COMBUSTION RESEARCH FACILITY

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Improving resolving power for complex compositions by combining tunable synchrotron radiation with advanced mass spectrometric techniques

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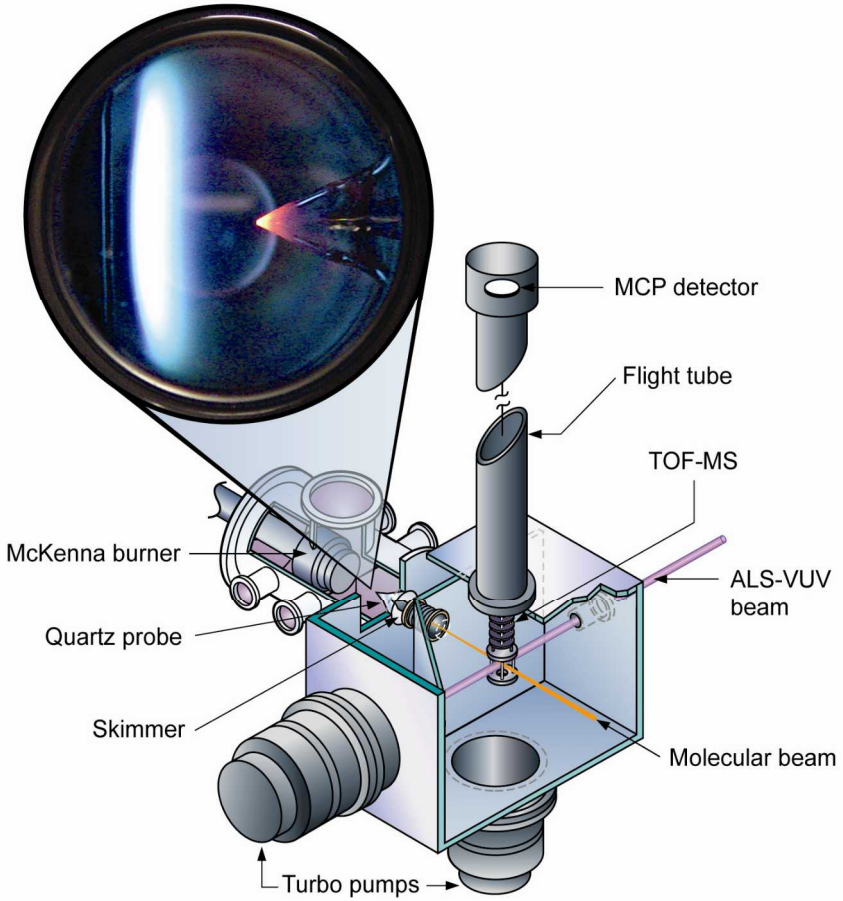
Outline

- Introduction
- Combustion research at the ALS
- Future ideas
- Conclusions and Summary

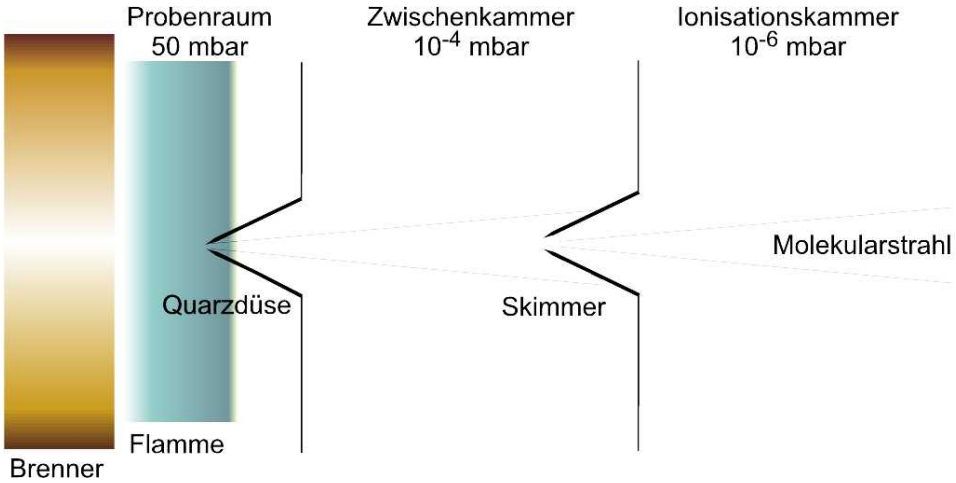
Introduction

- Detailed knowledge of combustion chemistry crucial for predictive control of combustion behavior
- Combustion Systems highly complex analytical problems
  - High number of Species
  - Instable species
  - Mixing gradients
  - Low concentrations
  - Harsh environments (high p and T)
- Use of simplified model systems to analyze different aspects

Instrumental setup

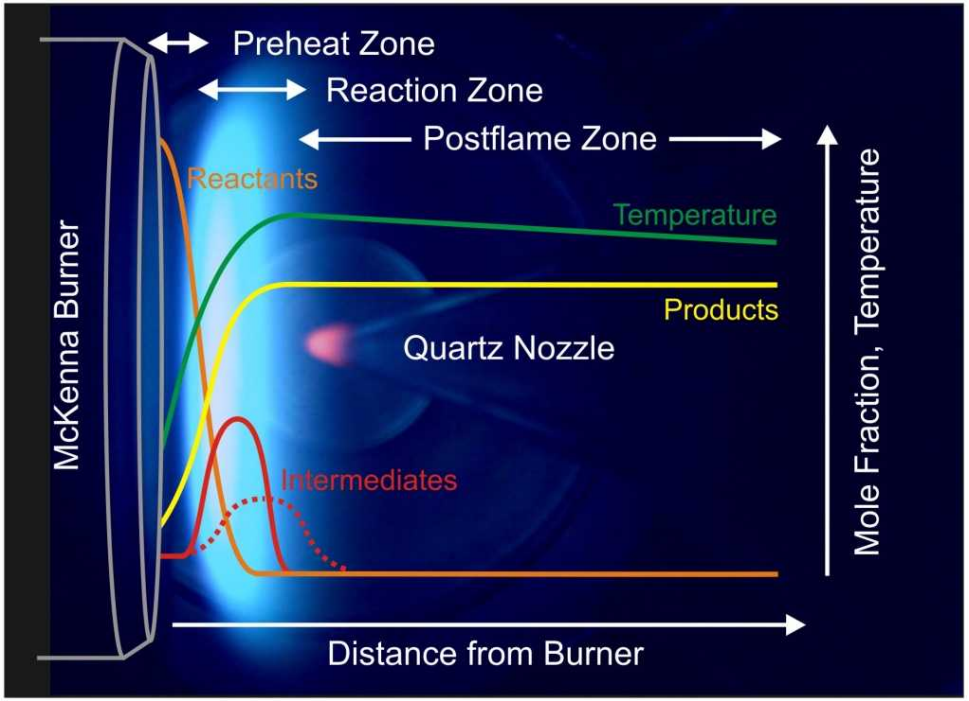


- Molecular beam sampling time-of-Flight Mass Spectrometry
- Offers rapid data collection and universal species overview

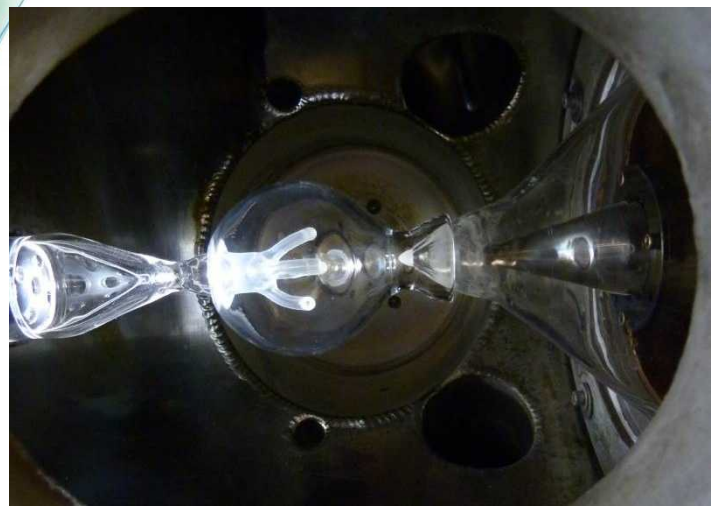


Model Flames

- laminar and premixed (oxygen + fuel)
- flat flame
  - one dimensional ➔ Distance from burner resambles reaction progress
  - low pressure ➔ higher spatial resolution

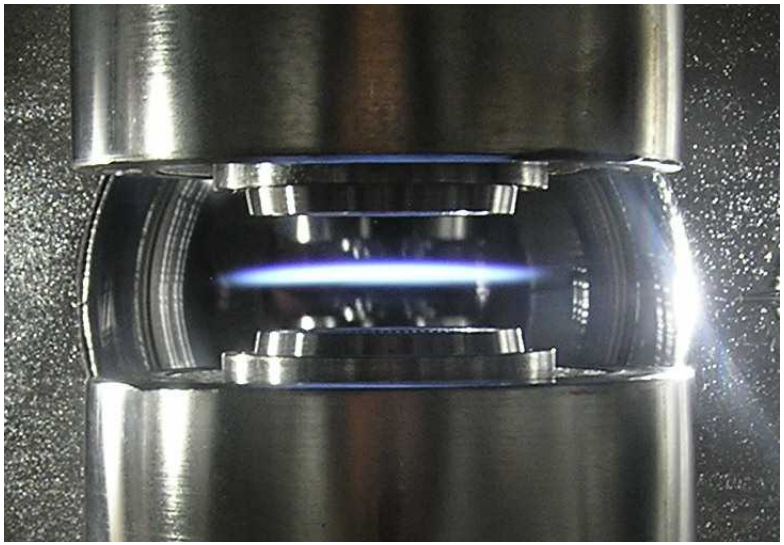


Other Model systems



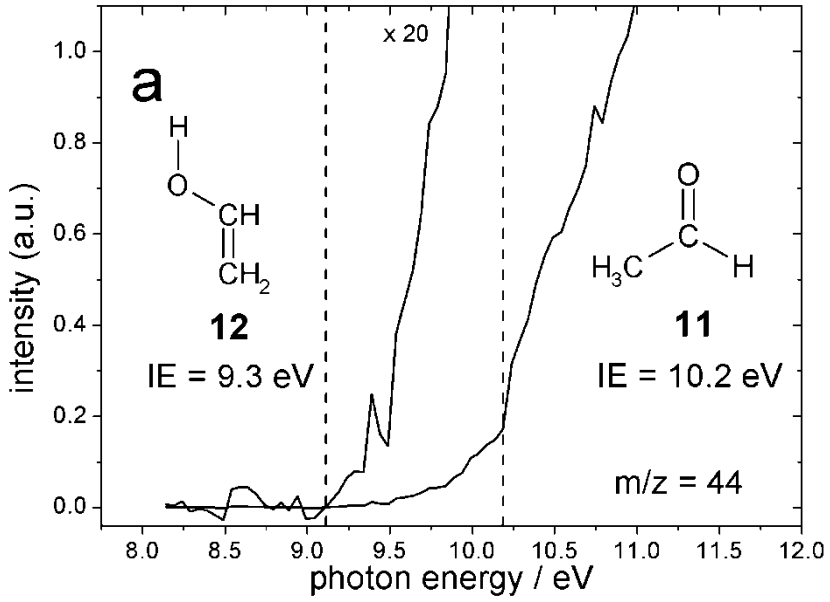
- Atmospheric and low pressure counter flow flames
- Observation of soot growth

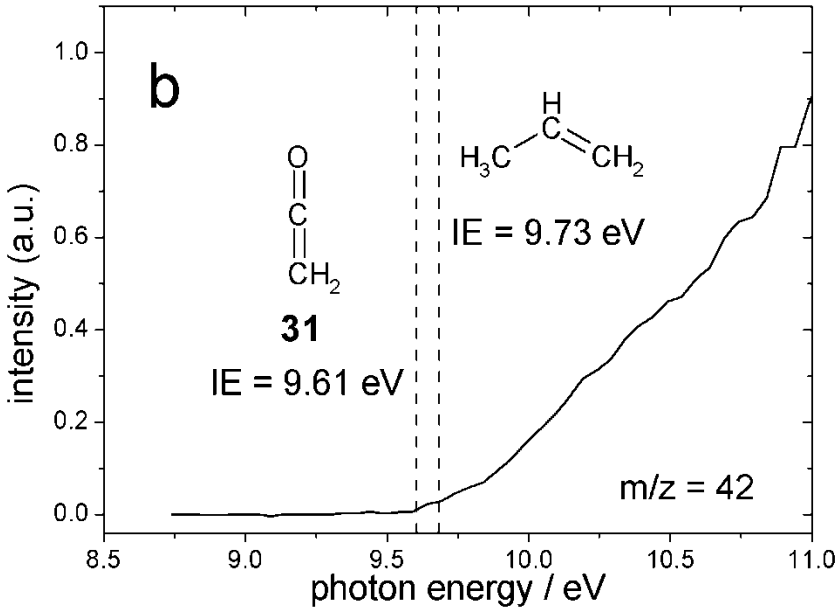
- Atmospheric pressure Jet Stirred Reactor
- Studies of low temperature oxidation



Isomer selective Ionization

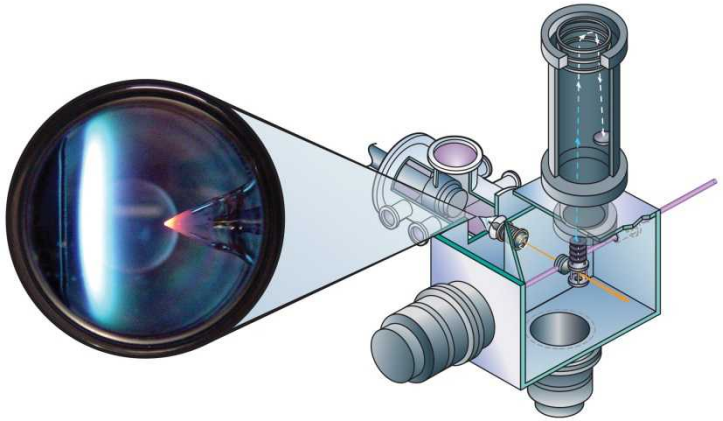
- Ionisation by Synchrotron Radiation at the Advanced Light Source
- Typical energy resolution (0.05 eV)
- Mass resolution limited by continous ionization
- Distinction between isobaric species with similar ionization energy challenging

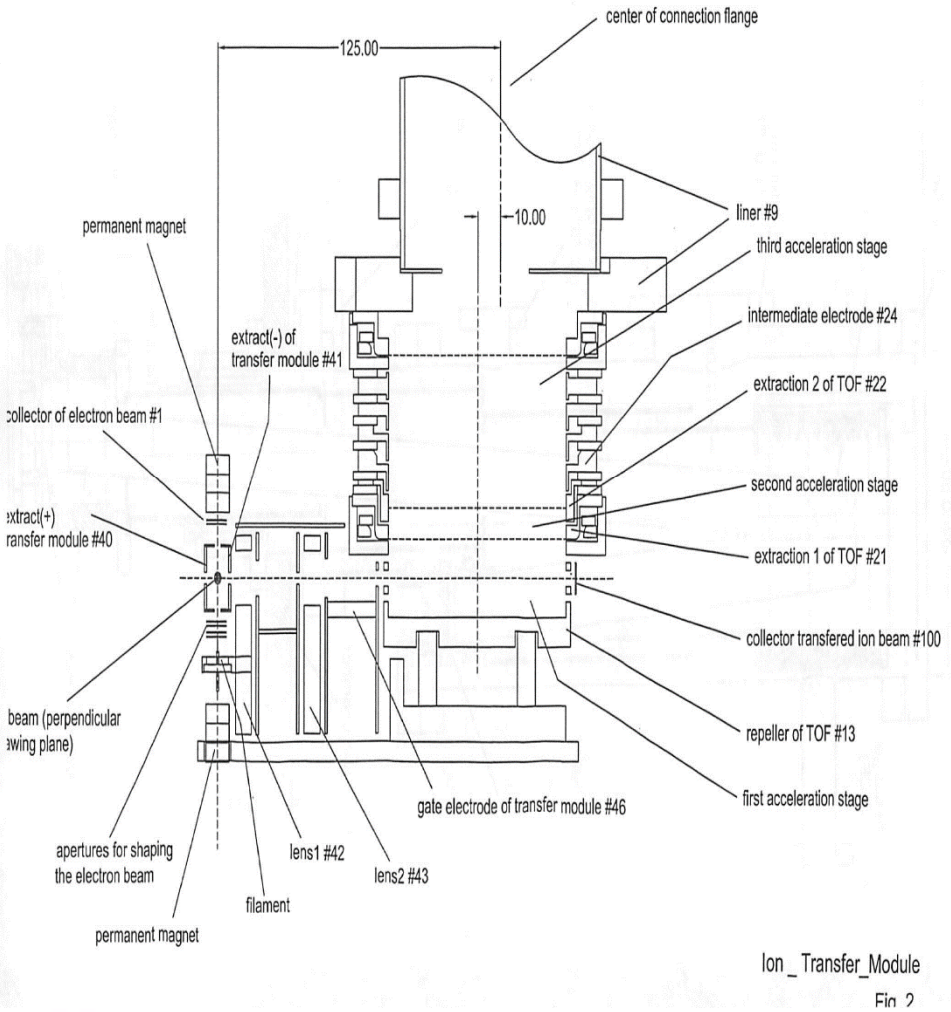




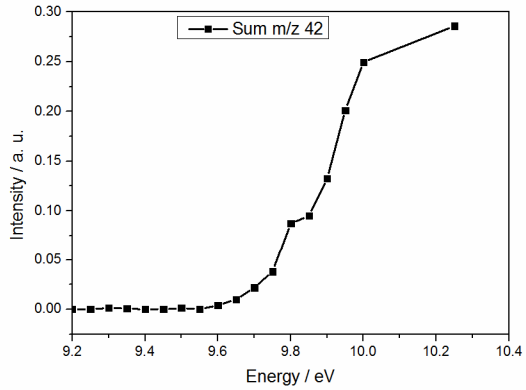
Updated mass spectrometer

- Orthogonal time of flight
  - Decoupling of ionization and extraction region
  - 2 stage extraction
  - Reflectron
  - High mass resolution at continuous ionization (R = 3000)

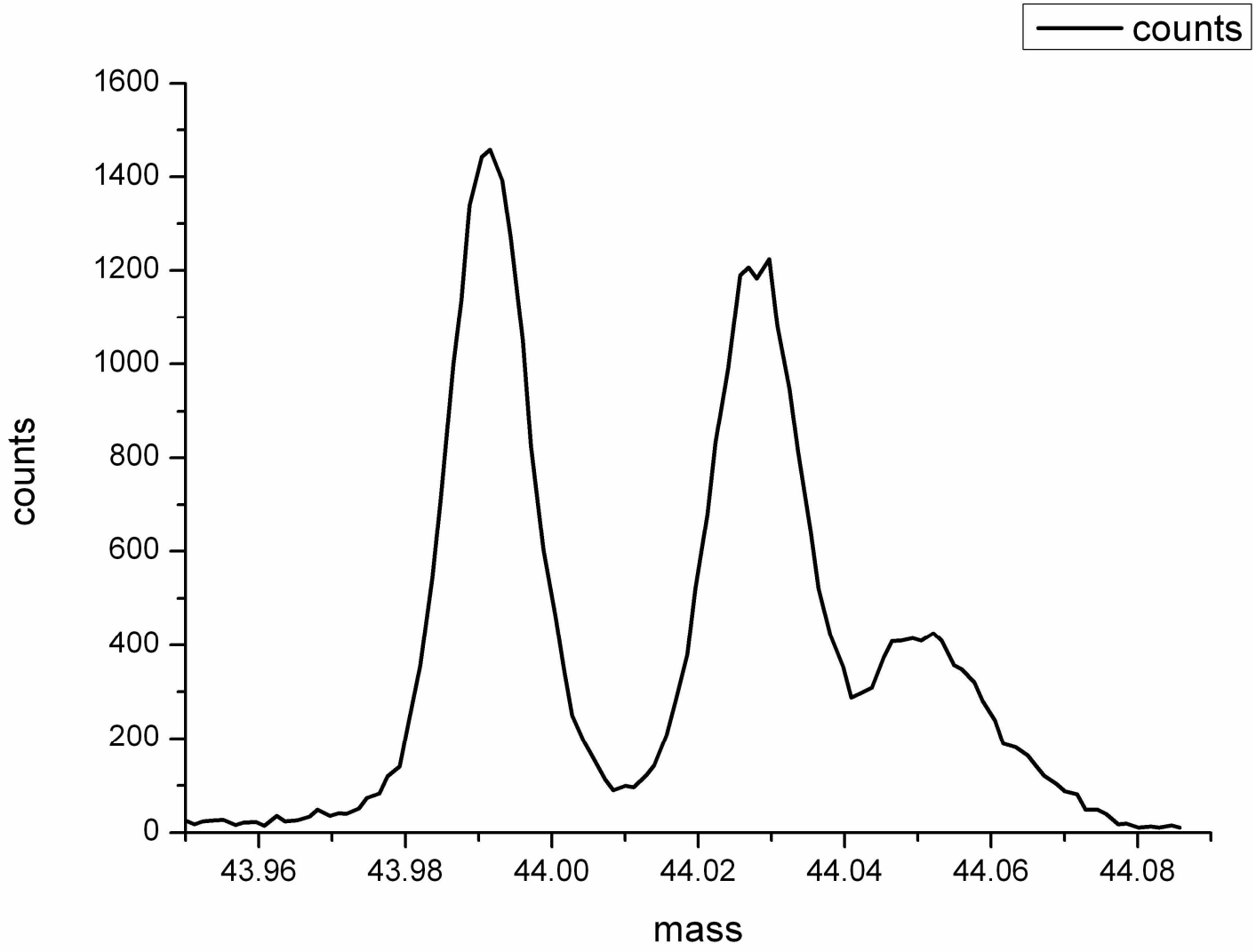




Identifying the Flame Components



Mass separation by peak fitting



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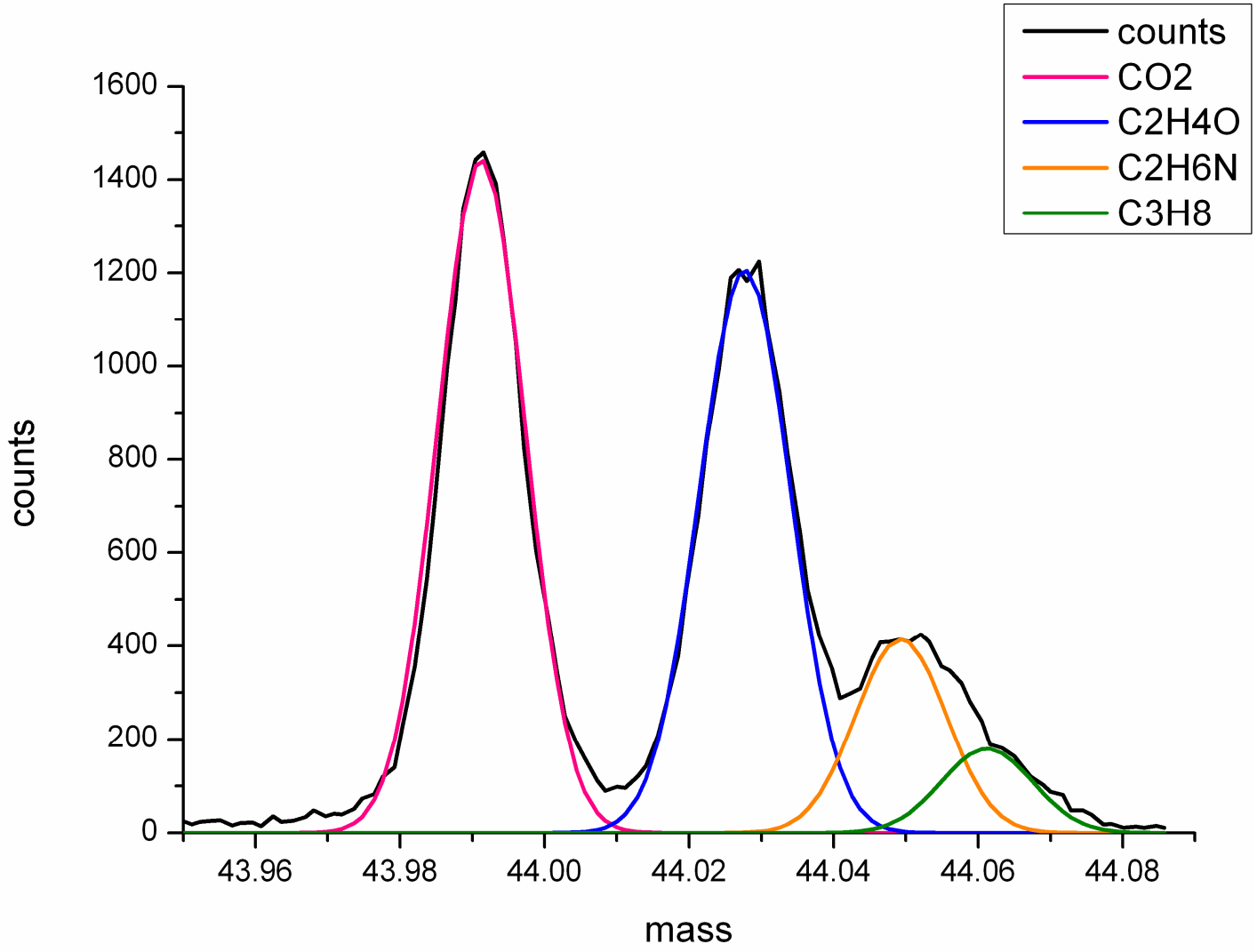

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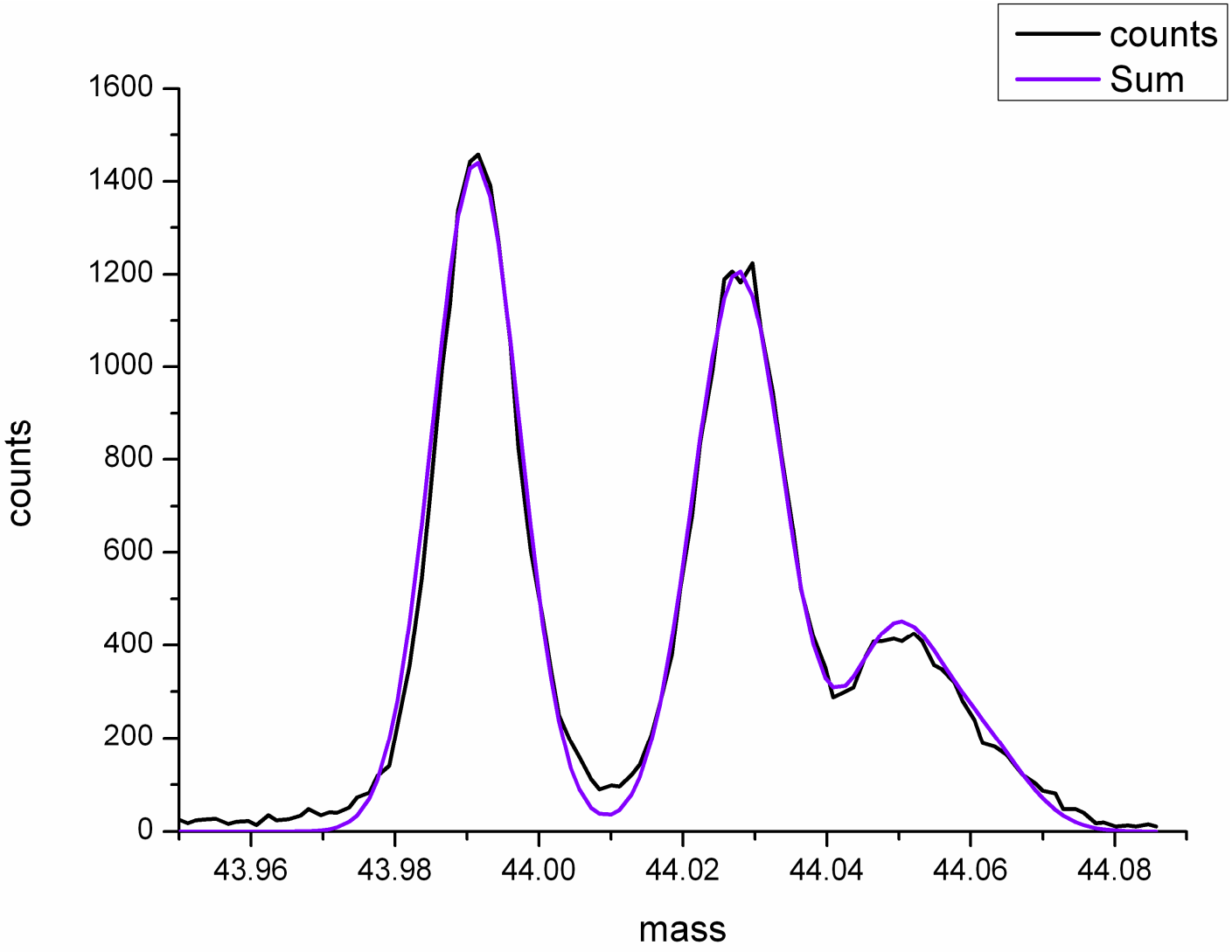

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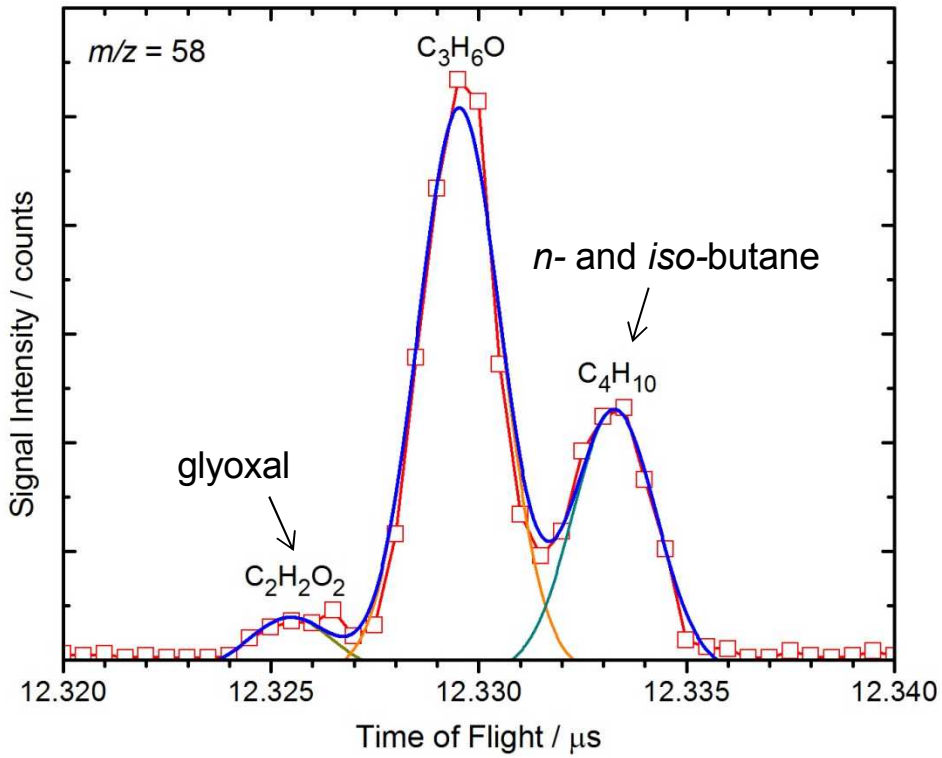
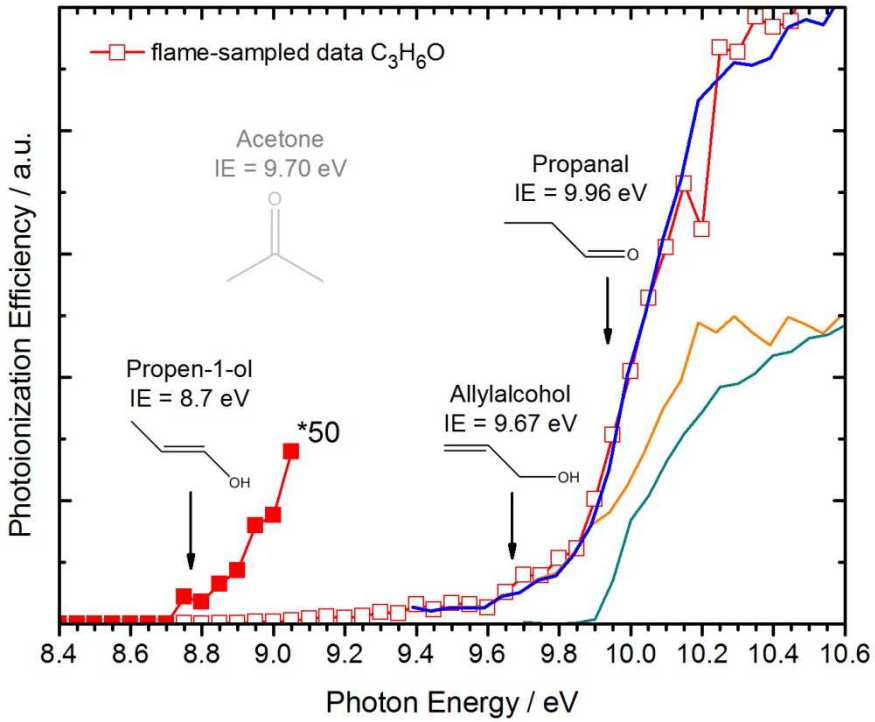
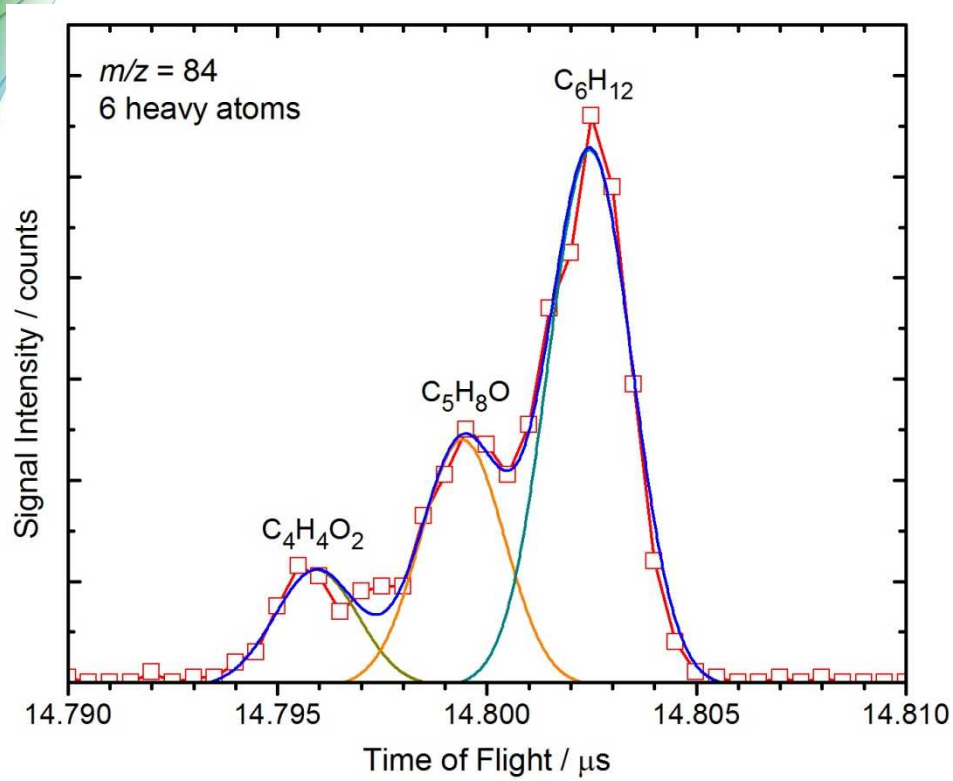


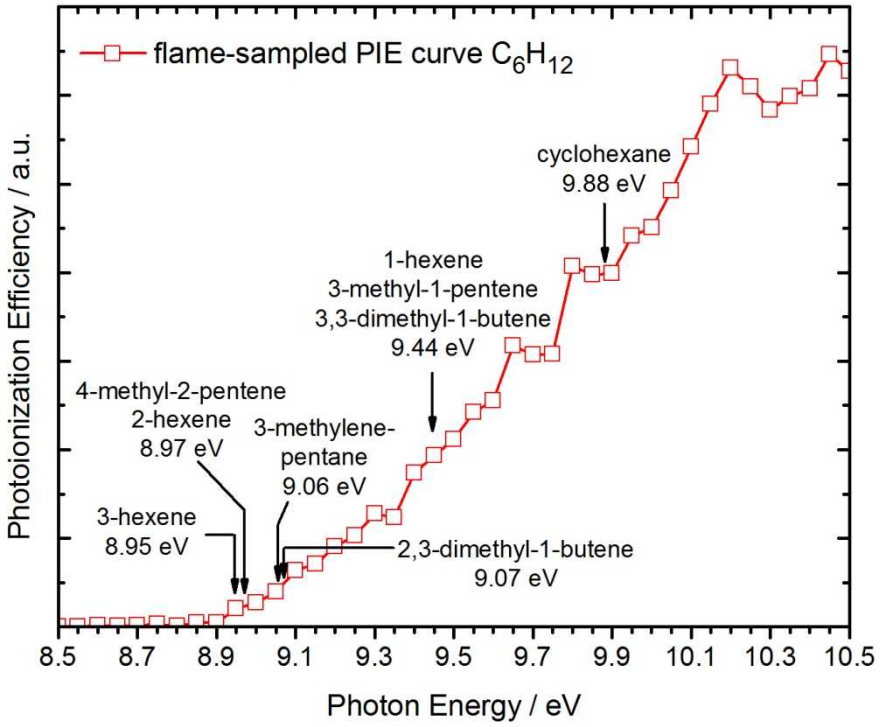


- Multiple isomers at exact mass
- Distinction by ionization energies and photoionization efficiency curves

A total of 6 species can be identified at *m/z* = 58,

Identifying the Flame Components



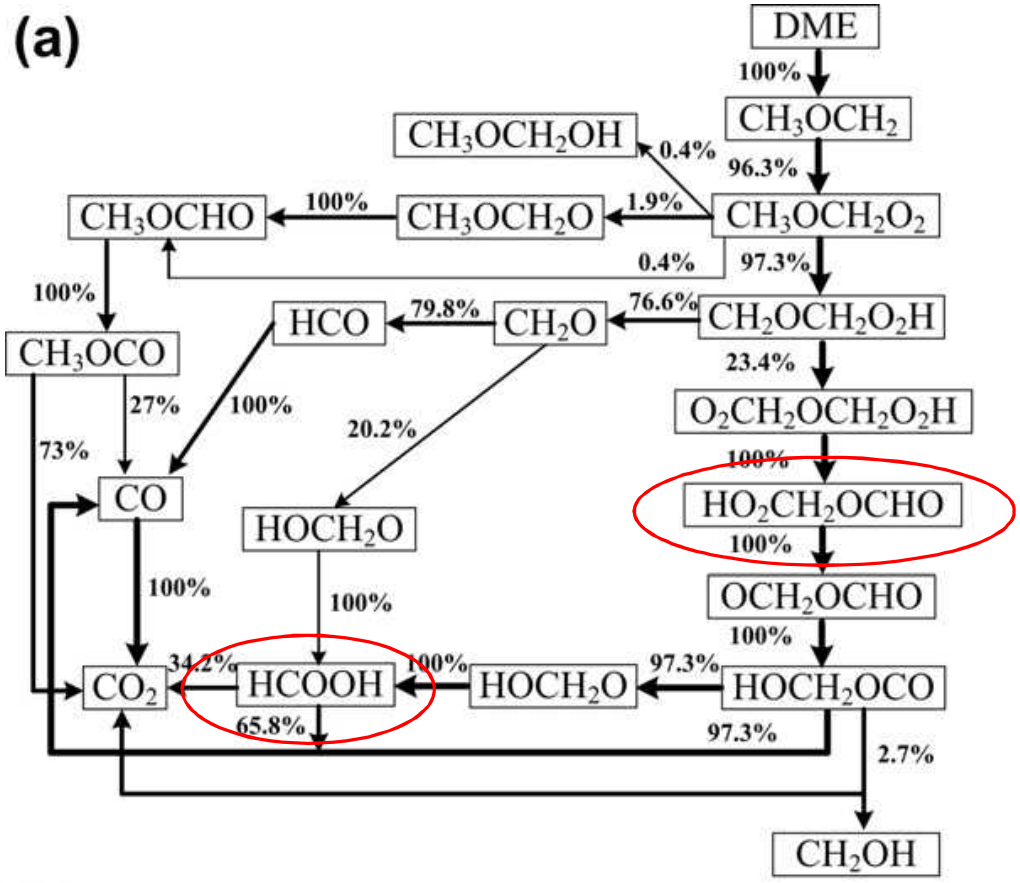


Challenges:

- 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

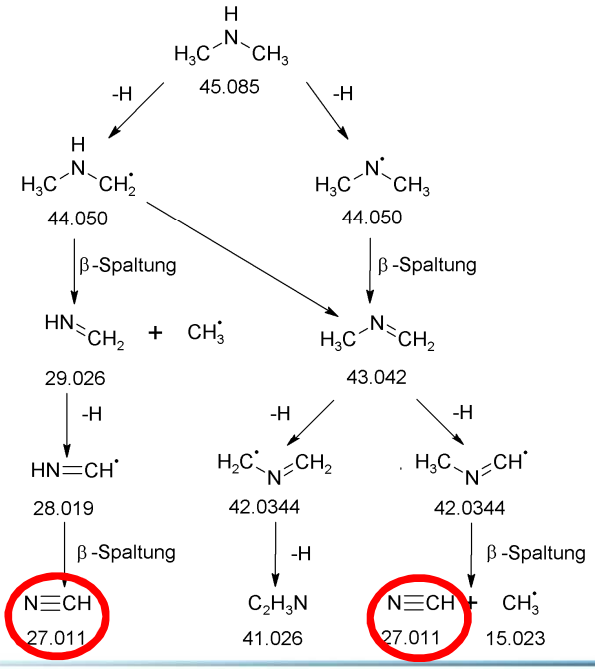
Low temperature oxidation

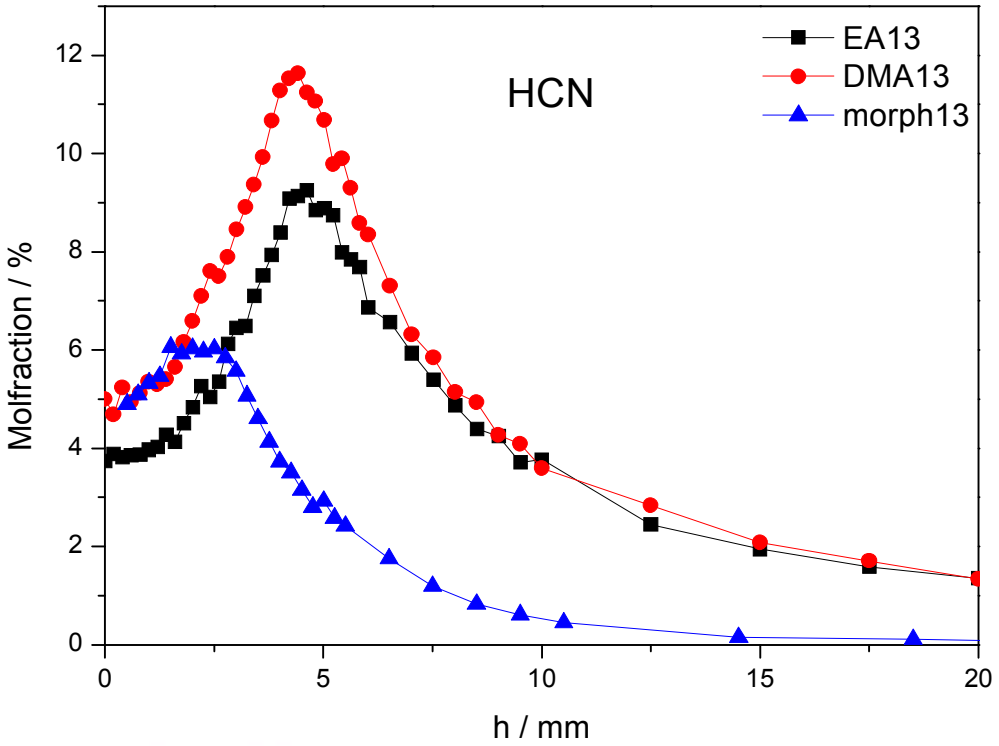
- Investigation of Ketohydroperoxid formation and destruction in lean mixtures of oxygenated and hydrocarbon fuels



Fuel nitrogen conversion

- High resolving power crucially needed because of the additional elemental compositions possible.
- HCN plays an important part in the fuel nitrogen conversion
  - Very high intermediate concentrations
  - Slow decomposition



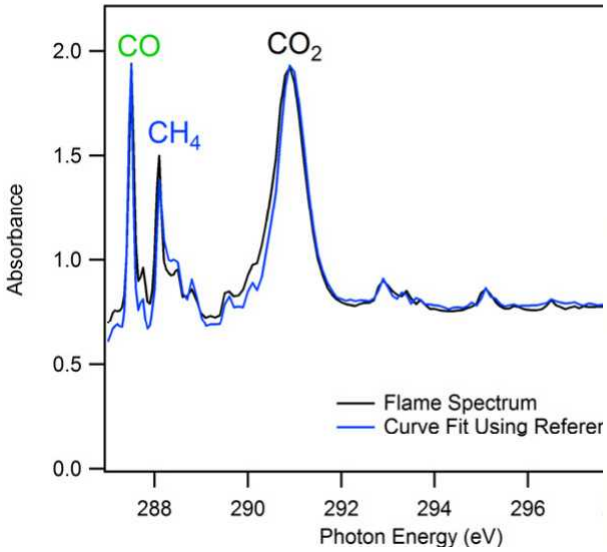


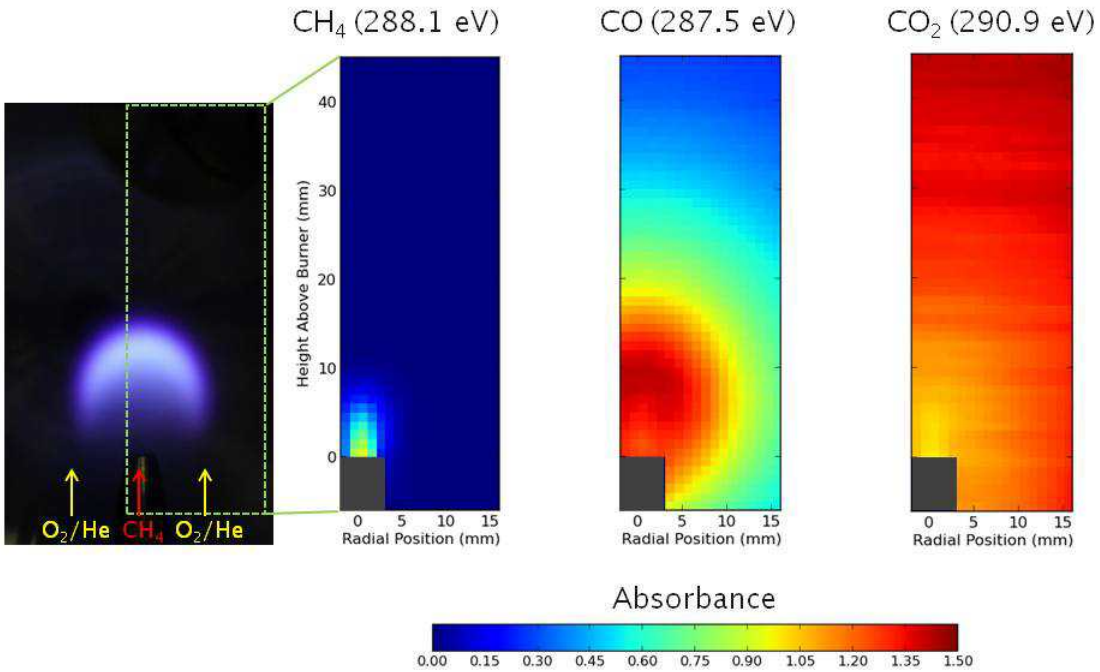
Future Prospects

- Isomer identification via post ionization dissociation
  - Spontaneous decay of metastable ions after soft ionization
  - Laser induced dissociation at turning point of reflectron
  - Laser or collision induced dissociation after linear TOF followed by reflectron TOF

X-ray techniques

- Soft x-ray absorption





Frank et. al. 8th US Combustion Meeting Utah 2013

Summary and Conclusions

- Orthogonal time of flight improves identification power significantly
- Isomer possibilities of larger species are still challenging
- In situ soft x-ray absorption viable option for non premixed flames

- Further enhancement possible by spontaneous or induced post ionization dissociation
- Soot formation may be possible to investigated by Small Angle x-ray scattering or x-ray Raman scattering

Acknowledgments

People:

Dr. Nils Hansen

Flame Team

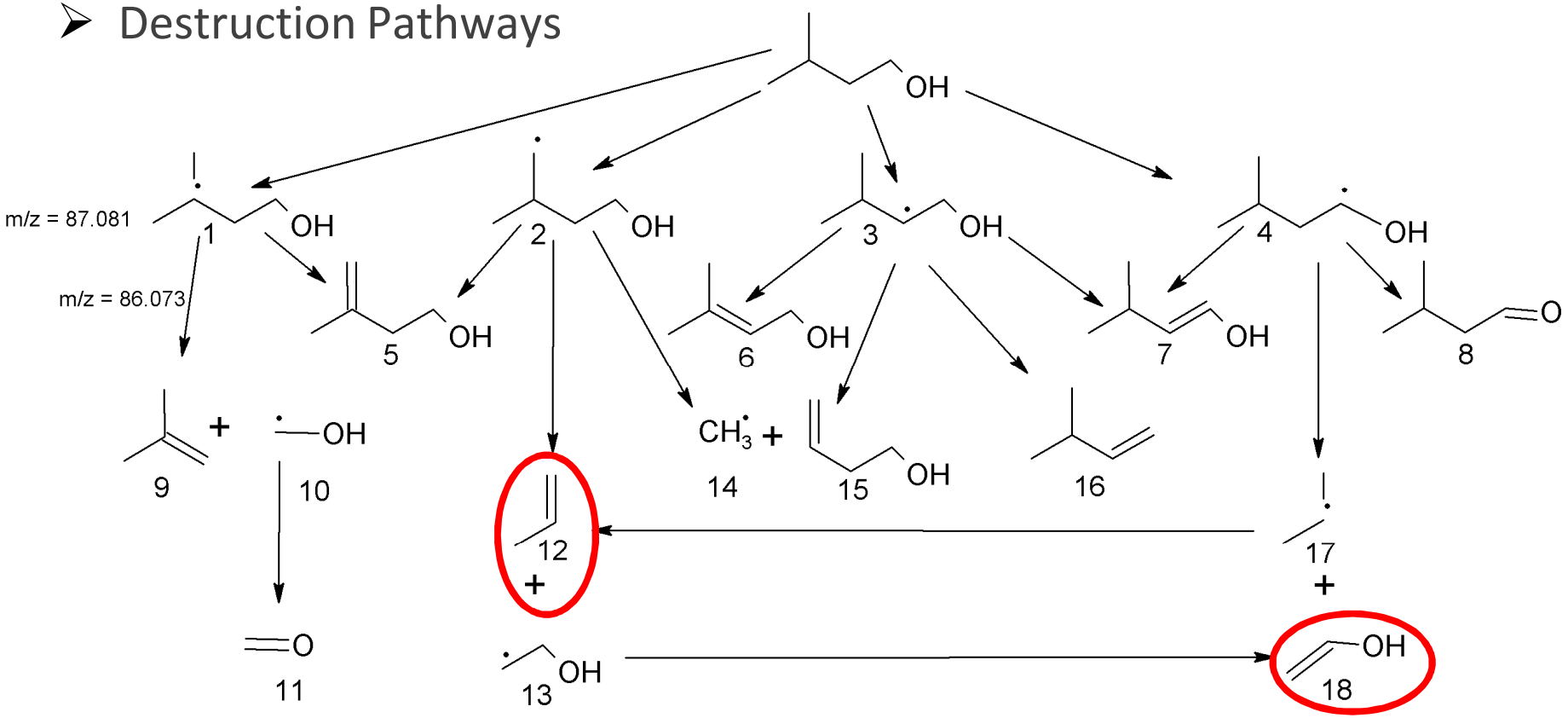
Funding:

- Office of Basic Energy Sciences
- Combustion Energy Frontier Research Center
- Avanced Light Source

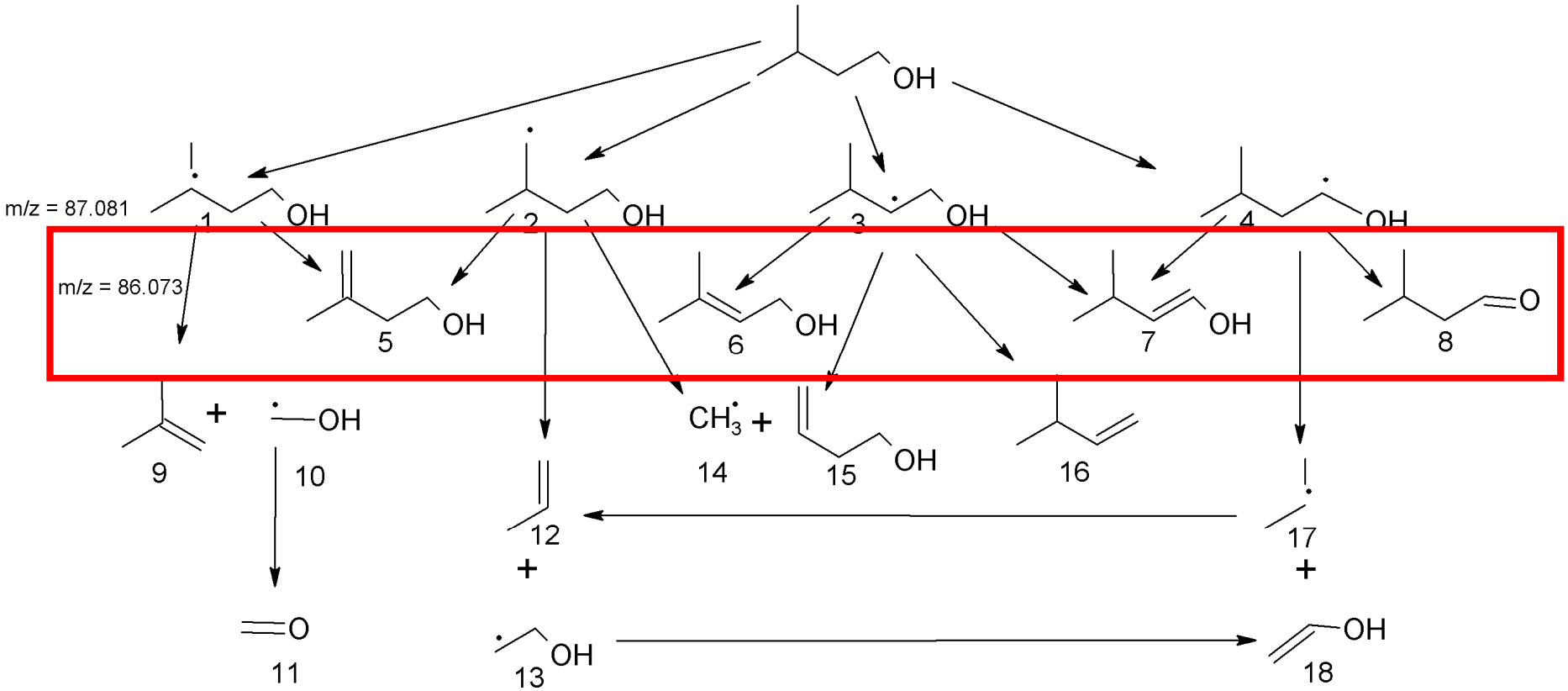
US Department of Energy

Isopentanol results

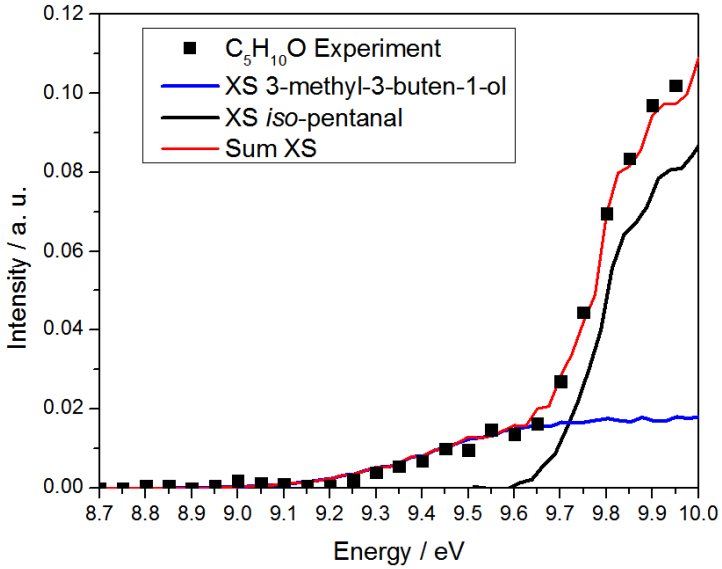
- Over 40 identified species
- Destruction Pathways

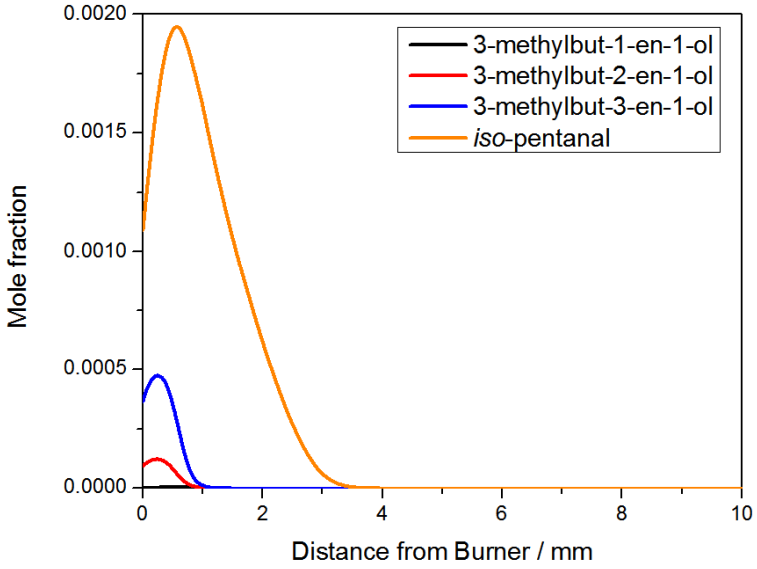


Destruction Pathways



C_5H_{10} Isomers





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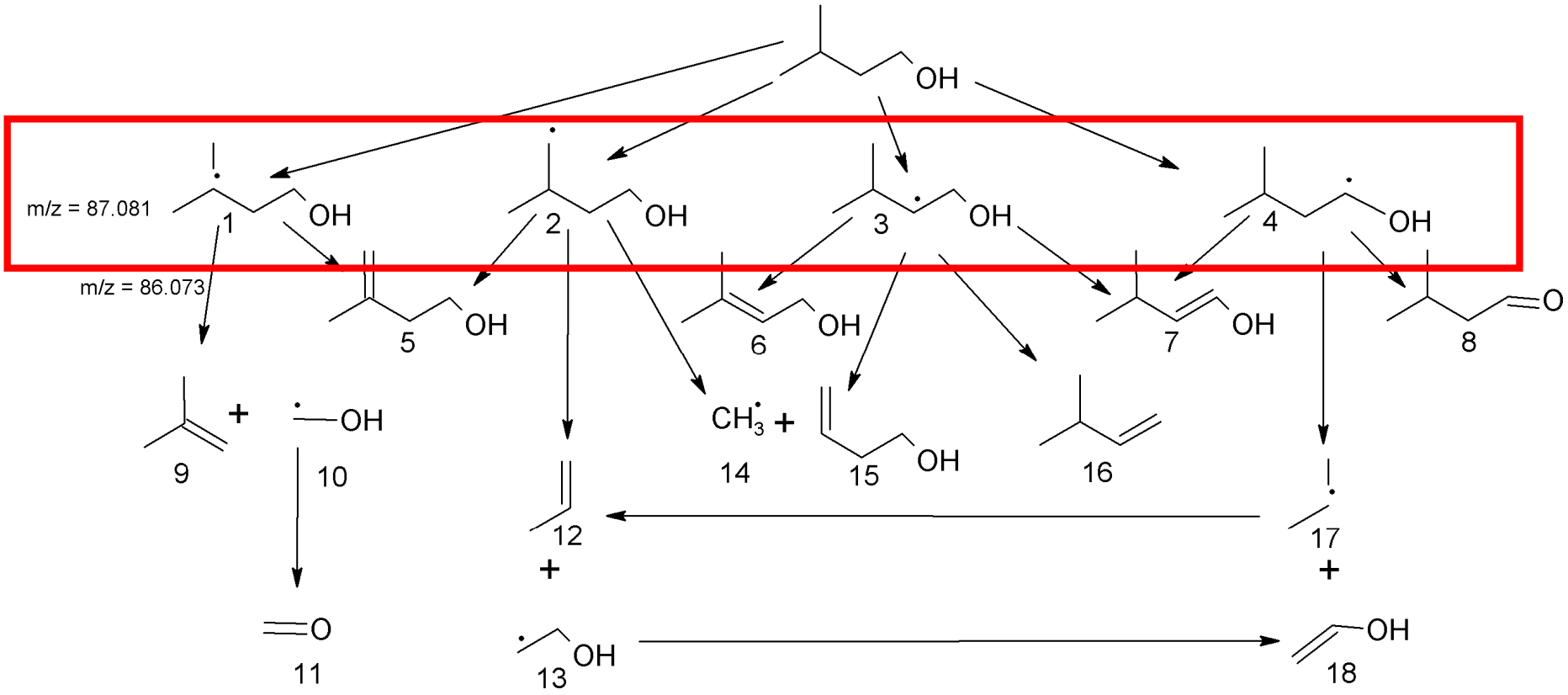
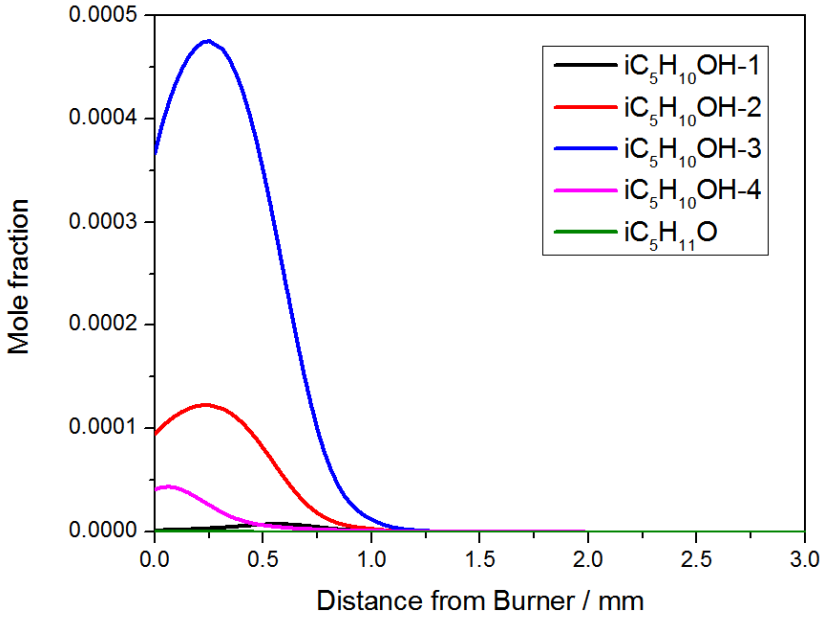
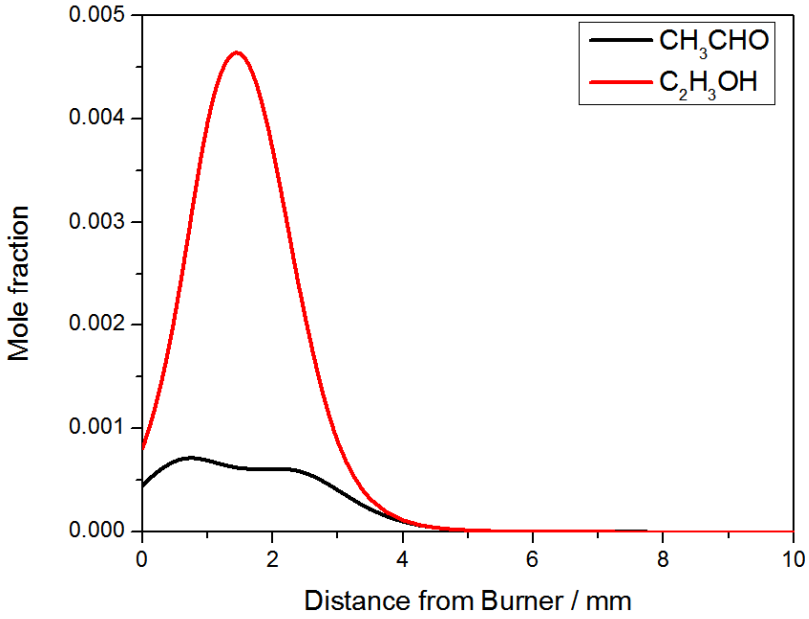
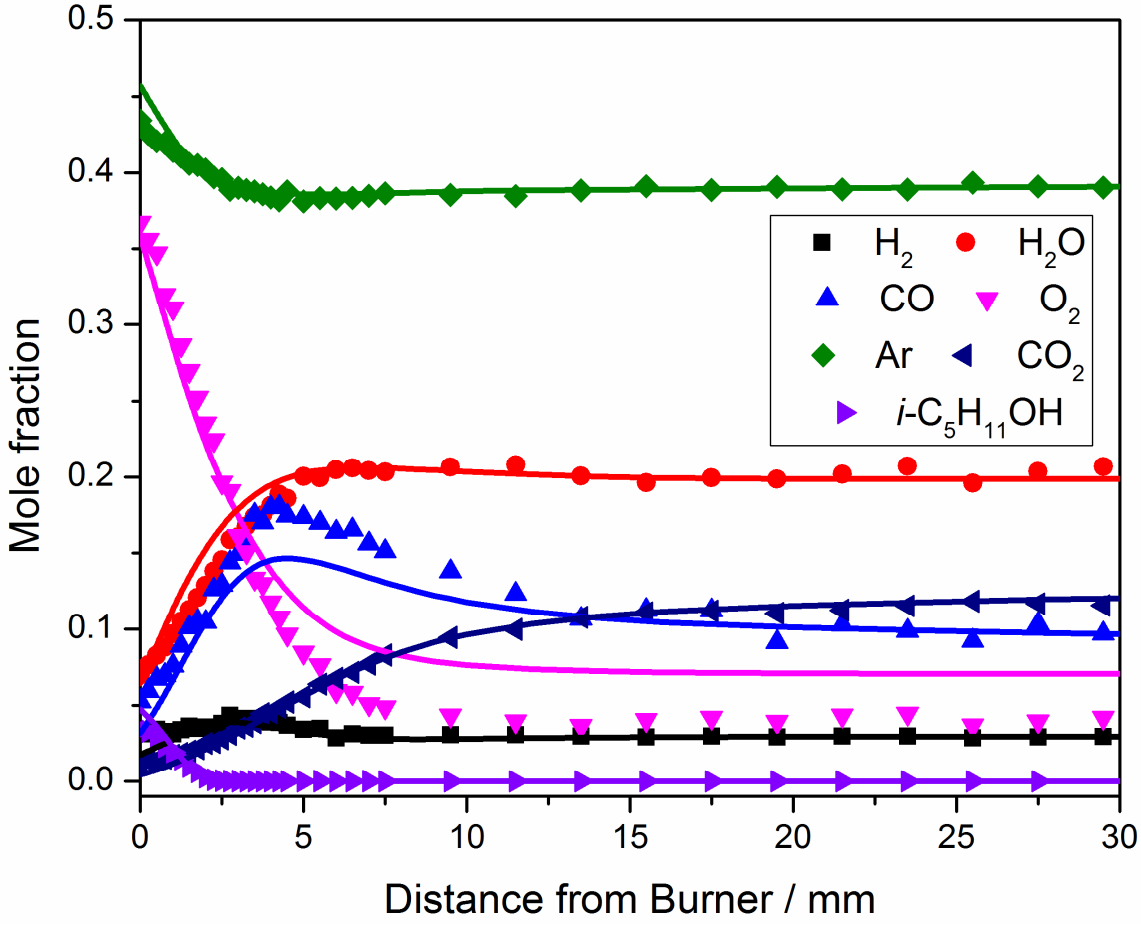
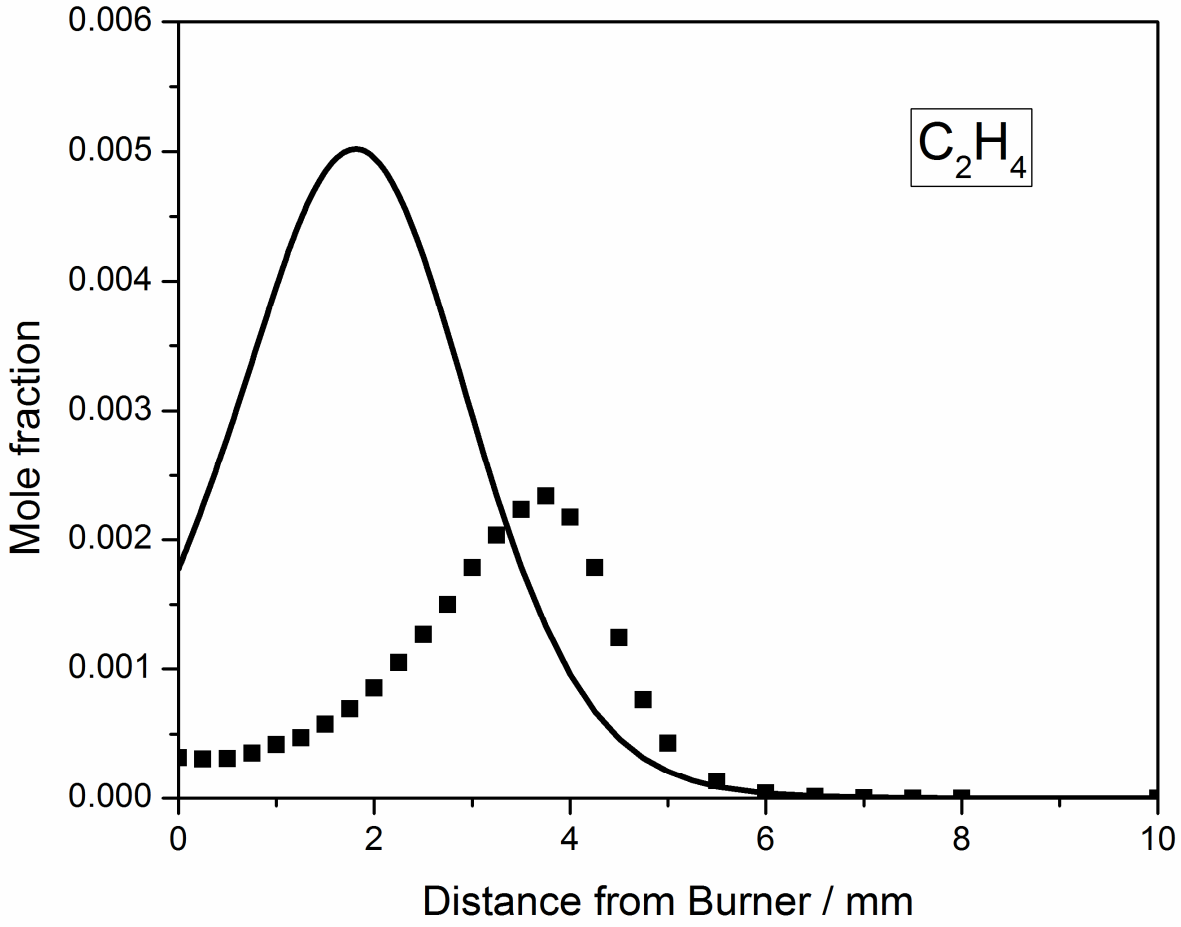


Model Results





Preliminary model comparisons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