SAND2020-8667PE

Exploring Combustion Processes in Laboratory-Scale Model Flames

From Soot Formation to Biofuels

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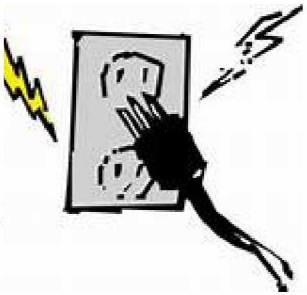
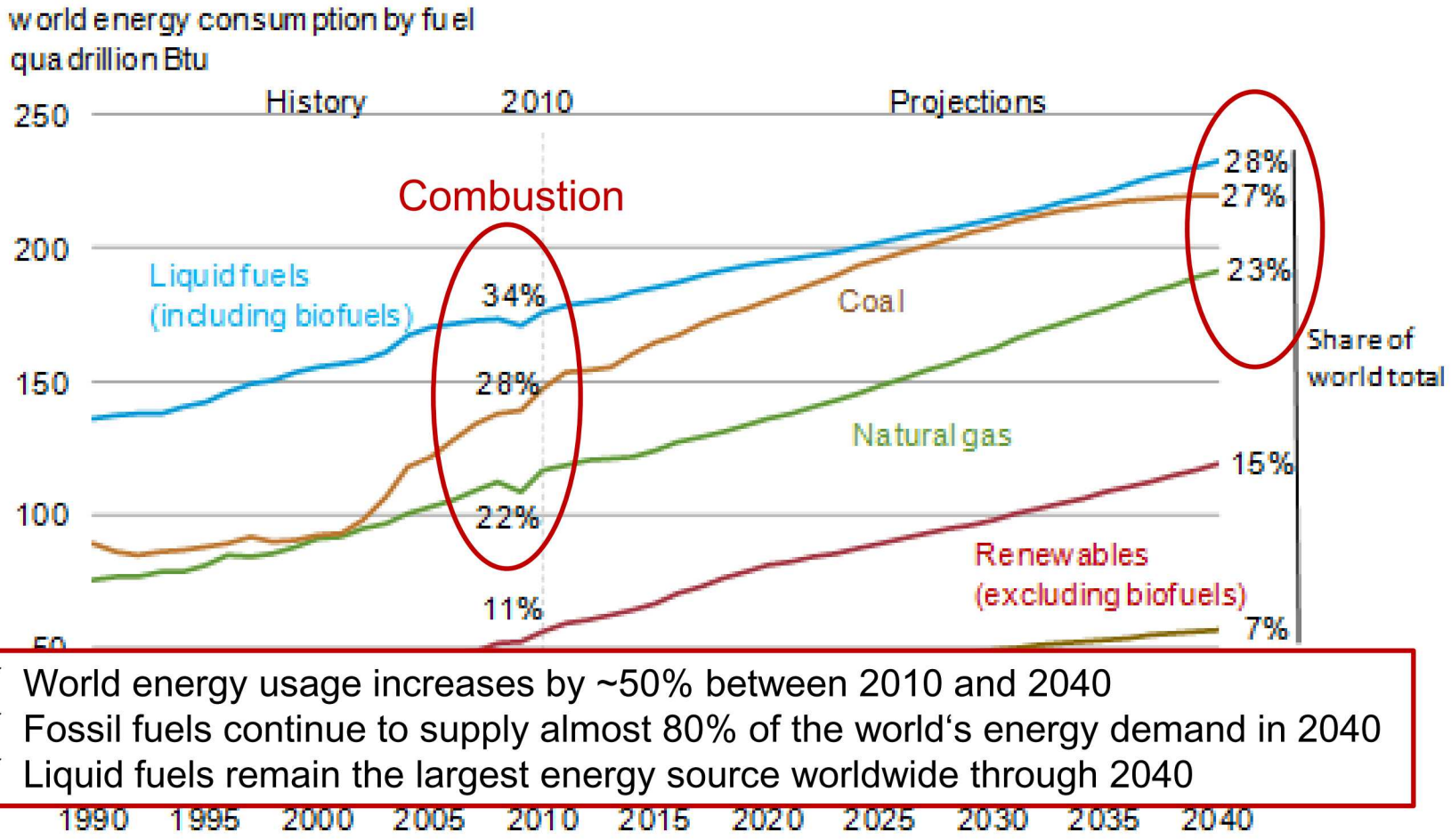
- ✓ **Background Information and Motivation**
- ✓ **Experiments**
  - ➢ Flame Configurations and Flame-Sampling Mass Spectrometry
- ✓ **Chemistry of Soot Formation**
  - ➢ Formation of the First Aromatic Ring
  - ➢ Chemical Composition of Soot Particles
- ✓ **Low-Temperature Oxidation Chemistry of DME**
  - ➢ A Jet-Stirred Reactor with Molecular-Beam Sampling Capabilities
- ✓ **Outlook and Conclusions**

Where Did The Energy Come From?

- Have you had a shower today?
- Do you wear clean clothes?
- Have you had tea or coffee and a hot meal?
- Have you used your mobile phone or computer today?
- Have you traveled by plane, train, bus, or car?



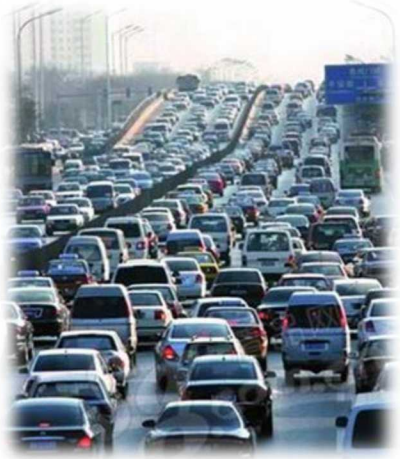
Combustion Energy Demands

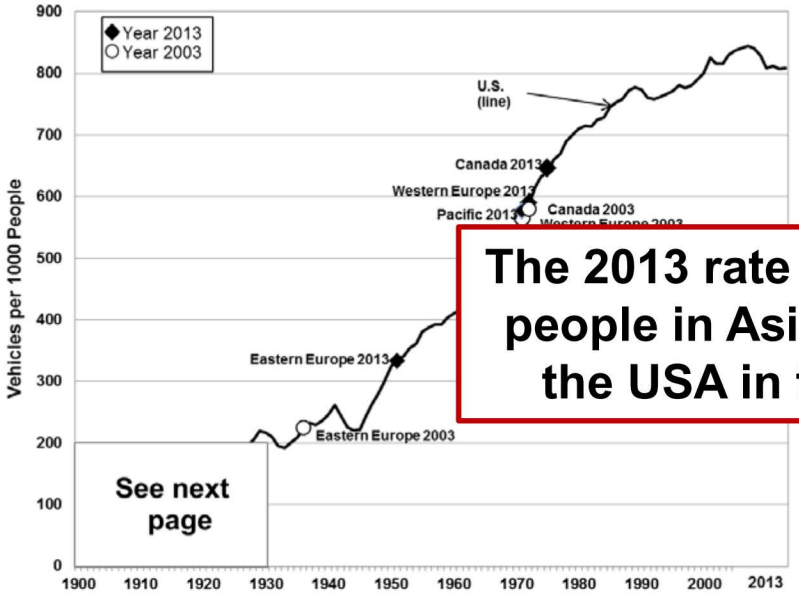


- ✓ World energy usage increases by ~50% between 2010 and 2040
- ✓ Fossil fuels continue to supply almost 80% of the world's energy demand in 2040
- ✓ Liquid fuels remain the largest energy source worldwide through 2040

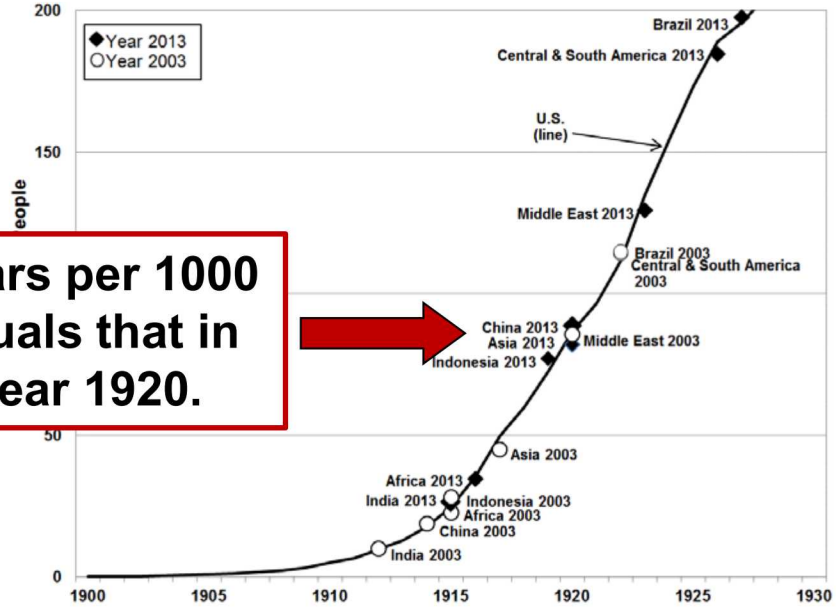
Source: EIA, International Energy Outlook 2013

Transportation Outlook





The 2013 rate of cars per 1000 people in Asia equals that in the USA in the year 1920.



From Transportation Data Book 2015, Published by Oak Ridge National Laboratory

Engine Combustion – A Complicated Process

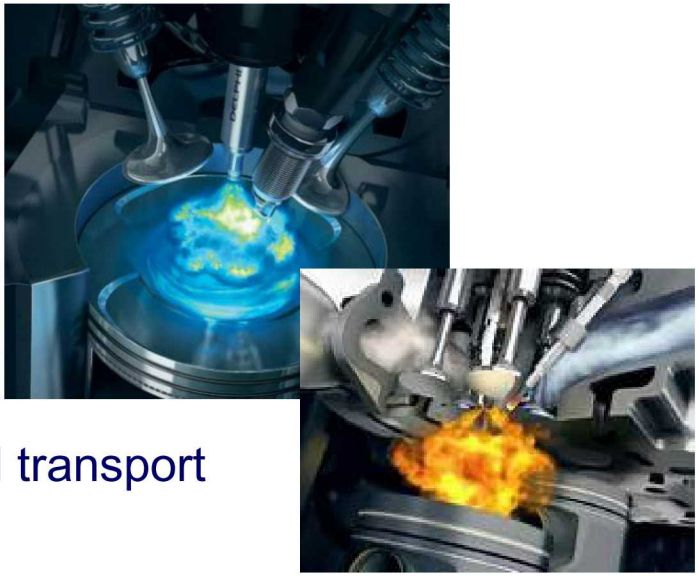
- fluid dynamics coupled with chemical reaction
- four-dimensional process in space – time.
- it‘s a multi-scale problem: (9 orders of magnitude)

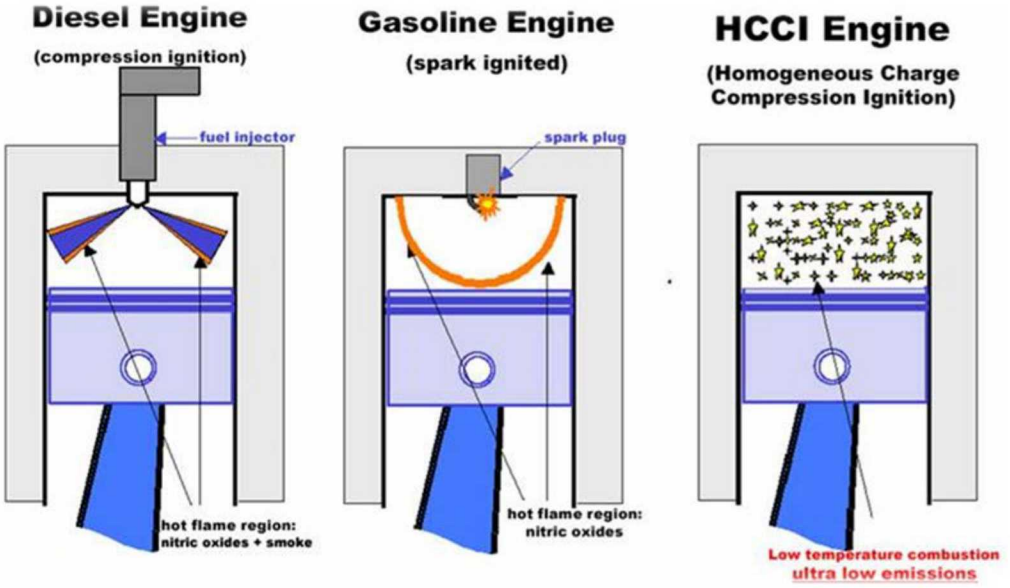
Length-Scale:

molecular scale ⇄ few centimeters

Time-Scale:

from fast molecular reactions ⇄ slow fluid transport





✓ It is more complicated than

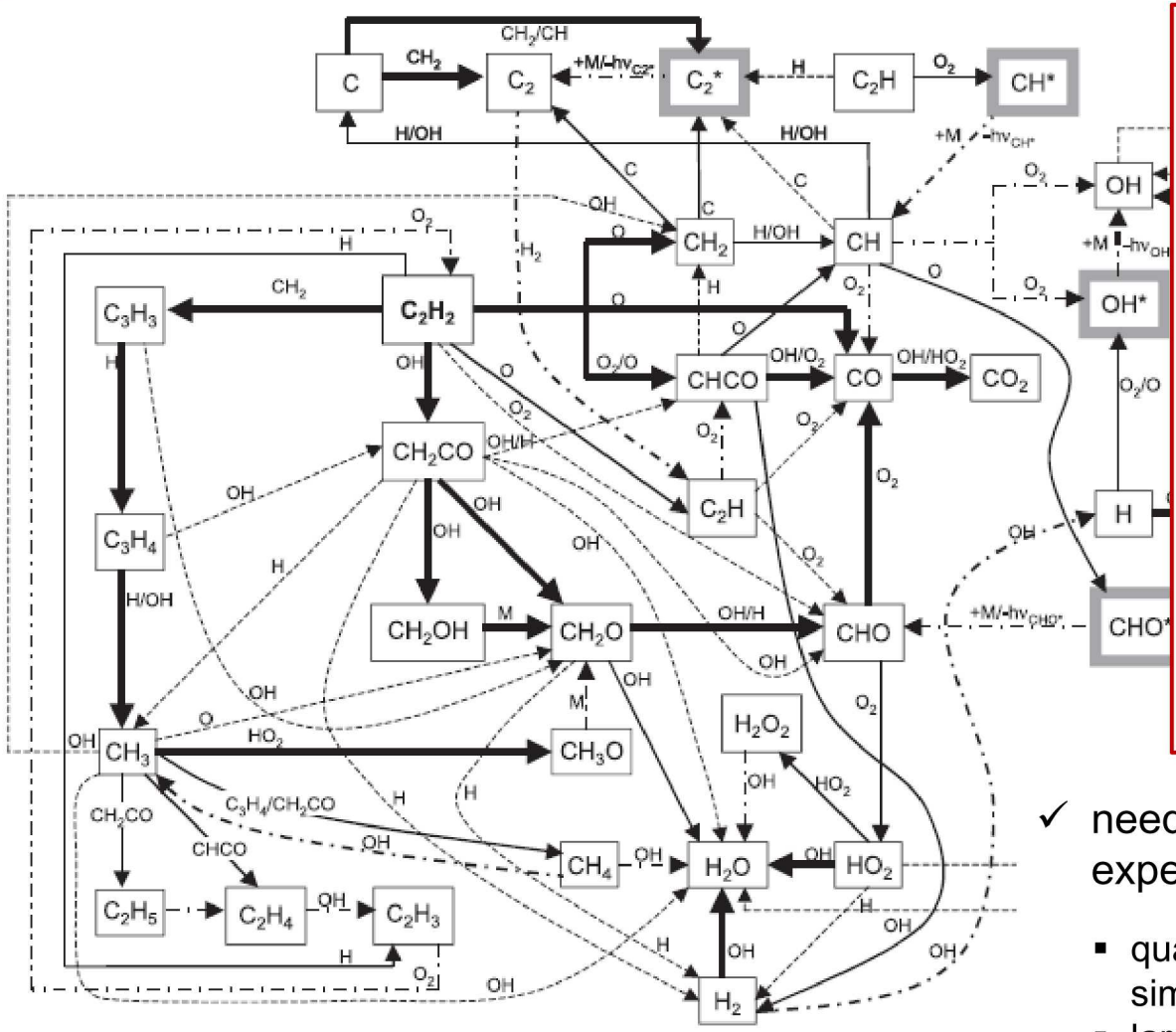
$$C_xH_y + (x+y/4)\ O_2$$

$$\updownarrow$$

$$x\ CO_2 + y/2\ H_2O + E$$

Chemistry can explain combustion emissions: soot, NO_x, CO_2

Wanted:
A Predictive Model for Combustion Chemistry



iBuOH+H=H2+C4H9Oi1	2.7e+07	1.76	7453.56
iBuOH+H=H2+C4H9Oi2	1.74e+07	1.48	3442.4
iBuOH+H=H2+C4H9Oi3	1.09e+07	1.59	3352.7
iBuOH+H=H2+C4H9Oi4	4.05e+04	2.38	9.34e+03
iBuOH+C2H3=C4H9Oi1+C2H4	1.10e-03	4.55	3505
iBuOH+C2H3=C4H9Oi2+C2H4	2.69e-02	3.9	684.9
iBuOH+C2H3=C4H9Oi3+C2H4	5.19e-02	3.9	861.37
iBuOH+CH3=CH4+C4H9Oi1	1.61e+00	3.59	7719.45
iBuOH+CH3=CH4+C4H9Oi2	4.14e+02	2.87	4899.5
iBuOH+CH3=CH4+C4H9Oi3	1.87e+00	3.50	6.00e+03
iBuOH+CH3=CH4+C4H9Oi4	2.32e+00	3.49	6.09e+03
iBuOH+CH2OH=C4H9Oi1+CH3OH	1.040E+06	1.800	15050.00
iBuOH+CH2OH=C4H9Oi2+CH3OH	0.99140E+06	1.753	12532.12
iBuOH+CH2OH=C4H9Oi3+CH3OH	0.99040E+06	1.786	13448.33
iBuOH+CH2OH=C4H9Oi4+CH3OH	0.250E-04	5.000	12580.00
iBuOH+OH=H2O+C4H9Oi3	3.61E+03	2.89	-2291
iBuOH+OH=H2O+C4H9Oi2	1.54	3.7	-4940
iBuOH+OH=H2O+C4H9Oi1	5.4E+06	2 5	12.64
iBuOH+OH=H2O+C4H9Oi4	5.88e2	2.82	-584.58
iBuOH+O2=C4H9Oi1+HO2	1.206E14	0.0	51.87e+03
iBuOH+O2=C4H9Oi2+HO2	1.588E14	0.0	47.69e+03
iBuOH+O2=C4H9Oi3+HO2	1.588E14	0.0	47.69e+03
iBuOH+O2=C4H9Oi4+HO2	2.325E12	0.0	74.12e+03
iBuOH+O=C4H9Oi1+OH	9.540E+04	2.710	2106.00
iBuOH+O=C4H9Oi2+OH	0.78E+05	2.5	1113.77
iBuOH+O=C4H9Oi3+OH	1.289E+05	2.79	2183.65
iBuOH+O=C4H9Oi4+OH	1.000E+13	0.000	4690.00
C4H9Oi3+O2=C4H8O-i3+HO2	5.28E+17	-1.638	8.39E+02
C4H9Oi1+O2=C4H8O-i1+HO2	7.23E+12	0.0	15998.4
O2+C4H9Oi3=HO2+C4H8O-i2	7.23E+12	0.0	15998.4
O2+C4H9Oi2=HO2+C4H8O-i1	7.23E+12	0.0	15998.4
O2+C4H9Oi2=HO2+C4H8O-i2	7.23E+12	0.0	15998.4
iBuOH+CH3O=C4H9Oi1+CH3OH	2.820E+11	0.000	7000.00
iBuOH+CH3O=C4H9Oi2+CH3OH	2.200E+11	0.000	4570.00
iBuOH+CH3O=C4H9Oi3+CH3OH	3.173E9	0.95	5644.0
C4H9Oi4+CH3OH=iBuOH+CH3O	2.820E+11	0.000	7000.00
C2H6+C4H9Oi1=iBuOH+C2H5	1.926e-05	5.28	7.78e+03
iBuOH+C2H5=C2H6+C4H9Oi2	1.41e-05	4.83	4.37e+03

- ✓ needs to be validated by suitable experiments
  - quantitative detection of many species simultaneously
  - large sensitivity and dynamic range

Marques *et al., J. Braz. Chem. Soc.*, 2006, **17,** 302-315

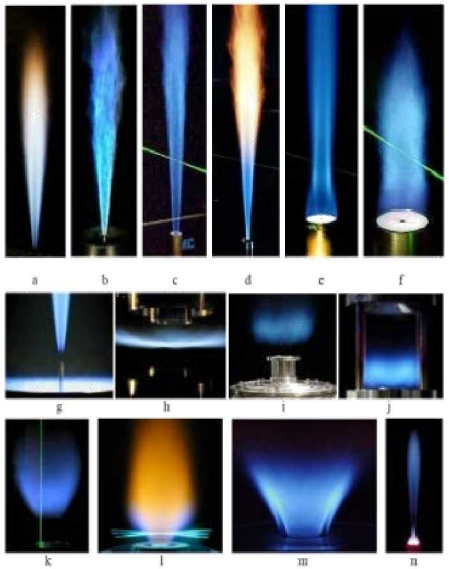
Combustion Research

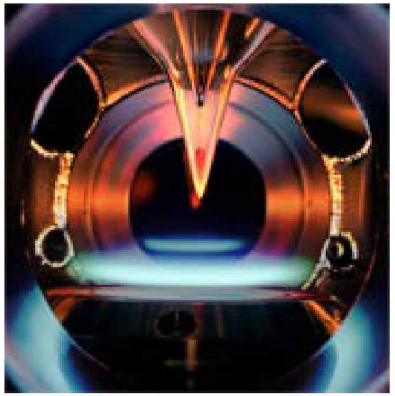
Multi-Scale Nature of Combustion and Model Flames

- ✓ Depending on the mixing state of the reactants laboratory flames are classified as *non-premixed* or *premixed.*

dominated by rate of mixing

dominated by chemistry

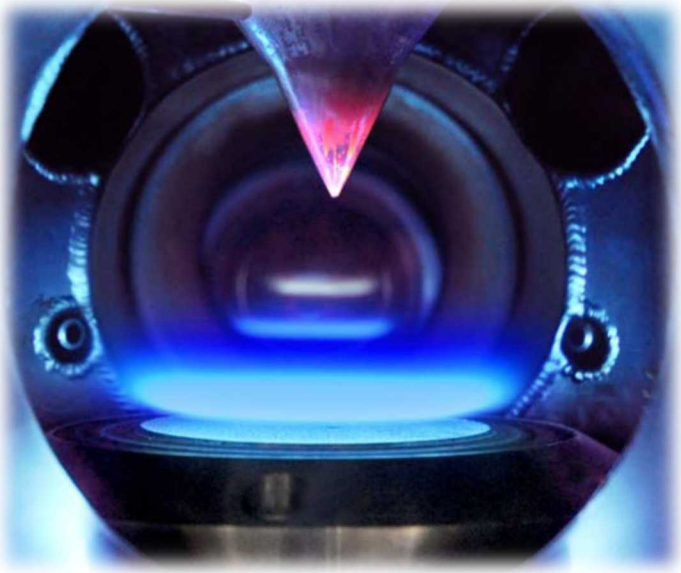




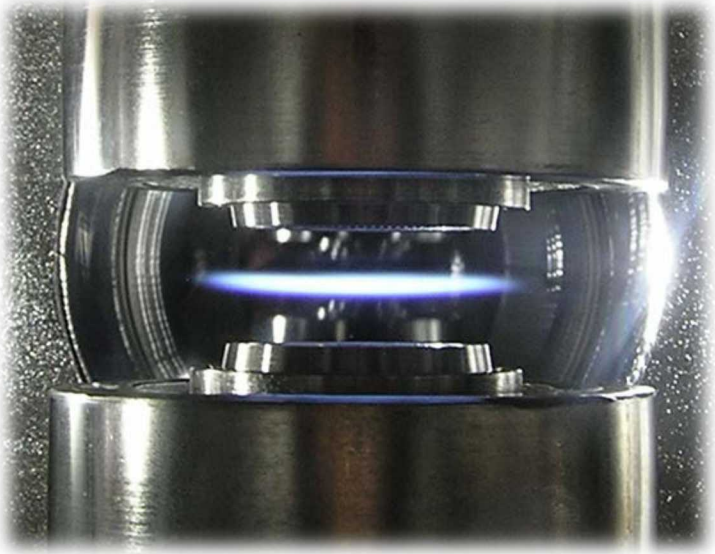
- ✓ Depending on their fluid dynamics, flames are further characterized as either *laminar* or *turbulent*.

Providing Experimental Data Under Idealized Conditions For Model Verification

Virtually all flame *chemistry* research has been performed in laminar flames.



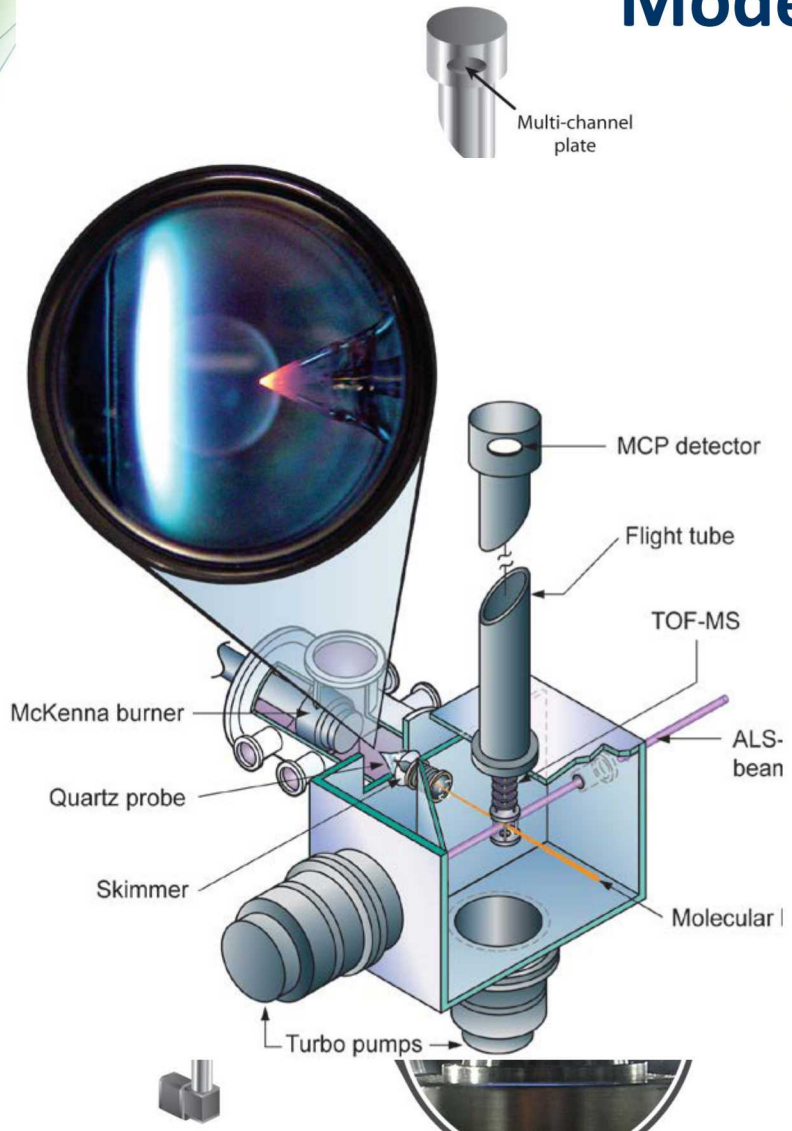
Low-Pressure Premixed Flames



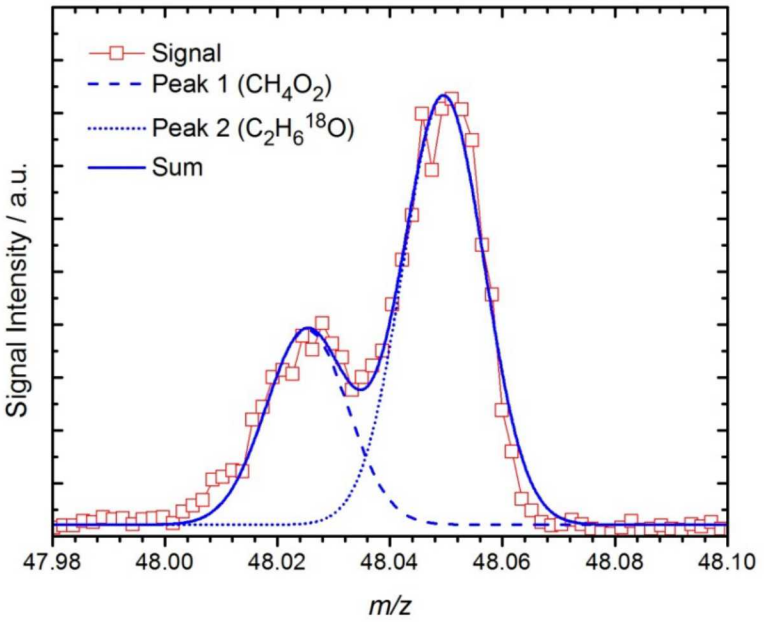
Counter-Flow Diffusion Flames
At Low- and Atmospheric Pressure

Can we predict the chemical structure of such simple model flames?

Providing Experimental Data For Model Verification



1. ✓ Orthogonal extraction reflectron time-of-flight
   ✓ Continuous ionization, rapid (35 kHz) ion extraction
   ✓ Electron and photon ionization
2. ✓ Detection limit: ~ 1ppm
   ✓ Mass resolution $m/\Delta m$ ~ 4000
3. Ide
   ❑
   ❑
4. Dev
   ❑
   ❑

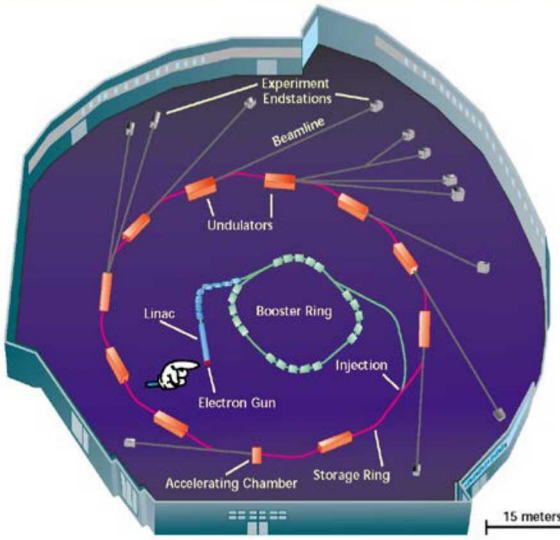


N. Hansen *et al., Prog. Energy Combust. Sci.*, **2009,** 35, 168-191

Advanced Light Source

Synchrotron Radiation at the Lawrence Berkeley National Laboratory

- ✓ 3rd Generation light source for vacuum ultraviolet (VUV) and soft X-rays
- ✓ Photons are generated by the acceleration of ultarelativistic electrons through magnetic fields

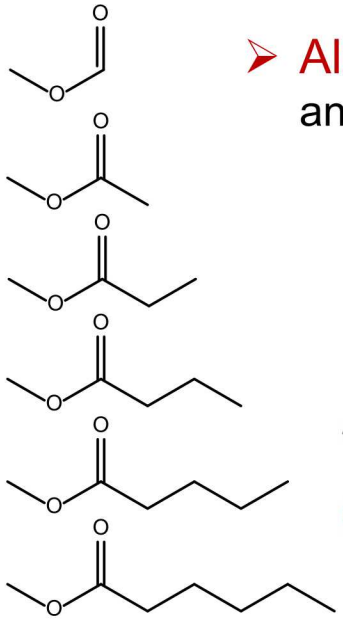


- ✓ easy to tune in the range from 7.3 to 24 eV
- ✓ energy resolution of $E/\Delta E$ = 250-400 sufficient for the identification of individual isomers of flame species

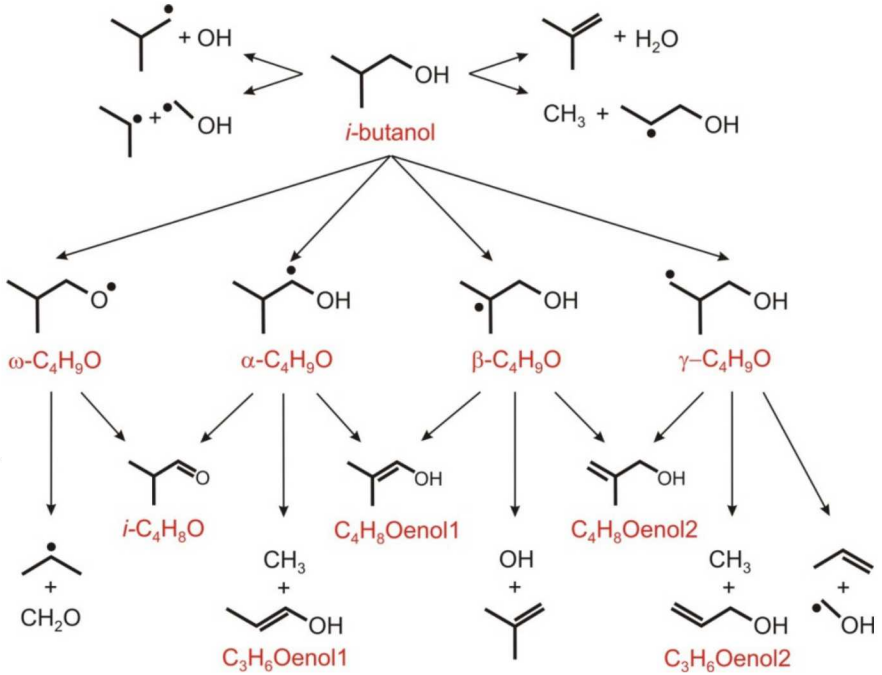
Combustion Chemistry of Oxygenated Fuels

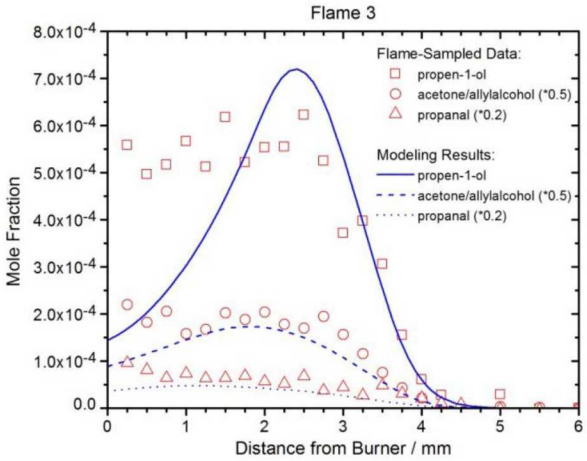
- performed for the Combustion Energy Frontier Research Center -

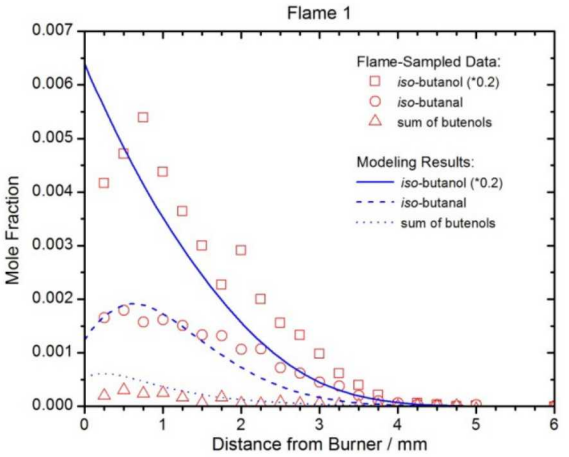
- **Biodiesel/Ester:** in collaboration with Yang (Tsinghua), Westbrook (LLNL), and Kohse-Höinghaus (Bielefeld)



- **Alcohols:** in collaboration with Green (MIT) and Sarathy (Kaust)



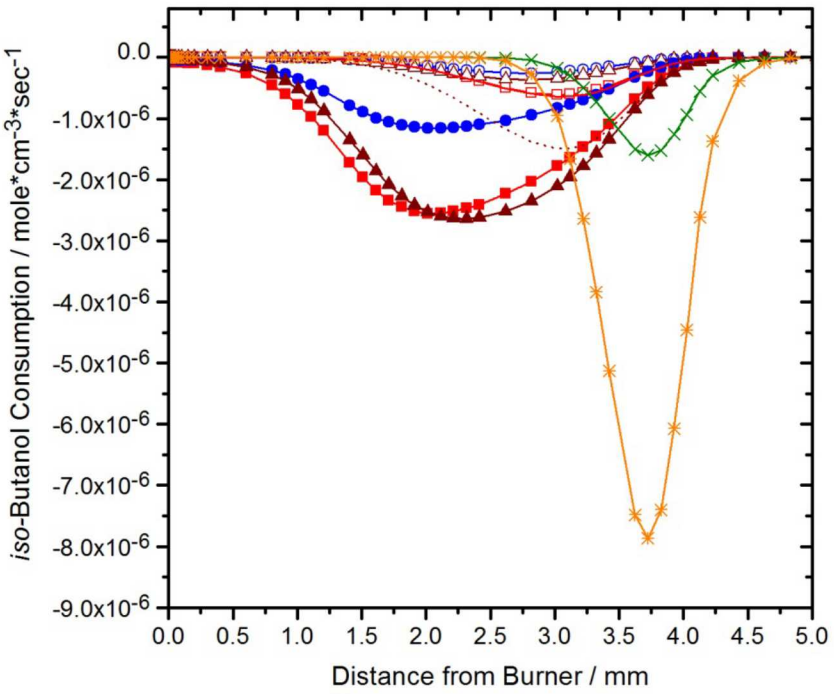




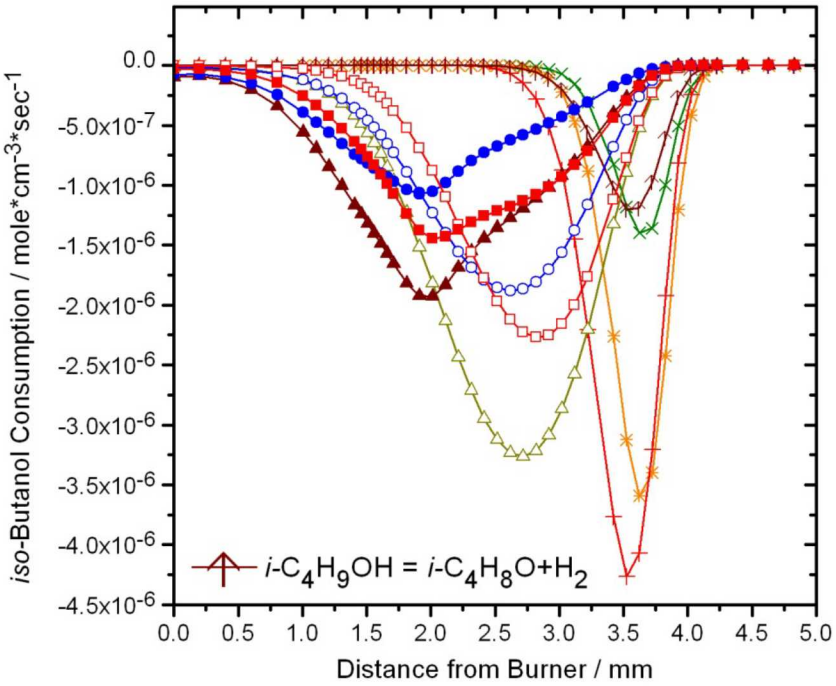
- largely predictive models can be generated for the combustion of these fuels

Combustion Chemistry of Oxygenated Fuels

MIT Model (Green *et al.*)



KAUST Model (Sarathy *et al.*)



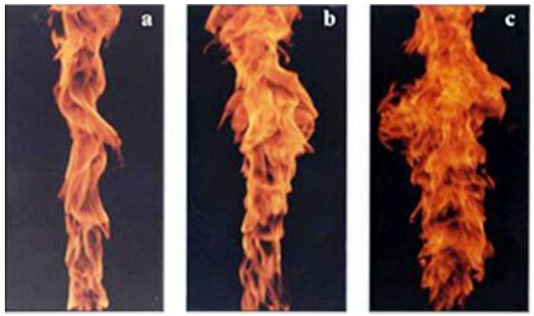
Reliable experimental data can be explained by "wrong" models.

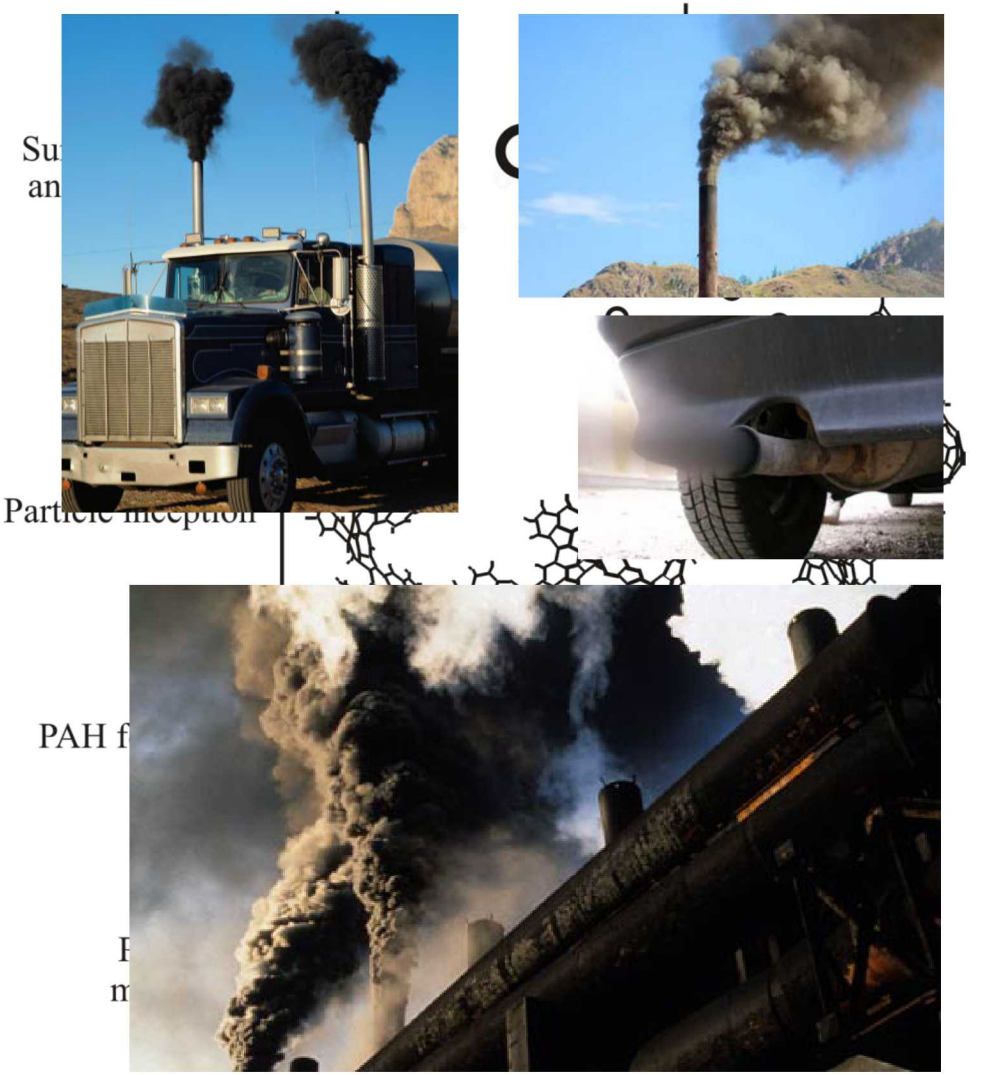
More accurate experimental data are required to further constrain the models.

N. Hansen *et al., Combust. Flame,* **2013,** 160, 2343-2351

Chemistry of Soot Formation

- ✓ Soot is a hazardous combustion emission
- ✓ Agreement has been achieved on the general features of the overall soot formation processes
- ✓ Soot is formed by molecular growth reactions from small unsaturated hydrocarbons
- ✓ Chemical reaction mechanisms in flame models must be tested against reliable experimental data

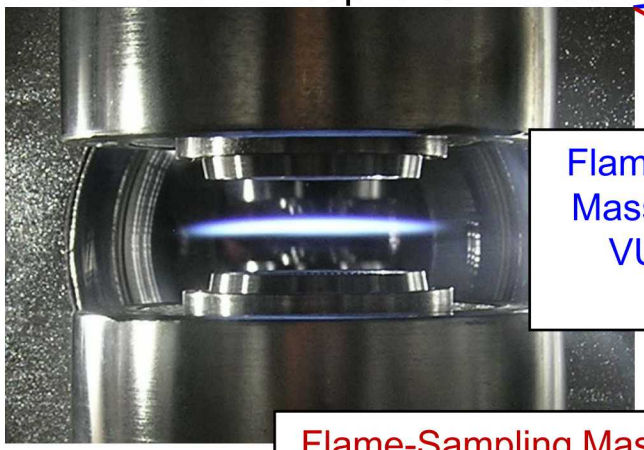




Chemistry of Soot Formation

Experimental Approaches

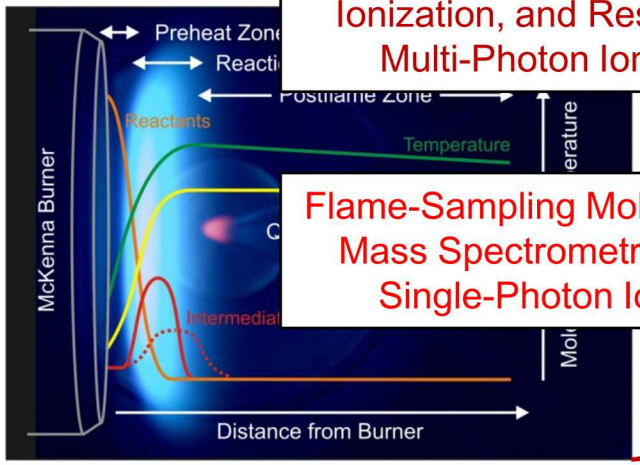
Counter-Flow Diffusion Flames
At Low- and Atmospheric Pressure



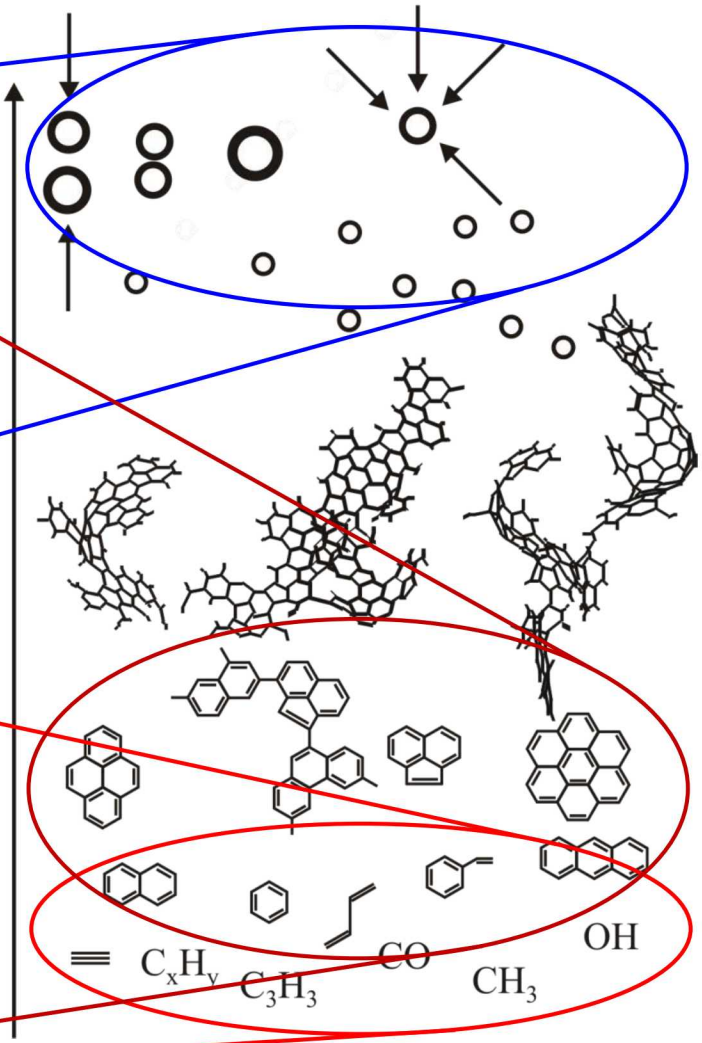
Flame-Sampling Aerosol Mass Spectrometry with VUV Single-Photon Ionization

Flame-Sampling Mass Spectrometry with VUV Single-Photon Ionization, Electron Ionization, and Resonance-Enhanced Multi-Photon Ionization (REMPI)

Low-Pressure



Flame-Sampling Molecular-Beam Mass Spectrometry with VUV Single-Photon Ionization



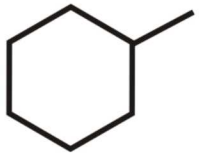
Fuel-Structure Dependence of Benzene Formation

Allene + Propyne

1,3-Butadiene

Cyclopentene

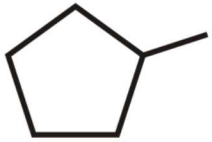
Methylcyclohexane



1-Hexene

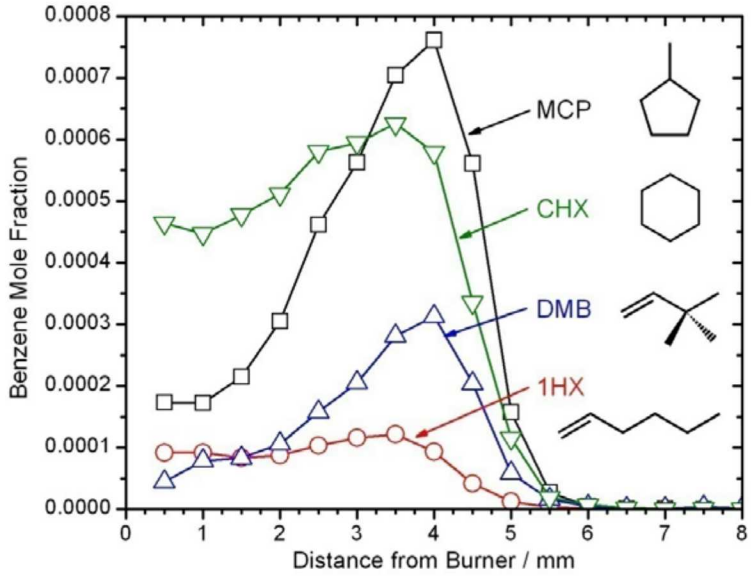
3,3-Dimethyl-1-Butene

Methyl-cyclopentane



Cyclohexane

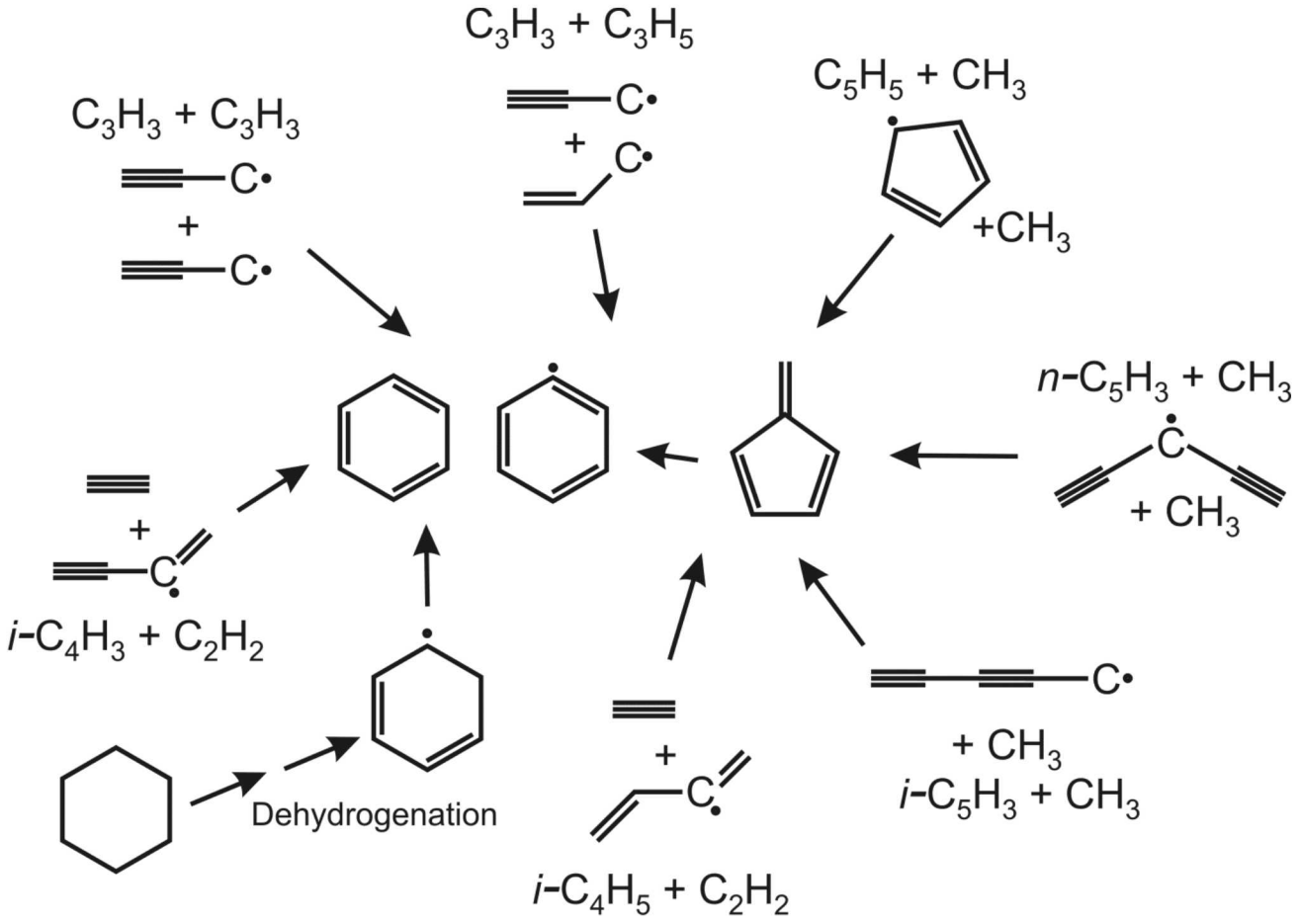
- selected fuels represent a variety of chemical structures, including *alkenes*, a *branched alkene*, an *alkyne*, a *cycloalkene*, a *cycloalkane*, and its *methyl-substituted* derivative



N. Hansen *et al., Proc. Combust. Inst.*, **2011,** 33, 585-592

Formation of the First Aromatic Ring

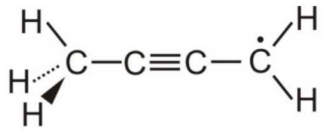
- Numerous formation pathways contribute
- Significance of different pathways depends on the fuel structure



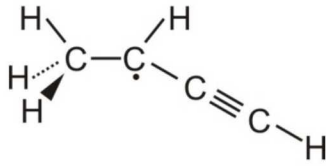
N. Hansen *et al., Combust. Expl. Shock Waves,* **2012,** 48, 508-515

Identification of C_4H_5 Radicals

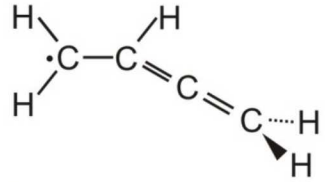
- **1-Methylallenyl:**



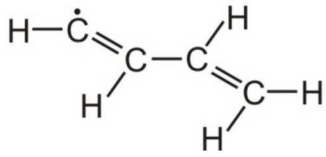
- **CH_3CHCCH:**



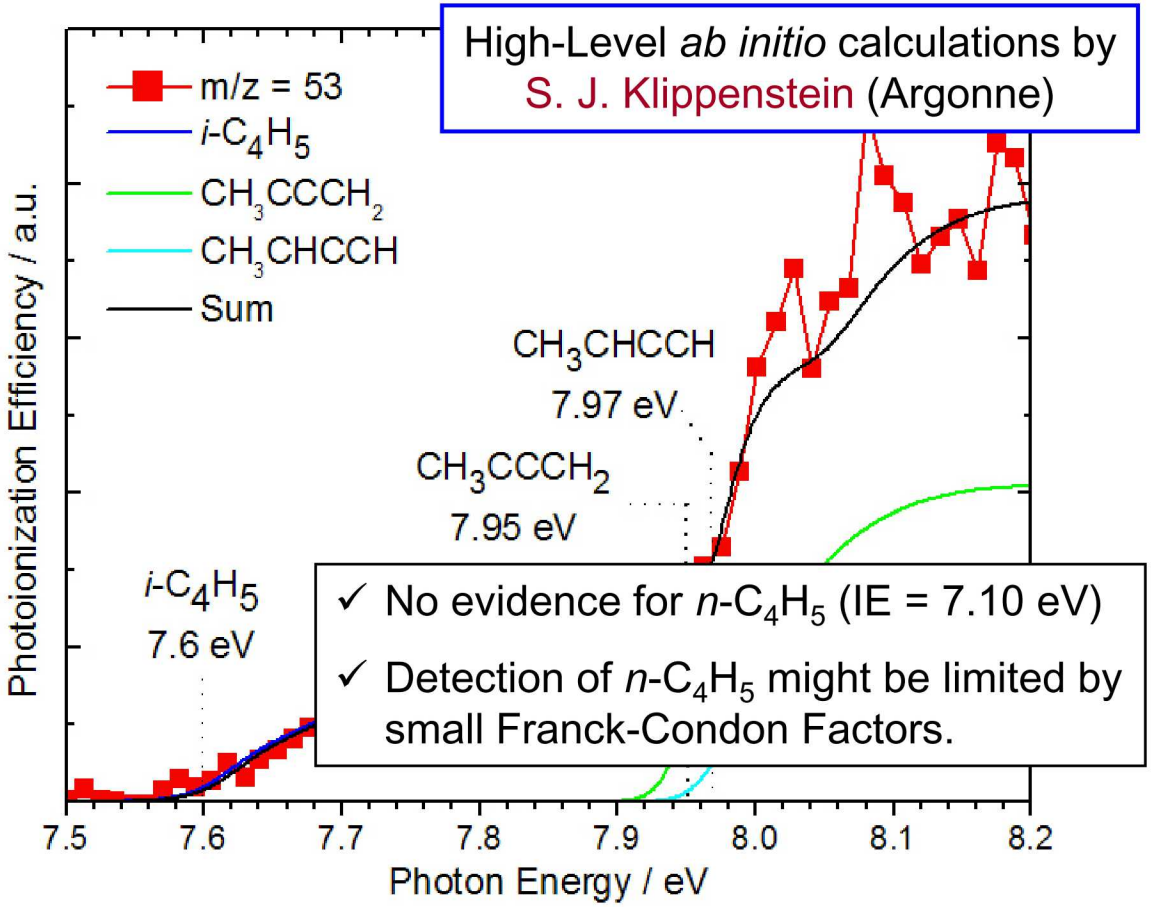
- ***i*-C_4H_5:**



- ***n*-C_4H_5:**



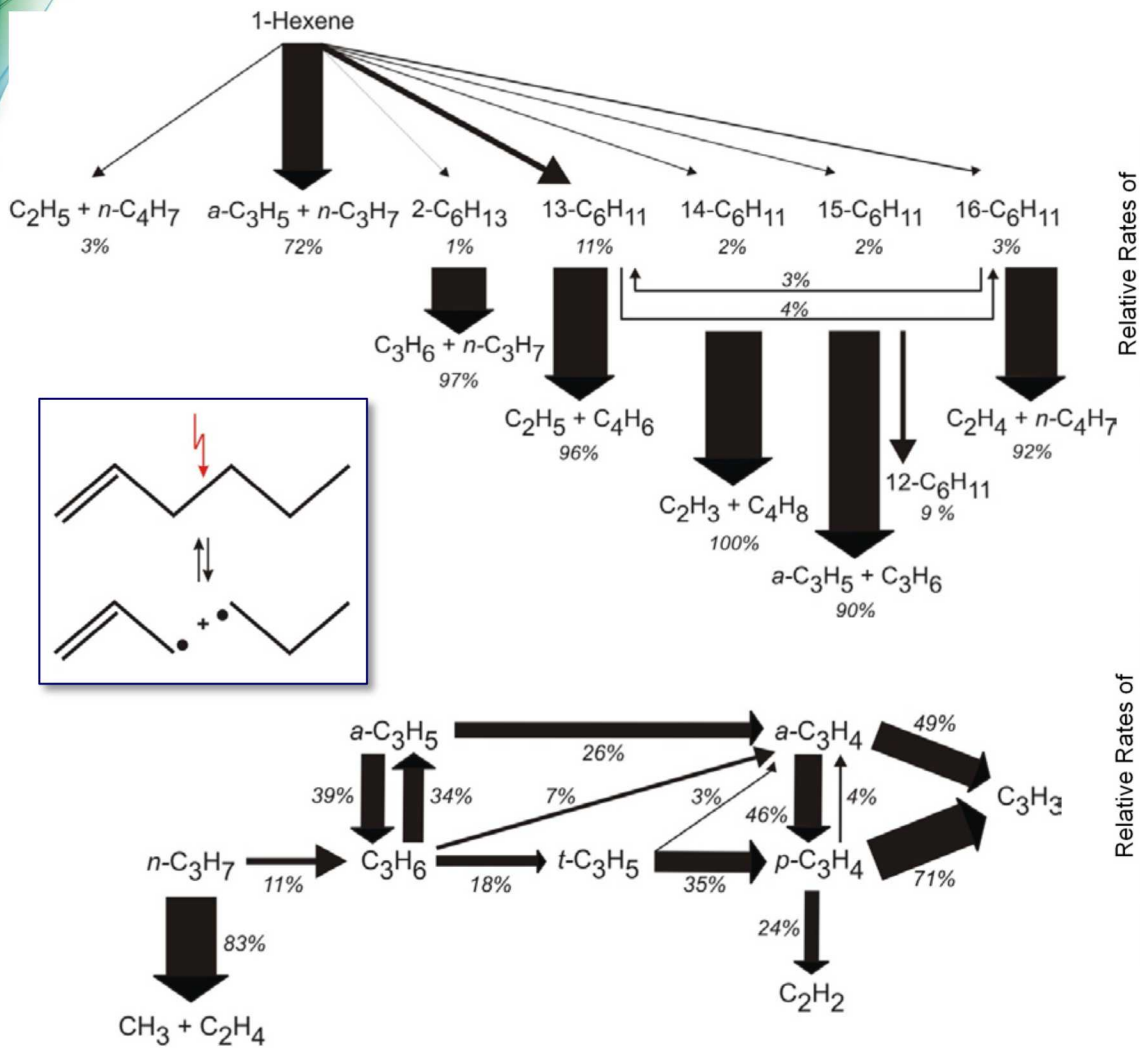
- **Flame-Sampled Photoionization Spectrum:**

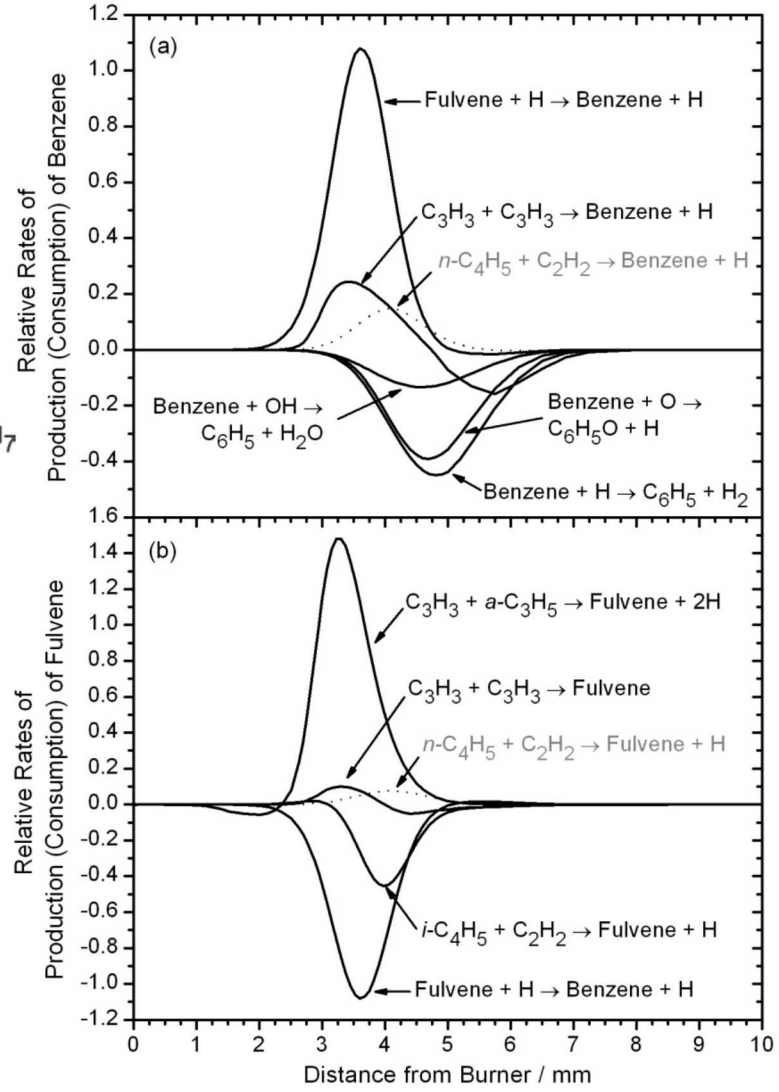


N. Hansen *et al., J. Phys. Chem. A,* **2006,** *110,* 3670-3678

Fuel-Rich 1-Hexene Flame:

Importance of Fuel Dissociation and C_3H_3+C_3H_5 Association



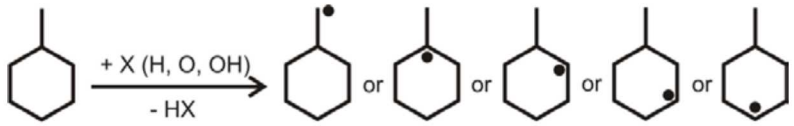


N. Hansen *et al., Phys. Chem. Chem. Phys.*, **2010**, 12, 12112-12122

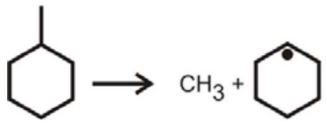
Methylcyclohexane Flames

Dehydrogenation, Dissociation and Isomerization

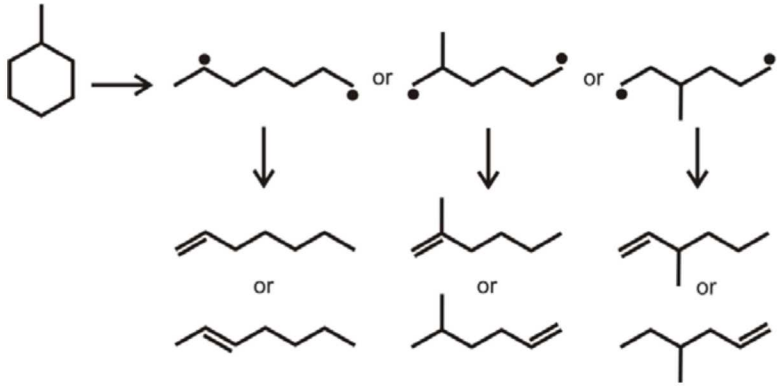
- H-Abstraction Reactions (dehydrogenation) ~70%

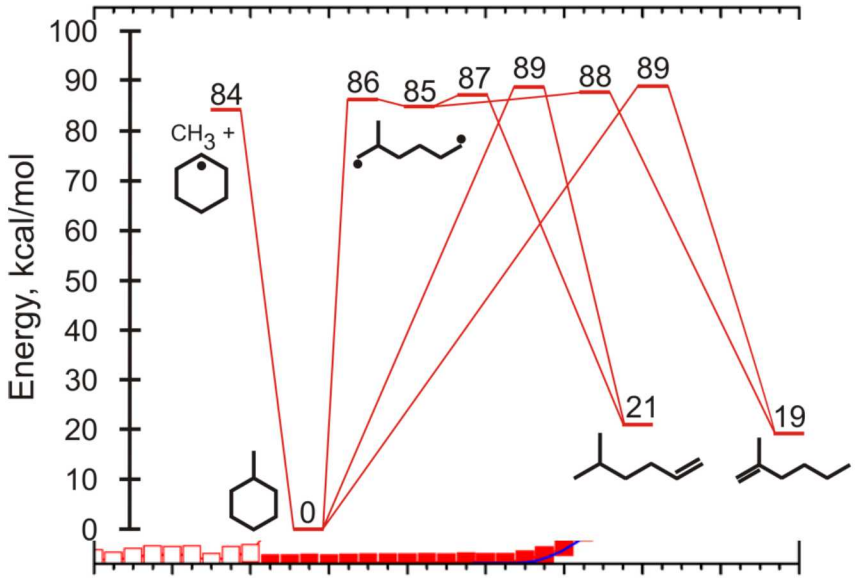


- Unimolecular Dissociation ~15%



- Unimolecular Isomerization (ring opening) ~15%





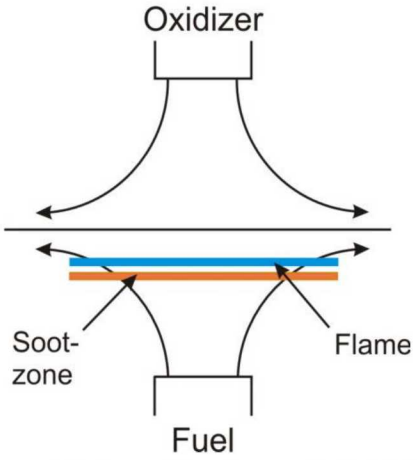
- ✓ stepwise via diradicals or through concerted processes
- ✓ β-scissions of the diradicals are energetically not favored
- ✓ low-lying carbenes are unlikely intermediates

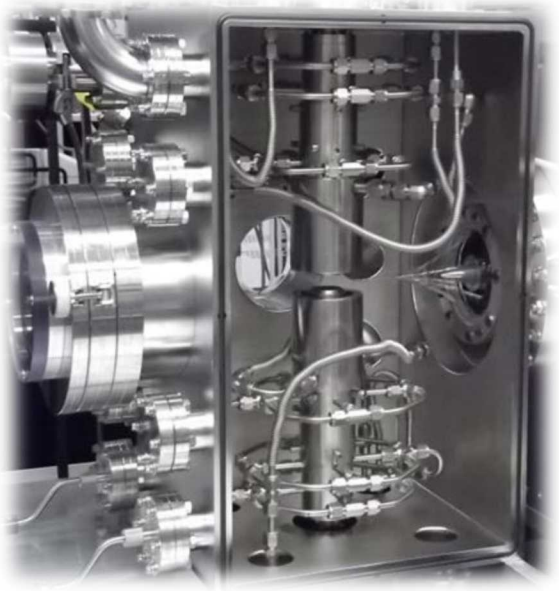
Isomerization of the fuel can be an important fuel consumption pathway.

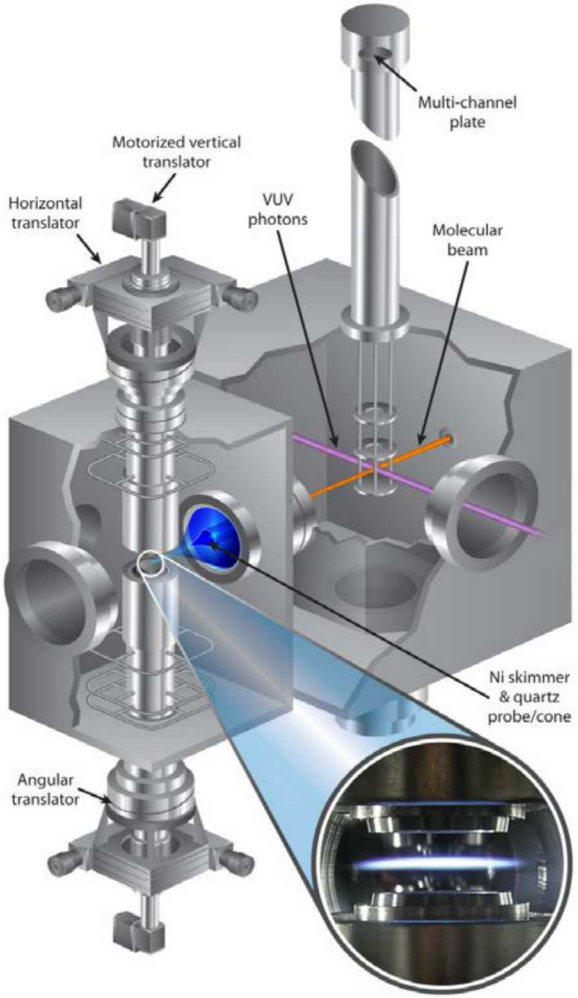
S. A. Skeen *et al., Energy Fuels,* **2011,** 25, 5611-5625

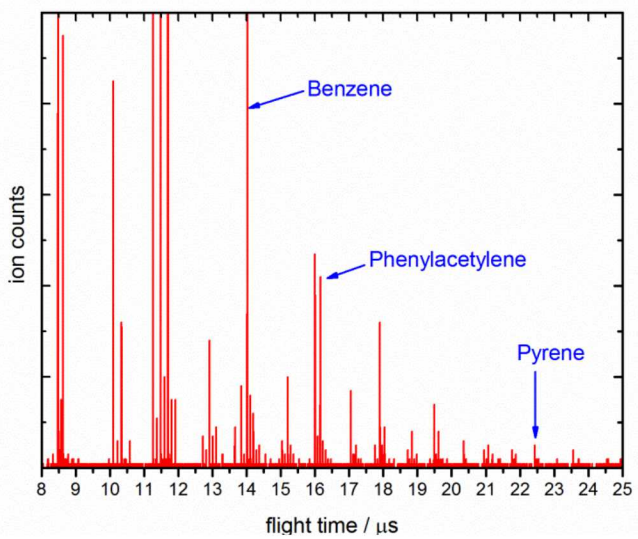
Molecular-Growth Chemistry:

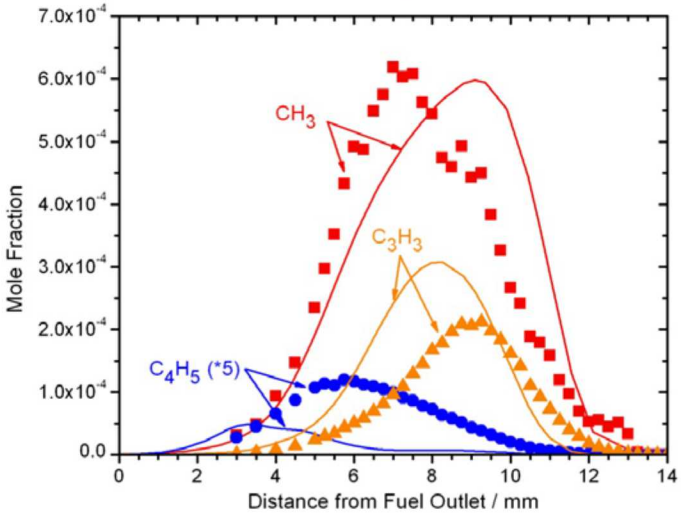
Laminar Opposed-Flow Diffusion Flames





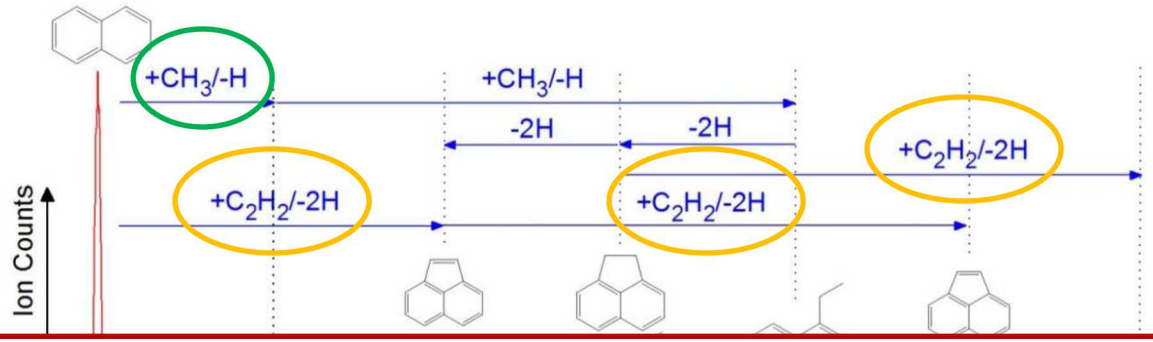


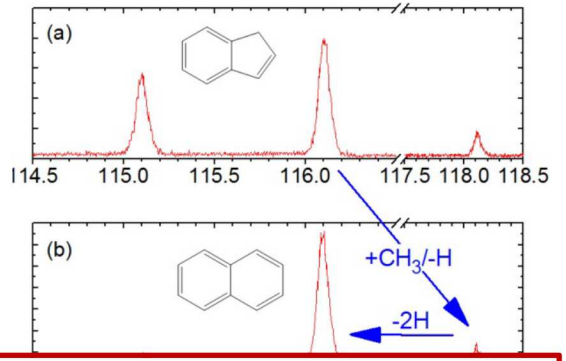


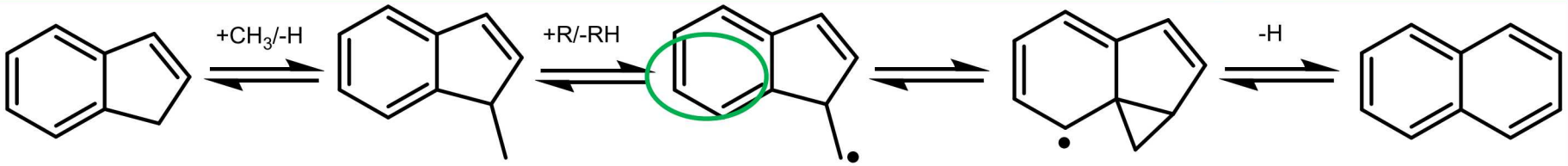


S. A. Skeen *et al., Proc. Combust. Inst.*, **2013,** 34, 1067-1075

Molecular-Growth Chemistry:
Formation of Polycyclic Aromatic Hydrocarbons



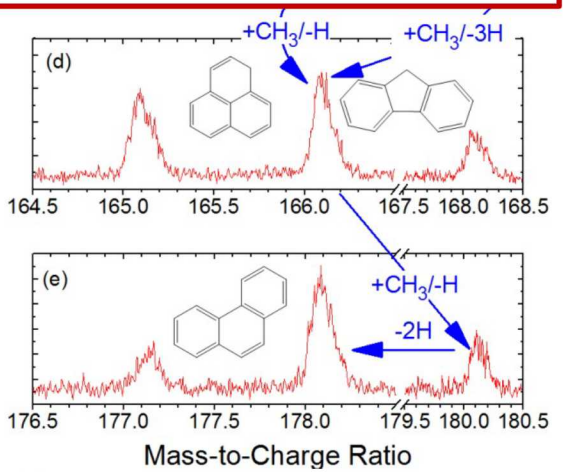




A. W. Jasper and N. Hansen, *Proc. Combust. Inst.*, **2013,** 34, 279-287

Multiple pathways are likely to contribute:

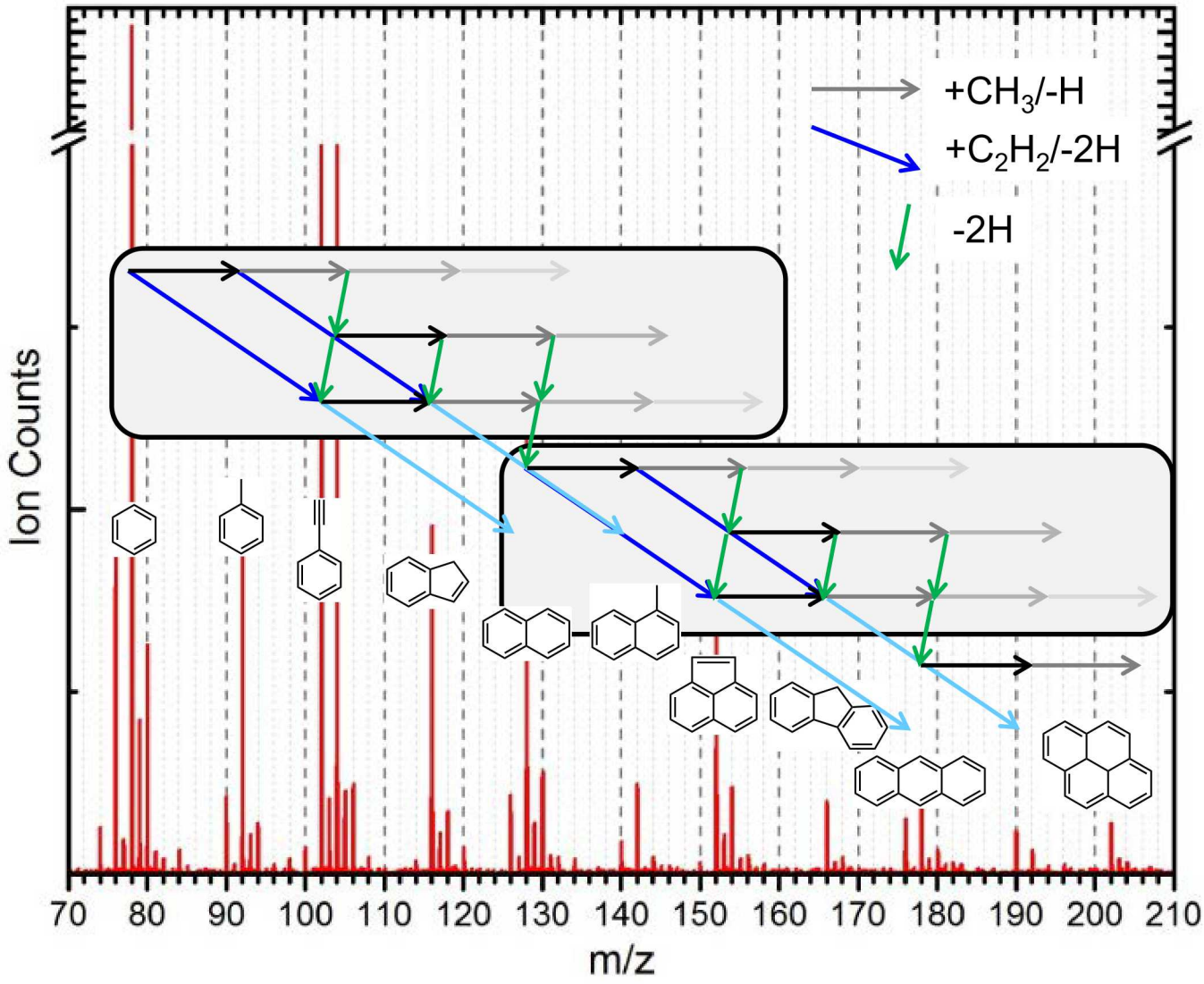
- H-abstraction-C_2H_2-addition (HACA?)
- H-abstraction-methyl-addition
  - ⇒ crucial for explaining the density of the spectra
- H-abstraction-phenyl-addition
  - ⇒ crucial for explaining fast and non-sequential growth



M. Schenk *et al., Proc. Combust. Inst.*, **2015,** 35, 1761-1769

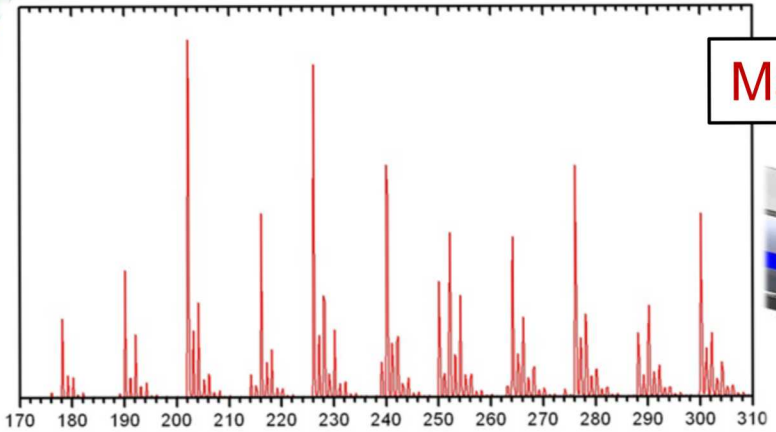
Molecular-Growth Chemistry:

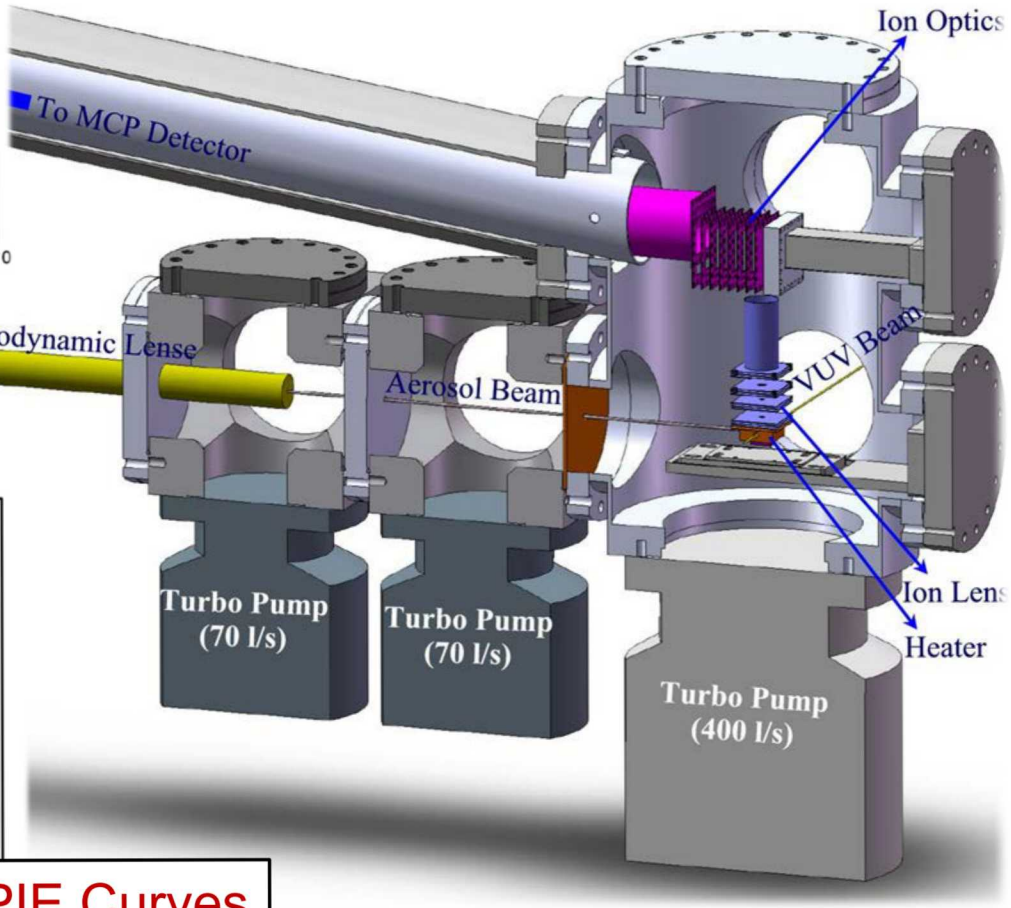
Formation of Polycyclic Aromatic Hydrocarbons

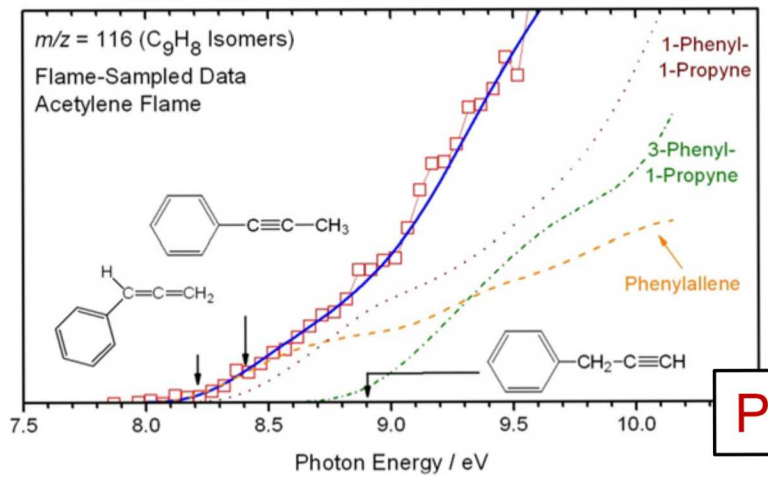


Flame-Sampling Aerosol Mass Spectrometry with VUV Single-Photon Ionization

Mass Spectra



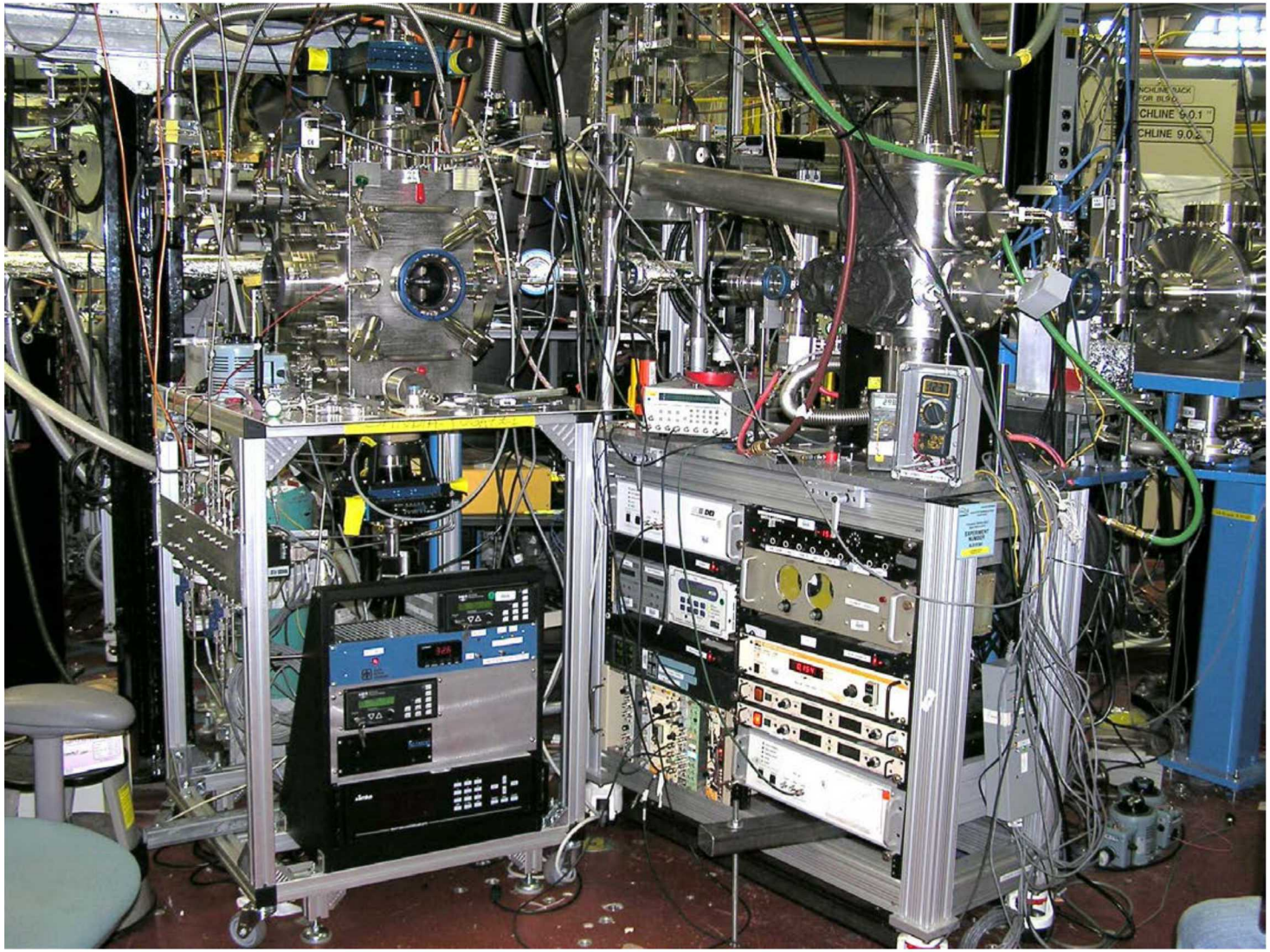




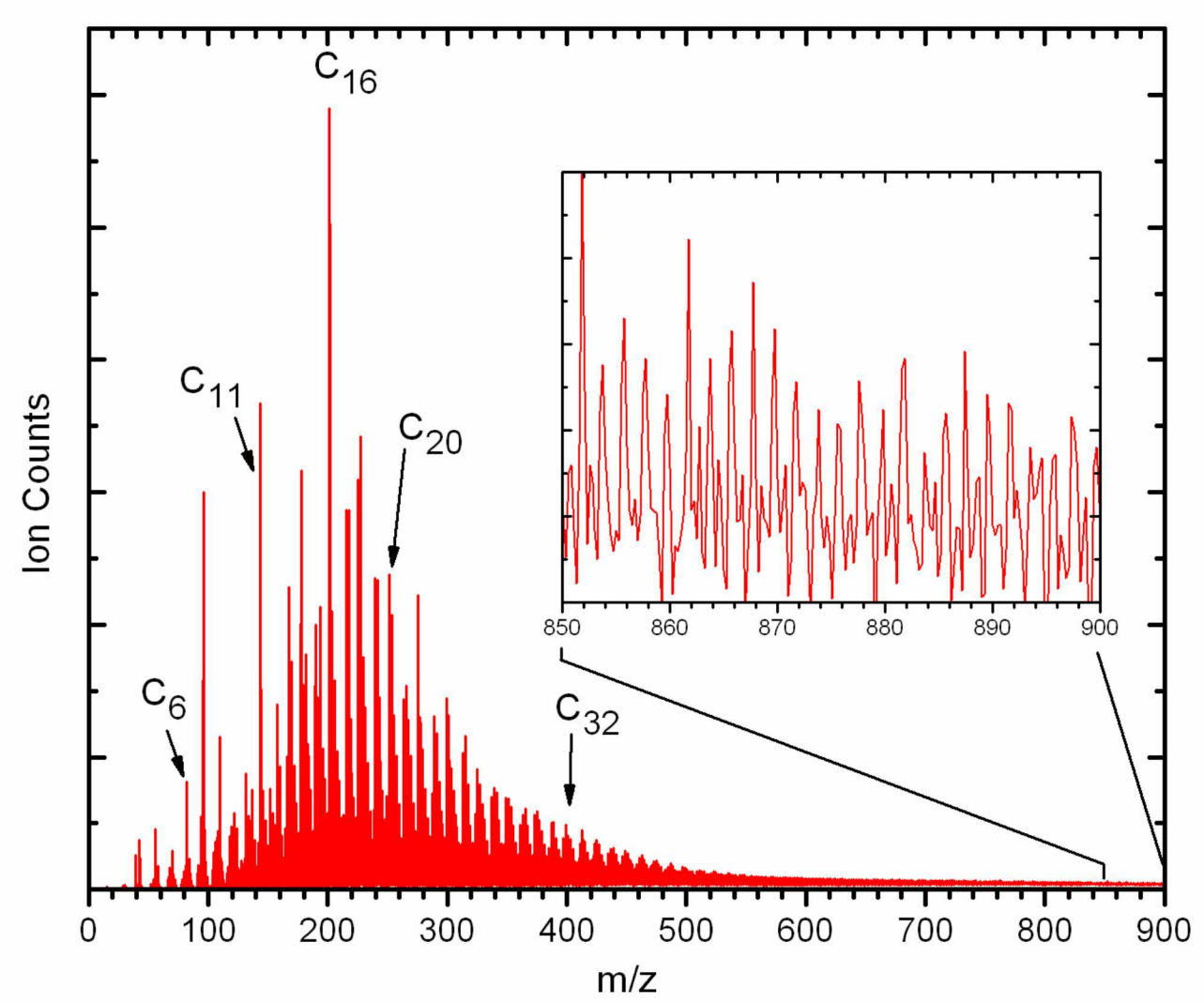
PIE Curves

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

Flame-Sampling Aerosol Mass Spectrometry with VUV Single-Photon Ionization

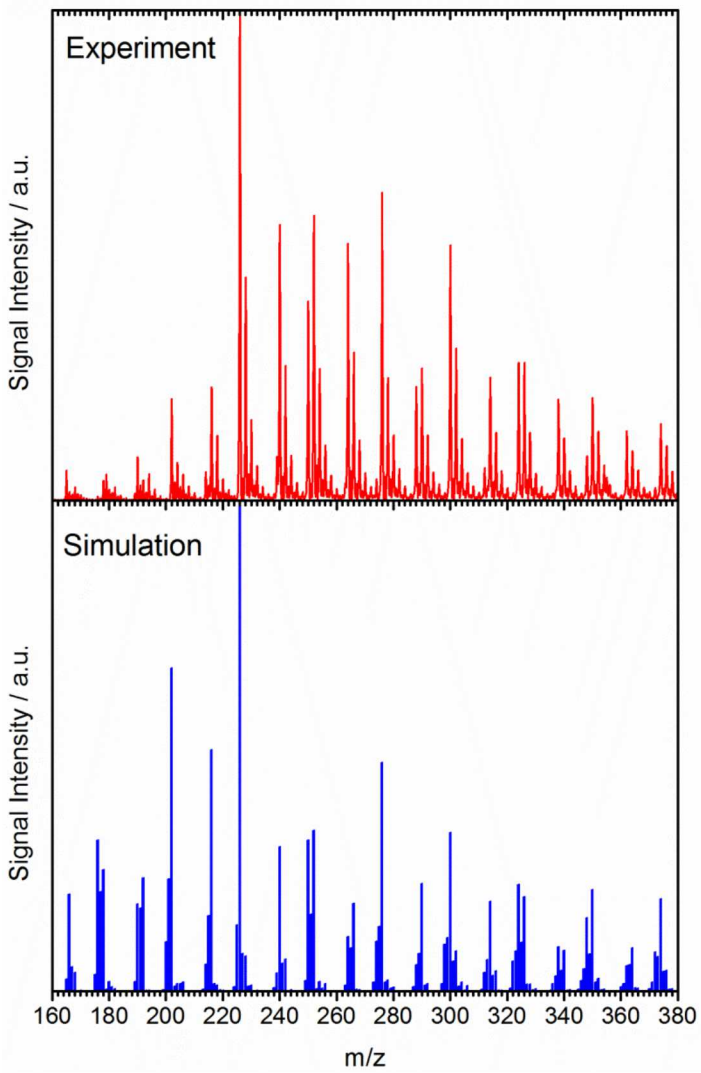


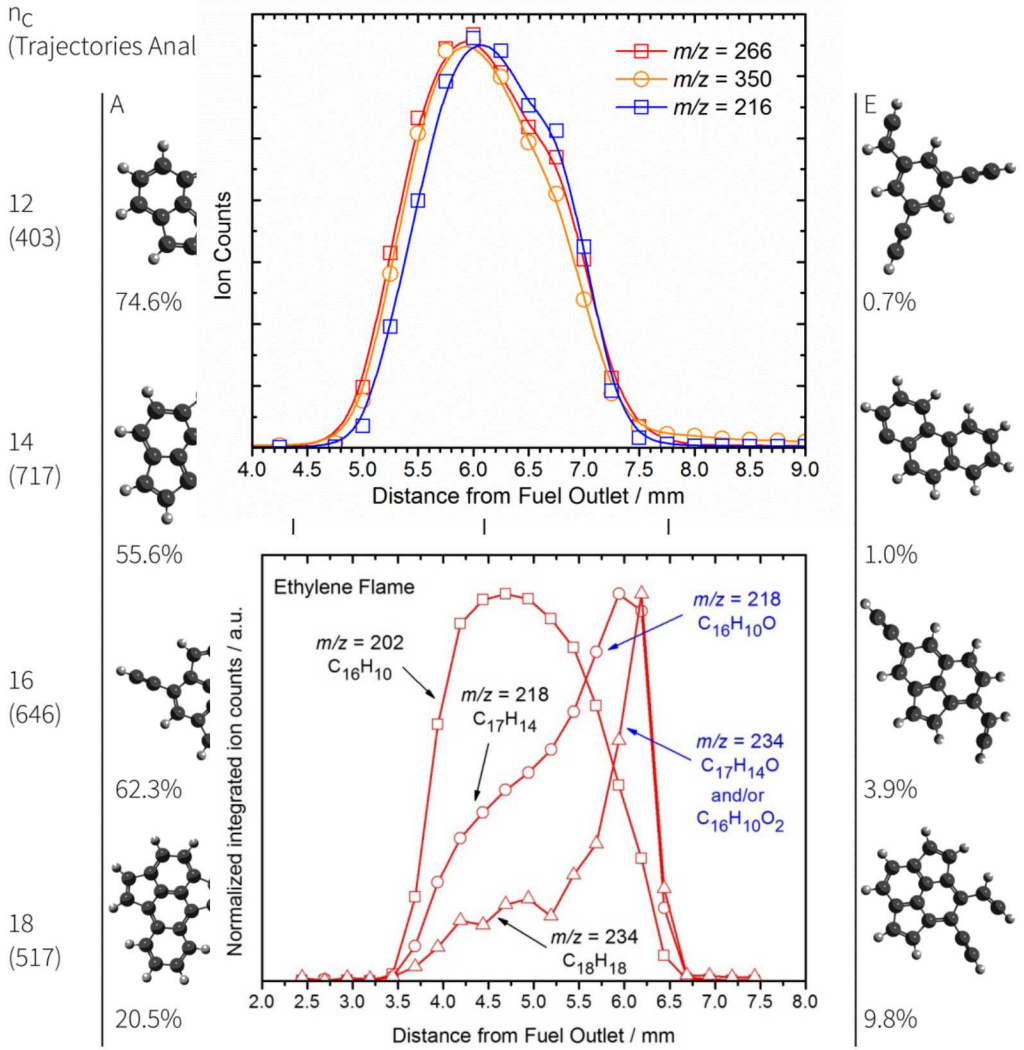
Soot Formation Chemistry Beyond Benzene



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

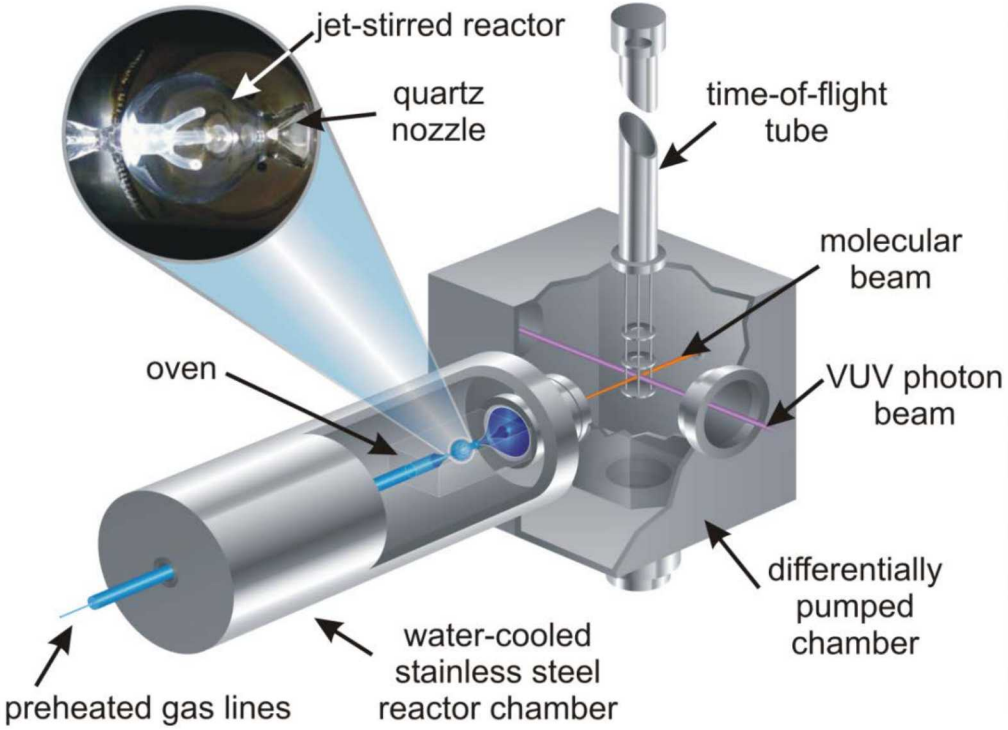
Flame-Sampling Aerosol Mass Spectrometry with VUV Single-Photon Ionization

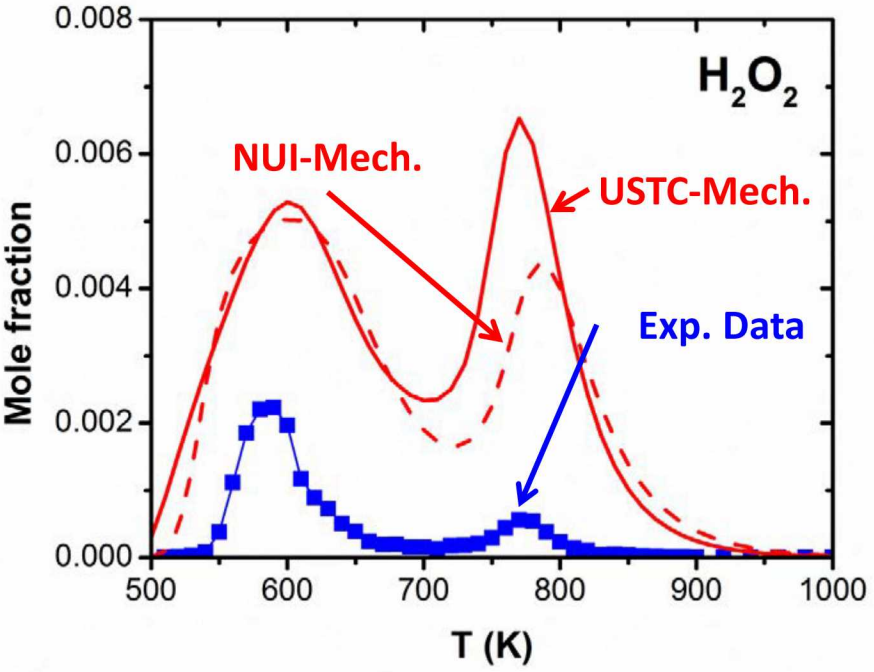




K. O. Johansson *et al., Proc. Combust. Inst.,* **2015,** 35, 1819-1826 and S. A. Skeen *et al., J. Aerosol Sci.,* **2013,** 58, 86-102

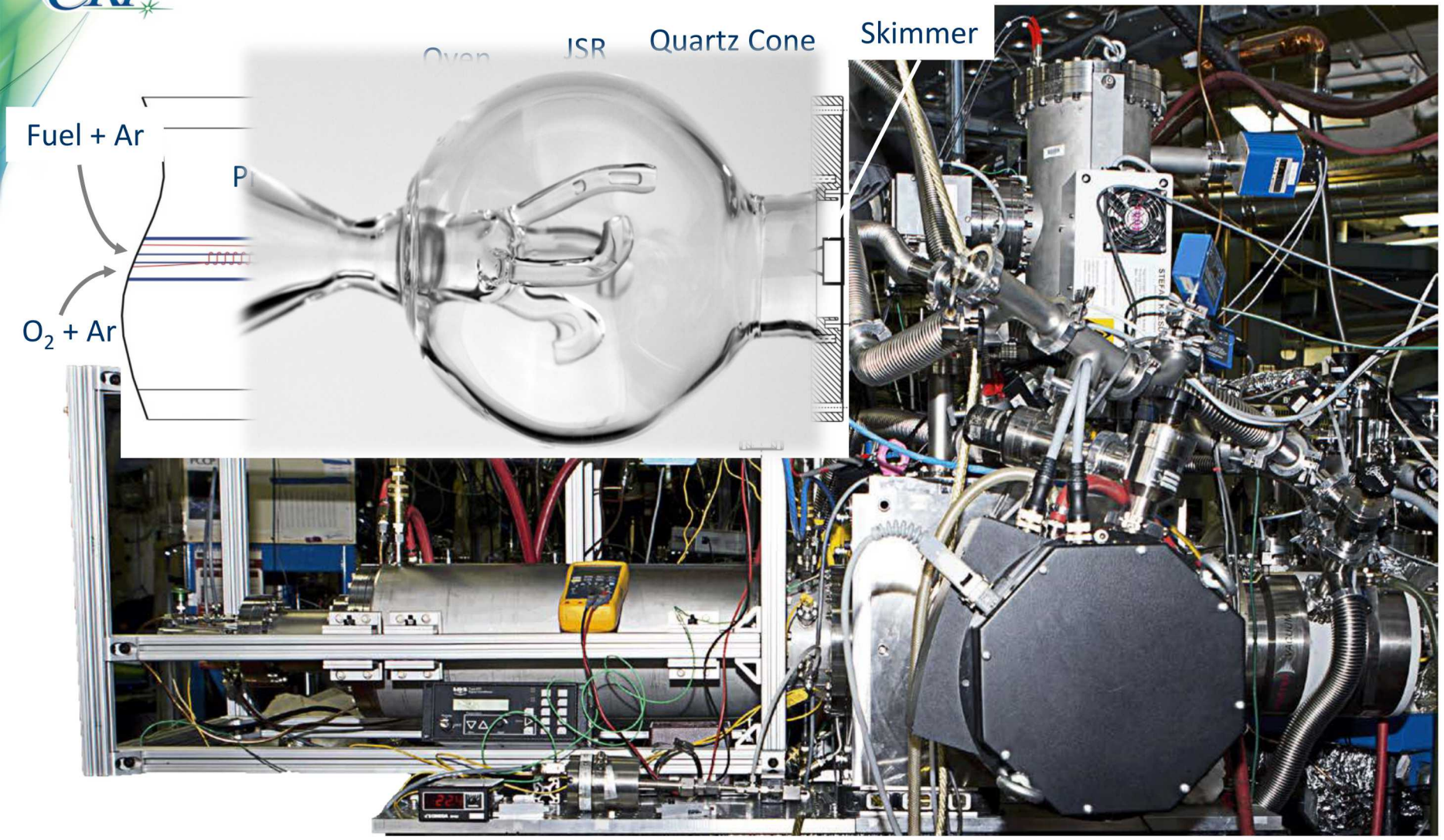
A Jet-Stirred Reactor with Molecular-Beam Sampling Capabilities





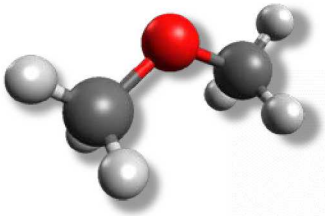
K. Moshammer *et al., J. Phys. Chem. A,* **2015,** in press

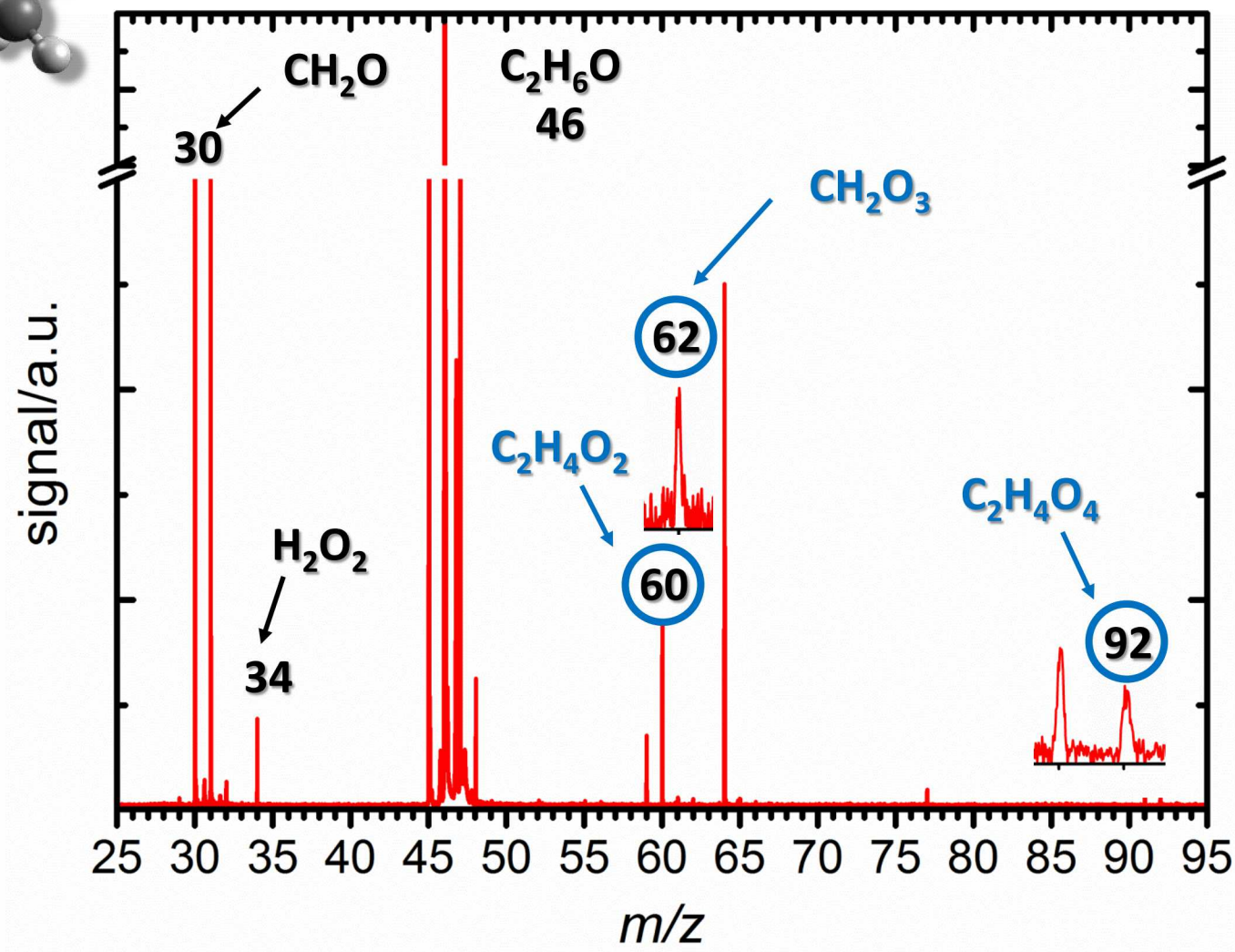
Molecular-Beam Jet-Stirred Reactor



Jet-stirred reactor system | Sampling | Product analysis

Low-temperature oxidation of DME



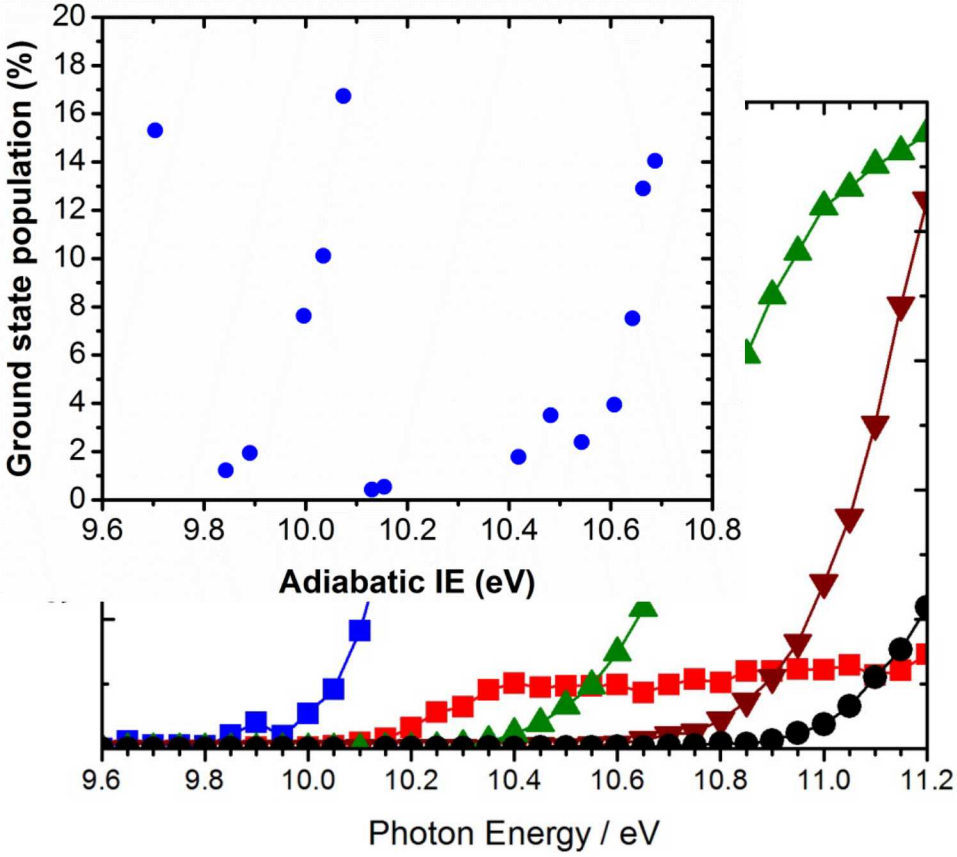


K. Moshammer *et al., J. Phys. Chem. A,* **2015,** in press

Detection of the Ketohydroperoxide

Conformer-dependent IEs for Larger Species

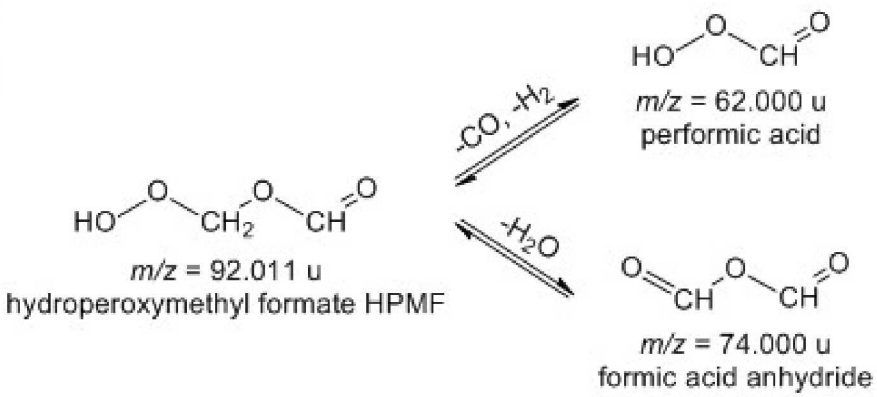
- Conformers characterized for both the neutral and cation species
- Neutral conformer populations estimated via a simple locally harmonic scheme
- Locally adiabatic IEs calculated for each conformer based on vertical excitations
- 3 conformers with ionization energies near ~10.05 eV make up 35% of the total population
- Conformer near 9.7 eV has a poor Franck-Condon overlap



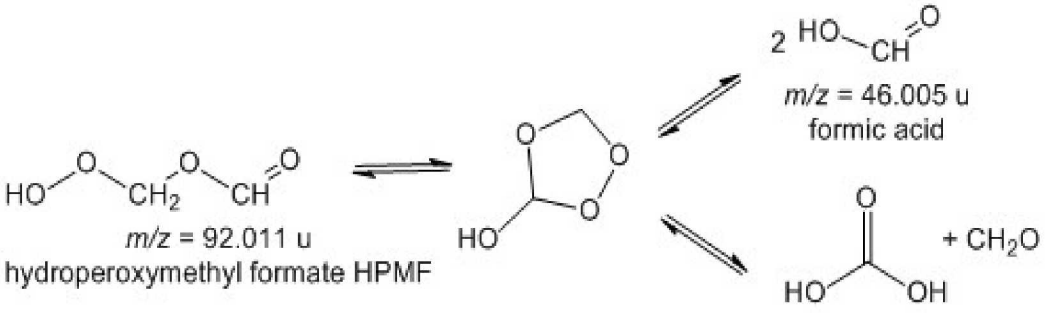
Fragment pattern gives additional evidence for the experimental detection of HPMF

K. Moshammer *et al., J. Phys. Chem. A,* **2015,** in press

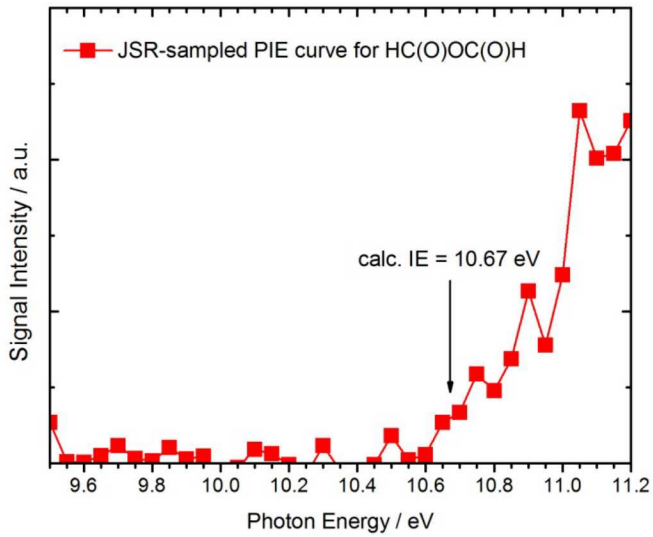
Additional Evidence for the Presence of the Ketohydroperoxide

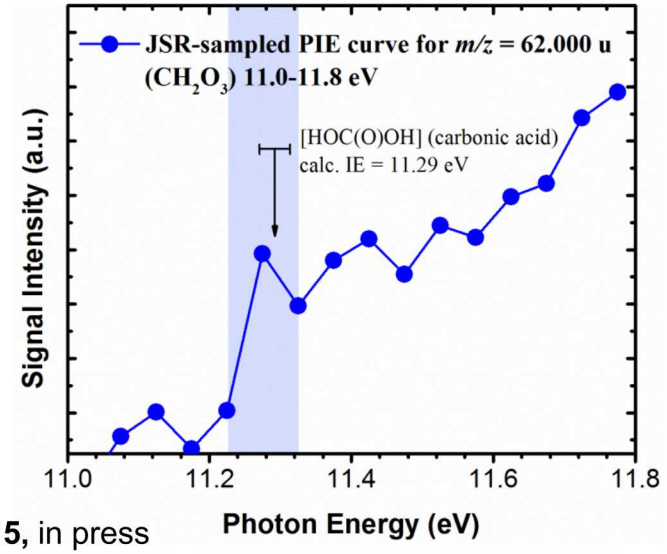


A. Andersen, E.A. Carter, *J. Phys. Chem. A,* **2003,** 107, 9463−9478.



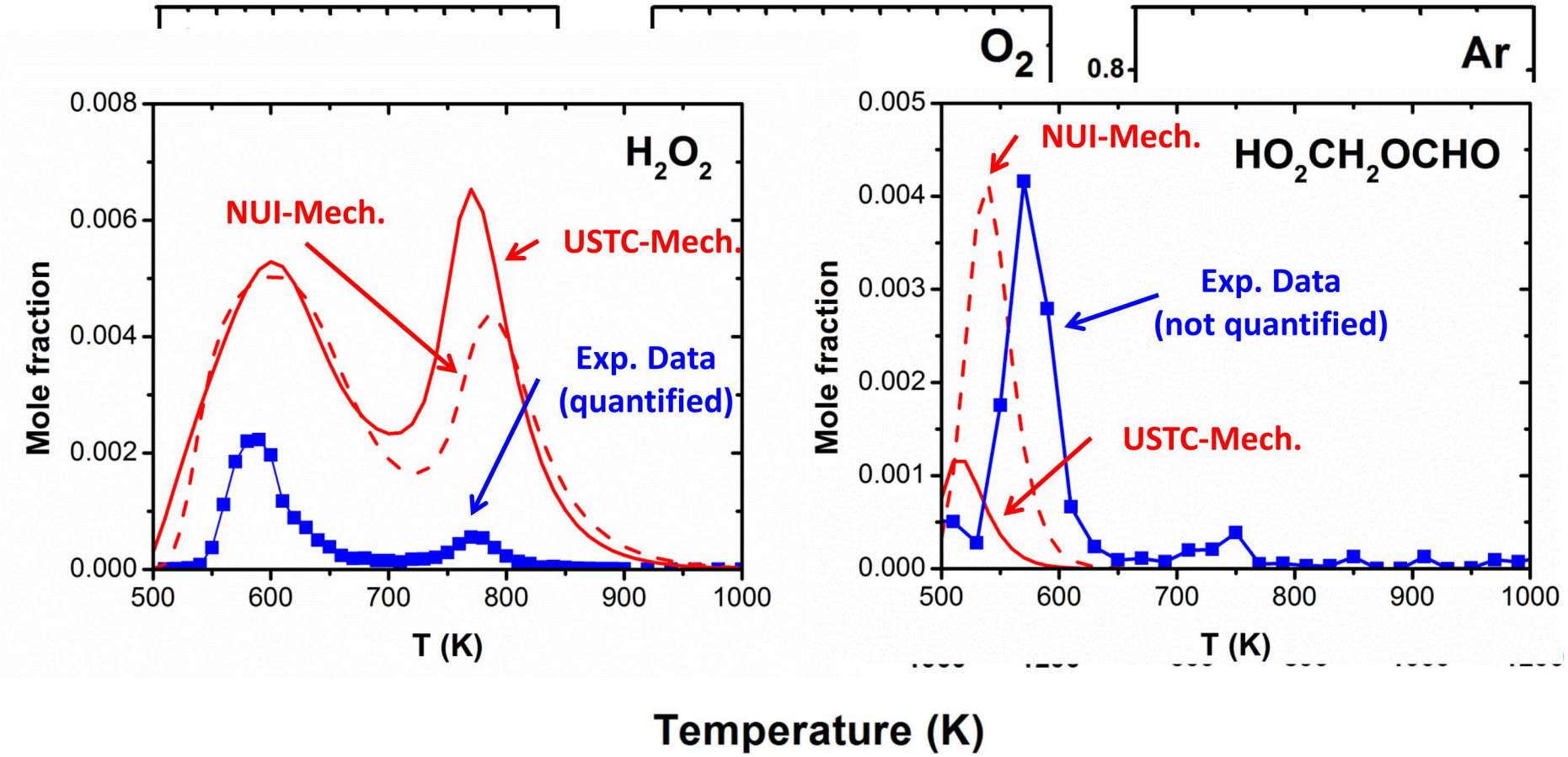
Detection of carbonic acid provides evidence for the Korcek decomposition mechanism!





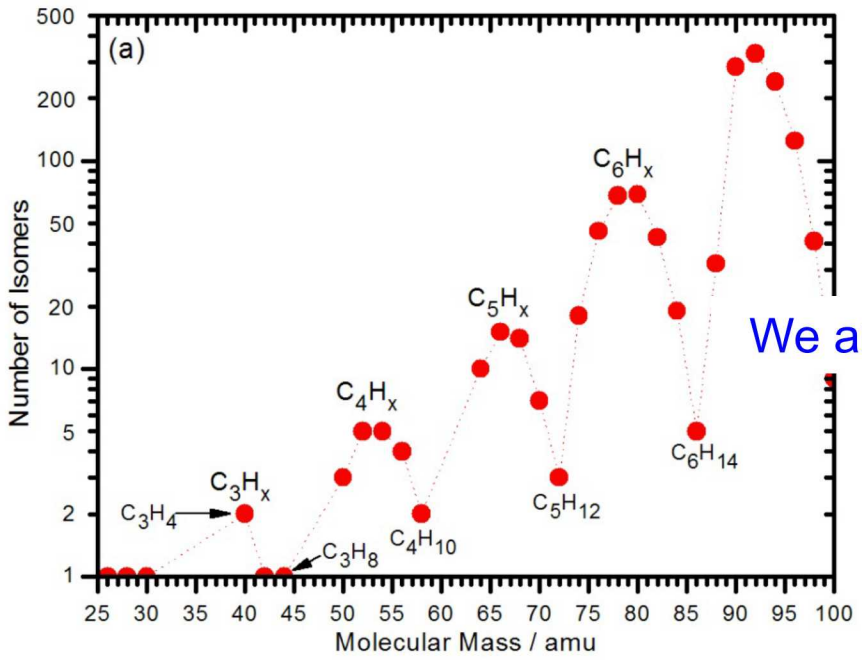
K. Moshammer *et al., J. Phys. Chem. A,* **2015,** in press

Quantification and Comparison with Model Calculations

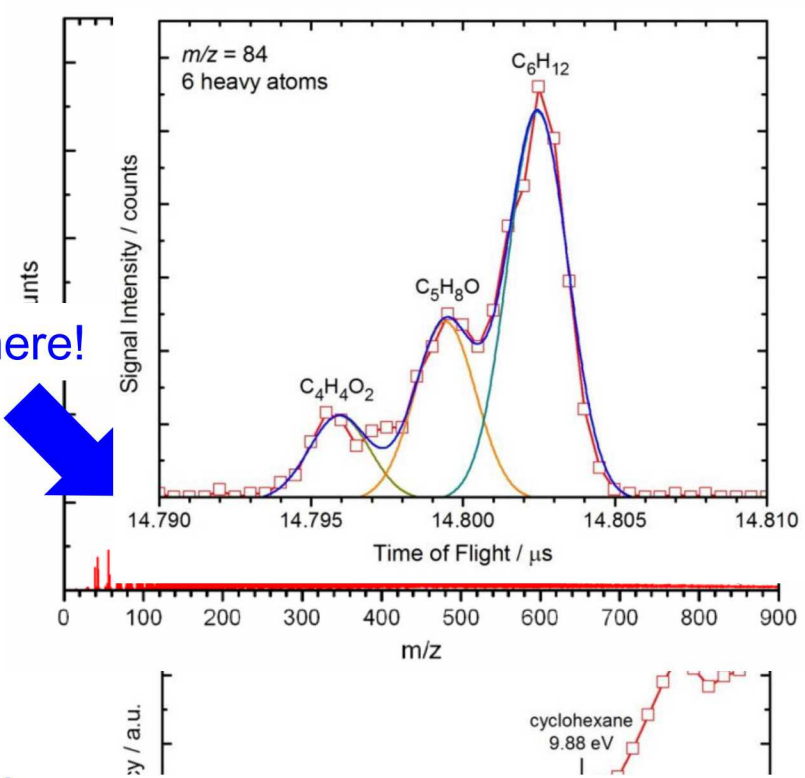


Model from: Z. Wang *et al., Combust. Flame,* **2015,** 162, 1113-1125 W. K. Metcalfe *et al., Int. J. Chem. Kin.,* **2013,** 45, 638-675

So, What Are The Problems?



We are here!



Challenges:

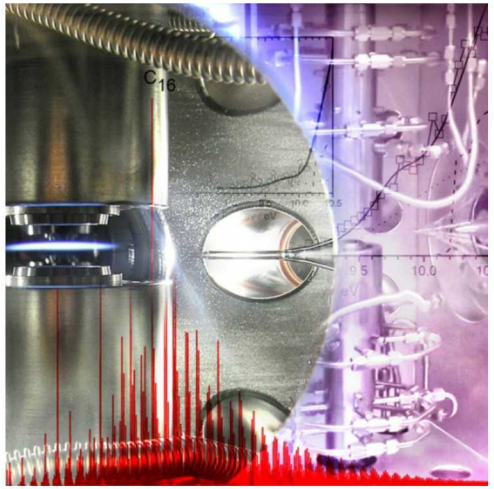
- Number of possible isomers increases with molecular size
- Smaller differences in heats of formation and similar structural features result in almost identical IE‘s and indistinguishable PIE curves
- IE‘s and PIE curves may not be known and need to be measured/calculated

Chemical Specificity!

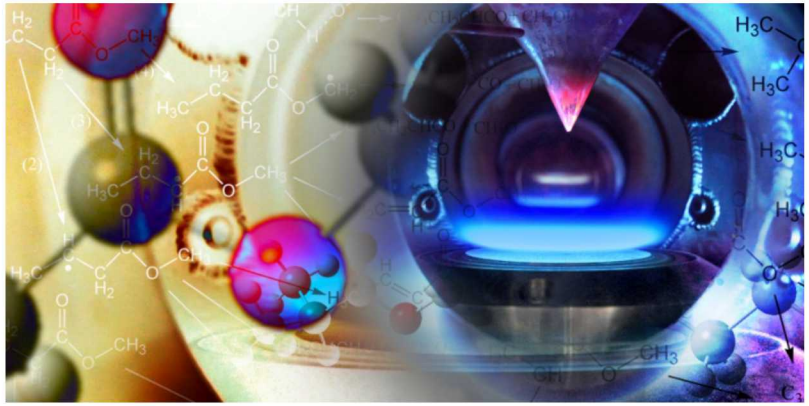
But, how much detail is needed?

Summary and Conclusions

- Four different experiments are currently performed in my group to guide the development of combustion chemistry models:
  - ✓ Low-pressure premixed flames
  - ✓ Low- and atmospheric-pressure counterflow diffusion flames
  - ✓ Flame-sampling aerosol mass spectrometry
  - ✓ Jet-stirred reactor



- Benzene Formation Chemistry is well understood.
- Our understanding of the molecular-weight growth processes remains vague and many different pathways are likely to contribute.
- Large kinetic models cannot be used to learn anything about the flame chemistry.
- More reliable experimental data are necessary to guide model development.
- New JSR capabilities provide detailed validation targets for low-temperature combustion chemistry modeling.



Thank You!

Flame Experiments:

- K. Kohse-Höinghaus (Universität Bielefeld, Germany)
- B. Yang (Tsinghua University, Beijing, China)
- T. Kasper (Universität Duisburg-Essen, Germany)
- S. M. Sarathy and S. Chung (KAUST, Saudi Arabia)
- P. R. Westmoreland (North Carolina State University)

Flame-Sampling Aerosol Mass Spectrometry:

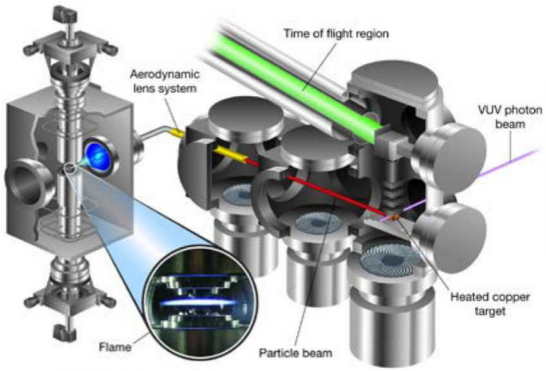
- H. A. Michelsen (Sandia National Laboratories)
- A. Violi (University of Michigan, Ann Arbor)
- K. R. Wilson (Lawrence Berkeley National Laboratory)

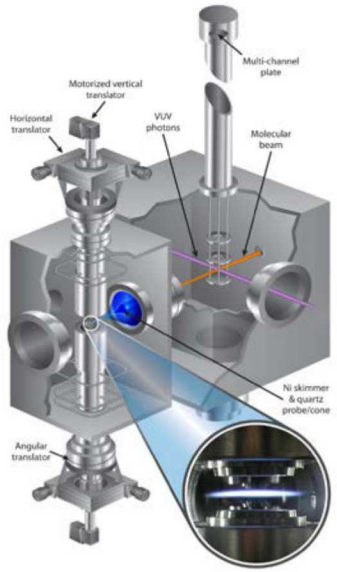
Jet-Stirred Reactor Experiments:

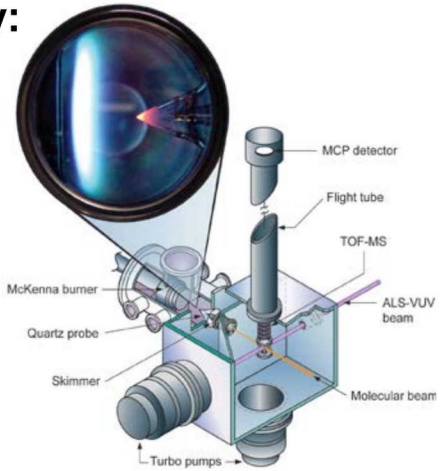
- S. R. Leone and D. M. Popolan-Vaida (UC Berkeley)
- S. M. Sarathy (KAUST, Saudi Arabia)
- K. Kohse-Höinghaus (Universität Bielefeld, Germany)
- P. Dagaut (CNRS Orleans, France)
- J. Yu (Princeton University)
- C. A. Taatjes (Sandia National Laboratories)

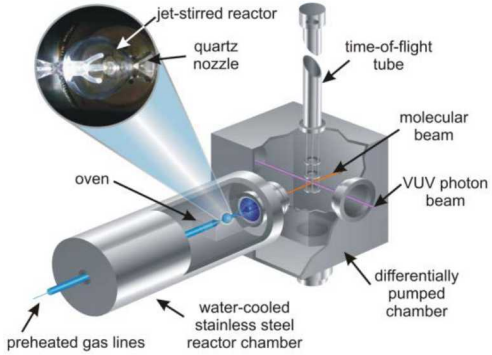
Postdocs:

- K. Moshammer, K. O. Johansson, A. Lucassen, and S. A. Skeen









Modeling and Theoretical Support:

- A. W. Jasper (Sandia National Laboratories)
- S. J. Klippenstein and J. A. Miller (Argonne National Laboratory)
- W. H. Green (Massachusetts Institute of Technology)
- F. Mauß and L. Seidel (Universität Cottbus, Germany)

Thank You!

- Office of Basic Energy Sciences, US Department of Energy