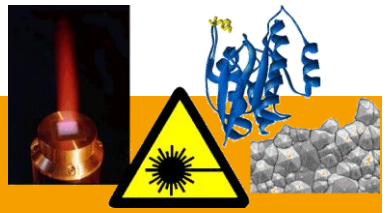


# The role of advanced diagnostics in combustion *chemistry* research

**Katharina Kohse-Höinghaus**

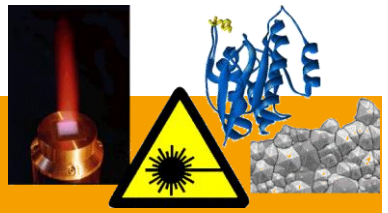
*Bielefeld University, Germany*

**Fei Qi**

*USTC, China*

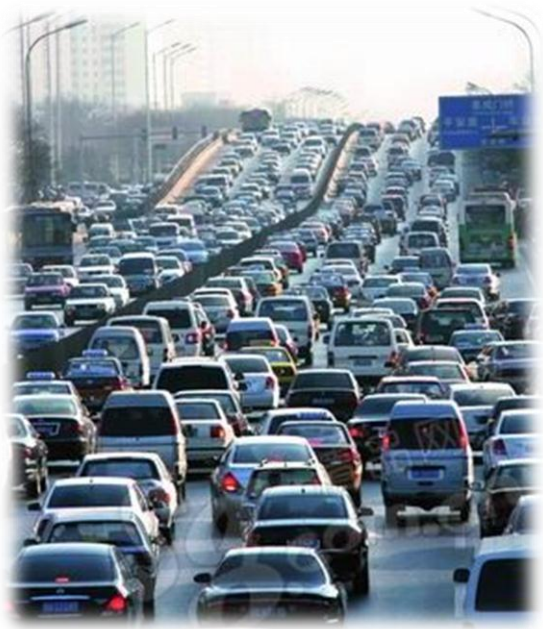
**Nils Hansen**

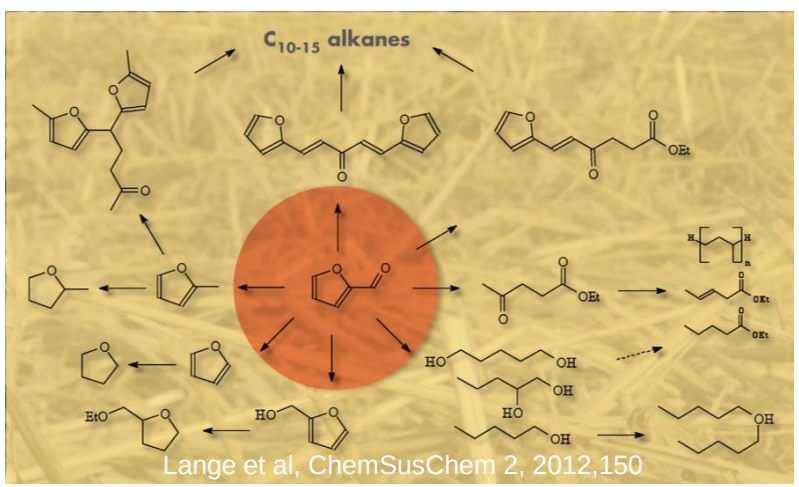
*Sandia National Lab, USA*



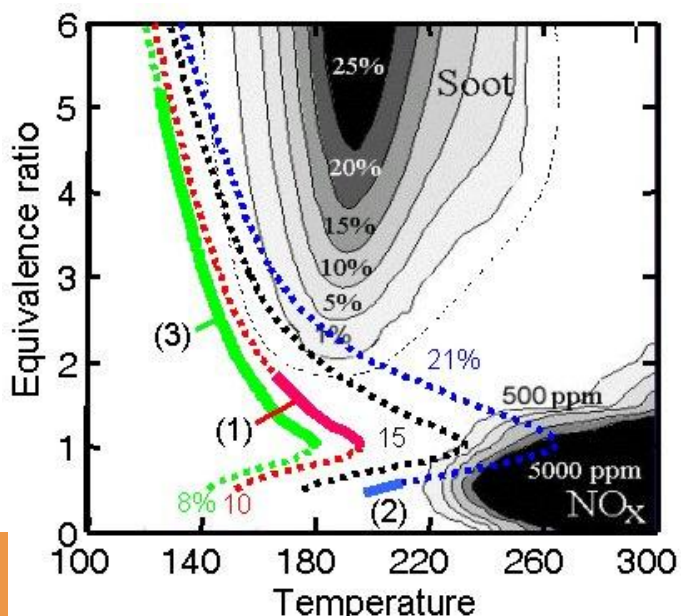
# Introduction: The problem

- **Clean combustion: high efficiency, low emissions**
- **Alternative transportation fuels: new chemistry**
- **Novel combustion regimes: influences of p, T, phi, mixture**





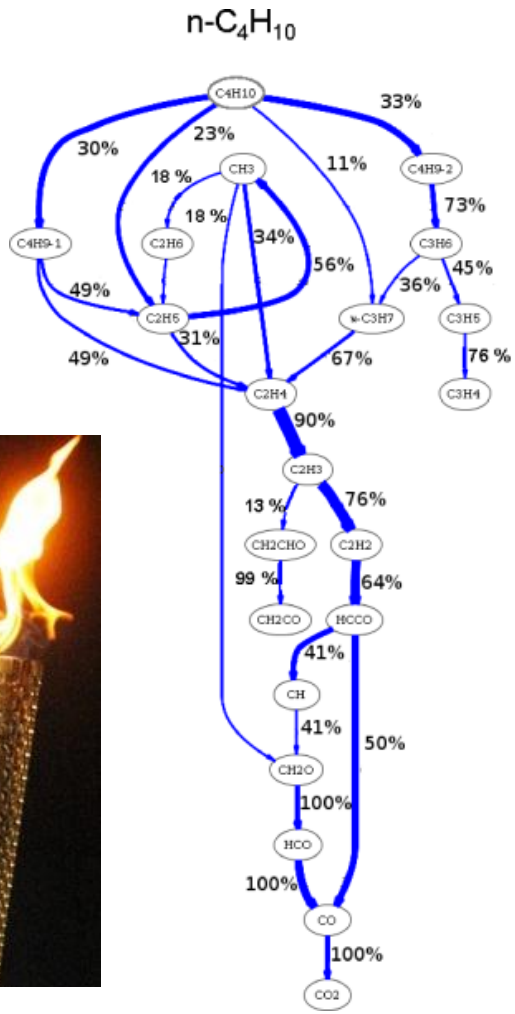
Lange et al, ChemSusChem 2, 2012,150

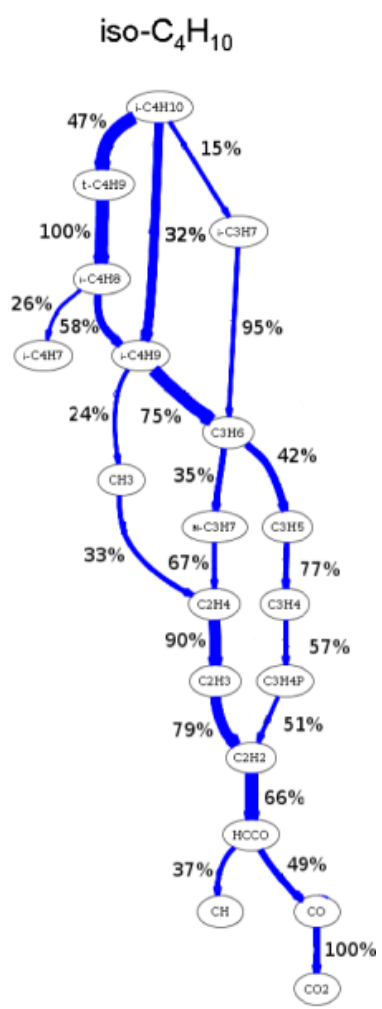



**Needed: Systematic knowledge on combustion chemistry**

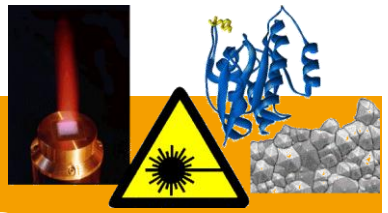
# Probing flame chemistry: Wanted

- **In situ information on unknown species mix: identification.**
- **Large dynamic range of mole fractions, labile species.**
- **Quantitative set of concentration-reaction time profiles.**
- ***Example*: butane combustion, ~ 40 species.**



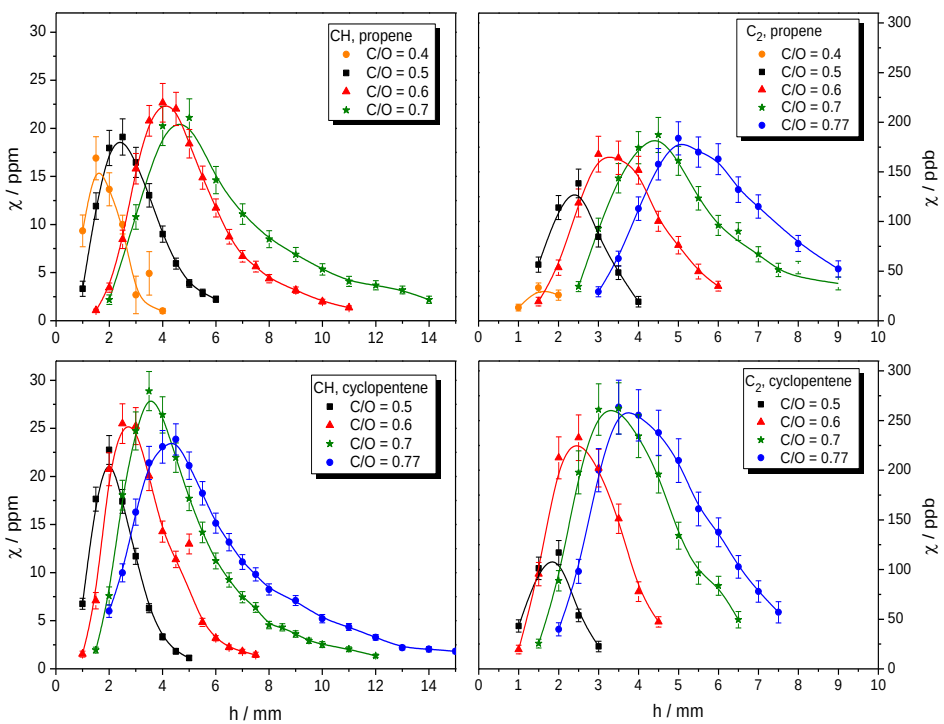




Oßwald et al, Z Phys Chem 225, 2011,1029



# Probing flame chemistry: laser diagnostics

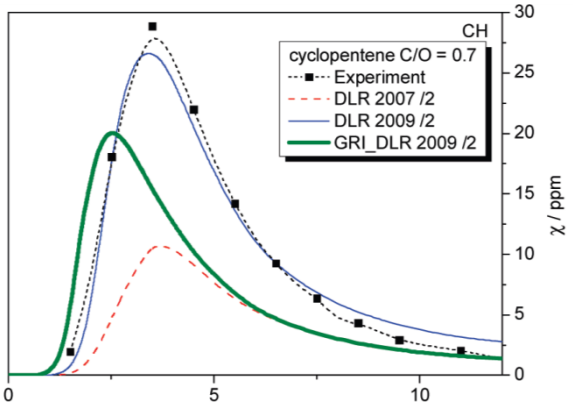
- **Laser spectroscopy: Raman, LIF, CRDS, IR absorption, etc.**
- **Quantitative, non-intrusive, *small* molecules: *e.g.* CH, $C_2$**
- **Not suitable for complete flame analysis**

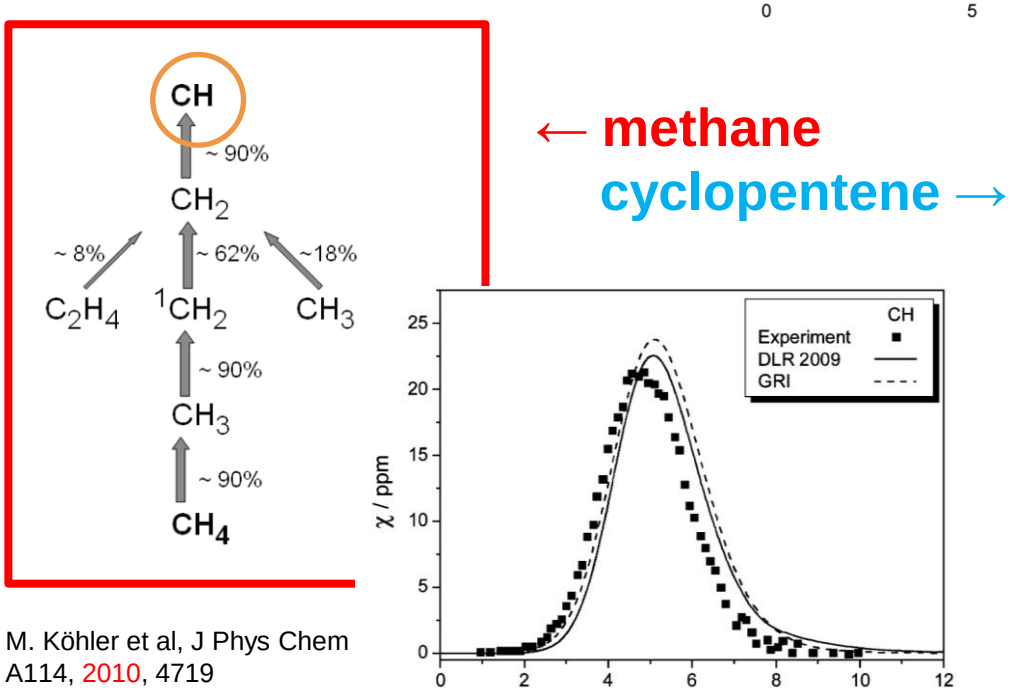




M. Köhler et al, J Phys Chem A114, 2010, 4719

# Small species and chemical mechanisms

- **One species *cannot* validate mechanisms.**
- **Small species are at *end* of reaction chain.**



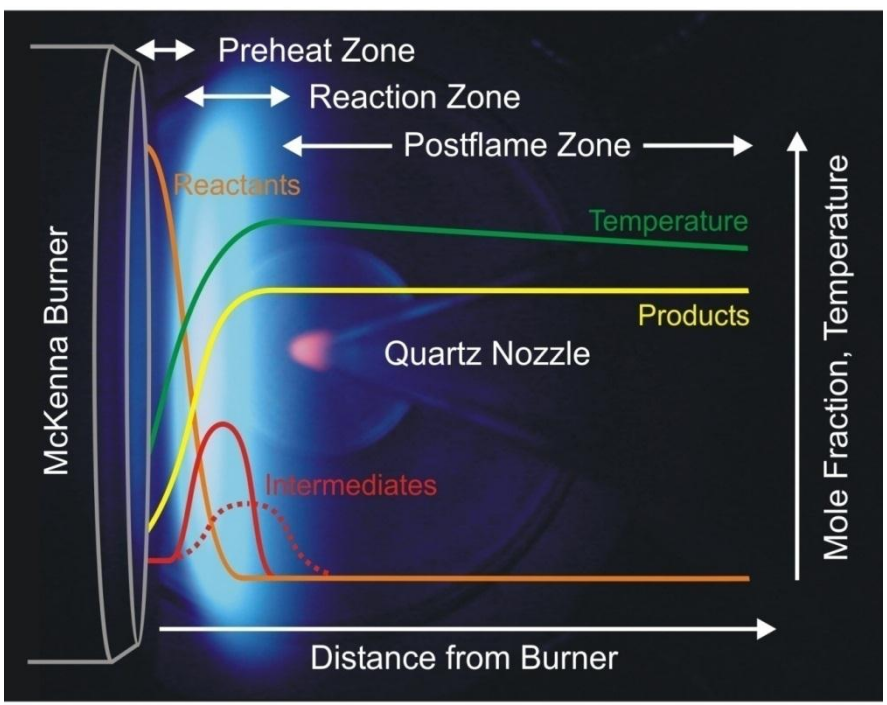


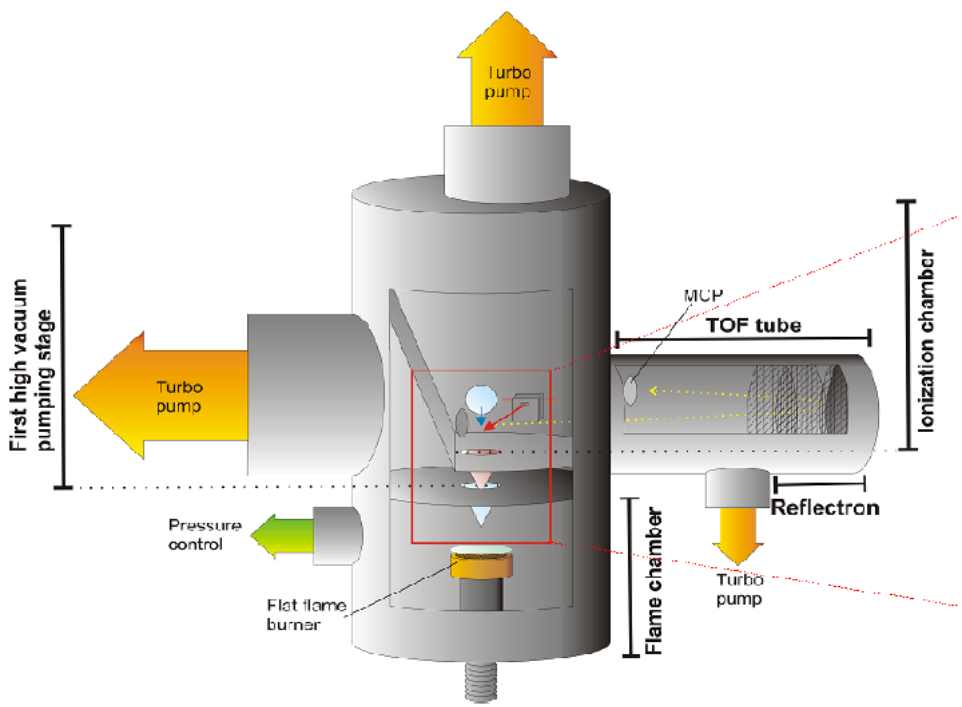


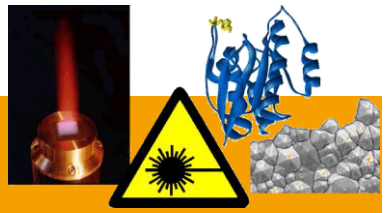
M. Köhler et al, J Phys Chem A114, 2010, 4719

# Probing flame chemistry: mass spectrometry

- **Molecular-beam mass spectrometry (MBMS):**
- ***Complete*** **species set (?!); structure-sensitive, isomers**
- **Quantitative –** ***but*****: fragmentation, overlaps, sampling, ….**

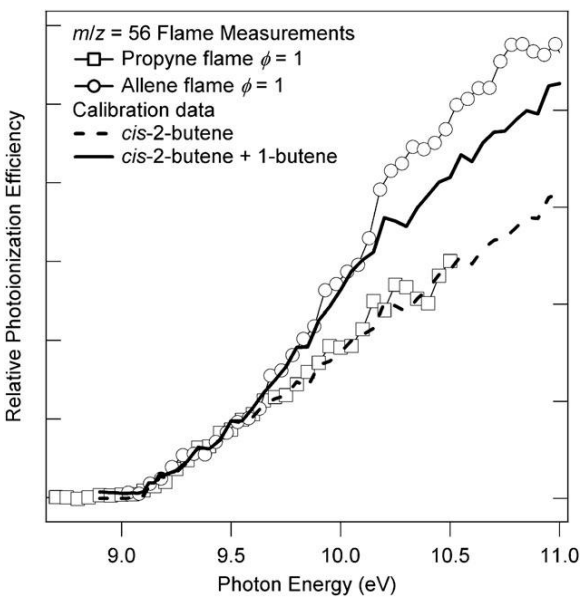


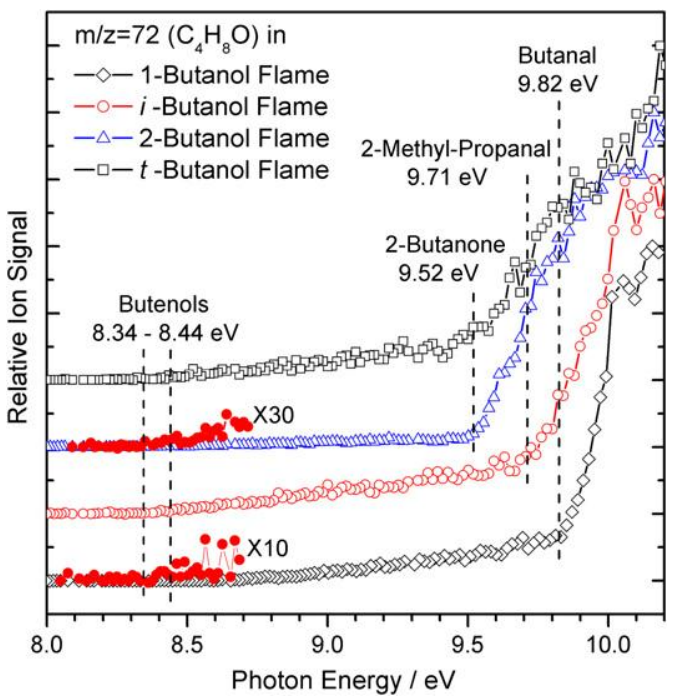


# Species- and structure-selective analysis

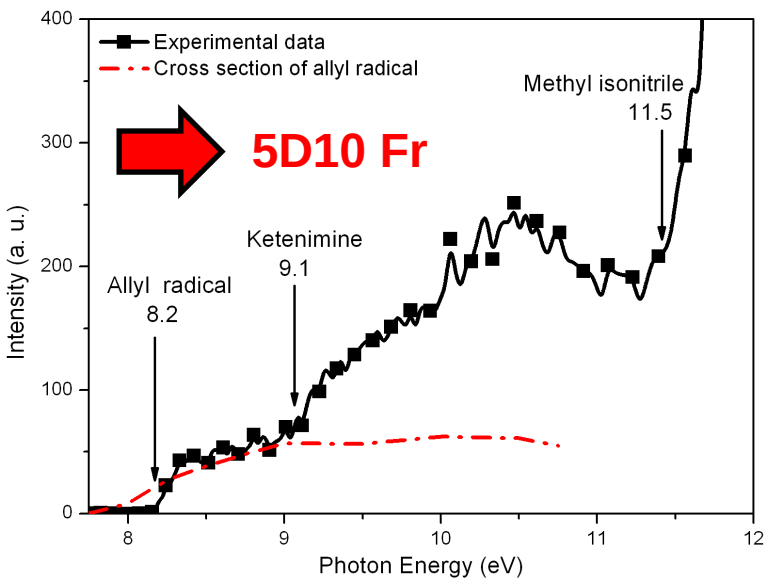
- **Tunable VUV single-photon PI-MBMS:**
- **Distinction of intermediates in C/H, C/H/O, and C/H/O/N systems**
- **Mass & photoionization efficiency (PIE) spectra as discriminators**




C.A. Taatjes et al, PCCP 10, 2008, 1

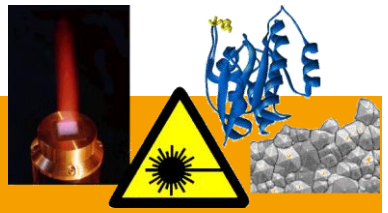



B. Yang et al, Combust Flame 148, 2007,198



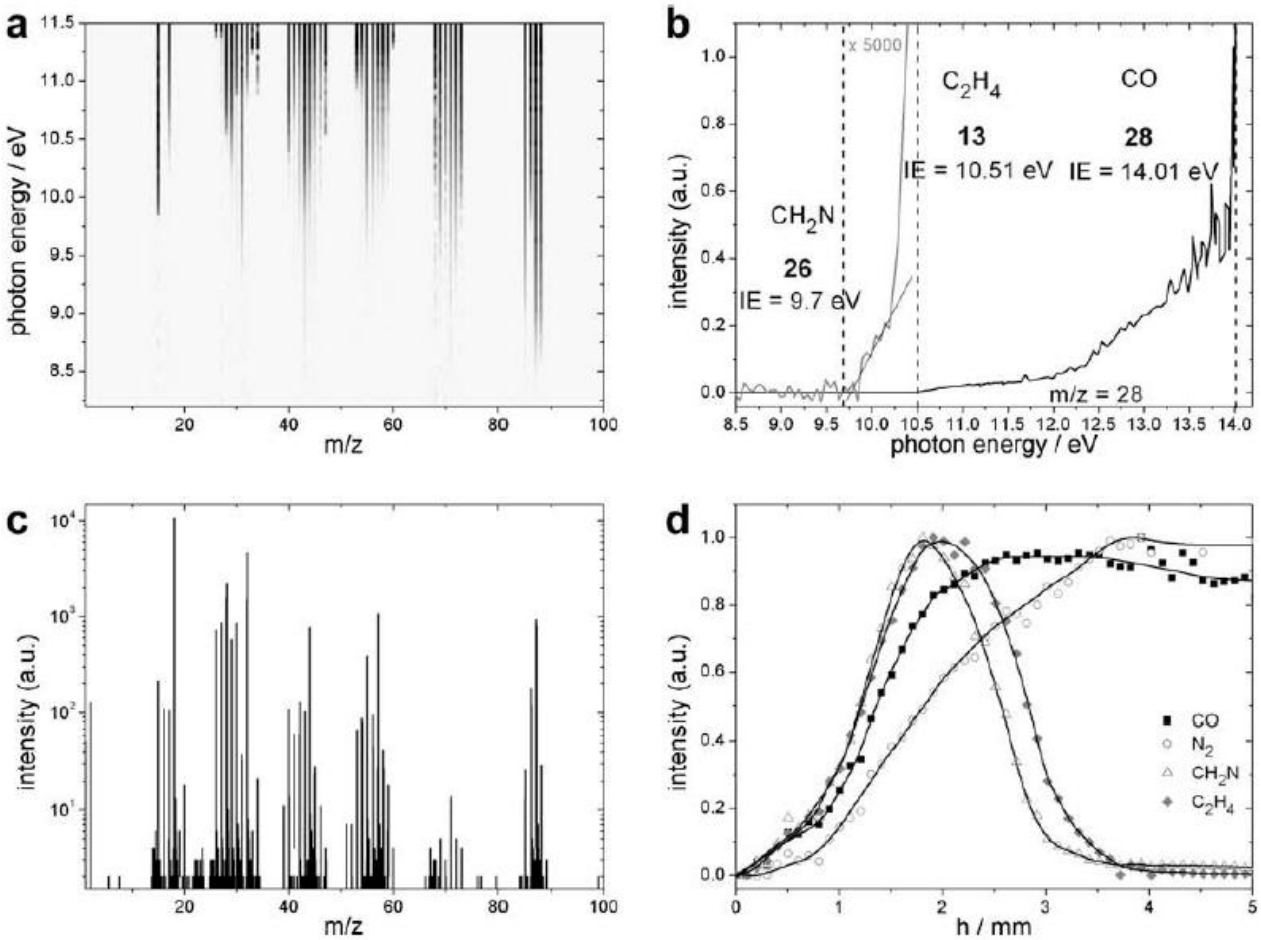

m/z=41, $C_3H_5$, $C_2H_2NH$, $CH_3NC$ ($CH_3CN$)

A. Lucassen et al, PROCI 34, 2012

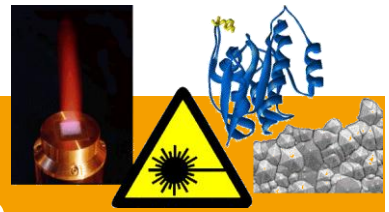


# Combining high mass + energy resolution

- **Fuel complexity: hydrocarbons → oxygenates → fuel-N.**
- **More elements need better *mass separation:* →EI-MBMS.**
- **Fuel structure and intermediate mix need *isomer separation:* →PI-MBMS.**
- ***Example:* morpholine flame.**

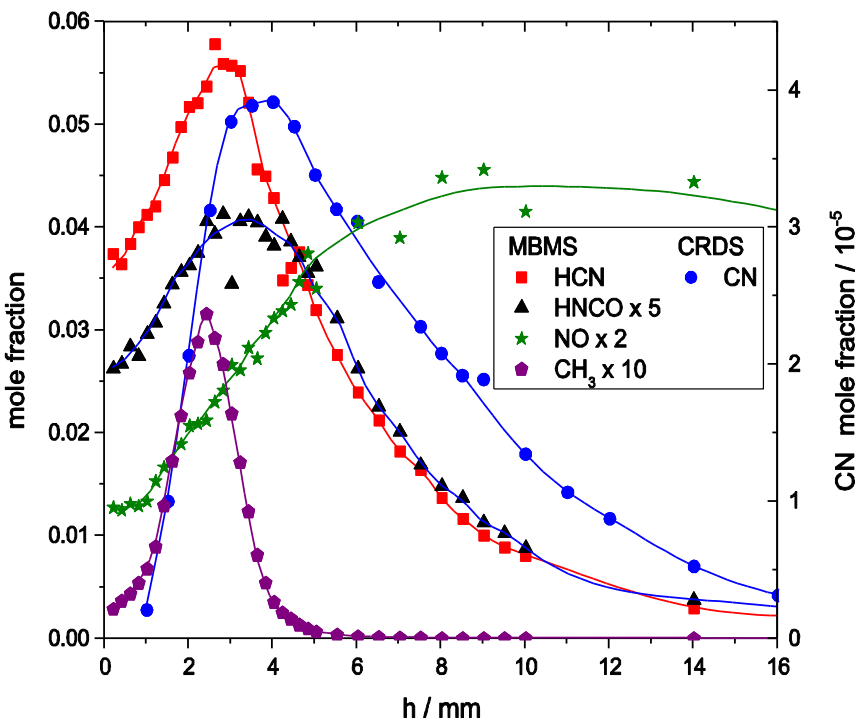


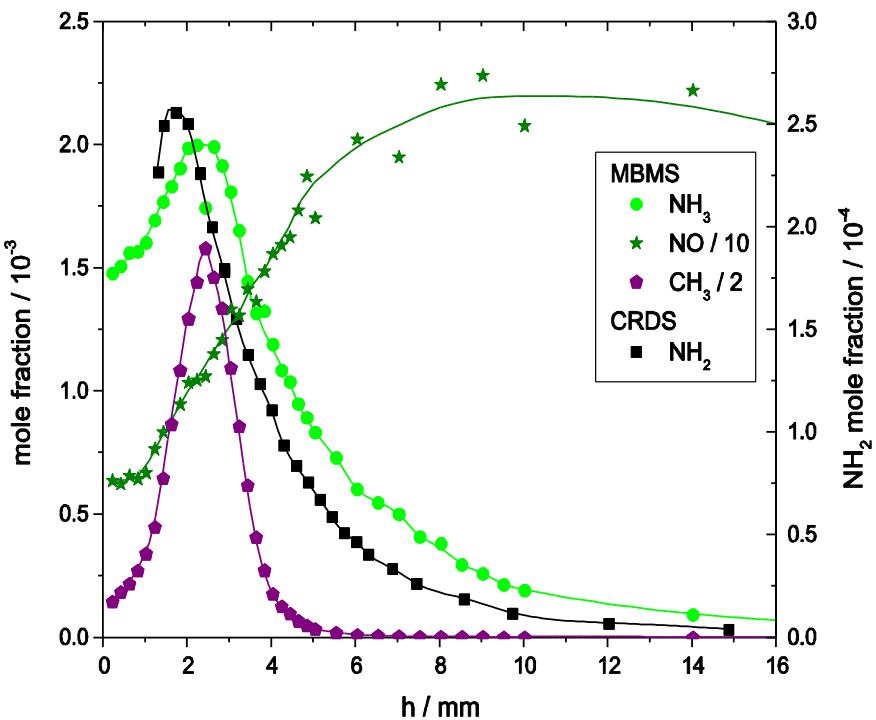

A. Lucassen et al, PROCI 32, 2009,1269



# Combining EI-MBMS+PI-MBMS+LIF+CRDS

- MBMS results for HCN, $NH_3$, NO, HNCO, $CH_3$, ...
- LIF temperature measurement
- CRDS results for $NH_2$, CN, CH, OH, …

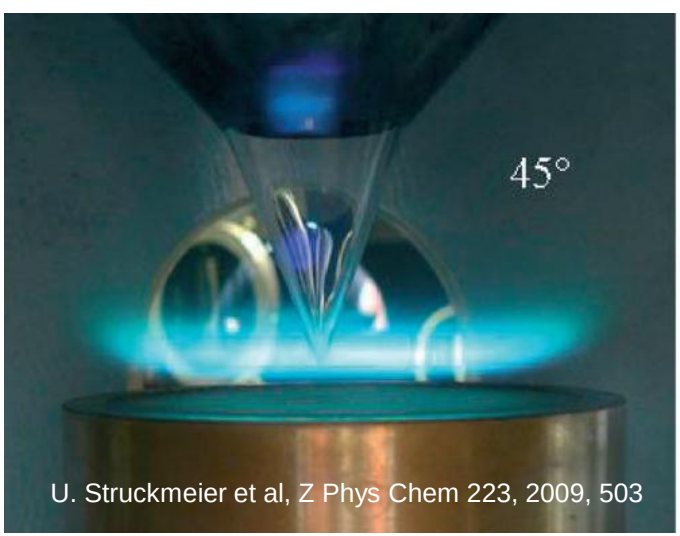


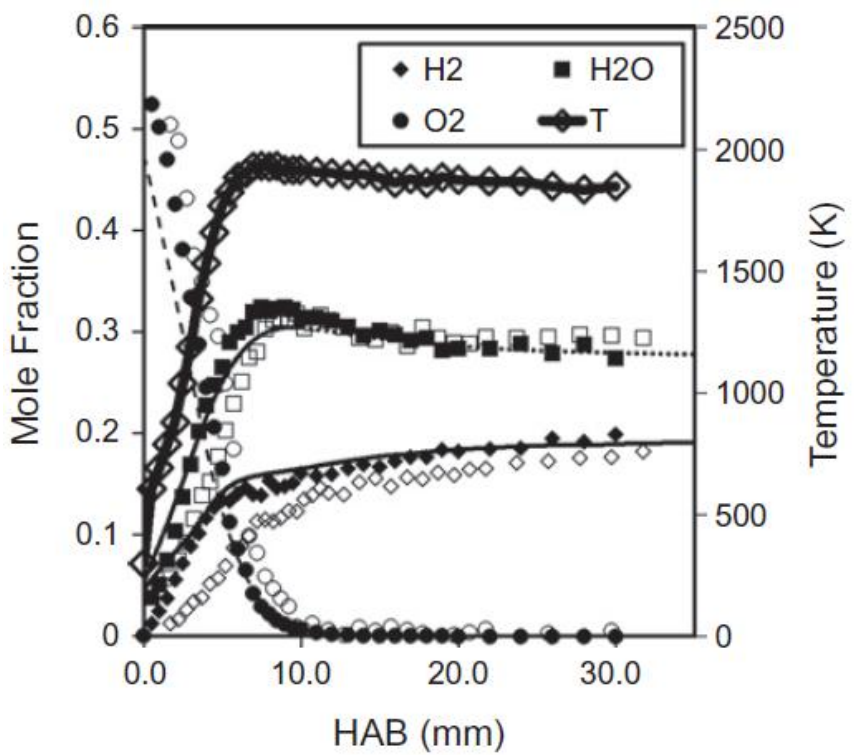

P. Nau et al, Exp Fluids 32, 2009,1269

# Experiment vs. model: (un)disturbed T profile

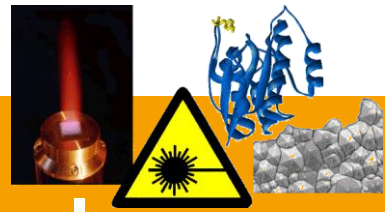
- ***T profile*** **for optical or MBMS sampling must be considered in comparison with models – no shifts!**
- ***Example:*** **butanol flames.**




U. Struckmeier et al, Z Phys Chem 223, 2009, 503

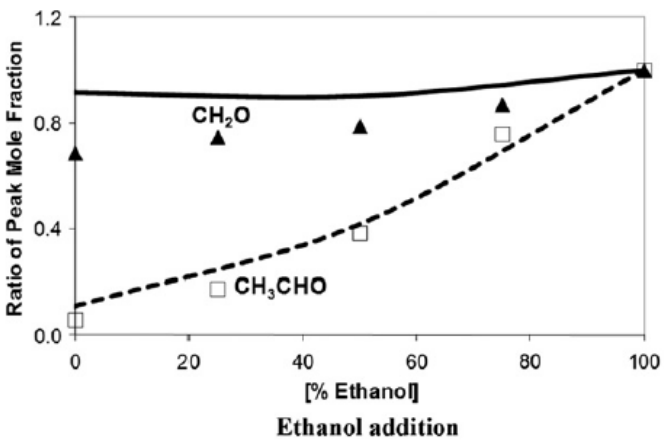


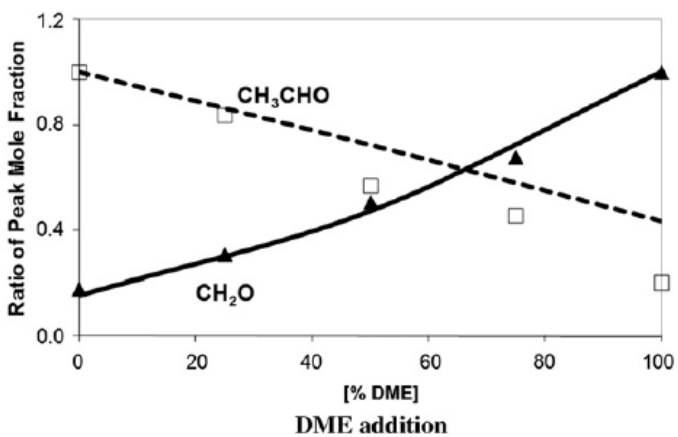

M. Sarathy et al, Combust Flame 159, 2012, 2028

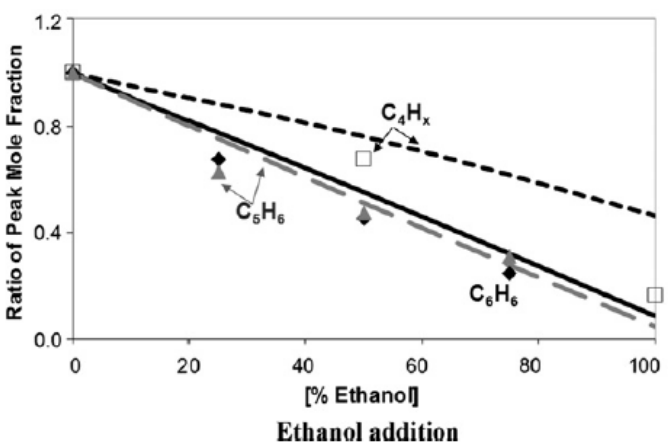


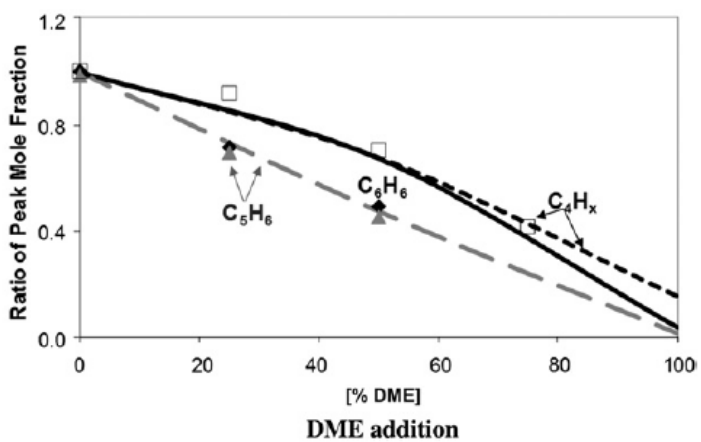
# New combustion details: study of isomeric fuels

- **Quantitative but *relative* species measurement is more forgiving.**
- **Chemical trends are more obvious.**
- **Model can probe mechanistic differences.**
- ***Example:* ethanol and DME addition to propene.**

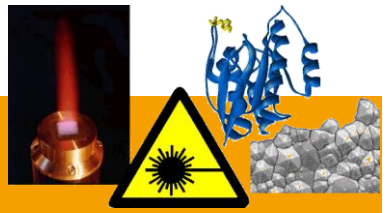


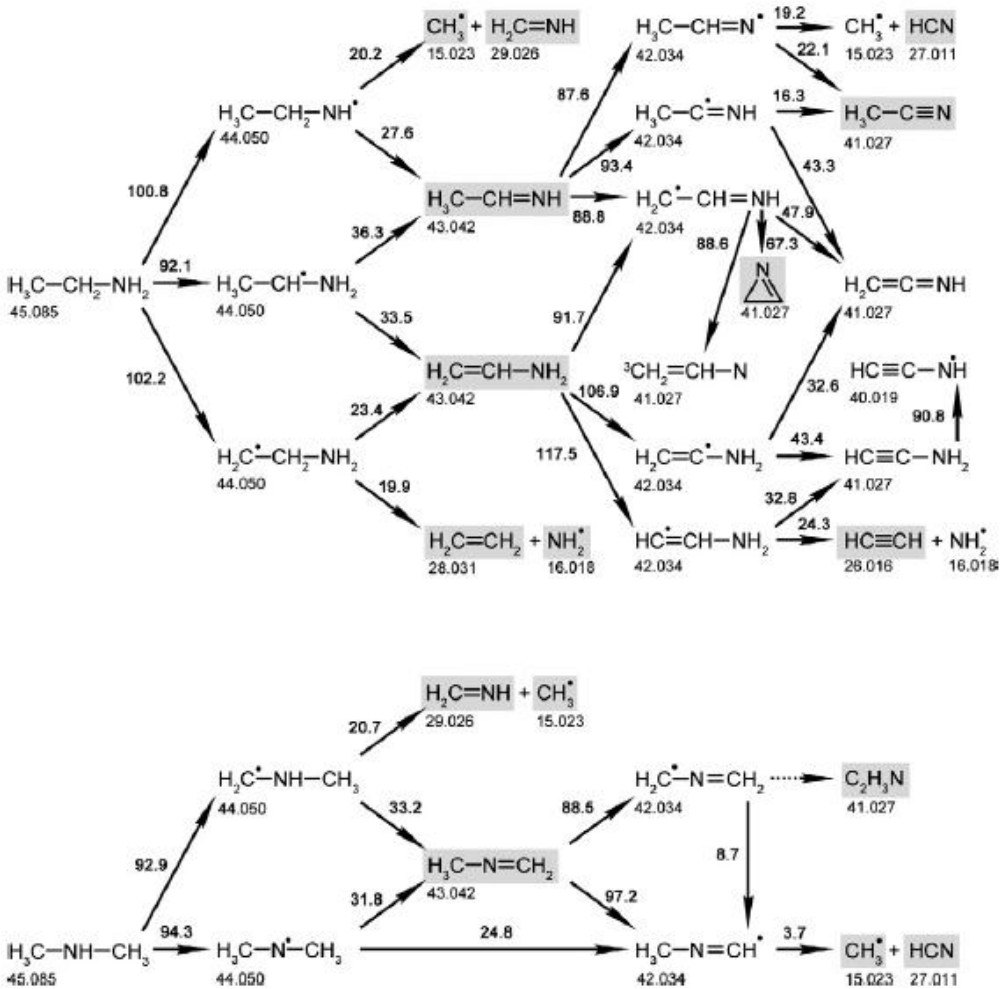




A. Frassoldati et al, Combust Flame 158, 2011, 1264



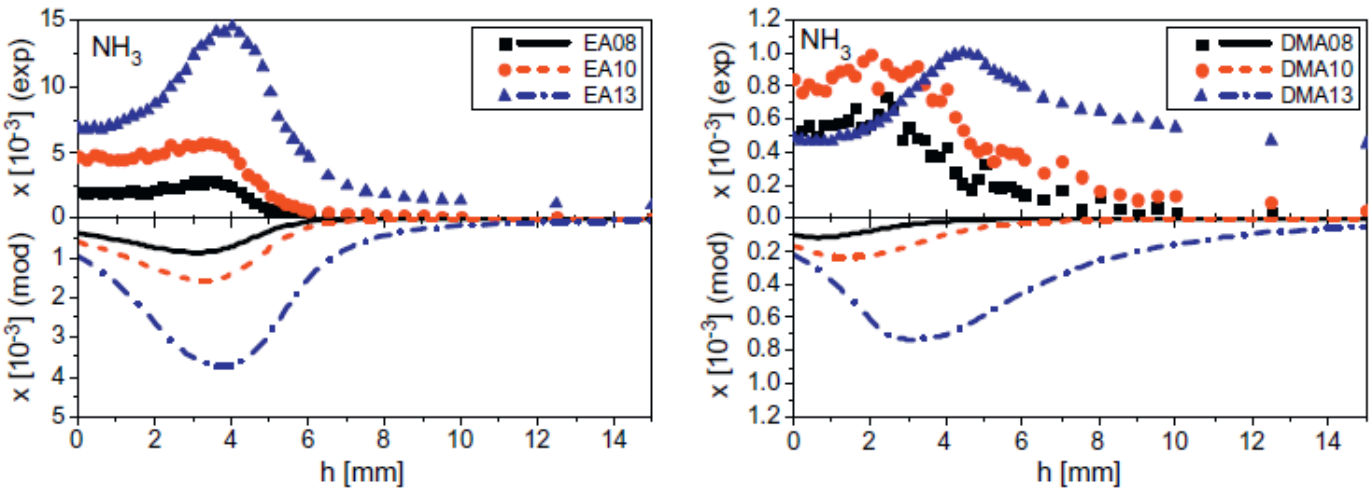
# Fuel-N conversion: biomass components




- ***Isomeric*** **fuel decomposition pathways different.**
- **Ethylamine break-down suggests early $NH_3$ formation.**
- **Substantial HCN mole fractions expected for both fuels.**
- ***Example:*** **ethylamine and dimethylamine combustion.**

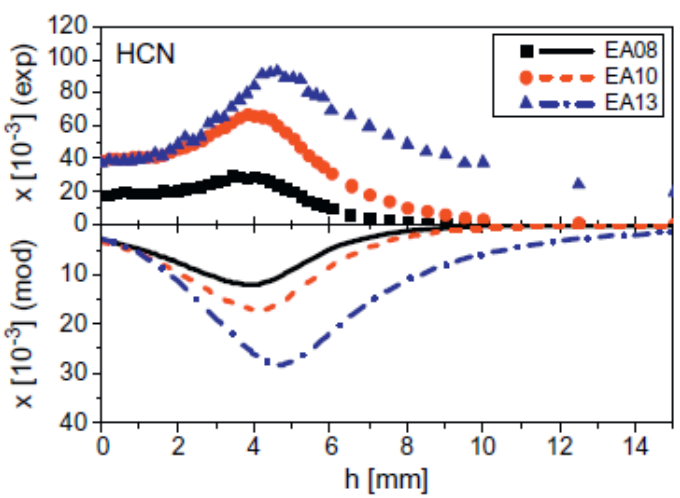
A. Lucassen et al, Combust Flame 159, 2012, 2254

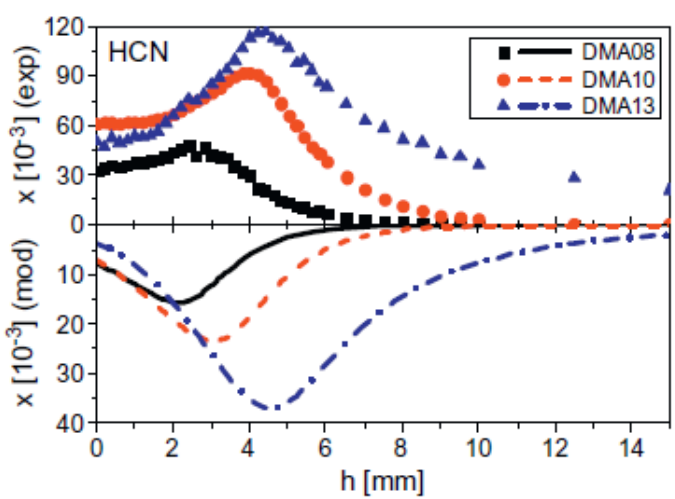
# Ethylamine vs. dimethylamine combustion





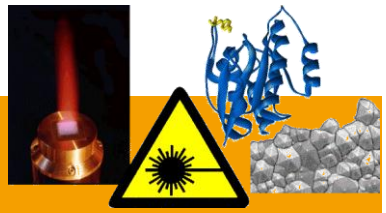




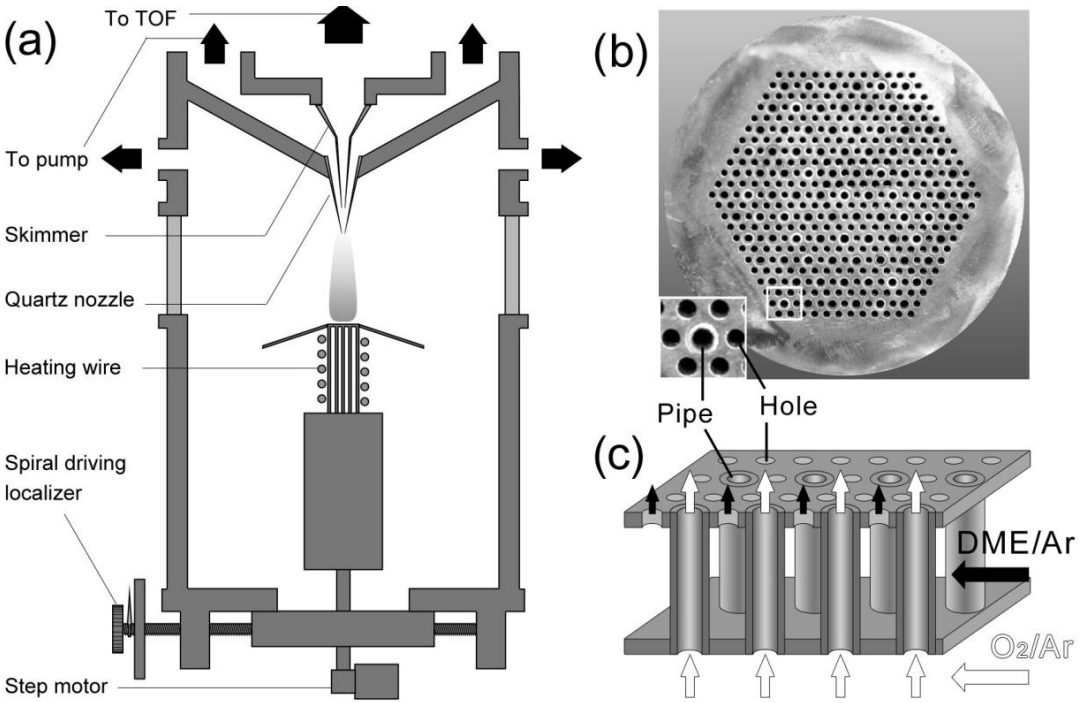



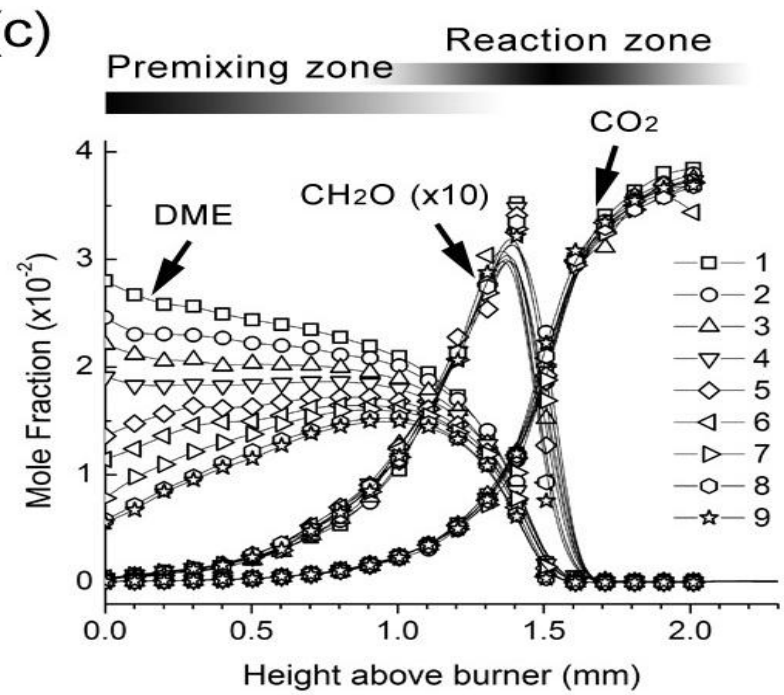

- $NH_3$ mole fractions much higher for EA.
- Model under-predicts $NH_3$ in both flame sets.
- High HCN mole fractions of up to 12%.
- Model under-predicts HCN.

A. Lucassen et al, Combust Flame 159, 2012, 2254



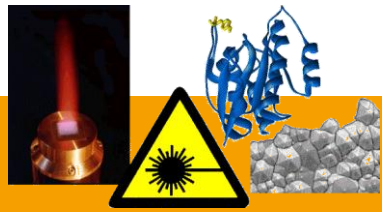
# Low-temperature combustion chemistry



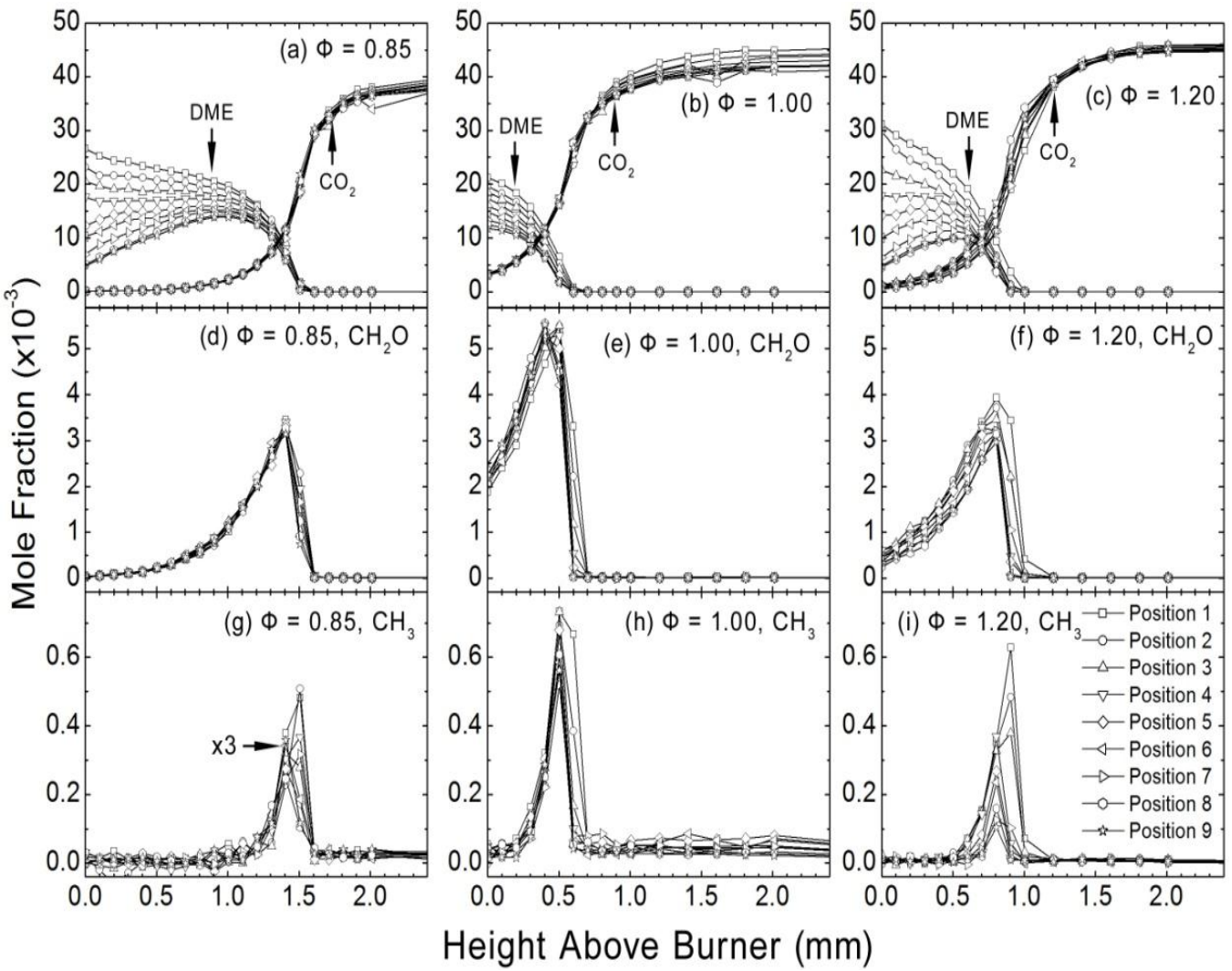




- **Sampling from highly-diluted, preheated, partially-premixed DME flame at 1 bar with T = 1400 K.**
- **Partially-premixing species profiles are *position*-dependent.**

K. Zhang et al, PROCI 34, 2012



# Low-temperature combustion chemistry

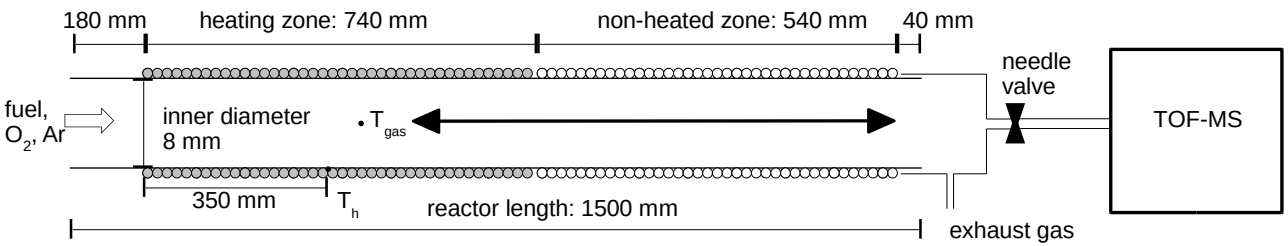


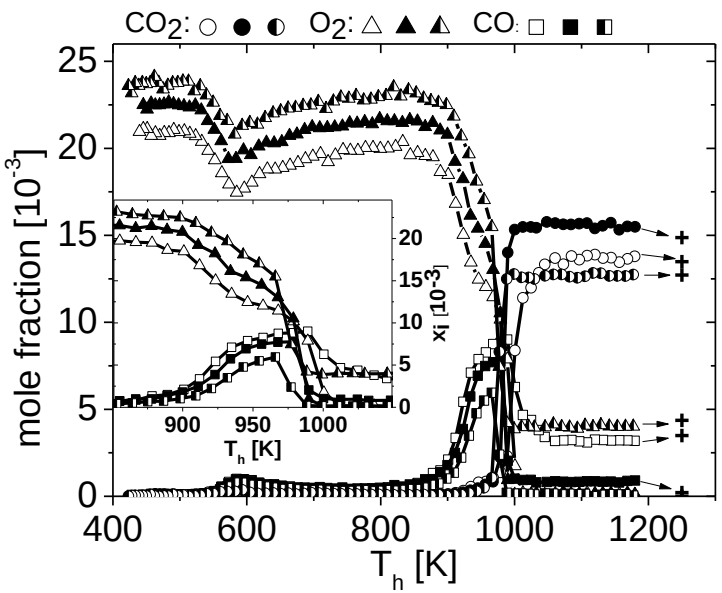

- **Highly diluted preheated DME combustion.**
- **Three stoichiometries: 0.85, 1.0, and 1.2. *Intermediate-T* behavior; e.g. $CH_3$ vs. $CH_2O$.**

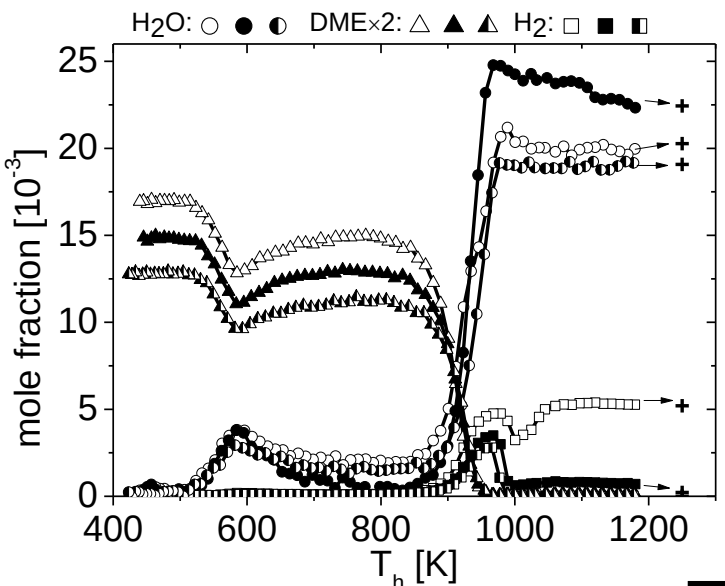
**1E06 Mon**

K. Zhang et al, PROCI 34, 2012

# Low-temperature combustion chemistry



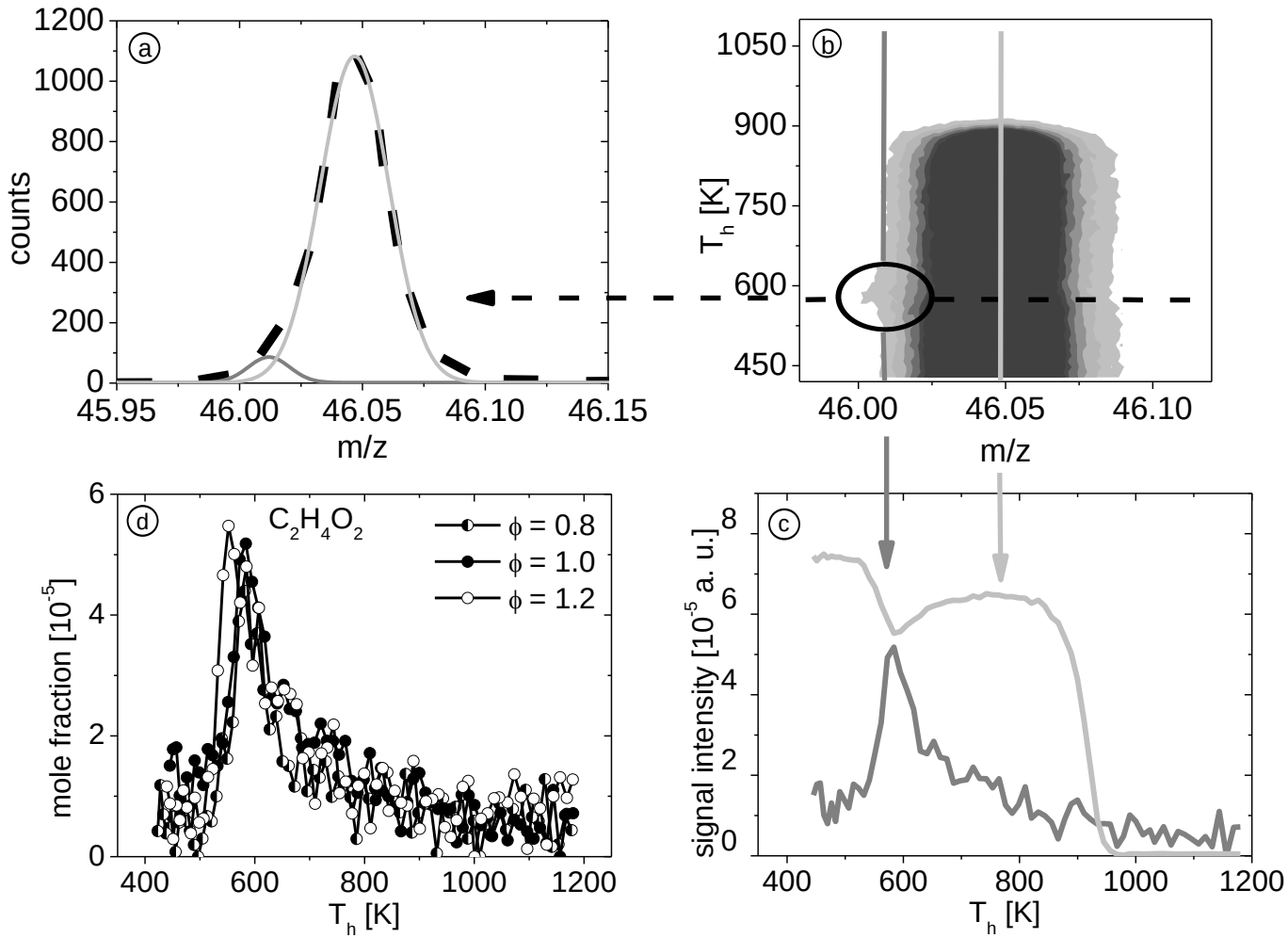




- **Highly diluted DME oxidation in flow reactor.**
- **Three stoichio-metries: 0.8, 1.0, and 1.2. *Expected* low-T behavior.**
- **Compare with model/ to EtOH: →WIP!**

**1E07 Mon, W5P070 Fri**

F. Herrmann et al, PROCI 34, 2012

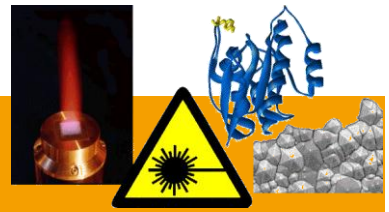
# Low-temperature combustion chemistry



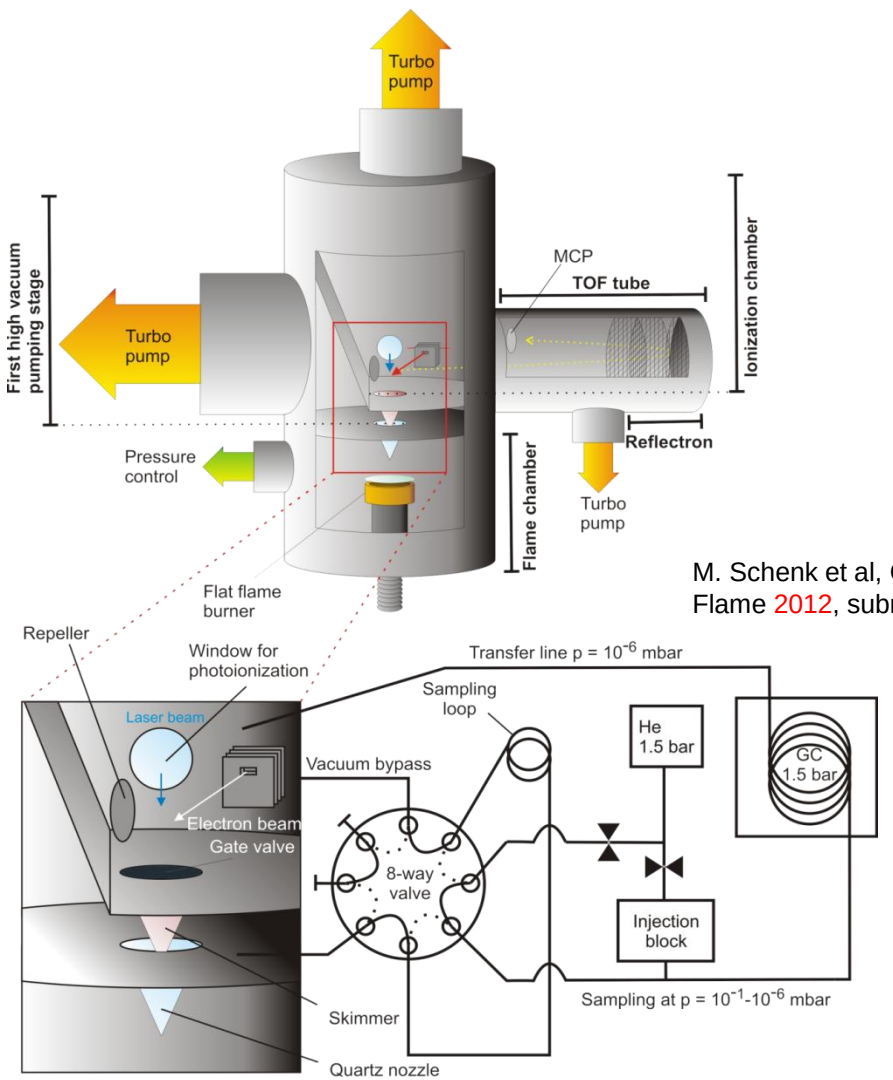

- **DME oxidation in low-T flow reactor.**
- **High mass resolution: fuel DME (46.042) and *formic acid* (46.010) at $T_h$ = 583 K are separated.**
- ***Methyl formate* is detected.**
- **More species, VUV-PI-MBMS: →WIP!**

**1E07 Mon, W5P072 Fri**

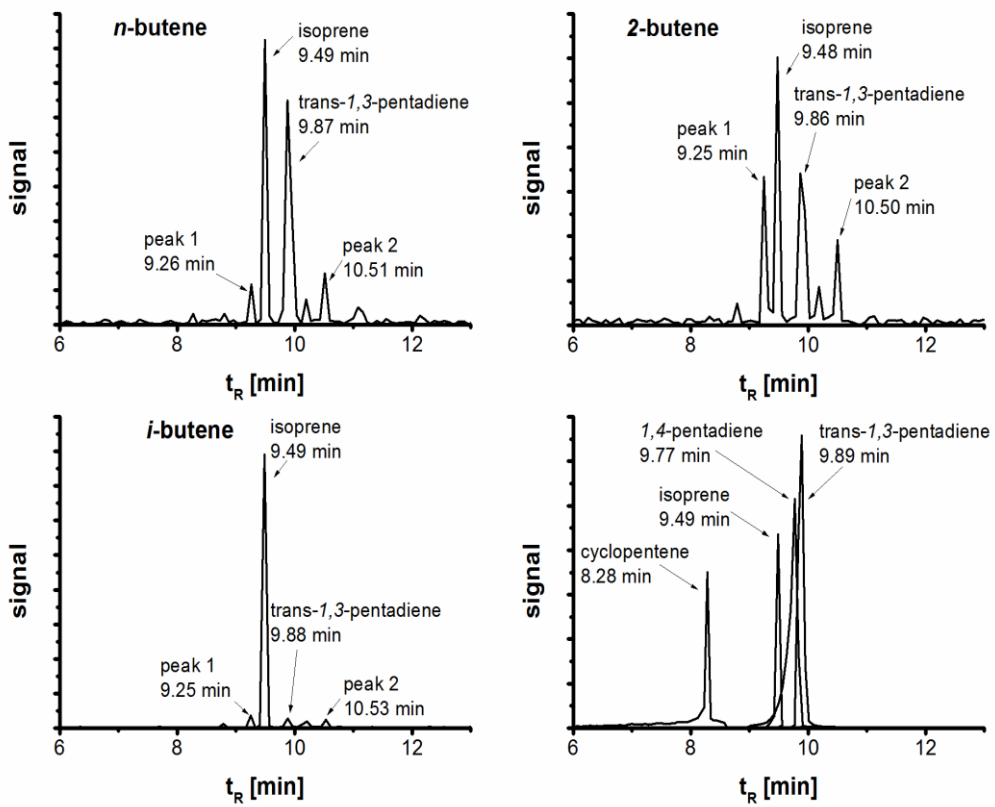
F. Herrmann et al, PROCI 34, 2012



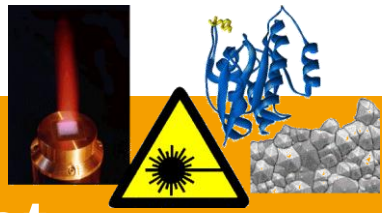
# EI-MBMS and GC from the same volume



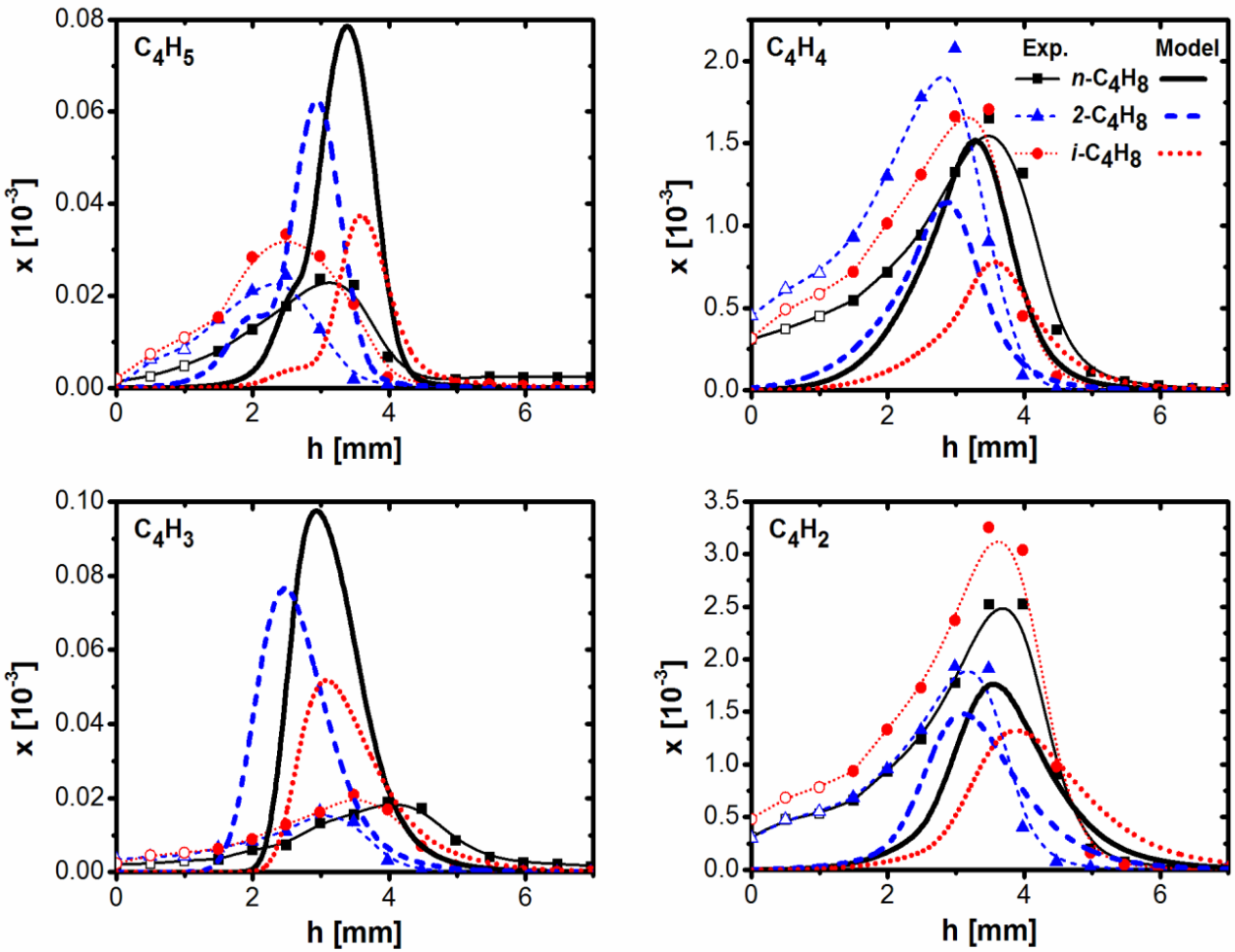

M. Schenk et al, Combust Flame 2012, submitted




- **In-situ isomer separation + EI-MBMS**
- ***Example:*** **butene flames, $C_5H_8$ m/z 68**



# Butene combustion as C4 chemistry subset




- **Different fuel break-down schemes for the 3 butene isomers.**
- ***C3 route* is of high importance for all butenes, almost exclusive for *i*-butene.**
- **Additional *C4 route* exists for the 2 linear butenes.**

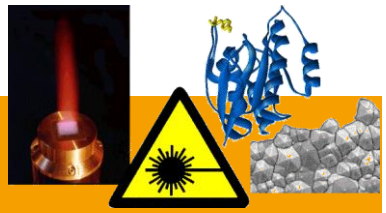
**W2P081 Tue**

M. Schenk et al, Combust Flame 2012, submitted

# Highly complex chemistry: Biomass pyrolysis

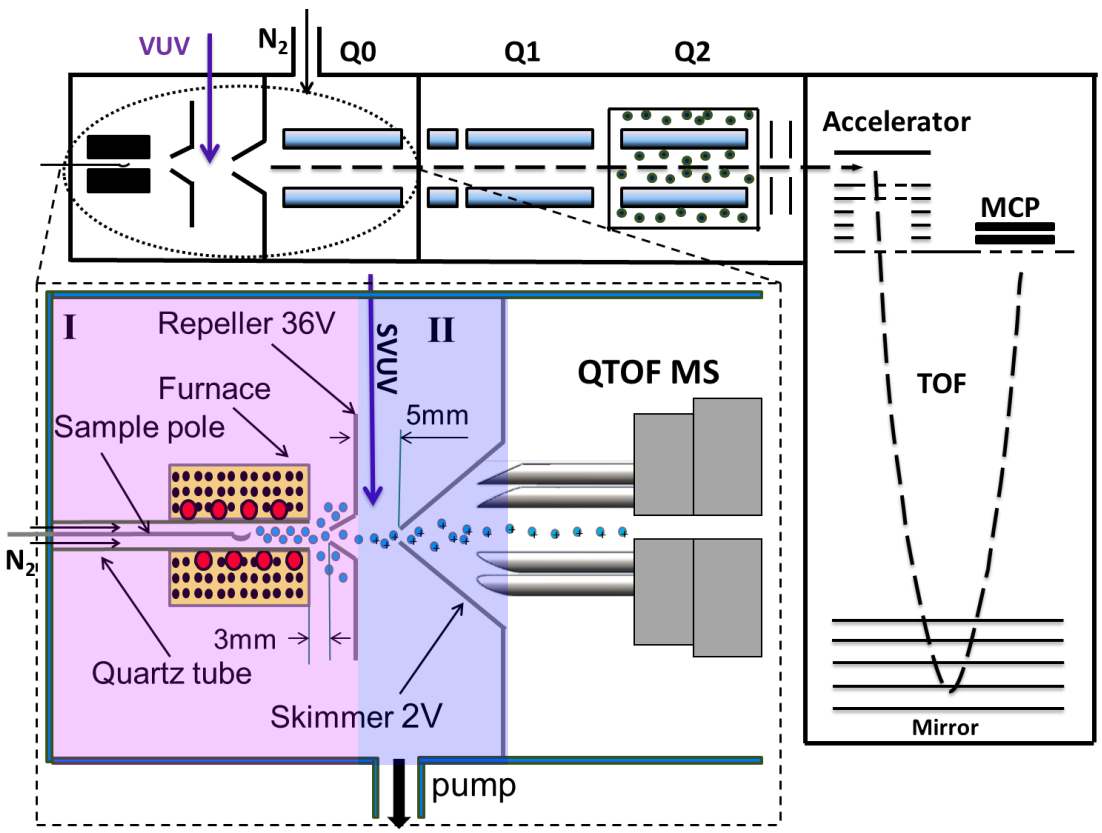

- **Tunable VUV PI-MBMS for analysis of pyrolysis profiles (T, time) of second-generation biofuels.**
- **Fast-growing poplar wood as potential corn replacement; carbon conversion to biofuels.**

J. Weng et al, PROCI 34, 2012



# Poplar pyrolysis set-up

- **Qstar triple quadrupole TOF-MS with mass range 30-20000 Da, *resolution 10000*.**
- **Reactor is heated to specific temperature, then sample inside the quartz pole is pushed into the furnace.**
- **Pyrolysis products pass through a repeller plate into the photoionization region, photoions are analyzed by the QTOF mass spectrometer.**

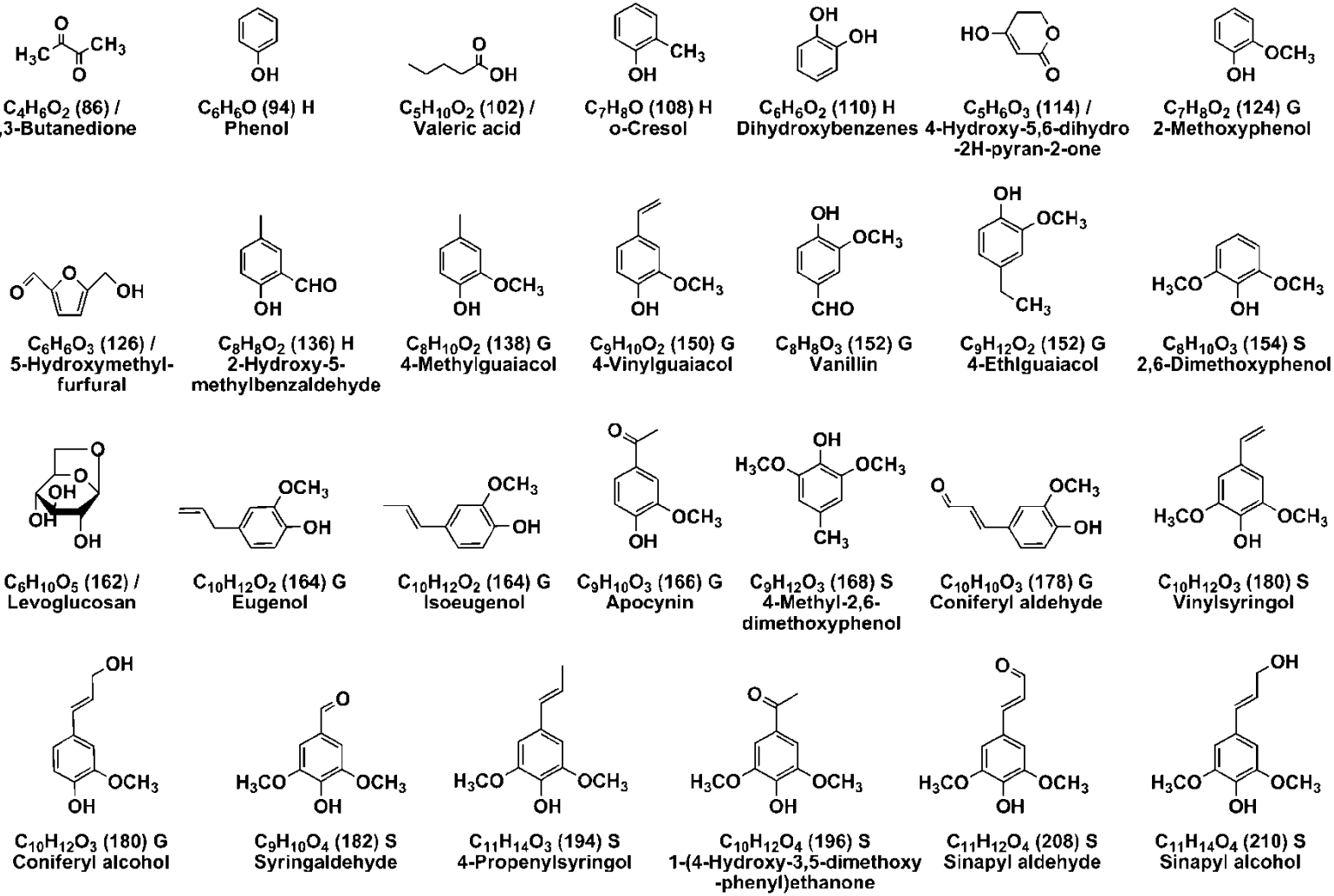



I. Pyrolysis, 20 mTorr

II. Photonionization

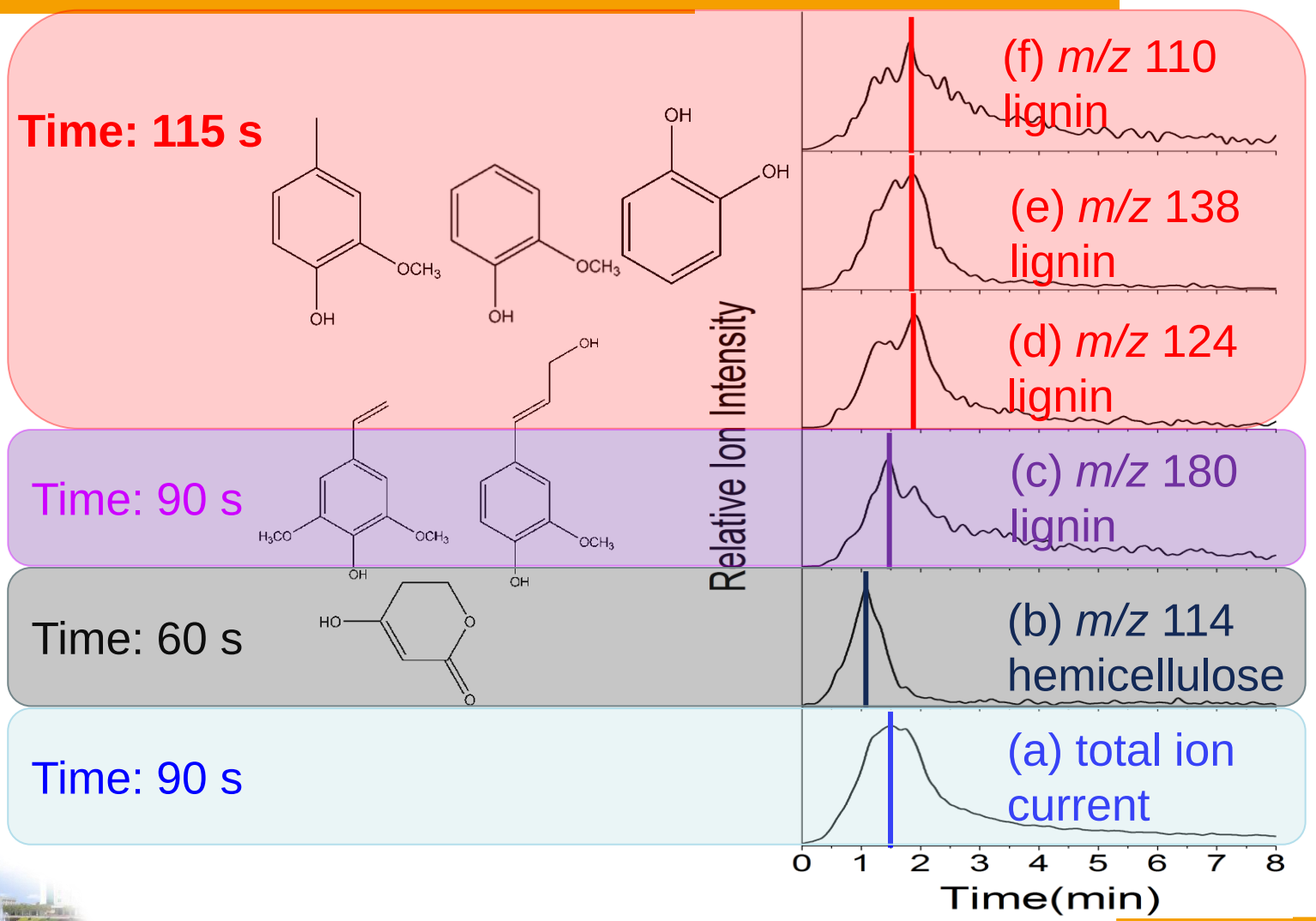
J. Weng et al, PROCI 34, 2012

# Major products from poplar pyrolysis




J. Weng et al, PROCI 34, 2012

# Time-resolved pyrolysis profiles

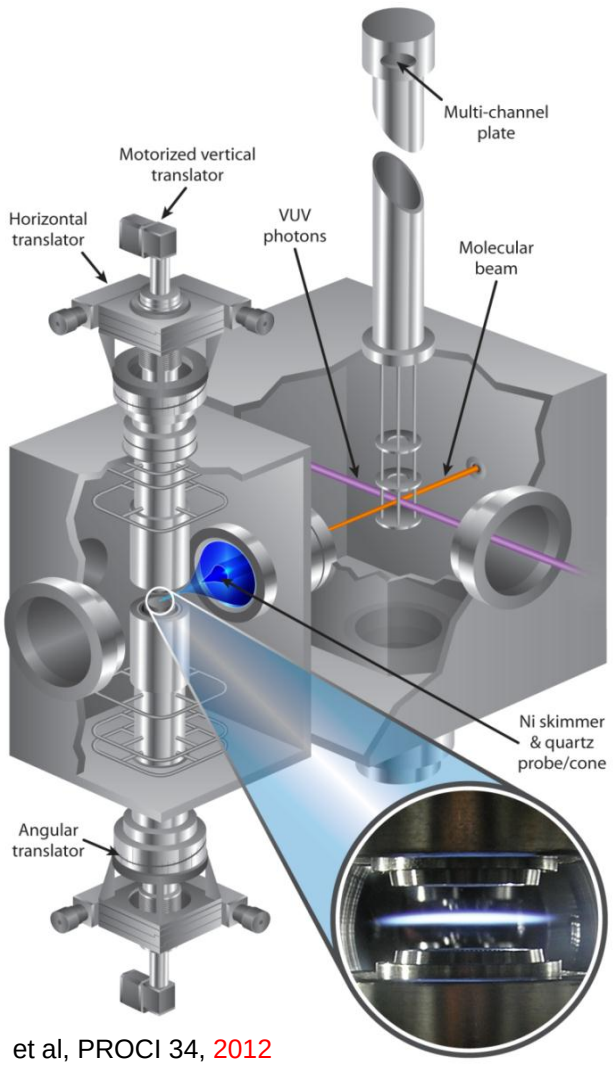


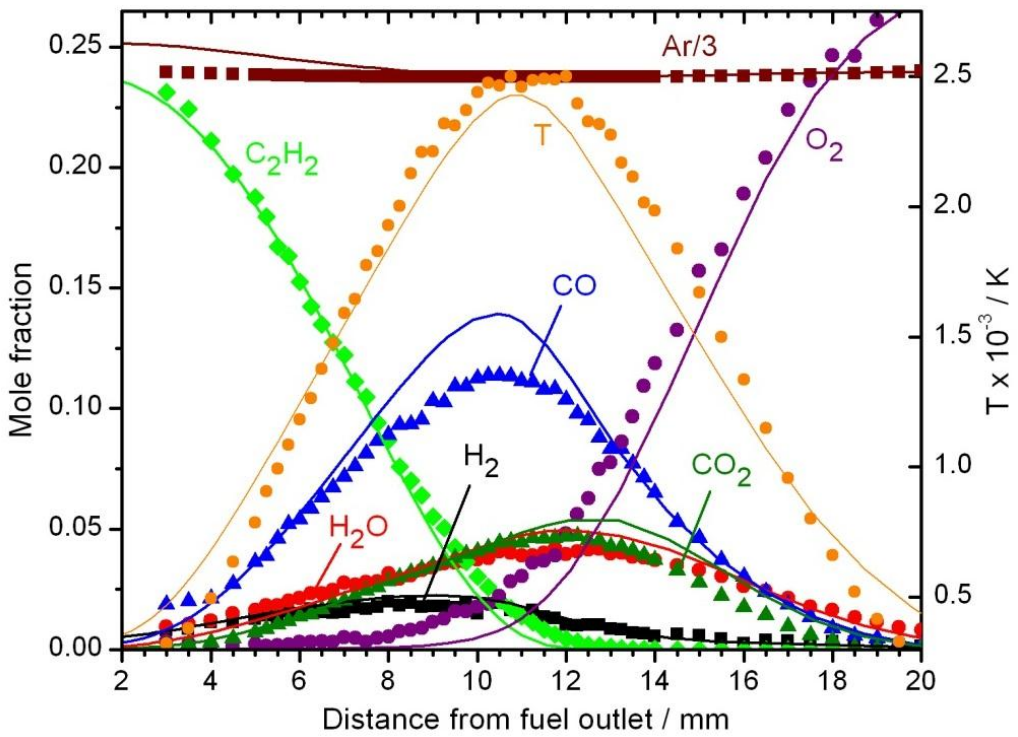

**500 °C**
**10.5 eV**

**2G10 Tue**

J. Weng et al, PROCI 34, 2012

# MBMS in non-premixed flames

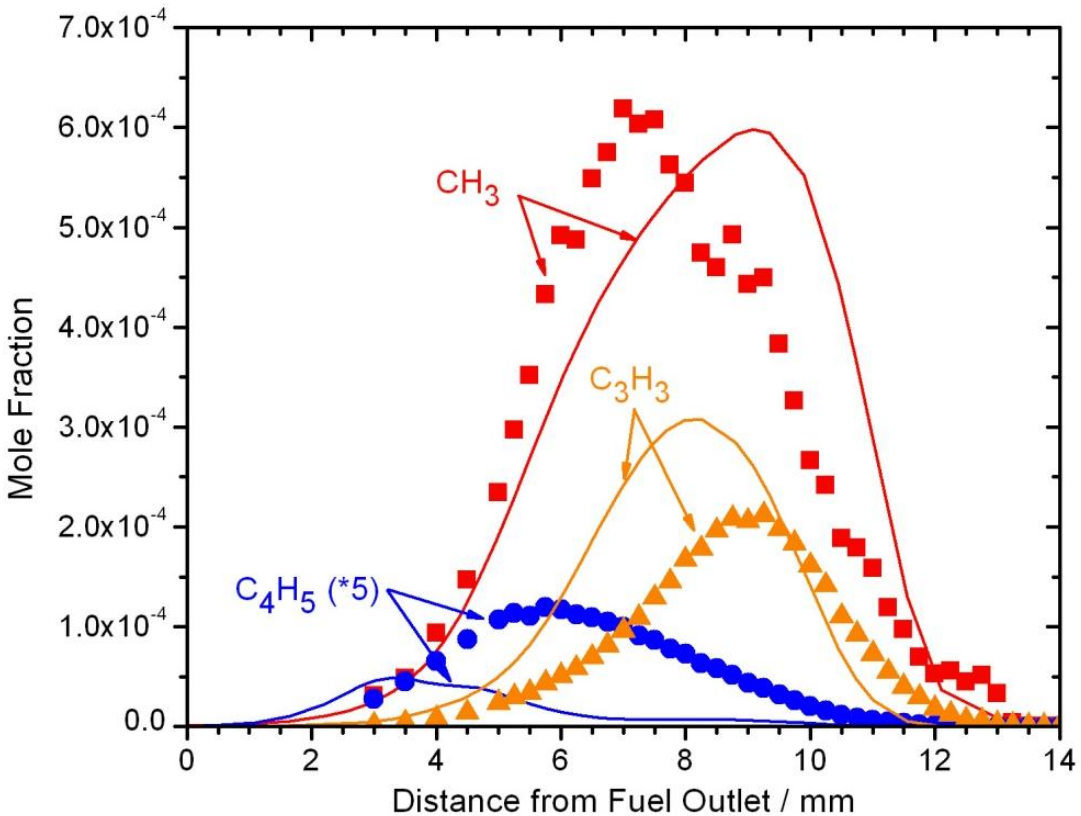


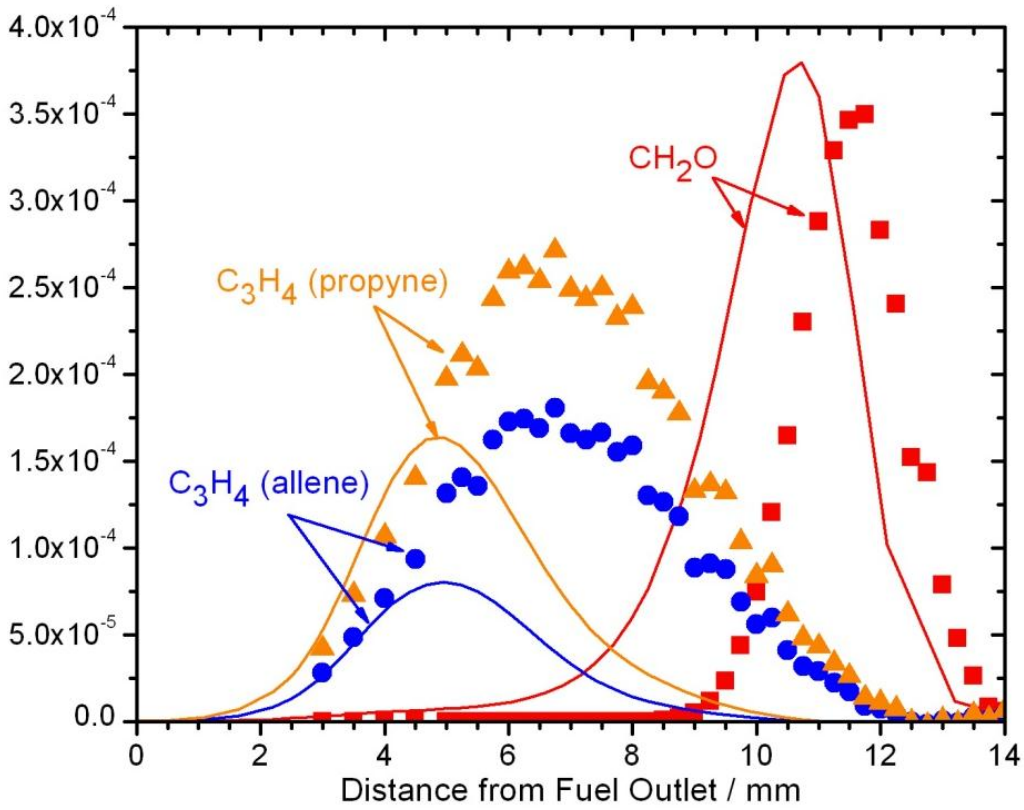




- $C_2H_2$ flame at 30 Torr
- Mole fractions vs. fuel outlet
- Agreement with model by Jim Miller

S.A.Skeen et al, PROCI 34, 2012

# MBMS in non-premixed flames



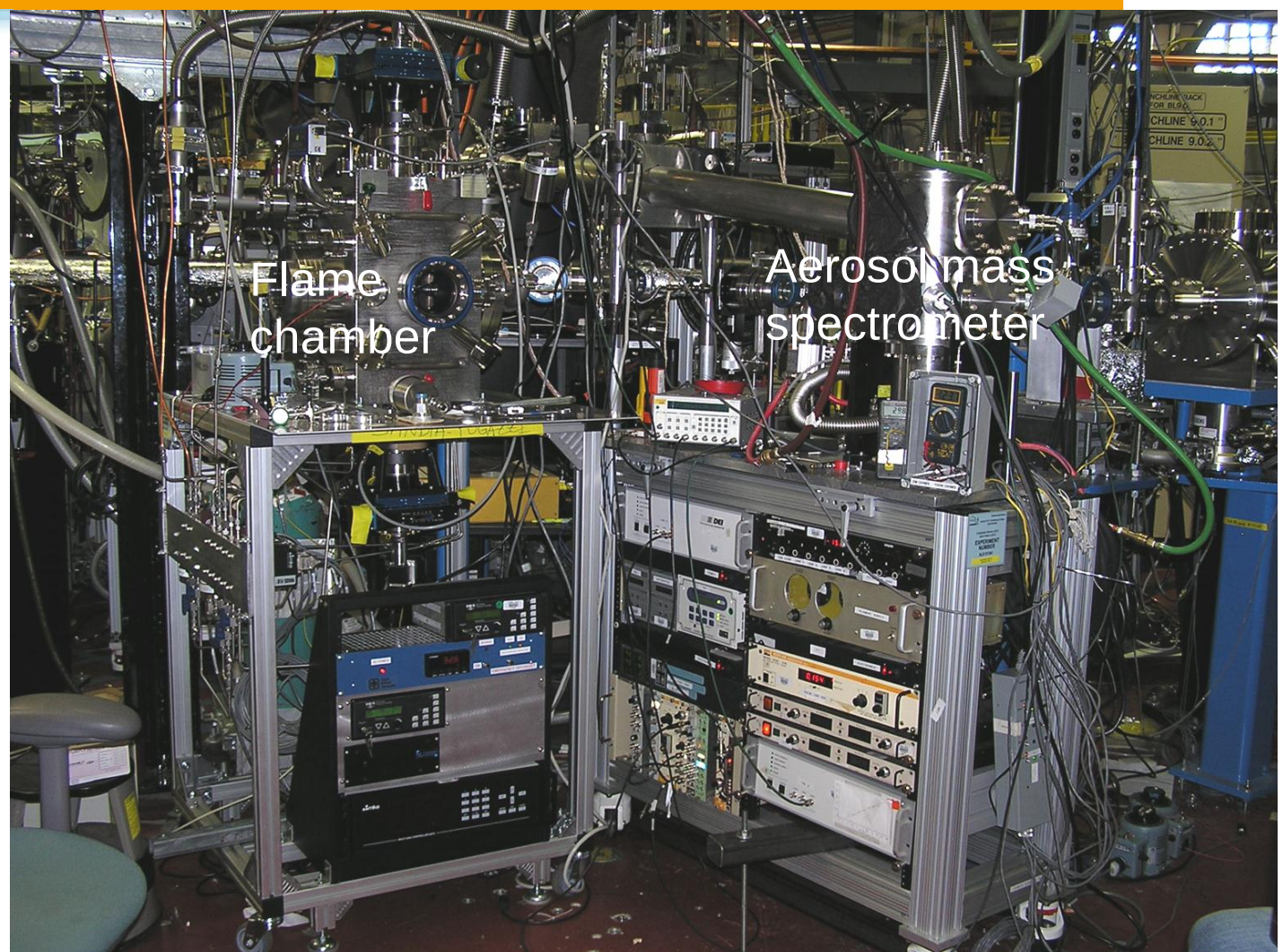



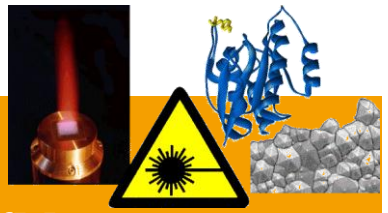

- **Radicals can be detected.**
- **Profiles appear shifted vs. model.**

**5E07 Fr**

S.A.Skeen et al, PROCI 34, 2012

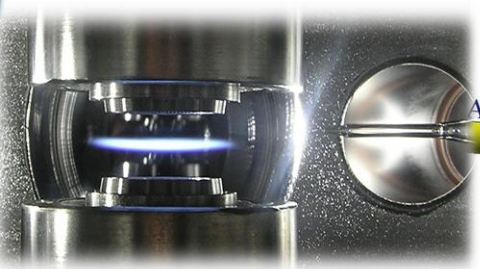
# Flame-sampling aerosol mass spectrometry

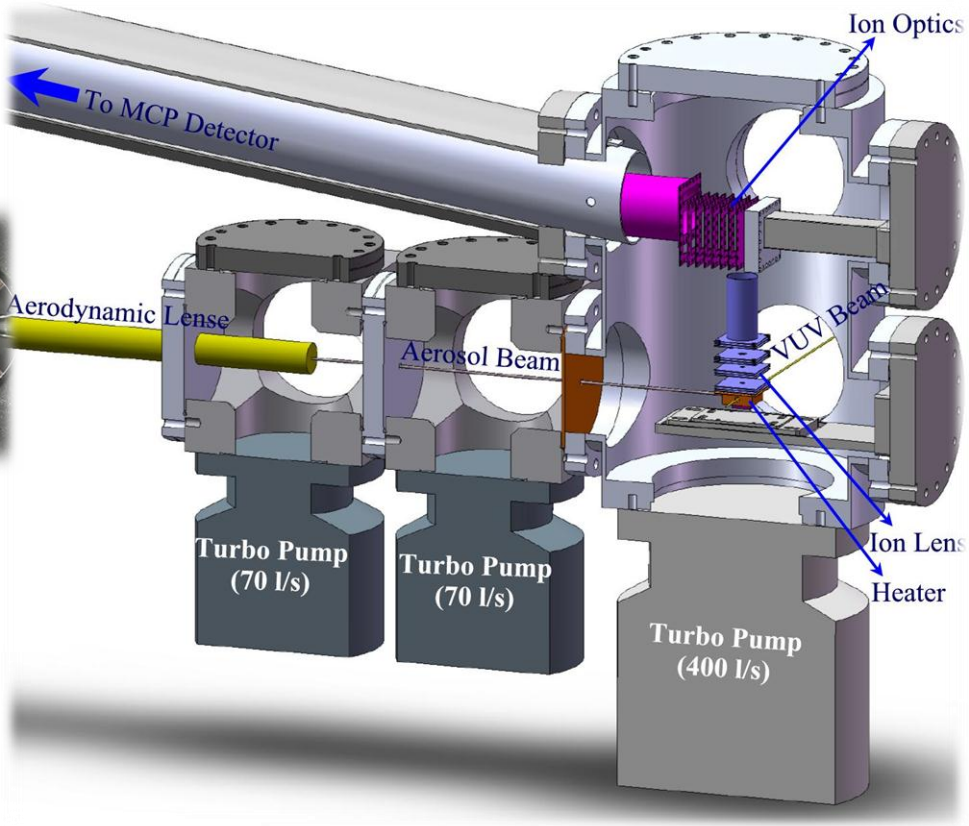




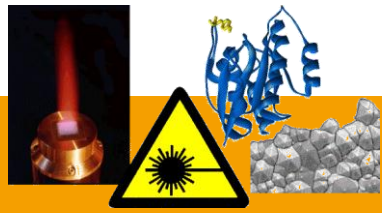
# Flame-sampling aerosol mass spectrometry

- **Gas phase species and *50-100 nm particles* are sampled from 700 Torr counterflow flame with quartz microprobe.**

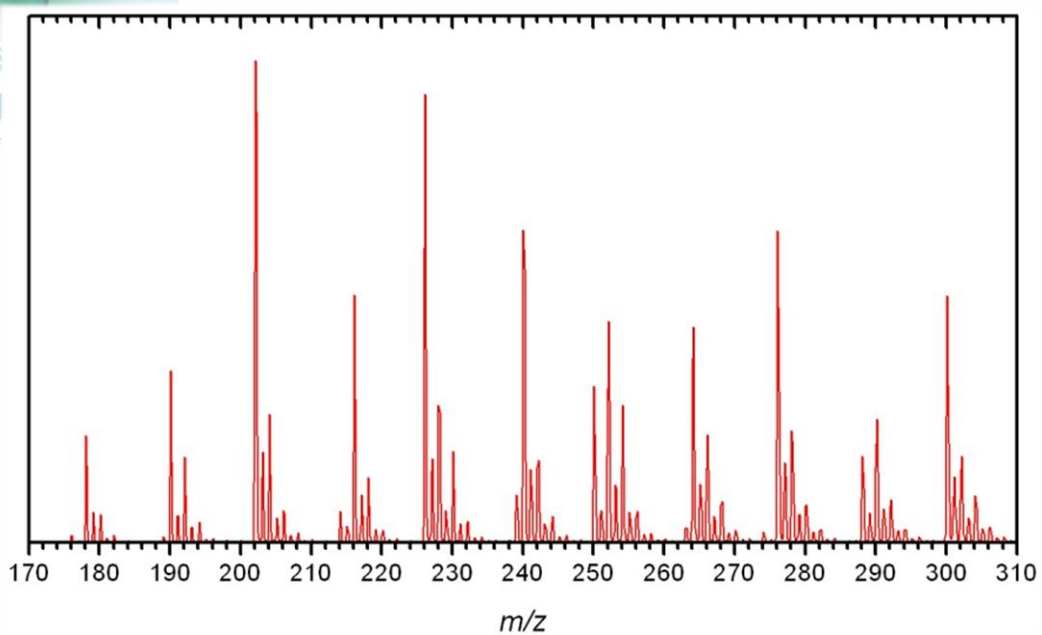


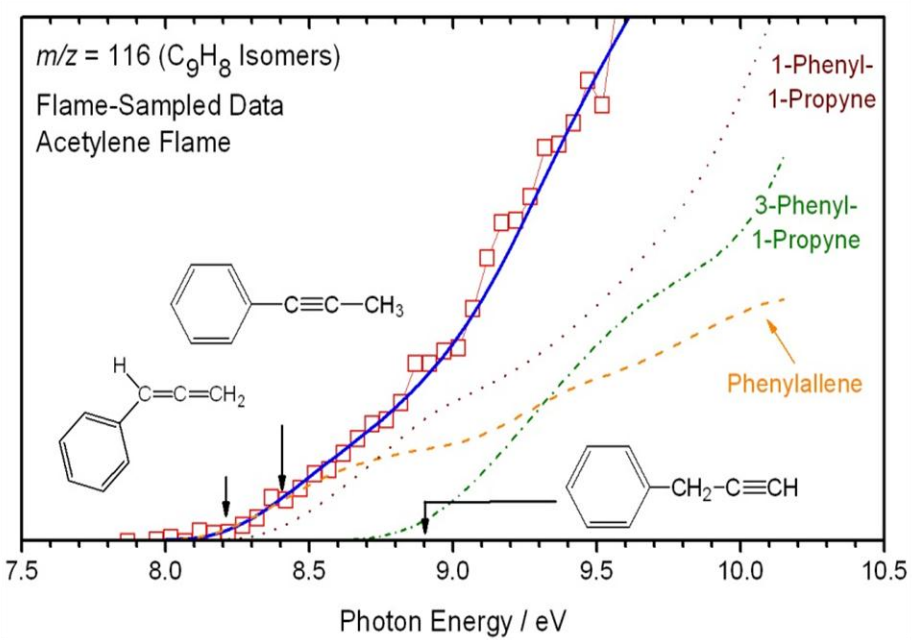



- **Particles are focused with aero-dynamic lens onto heated copper plate and flash-vaporized.**
- **Molecular con-stituents are VUV-photoionized and detected by TOF mass spectrometry.**

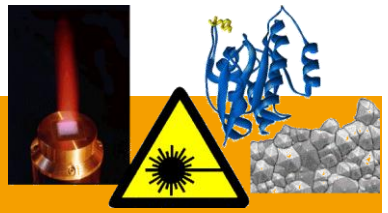


# Particle chemical composition: surprises

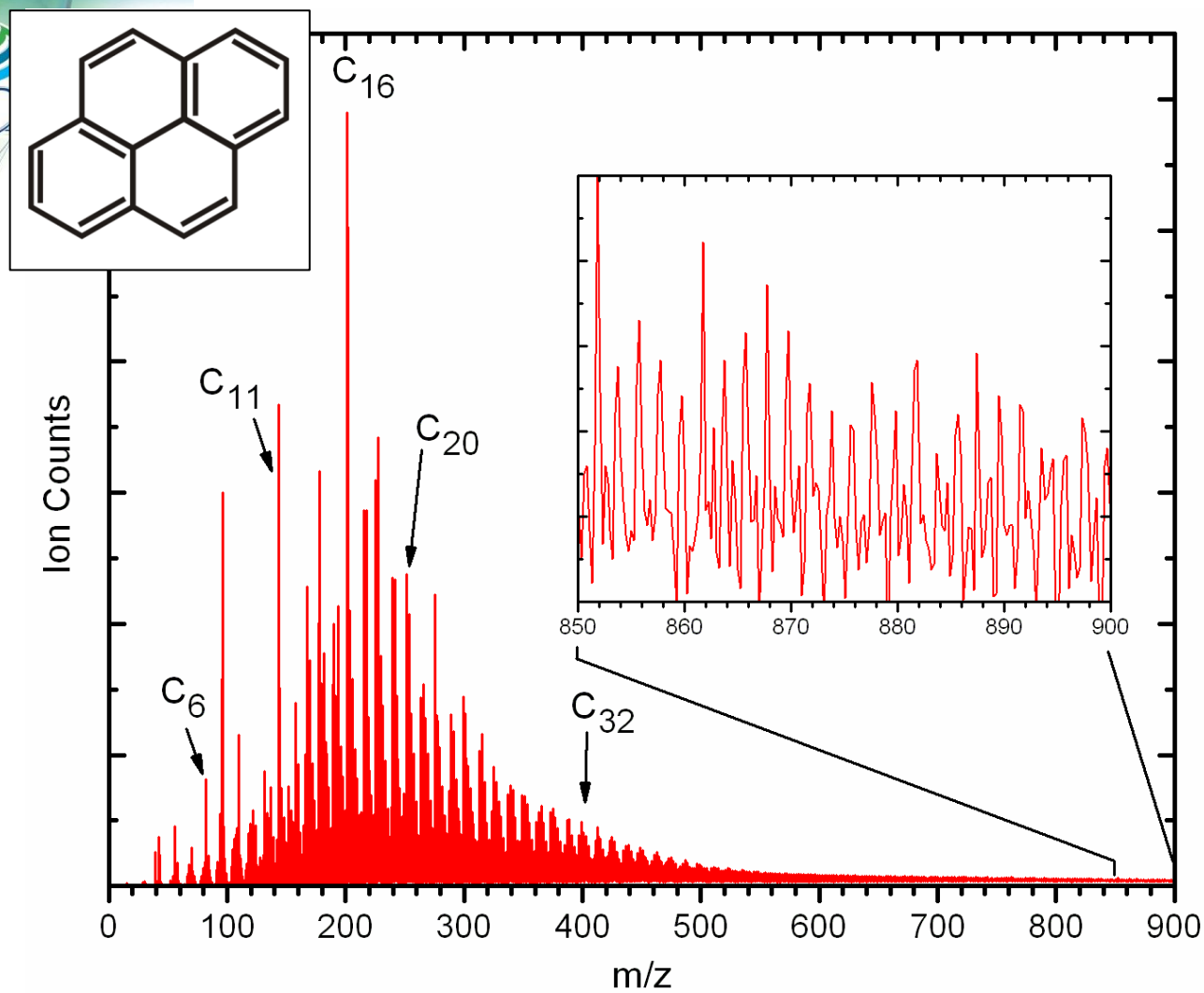


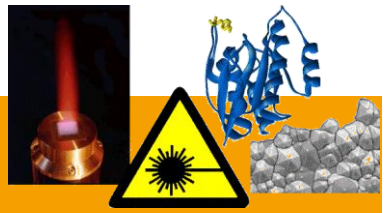

- **Mass spectra map chemical composition of the particles vs. distance from the fuel outlet; PIE spectra permit identification.**
- ***Example*** **m/z=116, normally only identified as indene, but PIE curve shows also** ***phenyl-substituted allene and propynes*****.**



# Soot formation beyond benzene




- Many species beyond benzene to ~1000 Da.
- Mass spectra peak at around 202 Da, i.e. pyrene.
- Detailed analysis in progress.

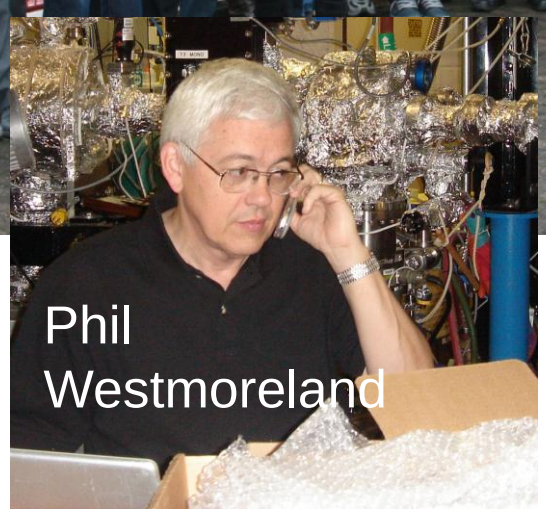


# Perspectives: Future trends and needs?

- ***New combustion chemistry:*** **more elements, higher mass range, structure-selective quantitative analysis.**
- ***New measurement domains:*** **larger p and T range, pyrolysis vs. highly-diluted oxidative systems, particles, aerosols, homogeneous vs. heterogeneous combustion chemistry.**
- ***Time-resolved*** **analysis.**
- ***Support by theory:*** **ionization energies, structures, simulation of spectra, kinetics, thermochemistry.**
- ***Combination of methods:*** **optical&MS techniques, in situ GC-MBMS, IR-absorption, MS-MS, PEPICO, ….**
- ***Caveat:*** **Let‘s get sampling problem solved!**


Kai Moshammer
Patrick Oßwald
Friederike Herrmann
Arnas Lucassen
Marina Schenk
Kuiwen Zhang
THANK YOU


Terry Cool


Phil Westmoreland


Nils Hansen
Tina Kasper


Fei Qi