SAND2016-3655C

Advancing kinetic mechanisms for low-temperature combustion through the detection of highly elusive intermediates

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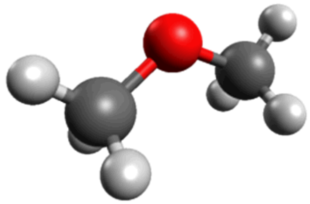
Focus of this talk

- Experimental detection of the ketohydroperoxide in dimethyl ether oxidation
- Determination of photoionization cross sections for elusive species
- Experimental evidence of the Korcek Decomposition Mechanism
- Extended low-temperature oxidation scheme for hydrocarbons

Introduction



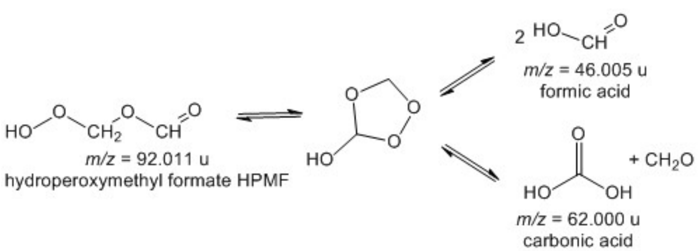
Dimethyl ether

Simple model fuel with similar characteristics like gasoline/diesel

Homogenized Low-Temperature Combustion: Reduction of NO_x and soot at the same time

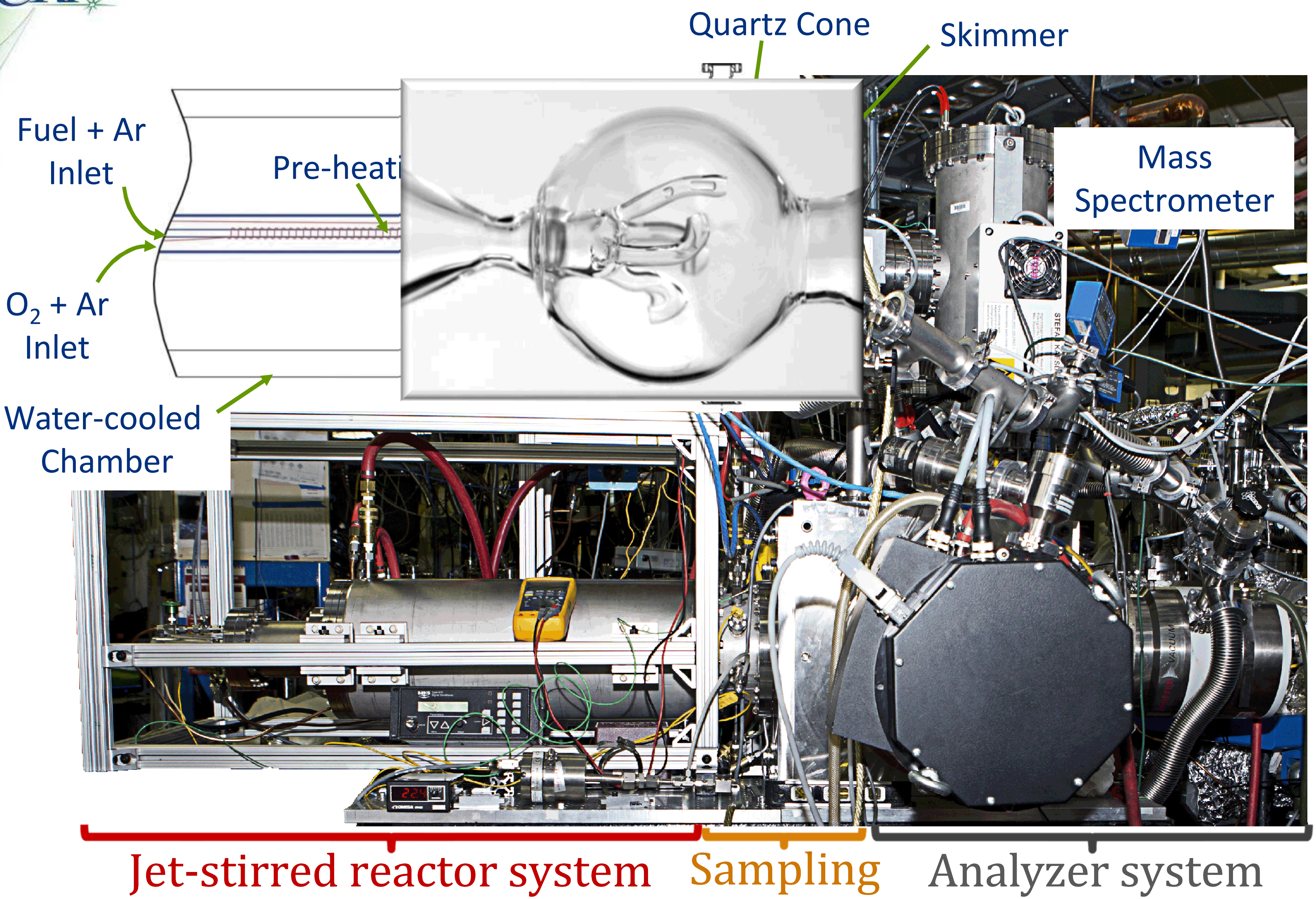
destructive instabilities
engine knocking
other pollutants
…

Understanding its chemical kinetics

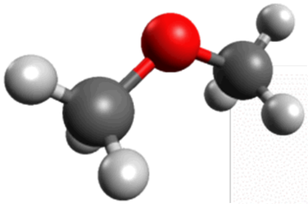


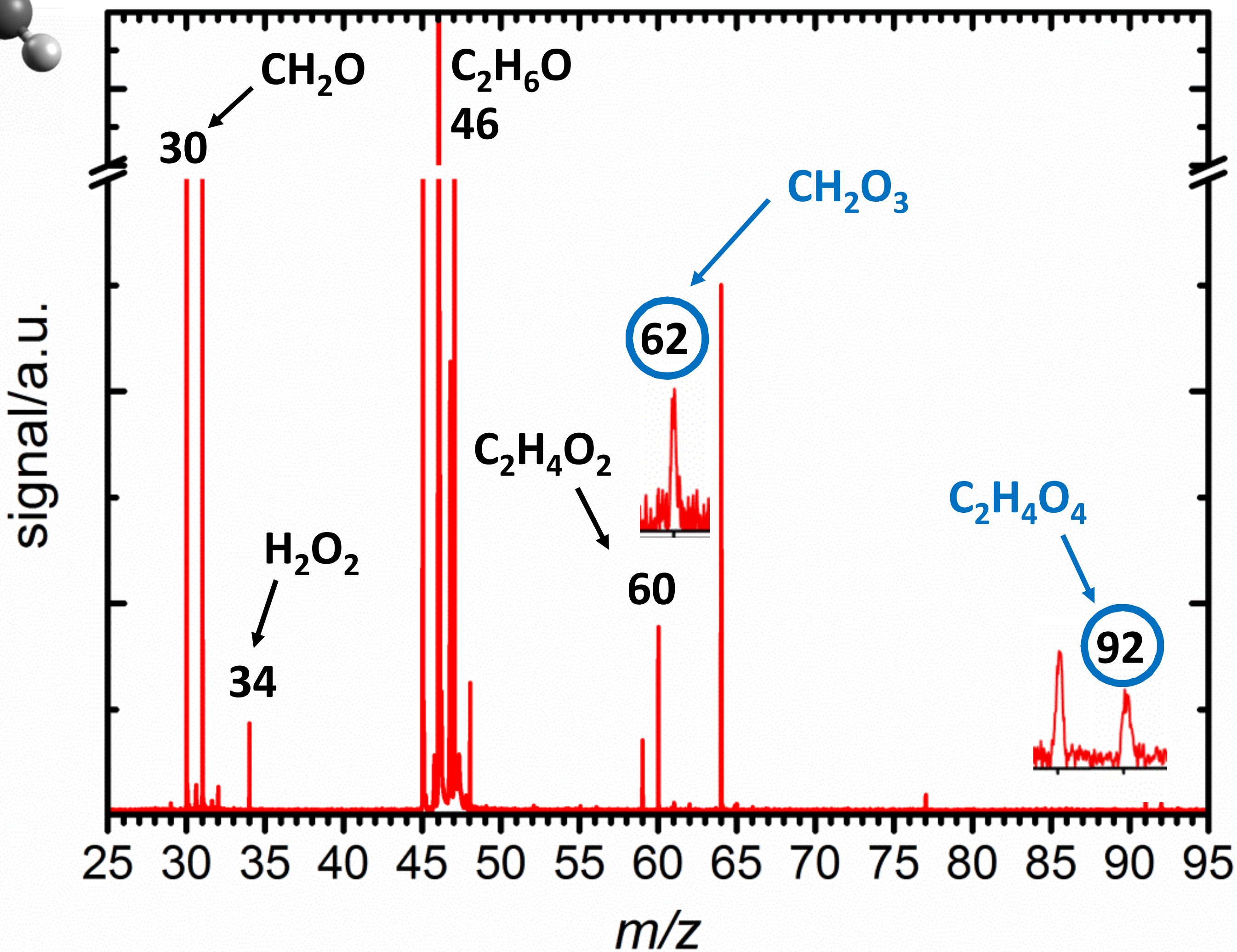
- Control autoignition
- Prevent pollutants

Experimental approach



Low-temperature oxidation of DME





Conditions:
T=540 K
τ=5000 ms
Photon energy=11.2 eV

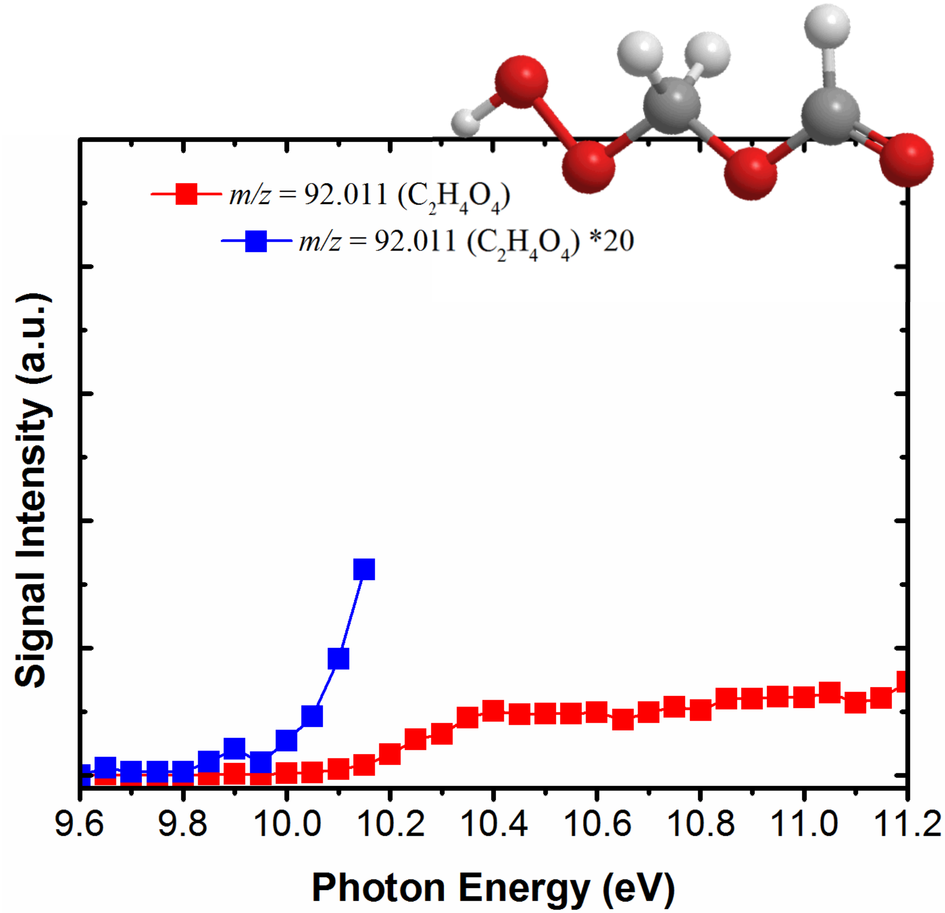
Detection of the Ketohydroperoxide

Theory

CH_3OCH_3
↓ **H-atom abstraction**
CH_3OCH_2
↓ **1st O_2-addition**
$CH_3OCH_2O_2$
↓ **Rearrangement**
$CH_2OCH_2O_2H$
↓ **2nd O_2-addition**
$O_2CH_2OCH_2O_2H$
↓ **OH elimination**
HO_2CH_2OCHO
↓

m/z=92.011 u

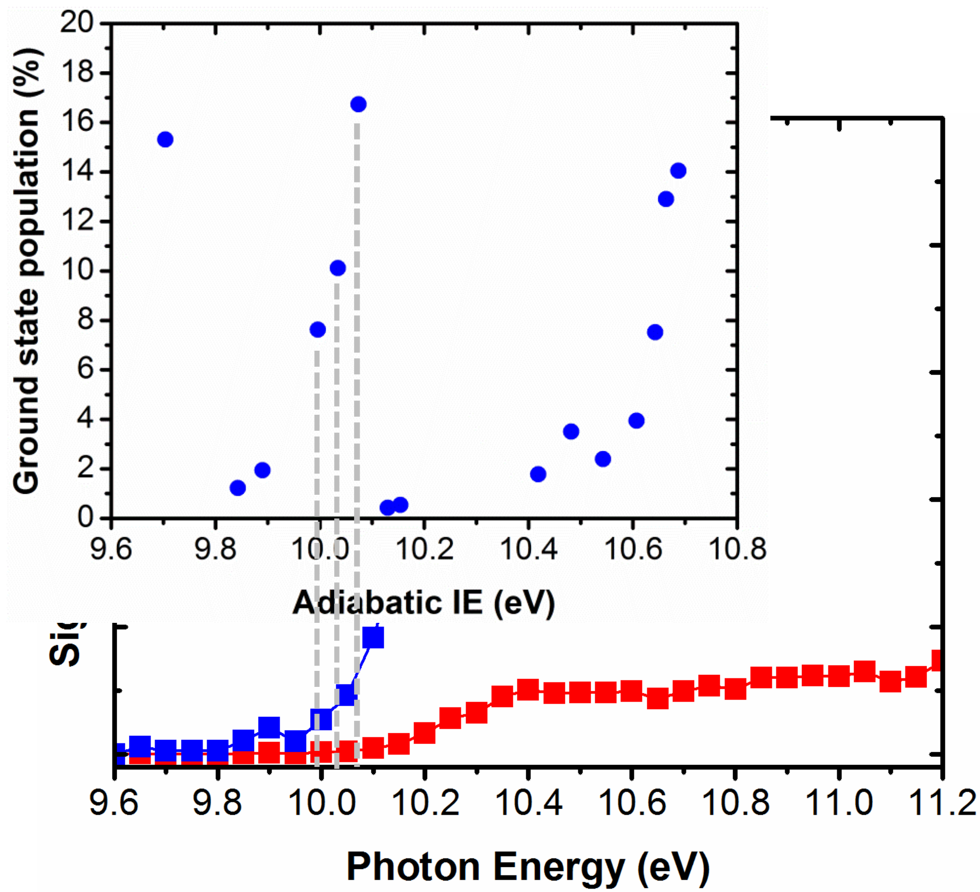
hydroperoxymethyl formate (HPMF)



Detection of the Ketohydroperoxide

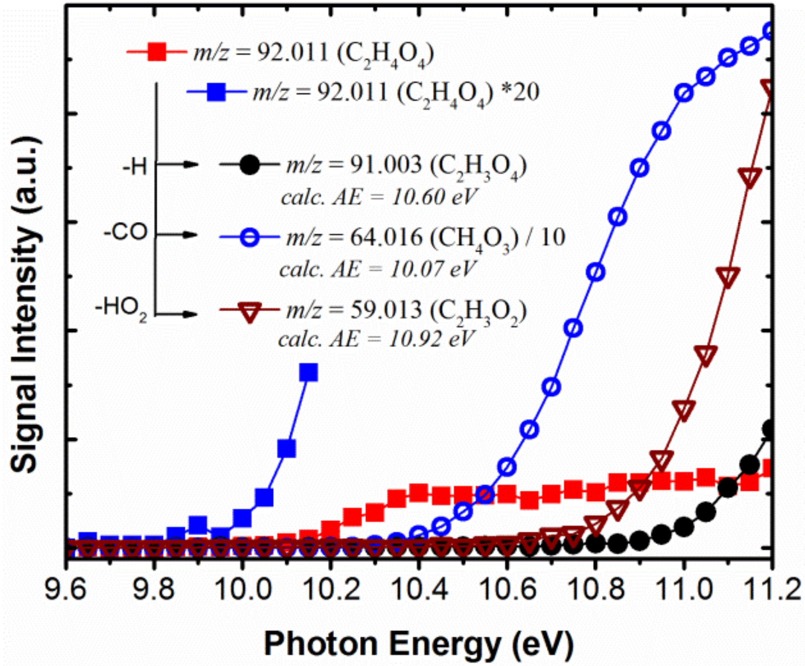
Conformer-dependent IEs for Larger Species

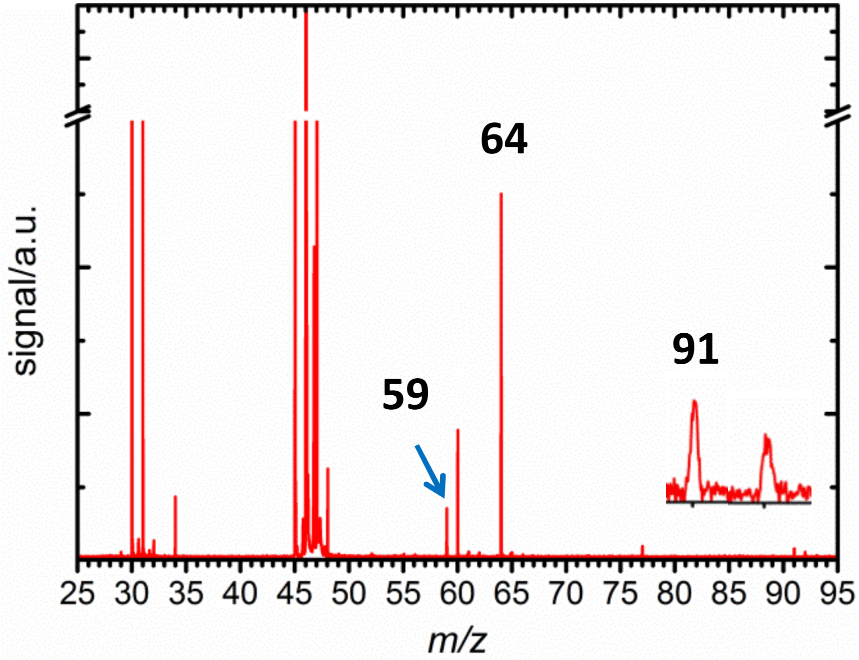
- Conformers characterized for both the neutral and cation species
- Neutral conformer populations estimated via a simple locally harmonic scheme
- Locally adiabatic IEs calculated for each conformer based on vertical excitations
- 3 conformers with ionization energies near ~10.05 eV make up 35% of the total population
- Conformer near 9.7 eV has a poor Franck-Condon overlap



K. Moshammer *et al., J. Phys. Chem. A,* **2015,** 119, 7361-7374

Detection of the Ketohydroperoxide





Hydroperoxymethyl formate (HPMF) ???

Fragment pattern gives evidence for the experimental detection of HPMF

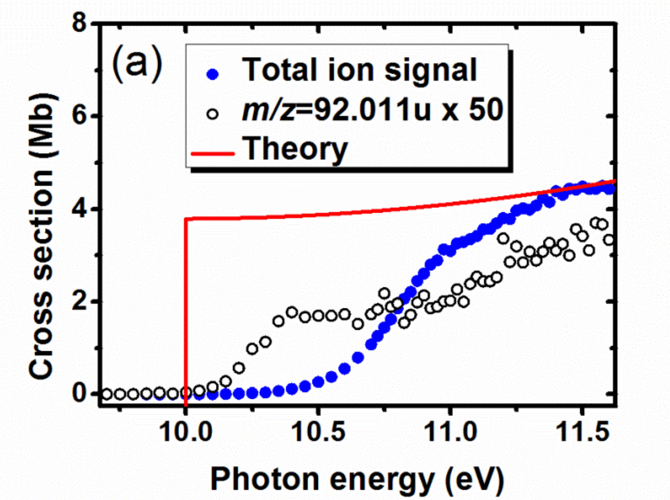
Quantification and Comparison with Model Calculations

- using calculated photoionization cross sections

  ePolyScat (version E3)

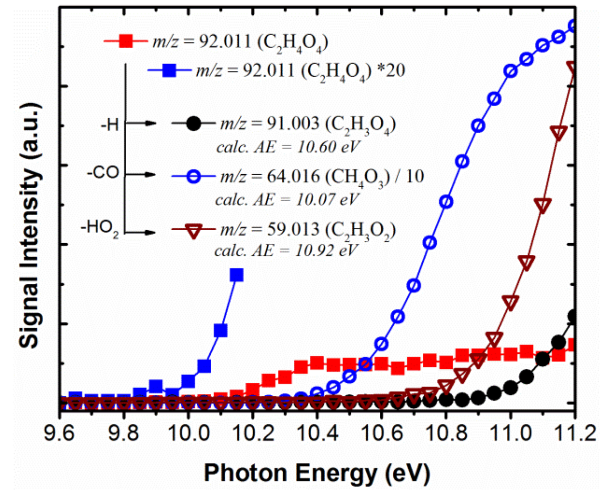
  F. A. Gianturco *et al., J. Chem. Phys.,* **1994,** 100, 6464-6471

  A.P.P. Natalense *et al., J. Chem. Phys.,* **1999,** 111, 5344-5348



- tested against a variety of known species
- it calculates total cross sections

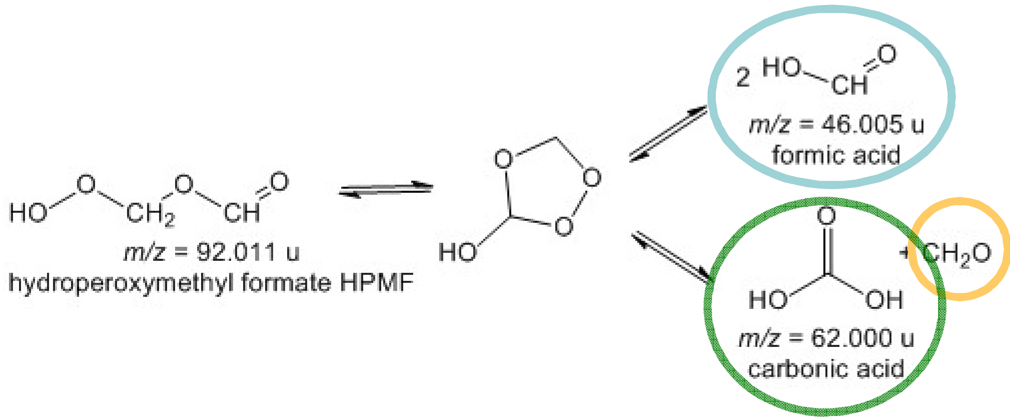
  ⇒ fragmentation pattern needs to be known

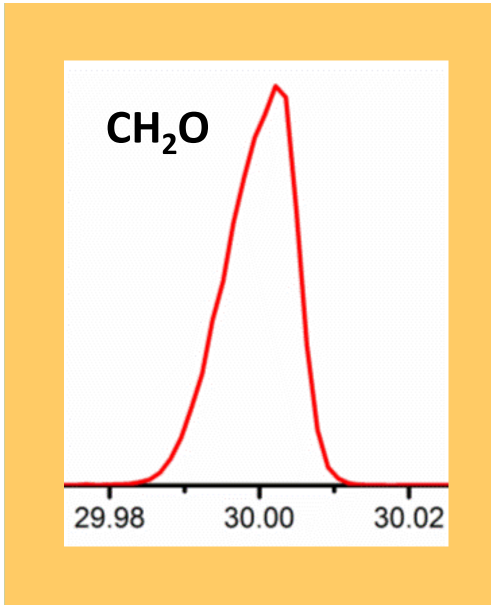


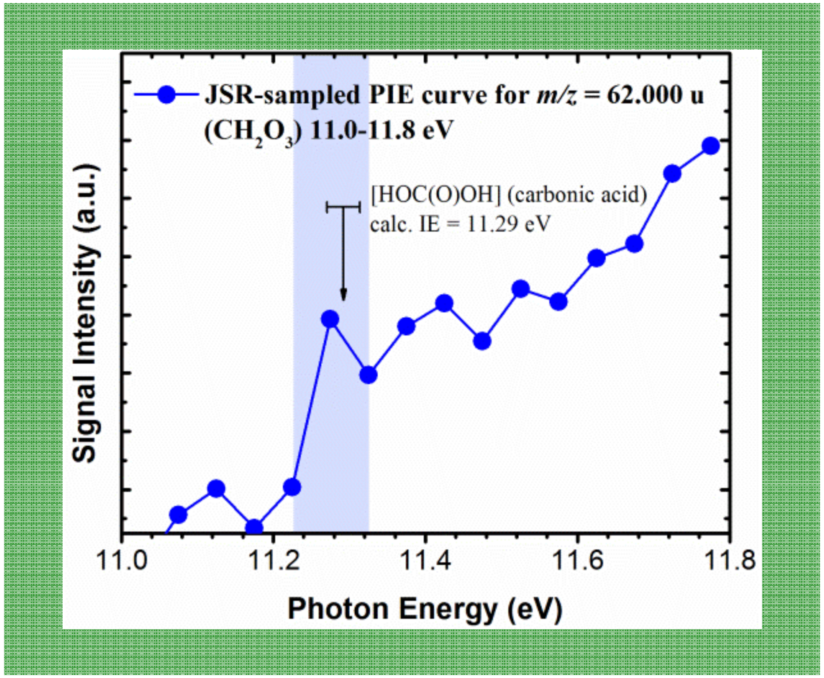
Models:
Z. Wang *et al., Combust. Flame,* **2015,** 162, 1113-1125 (USTC)
U. Burke *et al., Combust. Flame,* **2015,** 162, 315-330 (NUI)
A. Rodriguez *et al., J. Phys. Chem. A,* **2015,** 119, 7905-2923 (CNRS)

K. Moshammer *et al., J. Phys. Chem. A.,* **2016,** submitted

The Korcek Decomposition Mechanism







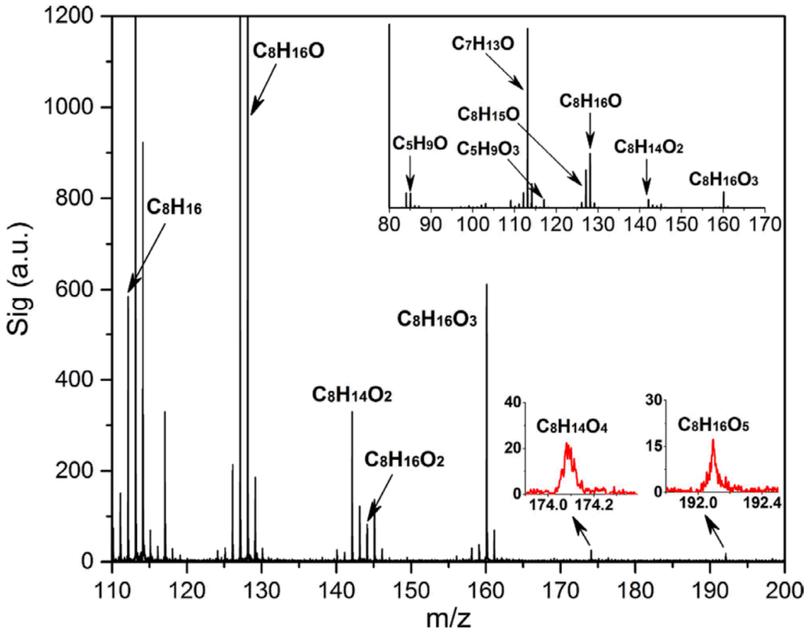
BUT:

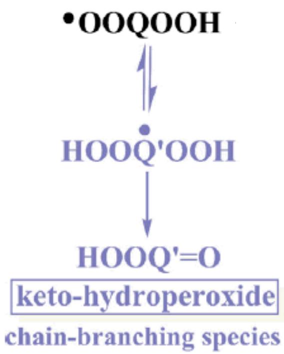
Formic acid and formaldehyde are also produced by several other pathways!!!

Detection of carbonic acid proofs Korcek decomposition mechanism!

Extended low-temperature oxidation scheme

- low-temperature oxidation of 2,5-dimethylhexane

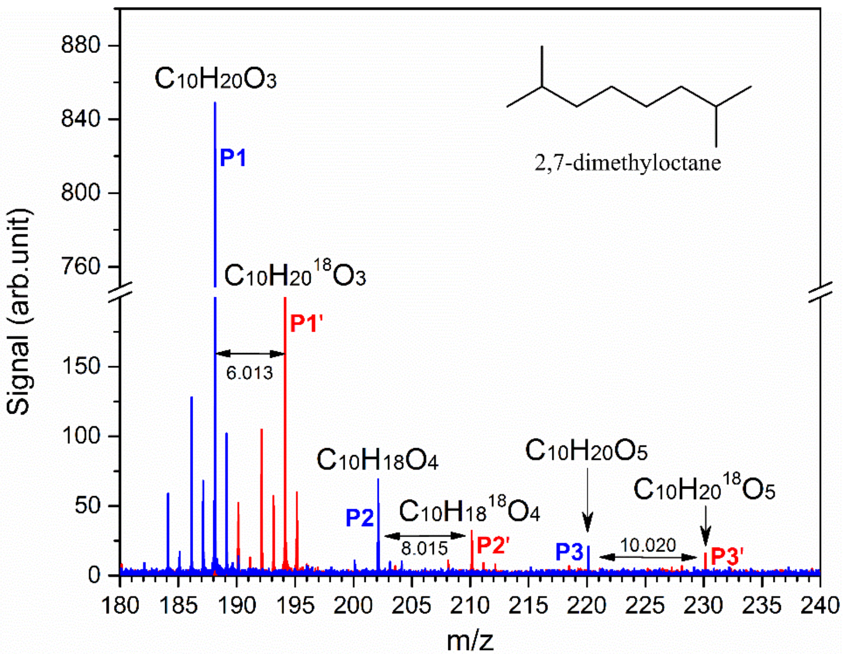




Z. Wang *et al., Combust. Flame,* **2016,** 164, 386-396

Confirmation through $^{18}O_2$ experiments

- low-temperature oxidation of 2,7-dimethyloctane



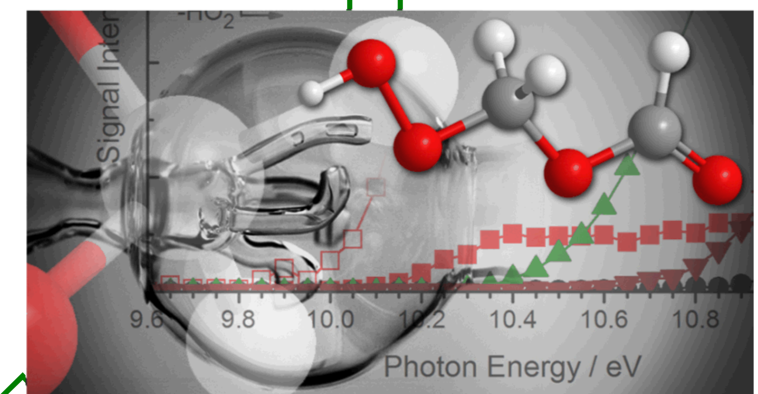
Species	$^{16}O_2$ exp.	$^{18}O_2$ exp.
$C_{10}H_{20}O_3$	*m/z*=188.14 u (P1)	*m/z*=194.149 u (P1′)
$C_{10}H_{18}O_4$	*m/z*=202.121 u (P2)	*m/z*=210.136 u (P2′)
$C_{10}H_{20}O_5$	*m/z*=220.127 (P3)	*m/z*=230.147 u (P3′)

The usage of $^{18}O_2$ instead of $^{16}O_2$ confirms the oxygenated chemical composition in the respective mass range

Summary

Experimental insights

- Detection of the ketohydroperoxide (HPMF)
- Quantified temperature profile of HPMF
- Carbonic acid as evidence for the Korcek Decomposition Mechanism
- Extended low-temperature oxidation scheme (3rd O_2 addition)



Theoretical insights

- Local adiabatic IPs
- Conformeric structure strongly affects adiabatic IP
- Calculation of PICS

Future model development

Comparisons of exp. data with model predictions

Acknowledgements

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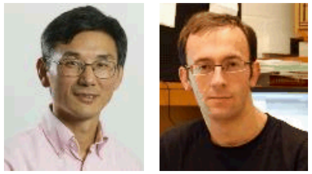
Universität Bielefeld



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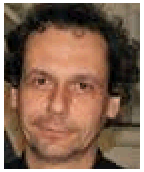

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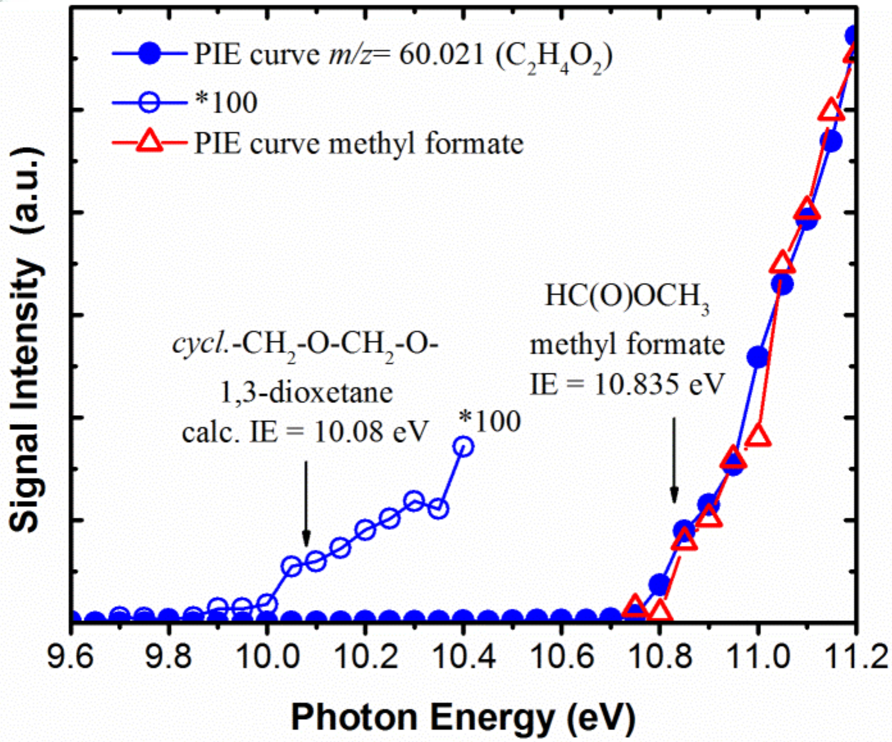
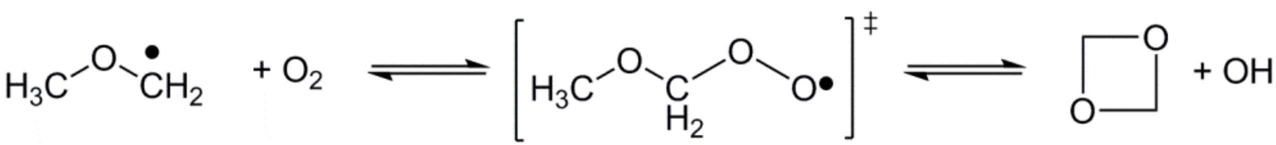
Thank you for your attention!!!

Cyclic ether at Mass 60



m/z	species	theory I[a]	theory II[b]
48	CH_3OOH	9.77	9.83
	$HOCH_2OH$	11.00	11.10
59	CH_2OCHO	7.93	7.78
	CH_2CHOO	10.18	9.79
60	$HC(O)OCH_3$	10.81	10.86
	CH_2CHOOH	9.07	9.19
	HOCHCHOH	8.27	8.41
	oxiran-2-ol	8.83	8.87
	3-CH_3-dioxirane	10.31	10.30
	cycl-CH_2OOCH_2–	9.35	9.37
	cycl-CH_2OCH_2O–	10.00	10.08

K. Moshammer et al., J. Phys. Chem. A, **2015**



Theoretically anticipated to be part of the LTC of DME