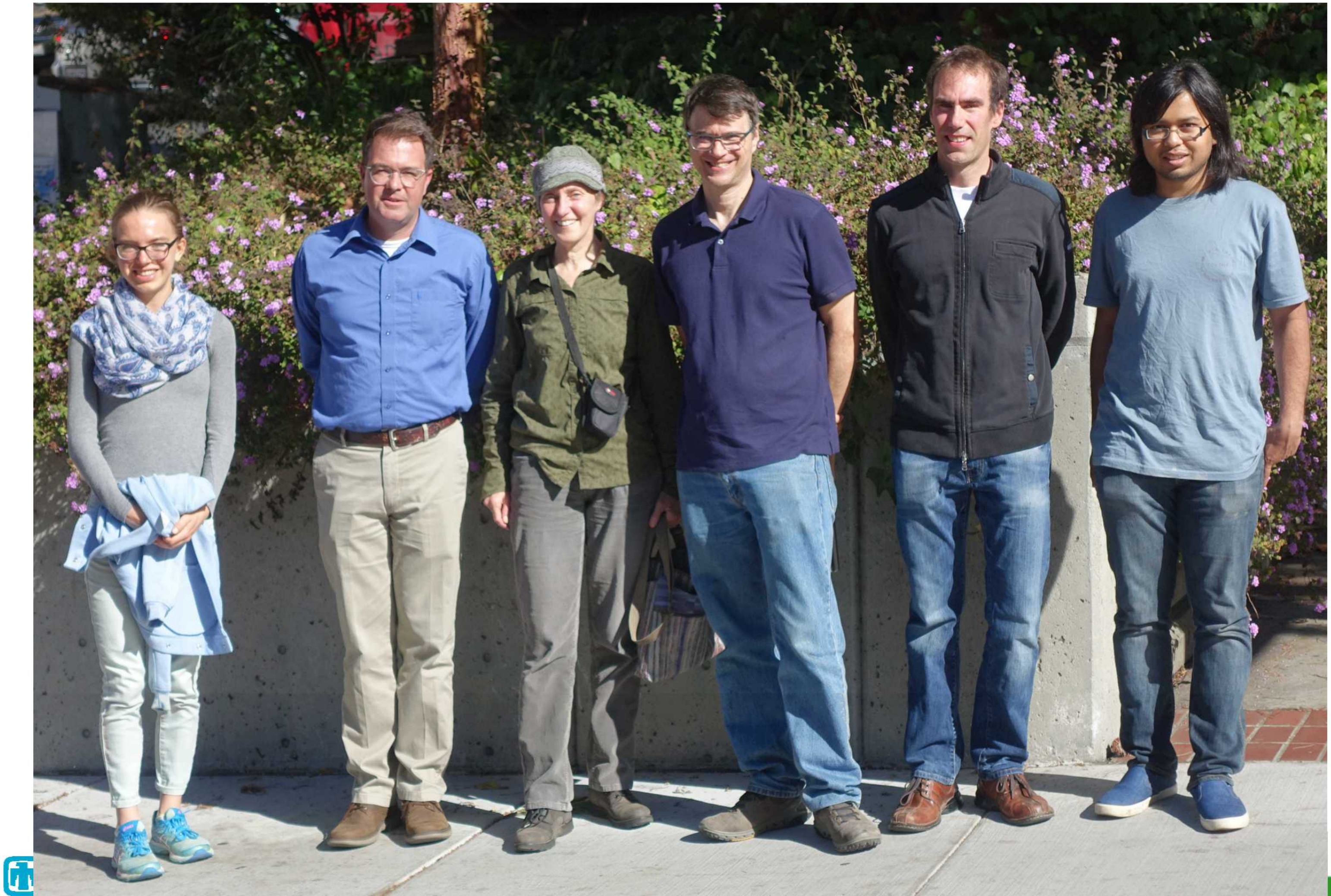

My Gratitude to

Olof Johansson, Paul Schrader

Brian Adamson, Scott Skeen, Nils Hansen,
Kai Moshammer

Kevin Wilson, Martin Head-Gordon,
Bruce Rude

US DOE Office of Basic Energy Sciences

Thank you