SAND2019-0859C

GAS PHASE CHEMICAL PHYSICS

Isomer-Resolved Probing of Complex Systems of Reactions

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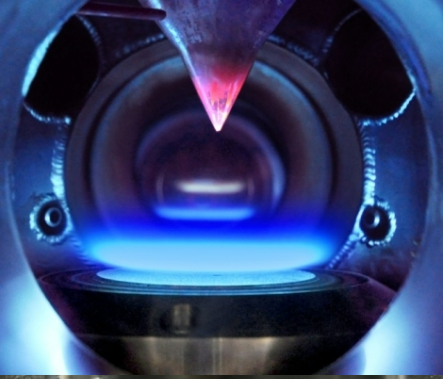

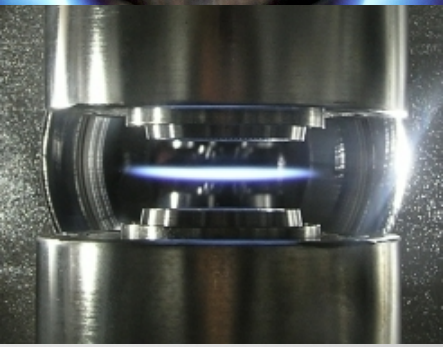

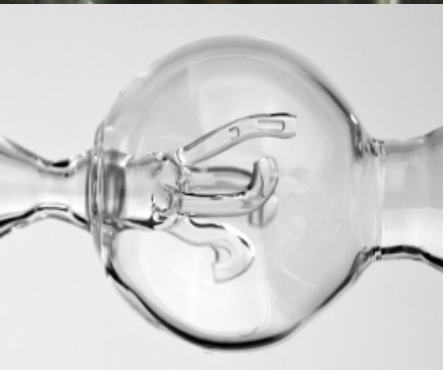

- ✓ Introduction
- ✓ Experimental Procedures
- ✓ Significance of Various PAH Formation Pathways in Flames
- ✓ 2D-Temperature Fields around the Quartz Sampling Probe
  - ➢ X-Ray Fluorescence Spectroscopy
- ✓ Low-Temperature Oxidation Studies
  - ➢ Jet-Stirred Reactor Sampling Molecular-Beam Mass Spectrometry
  - ➢ Identification and Quantification of Ketohydroperoxides
- ✓ Development of New Experimental Tools
  - ➢ Microwave Spectroscopy
  - ➢ 2D Mass Spectrometry (MS-MS)
- ✓ Summary and Outlook

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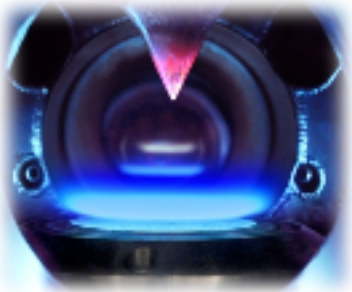
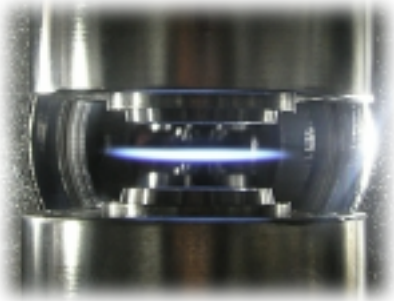
Complex Systems of Reactions and Combustion Mechanism Development

- ✓ Studying the chemistry of complex systems of reaction networks
- ✓ Gaining insights into the *scientifically relevant aspects* (key intermediates and chemical pathways) by addressing the "right" level of detail for
  - ➢ *formation of polycyclic aromatic hydrocarbons (PAHs)*
  - ➢ *low-temperature oxidation and ignition chemistry (detection, identification, and quantification of KHPs)*

- ✓ experiments and analysis procedures, theory, and new experiments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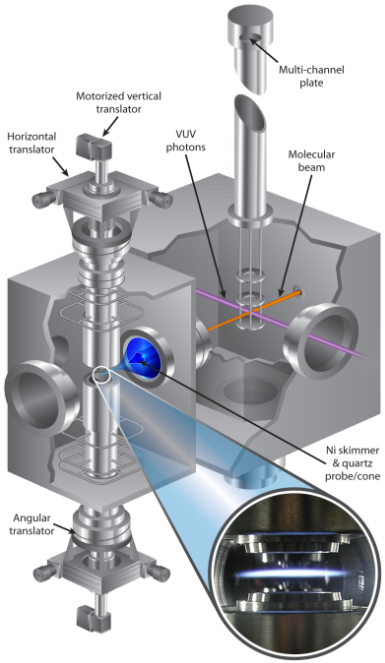
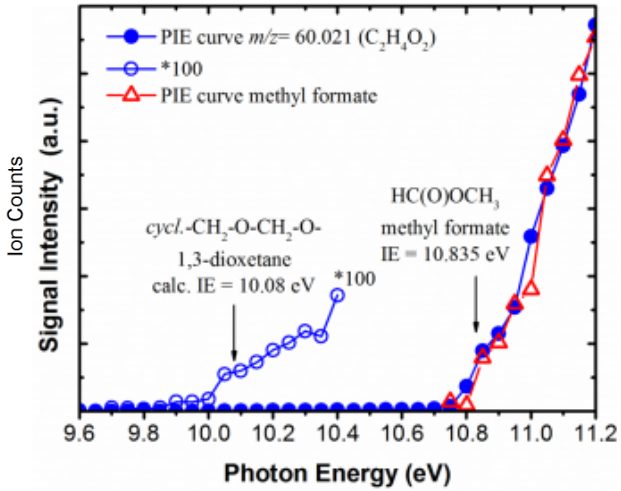
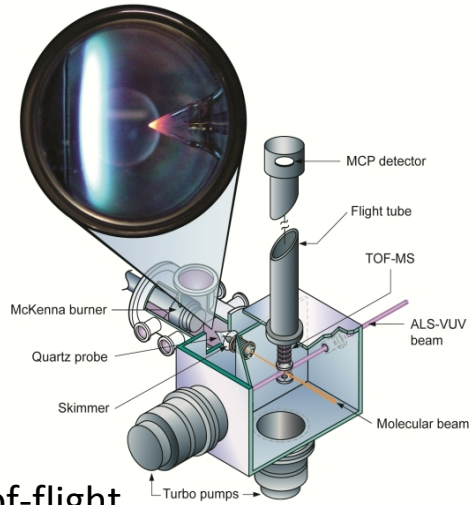
Gaining Experimental Insights Into Complex Systems of Reactions Under Idealized Conditions







- ✓ Orthogonal extraction reflectron time-of-flight
- ✓ Detection limit: ~0.5 ppm
- ✓ Mass resolution $m/\Delta m$ ~ 4000
- ✓ Electron and photon ionization (at the Advanced Light Source)
- ✓ Continuous ionization, rapid (35 kHz) ion extraction

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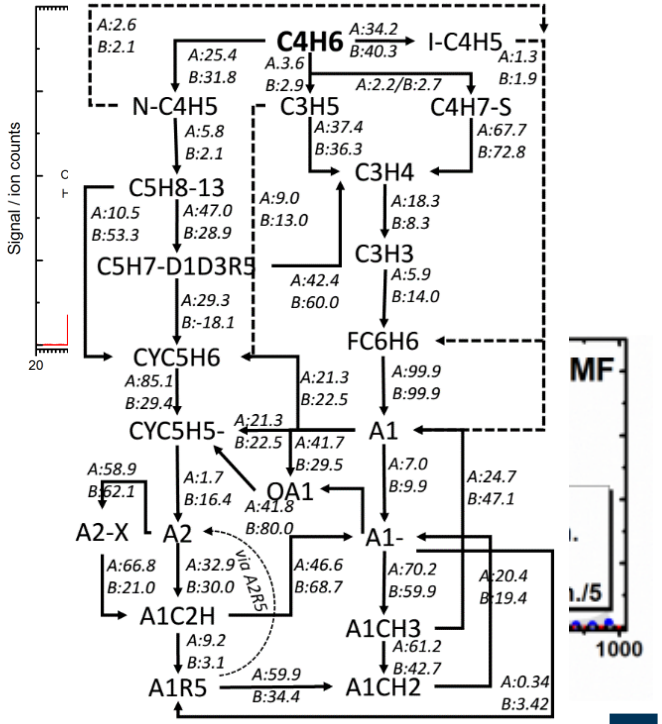
Gaining Experimental Insights Into Complex Systems of Reactions Under Idealized Conditions

1. **Sample from Complex Systems and record Mass Spectra**
   at various positions from and temperatures in the reactors
2. **Identify Key Components**
   based on m/z ratios, ionization thresholds, fragmentation patterns, PIE curves
3. **Determine the Quantitative Composition of the Reactors**
   calibrate the system (mass discrimination factors), measure (or calculate) photo- and electron ionization cross sections
4. **Identify Relevant Reaction Pathways**
   from species' identities and their mole fraction data
   combine measurements of mole fractions with kinetic modeling results
5. **Gaining Insights into Relevant Chemical Aspects**
   for PAH formation and low-temperature oxidation



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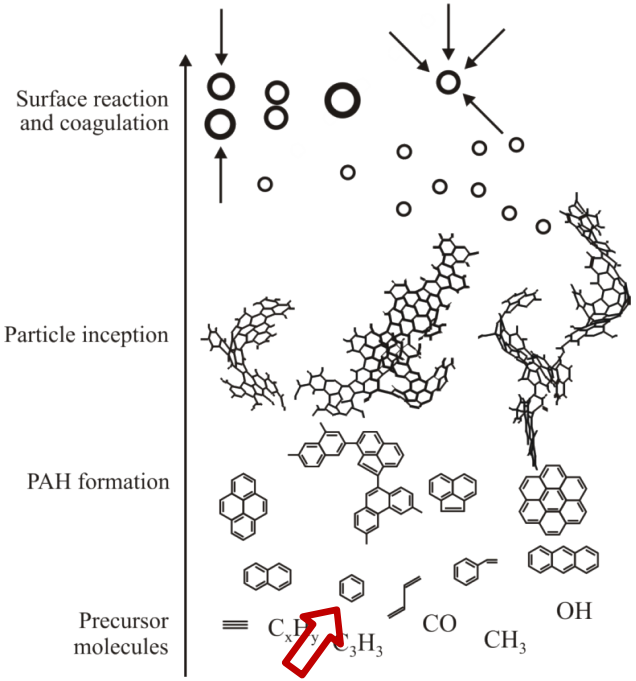
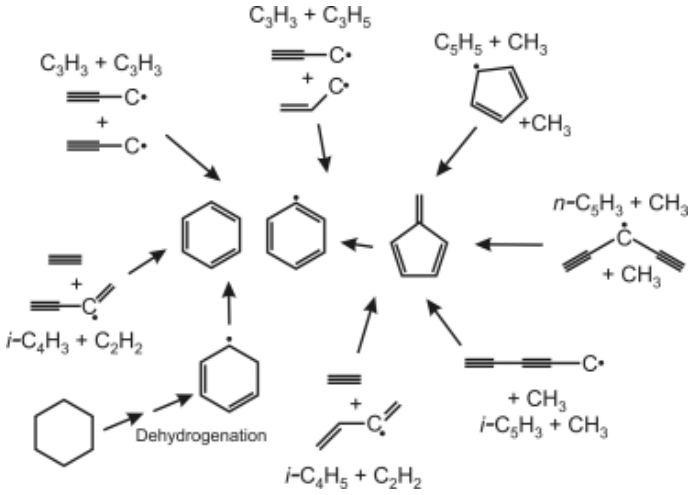
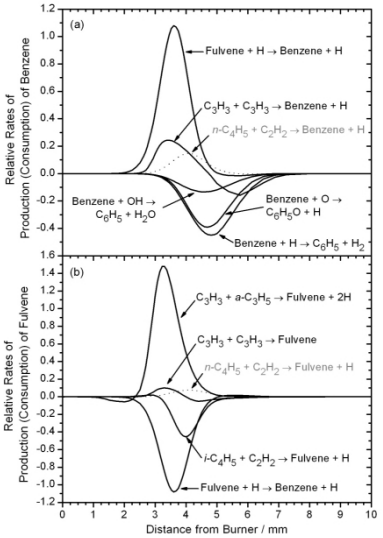
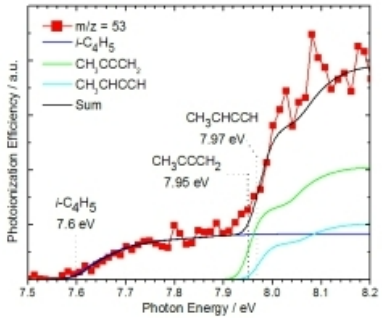
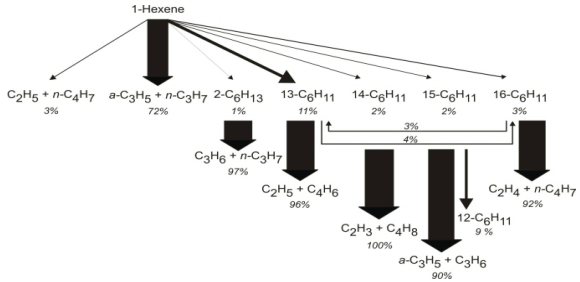
Formation of Benzene











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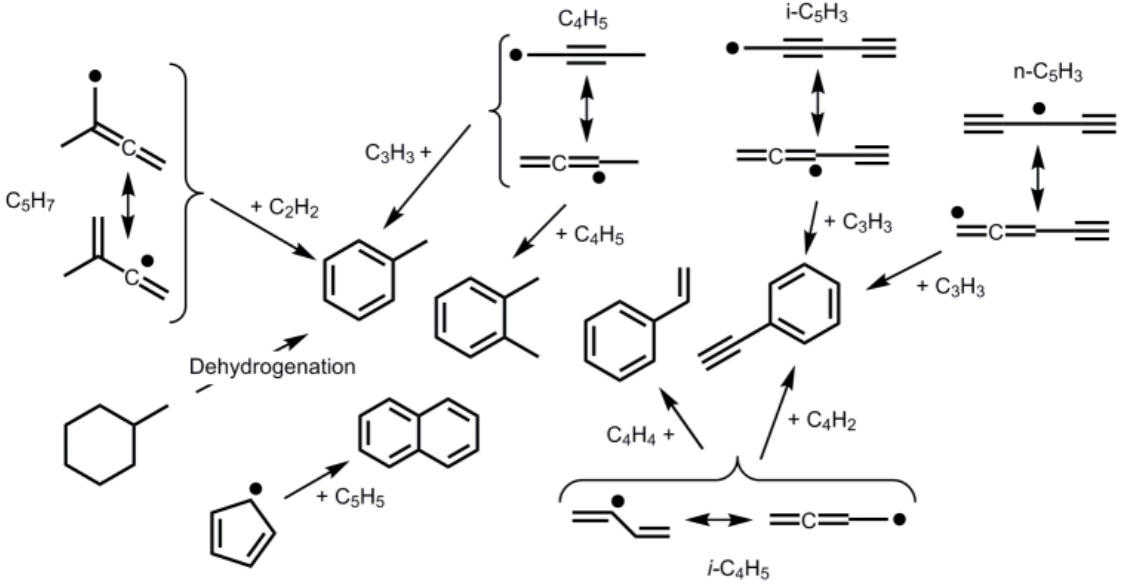
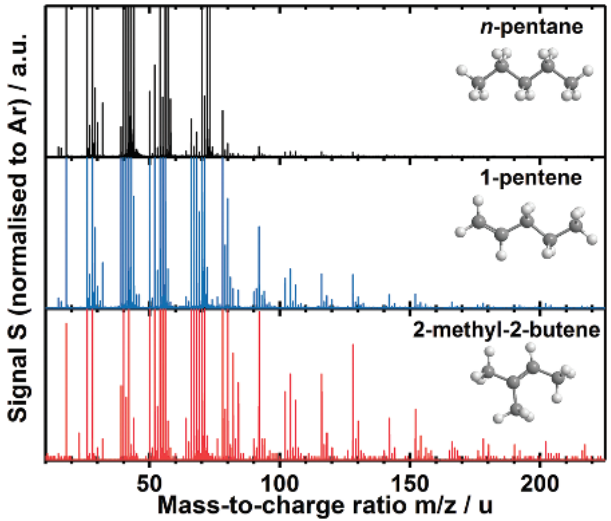
N. Hansen *et al., Combust. Expl. Shock Waves,* **2012,** 48, 508-515

Molecular-Growth From The First Aromatic Ring to Pyrene

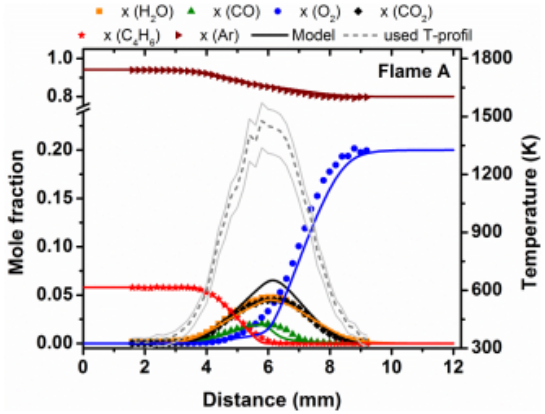
✓ What are the first aromatic species and how are they formed?

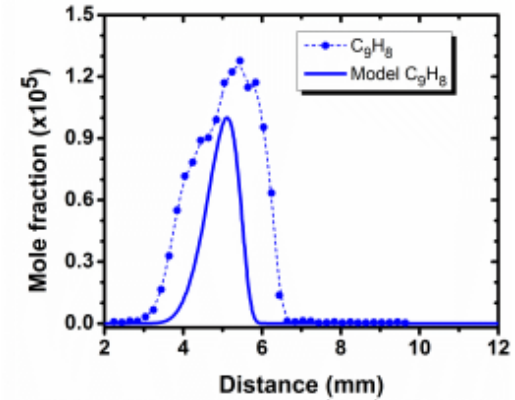


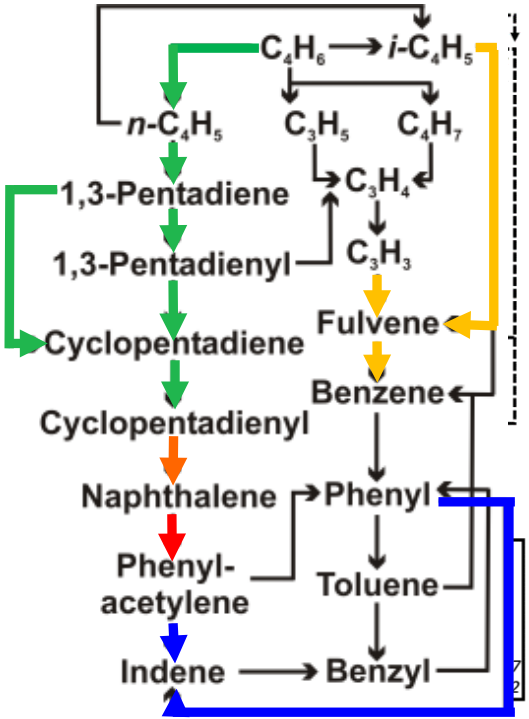


S. A. Skeen *et al., Energy Fuels,* **2011,** 25(12), 5611-5625
L. Ruwe *et al., Combust. Flame,* **2017,** 175, 34-46 and *Phys. Chem. Chem. Phys.,* **2018,** 20, 10780-10795

Molecular-Growth From The First Aromatic Ring to Pyrene







- ✓ indene (A1R5) is formed via $C_6H_5 + C_3H_3$ and CH_3 + phenylacetylene (A1C2H) reactions
- ✓ with A1C2H being formed through naphthalene oxidation

providing evidence for non-sequential growth

- ➢ highlights the need to better understand the 2nd ring formation

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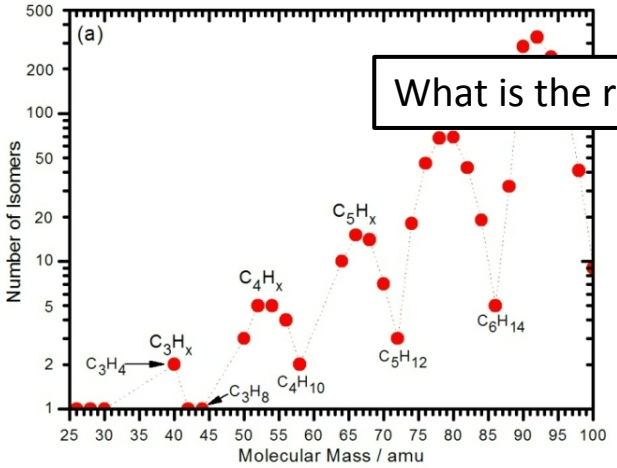
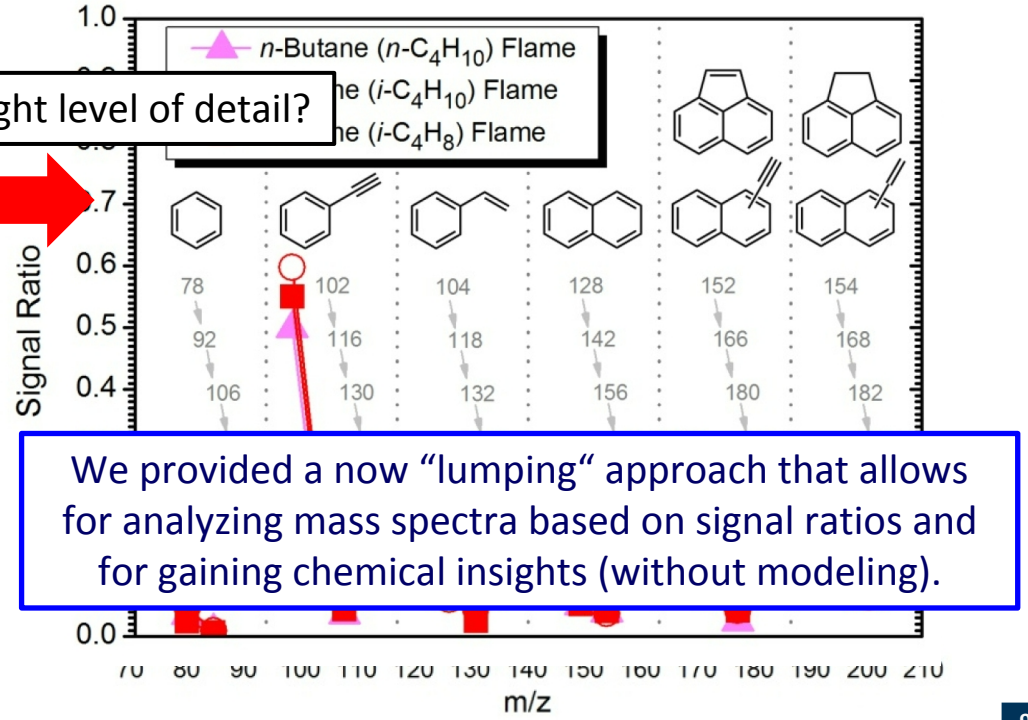
K. Moshammer *et al., Proc. Combust. Inst.*, **2017,** 36(1), 947-955

Molecular-Growth From The First Aromatic Ring to Pyrene



N. Hansen *et al., Prog. Energy Combust. Sci.*, **2009,** 35(2), 168-191

What is the right level of detail?



We provided a now "lumping" approach that allows for analyzing mass spectra based on signal ratios and for gaining chemical insights (without modeling).

N. Hansen *et al., Combust. Flame,* **2017,** 180, 250-261

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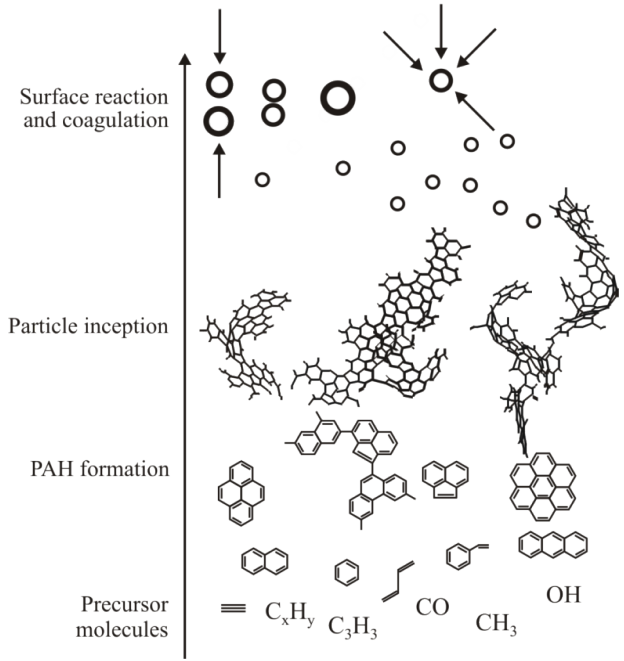
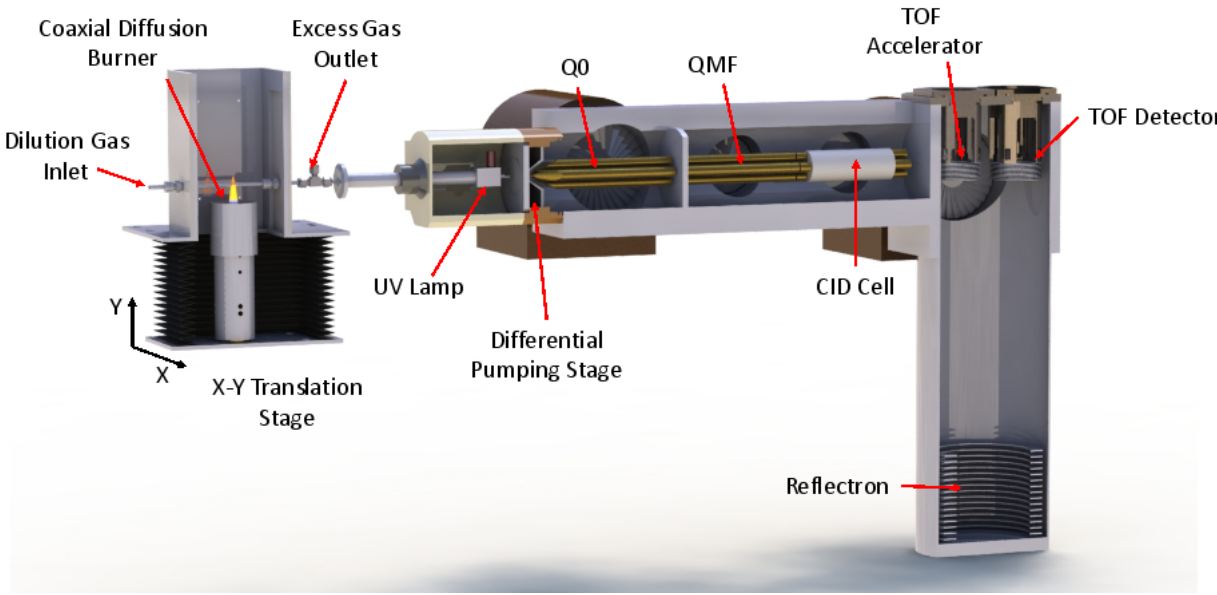
Addressing the Complexity of Reaction Systems: Tandem Mass Spectrometry





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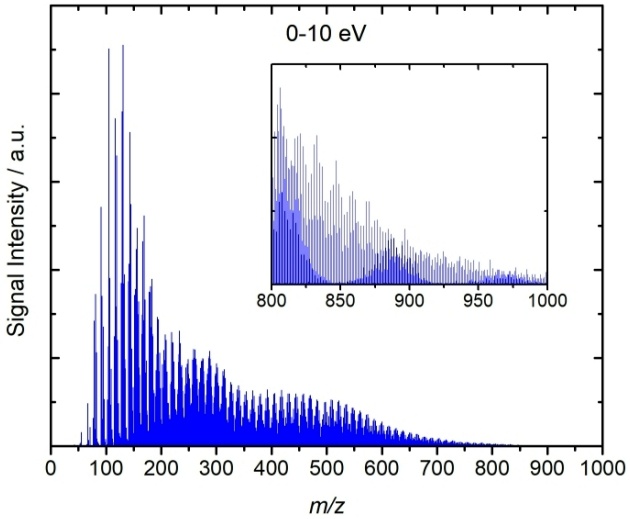
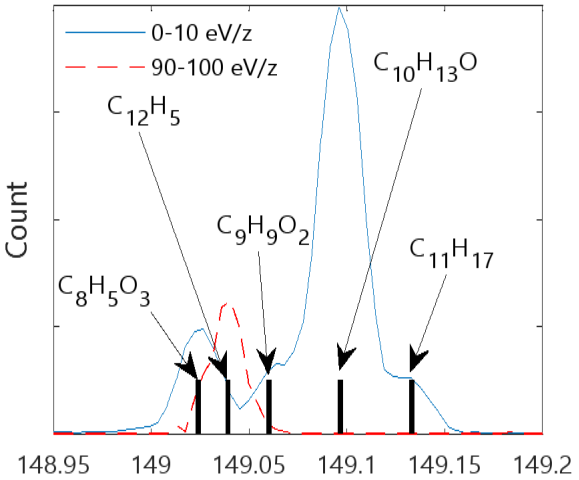
Tandem Mass Spectrometry: General Performance of the Mass Spectrometer

- ✓ atmospheric pressure photoionization (APPI)
- ✓ two modes of operation:
  - ➢ time-of-flight mode
  - ➢ MS-MS mode
- ✓ Resolution: QMF ~1, TOF ~8000
- ✓ collission gas: Ar
- ✓ sensitivity: tbd





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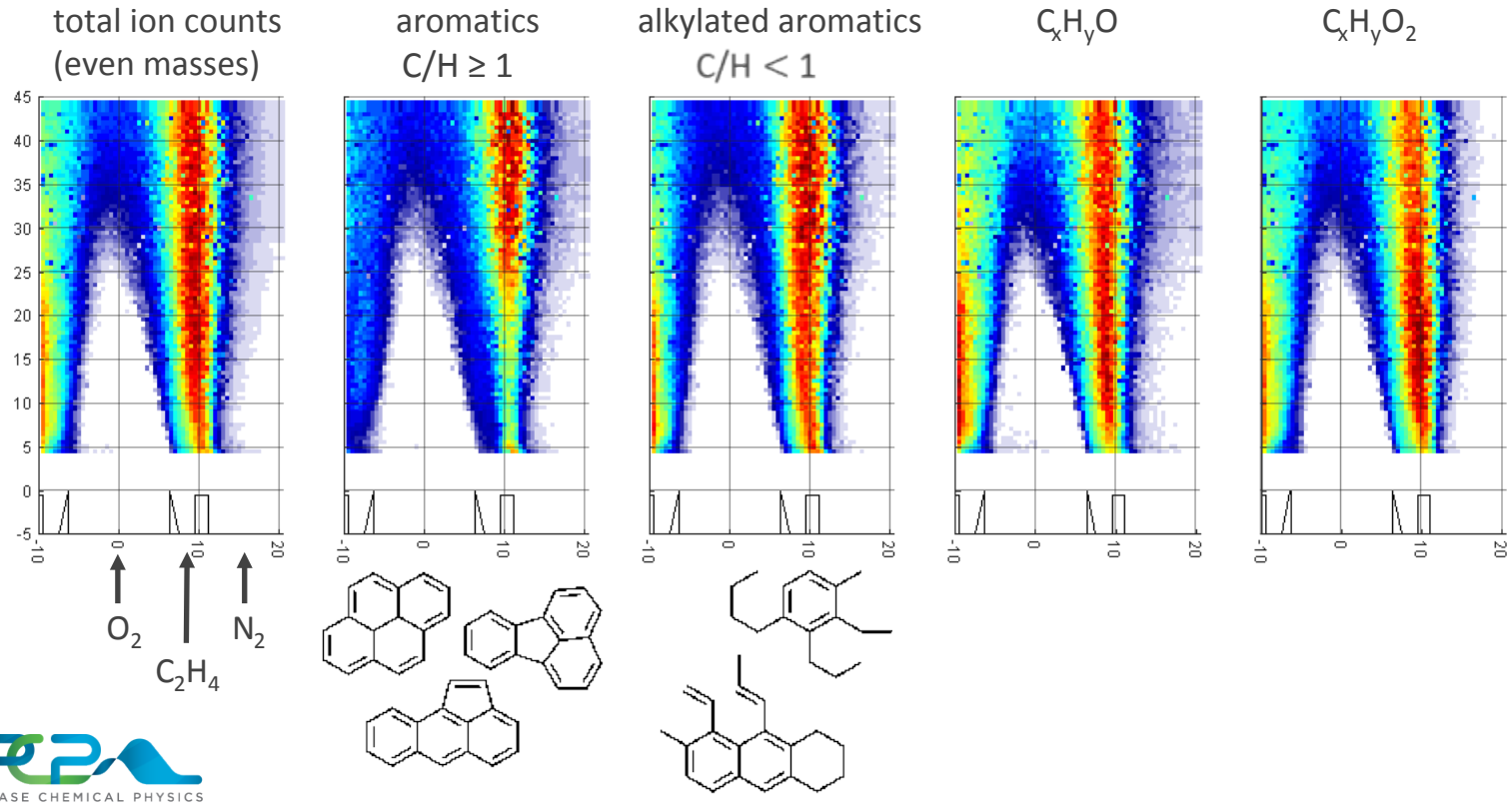
2D-Color Maps of PAHs in Co-Flow Diffusion Flames



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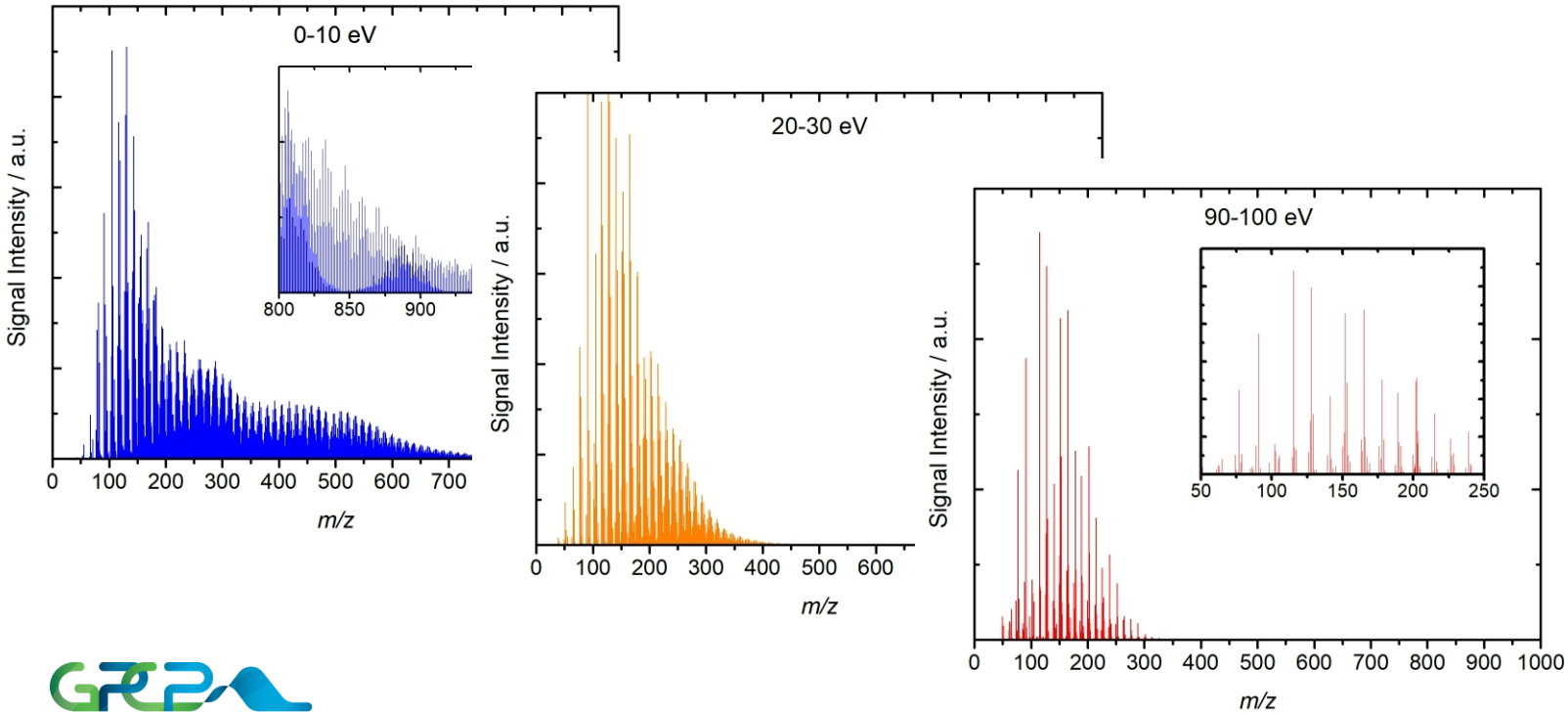
Fragmentation Scans: Identification of core-PAH Structures



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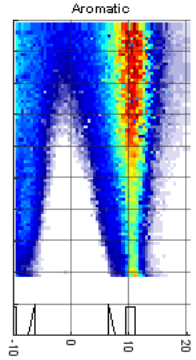
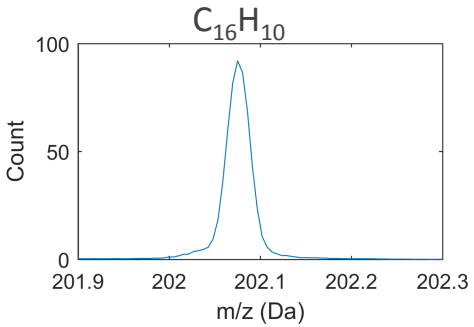
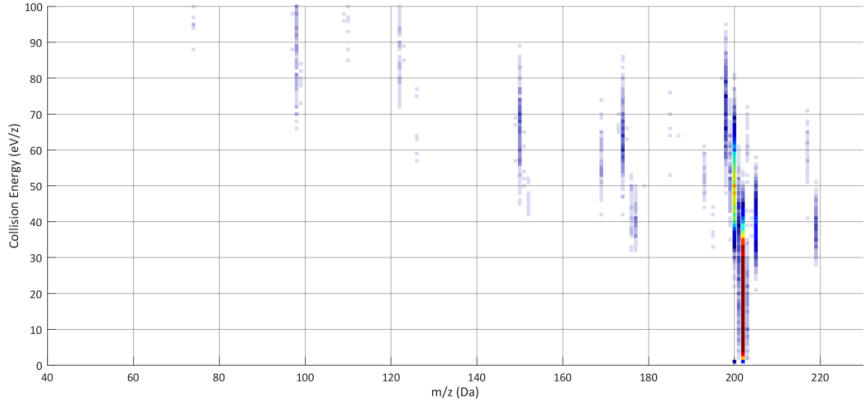
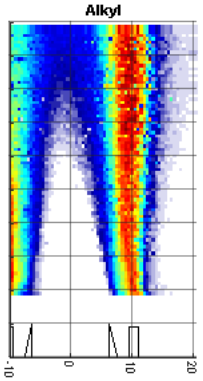
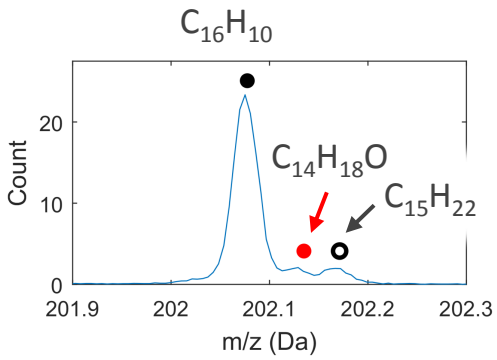
Fragmentation Scans: *m/z* = 202

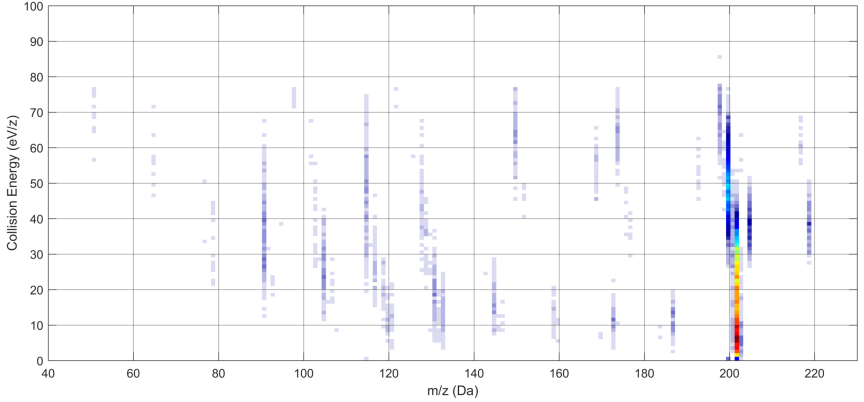












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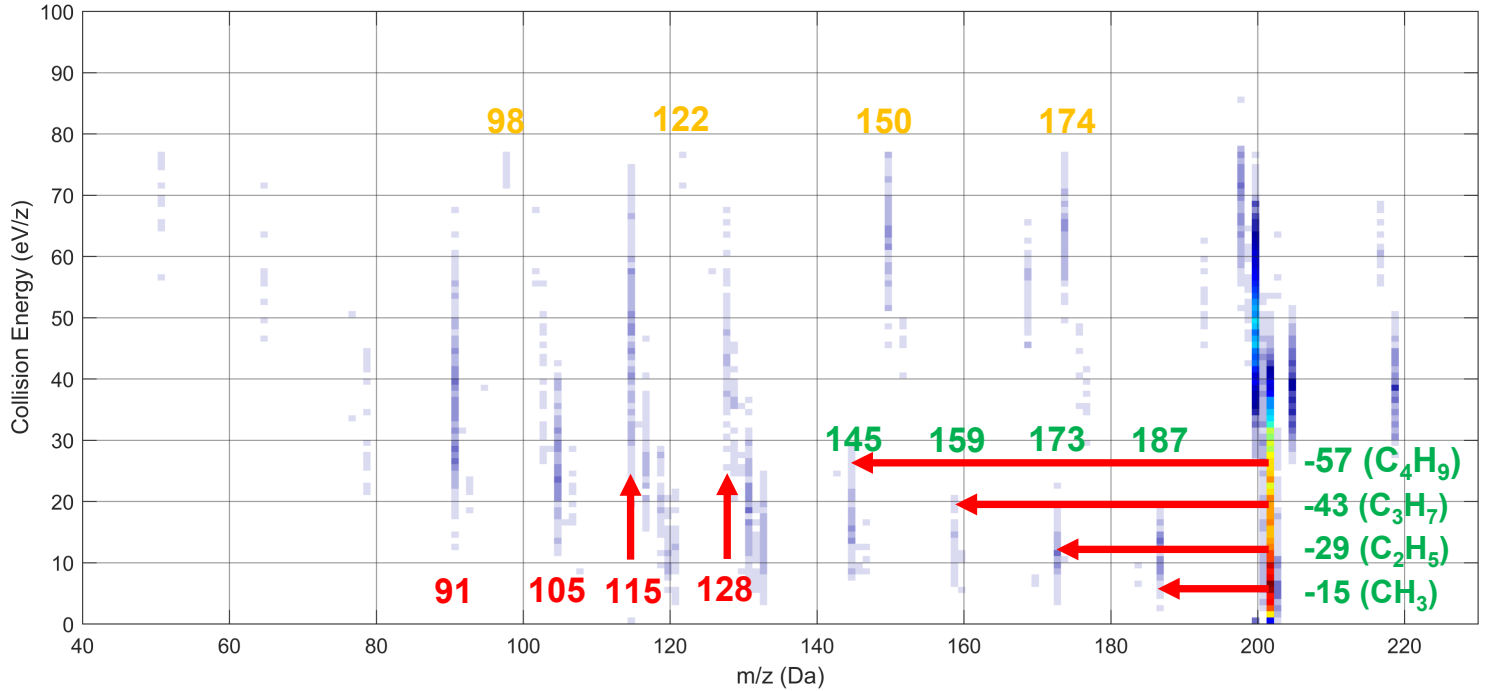
Identification of core PAH Structures and Aliphatic Chains



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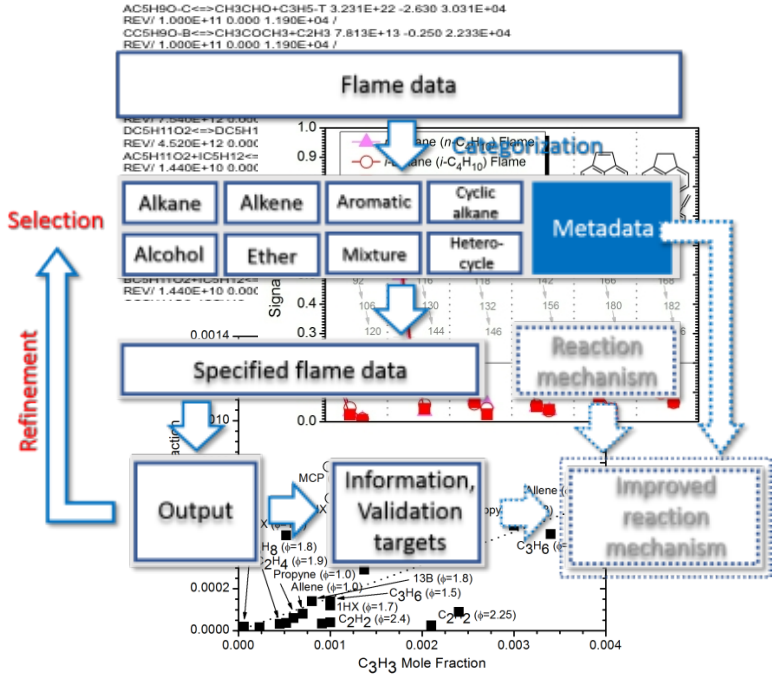
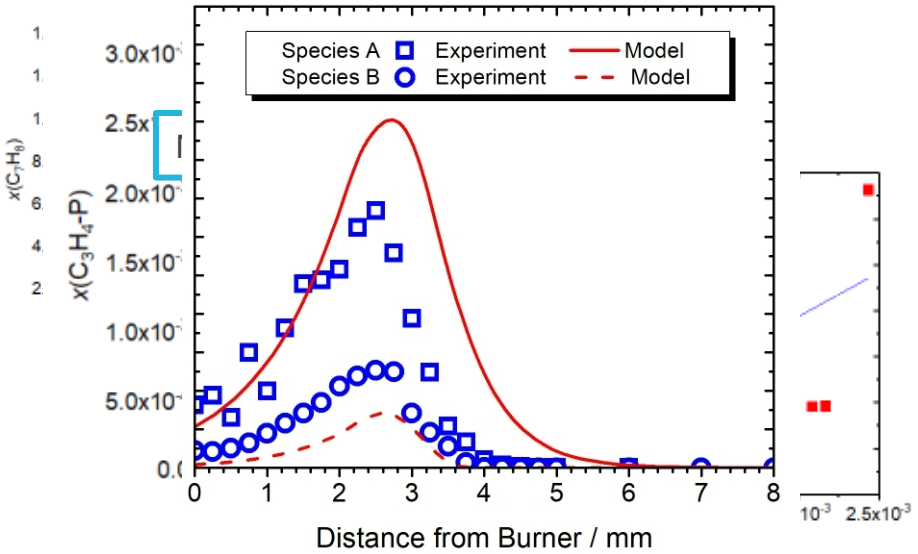
Addressing the Complexity of Reaction Systems: Innovative Modeling Approaches/ML



Development of a Low-Pressure Flame Database

more than 50 flames from five different labs



N. Hansen *et al., Proc. Combust. Inst.*, **2011,** 33, 585-592

N. Hansen *et al., Combust. Flame,* **2017,** 180, 250-261

N. Hansen *et al., Proc. Combust. Inst.,* **2019,** in press

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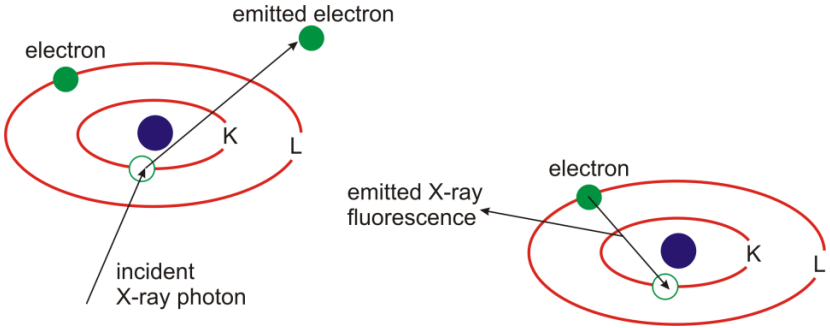
Measuring 2D Temperature Fields with Kr X-Ray Fluorescence

Beamline 7BM at the Advanced Photon Source (APS) of the Argonne National Laboratory

- X-ray fluorescence beamline
- Synchrotron-generated 5.1-22 keV
- High photon flux (2 x 10^{11} photons/s)
- Size of focal point: 5 x 7 μm
- Kr excitation at 15 keV and fluorescence detection at 12.6 keV (Kr Kα)



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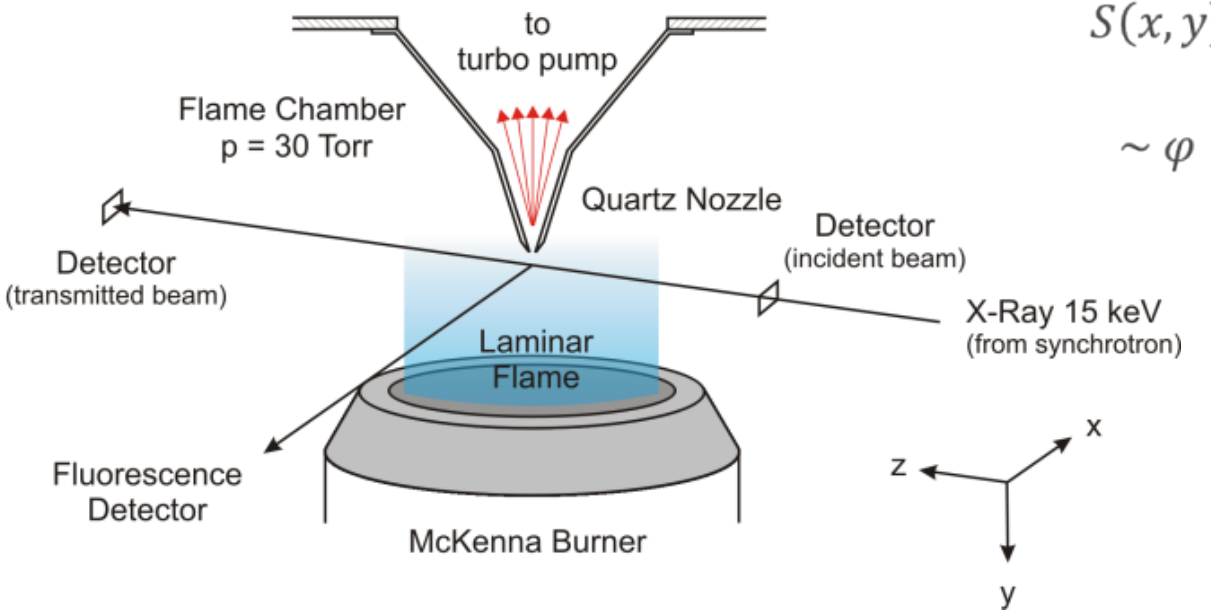
N. Hansen *et al., Combust. Flame,* **2017,** 181, 214-224 and *Proc. Combust. Inst.,* **2019,** in press

Measuring 2D Temperature Fields with Kr X-Ray Fluorescence



$$S(x,y) \sim \varphi \times x_{Kr}(x,y) \times \frac{n}{V}$$

$$\sim \varphi \times x_{Kr}(x,y) \times \frac{p}{T(x,y)}$$

$S(x,y)$: fluorescence signal

φ: photon flux incident X-ray beam

$x_{Kr}(x,y)$: Kr mole fraction

n: number density

p: pressure

$T(x,y)$: local temperature

Flame conditions: 14.5% C_2H_4, 25.5% O_2, 55% Ar, 5% Kr, Φ=1.7, 30 Torr, 0.00404 g/cm^2/sec

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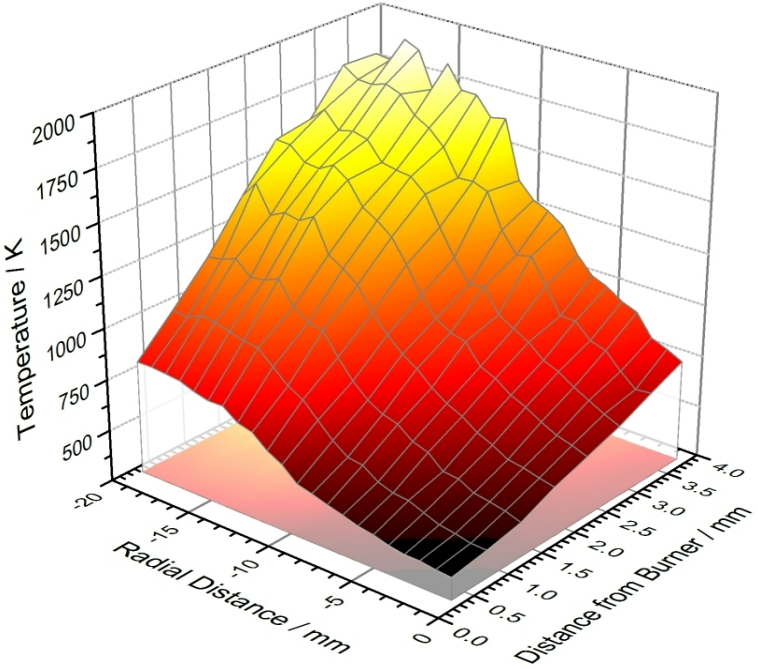

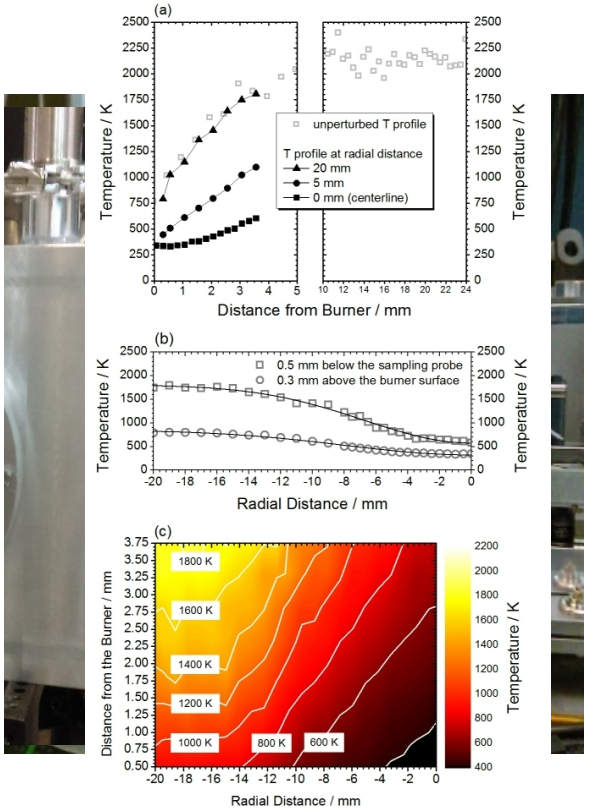

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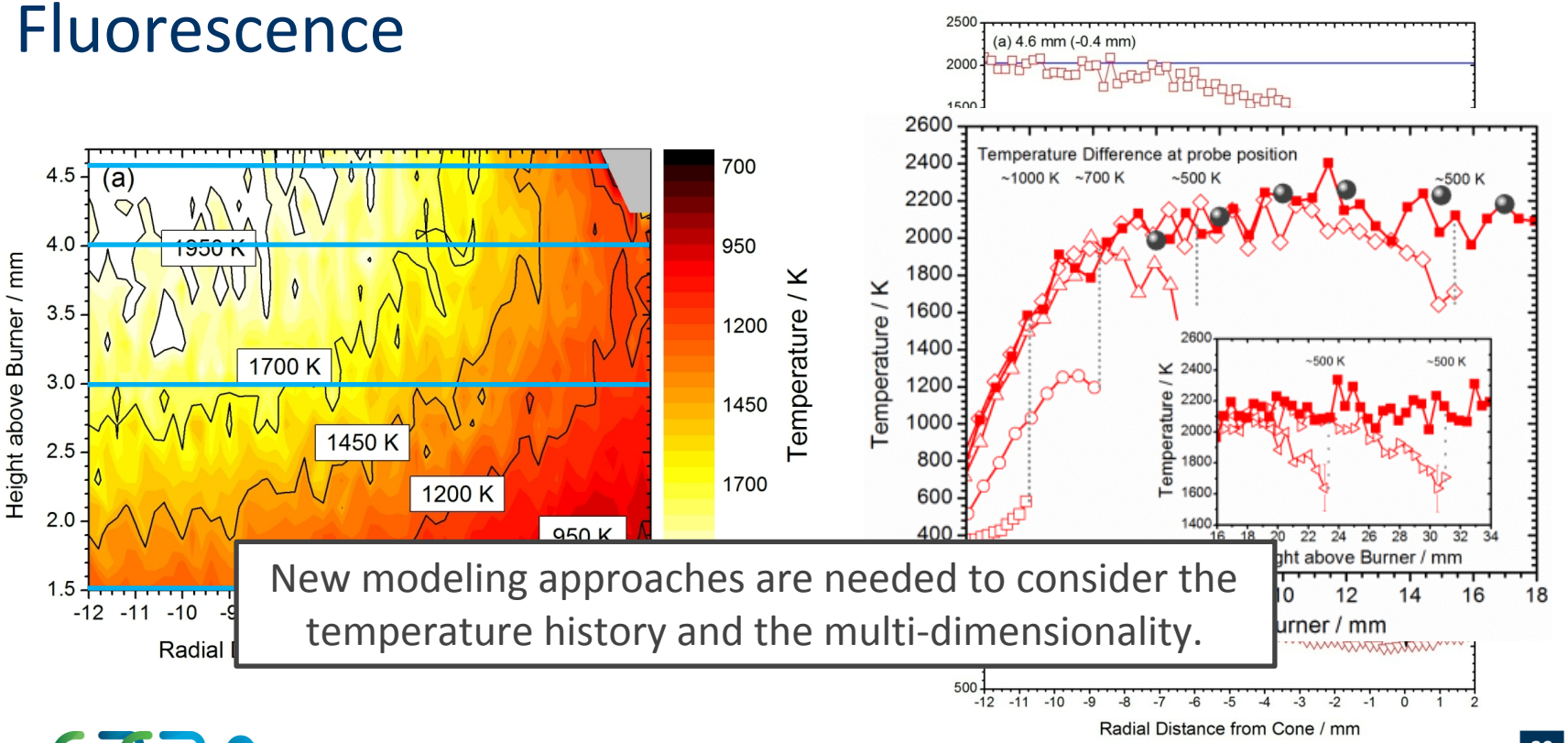

New modeling approaches are needed to consider the temperature history and the multi-dimensionality.

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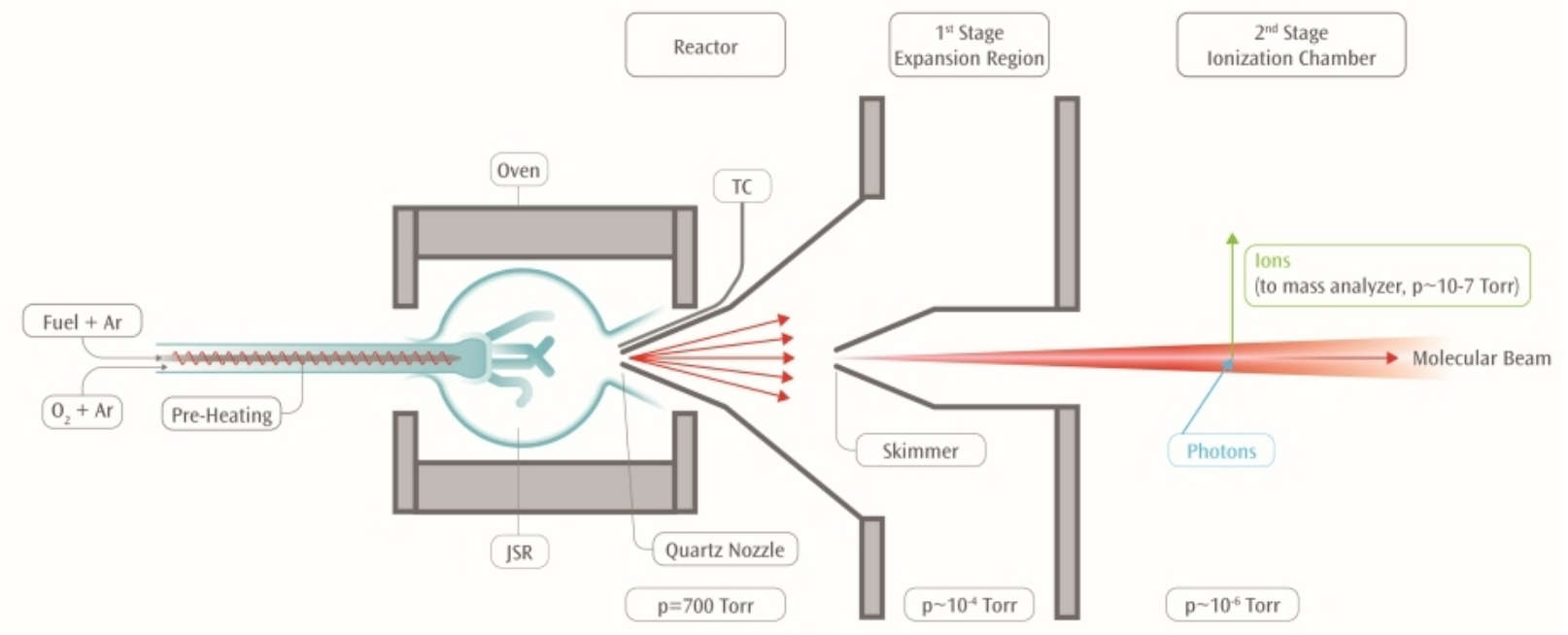
N. Hansen *et al., Combust. Flame,* **2017,** 181, 214-224 and *Proc. Combust. Inst.,* **2019,** in press

Low-Temperature Oxidation and Ignition Chemistry

Molecular-Beam Sampling Jet-Stirred Reactor



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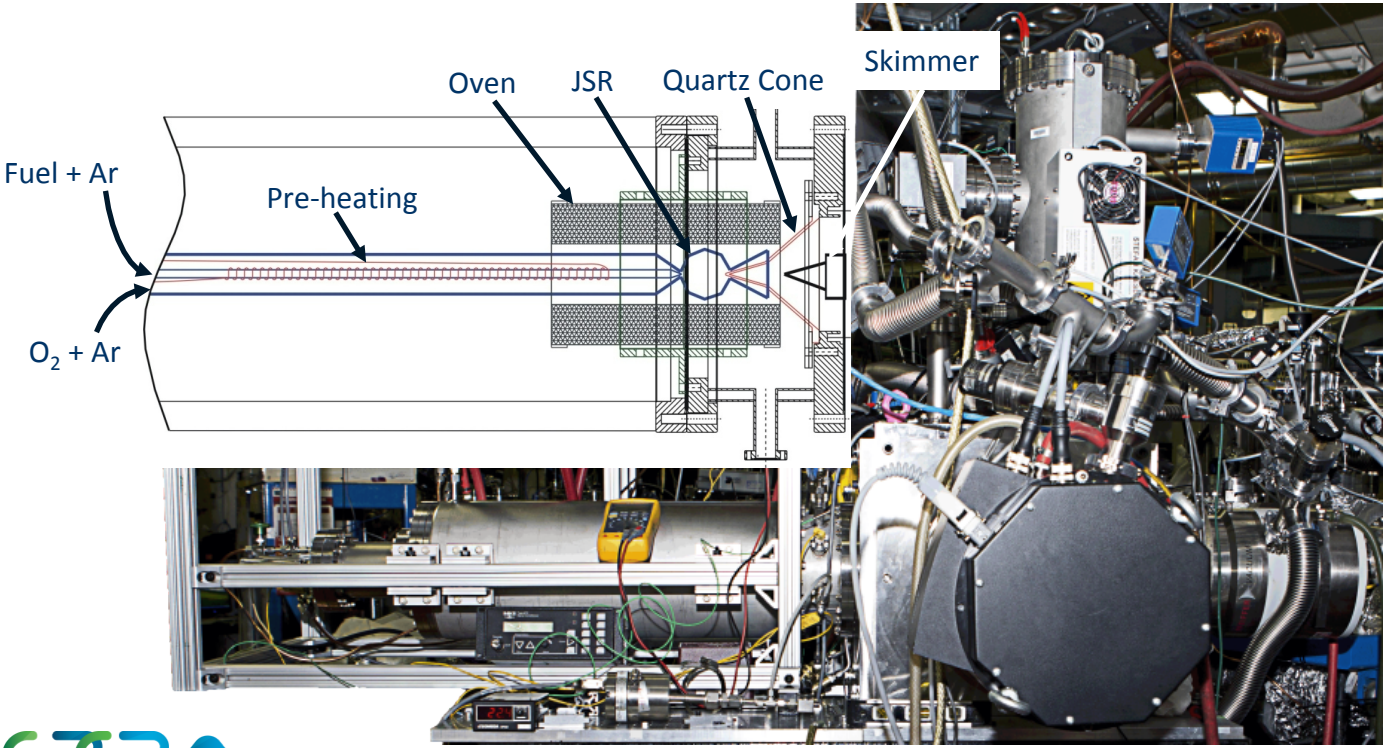
K. Moshammer *et al., J. Phys. Chem. A,* **2015,** 119, 7361-7374
K. Moshammer *et al., J. Phys. Chem. A,* **2016,** 120, 7890-7901

Low-Temperature Oxidation and Ignition Chemistry

Molecular-Beam Sampling Jet-Stirred Reactor



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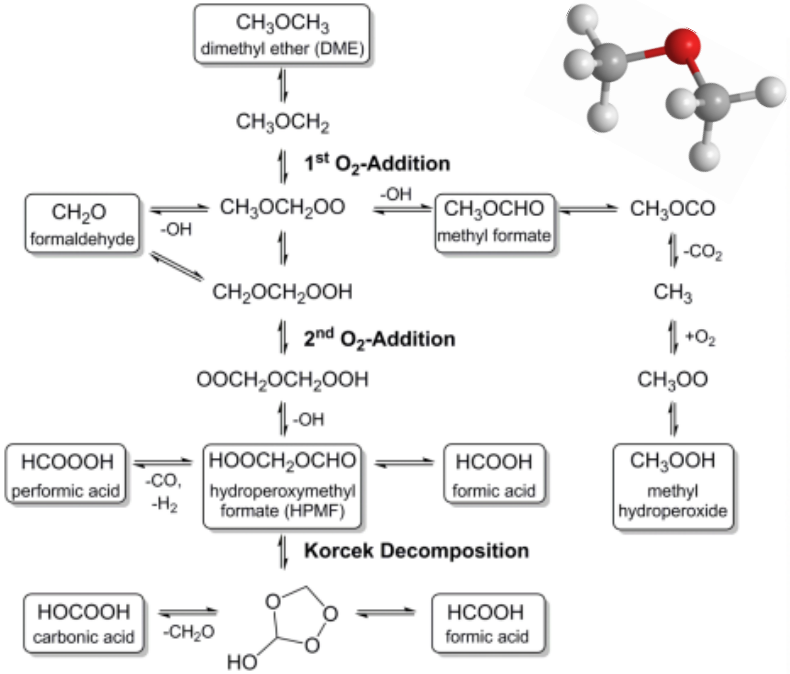
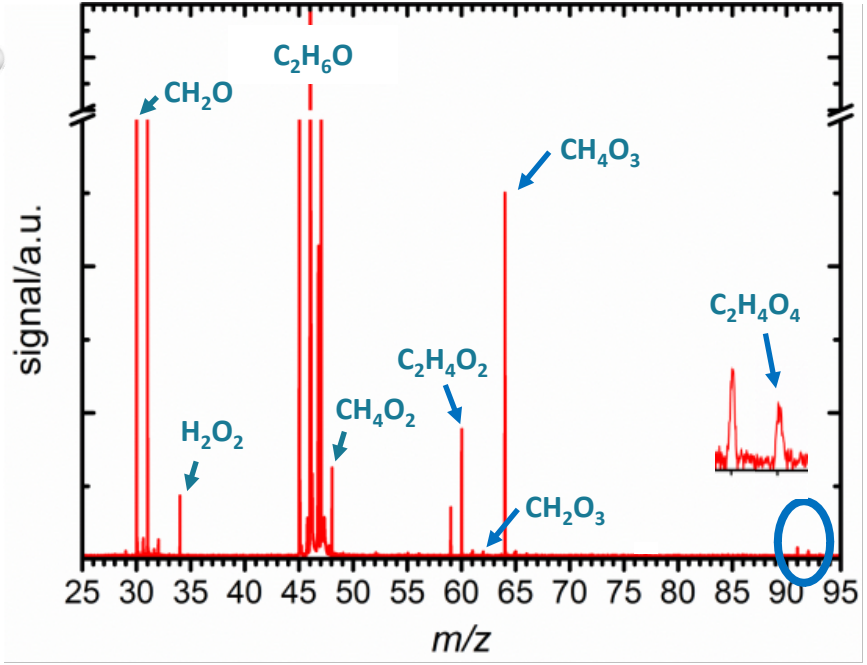
Low-Temperature Oxidation Chemistry of Dimethyl Ether (DME)





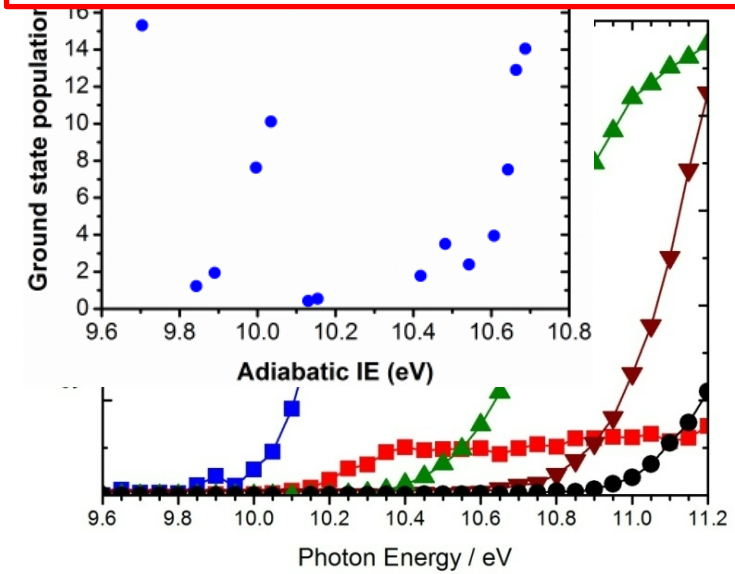
K. Moshammer *et al., J. Phys. Chem. A,* **2015,** 119, 7361-7374
K. Moshammer *et al., J. Phys. Chem. A,* **2016,** 120, 7890-7901

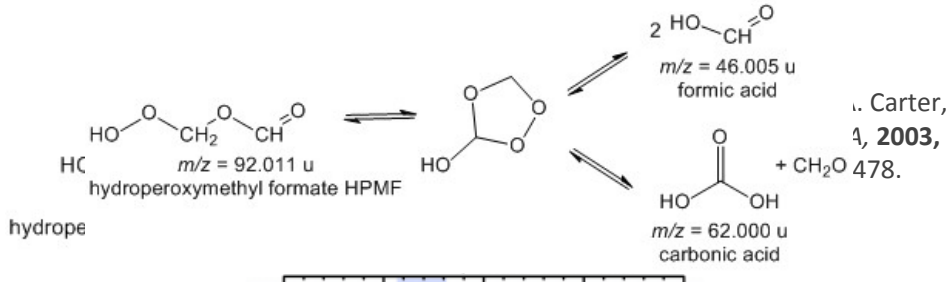
GAS PHASE CHEMICAL PHYSICS

Low-Temperature Oxidation of DME

Identification of the Ketohydroperoxide HPMF

Fragment pattern gives additional evidence for the experimental detection of HPMF





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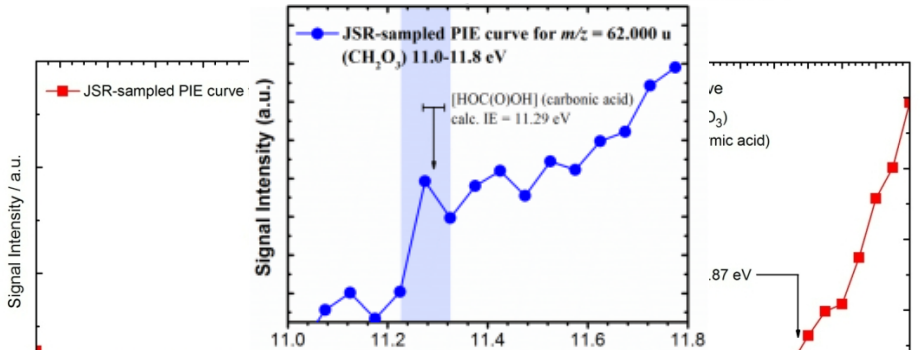
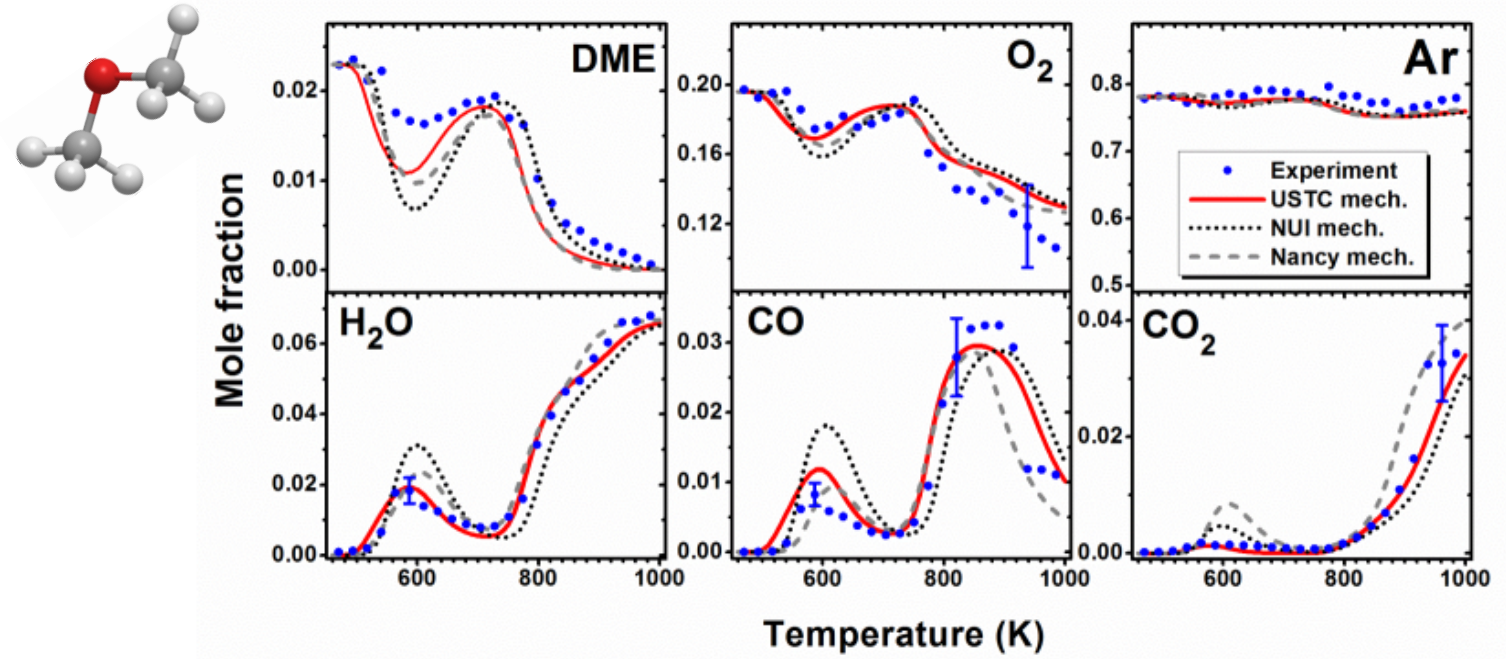


Detection of carbonic acid provides evidence for the Korcek decomposition mechanism!

K. Moshammer *et al., J. Phys. Chem. A,* **2015,** 119, 7361-7374
K. Moshammer *et al., J. Phys. Chem. A,* **2016,** 120, 7890-7901

Low-Temperature Oxidation of DME

Quantification of the Main Species

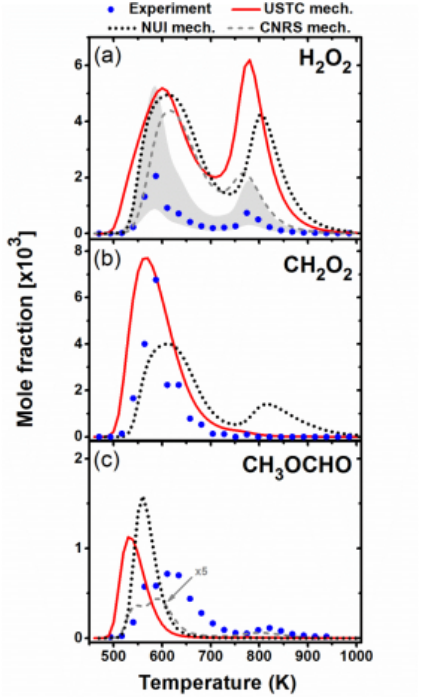


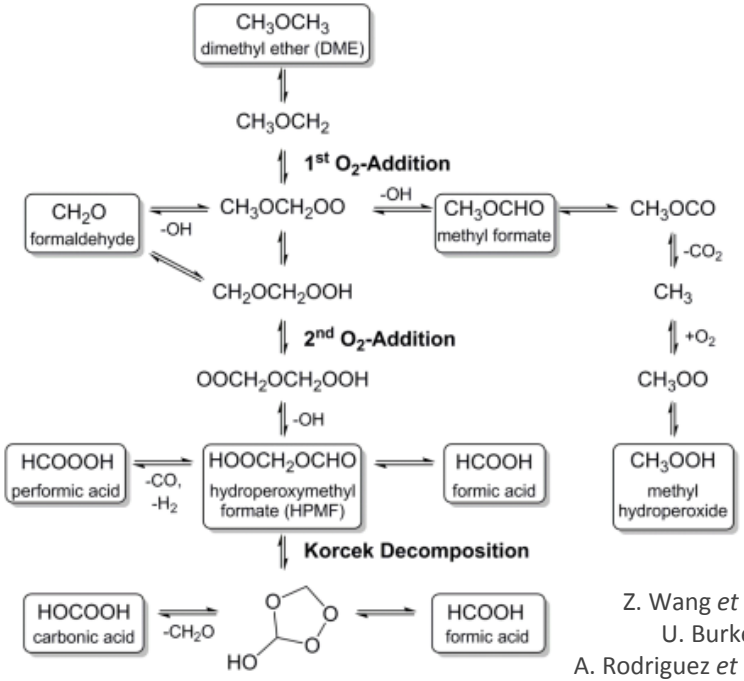
K. Moshammer *et al., J. Phys. Chem. A,* **2015,** 119, 7361-7374

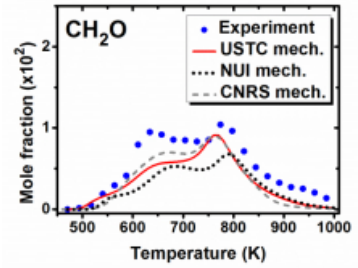
K. Moshammer *et al., J. Phys. Chem. A,* **2016,** 120, 7890-7901

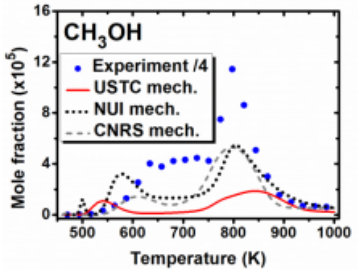
Low-Temperature Oxidation of DME

Quantification of Some Intermediates









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,* **2015,** 119, 7361-7374
K. Moshammer *et al., J. Phys. Chem. A,* **2016,** 120, 7890-7901

GAS PHASE CHEMICAL PHYSICS

Low-Temperature Oxidation of DME

Quantification of CH_3OOH and the Ketohydroperoxide HPMF

- using calculated photoionization cross sections

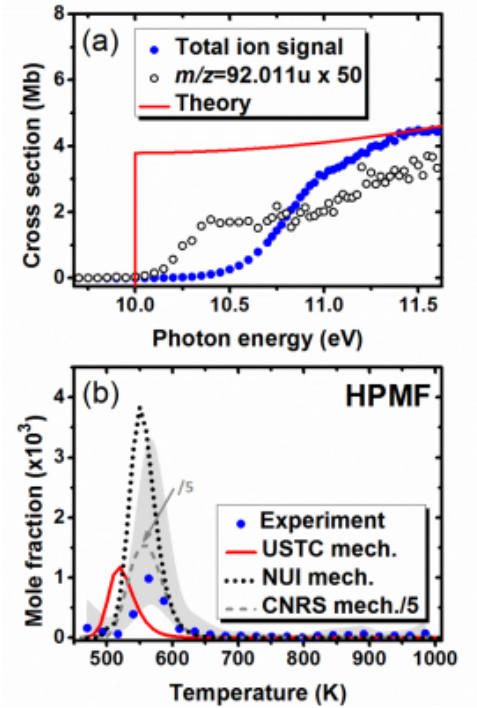
R. R. Lucchese, Texas A&M

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

A. W. Jasper, Argonne



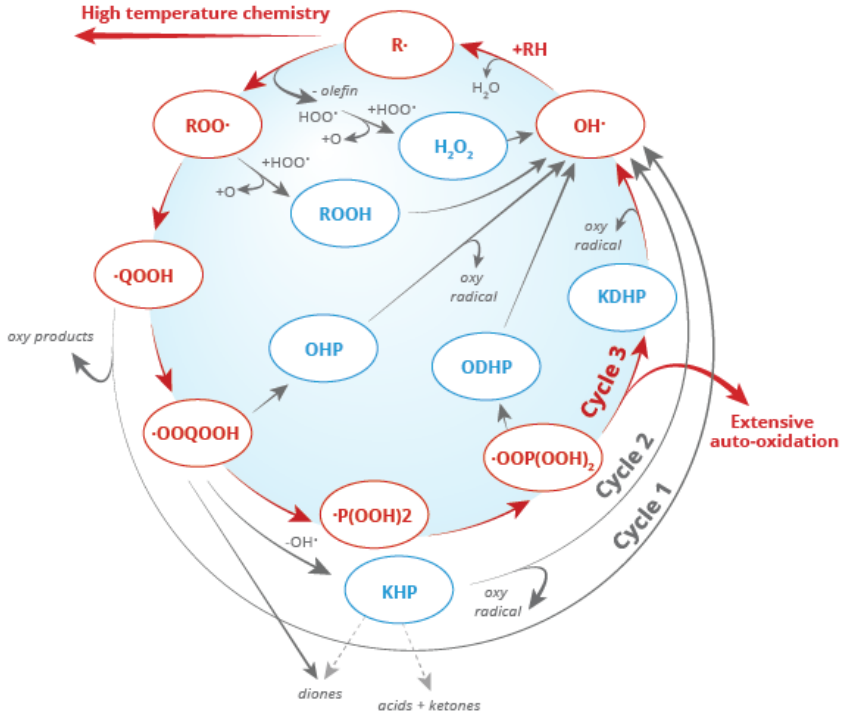
- tested against a variety of known species
  ⇒ uncertainty ≤ a factor of 2
- it calculates total cross sections
  ⇒ fragmentation pattern needs to be known
- it doesn't calculate Franck-Condon overlaps
  ⇒ scale to experimental photoionization efficieny curves

GAS PHASE CHEMICAL PHYSICS

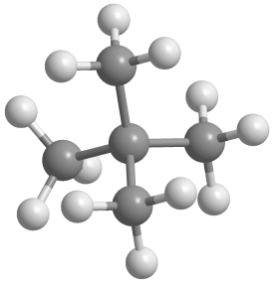
K. Moshammer *et al., J. Phys. Chem. A,* **2015,** 119, 7361-7374
K. Moshammer *et al., J. Phys. Chem. A,* **2016,** 120, 7890-7901

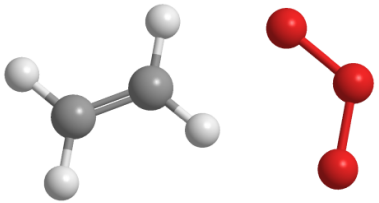
Low-Temperature Oxidation

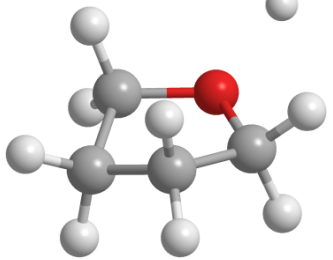
neo-Pentane and Tetrahydrofuran as Logical Extension



- apply the insights gained from the DME project to study the low-temperature oxidation of a more complex molecular system:
  - ✓ *neo*-pentane
  - ✓ tetrahydrofuran (THF)
  - ✓ ethylene ozonolysis





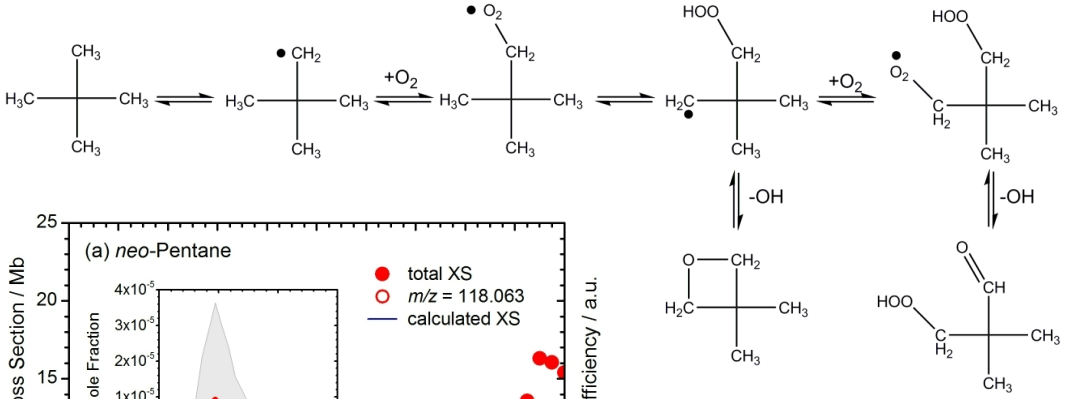


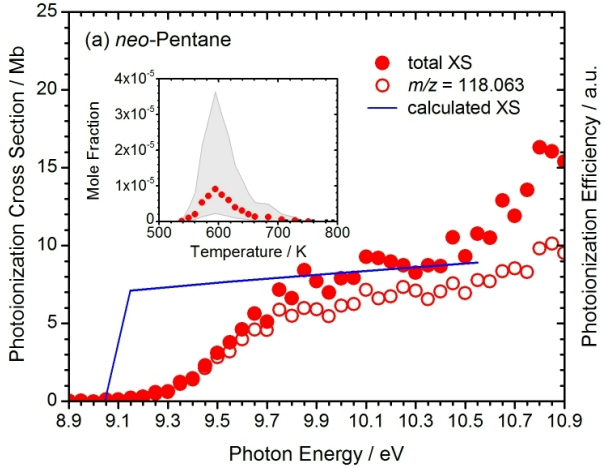
GAS PHASE CHEMICAL PHYSICS

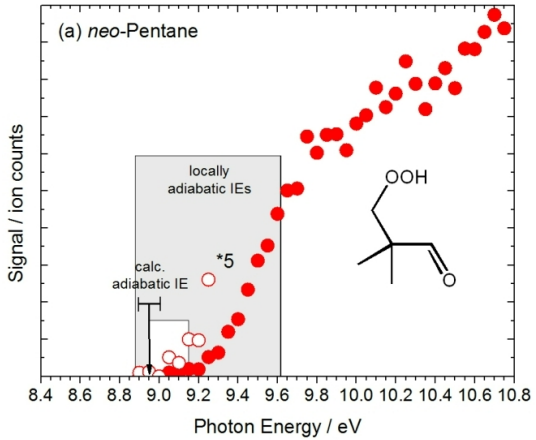
N. Hansen *et al., J. Phys. Chem. Lett.,* submitted

Low-Temperature Oxidation of *neo*-Pentane

Detection and Identification of the KHP







Fragmentation Channel	Calculated AE, eV[a]	Experimentally observed AE, eV
$HOO\text{-}CH_2\text{-}C(CH_3)_2H^+$ ($C_4H_{10}O_2^+$) + CO	9.41	9.40
$HOO\text{-}CH_2\text{-}C(CH_3)_2CO^{\cdot+}$ ($C_5H_9O_3^+$) + H	10.18	10.1
$HOO\text{-}CH_2\text{-}C(CH_3)_2^{\cdot+}$ ($C_4H_9O_2^+$) + ·CHO	10.44	10.5
$\cdot C(CH_3)_2CHO^+$ ($C_4H_7O^+$) + $\cdot CH_2OOH$	10.70	10.65

GAS PHASE CHEMICAL PHYSICS

N. Hansen *et al., J. Phys. Chem. Lett.,* submitted

Low-Temperature Oxidation of Tetrahydrofuran

Identification and Quantification of the Ketohydroperoxide

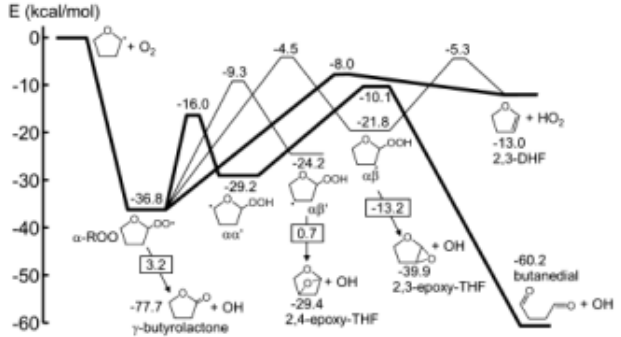
THE JOURNAL OF PHYSICAL CHEMISTRY A — Article — pubs.acs.org/JPCA

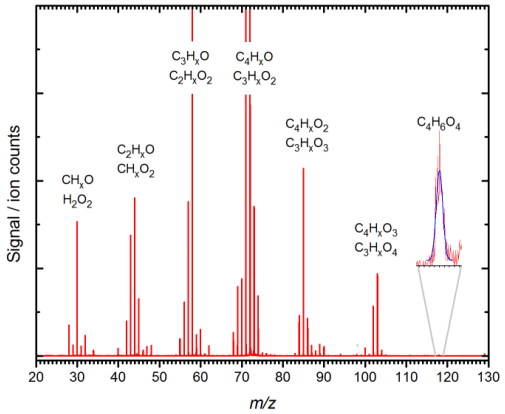
J. Phys. Chem. A **2016,** *120,* 6582−6595

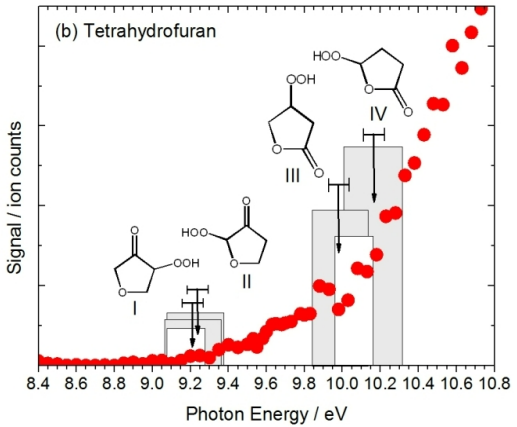
Pressure-Dependent Competition among Reaction Pathways from First- and Second-O_2 Additions in the Low-Temperature Oxidation of Tetrahydrofuran

Ivan O. Antonov, Judit Zádor, Brandon Rotavera, Ewa Papajak, David L. Osborn, Craig A. Taatjes, and Leonid Sheps*

Combustion Research Facility, Sandia National Laboratories, Livermore, California 94551, United States





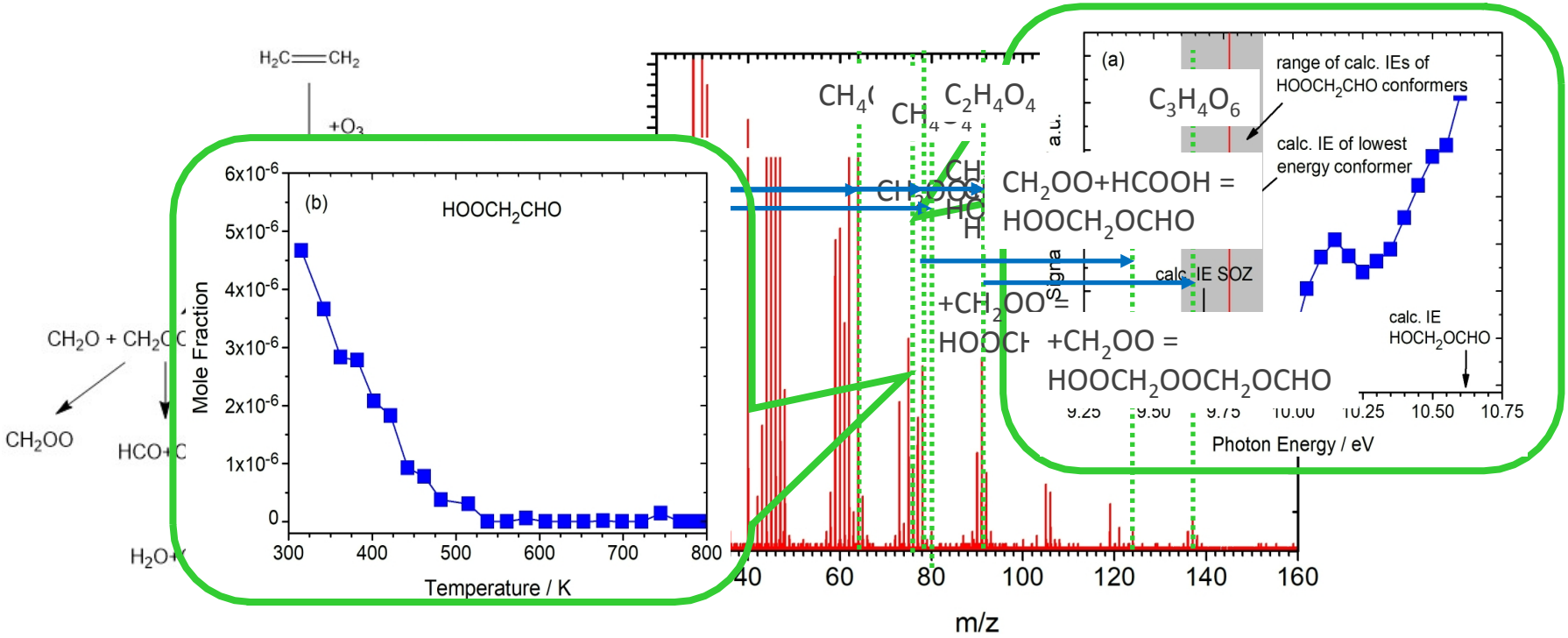


"…energies were calculated using M06-2X/cc-pVTZ geometries and frequencies and a high level energy correction that approximates the CCSD(T)/CBS result, where ~CCSD(T)/CBS = CCSD(T)/cc-pVTZ + MP2/CBS – MP2/cc-pVTZ and the CBS limit was approximated using a two point formula and the cc-pVTZ and cc-pVQZ basis sets." – Ahren Jasper (Argonne)

GAS PHASE CHEMICAL PHYSICS

Ozonolysis of Ethylene

Ketohydroperoxide and Criegee Intermediate Reactions



A. C. Rousso, A. W. Jasper, Y. Ju, N. Hansen, *J. Phys. Chem. A,* **2018,** submitted

Addressing the Complexity of Reaction Systems: Rotational Spectroscopy

- dissociative ionization might preclude a complete qualitative and quantitative interpretation of the sampled mass spectra
- similar ionization energies and photoionization efficiency curves may prevent isomer-specific assignments
- small Franck-Condon overlaps might hamper an adequate formation and sensitive detection of the corresponding ion
- access to synchrotron facilities for photoionization measurements might be very competitive and limited

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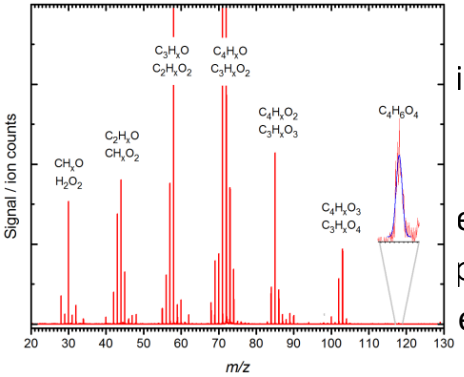
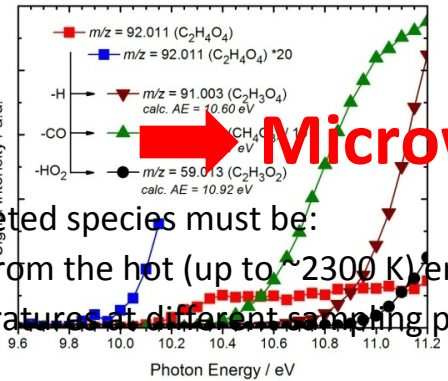
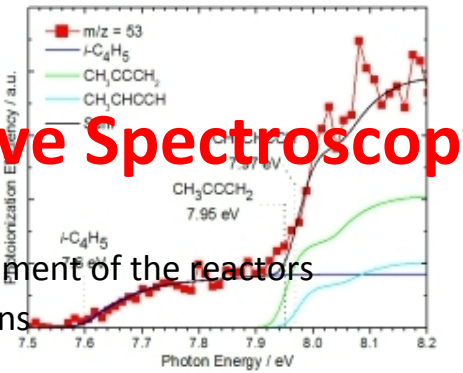
th e targeted species must be:

- pling from the hot (up to ~2300 K) environment of the reactors
- emperatures at different sampling positions







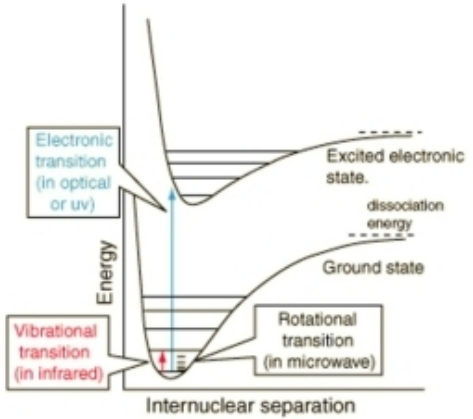
Microwave Spectroscopy

GAS PHASE CHEMICAL PHYSICS

Microwave Spectroscopy as a Diagnostic Tool

MW spectroscopy is the most accurate way to determine molecular structures

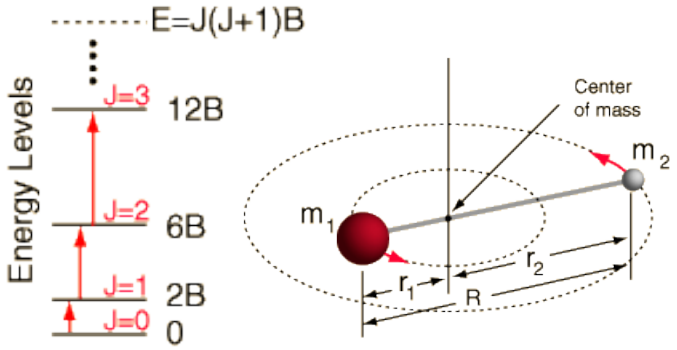
- ✓ rotational transitions are uniquely dependent on the molecular structure
- ✓ characteristic fingerprints due to *fine* and *hyperfine structures,* and *internal rotation effects*
- ✓ superior resolution ($E/\Delta E \sim 10^6$)



Challenges:

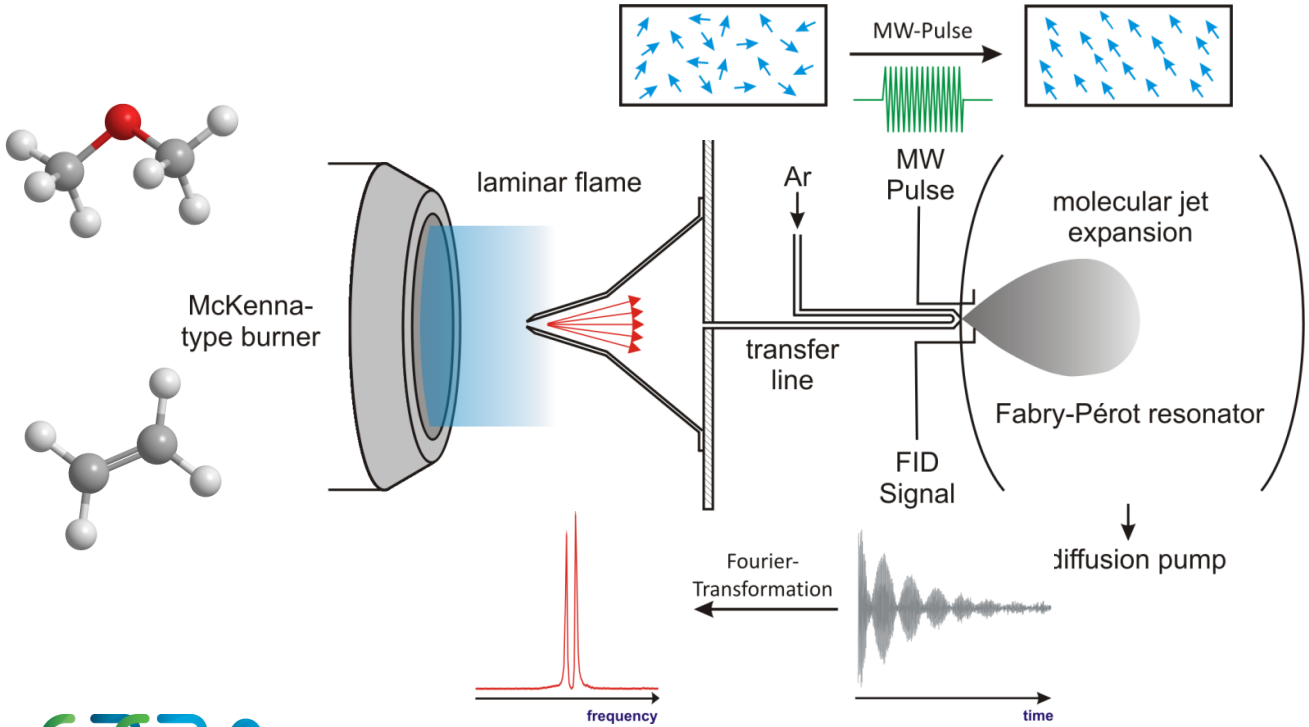
the rotational temperature of the targeted species must be:

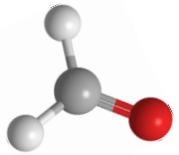
- ➢ sufficiently cooled after sampling from the hot (up to ~2300 K) environment of the reactors
- ➢ independent of the varying temperatures at different sampling positions



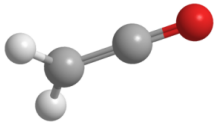
GAS PHASE CHEMICAL PHYSICS

Addressing the Complexity of Reaction Systems: Rotational Spectroscopy

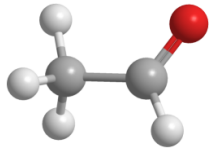




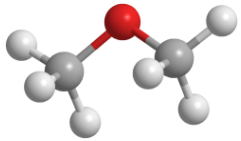
$2_{1,1}$-$2_{1,2}$ (14488.479 MHz)



$1_{0,1}$-$0_{0,0}$ (20209.201 MHz)



$1_{0,1}$-$0_{0,0}$ (19262.140 MHz)

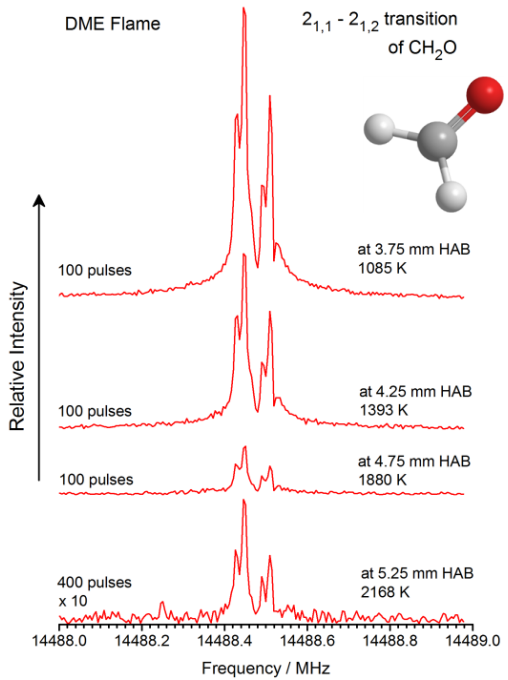


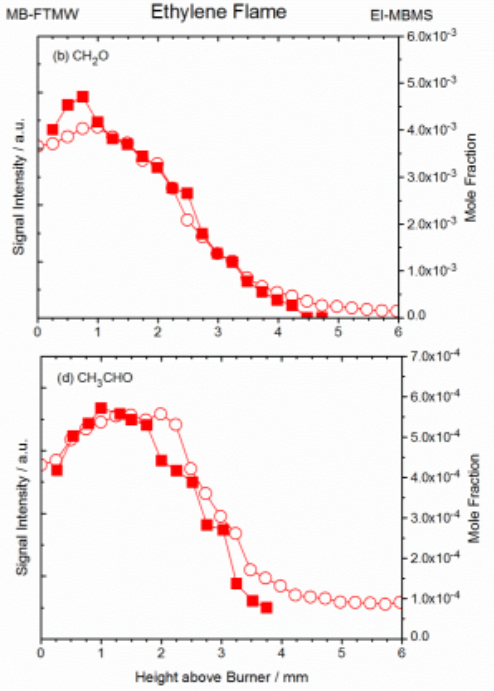
$2_{0,2}$-$1_{1,1}$ (9118.816 MHz)

N. Hansen *et al., RSC Advances,* **2017,** 7(60), 37867-37872

GAS PHASE CHEMICAL PHYSICS

Addressing the Complexity of Reaction Systems: Rotational Spectroscopy

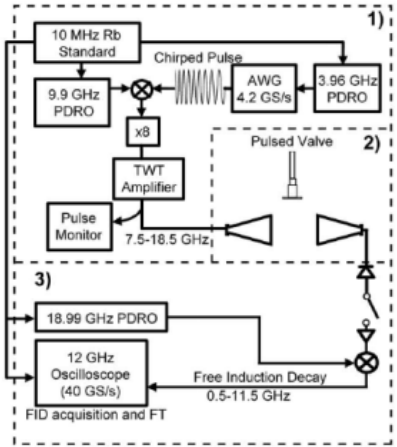




N. Hansen *et al., RSC Advances,* **2017,** 7(60), 37867-37872

GAS PHASE CHEMICAL PHYSICS

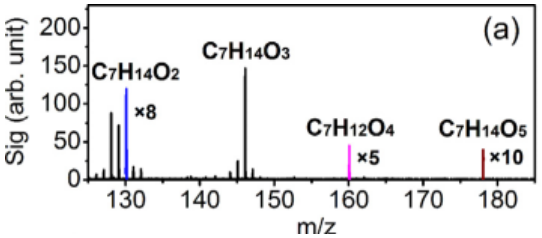
Addressing the Complexity of Reaction Systems: Rotational Spectroscopy

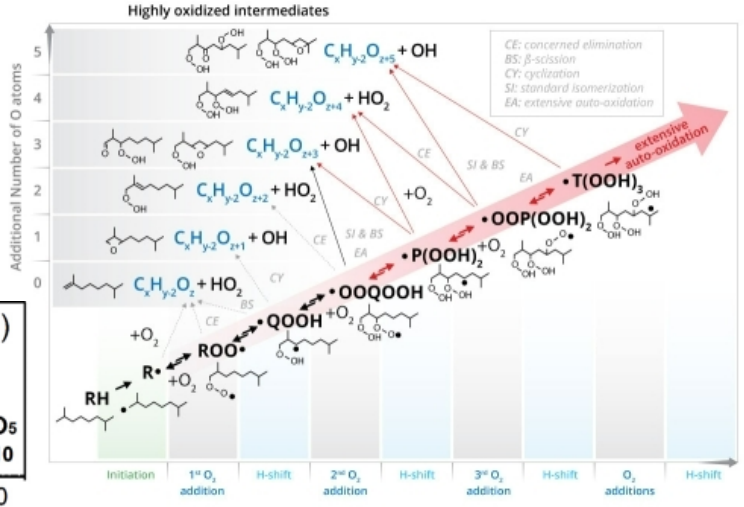


Chirped Pulse MW Spectroscopy
Brown *et al., Rev. Sci. Instrum.*, **2008,** 79, 053103

Potential Targets:

- ✓ Reactors (flames, JSR, *etc.*) can provide target species in a controlled manner that are hard to obtain otherwise
  - ⇒ isomer- and conformer specific spectroscopy
- ✓ Low-Temperature Oxidation:
  - ➢ *Identification and quantification of highly-oxygenated species*



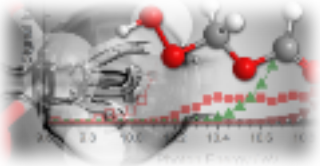
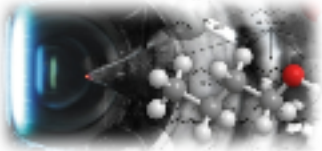
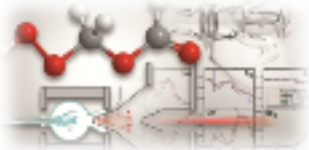
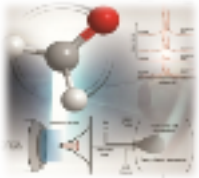


Z. Wang *et al., Combust. Flame,* **2016,** 280, 386-396, *Proc. Combust. Inst.,* **2017,** 36, 373–382, and *Proc. Nat. Acad. Sci.,* **2017,** 114(50), 13102-13107

GAS PHASE CHEMICAL PHYSICS

Conclusions and Outlook

- address the complexity of chemical reaction networks with a combination of experiments, data analysis procedures, and model development
  - ✓ identify reaction pathways, detect and quantify key intermediates
- fuel-structure dependence of molecular-weight growth reactions using an experimental lumping approach
- imaged 2D temperature fields around the quartz sampling probe
- detection, identification, and quantification of elusive highly oxygenated intermediates during the low-temperature oxidation of DME, *neo*-pentane, and THF
  - ✓ conformer-dependent ionization and appearance energies, photoionization cross sections
- address the complexity of the reaction networks with new experimental approaches, *i.e.* microwave spectroscopy and MS-MS

GAS PHASE CHEMICAL PHYSICS

Acknowledgments

Experiments:

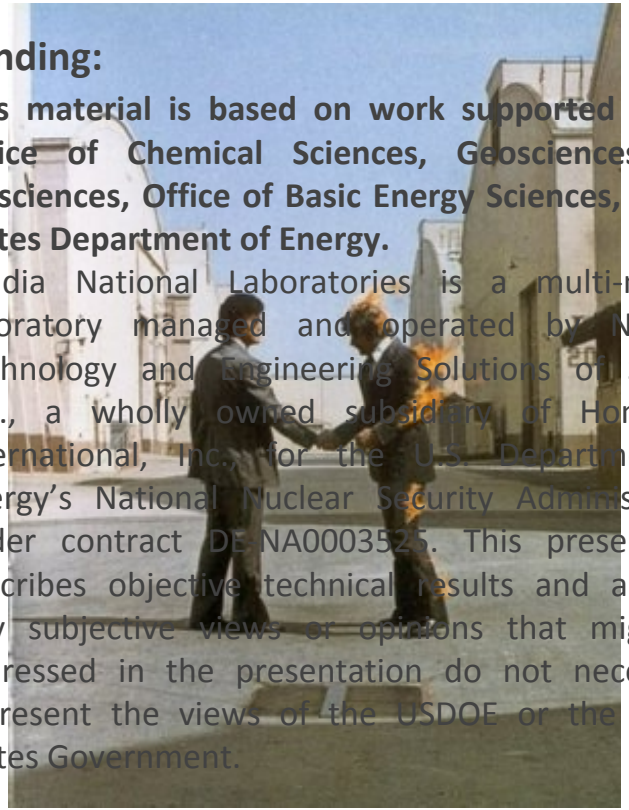
- P. Dagaut (CNRS Orleans, France)
- K. Kohse-Höinghaus (Universität Bielefeld, Germany)
- S. A. Skeen (Sandia National Laboratories)
- R. S. Tranter (Argonne National Laboratory)
- A. L. Kastengren (Argonne National Laboratory)
- J.-U. Grabow (Leibniz Universität Hannover, Germany)

Theory and Modeling:

- A. W. Jasper (Argonne National Laboratory)
- S. J. Klippenstein (Argonne National Laboratory)
- F. Mauss (Cottbus, Germany)

Postdocs and Vistors:

- K. Moshammer, A. Rousso, J. Wullenkord, L. Ruwe, and B. Adamson



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