



The Criegee Intermediate Reaction Network in Ethylene Ozonolysis

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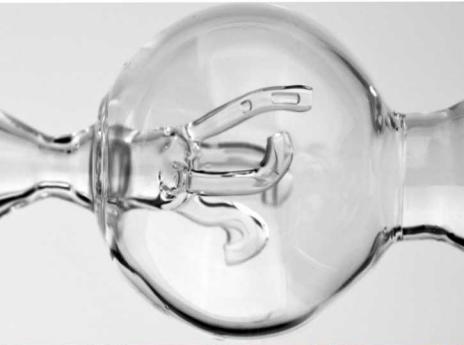
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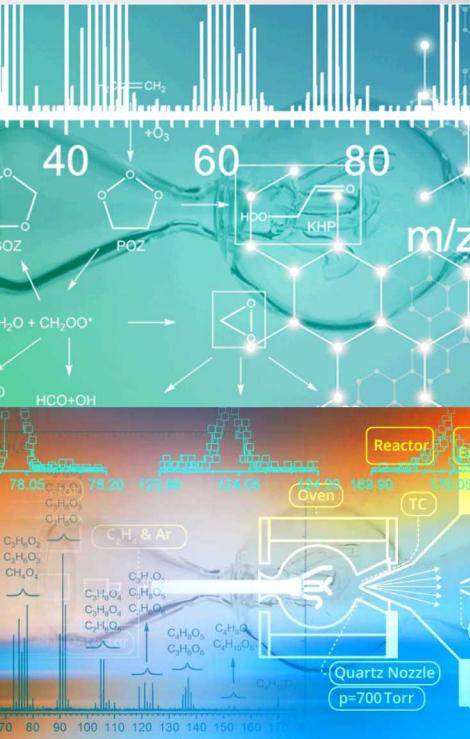
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Outline

- ✓ 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 NO_x , HO_x , intermediate generation and consumption
- ✓ flame chemistry
 - kinetic acceleration of low temperature chemistry
 - laboratory studies of stable cool flames



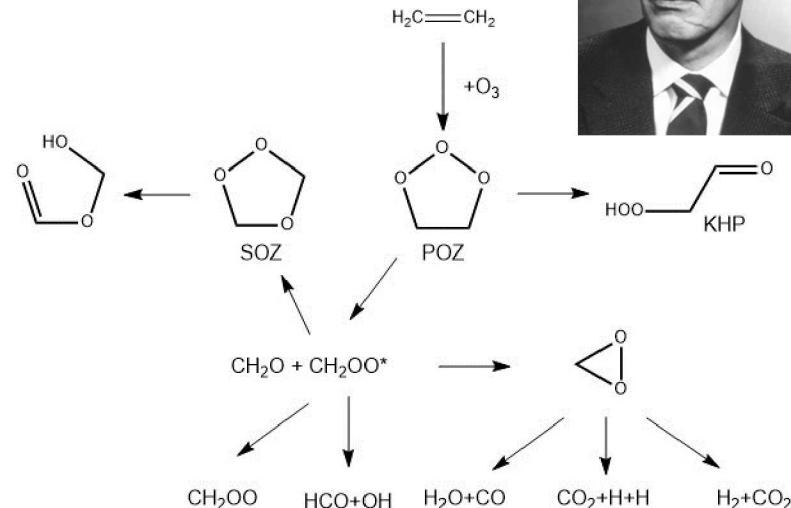
Background Information: Ozonolysis



- ✓ 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 – CH_2OO)
- cyclic secondary ozonide (SOZ)
 - hydroxy-methylformate
- CH_2O_2 either collisionally stabilizes, decomposes or isomerizes

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





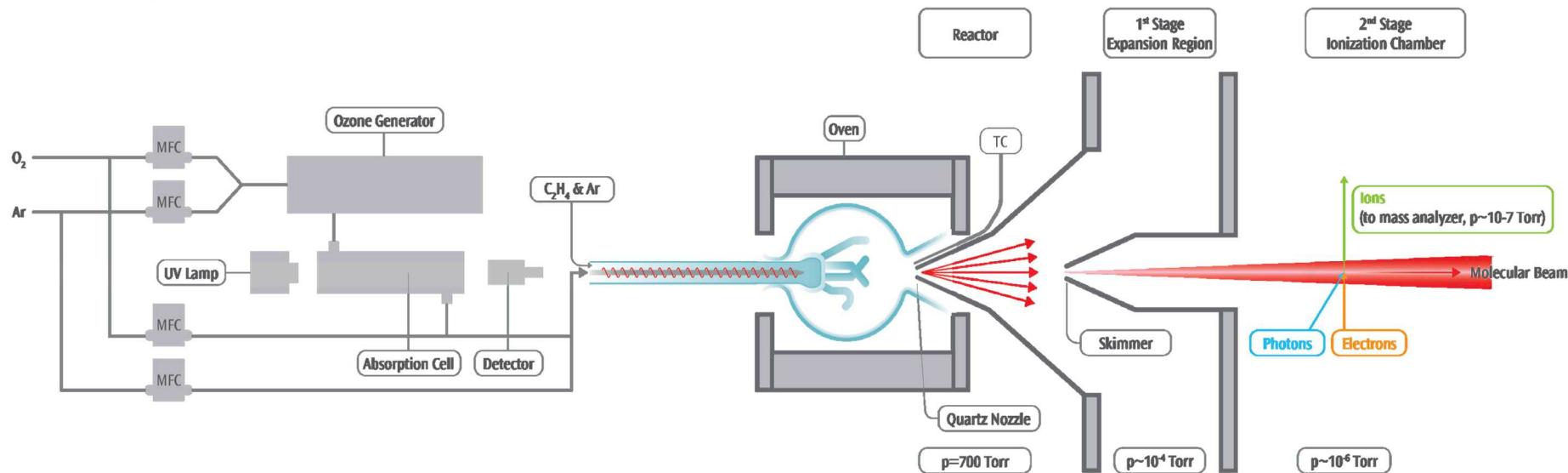
Challenges, Objectives, and Outcomes

- ✓ 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



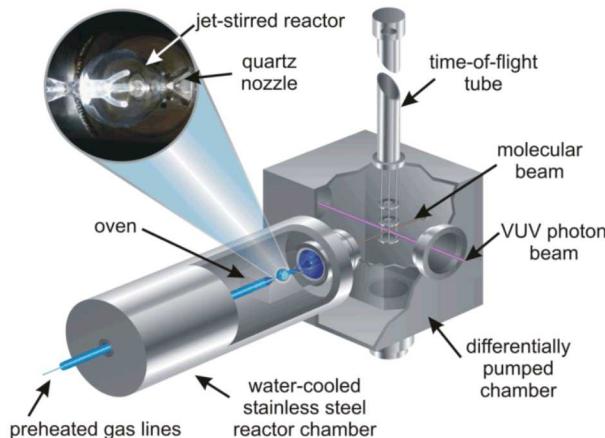
Experimental Details

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

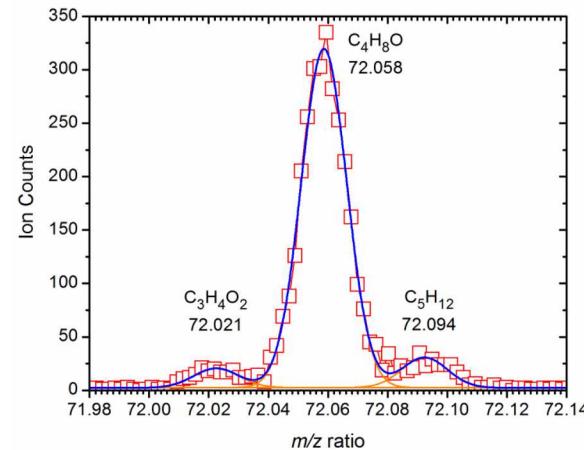


Experimental Details

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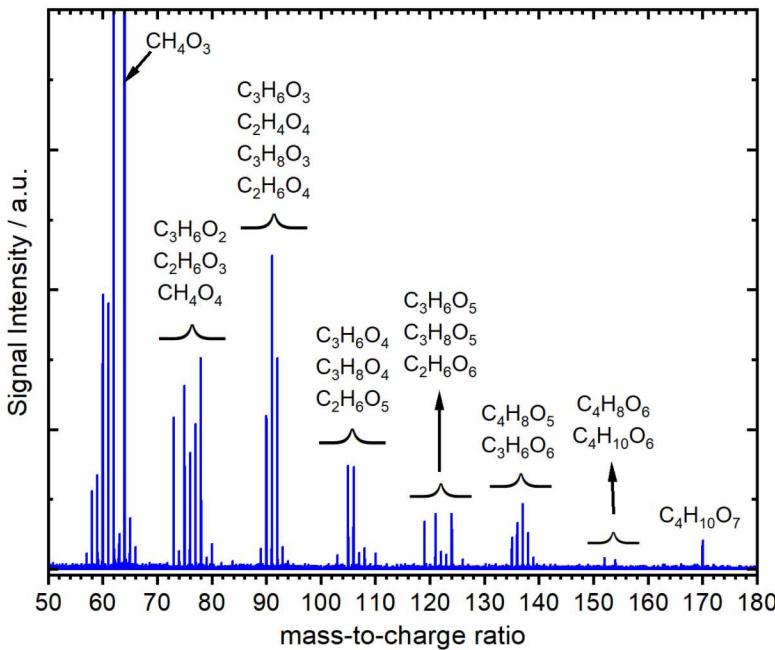


- ✓ orthogonal extraction reflectron time-of-flight
- ✓ detection limit: ~ 0.5 ppm
- ✓ mass resolution $m/\Delta m \sim 4000$
- ✓ electron and photon ionization (at the Advanced Light Source)
- ✓ continuous ionization, rapid (35kHz) ion extraction

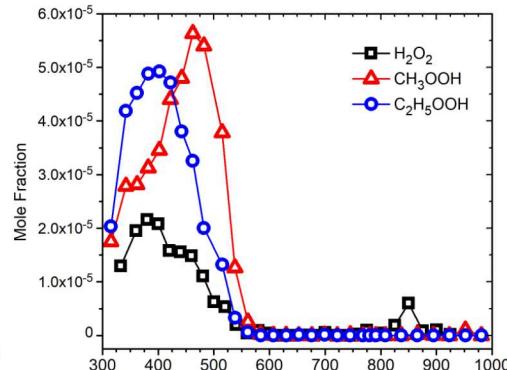
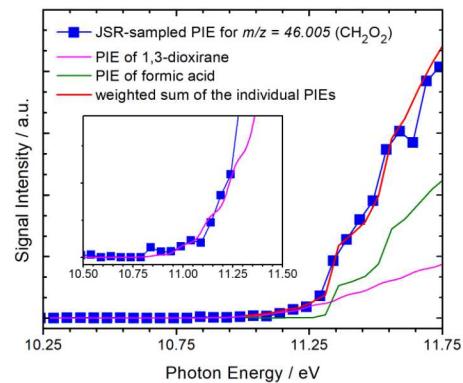


Experimental Details

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

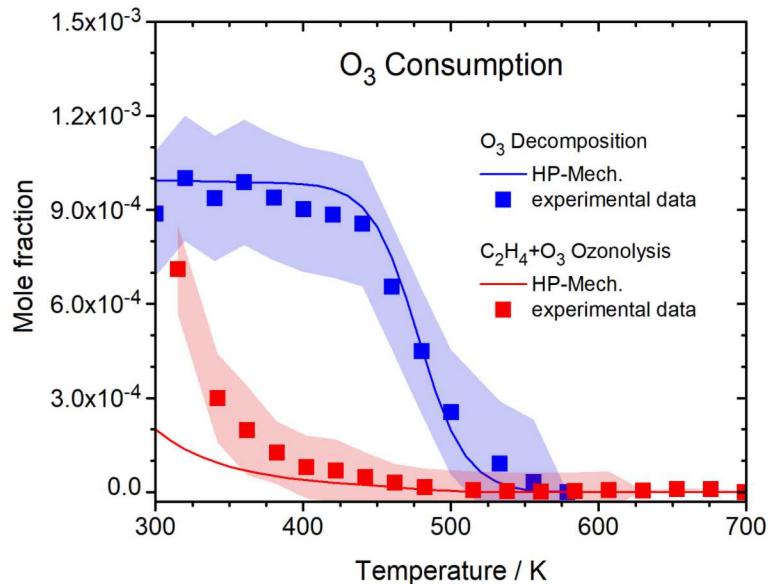


- 2% ethylene, 12% O_2 , and 86% argon ($\phi = 0.5$)
- $p = 0.92$ atm (700 Torr)
- residence time = 1.3 s
- 1000 ppm ozone addition
- $T = 300\text{--}1100$ K

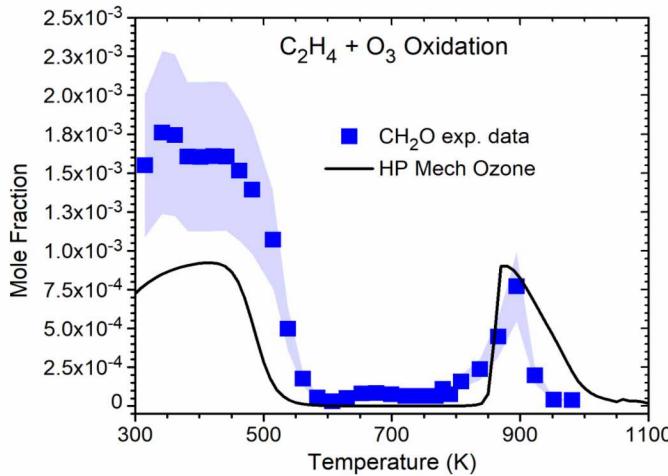
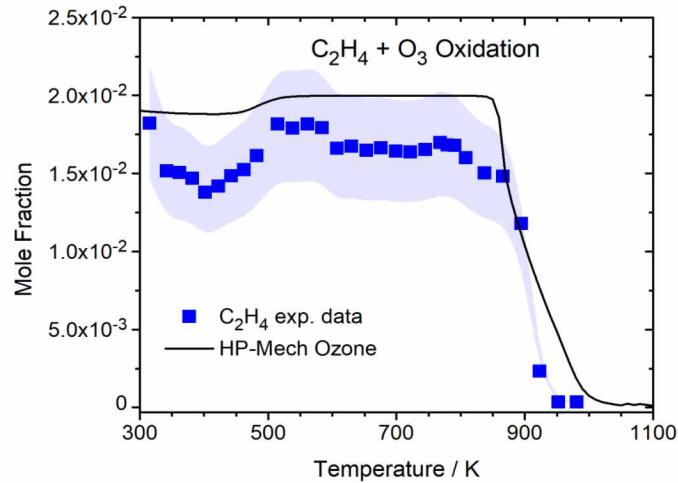


Ozone Thermal Decomposition

- 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



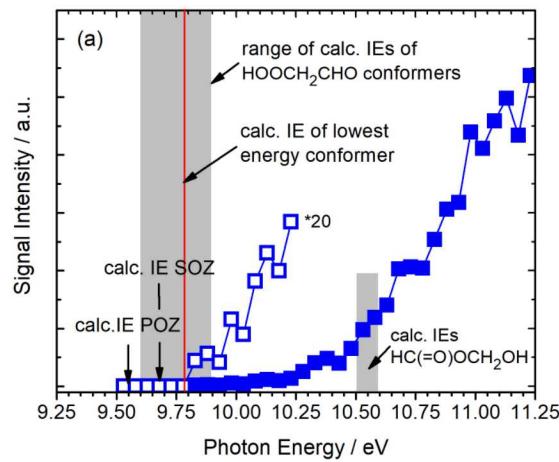
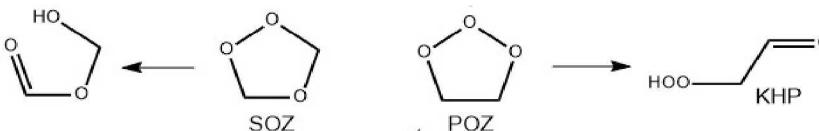
Low-Temperature Oxidation of Ethylene



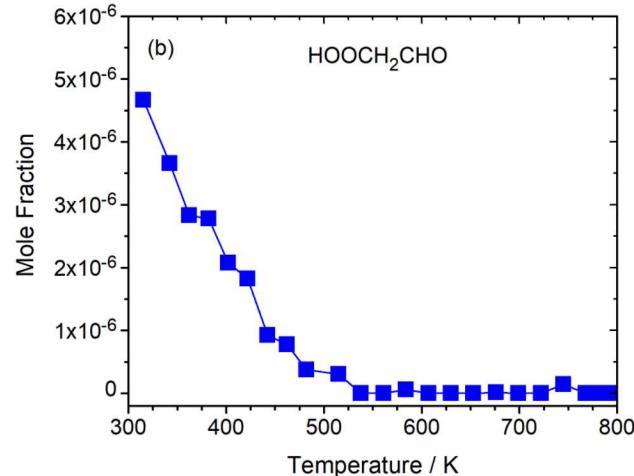
- clear LTC and NTC chemistry regimes, caused by ozonolysis
- model predicts high temperature chemistry fairly well
- IUPAC rates: do well at atmospheric conditions, but clearly missing reactions at higher temperatures
- to understand what is missing, we must identify and verify other species in the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

Low-Temperature Oxidation of Ethylene

Identification of the $\text{C}_2\text{H}_4\text{O}_3$ 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

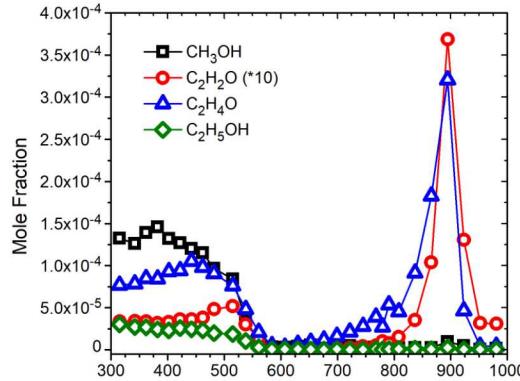
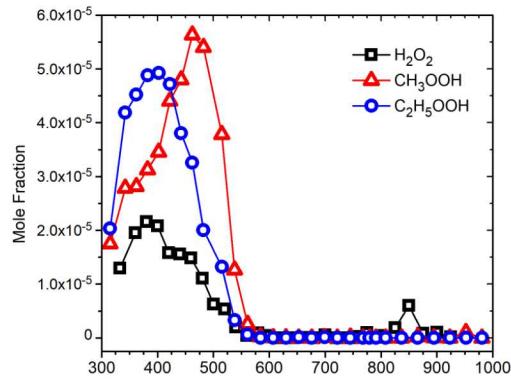


Low-Temperature Oxidation of Ethylene

Oxygenated LTC Intermediates

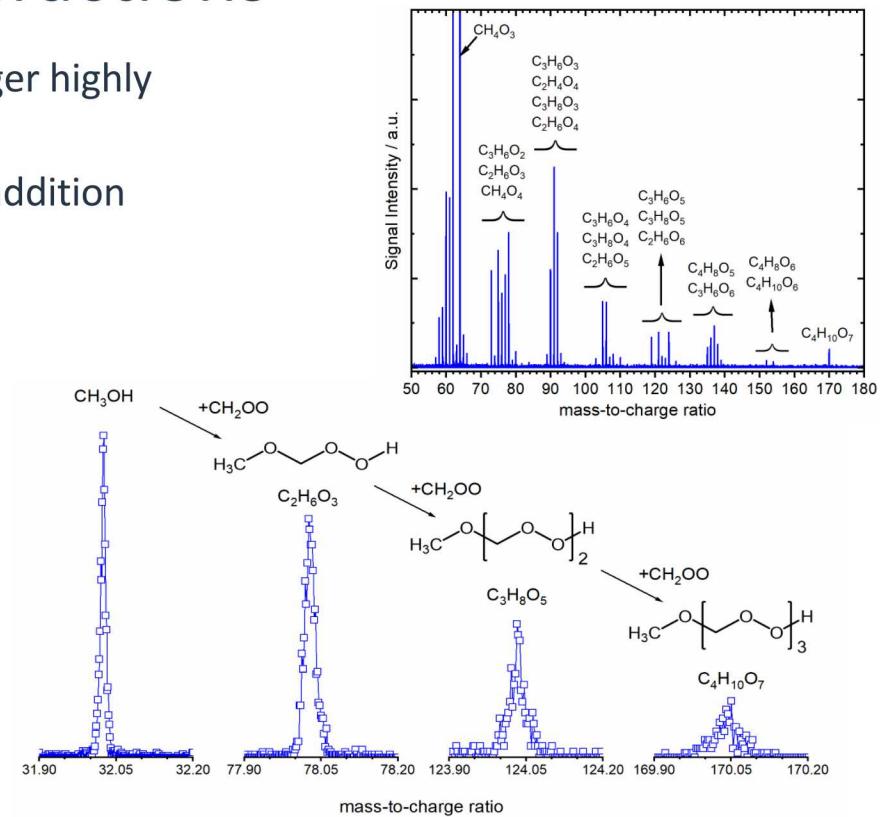
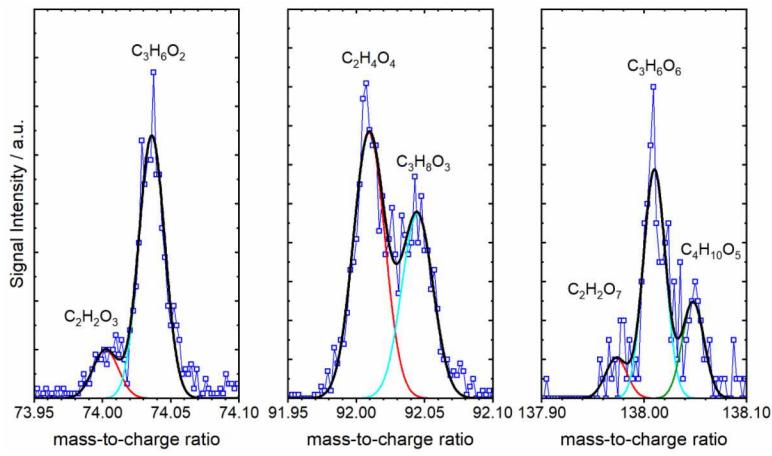
- Major intermediates identified that were either drastically underpredicted or not present in the current model
- Acetaldehyde concentration begins to grow again immediately after the NTC ozone regime
 - Suggestive of O radical chemistry due to ozone thermal decomposition

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



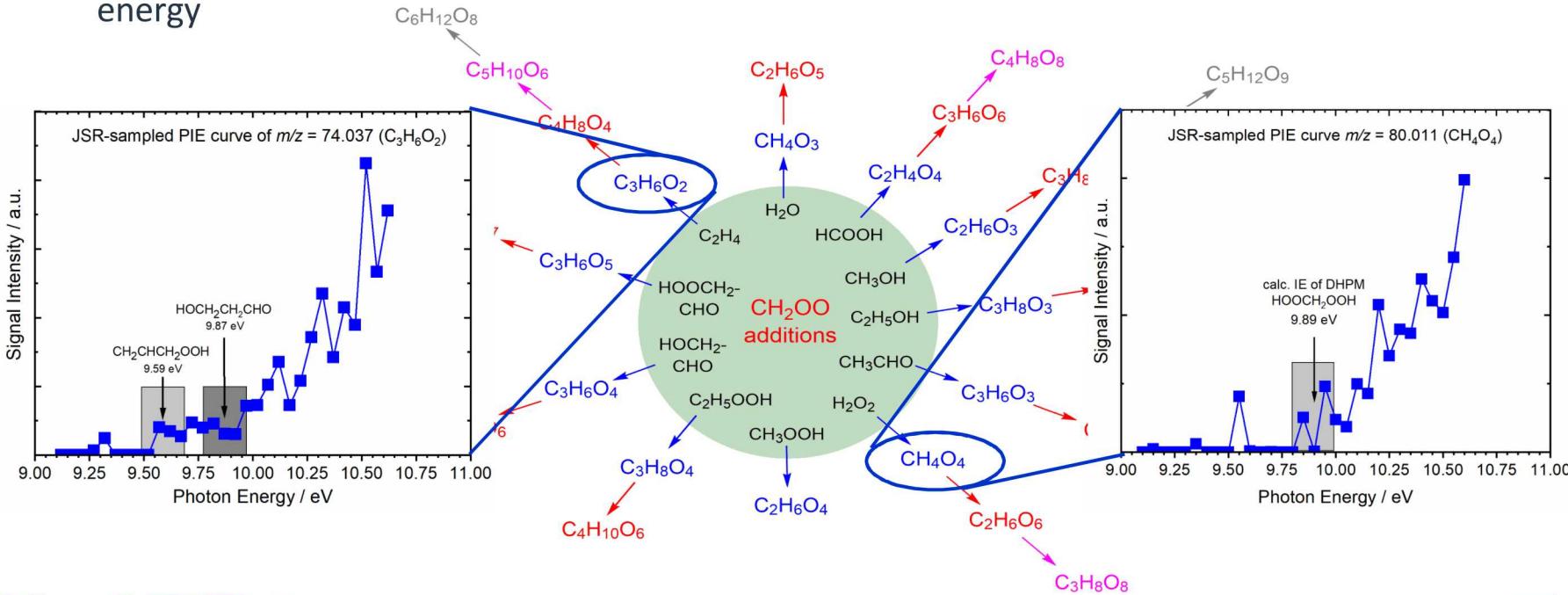
Criegee Intermediate Interactions

- 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 $\text{C}_2\text{H}_4 + \text{O}_3$ 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





Acknowledgements

- ✓ U.S. Department of Defense - National Defense Science & Engineering Graduate (NDSEG) Fellowship program
- ✓ NSF grant CBET-1507358
- ✓ Princeton SEAS innovation fund and ACEE grant.
- ✓ U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists, Office of Science Graduate Student Research (SCGSR) program, administered by the Oak Ridge Institute for Science and Education for the DOE under contract number DE-SC0014664.
- ✓ U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.
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- ✓ The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DEAC02-05CH11231.

