

Reactivity of Criegee Intermediates CH_2OO and CH_3CHO : Direct Detection and Conformer-Dependent Kinetics

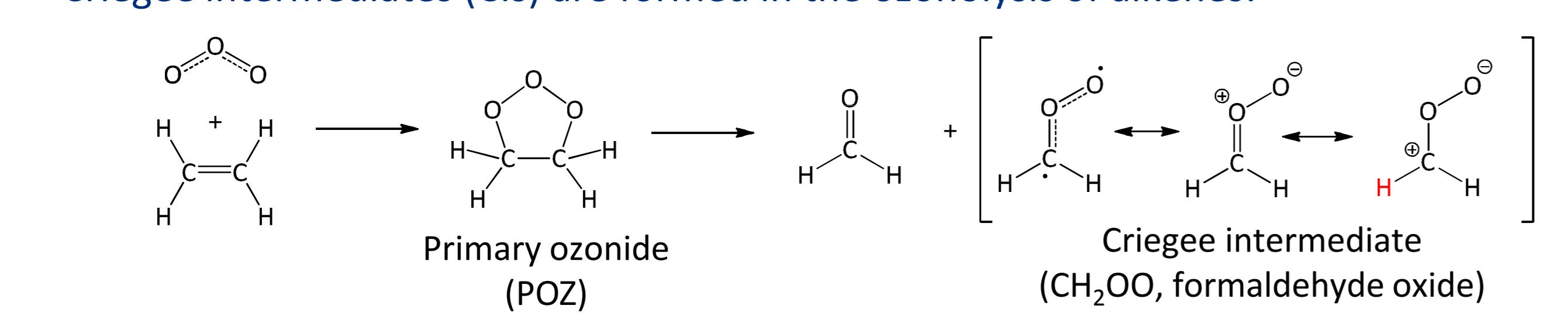
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Hot Topic Talk 10
Friday, 9:10 AM

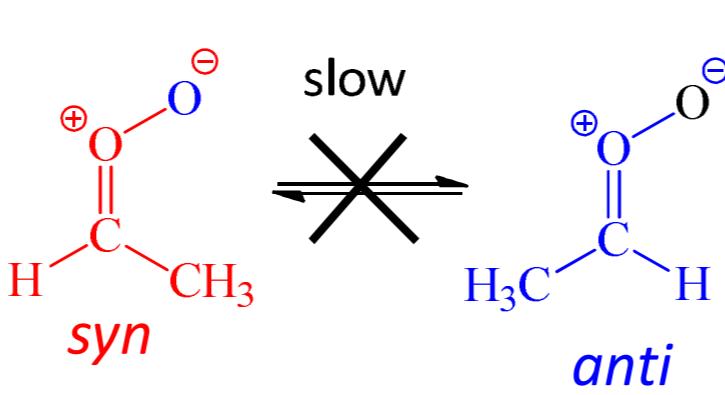
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Introduction

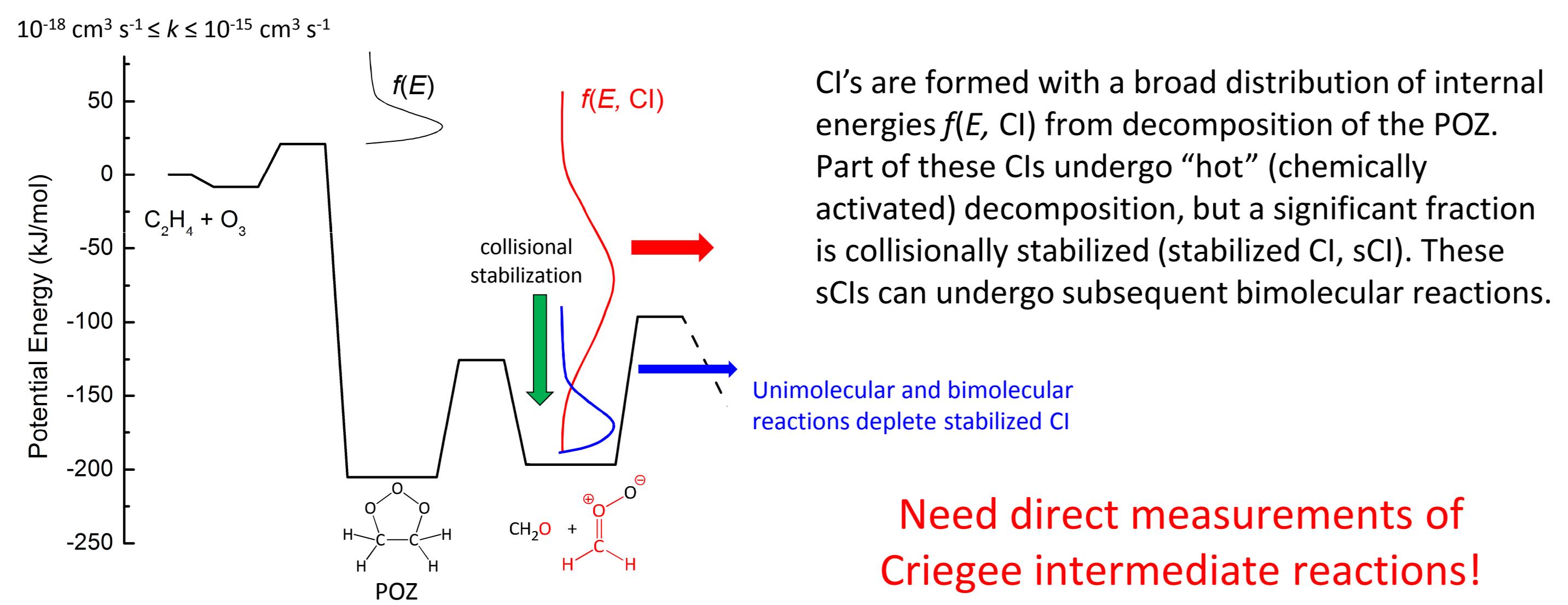
- Alkenes are emitted into the troposphere from biogenic and anthropogenic sources in large amounts (~ 15% of the non-methane emissions)
- Criegee intermediates (Clis) are formed in the ozonolysis of alkenes:



- COO fragment: 3-atom, 4 π -electron system
- Singlet zwitterion is the dominant configuration
- Barrier of ~120 kJ/mol for rotation about the CO bond \rightarrow slow at tropospheric conditions



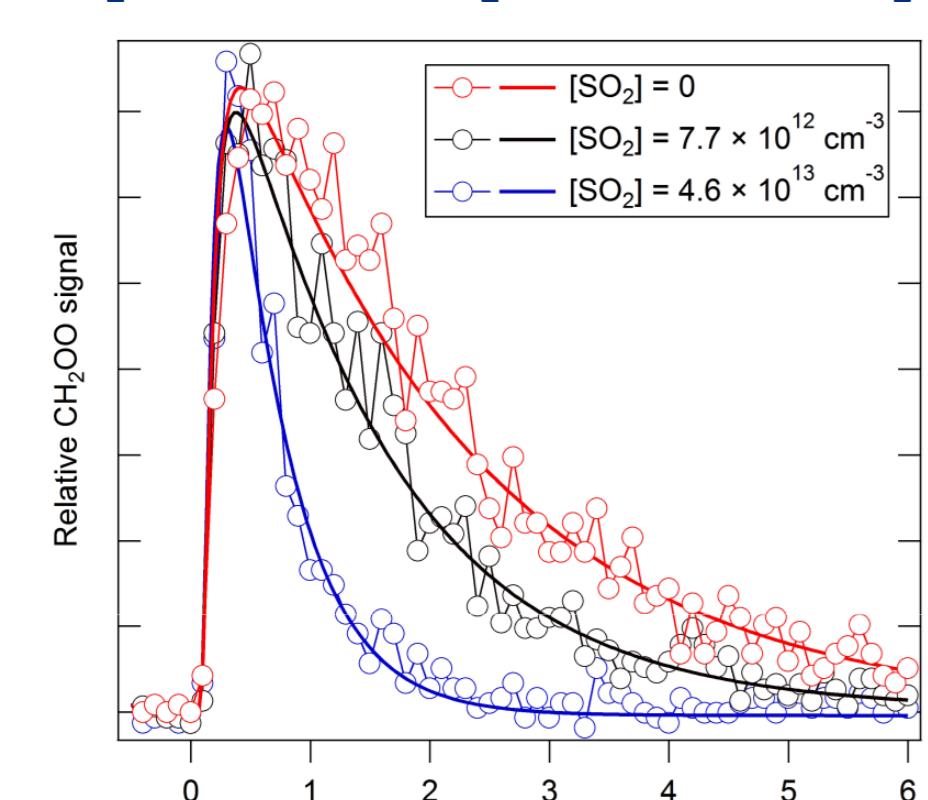
- Clis are key species in the troposphere \rightarrow non-photolytic source of OH, controlling the budgets of NO_x , NO_y , and secondary organic aerosols
- Rate coefficients of Clis with key atmospheric species (H_2O , NO , NO_2 , SO_2 , ...) are uncertain by orders of magnitude \rightarrow Significant uncertainty in the quantitative role of Clis in the troposphere
- No Cl has ever been detected in gas-phase ozonolysis: Ozonolysis forms Cls slowly, but they react away rapidly \rightarrow low steady-state concentrations



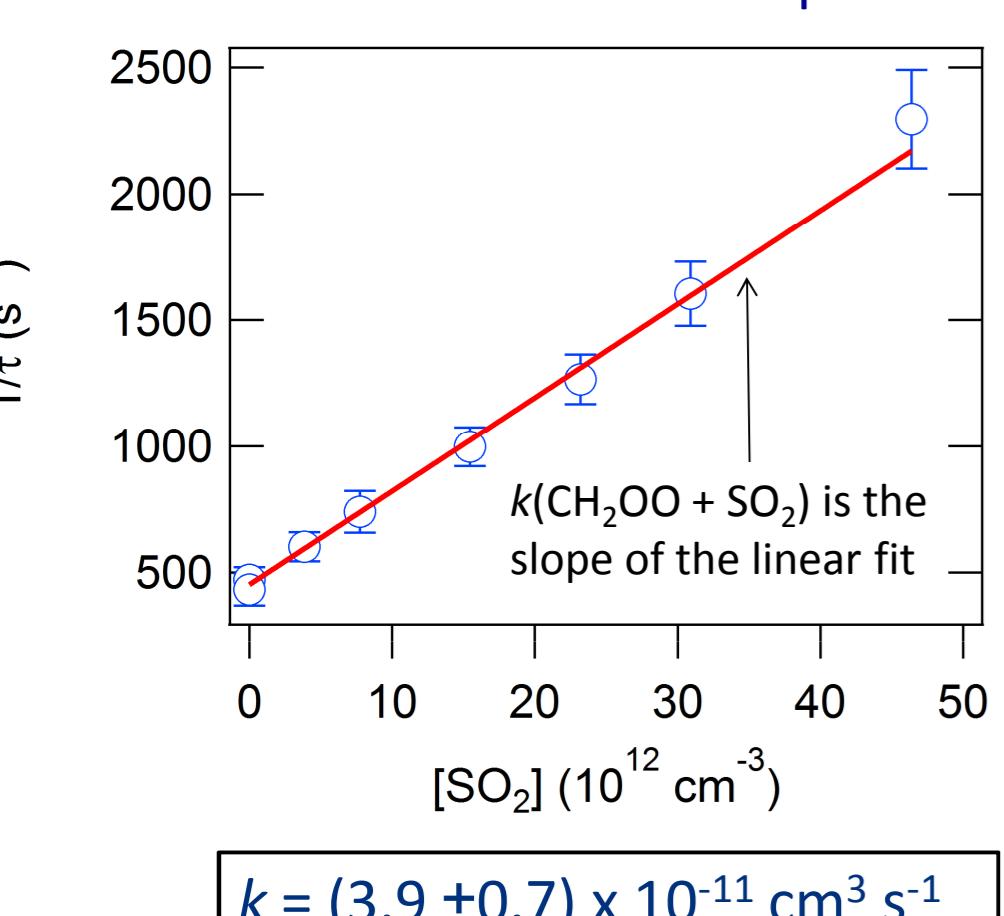
Direct Measurements of CH_2OO Kinetics¹ (4 Torr, 300 K)

$\text{CH}_2\text{OO} + \text{SO}_2$:

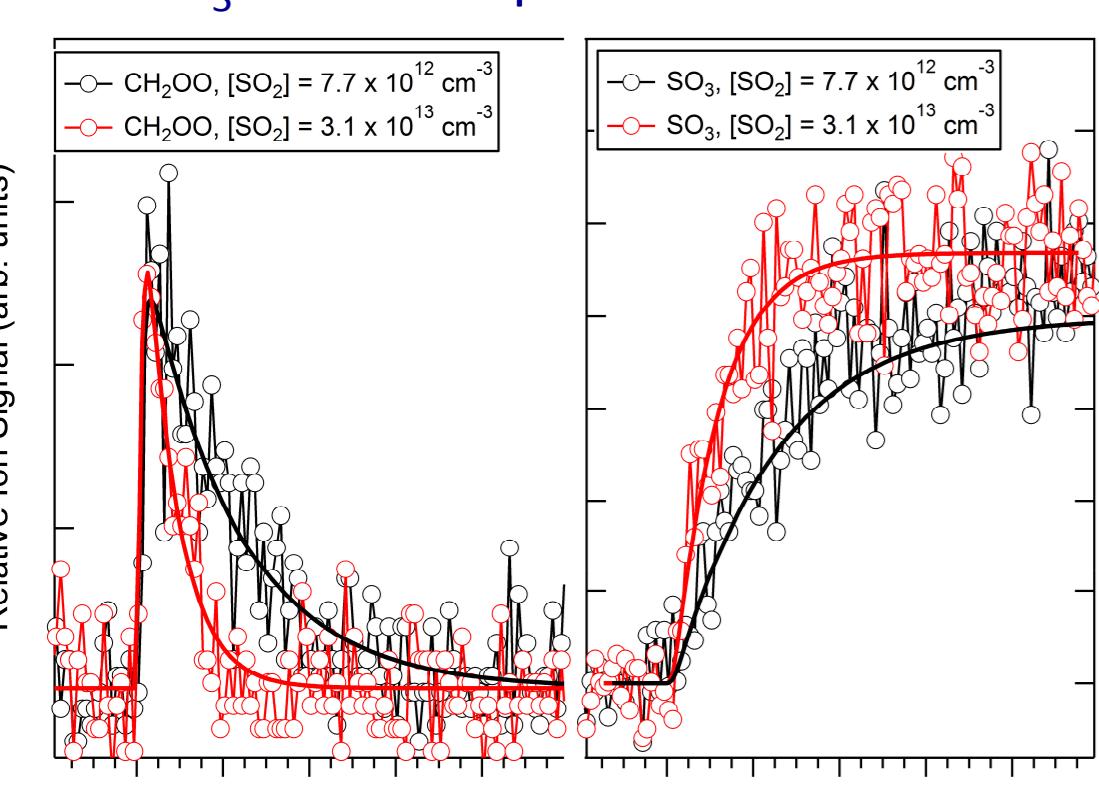
Addition of SO_2 makes the decay of CH_2OO faster: SO_2 reacts with CH_2OO !



Pseudo-first-order plot



SO_3 is a direct product at 4 Torr



Kinetics analysis:



$$[\text{SO}_2] \gg [\text{CH}_2\text{OO}]_0: k_{1st} = k_{loss} + k(\text{CH}_2\text{OO} + \text{SO}_2) [\text{SO}_2]$$

$$[\text{CH}_2\text{OO}] = [\text{CH}_2\text{OO}]_0 \exp(-k_{1st} t)$$

Kinetics results for CH_2OO reactions

$\text{CH}_2\text{OO} + \text{SO}_2: k = (3.9 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
 \rightarrow up to 10 000 times faster than what is used in models
 \rightarrow Cls might be major SO_2 oxidants

$\text{CH}_2\text{OO} + \text{NO}_2: k = (7^{+3/-2}) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
 \rightarrow 50 times faster than what is used in models
 \rightarrow Cls might play an important role in NO_x chemistry

Reactions of CH_2OO with NO and H_2O are too slow to be measured \rightarrow only upper limits could be obtained

$\text{CH}_2\text{OO} + \text{NO}: k \leq 6 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$
 \rightarrow ≥ 100 times slower than literature estimates

$\text{CH}_2\text{OO} + \text{H}_2\text{O}: k \leq 4 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$
 \rightarrow Tends to confirm values used in models

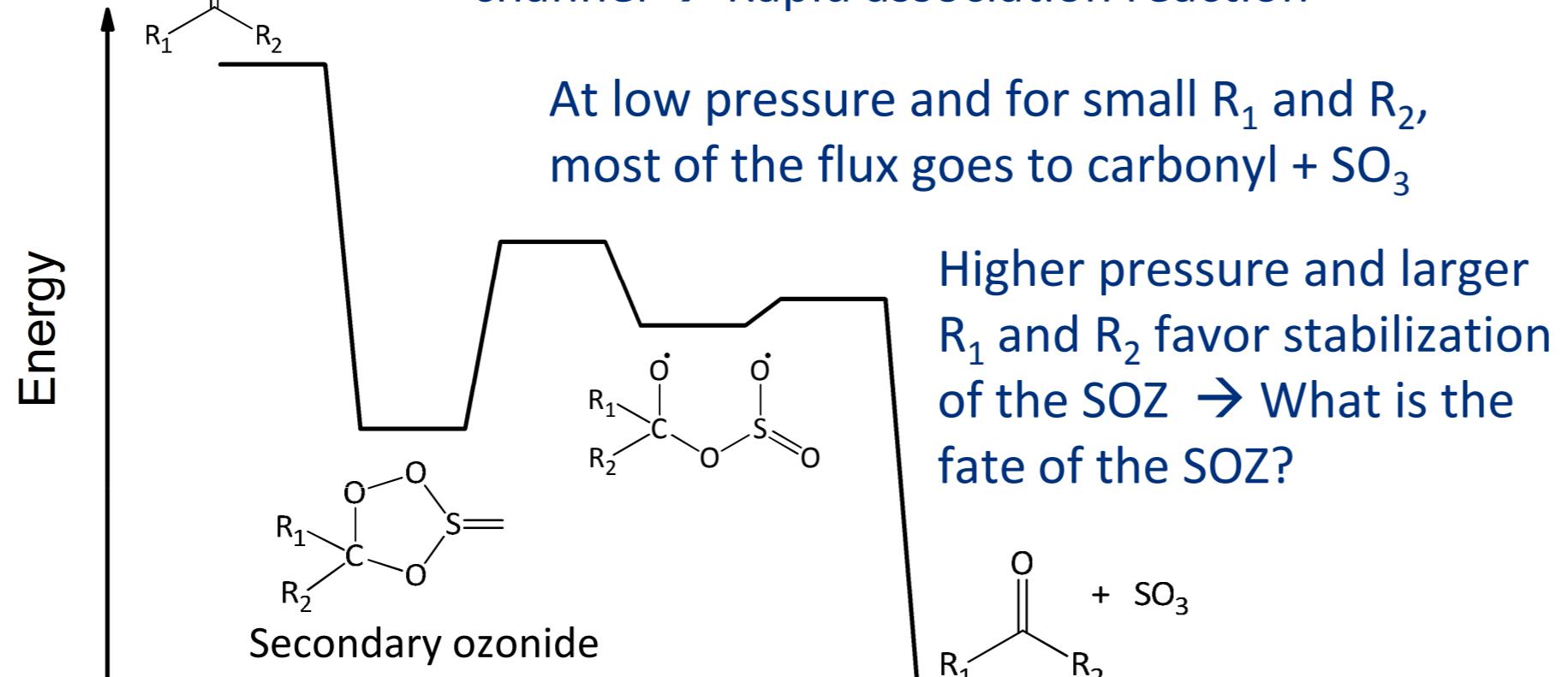
The rate coefficients at 4 Torr are lower limits to the values at atmospheric pressure!

Why is $\text{CH}_2\text{OO} + \text{SO}_2$ so fast?² How do the results at 4 Torr transfer to atmospheric conditions?

The Cl + SO_2 reaction has a barrierless entrance channel \rightarrow Rapid association reaction

At low pressure and for small R_1 and R_2 , most of the flux goes to carbonyl + SO_3

Higher pressure and larger R_1 and R_2 favor stabilization of the SOZ \rightarrow What is the fate of the SOZ?

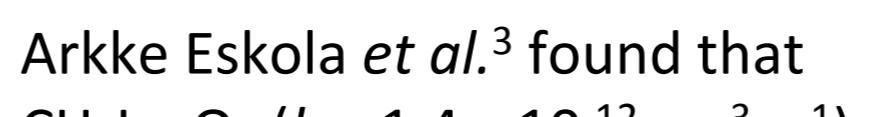


References

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2. L. Vereecken, H. Harder, A. Novelli, *Phys. Chem. Chem. Phys.* **2012**, *14*, 14682 - 14695.
3. A. J. Eskola, D. Wojcik-Pastuszka, E. Ratajczak, R. S. Timonen, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1416-1424.
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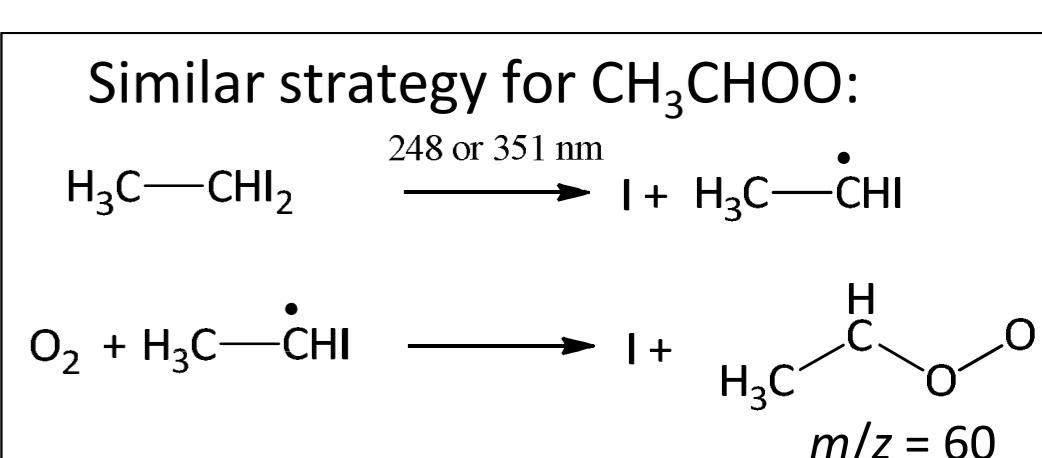
Direct Detection of Criegee Intermediates

- Method to produce Cls rapidly and internally cold:



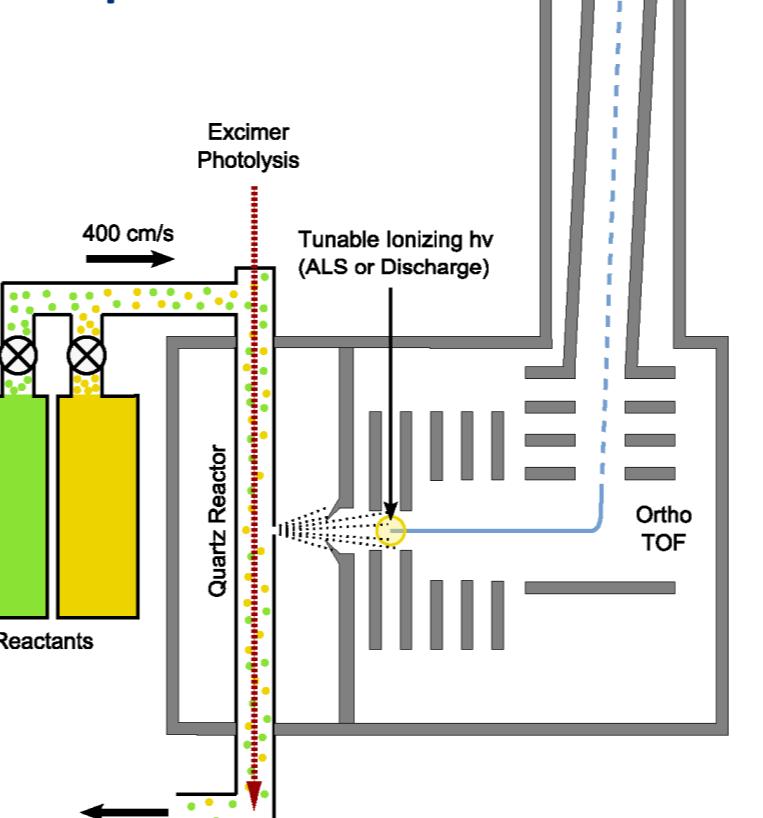
$$m/z = 46$$

$$T = 300 \text{ K}, P = 4 \text{ Torr}, [\text{O}_2] = 1 \times 10^{16} \text{ cm}^{-3}$$



- Unambiguous Detection of Cls using Multiplexed Synchrotron Photoionization Mass Spectrometry (MPIMS)

Experiment

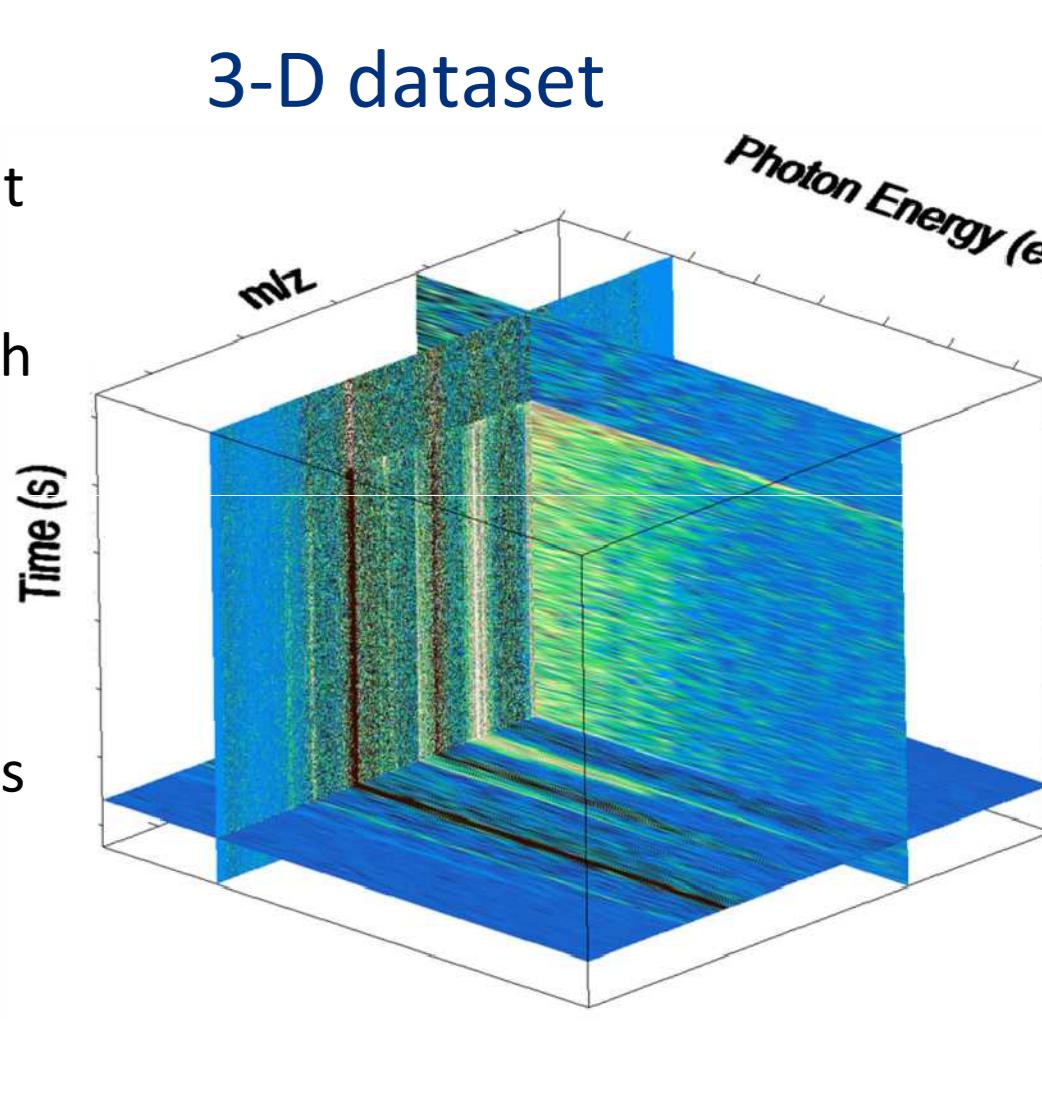


- Tunable vacuum ultraviolet synchrotron radiation using the Advanced Light Source at LBNL \rightarrow Isomer-resolved detection

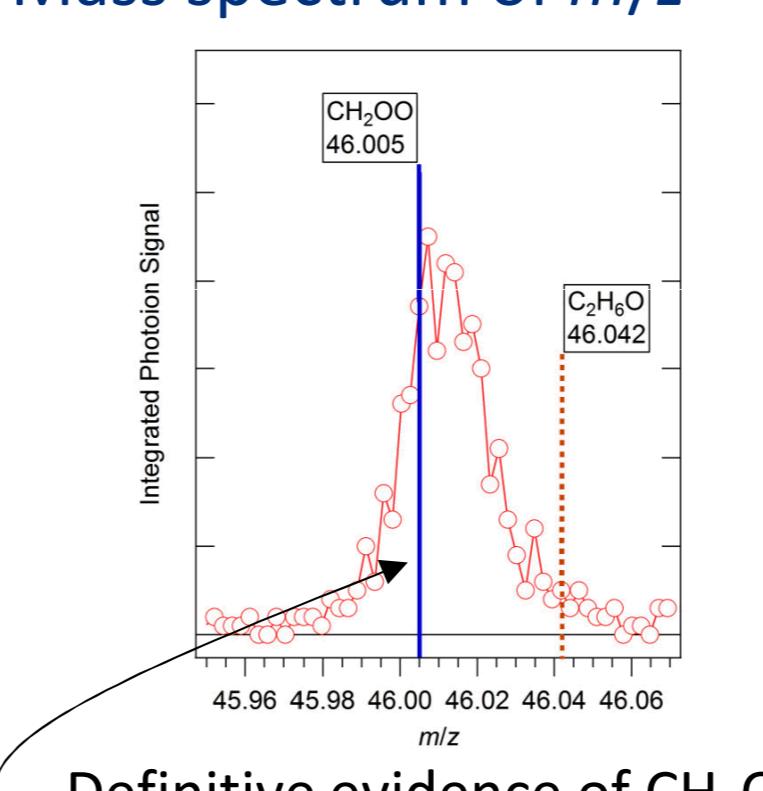
Mass resolution: $m/\Delta m = 1600 \rightarrow$ distinguish CH_4 from O units ($\text{CH}_2\text{O}_2 \leftrightarrow \text{C}_2\text{H}_6\text{O}$)

Mass spectra are recorded every 20 μ s

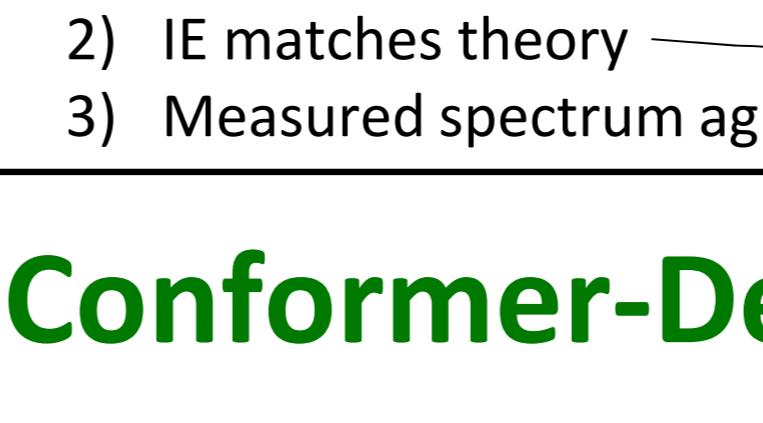
- Data is acquired as a function of
 - mass-to-charge ratio m/z ,
 - kinetic time t relative to the photolysis laser pulse
 - photon energy E .



Mass spectrum of $m/z = 46$



Photoionization spectrum of CH_2OO



Time profile of CH_2OO



Definitive evidence of $\text{CH}_2\text{OO}:$

- Exact mass is correct
- IE matches theory
- Measured spectrum agrees well with Franck-Condon factor simulations

9.37 eV: Only anti- is probed

10.5 eV: Mostly (~90%) syn-

no reaction observed for syn- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}$

Relative Ion Signal

mostly syn-

anti-

anti- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}:$

$k = (1.0 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$

syn- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}:$

$k \leq 4 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$

Determination of the rate coefficient for anti- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}$

$k_{1st} (s^{-1})$

$[H_2O] (10^{16} \text{ cm}^{-3})$

anti- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}$

10.5 eV

9.37 eV

no reaction observed for syn- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}$

Relative Ion Signal

mostly syn-

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anti- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}:$

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syn- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}:$

$k \leq 4 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$

Relative Ion Signal

mostly syn-

anti-

anti- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}:$

$k = (6.7 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

anti- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}:$

$k = (2.4 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

syn- $\text{CH}_3\text{CHO} + \text{H}_2\text{O}:$

$k = (6.7 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

Relative Ion Signal