COMBUSTION RESEARCH FACILITY

SAND2012-6135C

# Synchrotron studies of hydrocarbon oxidation and combustion science

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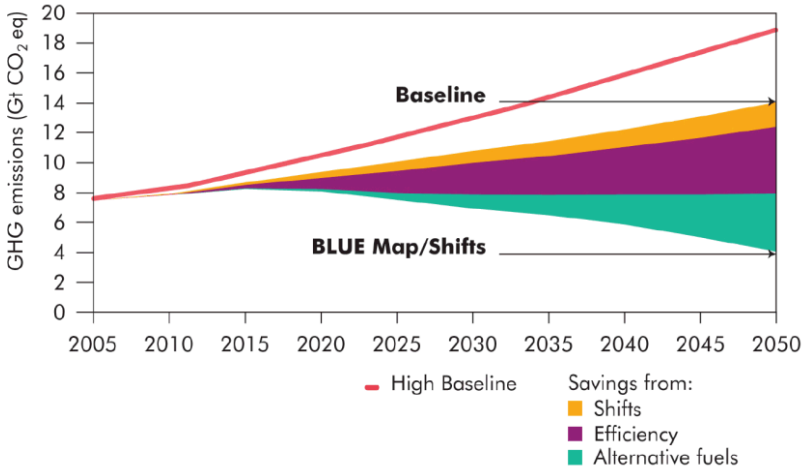
# Hydrocarbon Oxidation Powers Our Society and Is a Key Process in Earth's Atmosphere

Combustion produces ~ 85% of the United States' energy

- Hydrocarbon combustion provides nearly all of the energy for transportation
- Clean, efficient combustion is part of global energy strategies




Karol M Wikimedia commons

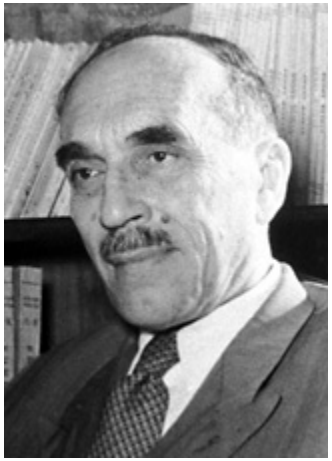
**Tropospheric Chemistry:**

- **Oxidation "cleanses" the troposphere**
- **Oxidation also produces aerosols, smog, other unwanted byproducts**

# Chemistry – Who Needs It? You Don't Need to Know Much Chemistry to Make an Engine!

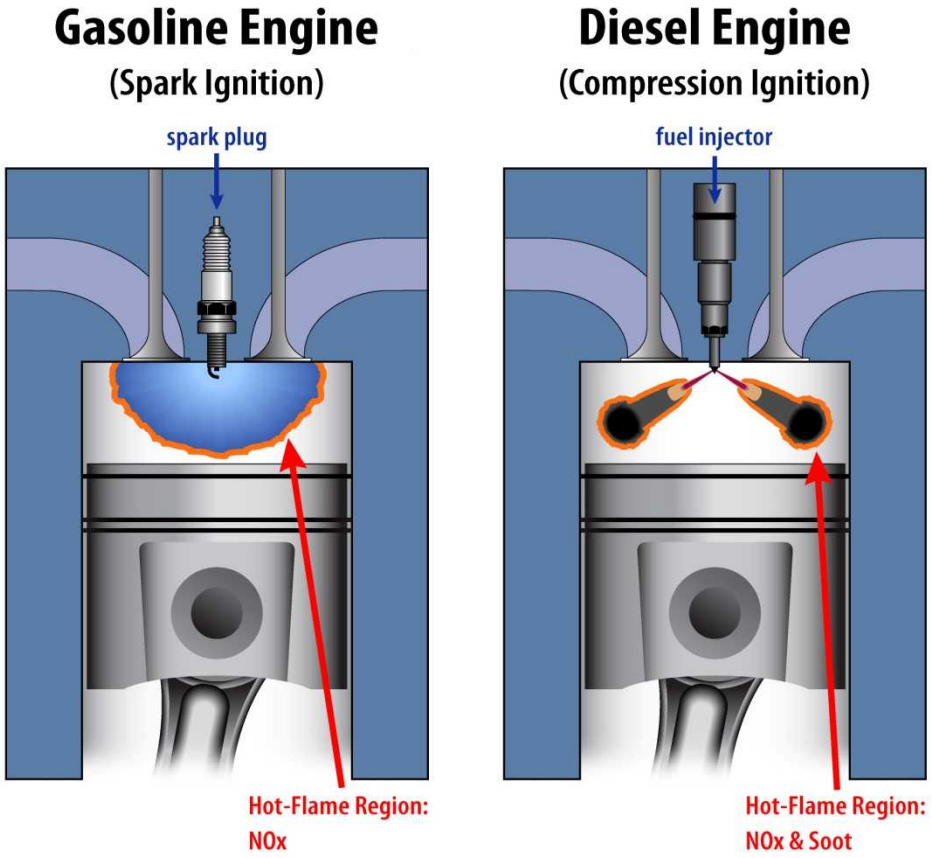
**Nikolaus August Otto** (1832-1891)

**Rudolf Christian Karl Diesel** (1858 –1913)



**Nikolai Nikolaevic Semenov** (Chemistry Nobel, 1956) "Some problems relating to chain reactions and to the theory of combustion"

# New Clean Efficient Combustion Strategies Depend on Autoignition Chemistry



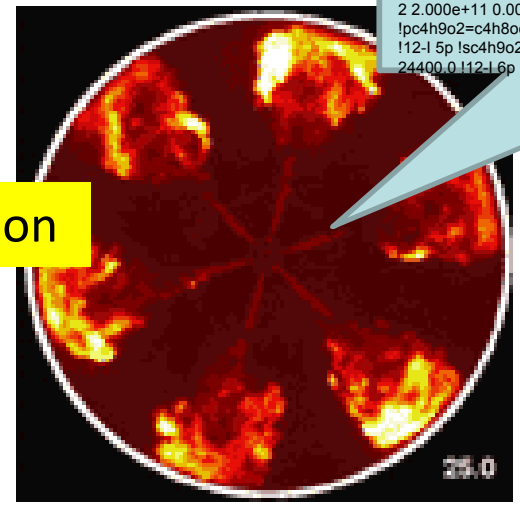

Manley et al., Physics Today, November 2008, 47–52

# Combustion is a Complicated Mix of Chemistry and Fluid Dynamics

Comprehensive Kinetic Mechanism

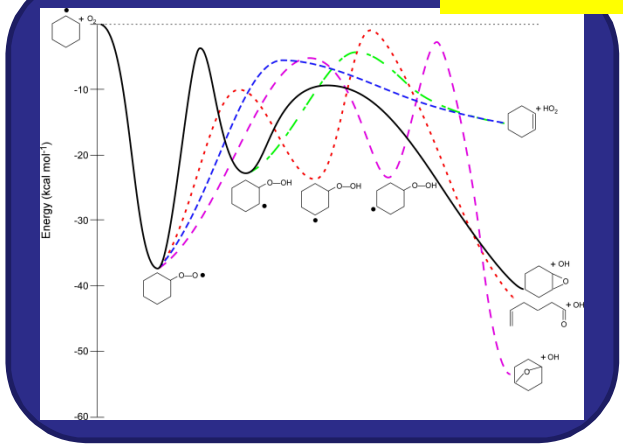

Detailed chemistry of single elementary fuel may have thousands of reactions and hundreds of species

Turbulent, multiphase flows interact with the chemistry



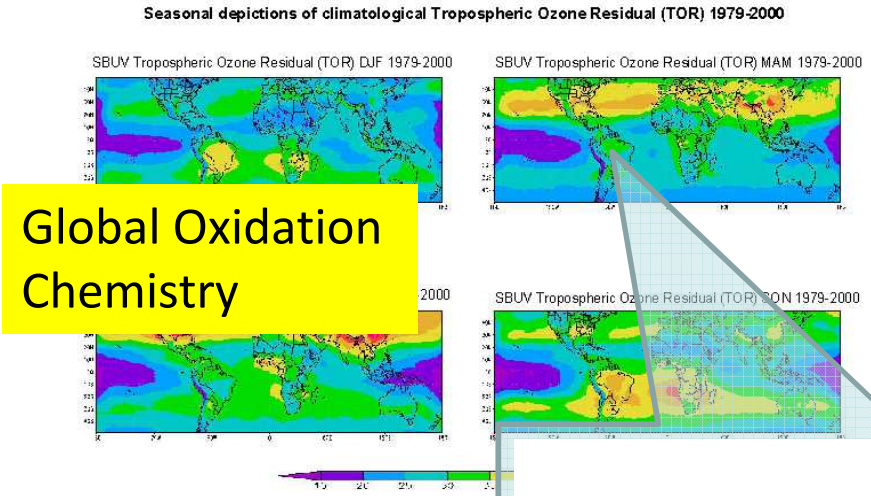

Autoignition

$R + O_2$ reactions




Charles Mueller, CRF

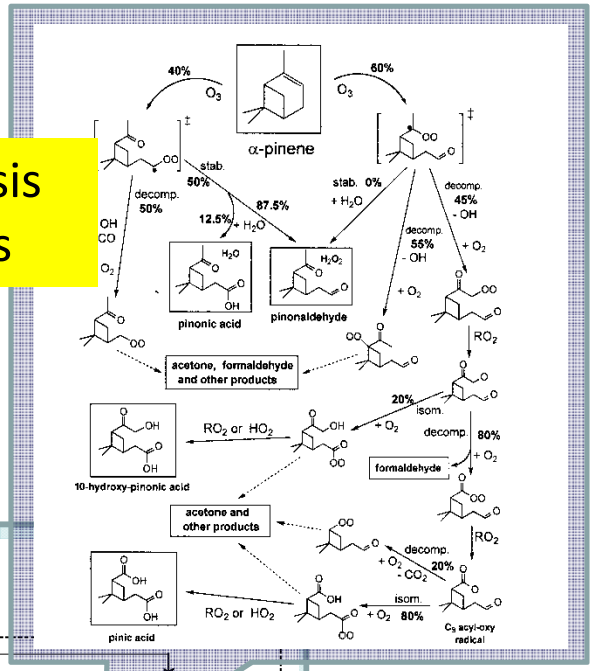
# Tropospheric Hydrocarbon Oxidation Depends on Chemistry and Transport




Atmos. Chem. Phys. Discuss., 3, 1453–1476, 2003

Global Oxidation Chemistry

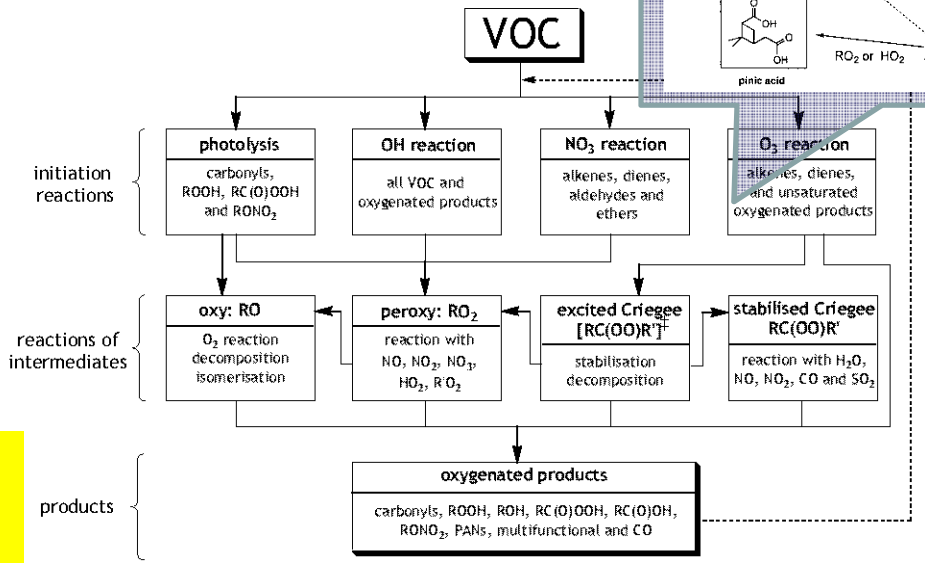
Ozonolysis reactions




Time and length scales are much different than in combustion

Transport changes chemistry

Comprehensive Kinetic Mechanism




Atmos. Chem. Phys., 3, 161–180, 2003

Detailed oxidation mechanism of a single compound is a complicated network of reactions

Jenkin et al., Atmospheric Environment 34 (2000) 2837-2850

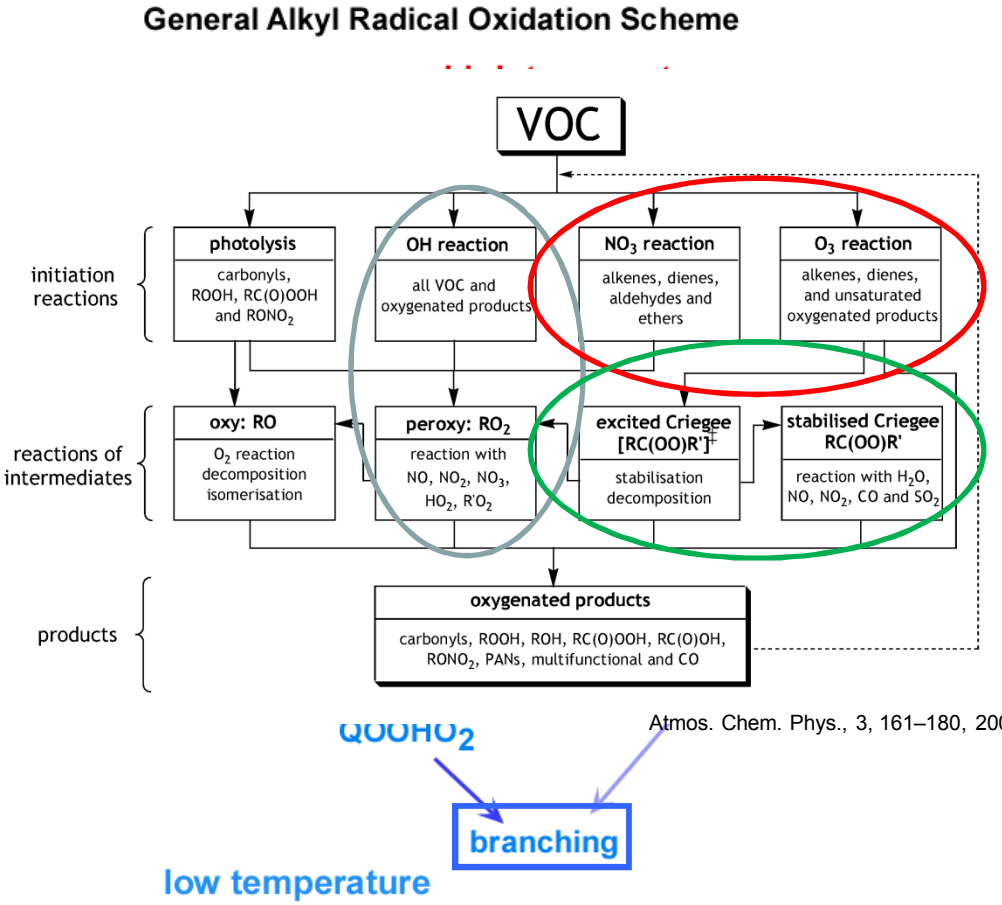
# Tropospheric and Engine Oxidation Processes Both Run on Radical Chain Chemistry

## Ignition Chemistry:

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

## Tropospheric Chemistry:

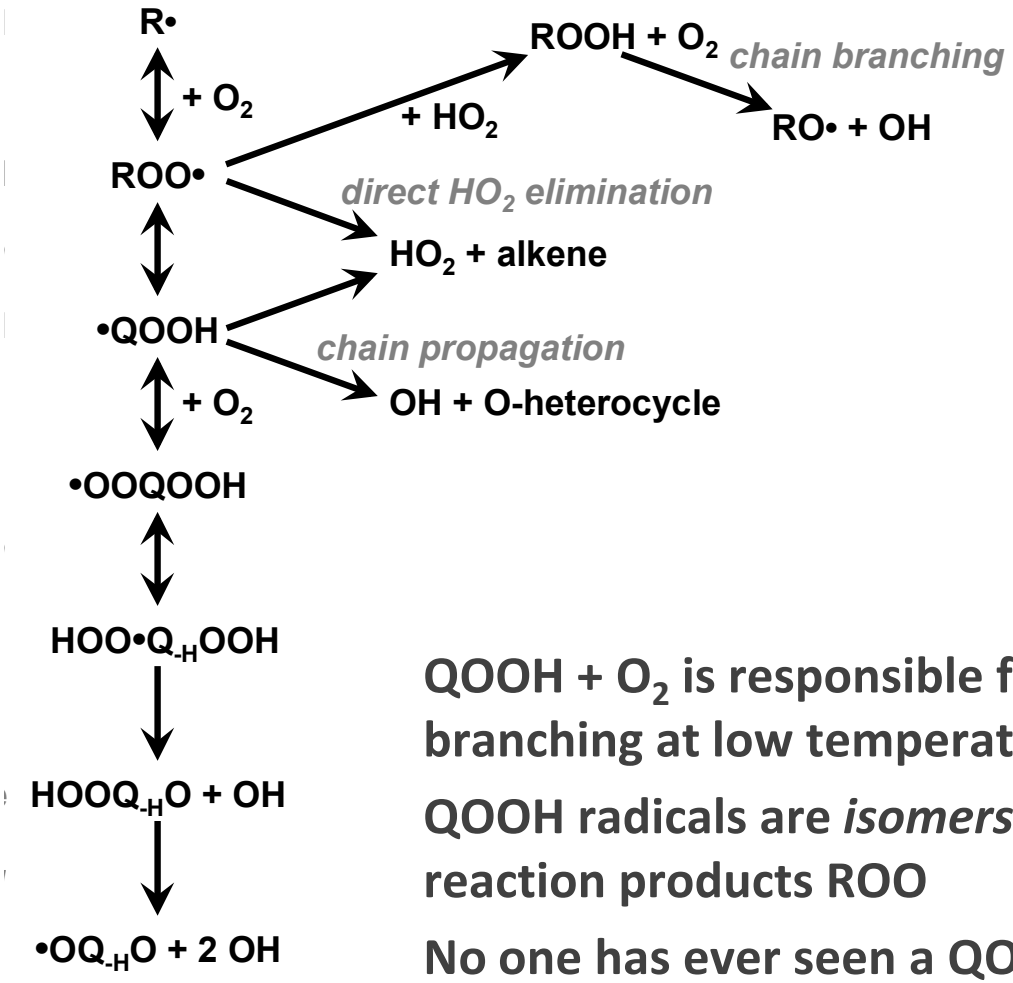
- Alkyl + $O_2$ reactions from OH-initiated oxidation also important in troposphere
- $NO_3$ and $O_3$ species are also important oxidation initiators
- *Criegee biradical intermediates* are important species for OH, aerosol formation, $NO_x$, $SO_x$

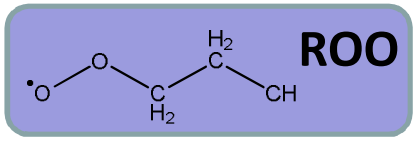


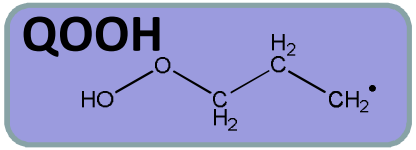

Atmos. Chem. Phys., 3, 161–180, 2003

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

# Predicting Ignition Chemistry Requires Knowing Reactions of "Intermediates"



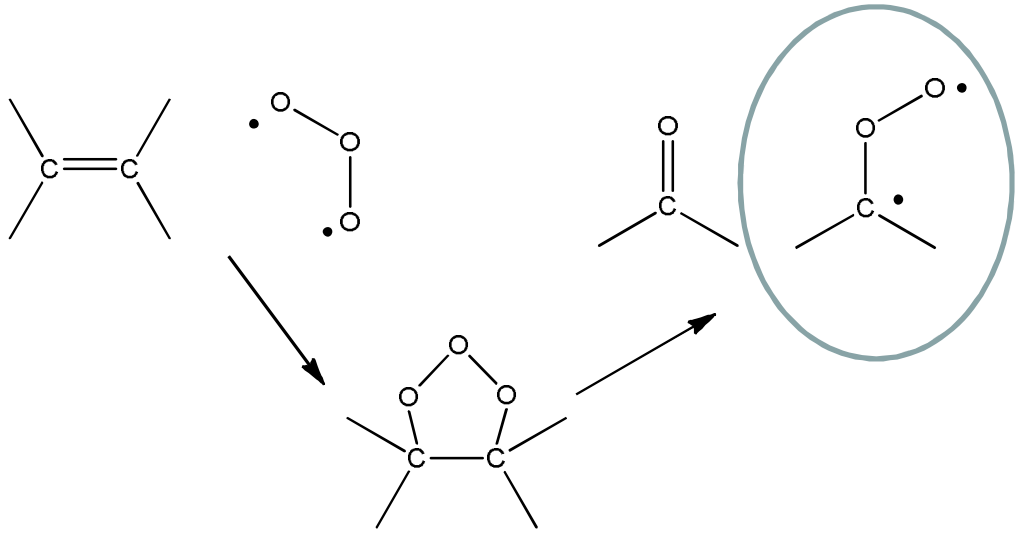

- QOOH + $O_2$ is responsible for chain branching at low temperature
- QOOH radicals are *isomers* of the major reaction products ROO
- No one has ever seen a QOOH by any means

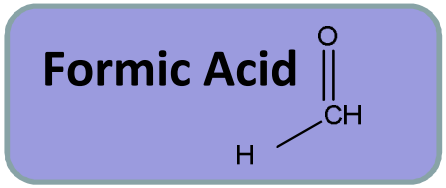
Zádor, J.; Taatjes, C. A.; Fernandes, R. X. *PECS* **2011**, *37*, 341.

# Modeling Tropospheric Chemistry Requires Knowing Reactions of "Intermediates"

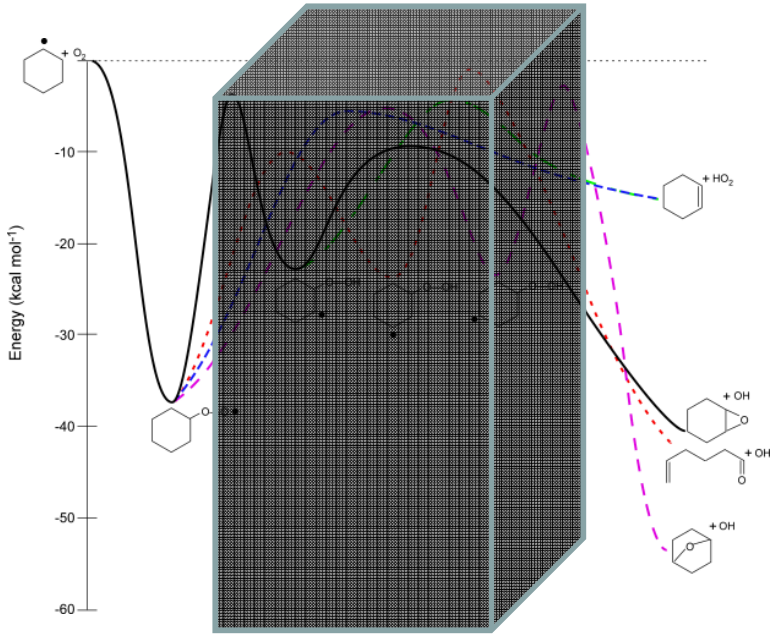


- Ozonolysis is a major component in tropospheric removal of hydrocarbons – makes Criegee intermediate
- Criegee intermediates also appear in QOOH + $O_2$ reactions Andersen and Carter, *J Phys. Chem. A.* 107, 9463-9478 (2003); Asatryan and Bozzelli, *J Phys. Chem. A.* 114, 7693-7708 (2010)
- Criegee intermediates are *isomers* of more stable products, organic acids or esters
- No one has directly measured a Criegee reaction



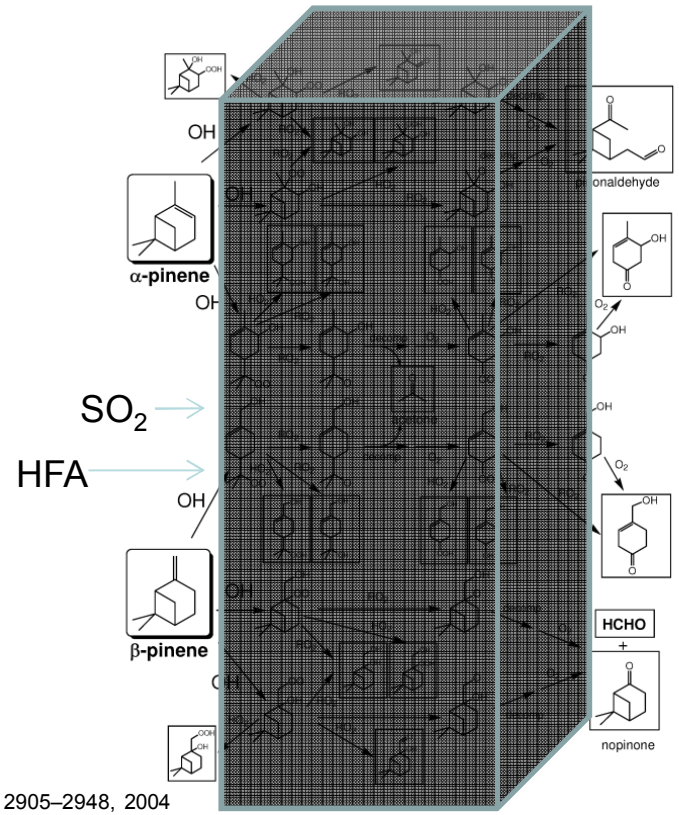



# How Can We Tell Anything about the Reactions of These Intermediates? Deal with the Black Box!




## Measure products of ozonolysis and compare to theory and models

**Add scavengers that are thought to remove Criegee intermediates, see what happens to stable product yields**




## Measure products of R + $O_2$ reactions and compare to theory

**Change conditions and see what happens to time behavior and product yields**

Atmos. Chem. Phys. Discuss., 4, 2905–2948, 2004

# Why are these things so hard to detect?

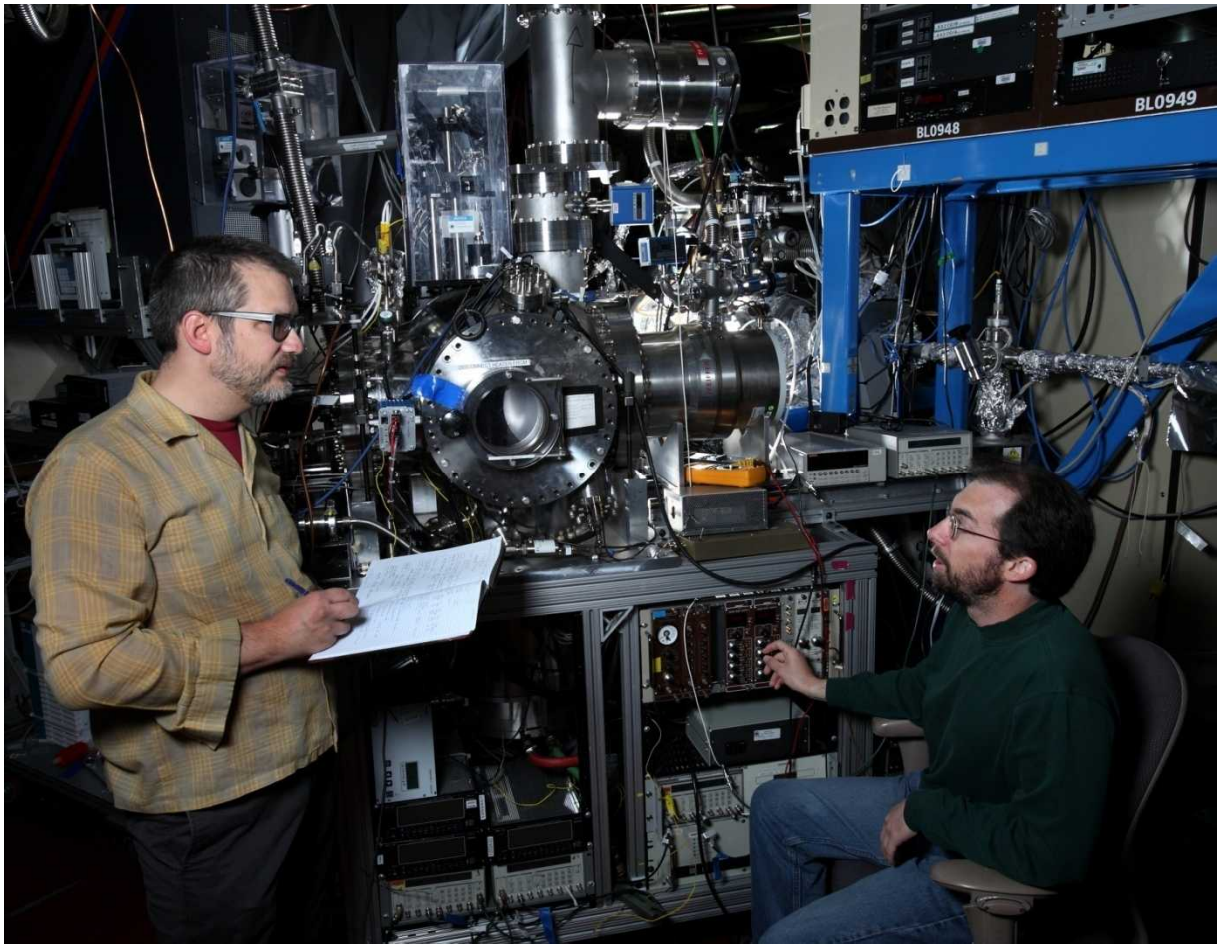
The hole in the bottom of the bucket is bigger than the hole at the top!

People get out of the rain!

They don't stay in their reactive configuration very long – they are made slowly and consumed rapidly

**We need sensitive and selective detection *and* a way to make intermediates directly**

# We have a machine that can sensitively detect specific isomers in chemical reactions!




Tunable synchrotron photoionization mass spectrometry

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

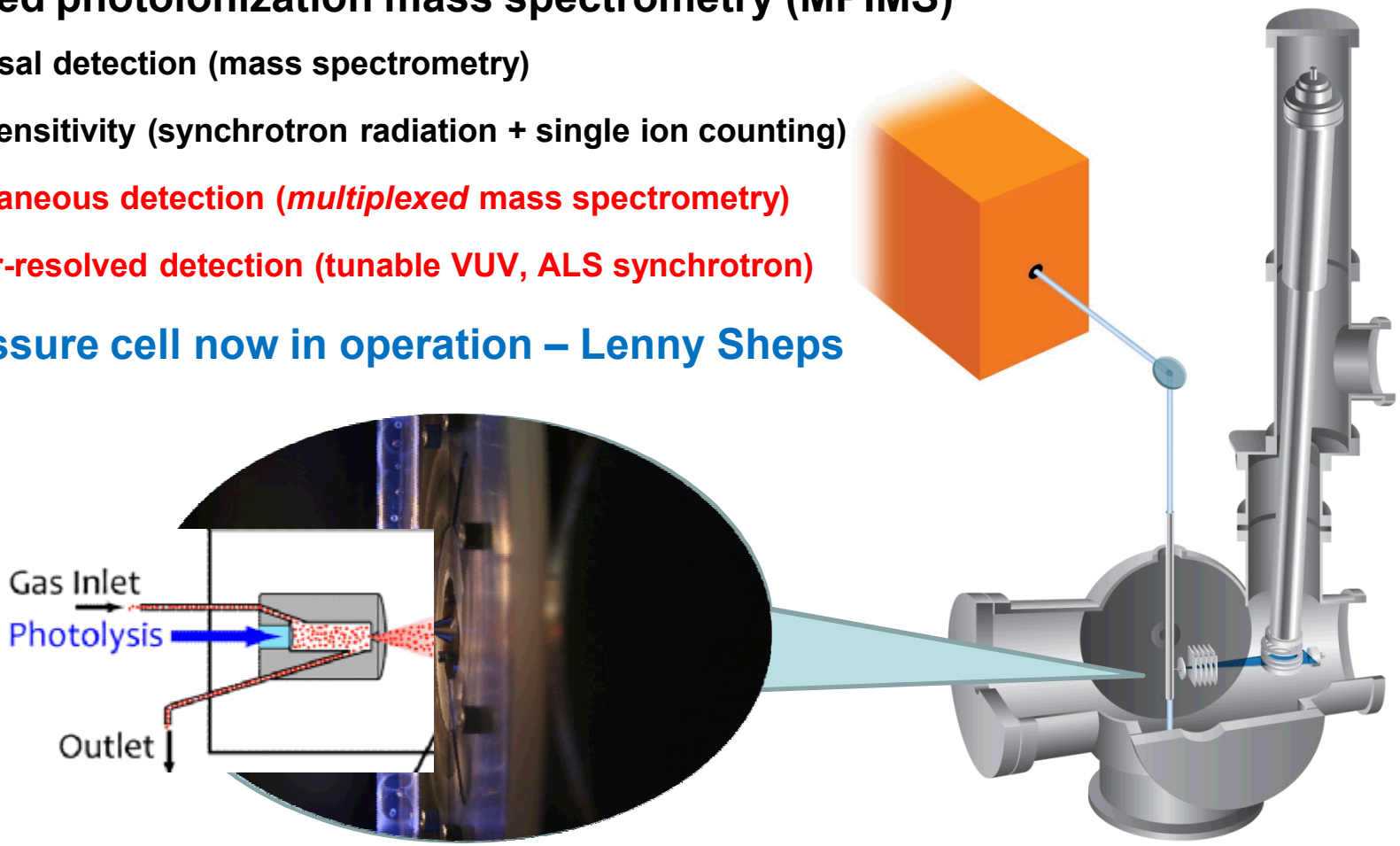
Osborn et al., *Rev. Sci. Instrum.* **79**, 104103 (2008)

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

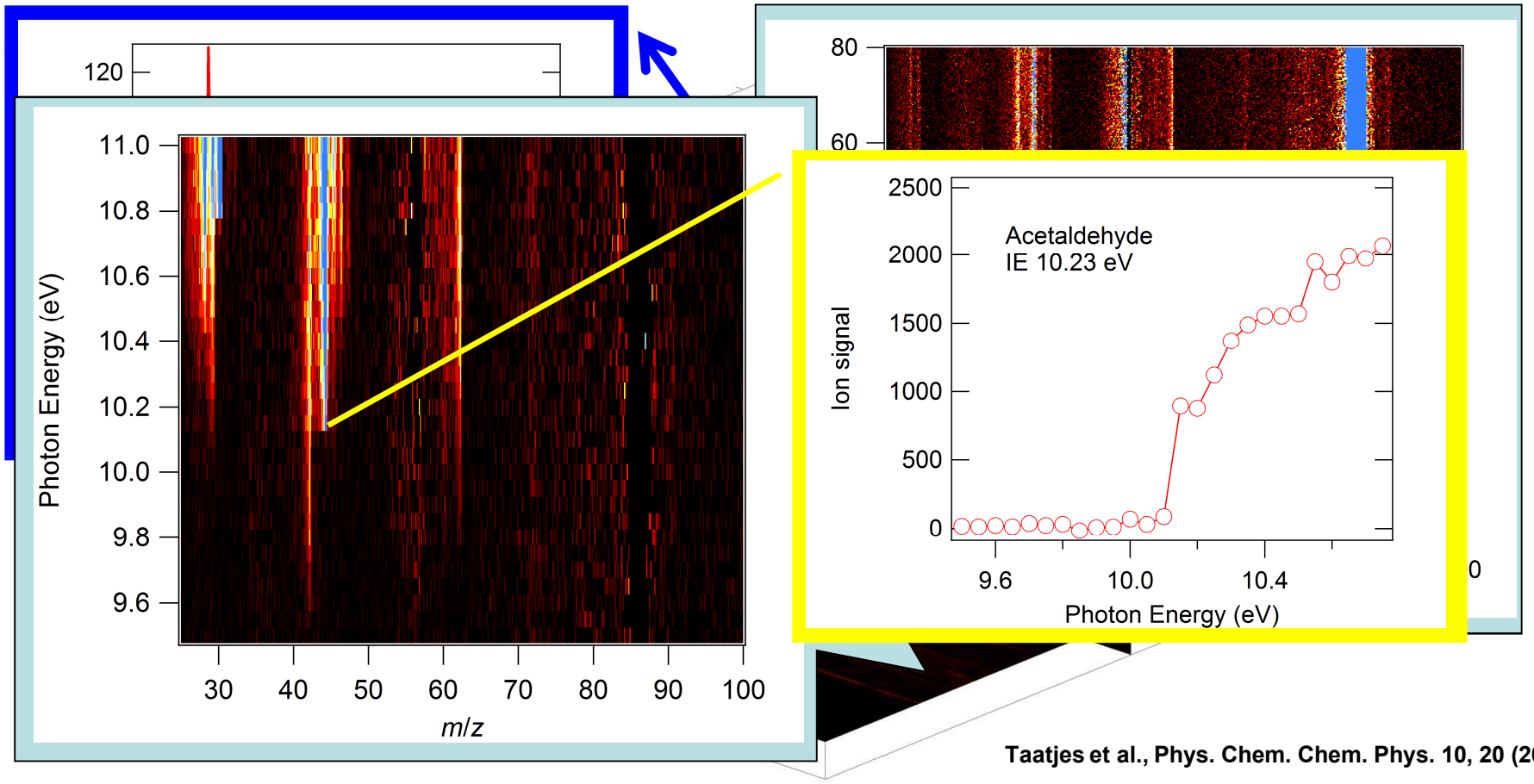
## Multiplexed photoionization mass spectrometry (MPIMS)

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

## High-pressure cell now in operation – Lenny Sheps



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




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

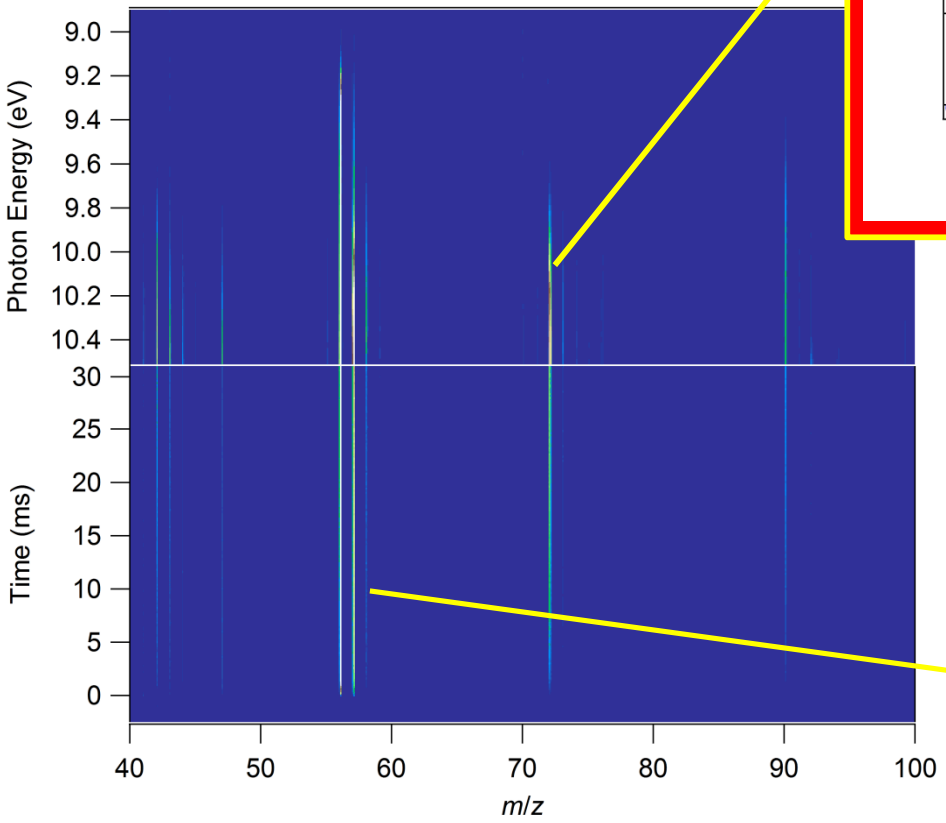
**3-D dataset can be "sliced" along different axes to probe different aspects of the reaction**

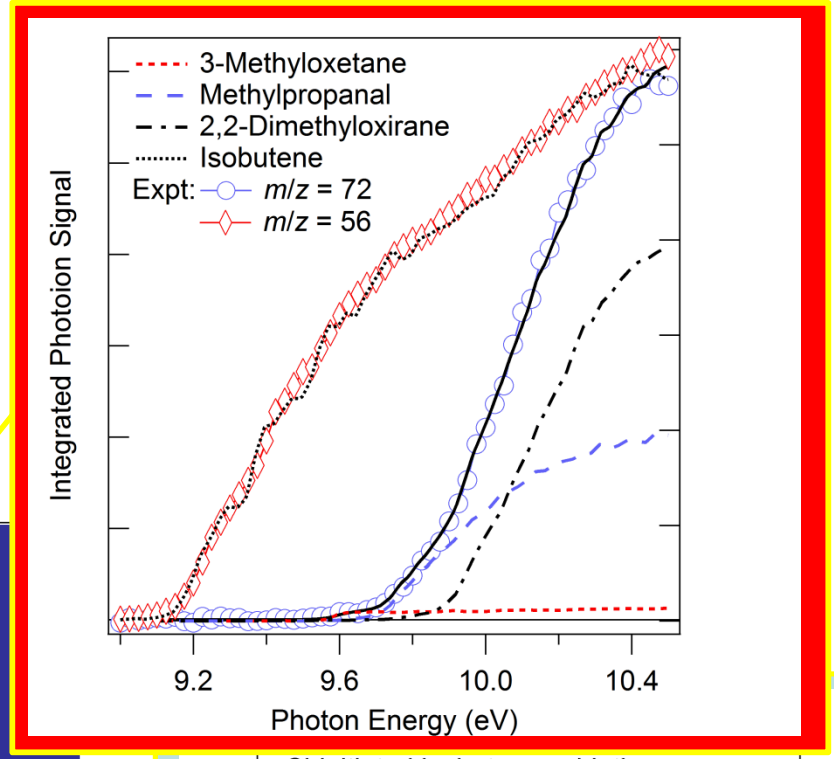
# Cl-initiated isobutane oxidation

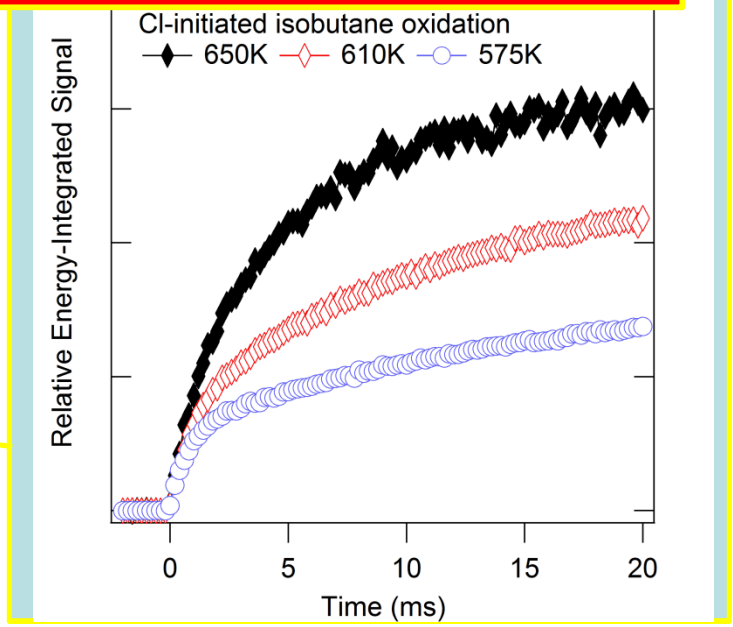
**Time behavior of product formation – prompt and delayed**

**Photoionization spectra identify product isomers**

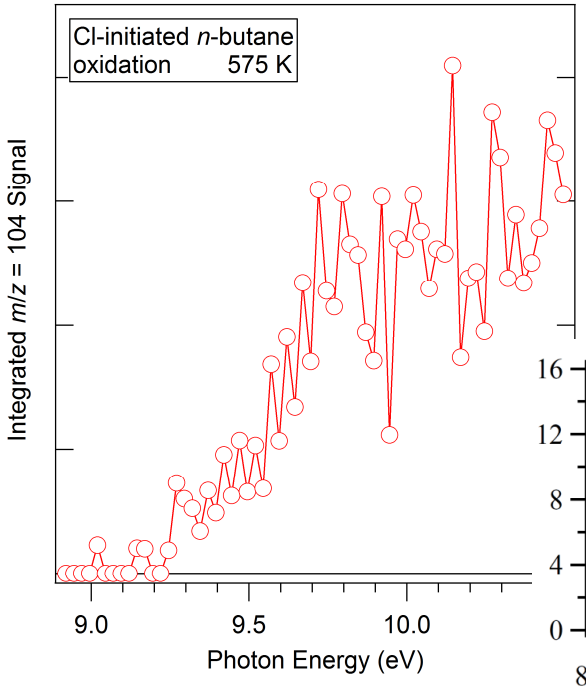
Eskola et al., *Proc. Combust. Inst.*, in press



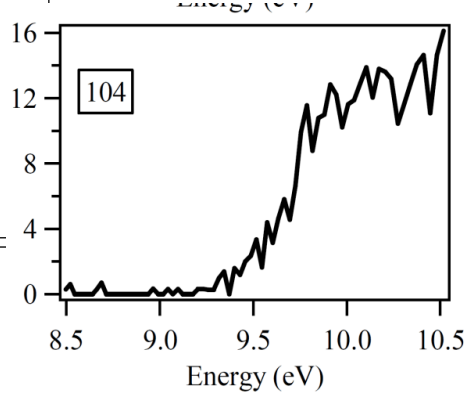



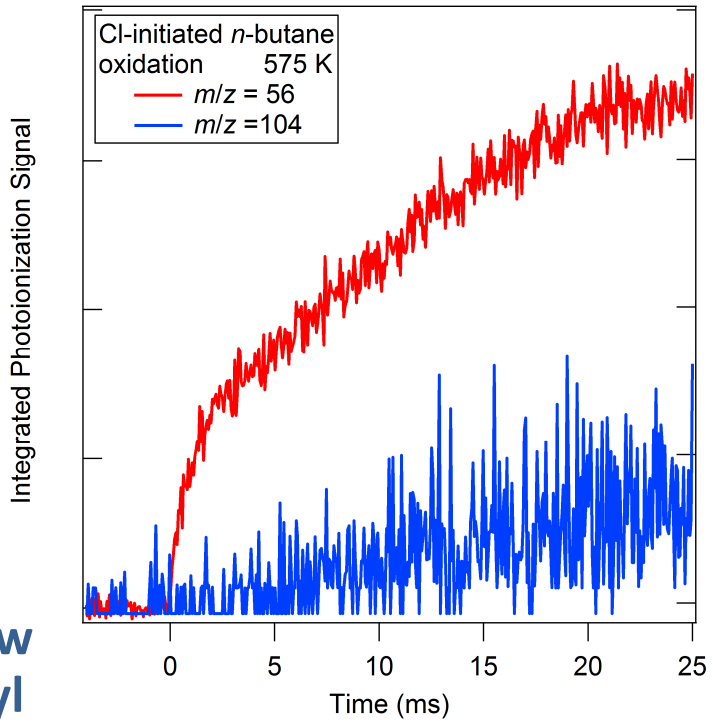
# Ketohydroperoxide Product at *m/z* = 104 Arises from QOOH + $O_2$




**Photoionization spectrum similar to that observed by Battin-Leclerc et al.** (Angew. Chem. 2010, **49**, 3169)




**Time profile is characteristic of a secondary product of R + $O_2$ reaction**




**Measurements with specific butyl isomers show ketohydroperoxide from low pressure *n*-butyl oxidation but not *sec*-butyl oxidation**

# What about QOOH? Can photoionization directly detect and characterize the elusive QOOH?

**Most ROO have no stable parent cation**
(Meloni et al., *J. Am. Chem. Soc.* 128, 13559 (2006)),
**but some $QOOH^+$ are stable**

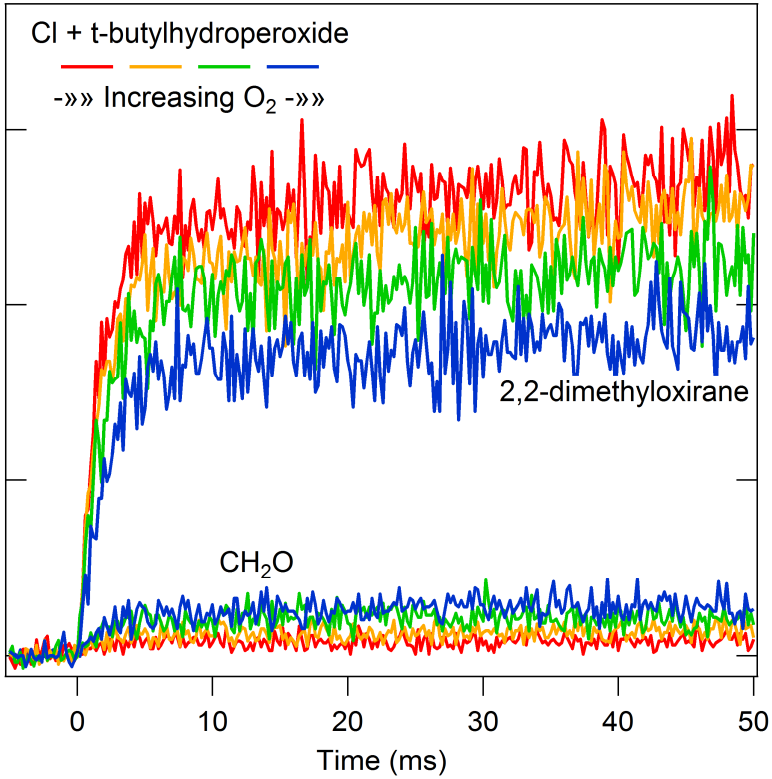
**Problem is to make enough!**

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

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

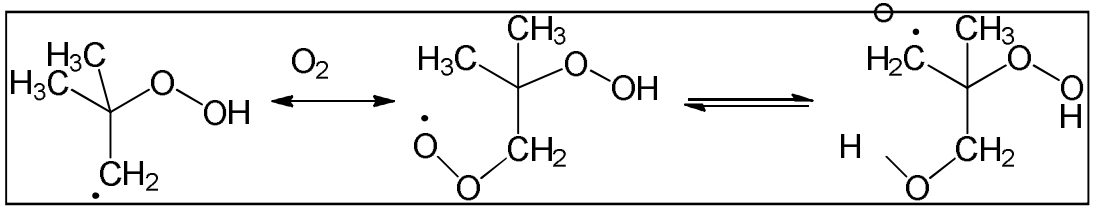
$(CH_3)_2C(CH_2)OOH \rightarrow$ 2,2-dimethyloxirane + OH

**Reaction with $O_2$ competes with dissociation – forms other products**




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

**Product detection can give *direct* measurements of QOOH reactions**
**Judit Zádor**

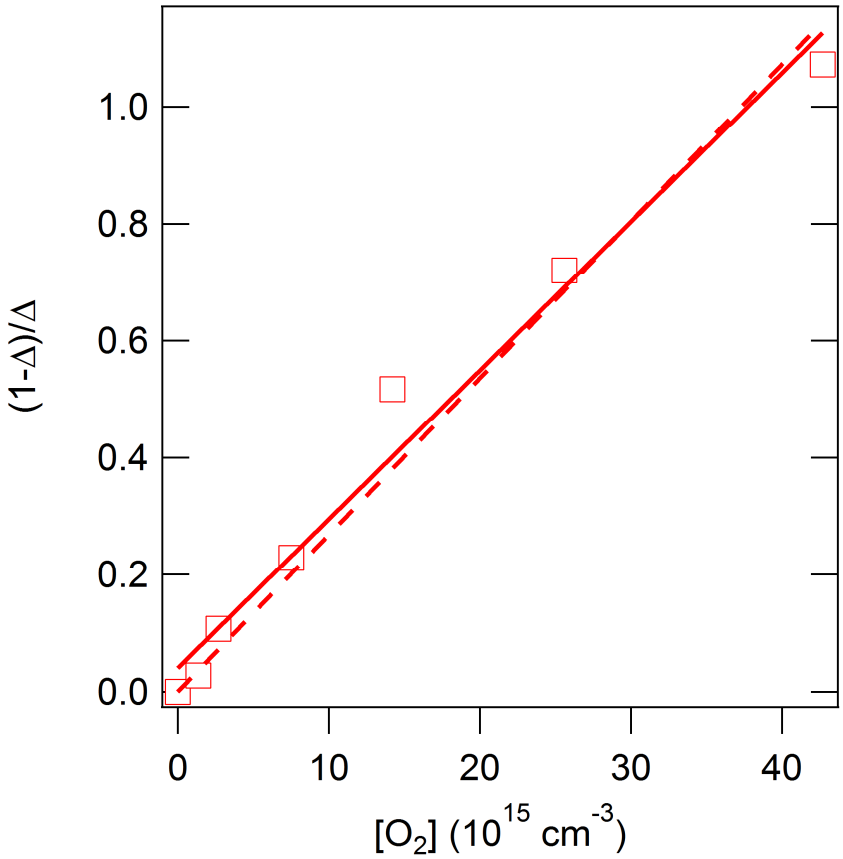


# Detection of Reaction Products Can Give Direct Kinetics Measurements

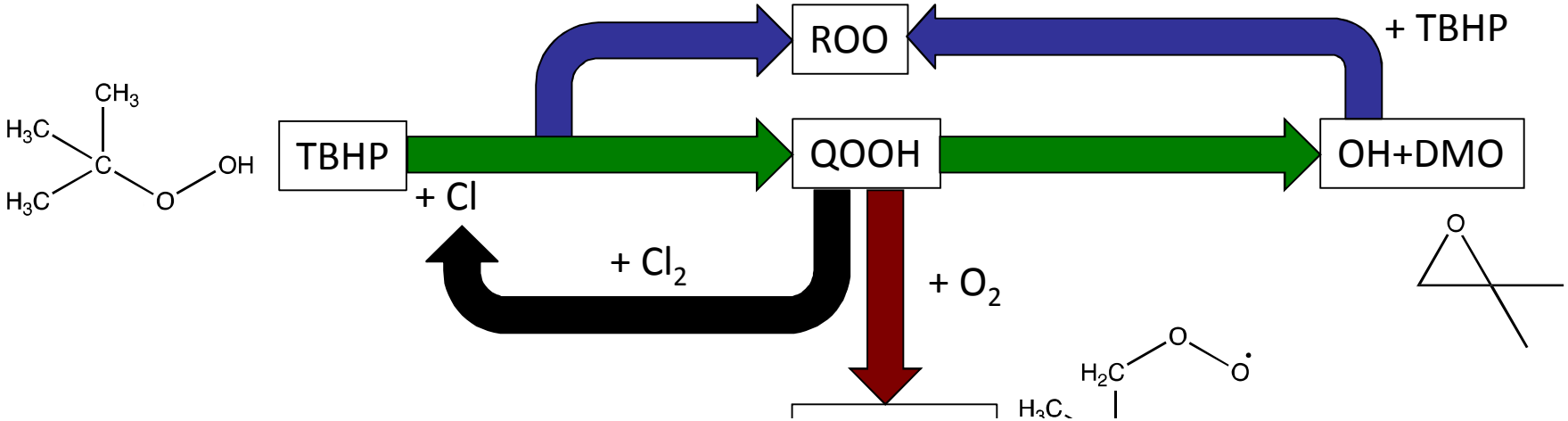
- $[O_2]$ dependence of $CH_2O$ formation identical to change in 2,2-dimethyloxirane
- Correctly scaled change in dimethyloxirane is linear in $[O_2]$
- Direct measurement of QOOH + $O_2$ rate coefficient relative to thermal dissociation

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

- ALS experiments can help design complementary optical studies

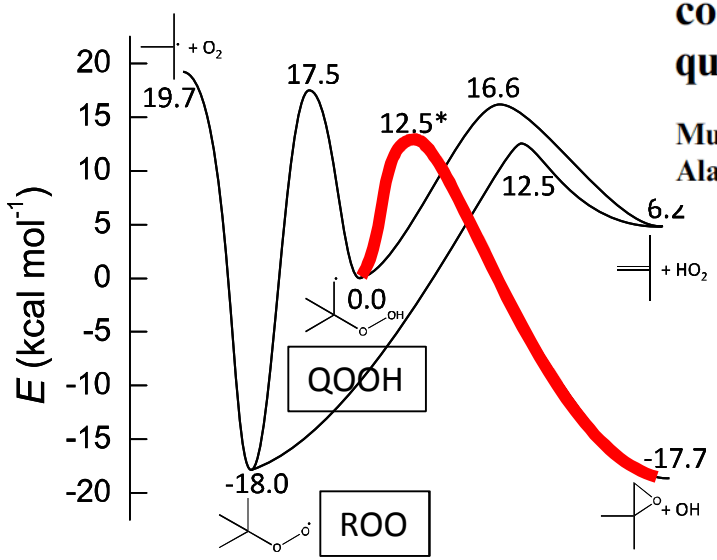


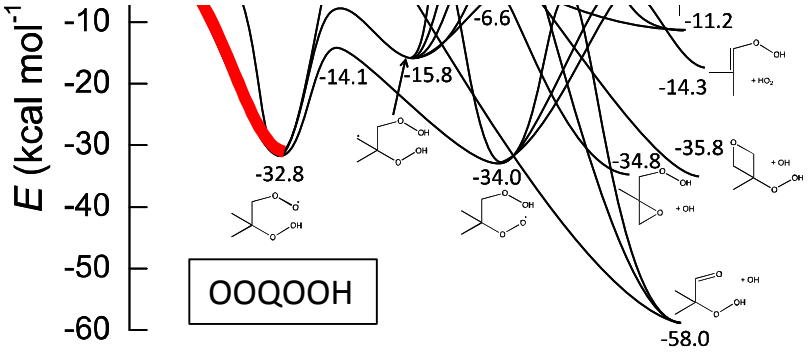
# At 300 K the QOOH reaction mechanism can be relatively simplified.




**$(CH_3)_3COOH$ (*tert*-butyl hydroperoxide): OH reaction rate coefficients between 206 and 375 K and the OH photolysis quantum yield at 248 nm†**

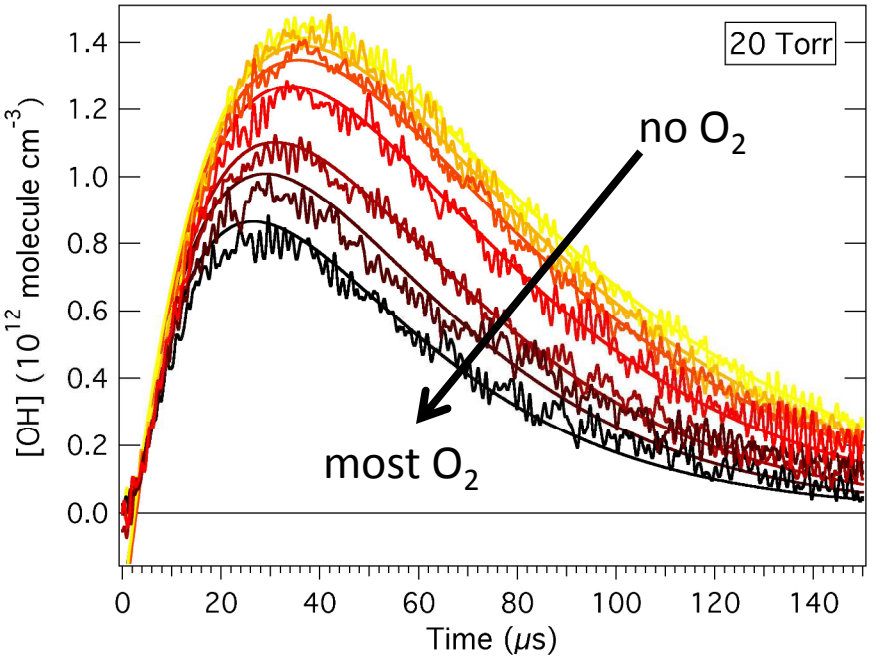
Munkhbayar Baasandorj,[ab] Dimitrios K. Papanastasiou,[ab] Ranajit K. Talukdar,[ab] Alam S. Hasson[c] and James B. Burkholder*[a]



# Measurement of OH directly probes rate constant for QOOH reactions

$$[OH]_t = (\alpha - 1)[Cl]_0 \frac{k_{QOOH\text{-->}OH} e^{-k_{OH+TBHP}[TBHP]t^*}}{K}\left(e^{-Kt^*} - 1\right); \quad K = \alpha k_{eff} + k_{QOOH\text{-->}OH} + k_{QOOH+O_2}[O_2] - k_{OH+TBHP}[TBHP]$$




unknowns w/o $O_2$

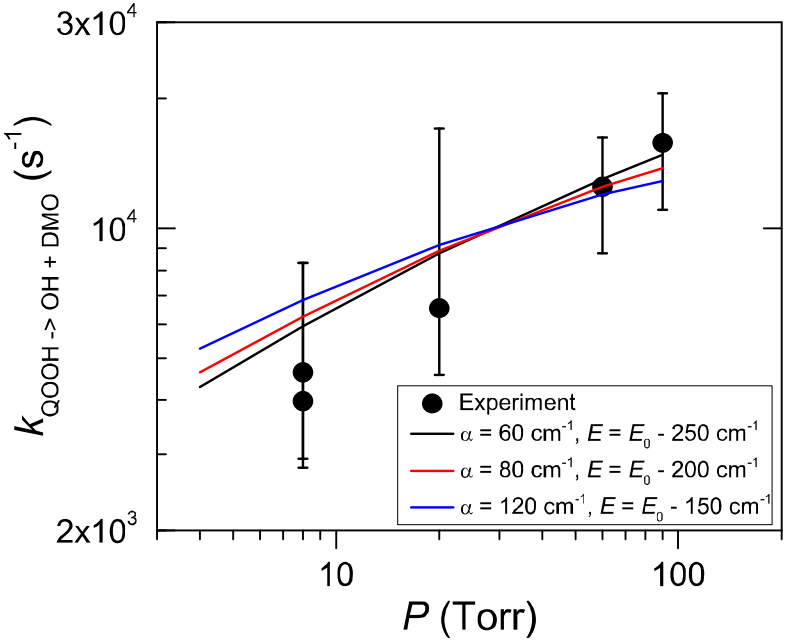
① $k_{QOOH \rightarrow OH}$

② chain chlorination ($k_{eff}$)

unknowns w/ $O_2$, same conditions

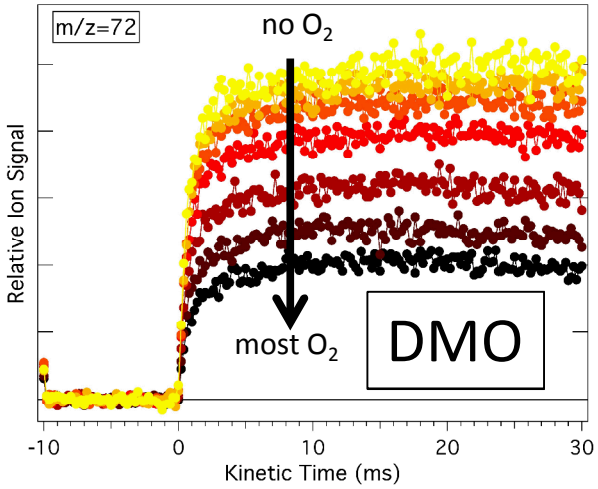
③ loss to ROO in Cl+TBHP (α)

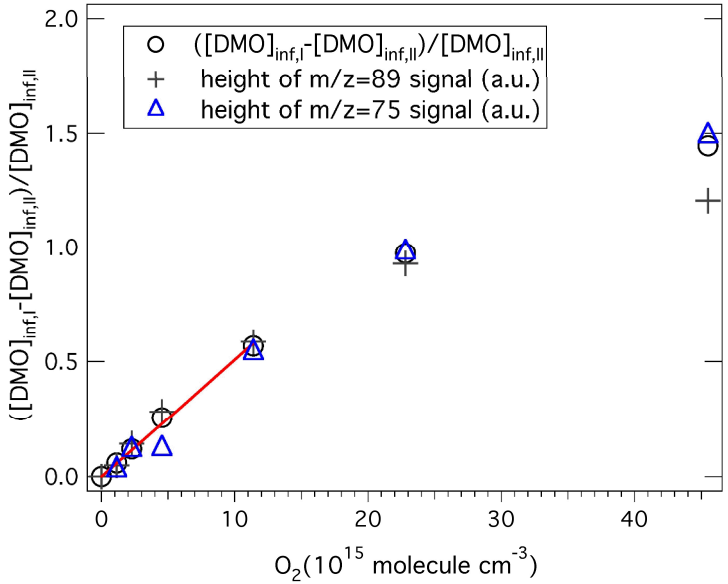
④ $k_{QOOH+O2}$



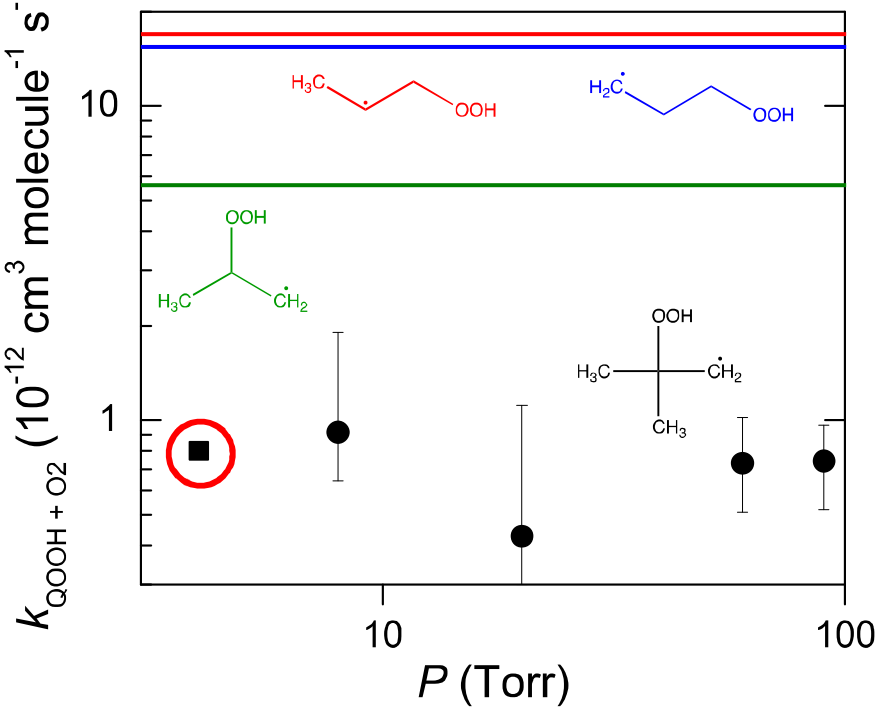

**Fit all data -- use competition between QOOH dissociation and addition of $O_2$ to get $k_{QOOH+O2}$ as well**

# Direct measurement of QOOH + $O_2$ reaction rate constant




Comparison of $k(QOOH+O_2)$ for various QOOH's

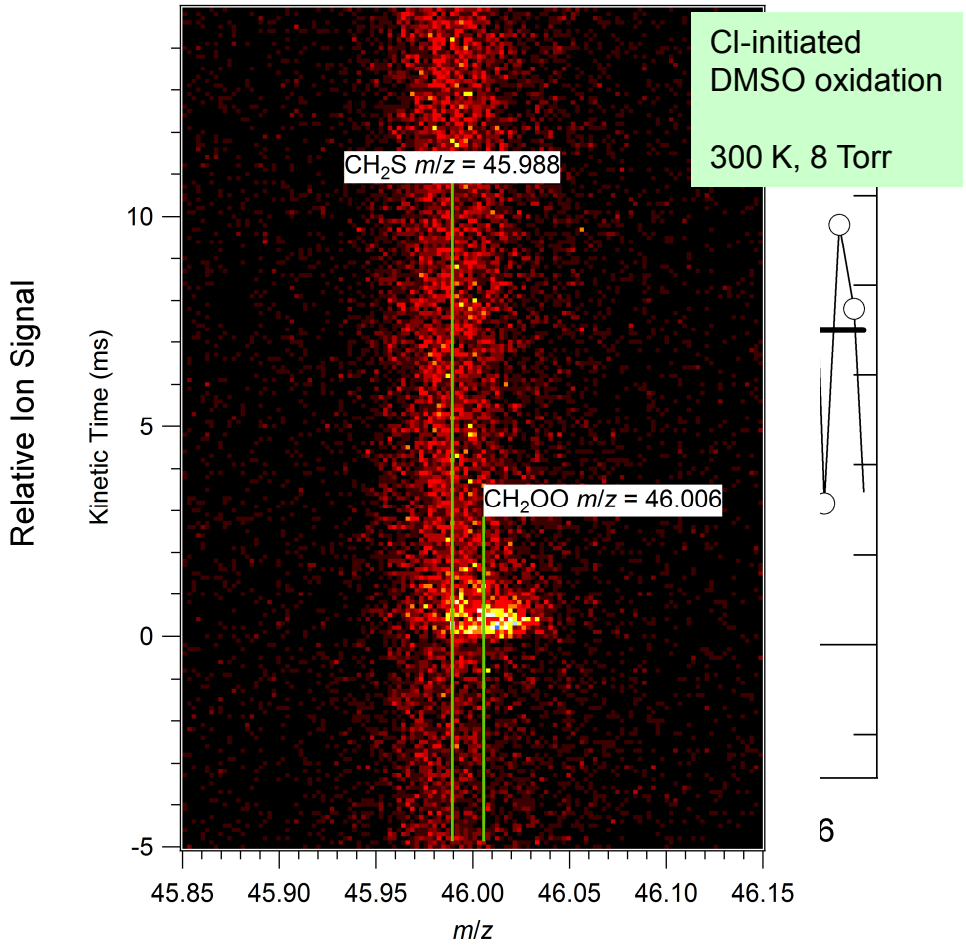



C. Franklin Goldsmith, William H. Green, and Stephen J. Klippenstein, J. Phys. Chem A 2012, *116*, 3325–3346

$$k_{QOOH+O2} = \frac{k_{QOOH-->OH} + L}{[O_2]} \times \frac{[DMO]_\infty^0 - [DMO]_\infty}{[DMO]_\infty}$$

# 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 $CH_2OO$




**Until 2008, no one had even seen a gas phase Criegee intermediate**

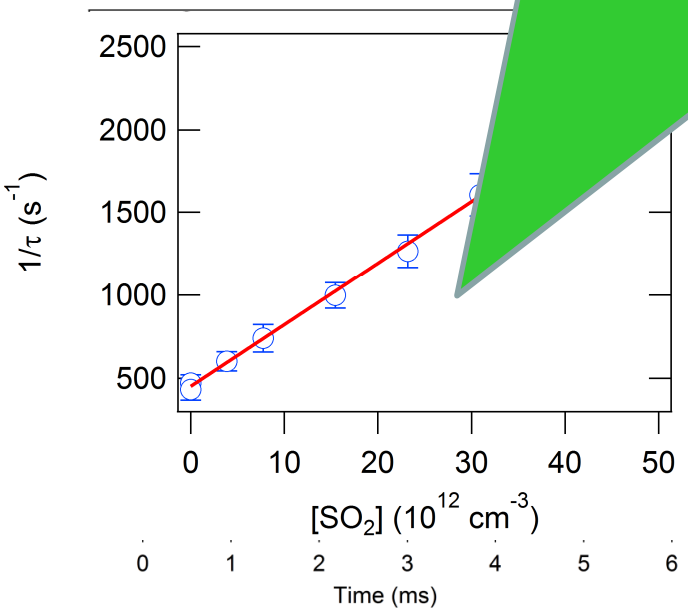
Taatjes et al., J. Am. Chem. Soc. 130, 11883 (2008)

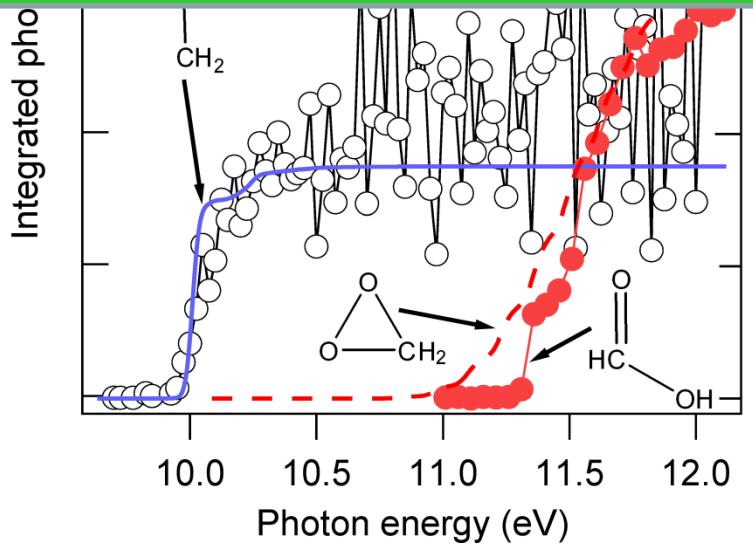
# Detection Is One Thing, Kinetics Is Another: Make More Criegee to Measure Reactions

- **Arkke Eskola** 1416 (2006) **fou made I atom Criegee inter**
- **Can make lot reactions wit species**

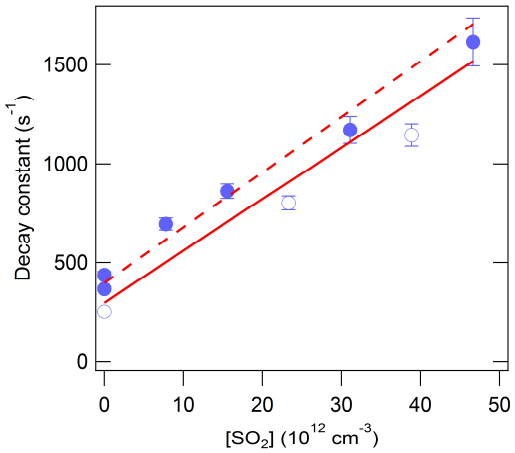
Reaction of $CH_2OO$ with $NO_2$ is **50 times** what is used in models
- If other Criegee intermediates react similarly, Criegee reactions are significant $NO_3$ source

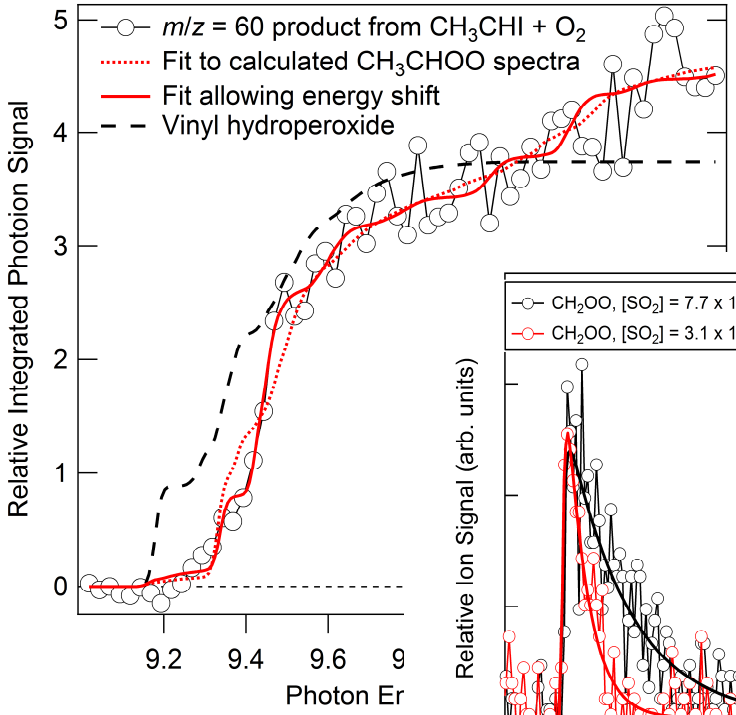
Reaction of $CH_2OO$ with $SO_2$ is up to **10 000 times** models
- If other Criegee intermediates react similarly, Criegee reactions are major $SO_2$ oxidant

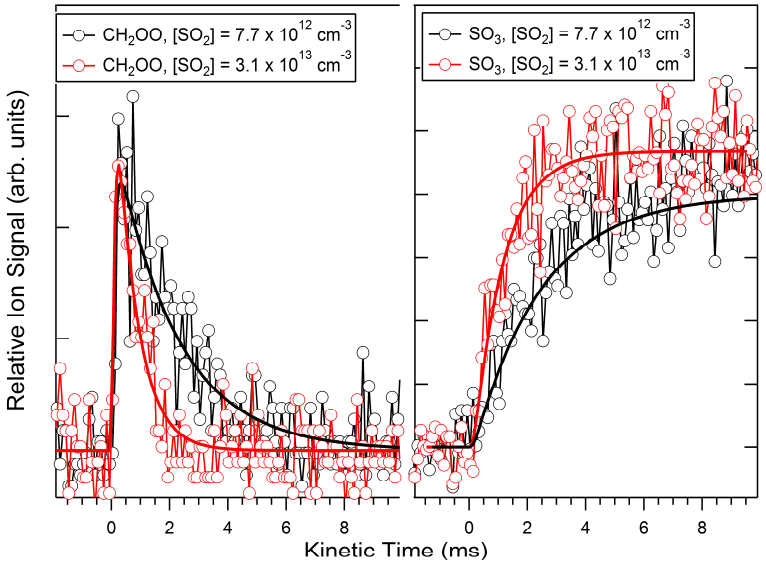


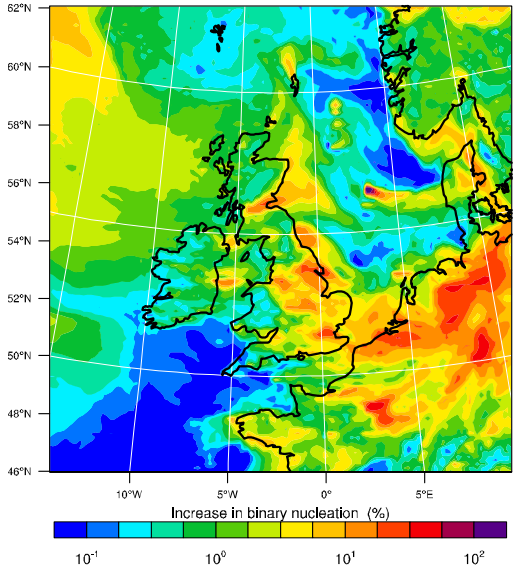

Welz, Savee, et al., *Science* **335**, 204 (2012)




**Tropospheric modeling (Dudley Shallcross, Carl Percival, Gordon McFiggans et al.) shows that a substantial amount of $H_2SO_4$ formation is via Criegee intermediate oxidation of $SO_2$**



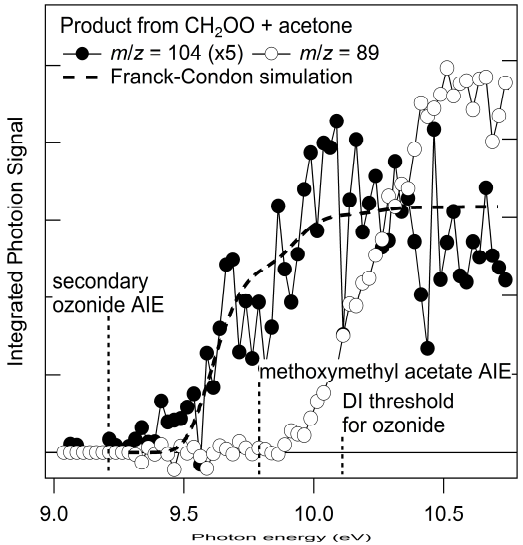

**Next larger Criegee intermediate can be produced in a similar way; also reacts rapidly with $SO_2$**

**$SO_3$ is a major product from $SO_2$ reactions**

# What does all this mean?

- **Sulfate chemistry makes aerosols**
  - Aerosols tend to reflect radiation
    - Criegee chemistry might be connected to “cooling”
  - Biggest Criegee contribution where there is a lot of ozone and alkenes

Photo: Christian von Wissel




Taatjes et al., PCCP **14**, 10391-10400 (2012)

**We are *just beginning* to understand how Criegee intermediates react**

Need to understand even larger Criegee molecules

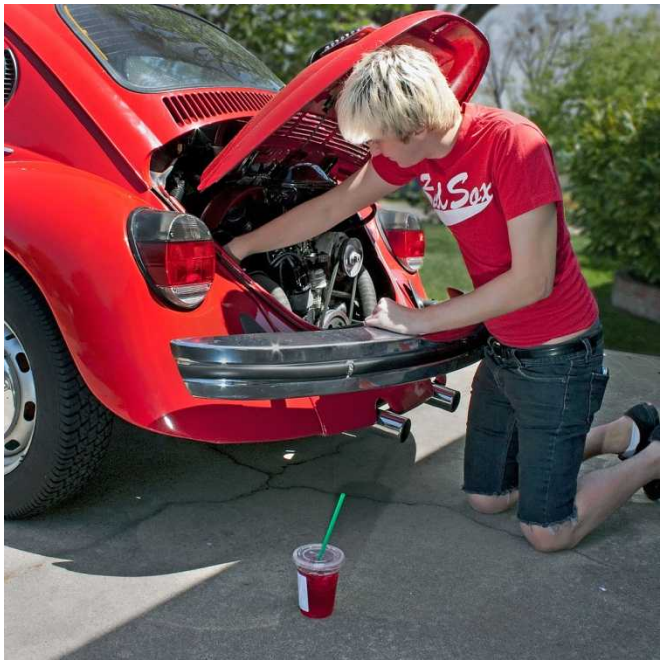
Need to understand more reactions:

Reactions with carbonyls make secondary ozonides

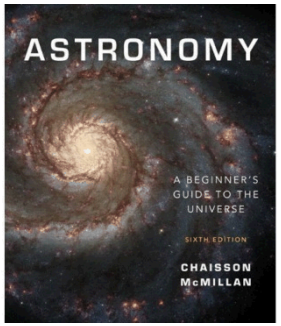
Need to know rate constant with water

Need to understand reactions and product branching at different conditions

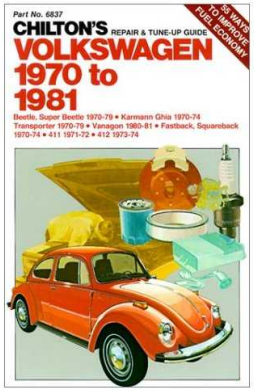
# What is the philosophy of atmospheric research?

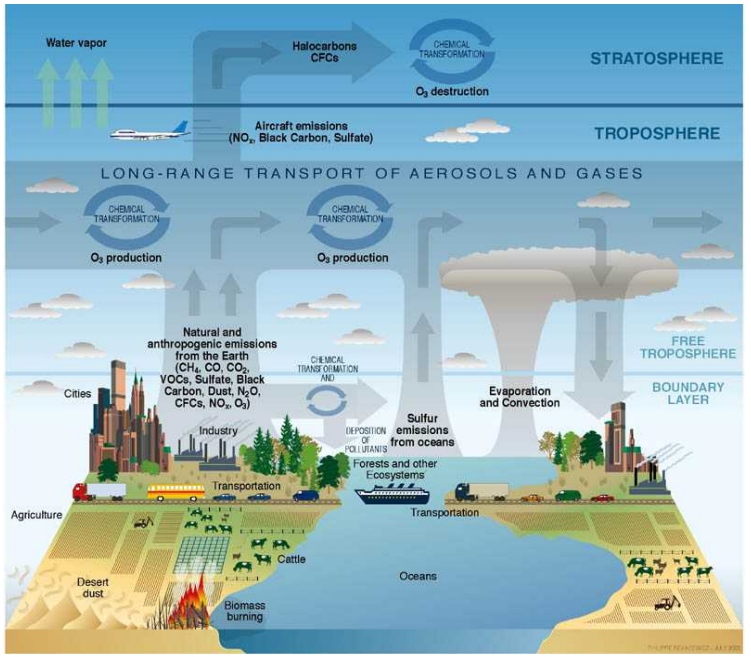


Robert Couse-Baker




Mbz1 Wikimedia commons

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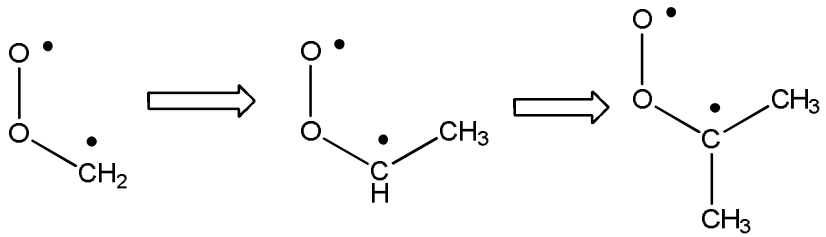
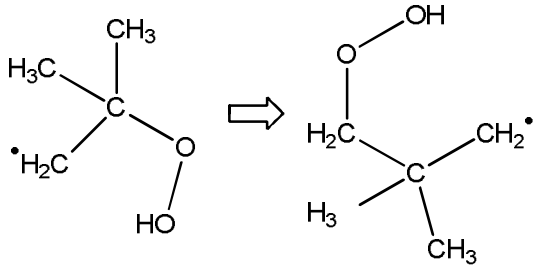
# Opening the "black box" is just the beginning for studies of these ephemeral intermediates

- Studies so far investigated conditions unlike actual combustion or troposphere




- Measurements of only the simplest or most convenient examples of intermediates




- **"Trailblazing" measurements may inspire new tools to investigate these species**

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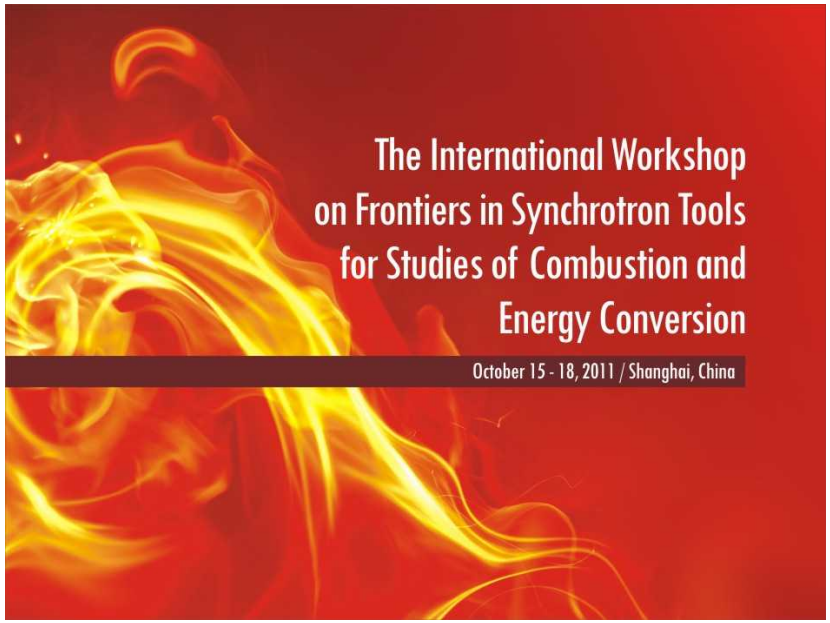
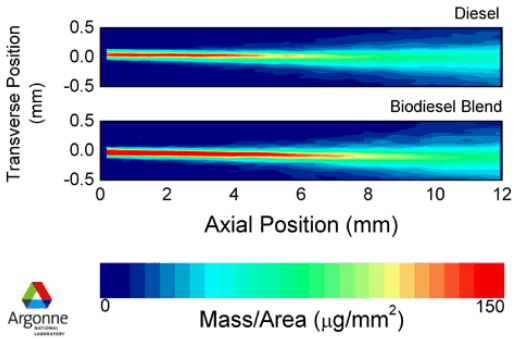
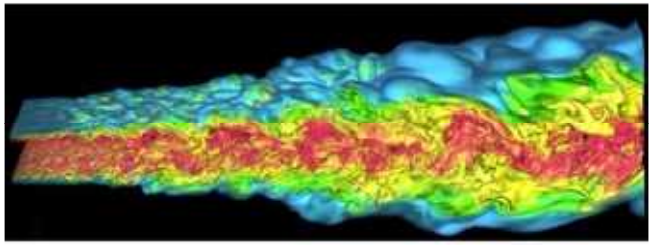
# Challenges for Future Light-Source Studies of Combustion Physics?



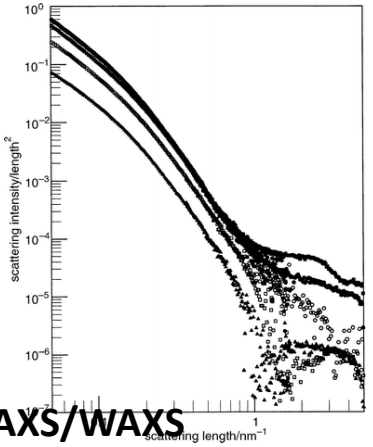

- **Current combustion applications of synchrotron radiation**
  - Strong emphasis on VUV for chemistry
  - X-ray measurements of particulate products
  - X-radiography of spray formation
- **Interfacial and multiphase processes are critical in many combustion problems**
  - Soot formation and oxidation
  - Mixture formation
  - Fluidized bed combustion




**Spray formation – X-radiography**



**Gas-phase chemistry – SPIMS**




**Soot formation – SAXS/WAXS**

*Faraday Discuss.* **119**, 395-407 (2002)

**Soot morphology – X-ray diffraction (CFEL-LCLS)**

# Challenges for Future Light-Source Studies of Combustion Physics?

U.S. DOE "PreSICE" initiative --

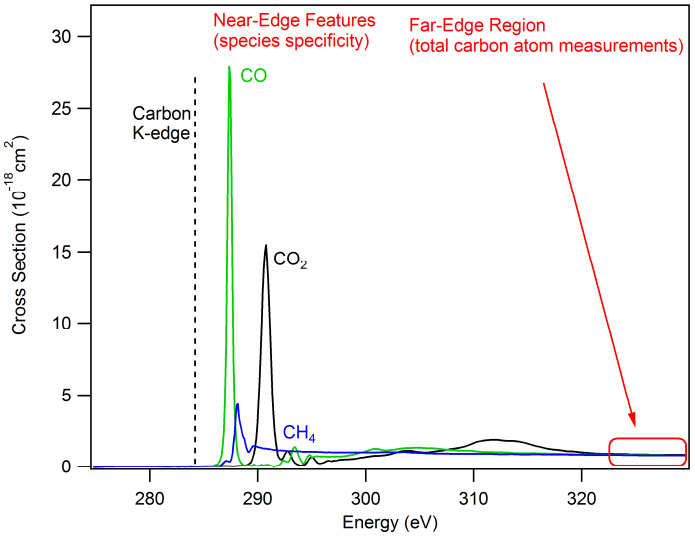
Experiments are important to discover and validate **fundamental physics** for predictive simulation

*"Stochastic" in-cylinder effects – sensitivity of combustion to initial conditions*

*Physics of mixture formation from injection of liquid fuels*

Highest impact experiments will require spatially resolved and chemically specific measurements

# Core-level spectroscopy may be an important tool to probe gas-phase turbulence



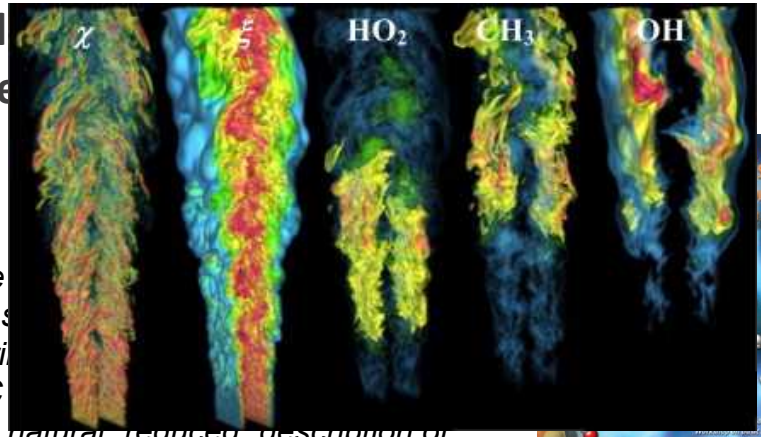

Far-edge region can see all carbon

- Carbon atom counting – directly probe mixing fraction

Near edge chemical-environment specific more than *molecule*-specific

- Possible relationship to reduced chemistry?

**DOE report "Basic Research Needs for Cl… Ce…**




*"The meas… distri… C=C … as a natural "reduced" description of complicated chemistry…"*

J.-H. Chen, *Proc. Combust. Inst.* **33**, 99-123 (2011)

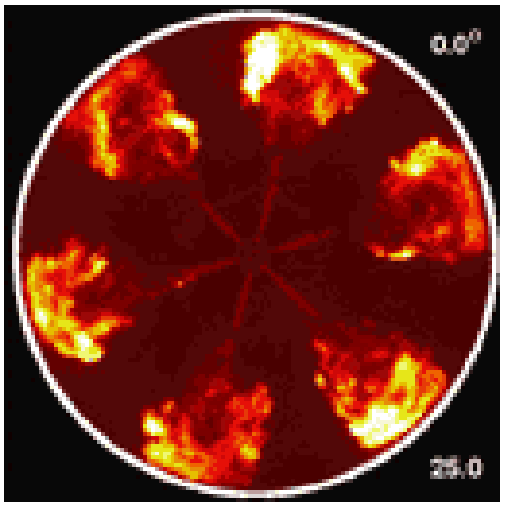


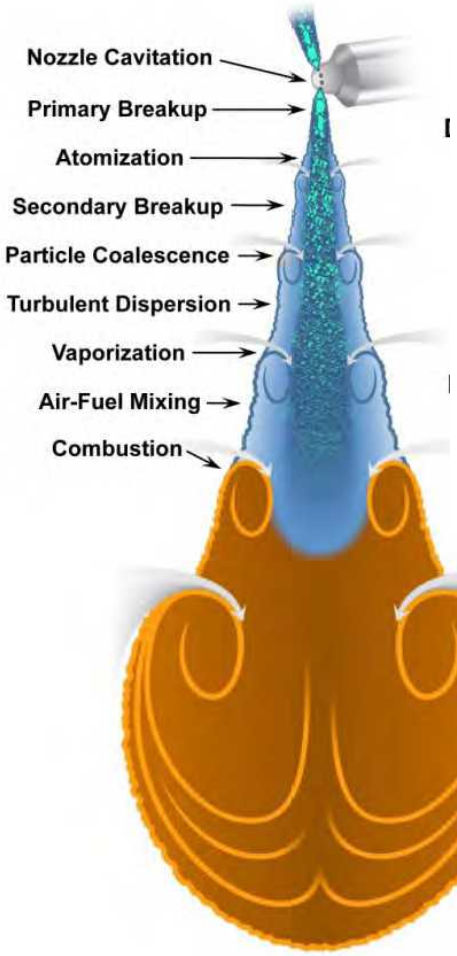

**Bellan and coworkers have developed a reduced kinetics that uses "constituents" – chemical groups** **Combustion and Flame 157 (2010) 1594–1609**

**Core-level spectroscopy applied to flame imaging -- Hendrik Bluhm (LBNL / ALS), Jonathan Frank, David Osborn (Sandia CRF).**

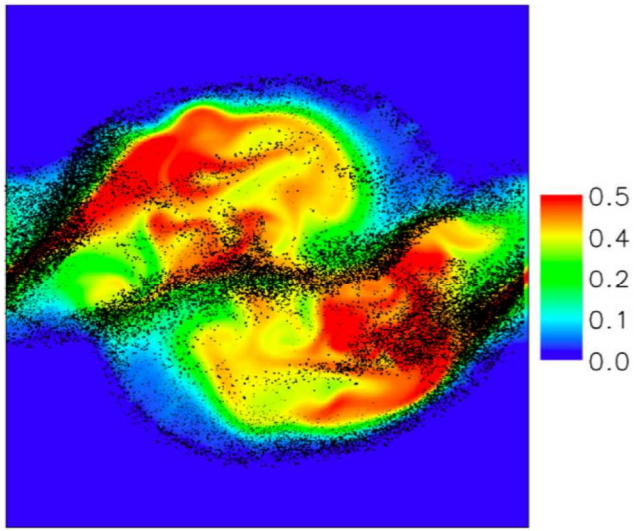
# Evaporation is an important part of the "multiphysics" problem of mixture formation

- High-momentum liquid fuel jet enters a dense hot gas environment
- Primary breakup of the liquid core leads to drops
- These drops evaporate and interact with the gas flow






Heinz Pitsch & Olivier Desjardins




Mixture fraction and droplets distribution

- X-ray measurements in droplet train have probed surface and bulk composition
- Differential evaporation of multicomponent liquids
- Interaction with flow and temperature fields

**Is there a role for x-ray measurements in this multiphase region?**

# Acknowledgements

David Osborn, Oliver Welz, Judit Zádor, John Savee, Haifeng Huang, Arkke Eskola, Howard Johnsen, Subith Vasu (UCF)

Collaborators: Carl Percival (Manchester), Dudley Shallcross (Bristol) and John Dyke (Southampton)

This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the United States Department of Energy (DOE);

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the DOE under Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory.