



# ***The Criegee Intermediate Reaction Network in Ethylene Ozonolysis***

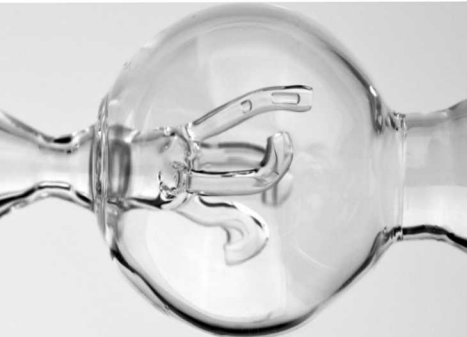
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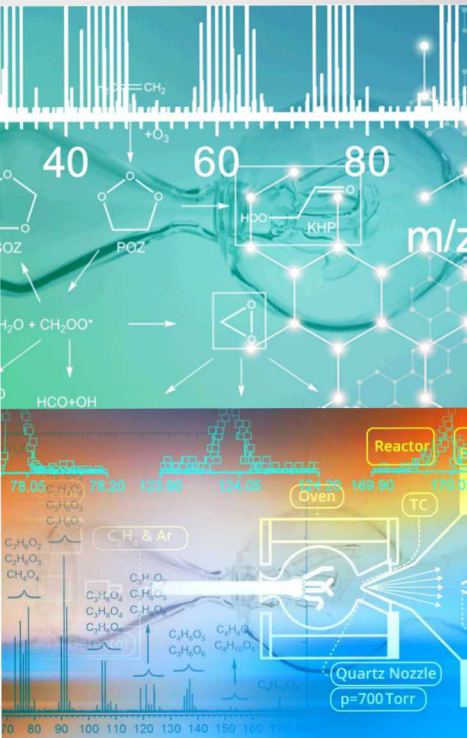
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# Outline

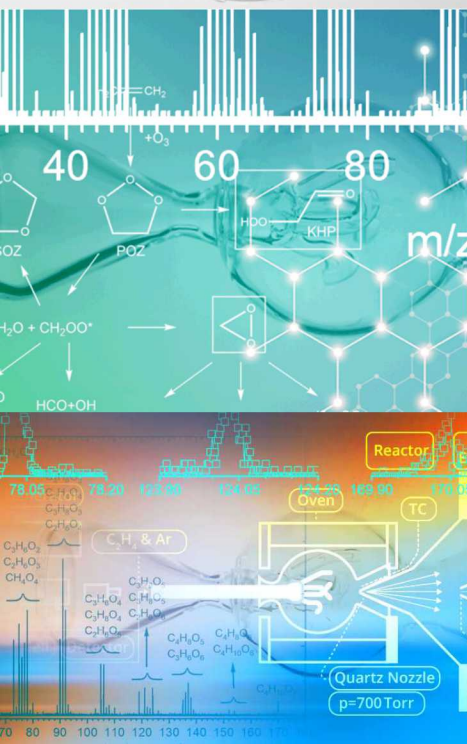
- ✓ Introduction: Motivation, Background, Challenges, and Objectives
- ✓ Experimental Procedures
- ✓ Ethylene Ozonolysis
  - Low-temperature oxidation of ethylene
  - Identification of the Criegee Intermediate reaction network
- ✓ Summary and Outlook





# Motivation

- ✓ for over 100 years researchers have studied the gas phase interaction of ozone with hydrocarbons
- ✓ atmospheric (tropospheric) chemistry
  - ozone is a major oxidant
  - understanding aerosol, pollution formation as well as  $\text{NO}_x$ ,  $\text{HO}_x$ , intermediate generation and consumption
- ✓ flame chemistry
  - kinetic acceleration of low temperature chemistry
  - laboratory studies of stable cool flames

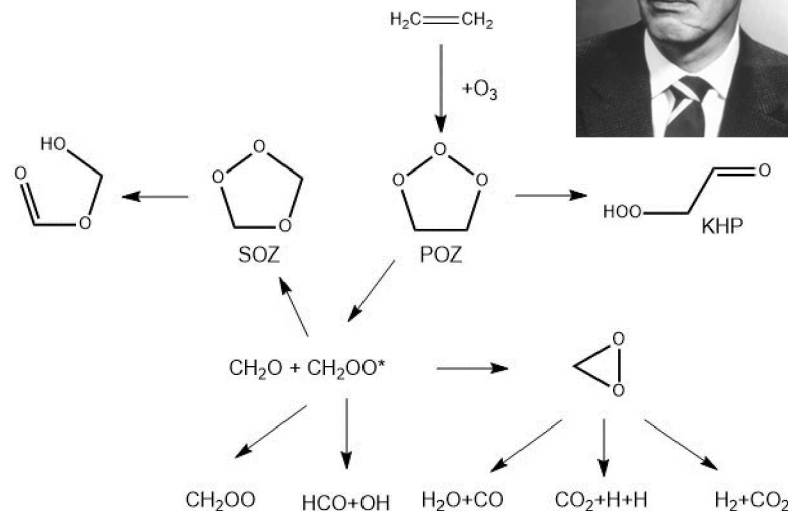


# Background Information: Ozonolysis

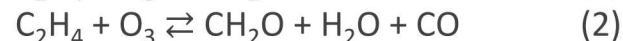
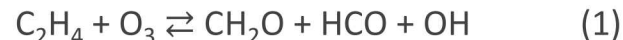


✓ mechanism laid out by Rudolf Criegee in 1975

- ❑ cleavage of unsaturated hydrocarbon double bond through ozone addition
- ❑ cyclic primary ozonide (POZ)
  - keto-hydroperoxide (hydroperoxy-acetaldehyde)
  - carbonyl group (formaldehyde) + carbonyl oxide (Criegee Intermediate –  $\text{CH}_2\text{OO}^*$ )
- ❑ cyclic secondary ozonide (SOZ)
  - hydroxy-methylformate
- ❑  $\text{CH}_2\text{O}_2$  either collisionally stabilizes, decomposes or isomerizes



✓ IUPAC recommends 4 reactions to model this process for atmospheric chemistry







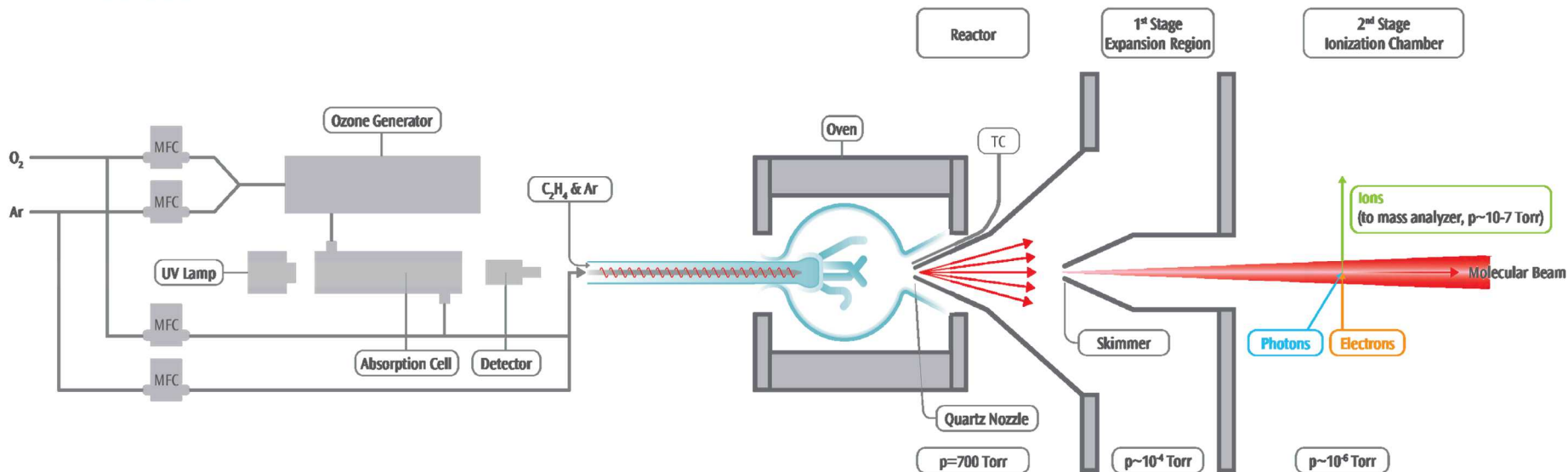
# Challenges, Objectives, and Outcomes

- ✓ Challenges: intermediate species difficult to measure directly
  - Criegee Intermediates are slow to form but extremely fast to react
  - many experiments exploring this chemistry rely on specialized mechanisms
  - most kinetic studies focus on atmospheric conditions
- ✓ Objectives: “Bridge the gap”
  - temperature dependent ethylene ozone oxidation from 300-1000 Kelvin
  - exploring the shift from ozone-assisted low temperature chemistry to intermediate oxidation chemistry
  - isomer-specific identification and quantification of intermediates
  - highlight areas for improvement for future LTC modeling
- ✓ Outcomes:
  - detailed chemical understanding of the ozone-assisted low-temperature oxidation of ethylene
  - insights into the Criegee Intermediate reaction network that can be related to formation of highly oxygenated species and SOA



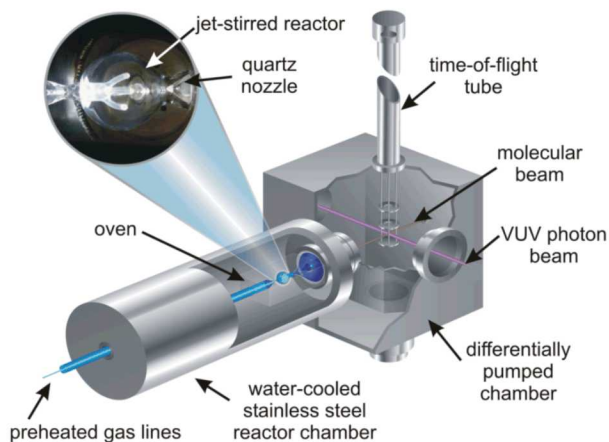
# Experimental Details

## Molecular-beam mass spectrometry after sampling from a jet-stirred reactor

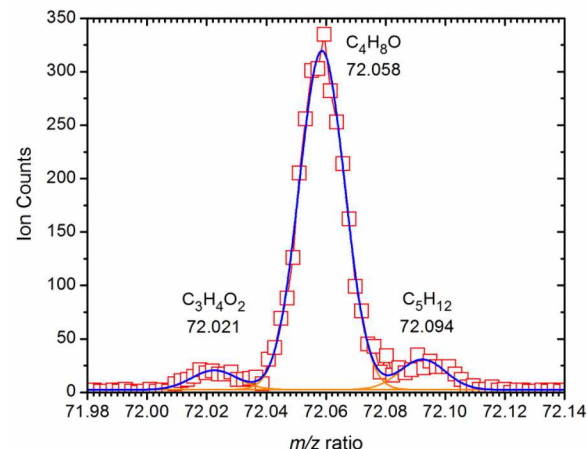


# Experimental Details

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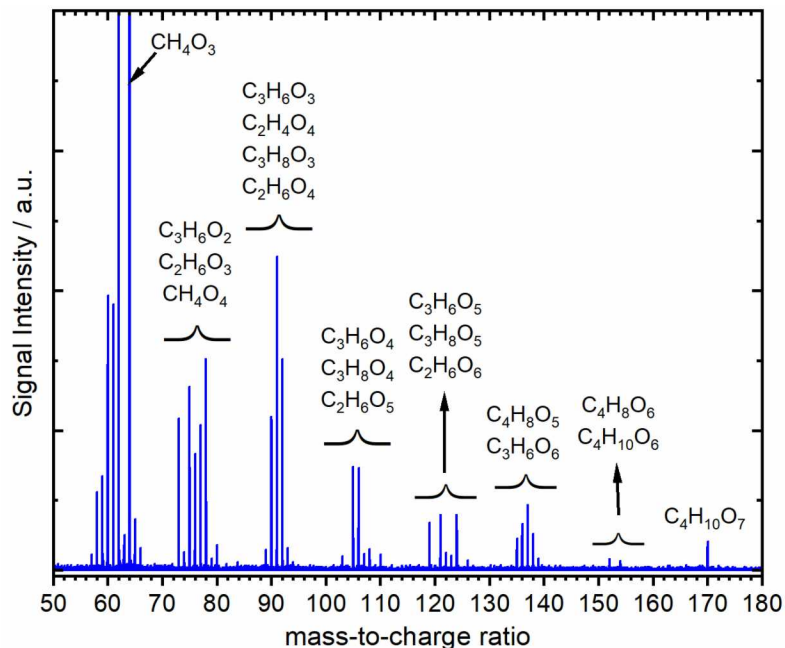


- ✓ orthogonal extraction reflectron time-of-flight
- ✓ detection limit:  $\sim 0.5$  ppm
- ✓ mass resolution  $m/\Delta m \sim 4000$
- ✓ electron and photon ionization (at the Advanced Light Source)
- ✓ continuous ionization, rapid (35kHz) ion extraction

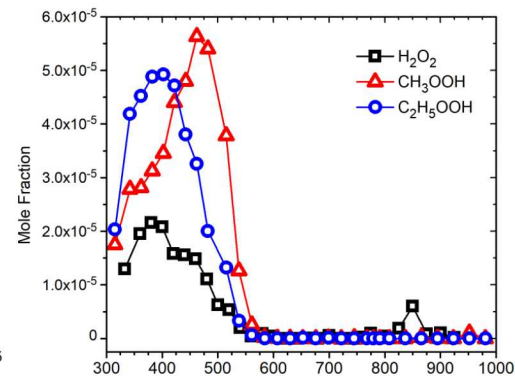
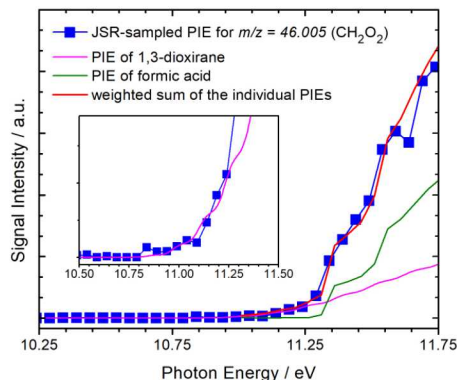


# Experimental Details

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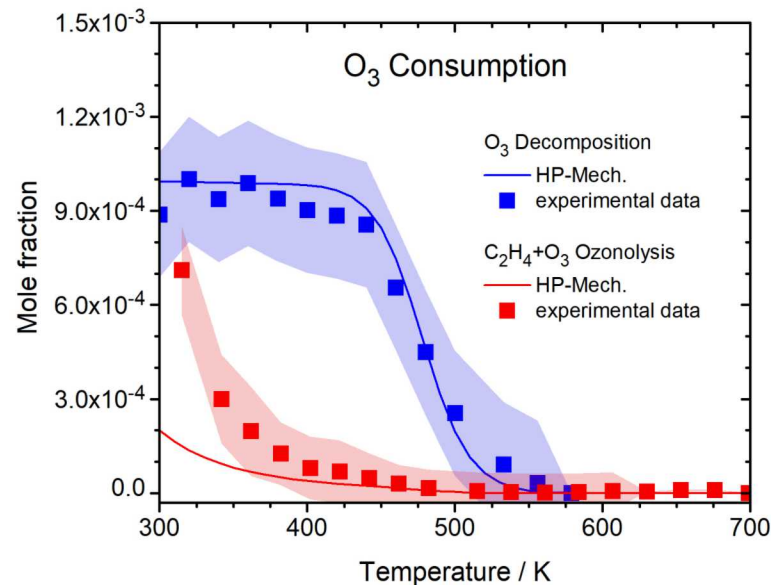
- ☐ 2% ethylene, 12%  $\text{O}_2$ , and 86% argon ( $\phi = 0.5$ )
- ☐  $p = 0.92$  atm (700 Torr)
- ☐ residence time = 1.3 s
- ☐ 1000 ppm ozone addition
- ☐  $T = 300\text{--}1100$  K



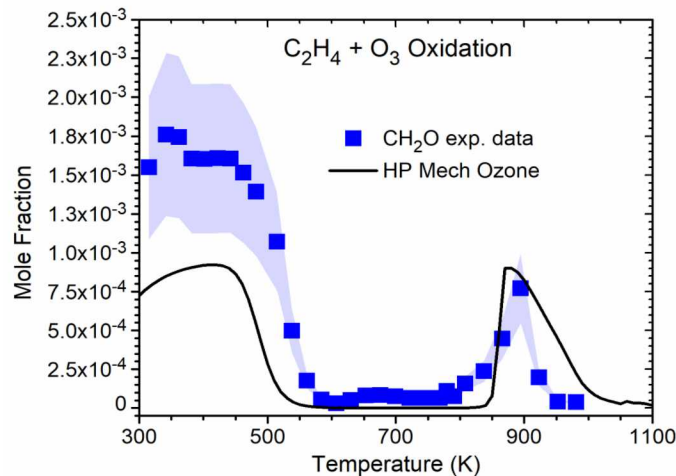
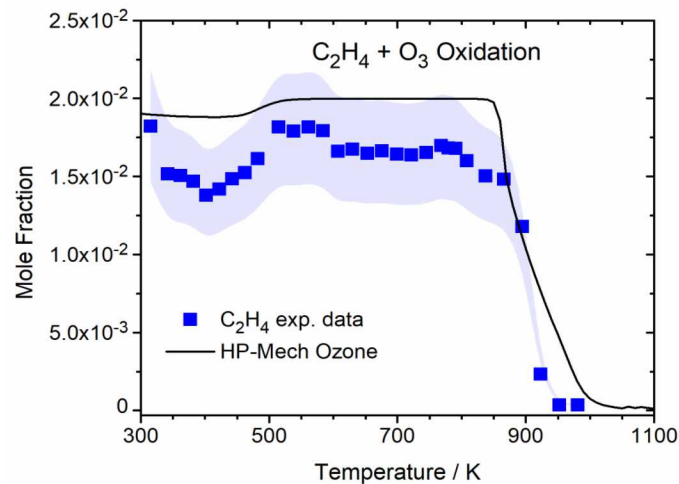


# Ozone Thermal Decomposition

- model for this work: HP-Mech with the addition of an ozone submechanism (Zhao *et al.*, *Combust. Flame*, 2017, **183**, 253-260)
- IUPAC global rates added to simulate  $\text{C}_2\text{H}_4 + \text{O}_3$  reactions
- ozone thermally decomposes with temperature by 600 K
- model accurately predicts ozone concentration
- fuel reactions are overpredicted at room temperature
- trends beyond 600 K are initiated by O atom addition, not ozonolysis



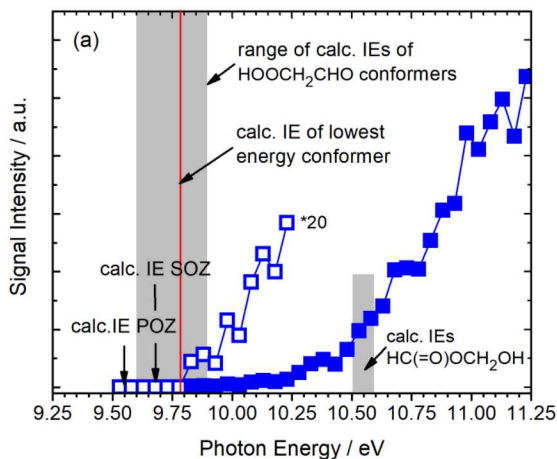
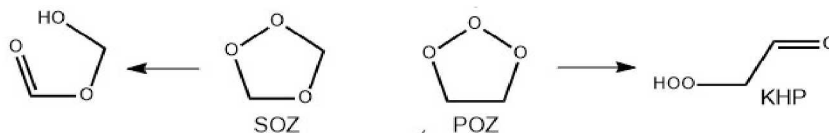
# Low-Temperature Oxidation of Ethylene



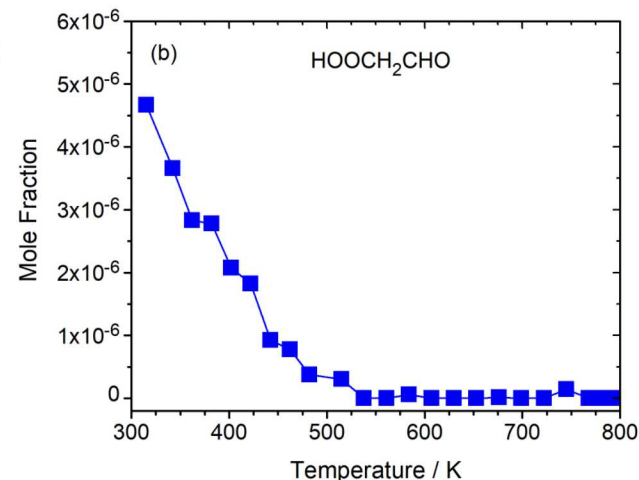
- clear LTC and NTC chemistry regimes, caused by ozonolysis
- model predicts high temperature chemistry fairly well
- IUPAC rates: do well at atmospheric conditions, but clearly missing reactions at higher temperatures
- to understand what is missing, we must identify and verify other species in the reaction mechanism not captured by the model

# Low-Temperature Oxidation of Ethylene

## Identification of the $C_2H_4O_3$ Intermediate



- the calculated IE of the lowest energy conformer of hydroperoxy-acetaldehyde (KHP) is 9.76 eV
- CCSD(T)/CBS//M06-2X/cc-pVTZ level of theory
- theoretically predicted as the most stable structure on the potential energy surface

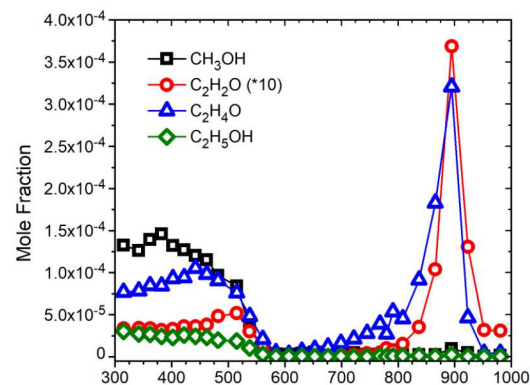
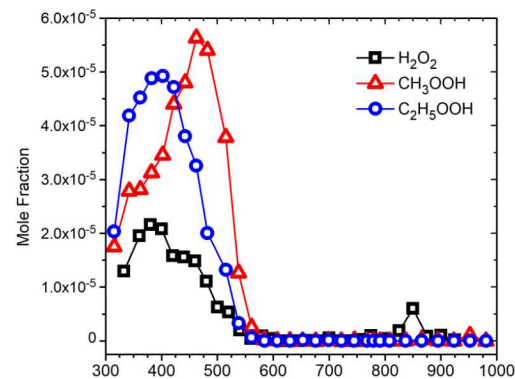


# Low-Temperature Oxidation of Ethylene

## Oxygenated LTC Intermediates

- Major intermediates identified that were either drastically underpredicted or not present in the current model
- Acetaldehyde concentration begins to grow again immediately after the NTC ozone regime
  - Suggestive of O radical chemistry due to ozone thermal decomposition

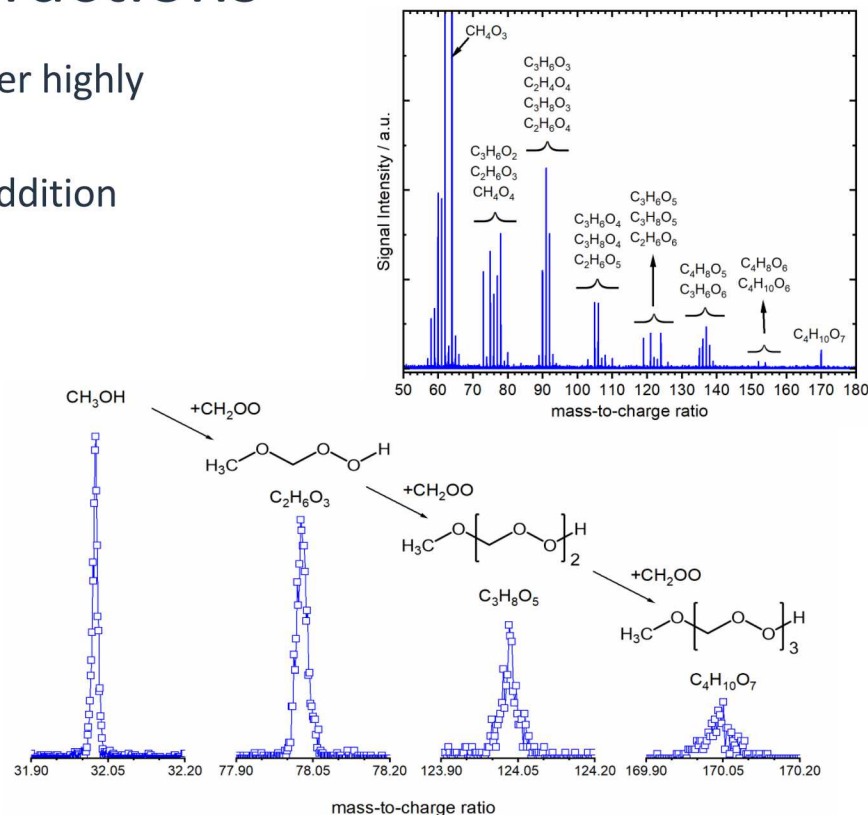
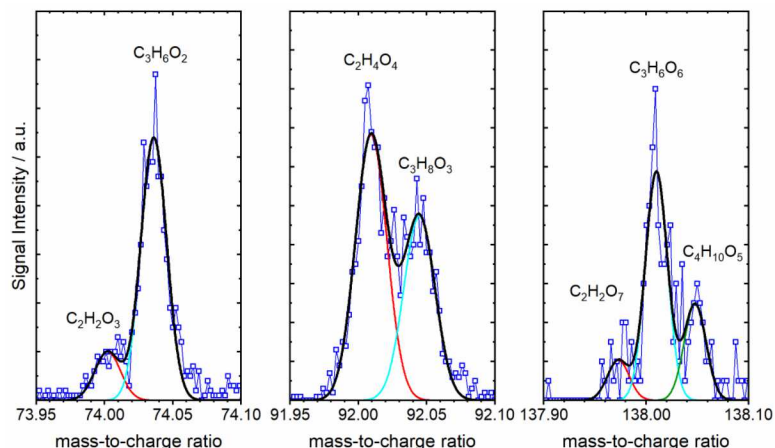
Species	Isomer	IE Threshold / eV	Cross Sections/Mb (Photon Energy/eV)
CH <sub>3</sub> OH	Methanol	10.84	3.6 (11)
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide	10.58	4.4 (11.5)
CH <sub>2</sub> CO	Ketene	9.62	24.8 (10.5)
CH <sub>3</sub> CHO	ethenol/acetaldehyde	9.33/10.23	7.4 (10.5)
C <sub>2</sub> H <sub>5</sub> OH	Ethanol	10.48	4.9 (11)
CH <sub>3</sub> O <sub>2</sub> H	methyl hydroperoxide	9.83	2.4 (10.5)
HOCH <sub>2</sub> CHO	hydroxy-acetaldehyde	9.98	6.1 (10.5)
C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> H	ethyl hydroperoxide	9.61	5.72 (10.0)
HOOCH <sub>2</sub> CHO	hydroperoxy-acetaldehyde	9.80	5.0 (10.5)



# Criegee Intermediate Interactions

- at close to ambient temperatures, many larger highly oxygenated species were detected
- most peaks can be explained by sequential addition reactions of the Criegee Intermediate

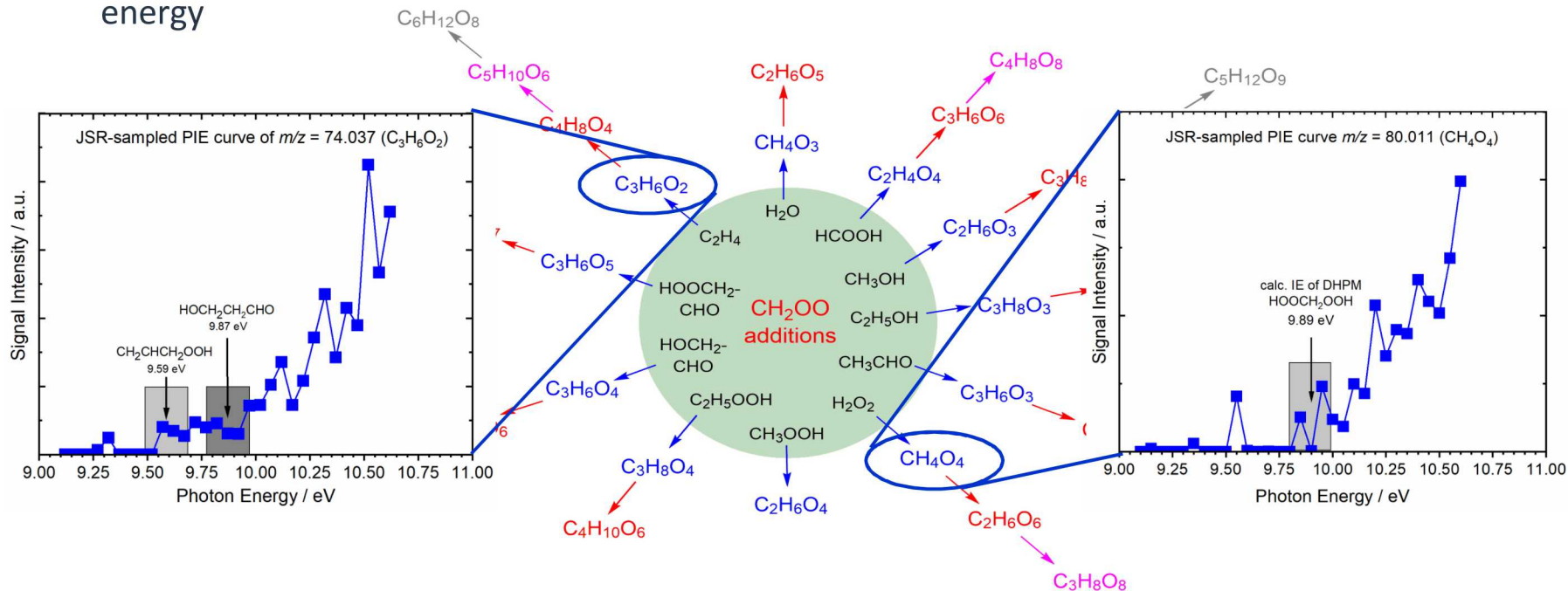
⇒ SOA formation





# Criegee Intermediate Interactions

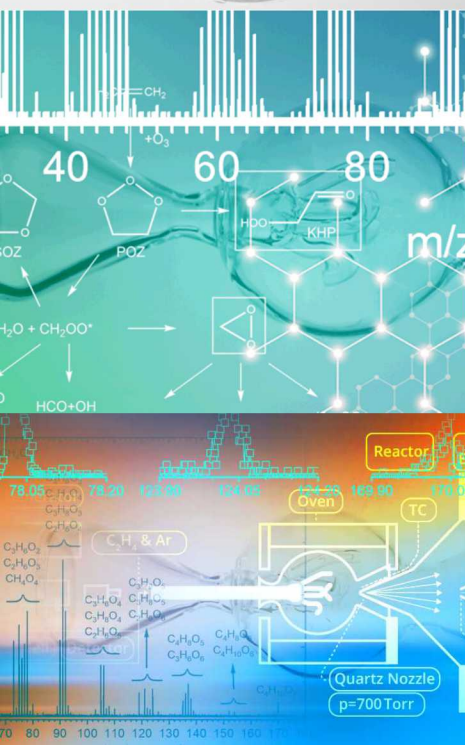
- 11 distinct chains were observed in this work
- first additions (blue) were all identified and quantified using PIE scans and calculated ionization energy





# Conclusions

- ✓ Major species and intermediates for ozone addition to ethylene were identified in the low and intermediate temperature regimes from 300 – 1000 K
  - Distinct “LTC” chemistry was seen below 450 K due to ozonolysis
  - NTC behavior between 450 and 600 K - where ozone is completely decomposed
- ✓ Key intermediates in the Criegee mechanism were identified and quantified.
  - KHP was found to be the most stable product of  $C_2H_4 + O_3$  reaction
- ✓ Modeling results using HP-Mech and IUPAC reactions rates
  - decent prediction of product species at room temperature, but becomes more inaccurate at higher temperatures
  - missing reactions for low and intermediate temperature modeling of this system
- ✓ Network of Criegee Intermediate adducts was identified and quantified
  - covering CI reactions with a variety of functional groups
  - up to 4 consecutive CI additions were observed





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