SAND2011-2305P

Laser and Synchrotron Investigations of Fundamental Combustion Chemistry

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MIT Modern Optics and Spectroscopy Seminar, April 5, 2011

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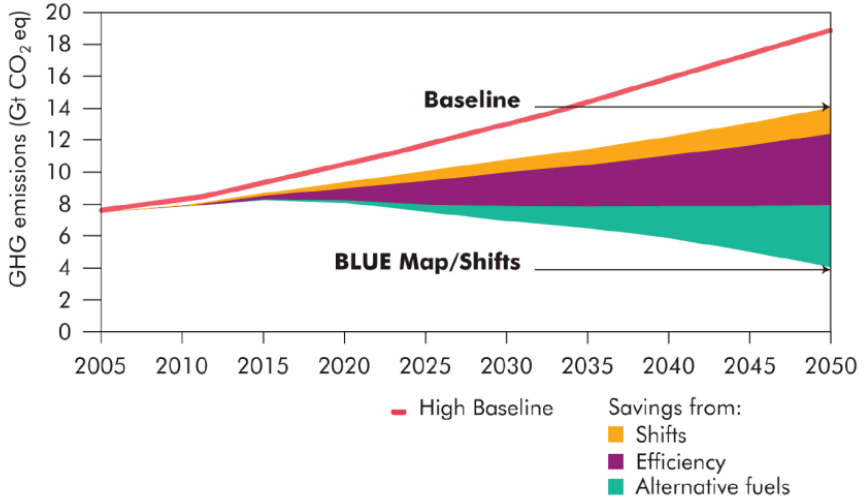
Climate Change and Energy Security Hold Huge Challenges for Transportation

- Reducing “foreign oil” 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.

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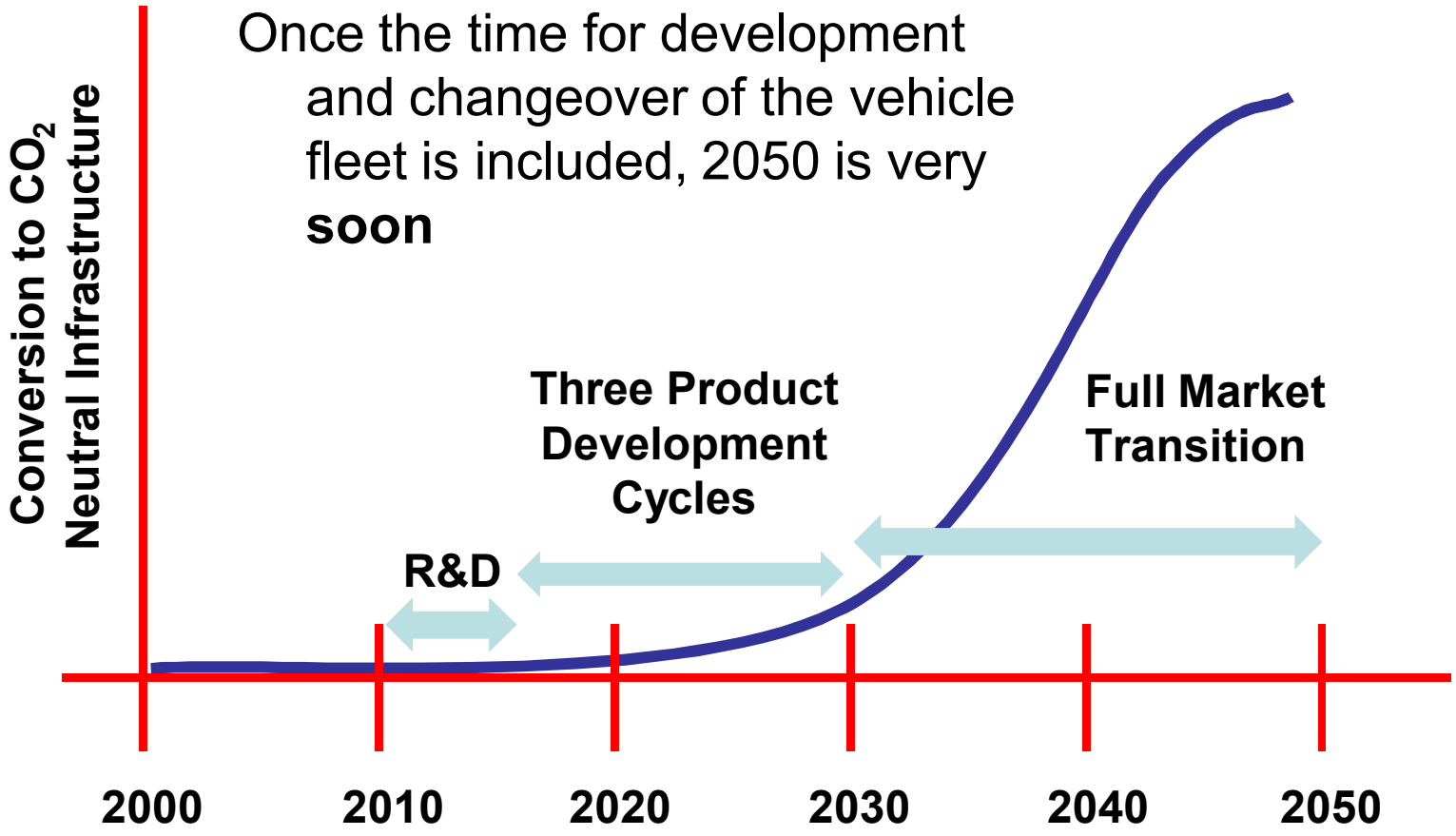
Predictive Simulation of Combustion Is Needed to Accelerate Development



Predictive simulation can shrink development time

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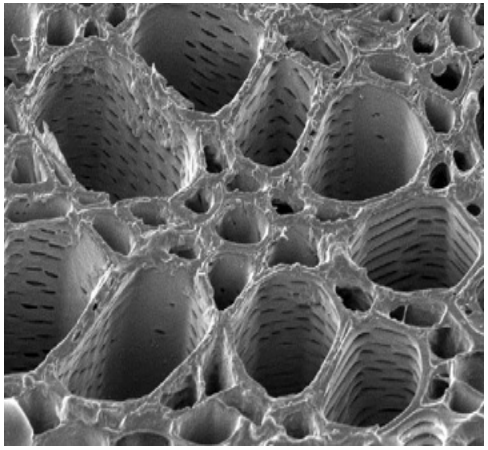
In Response to These Challenges the Fuel Stream Is Already Changing

- Non-traditional fossil sources can address "energy security"
  - Tar sands (Canada); oil shale (US)
  - **Not generally climate-friendly!**

Fuel chemistry is changing



- Biomass-derived fuels
  - Current biofuels – ethanol & biodiesel – give relatively small reduction of GHG relative to petroleum
  - **Cellulosic biofuels will give much greater GHG reduction, not compete with food production**
    - **Cellulose is challenging to deconstruct**
    - **Most efficient production may give novel fuel compounds**

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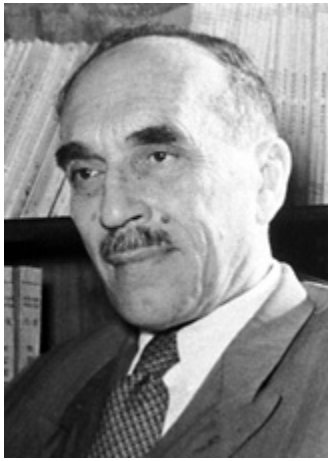
You Don't Need to Know Much Chemistry to Make an Engine!

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 Make a Big Difference

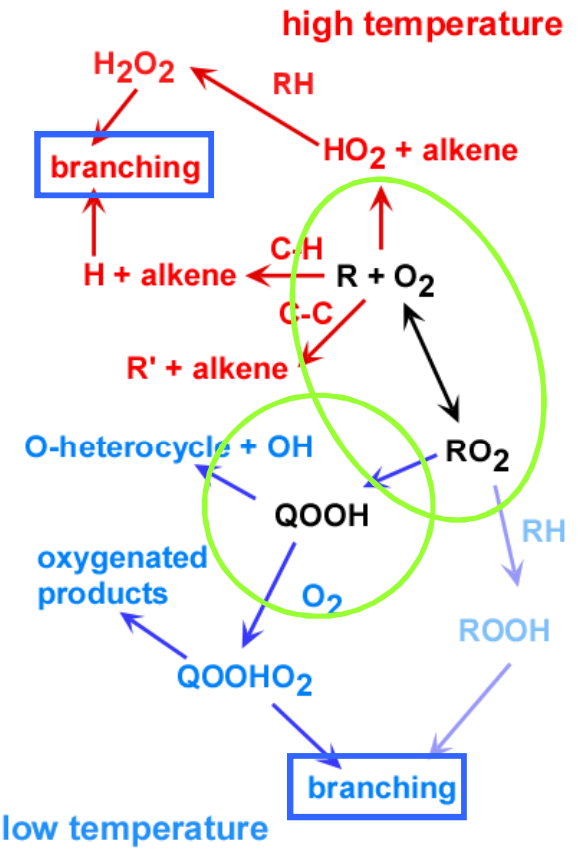
Pollutant Formation:

- 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

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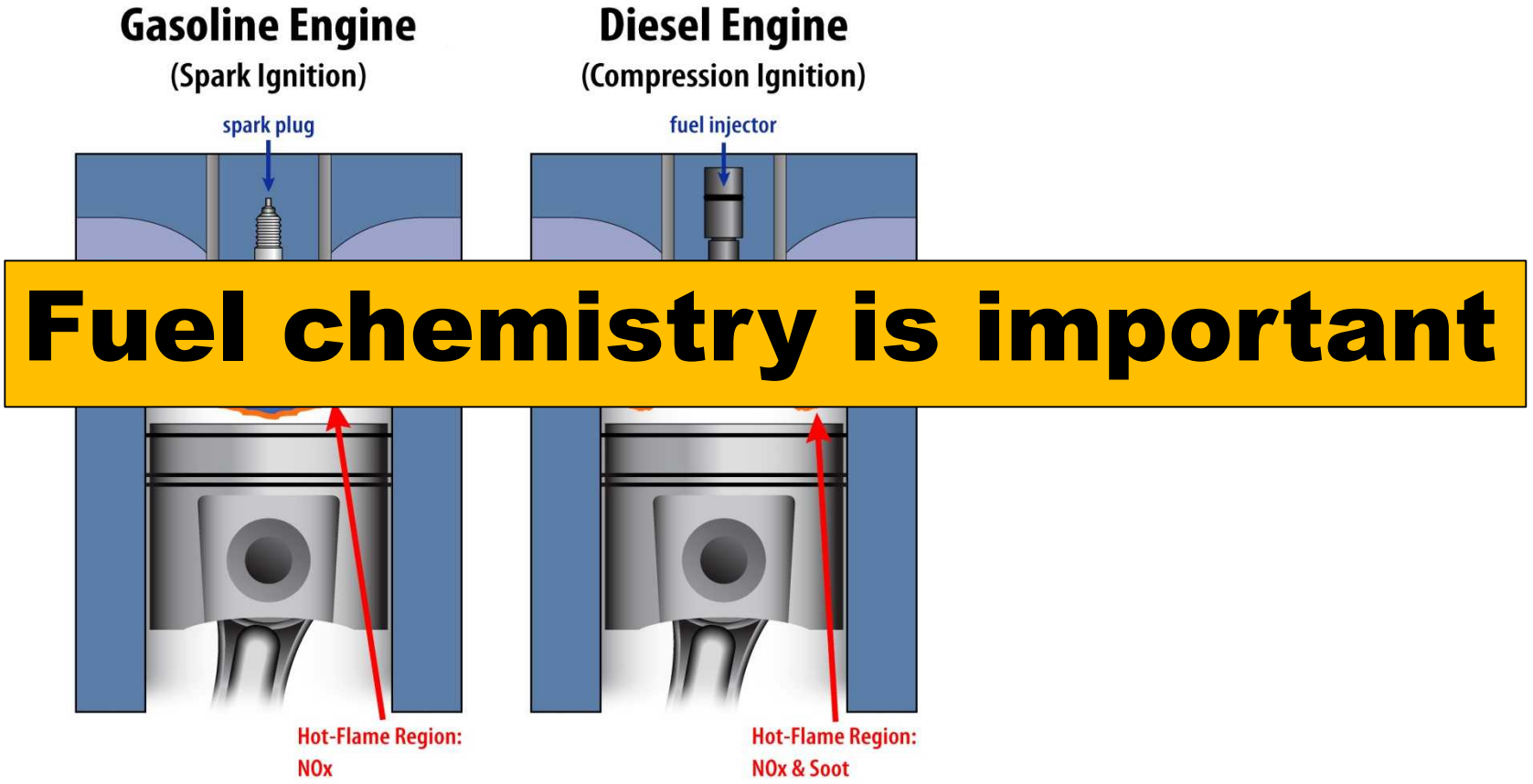
Advanced Engines Rely on Autoignition Chemistry to an Unprecedented Degree



Fuel chemistry is important – but fuel stream is already changing!

- Non-traditional hydrocarbon sources → cycloalkanes
- Alternative fuels → esters? alcohols? furans?!?

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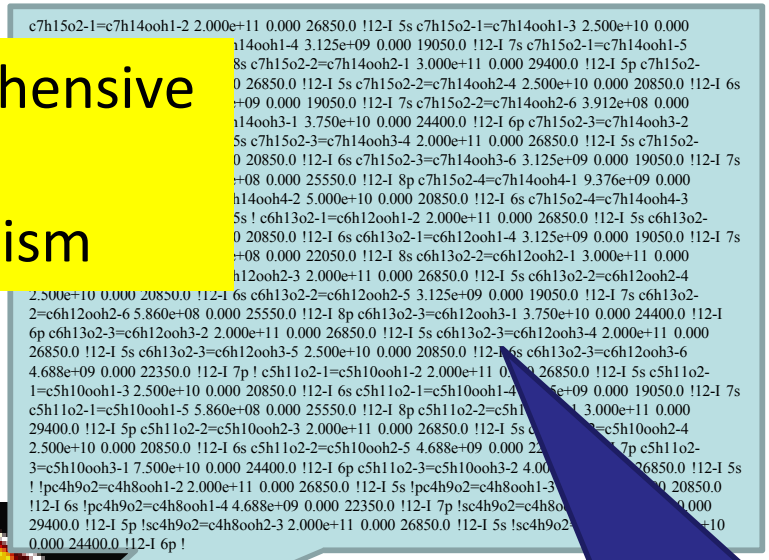
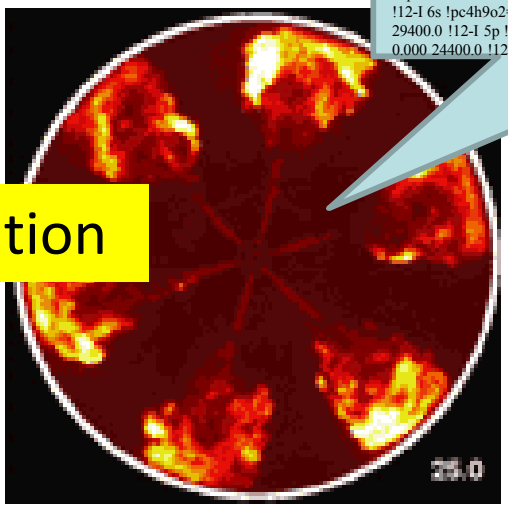
Even Complicated Chemistry Depends on a Few Key "Elementary" Reactions

Comprehensive Kinetic Mechanism



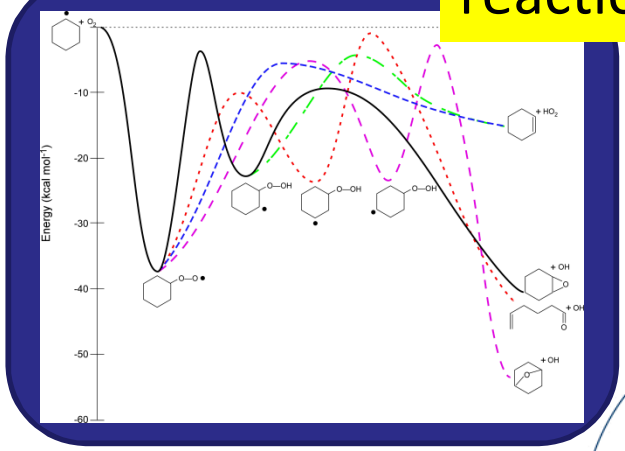
Detailed chemistry of single elementary fuel may have thousands of reactions and hundreds of species

Turbulent, multiphase flows interact with the chemistry



Autoignition

$R + O_2$ reactions



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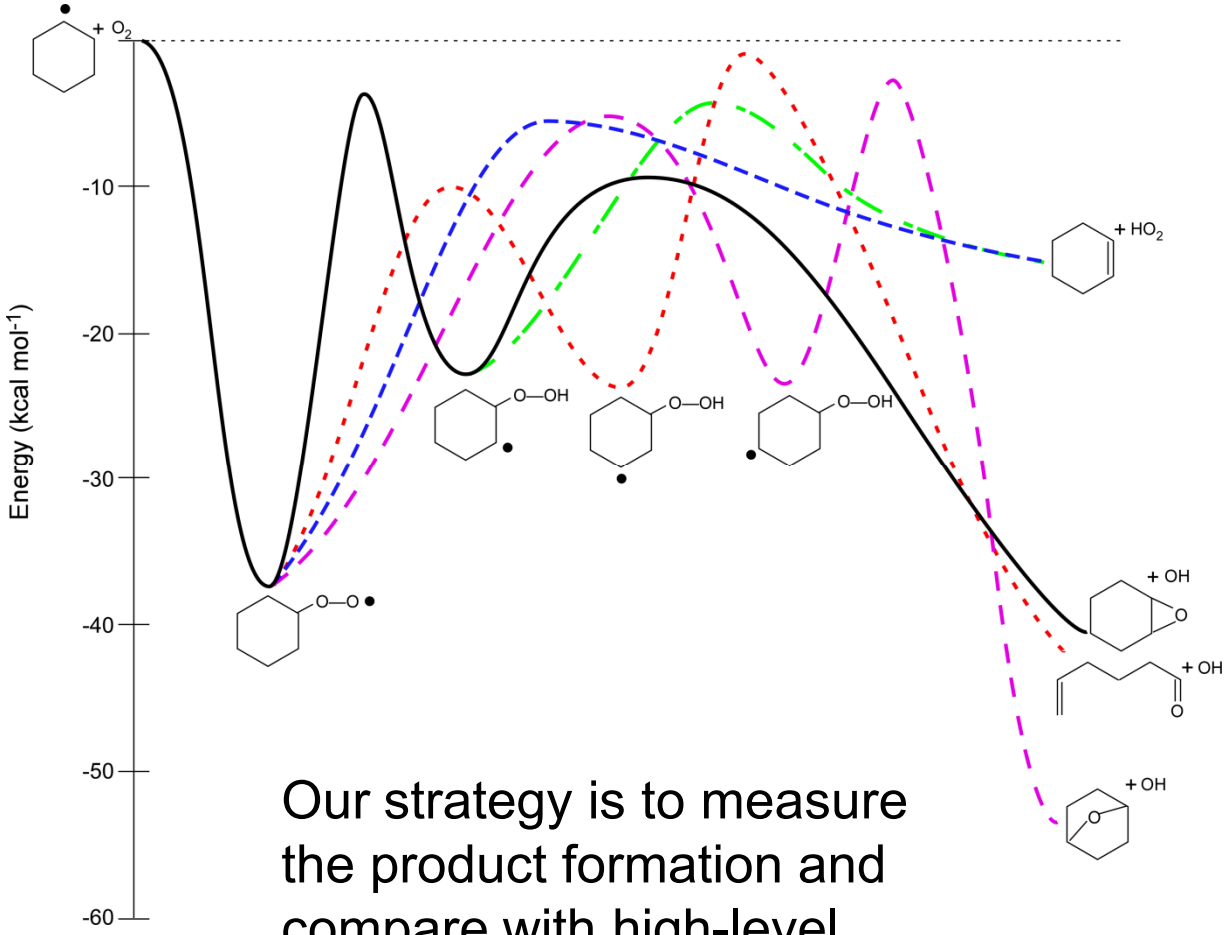
The R + O_2 Reactions Are Critical in Low- and Intermediate Temperature Oxidation



Our strategy is to measure the product formation and compare with high-level theoretical kinetics

- Balance between chain branching and chain termination is important for autoignition – changes with pressure and temperature
- Production of HO_2 is chain-terminating at low T
- Pathways to OH are chain propagating, and pass through “QOOH” intermediate

- Reactions of QOOH with O_2 give chain branching

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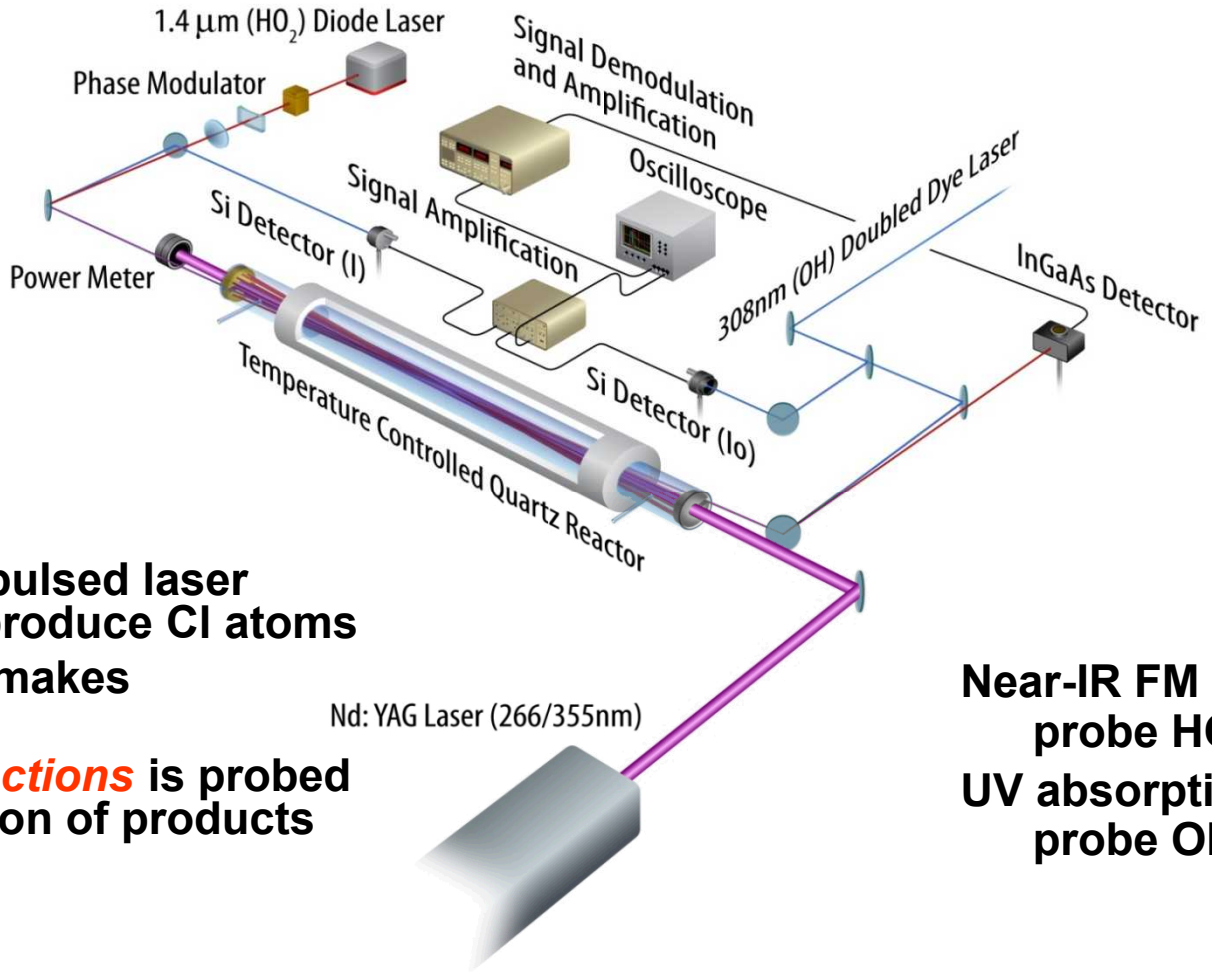
Laser Photolysis / Laser Absorption Method Is Used to Probe OH and HO_2



- Experiment uses pulsed laser photolysis to produce Cl atoms
- Cl + cyclohexane makes cyclohexyl
- Ensuing *set of reactions* is probed by cw absorption of products

- Near-IR FM to probe HO_2
- UV absorption to probe OH

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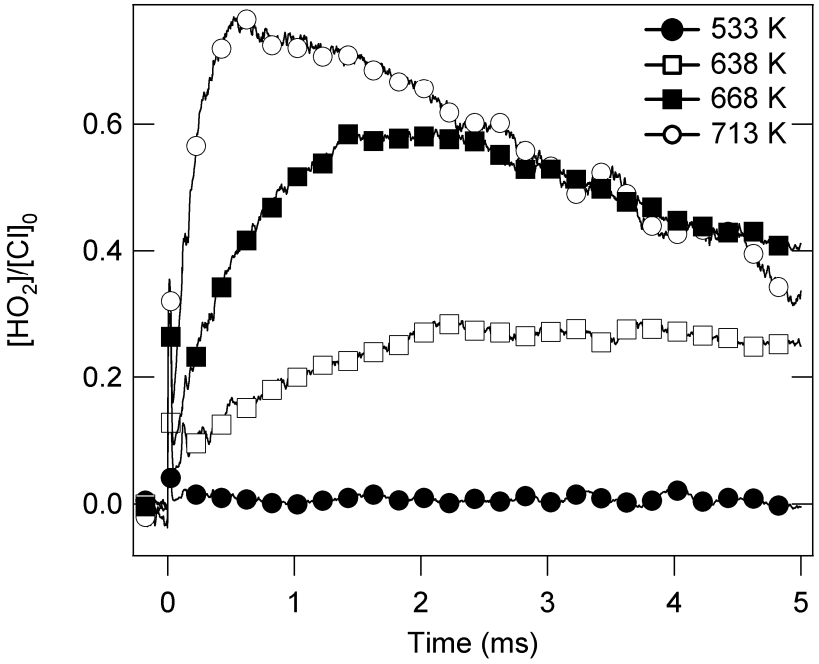
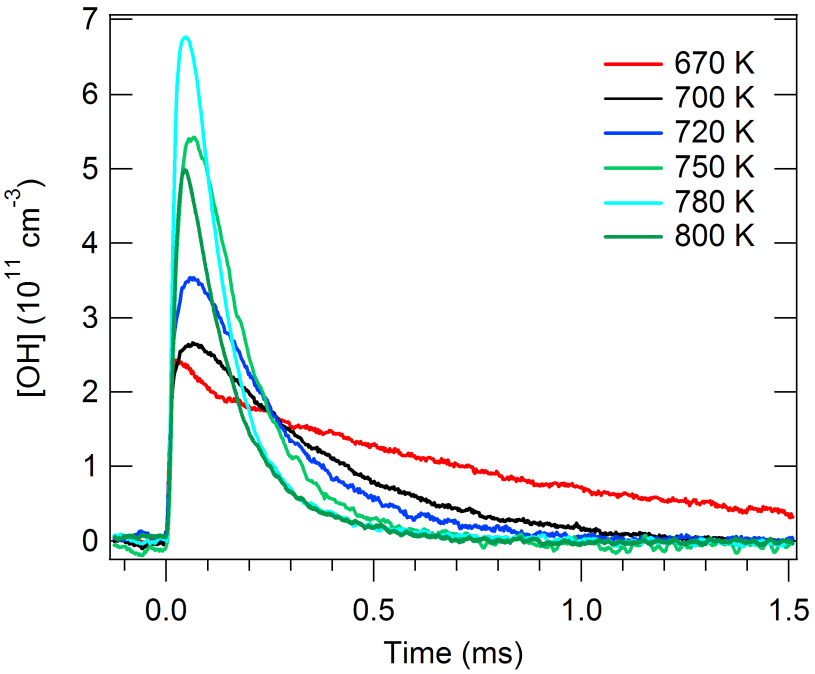
Measurements of HO_2 and OH Are Carried Out at Various Temperatures





Comparison to reference system (Cl-initiated methanol oxidation) gives HO_2 relative to initial Cl concentration

Absorption detection of OH radical yields absolute concentration

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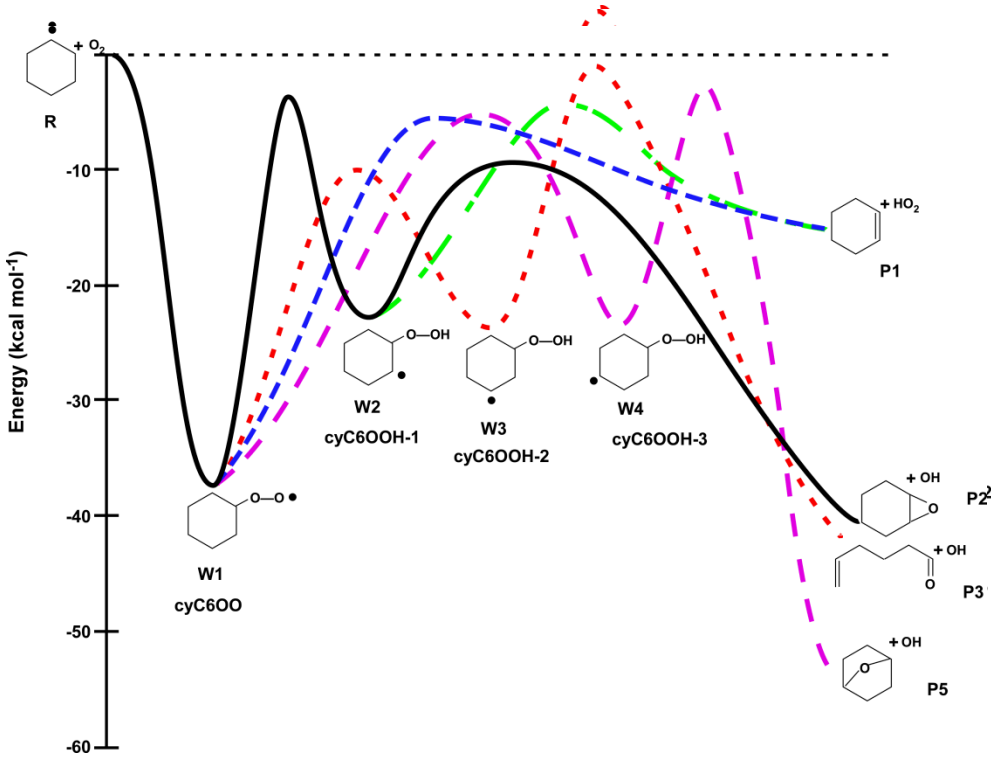
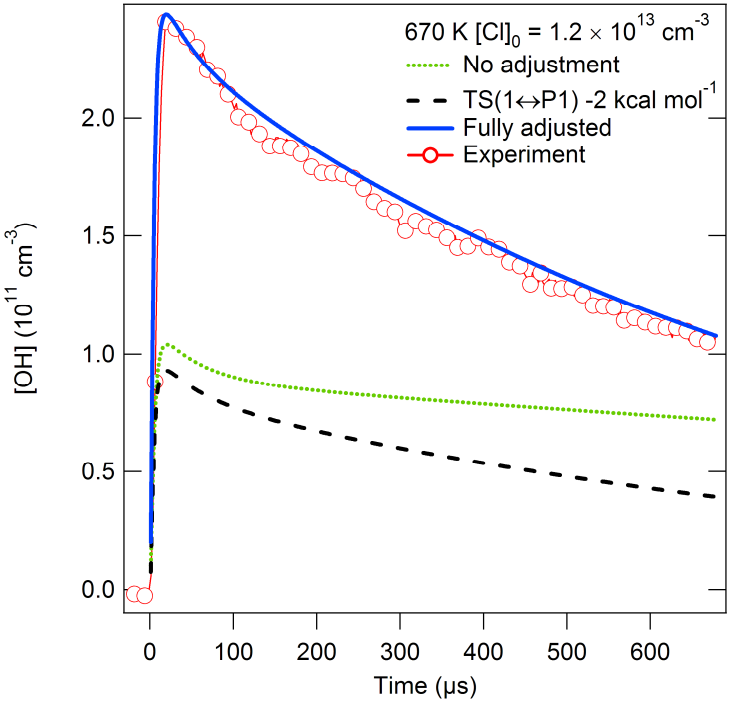
Stationary Point Energies Are Adjusted to Match Experiment





Because of chain reaction with cyclohexane, OH decay depends on overall branching to OH channels

Modeling amplitude and Walker et al. end products requires substantial lowering of transition states to hex-5-enal and cyclohexane oxide

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Stephen Klippenstein (Argonne)
Carlo Cavallotti (Milan)

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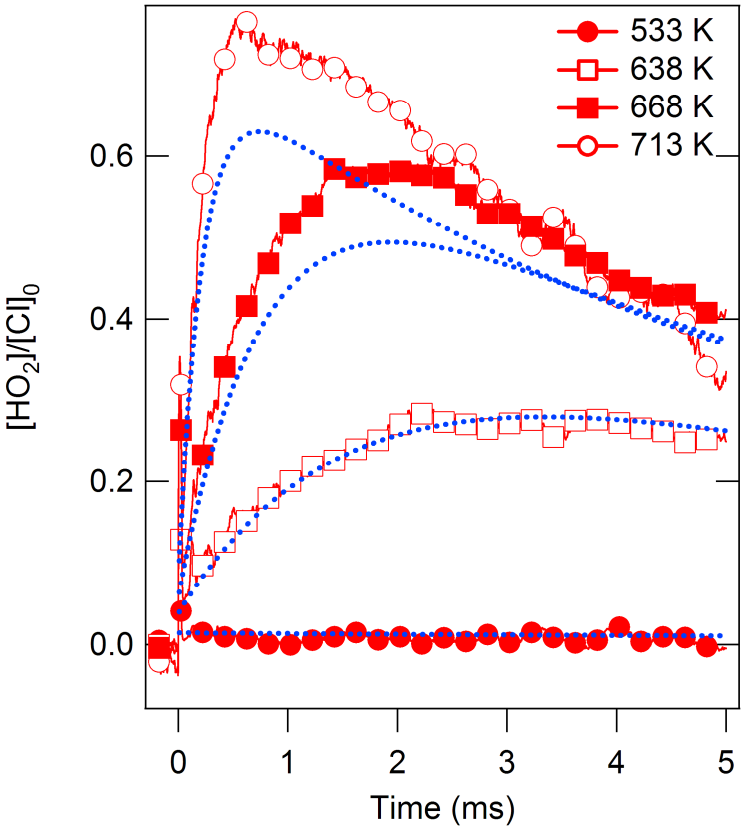
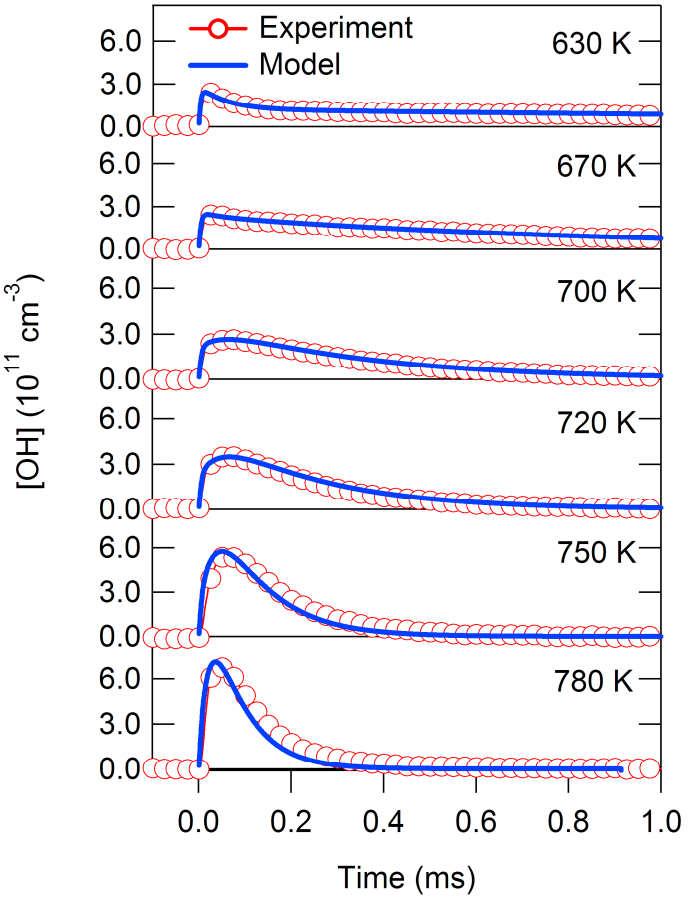
The Same Stationary Point Energies Are Used for All Temperatures





(Knepp et al., PCCP 9, 4315 (2007))

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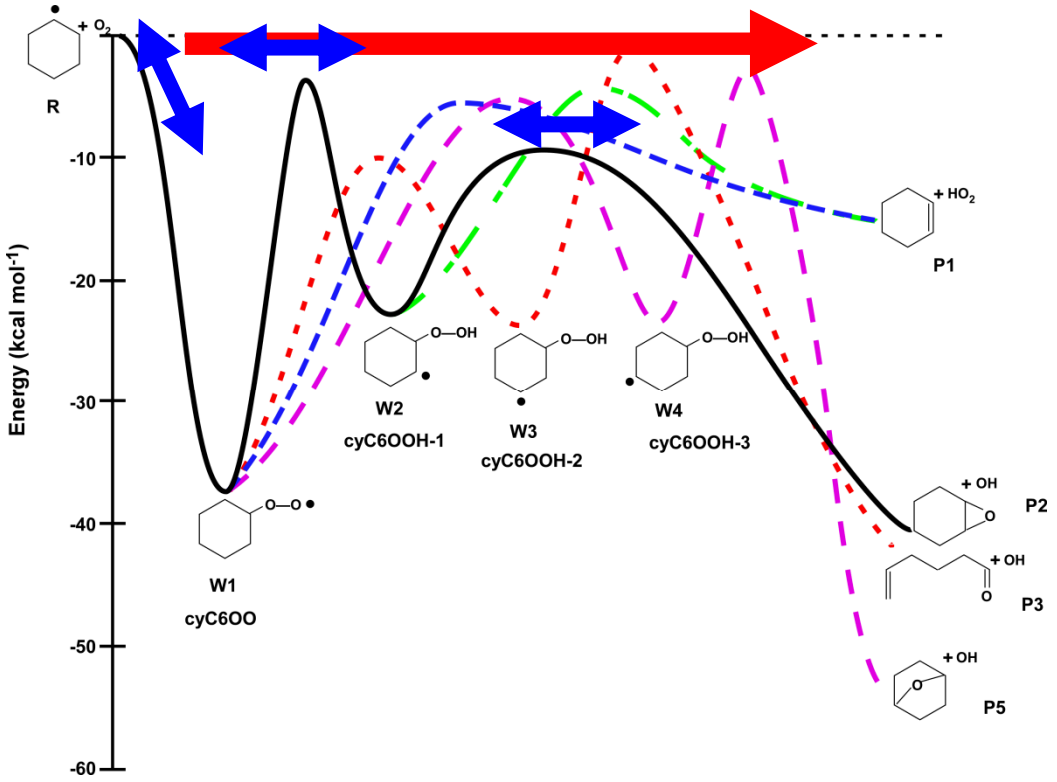
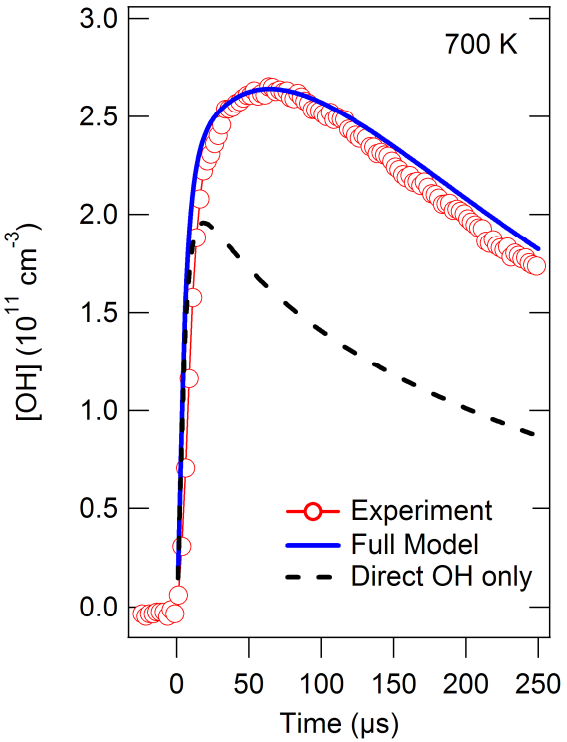
Both "Sequential" and "Formally Direct" Pathways Are Evident in Experiment





"Formally direct" path crosses more than one transition state in single step

"Sequential" OH formation from thermalized RO_2 and QOOH evident at longer times

Different timescales show mechanistic difference – has consequences for pressure dependence!

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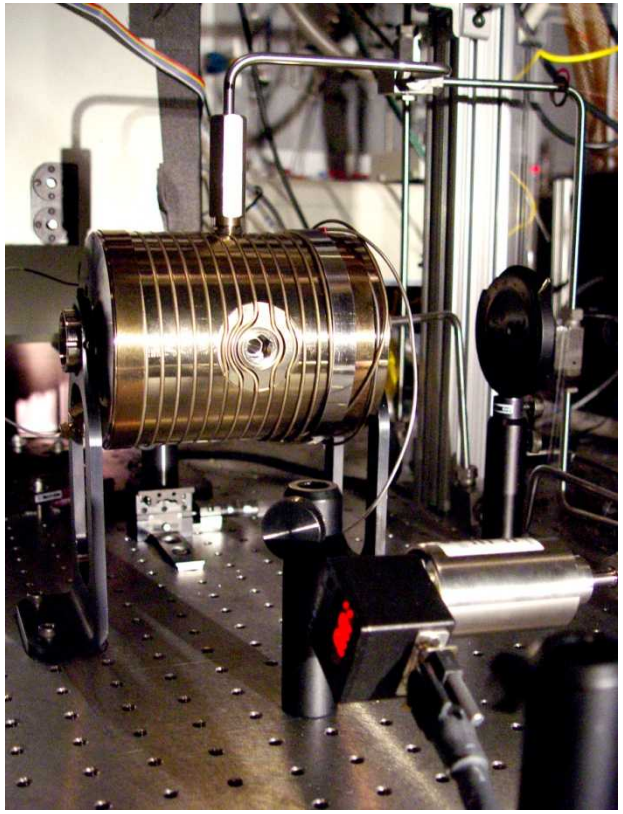
What Happens at the High Pressures Inside an Internal Combustion Engine!?

- Collisional energy transfer will change the product branching fractions
- Previous experiments were at < 100 Torr – in-cylinder pressures are 20 – 100 bar!
- Isn't everything just in the high-pressure limit in an engine?

- Carry out similar measurements of OH formation at high pressure

Are "formally direct" channels relevant at engine cylinder pressures?



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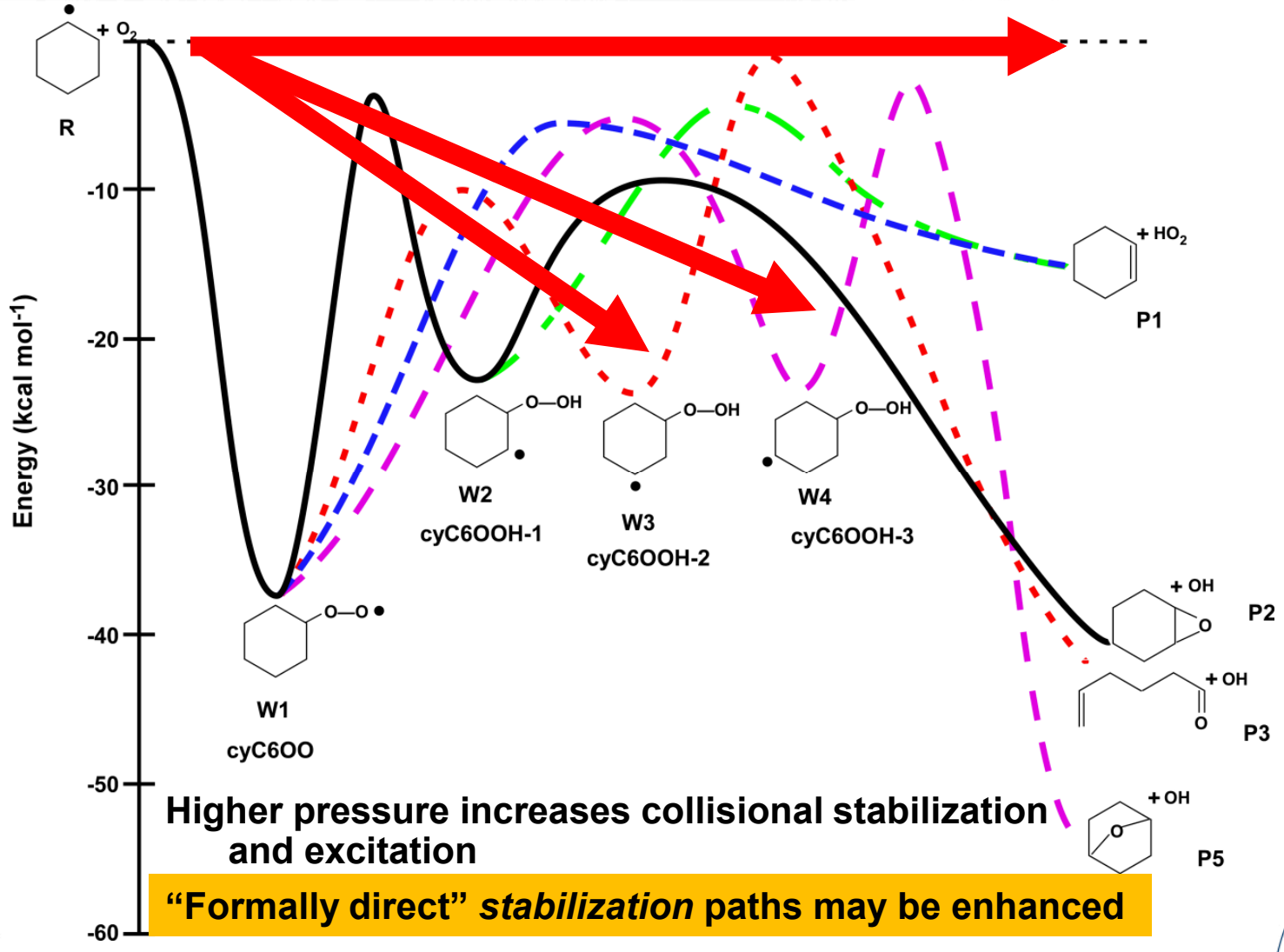
Both "Sequential" and "Formally Direct" Pathways Change at High Pressure



Higher pressure increases collisional stabilization and excitation

"Formally direct" *stabilization* paths may be enhanced

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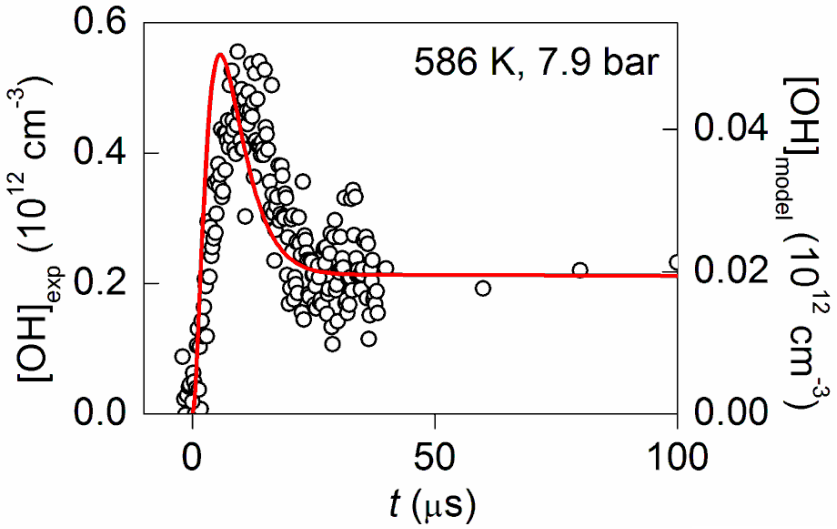
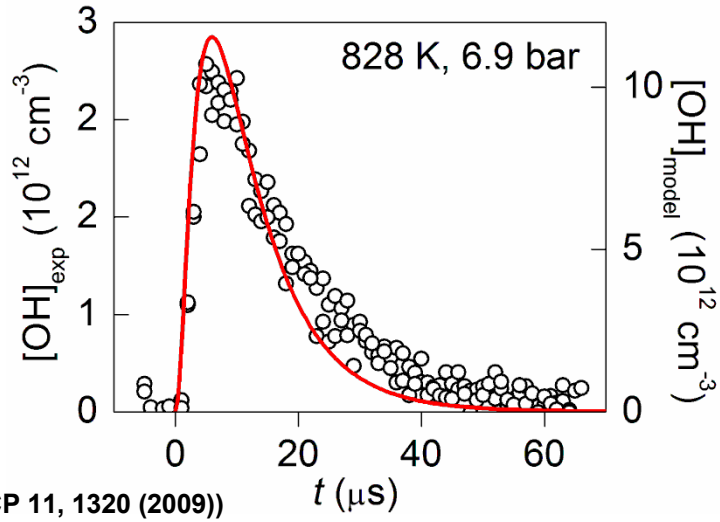
Cyclohexane Oxidation Shows Formally Direct Channels Even at High Pressure

- **High-pressure experiments are modeled using stationary points validated at low pressure**
  - **Formally-direct pathways**
  - **Correct shape of [OH]**
- **Amplitude is in substantial disagreement at low T!**



- **Adjusting R + O_2 does not reconcile model & experiment**

Rapid QOOH + O_2 branching reaction reconciles all data



(Fernandes et al., PCCP 11, 1320 (2009))

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$QOOH + O_2$ Is a Crucial and Mysterious Area of Ignition Chemistry

Reactions of QOOH with O_2, though central to low temperature combustion, are poorly characterized

Calculations exist for a few $QOOH + O_2$ reactions

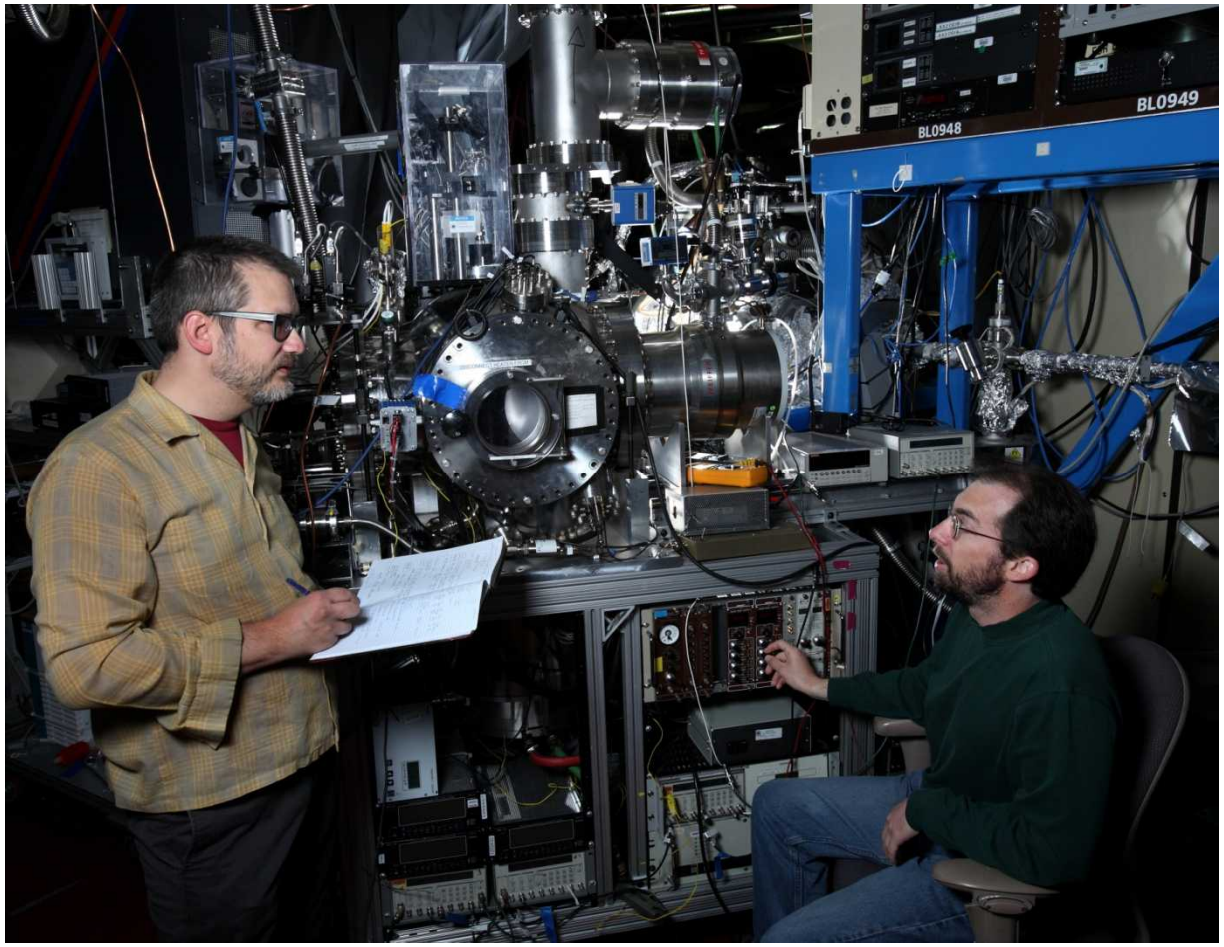
QOOH has never been directly seen

The characterization of the "second O_2 addition" is probably the most important unsolved problem in autoignition chemistry

Increased pressure *accentuates* QOOH chain-branching

Low- and intermediate-temperature heat release often increases for boosted engine operation

Although HO_2 and OH Are Important, Measuring Two Products Isn't 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)

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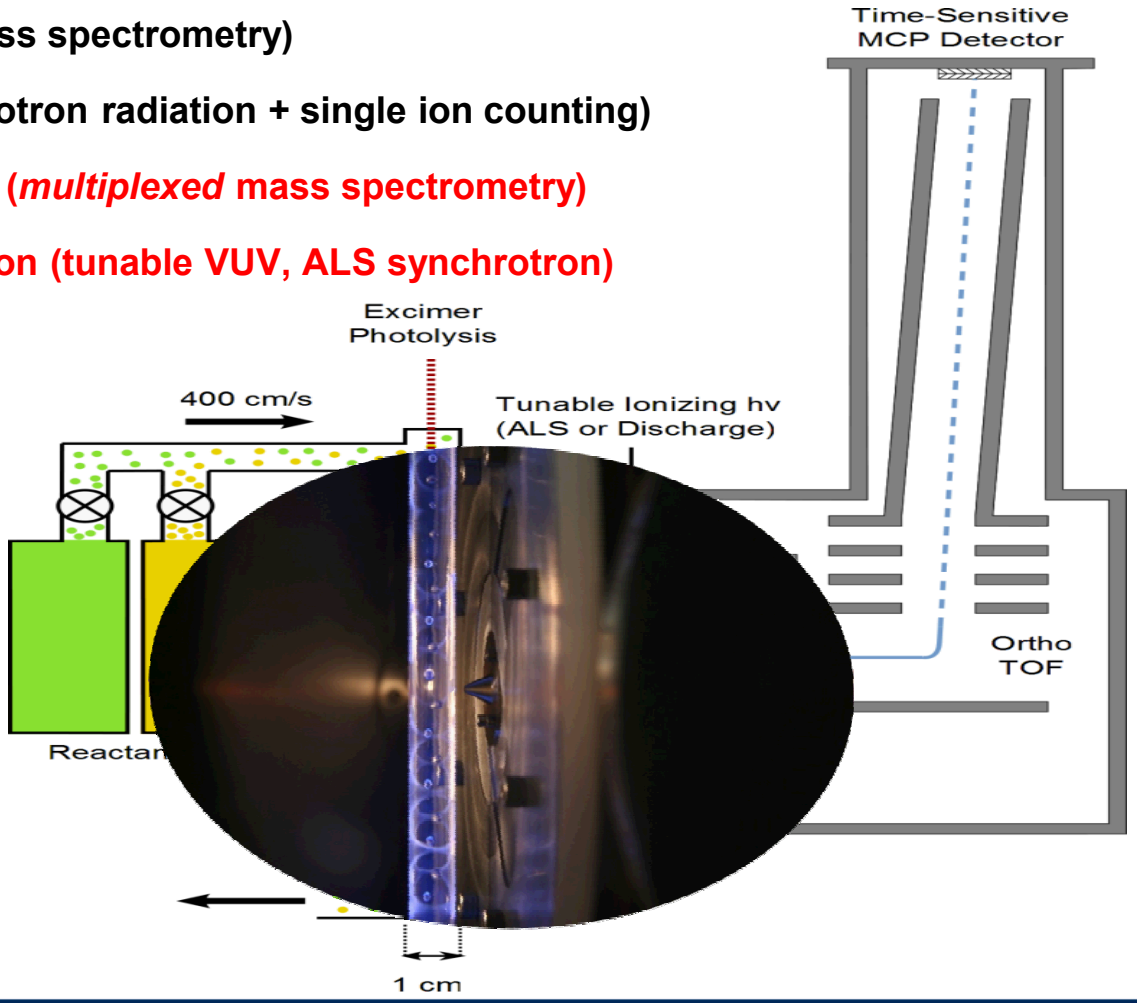
Laser Photolysis Reactor is Coupled to Time-of-Flight Mass Spectrometer

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)



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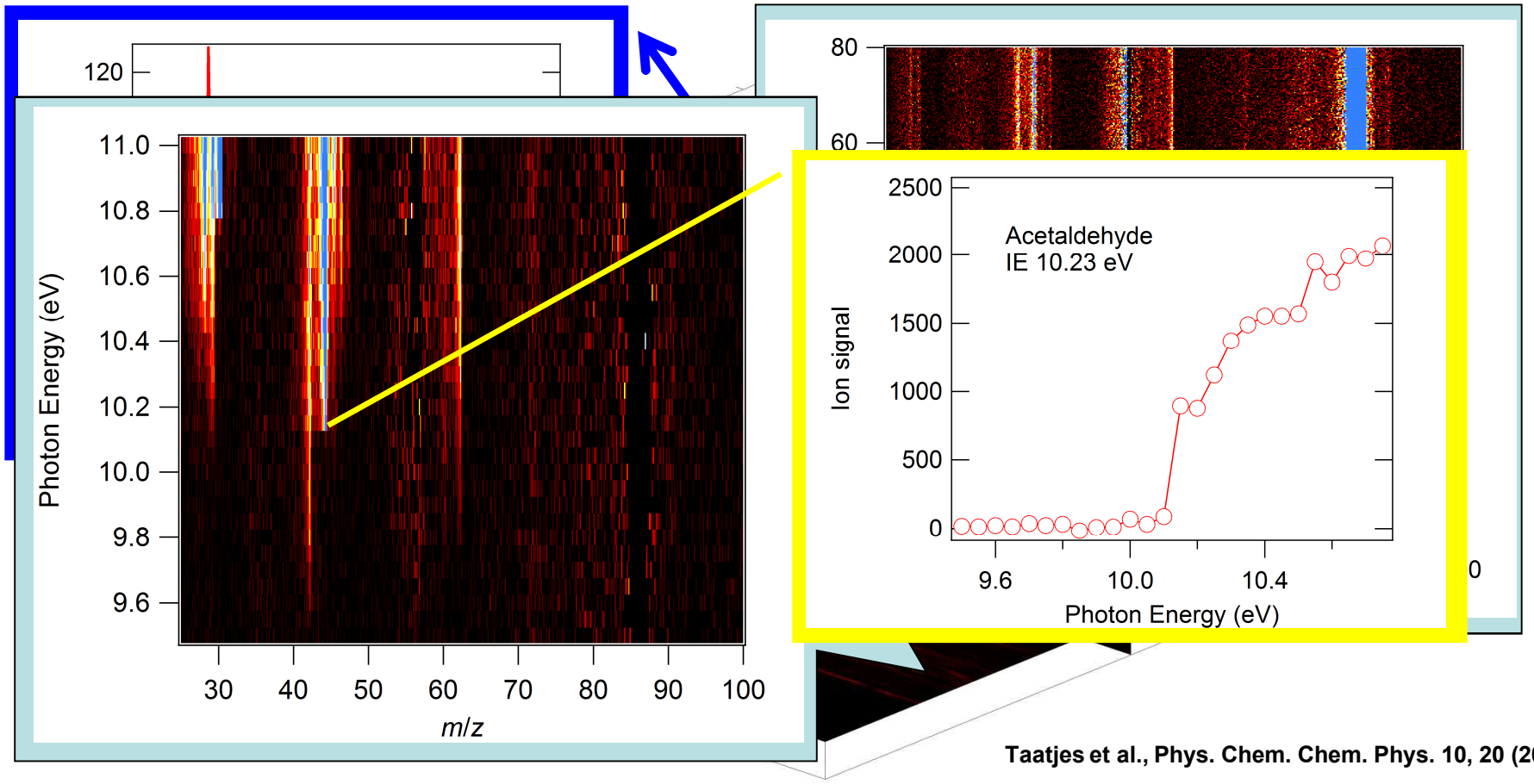
Kinetic Data is Acquired as a Function of Time, Mass, and Photoionization Energy



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

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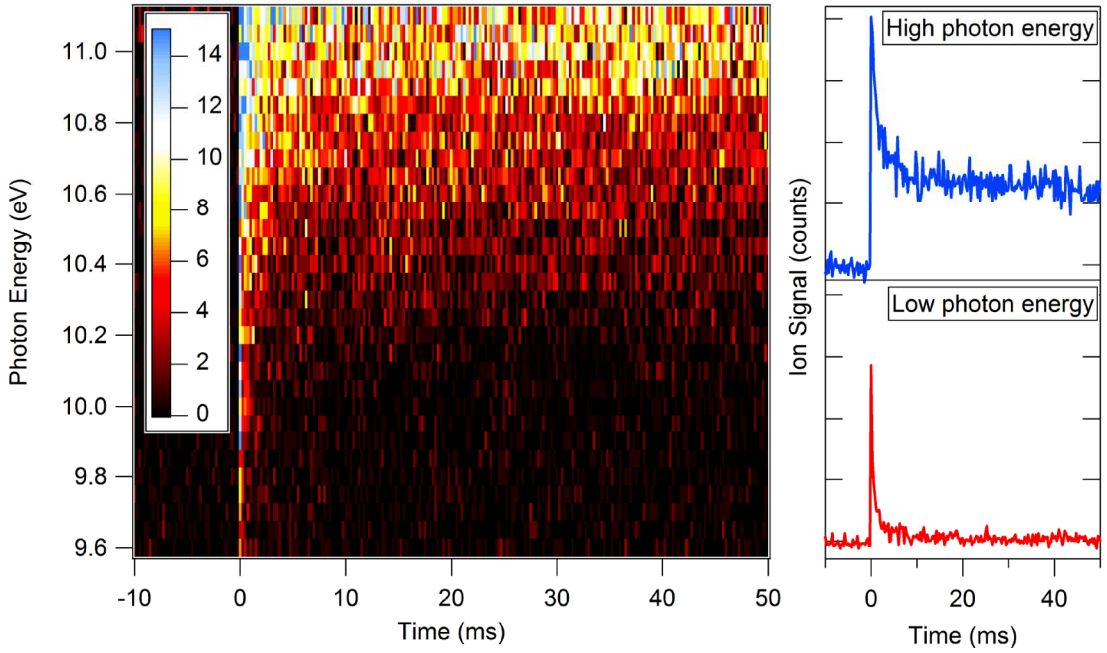
Time Resolution Permits Kinetic Discrimination of Ionization Processes



Reaction of ethyl with O_2 produces ethylperoxy radicals

Photoionization of C_2H_5OO is dissociative to form $C_2H_5^+ + O_2$

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**

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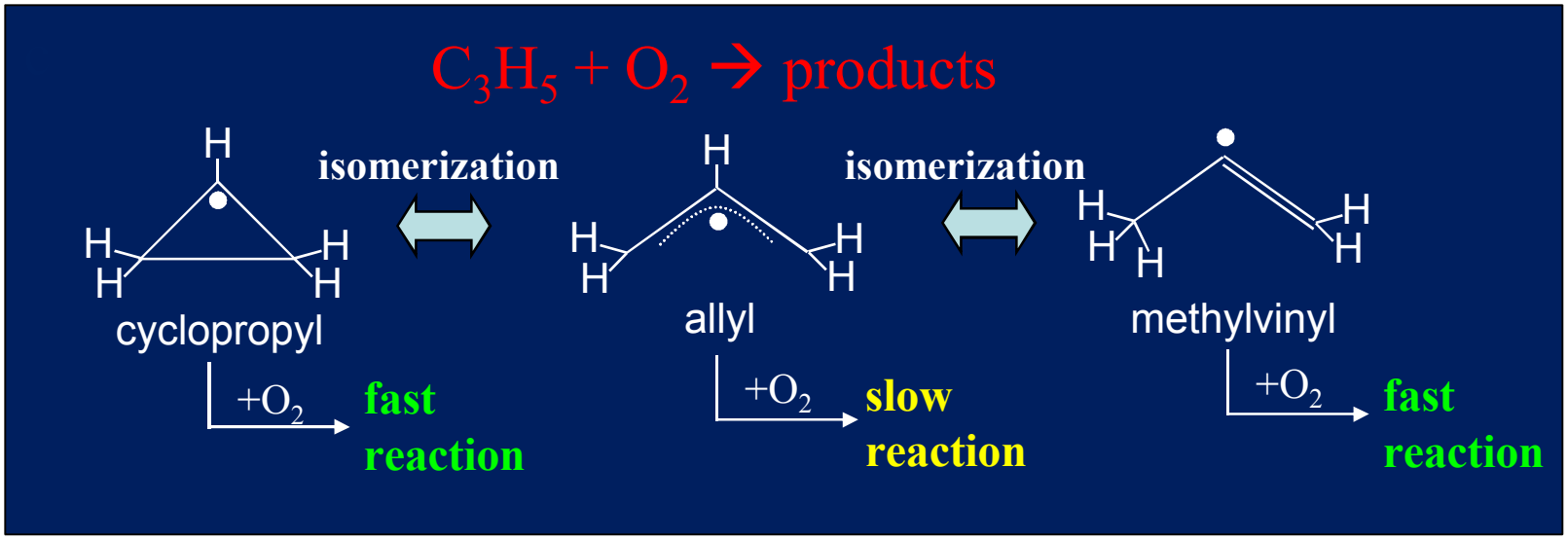
Full Characterization of Key Reactions Requires Isomer-Specific Kinetics

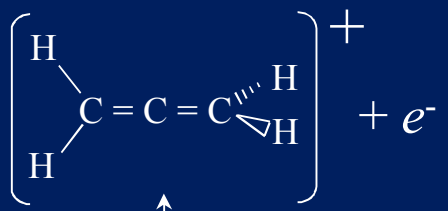
- Isomer-resolved product distributions are sensitive probes of reaction mechanisms.
- Different isomers may have vastly different reactivity, steering downstream chemistry in different directions.



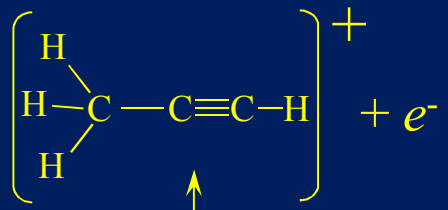
Distinguishing Isomers Is Possible by Photoionization Mass Spectrometry

Each isomer of a chemical usually has a distinct ionization energy, and a characteristic shape of its photoionization curve (Franck-Condon).

Potential Energy (eV)

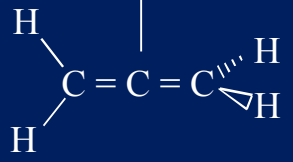


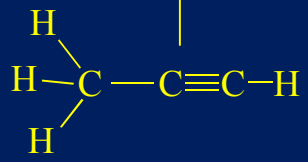
C_3H_4



IE=9.692 eV ($\lambda = 127.9$ nm)

IE=10.36 eV ($\lambda = 119.7$ nm)





Allene
$\Delta H_f = +47.4$ kcal/mol

Propyne
$\Delta H_f = +44.32$ kcal/mol

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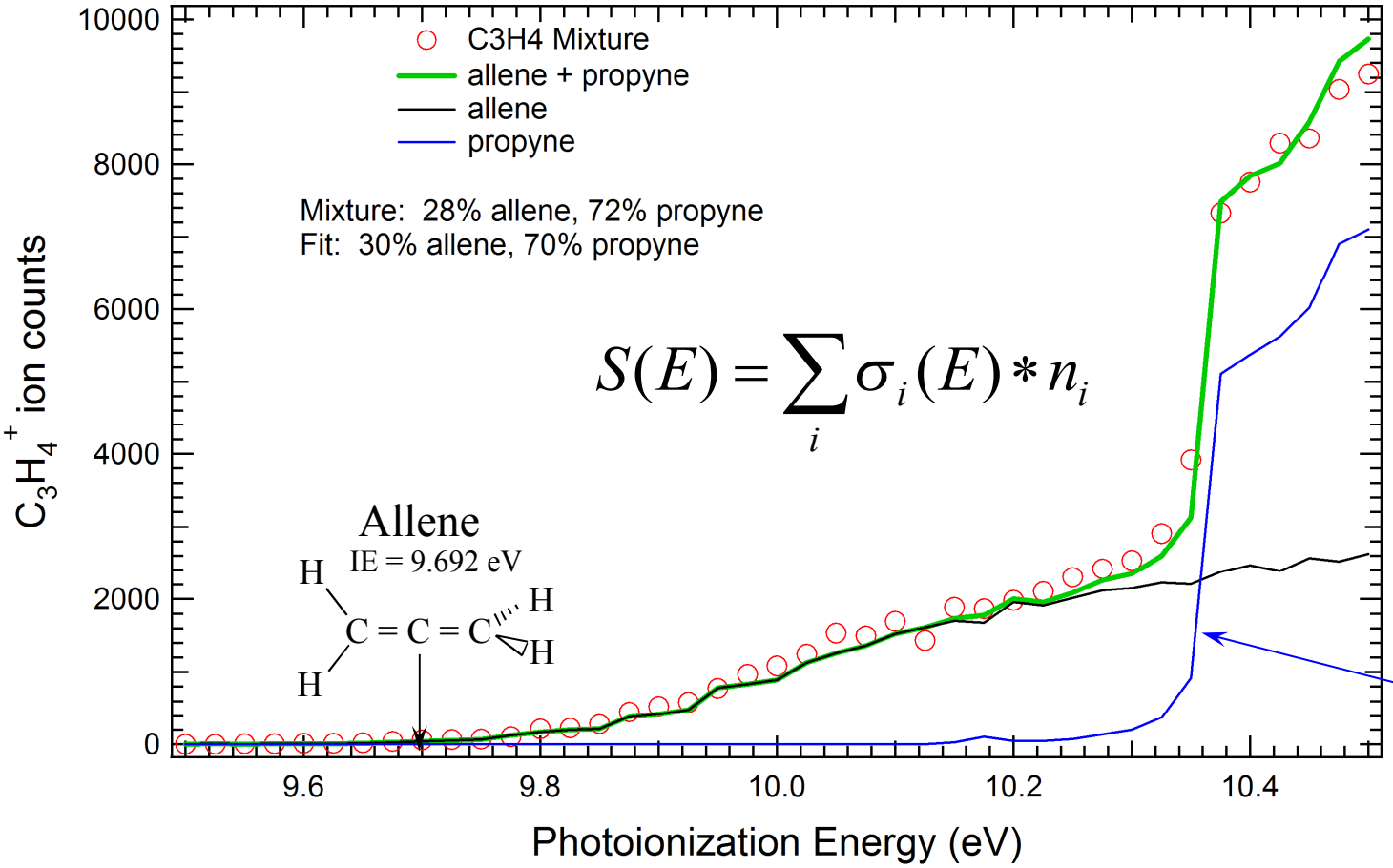
Photoionization Efficiency Spectra Can Give Quantitative Isomer Ratios



From PIE curves we can extract the proportion of each isomer present

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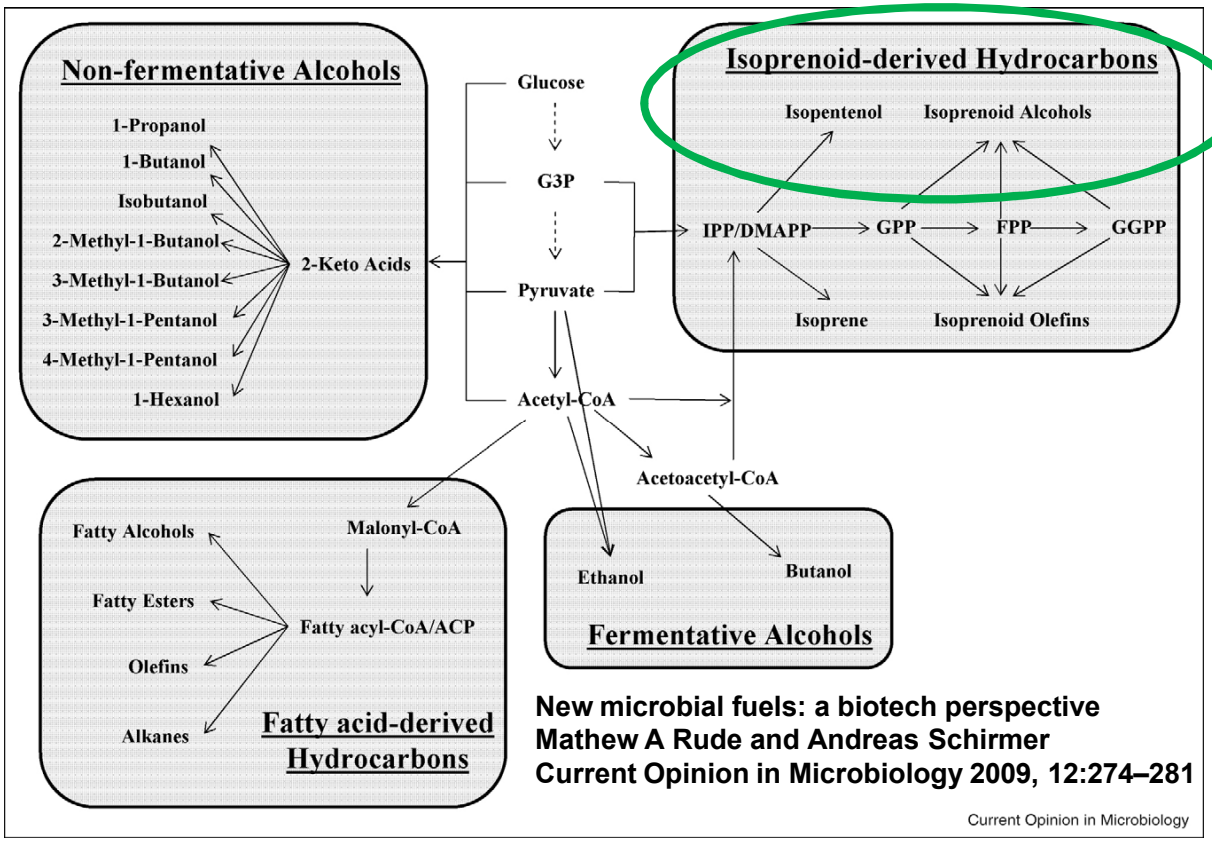
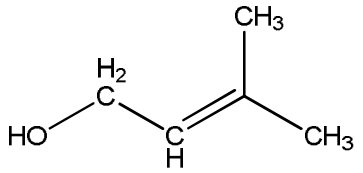
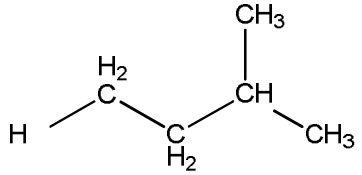
What Can These Tools Tell Us About Autoignition Chemistry of Biofuels?



New microbial fuels: a biotech perspective
Mathew A Rude and Andreas Schirmer
Current Opinion in Microbiology 2009, 12:274–281



prenol



isopentanol

Isoprenoid alcohols are a promising basis for biofuels
What is their autoignition chemistry like?
Consider the effects of OH group

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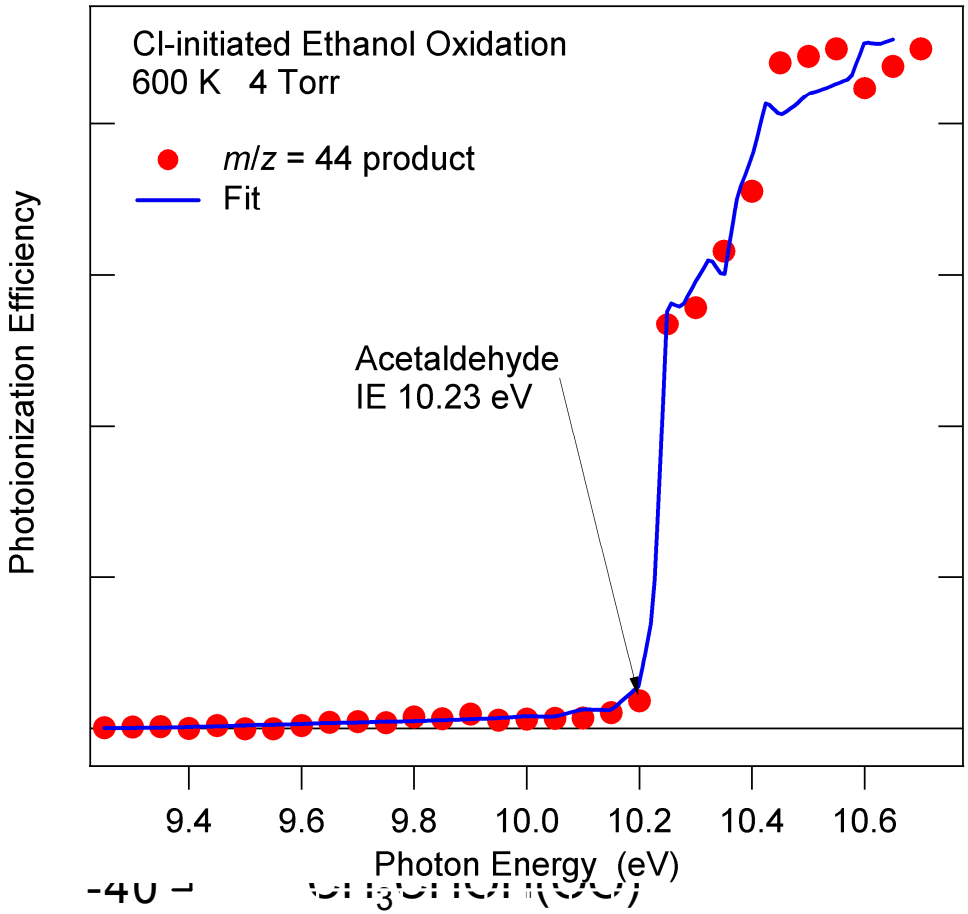
Ethanol Gives a Simple Example of Alcohol Ignition Chemistry

- Two initial radicals can be formed



1-hydroxyethyl + O_2 produces HO_2 + acetaldehyde

OOH)

CH_2CHOH + HO_2

J. Zádor et al., Proc. Combust. Inst. 32, 271-277 (2009)

CH_2CHOH + OH

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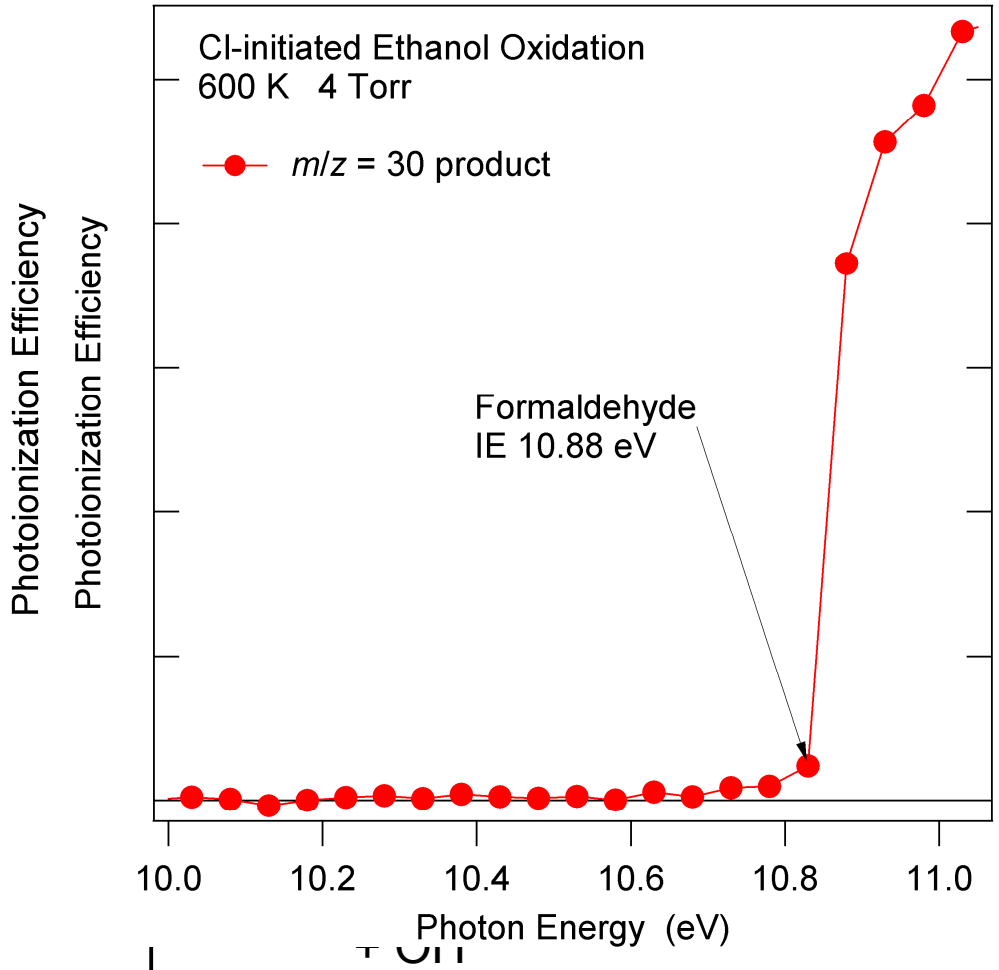
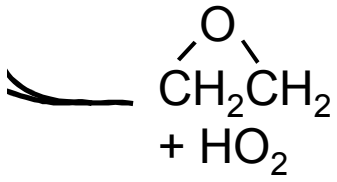
Ethanol Gives a Simple Example of Alcohol Ignition Chemistry



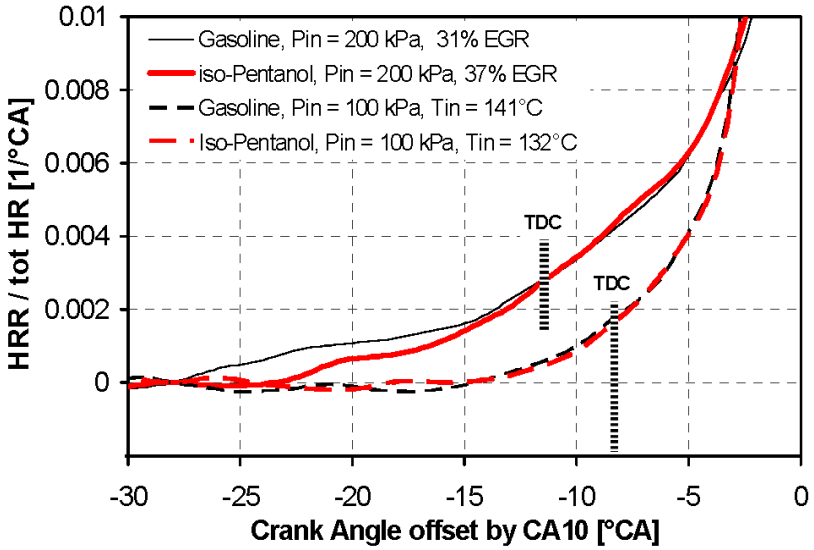
2-hydroxyethyl + O_2 produces HO_2 and OH

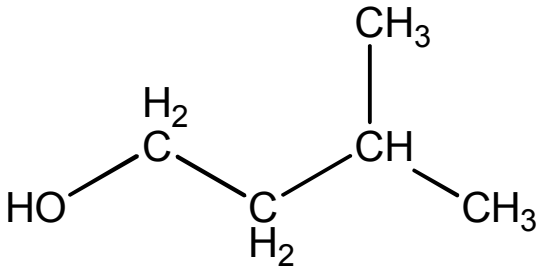


2 CH_2O + OH

J. Zádor et al., Proc. Combust. Inst. 32, 271-277 (2009)

Isopentanol May Combine Characteristics of Alcohol and Alkane





Isopentanol shows gasoline-like intermediate-temperature heat release (ITHR) in HCCI engine experiments (**Yi Yang, John Dec, et al.,** SAE technical paper **2010-01-2164**).

ITHR increased by boost – much greater ITHR than ethanol

Synchrotron investigations show rich chemistry

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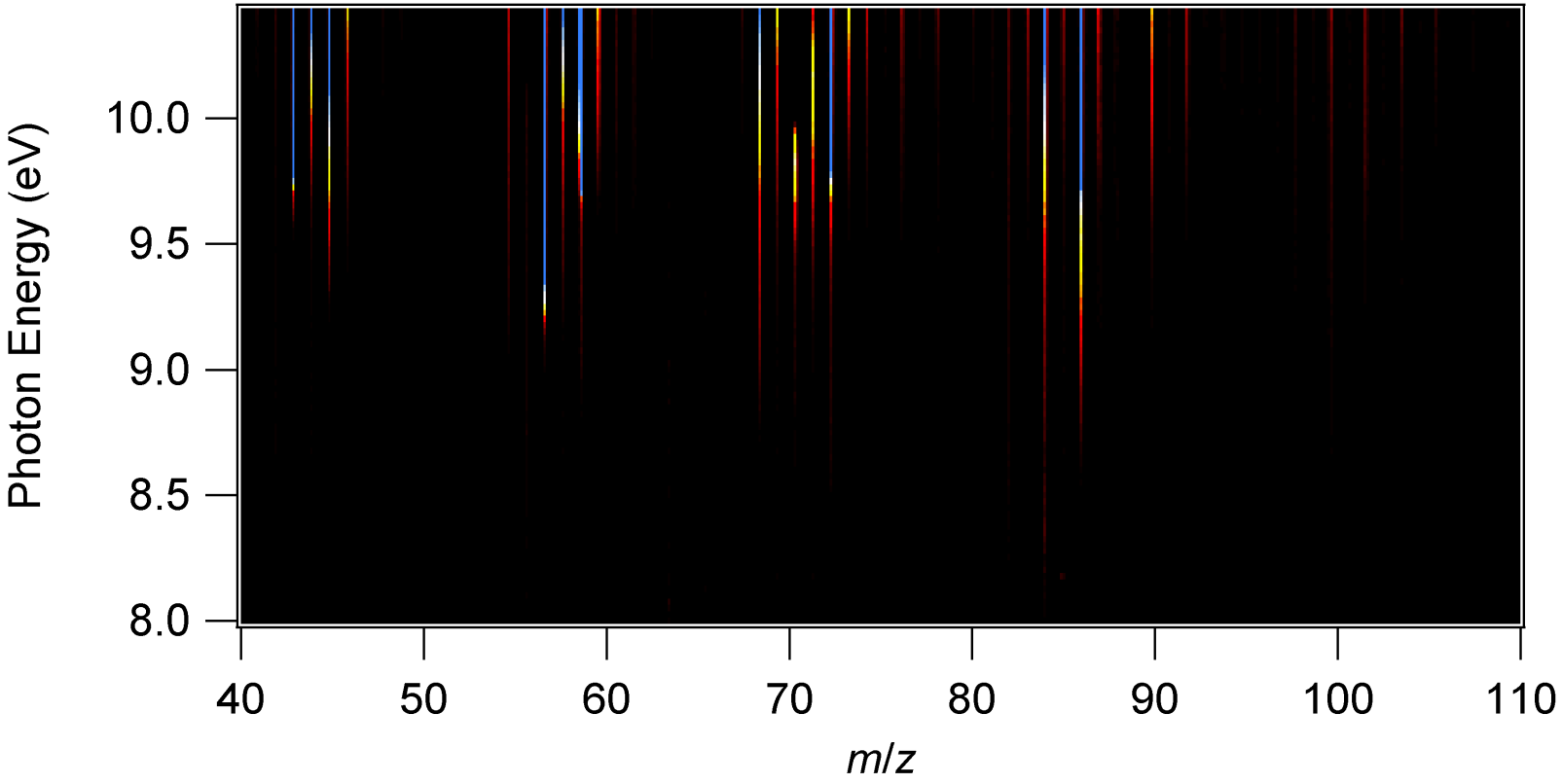
Cl-initiated Isopentanol Oxidation Shows Many Product Pathways



- Primary and secondary reaction products are observed
- C-C bond scission products and oxygen addition products

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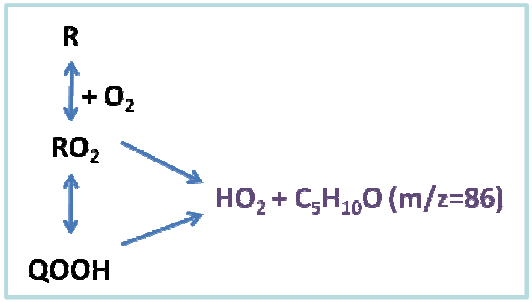
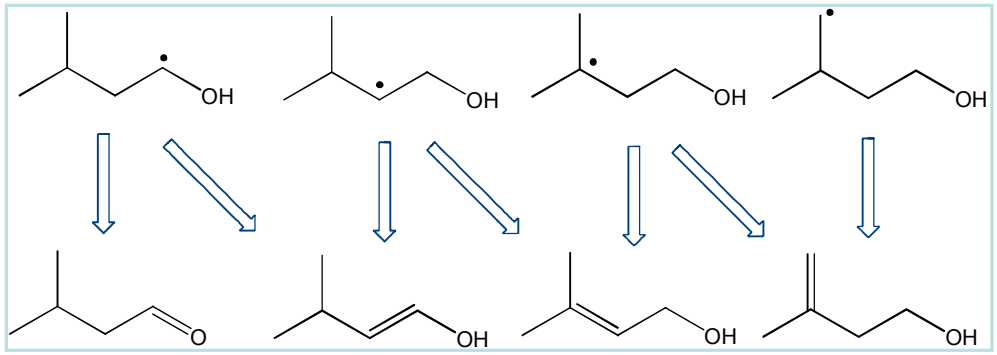
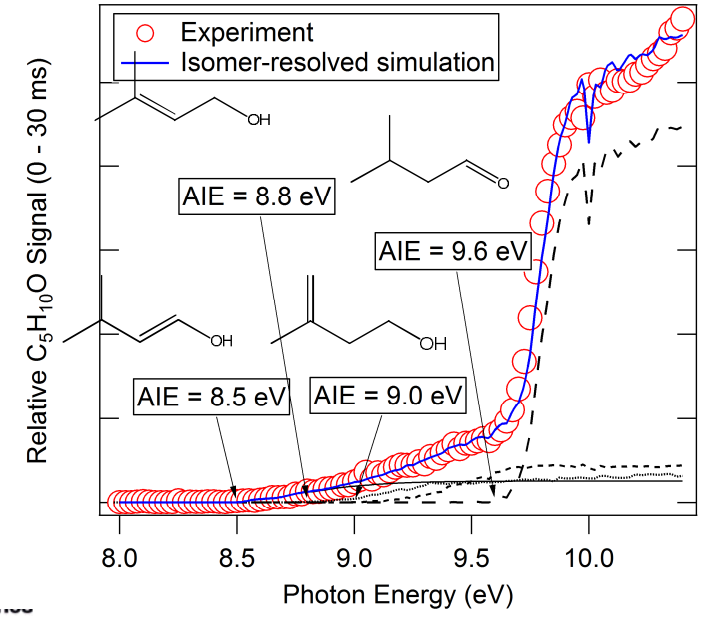
All Possible $C_5H_{10}O$ (m/z = 86) Isomers Contribute to HO_2 + $C_5H_{10}O$ Formation

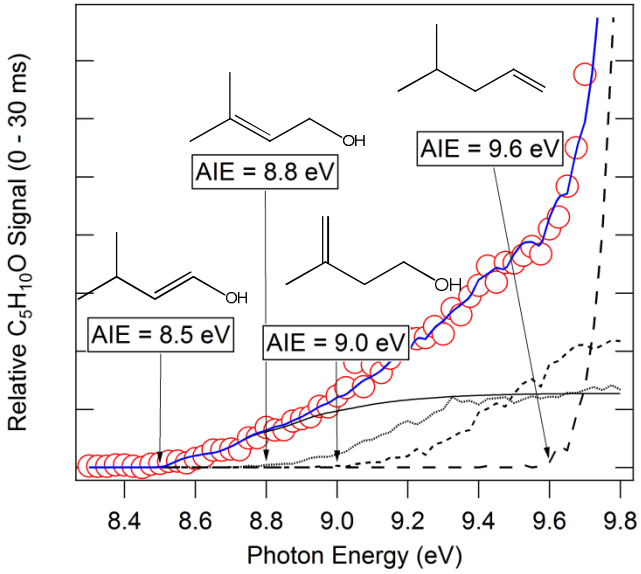
- Pathways:





- Photoionization efficiency curve of $C_5H_{10}O$ at 550K:





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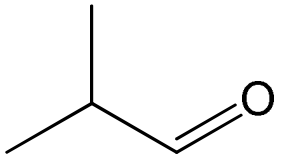
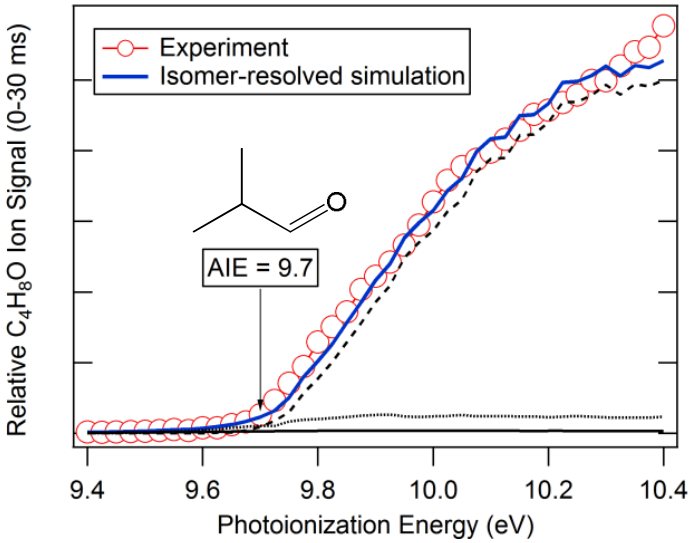
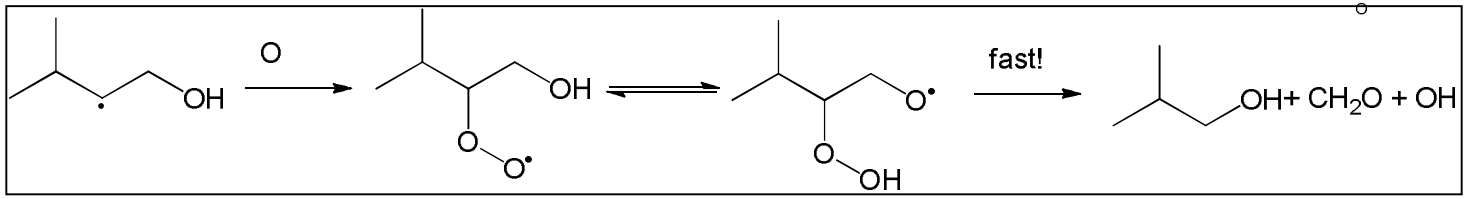
C-C Bond Fission Is Linked to Weakly Bound QOOH and Formation of OH

- m/z = 72 (C_4H_8O) contains mostly methylpropanal



- Possible formation pathway





- The corresponding channel is also present in the oxidation of **ethanol** (Zador *et al.*, Proc Combust. Inst. 2009) and **1-butanol** (unpublished results)

→**Is this pathway a general feature for alcohol oxidation?**

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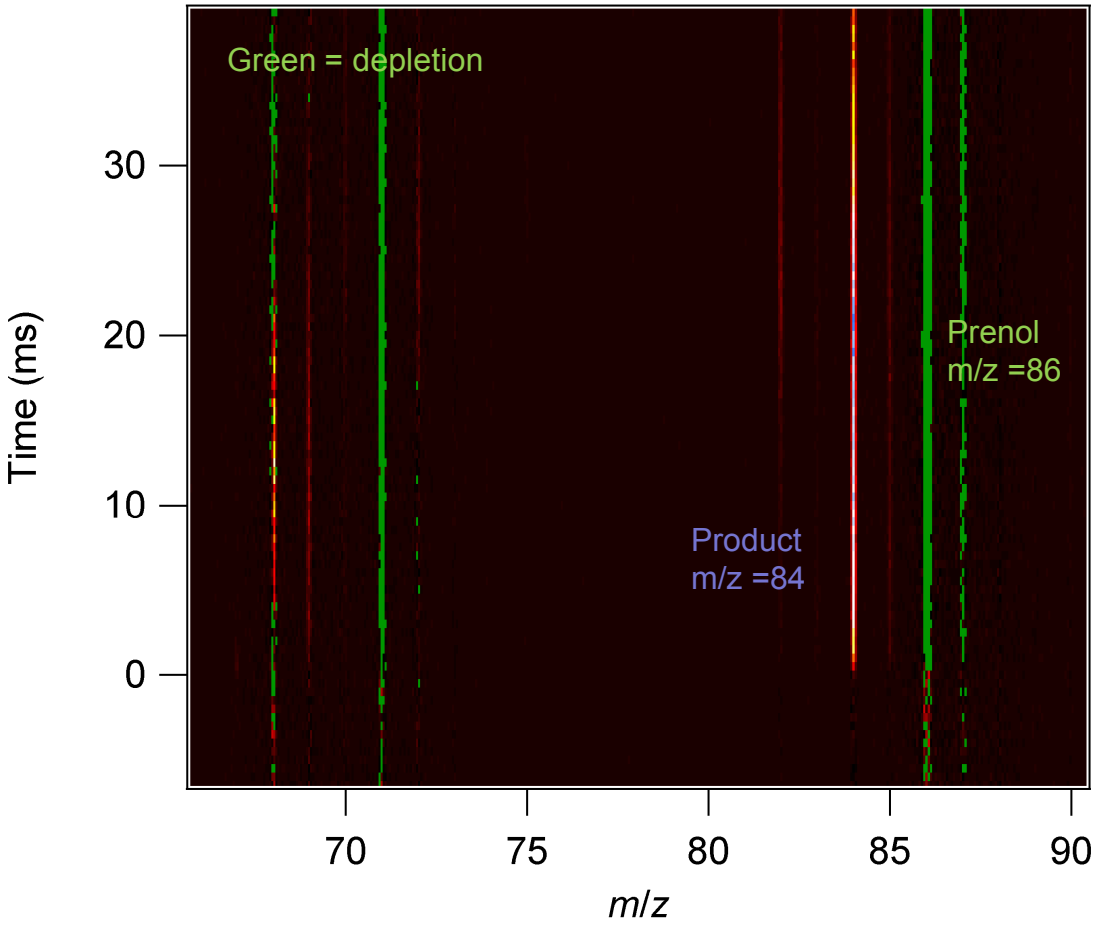
Products of Low-Temperature Cl-Initiated Prenol Oxidation Appear Far Simpler



- Cl-initiated prenol oxidation forms almost exclusively product with loss of 2 H atoms
- Presumably correlated with HO_2 formation
- More than one possible isomer at m/z=84.
- Isomeric products can tell us about the reactivity of prenol

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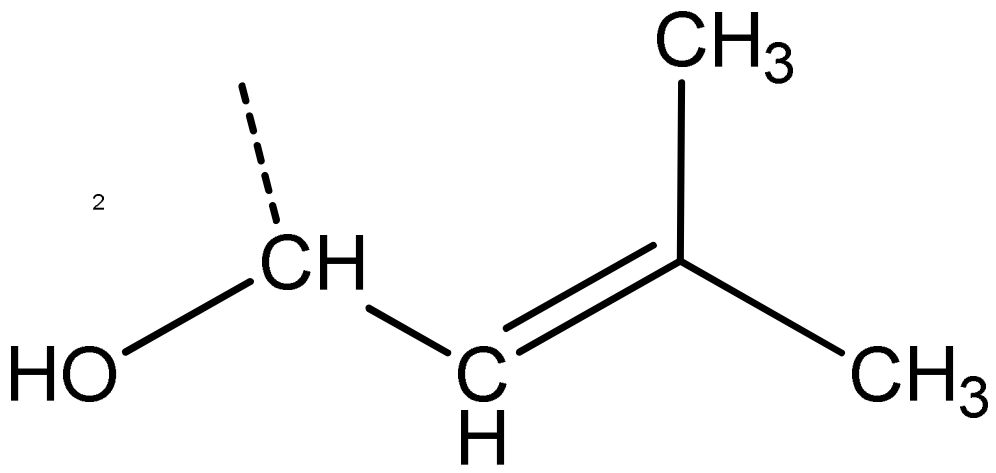
Weak Allylic C-H Bonds in Prenol May Shape Its Oxidation Chemistry

- Eight of the nine C-H bonds in prenol are allylic
- Allylic radicals are relatively unreactive with O_2
- The α C-H bond is doubly weakened – next to an OH *and* allylic



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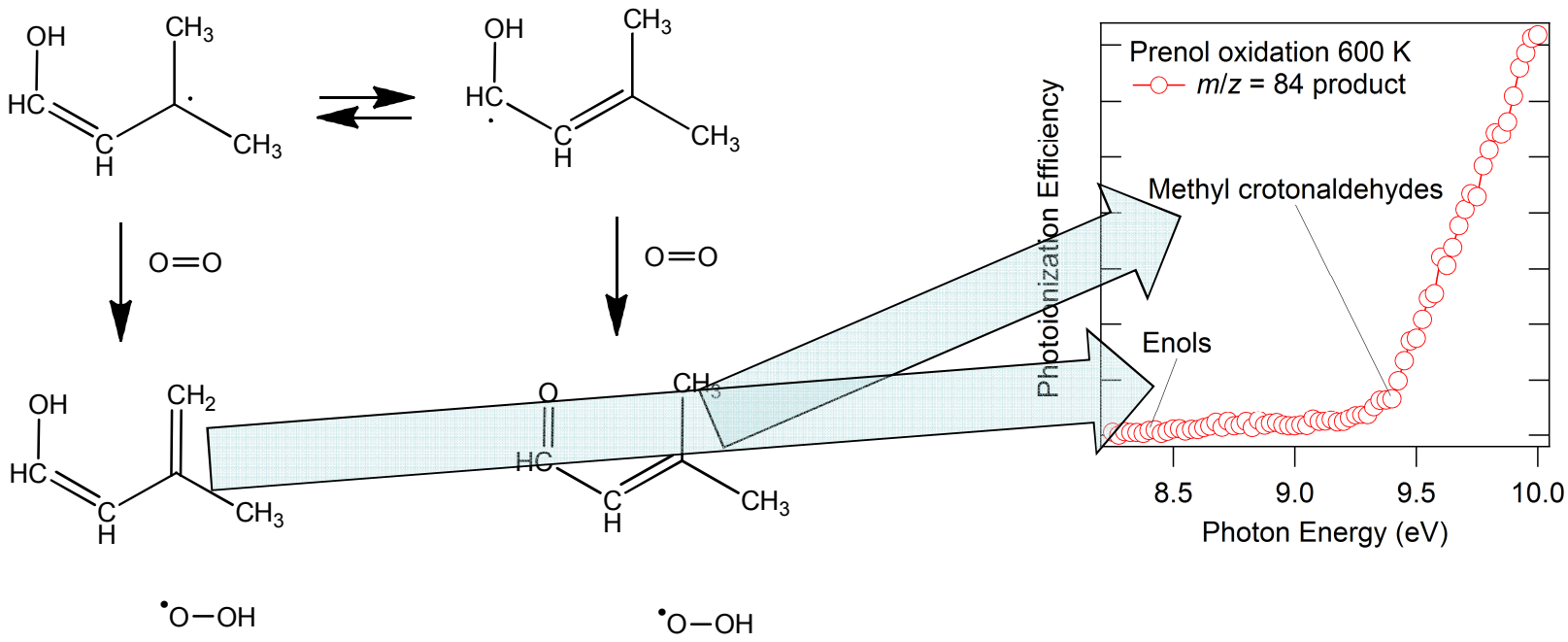
Products Show Low-Temperature Prenol Oxidation Occurs via α-Hydroxy Radical



Abstraction from the α-position gives a radical with two resonance structures, with the 1-hydroxy form likely favored

In 1-hydroxyethyl + O_2 the barrier to acetaldehyde formation is low

Analogous aldehyde product is dominant in prenol reaction

Enol can arise from other resonance structure

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Combustion Chemistry Is Important in a Changing Fuel Environment

- **New fuels bring new challenges**
  - Pressure-dependence is important at engine pressures – not in the high-pressure limit
  - QOOH reactions may be accentuated at high pressure
  - Oxygenated biofuels can have distinctly different reactivity because of the effect of oxygen on thermochemistry -- even allylic 1-hydroxy radicals appear to react readily
- **Comparison of detailed experiment and theory can reveal mechanisms**
- **Fundamental science is important for future transportation**

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

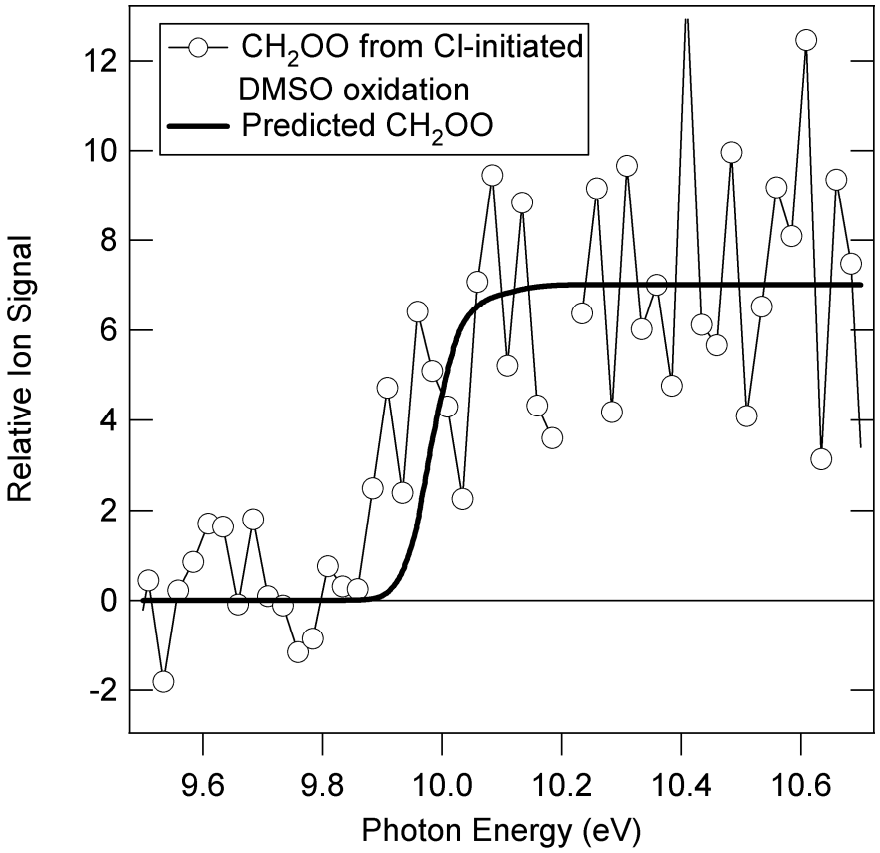
Tunable Synchrotron Photoionization Can Identify Novel Isomeric Products

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))



No one ~~has~~ had ever seen a gas phase Criegee intermediate
Taatjes et al., J. Am. Chem. Soc. 130, 11883 (2008)

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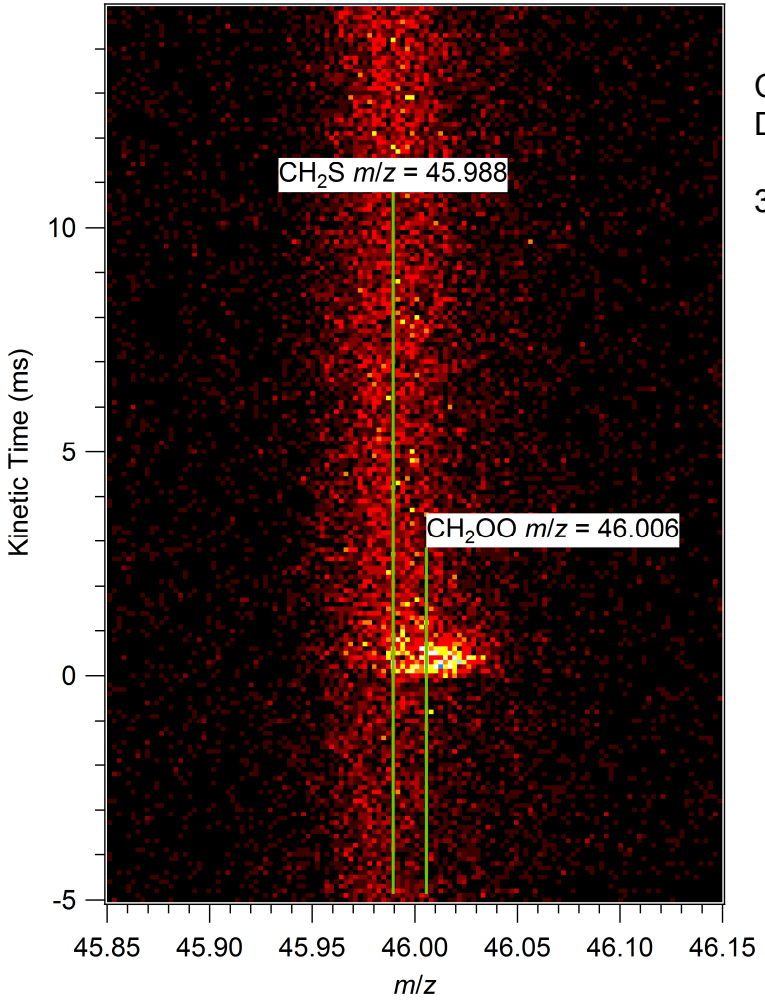
Orthogonal Acceleration Time-of-Flight Definitively Resolves CH_2OO and CH_2S

- **CH_2S and CH_2OO masses differ by about 1 part in 2600 – sufficient to distinguish in time-of-flight**
- **Criegee intermediate is consumed rapidly by homogeneous and heterogeneous reactions**
- **Increasing the CH_2OO lifetime (e.g., wall coatings, changes in reaction conditions) will enable *direct* kinetics measurements**



Cl-initiated DMSO oxidation

300 K, 8 Torr

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Will 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

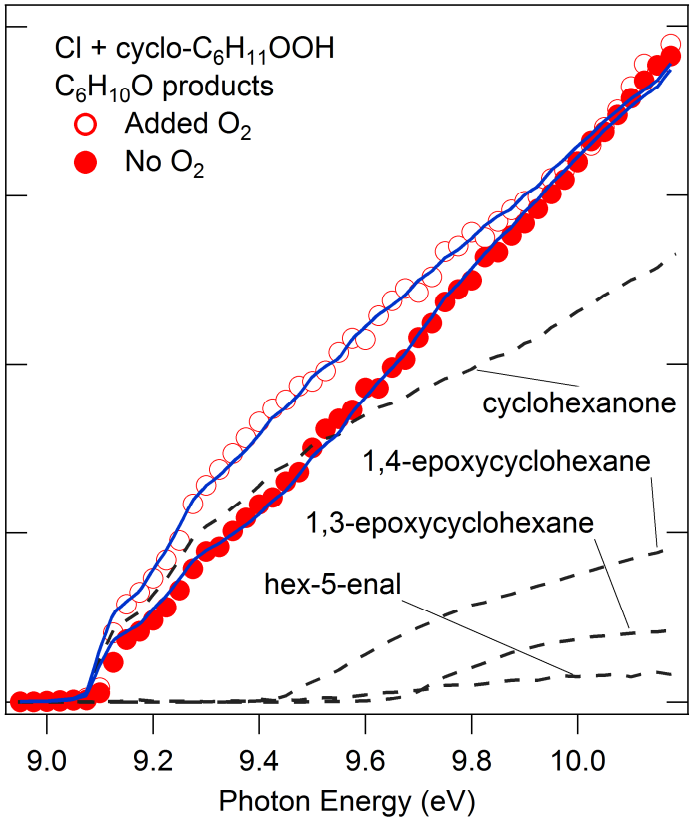
Problem is to make enough!

- Cl + alkylhydroperoxide reactions make QOOH: e.g.,

  $Cl + (CH_3)_3COOH \rightarrow (CH_3)_2C(CH_2)OH + HCl$

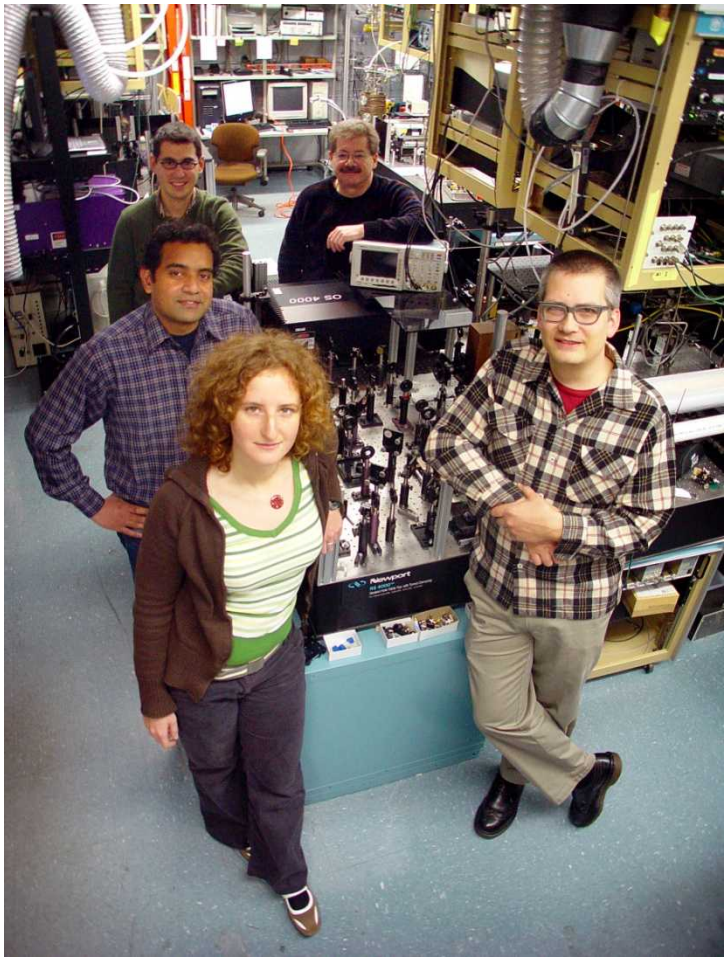
  $(CH_3)_2C(CH_2)OH \rightarrow$ 2,2-dimethyloxirane + OH

- Reaction with O_2 competes with dissociation – forms other products
- Cl + cyclohexylhydroperoxide forms several isomers that react differently with O_2



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

Acknowledgements



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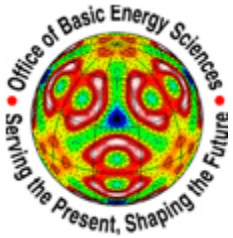

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