

# Reactivity of Criegee Intermediates $\text{CH}_2\text{OO}$ and $\text{CH}_3\text{CHOO}$ : Direct Detection and Conformer-Dependent Kinetics

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 Craig A. Taatjes<sup>1</sup>

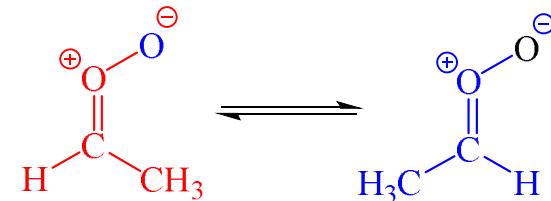
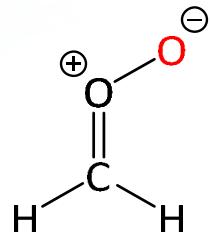
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32<sup>nd</sup> International Symposium on Free Radicals  
 Potsdam, Germany

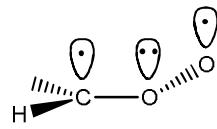
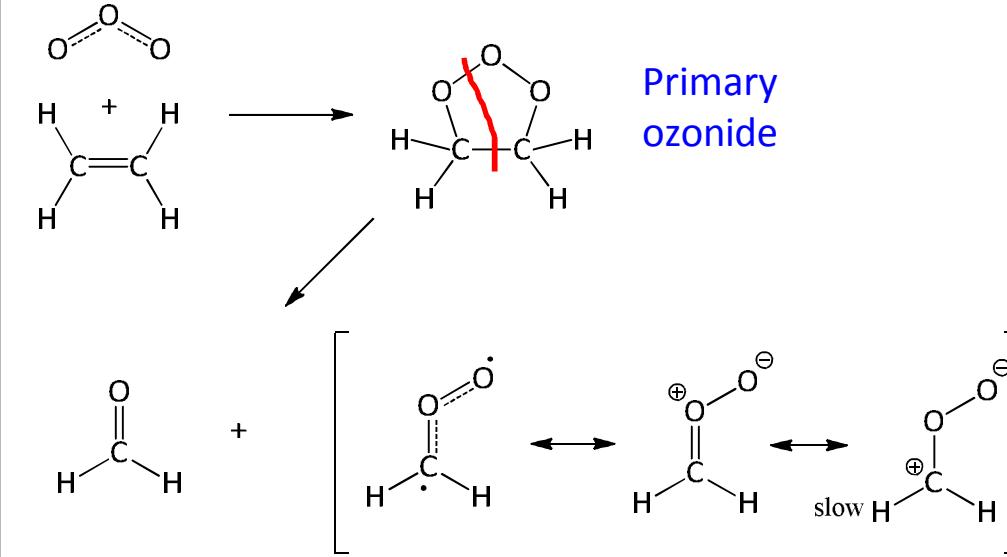
# Criegee intermediates are formed in ozonolysis of alkenes in the troposphere

Alkenes are emitted in large amounts  
(15% of the non-methane emission)



Tropospheric reactions, e.g., with OH,  $\text{NO}_3$ ,  $\text{O}_3$  consume alkenes

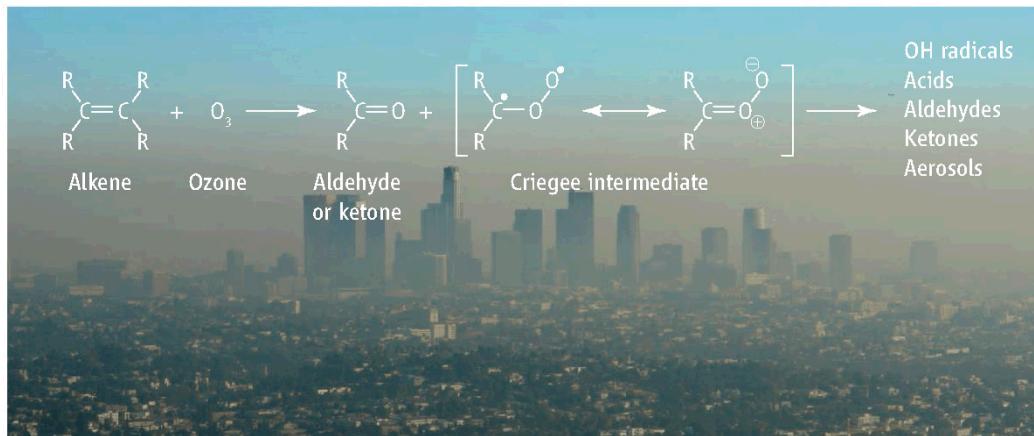
Ozonolysis: (Rudolf Criegee, 1949)



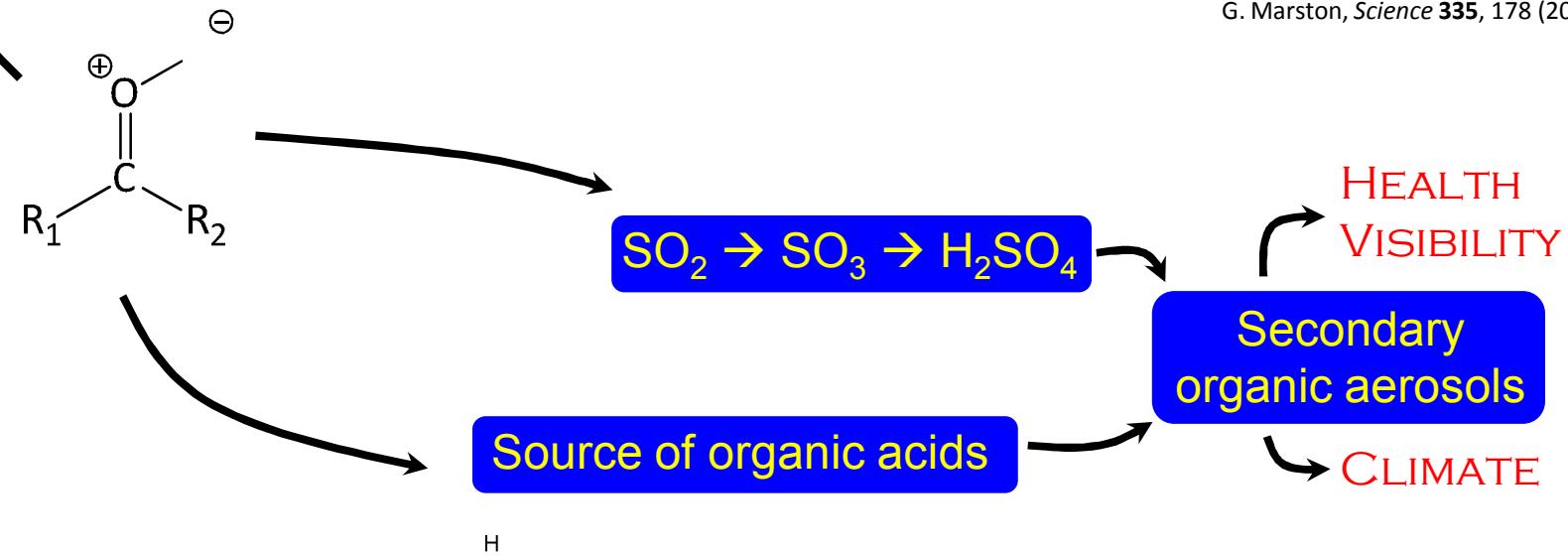
3-atom, 4  $\pi$ -electron system  
singlet zwitterion  
high barrier ( $\sim 120 \text{ kJ mol}^{-1}$ ) for rotation about CO bond

# Reactions of Criegee intermediates contribute to important tropospheric processes

Non-photolytic source of OH

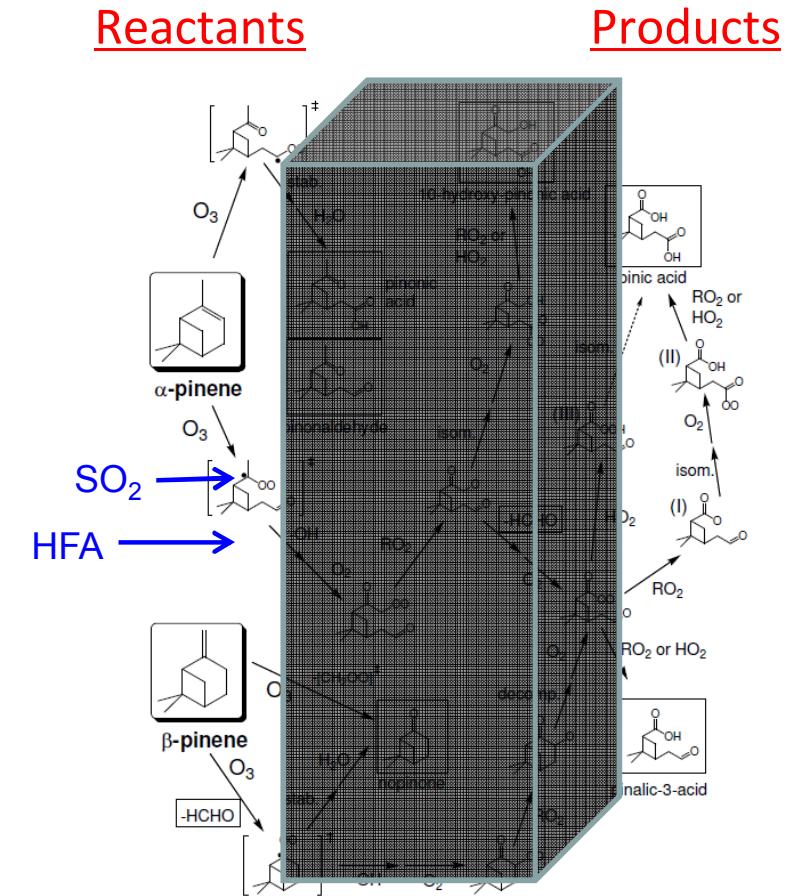


G. Marston, *Science* **335**, 178 (2012)



# Traditional approach to study Criegee chemistry

- 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
- **Problem:** Rate coefficients for Criegee reactions are uncertain by orders of magnitude!
  - Need *direct measurements*
- **But:** No Criegee intermediate has ever been detected in gas-phase ozonolysis!
- **Reason:** Ozonolysis forms Criegee intermediates slowly, but they react away rapidly



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

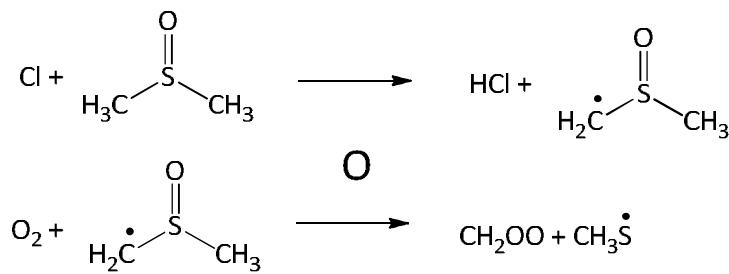


# “Recipe” for directly measuring Criegee reactions

1. Make a lot of Criegee intermediates and make them fast
2. Have a sensitive and selective detection technique for Criegee intermediates

# 1. Make a lot of Criegee Intermediates and make them fast

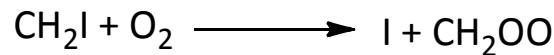
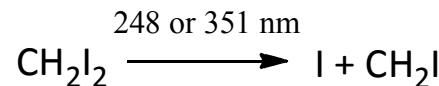
Asatryan and Bozzelli *Phys. Chem. Chem. Phys.* 10, 1769 (2008) predicted  $\text{CH}_2\text{OO}$  formation in dimethyl sulfoxide oxidation



Taatjes and co-workers *JACS* 130, 11883 (2008) detected  $\text{CH}_2\text{OO}$  in this system, but not enough for kinetic studies.

Make a lot of it and make it fast

Eskola *et al.* *Phys. Chem. Chem. Phys.* 8, 1416 (2006) found that  $\text{CH}_2\text{I}$  reaction with  $\text{O}_2$  made iodine atom with unity yield at low pressure – turns out that what's left is Criegee intermediate!



$$\Delta H_R \sim -4 \text{ kJ/mol}$$

$$T = 300 \text{ K}, P = 4 \text{ Torr}$$

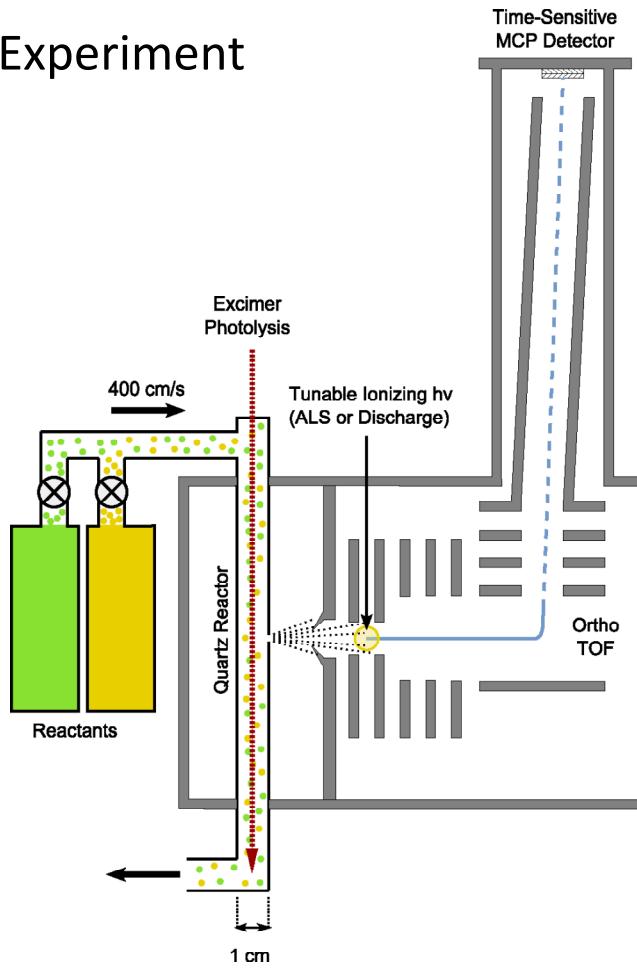
Make it fast

O. Welz, J.D. Savee, D. L. Osborn, S. V. Vasu, C. P. Percival, D. E. Shallcross, C. A. Taatjes, *Science* **335**, 204 (2012)

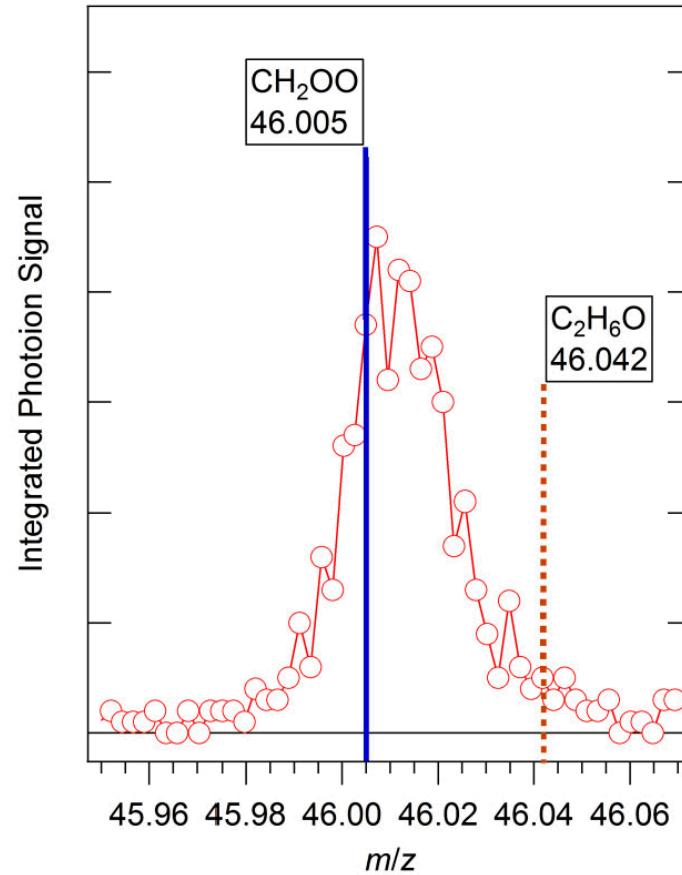
## 2. Have a sensitive and selective detection technique

→ Multiplexed Photoionization Mass Spectrometry (MPIMS)

### Experiment



### Mass spectrum of $m/z = 46$

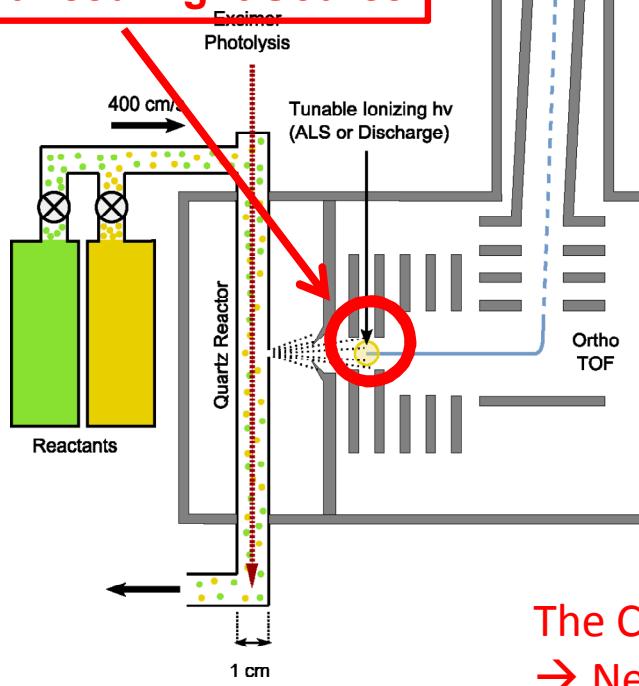


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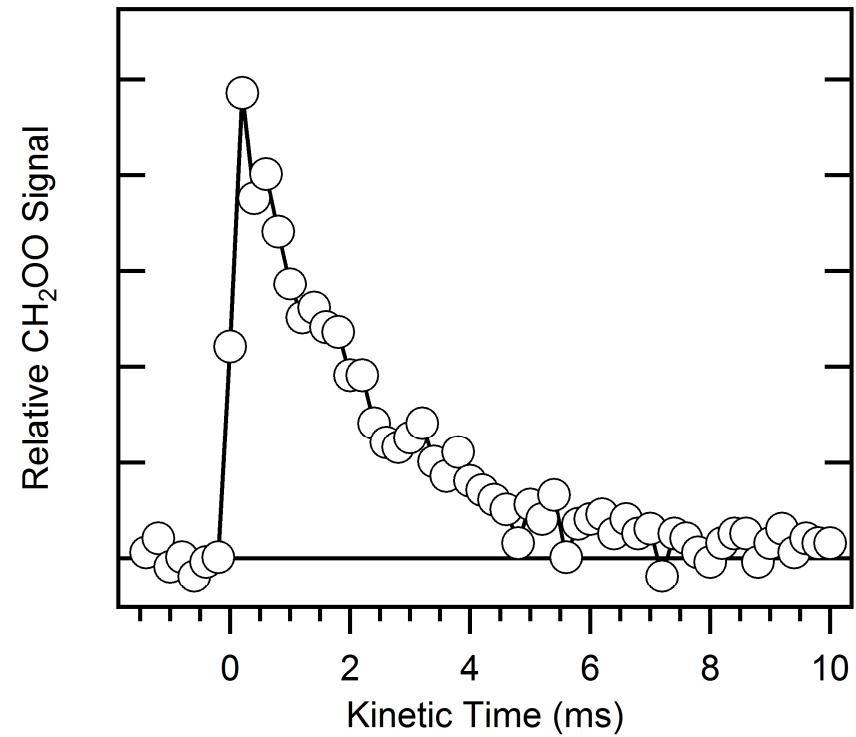
→ Multiplexed Photoionization Mass Spectrometry (MPIMS)

### Experiment

**Tunable VUV radiation  
from the  
Advanced Light Source**



### Time profile of $\text{CH}_2\text{OO}$



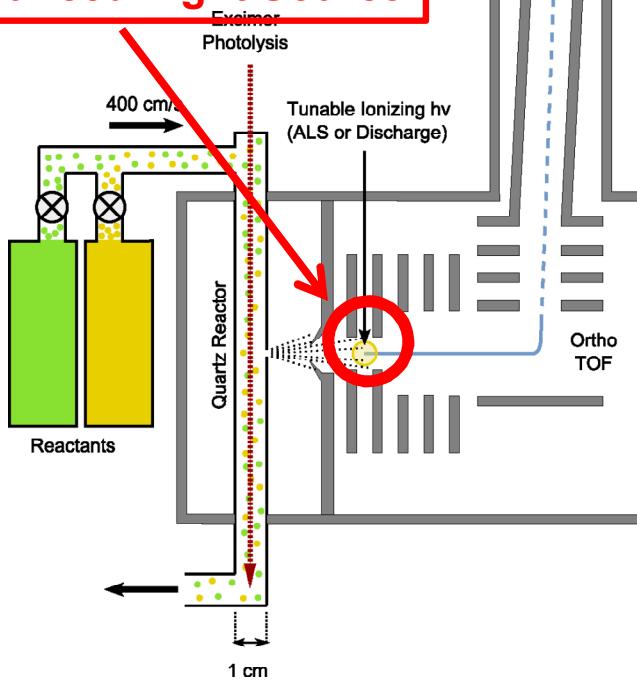
The Criegee intermediate is an *isomer* of more stable products  
→ Need isomer-resolved detection!

## 2. Have a sensitive and selective detection technique

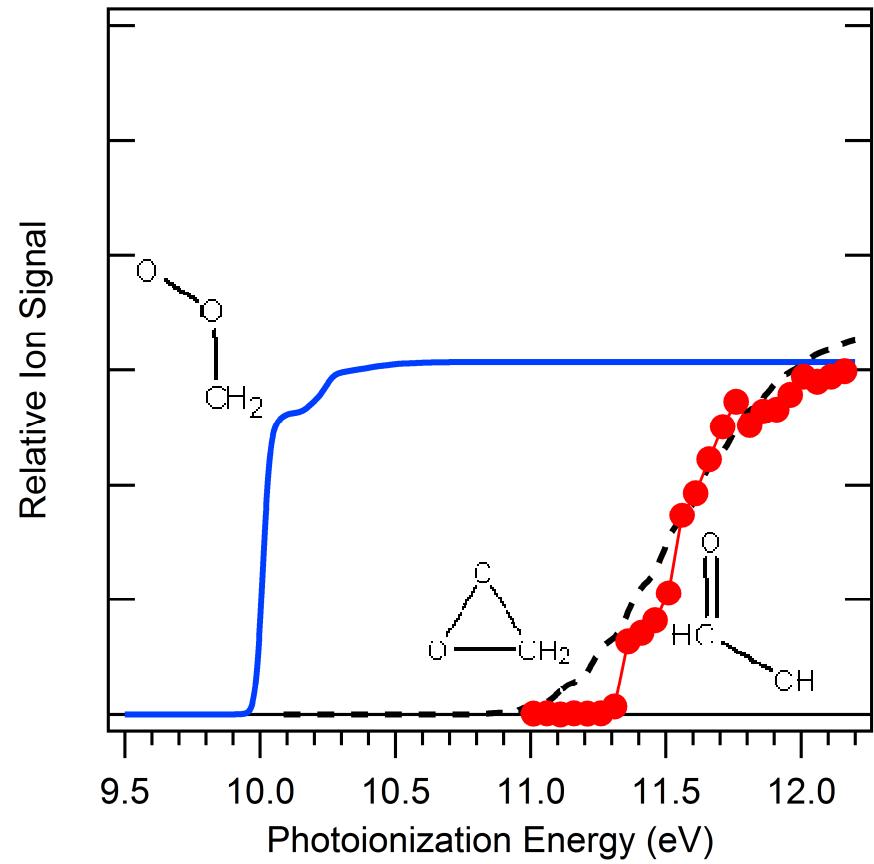
→ Multiplexed Photoionization Mass Spectrometry (MPIMS)

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**Tunable VUV radiation  
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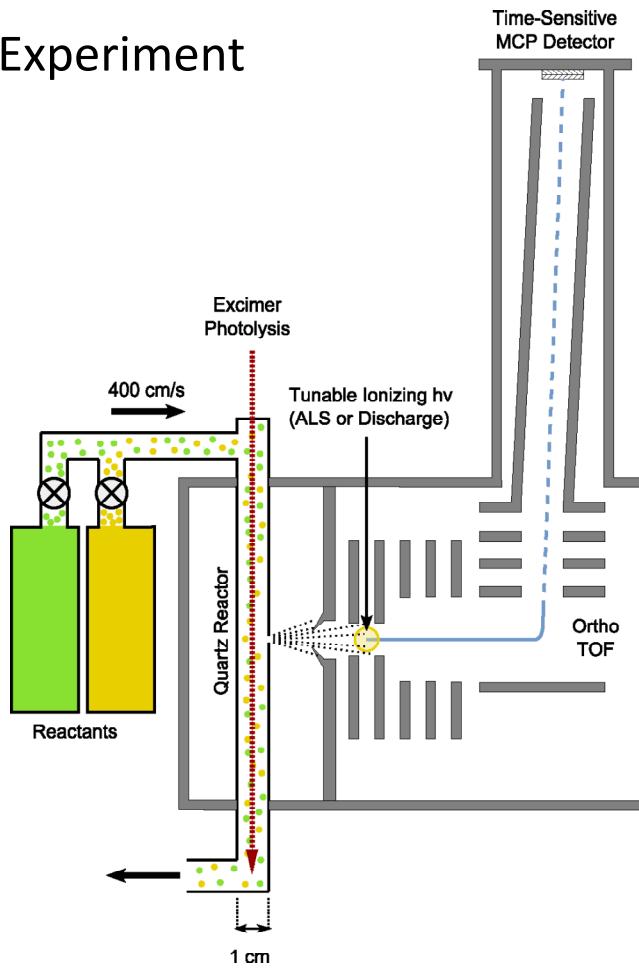
### Photoionization spectra of $\text{CH}_2\text{OO}$ isomers



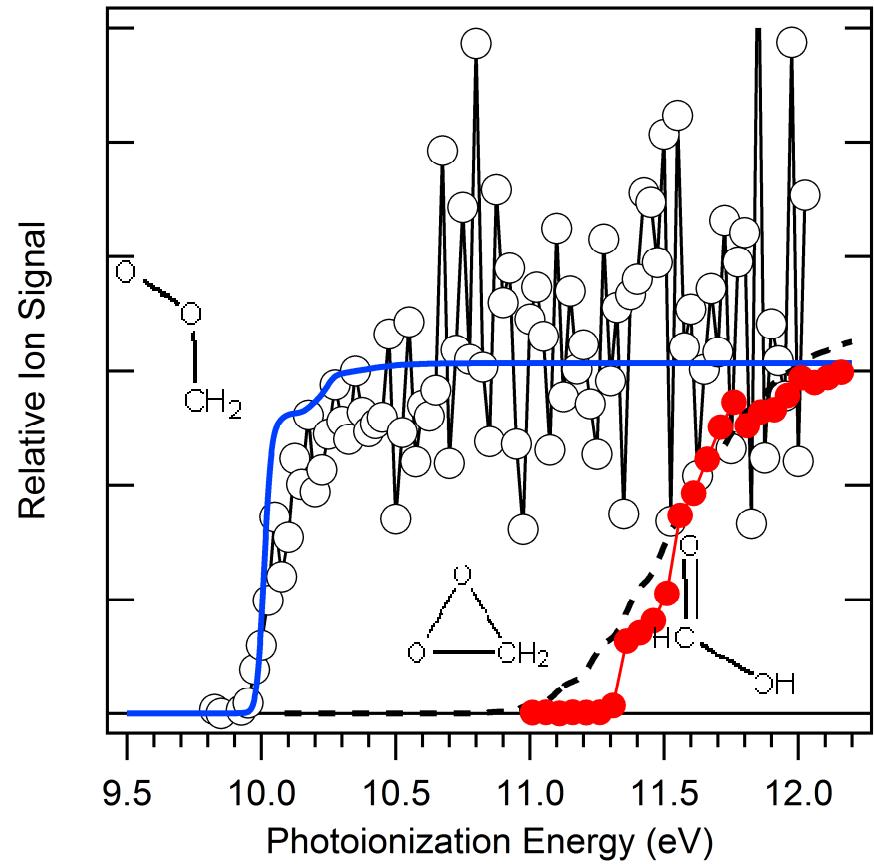
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### Experiment



### Photoionization spectra of $\text{CH}_2\text{OO}$ isomers

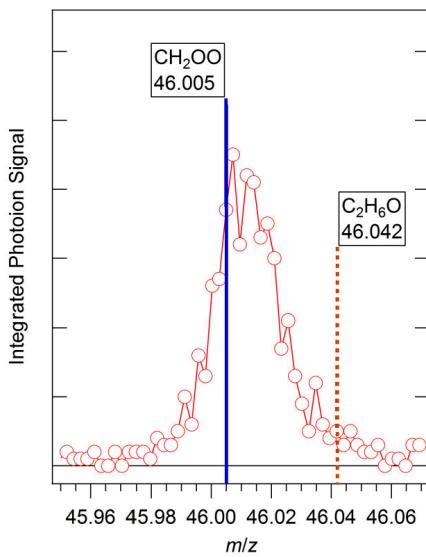


## 2. Have a sensitive and selective detection technique

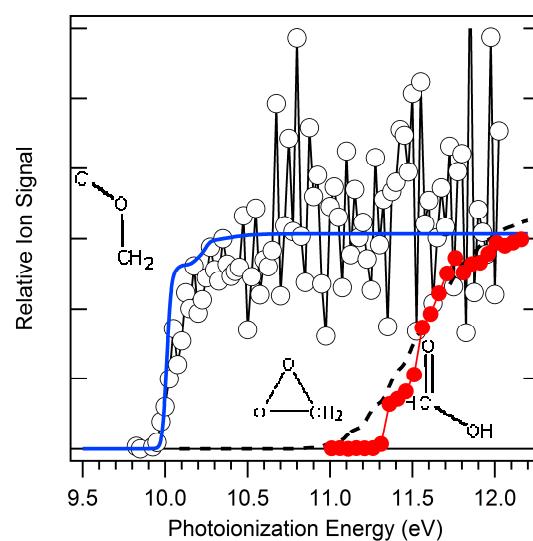
Definitive Evidence of the Criegee Intermediate  $\text{CH}_2\text{OO}$ :

1. Exact mass is correct
2. Ionization energy matches theory
3. Measured spectrum agrees well with Franck-Condon factor simulations

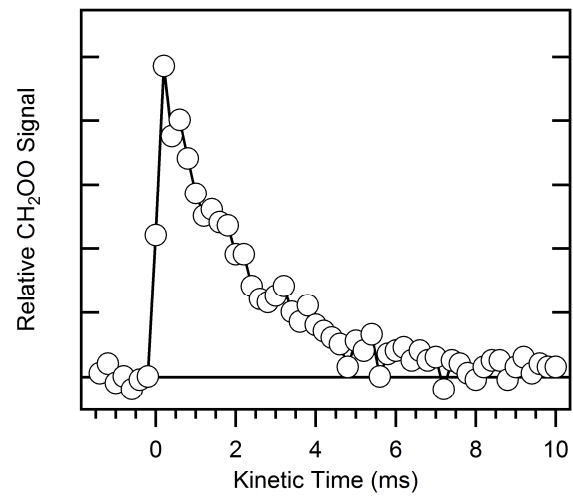
Mass spectrum of  $m/z = 46$



Photoionization spectrum of  $\text{CH}_2\text{OO}$



Time profile of  $\text{CH}_2\text{OO}$



# Measuring CH<sub>2</sub>OO reactions with important tropospheric species (H<sub>2</sub>O, SO<sub>2</sub>, NO<sub>2</sub>, NO)



→ up to **10 000 times** faster than what is used in models

If other Criegee intermediates react similarly, they are major SO<sub>2</sub> oxidants



→ **50 times** faster than what is used in models

If other Criegee intermediates react similarly, Criegee reactions might play an important role in NO<sub>x</sub> chemistry

Reactions of CH<sub>2</sub>OO with NO and H<sub>2</sub>O are too slow to be measured

→ only upper limits could be obtained



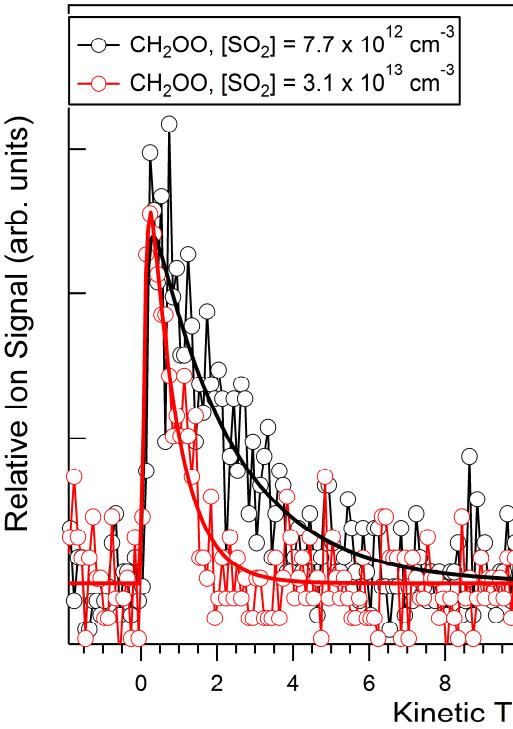
→ At least two orders of magnitude slower than literature estimates



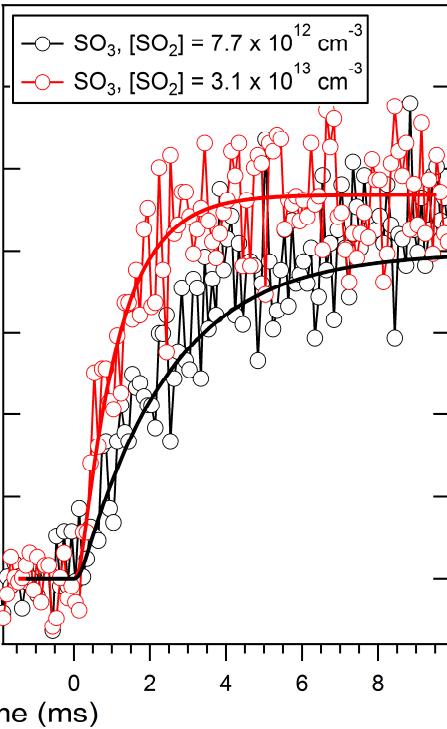
→ Tends to confirm values used in models

# $\text{SO}_3$ is a direct product of $\text{CH}_2\text{OO} + \text{SO}_2$ at 4 Torr

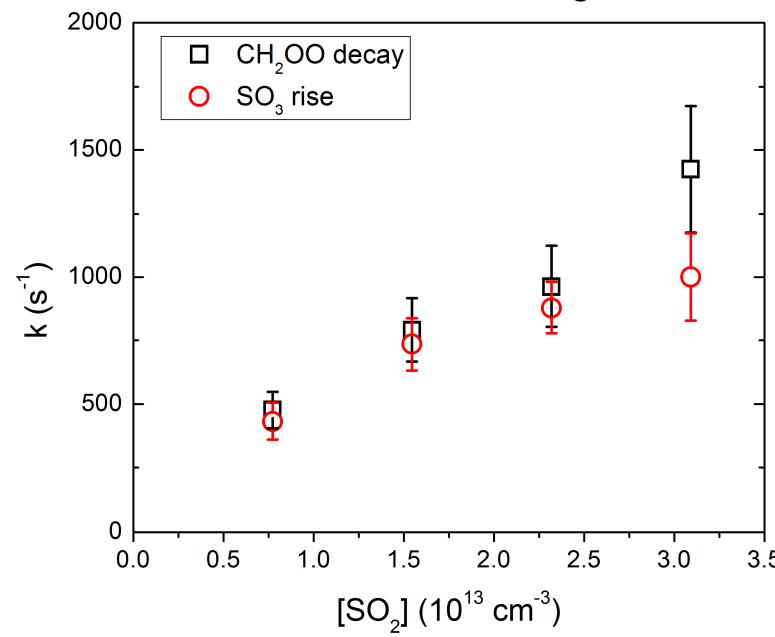
Time profiles of  
 $\text{CH}_2\text{OO}$



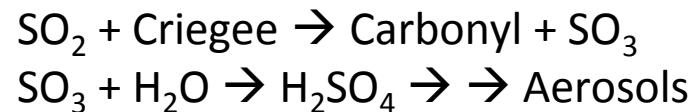
$\text{SO}_3$



The  $\text{CH}_2\text{OO}$  decay  
 matches the  $\text{SO}_3$  rise

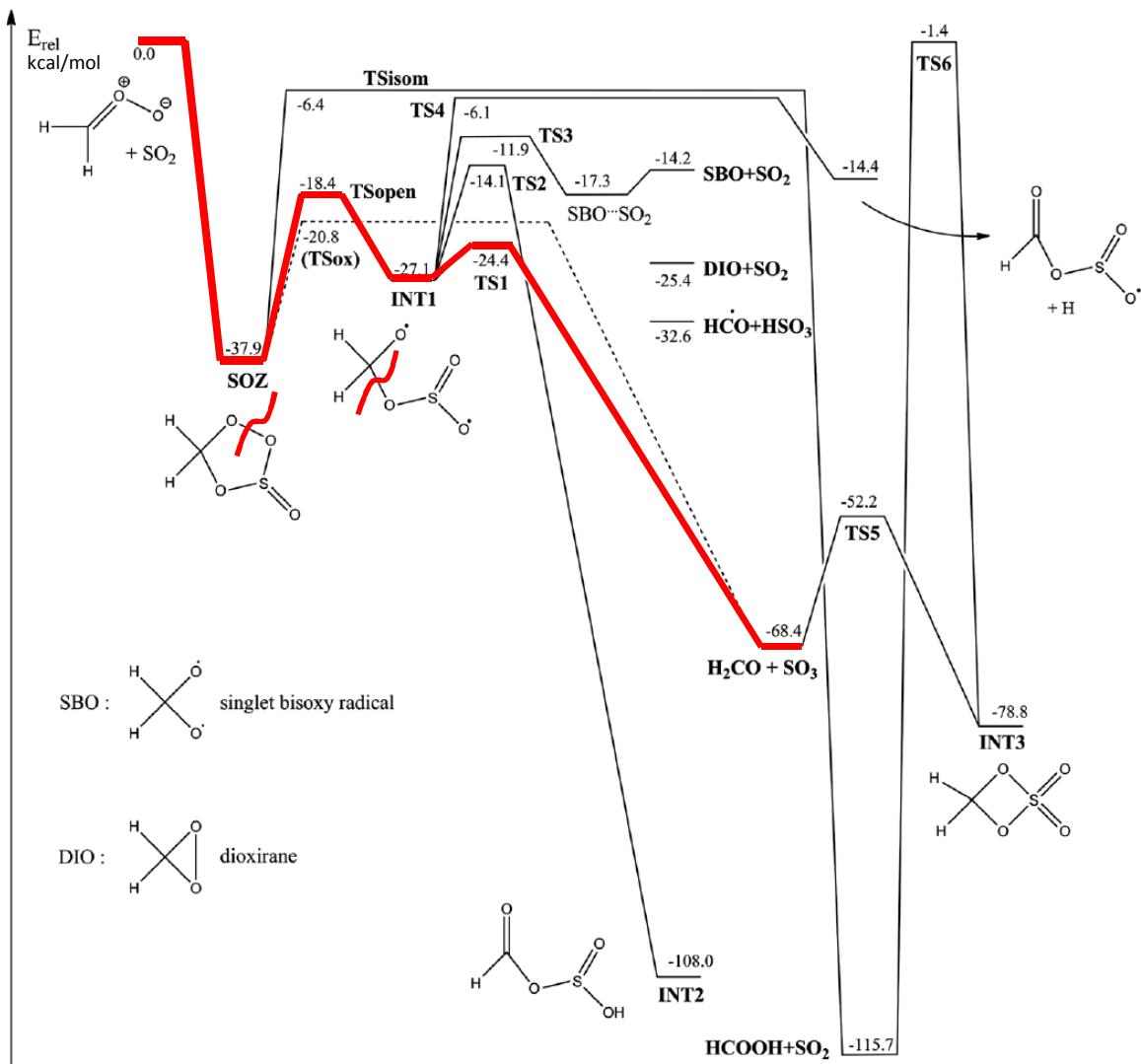


Criegee intermediates might  
 be an important source of  
 sulfuric acid!



Percival et al., Faraday  
 Discussions, 2013, accepted

Why is  $\text{CH}_2\text{OO}$  ( ${}^1\text{A}'$ ) +  $\text{SO}_2$  ( ${}^1\text{A}_1$ ) so fast? ( $k = 3.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ )  
How do the results at 4 Torr relate to atmospheric conditions?



The  $\text{CH}_2\text{OO} + \text{SO}_2$  reaction has a barrierless entrance channel.

The total rate coefficient at 4 Torr pressure is a lower limit to atmospheric conditions.

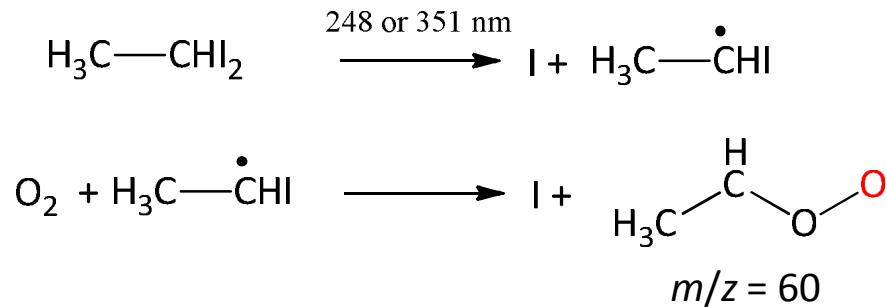
Increasing pressure will favor stabilization of the SOZ over  $\text{SO}_3$  + carbonyl formation

## What is the fate of the SOZ in the troposphere?

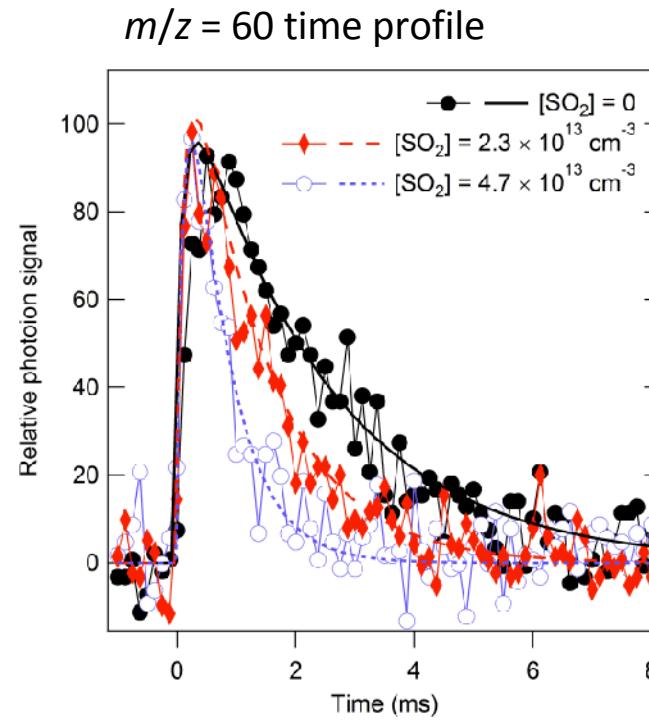
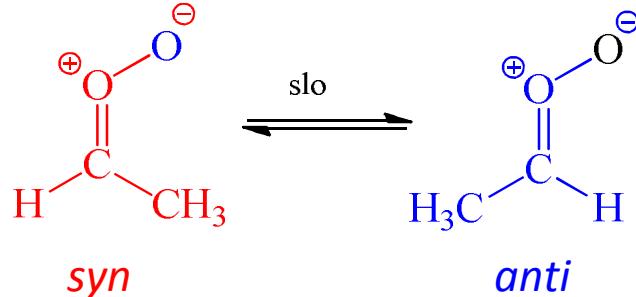
L. Vereecken, H. Harder, and A. Novelli,  
*Phys. Chem. Chem. Phys.* **14**, 14682 (2012).

# Production and characterization of the next larger Criegee Intermediate: acetaldehyde oxide ( $\text{CH}_3\text{CHOO}$ )

Similar strategy:

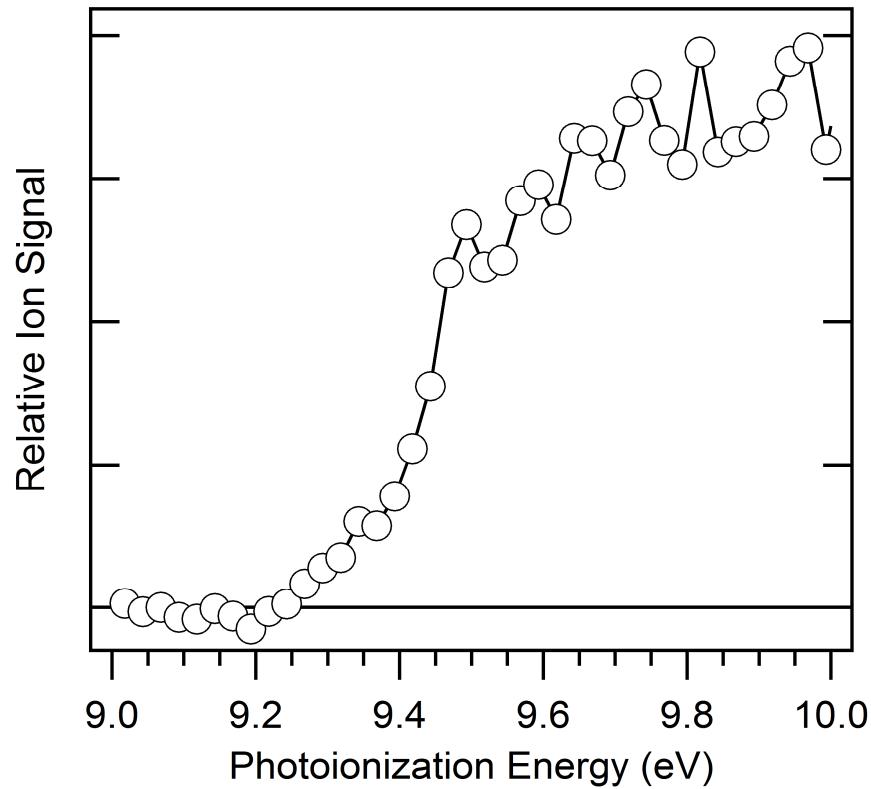


$\text{CH}_3\text{CHOO}$  exists in two distinct<sup>o</sup> conformeric forms



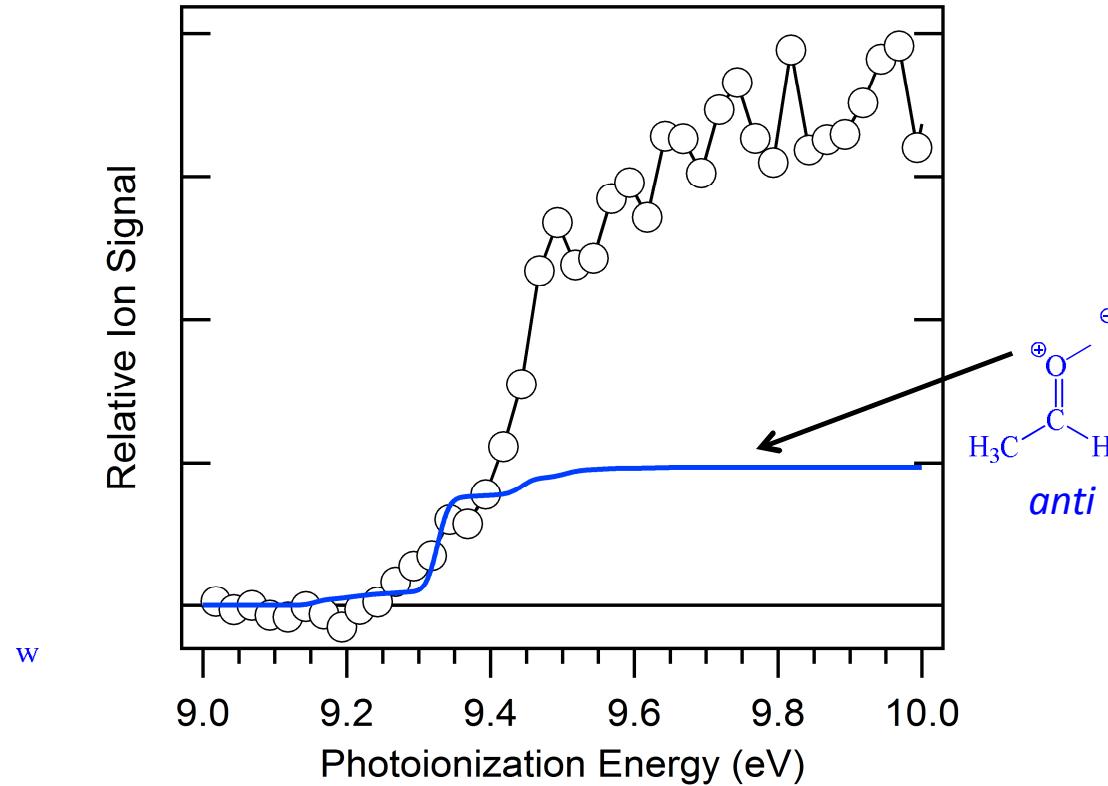
Calculations predict that *anti*- $\text{CH}_3\text{CHOO}$  reacts with  $\text{H}_2\text{O}$  five orders of magnitude faster than *syn*- $\text{CH}_3\text{CHOO}$   
 (Phys. Chem. Chem. Phys. 13, 13034 (2011))

# The $m/z = 60$ photoionization spectrum shows evidence of both *syn*- and *anti*- conformers of $\text{CH}_3\text{CHOO}$



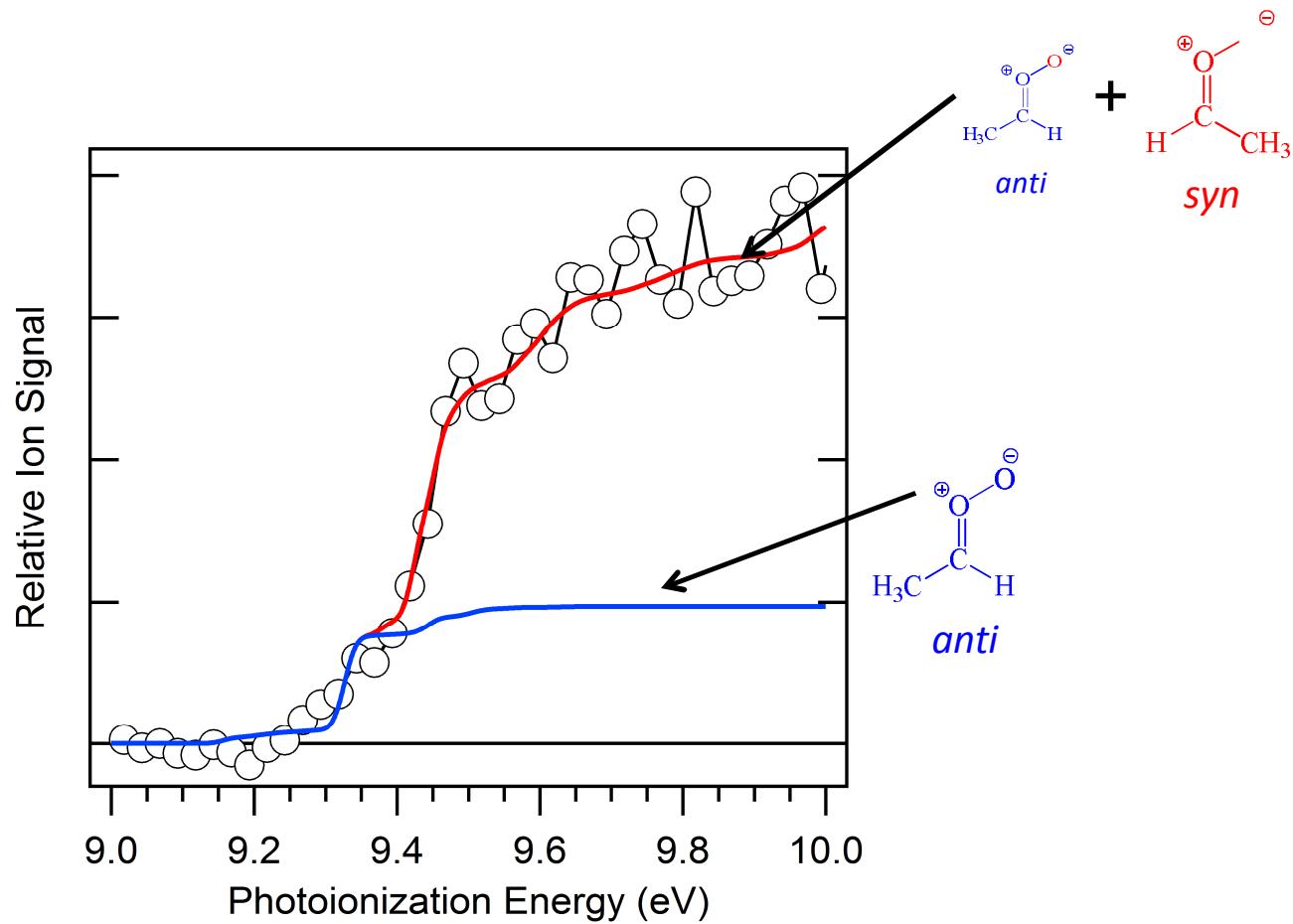
Taatjes *et al.*, *Science* **340**, 177 (2013)

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Taatjes *et al.*, *Science* **340**, 177 (2013)

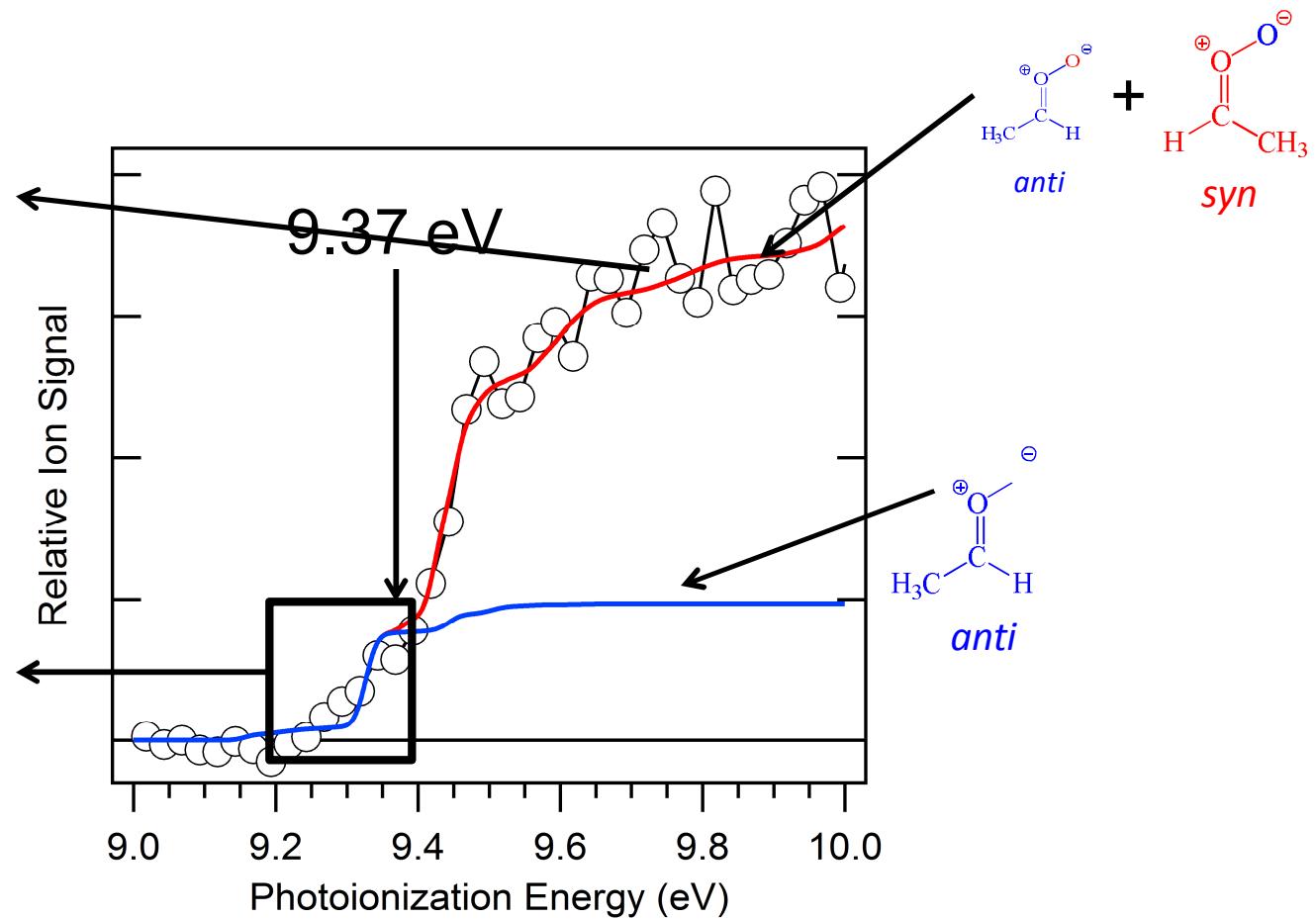
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Taatjes *et al.*, *Science* **340**, 177 (2013)

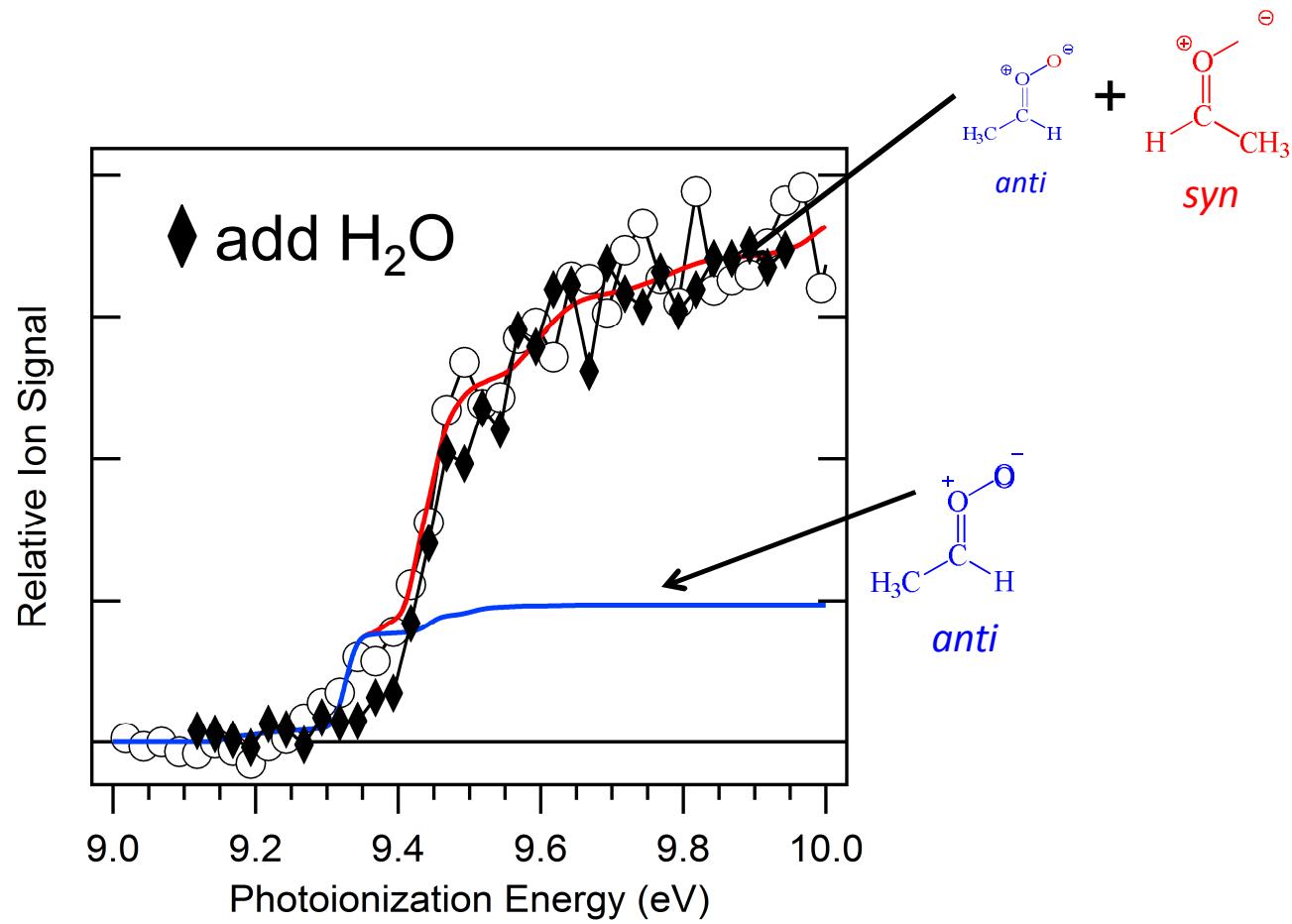
# The low-energy part $m/z = 60$ photoionization spectrum is dominated by *anti*-CH<sub>3</sub>CHO

both conformers contribute, but *syn*-dominates  
 10.5 eV: ~ 85% of the signal is *syn*-  
*anti*-conformer can be probed separately from *syn*-



Taatjes *et al.*, *Science* **340**, 177 (2013)

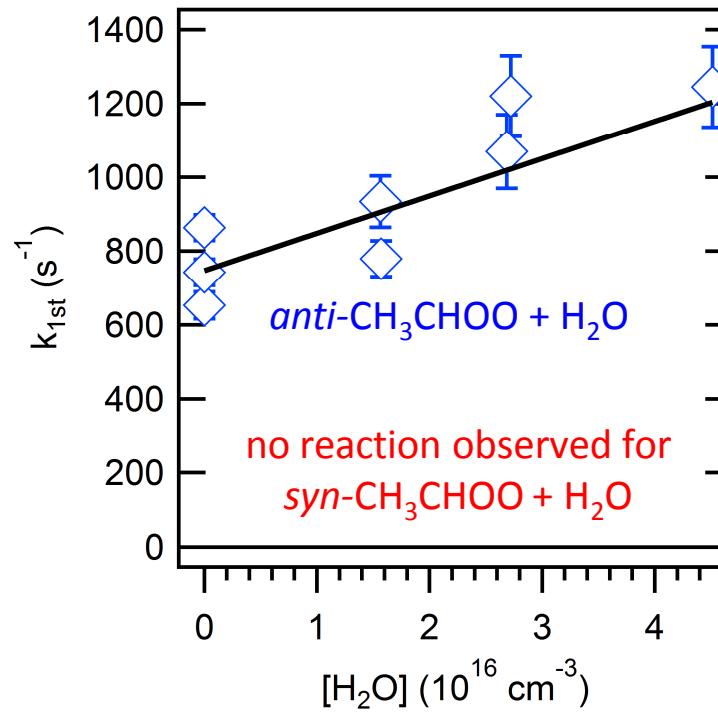
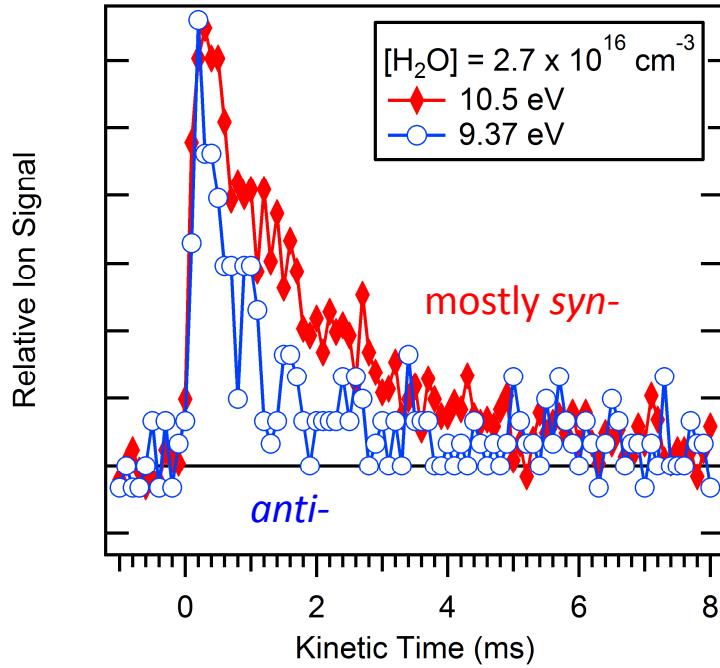
# Addition of water preferably removes the *anti*- conformer of $\text{CH}_3\text{CHOO}$



Conformer-dependent reactivity!

Taatjes *et al.*, *Science* **340**, 177 (2013)

# Measuring the rate coefficient of *anti*-CH<sub>3</sub>CHO with H<sub>2</sub>O

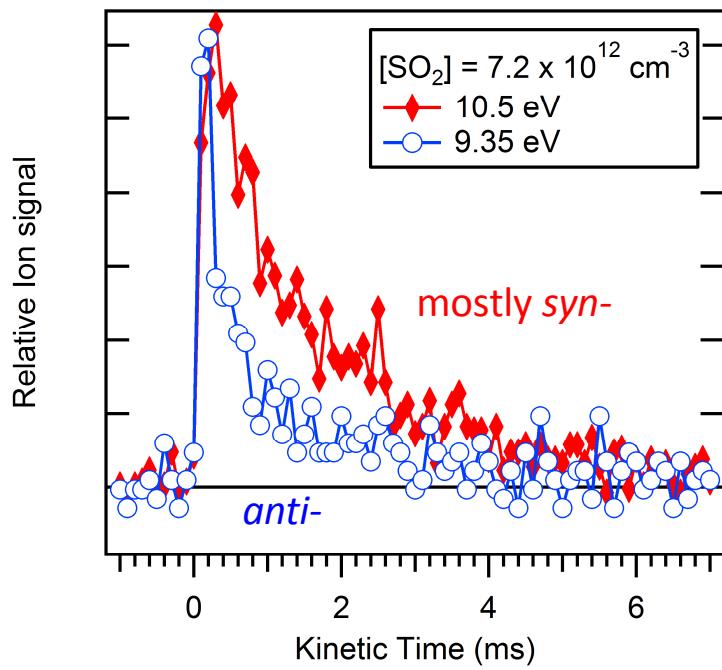


$$k(\text{anti-CH}_3\text{CHO} + \text{H}_2\text{O}) = (1.0 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$$

$$k(\text{syn-CH}_3\text{CHO} + \text{H}_2\text{O}) \leq 4 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$$

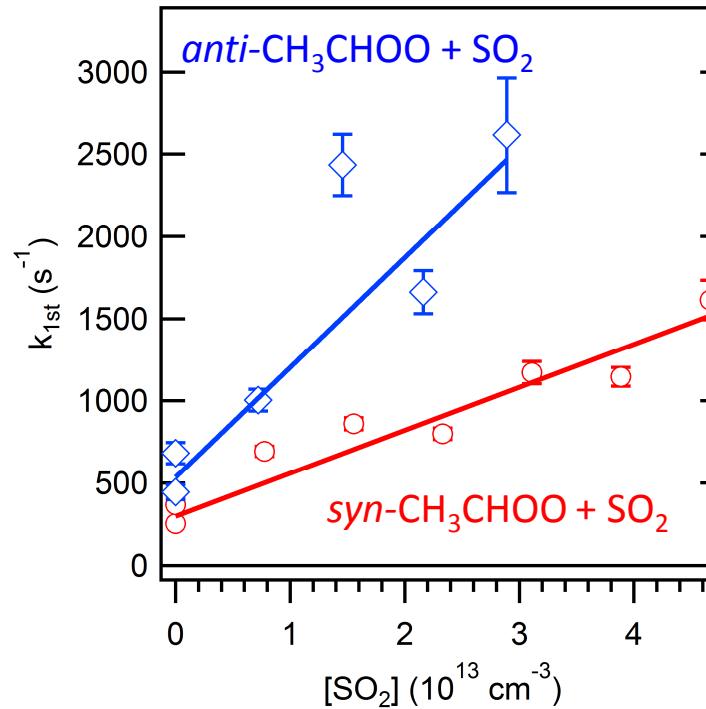
- A factor of 10 lower than predictions for the high-pressure limit from Anglada *et al.* (Phys. Chem. Chem. Phys. 13, 13034 (2011)), but larger than other calculations
- Substantially larger than predictions for other Criegee Intermediates

# The $\text{CH}_3\text{CHOO} + \text{SO}_2$ reaction shows conformer-dependent reactivity as well



$$k(\text{anti-CH}_3\text{CHOO} + \text{SO}_2) = (6.7 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

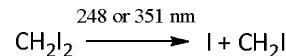
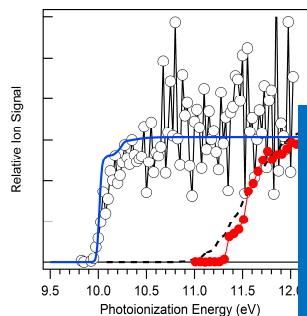
$$k(\text{syn-CH}_3\text{CHOO} + \text{SO}_2) = (2.4 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$



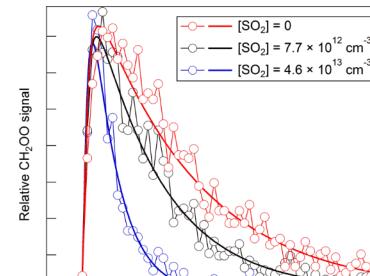
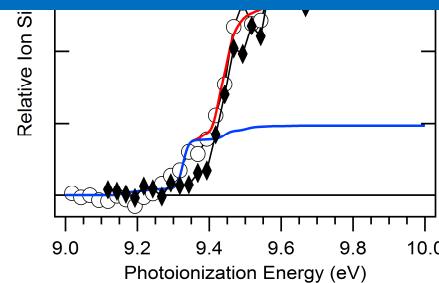
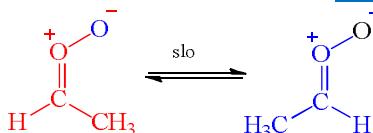
Similarly fast as the  $\text{CH}_2\text{OO}$  reaction

# Summary and Outlook

1,1-Diiodoalkane oxidation combined with MPIMS is a suitable strategy to directly probe reactions of Criegee Intermediates



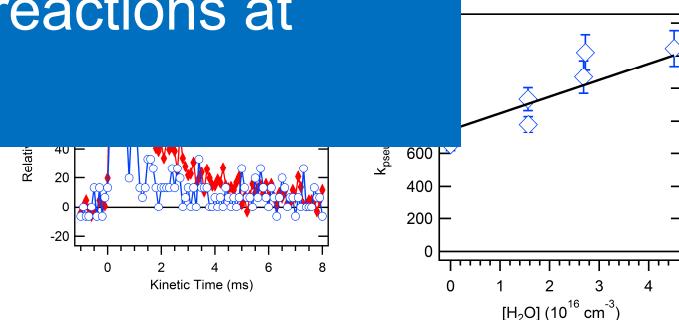
The two conformers can be distinguished by photoionization spectra



We determined rate  $k_{\text{pse}}$  coefficients for  $\text{CH}_2\text{OO}$  reactions with atmospherically relevant species; substantial

values to values used in chemical models exist in these

with  $\text{H}_2\text{O}$  and termination of the coefficient





# Acknowledgements

Craig A. Taatjes

Arkke J. Eskola

John D. Savee

Adam M. Scheer

Brandon Rotavera

David L. Osborn

Edmond P. F. Lee

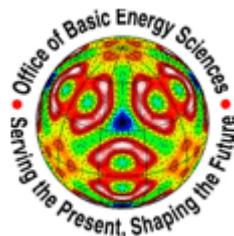
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Dudley E. Shallcross

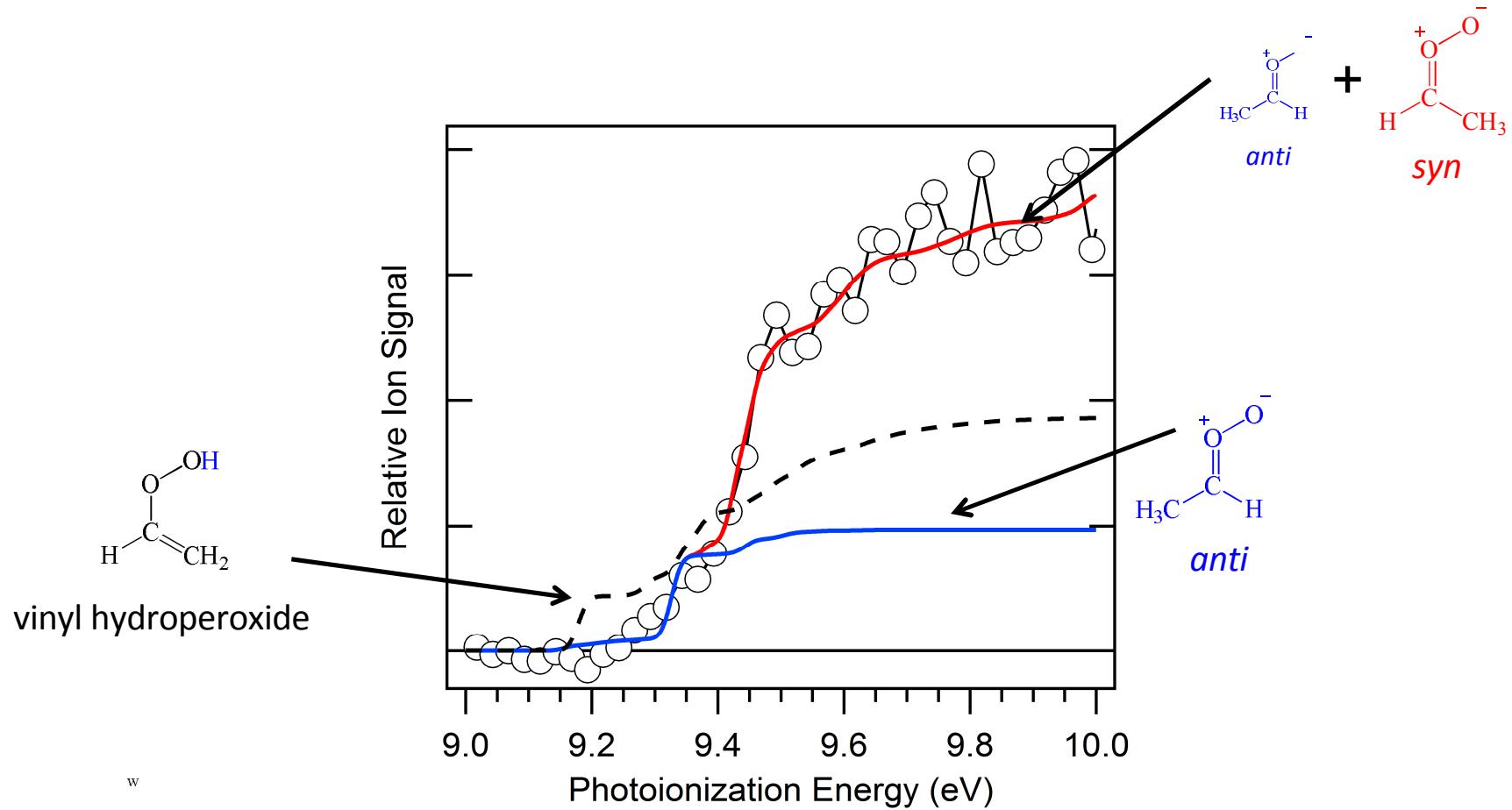
- Howard Johnsen (Sandia) and the staff of the Chemical Dynamics Beamline at the ALS for technical support



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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.

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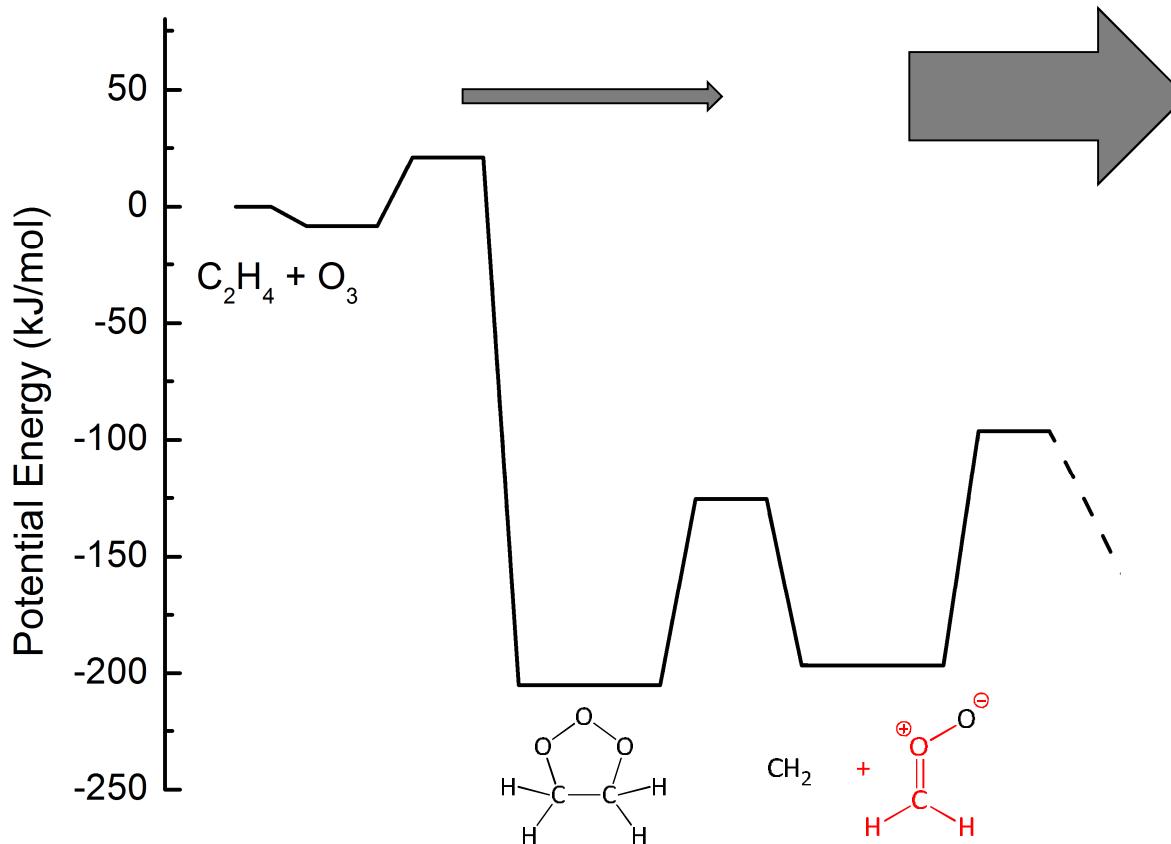


# Why are Criegee intermediates so hard to detect?

Ozonolysis forms Criegee intermediates slowly, but they react away rapidly

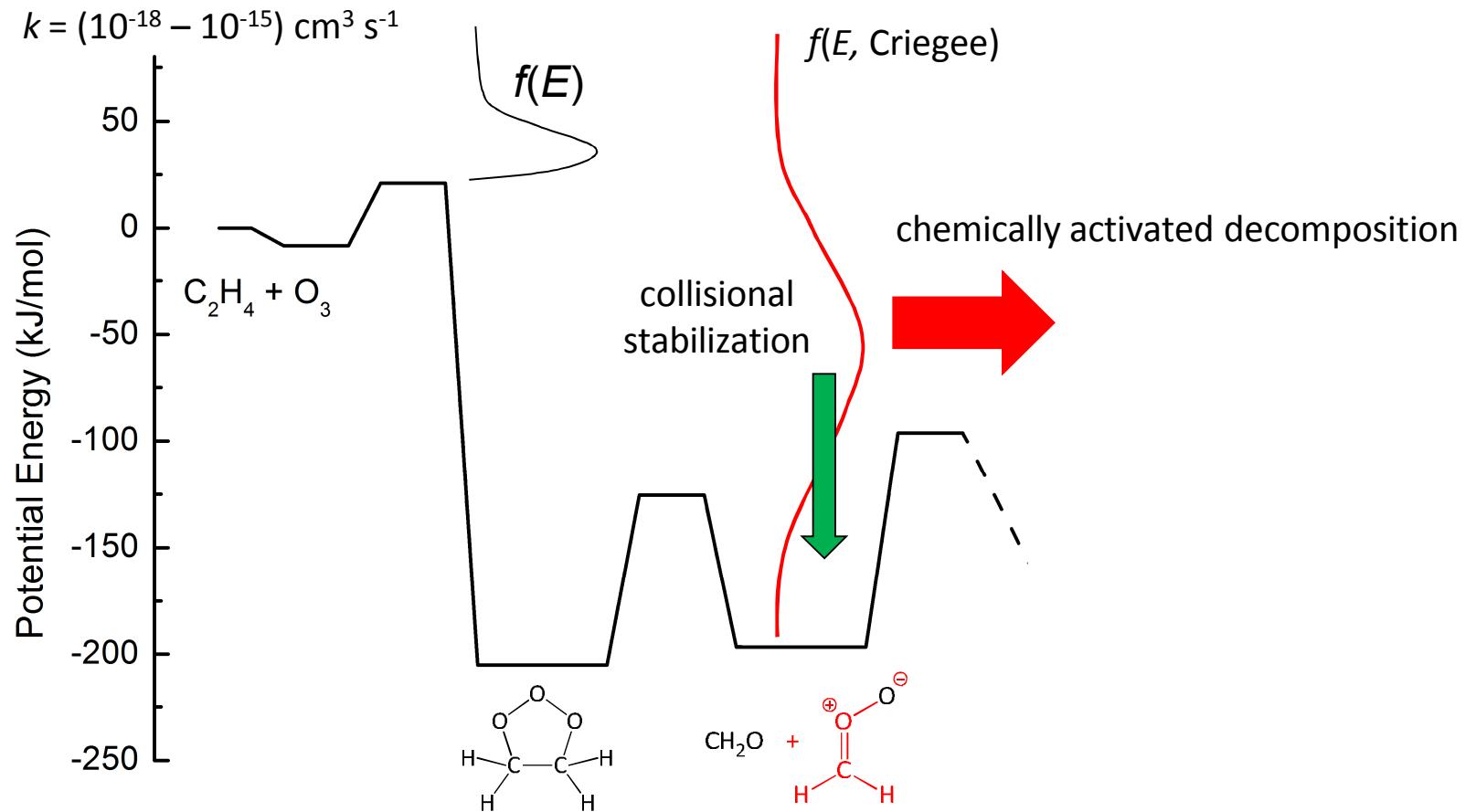
→ low steady-state concentrations

$$10^{-18} \text{ cm}^3 \text{ s}^{-1} \leq k \leq 10^{-15} \text{ cm}^3 \text{ s}^{-1}$$



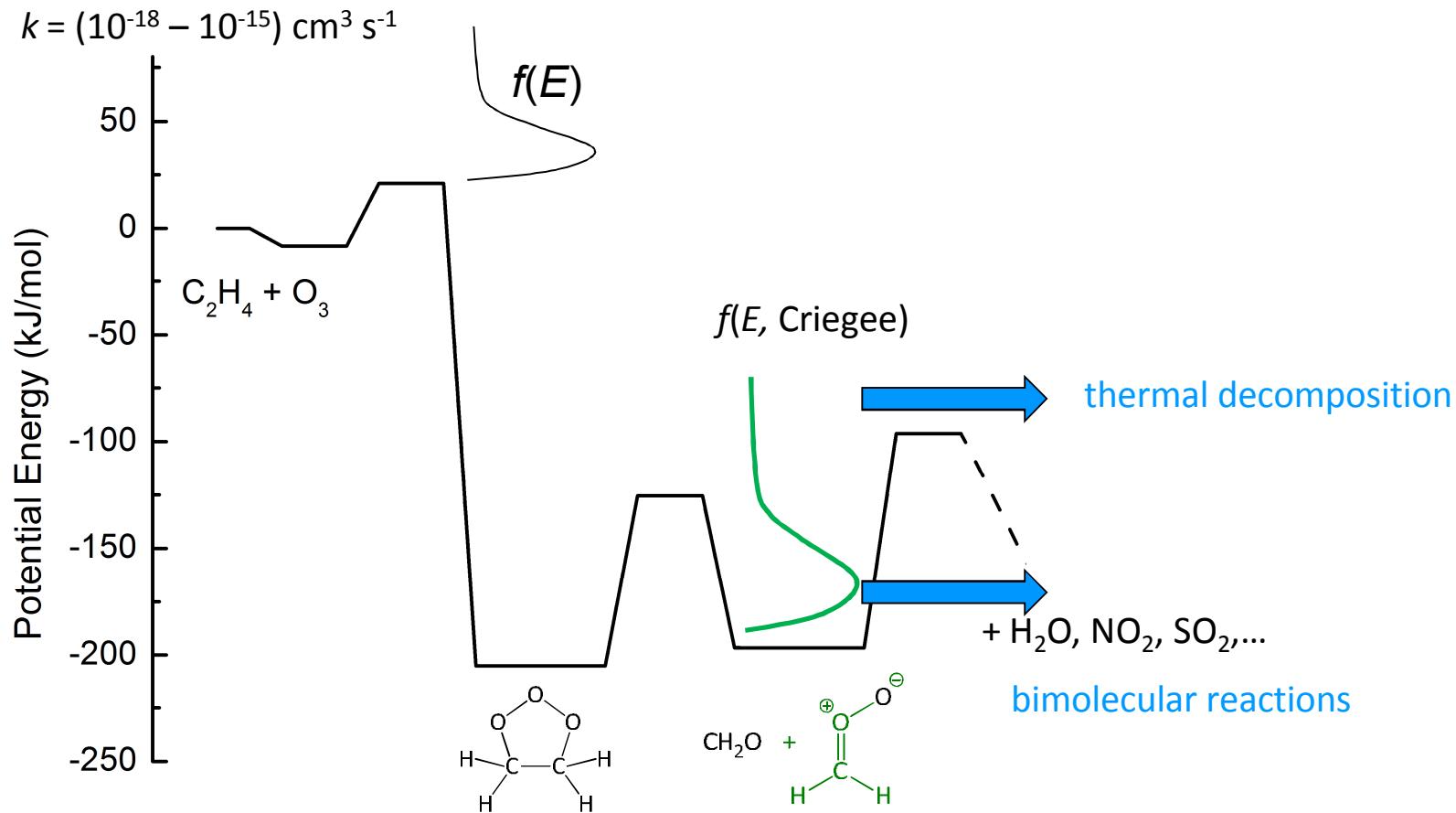
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