COMBUSTION RESEARCH FACILITY

SAND2014-17496PE

# Decomposition Pathways and Product Formation from R + $O_2$ Reactions in Low-Temperature Oxidation of 2,5-dimethylhexane

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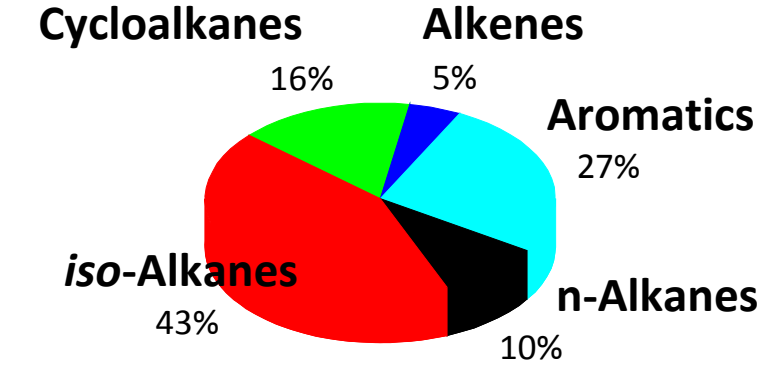
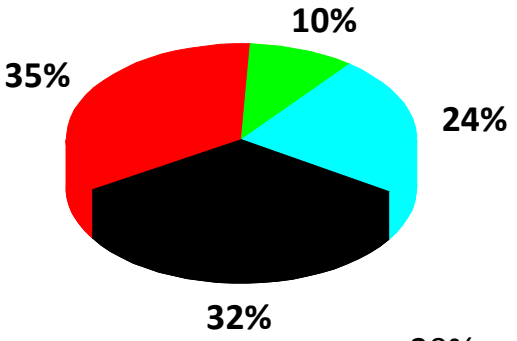
**October 9, 2014**

# Conventional Transportation Fuels Contain Different Distributions of Hydrocarbon Classes and Species

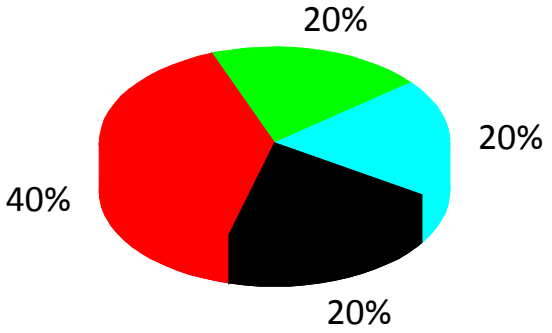
**Gasoline**
- High octane number
- Short-chain alkanes
- Highly branched species
- Aromatics




**Diesel Fuel**
- High cetane number
- Long-chain alkanes
- Limited branched species
- Aromatics




**Jet Fuel**
- Long-chain alkanes
- Limited branched species
- Aromatics



# EtOH, Methyl Esters Impose Blending Limits for Practical Engines, Fuel-Transport Infrastructure

**Gasoline**
- High octane number
- Short-chain alkanes
- Highly branched species
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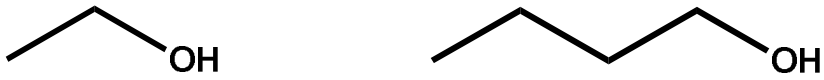
**Diesel Fuel**
- High cetane number
- Long-chain alkanes
- Limited branched species
- Aromatics

**Jet Fuel**
- Long-chain alkanes
- Limited branched species
- Aromatics

**Comparison of Alcohol Properties to Gasoline**

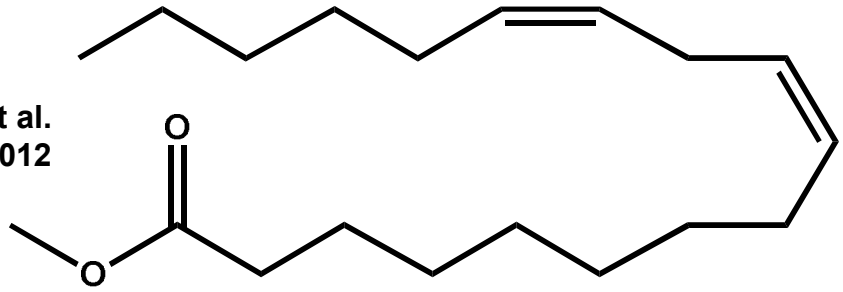
| Fuel | Energy Content ($MJ \cdot L^{-1}$) | Octane Number (MON) | Viscosity (15 °C) ($mPa \cdot s$) |
|---|---|---|---|
| Gasoline | 32.0 | 84 – 93 | 0.700 |
| Ethanol | 19.6 | 102 | 1.337 |
| 1–Butanol | 29.2 | 78 | 3.515 |




**Comparison of Biodiesel Properties to Diesel**

| Fuel | Density ($g \cdot mL^{-1}$) | Cetane Number | Viscosity ($mPa \cdot s$) |
|---|---|---|---|
| Diesel | 0.85 | 40 – 55 | 1.3 – 4.1 |
| Biodiesel | 0.88 | 48 – 65 | 4.0 – 6.0 |

Peralta-Yahya et al.
*Nature*, 2012



# “Ideal” Biofuels Share Similar Fuel Properties with Conventional Hydrocarbons

**Gasoline**
- High octane number
- Short-chain alkanes
- Highly branched species
- Aromatics

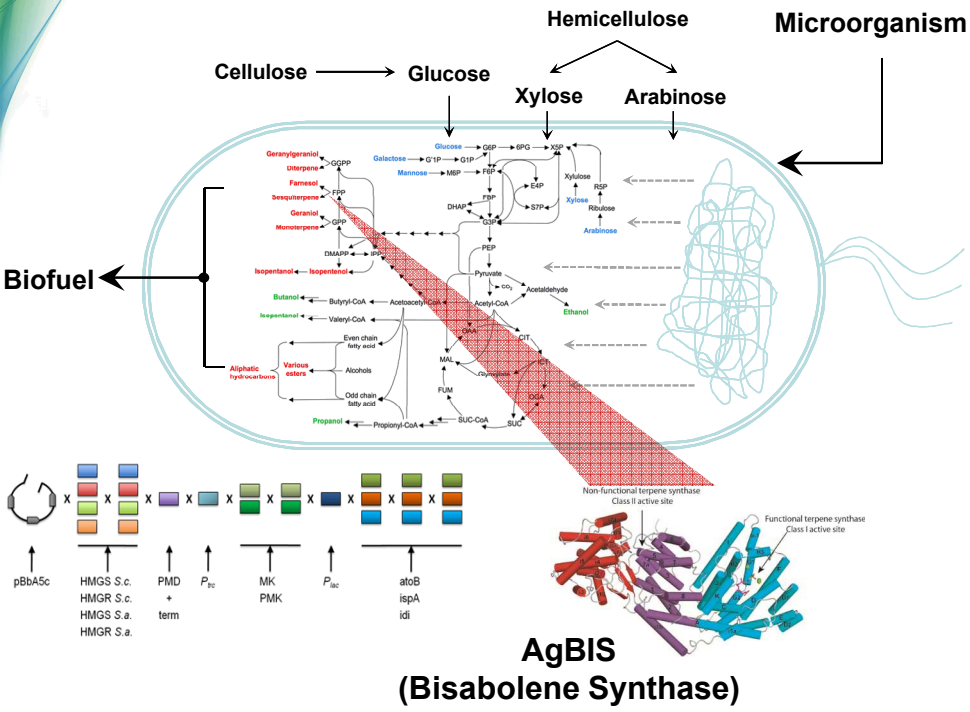
**Diesel Fuel**
- High cetane number
- Long-chain alkanes
- Limited branched species
- Aromatics

**Jet Fuel**
- Long-chain alkanes
- Limited branched species
- Aromatics

Ideal Biofuel Target:

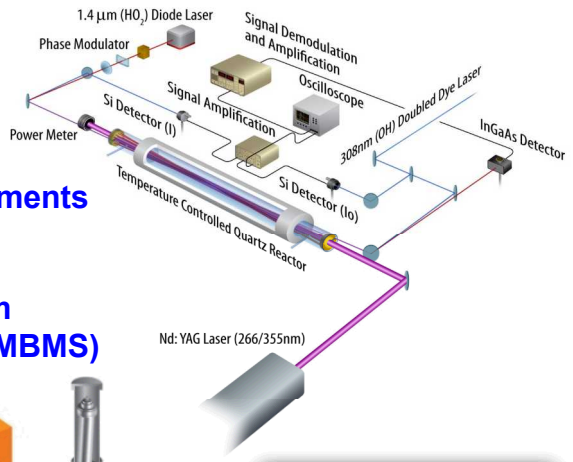
Biofuels with **properties similar to petroleum-based fuels** for all engines types

# Joint Effort Towards Synthesis and Combustion Characterization of "Ideal" Biofuels



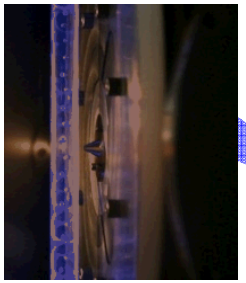


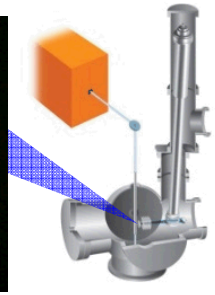

AgBIS
(Bisabolene Synthase)

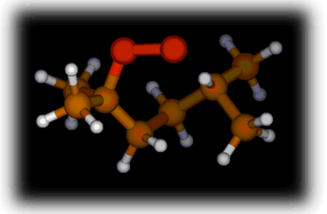



OH, $HO_2$ Measurements

Molecular Beam
Mass Spectrometry (MBMS)







Sandia National Laboratories

UNIVERSITY OF MICHIGAN

**Joint BioEnergy Institute (JBEI):**
**Synthesis of Advanced Biofuels**

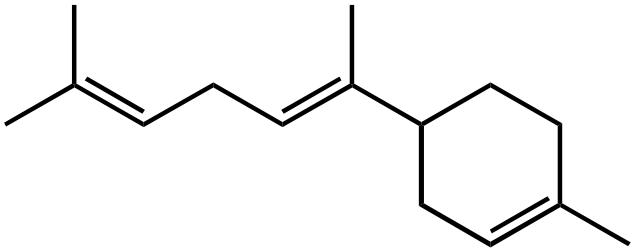
jbei
Joint BioEnergy Institute

**Sandia National Laboratories,**
**University of Michigan:**
**Fundamental Oxidation Measurements,**
***ab initio* Calculations**

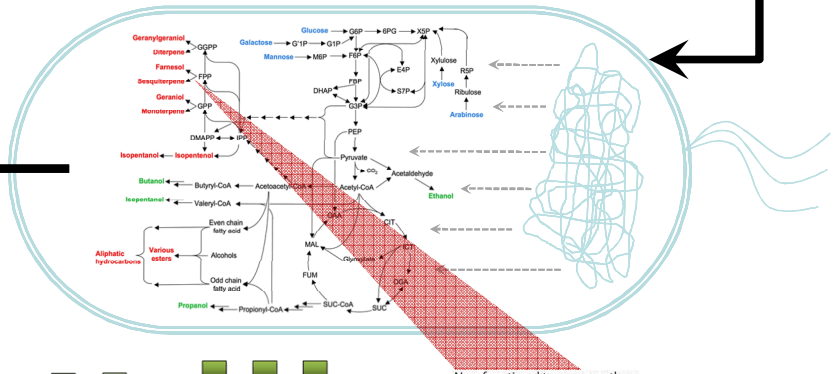
***Direct Feedback* of Experimental Results**
**Supports Further Development of Advanced Biofuels**

# Microbially-Derived Sesquiterpenoid Biofuel Produced with Structural Characteristics of Diesel

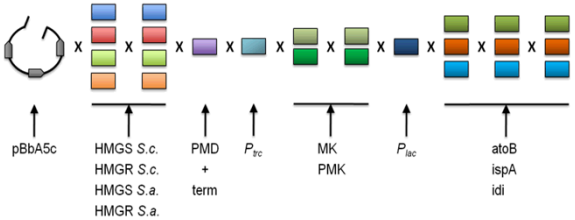
Bisabolene ($C_{15}H_{24}$)

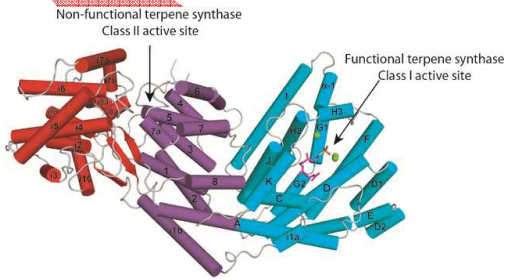


Micro-organism




Hydrogenation




**AgBIS**
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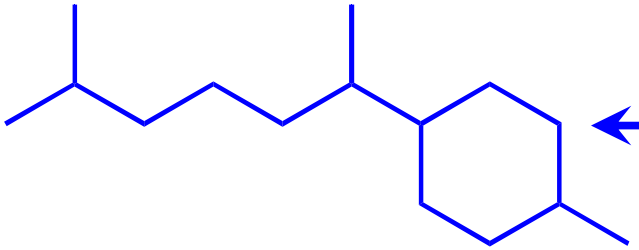


Bisabolane ($C_{15}H_{30}$)

**Biosynthetic Alternative to D2 Diesel Fuel**

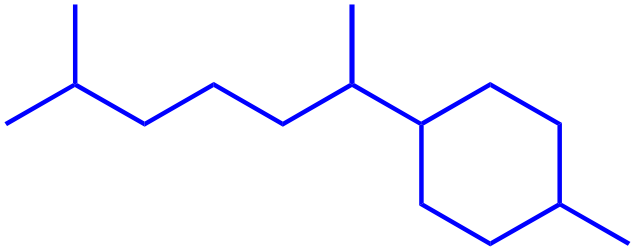
jbei
Joint BioEnergy Institute


Peralta-Yahya, Zhang, del Cardayre, and Keasling, (2012).
Microbial engineering for the production of advanced biofuels. *Nature*, 488, 320.

# Physical Properties of Bisabolane Compatible with Conventional Diesel Fuel

| *Properties* | *D2 Diesel* | *Biodiesel* | *Hydrogenated bisabolene* |
|---|---|---|---|
| Density (g/ml) | 0.85 | 0.88 | 0.82 |
| API Gravity | 35.0 | 29.3 | 41.1 |
| Flash point (°C) | 60–80 | 100–170 | 111 |
| Viscosity ($mm^2/s$) | 1.3–4.1 | 4.0–6.0 | 2.9 |
| Boiling point (°C) | 180–340 | 315–350 | 267 |
| Cloud point (°C) | −35 to 5 | −3 to 15 | <−78 |
| Cetane number | 40–55 | 48–65 | 42 |

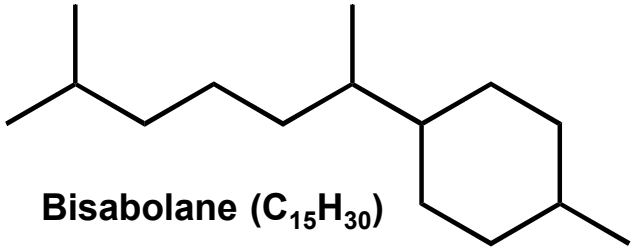
Peralta-Yahya et al.
*Nature Communications*, 2011



Bisabolane ($C_{15}H_{30}$)

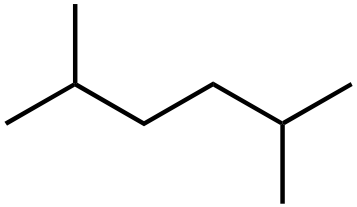
# Component-Centered Approach Towards Oxidation Studies on Microbially-Derived Bisabolane

## Target Molecule

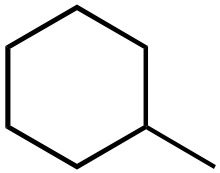


Bisabolane ($C_{15}H_{30}$)

## Component System 1

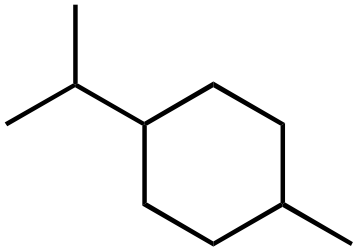


2,5-dimethylhexane



MCH

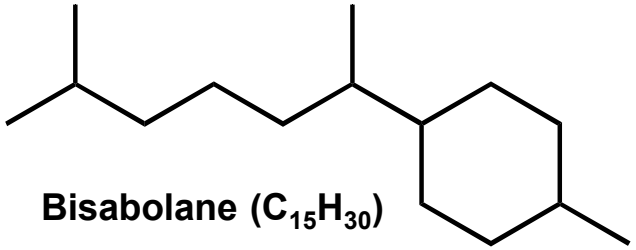
## Component System 2



Limonane

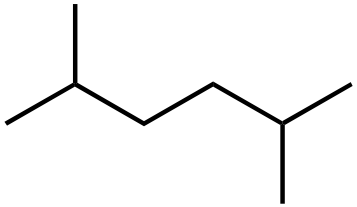
# Component-Centered Approach Towards Oxidation Studies on Microbially-Derived Bisabolane

## Target Molecule



Bisabolane ($C_{15}H_{30}$)

## Component System 1



2,5-dimethylhexane



MCH

## Component System 2



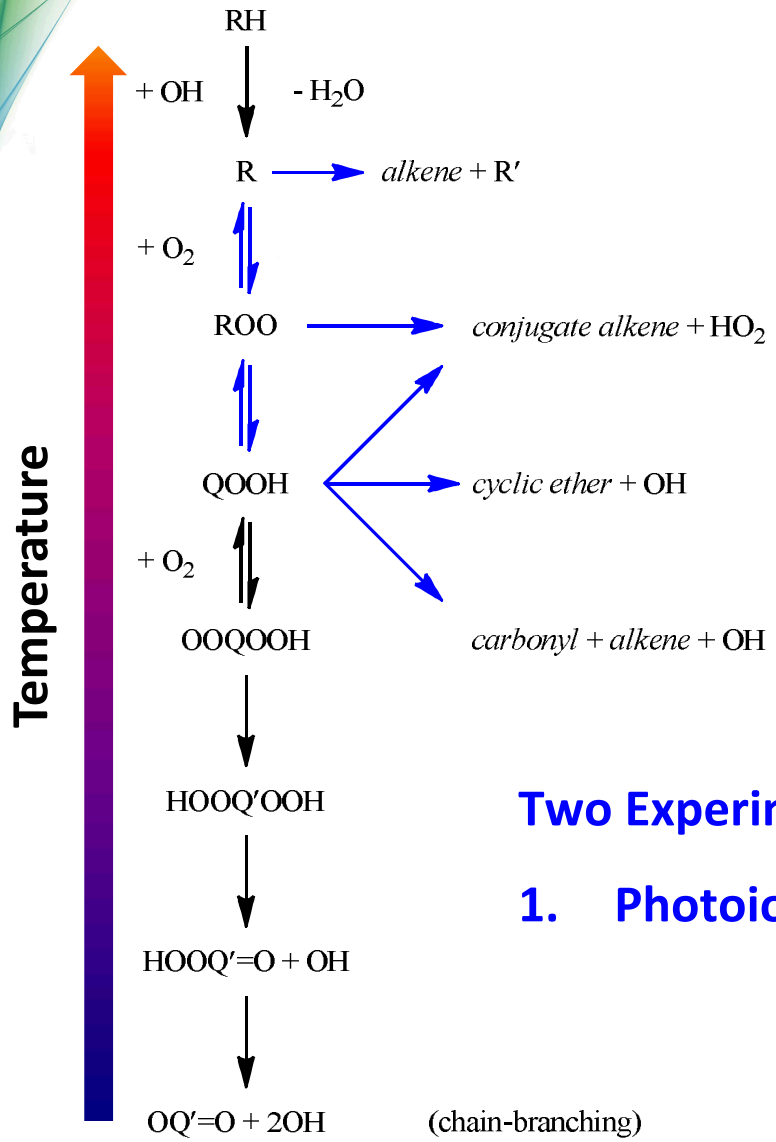
Limonane

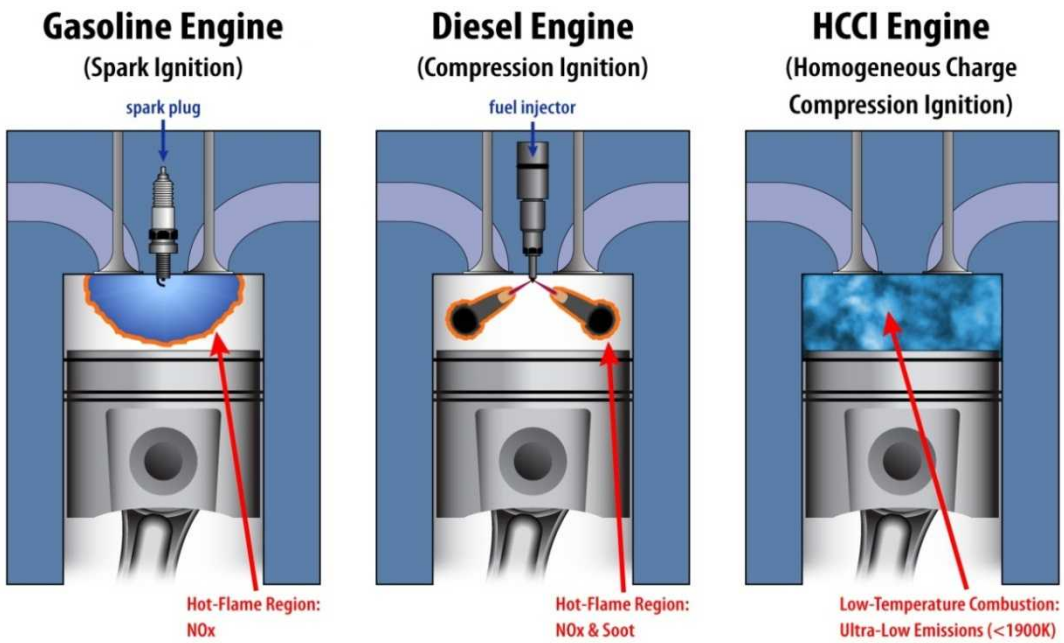
## Objectives

1. Experimental: characterization of low-temperature $RO_2$-related oxidation mechanisms of component analogs (cyclic ether formation, alkene formation, OH, $HO_2$, …)
2. Computational: Quantum chemical, *ab initio* calculations (PES, rate coefficients, …)

# Experimental and Computational Methods

# Characterization of Initial Low-Temperature Oxidation Steps from R + $O_2$ in Hydrocarbons

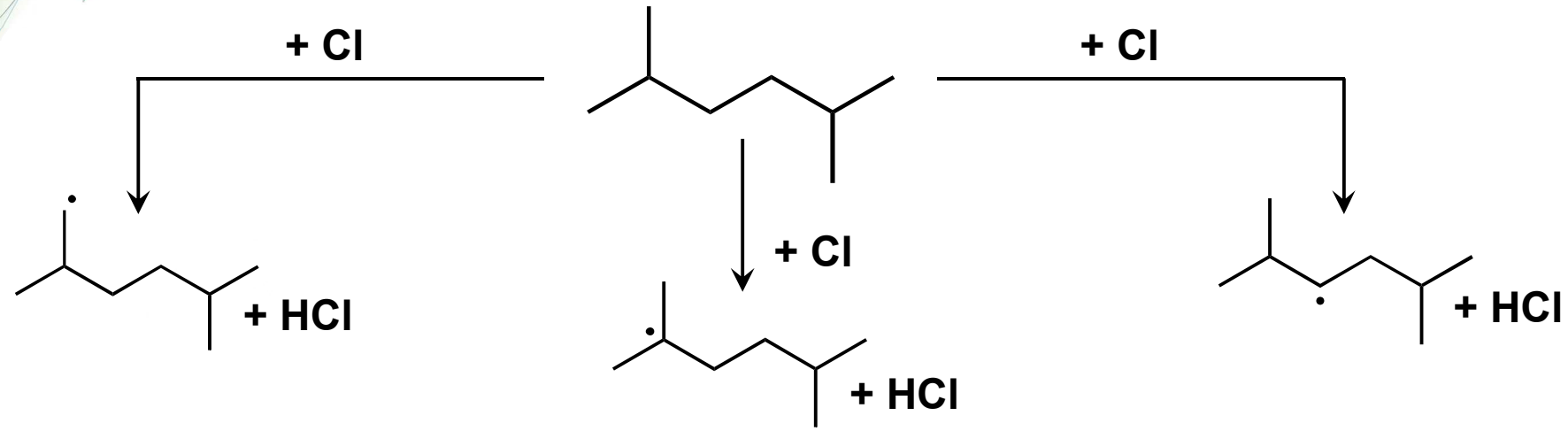


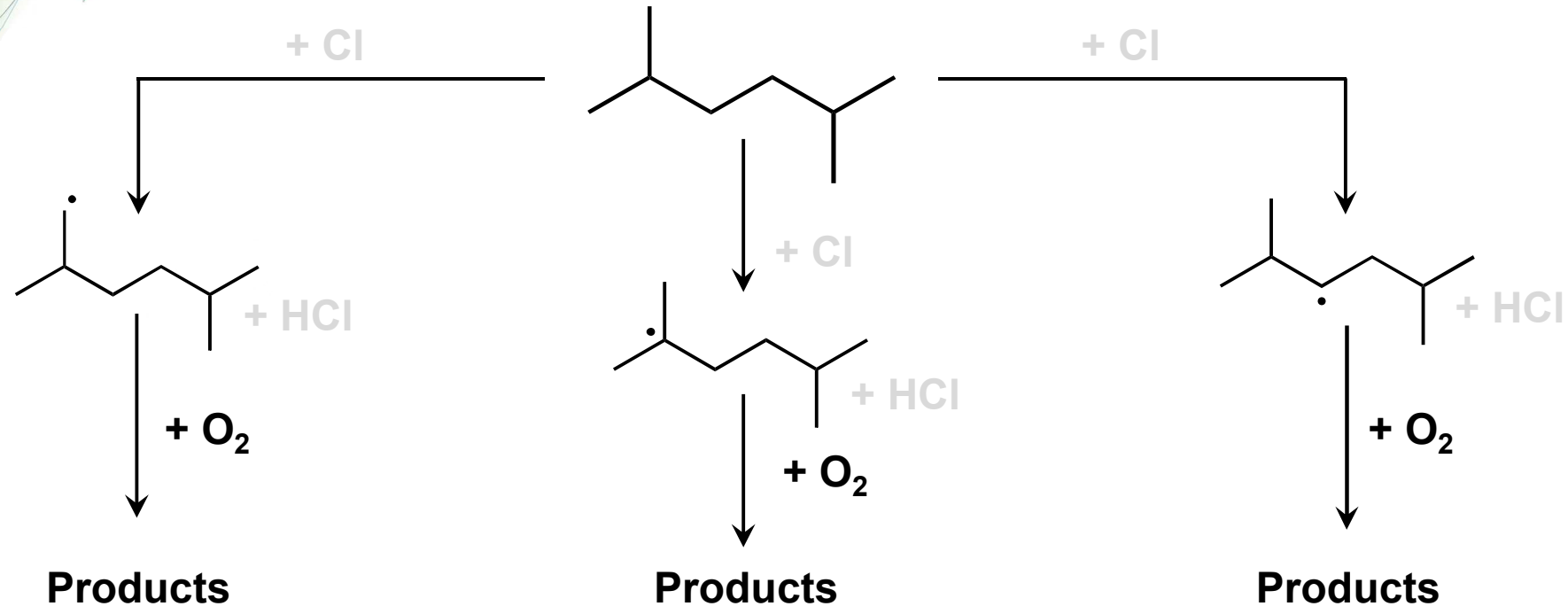

## Two Experimental Approaches:

1. Photoionization Mass Spectrometry (PIMS)

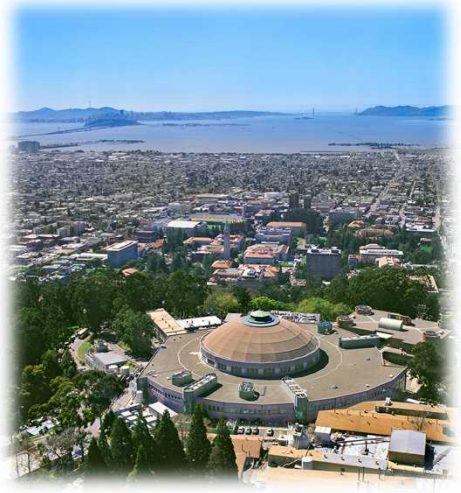
# Initial Alkyl Radicals Generated using Photolyzed $Cl_2$

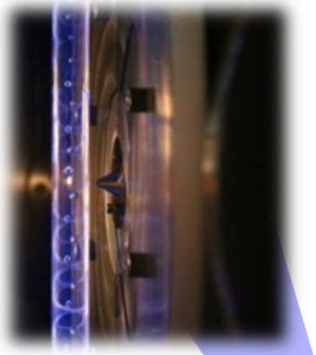


# Pseudo-First-Order Conditions for Reaction of R with $O_2$



# Experimental Approach – Studying R + $O_2$ Chemistry using Multiplexed Photoionization Mass Spectrometry (MPIMS)








Multiplexed Photoionization Mass Spectrometer

Number Densities (molecules/$cm^3$):

$RH = 1.3\ 10^{14}$ $O_2 = 2.8\ 10^{16}$

$Cl_2 = 1.4\ 10^{14}$ $He = 1.0\ 10^{17}$

Initial Conditions:

$O_2/RH \sim 220$

$O_2/Cl_2 \sim 200$

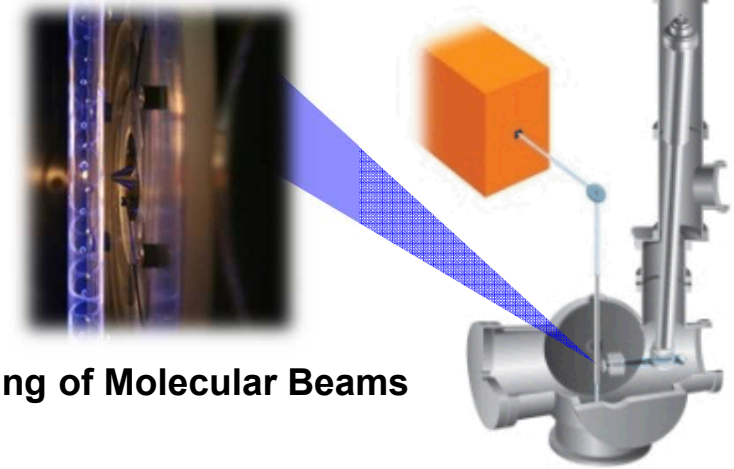
$RH/Cl \sim 30$

550 K, 650 K

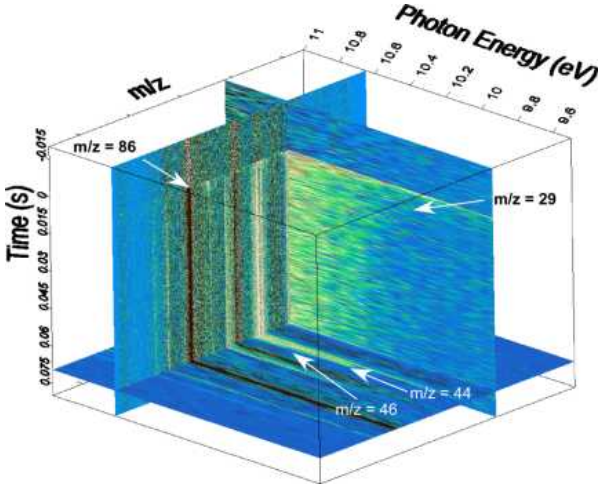
8 Torr

Osborn et al., *Rev. Sci. Inst.* (2008)

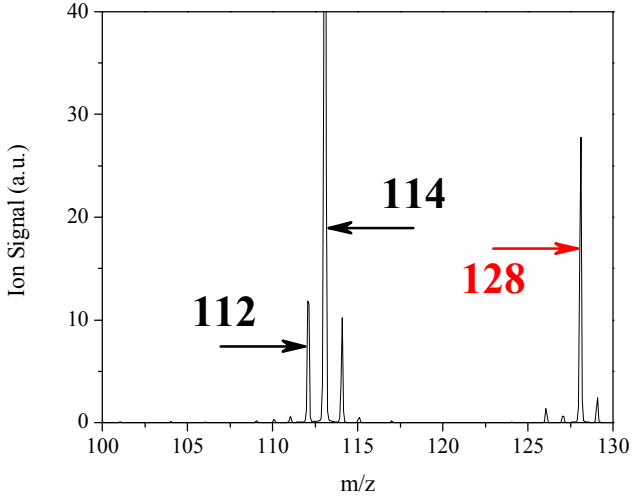
# Experimental Approach – Studying R + $O_2$ Chemistry using Multiplexed Photoionization Mass Spectrometry (MPIMS)



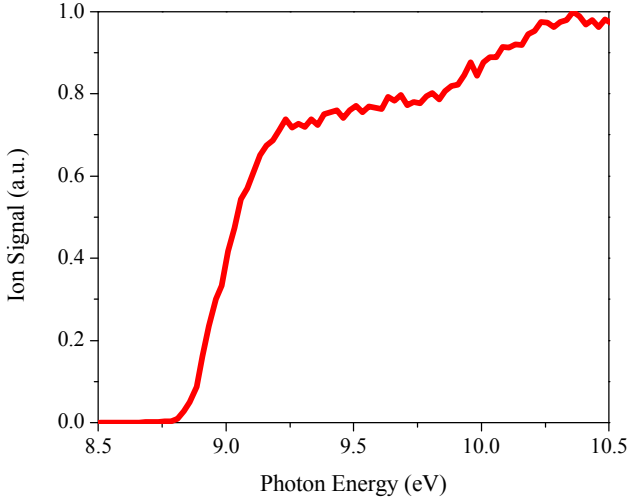
Probing of Molecular Beams



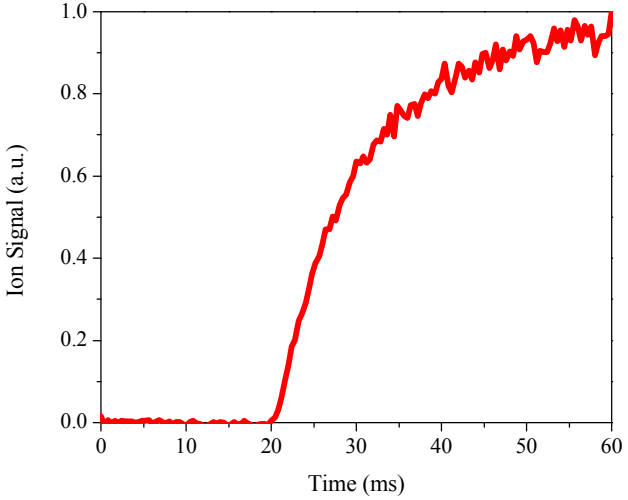

**High-Resolution Mass Spectra**



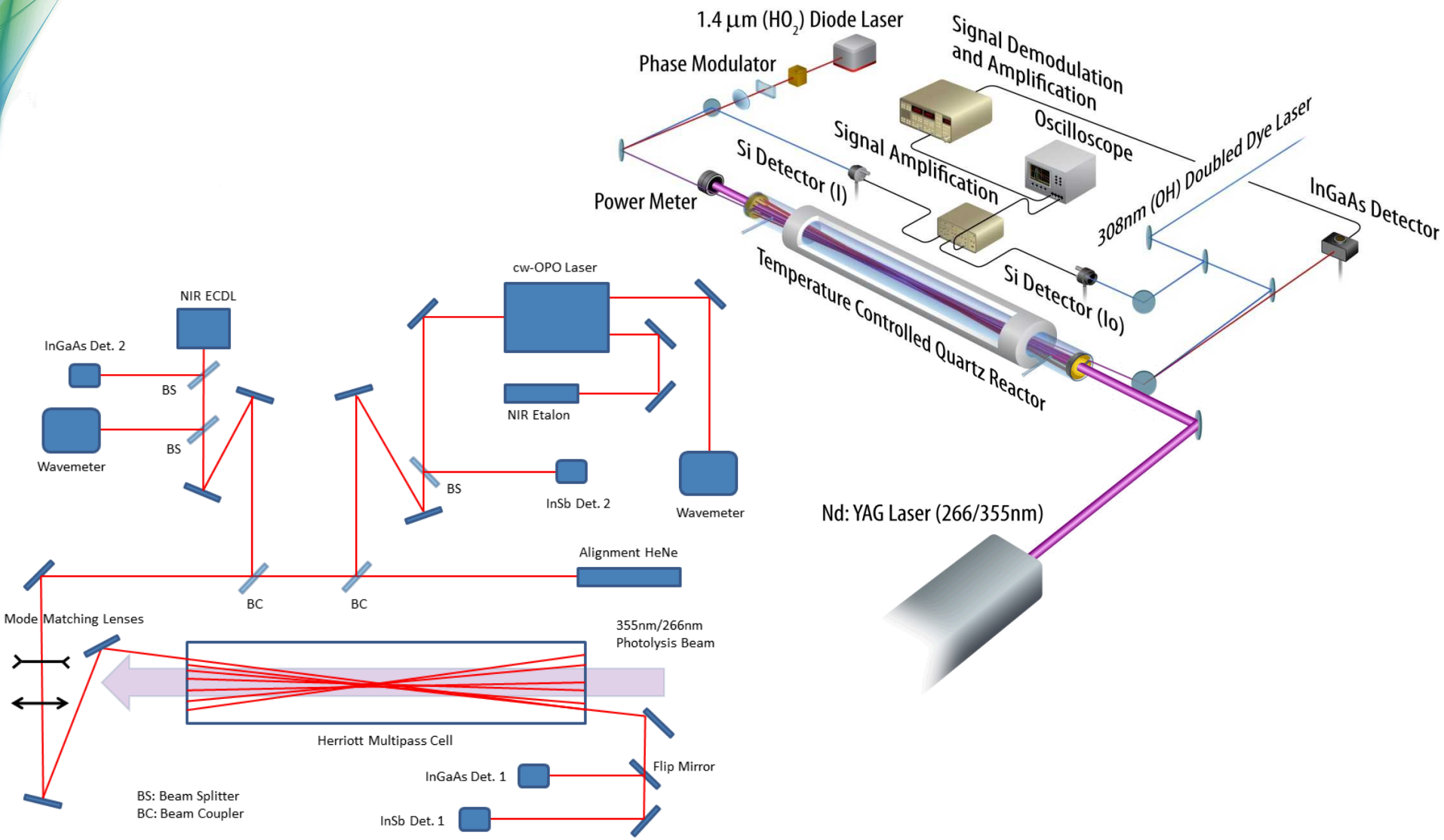

**Isomer-Resolved Species Identification**




**Time-Dependent Chemical Kinetics**



# Experimental Approach – Multi-Pass Laser-Absorption Measurements of OH and $HO_2$ Time Histories



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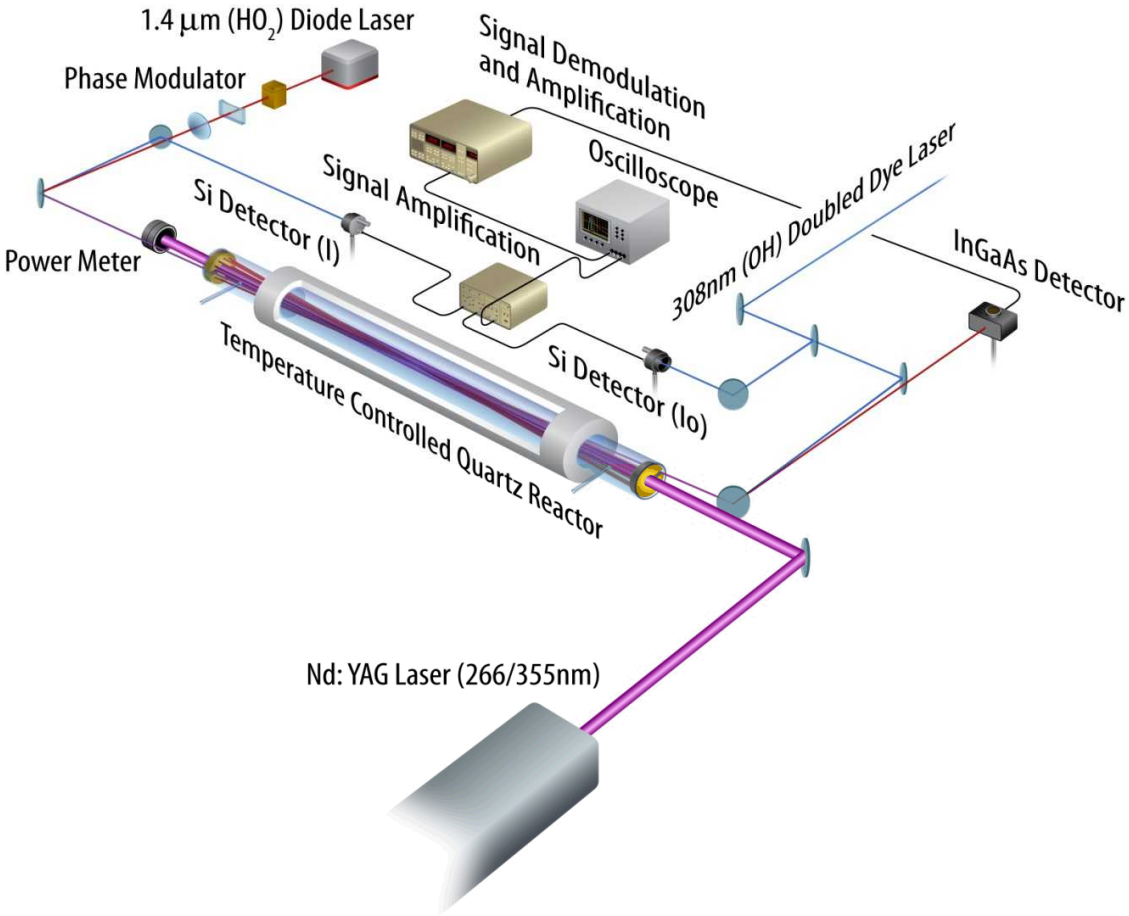
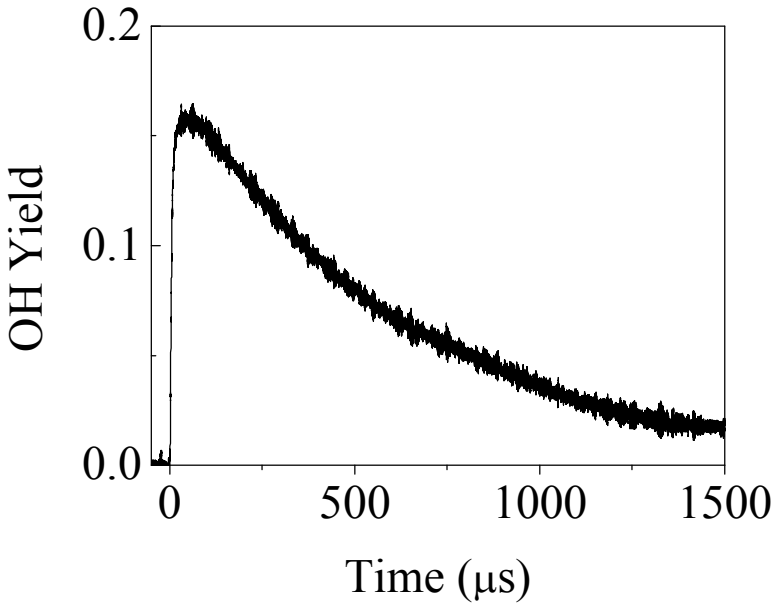
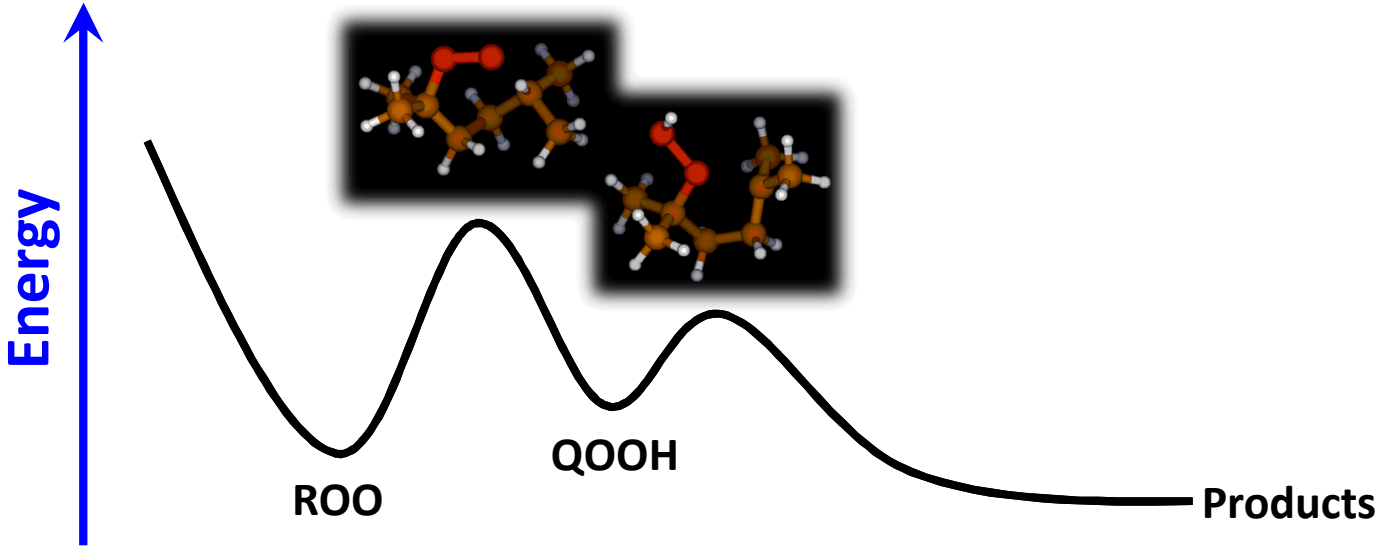



**OH Time History (600 K, 20 Torr)**



# Computational Approach




**Objectives –**

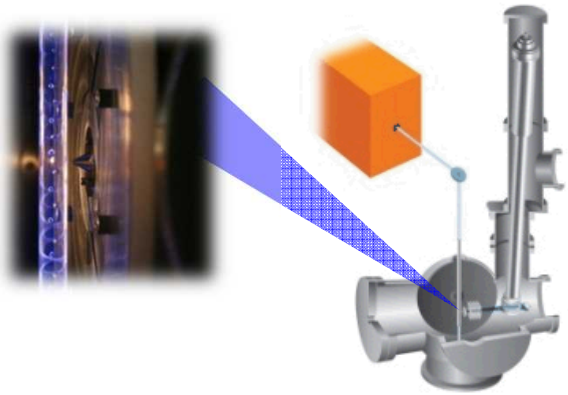
1. **Stationary point energies calculated at CBS-QB3 level of theory**
   - **2,5-dimethyl-1-hexyl + $O_2$**
   - **2,5-dimethyl-2-hexyl + $O_2$**
   - **2,5-dimethyl-3-hexyl + $O_2$**
2. **Master Equation calculations (low-temperature reactions)**

# Organization of Results

**MPIMS Results (550 K, 650 K)**

**(1) Mass spectra**
**(2) $HO_2$ + conjugate alkene from R + $O_2$**
**(3) Cyclic ether from R + $O_2$**
**(4) Role of primary alkyl isomerization**
**(5) QOOH decomposition via $\beta$-scission**

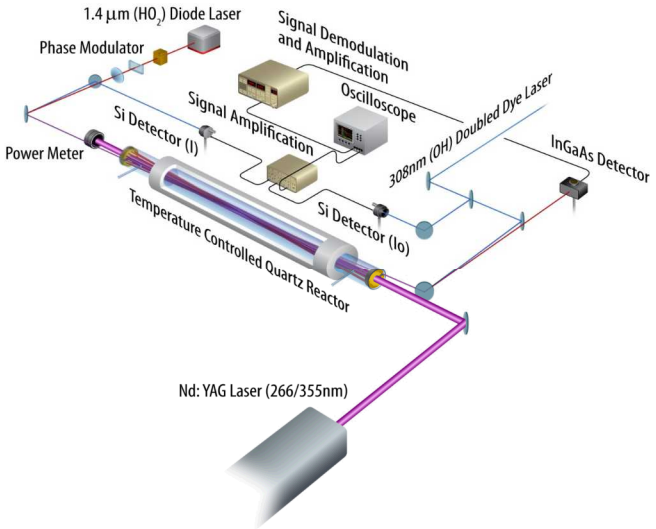
**(Rotavera et al., J. Phys. Chem. A, *in-press*)**



**OH- and HOO-Absorption Results**

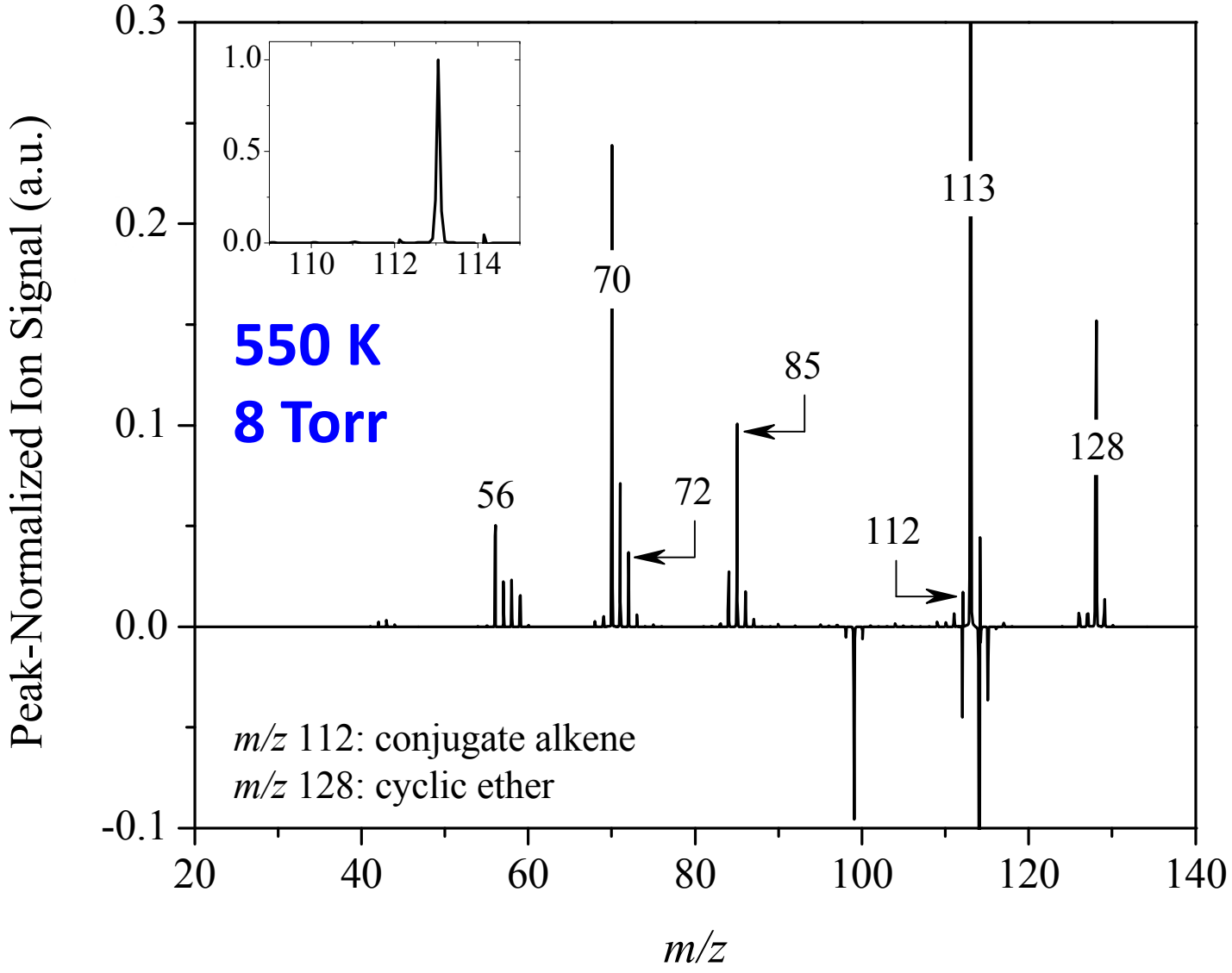
**(1) OH time histories (500 – 750 K)**
**(2) $HO_2$ time histories (600 – 750 K)**

**(Chong et al., in preparation)**



# PIMS Results: Mass Spectra

# Mass Spectra: 2,5-dimethylhexane Oxidation



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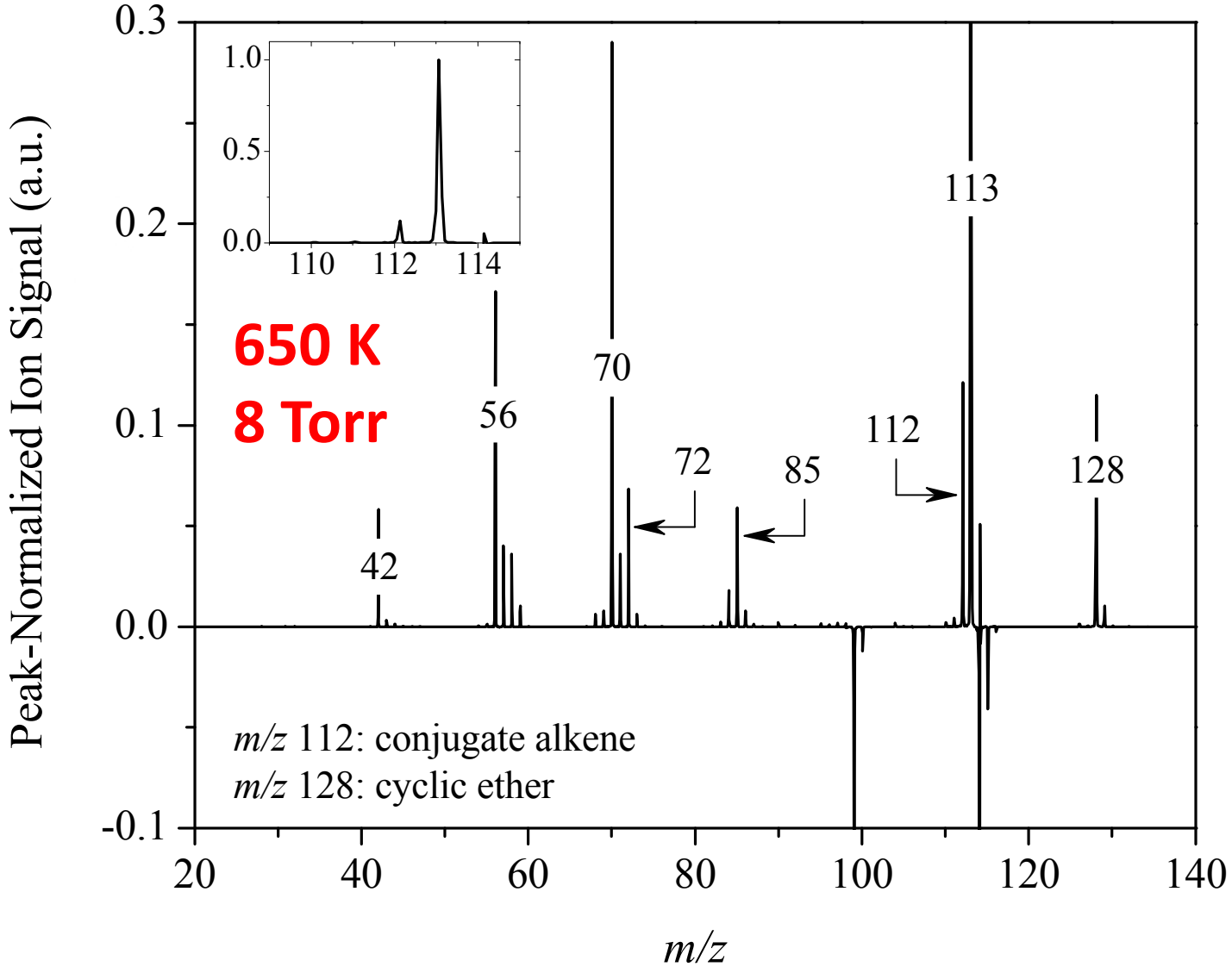
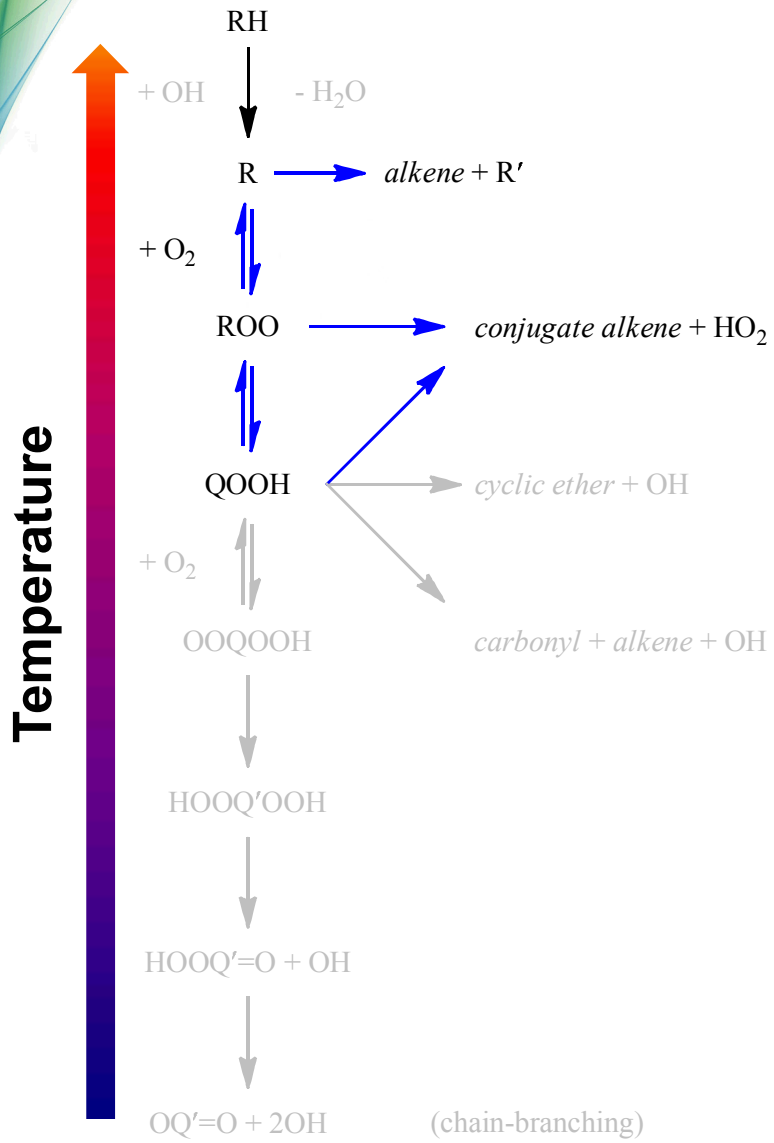
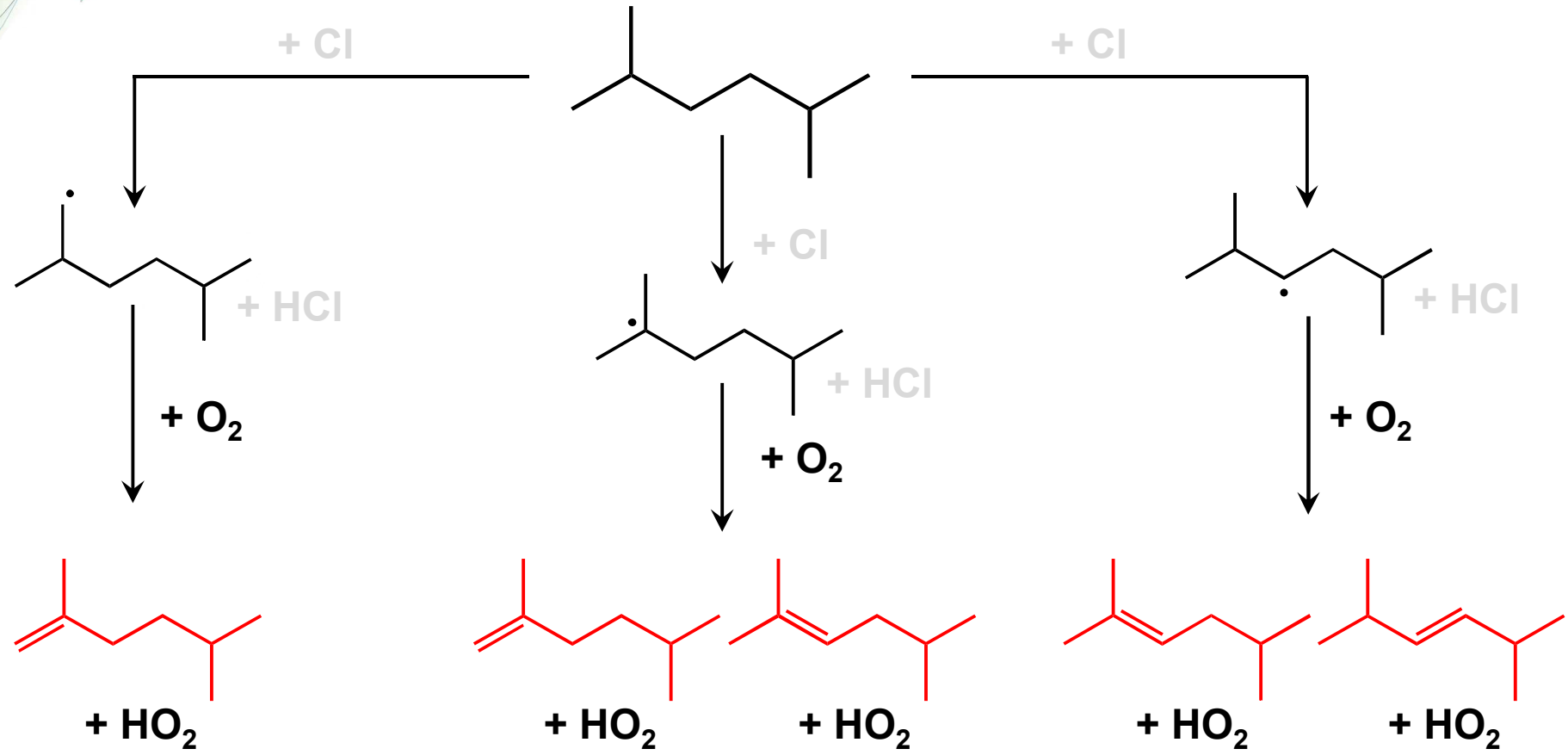


# MPIMS Results: $HO_2$ + Conjugate Alkene

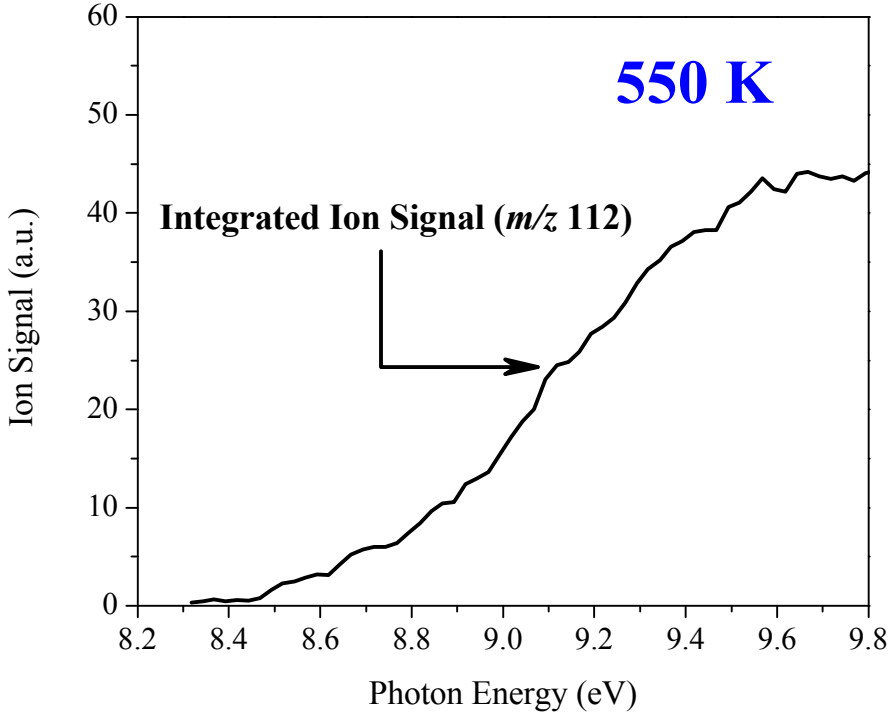
# Direct Measurement of $HO_2$-Elimination Channel



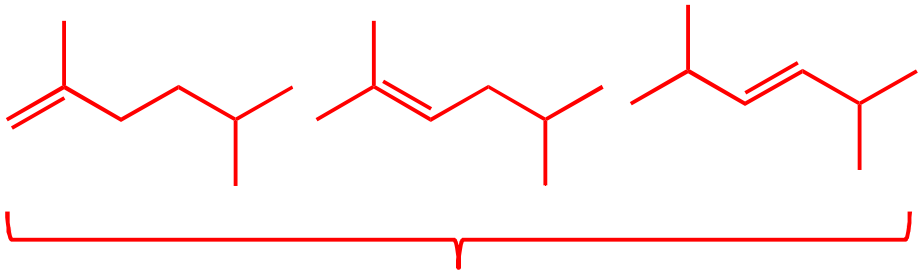
# Conjugate Alkene Species from R + $O_2$



# Integrated Ion Signal of *m/z* 112 Contains Contributions from All Conjugate Alkenes

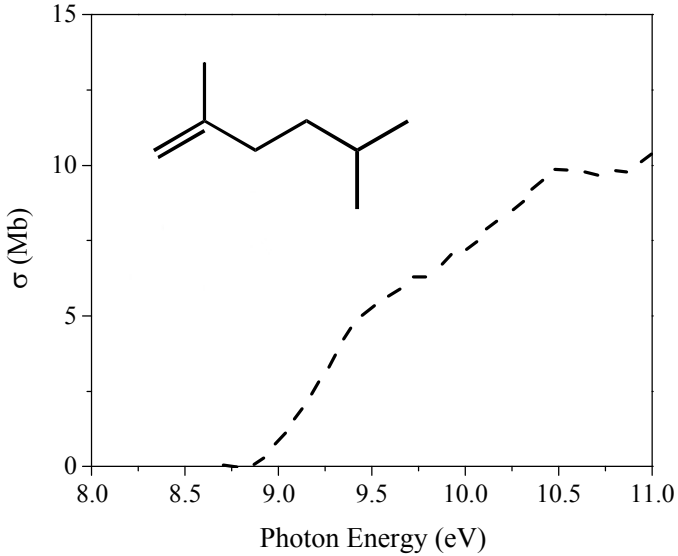


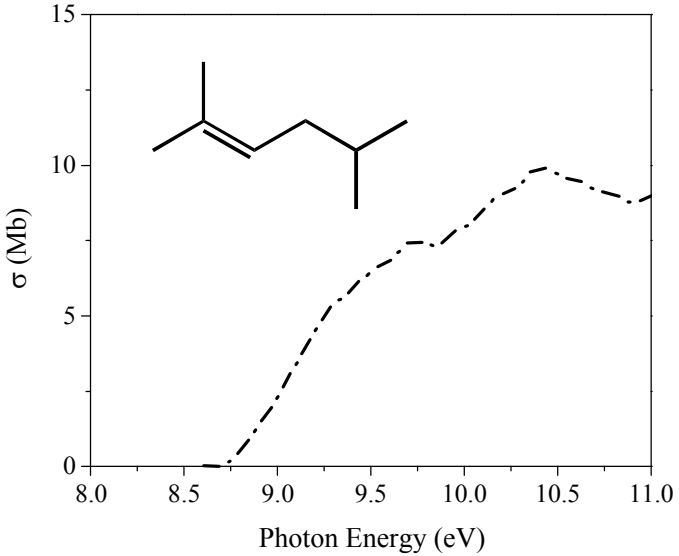

*Unknown, temperature-dependent contributions to integrated ion signal*

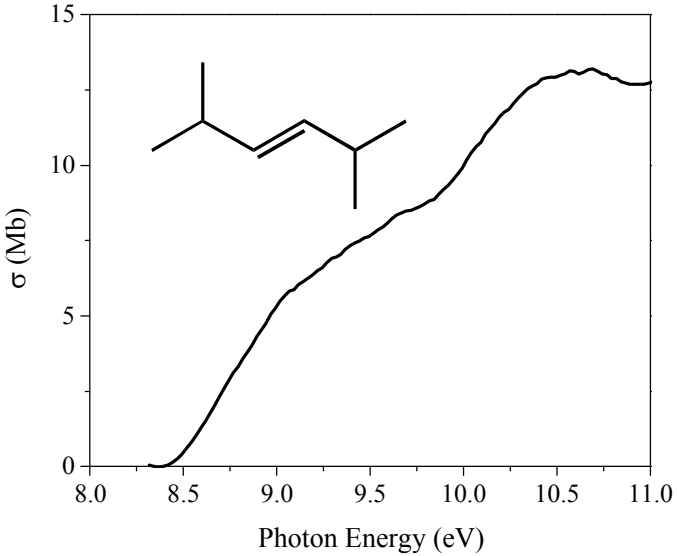


**Isomers of *m/z* 112**

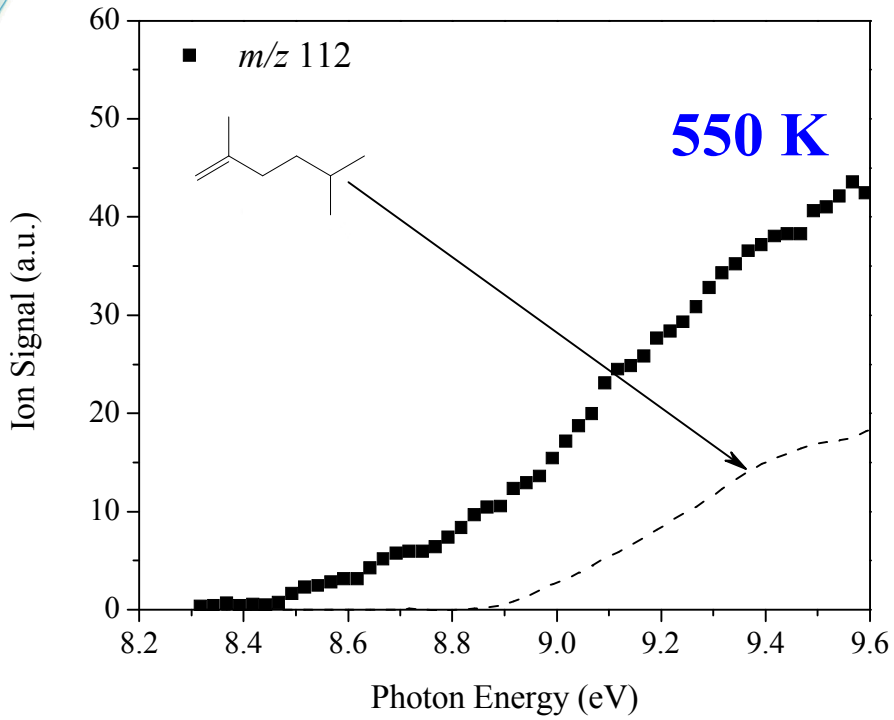
# Isomeric Composition Quantified using Absolute Photoionization Cross-Sections

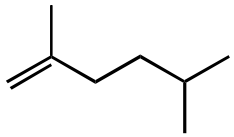


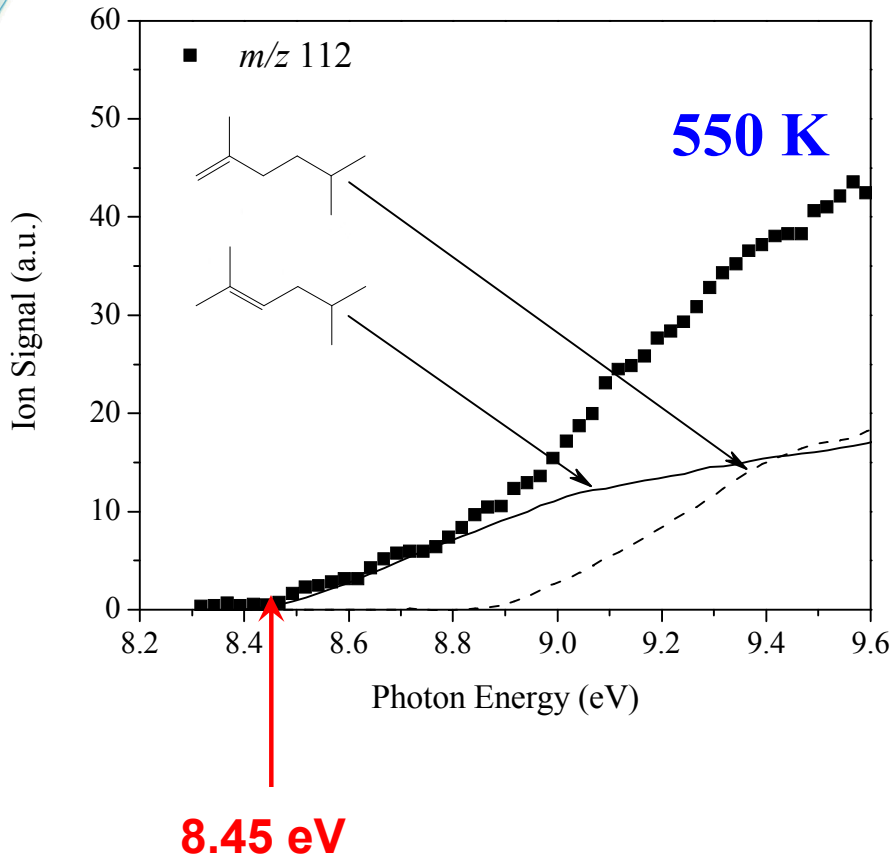



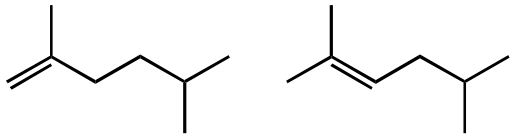
# Temperature-Dependent Branching Ratios of Conjugate Alkenes from R + $O_2$



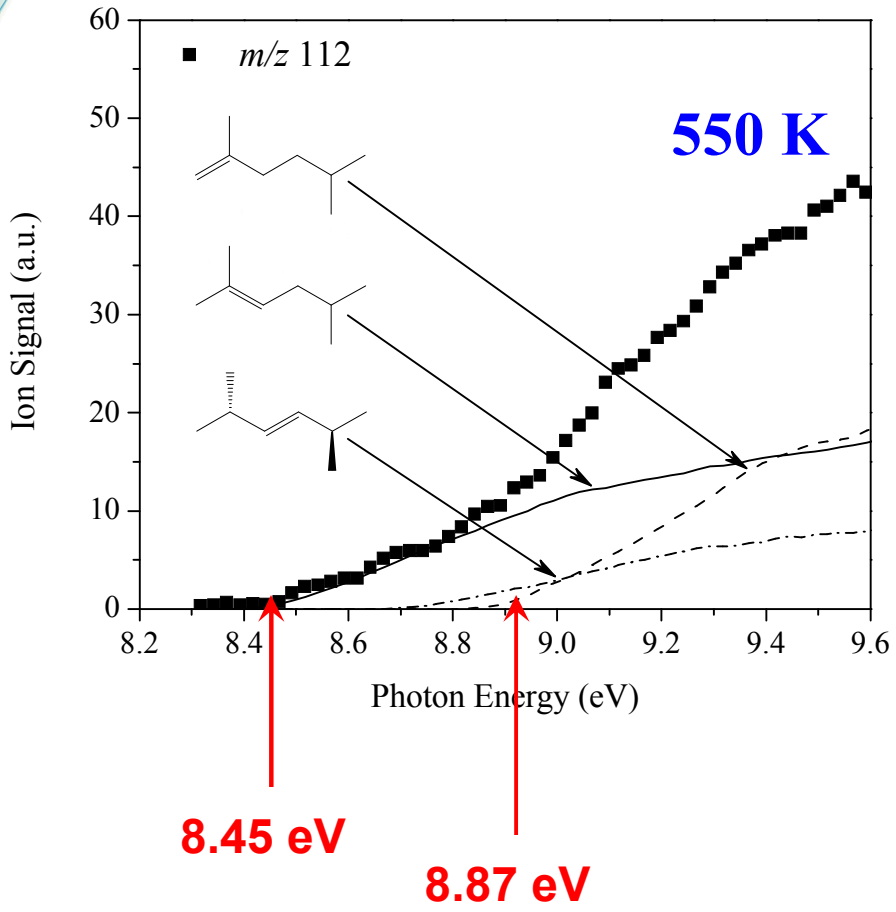



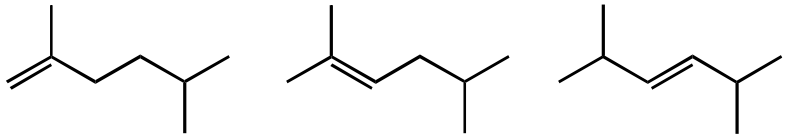
# Temperature-Dependent Branching Ratios of Conjugate Alkenes from R + $O_2$



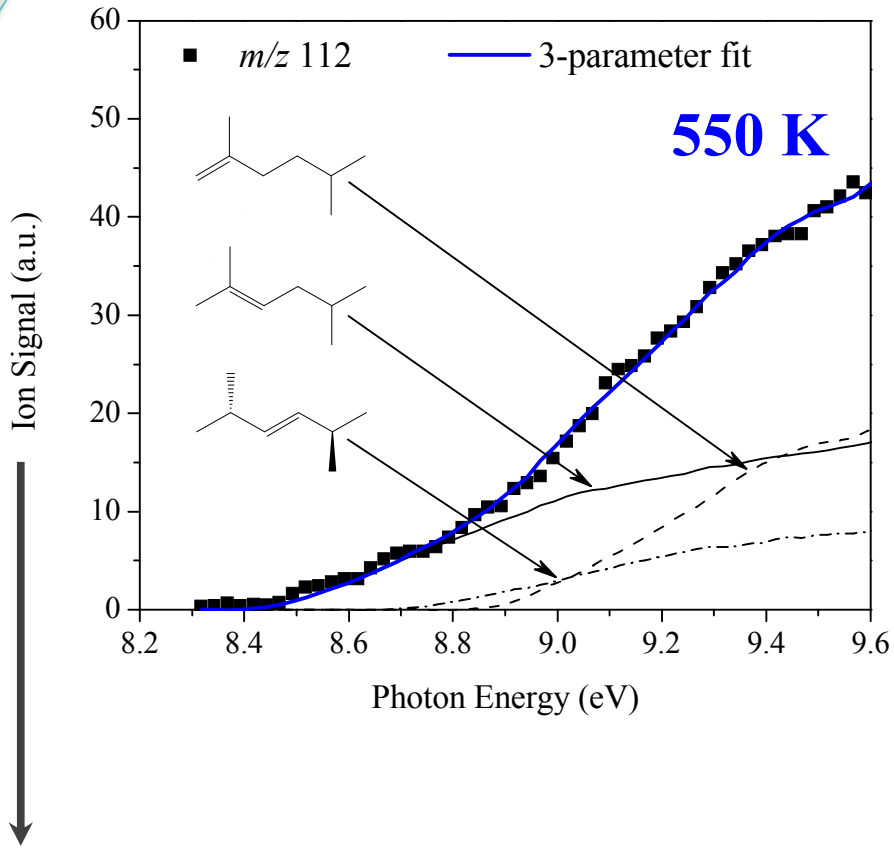



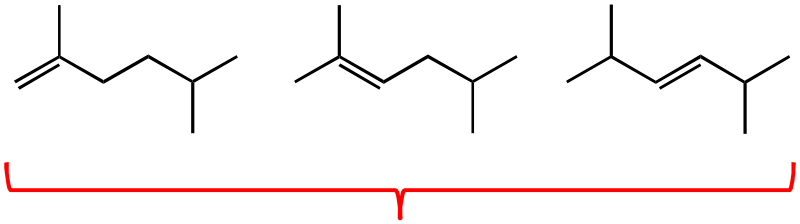
# Temperature-Dependent Branching Ratios of Conjugate Alkenes from R + $O_2$



# Temperature-Dependent Branching Ratios of Conjugate Alkenes from R + $O_2$



**Isomers of *m/z* 112**

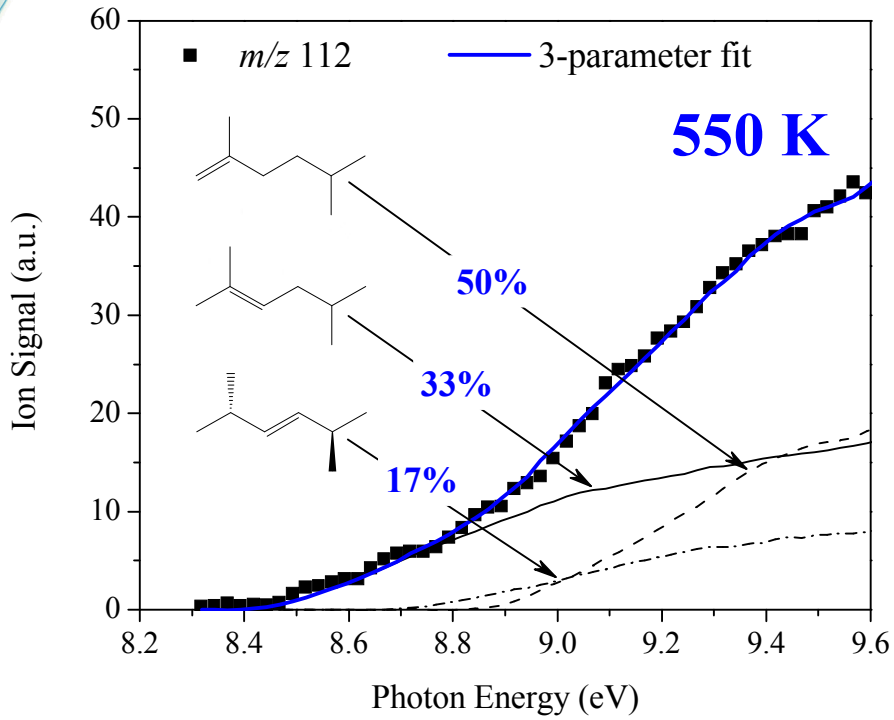
**Isomer-specific contributions quantified using results from separate measurements of absolute photoionization cross-sections $\sigma_i(E)$ for each species and application of fitting routine:**

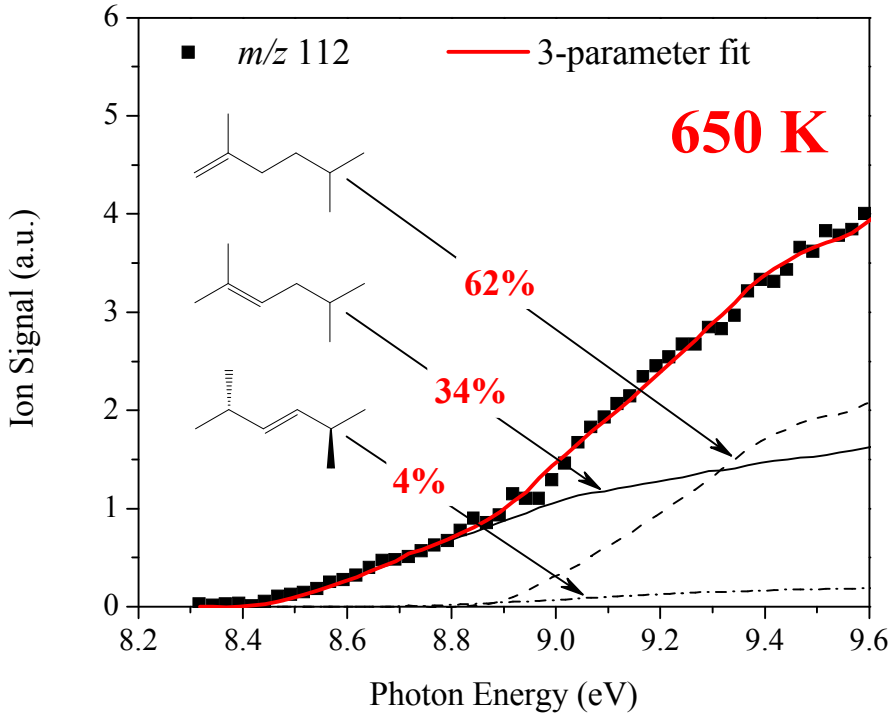
$$S_{m/z}(E) = \sum_{i}^{N} A_i \sigma_i(E)$$

**Ion Signal Definition:**

$$S_i(E) = \Lambda \sigma_i(E) c_i \alpha_i$$

# Temperature-Dependent Branching Ratios of Conjugate Alkenes from R + $O_2$



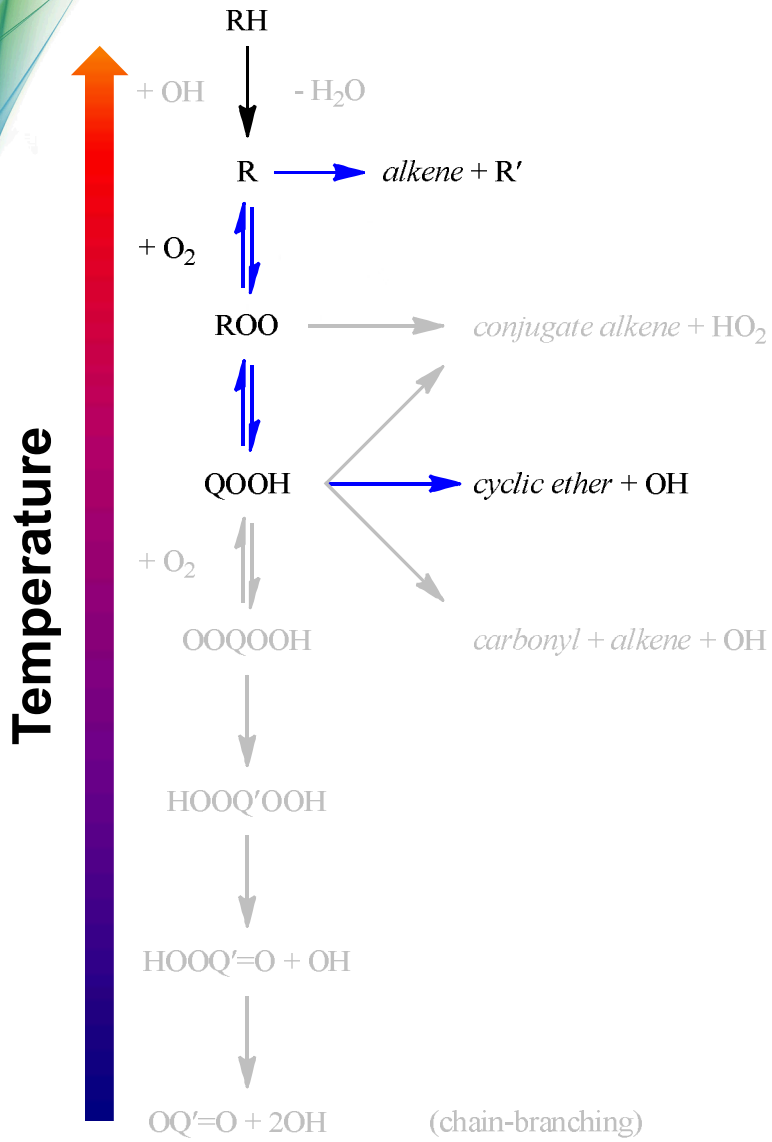




| Conjugate Alkene | 550 K | 650 K |
|---|---|---|
| 2,5-dimethyl-1-hexene | 0.50 ± 0.25 | 0.62 ± 0.31 |
| 2,5-dimethyl-2-hexene | 0.33 ± 0.16 | 0.34 ± 0.17 |
| 2,5-dimethyl-3-hexene | 0.17 ± 0.08 | 0.04 ± 0.02 |

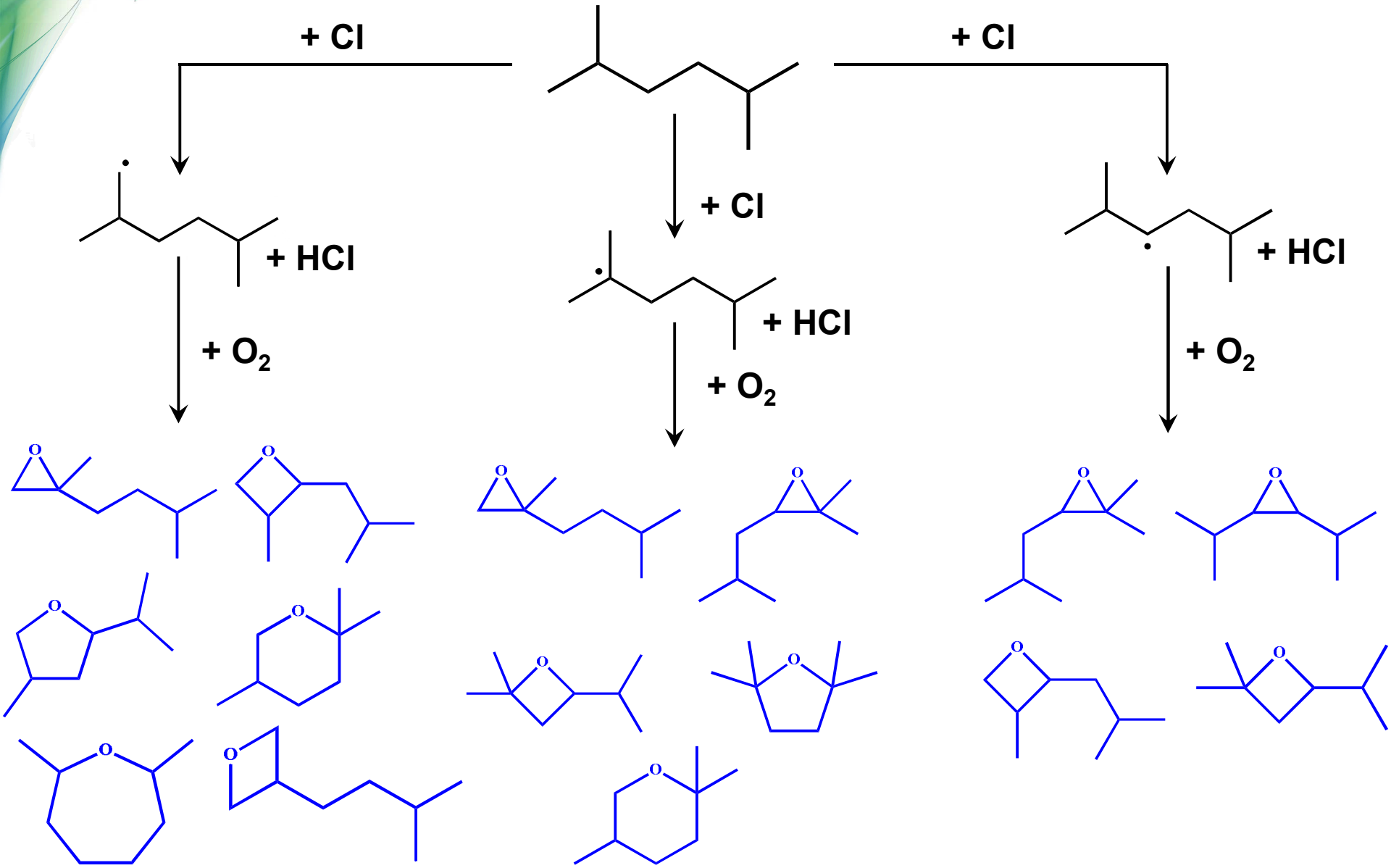
Branching Ratios

# MPIMS Results: Cyclic Ether Formation

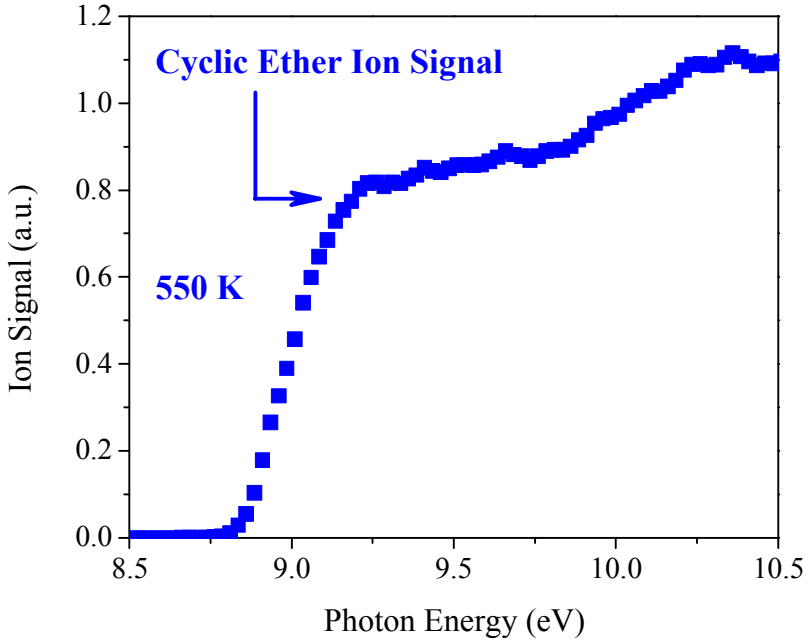
# OH-Loss Co-Products from QOOH Species

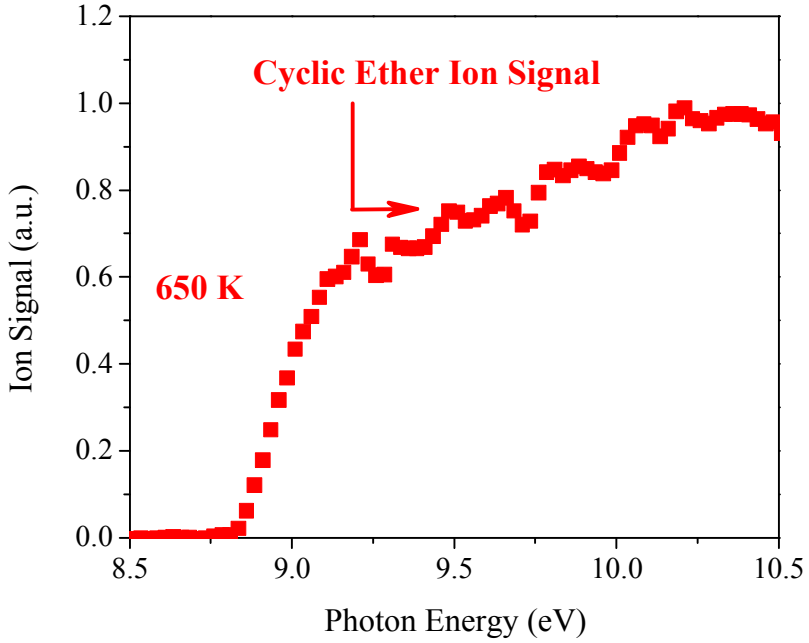


# 10 Cyclic Ether Species Coincident with OH

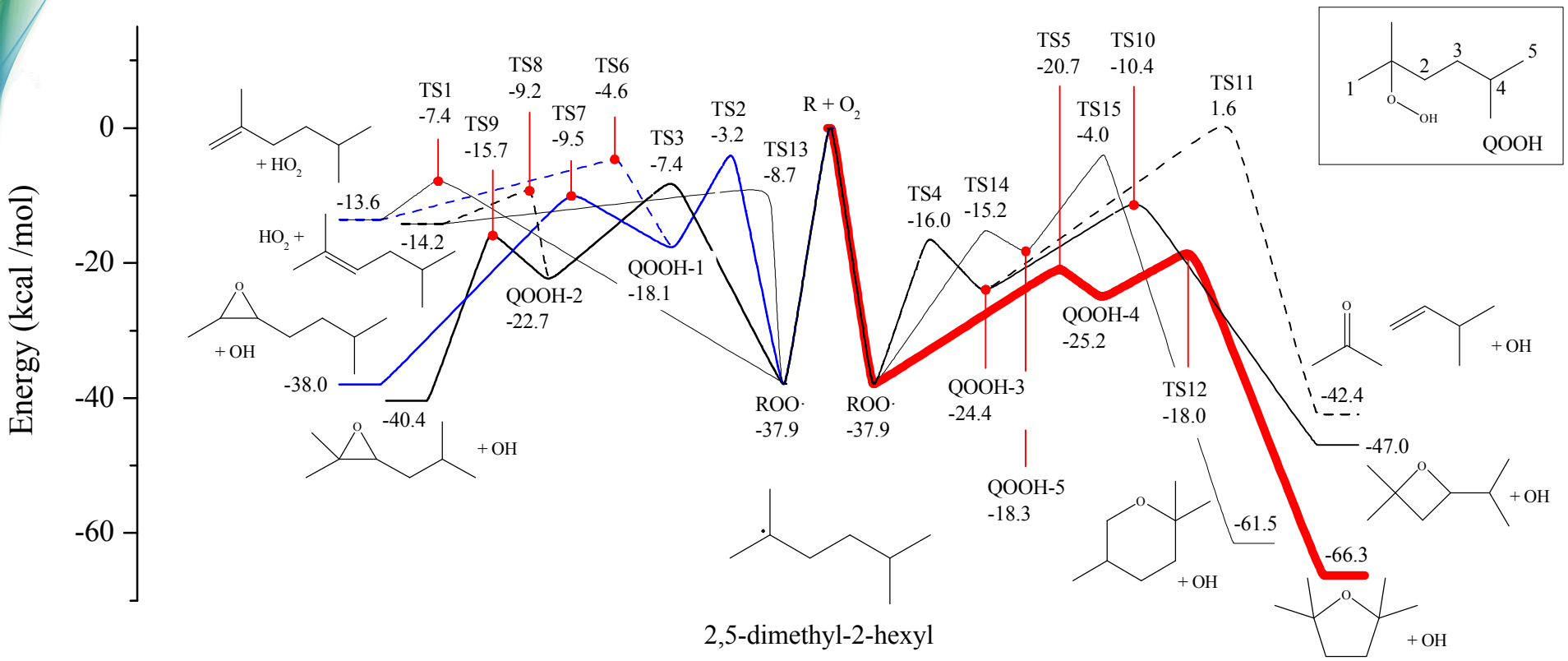


# Integrated Ion Signal of *m/z* 128 (Cyclic Ether) Contains Contributions Potentially from All 10 Species



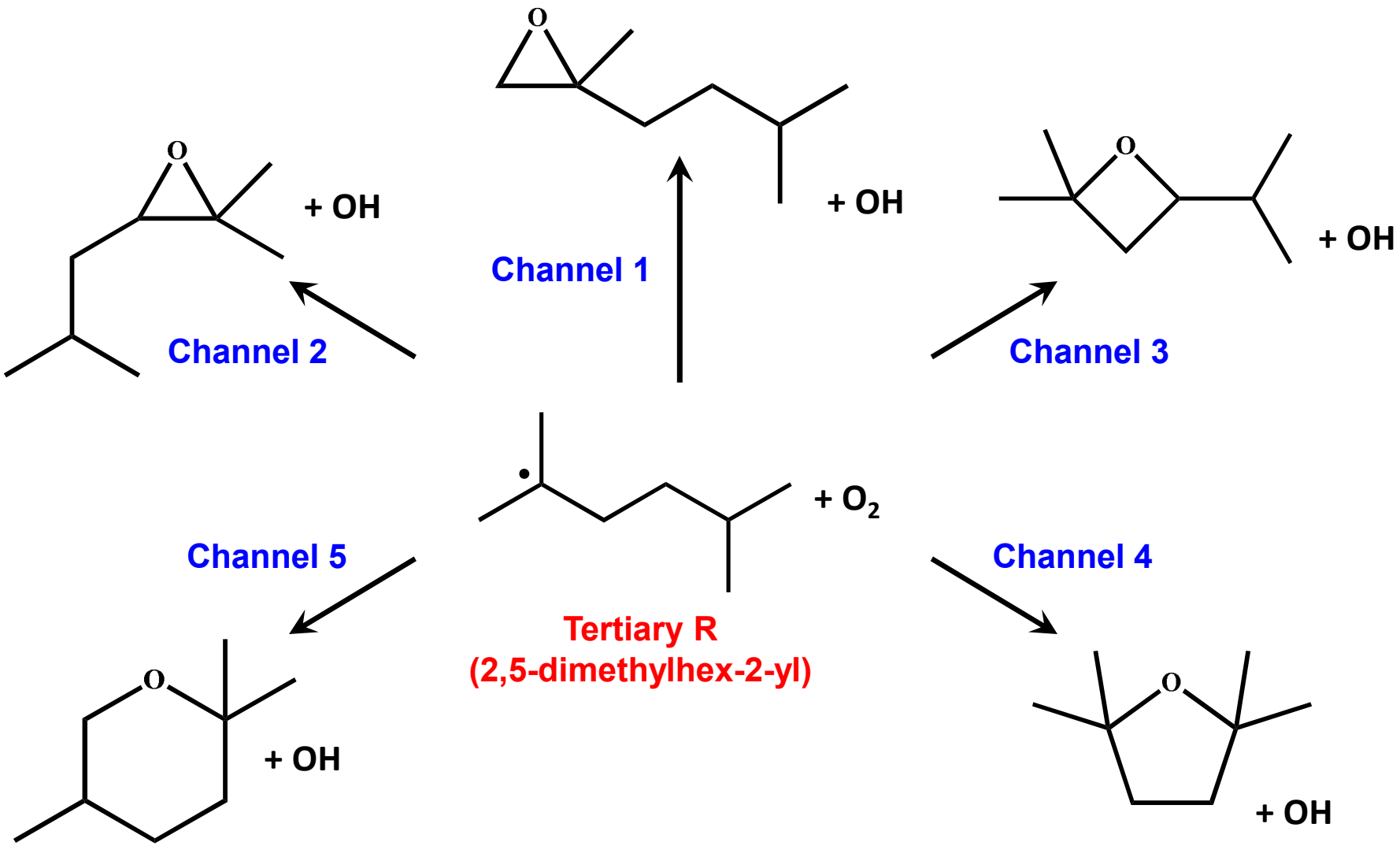



# CBS-QB3 Stationary Points: 2,5-dimethyl-2-hexyl + $O_2$

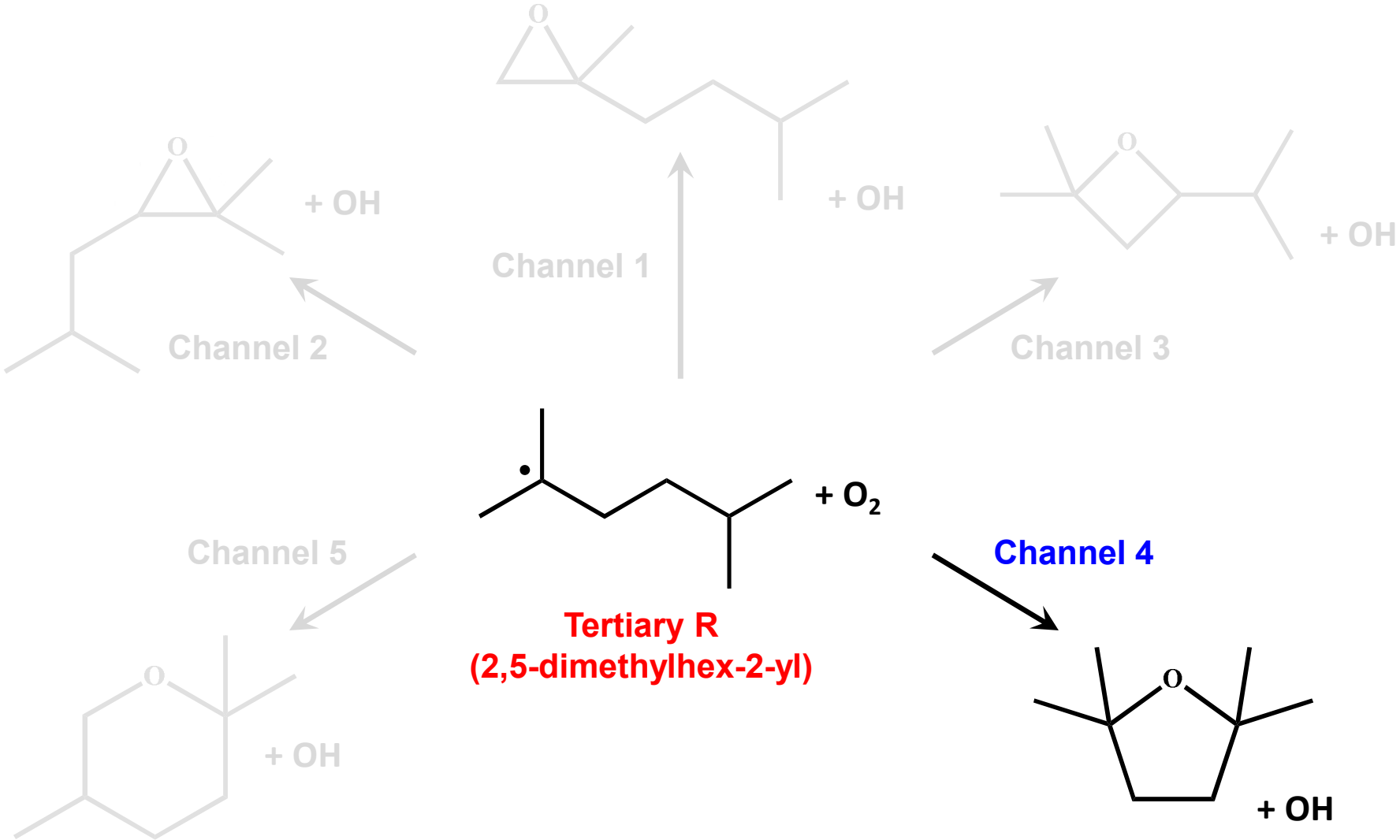



**Lowest-energy pathway leads to 2,2,5,5-tetramethyltetrahydrofuran**

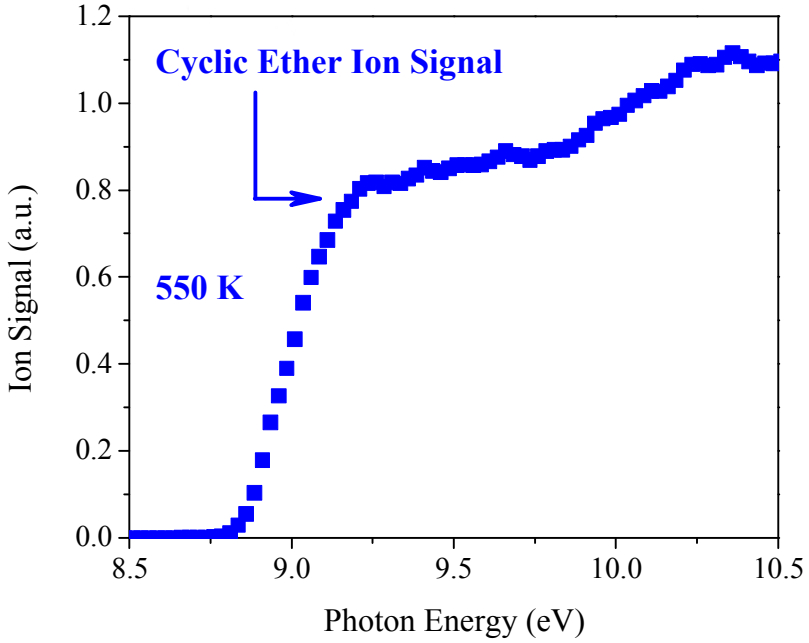
# Cyclic Ether Formation from $O_2$-Addition to Tertiary R

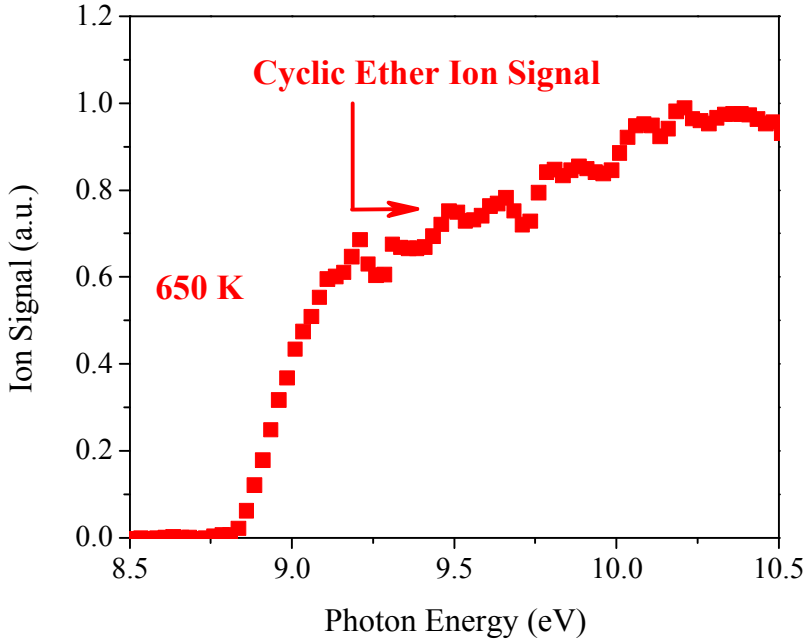


# Cyclic Ether Formation: 2,2,5,5-tetramethyl-THF

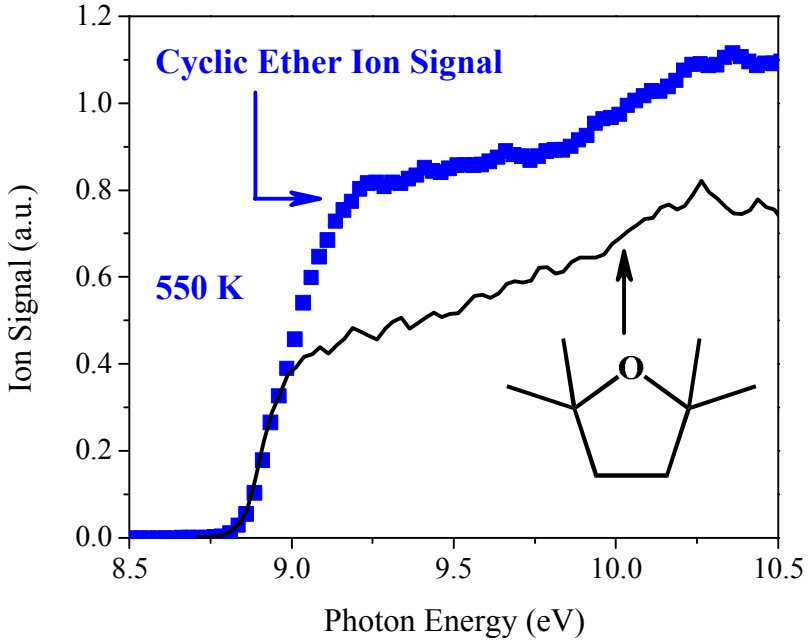


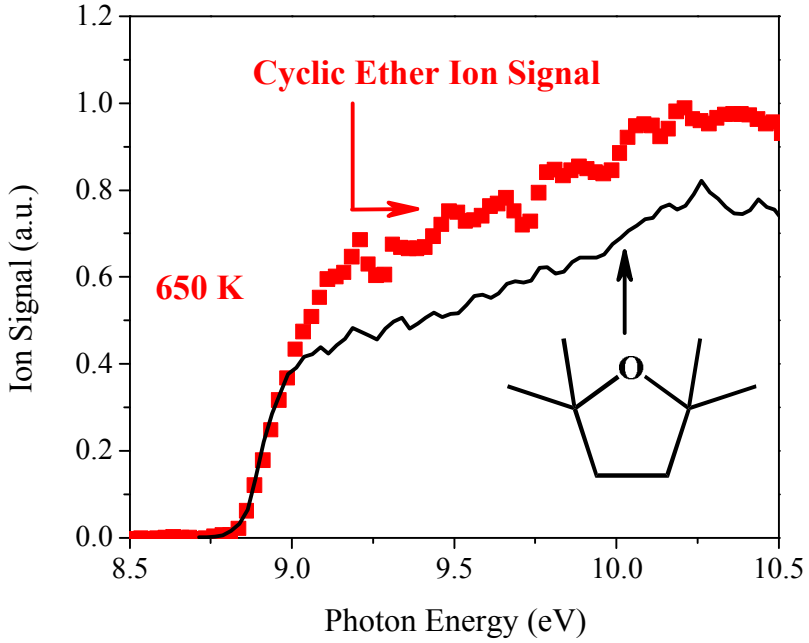
# Integrated Ion Signal of *m/z* 128 (Cyclic Ether) Contains Contributions Potentially from All 10 Species



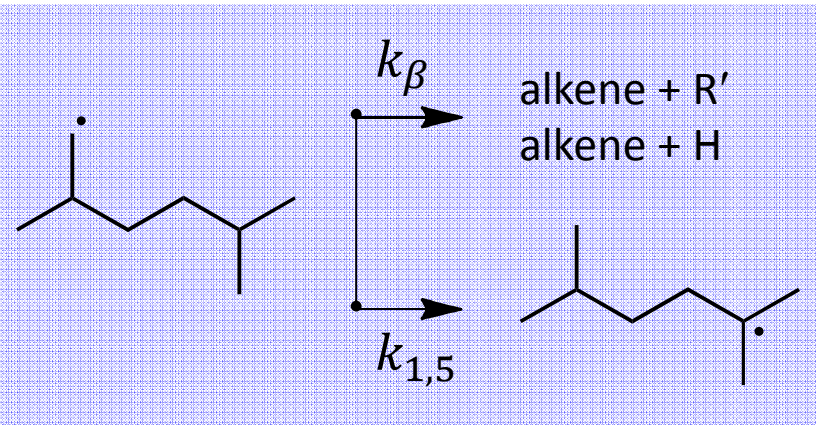
# Relative Importance of 2,2,5,5-tetramethyl-THF to Cyclic Ether Channel Increases with Temperature

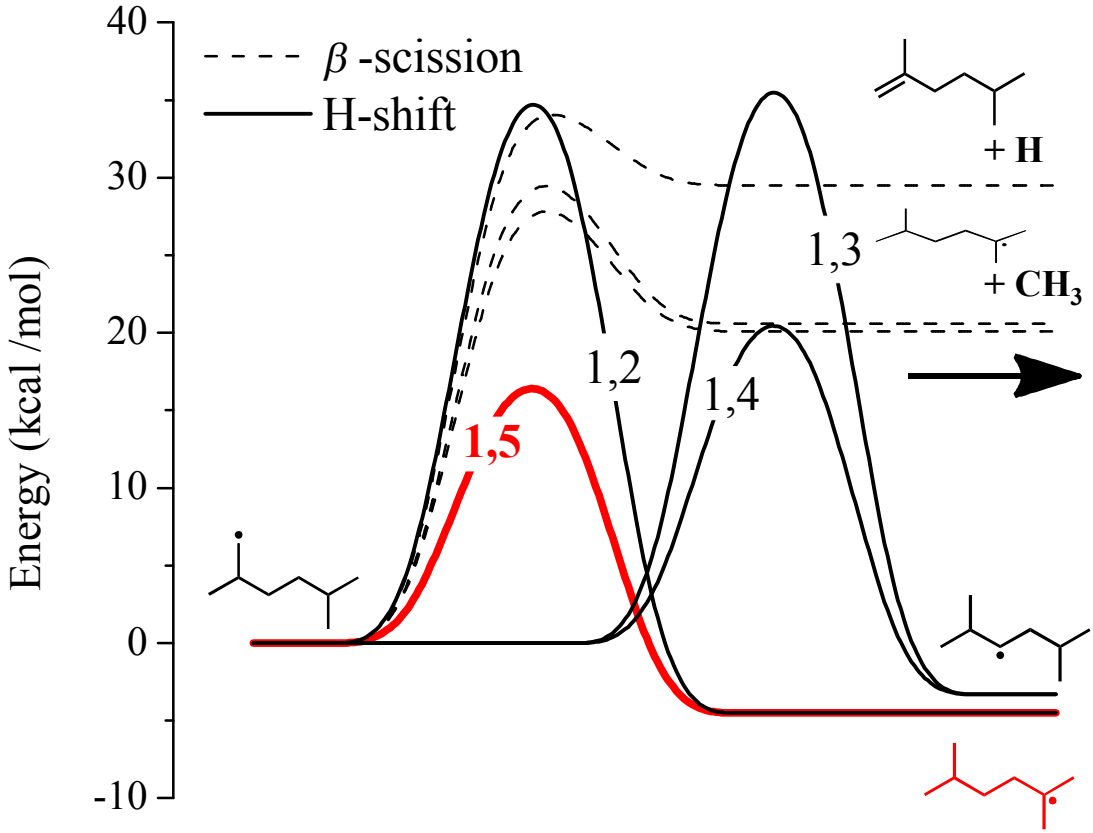


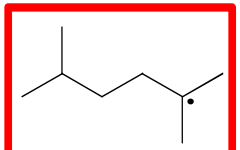
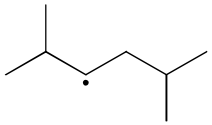
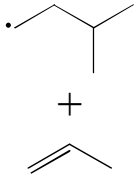
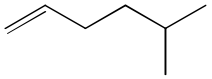
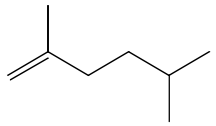
# MPIMS Results: Role of Primary Radicals in 2,2,5,5-tetramethyl-tetrahydrofuran Formation

# CBS-QB3 ZPE-Corrected Barrier Heights: 1,5-H-Shifting Dominates Primary Alkyl Decomposition

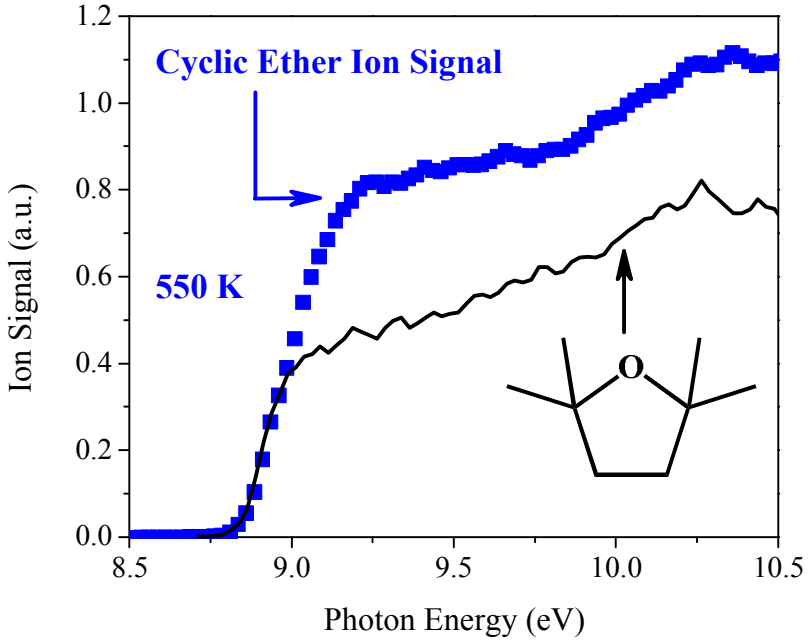


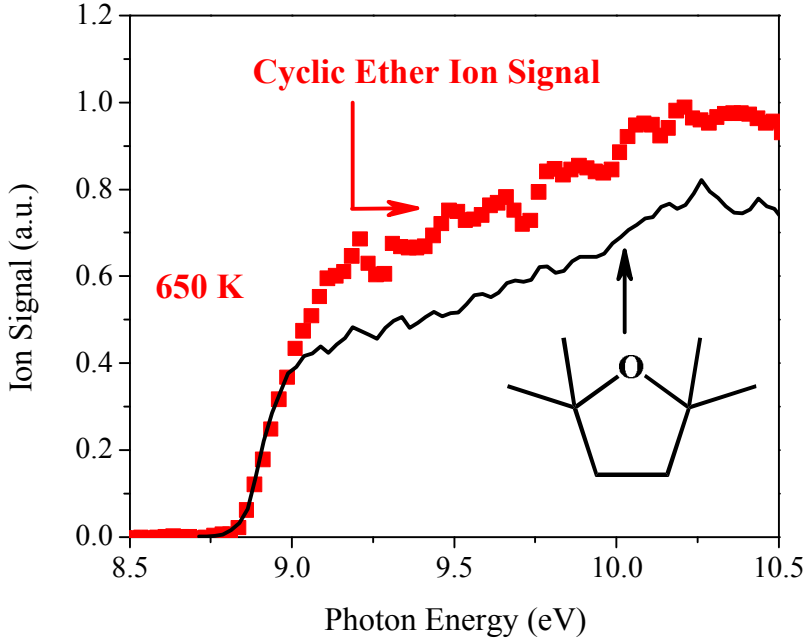



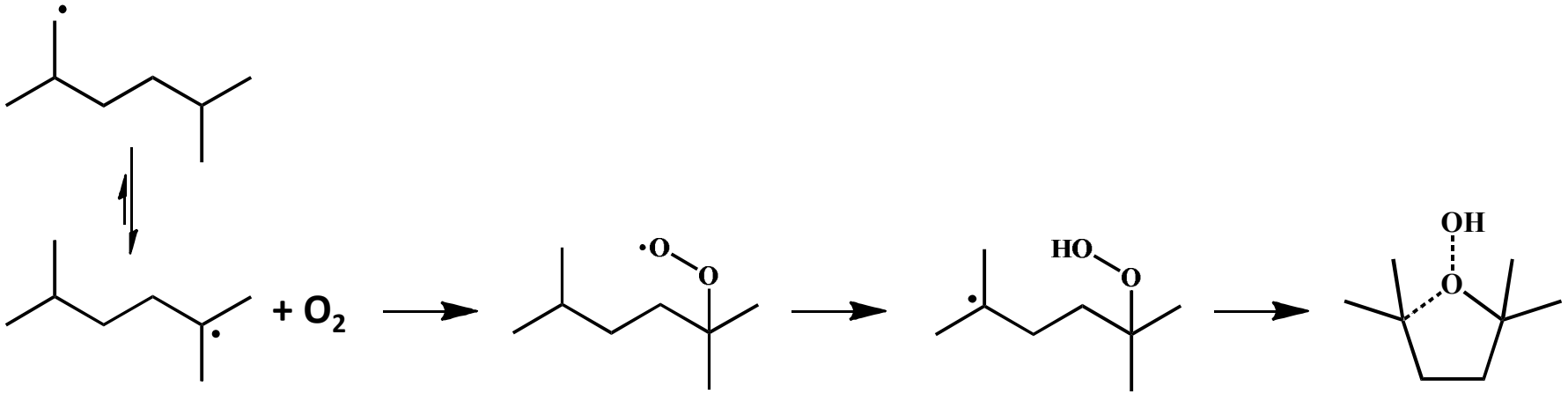
# CCSD(T)-F12a/cc-pVDZ Unimolecular Decomposition Rates: 1,5-H-atom Shifting Dominates Primary Alkyl

| | |  |  |  + |  + $CH_3$ |  + H |
|---|---|---|---|---|---|---|
| ZPE-corrected barrier height (kcal $mol^{-1}$) | CBS-QB3 | 36.1/16.2 | 37.0/20.8 | 27.1 | 28.9 | 33.4 |
| | CCSD(T)-F12a | 36.3/17.2 | 37.1/21.4 | 28.4 | 30.1 | 34.5 |
| $k_{550\ K}$ ($s^{-1}$) | CBS-QB3 | **$2.8 \cdot 10^4$** | $2.7 \cdot 10^3$ | $1.1 \cdot 10^3$ | 41.0 | 0.07 |
| | CCSD(T)-F12a | **$7.9 \cdot 10^3$** | $1.3 \cdot 10^3$ | $4.4 \cdot 10^2$ | 17.0 | 0.05 |
| $k_{650\ K}$ ($s^{-1}$) | CBS-QB3 | **$1.3 \cdot 10^5$** | $2.2 \cdot 10^4$ | $2.3 \cdot 10^4$ | $1.0 \cdot 10^3$ | 3.0 |
| | CCSD(T)-F12a | **$4.9 \cdot 10^4$** | $1.3 \cdot 10^4$ | $1.2 \cdot 10^4$ | $5.8 \cdot 10^2$ | 3.0 |

# Relative Importance of 2,2,5,5-tetramethyl-THF to Cyclic Ether Channel Increases with Temperature

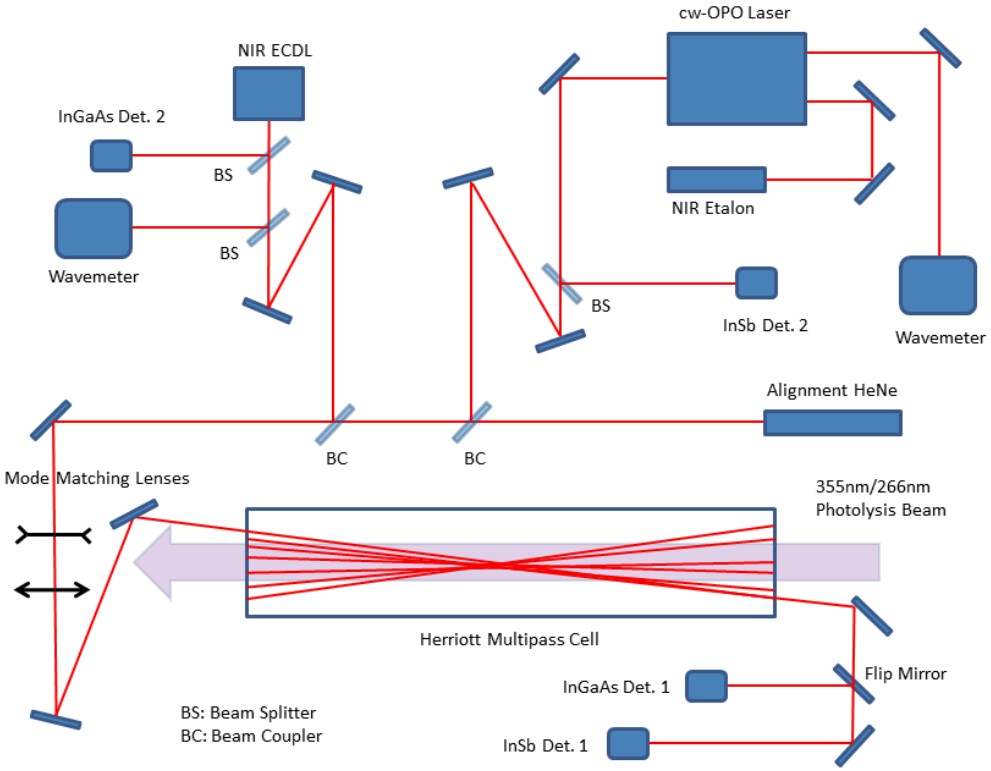


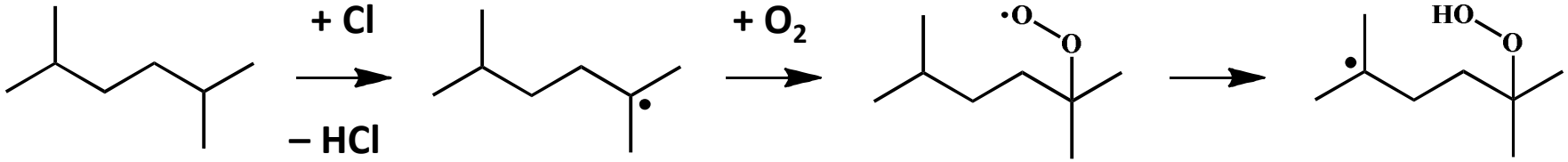



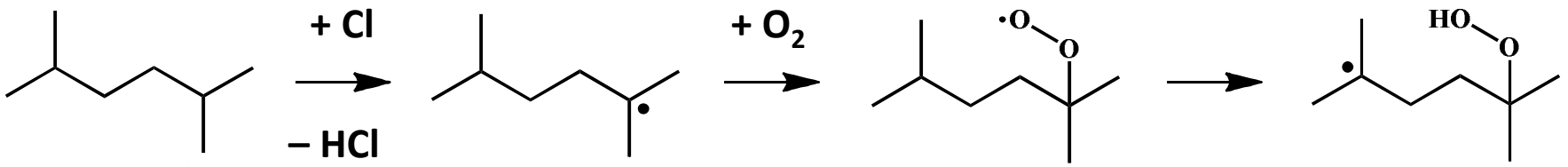
# Laser-Absorption Results: OH, $HO_2$ Time Histories

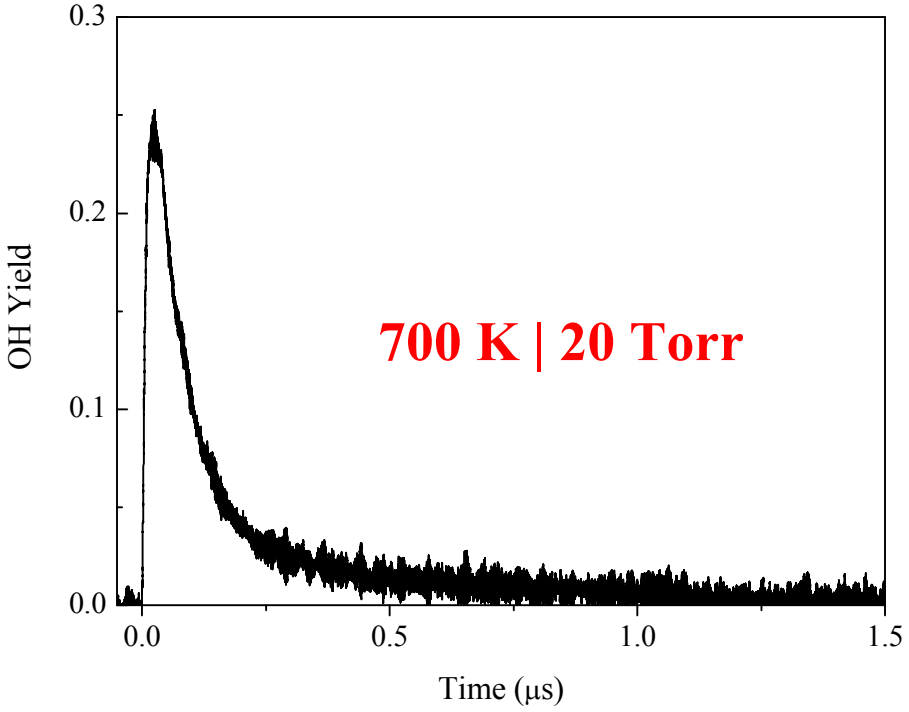
# Direct Measurement of OH and $HO_2$ Time Histories from R + $O_2$ Initiated Reactions

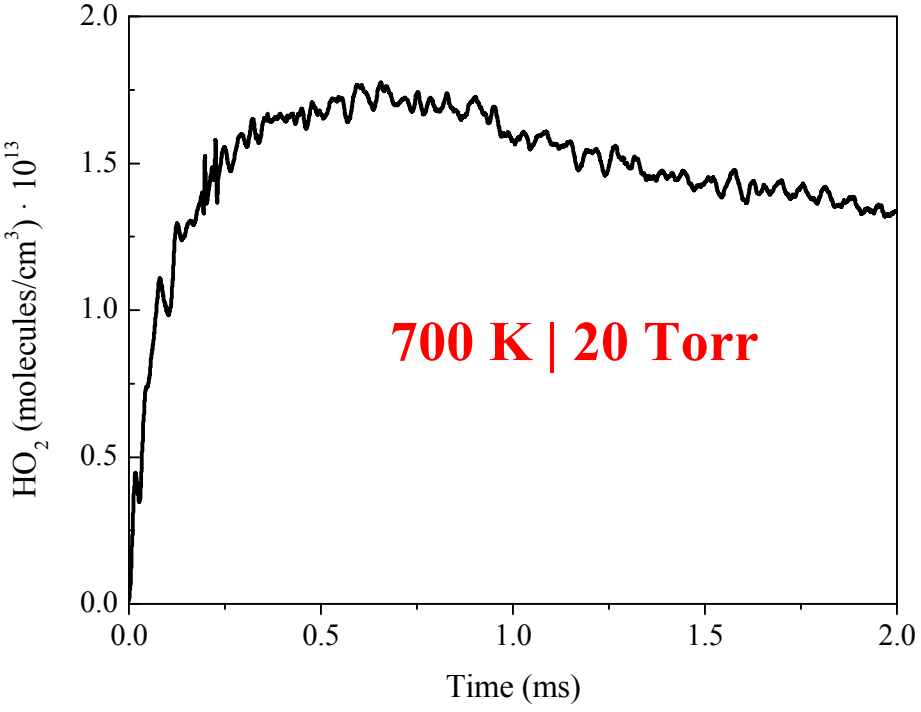


# Direct Measurement of OH and $HO_2$ Time Histories from R + $O_2$ Initiated Reactions

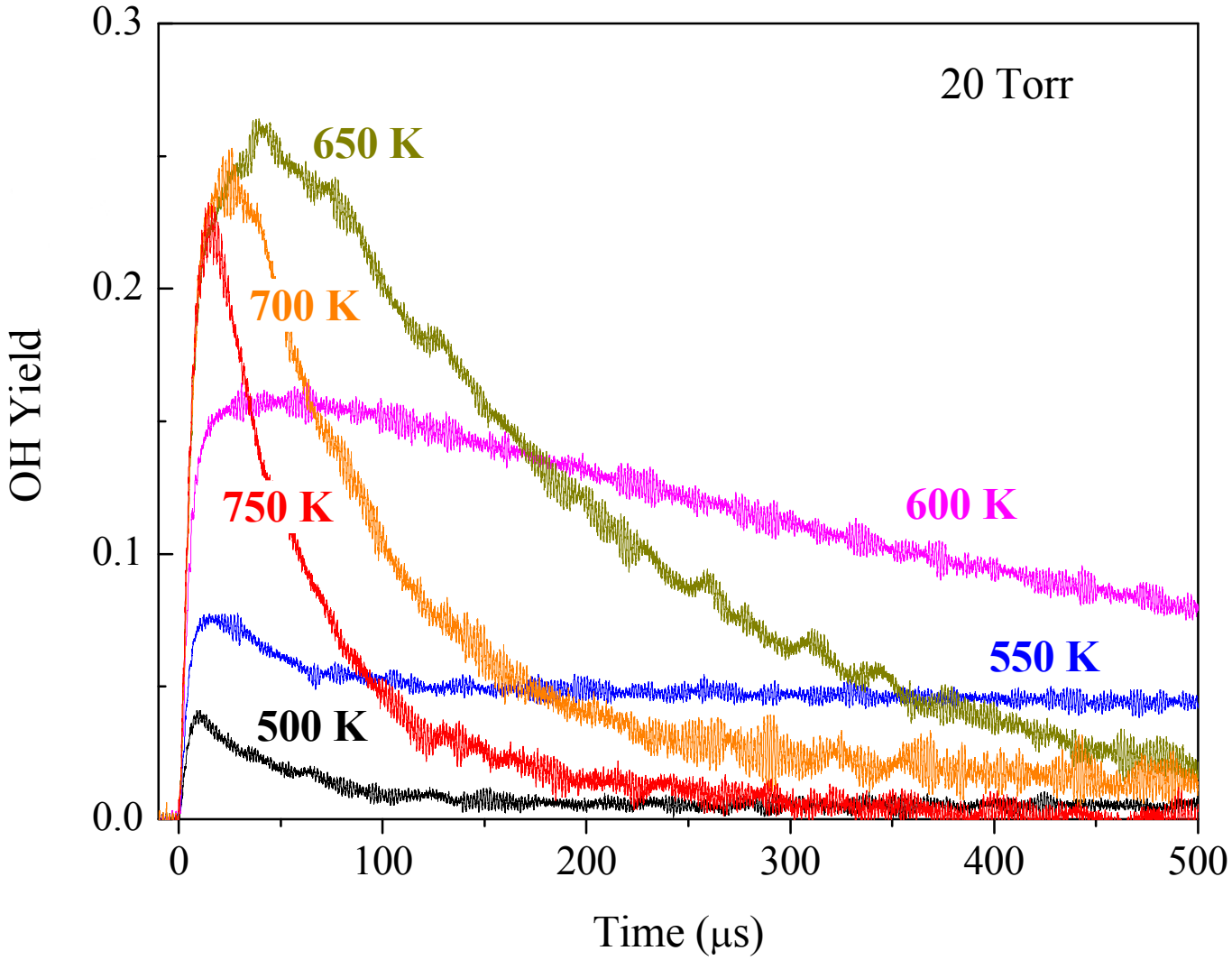


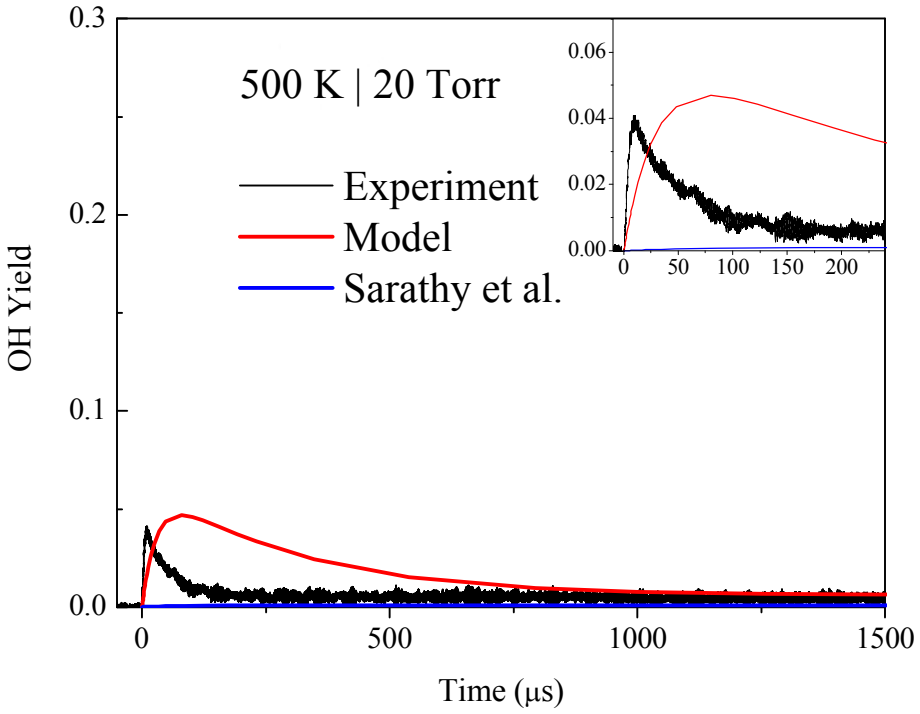



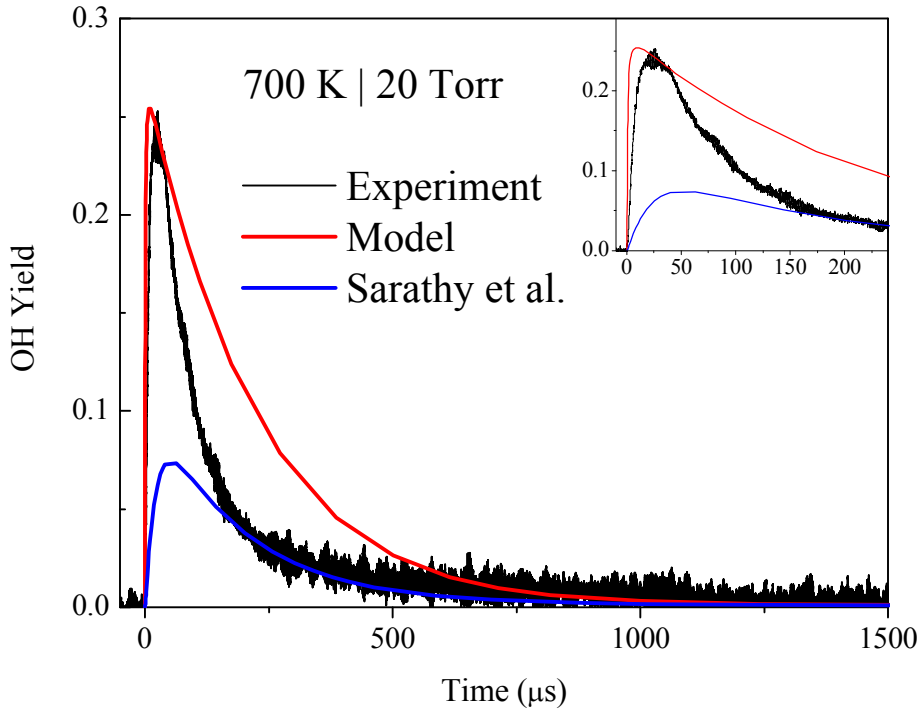

**Comprehensive Model for 2,5-dimethylhexane: Sarathy et al., *Comb. Flame*, 161 (2014)**

# OH Time History Measurements

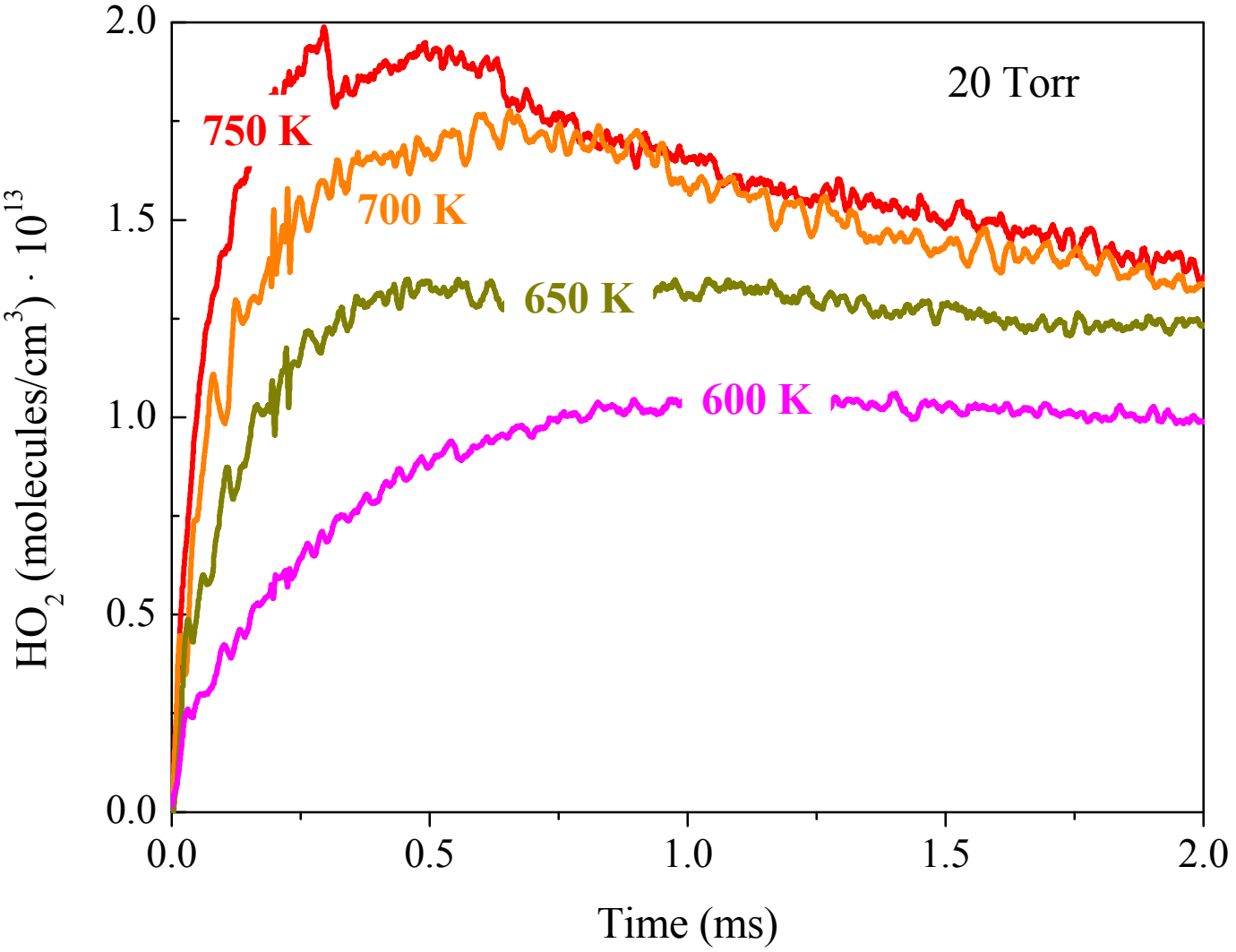


# OH Time History Measurements and Comparison with Detailed Chemical Kinetics Modeling

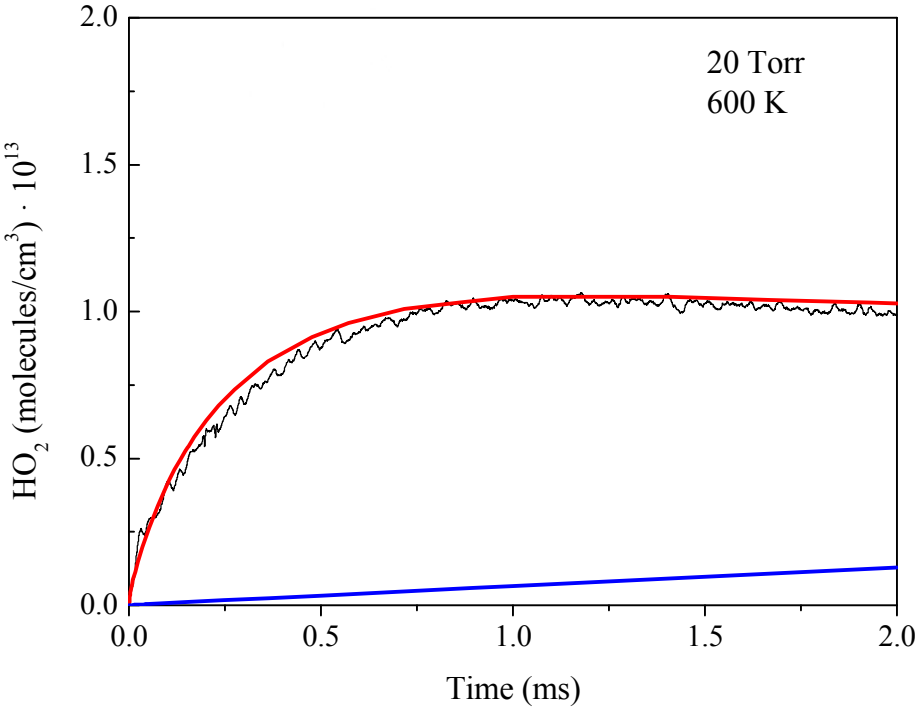


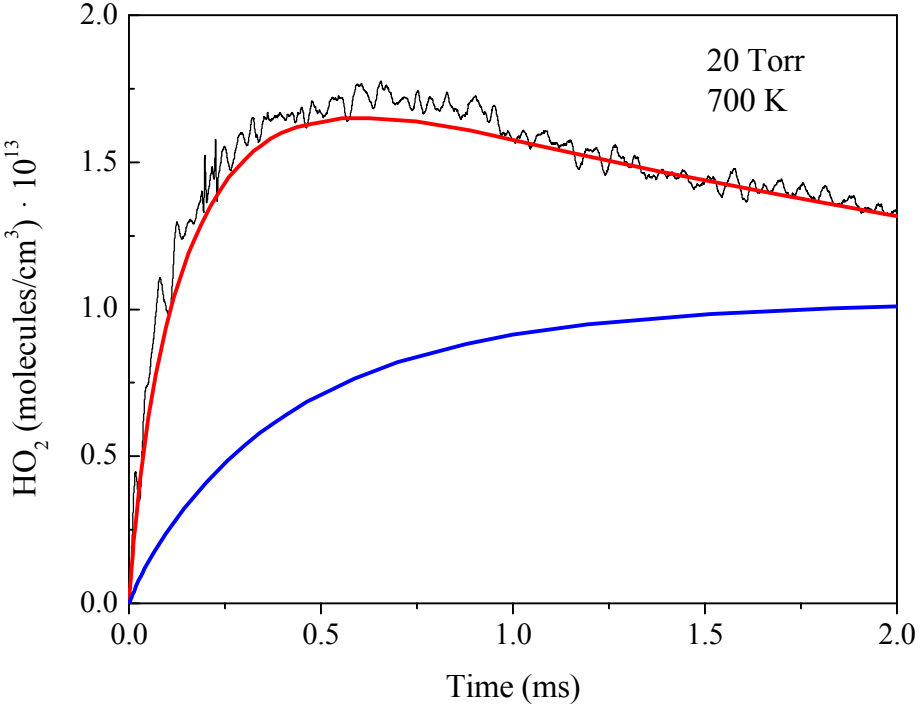



# $HO_2$ Time History Measurements



# $HO_2$ Time History Measurements and Comparison with Detailed Chemical Kinetics Modeling



# Changes Implemented into Sarathy et al. Model: *ab intio* Calculations of Rate Coefficients

**Class 1: R + $O_2$ = ROO**
**Class 5: ROO Isomerization to QOOH**
**Class 6: ROO = $HO_2$ + Alkene**
**Class 13: QOOH = Cyclic Ether + OH**
**Class 14: QOOH = Alkene + $HO_2$**
**Class 15: QOOH = Alkene + Carbonyl + OH**

**MultiWell (Time-Dependent Master Equation Solver)**

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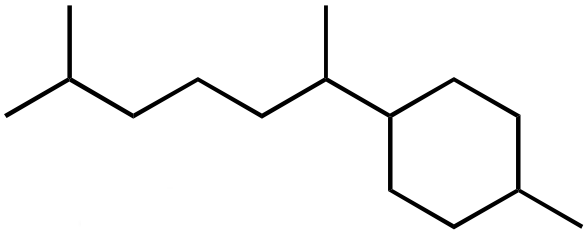
# Concluding Remarks

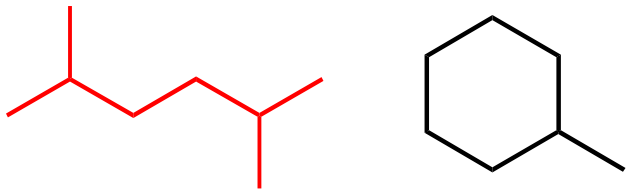
# Concluding Remarks

**Bisabolane ($C_{15}H_{30}$)**



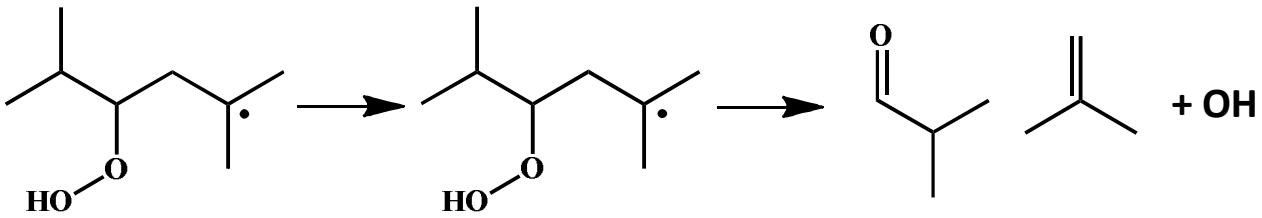
**Target Fuel**

**2,5-dimethylhexane** **MCH**



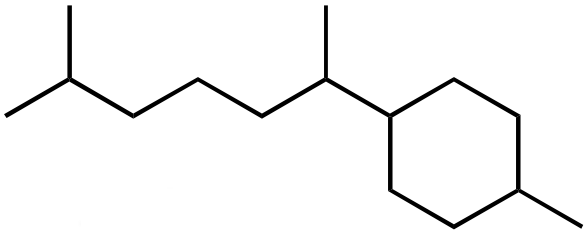
**Component Analogs**

- $RO_2$-related oxidation of 2,5-dimethylhexane studied at 550 K, 650 K using PIMS
  - Branching ratios of $HO_2$-elimination pathways quantified
  - 2,2,5,5-tetramethyl-THF vital to characterizing low-temperature chain-propagation
  - primary R ⟶ tertiary R favored over unimolecular decomposition and $O_2$-addition
  - Relevance of concerted QOOH decomposition (methylpropanal ⟶ significant)



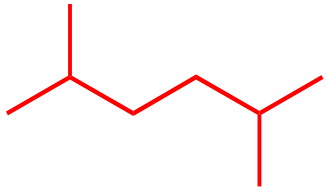
# Concluding Remarks

**Bisabolane ($C_{15}H_{30}$)**

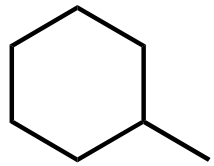


**Target Fuel**

**2,5-dimethylhexane**



**MCH**



**Component Analogs**

- OH, $HO_2$ time histories, *ab initio* rate coefficient calculations
  - Improved predictions of OH yield
  - Improved predictions of HOO yield
  - Improved $\phi$ = 1.0, 2.0 ignition delay time predictions in NTC region

- Remaining issues
  - RH + OH rate coefficients
  - Fuel-lean ($\phi$ = 0.5) ignition delay time predictions from high- to low-temperature


Sandia National Laboratories

University of Michigan

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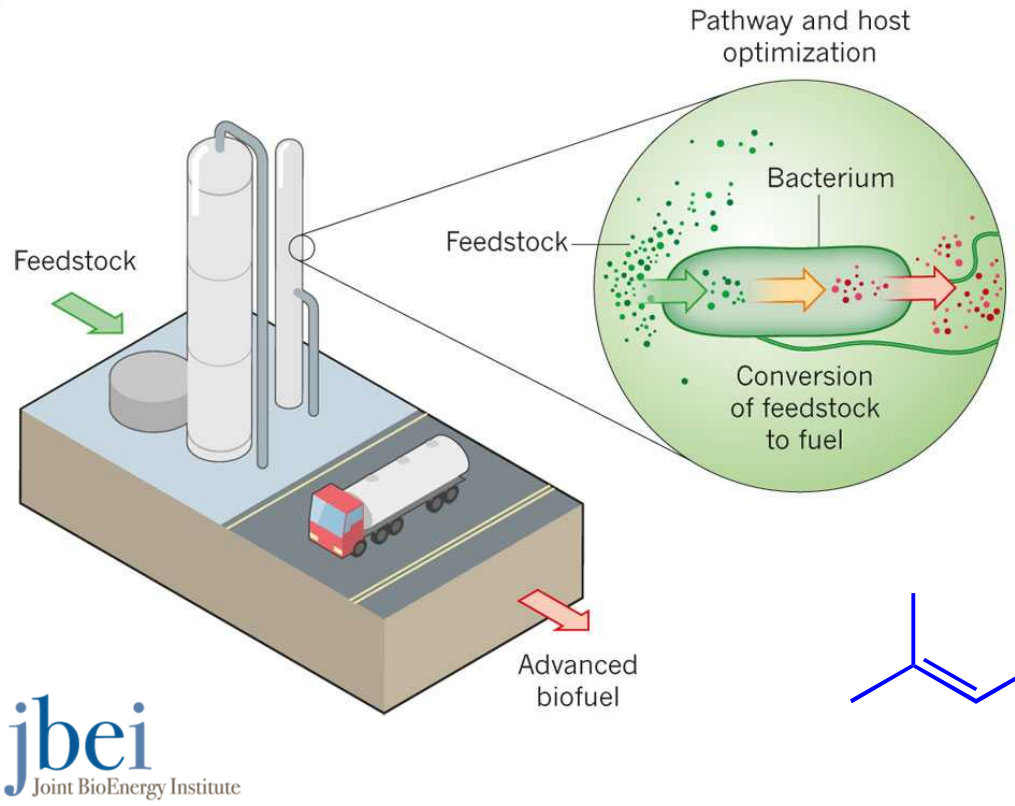
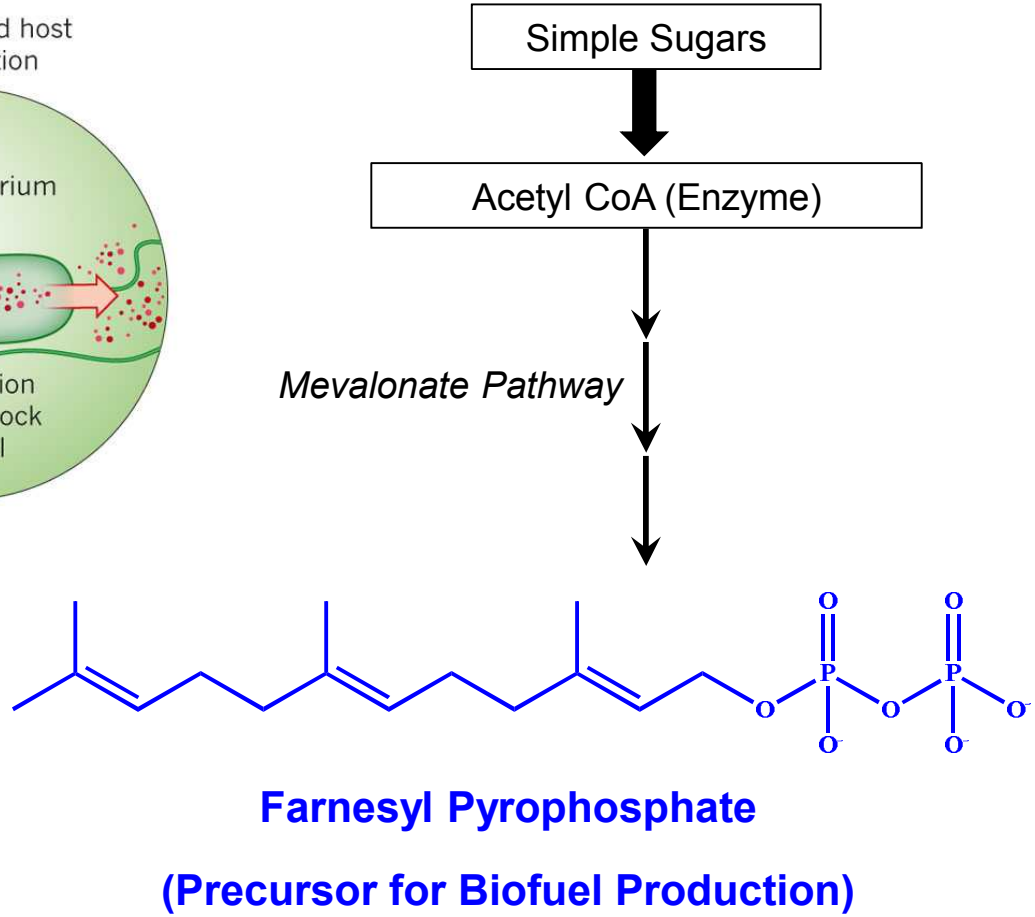
*Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the NNSA under contract DE-AC04-94AL85000*

*Funded by U.S.-China Clean Energy Research Center for Clean Vehicles*

# Targeted Biofuel Production using Microbial Synthesis




**Farnesyl Pyrophosphate**

**(Precursor for Biofuel Production)**

Peralta-Yahya, Zhang, del Cardayre, and Keasling, (2012).
Microbial engineering for the production of advanced biofuels. *Nature*, 488, 320.

# Microbial Production of Biofuel Provides Some Control Over Fuel Structure

| Sesquiterpenes | Production using *S. cerevisiae* | Production using *E. coli* |
|---|---|---|
| Farnesene | 2 µg/L | 240 mg/L |
| Bisabolene | 150 µg/L | 517 mg/L |
| Curcumene | Not detected | 130 µg/L |
| Vetispiradiene | 300 µg/L | 73 mg/L |
| Cadinene | 3.6 mg/L | 10.3 µg/L |
| Aristolochene | 190 µg/L | 33 mg/L |
| Amorphadiene | 120mg/L | 20 g/L |

Peralta-Yahya et al.
*Nature Communications*, 2011

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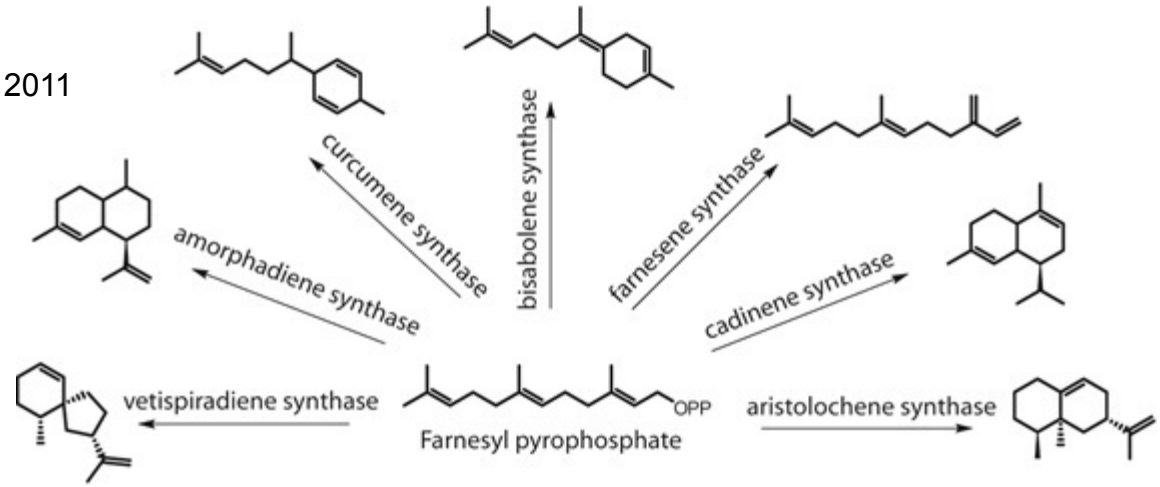

# Selected Biosynthetic Pathway Leads to Diesel-like Fuel Molecule

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|---|---|---|
| Farnesene | 2 µg/l | 240 mg/l |
| **Bisabolene** | **150 µg/L** | **517 mg/L** |
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Peralta-Yahya et al.
*Nature Communications*, 2011

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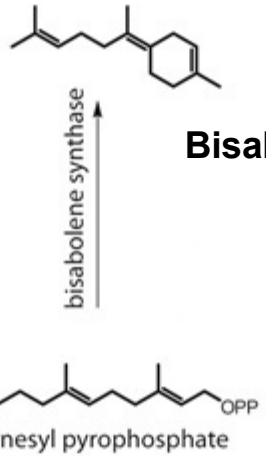


**Bisabolene ($C_{15}H_{24}$)**

# Overview of Species Detected in Mass Spectra

| m/z | Linear Formula | 550 K | 650 K | |
|---|---|---|---|---|
| **128** | $C_8H_{16}O$ | 2,2,5,5-tetramethyl-tetrahydrofuran | 2,2,5,5-tetramethyl-tetrahydrofuran | **Cyclic Ether** |
| **126** | $C_8H_{14}O$ | (unidentified) | (unidentified) | |
| **112** | $C_8H_{16}$ | 2,5-dimethyl-1-hexene | 2,5-dimethyl-1-hexene | **Alkene ($HO_2$-Elimination)** |
| | | 2,5-dimethyl-2-hexene | 2,5-dimethyl-2-hexene | |
| | | 2,5-dimethyl-3-hexene | 2,5-dimethyl-3-hexene | |
| **104** | $C_4H_8O_3$ (minor) | (unidentified) | (unidentified) | |
| **98** | $C_7H_{14}$ | – | 5-methyl-2-hexene | **Alkene** |
| **90** | $C_3H_6O_3$ (minor) | (unidentified) | (unidentified) | |
| **86** | $C_5H_{10}O$ | (unidentified) | (unidentified) | |
| **84** | $C_5H_8O$ | (unidentified) | (unidentified) | |
| **72** | $C_4H_8O$ | methyl-propanal | methyl-propanal | **Aldehyde** |
| **70** | $C_5H_{10}$ | (unidentified) | (unidentified) | |
| **68** | $C_5H_8$ | isoprene | isoprene | **Diene** |
| **58** | $C_3H_6O$ | acetone | acetone | **Ketone** |
| | | methyloxirane | – | |
| **56** | $C_4H_8$ | *iso*-butene | *iso*-butene | **Alkene** |
| **44** | $C_2H_4O$ | acetaldehyde | acetaldehyde | **Aldehyde** |
| | | vinyl alcohol | vinyl alcohol | **Alcohol** |
| **42** | $C_3H_6$ | propene | propene | **Alkene** |

# Quantification of Fractional Yields of Products

| m/z | Species | Fractional Yield | |
|---|---|---|---|
| | | 550 K | 650 K |
| 42 | propene | 0.10 | 0.38 |
| 44 | acetaldehyde | 0.04 | 0.02 |
| | vinyl alcohol | 0.02 | 0.01 |
| 56 | *iso*-butene | 1.05 | 0.88 |
| 58 | acetone | 0.49 | 0.21 |
| | methyloxirane | 0.21 | 0.00 |
| 68 | isoprene | 0.01 | 0.01 |
| 72 | methyl-propanal | 1.46 | 0.58 |
| 98 | 5-methyl-2-hexene | 0.00 | 0.07 |
| 112 | ***2,5-dimethyl-1-hexene*** | ***1.00*** | ***1.00*** |
| | 2,5-dimethyl-2-hexene | 1.13 | 0.71 |
| | 2,5-dimethyl-3-hexene | 1.16 | 0.41 |
| 128 | 2,2,5,5-tetramethyl-THF | 73.69 | 12.91 |

**Ion Signal:**

$$S_i(E) = \Lambda \sigma_i(E) c_i \alpha_i$$

**Absolute Photoionization Cross-Section:**

$$\sigma_i(E) = \sigma_{ref.}(E) \left(\frac{S_i(E)}{S_{ref.}(E)}\right)\left(\frac{c_i}{c_{ref.}}\right)\left(\frac{m_i}{m_{ref.}}\right)^{\beta(P,T)}$$

$$\sigma_i(E) = S_i(E)\left(\frac{\gamma(P,T)}{c_i m_i^{\beta(P,T)}}\right)$$

**Fitting Coefficients:**

$$S(E) = \sum_i^N A_i \sigma_i(E)$$

**Fractional Yield:**

$$\rho = \left(\frac{A_i}{A_{2,5-dimethyl-1-hexene}}\right)\left(\frac{m_i}{112.125}\right)^{\beta(P,T)}$$

# Quantification of Fractional Yields of Products

| m/z | Species | Fractional Yield | |
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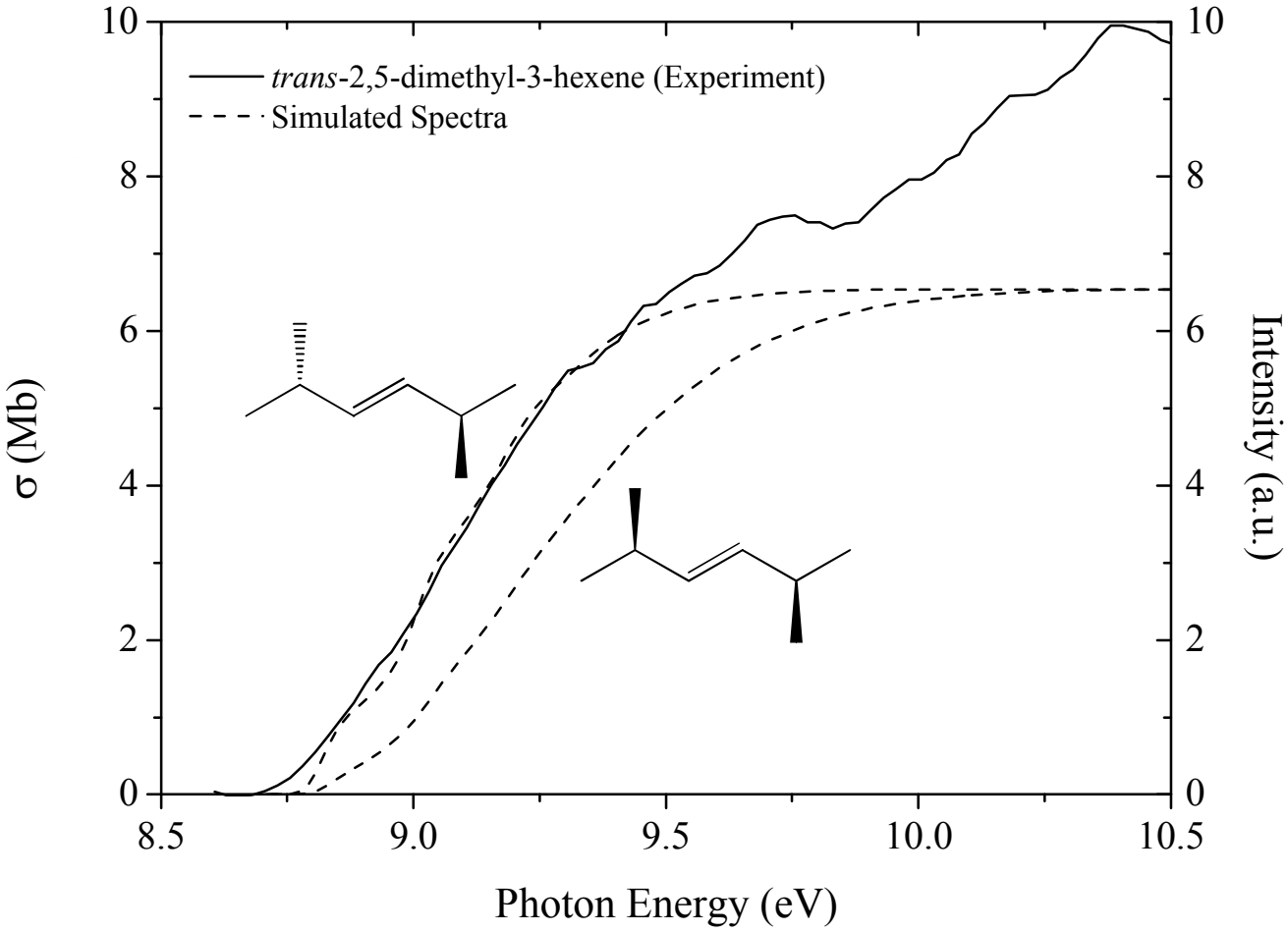
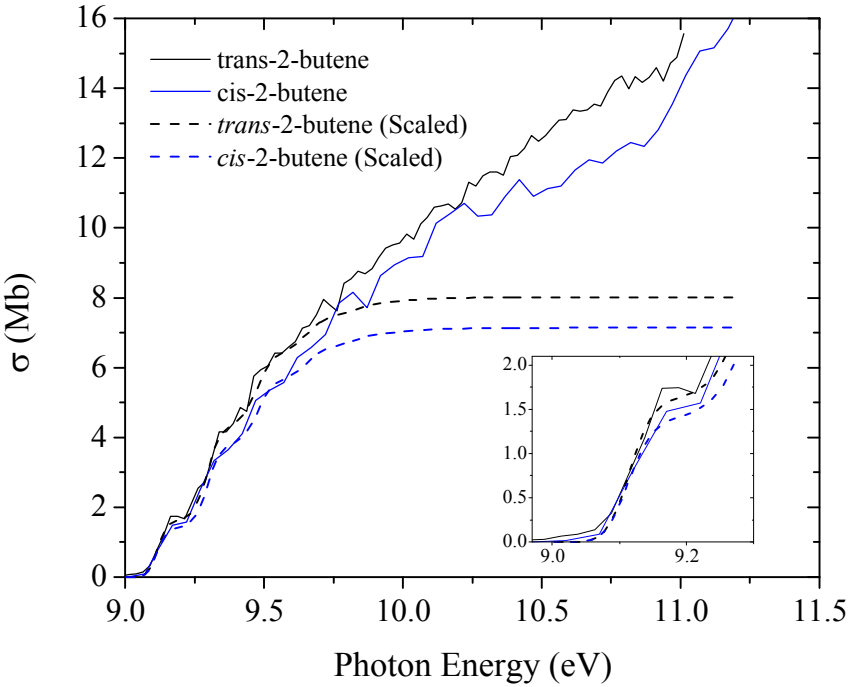
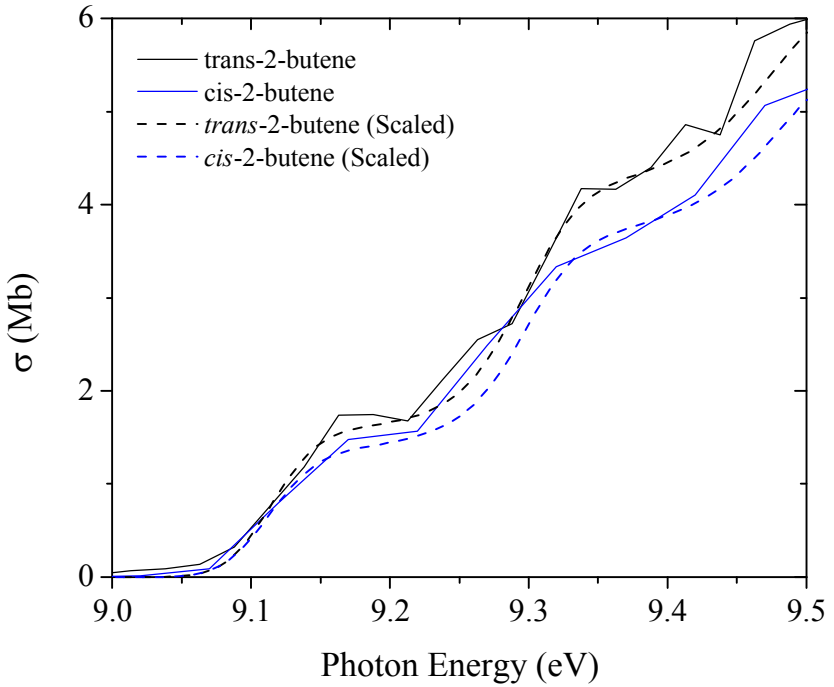
| | 2,5-dimethyl-3-hexene | 1.16 | 0.41 |
| 128 | 2,2,5,5-tetramethyl-THF | 73.69 | 12.91 |

**Fractional yields defined relative to formation of $HO_2$-elimination co-product 2,5-dimethyl-1-hexene:**

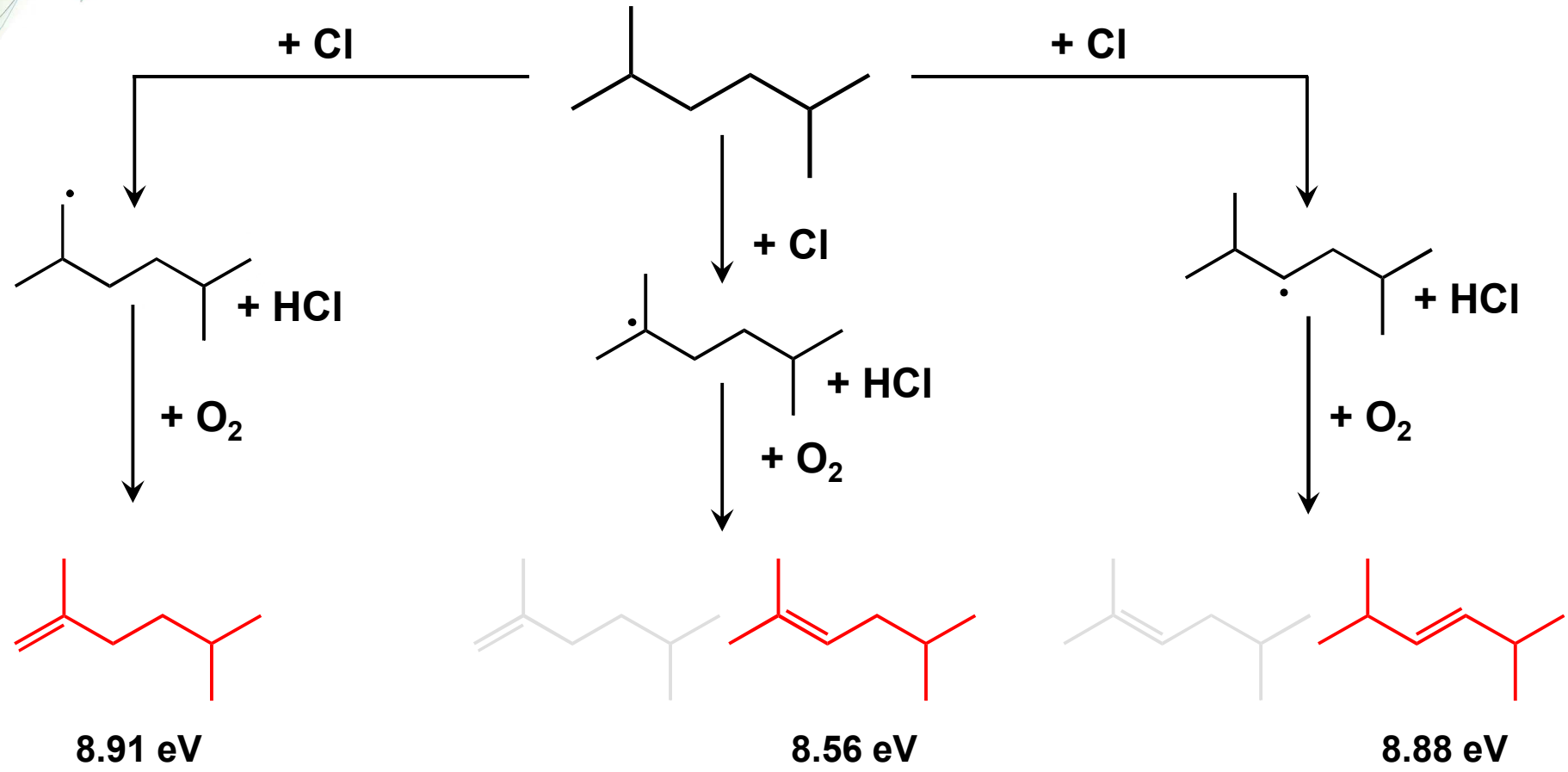
$$Fractional\ Yield = \frac{[Species\ i]}{[2,5{-}dimethyl{-}1{-}hexene]}$$


trans-2,5-dimethyl-3-hexene (Experiment)
Simulated Spectra
σ (Mb)
Intensity (a.u.)
Photon Energy (eV)
0
2
4
6
8
10
8.5
9.0
9.5
10.0
10.5


trans-2-butene
cis-2-butene
trans-2-butene (Scaled)
cis-2-butene (Scaled)
σ (Mb)
Photon Energy (eV)
0
2
4
6
8
10
12
14
16
9.0
9.5
10.0
10.5
11.0
11.5
2.0
1.5
1.0
0.5
0.0
9.0
9.2

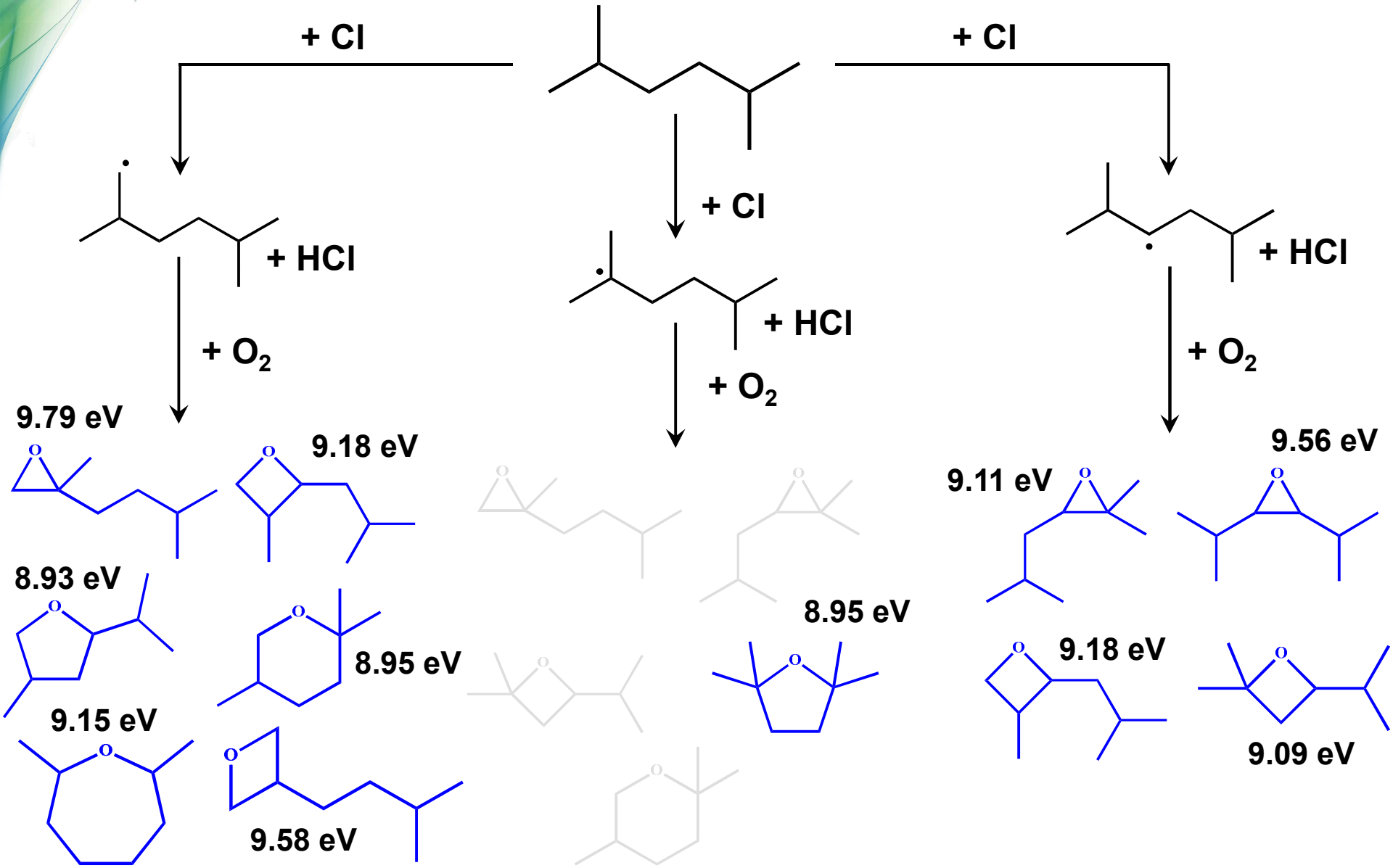

trans-2-butene
cis-2-butene
trans-2-butene (Scaled)
cis-2-butene (Scaled)
σ (Mb)
Photon Energy (eV)
0
2
4
6
9.0
9.1
9.2
9.3
9.4
9.5

# $HO_2$-Elimination Co-Products of R + $O_2$

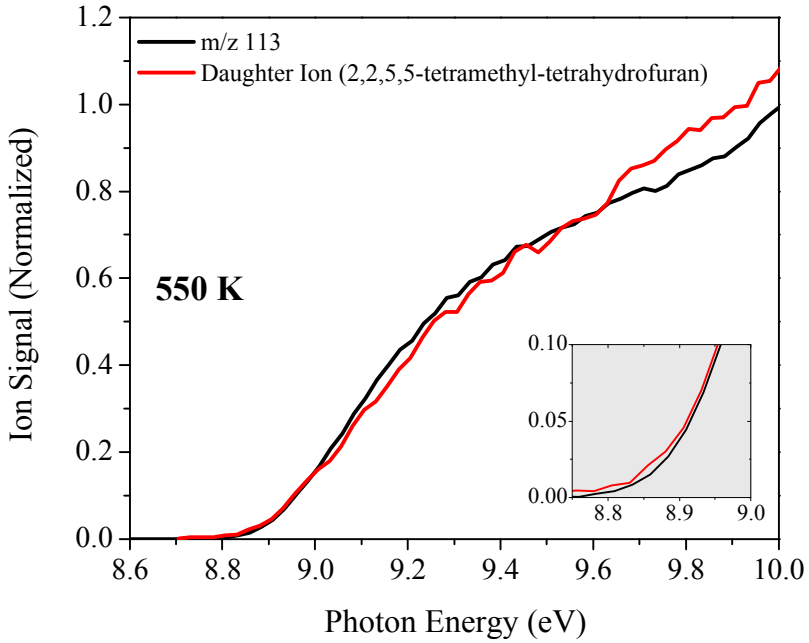



**CBS-QB3-Calculated Adiabatic Ionization Energies**

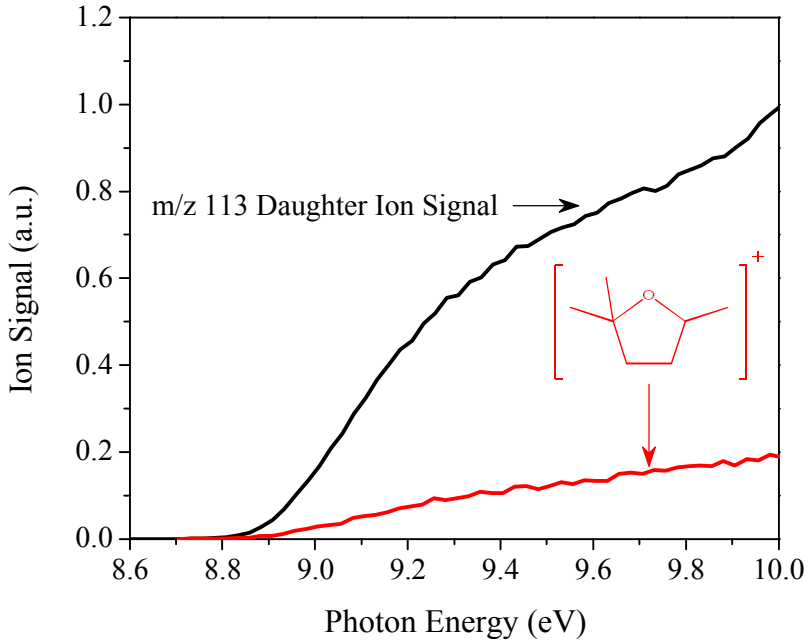
# OH-Loss Co-Products from QOOH Species



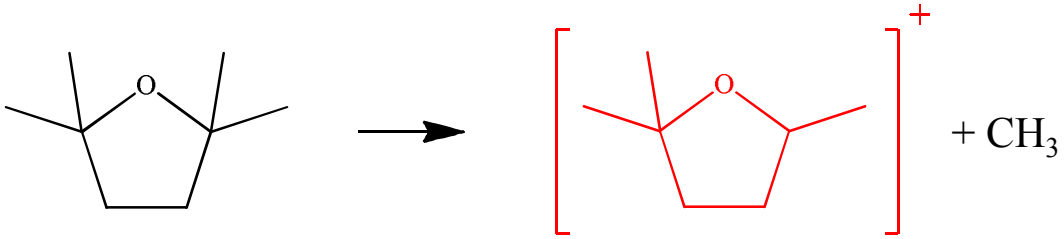
# Daughter Ion Measurements Support Quantification of Upper Limit to 2,2,5,5-tetramethyl-THF



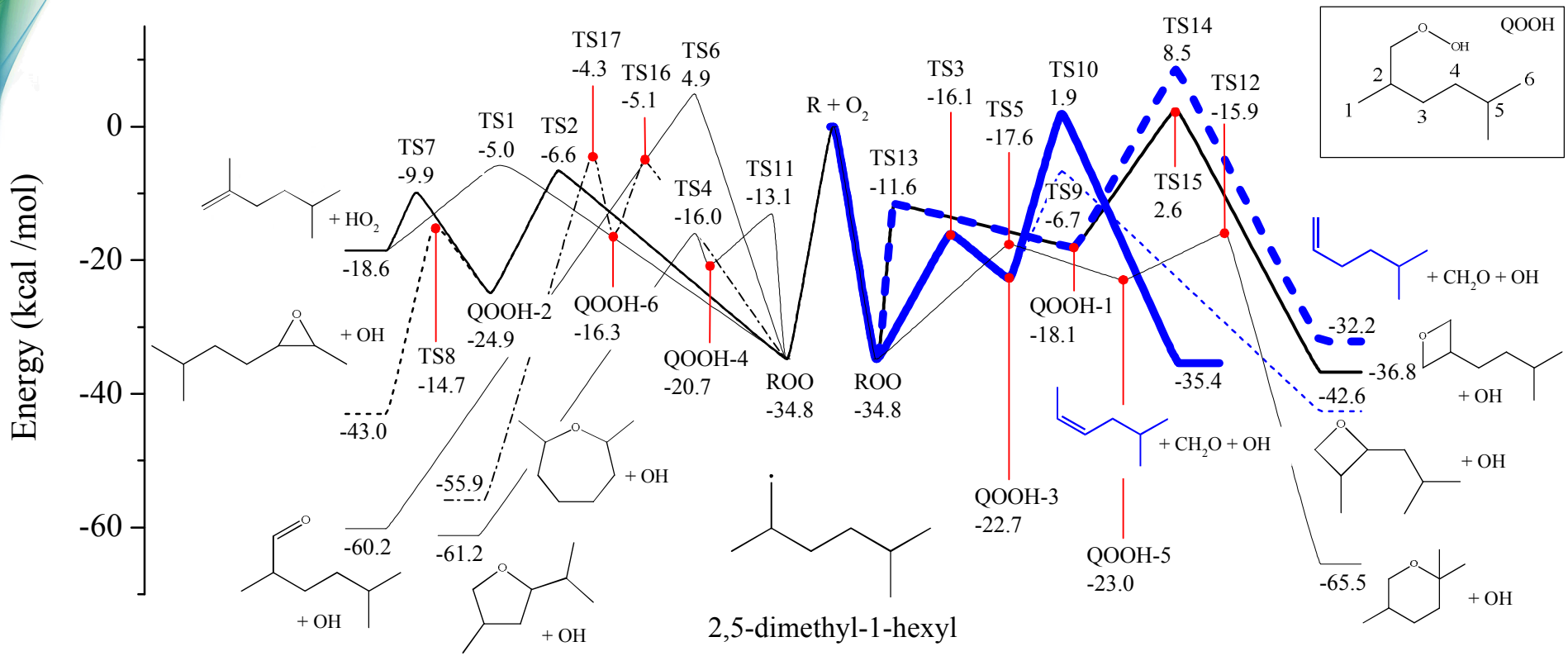

**Normalized m/z 113 daughter ion signals**




**Scaled m/z 113 daughter ion signals**

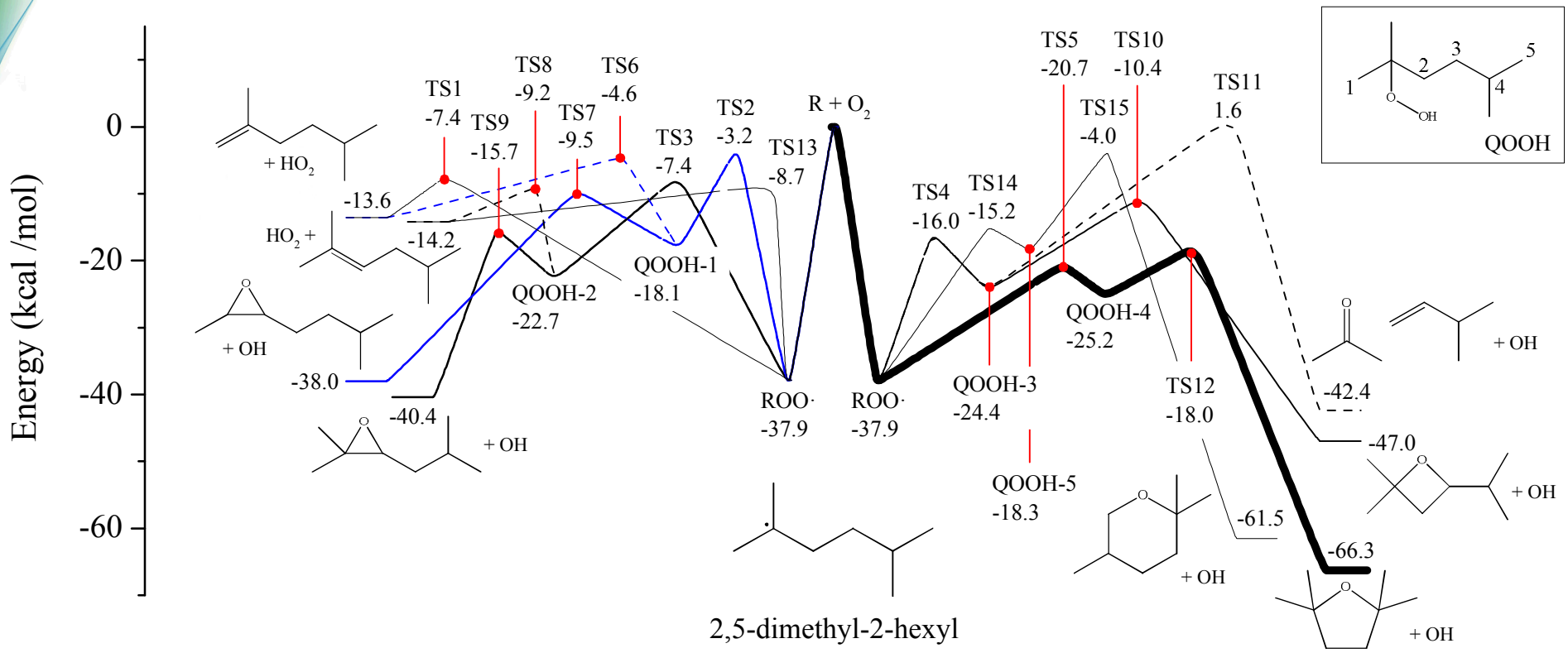


# Stationary Points: 2,5-dimethyl-1-hexyl + $O_2$

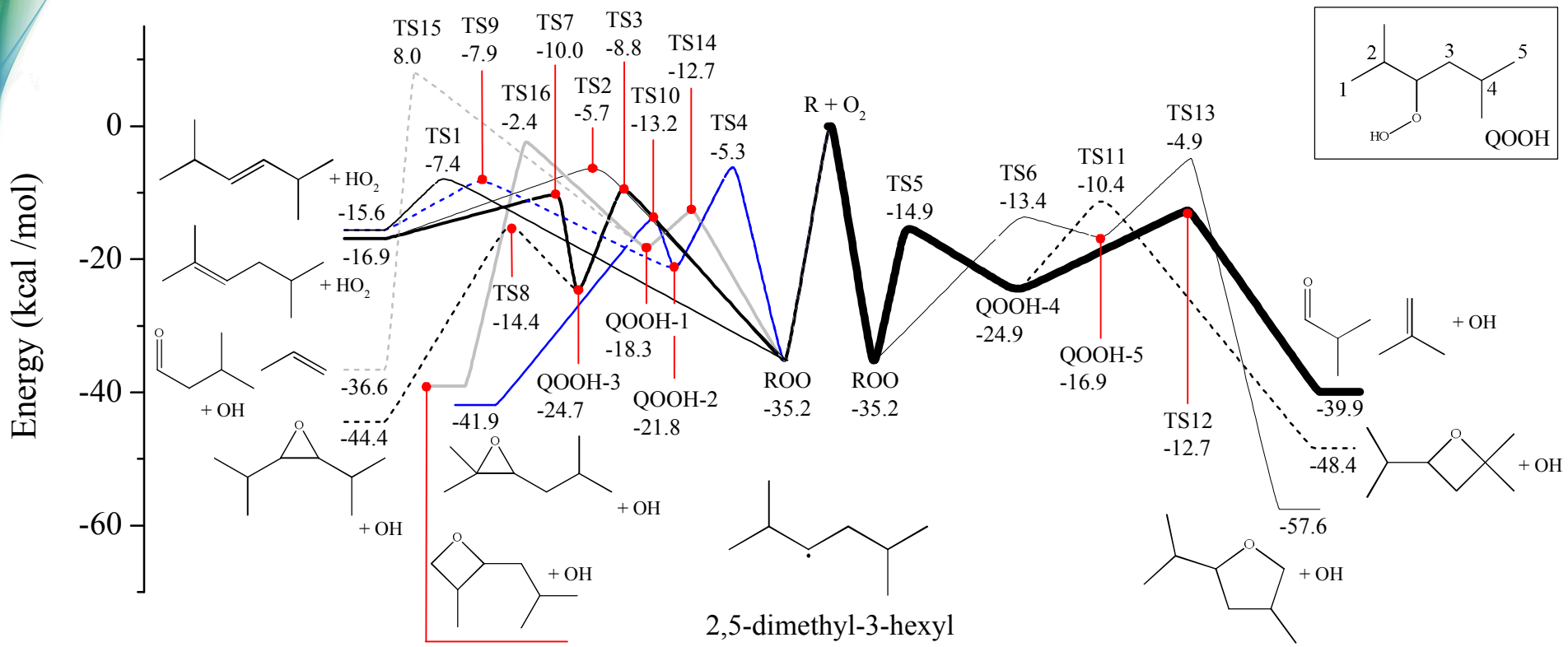


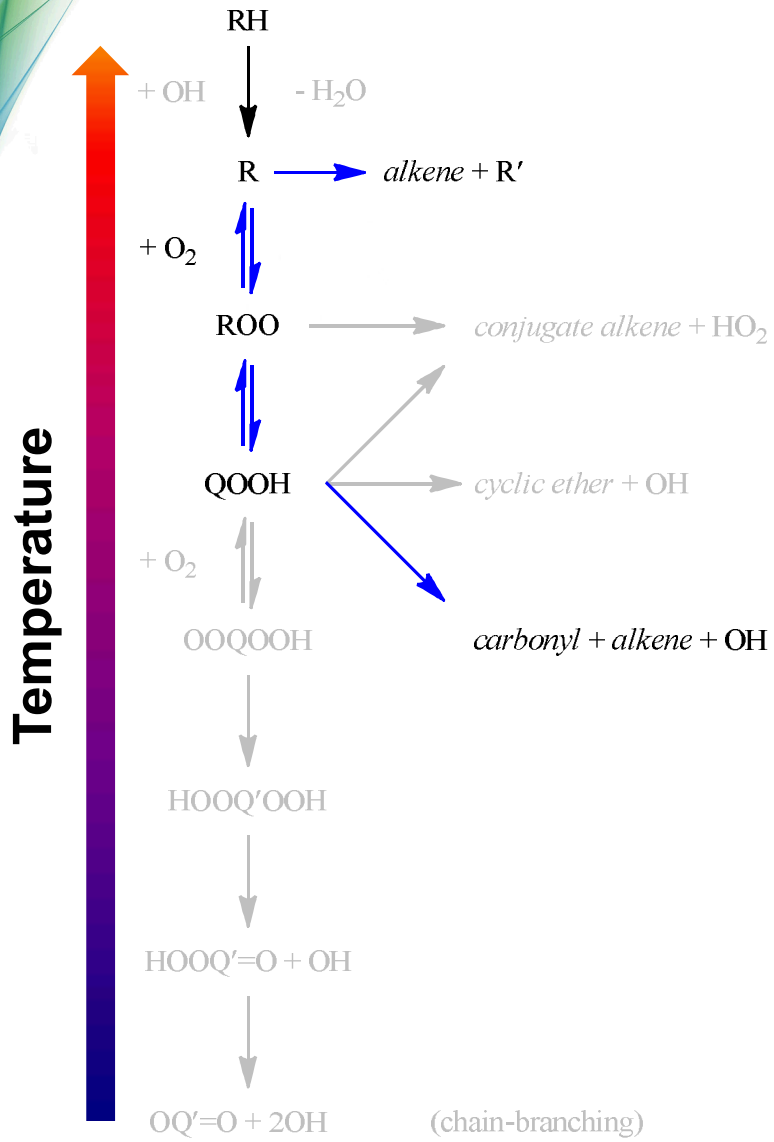

**Energy barriers to m/z 98 alkene formation from QOOH lie above entrance channel for R + $O_2$**

# Stationary Points: 2,5-dimethyl-2-hexyl + $O_2$ Calculated at CBS-QB3 Level

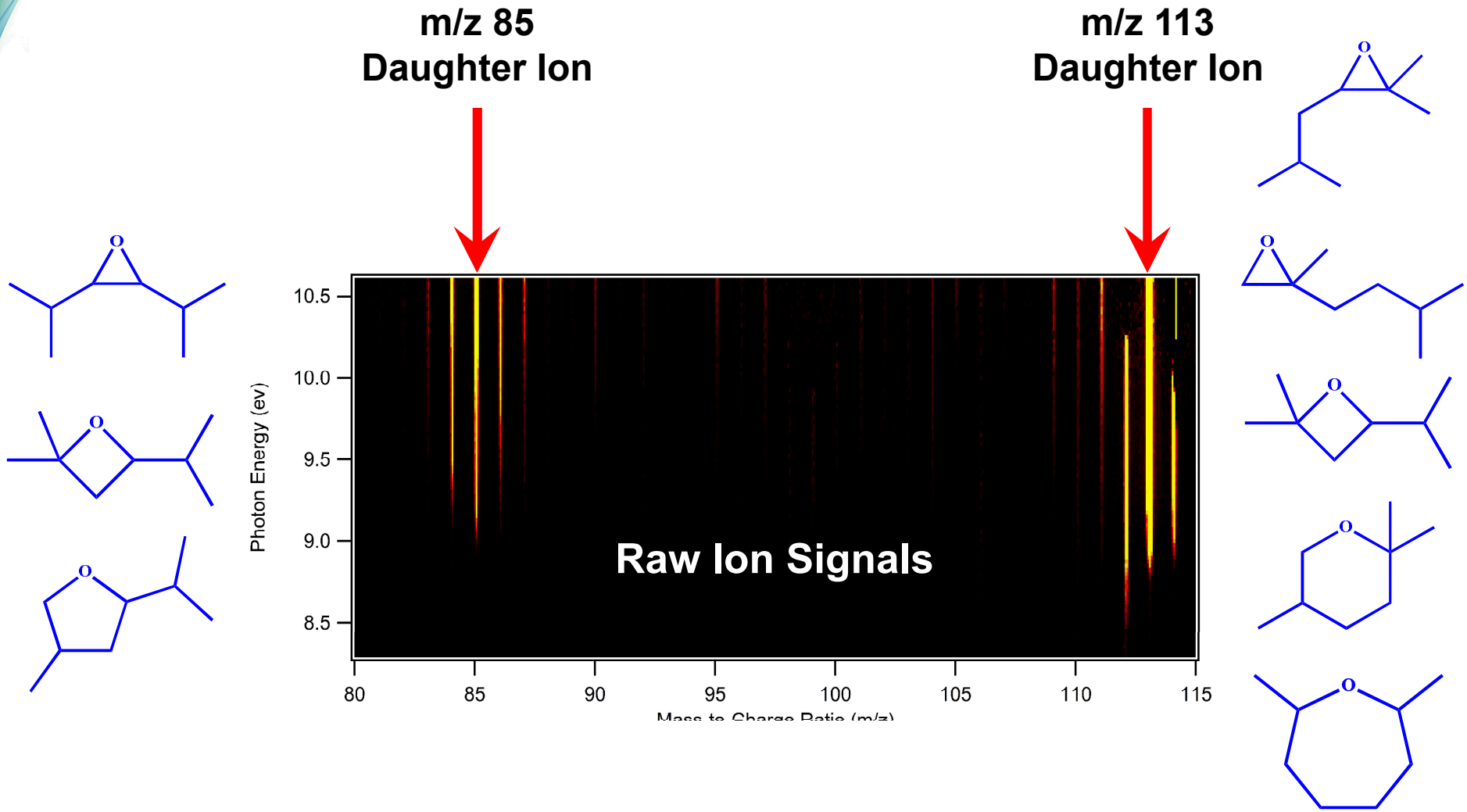


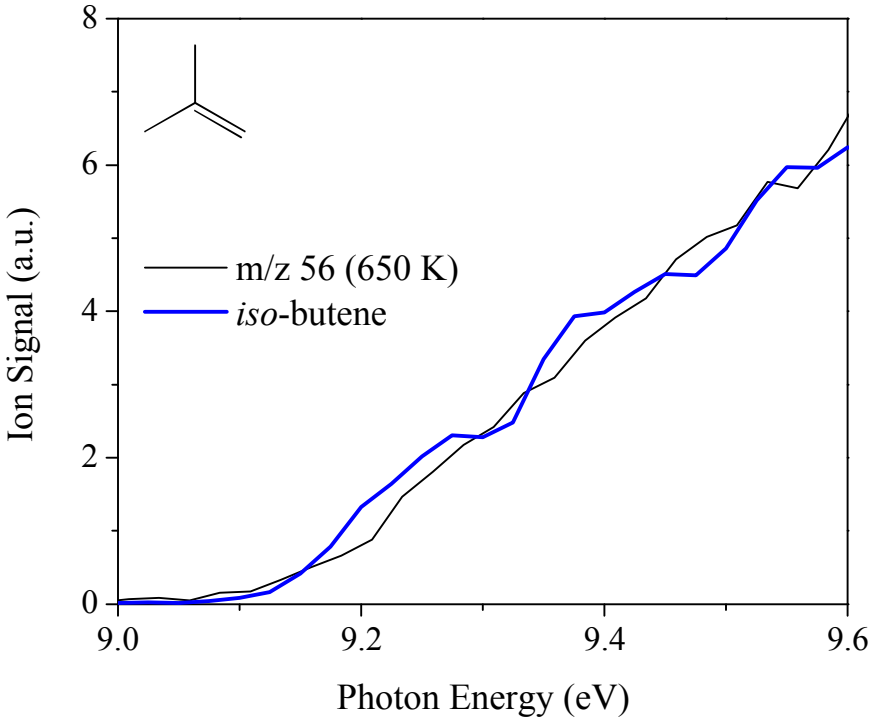
# Stationary Points: 2,5-dimethyl-3-hexyl + $O_2$



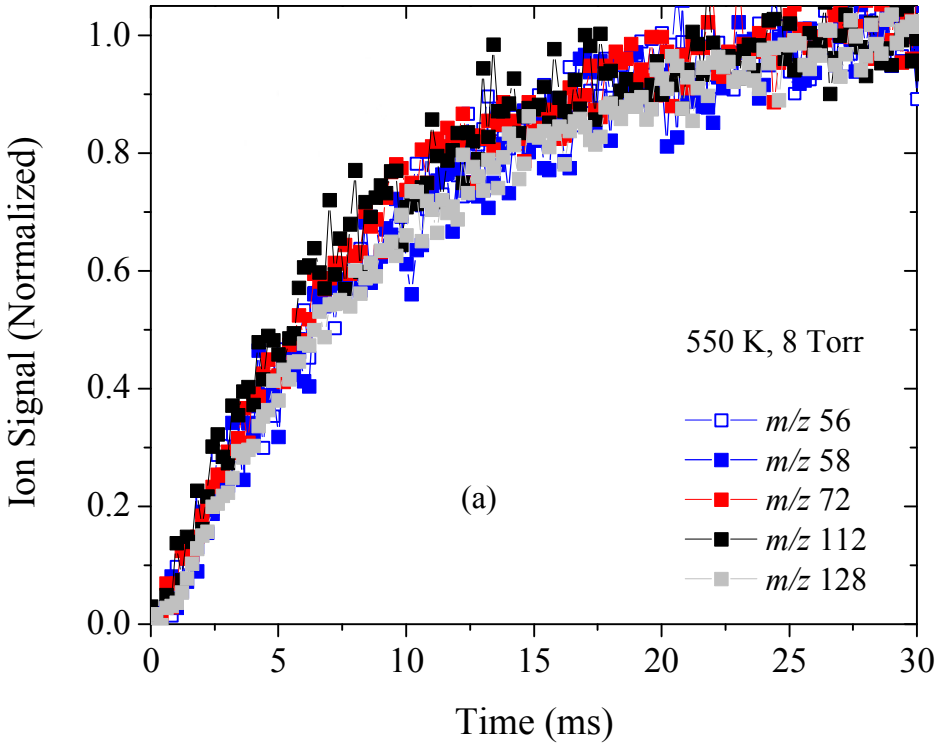

RH
+ OH
- $H_2O$
R
*alkene* + R′
+ $O_2$
ROO
*conjugate alkene* + $HO_2$
QOOH
*cyclic ether* + OH
+ $O_2$
OOQOOH
*carbonyl* + *alkene* + OH
HOOQ′OOH
HOOQ′=O + OH
OQ′=O + 2OH
(chain-branching)
Temperature

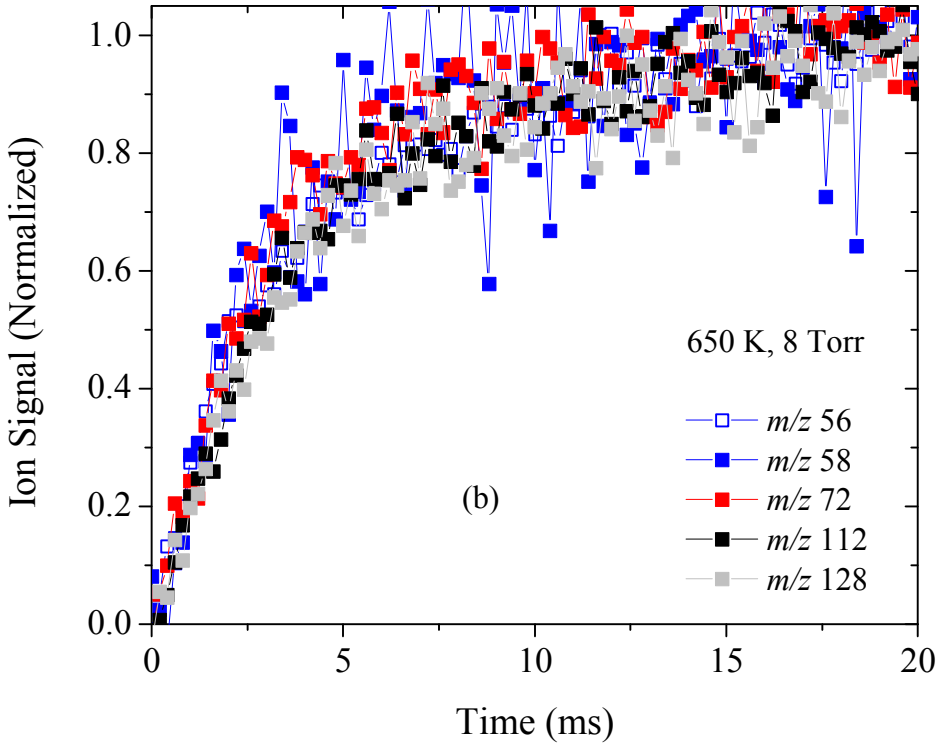
# Daughter Ion Signals Indicate Potential for Other Cyclic Ethers Formed by QOOH Decomposition



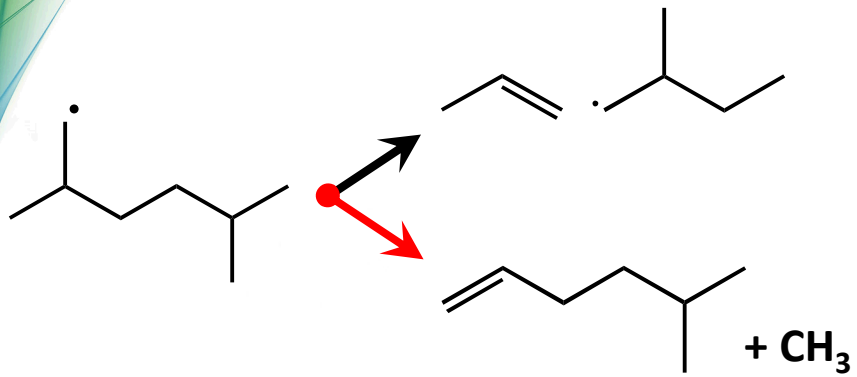

8
6
4
2
0
Ion Signal (a.u.)
m/z 56 (650 K)
iso-butene
9.0
9.2
9.4
9.6
Photon Energy (eV)

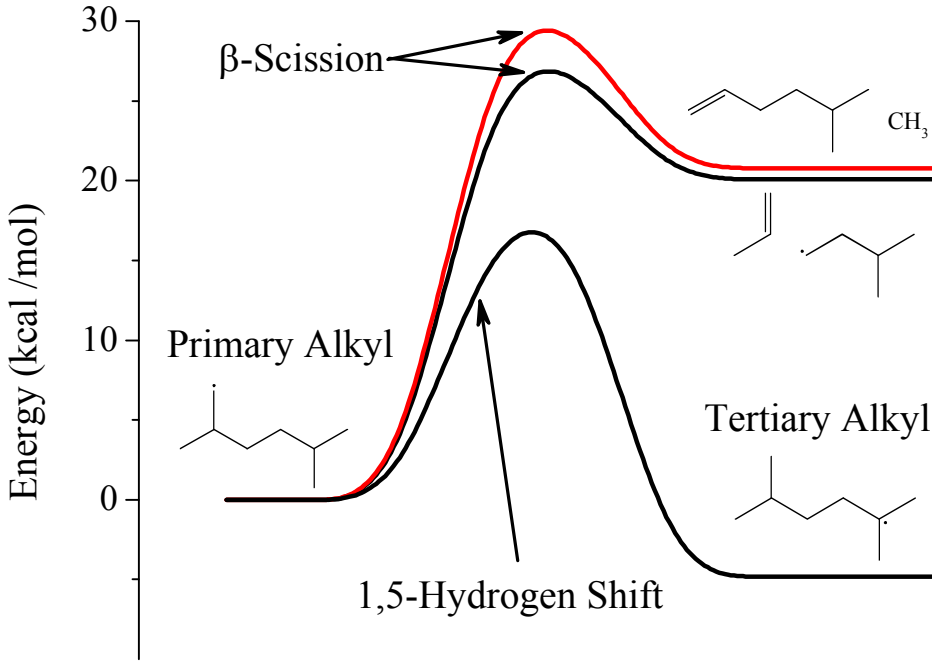
# Time Histories



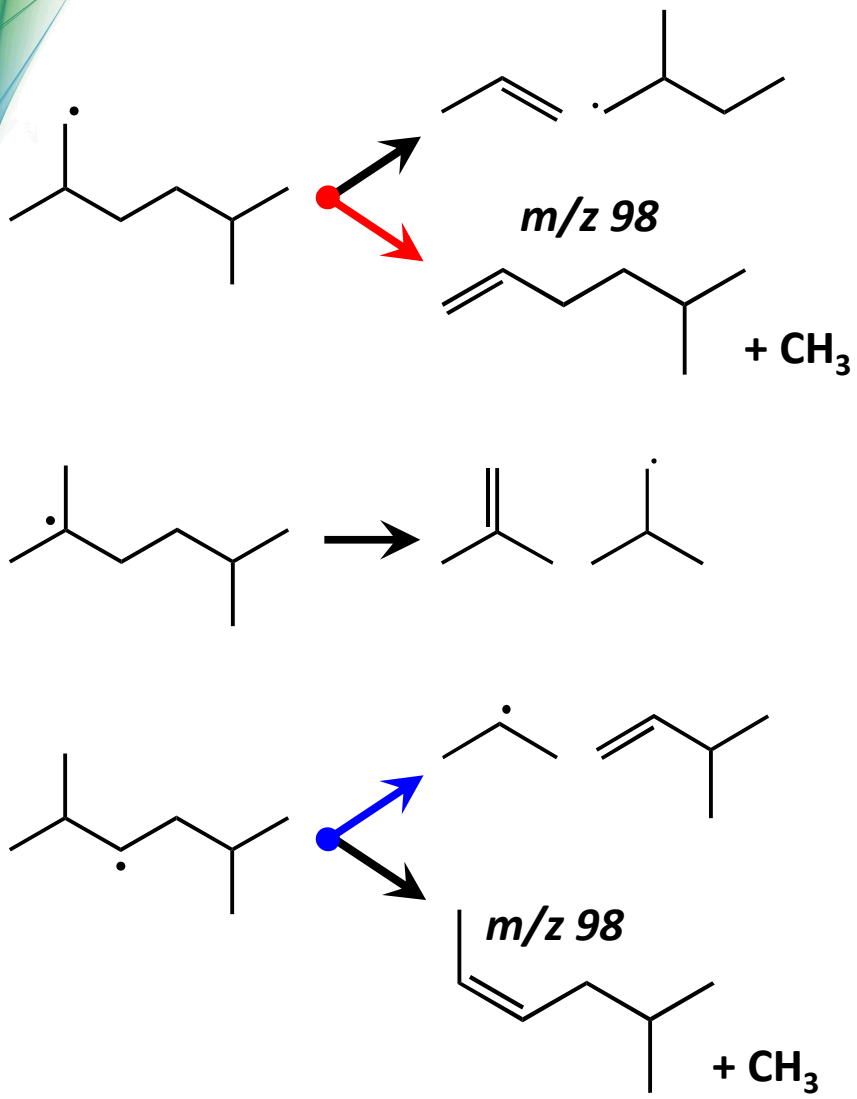



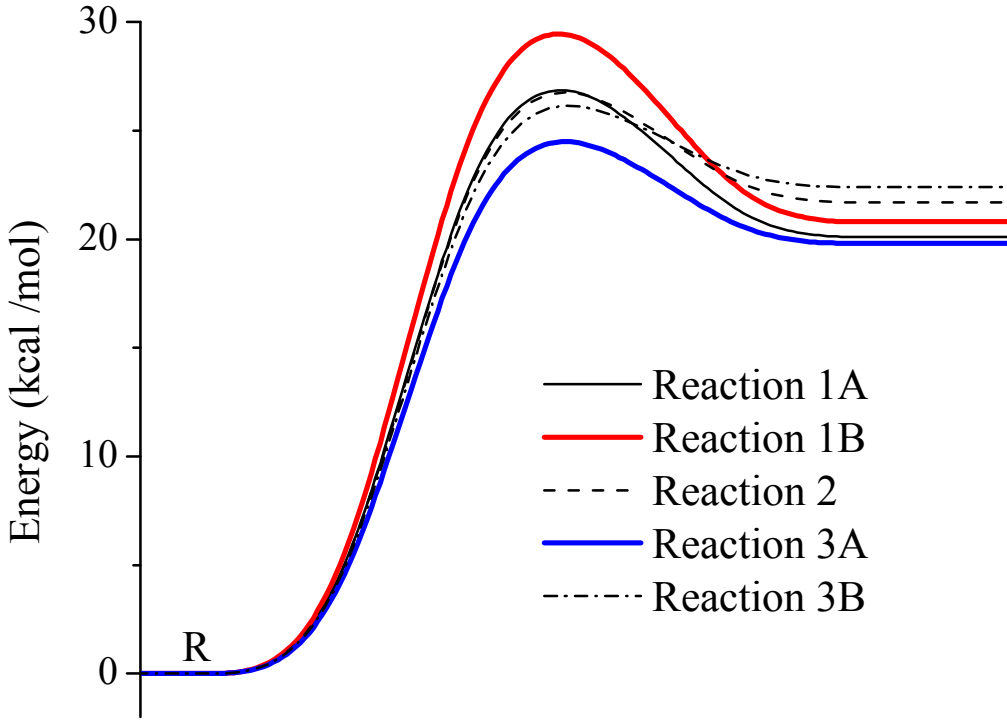
# Role of Primary Alkyl Radicals in Forming 2,2,5,5-tetramethyl-THF



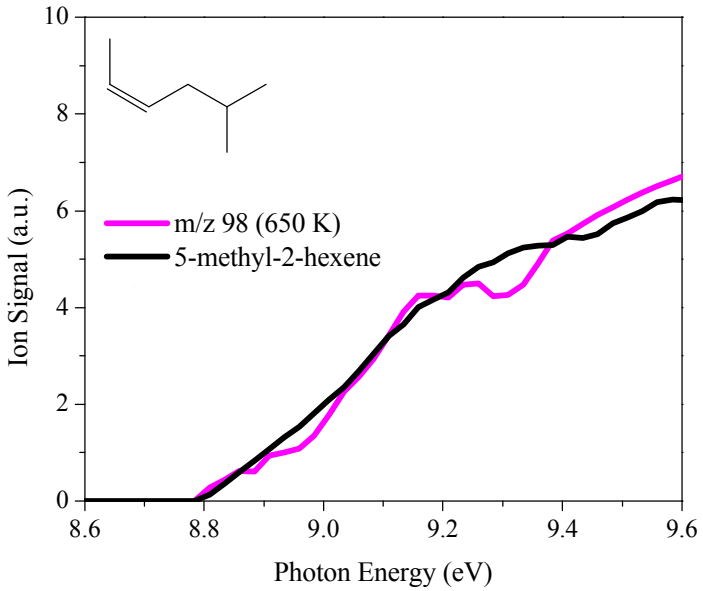



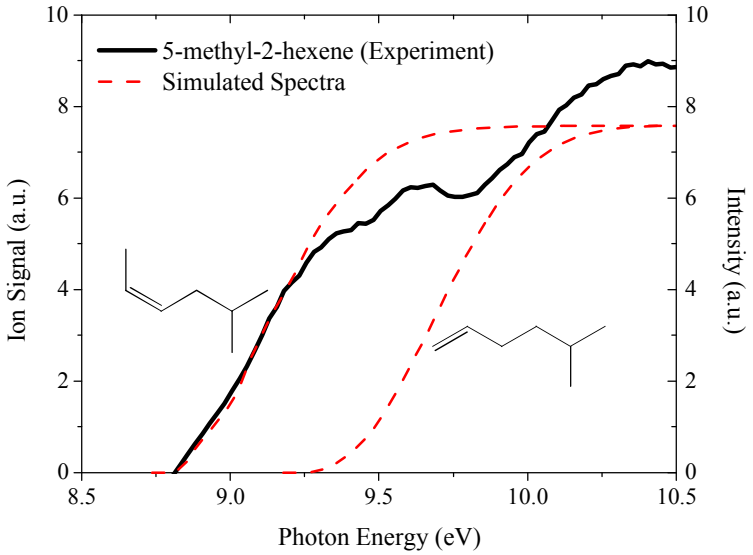
# β-Scission Pathways in 2,5-dimethylhexane

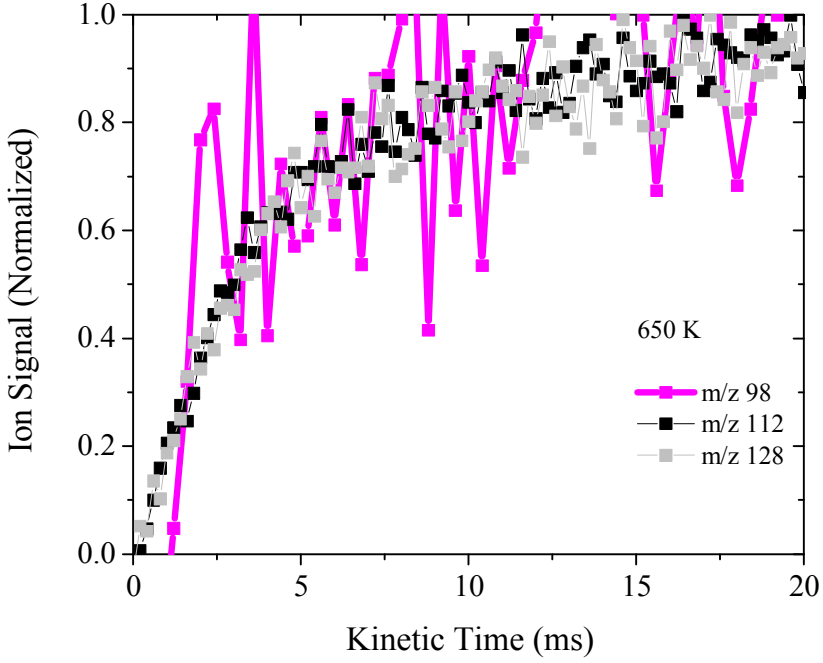


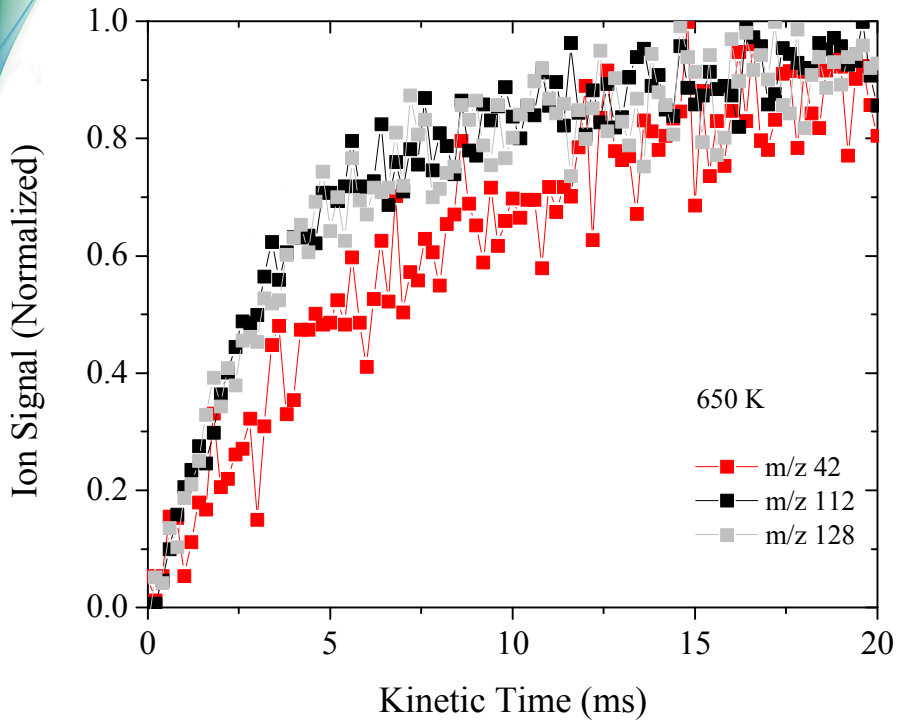
# Evidence of β-Scission: m/z 98 (5-methyl-2-Hexene)

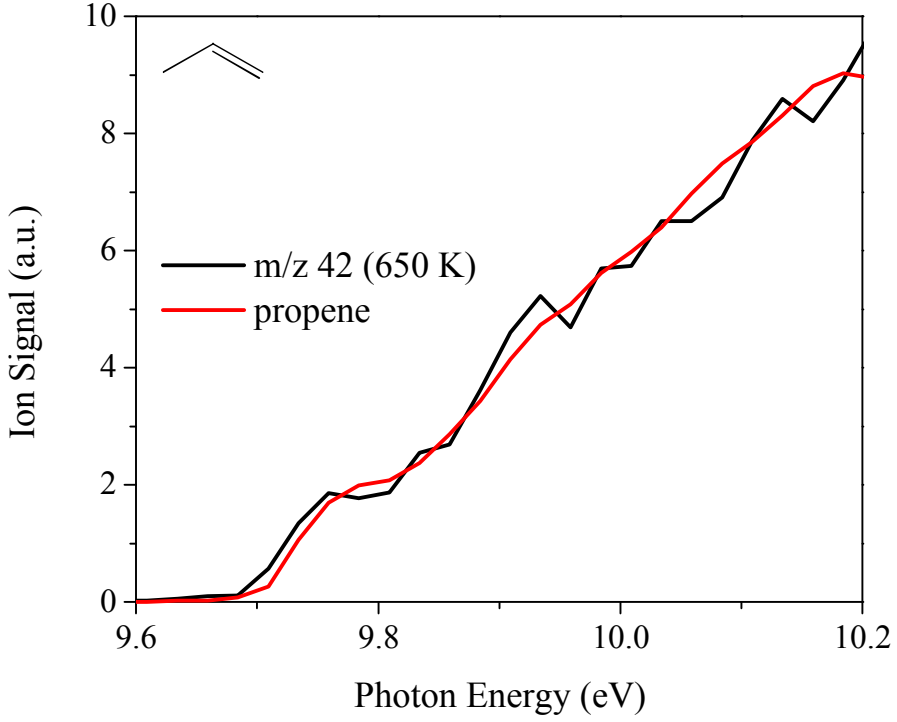


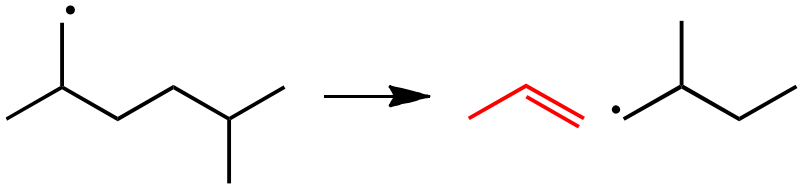



# Evidence of β-Scission: m/z 42 (Propene)

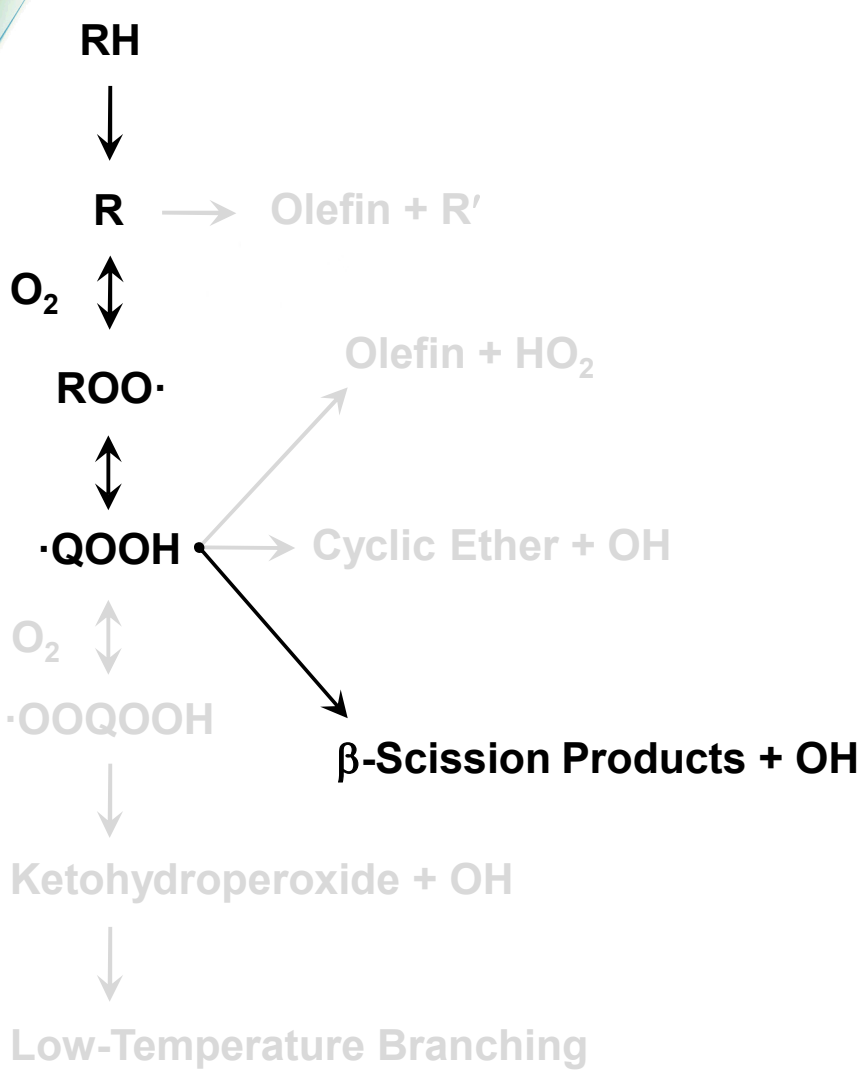


# Results (3): Other Channels

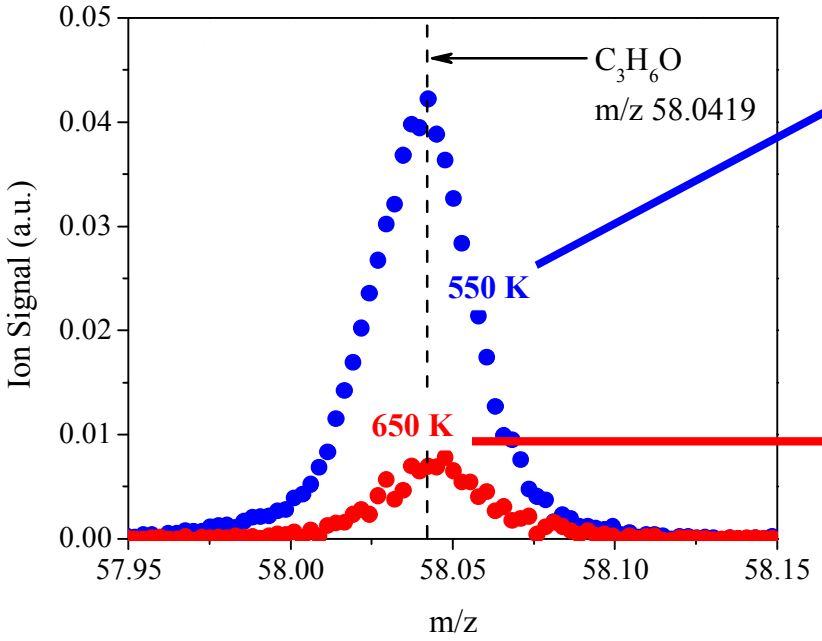
# β-Scission Products of QOOH Species

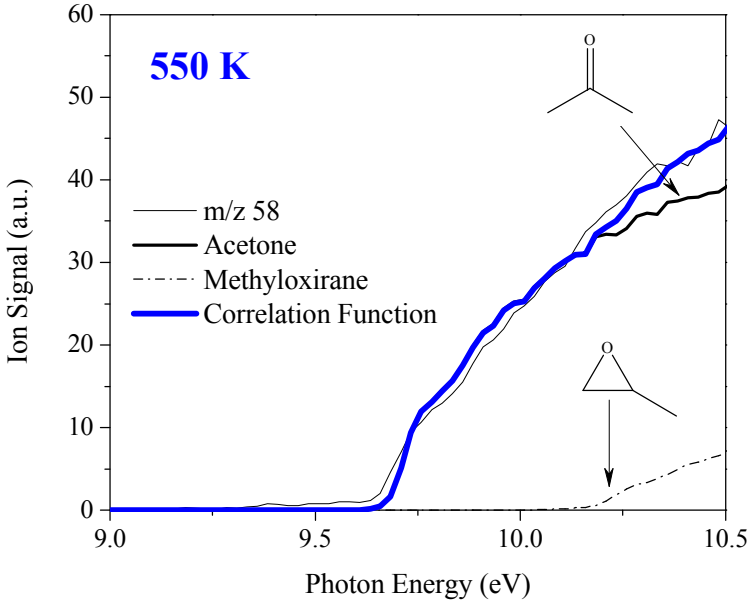


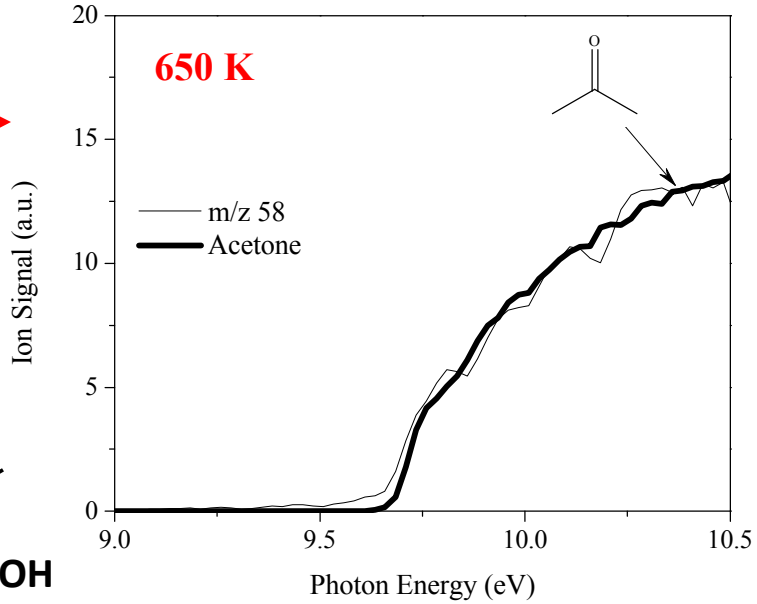
# Integrated Ion Signal (m/z 58): Acetone

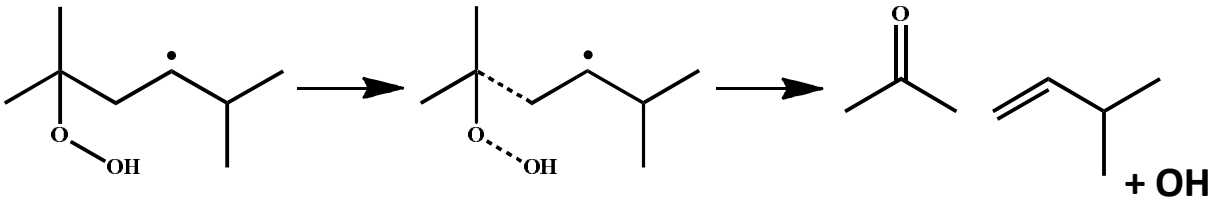
$$Acetone\ Fractional\ Yield\ (550\ K) = 0.49$$

$$Acetone\ Fractional\ Yield\ (650\ K) = 0.21$$

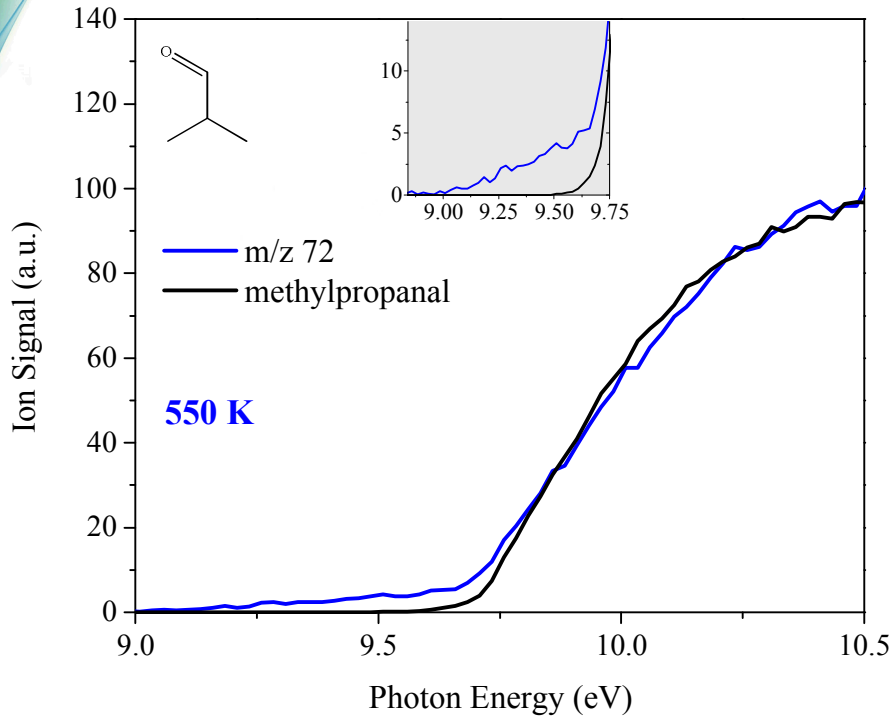


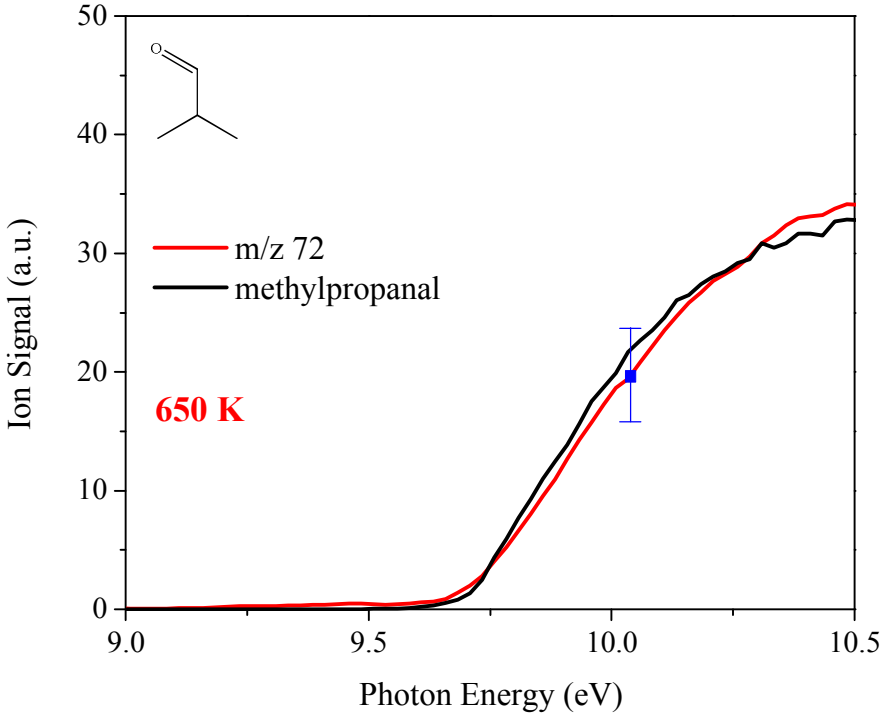



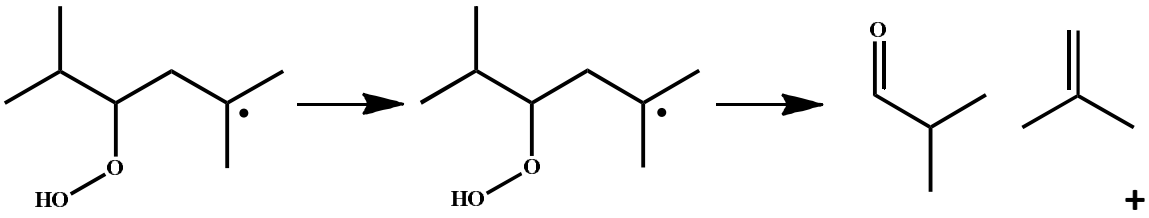
# Integrated Ion Signal (m/z 72): Methylpropanal



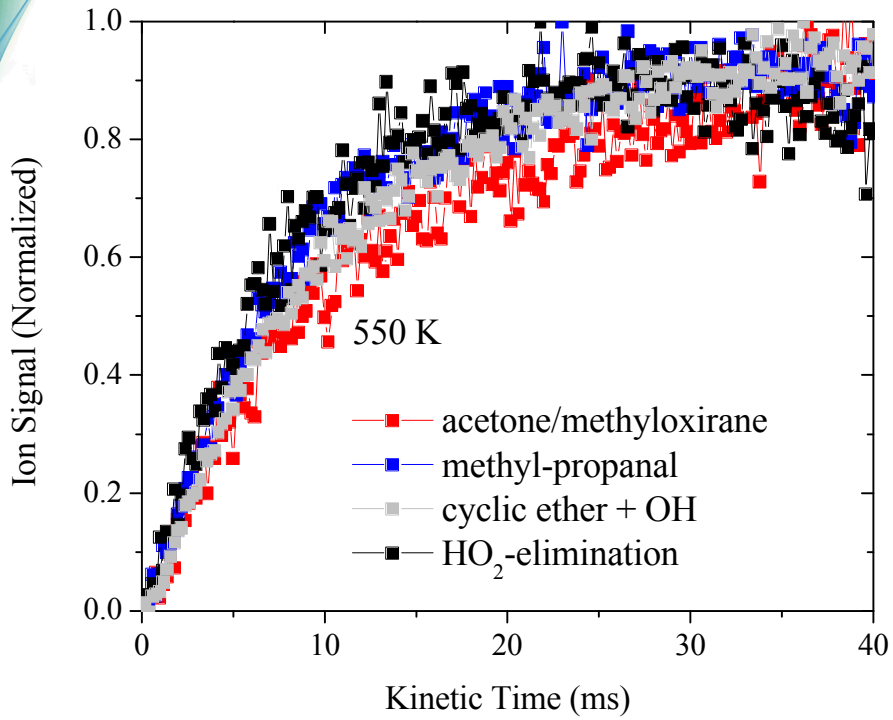



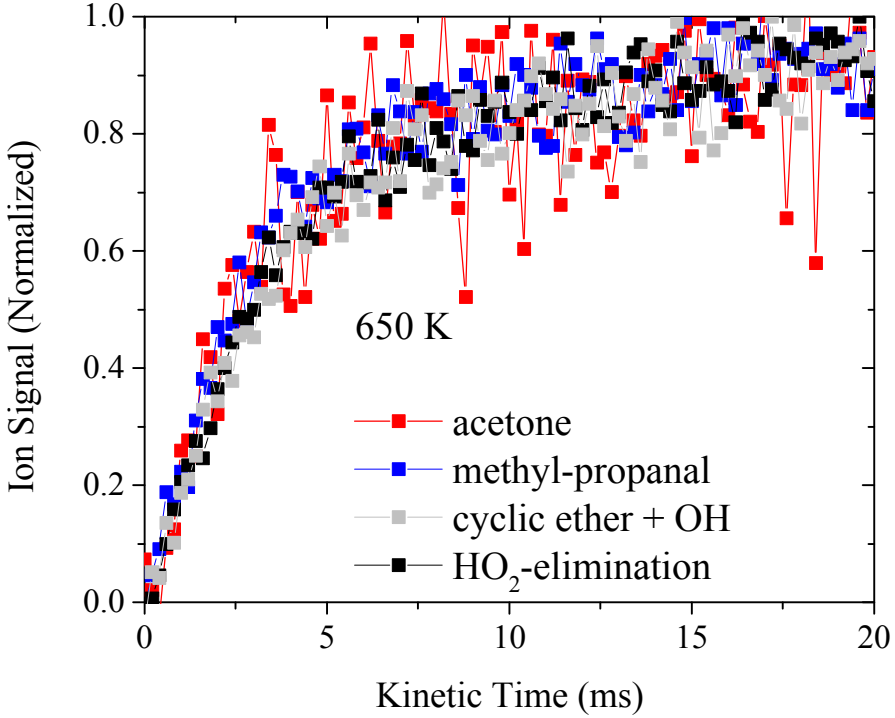

$$\textit{Fractional Yield}\ (550\ K) = 1.46$$

$$\textit{Fractional Yield}\ (650\ K) = 0.58$$



# Comparison of m/z 58, 72 Time Histories to Cyclic Ether and $HO_2$-Elimination



# $HO_2$ Time History Measurements and Comparison with Detailed Chemical Kinetics Modeling