

Reactivity of Criegee Intermediates CH_2OO and CH_3CHOO : Direct Detection and Conformer-Dependent Kinetics

Oliver Welz,¹

Arkke J. Eskola,¹ John D. Savee,¹ Adam M. Scheer,¹ Brandon Rotavera,¹ David L. Osborn,¹
Edmond P. F. Lee,^{2,3} John M. Dyke,² Daniel M. K. Mok,³ Carl J. Percival,⁴ Dudley E. Shallcross⁵,
Craig A. Taatjes¹

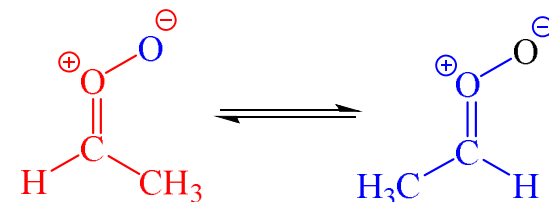
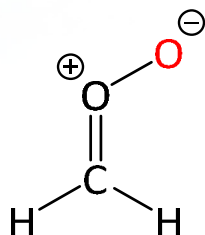
¹Sandia National Laboratories, Livermore, USA

²University of Southampton, UK

³Hong Kong Polytechnic University, Hong Kong

⁴University of Manchester, UK

⁵University of Bristol, UK



32nd International Symposium on Free Radicals
Potsdam, Germany

Criegee intermediates are formed in ozonolysis of alkenes in the troposphere

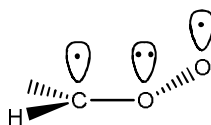
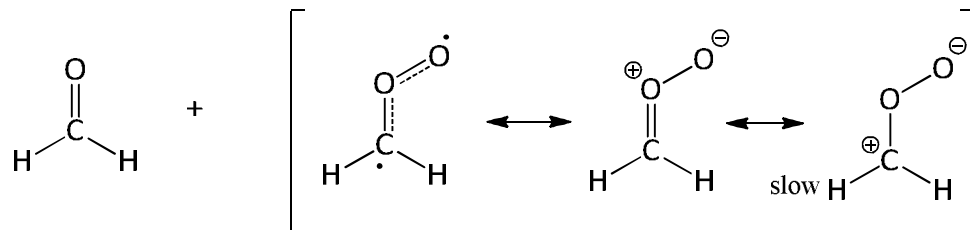
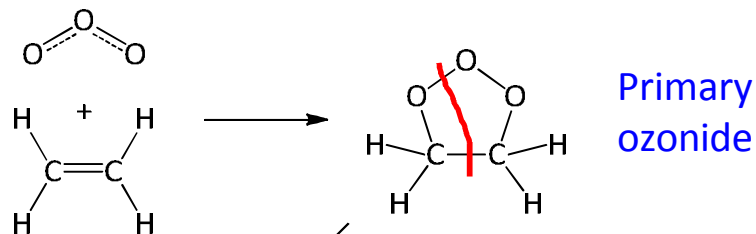
Alkenes are emitted in large amounts

(15% of the non-methane emission)



Tropospheric reactions, e.g., with OH, NO₃, O₃ consume alkenes

Ozonolysis: (Rudolf Criegee, 1949)



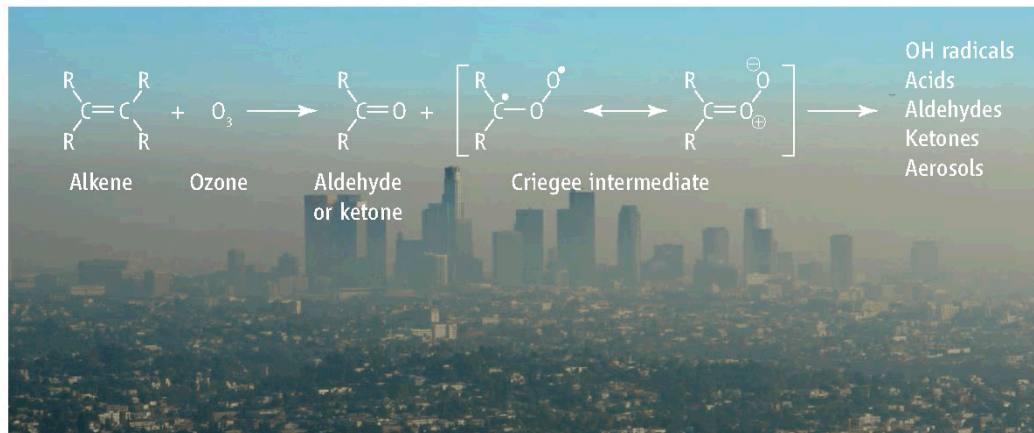
3-atom, 4 π -electron system

singlet zwitterion

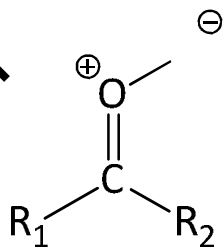
high barrier ($\sim 120 \text{ kJ mol}^{-1}$) for rotation about CO bond

Reactions of Criegee intermediates contribute to important tropospheric processes

Non-photolytic source of OH



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



$\text{SO}_2 \rightarrow \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$

Source of organic acids

Secondary organic aerosols

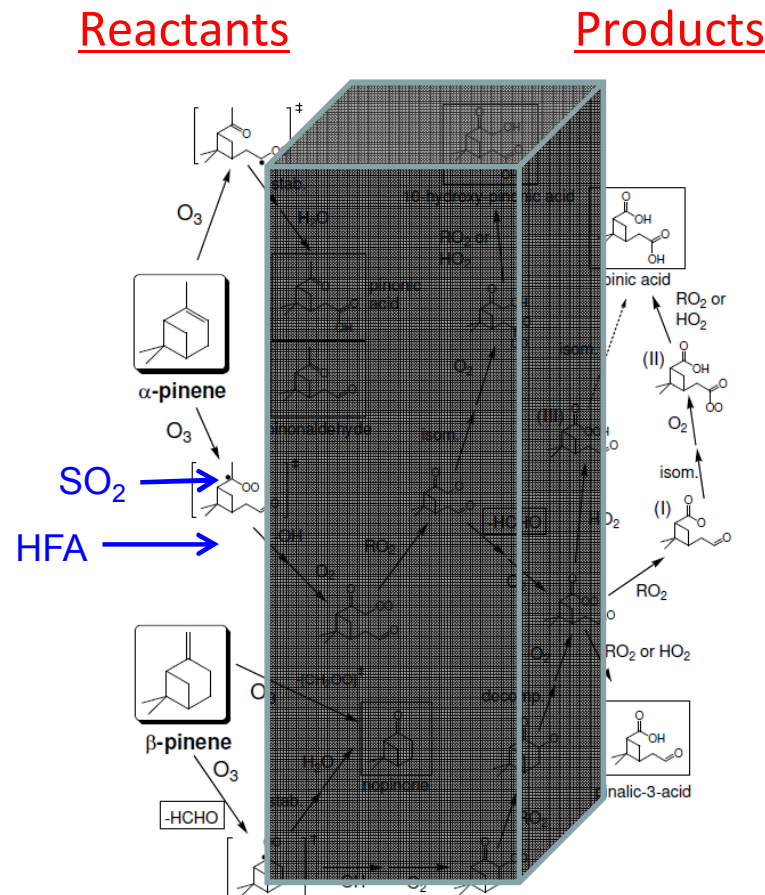
HEALTH
VISIBILITY

CLIMATE

H

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



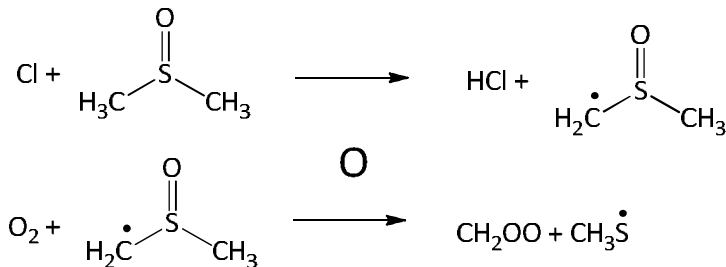


“Recipe” for directly measuring Criegee reactions

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 CH_2OO formation in dimethyl sulfoxide oxidation

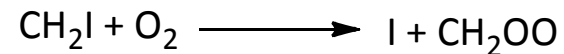
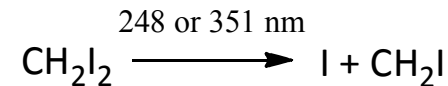


Taatjes and co-workers *JACS* 130, 11883 (2008) detected CH_2OO in this system, but not enough for kinetic studies.

Make it fast

Make a lot of it and make it fast

Eskola *et al.* *Phys. Chem. Chem. Phys.* 8, 1416 (2006) found that CH_2I reaction with O_2 made iodine atom with unity yield at low pressure – turns out that what's left is Criegee intermediate!



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

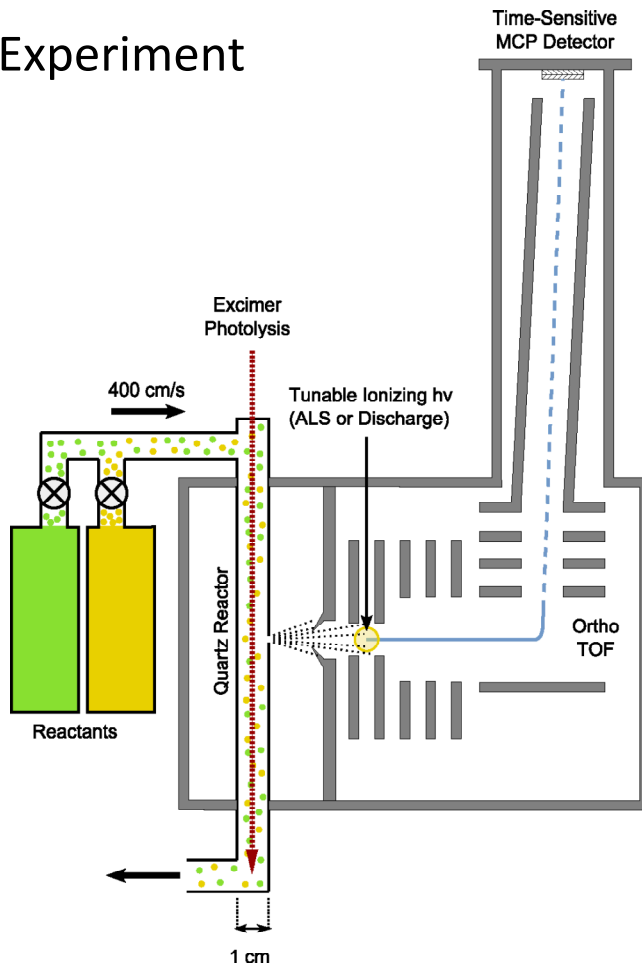
$$T = 300 \text{ K}, P = 4 \text{ Torr}$$

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

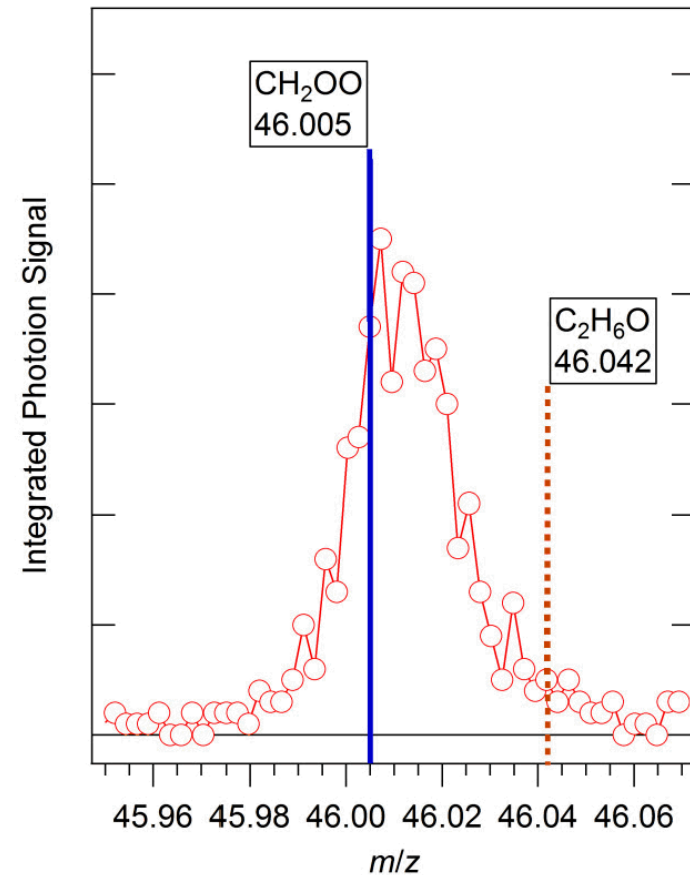
2. Have a sensitive and selective detection technique

→ Multiplexed Photoionization Mass Spectrometry (MPIMS)

Experiment



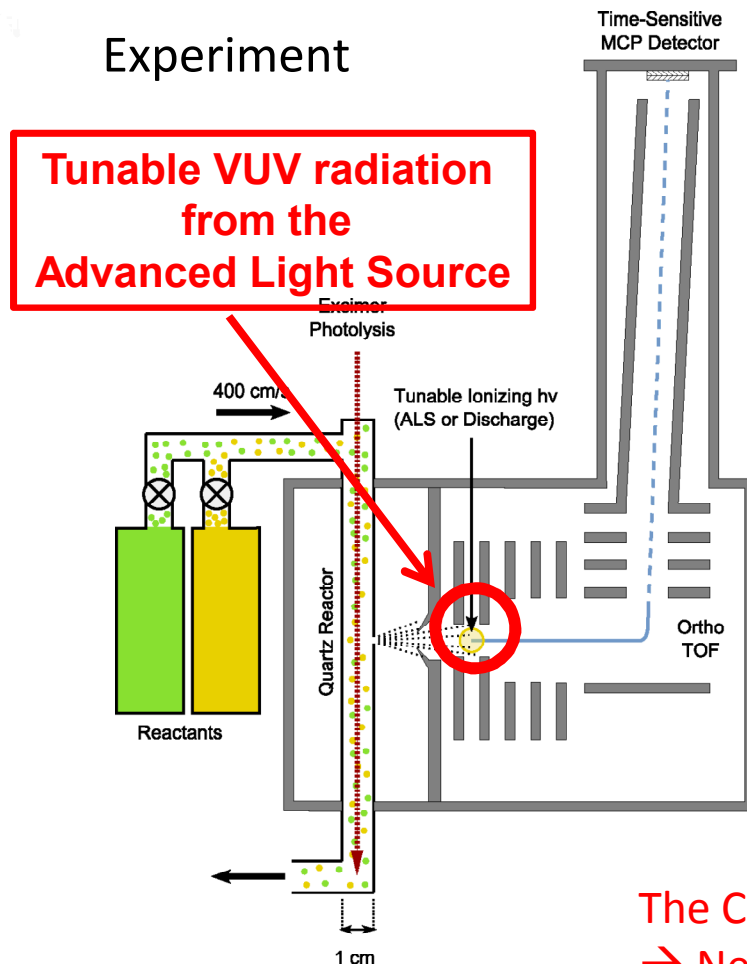
Mass spectrum of $m/z = 46$



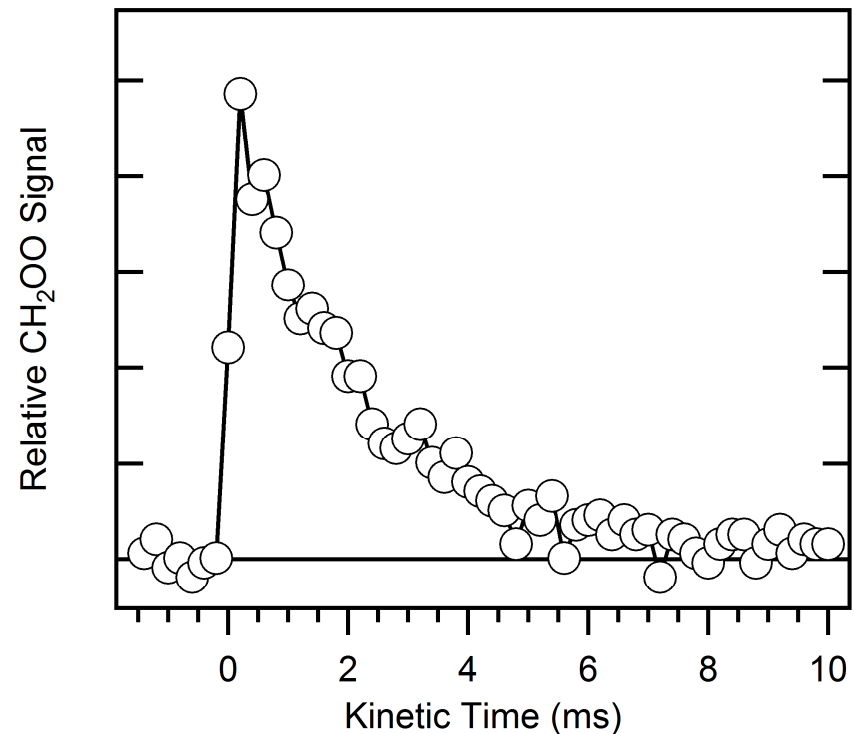
2. Have a sensitive and selective detection technique

→ Multiplexed Photoionization Mass Spectrometry (MPIMS)

Experiment



Time profile of CH_2OO

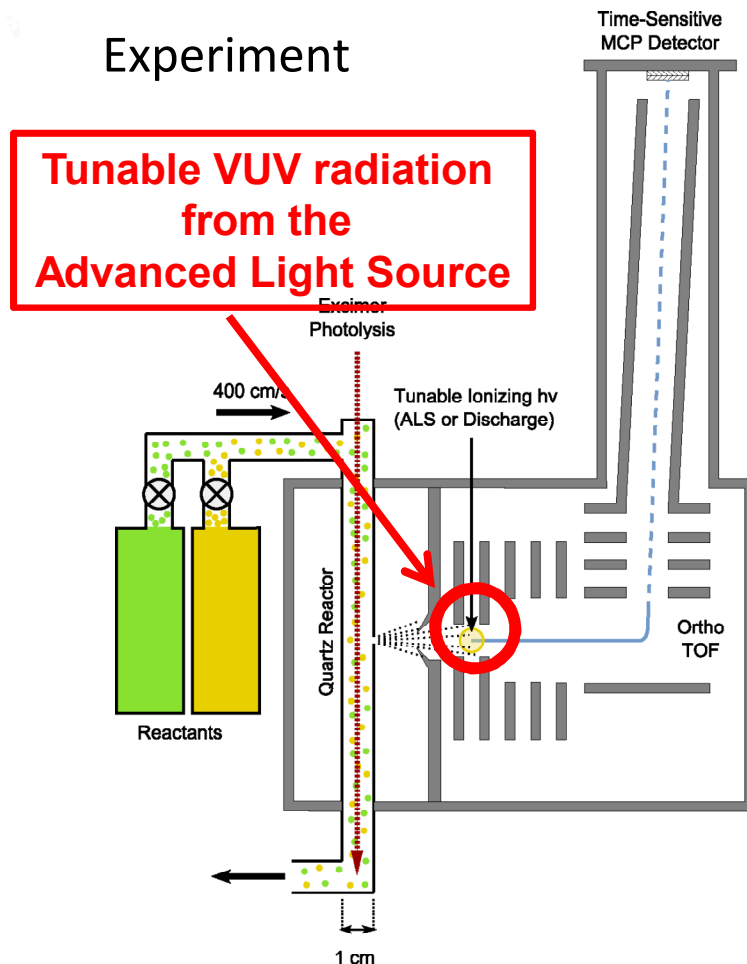


The Criegee intermediate is an *isomer* of more stable products
→ Need isomer-resolved detection!

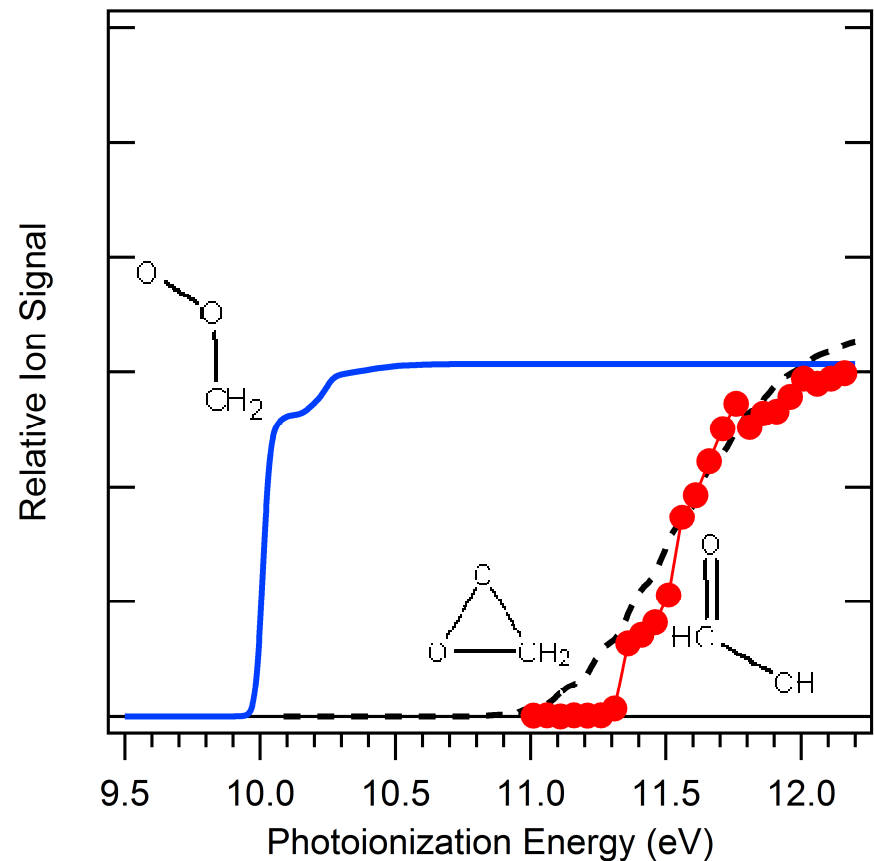
2. Have a sensitive and selective detection technique

→ Multiplexed Photoionization Mass Spectrometry (MPIMS)

Experiment



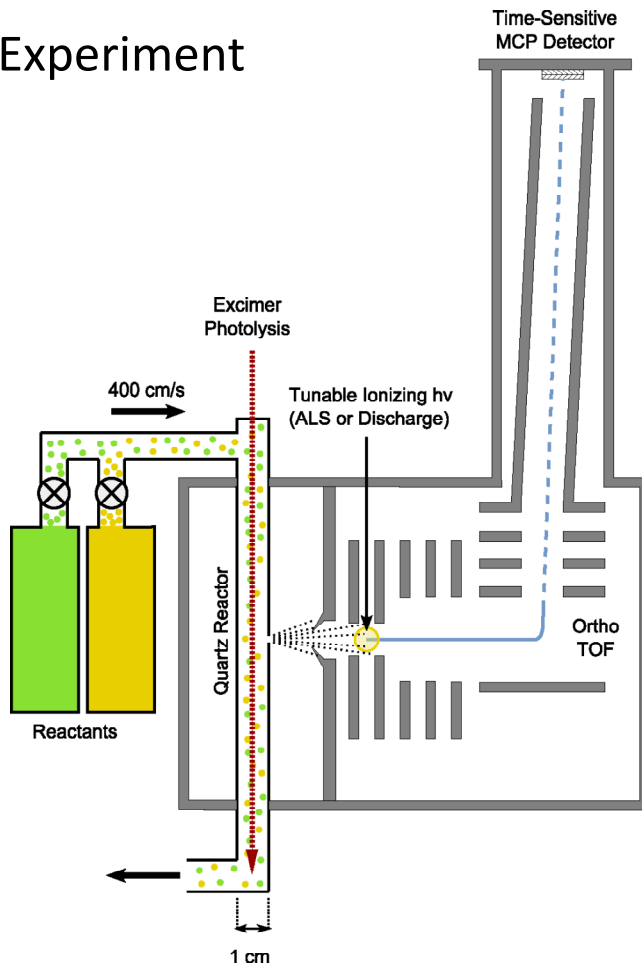
Photoionization spectra of CH_2OO isomers



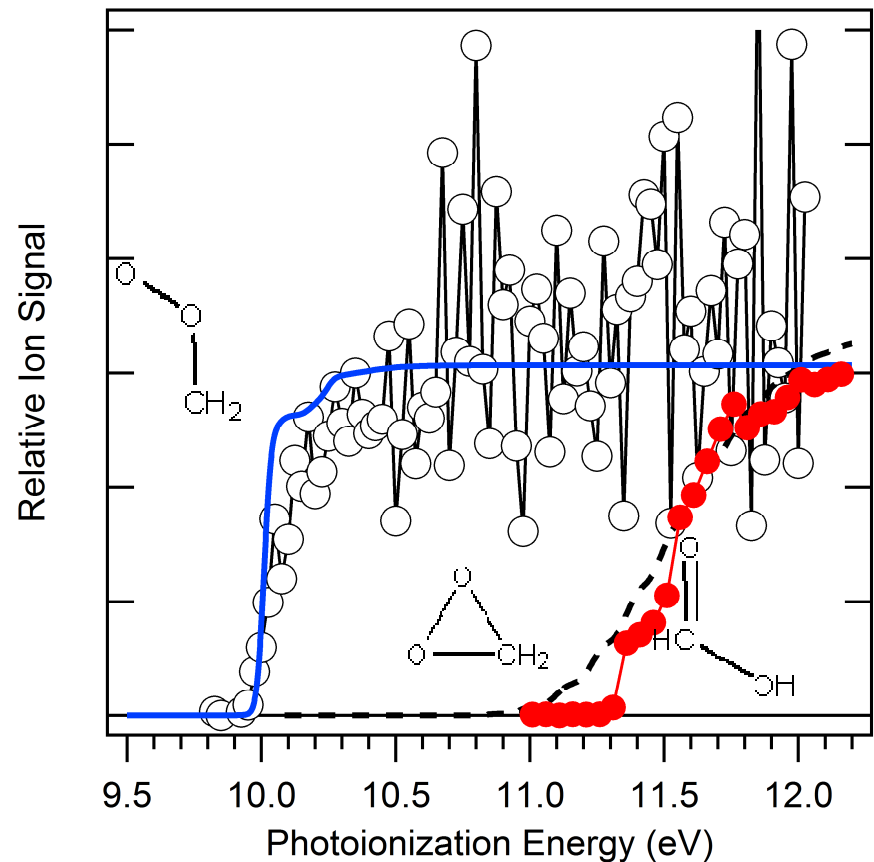
2. Have a sensitive and selective detection technique

→ Multiplexed Photoionization Mass Spectrometry (MPIMS)

Experiment



Photoionization spectra of CH_2OO isomers

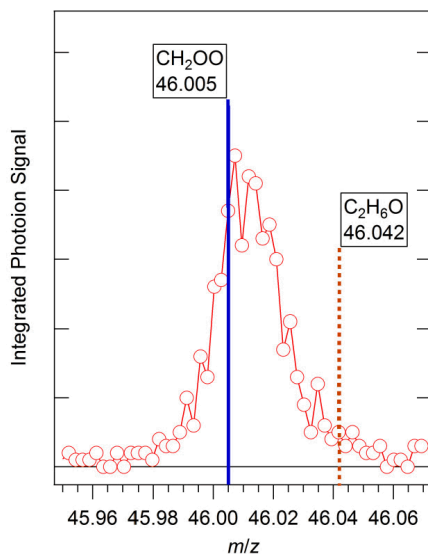


2. Have a sensitive and selective detection technique

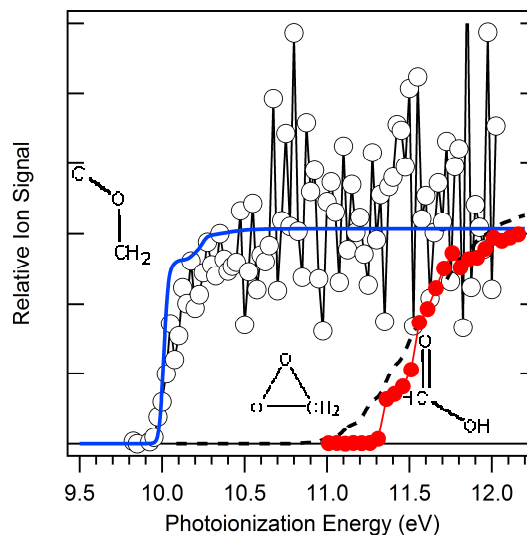
Definitive Evidence of the Criegee Intermediate CH_2OO :

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

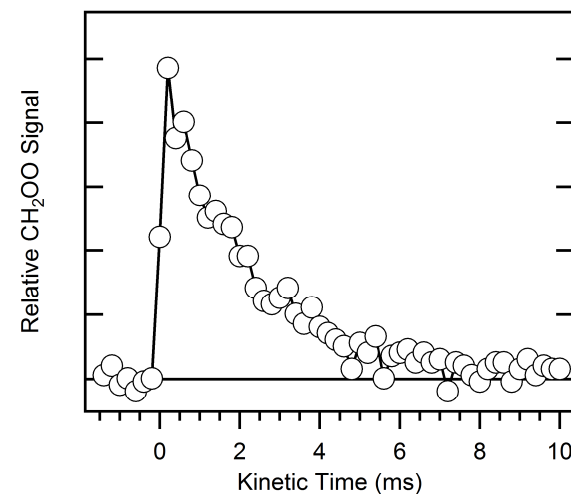
Mass spectrum of $m/z = 46$



Photoionization spectrum of CH_2OO



Time profile of CH_2OO





Measuring CH₂OO reactions with important tropospheric species (H₂O, SO₂, NO₂, NO)



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

If other Criegee intermediates react similarly, they are major SO₂ oxidants



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

If other Criegee intermediates react similarly, Criegee reactions might play an important role in NO_x chemistry

Reactions of CH₂OO with NO and H₂O are too slow to be measured

→ only upper limits could be obtained



→ At least two orders of magnitude slower than literature estimates

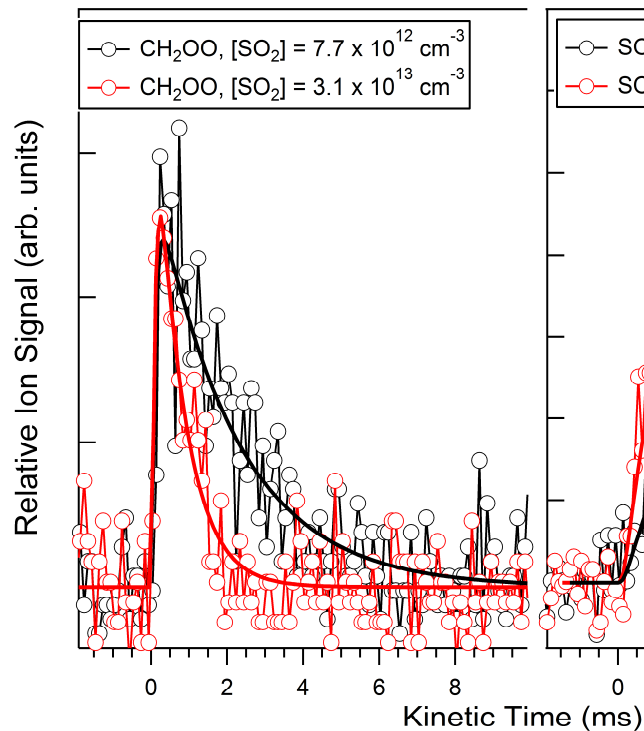


→ Tends to confirm values used in models

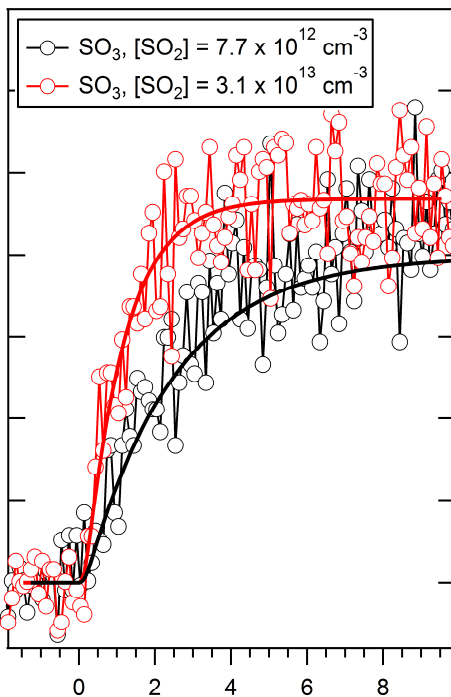
[SO₂] (10⁻¹¹ cm³)

SO₃ is a direct product of CH₂OO + SO₂ at 4 Torr

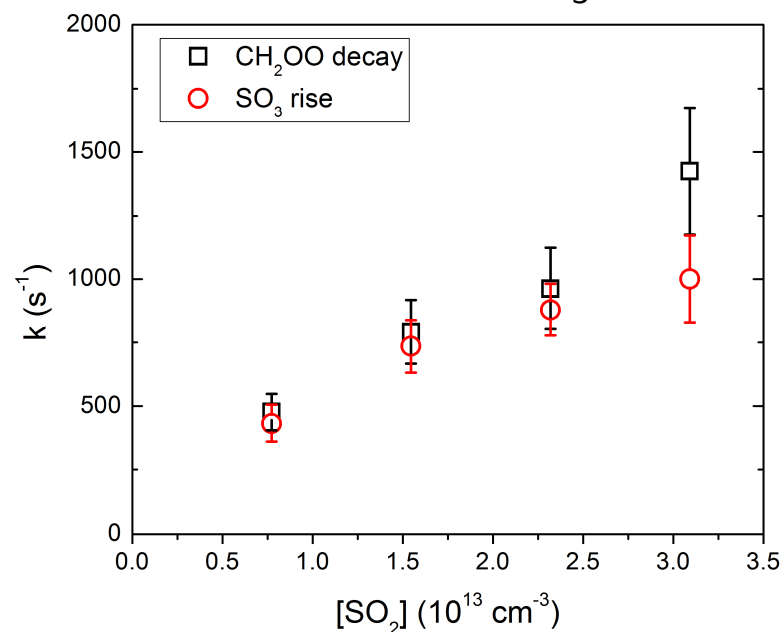
Time profiles of
CH₂OO



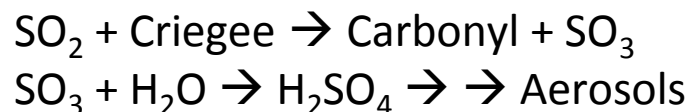
SO₃



The CH₂OO decay
matches the SO₃ rise



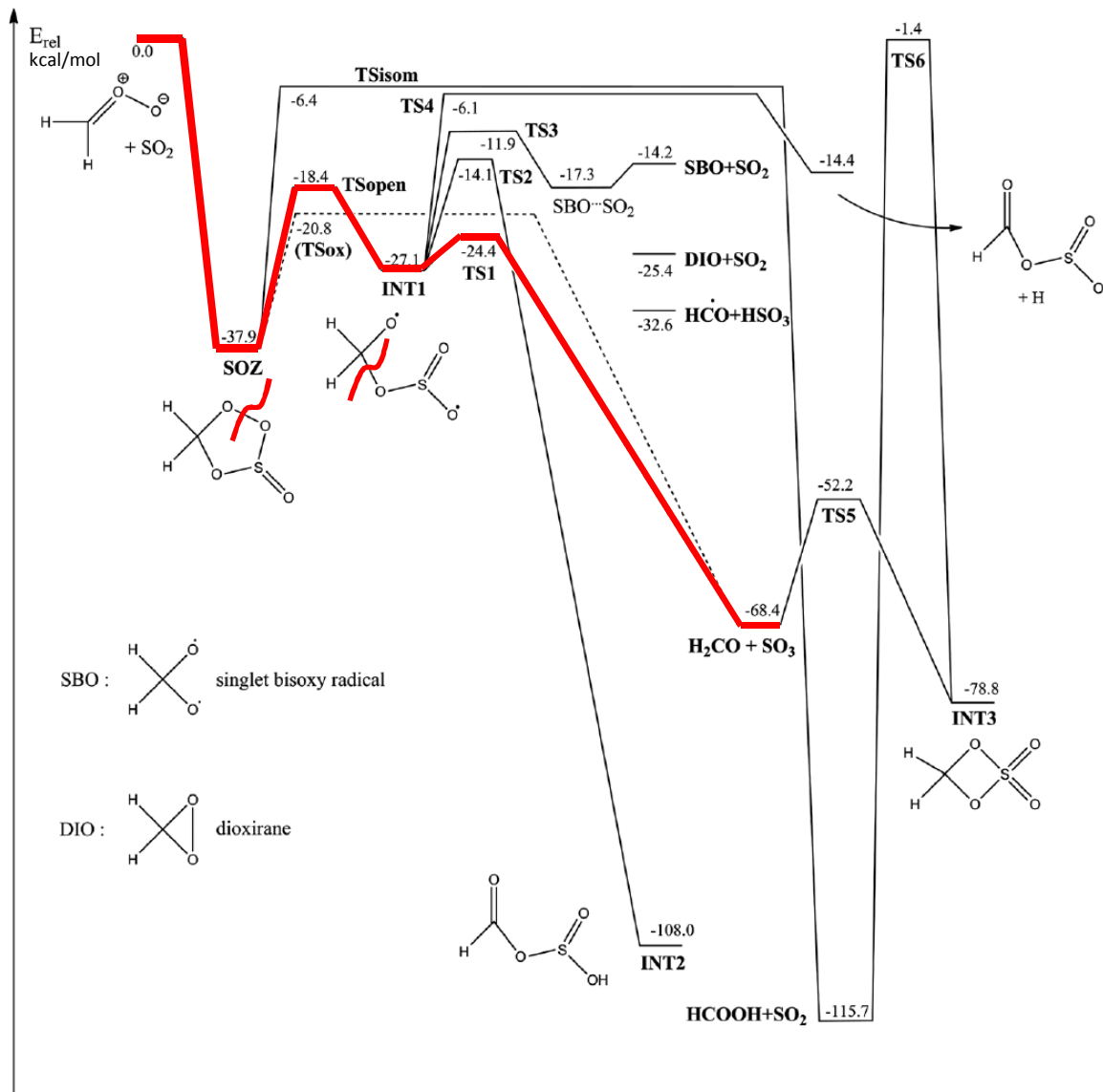
**Criegee intermediates might
be an important source of
sulfuric acid!**



Percival et al., Faraday
Discussions, 2013, accepted

Why is CH_2OO ($^1\text{A}'$) + 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.

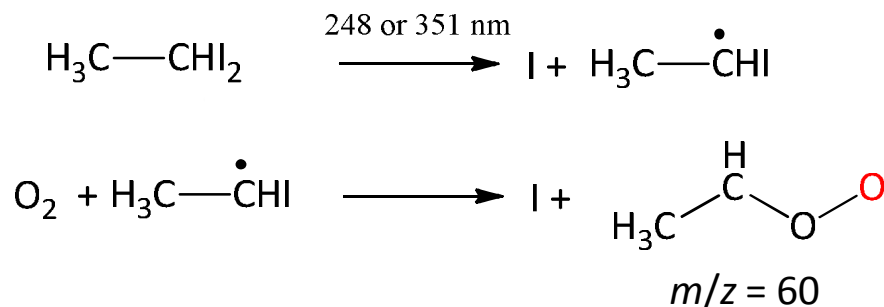
The total rate coefficient at 4 Torr pressure is a lower limit to atmospheric conditions.

Increasing pressure will favor stabilization of the SOZ over SO_3 + carbonyl formation

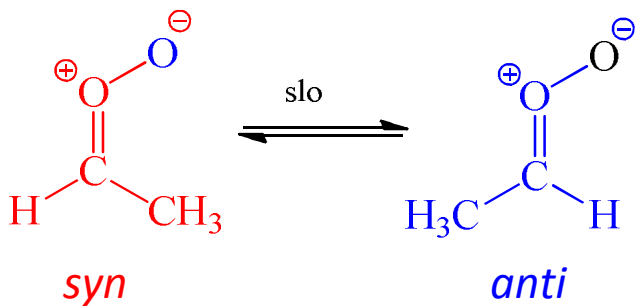
What is the fate of the SOZ in the troposphere?

Production and characterization of the next larger Criegee Intermediate: acetaldehyde oxide (CH_3CHOO)

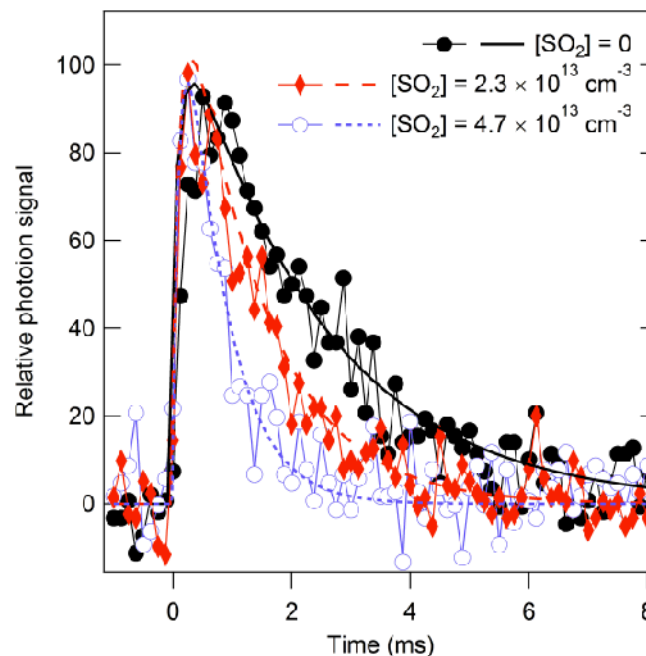
Similar strategy:



CH_3CHOO exists in two distinct conformeric forms

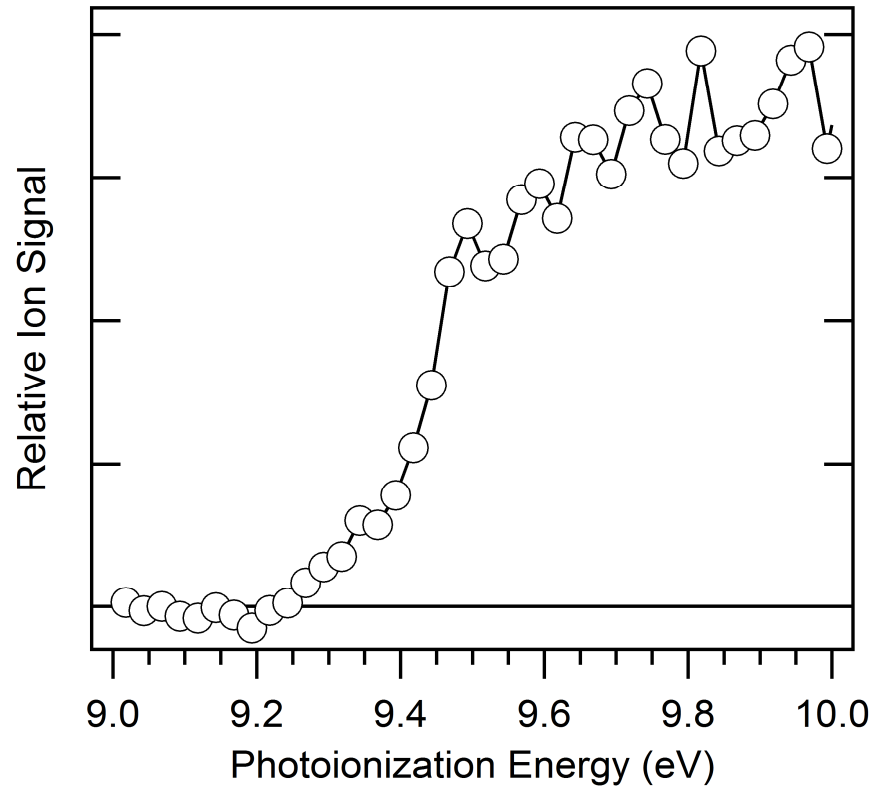


$m/z = 60$ time profile



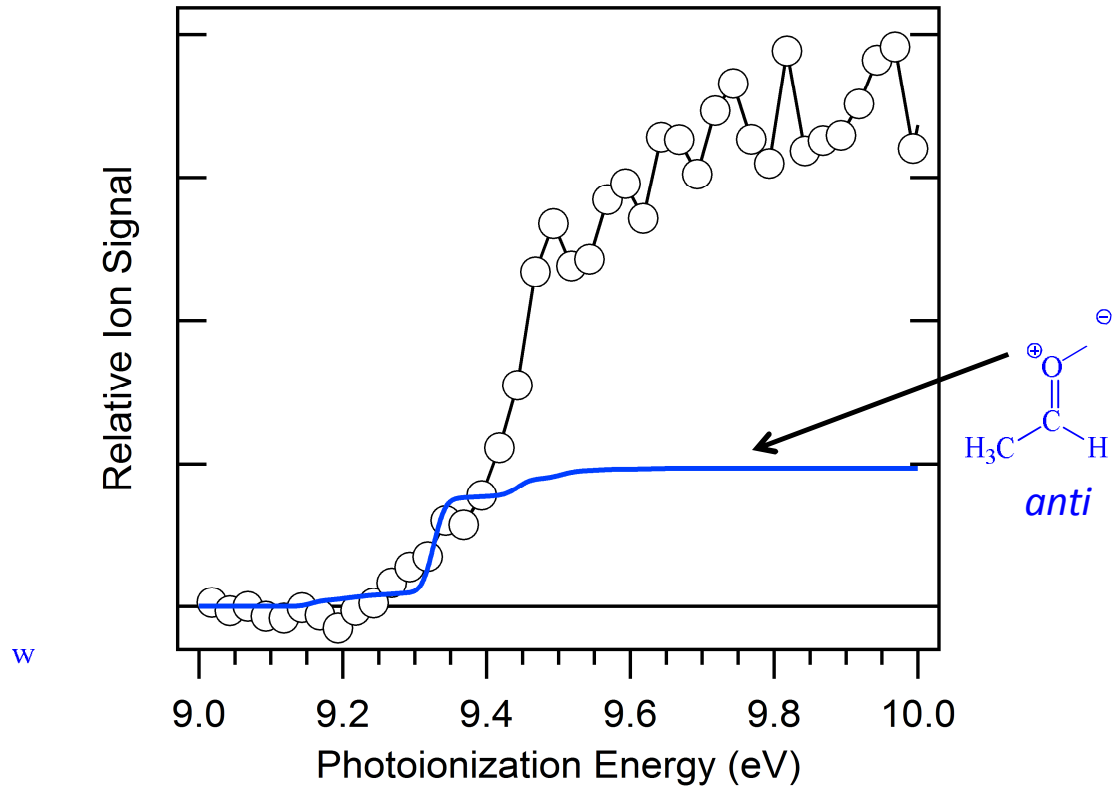
Calculations predict that *anti*- CH_3CHOO reacts with H_2O five orders of magnitude faster than *syn*- CH_3CHOO (Phys. Chem. Chem. Phys. 13, 13034 (2011))

The $m/z = 60$ photoionization spectrum shows evidence of both *syn*- and *anti*- conformers of CH_3CHOO



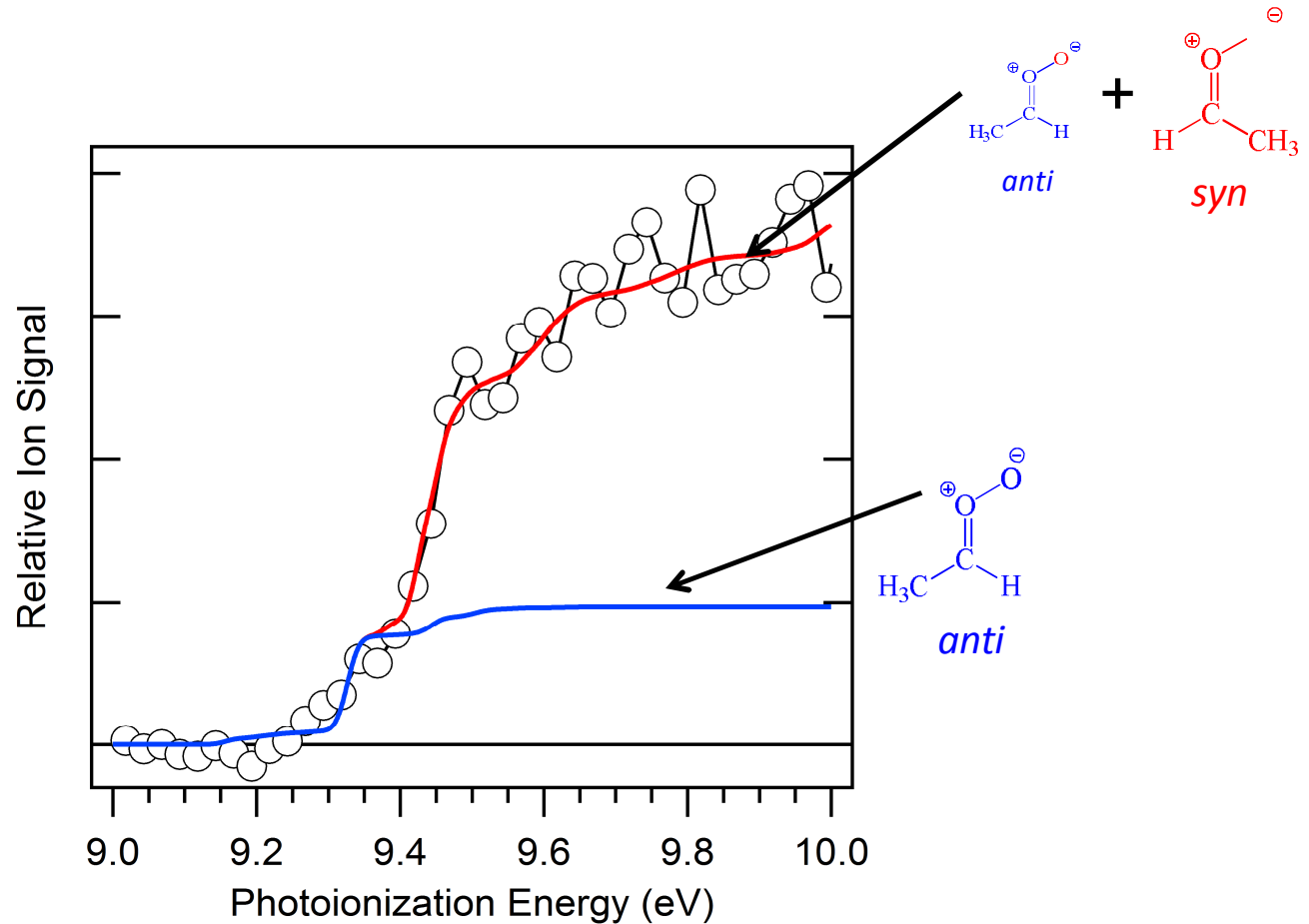
Taatjes *et al.*, *Science* **340**, 177 (2013)

The $m/z = 60$ photoionization spectrum shows evidence of both *syn*- and *anti*- conformers of CH_3CHOO



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

The $m/z = 60$ photoionization spectrum shows evidence of both *syn*- and *anti*- conformers of CH_3CHOO



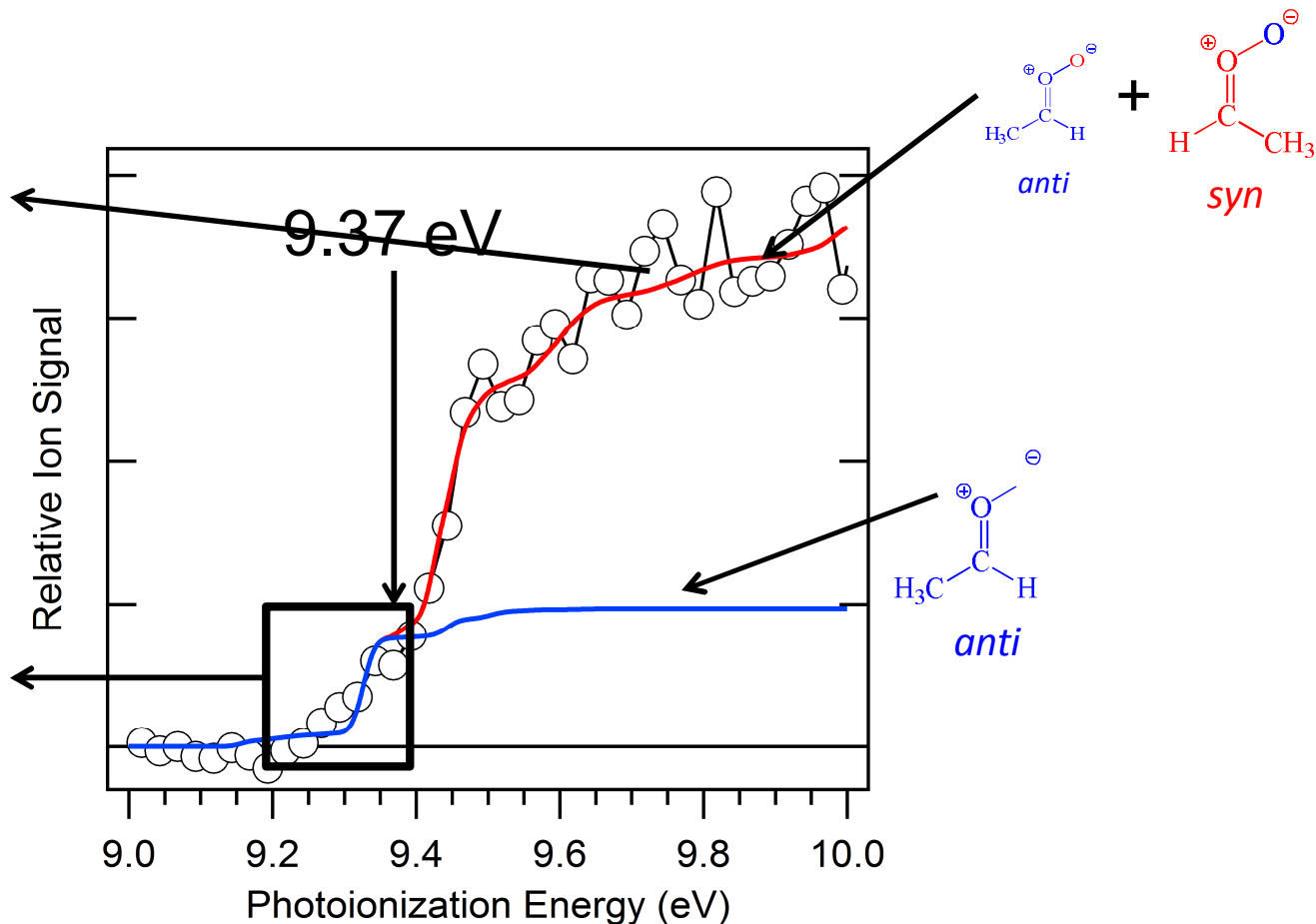
Taatjes *et al.*, *Science* **340**, 177 (2013)

The low-energy part $m/z = 60$ photoionization spectrum is dominated by *anti*-CH₃CHOO

both conformers contribute, but *syn*-dominates

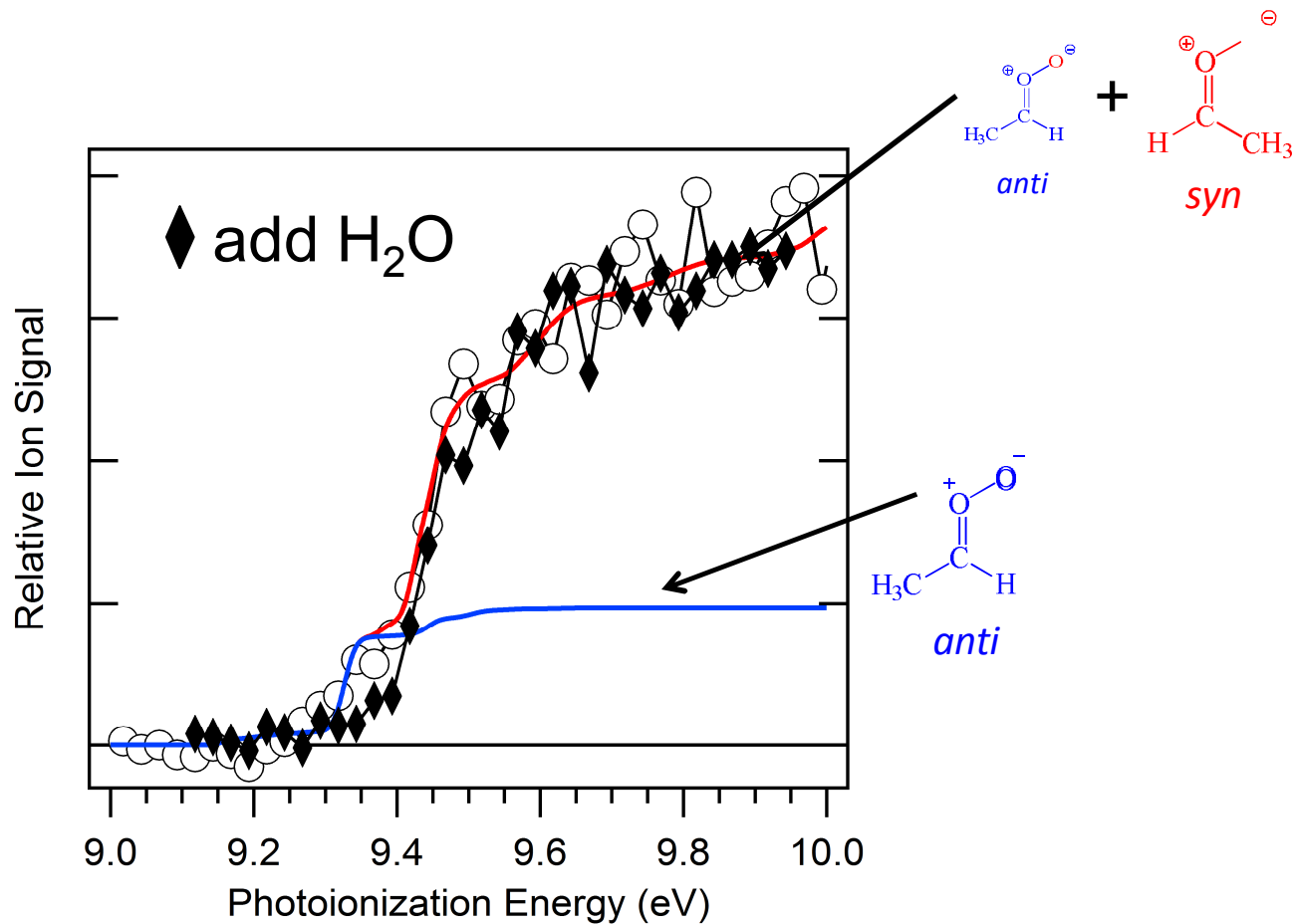
10.5 eV: ~ 85% of the signal is *syn*-

anti- conformer can be probed separately from *syn*-



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

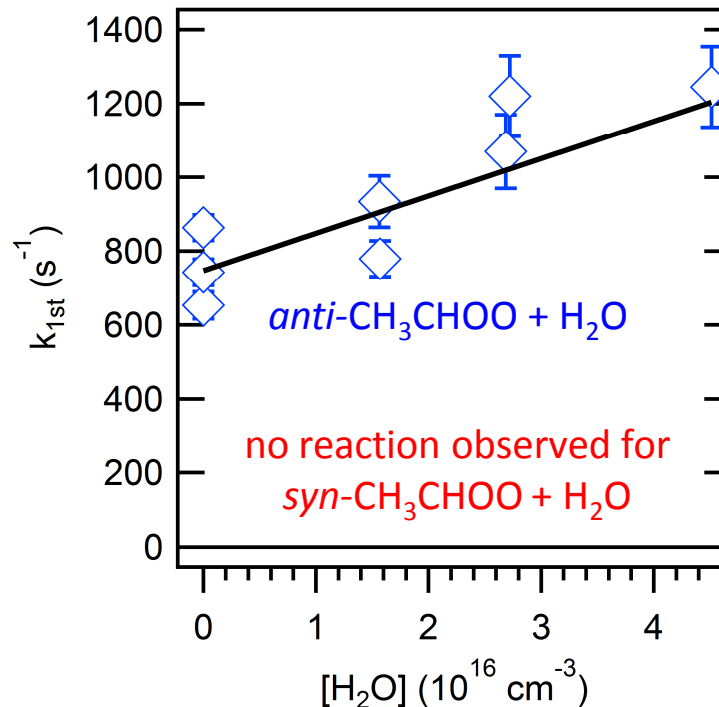
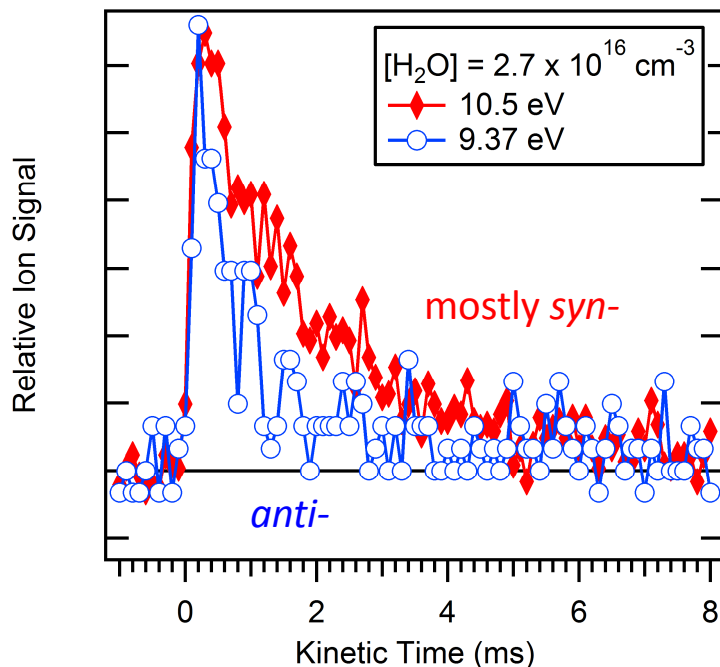
Addition of water preferably removes the *anti*- conformer of CH_3CHOO



Conformer-dependent reactivity!

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

Measuring the rate coefficient of *anti*-CH₃CHOO with H₂O

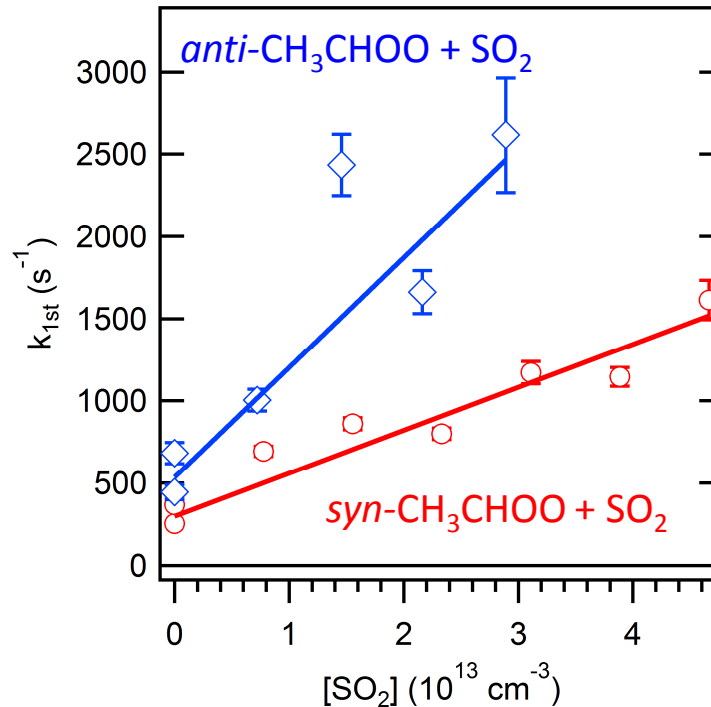
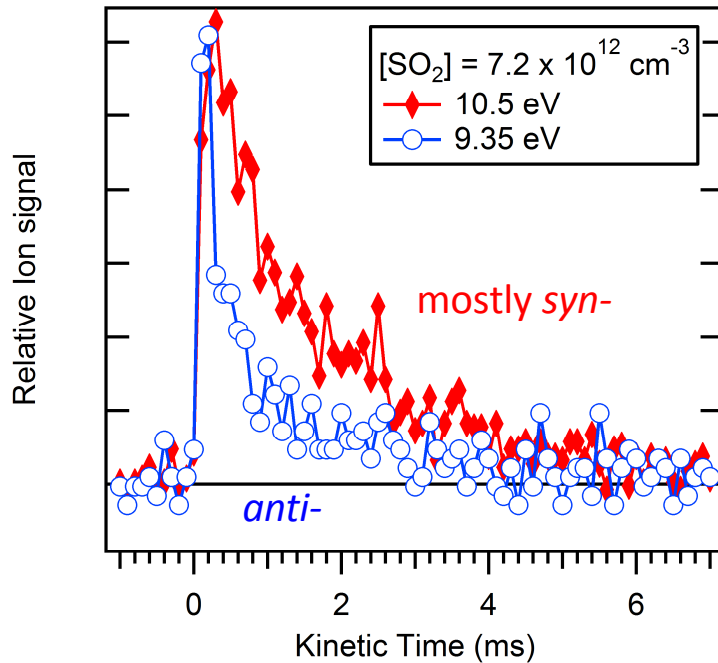


$$k(\text{anti-CH}_3\text{CHOO} + \text{H}_2\text{O}) = (1.0 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$$

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

- 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



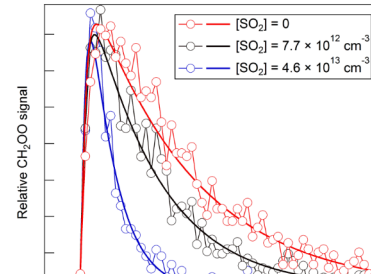
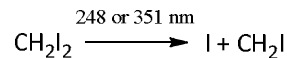
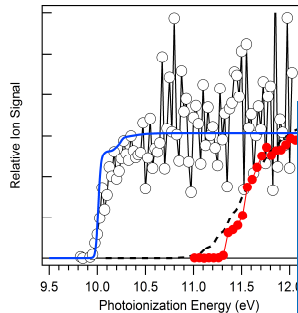
$$k(\text{anti-CH}_3\text{CHOO} + \text{SO}_2) = (6.7 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

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

Similarly fast as the CH_2OO reaction

Summary and Outlook

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



We determined rate coefficients for CH_2OO reactions with atmospherically relevant species; substantial

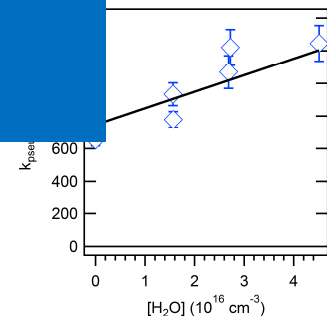
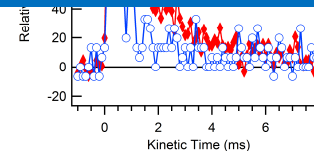
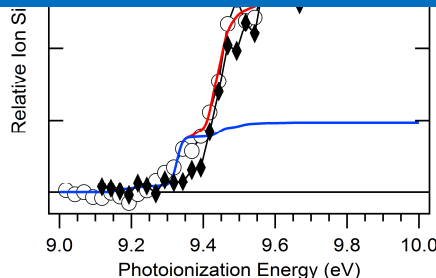
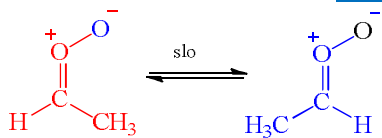
We are just beginning to understand how Criegee intermediates react

- Need to understand larger Criegee molecules
- Need to understand more reactions
- Need to understand reactions at different conditions

es to values used in
meric models exist in
ses

r with H_2O and
mination of the
coefficient

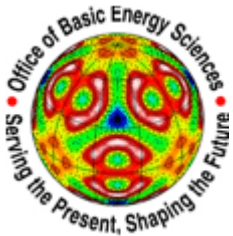
The two conform
can be distinguish
photoionization s



Acknowledgements

Craig A. Taatjes	Edmond P. F. Lee
Arkke J. Eskola	John M. Dyke
John D. Savee	Daniel M. K. Mok
Adam M. Scheer	Carl J. Percival
Brandon Rotavera	Dudley E. Shallcross
David L. Osborn	

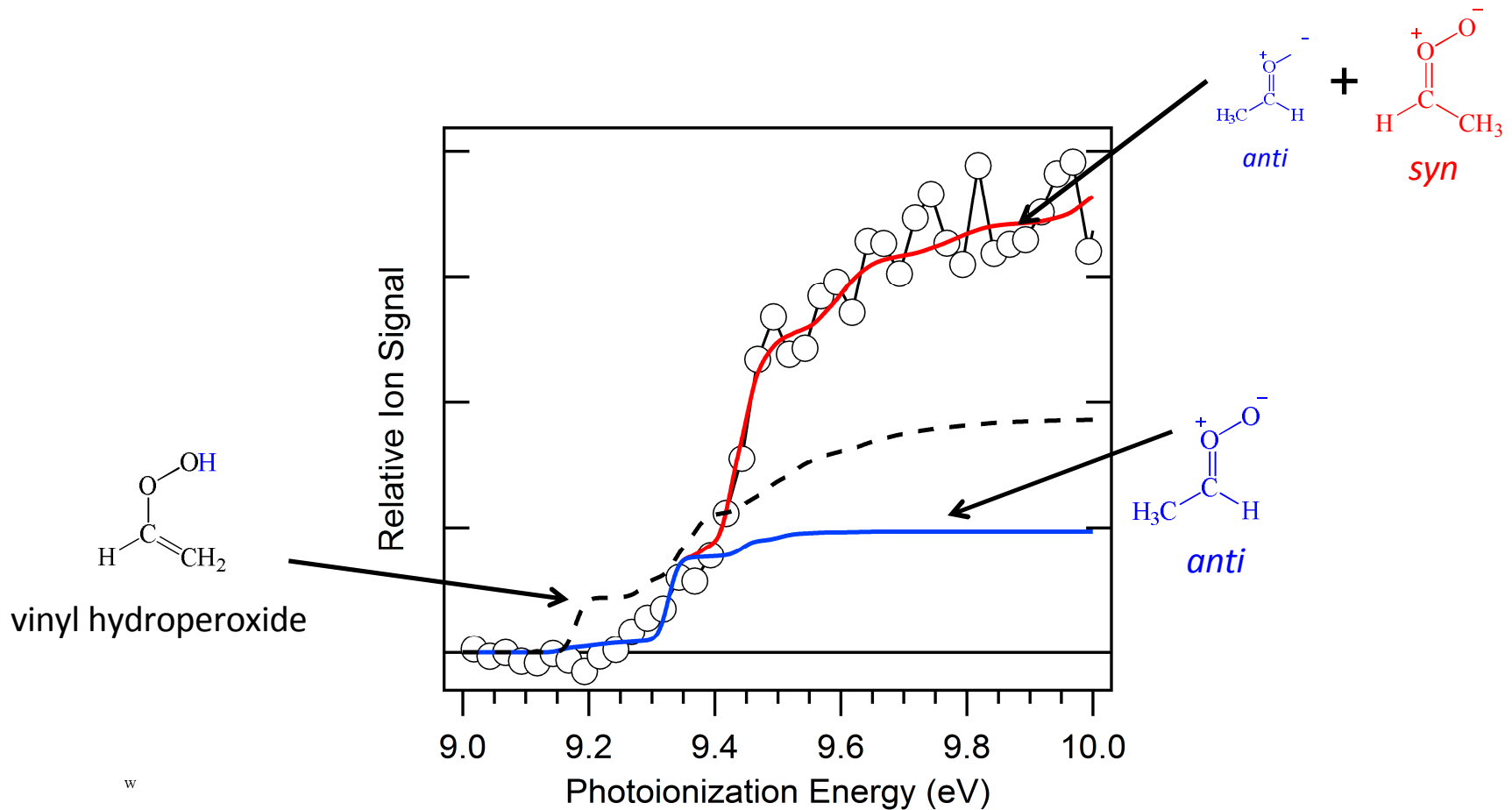
- Howard Johnsen (Sandia) and the staff of the Chemical Dynamics Beamline at the ALS for technical support



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.

The $m/z = 60$ photoionization spectrum shows evidence of both *syn*- and *anti*- conformers of CH_3CHOO

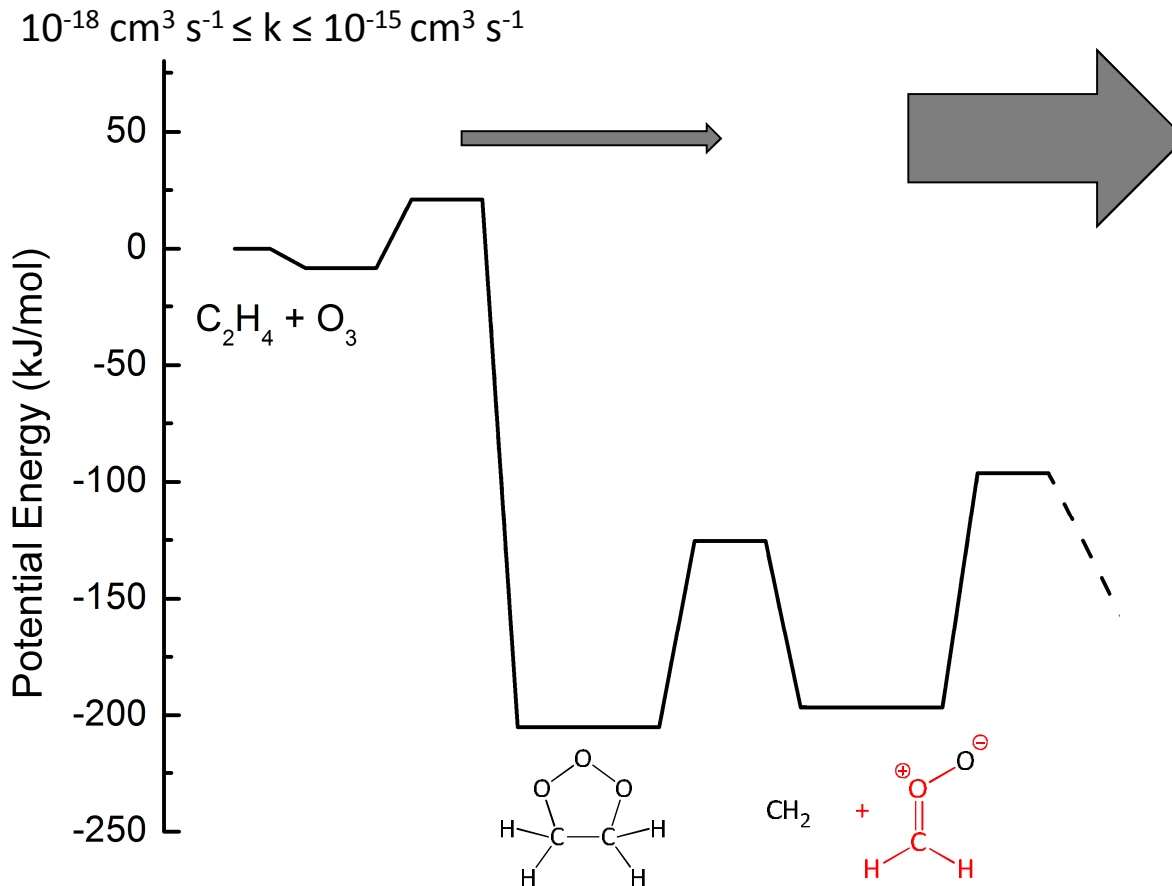


Why are Criegee intermediates so hard to detect?

Ozonolysis forms Criegee intermediates slowly, but they react away rapidly

→ low steady-state concentrations

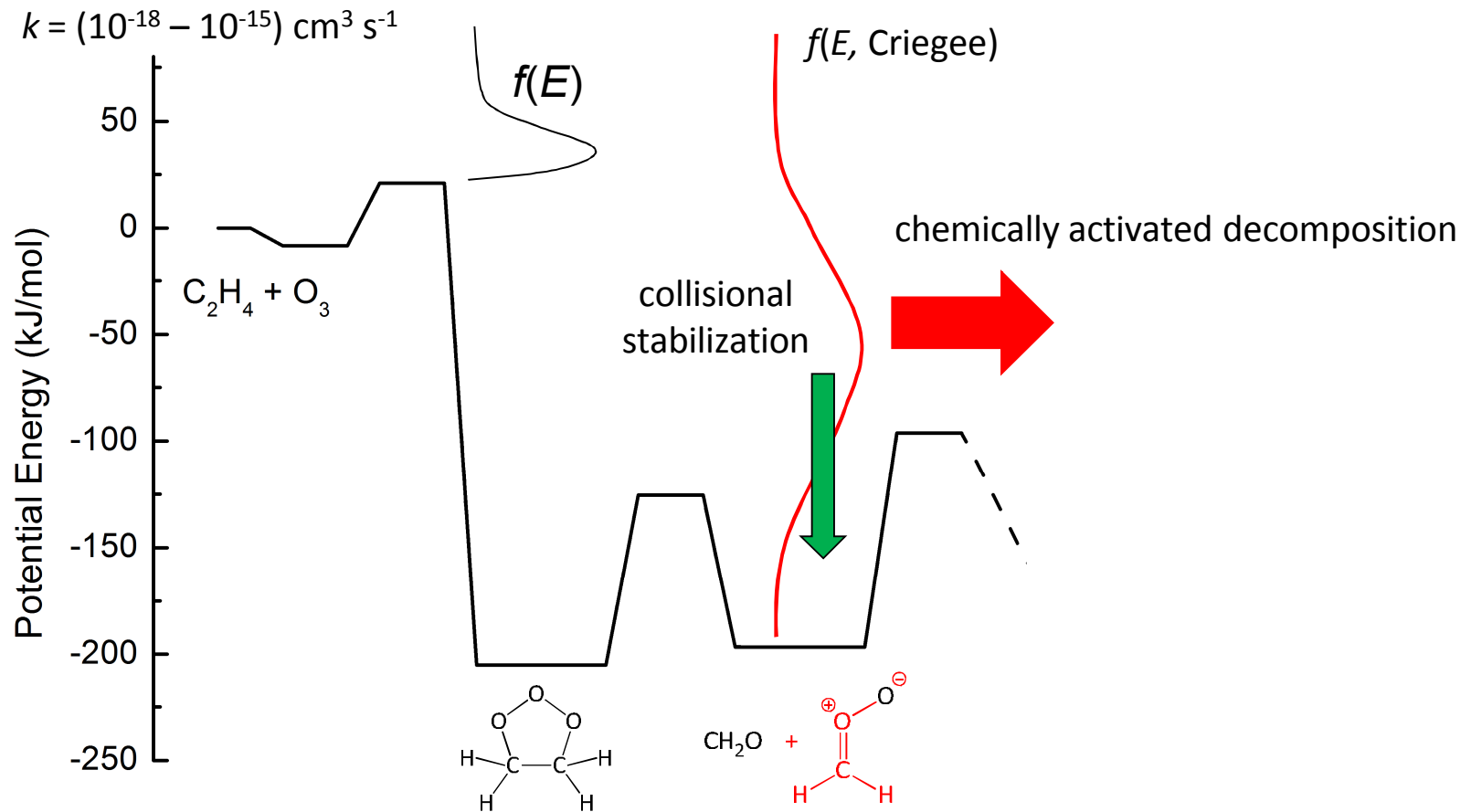
o



Why are Criegee intermediates so hard to detect?

Ozonolysis forms Criegee intermediates slowly, but they react away rapidly

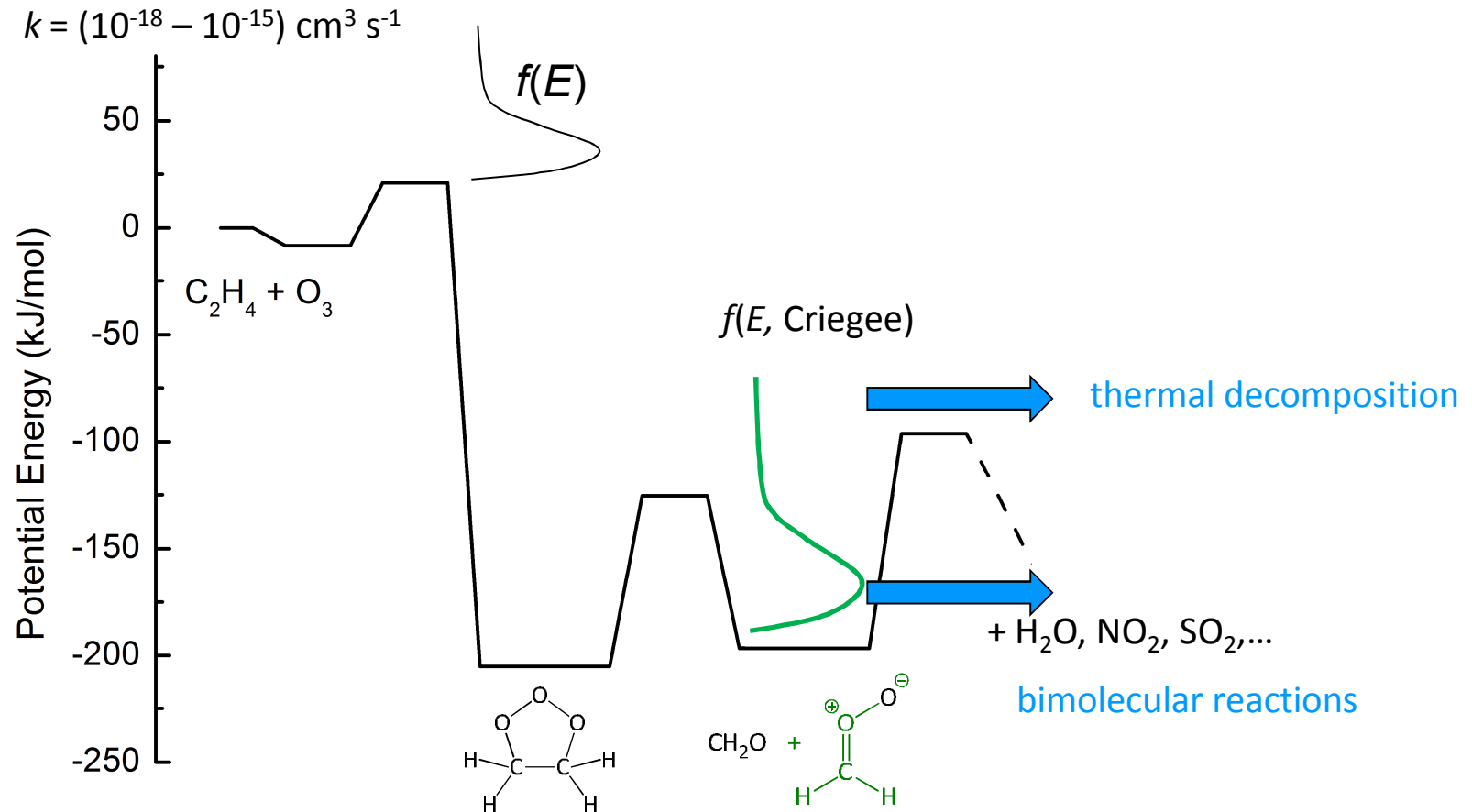
→ low steady-state concentrations



Why are Criegee intermediates so hard to detect?

Ozonolysis forms Criegee intermediates slowly, but they react away rapidly

→ low steady-state concentrations



Why are Criegee intermediates so hard to detect?

Ozonolysis forms Criegee intermediates slowly, but they react away rapidly

→ low steady-state concentrations

