SAND2022-8317C

Quantitative Probing of Autoignition Intermediates at High Pressures by Time-Resolved VUV Photoionization Mass Spectrometry

Leonid Sheps
Combustion Research Facility
Sandia National Laboratories, USA

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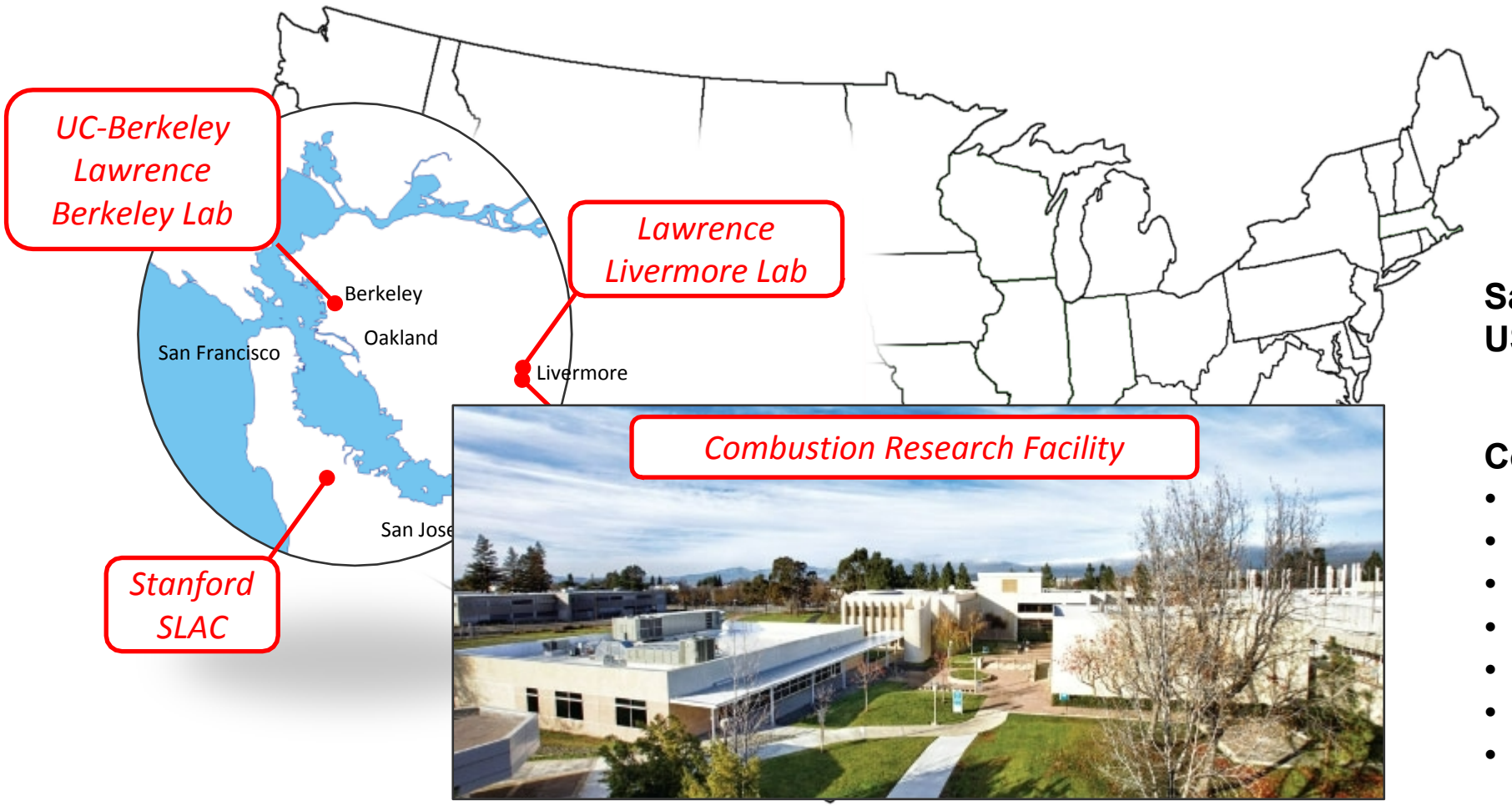

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US Department of Energy

Combustion Research Facility

- Fuel & engine research
- Energy storage and conversion
- Turbulence/chemistry interactions
- Experimental diagnostics
- Chemical kinetics
- Gas-phase chemical physics
- *New* Multi-phase (gas-surface) interactions

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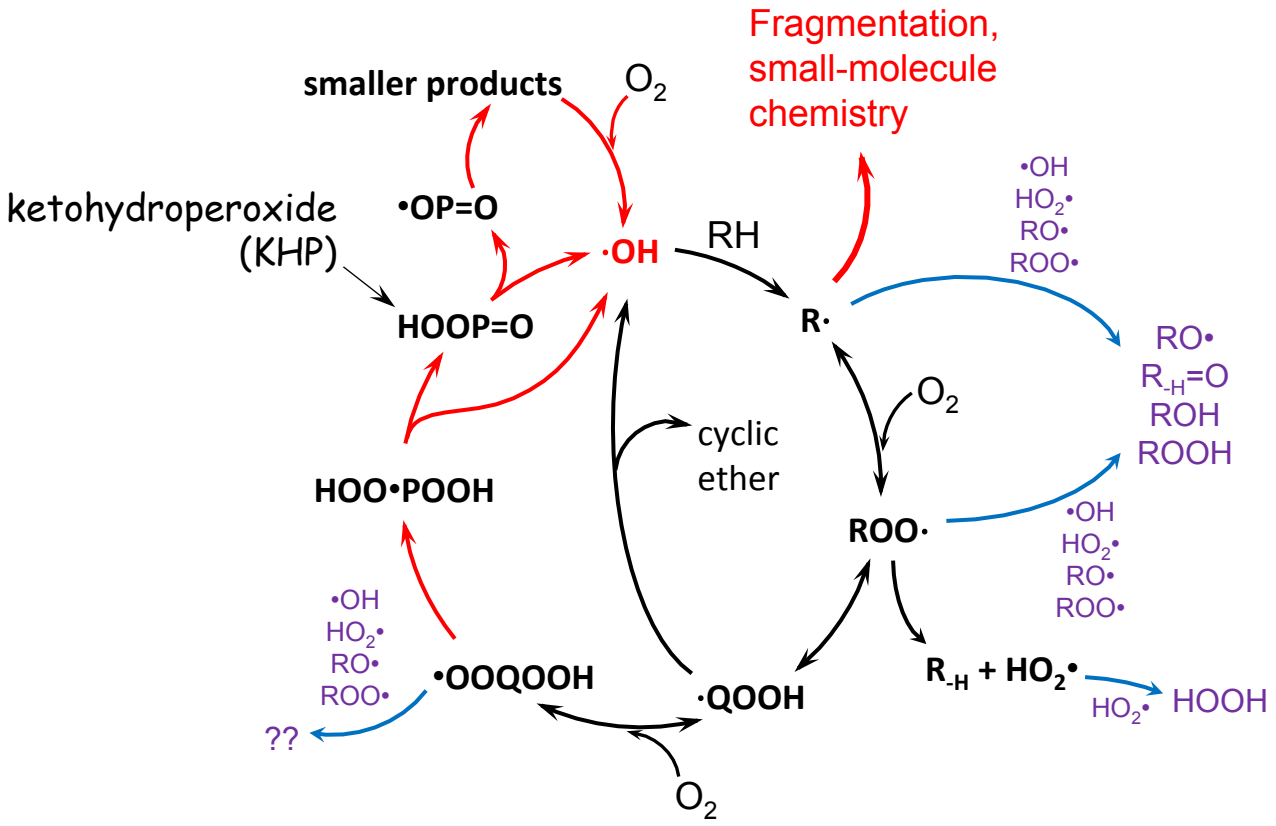
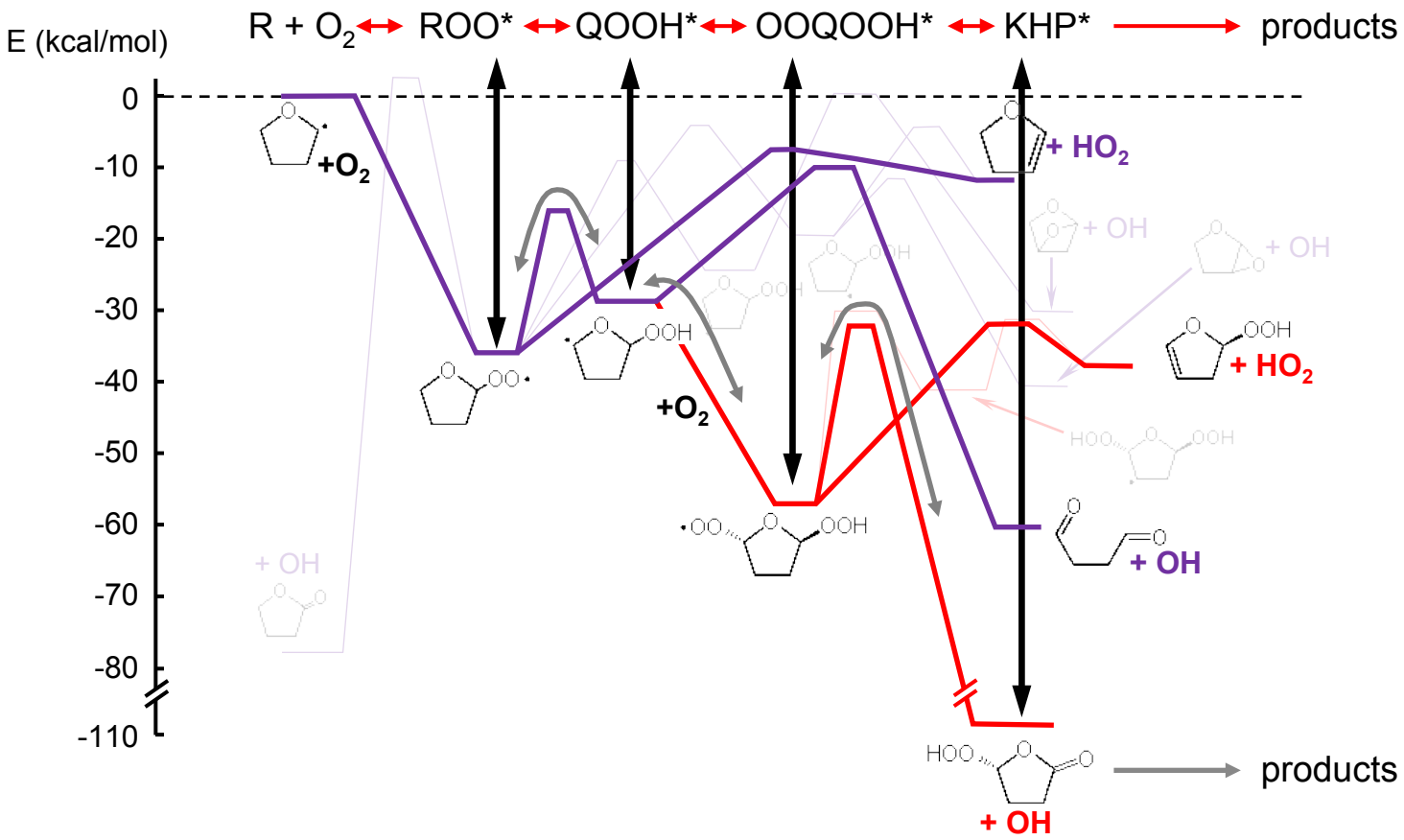
Autoignition – a chemical feedback loop

Adapted from Merchant *et al.* *Comb. Flame*, **162**, 3658 (2015)





Fundamental Chemical Physics challenges

- Molecular structure-dependence
- Temperature dependence
- Pressure-dependence and non-Boltzmann reactions

Modeling challenges

- 100s of species/1000s of reactions
- uncertain rate and energy transfer parameters

Experimental challenges

- Short-lived, reactive intermediates
- No prior characterization

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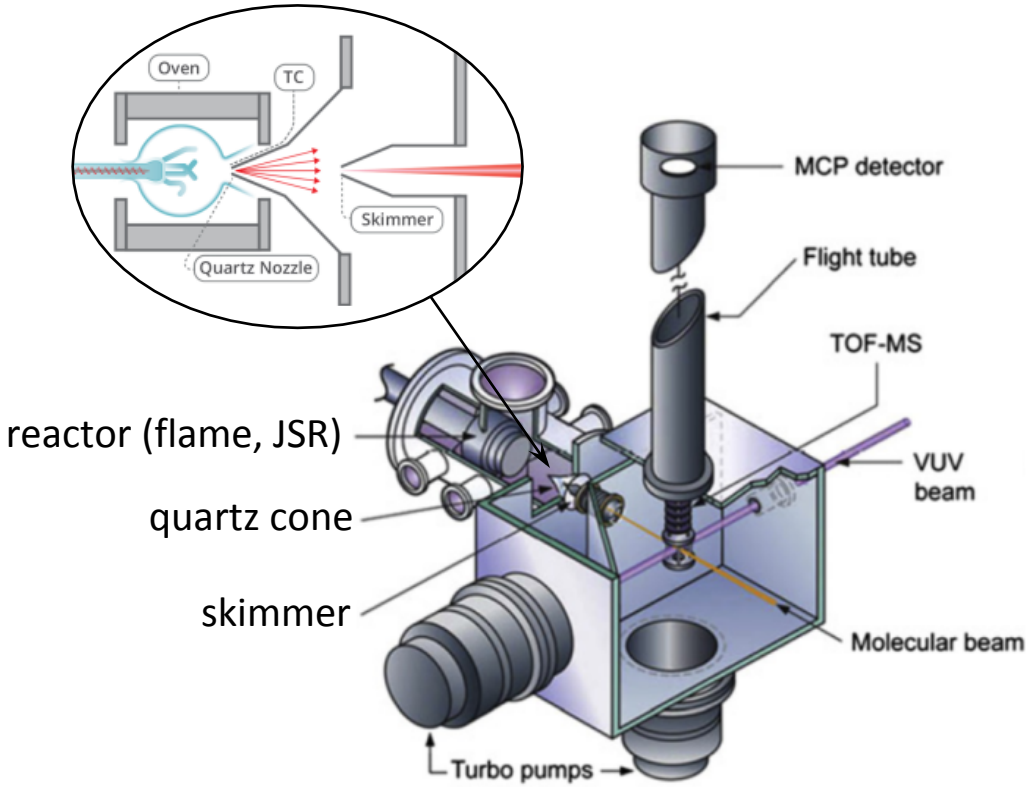
SVUV Photoionization mass spectrometry



Cool *et al.*, ALS, circa 2005 - present

- Universal detection*
- Multiplexed, high-throughput
  - Orthogonal acceleration TOF-MS
  - Quasi-CW ionization, duty cycle ~1
- Isomer-level selectivity*
  - Soft VUV ionization
  - Distinct PI spectra
- Quantitative*
  - Large database of abs. PICS is available

- Other SVUV-PIMS setups: NSRL, Soleil, others?
- Also: shock tubes, plug flow reactors, catalytic reactors
- Advanced photoionization methods (PEPICO, false coincidence rejection)

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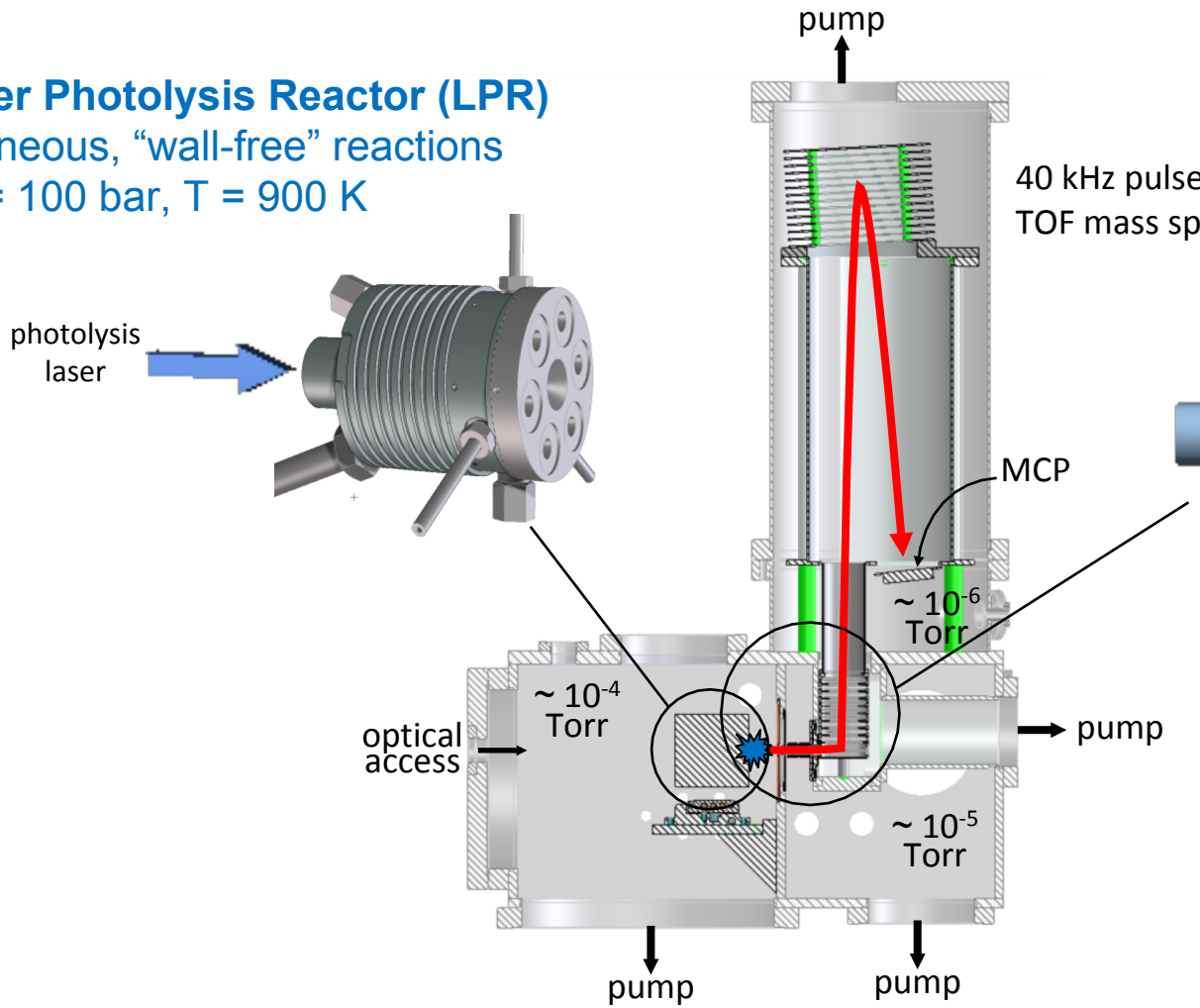
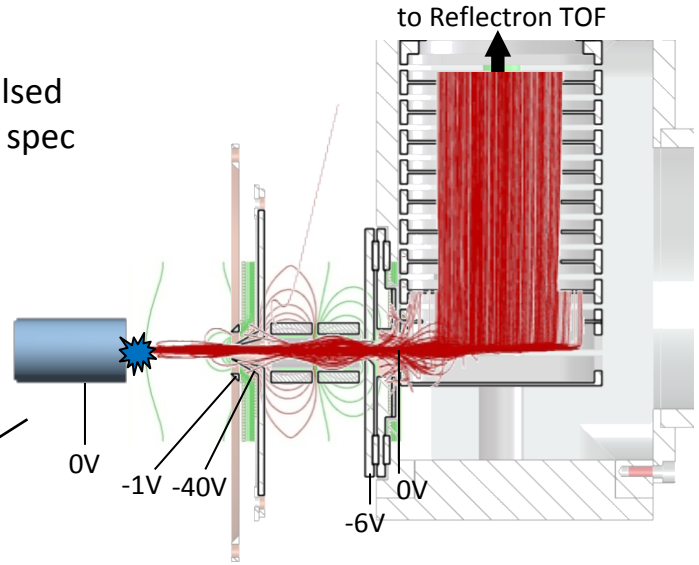
Sandia high-pressure PIMS endstation

high-P Laser Photolysis Reactor (LPR)

- Homogeneous, "wall-free" reactions
- up to P = 100 bar, T = 900 K





Ivan Antonov

J. Phys. Chem. A, 123 **(2019)**, 10804

Custom photoionization mass spec

- High-density ionization = high sensitivity (including reactive molecules, e.g. radicals)

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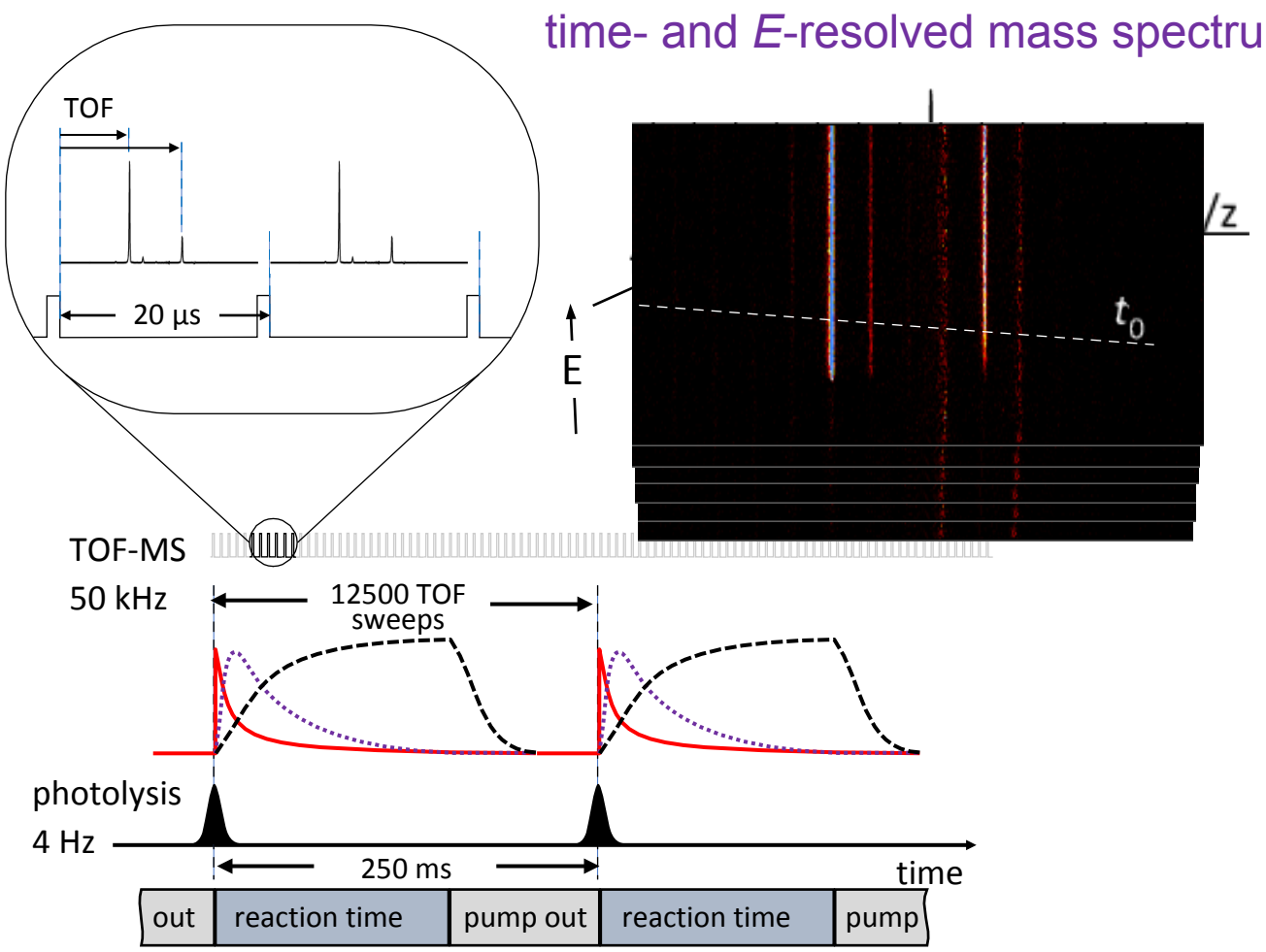
Laser flash photolysis/time-resolved SVUV-PIMS



- Real-time speciation data
  - Helps unravel sequential kinetics
  - A new dimension for model targets
- Works at T << autoignition
- Enables detection of radicals, other short-lived intermediates

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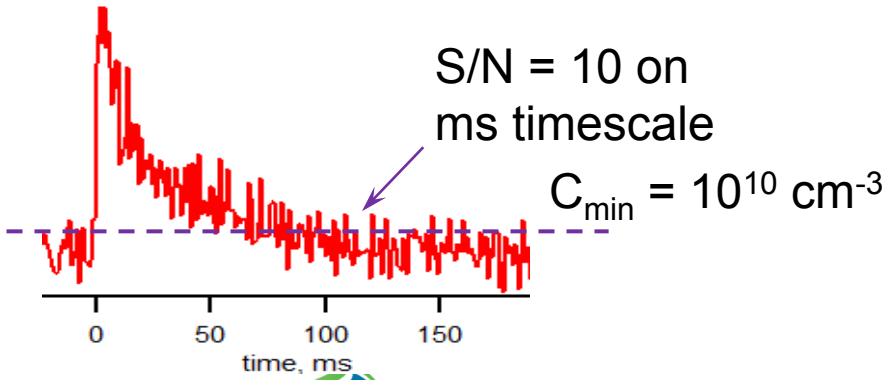
Sensitivity loss of MBMS-PIMS as a function of P

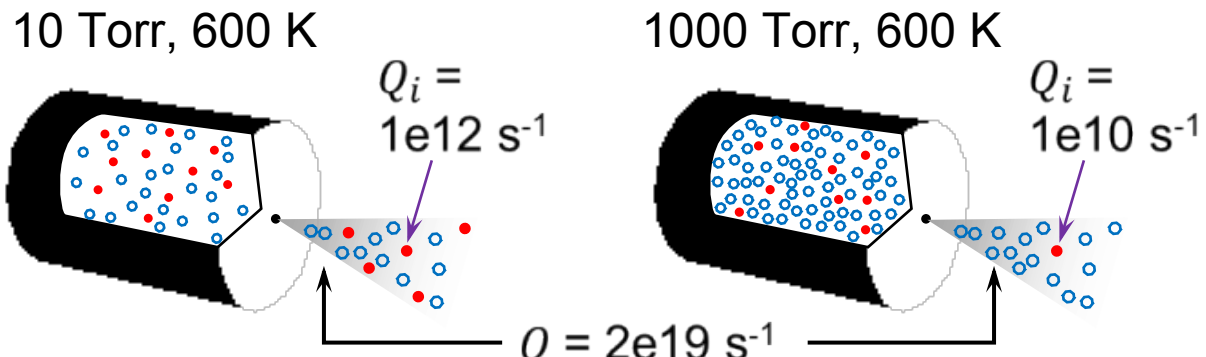
1e-17 cm^2 1e15 $cm^{-2}s^{-1}$ 1e-9 s

$$S_i(Et) = Q \cdot \chi_i(t) \cdot \sigma_i(E) \cdot F_{VUV}(E) \cdot O_s$$

ionization probability ~1e-11

- Q: sampling flow
- $\chi_i(t)$: mole fraction
- $\sigma_i(E)$: PICS
- $F_{VUV}(E)$: VUV fluence
- O_s: "overlap" factor





10 counts·s^{-1}

~10^4 shots averaging
(42 minutes)

0.1 counts·s^{-1}

~10^6 shots averaging
(70 hours)

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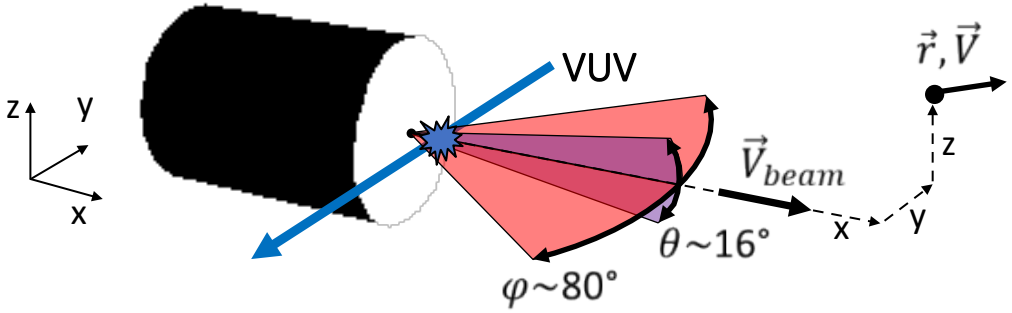
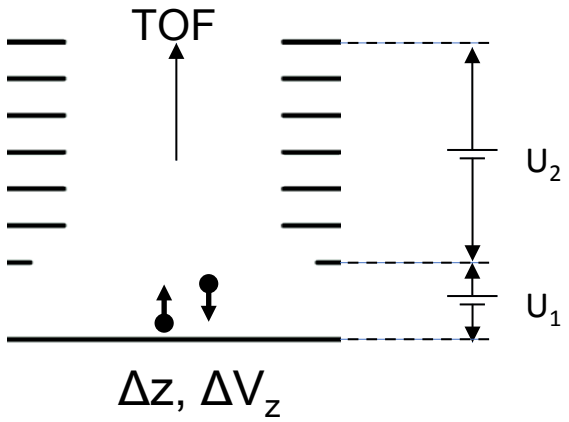
High-density ionization – a new mass spectrometer design

- Pro: high ionization efficiency (ρ ~ $1/x^2$)
- Con #1: ion beam divergence

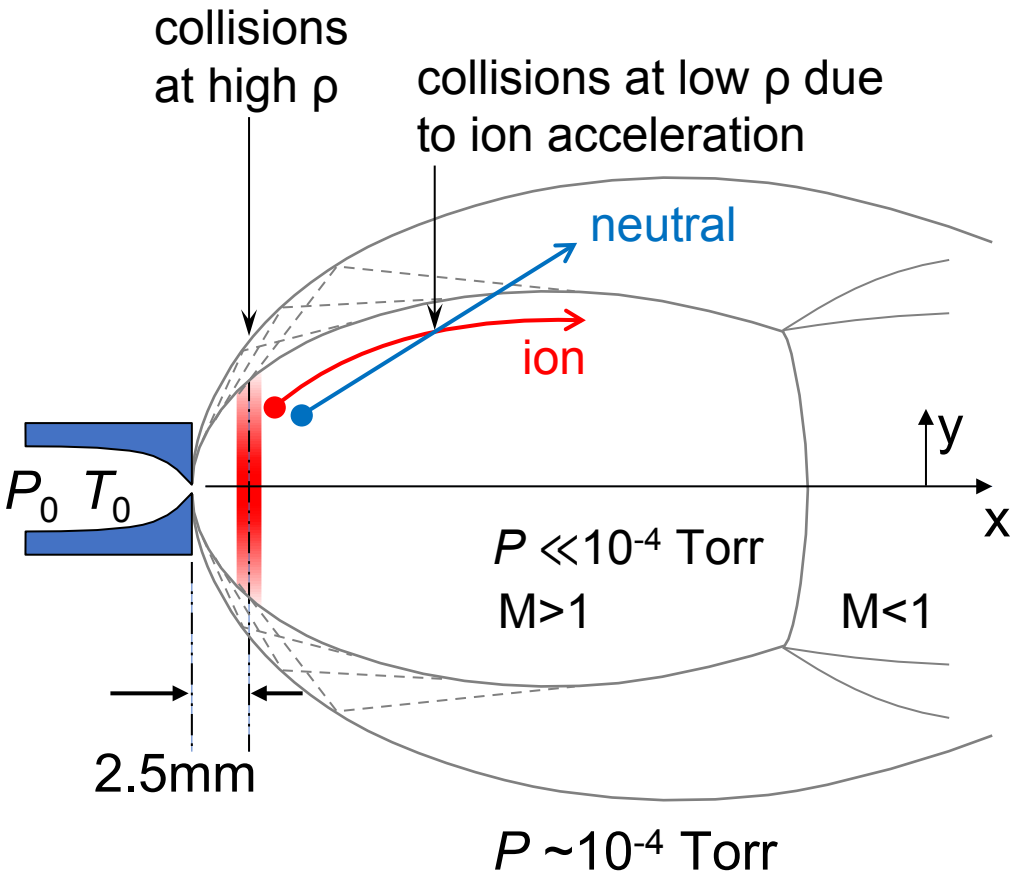




Transverse $\Delta\vec{V}$ leads to TOF dispersion

- cannot compensate for $\Delta\vec{V}_z$
- degrades mass resolution

- Con #2: ion-molecule collisions



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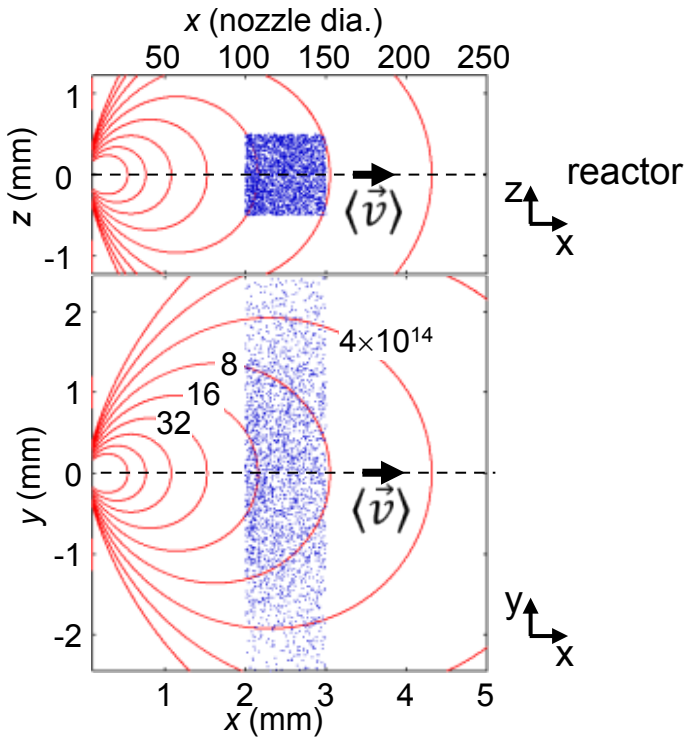
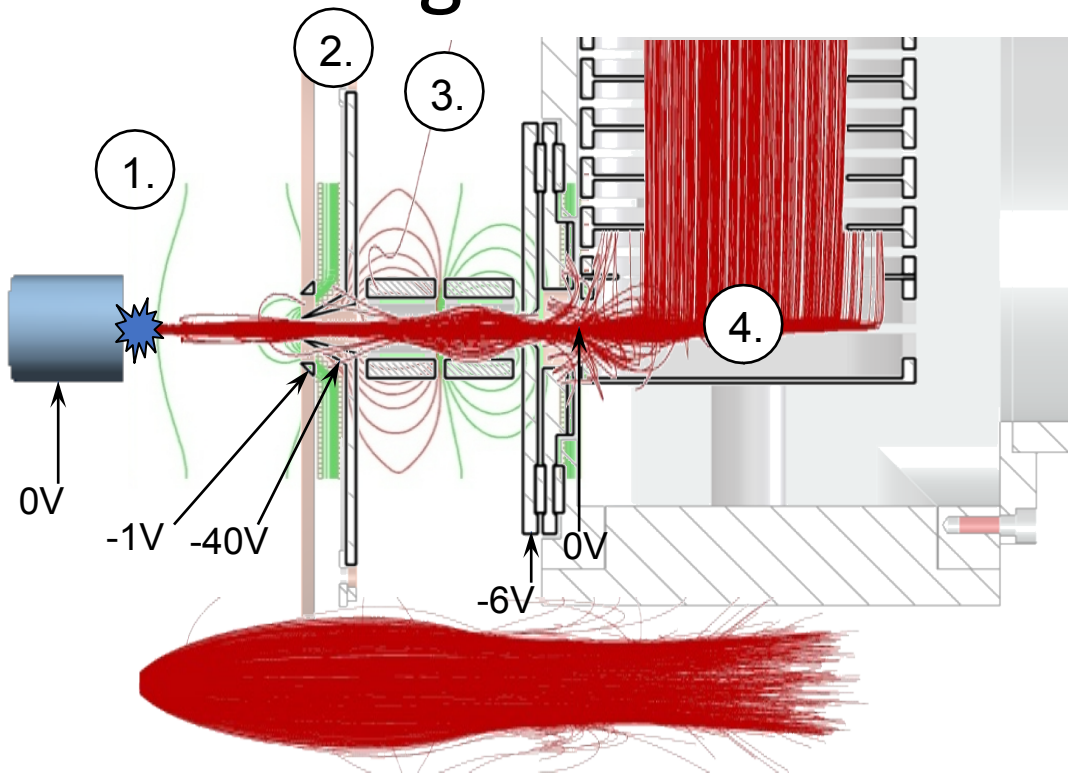
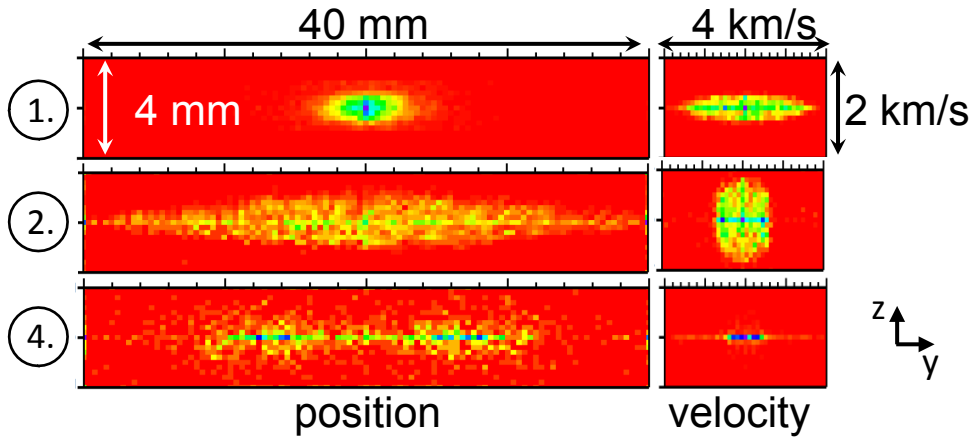
High-density ionization – the “digital twin”





1. Ionization
2. Nested apertures (4mm x 40mm)
3. ES quadrupole focusing doublet
4. Pulsed acceleration

- Ensemble of initial $\vec{r}, \vec{V}$
- Hard-sphere collisions
- Iterative design optimization



- $P_{collision}$ ~20%
- $P_{detection}$ ~1e-9
- m/Δm ~1600

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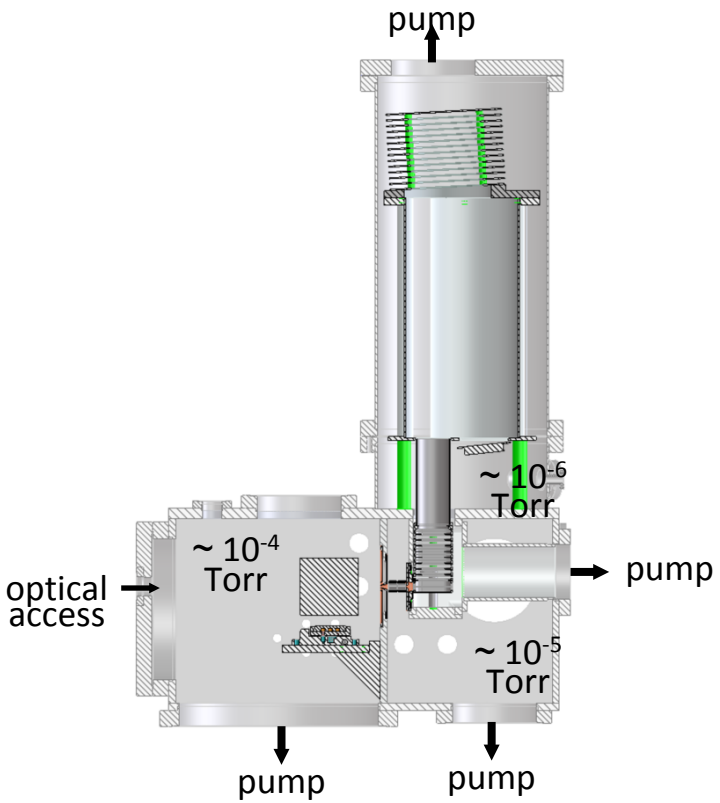
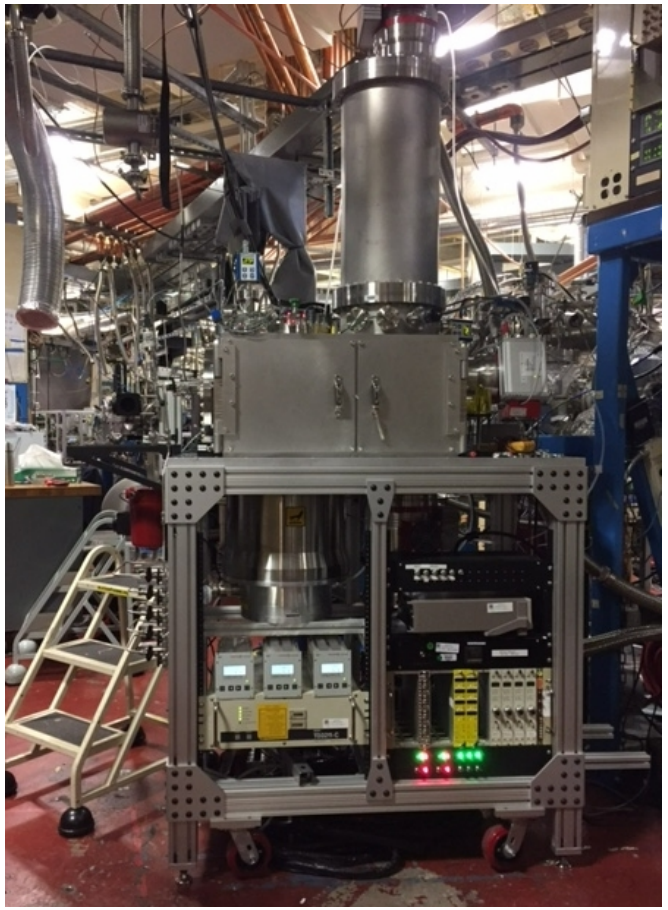
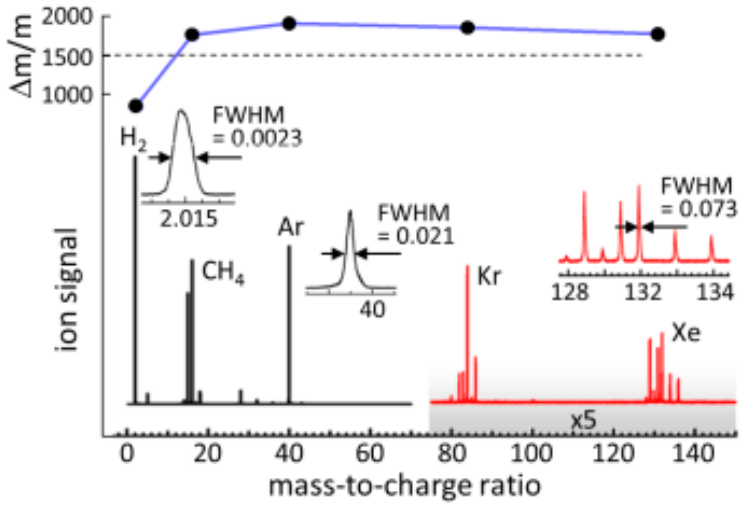
Sandia high-pressure PIMS – V2.0





Installed at beamline 9.0.2



- Mobile endstation (SNL or ALS)
- m/Δm ~1600
- 100x sensitivity over version 1.0
- P up to 50 bar, T up to 900 K
- “Wall-free”, sensitive to radicals
- 25µs time resolution

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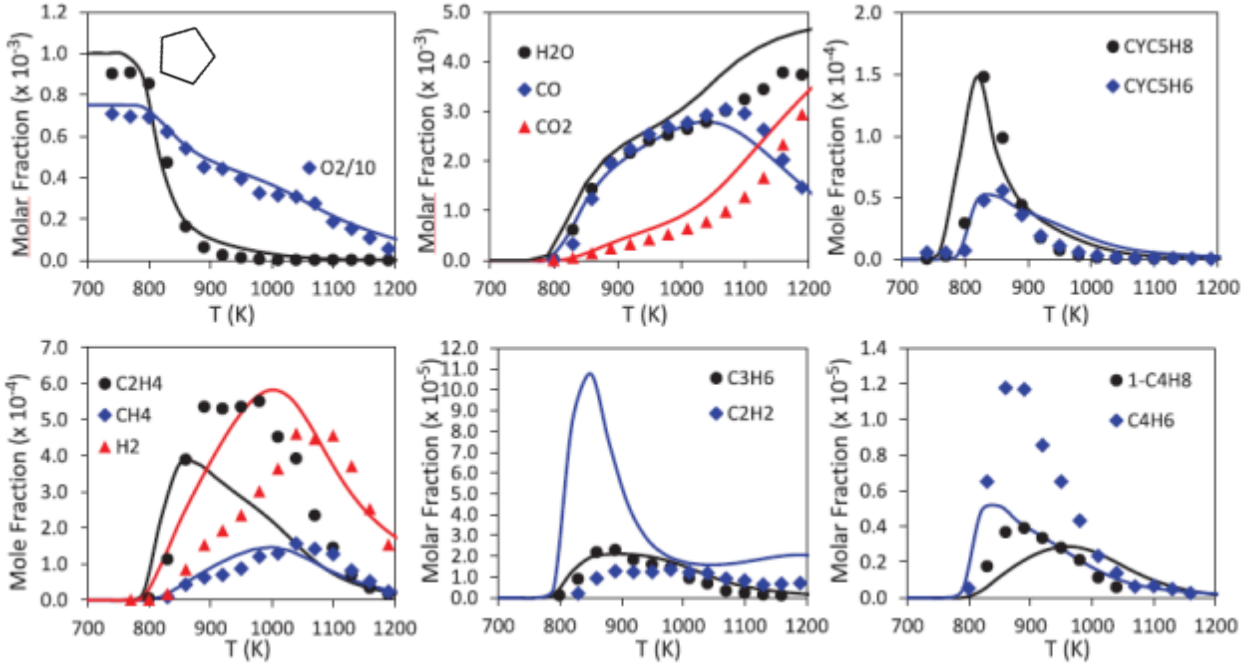
Oxidation of a prototypical cycloalkane: cy-C_5H_{10}

Experiments
- Wu and Bayes (1986), direct R + O_2 kinetics @3.5 Torr, 298 K
- DeSain and Taatjes (2001), HO_2 time traces up to 60 Torr, 723 K
- Daley *et al*. (2008), shock tube ignition delays

Theory:
- Sirjean *et al*. (2009): ROO ⟶ products, CBS-QB3
- Miyoshi (2019): R + O_2, γ-QOOH + O_2, CBS-QB3

Theory, modeling, experiments
- Al Rashidi *et al*. (2017), 3 papers:
  - R + O_2, γ-QOOH + O_2, CCSD(T)-F12//MO6-2X
  - master-equation modeling
  - shock tubes, RCM, JSR

Our goal:
- Direct, time-resolved probe of critical intermediates and products
- Coupled to theoretical kinetics, master equation modeling
- Elucidate primary oxidation sub-mechanism



Al Rashidi et al, PROCI 36 (2017) 469

- ST, JSR, RCM probe mostly stable products
- "no low-T chemistry"

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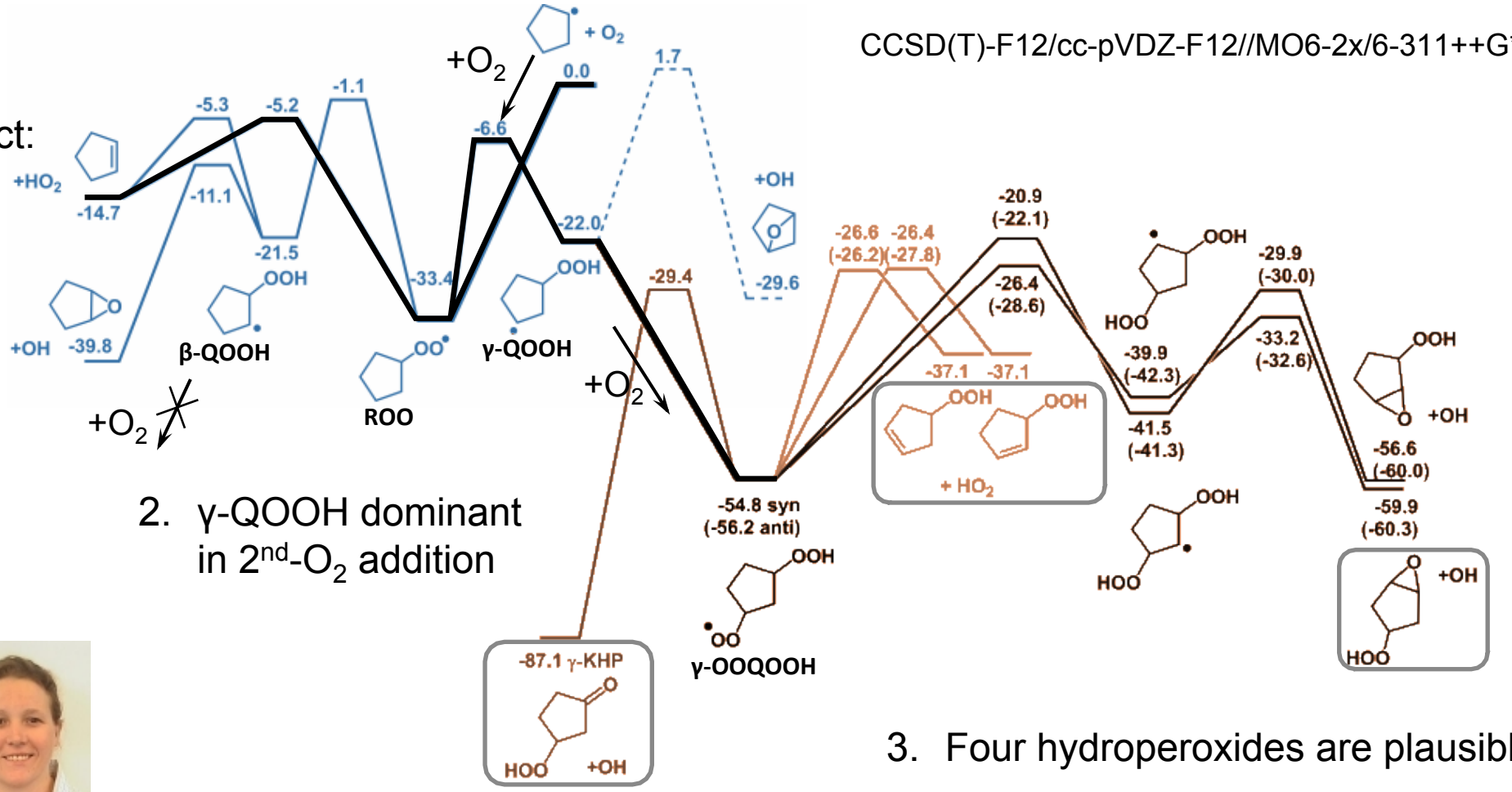
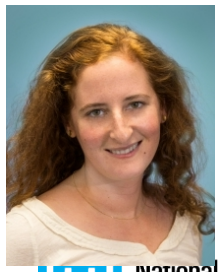
Calculated R + O_2 + O_2 PES and theoretical kinetics

1. Major product: cy-C_5H_8



2. γ-QOOH dominant in 2nd-O_2 addition

3. Four hydroperoxides are plausible



Judit Zádor

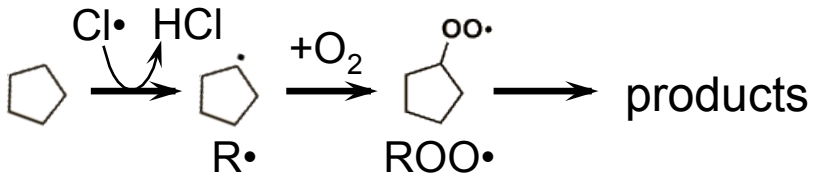
Amanda Dewyer

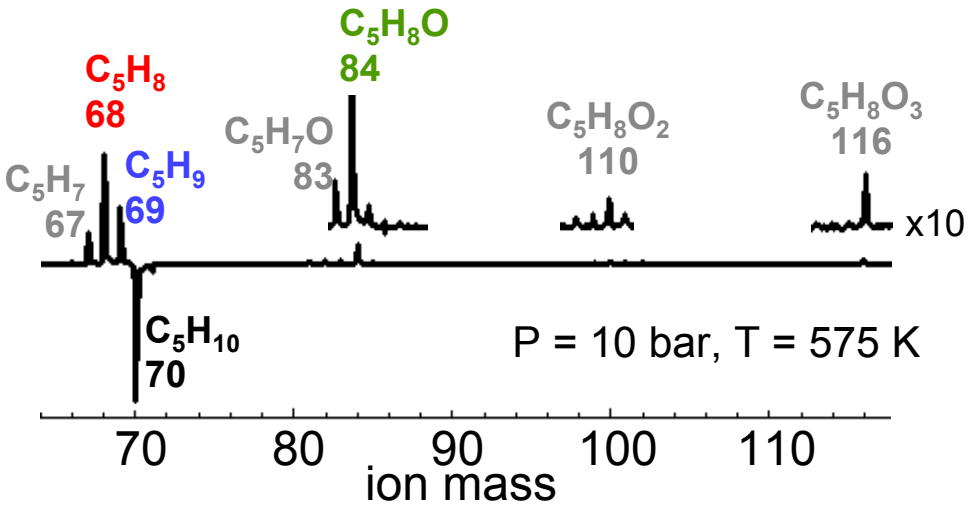
Time-resolved SVUV-PIMS at P = 10 bar, T = 450 – 650 K

Maria Demireva

Cl_2/cy-C_5H_{10}/O_2/He

Cl_2 + hv(351nm) ⟶ 2Cl•





- Most of these species have not been detected before
- Unknown PI cross-sections, fragmentation patterns

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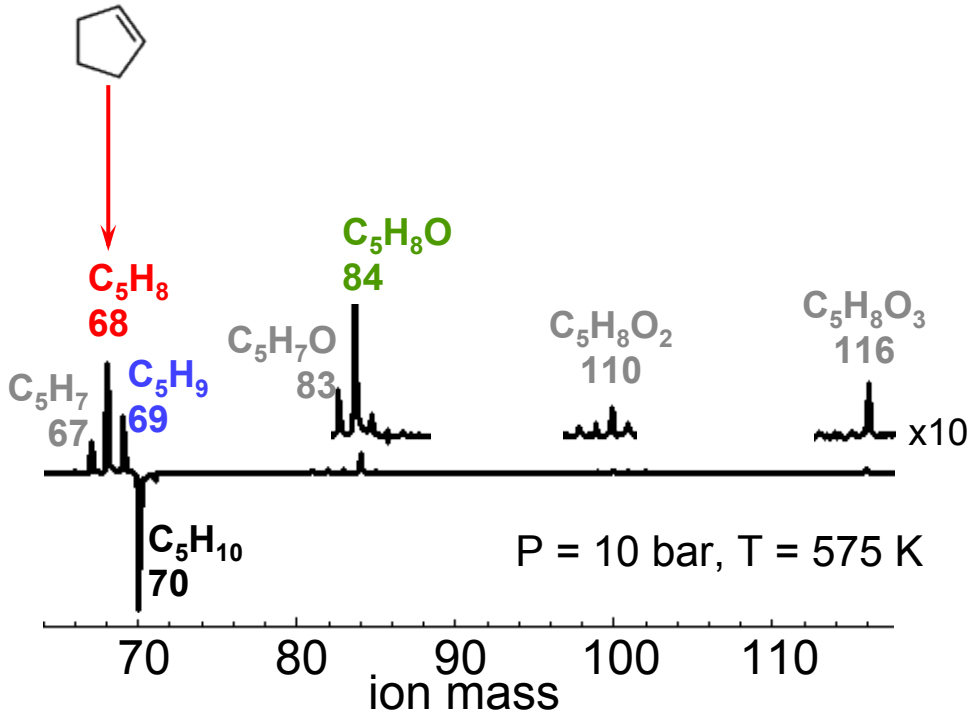
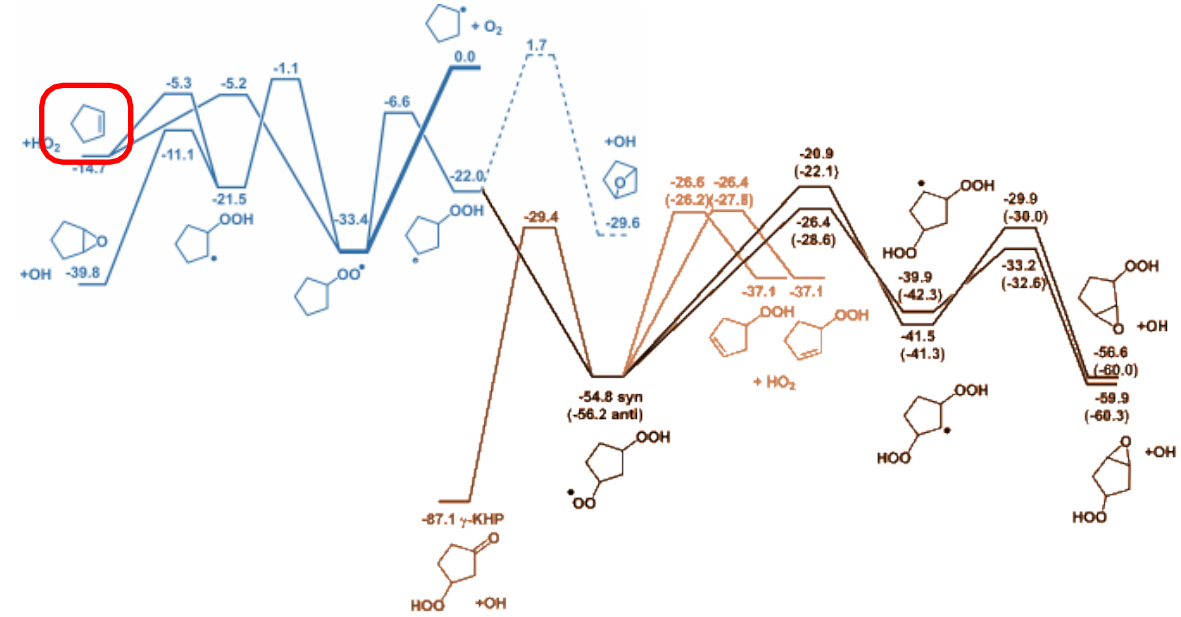
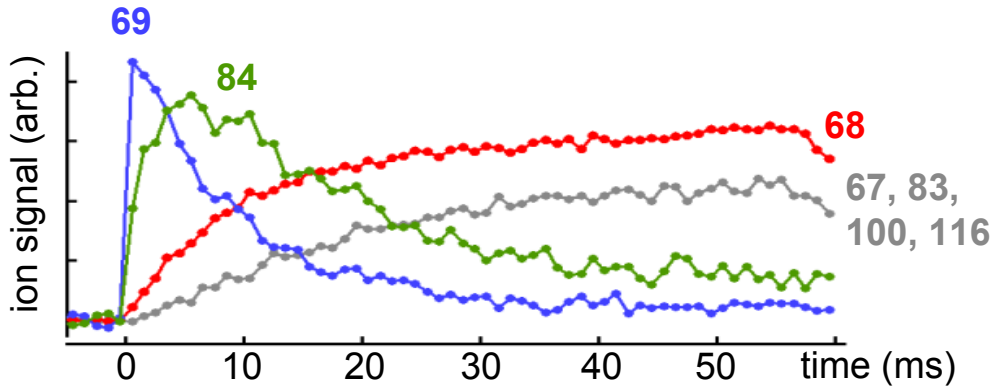
Species assignments and photoionization spectroscopy







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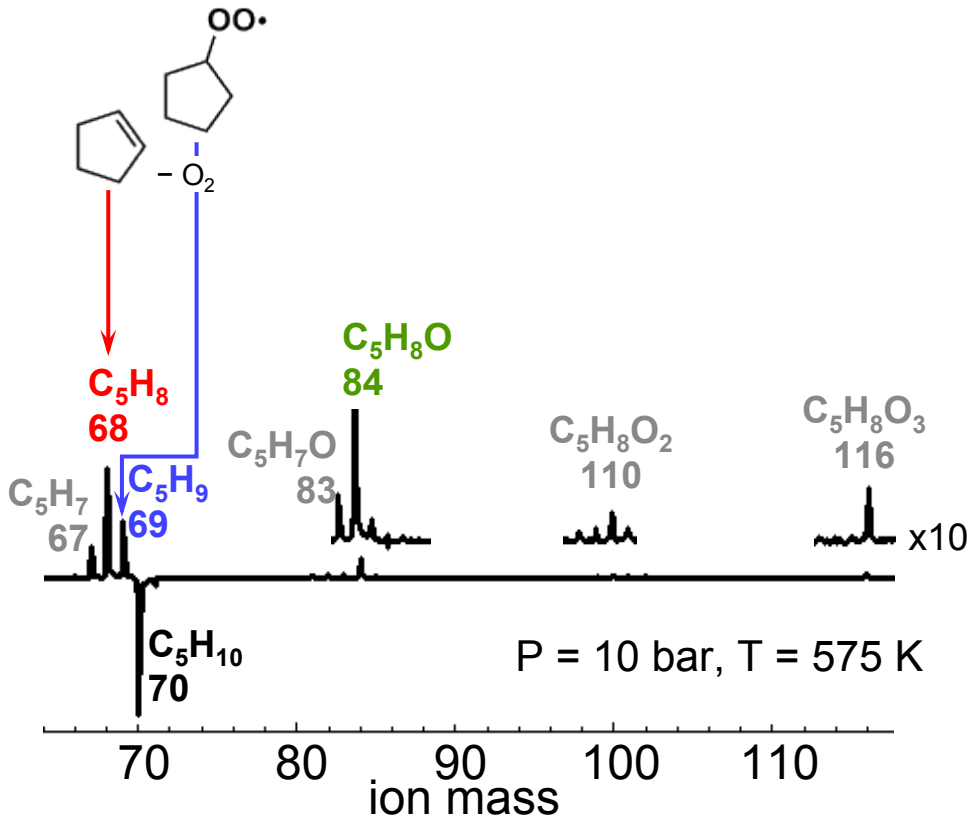
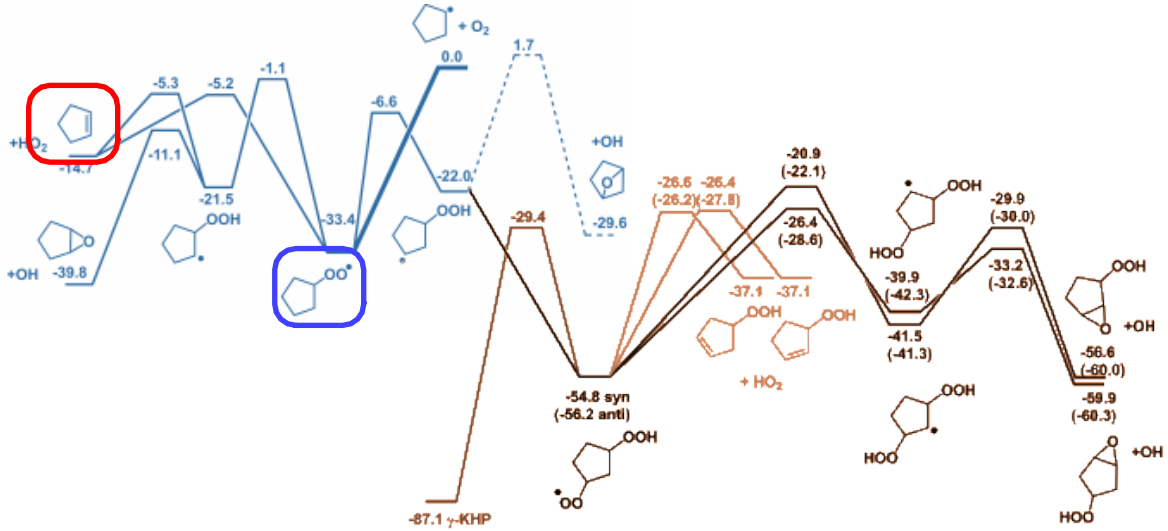
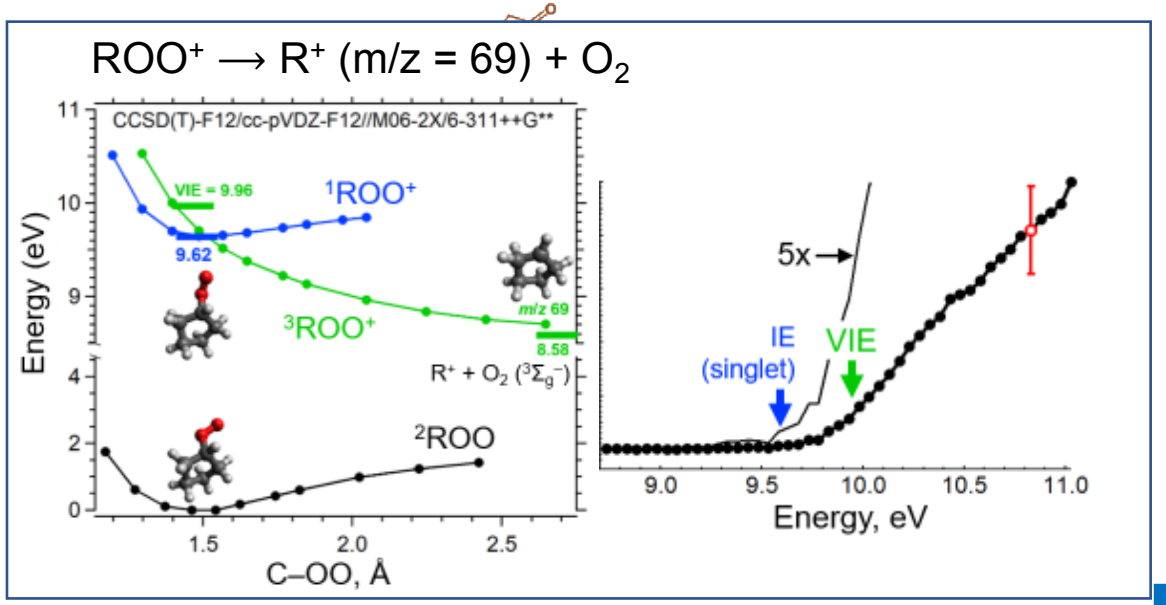
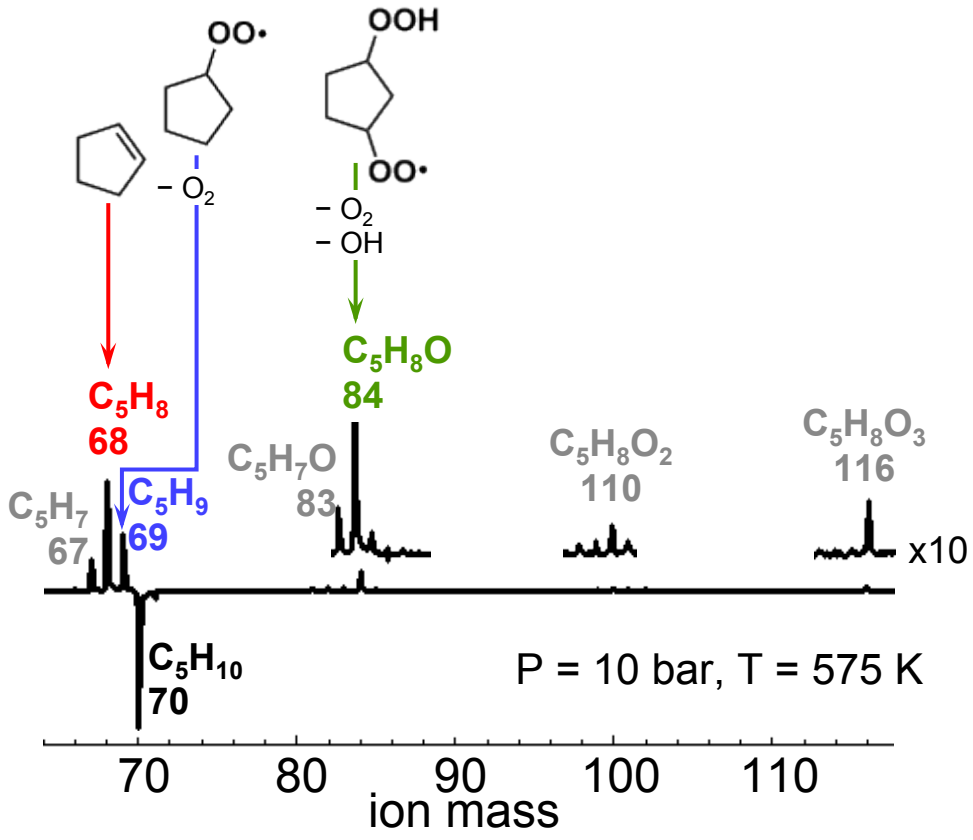
Species assignments and photoionization spectroscopy

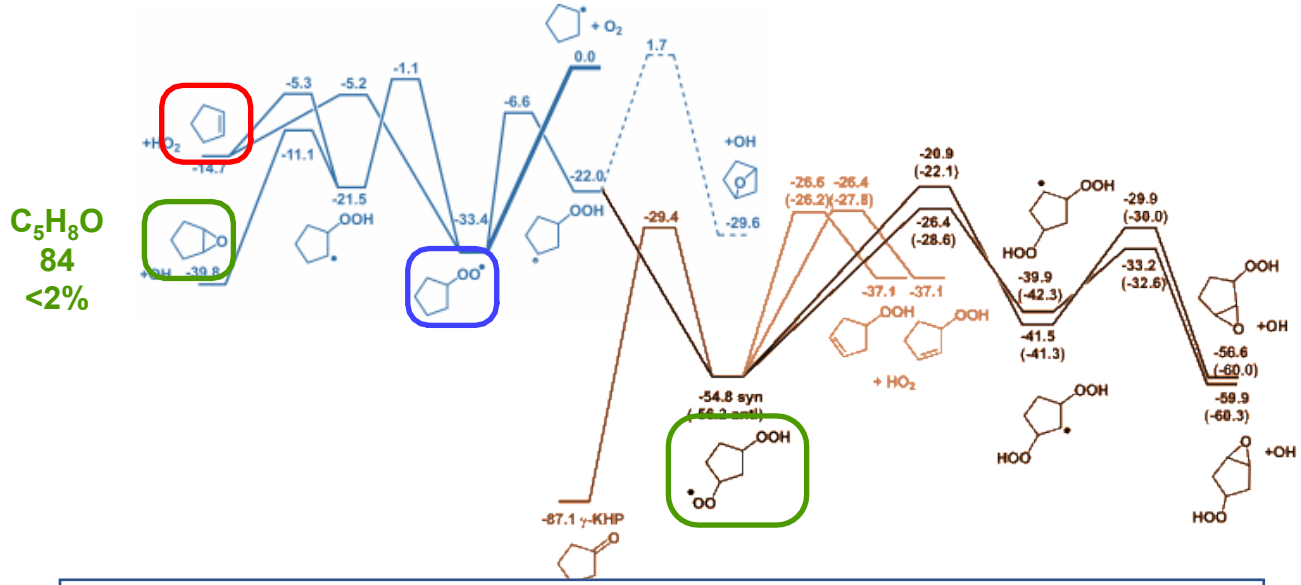


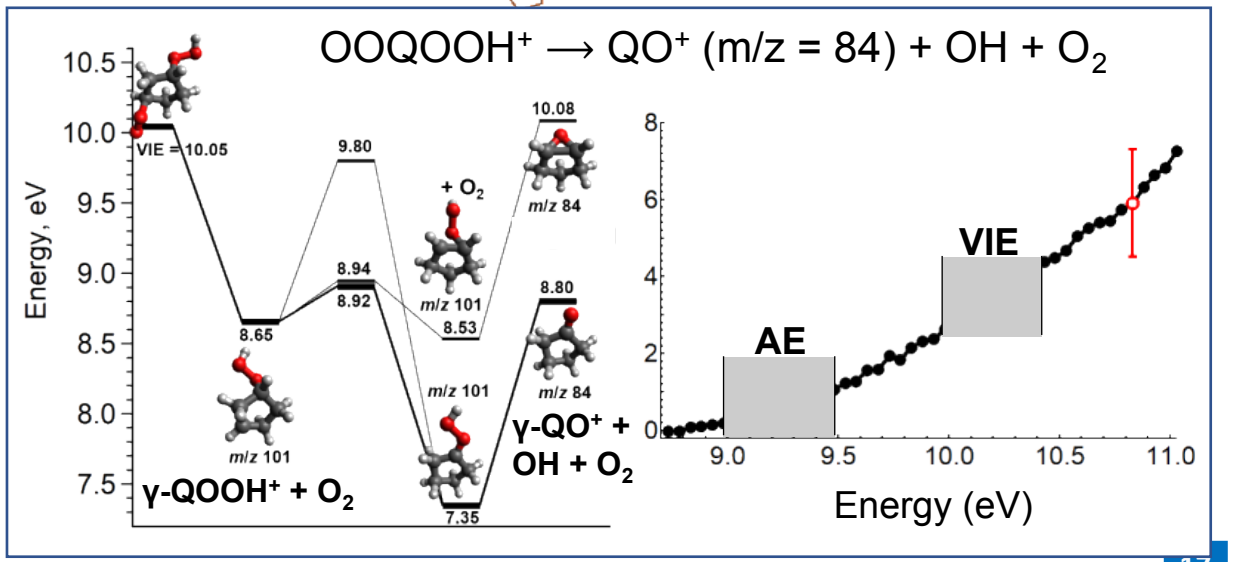




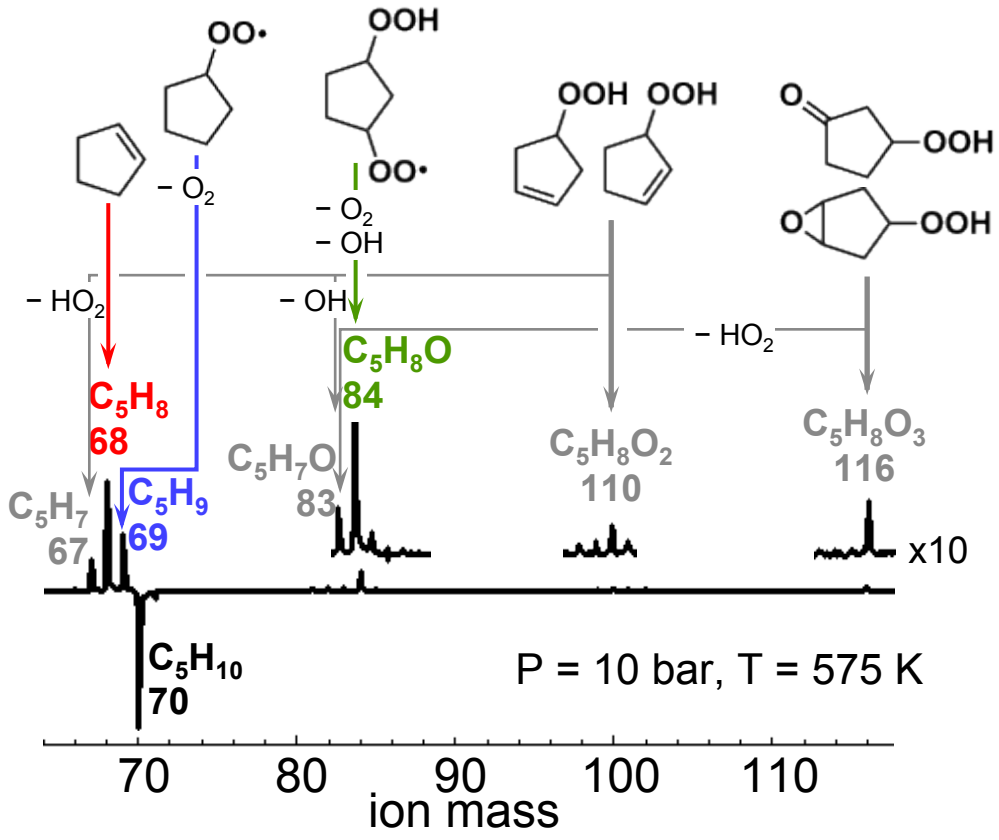
Species assignments and photoionization spectroscopy

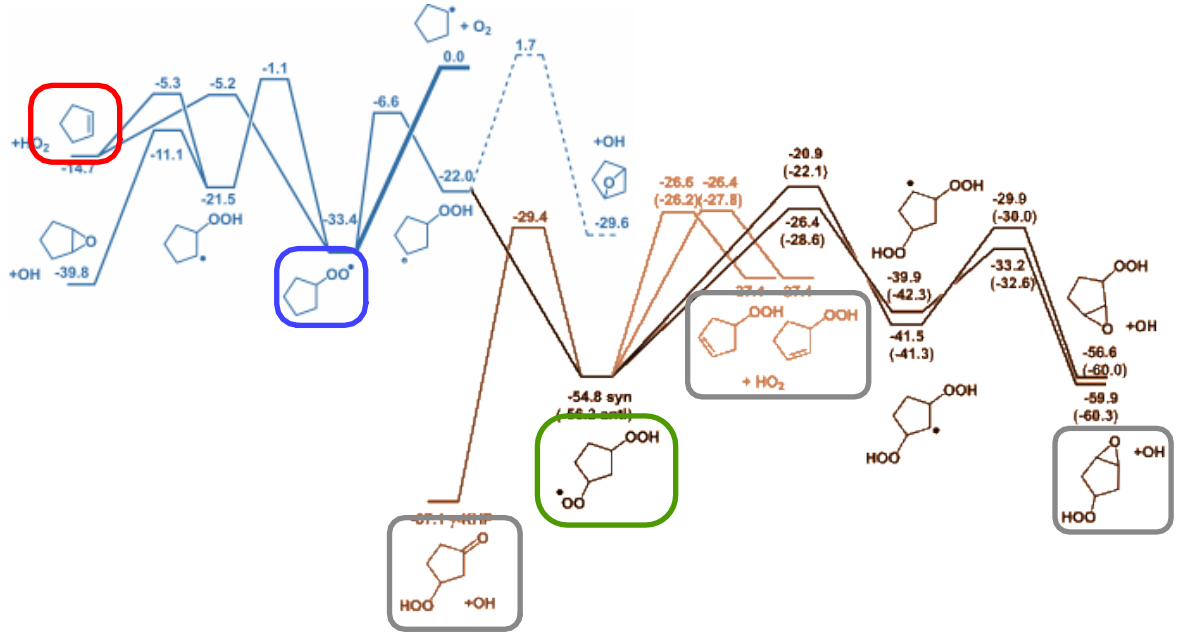


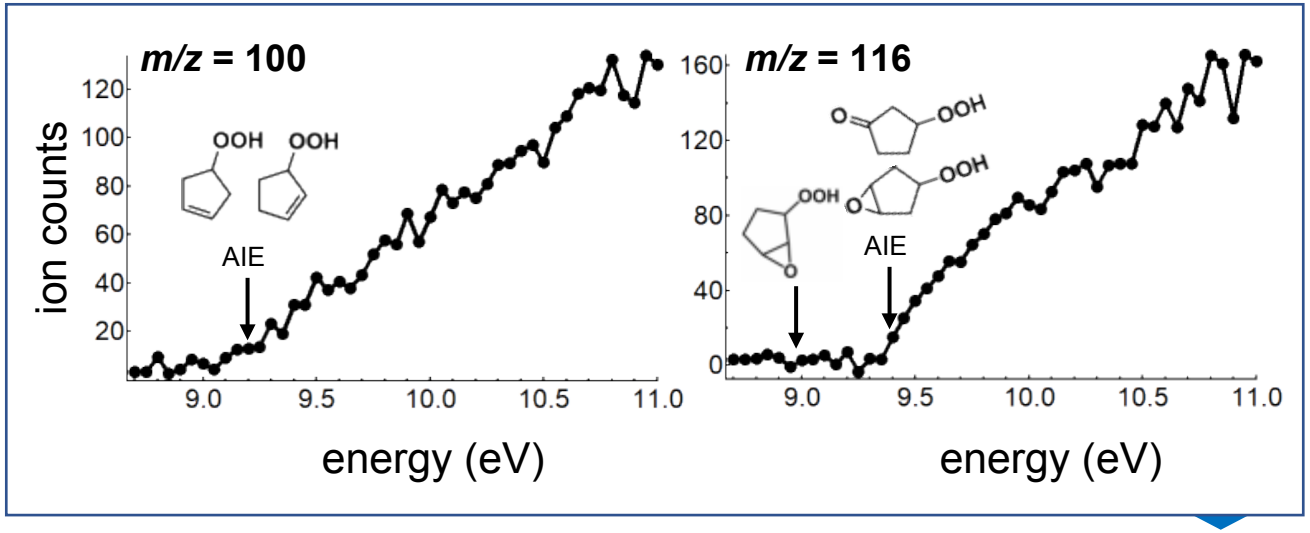




Species assignments and photoionization spectroscopy







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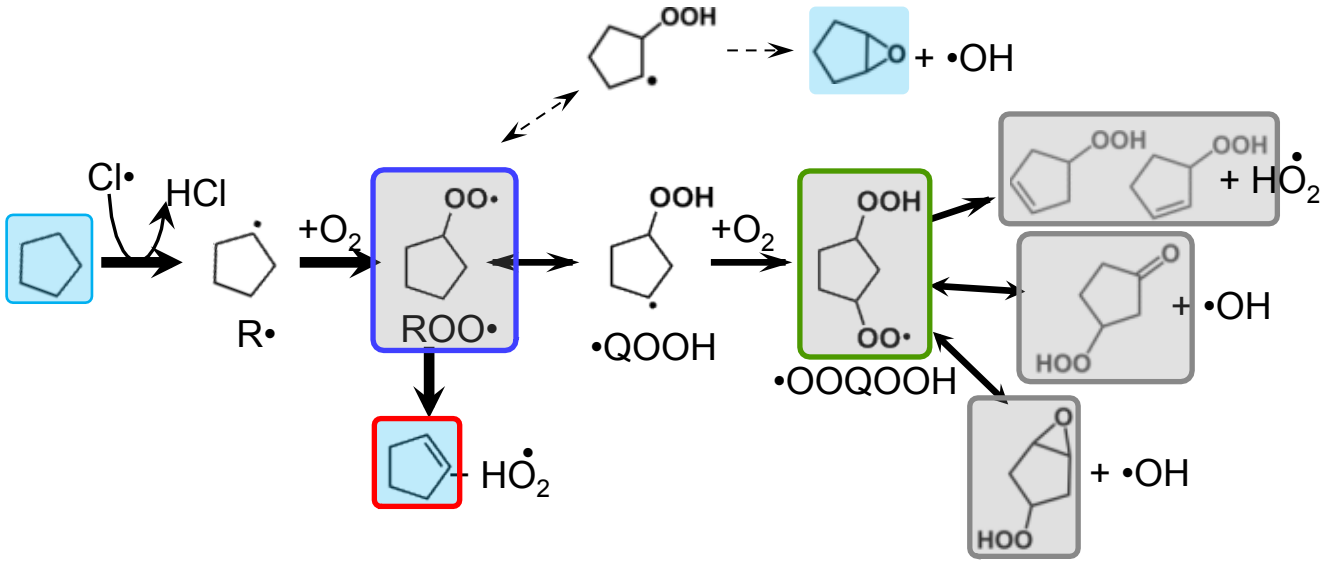
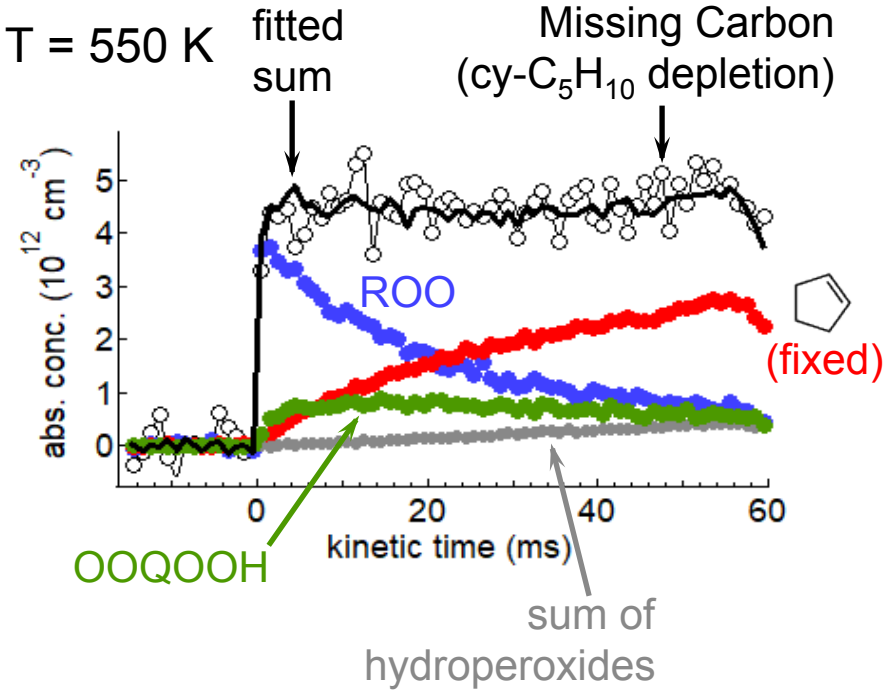
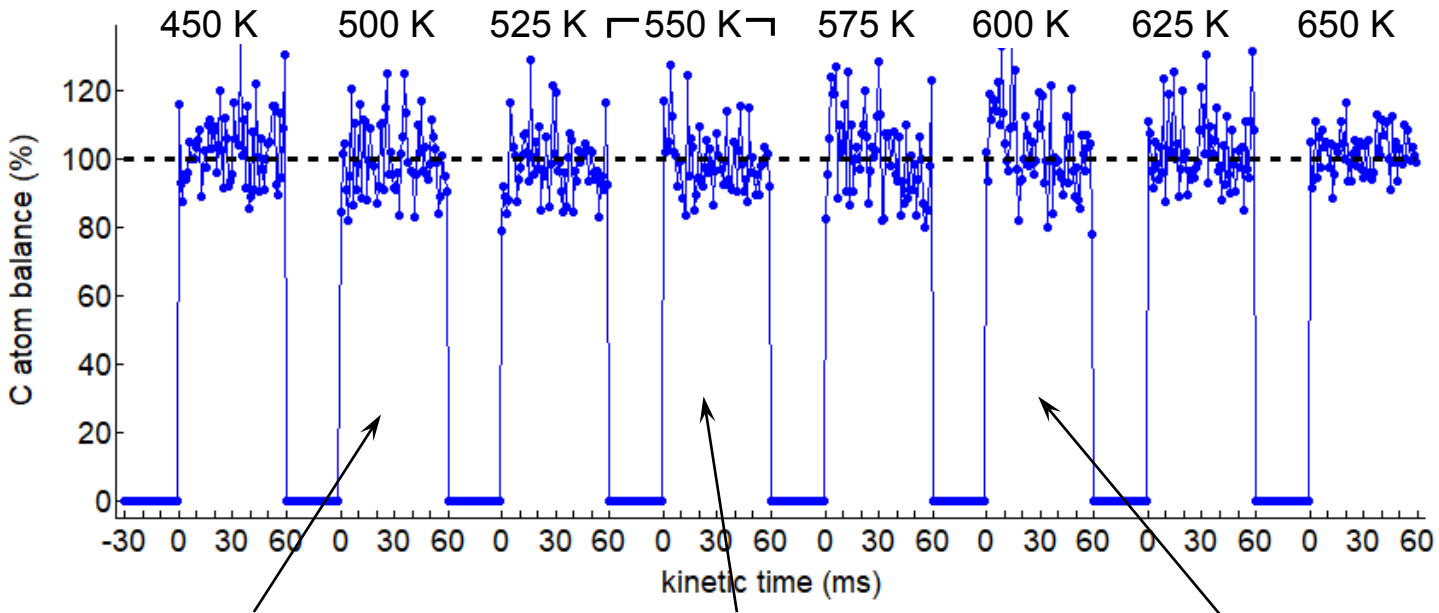
Quantification from C atom balance

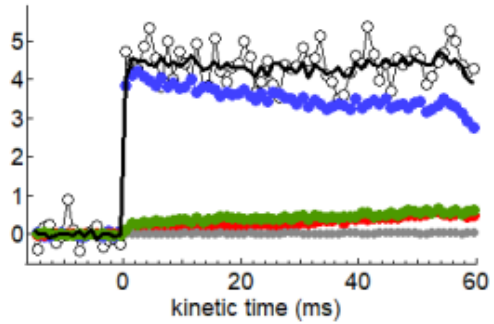


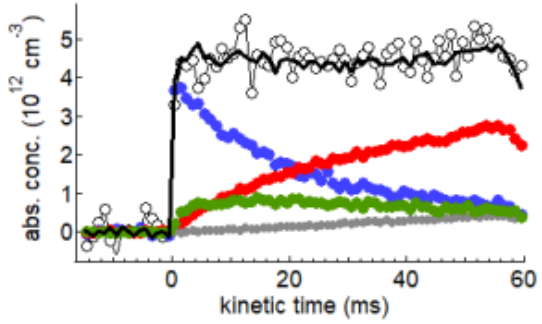
= directly detected = quantified from reference PIXS

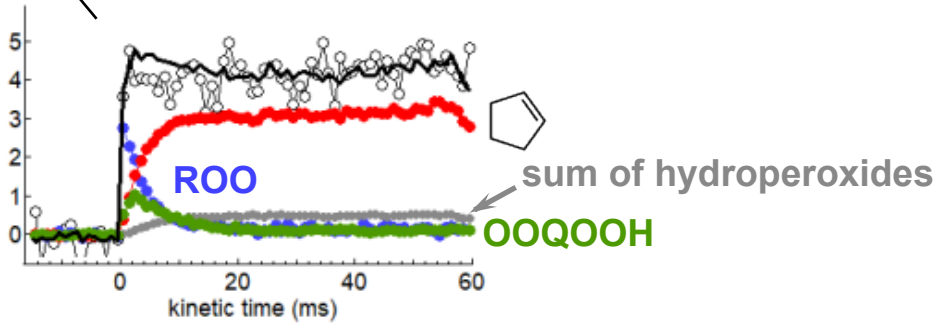


Quantification from C atom balance – global fit









- Global fit at all T
- cy-C_5H_{10}, minor products fixed
- Adjustable (T-independent) total PICS:
  - ROO
  - OOQOOH
  - "Effective" PICS of hydroperoxides

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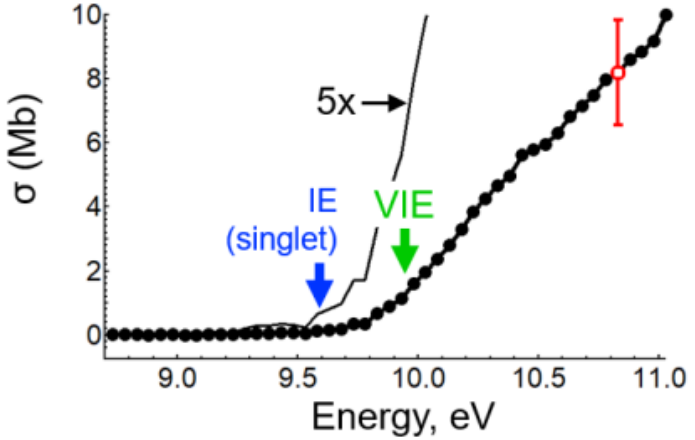
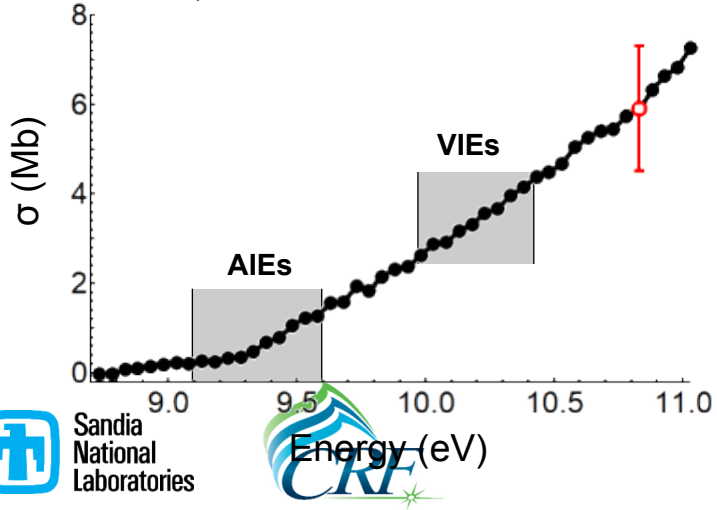
Quantification from C atom balance

Absolute photoionization cross-sections

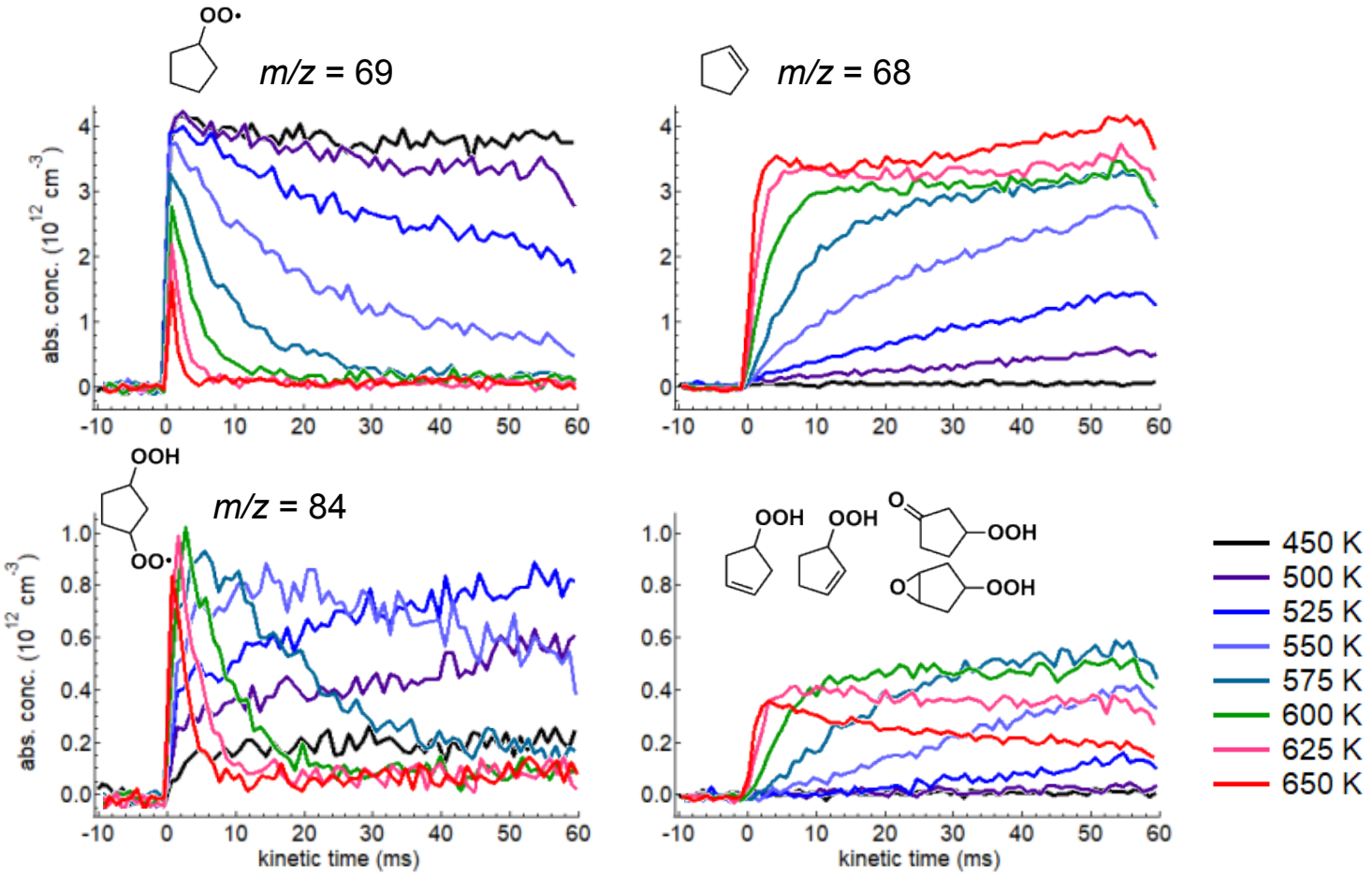
ROO, *m/z* = 69 channel



OOQOOH, *m/z* = 84 channel



Absolute concentration-time profiles



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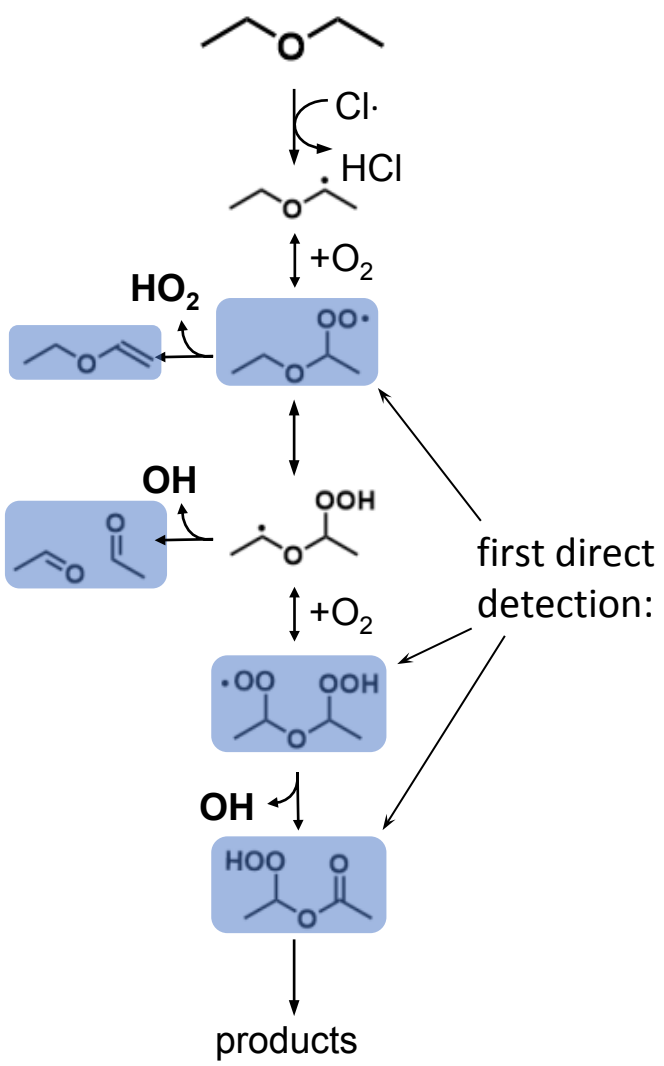
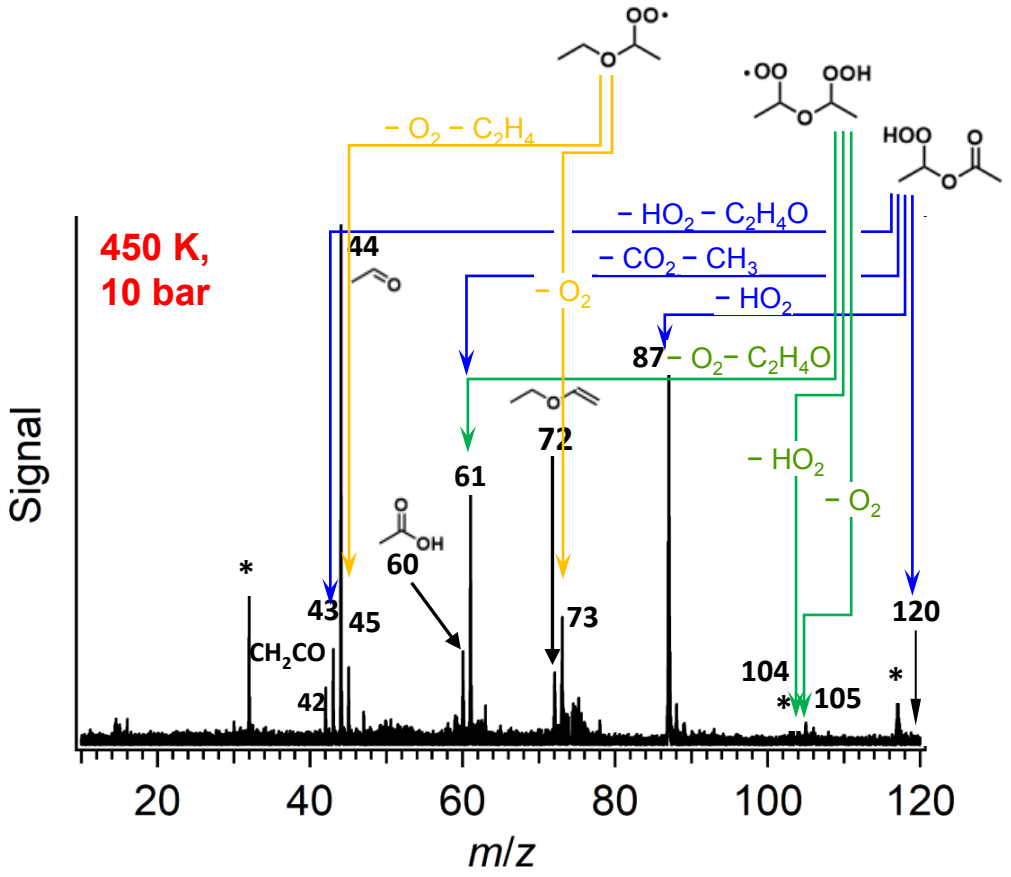
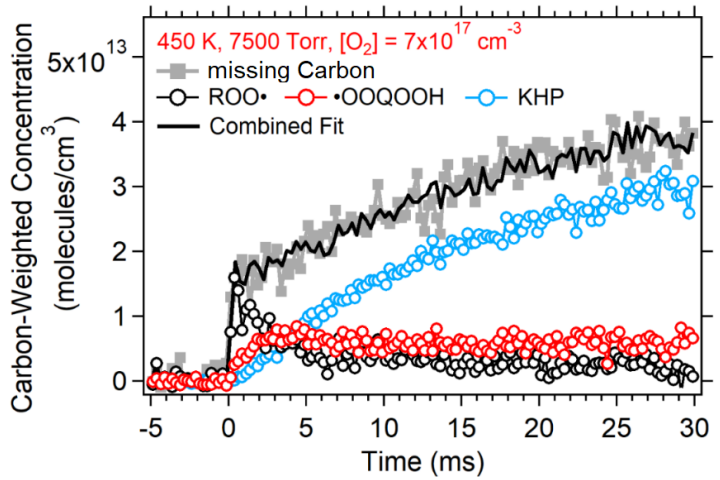
Diethyl ether – prototypical small linear ether



Demireva *et al.*, *PCCP*, 22 (2020), 24649



Maria Demireva



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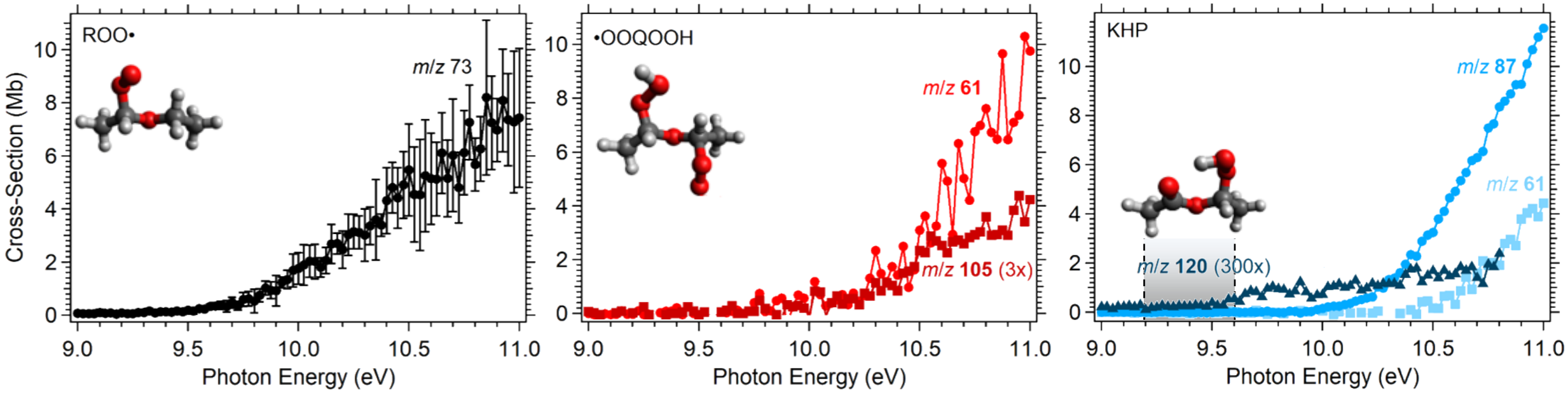
Diethyl ether – prototypical small linear ether

Experimental quantification ⟶ absolute PI cross-sections for ROO, OOQOOH, KHP



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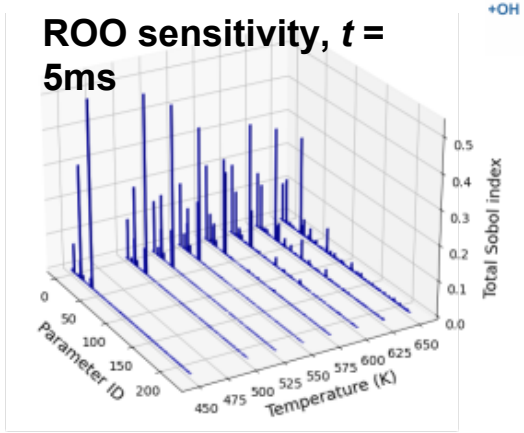
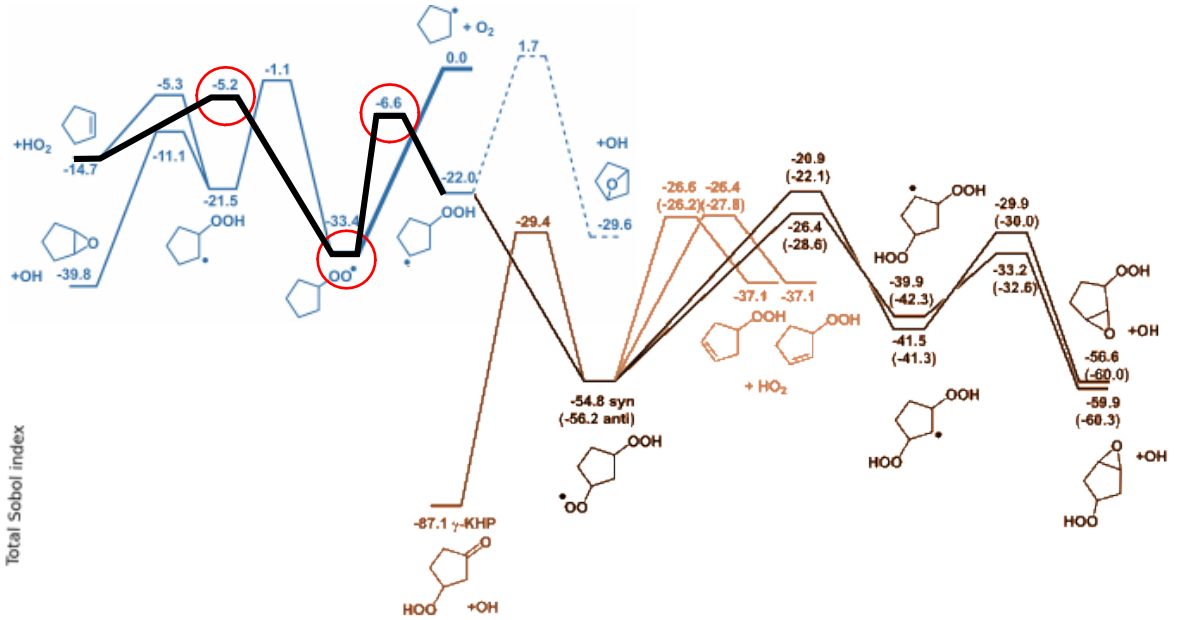
back to cyclopentane – Master Equation model optimization

Modeling and mechanism construction

- Master equation for primary reactions
- ME parameters: energies, vibrational frequencies, hindered rotors, energy transfer
- only 6 out of 223 parameters are highly sensitive at T < 600K:
  - ROO ⟶ cy-C_5H_8 + HO_2
  - ROO ⟶ γ-QOOH





Genetic algorithm optimization

- Monte Carlo parameter sampling
- Well energies ± 0.5 kcal/mol; barriers ± 1 kcal/mol; frequencies ± 5%; tunneling ± 20%
- Master Equation sub-mechanism embedded in comprehensive cyclopentane mech. (LLNL + NUIG, *Comb. Flame*, 225 (2021), 255)

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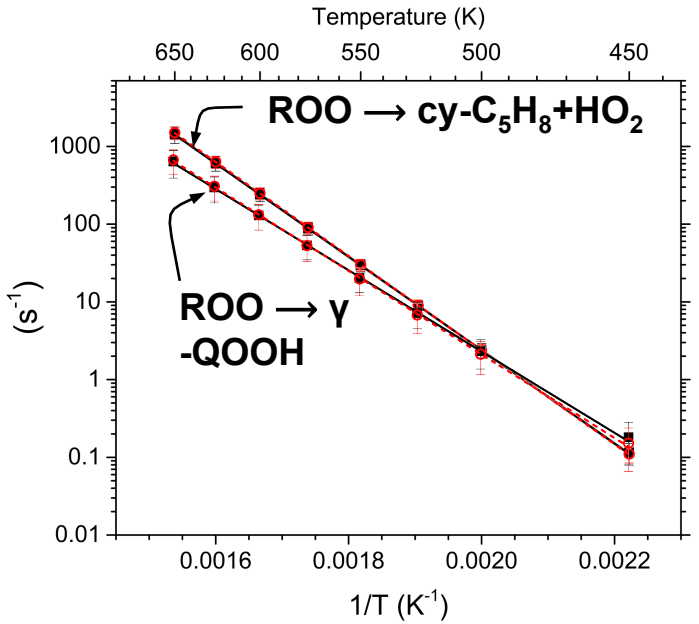
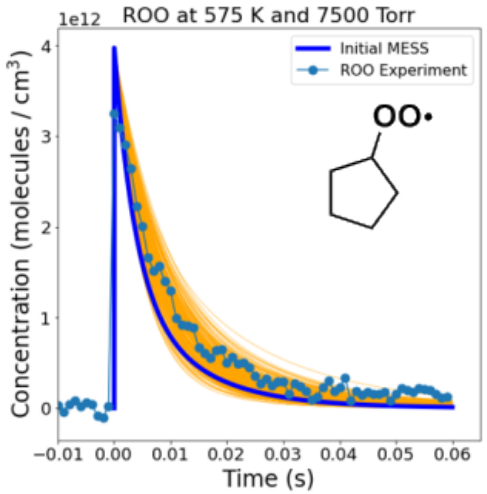
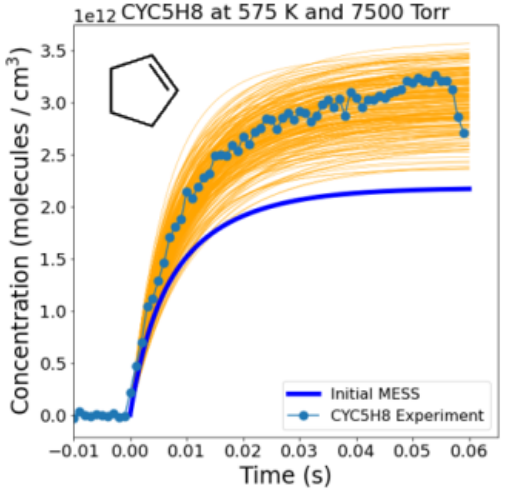
back to cyclopentane – Master Equation model optimization

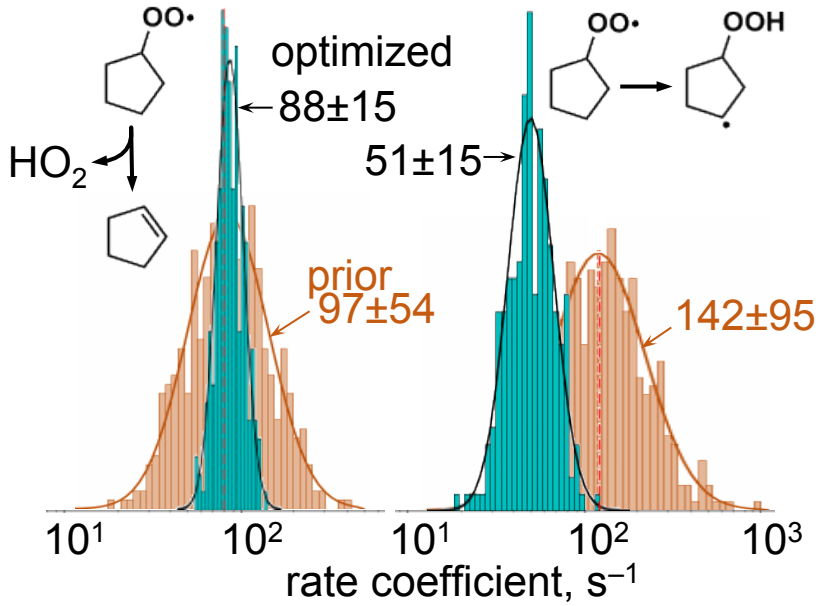
Genetic algorithm optimization

- 500 model realizations per generation
- Model predictions comparison with time-resolved experiments for cy-C_5H_{10}, ROO, OOQOOH, cy-C_5H_8
- Simultaneous comparison at T = 450 – 575 K









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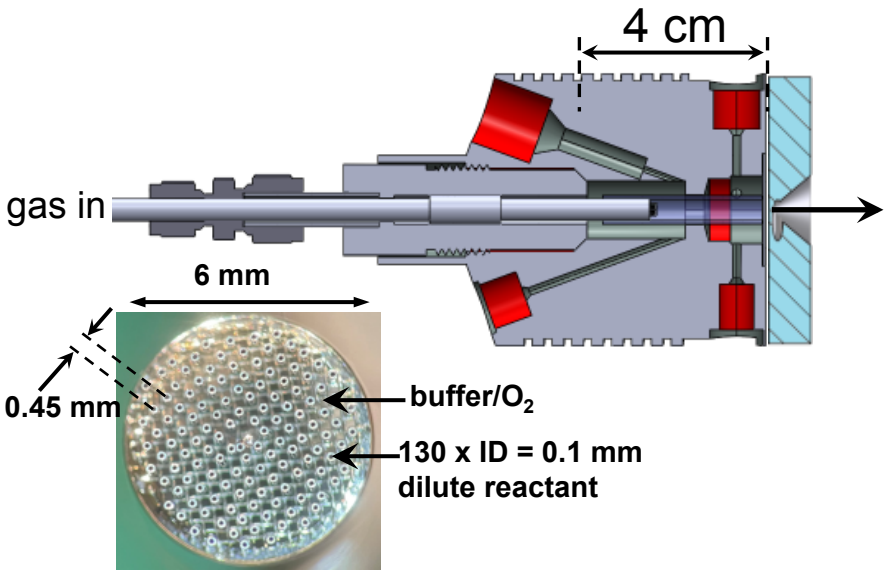
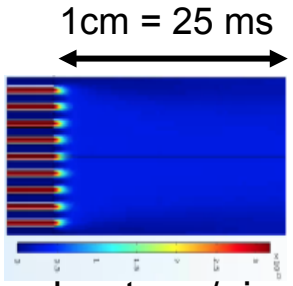
Outlook: complementary reactors, probe methods

High-Pressure Laminar Flow Reactor

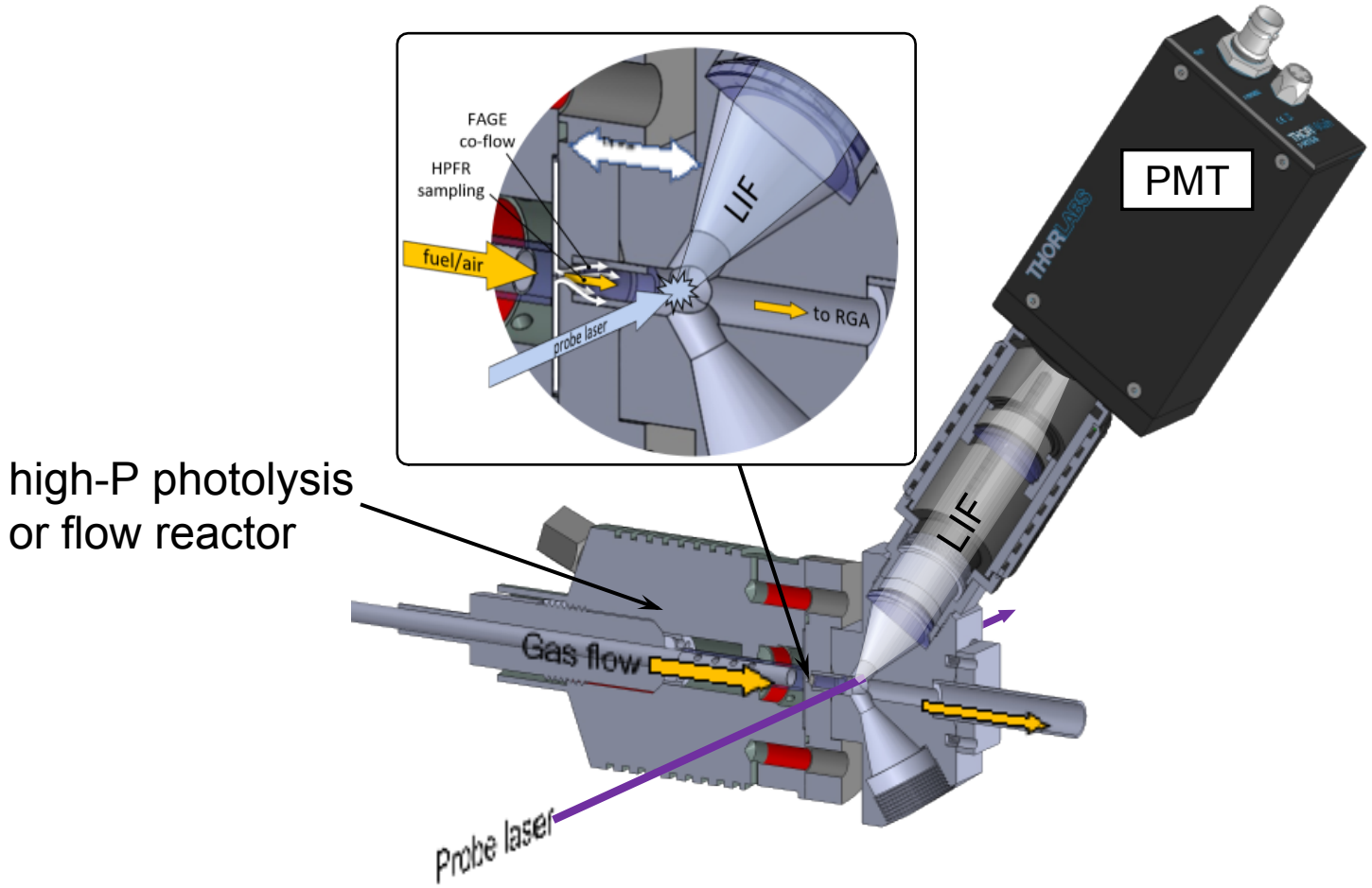




n-heptane/air,
10 bar, 600K

- up to 100 bar, 1000 K
- thermal initiation
- residence times 0 – 2 s with < 10 μs resolution

Quantitative OH, HO_2 detection *via* high-P FAGE



Fluorescence **A**ssay by **G**as **E**xpansion

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Conclusions

New highly sensitive time-resolved SVUV-PIMS setup

- Homogeneous, 0-D high-pressure laser photolysis reactor
- High-density ionization scheme
- Detection of radicals and reactive intermediates

Experimental quantification from time-resolved C atom balance

- Absolute concentration-time histories
- PI cross-sections for detection in more complex reactions
- Approaches the accuracy of stable, commercially available compounds

Coupling of detailed chemical speciation to theory and modeling

- ME model optimization of cyclopentane low-T oxidation
- Near-term plans: combine with time-resolved OH, HO_2 measurements *via* FAGE/LIF
- Combine with complementary experiments (JSR, possibly others)

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Thank you!

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