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Combustion Chemistry of Next-Generation Biofuels:

Detailed Investigation of iso-Pentanol Flames

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- ✓ **Introduction**
- ✓ **Investigation techniques**
  - ➢ Model Flames
  - ➢ Molecular Beam mass spectrometry
- ✓ ***2-Methyl*butanol**
    - ➢ Destruction Pathways
    - ➢ Preliminary model comparisons
- ✓ **Conclusions and Summary**

Introduction

- Wide variety of potential biofuels
- New chemical classes: alcohols, ester, ethers
- Previous studies: Combustion behavior and pollution potential structure dependent
- Currently: based on starch or oils
- Future: based on cellulosic biomass

Pollutants

Various biofuels show high concentrations of aldehydes

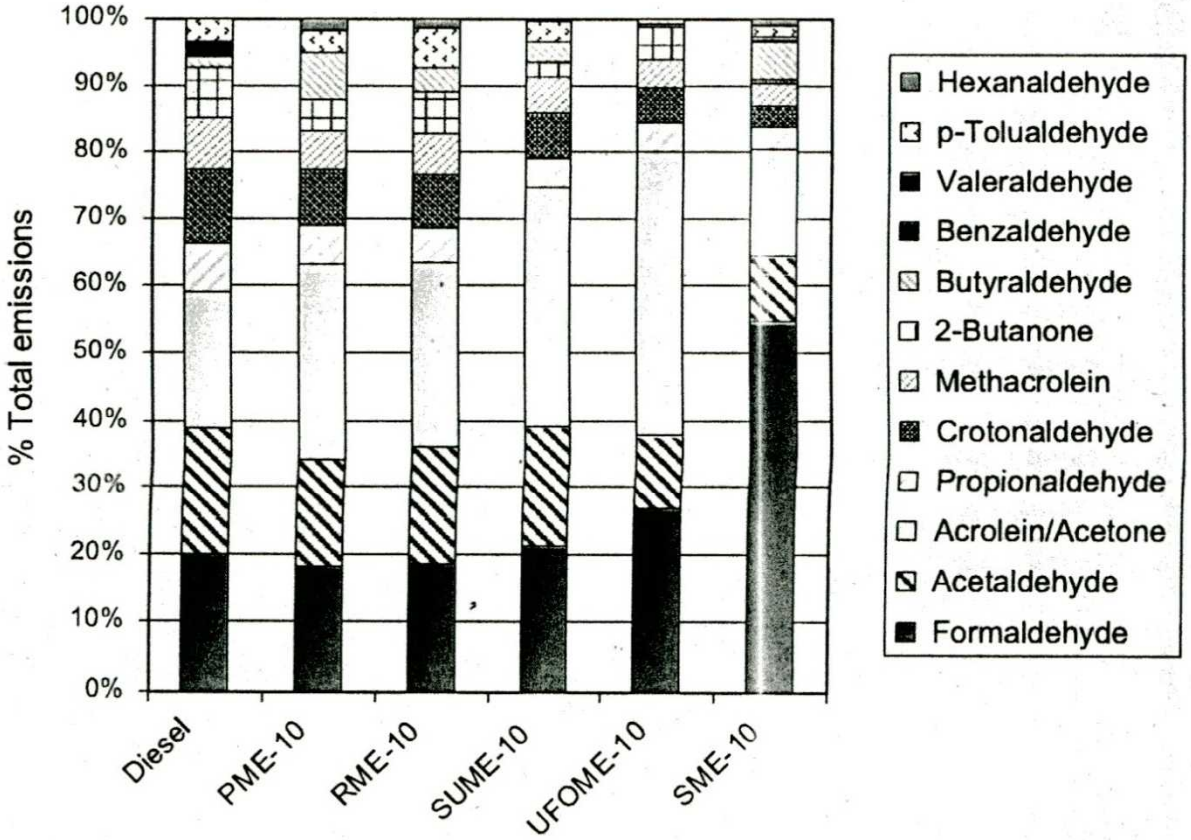
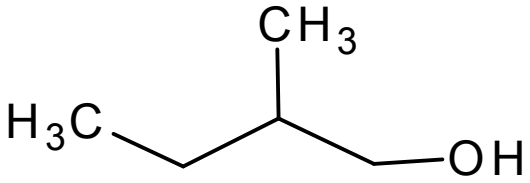


Fig. 2. Percentage of each individual compound on total emissions for each fuel tested.

Fontaras et al. Environnemental Pollution 158 2010 2496-2503

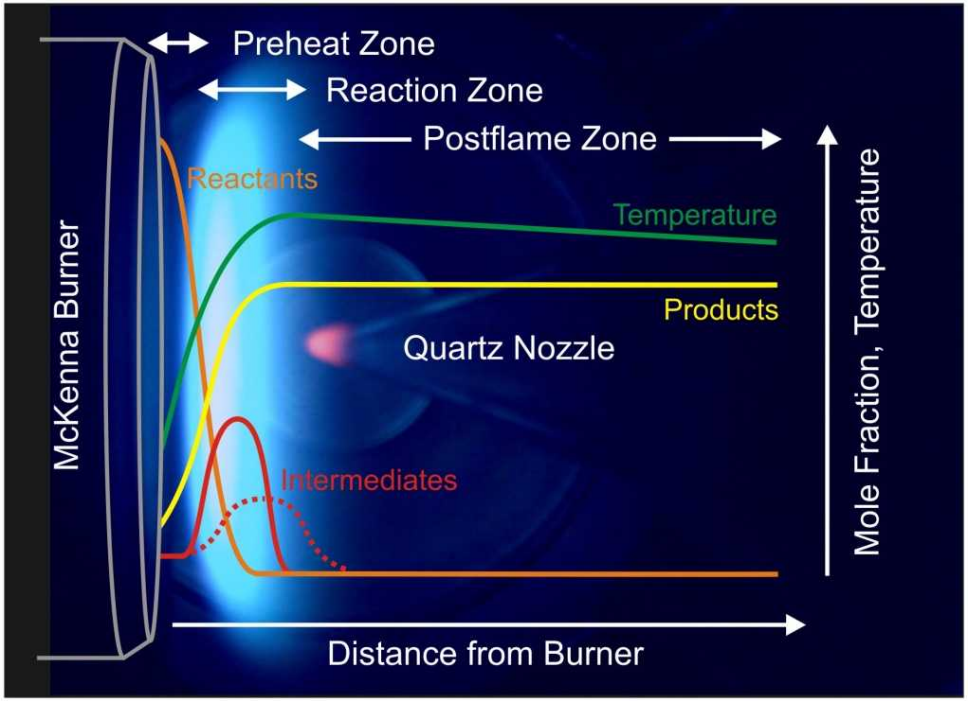
2-Methylbutan-1-ol



- Can be produced from cellulosic biomass by fungi
- Promising combustion behavior
- Isopentanol model based on butanol model available already validated against various other experiments

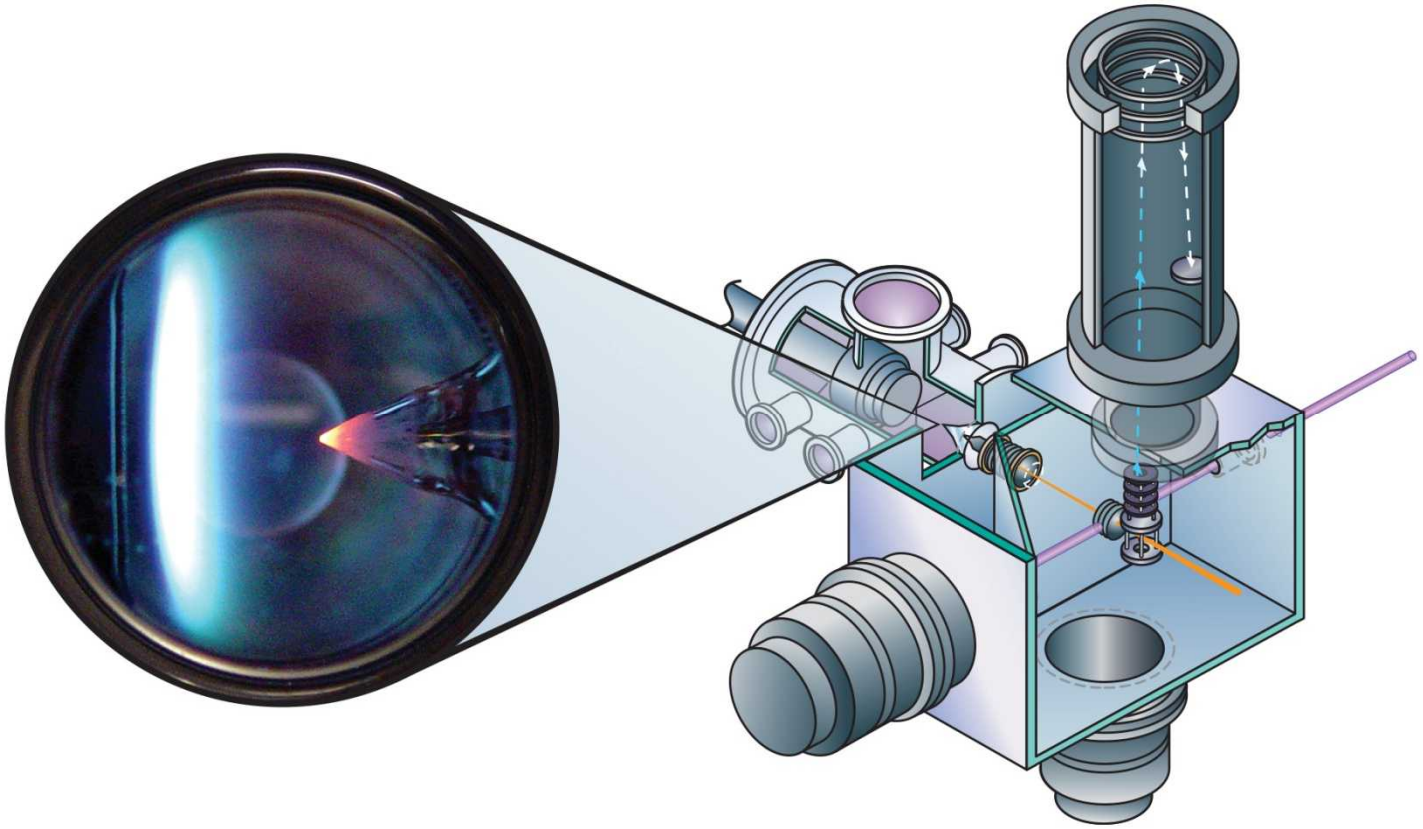
Model Flames

- laminar and premixed (oxygen + fuel)
- flat flame
  - one dimensional ➔ Distance from burner resembles reaction progress
  - low pressure (15 Torr) ➔ higher spatial resolution

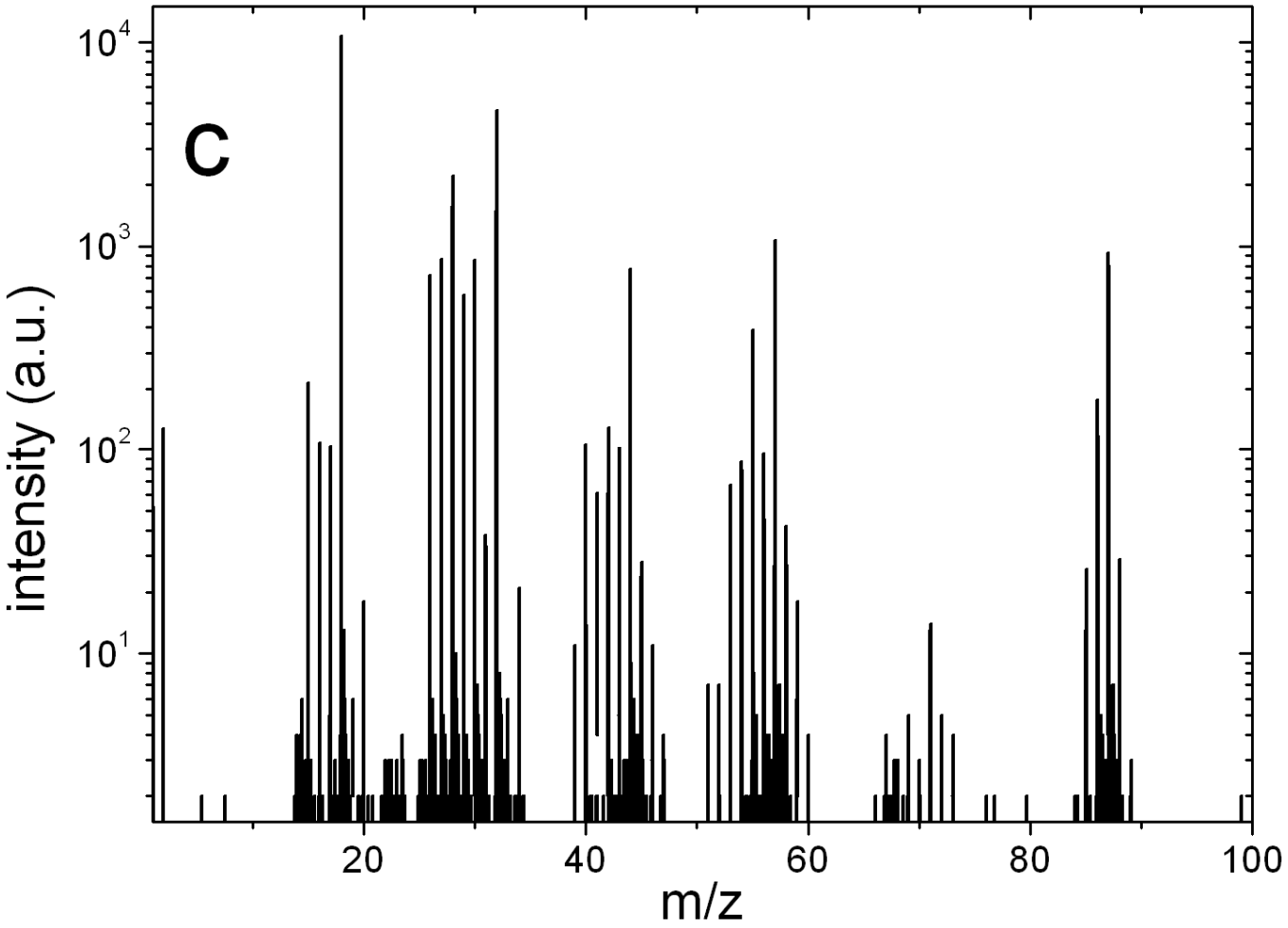


Instrumental setup

- Flame-Sampling Time-of-Flight Mass Spectrometry
- This technique offers rapid data collection and universal species overview



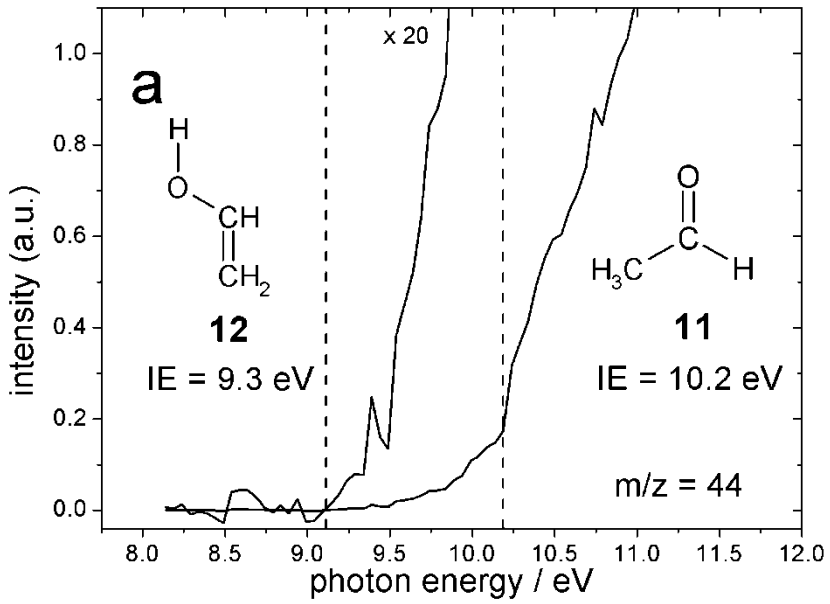
Separation

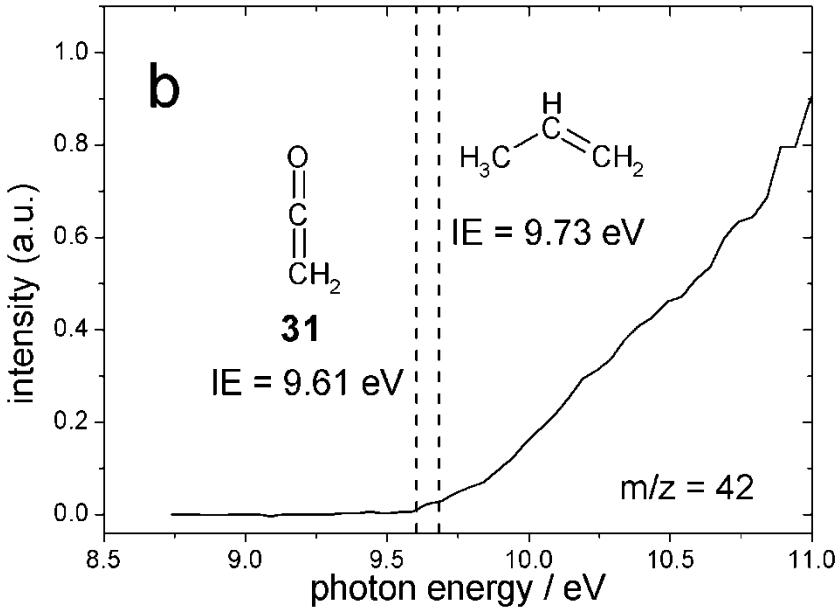


- Complex mass spectra
- Separation can be achieved in two ways

Energy Distinction

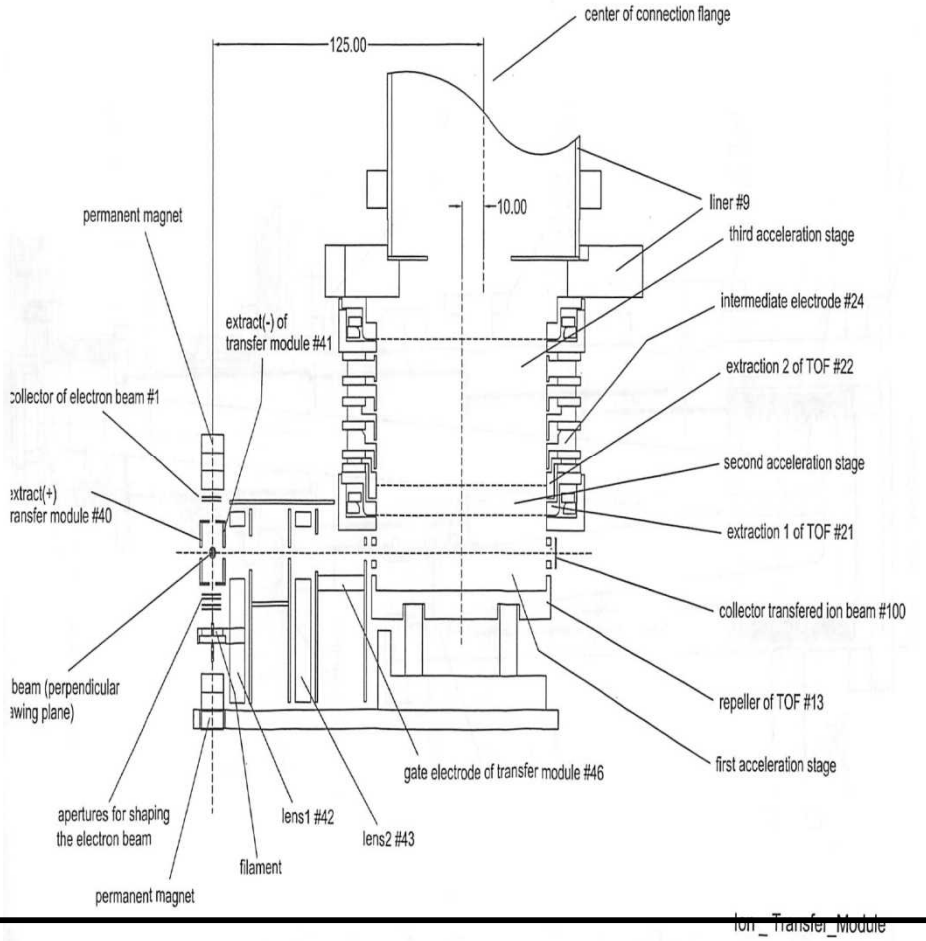
- Ionization by Synchrotron Radiation at the Advanced Light Source
- Energy resolution (0.05 eV)
  - Isomer separation relying on known cross sections for all possible species
  - Mass resolution 1000 ➔ overlap between species on one nominal mass





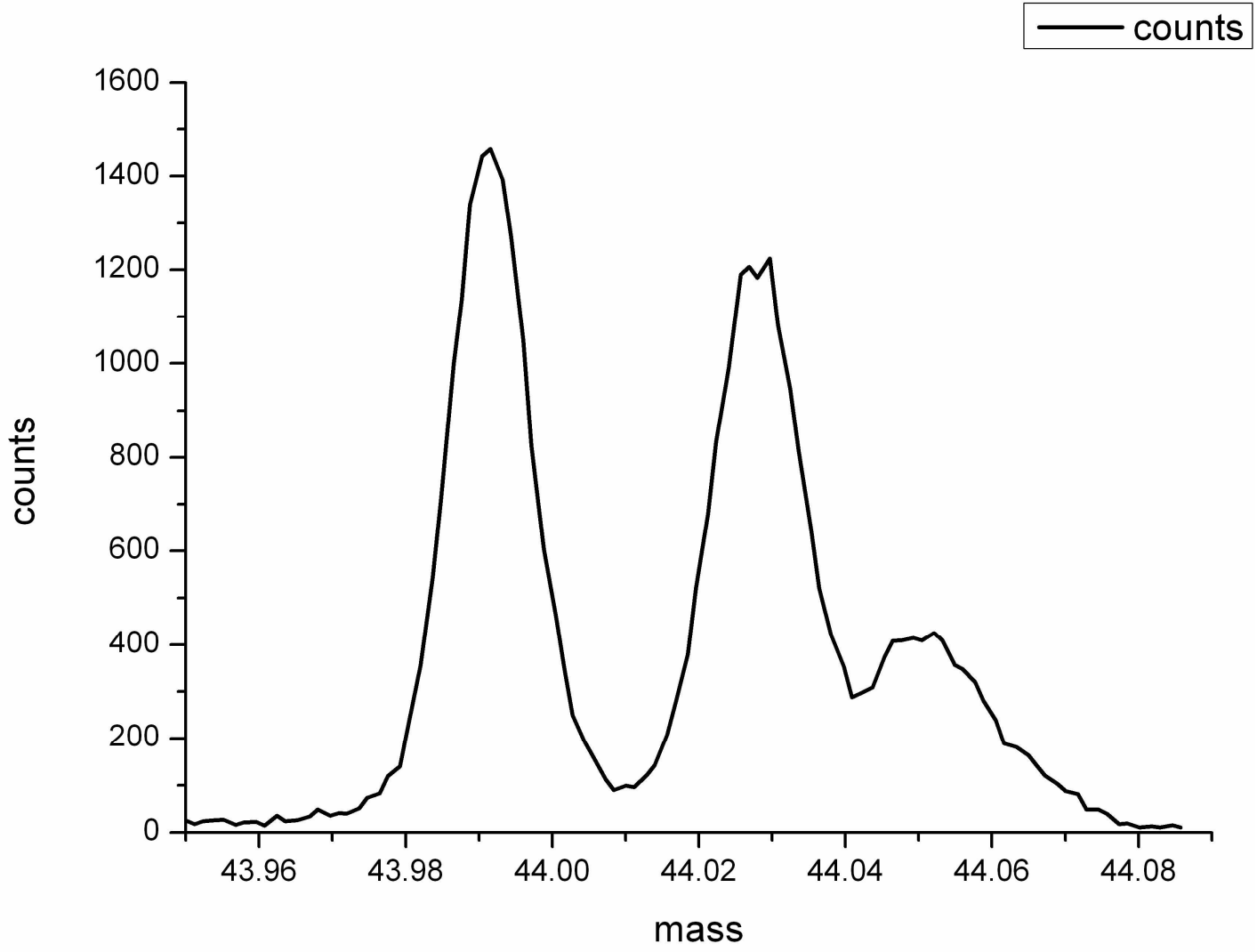
New mass spectrometer

- Orthogonal time of flight
  - Decoupling of ionization and extraction region
  - 2 stage extraction
  - Reflectron
  - High mass resolution R>3000 at continuous ionization
- Remaining overlaps resolved by fitting software
- Variety of other ionization methods available (Electron Impact, REMPI)

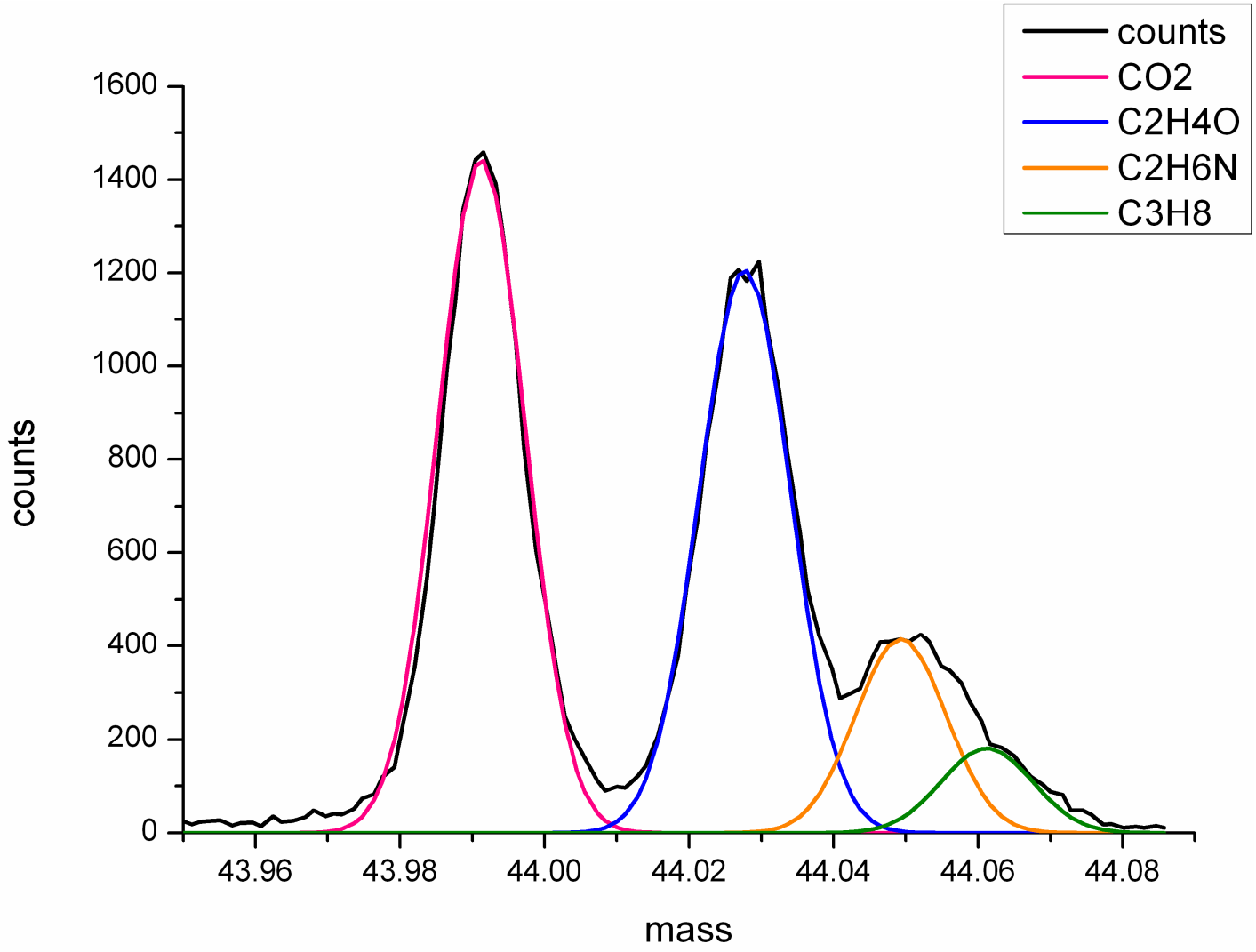


By Utilizing this instrument with Synchrotron radiation separations are possible which where only possible combining results of different machines. Furthermore species assignments are achievable which remained ambiguous before.

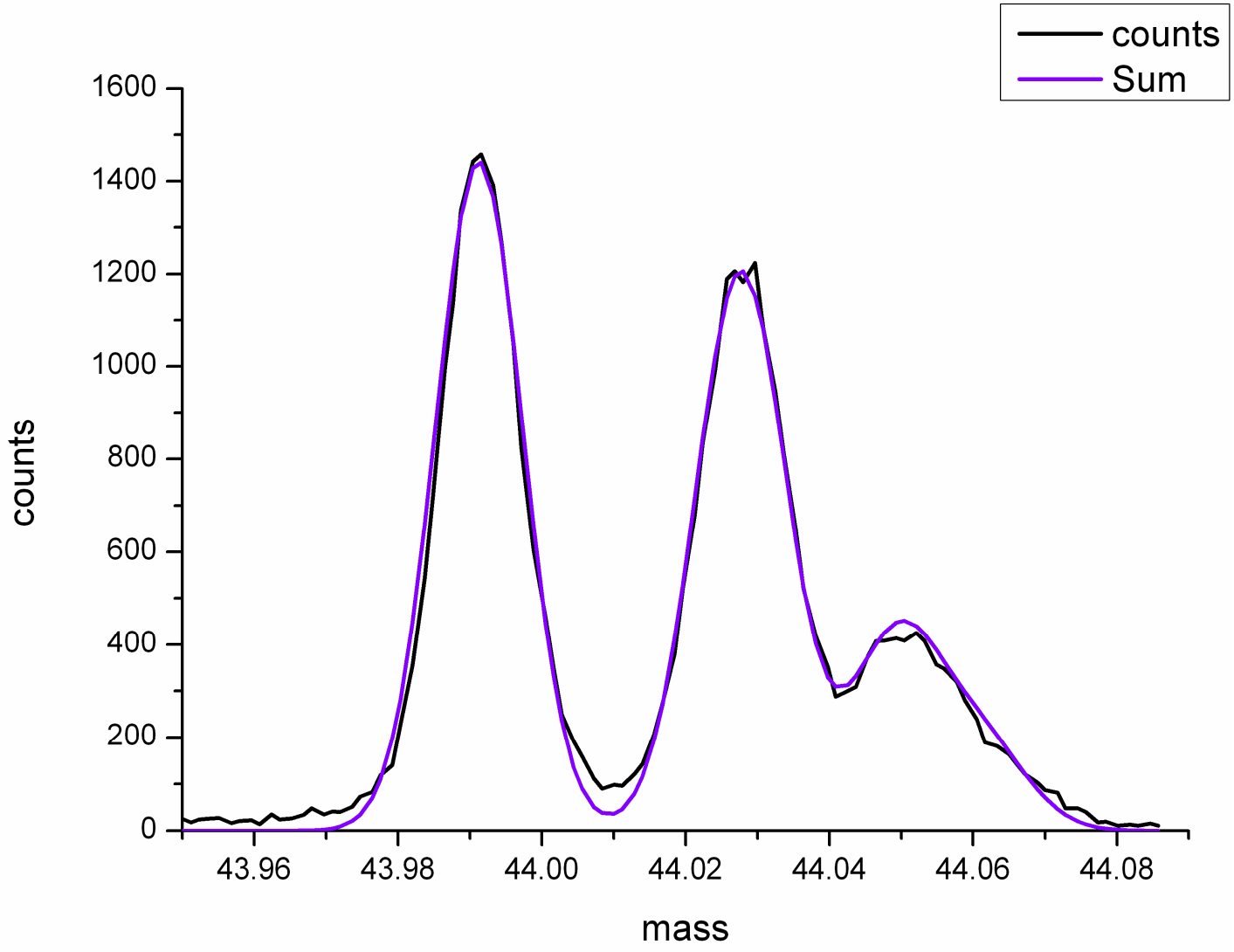
Mass separation



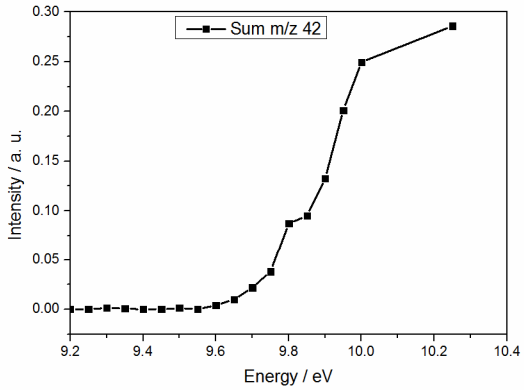
Mass separation



Mass separation

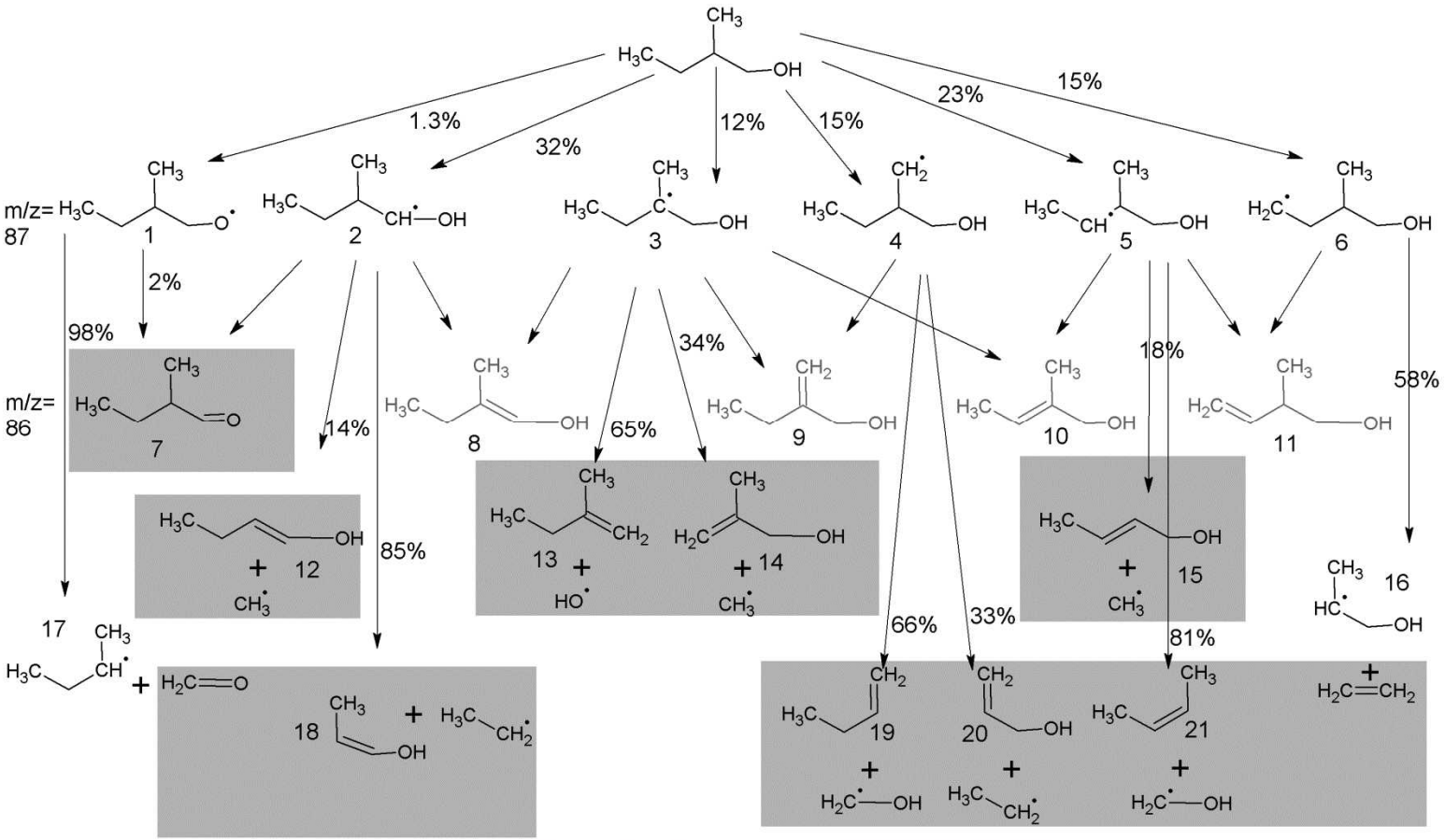


Identifying the Flame Components



Methylbutanol results

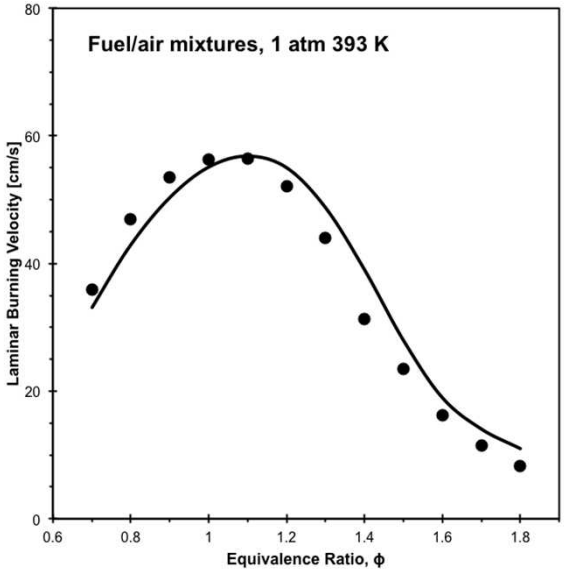
- Over 40 identified species
- Destruction Pathways

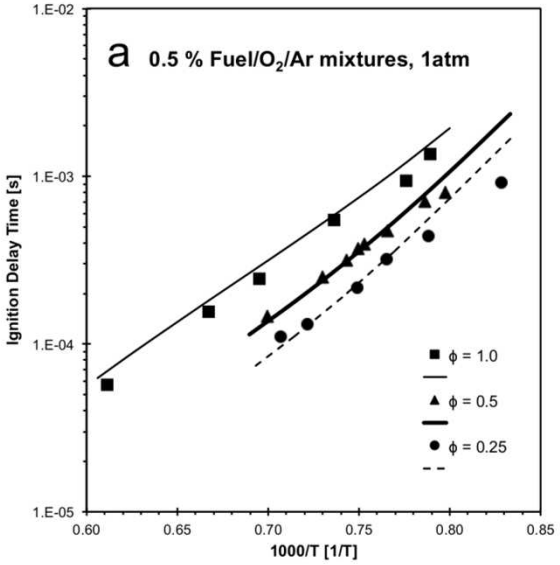


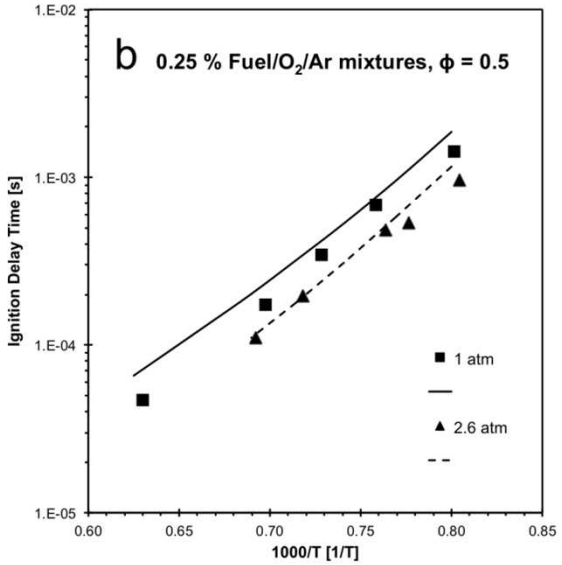
Model

- Adapted at KAUST from their Isopentanol model
  - Isopentanol model validated against various other experiments
  - 2-methylbutanol modell validated against flame speed and ignition delay data
- 2086 reactions 324 species
- Overall good agreement

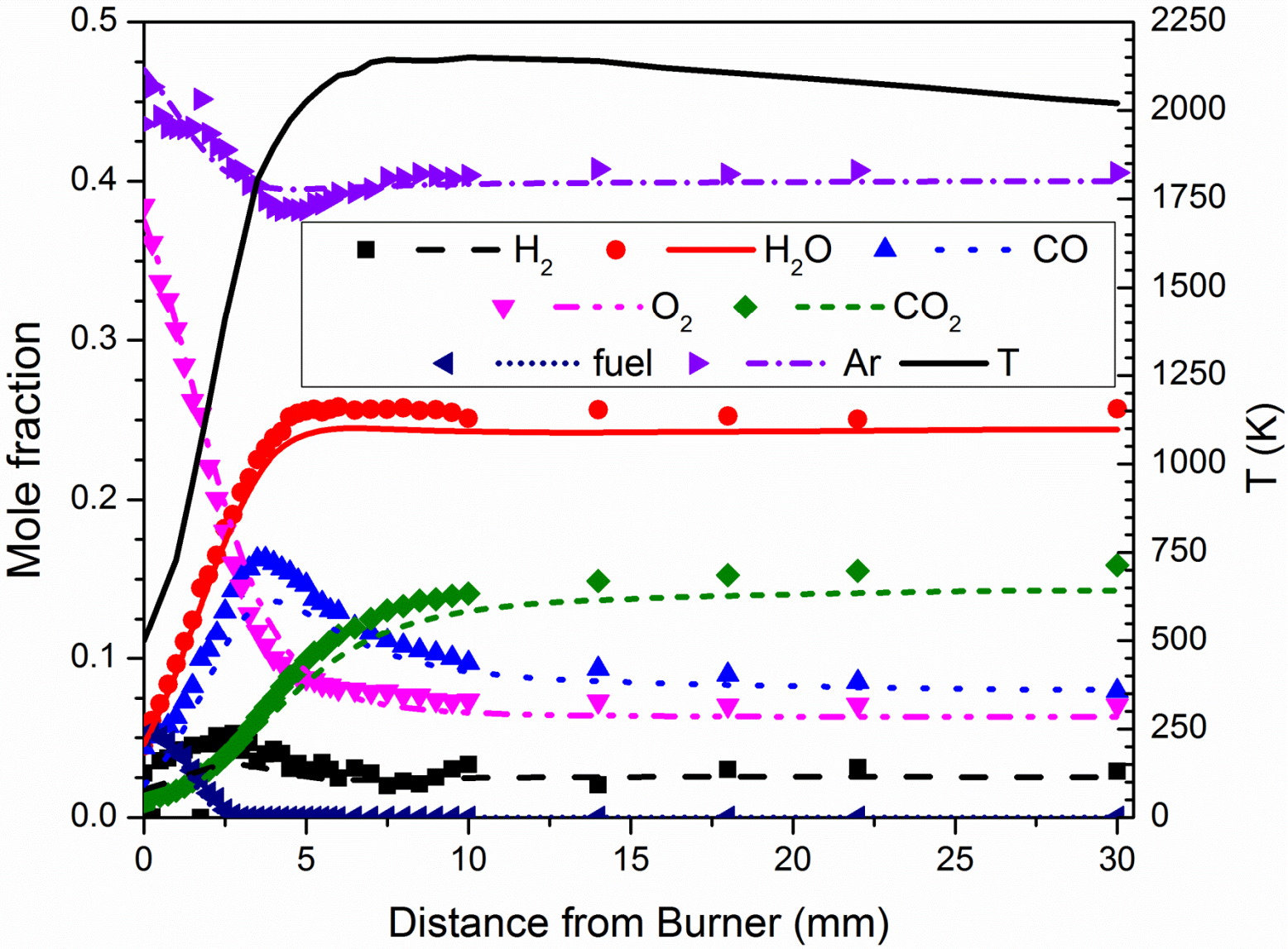
Model


Fuel/air mixtures, 1 atm 393 K
Laminar Burning Velocity [cm/s]
Equivalence Ratio, ϕ
0
20
40
60
80
0.6
0.8
1
1.2
1.4
1.6
1.8


a 0.5 % Fuel/O2/Ar mixtures, 1atm
Ignition Delay Time [s]
1000/T [1/T]
1.E-02
1.E-03
1.E-04
1.E-05
0.60
0.65
0.70
0.75
0.80
0.85
ϕ = 1.0
ϕ = 0.5
ϕ = 0.25

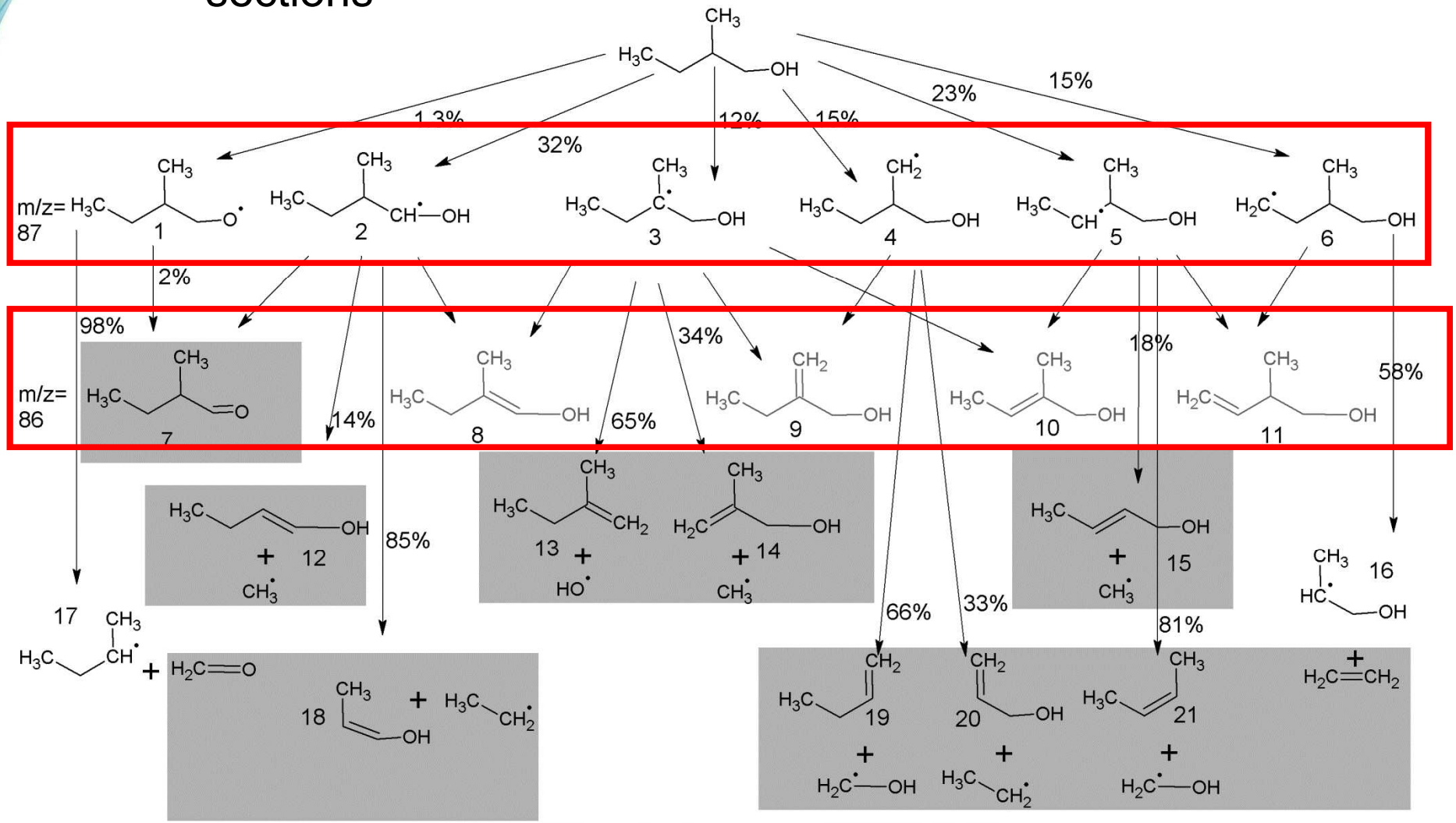

b 0.25 % Fuel/O2/Ar mixtures, ϕ = 0.5
Ignition Delay Time [s]
1000/T [1/T]
1.E-02
1.E-03
1.E-04
1.E-05
0.60
0.65
0.70
0.75
0.80
0.85
1 atm
2.6 atm

Modell Comparison



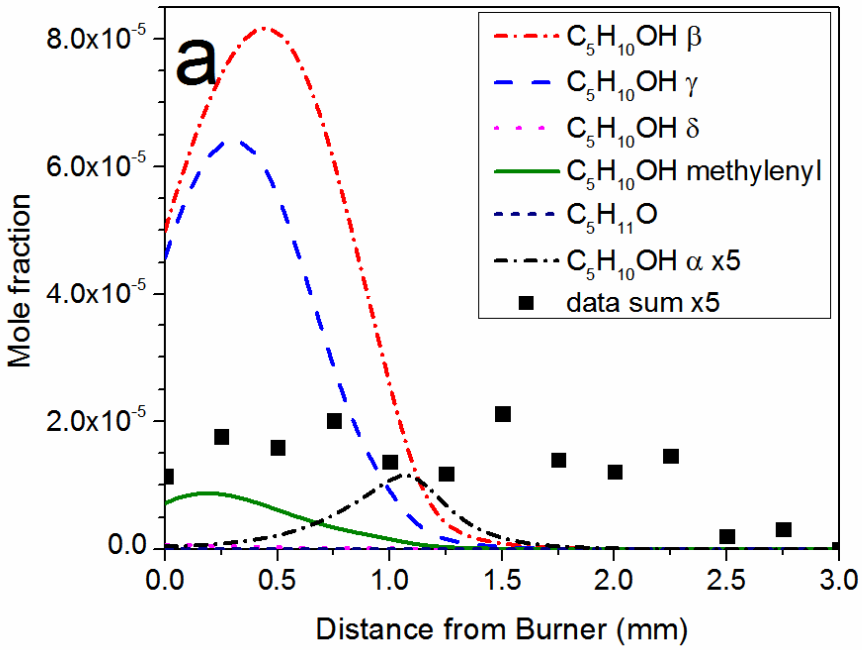
Destruction Pathways

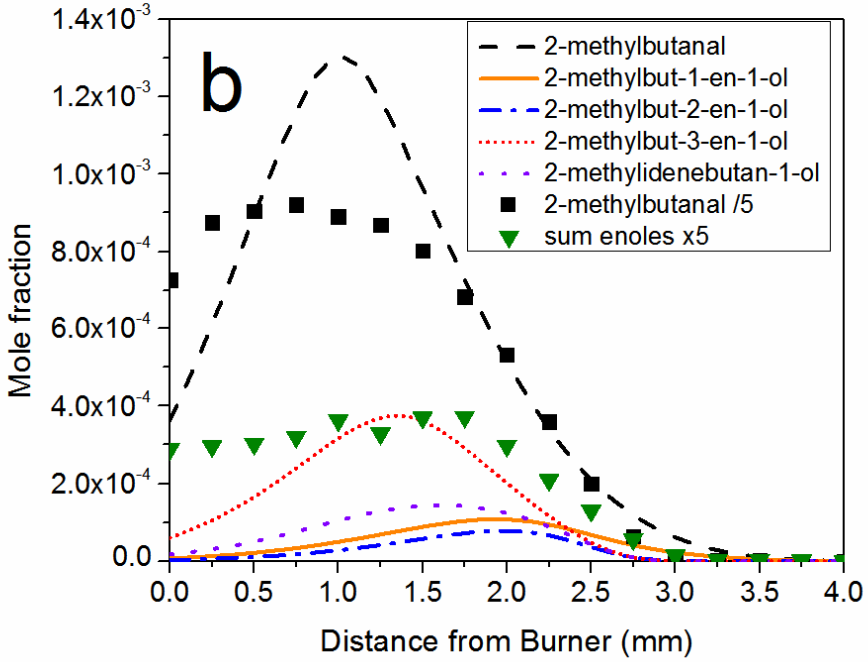
- -H separation not possible because limited cross sections



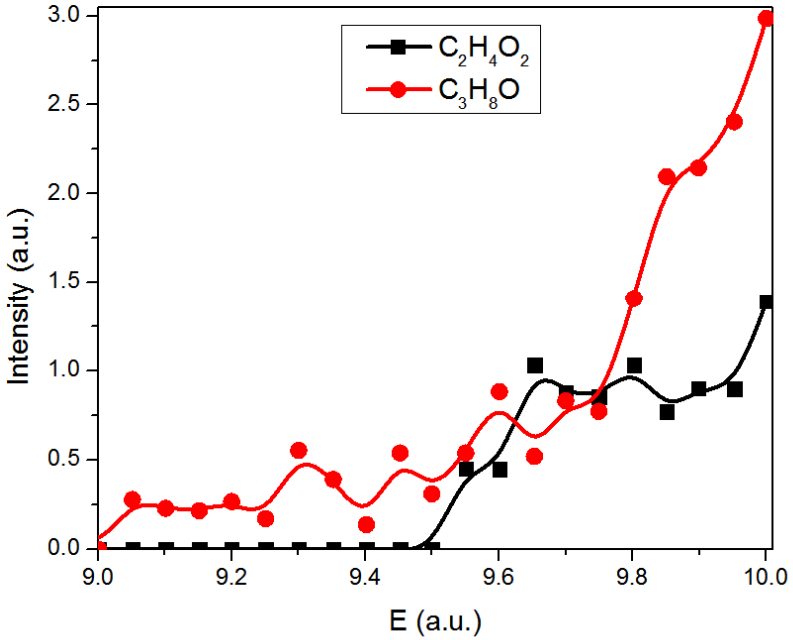
$C_5H_{10}O$ and $C_5H_{10}O$ Isomers

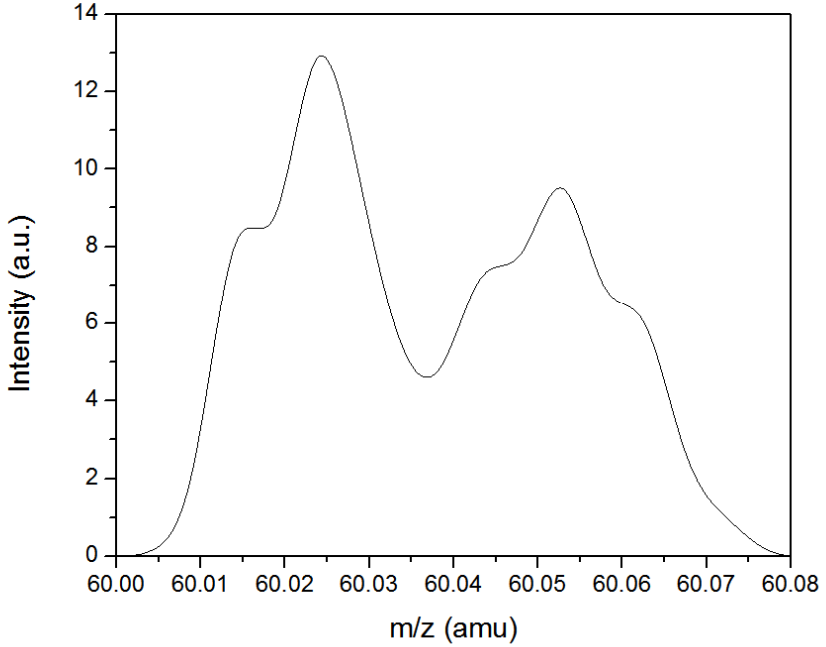
- Fuel radicals elude detection even in recend experiments at SLS despite higher radical sensitivity
- Enols Lumped in Sub model and in experiment
  - both rate constants and cross sections missing





Further Species





Summary and Conclusions

- A new mass spectrometer was built combining capabilities so far only available in different laboratories
- First time detectability of several instable species
  - Impact on combustion chemistry still to be investigated
  - Reference data (absolute cross sections) desperately needed
- 2-Methylbutanol and Isopentanol are a good model substance isomer pair to study the oxidation chemistry of higher alcohols.
  - Further investigation by Flame-PEPICO (Presentation 3B10 Ballroom B)
- Preliminary model comparisons promising but still needs improvement
  - measurement of currently analogy derived or calculated rate constants

Acknowledgments

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