SAND2007-5208C

“Imaging” Combustion Chemistry with Multiplexed Synchrotron Photoionization Mass Spectrometry

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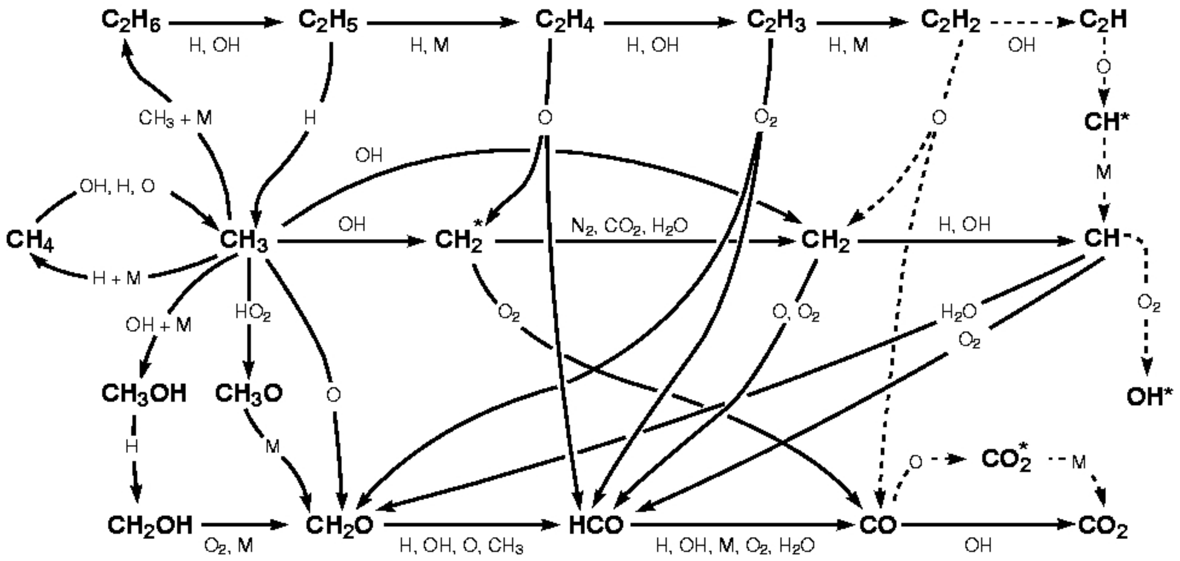
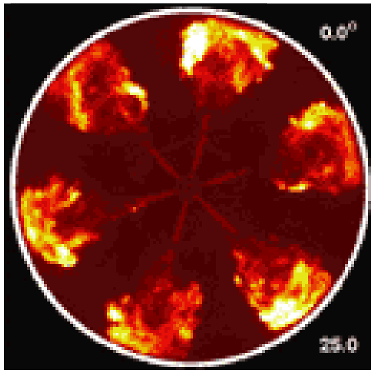
Combustion is a Complicated Mix of Chemistry and Fluid Dynamics



Najm, H.N.; Paul, P.H.; Mueller, C.J.; Wyckoff, P.S. *Combust. Flame* **1998**, 113, 312.

Fuels Research Lab (C.J. Mueller, Sandia)



Detailed chemistry of single elementary fuel may have thousands of reactions and hundreds of species

Combustors operate at 300 – 3000 K, 10 – 10^6 Torr

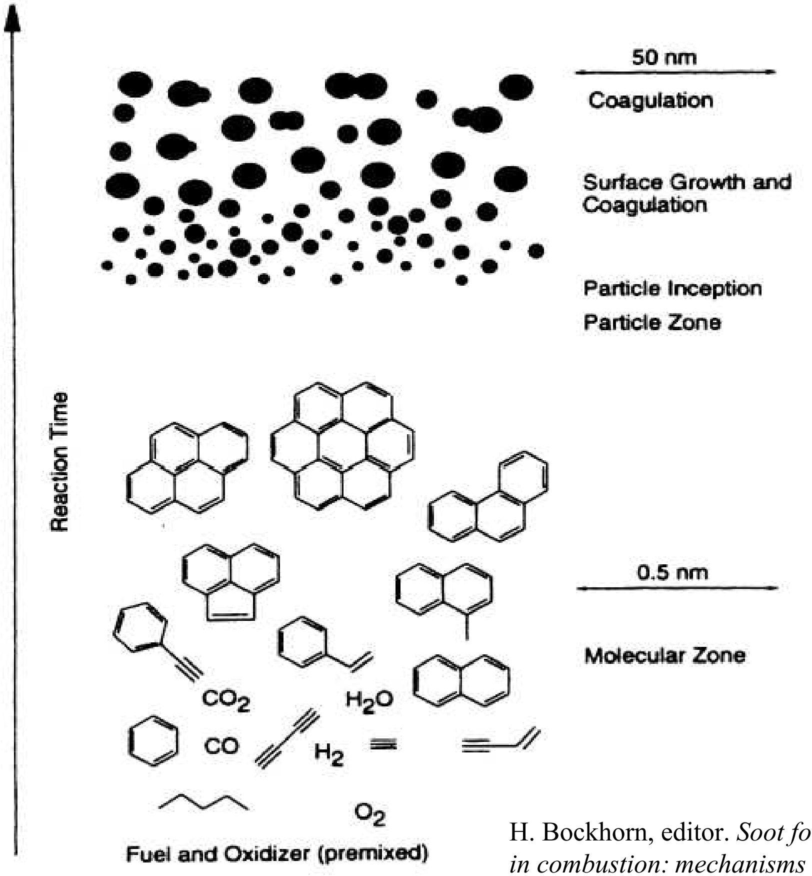
Turbulent, multiphase flows interact with the chemistry

Knowledge of Detailed Flame Chemistry is Important in Pollution Control

Detailed combustion chemistry, including isomers, determines nature and amount of pollutants

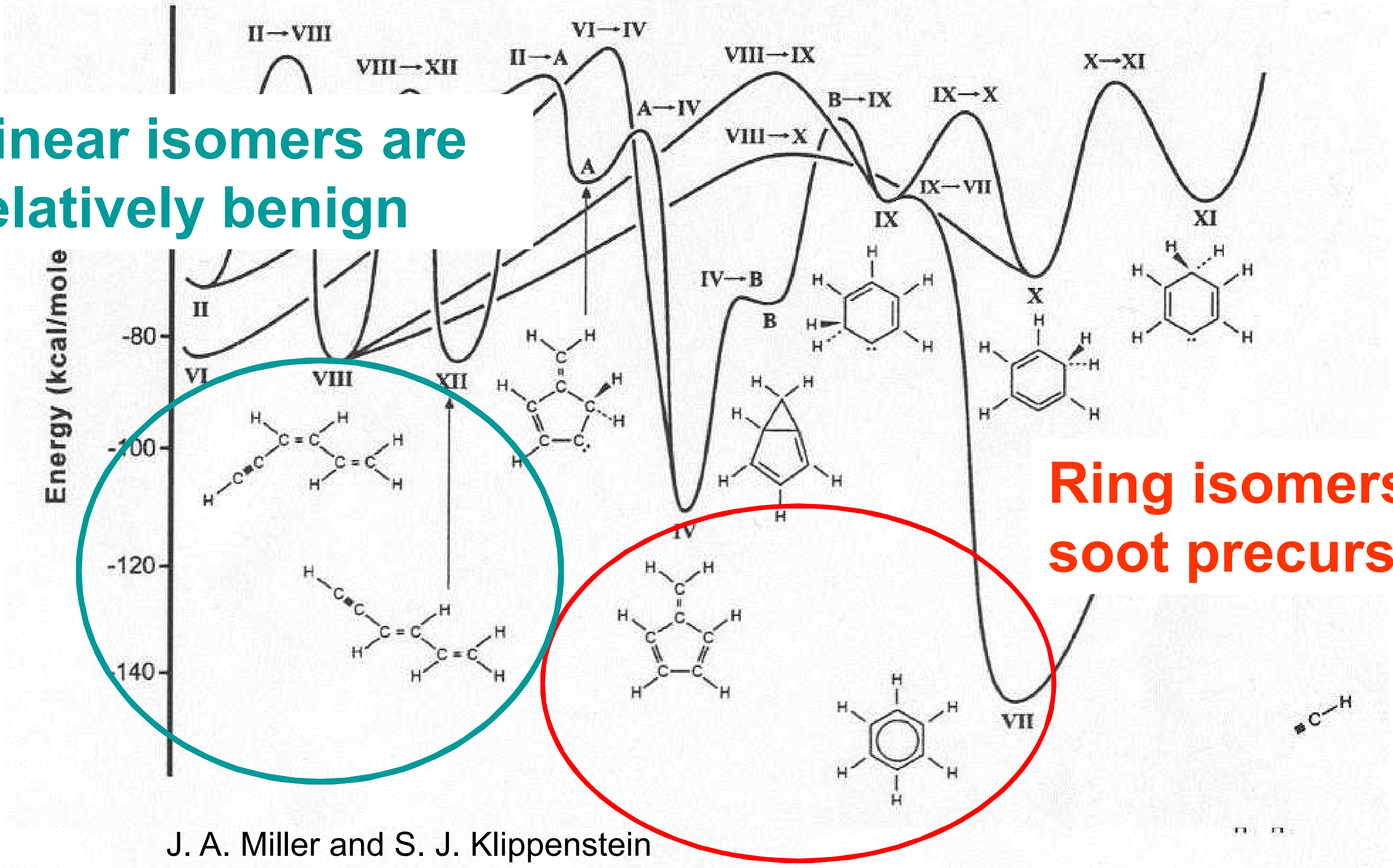
Soot is formed by molecular growth reactions from small unsaturated hydrocarbons

Individual reactions and full mechanisms in flame models must be validated experimentally



H. Bockhorn, editor. *Soot formation in combustion: mechanisms and models*. Berlin: Springer, 1994.

Recombination of Propargyl Radicals Occurs on a Complicated C_6H_6 Potential



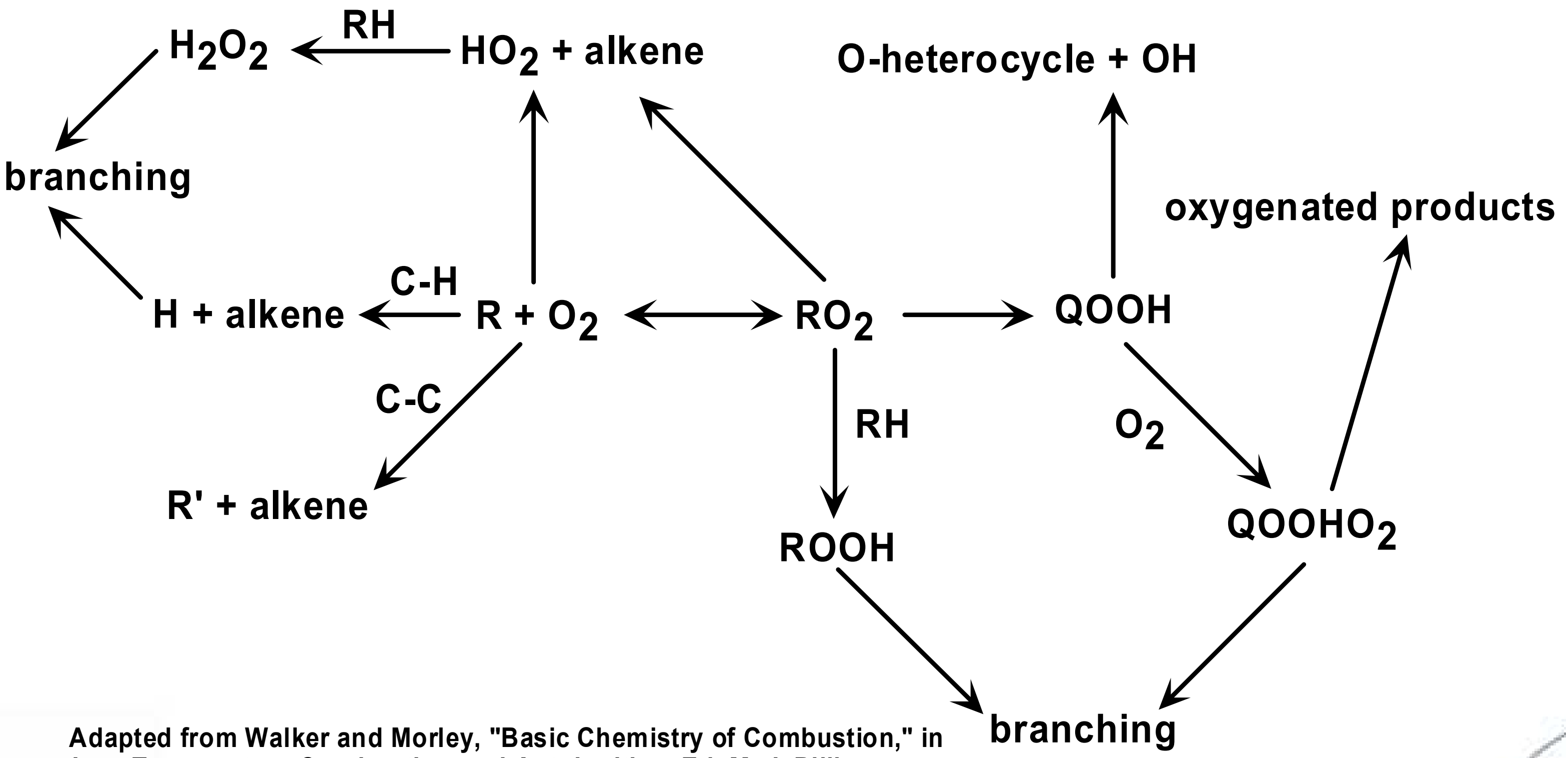
Linear isomers are relatively benign

Ring isomers are soot precursors

J. A. Miller and S. J. Klippenstein
J. Phys. Chem. A, **2003,** *107*, 7783

Details of Alkyl + O_2 Reactions Are Central to Ignition Chemistry

General Alkyl Radical Oxidation Scheme



high temperature

low temperature

H_2O_2

RH

HO_2 + alkene

O-heterocycle + OH

branching

oxygenated products

C-H

H + alkene

R + O_2

RO_2

QOOH

C-C

RH

O_2

R' + alkene

ROOH

$QOOHO_2$

branching

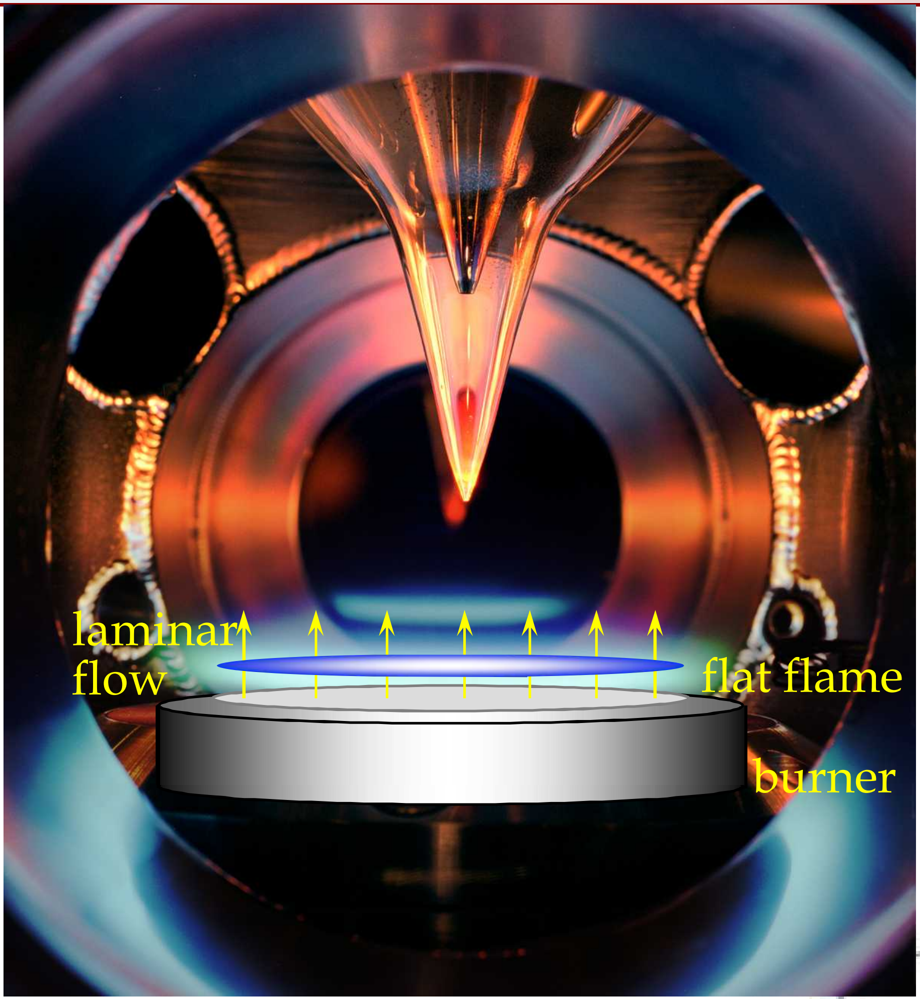
Adapted from Walker and Morley, "Basic Chemistry of Combustion," in *Low Temperature Combustion and Autoignition*, Ed. M. J. Pilling, (Comprehensive Chemical Kinetics Vol. 35) Elsevier, 1997

Low-Pressure Flames are a Controlled Environment to Study Chemistry

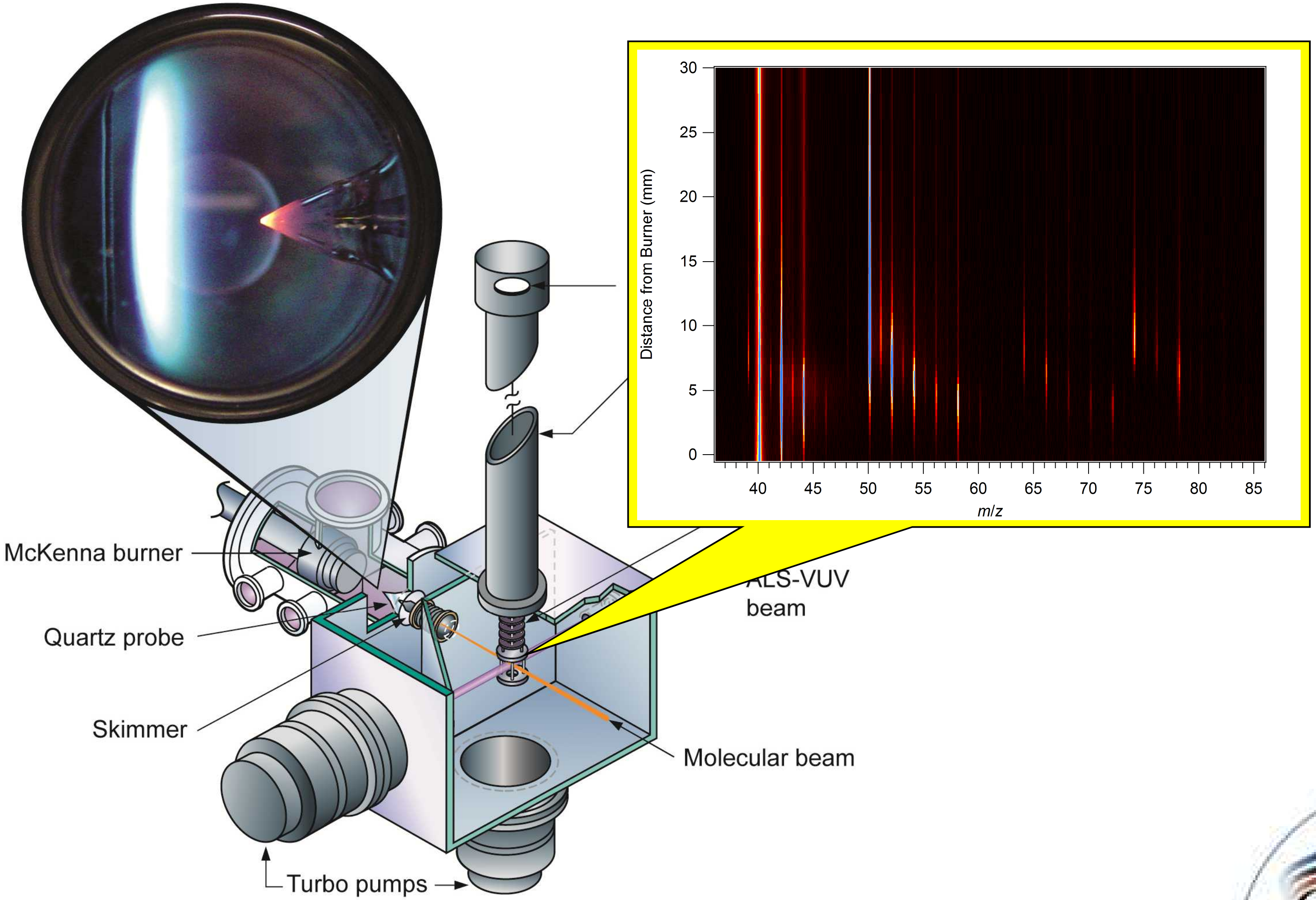
Laminar premixed flames reduce fluid dynamics to (nearly) one dimension

Low pressure expands reaction zone (but changes some three-body chemistry)

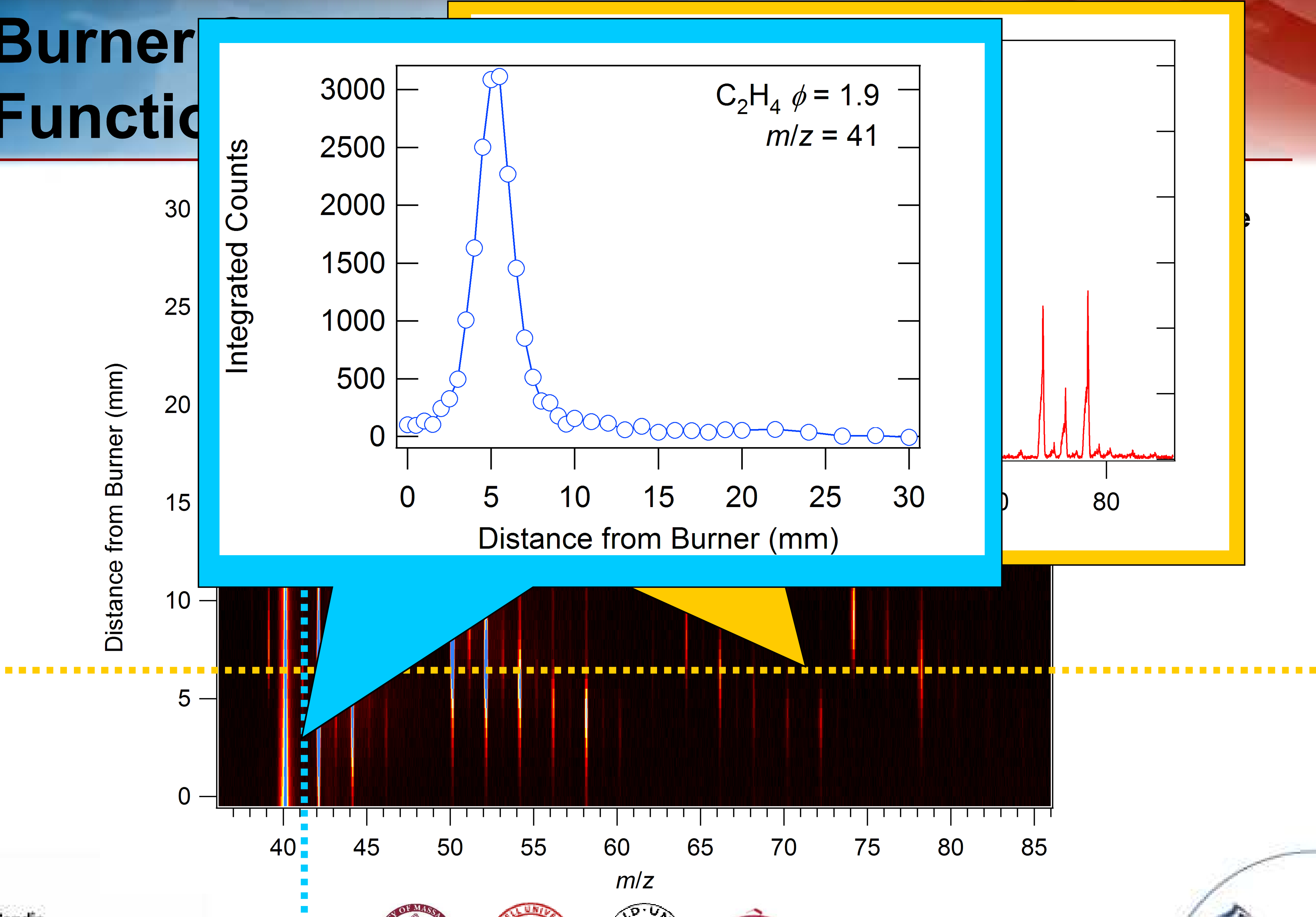
Molecular **B**eam **M**ass **S**pectrometry (MBMS) is a venerable technique for combustion studies and can detect intermediates and radicals *in situ*



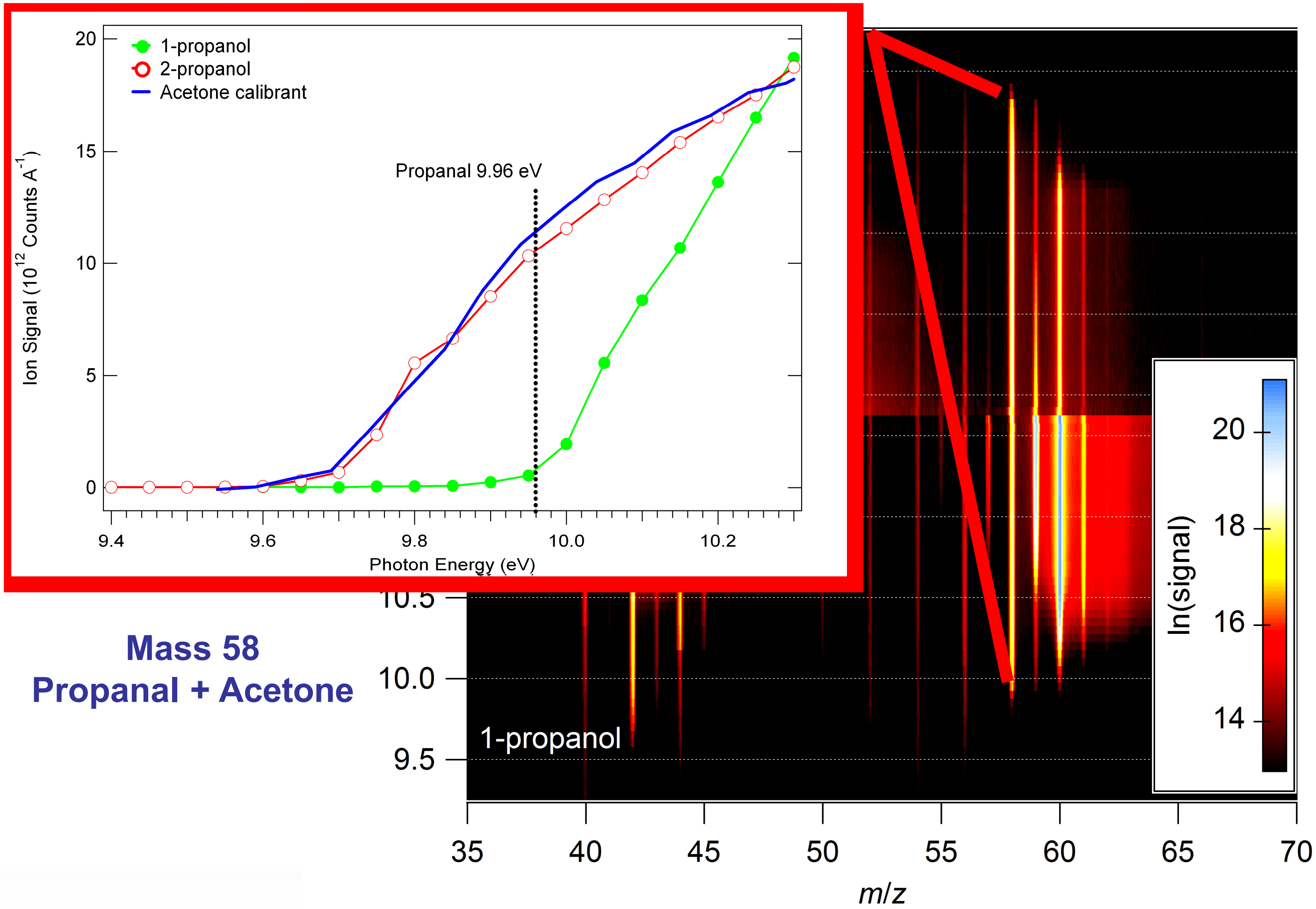
Flame Machine at the Advanced Light Source Employs Photoionization MBMS



Burner
Functi



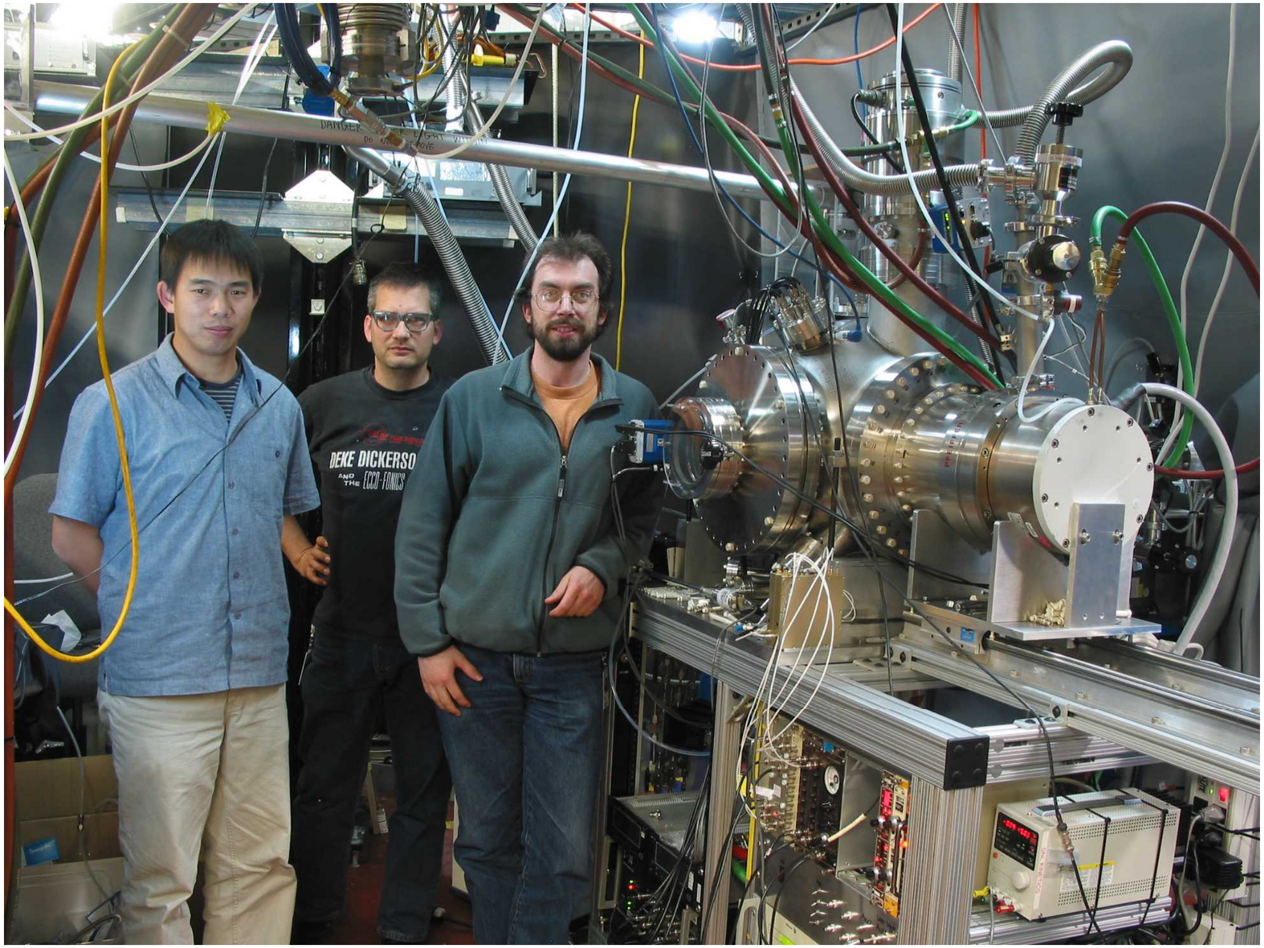
Scan of Photon Energy Gives Photoionization Efficiency (PIE) Curve



Tunable photoionization can distinguish isomers

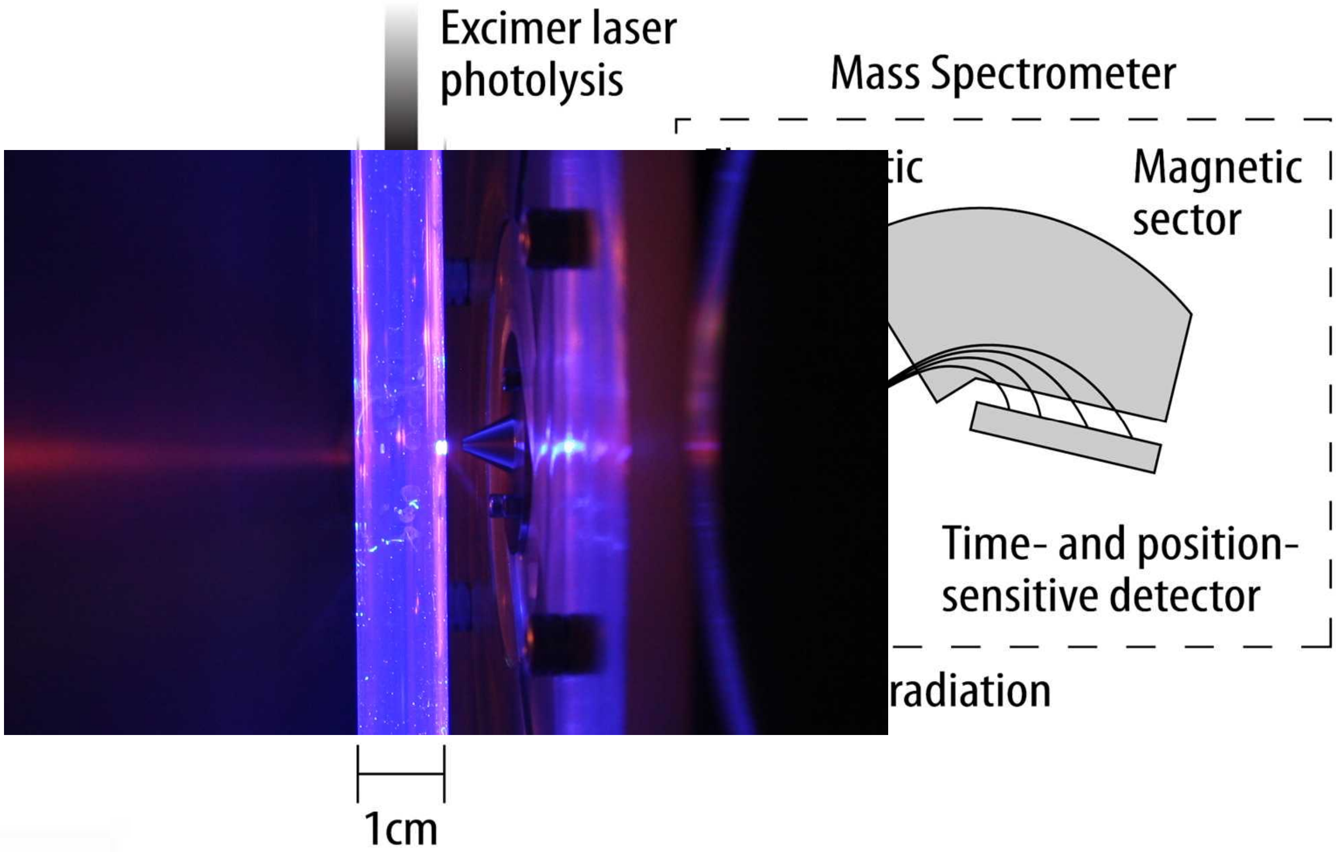
Mass 58
Propanal + Acetone

Kinetics Machine at ALS Applies Synchrotron to Elementary Reactions

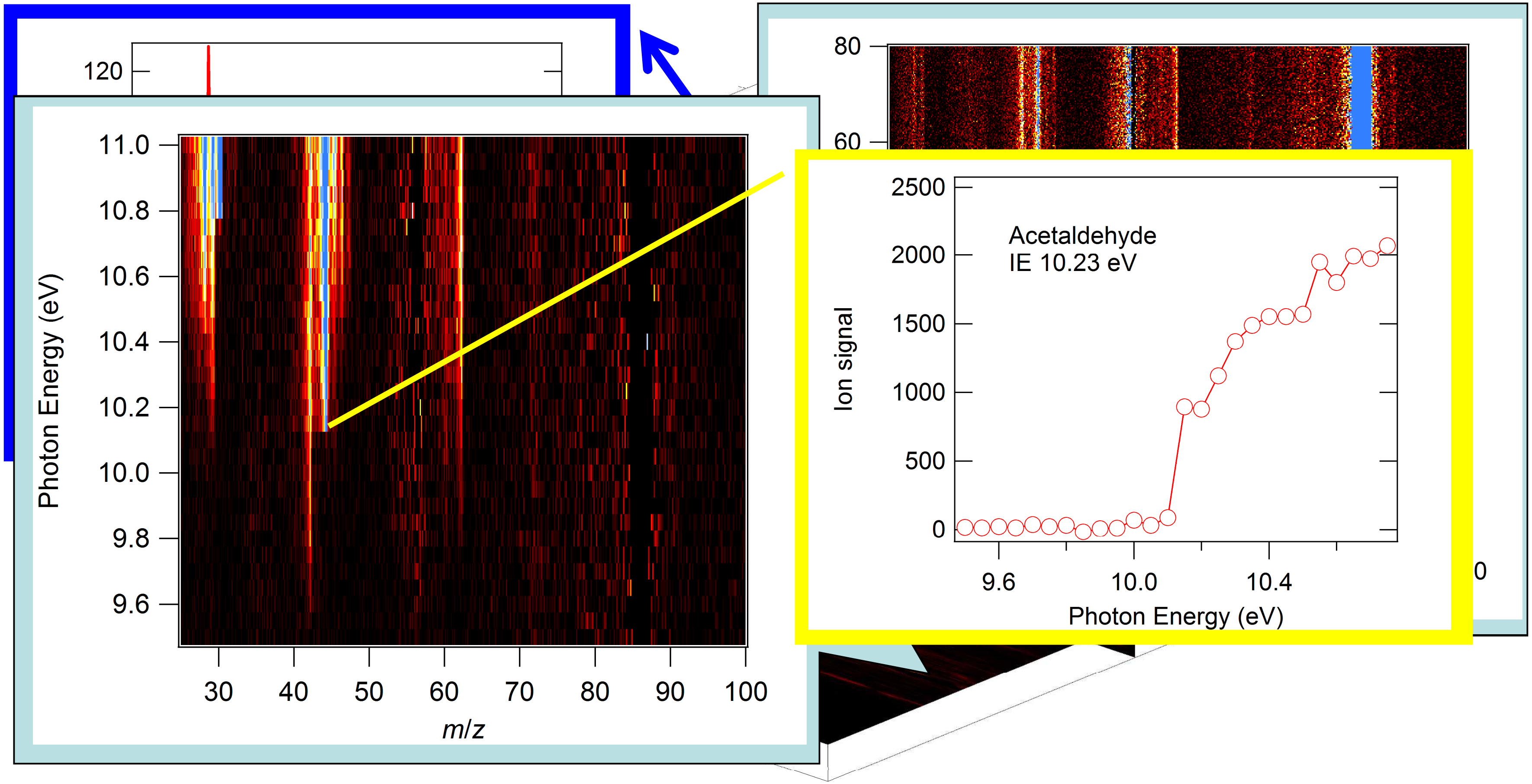


Collaboration between Sandia CRF (David Osborn, C.A.T.) and LBNL

Laser Photolysis Reactor is Coupled to Miniature Magnetic Sector Spectrometer

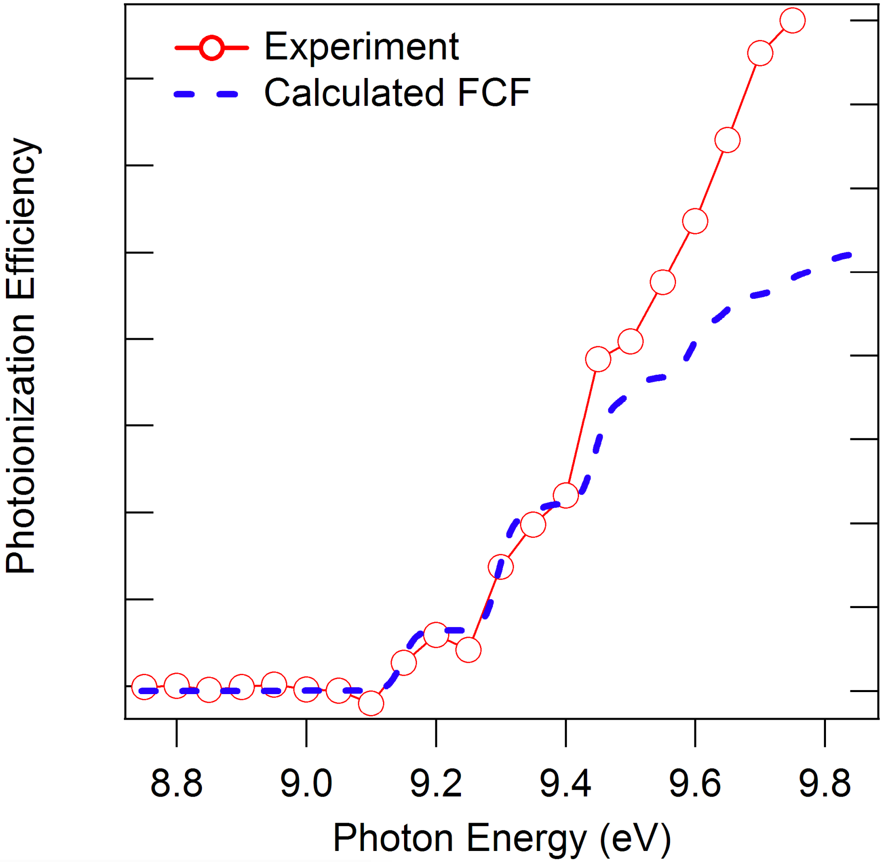


Kinetic Data is Acquired as a Function of Time, Mass, and Photoionization Energy



3-D dataset can be "sliced" along different axes to probe different aspects of the reaction

Change of PIE with Time Can Indicate Different Isomeric Reactivity

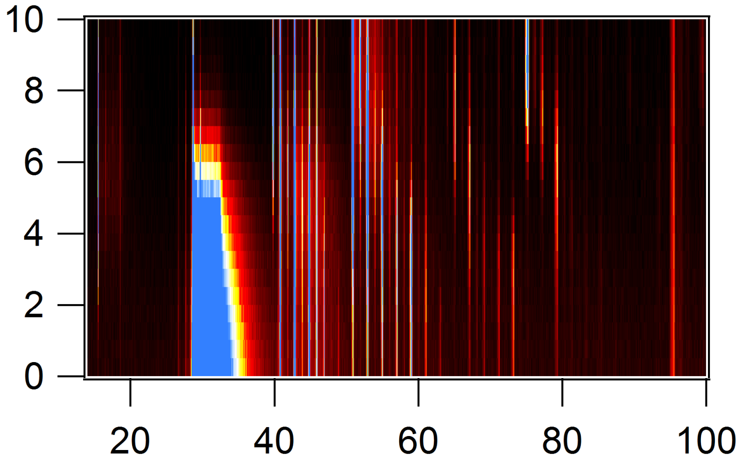


- Allene photolysis at 193 nm produces C_3H_2
- PIE at this mass changes with time after photolysis
- Early-time C_3H_2 signal decays rapidly by isomerization, relaxation, or reaction
- Long-time C_3H_2 is from the most stable isomer, cyclopropenyidene

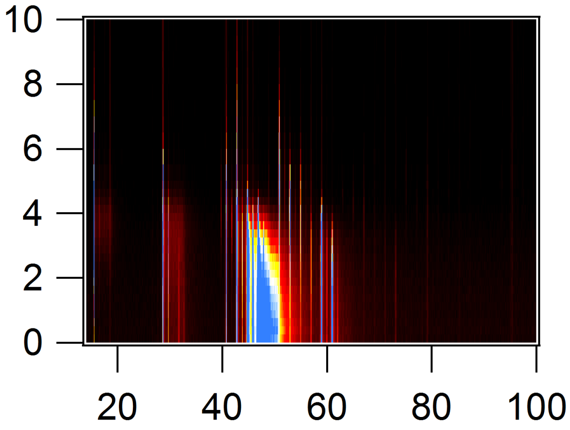
Multidimensional Photoionization Data Illuminate Combustion Chemistry

- Low-pressure flame images
  - Show global pathways of combustion chemistry
  - Are a powerful tool for comparing isomeric flames
- Multiplexed kinetic measurements with time, mass, and photon-energy resolution can
  - Distinguish competing ionization processes
  - Identify new pathways in chemical reactions
  - Determine isomeric products of reactions (Fabien Goulay poster B-9)

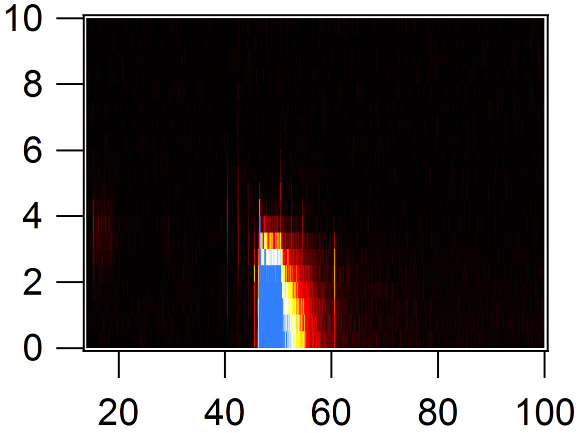
Global Picture of Flame Chemistry is Directly Visible in Images



Ethene flame
$\phi = 1.9$



Ethanol flame
$\phi = 1.97$



Dimethyl ether flame
$\phi = 2.0$

Oxygenated fuels or additives reduce soot formation

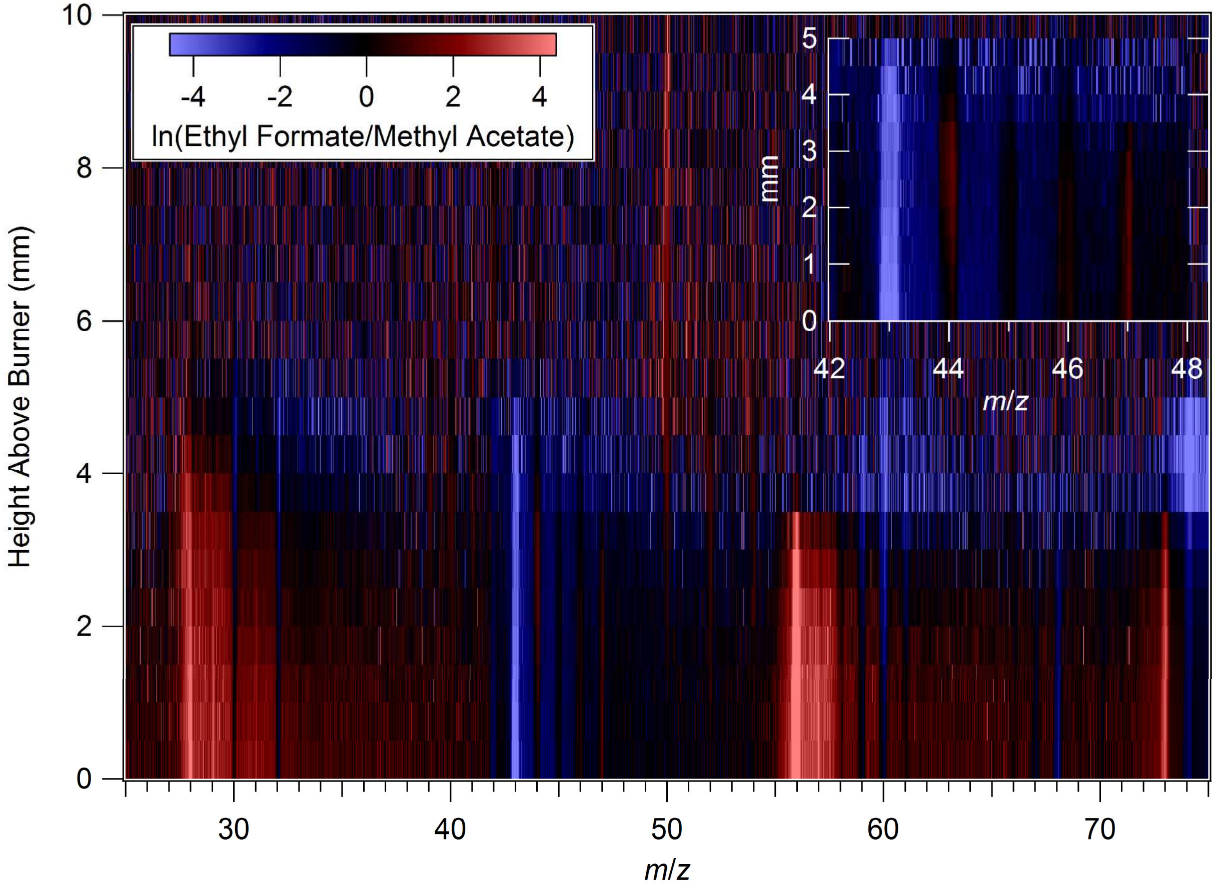
Ethene images shows molecular weight growth chemistry

Production of soot precursors in premixed flames diminishes for oxygenates

Also true for doping with oxygenates
(Kohse-Höinghaus et al., *Proc. Combust. Inst.* 31, 1119 (2007))

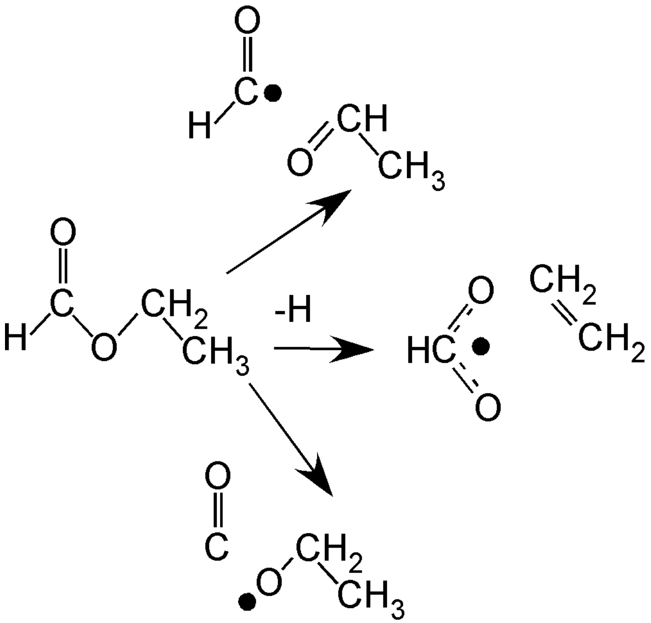
Fuel-Dependent Chemistry is Seen in Isomeric Ester Flames

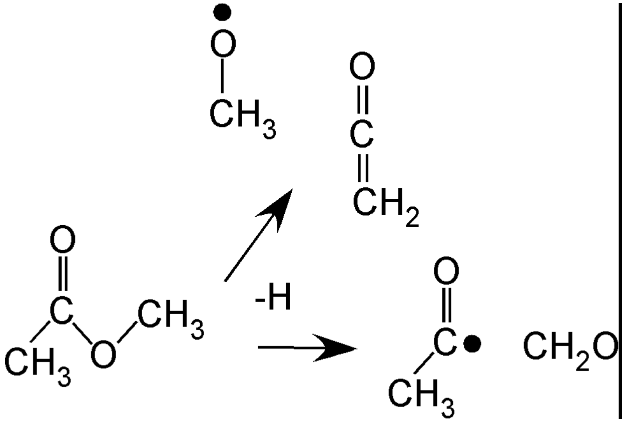
- **Biodiesel consists of long-chain methyl or ethyl esters**
- **Comparison of isomeric flames highlights specific chemical pathways**
- **Methyl acetate: more formaldehyde, methanol, ketene**
- **Ethyl formate: more acetaldehyde, ethene, C_4 species**

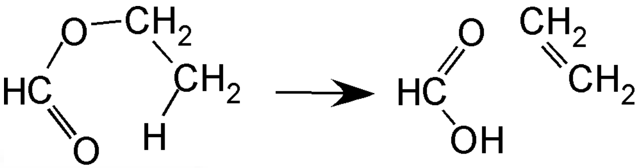


Oßwald et al., *J. Phys. Chem. A* 111, 4093 (2007)

Differences in Ester Flames Reflect First Steps of Fuel Decomposition





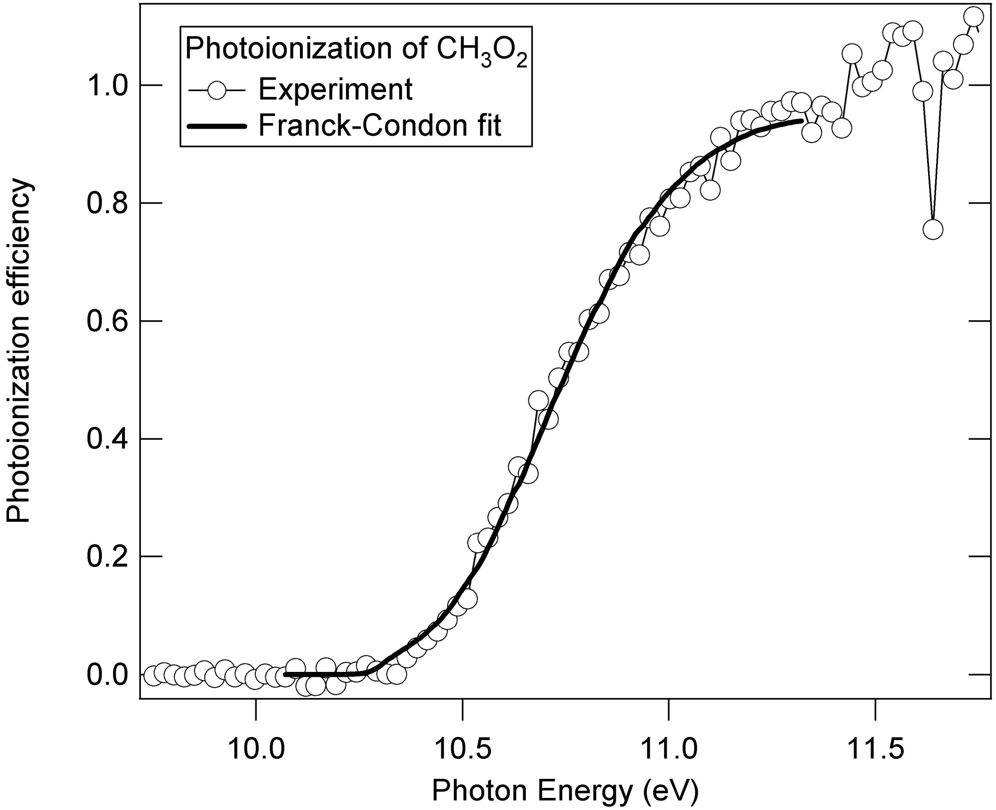


- Initial removal of esters by H abstraction creates radicals that will decay differently for the two isomers
- Ethyl formate can also undergo elimination reaction to form ethene and formic acid

Measurement of RO_2 Would Be Useful for Oxidation Chemistry Studies

- Alkylperoxy radicals are key intermediates in the $R + O_2$ reactions
- Alkylperoxy radicals are also important chain carriers in tropospheric chemistry
- Can these radicals be detected by photoionization?
  - CH_3OO was detected in PIMS kinetics experiments
  - No PIE or ionization energies reported
- Use $R + O_2$ reactions at 300 K to look for RO_2

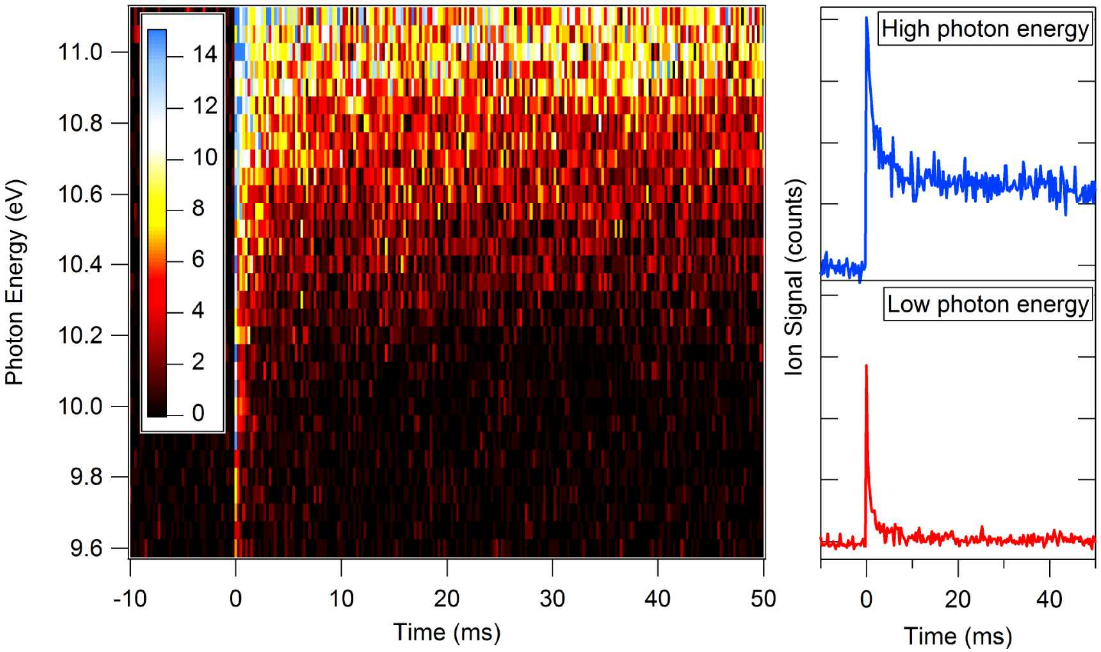
Methylperoxy Radical Is Observed from the Reaction of Methyl with O_2



Ionization energy is derived from a 300 K Franck-Condon fit

IE of 10.33 eV in excellent agreement with calculation

Time Resolution Permits Kinetic Discrimination of Ionization Processes



- Reaction of ethyl with O_2 produces ethylperoxy radicals
- Photoionization of ethylperoxy is dissociative to form ethyl cations
- Ethyl cation signal as a function of ionization energy shows:
  - Direct ionization of ethyl radical at low photon energy
  - Dissociative ionization of ethylperoxy emerging at higher photon energy

Dissociative Ionization Gives Information on Alkylperoxy Radical Thermochemistry

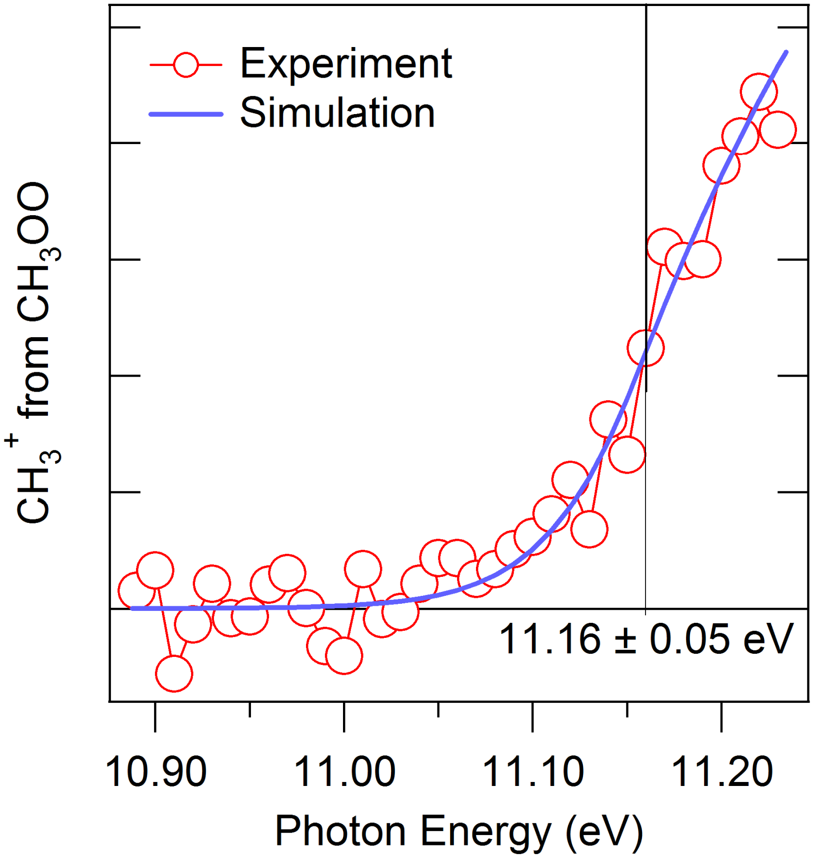
Dissociative ionization of methylperoxy (CH_3OO) can be identified by kinetics

Methyl radical ionization energy is very well known

Appearance energy of CH_3^+, 11.16 eV, gives bond energy of CH_3OO

$D_0(CH_3\text{-}OO) = (80 \pm 7)\ \text{kJ mol}^{-1}$

G. Meloni et al., *J. Am. Chem. Soc.* **128**, 13559 (2006)

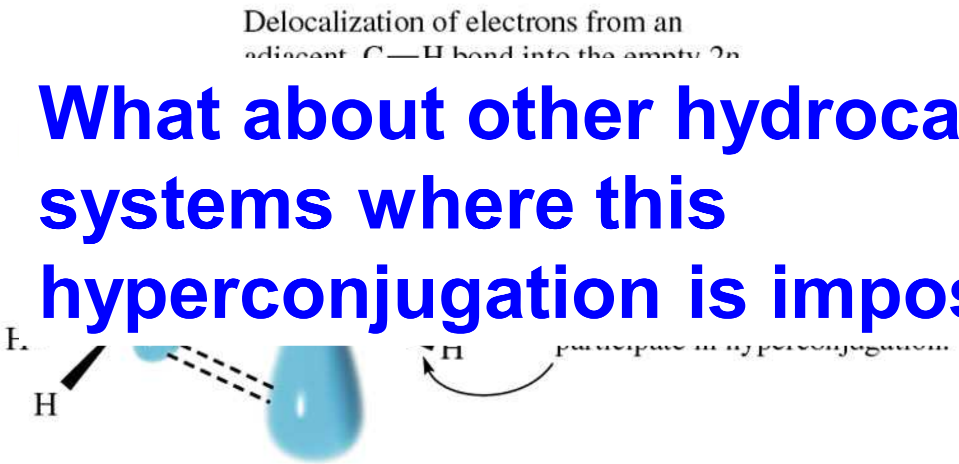


Alkylperoxy Ionization Is Affected by the Stabilization of the Alkyl Cation

Of experimentally studied peroxy cations: CH_3OO^+,[a] $C_2H_5OO^+$,[a,b] and $C_3H_7OO^+$,[a,b] only CH_3OO^+ shows thermodynamic stability [a]

Larger alkylperoxy cation triplet ground states are unbound [a,b]

Increasing relative stability of alkyl cation fragments as result of hyperconjugation



What about other hydrocarbon-O_2 systems where this hyperconjugation is impossible?

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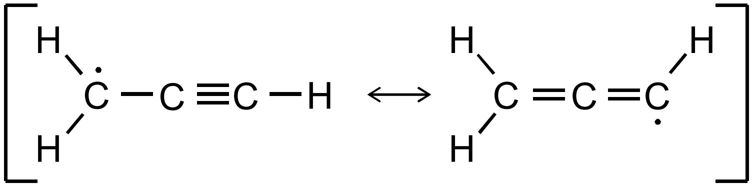
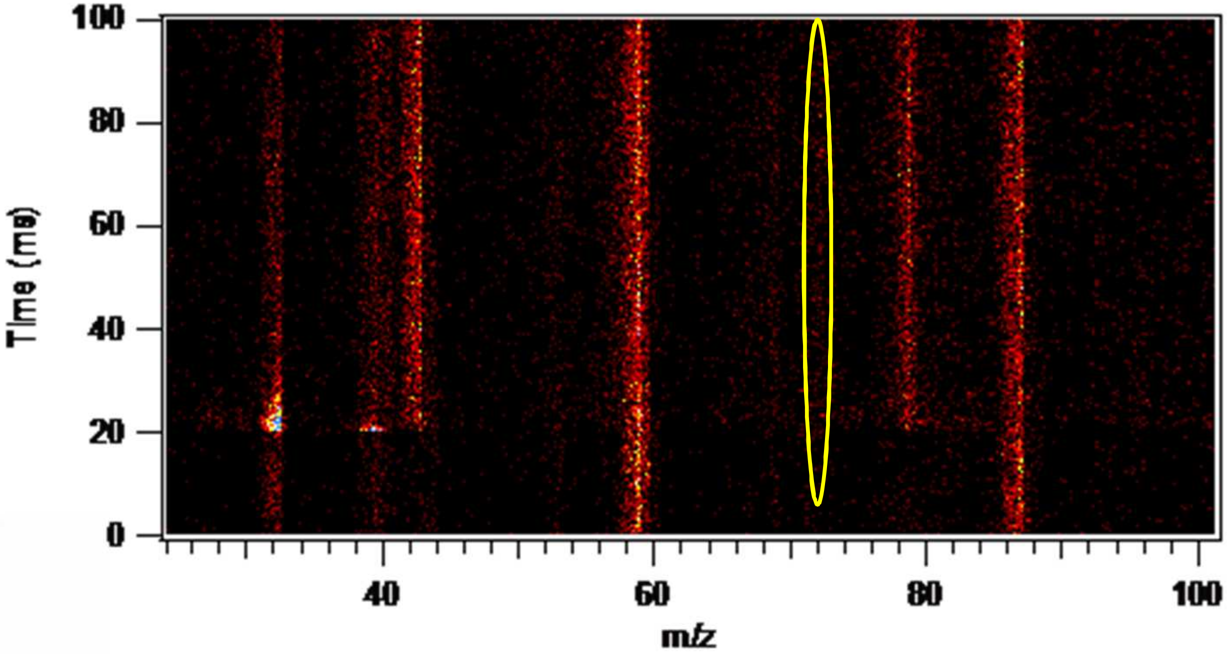
[a] Meloni *et al.*, J. Am. Chem. Soc. **2006**, *128*, 13559-13567.
[b] Fu *et al.*, J. Chem. Phys. **2006**, *125*, 014310.

The Reaction of Propargyl with O_2 Can Form Two Different Peroxy Radicals

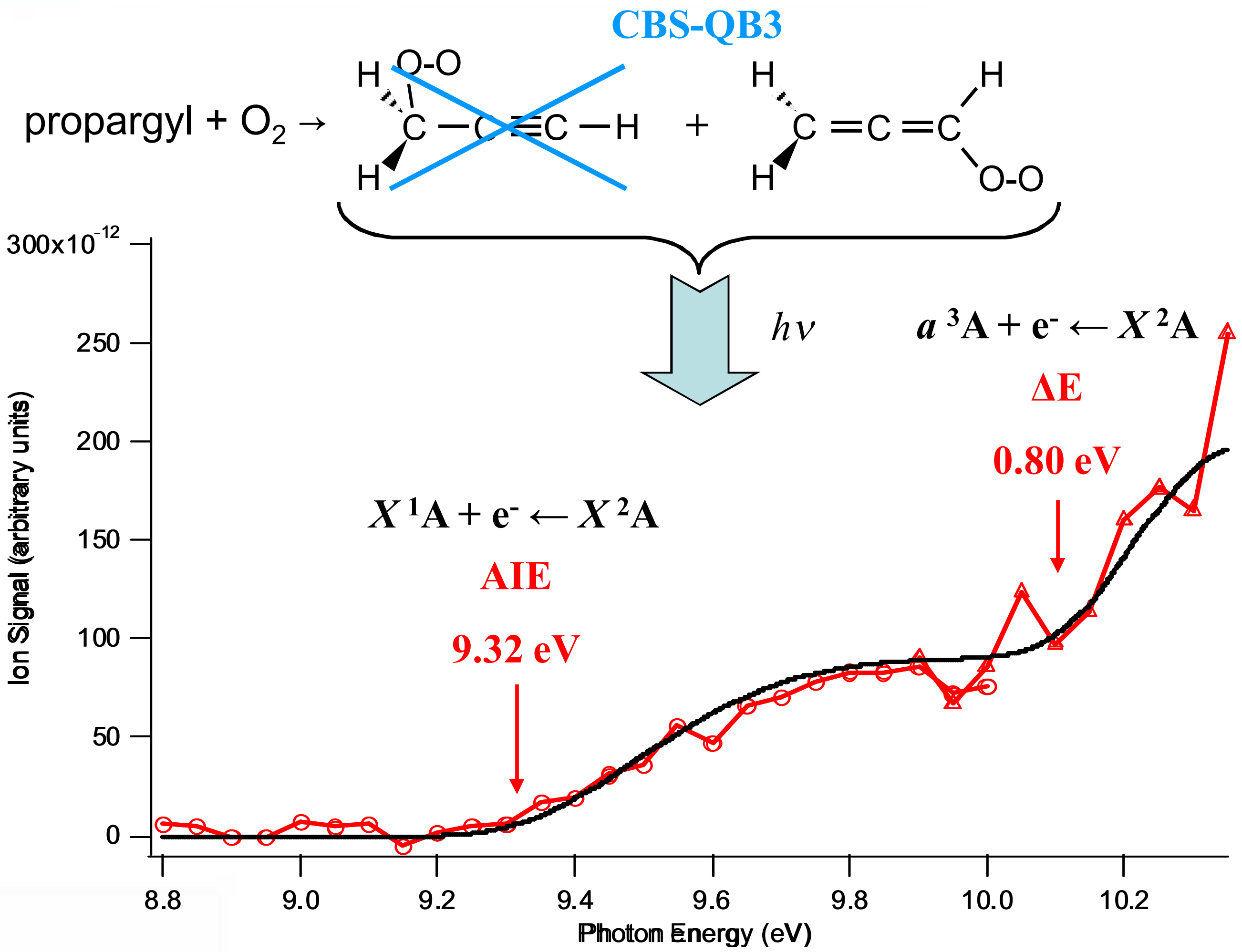
$C_3H_3Br \xrightarrow{h\nu}$ propargyl



+ O_2 → **propargylperoxy**



Only One of the $C_3H_3O_2$ Radicals Is Calculated to Have a Stable Cation



P = 6 Torr
T = 298 K

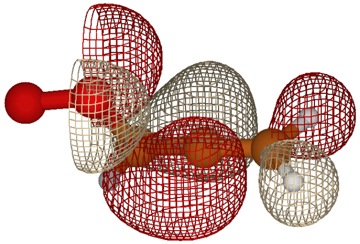
Experimental photoionization efficiency matches computed Franck-Condon factors and ionization energies for the CH_2=C=CHOO isomer

Cations of 1-Alkenylperoxy Radicals Have Stable Singlet Ground States

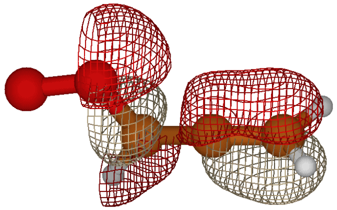
As a rule, the HOMO of 1-alkenylperoxy radicals is singly occupied

This molecular orbital has C-O anti-bonding character

Singlet ground state of the cation has shorter C-O and longer C-C bonds than the neutral



HOMO



HOMO-1

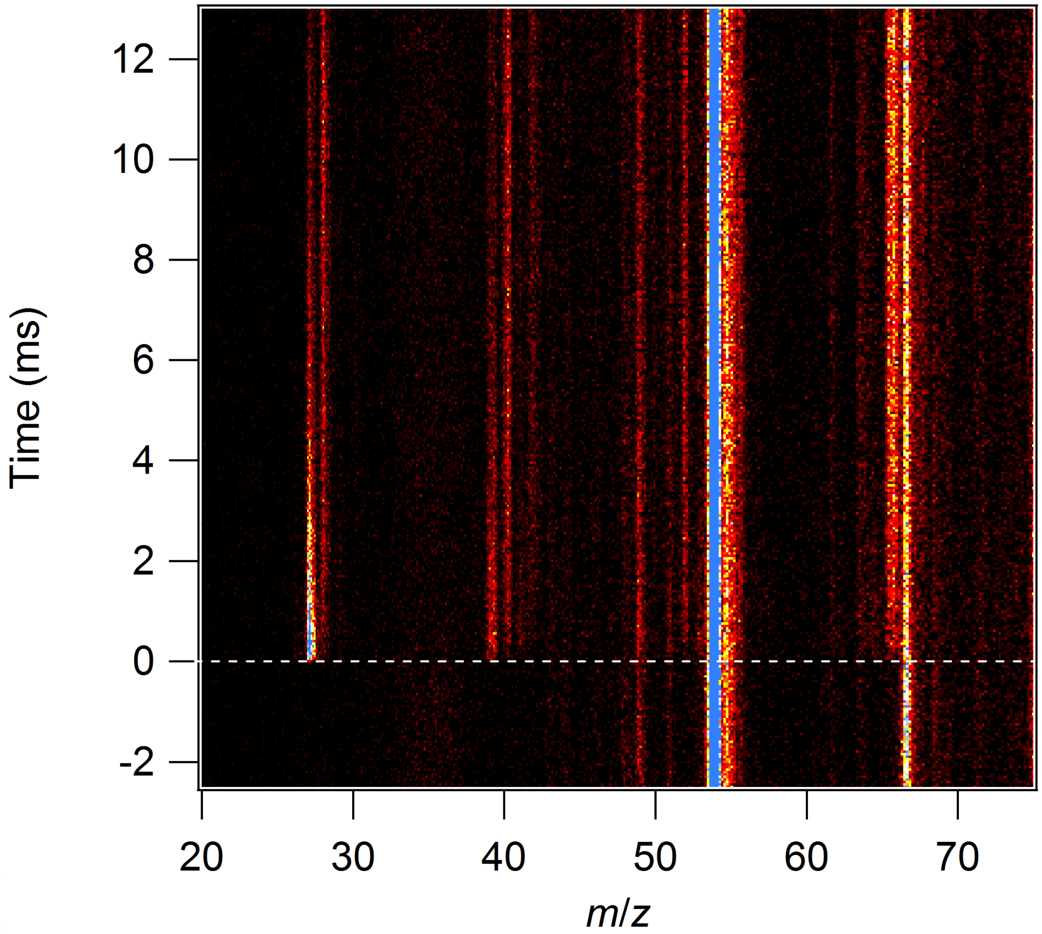
Recently Disagreement Has Emerged About the Vinyl Self-Reaction

Literature values for total rate coefficient (Askar Fahr and coworkers) are ~> 1 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1}

Laser absorption experiments at CRF (C.A.T.) and at MIT (Bill Green group) show much (2-3x) smaller rate coefficient

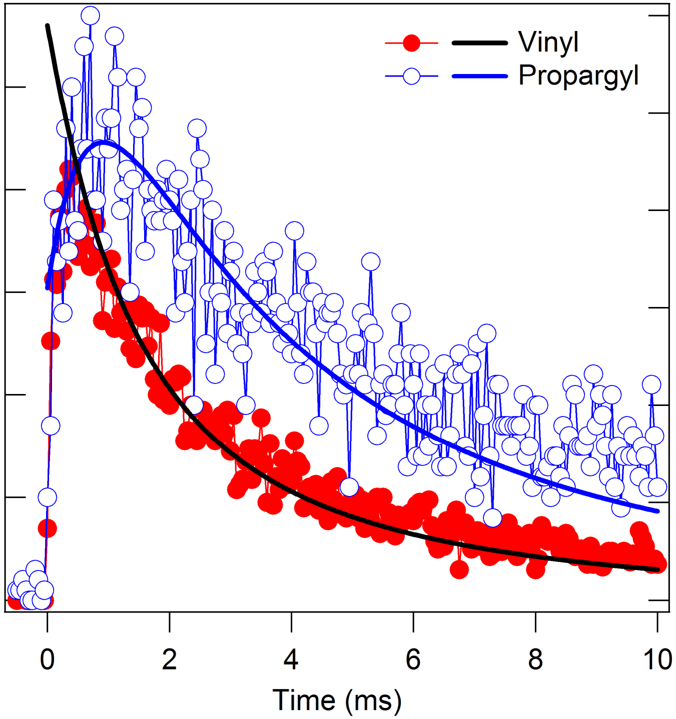
Why??

Measurements at the ALS Confirm Low Value of Vinyl + Vinyl Rate Coefficient



- Photolysis of Methyl Vinyl Ketone and Divinyl Ketone
- Initial radical concentrations determined from precursor depletion
- From both precursors, a propargyl radical signal is seen
- Propargyl not instantaneous
- Could vinyl + vinyl make propargyl + methyl?

Could Substantial Propargyl + Methyl Branching Reconcile Studies?



Including propargyl in analysis of previous experiments would increase initial concentration and reduce rate coefficient

Data from both experiments consistent with propargyl as product of vinyl + vinyl

Small amounts of ethene + acetylene formed

Pyrolysis and photolysis of initial adduct 1,3-butadiene is known to produce propargyl and methyl

Previous measurements probed 1,3-butadiene and used assumed branching to get initial concentration

Isomeric Reaction Products Can be Probed

- C_2H reactions (Goulay et al., *PCCP* 9, 4291 (2007))
- CH reactions (Fabien Goulay poster B-9)
- Enol formation in OH + alkene reactions:
  - Enols recently found in many low-pressure flames
  - Enols could contribute to tropospheric acid formation (Archibald et al., *Geophys. Res. Lett.*, in press)
  - OH + alkenes predicted to be major source of enols

Synchrotron Measurements Confirm Enol Production from OH + Alkenes

OH is formed by 248 nm photolysis of H_2O_2

Alkene is in great excess

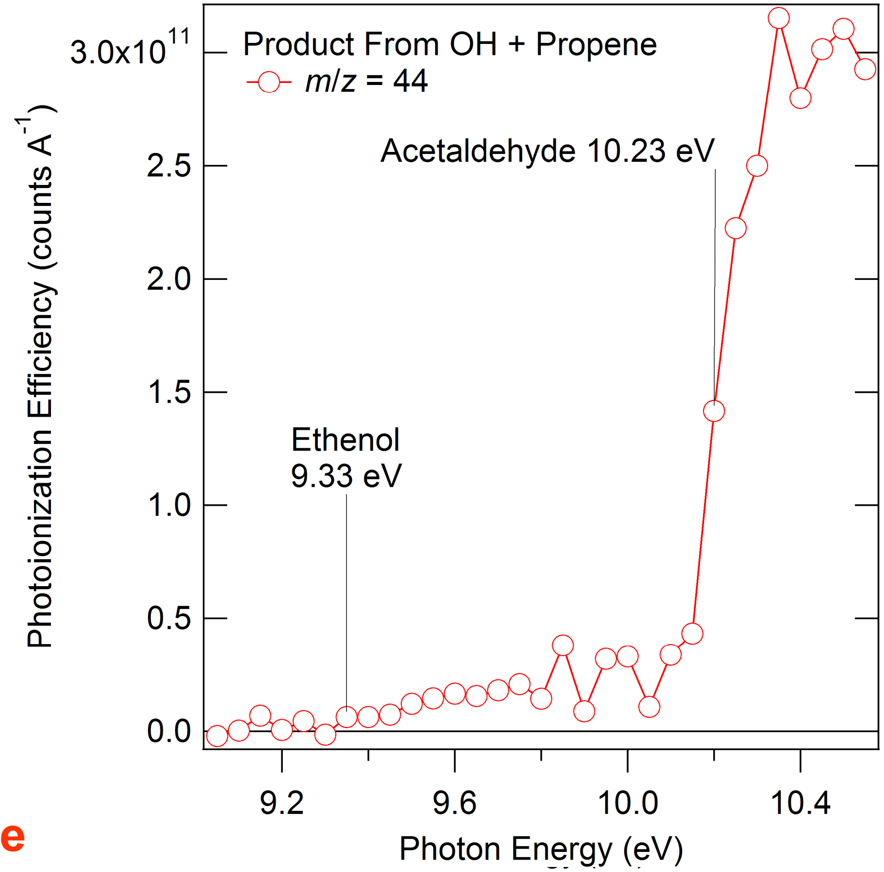
At 500 K, substantial ethenol is observed from OH + ethene

OH + propene reaction has been shown to produce C_2H_4O and C_3H_6O products (Hoyermann, K.; Sievert, R. *Ber. Bunsen-Ges. Phys. Chem.* 1979, *83*, 933)

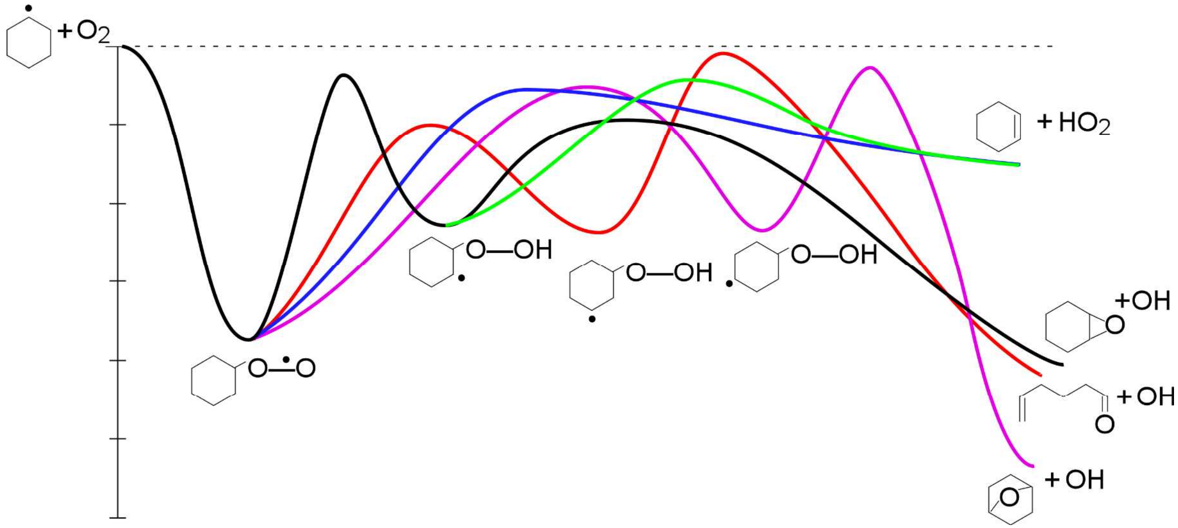
Are these products the enols??

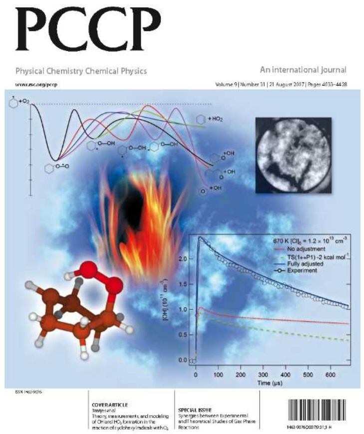
***m/z* = 58 is propenol**

But *m/z* = 44 is mostly acetaldehyde



Ignition Chemistry of Cycloalkanes is of Increasing Technological Importance




PCCP

Physical Chemistry Chemical Physics

An international journal

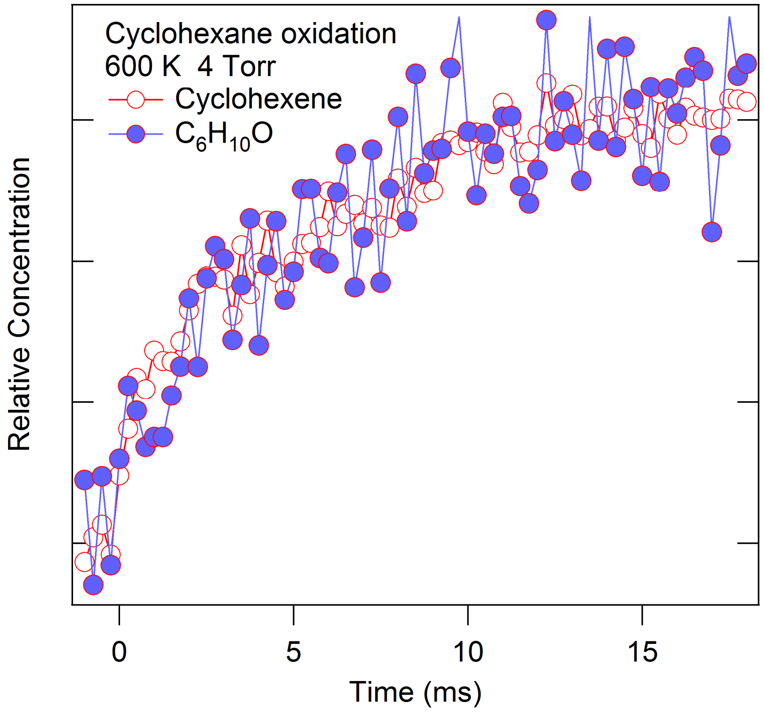
Fuels from non-traditional hydrocarbon sources (e.g., oil sands) have more cyclic alkanes (napthenes)

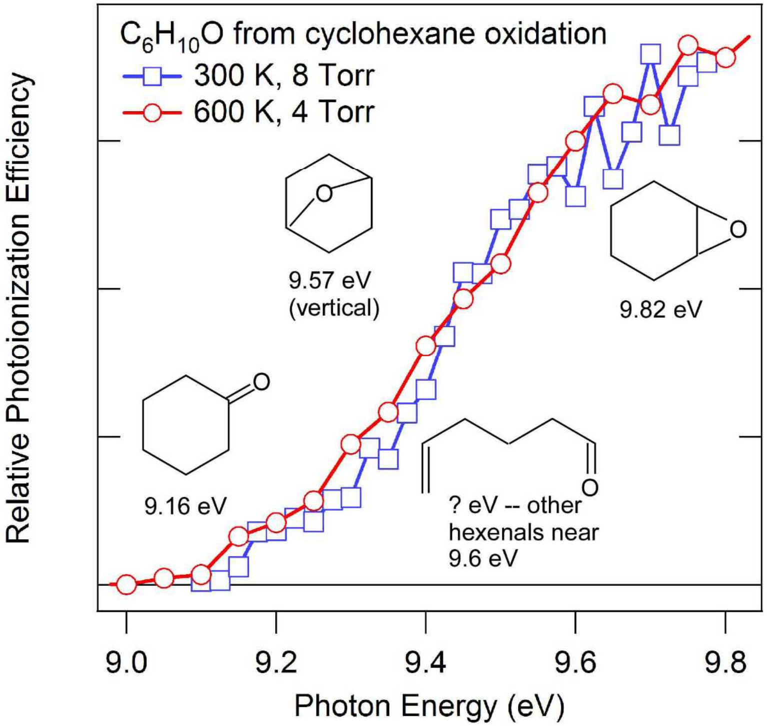
Advanced engines (e.g., HCCI) rely on chemistry to time ignition

Need to better characterize naphthene ignition chemistry

Measurements of OH and HO$_2$ from cyclohexyl + O$_2$ were combined with ab initio and master equation calculations to generate model (Knepp, Meloni, Jusinski, Taatjes, Cavallotti, & Klippenstein, PCCP 9, 4315 (2007))

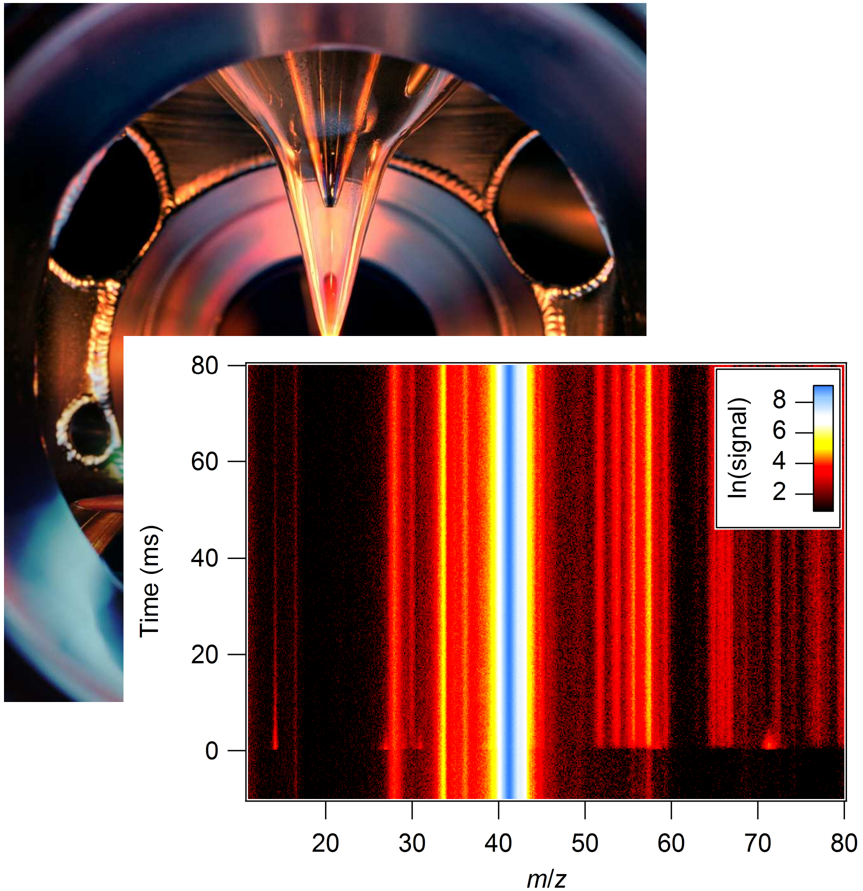
Photoionization Is Being Applied to Outstanding Cyclohexyl + O_2 Questions





Cyclohexene at 600 K is well-predicted by model
$C_6H_{10}O$ signal follows same time curve (as expected)
Understanding PIE spectra will require new spectroscopy!

Even After 150 Years of Research, Now is a Good Time to Study Combustion



Flame chemistry has a long history

Multiplexed Synchrotron photoionization is a powerful tool to “image” flames

and kinetics

The chemistry is important …

The ALS Flame Team

C.A.T., Nils Hansen, Tina Kasper (Sandia)

Terrill A. Cool, Juan Wang (Cornell University)

Phillip R. Westmoreland, Matt Law (U. Massachusetts)

Katharina Kohse-Höinghaus, Patrick Osswald (Bielefeld)

The ALS Kinetics Team

David Osborn, Peng Zou, Giovanni Meloni, Talitha Selby
Howard Johnsen

Fabien Goulay, Steve Leone (UC Berkeley)
Simon North, Erin Greenwald Tullos (Texas A&M)
Askar Fahr (Howard University)