ISF-4 Workshop Table of Contents

International Sooting Flame (ISF) Workshop
Proceedings Table of Contents

International Sooting Flame (ISF) Workshop
Aims and Objectives

Aims of the ISF Workshop

- To advance understanding and predictive capability of flames with soot, to identify gaps in this understanding and to coordinate research programs to address them;
- To identify well defined target flames and coordinate additional experiments that provide suitable data for model development and validation, spanning a variety of flame types and fuels in each of the research programs;
- To establish an archive of the detailed data sets of target flames with defined accuracy and to provide a forum for the exchange and dissemination of these data;

Objectives and Targets for ISF-4

Objective 1**:** To advance understanding and prediction of inception-dominated ethylene flames:

Target 1: obtain new systematic data in inception-dominated laminar ethylene flames (such as counter-flow flames) to achieve conditions for key controlling parameters (such as residence time) that better match those that apply in the existing data sets for turbulent ethylene jet target flames. Data is sought for both atmospheric and elevated pressure conditions.

Objective 2**:** To advance prediction of sooting flames in the growth/agglomeration regimes of ethylene flames:

Target 2**:** obtain new systematic data in growth/agglomerated-dominated regimes of turbulent ethylene flames (such as the recirculation region of bluff-body flames) to achieve conditions for key controlling parameters such as residence time that better match those that apply in the existing data sets for laminar ethylene jet flames. Data is sought for both atmospheric and elevated pressure conditions.

Objective 3**:** To advance prediction of sooting flames with more practical fuels:

Target 3: establish a coordinated data base, building on existing data, in the laminar and turbulent regimes, and at a range of pressures, for

- methane flames and
- pre-vaporised heptane flames;

Objective 4**:** To engage with the international community through joint sessions with members of the Flame Chemistry and Measurement and Computation of Turbulent Flames (TNF) workshops to:

- advance both understanding and global coordination in the ongoing development of models of soot evolution, addressing PAH chemistry, soot inception, and soot oxidation;
- advance both understanding and global coordination in the ongoing development of models of turbulence-chemistry interactions;

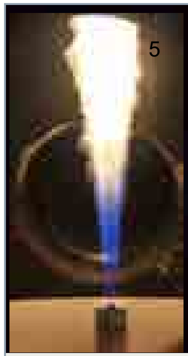
Workshop Programs

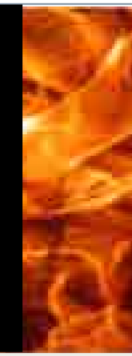
For ISF-4, the workshop will be organised around the following two Research Programs:

- Laminar flames as a function of pressure: Chemical Kinetics (PAH, inception, growth and oxidation); Particle dynamics (moment methods, sectional models, coalescence vs. aggregation);
- Turbulent flames as function of pressure: jet flames, bluff body flames, swirl flames, pool fires, influence of scale;

International Sooting Flame (ISF) Workshop
Program (Final Draft)

Date	Time	Topic	Chair/Presenter
Friday 27th	9:00 - 10:00	Registration and coffee	
	10:00 - 10:20	Welcome, aims and agenda	Speaker: Nathan
	10:20 - 10:50	Industry perspective "Carbon black challenges & technology frontiers"	Speaker: Roscoe Taylor, Orion Engineered Carbons Chair: Wang
	10:50 - 11:10	Discussion	
	11:10 - 11:40	Soot inception and growth: What do we know, and where do we go from here?	Speaker: Michelsen Chair: Shaddix
	11:40 - 12:00	Discussion	
	12:00 - 12:20	Review key outcomes from ISF-3	Speaker: Thomson
	12:20 - 13:00	Discussion	Chairs: Pitsch / Thomson
	13:00 – 14:00	**Lunch**	
	14:00 - 15:30	Turbulent flames (Atmospheric & pressurised)	Speakers: Mueller / Sun / Dreier Chair: Dally
	15:30 - 16:00	**Coffee**	
	16:00 - 17:30	Discussion: Turbulent flames	Chair: Geigle / Dally
		Break	
	19:00 - 22:00	**Posters and Informal Dinner**	
Saturday 28th	8:30 - 8:50	Progress and capabilities for turbulent sooting flames	Speakers: Dally / Mueller
	8:50 – 9:30	Configurations and techniques for flames series from non-sooting to sooting	Discussion Panel: Simone Hochgreb, Venkat Raman, Bill Roberts
	9:30 - 10:00	Joint discussion session with the TNF Workshop	Chairs: Dally / Mueller
	10:00 - 10:30	**Coffee**	
	10:30-10:50	Current knowledge on PAH chemistry: Mechanisms view	Speaker: Tiziano Faravelli Chair: Wang
	10:50-11:10	Current knowledge on PAH chemistry: Reactions view	Speaker: Stephen Klippenstein Chair: Wang
	11:10-11:30	Potential validation experiments for PAH chemistry	Speaker: Nils Hansen Chair: Thomson
	11:30 - 12:30	Joint discussion session with Flame Chemistry Workshop	Chair: Pitsch / Wang
	12:30 - 13:30	**Lunch**	
	13:30 - 15:30	Laminar flames (Atmospheric & pressurised)	Speakers: Dworkin/Bisetti/Sirignano Chair: Wang / Thomson
	15:30 - 16:00	**Coffee**	
	16:00 - 17:00	Discussion: Outcomes and next target flames	Chairs: Shaddix / Wang
	17:00 - 17:15	Feedback on Workshop	Chairs: Dally / Geigle
	17:15 - 17:30	Closing remarks	Speaker: Nathan
	17:30	**Nominal closing time**	





Welcome

Welcome to ISF-4

Fourth International Sooting Flame (ISF) Workshop

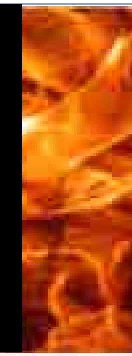
Friday July 27th – Saturday July 28th, 2018

Dublin, Ireland

www.adelaide.edu.au/cet/isfworkshop

ISF Workshop

Welcome



Organising Committee

Prof Gus Nathan
Prof Heinz Pitsch
Prof Hai Wang
Prof Bassam Dally
Dr Chris Shaddix
Dr Klaus-Peter Geigle
Prof Murray Thomson

Scientific Advisory Committee

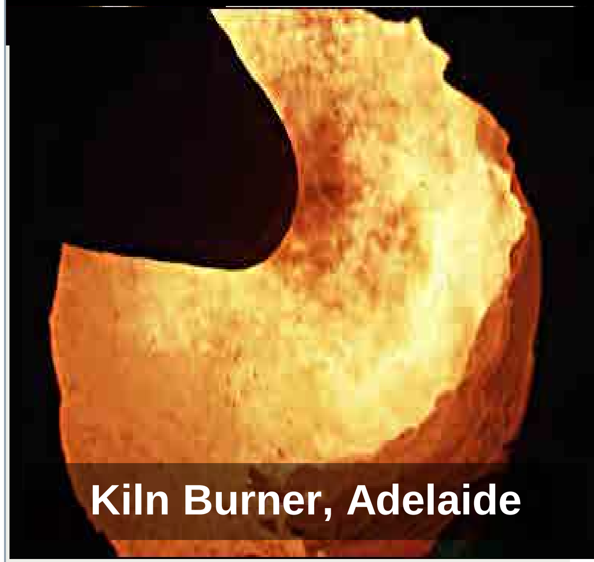
Prof Ömer Gülder
Dr Hope Michelsen
Dr Meredith Colket
Prof Andrea D'Anna
Prof Henning Bockhorn
Prof Peter Lindstedt
Prof Pascalle Desgroux
Prof Mitch Smooke
Prof Dan Haworth
Prof. Bill Roberts

Program Leaders and Co-leaders

Laminar Flames: Prof Guillame Blanquart, Dr Mariano Sirignano, Prof Thomas Dreier

Turbulent Flames: Prof Michael Mueller; Dr Zhiwei Sun, Prof Fabrizio Bisetti

ISF – Aims to develop predictive models relevant to practical sooting flames

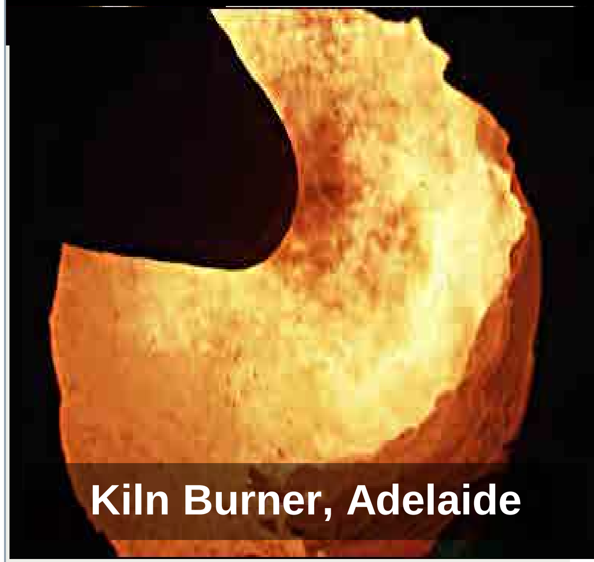


- $\tau_{res} \sim 10$ sec
- Soot desirable for radiant heat transfer

- $\tau_{res} \sim 0.01$ sec
- Soot & radiation undesirable

- $\tau_{res} \sim 0.001$ sec
- Soot & radiation undesirable

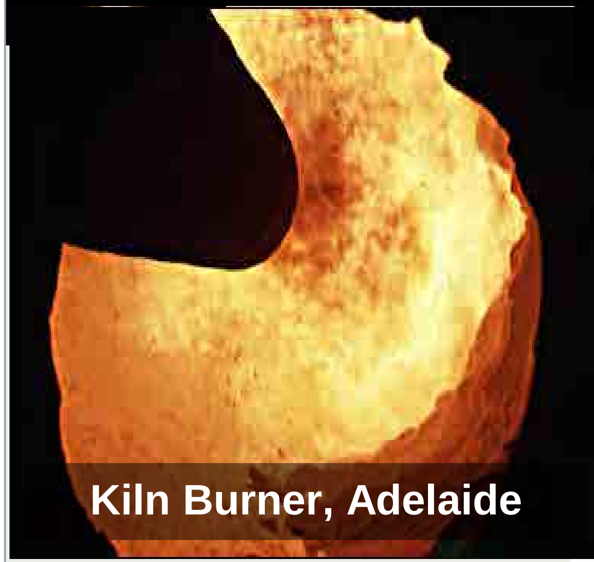
ISF – Aims to develop predictive models relevant to practical sooting flames



Apriori prediction is challenging because:

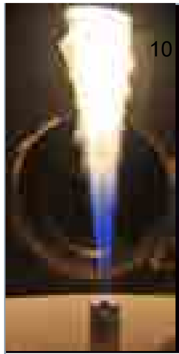
- Multi-scale physics
- Coupled, non-linear mechanisms
- Range of multi-component fuels
- Wide range of regimes (T, τ_{res}, ξ, P, C_xH_y, M)

ISF Approach

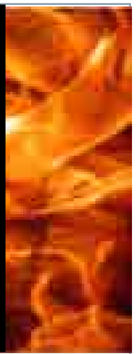


To establish a series of well defined and linked “target flames” with known accuracy suitable for model development and validation, spanning a variety of flame types relevant to application;

To develop progressively improved prediction through comparison of alterative models against the data;

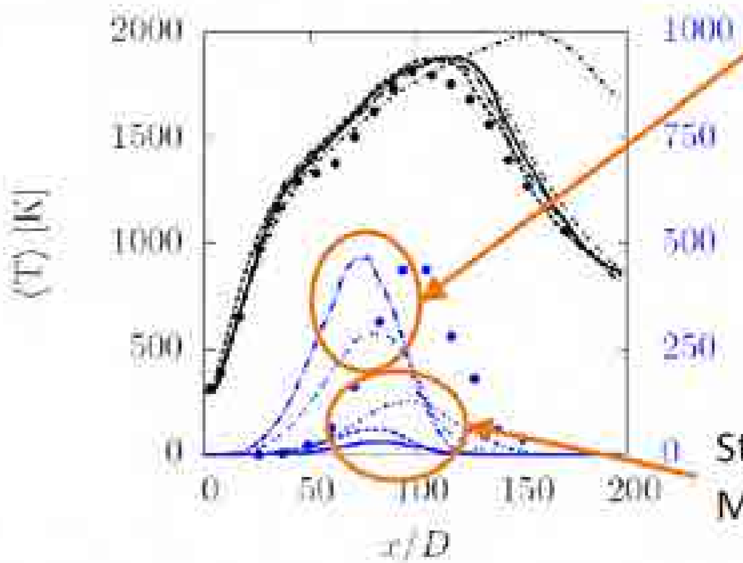


ISF Workshop



Predicting turbulent flames is still a challenge at ISF-3

- Sensitivity to Chemical Mechanism
  - LES results for Adelaide simple jet flame (middle strain rate)

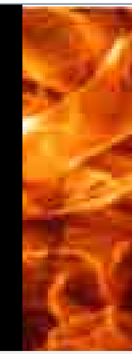


KAUST Mechanism

Note: LES volume fraction multiplied by 10x!

Stanford/Aachen Mechanism

  - Both mechanisms underpredict the soot volume fraction significantly, which means there is something still really wrong with the models



Progressive Targets for ISF

ISF-I: Established "Buy-in" for process of linked "Target flames"

Poor prediction with $CH_4 \rightarrow$ moved to C_2H_4

ISF-2: Achieved first "Linked flames" through the programs

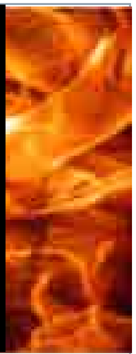
Poor prediction with $C_2H_4 \rightarrow$ expanded data bases

ISF-3: Established more extensive data based of "Linked flames"

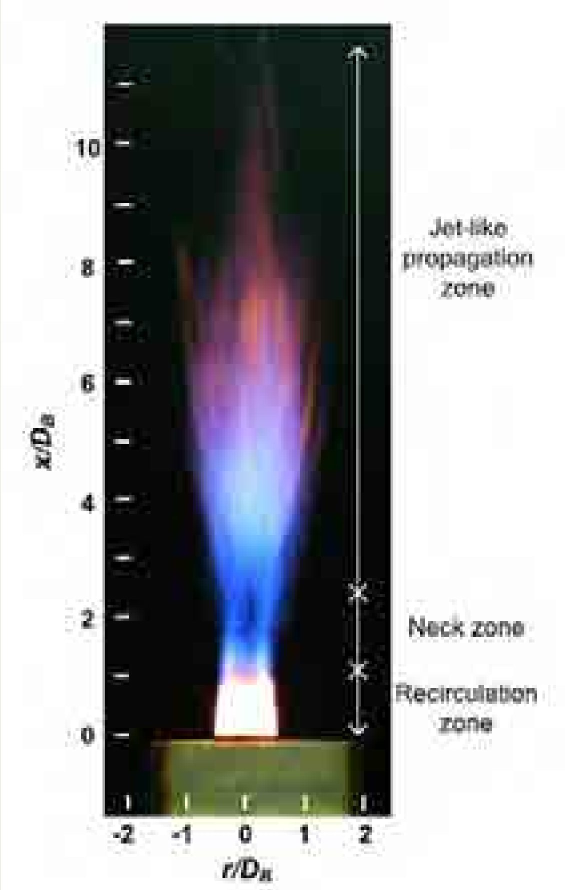
Identified improved prediction in "growth-dominated" over "inception-dominated" flame regimes (also C_2H_4)

ISF-4: Called for more data in two regimes and additional fuels

ISF Workshop



Turbulent flames with both zones



Inception – dominated regime

- High strain, short residence time
- poor prediction
- Approaching gas turbine type applications

Growth/agglomeration – dominated regime

- Low strain, long residence time
- Improved prediction
- Approaching furnace & kiln applications

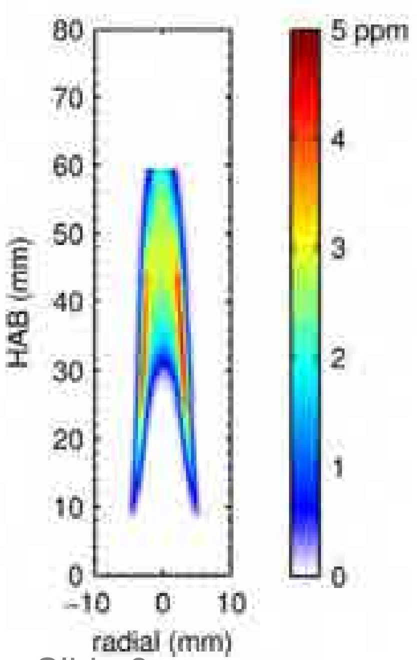
Mueller et al. Comb. Flame (2016)

ISF Workshop

Plausible explanation for discrepancies in inception-dominated regimes

Models developed and applied in different dominant regimes:

- Models developed: Laminar $\rightarrow$ growth/agglom -dominated
- Models applied: Turbulent $\rightarrow$ inception-dominated



τ_{glob} **=L/u** ~ 0.3 sec

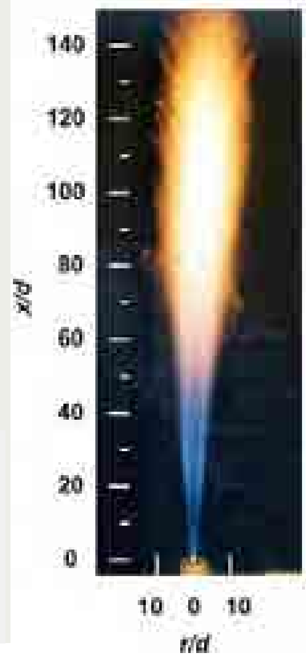
$\tau_{loc} \sim \tau_{glob}$

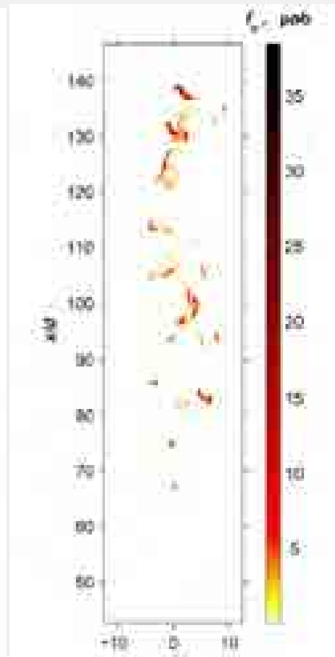
Sun et al. Comb. Flame (2017)

τ_{glob} **=L/u** ~ 0.03 sec

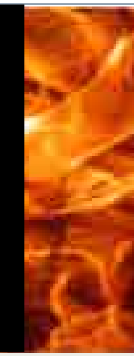
$\tau_{loc} \sim \tau_{glob}$ **/ 10**

Qamar et al. Comb. Flame (2009)



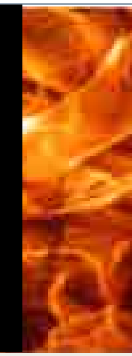


Objectives for ISF-4



Objective 1: To advance understanding and prediction of **inception-dominated ethylene flames**:

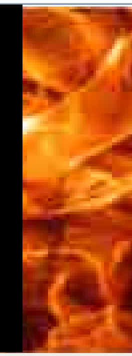
Target 1: obtain new systematic data in inception-dominated laminar ethylene flames (e.g. counter-flow flames) to better match controlling parameters (such as residence time) in the “plume” of turbulent ethylene jet target flames (atmospheric and pressurised).



Objectives for ISF-4

Objective 2: To advance prediction of sooting flames in the **growth/agglomeration regimes of ethylene flames**:

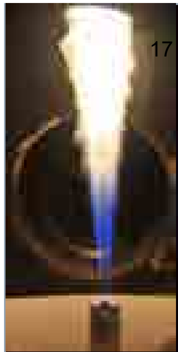
Target 2: obtain new systematic data in growth/agglomerated-dominated regimes of turbulent ethylene flames (e.g. recirculation zone of bluff-body flames) to better match the existing data sets for laminar ethylene jet flames (atmospheric and pressurised).



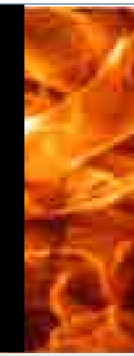
Objectives for ISF-4

Objective 3: To advance prediction of sooting flames with more practical fuels:

Target 3 establish a coordinated data base, linked to existing data, in both the laminar and turbulent regimes and at various pressures, for methane flames and pre-vaporised heptane flames;

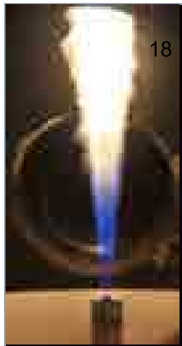


Objectives for ISF-4

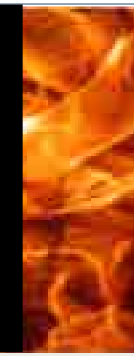


Objective 4: To increase international engagement through **joint sessions with**:

- **the flame chemistry workshop** to address both:
  - PAH chemistry, soot inception, and
  - soot oxidation
- **the TNF workshop** to address:
  - Lessons learned from modelling turbulent flames
  - Better leverage and coordination of data



Program Features for ISF-4



Industrial Keynote Speaker
Roscoe Taylor (Orion Engineered Carbons)

Research Keynote Speaker
Dr Hope Michelsen (Sandia National Laboratory)

Invited Panellists for Joint Session with TNF Workshop
Prof Simone Hochgreb (Cambridge University)
Prof Venkat Raman (University of Michigan)
Prof Bill Roberts (King Abdullah University of Science and Technology)

Invited Panellists for Joint Session with Flame Chemistry Workshop
Prof Tiziano Faravelli (Politecnico di Milano)
Prof Stephen Klippenstein (Argonne National University)
Prof Nils Hansen (Sandia National Laboratory)

Local Host
Prof. Stephen Dooley (Trinity College, Dublin)


International Sooting Flame Workshop
An Open Forum for Discussions and Interaction
Probability
0.8
0.6
0.4
0.2

Discussion?

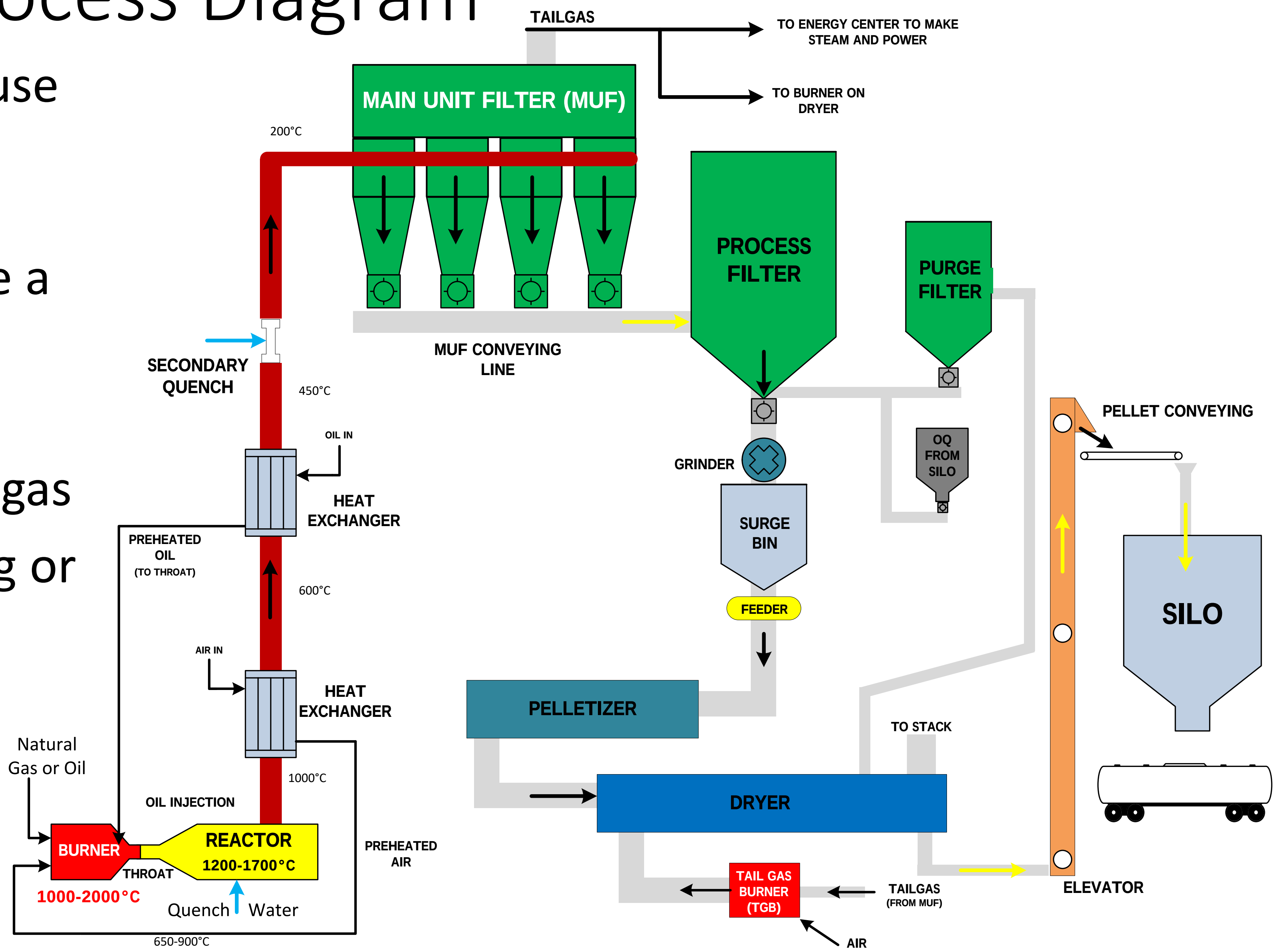
Carbon Black

Challenges and Technology Frontiers

Carbon Black Process Diagram

1. Create a hot gas and use to heat/burn a hydrocarbon
2. Boil burn and pyrolyse a hydrocarbon
3. Quench reactions
4. Collect Particles from gas
5. Optional coke grinding or separation
6. Pelletise (wet or dry)
7. Pack and Ship

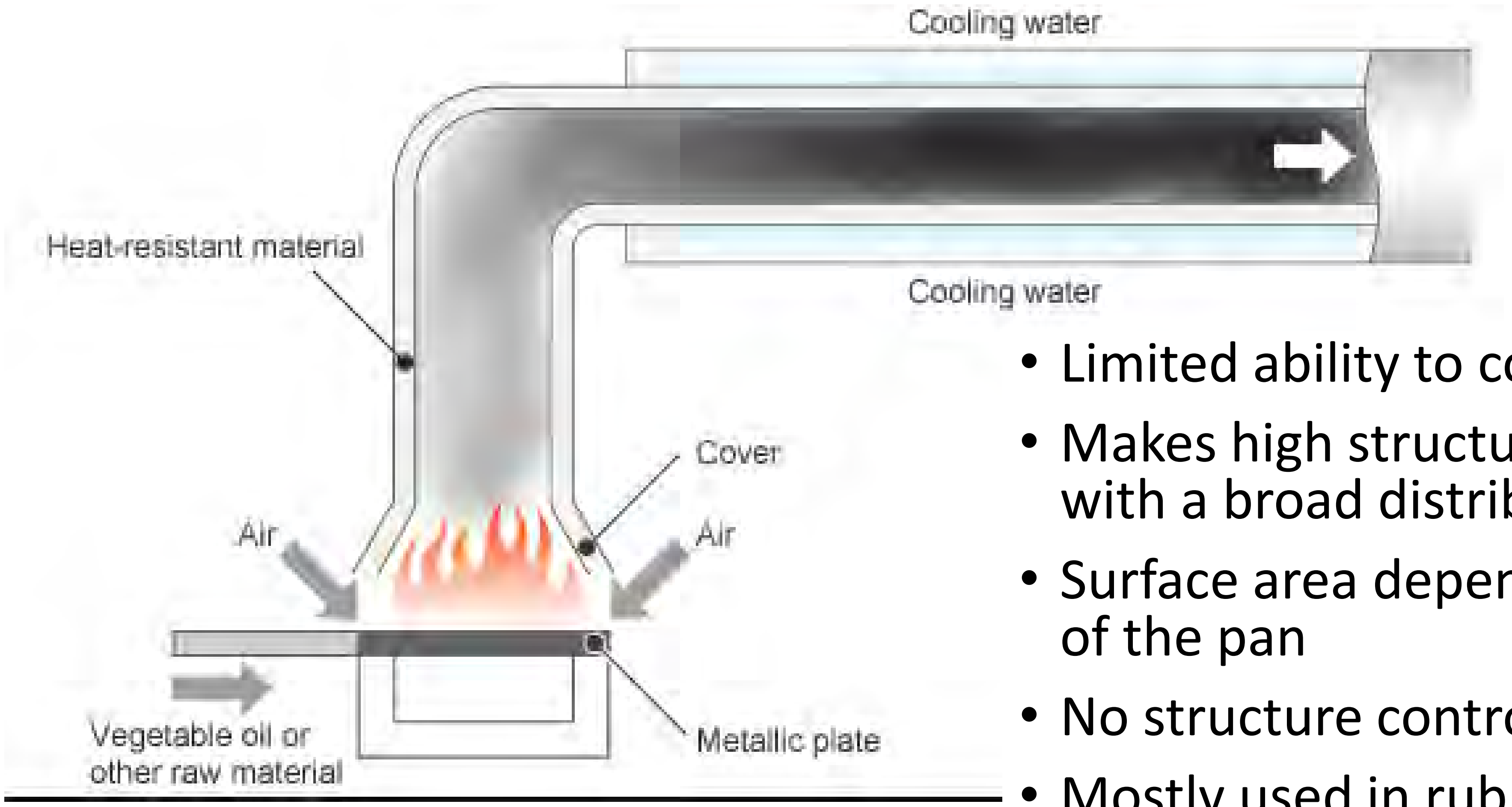
Up to ~300 T/day



Different Carbon Black Processes

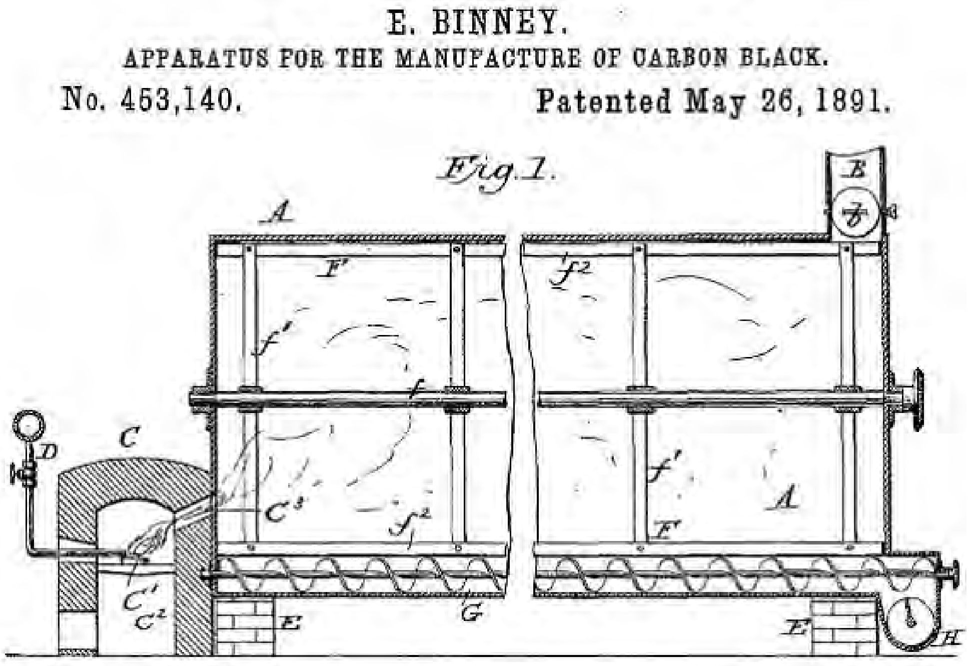
- Lamp Black -- Pan of evaporating oil covered to limit air
  (process invented in China 2000 BC, <1% production)
- Channel Process -- Natural Gas flame on cold channel iron
  (dirty & dominant process pre 1970, no longer in use)
- Gas Process -- Vapour flame on a rotating drum
  (modern channel process, <1% of production)
- Thermal Process -- Natural Gas on hot bricks. Semi Continuous
  (makes the largest particle size blacks, <2% production)
- Acetylene Process – Exothermic Decomposition of Acetylene
  (highly conductive and crystalline blacks, <1% production)
- Furnace Process -- Partial combustion of aromatic oils
  (>90% of current black produced)

Lamp Black Process



- Limited ability to control particles
- Makes high structure large particles with a broad distribution
- Surface area dependent on diameter of the pan
- No structure control
- Mostly used in rubber extrusions, some conductive applications

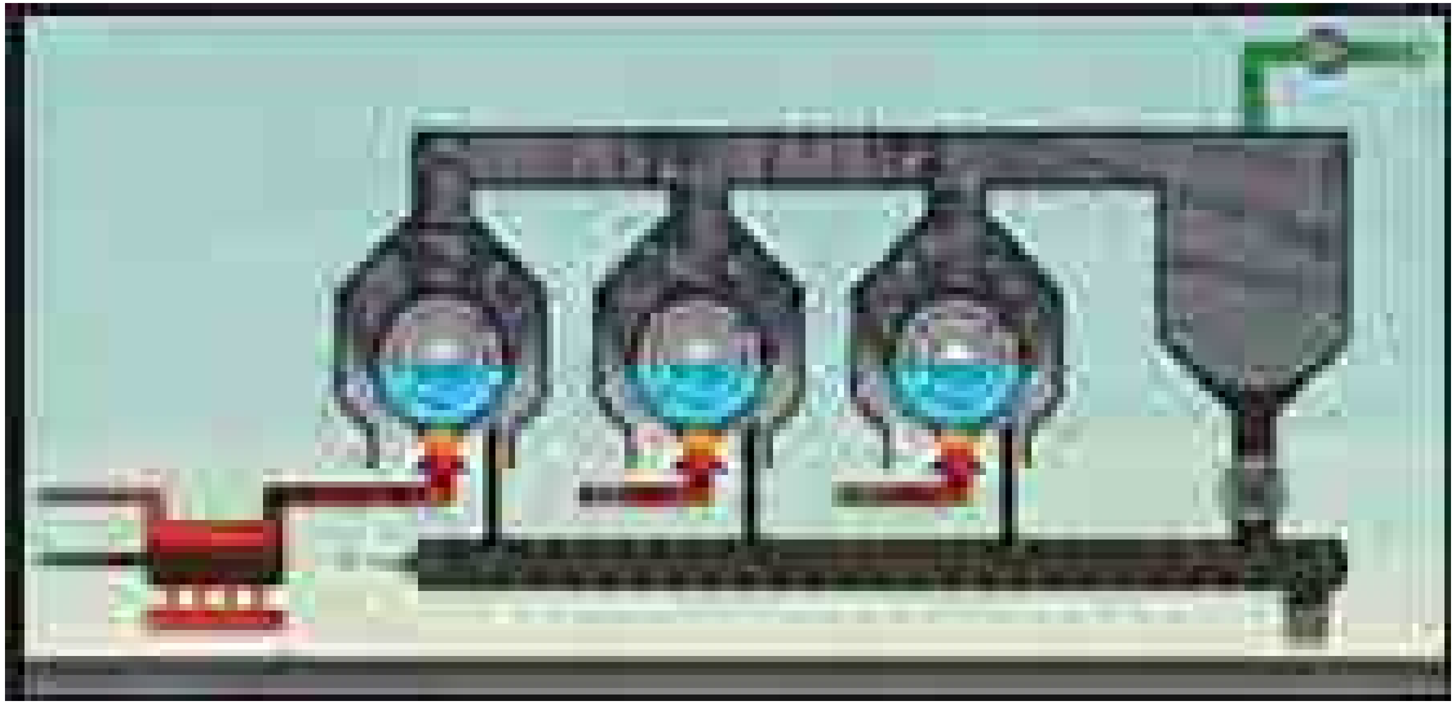
Channel Black



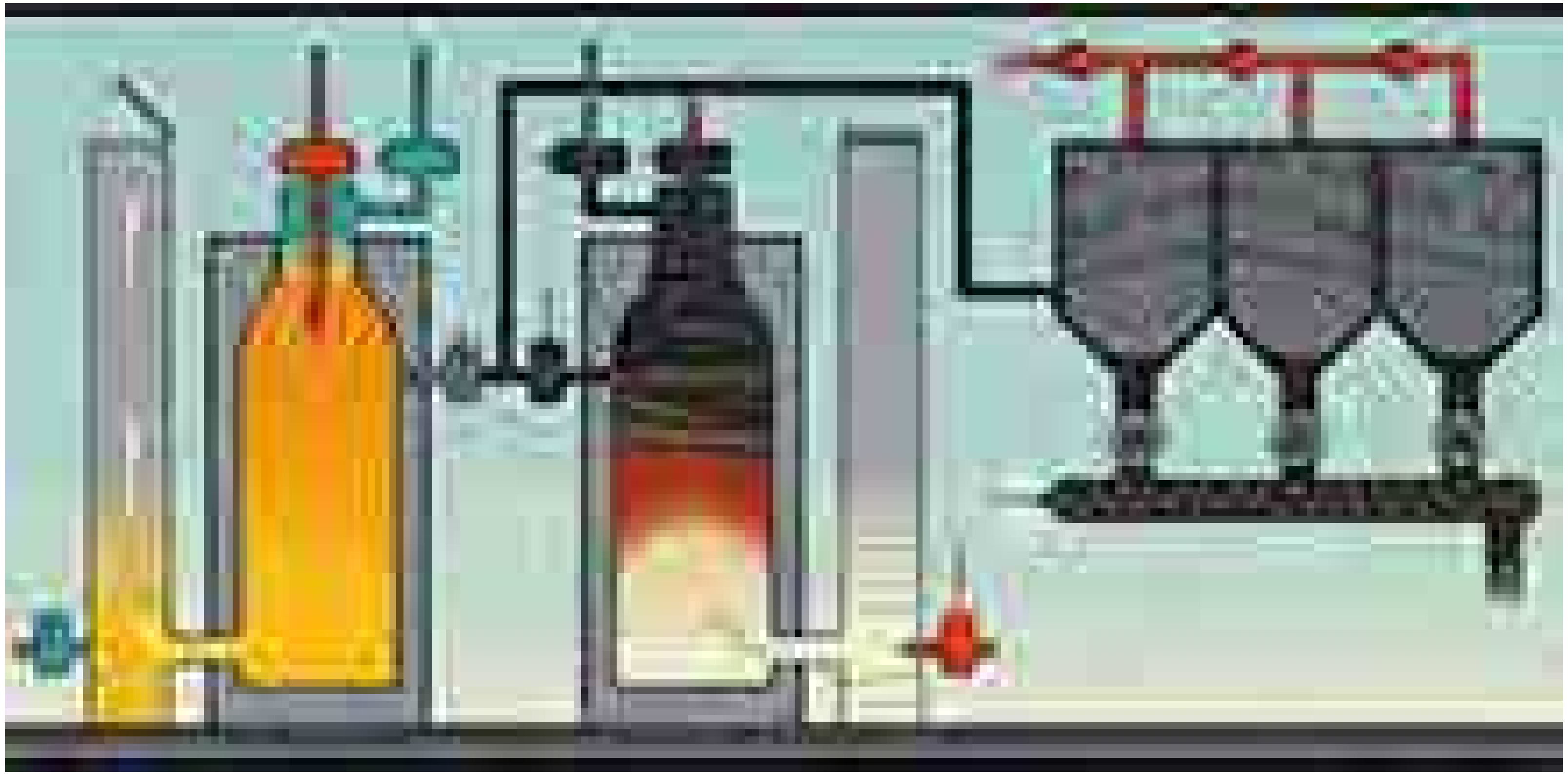
- Main process until ~1960’s
- Low recovery, high emissions
- Natural Gas feedstock
- Used as aeroplane navigational aids

Gas Black (Similar to Channel Black)

- Oil based channel black process.
- Oil Flame playing on a water cooled drum
- Produces some of the smallest particles
- Can produce highly hydrophilic surfaces
- Often used in aqueous based paints and toners

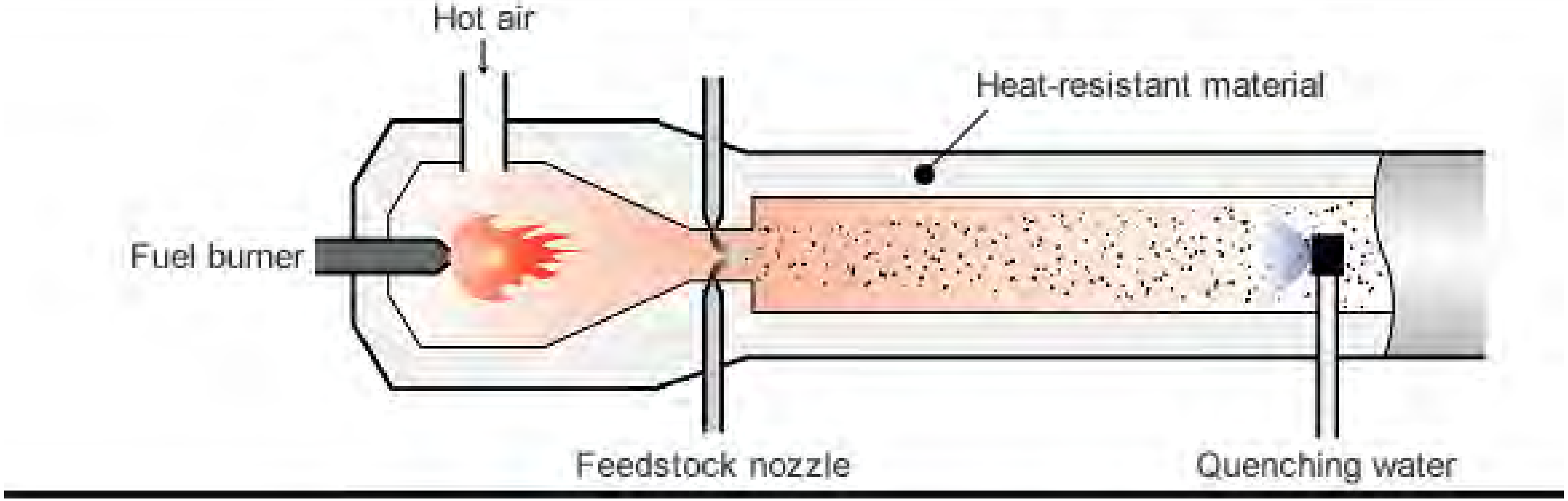


Thermal Black Process



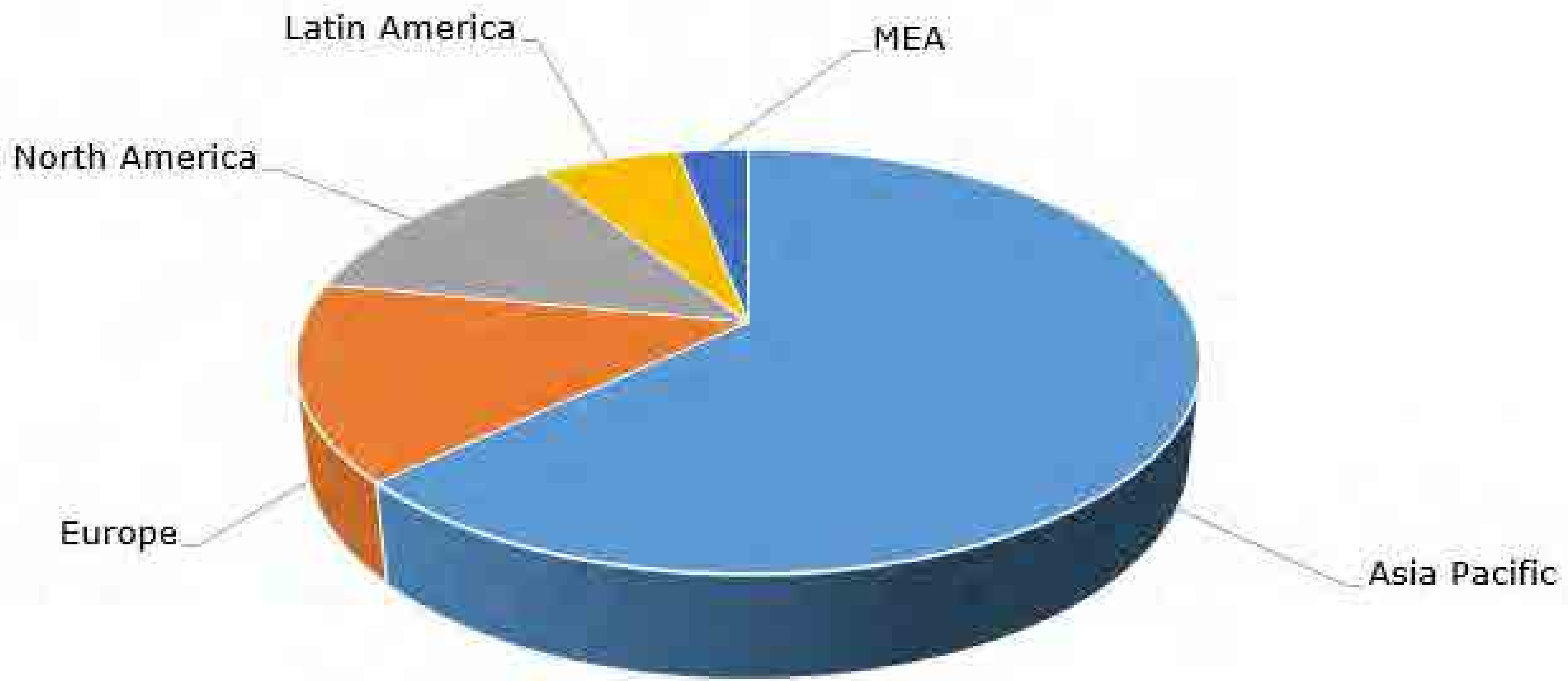
- Only makes large particles with little or no structure
- Only NG based process in commercial production
- Converts NG to Pyrene in Upper Portions of Reactor
- Makes product almost entirely from surface growth. No apparent relationship between temperature and surface area.
- Surface area dependent on Concentration

Furnace Process: Most Flexible. >90% Production



- Makes the widest variety of products
- Typically a two stage combustion process
  - First stage 1000-2000+°C
  - Second stage reactor temperatures generally 1200-1800°C
- Feedstock starts with PAHs in the 3-5 fused ring range
- Controls aggregation with potassium salt addition, charging the forming particles to reduce aggregation
- Quenching to control particle porosity and influence surface chemistry

Regional Distribution of Production: China represents the largest supplier (>30%)



Industry Challenges

- **Increasing the yield**: burning less oil turns more of it into black
- **Tighter environmental regulation** around particulates, SO_x and NO_X emissions
- **Competition from alternative materials**

Challenges: Increasing Yield

- In general the feedstock represents the largest cost in producing CB
  - Feedstock quality is declining as technology in refineries changes, reducing yield
- Reactor equivalence ratios run in the range of 3-8
  - Of this the primary fire is 0.5-0.8
- Yield for a grade increases with higher air and oil preheat temperatures.
  - Air preheat at the metal temperature limits of heat exchangers
  - Oil preheat at the limit of coking in the oil heater

Reaction temperature, °C[a]	Primary particle size, nm
1450	44
1500	35
1570	26
1580	24
1630	21
1680	19

- This leaves the goal of making the same product at a lower reactor temperature e.g. by improving the oil and fire mixing
- All of the above supports a collision coalescence model of carbon black formation although also not inconsistent with a surface growth model

Challenges: More Strict Emissions Controls

Many countries now require emissions control equipment for NO_x.

- Nitrogen in the feedstock converts to chemical NO_x precursors
- SCR required for the more strict regimes
- SNCR used on combusted tail gas, but not the dryer stack (too low temperature)

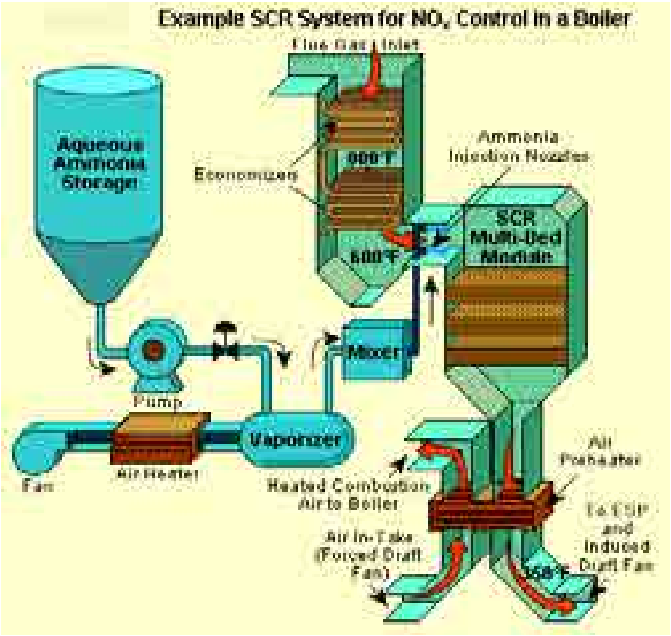
For SO_x control some internationally located plants use dry scrubbing

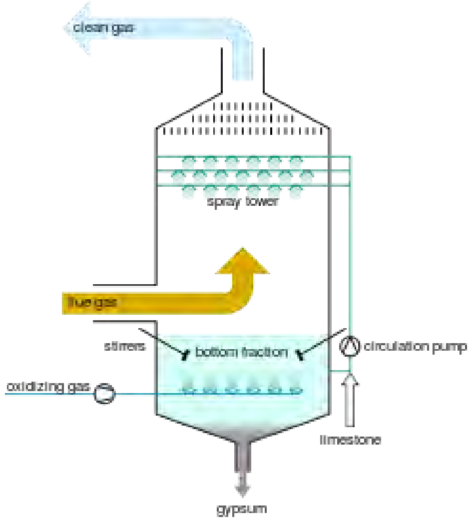
- US EPA requiring widespread adoptions of SO_x wet scrubbing
  - Cost of around $150+/T or 10-15% of current prices
  - Will make importing black significantly more attractive
  - EPA previously used 3% limits to feedstock Sulfur vs 1-2% elsewhere
  - Some US plants will avoid scrubbing by using 1% Sulfur feedstock

China enforced a Winter shutdown of CB plants in Hubei province

Continental plant in India shutdown indefinitely over particulate emissions

Other plants constrained in production by particulate emissions limits

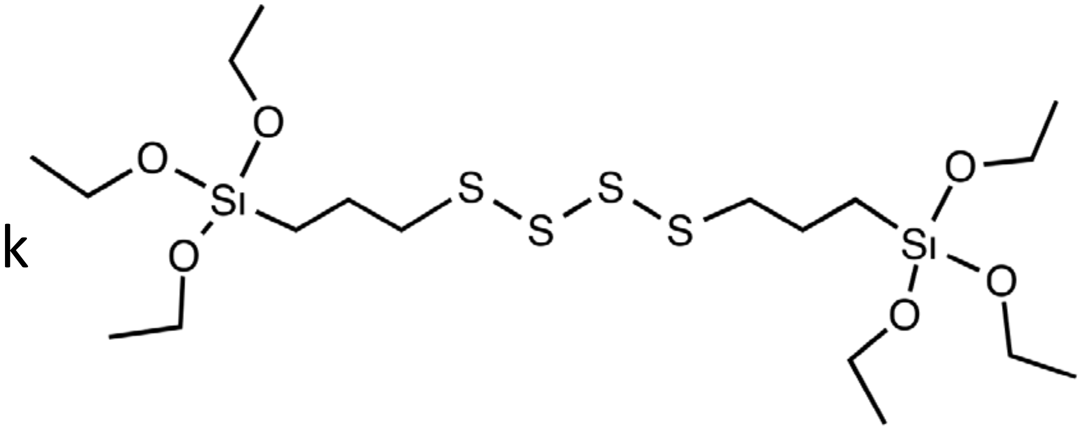




Challenges: Alternative Materials

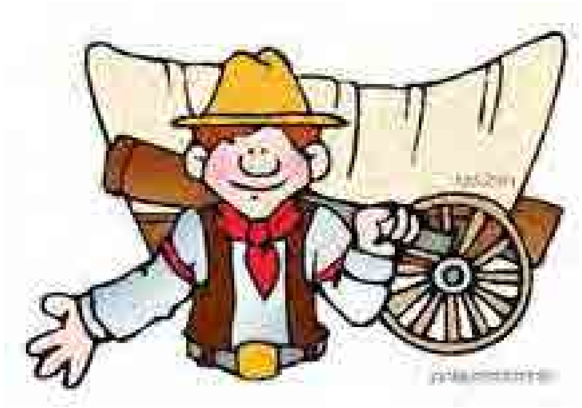
- Recycled Carbon Black
  - Tyre producers use some carbon black from pyrolised tyres
  - Used as a low cost filler as the material provides much less reinforcement
  - At best recycled carbon black is a blend of many grades (tread, sidewall etc)

- Precipitated Silica plus a coupling agent
  - Replace carbon black with silica coupled to the rubber through the use of bis [(3-triethoxysilylpropyl) tetra sulfide], TESPT, or Si-69.
  - Changes tread wear hysteresis trade off
  - Improves wet traction
  - Present in many "green" tyres
  - Typically used in a blend with Carbon Black



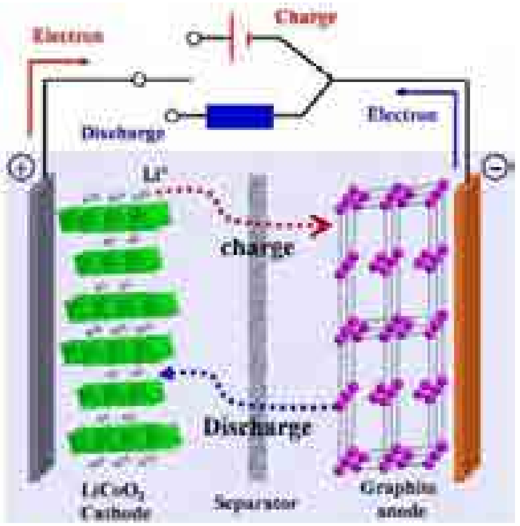
Technology Frontiers

- Strict purity requirements products for lithium ion batteries
- Plasma blacks, carbon black by an alternative cleaner process
- Improving interaction between CB and natural rubber
- Modelling a carbon black reactor



Battery Blacks: High Growth High Margin

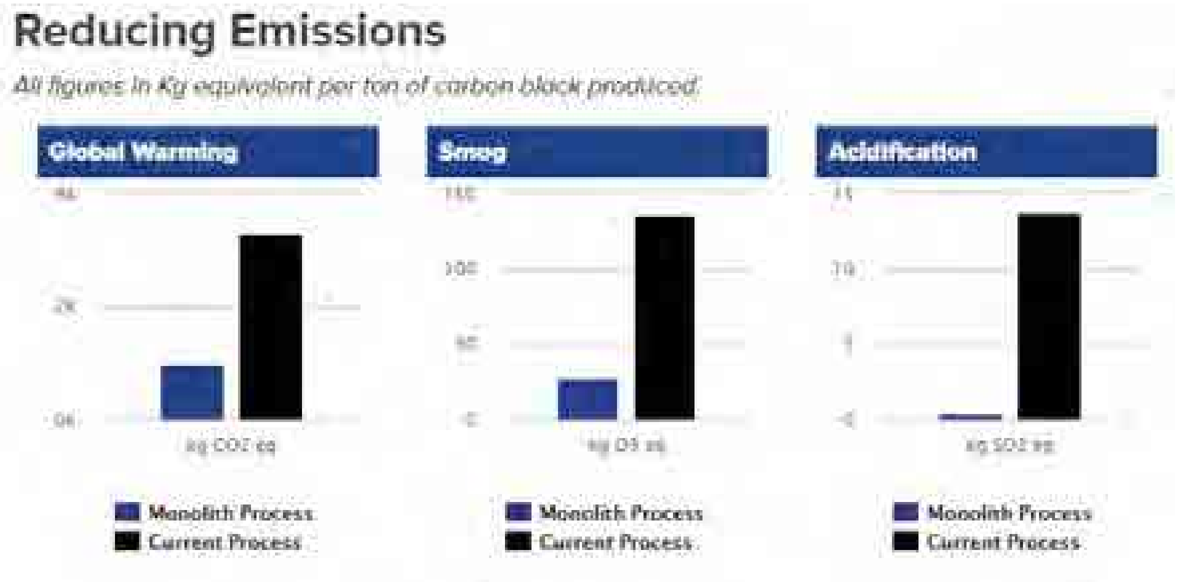
- Batteries use blacks to overcome resistance in battery components
  - For example in lead acid batteries lead oxide has a low conductivity
- Li ion batteries utilise blacks in both the cathode and the anode to create conductive contact points between non-conductive material (e.g. Lithium Iron Phosphate) and conductive material (e.g. graphite).



- Current colloidal requirements 45 m2/g 200 OAN
  - Next generation blacks desire more conductivity, 100 m2/g 150 OAN.
  - Driven by higher current requirements that require more contact points.
  - The next generation CB then enables higher charge and discharge rates.
- Requirements for purity are 5-10 ppm Fe going to 2 ppm.
  - Fe diffuses to the membrane and forms spinals that then can short the battery causing catastrophic failure with rapid discharge.
- Low sulphur <10ppm and low other base metal ions (currently <30 ppm)
- Oil based blacks are unlikely to manage to achieve this purity
- Steam activated blacks and carbons, acetylene blacks, and graphenes compete in this area

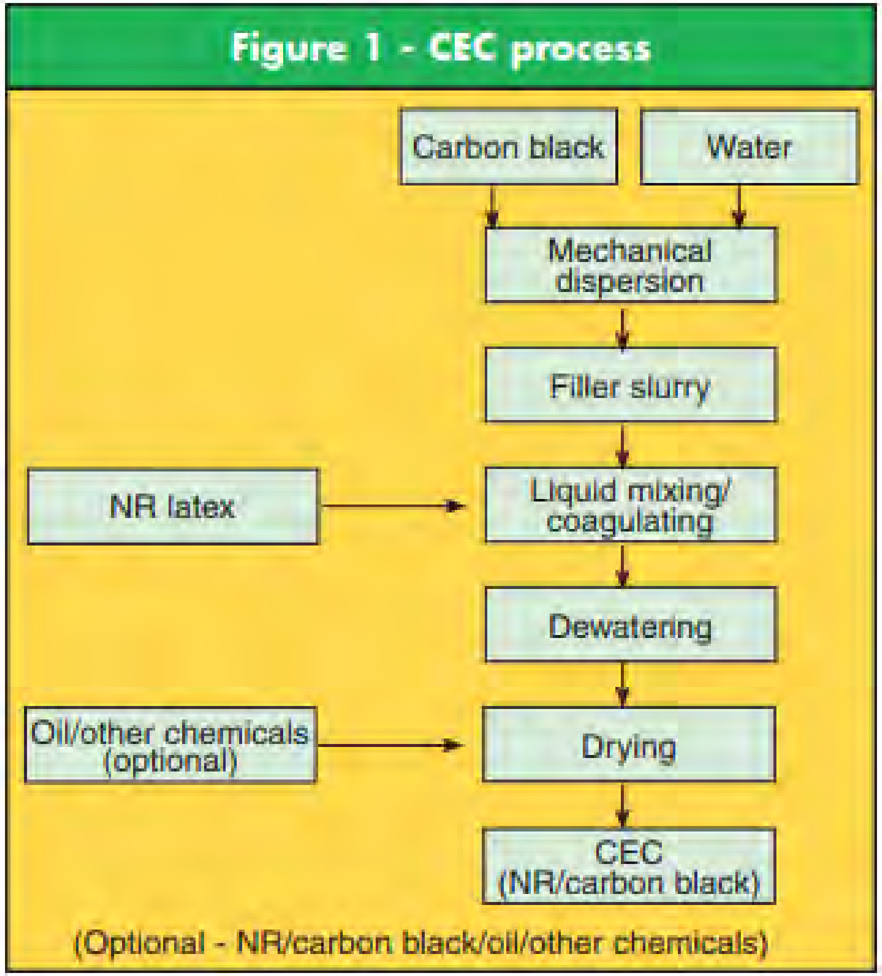
Plasma Process

- Uses Natural Gas and Electricity to make black
- Should produce blacks of a high chemical purity
- Much reduced CO_2 and SO_x emissions
- Rubber applications are mostly compete on cost:
  - Natural Gas is much cheaper than oil even on a carbon basis
  - Electricity is more expensive than combustion heat
  - Hydrogen by product available as a fuel
  - Reaction temperature vs surface area determines the required energy
- Specialty applications mostly compete on quality. Plasma blacks have:
  - Purity advantage
  - Oxygen free surface chemistry
  - Clean Slate surface chemistry



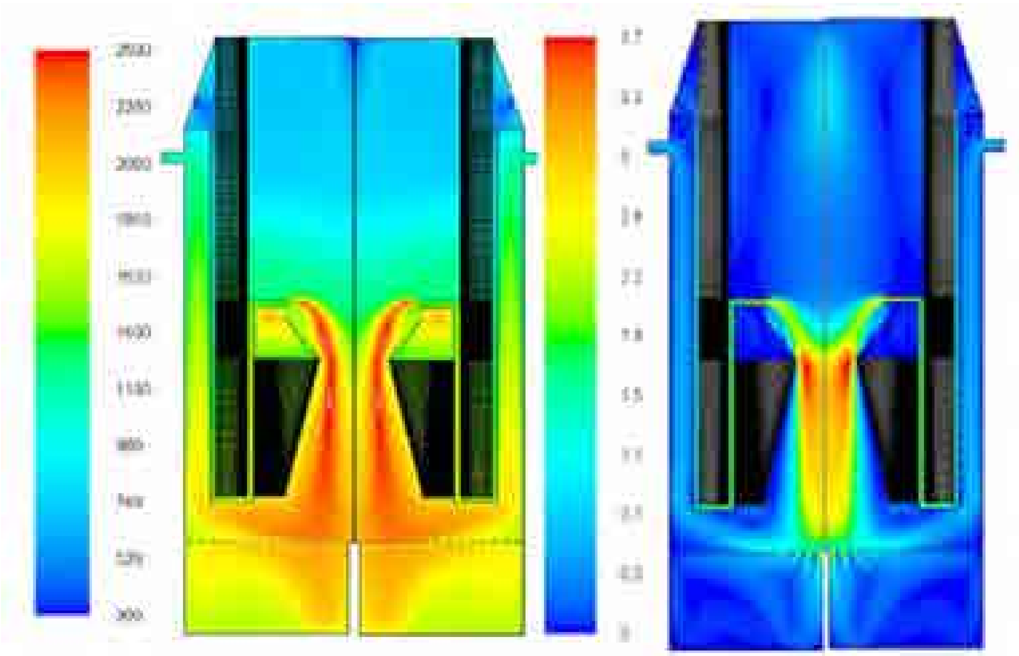
Improving Rubber Black Interaction

- Rubber is mostly hydrophilic and black mostly hydrophobic
- The mixing process is thought to create free radicals in the rubber that then bond with the carbon black surface reinforcing the rubber
- Not all carbon surfaces contact the rubber and at the small scale dispersion is inconsistent
- CEC process achieves near perfect dispersion by incorporating the black into natural rubber when it coagulates
- Improves hysteresis tread wear trade off and cut chip resistance through better dispersion
- Patents held by Cabot and Bridgestone
- Under development by Cabot Michelin JV



CFD Modelling of Carbon Black Reactors

- Steady state turbulent modelling most commonly used
- Simplified reaction system
  - Feedstock to black nucleate, perhaps with an intermediate
  - This may be good enough as feedstock starts as 3-6 fused rings
- May track the number of nuclei and mass of carbon
  - Tracking these enables estimation of surface area and tuning of model
- Typically mixed is burnt for gas phase
  - Consequently system is mostly transport limited
  - Solids at times assumed to be unreactive
- Process mostly appears to match what aerosol dynamics would predict
  - Some think surface growth dominates
- Little mechanistic understanding of aggregation
  - Measured by mixing with an oil (ASTM D2414).
  - Controlled by adding Potassium salts to the reactor



How Can Academia & Modelling Help?

What can be done to improve the yield, or make smaller particles?

- Overall making carbon black is a non-equillibrium process. Water of combustion and CO2 survive the reactor resulting in a higher yield. What would maximise the amount of these?
- Quenching before reactions are complete greatly enlarges particles and results in high residual aromatics which cannot go to customers
- How to maximise nucleation rates so that we make smaller particles?
- How to reduce coalescence of nuclei after they form?

What are the mechanics of aggregation?

How can we make more highly aggregated particles without losing surface area?

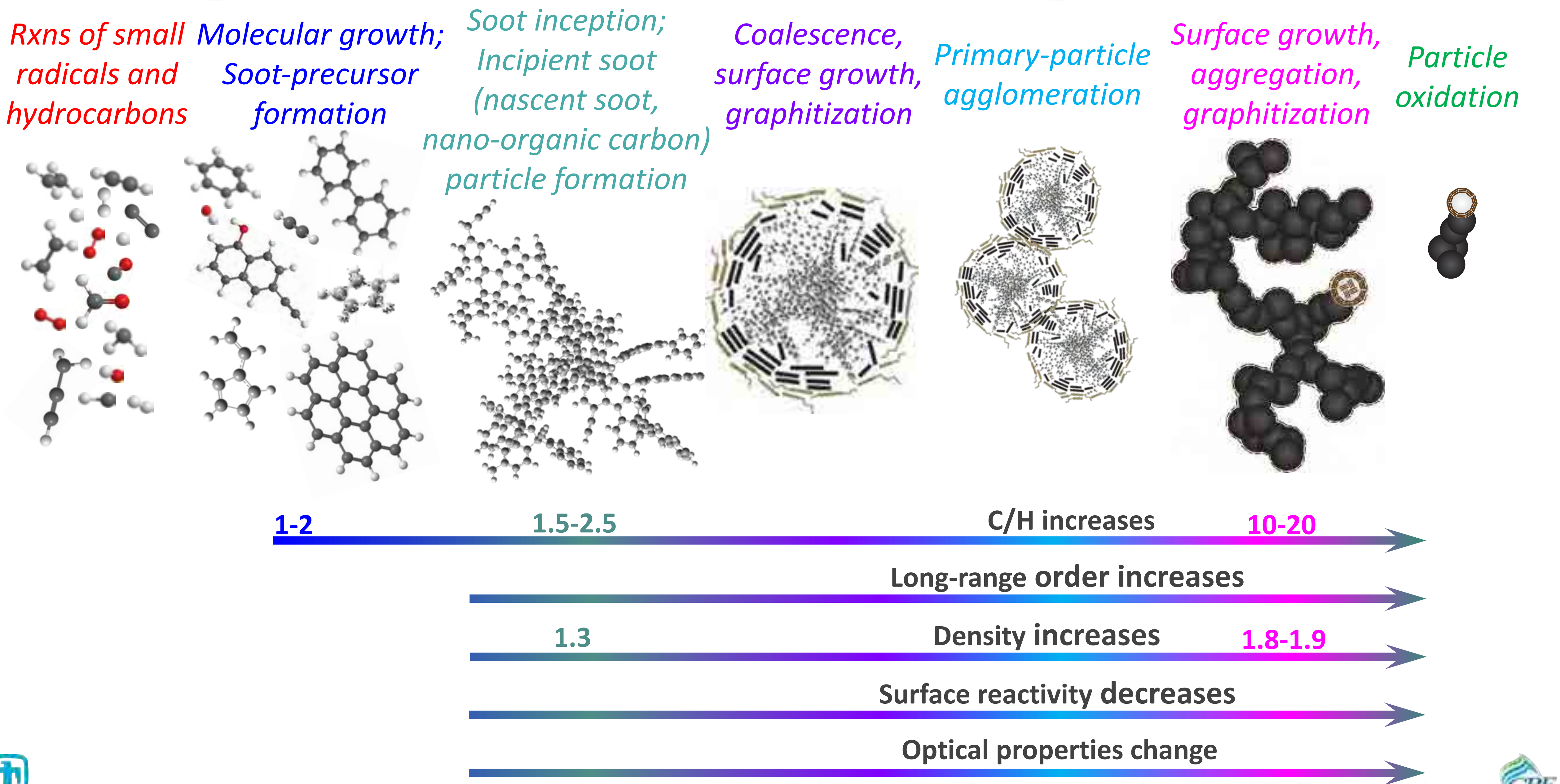
Main Uses of Carbon Black

- Rubber Reinforcement (90+%)
  - Tyres
  - Industrial Rubber Products (belts, seals, hoses, roofing)
- Pigmentation
  - Inks (newsink, gloss, gravure, UV curable)
  - Paint (automotive top coat, industrial coatings)
  - Plastic (car parts, decorative)
  - Toners (laser printers, photo copiers)
- Conductivity
  - Under Ground Power Cables
  - Anti static applications
  - Conductive inks
  - Batteries
- UV resistance
  - Agricultural film
  - Pipe
  - Coatings

Soot Inception and Growth

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

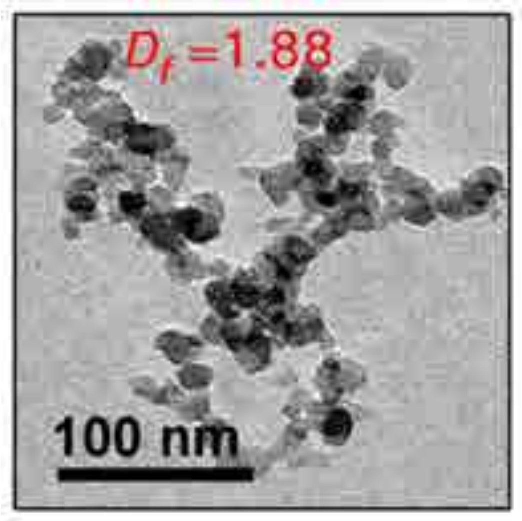
Stages of Particle Evolution During Combustion



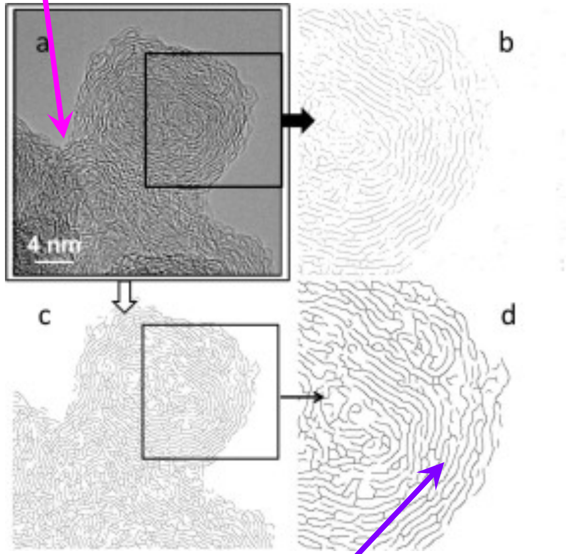
Characteristics of Mature-Soot Particles

The Product

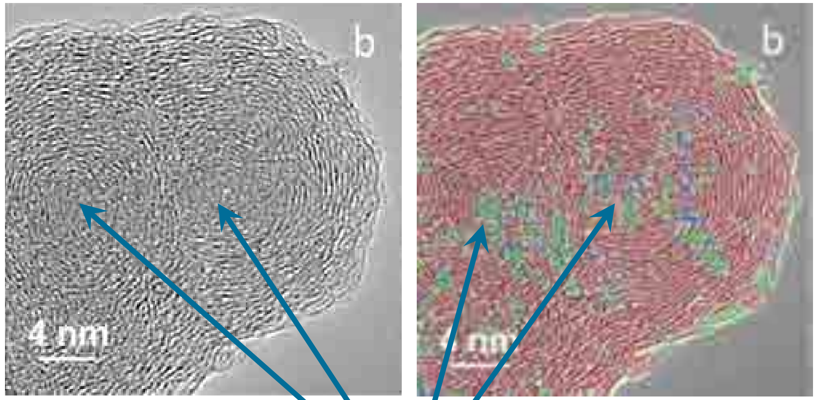
Graphitic overlayers hold aggregate together



Bambha, Dansson, Schrader, Michelsen 2013



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



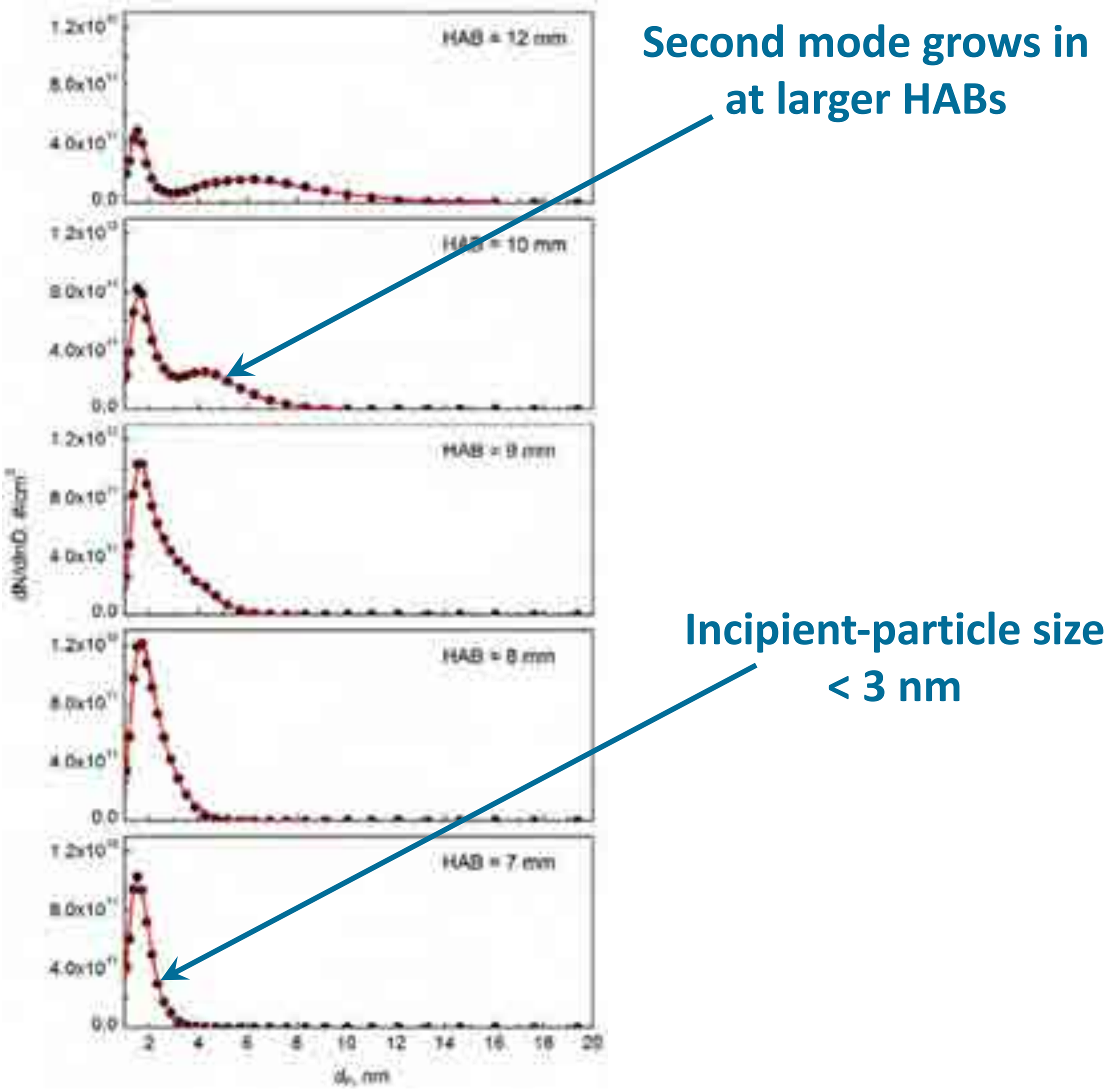
Disordered foci or growth centers, 1-4 nm in diameter

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

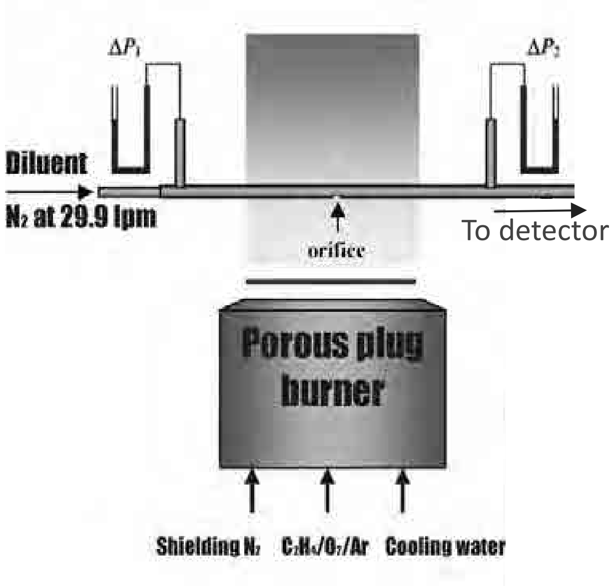
Characteristics of Incipient Particles

Incipient-Particle Size

Premixed ethylene/air, C/O=0.67, Φ=2.03



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



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

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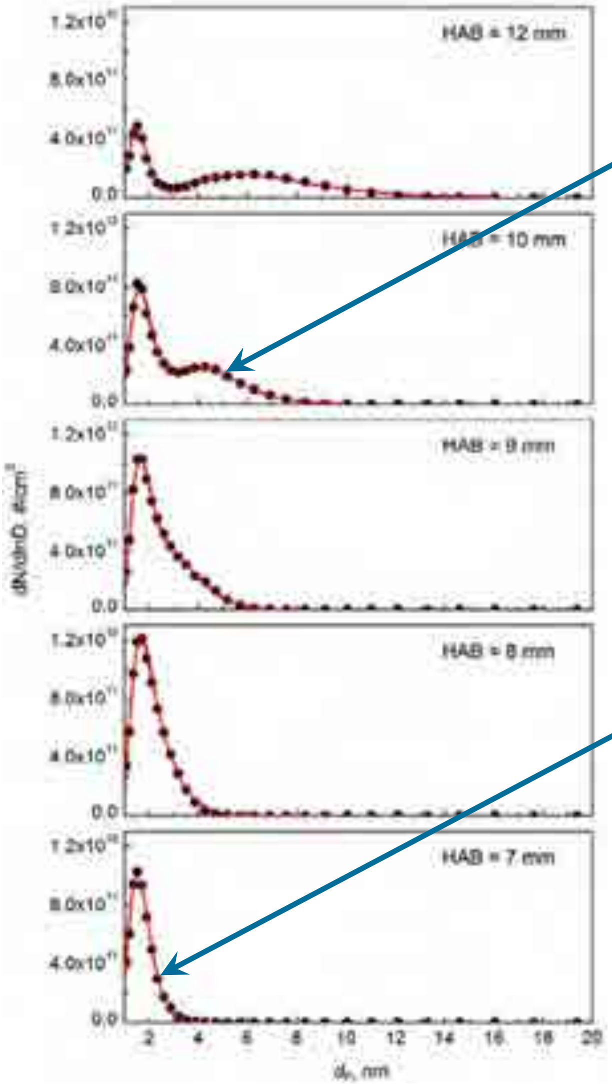
Incipient-Particle Size

Premixed ethylene/air, C/O=0.67, Φ=2.03

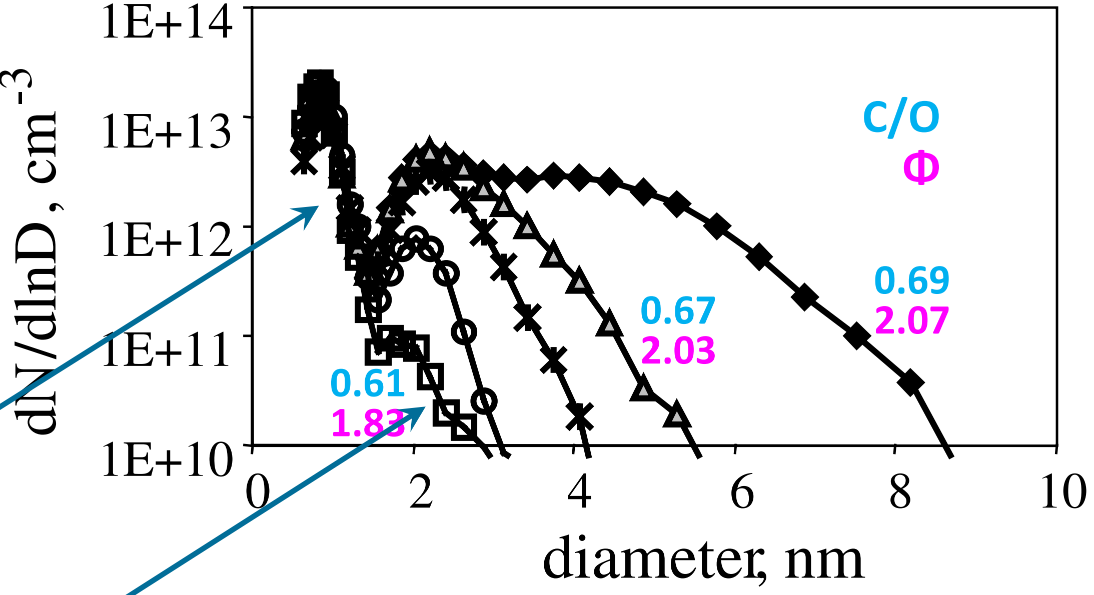


Commodo, De Falco, Bruno, Borriello, D'Anna 2015

Second mode grows in at larger HABs

Incipient-particle size < 3 nm

Premixed ethylene/air, HAB=10 mm



Sgro, De Filippo, Lanzuolo, D'Alessio 2007

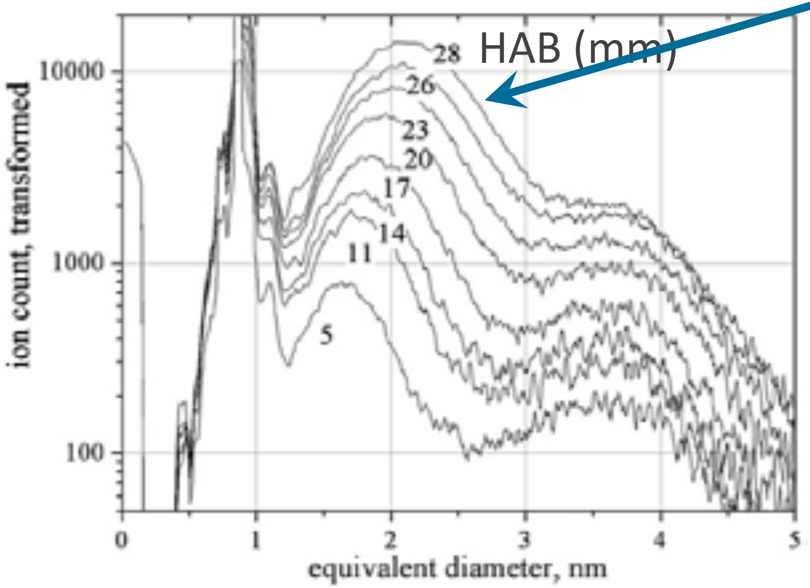
Second mode disappears at lower C/O

Characteristics of Incipient Particles
Incipient-Particle Size

Photoionization mass spectrometry

Premixed ethylene/air

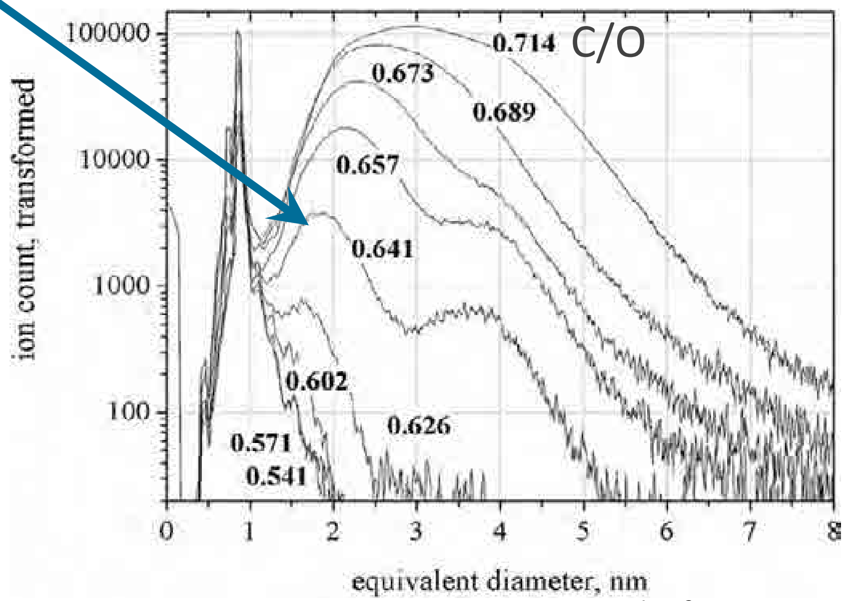
C/O=0.64, Φ=1.92



assuming density of 1 g/cm³

Appears to be growth mode; required for soot formation

HAB = 15 mm



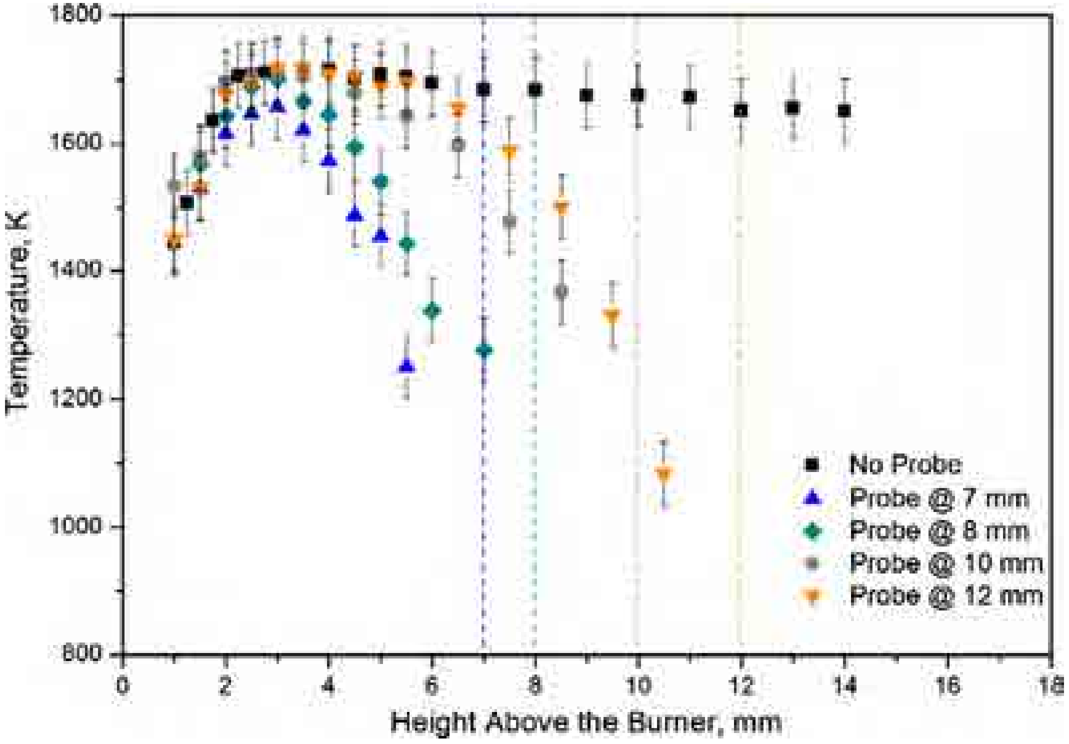
assuming density of 1 g/cm³

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, Φ=2.03



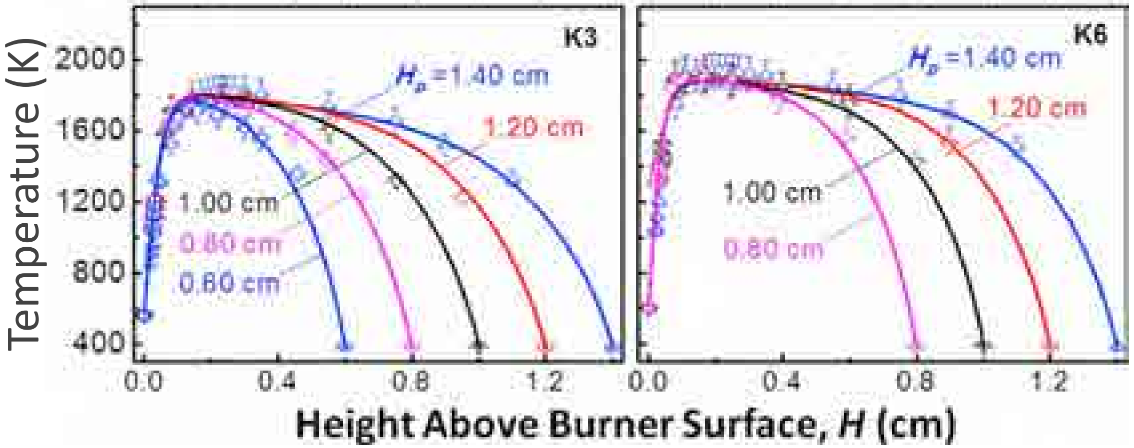
Commodo, De Falco, Bruno, Borriello, D'Anna 2015

Burner-stabilized stagnation flame

Premixed ethylene/air

C/O=0.60, Φ=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

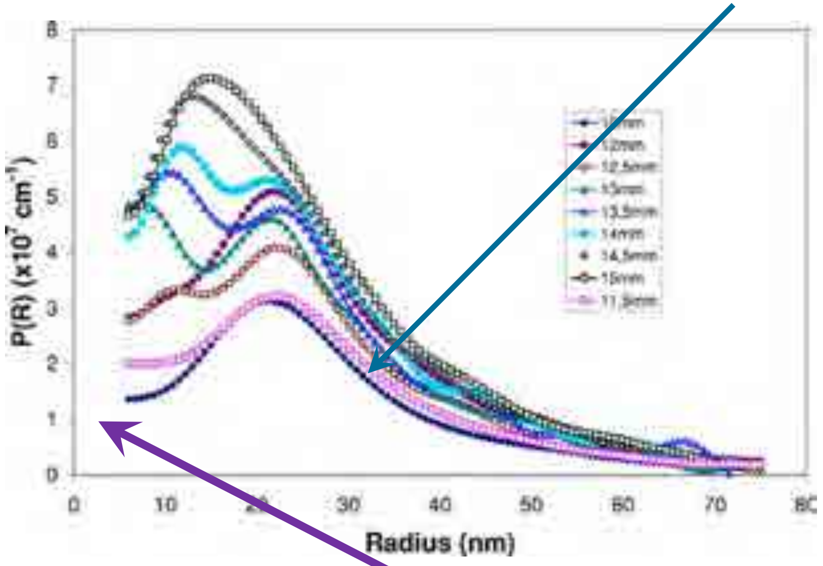
Incipient-Particle Size

Ethylene co-flow diffusion flame
Particle size distributions

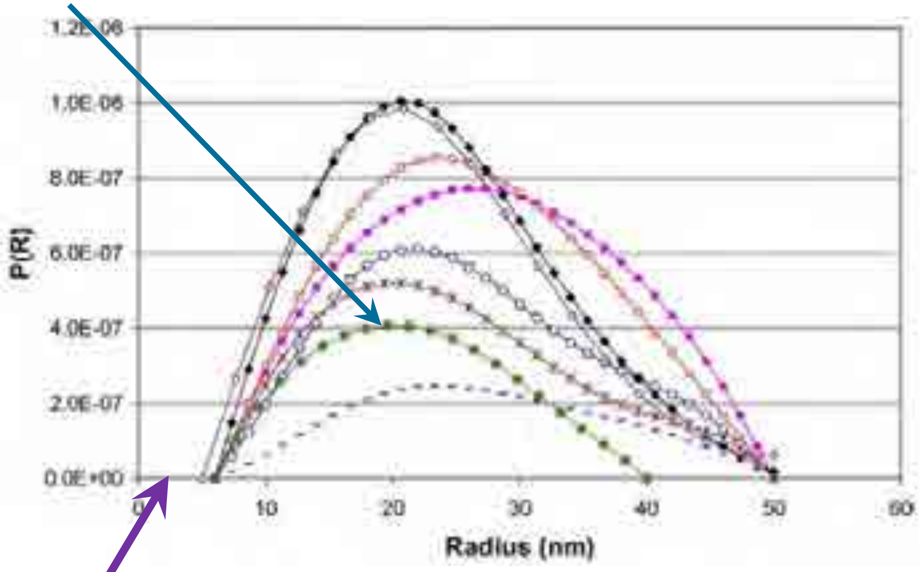
Small-angle X-ray scattering

HAB=10 mm

Small-angle neutron scattering



Mitchell, Courbe, Florescu-Mitchell, di Stasio, Weiss 2006



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

Retrieval of incipient particle size and shape is difficult

What do we know about incipient particles?

They have C/H ratios of ~1.5-2.5.

They are <~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 (>~4-6 nm).

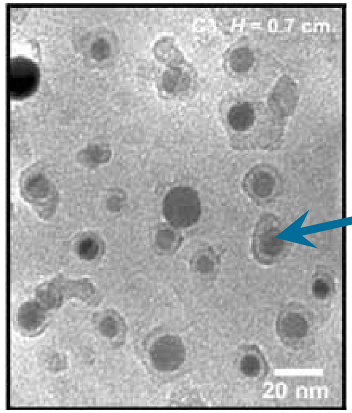
They appear to be the source of the larger mode.

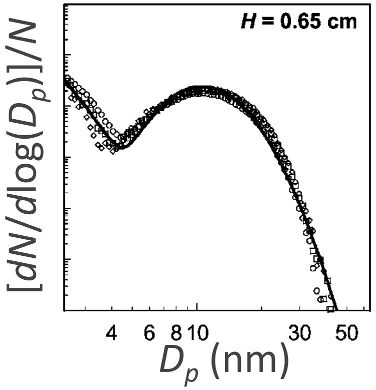
Characteristics of Incipient Particles

Incipient-Particle Consistency and Shape

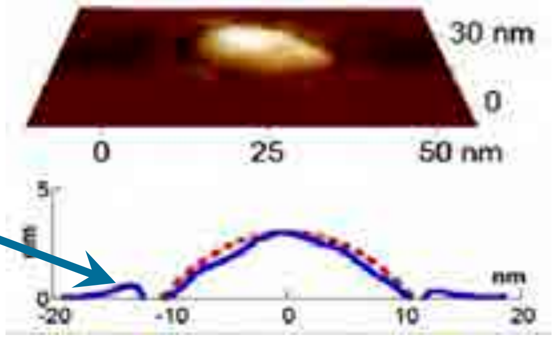
Premixed ethylene/O_2/Ar, C/O=0.69, Φ=2.07

Transmission electron microscopy (TEM)





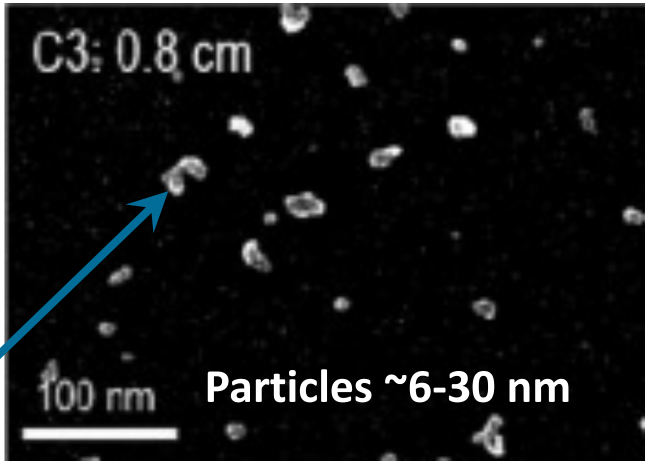
Atomic force microscopy (AFM)

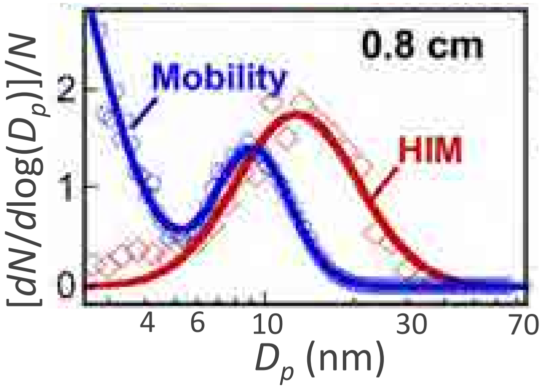


Halo suggests spreading and fluidity

Particles of both modes appear spherical

Helium ion microscopy (HIM)





Some particles in the larger mode may not be spherical

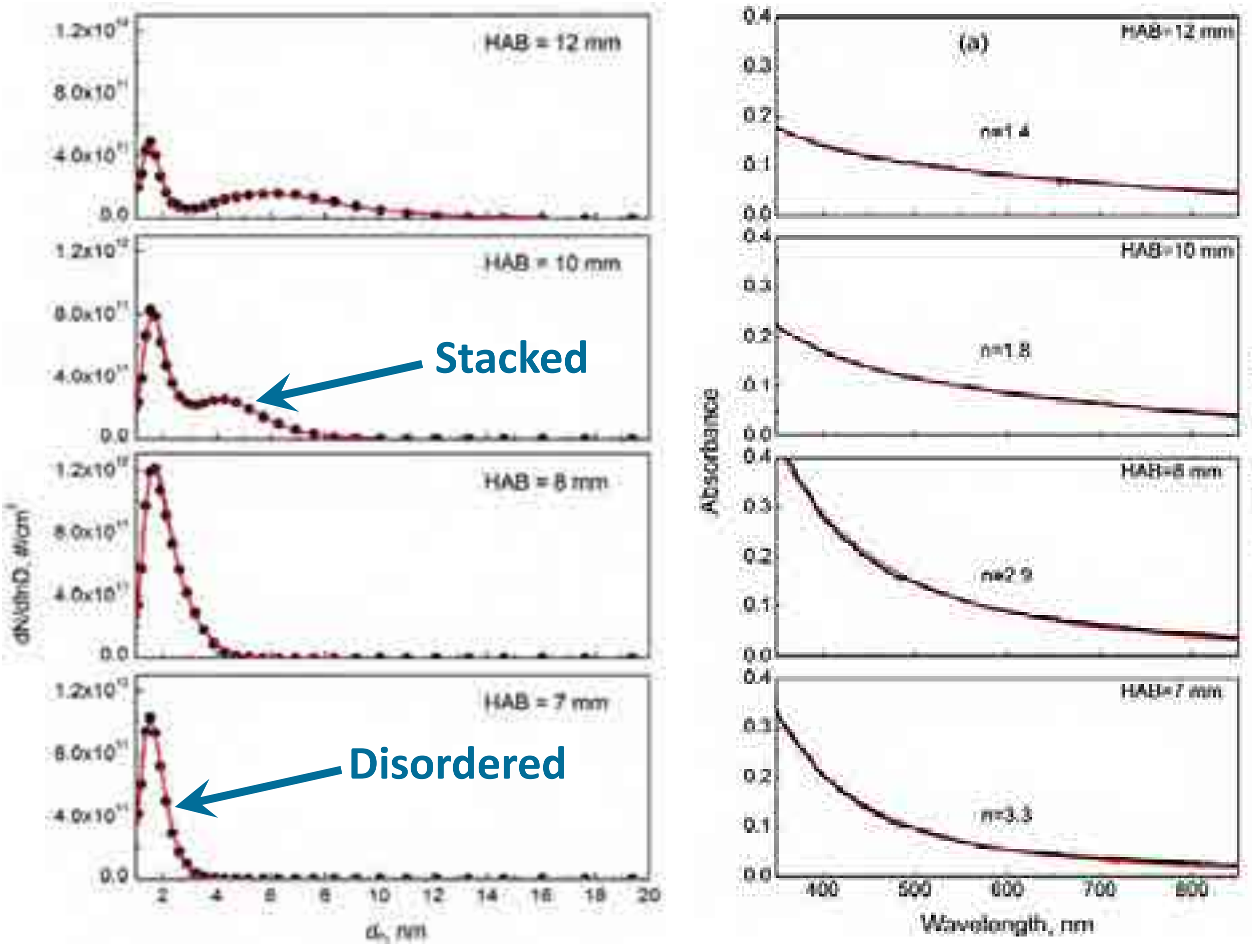
Abid, Heinz, Tolmachoff, Phares, Campbell, Wang 2008

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

Characteristics of Incipient Particles

Incipient-Particle Optical Properties

Premixed ethylene/air, C/O=0.67, Φ=2.03



Ångström exponent Dispersion exponent	Optical band gap
1.4	0.5 eV
1.8	0.8 eV
2.9	1.4 eV
3.3	1.6 eV

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

Characteristics of Incipient Particles
Incipient-Particle Optical Properties

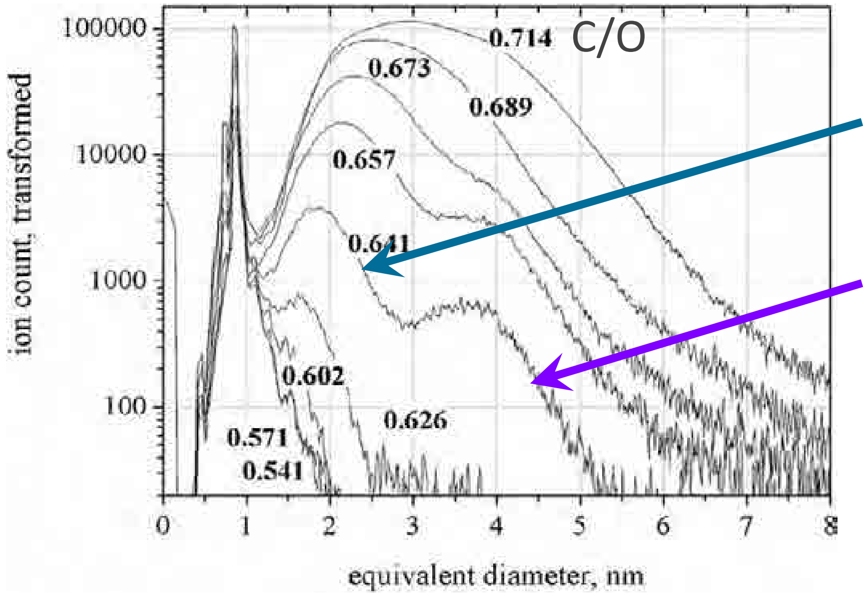
Photoionization mass spectrometry

Premixed ethylene/air, HAB=15 mm

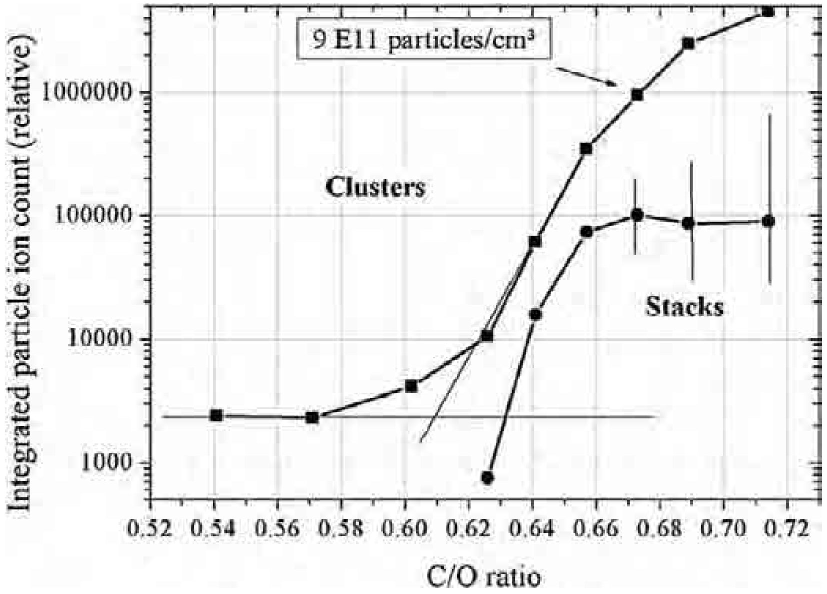
Photoionization at 193 nm, 6.3 eV

2 photons Disordered clusters

1 photon Stacked large PAHs



assuming density of 1 g/cm^3



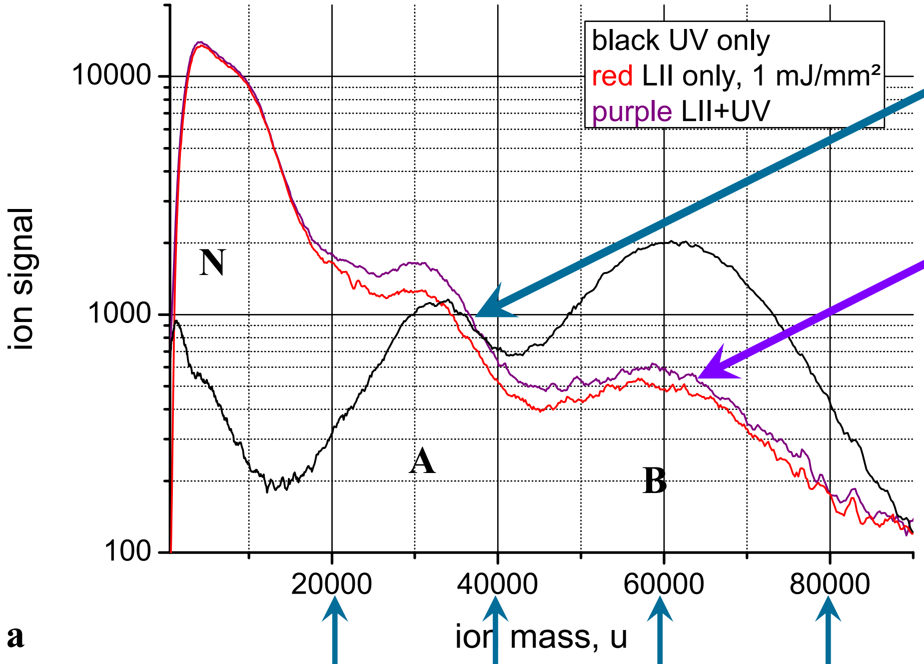
Grotheer, Hoffmann, Wolf, Kanjarkar, Wahl, Aigner 2009

Characteristics of Incipient Particles

Incipient-Particle Optical Properties

Photoionization mass spectrometry

Irradiation at 1064 nm



Clusters do not absorb in near-IR

Stacks absorb and vaporize

3.65 nm **4.60 nm** **5.27 nm** **5.80 nm**

Particle sizes assuming density of 1.3 g/cm^3

Grotheer, Wolf, Hoffmann 2011

What do we know about incipient particles?

They have C/H ratios of ~1.5-2.5.

They are <~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 (>~4-6 nm).

They appear to be the source of the larger mode.

They appear spherical and fluid.

They absorb in the UV but weakly at longer wavelengths.

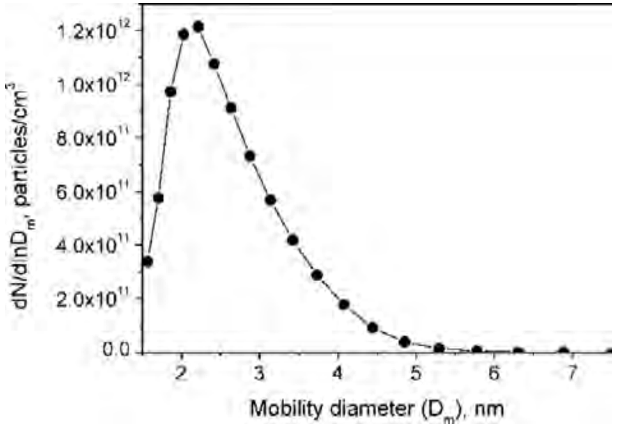
Their photoionization threshold is >6.3 eV.

They have disordered fine structure.

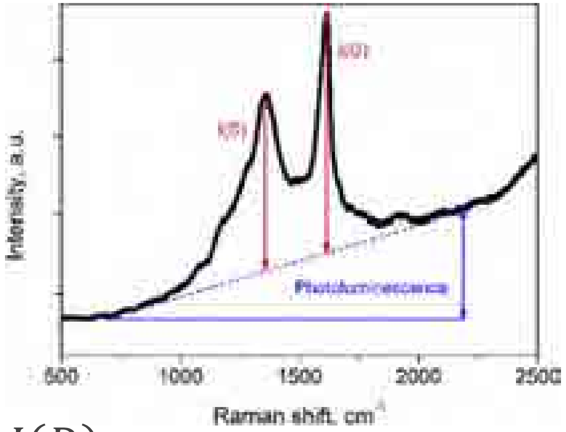
Characteristics of Incipient Particles

Incipient-Particle Composition

SMPS size distribution



Raman spectroscopy

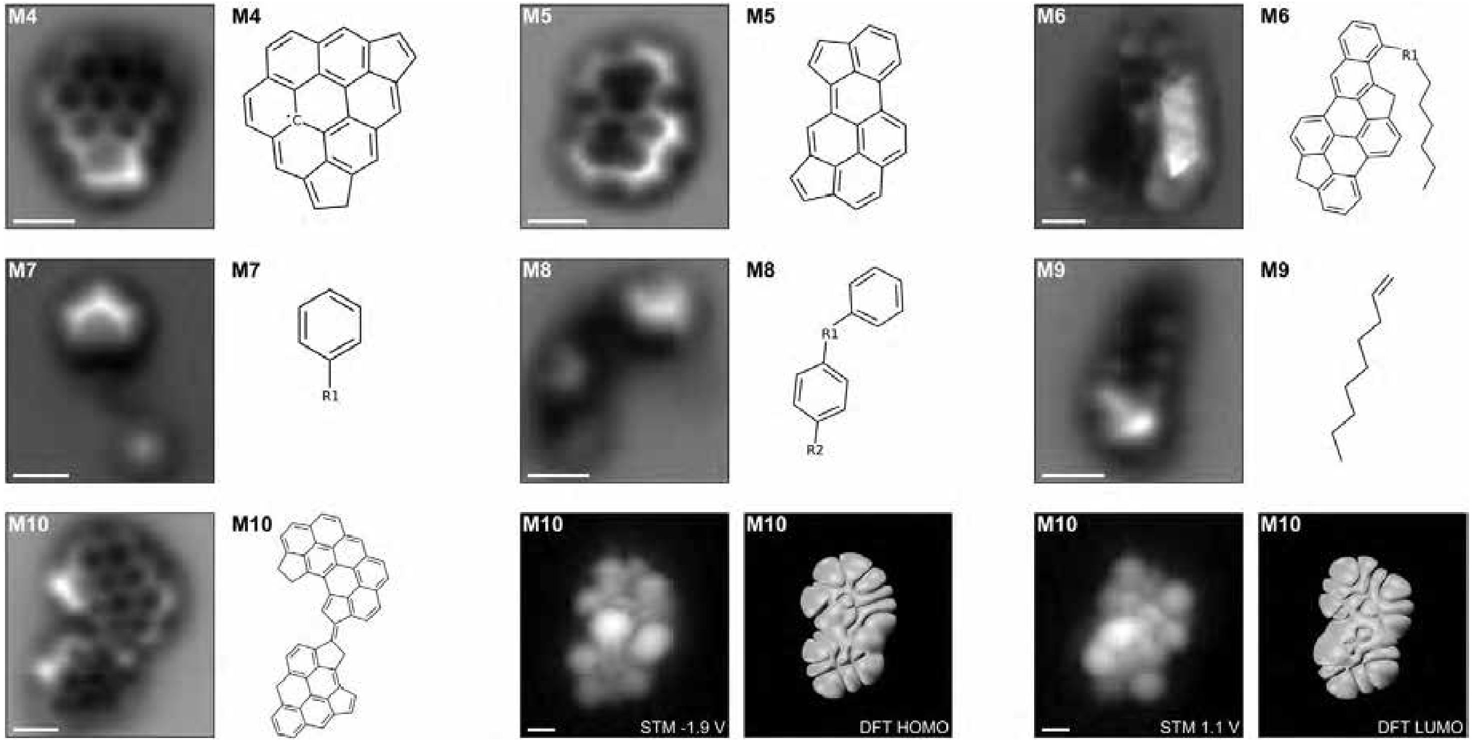


$$\frac{I(D)}{I(G)} \longrightarrow L_a\text{=1.1 nm}$$

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

Premixed ethylene/air, C/O=0.67, Φ=2.03, HAB=8 mm

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



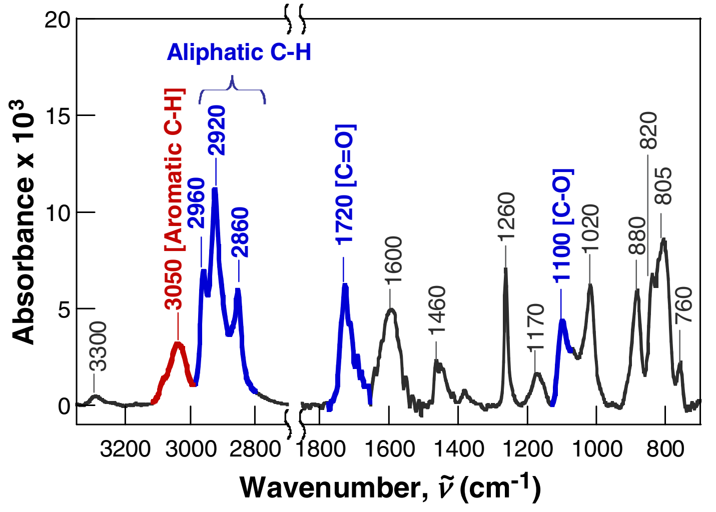
Schulz, Commodo, Kaiser, De Falco, Minutolo, Meyer, D'Anna, Gross 2018
Combustion Symposium talk 4C01

Significant abundance of 5-membered rings and aliphatic groups

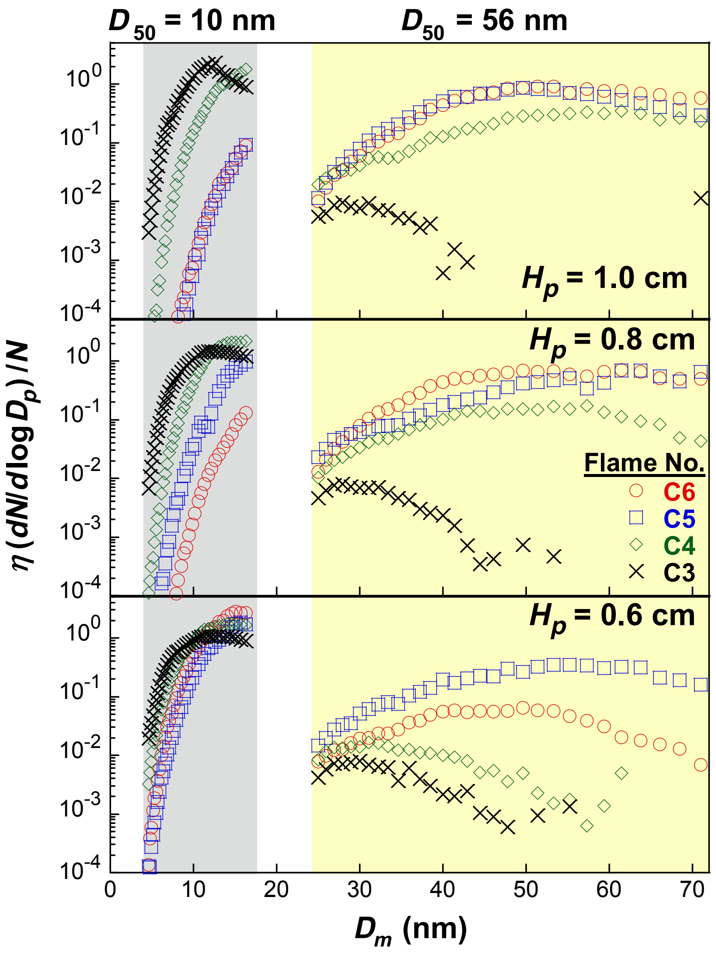
Characteristics of Incipient Particles
Incipient-Particle Composition

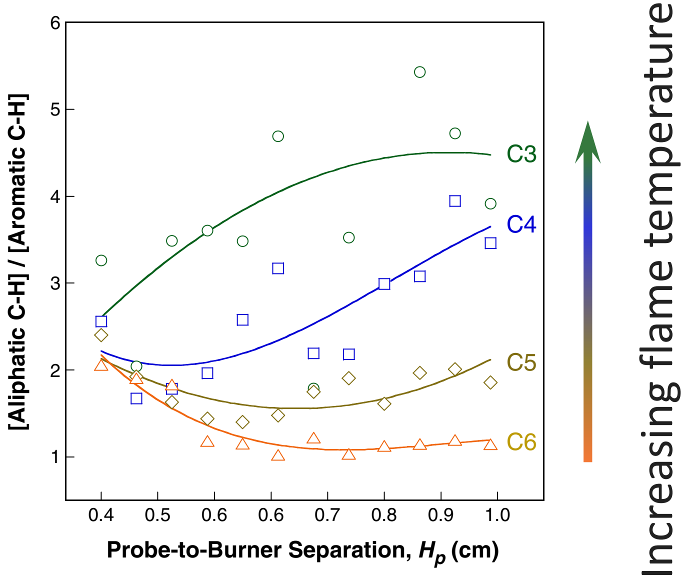
Premixed ethylene/O_2/Ar, C/O=0.69, Φ=2.07

Infrared spectroscopy



Nano-MOUDI stages





Particles have high aliphatic content

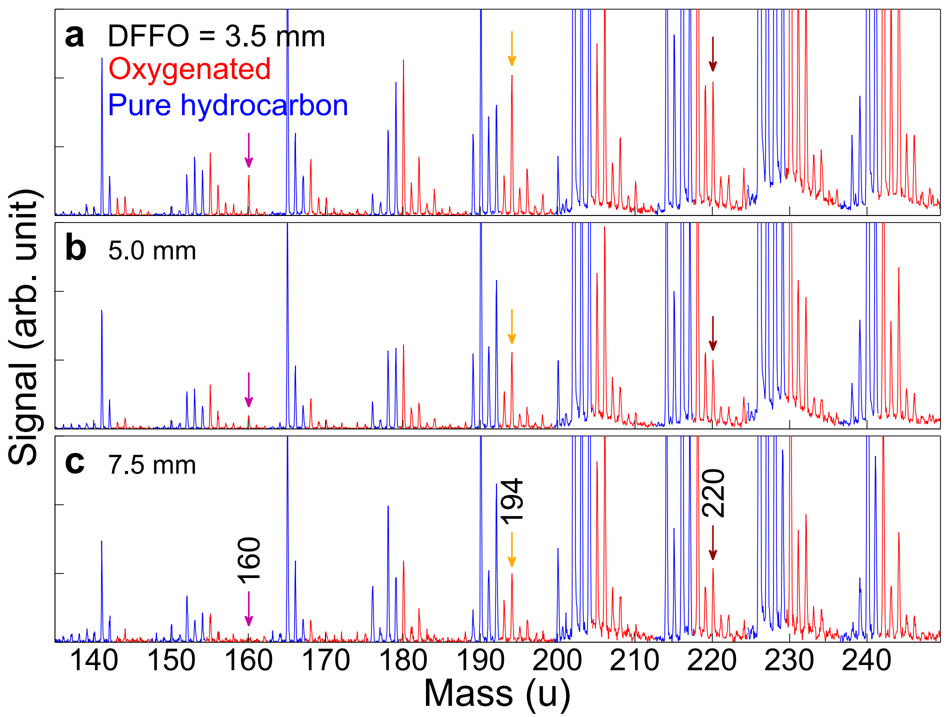
Oxygenated species also present

Cain, Camacho, Phares, Wang, Laskin 2011

Characteristics of Incipient Particles

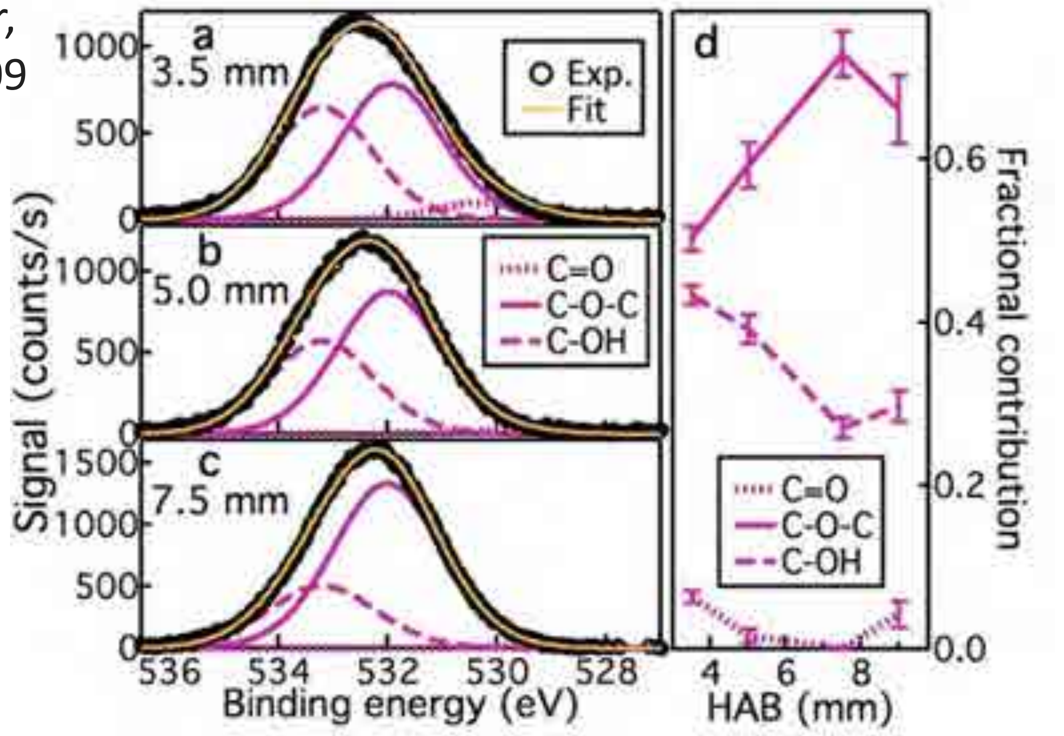
Incipient-Particle Composition

Aerosol mass spectrometry (AMS)

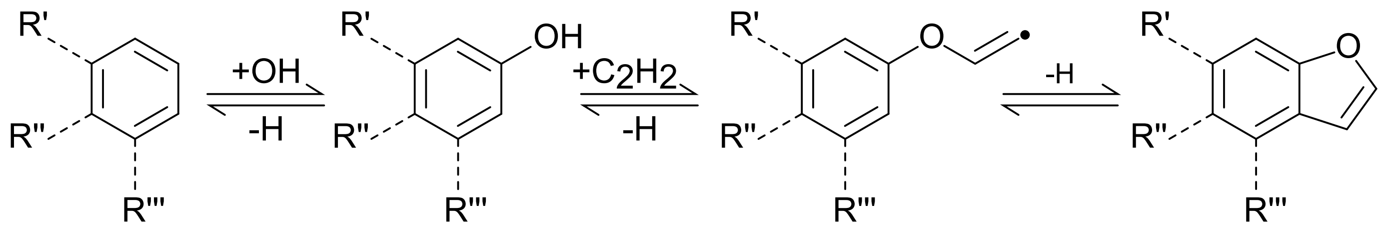


Premixed ethylene/O_2/Ar, C/O=0.7, Φ=2.09

X-ray photoelectron spectroscopy (XPS)



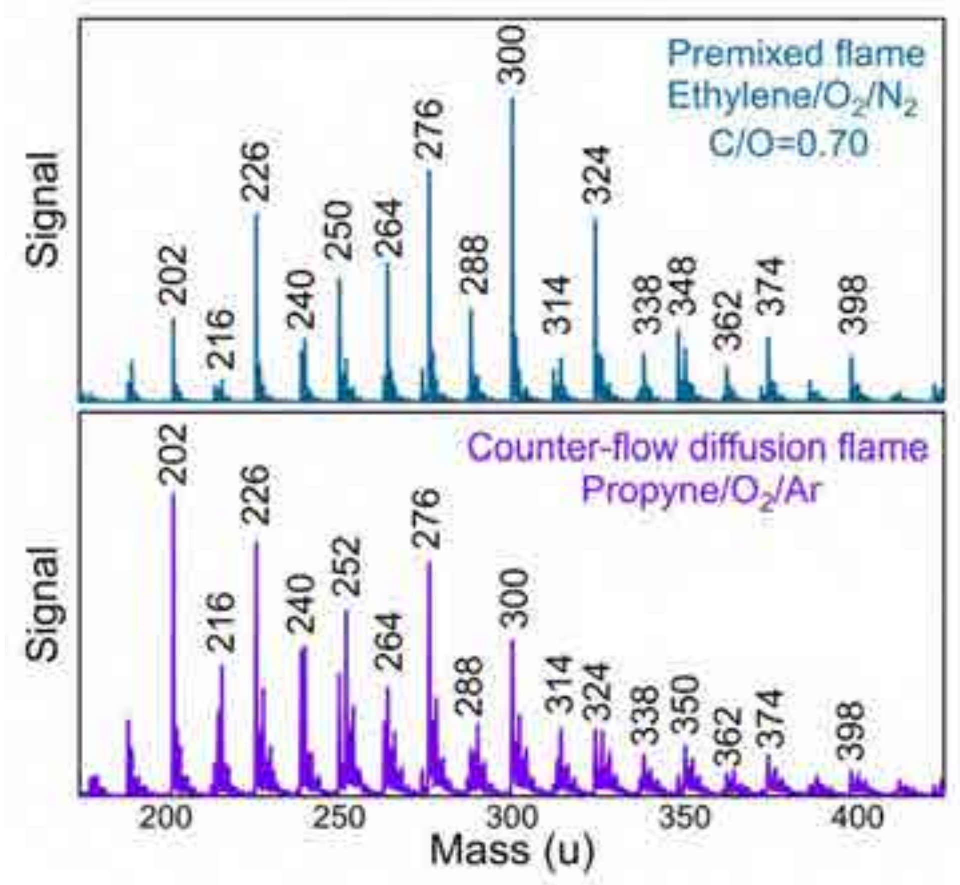
Johansson, Dillstrom, Monti, El Gabaly, Campbell, Schrader, Popolan-Vaida, Richards-Henderson, Wilson, Violi, Michelsen 2016



Characteristics of Incipient Particles

Incipient-Particle Composition

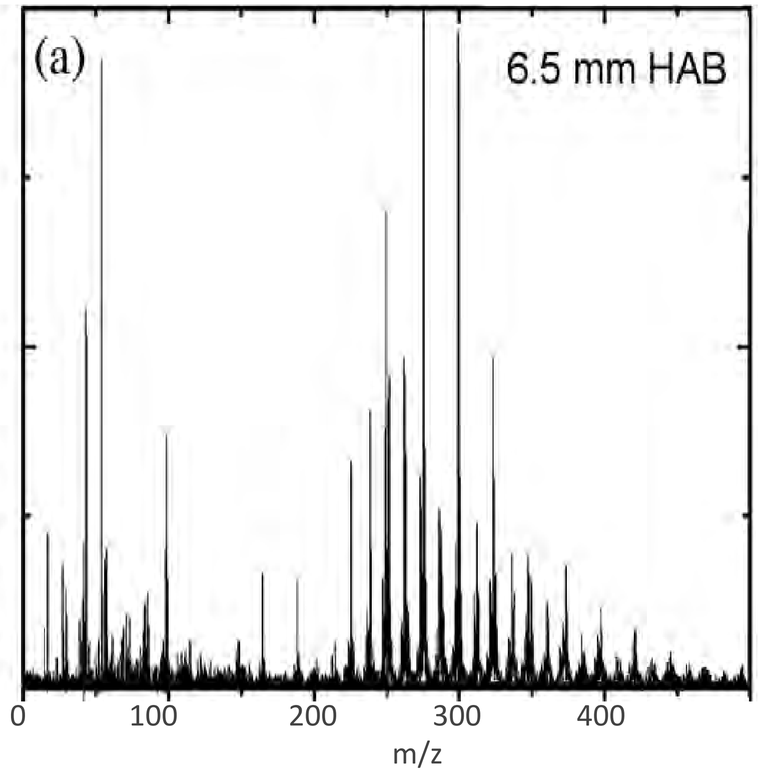
Aerosol mass spectrometry



Photoionization Aerosol Mass Spectrometry

PIAMS mass spectrum of incipient soot using 1064-nm laser desorption, 118-nm photoionization

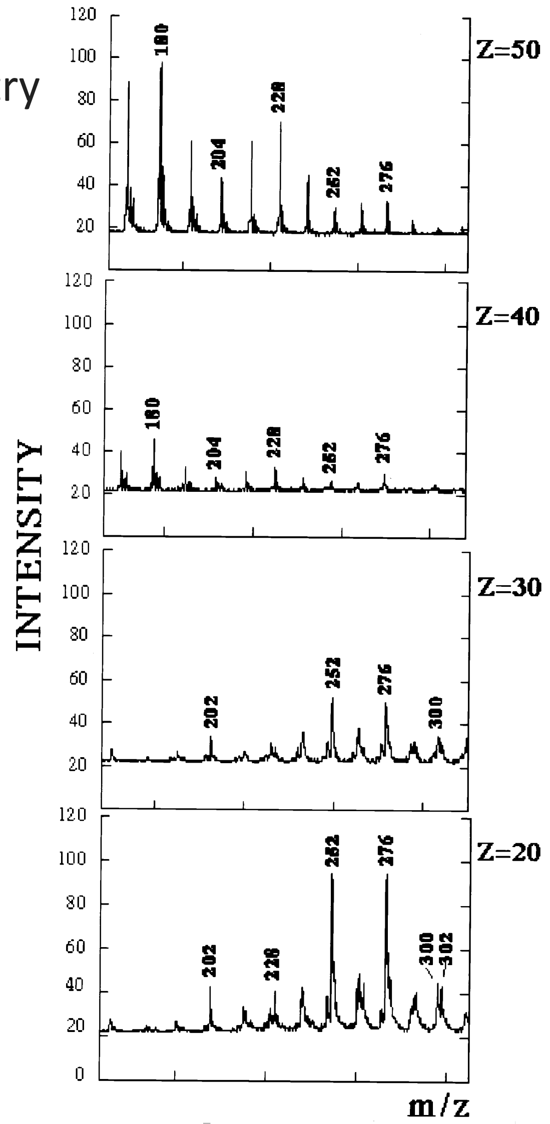
Premixed ethylene/O_2/Ar flame



Öktem, Tolocka, Zhao, Wang, Johnston 2005

Laser microprobe mass spectrometry

Coflow diffusion flame

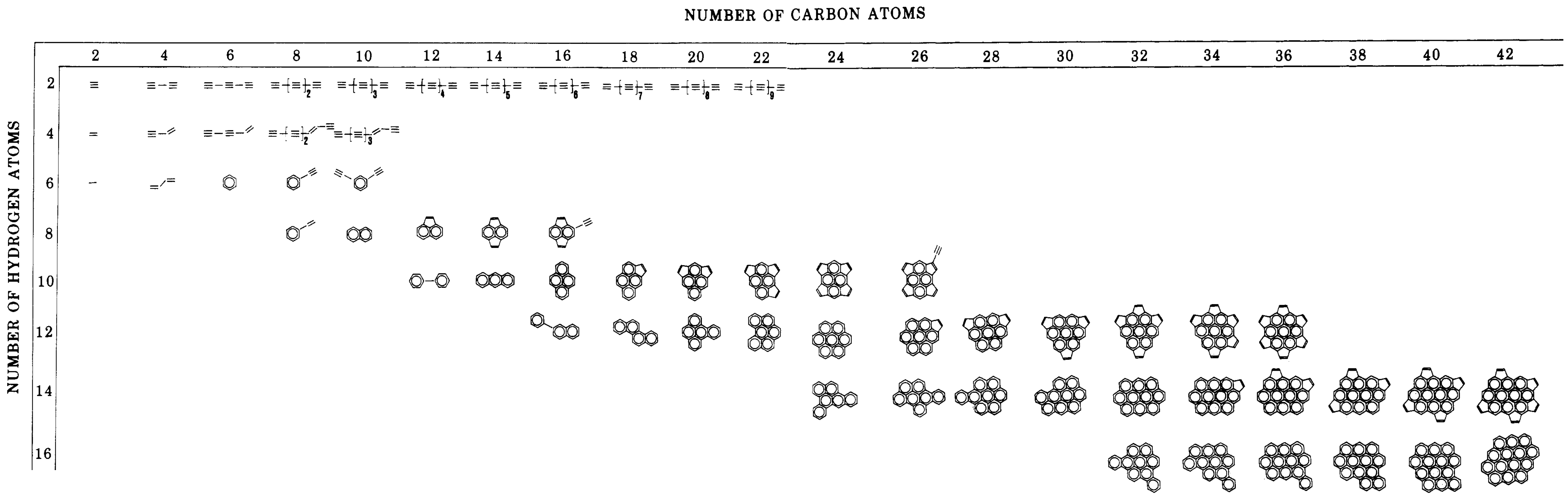


Dobbins, Fletcher, Chang 1998

Characteristics of Incipient Particles

Incipient-Particle Composition

Stabilomers

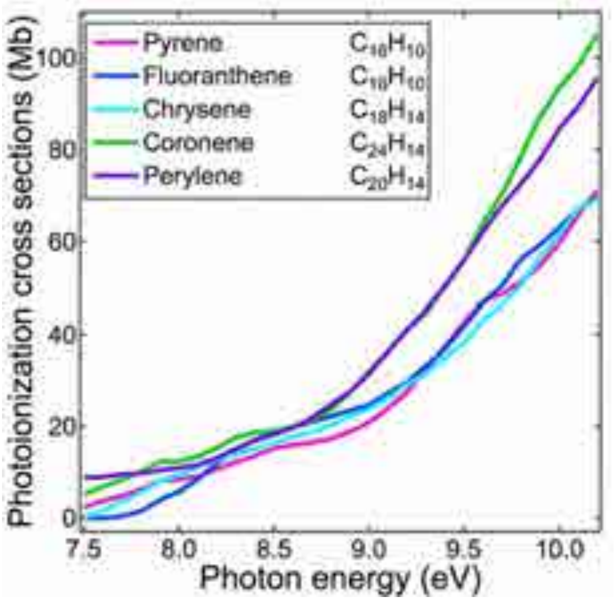


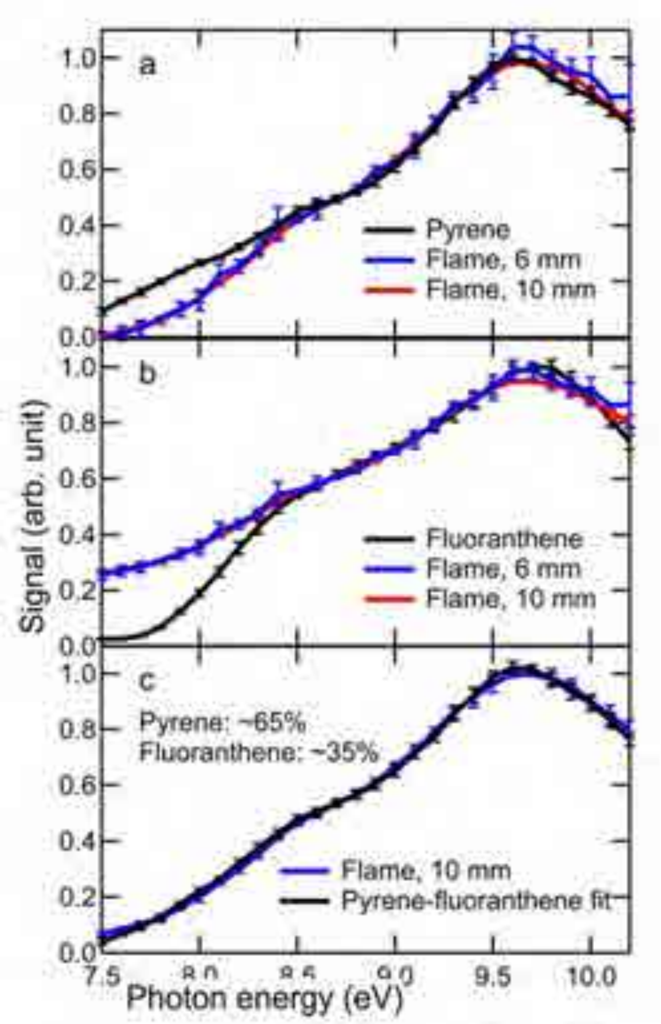
Stein, Fahr 1985

Characteristics of Incipient Particles

Incipient-Particle Composition

Premixed ethylene/O_2/N_2, C/O=0.70, Φ=2.09





Evidence for non-stabilomer precursors

Johansson, Campbell, Elvati, Schrader, Zádor, Richards-Henderson, Wilson, Violi, Michelsen, *J. Phys. Chem. A* 2017

Johansson, Zádor, Elvati, Campbell, Schrader, Richards-Henderson, Wilson, Violi, Michelsen, *J. Phys. Chem. A* 2017

What do we know about incipient particles?

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They are <~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 (>~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 may have significant abundances of 5-membered rings.

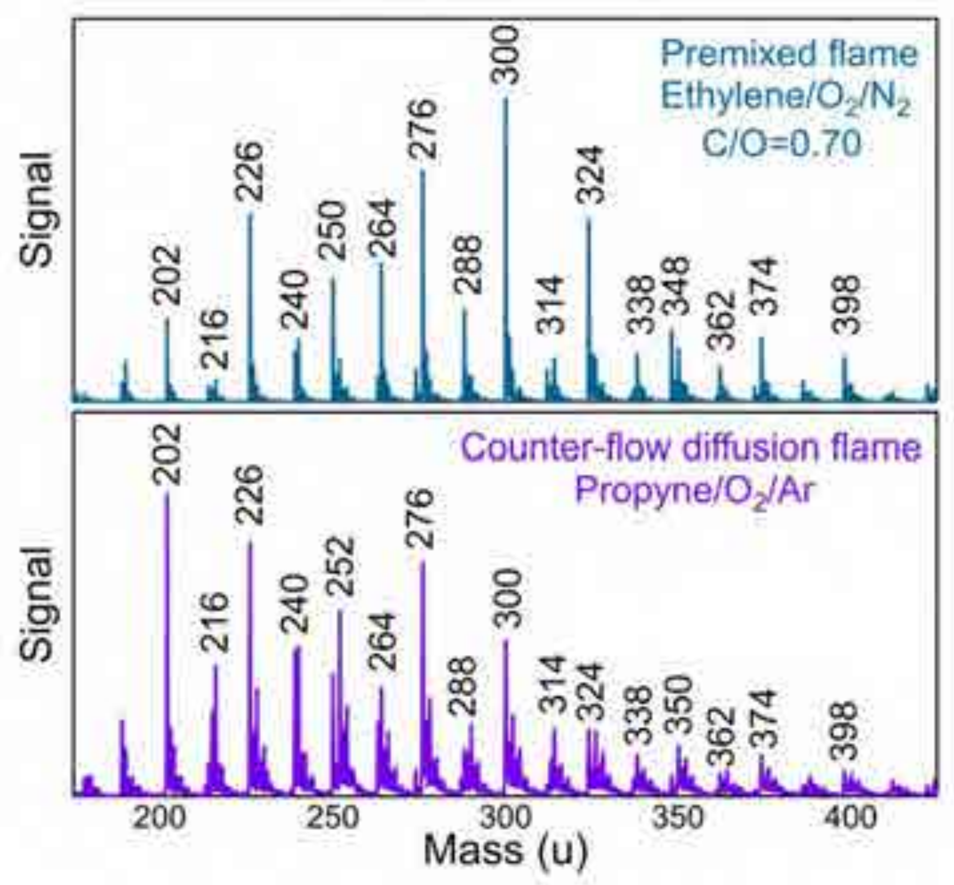
Their precursor masses are consistent between flames, fuels.

Their precursors may not be the most thermodynamically stable isomers.

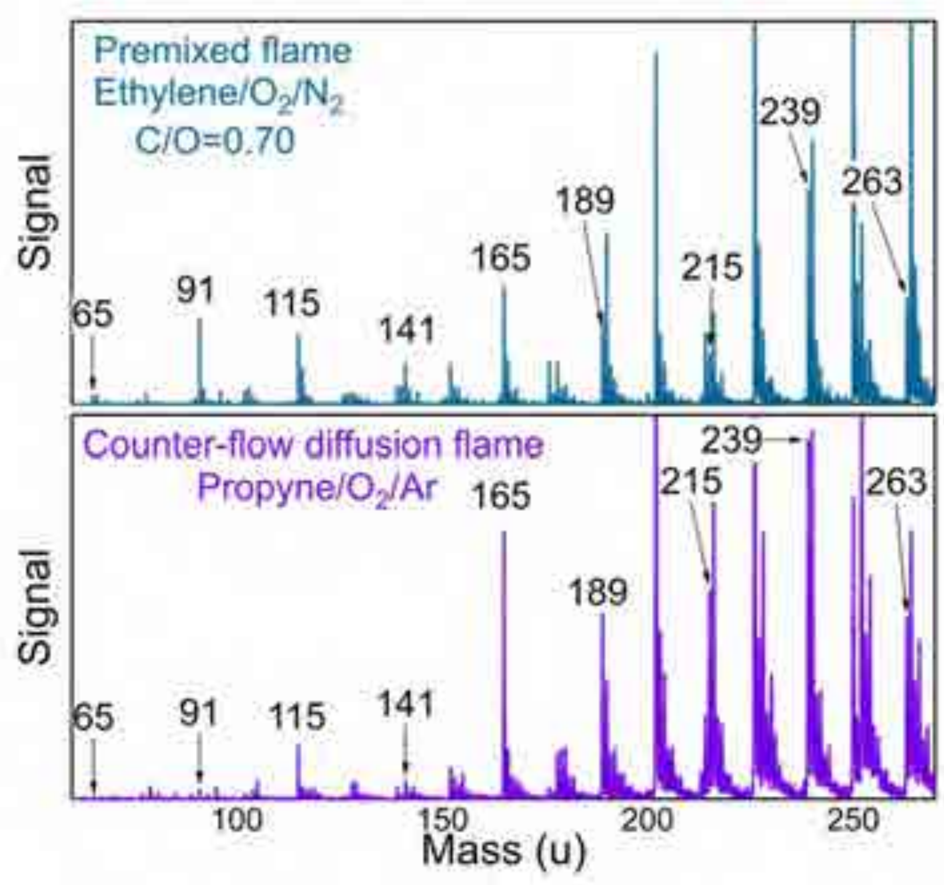
Characteristics of Incipient Particles

Incipient-Particle Composition

Aerosol mass spectrometry



Johansson, Dillstrom, Elvati, Campbell, Schrader, Popolan-Vaida, Richards-Henderson, Wilson, Violi, Michelsen, *Proc. Combust. Inst*. 2017



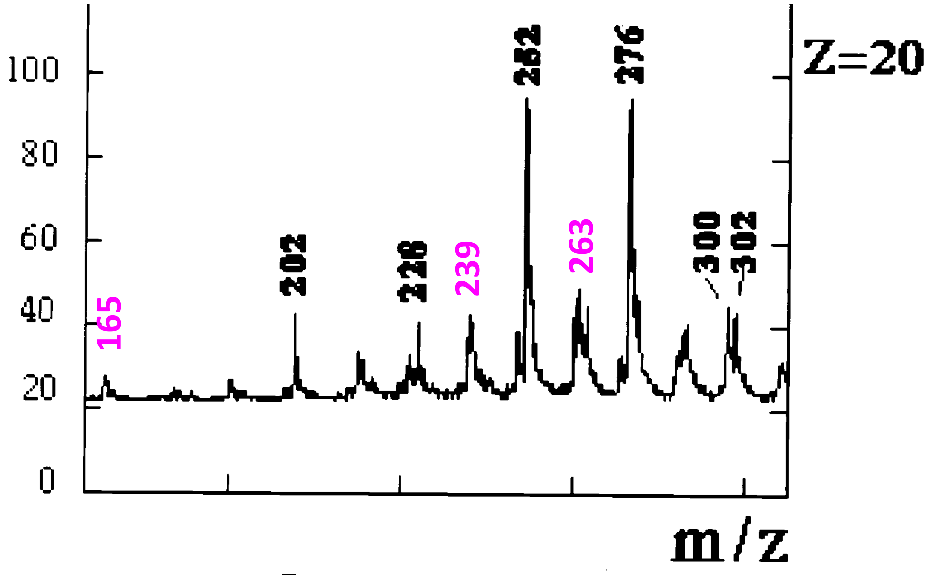
Johansson, Head-Gordon, Schrader, Wilson, Michelsen, *Science*, 2018 September 7th

Characteristics of Incipient Particles

Incipient-Particle Composition

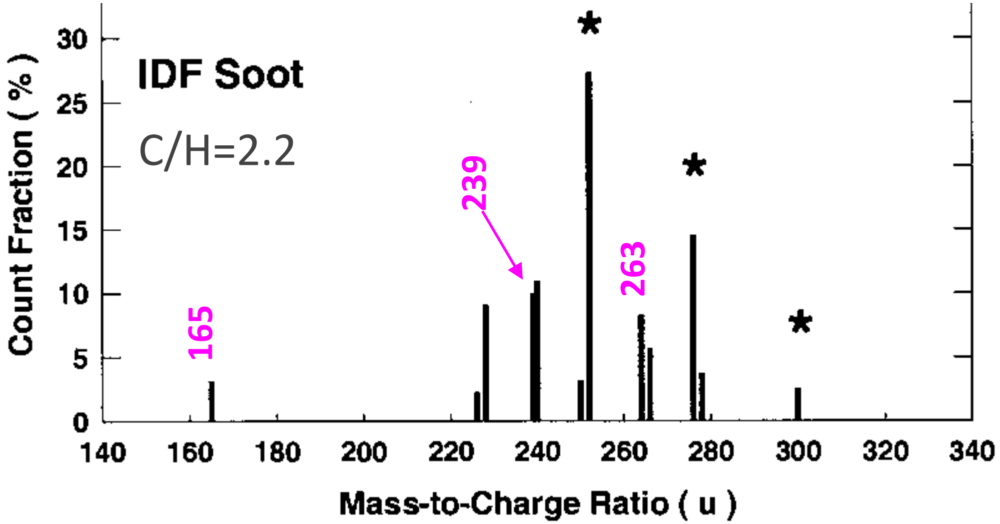
Laser microprobe mass spectrometry

Ethylene/air co-flow diffusion flame



Dobbins, Fletcher, Chang 1998

Ethylene/air inverse diffusion flame



Blevins, Fletcher, Benner, Steel, Mulholland 2002

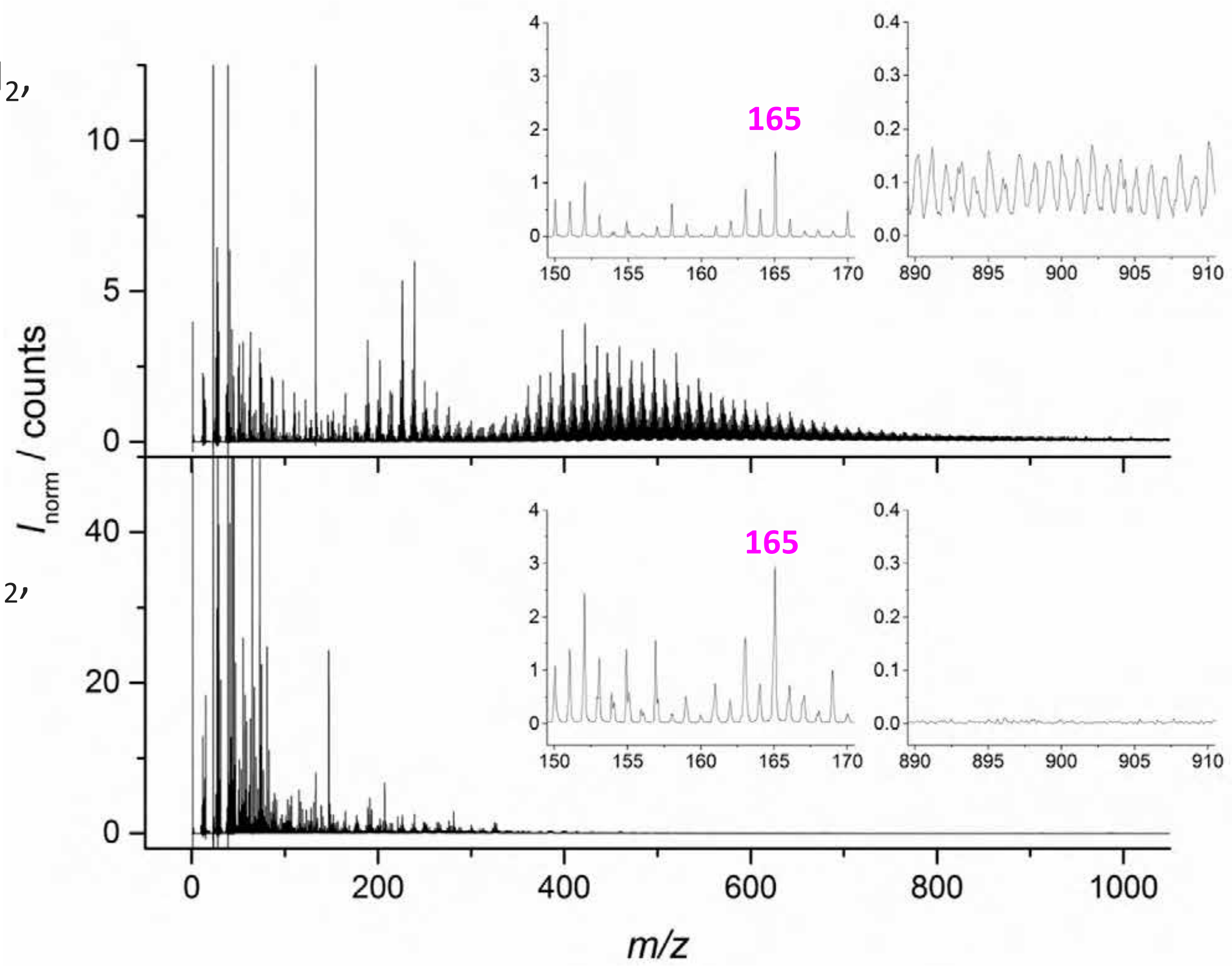
Characteristics of Incipient Particles

Incipient-Particle Composition

Time of flight secondary ion mass spectrometry

Low pressure (200 Torr)
Premixed methane/O_2/N_2,
C/O=0.49, Φ=1.95

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

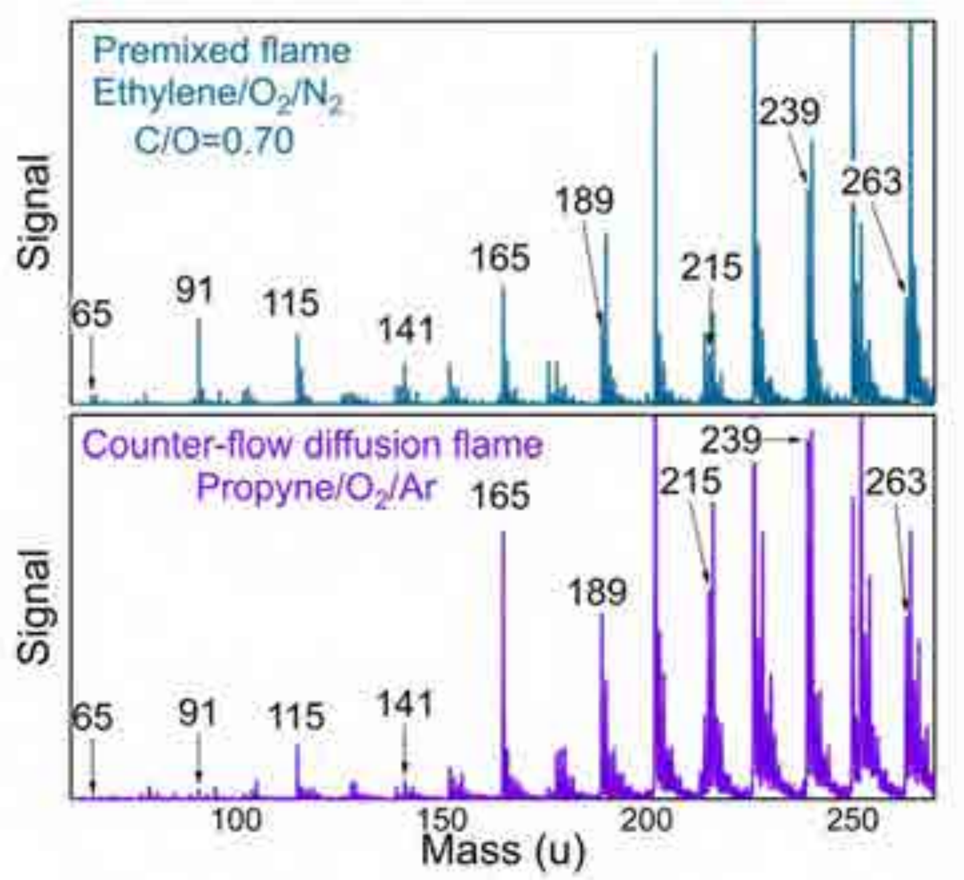


Desgroux, Faccinetto, Mercier, Mouton, Karkar, El Bakali 2017

Characteristics of Incipient Particles

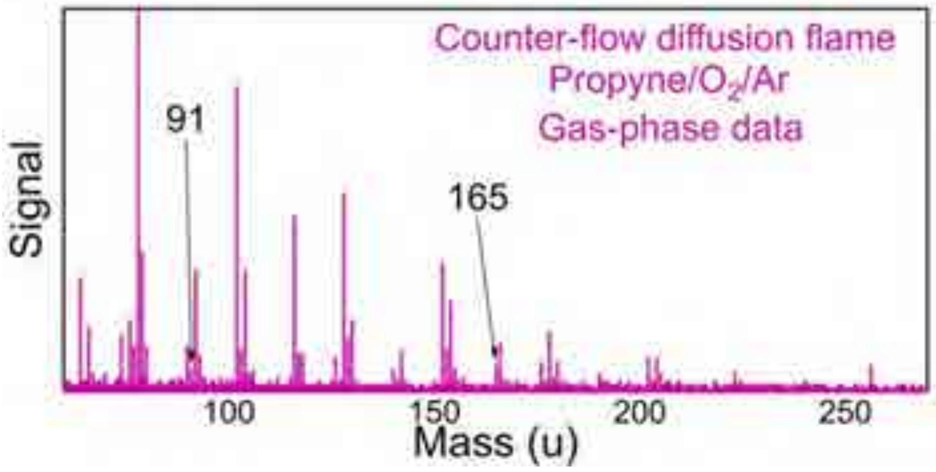
Incipient-Particle Composition

Aerosol mass spectrometry



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

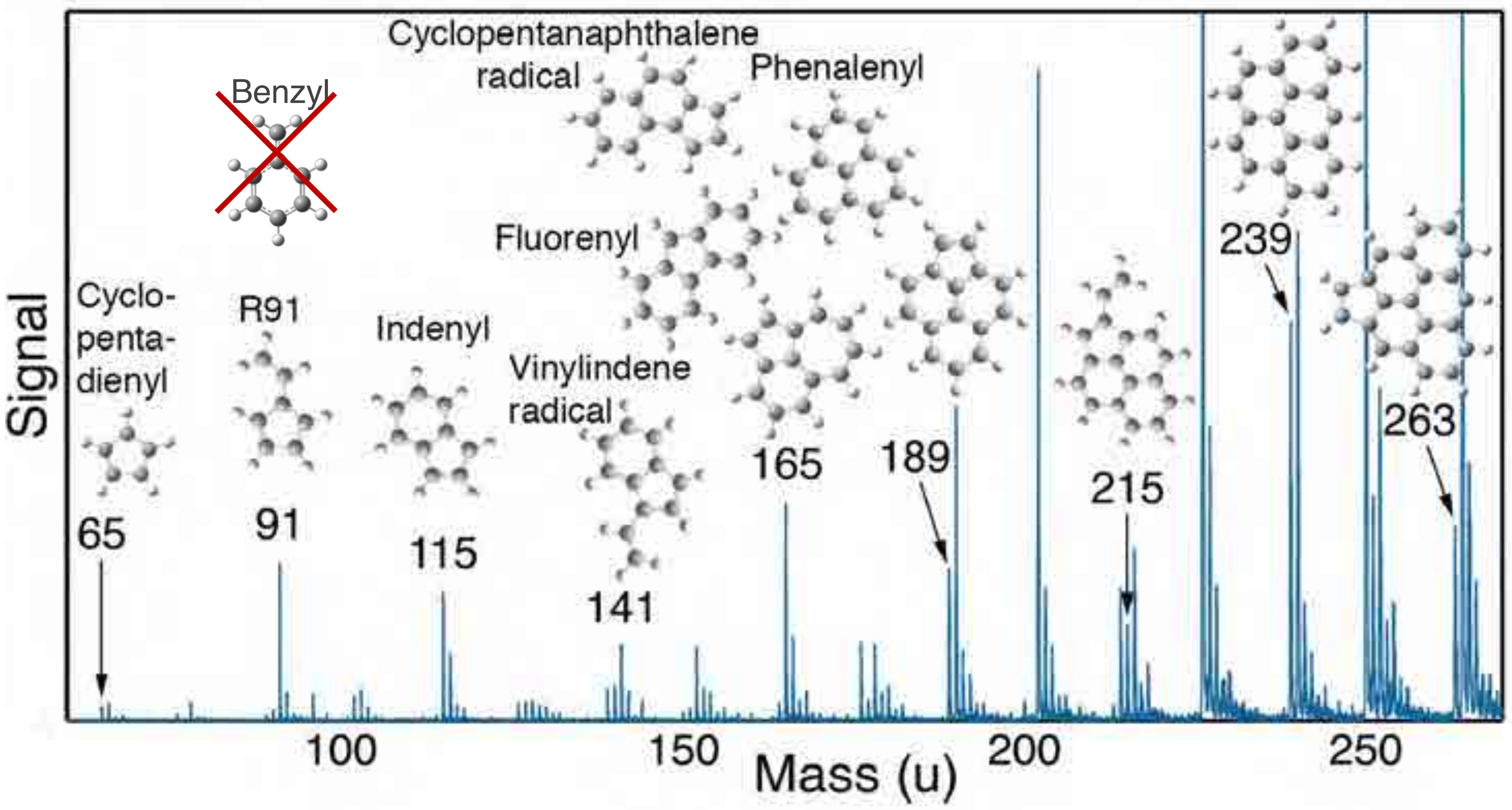
Molecular beam mass spectrometry



Nils Hansen and Kai Moshammer, private communication

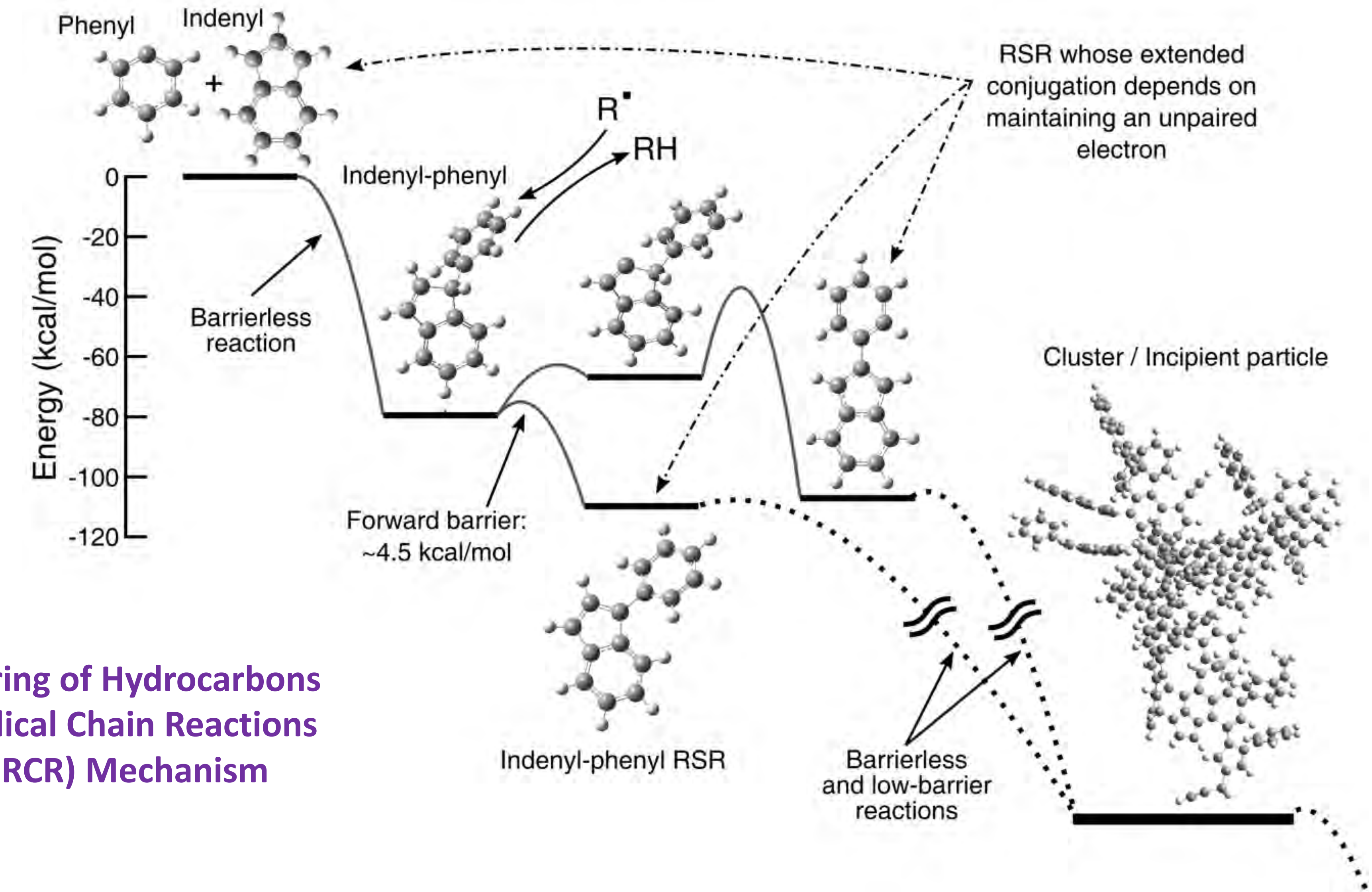
Characteristics of Incipient Particles

Incipient-Particle Composition



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

Particle Inception by Radical Chain Reactions



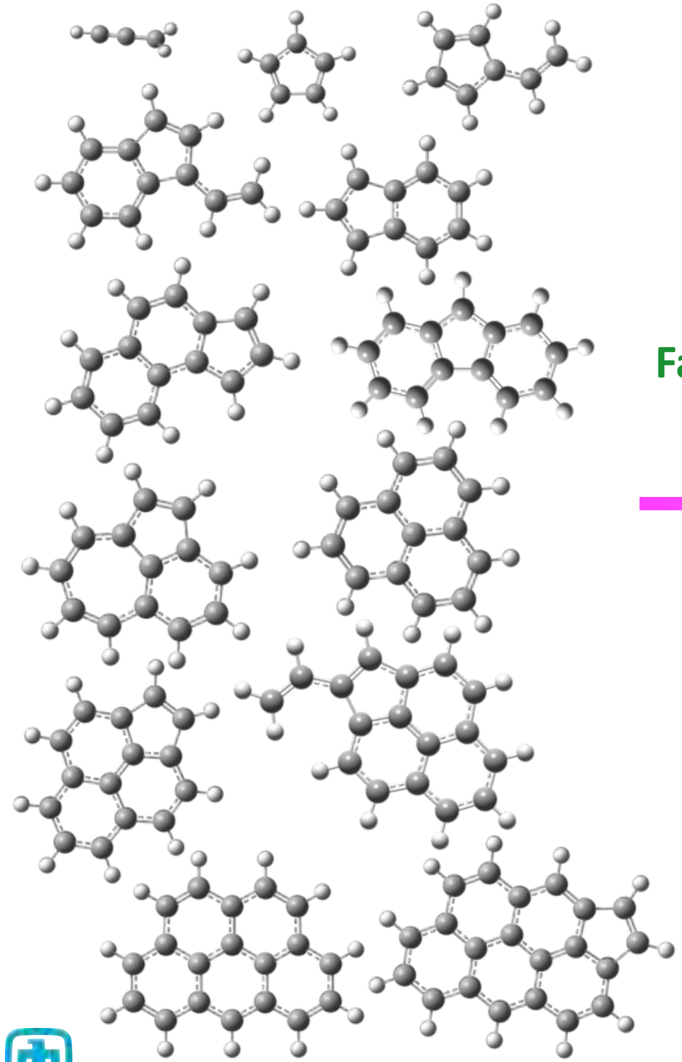
Clustering of Hydrocarbons by Radical Chain Reactions (CHRCR) Mechanism

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

Particle Growth by Radical Chain Reactions

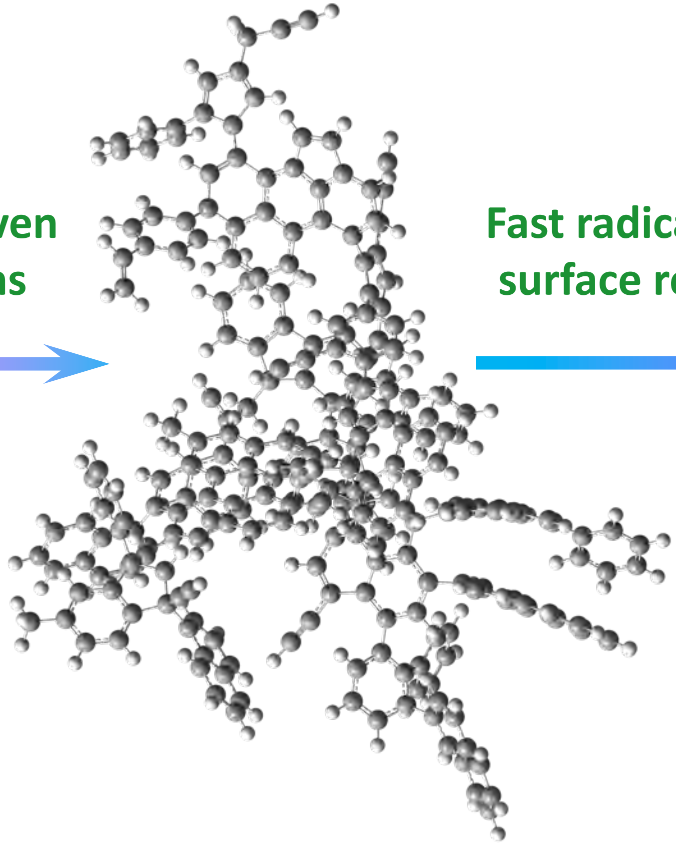
Clustering of Hydrocarbons by Radical Chain Reactions (CHRCR) Mechanism

Resonance-stabilized radicals



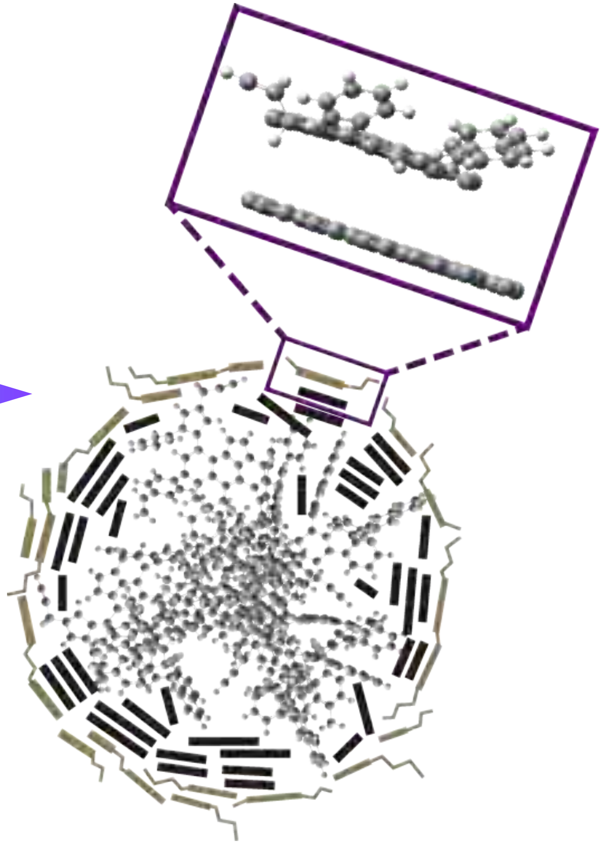
Fast radical-driven chain reactions

Incipient particles
Hydrocarbon clusters



Fast radical-driven surface reactions

Primary particles
Soot aggregates



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

What do we know about incipient particles?

They have C/H ratios of ~1.5-2.5.

They are <~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 (>~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 may 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 via radical-chain reactions.

Olof Johansson **Paul Schrader**

Martin Head-Gordon Kevin Wilson

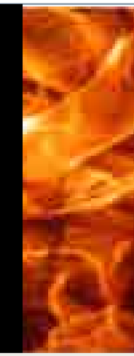

Thank you

Major Elements of ISF3 Program

Topic	Presenter
Welcome & Introduction	Nathan
Industry Perspective	Duksang 'Andy' Kim (Doosan Group)
Engine Combustion Network	Scott Skeen (Sandia)
Review outcomes from ISF-2	Pitsch
Turbulent Flames (Atmospheric and Pressurised)	Mueller/Geigle/Haworth
Pressurised Laminar Flames	Haworth/Geigle
Topical Discussion: Soot Data Uncertainty & Standardisation	Shaddix
Atmospheric Laminar Flames	Blanquart/Sirignano
Invited Reflections	Gülder/Roberts

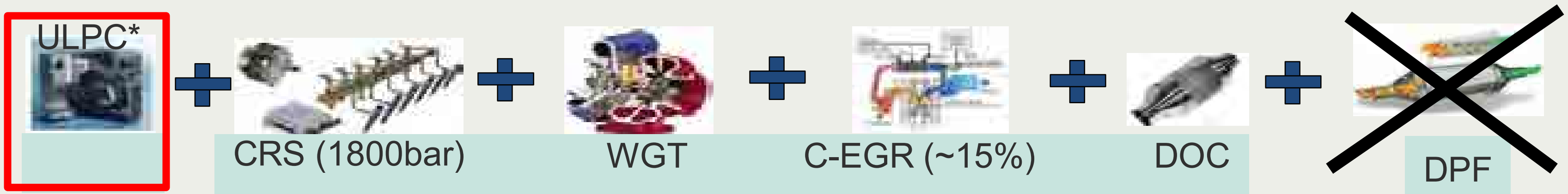
ISF Workshop #3

Industry Perspective



- Speaker: Duksang ‘Andy’ Kim (Doosan Group)
- Key Points:
  - Stringent PM (particulate matter) emission regulations
  - Low Temperature Combustion (LTC) can achieve Tier 4 emission targets without Aftertreatment

1 Emission Strategy of LD machinery (< 56KW, NOx=4.0 g/kWh)

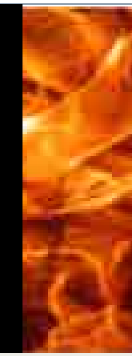


* **U**ltra **L**ow **PM** **C**ombustion

- Discussion Points:
  - Our Science vs Technology
  - How can we better collaborate with industry to help achieve these targets?

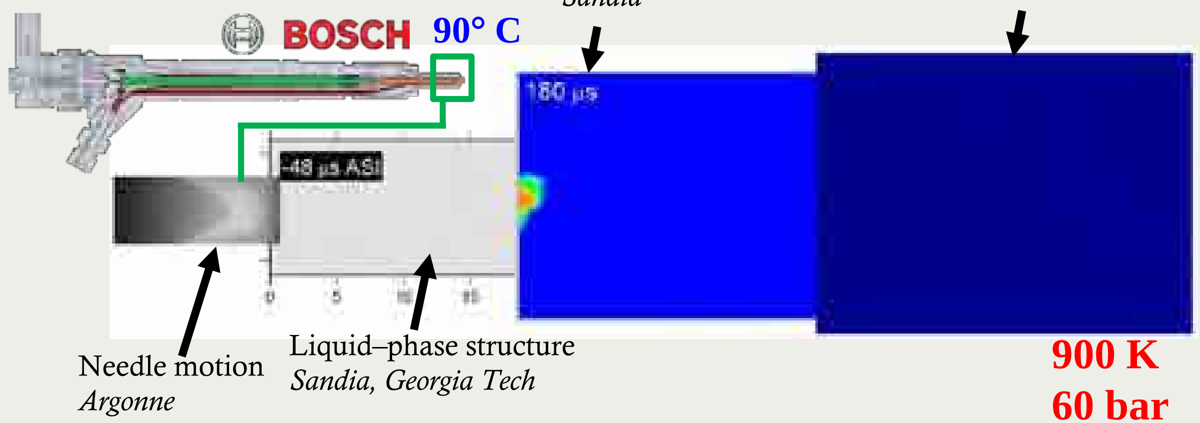
ISF Workshop #3

Engine Combustion Network

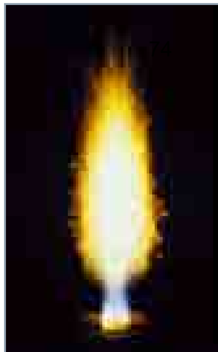


- Speaker: Scott A. Skeen, (Sandia National Laboratories)
- Key Points:
  - ECN very active in experiments and modeling that include soot
  - Potential for collaboration

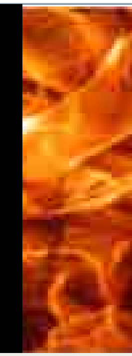
Diesel Spray A



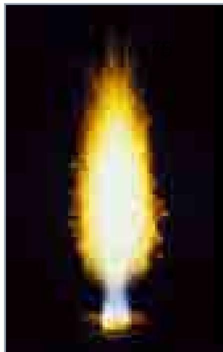
- Discussion Points:
  - Are we taking advantage of potential synergies with ECN?



REFLECTIONS: Outreach to other workshops

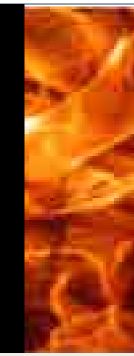


- Over the past 20 years, have seen ‘silo-ing’ of communities.
  - TNF and PTF have been very successful.
- Now, need to break down these barriers and build more collaborations between these workshops and ISF.
  - How to include LII workshop, ECN, and Chemistry workshop, etc.
    - Having Andy and Scott open workshop a great idea
  - How do we build these bridges and establish effective dialog?
  - Expand beyond our typical communities, e.g., the atmospheric chemistry and toxicology communities?

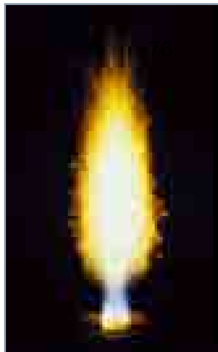


ISF Workshop #3

Turbulent Flames: Atmospheric and Pressurized

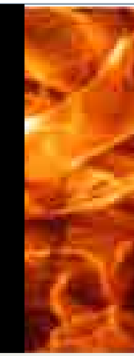


- Speakers:
  - Michael E. Mueller (Princeton University)
  - Klaus-Peter Geigle (German Aerospace Center, DLR)
  - Daniel C. Haworth (Pennsylvania State University)
  - Bassam Dally (University of Adelaide)

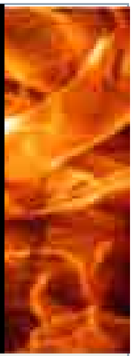


ISF Workshop #3

New Experimental Techniques and Measurements (Dally)



- Adelaide (Sun/Nathan/Dally/Alwahabi)
  - Simultaneous Soot Volume Fraction, Temperature and Primary Particle Size using LII, TLAF and TiRe-LII, respectively
- Sydney (Masri/Dunn/Bartos) and Napoli (D’Anna/Sirignano)
  - Multi-laser measurements in turbulent flames
- KAUST (Chowdhury/Boyette/Roberts)
  - Particle size distributions in turbulent flames
- Sandia (Kearney/Hewson)
  - CARS temperature measurements in Sandia turbulent sooting flames



Atmospheric Pressure Turbulent Targets (Mueller)

- Key Findings and Takeaways
  - Soot "shift" in Delft/Adelaide flame consistent across modeling approaches
    - ISF-1: Methane fuel potentially higher uncertainty than ethylene
  - With acetylene inception models, mean soot is about right in ethylene jet flames but fluctuations underpredicted
  - With PAH inception models, soot is almost universally underpredicted in ethylene jet flames but relative fluctuations about correct
    - Trend seems to be true whether simple, piloted, or lifted
    - Trend seems to be true independent of mixing with hydrogen

WHY?

Turbulent Flame Regimes and Mechanisms (Mueller)

- Summary of Potential Issues in Turbulent Jets
  - Soot Precursor Chemistry
    - Do we need to worry about centerline of laminar coflow flames?
    - Would very rich premixed flames be useful?
  - Subfilter Molecular Transport
    - Subfilter differential diffusion between soot and flame requires more sophisticated subfilter PDF and mixing models.
  - Gas-Phase Differential Diffusion
    - This is potentially important for some species but not all but cannot be a priori neglected.

Turbulent Flame Regimes and Mechanisms (Mueller)

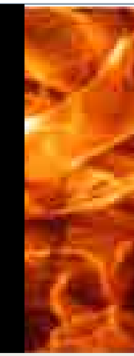
- Beyond Mean Soot Volume Fraction
  - Overemphasis on predictions of mean soot volume fraction?
  - Should we be comparing the models with other experimental measurements (PDFs, intermittency, particle size) to better understand where we are going wrong?
  - Should these comparisons be normalized
- What can we do about mixture fraction?
  - This is a leading order effect in turbulent flames.
    - Recirculating Flow: Dictates dominant growth mechanism in RZ
    - Jet Flames: Relative distribution/transport of mixture fraction and soot
  - If mixture fraction measurements are impossible, what else could be measured to help understand and validate models?

Turbulent Flame Regimes and Mechanisms (Mueller)

- Do we need to think about using numerical experiments?
  - Subfilter transport processes can be directly evaluated with DNS.
  - Of course, if there is a fundamental problem with soot chemistry or soot models, then DNS is meaningless…
- Future Target Flames
  - Do we need a canonical recirculating flow flame (e.g., bluff body)?
    - Variations in recirculation zone mixture fraction to vary the dominant soot evolution mechanisms
  - Would unsteady laminar flames be helpful?
    - Is response of PAH to unsteady straining an issue?

ISF Workshop #3

REFLECTIONS: Turbulent Flames



Experiments

- Desire to move more towards practical combustion device-relevant conditions
  - Focus has been on ethylene; are we missing opportunities by not looking at more realistic fuels? Single component surrogates sufficient? Sprays?
- Are the current suite of flame geometries sufficient to elucidate the underlying physics and chemistry?
- In most cases, experiments are done first and models follow. Need to have more feedback from modelers on what should be measured

Modeling

- Why so much disparity in model predictions?
- Issues identified:
  - Soot precursor chemistry (PAH and acetylene-based approaches)
  - Sub-filter molecular transport and Gas-phase differential diffusion
- Are existing turbulent combustion modeling approaches applicable to slow chemical processes (like soot formation)?
- Does one need to accurately predict soot statistical properties in order to get the mean behavior correct?

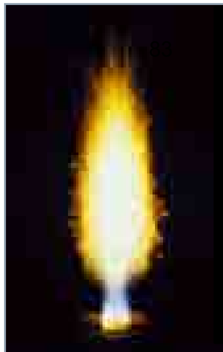
Elevated Pressure Turbulent Flames (Geigle / Haworth): DLR Swirl Combustor

Significant issues of calculations

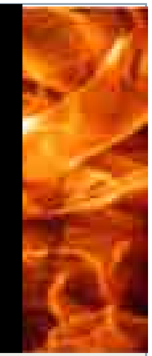
- Extent of mesh refinement near the inlet areas
- How far upstream and downstream you simulate greatly affects the accuracy of the simulation
- The instable behavior of the reactive flow of simulations

Issues with potential for optimization

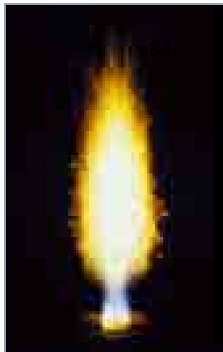
- More representative inlet boundary conditions.
- We have to use more complex soot models than the Leung and Lindstedt model to improve the predictive capability, but this imply:
  1) more detailed chemistry and soot morphology
  2) a more expensive simulation

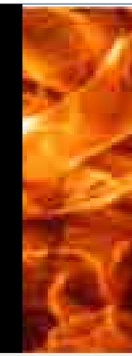


Laminar Flames: Atmospheric and Pressurized



- Speakers:
  - Mariano Sirignano (University of Naples)
  - Guillaume Blanquart (Caltech)
  - Klaus-Peter Geigle (German Aerospace Center, DLR)
  - Daniel C. Haworth (Pennsylvania State University)





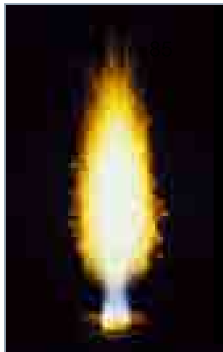
Elevated Pressure Laminar Flames (Geigle / Haworth):

Significant issues of calculations

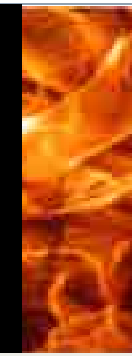
- Computation cost:
  - Fine mesh to resolve thin flame structure at high pressures
  - Large chemical mechanism to include detailed PAH chemistry
  - Long run-time to get rid of flame oscillation triggered at high pressure
  - Small time step to avoid numerical issues
- Ambiguity in boundary conditions

Issues with potential for optimization

- Better specification of the boundary conditions
  - Inlet velocity profile (Is bulk velocity profile good enough at the inlet? Is the result sensitive to the distance between the honeycomb and the nozzle exit)
  - Inlet flow temperature (Is heat transfer to the nozzle important?
- Centerline soot: Better understanding on PAH-based soot formation processes and improving centerline predictability



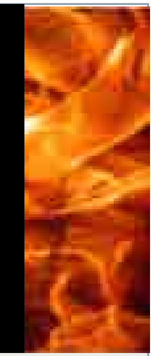
REFLECTIONS: Laminar Flames P>1 atm



Modeling

- Encouraging results for
  - Normalized peak soot volume fraction
  - Particle size
  - Centerline temperature (experimental data will be re-evaluated)
  - Centerline species
- Ambiguity in experimental boundary conditions
  - Importance of boundary conditions; can/should we design new experiments where we have better control over boundary conditions?
- Experiments
  - Are the current suite of flame geometries sufficient to elucidate the underlying physics and chemistry?

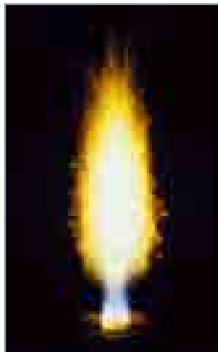
Atmospheric Pressure Laminar Flames (Sirignano/Blanquart): Numerical



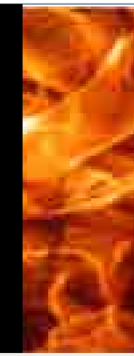
- **Spheres vs. aggregates**
  - Some models assume purely spheres, some aggregates
  - How does the transition from spheres to aggregates occur?
- **Nucleation**
  - What species nucleate into soot?
  - What are the coagulation efficiency for PAH and small particles?
    - Sensitivity?
- **Oxidation**
  - Are we using the same oxidation rates (OH and O_2)
  - Are the models considering different soot aging in the oxidation?
  - Are the models considering fragmentation and which impact does it have?
- **Should we force/encourage “turbulent people” to simulate laminar flames?**

Atmospheric Pressure Laminar Flames (Sirignano / Blanquart): Experimental

- **LII vs. soot**
  - Do we compare LII with the right “particles/aggregates”?
- **Nanoparticles: PSD and optical**
  - Providing PSDs both with BSS and horizontal probes
  - Comparing PSD volume fraction also with optical technique (absorption , LIF)
- **Parametric studies**
  - Good efforts spent in providing series of flame rather than single.
  - Can we do better? (changing less parameters at a time)
- **New flames**
  - Why only <u>one</u> new result on the designed coflow Yale burner?
  - Which aspect(s) should they be able to cover?



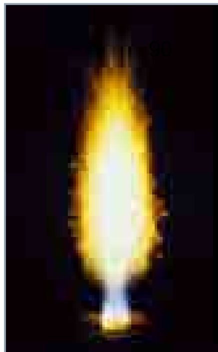
REFLECTIONS: Lamiar Flames



- What do we want to learn/get from laminar flames?
  - Improved understanding of soot processes or improved soot models
  - How soot processes respond to perturbations (thermal, chemical, density, strain, etc.)
  - Are the current suite of flame geometries sufficient to elucidate the underlying physics and chemistry?
    - Are coflow diffusion flames relevant to soot production in turbulent flames?
  - Soot models calibrated for relatively large values of f_v, whereas in turbulent flames f_v are much lower
- PAH
  - How accurate are PAH models? How accurate do they need to be?
  - Can we effectively co-validate PAH chemistry and soot formation in flames, or do these need to be treated separately?
- Soot Morphology
  - Do we need to distinguish “immature” from “mature” soot (to mimic experimental measurements and to treat differences in reactivity, etc.)? If so, how can we do this?

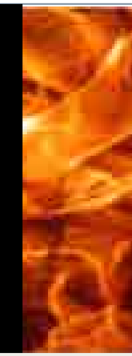
ISF Data Standardisation and Uncertainties

- Speakers:
  - Chris Shaddix, (Sandia National Labs)
  - KP Geigle, (DLR)
  - Gus Nathan, (University of Adelaide)
  - Omer Gulder, (University of Toronto)
- Topics
  - Standardization of assumed soot optical properties
  - Challenges of determining uncertainties of measurements
  - Uncertainties of the flame experiment
- Discussion Points:
  - Reporting observables/raw data rather than processed data?



ISF Workshop #3

REFLECTION: Soot Morphology



- Soot morphology – primary soot particle size, soot agglomerate size, fractal characteristics, etc.
  - Orders of magnitude differences in volume fraction in turbulent flame models and experiments, but morphology perhaps more important
  - What is our interest in soot morphology?
  - Does this information help us to improve our soot models?
  - Species condensed on surface dictate toxicology; can we model EC/OC ratio etc.
- Soot maturity determination and modeling continues to be a real challenge
  - Uncertainty in index of refraction
- Do we need a discussion session on soot morphology re: what diagnostics to use?

Turbulent Flames

Michael E. Mueller

Department of Mechanical and Aerospace Engineering

Princeton University

Thomas Dreier

Institute for Combustion and Gas Dynamics

University of Duisburg-Essen

Zhiwei Sun

Centre for Energy Technology

School of Mechanical Engineering

University of Adelaide

4th International Sooting Flame (ISF) Workshop

Dublin, Ireland

July 27-28, 2018

Session Plan

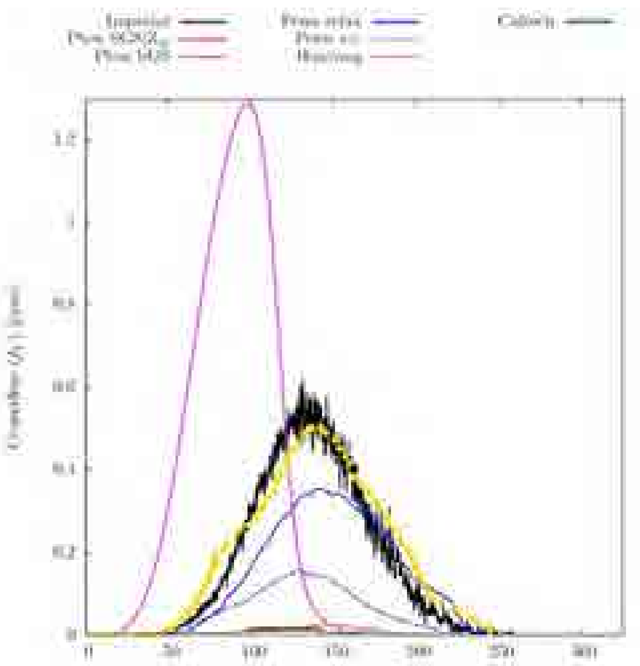
- Part I: Updates and Progress
  - Introductory Remarks (Mueller)
  - New Experimental Measurements (Sun/Dreier)
    - Jet Flames (Boyette)
    - Swirl Combustor (Geigle)
    - Bluff Body Flames (Dally)
  - Target Flame Comparisons (Mueller)
- Part II: Discussion
  - Target Flame Discussion (Mueller)
  - Survey of Simultaneous Measurements (Dreier/Sun)
  - Open Discussion (Mueller/Dreier/Sun)

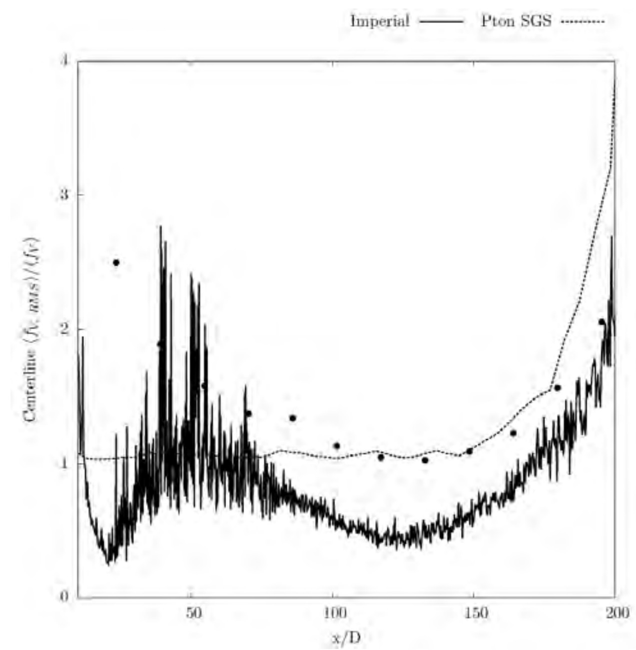
Discussion Throughout

Introductory Remarks

Introductory Remarks

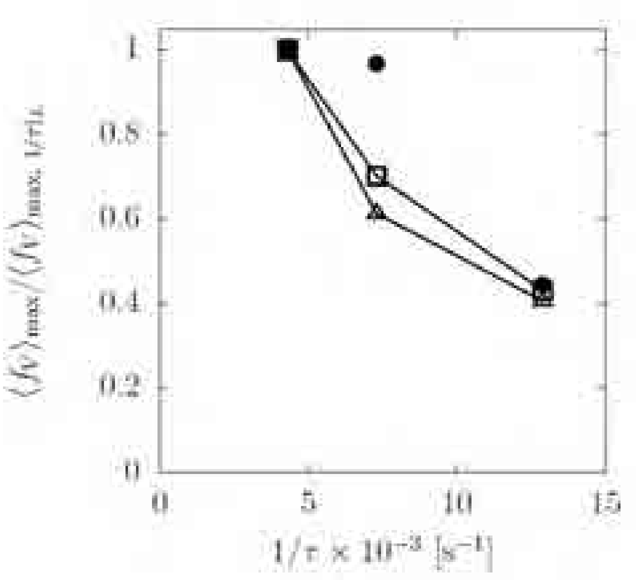
- ISF-3 Outcomes: Sandia Piloted Jet Flame
  - Several groups continued to struggle with severely underpredicting soot volume fraction in jet flames.
  - However, we are not getting everything wrong…





Introductory Remarks

- ISF-3 Outcomes: Adelaide Jet Flames
  - Underprediction of soot volume fraction, consistent with Sandia flame despite introduction of hydrogen into fuel.
  - However, response to strain trend is consistent with measurements.
    - Is this a model success?
    - Is this a coincidence?



Introductory Remarks

- ISF-3: Identified Modeling Needs
  - Soot Precursor Chemistry
    - How do we validate this at conditions relevant to turbulent flames?
    - How sensitive are results to variations in mechanism?
  - Subfilter Transport
    - Neglect of differential transport between soot and flame in most presumed and transported PDF models.
  - Gas-Phase Differential Diffusion
    - Spatially intermittent PAH not subject to convenient unity Lewis number approximation, but differential diffusion not important for all species.

Introductory Remarks

- From ISF-3 to ISF-4
  - Program Change
    - Atmospheric and pressurized turbulent flames combined into a unified turbulent flames program
  - Quarterly Teleconferences
    - Engaging community between workshops
    - Community sets agenda
    - Great opportunity for graduate students and postdocs to present new work and get instant feedback
    - Current mailing list of more than 70 researchers (contact program leaders to be added to the email list)
    - 20-30 researchers on each call
    - Typically 3-5 contributors per call

Introductory Remarks

- ISF-4 Objectives
  - *To advance prediction of sooting flames in the growth/agglomeration regimes of ethylene flames*
    - Continued emphasis on DLR confined swirl flame including new experimental data and numerous computational contributions
    - Introduction of a bluff body configuration as a target flame
  - *To engage with the international community through joint sessions with members of the…TNF workshop*
    - Joint session tomorrow morning at 8:30
    - Co-chaired by B.B. Dally and M.E. Mueller
    - Panelists: S. Hochgreb, V. Raman, W.L. Roberts

Introductory Remarks

- ISF-4 Further Goals
  - Address some of the modeling challenges identified above
    - Some of the model progress since the last workshop directly addresses these challenges
    - See the posters for more information
  - Begin to discuss simultaneous measurements and model predictions beyond spatial statistics
    - Do all models predict the same *relationships* between quantities?
    - Can these relationships be measured?

New Experimental Measurements

Target Flame Comparisons

Thanks to Dr. Suo Yang for assistance in preparing the plots!

Sandia Flame

- Configuration
  - Piloted jet flame
  - Fuel: Ethylene
  - Pilot: Ethylene/Air ($\phi = 0.9$)
  - Reynolds Number: 20,000

  - Measurements
    - Soot volume fraction (LII)
    - Soot temperature (2-Color Pyrometry)
    - PAH PLIF
    - OH PLIF
    - Flame radiation

Sandia Flame

- Contributions: Models

	Princeton	Imperial
PI	Mueller	Lindstedt
PoC	Yang	Schiener
LES/RANS	LES	RANS
Combustion Model	Flamelet	Exp. Chem.
Turbulence Model	Dyn. Smag.	SSG
Turbulence-Chemistry	PPDF	TPDF
Radiation	Opt. Thin	Opt. Thin
Soot Model	HMOM	Sectional
Inception	PAH	**Acetylene**
Sensitivity	PPDF	“Alpha”
Grid Points	590k	

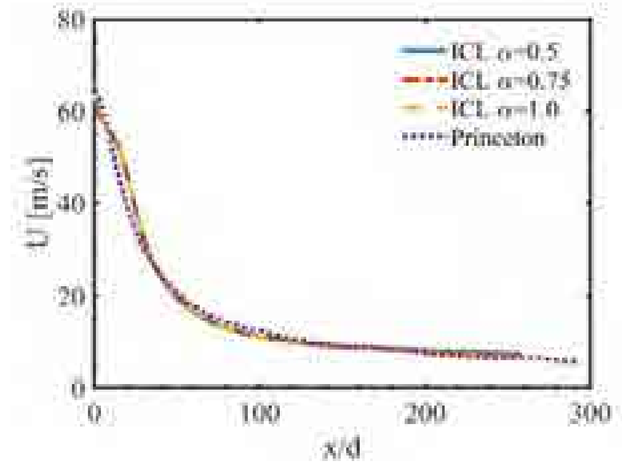
Sandia Flame

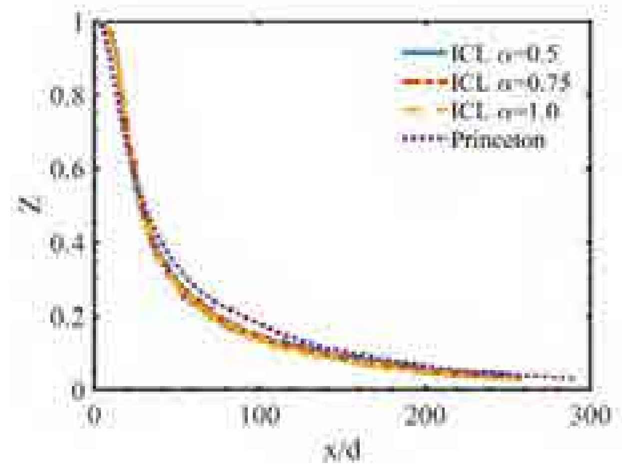
- Contributions: Boundary Conditions

	Princeton	Imperial
Central Jet	Fully Developed Pipe Flow	Fully Developed Pipe Flow
Pilot Profile	Flat	Flat
Pilot Mass Flow	Exp.	Exp.
Pilot Condition	Burned	Equil.
Coflow Profile	Flat	Flat
Coflow Turbulence	No	1%

Sandia Flame

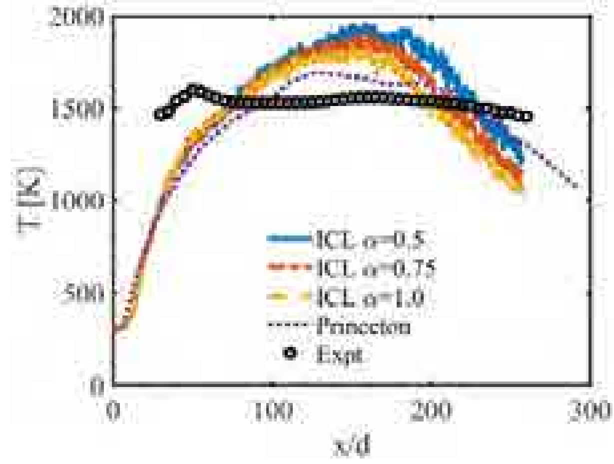
- Axial Velocity and Mixture Fraction
  - Despite the very different approaches to the fluid mechanics, the basic flow structure is essentially the same
  - Princeton results show slightly richer mixture fraction downstream, so a downstream shift in soot volume fraction might be anticipated
  - In Imperial results, essentially no effect of soot model parameters on flow and mixing





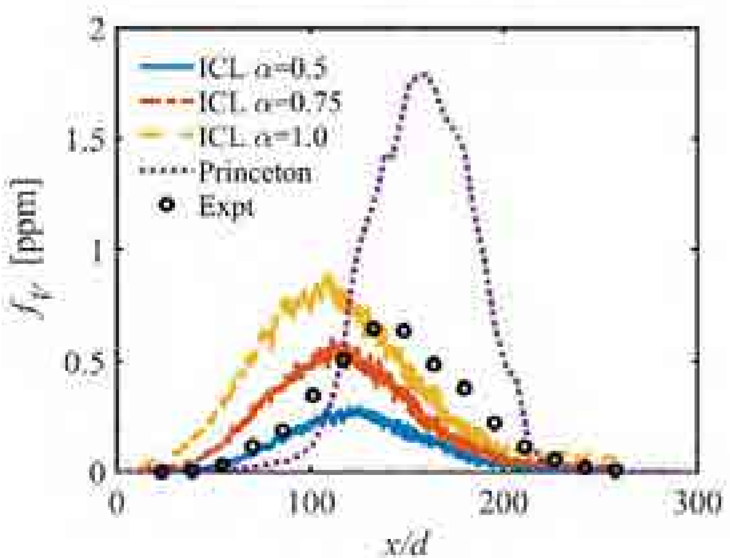
Sandia Flame

- Temperature
  - Somewhat larger differences between the two approaches
    - Princeton is slightly richer downstream so consistent with lower temperature until flame "tip"
    - Princeton also forms more soot so lower temperature
  - In Imperial results, some influence of soot model on temperature due to influence of soot radiation
  - Experimental measurements are the soot temperature, so the gas temperature is
    - Lower upstream: mean centerline mixture fraction richer than "soot mixture fraction"
    - Higher downstream: mean centerline mixture fraction leaner than "soot mixture fraction"



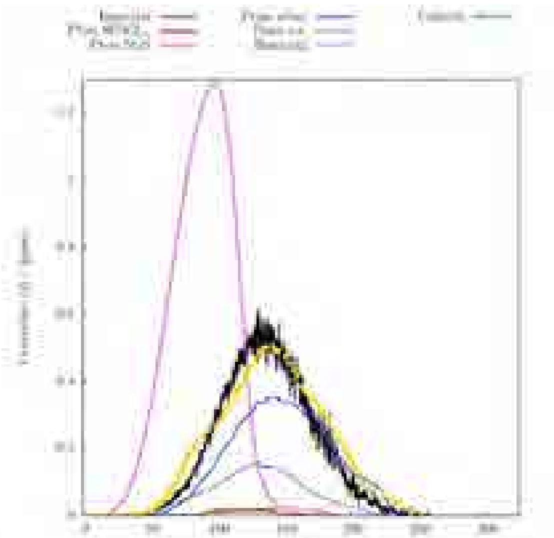
Sandia Flame

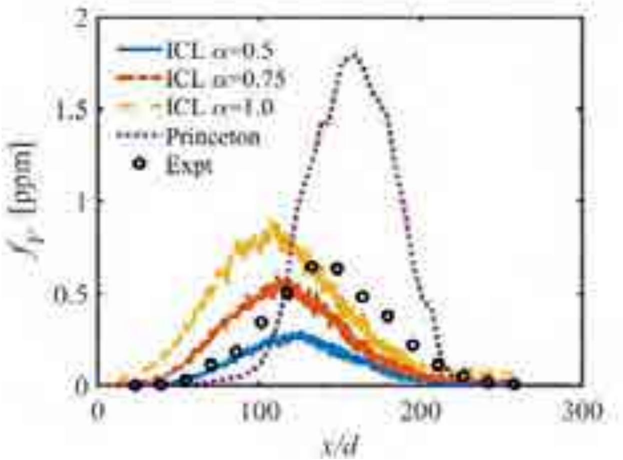
- Mean Soot Volume Fraction
  - Approach to soot modeling is quite different, but the magnitude matches the measurements quite well in both cases
    - Imperial peaks earlier than the experimental measurements
    - Princeton peaks later than the experimental measurements
  - Volume fraction scales more or less linearly with “alpha”



Sandia Flame

- Mean Soot Volume Fraction
  - My own results have changed dramatically from ISF-3!
  - Influence to the presumed subfilter soot PDF is extremely strong
    - Old marginal subfilter PDF: Ignored any correlation between soot and mixture fraction
    - New conditional subfilter PDF: Soot confined only to mixture fractions where growth faster than oxidation and eliminates “spurious oxidation”
    - See poster for more discussion and details





Adelaide Jet Flames

- Configuration
  - Simple jet flames
  - Fuel: Ethylene/Hydrogen/Nitrogen
    - 40/40/20 by volume

	Flame 1	Flame 2	Flame 3
Reynolds Number	15,000		
Strain Rate (U/D) [1/ms]	12.95	7.35	3.95

  - Measurements
    - Soot volume fraction (LII)
    - Centerline temperature
    - Exit velocity profiles
    - Flame radiation

Adelaide Jet Flames

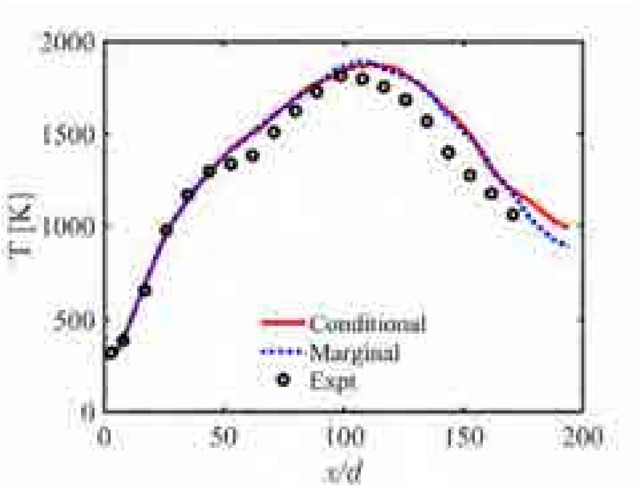
- Contributions

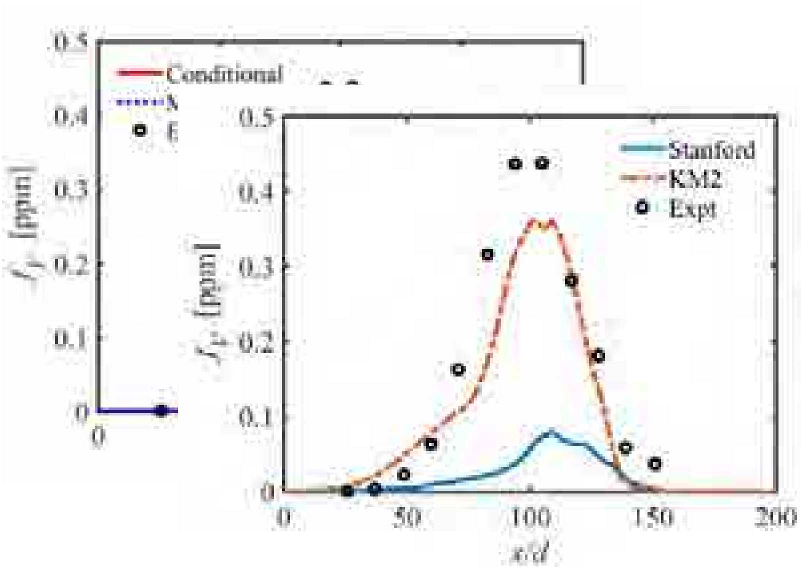
	Princeton
PI	Mueller
PoC	Yang
LES/RANS	LES
Combustion Model	Flamelet
Turbulence Model	Dyn. Smag.
Turbulence-Chemistry	PPDF
Radiation	Opt. Thin
Soot Model	HMOM
Inception	PAH
Sensitivity	PPDF
Grid Points	800k

	Princeton
Central Jet	Fully Developed Pipe Flow
Coflow Profile	Flat
Coflow Turbulence	No

Adelaide Jet Flames

- Sample Results: Flame 2





  – Like the Sandia flame, soot volume fraction is very sensitive to the soot subfilter PDF; reasonable predictions with new model
  – Another chemical mechanism gives better results at this higher H/C ratio; currently assessing whether this holds in laminar flames

Bluff Body Flames

- Configuration
  - Bluff body flames
  - Fuels: Ethylene/Hydrogen mixtures and LPG
    - Increasing hydrogen content in Flames 1-3

	Flame 1	Flame 2	Flame 3	Flame 4
Reynolds Number	~30,000			
Ethylene (Mole)	1.000	0.671	0.487	LPG
Hydrogen (Mole)	0.000	0.329	0.513	

  - Measurements
    - Soot volume fraction (LII)

Bluff Body Flames

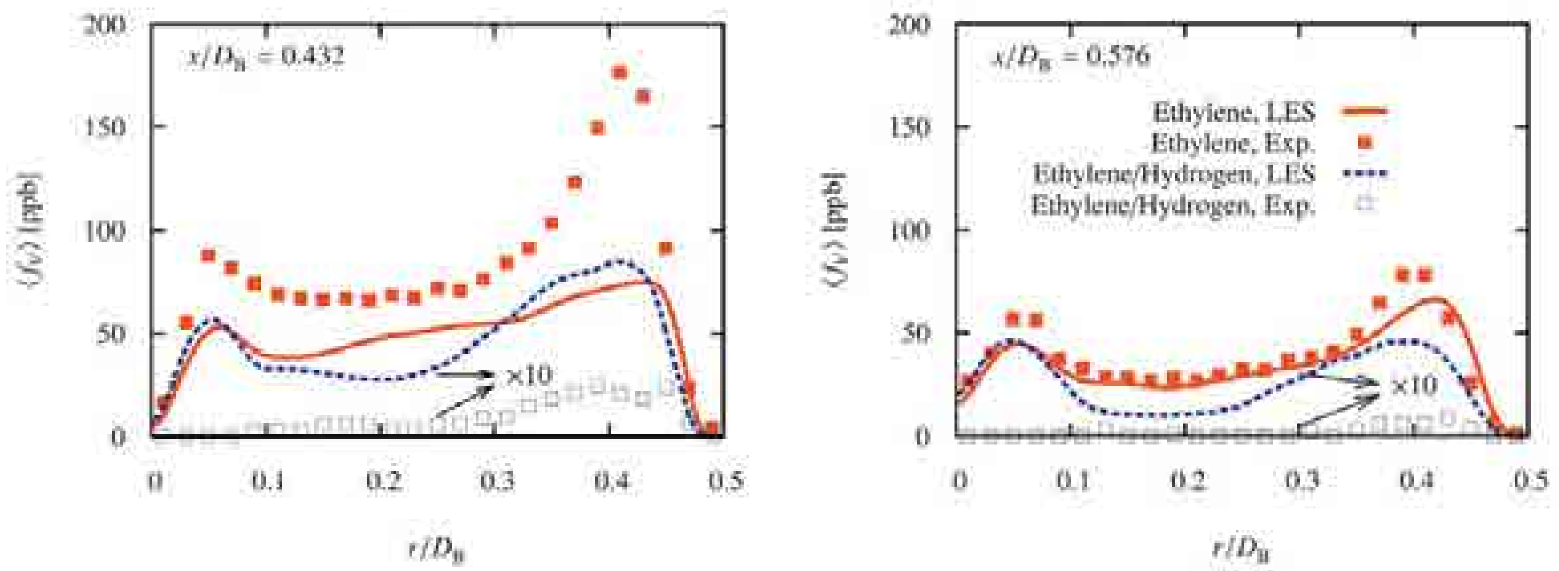
- Contributions

	Princeton
PI	Mueller
PoC	Mueller
LES/RANS	LES
Combustion Model	Flamelet
Turbulence Model	Dyn. Smag.
Turbulence-Chemistry	PPDF
Radiation	Opt. Thin
Soot Model	HMOM
Inception	PAH
Sensitivity	PPDF
Grid Points	800k

	Princeton
Central Jet	Fully Developed Pipe Flow
Coflow Profile	Turbulent Boundary Layer

Bluff Body Flames

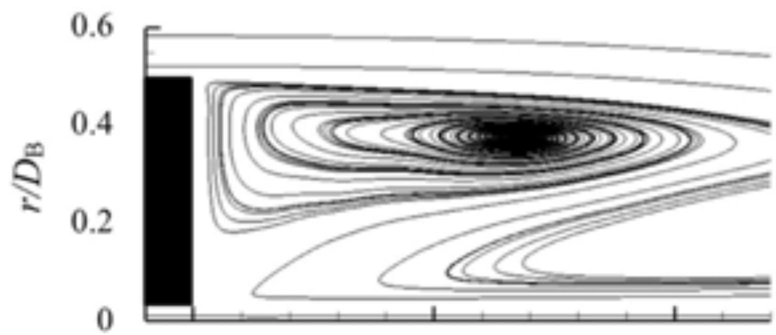
- Results: Flames 1-2 within Recirculation Zone

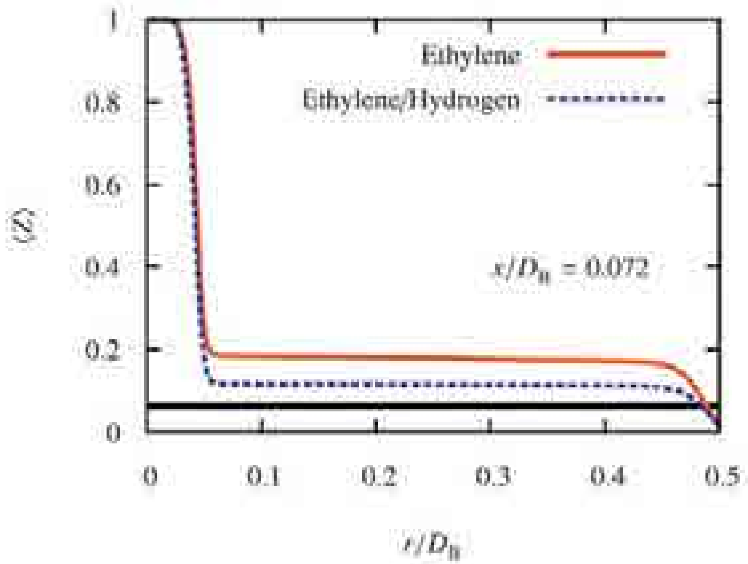


  – LES agrees well with experiments for the ethylene flame but significantly overpredictions soot with hydrogen addition
    - Opposite trend as in the jet flames

Bluff Body Flames

- Results: Flames 1-2 within Recirculation Zone

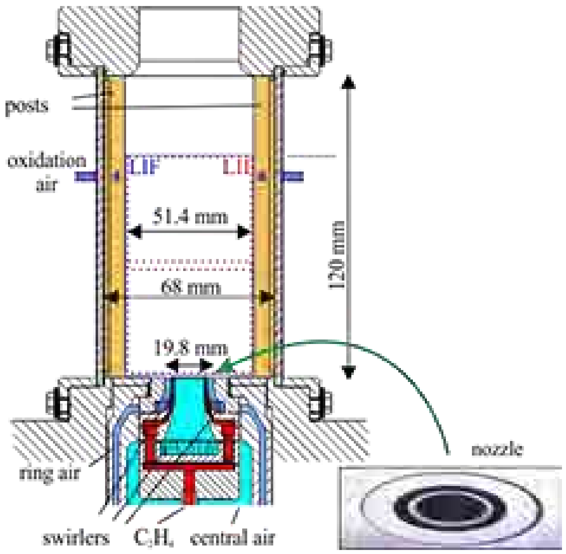




  – Challenge to models in the bluff body flame is prediction of entrainment of fuel into the recirculation zone
    - With hydrogen addition, to maintain Reynolds number, momentum flux of fuel jet increase so less entrainment
    - Is the recirculation zone mixture fraction correct in LES?

DLR Combustor

- Configuration
  - Confined swirl flame
  - Fuel: Ethylene
  - Variations
    - **3 bar** and 5 bar pressure
    - With and without secondary oxidation air
  - Measurements
    - Soot volume fraction (LII)
    - Temperature (CARS)
    - Velocity (PIV)
    - OH PLIF
    - PAH PLIF



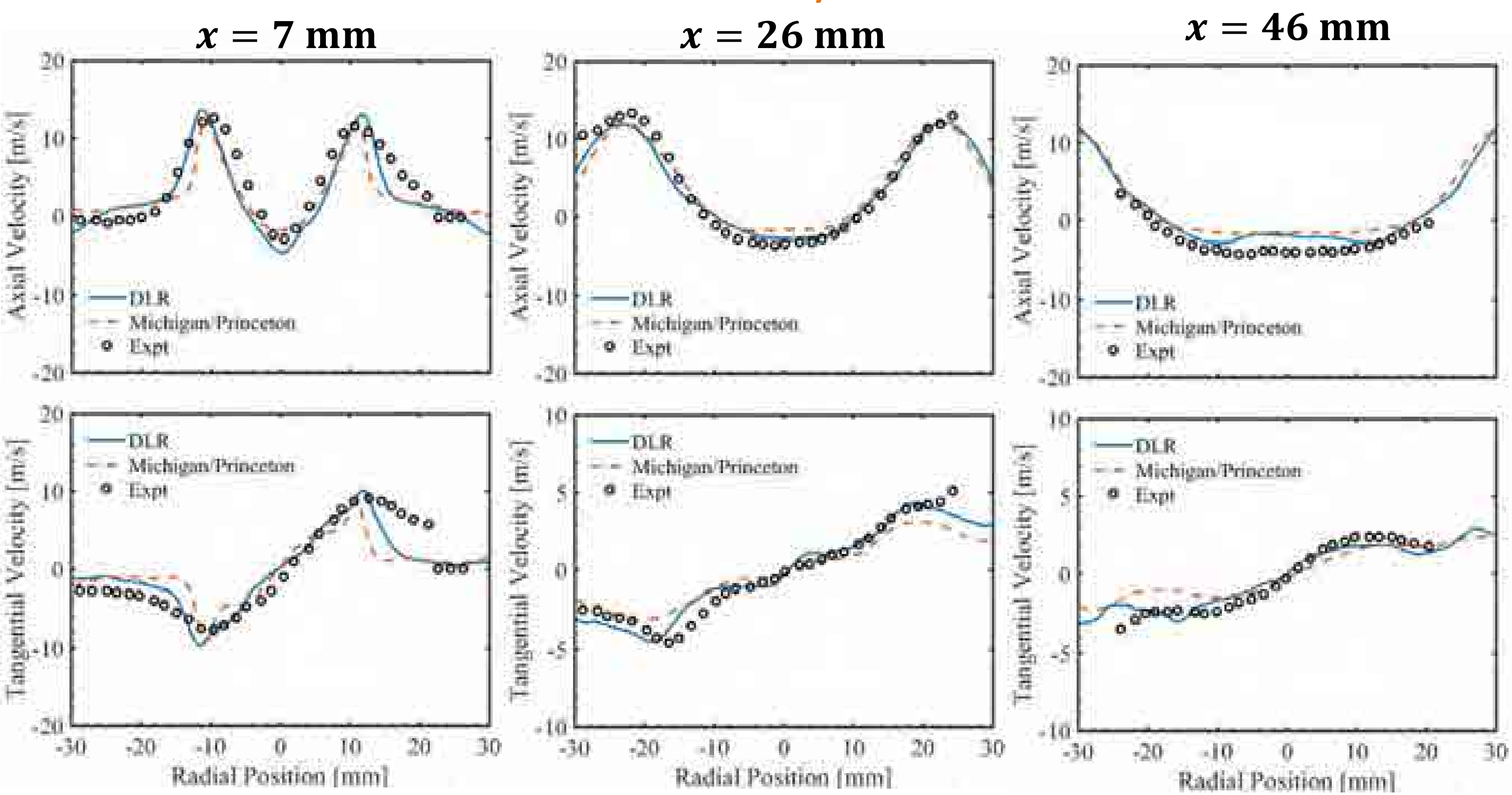
DLR Combustor

- Contributions

	Michigan/ Princeton	DLR	Rolls-Royce	EM2C	CERFACS
PI	Raman/ Mueller	Grader	Eggels	Franzelli	Cuenot
PoC	Chong	Grader	Eggels	Tardelli	Gallen
LES/RANS	LES	LES	LES	LES	LES
Combustion Model	Nonpremixed Flamelet	Explicit Chemistry	Premixed Flamelet	Nonpremixed Flamelet	Explicit Chemistry
Turbulence Model	Dyn. Smag.	Wale	Vreman	SIGMA	Wale
Turbulence-Chemistry	PPDF	PPDF	PPDF	PPDF	Thickened Flame
Radiation	Opt. Thin	Opt. Thin	None	Opt. Thin	None
Walls	Adiabatic	Isothermal	Isothermal	Isothermal	Adiabatic
Soot Model	HMOM (SEMI)	Sectional	SEMI	Sectional	SEMI
Inception	PAH (Acetylene)	PAH	Acetylene	PAH	Acetylene
Cases	Both	Both	w/ Ox	w/ Ox	w/ Ox
Grid Cells	12M	36M	30M	40M	40M

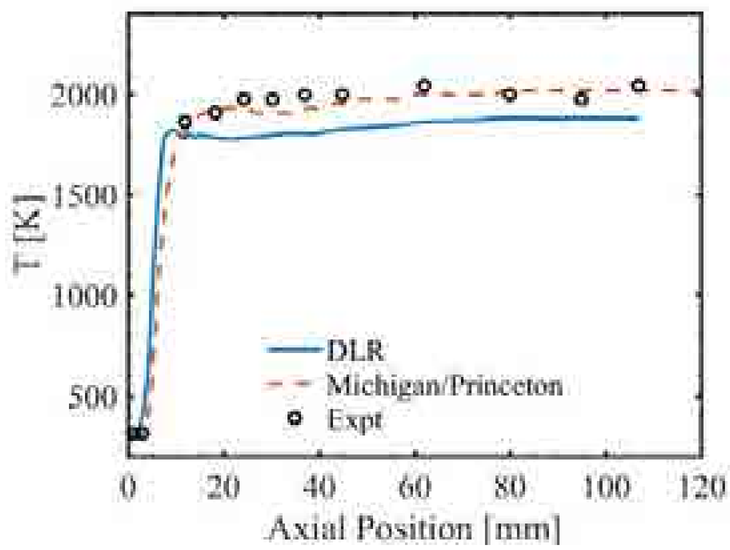
DLR Combustor

- Flow Field Results: No Secondary Oxidation Air



DLR Combustor

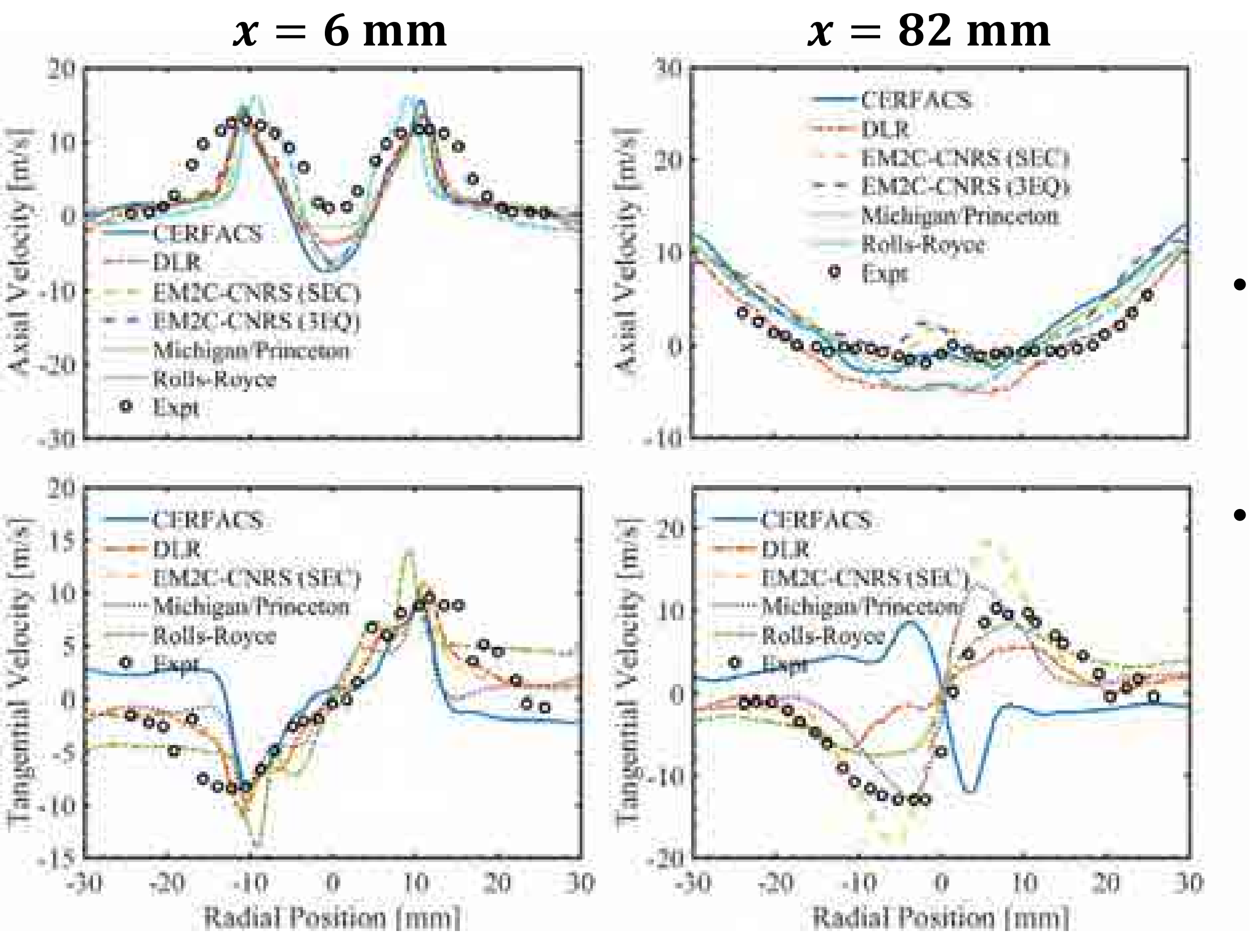
- Temperature Results: No Secondary Oxidation Air



  – Reduced temperature in DLR results due to isothermal wall boundary condition
    - More sophisticated heat transfer needed?

DLR Combustor

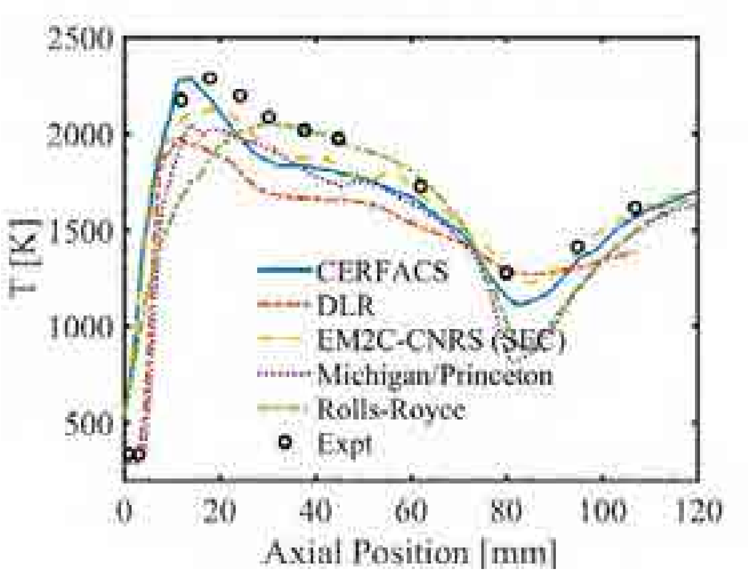
- Flow Field Results: With Secondary Oxidation Air



- More scatter than without secondary oxidation air but overall consistent with measurements
- Minor differences in persistence of recirculation zone and inflow swirl

DLR Combustor

- Temperature Results: With Secondary Oxidation Air

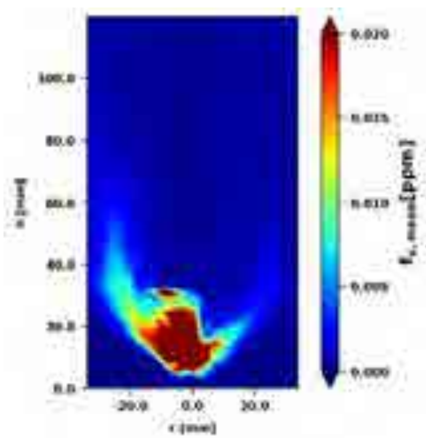


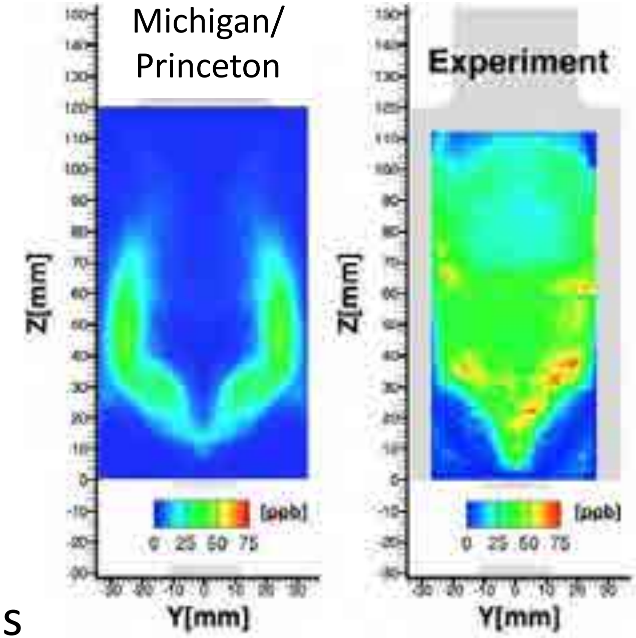
  - Some scatter but overall consistent with experimental measurements
  - Less clear trend with respect to heat transfer models but challenged with statistical convergence

DLR Combustor

- Soot Volume Fraction Results: No Secondary Oxidation Air

DLR

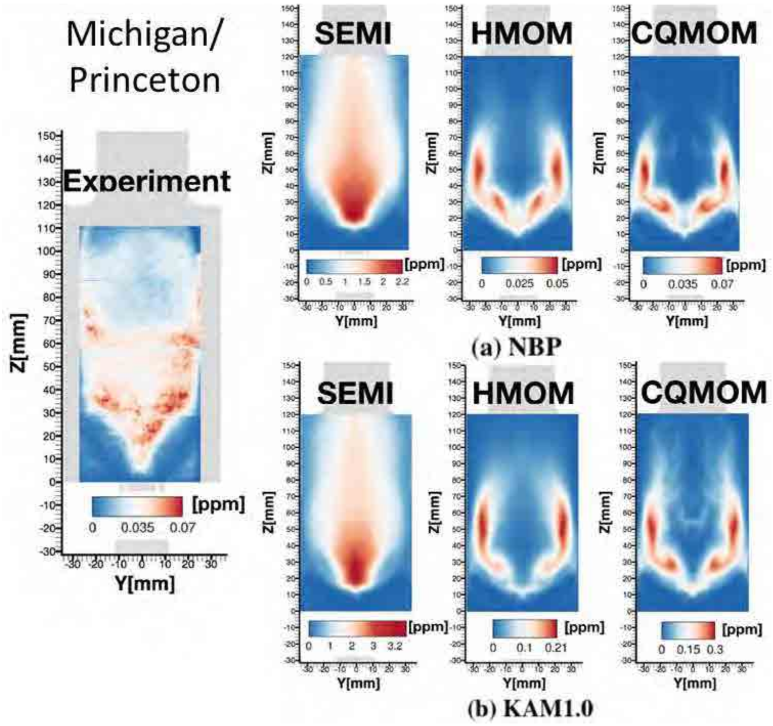




  – Qualitatively different soot predictions
    - DLR: Concentrated in recirculation zone near injection region
    - Michigan: Concentrated in fuel jets, little in recirculation
    - Experiments: More in fuel jets but some in recirculation zone
      – What is the mixture fraction in the recirculation zone?

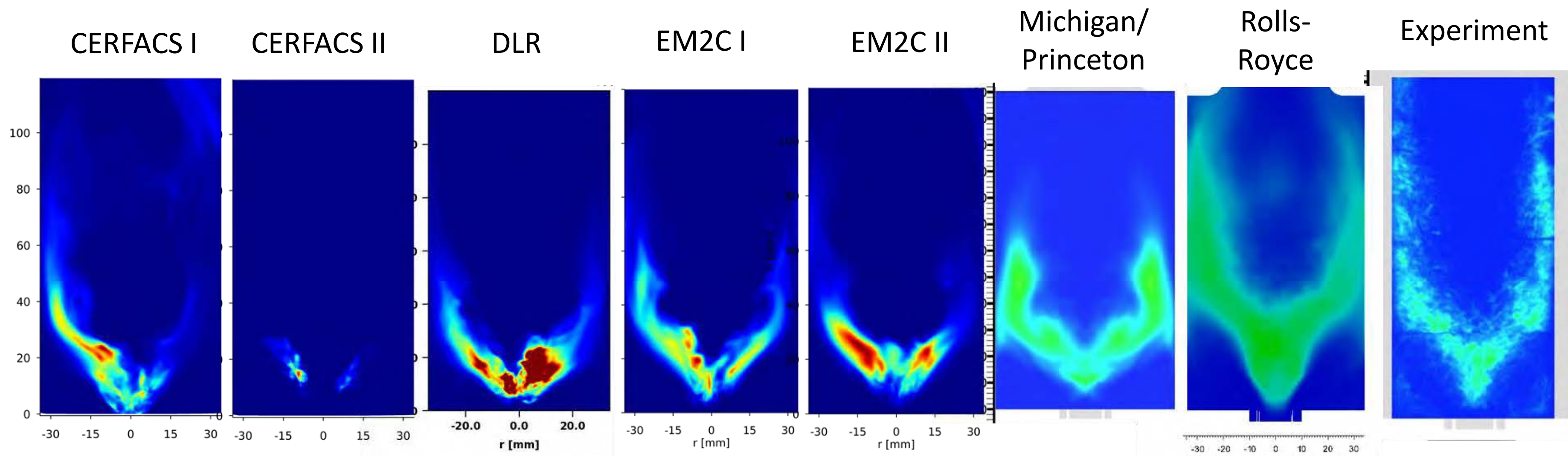
DLR Combustor

- Soot Volume Fraction Results: No Secondary Oxidation Air
  - The moment method has little influence on the magnitude of the soot volume fraction.
  - The chemical mechanism can significantly change the magnitude of the soot volume fraction, but the qualitative structure is the same.
  - A different inception model quantitatively and qualitatively modifies the soot volume fraction.



DLR Combustor

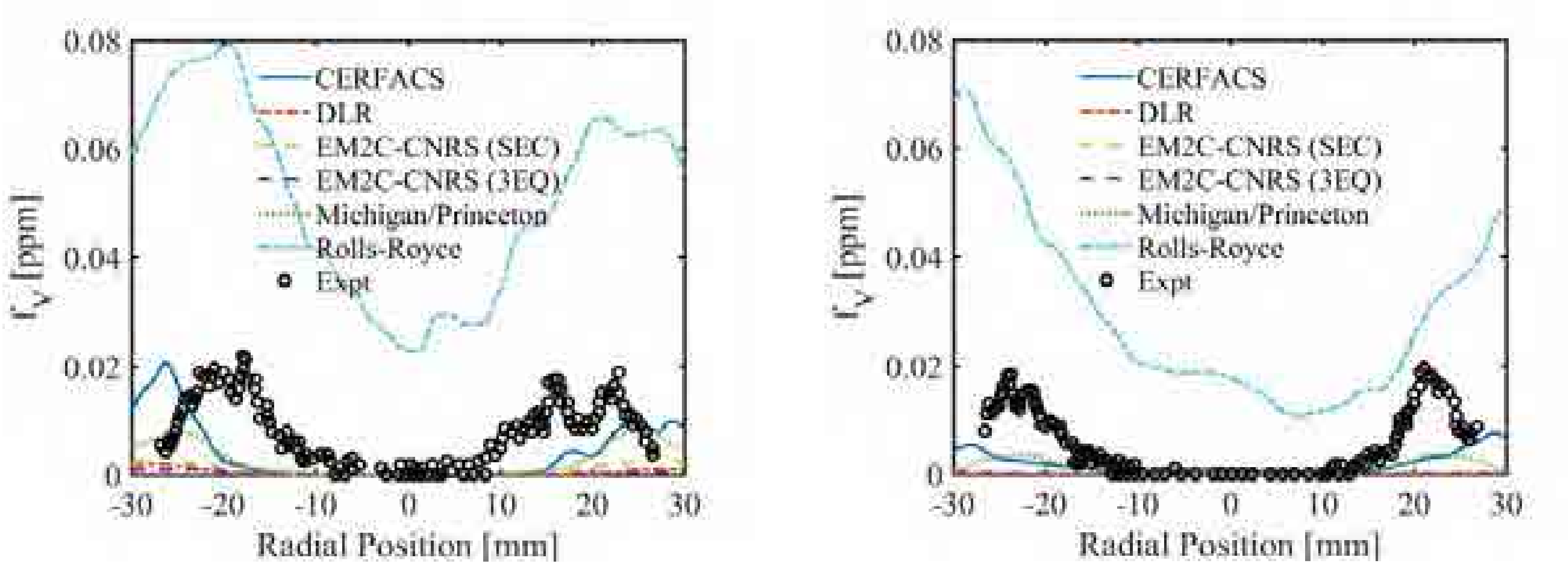
- Soot Volume Fraction Results: With Secondary Oxidation Air



- – Qualitatively, all of the models tend to predict similar soot structure
  - Secondary air oxidizes soot at a specific location
  - More importantly, recirculation zone becomes too lean to support soot

DLR Combustor

- Soot Volume Fraction Results: With Secondary Air Injection



  - Quantitatively, more variation between the models with some overpredicting soot and some underpredicting soot
    - Must correctly capture delicate balance between formation and oxidation to get correct magnitude of soot volume fraction
    - What measurement would be required to provide insight?

Summary

- Key Findings and Takeaways
  - Some significant progress in understanding and model development since ISF-3:
    - With PAH-based soot model, soot volume fraction in jet flames now in significantly better agreement with experimental
    - Significant improvements in modeling correlations between soot and mixture fraction
  - Emerging consensus:
    - Different models predict essentially the same velocity, mixture fraction, temperature.
    - Soot predictions can be both quantitatively and qualitatively different between models.
    - Models must be predicting different *relationships* between soot and other quantities.
    - **How can experiments help?**

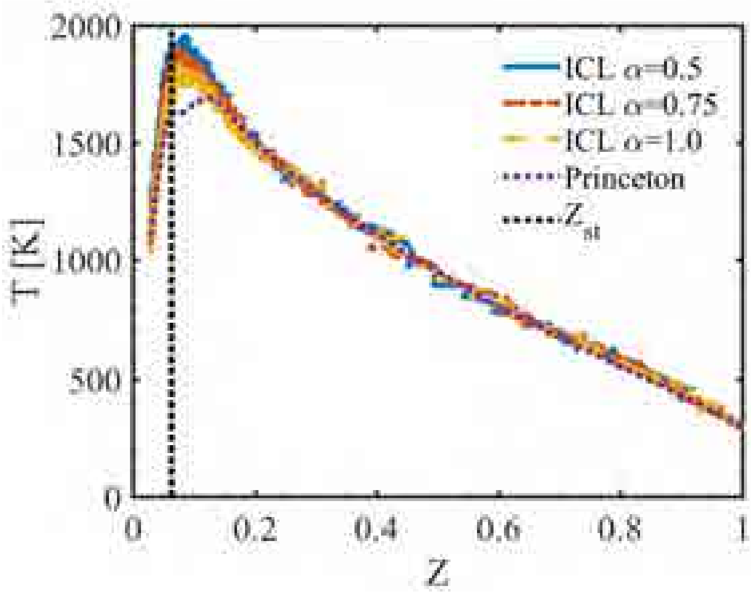
Discussion

Discussion

- Relationships between soot and…: Statistics
  - In essentially all of the comparisons in ISF to date, we have been considering spatial statistics, which miss relationships between variables.
    - Common practice in, for example, nonpremixed turbulent flames, would be to look at mixture fraction conditioned statistics.
    - Conditional statistics remove some of the biases associated with an incorrect flow field or mixing field.
    - For example, the mean soot volume fraction may be wrong only because the mean mixture fraction is wrong; conditional statistics remove that bias in part.
  - Unfortunately, not all of the groups computed any sort of conditional statistics, so we will just analyze relationships between means.

Discussion

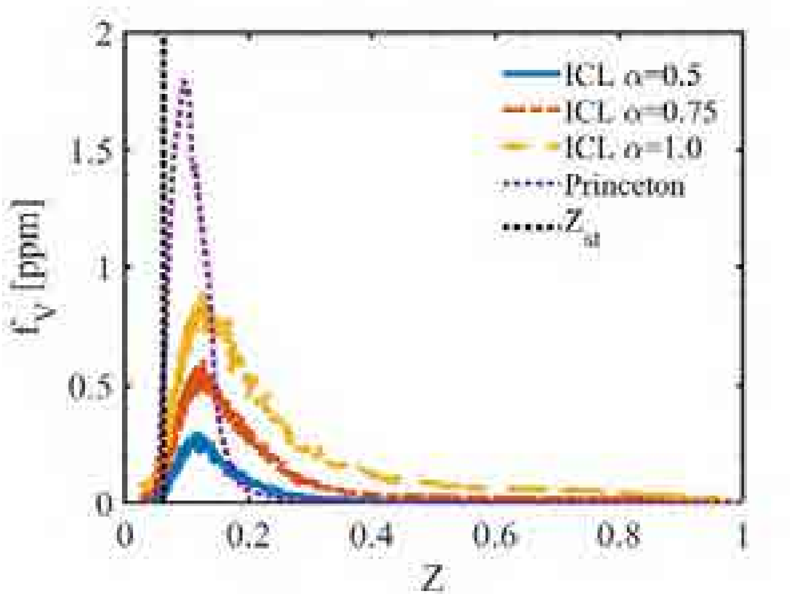
- Relationships between soot and…: Sandia Flame
  - Mean Temperature versus Mean Mixture Fraction



- Both models are essentially identically excepting differences in the peak temperature due to soot radiation.

Discussion

- Relationships between soot and…: Sandia Flame
  - Mean Soot Volume Fraction versus Mean Mixture Fraction



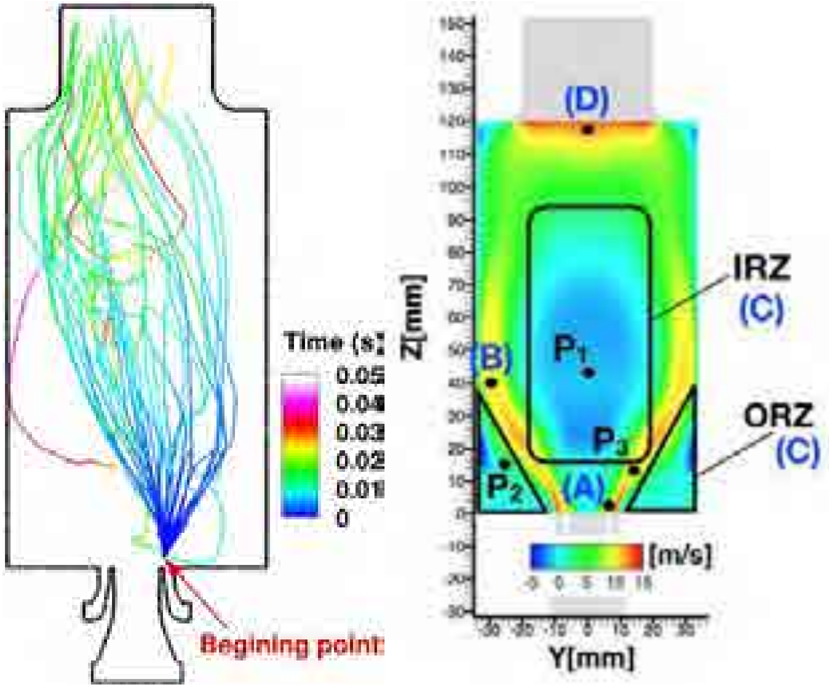
- Both models are very different, with the PAH-based model predicting mean soot volume fraction at leaner mean mixture fractions.
  - Caveat: This is not the same as a true conditional statistic!

Discussion

- Relationships between soot and…: Dynamics
  - Like it or not, we know that soot is kinetically controlled since the chemistry is relatively slow compared to other time scales.
  - For kinetically controlled processes, the pathway is very important.
    - Stated different, locations in physical space or composition space where soot source terms are large is not sufficient for predicting soot evolution.
    - The residence times and residence times histories at these locations will ultimately dictate soot evolution.
  - Consider Lagrangian time histories in the DLR combustor…

Discussion

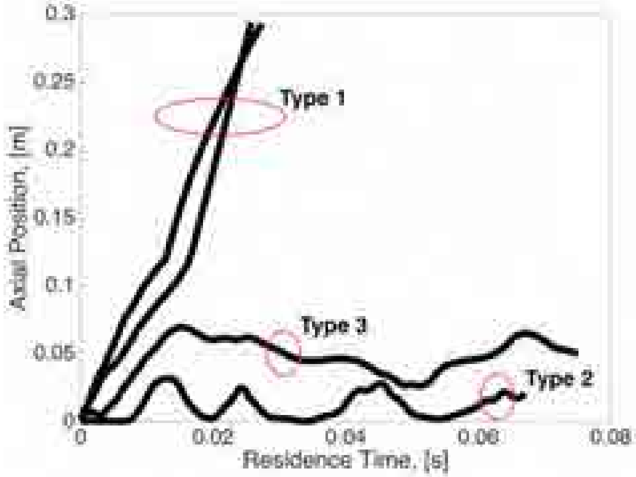
- Relationships between soot and…: DLR Combustor
  - Track Lagrangian history of notional fluid particles
  - Classification
    - Type 1: Rides shear layers and quickly exits combustor
    - Type 2: Entrained into outer recirculation zone (ORZ)
    - Type 3: Entrained into inner recirculation zone (IRZ) from downstream



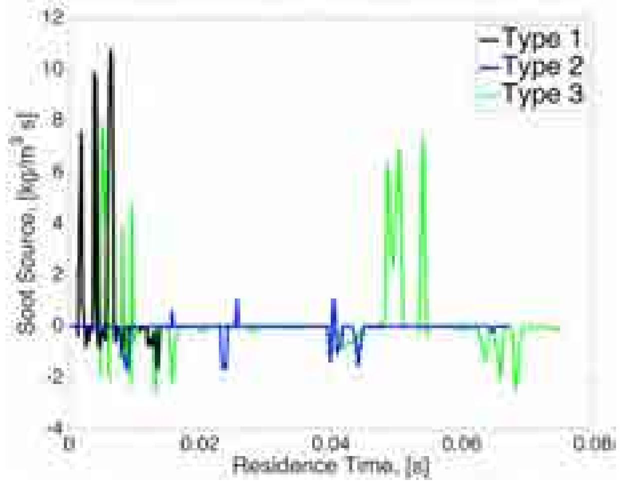
Discussion

- Relationships between soot and…: DLR Combustor

Particle trajectory by type



Intermittent soot source



- Very different time histories
- Changes in conditions affect distribution of time histories

Case	Particle Type 1 (%)	Particle Type 2 (%)	Particle Type 3 (%)
3 bar, No sidejet	76.3	21.3	2.4
3 bar, Sidejet	78.6	21.1	0.3
5 bar, No sidejet	83.1	16.5	0.4
5 bar, Sidejet	84.8	14.9	0.3

Discussion

- Computational Progress
  - Progress is being made in improving the models and incorporating more physics.
  - However, there are some significant differences between different modeling approaches.
  - What are the most important features to include in the models?

- Relationships
  - Different modeling approaches can predict the same temperature but very different soot volume fraction.
    - Relationships between quantities are fundamentally different.
  - Can these relationships be measured?
  - Can certain configurations isolate certain relationships?

Discussion

- Linkages with Laminar Flames Program
  - Chemistry will always be a significant need.
    - Is there a benefit to moving toward a common chemical mechanism?
    - Is there a benefit to more studies on non-C_2H_4 fuels?
    - Is the exact fuel more important for kinetic studies or simply another parameter such as H/C ratio?
  - Time histories in turbulent flames can be very different from laminar flames.
    - Are there “exotic” configurations that could provide more relevant conditions and histories in laminar flames compared to turbulent flames?

Simultaneous optical measurements in turbulent sooting flames

Soot + **X** (**X** = temperature, velocity, Z, ...)

Thomas Dreier and Zhiwei Sun

Outline

- Experimental work review
- Open discussion

ISF-4 Target Flame 2 (Sandia)

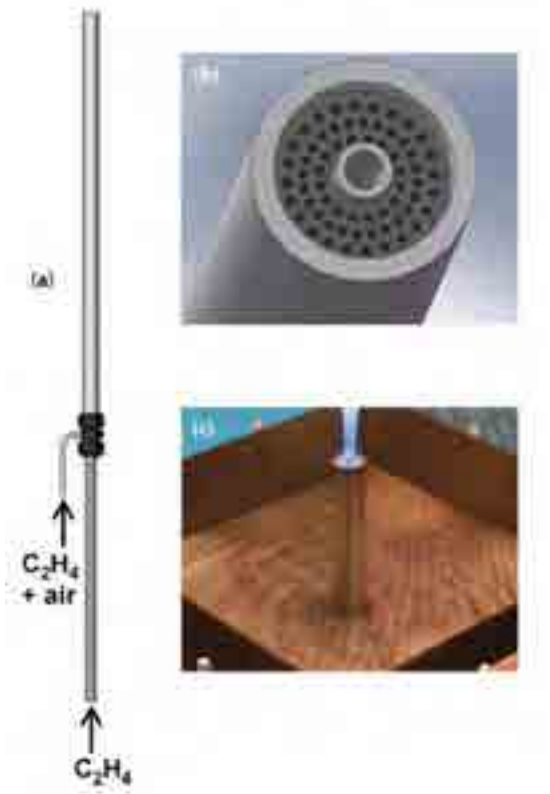
Dimensions
- Nozzle internal diameter = 3.2 mm
- Inner wall thickness = 0.65 mm
- Pilot outer diameter = 19.1 mm
- Outer wall thickness = 1.95 mm

Fuel jet: Ethylene

Pilot: Ethylene/air at equivalence ratio of 0.9 and thermal power of 2%

Flow Conditions
- Fuel average jet velocity = 54.7 m/s
- Co-flowing air mean velocity = 0.6 m/s
- Exit Reynolds number = 20,000
- Fuel temperature = 294 K

Measurements
- SVF → LII
- **Simultaneous SVF and temperature (3-line soot pyrometry)**
- OH PLIF
- PAH PLIF
- Radiant emission



Zhang et al.: Rev. Sci. Instrum. **82**, 074101 (2011)

ISF-4 Target Flame 4 (DLR)

Flame type

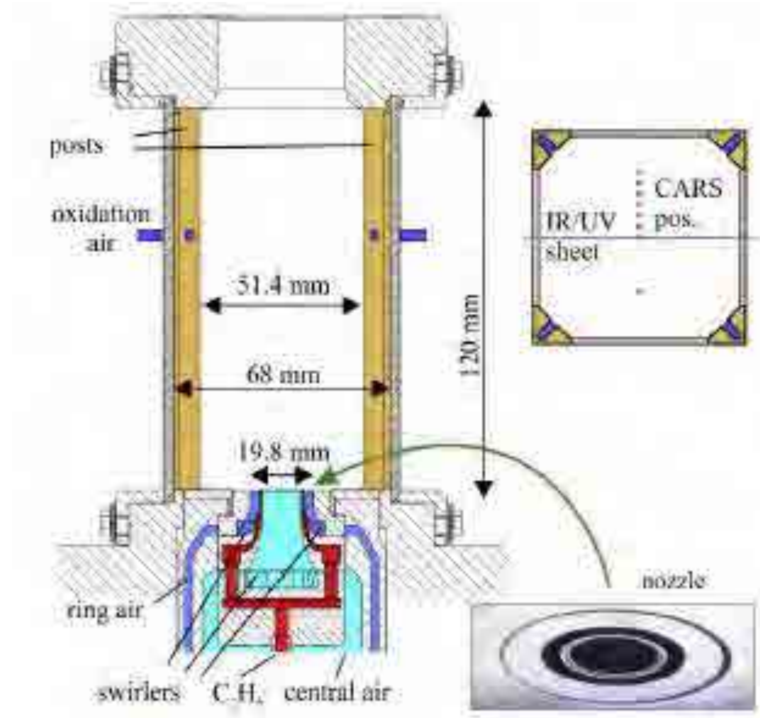
- Pressurized (3 bar)
- swirl

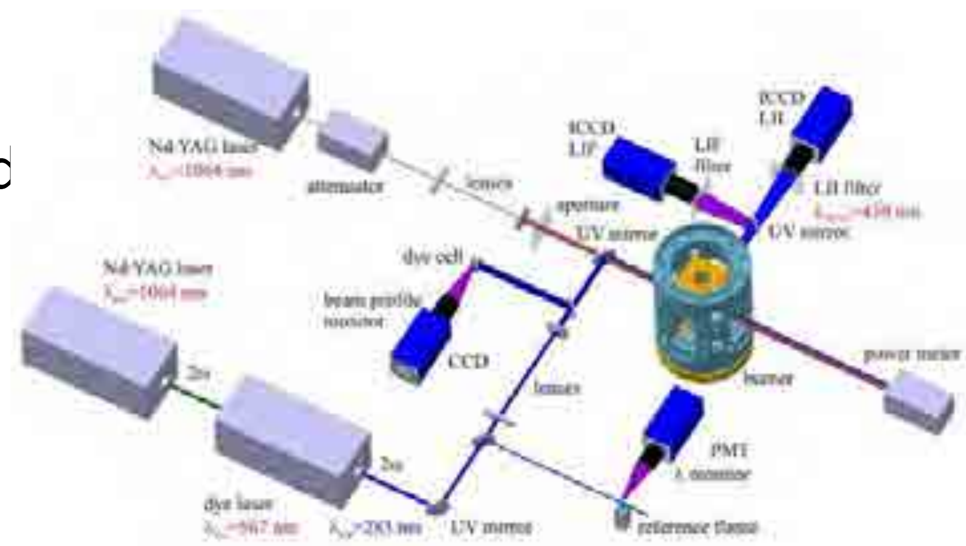
Measured Parameters

- Temperature → CARS (point-wise)
- Flame structure → OH-LIF (2D)
- SVF → LII (2D)

Main focus

- Effect of injection of second
  - Fuel-rich product gas stream





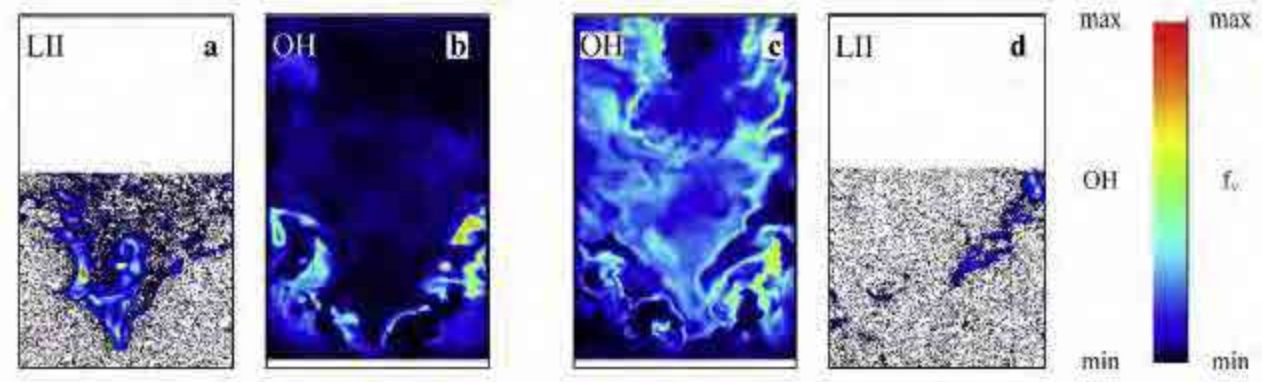
Geigle et al.: Proc. Combust. Inst. **35**, 3373 (2015)

ISF-4 Target Flame 4 (DLR)

Simultaneous Soot + OH

- Found between primary combustion zone (fed by combustion air and ethylene) and inner recirculation zone (oxidation air + transported unburned hydrocarbons (UHC)

w/o   w/ oxidation air



3 bar, instantaneous values

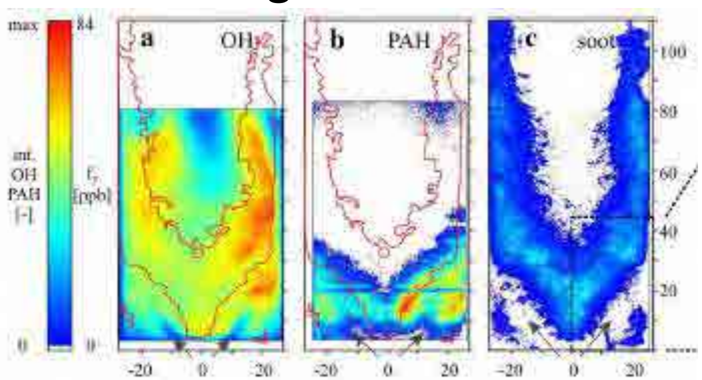
temperature / f_v-distributions

Geigle et al.: Proc. Combust. Inst. **35**, 3373 (2015)

ISF-4 Target Flame 4 (DLR)

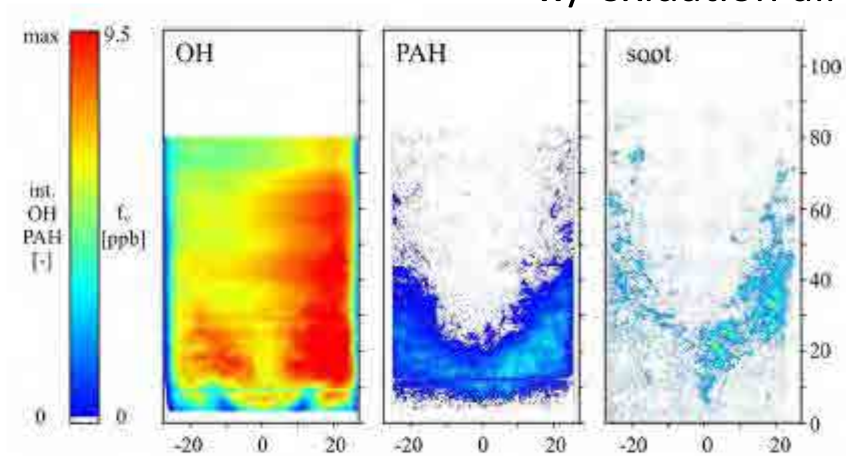
Simultaneous Soot + OH + PAH

- PAH signatures discontinuous
  - Contrary to OH
- Identification of wide range of soot formation progress
  - Isolated soot/PAH as well as transitioning
- Occurrence and distributions strongly dependent on flow field characteristics
  - Distinguish between transport and soot chemistry!



Prim. rich
w/ oxidation air

Moderately lean
w/ oxidation air



Ensemble-averaged

Geigle et al.: Appl. Phys. B **119**, 717 (2015)

ISF-4 Target Flame 4 (DLR)

Flame type

- Pressurized (3 bar)
- swirl

Measured Parameters

- Soot distribution → Rayleigh scattering (532 nm, 2D)
- Velocity → Stereo PIV (cold, reactive, 2D)

Main focus

- Effect of injection of secondary oxidation air
- Correlations between quantities

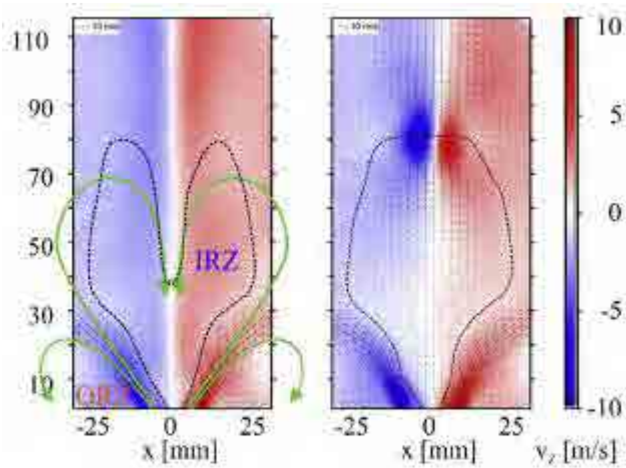
Geigle et al.: Proc. Combust. Inst. **36**, 3917 (2017)

ISF-4 Target Flame 4 (DLR)

Simultaneous Soot + Velocity

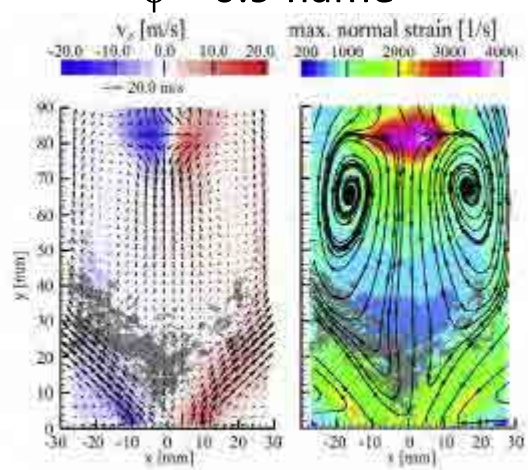
- Soot mainly formed in inner rich recirculation zones
- Secondary air injection separates flow field
  - Stagnation zone: upwards / downwards transport
- Flow field POD-anaylsis
  - Prescence of a PVC → impacts soot distribution
  - Soot present in high strain rate regions due to transport

w/o   w/ oxidation air



Geigle et al.: Proc. Combust. Inst. **36**, 3917 (2017)

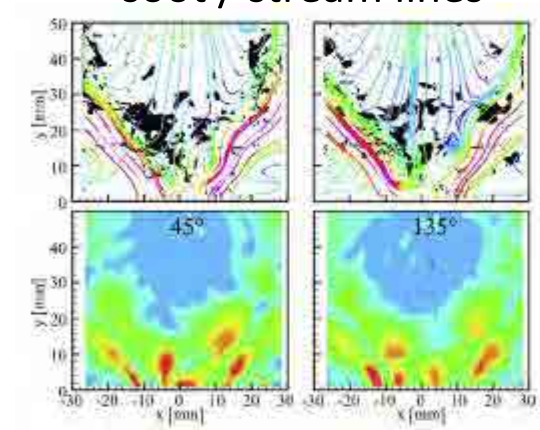
ϕ = 0.9 flame



Mean flow field + soot

Stream/ Strain lines

Phase-resolved soot / stream lines



Local extensive strain rates

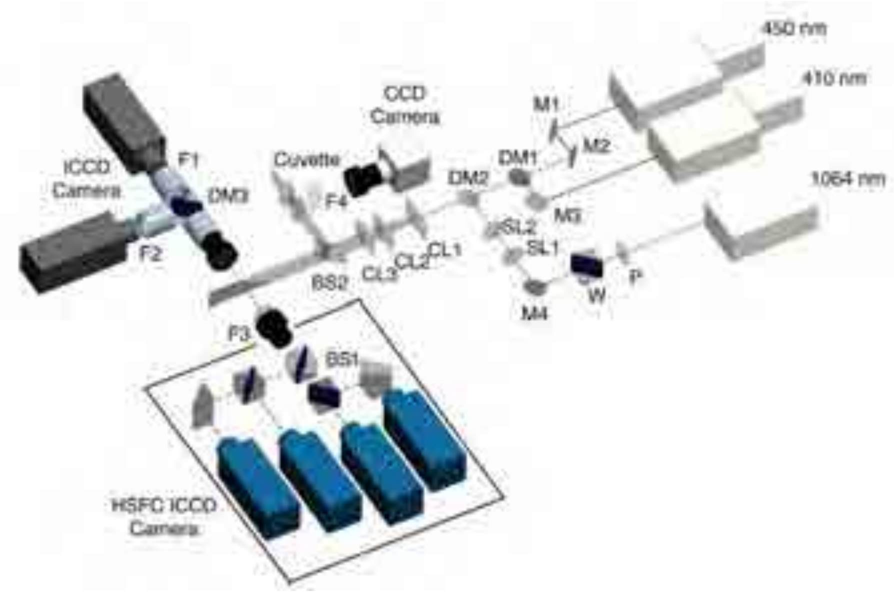
ISF-4 Other Flame 2 (DLR)

Simultaneous Soot + T + dp

- Temperature → nTLAF (In, VIS, 2D)
- SVF → prompt-LII (1064 nm, 2D)
  - Primary particle diameter (d_p) TiRe-LII →
  - Mean d_p number density (N_p)

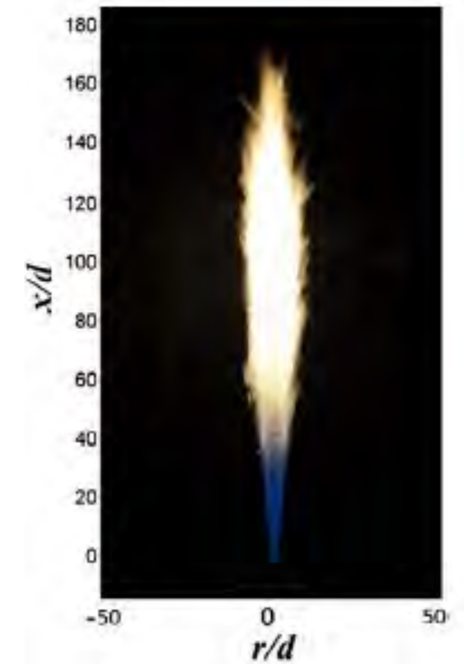
Main focus

- Joint statistics (pdf's), e.g., {T, f_v}



Gu et al.: Combust. Flame **179**, 33 (2017)

ISF-4 Target Flame 1 (Adelaide)



Simultaneous Soot + Temperature

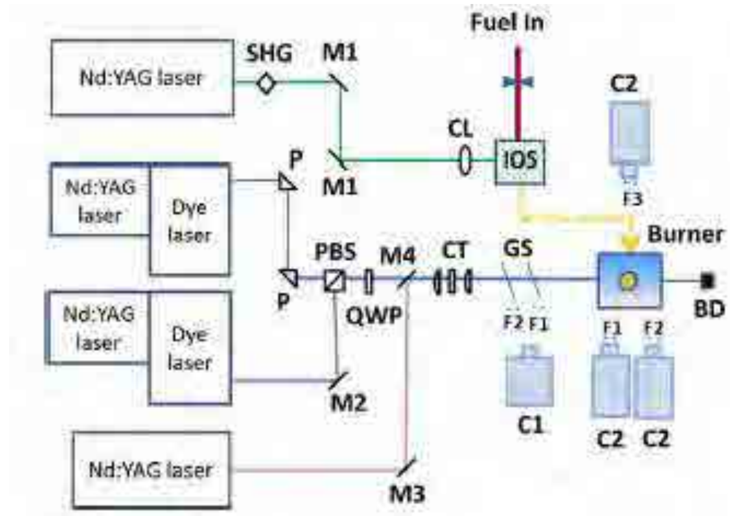
- 1 atm, $C_2H_4/H_2/N_2$/air (non-premixed)
- Lifted jet flame
  - Jet exit Re 5,000 – 15,000
  - Exit strain rate: 4,100 – 12,900 s^{-1}

Measured Parameters

- Temperature → nTLAF (In, VIS, 2D)
- Soot f_v → prompt-LII (1064 nm, 2D)
  - Primary

Main focus

- Soot – temperature correlation
- {T, SVF} joint pdf's



Mahmoud et al.: Proc. Combust. Inst. **35**, 1931 (2015)

Other Flame (Austin)

Flame type

- 1 atm, C_2H_4(50%)/N_2(46%)/air
- Turbulent, non-premixed jet flame
  - Jet exit Re 8,300

Simultaneous SVF + Velocity and SVF + mixture fraction (Z)

- Mixture fraction (Z) / Temperature → Kr-LIF
  - UV (2x214 nm), 1D
  - Calibrated at reference position (jet exit)
  - Density, quenching corrected
- SVF → prompt-LII (532nm, 2D)
  - Calibrated by extinction (632 nm)
- Velocity (532 nm, 3-component, 2D)

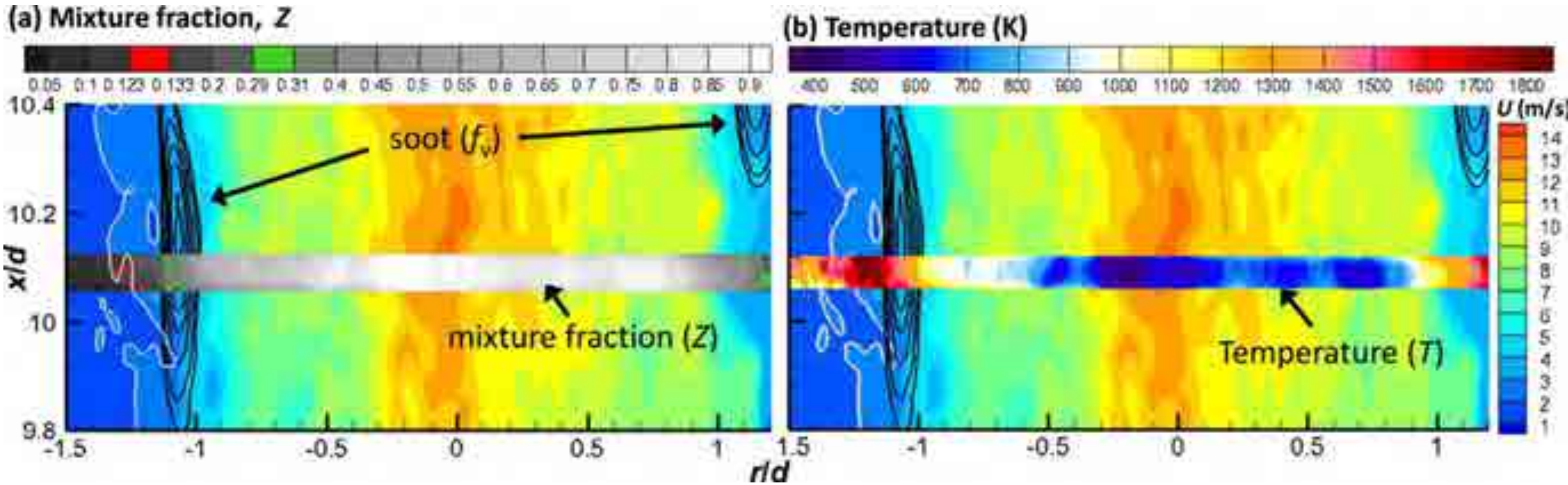
Main focus

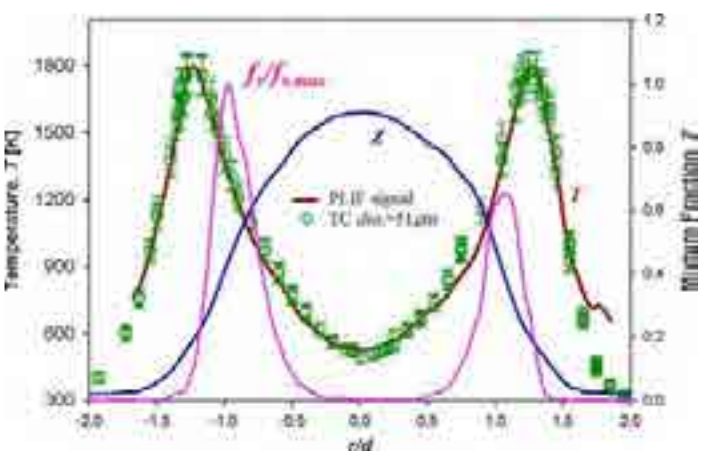
- Kinematics, thermo-physical state, dissipation fields (gradient evaluation) near soot formation regions

Park et al.: Proc. Combust. Inst. **36**, 899 (2017)

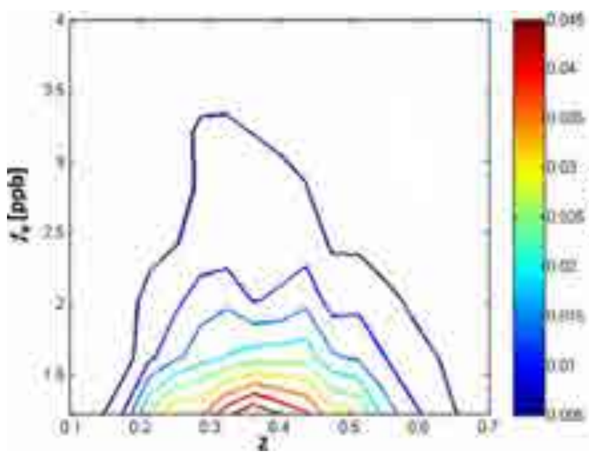
Other Flame (Austin)

Results (x/d = 10)

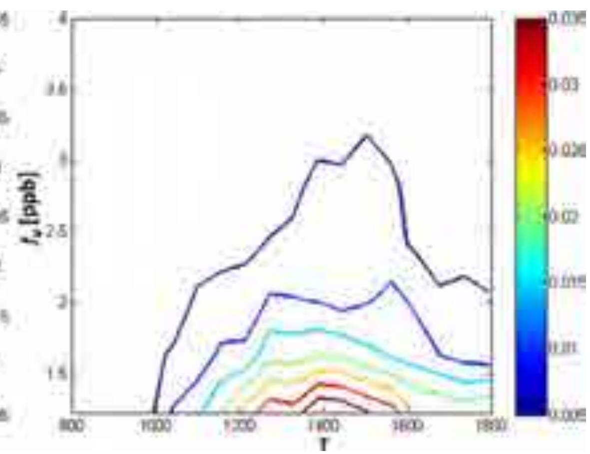




Park et al.: Proc. Combust. Inst. **36**, 899 (2017)



Joint PDF {fv, Z}



Joint PDF {fv, T}

Summary – simultaneous measurements

Benefits

- Improve understanding of soot formation
- Support model developments

Simultaneously measured Quantities	Diagnostic Methods	Spatial Dimen-sions	Data Interpretation
T, Z SVF Velocity	Kr-LIF + strained flame simul. LII 3c-PIV	1 2 2	Contour plots, Spatial profiles (mean / ss), Joint pdf's
T SVF (d_p, N_p)	In-nTLAF (TiRe-)LII	2 2	Contour plot overlays, Mean profiles Joint pdf's
Soot distrib. Velocity	Rayleigh PIV	2 2	Mean flow fields, stream lines, Strain rates
Soot distrib. PAH, OH	LII (2D) UV-PLIF	2 2	Scalar fields (overlays)
OH, PAH Velocity Soot lumen. / Fuel	UV-PLIF PIV LOS Image/Acetone PLIF	2 2 2	Scalar / vector fields (overlays)

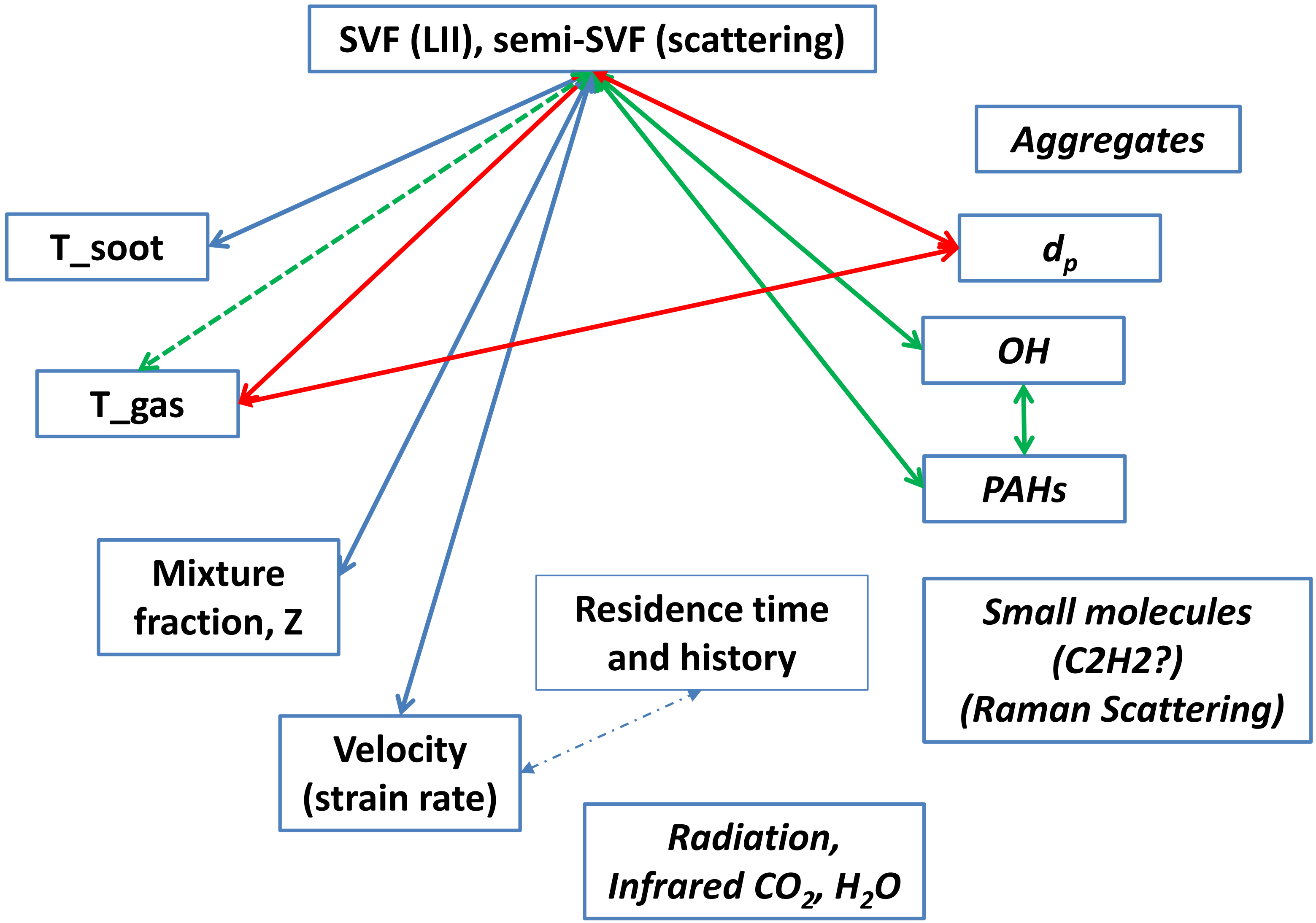
Summary – simultaneous measurements (cont.)

Simultaneously measured Quantities	Diagnostic Methods	Spatial Dimen-sions	Data Interpretation
d_p, Aggregate size SVF, N_p	Two-angle Rayleigh scattering Extinction	0 LOS (1)	Spatial profiles (mean / ss), Size distributions
SVF d_p	TiRe-LII	2	Engine measurements Calibration via point TiRe-LII measurements
d_p, Aggregate size SVF	Two-angle Rayleigh scattering LII	0 1	Spatial profiles (mean / ss), Size distributions
Soot distribution OH	LII LIF	2 2	Engine measurements Imaging (overlays)
SVF d_p Aggregate size	Extinction LII Rayleigh	2 2 2	RAYLIX-method

Discussion: Soot + X

- Which gas phase **X** should we measure simultaneously with soot?
- Do we have a suitable technique, or a potential new technique?
- What kind of results can we get? 2D necessary?
- Is accuracy sufficient to answer our questions?
- …

Simultaneous measurements of soot + X



Outline

- Literature review „Simultaneous measurements“ in turbulent sooting flames
- Open questions/discussion

ISF-4 Target Flame 2 (Sandia)

Dimensions
- Nozzle internal diameter = 3.2 mm
- Inner wall thickness = 0.65 mm
- Pilot outer diameter = 19.1 mm
- Outer wall thickness = 1.95 mm

Fuel jet: Ethylene

Pilot: Ethylene/air at equivalence ratio of 0.9 and thermal power of 2%

Flow Conditions
- Fuel average jet velocity = 54.7 m/s
- Co-flowing air mean velocity = 0.6 m/s
- Exit Reynolds number = 20,000
- Fuel temperature = 294 K

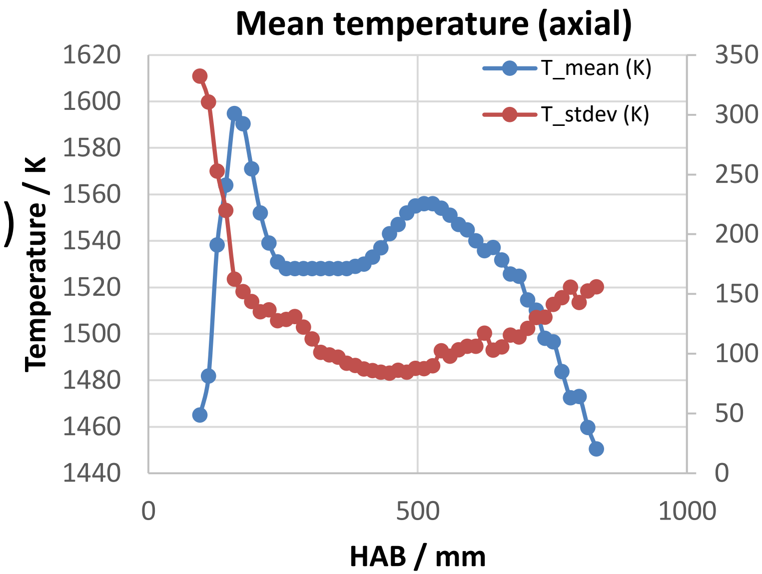
Measurements
- SVF → LII
- Simultaneous SVF and temperature (3-line soot pyrometry)
- OH PLIF
- PAH PLIF
- Radiant emission

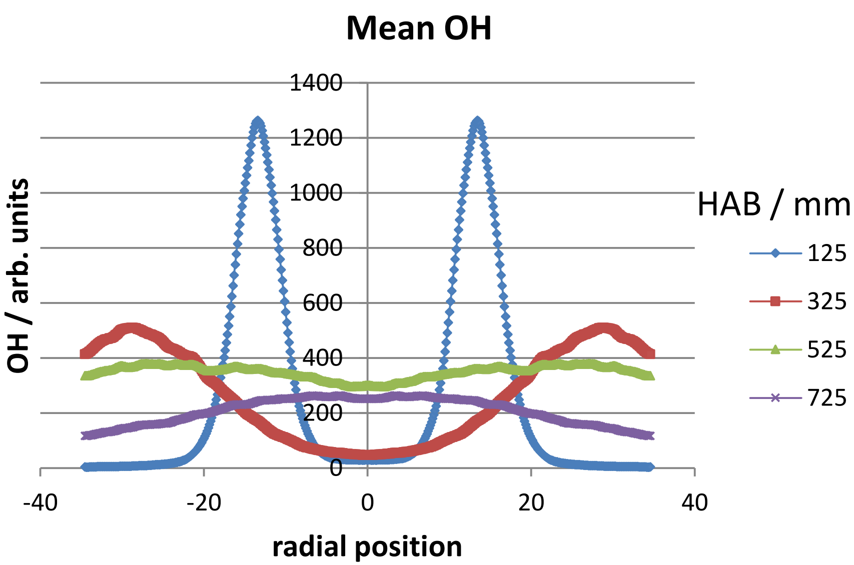
Zhang et al.: Rev. Sci. Instrum. **82**, 074101 (2011)

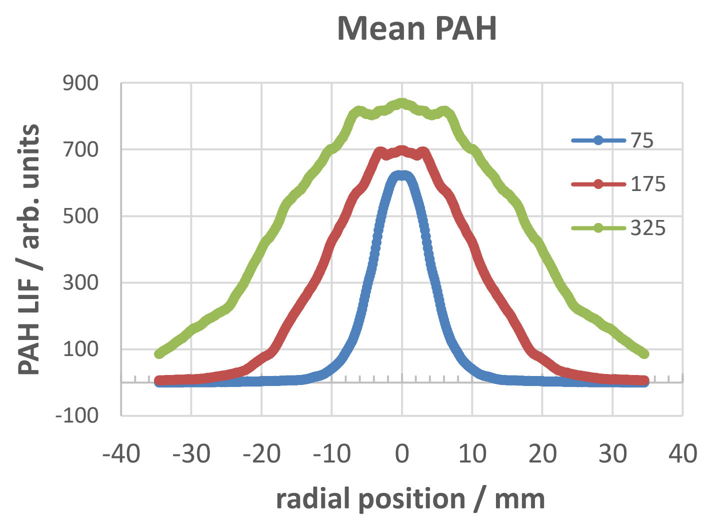
ISF-4 Target Flame 2 (Sandia)

Measurements

- Simultaneous soot volume fraction and temperature (3-line soot pyrometry)
- OH PLIF
- PAH PLIF
- Radiant emission







Zhang et al.: Rev. Sci. Instrum. **82**, 074101 (2011)

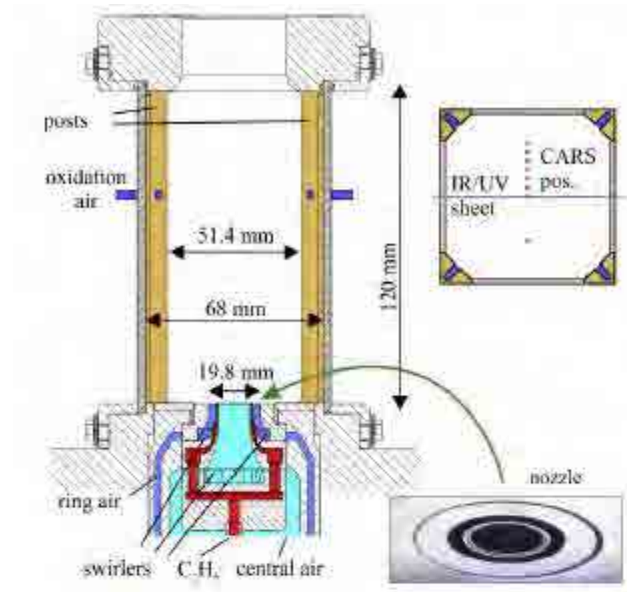
ISF-4 Target Flame 4 (DLR)

Flame type

- Pressurized (3 bar)
- swirl

Measured Parameters

- Temperature → CARS (pointwise)
- Flame structure → OH-LIF (2D)
- SVF → LII (2D)



Main focus

- Effect of injection of secondary oxidation air
  - Fuel-rich product gas stream of prim. combust. Zone

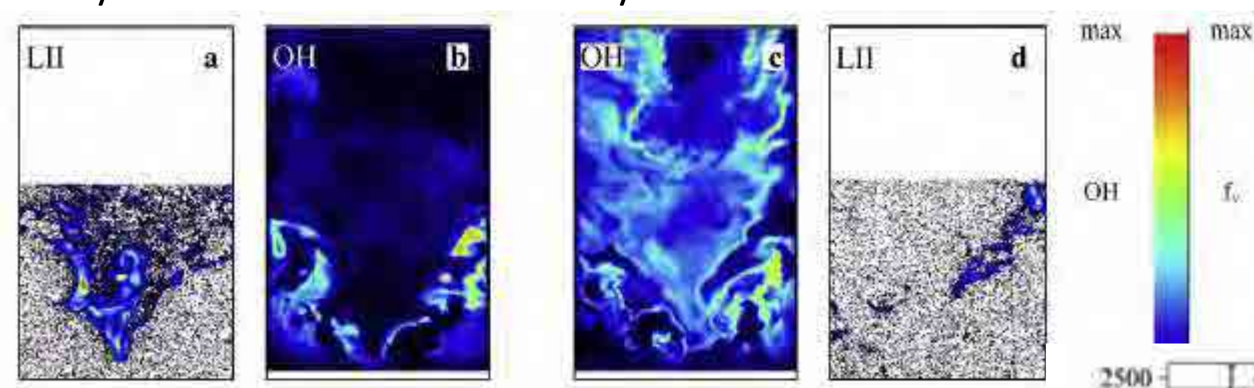
Geigle et al.: Proc. Combust. Inst. **35**, 3373 (2015)

ISF-4 Target Flame 4 (DLR)

Results

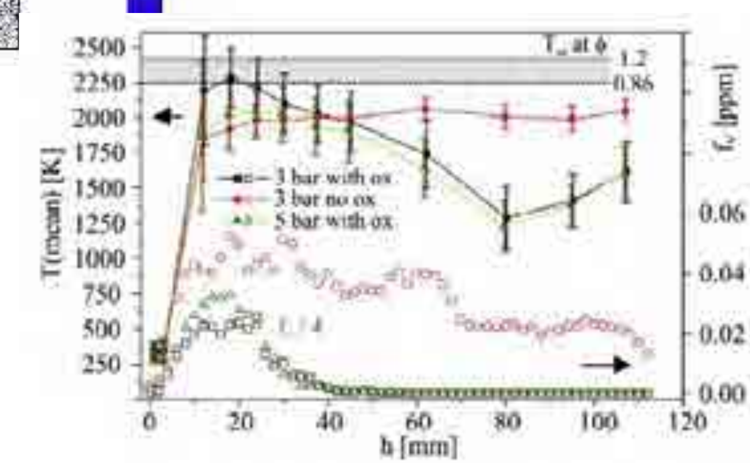
- Filament-like LII regions without OH
  - Found between primary combustion zone (fed by combustion air and ethylene) and inner recirculation zone (oxidation air + transported unburned hydrocarbons (UHC)

w/o w/ oxidation air



3 bar, instantaneous values

- Combined temperature (mean) / f_v-profiles



Geigle et al.: Proc. Combust. Inst. **35**, 3373 (2015)

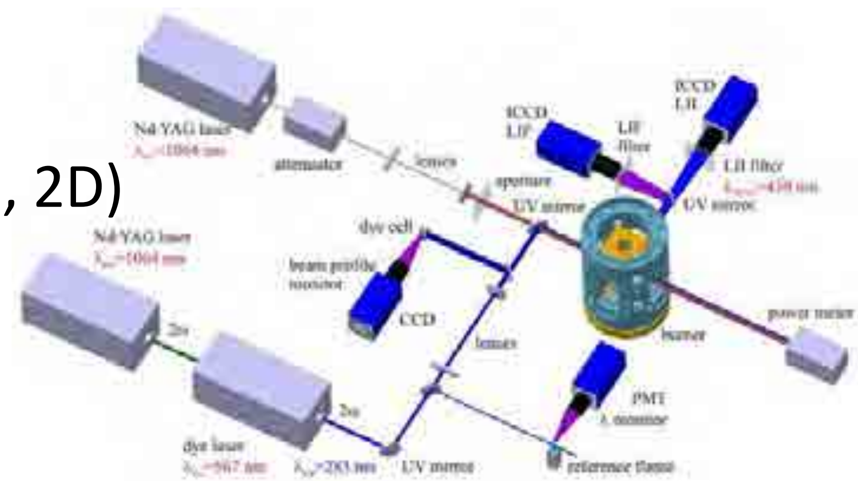
ISF-4 Target Flame 4 (DLR)

Flame type

- Pressurized (3 bar)
- swirl

Measured Parameters

- Soot distribution → LII (1064 nm, 2D)
- PAH → UV-LIF (2D)
- OH → UV-LIF (2D)



Main focus

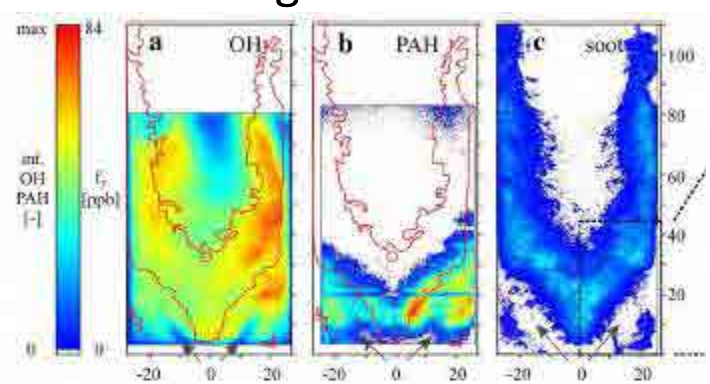
- Effect of injection of secondary oxidation air
- Correlations between quantities

Geigle et al.: Appl. Phys. B **119**, 717 (2015)

ISF-4 Target Flame 4 (DLR)

Results

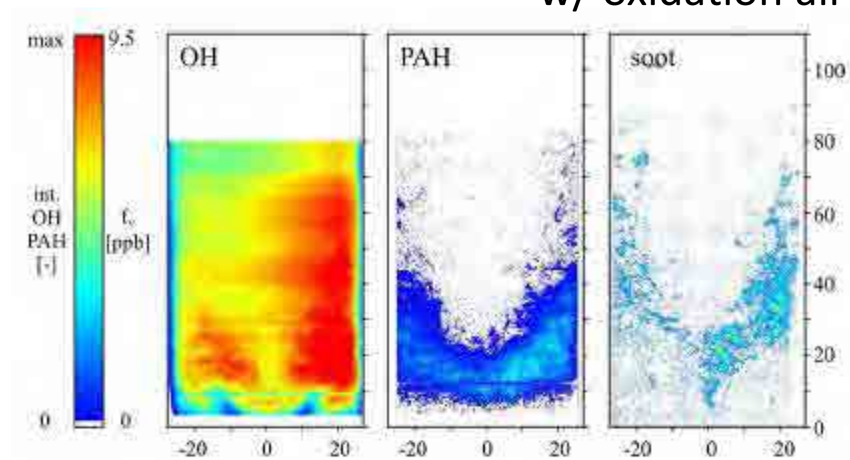
- PAH signatures discontinuous
  - Contrary to OH
- Identification of wide range of soot formation progress
  - Isolated soot/PAH as well as transitioning
- Occurance and distributions strongly dependent on flow field characteristics
  - Distinguish between transport and soot chemistry!



Prim. rich
w/ oxidation air

Geigle et al.: Appl. Phys. B **119**, 717 (2015)

Moderately lean
w/ oxidation air



Ensemble-averaged

ISF-4 Target Flame 4 (DLR)

Flame type

- Pressurized (3 bar)
- swirl

Measured Parameters

- Soot distribution → Rayleigh scattering (532 nm, 2D)
- Velocity → Stereo PIV (cold, reactive, 2D)

Main focus

- Effect of injection of secondary oxidation air
- Correlations between quantities

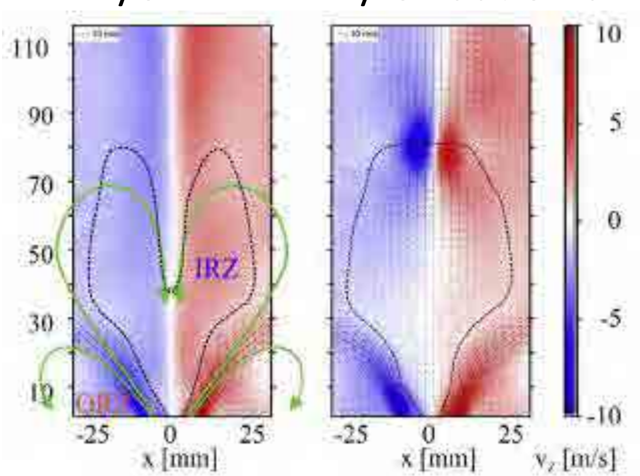
Geigle et al.: Proc. Combust. Inst. **36**, 3917 (2017)

ISF-4 Target Flame 4 (DLR)

Results

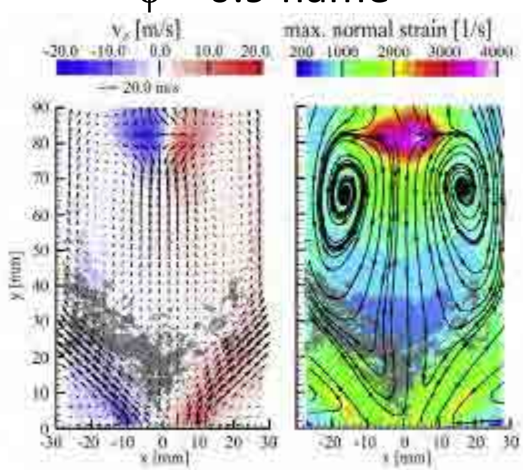
- Secondary air injection separates flow field
  - Stagnation zone: upwards / downwards transport
  - Flow field POD-analysis
  - Prescence of a PVC → impacts soot distribution
- Soot present in high strain rate regions due to transport
  - Soot mainly formed in inner rich recirculation zones

w/o w/ oxidation air



Geigle et al.: Proc. Combust. Inst. **36**, 3917 (2017)

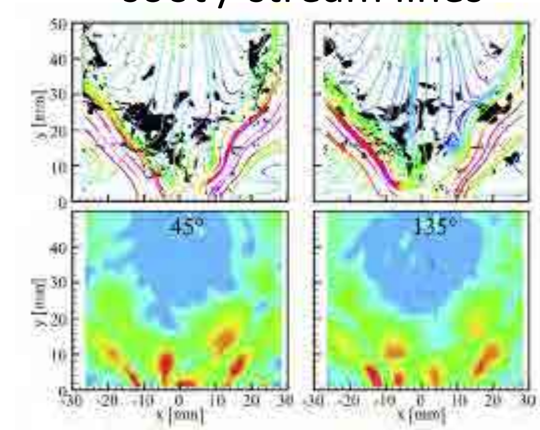
ϕ = 0.9 flame



Mean flow field + soot

Stream/ Strain lines

Phase-resolved soot / stream lines



Local extensive strain rates

ISF-4 Other Flame 2 (DLR)

Flame type

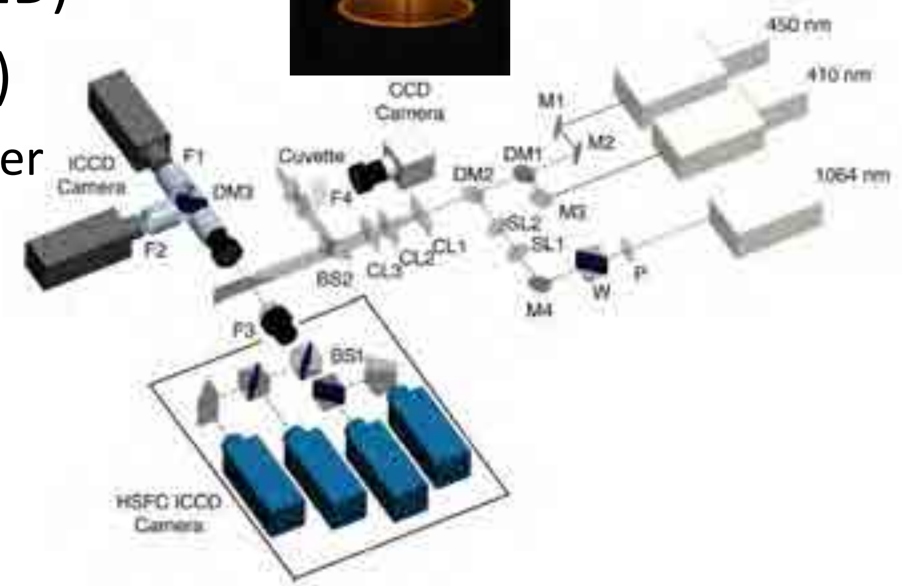
- 1 atm, Ethylene/air (non-prmxd)
- Lifted (26.3 mm) jet flame (Re 10,000)
  - Fuel mass flow: 10.4 g/min

Measured Parameters

- Temperature → nTLAF (In, VIS, 2D)
- SVF → prompt-LII (1064 nm, 2D)
  - TiRe-LII → Primary particle diameter
  - Number density (N_p)

Main focus

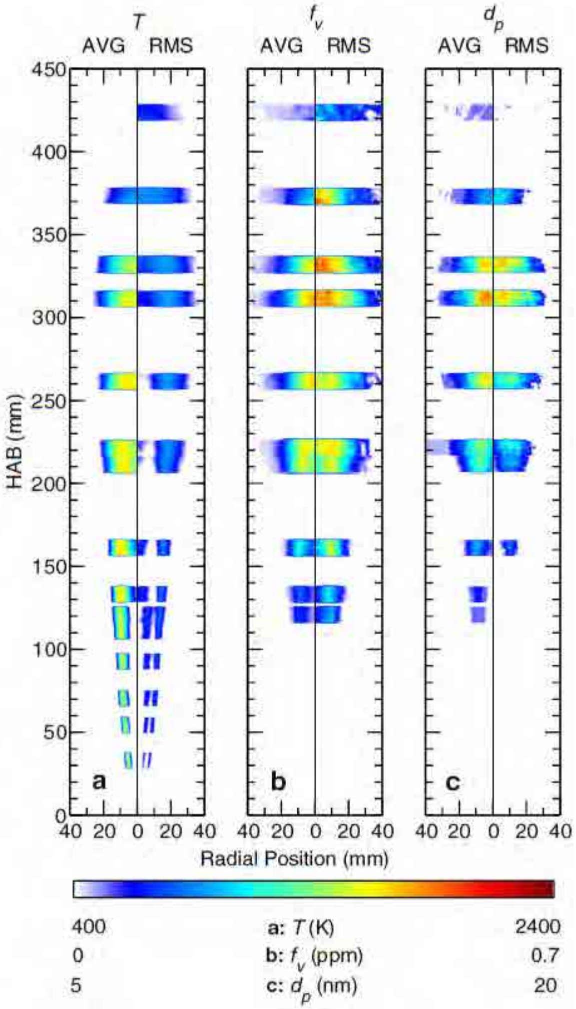
- Measurement accuracy
- Joint statistics (pdf's), e.g., {T, f_v}

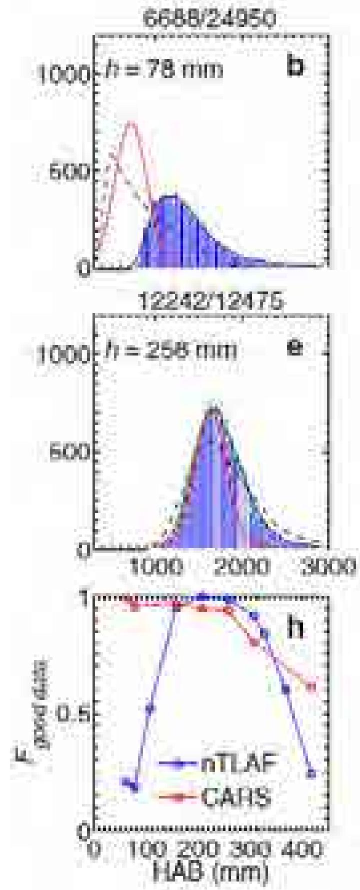


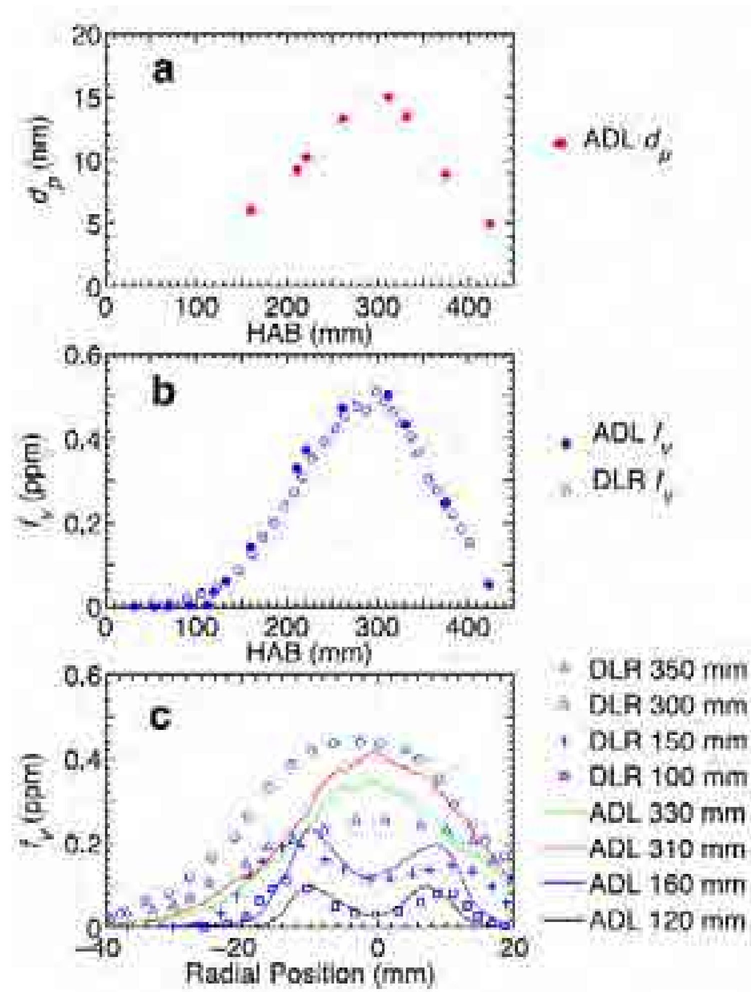
Gu et al.: Combust. Flame **179**, 33 (2017)

ISF-4 Other Flame 2 (DLR)

Results





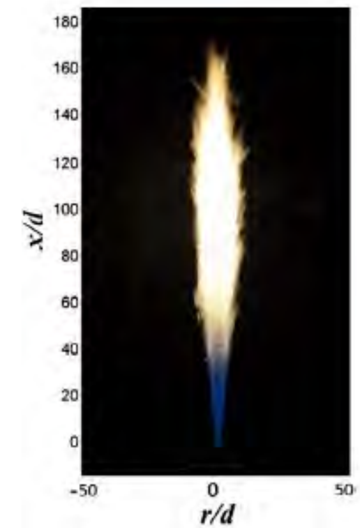


Gu et al.: Combust. Flame **179**, 33 (2017)

ISF-4 Target Flame 1 (Adelaide)

Flame type

- 1 atm, $C_2H_4/H_2/N_2$/air (non-prmxd)
- Lifted jet flame
  - Jet exit Re 5,000 – 15,000
  - Exit strain rate: 4,100 – 12,900 s^{-1}

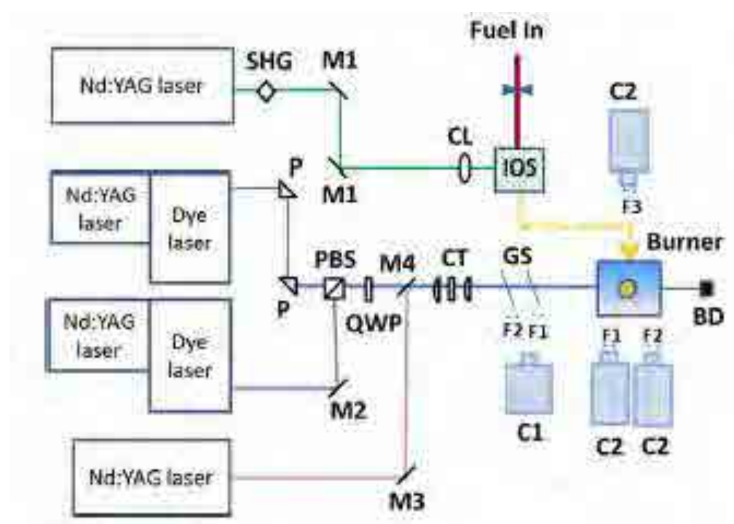


Measured Parameters

- Temperature → nTLAF (In, VIS, 2D)
- Soot f_v → prompt-LII (1064 nm, 2D)

Main focus

- Soot – temperature correlation
- {T, SVF} joint pdf's

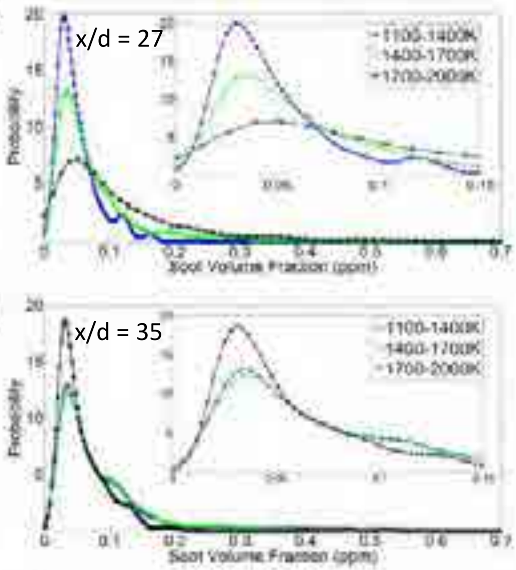


Mahmoud et al.: Proc. Combust. Inst. **35**, 1931 (2015)

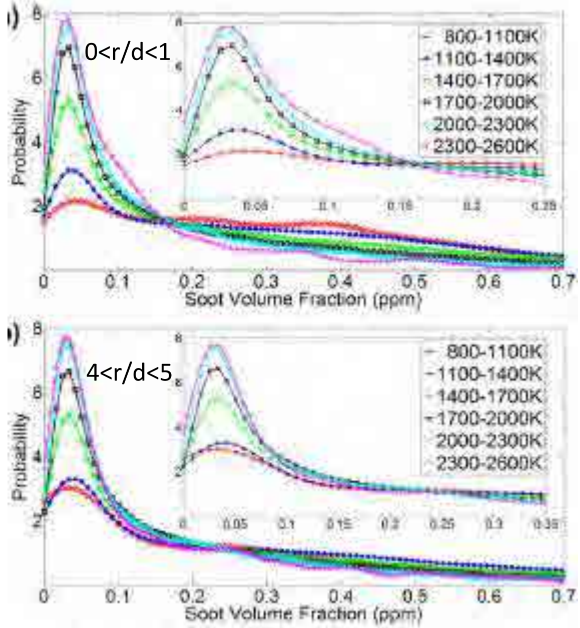
ISF-4 Target Flame 1 (Adelaide)

Results

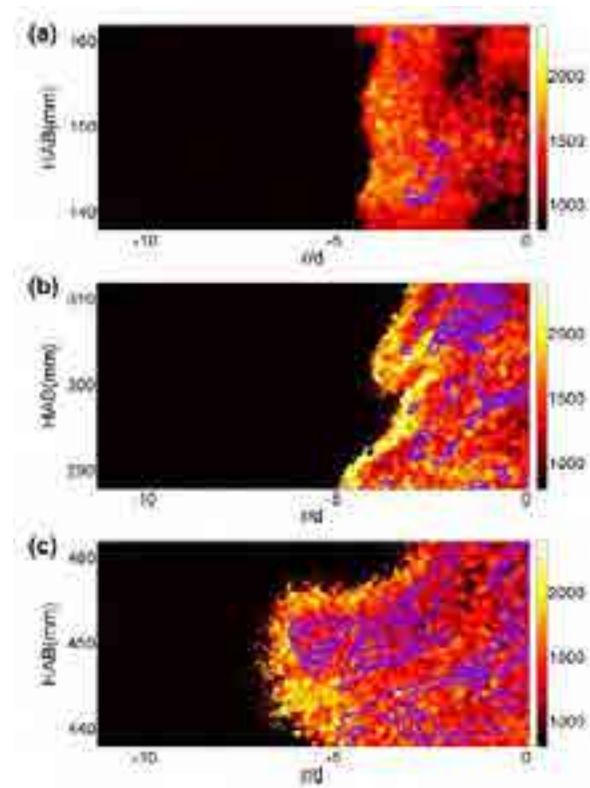
- Single-shot T, SVF fields
- Axial / radial mean SVFs
  - Strong T-influence of fv
  - SVF is function of T and axial distance



@ r/d = 0



@ x/d = 100



Mahmoud et al.: Proc. Combust. Inst. **35**, 1931 (2015)

Other Flame (Austin)

Flame type

- 1 atm, C_2H_4(50%)/N_2(46%)/air
- Turbulent, non-prmxd jet flame
  - Jet exit Re 8,300

Measured Parameters

- Mixture fraction (Z) / Temperature → Kr-LIF
  - UV (2x214 nm), 1D
  - Calibrated at reference position (jet exit)
  - Density, quenching corrected
- SVF → prompt-LII (532 nm, 2D)
  - Calibrated by extinction (632 nm)
- Velocity (532 nm, 3-component, 2D)

Main focus

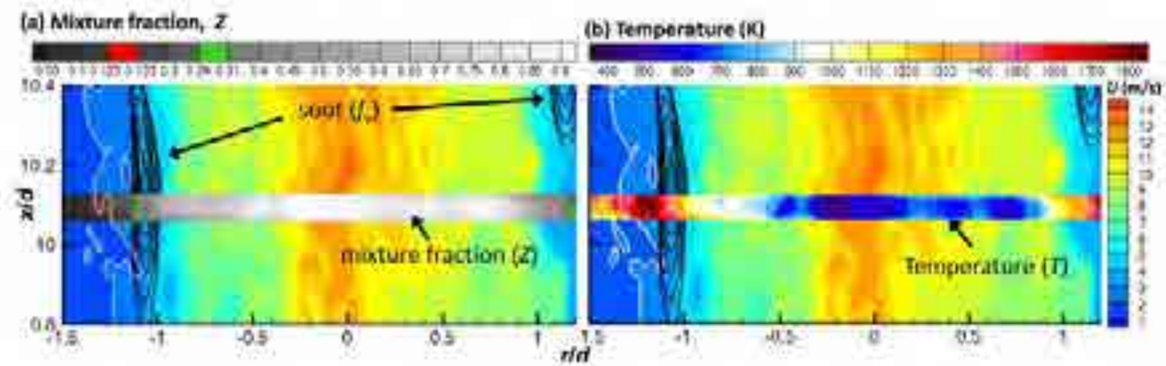
- Kinematics, thermo-physical state, dissipation fields (gradient evaluation) near soot formation regions

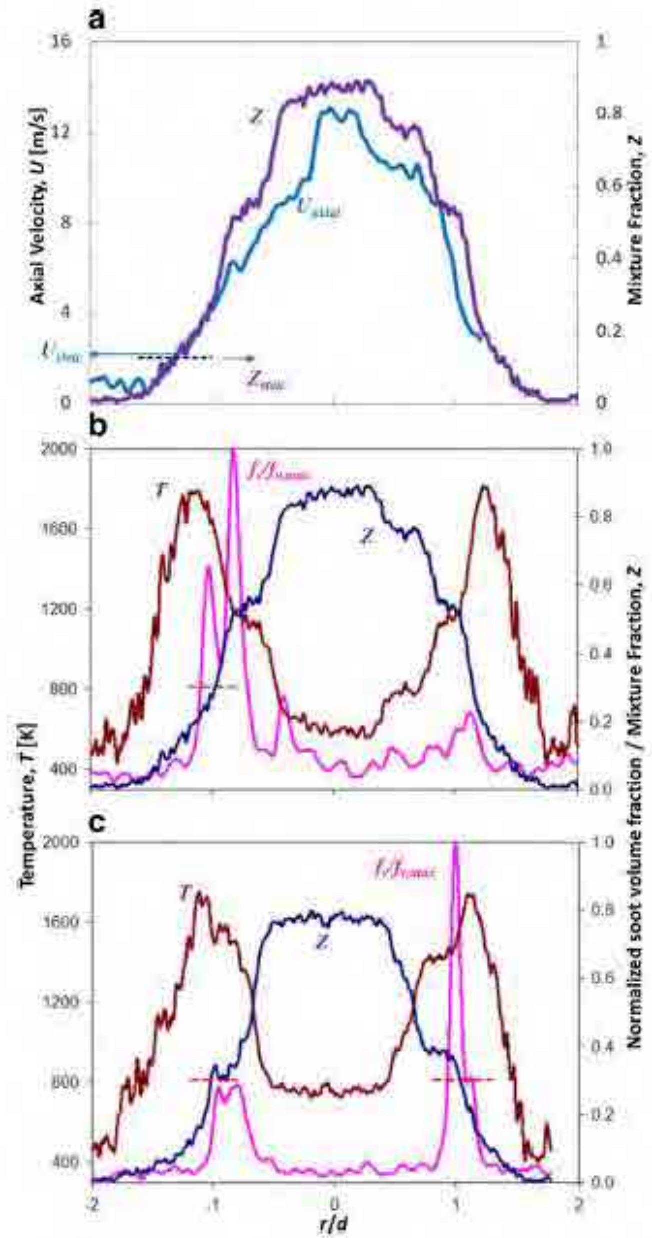
Park et al.: Proc. Combust. Inst. **36**, 899 (2017)

Other Flame (Austin)

Results

- Contour plot (below) of Axial **Velocity** + **SVF**
  - Overlaid:
    <u>left</u>: **mixture fraction** (1 mm height)
    <u>right</u>: **temperature**
- Single-shot profiles
  - Peak soot associated with rich side of flame
  - f_v peaks around Z of soot precursor species → also seen in mean profiles





Park et al.: Proc. Combust. Inst. **36**, 899 (2017)

Summary – simultaneous measurements

Benefits

- Improve understanding of soot formation
- Support model developments

Simultaneously measured Quantities	Diagnostic Methods	Spatial Dimen-sions	Data Interpretation
T, Z SVF Velocity	Kr-LIF + strained flame simul. LII 3c-PIV	1 2 2	Contour plots, Spatial profiles (mean / ss), Joint pdf's
T SVF (d_p, N_p)	In-nTLAF (TiRe-)LII	2 2	Contour plot overlays, Mean profiles Joint pdf's
Soot distrib. Velocity	Rayleigh PIV	2 2	Mean flow fields, stream lines, Strain rates
Soot distrib. PAH, OH	LII (2D) UV-PLIF	2 2	Scalar fields (overlays)
OH, PAH Velocity Soot lumen. / Fuel	UV-PLIF PIV LOS Image/Acetone PLIF	2 2 2	Scalar / vector fields (overlays)

Summary – simultaneous measurements (cont.)

Simultaneously measured Quantities	Diagnostic Methods	Spatial Dimen-sions	Data Interpretation
d_p, Aggregate size SVF, N_p	Two-angle Rayleigh scattering Extinction	0 LOS (1)	Spatial profiles (mean / ss), Size distributions
SVF d_p	TiRe-LII	2	Engine measurements Calibration via point TiRe-LII measurements
d_p, Aggregate size SVF	Two-angle Rayleigh scattering LII	0 1	Spatial profiles (mean / ss), Size distributions
Soot distribution OH	LII LIF	2 2	Engine measurements Imaging (overlays)
SVF d_p Aggregate size	Extinction LII Rayleigh	2 2 2	RAYLIX-method

Discussion – burning issues

Combination of diagnostics techniques

- Which combination of techniques might be the most useful?
  - E.g., a strong discrepancy between mean gas phase and mean soot → correlation between gas phase and soot is not correct
- Chemistry: PAH-based models vs. acetylene-based models
  - Variation in soot predictions are far greater than variances in other predictions (e.g., temperature, etc.)
- …

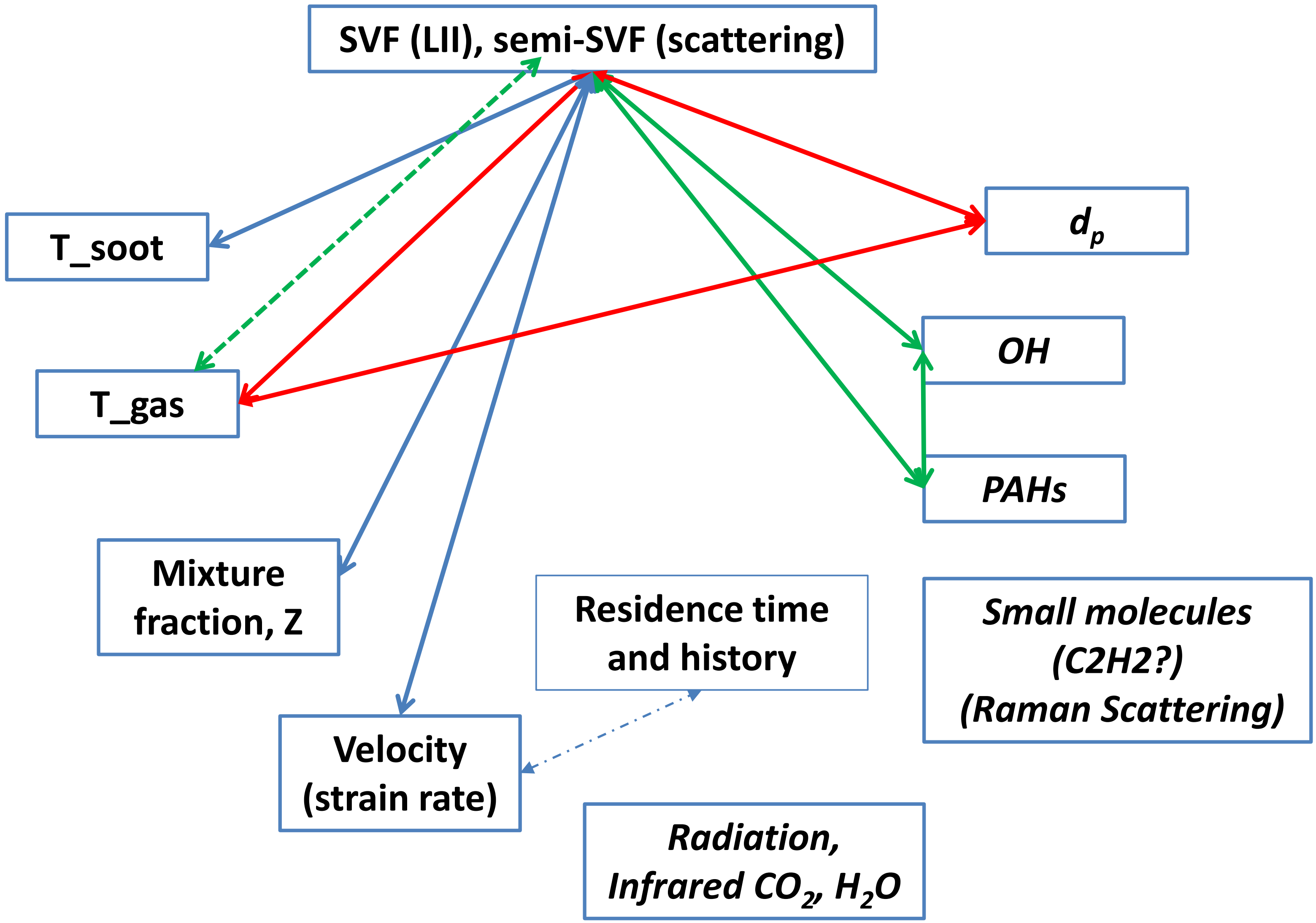
➡ What do we really need to measure to help better understand soot?

Discussion – burning issues (2)

Looking ahead

- Do we better understand what we know / not know w.r.t.
  - Modeling soot / turbulence / chemistry interaction?
  - What experimental measurements do we need
  - Are there specific configurations that will isolate phenomena we do not know much about?
- …

Simultaneous measurements of soot + X



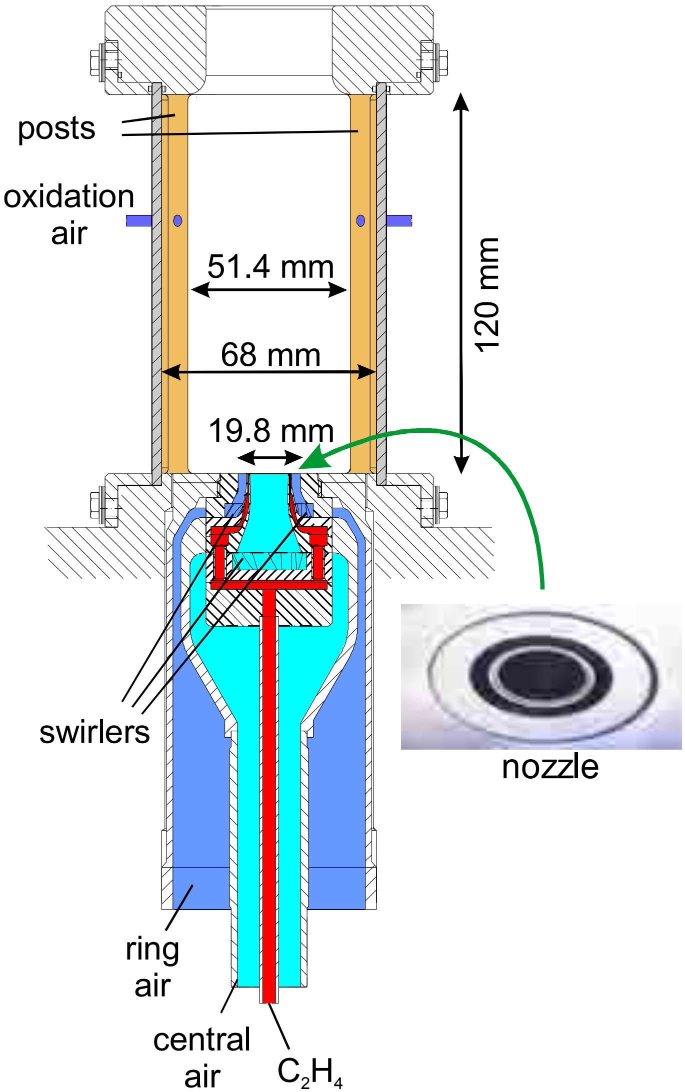
Complementing diagnostics for DLR pressurized swirling flame, ISF4 target flame 4

Achievements past ISF3:

- Combustor window temperatures by phosphor thermometry: Nau et al. APB 2017
- Time history of flow field, OH and soot: Stöhr et al. PROCI 2019, accepted

Plans past ISF4:

- Monitoring of fuel/air mixture

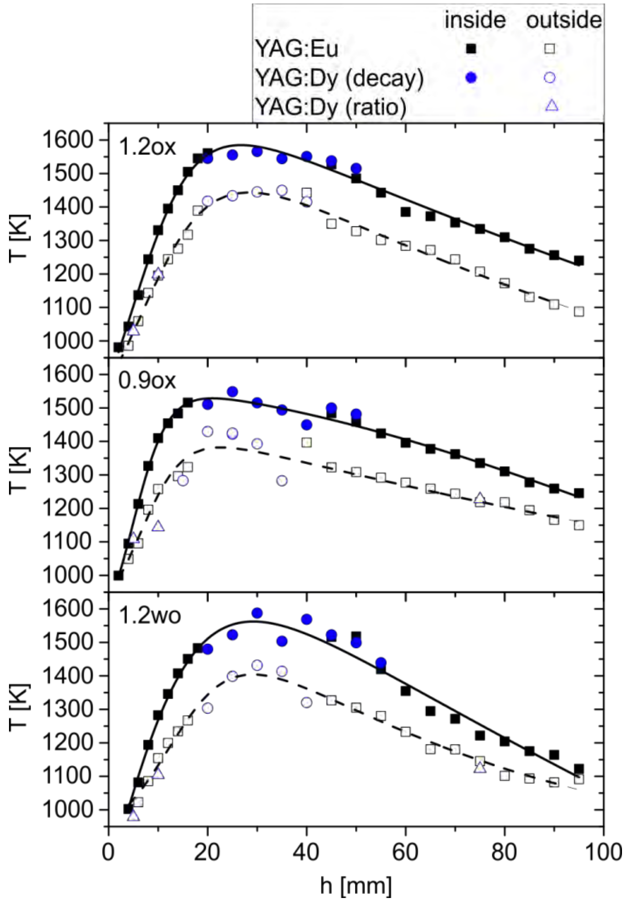


DLR

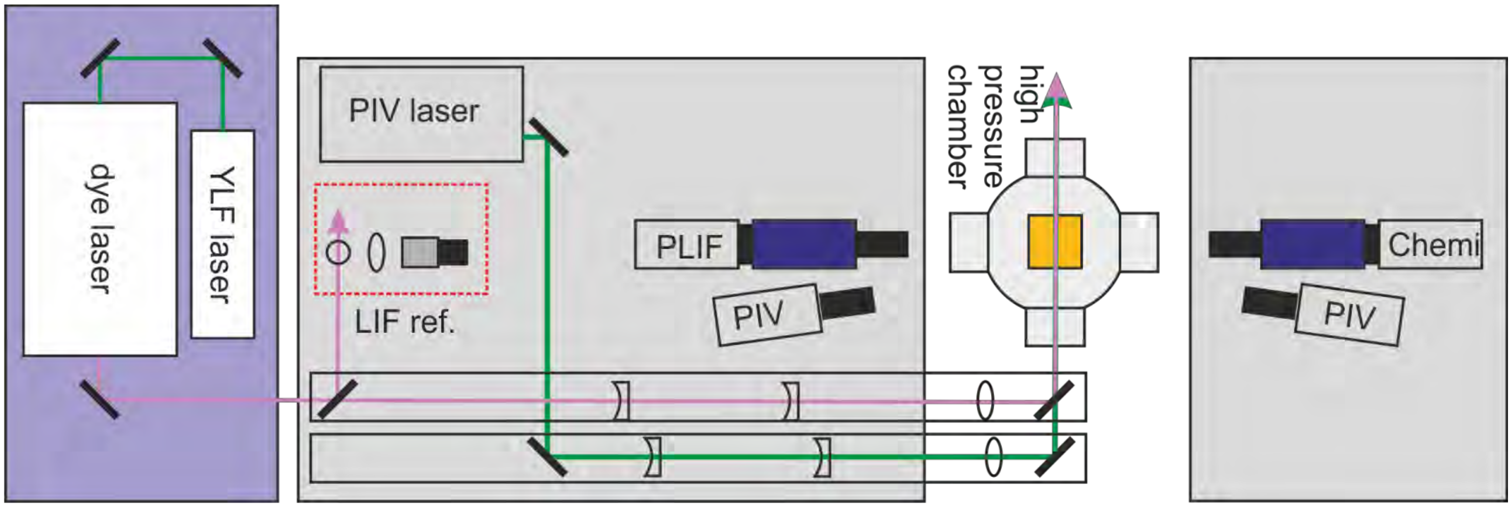
Nau et al. Appl. Phys. B 2017

Window temperature measurements

- Measurements along vertical window axis
- Inside and outside surface
- 3 operating conditions
    - 3 bar, ϕ=1.2, with oxidation air
    - 3 bar, ϕ=0.9, with oxidation air
    - 3 bar, ϕ=1.2, without oxidation air
- Challenging, very hot temperatures where flame impinges on window surface i.e. very short signal
- Good agreement of peak temperatures with visual surface damage



Coupled kHz laser diagnostics for soot monitoring



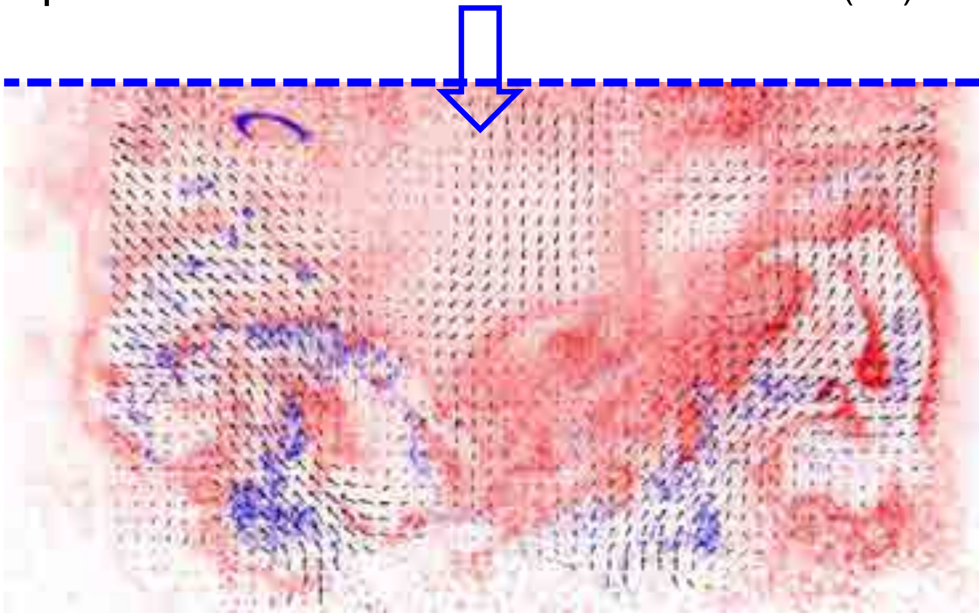
- PIV excitation at 532 nm, 9 mJ/pulse at 9.3 kHz (Edgewave)
- PIV detection: Lavision HSS8
- Soot luminescence detection at 450 nm (Lavision HSS6 plus HS-IRO)
- OH excitation at 283.2 nm, 280 µJ/pulse at 3.1 kHz (Edgewave/Sirah)
- OH detection: Lavision HSS 6 plus HS-IRO

Stöhr et al. PCI 2019, accepted
LES: Grader et al., ISF Poster
Exp: Geigle et al., ISF Poster

Results from kHz diagnostics

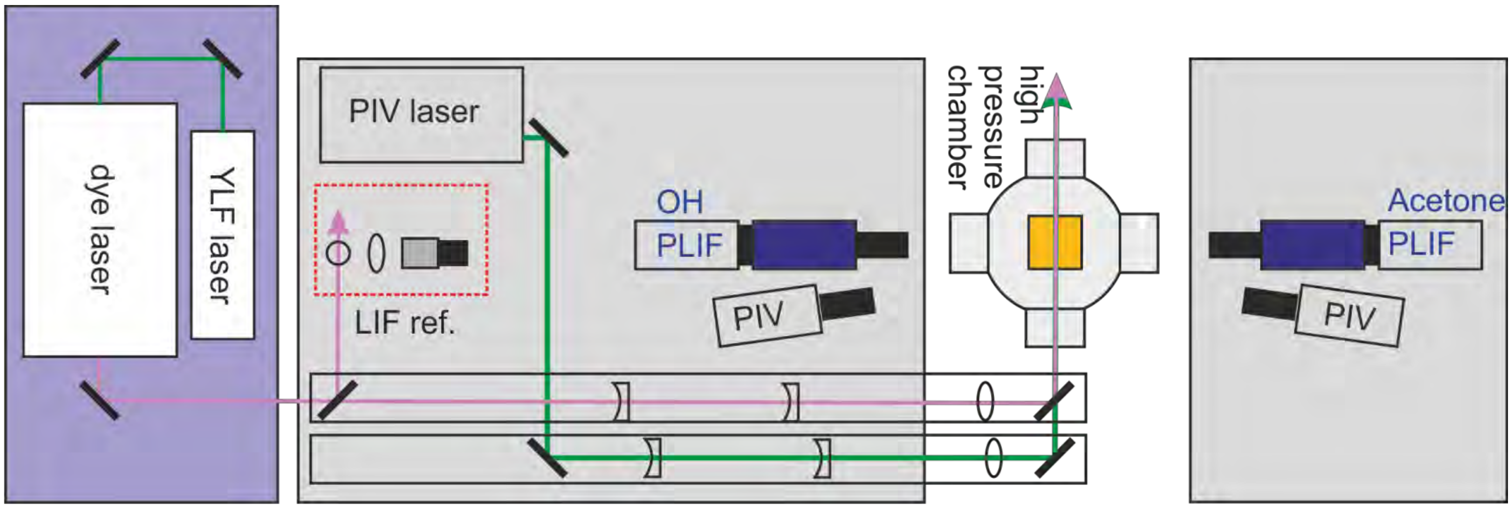
- Dense-seed packages (fresh gas) leak into post-flamefront regions / pockets of low OH → fuel rich zones between primary and secondary combustion
- Soot frequently aligns with edges of OH distribution → oxidation
- Soot can also be present in regions of OH
- Frequent upstream propagation of soot pockets
- Soot comes and goes in waves
- Integrated backflow is inversely correlated with soot formation → effect of oxidation air on local equivalence ratio → jet flapping (!)
- Tracking of zones of rich burnt gases and correlation with soot formation is possible

Red: OH
Dotted blue: fresh gas
Blue filaments: soot
Arrows: flow field (3C)



DLR

Coupled kHz laser diagnostics for soot monitoring



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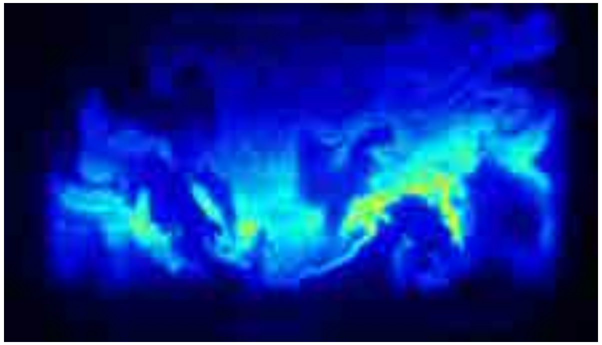
- PIV detection: Lavision HSS8
- Soot luminescence detection at 450 nm (Lavision HSS6 plus HS-IRO)
- OH excitation at 283.2 nm, 280 µJ/pulse at 3.1 kHz (Edgewave/Sirah)
- OH detection: Lavision HSS 6 plus HS-IRO

Air/fuel mixture

- Use acetone seeding into C_2H_4 to image fuel distribution and mixture with combustion air (acetone LIF)
- Combine with information on OH (LIF), soot and flow field (PIV)
- High (kHz) repetition rates to spatially resolve turbulent structures and deduce full statistical convergence
- Reference operating point at 3 bar, ϕ=1.2, with oxidation air
- 10% of total fuel is acetone, air flows as in reference conditions – soot certainly different
- Data evaluation ongoing



OH LIF

Acetone LIF

Challenges

- What should be measured?
  - How do we make "TNF" measurements in sooting flames?
    - Maybe this is not even possible…
    - Are there lesser techniques not utilized in non-sooting flames that would be appropriate for sooting flames?
  - Should we make measurements in a family of flames ranging from non-sooting to sooting with the same basic flame structure?
    - "TNF" measurements in the non-sooting flames
    - "ISF" measurements in the sooting flames
    - What would be a suitable flame series in terms of configurations, fuels, etc. considering both experimental and computational constraints?
    - What would be the best parameter to vary from sooting to non-sooting?

A range of flame experiments

	non-premixed ..premixed	Examples	Measurements	Fuel	Pressure
jet		TUD, Sandia, DLR	T Y_i U OH NO	CH_4 H_2	
piloted jet/bluff		Sandia/TUD C-F, Cabra PPJB, DJHC	T Y_i U OH NO	CH_4 H_2 DME CO CH_3OH	
stratified		TUD, CAM, Sydney	T Y_i U OH CH2O	CH_4 CH_4 H_2	
technical		TECFLAM, PRECCIINSTA, GTMC, Siemens, NASA LDI	T Y_i U OH CH2O	CH_4 H_2	P
soot		DLR-Adelaide DJHC, DLR-RQL	T f_v OH	CH_4 C_2H_4	P
spray		Sydney, Cambridge, DLR, DHSC, NASA LDI, CORIA	T* U d OH CH2O	Ethanol, methanol, alkanes, jet A1	P

50,000 <Re <100,000

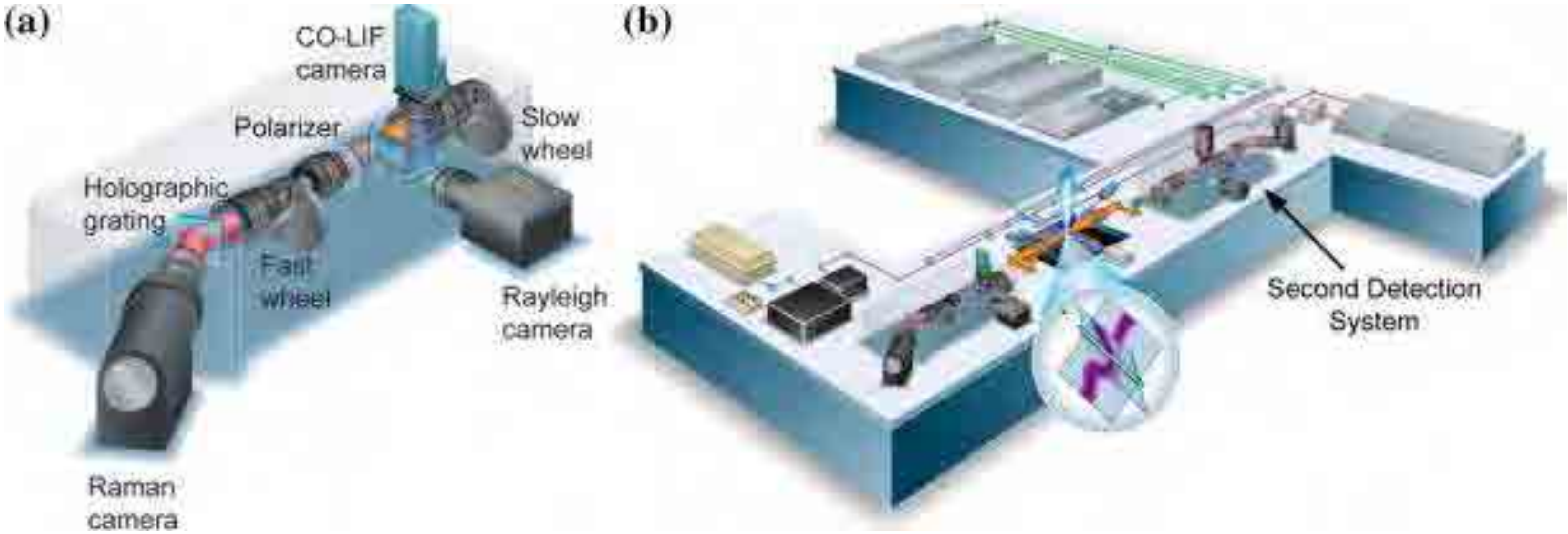
10 <Ka <5000

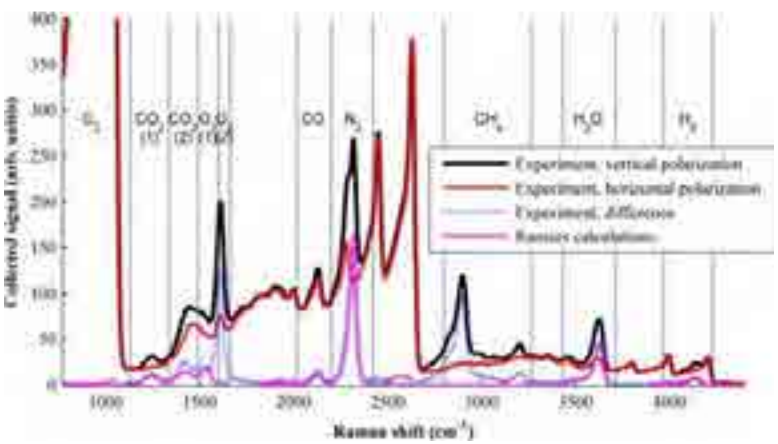
Radiant background!

Measurement techniques for radiant backgrounds

				Resolution	Pros/Cons	Cost	Expertise
correlation	PIV	**u**	velocity	kHz, µm..mm (image)	High signal *Radiant interference*	$$	-
correlation	LDA	**u**	velocity	kHz, µm..mm (point)	High signal *Radiant interference*	$$	-
scattering	LIF	Y,T	selected species mass fraction temperature	kHz, 0.1-1 mm	Good signal *Species specific* *Quenching, calibration*	$$	+
scattering	Rayleigh	T,ρ	density, temperature	(k)Hz, 0.1-1 mm	Simple bulk technique *Low signal*	$$	++
scattering	Raman	**Y**, T	major species mass fraction, temperature	Hz, 0.1-1 mm	Multiple species *Low signal* *Many interferences*	$$$	+++
coherent	CARS	**Y**, T	major species mass fraction, temperature	(k)Hz, 1 mm	Coherent *Alignment*	$$$$	+++
coherent	LIGS LIEGS	T	temperature	Hz, 1-5 mm	Coherent *Needs absorber/low signal* *Alignment*	$$	++
coherent	DFWM	Y	selected species mass fraction	Hz, 1-5 mm	Coherent *Species specific* *Alignment*	$$	++

Polarization separation – remove C_2 bands

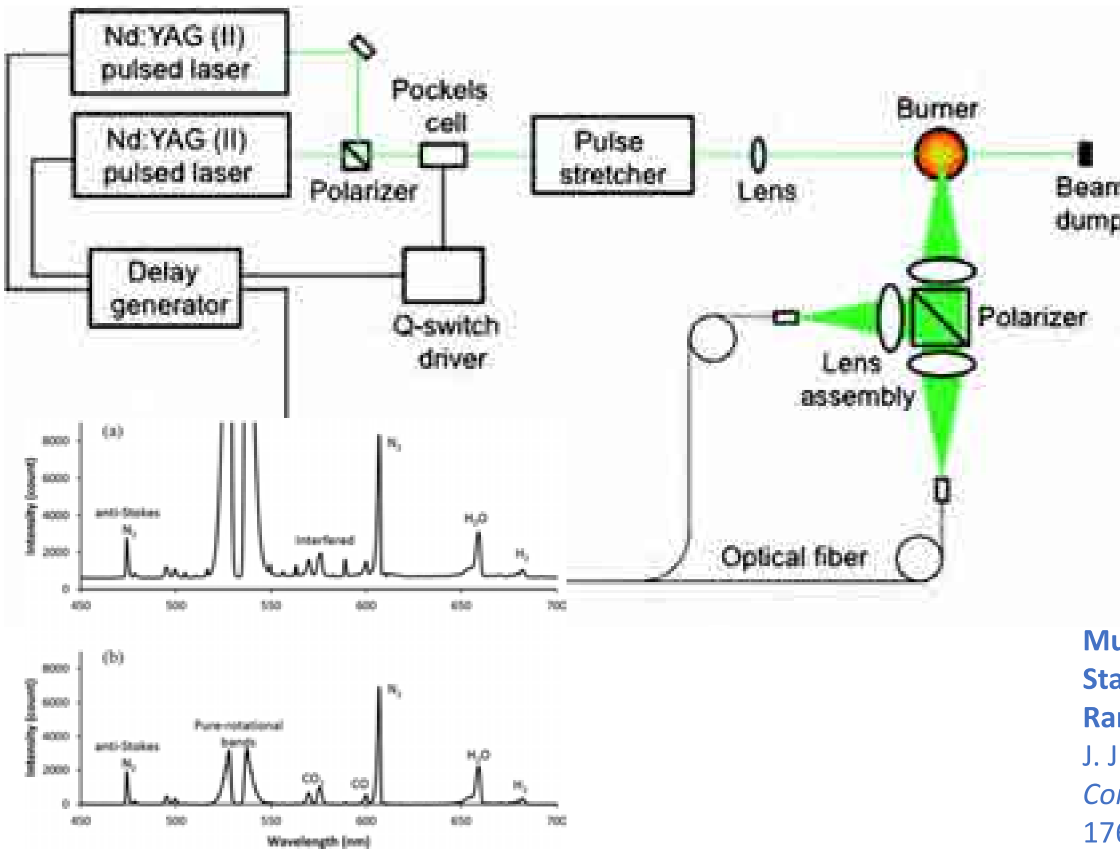


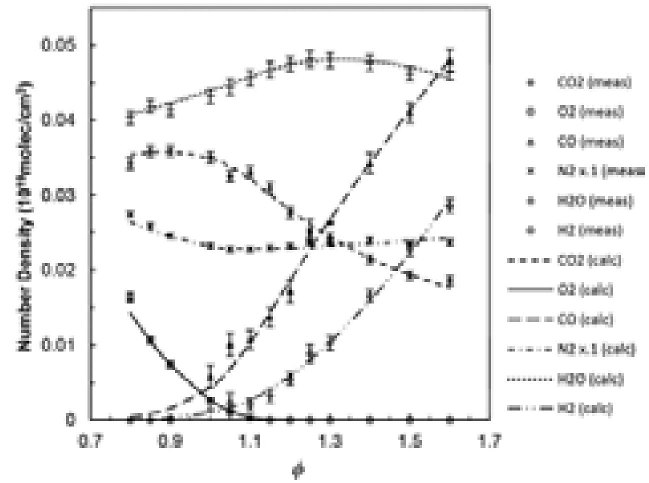


Higher accuracy (no interference)
Lower precision (loss of signal)

Interference free spontaneous Raman spectroscopy for measurements in rich hydrocarbon flames
G. Magnotti and D. Geyer and R. S. Barlow
Proceedings of the Combustion Institute **35** 3765 - 3772 (2015)

Dual SBG Raman spectroscopy + polarization

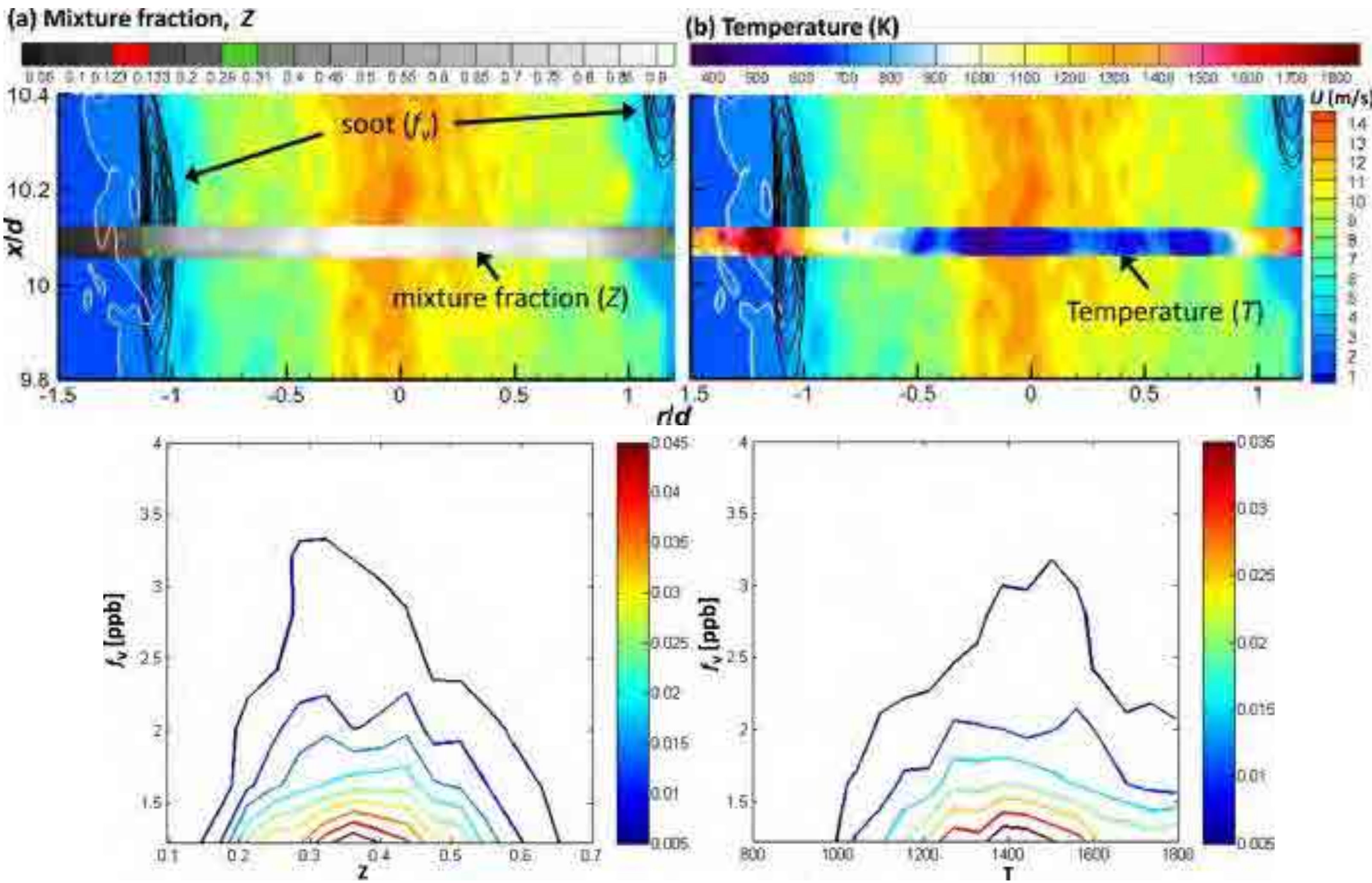




Multiscalar Analyses of High-Pressure Swirl-Stabilized Combustion via Single-Shot Dual-SBG Raman Spectroscopy
J. J. Kojima and D. G. Fischer
Combustion Science and Technology **185** 1735-1761 (2013)

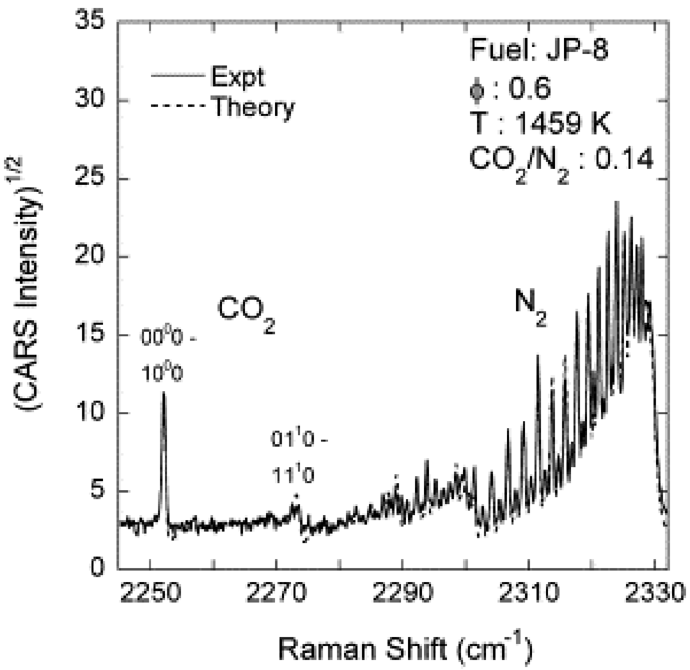
Subframe burst gating (stokes+anti-stokes)
Removal of interferences from fluorescence

Kr-LIF (soot and mixture fraction)

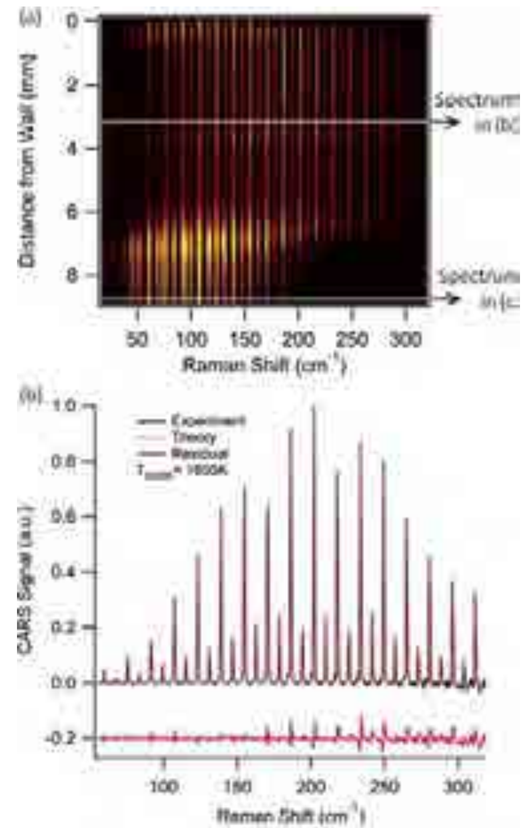


O. Park and R. A. Burns and O. R. H. Buxton and N. T. Clemens
Proceedings of the Combustion Institute **36** 899-907 (2017)

Dual pump and PS/FS CARS



S. Roy and T. R. Meyer and R. P. Lucht and V. M. Belovich and E. Corporan and J. R. Gord
Combustion and Flame **138** 273 - 284 (2004)



A. Bohlin and B. D. Patterson and C. J. Kliewer
The Journal of Chemical Physics **138** (2013)

Dual pump: downstream of flame

PS/FS: possibly workable in sooty flames

LIGS in flames

Pump energy = 100-200 mJ, Probe power = 2 W

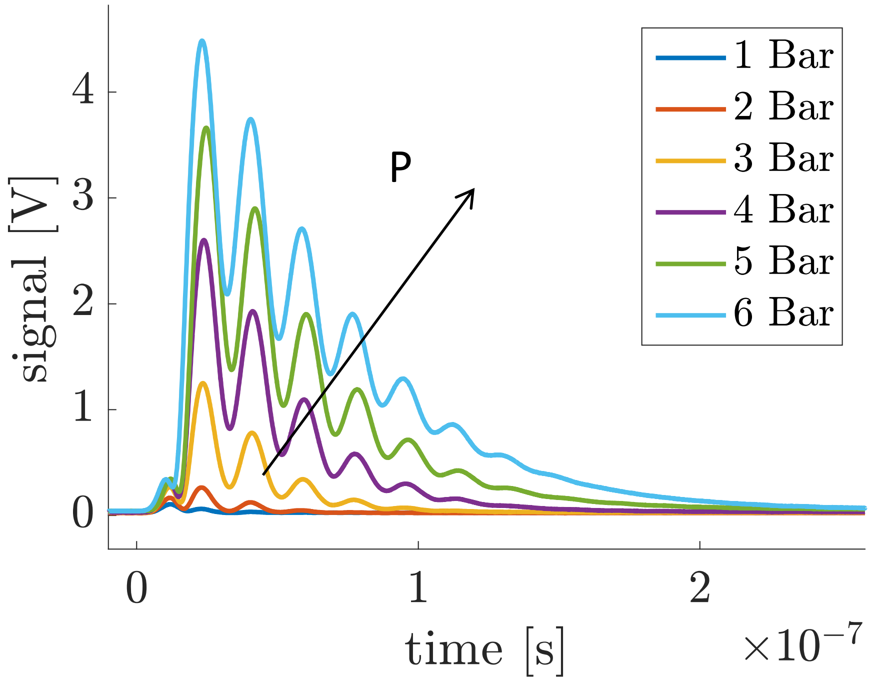
$$SIGNAL\ INTENSITY:\ I \leftrightarrow \rho^2 = \left(\frac{P}{RT}\right)^2$$

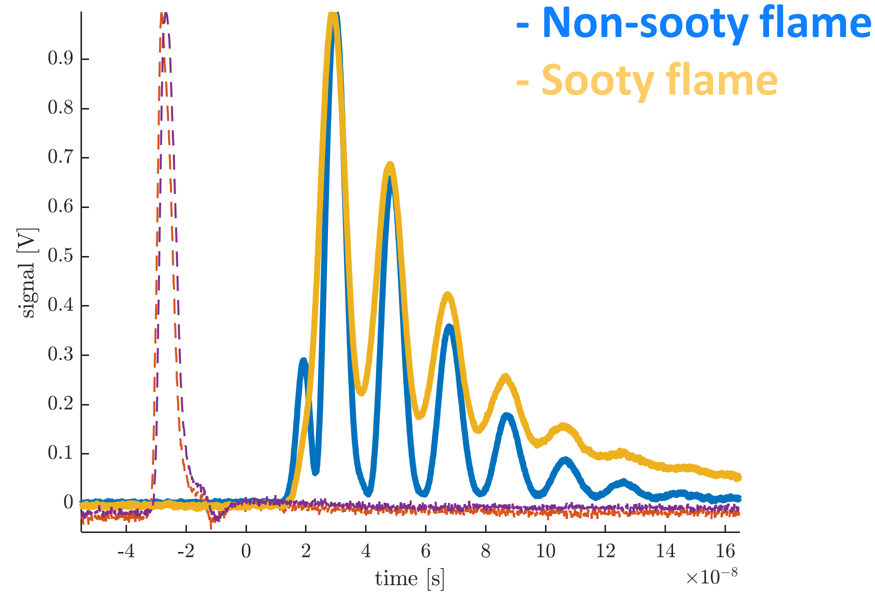
$$DAMPING\ RATE:\ \Gamma \leftrightarrow \frac{1}{\rho} = \frac{RT}{P}$$

ABSORBERS:

Non-sooty flames: water

Sooty flames: soot



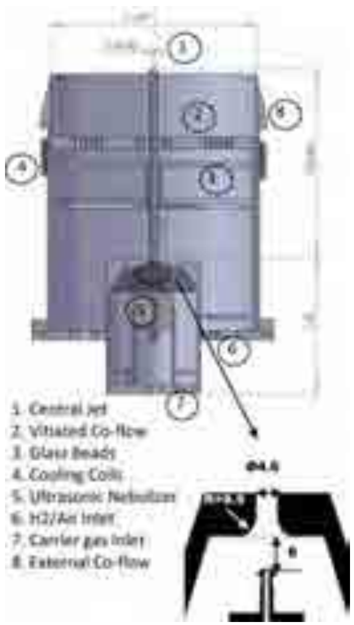


Differences:
- Rising time
- Contrast
- Damping rate

KAUST-Cambridge, unpublished
De Dedomenico, 2018

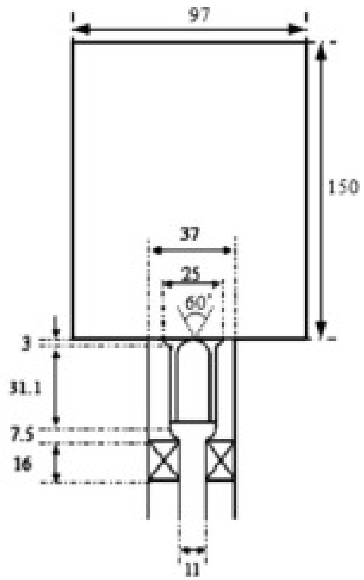
UNIVERSITY OF CAMBRIDGE

Not many measurements of scalars + soot in *liquid* spray flames



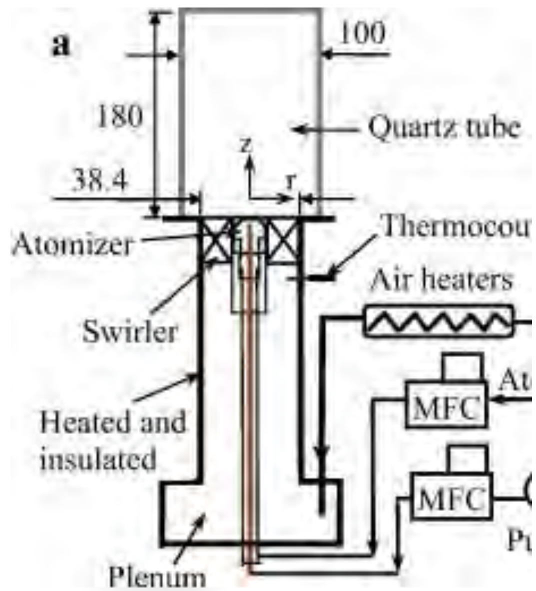
W. O'Loughlin and A. R. Masri
Combustion and Flame **158** 1577 - 1590 (2011)

U | d | OH | CH2O



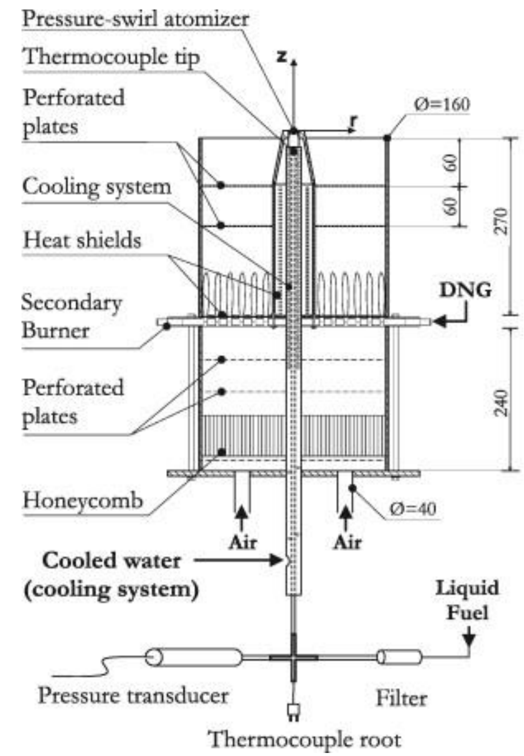
R. Yuan and J. Kariuki and A. Dowlut and R. Balachandran and E. Mastorakos
Proceedings of the Combustion Institute 35 1649-1656 (2015)

U | d | OH | CH2O



C. T. Chong and S. Hochgreb
Applied Energy 185 1383-1392 (2017)
C. T. Chong and S. Hochgreb
Fuel 115 551-558 (2014)

U | d | OH*

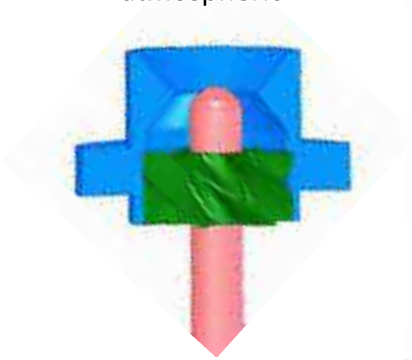


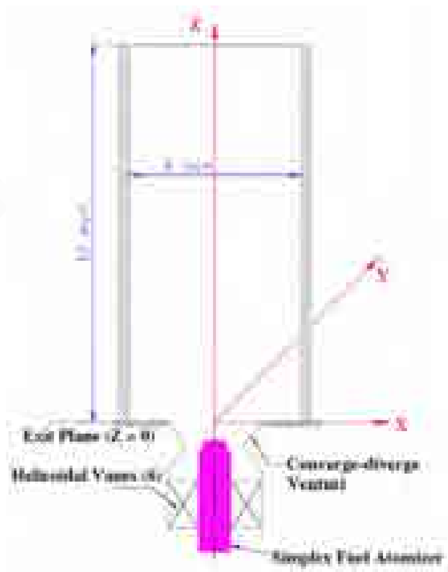
H. Correia Rodrigues and M. J. Tummers and E. H. van Veen and D. J. E. M. Roekaerts
International Journal of Heat and Fluid Flow 51 309-323 (2015)

T | U | d

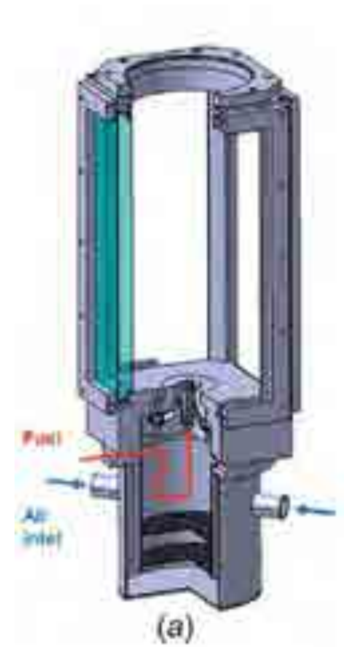
Technical/high pressure spray flames

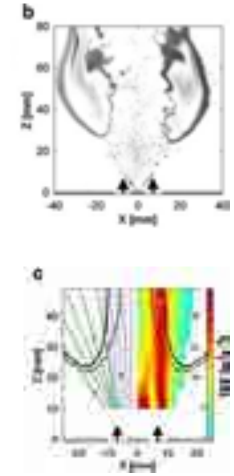
NASA-LDI
atmospheric





CORIA
pressure





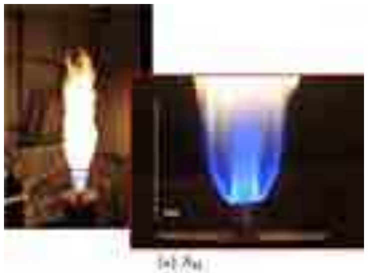
A. Iannetti, N.-S. Liu, F. Davoudzadeh
The Effect of Spray Initial Conditions on Heat Release and Emissions in LDI CFD Calculations
NASA Report No. NASA/TM—2008-214522, NASA Glenn Research Center, Cleveland, OH (2008)

The Structure of a Swirl-Stabilized Reacting Spray Issued from an Axial Swirler ,
J. Cai and S. M. Jeng and R. Tacina
AIAA 2005-1424 43rd AIAA Aerospace Sciences Meeting, Reno, Nevada (2005)

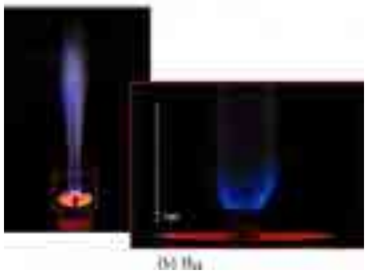
J. Marrero-Santiago and A. Verdier and C. Brunet and A. Vandel and G. Godard and G. Cabot and M. Boukhalfa and B. Renou
J. Eng. Gas Turbines Power 140 (2018)

A. Verdier and J. M. Santiago and A. Vandel and S. Saengkaew and G. Cabot and G. Grehan and B. Renou
Proceedings of the Combustion Institute 36 2595 - 2602 (2017)

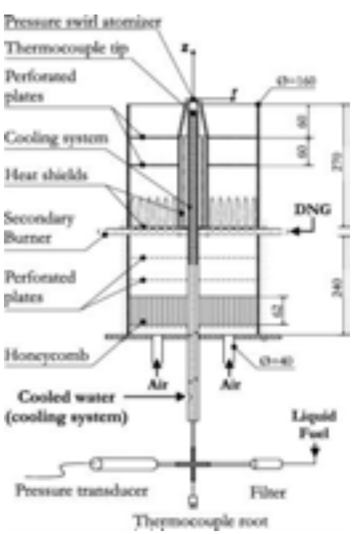
Dilute spray flames DHSC: sensible place to start?

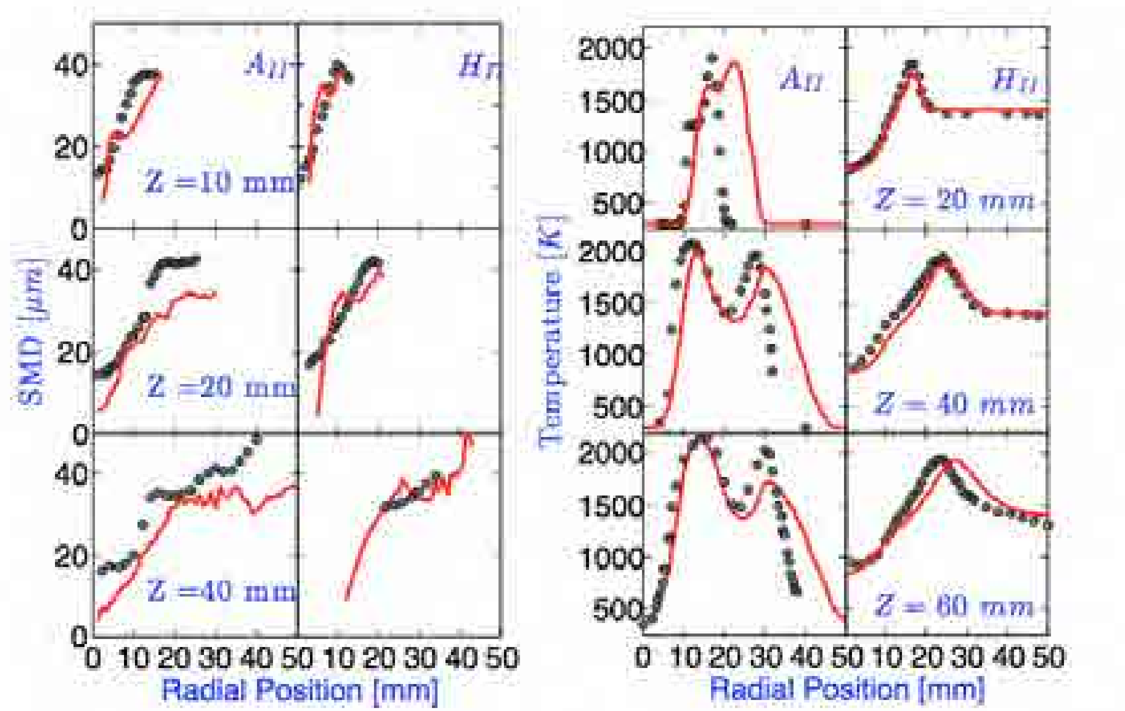


air (A)



hot pilot (H)





H. Correia Rodrigues and M. J. Tummers and E. H. van Veen and D. J. E. M. Roekaerts
Combustion and Flame 162 759-773 (2015)

L. Ma and D. Roekaerts
Proceedings of the Combustion Institute 36 2603-2613 (2017)

Soot/spray measurement needs: Input from industry and collaborators

Fuels and operating conditions

- CH_4/C_2H_4: significantly higher discrepancy with CH_4 : kinetic pathways probably not well worked out.
- Liquid fuels: approaching real kerosene (perhaps synthetic). Intermediate step could be addition of liquid fuels to C_2H_4
- Pressure: Need further validation mechanisms including total soot and soot size (common needs with IC engines), primary but also agglomerates. PAH measurements and techniques needed at pressure.
- Temperature: mechanisms are typically validated for low pressure flames, which do not reach high temperatures (unlike high pressure flames, up to 2300 K)
- Laminar vs. turbulent: residence time at microscale key: experiments in vitiated JSR (i.e. not flames) at high T possibly useful

Soot/spray measurement needs:
Input from industry and collaborators

Geometries:

- Swirl stabilized flames (such as DLR): more representative
- Fully characterized boundary conditions

Soot as an issue:

- Top of the radar for e.g. Rolls-Royce
- Not on the radar for e.g. GE, Siemens, P&W

THE UNIVERSITY of ADELAIDE

Bluff Body Turbulent Sooting Flames

Amir Rowhani, Bassam Dally, Zhiwei Sun, Graham Nathan

and many other contributors

ISF4 Dublin, August/2018

Previous Soot Data

Dimensions: Nozzle internal diameter: 3.6 mm; Bluff Body Diameter: 50.0 mm

Fuel jet: Flames 1-3 Ethylene-Hydrogen: Flame 4 LPG

Flow Conditions: Bulk jet exit Reynolds number: ~30,800

Fuel Composition:

Ethylene – 99.0% purity

Hydrogen – 99.0% purity

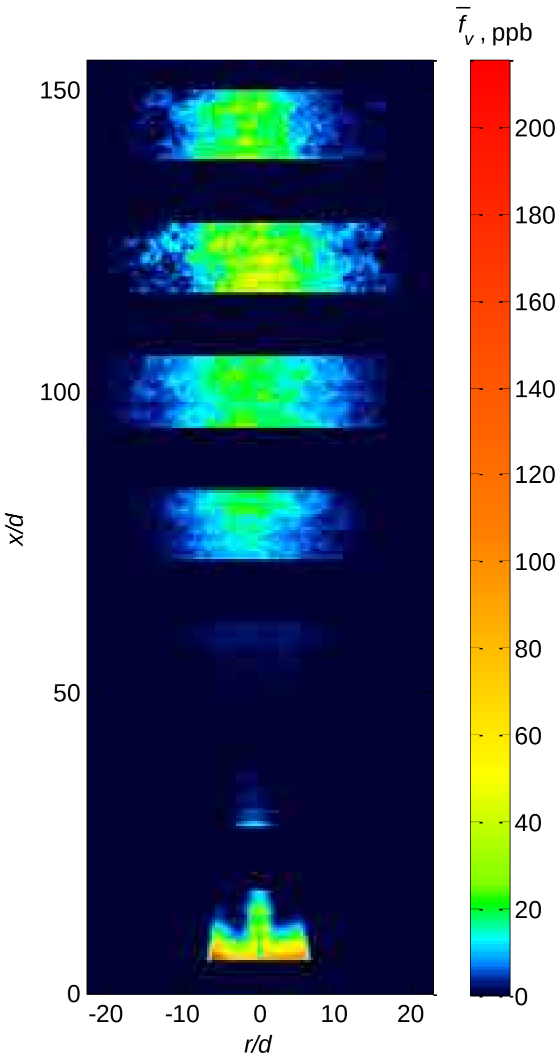
LPG (molar)– 97.35% propane, 1.35% ethane, 1.20% butane, 0.07% nitrogen, and 0.03% carbon dioxide.

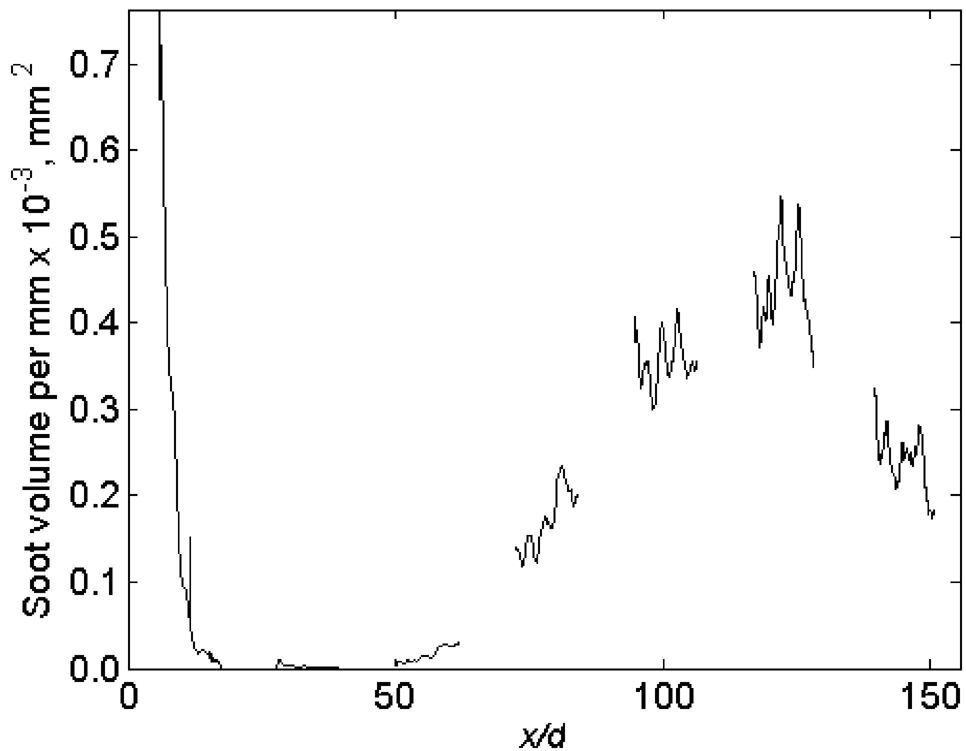
Previous Soot Data

Flame Type	Fuel (mole fraction)	Jet exit velocity (m/s)	Jet exit Reynolds Number (cold flow)	Heat output (kW)	Coflow Velocity (m/s)
Flame A	Ethylene: 1.000 Hydrogen: 0.000	74.2	30900	41.7	23
Flame B	Ethylene: 0.671 Hydrogen: 0.329	102.1	30800	41.9	23
Flame C	Ethylene: 0.487 Hydrogen: 0.513	130.7	30440	42.6	23
Flame D	LPG: 1.000	36.3	30474	32.0	23

- Mean Soot Volume fraction and Intermittency are available for Radial profiles at different axial positions above the burner exit z/DJ = 5 to 148.

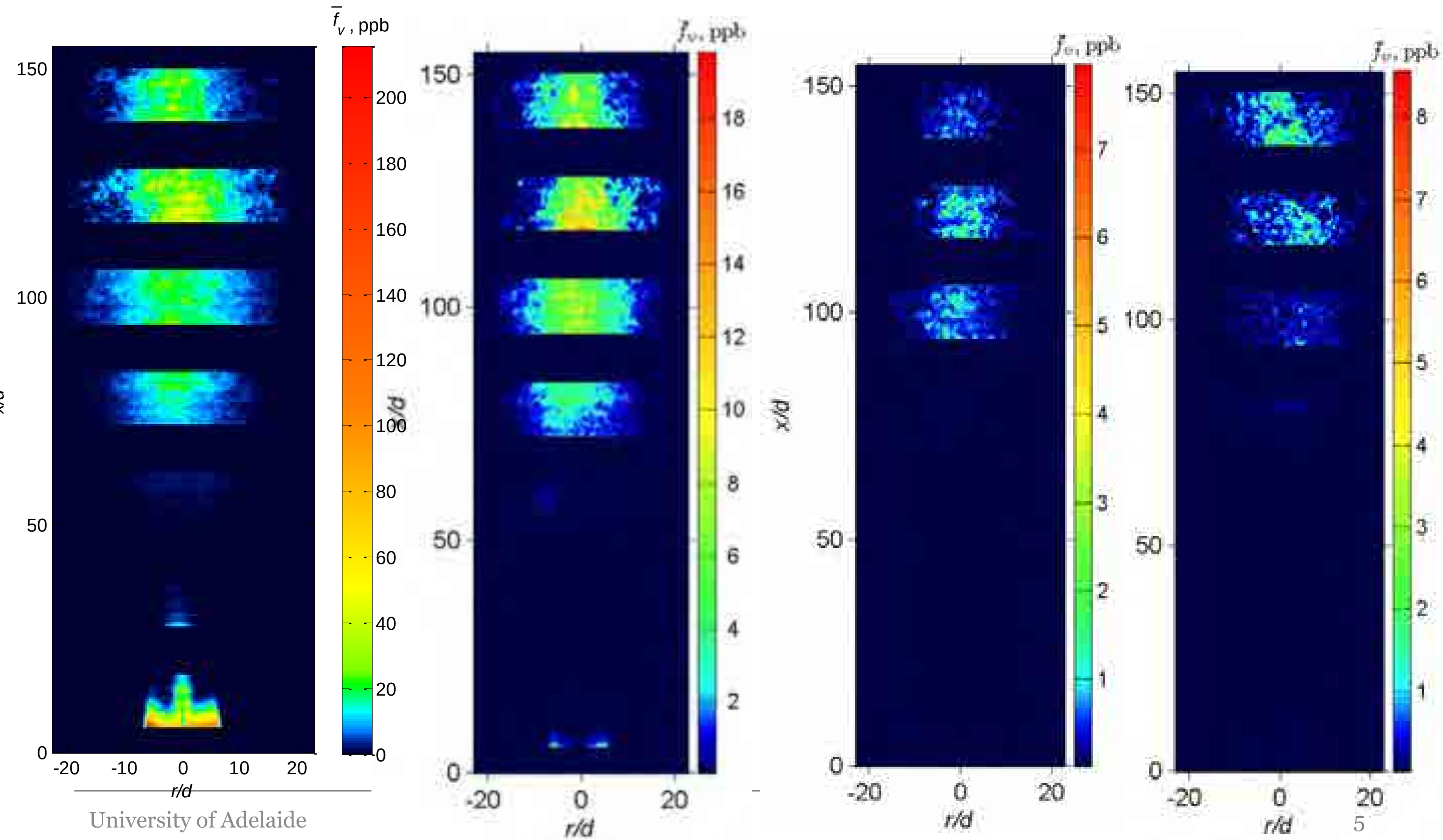
Pure Ethylene Flame





Pure Ethylene Flame

C2H4 | **C2H4/H2 (0.671/0.329)** | **C2H4/H2 (0.487/0.513)** | **LPG**



Previous Soot Data

Experimental Technique:

- LII measurements using Nd: YAG laser at 1064 nm was used for the LII excitation;
- Laser sheets ~80 mm high, ~0.3 mm thick
- The LII operating fluence was maintained at ~0.9 J/cm2 throughout the experiment to ensure that the LII signal observed is independent of laser fluence variation;
- The prompt signal was collected via an intensified CCD (ICCD) camera with 430 nm optical filter;
- The LII signal was calibrated via laser beam extinction measurements.

Plans for New Bluff Body Sooting Flames Data

Burner:

- Fixed jet diameter at 4.5 mm
- Three Bluff-Body diameters: 38mm, 50mm, 64mm
- Round coflow contraction 250mm diameter

Fuels:

- Ethylene/H2/N2 blends
- Pre-vaporised n-Heptane

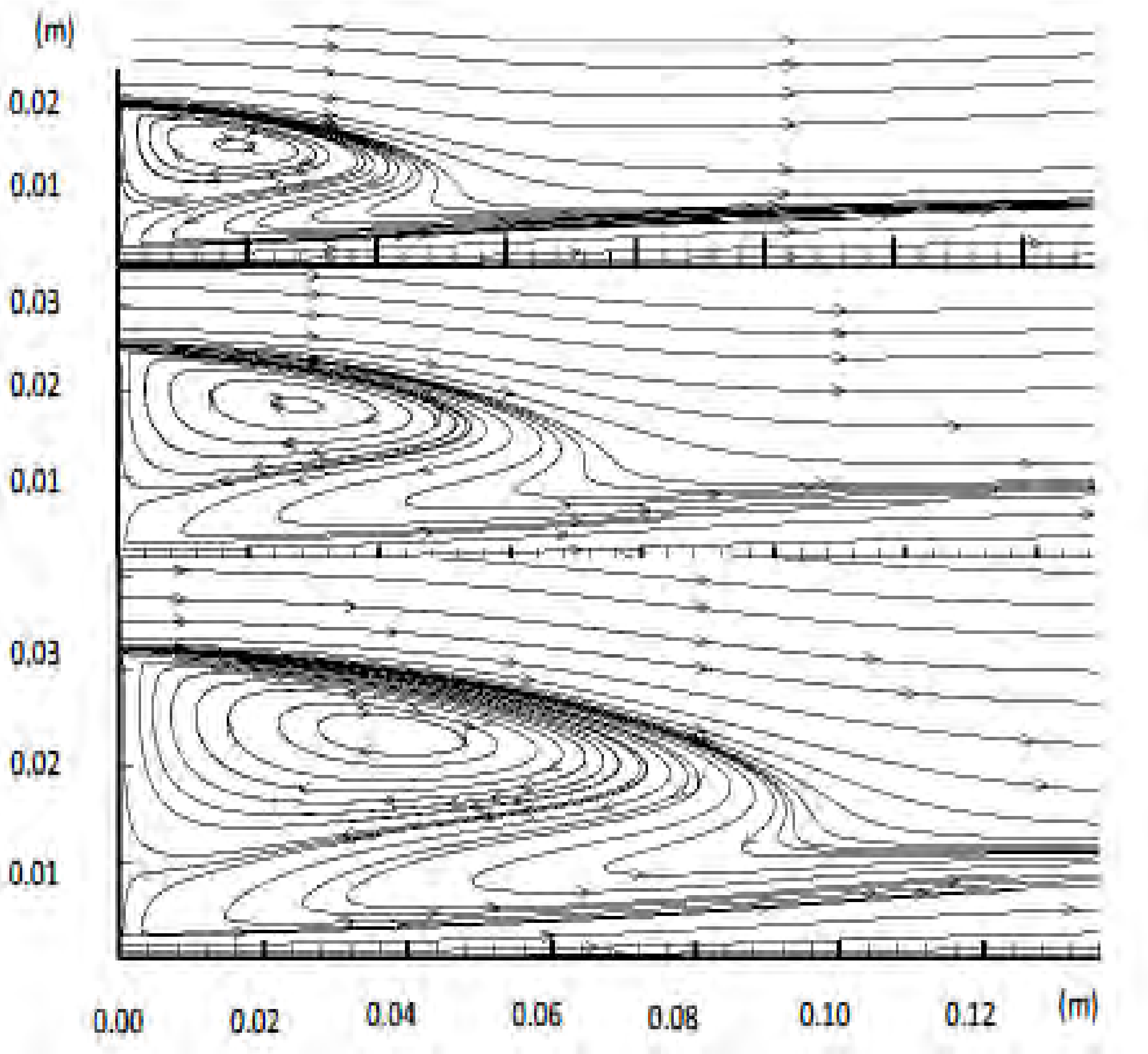
Variables:

- Ratio of jet to coflow momentum flux
- Jet Reynolds number
- Dilution

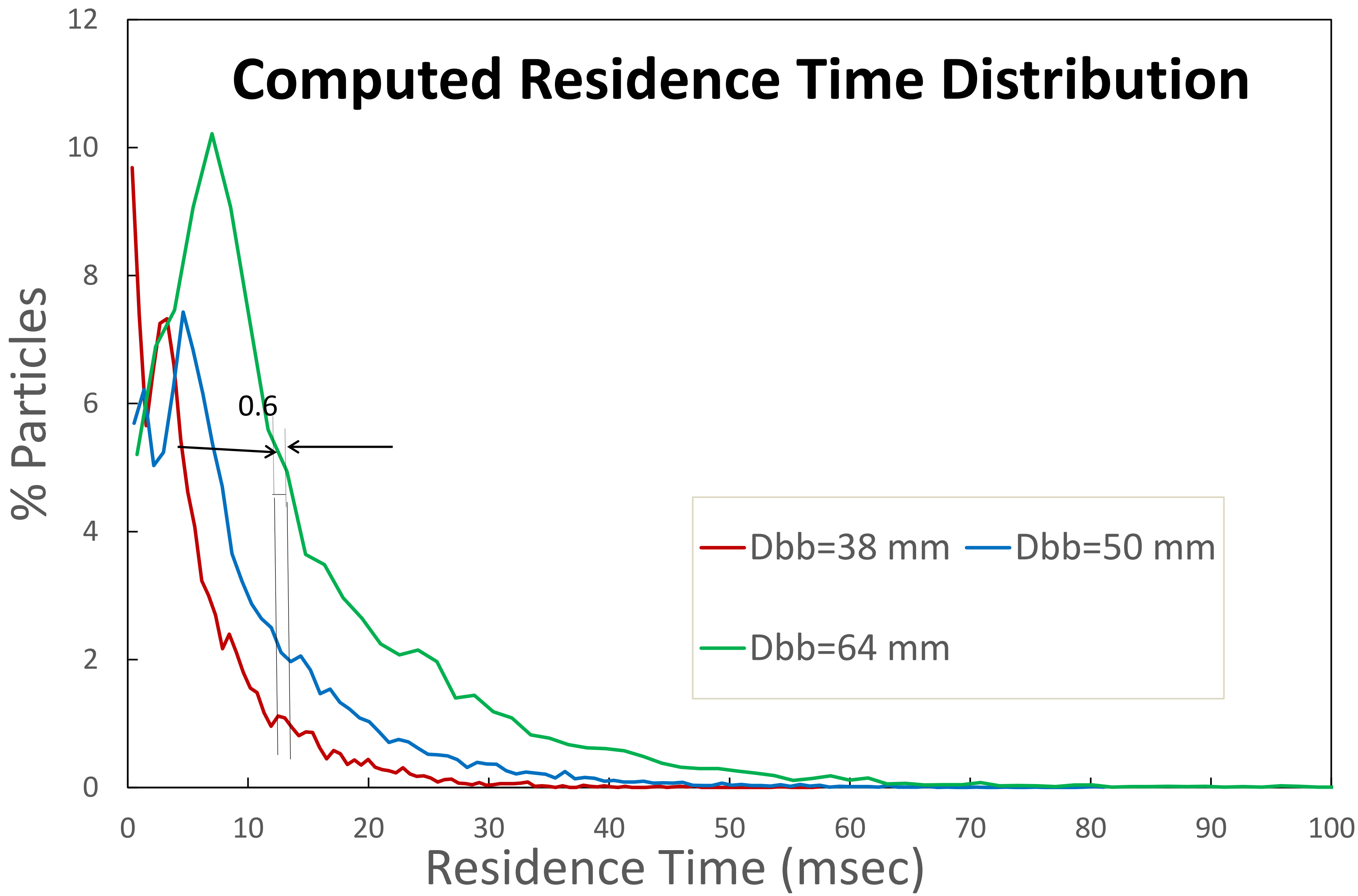
Flame Luminosity: Re=25000, Different D_j

Pure Ethylene Flames

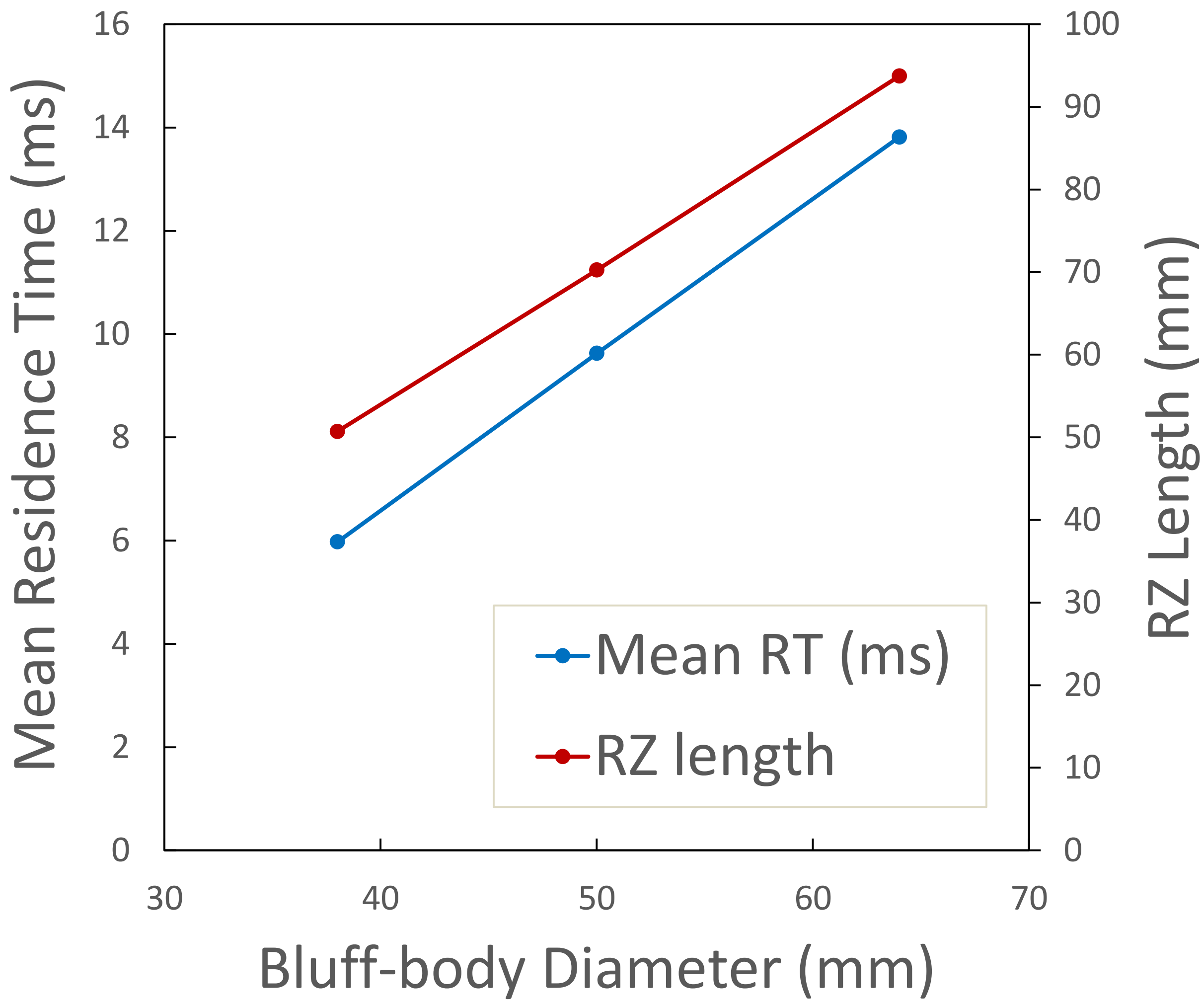
RZ Structure: Same Re# and Different D_j



Residence Time Distribution in RZ



Mean Residence Time in RZ



Planned Measurements

Flow Field using PIV:

- Non-reacting flows
- Lightly sooting flames

Simultaneous T-dp-fv-OH:

- Using nTLAF technique to measure temperatures in RZ, Neck Zone and few positions in the Jet-Like Zone
- PLIF of OH to identify the reaction zone
- TiRe-LII to measure fv and dp

Radiation measurements:

- Using standard PMT

Centreline Temperature measurements:

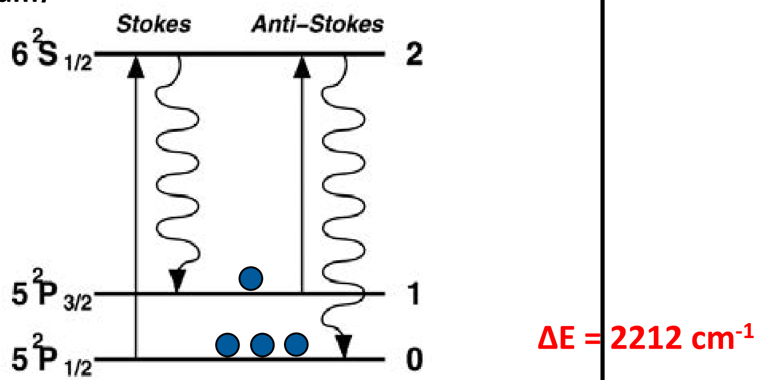
- Using a small bead thermo-couple

Bluff Body surface temperature:

- Using two-colour pyrometer

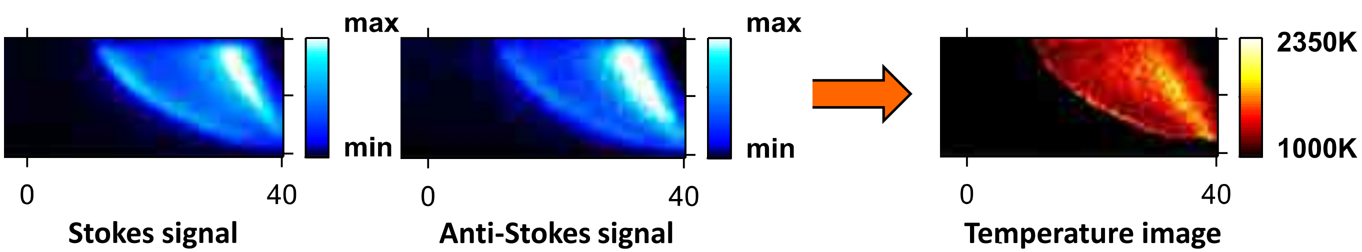
TLAF using Indium as thermometry tracer

Two-line atomic fluorescence (TLAF using Indium)

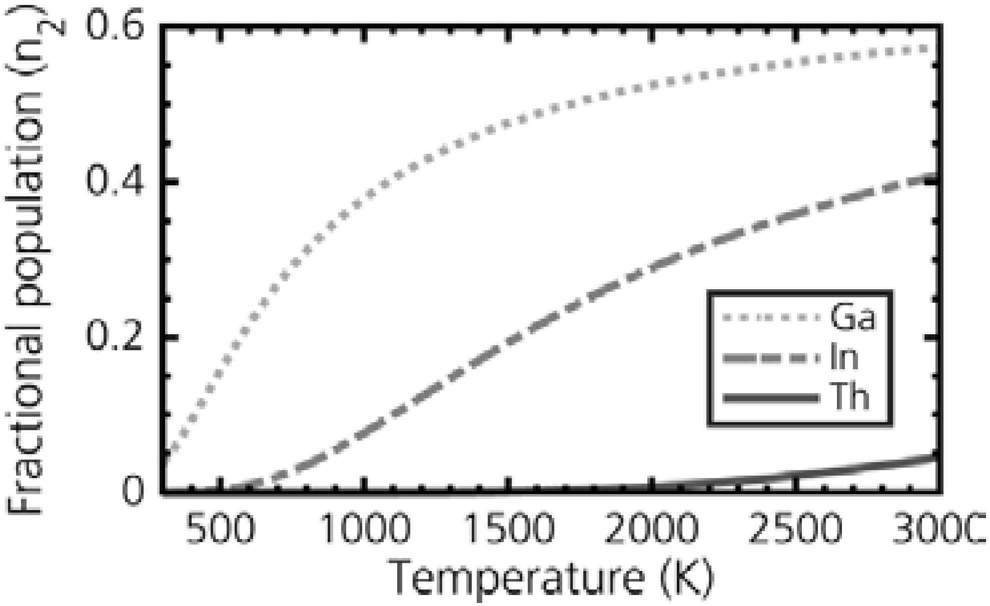


Because of the large **ΔE (2212 cm^{-1})**

- TLAF using Indium is sensitive in high temperature region of > 1000 K.
- Low fractional population at the first excited state, resulting in low Anti-Stokes signals and low S/N, so that low precision of temperature in single-shot imaging.



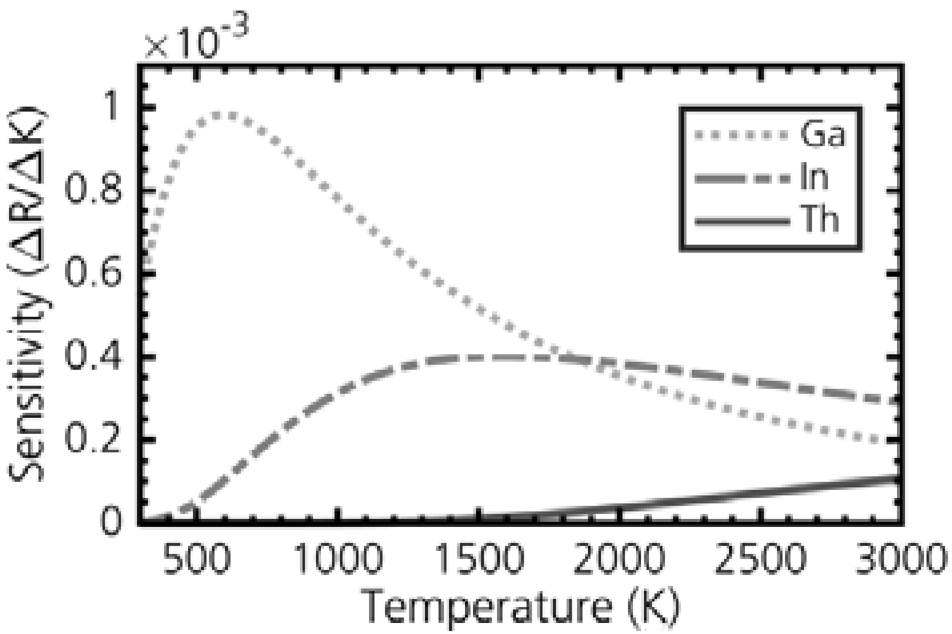
Other atomic tracers, e.g. Gallium with a small ΔE (826 cm^{-1}) but similar Einstein coefficients (A)



Jesper Borggren,
Doctoral thesis, (2018), Lund, Sweden

Fractional population of the first excited state of different atomic tracer as a function of temperature

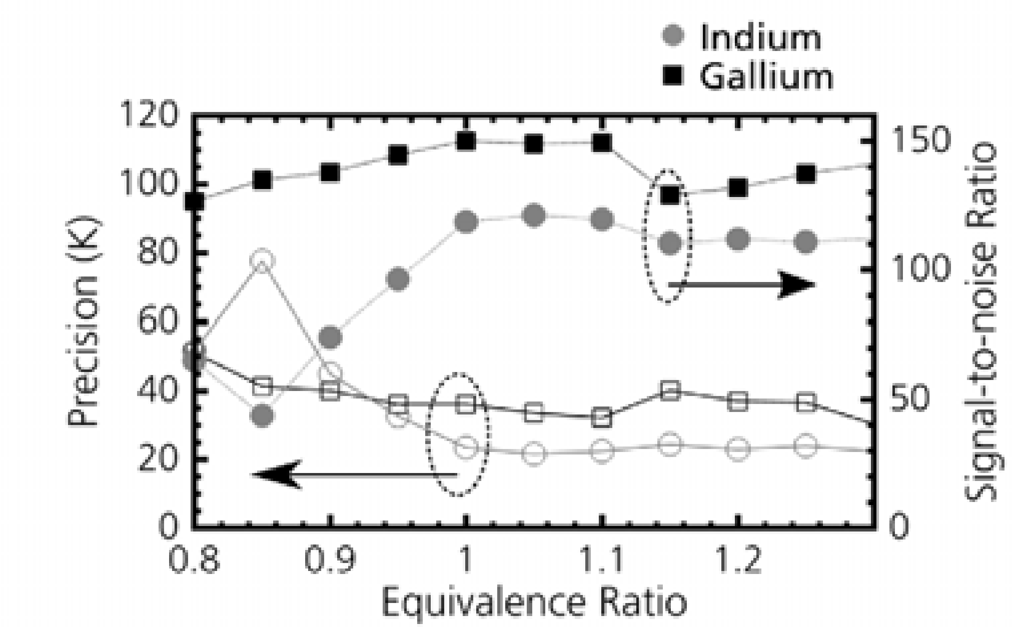
Sensitivity ($\Delta R/\Delta T$), where R is the ratio of Stokes and Anti-Stokes LIF signals.



Jesper Borggren,
Doctoral thesis, (2018), Lund, Sweden

Temperature sensitivity of the atoms (Ga, In and Th) for TLAF measurement.

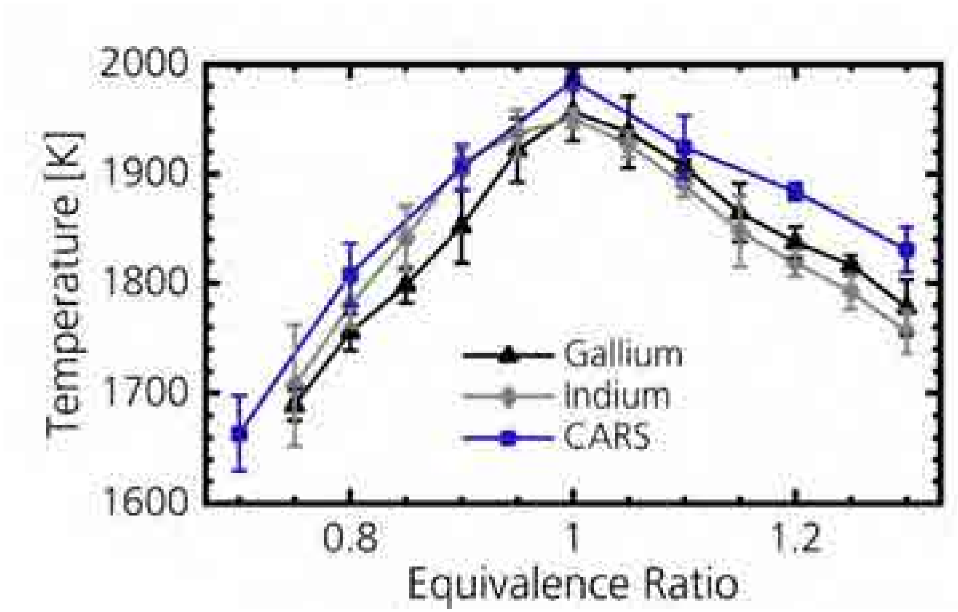
Precision (hollow markers) and the corresponding signal-to-noise ratio (filled markers) for gallium and indium for different equivalence ratios.



Jesper Borggren,
Doctoral thesis, (2018), Lund, Sweden

Temperature precision of 20-30K in region of interest and TLAF.

Comparison of mean temperature using TLAF technique with CARS. Error bars are STDev.



Jesper Borggren,
Doctoral thesis, (2018), Lund, Sweden

Mean temperature is within the different techniques accuracy.

Potential advantages of Ga-TLAF over Indium TLAF

1. High Anti-Stokes signals, so that high precision is expected in **instantaneous** planar measurements
2. High sensitivity, particularly in the range of 500 – 1200 K.
3. Low temperature regions are accessible (> 300 K for Gallium TLAF, while > 800 K for Indium TLAF)
4. An accuracy in the order of 2-3 % at flame temperatures around 1800 K is typical for the TLAF technique and the precision is for many cases below 1 % for averaged measurements.
5. Gallium melts at 40^{o}C which poses a challenge for seeding it as particulates. Trimethylgallium (TMG) is also possible, except it is a nasty chemical to deal with.

Discussion Points

1. Mixture fraction is hard to measure in sooting flames, how useful is the mixture fraction distribution in a ‘clean’ flame of similar flow dynamics?
2. Adding hydrogen will introduce issues with differential diffusion? Does the addition of methane, instead, be any better?
3. Is the rest of the flame important?

Atmospheric pressure turbulent flames

- The "simple" configuration of unconfined turbulent jet flames has been used extensively to study important aspects of flames:

Delft/Sandia flame III

Sydney inhomogeneous inlets flame

Adelaide jet flame

Sandia/ETH syngas flame

DLR lifted flame

- Piloted or non-piloted,
- Attached or lifted,
- Sooty or blue,
- Large range of fuels

- These flames allow isolating effects and are amenable to modeling.
- However, they are not compatible with most available pressure rigs because they need to be vertical to preserve symmetry and tall (> 2m)

High pressure flames

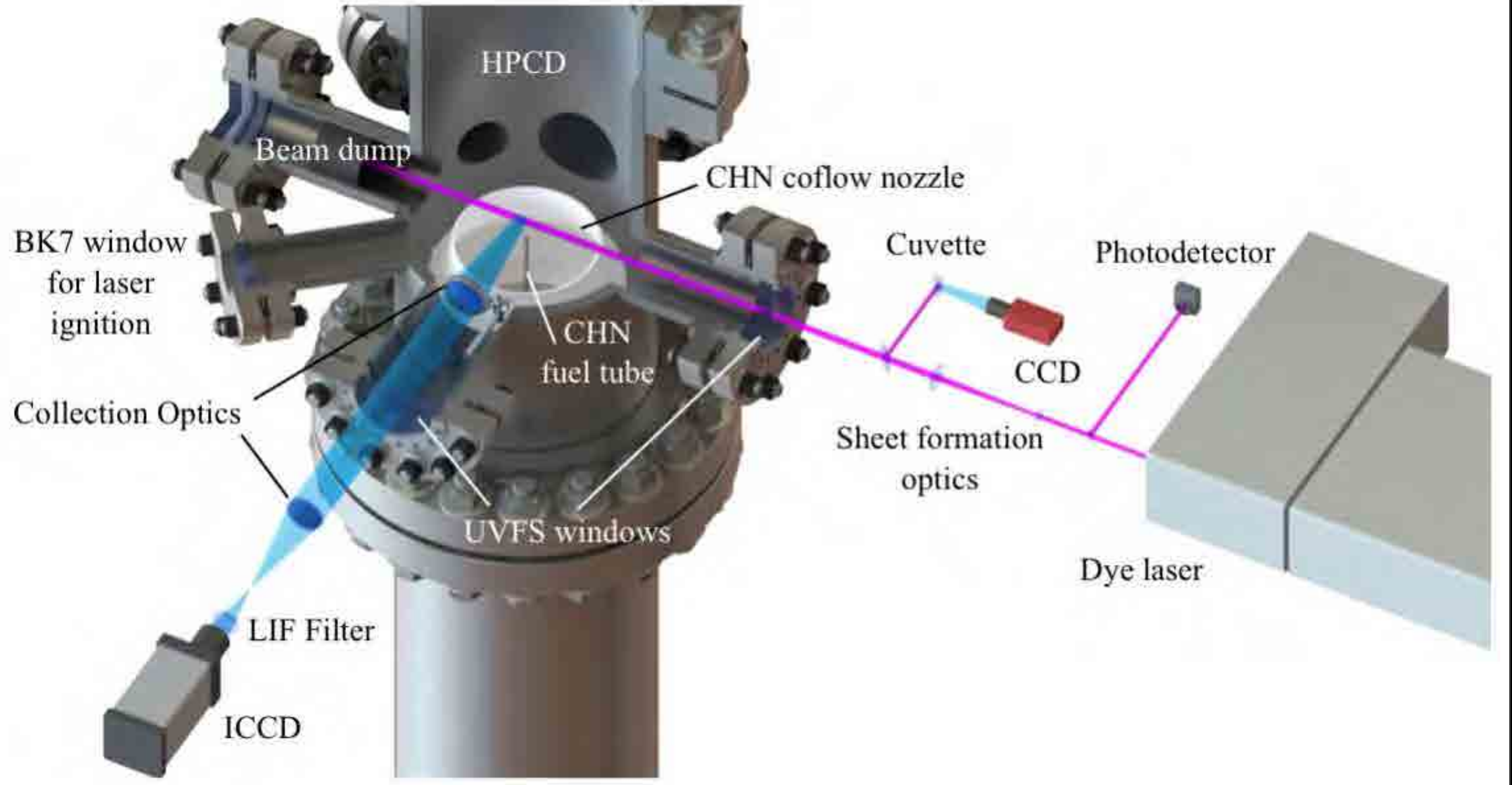
- One of the most successful features of TNF was ability to replicate the different burners
  - Confirmation of measurements by applying different diagnostic techniques
- With the complexities of high pressure facilities, this model doesn't work any more
  - Need to bring burners and diagnostics to the few facilities available
  - High cost dictates very judicious choices of experiments
  - Employ as many simultaneous diagnostics as possible to maximize data yield
  - High rep rate diagnostics highly advantageous (but do you get statistically independent data?)
- Only go to pressure when necessary

High Pressure Combustion Duct

- KAUST high pressure combustion lab
  - Supply of high air & nitrogen flow rates (0.56 kg/s continuous, higher for intermittent)
  - High pressure (45 bar)
- KAUST high pressure combustion duct (HPCD)
  - Designed for turbulent non-premixed flames at high pressure
  - Wide inner diameter (~ 400 mm) allows wide variety of burners
  - Height (~ 9 m) allows very long flames
  - Design pressure: 40 atm
  - Optical access: 6 UV fused silica windows

Vessel and Facility Mods

- Now placing collection optics inside duct. Will be an issue for very radiant flames.
- Adding y and z translation capability to burners (60 mm)
- 200 kg of air storage for short duration runs with higher mass flux
- Will have liquid fuel capability soon
- Redesigning exhaust to allow higher power and also better atmospheric pressure environment
- Continually expanding suite of diagnostic tools available



KAUST's HPCD timeline

Flames

Lifted-flame

Syngas jet flame

Sydney inhomogeneous inlets

Cambridge Bluff-body

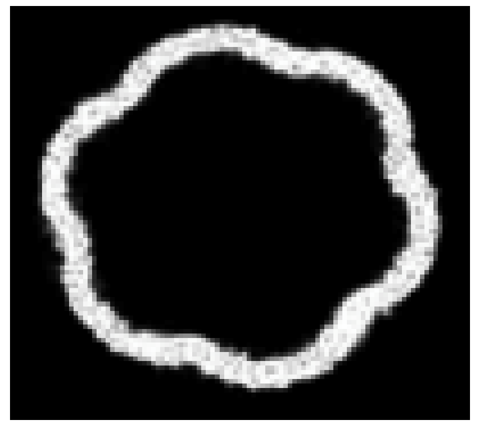
Piloted ethylene

Syngas jet flame

Inverse diffusion flame

Premixed swirl flame

Vanderbilt Tubular flame



Lifted-flame

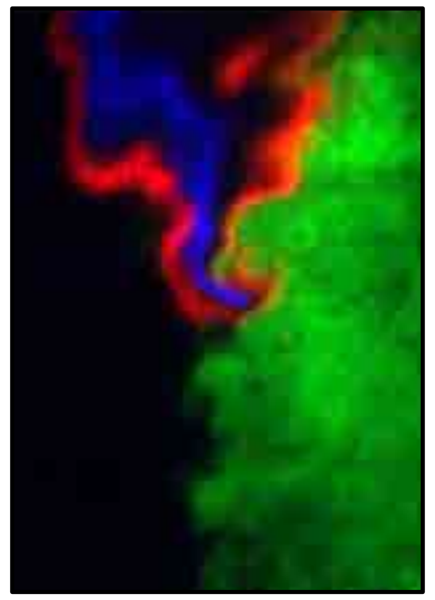
Syngas jet flame

TBD
Open to Collaborations!

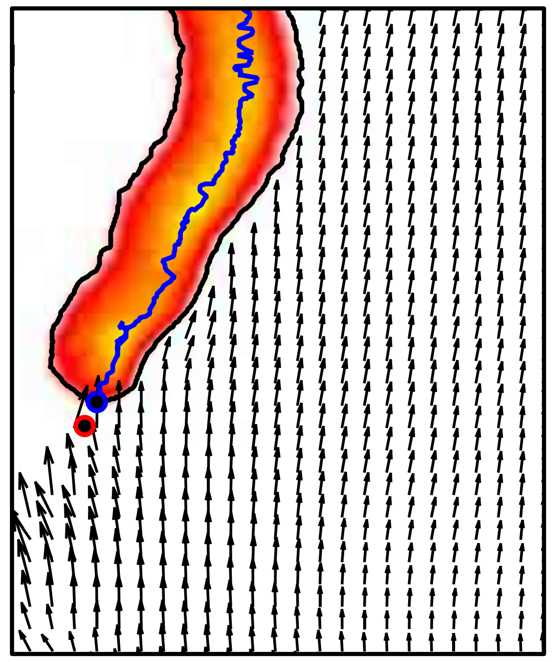
2019
Fall
Winter

2018
September | October | November | December | 2019 January | February | March | April | May | June

2-D scalar imaging
Raman (CH_4/N_2)
OH/CH_2O PLIF

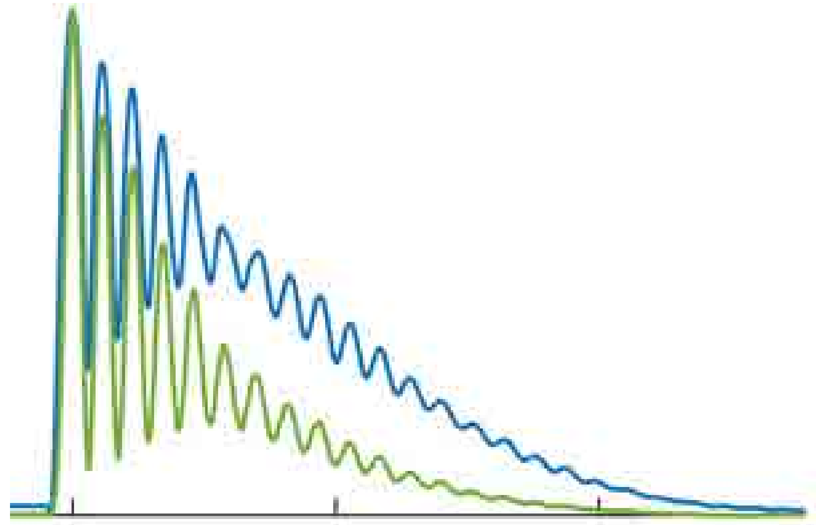


Velocimetry
PIV

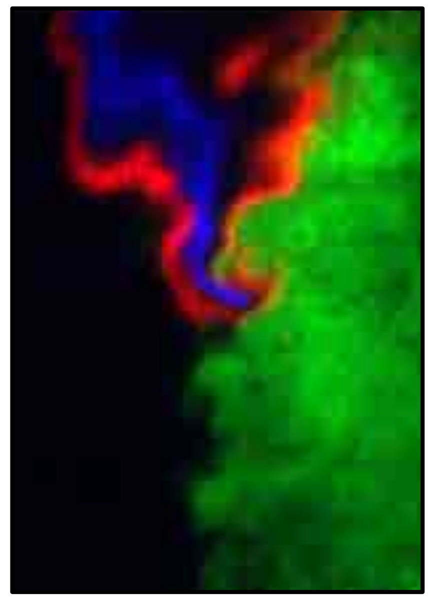


2-D scalar imaging
CH PLIF

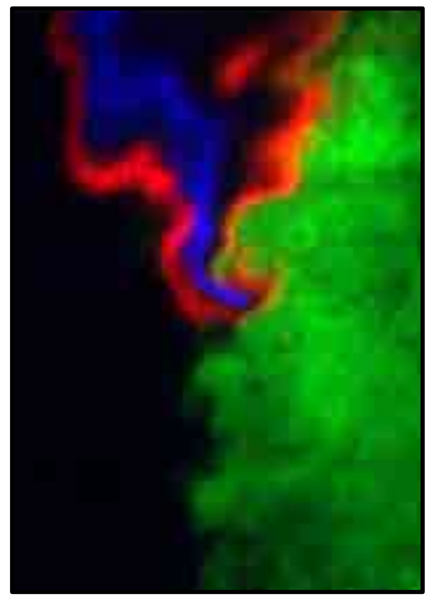
Thermometry
Thermographic phosphors
LIGS



2-D scalar imaging
Raman (CH_4/N_2)
CH PLIF

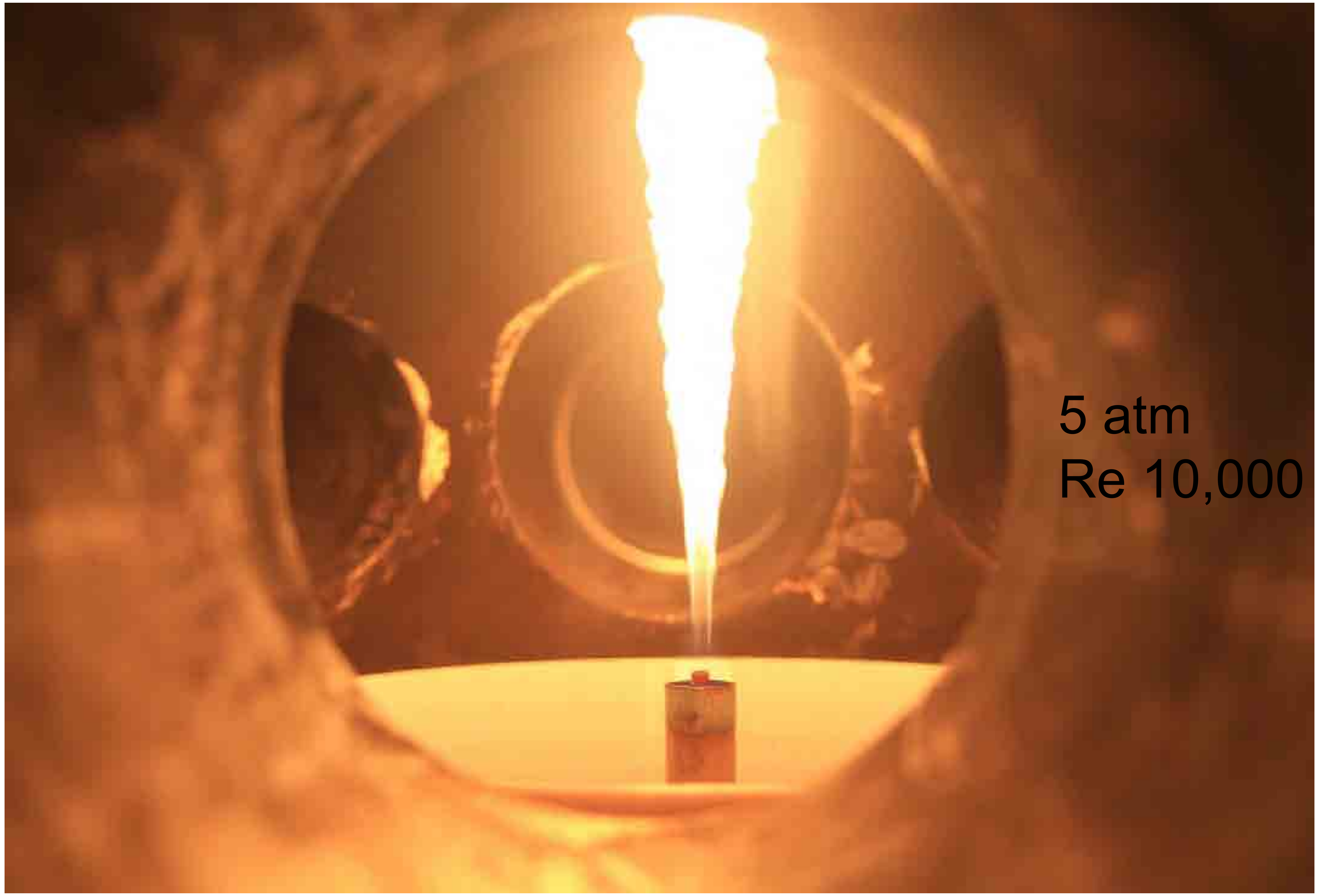


2-D scalar imaging
Raman ($CH_4/N_2/H_2/CO_2$)
Filtered Rayleigh scattering



Diagnostics

HP Turbulent Sooting Flames



Issues to discuss

- Better linkage between laminar and turbulent flames;
  - Unsteady (forced) co-flow and counterflow flames offer many advantages
- Is nitrogen dilution preferable way to suppress soot at high pressures? Adding Hydrogen? Changing H/C ratio problematic.
- Partial premixing? Sydney inhomogeneous burner at pressure?
- Liquid fuels? (n-Heptane? Multi-component surrogate?) Spray flames or pre-vaporized?
- Is there still utility is in pushing jet flames to higher power and Re? Lifted vs piloted?
- Adelaide ethylene/hydrogen/nitrogen attached flames to high pressure?
- Turbulent counter-flow flames? Much smaller physical region, more amenable to DNS
- How necessary is confinement for swirl flames? Removing confinement simplifies diagnostics and the prescription of thermal boundary conditions.

Understanding PAH chemistry: challenges for mechanism development

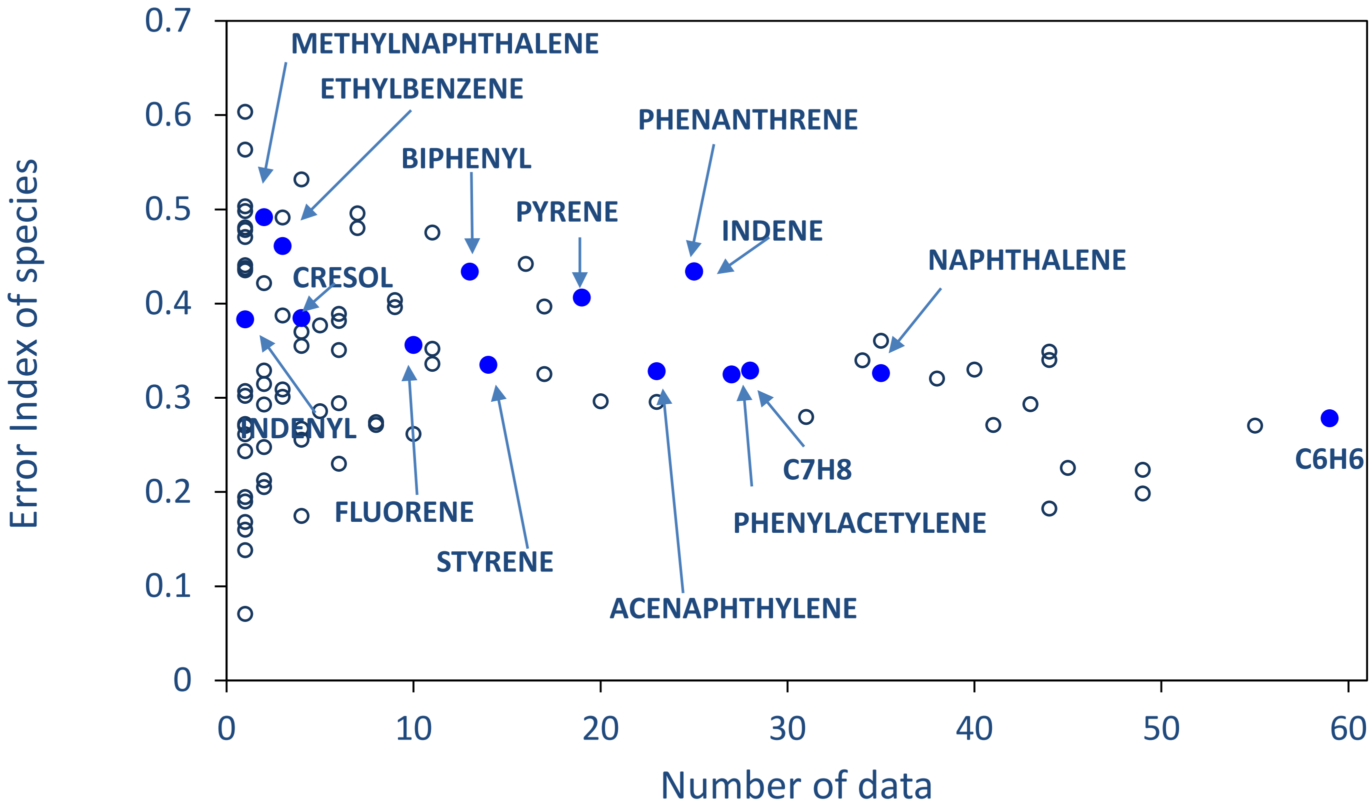
Tiziano Faravelli

CRECK Modeling Lab
Department of Chemistry, Materials, and Chemical Engineering
Politecnico di Milano (Italy)

Outline

- This presentation aims at arising questions not at giving answers
- No exciting or fundamental novelties
- Mechanisms and not rate constants
- Many and large uncertainties and not only related to the experimental data
- A lot of conditionals

Experimental data



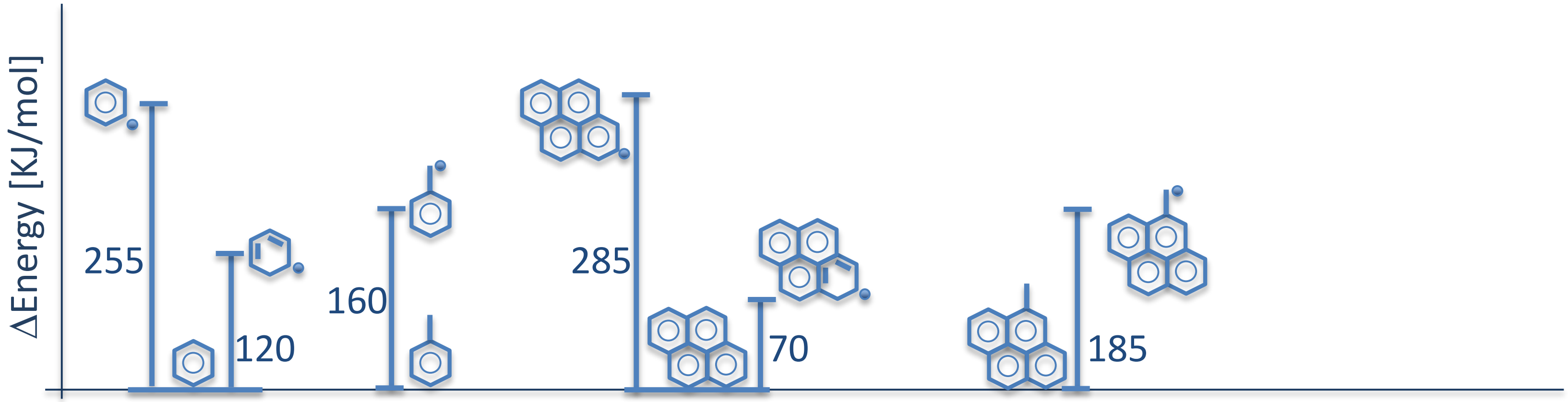
W. Pejpichestakul et al., Soot effect on intermediate PAHs concentration in premixed laminar flames. Wednesday, presentation 3C01

Kinetic models

ABF	Appel et al. (2000), Wang and Frenklach (1997)
ITV/Caltech	Blanquart et al. (2009), Narayanaswamy et al. (2010)
KAUST	Wang et al. (2013), Park et al. (2017)
Cottbus	Moshammer et al. (2017)
Shanghai	Yang et al. (2015), Yuan et al. (2015)
DLR	Slavinskaya et al. (2009), Slavinskaya et al. (2012)
Lille	El Bakali et al. (2012), Desgroux et al. (2017)
MIT	Richter et al. (2005), Ergut et al. (2009)
LLNL	Marinov et al. (1998), Nakamura et al. (2015)
CRECKM	http://creckmodeling.chem.polimi.it/

Only a few mechanisms. Above all, with different PAH formation and growth pathways

Radical stability

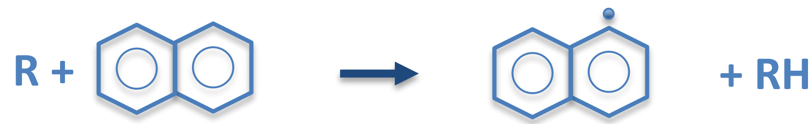


“The experiments show that there is no difference in reactivity between the large open- and closed-shell PAH. The radicals are not of the σ-type with localized reactive sites but π-radicals with no extra reactivity because of delocalization of the unpaired electron. The tendency to form π-radicals increases with the size of the polyaromatic species. Thus, it must be concluded that unpaired electrons in soot particles are also of the π-type and therefore delocalized.”

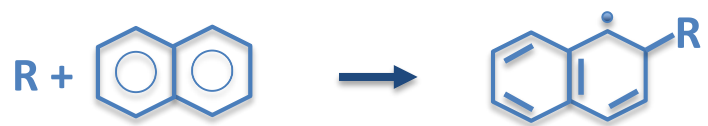
A. Keller, R. Kovacs and K.-H. Homann, Phys. Chem. Chem. Phys., 2000, 2, 1667-1675

More than

abstraction

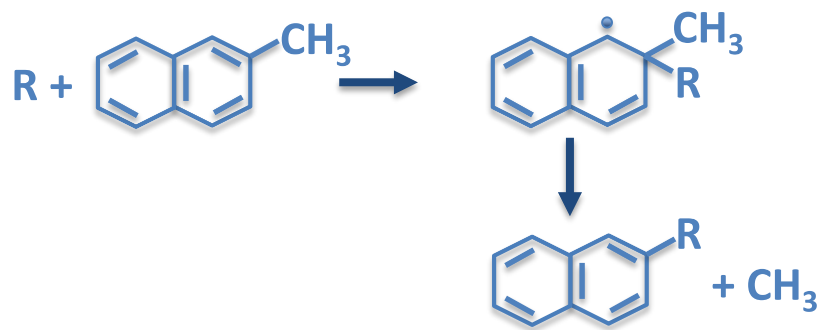


addition



and

ipso addition

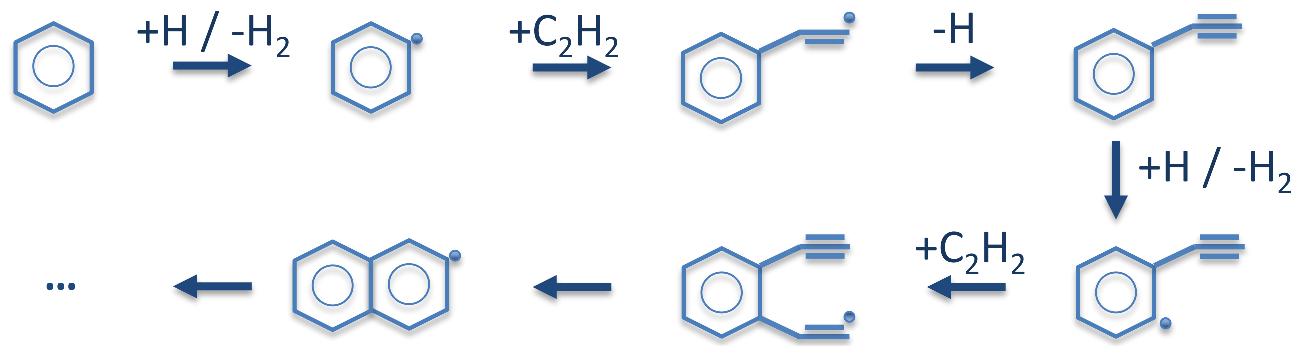


could be important

HACA mechanisms

223

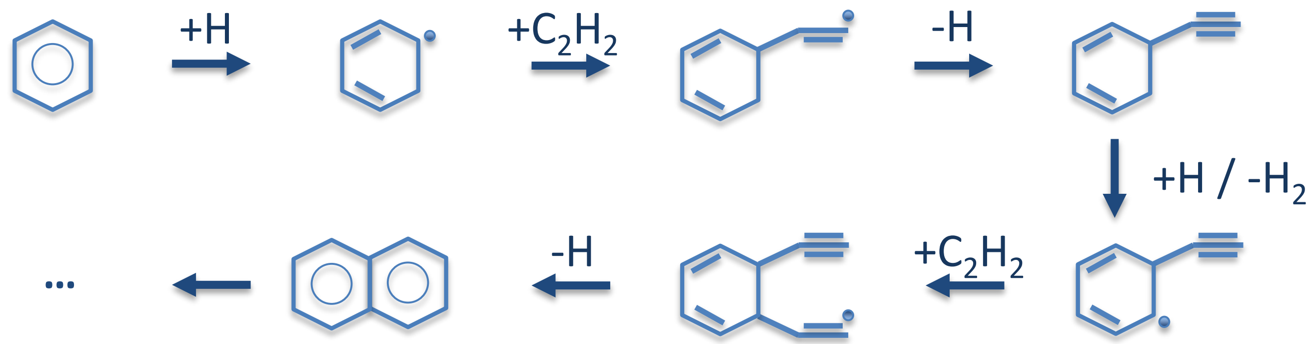
H Abstraction **C**arbon **A**ddition



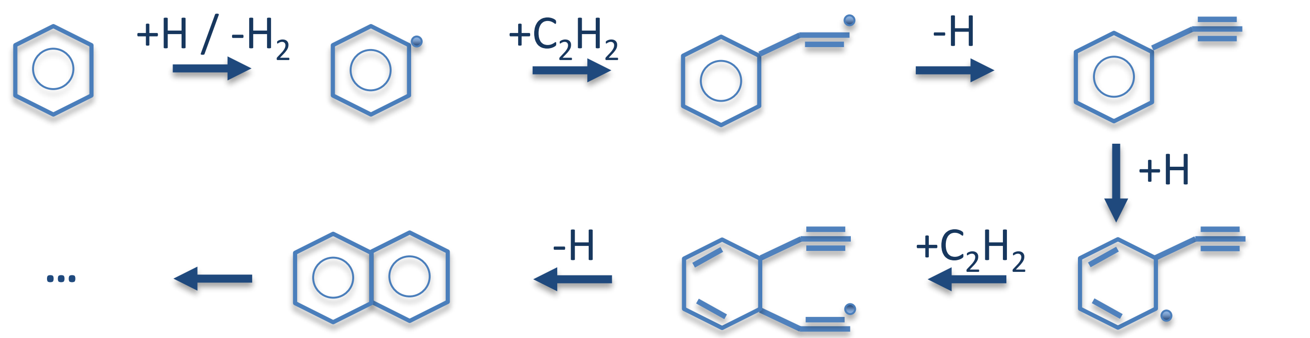
Frenklach and Wang, Proc. Combust. Inst., 23 (1991) 1559-1566
and successive modifications

Possible HACAs

H Addition/abstraction Carbon Addition

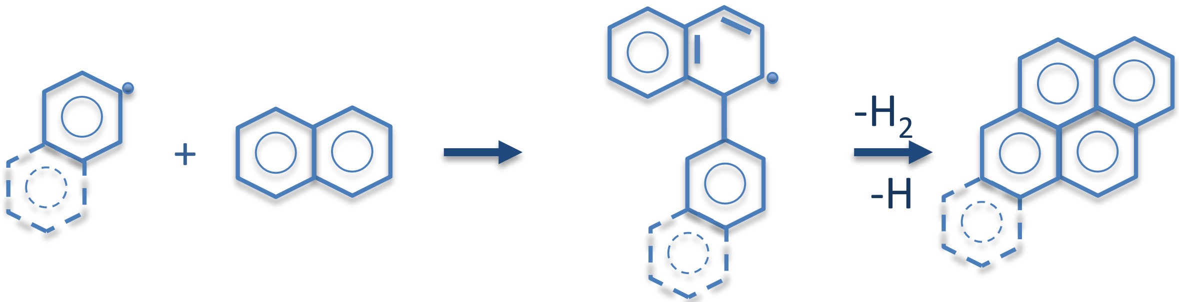


H Abstraction/addition Carbon Addition



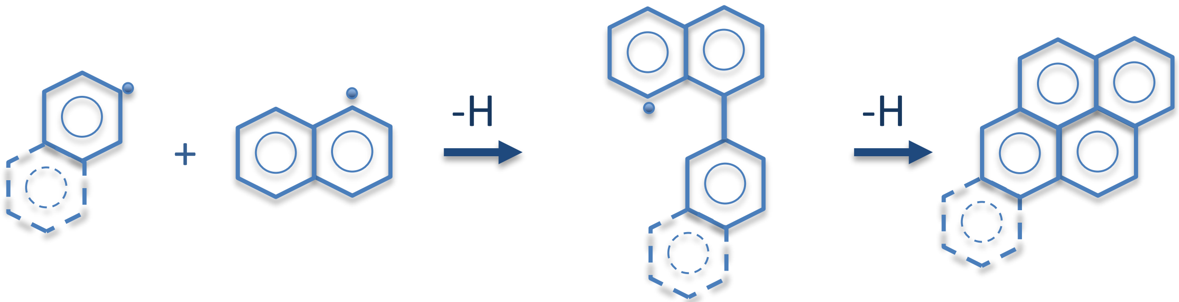
S. Klippenstein private communication

Aryl Addition Cyclization (AAC) mechanism



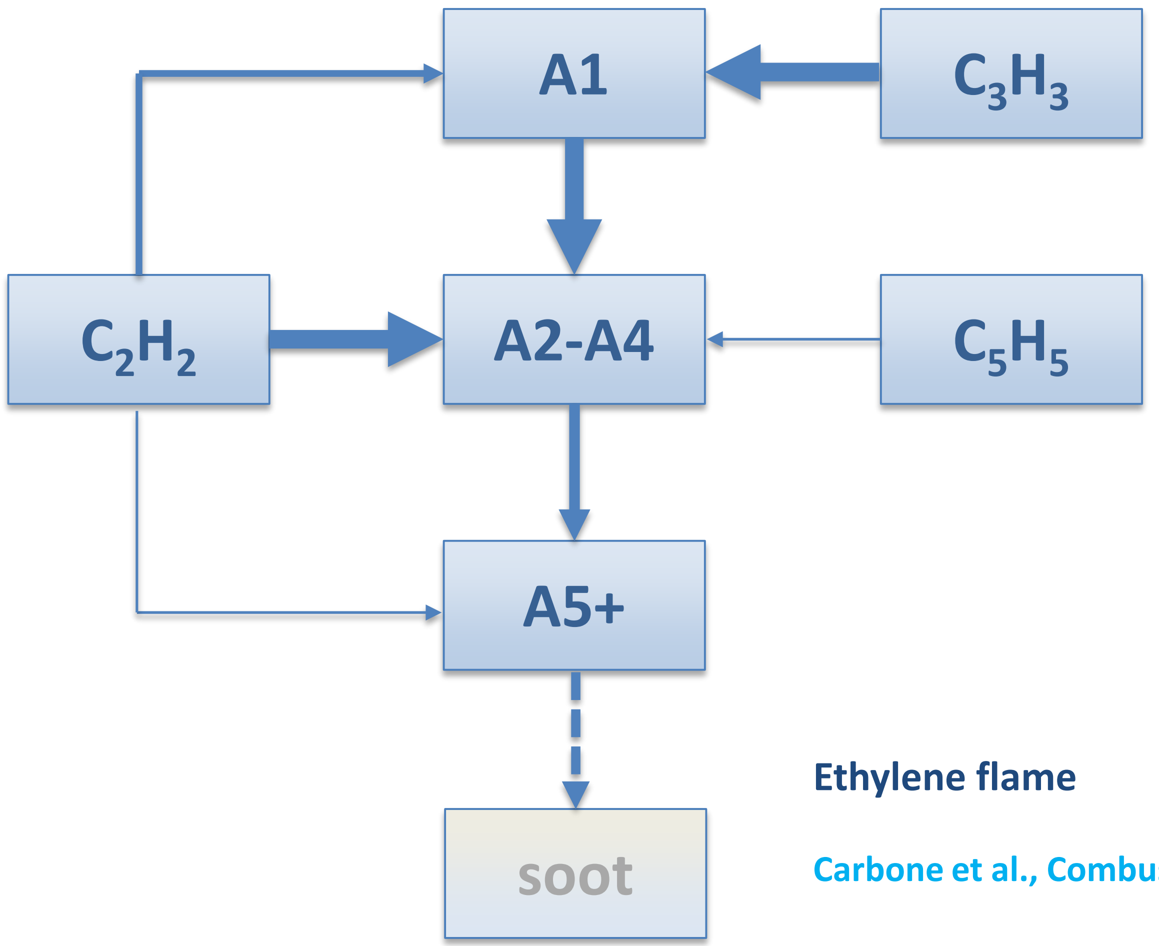
Shukla and Koshi, Combust. Flame, 158 (2011) 369-375

Aryl Recombination Cyclization (ARC) mechanism



Shukla and Koshi, Combust. Flame, 158 (2011) 369-375

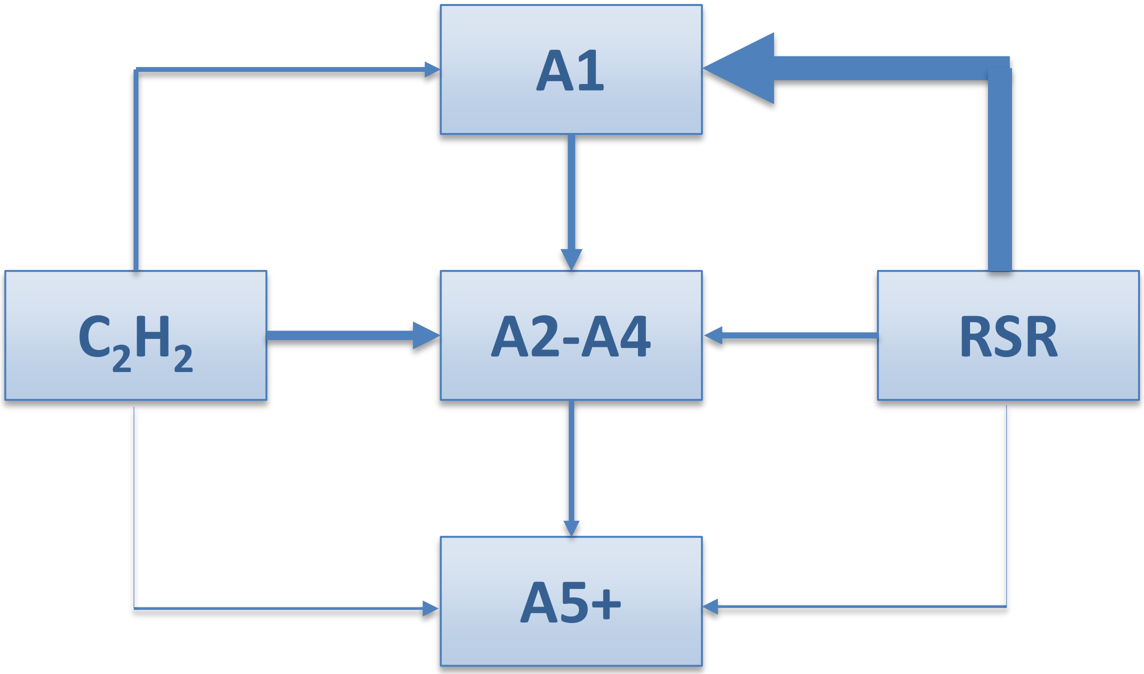
Mechanism summary CRECKModeling



Ethylene flame

Carbone et al., Combust. Flame 181 (2017) 315–328

Mechanism summary ITV/Caltech

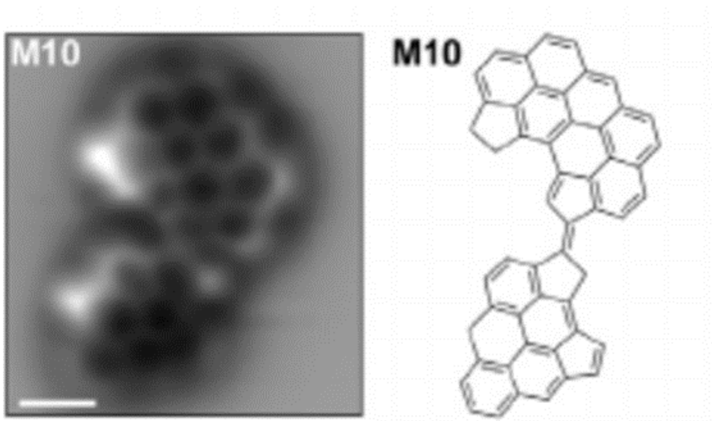


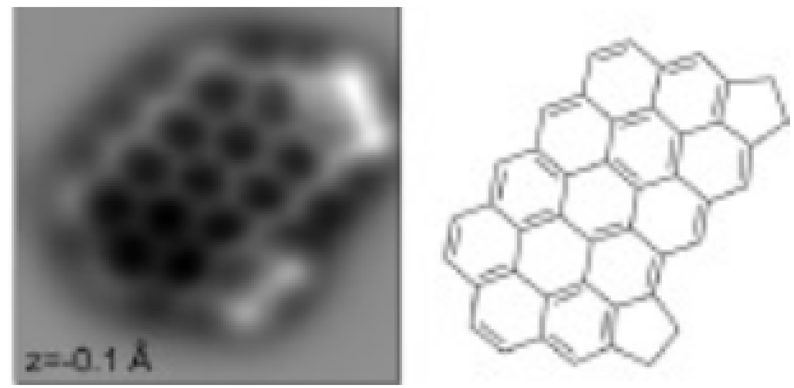
Ethylene flame

Carbone et al., Combust. Flame 181 (2017) 315–328

Some interesting images

Laminar premixed ethylene–air flame. C/O= 0.67. Incipient soot particles collected at HAB of 8 mm. High-dilution horizontal tubular probe.

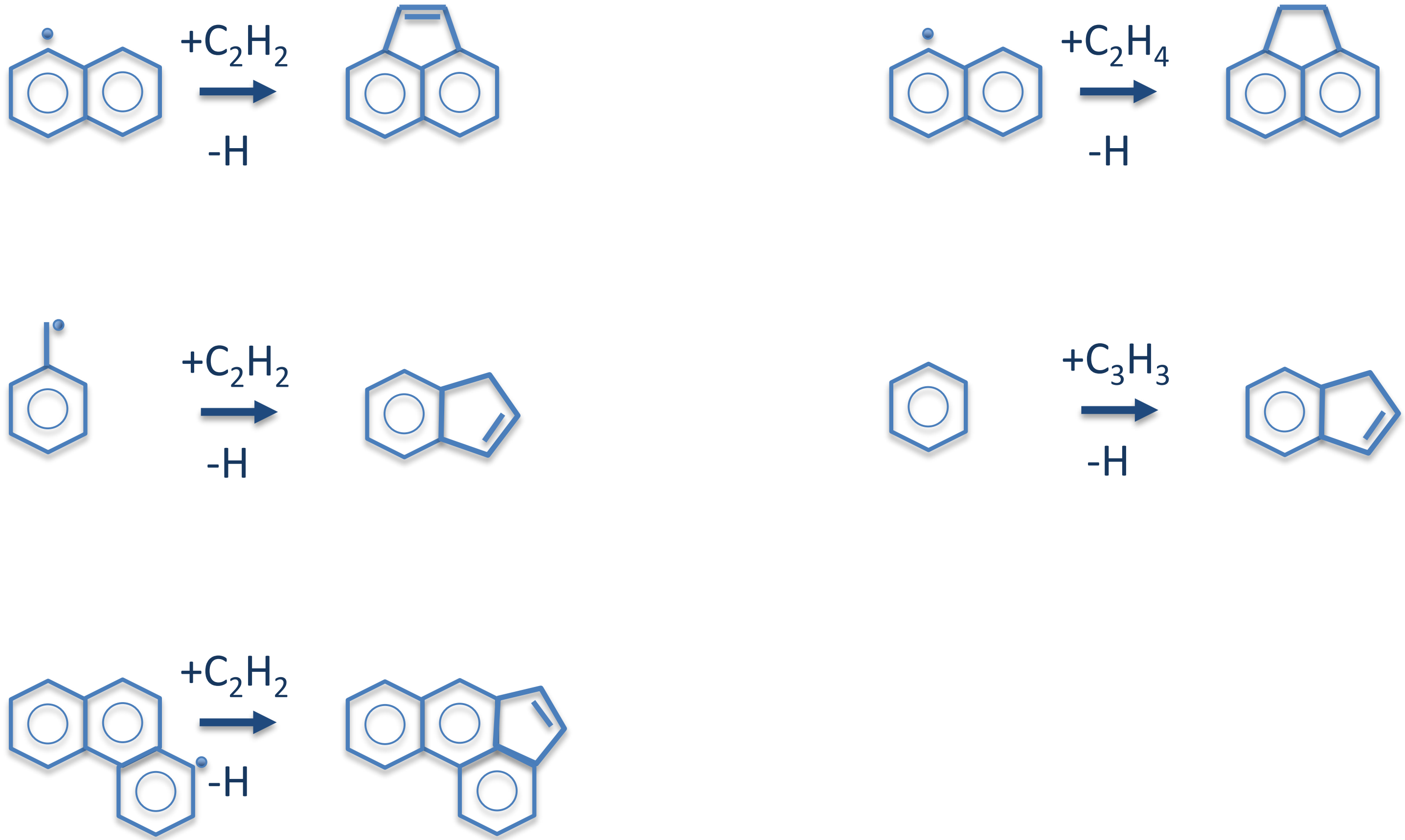




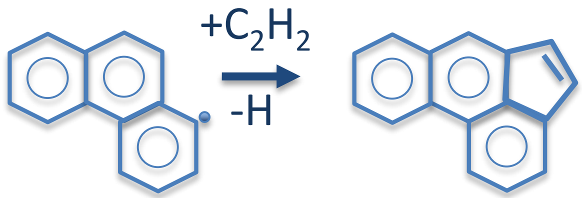
Several 5 membered rings and some aliphatic bridges. Number of needed species is very high.

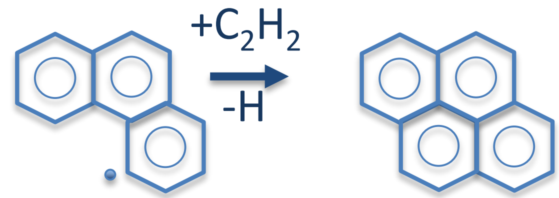
F. Schulz, M. Commodo, K. Kaiser, G. De Falco, P. Minutolo, G. Meyer, A. D'Anna, L. Gross, *Insights into incipient soot formation by atomic force microscopy*, Proceedings of the Combustion Institute 000 (2018) 1–8

Five membered ring formation

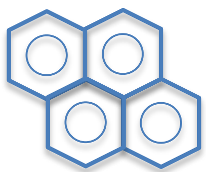


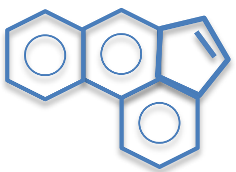
The number of isomers

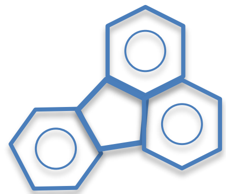




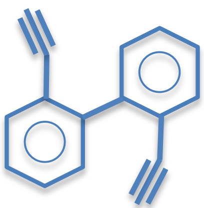
Some isomers of $C_{16}H_{10}$

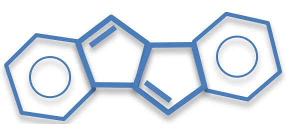

Pyrene

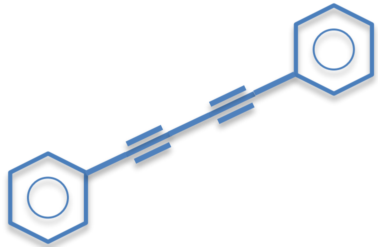

Acephenanthrylene


Fluoranthene

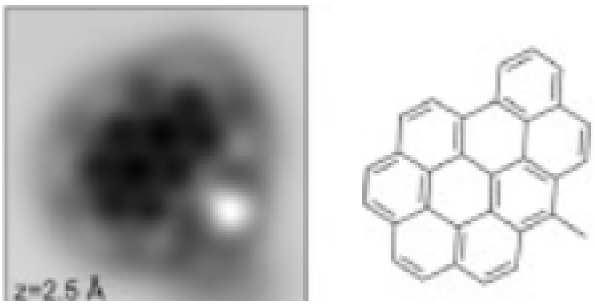

aceanthrylene


1,1'-Biphenyl,2,2'-diethynyl-

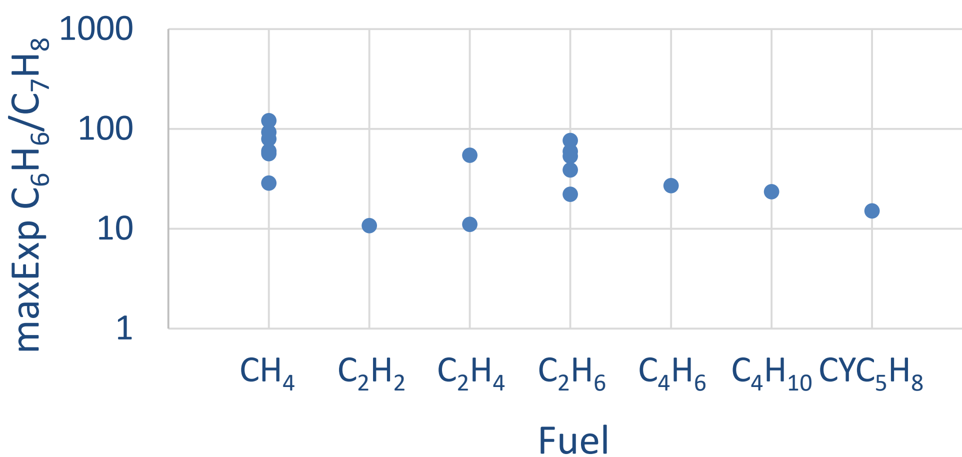

indenoindene


Benzene, 1,1'-(1,3-butadiyne-1,4-diyl)bis-

Methyl aromatics

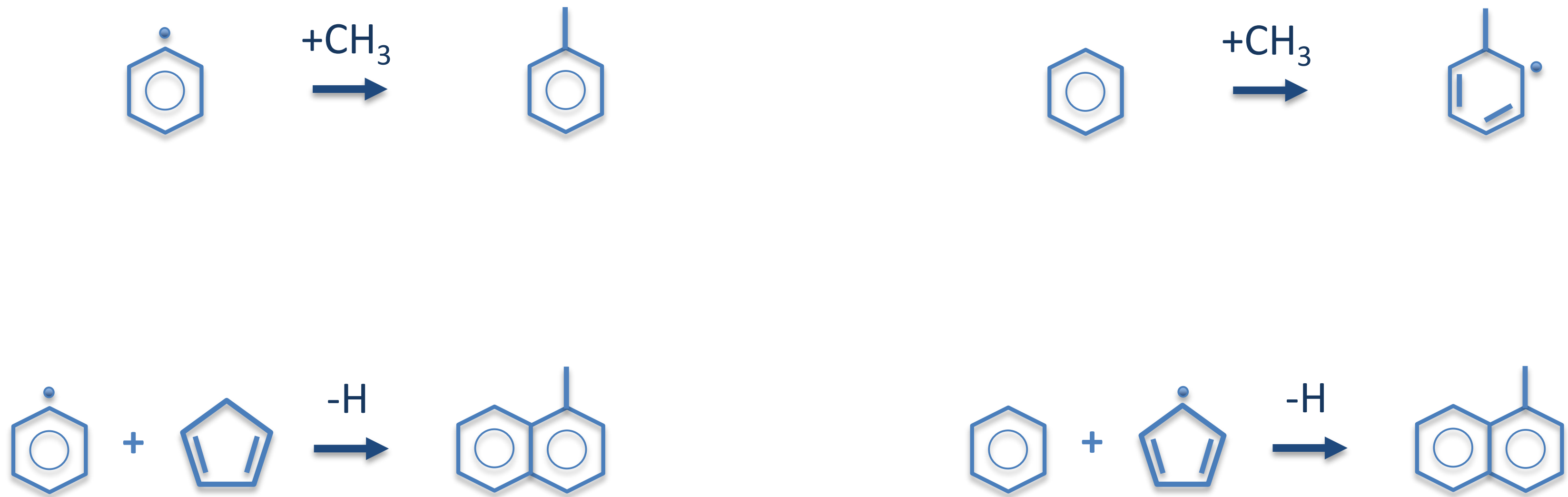


F. Schulz, M. Commodo, K. Kaiser, G. De Falco, P. Minutolo, G. Meyer, A. D'Anna, L. Gross, *Insights into incipient soot formation by atomic force microscopy*, Proceedings of the Combustion Institute 000 (2018) 1–8



From the experimental data base, toluene is one order of magnitude lower than benzene, at least

Aromatic methylation

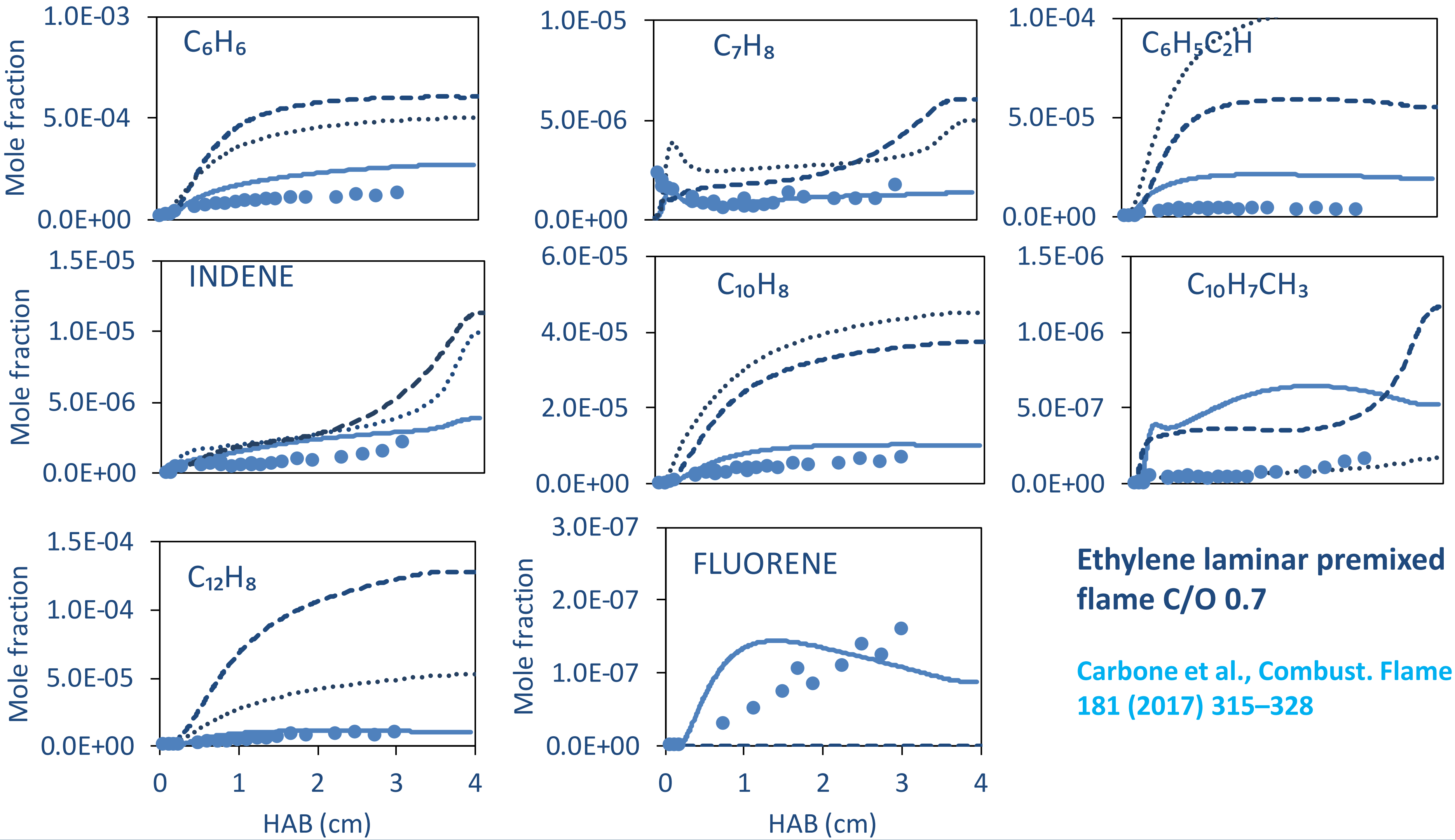


Cavallotti et al., JPCA, 116 (2012) 3313-3324

Cavallotti et al., Proc. Comb. Inst., 34 (2013) 557-564

Do actual mechanisms work?

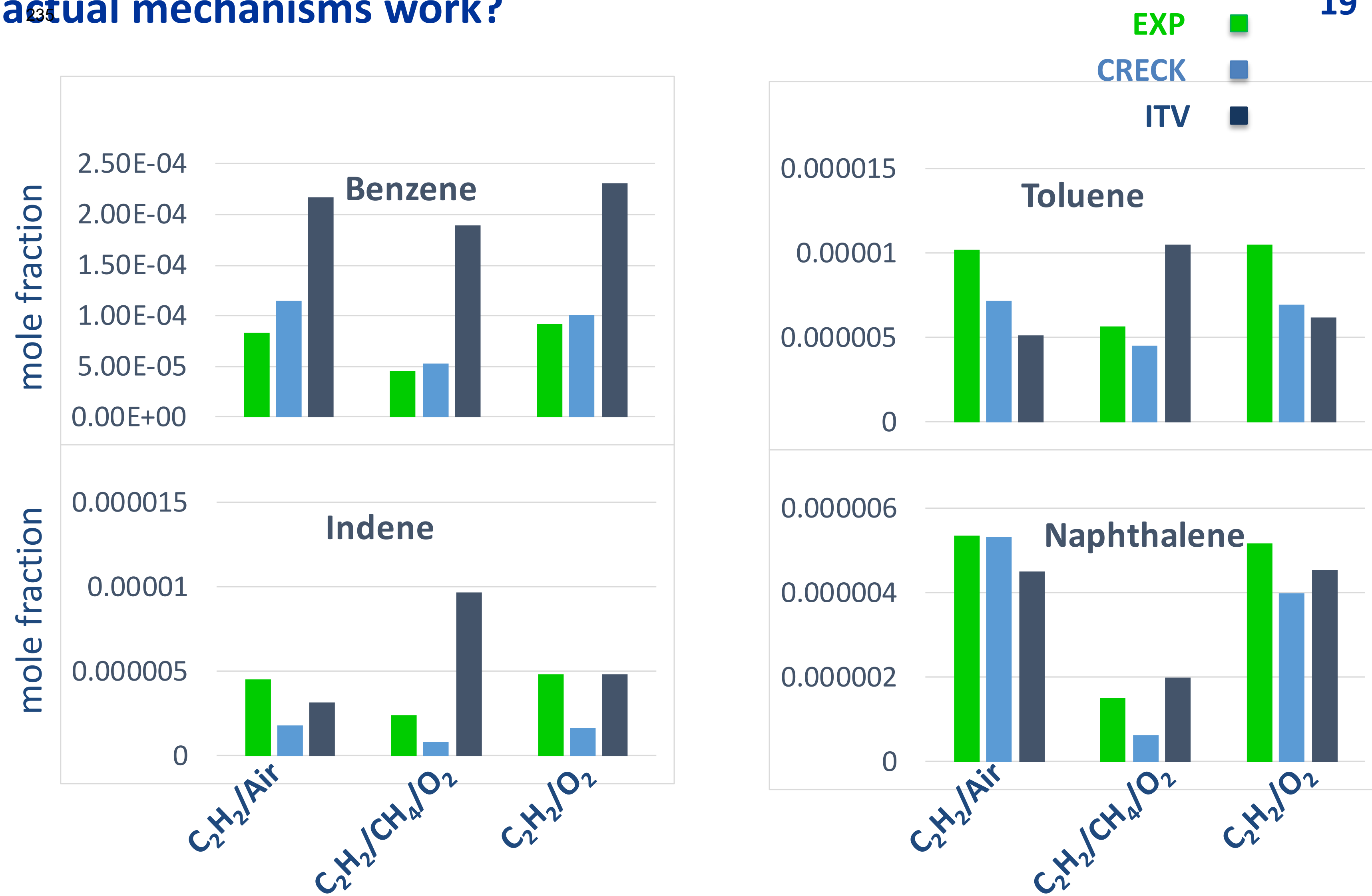
CRECK ——
ITV/Caltech ·······
KAUST - - - -



Ethylene laminar premixed flame C/O 0.7

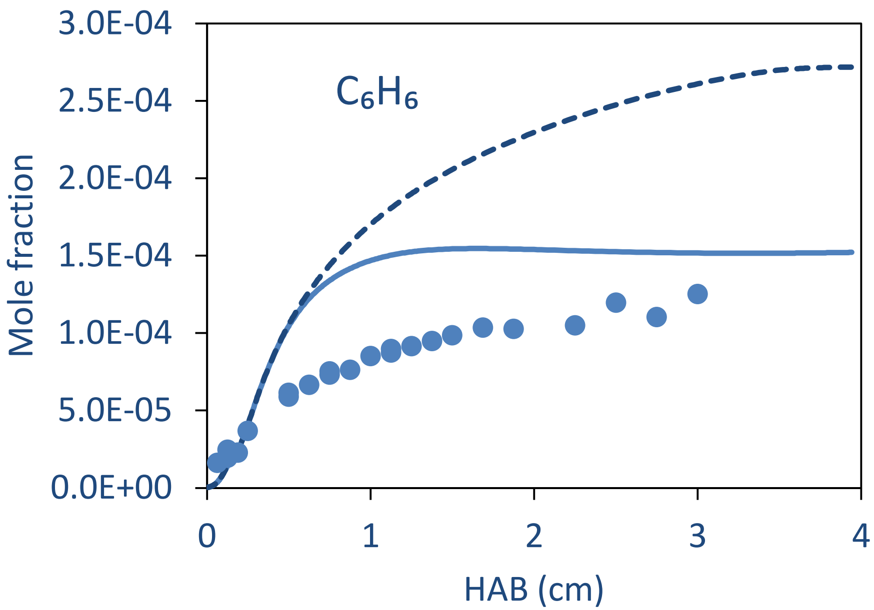
Carbone et al., Combust. Flame 181 (2017) 315–328

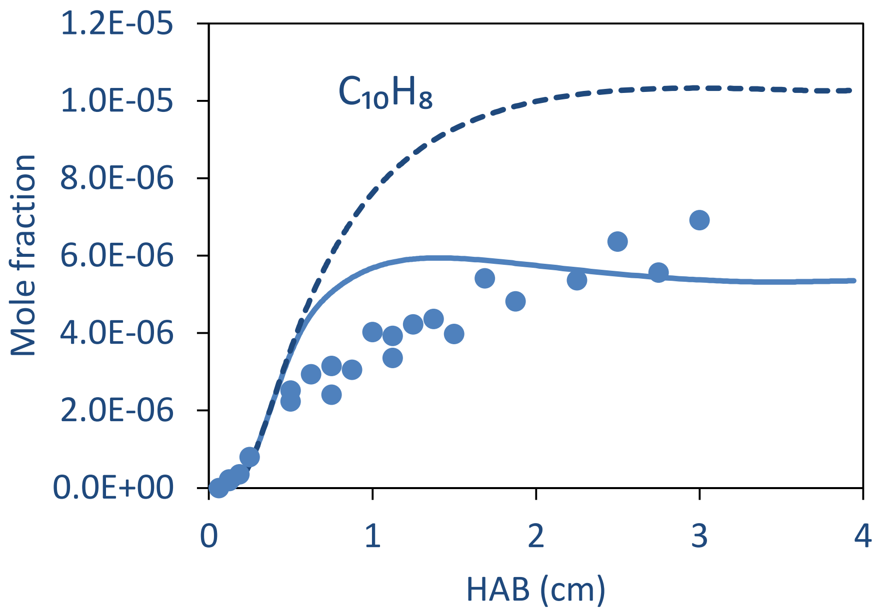
Do actual mechanisms work?



M. Baroncelli, D. Felsmann, N. Hansen, H. Pitsch, Investigating the effect of carbon dioxide and methane addition on acetylene counterflow flames: a mass spectrometric study, submitted to Combustion and Flame

Soot formation effect





with soot

without soot

W. Pejpichestakul et al., Soot effect on intermediate PAHs concentration in premixed laminar flames, Wednesday, presentation 3C01

Opening discussion

- Experimental data are still a few and in many cases not complete.
- Rate constants are a challenge because of the difficulties of applying ab-initio techniques to these large and very large molecules. Above all, rate rules for classes of reactions have to be identified.
- Several open questions on mechanisms. HACA or CAHM are still in progress.
- Number of species and isomers is another open issue. Lumping (both horizontal and vertical) or other possible approaches have to be adopted.
- Soot mechanism is necessary for PAH model development and validation.
- Despite all these difficulties, actual mechanisms can give some reasonable results, even though the work is not finished.

Acknowledgements

This presentation is the result of the work of many colleagues and especially students during the last years.

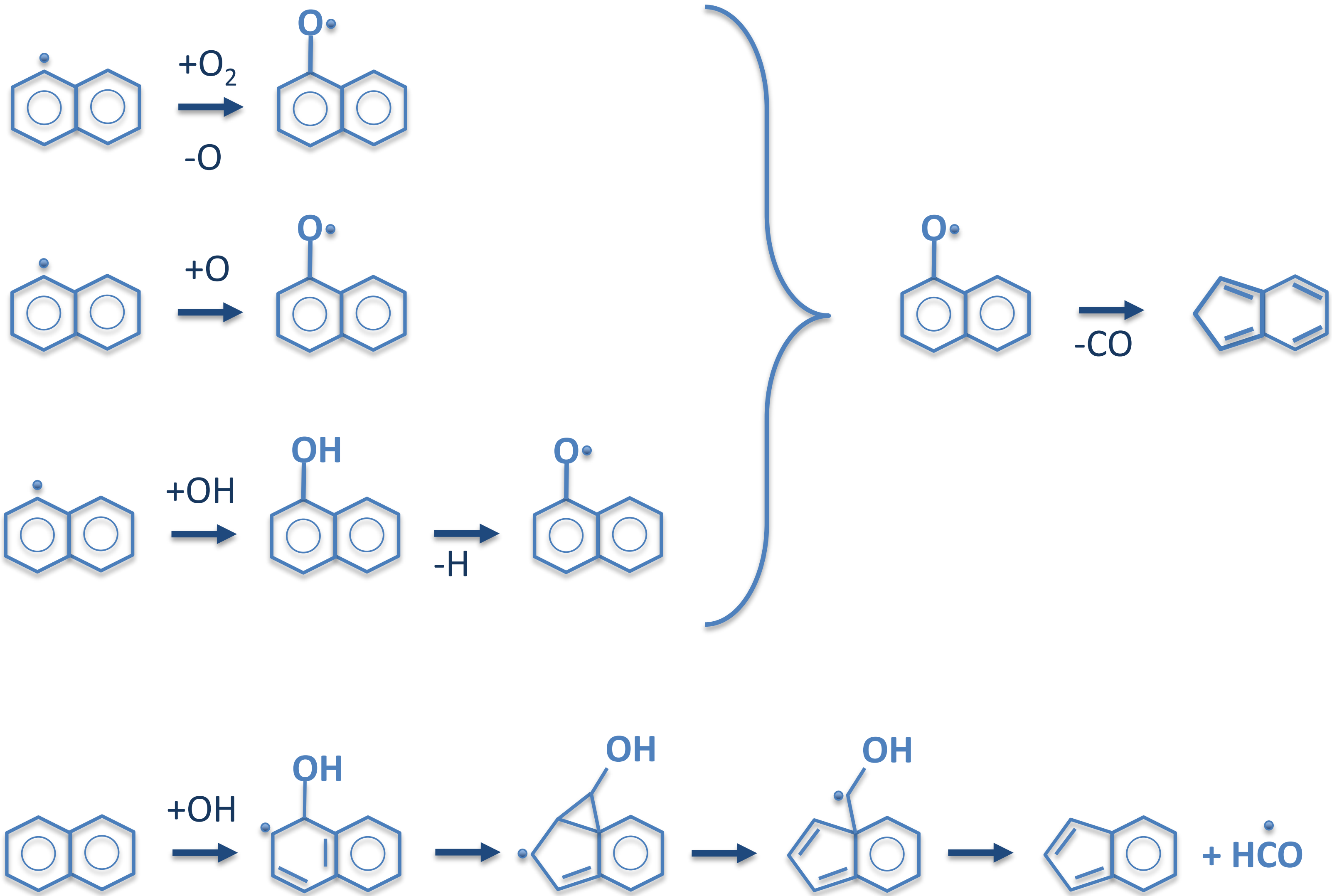
I acknowledge the fundamental support of:

Eliseo **Ranzi**
Alessio **Frassoldati**
Alberto **Cuoci**
Carlo **Cavallotti**
Marco **Mehl**
Matteo **Pelucchi**
Warumporn **Pejpichestakul**

Stephen **Klippenstein**

THANK YOU FOR YOUR ATTENTION

Oxidation



KAUST Piloted Turbulent Nonpremixed Flames at Elevated Pressure

Wesley Boyette, PhD Student, KAUST

In collaboration with Anthony Bennett, Thibault F. Guiberti, & William L. Roberts

4th International Sooting Flame (ISF) Workshop

Dublin, Ireland

27 July – 28 July, 2018

Pressurized Turb. Diffusion Flames?

Turbulent flames

1. Adelaide

2. Sandia

3. Delft/Adelaide

4. DLR

KAUST Pressurized Turbulent Nonpremixed Flames

Pressurized flames

1. Swirled pressurized

3. Laminar premixed pressurized

2. Laminar diffusion pressurized

High Pressure Combustion Duct

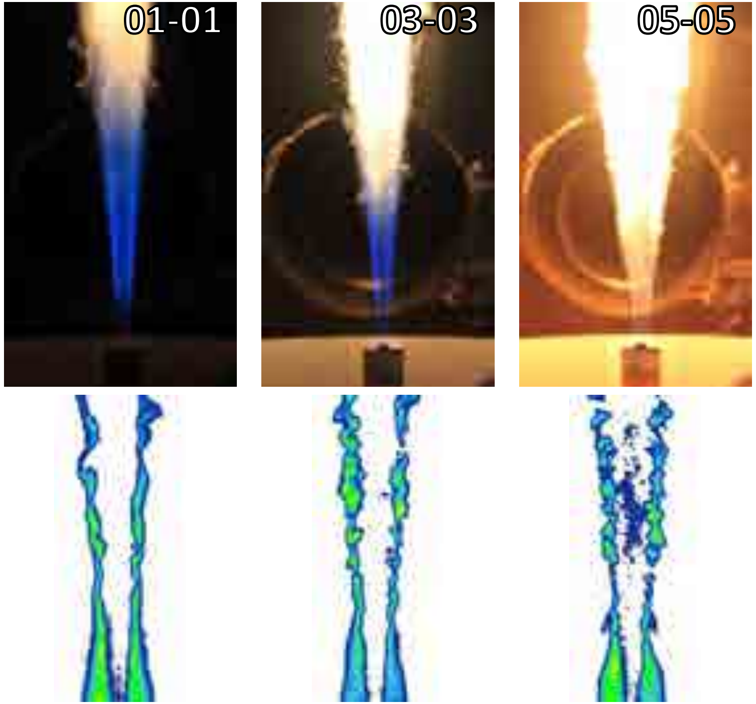
- Designed for turbulent non-premixed flames at high pressure
- Wide inner diameter (~ 400 mm)
  - Accommodates wide variety of burners
  - Minimizes flame-wall interactions
- Height (~ 9 m) allows very long flames
  - Vertical orientation eliminates buoyancy induced asymmetries
- Design pressure: 40 atm
- Optical access: 6 UV fused silica windows
- High air flow rates for coflow & cooling

KAUST C_2H_4/N_2 (KEN) Flames

- $35\%\ C_2H_4$, $65\%\ N_2$ by volume
  - Geometry identical to ISF-4 turbulent target flame 2 (Sandia) (1)
    - $D = 3.4$ mm
  - Piloted (C_2H_4/air, $\phi = 0.9$)
    - 6% of main jet heat release

Flame	p (atm)	Re_D	U_j (m/s)	U_{cf} (m/s)	Pilot
01-01	1	10,000	37.9	0.6	6%
03-03	3	30,000	37.9	0.6	6%
05-05	5	50,000	37.9	0.6	6%

Direct images (top) and OH-PLIF (bottom) for KEN flames.
Note: Different scales

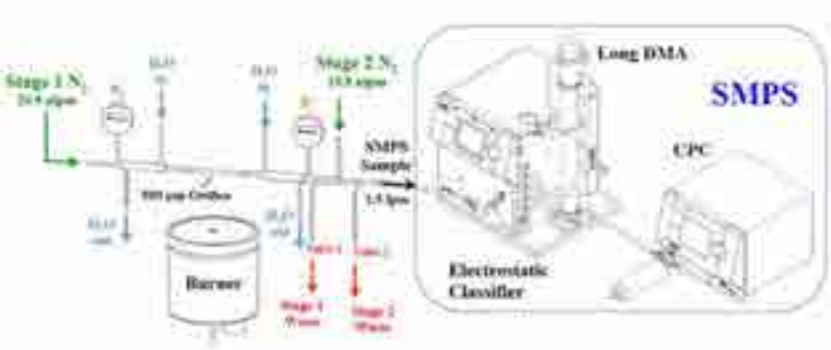


(1) Zhang, Shaddix, Schefer. *Rev Sci Inst*. 82:074101 (2011)

Soot Diagnostics

Scanning Mobility Particle Sizer (1 atm)

- time-averaged particle size distributions
- intrusive technique
- adequate N_2 dilution of sample critical to avoid soot coagulation in sample line
- requires low soot concentrations



Laser Induced Incandescence (1-5 atm)

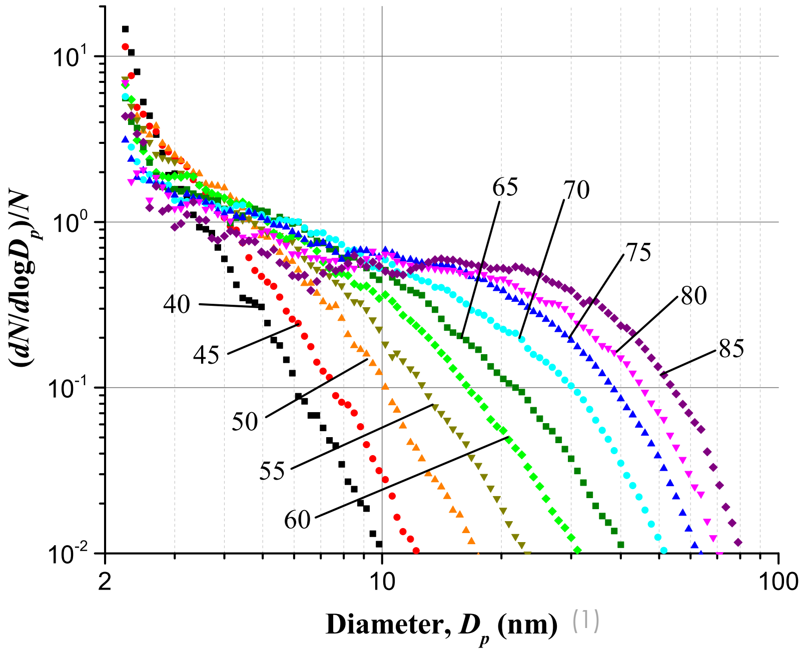
- 10 Hz, 1064 nm
- collection wavelength: 655 nm
- gate: 50 ns
- image entire flame at 40 mm increments
- background image immediately before laser
- calibration with laminar flames
    - different calibration for each pressure

KEN 01-01 Particle Size Distributions

KAUST

- Centerline soot particle size distributions in increments of *x/D* = 5
  - Time-averaged
- Gradual shift to larger particle diameters as *x* increases
- Recent transported PDF modelling by Schiener & Lindstedt (PROCI 2018) shows good agreement
  - *Session 5C01*

KEN 01-01 Centerline soot PSDFs

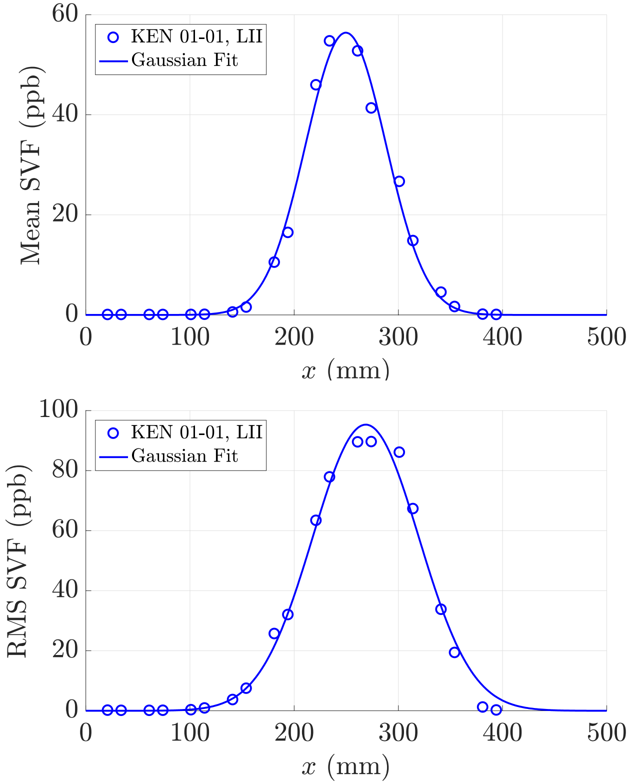


(1)

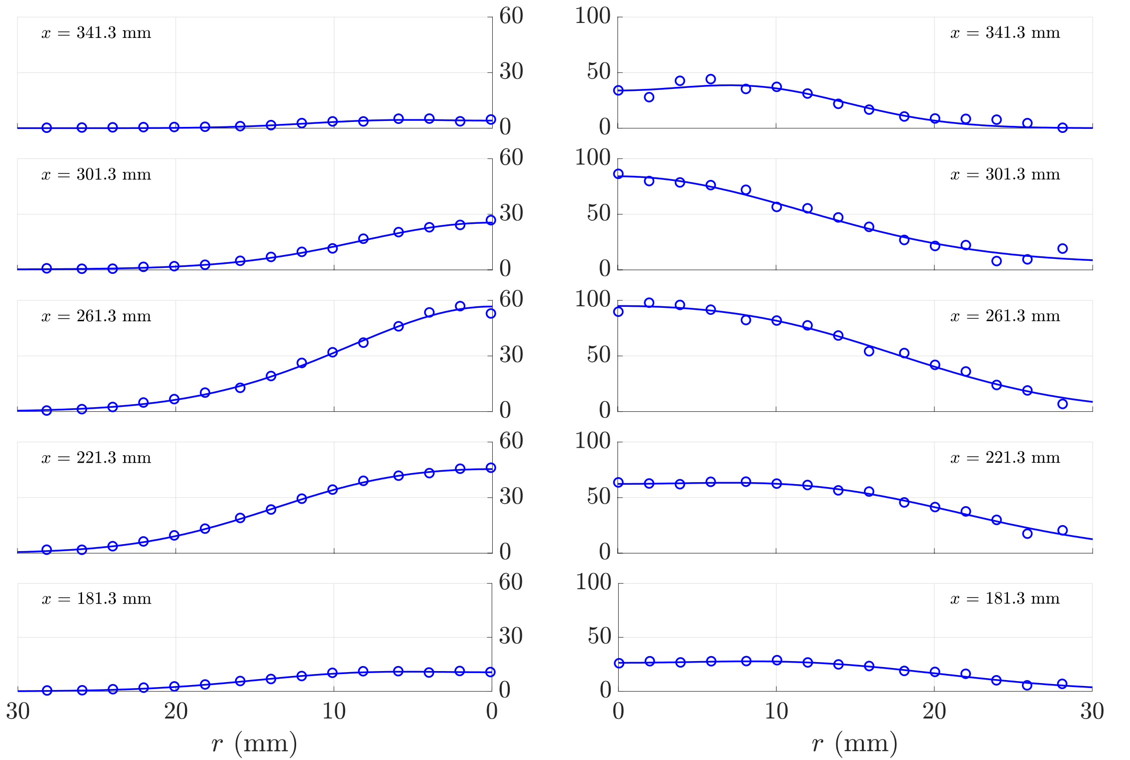
(1) Chowdhury, Boyette, Roberts. *J Aero Sci.* 106:56-67 (2017)

KEN 01-01 Soot Volume Fraction

KEN 01-01 Centerline mean & RMS SVF



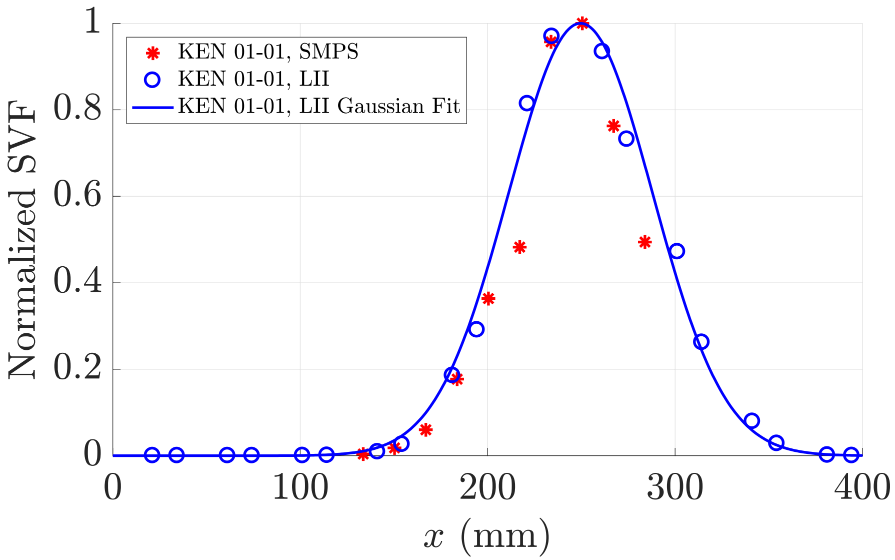
KEN 01-01 Radial mean & RMS SVF



KEN 01-01 SMPS & LII Comparison

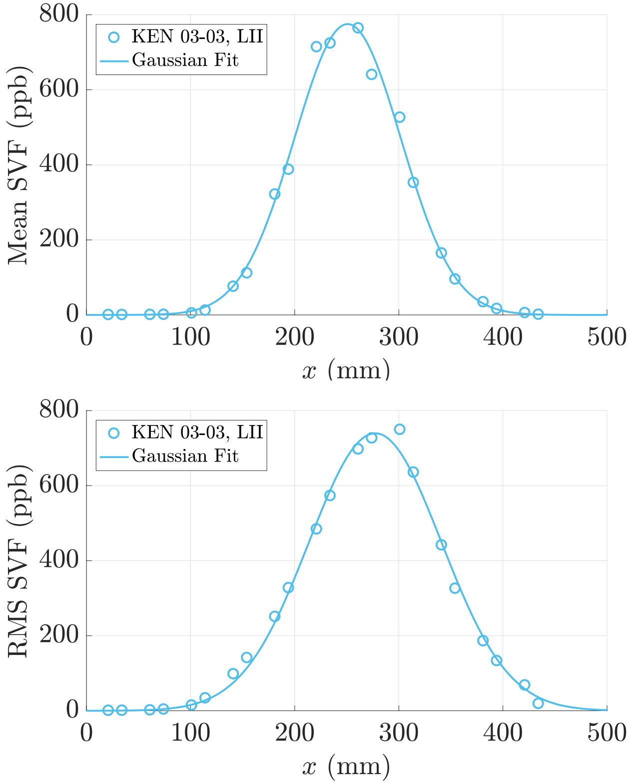
- Normalized centerline SVF profiles from SMPS and LII
  - Excellent agreement
  - Assumes constant SMPS N_2 dilution ratio
- Reasons for discrepancies
  - Very different techniques
    - Aggregation high in flame: particles not necessarily spherical
  - SMPS N_2 dilution ratio not measured directly and may not be constant
  - SMPS is intrusive
  - Slight differences in burner construction & coflow

KEN 01-01 Normalized centerline mean SVF

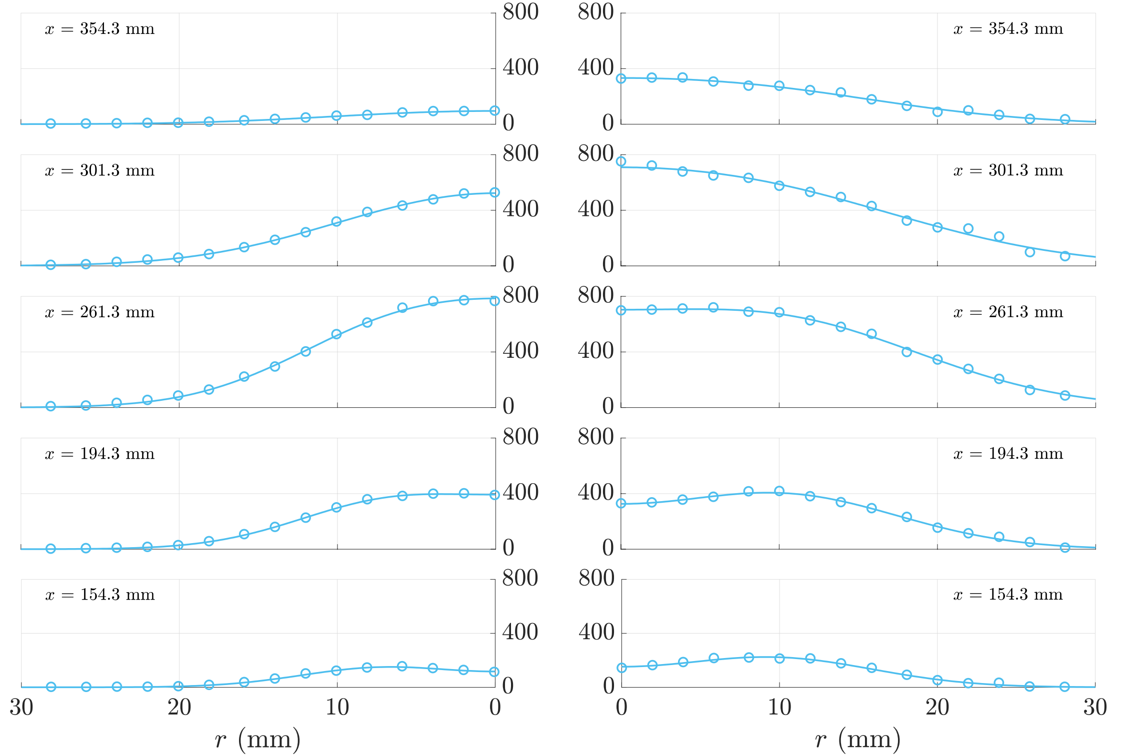


KEN 03-03 Soot Volume Fraction

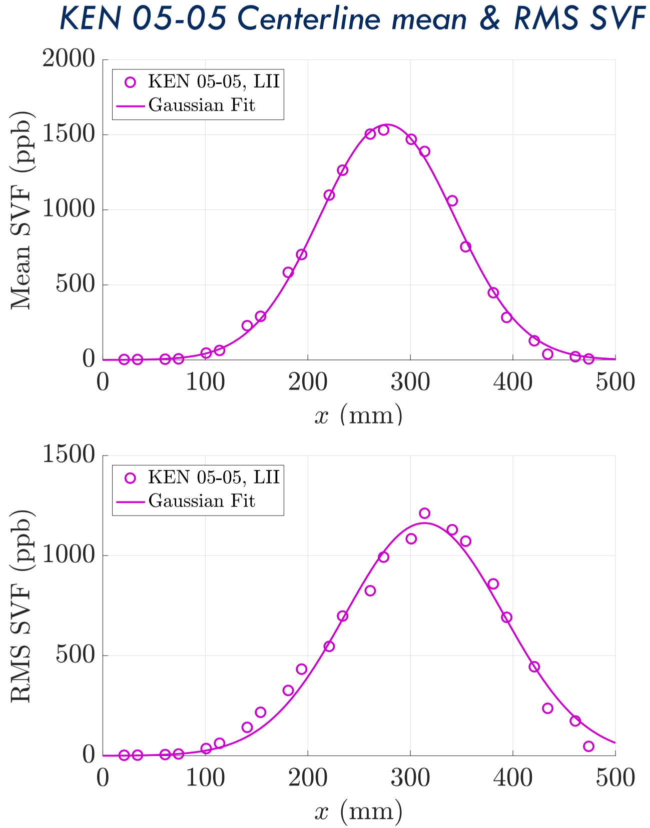
KEN 03-03 Centerline mean & RMS SVF

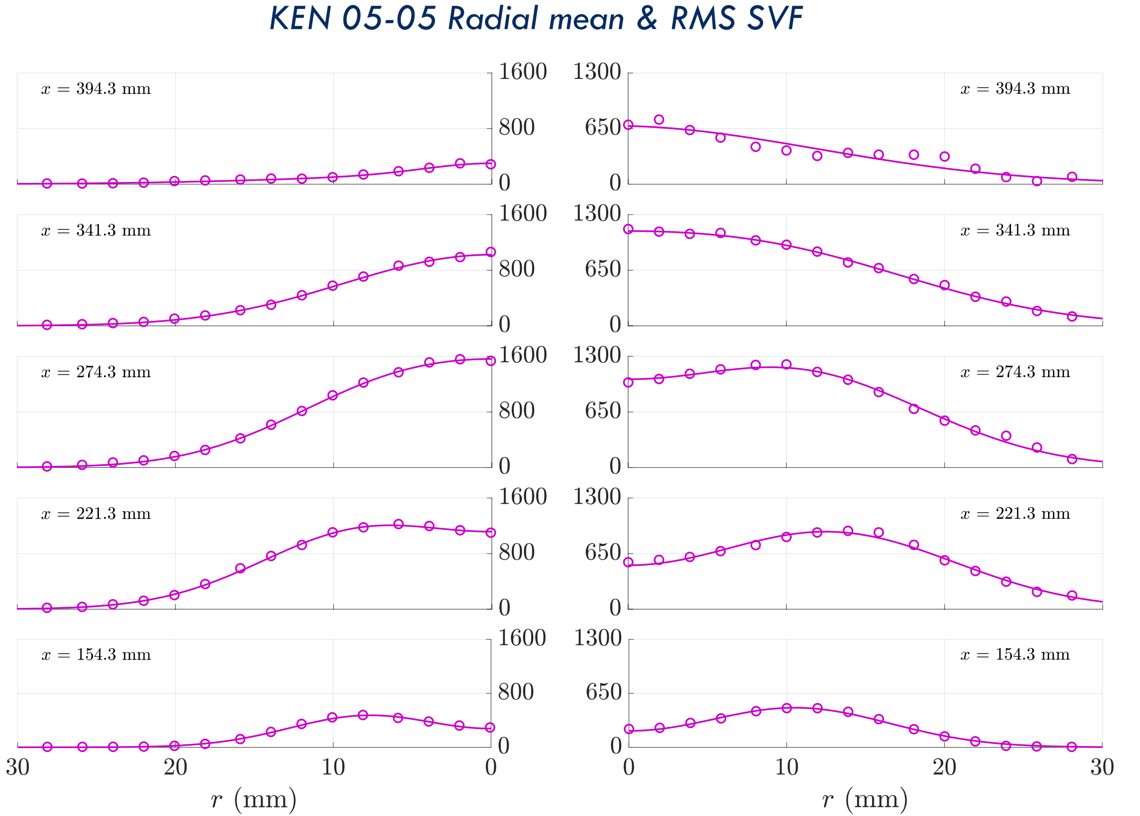


KEN 03-03 Radial mean & RMS SVF



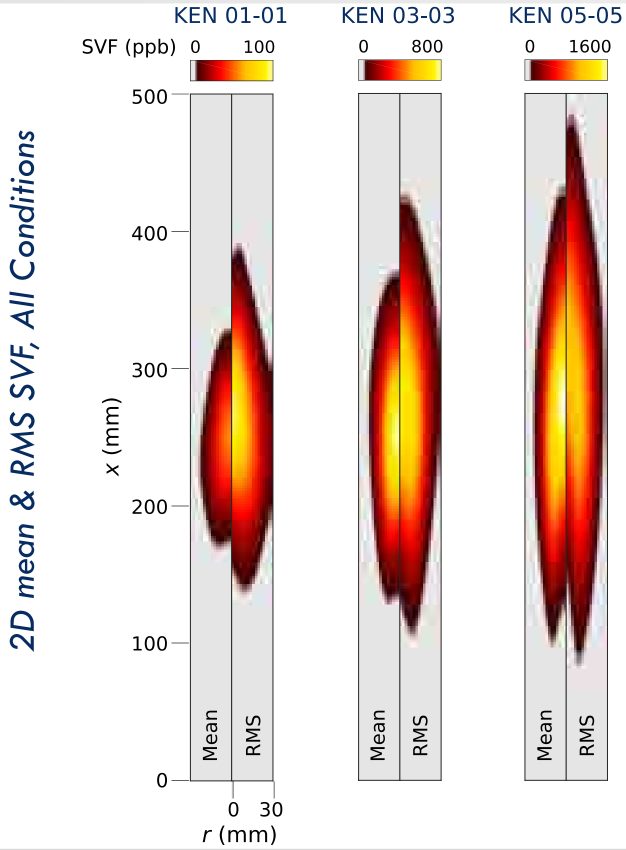
KEN 05-05 Soot Volume Fraction





SVF Comparisons 1

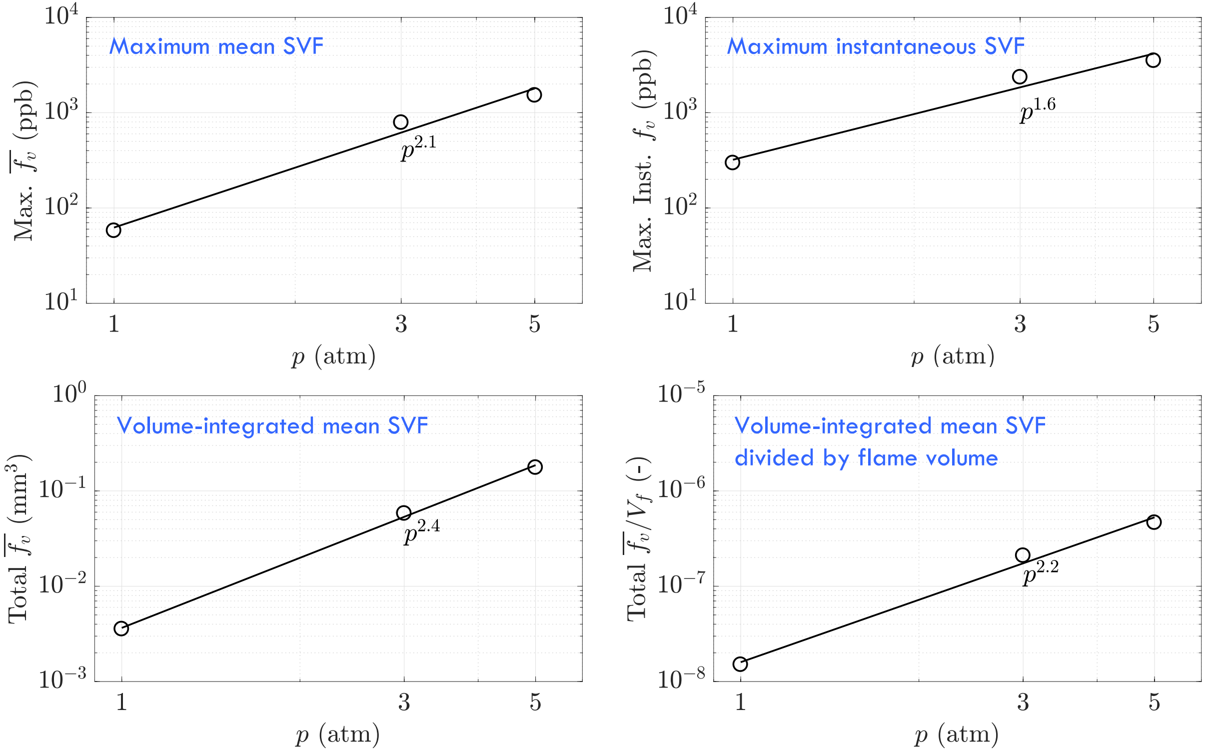
251



- As pressure/Re increase
  - Flames get longer (volume increases)
  - Axial distance to soot inception decreases
  - Axial location of maximum mean SVF changes very little

SVF Comparisons 2

Trends of Global Soot Parameters versus Pressure



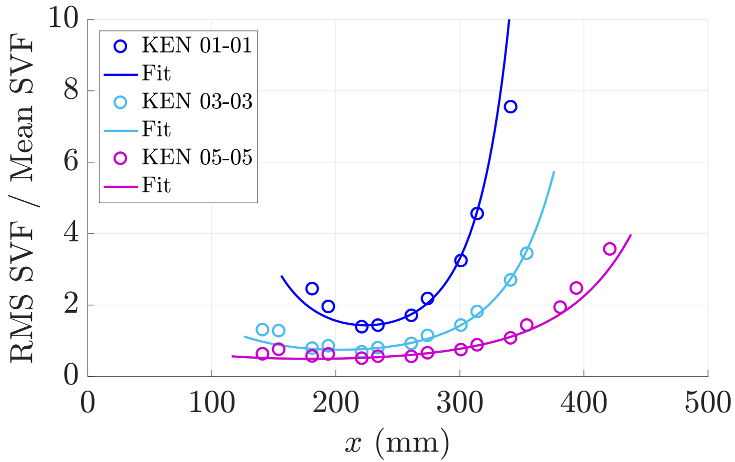
- Reynolds number effects outweighed by pressure effects
- Other studies show p^n relationship with SVF
  - Turbulent diffusion flames: $p^{1.4}$ (1)
  - Laminar diffusion flames: $p^{2.2}$ (2)

(1) Flower. *Proc. Combust Inst.* 22:425-435 (1988)
(2) Steinmetz, Fang, Roberts. *Combust Flame.* 169:85-93 (2016)

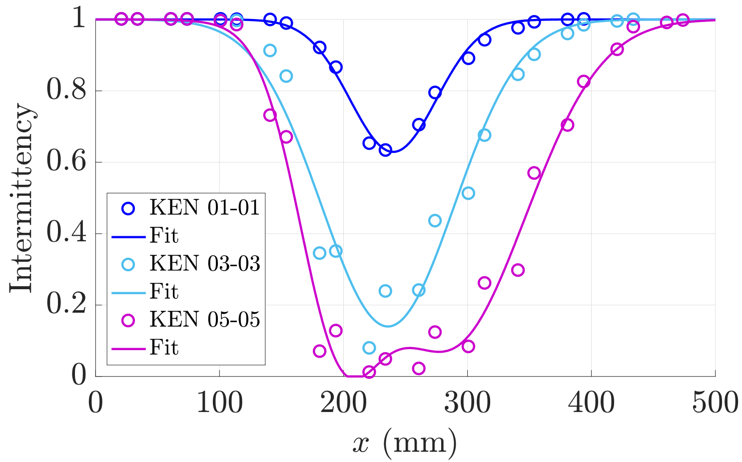
SVF Comparisons 3

- Centerline RMS & mean same order of magnitude
  - Decreases with increasing pressure
- Centerline intermittency strong function of pressure/Re
  - Soot almost always present near peak of 5 atm flame

Centerline RMS/Mean SVF for All Conditions

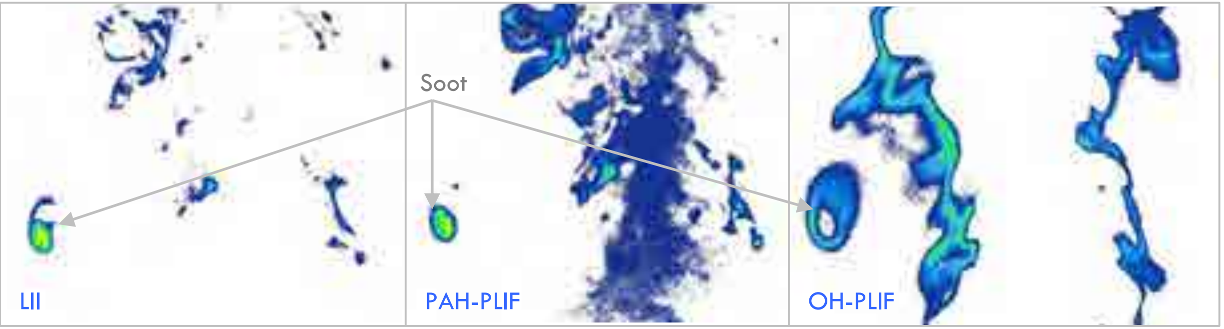


Centerline Intermittency for All Conditions

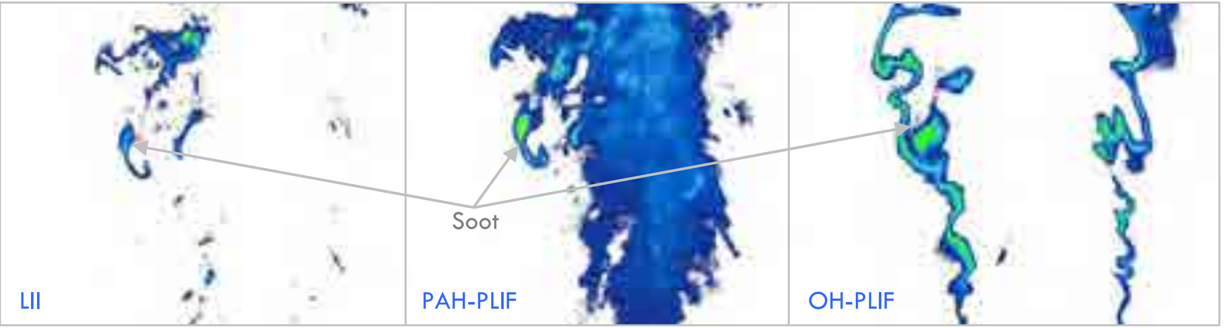


Data Being Processed

Simultaneous Soot, PAH, OH: KEN 05-05, Station 3



Simultaneous Soot, PAH, OH: KEN 05-05, Station 2



- Simultaneous LII/PAH-LIF/OH-LIF
- Data collected; still processing
- Images shown are uncorrected
- Details
  - LII
    - laser: λ = 1064 nm
    - collection: λ = 655 nm
  - PAH-PLIF
    - laser: λ = 283 nm
    - collection: λ = 500 nm shortpass + λ = 325 nm longpass
  - OH-PLIF
    - laser: λ = 283 nm
    - collection: λ = 310 nm

Future Work

255

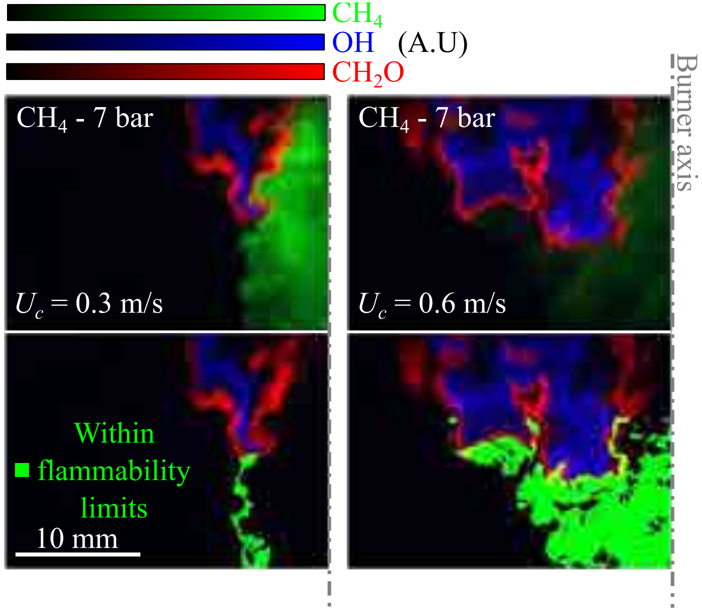
- Flame type
  - KEN flames
    - Extension to other conditions in 1-5 atm range
      - Constant Re series in addition to constant U
    - Probably limited to 5-7 atm maximum pressure
  - Lifted flames?

Lifted Flames

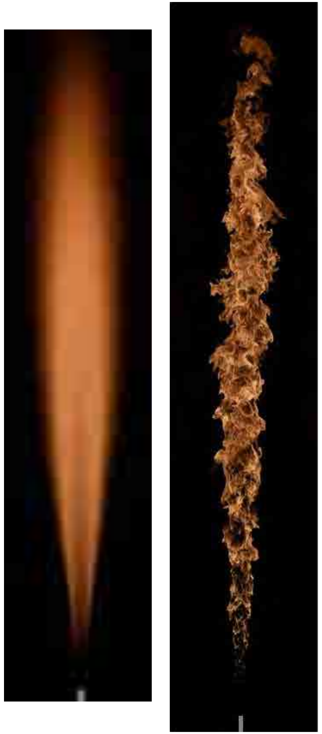
256

- Some experimental advantages over piloted flames
  - Not limited to 5-7 atm
  - Full characterization of flow & scalars upstream of flame possible
  - Can easily change tube diameter if needed
- Will still need N_2 dilution at pressure
  - Lower soot concentration, shorter, less powerful

$CH_4 - 7$ bar
OH-PLIF/CH_2O-PLIF/2D-CH_4-Raman



$C_2H_6 - 6$ bar
DSLR



Future Work

257

- Flame type
  - KEN flames
    - Extension to other conditions in 1-5 atm range
      - Constant Re series in addition to constant U
    - Probably limited to 5-7 atm maximum pressure
  - Lifted flames?
- Fuel
  - in order of preference: CH_4, C_2H_4, C_2H6
- Data collection
  - 2D velocity: non-reacting + reacting, base only
  - Temperature: LITGS
  - SVF: for any new conditions

What is current knowledge in PAH chemistry - Elementary reaction point of view

From 1 to 3 Rings and Beyond: Status of Theory

Stephen J. Klippenstein

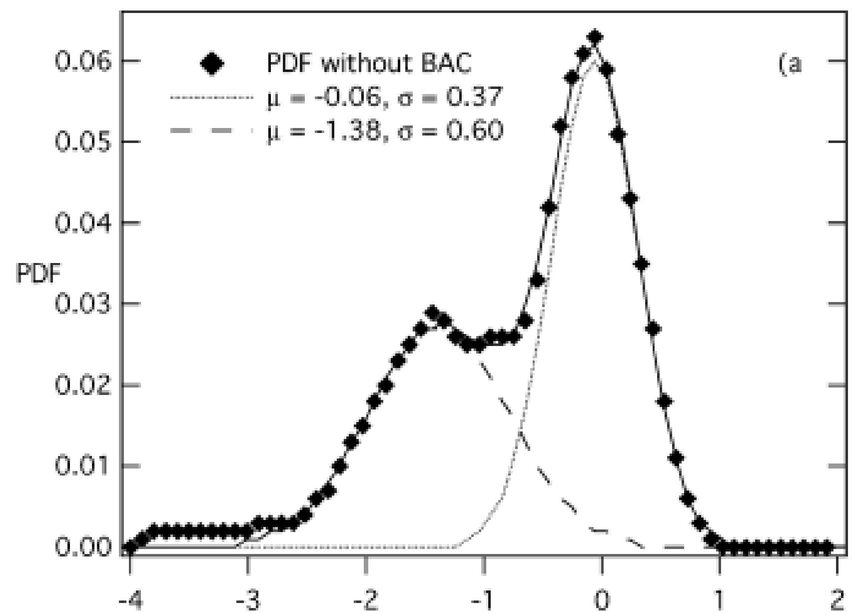
4th International Workshop on Flame Chemistry, Dublin, July 28, 2018

Progress in Theory — High Pressure Limits

1. Potential Energy Surface Mapping
   - Mebel, Mebel, Mebel, …
   - Cavallotti, Miyoshi, Comandini, Koshi, Green
   - Others
2. Energies

	2σ (kcal/mol)	Boltzmann(2σ) at 1500 K
Current		
❑ CBS-QB3	2.5	2.3
❑ G2M	~2-3	2.0-2.7
Future		
❑ CCSD(T)/CBS	~1.5	1.7
❑ Isodesmics		
❑ Bond Additivity Corrections		
❑ Connectivity Based Hierarchy		
❑ Machine Learning - Green		

Goldsmith, Magoon, Green
JPCA 116 (2012), 9033



3. Partition Functions
   - Density Functional Theory
     - ❑ B3LYP -> M062X -> B2PLYPD3
   - Hindered Rotors
   - Variational

Overall Uncertainty ~ Typically - Factor of 4-10
State of the Art ~ 2

Progress in Theory Pressure Dependence

Most Studies have Ignored Pressure Dependence

Mechanisms Change with Pressure

- 1 Atm and Lower
  - ❑ Bimolecular Products
  - ❑ Direct/Well Skipping
  - ❑ Unstable Species
- 100 Atm
  - ❑ Stabilization
  - ❑ But Still not High Pressure Limit Because of Back Flux

Master Equation

- Chemically Significant Eigenvectors
  - ❑ Mebel, SJK, Miyoshi
- Stochastic Solvers
  - ❑ Cavallotti, Frenklach
- ME + Modified Strong Colliders (??)
  - ❑ Green

Lingering Questions - Unstable Species, Direct Decomp., Non-Thermal

Uncertainty ~ Another Factor of 2 – 3

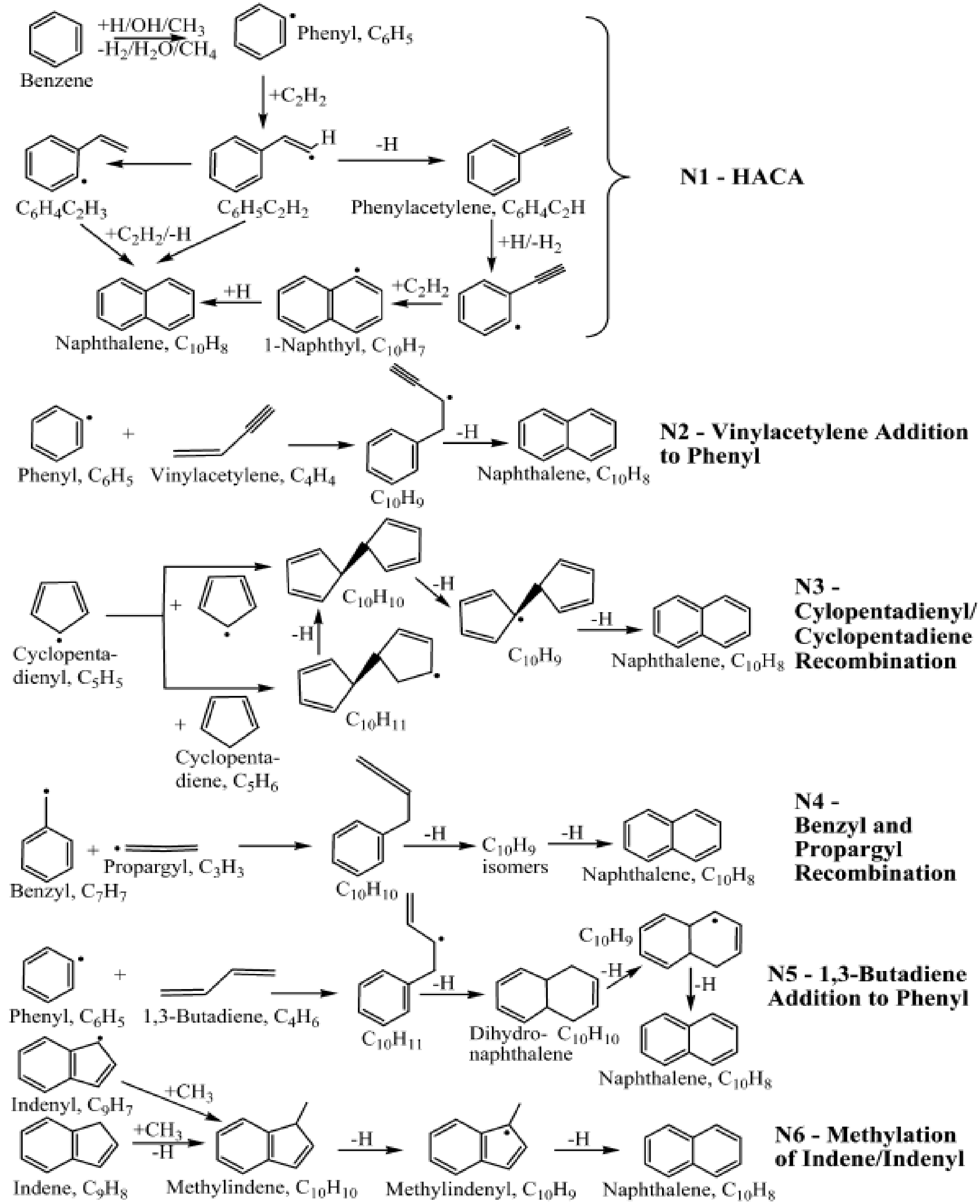
Pathways to Naphthalene $C_{10}H_8$

Mebel, Landera, Kaiser, JPCA 121 (2017) 901-926

- HACA
- $C_5H_5 + C_5H_{6/5/4}$
- $C_6H_5 + C_4$ Alkenes
- Reson. Stab. Rad. + Reson. Stab. Rad.
- Indene/Indenyl + CH_3

Other Pathways

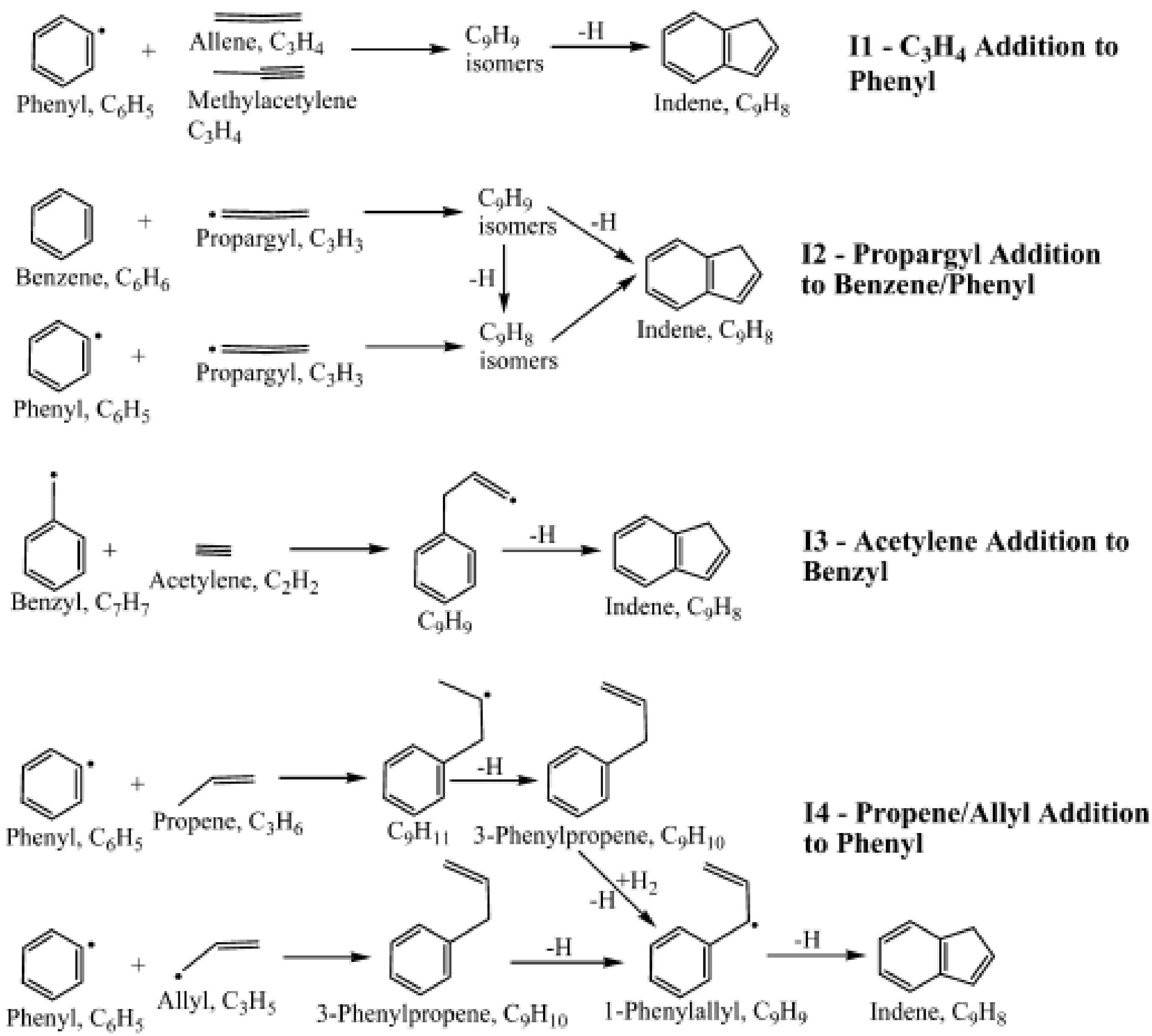
- Phenyl Assisted Cyc./ Aromatic + Aromatic
- CH_3 + Aromatic
- Benzyne
- Fulvene
- Triplets



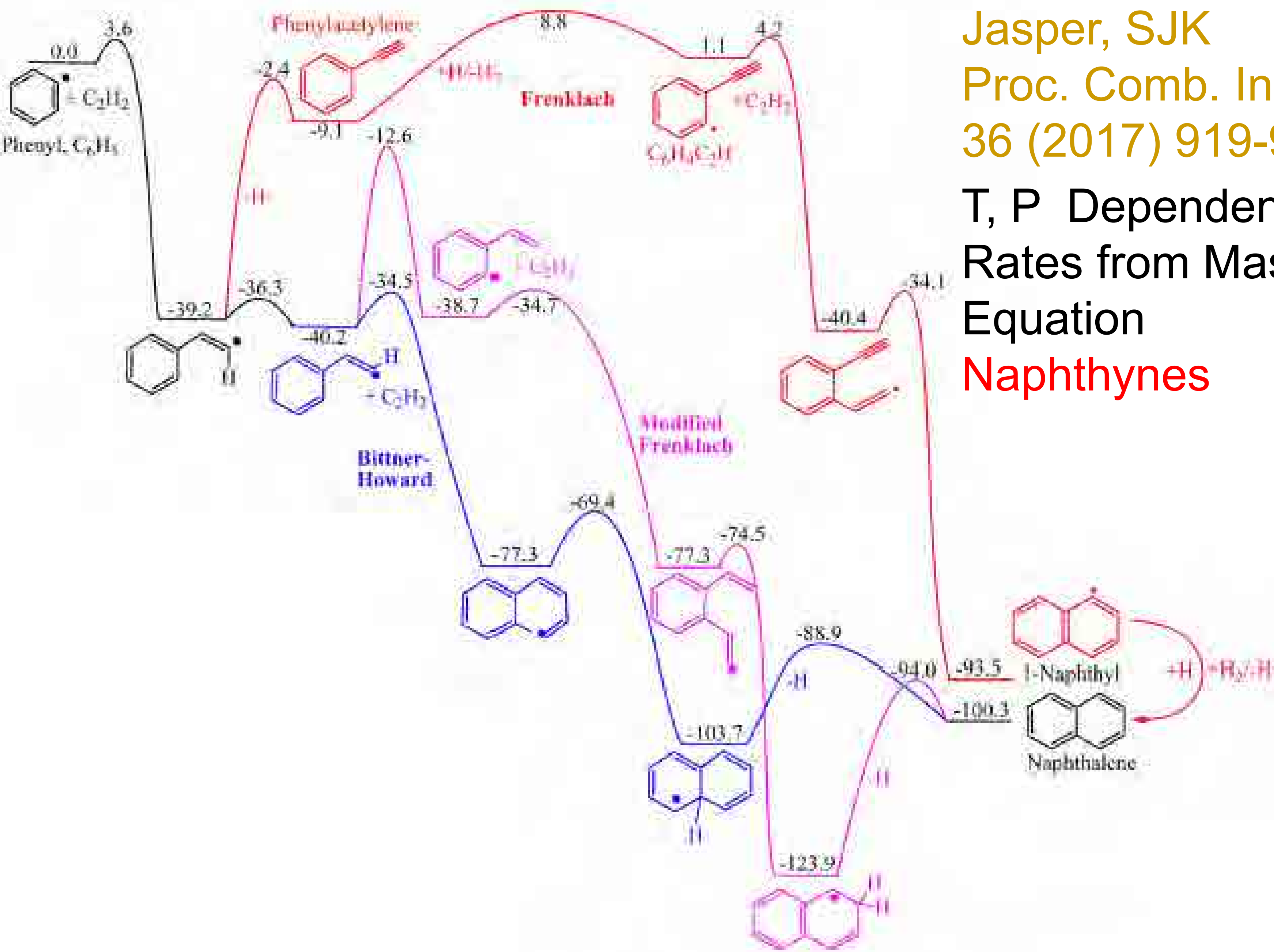
Pathways to Indene C_9H_8

Mebel, Landera, Kaiser, JPCA 121 (2017) 901-926

- Phenyl + C3 Alkene
- C_6H_6 + C3 Res. Stab. Rad.
- Phenyl + C3 Res. Stab. Rad.
- $C_7H_7 + C_2H_2$



HACA

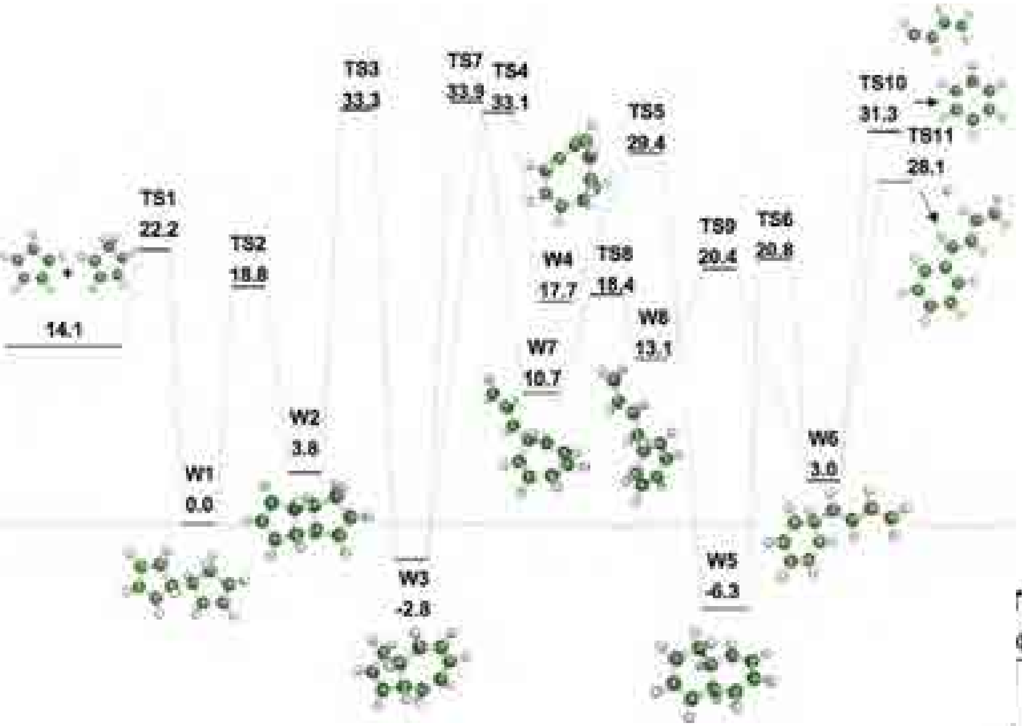


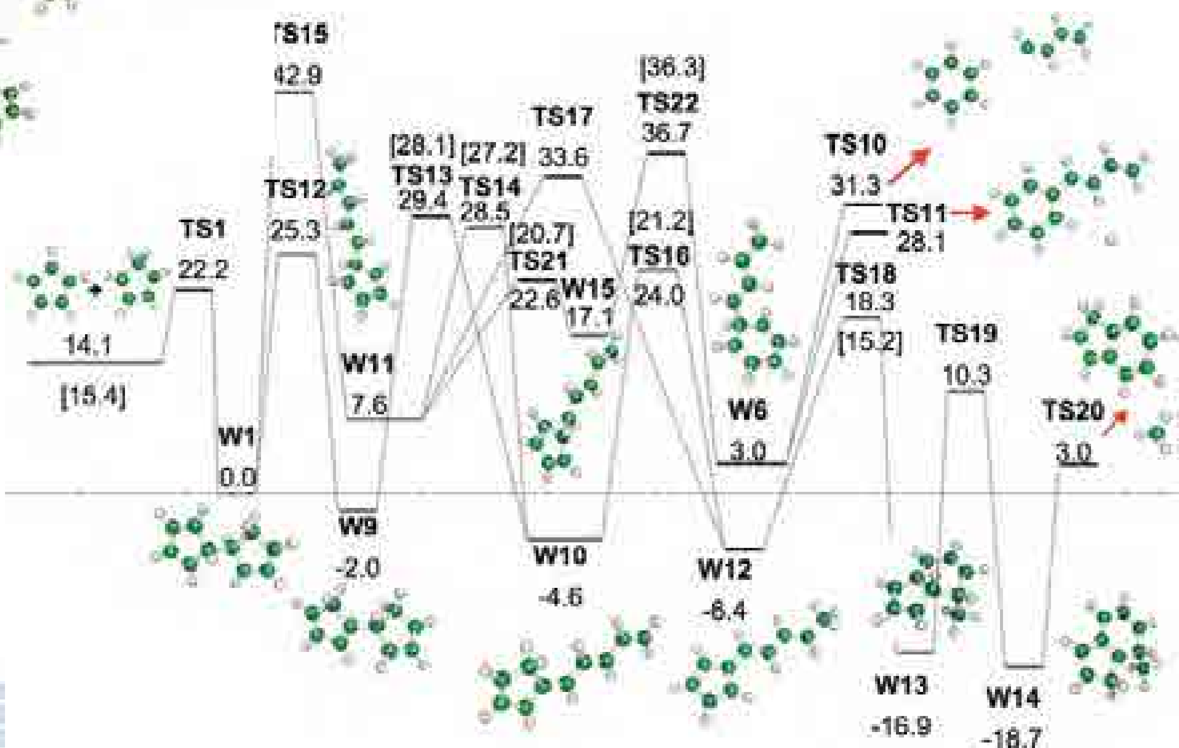
Mebel, Georgievskii, Jasper, SJK
Proc. Comb. Inst. 36 (2017) 919-926

T, P Dependent Rates from Master Equation

Naphthynes

$C_5H_5 + C_5H_6$

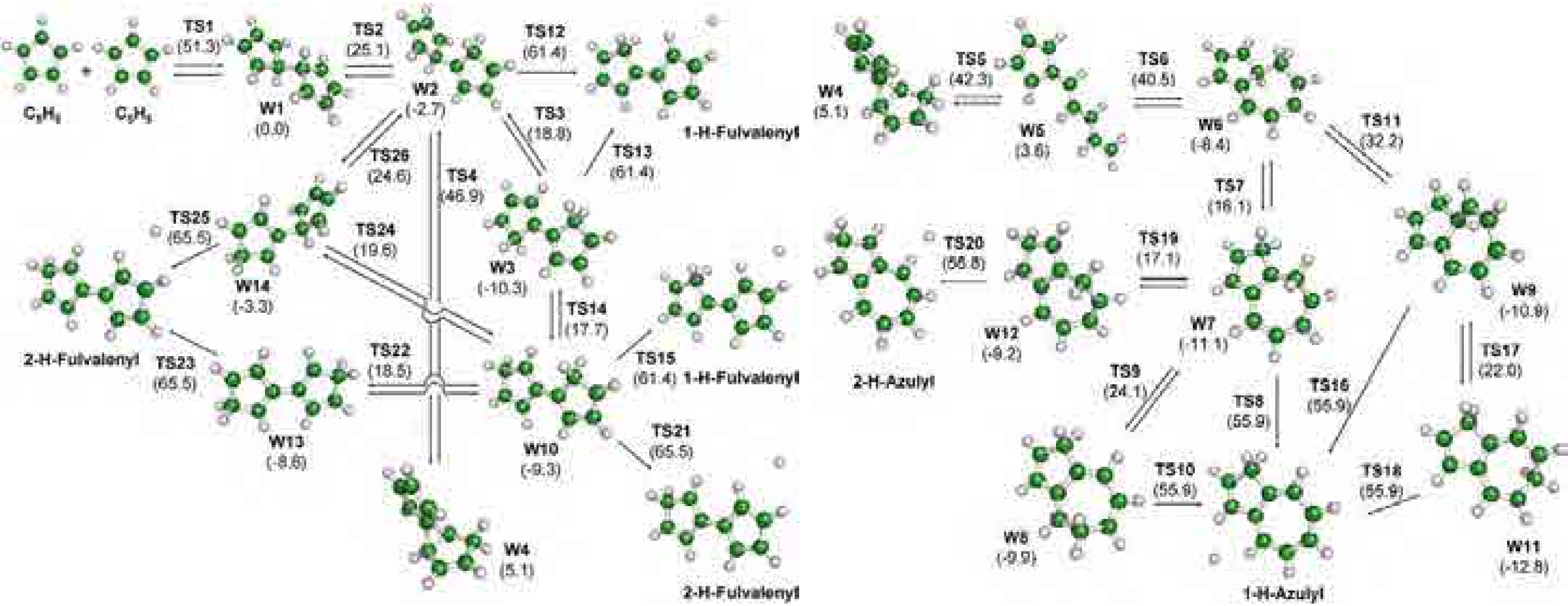




Cavallotti, Polino, Frassoldati, Ranzi, J. Phys. Chem. A 116 (2012) 3313-3324

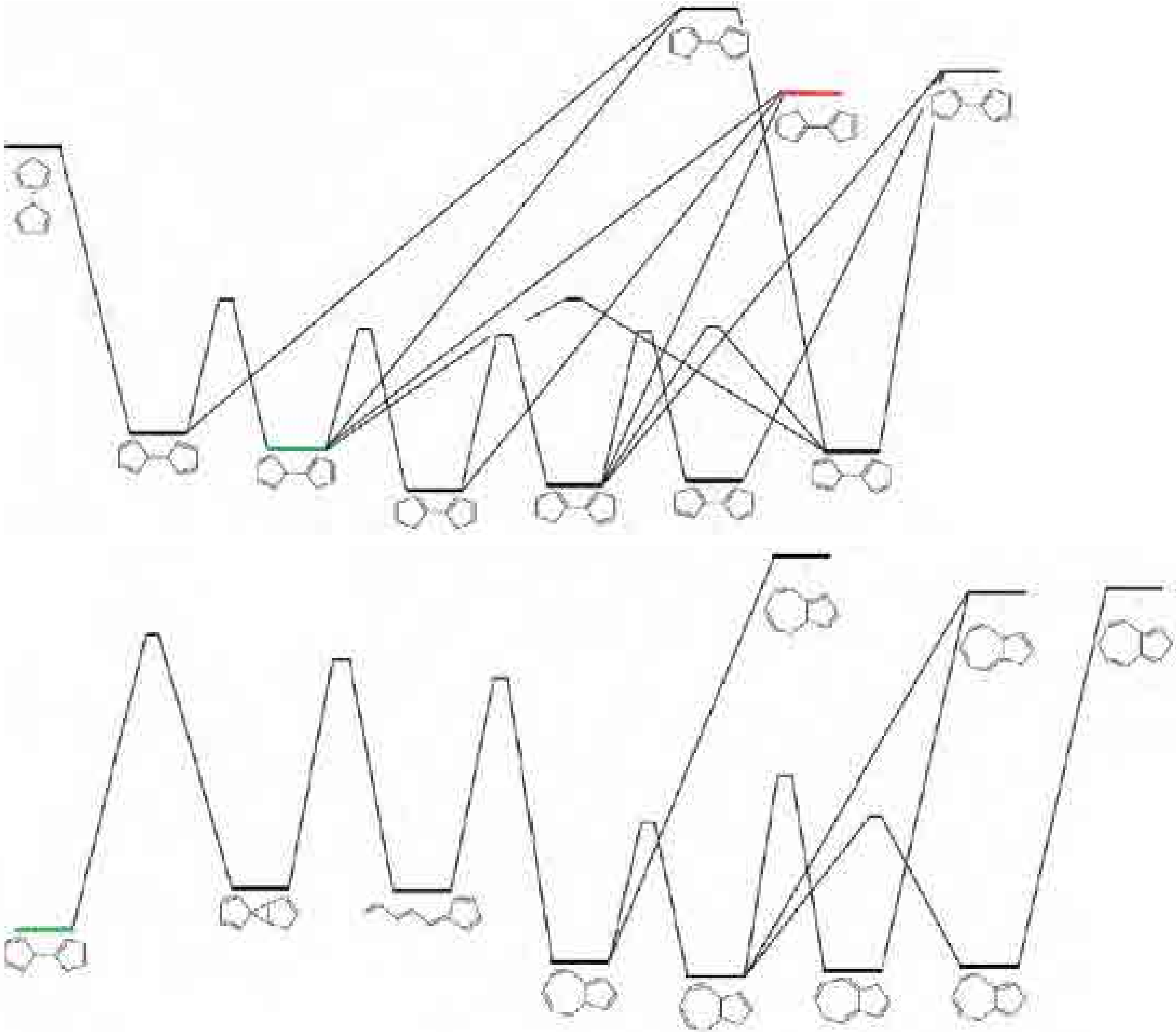
$C_5H_5 + C_5H_5$

Cavallotti, Polino, Proc. Combust. Inst. 34 (2013) 557-564



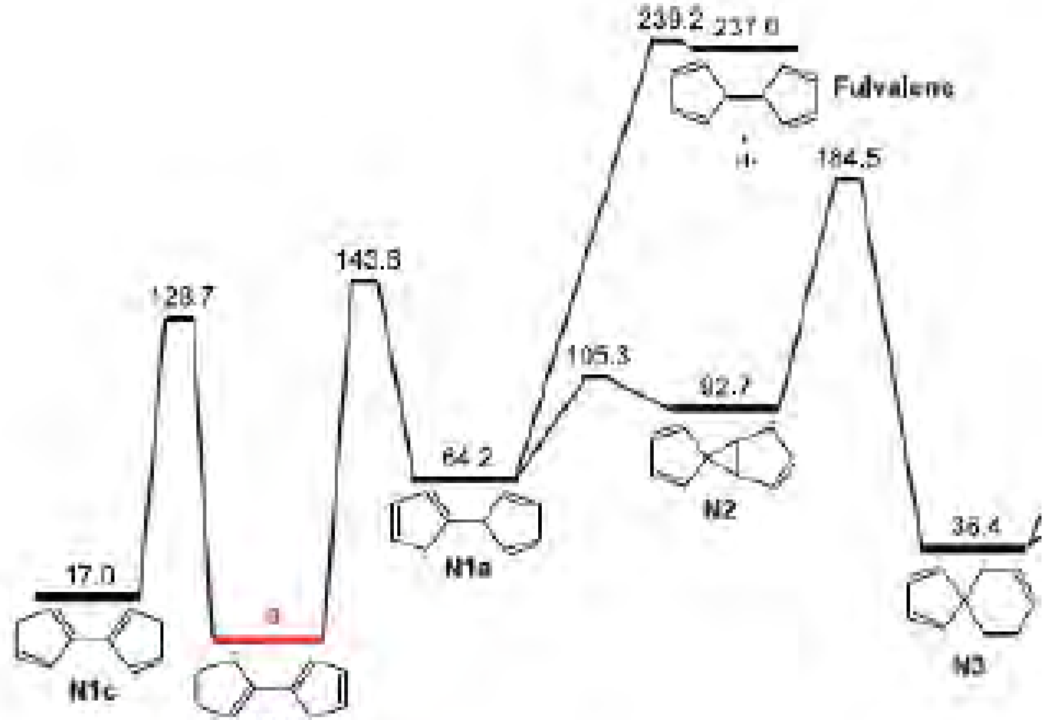
$C_5H_5 + C_5H_5$

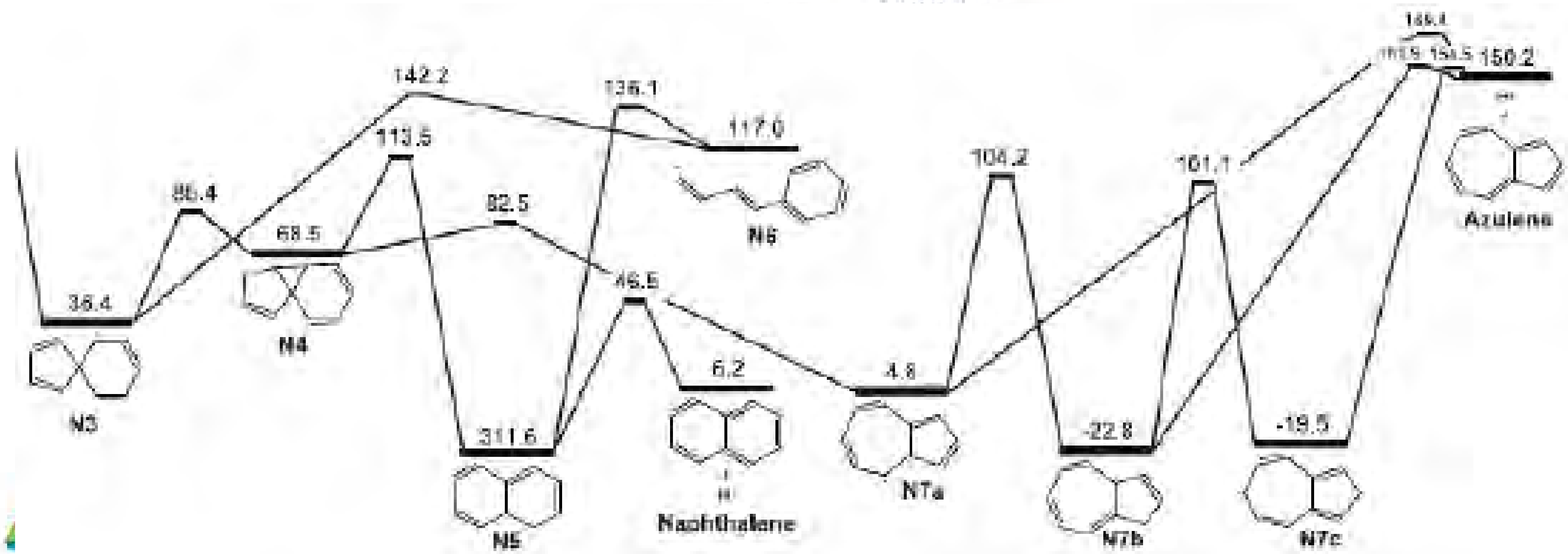
Long, Merchant, Vandeputte, Carstensen, Vervust, Marin, van Geem, Green, Combust. Flame, 187 (2018) 247-256.



$C_{10}H_9$

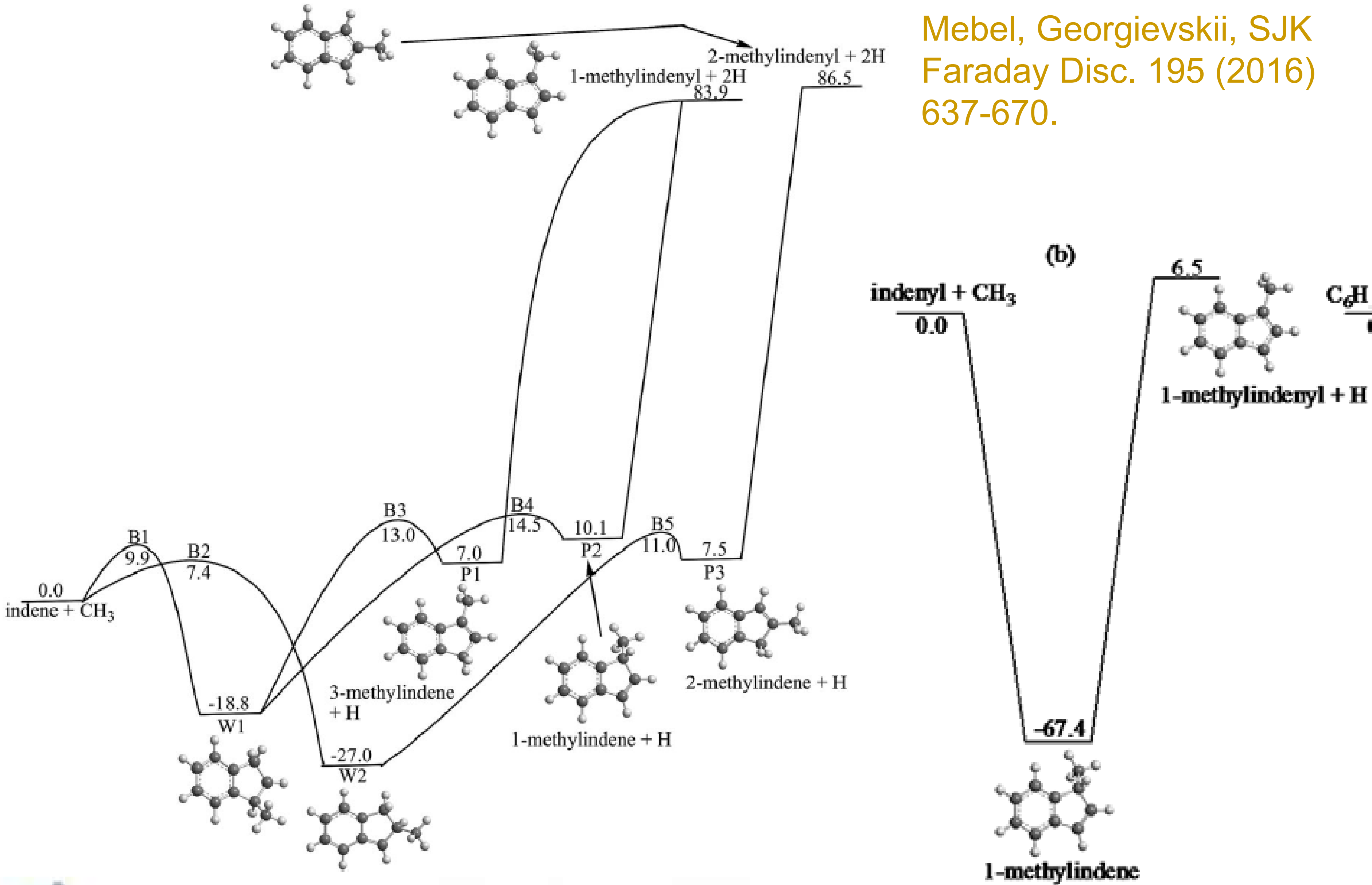
Long, Merchant, Vandeputte, Carstensen, Vervust, Marin, van Geem, Green, Combust. Flame, 187 (2018) 247-256.





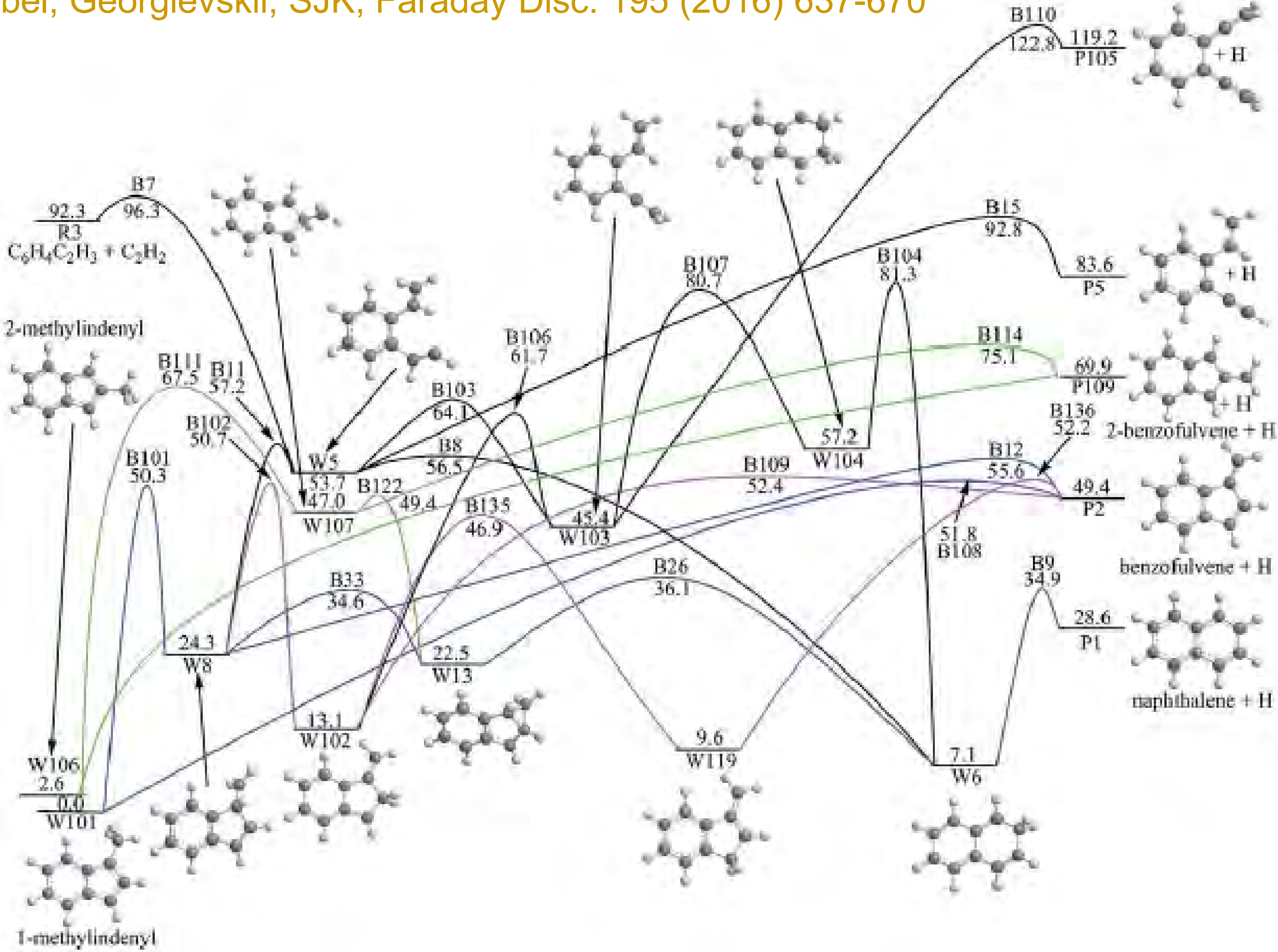
Conversion from Indene to MethylIndene

Mebel, Georgievskii, SJK Faraday Disc. 195 (2016) 637-670.



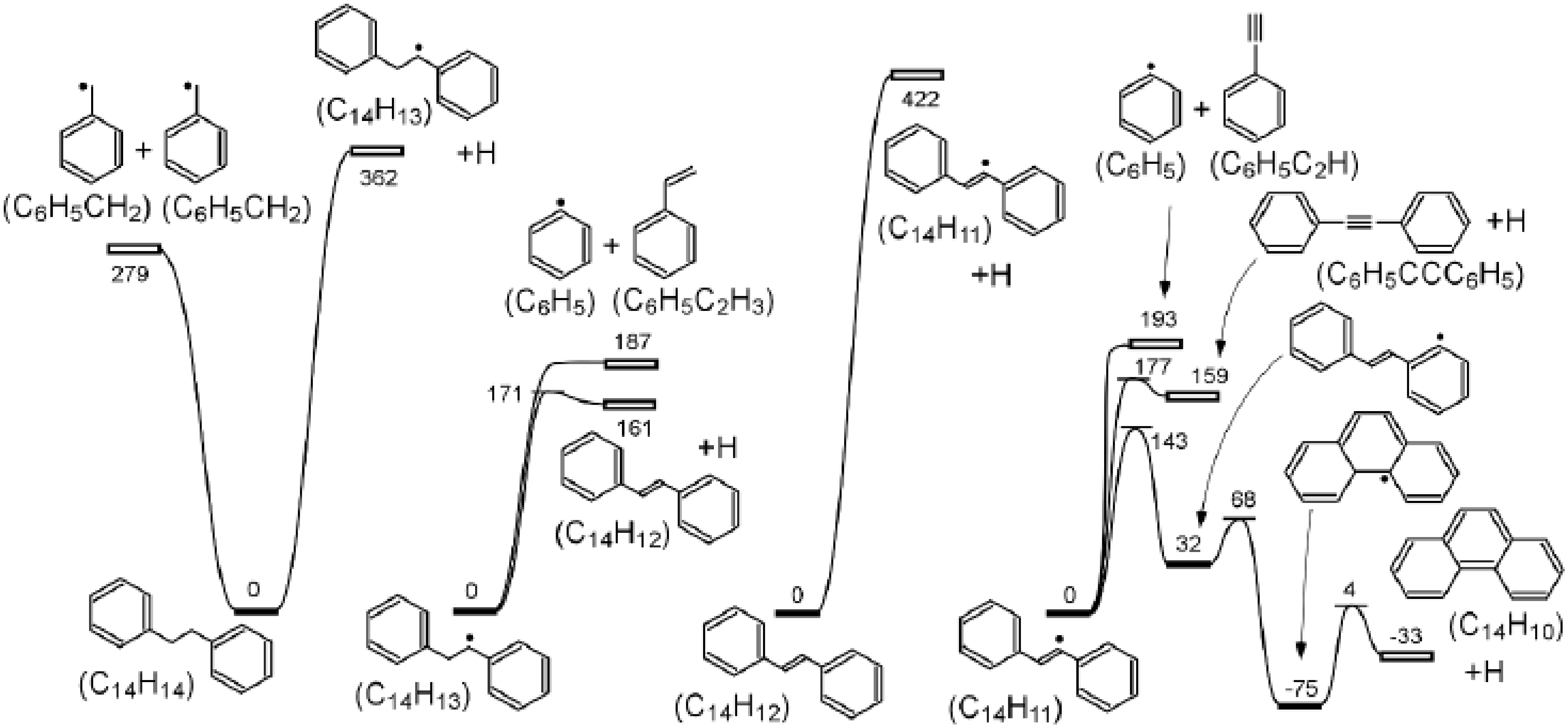
Conversion from MethylIndenyl to Naphthalene

Mebel, Georgievskii, SJK, Faraday Disc. 195 (2016) 637-670



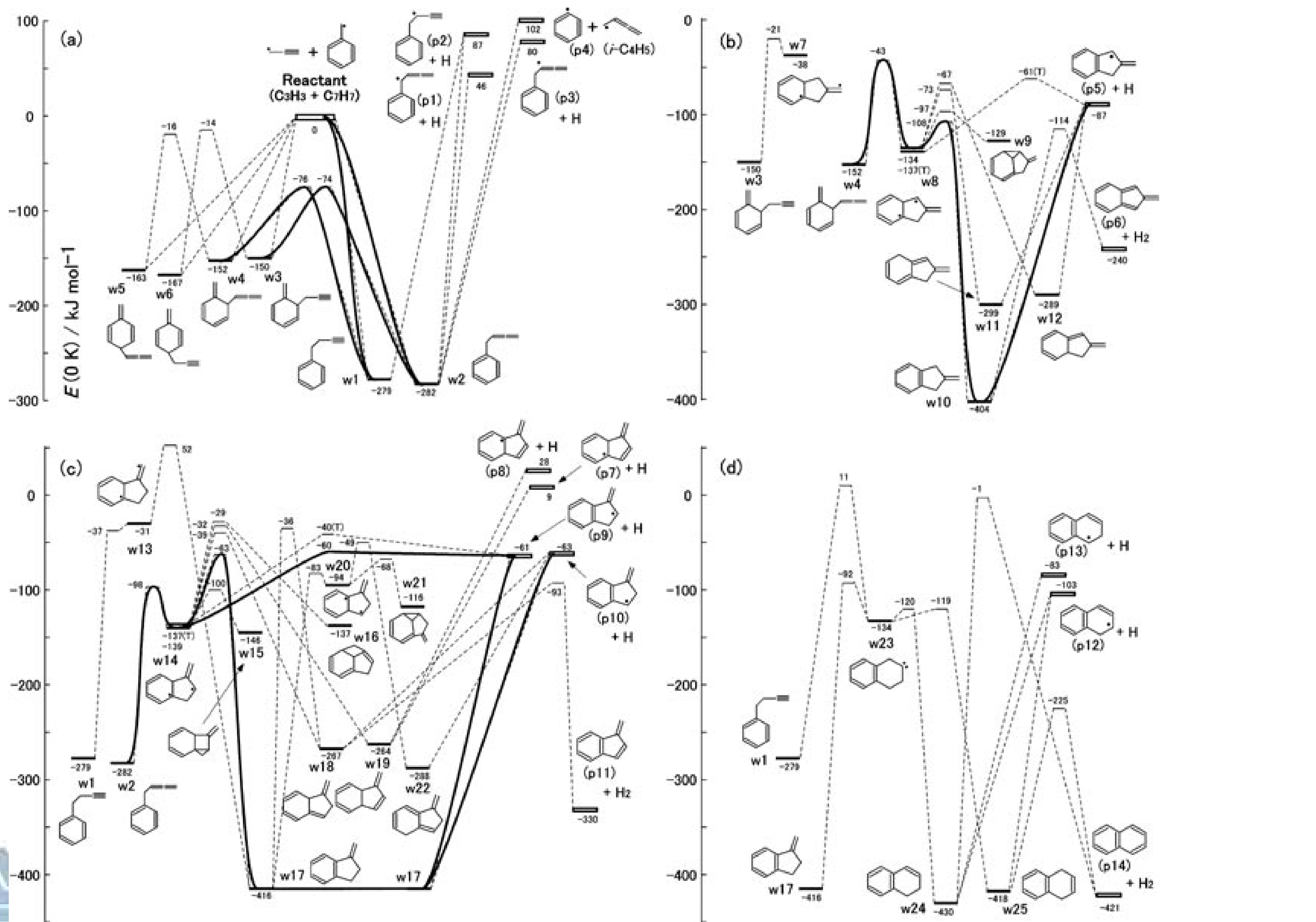
$C_7H_7 + C_7H_7$

A. Matsugi, A. Miyoshi,
Proc. Combust. Inst. 34 (2013) 269-277.



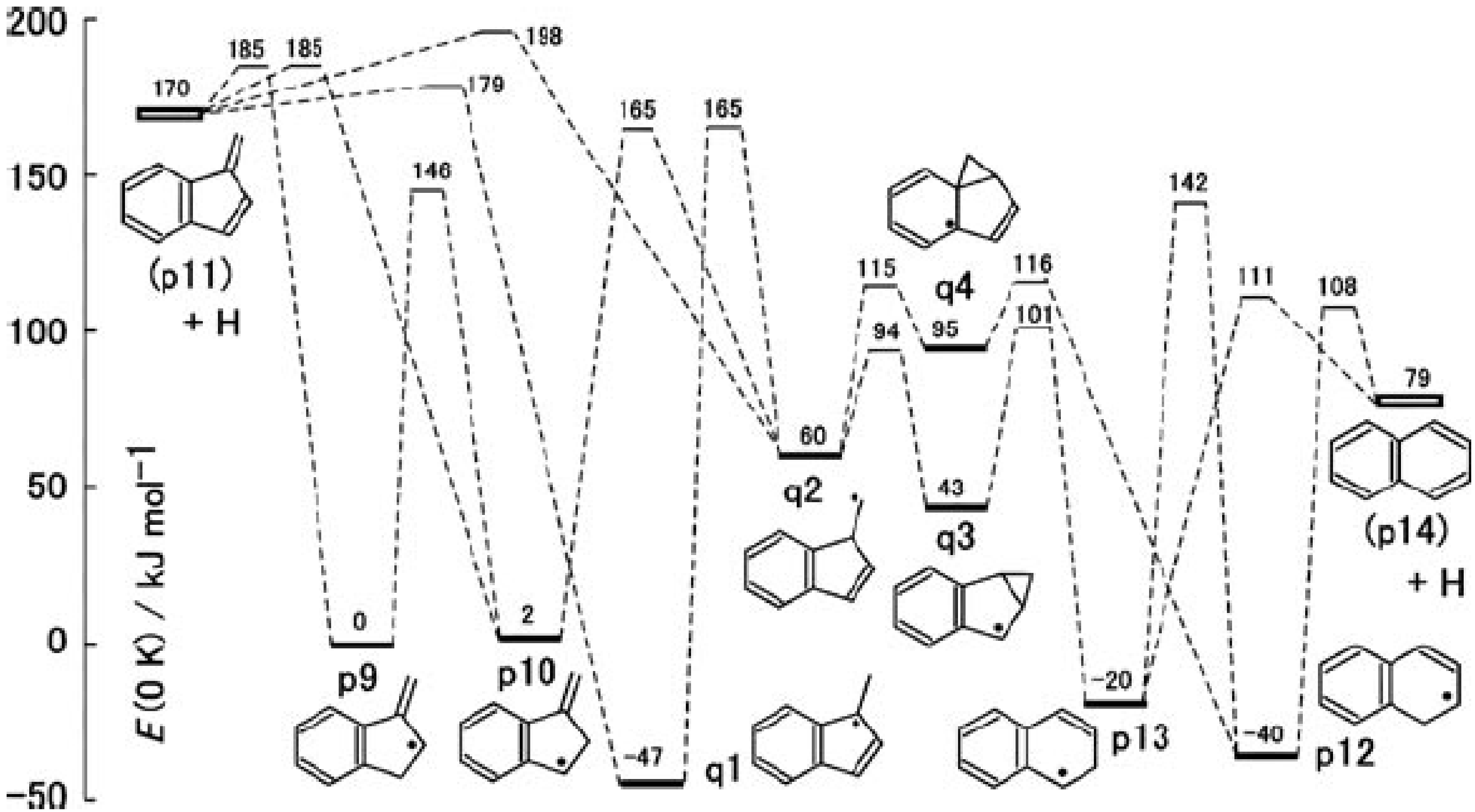
$C_7H_7 + C_3H_3$

A. Matsugi, A. Miyoshi, Int. J. Chem. Kinet. 44 (2012) 206-218.



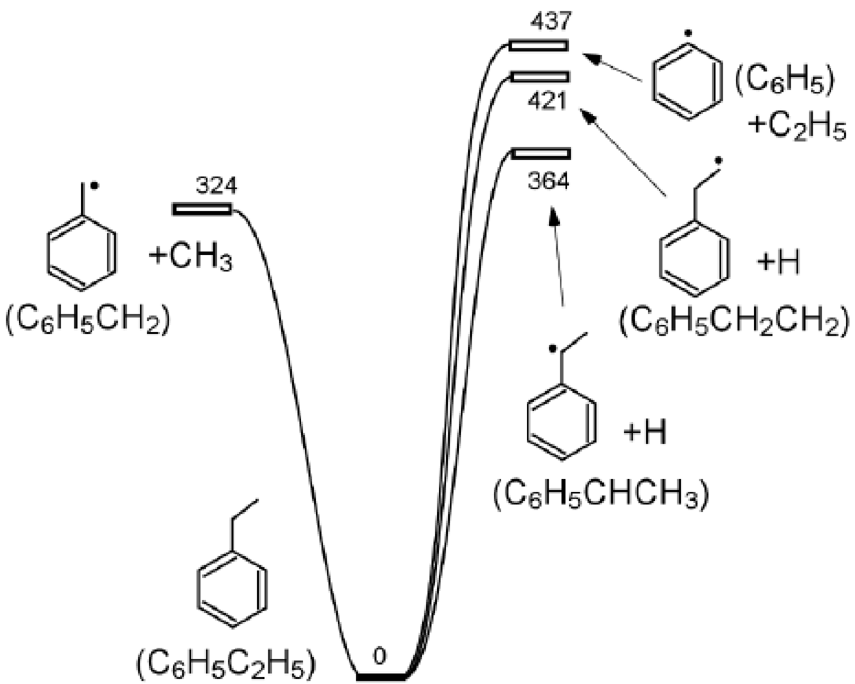
$C_7H_7 + C_3H_3$

A. Matsugi, A. Miyoshi, Int. J. Chem. Kinet. 44 (2012) 206-218.

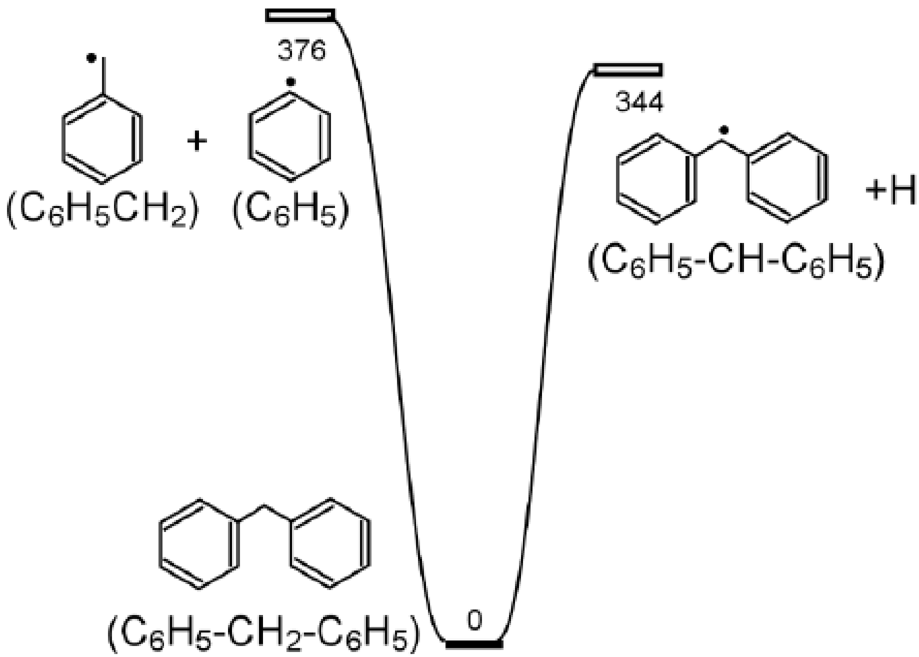


A. Matsugi, A. Miyoshi
Proc. Combust. Inst. 34 (2013) 269-277.

$C_7H_7 + CH_3$

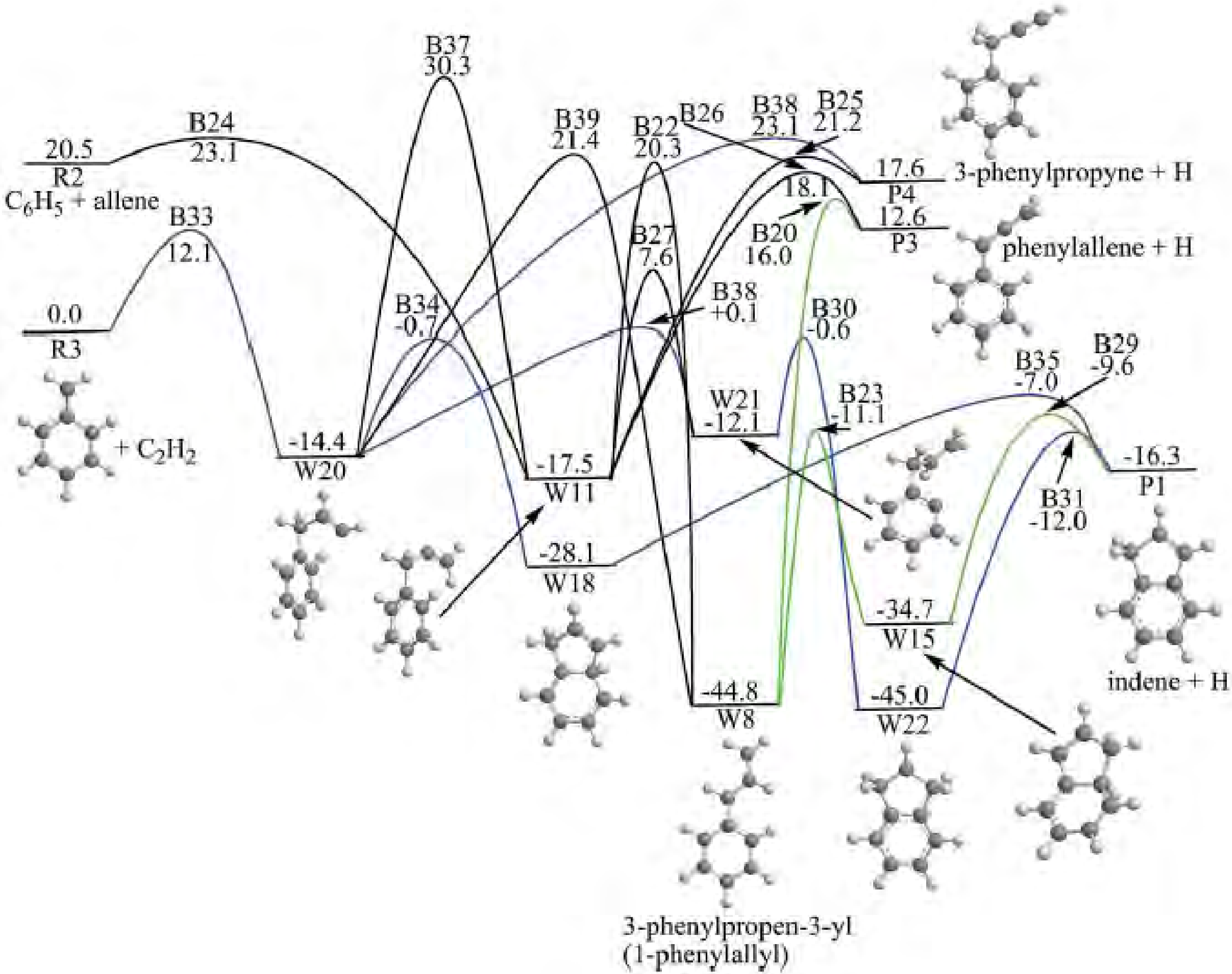


$C_7H_7 + C_6H_5$



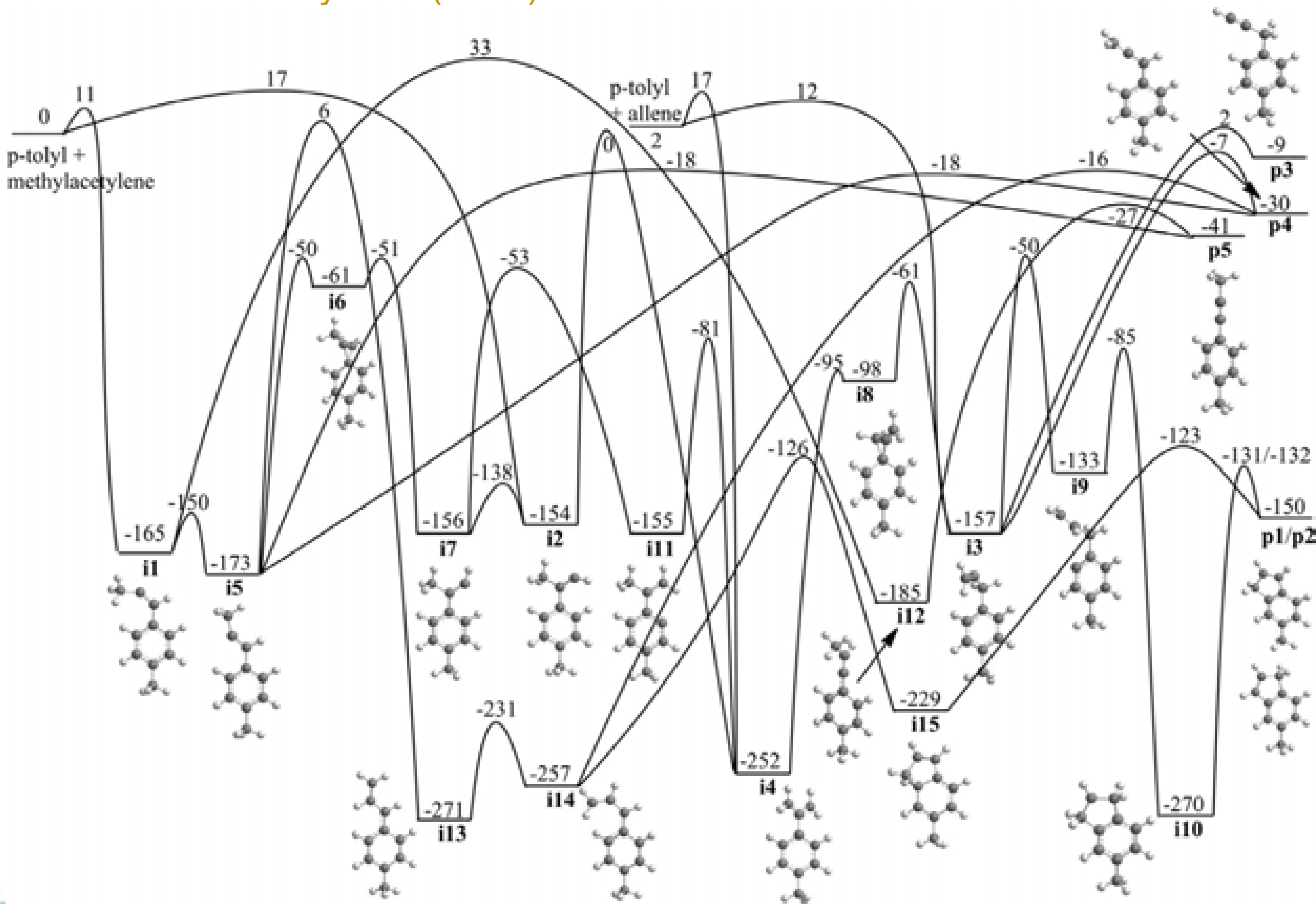
$C_7H_7 + C_2H_2$

Mebel, Georgievskii, SJK
Faraday Disc. 195 (2016) 637-670.



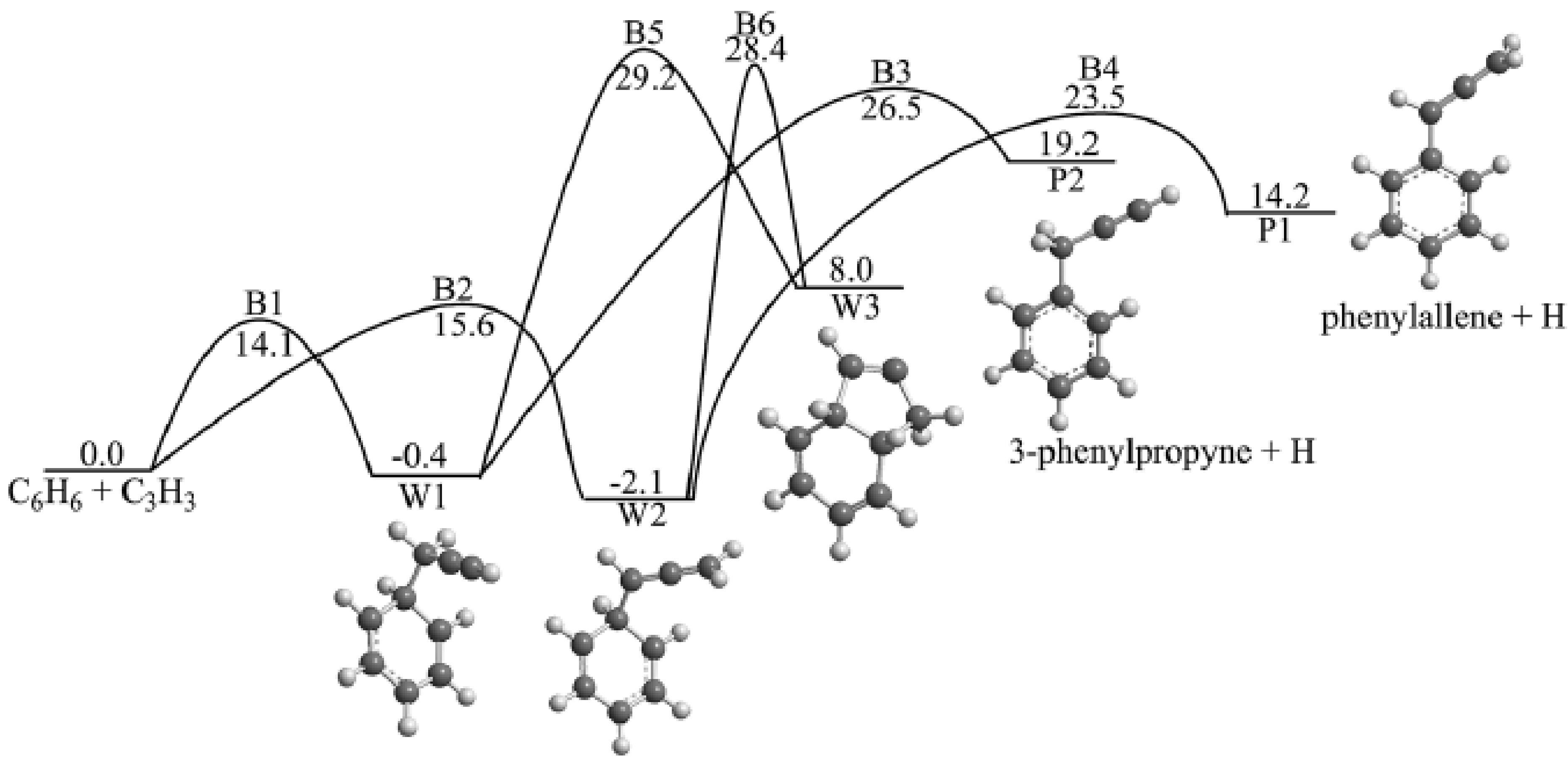
C_7H_7 + C_3H_4 Paratolyl No Rates

Yang, Parker, Dangi, Kaiser, Mebel, Phys. Chem. Chem. Phys. 17 (2015) 10510-10519



$C_6H_6 + C_3H_3$

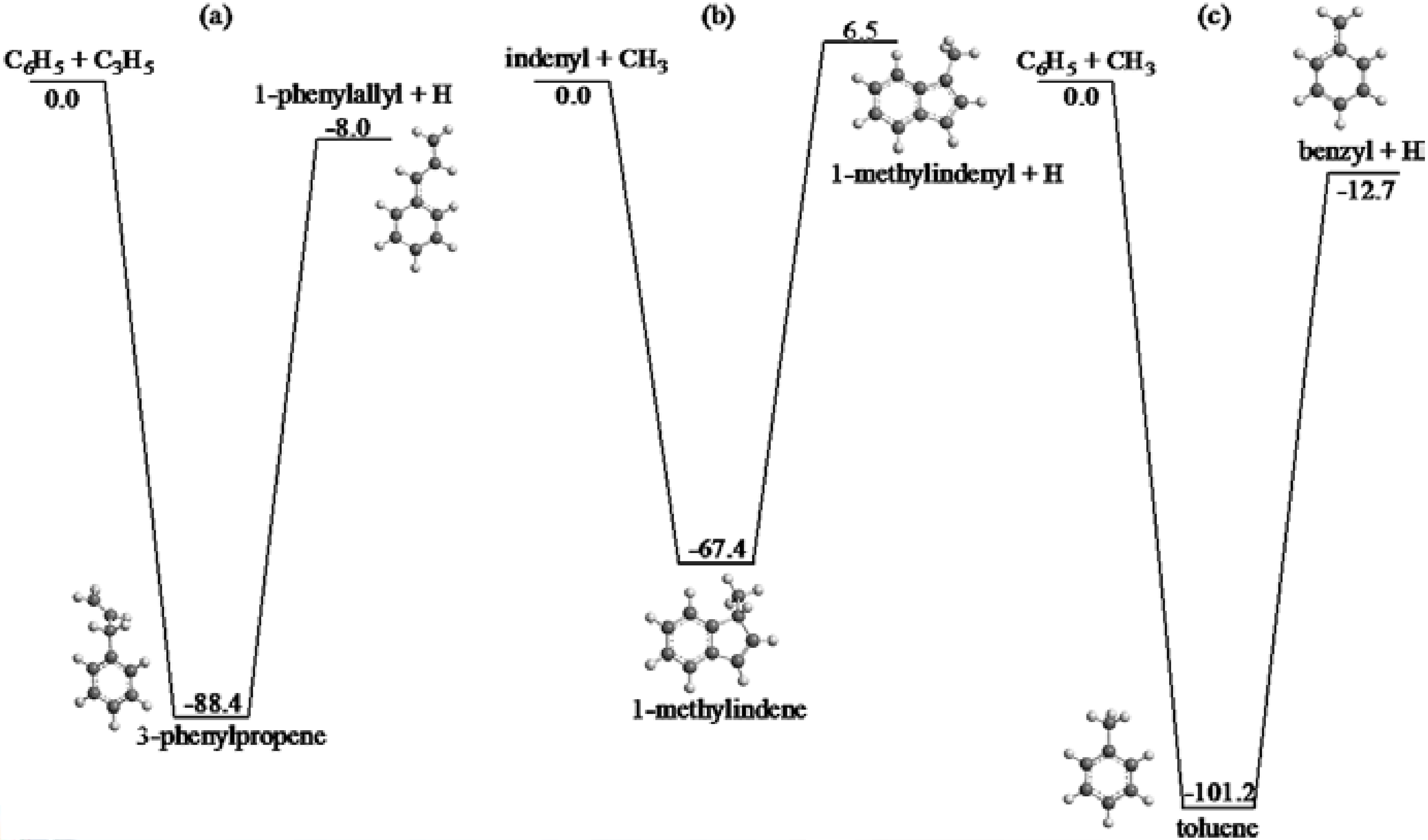
Mebel, Georgievskii, SJK
Faraday Disc. 195 (2016) 637-670.



$C_6H_5 + C_3H_5$ $C_9H_7 + CH_3$ $C_6H_5 + CH_3$

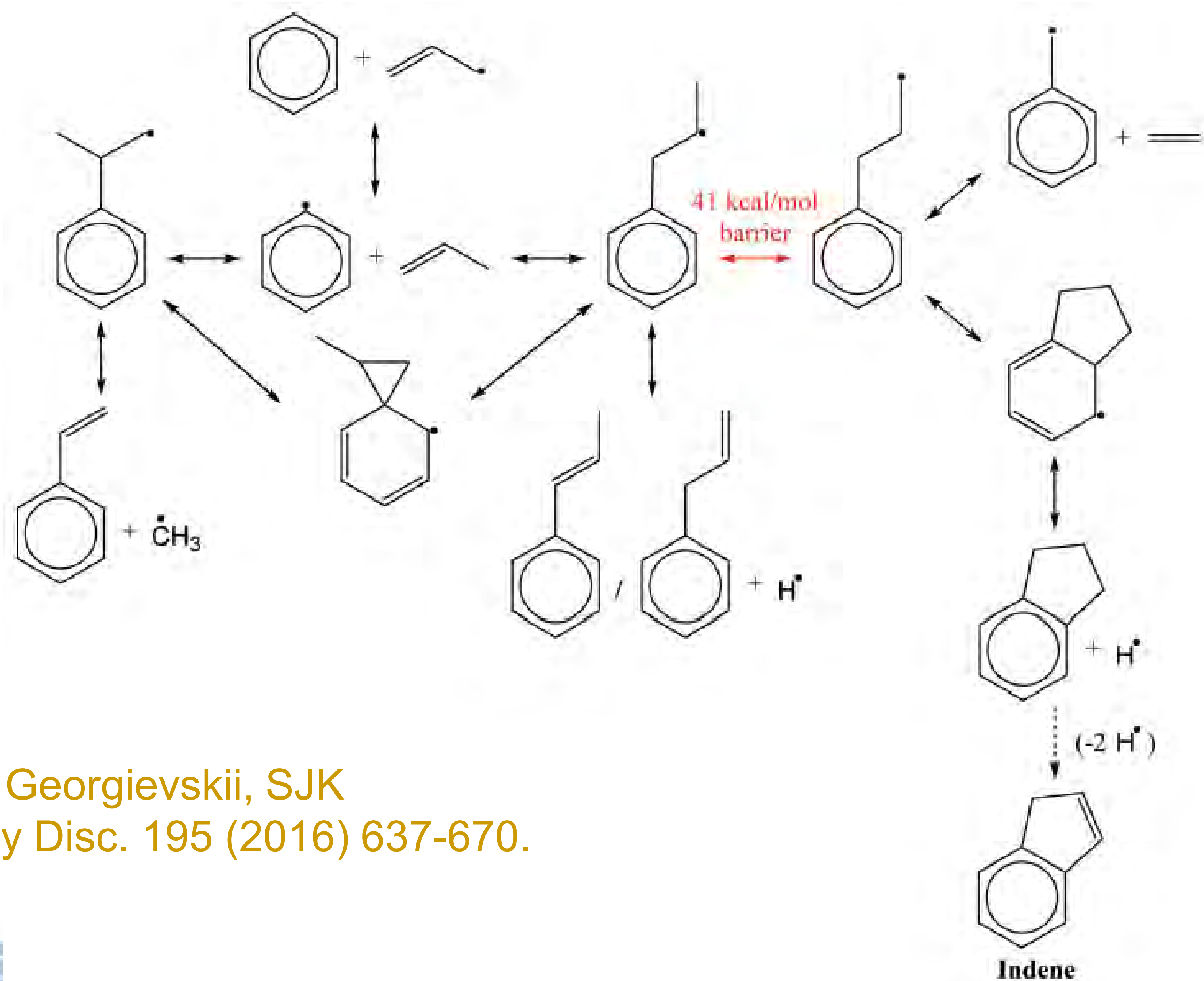
Mebel, Georgievskii, SJK, Faraday Disc. 195 (2016) 637-670

Barrierless Reactions



$C_6H_5 + C_3H_6$

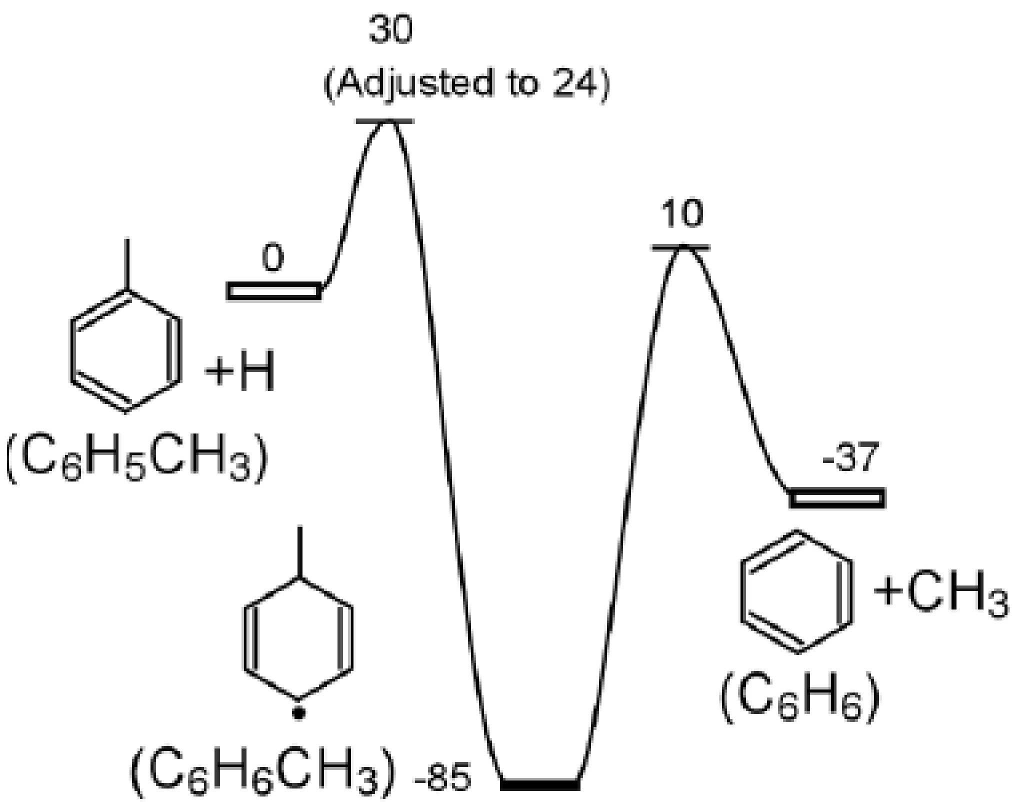
Buras, Chu, Jamal, Yee, Middaugh, Green, Phys. Chem. Chem. Phys. 20 (2018) 13191-13214.



Mebel, Georgievskii, SJK
Faraday Disc. 195 (2016) 637-670.

$C_6H_6 + CH_3$

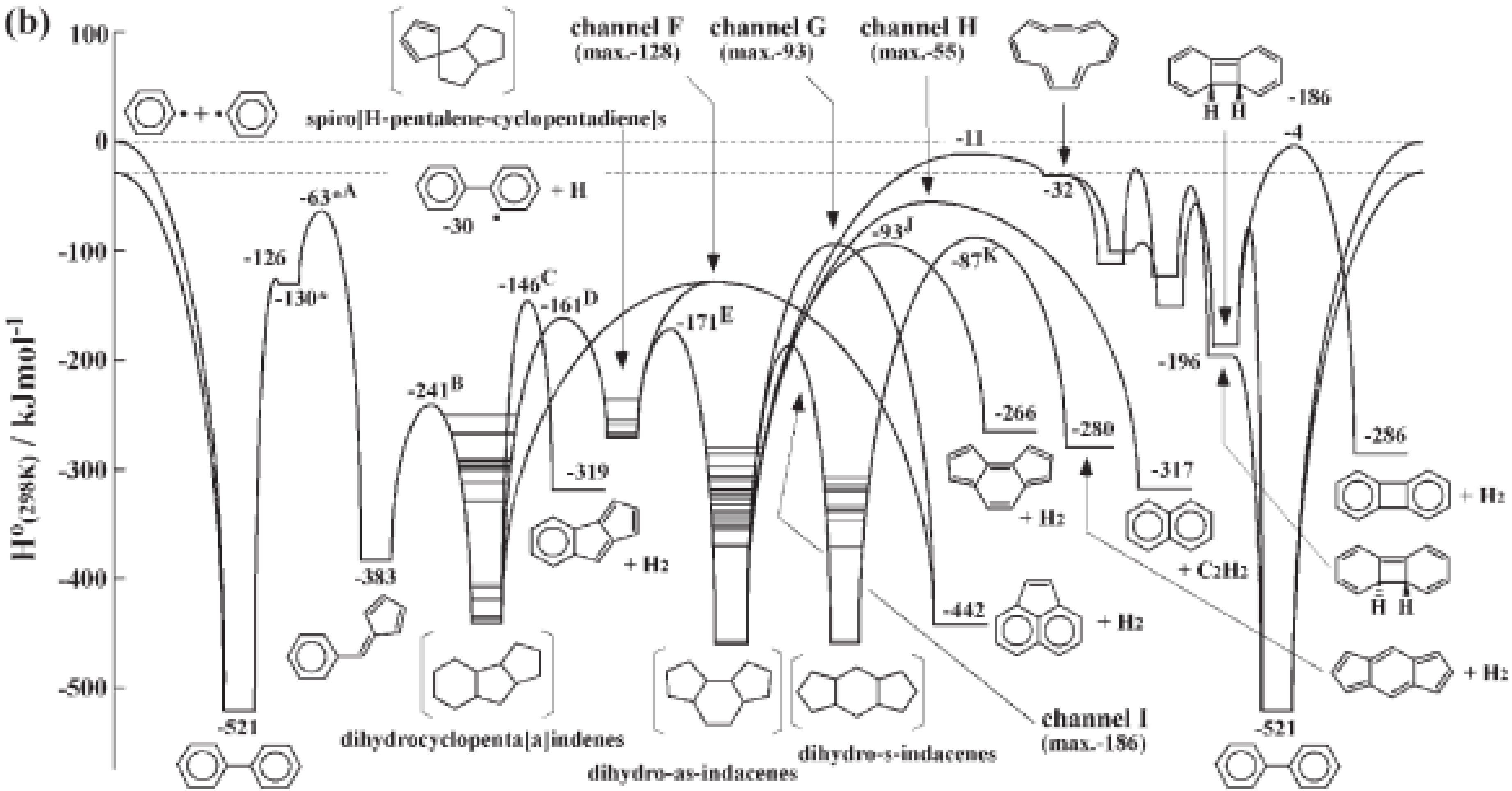
A. Matsugi, A. Miyoshi, Proc. Combust. Inst. 34 (2013) 269-277.



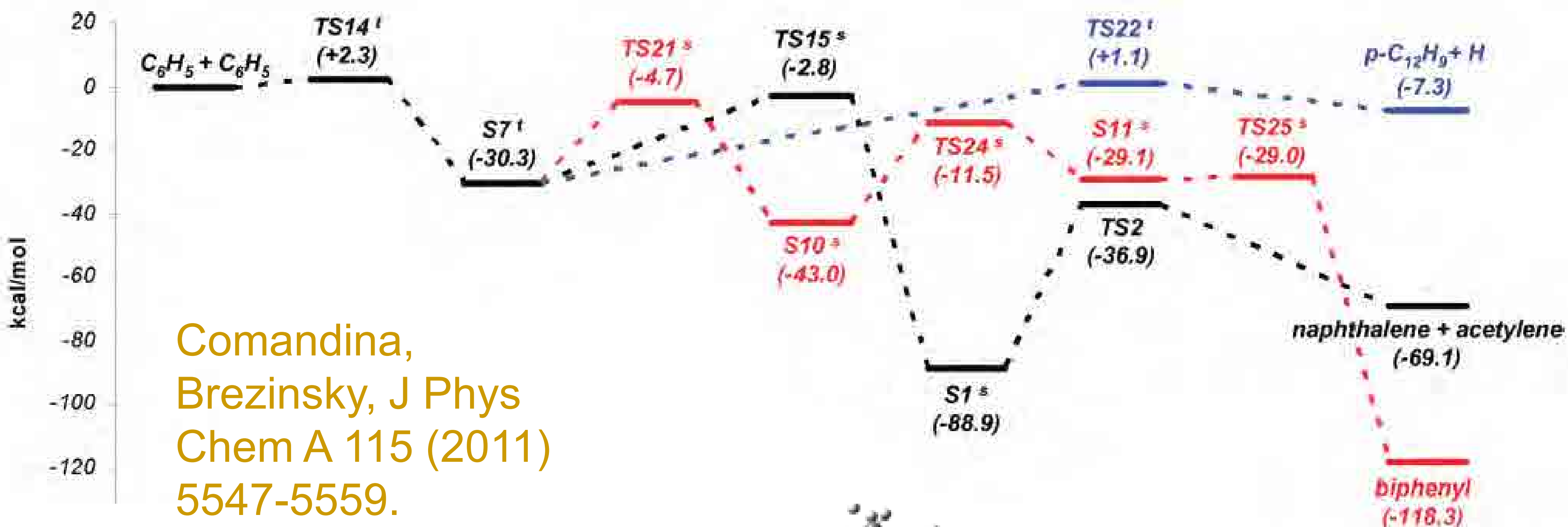
Phenyl Assisted Cyclization (PAC)

$C_6H_5 + C_6H_5$ High P Limit

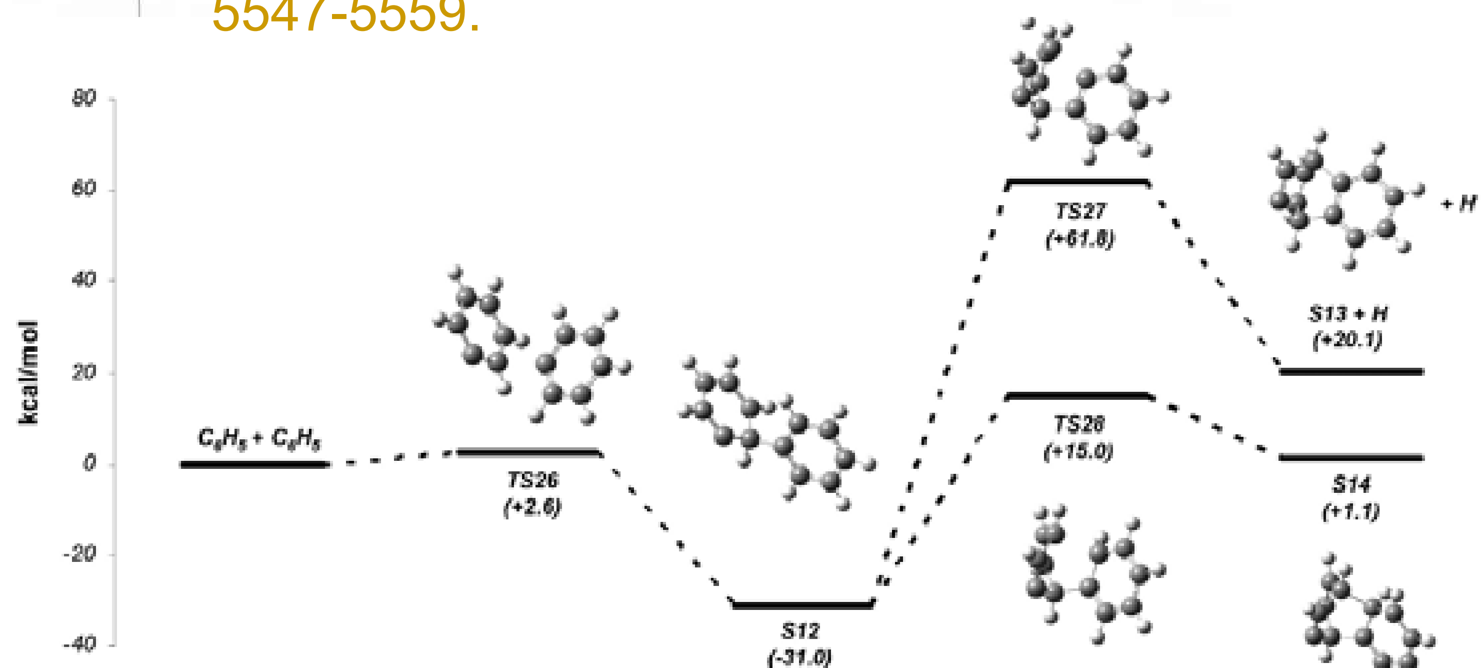
Shukla, Tsuchiya, Koshi, J Phys Chem A 115 (2011) 5284-5293.



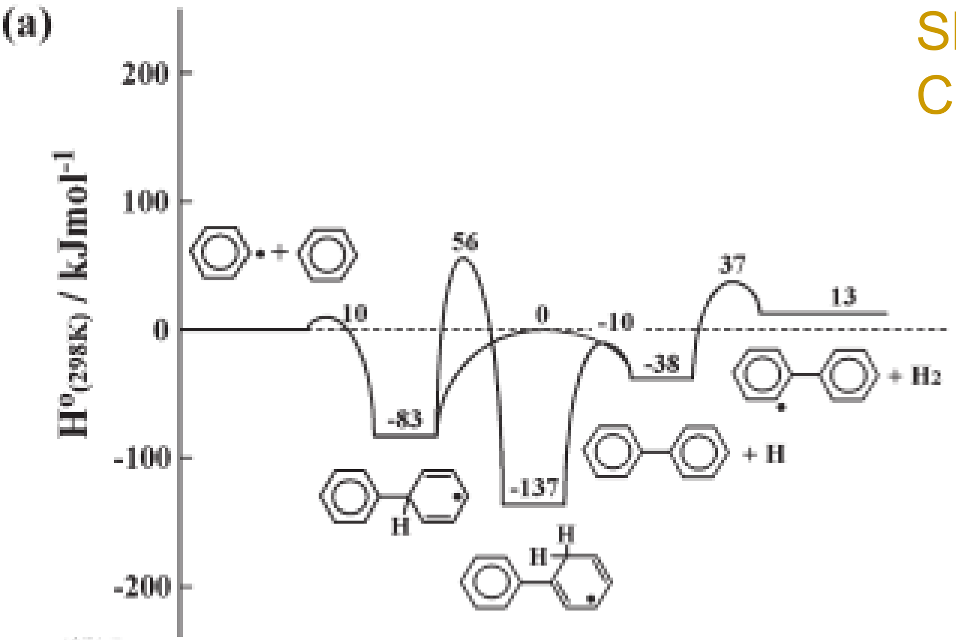
C_6H_5 + C_6H_5 High P Limit



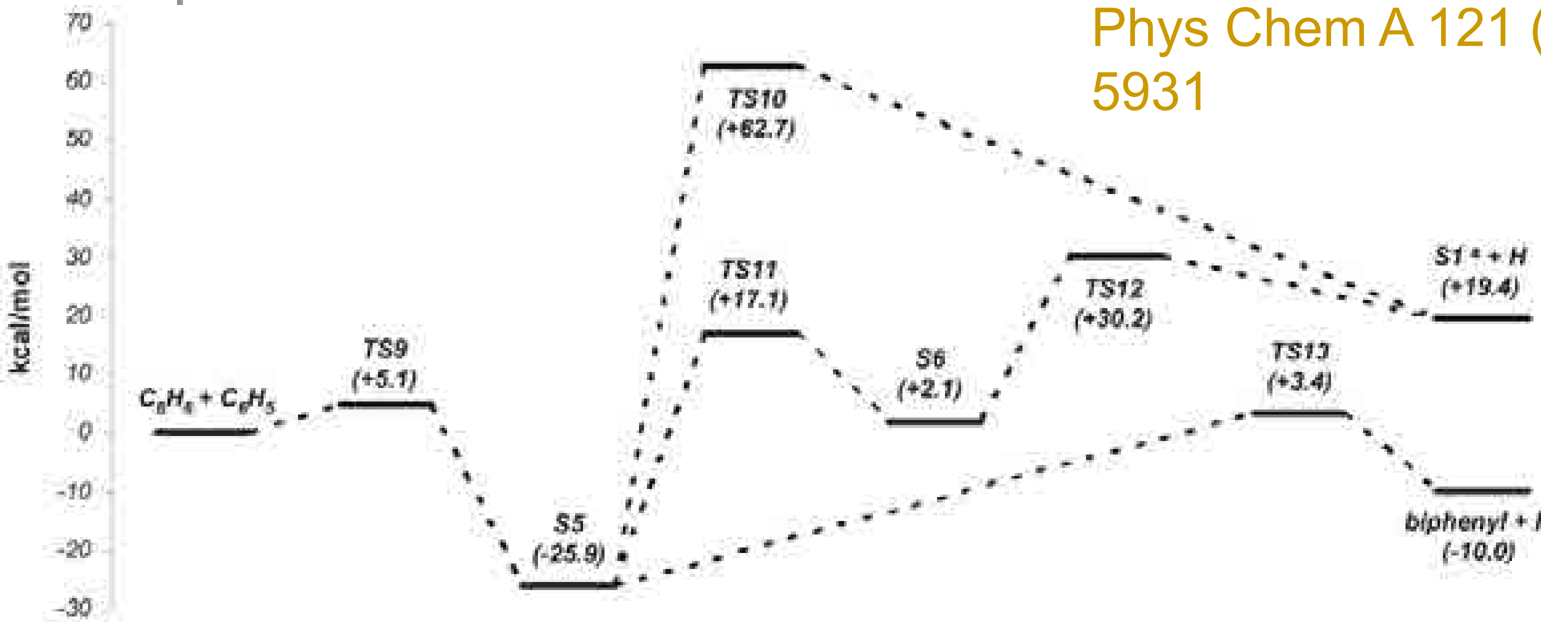
Comandina, Brezinsky, J Phys Chem A 115 (2011) 5547-5559.



$C_6H_5 + C_6H_6$ High P Limit



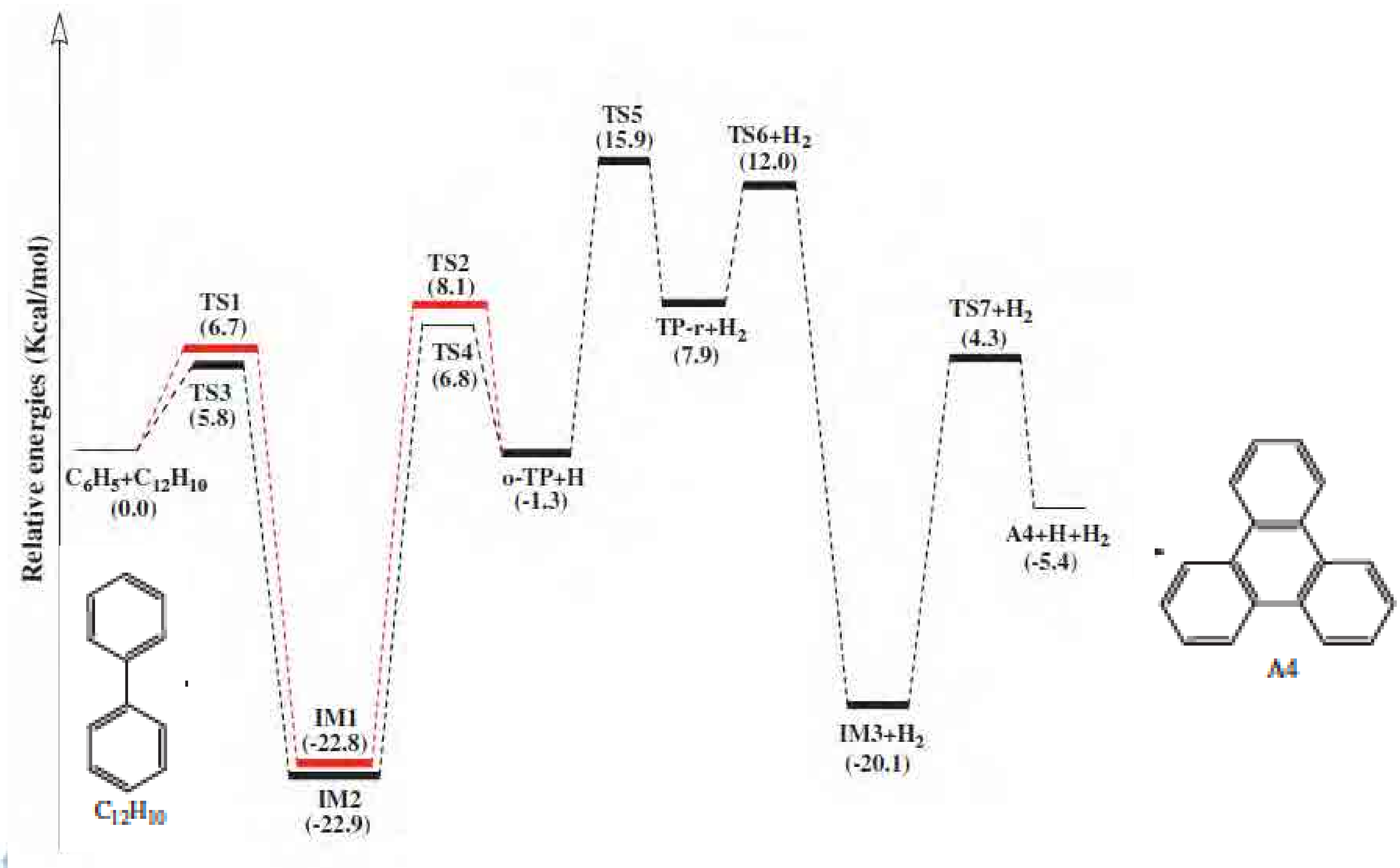
Shukla, Tsuchiya, Koshi, J Phys Chem A 115 (2011) 5284-5293.



Comandini, Abid, Chaumeix, J Phys Chem A 121 (2017) 5921-5931

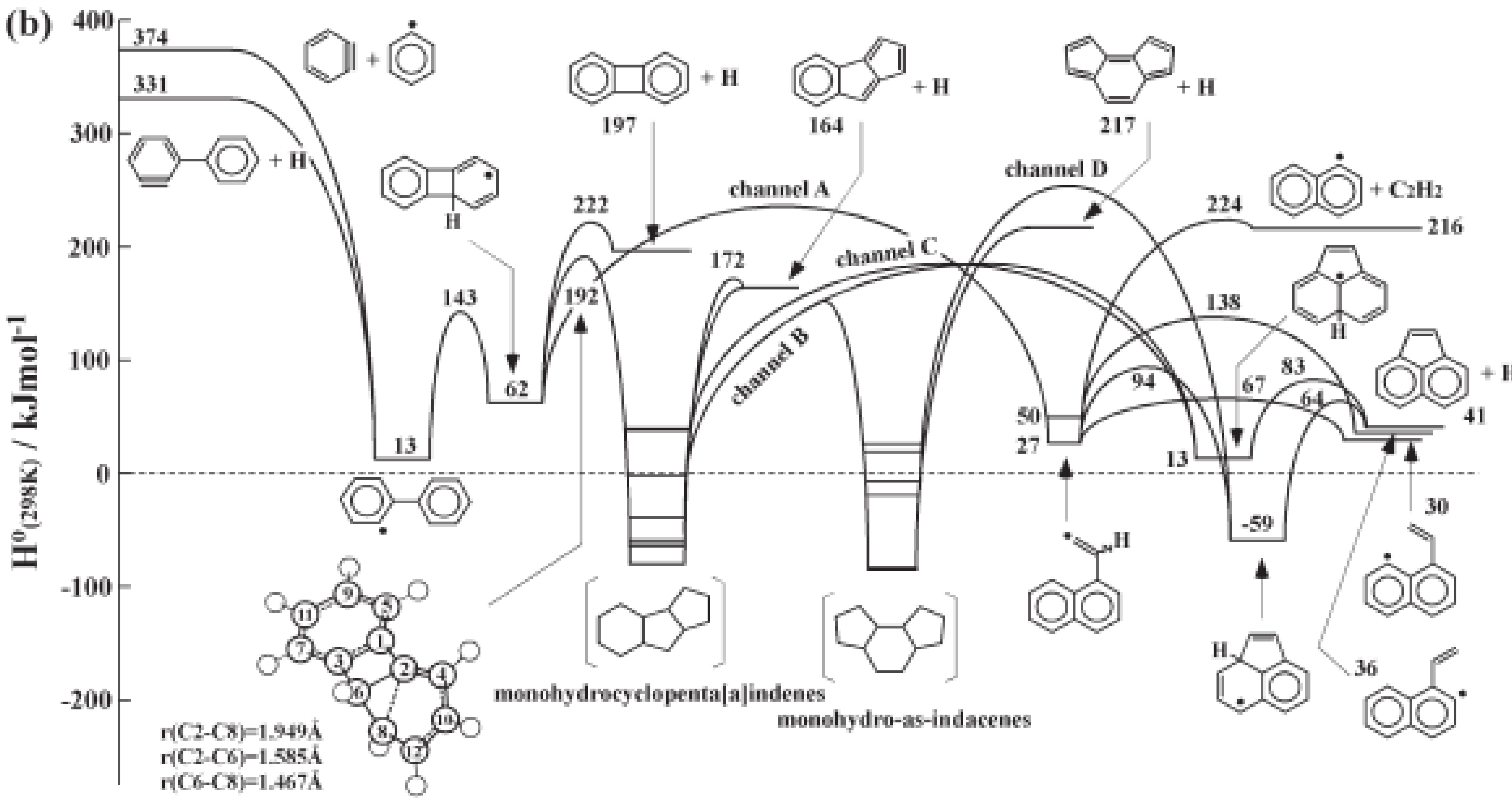
C_6H_5 + $C_{12}H_{10}$ High P Limit

Xiong, Li, Wang, Li, Li Comp. Theo. Chem. 984 (2012) 1-7.



$C_6H_5 + C_6H_4$ — High P Limit

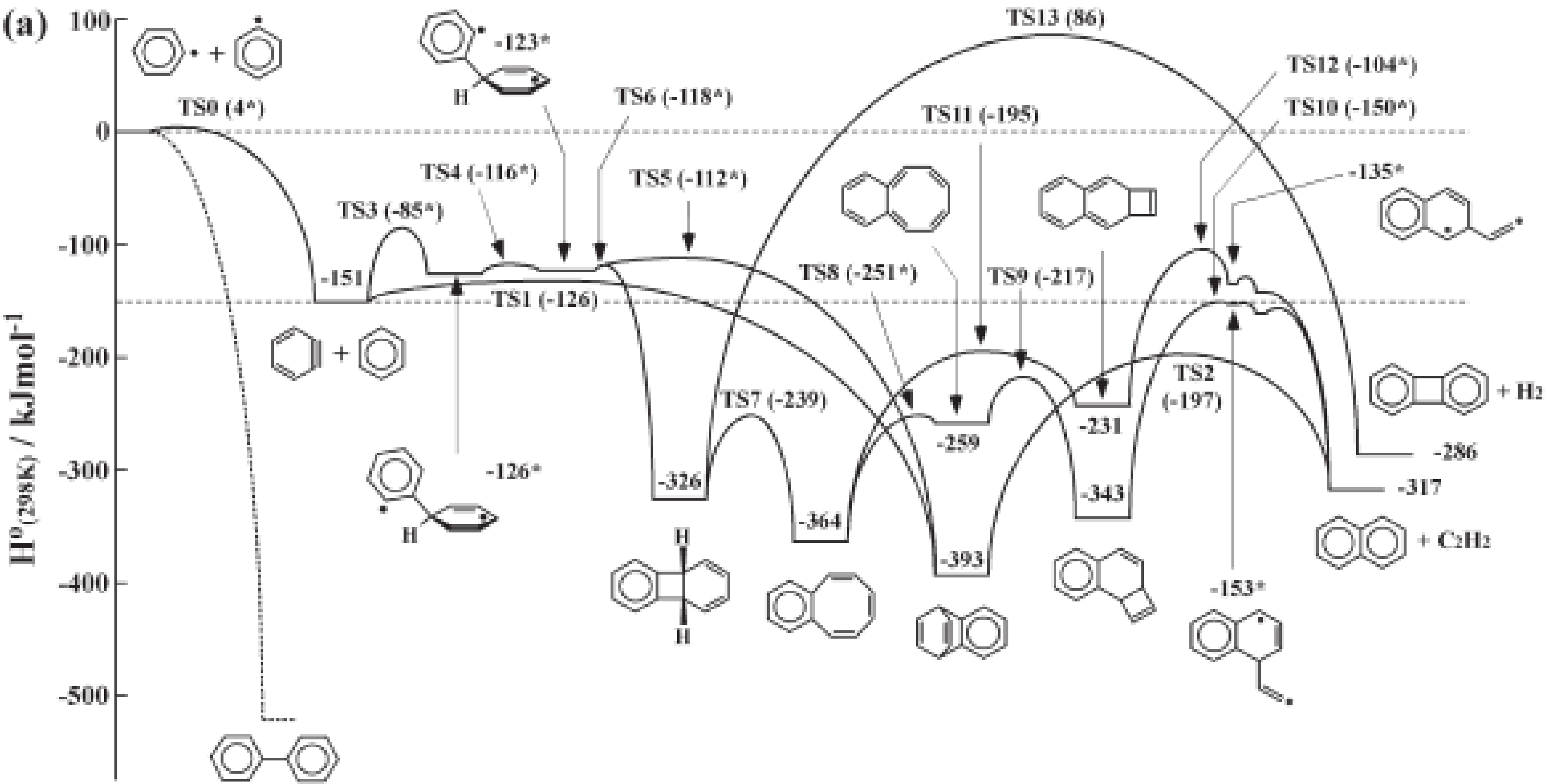
Shukla, Tsuchiya, Koshi, J Phys Chem A 115 (2011) 5284-5293.



Benzyne High Reactivity

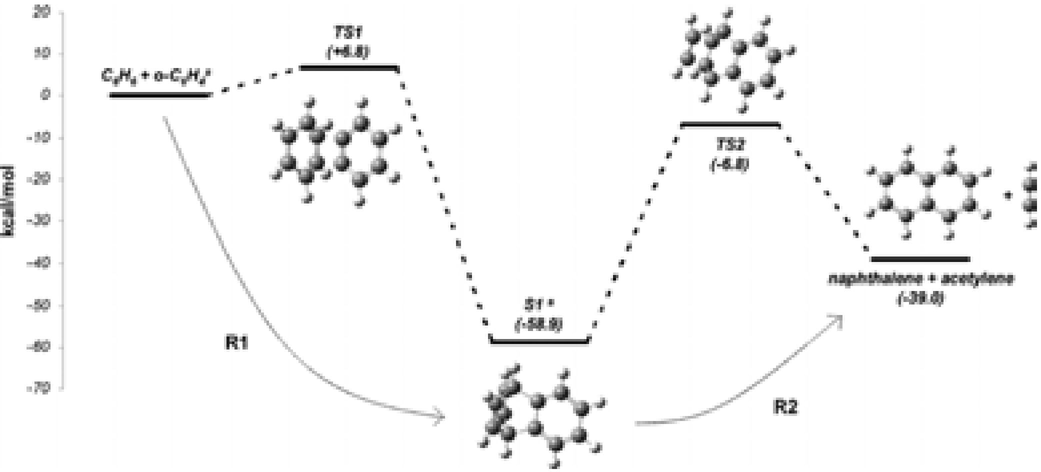
$C_6H_4 + C_6H_6$ High P Limit

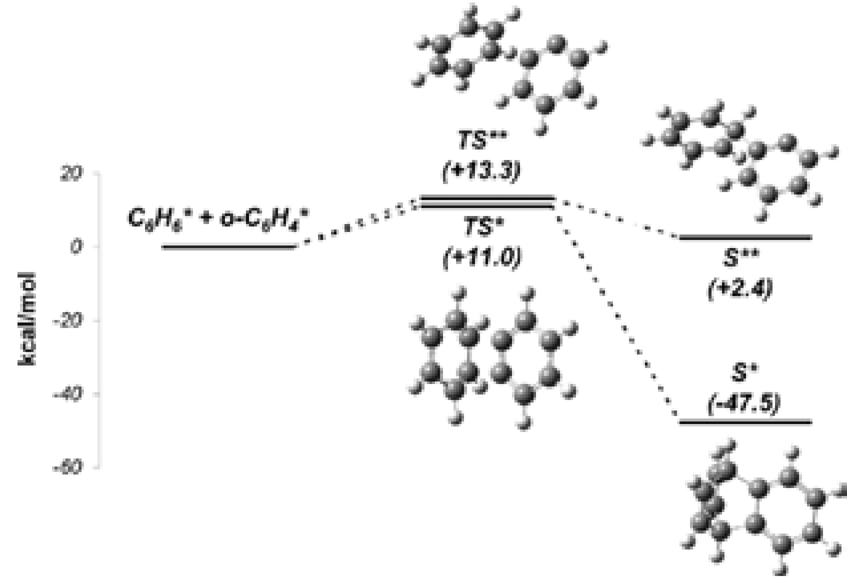
Shukla, Tsuchiya, Koshi, J Phys Chem A 115 (2011) 5284-5293.

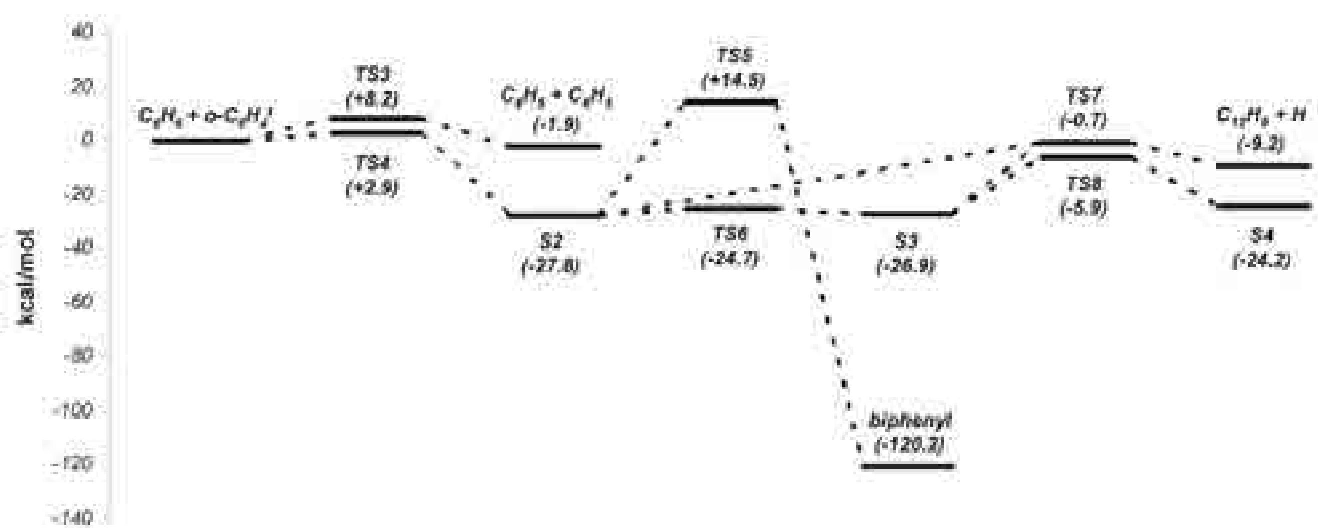


C_6H_4 + C_6H_6 High P Limit

Comandina, Brezinsky J Phys Chem A 115 (2011) 5547-5559.

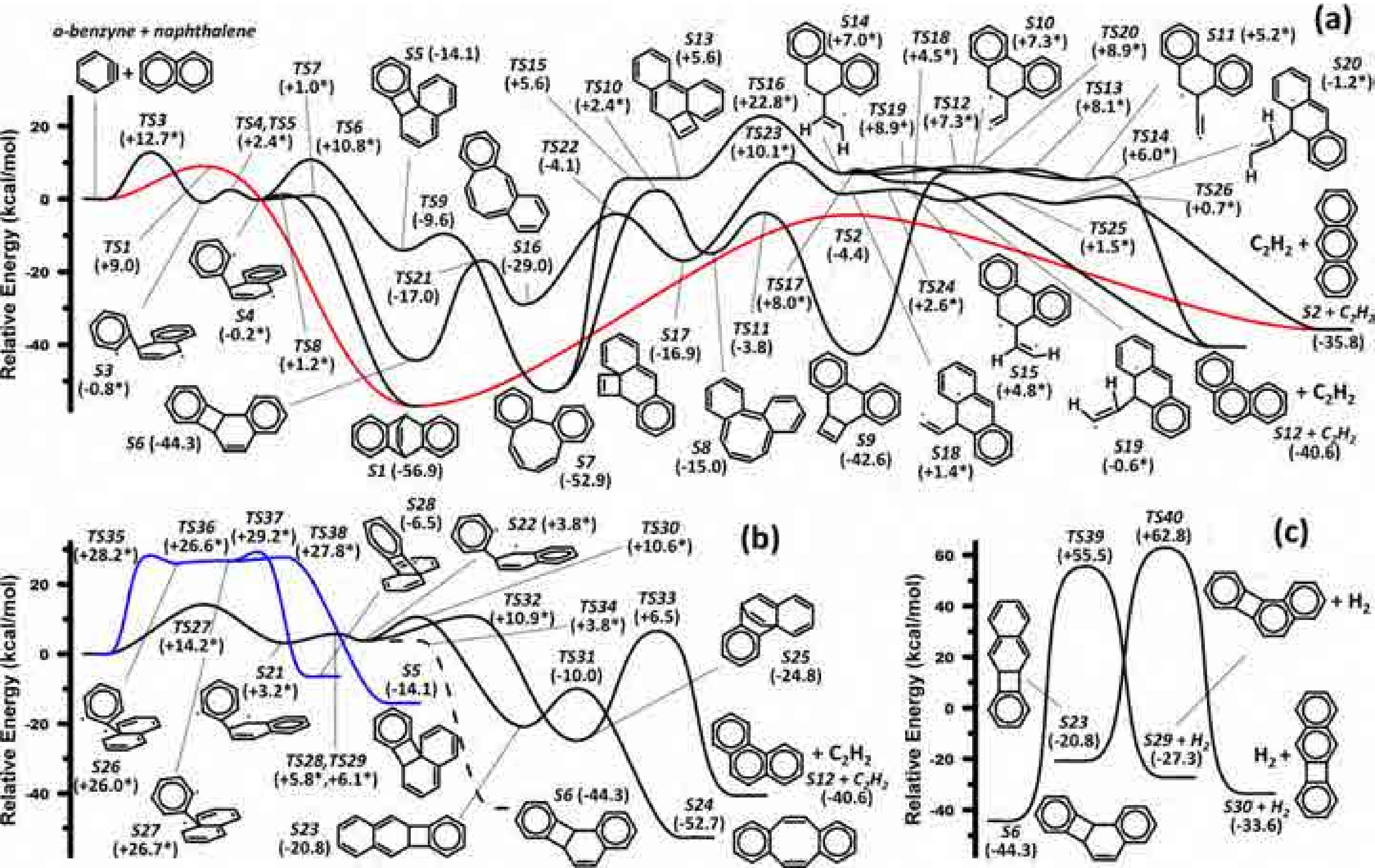






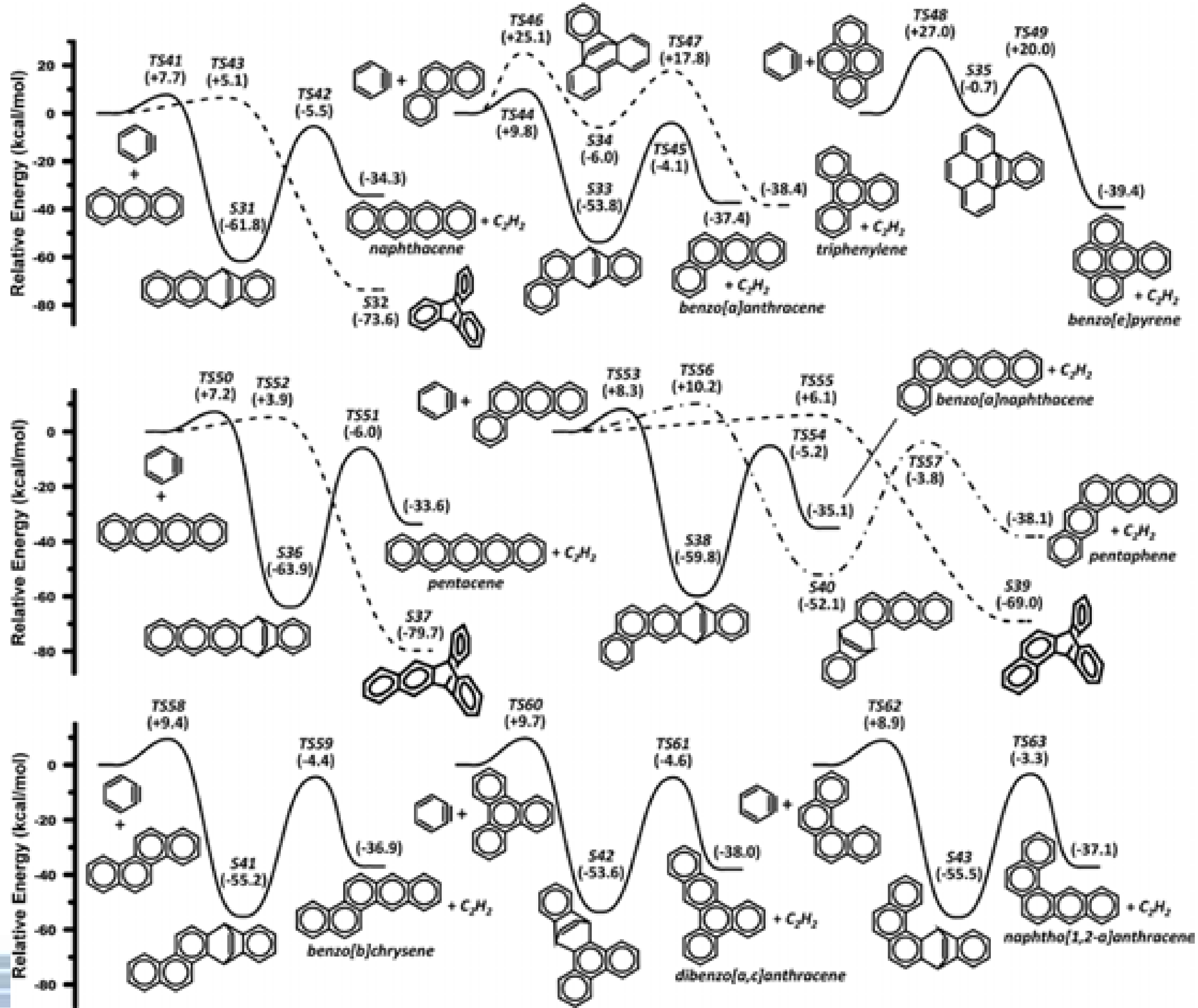
C_6H_4 + $C_{10}H_8$ PES Only

Comandini, Abid, Chaumeix, J Phys Chem A 121 (2017) 5921-5931



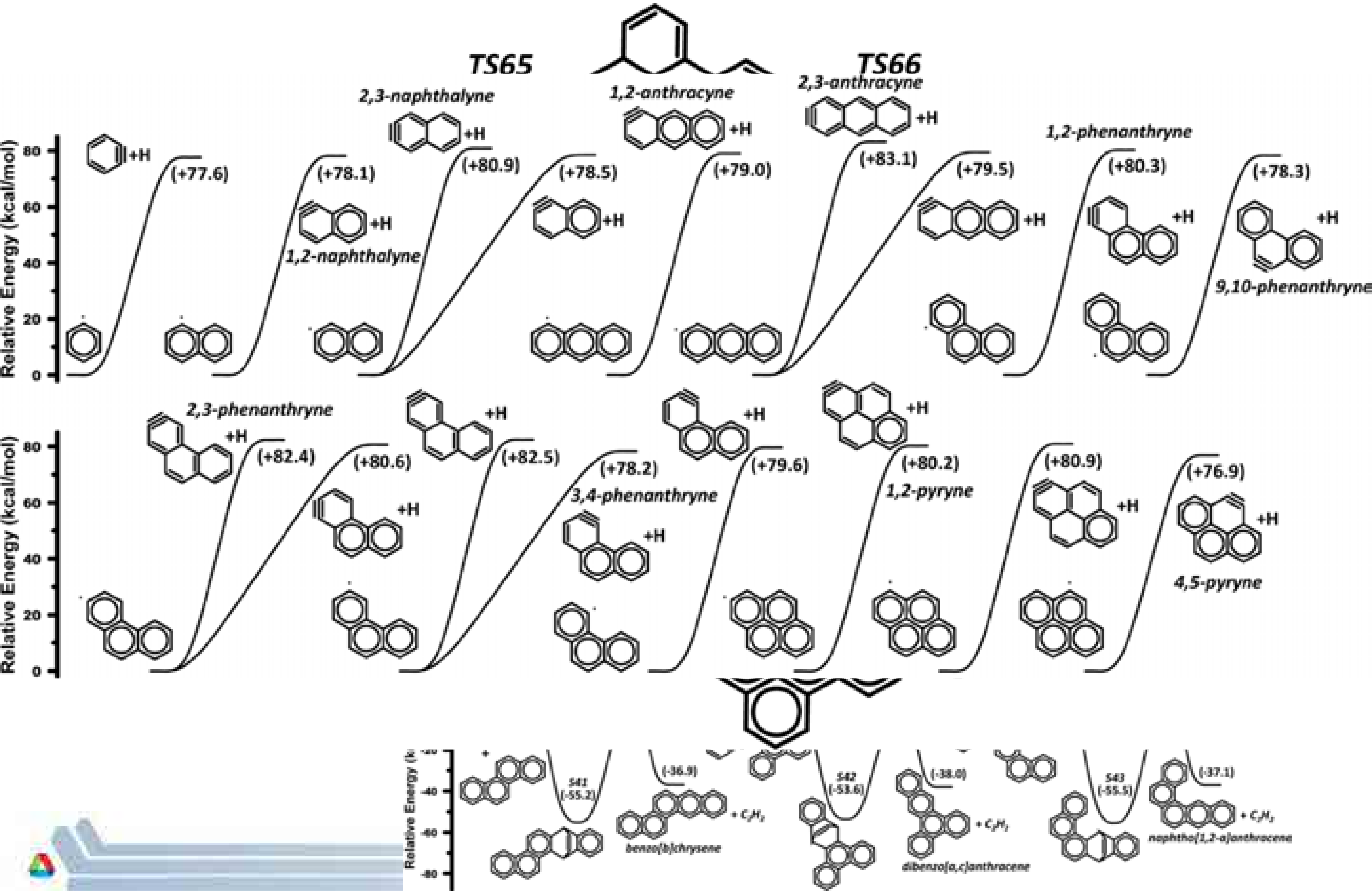
$C_6H_4 + C_{14}H_{10}$ and $C_6H_4 + C_{16}H_{12}$ **PES Only**

Comandini, Abid, Chaumeix, J Phys Chem A 121 (2017) 5921-5931

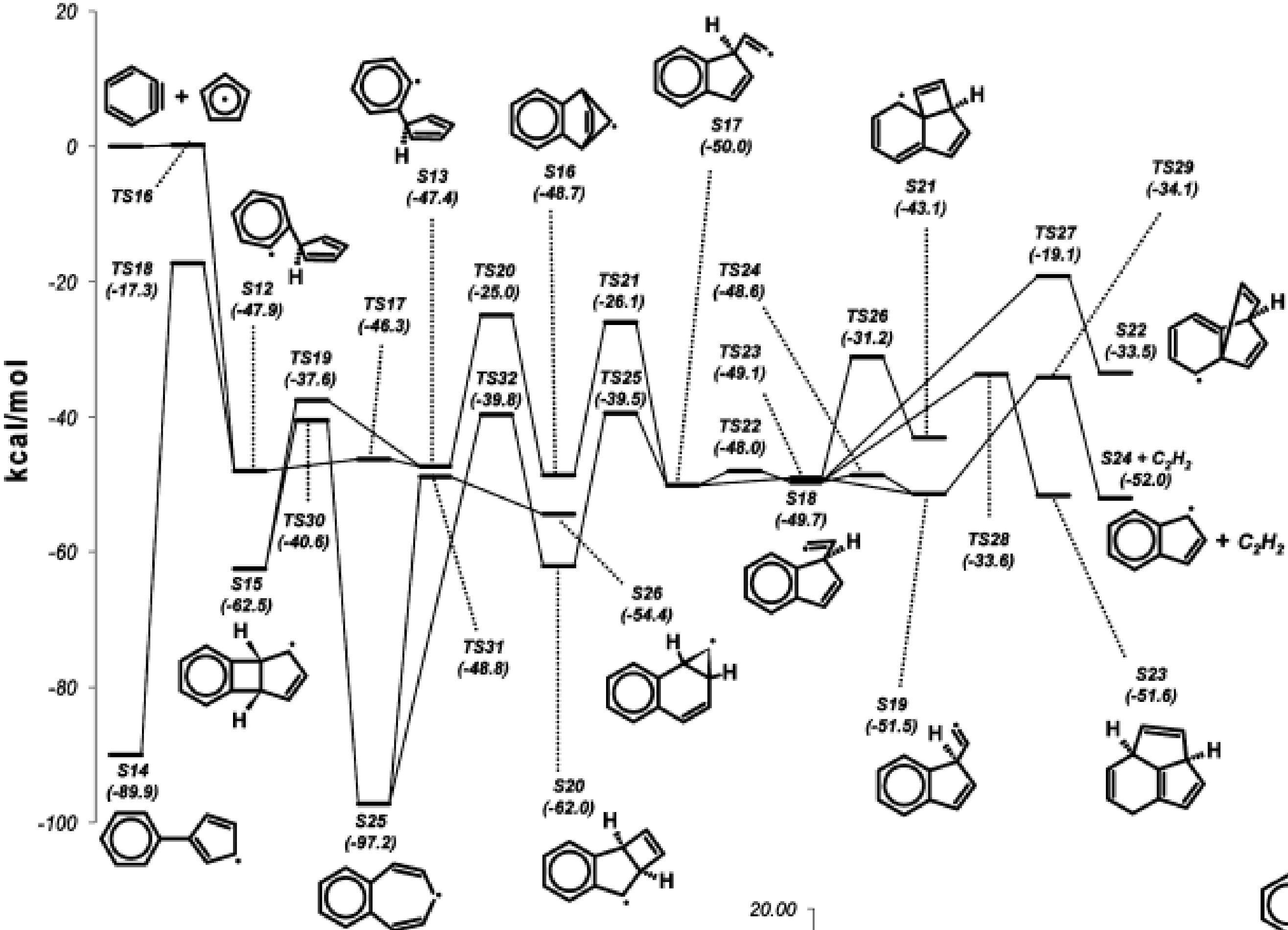


$C_6H_4 + C_{10}H_8$ High P Limit

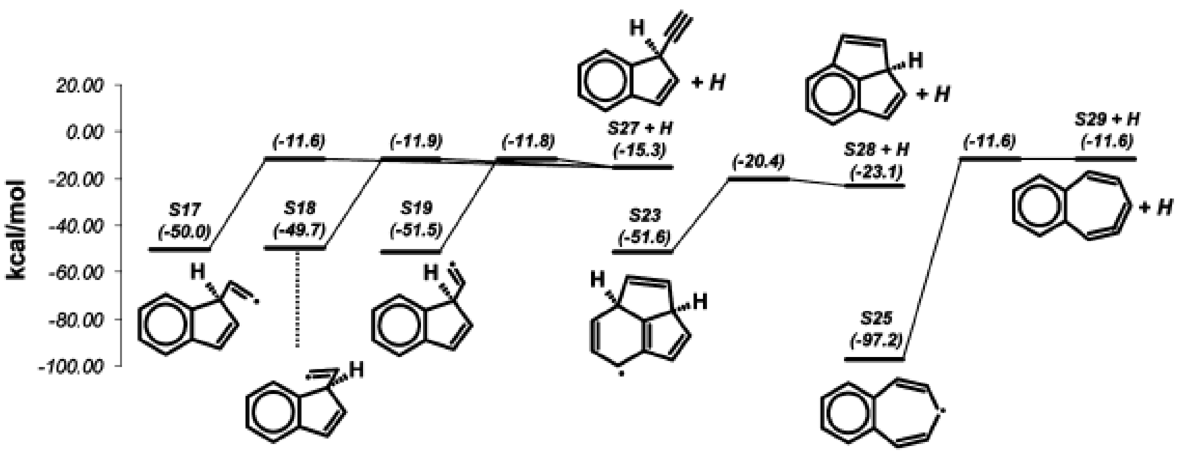
Comandini, Abid, Chaumeix, J Phys Chem A 121 (2017) 5921-5931



$C_6H_4 + C_5H_5$ High P Limit

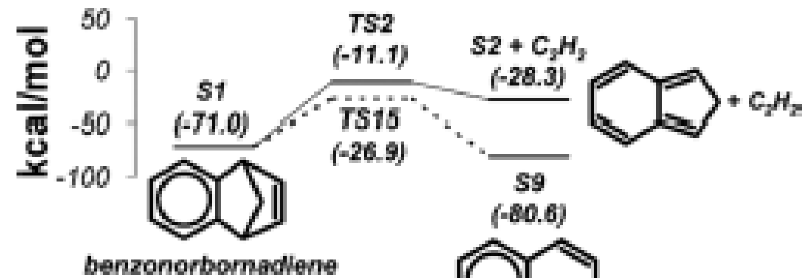


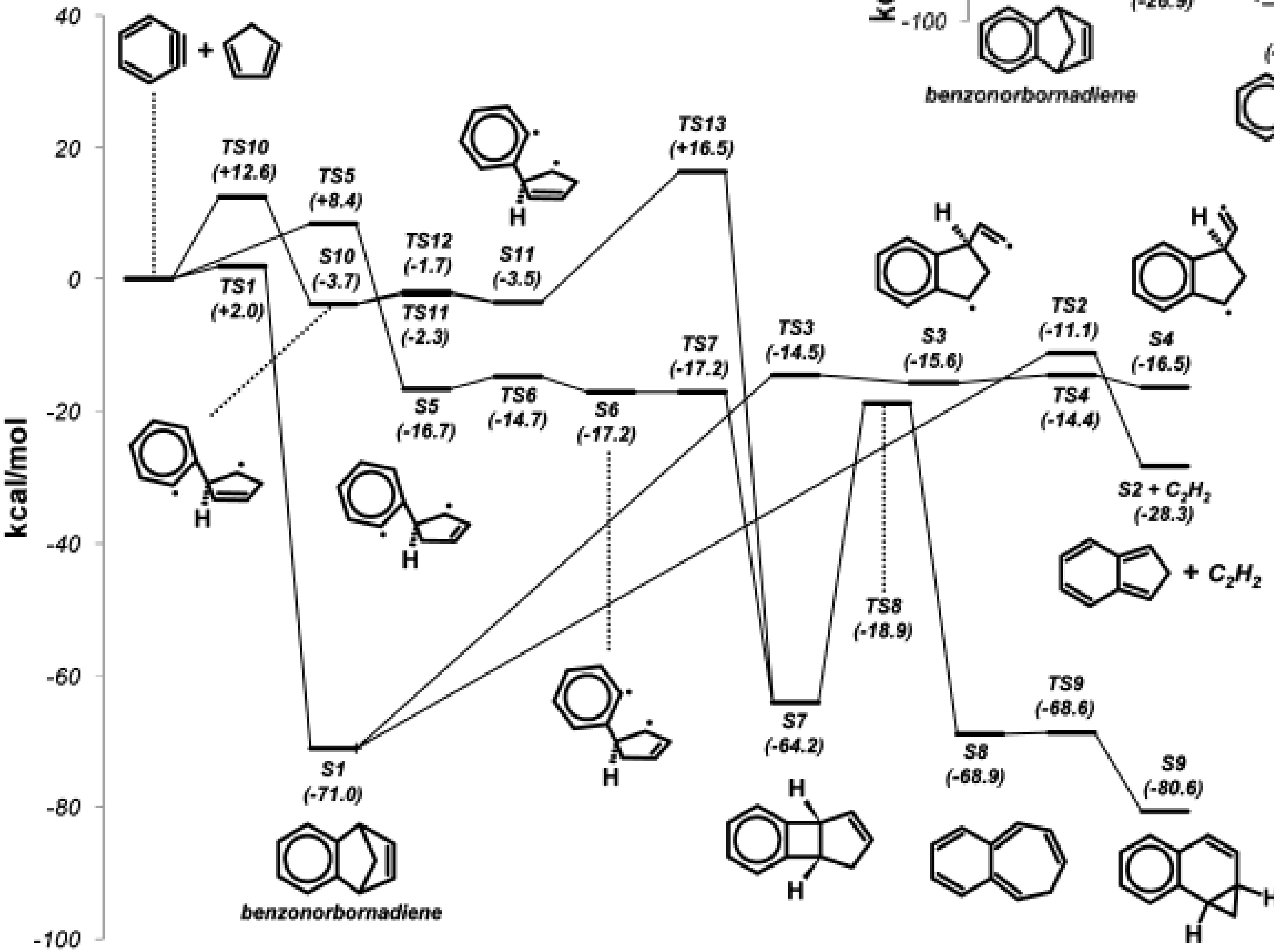
Comandini, Brezinsky, J Phys Chem. A 116 (2012) 1183-1190.



$C_6H_4 + C_5H_6$ High P Limit

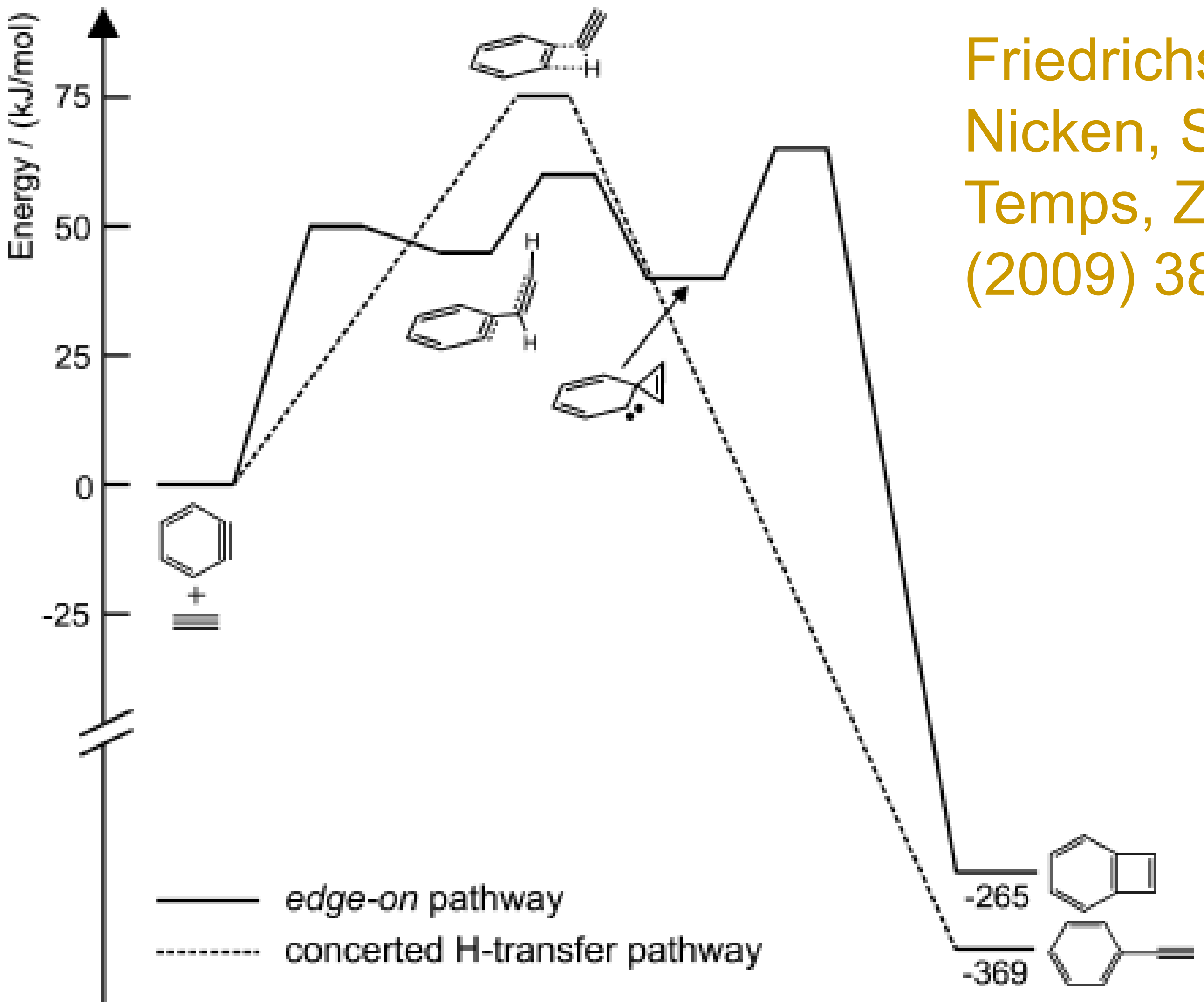
Comandini, Brezinsky, J Phys Chem. A 116 (2012) 1183-1190.





$C_6H_4 + C_2H_2$

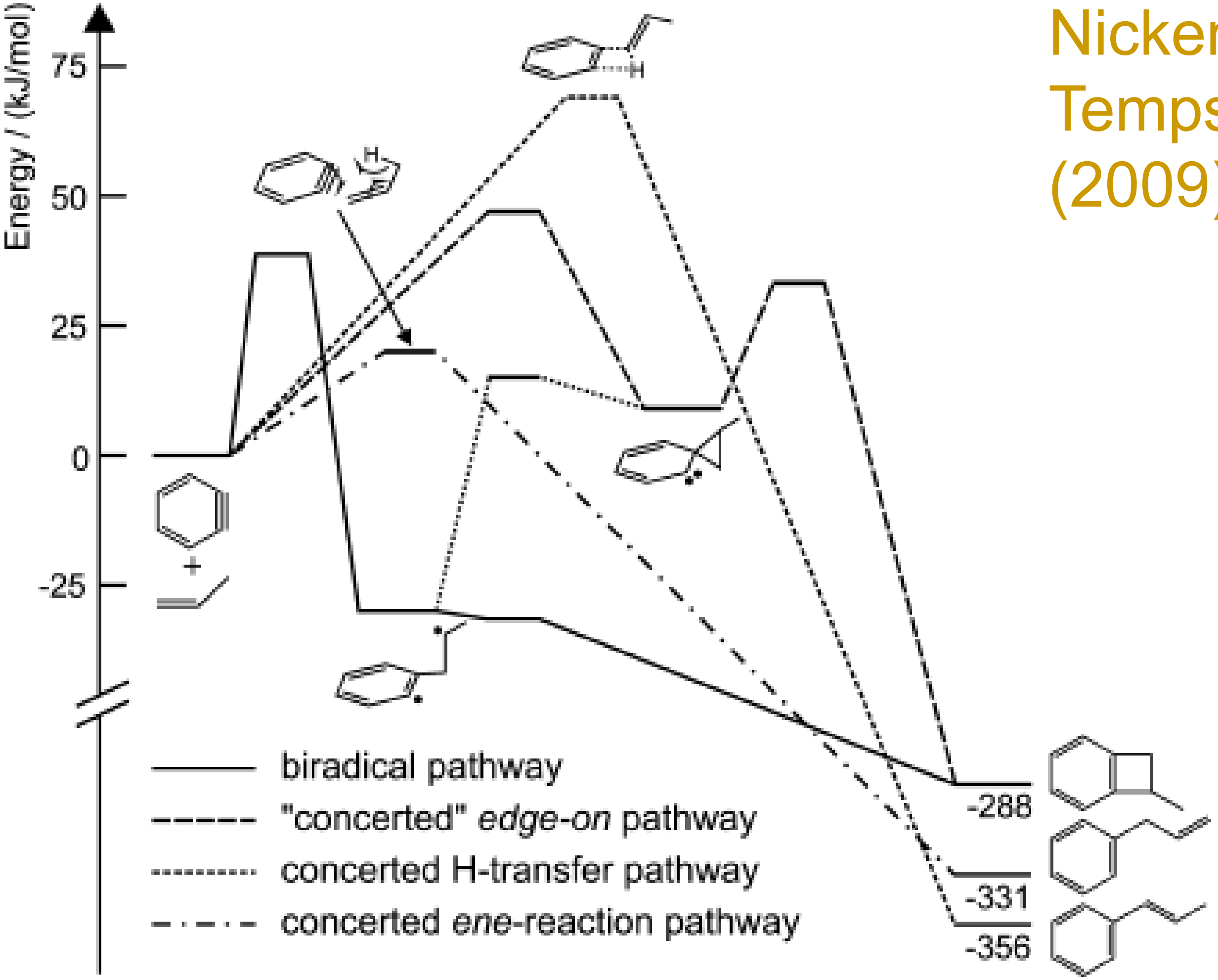
High P Limit



Friedrichs, Goos, Gripp, Nicken, Schonborn, Vogel, Temps, Z. Phys. Chem. 223 (2009) 387-407.

$C_6H_4 + C_2H_4$

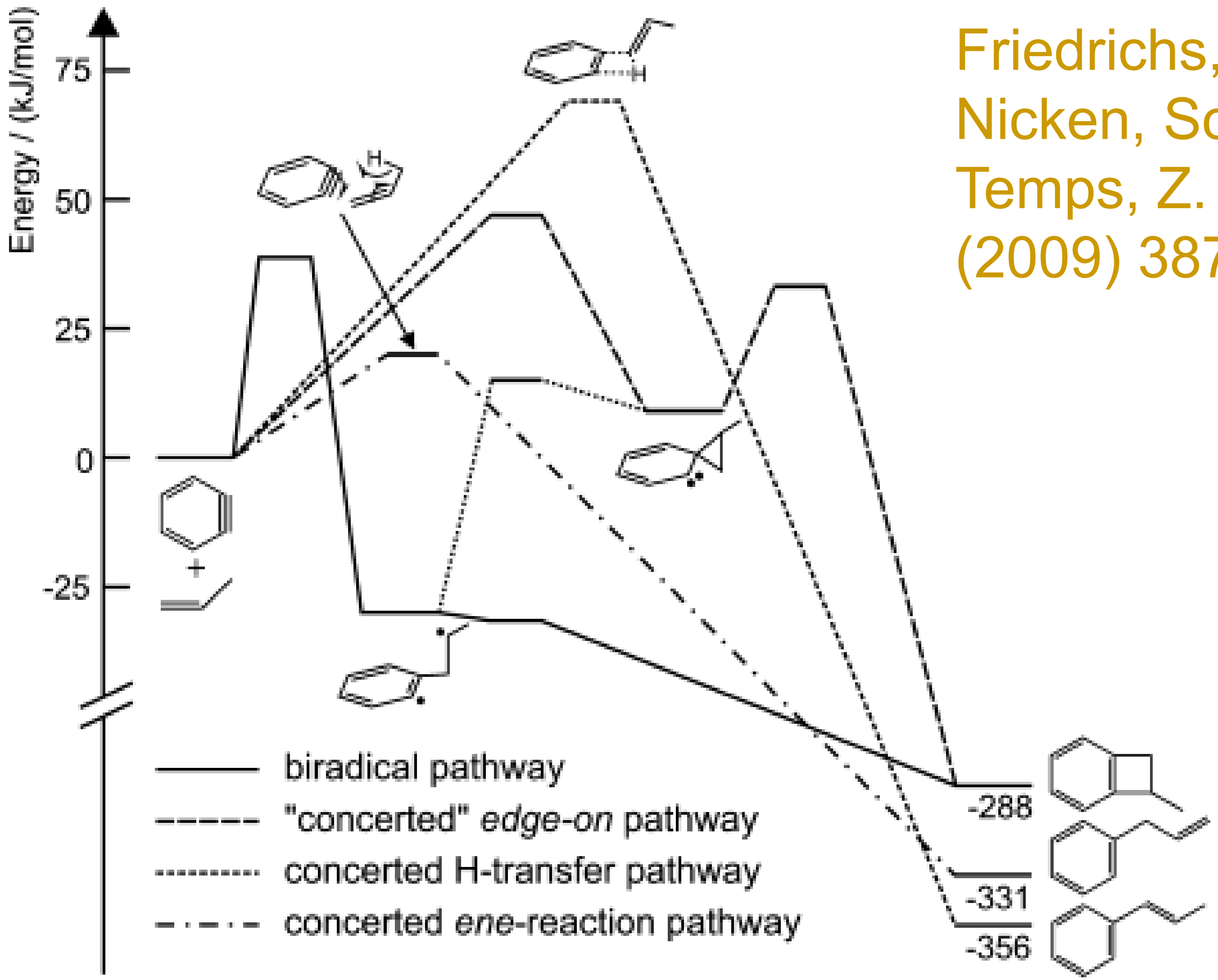
High P Limit



Friedrichs, Goos, Gripp, Nicken, Schonborn, Vogel, Temps, Z. Phys. Chem. 223 (2009) 387-407.

$C_6H_4 + C_3H_6$

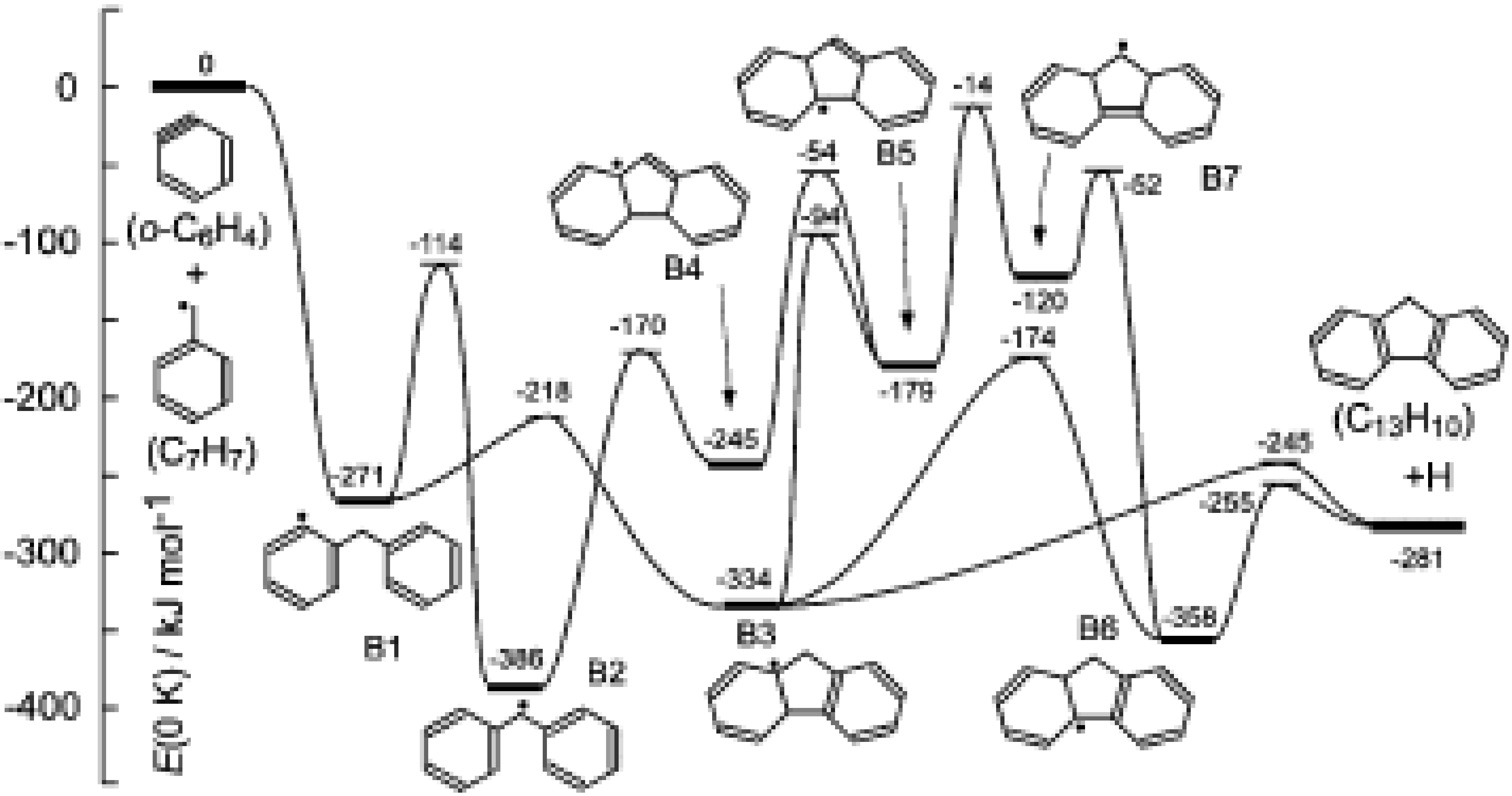
High P Limit



Friedrichs, Goos, Gripp, Nicken, Schonborn, Vogel, Temps, Z. Phys. Chem. 223 (2009) 387-407.

C_6H_4 + C_7H_7 P Dependent

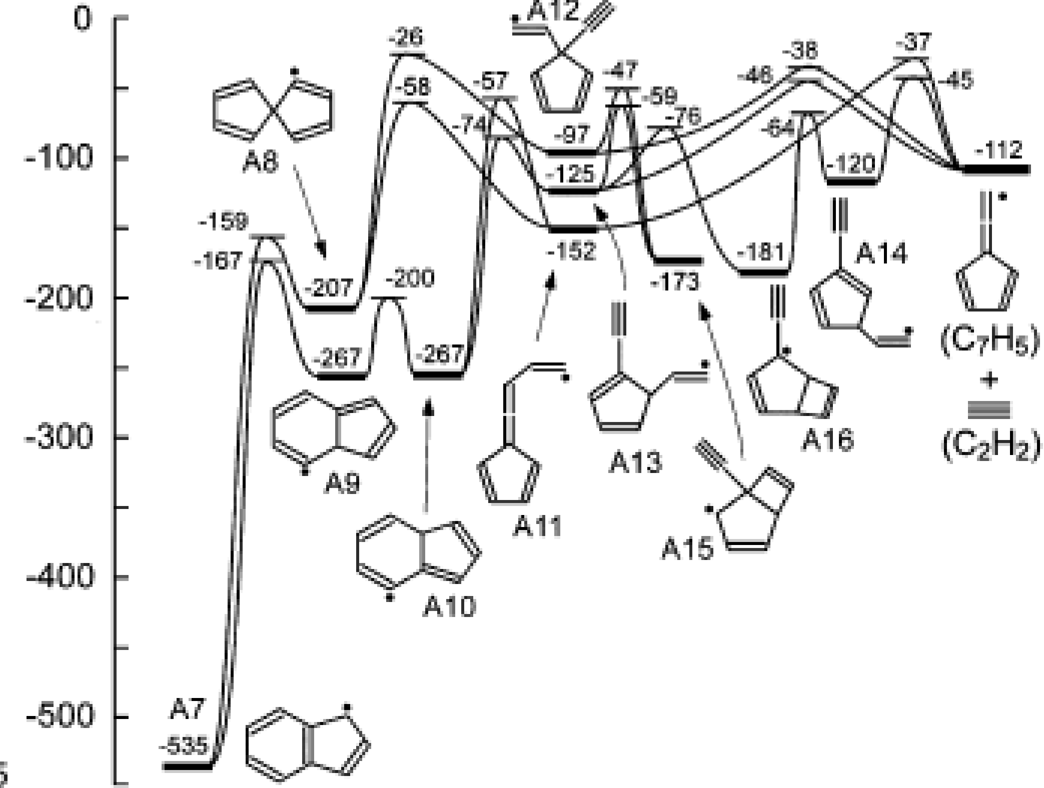
Matsugi, Miyoshi
Phys. Chem. Chem. Phys.
14 (2012) 9722-9728

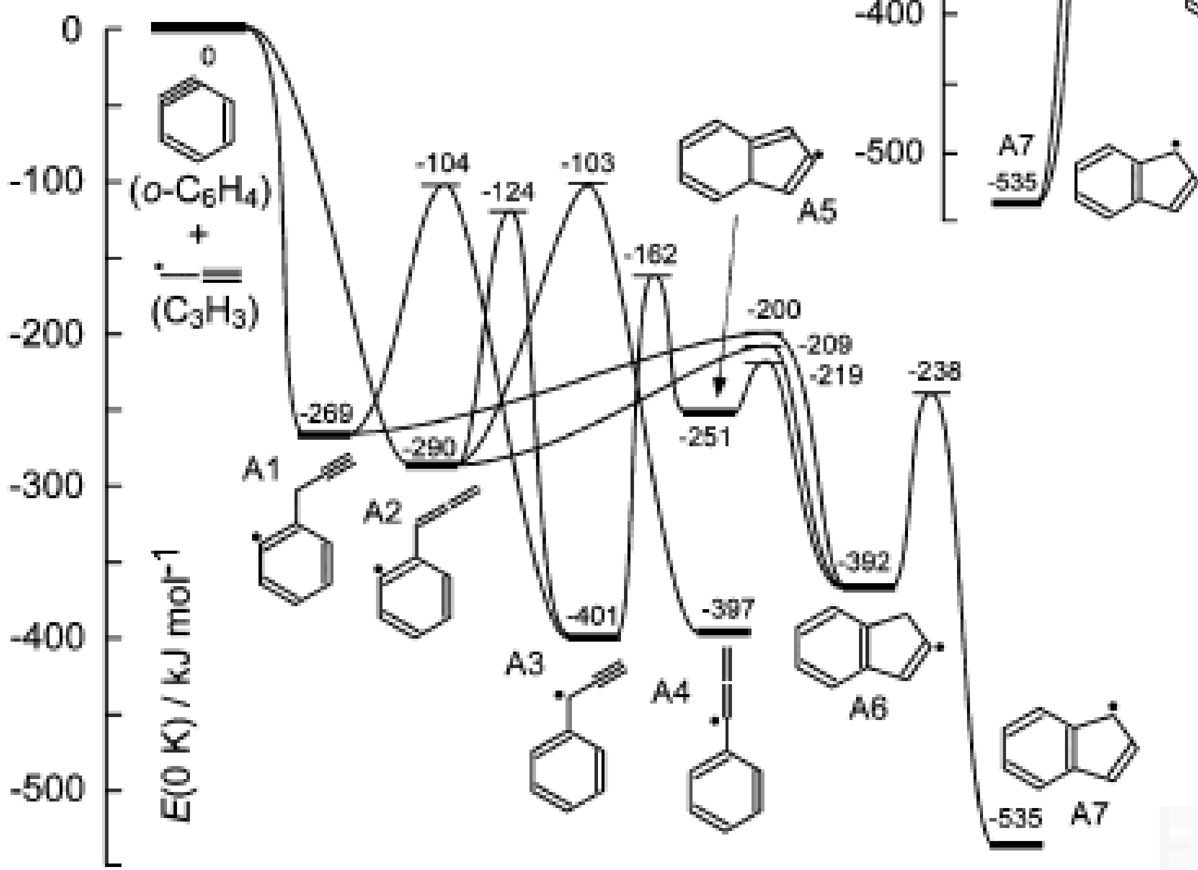


C_6H_4 + C_3H_3

P Dependent

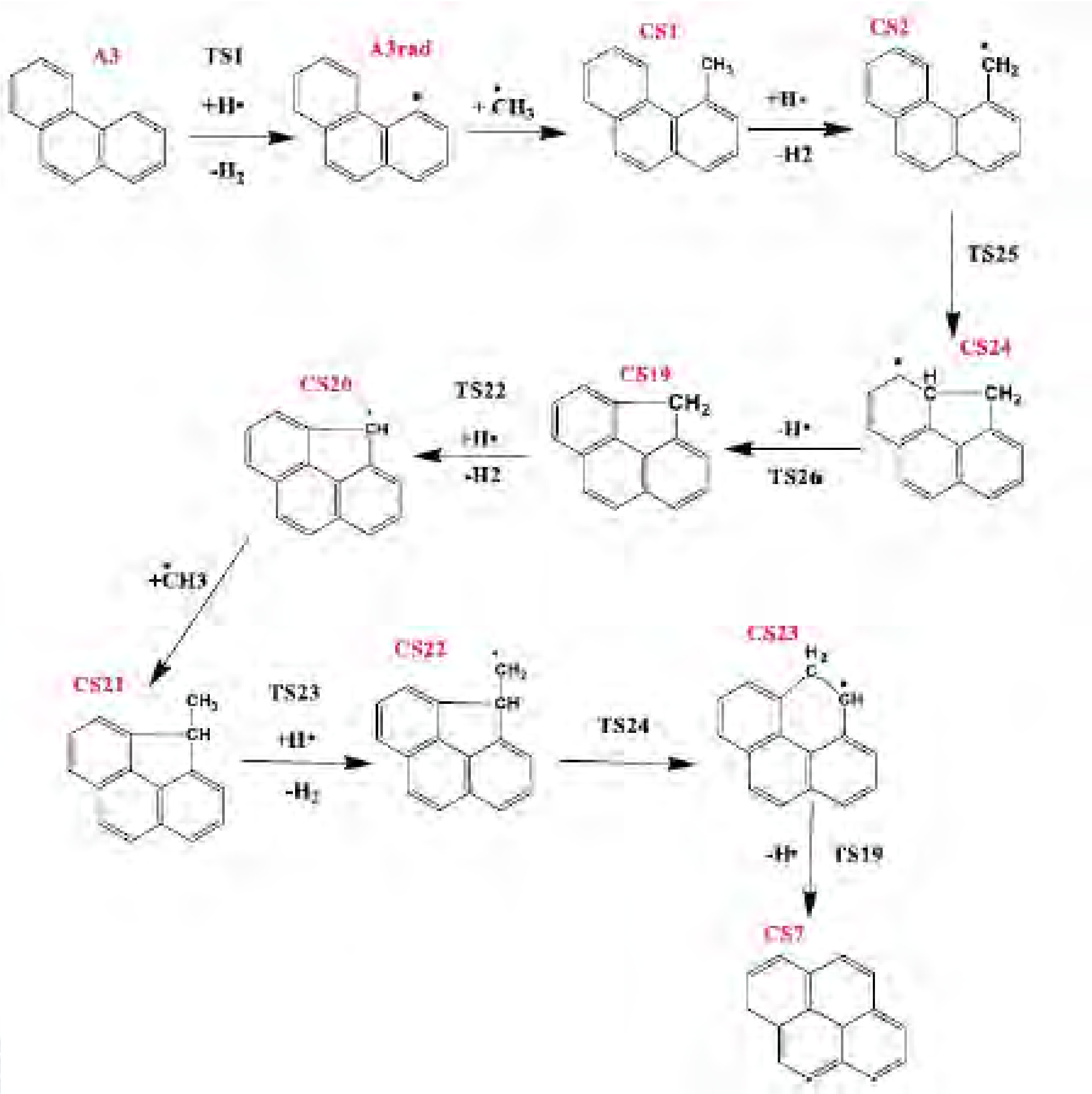
Matsugi, Miyoshi
Phys. Chem. Chem. Phys.
14 (2012) 9722-9728





Methyl Addition Cyclization (MAC) No Rates

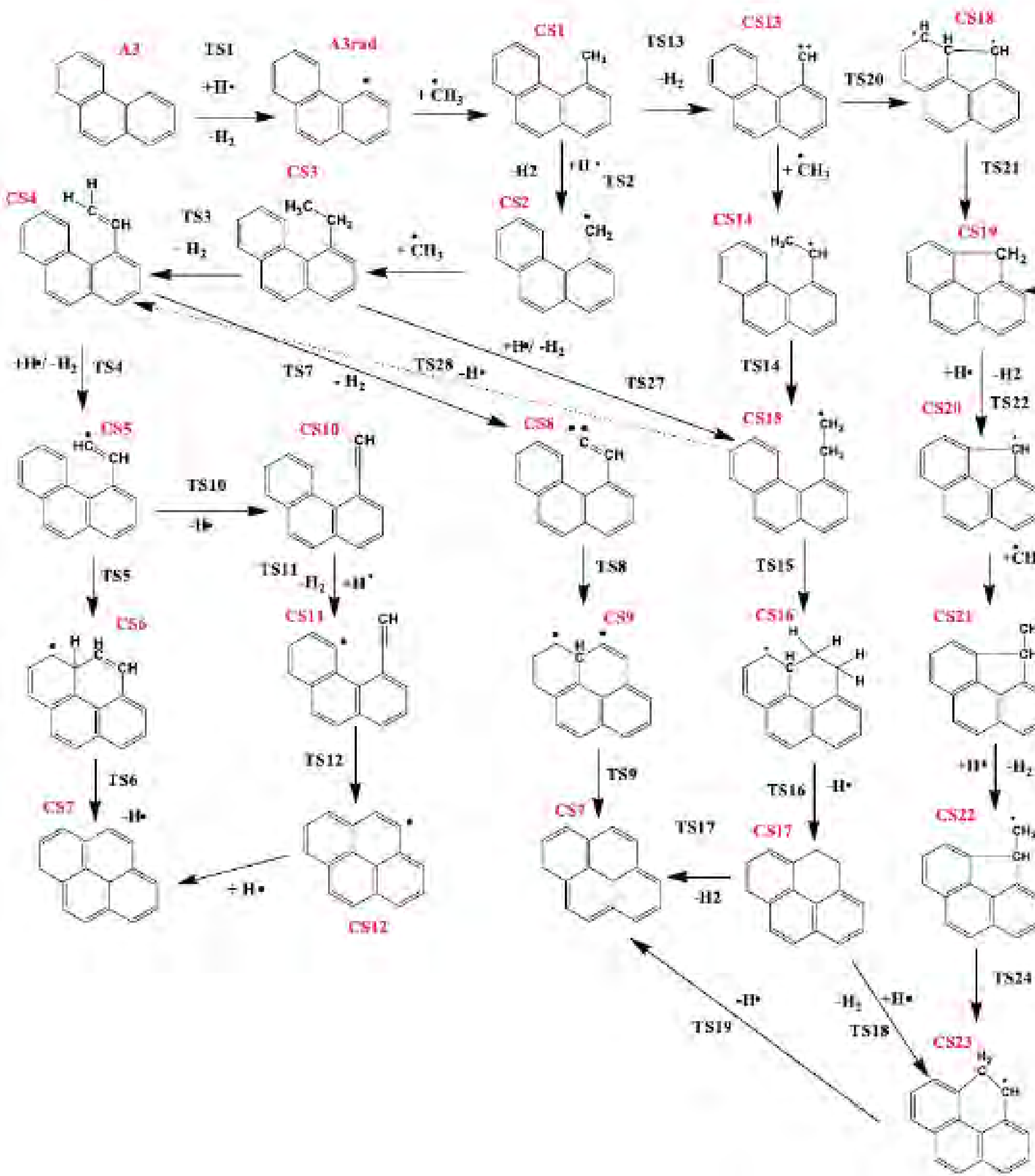
Shukla, Miyoshi, Koshi, J. Am. Soc. Mass Spectrom. 21 (2010) 534-544.



Role of CH_3

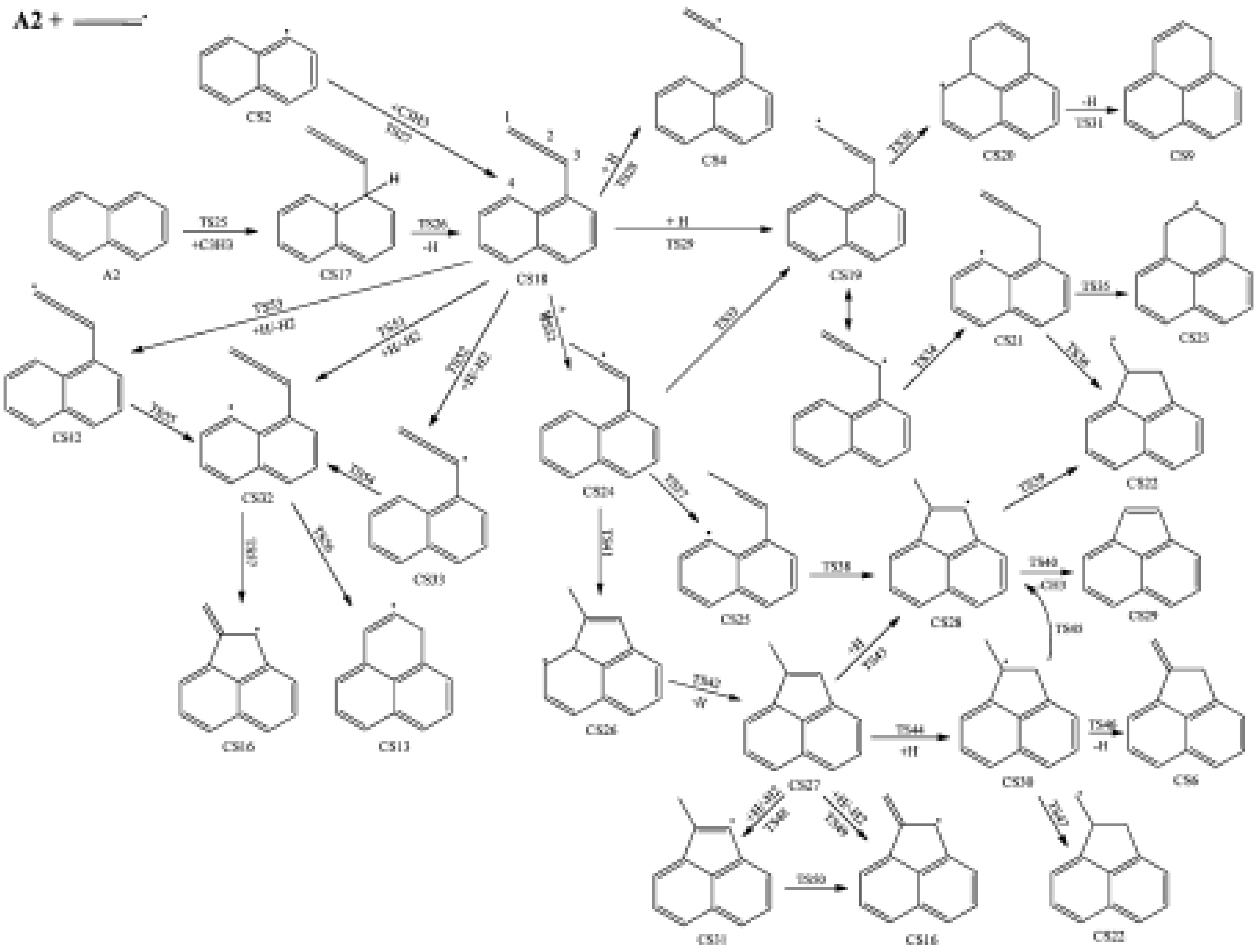
High P Limit

Georganta, Rahman, Raj, Sinha, Combust. Flame 185 (2017) 129-141.



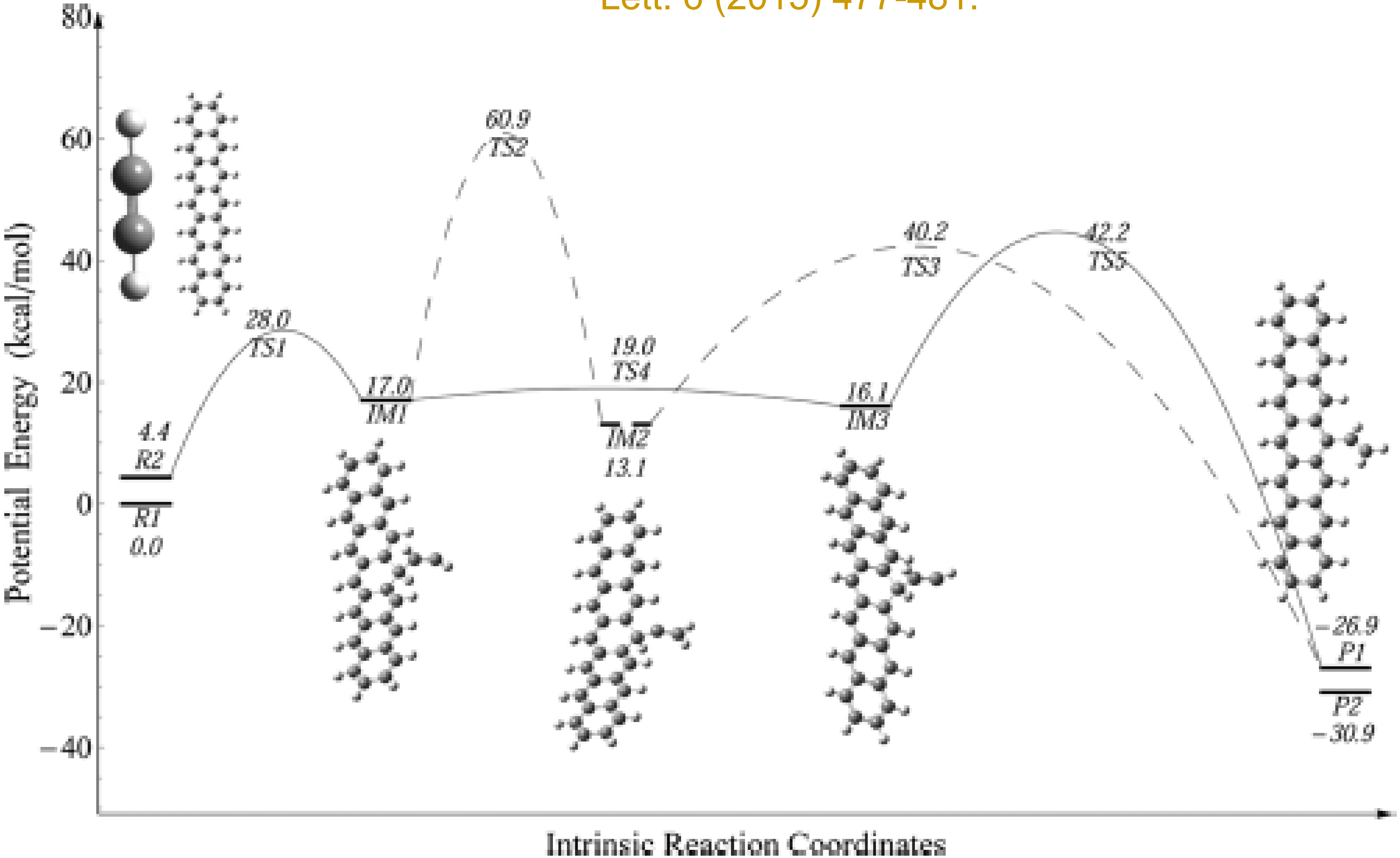
C_3H_3 Addition to Aromatics High P Limit

Raj, Rashidi, Chung, Sarathy, J. Phys. Chem. A 118 (2014) 2865-2885.



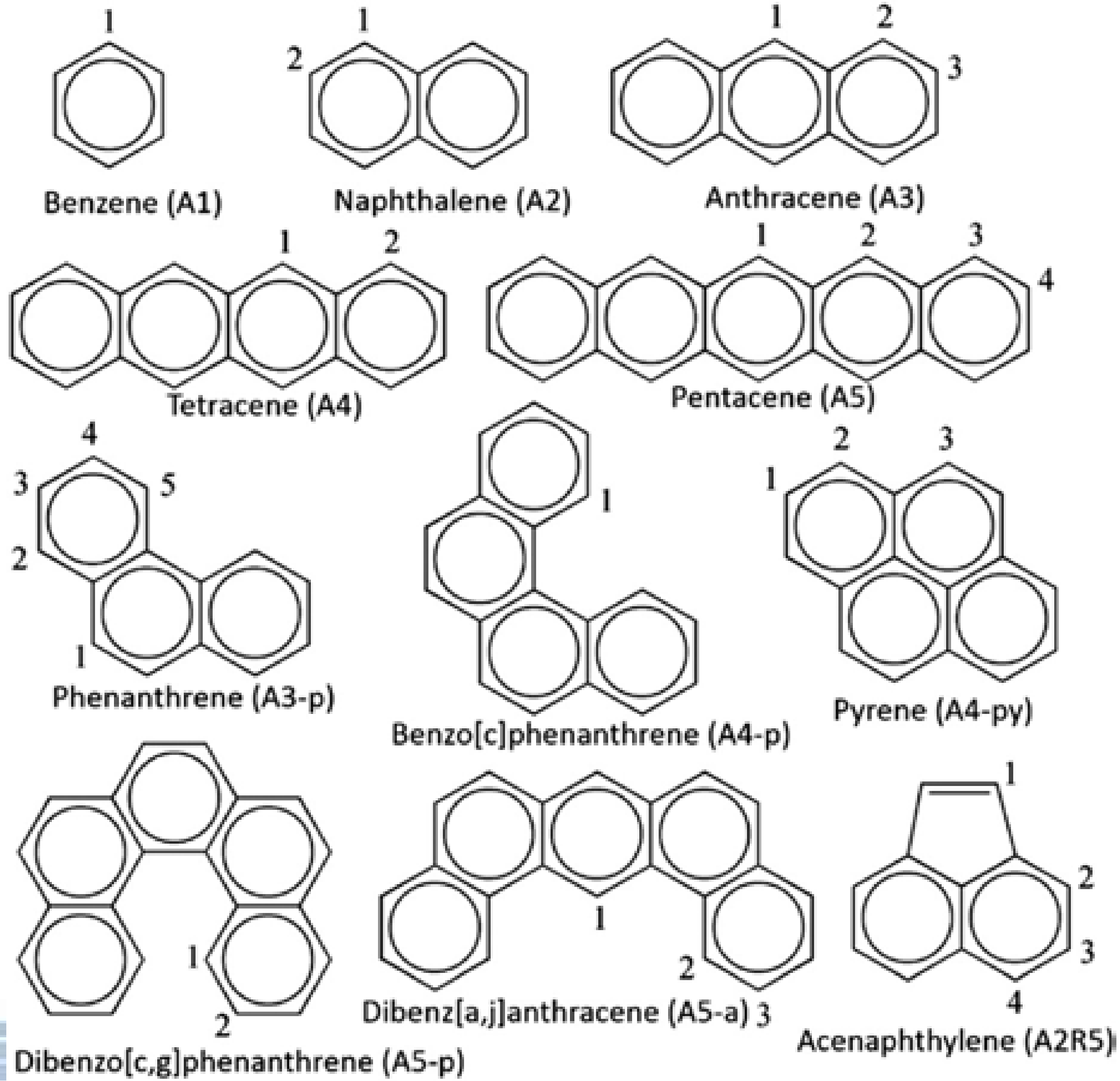
Triplet Radicals High P Limit

Zhang, You, Law, J. Phys. Chem. Lett. 6 (2015) 477-481.



H Abstraction by H from Aromatics

Hou, You, Phys. Chem. Chem. Phys. 19 (2017) 30772-30780



PES Perspective C_9H_8

C_9
- $C_9H_7 + H$
- $C_9H_6 + H_2$

C_5
- $C_5H_8 + C_4$
- $C_5H_7 + C_4H$
- $C_5H_6 + C_4H_2$
- $C_5H_5 + C_4H_3$
- $C_5H_4 + C_4H_4$
- $C_5H_3 + C_4H_5$
- $C_5H_2 + C_4H_6$
- $C_5H + C_4H_7$
- $C_5 + C_4H_8$

C_8
- $C_8H_8 + C$
- $C_8H_7 + CH$
- $C_8H_6 + CH_2$
- $C_8H_5 + CH_3$
- $C_8H_4 + CH_4$

C_7
- $C_7H_8+C_2$
- $C_7H_7+C_2H$
- $C_7H_6+C_2H_2$
- $C_7H_5+C_2H_3$
- $C_7H_4+C_2H_4$
- $C_7H_3+C_2H_5$
- $C_7H_2+C_2H_6$

C_6
- $C_6H_8 + C_3$
- $C_6H_7 + C_3H$
- $C_6H_6 + C_3H_2$
- $C_6H_5 + C_3H_3$
- $C_6H_4 + C_3H_4$
- $C_6H_3 + C_3H_5$
- $C_6H_2 + C_3H_6$
- $C_6H + C_3H_7$
- $C_6 + C_3H_8$

Summary

~ Ready for Mechanism that Includes all Relevant Pathways from 1 to 2 Rings

- More Pressure Dependent Studies
- PES Perspective
- Reactions Producing and Growing from C_8H_x
- More CH_3 Reactions

Theory Could be Improved

- Higher Level Ab Initio
- Machine Learning
- Variational
- Hindered Rotors

Oxidation – Same But Much Less Complete

Funding DOE BES

GAS PHASE CHEMICAL PHYSICS

PAH Formation Chemistry- Potential Validation Experiments

Nils Hansen

Sandia National Laboratories

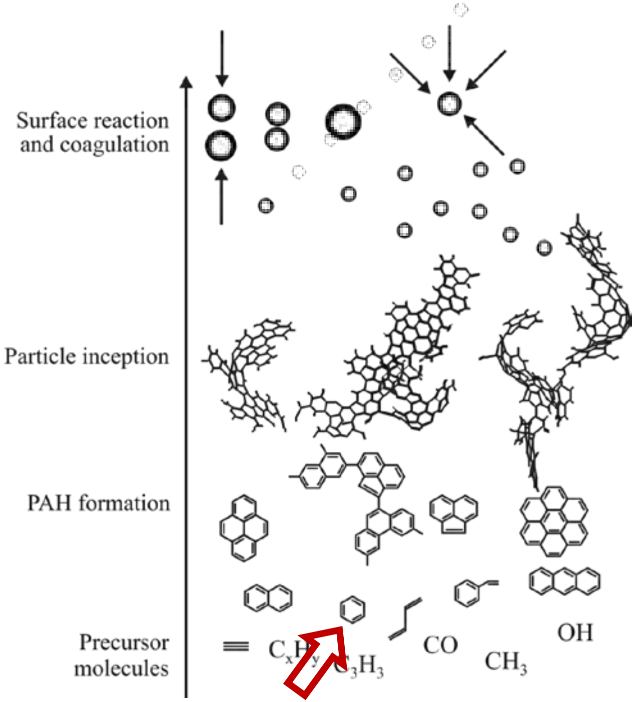
CRF

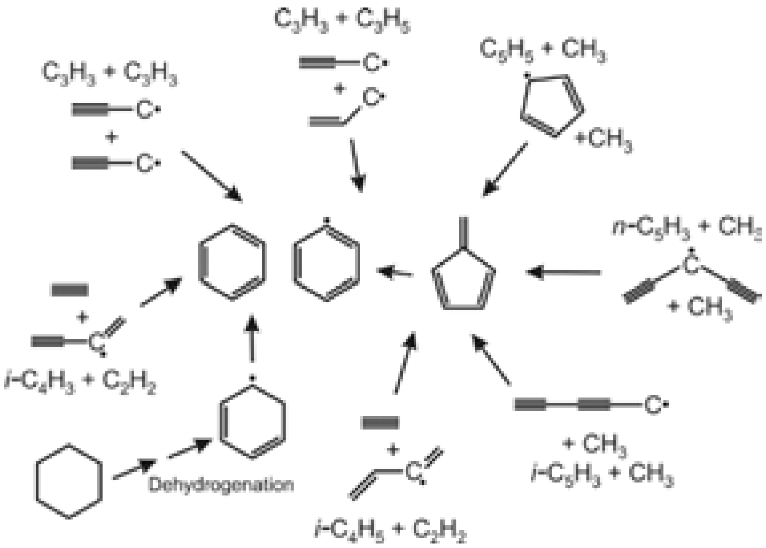
PAH Formation Chemistry- Potential Validation Experiments

- What do we know about PAH Formation Chemistry?
- Experimental Approaches
  - Flame-sampling molecular-beam mass spectrometry
  - Gas-Chromatography
  - PIE/PEPICO
  - Aerosol Mass Spectrometry
- Experimental Challenges
- Tandem (2D) Mass Spectrometry
- Sampling-Probe Effects

GAS PHASE CHEMICAL PHYSICS

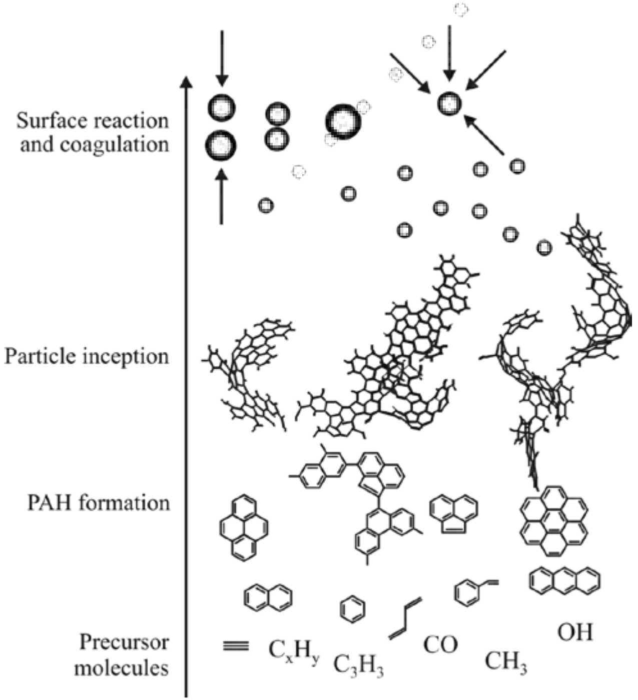
PAH and Soot Formation Chemistry: What do we know?

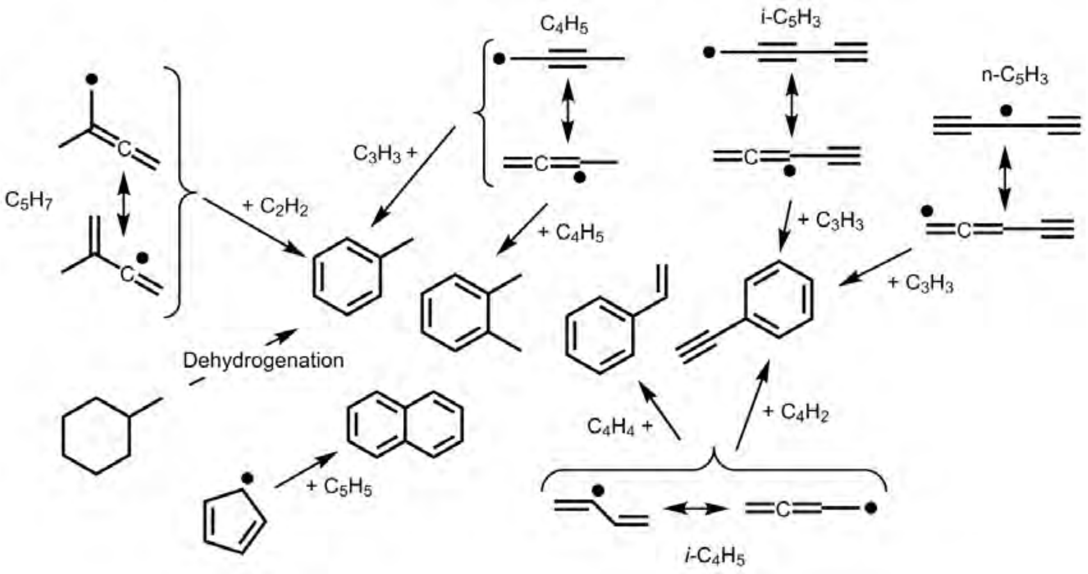




N. Hansen *et al.*, *Combust. Expl. Shock Waves*, **2012,** 48, 508-515

PAH and Soot Formation Chemistry: What do we know?

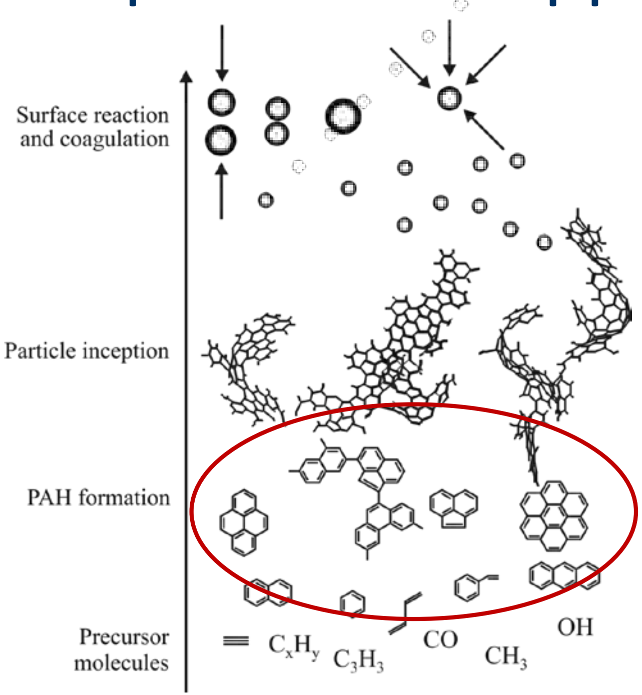


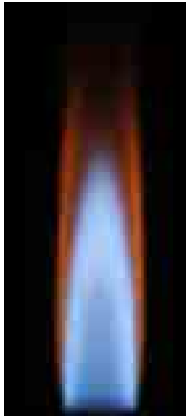


- ✓ Benzene is not necessarily the "first aromatic ring"
- ✓ Larger aromatic species can be formed while bypassing benzene

Energy Fuels, **2011,** 25(12), 5611-5625
Combust. Flame, **2017,** 175, 34-46 and *Phys. Chem. Chem. Phys.*, **2018,** 20, 10780-10795

PAH and Soot Formation Chemistry: Experimental Approaches





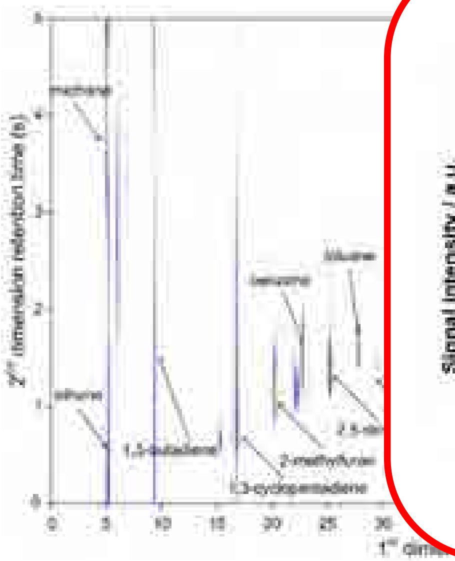
Mass spectrometry is a universal diagnostics tool that enables the detection of all intermediates simultaneously without prior knowledge of their identity.

- ✓ Flame-Sampling Gas-Chromatography
  - ➢ 2D-GC/VUV Mass Spectrometric Detection

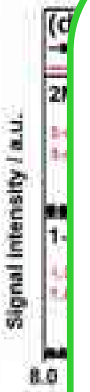
GAS PHASE CHEMICAL PHYSICS

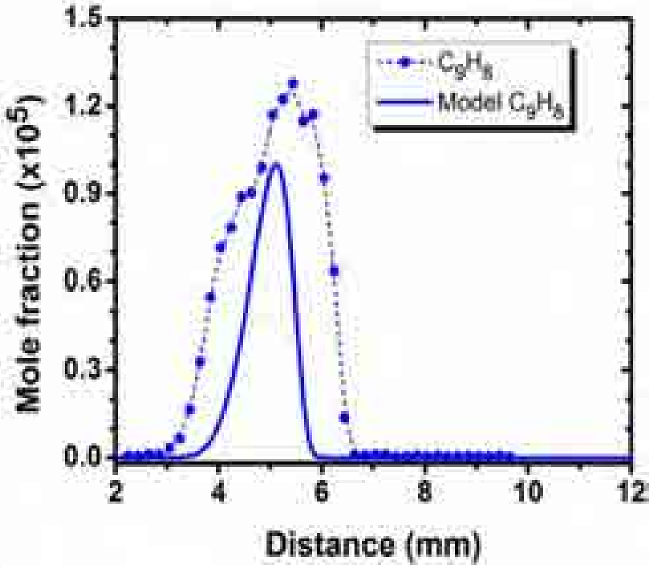
PAH and Soot Formation Chemistry

✓ 2D-Gas Chromatography

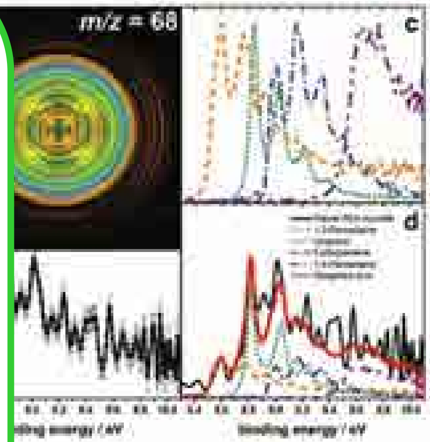


✓ Structures information
✓ Unidentifiable features





✓ Ga… Photo-Electron-PhotoIon Coincidence



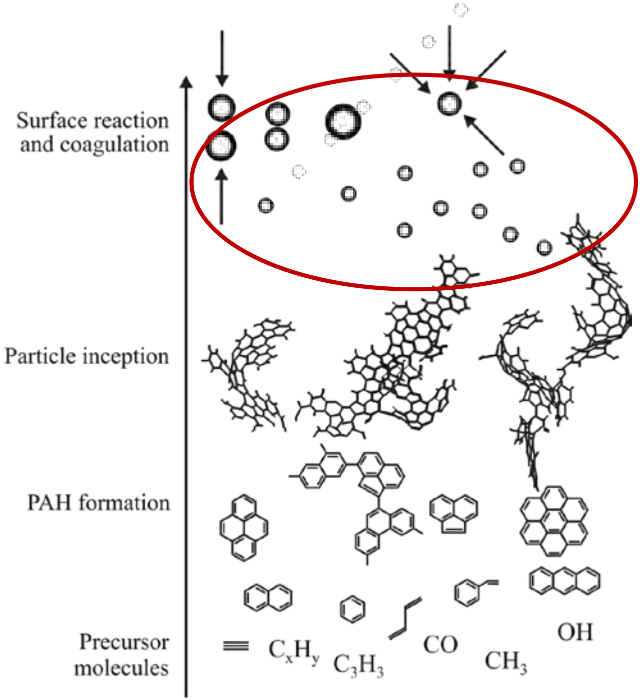
…per *et al.*, *Z. Phys. Chem.*, **2018,** 232(2), 153-187

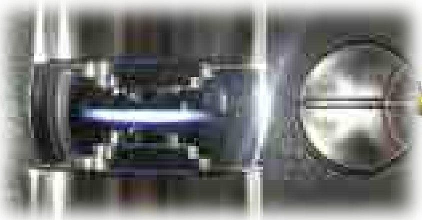
…ass-to-charge ratio
✓ Everything detected

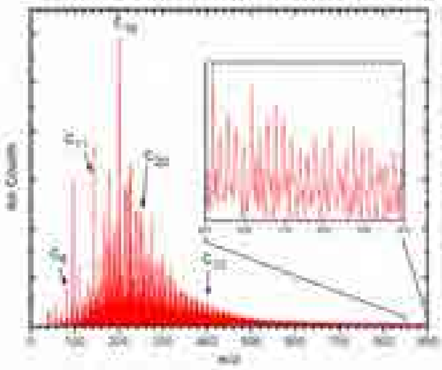
Information can be converted into mole fraction profiles

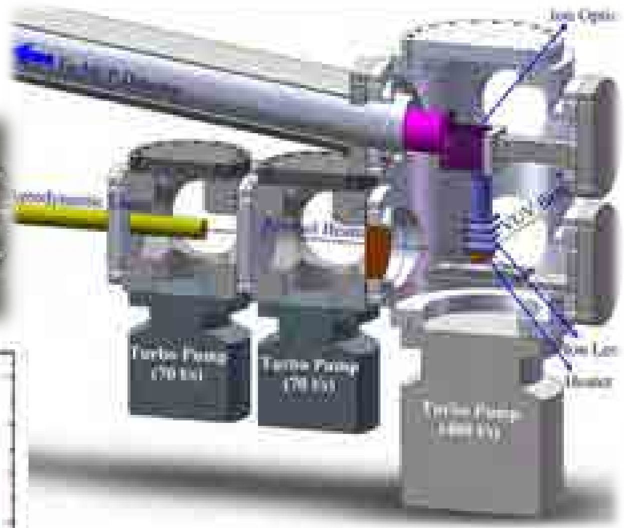
L. Ruwe *et al., Phys. Chem. Chem. Phys.*, **2018,** 20, 10780-10795

PAH and Soot Formation Chemistry



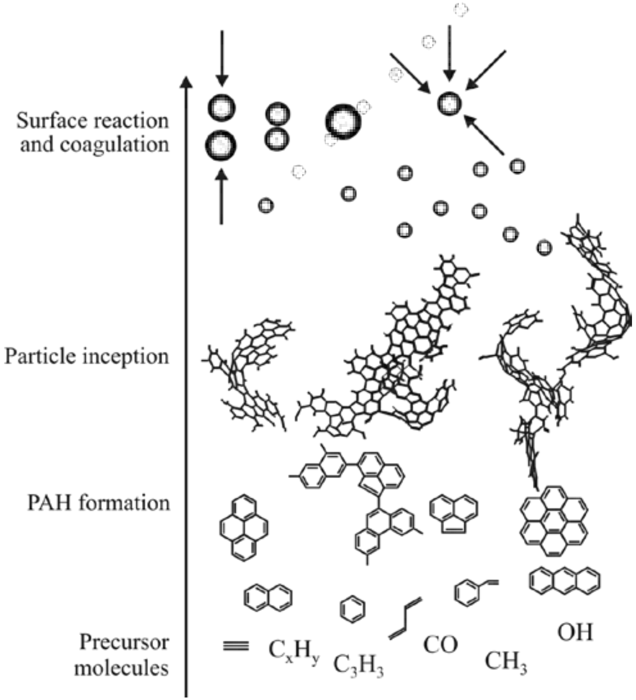


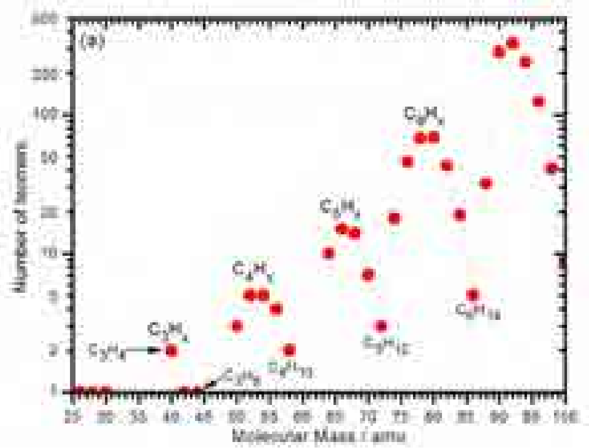




S. A. Skeen *et al., J. Aerosol Sci.*, **2013,** 58, 86-102

PAH and Soot Formation Chemistry



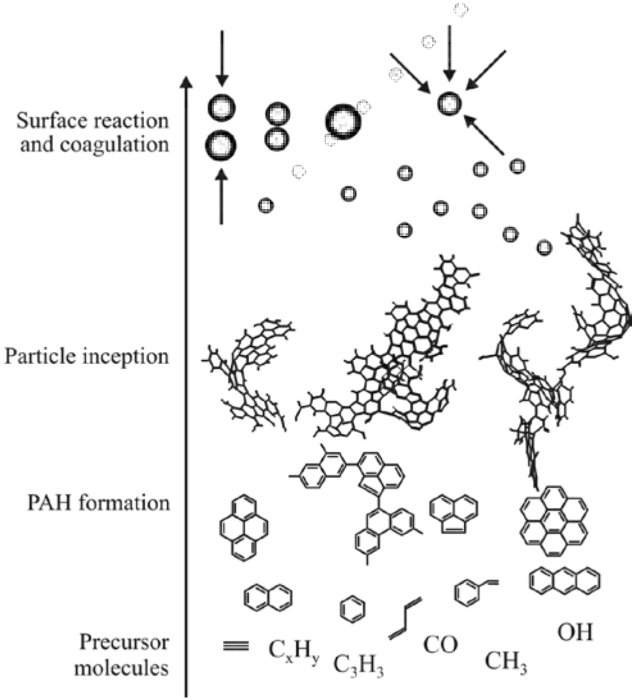


Challenges:

- Already the formation of the „first“ aromatic ring is governed by many different reactions involving many different reactants
- Number of possible isomers increases with molecular size
- The isomer-selective approach will break down

What is the right level of detail?

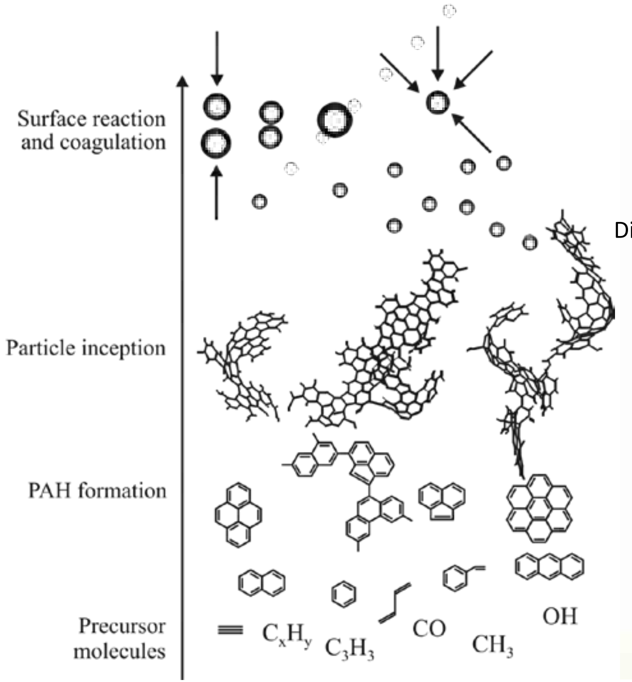
PAH and Soot Formation Chemistry

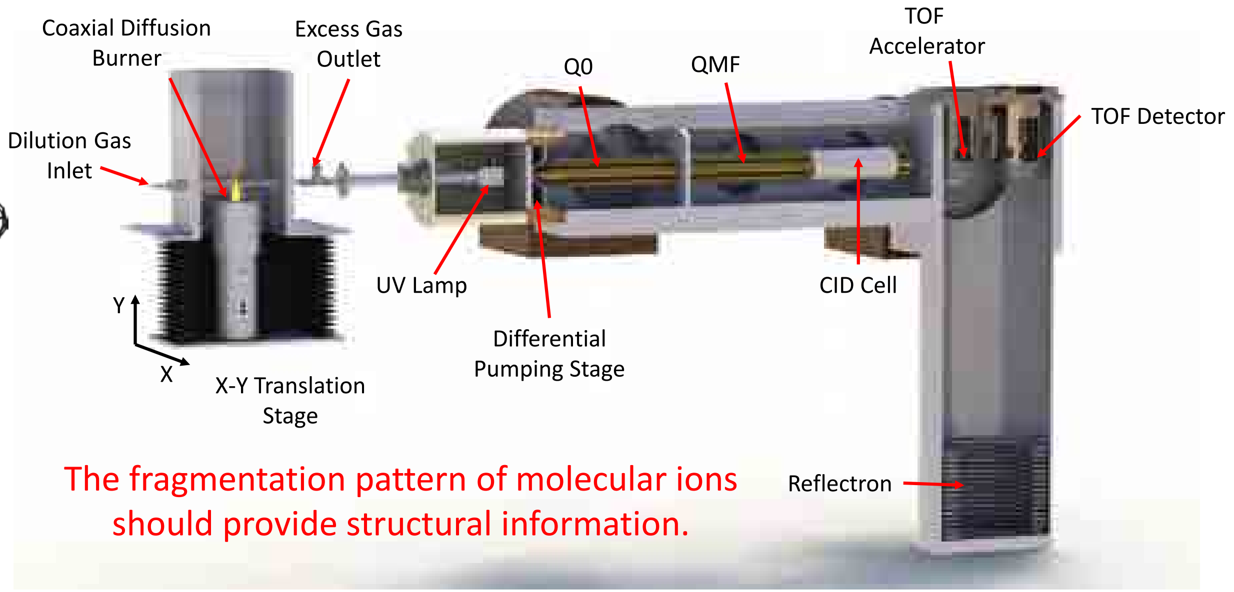


- ✓ the goal is not to identify all possible isomeric structures
- ✓ the goal is to identify the important intermediates at the right level of detail

  ⇒ **re-occurring reactive structural features**
- ✓ The diagnostic technique should be able to:
  - ➢ identify five-membered ring structures
  - ➢ aliphatically bridged PAHs
  - ➢ reactive side chains
  - ➢ functional groups, etc.

GAS PHASE CHEMICAL PHYSICS

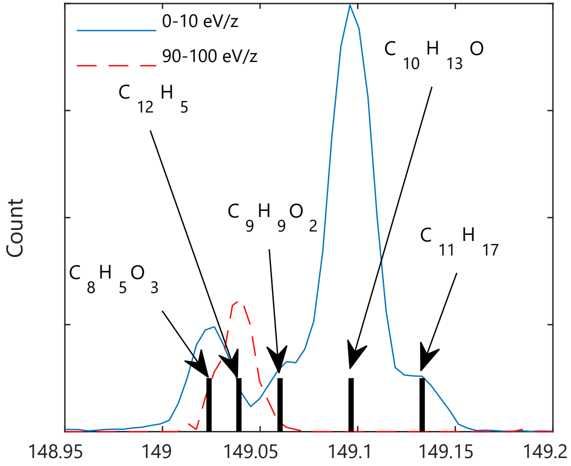




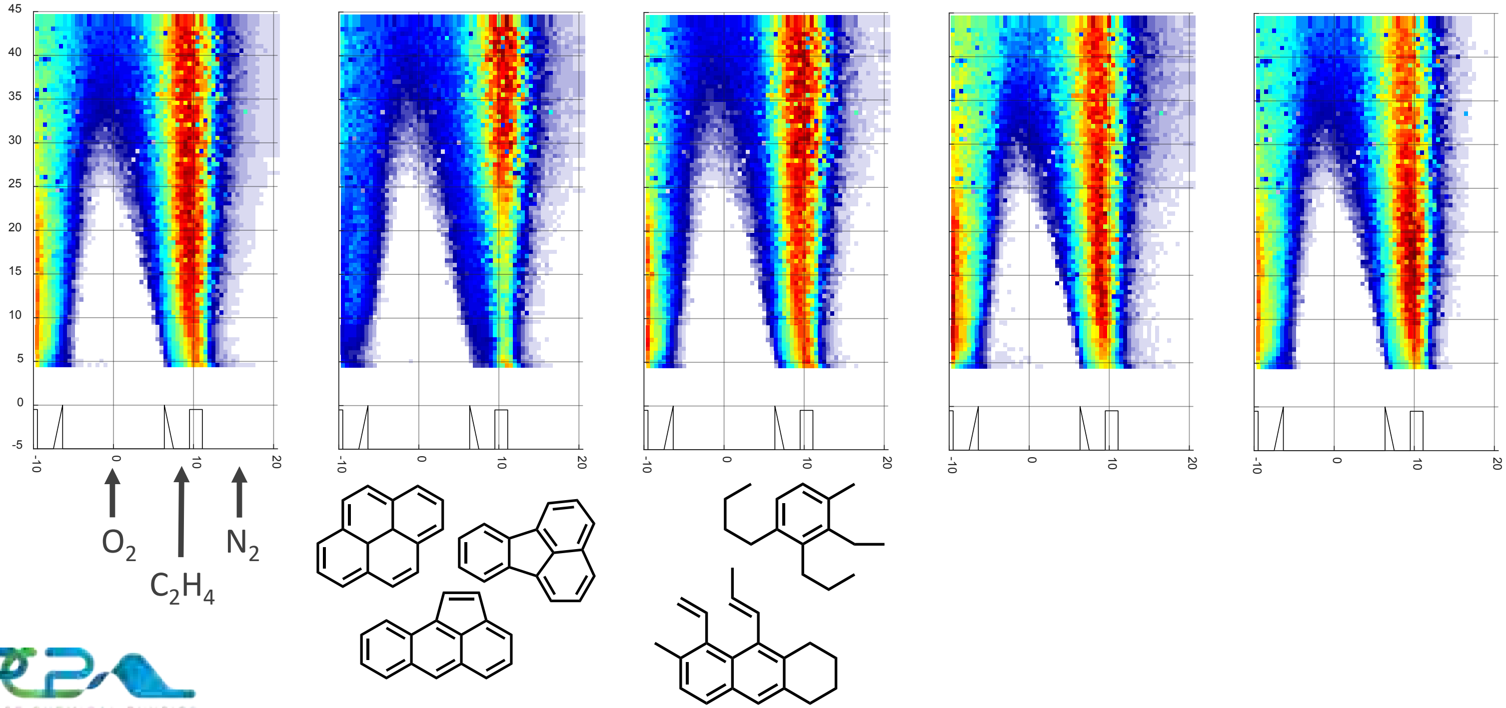
The fragmentation pattern of molecular ions should provide structural information.

B. D. Adamson *et al., J. Phys. Chem. A,* to be submitted

- atmospheric pressure photoionization (APPI)
- two modes of operation:
  - time-of-flight mode
  - MS-MS mode
- Resolution: QMF ~1, TOF ~8000
- collission gas: Ar
- sensitivity: tbd



B. D. Adamson *et al.*, *J. Phys. Chem. A,* to be submitted total ion counts (even masses) | aromatics C/H ≥ 1 | alkylated aromatics C/H < 1 | C_xH_yO | $C_xH_yO_2$

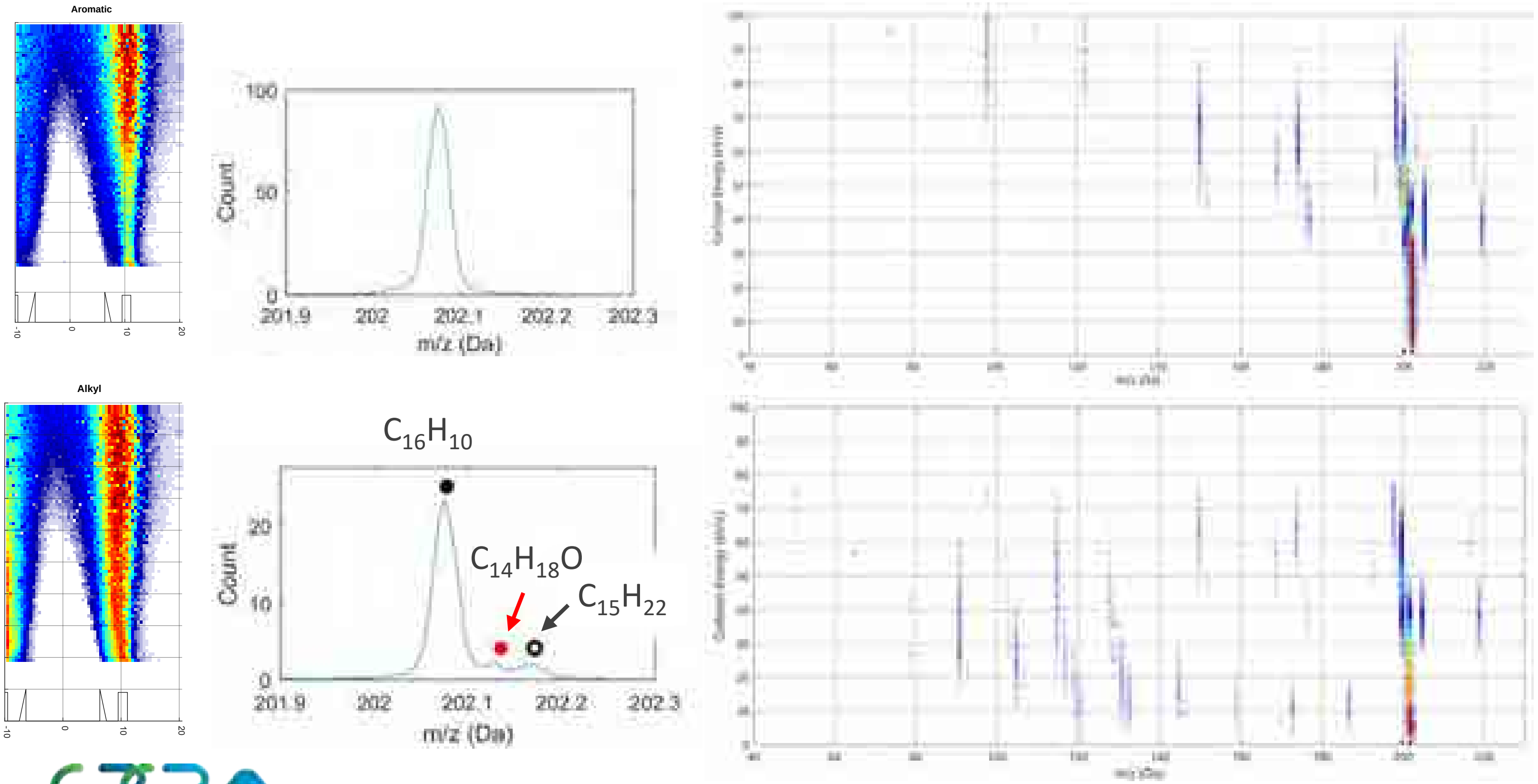


Evidence for aliphatically bridged PAHs

Identification of core-PAH structures

B. D. Adamson *et al., J. Phys. Chem. A,* to be submitted

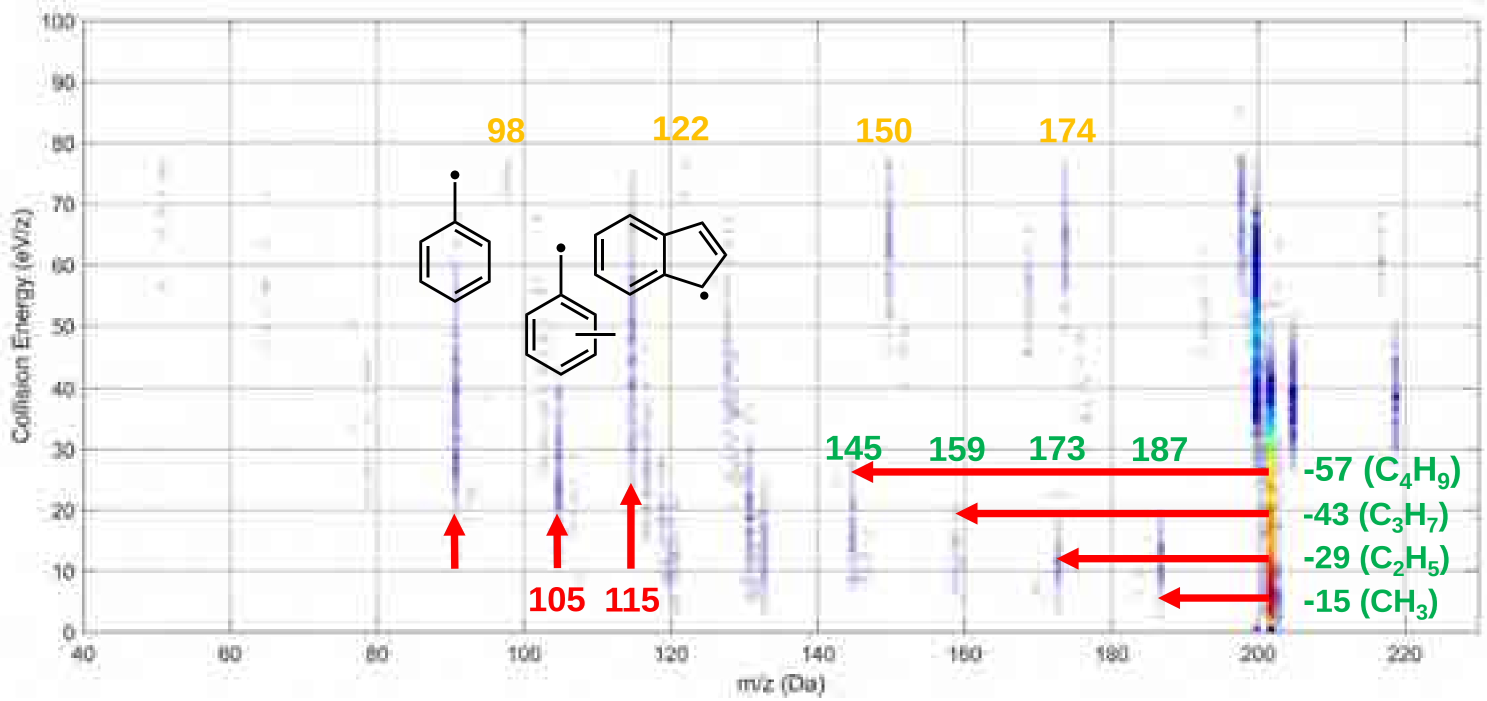
Fragmentation Scans: *m/z* = 202



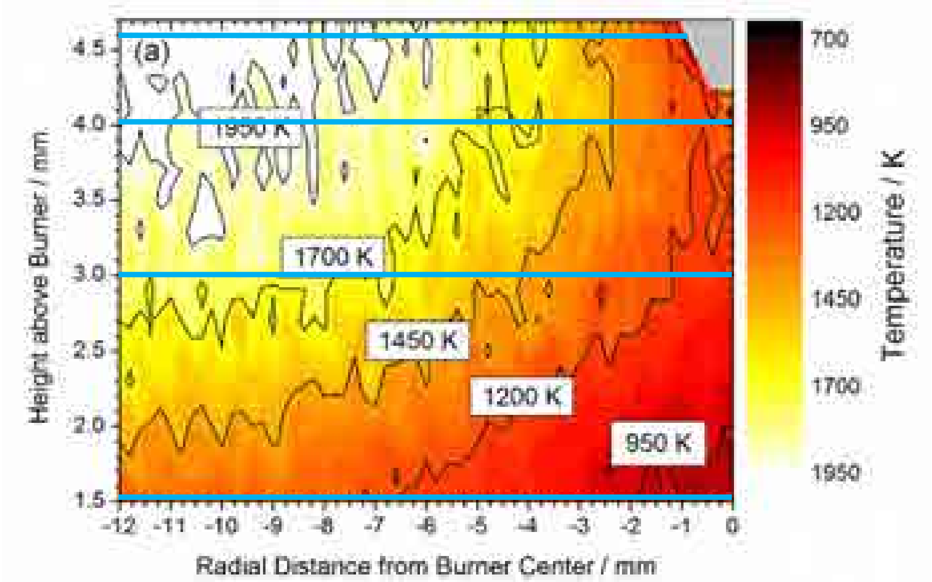
GAS PHASE CHEMICAL PHYSICS

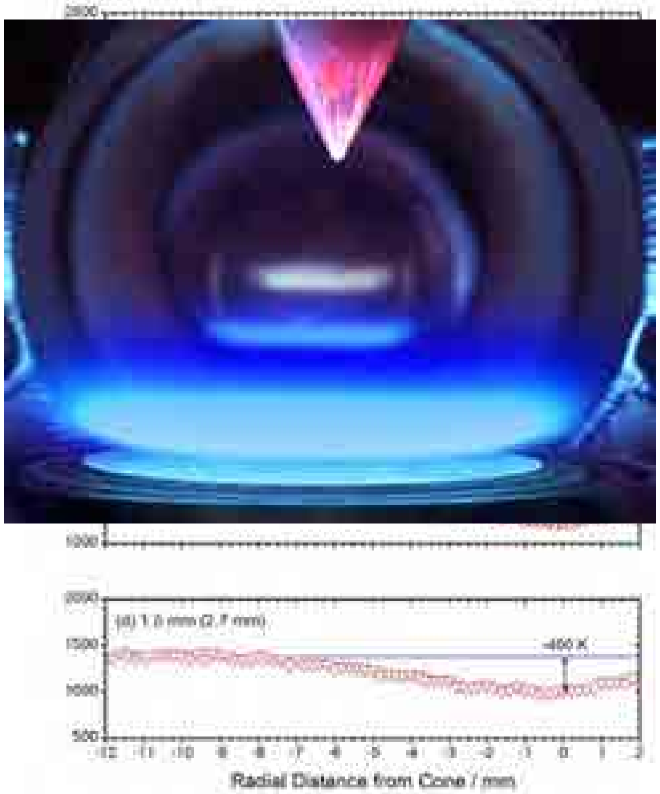
B. D. Adamson *et al.*, *J. Phys. Chem. A*, to be submitted

Identification of core PAH Structures and Aliphatic Chains



B. D. Adamson *et al., J. Phys. Chem. A,* to be submitted





New modeling approaches are needed to consider the temperature history and the multi-dimensionality.

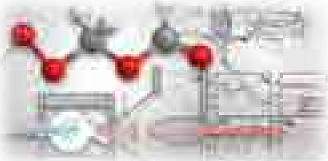
GAS PHASE CHEMICAL PHYSICS

N. Hansen *et al.*, *Combust. Flame*, **2017,** 181, 214-224 and *Proc. Combust. Inst.*, **2019,** in press

Conclusions and Outlook

“right level of detail“

five-membered rings, aliphatically bridged
PAHs, reactive side chains, ...)



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Experiments:

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- R. S. Tranter (Argonne National Laboratory)
- A. L. Kastengren (Argonne National Laboratory)

Theory and Modeling:

- A. W. Jasper (Argonne National Laboratory)
- S. J. Klippenstein (Argonne National Laboratory)
- F. Mauss (Cottbus, Germany)

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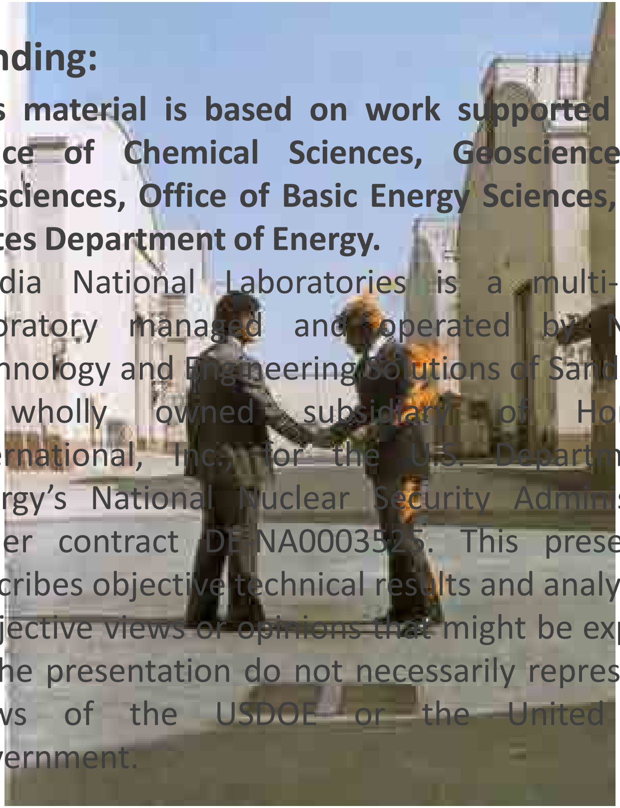


ISF - LAMINAR FLAME SECTION

ISF - LAMINAR FLAME SECTION

Outline:

Introduction

Focus topic(s)

Contributions & Discussion

Final Remarks

INTRODUCTION

ISF - PAST MEETINGS

LARGE NUMBER OF CONTRIBUTIONS

Many target flames - Many modelling results

PROs

Sharing and discuss data

Individuating common lines of research

Define the standards for a «useful» experiment/modelling

Open collaborations

CONs

Too many operative conditions?

Too many aspects to focus on?

Lack of consensus on key topics

Lack of clear outcome from the community

ISF - LAMINAR FLAME SECTION

INTRODUCTION

ISF - THIS MEETINGS

After an internal (***committee***) and external (***telecon and survey***) evaluation, a topic was identified as fundamental to advance knowledge

INCEPTION

PRO

Establishing consensus on this topic can advance the reliability and the performance of the models and guide future experiments

CON

Focusing on a single topic can diminish the general mission of the workshop

INCEPTION

DEFINITION (?)

THE PROCESS THAT LEADS FROM GAS PHASE COMPOUNDS TO A CONDENSED PHASE, i.e., A THREE DIMENSIONAL STUCTURE

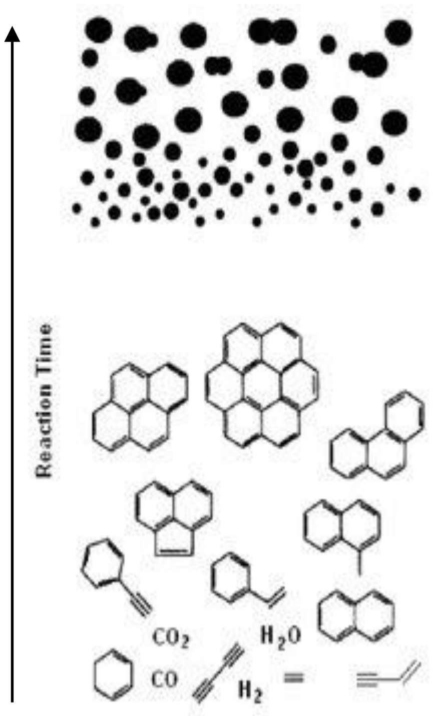
The definition has to be as broad as possible in order to not «restrict» any possibility of mechanism

Let's start from what we know and move to what we don't know

ISF – LAMINAR FLAME SECTION

WHY INCEPTION?

After Round Table 1994 in Heidelberg



General consensus on the «top» of the figure

(shape, distribution, size, H/C, reactivity

and name *SOOT*)

INCEPTION WAS ALREADY A «***DARK REGION***[1]»

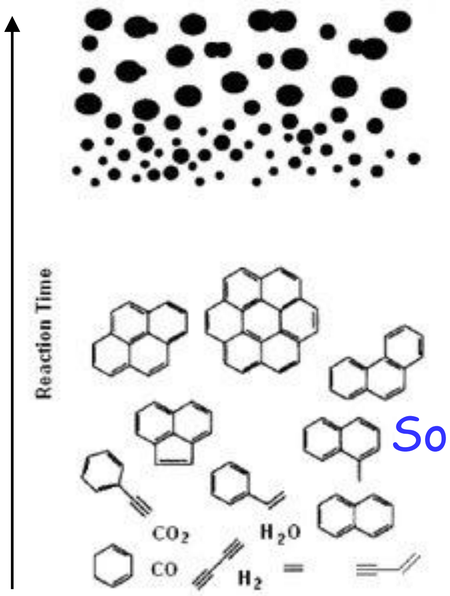
General consensus on the «bottom» of the figure

(main oxidation, formation of PAH – HACA+RFSR)

[1]Vander Wal, R. L. Symp. Int. Comb. (26) 1996

WHY INCEPTION?

After Round Table 1994 in Heidelberg



The community «felt» that in this «dark region» something was different:

The **existence** of «particles» of few nanometers was indipendently discovered by ***Dobbins***[1] (Brown Uni) and ***D'Alessio***[2] (Naples Uni) in 1991

Many definitions:

Soot precursors Precursor Nanoparticles Nanodroplets

Incipient Soot White soot Soot nuclei

Precursors Nanoparticles (PNPs) NanoOrganicCarbon-(NOC)

Condensed Phase Nanostructures-(CPN)

and also just SOOT

[1] Dobbins Subramanisivam in Soot Formation in Combustion 1994

[2] D'Anna D'Alessio Minutolo in Soot Formation in Combustion 1994

WHY ALL THESE DEFINITIONS?

These particles were clearly «fresh»!

Closest as possible to the «first» particle that could be hypothesized

NUCLEATED PARTICLES DEFINITION

NUCLEATED PARTICLES PROPERTIES[1,2]

Size distribution

Optical properties

H/C

Physico-chemical properties

INCEPTION MECHANISM[1,2]

Growth of "two-dimensional" PAHs into ***curved***

Physical PAH coalescence into ***stacked clusters***

coalescence of PAHs into ***cross-linked*** three-dimensional structures

[1]D'Anna, A. (2009). PROCI 32 [2]Wang, H. (2011). PROCI 33

ISF – LAMINAR FLAME SECTION

MANY DEFINITIONS – LOT OF WORK

	GROUPS CONTRIBUTING TO THIS FIELD
Optical properties (extinction, Scattering, LIF, LII, RAMAN, photoionization, Band gap)	D'Alessio-D'Anna, Dobbins, J.H. Miller, Roth, Bockhorn, Ossler, Desgroux, Michelsen, Schulz, K.A. Thomson, Kohse-Höinghaus, Vander Wal, Wang, Liu, Smallwood
Particle size distribution	Wang, D'Alessio-D'Anna, Grotheer, Kohse-Höinghaus, Maricq, Kohse-Höinghaus
TEM and AFM images	Wang, D'Alessio-D'Anna, Dobbins, Vander Wal, M.J. Thomson, Kraft
Chemical properties (H/C, reactivity, solubility in water and organic solvents)	Ciajolo, Homman, Wagner, Howard, Mulholland, M.J. Thomson, Wang, Kohse-Höinghaus
Physical properties (density, emissivity, coagulation efficiency)	Wang, Kohse-Höinghaus, Desgroux, M.J. Thomson, D'Alessio-D'Anna, Dobbins,
Advanced Modelling (MOM, MC, Sectional Method, AMPI, MD)	Frenklach, Violi, Kraft, D'Anna, Thomson, J.H. Miller, Ranzi-Faravelli, Howard, Blanquart, Pitsch, Lindstedt, Smooke

ISF – LAMINAR FLAME SECTION

MANY DEFINITIONS – LOT OF WORK

NUCLEATED PARTICLES	SOOT
Condensed phase physic state ("solid" is not appropriate for these entities)	"solid" is appropriate for these entities
Able to splash on a surface	NOT Able to splash on a surface
Hardly or not absorbing in the visible but strongly in the UV range (Eg 0.7-2.3)	Absorbing in the visible AND in the UV range (Eg 0.1:0.5)
Not having size larger than few nm (generally not larger than 3 nm)	HAVING size up to hundreds of nm
Able to fluoresce in the UV and in the Visible also with high quantum yields	NOT Able to fluoresce but easily incandescing
H/C between 0.8 and 0.3	H/C between 0.3 and 0.05
RAMAN spectra typical of amorphous carbon	RAMAN spectra typical of graphitic carbon
Partially soluble in water (and organic sovent - DCM)	NOT soluble in water
Generating hydrophilic surfaces,	Generating hydrophobic surfaces
Having a very low and size-dependent coagulation efficiency at flame Temp (10^{-3})	Having a unitary coagulation efficiency at flame Temp
Contributing for more than 90% to the total number, but negligible in mass,	Contributing for more than 90% to the total MASS, but negligible in number
Density that ranges from 1.0 to 1.4 g/cm3,	Density that ranges from 1.4 to 2.0 g/cm3,
Emissivity close to 0.5.	Emissivity close to 1

NUCLEATED PARTICLES PROPERTIES

Different properties can lead the individuation of different

INCEPTION MECHANISMS?

Condensed phase physic state

Not solid – more liquid-like (Splash)

→ Inception has to pass through disordered/loose/non-cristalline structure

Raman of amorphous carbon

LIF most centered in the UV

→ Main components unlikely to be very large PAHs (not larger than pyrene?)

H/C between 0.8 and 0.3

NUCLEATED PARTICLES PROPERTIES

Different properties can lead the individuation of different

INCEPTION MECHANISMS?

Can the properties analysis help to rule out or reduce the role of certain pathways?

Pyrene dimerization → **Would lead immediately to rigid/ordered structures**

LIF signal will be far in the visible (red-shift)

H/C will be closer to soot (dehydrogenation and growth)

The fact that many MD simulation found not feasible this pathway is a logic consequence and a support to all the other experimental measurements

CONTRIBUTIONS FROM THE COMMUNITY

LILLE GROUP - EXPERIMENTAL

MOTIVATION: Origin of Visible LIF in Diffusion Flames

Unexplained Visible Fluorescence Emission Band in Sooting Flames

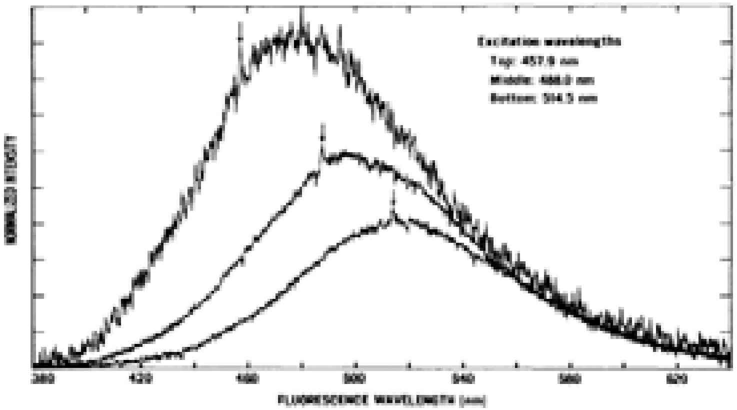


Fig. 3. Unstructured fluorescence observed using the slot burner for three excitation wavelengths (denoted by an arrow on each spectrum). The spectra have been normalized for the laser intensity; the actual powers at each wavelength were 1.70 W at 514.5 nm, 1.73 W at 488.0 nm, and 0.23 W at 457.9 nm. The cold flow velocities were 17 cm/s for methane and 24 cm/s for air.

J. Houston Miller et al., Comb. Flame ***1982***

- **Up to now:** No clear explanation (Large PAHs? Hot Bands of PAHs?)
- **Other considered possibilities:** Dimers of moderate-sized PAHs (Sirignano, Houston Miller…)
- **Problem:** The formation of such dimers is not thermodynamically favored at typical flame temperature

Aim of this work

Provide explanations for these large unstructured fluorescence emission bands observed for a long time in sooting flames

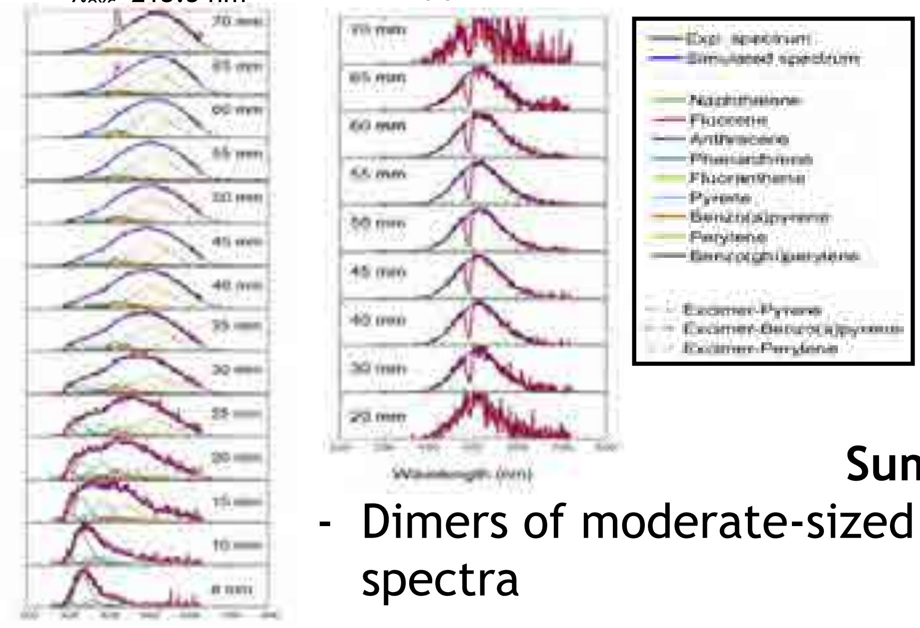
ISF – LAMINAR FLAME SECTION

LILLE GROUP – EXPERIMENTAL

MOTIVATION: Origin of Visible LIF in Diffusion Flames

Analysis of the Fluorescence Emission Spectra with the Simulation Code

λ_{exc}=213.5 nm λ_{exc}=488 nm



Wavelength (nm)

Analysis:

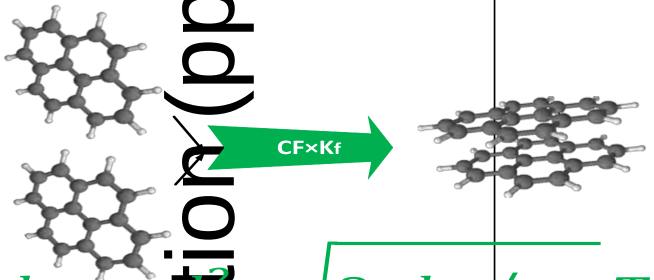
- **UV part** of the fluorescence spectra
  - Well reproduced by **PAHs fluorescence contributions**
- **Visible part** of the fluorescence spectra:
  - **Cannot correspond to PAH fluorescence**
    No PAH can provide intense fluorescence signals above 450 nm
    No PAH can be excited at 488 nm
  - Very well reproduced by the fluorescence contributions of **dimers of moderate-sized PAHs** whatever the excitation wavelength

Summarizing remarks:

- Dimers of moderate-sized PAHs account for the visible part of these spectra
- Is dimer formation the key step of nucleation (meaning kinetic over thermodynamic)?

ETH – U.Toronto- PTL – NSERC – MODELLING

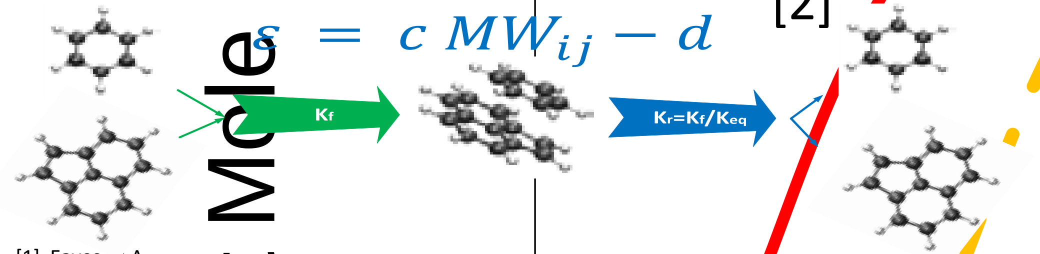
MOTIVATION: Feasibility of PAH dimerization

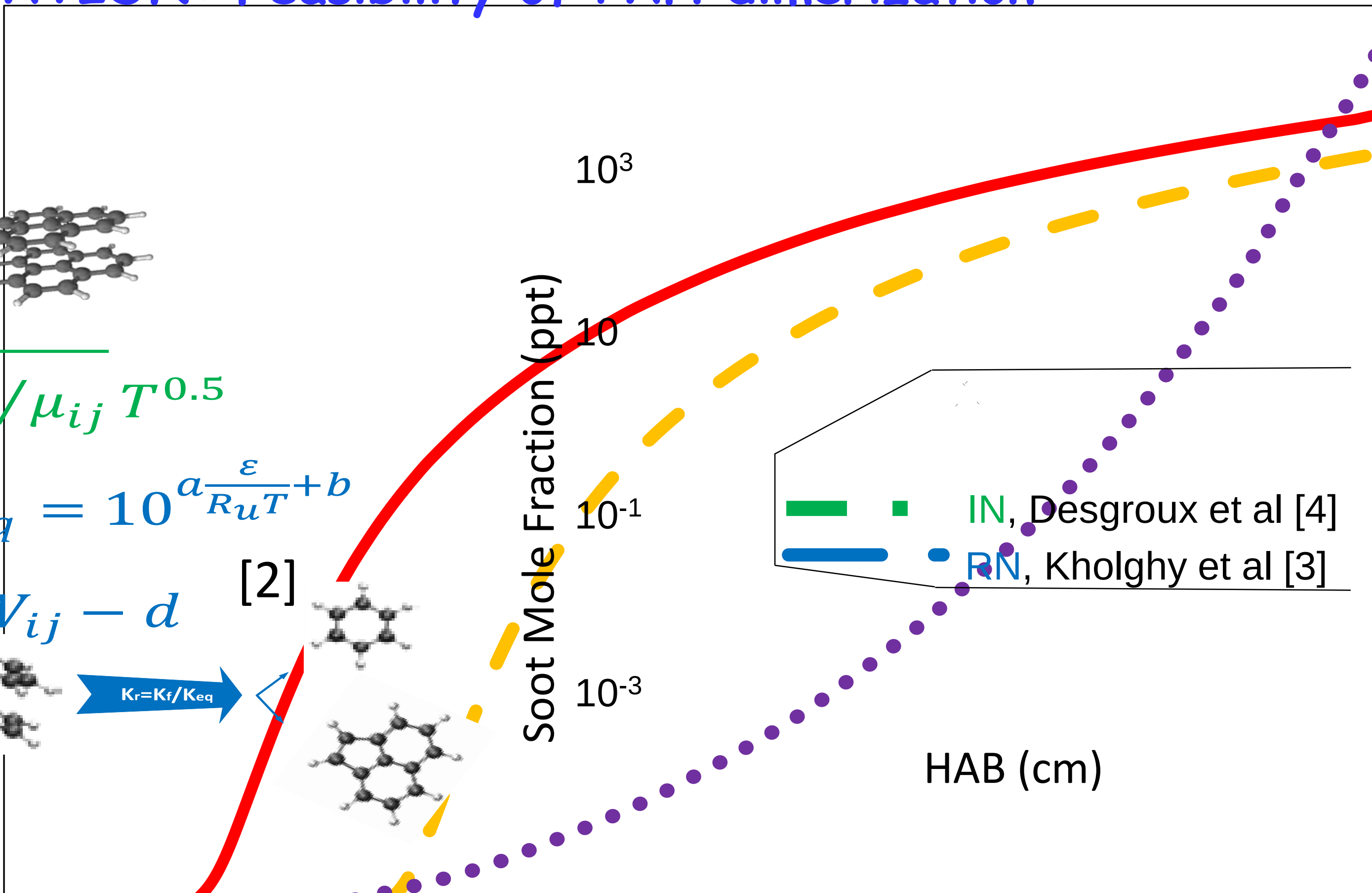


$$k_f \approx d_{ij}^2 \sqrt{8\pi k_B/\mu_{ij}}\, T^{0.5}$$

$$k_r = \frac{k_f}{k_{eq}} \qquad k_{eq} = 10^{a\frac{\varepsilon}{R_u T}+b}$$

$$\varepsilon = c\, MW_{ij} - d$$



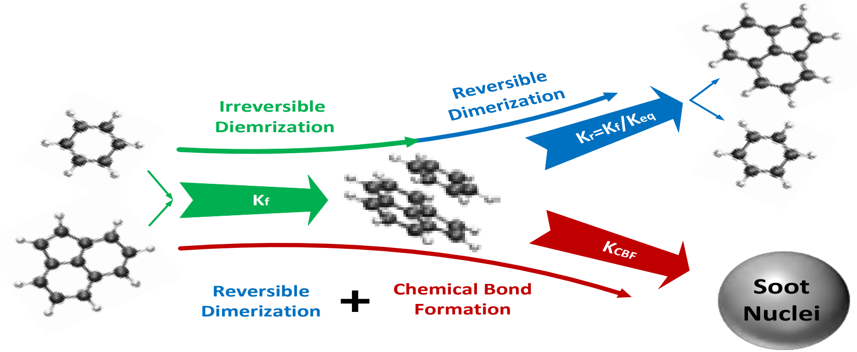


[1] Eaves. N A,
[2] Miller. H J, /

ETH - U.Toronto- PTL - NSERC - MODELLING

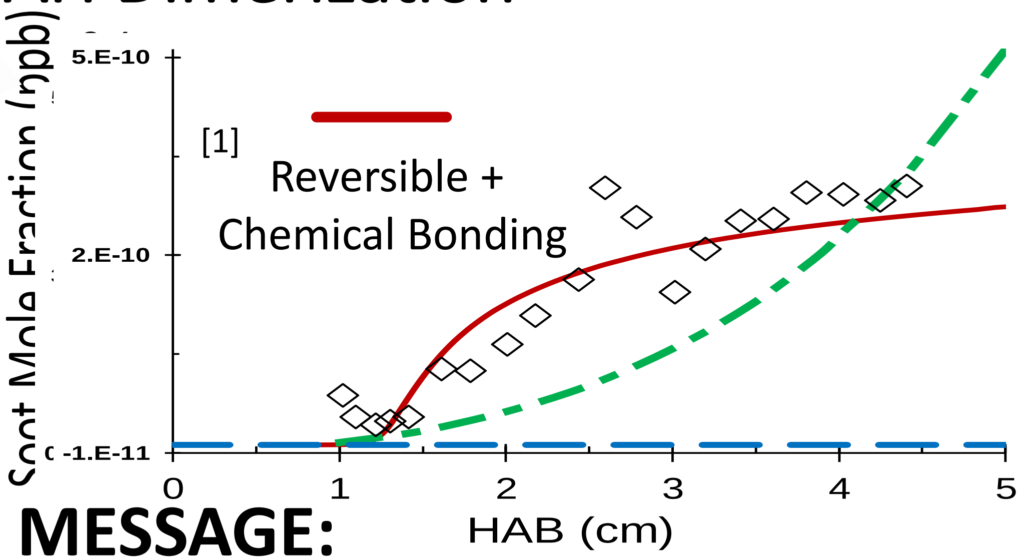
MOTIVATION: Feasibility of PAH dimerization

Reactive PAH Dimerization



$$k_{CBF} \approx T^{0.5} e^{(-E_a/R_u T)}$$

$$E_a \approx 25\ kcal/mole$$



FINAL MESSAGE:

The ***formation of chemical bond after the collision of gas phase PAH*** drastically changes the overall nucleation rate

The nucleation rate influences the ***shape of the particle profile*** and the final concentration in the investigated conditions

ISF - LAMINAR FLAME SECTION
U.Toronto - MODELLING

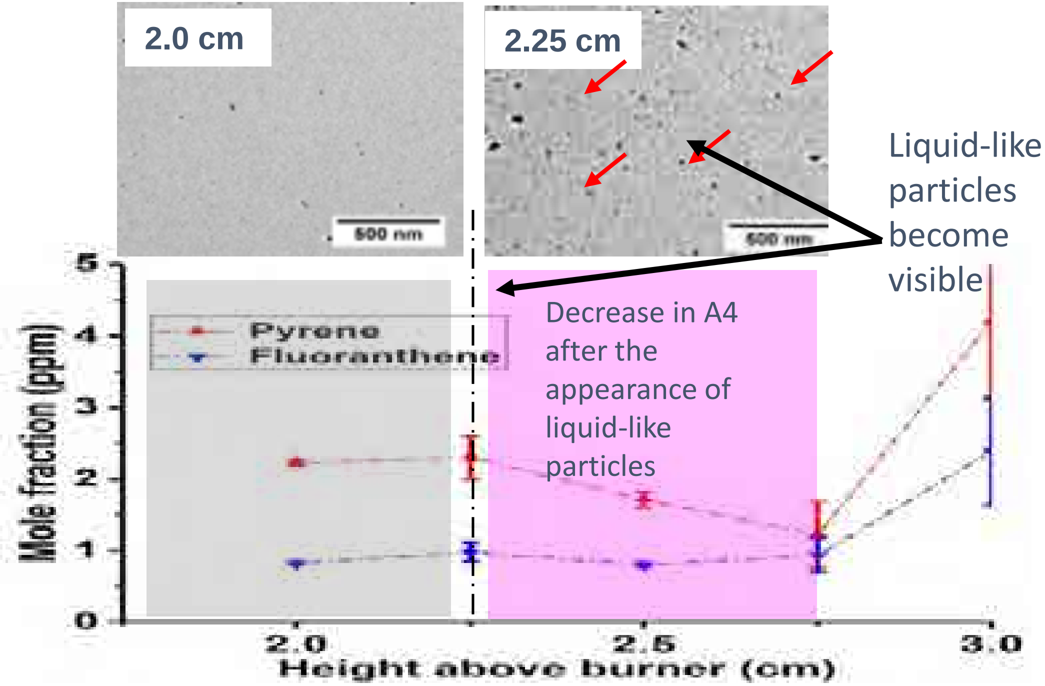
MOTIVATION: Composition and nature of first Particle

First particles are not solid (liquid-like)

n-dodecane=3%
methane=97%

TEM

GC/MS



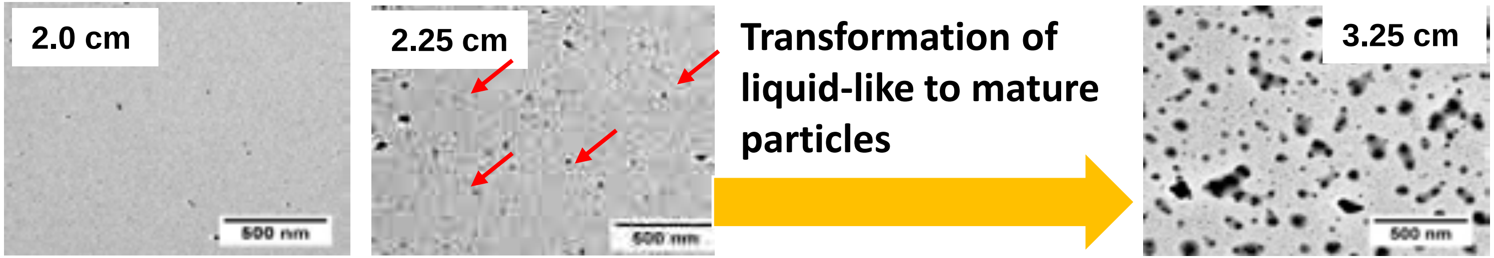
No larger PAHs than Pyrene were observed

ISF – LAMINAR FLAME SECTION

U.Toronto – MODELLING

MOTIVATION: Composition and nature of first particle

n-dodecane=3%
methane=97%



- **Liquid-like particles prevents PAH growth**
- **Mass spectra of liquid particles shows species larger than A4[1]**
  - *Species rearranging within the particles?*
  - *Higher masses represent chemically bonded dimers/ PAH radicals?*
  - *Large PAHs behaving as intermediates?*
- **A4 rises rapidly as liquid particles transform to mature soot**
  - *Large PAHs released from the particles surface?*
  - *Growth in gaseous phase resumes as particles mature?*

Ryerson – U. Michigan – U. Windsor – MODELLING

MOTIVATION: the role of aliphatic in the Inception process

- Literature suggests that for premixed flames [1, 2]:
    - (1) Nascent soot can be rich in aliphatics
    - (2) Soot mass growth can occur without the presence of gas-phase hydrogen atoms
- Neither of these observations can be explained by current models that rely on PAH-based inception
- Soot growth in the absence of hydrogen atoms indicates another mechanism possibly involving aliphatics aside from the HACA mechanism

[1] Wang, H. *Proceedings of the Combustion Institute, 33*, 41-67, 2011.
[2] Öktem, Berk, et al. *Combustion and Flame*, *142*, 364-373, 2005.

Ryerson – U. Michigan – U. Windsor - MODELLING

MOTIVATION: the role of aliphatic in the Inception process

How do aliphatics become part of the soot particle?

- Directly through aliphatic/soot interaction?

- As an aliphatic chain on a PAH which either nucleates or condenses?

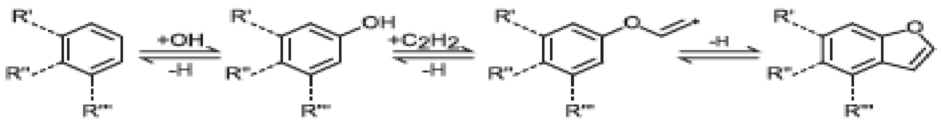
- A different mechanism?

- Ongoing work focuses on combining MD with CFD efforts to begin to address this knowledge gap

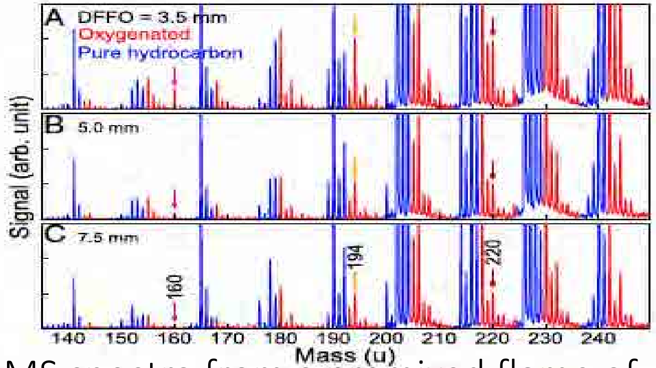
Other possible parameters influencing Inception process

Formation of *oxy-PAHs*

Atomistic simulations and experiments identify presence of oxygenated polycyclic aromatic compounds in flames of hydrocarbons.



Reaction sequence leading to the formation of a furan group.



AMS spectra from a premixed flame of ethylene. Red peaks correspond to oxygenated species.

<u>DIFFERENT STICKING EFFICIENCY?</u>

<u>DIFFERENT REACTIVITY?</u>

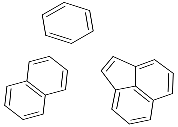
Johanson, Dillstrom, Monti, El Gabaly, Campbell, Schrader, Popolan, Henderson, Wilson, Violi, Michelsen, PNAS 1604772113
Elvati, Violi Fuel 222, 307 (2018)

NAPLES Group- EXPERIMENTAL & MODELLING

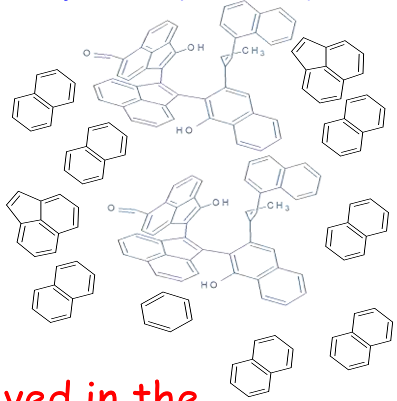
MOTIVATION: Predicting particle properties by Inception mechanism

GAS PHASE | **CONDENSED PHASE**

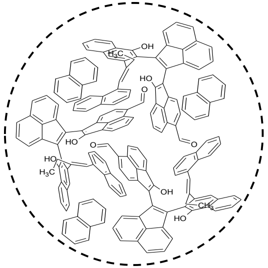
PAH FORMATION



LARGE MOLECULES FORMATION



INCEPTION



PARTICLE EVOLUTION INCREASES:

Dimer formation

Π- Π dimer

Cross-linking

The main species involved in the inception process would be ***small PAH 2-4 rings linked by aliphatic bonds***, with the occasional presence of ***aliphatic groups (methyl) and oxygen***.

This first «particle» would be:

UV absorbing and fluorescing (as the constituting PAHs but with higher q.y.)

Liquid-like or non solid (no lattice structure)

H/C similar to constituting PAH (almost a polymer)

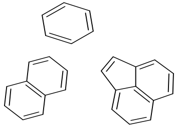
ISF – LAMINAR FLAME SECTION

NAPLES Group- EXPERIMENTAL & MODELLING

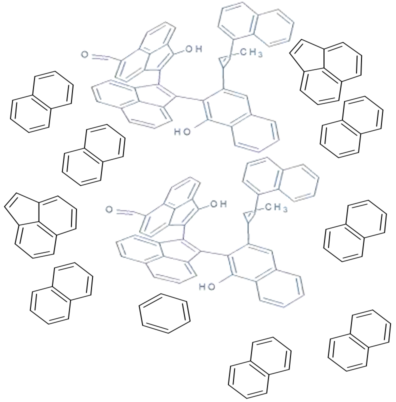
MOTIVATION: Predicting particle properties by Inception mechanism

We put this phenomelogical model into ***MULTI SECTIONAL*** approach

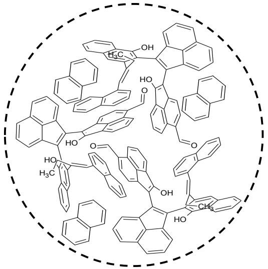
PAH FORMATION



LARGE MOLECULES FORMATION



INCEPTION



PARTICLE EVOLUTION INCREASES:

Dimer formation

Π- Π dimer

Cross-linking

GAS PHASE

"MOLECULES"

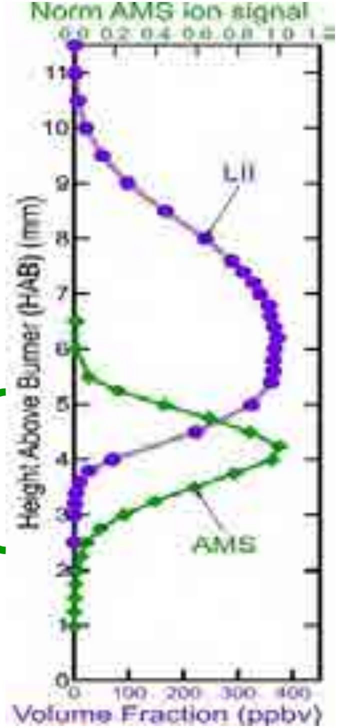
"CLUSTERS of MOLECULES" or PARTCILES

SANDIA- EXPERIMENTAL

MOTIVATION: Assessing features of first Particles

LII signal from mature soot

AMS total ion signal indicates incipient-particle formation



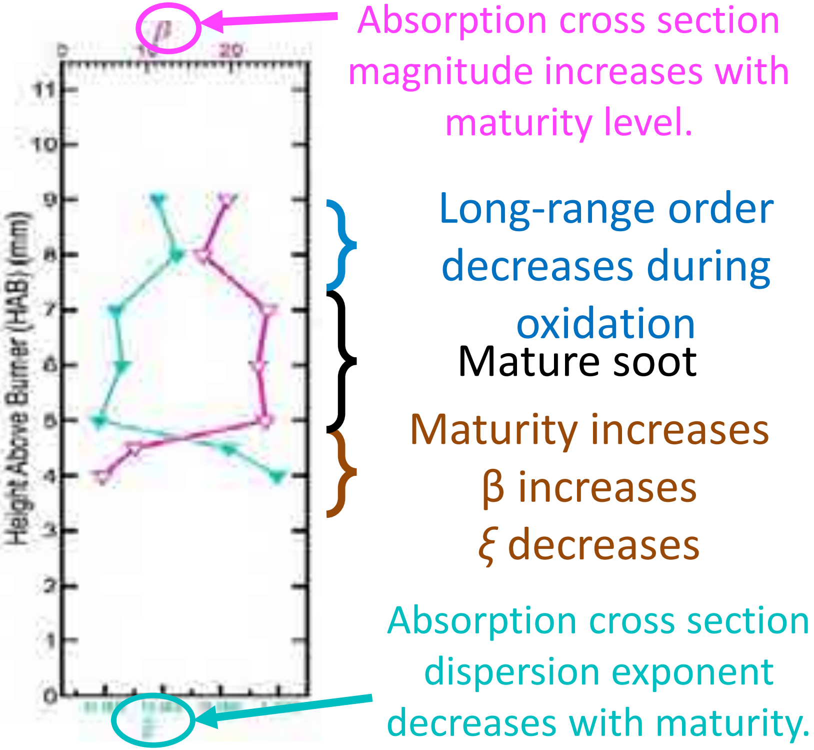
- Aerosol mass spectrometry (AMS) signal can only be observed if there are particles and semi-volatile species to vaporize.
- AMS total ion signal gives indication of incipient particle formation and availability of hydrocarbons for growth.
- These incipient particles are not observable with LII.

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

SANDIA- EXPERIMENTAL

MOTIVATION: Assessing features of first Particles

- Particle mature very quickly
- XPS indicates that surface matures more slowly than bulk.
- Surface growth may keep particle from maturing at the surface.



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

SUMMARY OF INFORMATION AND OPEN QUESTIONS

1. SHOULD A PHENOMENOLOGICAL MODEL COME BEFORE AMATHEMATICAL ONE?
2. WHICH ARE THE MAIN OBSTACLES TO A CORRECT PHENOMENOLOGICAL MODEL?
3. IS IT TIME TO FOCUS LESS ON MATCHING EXPERIMENTAL DATA AND MORE ON TRYING TO IMAGINE/PREDICT/MODEL THE TRUE PHYSICAL CHARACTERISTICS OF THE FIRST PARTICLES?

SUMMARY OF INFORMATION AND OPEN QUESTIONS

1. FORMATION OF DIMER IS EVIDENT: IS DIMERIZATION THE INCEPTION PROCESS OR THE EFFECT OF (RAPID) PARTICLE EVOLUTION?
2. PAHs INVOLVED IN INCEPTION PROCESS SEEM TO BE NO LARGER THAN 4-5 RINGS (LOTS OF 2-3 RINGS): HOW DO SUCH SMALL PAH FORM A CONDENSED PHASE STRUCUTRE?
3. HOW SHOULD ALIPHATIC AND OXY-PAHs PARTICIPATE IN INCEPTION?
4. WHAT WE CAN DO TO GET BETTER CONDITIONS (FLAMES) WHERE THESE PROCESSES ARE STRESSED/EVIDENT?

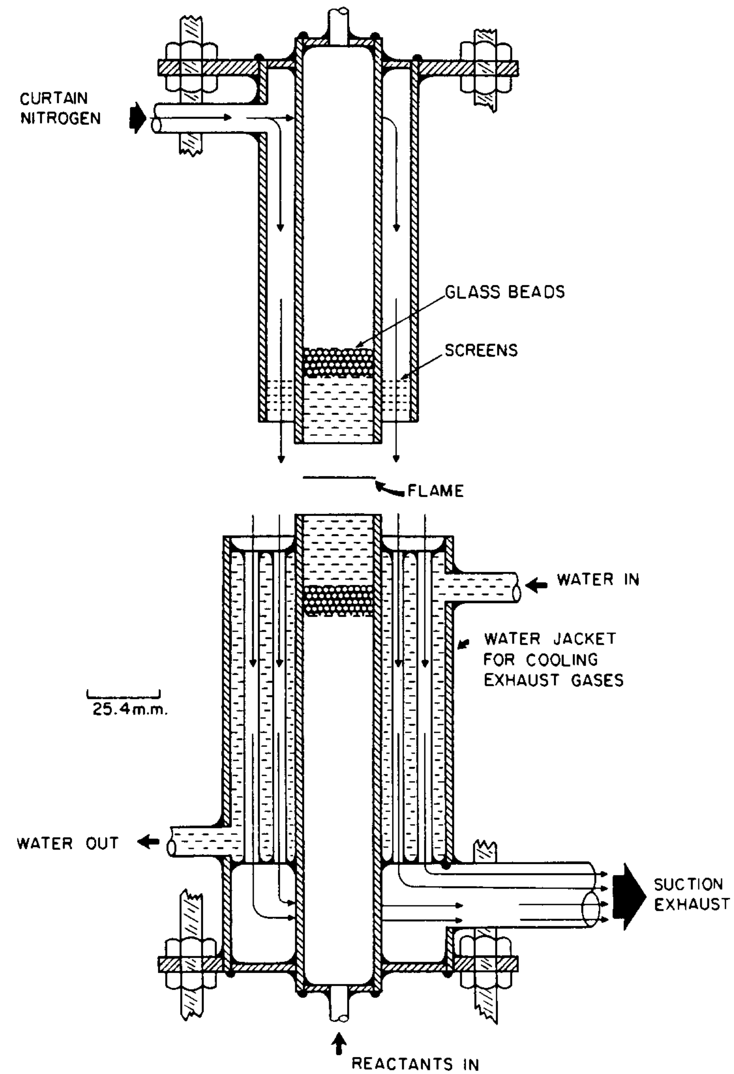
Counterflow burner

An effective tool to study soot formation and growth in flames?

Prepared by F. Bisetti (UT Austin)

with contributions from

Yale U, U Virginia, RWTH Aachen & U Adelaide

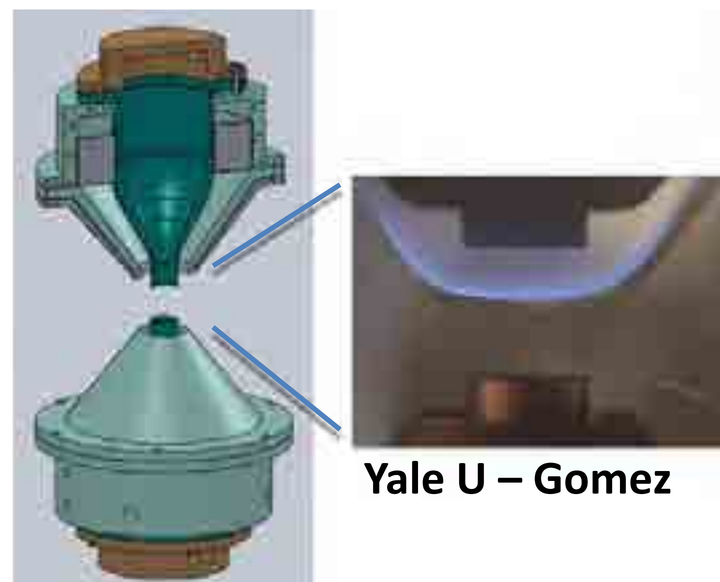


from Puri & Seshadri CNF 65 (1986)

Counterflow burner: 3 contributions

- We received contributions from 3 groups that conduct experiments
  - Yale University (Gomez)
  - U Virginia (Chelliah)
  - RWTH Aachen/U Adelaide (Pitsch/Medwell)
- Two questions
  - Strengths/Challenges of CF for soot studies?
  - What data are available?

U Virginia – Chelliah

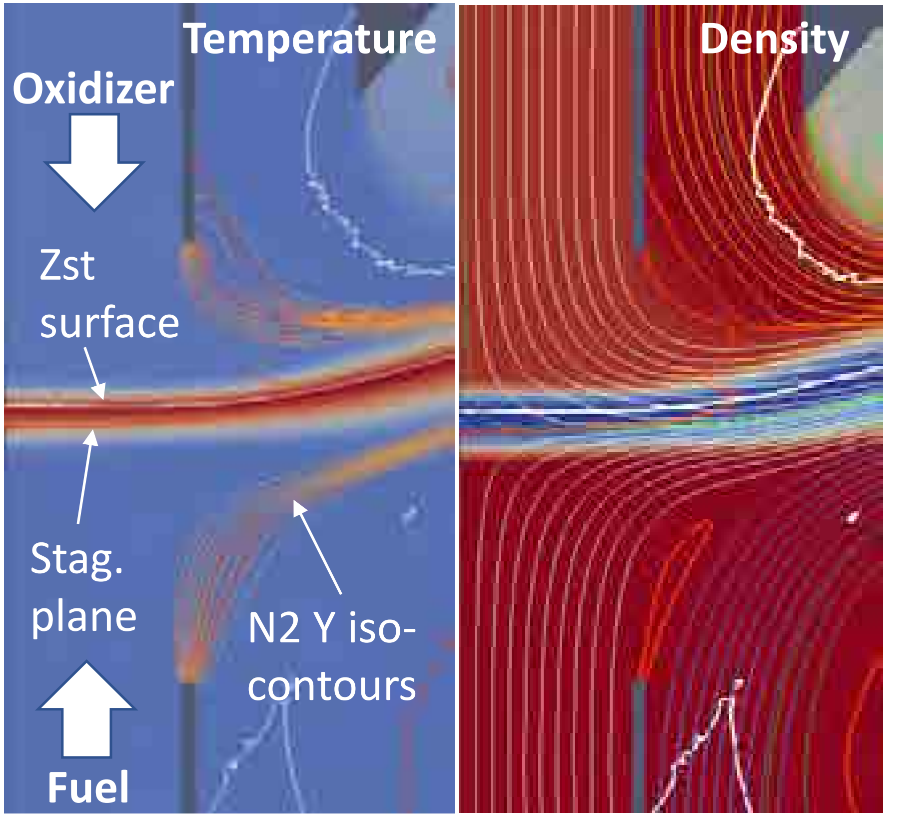


Counterflow: strengths

STRENGHTS

- No heat losses to walls
- Buoyancy-driven instabilities may be suppressed
- Direct control on mixing layer & soot yield
  - Strain controls soot inception rates
  - Dilution controls soot yield
- One-dimensional modeling applies
  - …but require boundary conditions

Reynolds nr = 600 & Richardson nr = 1

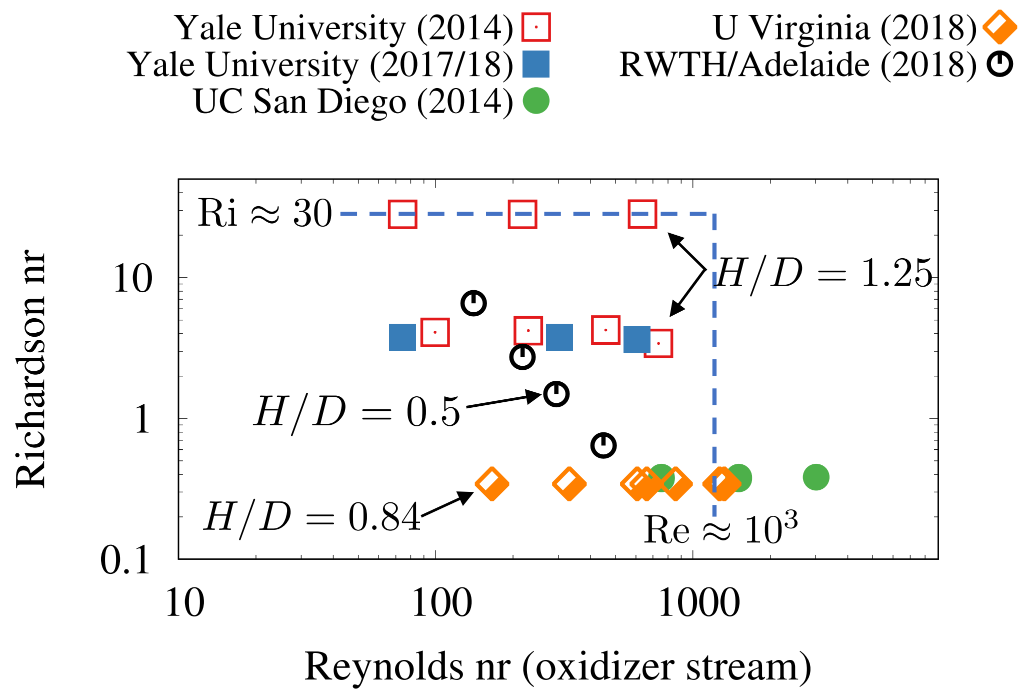


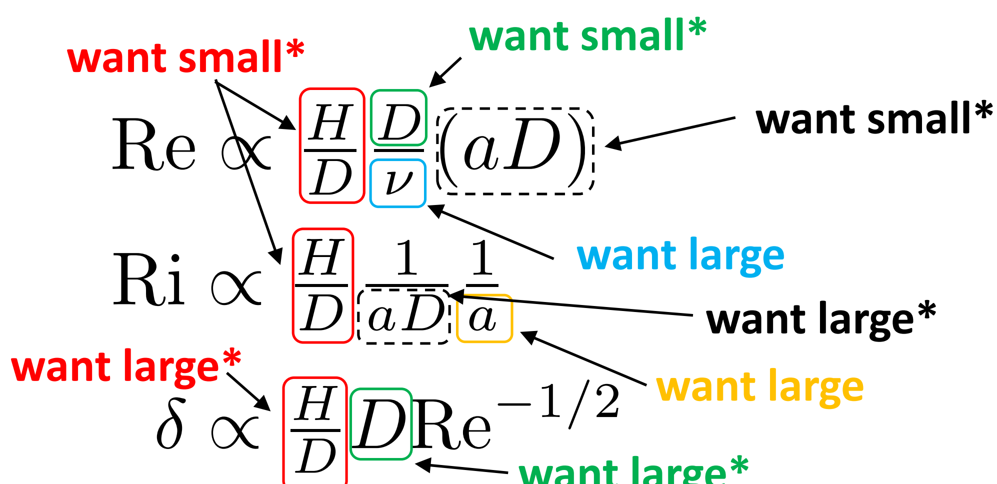
Axisymmetric simulations by UT Austin (Bisetti) & Politecnico di Milano (Cuoci) for the Yale U burner (Gomez) at 8 atm.

Counterflow: challenges

CHALLENGES

- Need to keep Reynolds and Richardson nr "small"
- Hydrodynamic instabilities (of various kinds) are observed as Reynolds & Richardson nrs increase
- As pressure increases
  - The set of suitable flow configurations and burner designs shrinks
  - I.e. burner and flame (mixing layer) become "small"





Yale University (A. Gomez)

- Non-premixed and partially premixed flames
- Various fuels & doped fuels
- Pressures from 1 to 25 atm
- Measurements/Diagnostics
  - Quartz probe sampling followed by GC-MS
  - Thermocouples and thin-filament pyrometry
  - Multicolor pyrometry (soot volume fraction)
- **Focus on soot nucleation/inception with aim of kinetics model development**
- Large number of publications (2012-2018) provide data, experimental details and validation of sampling technique

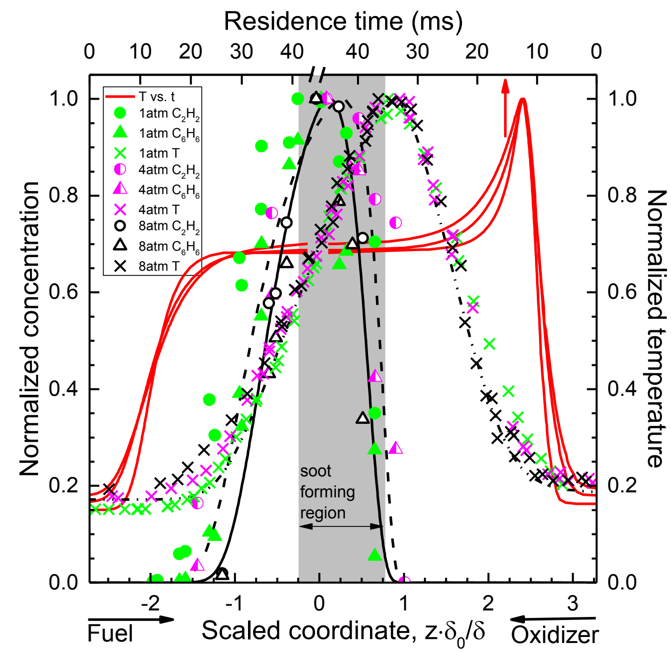
Yale University (A. Gomez)

Ethylene/oxygen with N2 and HE dilution

Stoichiometric mixture fraction Z_{st}=0.408				
P [MPa]	T_{max} [K]	Strain rate [s^{-1}]	Measurements performed: Gas phase up to 3-rings	Measurements performed: Soot volume fraction
0.1	1712	57	[1]	N/A
0.2	1790	57	[1]	N/A
0.4	1826	57	[1]	N/A
0.8	1868	57	[1]	N/A
0.29	1563	18.4	[2]	N/A
0.85	1600	18.4	[1]	N/A
2.5	1615	18.4	[1,2]	N/A

[1] L. Figura, A. Gomez, CNF 161 (2014) 1587–1603.
[2] L. Figura, F. Carbone, A. Gomez, PCI 35 (2015) 1871–1878.
[3] F. Carbone, K. Gleason, A. Gomez, PCI 36 (2017) 1395–1402.
[4] K. Gleason, F. Carbone, A. Gomez, CNF 192 (2018) 283–294.
[5] K. Gleason, F. Carbone, A. Gomez, PCI 37 (2019).

$$D \approx 6.5 \text{ mm}$$
$$H \approx 8 \text{ mm}$$
$$U \approx 20 \text{ cm/s}$$



Ethylene/oxygen with N2

Stoichiometric mixture fraction Z_{st}=0.183				
P [MPa]	T_{max} [K]	Strain rate [s^{-1}]	Measurements performed: Gas phase up to 3-rings	Measurements performed: Soot volume fraction*
0.1	1984	50	[3]	[4]
0.4	1787	50	[3]	[5]
0.8	1656	50	[3]	[5]

*Includes additional measurements at different T_{max}

University of Virginia (H. Chelliah)

- Ethylene/oxygen flames with nitrogen and helium dilution
- Pressures from 1 to 30 atm
- Laser-based m
  - PIV for flow f
  - LII for soot (v dimensional model paran
- Focus on scali pressure of int
- **Broad range o suppression o**

Soot Nucleation Limits of Ethylene-Oxygen-Nitrogen-Helium Non-premixed Laminar Counterflow Flames up to 30 atm Pressure

Harsha Chelliah
University of Virginia

Undiluted (up to 4 atm) and fixed global strain rate of 500 s^{-1}

p = 1 atm

p = 2 atm

p = 4 atm

Some Key Features:

- Nozzle diameter of 6.5 mm with nozzle separation distance of 5.45 mm
- Momenta is balanced for every case considered
  - with oxidizer side velocity (including the velocity gradient at the nozz

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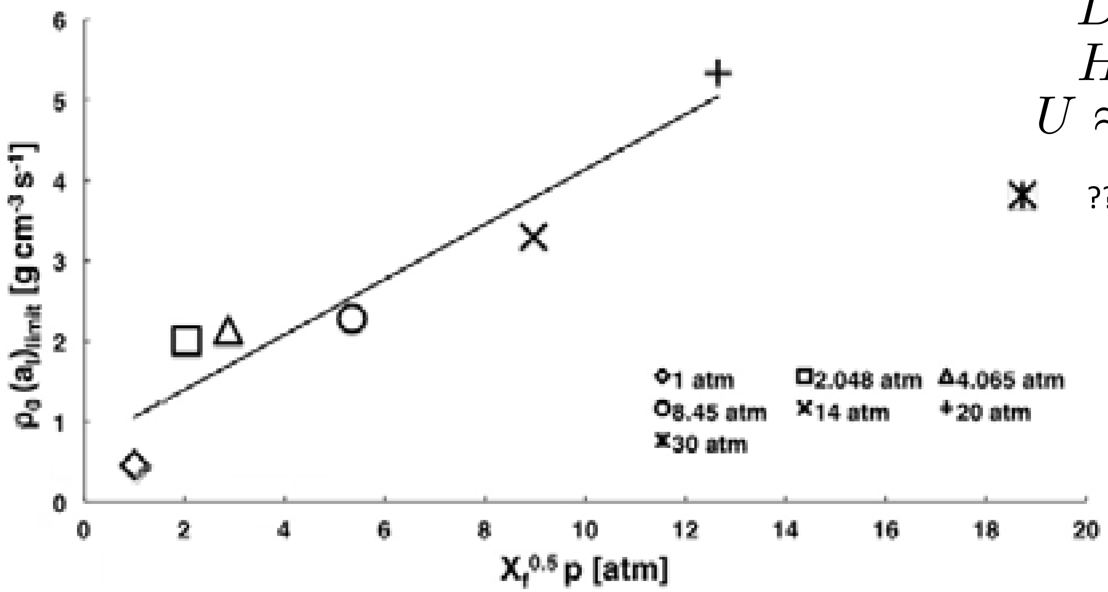
Effect of Pressure on Soot Nucleation Limit

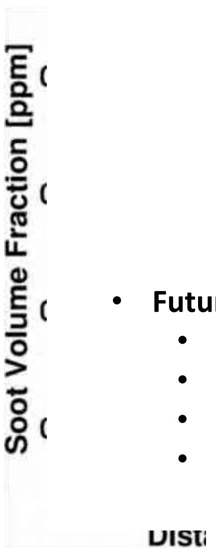
- Comparison with the linear correlation proposed by Du, Wang, Law (1998)



$$D = 6.5 \text{ mm}$$
$$H = 5.5 \text{ mm}$$
$$U \approx 40 - 80 \text{ cm/s}$$

???

- **Future work:**
  - Repeat 30 atm and other pressures
  - Focus on oxidation, growth?
  - Gas-phase temperature and species measurements with CARS, explore excitation wave lengt m; …
  - Fixed mixture fraction for the entire pressure range, other fuels, ….



Soot volume fraction (
flame at 20 atm and lc

0 2 4 6 8 10 12 14 16

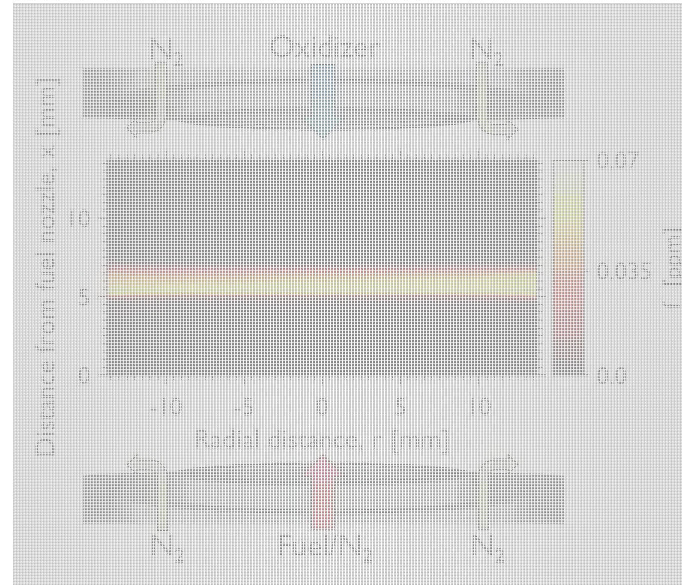
$X_f^{0.5}$ p [atm]

- *Sarnacki and (*

- **Future work:**
  - Repeat 30 atm and other pressures

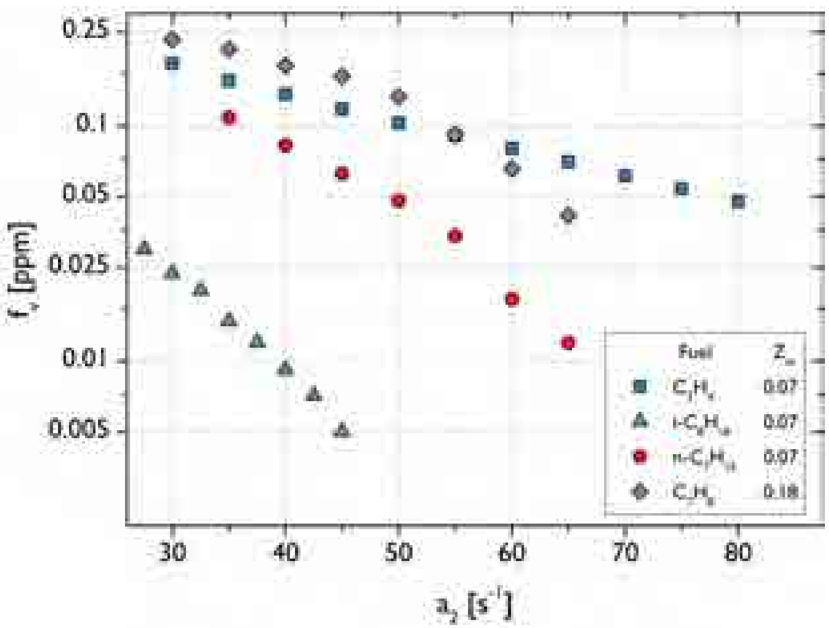
RWTH Aachen & U Adelaide (Pitsch/Medwell)

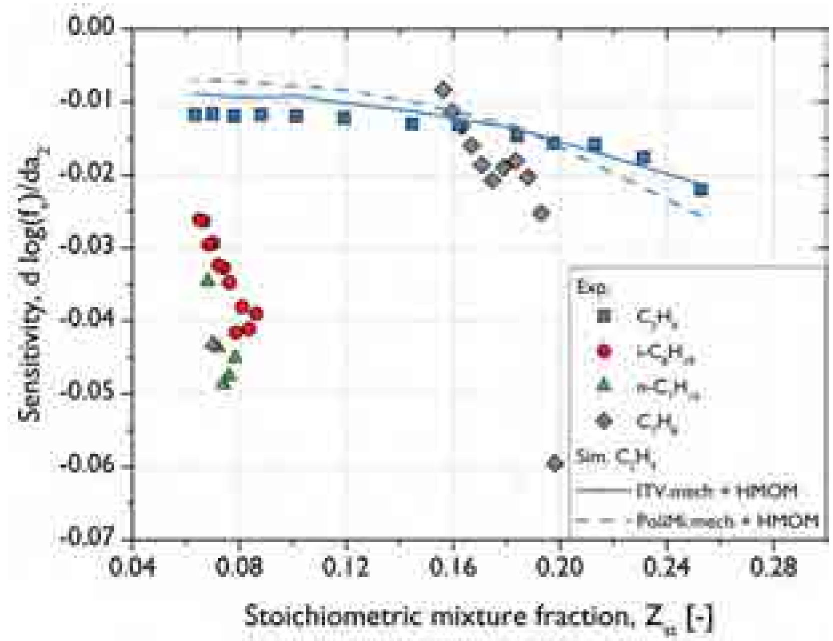
- Non-premixed flames
- <u>Atmospheric pressure</u>
- Various gaseous and liquid fuels (nitrogen dilution)
  - Ethylene, iso-octane, toluene, and n-heptane
- Varying dilution and strain rate cases
- Soot volume fraction from Laser induced incandescence (LII) at 1064 nm
- **Focus on strain rate effects on soot formation and comparison to models**



$D = 2.7$ cm
$H = 1.35$ cm
$U \approx 10 - 30$ cm/s

RWTH Aachen & U Adelaide (Pitsch/Medwell)





- As strain rate increases, soot decreases with significant dependence on <u>fuel</u> and <u>stoichiometry</u>
- Large sensitivity of soot to mixing can be exploited for model validation (precursor chemistry)

Take-away messages

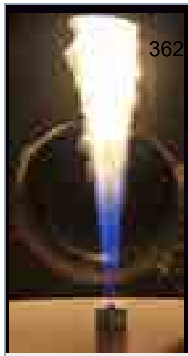
- Counterflow provides a flame without heat losses and buoyancy driven instabilities and direct control of mixing rates
- Experimental challenges exist for higher pressures (limits depend on burner and technique)

- Data are available with focus on (a) gaseous precursors; (b) soot response to strain (c) at pressures from 1 to 30 atm and various fuels/dilutions.

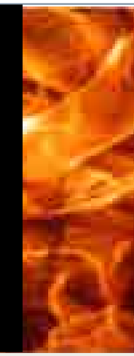
- Are there specific barriers to usage of counterflow for nucleation studies (resolution, boundary conditions)?
- Use response of soot yield to strain for precursor chemistry assessment?

From gas phase to mature soot

Entity	Clusters, dimers…	« young soot »	Mature soot
Physical state	Liquid? Condensed phase?	Solid?	Solid
Size	<5 nm	2-20 nm primary particles	2-50 nm primary particles
Fine structure	Disordered	Partially ordered/ stacked/graphitic	Polycrystalline turbostratic graphite
Experimental in situ identification	LIF, absorption?	LII, extinction	LII, extinction
density	1.1-1.3	1.3-1.8	1.8-2.1
C/H	1.5-2.5	2.5-10	10-20
Optical properties	Absorb in the UV and the visible but not in the IR	Absorb continuously from UV to IR E(m) lower than from mature soot	Absorb continuously from UV to IR
Experimental ex situ identification	LIF, Absorption, AFM, AMS	SMPS, TEM, HIM, AFM…	SMPS, TEM, HIM, AFM…
Proposed terminologies: which one?	SOOT (without any distinction from the first condensed entities to mature soot)		
	Clusters? Incipient particles? Incipient soot particles	Young soot Partially graphitized soot	Mature soot Graphitized soot



Welcome



ISF-4 Closing comments

Fourth International Sooting Flame (ISF) Workshop

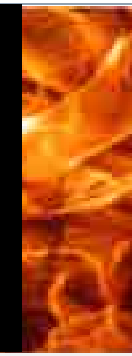
Friday July 27th – Saturday July 28th, 2018

Dublin, Ireland

www.adelaide.edu.au/cet/isfworkshop

ISF Workshop

Thank you!



Organising Committee

Prof Gus Nathan
Prof Bassam Dally
Prof Murray Thomson
Prof Heinz Pitsch
Dr Chris Shaddix
Prof Hai Wang
Dr Klaus-Peter Geigle

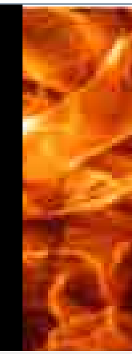
Scientific Advisory Committee

Prof Ömer Gülder
Prof Andrea D'Anna
Prof Pascalle Desgroux
Prof. Bill Roberts
Dr Hope Michelsen
Prof Henning Bockhorn
Prof Mitch Smooke
Dr Meredith Colket
Prof Peter Lindstedt
Prof Dan Haworth

Program Leaders and Co-leaders

Laminar Flames: Prof Guillame Blanquart, Prof Thomas Dreier, Dr Mariano Sirignano

Turbulent Flames: Prof Michael Mueller; Dr Zhiwei Sun, Prof Fabrizio Bisetti



Plans for ISF-5

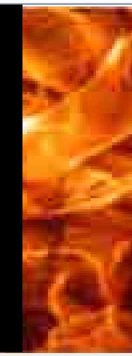
Anticipated Details:

- Fri 10 – Sat 11 July, 2020
- Coordinated with other workshops
- University of Adelaide Campus
- Joint sessions

Actions arising

- Terminology to be documented
- Release of presentations on the web
  - Please advise of any limitations

ISF Workshop



Plans for ISF-5

Targets

Preliminary targets to be released after Workshop

Updated targets to be set in mid 2019 by Joint Committee

Participation of data for ISF-5

Work through program leaders beginning NOW!

Please add data and conditions to ISF web-site

We are looking forward to welcoming you all to Adelaide 2020!