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Interactions of Theory, Modeling and Experiment in Determining the Kinetics and Mechanisms of Fundamental Autoignition Reactions

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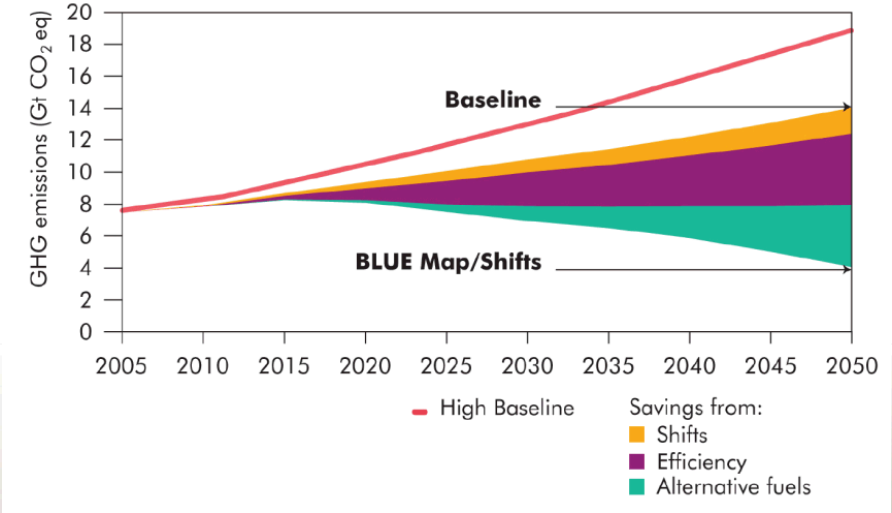
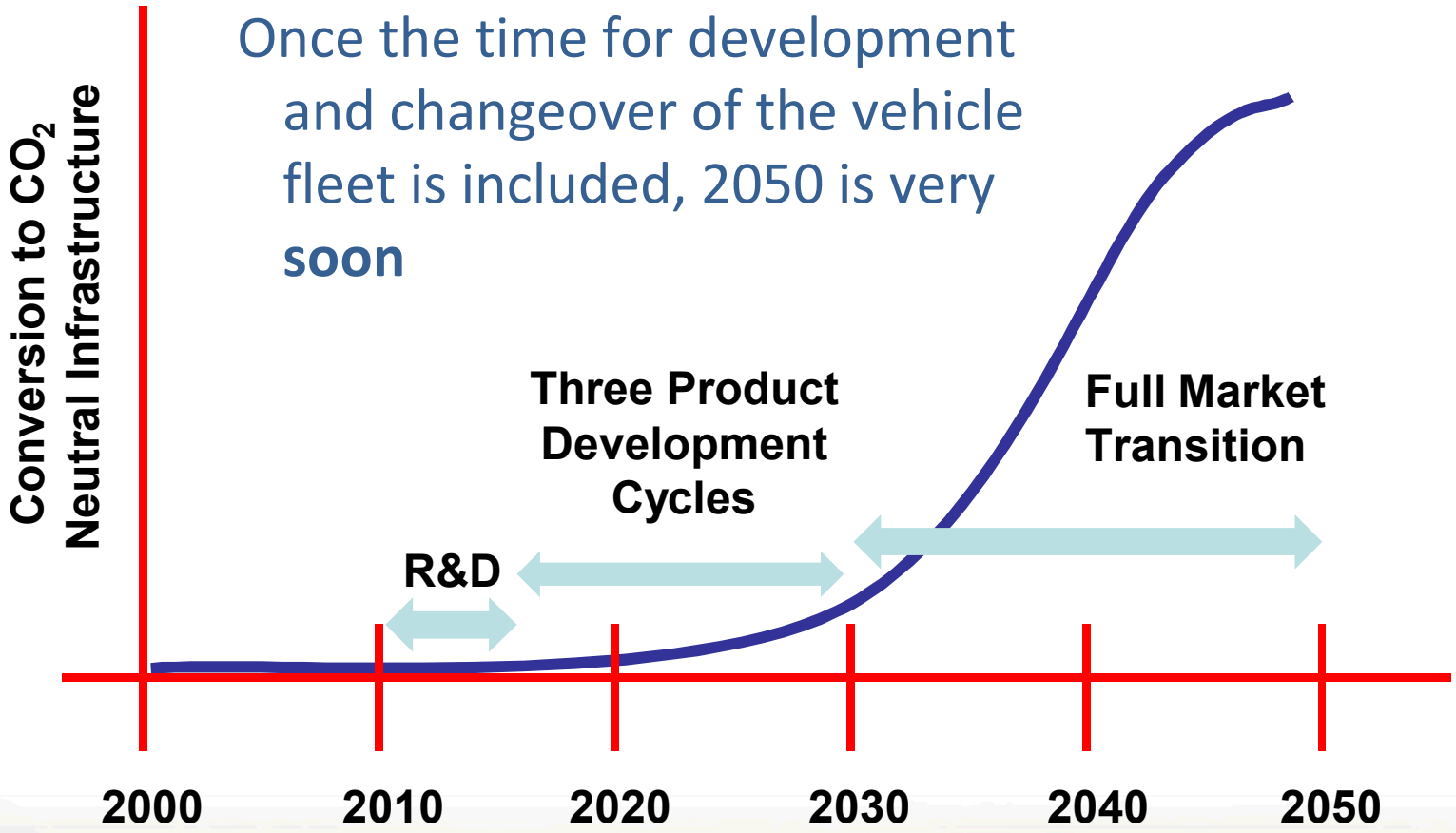
Climate Change and Energy Security Hold Huge Challenges for Transportation

- Reducing petroleum dependence requires new energy sources
- Mitigation of climate change demands **multifaceted urgent** action
  - The transportation sector accounts for two-thirds of United States oil use and one-quarter of its greenhouse gas emissions.
  - The *American Clean Energy and Security Act of 2009* includes a goal for reducing CO_2 emissions by **80% of 2005 levels** by 2050.
- *Advanced biofuels* and *combustion efficiency* are important parts of the path forward



from *Transport, Energy and CO_2: Moving Toward Sustainability*, International Energy Agency 2009.

Predictive Simulation of Combustion Is Needed to Accelerate Development



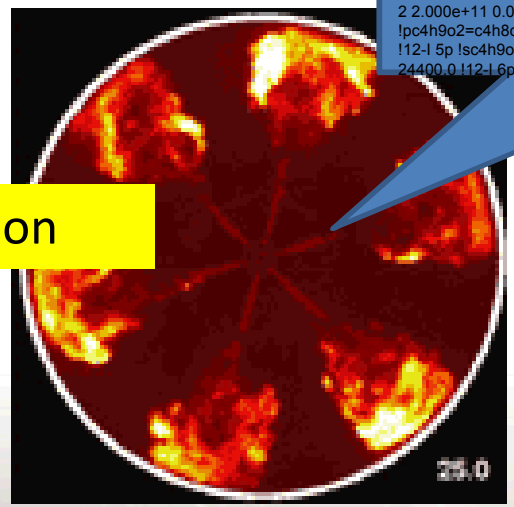
Predictive simulation can shrink development time

Combustion is a Complicated Mix of Chemistry and Fluid Dynamics

Comprehensive Kinetic Mechanism

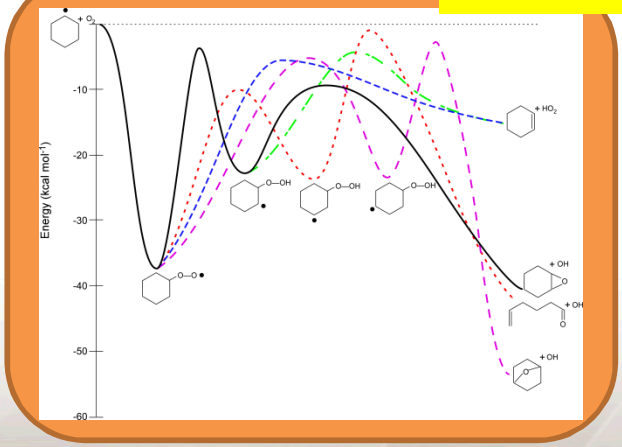
Detailed chemistry of single elementary fuel may have thousands of reactions and hundreds of species

Turbulent, multiphase flows interact with the chemistry



Autoignition

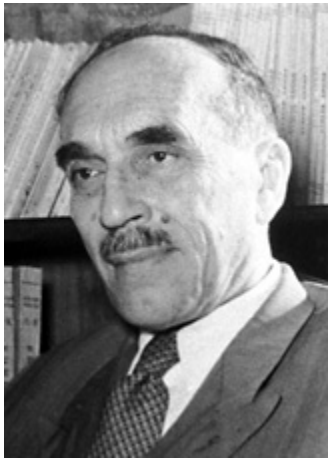
$R + O_2$ reactions



You Don't Need to Know Much Chemistry to Make an Engine!

Nikolaus August Otto (1832-1891)

Rudolf Christian Karl Diesel (1858 –1913)



Nikolai Nikolaevic Semenov (Chemistry Nobel, 1956)

"Some problems relating to chain reactions and to the theory of combustion"

In Some Key Areas the Details of the Chemistry Are Very Important

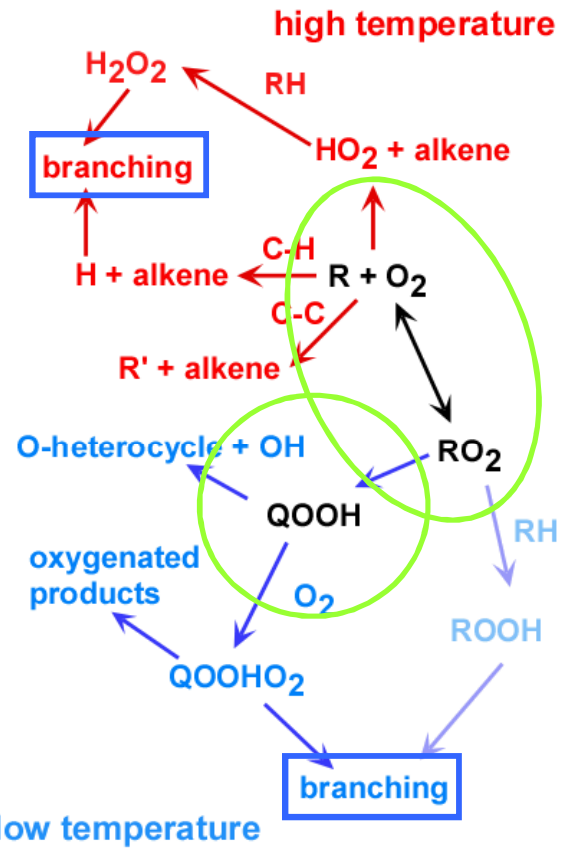
Pollutant Formation:

- Detailed combustion chemistry determines nature and amount of pollutants
- Soot is initiated by reactions of small unsaturated hydrocarbon radicals

Ignition Chemistry:

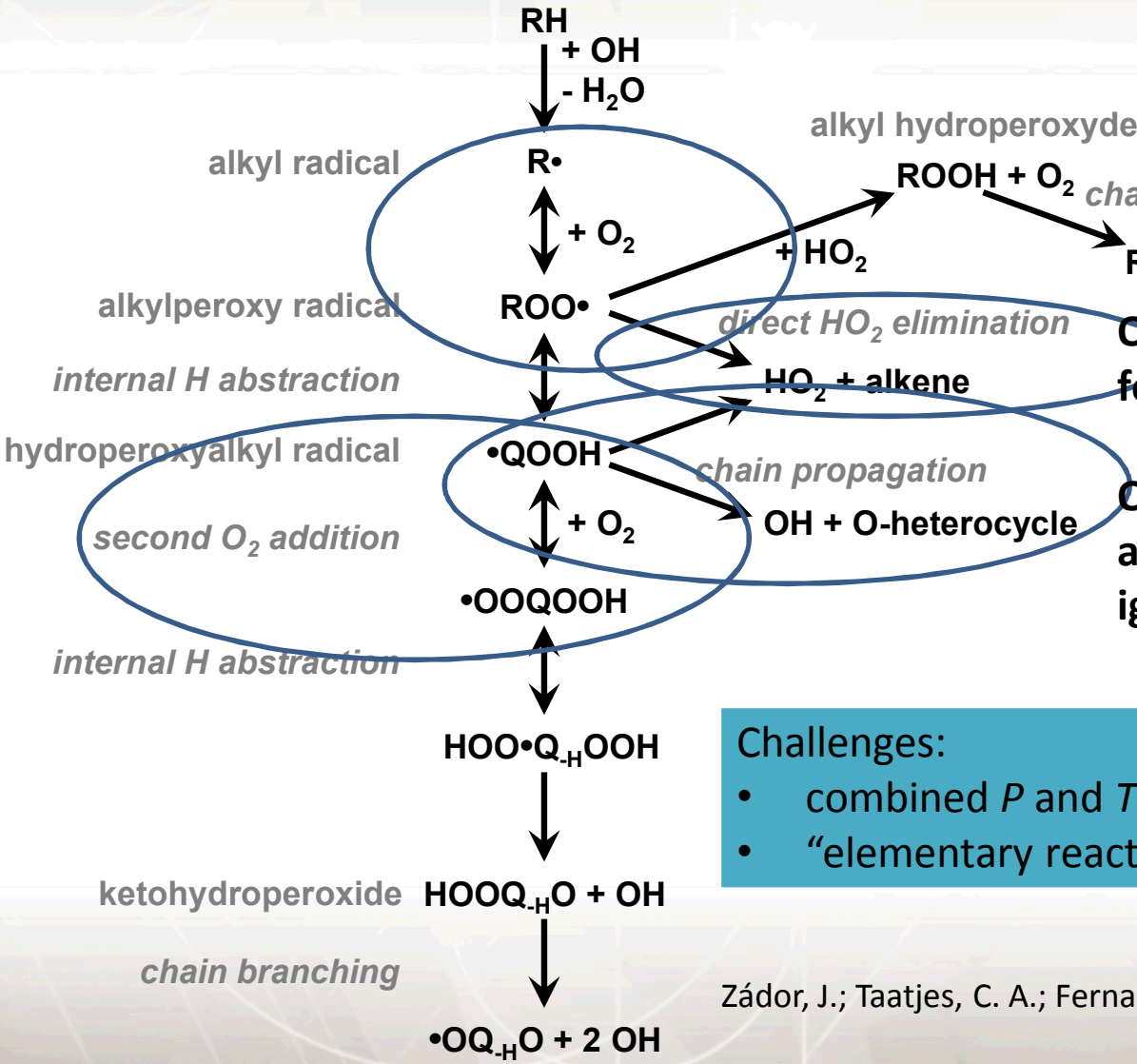
- Chain-branching pathways are a "nonlinear feedback" for autoignition
- Alkyl + O_2 and "QOOH" reactions are central to low-temperature chain branching

General Alkyl Radical Oxidation Scheme



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

Reactions of alkyl radicals with O_2 are critical to controlling hydrocarbon autoignition.



QOOH is responsible for chain branching

HO_2 elimination is chain-terminating

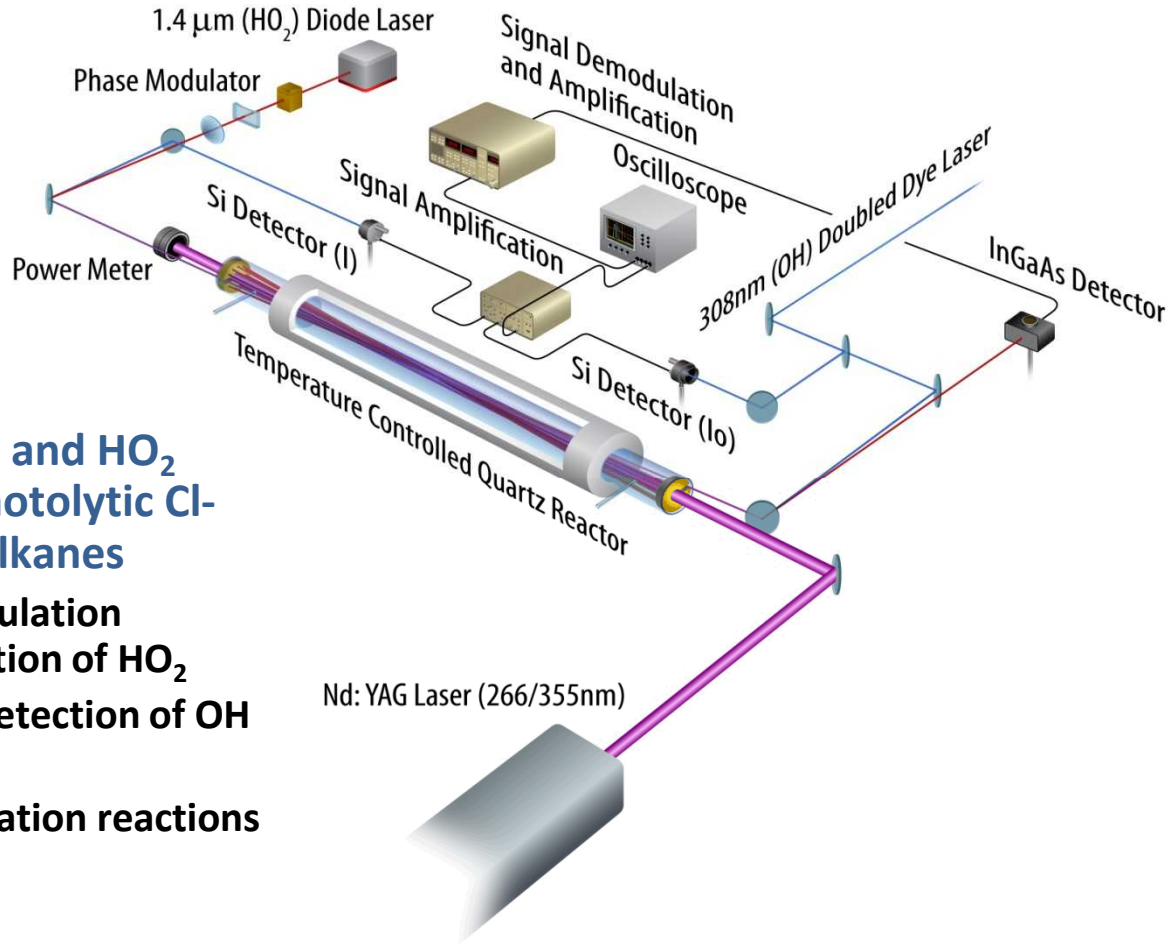
$QOOH + O_2$ is a crucial and mysterious area of chain-propagating ignition chemistry

Challenges:

- combined *P* and *T* dependence
- "elementary reaction" has many paths!

Zádor, J.; Taatjes, C. A.; Fernandes, R. X. *PECS* **2011**, *37*, 341.

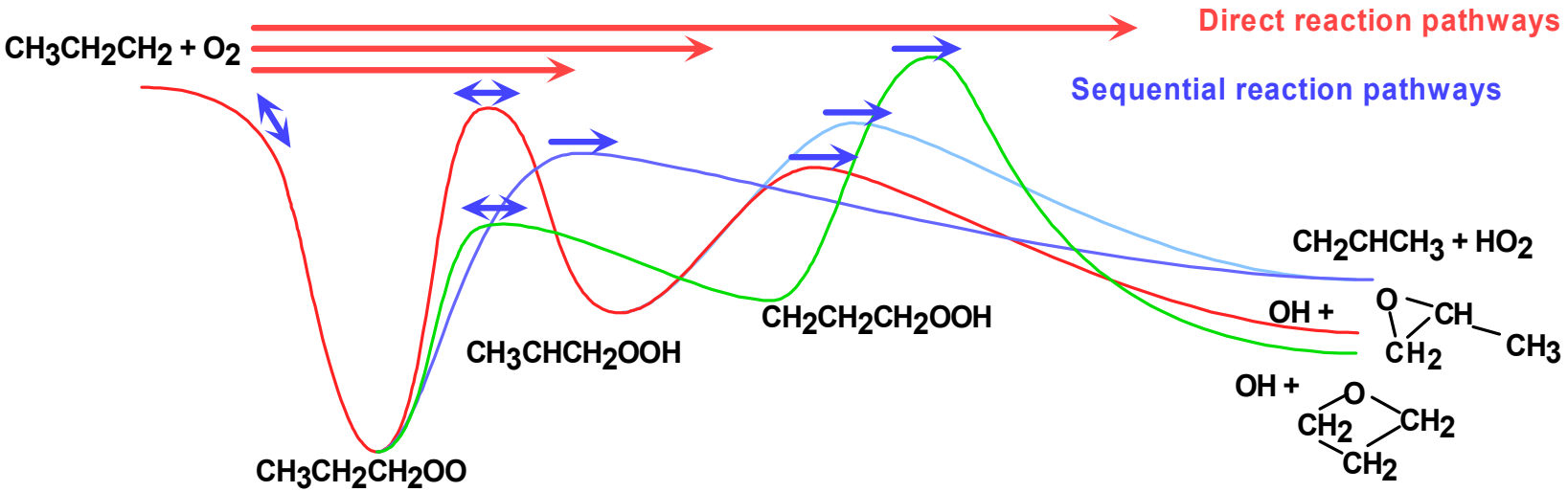
Basis of our strategy: Comparison of experiment and detailed calculations can reveal mechanisms



Experiment: Measure OH and HO_2 formation in pulsed-photolytic Cl-initiated oxidation of alkanes

- **Infrared frequency-modulation spectroscopic detection of HO_2**
- **Ultraviolet absorption detection of OH radicals**
- **Probes *set* of initial oxidation reactions**

Basis of our strategy: Comparison of experiment and detailed calculations can reveal mechanisms

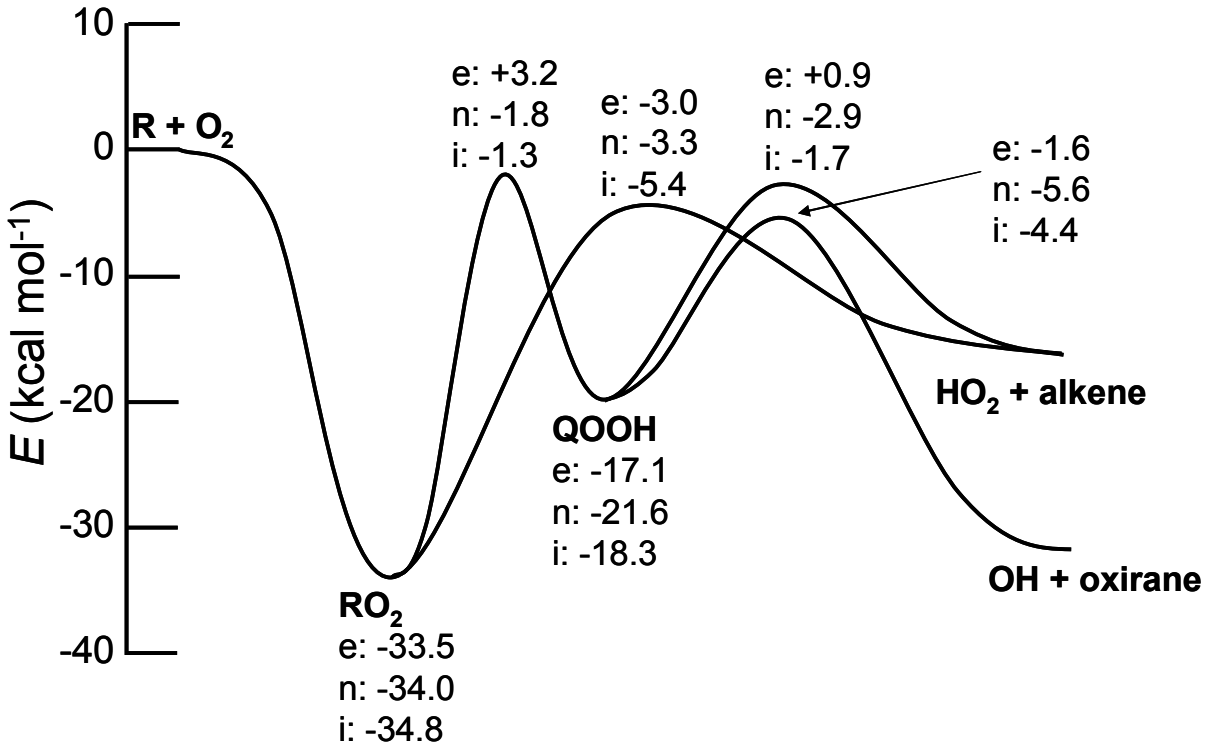


Compare to time-dependent multiple-well master equation solutions

- *Ab initio* characterization of stationary points on the potential surface (Stephen Klippenstein, Jim Miller, Judit Zádor)
- Parameterization of ME solution (SJK / JAM/ JZ) input to kinetic models
- Includes formally direct pathways for isomer and product formation

We have reinvestigated OH production in ethyl + O_2 and propyl + O_2 reactions

Ethyl and propyl radical reactions with O_2 are prototypical

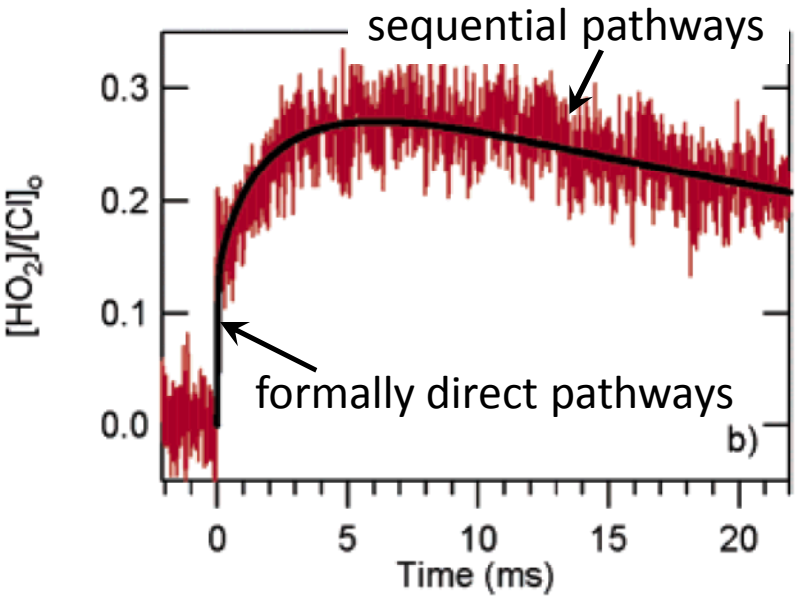


Although the PES's are similar, ethyl + O_2 reaction has barriers for OH formation above reactants while for the propyl + O_2 reactions barriers are below reactants

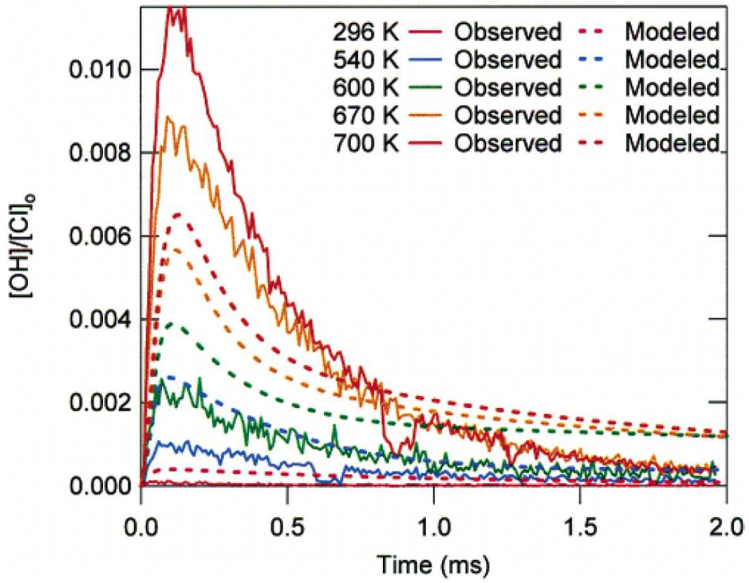
DeSain, J. D.; Taatjes, C. A.; Miller, J. A.; Klippenstein, S. J.; Hahn, D. K. *Faraday Discuss.* **2001**, *119*, 101.
DeSain, J. D.; Klippenstein, S. J.; Miller, J. A.; Taatjes, C. A. *J. Phys. Chem. A* **2003**, *107*, 4415.
Huang, H.; Merthe, D.; Zádor, J.; Jusinski, L. E.; Taatjes, C. A. *Proc. Combust. Inst.* **2010**, *33*, 293.

In previous work, HO_2 profiles were modeled perfectly, but OH profiles could not be reconciled

Model using best R + O_2 rate coefficients from rigorous ME treatment



Estupiñán, E. G.; Klippenstein, S. J.; Taatjes, C. A. *J. Phys. Chem. B* **2005**, *109*, 8374.

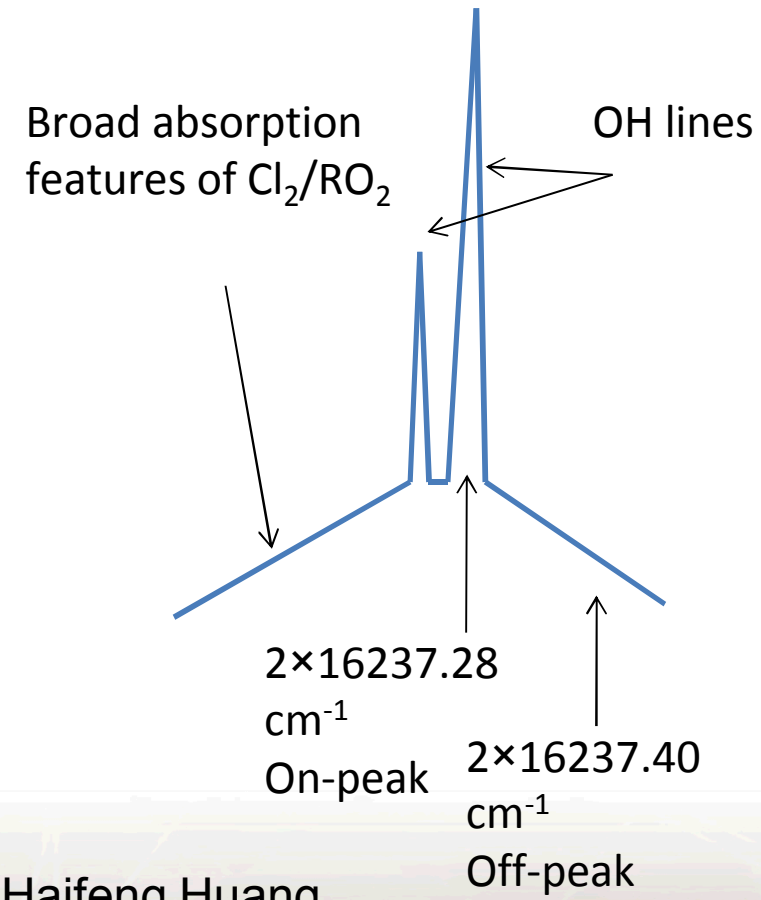


DeSain, J. D.; Klippenstein, S. J.; Miller, J. A.; Taatjes, C. A. *J. Phys. Chem. A* **2003**, *107*, 4415.

Validation of the Master Equation calculations for the OH channels requires more accurate experimental results.

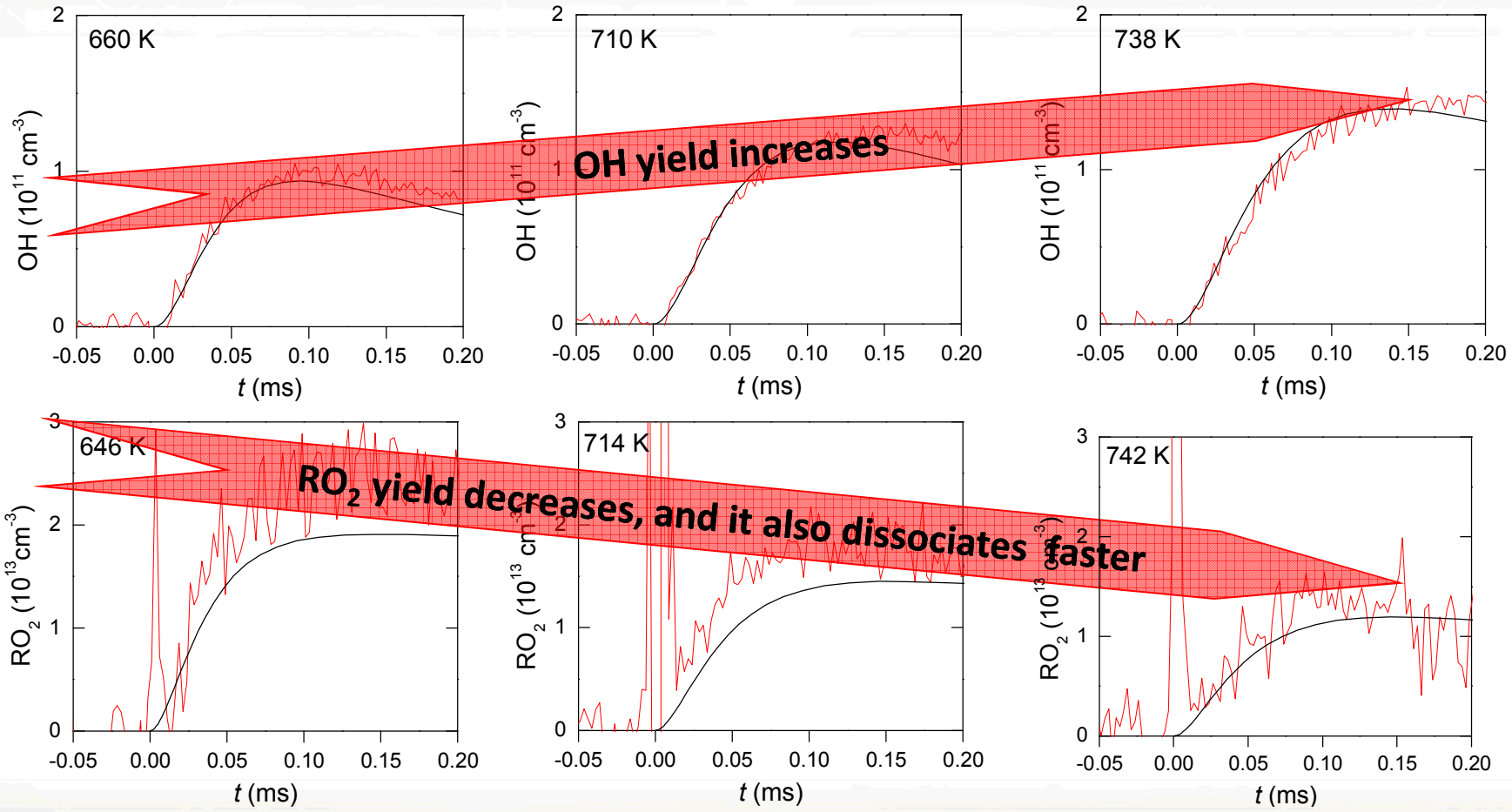
New OH experiments improved upon the previous measurements in two very important aspects.

- **Cl_2 or $(COCl)_2$ radical source**
  - ➔ Few unwanted side-reactions (chain-chlorination is negligible).
- Detection by **differential direct long-path absorption at 308 nm** (frequency doubled 616 nm CW ring dye laser)
  - ➔ Yields OH concentrations directly.
  - ➔ Detection limit is ~10^{10} cm^{-3} (total density is ~10^{17} cm^{-3}).
  - ➔ Absorption spectroscopy also allows the measurement of other species.



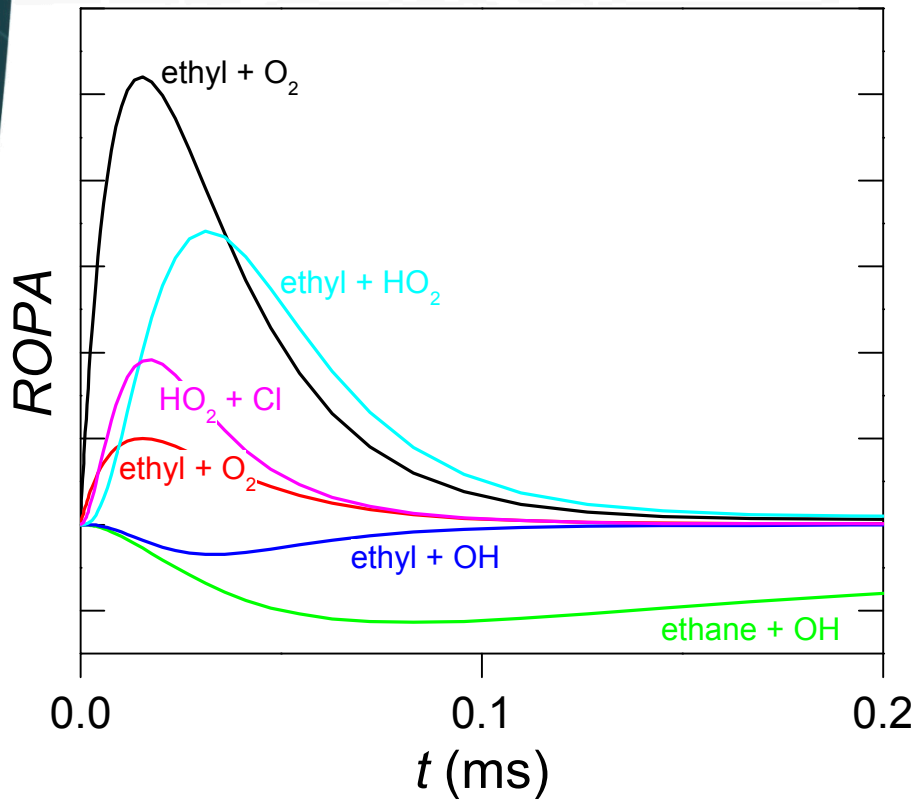
Haifeng Huang

RO_2 and OH production in Cl-initiated ethane oxidation has been remeasured from 660-740 K



Measured and calculated OH concentrations agree very well up to 200 μs.
Note that all curves are **unscaled absolute concentrations**!

Ethyl + O_2 contribution takes place mostly in the first ~200 μs after photolysis



OH is formed principally via "formally direct" pathways.

➔ These experiments probe (and confirm) $RO_2 \leftrightarrow$ QOOH barrier height

A significant contribution comes from ethyl + HO_2. The rate coefficient is based on methyl + HO_2 (Jasper et al. 2009 PCI).

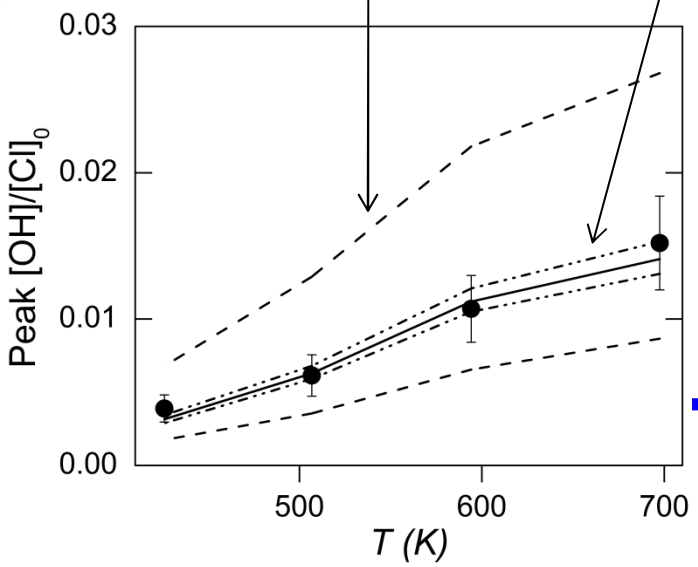
Also, HO_2 + Cl produces some OH, but it is a relatively well-characterized reaction.

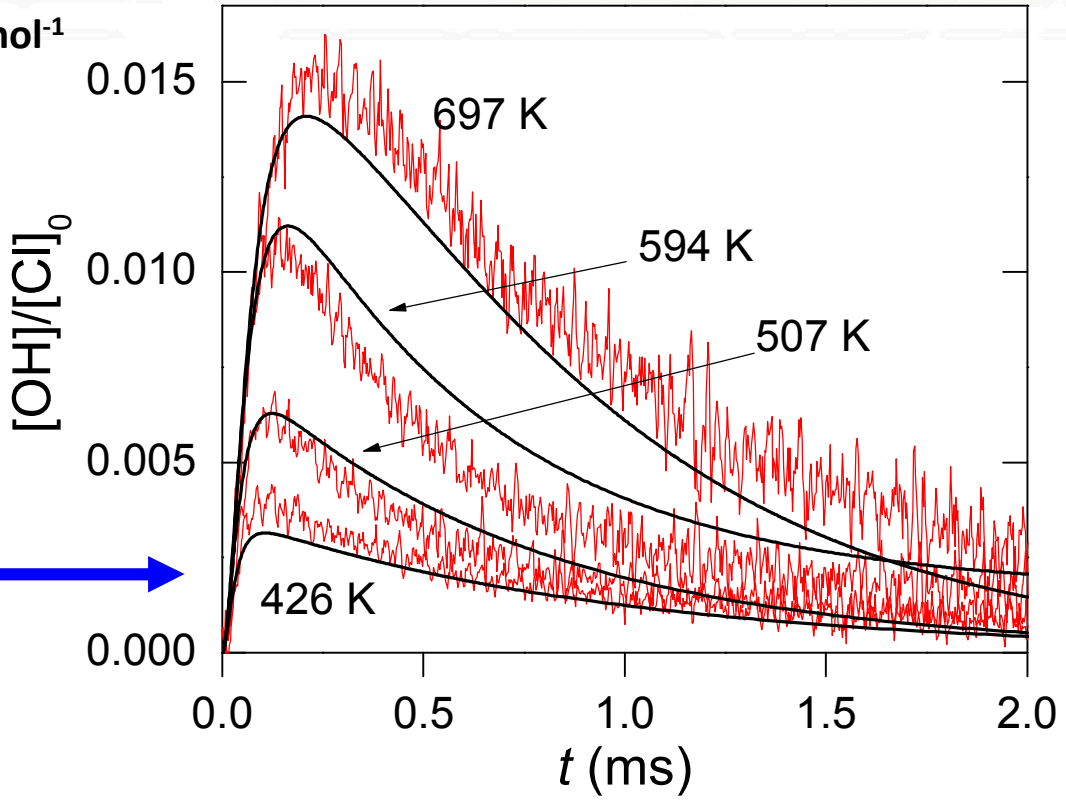
After 200 μs ethane + OH is expected to dominate OH profile with a small contribution from $C_2H_5 + O_2 \rightarrow$ OH induced by RO_2 backdissociation.

OH production in Cl-initiated propane oxidation (426-697 K) is also well-modeled

ΔE (QOOH→OH + *c*-C_3H_6O) = ± 1 kcal mol^{-1}

ΔE ($RO_2 \leftrightarrow$ QOOH) = ± 1 kcal mol^{-1}





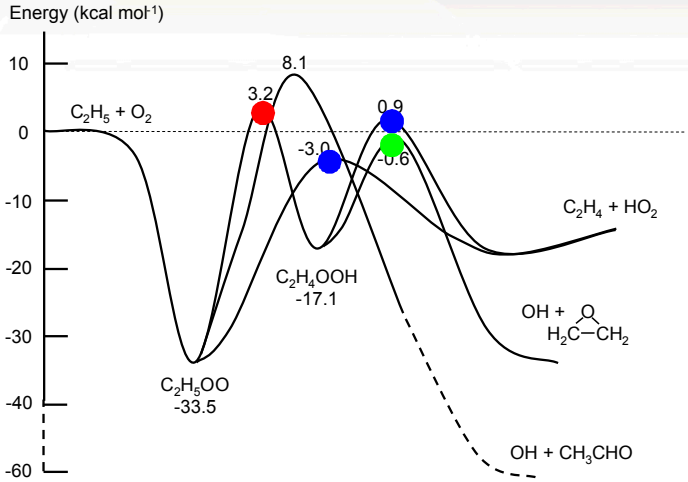
The propyl + O_2 reaction produces more OH, therefore, secondary chemistry is relatively less important than for ethane, even at longer times.

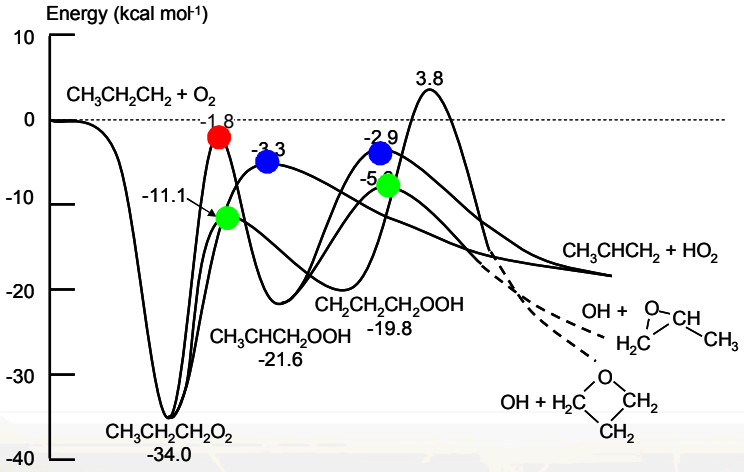
The OH formation is very sensitive to the ROO $\leftrightarrow$ QOOH transition state

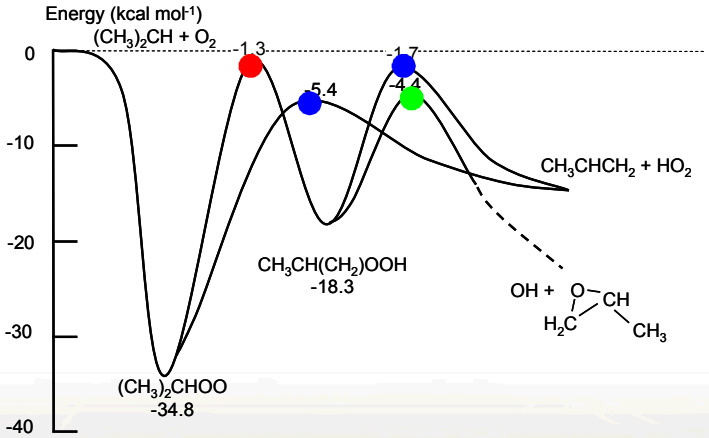
Huang, H.; Merthe, D.; Zádor, J.; Jusinski, L. E.; Taatjes, C. A. *Proc. Combust. Inst.* **2010**, *33*, 293.

Experiments validate stationary points on the ethyl + O_2 and propyl + O_2 potential energy surfaces

- Previous HO_2 measurements at Sandia
- Current OH measurements
- High-pressure experiments are underway **Lenny Sheps**

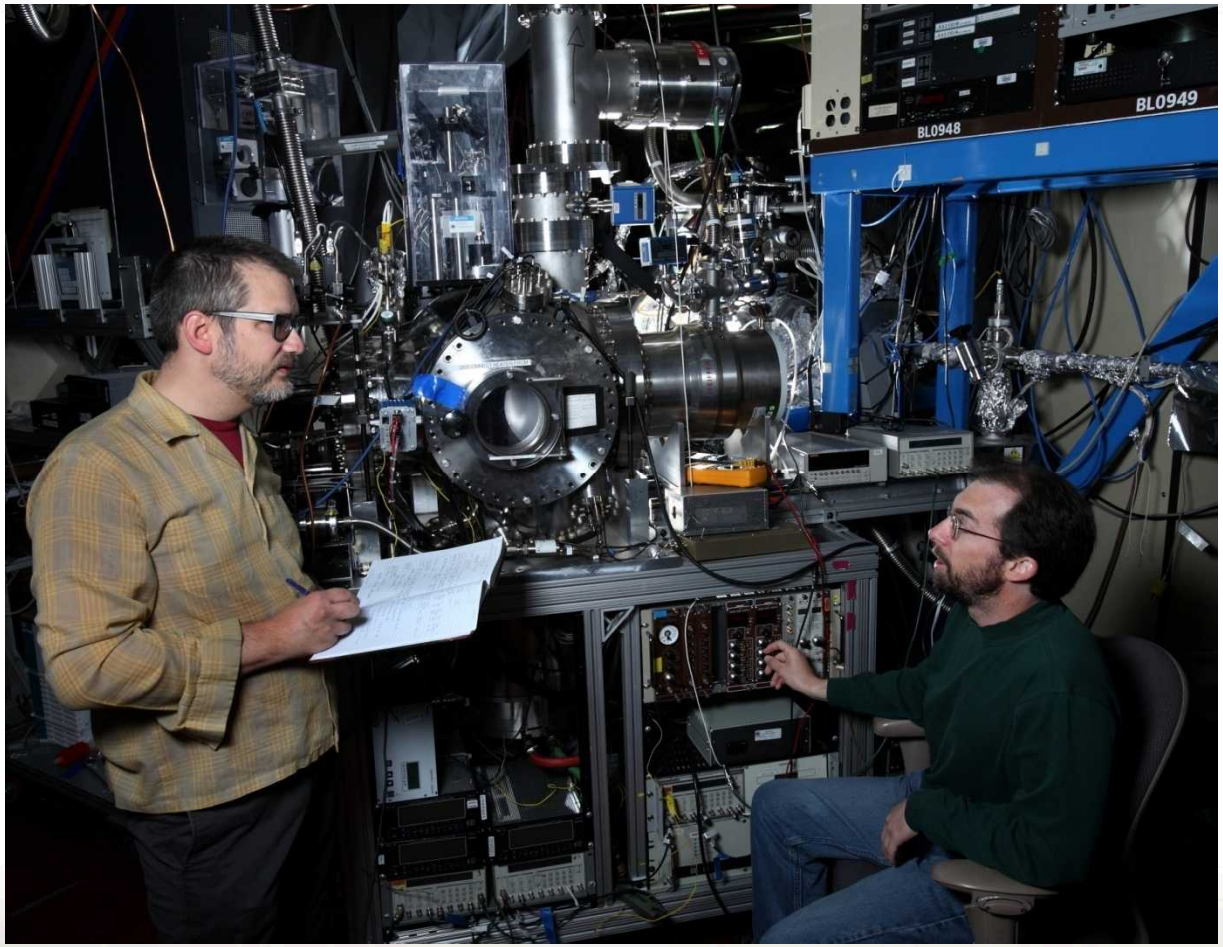






High-pressure experiments will help refine the potential energy surface.

Although HO_2 and OH are important, measuring only two products isn't always enough



Larger systems demand more information

Photoionization mass spectrometry can give us this detail

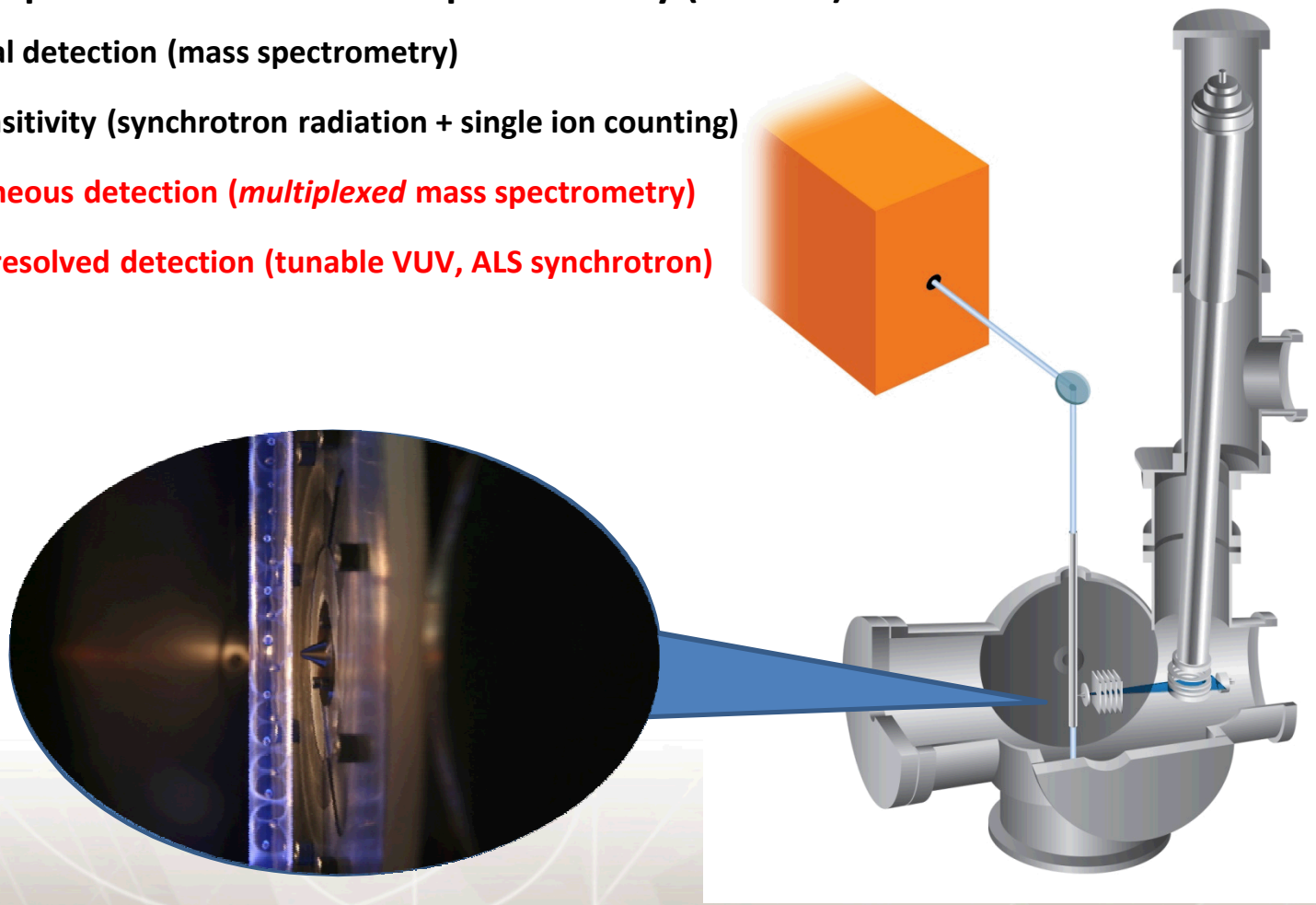
Collaboration between Sandia CRF (**David Osborn**, C.A.T.) and LBNL (Musa Ahmed, Kevin Wilson, Steve Leone)

Osborn et al., *Rev. Sci. Instrum.* **79**, 104103 (2008)

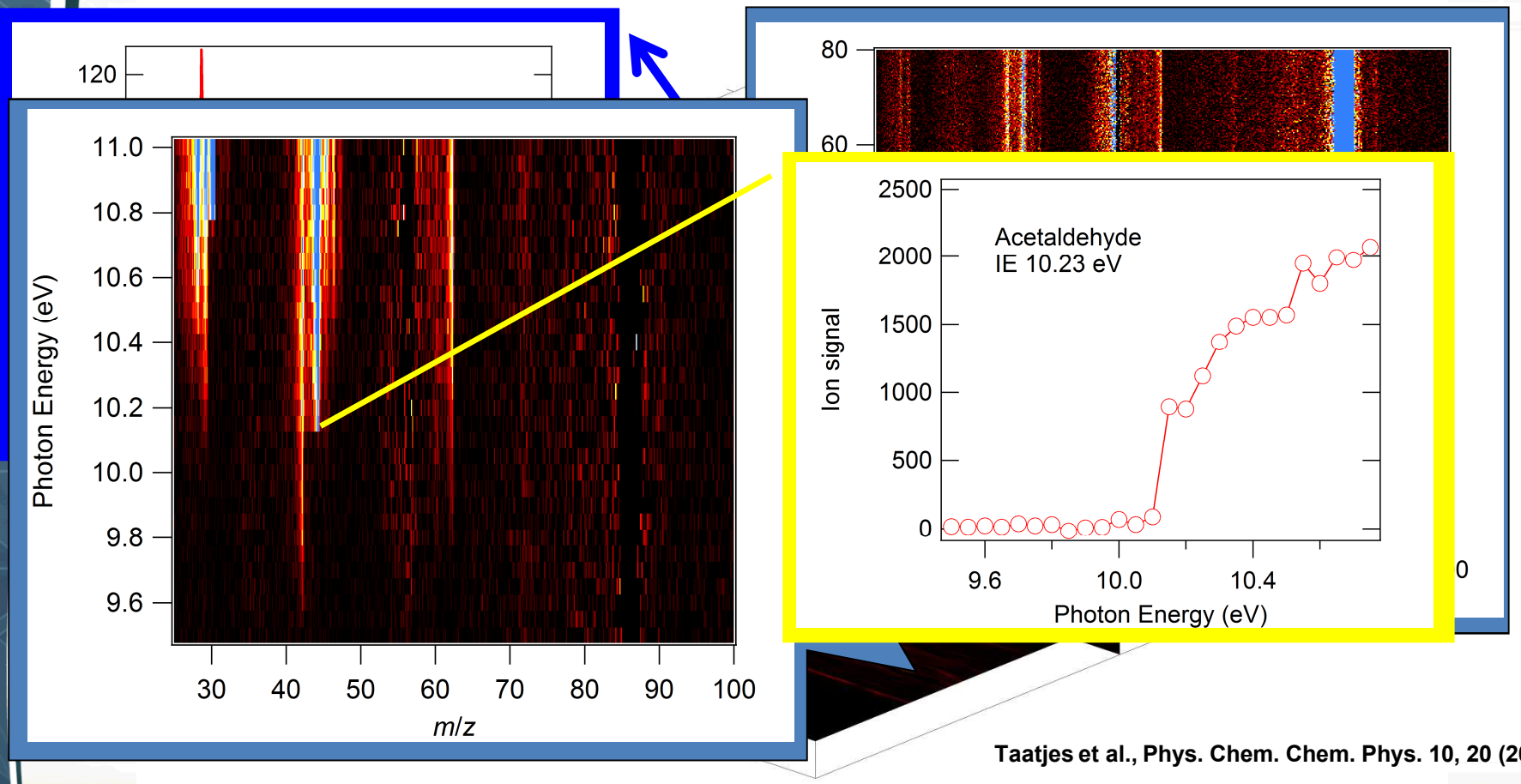
Laser photolysis reactor is coupled to time-of-flight mass spectrometer with synchrotron photoionization

Multiplexed photoionization mass spectrometry (MPIMS)

- Universal detection (mass spectrometry)
- High sensitivity (synchrotron radiation + single ion counting)
- Simultaneous detection (*multiplexed* mass spectrometry)
- Isomer-resolved detection (tunable VUV, ALS synchrotron)



Kinetic data is acquired as a function of kinetic time, mass, and photoionization energy



Taatjes et al., Phys. Chem. Chem. Phys. 10, 20 (2008).

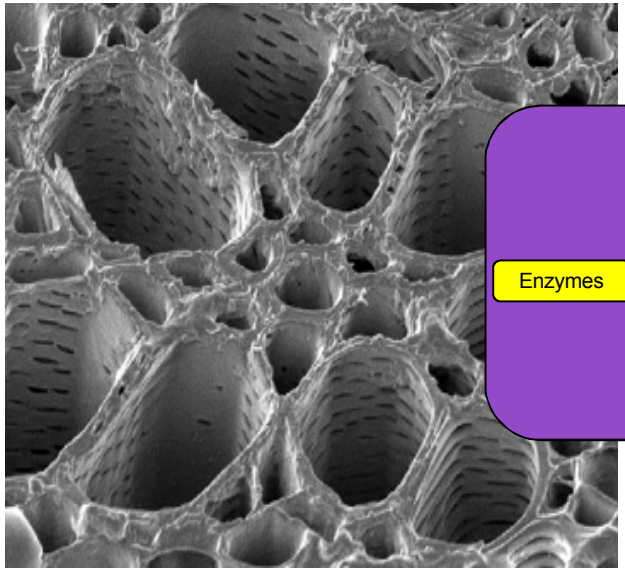
3-D dataset can be "sliced" along different axes to probe different aspects of the reaction

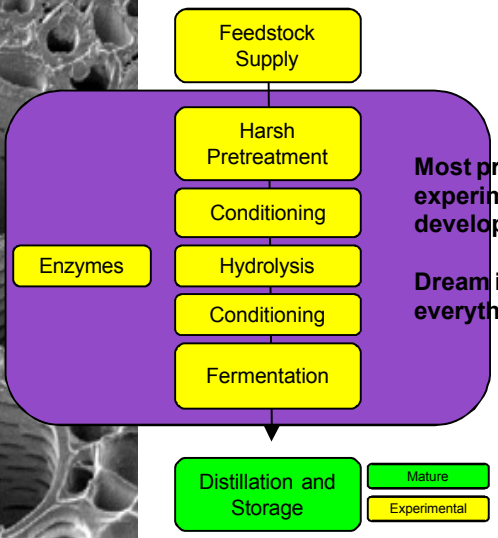
What can these tools tell us about autoignition chemistry of biofuels?

- Current biofuels – corn ethanol and biodiesel – involve relatively small reduction of GHG relative to petroleum
- Next-generation cellulosic biofuels will give much greater GHG reduction

Cellulose is the most abundant component of plant biomass, assembled with lignin and hemicellulose into fibers – challenging to deconstruct

Deconstruction strategies – including synthetic biology – produce some novel fuel compounds





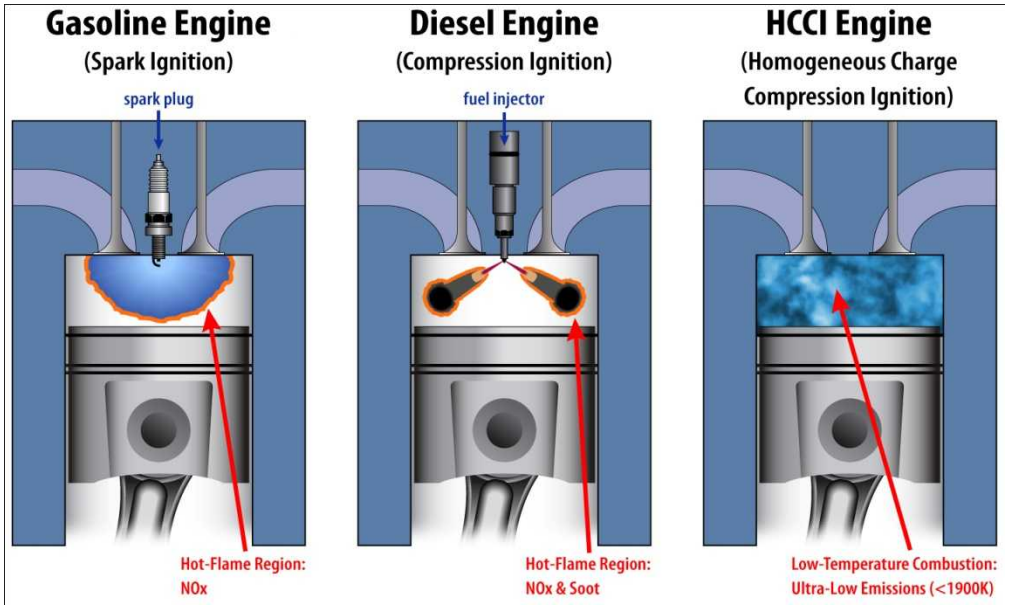
Most processes are experimental / in development

Dream is to consolidate everything in the purple box

Most effective deployment of biofuels may entail a substantial change in fuel chemistry

Fuel Chemistry and Engine Combustion Efficiency are Interdependent

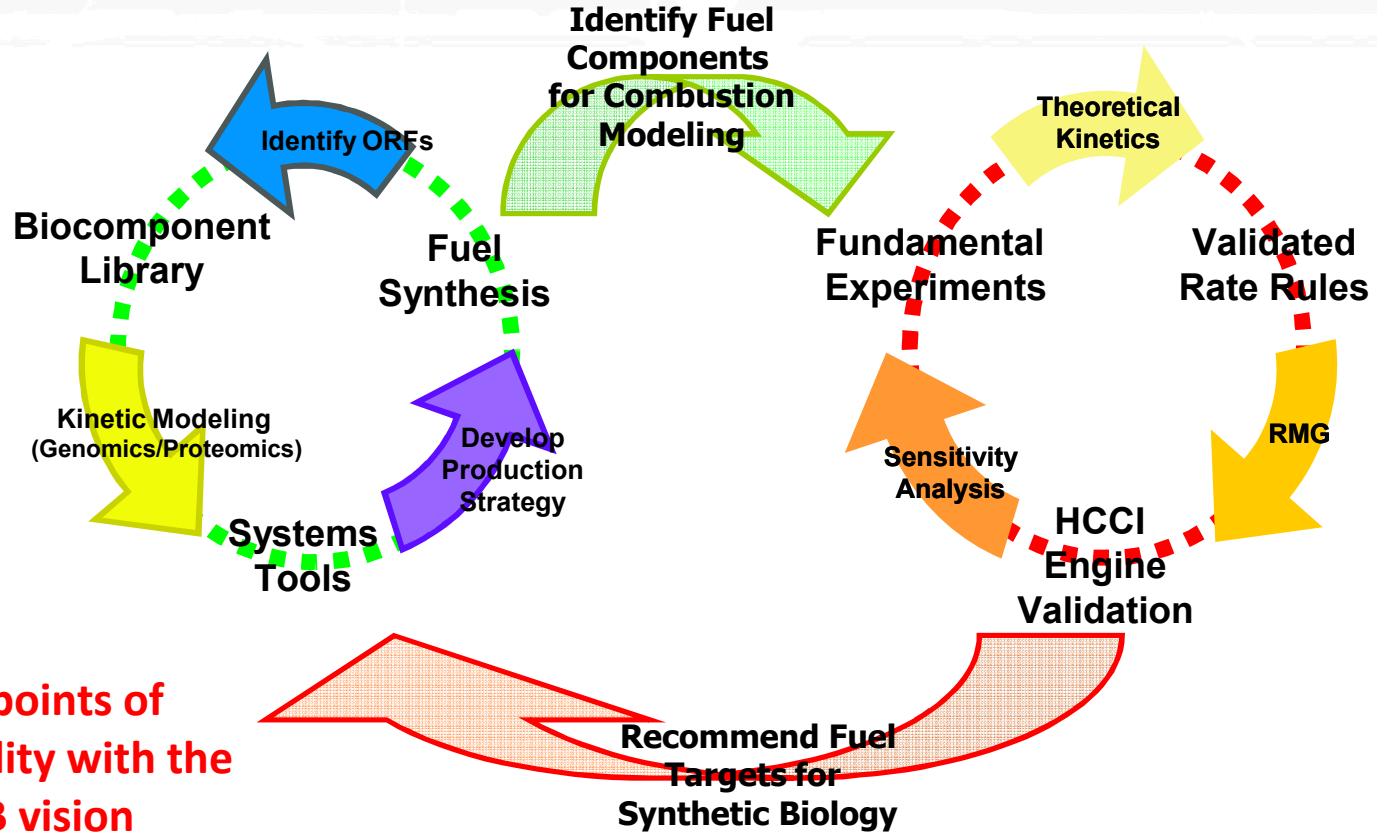
Advanced clean efficient (>30% improvement) engines (e.g., HCCI) rely on compression ignition – chemistry – to time combustion



- **Increased use of biofuels will change fuel chemistry dramatically**
- **Previous (even minor) fuel changes have been disruptive**
- **New fuel chemistry could *enable* advanced engines**

However, biofuel development is typically isolated from combustion performance investigations

Overarching goal: *Robust framework* for biofuel / engine co-development



Many points of commonality with the TMFB vision

Adaptable framework – beyond any specific set of production or utilization platforms

Represents a new way to engineer biofuels

Endophytic fungi have potential advantages as a biofuel production platform

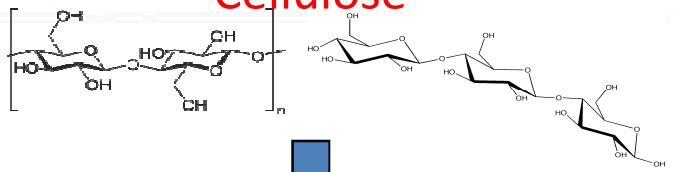
Endophytic fungi live in a symbiotic relationship with a plant host

Fungi can directly consume cellulose and other renewable carbon compounds, produce a spectrum of potentially useful volatile organic compounds (VOC)

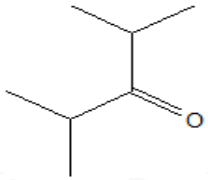
For example, one fungus produces hydrocarbons, but also compounds like hexadecanoic acid (Strobel et al., 2008)

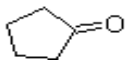
Optimization for fuel production requires a knowledge of the combustion benefits and drawbacks of the VOC components

Cellulose



Fuels



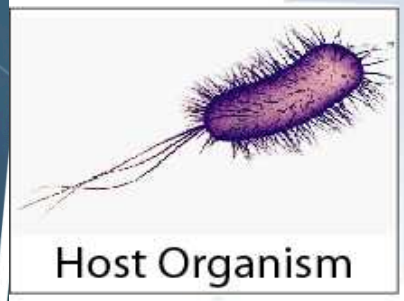


$C_7H_{14}O$ (m/z=114)

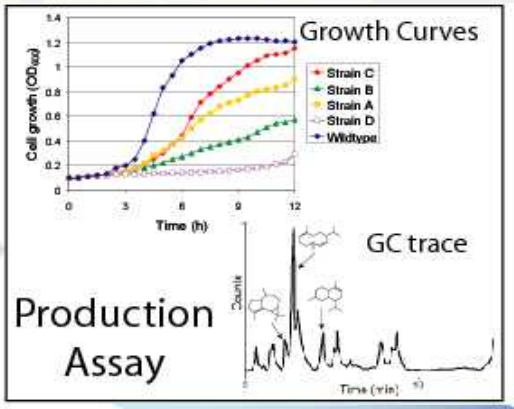
C_5H_8O (m/z=84)

Optimization loop for biofuel production should mesh with combustion investigations

Natural fungus is starting point

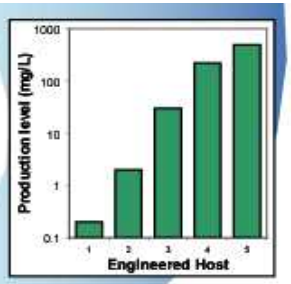


Metabolic Engineering



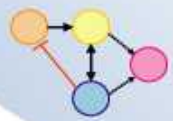
First "mesh point" is analysis of VOC output, identification of targets for combustion studies

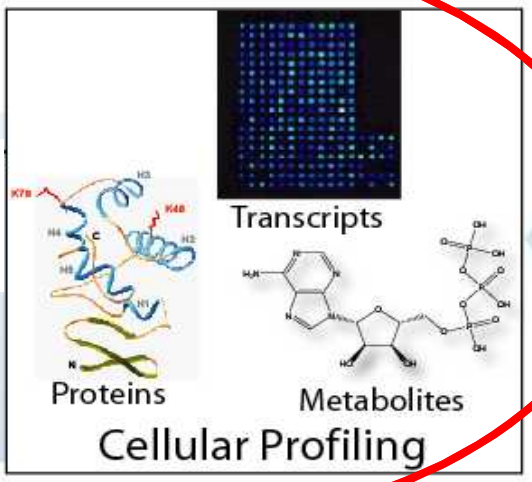
Achieved desired production level ?



Second mesh point: Combustion performance is part of feedback for desired production level

Develop cellular models and redesign





While the combustion modeling tools are being developed, the biochemical engineering toolkit is assembled – "pathway prospecting"

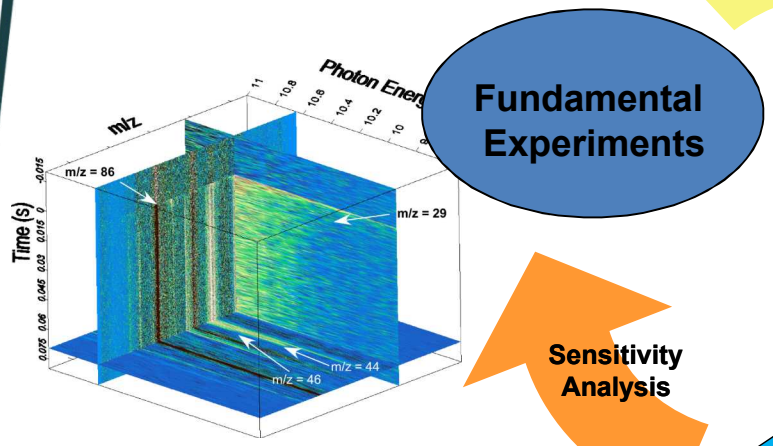
Fundamental chemistry measurements are the first step in the combustion model

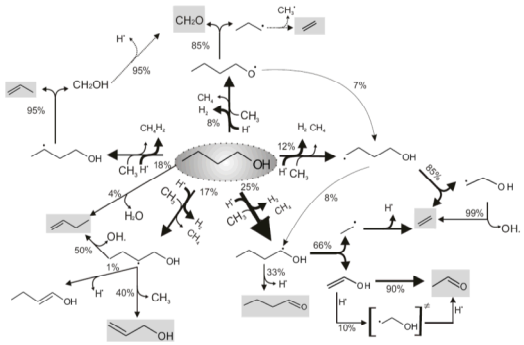
Molecular structure affects key elementary autoignition reactions

Mesh point – target representatives of classes of molecules in fungal VOC profiles

Integrating the key reactions into an overall ignition model uses the RMG toolkit from Bill Green (MIT)

Structure-dependent rate rules are the basis for model generation





Analysis of model / experiment discrepancies and new input from biofuel production team determine next targets

Ignition model is tested in HCCI engine or by bulk ignition measurements

Mesh point -- validated model allows fuel performance feedback to the production side

GC analysis of fungal VOC profiles gives first combustion targets

1	1-Butanol,2-methyl-
2	1,4-Cyclohexadiene,1-methyl-
	1,3,5-Heptatriene,[E,E)-
	Bicyclo[4.1.0]hept-2-ene
	1,3,5-Hexatriene,3-methyl-,(2-methyl isomer)-
	1,3-Cyclopentadiene,5,5-dimethyl-(1,2-dimethyl-3somer)
3	Cyclopentene,1,2,3-trimethyl-
	1,3-Dimethyl-1-cyclohexene
	Ethanone,1-(1H-pyrazol-4-yl)
	Cyclopropane,2-(1,1-dimethyl-2-pentenyl)-1,1-dimethyl-
	1,4-Pentadiene,2,3,3-trimethyl-
	1,4-Hexadiene,2,3-dimethyl-
4	Butanoic acid,2,3-dimethyl-,methyl ester
5	Styrene
6	4-Heptyn-2-ol
	1-Pentene,5-methoxy-
7	Cyclohexane,(ethenylthio)-
8	1H-Pyrazole-3,4-diamine,1,5-dimethyl-
	1,3-Cyclopentanedione,2,5-dimethyl-
9	1-Hexanol,2-ethyl-
10	2(3H)-Furanone,dihydro-3-methylene-
11	*Undecane,3,7-dimethyl-*
12	Dodecane,2,6,10-trimethyl-
13	1H-Cycloprop[e]azulene,1a,2,3,4,4a,5,6,7b-octahydro-1,1,4,7-
14	1
15	T
16	C

C14-A

1	1-Butanol,3-methyl-
2	1,4-Cyclohexadiene,1-methyl-
	1,3,5-Hexatriene,3-methyl-,(Z)-
	1,3,5-Heptatriene,[E,E)-
	Bicyclo[4.1.0]hept-2-ene
	1,3-Cyclopentadiene,5,5-dimethyl-
	1,3-Cycloheptadiene
3	Benzene,1-ethyl-3-methyl-(3isomers)
4	Oxime-,methoxy-phenyl-_
5	Cyclohexene,1-(1-propynyl)-
	Spiro[4.4]nona-1,6-diene,(S)-
6	*4,7-Ethano-1H-isoindole-1,3(2H)-dione,3a,4,7,7a-tetrahydro-*
7	Phenol
8	3-Methylene-2-norbornanone
9	Benzene,2-propenyl-(isomers)
	Tetracyclo[3.3.1.0(2,8).0(4,6)]-non-2-ene
	Bicyclo[4.2.0]octa-1,3,5-triene,7-methyl-
10	Eucalyptol
11	Cyclohexane,1,2,4-tris(methylene)-
12	1,3-Cyclopentadiene,5-(1-methylpropylidene)-
13	2,5-Heptadien-3-yne,2,4-dimethyl-
14	3-Heptanone,5-ethyl-4-methyl-
15	Phenylethyl Alcohol
16	*Thiophene,2-ethyl-5-propyl-*
17	*1,2,4a,5,8,8a-Hexahydro-naphthalene*
18	Cyclohexane,1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-
	Tricyclo[5.4.0.0(2,8)]undec-9-ene,2,6,6,9-tetramethyl-
19	Caryophyllene

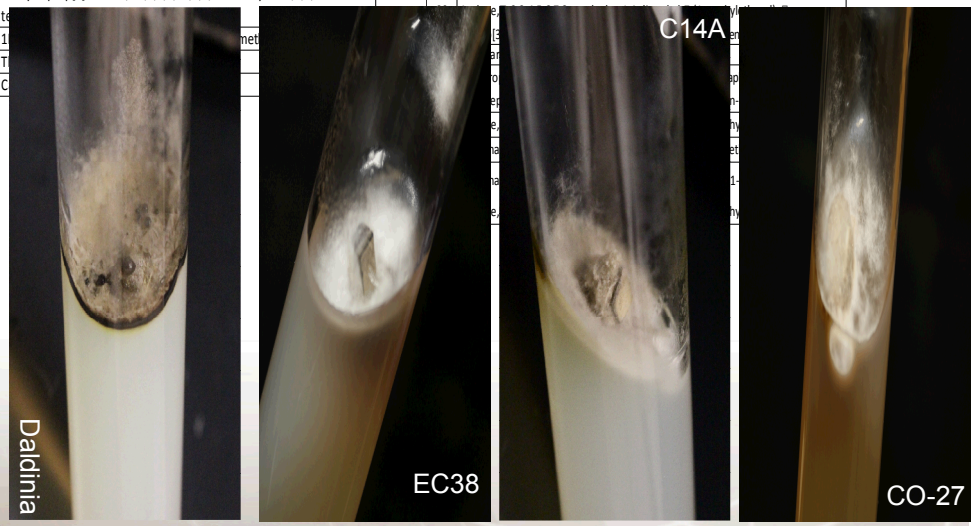
EC 38

1	1-Butanol,3-methyl-
2	Cyclohexane,1,2,4-tris(methylene)-
3	Benzene,methoxy-
4	Oxime-,methoxy-phenyl-_
5	Benzene
6	Benzeneethanol,beta.-ethenyl-
7	Eucalyptol
8	1,3-Cyclopentadiene,5-(1-methylpropylidene)-
9	trans-.alpha.-Bergamotene
10	Caryophyllene
11	1,6-Cyclodecadiene,1-methyl-5-methylene-8-(1-methylethyl)-,
	1H-Cyclopenta[1,3]cyclopropa[1,2]benzene,octahydro-7-methyl-3-methylene-4-(1-methylethyl)-,

CO 27

1	1-Butanol,2-methyl-
2	1,4-Cyclohexadiene,1-methyl-
	1,3,5-Heptatriene,[E,E)-
	Bicyclo[4.1.0]hept-2-ene
	1,3,5-Hexatriene,3-methyl-,(2-methyl isomer)-
	1,3-Cyclopentadiene,5,5-dimethyl-(1,2-dimethyl-3somer)
3	Cyclopentene,1,2,3-trimethyl-
	1,3-Dimethyl-1-cyclohe
	Ethanone,1-(2-furanyl)-
	Ethanone,1-(1H-pyrazo
	Cyclopropane,2-(1,1-dimethyl-2-pentenyl)-1,1-dimethyl-
	1,4-Pentadiene,2,3,3-trimethyl-
	1,4-Hexadiene,2,3-dimethyl-
4	Butanoic acid,2,3-dimethyl-,methyl ester
5	Styrene
6	4-Heptyn-2-ol
	1-Pentene,5-methoxy-
7	Cyclohexane,(ethenylthio)-

Daldinia



Criteria for combustion chemistry study:

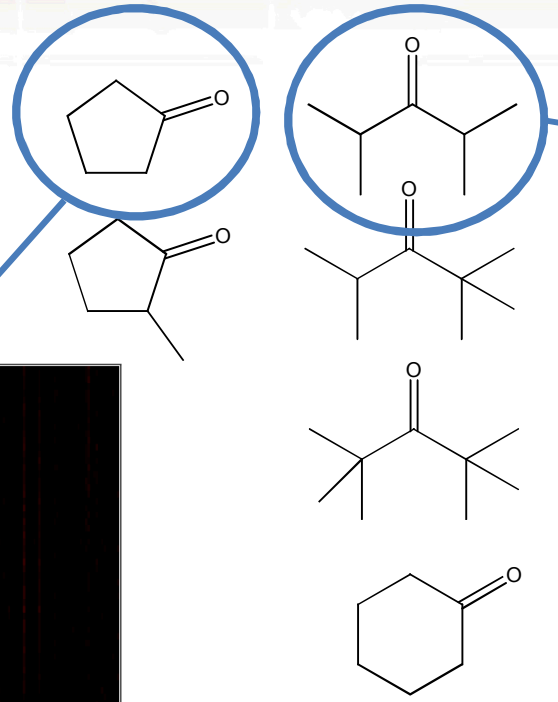
- Prominence in VOC profile
- Poor existing understanding of ignition chemistry

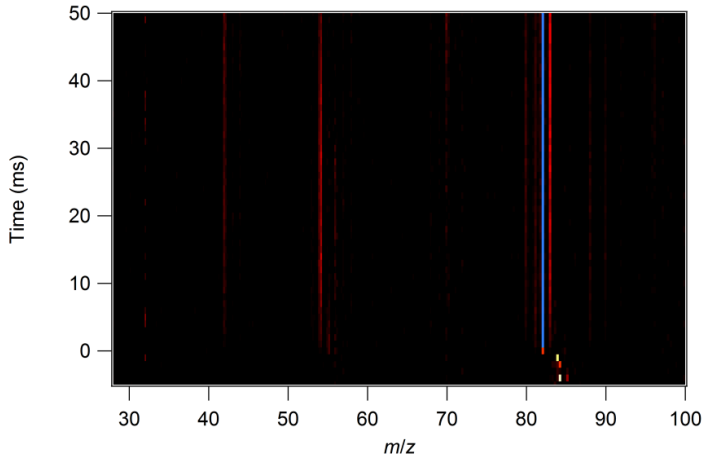
Ketones are prominent products in assays at Sandia and at Montana State University

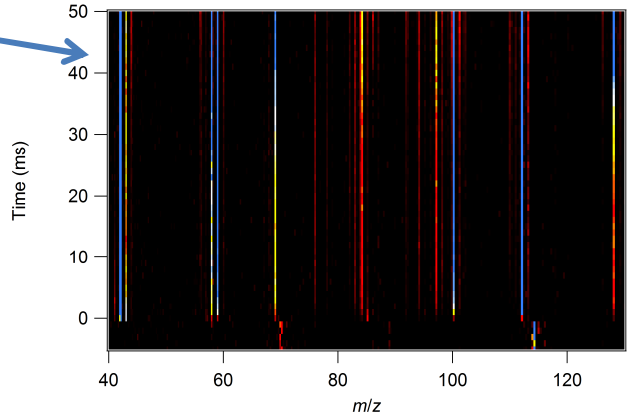
Terpene and sesquiterpene derivatives include cyclic ether function, e.g. cineole

First targets are fundamental ignition chemistry of representative ketones and cyclic ethers

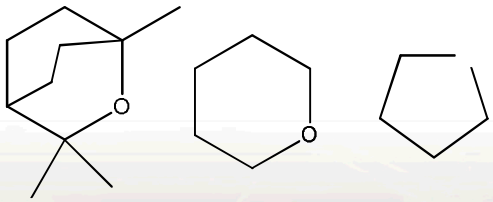
2,4-dimethyl-pentan-3-one (Di-Isopropyl Ketone –DIK) and cyclopentanone







Measurements for cyclic ethers have also been carried out – cineole, oxane, oxolane

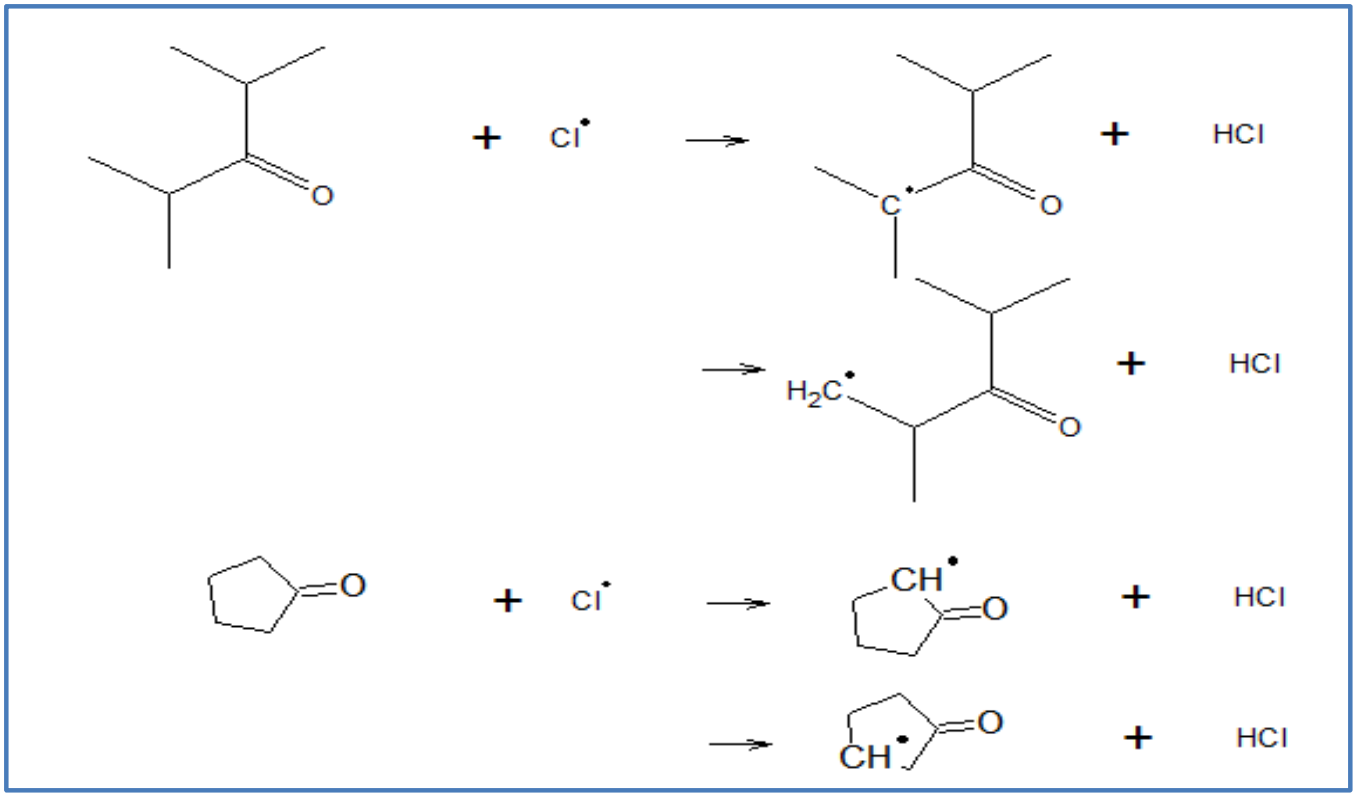


Measurements at the Advanced Light Source probe isomeric products of initial oxidation reactions

Representative ketones chosen to constrain rules for branching near carbonyl site, ring strain

Revealing low-temperature oxidation pathways of ketones by product detection (T= 550 – 750 K, P = 8 torr)

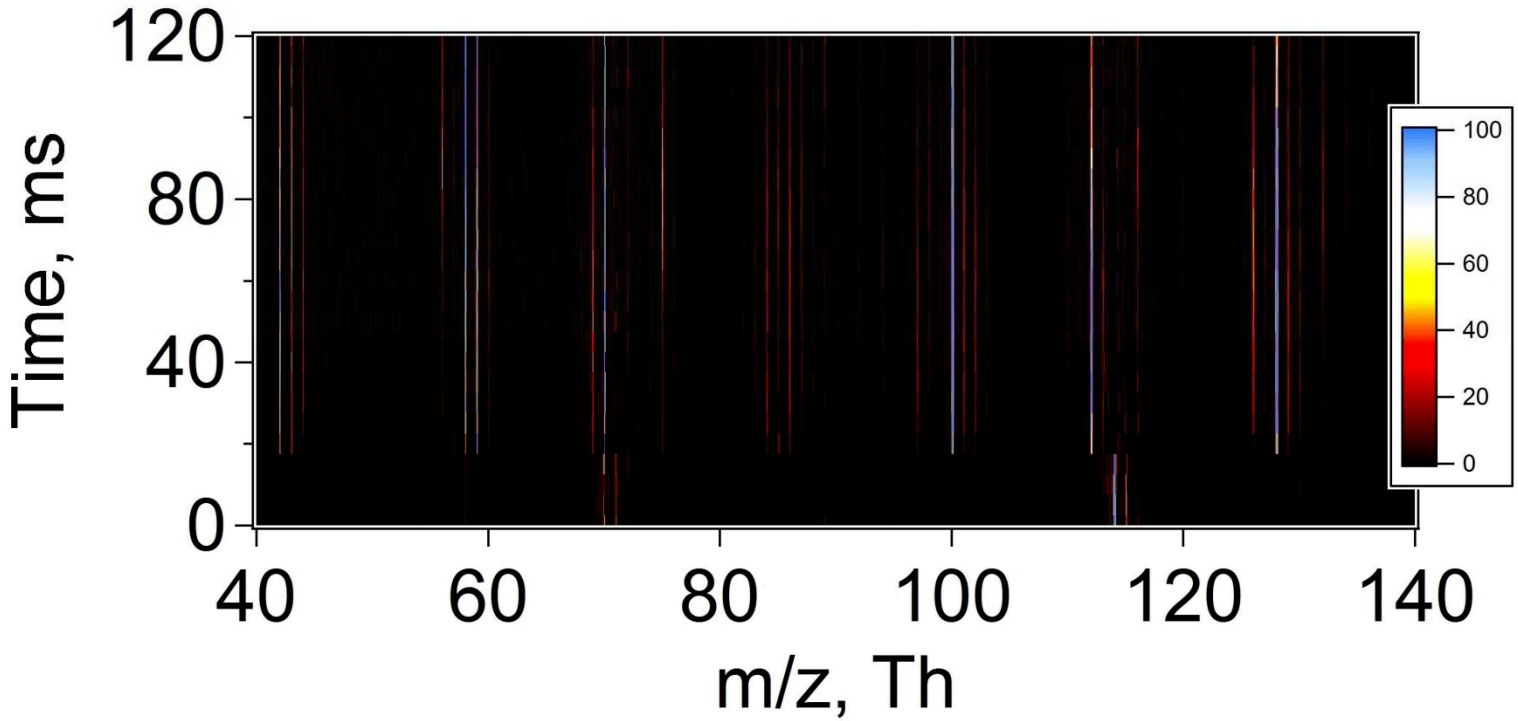
- Pulsed-photolytic Cl initiation at 4 Hz: $Cl_2 + h\nu$ (351 nm)$\rightarrow 2Cl^{\bullet}$



Fuel radicals react with O_2 forming various products: Detected by time-resolved synchrotron photoionization mass spectrometry

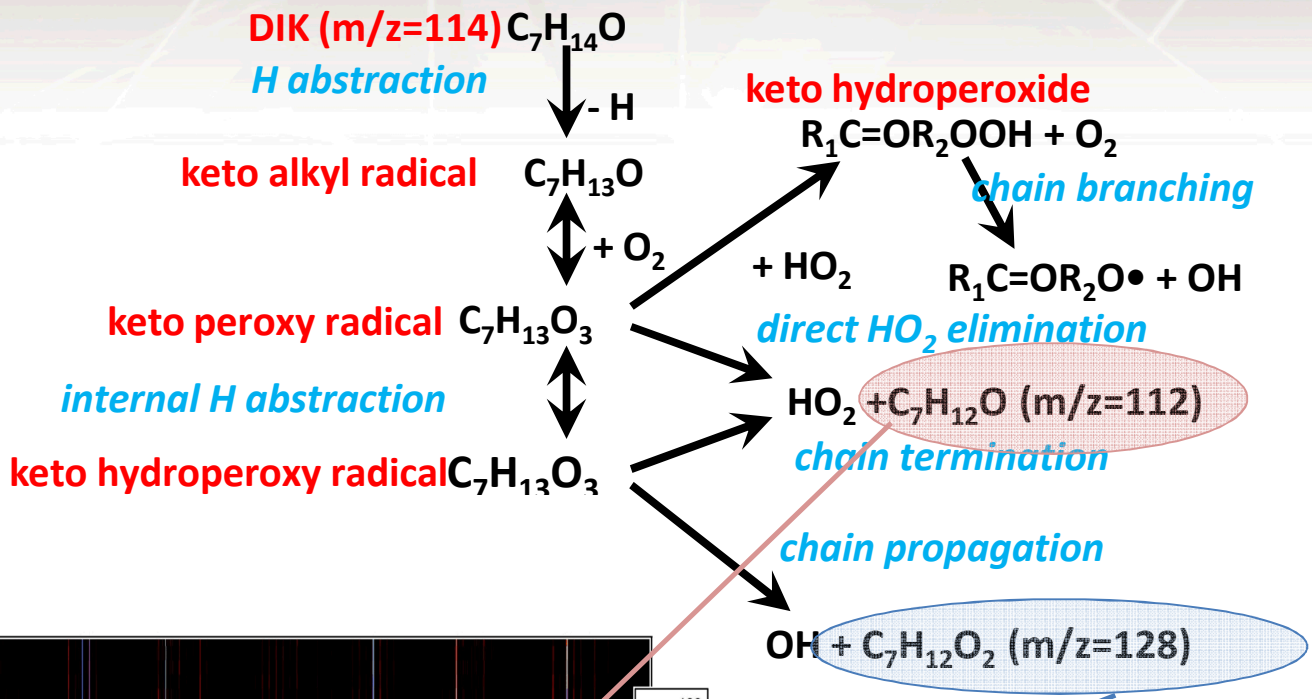
DIK (m/z=114) has a rich low-temperature oxidation chemistry

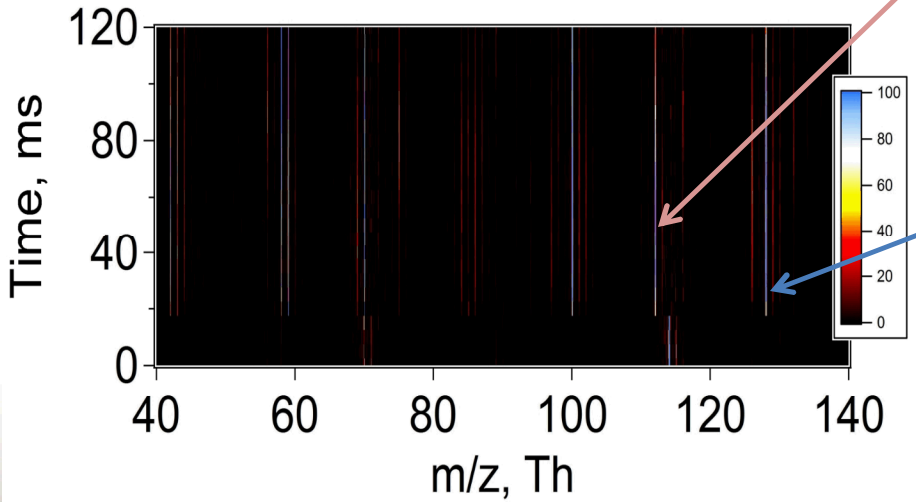
Time-resolved product mass spectrum at 550 K (Photon energy range: 8.0 - 10.5 eV)



→ Multiple product channels are present!

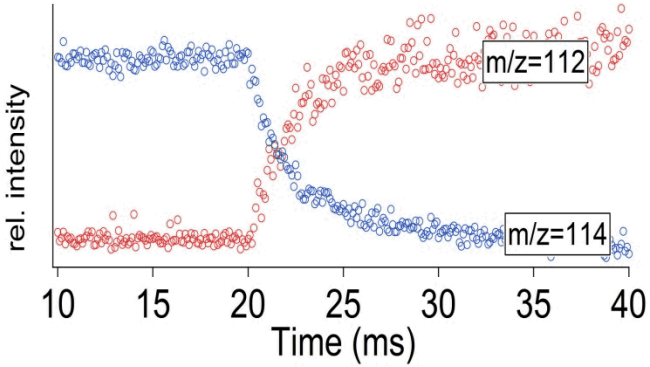
General low-temperature oxidation scheme: DIK



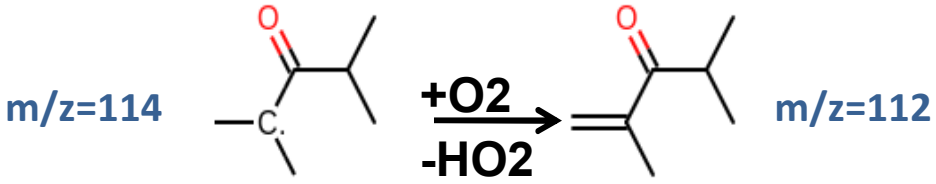


HO_2 elimination channel: $C_7H_{12}O$

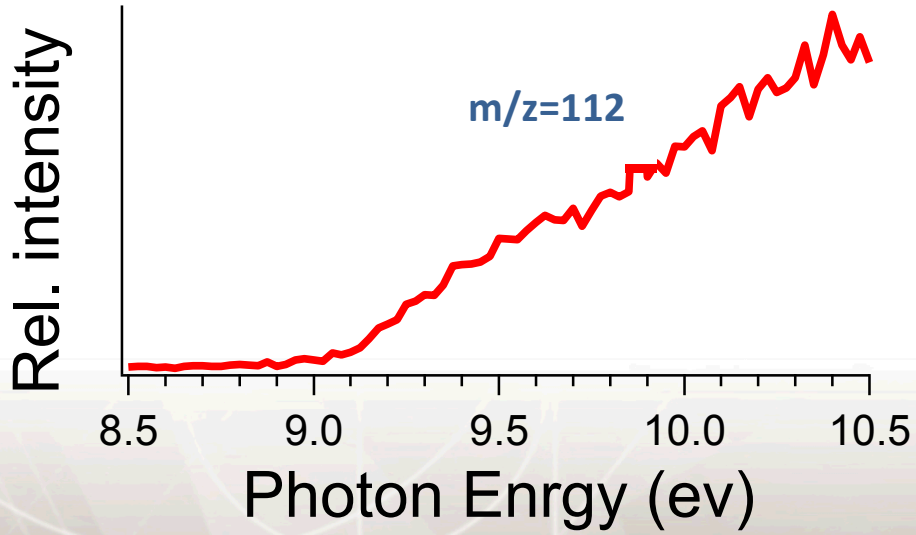
$C_7H_{12}O$ formation



Expected pathway:

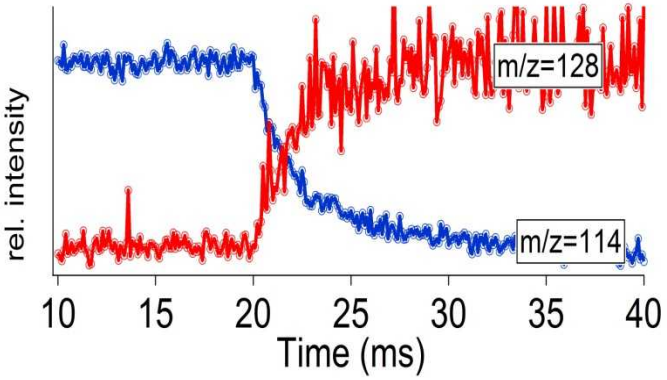


PIE spectrum of $C_7H_{12}O$

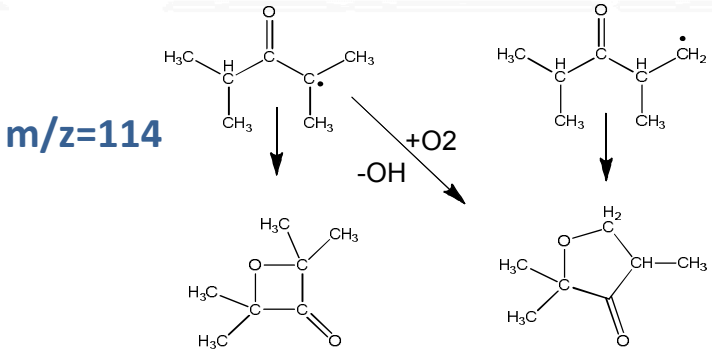


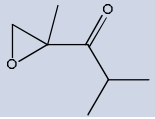
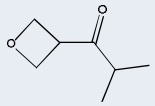
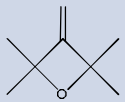
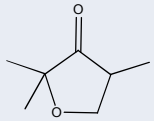
Cyclic ether channels: $C_7H_{12}O_2$

$C_7H_{12}O_2$ formation

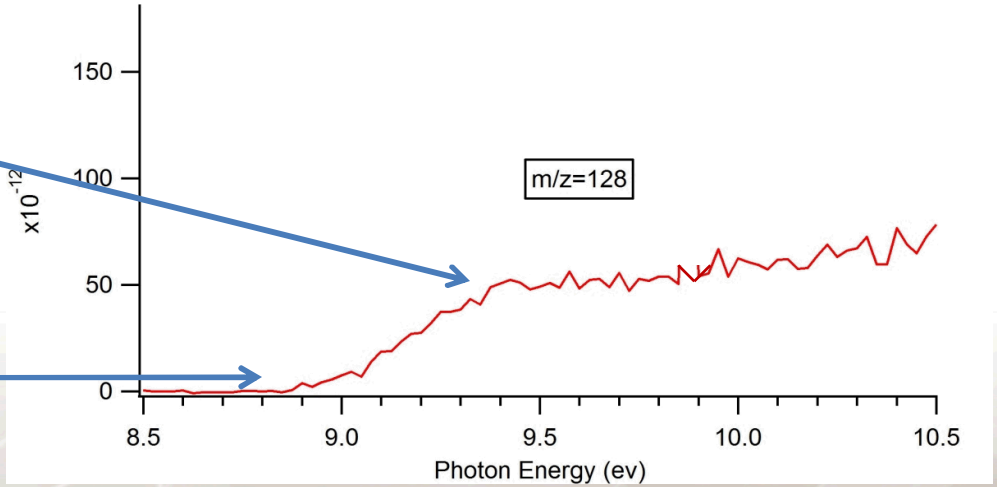


Expected pathways (4 total):

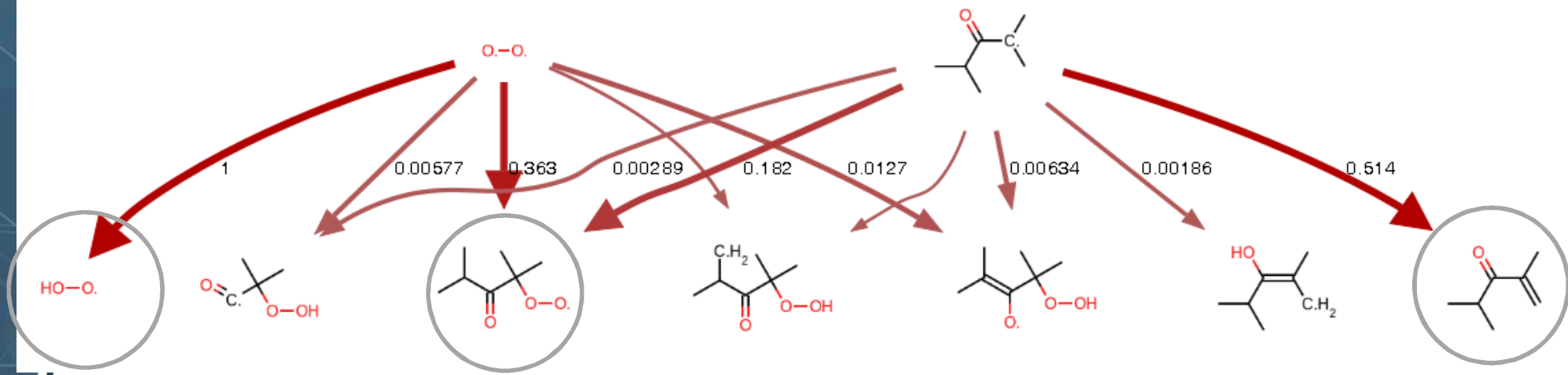


Species	AIE / eV (CBS-QB3)
	9.14
	9.41
	8.90
	8.80

PIE spectrum of $C_7H_{12}O_2$



RMG reaction flux model shows pathways in DIK oxidation mechanism

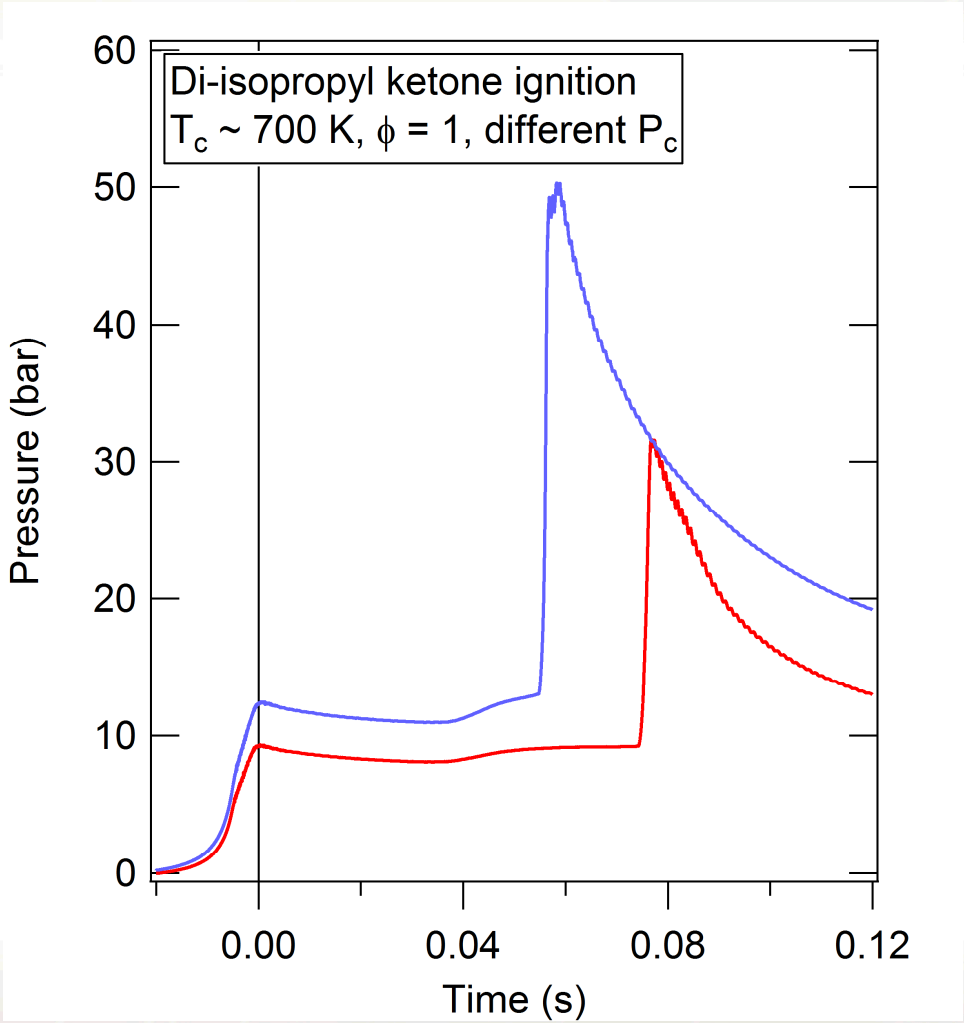


Initially, mainly chain terminating reactions:
direct elimination of HO_2 and formation of alkene

Some formation of ketoperoxy radical, which can go on to form OH (chain propagation) or hydroperoxyalkyl radicals (chain branching)

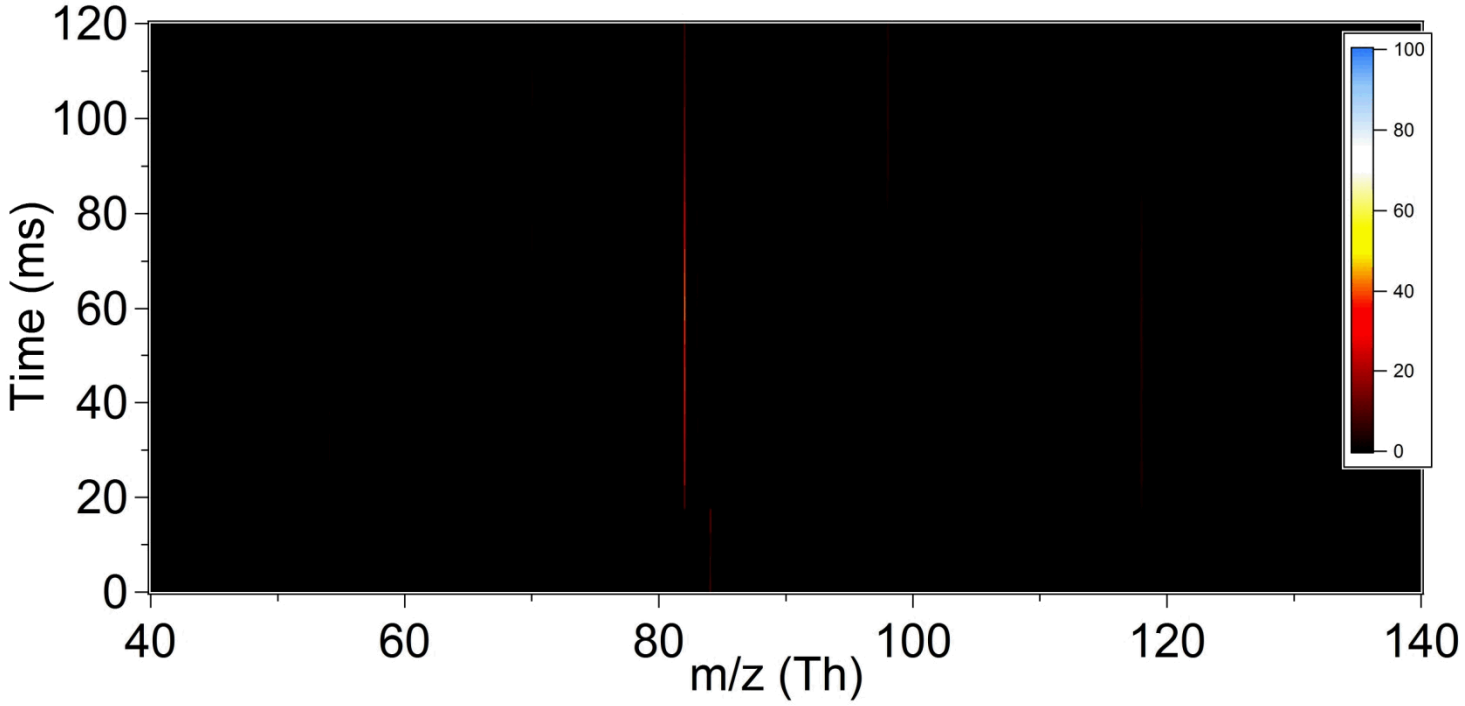
Validated elementary rate rules allow RMG to develop a complete ignition model

- Rapid-compression machine measurements in the SWL show two-stage ignition
- RMG model, using new rate rules for initiation reactions, predicts two-stage ignition, same magnitude for delay
- Negative temperature coefficient region reflects contribution from ROO / QOOH chemistry
- Ignition validation helps develop model for HCCI



Cyclopentanone (m/z=84) chemistry is relatively simpler

Time-resolved product mass spectrum at 700 K (Photon energy range: 8.0 - 10.5 eV)

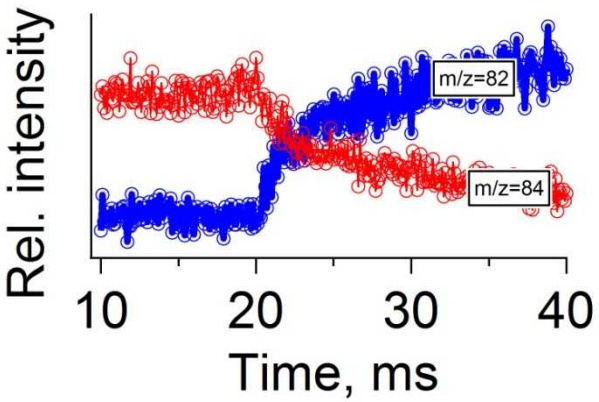


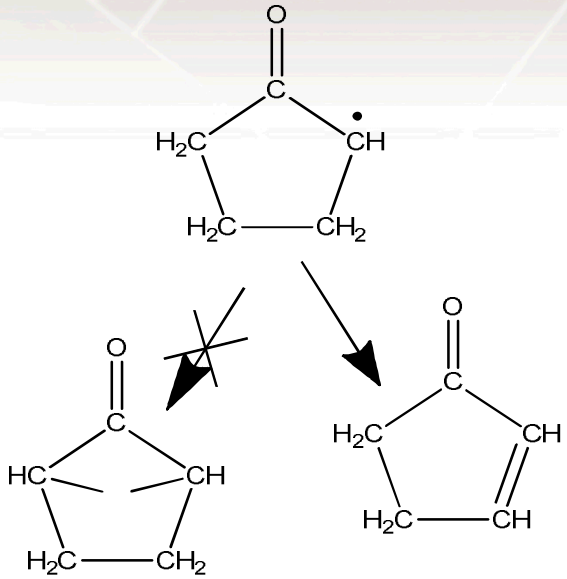
→ Cyclic ether formation is absent: essentially zero intensity at m/z = 98 suggests no cyclic ethers (high barriers?)– in contrast to alkane oxidation

→ **But**: Barrier for HO_2 elimination seems to be below the energy of the reactants (strong intensity at m/z=82)

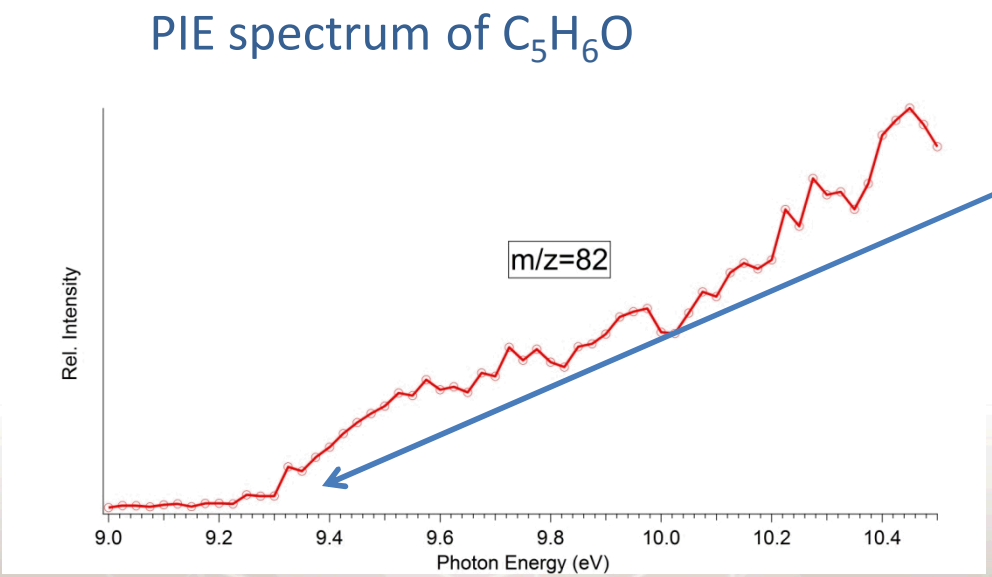
HO_2 elimination channel: C_5H_6O

C_5H_6O formation





PIE spectrum of C_5H_6O

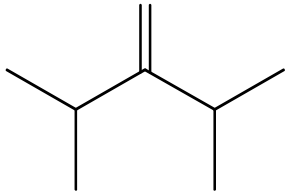


IE=9.3eV

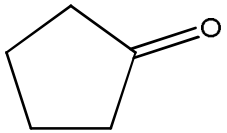
Ketone Structure affects Reaction Pathways

- Two ketones are representative of molecular-structure effects.

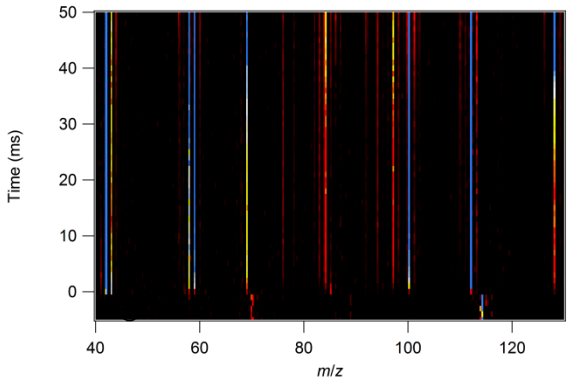
- **Di-isopropyl ketone**: shows species associated with chain-propagating OH formation.
  - Expect significant ITHR in engine with associated benefits for HCCI.

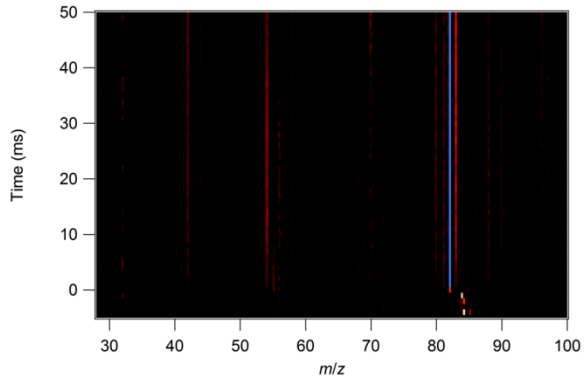


- **Cyclopentanone:** shows almost exclusively cyclopentenone formation, associated with chain-terminating HO_2 formation.
  - Expect very little ITHR in engine.



ALS Mass Spectra





- Engine experiments will be conducted to verify the expected changes in performance with ketone structure.
- Feedback to Bio-Side for tuning production by the fungus.

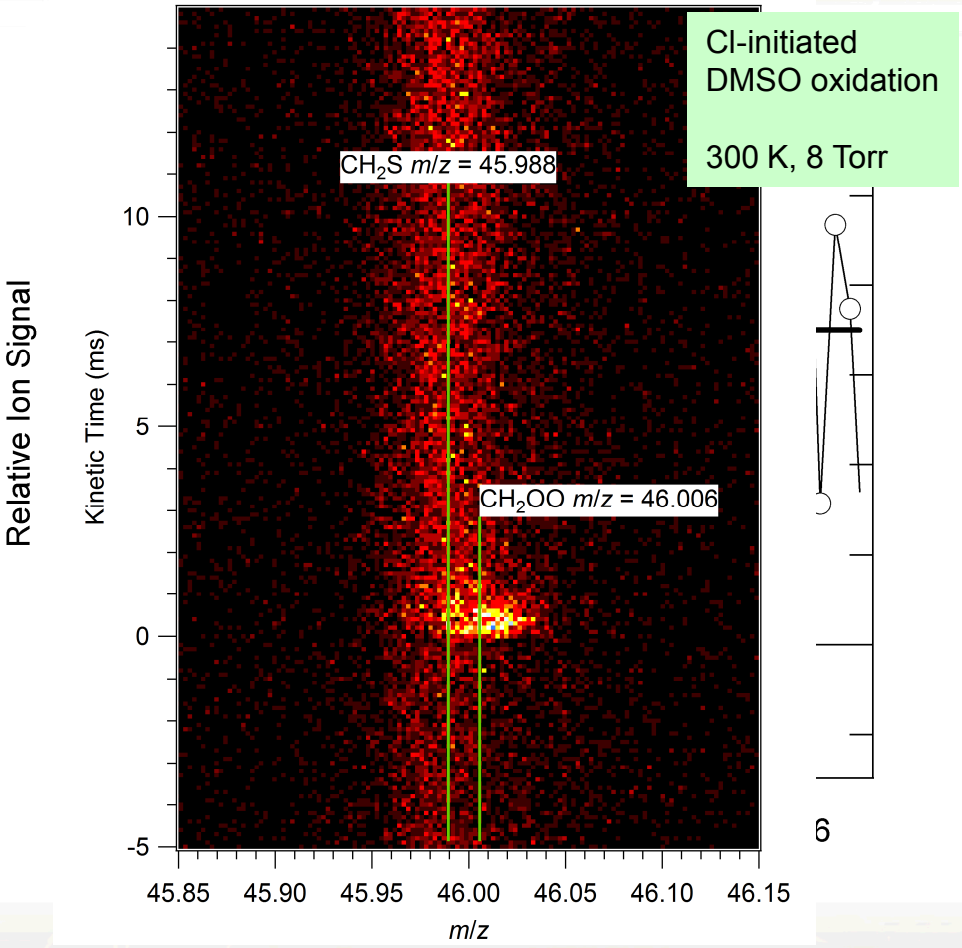
Combustion Chemistry Is Important in a Changing Fuel Environment

- **Comparison of detailed experiment and theory can reveal mechanisms**
- **New fuels bring new challenges**
  - Oxygenated biofuels can have distinctly different reactivity because of the effect of oxygen on thermochemistry
  - Connecting molecular structure to autoignition chemistry is a path towards predictive models
- **Fundamental science is important for future transportation**

What might synchrotron photoionization be able to do *next*?

Tunable synchrotron photoionization can identify novel isomeric products

- Ozonolysis of alkenes proceeds via a carbonyl oxide intermediate ("Criegee intermediate")
- They are important tropospheric reactants but only indirect measurements exist
- **Problem is to make enough**
- Dimethyl Sulfoxide (DMSO) oxidation may form CH_2OO (Asatryan and Bozzelli, PCCP 10, 1769 (2008))
- Time-of-flight can resolve CH_2S from CH_2OO



had

No one ~~has~~ ever seen a gas phase Criegee intermediate

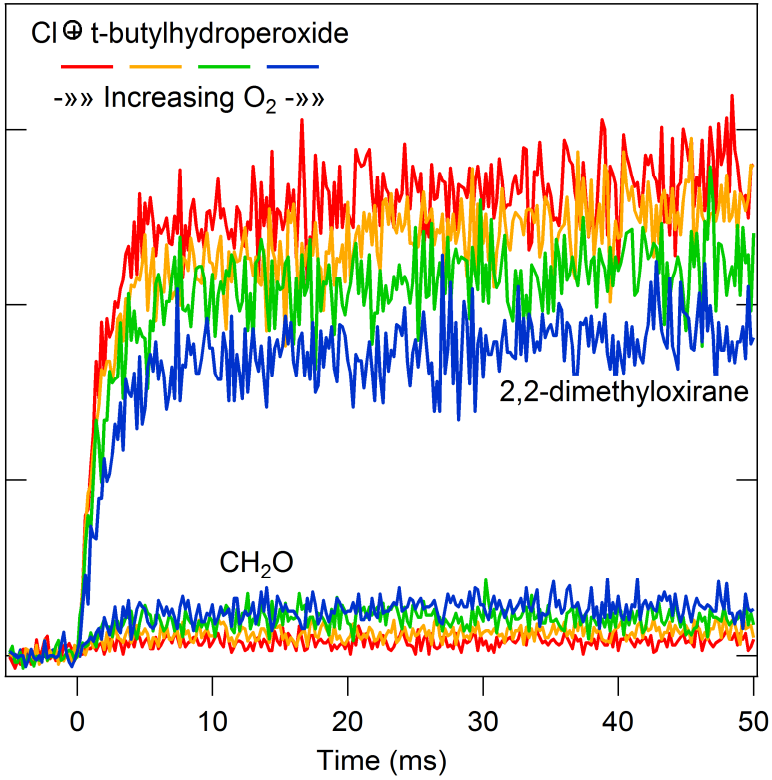
Taatjes et al., J. Am. Chem. Soc. 130, 11883 (2008)

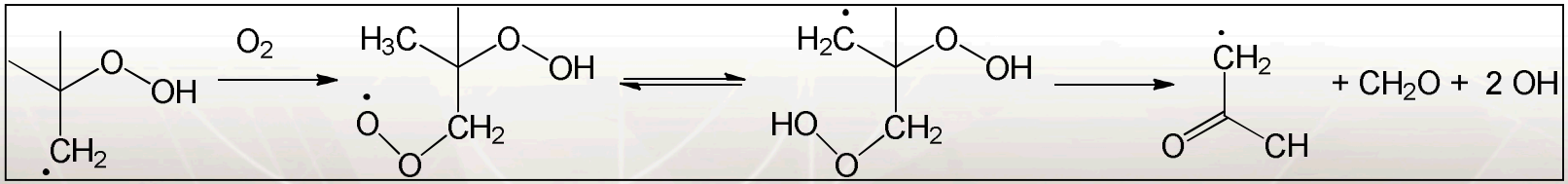
Can photoionization directly detect and characterize the elusive QOOH?

- QOOH reactions are critical for autoignition but only indirect measurements exist
- Most ROO isomers have no stable parent cation (Meloni et al., *J. Am. Chem. Soc.* **128**, 13559 (2006)), but some $QOOH^+$ are stable

Problem is to make enough!

- Cl + alkylhydroperoxide reactions make QOOH: e.g.,
  - $Cl + (CH_3)_3COOH \rightarrow (CH_3)_2C(CH_2)OH + HCl$
  - $(CH_3)_2C(CH_2)OH \rightarrow$ 2,2-dimethyloxirane + OH
- Reaction with O_2 competes with dissociation – forms other products





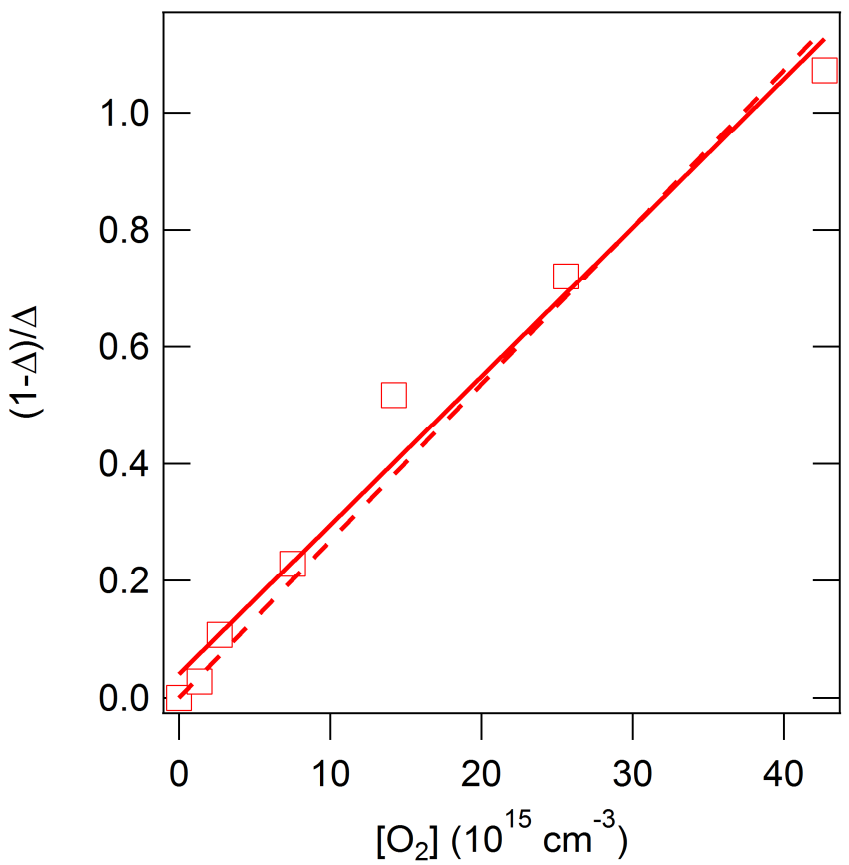
Detection of Reaction Products Can Give Direct Kinetics Measurements

- $[O_2]$ dependence of CH_2O formation identical to change in 2,2-dimethyloxirane
- Correctly scaled change in dimethyloxirane is linear in $[O_2]$
- Direct measurement of QOOH + O_2 rate coefficient relative to thermal dissociation

Problem is we don't know the absolute k of either process!

- Fix this by doing experiments with better time resolution

$k(QOOH+O_2)/k(dissociation) = (2.5 +/- 0.4) \times 10^{-17}$ cm^3



$k(dissociation) \sim 3 \times 10^4$ s^{-1} → $k(QOOH+O_2) \sim 8 \times 10^{-13}$ cm^3 s^{-1}

Can photoionization directly detect and characterize the elusive QOOH?

- QOOH reactions are critical for autoignition but only indirect measurements exist
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- **Problem is to make enough!**
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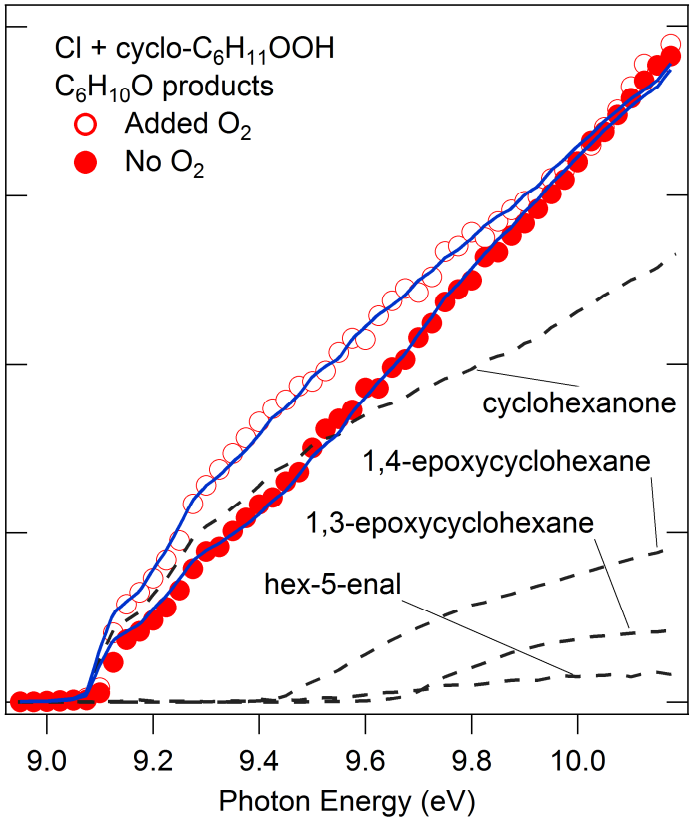
  - $Cl + (CH_3)_3COOH \rightarrow (CH_3)_2C(CH_2)OH + HCl$
  - $(CH_3)_2C(CH_2)OH \rightarrow$ 2,2-dimethyloxirane + OH
- Reaction with O_2 competes with dissociation – forms other products
- Cl + cyclohexylhydroperoxide forms several isomers that react differently with O_2



However, no $QOOH^+$ (yet!)

Combustion Chemistry Is Important in a Changing Fuel Environment

- **Comparison of detailed experiment and theory can reveal mechanisms**
- **New fuels bring new challenges**
  - Oxygenated biofuels can have distinctly different reactivity because of the effect of oxygen on thermochemistry
  - Connecting molecular structure to autoignition chemistry is a path towards predictive models
- **Fundamental science is important for future transportation**

- **Direct measurements of QOOH reactions**

Acknowledgements

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Ravi Fernandes, Changyoul Lee (RWTH Aachen University)

Giovanni Meloni (University of San Francisco)

Daniel Merthe (USF → LBNL →)

Leonard Jusinski (→ San Jose State)

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