High-Temperature Oxidation of *n*-Butanol, *iso*-Butane, and *iso*-Butene in Low-Pressure Premixed Flames

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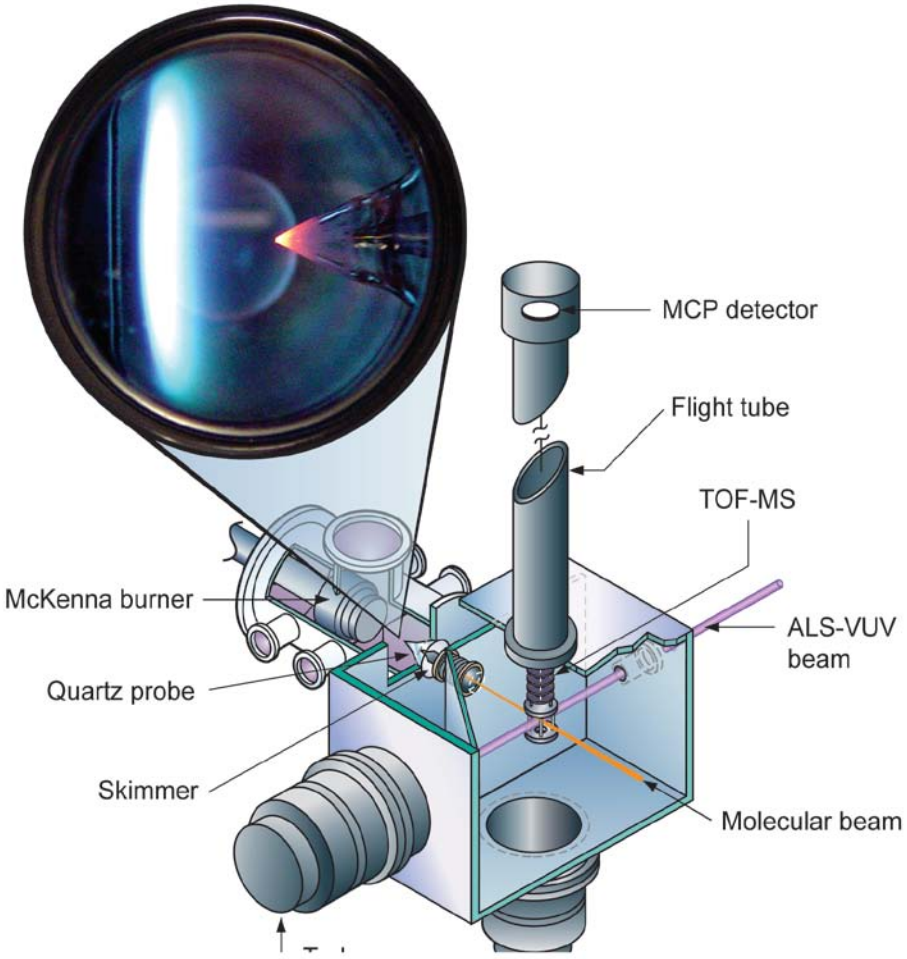
Outline

- ✓ **Experimental Details**
  - Photoionization Mass Spectrometer
  - Flame Conditions
- ✓ **Flame Chemistry Insights (*n*-butanol flame)**
  - Experiment *vs.* Model
  - Fuel-Consumption Pathways
  - Enols and Aldehydes: Reaction Path Analysis
- ✓ **Summary and Outlook**

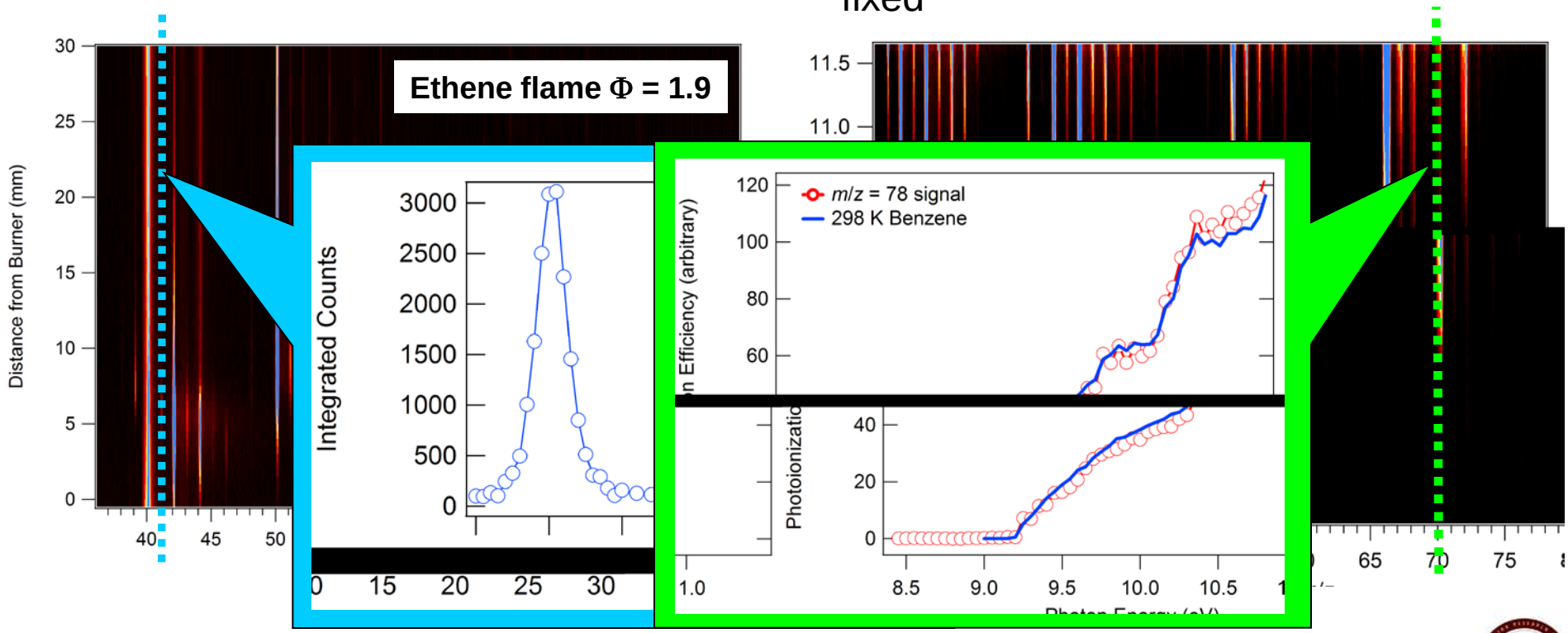
Experimental Details: Synchrotron Photoionization Molecular-Beam Mass Spectrometry



- ✓ Premixed laminar low-pressure flames
- ✓ Molecular beam sampling ”freezes“ chemistry
- ✓ Time-of-flight mass spectrometry offers the appeal of universal and relatively rapid data collection
- ✓ Photoionization mass spectrometry allows identification of species
  - by mass
  - by ionization energy
  - ✓ Energy Scan:
  - to identify species by photoionization efficiency curves
- ✓ Burner Scan:
- to get spatial profiles the burner is moved relative to the quartz cone and photon energy is fixed

Experimental Details: Synchrotron Photoionization Molecular Beam Mass Spectrometry

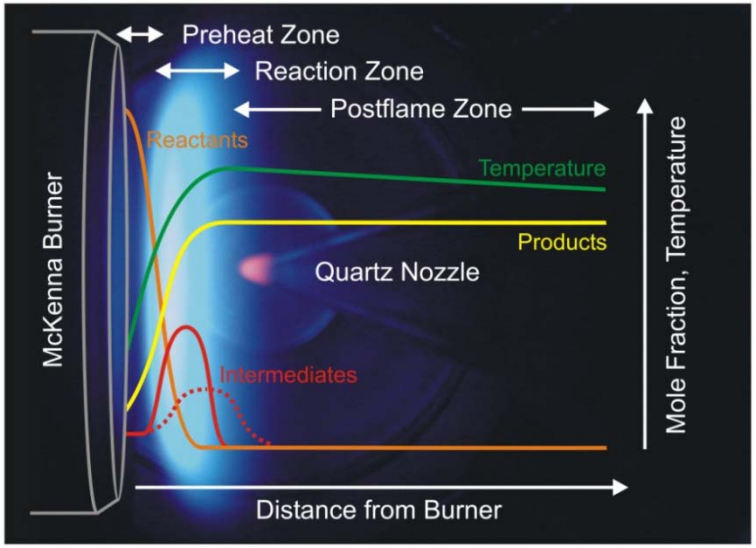
- ✓ **Burner Scan**
  to get spatial profiles the burner is moved relative to the quartz cone and photon energy is fixed
- ✓ **Energy Scan**
  to identify species by photoionization efficiency curves the photon energy is scanned and the burner position is fixed



Experimental Details: Flame Conditions and Combustion Chemistry Models

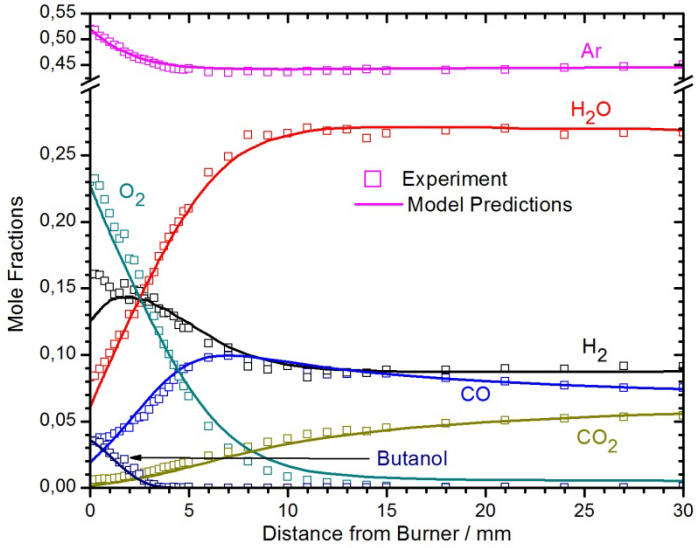
	n-butanol	*n*-butanol	*i*-butanol	*i*-butane	*i*-butene	
fuel	3.32	3.52	3.52	9.87	10.53	mol%
H_2		24.12	24.12			mol%
O_2	16.68	24.12	24.12	40.13	39.47	mol%
Ar	80	48.24	48.24	50	50	mol%
pressure	25	15	15	30	30	Torr
Stoichiometry	1.2	1.38	1.38	1.6	1.6	

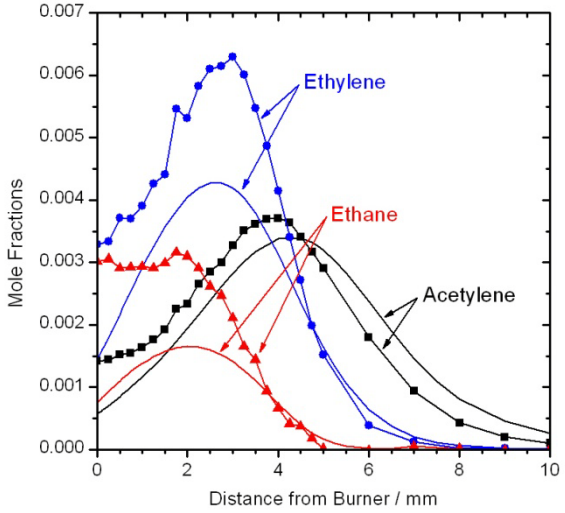
- about 30 to 40 species were quantified for each flame
- temperature profiles were measured using OH LIF
- resulting mole fraction data are compared with combustion chemistry model predictions
  - ✓ M. R. Harper *et al., Combust. Flame,* doi:10.1016/j.combustflame.2010.06.002 (2010)
  - ✓ H. Wang *et al.,* USC Mech V2.0, http://ignis.usc.edu/USC_Mech_II.htm, May 2007

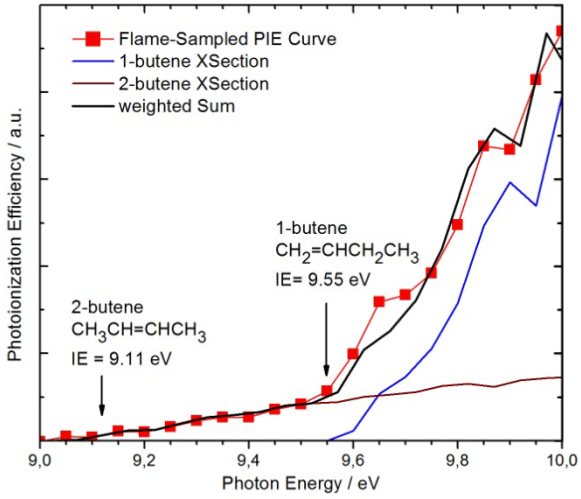


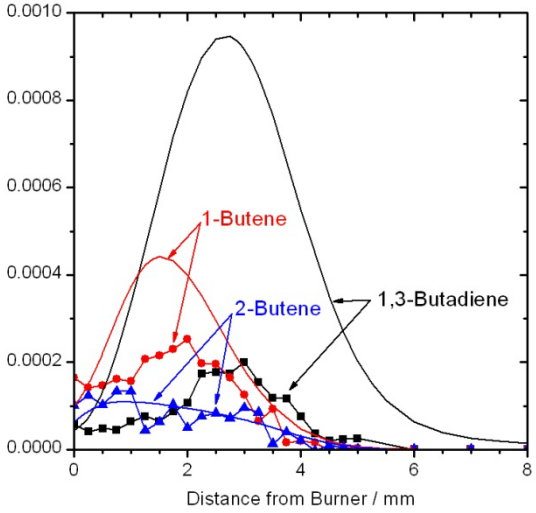
n-butanol: Experiment *vs.* Modeling (Harper *et al.*)

- The updated model includes additional pressure-dependent rate coefficients
  - ✓ *the model was insensitive to these kinetic parameters for the previous validation targets*
- experimentally determined major species profiles agree satisfactorily with modeled results
- larger discrepancies for some minor species, including C_3's and C_4's





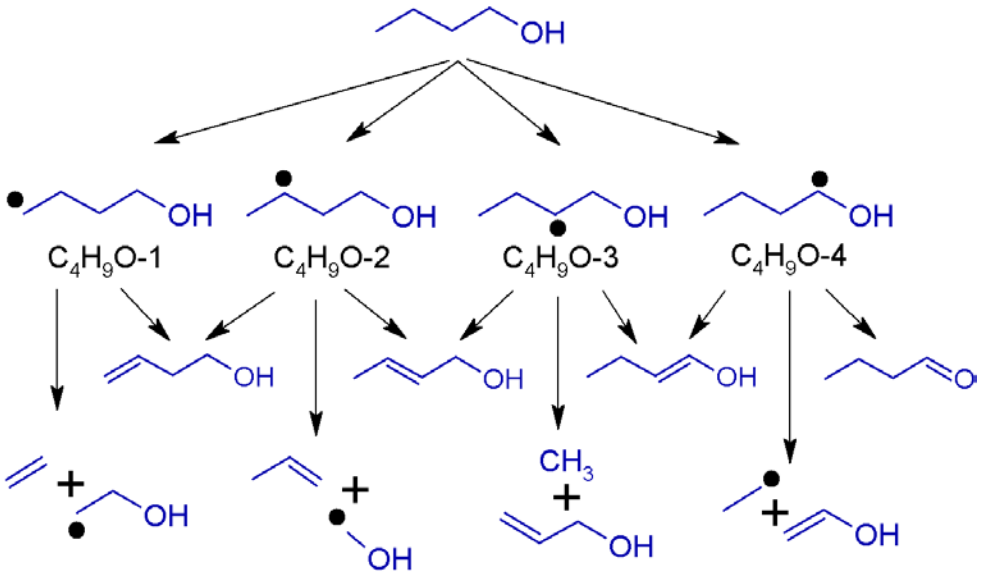




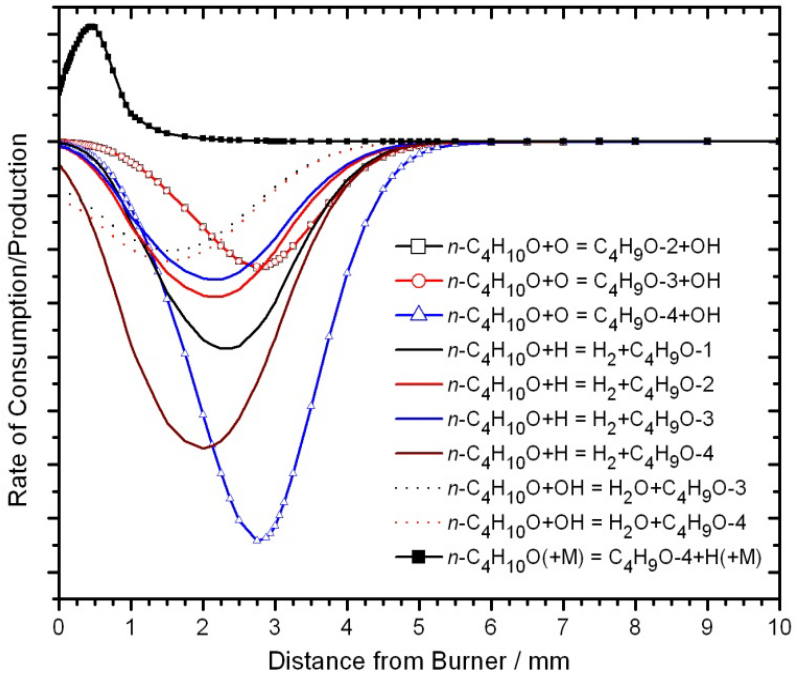
n-butanol: Fuel-Consumption by H-Abstraction Reactions

✓ First Steps in Fuel-Consumption:

- Fuel-consumption is initiated by H-abstraction reaction with H, O, and OH and formation of the isomeric C_4H_9O radicals



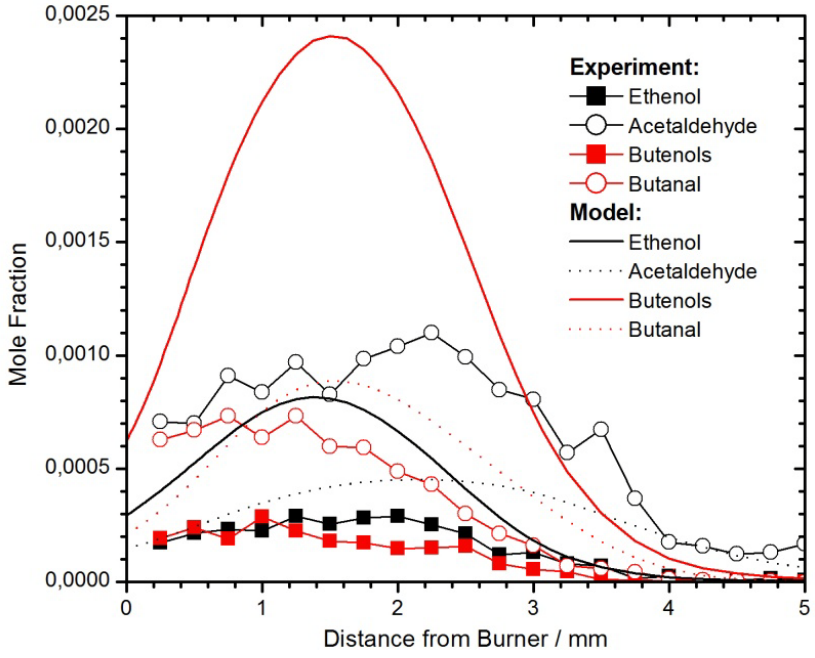
✓ Relative Rate of Consumption:



- C_4H_9O radicals dissociate and form butenols/butanal, or smaller fragments including CH_3, C_2H_4, C_2H_5, C_3H_6, and enols (ethenol + propenol)
- C_4H_9O radicals also react with other radical species, mainly H and O

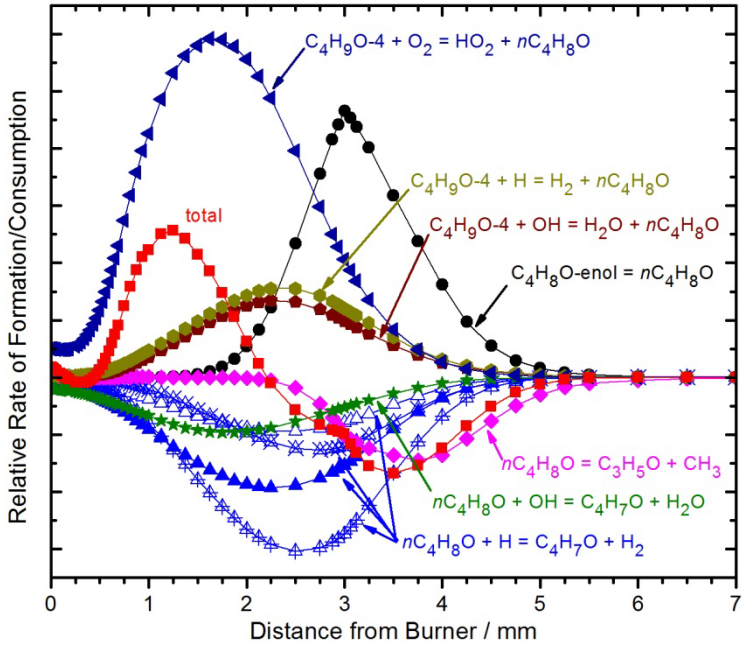
n-butanol: Reaction Path Analysis – Enols and Aldehydes

✓ Mole Fraction Profiles:



- the model over-estimates the importance of enols (ethenol, propenol, and butenol)
- with the exception of butanal, the importance of aldehydes is under-estimated

✓ Relative Rates of Formation:



- butenol ($CH_3CH_2CHCHOH$) and butanal ($CH_3CH_2CH_2CHO$) are formed via H-abstraction reactions of the C_4H_9O radicals

Summary and Outlook

✓ Summary:

- PI-MBMS is employed to study the isomeric composition of low-pressure flat flames fueled by

  ***n*-butanol** ***iso*-butanol** ***iso*-butane** ***iso*-butene**

- mole fraction profiles are used to improve detailed chemical models
- only *n*-butanol combustion chemistry discussed here in detail
  - ✓ reaction path analysis reveals important fuel-consumption pathways and uncovers uncertainties for C_4H_9O radical reactions
  - for *iso*-butane and *iso*-butene combustion chemistry insights see Bin's poster

✓ Outlook:

- provide more experimental data for further model refinements
- consolidate the different mechanisms under development
- low-temperature oxidation chemistry in a jet-stirred reactor (with Y. Ju)