Formation of Nascent Soot and Other Condensed-Phase Materials in Flames

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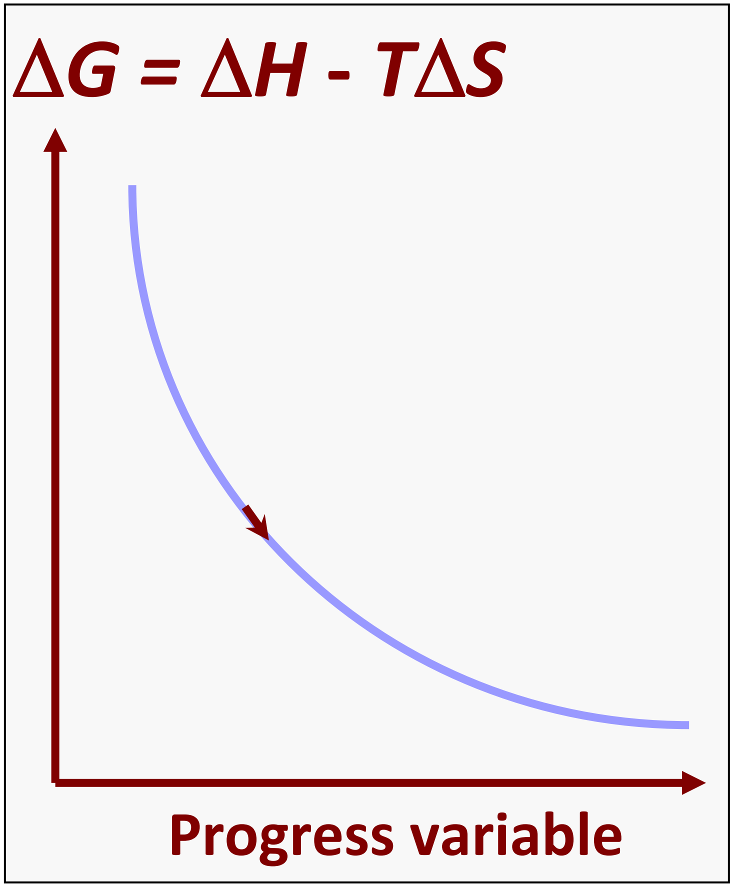
Work supported by NSF, SERDP and DOE (CEFRC)

Why Does Condensed-Phase Matter Form?



Gas-to-Solid Transformation

- **Type 1: enthalpy driven (heat release)**

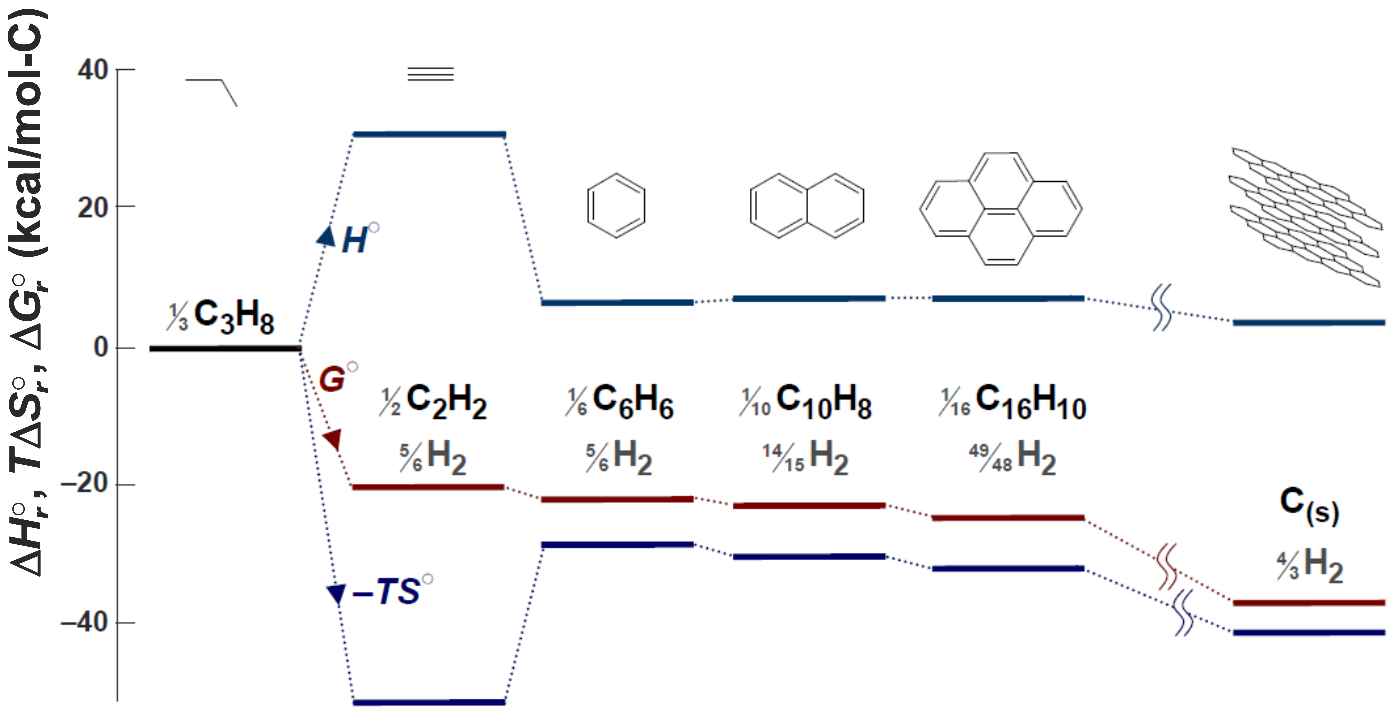
  metal oxides
  carbides, nitrides

- **Type 2: entropy driven**

  soot

  $C_3H_8 \rightarrow$ solid carbon + $4H_2$
  ($\Delta H > 0$, but $\Delta S > 0$)

Driving Force – Soot



- Soot formation is entropy driven (H_2 goes free).
- Condensed-phase carbon forms as an aerosol (kinetics driven).

Condensed-phase material is ubiquitous in flames

http://www.historyforkids.org/learn/science/fire.htm

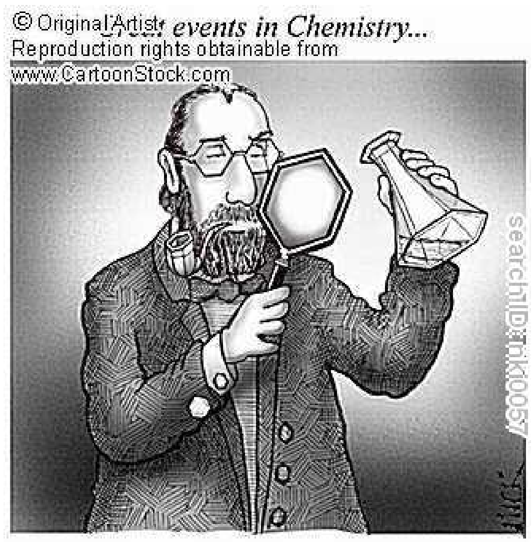
http://hearth.com/what/historyfire.html

Lampblack (soot) used in prehistoric cave paintings (35,00 -10,000 ybp)

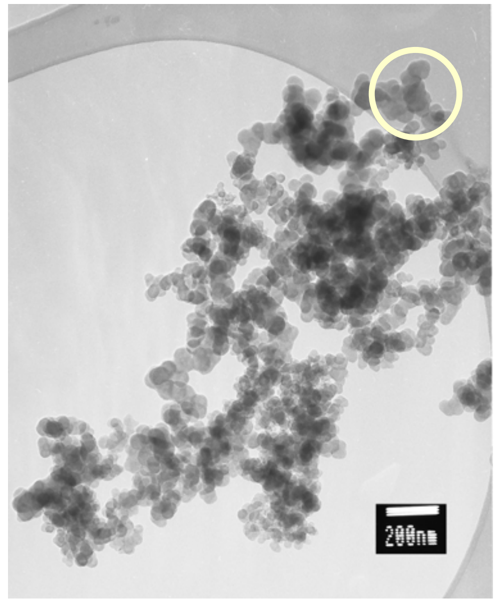
G. Nelson Eby, http://faculty.uml.edu/nelson_eby/Forensic%20Geology/PowerPoint%20Presentations.htm

World's oldest tattoos (Tyrolean iceman, Ötzi) were etched in soot (c. 3,300 BC)

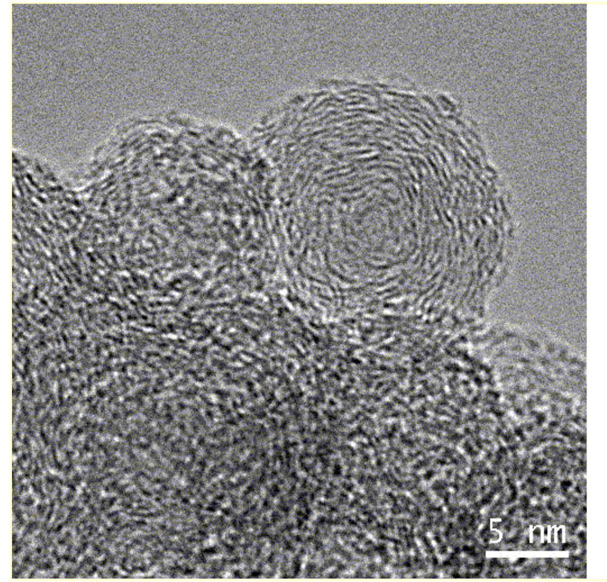
Soot Microstructures/Composition



1865: Kekulé, moments before his brilliant insight into the structure of benzene.



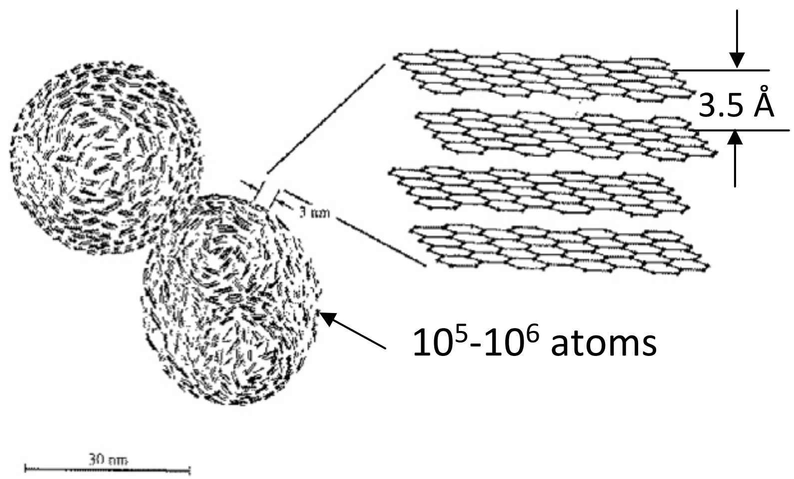
http://www.asn.u-bordeaux.fr/images/soot.jpg



Courtesy: Boehman

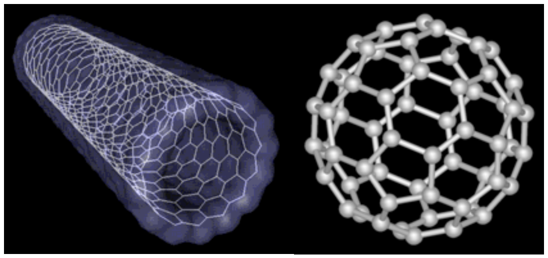
Mature soot:

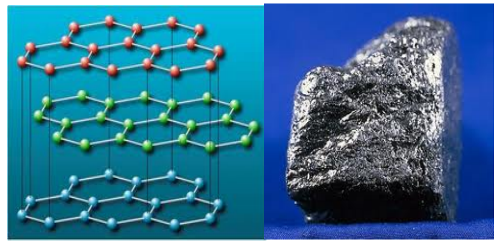
C/H ~ 8/1
ρ = 1.8 g/cc

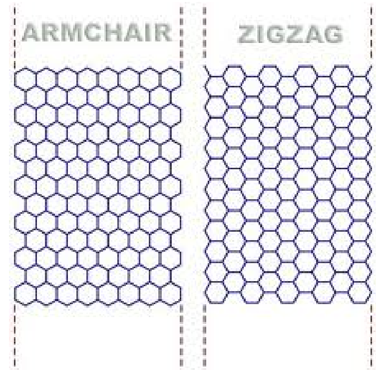


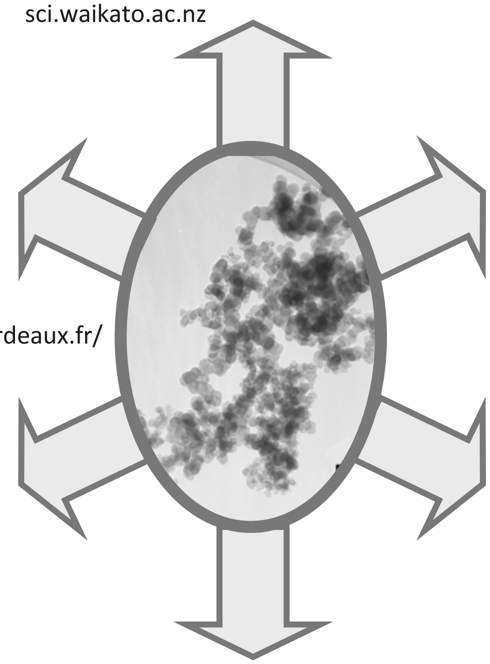
http://www.atmos.umd.edu/~pedro/soot2.jpg

Soot as a Versatile Material – Old and New


daneshema.com

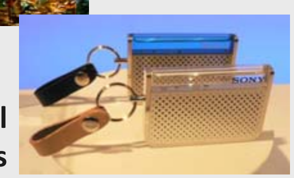

sci.waikato.ac.nz




http://www.asn.u-bordeaux.fr/images/soot.jpg

renewable energy


3rd generation solar cells

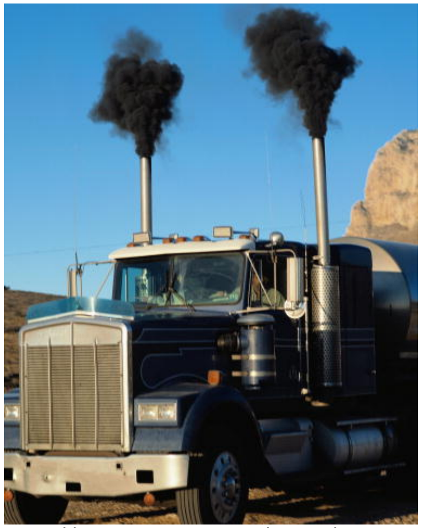

direct methanol fuel cells

Soot as Particulate Air Pollutants

http://farm1.static.flickr.com/216/499969453_44089c6c1d.jpg

http://www.spacemart.com/images/cruis
e-ship-smoke-stack-emission-bg.jpg]

http://www.parks.ca.gov/pages/491/images/sierra_3
_steam_locomotive.jpg



http://www.sfgate.com/blogs/ima
ges/sfgate/green/2009/06/03/dies
el-smoke.jpg

http://www.soot.biz/images/soot/soot
_250x251.jpg

Soot and the Climate

- **Soot deposition responsible for 95% polar ice melting**

- **Dirty snow reduces ice albedo**

- **Brown clouds causes regional warming**

- **Contrail related cloud albedo**

Driving Forces behind Soot Research (1)

The 80s' & 90s':

"A major break-through in understanding carbon formation will have been achieved when it becomes possible in at least one case to account for the entire course of nucleation and growth of carbon on the basis of a fundamental knowledge of reaction rates and mechanisms."

Palmer & Cullis, 1965

Frenklach, **Wang**, *Proc. Combust. Inst.* 23 (1990) 1559.

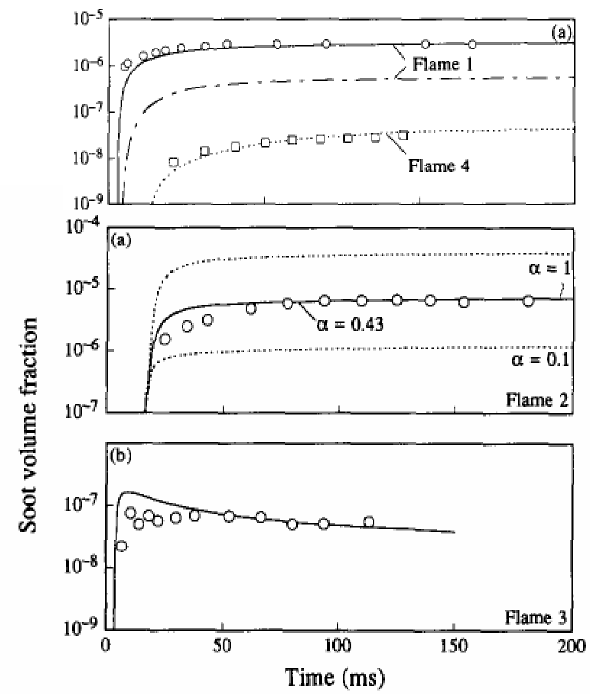
Frenklach, **Wang**, in: *Soot Formation in Combustion: Mechanisms and Models of Soot Formation*, Bockhorn, Ed. Springer-Verlag, Berlin, 1994, pp 162-190.

Colket, Hall, in *Soot Formation in Combustion: Mechanisms and Models of Soot Formation,* Bockhorn, Ed. Springer-Verlag, Berlin, 1994, pp 442-468.

Mauss, Schafer, and Bockhorn, *Combust. Flame* 99, 697-705 (1994)

Bockhorn, ed. *Soot Formation in Combustion: Mechanisms and Models of Soot Formation,* Springer-Verlag, Berlin, 1994.

Kennedy "Models of soot formation and oxidation," *Prog. Energy Combust. Sci.* 23 (1997) 95-132.

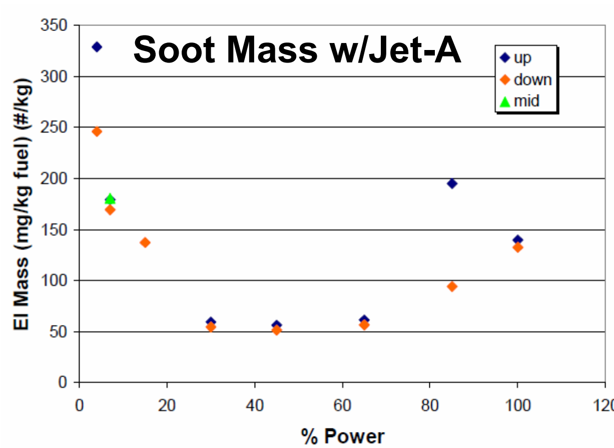


Data: Jander & Wagner, Simulation: Kazakov, Wang, Frenklach (1994)

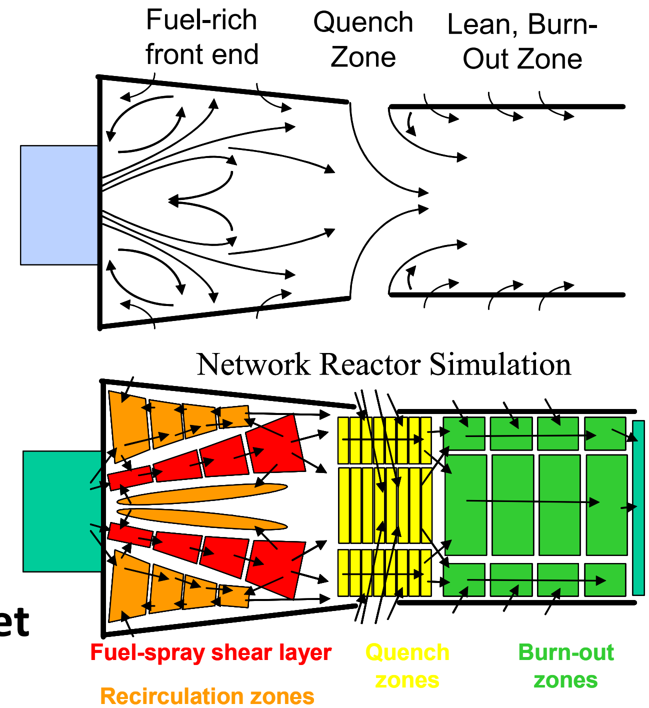
Driving Forces behind Soot Research (2)

The most recent decade:

Predictive tools for combustion engine designs



Fuel injector/swirler



Courtesy of Colket

Bai, Balthasar, **Mauss**, Fuchs *Proc. Combust. Inst.* 27 (1998) 1623.

Pitsch, Riesmeier, **Peters** *Combust. Sci. Technol.* 158 (2000) 389.

Wen, Yun, **Thomson**, Lightstone *Combust. Flame* 135 (2003) 323.

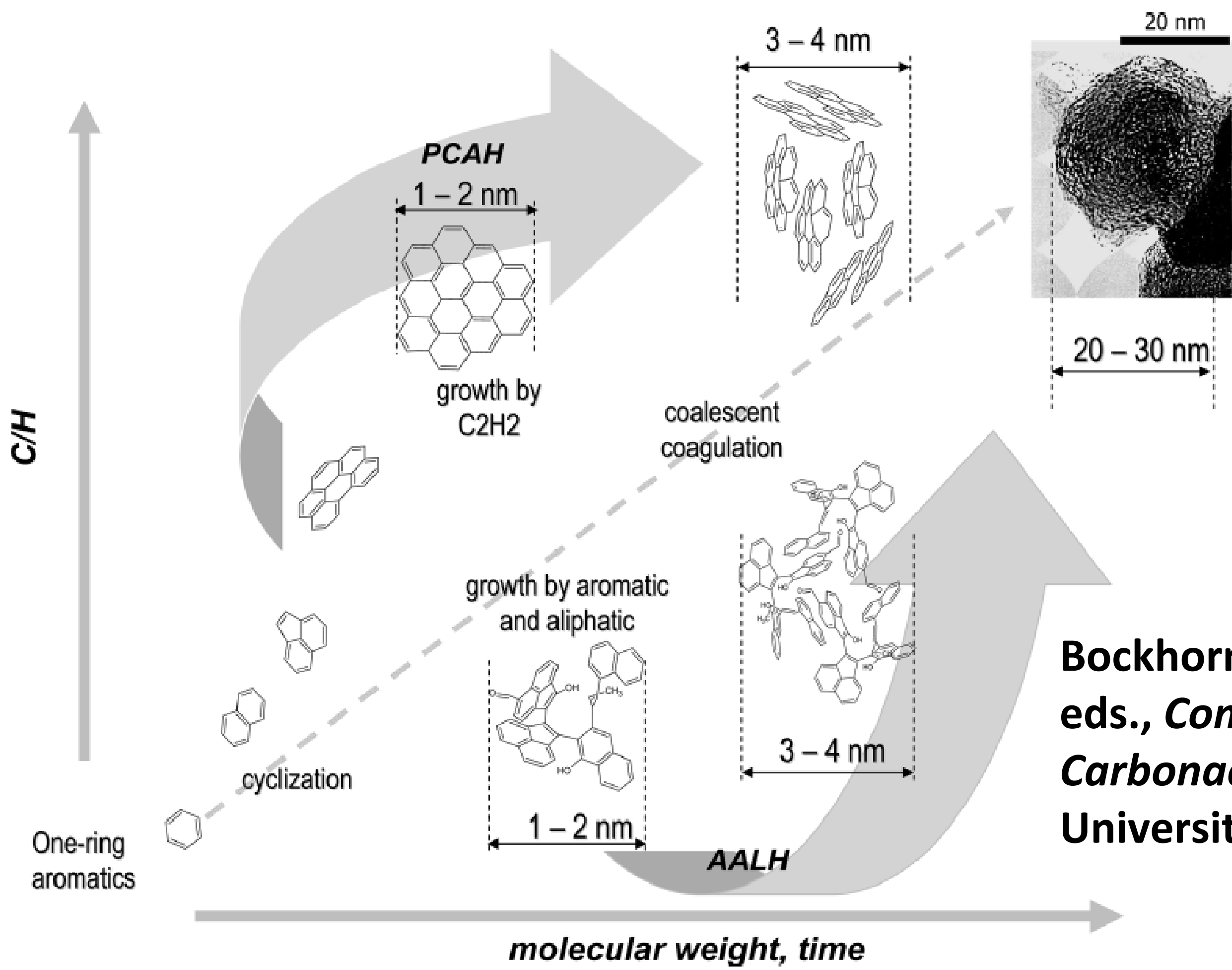
Wang, **Modest**, **Haworth**, Turns *Combust. Theor. Model.* 9 (2005) 479.

Lignell, **Chen**, Smith, Lu, Law *Combust. Flame* 151 (2007) 2.

Mosback, Celnik, Raj, **Kraft**, Zhang, Kubo, Kim *Combust. Flame* 156 (2009) 1156.

Haworth *Prog. Energy Combust. Sci.* 36 (2010) 168-259.

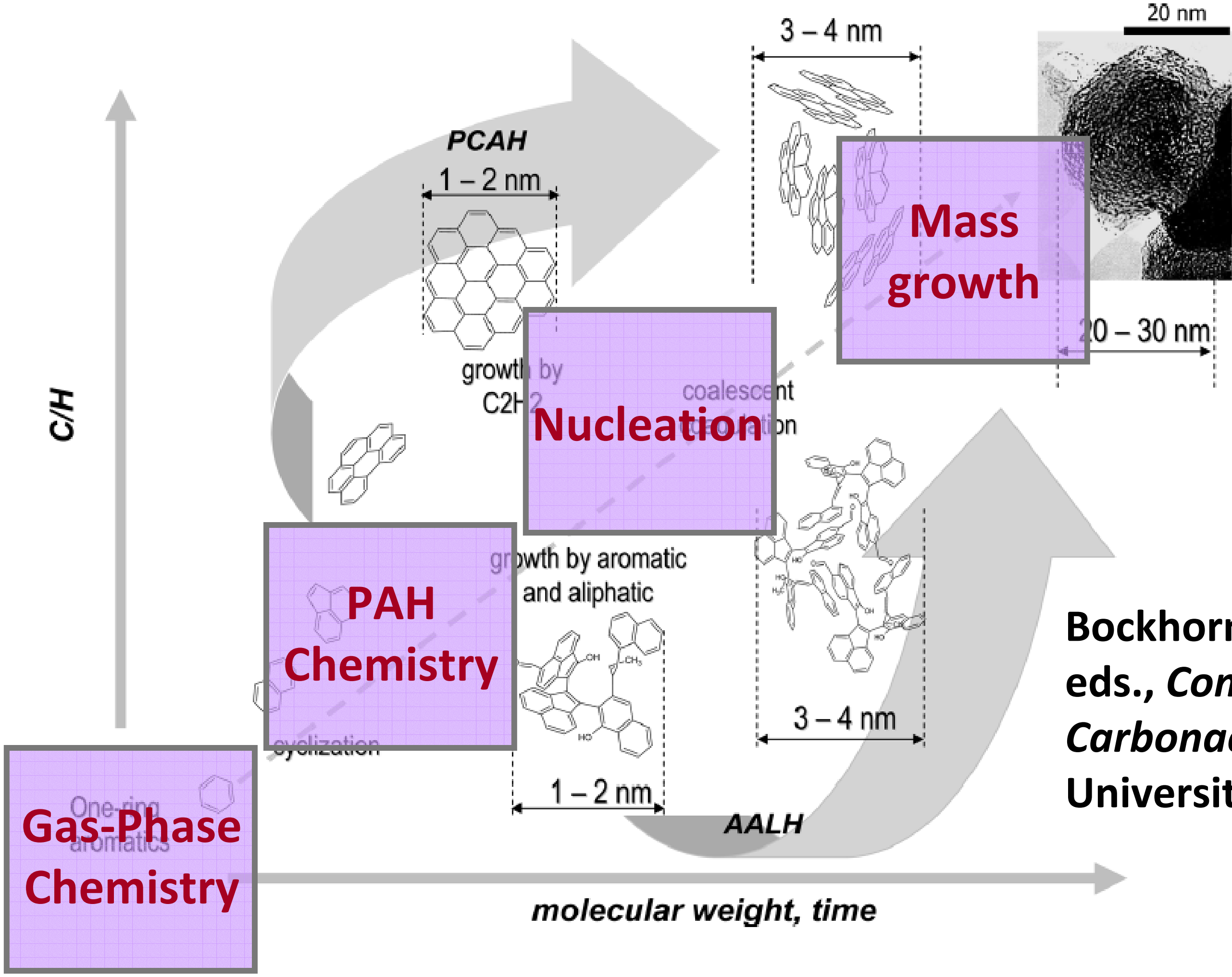
Kinetic Mechanism of Soot Formation



Bockhorn, D’Anna, Sarofim, Wang, eds., *Combustion Generated Fine Carbonaceous Particles*, Karlsruhe University Press, 2009.

Courtesy of D’Anna

Kinetic Mechanism of Soot Formation

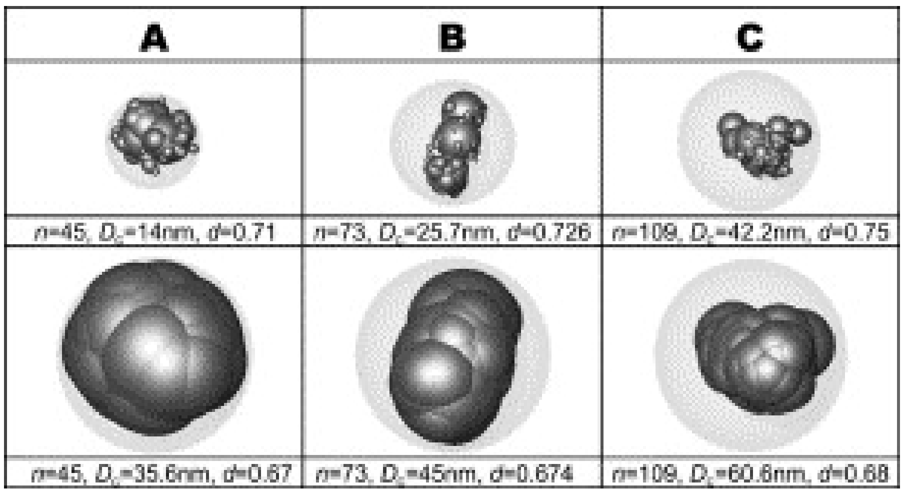


Courtesy of D'Anna

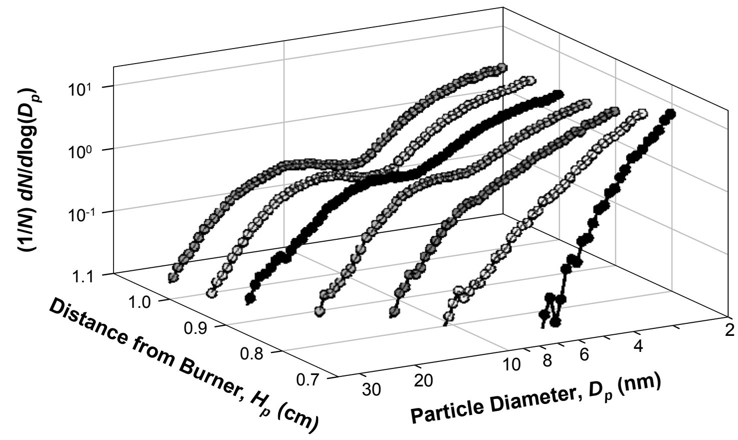
Bockhorn, D'Anna, Sarofim, Wang, eds., *Combustion Generated Fine Carbonaceous Particles*, Karlsruhe University Press, 2009.

Recent Highlights (2)

- **Kinetic Monte Carlo simulation explains the origin of sphericity of nascent soot particles**

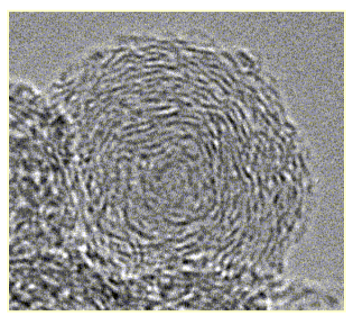


Balthasar, Frenklach (2005)



Abid et al. (2009)
C_2H_4-O_2-Ar flame ϕ = 2.1

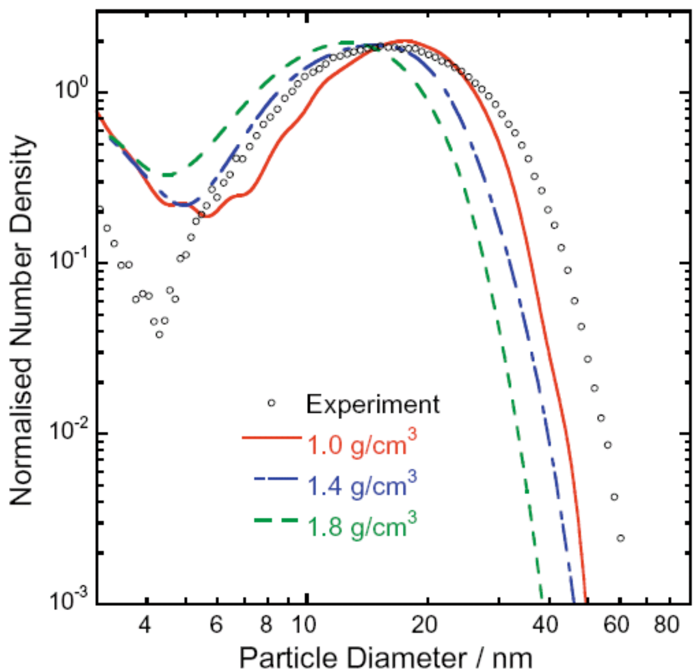
Eventually



Recent Highlights (3)

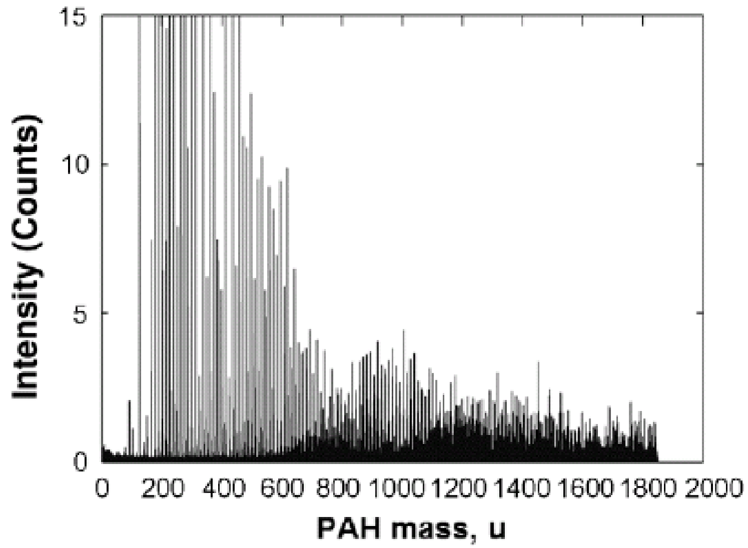
- **Stochastic simulations with detailed chemistry and aerosol dynamics are able to predict particle size distribution & soot chemical compositions**

Particle Size Distributions

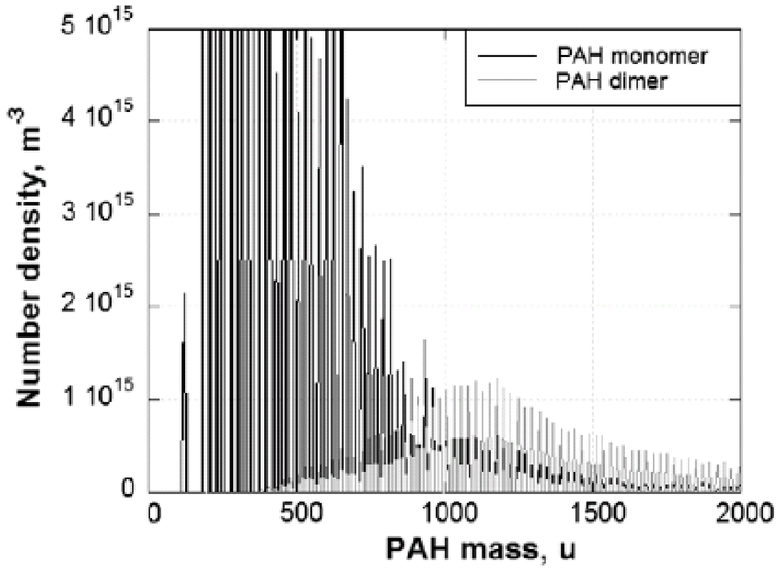


Courtesy of Kraft

Chemical makeup



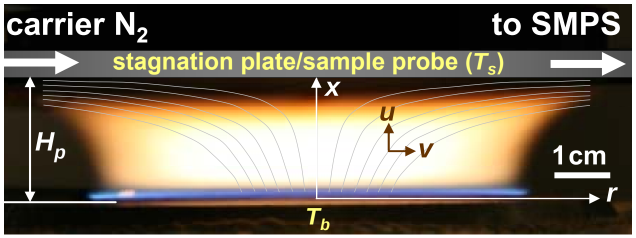
(a) Experimental mass spectra



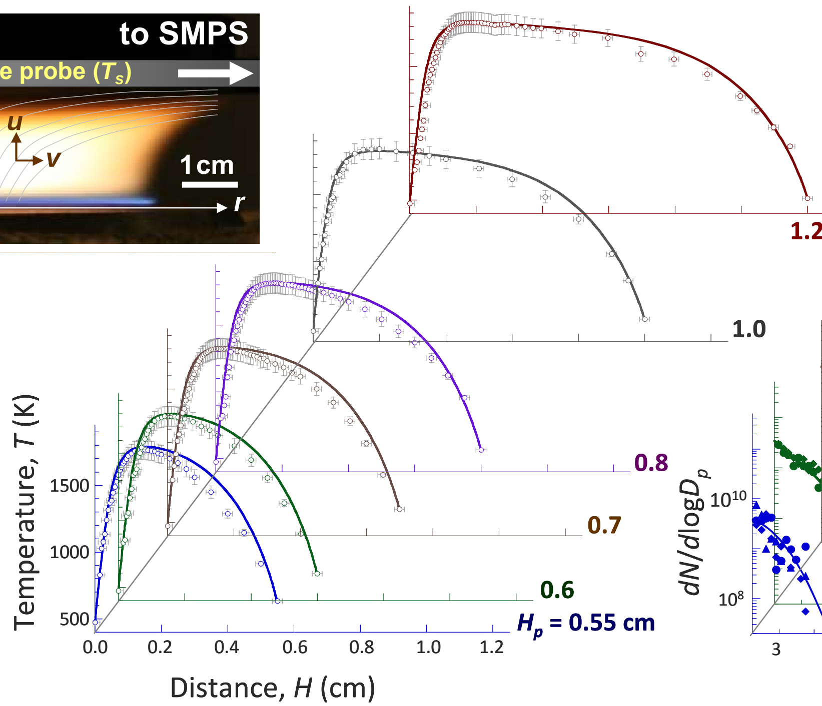
(b) Computed mass spectra

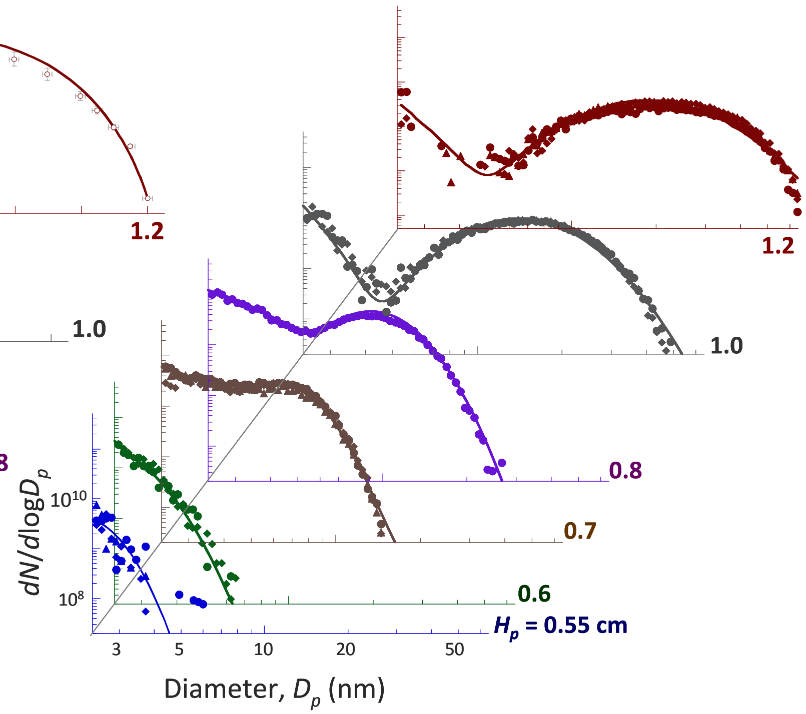
Experiments Facilitate Model Comparison

Burner-stabilized stagnation flame approach



$C_2H_4/O_2/Ar$ flame ($\phi = 2.1$)





Measured and computed (USC Mech II) temperature in close agreement) – removed the need to "shift" time zero.

Detailed PSDFs by mobility sizing provide added resolution to probing soot nucleation and mass/size growth chemistry

Abid et al. (2009)

Current Problems & Questions

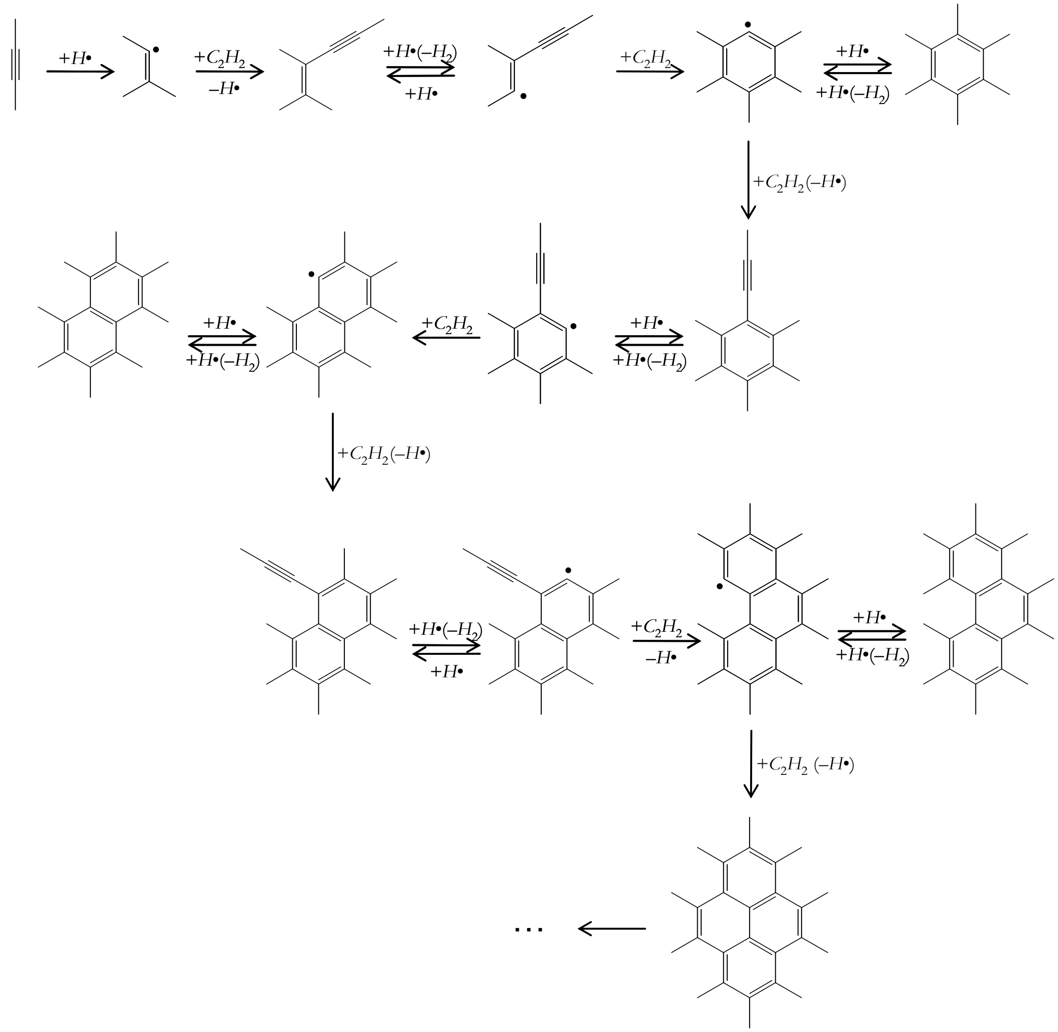
- PAH precursor chemistry and its dependency on fuel structures;
- What is the mechanism of particle inception?
- Is the composition of nascent soot identical to mature soot?
- Is the HACA mechanism compete?

PAH Precursor Chemistry (1)

The Hydrogen-Abstraction—Carbon Addition (HACA) Mechanism (Frenklach)

- Stein's stabilomers as soot building block
- Capture three important factors of molecular weight growth

	Flame chemistry	PAH formation
H atom	chain branching	activation
C_2H_2	dominant species	building block
High T	heat release	Arrhenius kinetics

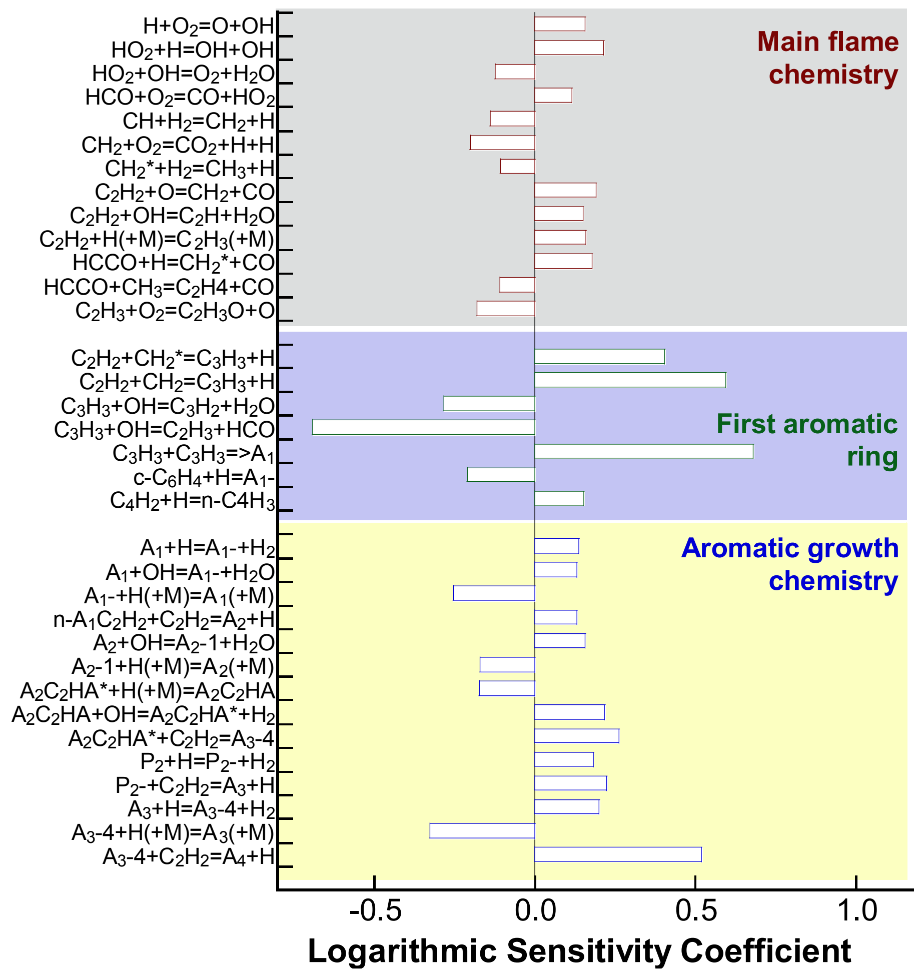


PAH Precursor Chemistry (2)

- **Earlier work aimed at developing consistent**
  thermodynamic
  J Phys Chem 97 (1993) 3867.
  transport
  Combust Flame 96 (1994) 163.
  chemical kinetic
  J Phys Chem 98 (1994) 11465;
  Combust Flame 110 (1997) 173;
  Proc Combust Inst 23 (1990) 1559.
  descriptions of PAH formation

- **Lessons learned:**
  PAH formation is sensitive to a multitude of elementary reactions and local flame conditions.

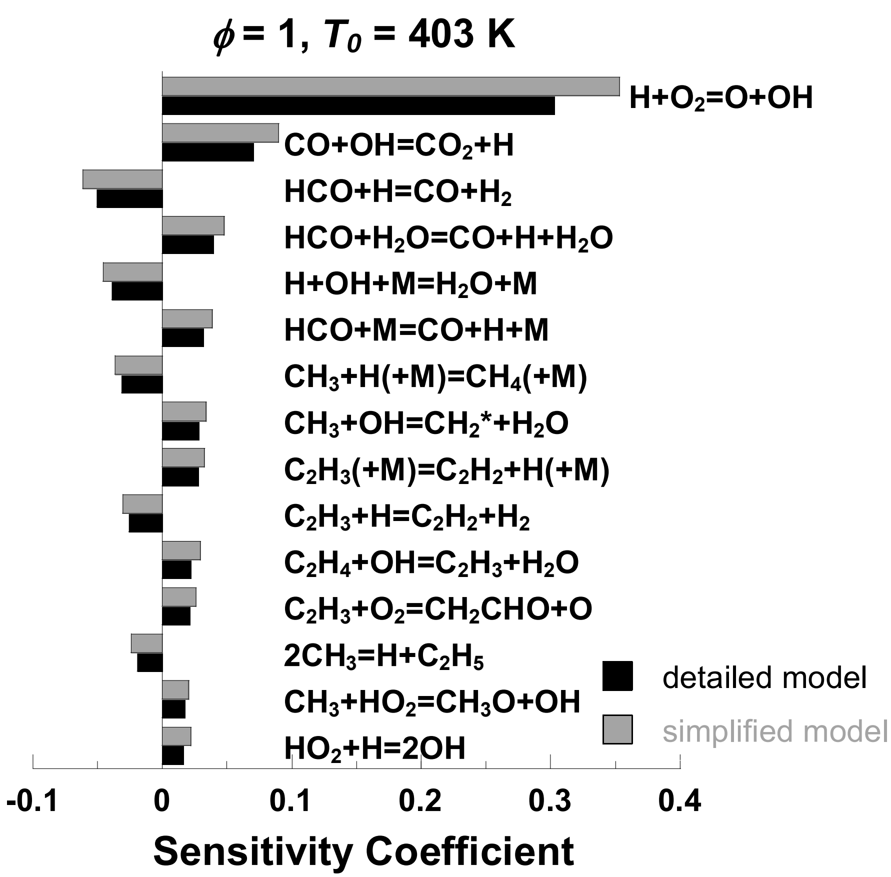
Spectral sensitivity of pyrene concentration 90 Torr burner stabilized $C_2H_2/O_2/Ar$ flame (Bockhorn), *H* = 0.55 cm



Wang & Frenklach, C&F (1997)

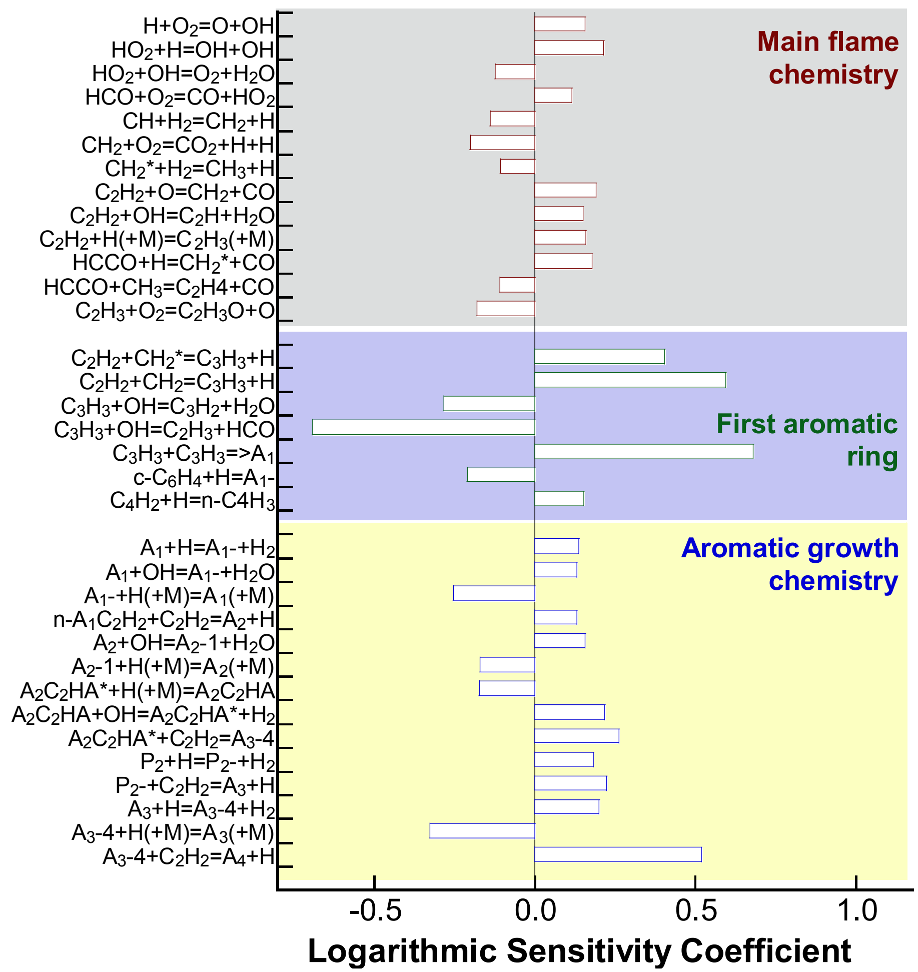
PAH Precursor Chemistry (3)

***n*-dodecane-air flame speed**



You et al. Proc. Combust. Inst. (2009)

Spectral sensitivity of pyrene concentration 90 Torr burner stabilized $C_2H_2/O_2/Ar$ flame (Bockhorn), *H* = 0.55 cm



Wang & Frenklach, C&F (1997)

PAH Precursor Chemistry (3)

Lessons learned:

- PAH formation is sensitive to a multitude of elementary reactions.

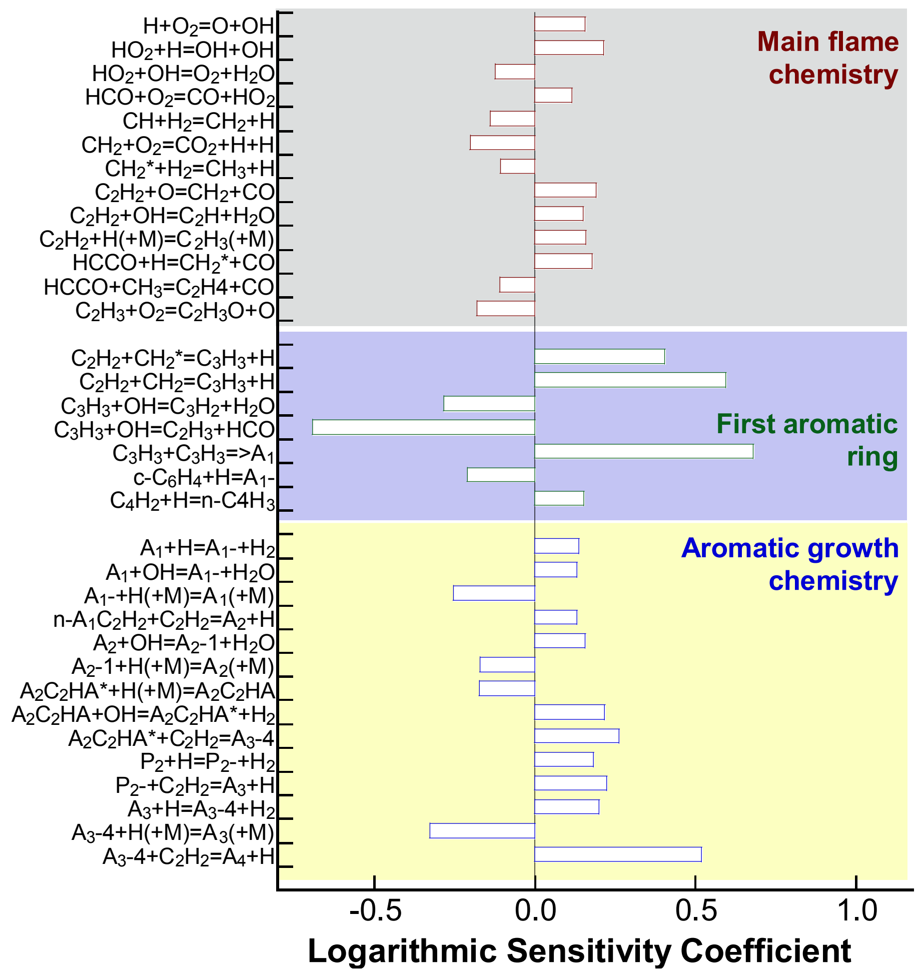
- Accurate prediction of PAH formation may require a precision in main flame chemistry currently unavailable.

- PAH formation can be highly sensitive to fuel structures.

  4D01: Hansen, Kasper, Yang, Cool, Li, Westmoreland, Oβwald, Kohse-Höinghaus, Fuel structure dependence of benzene formation processes in premixed flames fueled by C_6H_{12} isomers

- Possibly a large number of pathways to PAHs have yet been considered.

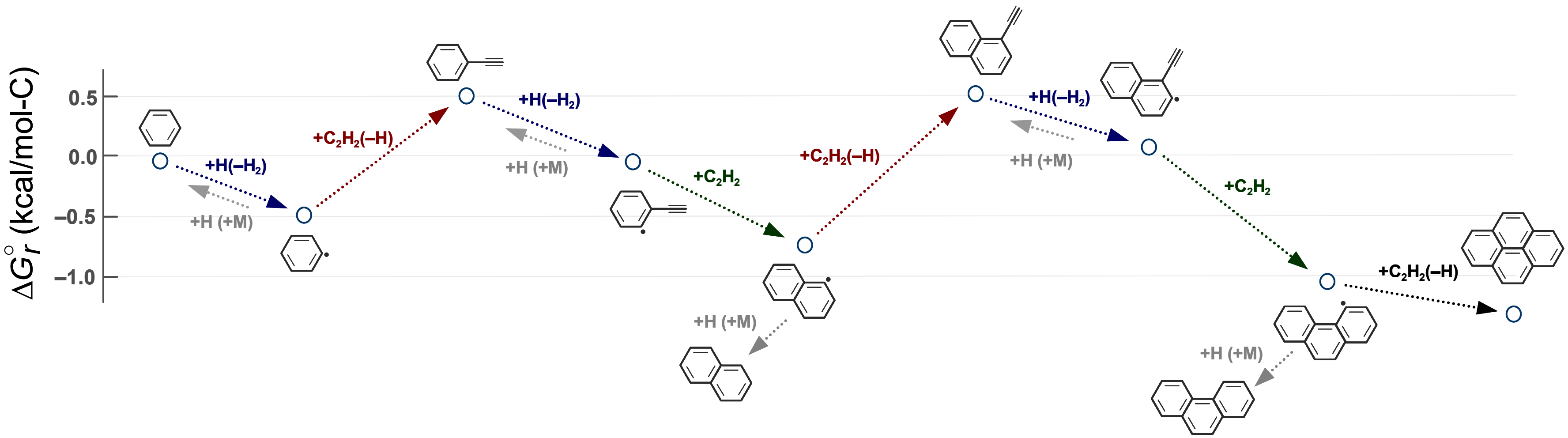
Spectral sensitivity of pyrene concentration 90 Torr burner stabilized $C_2H_2/O_2/Ar$ flame (Bockhorn), *H* = 0.55 cm



Wang & Frenklach, C&F (1997)

PAH Precursor Chemistry (4)

Thermodynamic Origin of PAH Formation/Growth Beyond HACA



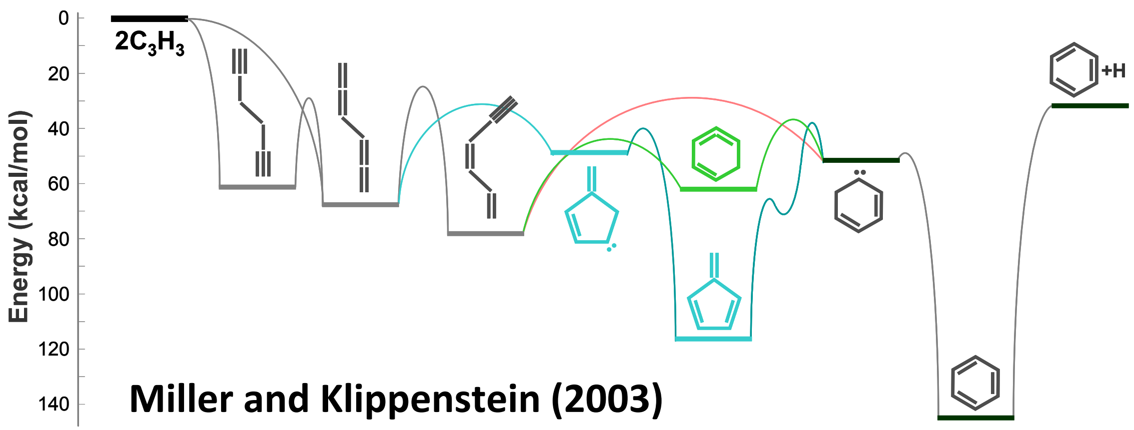
C_2H_2	5	5	4	4	3	2	2	1	0
H	1	0	1	0	0	1	0	0	1
H_2	0	1	1	2	2	2	3	3	3

- **While HACA captures the thermokinetic requirements for PAH formation, its reversibility opens it to competitions from other pathways**

PAH Precursor Chemistry (5)

Known Pathways beyond HACA

- Propargyl combination (Fahr & Stein 1990)



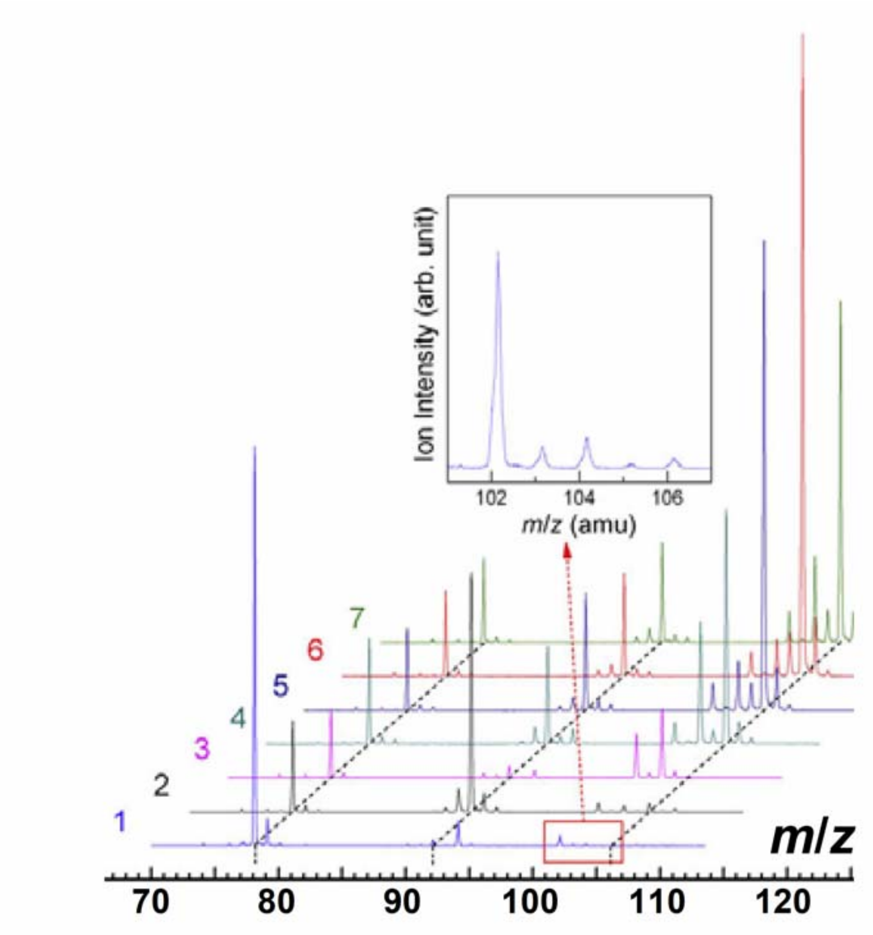
Miller and Klippenstein (2003)

Rate coefficient calculation require high-quality PES (e.g., CASPT2), RRKM/Master equation modeling, flexible, variational transition state theory

- Sequential dehydrogenation from cycloparaffins (Westmoreland 2007)
- Phenyl addition/cyclolization pathway (Koshi 2010)
- Fulvenallene + acetylene (Bozzelli 2009)
- Cyclopentadienyl + acetylene (Carvallotti et al. 2007)
- Cyclopentadienyl + cyclopentadienyl (Colket 1994; Mebel 2009)

PAH Precursor Chemistry (6)

Recent advance in probing flame by molecular beam synchrotron photoionization mass spectrometry will be critical to further progress.



Courtesy of Qi

Photoionization mass spectra of flame species of burner stabilized aromatics/oxygen/50% argon flames (30 Torr, C/O = 0.68) determined by molecular beam synchrotron photoionization mass spectrometry.

1: benzene
2: toluene
3: styrene
4: ethylbenzene
5: *o*-xylene
6: *m*-xylene
7: *p*-xylene

PAH Precursor Chemistry - Summary

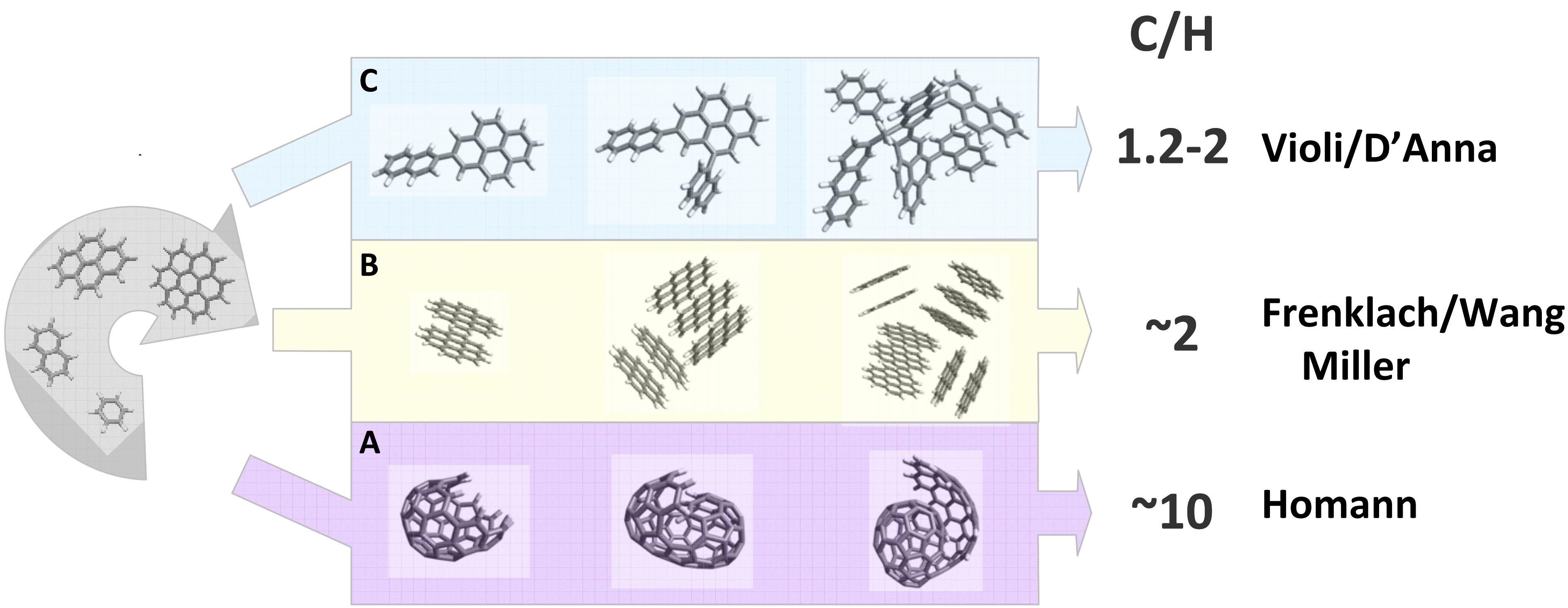
1. PAH formation is sensitive to main flame chemistry, local flame conditions, fuel structure and composition.

2. For real fuels and their surrogate, the number of pathways to aromatics is currently undefined; and it remains to be seen whether this number is finite.

3. Requires theoretical approaches beyond one-reaction-at-a-time type calculations.

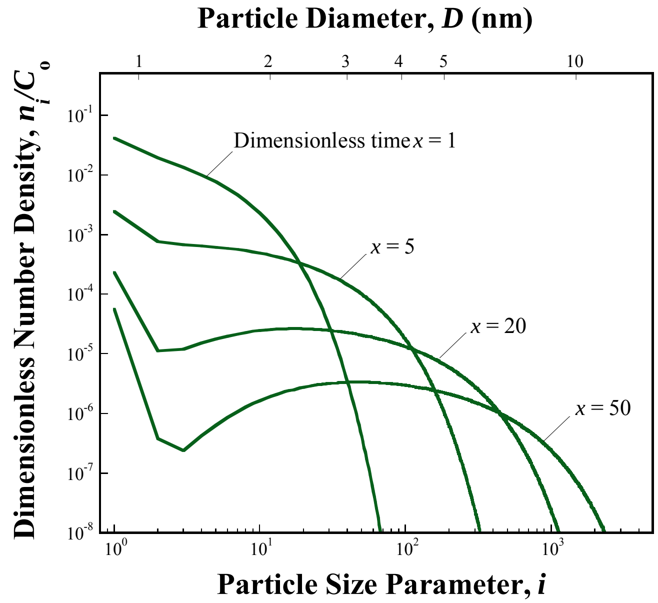
4. Need to account for the formation of aromatic π radicals

Soot Nucleation (1)

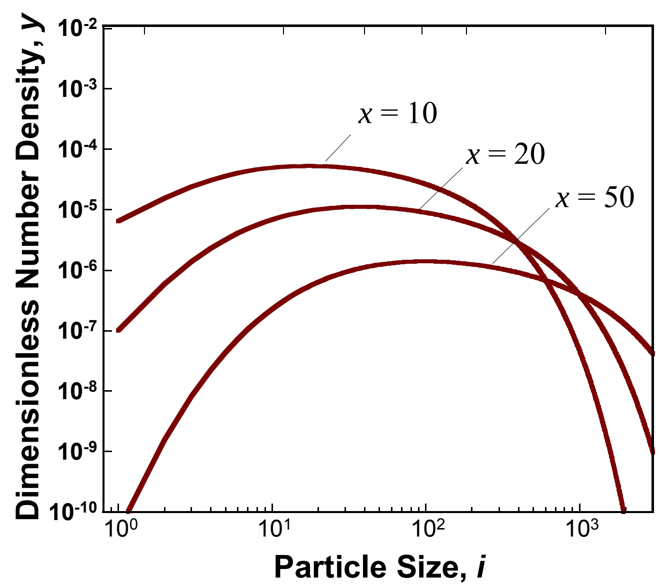


Soot Nucleation (2)

- **Second-order nucleation kinetics – dimerization of soot precursors – leads to Persistent *bimodality*.**



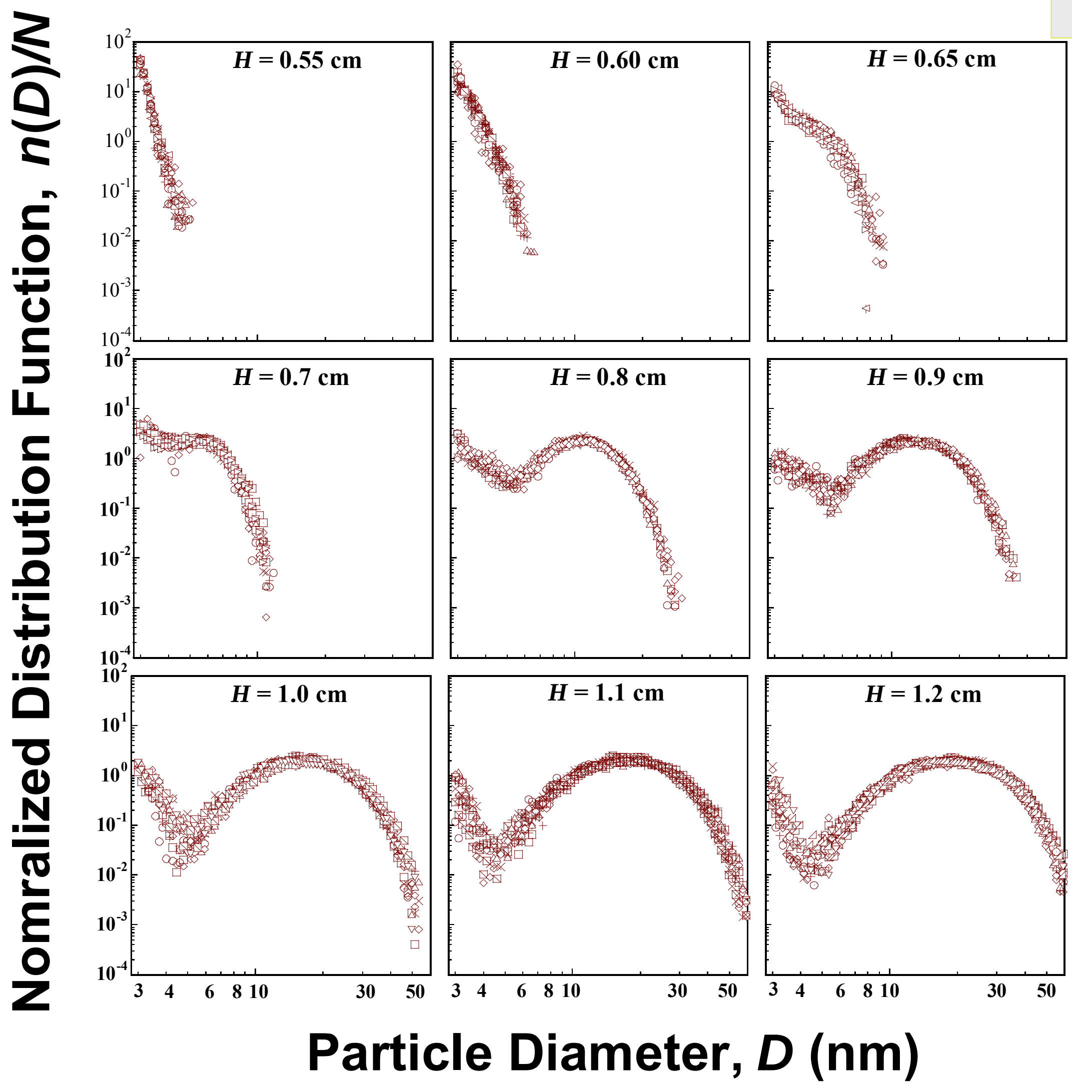
- **First-order nucleation kinetics gives PSDFs that are persistently unimodal.**

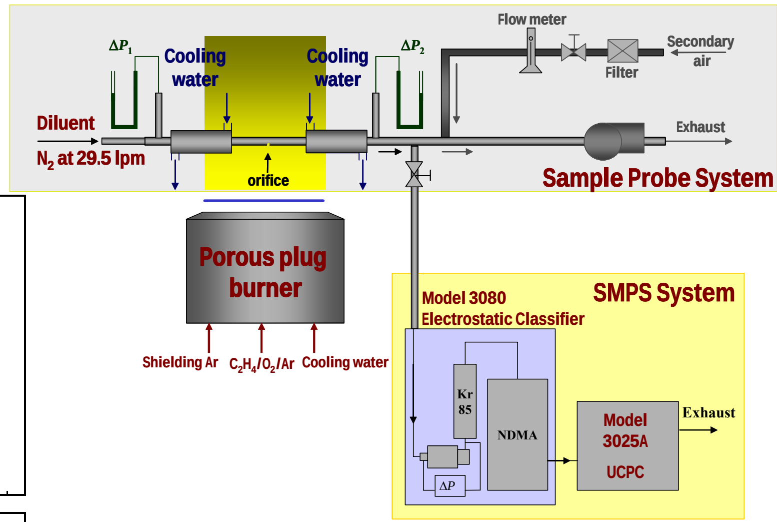


Zhao et al. (2003a)

Soot Nucleation (3)

Measured PSDFs are indeed bimodal

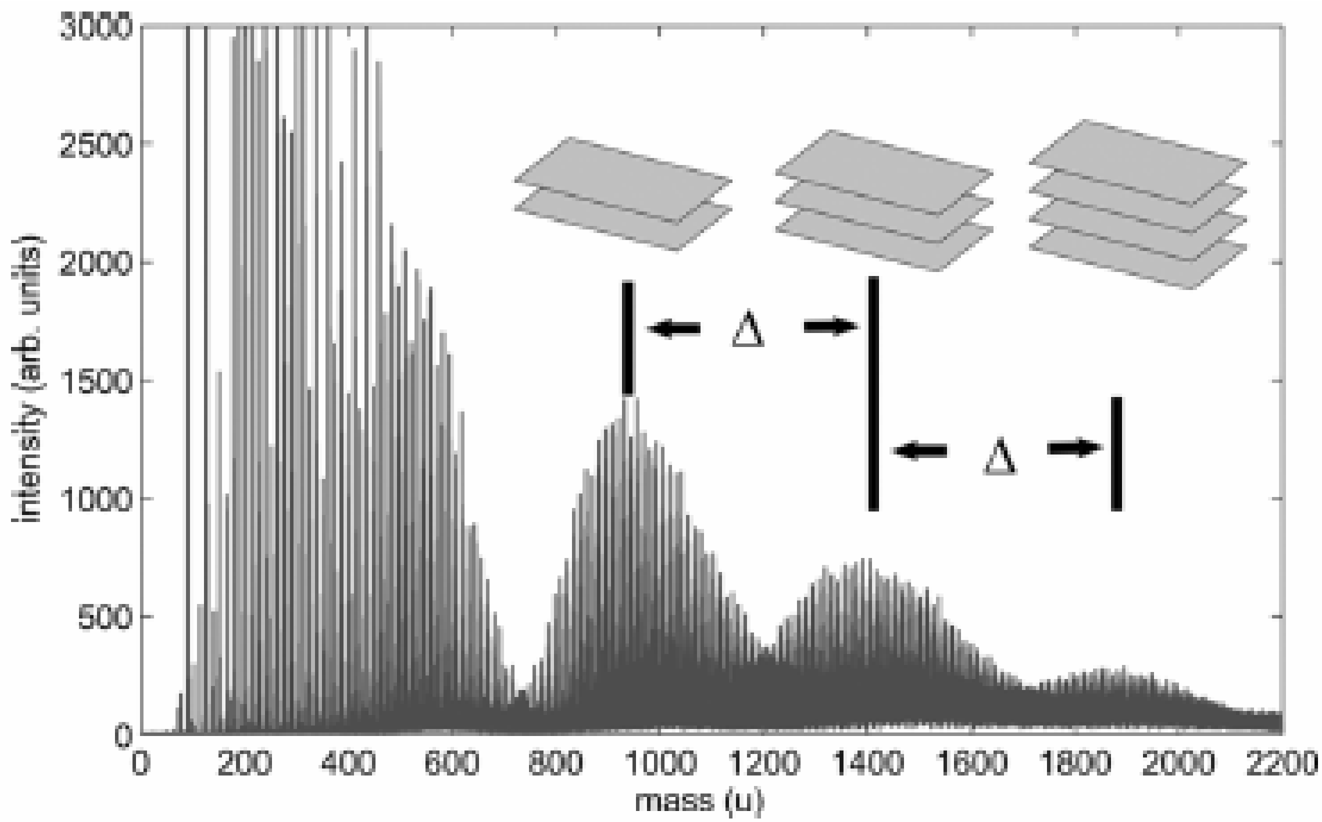




Zhao et al. 2003

Soot Nucleation (5)

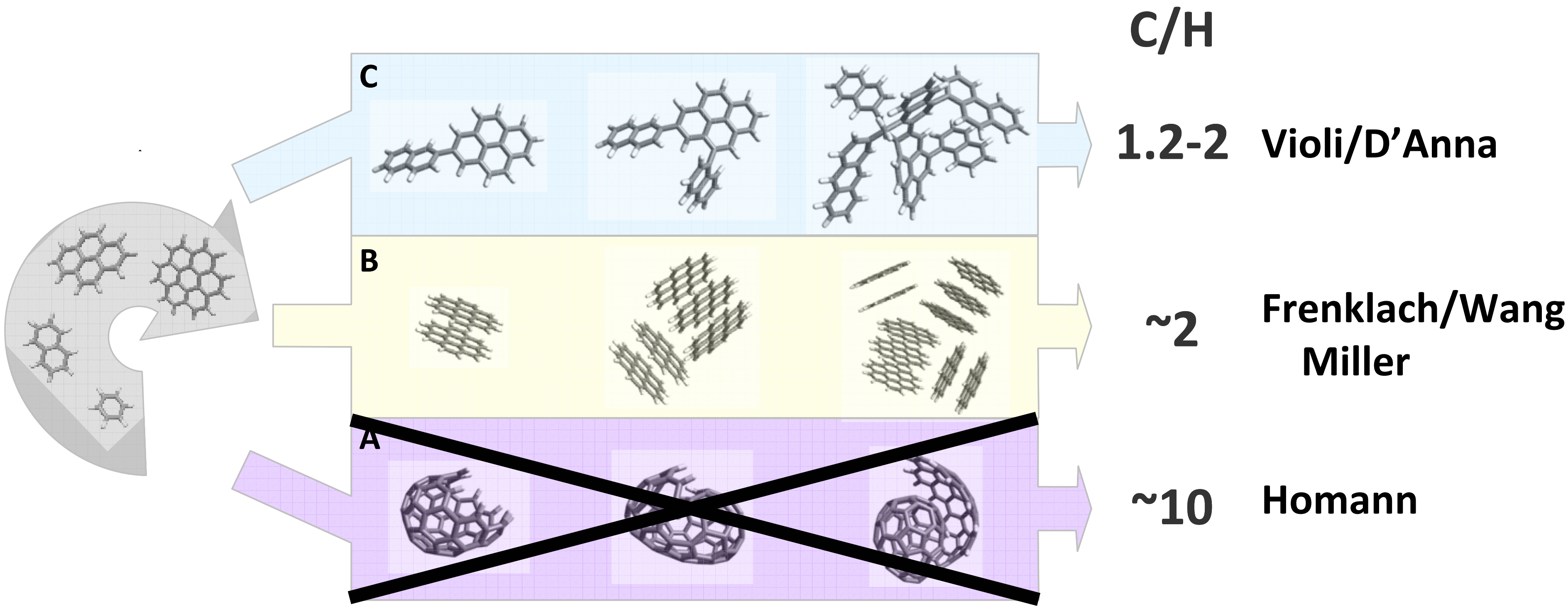
Mass spectrum of fragments from photoionization of nascent soot show periodicity



100-Torr acetylene-oxygen flame (ϕ = 3.25)

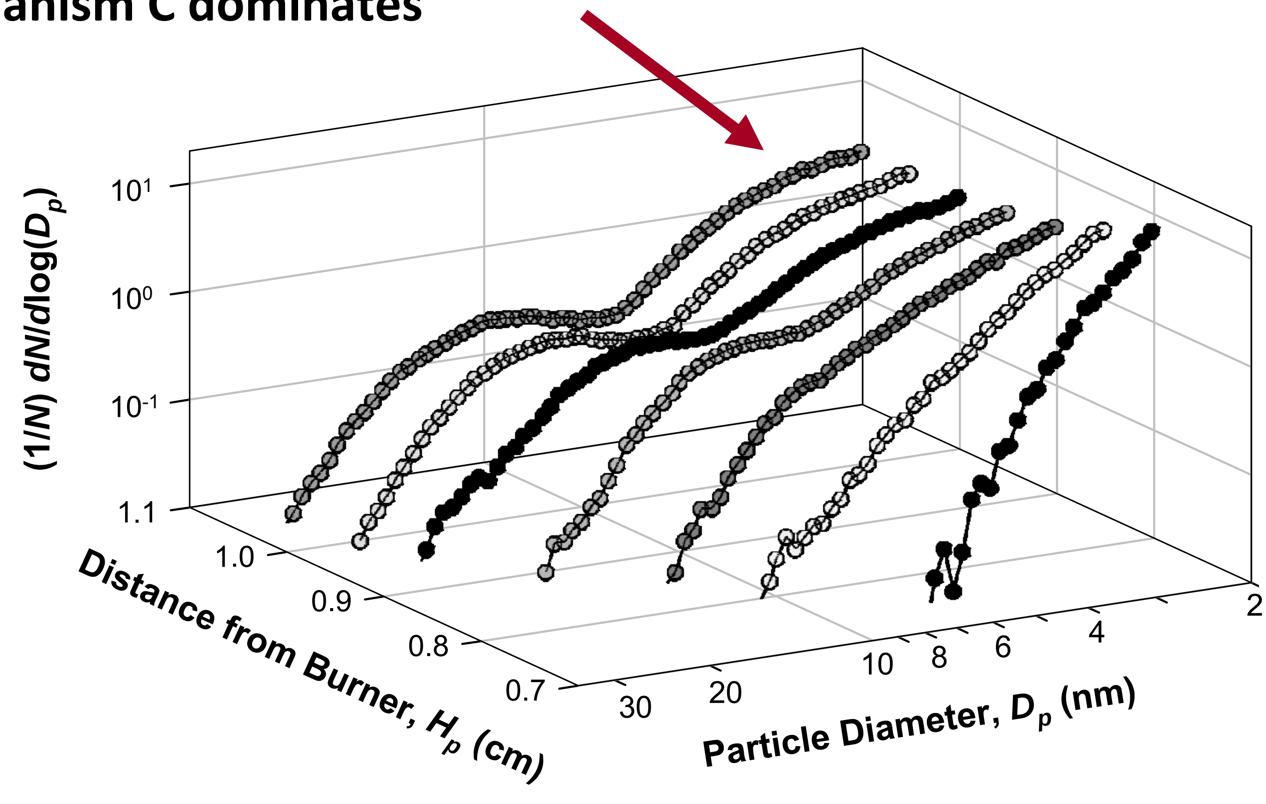
Courtesy of Grotheer

Soot Nucleation (1)



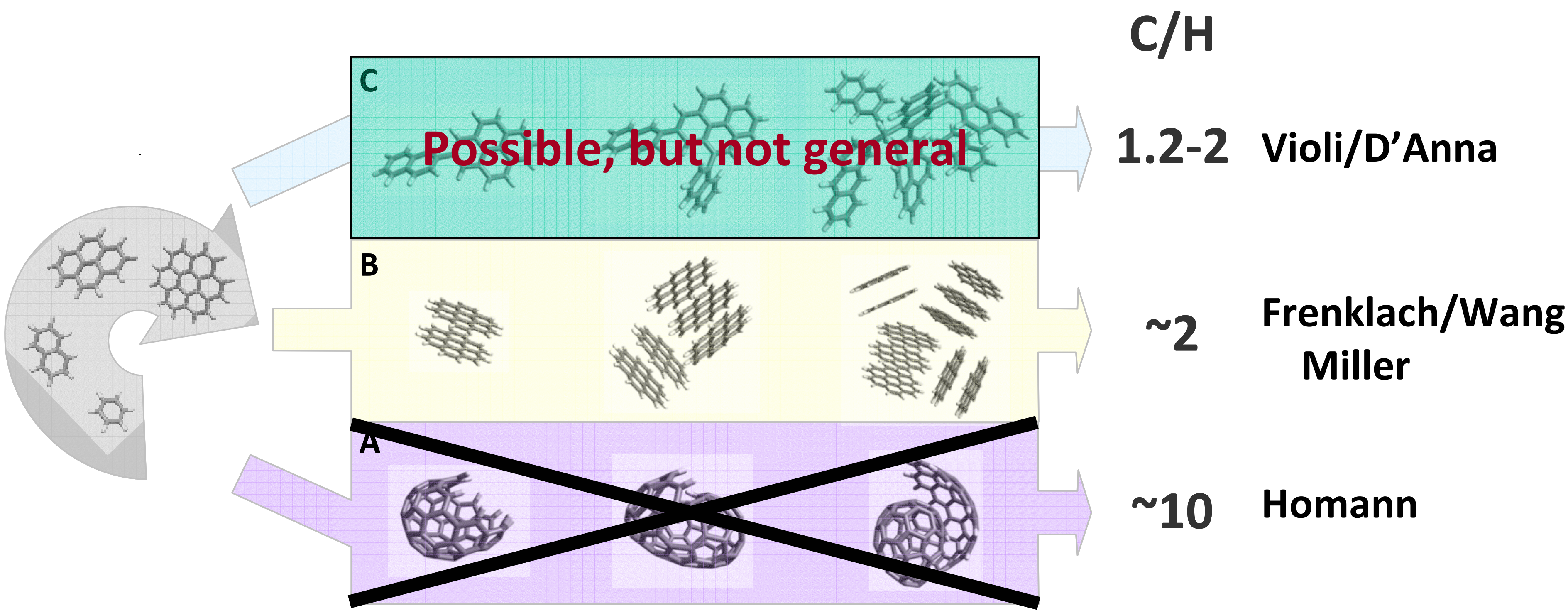
Soot Nucleation (6)

- $T < 1500$ K, $x_H < 10^{-5}$
- Temperature is too low to explain persistent nucleation if mechanism C dominates

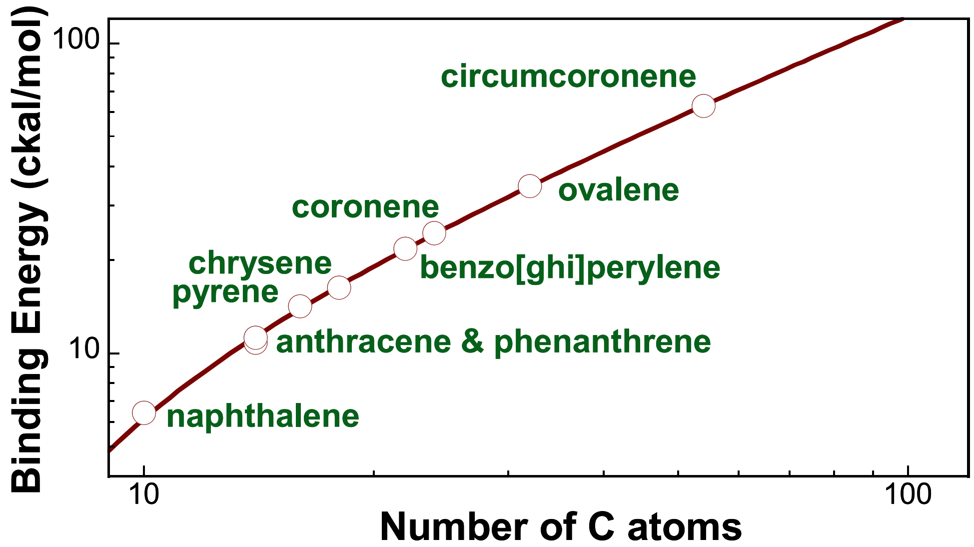


Abid et al. (2009)

Soot Nucleation (1)

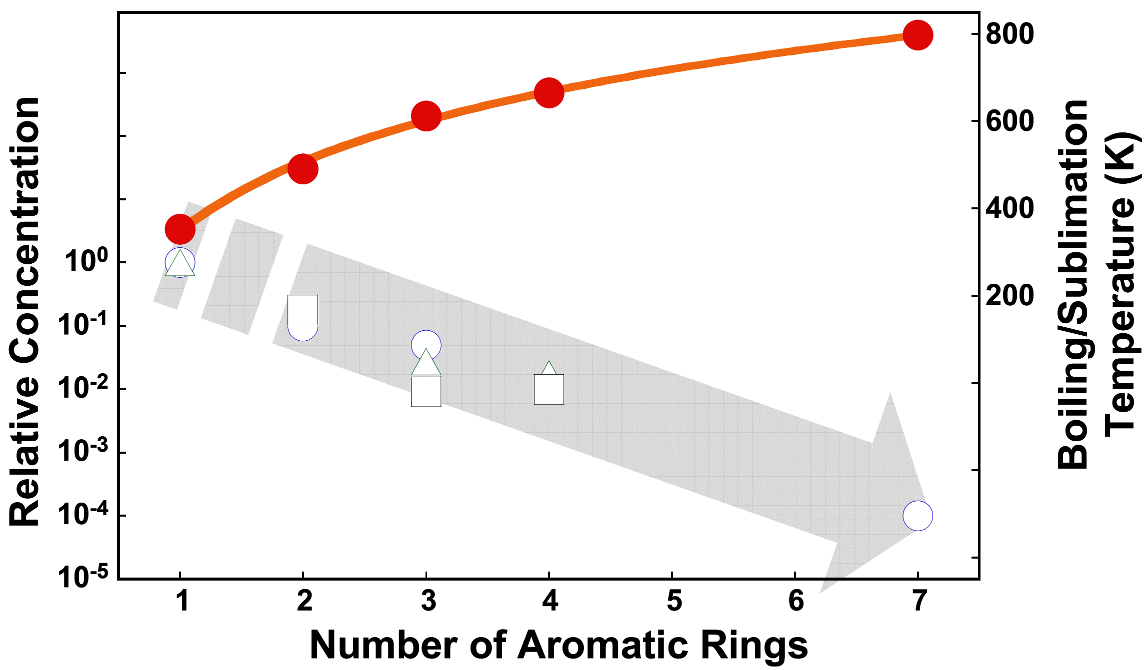


Soot Nucleation (7)



Herdman and Miller (2008)

Binding energy of coronene = 25 kcal/mol



Soot Nucleation (8)

Is 25.4 kcal/mol enough to bind a pair of coronene together?

2 coronene → (coronene)$_2$

$$\Delta H^\circ \cong -E_0 + \sum_{i=1}^{6}\left\{1+\frac{1}{\exp\left[h\nu_i/(k_B T)\right]-1}\right\}h\nu_i - 4k_B T$$

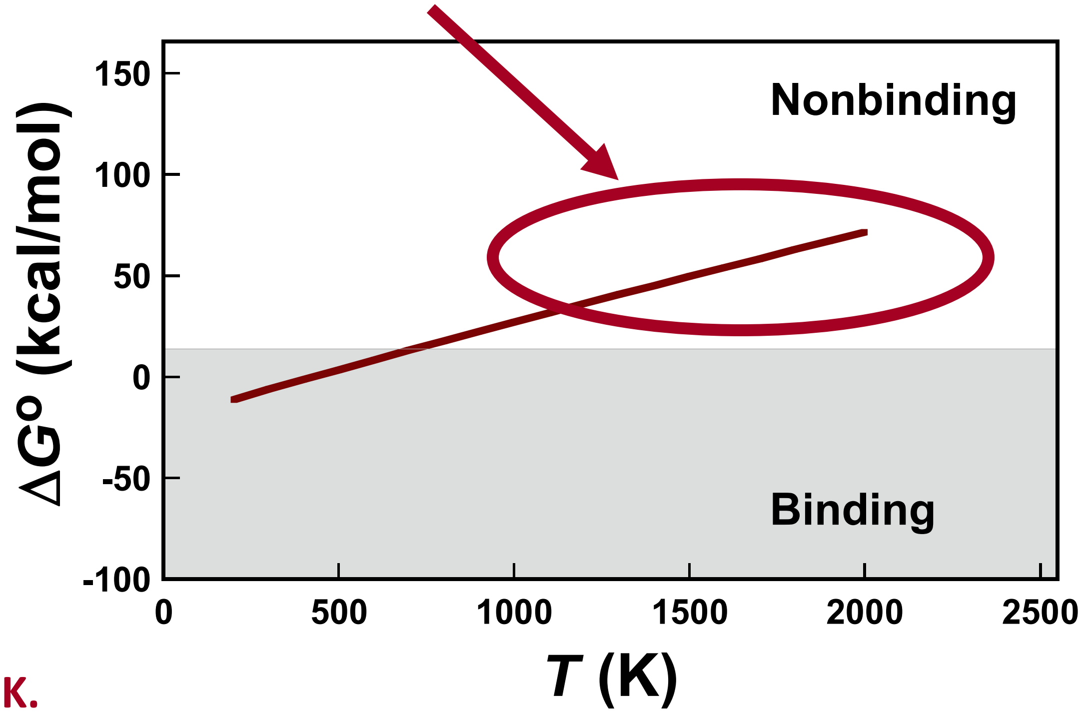
$$\frac{\Delta S^\circ}{R_u} \cong \ln\left[\left(\frac{2\bar{B}}{m}\right)^{3/2}\frac{h^3 p^0}{\pi^2 (e k_B T)^4}\frac{\sigma_1^{\,2}}{\sigma_2}\right] + \sum_{i=1}^{6}\left[\frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T}-1} - \ln\left(1-e^{-h\nu_i/k_B T}\right)\right]$$

Assumptions:

- ν_i = 200 cm^{-1}
- B (cm^{-1}) = 1510 x $MW^{-2.12}$
- σ_2 = 1

Ovalene E_0 = 35 kcal/mol
Circumcoronene E_0 = 63 kcal/mol
Even they would not bind > 1600 K.

- **ΔG° too positive to allow binding above 700 K**
- **Entropy tears the dimer apart.**



Soot Nucleation (8)

Is 25.4 kcal/mol enough to bind a pair of coronene together?

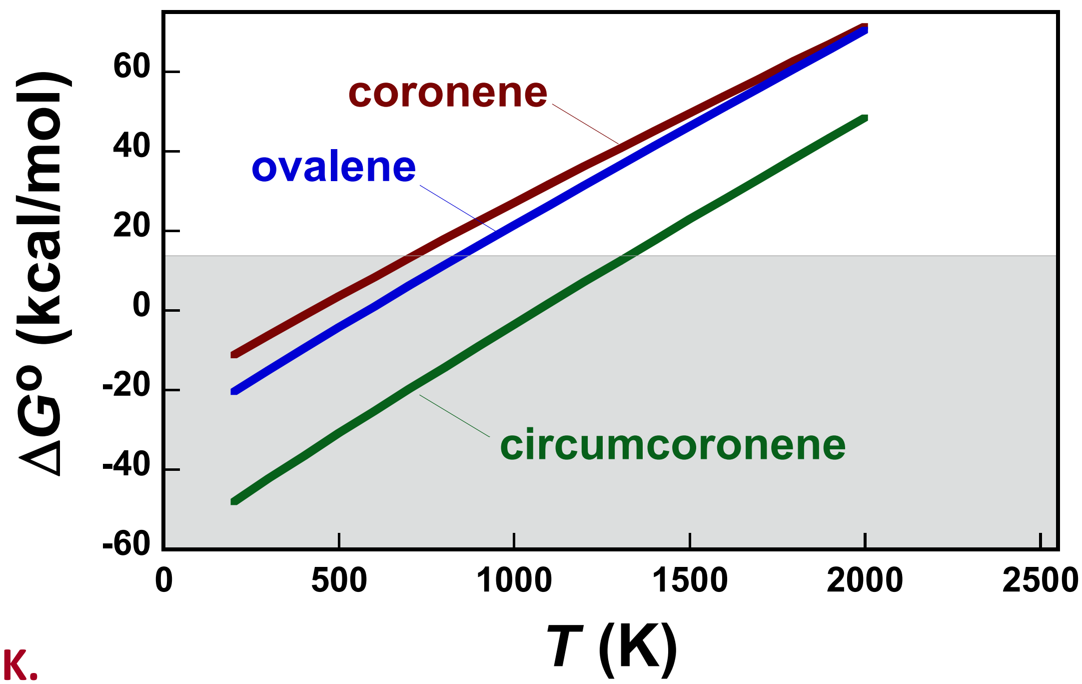
2 coronene → (coronene)$_2$

$$\Delta H^\circ \cong -E_0 + \sum_{i=1}^{6} \left\{ 1 + \frac{1}{\exp\left[h\nu_i/(k_B T)\right] - 1} \right\} h\nu_i - 4k_B T$$

$$\frac{\Delta S^\circ}{R_u} \cong \ln\left[\left(\frac{2\bar{B}}{m}\right)^{3/2} \frac{h^3 p^0}{\pi^2 (e k_B T)^4} \frac{\sigma_1^{\,2}}{\sigma_2} \right] + \sum_{i=1}^{6} \left[\frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T} - 1} - \ln\left(1 - e^{-h\nu_i/k_B T}\right) \right]$$

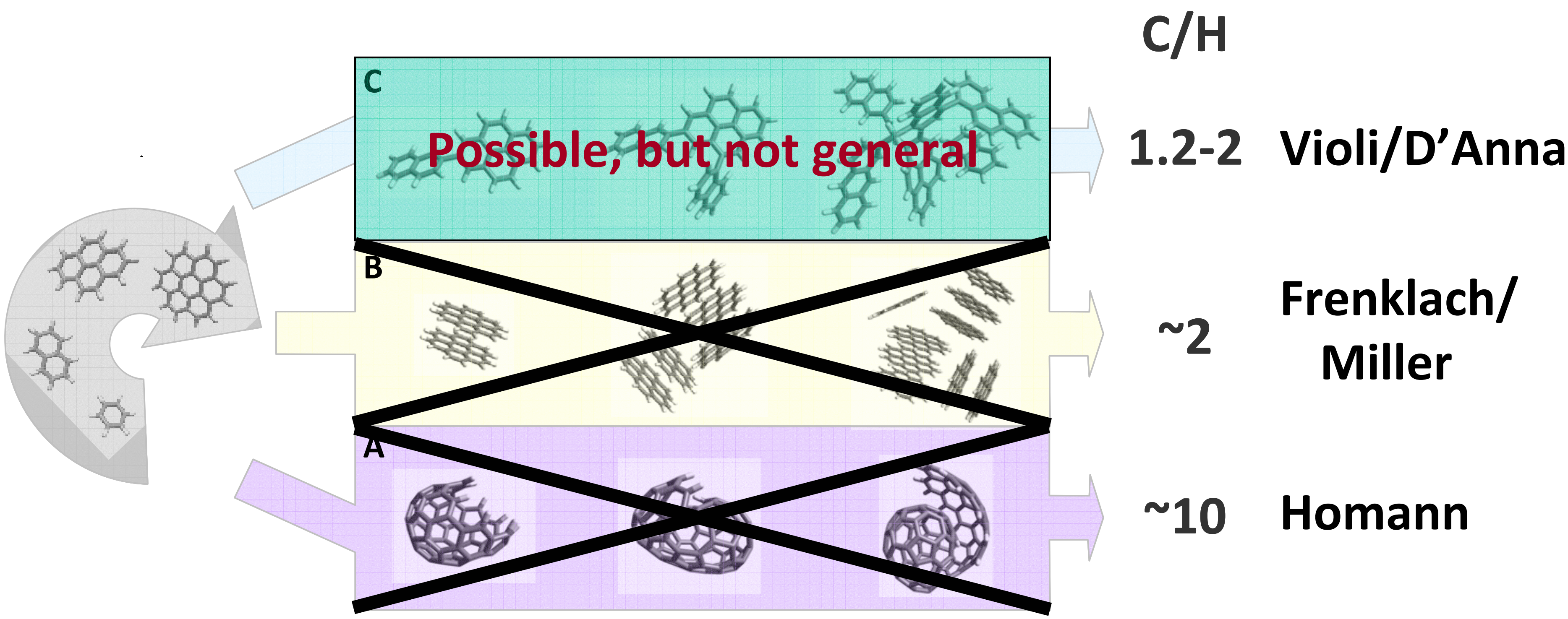
Assumptions:

- ν_i **= 200 cm^{-1}**
- B **(cm^{-1}) = 1510 x** $MW^{-2.12}$
- σ_2 **= 1**



Ovalene E_0 = 35 kcal/mol
Circumcoronene E_0 = 63 kcal/mol
Even they would not bind > 1600 K.

Soot Nucleation (1)



Soot Nucleation (9)

- **Polyacenes are singlet diradicals (though arguable).**
- **Ground-state polyacenes are close-shell singlets, but the adiabatic S0-T1 excitation energy is only 13 kcal/mol for heptacene - Hajgató et al. (2009).**
- **Applications in organic light emitting diodes and organic semiconductors and capacitors.**

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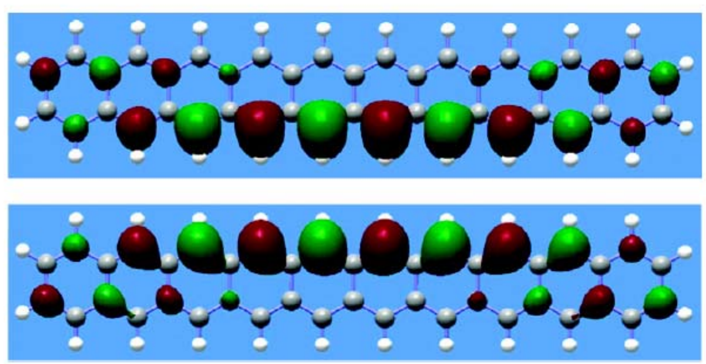
Communication

Oligoacenes: Theoretical Prediction of Open-Shell Singlet Diradical Ground States

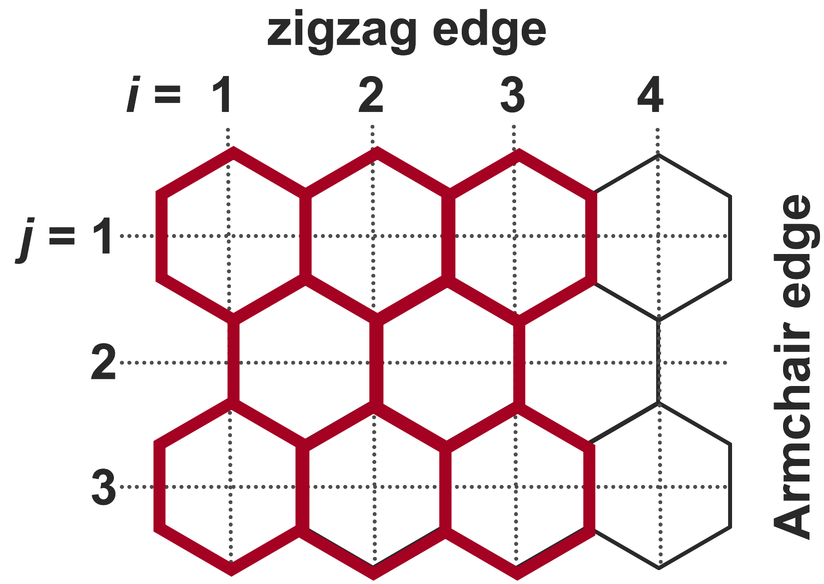
Michael Bendikov, Hieu M. Duong, Kyle Starkey, K. N. Houk, Emily A. Carter, and Fred Wudl

J. Am. Chem. Soc., **2004**, 126 (24), 7416-7417• DOI: 10.1021/ja048919w • Publication Date (Web): 14 May 2004



Soot Nucleation (10)

- Zigzag edges of graphene have localized π-electronic states
  Kobayashi 1993; Klein 1994
- Zigzag edges have an open-shell singlet ground state
  e.g., Fujita et al. 1996; Nakada 1996
- Finite-sized graphenes have radical or even multiradical characteristics.
  e.g., Nakano et al. 2008, Nagai 2010
- Side chain can induce π-radical characteristics
  Nakano et al. 2007
- Nonlinear optics applications.



i	*j*	*y*	*i*	*j*	*y*
1	1	0.000	1	3	0.037
2	1	0.050	2	3	0.217
3	1	0.149	3	3	0.510
4	1	0.281	4	3	0.806

Nagai et al. 2010
UBHandHLYP/6-31G(D) calculations
$0 \leqslant y \leqslant 1$
y = 0: close shell singlet
y = 1: open shell singlet (diradical)

Soot Nucleation - Summary

- If PAHs with π-radicals do play a role in soot nucleation, we need to
  - Understand the nature and structures of these PAH species,
  - Determine their binding energies with relevant species, including aromatics,
  - Probe them in flames (however small their concentrations may be),
  - Account for the mechanism of their formation.

Soot Mass Growth (1)

HACA Mechanism

$$\mathrm{S}_i\text{–H} + \mathrm{H}\bullet \leftrightarrow \mathrm{S}_i\bullet + \mathrm{H}_2 \qquad (1)$$

$$\mathrm{S}_i\bullet + \mathrm{H}\bullet \rightarrow \mathrm{S}_i\text{–H} \qquad (2)$$

$$\mathrm{S}_i\bullet + \mathrm{C}_2\mathrm{H}_2 \rightarrow \mathrm{S}_{i+2}\text{–H} + \mathrm{H}\bullet \qquad (3)$$

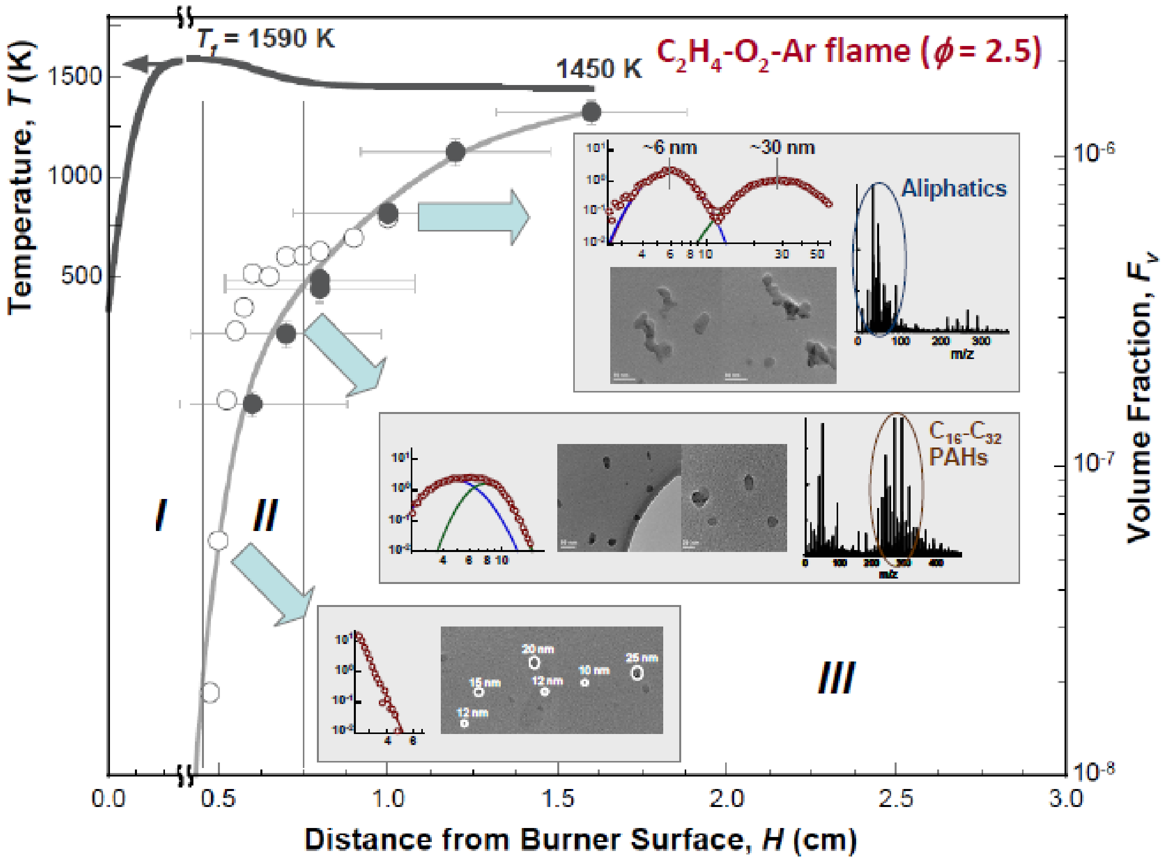
$$\omega_s\left(\frac{\text{mol C-atom}}{\text{cm}^3\text{s}}\right) \approx 2k_3 \frac{k_{1f}}{k_{1b}} \frac{[\mathrm{H}\bullet]}{[\mathrm{H}_2]} [\mathrm{S}_i\text{-H}][\mathrm{C}_2\mathrm{H}_2]$$

- **The mass growth rate is proportional to H atom concentration**

Soot Mass Growth (2)

Baby soot is entirely unlike mature soot.

- Comparison of mobility and TEM measurements shows nascent soot is liquid-like rather than being carbonized and rigid.
- Small angle neutron scattering and thermocouple densitometry suggest that nascent soot has C/H ~ 1 and ρ = 1.5 g/cc.
- Photoionization aerosol mass spectrometry indicates that nascent soot is rich in aliphatics (in addition aromatics).

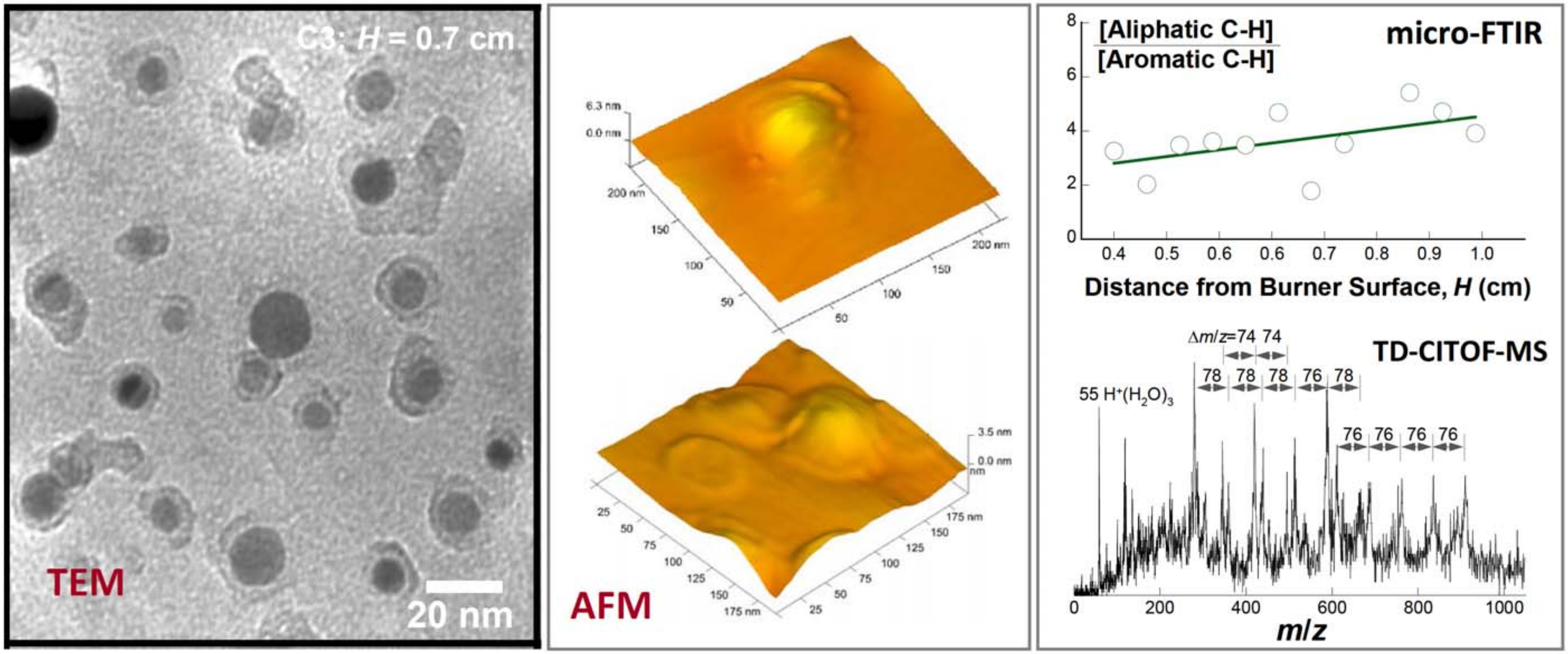


- **The presence of aliphatics suggests that nascent soot is not always purely aromatic.**
- **The mass of nascent soot continue to increase in post flame where H atoms are depleted, in contrast to HACA prediction – presence of persistent free radicals on soot surface?**

Wang et al. 2003; Oktem et al. 2005, Zhao et al. 2007

Soot Mass Growth (3)

C_2H_4-O_2-Ar flame (ϕ = 2.07, T_f = 1736 ± 50 K)



- "Sunny-side up" morphology (TEM & AFM) suggests an aromatic core-aliphatic shell structure.
- Micro-FTIR measurements again show aliphatic dominance
- Thermal desportion/chemical ionization (extreme soft) show broad mass spectrum, suggesting that nascent soot is alkylated.
- The large aliphatic/aromatic ratio again suggest that the initial aromatic core may contain persistent free radicals.

Abid et al. 2008; Cain et al. 2010

Soot Mass Growth (4)

Evidence supporting persistent free radicals

- Electron Spin Resonance spectra of anthracite, a coal containing little to no oxygenated compounds, show a measurable concentration of free radicals (Retcofsky, Stark & Friedel 1968).
- Soot volume fraction observed towards the stagnation surface can be predicted only if soot surface persists its radical nature (Wang et al 1996).
- Soot from pyrolysis of C_2H_4, C_2H_2 and jet fuel surrogates has appreciable amounts of free radicals of aromatic π nature. The spin concentrations is ~10^{21} per gram (1 in 50 every C atoms) (Eddings, Sarofim & Pugmire 2005).
- Soot, an otherwise hydrophobic material, has the ability to uptake water (Popovicheva 2003).
  - Binding energy between CH_3 and H_2O is 1.5 kcal/mol (Crespo-Otero et al. 2008), increases to 2–4 kcal/mol for C_2-C_4 alkyl radicals (Li et al. 2009).

Soot Mass Growth - Summary

- Nascent soot has aromatic core/aliphatic shell structure.
- Soot mass growth without the presence of H atom.

- Immediate questions and hypothesis:

  Is HACA mechanism complete?

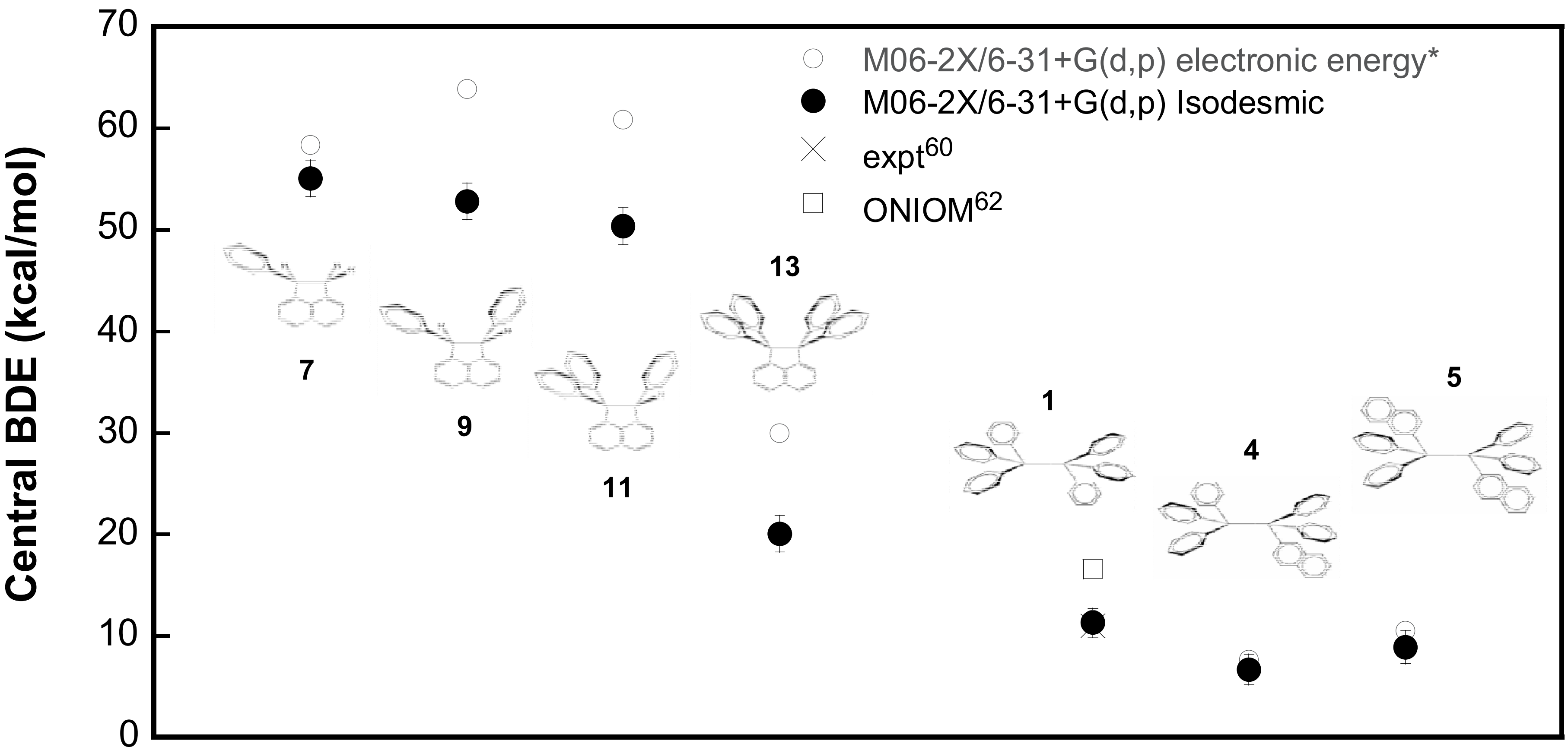
  Do persistent free radicals exist on nascent soot surfaces?

  Resonantly stabilized free radicals of semiquinone and phenoxyl origins (Dellinger 2001).

  Radicals due to strain energy in hexaphenylethane and acenaphthene derivatives (Dames et al. 2010).

Soot Mass Growth - Summary

Radicals due to strain energy in hexaphenylethane and acenaphthene derivatives (Dames, Sirjean, Wang 2010).



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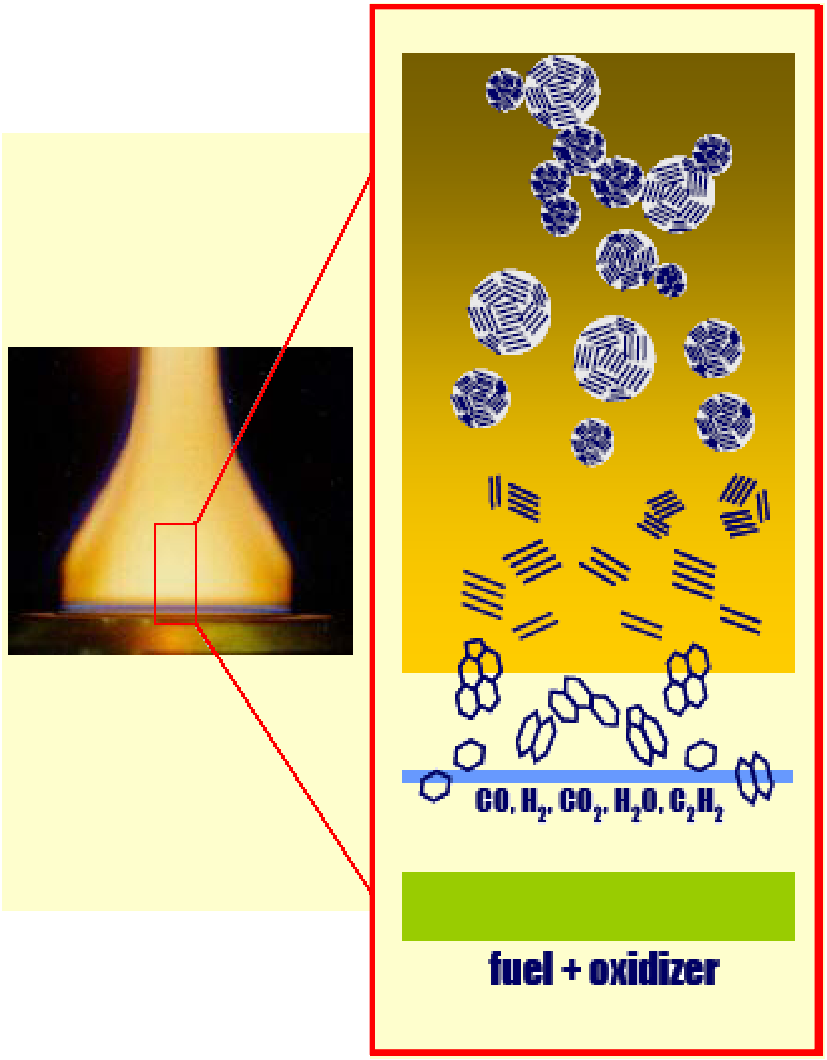
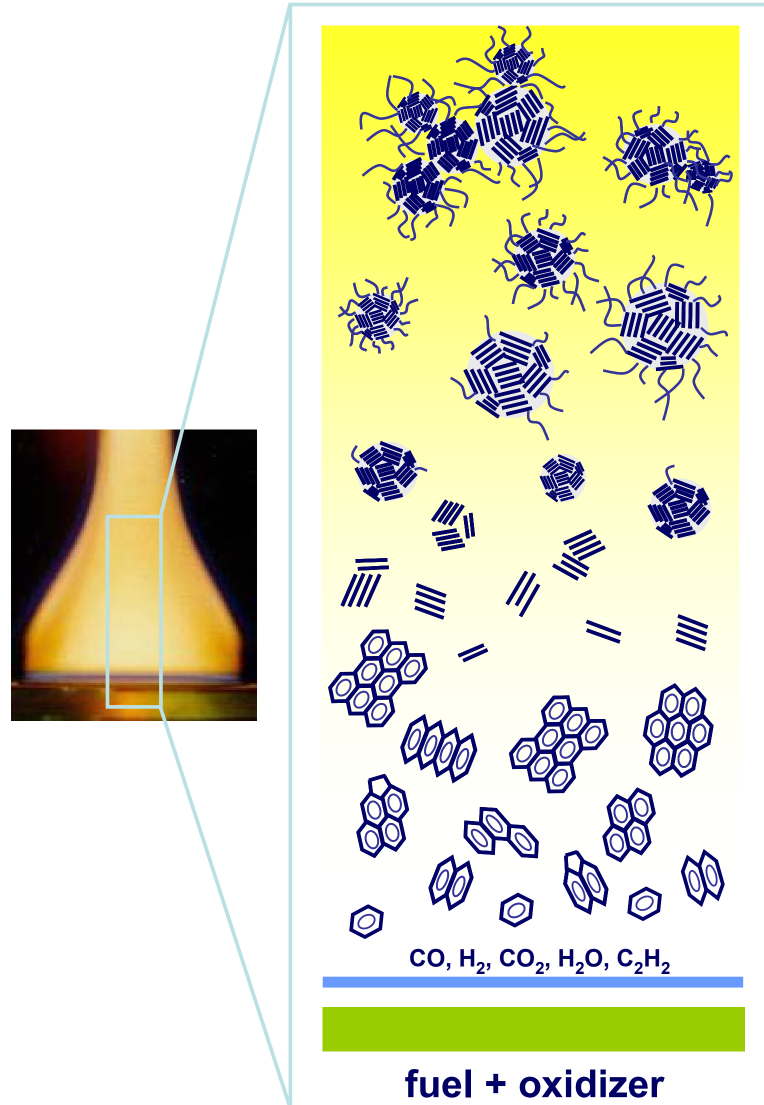
  Delocalized aromatic π radicals on zigzag edges propagated into soot structures (Cain et al. 2010 – 3D02).

Soot Formation



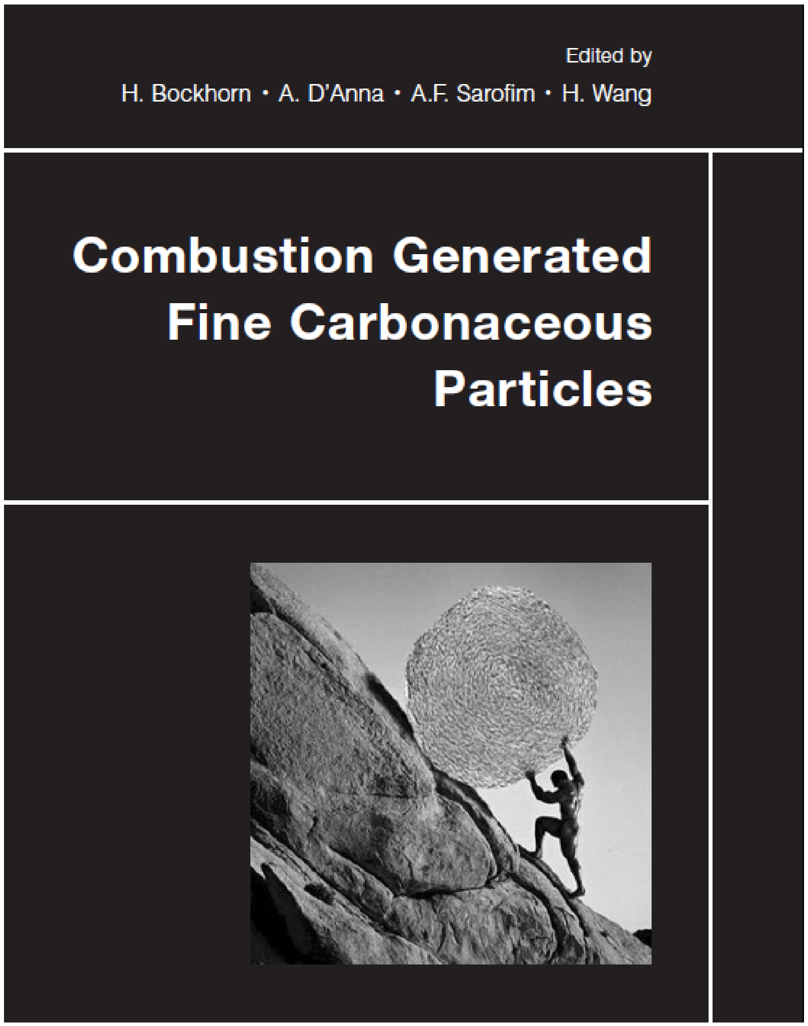
Previous (Calcote 1982, Bockhorn 1994)



Current

The Science of Soot Formation

Our View



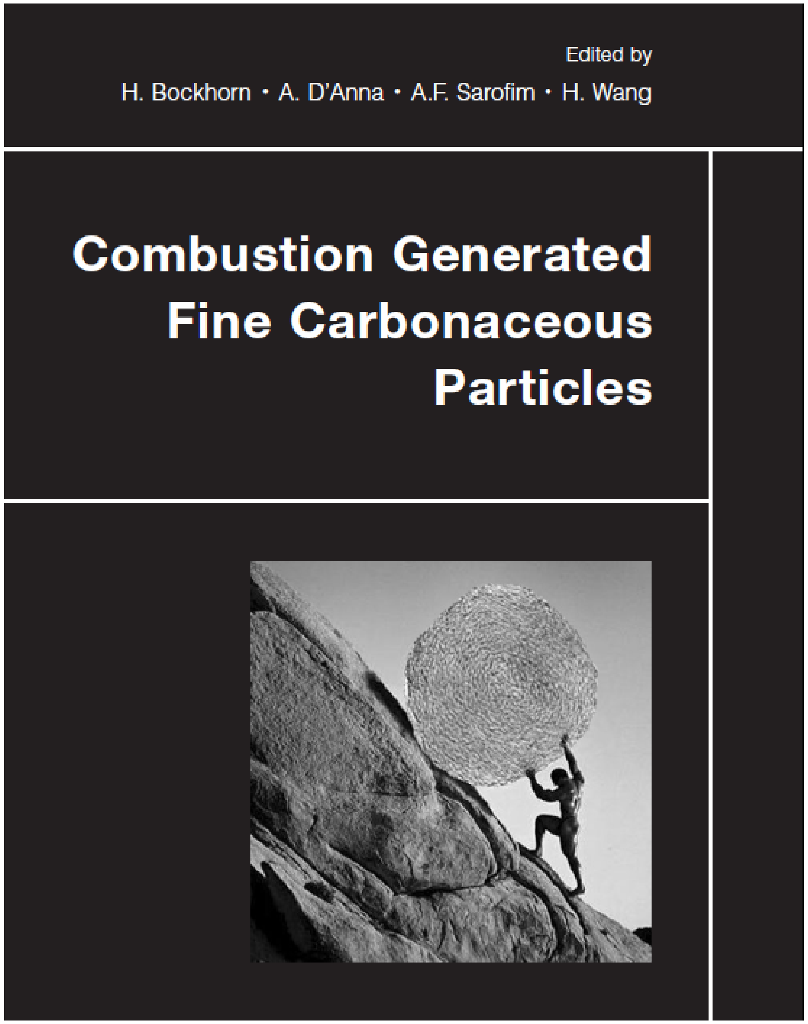
A. Ciajolo and A. Tregrossi
"Sysiphus rolling a soot particle up hill".

Nature's View

http://www.historyforkids.org/learn/science/fire.htm

The Science of Soot Formation

Our View | **Nature's View**



A. Ciajolo and A. Tregrossi
"Sysiphus rolling a soot particle up hill".

"Sysiphus stoping a soot particle falling off a potential energy cliff".

Other Condensed-Phase Matters – Metal Oxide

Titania
TiO_2

Courtesy of Pratsinis

Silicate
SiO_2

Courtesy of Pratsinis