

Aromatic ring formation in opposed-flow diffusive 1,3-butadiene flames

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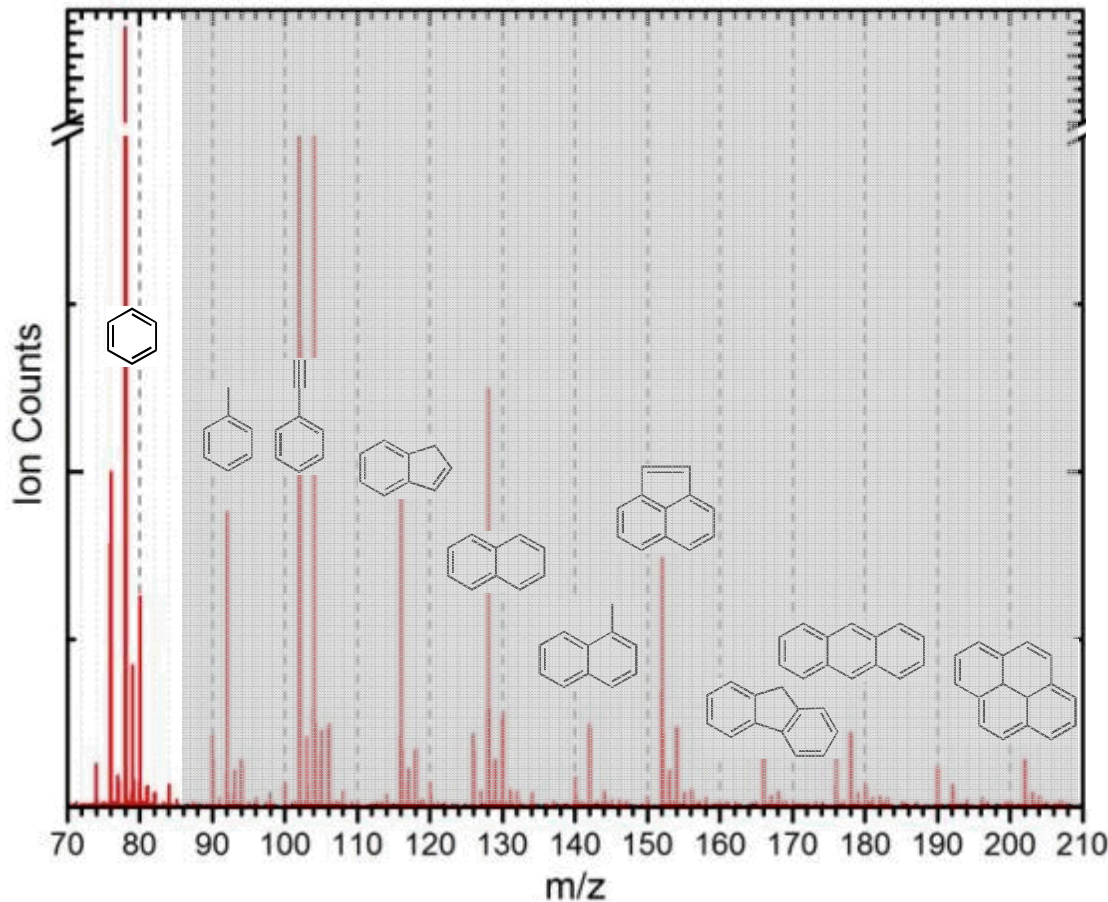


Focus of this Talk

- ❑ Obtaining detailed experimental insights in molecular-growth chemistry
- ❑ The development of a comprehensive, hierarchical model
- ❑ The formation of two-ring aromatic structures in 1,3-butadiene flames

Introduction

PAH formation – How much chemical detail is known?



White box:

- Chemical details of benzene formation are fully understood

Grey box:

- Chemical details of the formation reactions of PAHs are partially known and still evolving



Aim of this study:

- Extension of the white box up to naphthalene

Experimental and modeling study of opposed-flow diffusive 1,3-butadiene flames

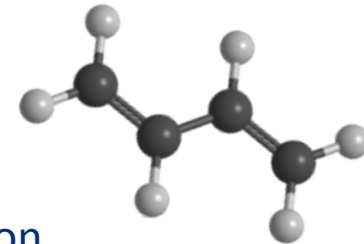
Introduction

PAH formation – How much chemical detail is known?

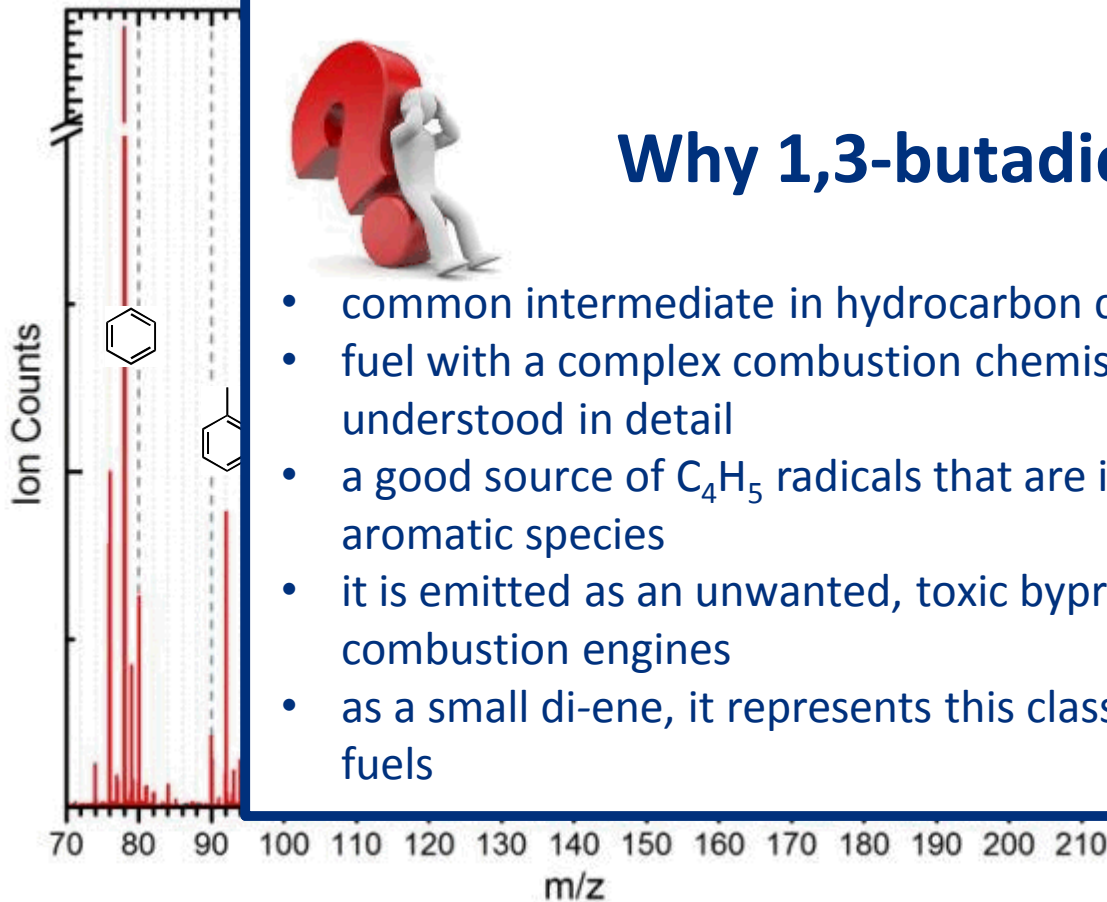
White box:



Why 1,3-butadiene?



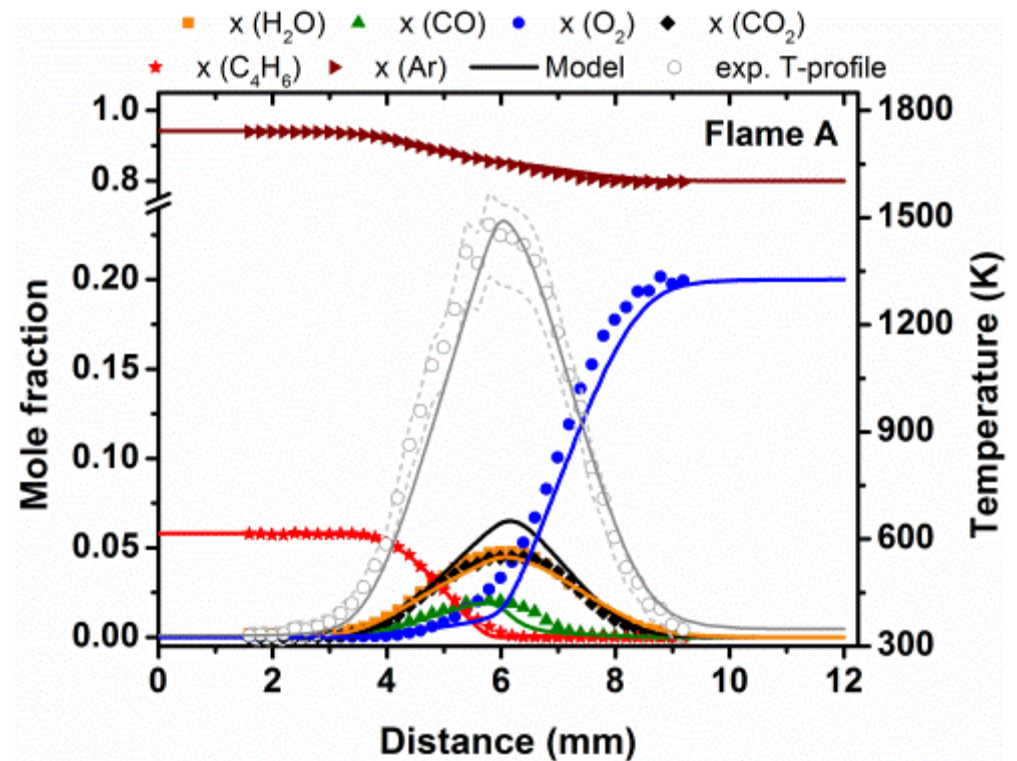
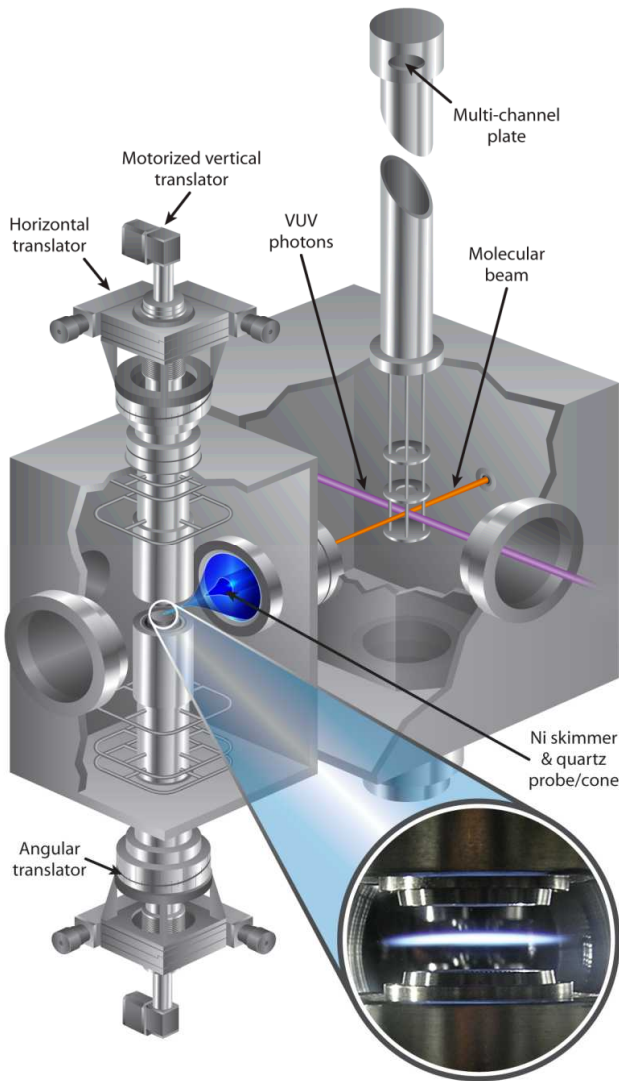
- common intermediate in hydrocarbon combustion
- fuel with a complex combustion chemistry, which is not yet understood in detail
- a good source of C_4H_5 radicals that are involved in the formation of aromatic species
- it is emitted as an unwanted, toxic byproduct from internal combustion engines
- as a small di-ene, it represents this class of compounds in practical fuels



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Experimental Approach

- Flame-Sampling Time-of-Flight Mass spectrometry
- This technique offers nearly full speciation of reactants, intermediates, and products



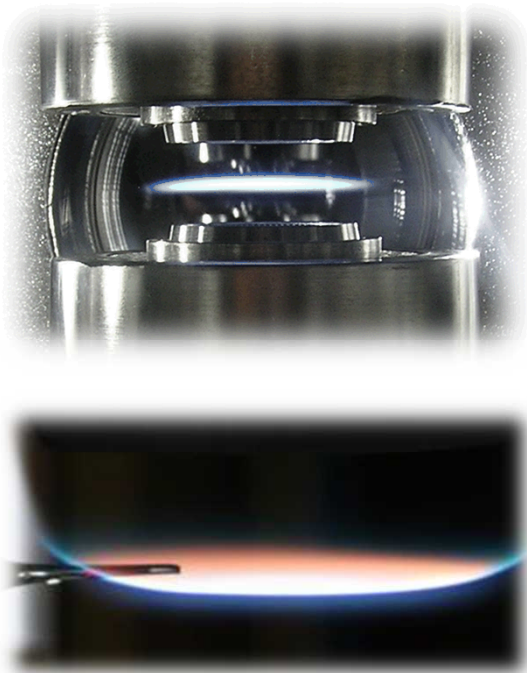
Experimental Approach



Mass spectrometer

- Orthogonal extraction reflectron time-of-flight
- Detection limit: ~ 1 ppm
- Mass resolution $m/\Delta m \sim 4000$
- Electron and photon ionization
- Continuous ionization, rapid (35 kHz) ion extraction

Experimental Approach



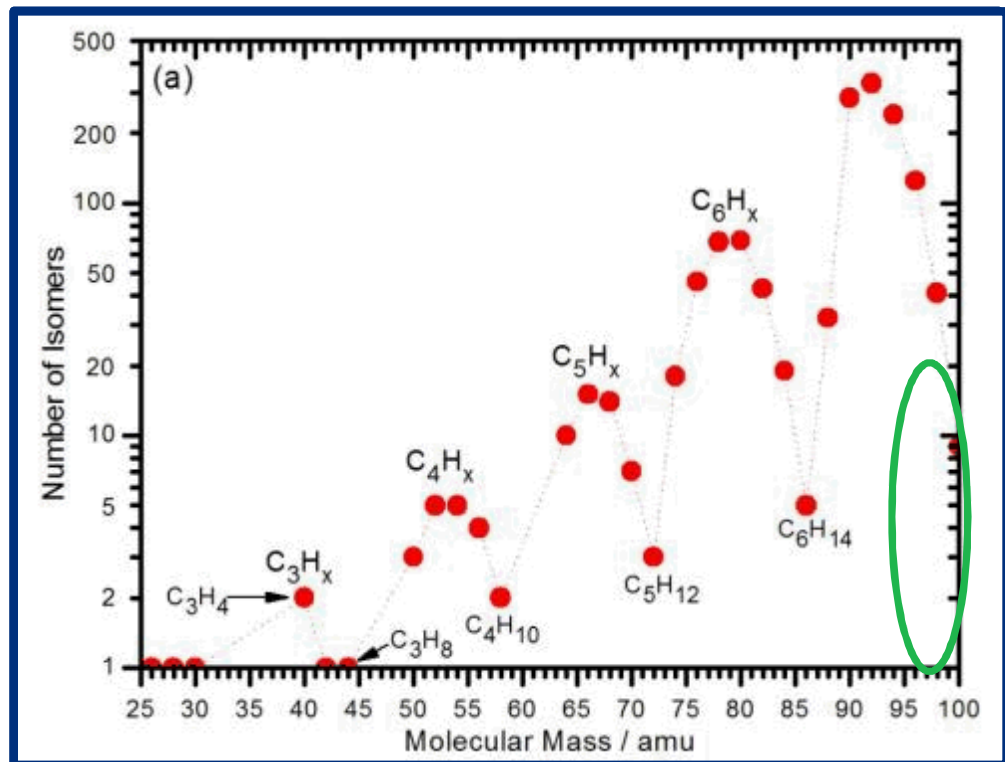
Investigated 1,3-butadiene flames

- *Flame A:*
 - 7.7% fuel – mainly particle free
 - allows the investigation of the formation of the first aromatic ring
- *Flame B:*
 - 10% fuel – slight soot layer
 - enables the detection of larger aromatic species (PAHs)

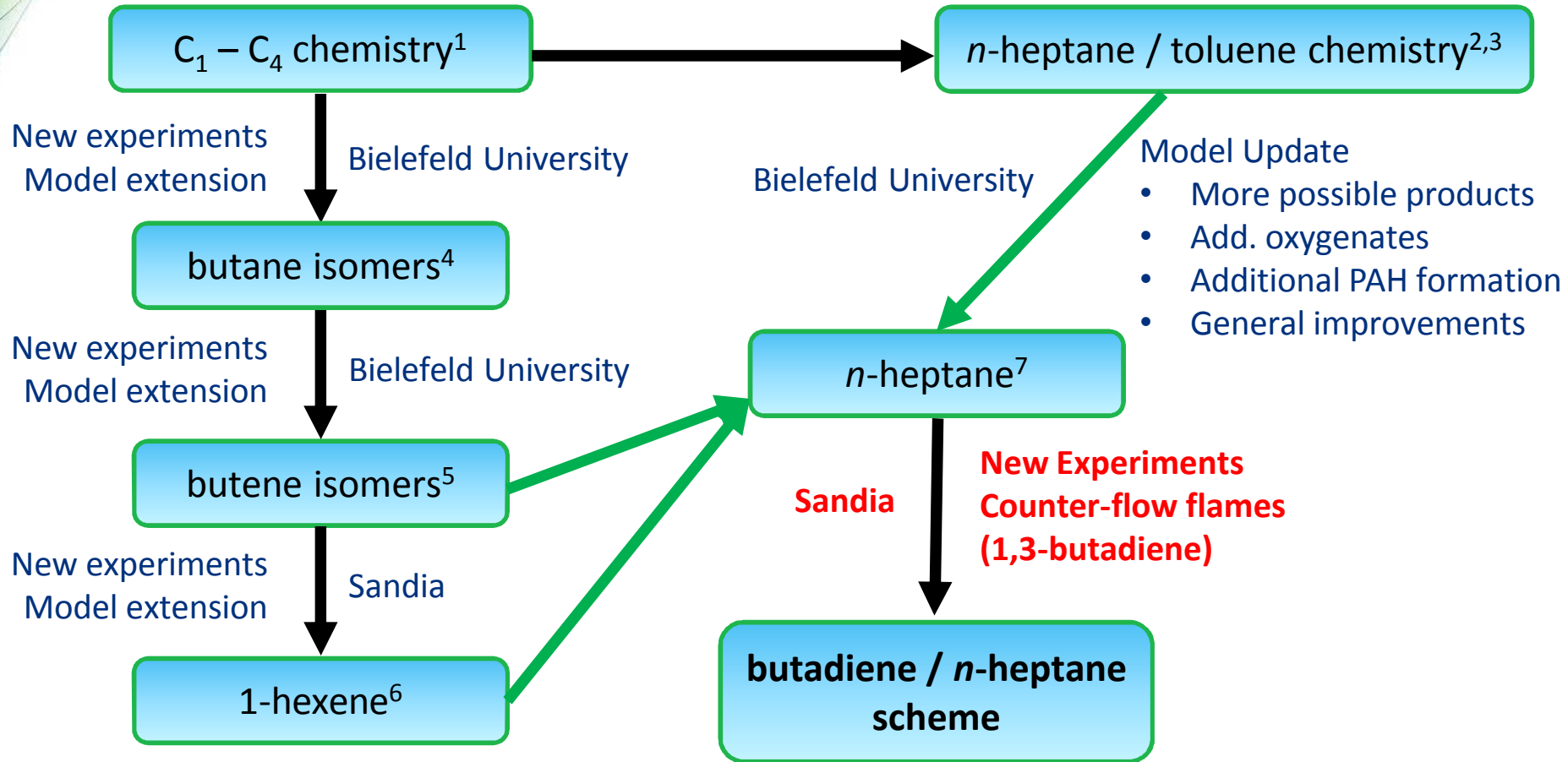
Isomer-specific Information

Chemical Dynamics Beamline at the Advanced Light Source

- Ionization through synchrotron VUV radiation (70-150nm)
- High photon flux (10^{14} photons/s)
- High energy resolution ($\Delta E=0.05$ eV) sufficient for the identification of individual isomers of flame species



The Mechanism – Development History



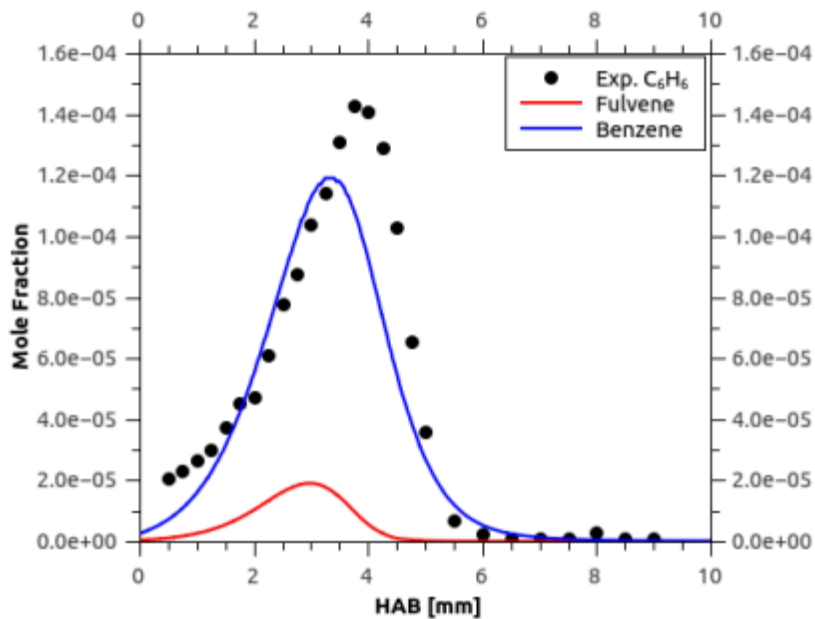
- 1) K. Hoyermann *et al.*, Phys. Chem. Chem. Phys. 6 (2004) 3824–3835
- 2) S. Ahmed *et al.*, Phys. Chem. Chem. Phys. 9 (2007) 1107–1126
- 3) T. Zeuch *et al.*, Combust. Flame 155 (2008) 651–674
- 4) P. Oßwald *et al.*, Zeitschrift für Phys. Chemie 225 (2011) 1029–1054
- 5) M. Schenk *et al.*, Combust. Flame 160 (2013) 487–503
- 6) A. Nawdiyal *et al.*, Proc. Combust. Inst. 35 (2015) 325–332
- 7) L. Seidel *et al.*, Combust. Flame 162 (2015) 2045–2058

- Model Update**
- Revised 1,3-butadiene decomposition chemistry
 - Additional PAH formation
 - General improvements

General Performance of the Mechanism

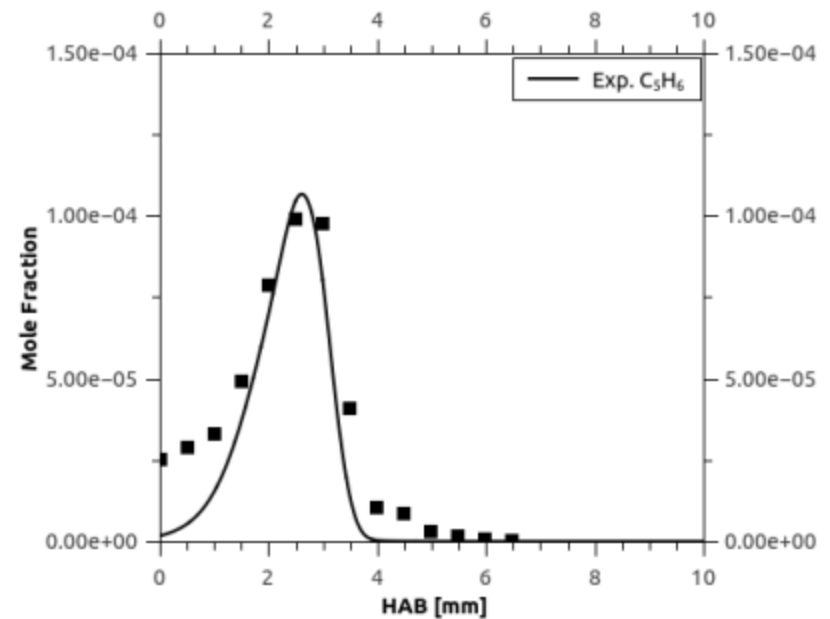
Premixed Flames

1,3-butadiene flame



N. Hansen *et al.*, Proc. Combust. Inst. 32 (2009) 623–630

n-heptane flame

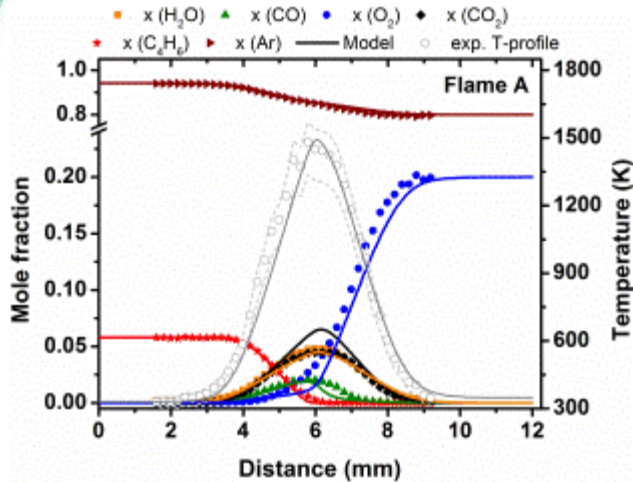


L. Seidel *et al.*, Combust. Flame 162 (2015) 2045–2058

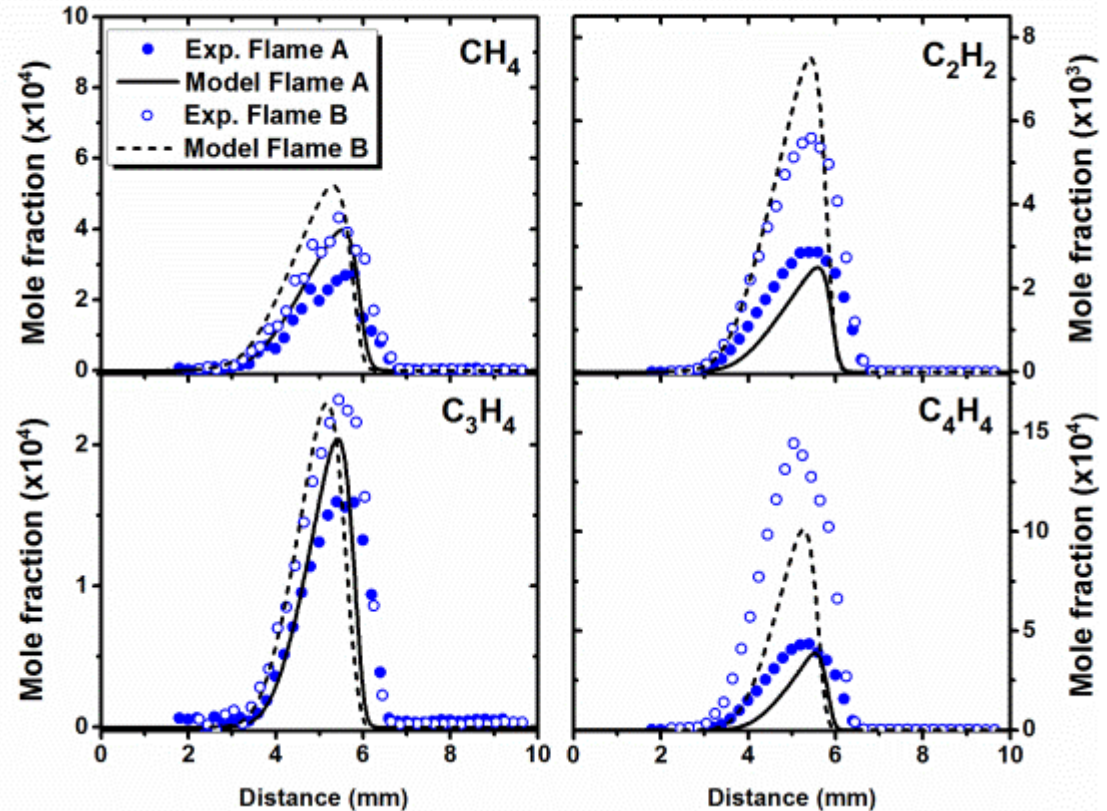
General Performance of the Mechanism

1,3-Butadiene Diffusion Flames

Major species



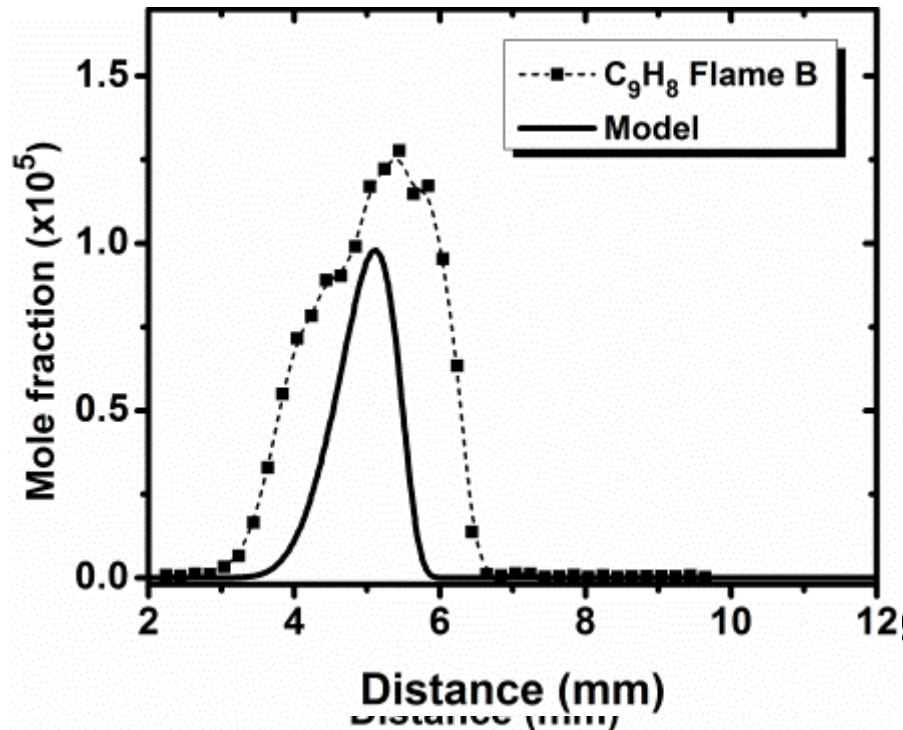
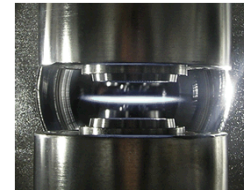
C_1 - C_4 intermediates



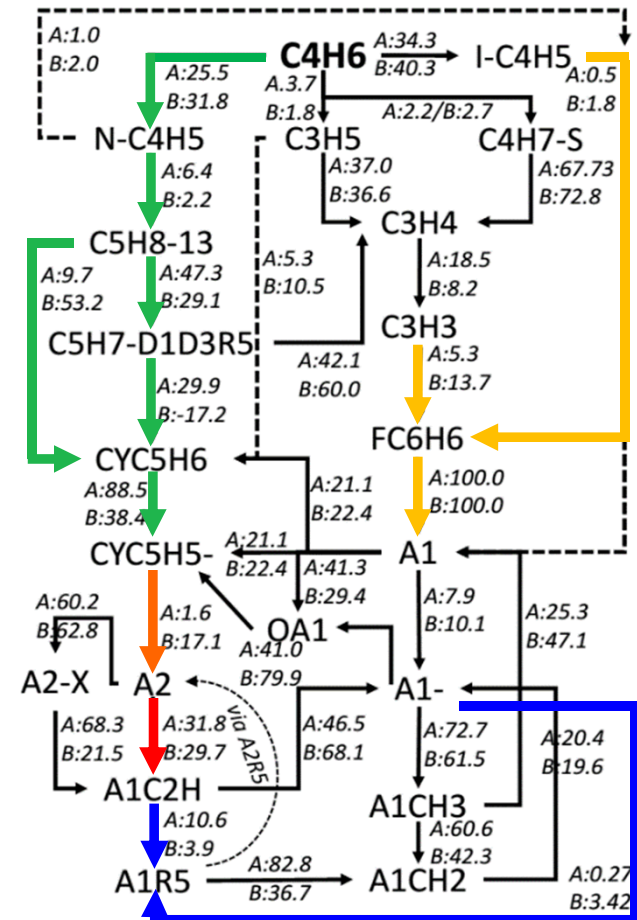
Temperature profiles:

- *Experiment:*
extracted from the Sampling function (\rightarrow probe-disturbed T-profile)
- *Modeling:*
radiation heat losses adjusted to match calculated and measured peak temperatures

Molecular-Growth Chemistry: Aromatics Formation in 1,3-Butadiene Flames



- indene is formed via $C_6H_5 + C_3H_3$ reactions and $CH_3 +$ phenylacetylene (A1C2H)
- providing evidence for non-sequential growth reaction



Summary

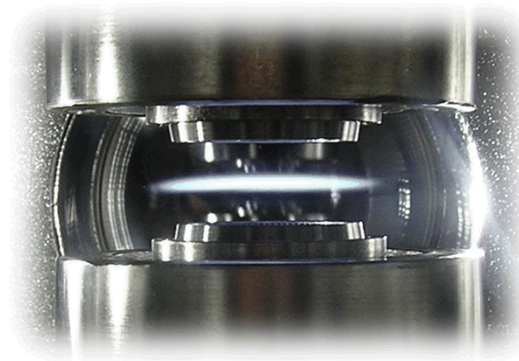
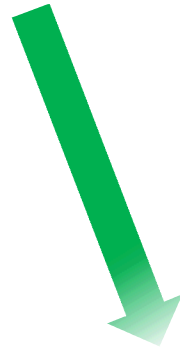
Experiments

- Mass spectrometric investigation of two different 1,3-butadiene opposed-diffusion flames
- Important isomer-specific information
- 47 species quantified



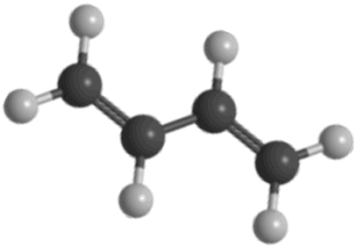
Mechanism Development

- Revised 1,3-butadiene decomposition chemistry
- Additional PAH formation reaction
- Tested against several validation targets and for different conditions

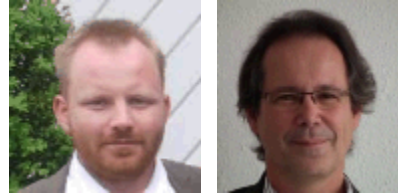


New chemical insights

- C₅ chemistry important for full description of molecular-growth
- Naphthalene oxidation to phenylacetylene provides evidence for non-sequential growth of two- ring aromatic species



Acknowledgement



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Thank you for your attention!!!