



# Reactivity of Criegee Intermediates CH<sub>2</sub>OO and CH<sub>3</sub>CHOO: Direct Detection and Conformer-Dependent Kinetics

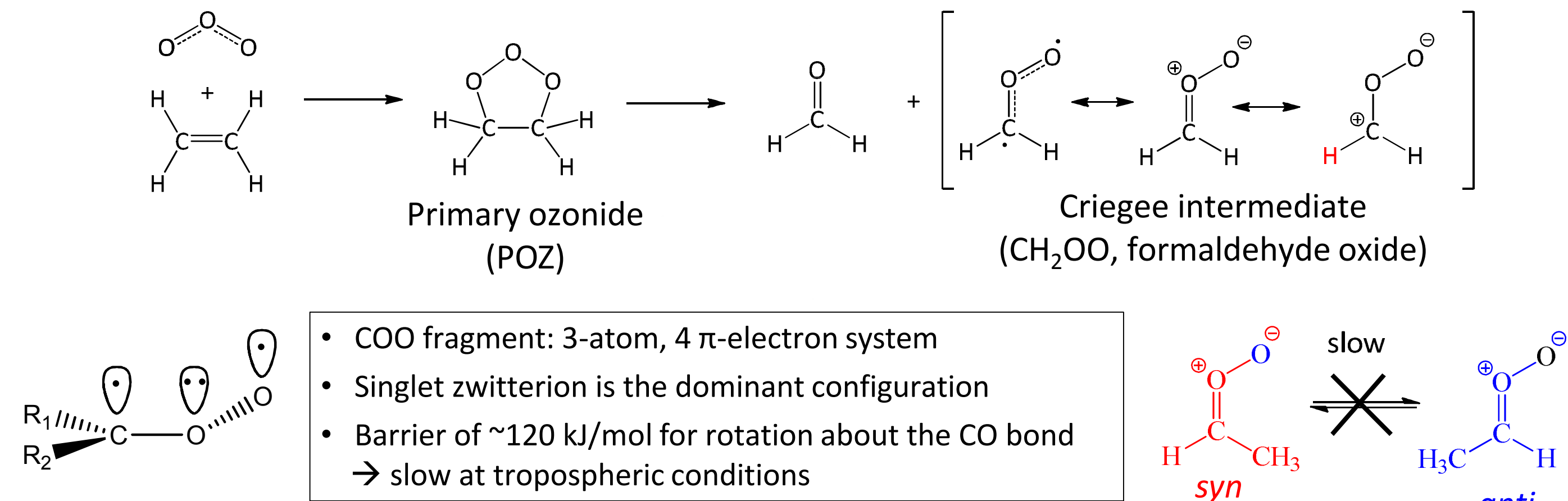
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Hot Topic Talk 10  
Friday, 9:10 AM

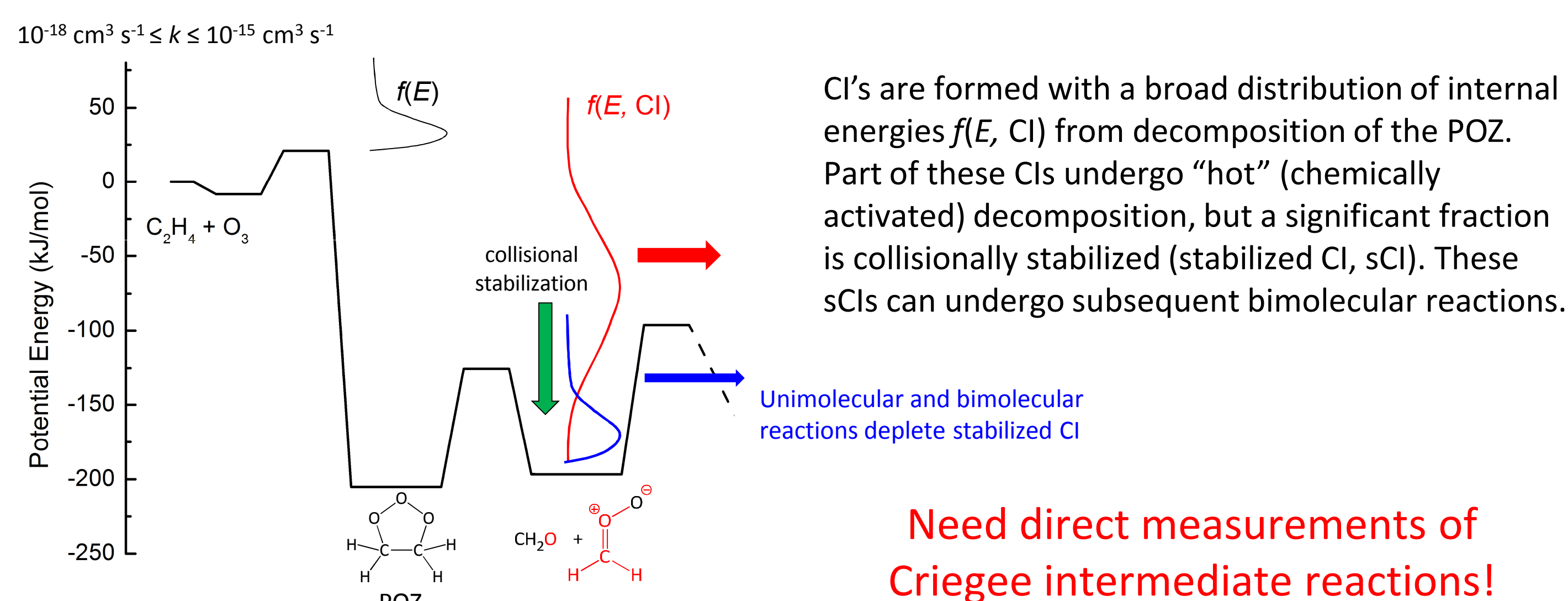
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## Introduction

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



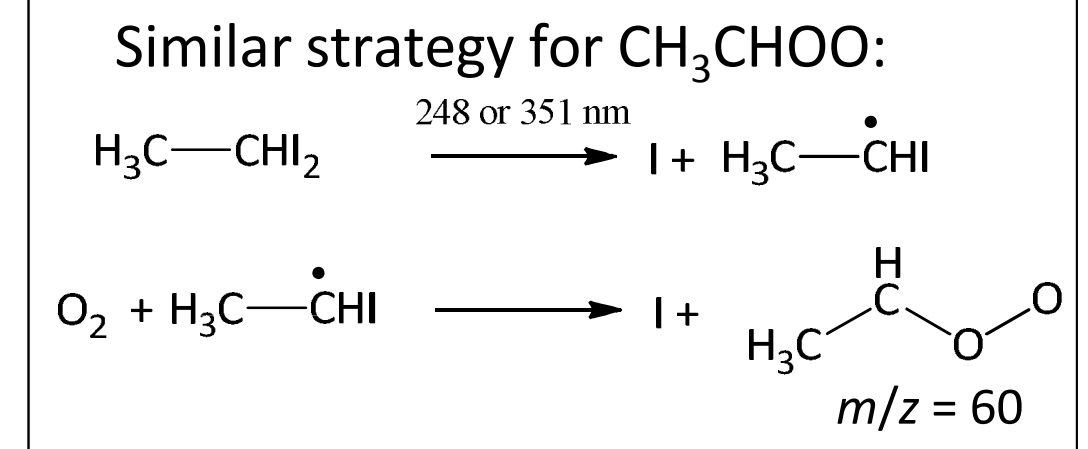
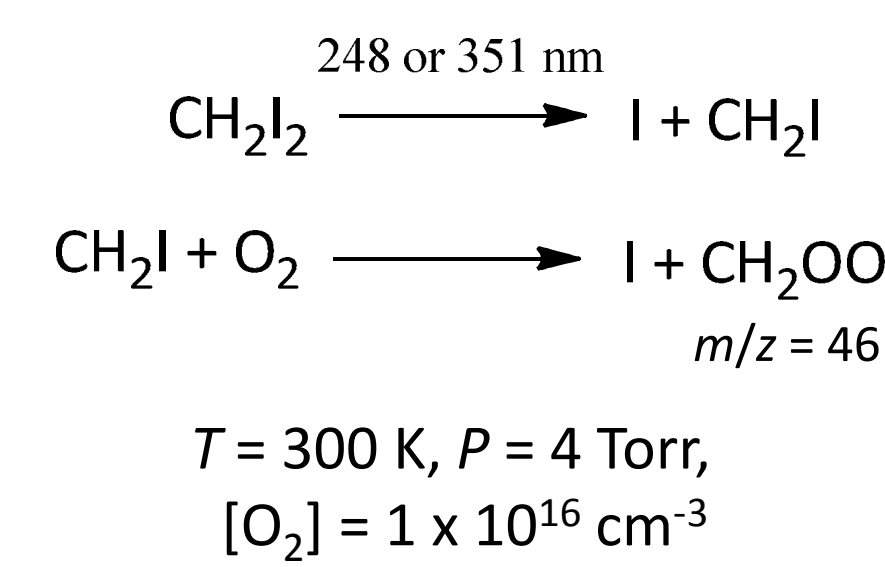
- CIs are key species in the troposphere → non-photolytic source of OH, controlling the budgets of NO<sub>x</sub>, NO<sub>y</sub>, and secondary organic aerosols
- Rate coefficients of CIs with key atmospheric species (H<sub>2</sub>O, NO, NO<sub>2</sub>, SO<sub>2</sub>, ...) are uncertain by orders of magnitude → Significant uncertainty in the quantitative role of CIs in the troposphere
- No CI has ever been detected in gas-phase ozonolysis: Ozonolysis forms CIs slowly, but they react away rapidly → low steady-state concentrations



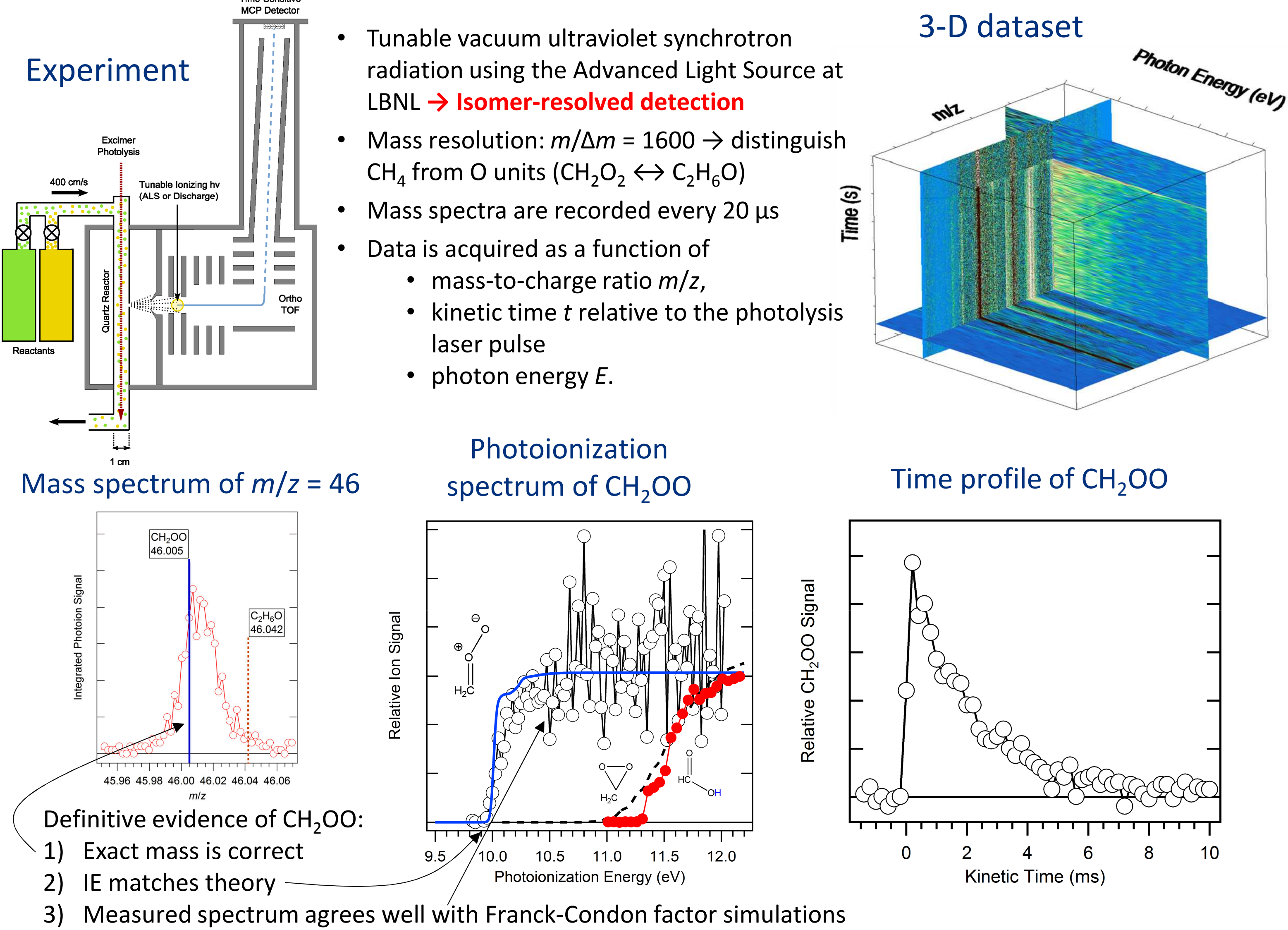
## Direct Detection of Criegee Intermediates

- Method to produce CIs rapidly and internally cold:

Arkke Eskola *et al.*<sup>3</sup> found that CH<sub>2</sub>I + O<sub>2</sub> (k = 1.4 × 10<sup>-12</sup> cm<sup>3</sup> s<sup>-1</sup>) made iodine atoms with unity yield at low pressure – it turns out that the co-product is the Criegee intermediate CH<sub>2</sub>OO!



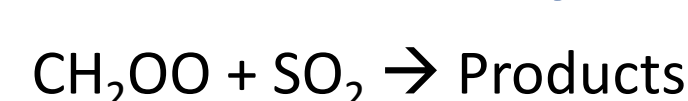
- Unambiguous Detection of CIs using Multiplexed Synchrotron Photoionization Mass Spectrometry (MPIMS)



## Direct Measurements of CH<sub>2</sub>OO Kinetics<sup>1</sup> (4 Torr, 300 K)

### CH<sub>2</sub>OO + SO<sub>2</sub>:

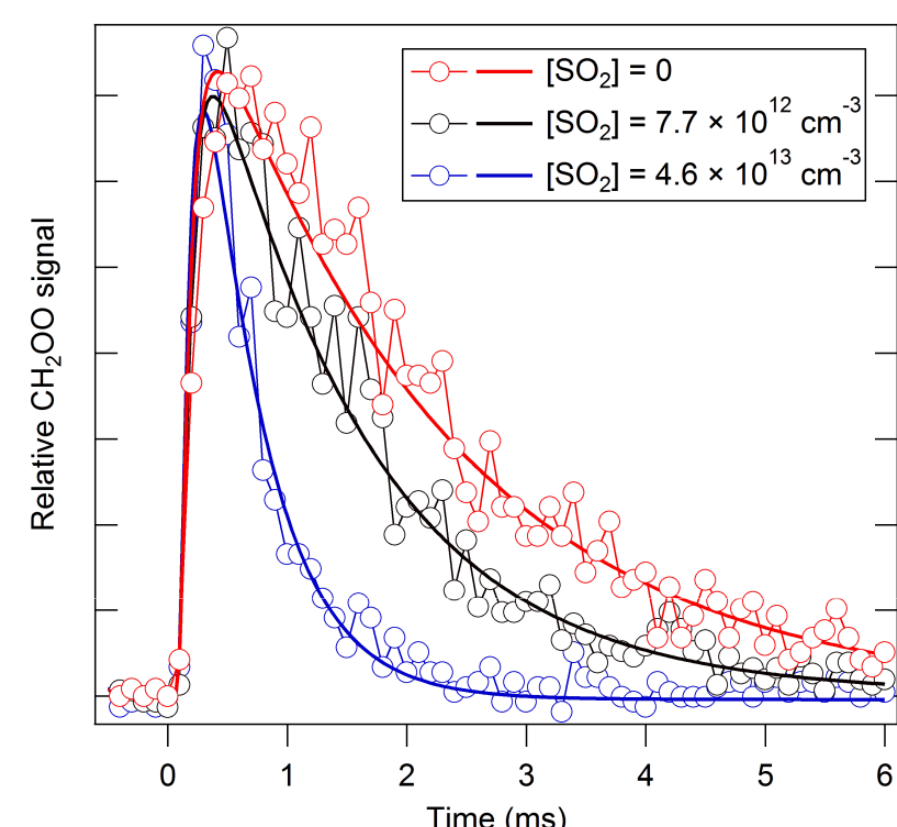
#### Kinetics analysis:



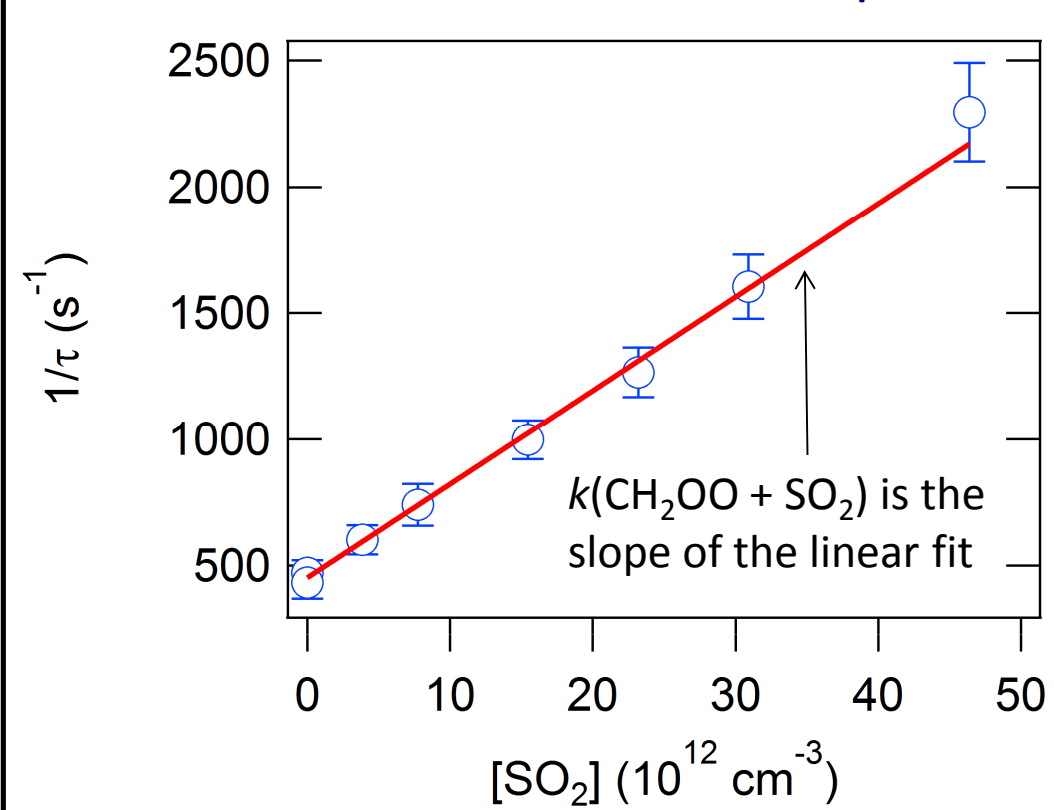
$$[\text{SO}_2] \gg [\text{CH}_2\text{OO}]_0: k_{1st} = k_{loss} + k(\text{CH}_2\text{OO} + \text{SO}_2) [\text{SO}_2]$$

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

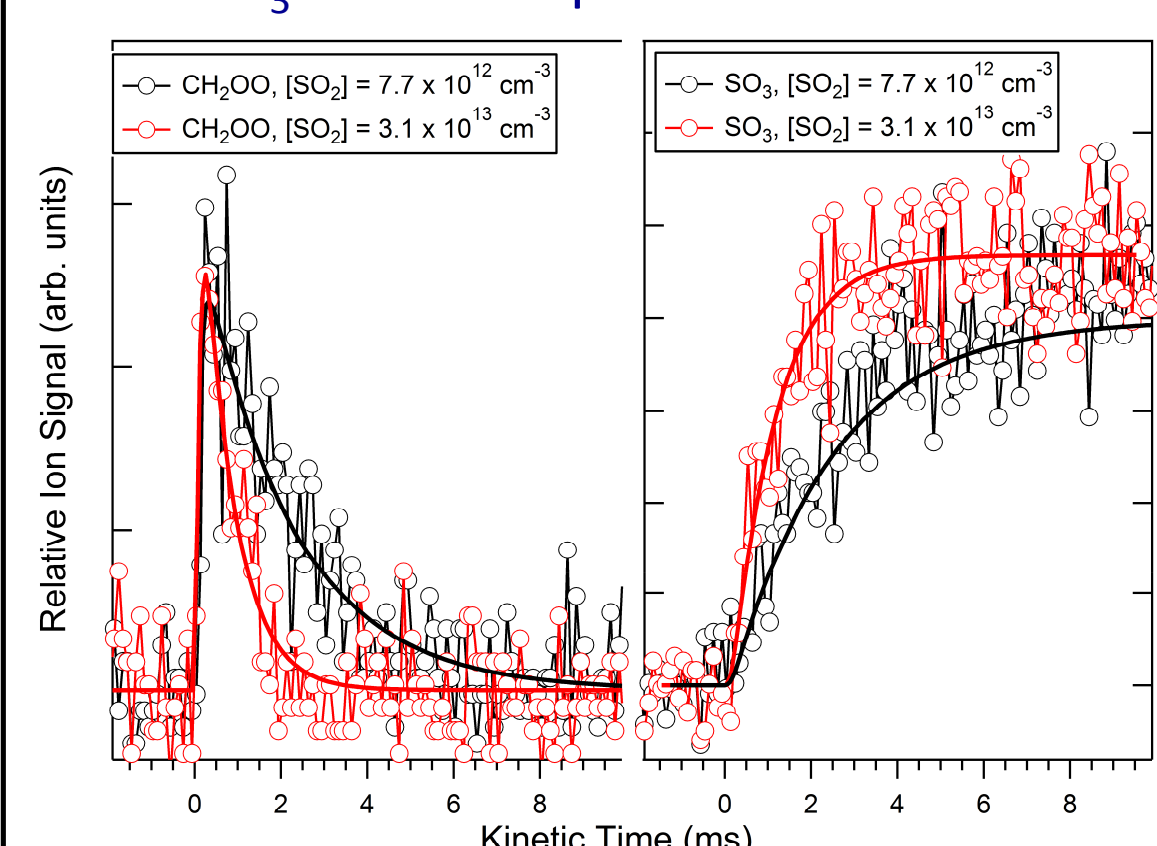
Addition of SO<sub>2</sub> makes the decay of CH<sub>2</sub>OO faster: SO<sub>2</sub> reacts with CH<sub>2</sub>OO!



#### Pseudo-first-order plot



SO<sub>3</sub> is a direct product at 4 Torr



### Kinetics results for CH<sub>2</sub>OO reactions

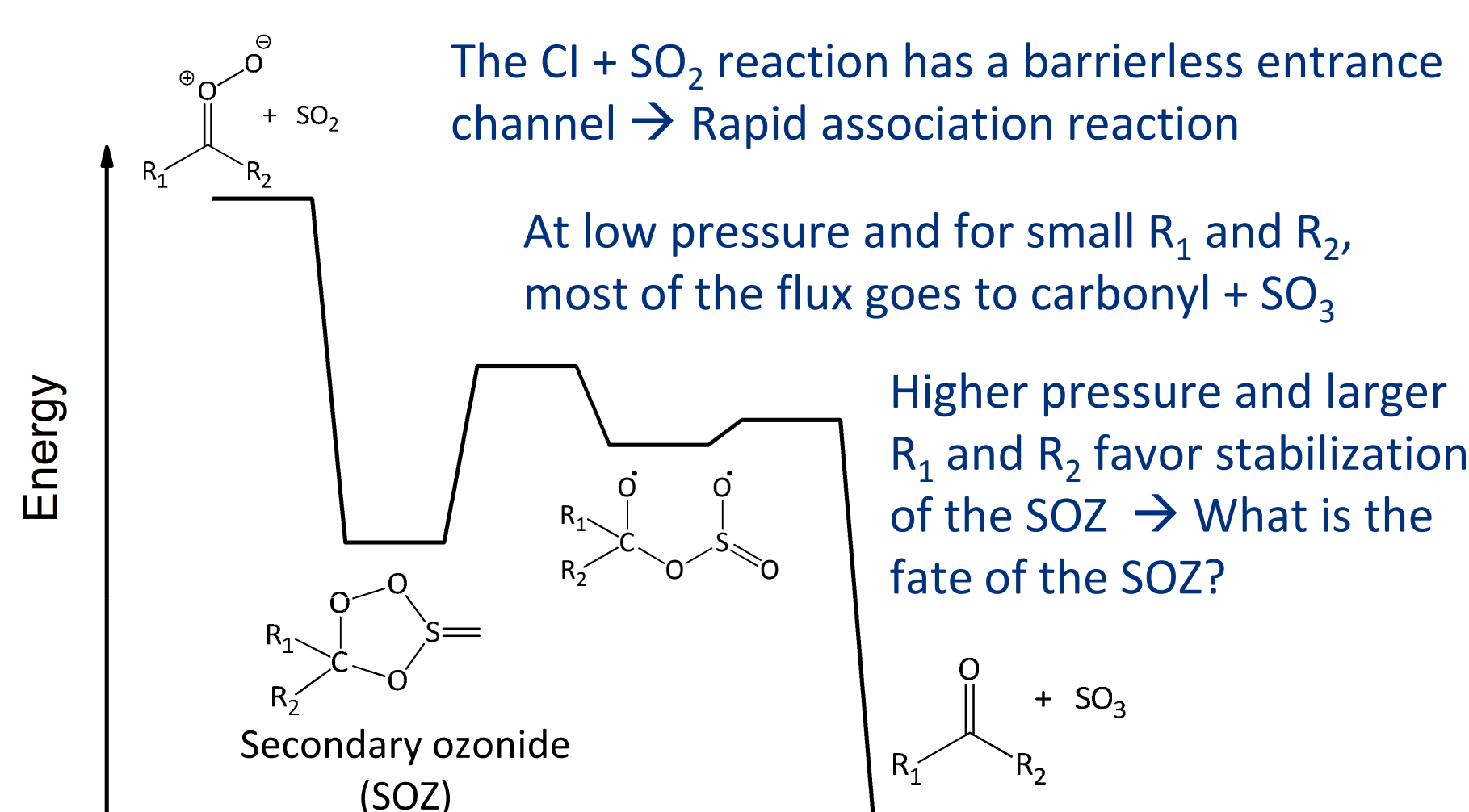
CH<sub>2</sub>OO + SO<sub>2</sub>: k = (3.9 ± 0.7) × 10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>  
→ up to 10 000 times faster than what is used in models  
→ CIs might be major SO<sub>2</sub> oxidants

CH<sub>2</sub>OO + NO<sub>2</sub>: k = (7<sup>+3</sup>/<sub>-2</sub>) × 10<sup>-12</sup> cm<sup>3</sup> s<sup>-1</sup>  
→ 50 times faster than what is used in models  
→ CIs 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  
CH<sub>2</sub>OO + NO: k ≤ 6 × 10<sup>-14</sup> cm<sup>3</sup> s<sup>-1</sup>  
→ ≥ 100 times slower than literature estimates  
CH<sub>2</sub>OO + H<sub>2</sub>O: k ≤ 4 × 10<sup>-15</sup> cm<sup>3</sup> s<sup>-1</sup>  
→ Tends to confirm values used in models

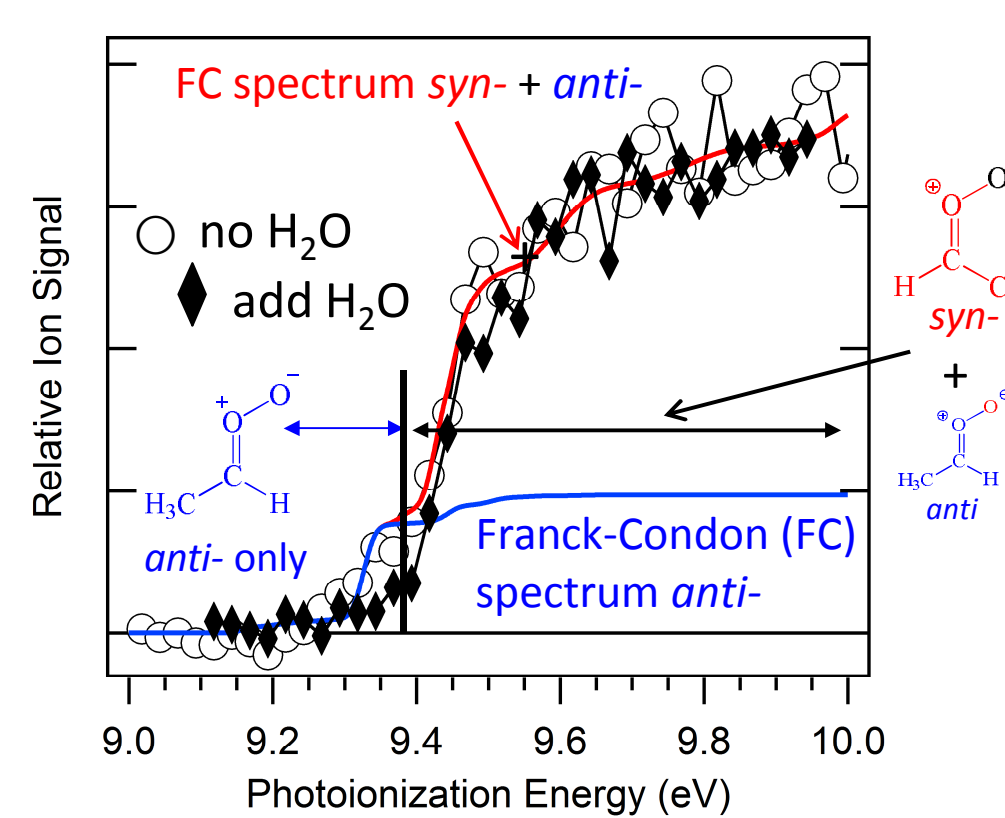
The rate coefficients at 4 Torr are lower limits to the values at atmospheric pressure!

### Why is CH<sub>2</sub>OO + SO<sub>2</sub> so fast?<sup>2</sup> How do the results at 4 Torr transfer to atmospheric conditions?



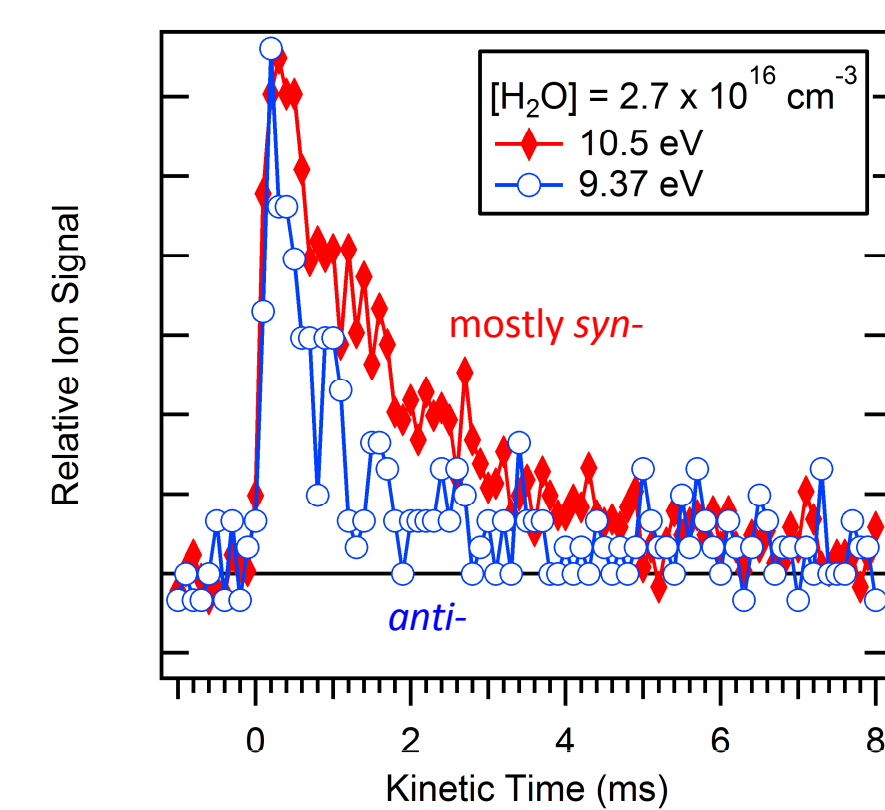
## Conformer-Dependent Kinetics<sup>4</sup> of CH<sub>3</sub>CHOO + H<sub>2</sub>O

Addition of H<sub>2</sub>O depletes the low-E part of the CH<sub>3</sub>CHO photoionization spectrum arising from *anti*-CH<sub>3</sub>CHOO

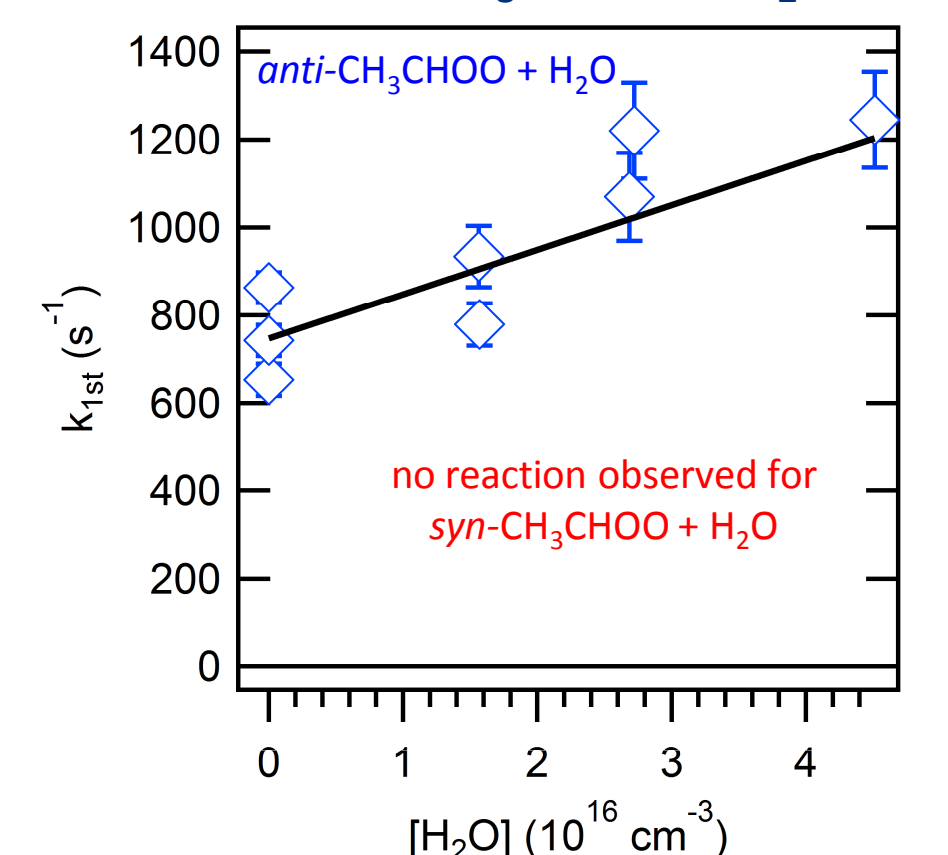


→ *anti*-CH<sub>3</sub>CHOO reacts with water!

9.37 eV: Only *anti*- is probed  
10.5 eV: Mostly (~90%) *syn*-



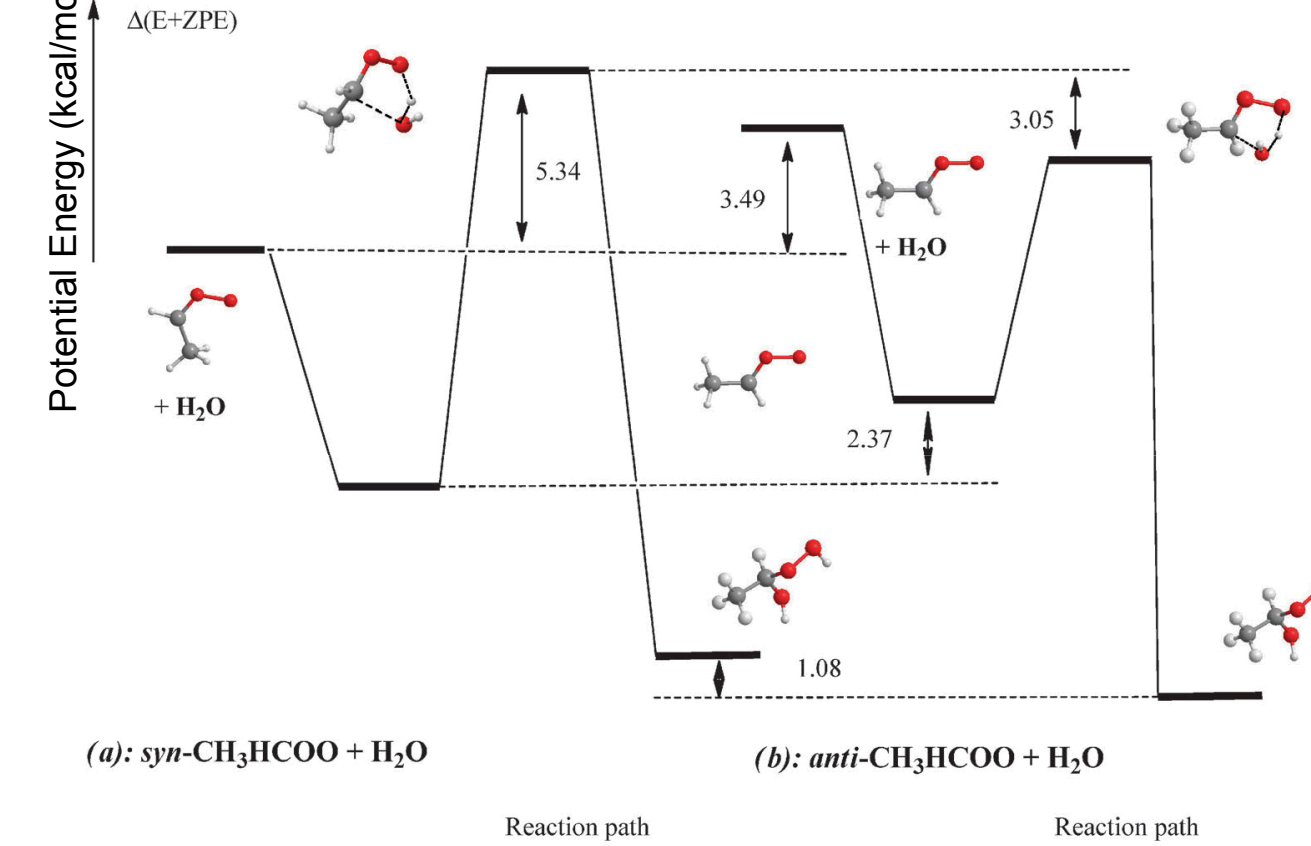
Determination of the rate coefficient for *anti*-CH<sub>3</sub>CHOO + H<sub>2</sub>O



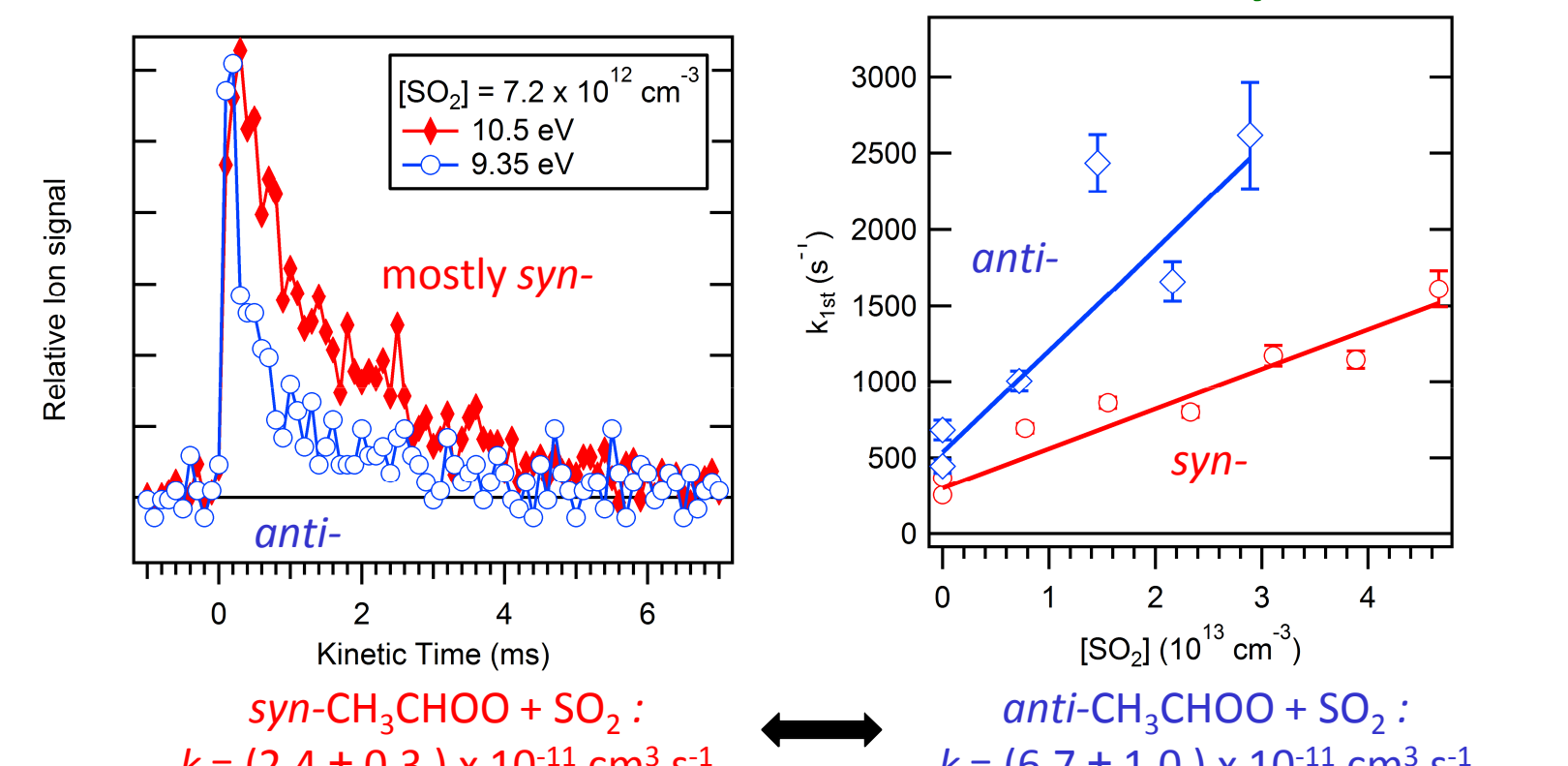
*anti*-CH<sub>3</sub>CHOO + H<sub>2</sub>O:  
k = (1.0 ± 0.4) × 10<sup>-14</sup> cm<sup>3</sup> s<sup>-1</sup>

*syn*-CH<sub>3</sub>CHOO + H<sub>2</sub>O:  
k ≤ 4 × 10<sup>-15</sup> cm<sup>3</sup> s<sup>-1</sup>

Conformer-dependent reactivity was predicted by Anglada *et al.*<sup>5</sup>



CH<sub>3</sub>CHOO + SO<sub>2</sub> is rapid; *anti*- reacts ~ 3 x faster than *syn*-



*syn*-CH<sub>3</sub>CHOO + SO<sub>2</sub>:  
k = (2.4 ± 0.3) × 10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>

*anti*-CH<sub>3</sub>CHOO + SO<sub>2</sub>:  
k = (6.7 ± 1.0) × 10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>

## Conclusions and Outlook

- The reaction of photolytically produced α-iodoalkyl radicals with O<sub>2</sub> forms CIs rapidly and with low internal energies. Combined with MPIMS, direct kinetics measurements of CH<sub>2</sub>OO and CH<sub>3</sub>CHOO with key atmospheric species were performed for the first time.
- Conformer-dependent reactivity of CH<sub>3</sub>CHOO with H<sub>2</sub>O and SO<sub>2</sub> was observed and might persist for reactions with other atmospheric species.
- The reaction of CIs with SO<sub>2</sub> is rapid, suggesting that CIs are major oxidants of SO<sub>2</sub>. SO<sub>3</sub> is a direct product of CH<sub>2</sub>OO and CH<sub>3</sub>CHOO + SO<sub>2</sub> at 4 Torr and 300 K.
- Investigations of larger CIs, measurements of rate coefficients and products of more reactions and at more (especially atmospheric) conditions are necessary to fully understand the role of CIs in the troposphere.

## References

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