Experimental Validation for Combustion Mechanism Development

SAND2006-4839C

From Reaction Kinetics to Flame Chemistry

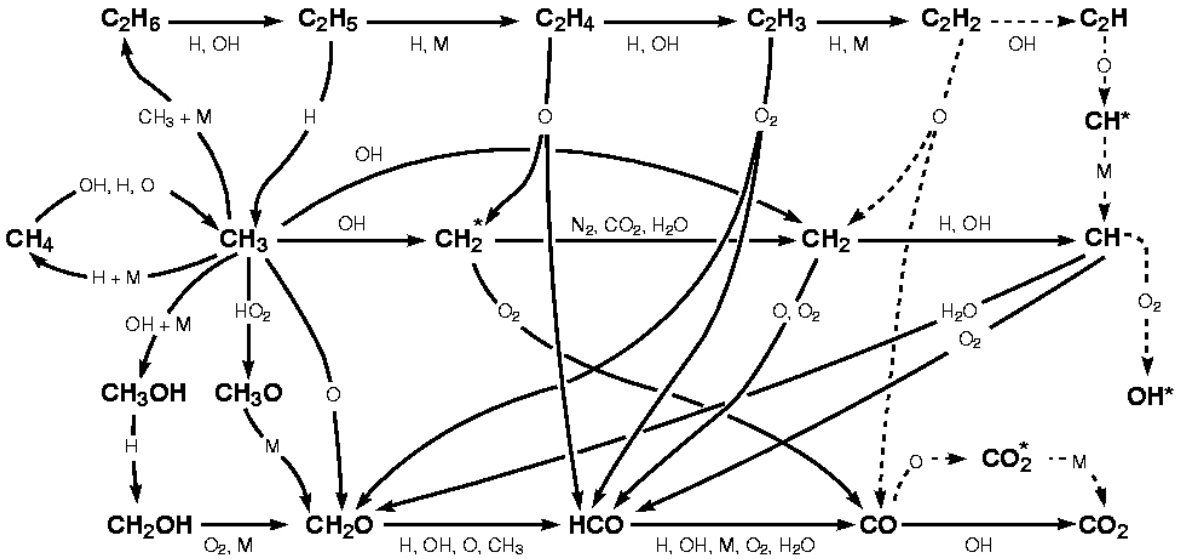
Craig A. Taatjes

Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94551

Sandia National Laboratories

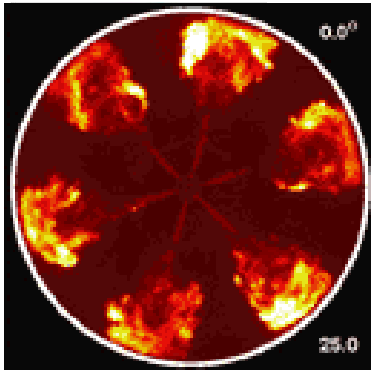
CRF

Real 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

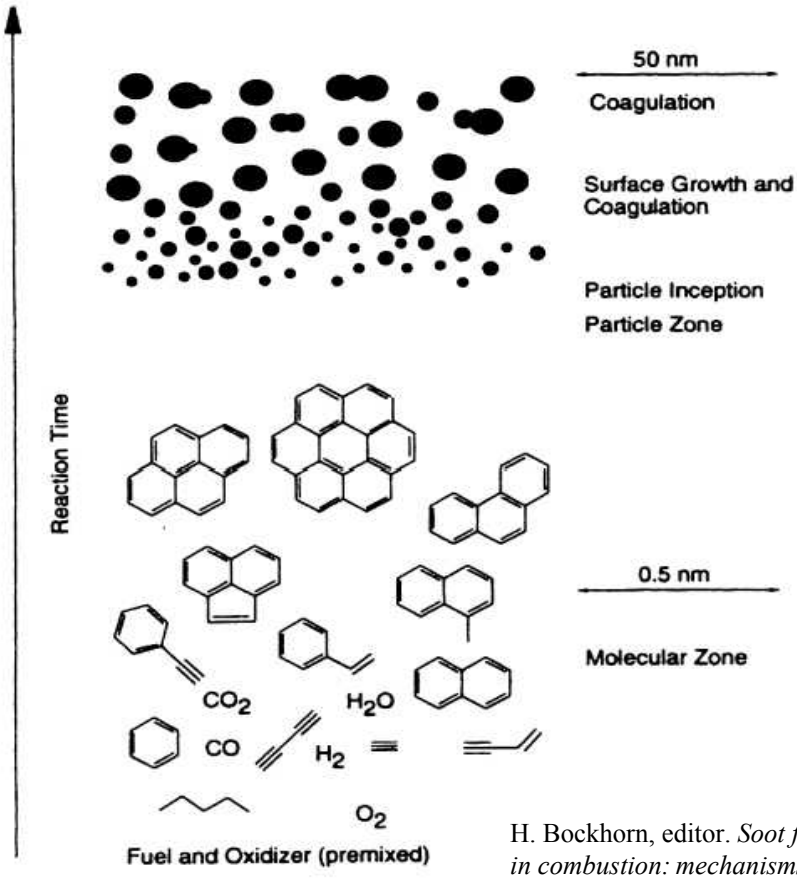
Turbulent, multiphase flows interact with the chemistry

Sandia National Laboratories

CRF

Knowledge of Detailed Flame Chemistry is Important in Pollution Control

- Detailed combustion chemistry determines nature and amount of pollutants
- Soot is formed by molecular growth reactions from small unsaturated hydrocarbons
- Chemical reaction mechanisms in flame models must be validated experimentally

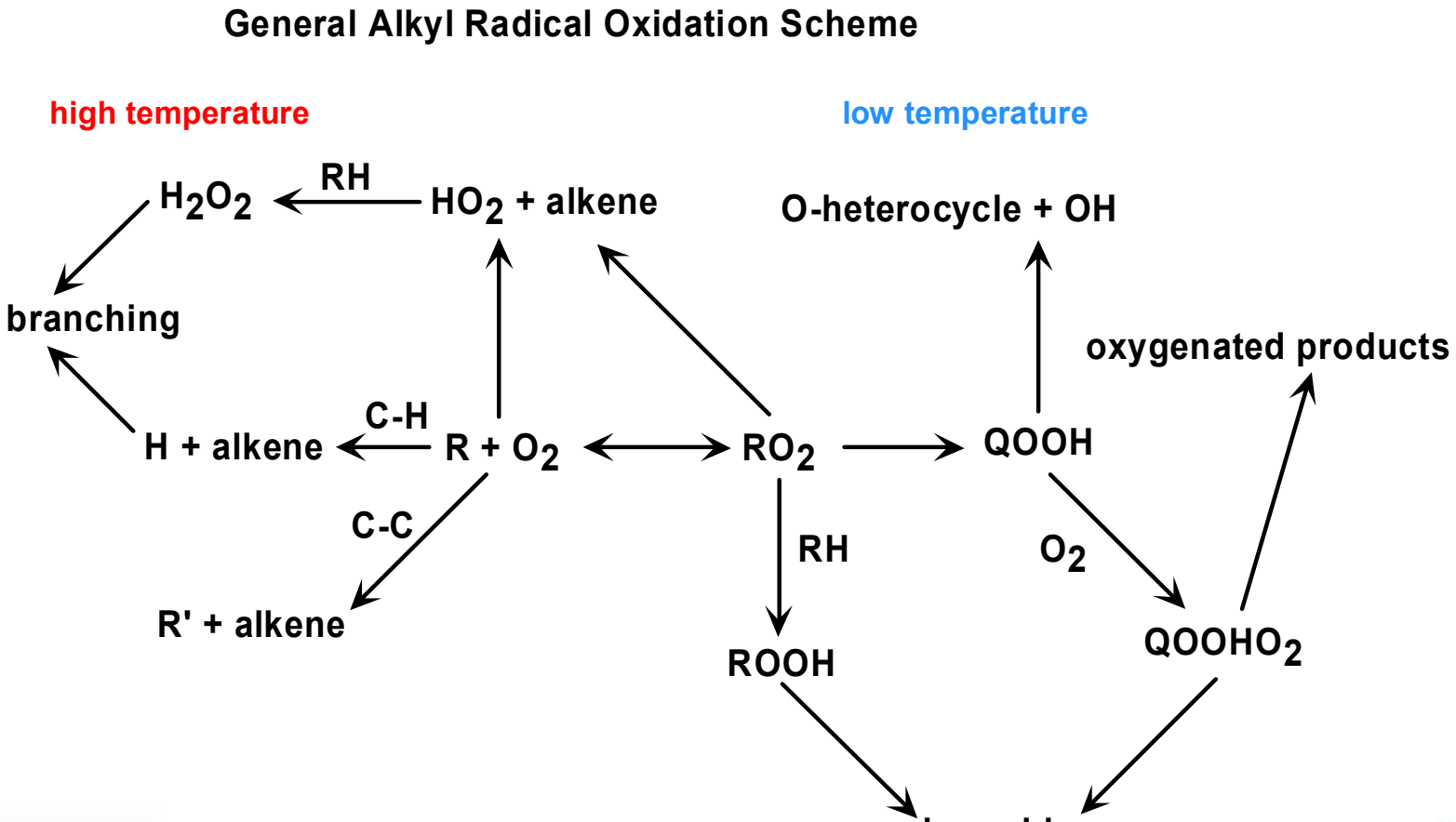


H. Bockhorn, editor. *Soot formation in combustion: mechanisms and models*. Berlin: Springer, 1994.

Sandia National Laboratories

CRF

Details of the Alkyl + O_2 Reactions Are Central to Ignition Chemistry

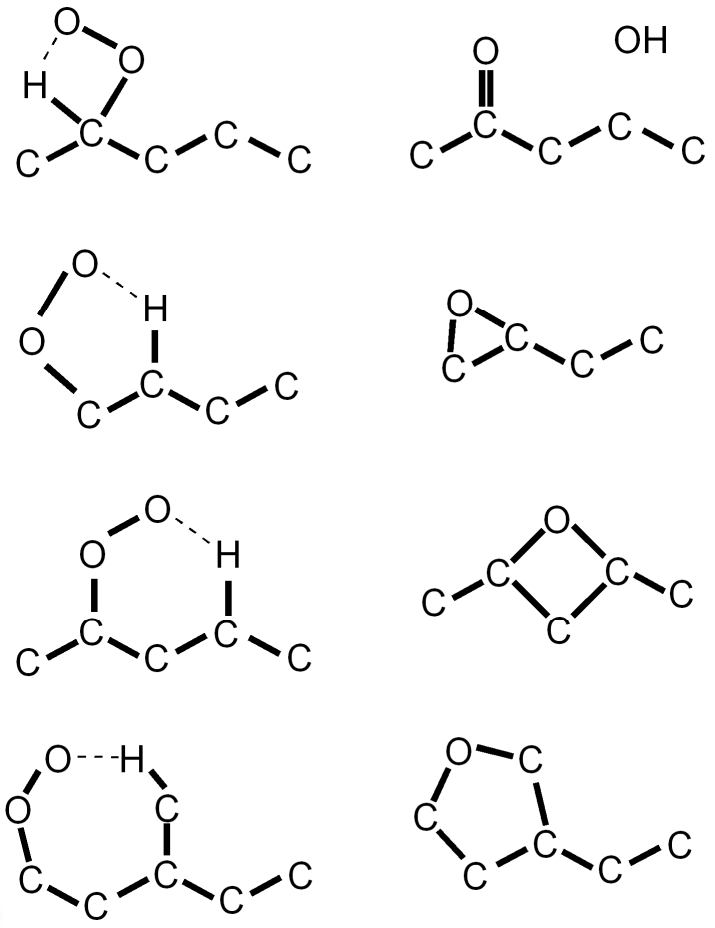


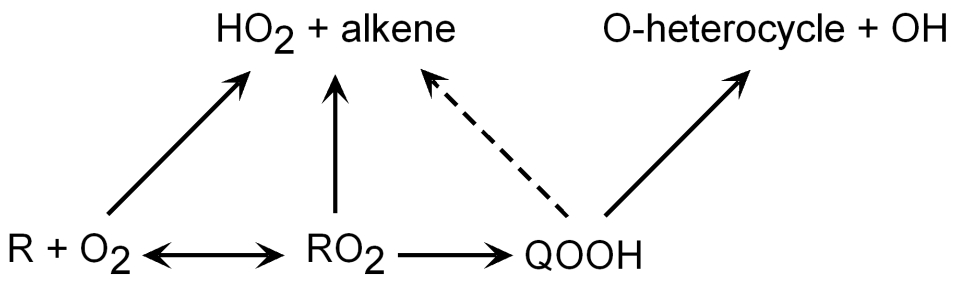
Adapted from Walker and Morley, "Basic Chemistry of Combustion," in *Low Temperature Combustion and Autoignition*, Ed. M. J. Pilling, (Comprehensive Chemical Kinetics Vol. 35) Elsevier, 1997

Sandia National Laboratories

CRF

The R + O_2 Reactions Have Various Possible Product Pathways





- At room temperature RO_2 formation dominates the reactions
- HO_2 formation is essentially chain terminating until high temperature
- Isomerization to QOOH can form OH and cyclic ethers
- Reactions of QOOH are responsible for chain branching at lower temperature

Comparison of Detailed Modeling and Experiment Can Reveal Mechanisms

Experiment: Measure product formation in pulsed-photolytic Cl-initiated oxidation of alkanes (or use R-I photolysis initiation)

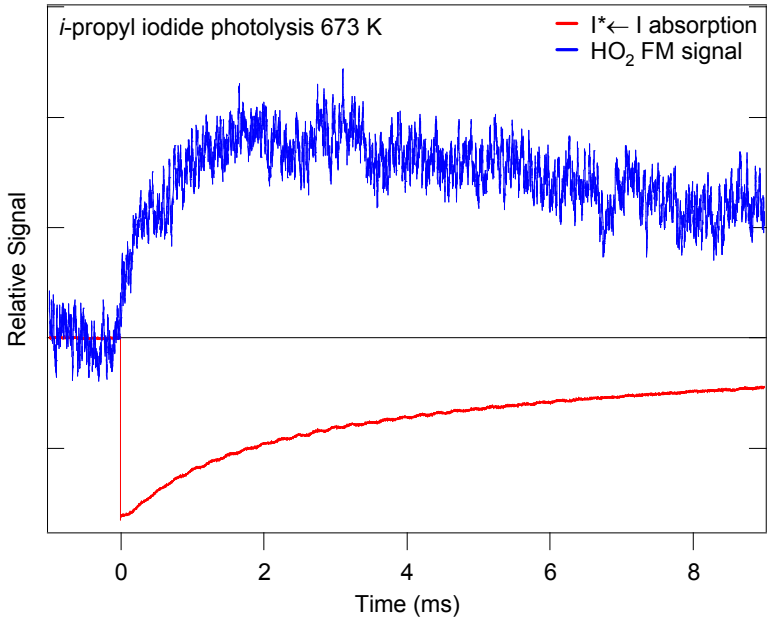
- **Infrared frequency-modulation spectroscopic detection of HO_2 radicals**
- **Laser-induced fluorescence or absorption detection of OH radicals**

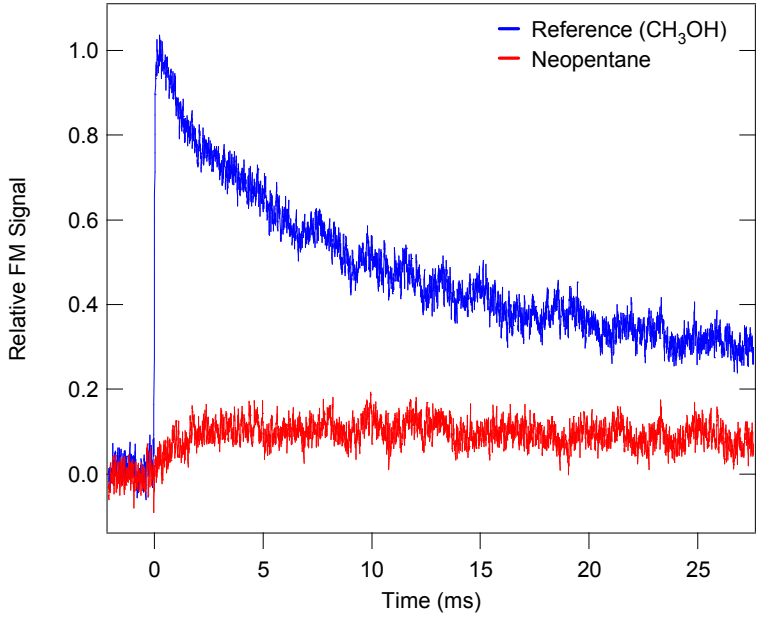
Compare to time-dependent multiple-well master equation solutions

- ***Ab initio* characterization of stationary points on the potential energy surface (Stephen Klippenstein and Jim Miller)**
- **Parameterization of ME solution and kinetic modeling (SJK and JAM)**
- **Includes formally direct pathways for isomer and product formation**

Adjust stationary point energies (within estimated uncertainties!) to match available experimental data (ours and literature)

R + O_2 Reaction Studies Use R-I Photolysis or Cl-initiated Oxidation



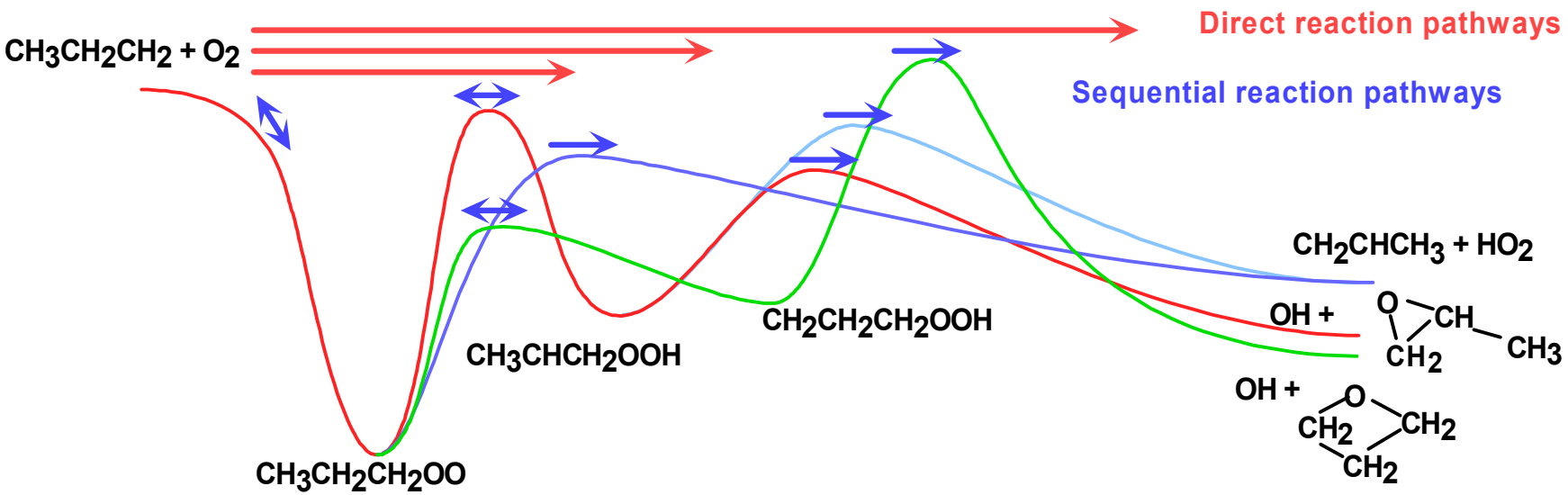


- Cl-initiated oxidation produces thermal radicals, allows calibration of relative HO_2 yield, gives HO_2 self-reaction correction
- Alkyl Iodide photolysis selects individual isomers, allows measurement of absolute initial radical concentration
- Secondary chemistry differs in the two systems

Sandia National Laboratories

CRF

Time-Dependent Master Equation Includes "Direct" Pathways for Isomerizations



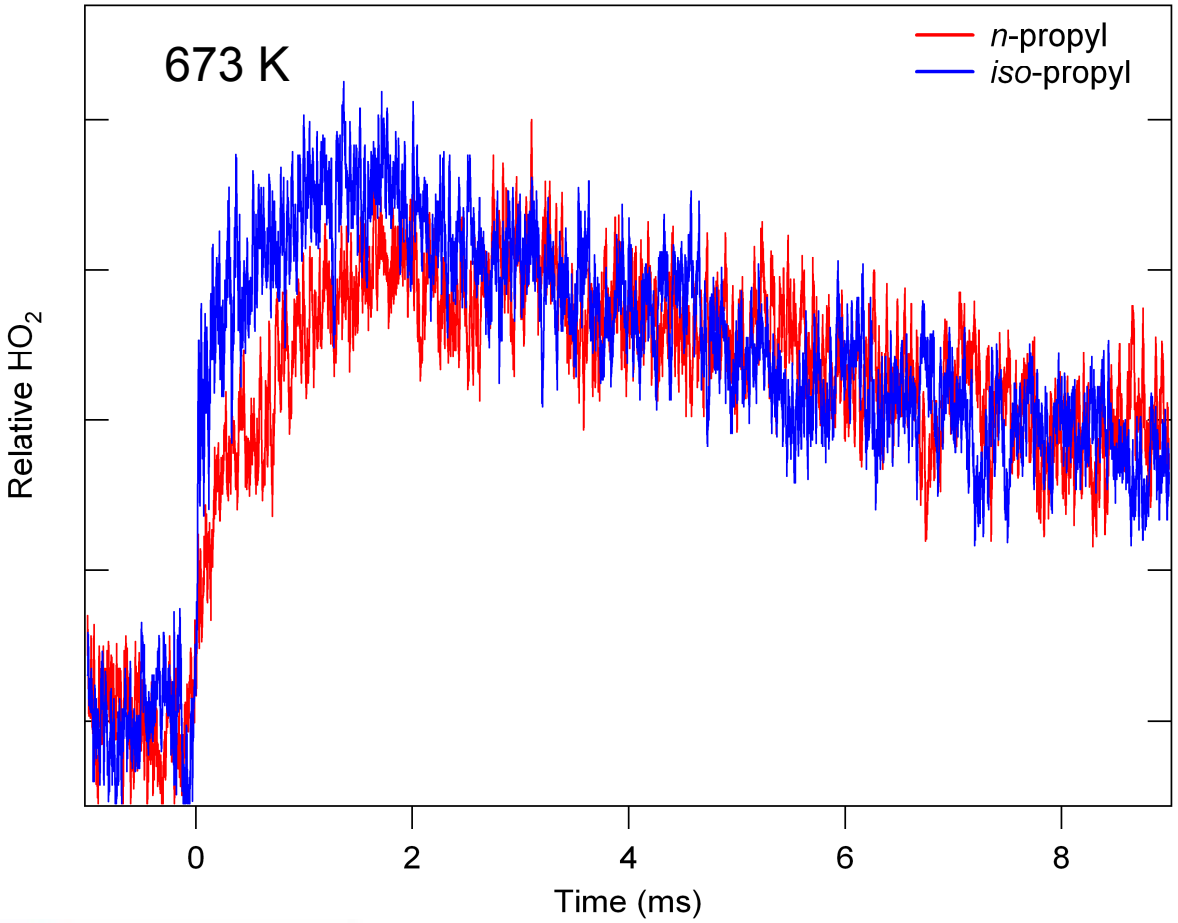
Direct formation pathway is reaction or isomerization of the chemically activated species prior to stabilization

Phenomenological rate constants from ME are incorporated into a rate equation model of the experiment

Sandia National Laboratories

CRF

Propyl Iodide Photolysis Is Used to Study *n*-Propyl & *i*-Propyl + O_2 Reactions



- Two stages of HO_2 production
  - "Direct" chemically-activated process
  - Re-dissociation of RO_2
- Propyl isomers show different behavior

Sandia National Laboratories

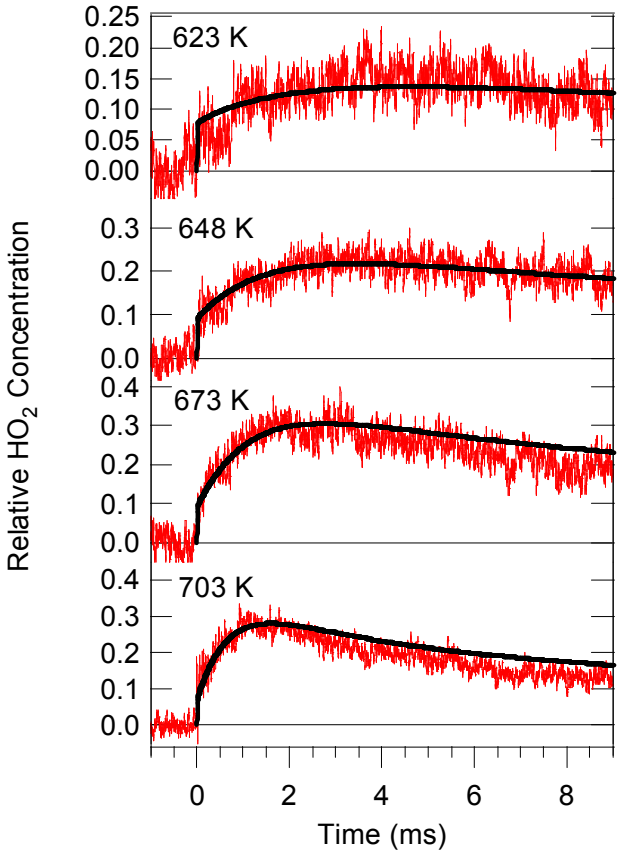
CRF

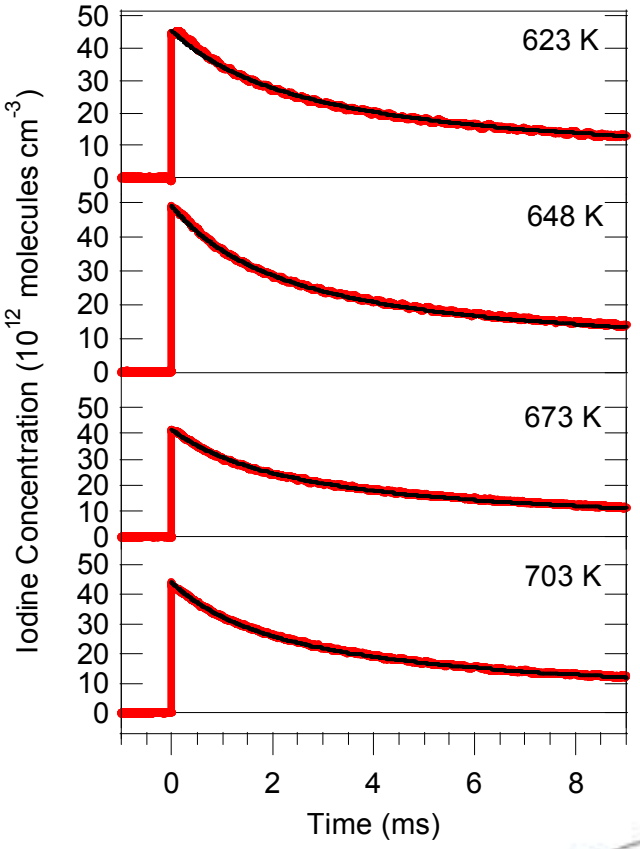
Small Adjustments in Stationary Points Yield Good Agreement for *n*-C_3H_7 + O_2

D_0 = 33.9 kcal mol^{-1} (reduced from ab initio by 1 kcal mol^{-1})

TS_{elim} = -3.8 kcal mol^{-1} (raised from ab initio by 1.4 kcal mol^{-1})

Density = 3.65 x 10^{17} cm^{-3}
[O_2] = 1.50 x 10^{17} cm^{-3}

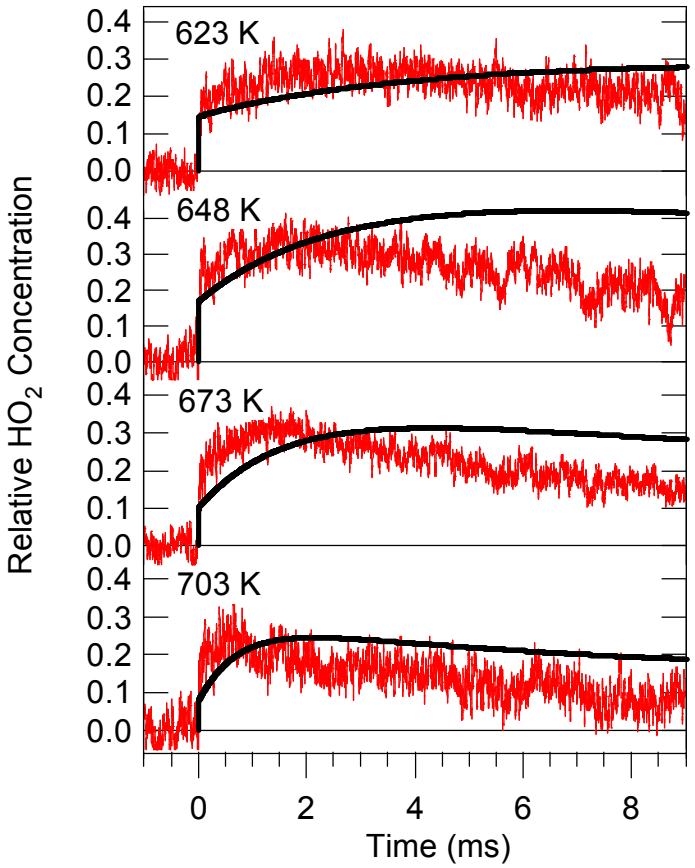


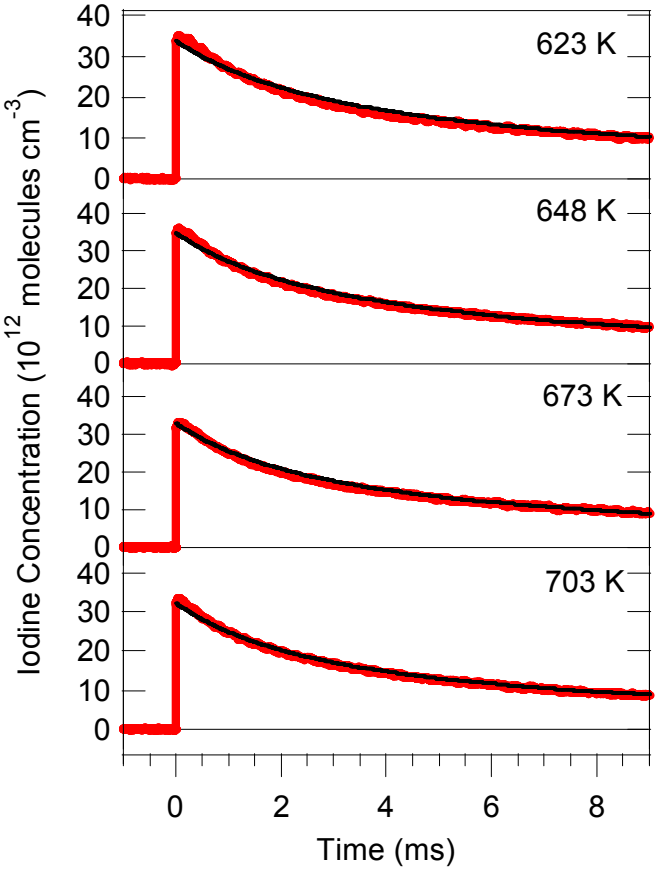


Sandia National Laboratories

CRF

Prediction of HO_2 from *i*-C_3H_7 + O_2 Is More Problematic





Density = 3.65 x 10^{17} cm^{-3}

$[O_2]$ = 1.50 x 10^{17} cm^{-3}

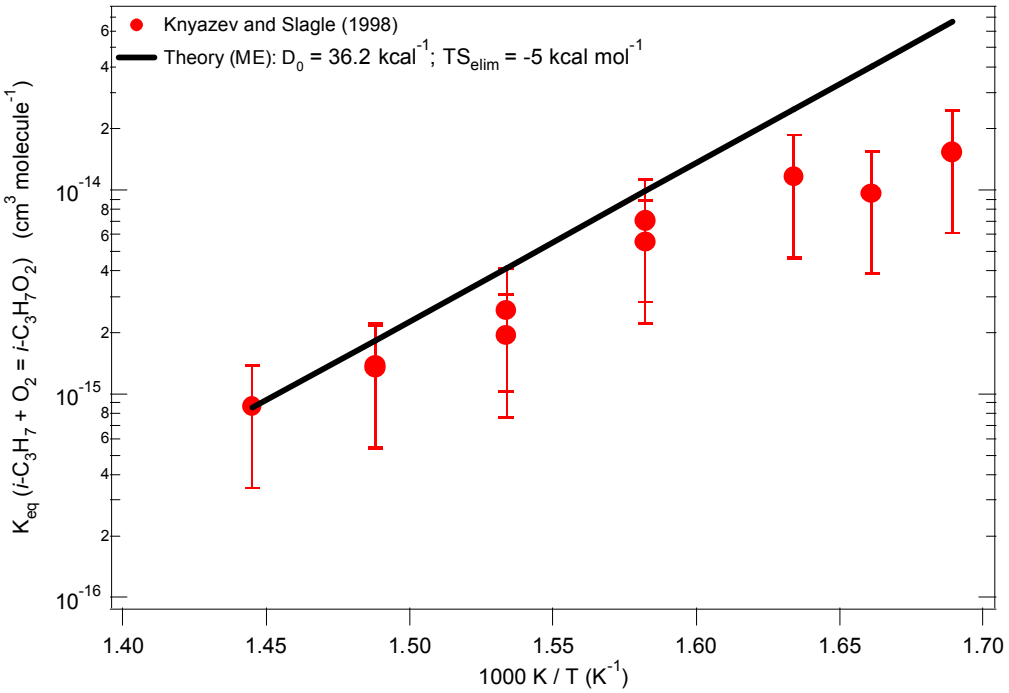
D_0 reduced by 0.6 kcal mol^{-1}, to 36.2 kcal mol^{-1}

TS_{elim} raised by 2 kcal mol^{-1}, to -5 kcal mol^{-1}

Sandia National Laboratories

CRF

Adjustment of Stationary Point Energies Is Constrained by Literature Studies



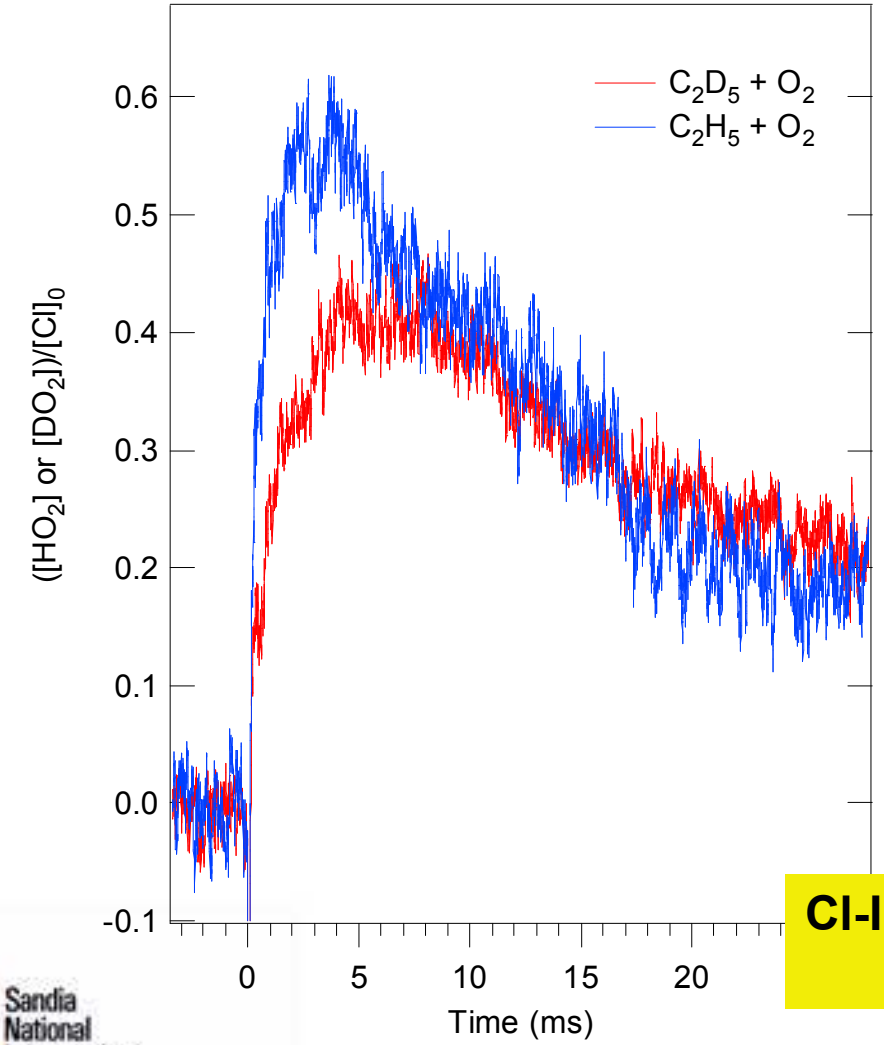
Equilibrium constant for addition of *i*-propyl to O_2 has been measured (V. D. Knyazev & I. R. Slagle, *J. Phys. Chem. A* **1998**, *102*, 1770)

High-temperature rate constant for *i*-propyl + $O_2 \rightarrow HO_2$ + propene has been reported (S. K. Gulati & R. W. Walker, *J. Chem. Soc. Faraday Trans 2*, **1988**, *84*, 401)

Sandia National Laboratories

CRF

Reactions of Deuterated Species Offer Additional Tests to Models



DO_2 Formation from $C_2D_5 + O_2$:

- Smaller prompt yield
- Longer time constant for DO_2 elimination

The overall observed kinetic isotope effect is a convolution of kinetic isotope effects for the ***stabilization, redissociation, and elimination pathways.***

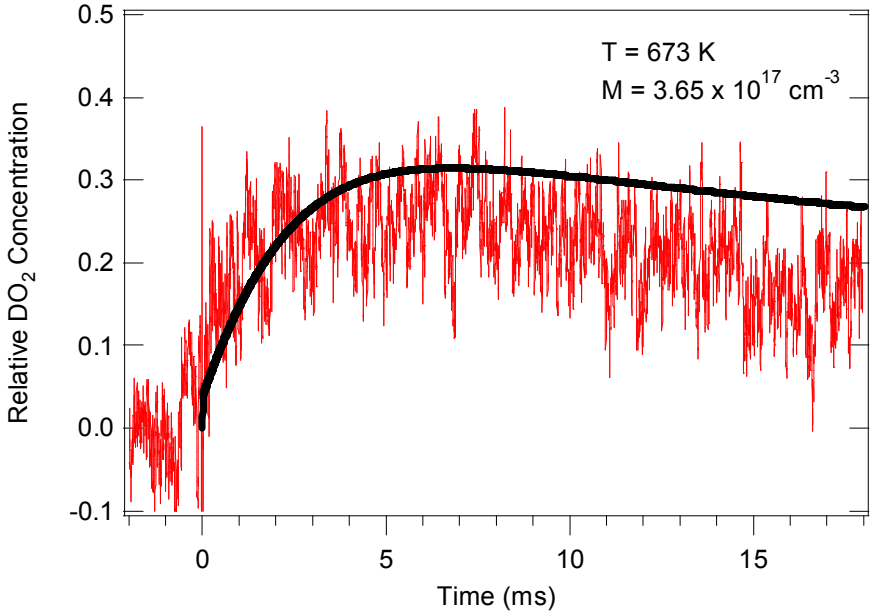
Cl-Initiated Oxidation of Ethane
698 K, 60 Torr

Sandia National Laboratories

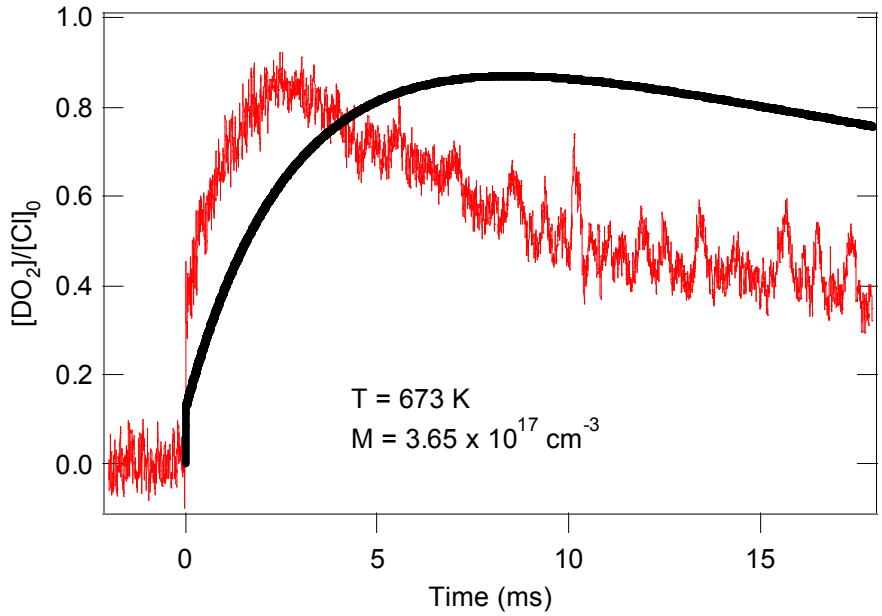
CRF

DO_2 Has Been Observed from *n*-Propyl + O_2 and *i*-Propyl + O_2 Reactions

Photolysis of *n*-Propyl Iodide



Photolysis of *i*-Propyl Iodide



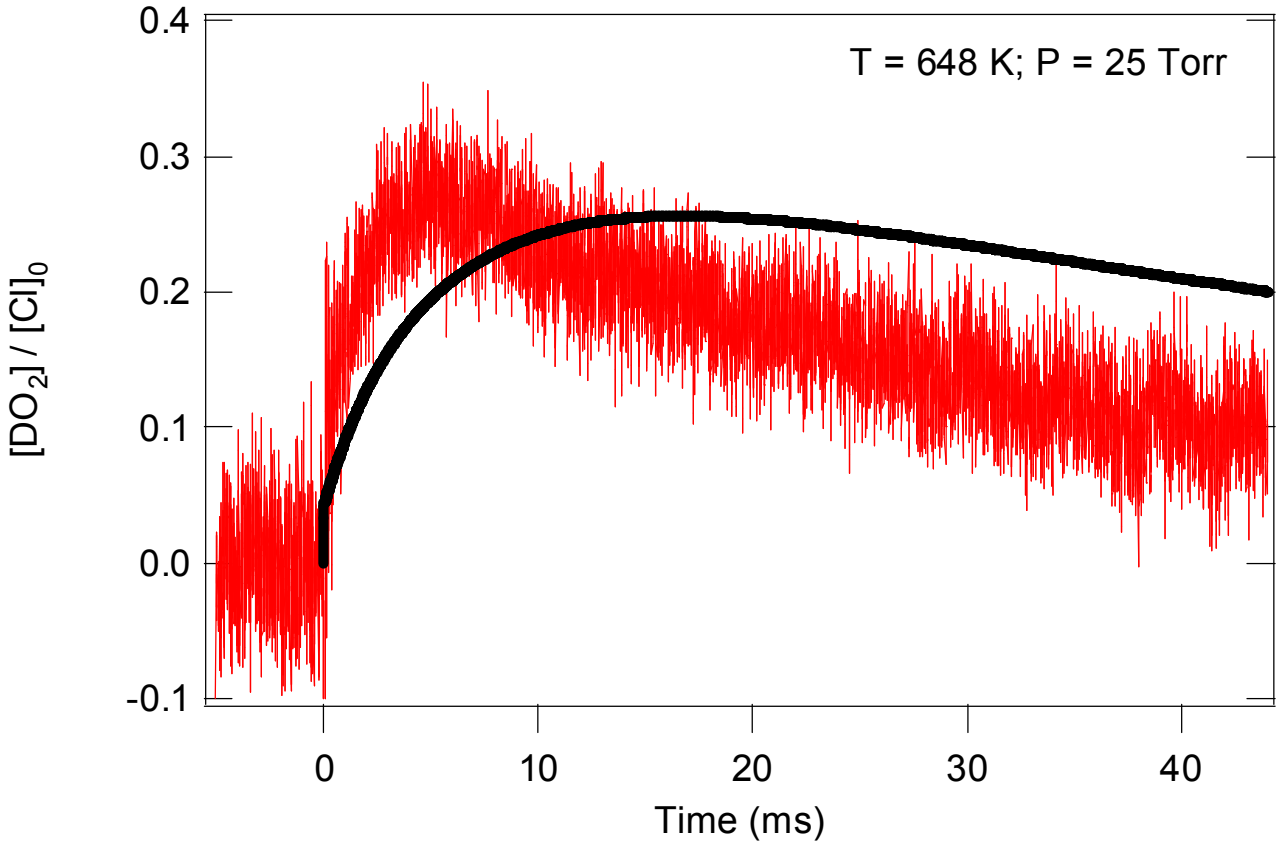
Model works well for DO_2 formation from *n*-C_3D_7 + O_2

Disagreement for *i*-propyl-d_7 + O_2 is similar to the *i*-C_3H_7 + O_2 reaction

Sandia National Laboratories

CRF

Prediction of DO_2 from Oxidation of C_3D_8 Reflects *i*-Propyl + O_2 Disagreement



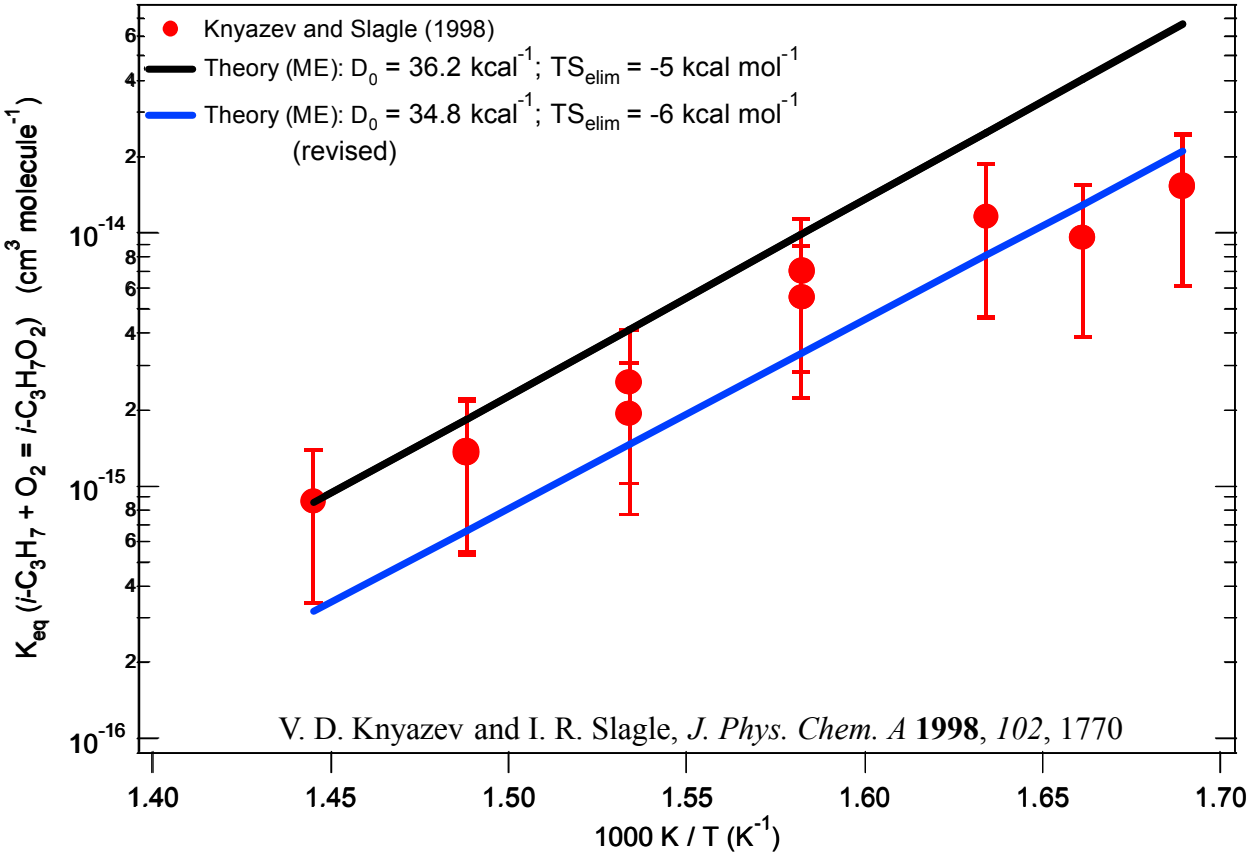
$Cl + C_3D_8 \rightarrow DCl + n\text{-}C_3D_7$ (~30%)

$Cl + C_3D_8 \rightarrow DCl + i\text{-}C_3D_7$ (~70%)

Sandia National Laboratories

CRF

Accumulated Evidence Suggests an Alternative Weight for Literature Studies

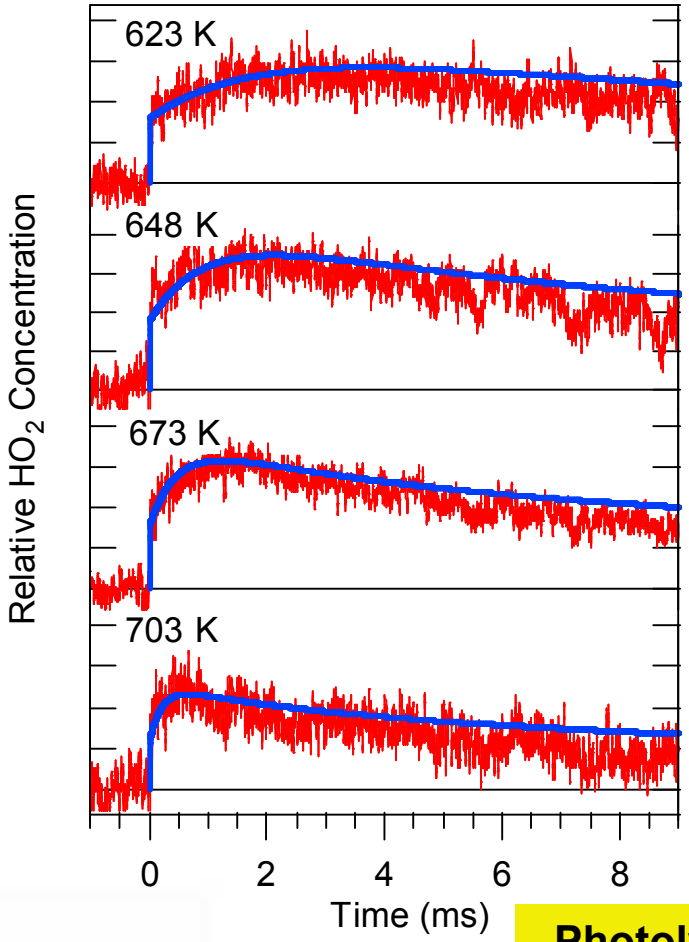


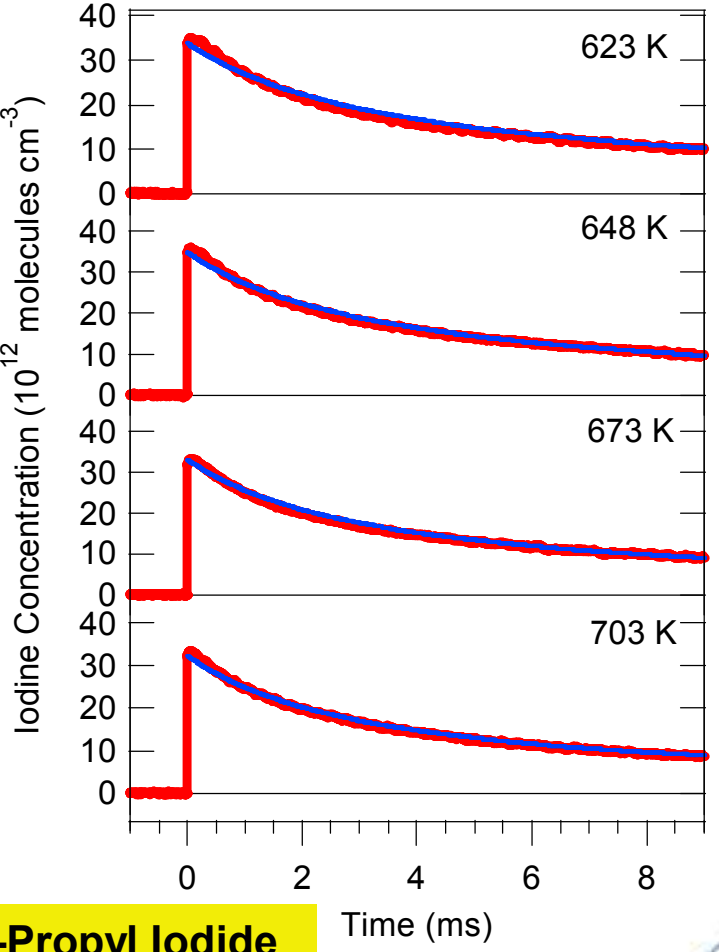
D_0 reduced by 2 kcal mol^{-1} and TS_{elim} raised by 1 kcal mol^{-1} from ab initio values
Maintains reasonable agreement for K_{eq}, increases disagreement with Gulati and Walker (to factor of 6)

Sandia National Laboratories

CRF

Revised Model Matches Measurements of HO_2 Formation From *i*-C_3H_7 + O_2





Photolysis of *i*-Propyl Iodide

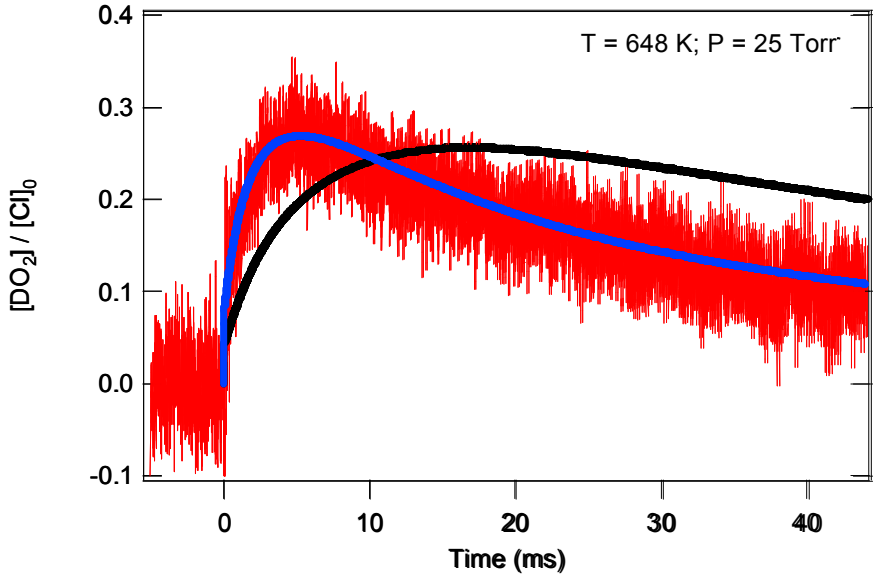
Density = 3.65 x 10^{17} cm^{-3} ; $[O_2]$ = 1.50 x 10^{17} cm^{-3}

Sandia National Laboratories

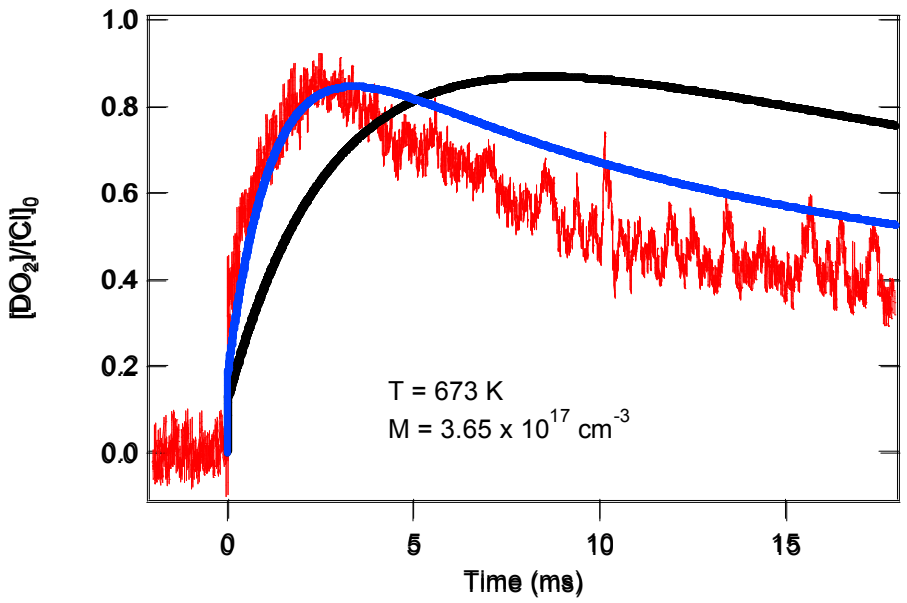
CRF

Revised Model Also Matches Observed DO_2 from Deuterated Propyl + O_2

Cl-Initiated Oxidation of Propane-d_8



Photolysis of *i*-Propyl-d_7 Iodide



D_0 = ab initio – 0.6 kcal mol^{-1}; E(TS_{elim}) = ab initio + 2 kcal mol^{-1}

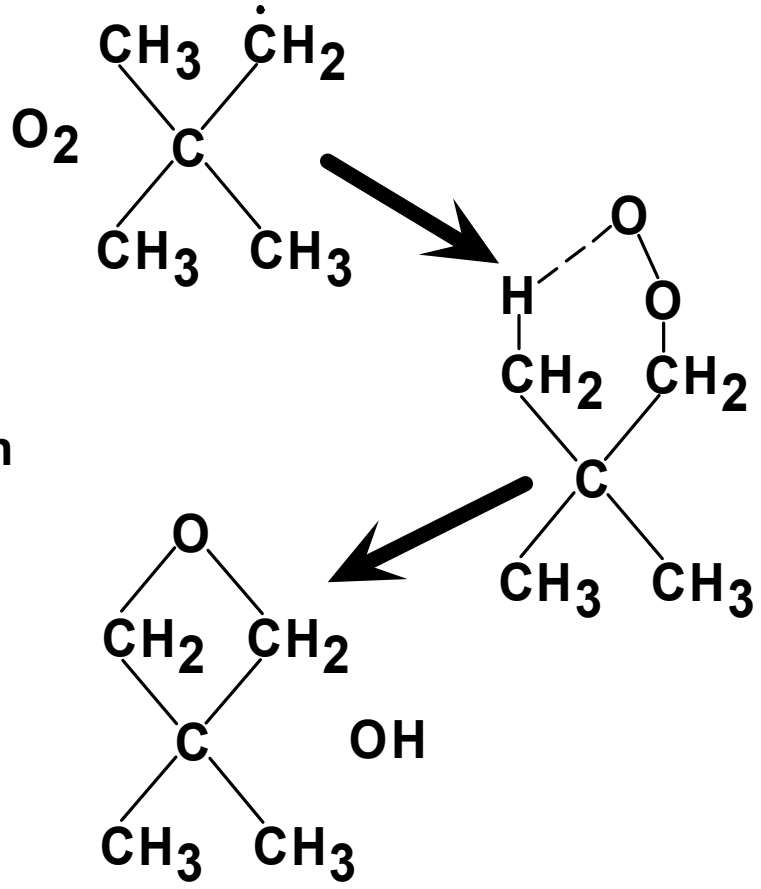
D_0 = ab initio – 2 kcal mol^{-1}; E(TS_{elim}) = ab initio + 1 kcal mol^{-1}

Sandia National Laboratories

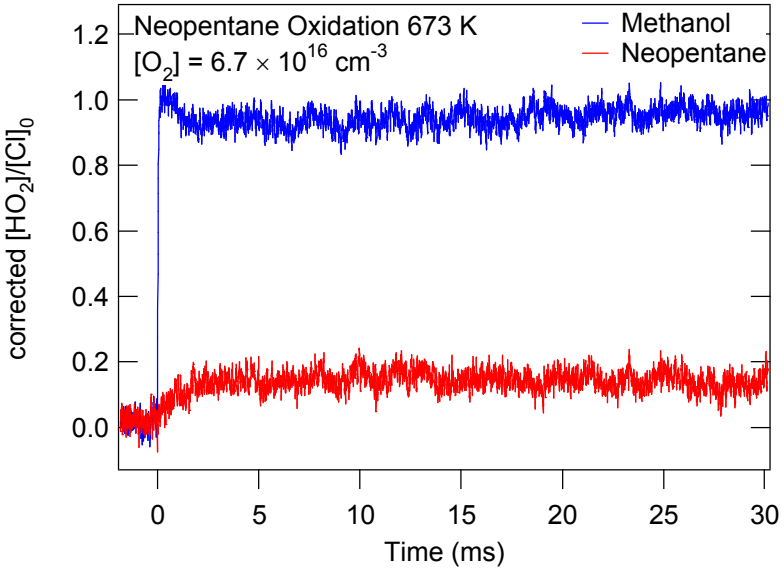
CRF

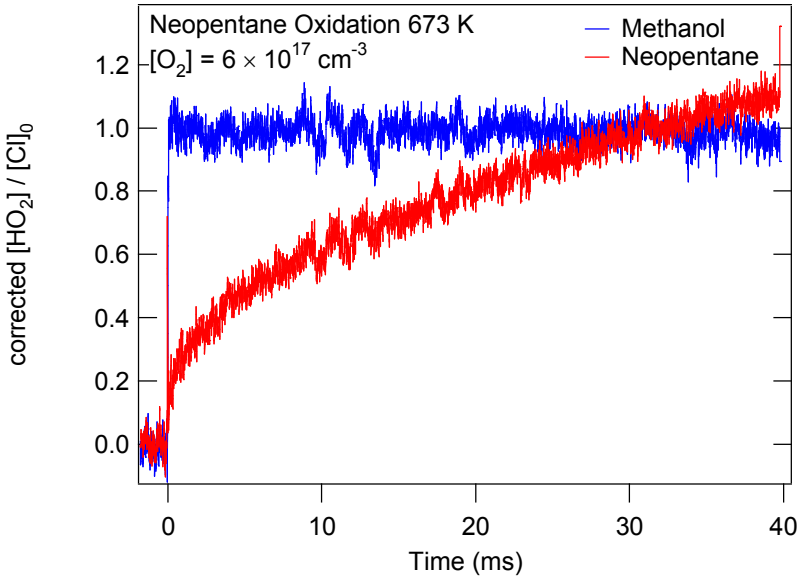
Neopentane Oxidation Is an Important Test System for QOOH Formation

- Neopentyl + O_2 focuses on the isomerization to QOOH
  - No conjugate alkene exists
  - No direct path to HO_2
- Pilling and co-workers -- OH formation probes isomerization rate
- Calculations of *n*-propyl + O_2 suggest rapid isomerization



Neopentane Oxidation May Provide Means to Investigate QOOH Chemistry





Neopentyl + O_2 cannot form HO_2 directly: no conjugate alkene exists

Formation of HO_2 results from subsequent reactions of RO_2 and QOOH

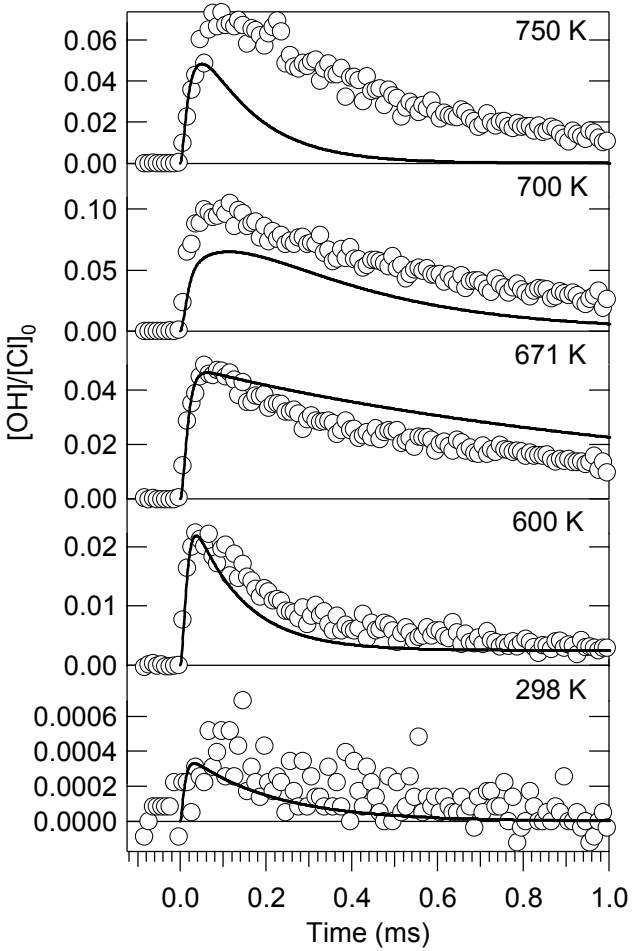
Chain-branching is evident for higher O_2 concentrations

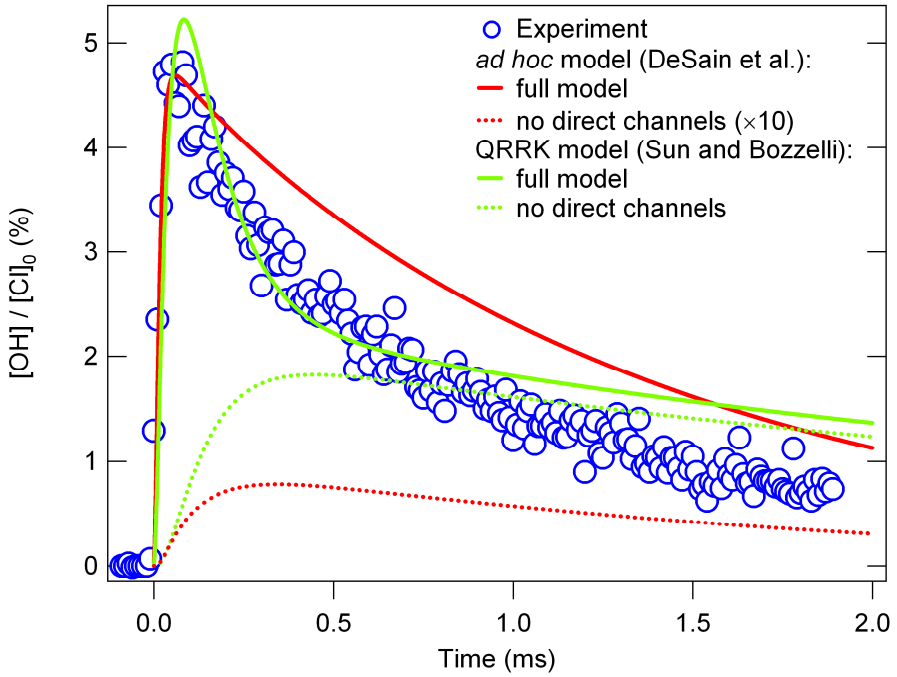
Simple models failed to reproduce chain branching behavior (DeSain, J. D.; Klippenstein, S. J.; Taatjes, C. A. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1584)

Sandia National Laboratories

CRF

Measurement of OH in Neopentane Oxidation Shows Direct Path to OH





Clear effects of direct OH + methyloxetane path

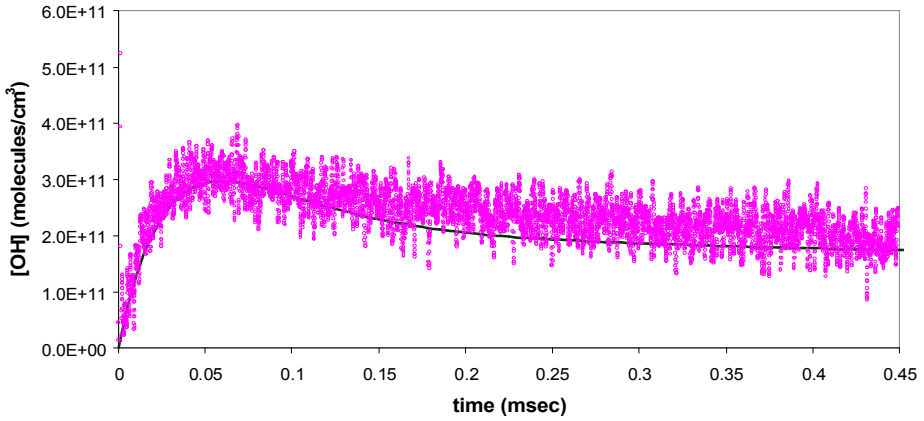
Can model CRF experiments and Pilling experiments with fast isomerization, based on analogy to n-C_3H_7

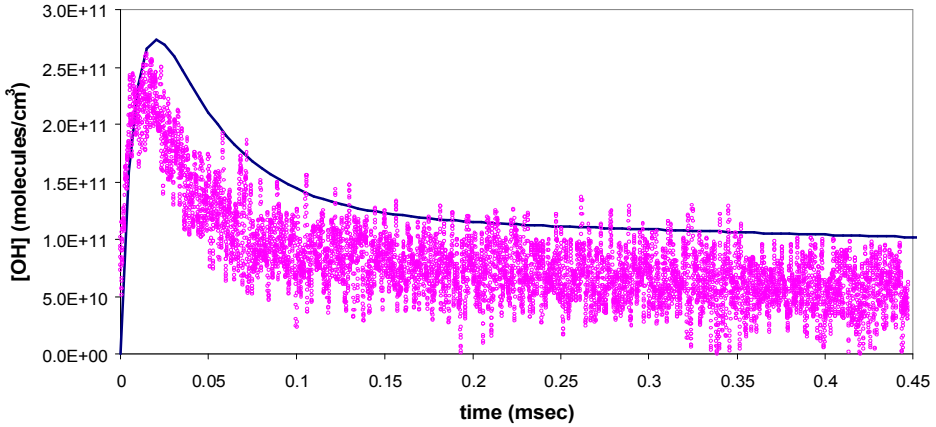
Sandia National Laboratories

CRF

Reinvestigation of Neopentane Oxidation with Automated Mechanism Generation

- Collaboration with Bill Green's group (MIT)
- Remeasure HO_2 and OH formation
- RMG methods point to key reactions
  - Re-emphasize direct OH
  - Search for conditions that probe isomerization
- Direct sensitivity to isomerization is small
  - Contributes via pressure-dependent network





Huzeifa Ismail, Sally Petway

Sandia National Laboratories

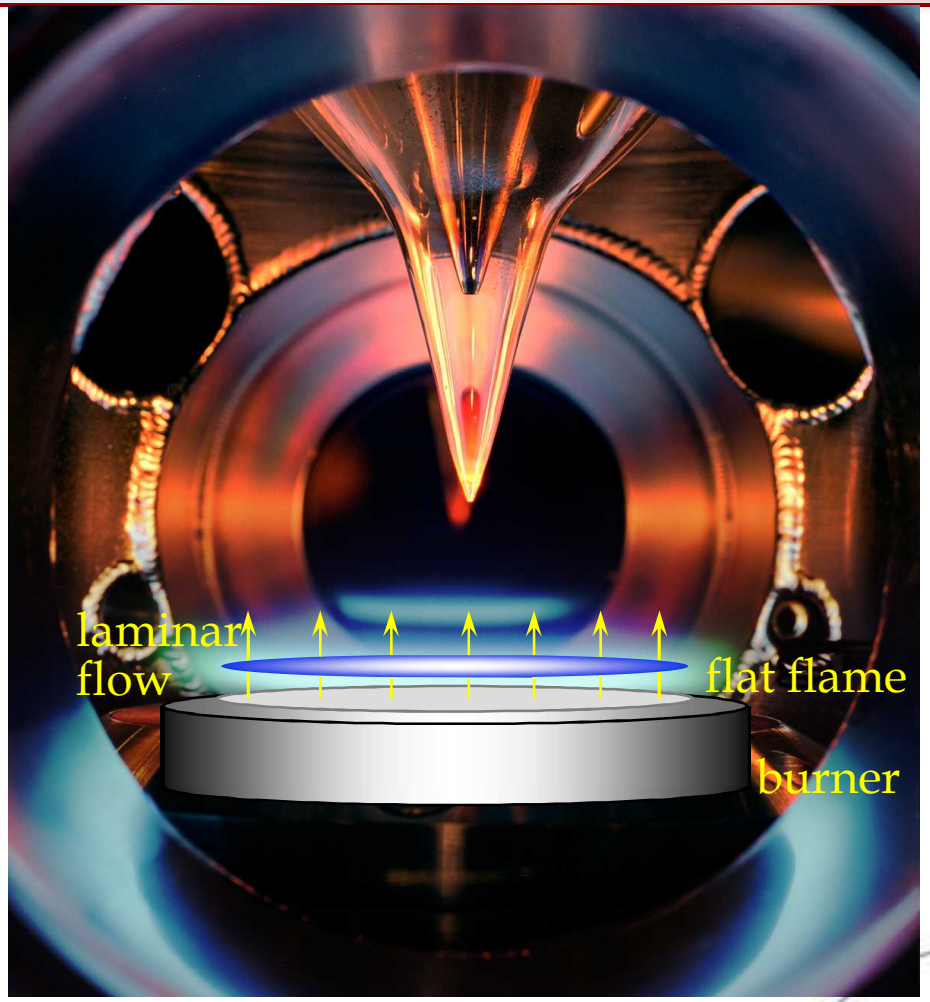
CRF

Measurements and Modeling of Product Formation Illuminate R + O_2 Reactions

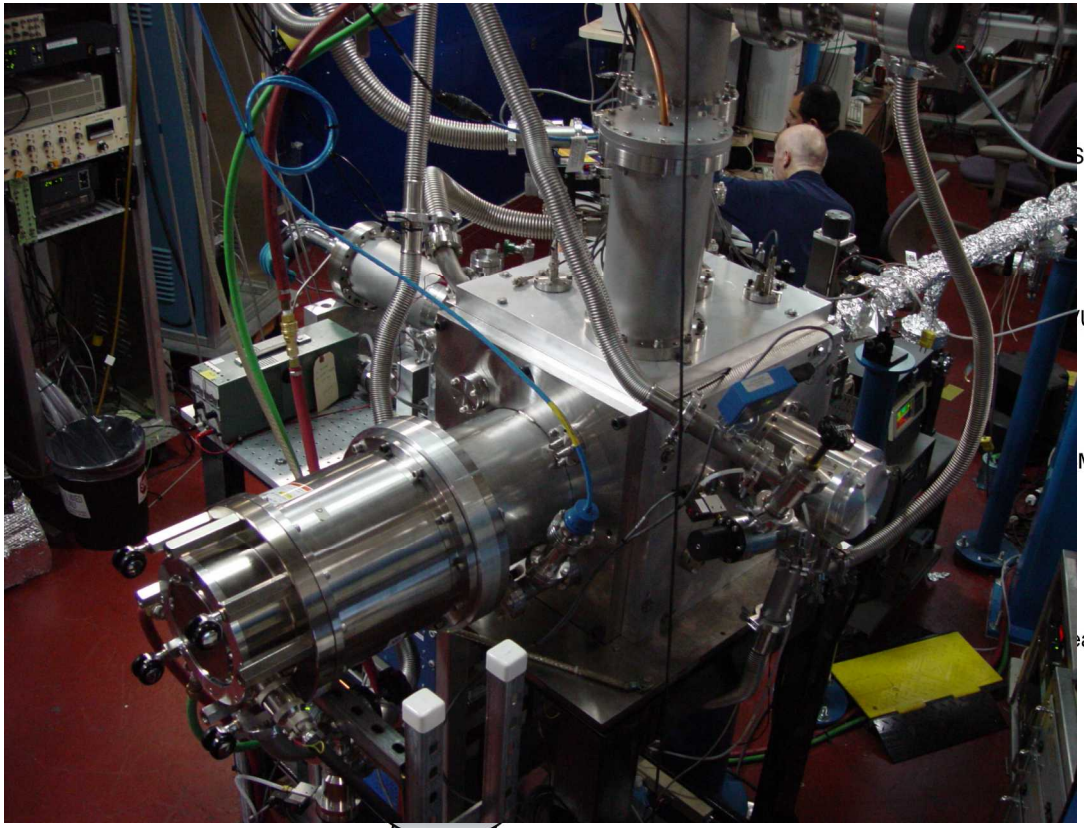
- HO_2 formation in propyl + O_2 now understood at nearly the same level as in ethyl + O_2
  - Propyl isomers are prototypical for larger alkyl radicals
  - Deuterated radicals offer additional test for stationary point energies
- Route to successful modeling of larger alkyl radicals may involve larger reaction mechanisms
- Quest for experimental measurement of QOOH continues

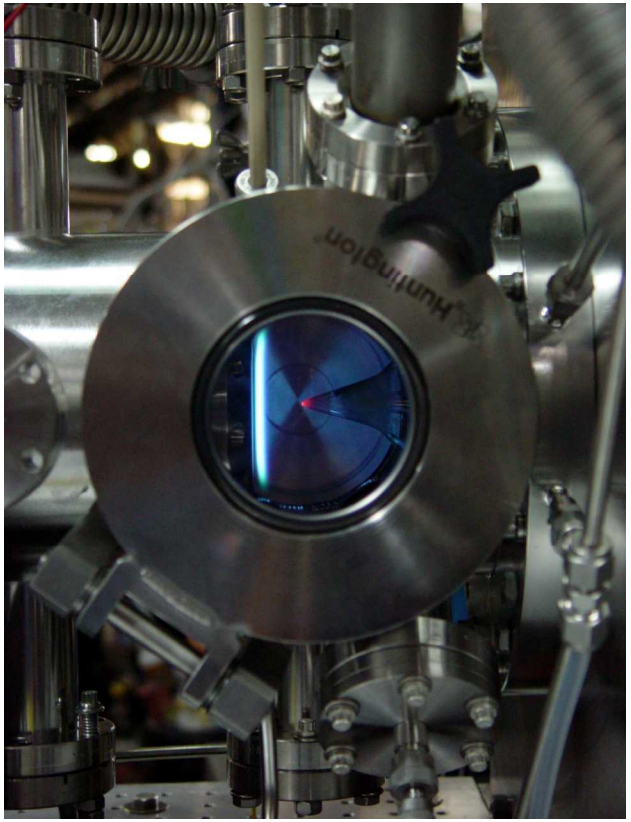
Low-Pressure Flames are a Controlled Environment to Study Chemistry

- Laminar premixed flames reduce fluid dynamics to (nearly) one dimension
- Low pressure expands reaction zone (but changes some three-body chemistry)
- **M**olecular **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: Photoionization MBMS



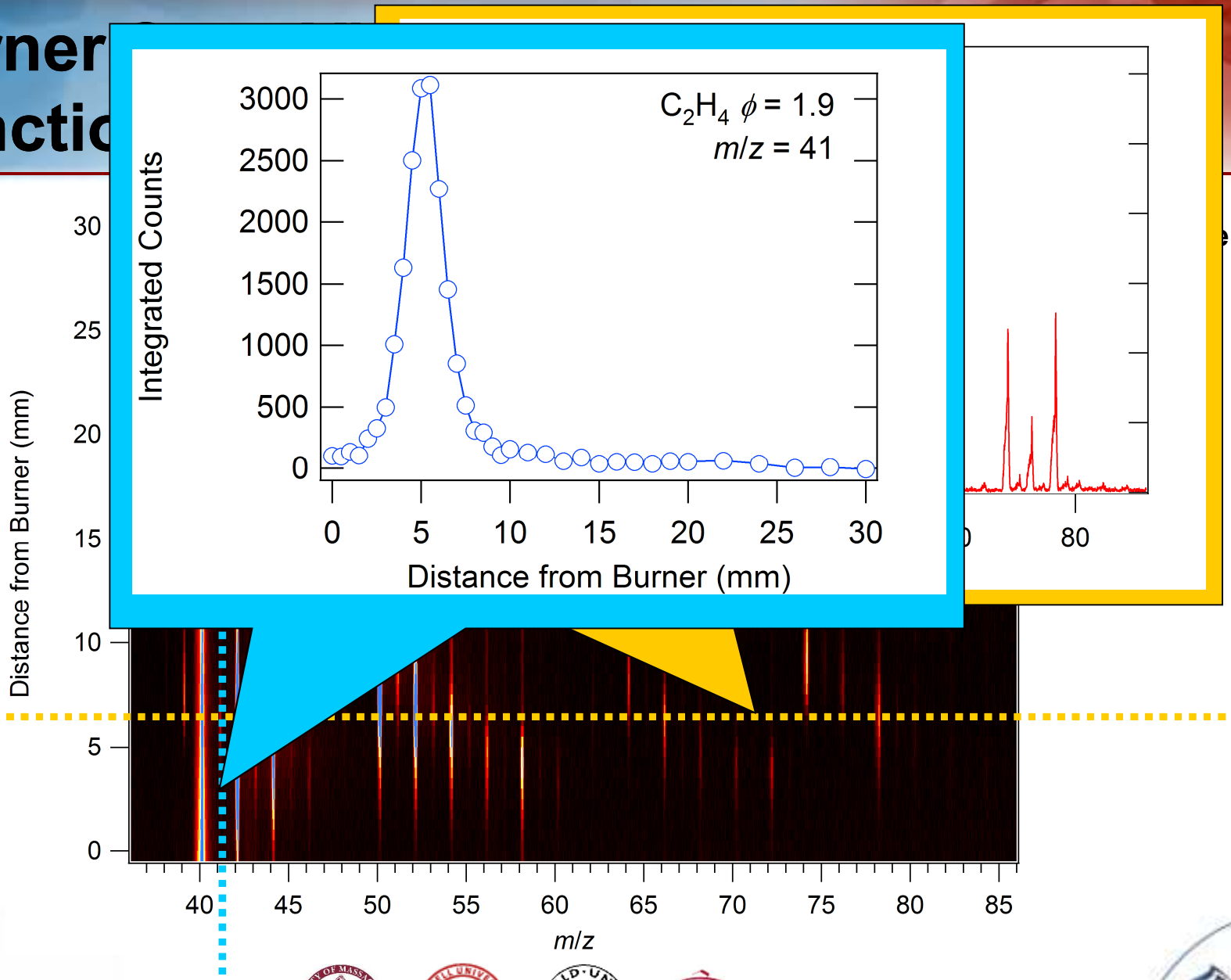


Sandia National Laboratories

BERKELEY LAB

CRF

Burner
Functio



Sandia National Laboratories

UNIVERSITY OF MASSACHUSETTS AMHERST 1863

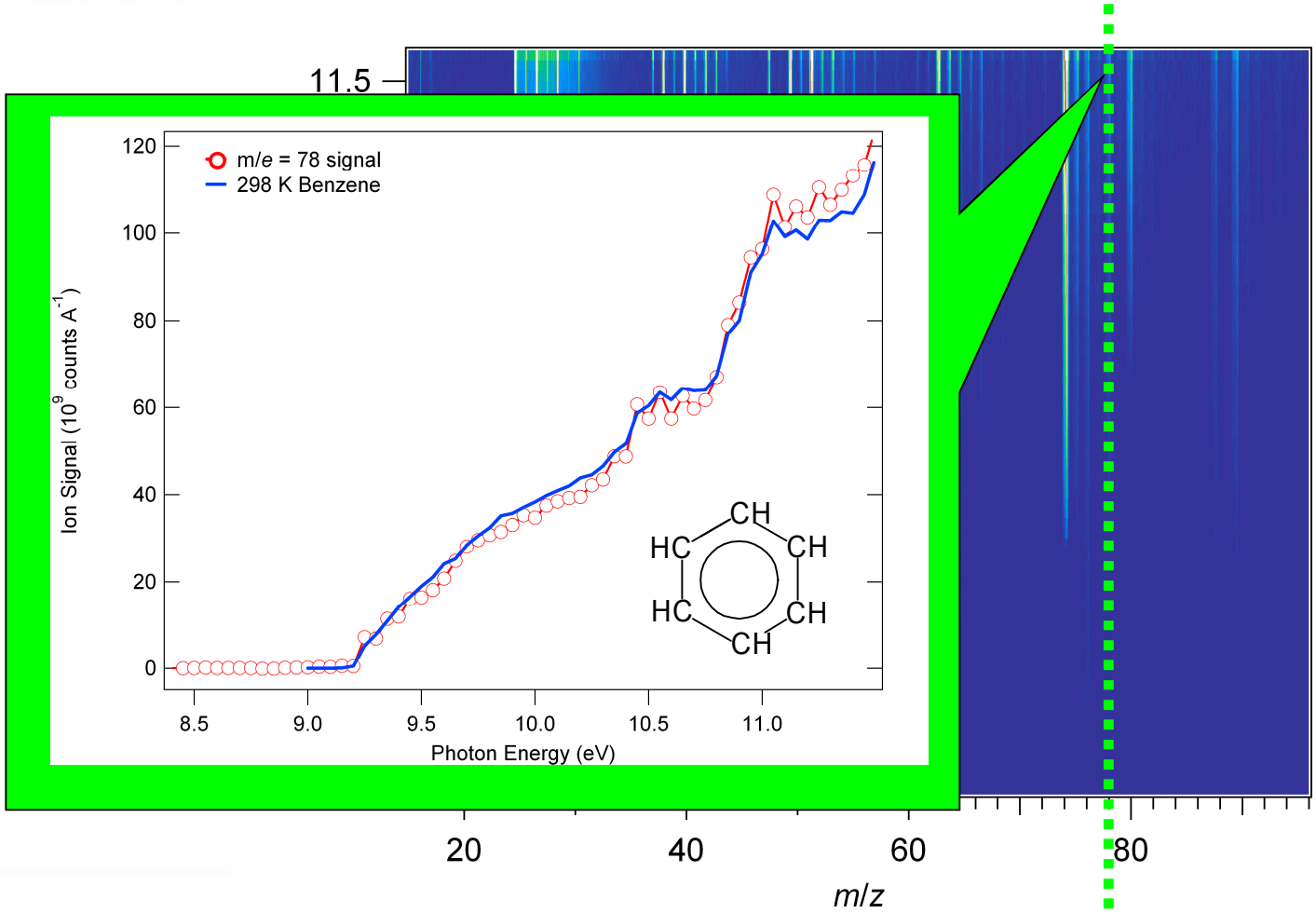
CORNELL UNIVERSITY FOUNDED A.D. 1865

BIELEFELD UNIVERSITÄT

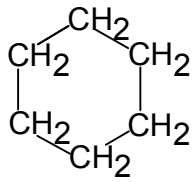
BERKELEY LAB

CRF

Scan of Photon Energy Gives Photoionization Efficiency (PIE) Curve



Cyclohexane flame
ϕ = 1.0



Sandia National Laboratories

Berkeley Lab

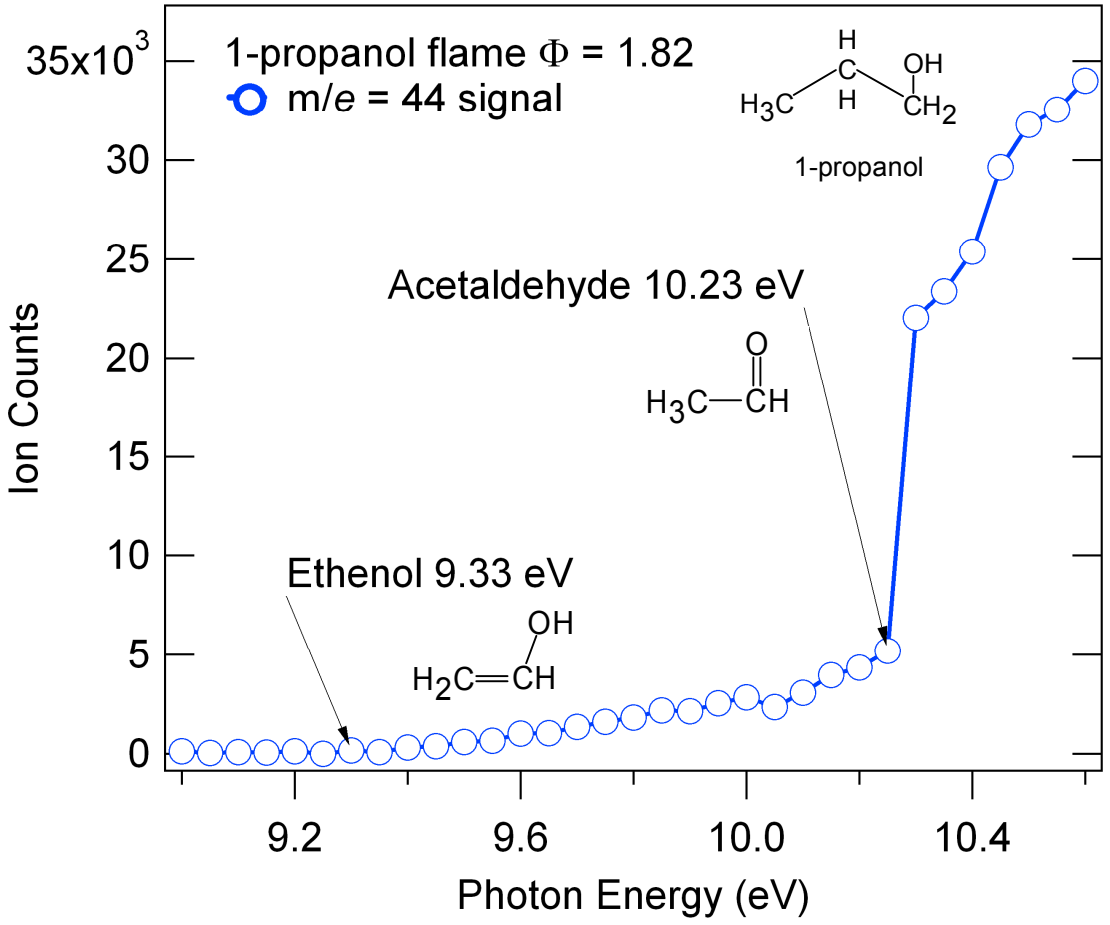
CRF

Tunable Photoionization Can Distinguish Isomers

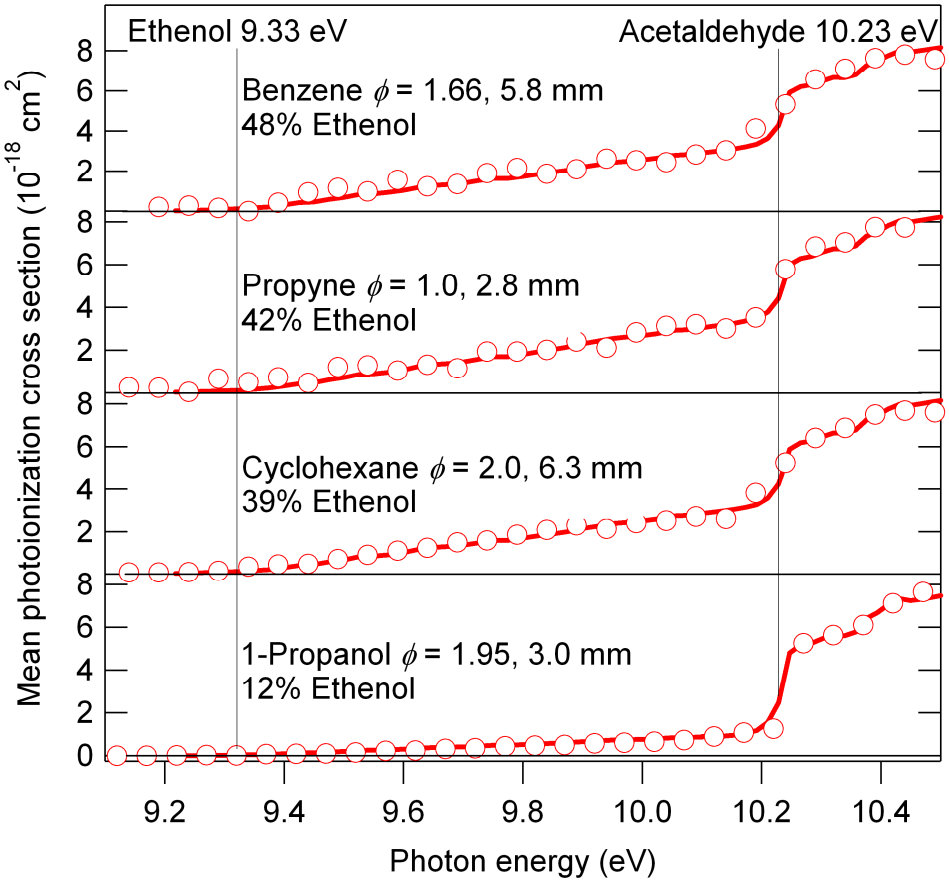
Enols (ethenol is the simplest) have C=C double bonds next to an alcohol (OH) group

Keto tautomers have C-C single bond and a C=O double bond

Keto-enol tautomerization is a famous isomerization in organic chemistry



Ethenol Appears in Flames of Many Different Fuels and Stoichiometries



- Relative concentrations of ethenol and acetaldehyde can be determined using an estimated photoionization cross section for ethenol
- Ethenol fractions are far above the equilibrium values

Sandia National Laboratories

BERKELEY LAB

CRF

Enols Are "New" Flame Intermediates

Enols (alcohol with adjacent double bond) – postulated to be transient intermediates by Erlenmeyer in 1880

Ethenol (simplest enol) went undetected for ninety years afterwards

- Measured in 1973 by NMR
- First observed in the gas phase in 1976

Keto tautomers are more stable, well-known in combustion chemistry

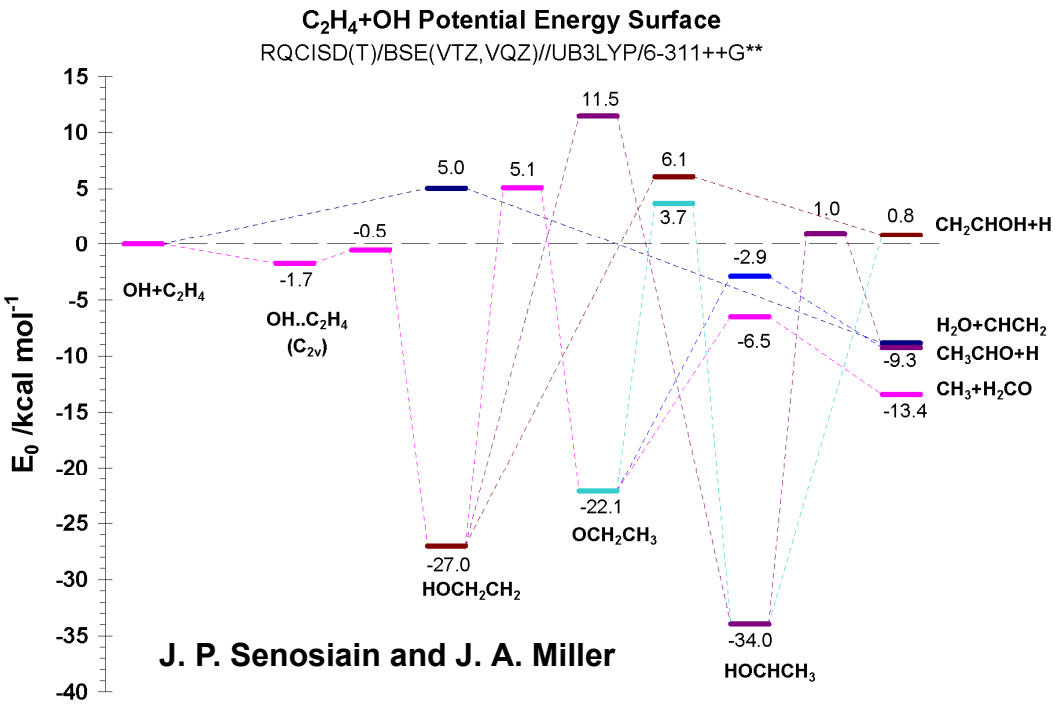
Enols appear^ed in no flame chemistry models

New chemistry needed for formation and removal of enols in flames

Reaction of C_2H_4 with OH Is One Possible Mechanism to Form Ethenol

- Ethene (C_2H_4) is a common intermediate in hydrocarbon flames
- OH is one of the most abundant radical species in flames
- Calculations (but no experiments yet) predict that OH + C_2H_4 produces ethenol at high temperatures

Juan Senosiain, James Miller, Stephen Klippenstein, *J. Phys. Chem. A*, **110**, 6960 (2006)

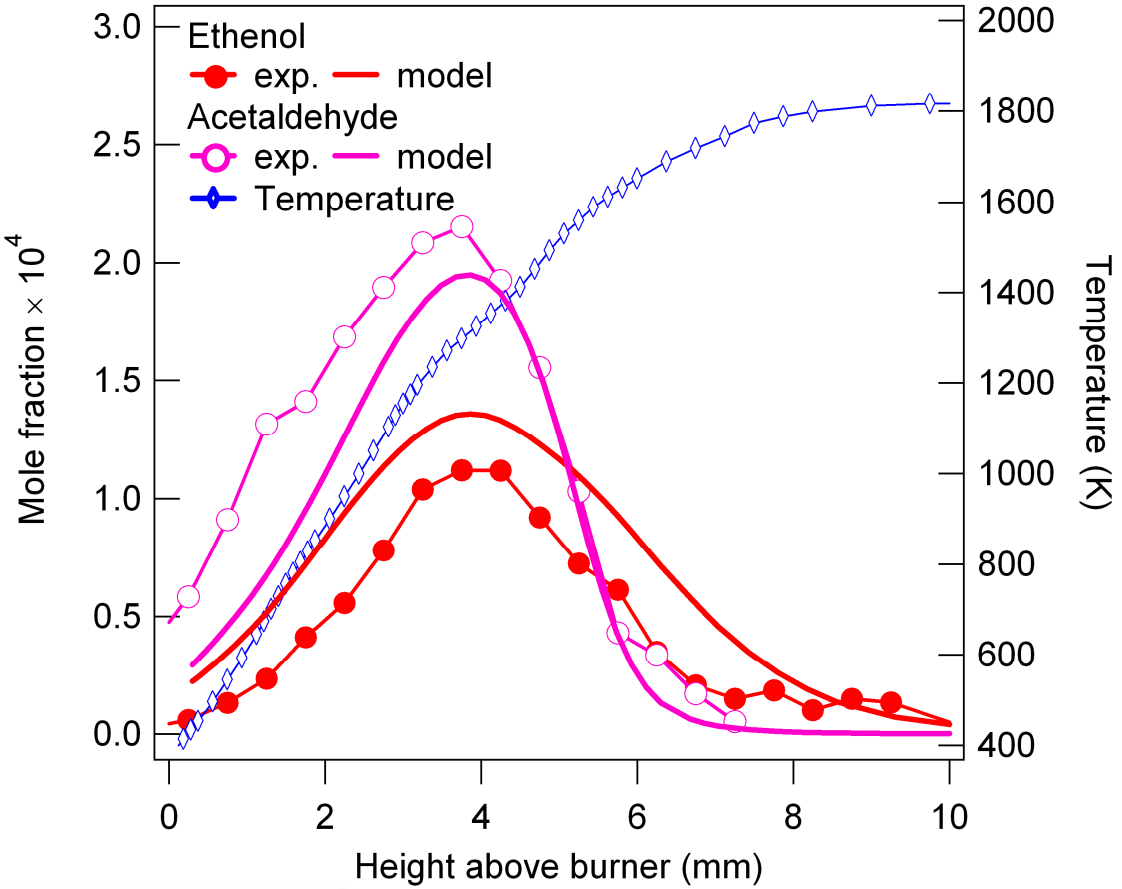


Sandia National Laboratories

BERKELEY LAB

CRF

Correction of OH + Ethene Reaction Can Model Ethenol Profiles in Several Flames



Ethene flame model has been modified to include new calculations for OH + C_2H_4 rate constants

Model now predicts formation of ethenol nearly quantitatively

Sandia National Laboratories

BERKELEY LAB

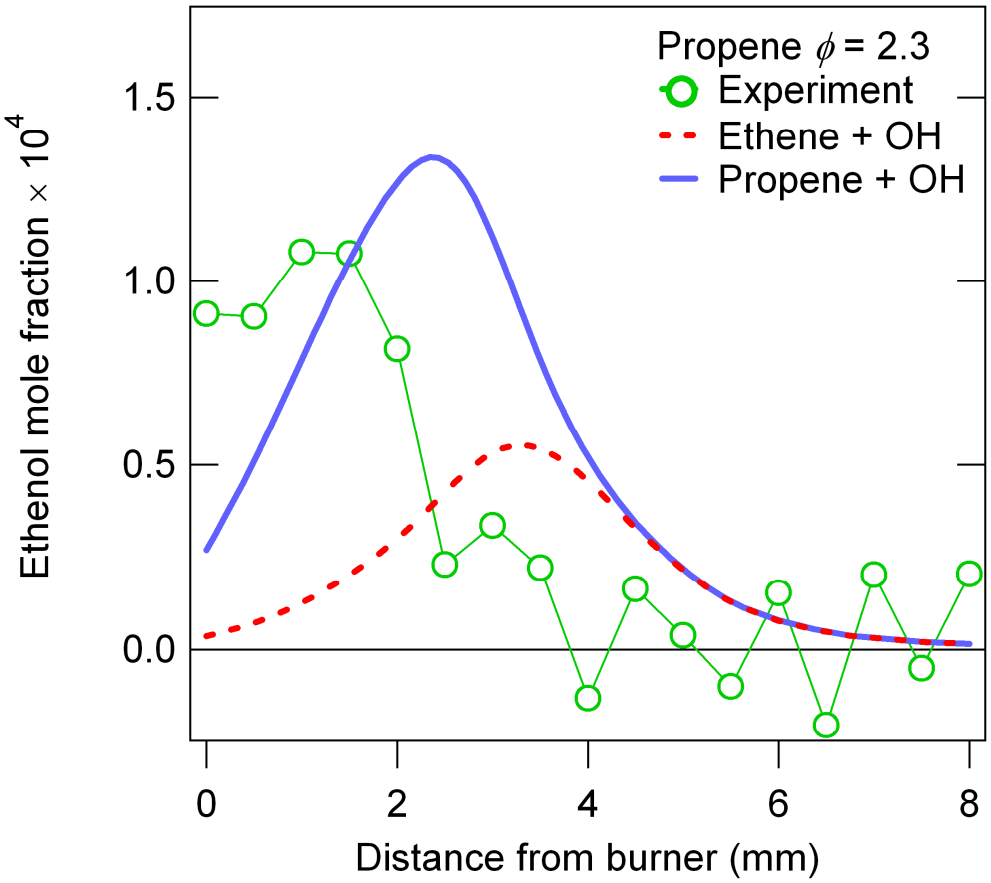
CRF

Further Refinements to Enol Chemistry Are Needed for Combustion Models

Other reactions may contribute to ethenol formation in other flames

- OH + propene
- Dehydrogenation of alcohols

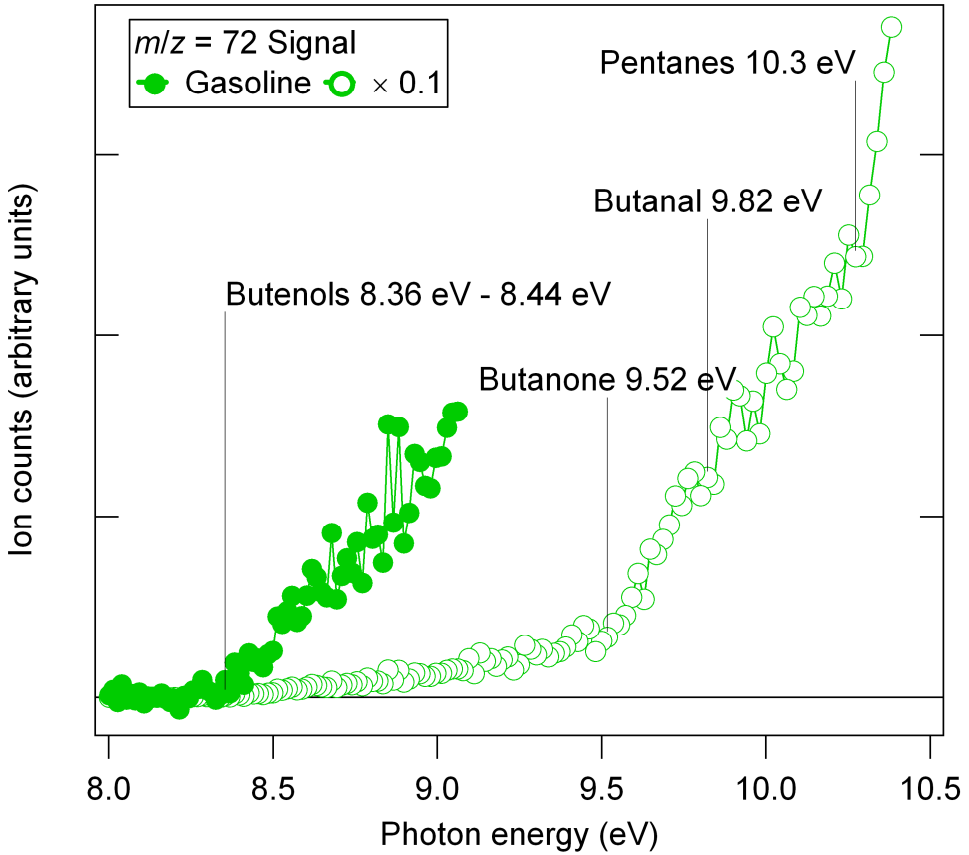
Higher enols are also significant – what are their formation and removal reactions?



Propenols and Butenols Are Observed in Hydrocarbon Flames

- Propenols and butenols have ionization energies significantly below the keto-tautomers
- Propenols and butenols are observed in pure fuels
- Enols are also observed in real fuels (Fei Qi, Luisi Sheng, Yunwu Zhang at the National Synchrotron Radiation Laboratory in Hefei, China)

The work at the National Synchrotron Radiation Laboratory is supported by the Chinese Academy of Sciences and the National Natural Science Foundation of China



What Effect Will Enol Chemistry Have on Combustion Modeling?

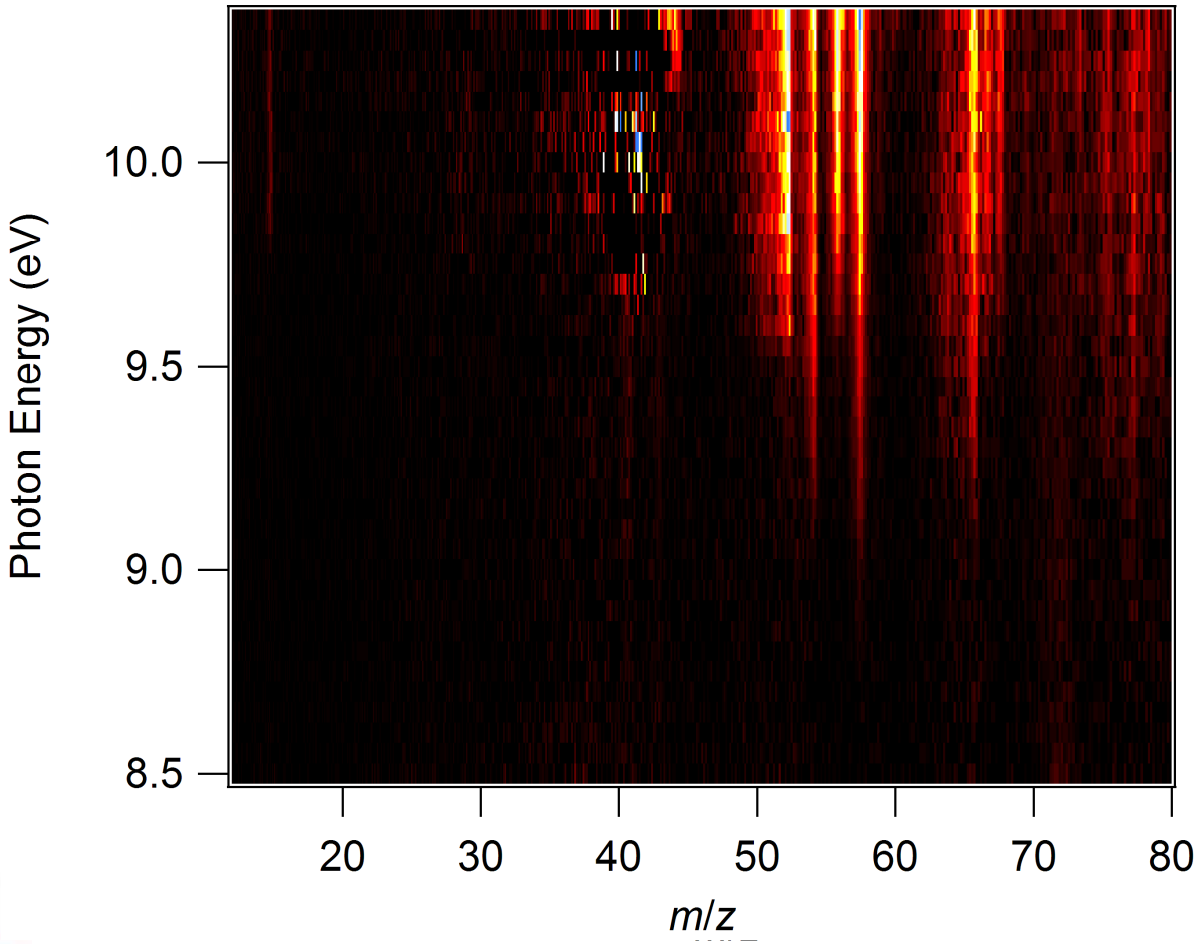
Enols are seen in flames of prototypes of chemicals used in modern fuel blends: alkenes, cyclic compounds, and biologically-derived fuels.

Present work shows enols do not simply isomerize to keto-form

Reactions of gas-phase neutral enols remain nearly unstudied

New fundamental chemistry measurements are needed

New Kinetics Machine at ALS Applies Synchrotron to Elementary Reactions



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

Pulsed photolysis / time-resolved mass spectra

Photoionization can resolve isomers

Enol chemistry is an early target of study

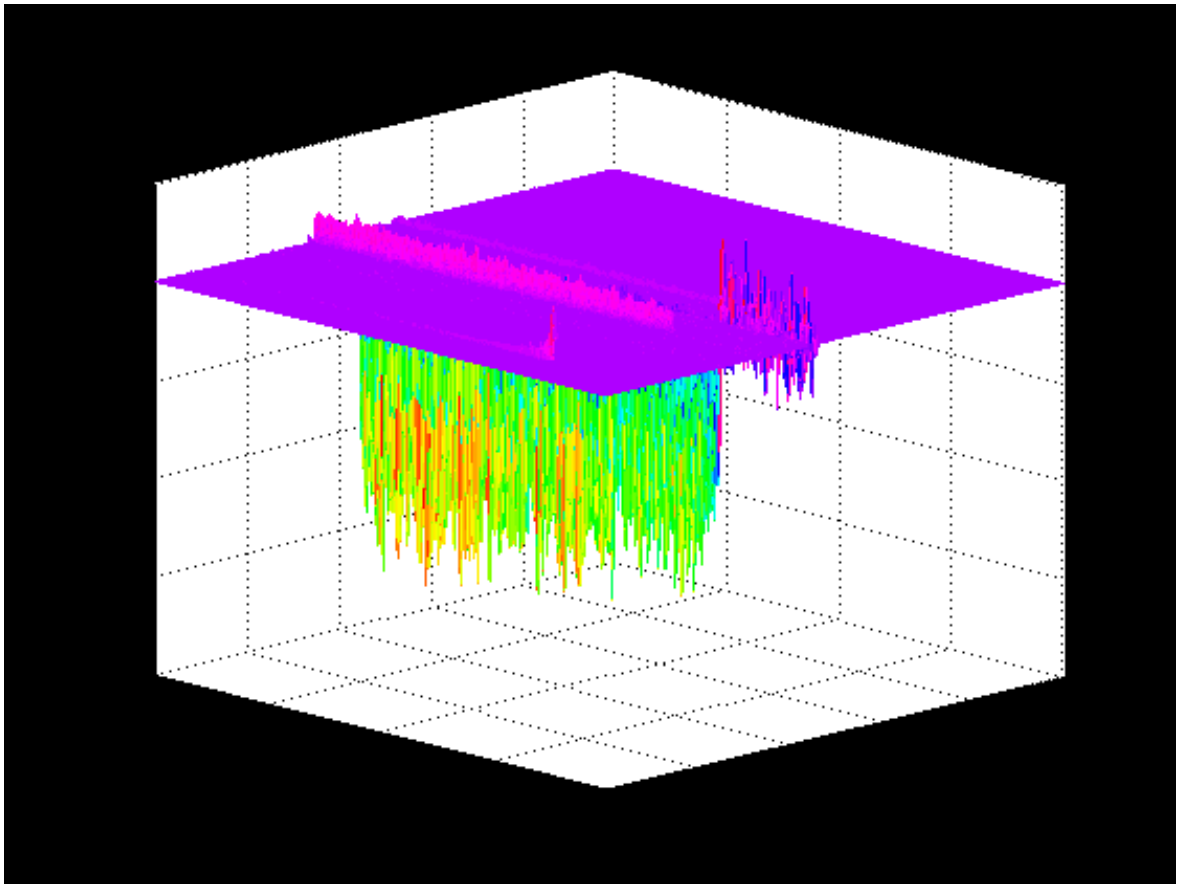
Sandia National Laboratories

CRF

Multiplexed Spectrum Gives Reactant Depletion and Product Formation

Branching fractions determinable if photoionization cross sections are known

Photoionization cross sections can be derived if the branching fraction is known



Preliminary Measurements Confirm Enol Production from OH + Alkenes

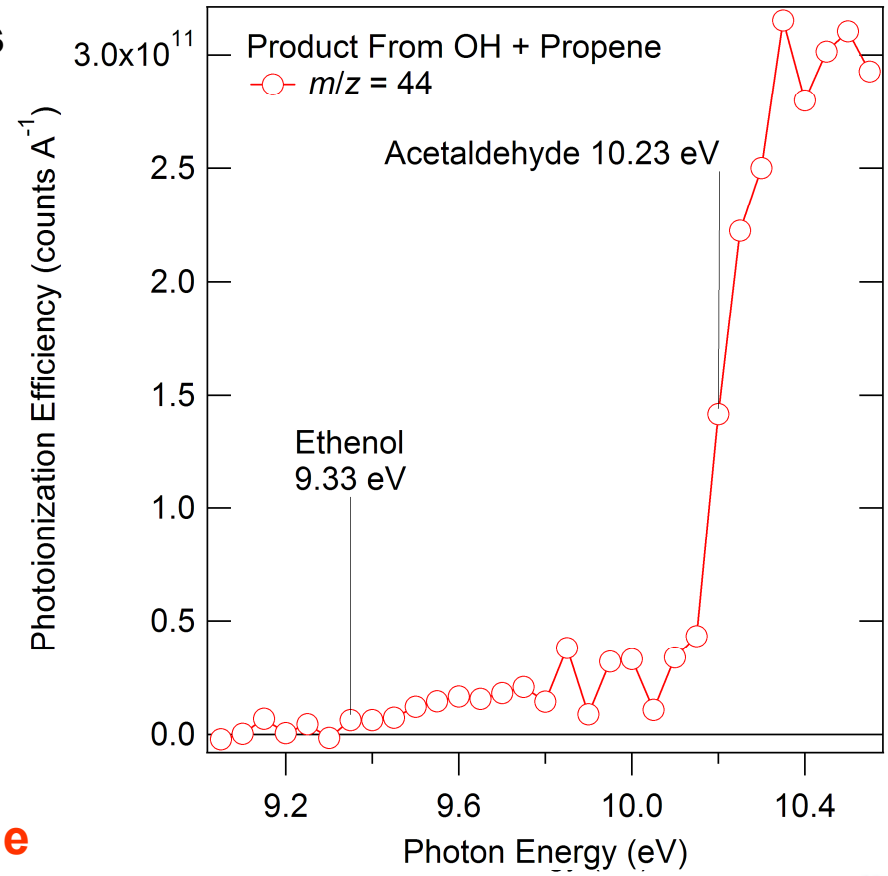
- OH is formed by 193 nm photolysis of H_2O_2
- Alkene is in great excess
- At 500 K, substantial ethenol is observed from OH + ethene

- 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**

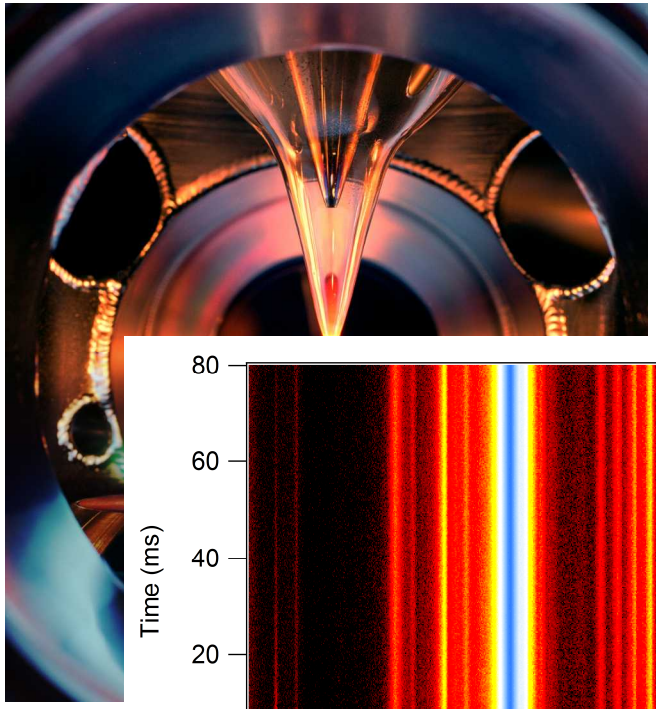
But *m/z* = 44 is mostly acetaldehyde

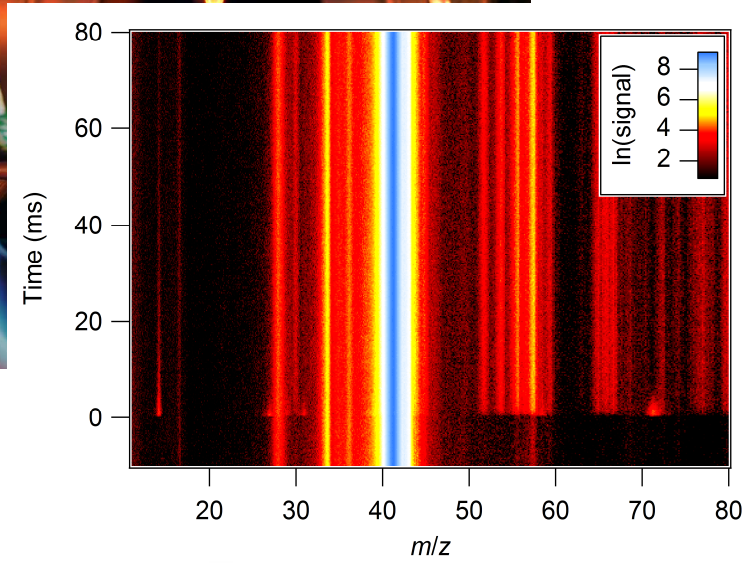


Sandia National Laboratories

CRF

Even After 150 Years of Research There Is Still A Lot to Learn in Combustion





- Flame chemistry has a long history
- Synchrotron photoionization is a powerful tool to study flames
  - and kinetics
- New chemistry is waiting…

Sandia National Laboratories

UNIVERSITY OF MASSACHUSETTS AMHERST 1863

CORNELL UNIVERSITY FOUNDED A.D. 1865

BIELEFELD UNIVERSITÄT

BERKELEY LAB

CRF

The ALS Flame Team

C.A.T., Andrew McIlroy, Nils Hansen (Sandia)

Terrill A. Cool, Juan Wang (Cornell University)

Phillip R. Westmoreland, Matthew E. Law, Aude Morel (University of Massachusetts)

Musahid Ahmed, Darcy S. Peterka (LBNL)

Katharina Kohse-Höinghaus, Tina Kasper (Bielefeld)

The Home Team

Leonard Jusinski, Giovanni Meloni

Edgar Estupiñán (Osram Sylvania)

John DeSain (The Aerospace Corporation)

Huzeifa Ismail, Sally Petway, Bill Green (MIT)

Adam Knepp (Stanford), Andrew Madewell (Arizona)

David Osborn, Peng Zou, Howard Johnsen

Fabien Goulay (UC Berkeley)

Sandia National Laboratories

CRF