SAND2018-13820C

The Role of Criegee Intermediate + ROOH Reactions towards Secondary Organic Aerosol Formation: Laboratory, Modelling and Field Studies

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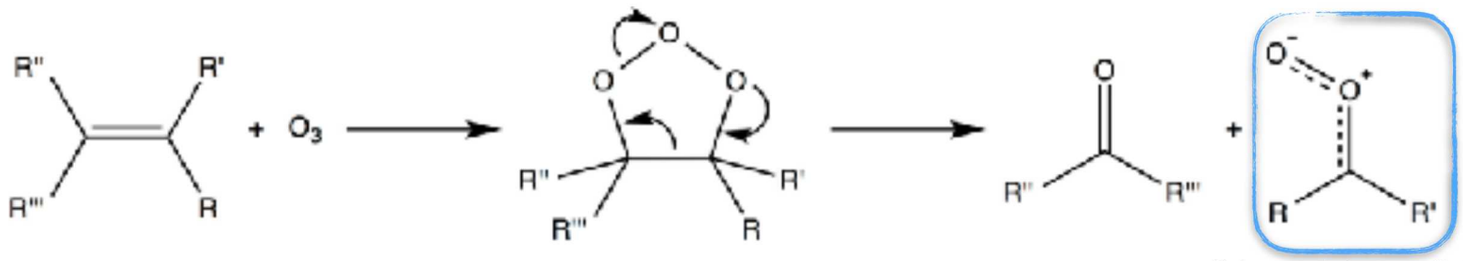
Chemical Sciences Division, Argonne National Laboratories, Lemont, IL, USA

ACM meeting, December 2018

Criegee Intermediates (CI)



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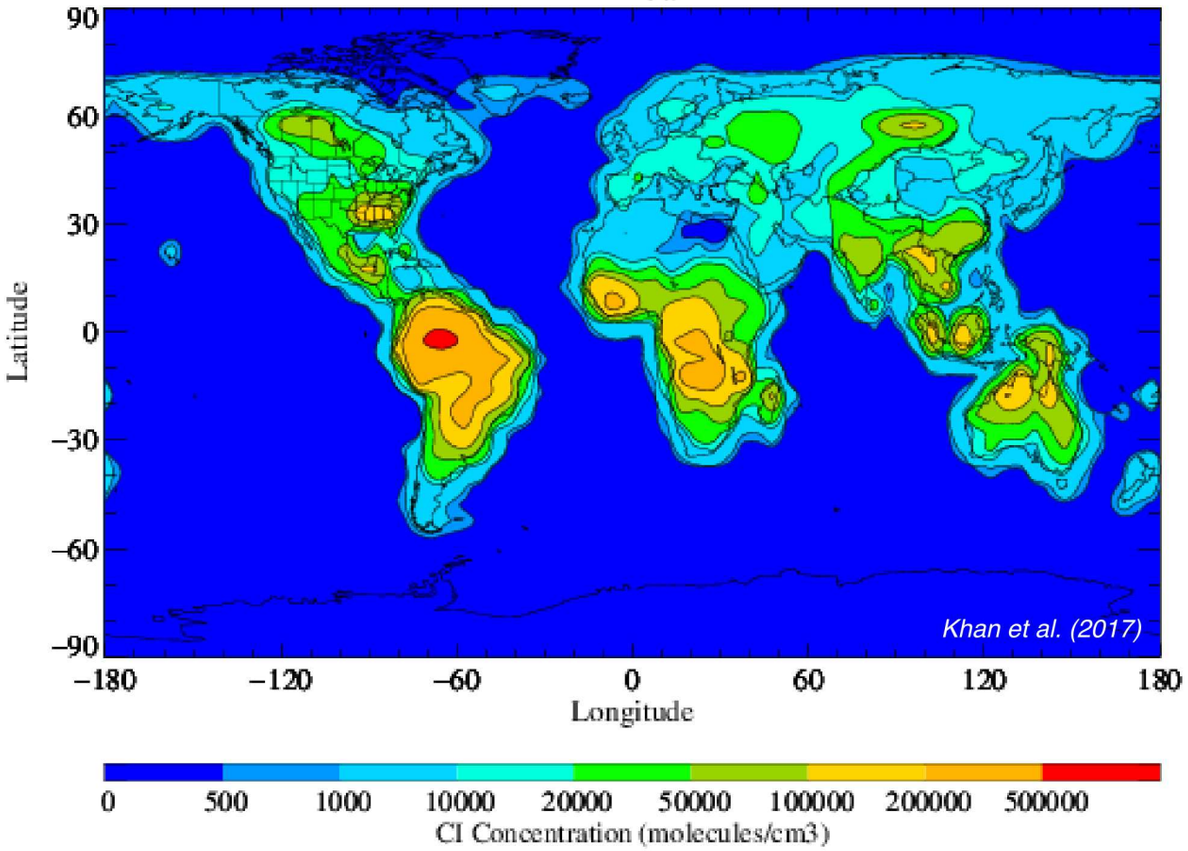
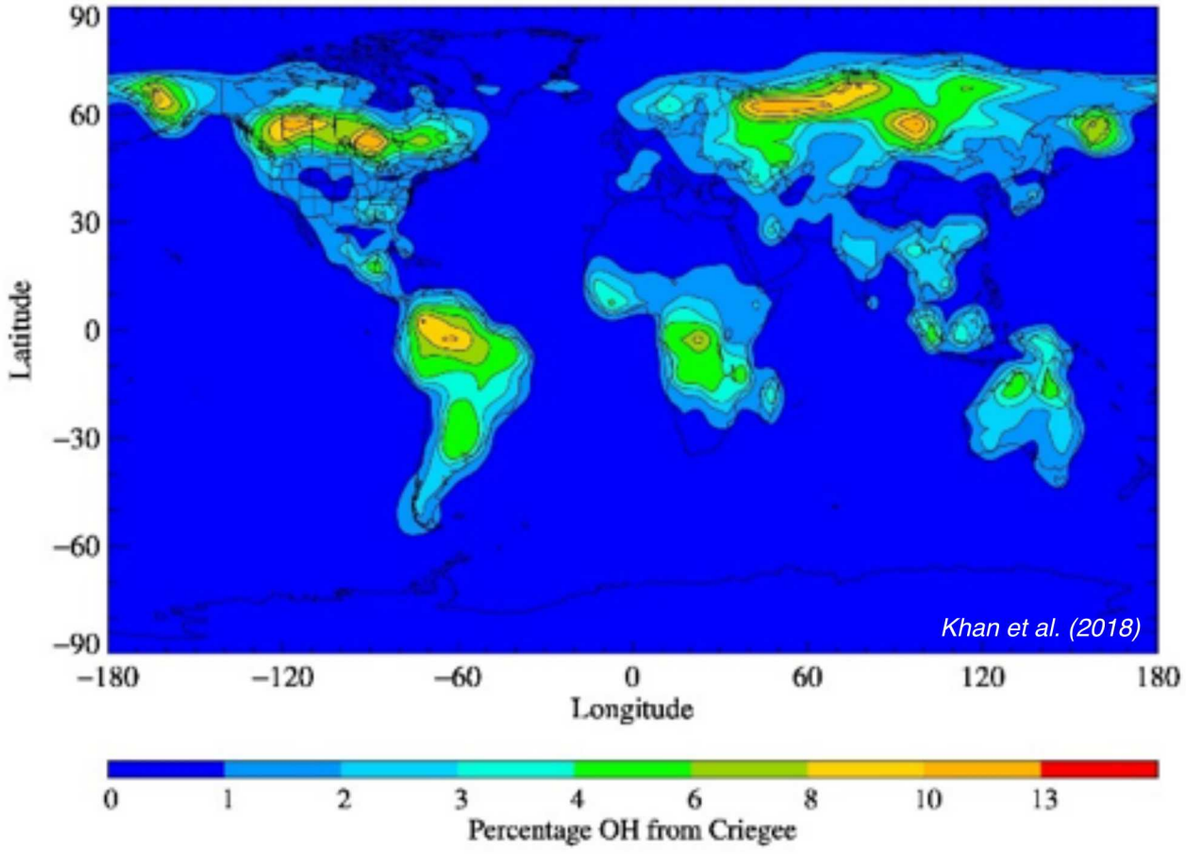
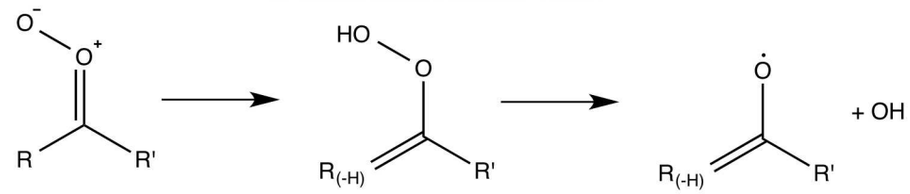


Criegee concentrations highest over amazon rainforest where biogenic alkene emissions are highest





R. Criegee, *Angewandte Chemie International Edition in English*, 1975, 14, 745-752.
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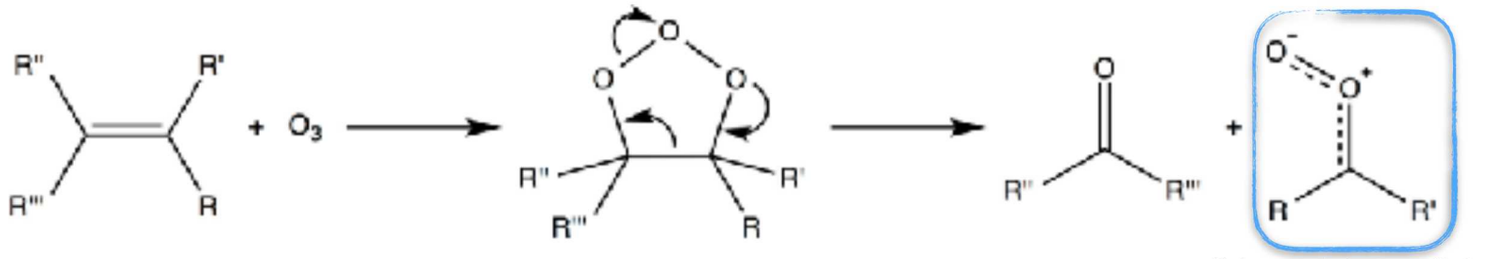

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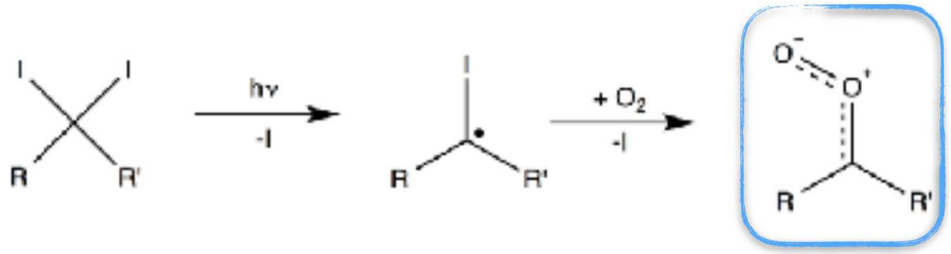

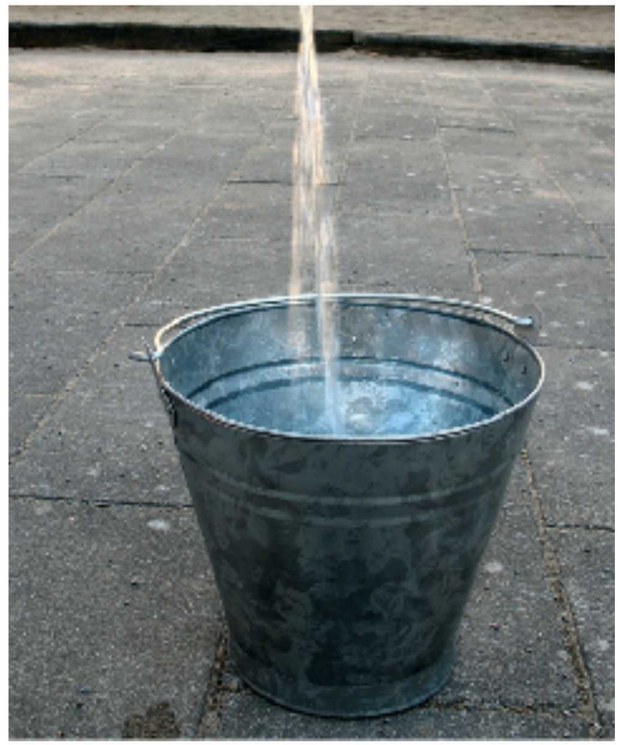

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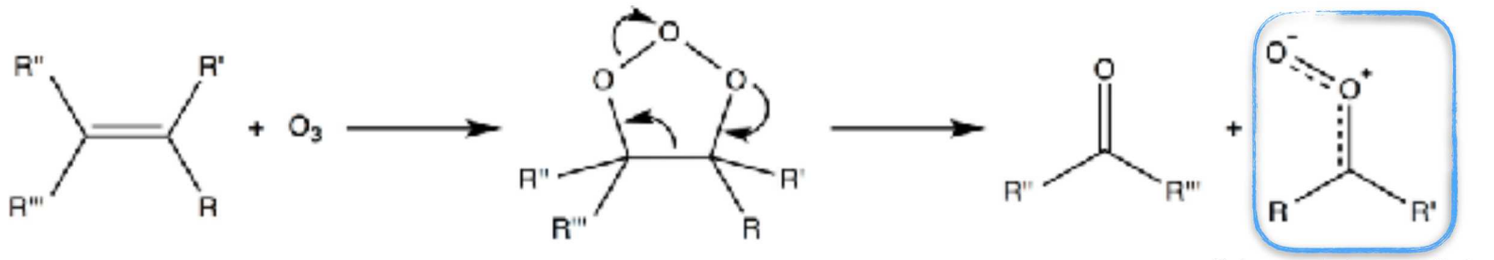

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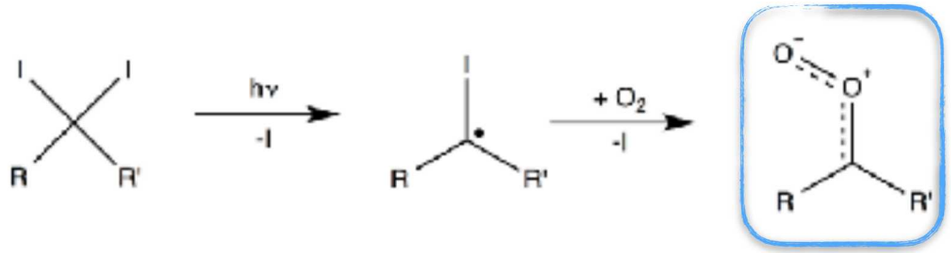
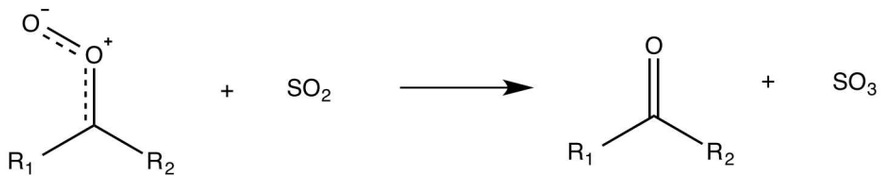
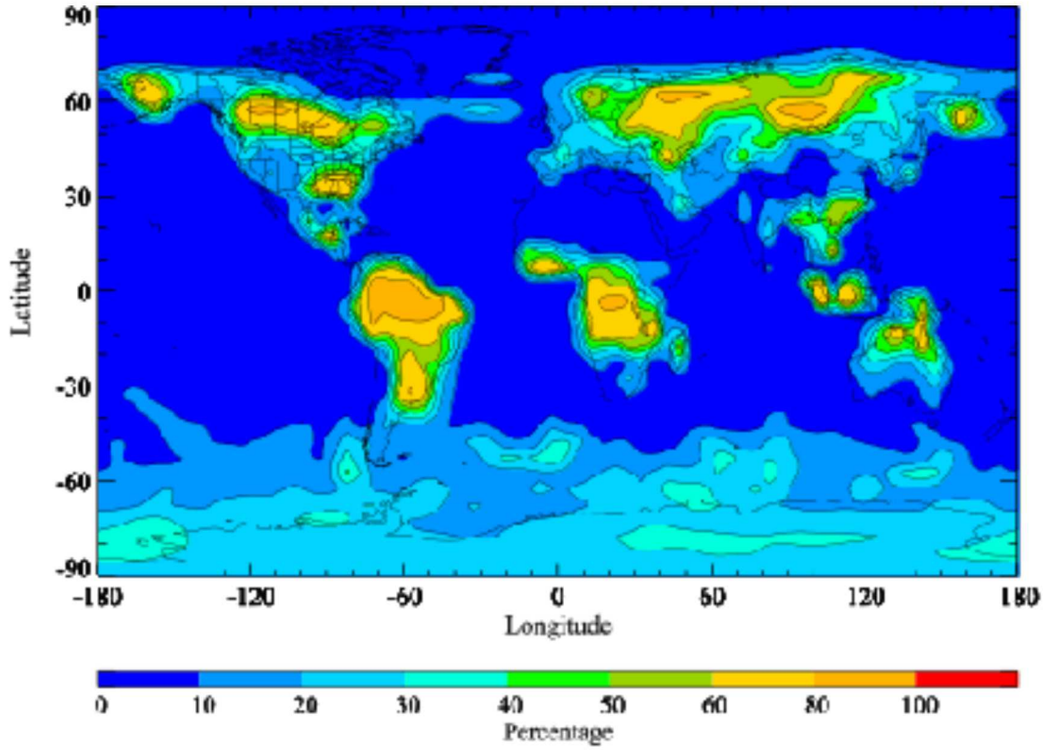


- Direct studies have revealed rapid CI reactivity:
  - i.e./ the reaction of C1-CI + SO_2 (3.4×10^{-11} cm^3 s^{-1}) ***~ 10,000 times faster*** than previously thought.
  - H_2SO_4 precursor → SOA (Cox & Penkett).





% of SO_2 oxidized by Criegee c.f. OH

Can CI reactions can lead to SOA formation ?

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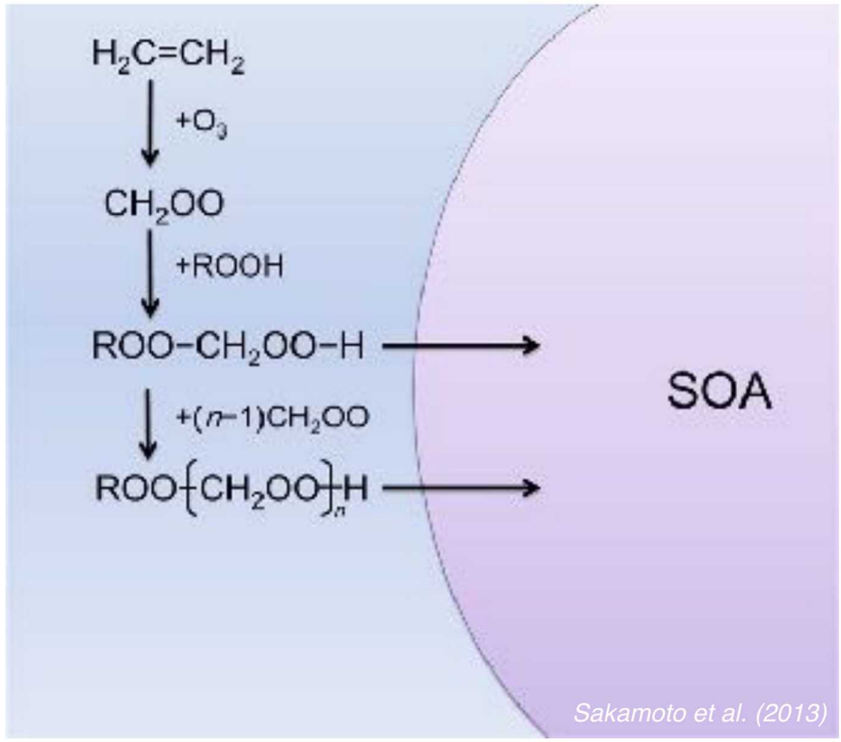

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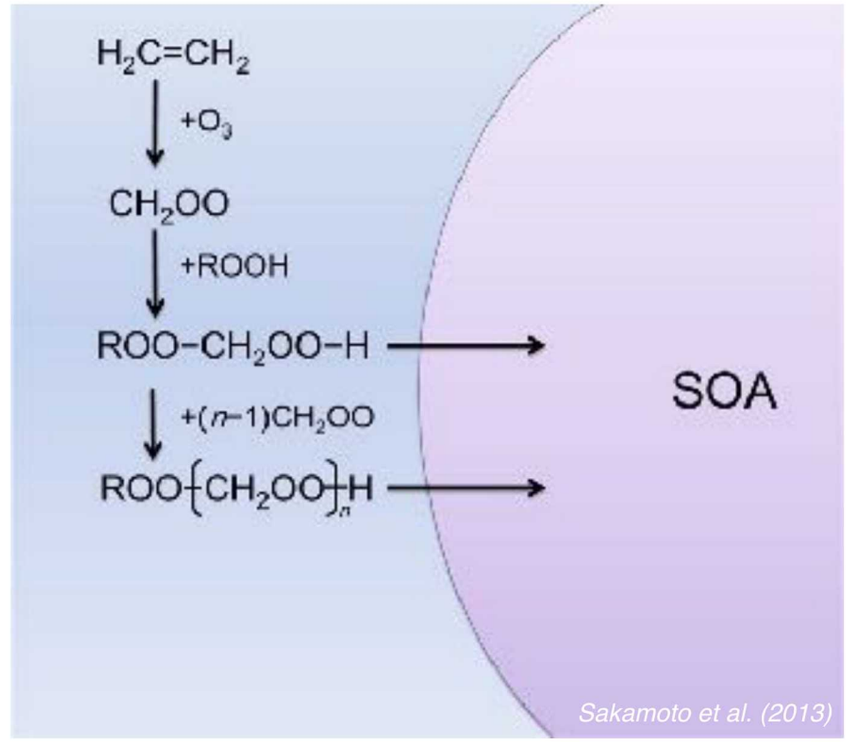

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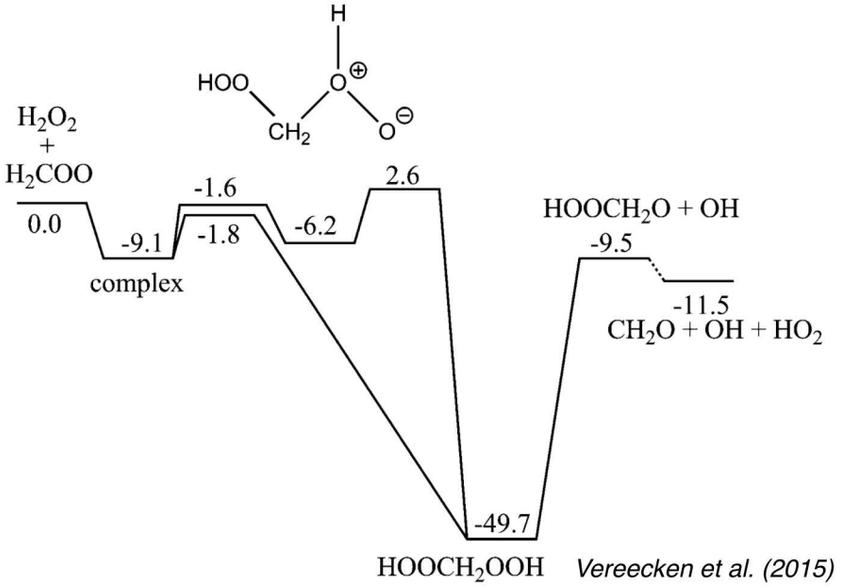

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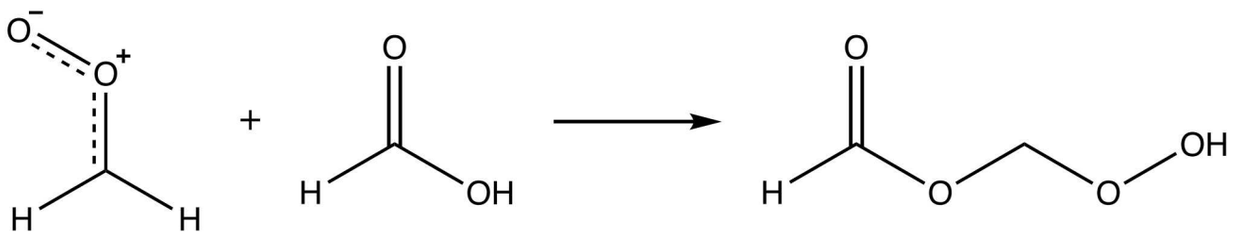

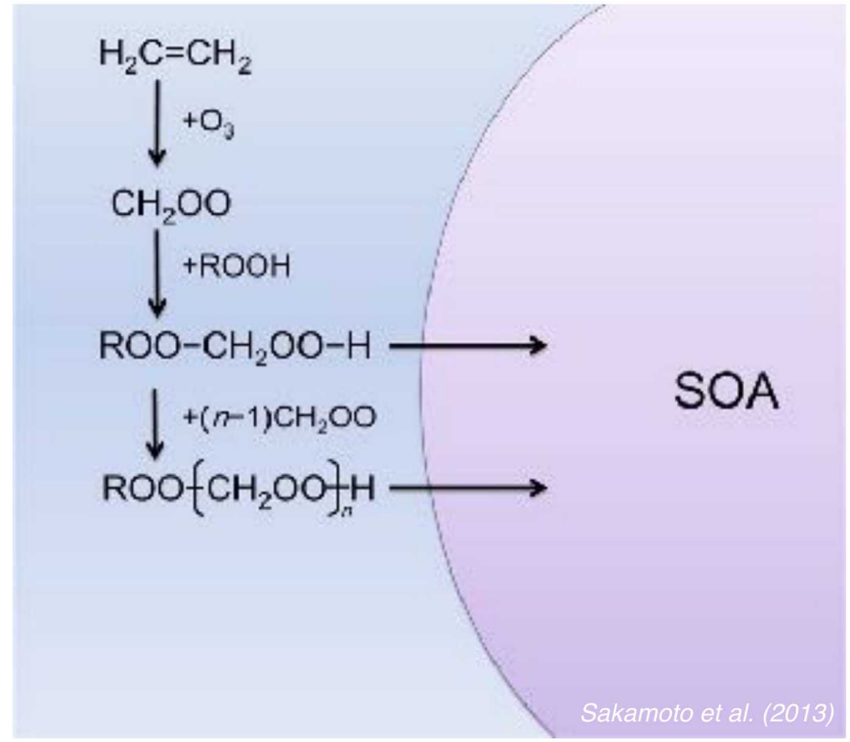

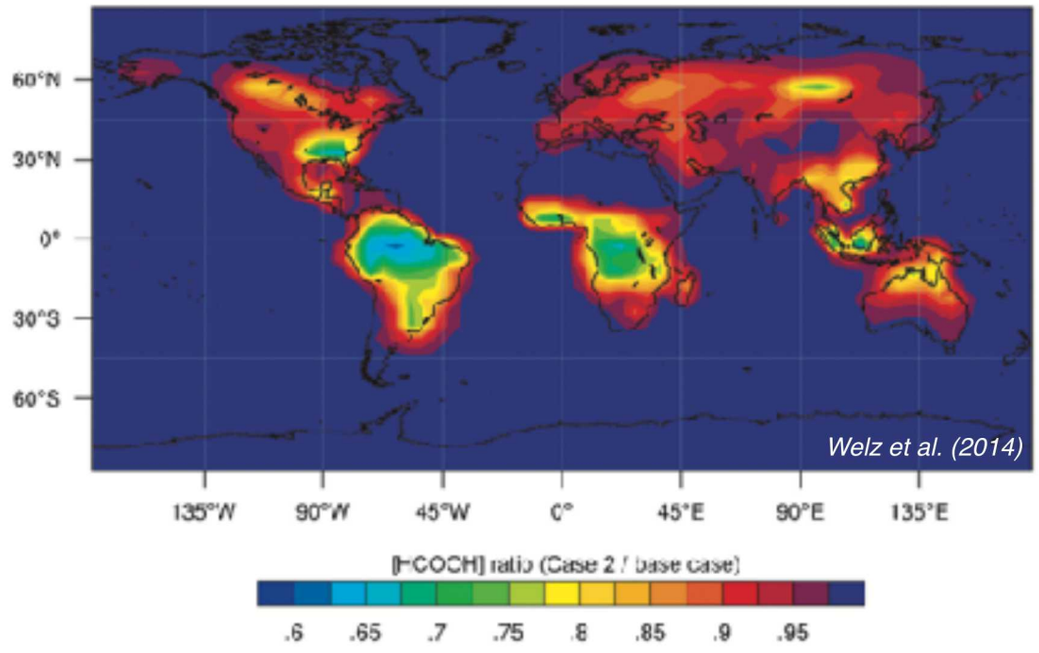

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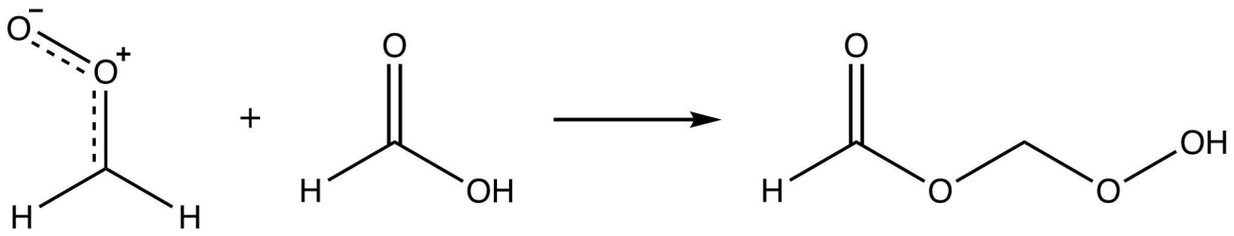
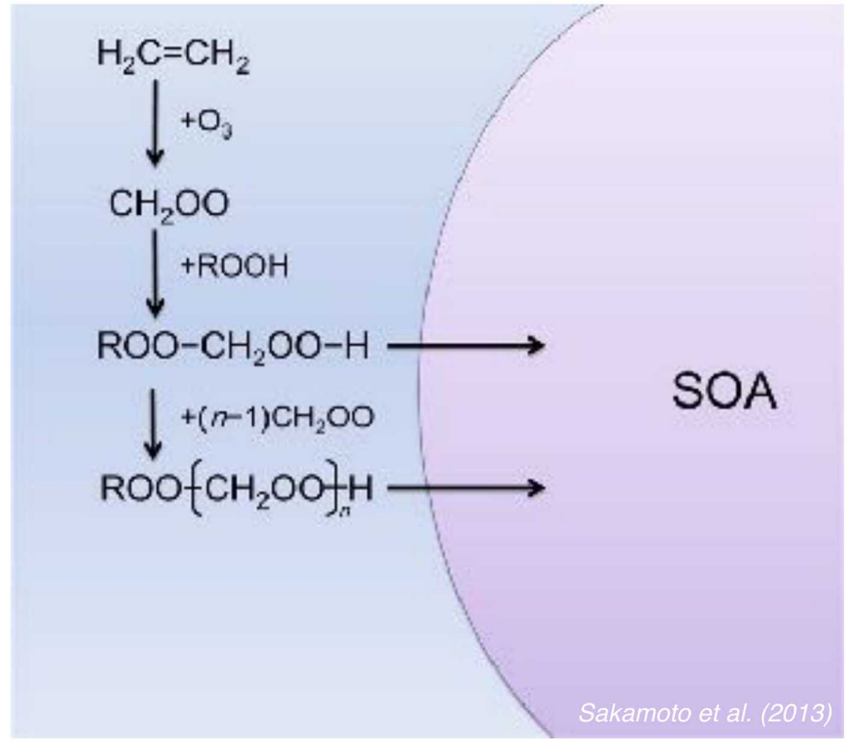
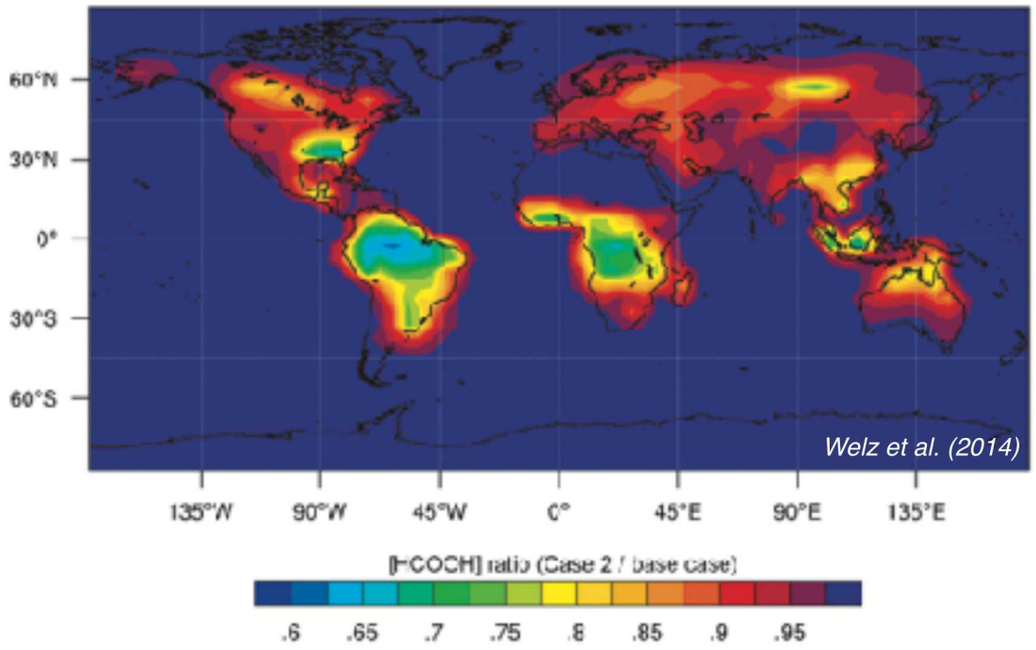


- Could sequential additions of CI into functionalized ROOH lead to high MW, highly oxygenated, low volatility SOA precursors ?





K.S. Docherty, W. Wu, Y. Bin Lam & P. Ziemann, *Environmental Science & Technology*, (2005), 39, 4049-4059.
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A. Sadezky, P. Chaimbault, A. Mellouki, A. Römpp, R. Winterhalter, G. Le Bras, & G.K. Moortgat, *Atmospheric Chemistry & Physics*, (2006), 6, 5009-5024.
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Y. Sakamoto, S. Inomata & J. Hirokawa, *Journal of Physical Chemistry A,* (2013), 117, 12912-12921 .
Q. Zhao, W. Wang, F. Liu, J. Lü, W. Wang, Atmospheric Environment, (2017), 166, 1-8.
L. Vereecken, A.R. Rickard, M.J Newland & W.J. Bloss, *Physical Chemistry Chemical Physics,* (2015), 17, 23847-23858.
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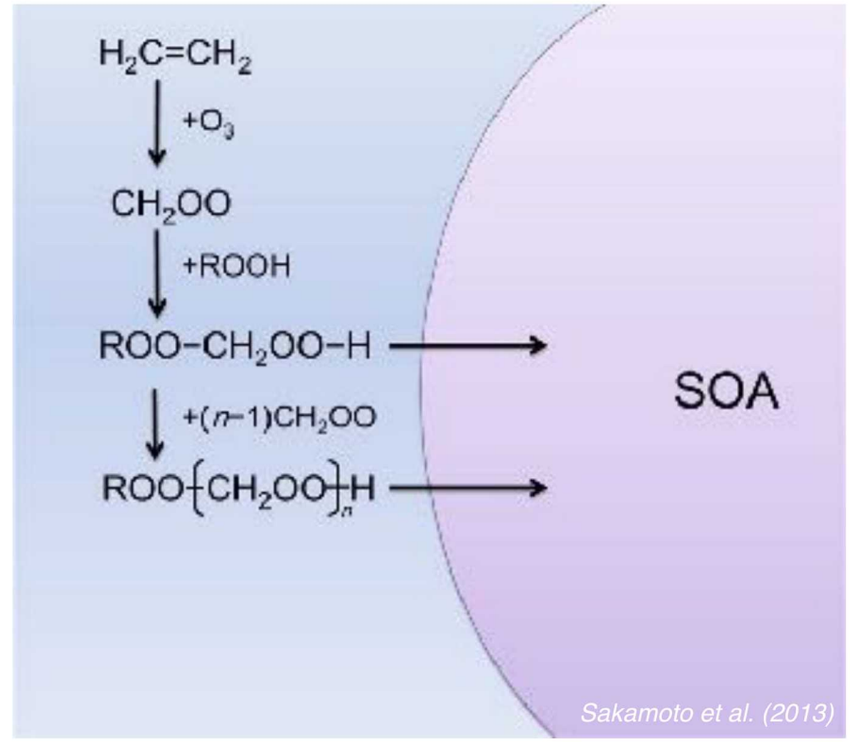
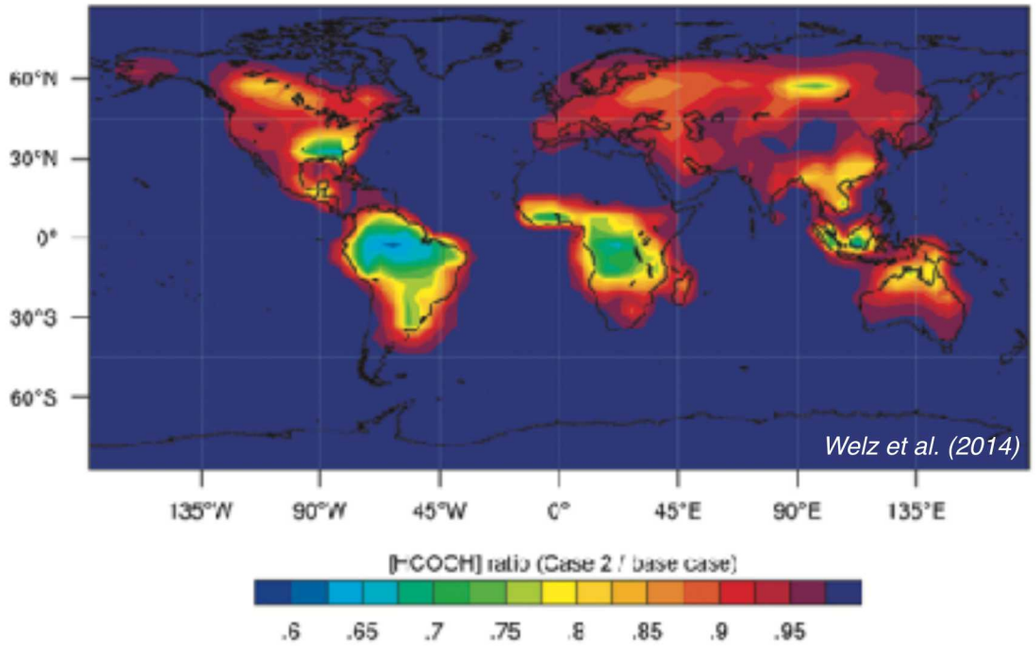
A.C. Rousso,, N. Hansen, A.W. Jasper & Y. Ju, *Journal of Physical Chemistry A,* (2018), 122(43), 8674-8685.

HOM from Criegee Intermediate reactions ?

- ROOH determined to be significant component of SOA (i.e. Docherty *et al.*, *Bonn et al.*)
- CI reactions leading to ROOH production implicated in the formation of SOA (Sadezky *et al.*, Sakamoto *et al.*)
  - i.e./ Ozonolysis of ethene: ***SOA suppressed in the presence of CI scavenger. CI-based oligomers observed in the gas + particle phase***. (Sakamoto *et al.*)
  - ***Sequential addition of CI into ROOH proposed → SOA***
- Rate and yield of CI insertion into O-H bond of ROOH calculated to be structure dependent:
  - CH_2OO + HOROOH $k \sim 1 \times 10^{-11}$ cm^3 s^{-1} (Zhao *et al.*)
  - $CH_2OO + H_2O_2$ $k \sim 3 \times 10^{-13}$ cm^3 s^{-1}, $CH_2OO + CH_3OOH$ $k \sim 6 \times 10^{-12}$ cm^3 s^{-1} (Vereecken *et al.*)
    - Ether oxide and organic hydroperoxide products predicted - yields dependent on ROOH and CI structure.
- ***Functionalized organic hydroperoxides also formed from CI + acid reactions.***
  - CH_2OO + formic acid. $k = 1.1 \times 10^{-10}$ cm^3 s^{-1} (Welz *et al.*)
  - Formic acid removal enhanced by up to 40% by reaction with CI.





Examine the initial steps towards SOA formation via:

(1) Direct (photolytic) generation of CI: Targeted study of reactions with characteristic ROOH (H_2O_2, tbhp) (MPIMS, time-resolved)

(2) Ozonolysis generation of CI (O_3 + ethene): Study of subsequent reaction products (JSR, steady-state) - Nils Hansen, Sandia (Rousso *et al.*)

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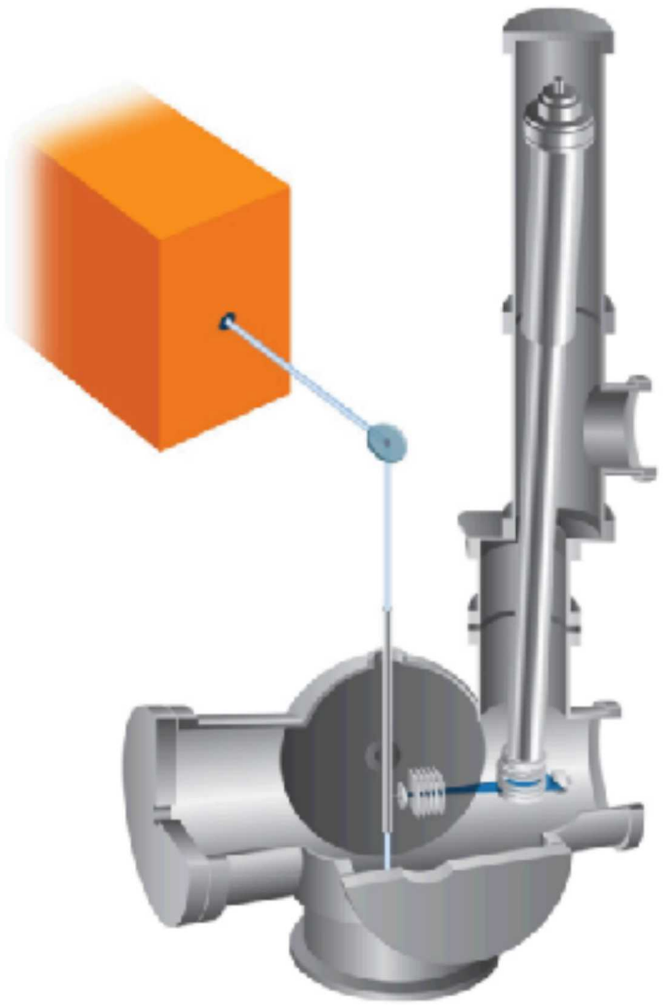
3D datasets from MPIMS

- Halocarbon wax coated quartz reactor - typical operating conditions of ~1-40 Torr, 300-373 K.



3D datasets from MPIMS

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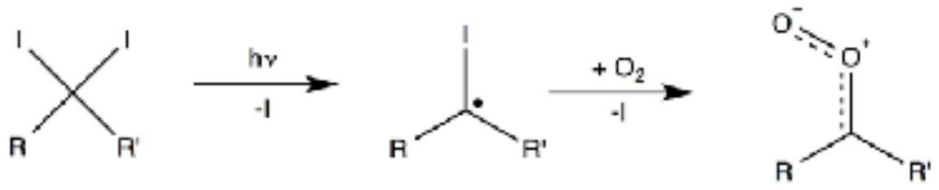

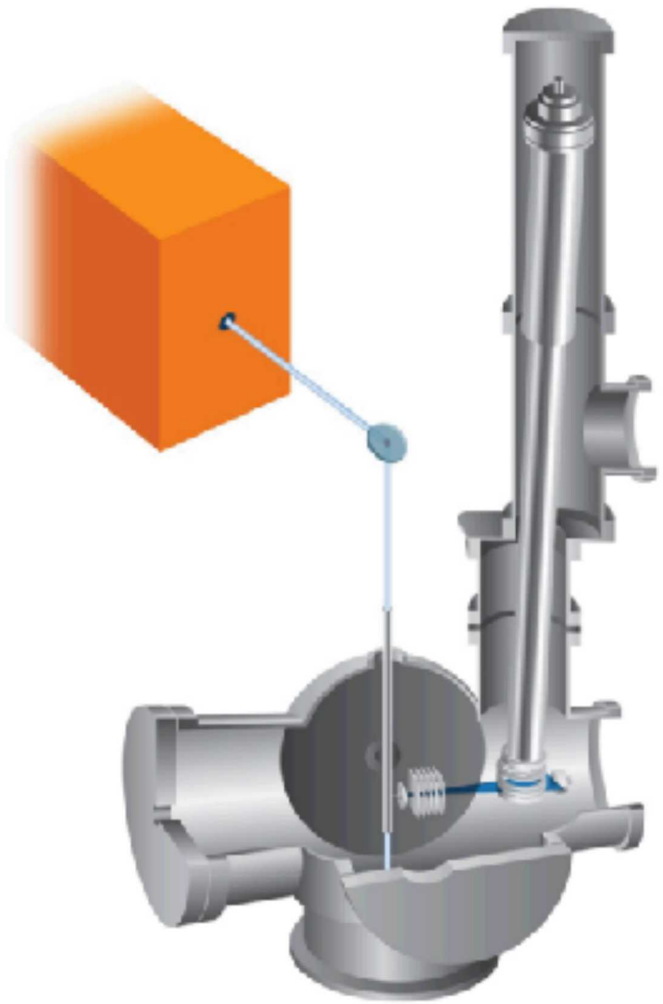

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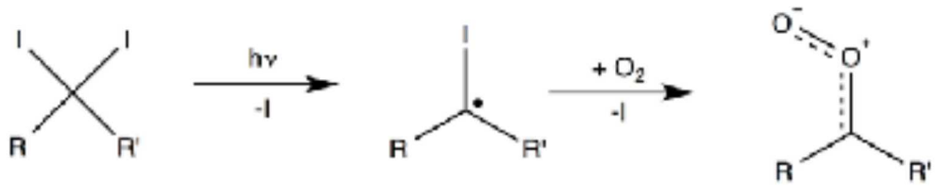

- Reactants, intermediates and products are continuously sampled via small pinhole in side wall of quartz reactor.
- Gas enters ionization region via skimmer where it is intercepted by VUV radiation.
- Ions are subsequently detected via orthogonal-acceleration TOF mass spectrometry - can see all masses at once.

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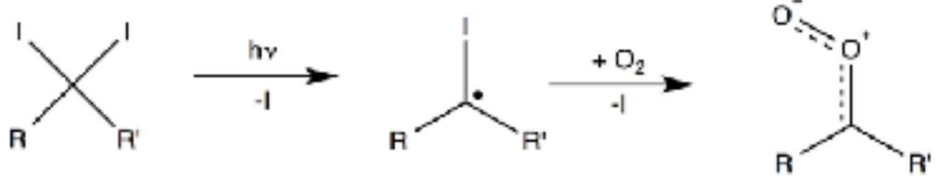

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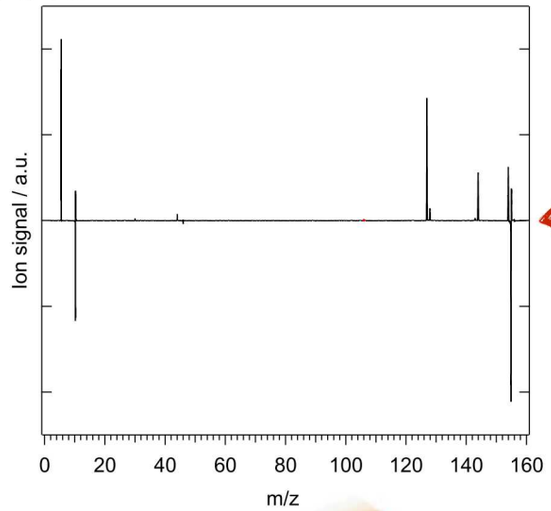

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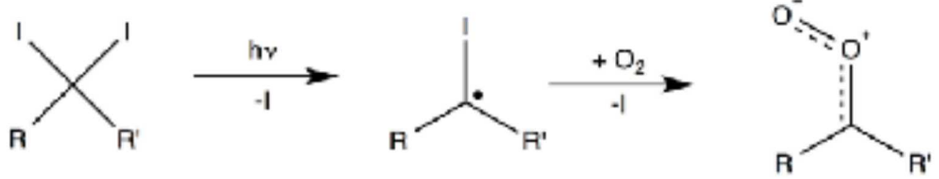

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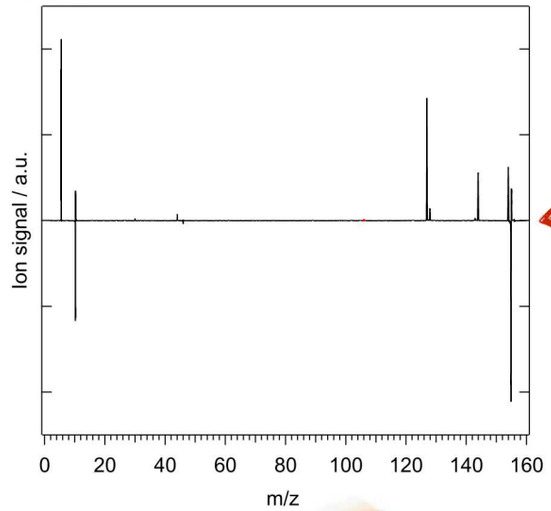

1. *High resolution mass spectra (TOF-MS)*

3D datasets from MPIMS

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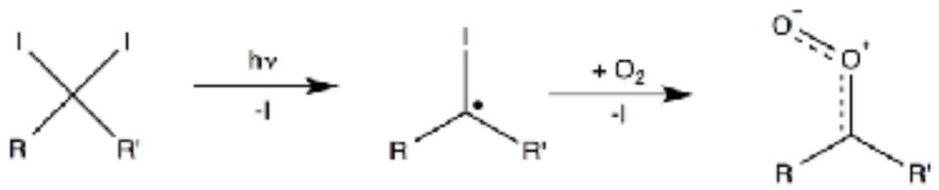

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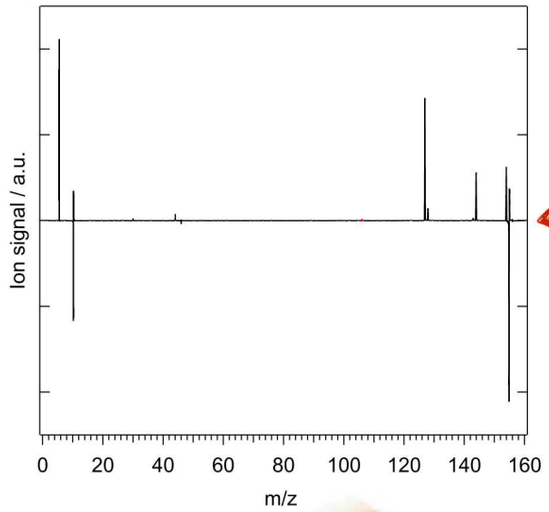
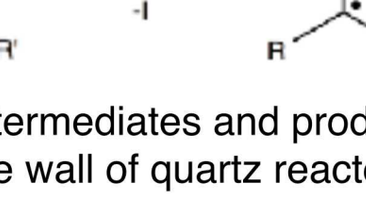
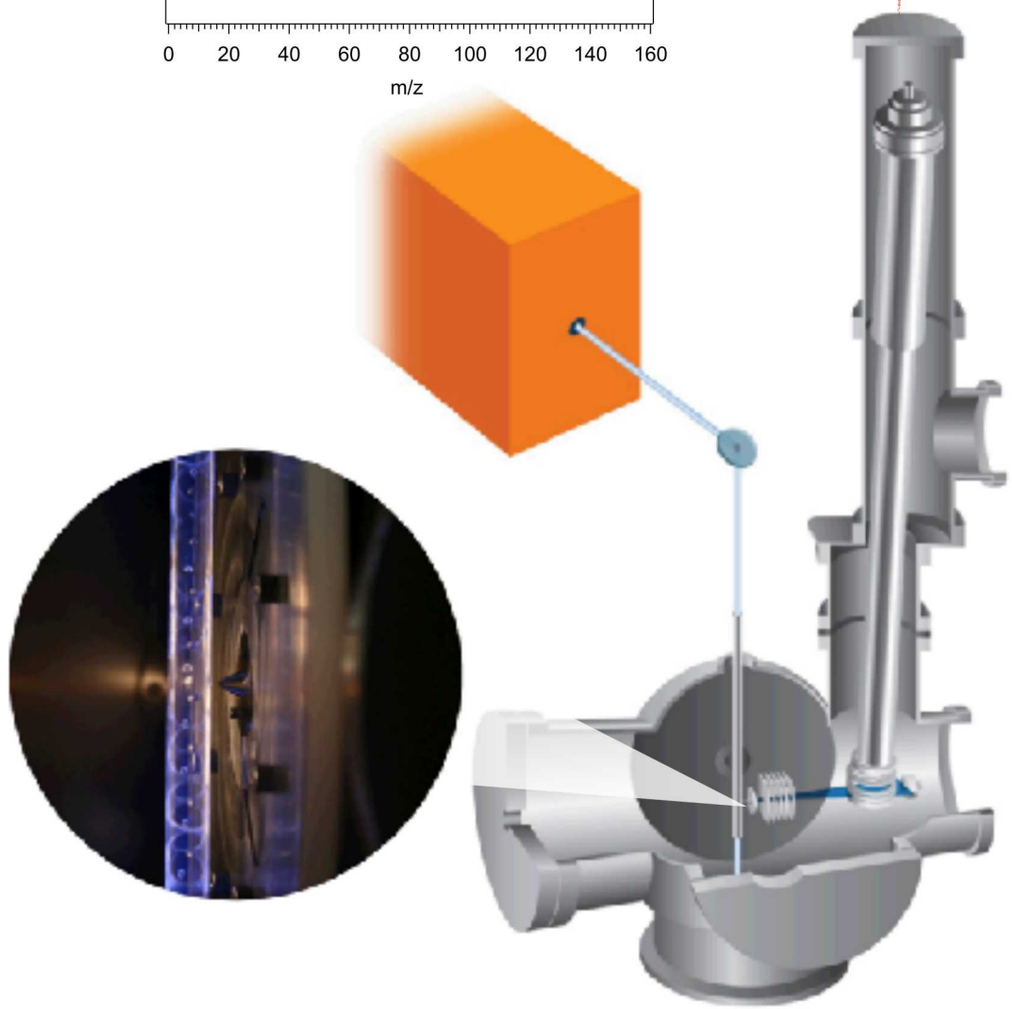


1. *High resolution mass spectra (TOF-MS)*
2. *Time resolved detection (photolysis laser + flow-tube)*





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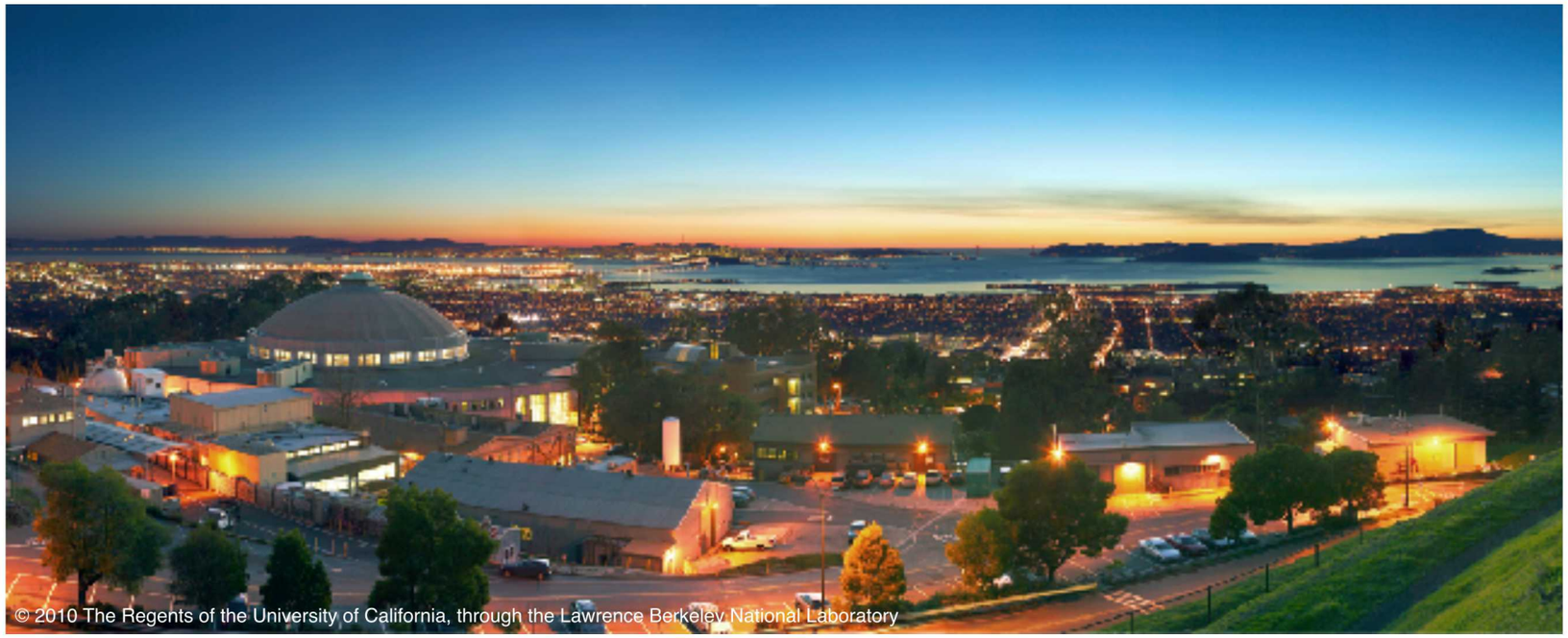

1. *High resolution mass spectra (TOF-MS)*
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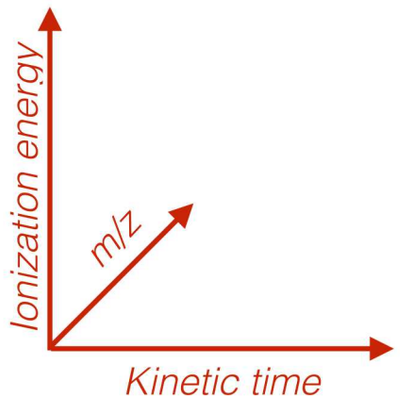
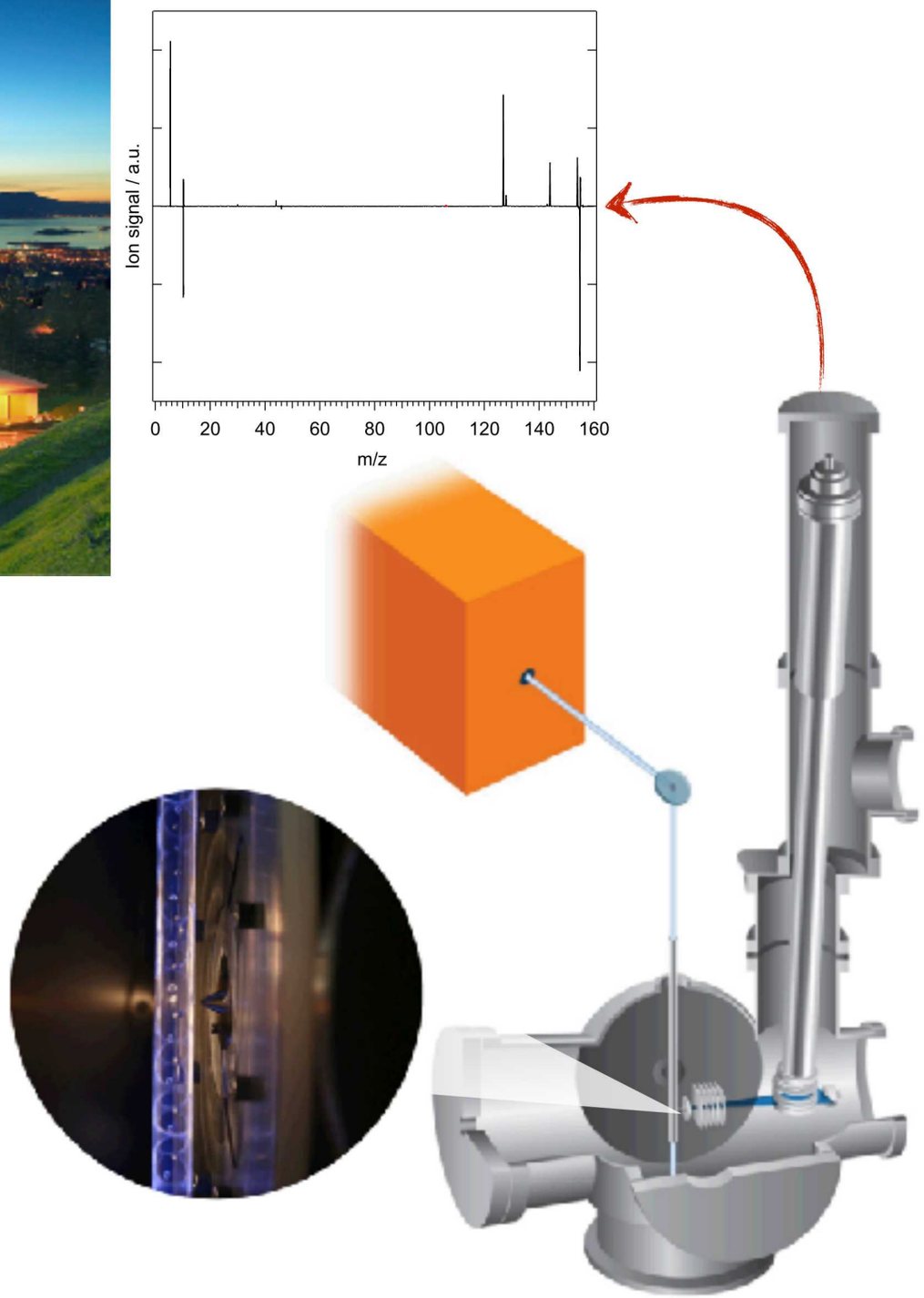
3. *Spectroscopy using tunable VUV (synchrotron - Advanced Light Source, LBL)*





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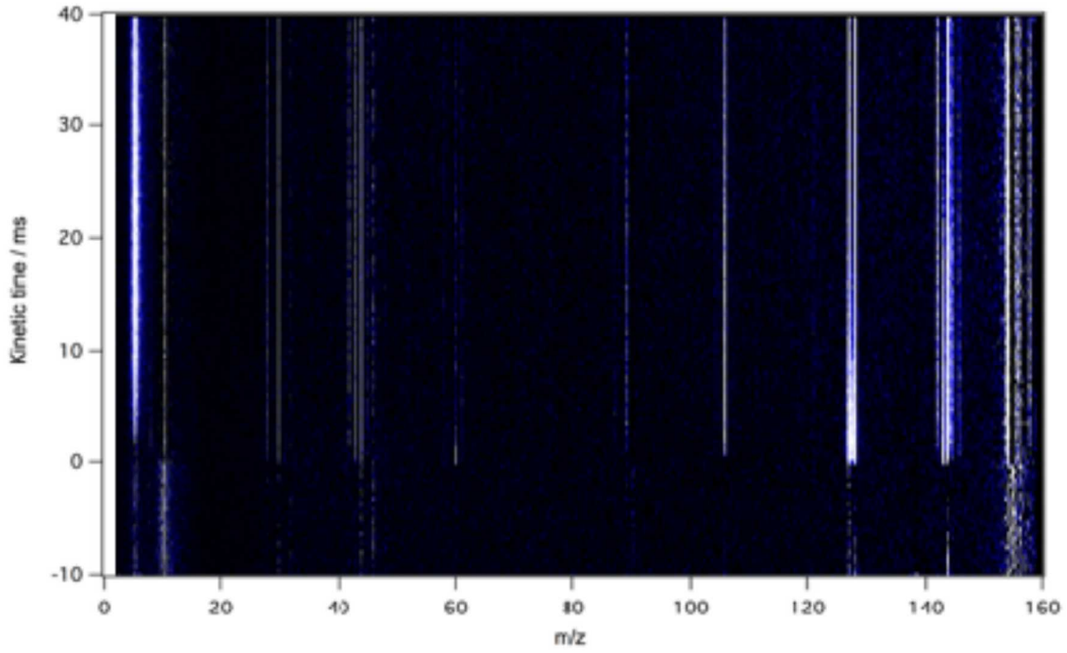
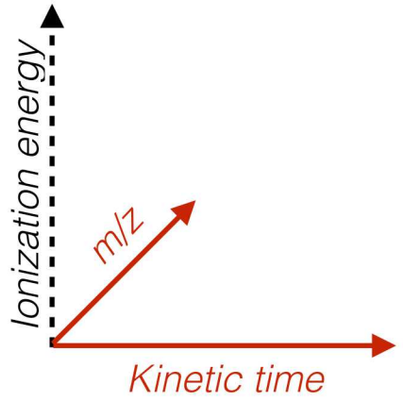
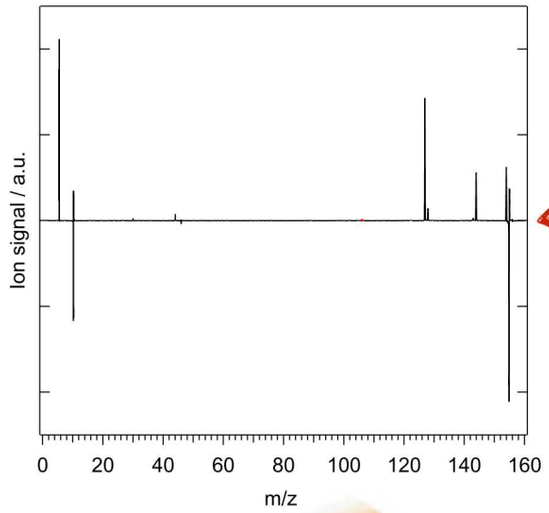
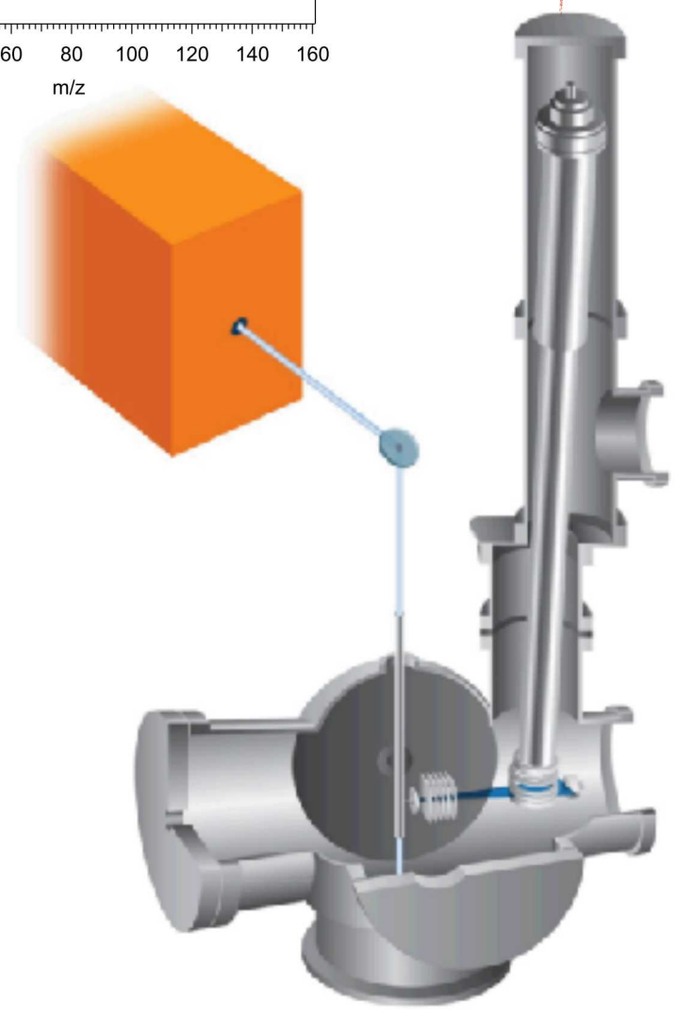
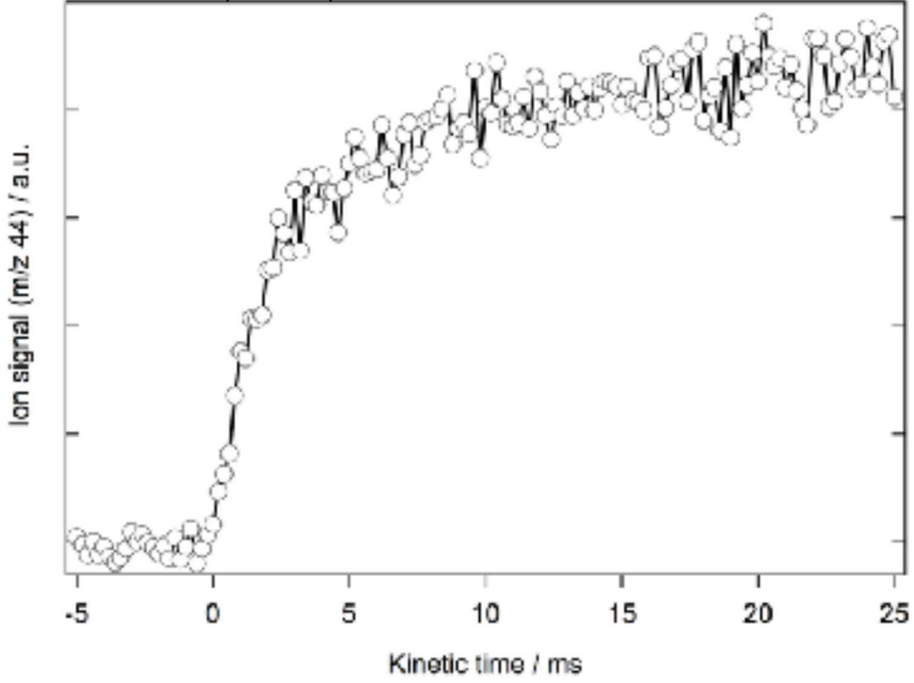




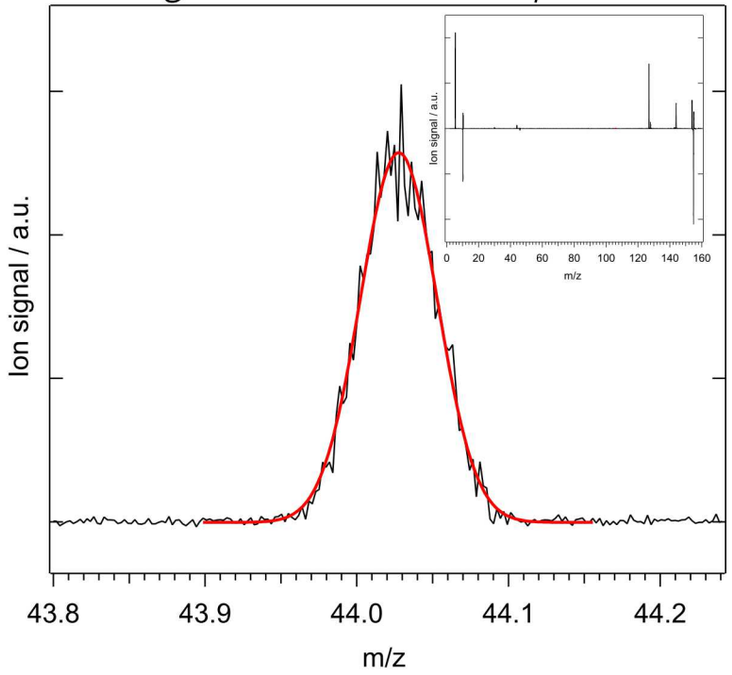




Temporal profiles: Kinetic information



High resolution mass spectra



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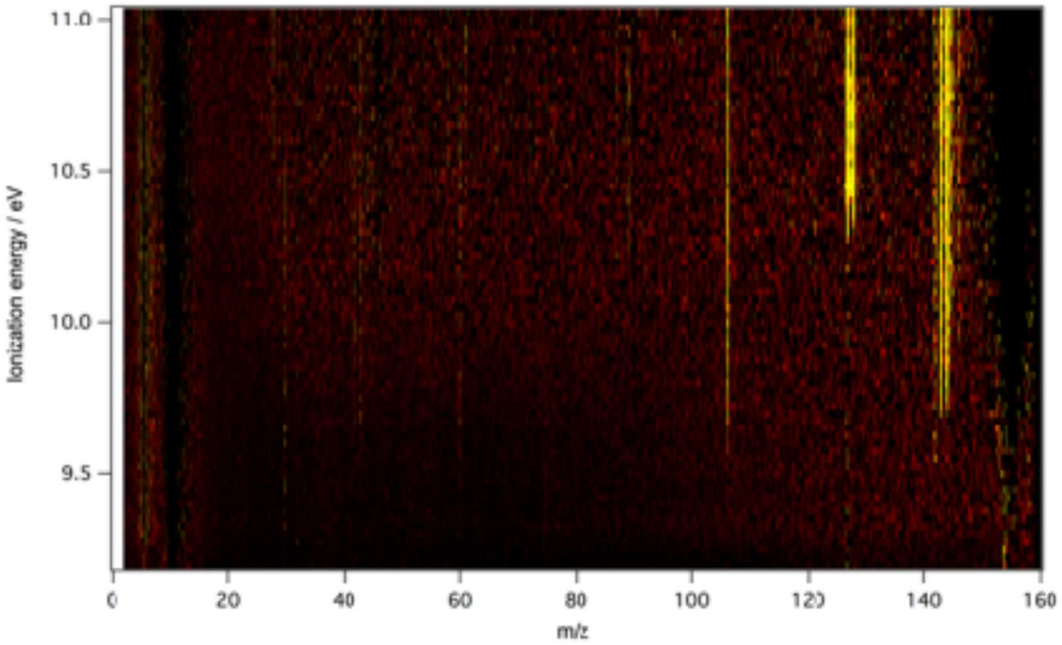
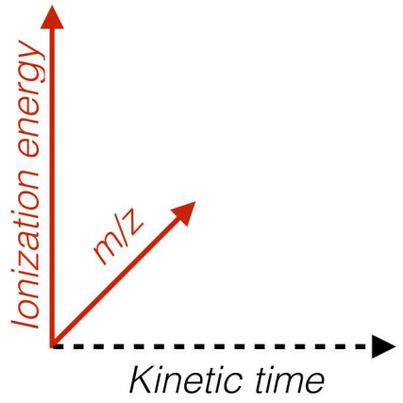
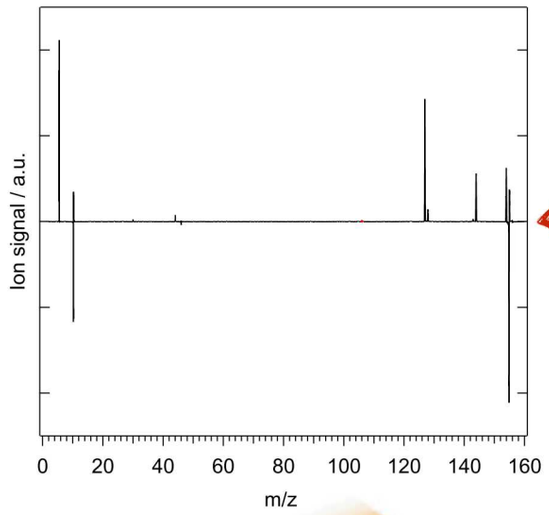
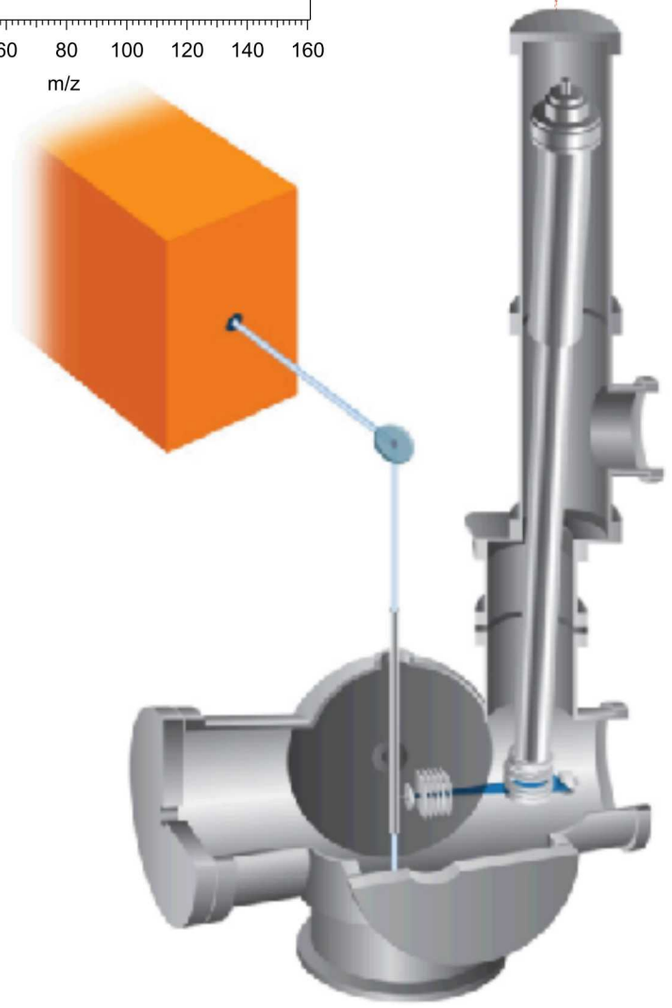
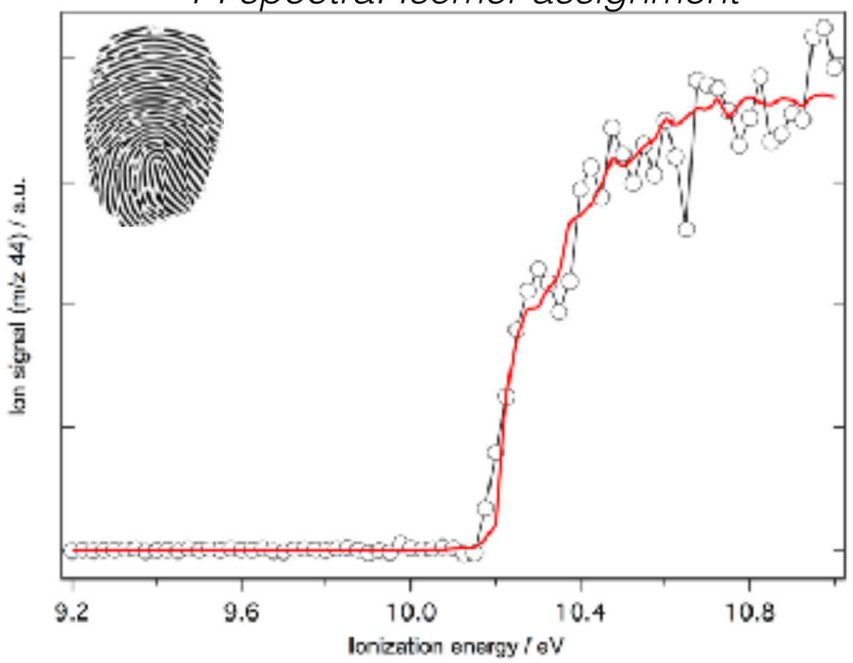








PI spectra: Isomer assignment



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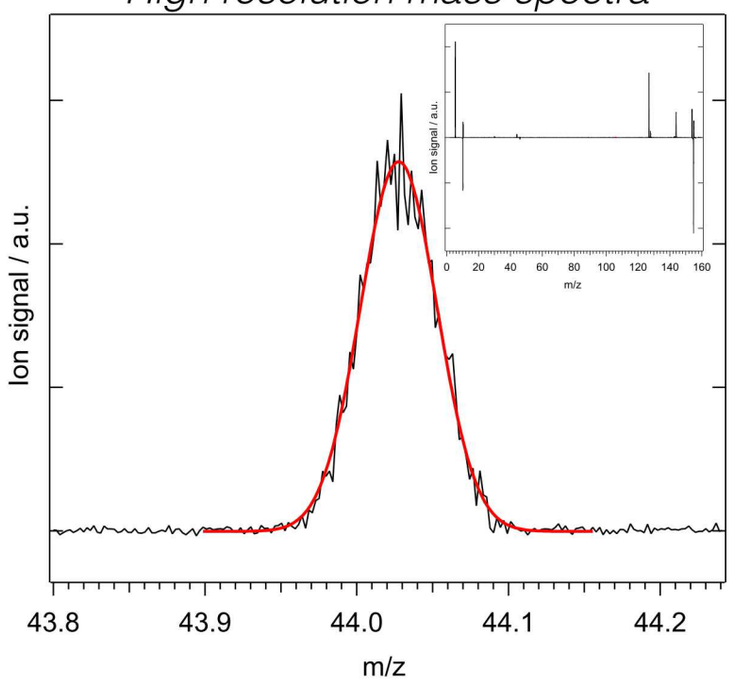
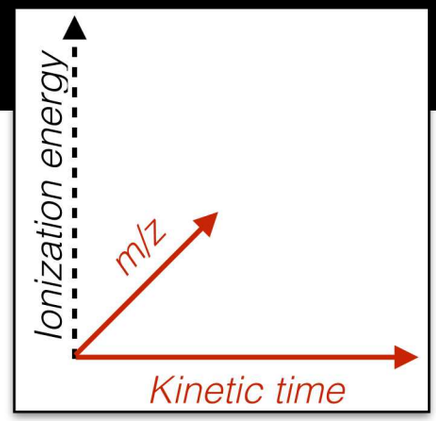
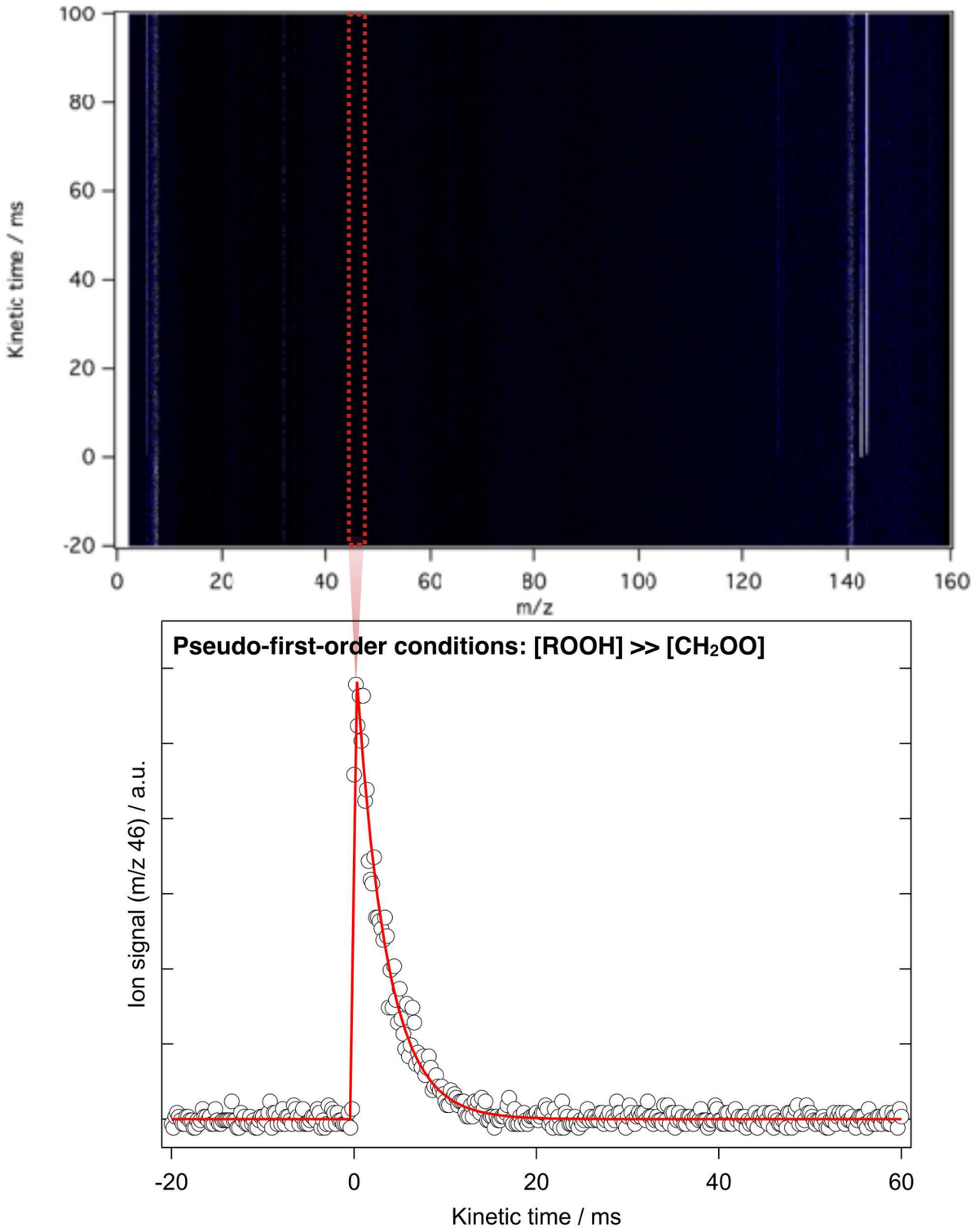


Direct kinetics measurements of CI + ROOH





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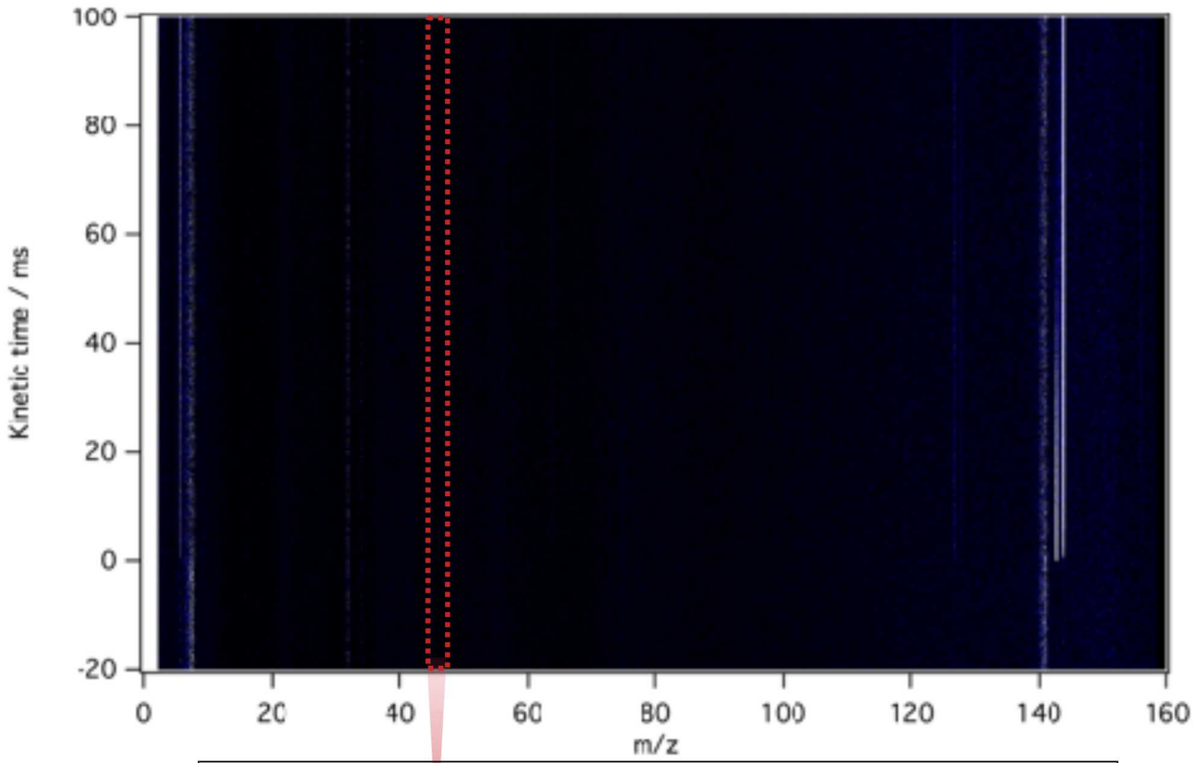

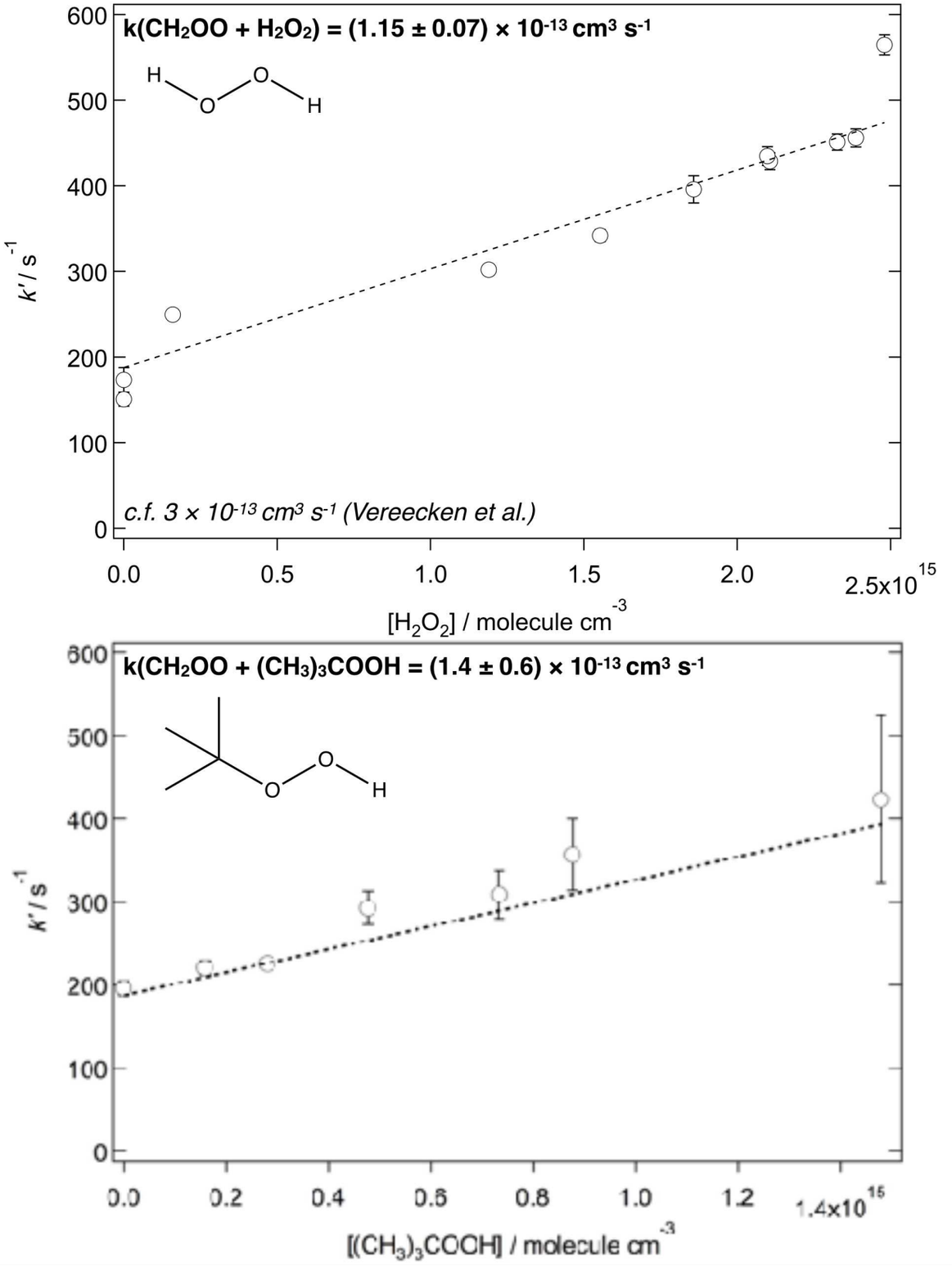

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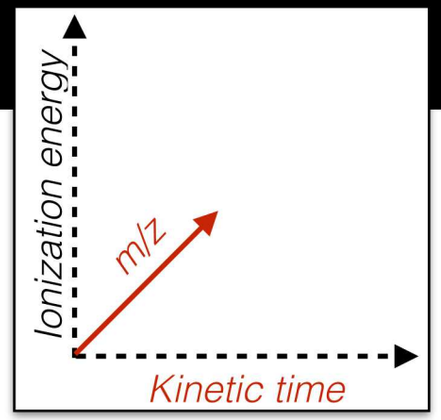
Observation of insertion products

- *High resolution mass spectra:* Signal at the exact m/z of Criegee-ROOH insertion products



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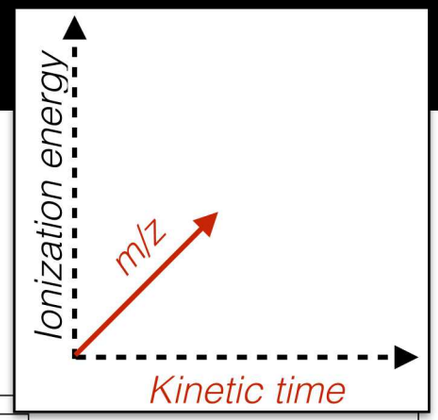

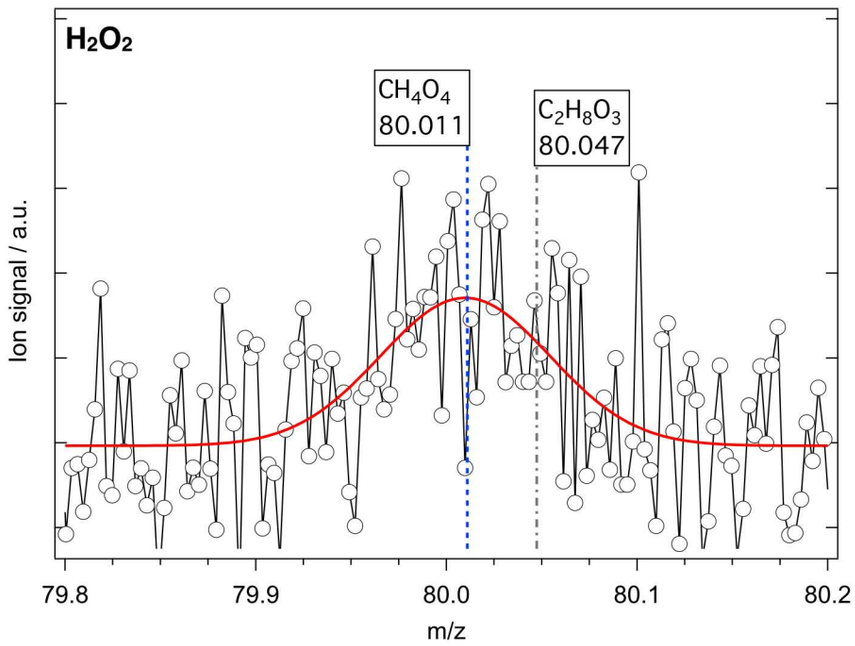

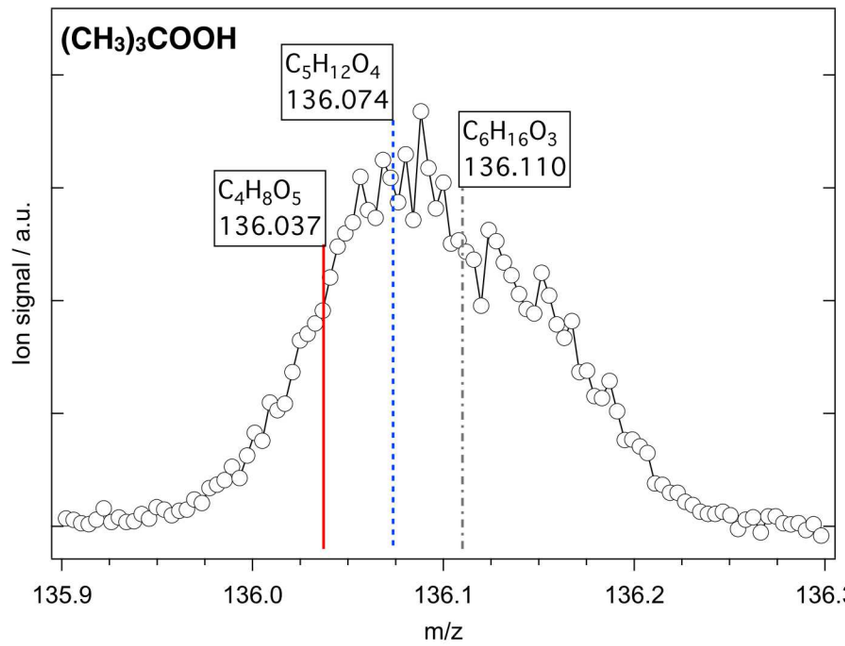

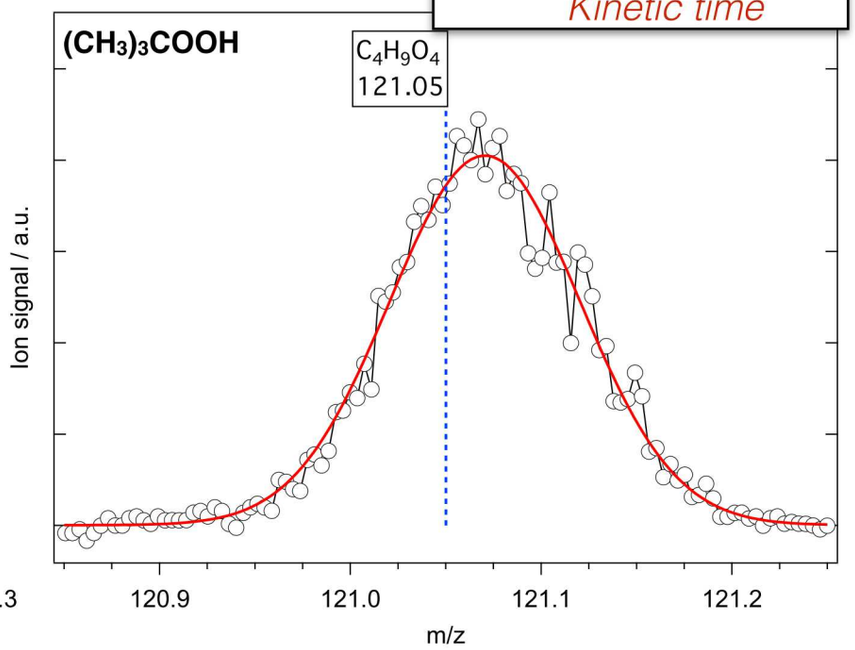

Observation of insertion products

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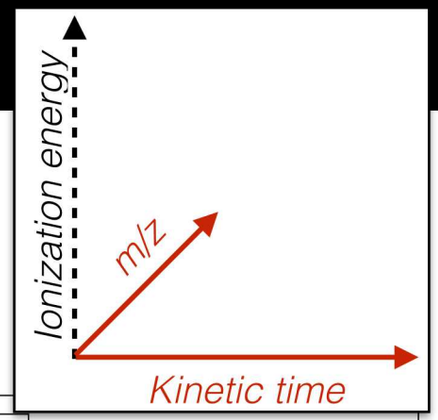

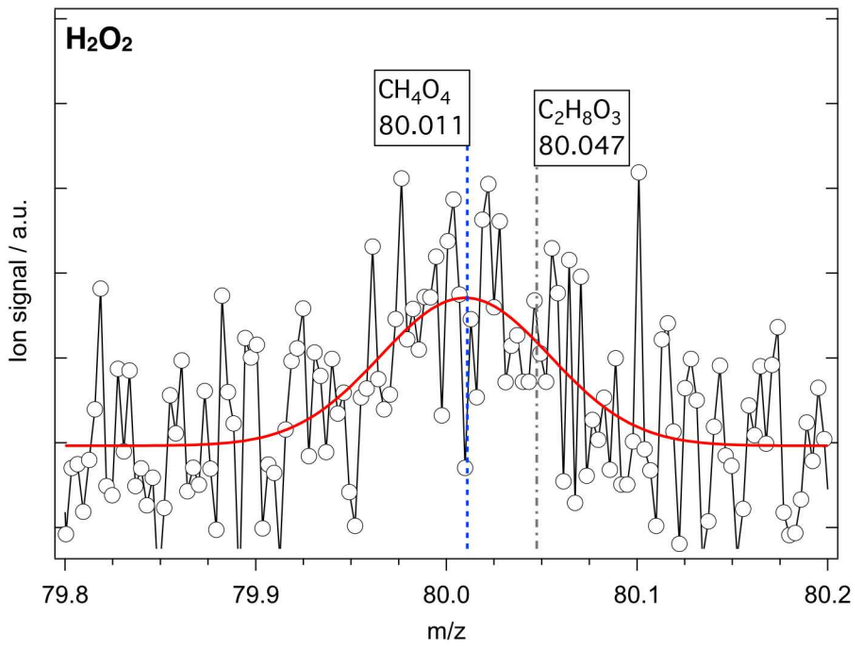

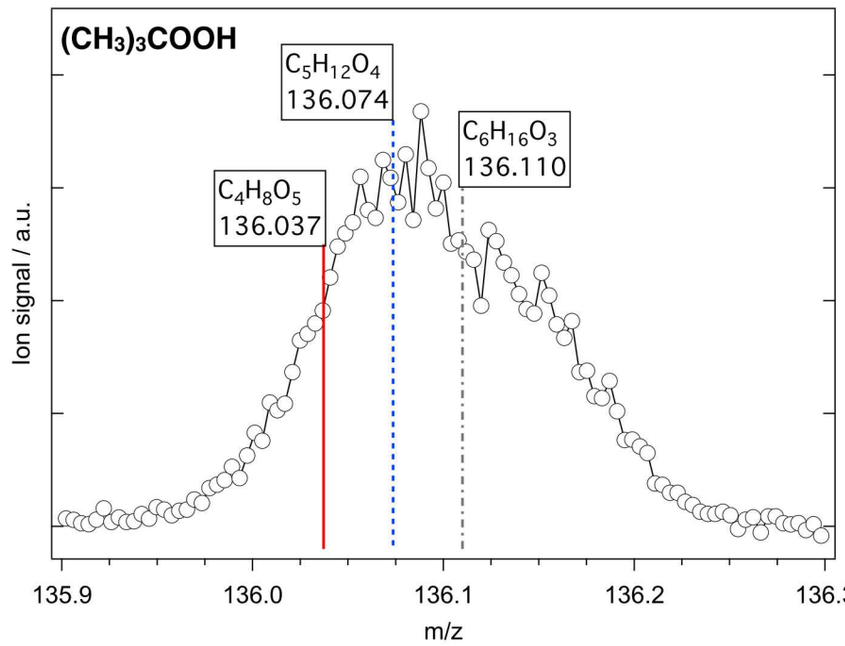

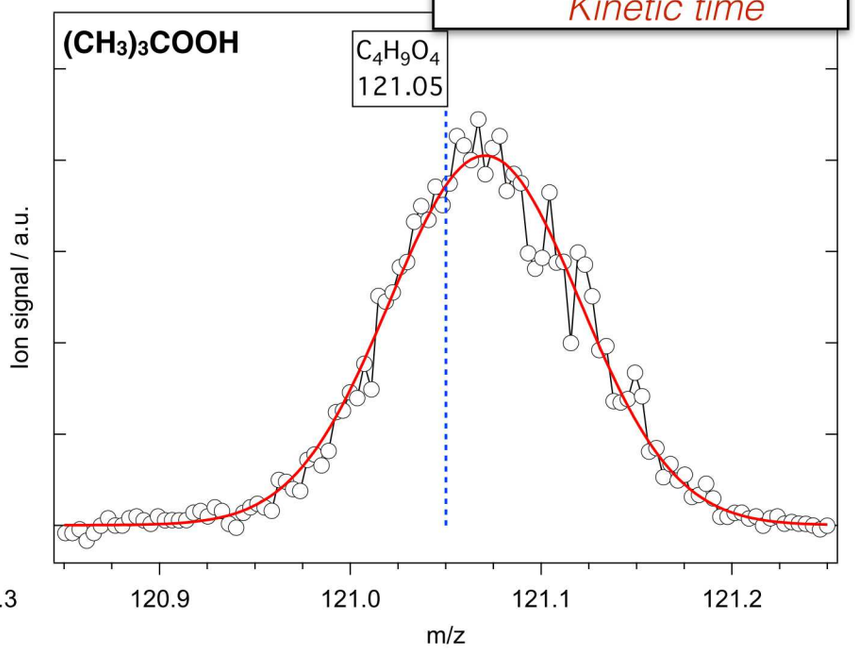

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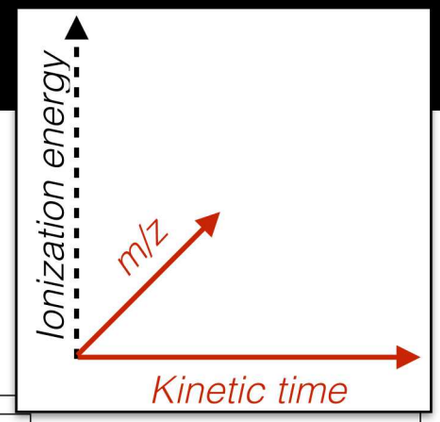

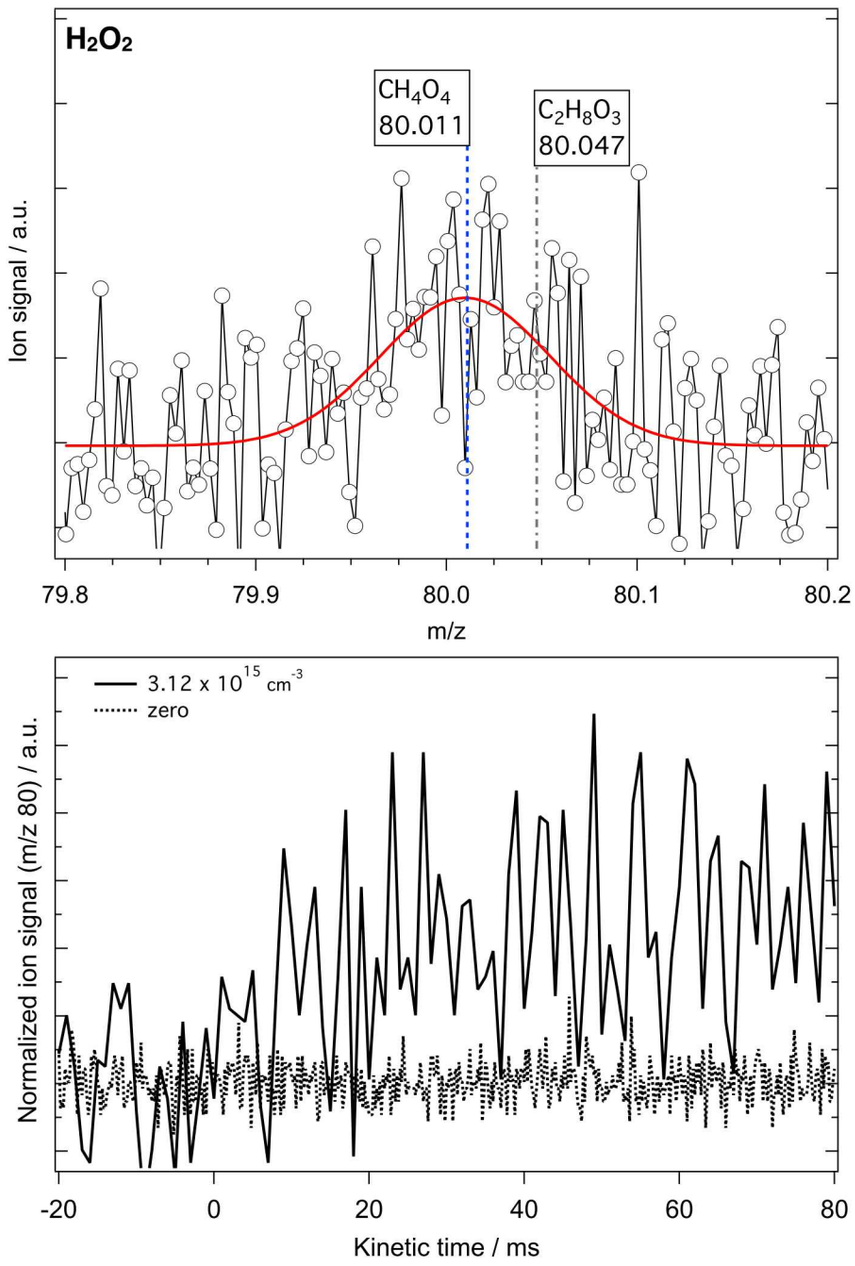

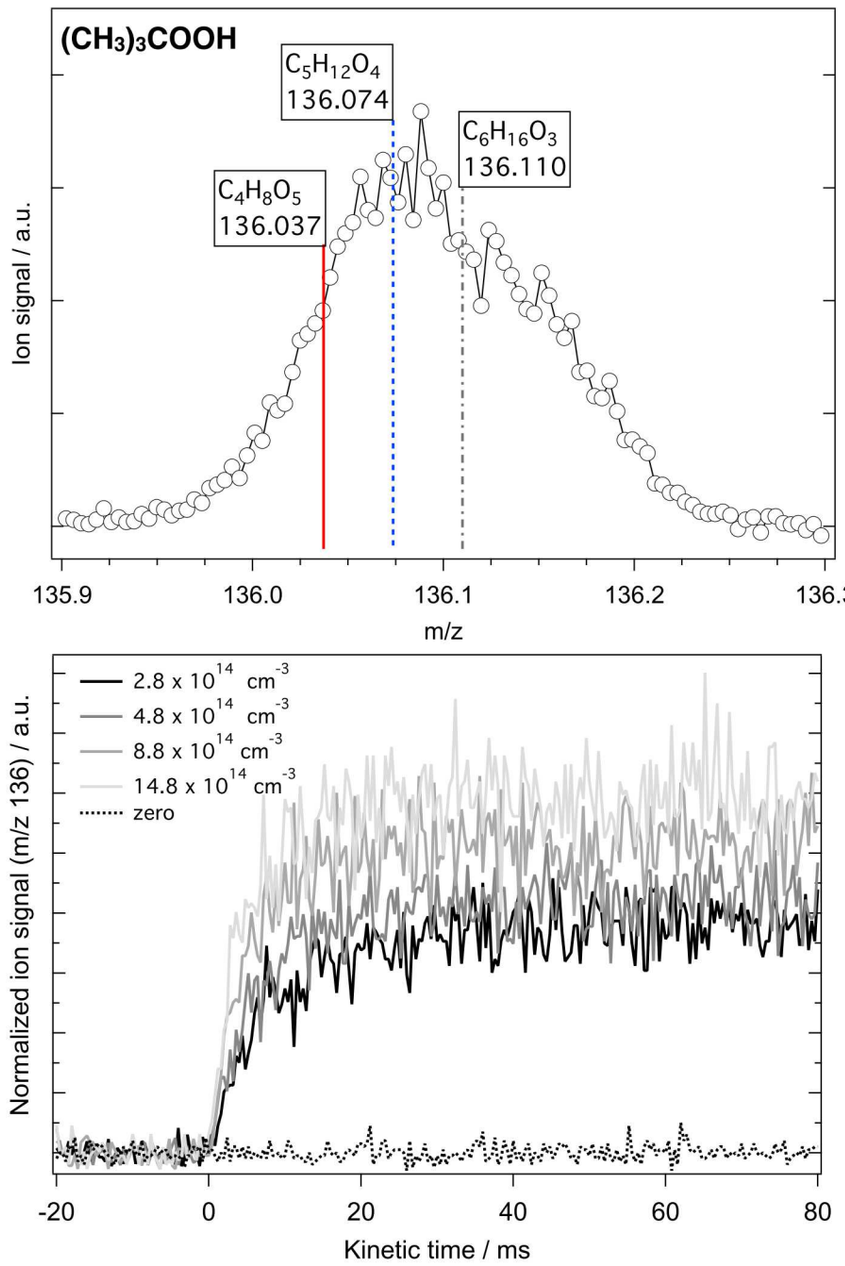

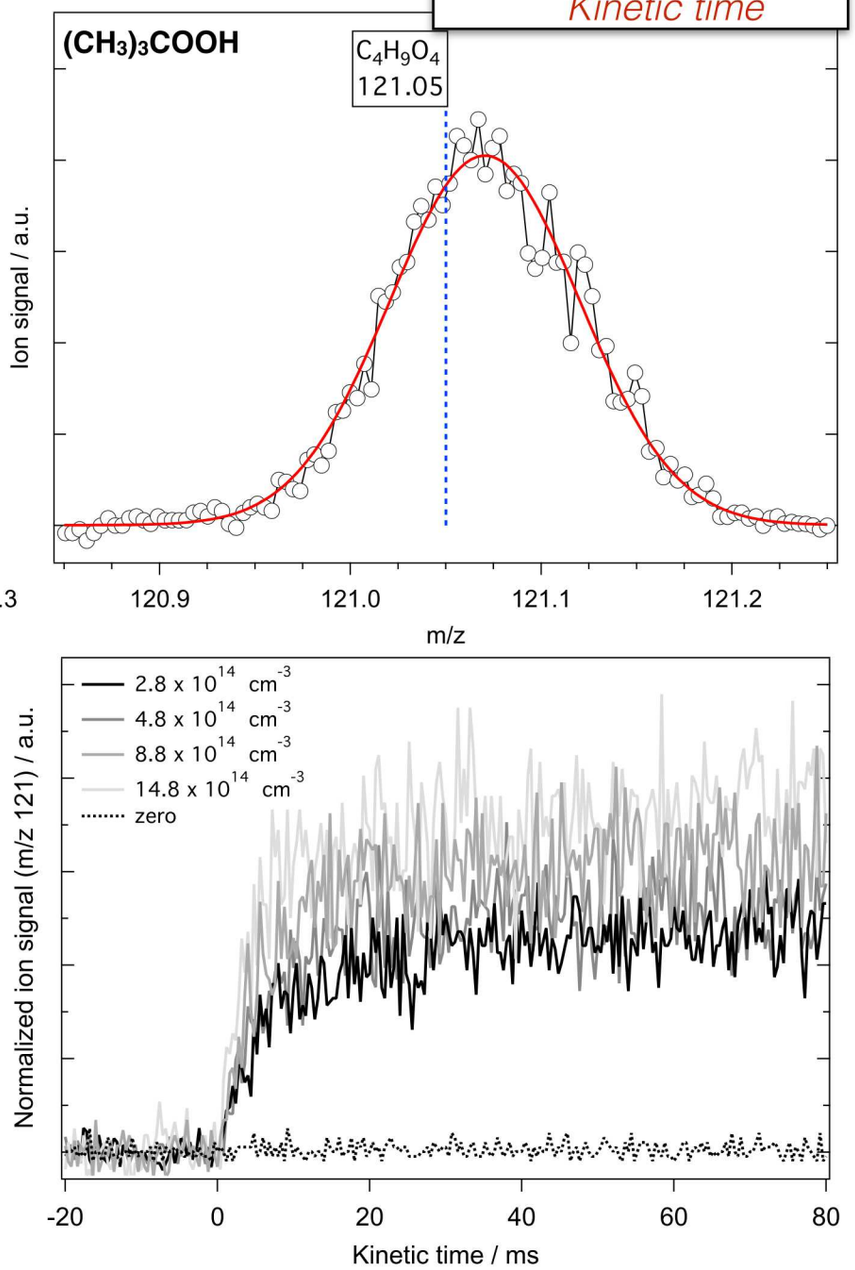

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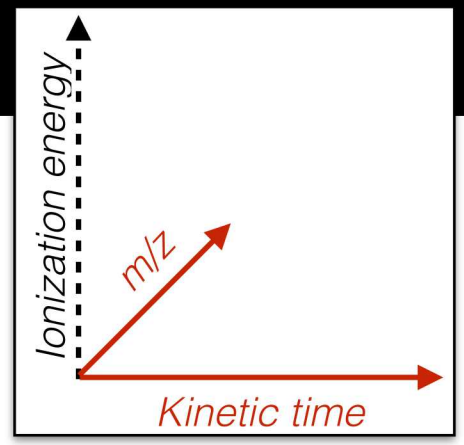

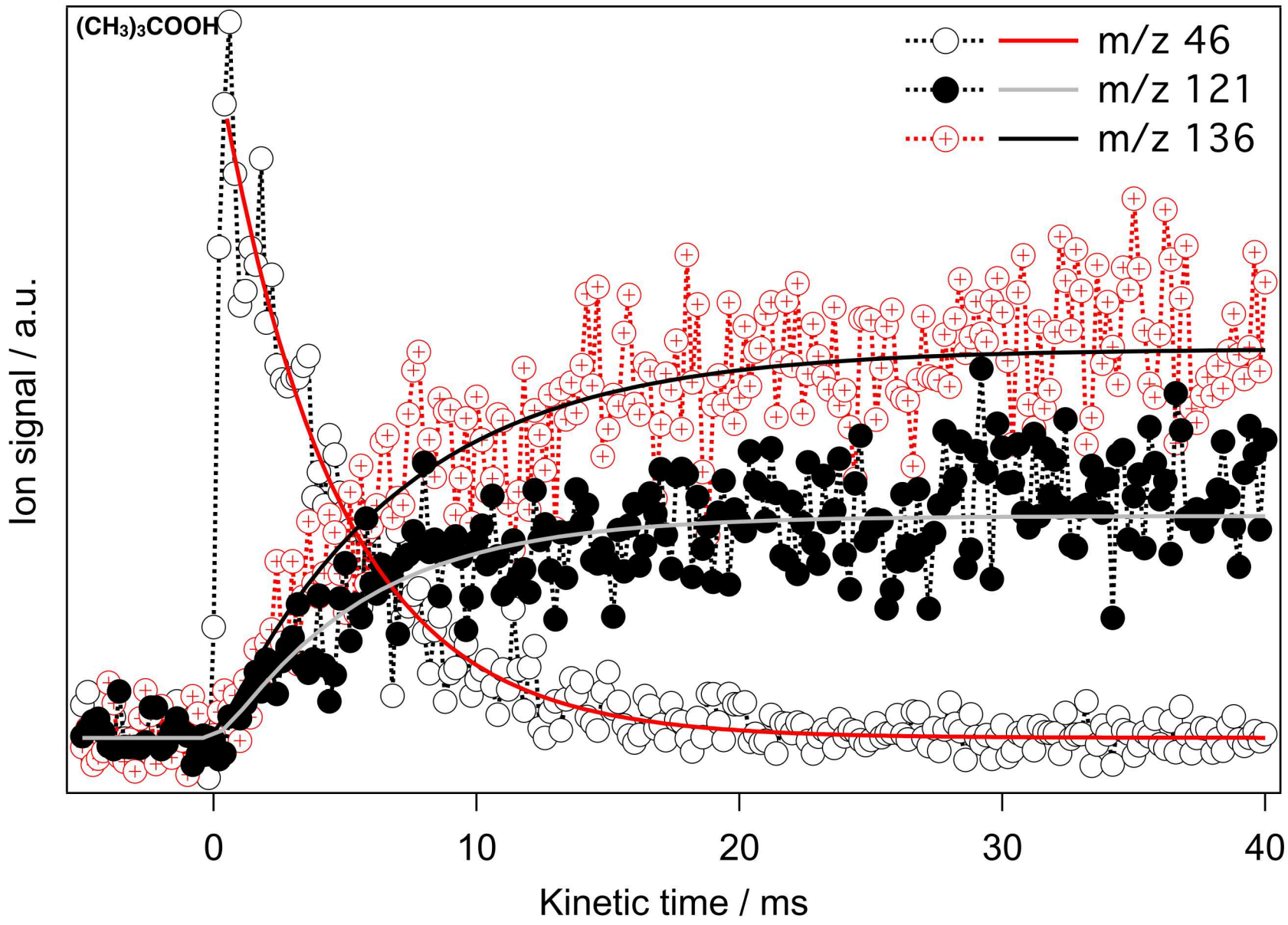

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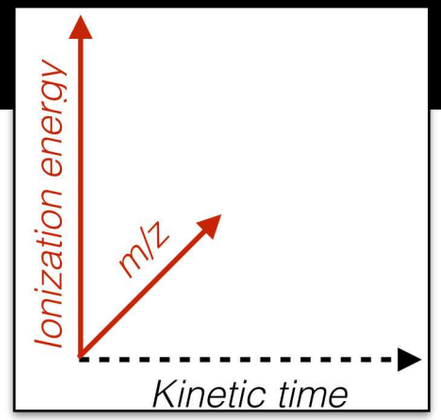

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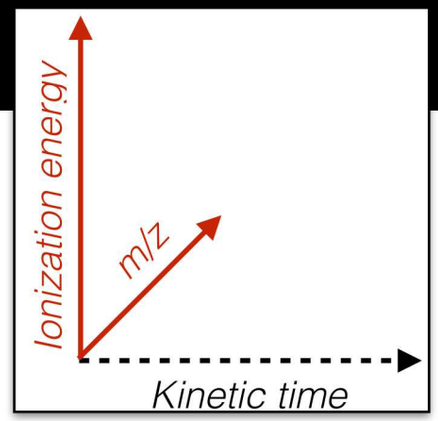

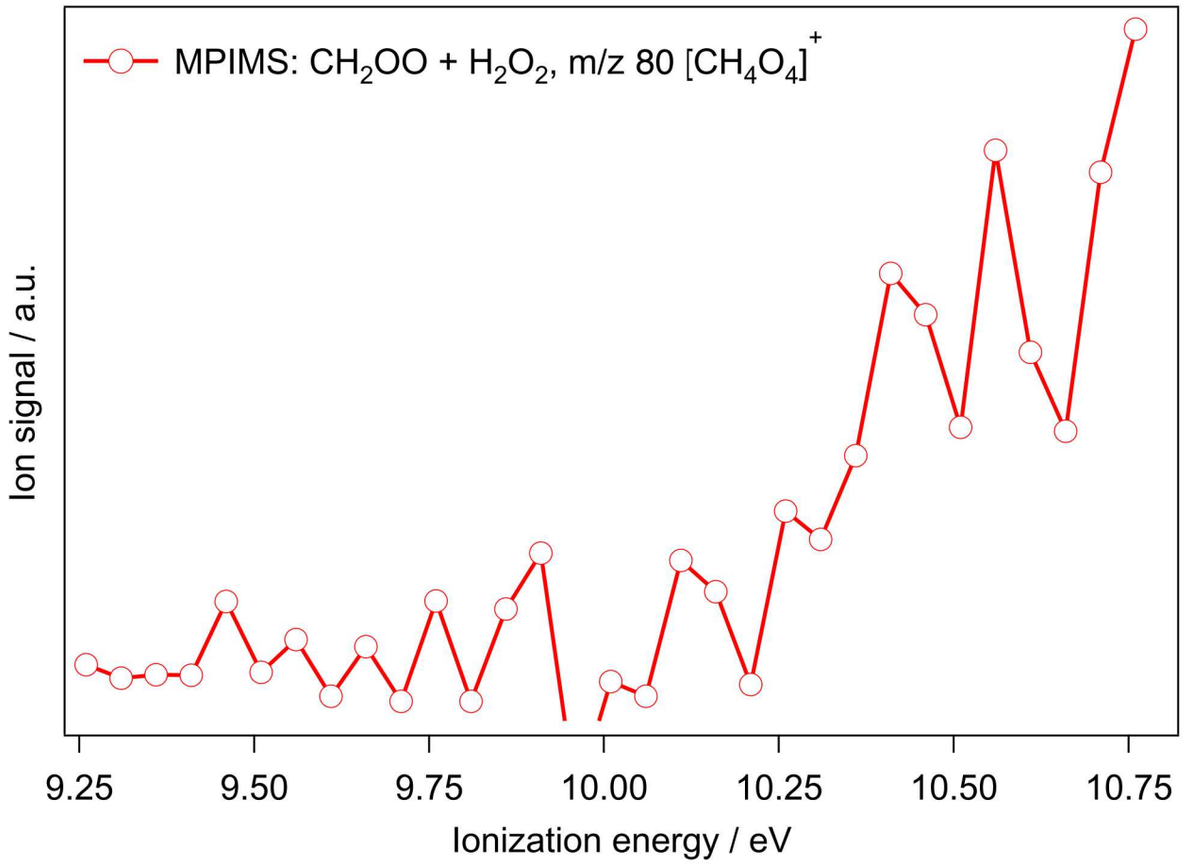

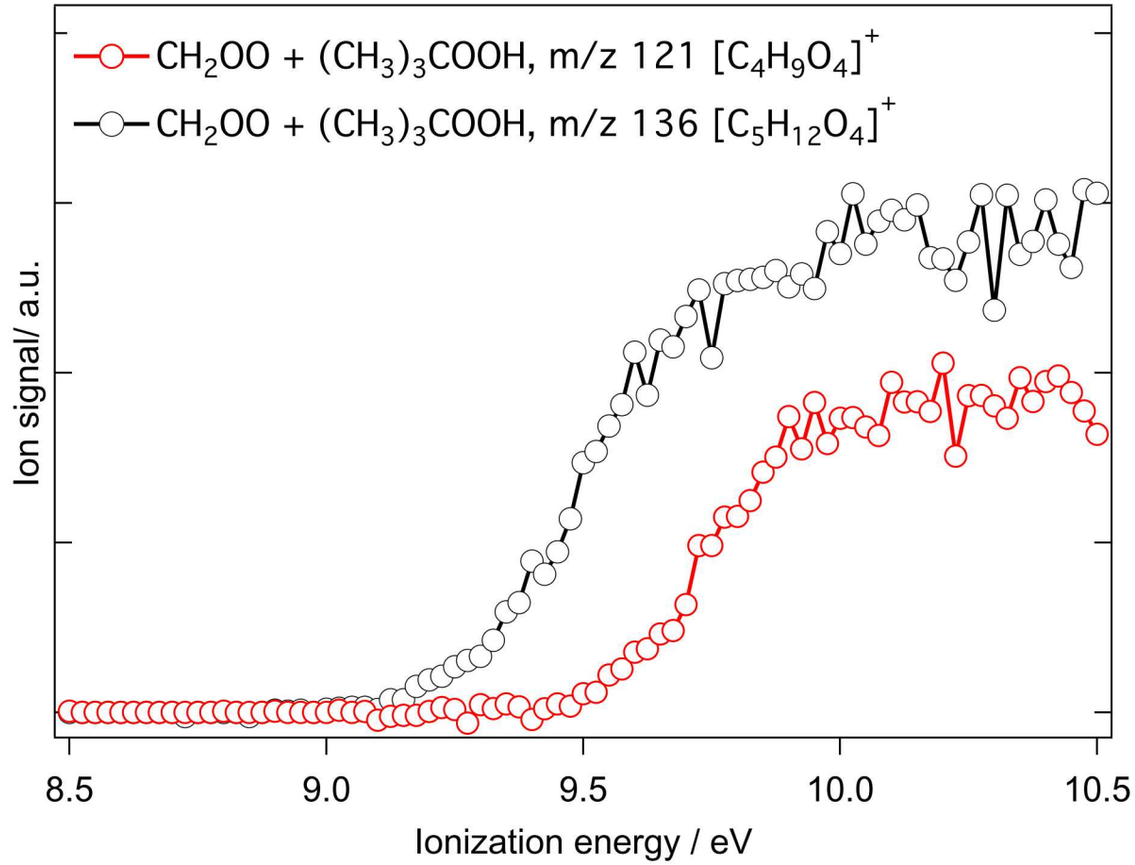

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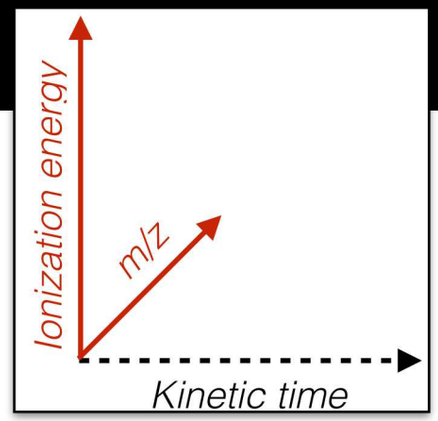

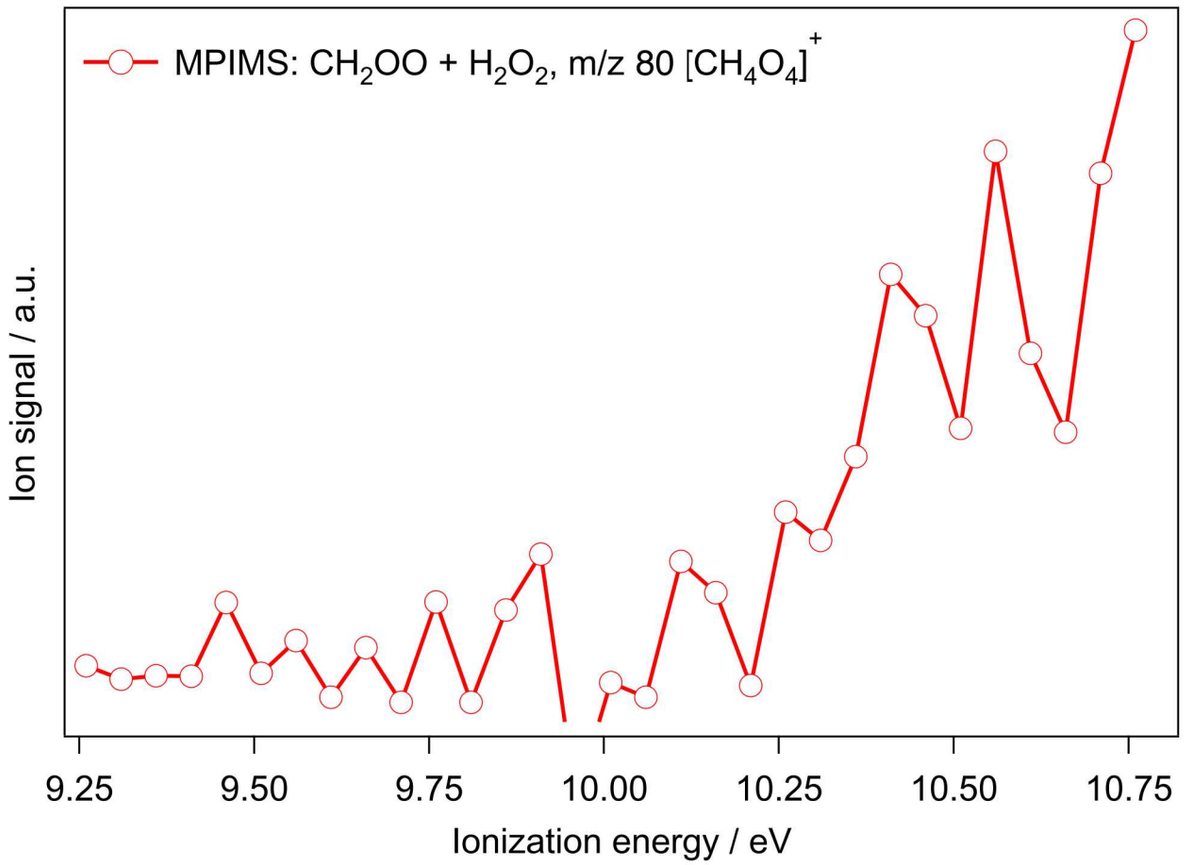

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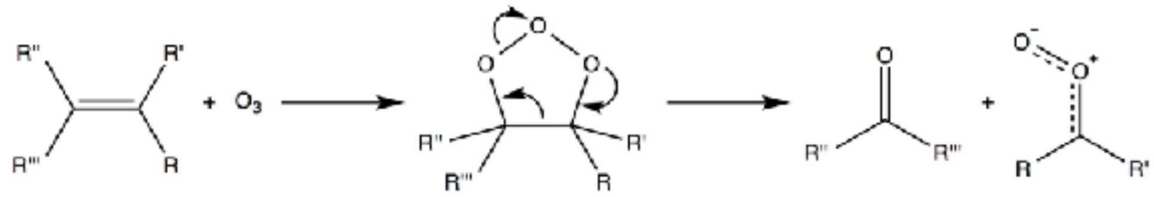
- PIE spectra of adduct from direct kinetic studies can also be compared with ozonolysis studies from JSR experiments also undertaken at the Advanced Light Source.
- *Hansen & Rousso,* Sandia
- 300 K, 700 Torr.



A.C. Rousso,, N. Hansen, A.W. Jasper & Y. Ju, *Journal of Physical Chemistry A,* (2018), 122(43), 8674-8685.

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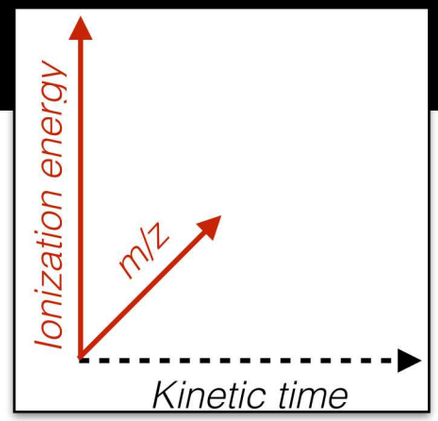

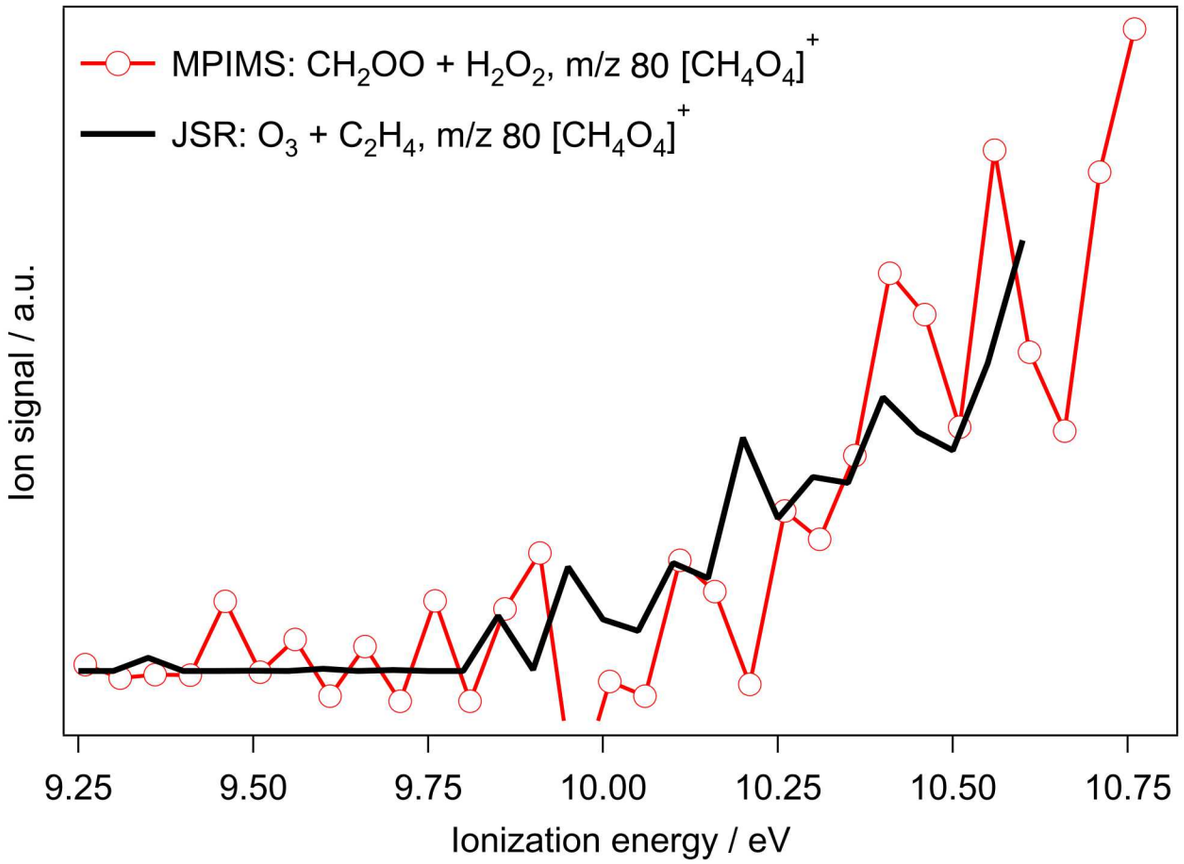

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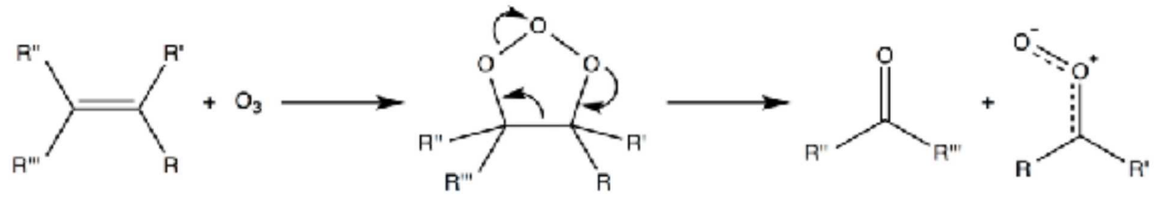

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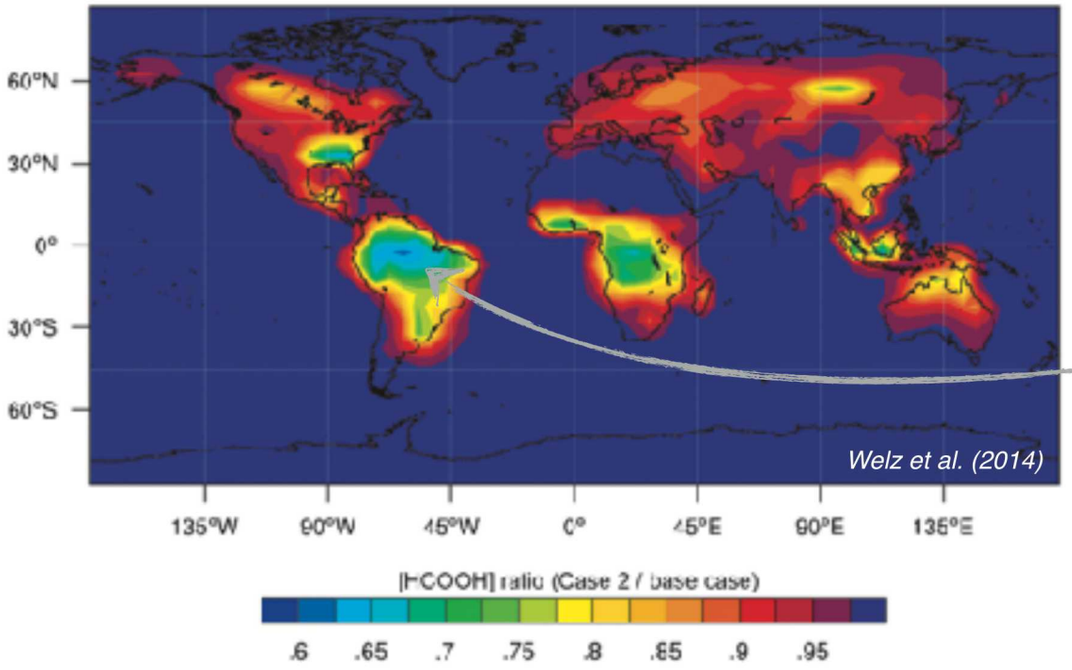
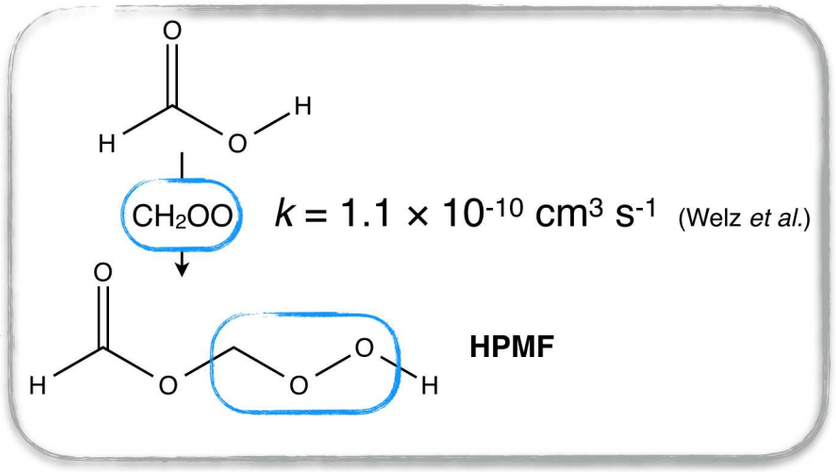
Criegee + HMPF: Theoretical investigations





1

O. Welz, A.J. Eskola, L. Sheps, B. Rotavera, J.D. Savee, A.M. Scheer, D.L. Osborn, D. Lowe, A.M. Booth, P. Xiao, M.A.H. Khan, C.J. Percival, D.E. Shallcross & C.A. Taatjes, *Angewandte Chemie*, (2014), 53 (18), 4547-4550.

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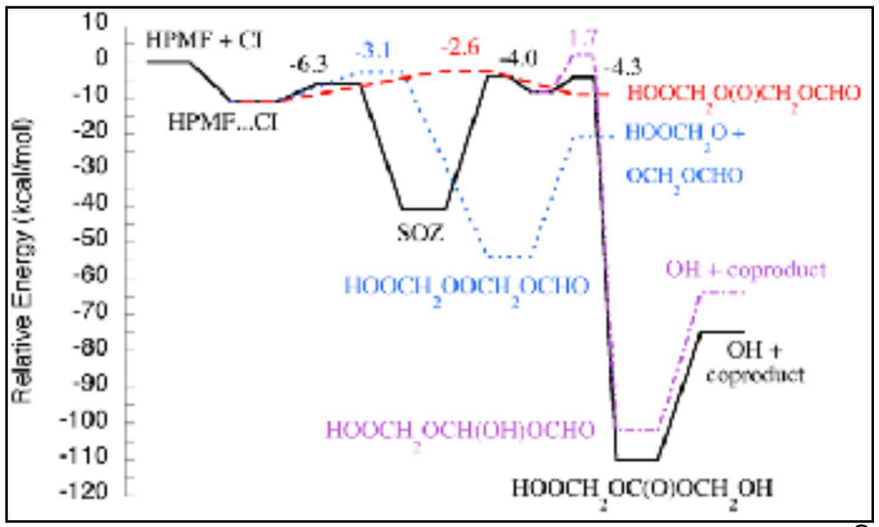
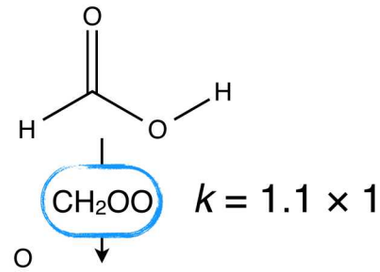


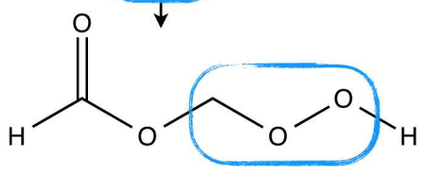
Klippenstein & Jasper, Argonne

CCSD(T)-F12/cc-pVTZ-F12//B2PLYPD3/cc-pVTZ

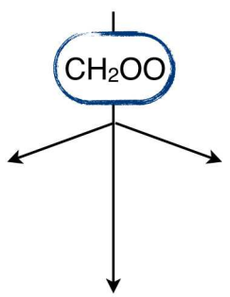


$k = 1.1 \times 10^{-10}$ cm^3 s^{-1} (Welz *et al.*)

1

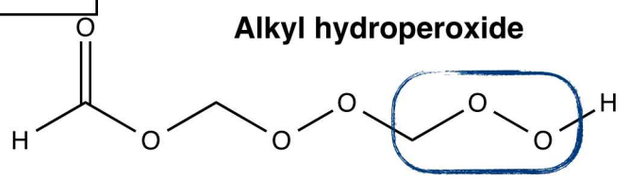


HPMF

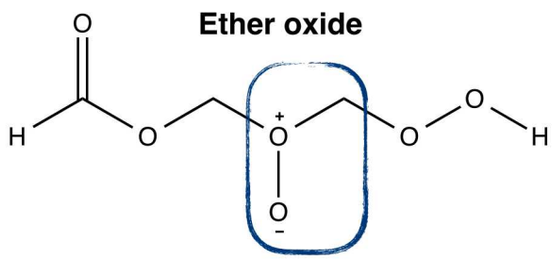


2

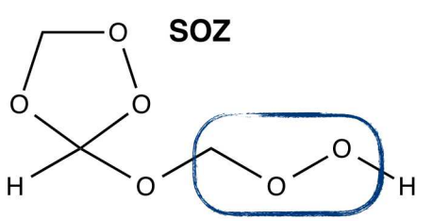
Alkyl hydroperoxide



Ether oxide



SOZ



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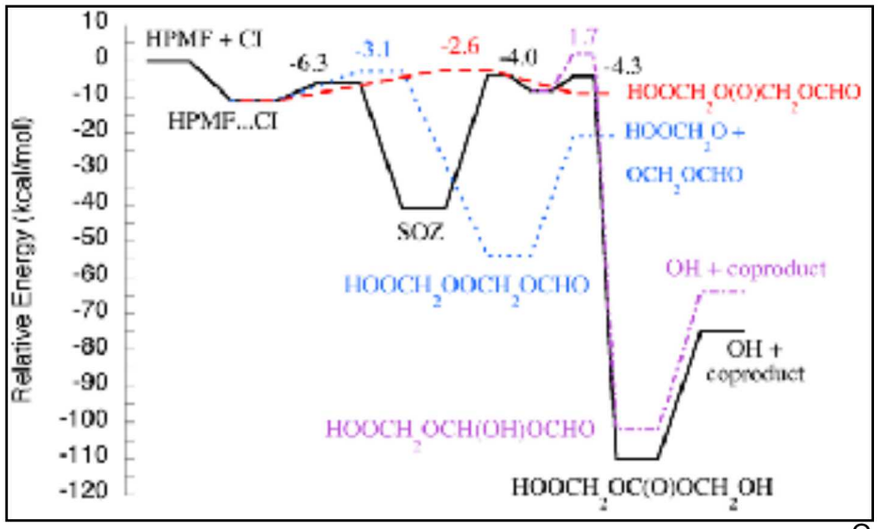

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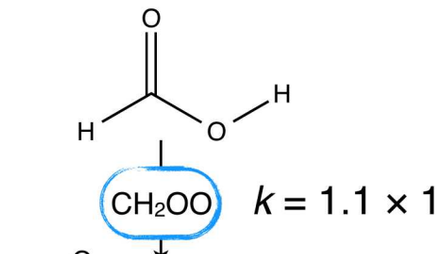

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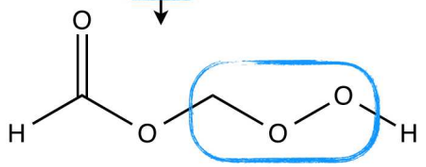

HPMF

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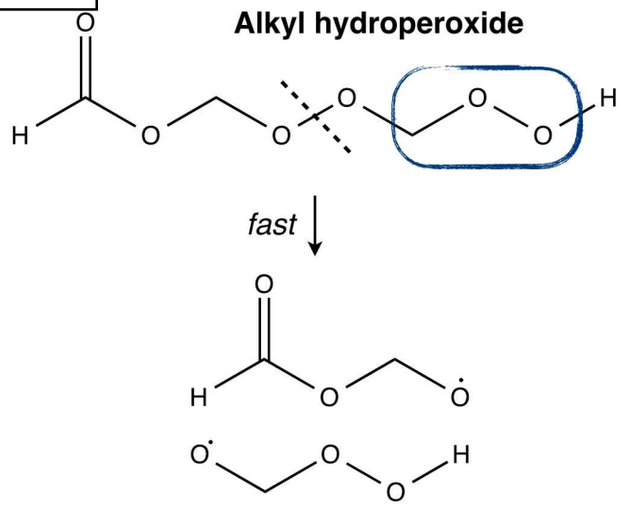

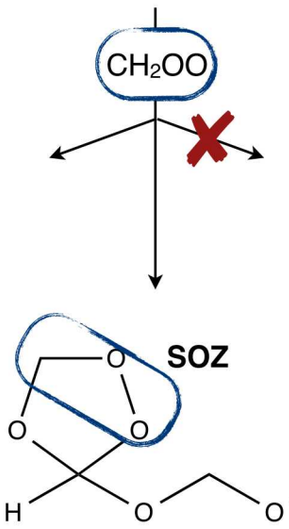

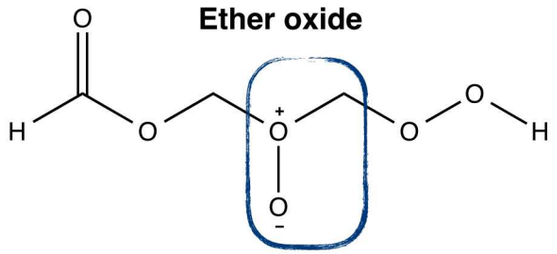

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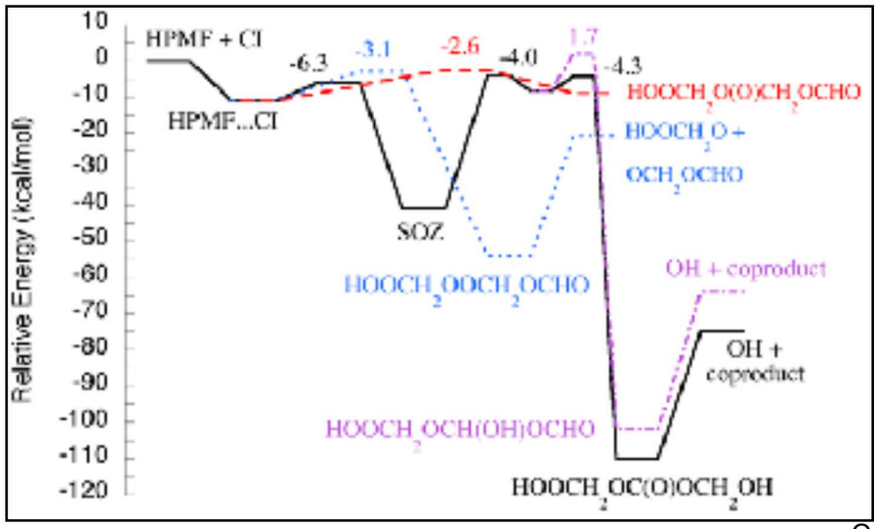

Klippenstein & Jasper, Argonne

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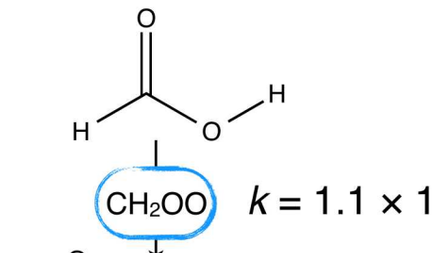

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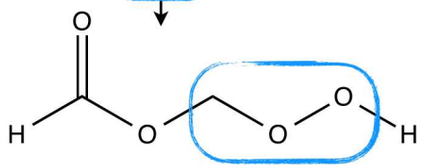

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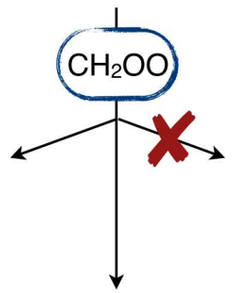

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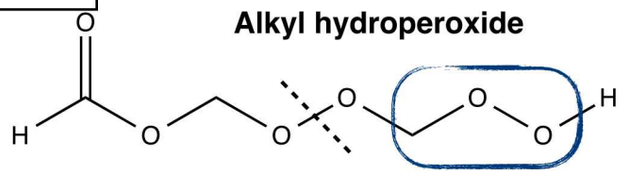

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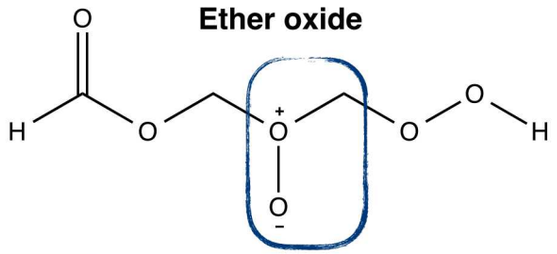
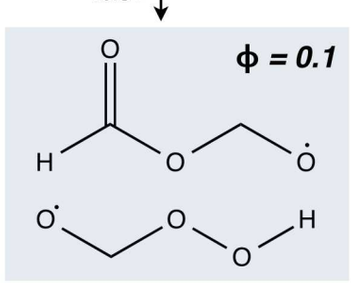
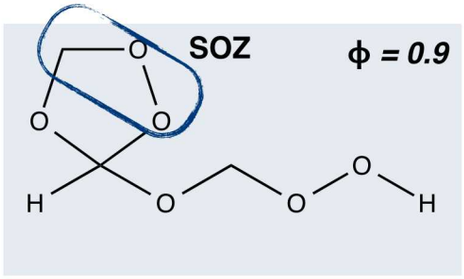


fast





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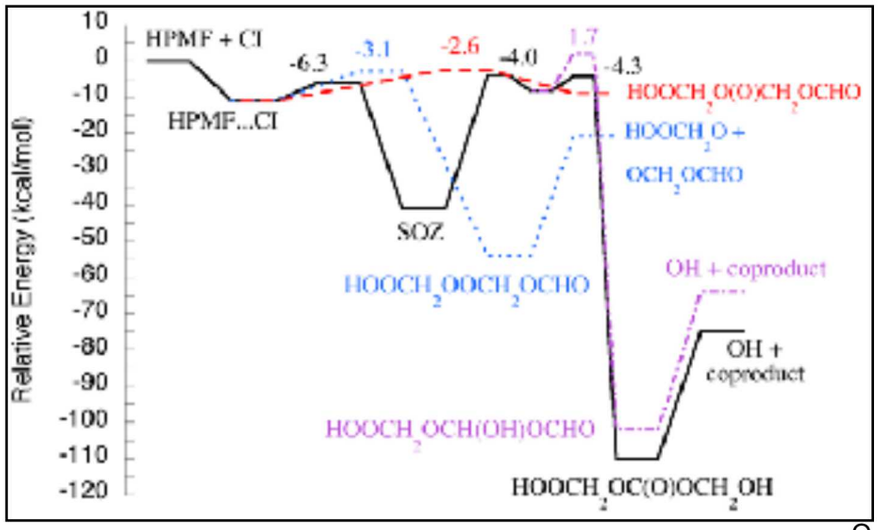

Klippenstein & Jasper, Argonne

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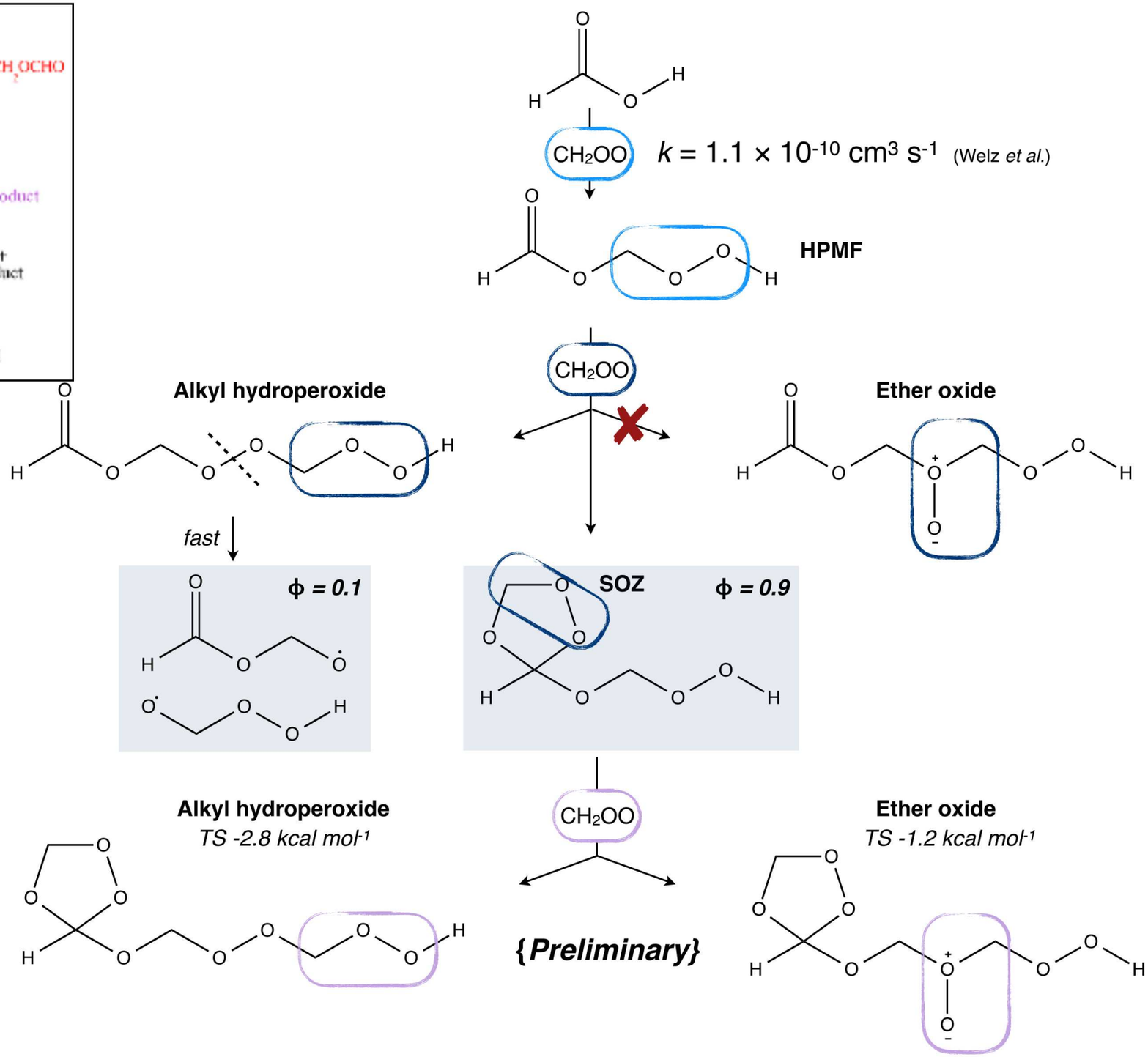

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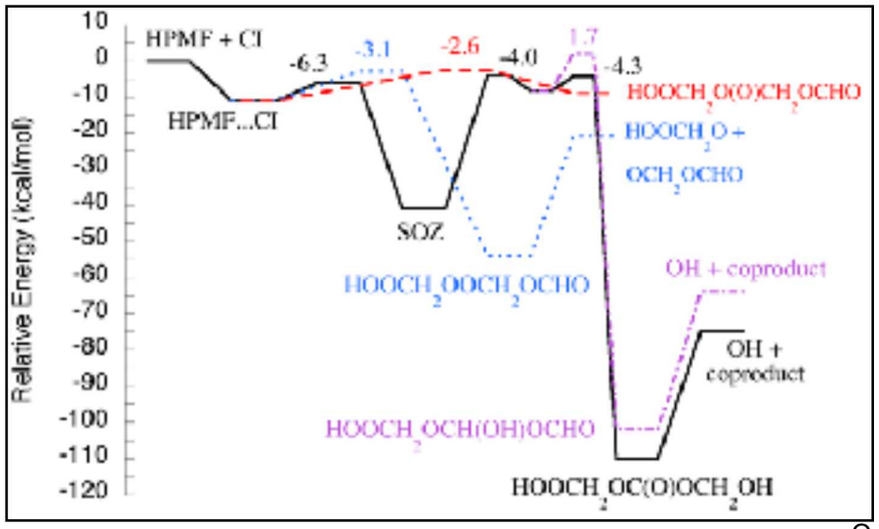

Klippenstein & Jasper, Argonne

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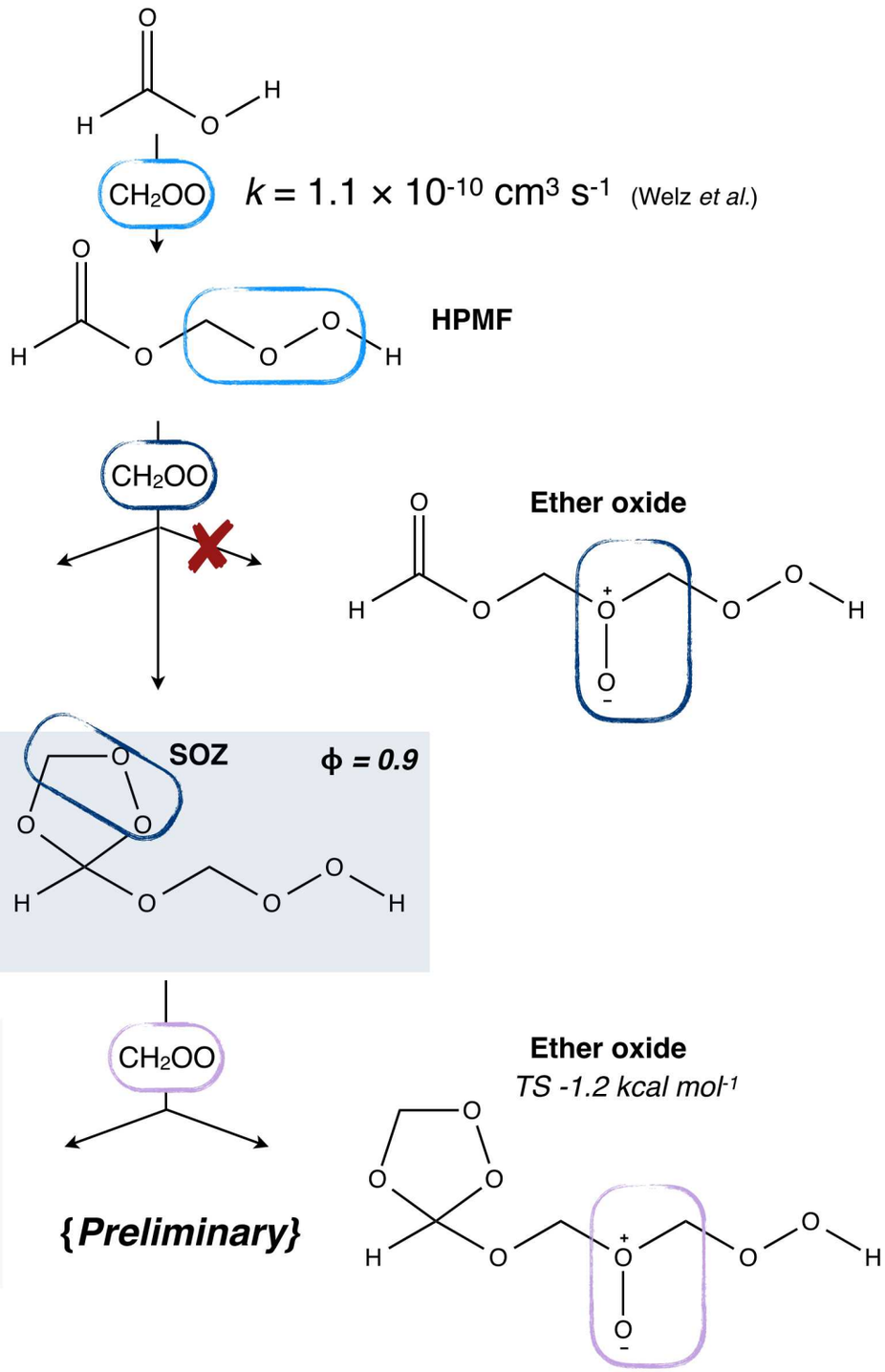
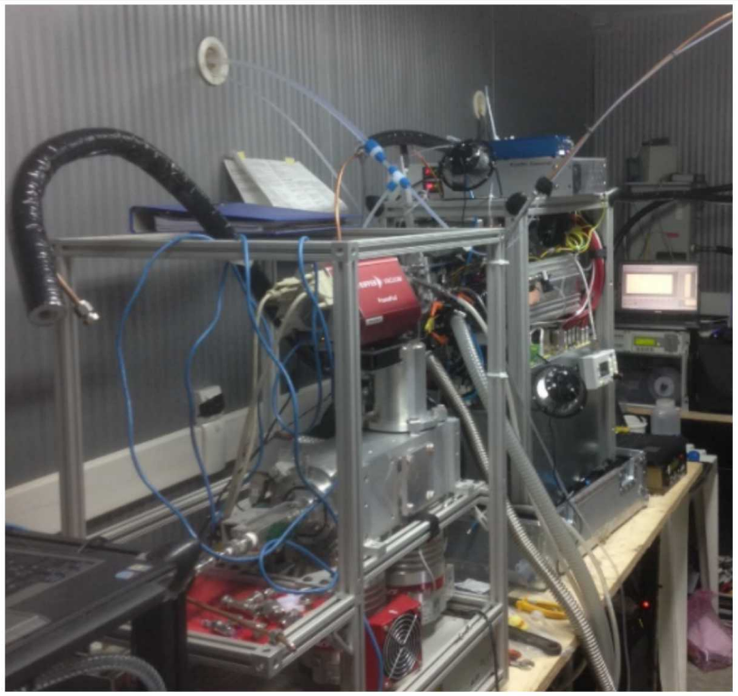
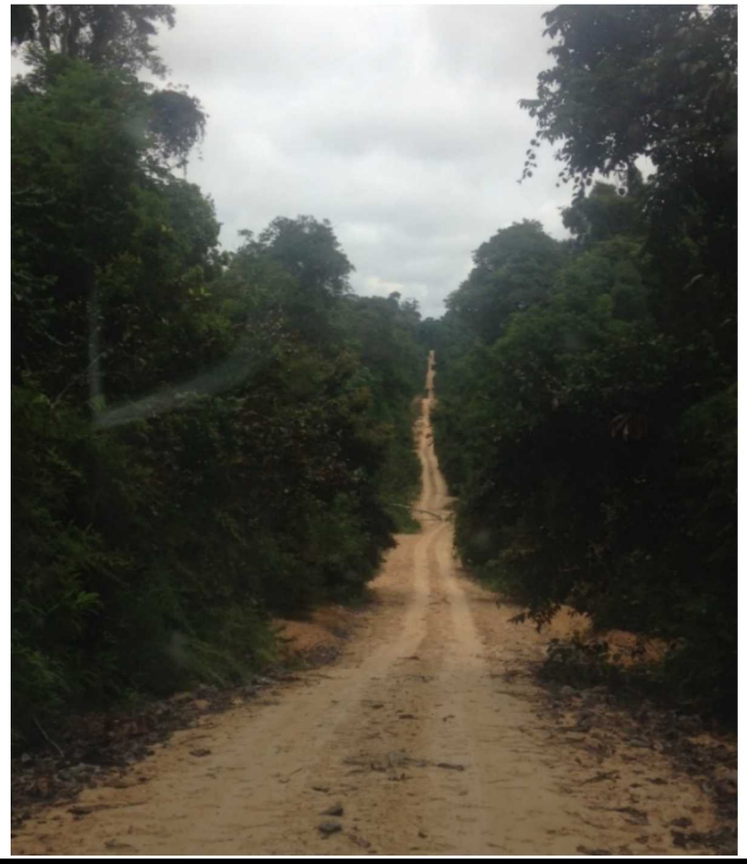


Energetically viable sequential Criegee Intermediate insertions from formic acid leading to oligomer formation.

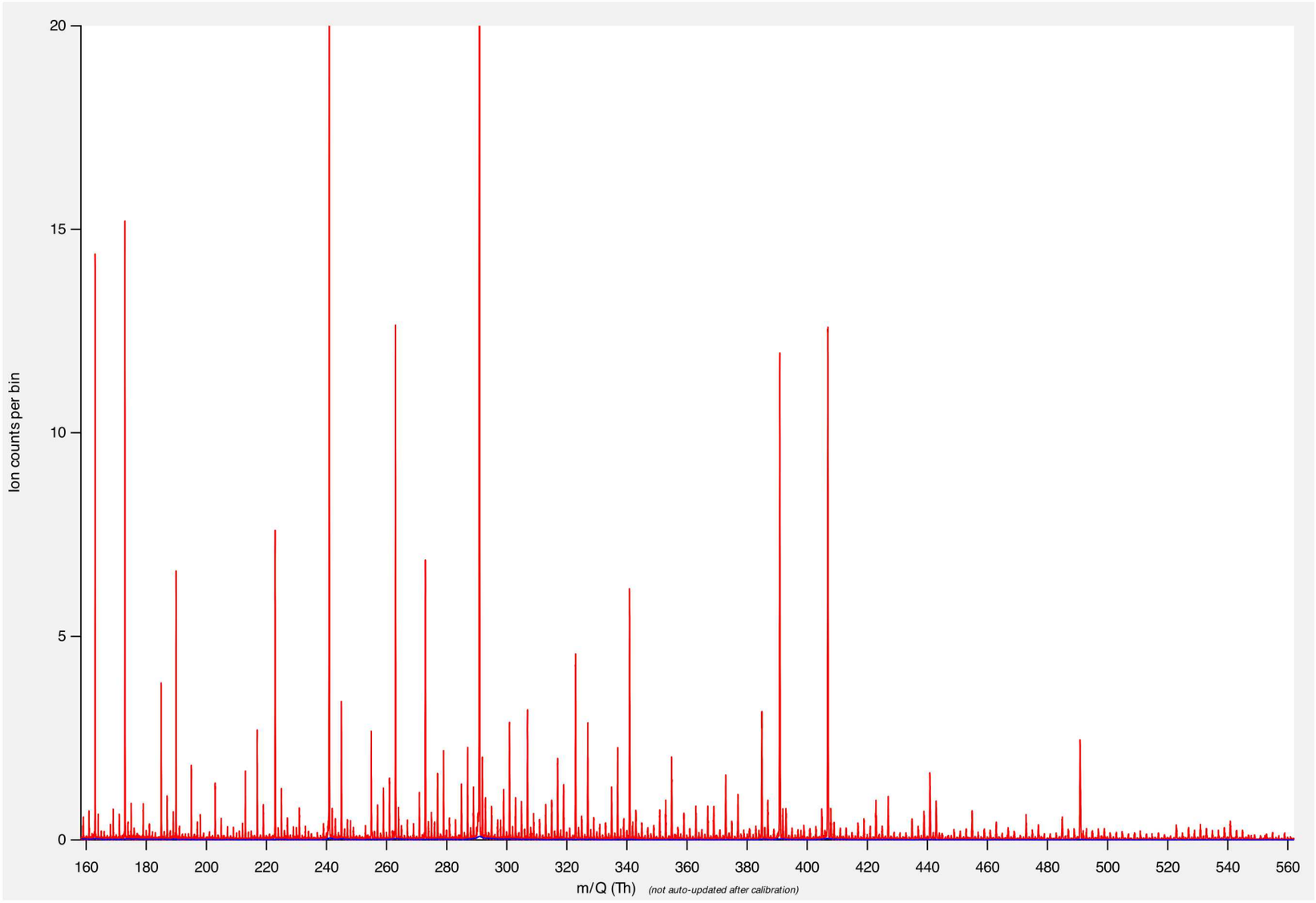
O. Welz, A.J. Eskola, L. Sheps, B. Rotavera, J.D. Savee, A.M. Scheer, D.L. Osborn, D. Lowe, A.M. Booth, P. Xiao, M.A.H. Khan, C.J. Percival, D.E. Shallcross & C.A. Taatjes, *Angewandte Chemie*, (2014), 53 (18), 4547-4550.

Insertion products in the field





- Brazil rainforest, June 2016.
- TOF-CIMS (*Bannan & Percival*, Manchester & JPL) detection of the gas and aerosol phase:
  - A- + B →A + B-



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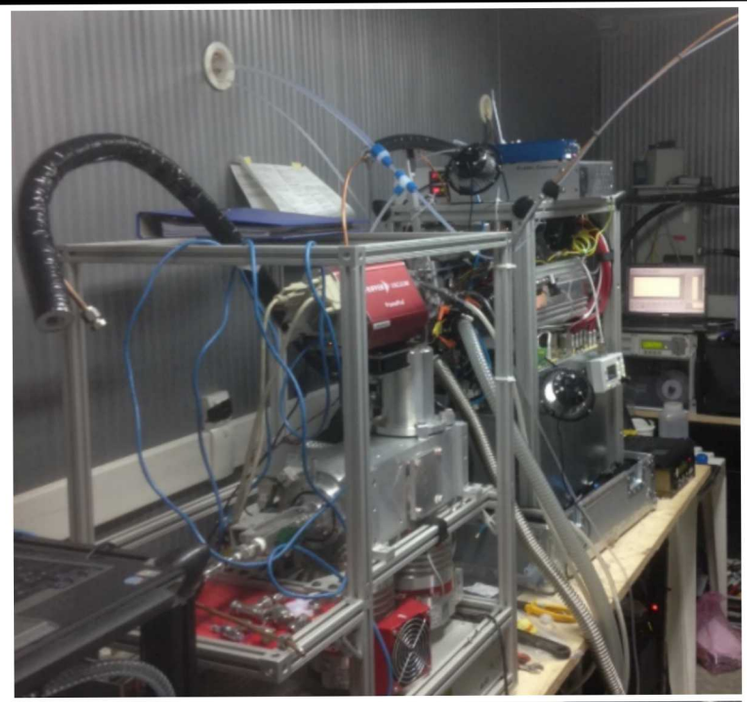

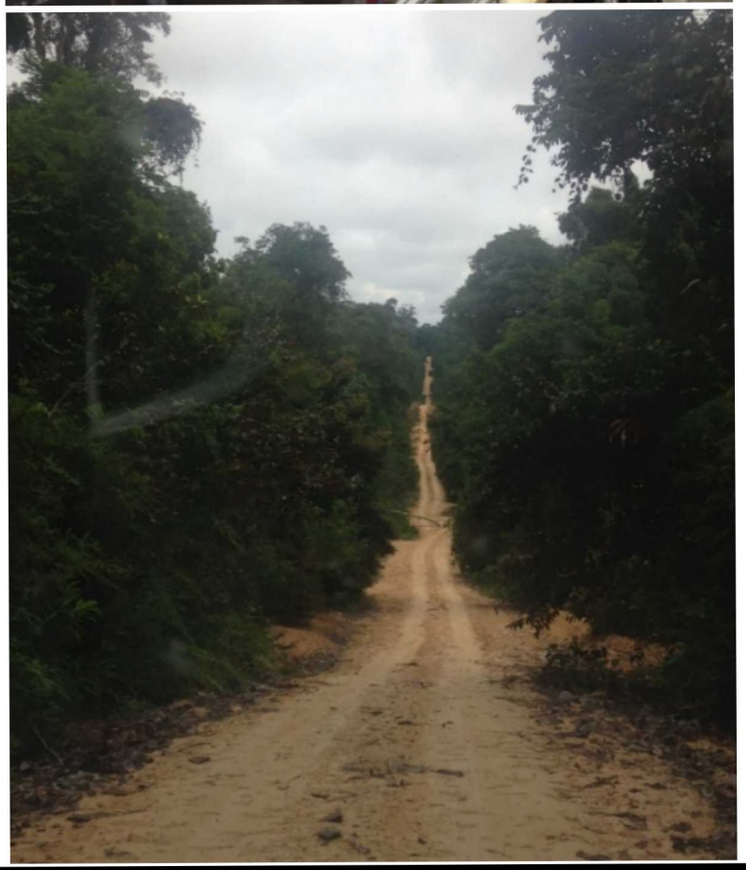

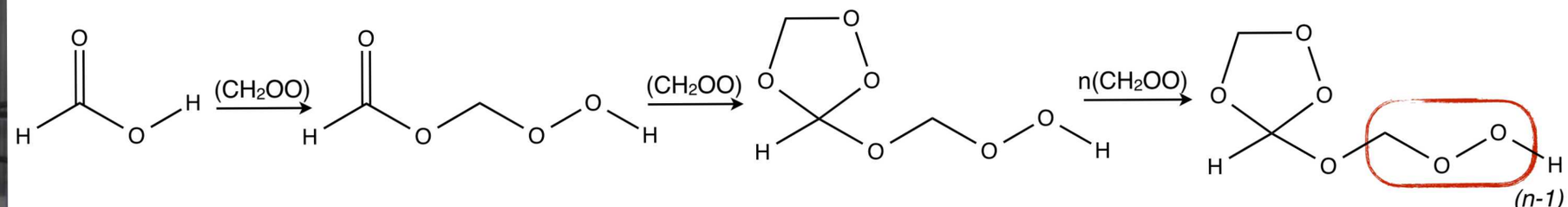

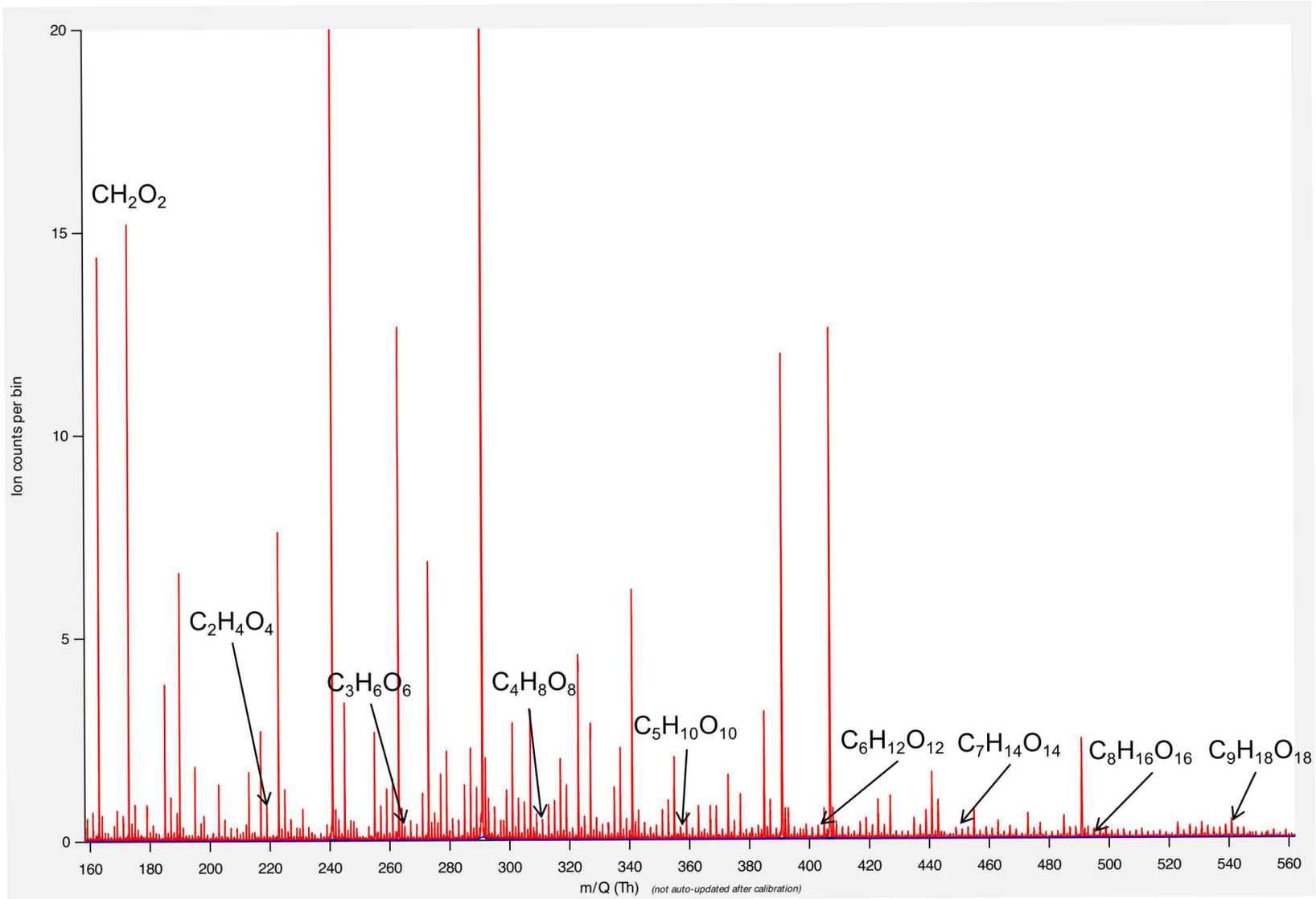

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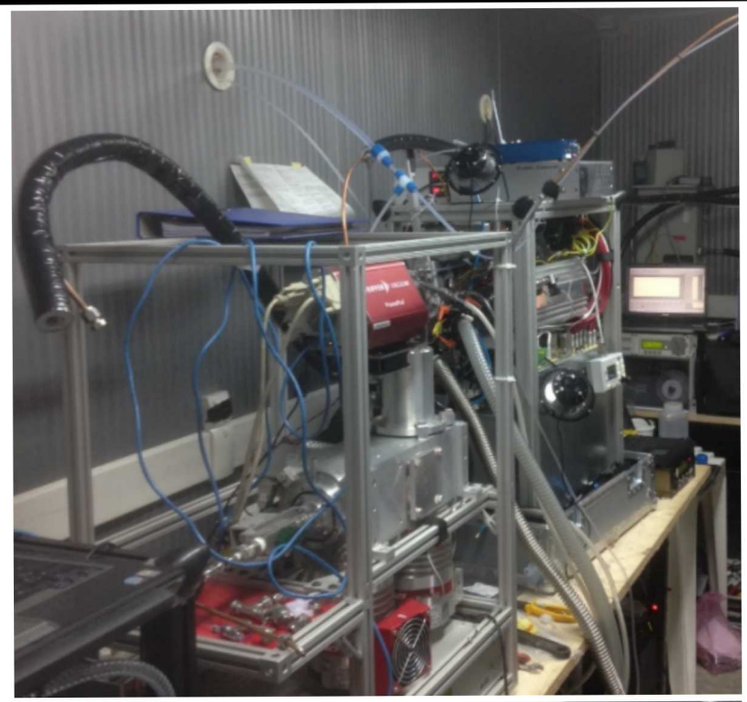
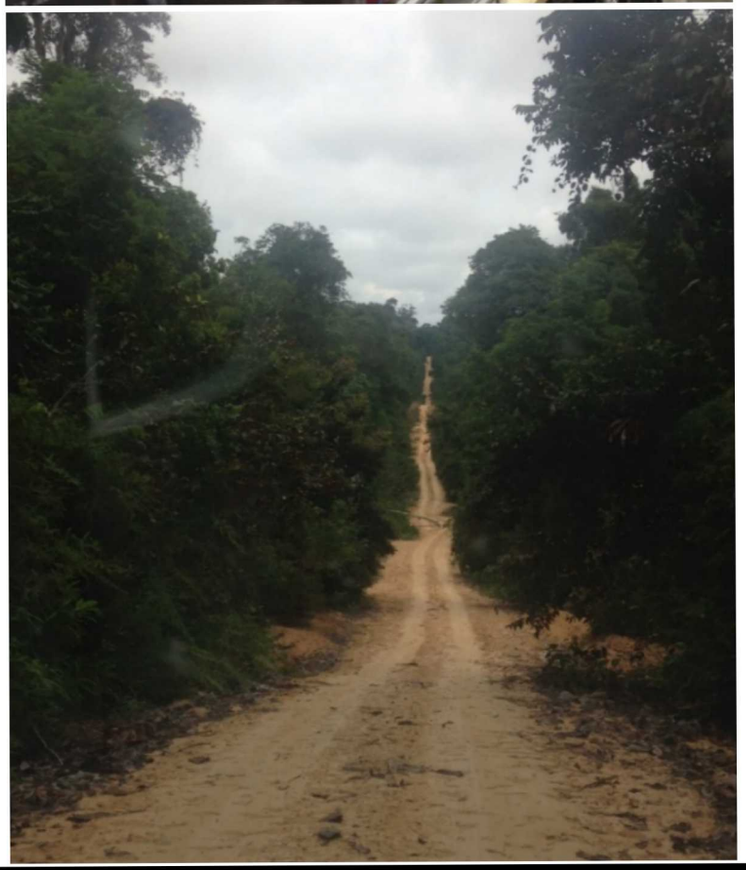
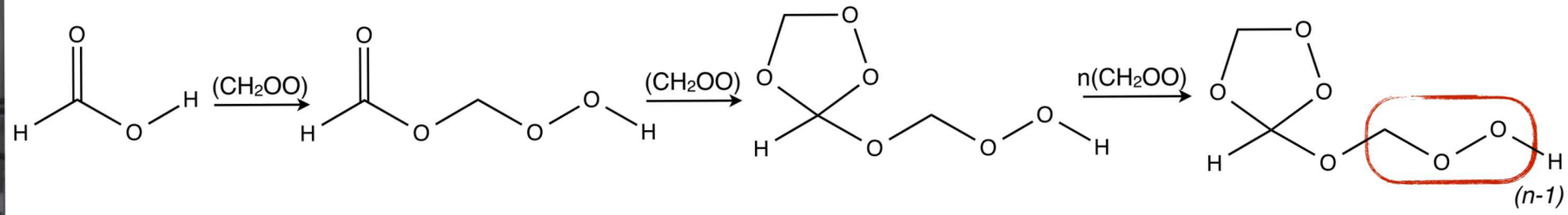
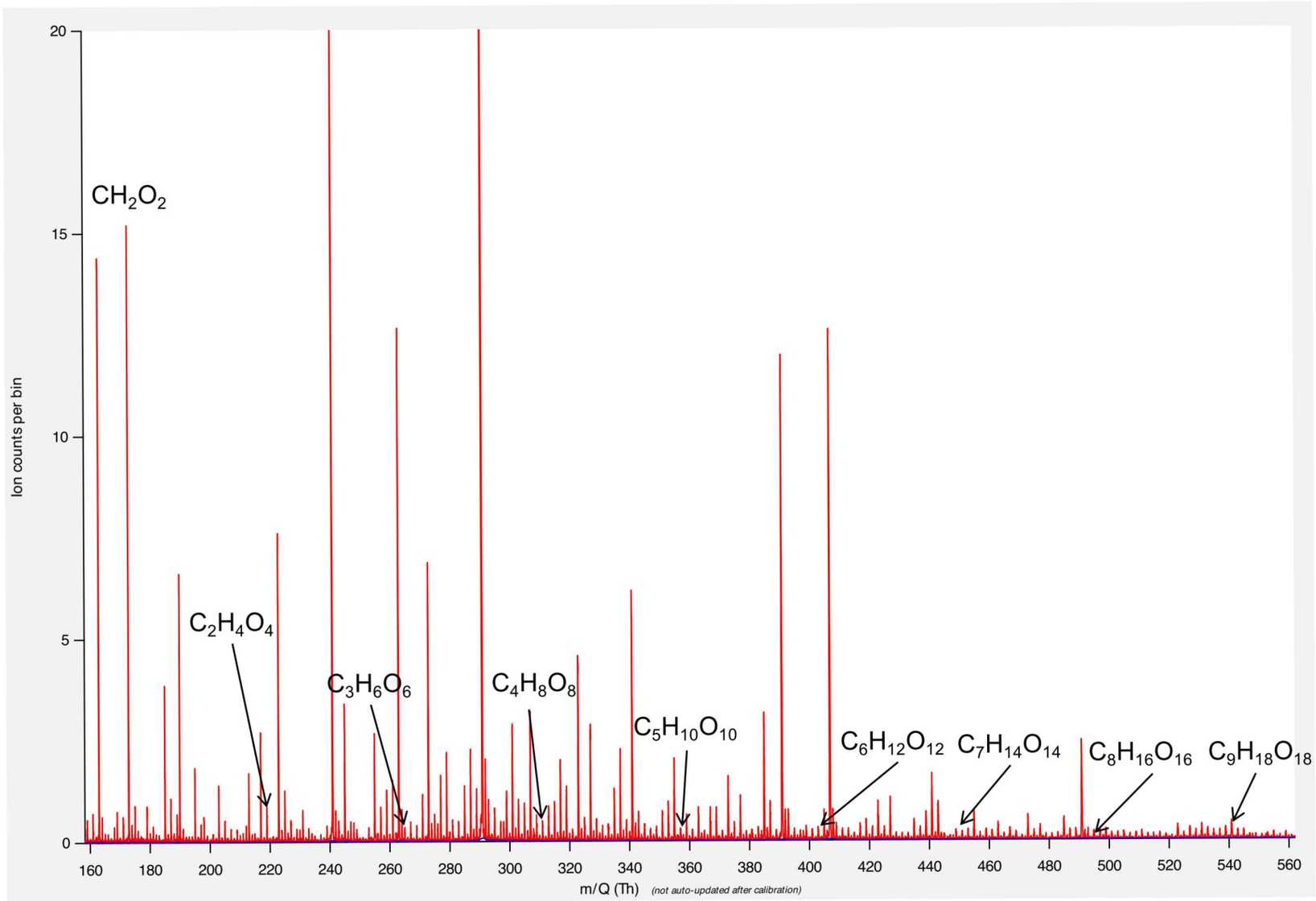






Criegee-ROOH insertion products ≤n=10 observed in the aerosol phase also



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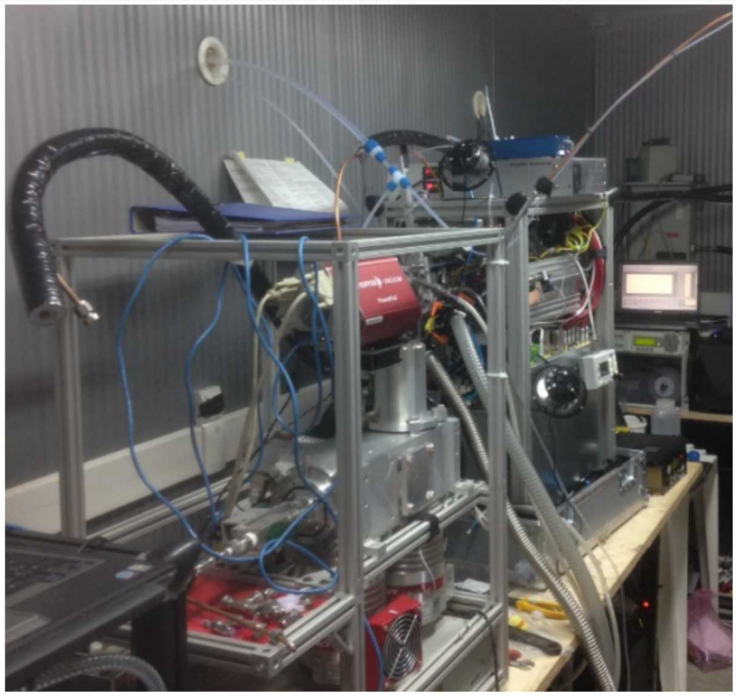

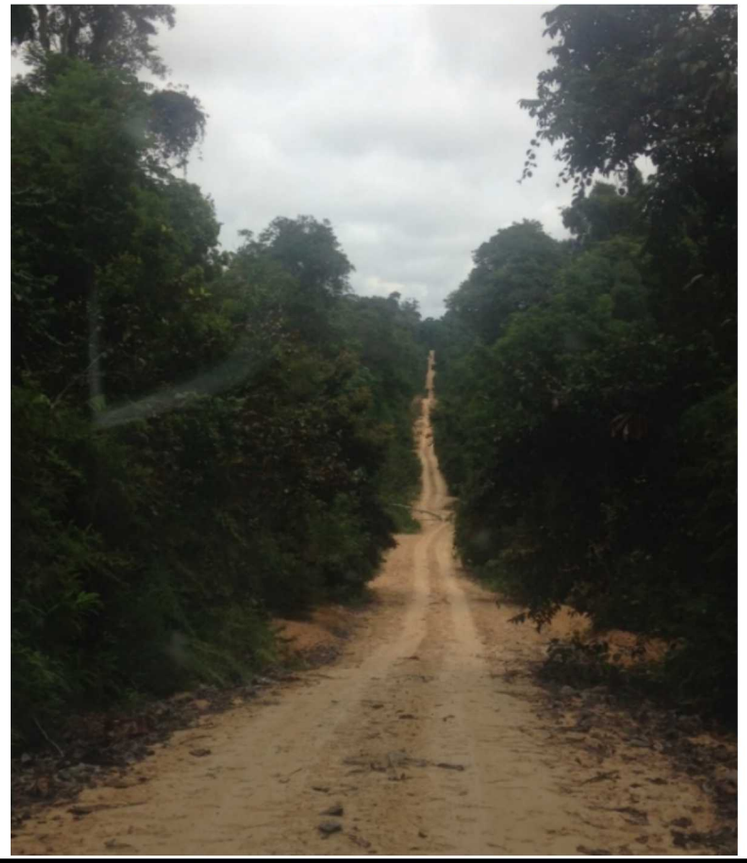

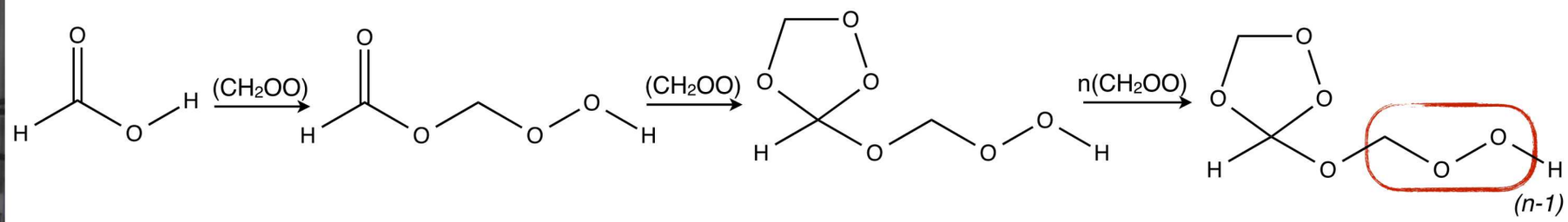

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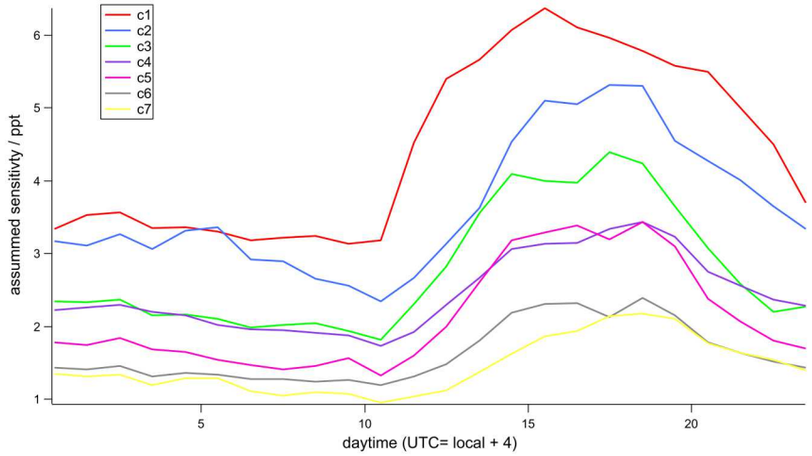
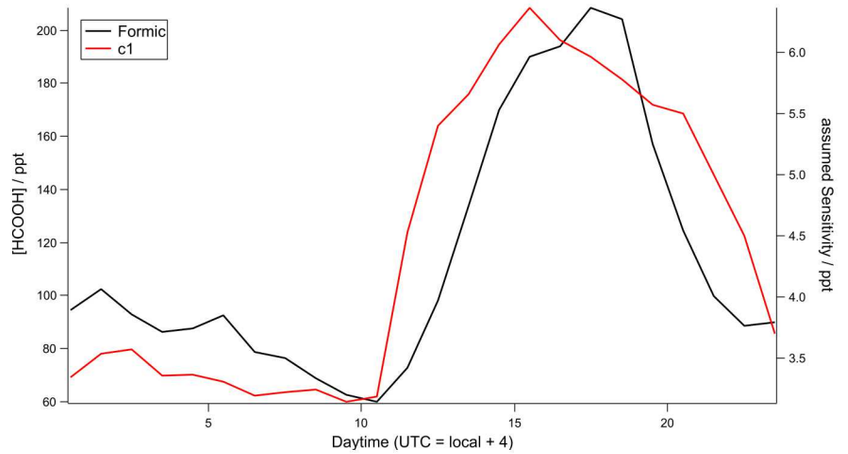




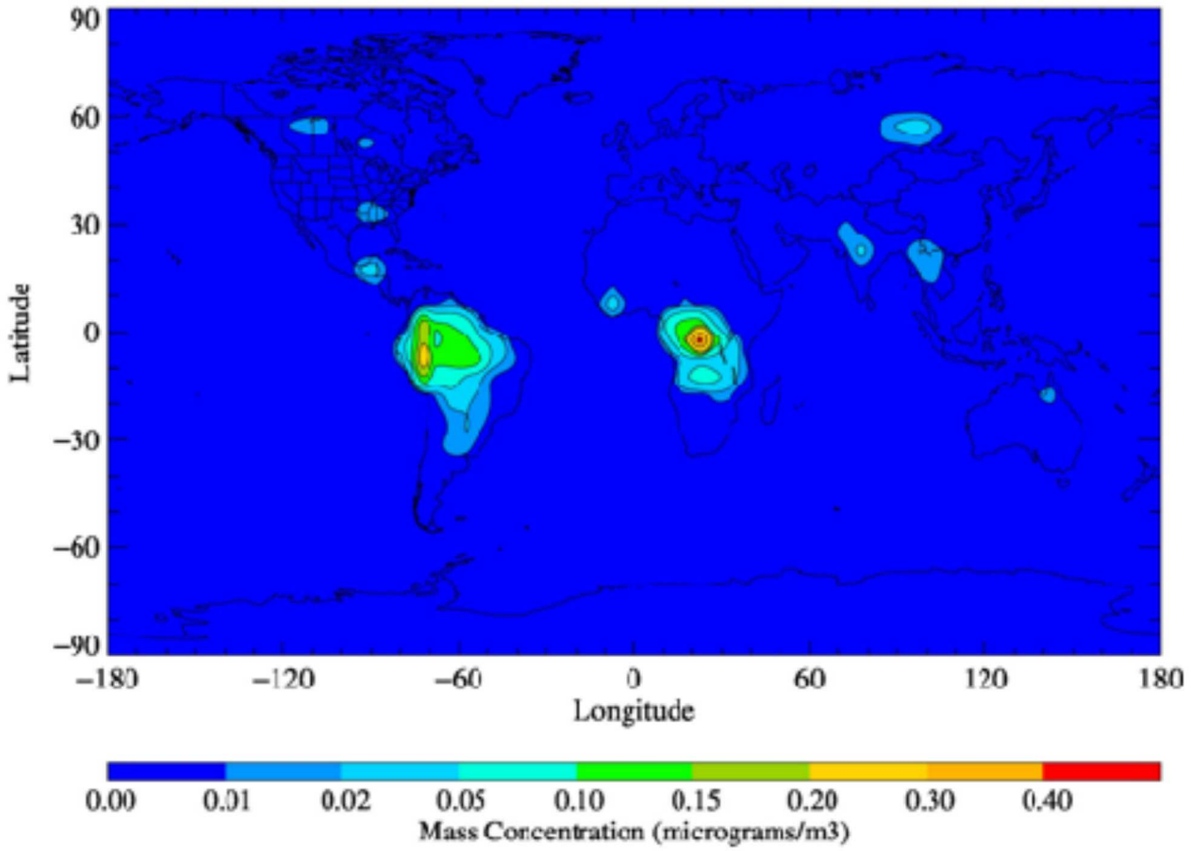
- Time behavior of insertion products follows that of formic acid
- Criegee + ROOH products now observed in both direct and ozonolysis lab studies, and the field.
- Criegee oligomerization products from ROOH measured in the field in gas and aerosol phase.
- What are the ***potential global atmospheric implications of these reactions for SOA*** ?

Examining the impacts with modelling

- Calculations of rate coefficient for CH_2OO + HPMF (from CH_2OO + formic acid) in progress (*Klippenstein*, Argonne) - early indications suggest the reaction is rapid.

- Preliminary global modeling of potential impact of Criegee + ROOH reactions have been undertaken (*Khan & Shallcross*, Bristol) using the 3D global chemical transport model STOCHEM-CRI

$k = 1 \times 10^{-12}$ cm^3 s^{-1}



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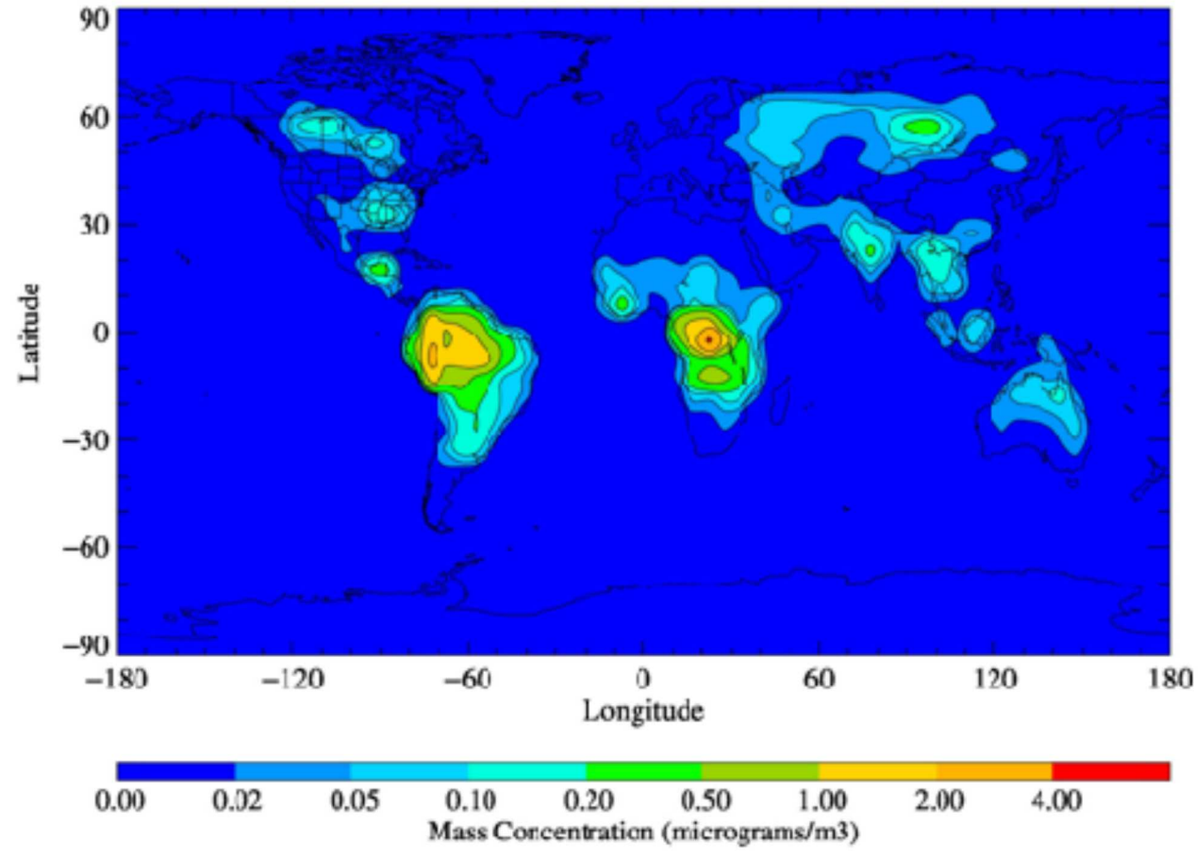

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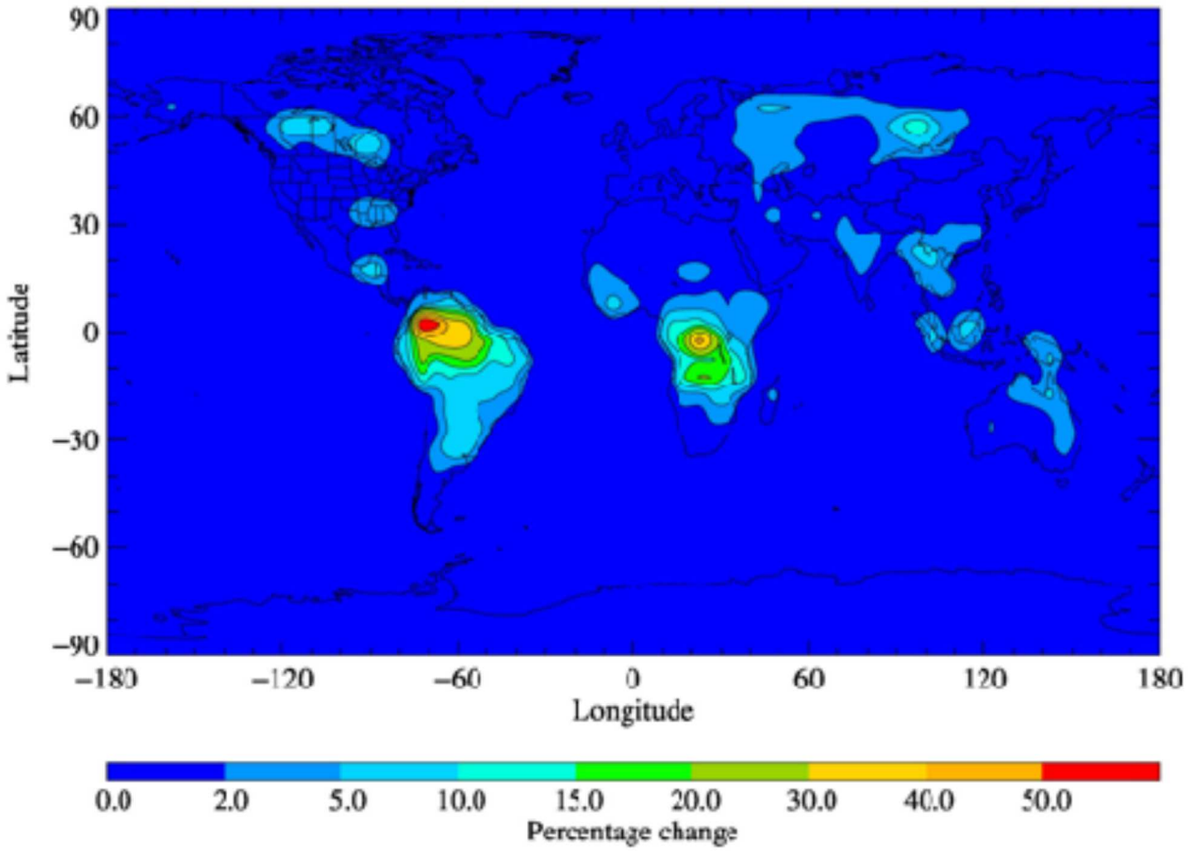
Up to 50% increase in modelled SOA mass



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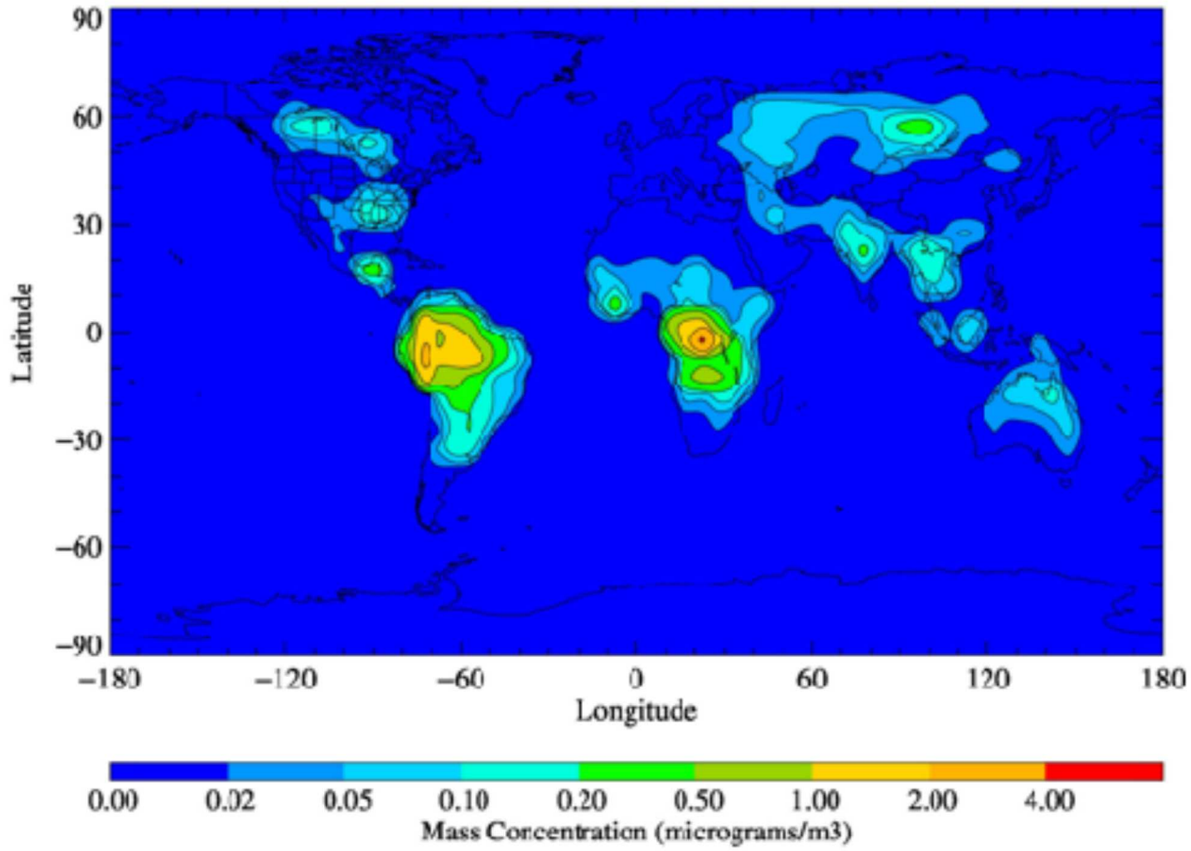

- Substantial increase in modeled SOA from Criegee + ROOH reactions if they are as fast as early indications suggest.

Summary

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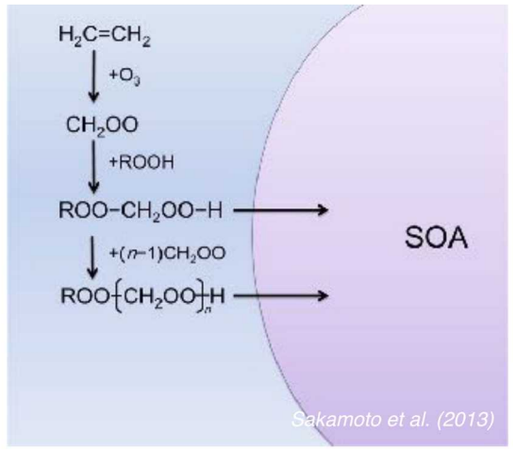

Y. Sakamoto, S. Inomata & J. Hirokawa, *Journal of Physical Chemistry A,* (2013), 117, 12912-12921 .
L. Vereecken, A.R. Rickard, M.J Newland & W.J. Bloss, *Physical Chemistry Chemical Physics,* (2015), 17, 23847-23858.

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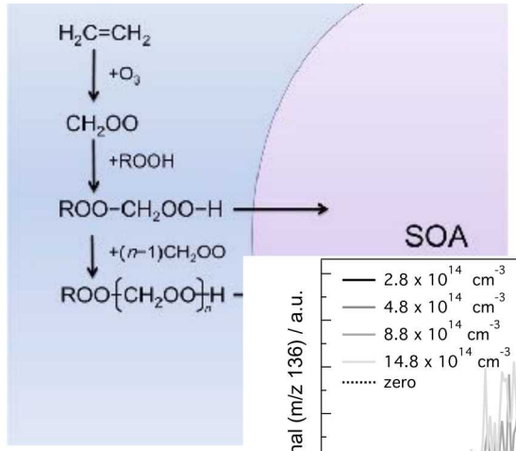
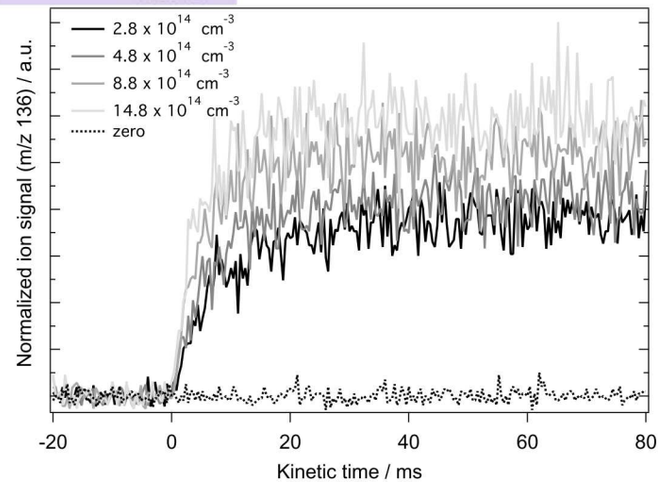
  c.f. Vereecken calculations.





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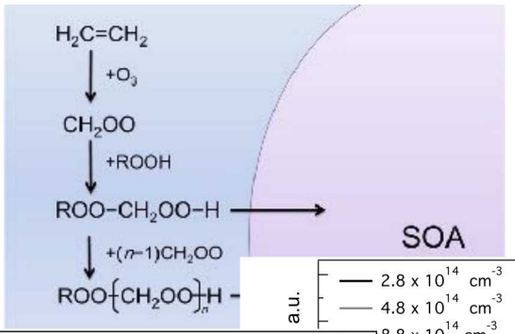

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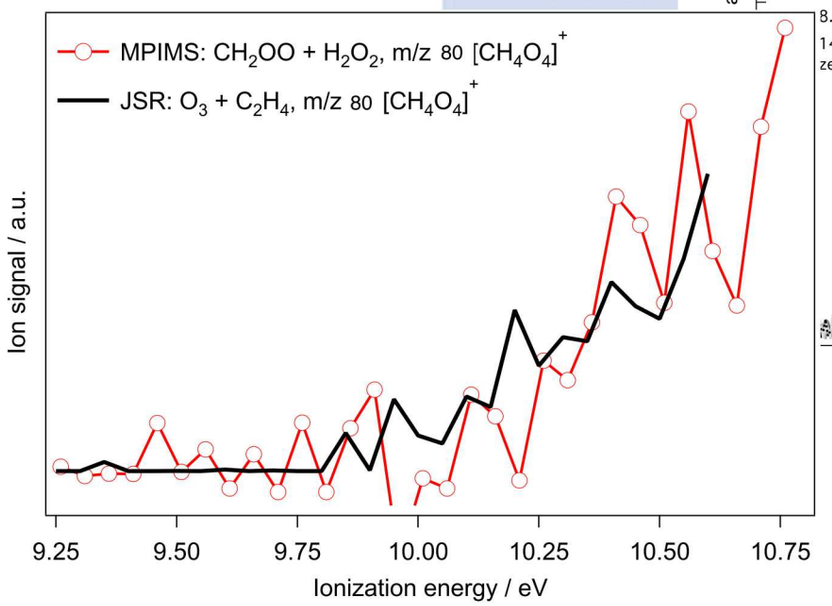

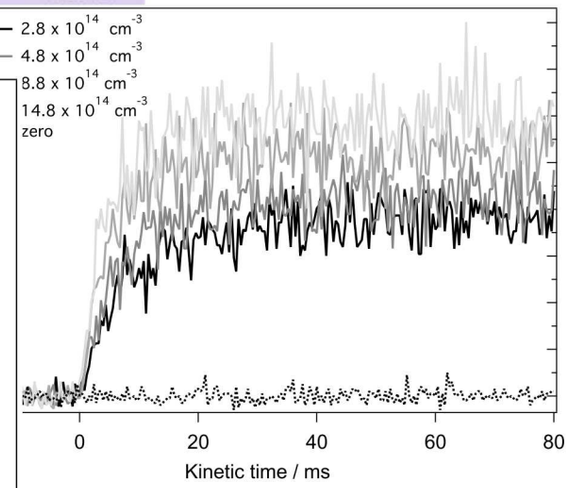

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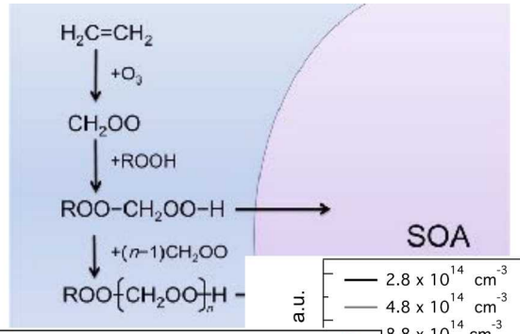

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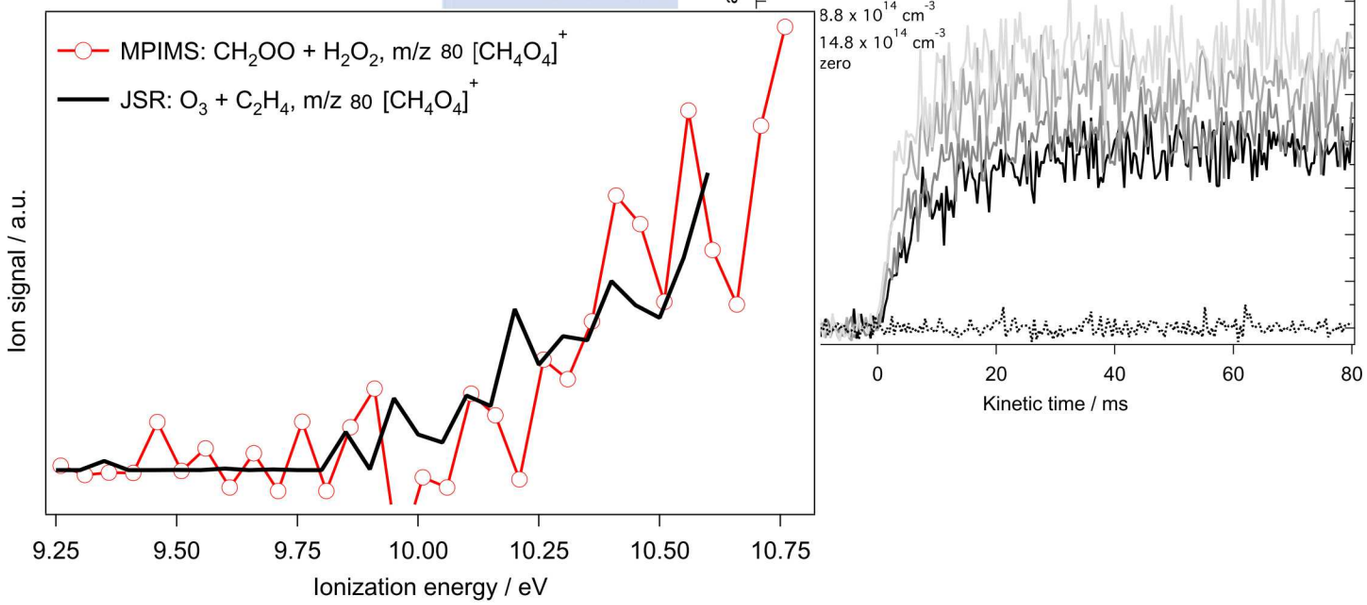

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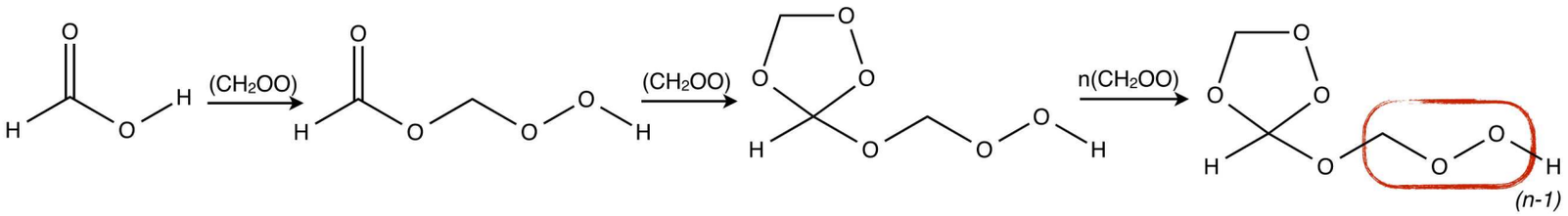

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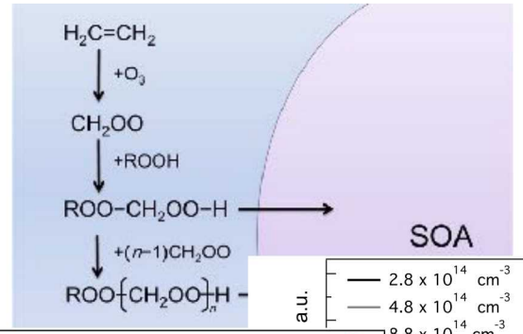

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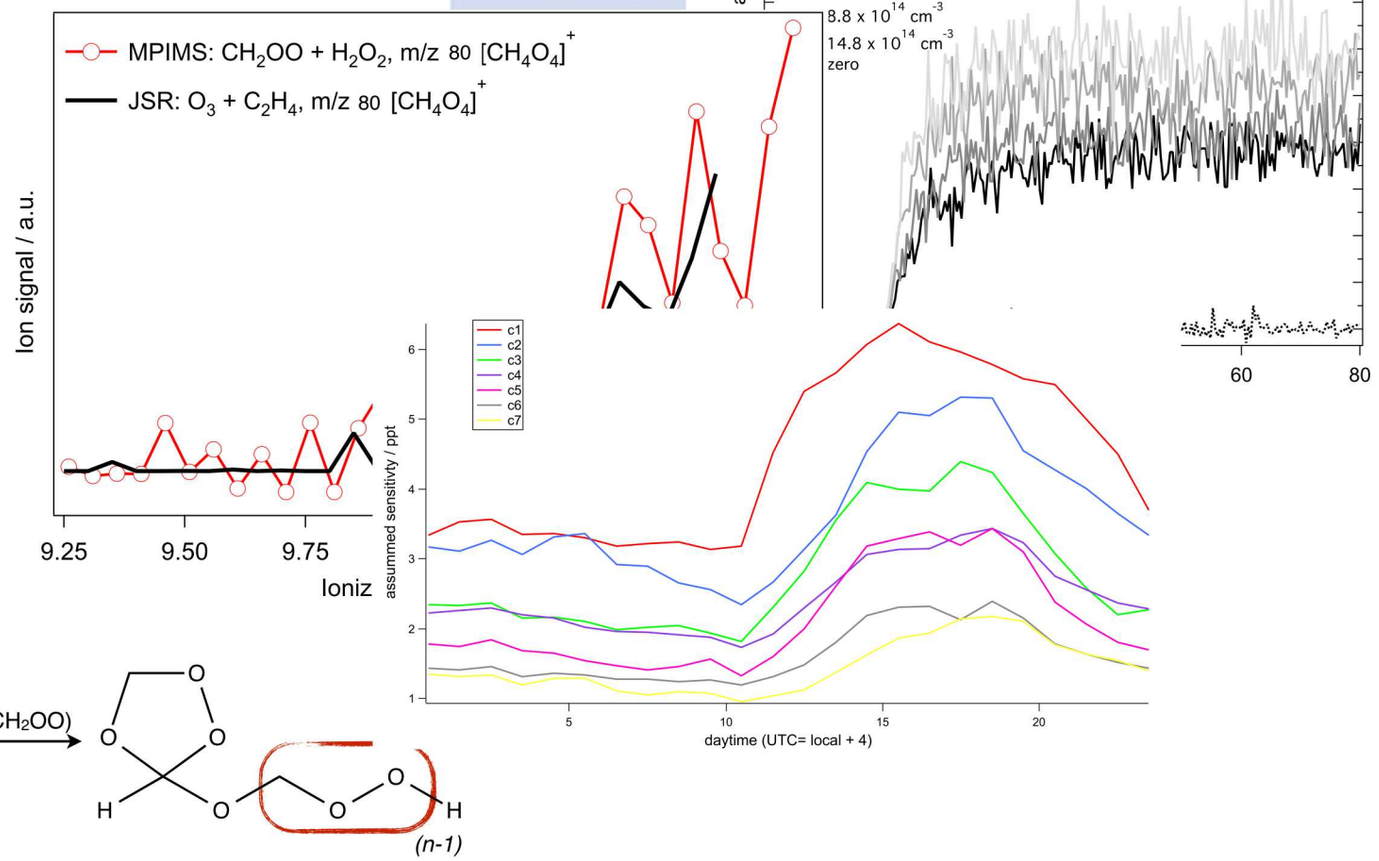

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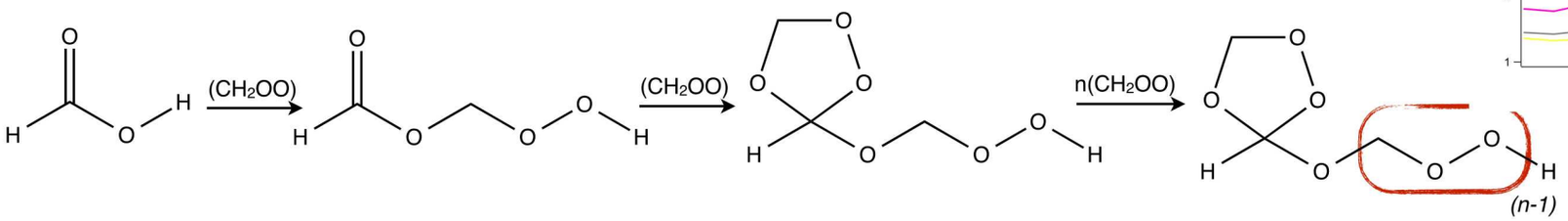

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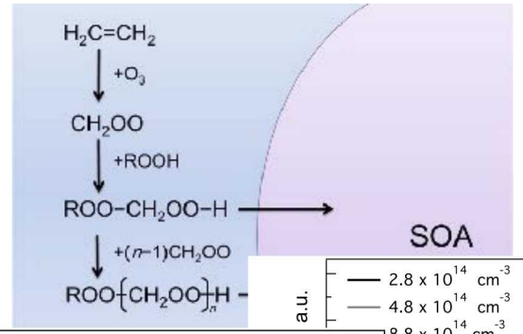

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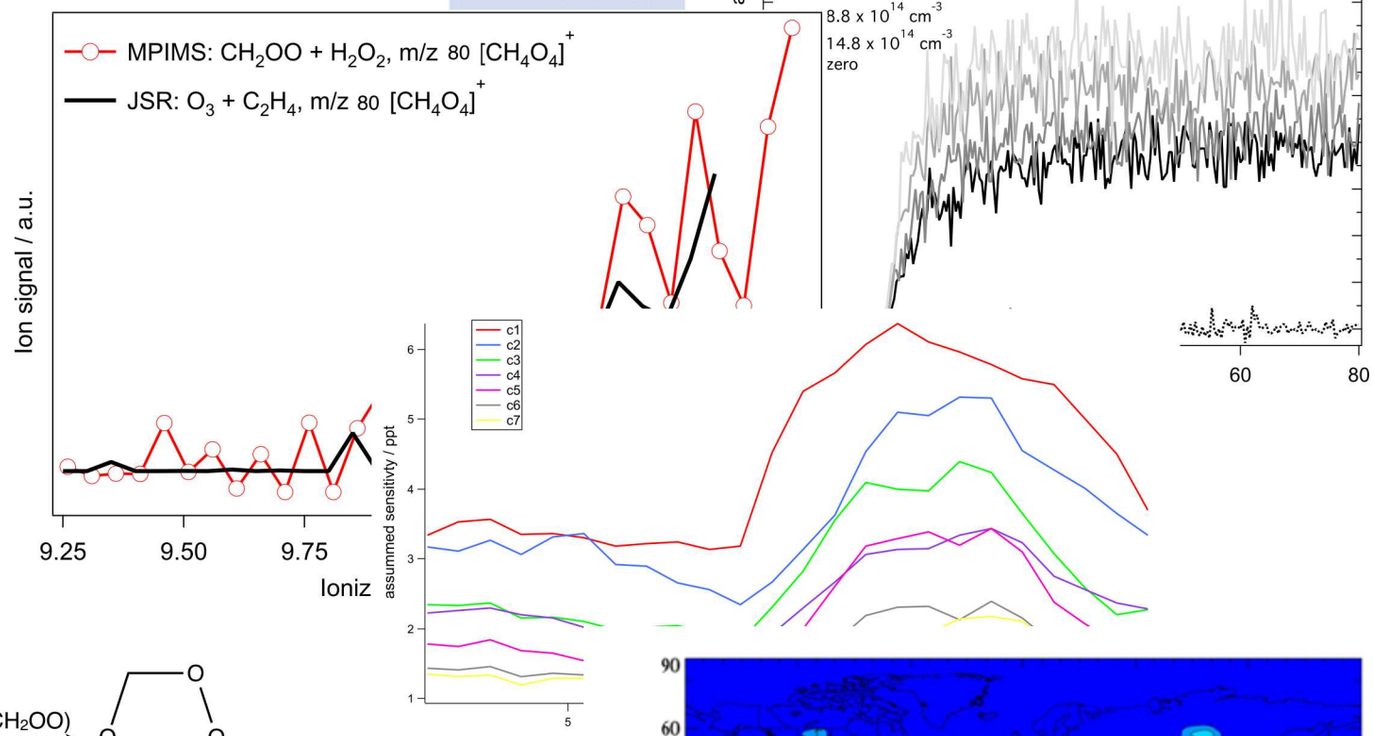

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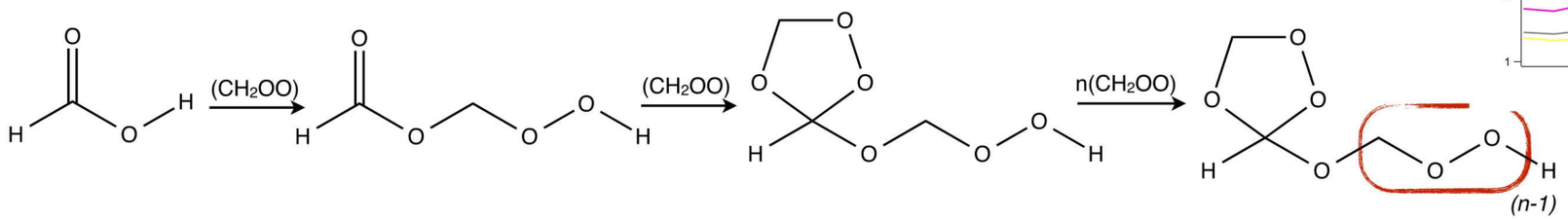

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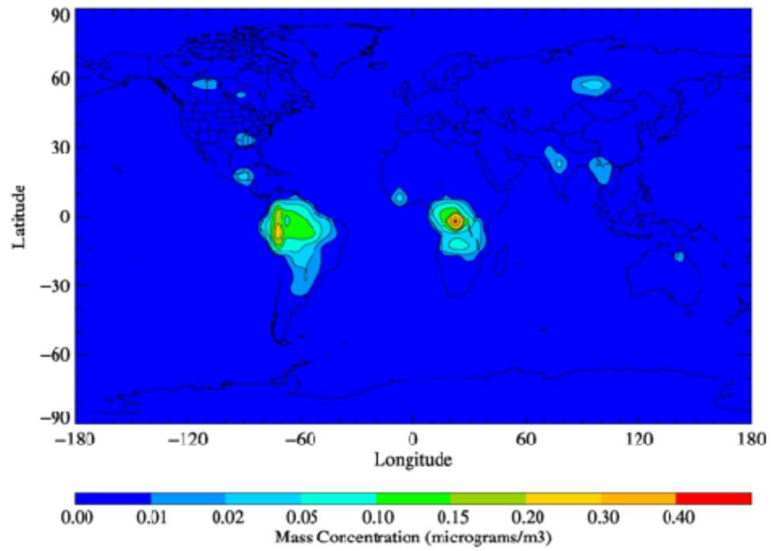
- Global modelling reveals Criegee + ROOH ***could be a significant source of SOA,*** especially over Brazil rainforest.



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Acknowledgements

Lab work

Raybel Almeida
Kendrew Au
Paul Fugazzi
Nils Hansen
David Osborn
Aric Rousso
Craig Taatjes

Jet Propulsion Laboratory
California Institute of Technology

Kyle Bayes
Carl Percival
Stan Sander
Frank Winiberg
Kristen Zuraski

Beamline support

Oleg Kostko
Bruce Rude
Doug Taube
Kevin Wilson

This material is based upon work supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (BES), U.S. Department of Energy (USDOE). Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the USDOE's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the USDOE or the United States Government.

This research used resources of the Advanced Light Source of Lawrence Berkeley National Laboratory, which is a USDOE Office of Science User Facility. The Advanced Light Source is supported by the Director, Office of Science, BES/USDOE, under contract DE-AC02- 05CH11231 between Lawrence Berkeley National Laboratory and the USDOE.

Field work

James Allan
Asan Bacak
Tom Bannan
Hugh Coe
Carl Percival
Stephen Worrall

Instituto de Física
Universidade de São Paulo

Paulo Artaxo
Joel Brito

Modelling

University of Bristol

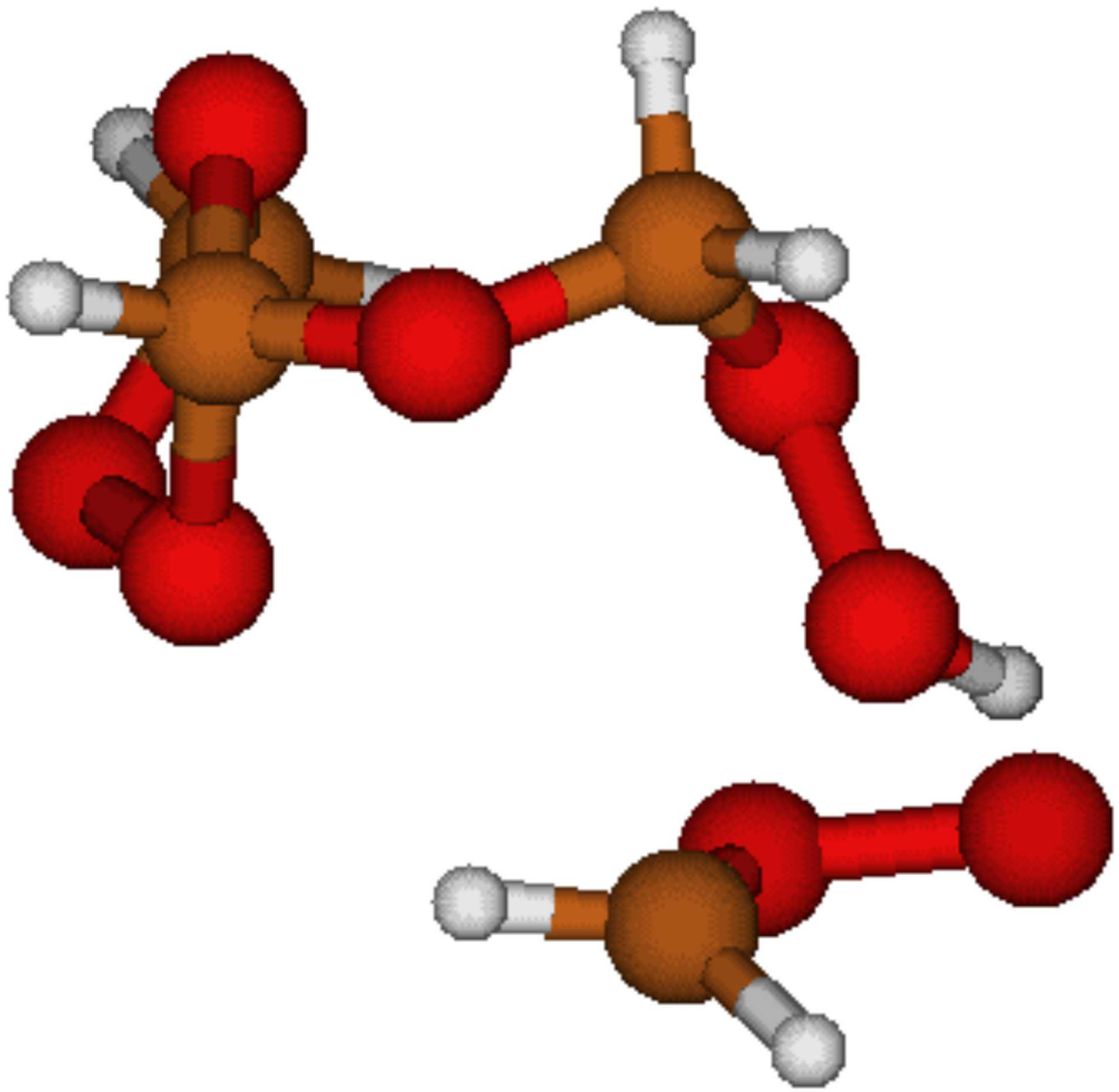
M. Anwar H. Khan
Dudley Shallcross

Theory

Argonne National Laboratory

Ahren Jasper
Stephen Klippenstein

Calculated TS for CH_2OO + SOZ insertion



Calculated PES for CH_2OO + HPMF