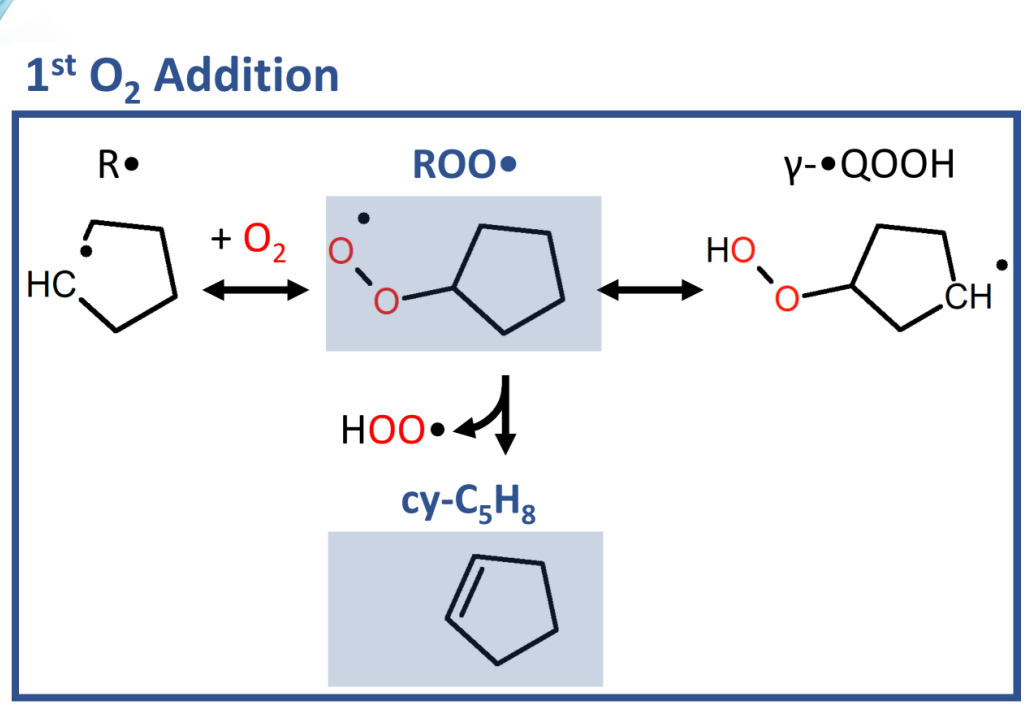
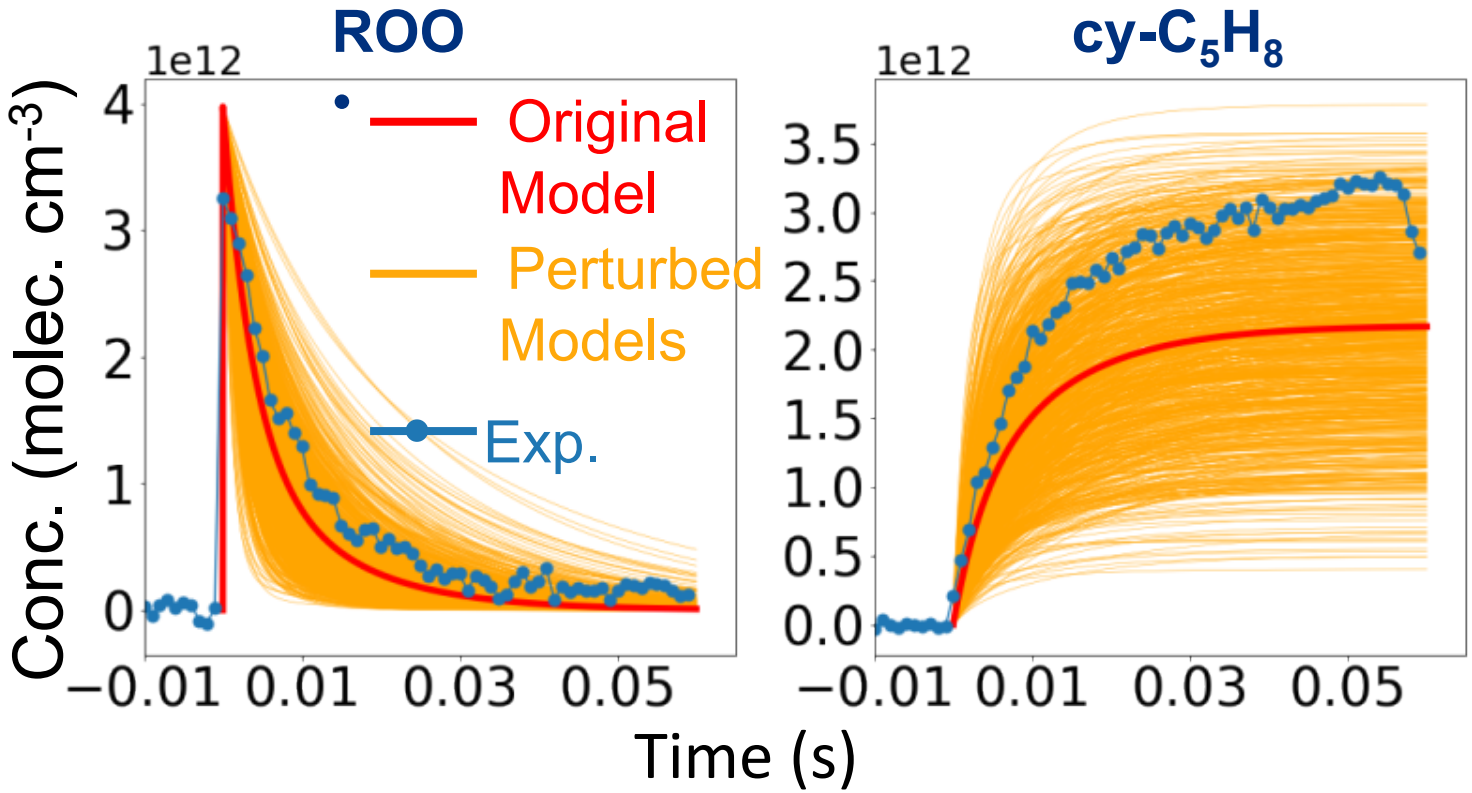
SAND2022-7518C

A Low-Temperature Cyclopentane Oxidation Kinetics Model:

Optimization of A Theory-Based Sub-Mechanism Against Experiment





Maria Demireva, James Oreluk, Amanda L. Dewyer, Judit Zádor, and Leonid Sheps

Sandia National Laboratories, Livermore, CA, USA

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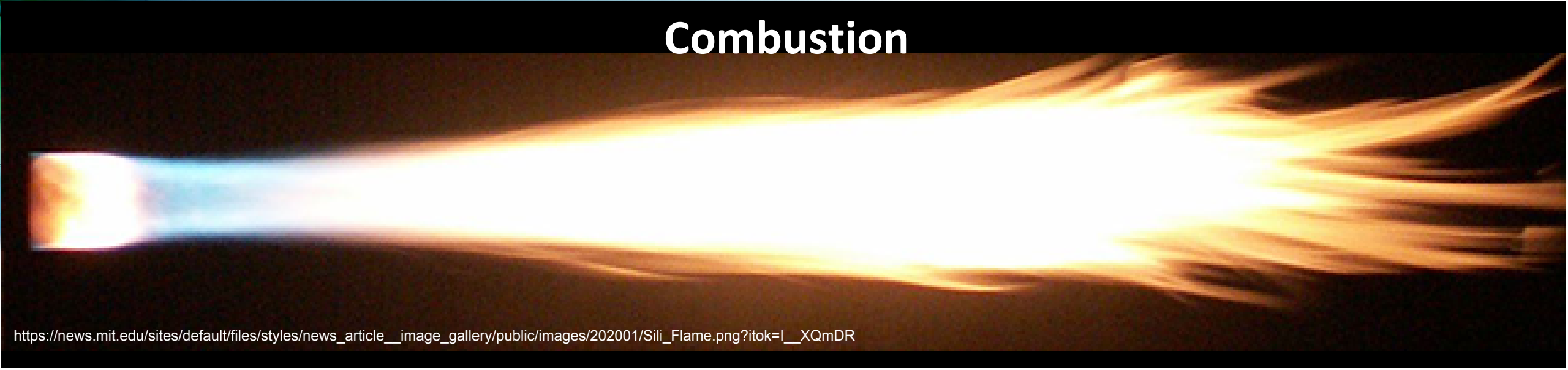
Combustion



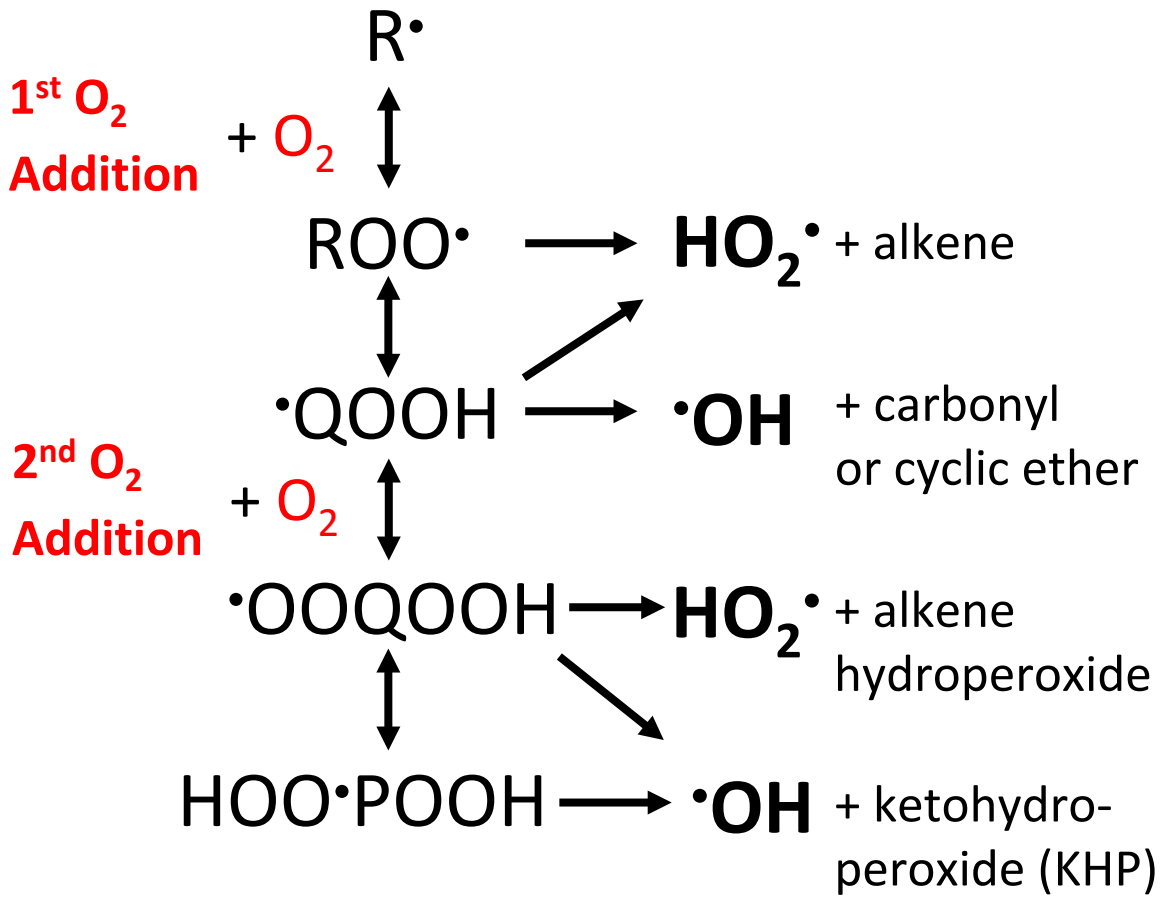
https://news.mit.edu/sites/default/files/styles/news_article__image_gallery/public/images/202001/Sili_Flame.png?itok=I__XQmDR

- Major motivation for combustion research is to develop advanced fuels and technologies that improve engine efficiencies and lower pollutant emissions.
- Low-temperature (LT) combustion engines are one recent promising innovation.
  - Aim to convert fuel at sufficiently low temperatures to avoid soot and nitrogen oxide formation, while increasing thermal efficiency.
- Accurate models of LT chemistry can help predict fuel properties and advance applications.

Low-Temperature (Below ~1000 K) Combustion

Hydrocarbon fuel: RH

Initiation: $\bullet OH + RH \leftrightarrow R\bullet + H_2O$



Low-Temperature (Below ~1000 K) Combustion

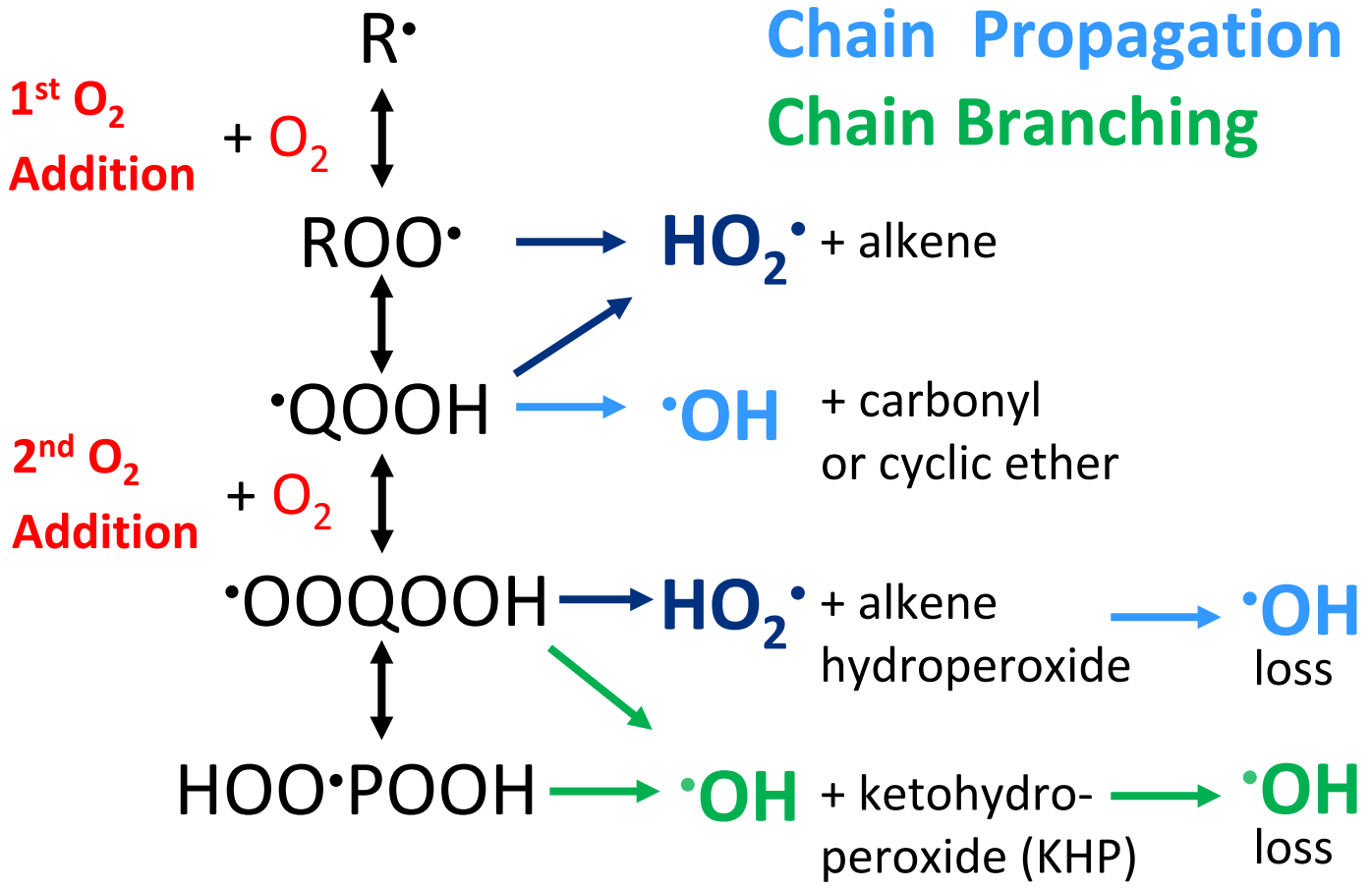
Hydrocarbon fuel: RH

Recycling: $\cdot OH + RH \leftrightarrow R\cdot + H_2O$

Chain Inhibition

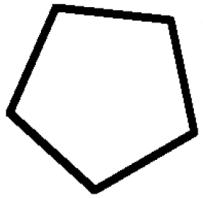
Chain Propagation

Chain Branching



Cyclopentane (CPT) Oxidation

Cyclopentane (CPT)



Simple model system:

- Exhibits typical alkane oxidation pathways.
- Symmetrical structure results in single initial isomer.
- Reactivity dominated by chain inhibition.
- Intermediates and products have been quantified.

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Hydrocarbon fuel: RH

Recycling: $\cdot OH + RH \leftrightarrow R\cdot + H_2O$

Chain Inhibition

Chain Propagation

Chain Branching

$R\cdot$

1st O_2 Addition $+ O_2$

$ROO\cdot \rightarrow HO_2\cdot$ + alkene

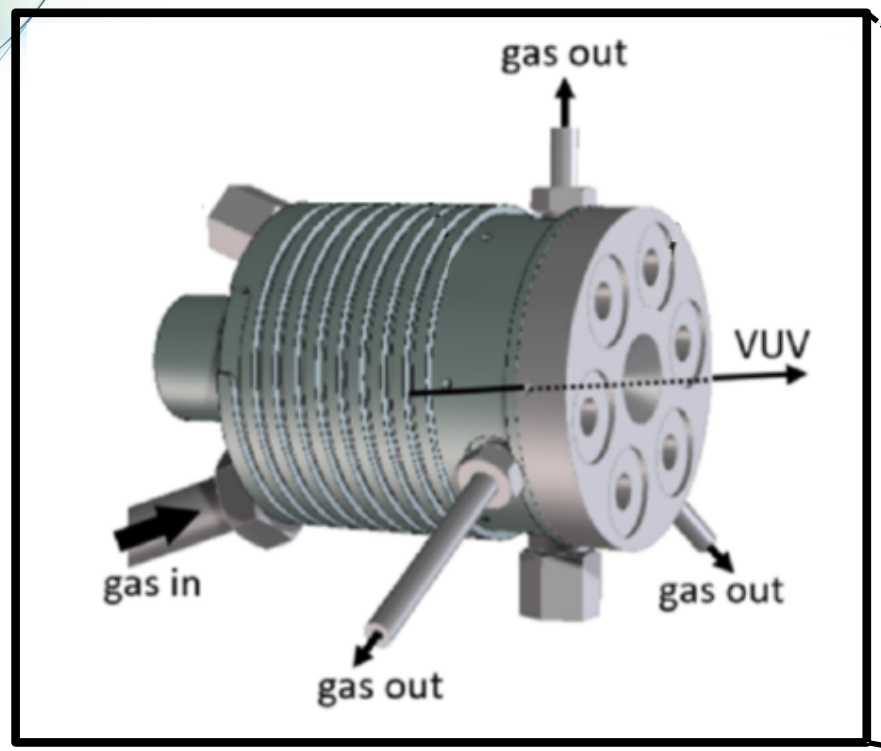
$\cdot QOOH \rightarrow \cdot OH$ + carbonyl or cyclic ether

2nd O_2 Addition $+ O_2$

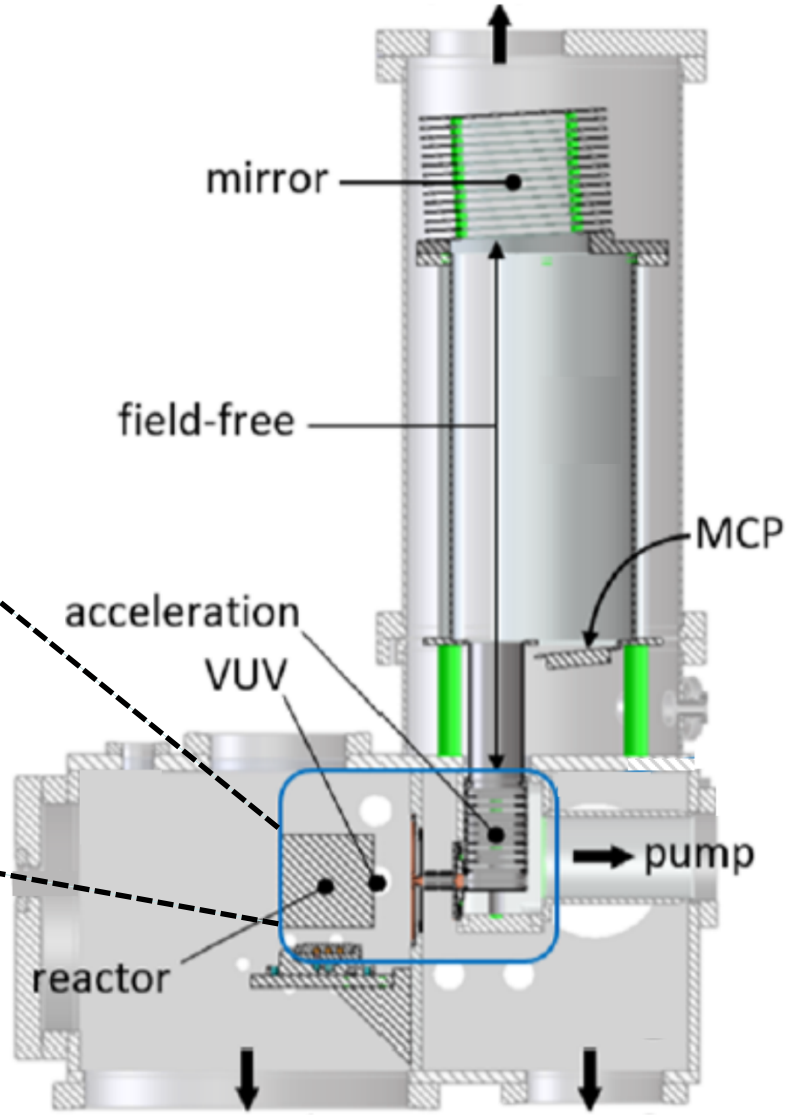
$\cdot OOQOOH \rightarrow HO_2\cdot$ + alkene hydroperoxide $\rightarrow \cdot OH$ loss

$HOO\cdot POOH \rightarrow \cdot OH$ + ketohydro-peroxide (KHP) $\rightarrow \cdot OH$ loss

Multiplexed Photoionization Mass Spectrometry (MPIMS)

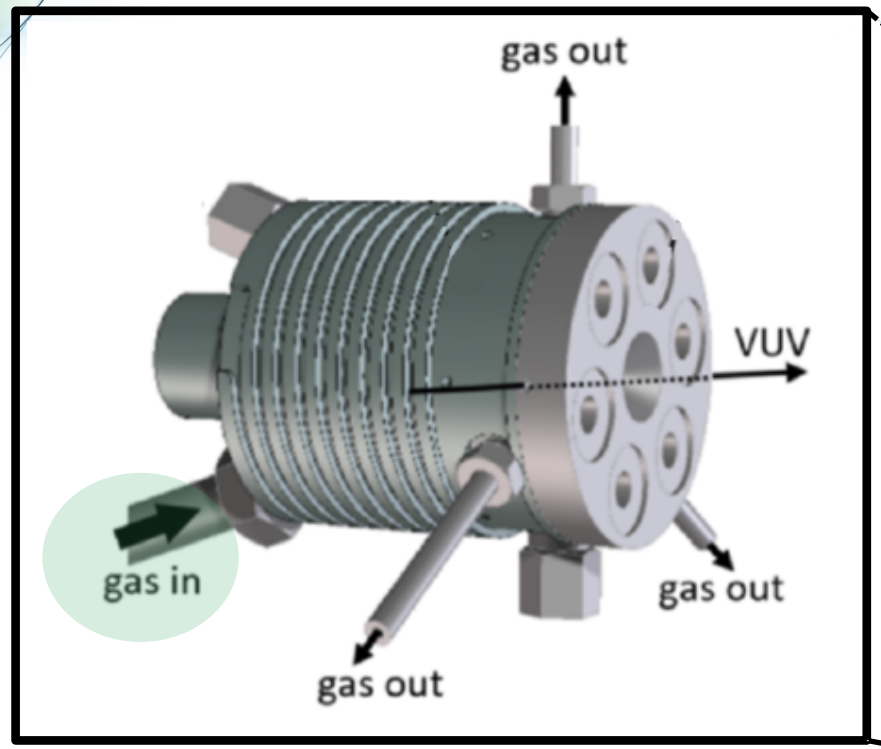


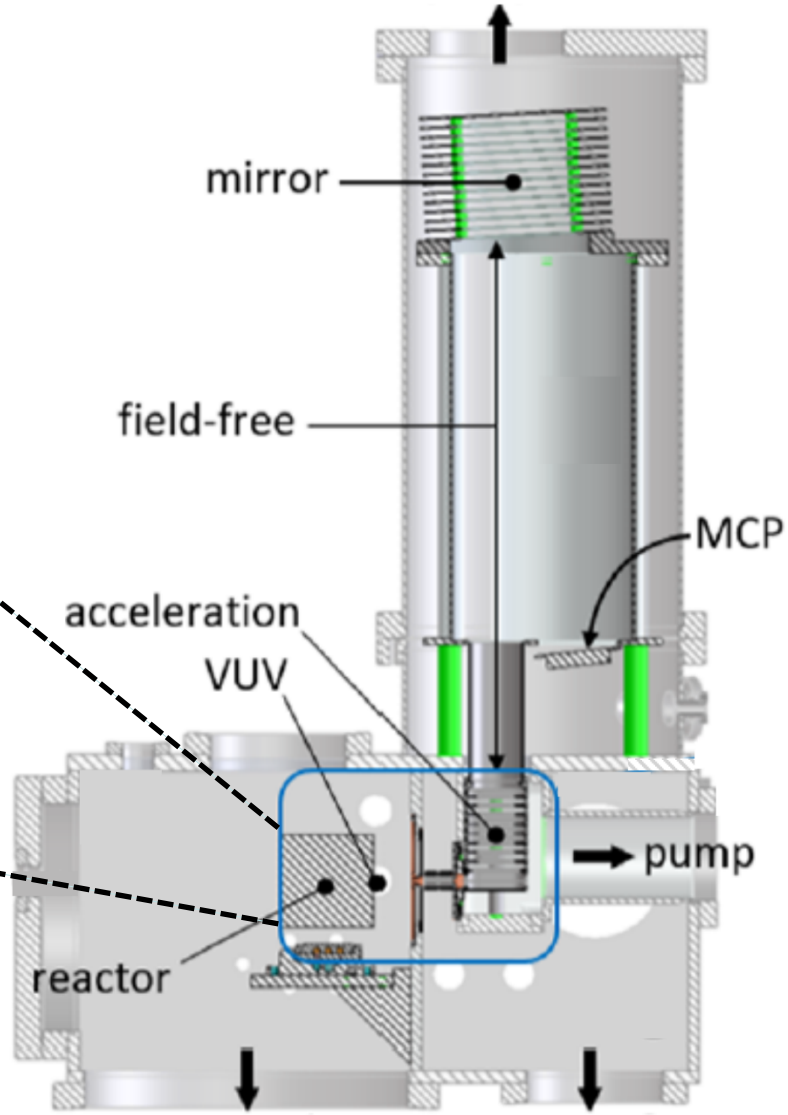
High-pressure photolysis reactor.



Sheps, Antonov, Au *JPCA*, **2019**, *123*, 10804.

Multiplexed Photoionization Mass Spectrometry (MPIMS)





Pressure: 7500 Torr, T: 450-650 K

CPT (cm^{-3}): 1×10^{14}

O_2 (cm^{-3}): 3×10^{19}

Cl_2 (cm^{-3}): 8.9×10^{14}

He (cm^{-3}): $(1.3 - 0.8)\times10^{20}$

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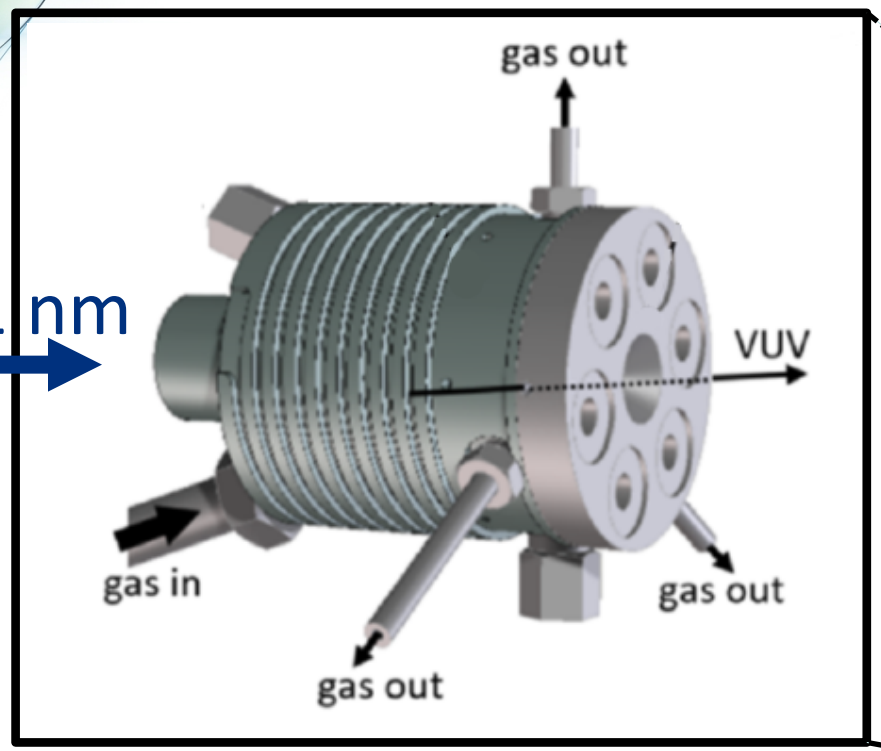
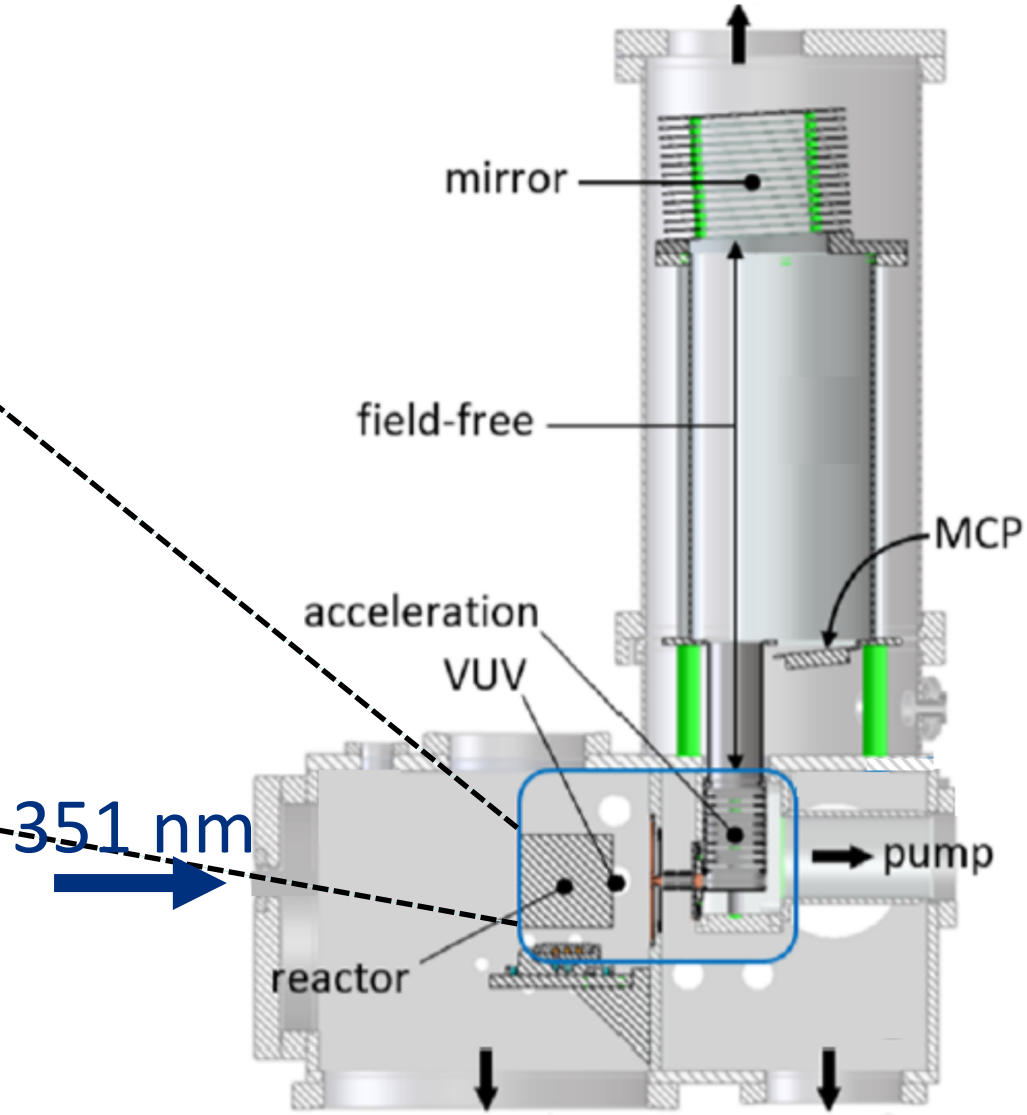
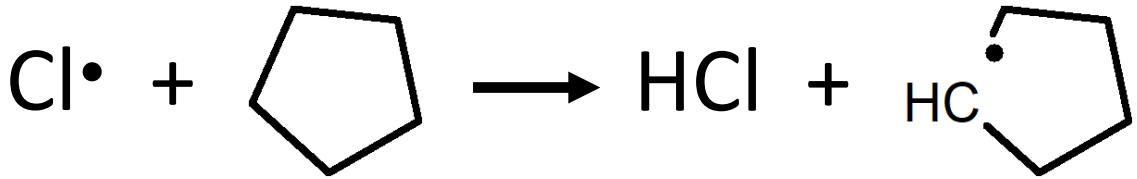
Multiplexed Photoionization Mass Spectrometry (MPIMS)





Photolysis at 351 nm of Cl_2 produces 2 Cl•, initiating H abstraction from CPT.



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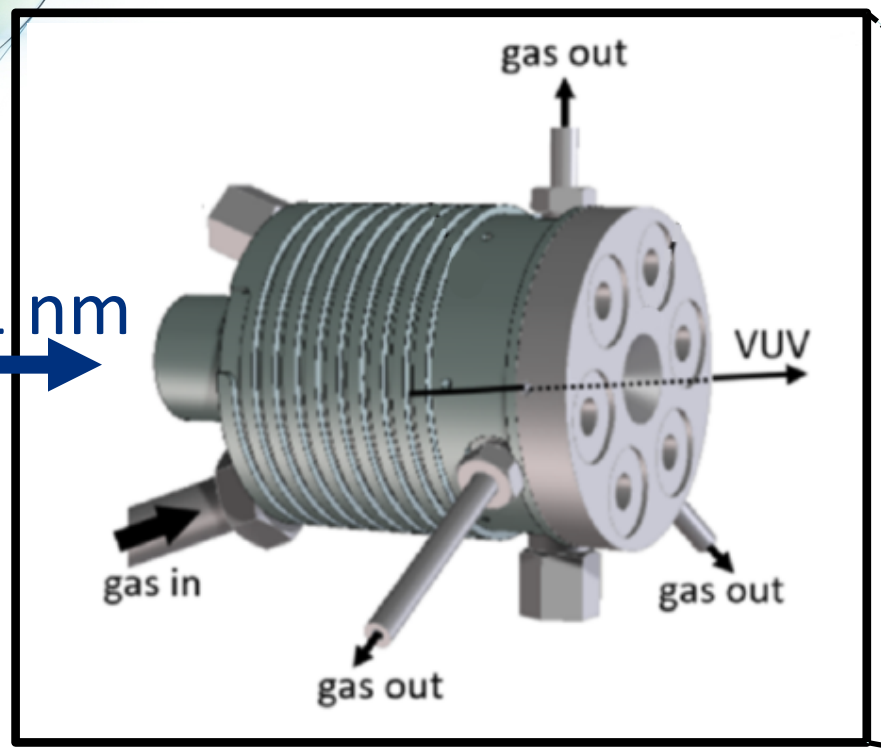
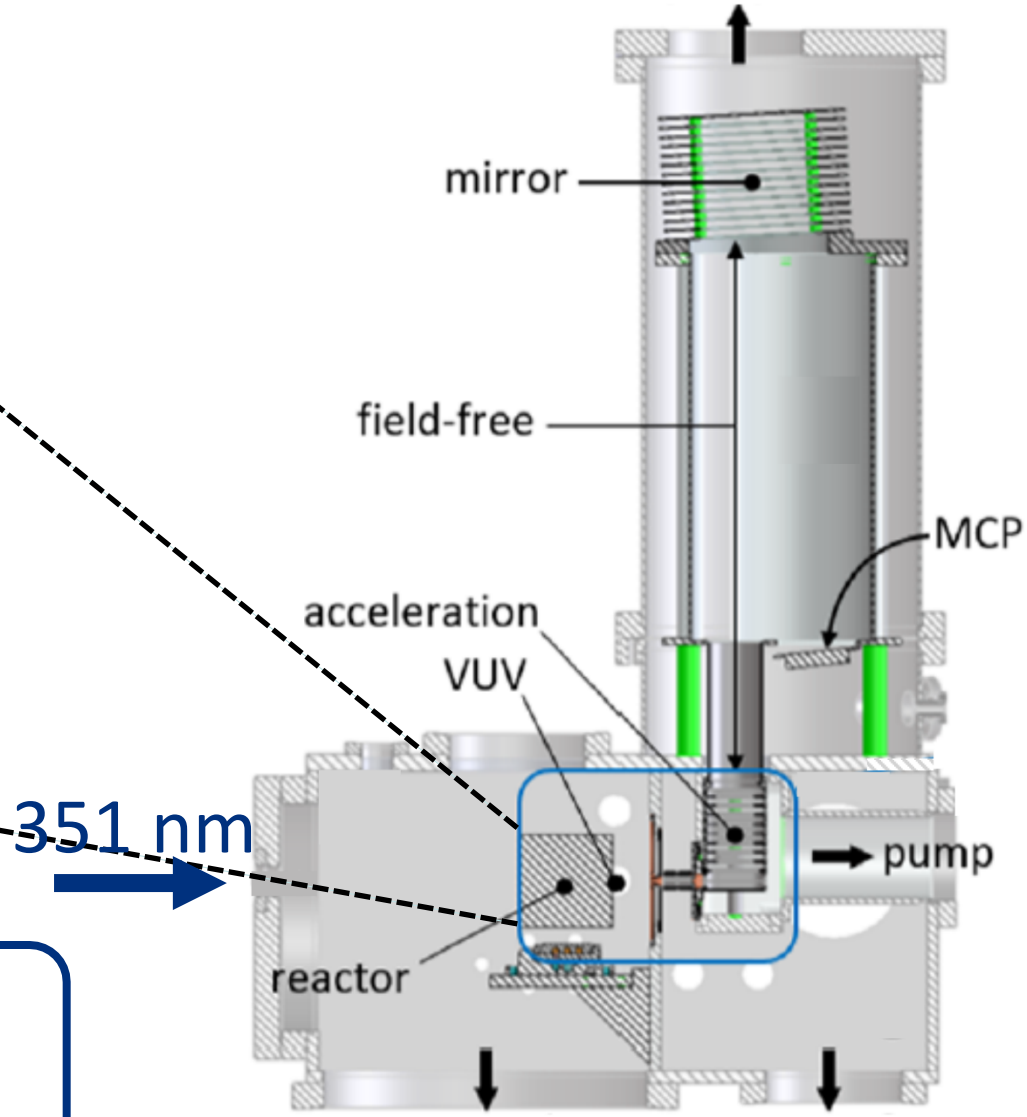
Multiplexed Photoionization Mass Spectrometry (MPIMS)





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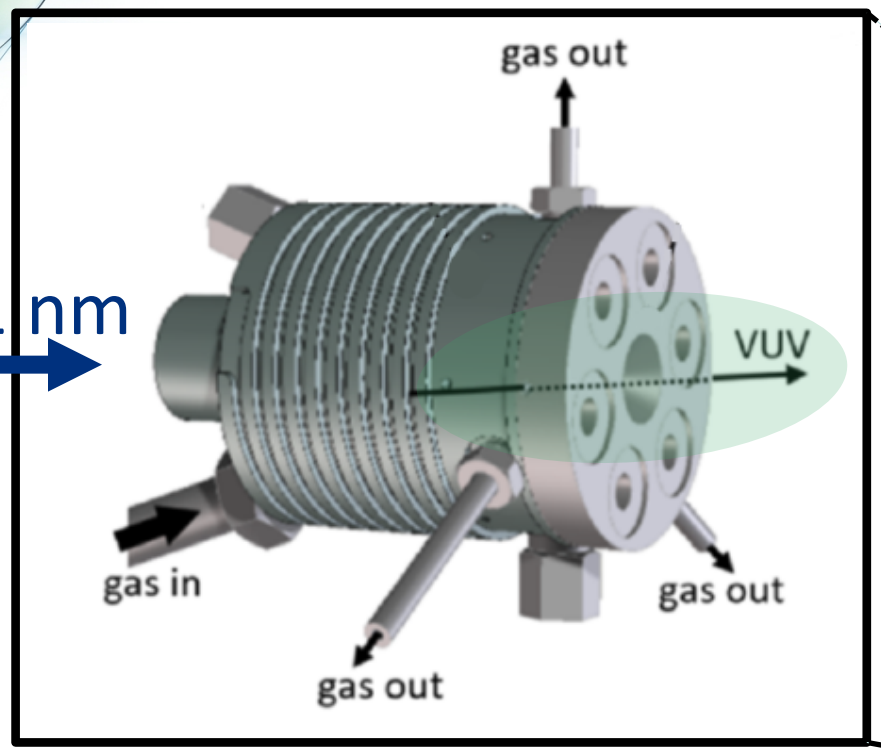
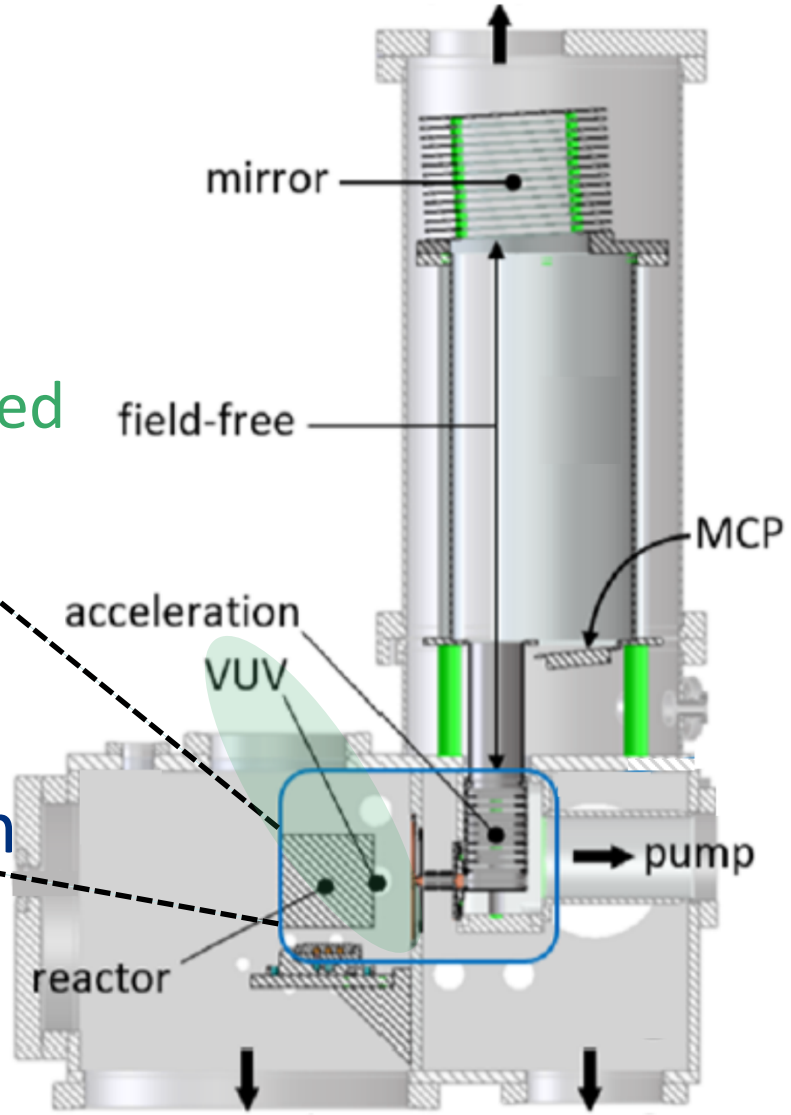
Multiplexed Photoionization Mass Spectrometry (MPIMS)



- Ionization of species with tunable vacuum ultraviolet (VUV) light from Berkeley Advanced Light Source.
- Detection with reflectron TOF-MS.



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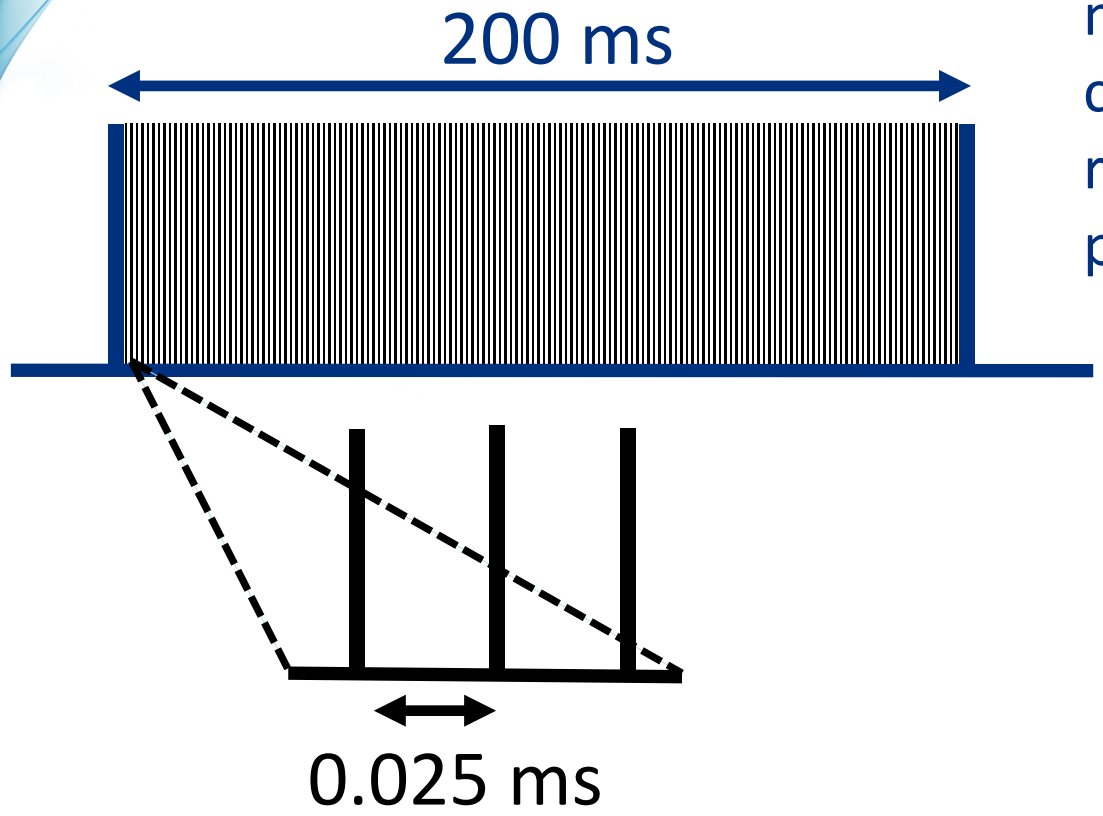
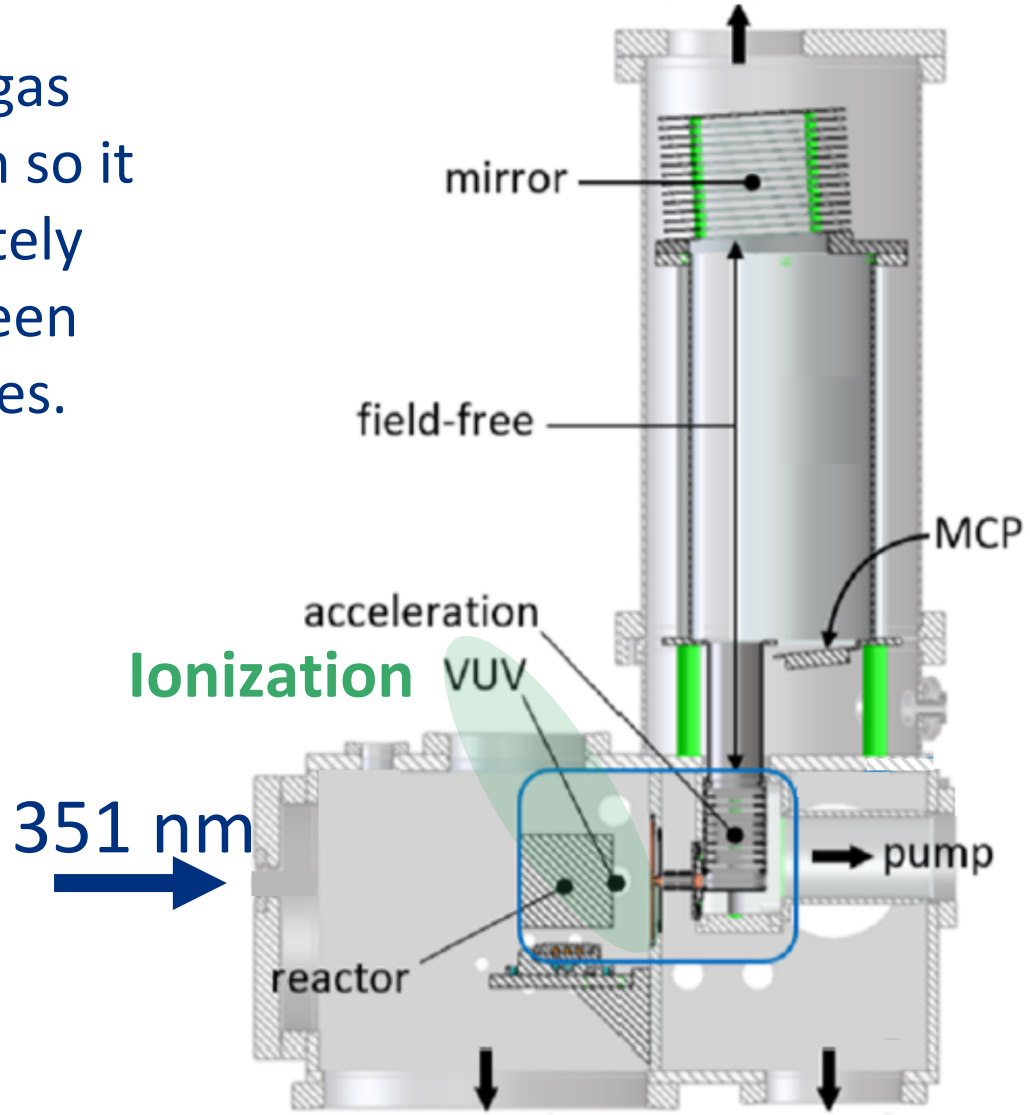
Time and Energy-Resolved Studies

351 nm Photolysis Laser: 5 Hz



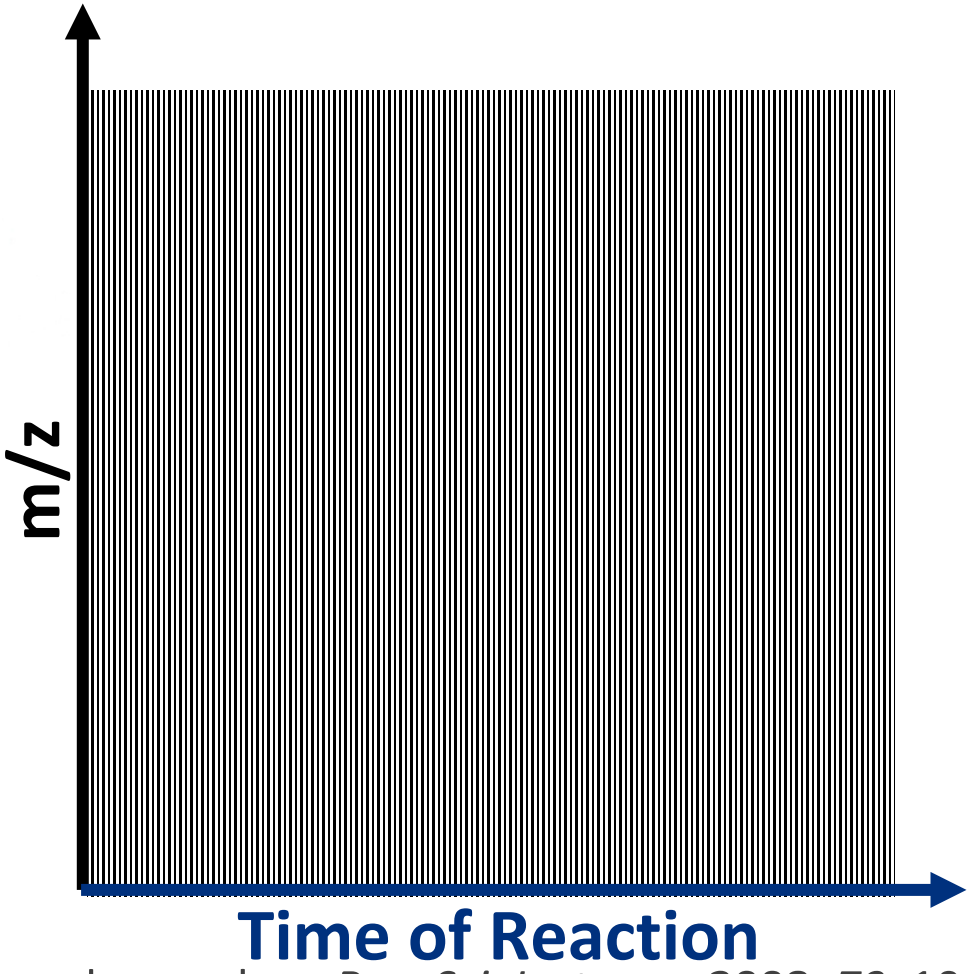
TOF Repetition Rate: 40 kHz

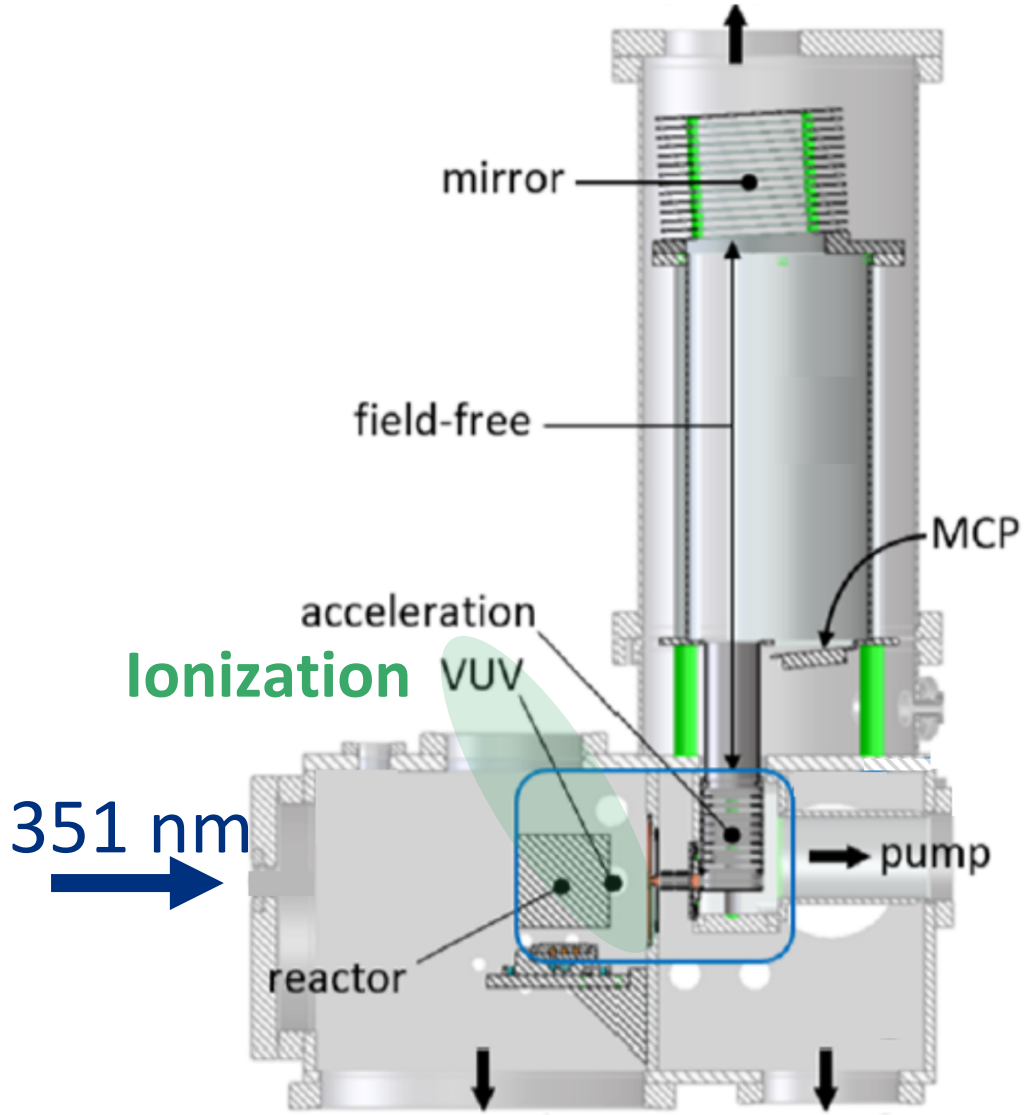
Flow speed of gas mixture chosen so it can be completely replaced between photolysis pulses.



Osborn, Taatjes, and coworkers *Rev. Sci. Instrum.*, **2008**, *79*, 104103.

Time and Energy-Resolved Studies





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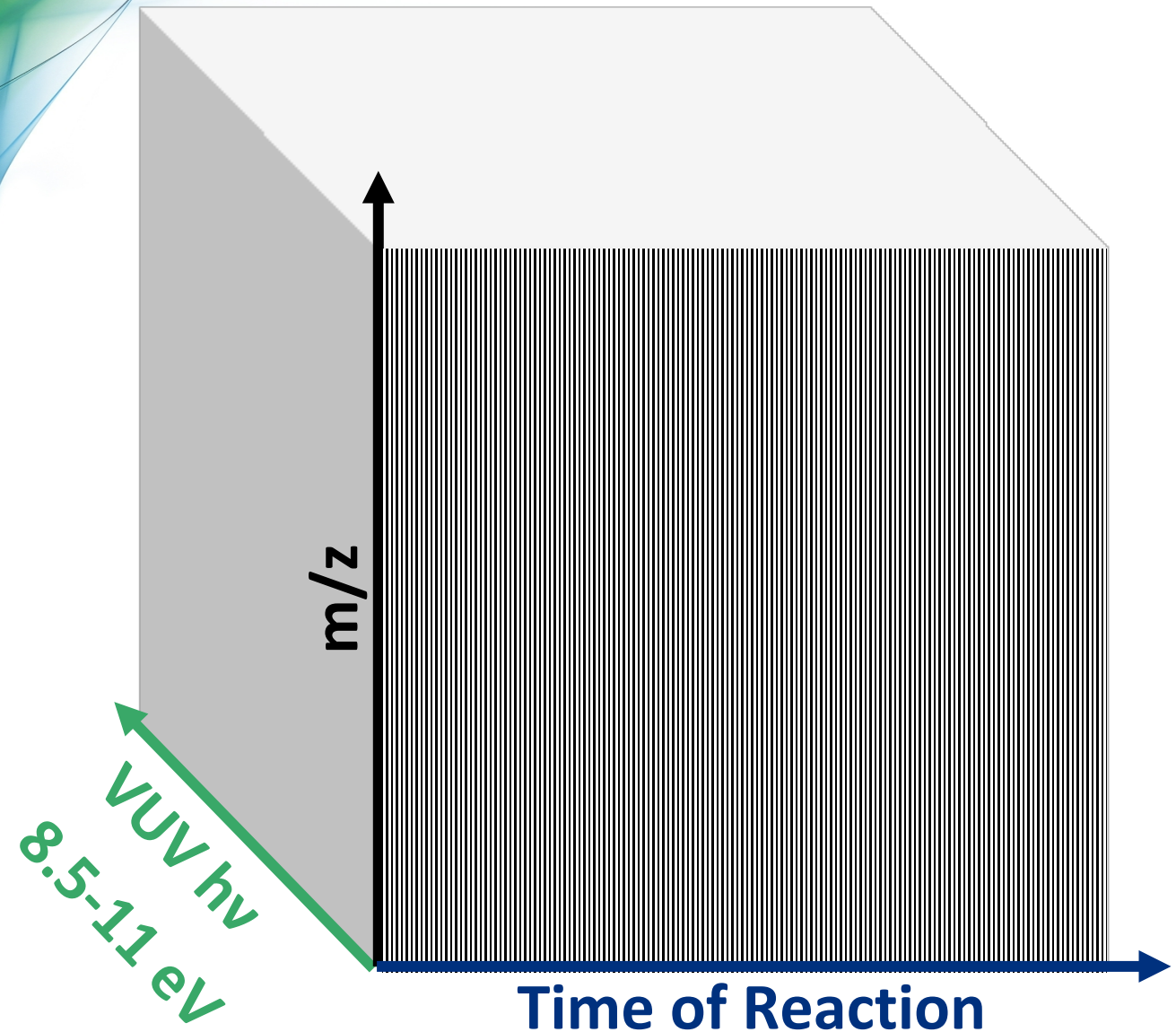
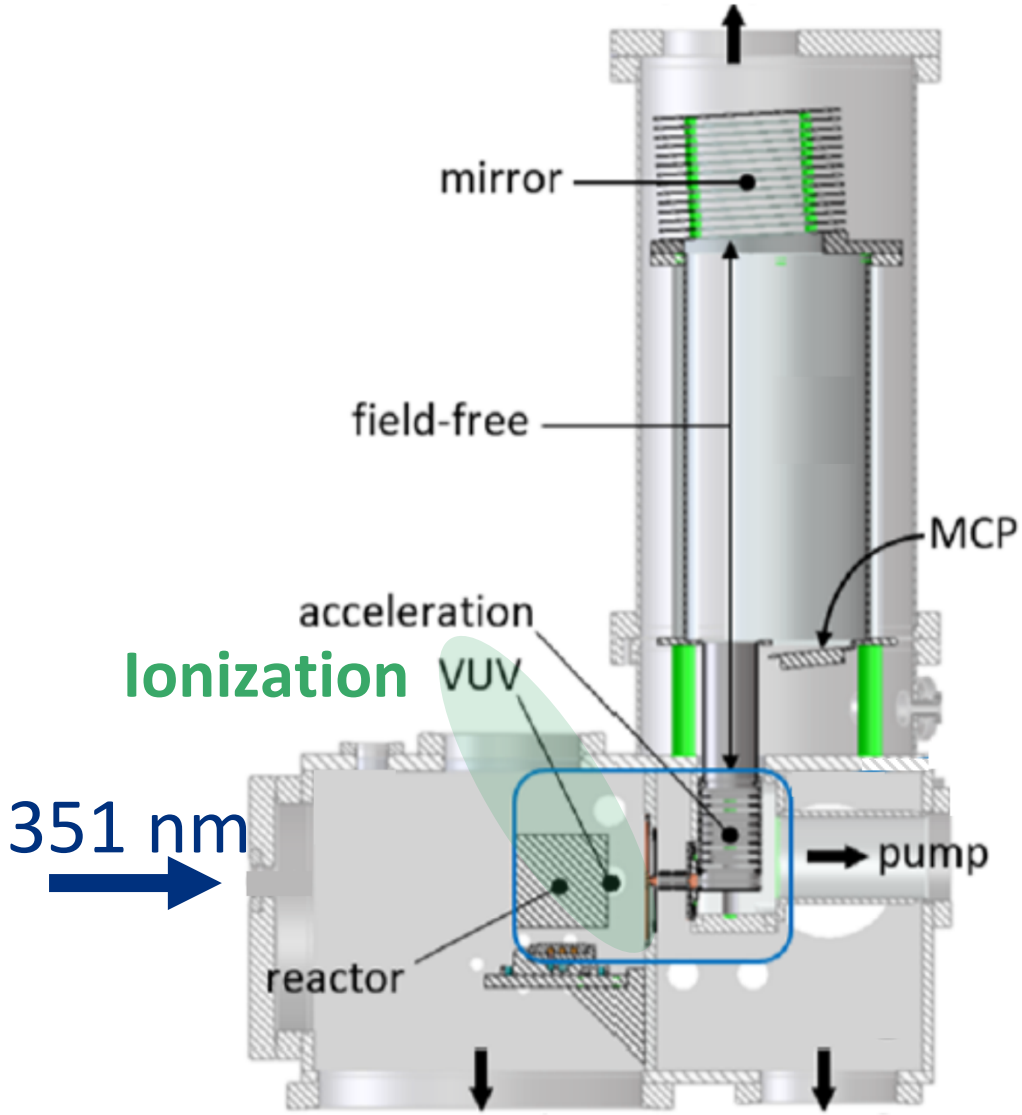
Time and Energy-Resolved Studies





Osborn, Taatjes, and coworkers *Rev. Sci. Instrum.*, **2008**, *79*, 104103.

Identification and Quantification Species

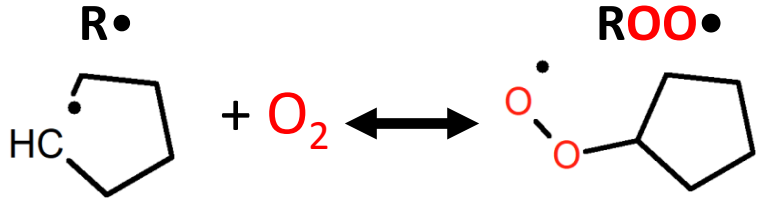
- Species identification from accurate mass and from photoionization thresholds by comparison with references and calculations.
- Species quantification:
  - Reference photoionization cross sections when available.
  - Quantification of remaining species from carbon balancing against fuel consumption from distinct time-behavior.

Demireva, Au, Sheps *PCCP* **2020**, *22,* 24649.
Sheps, Dewyer, Demireva, Zádor *JPCA* **2021**, *125*, 4467.

Potential Energy Surfaces (PESs) of CPT Sub-Mechanism

5 Separate PESs:

1st O_2: CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/6-311++G**



Amanda Dewyer and Judit Zádor

Sheps, Dewyer, Demireva, Zádor *JPCA* **2021**, *125*, 4467.

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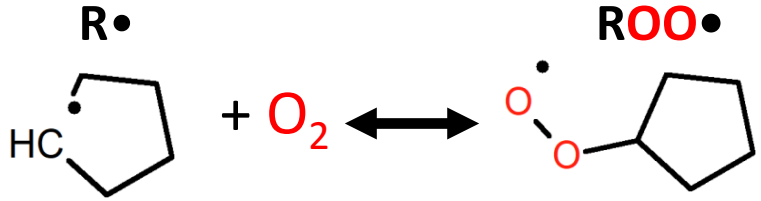
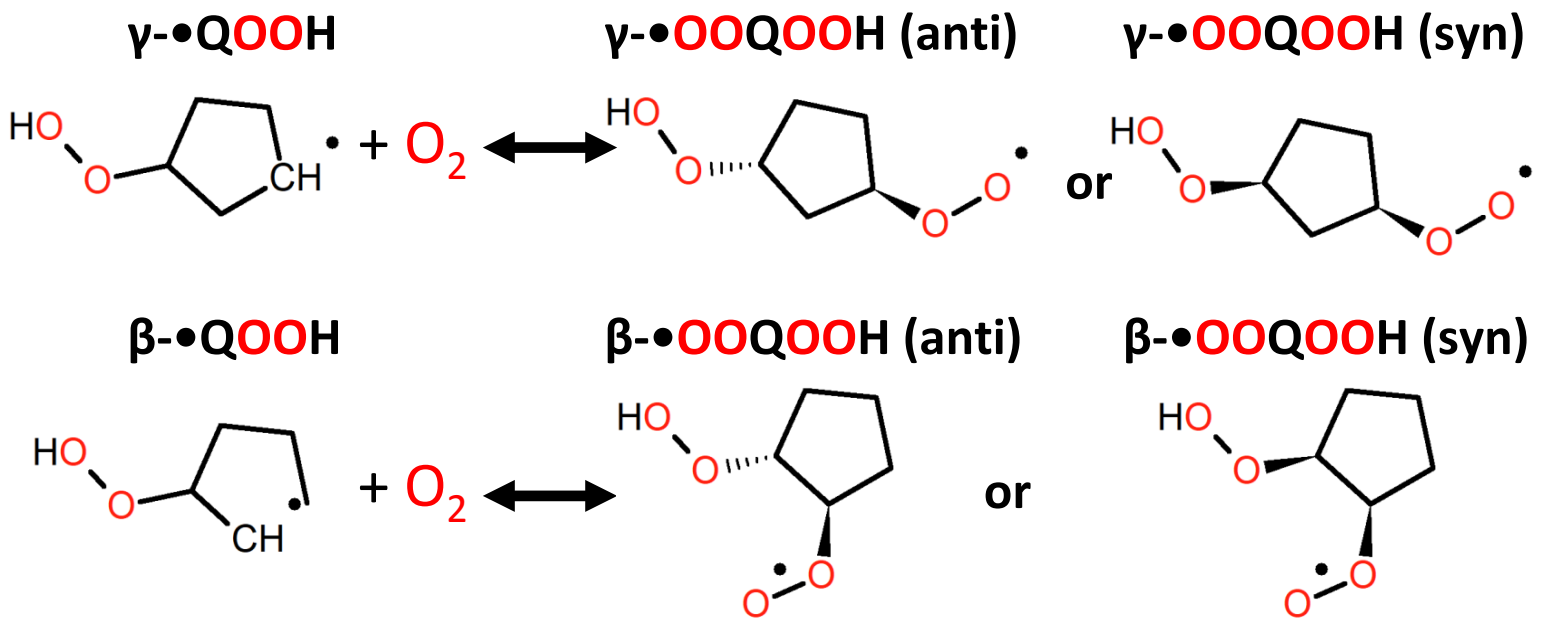


2nd O_2: CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/6-311++G**



Amanda Dewyer and Judit Zádor

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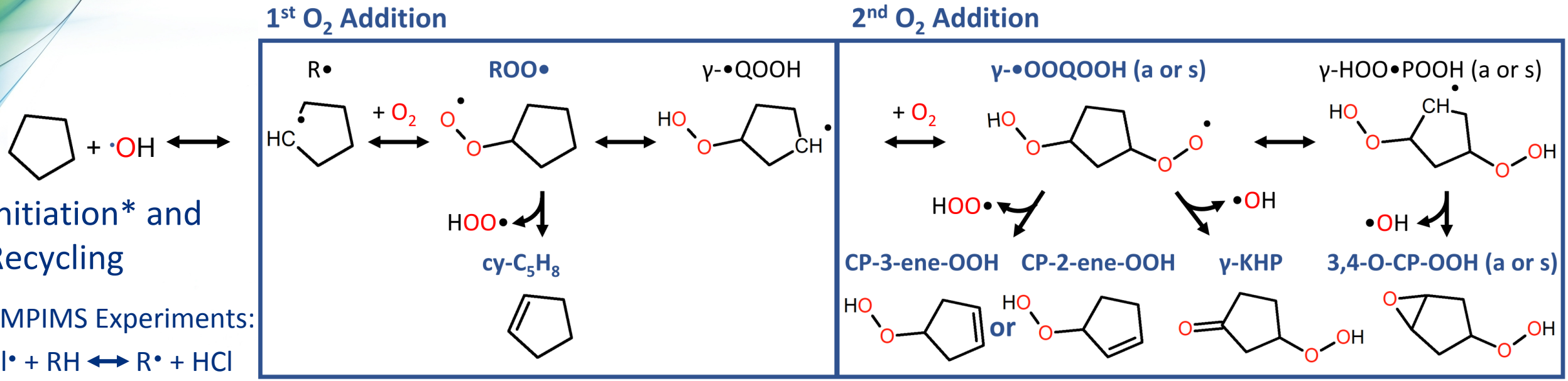
Dominant Pathways in Sub-Mechanism



Initiation* and Recycling

*MPIMS Experiments:

$Cl^{\bullet} + RH \leftrightarrow R^{\bullet} + HCl$

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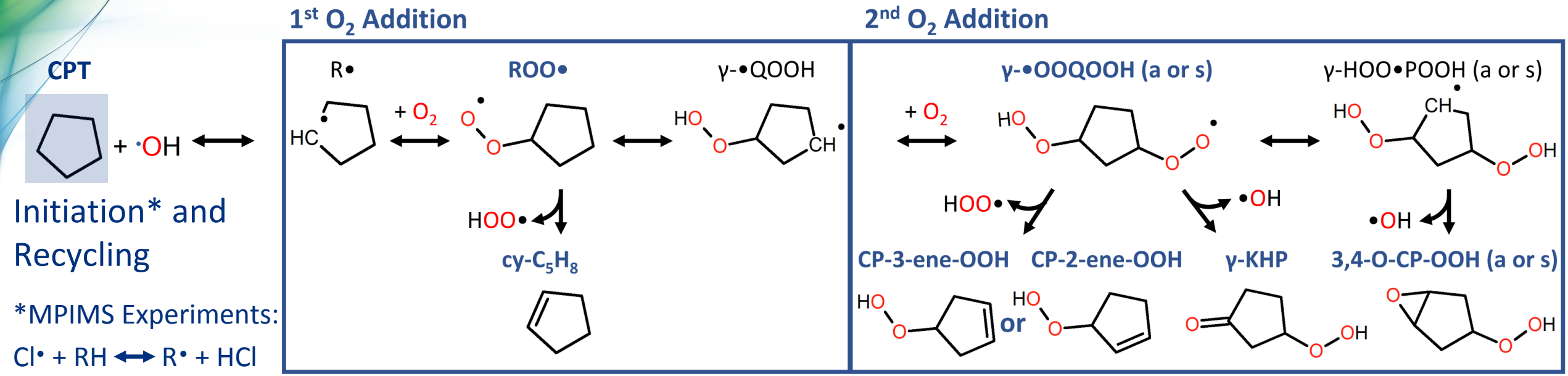
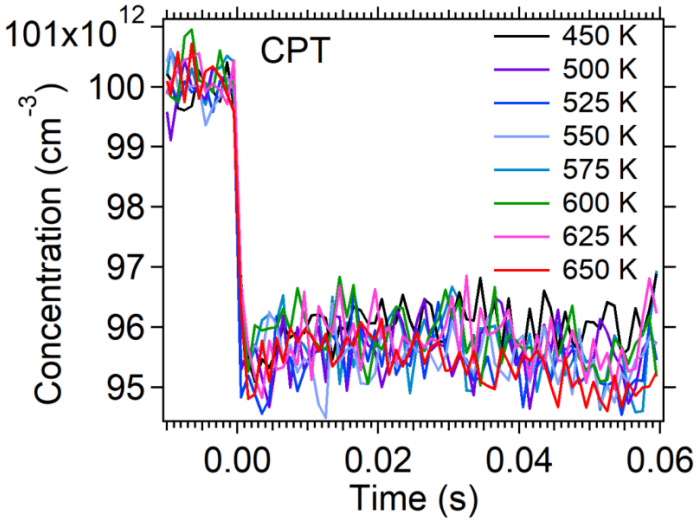
Dominant Pathways in Sub-Mechanism





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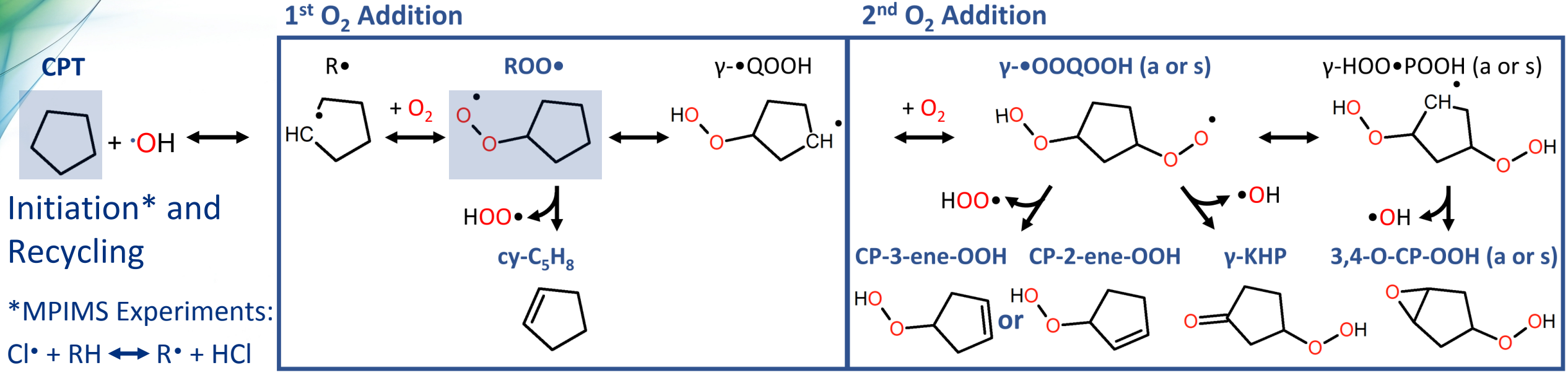

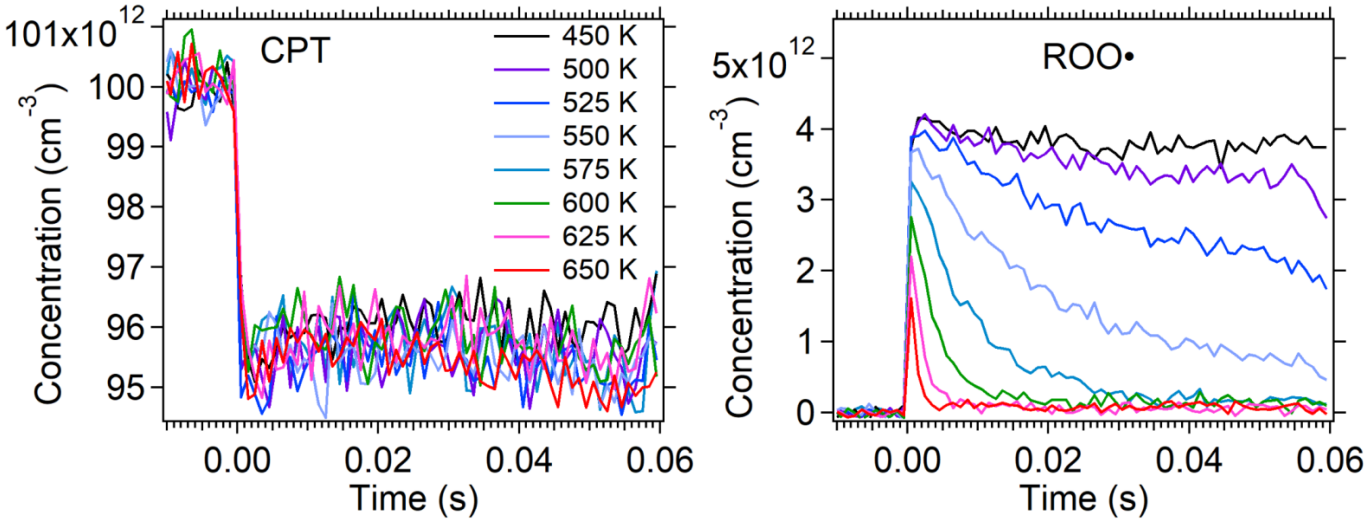

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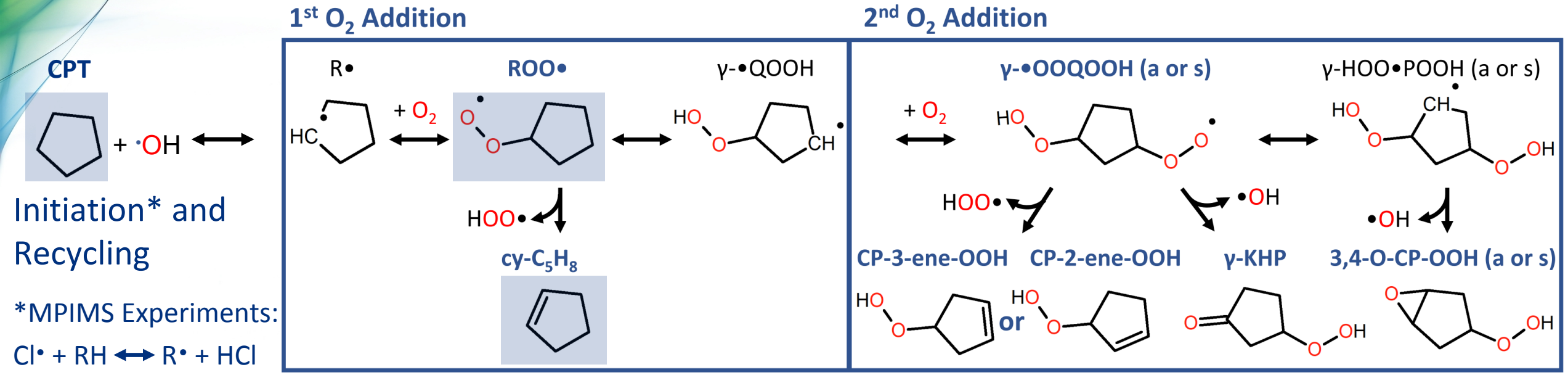
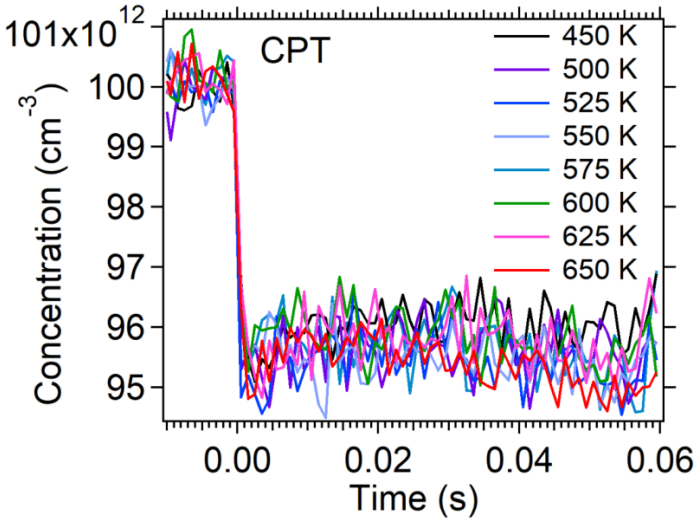
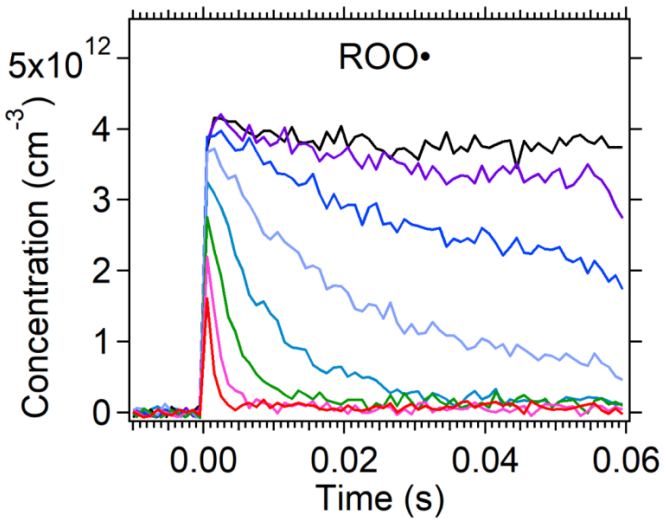
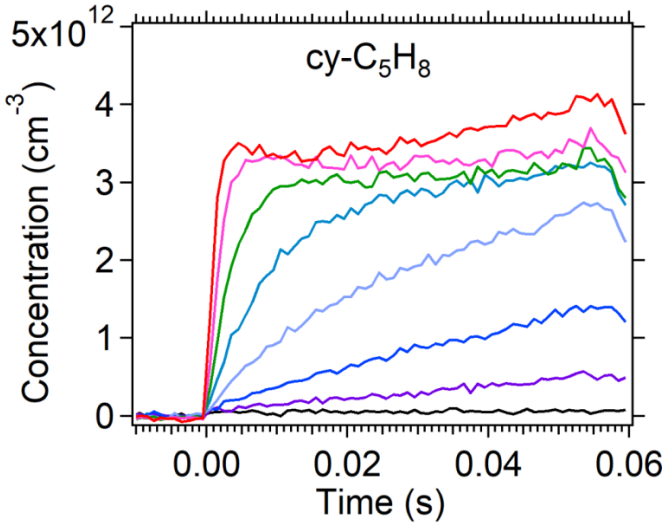
Dominant Pathways in Sub-Mechanism





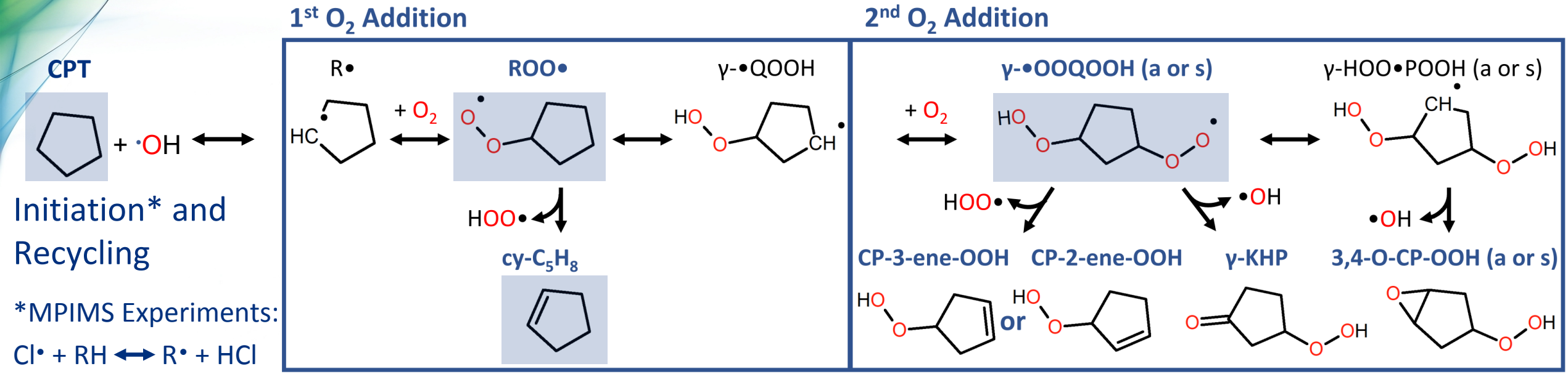


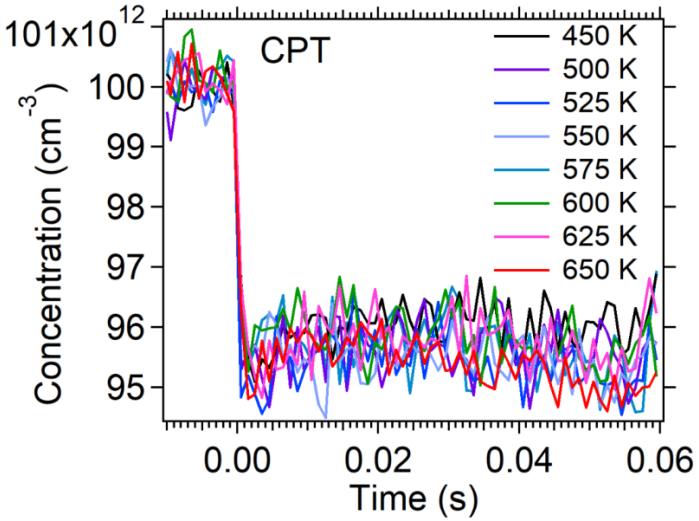


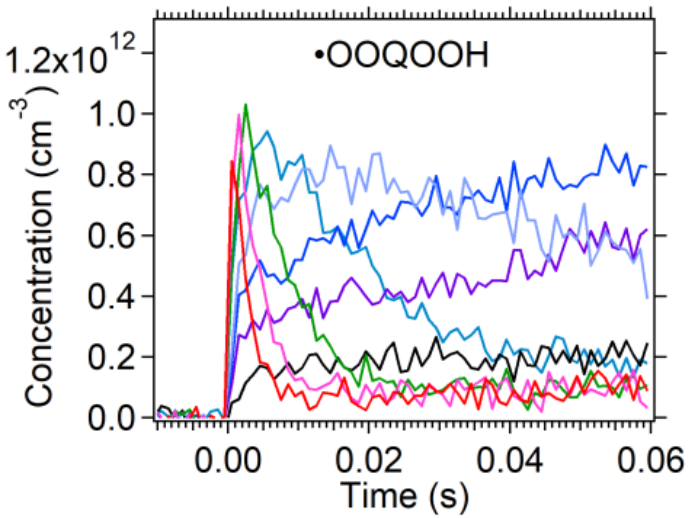
Primarily observe 1st O_2 addition species.

Sheps, Dewyer, Demireva, Zádor *JPCA* **2021**, *125*, 4467.

Dominant Pathways in Sub-Mechanism

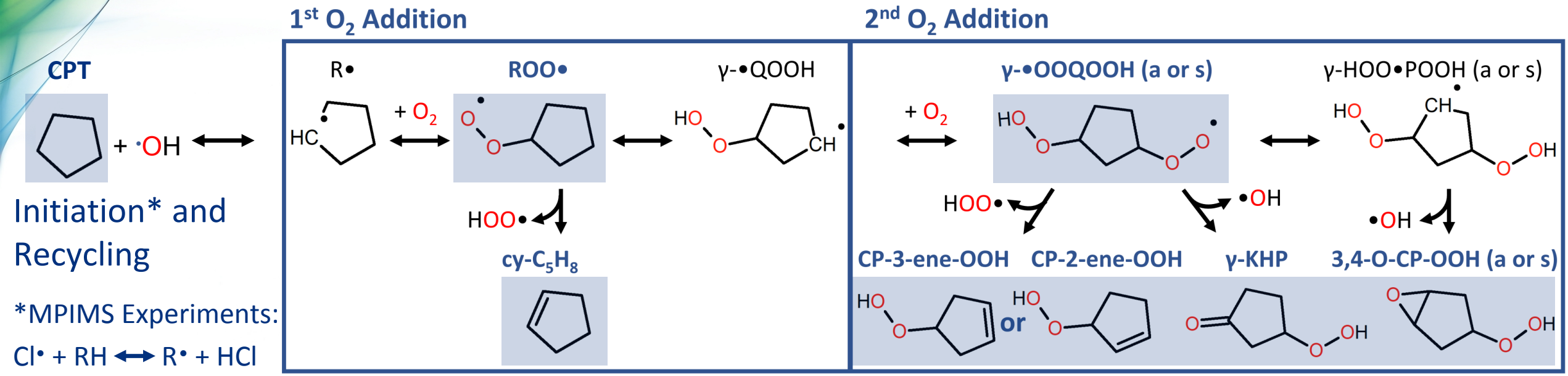


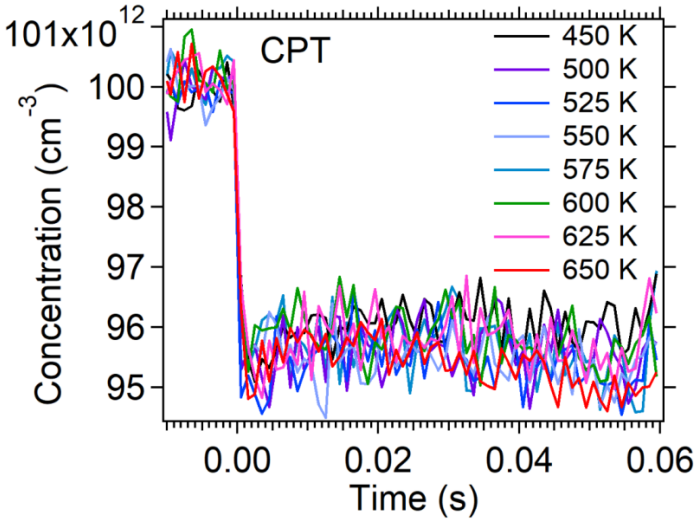


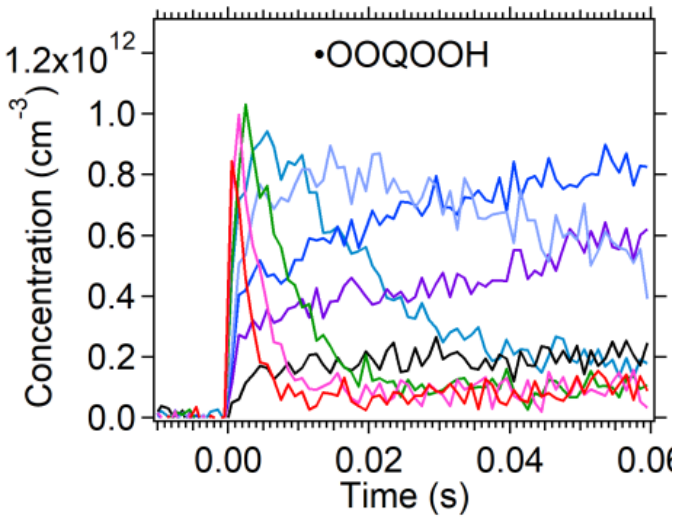


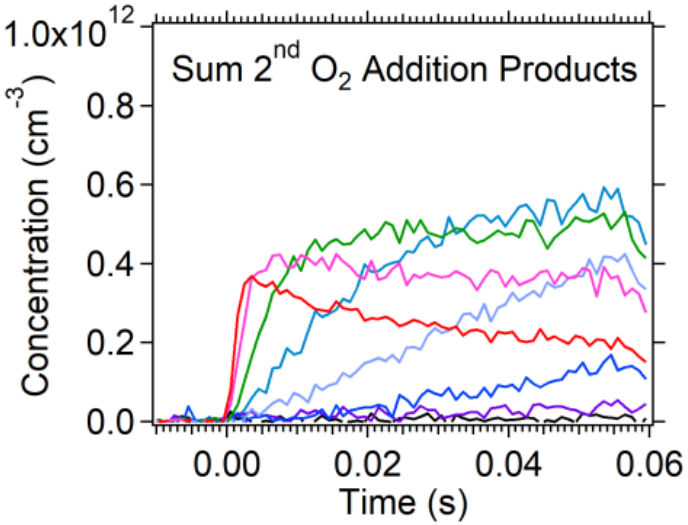
Sheps, Dewyer, Demireva, Zádor *JPCA* **2021**, *125*, 4467.

Dominant Pathways in Sub-Mechanism









Small concentration of 2nd O_2 addition species.

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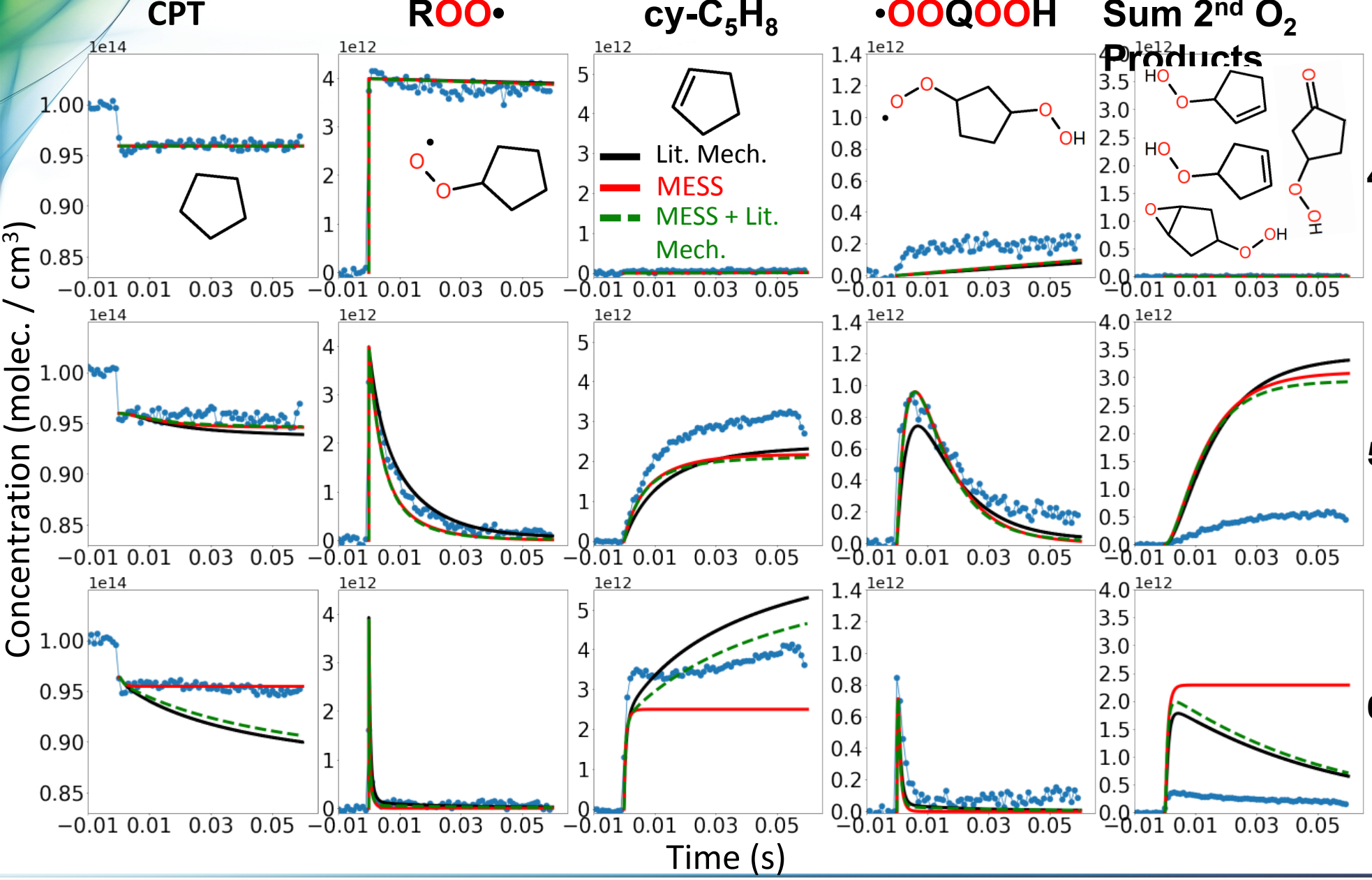
Performance of Kinetics Models Against MPIMS Data

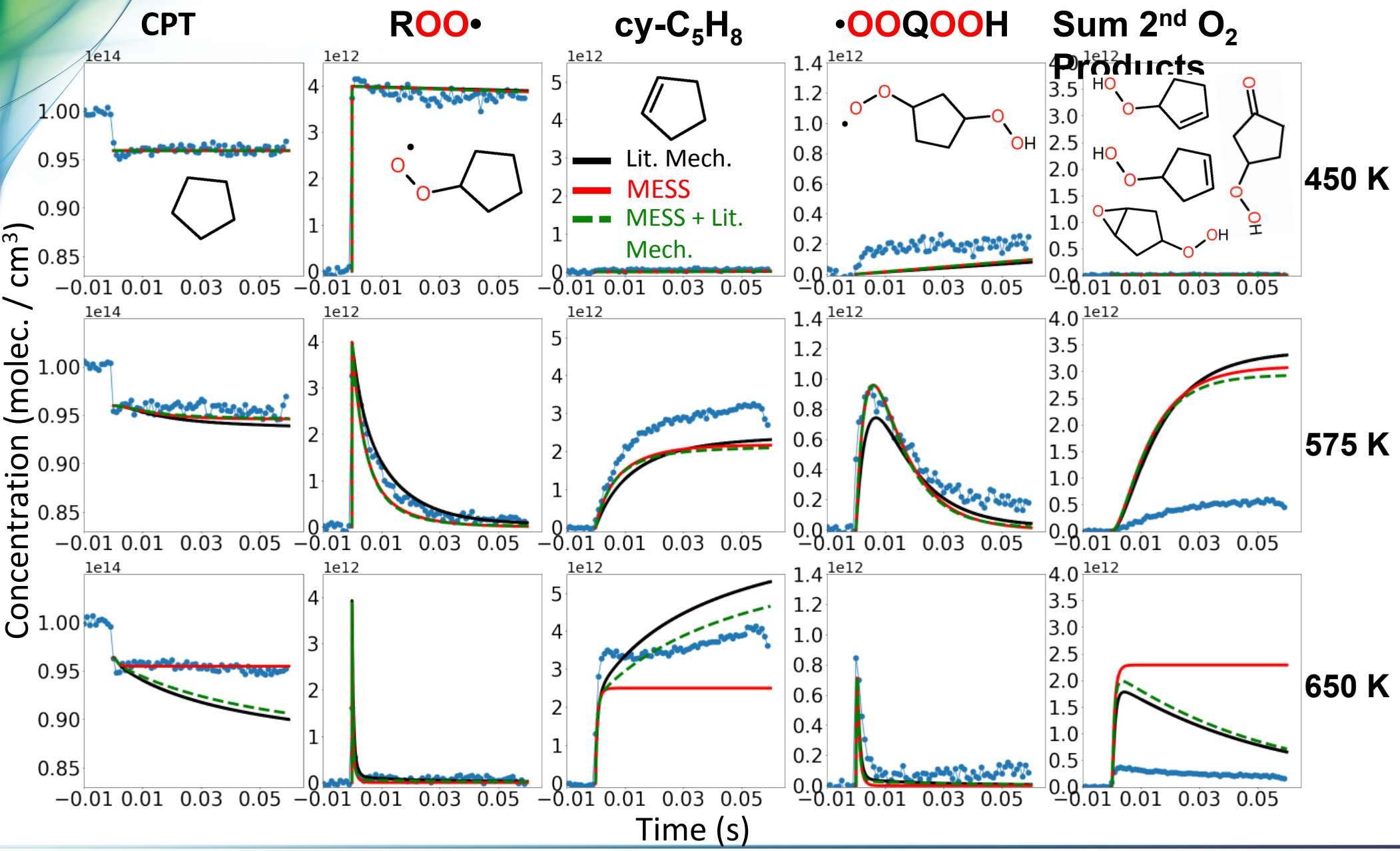


- **Lit. mech:**
  Full-scale CPT oxidation mechanism:
  Lokachari, Wagnon, Kukkadapu, Pitz, Curran *Combust. Flame* **2021**, *225*, 255.

- **MESS:**
  Rate coefficients for theory-based sub-mechanism calculated with Master Equation System Solver (MESS).

- **MESS + Lit. Mech:**
  Theory-based sub-mechanism embedded into full-scale CPT model.

Performance of Kinetics Models Against MPIMS Data



At high T, full scale models overpredict CPT consumption. All models overpredict 2nd O_2 products, while underpredicting cy-C_5H_8.

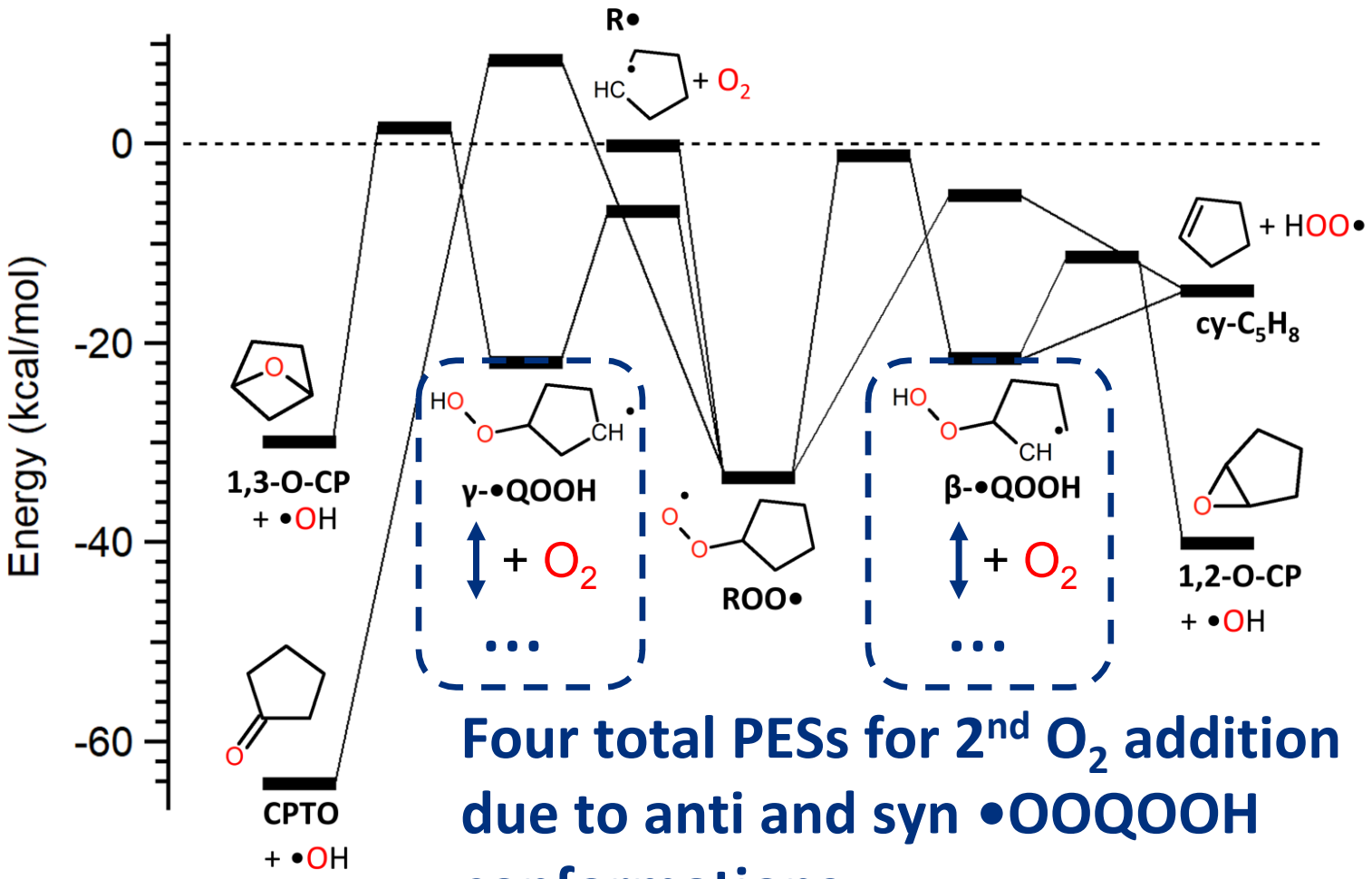
At or below 575 K, **MESS** and **MESS + Lit. Mech** result in nearly identical concentration profiles.

Optimization of Theory-Based Sub-Mechanism

223 parameters in sub-mechanism to be perturbed, such as well energies, barrier heights, frequencies, imaginary frequencies, and hindered rotor potentials.

1st O_2 Addition PES:

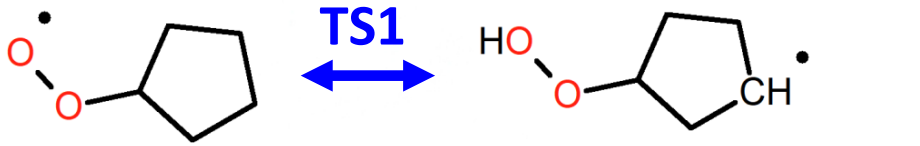
CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/6-311++G**



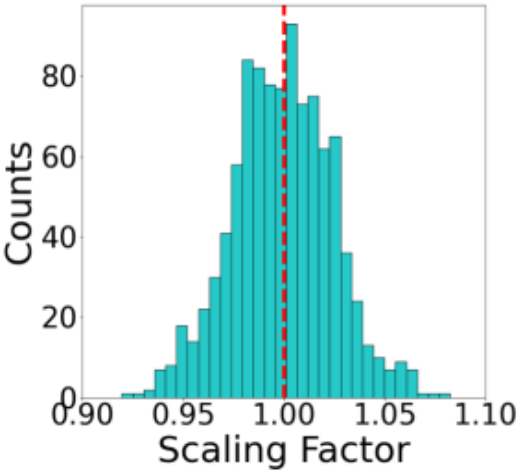
Four total PESs for 2nd O_2 addition due to anti and syn •OOQOOH conformations.

Global Sensitivity Analysis

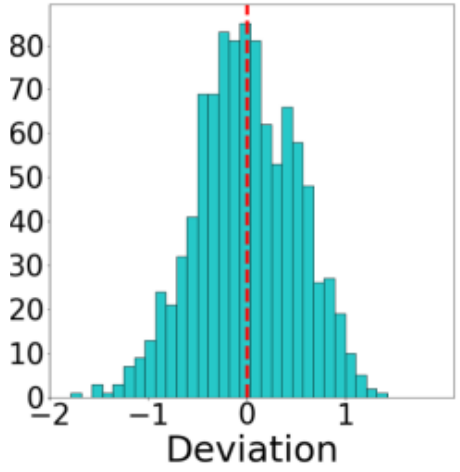
- Perturb 223 parameters randomly within expected uncertainties.
- Create 1000 perturbed models.



Frequency ± 5%

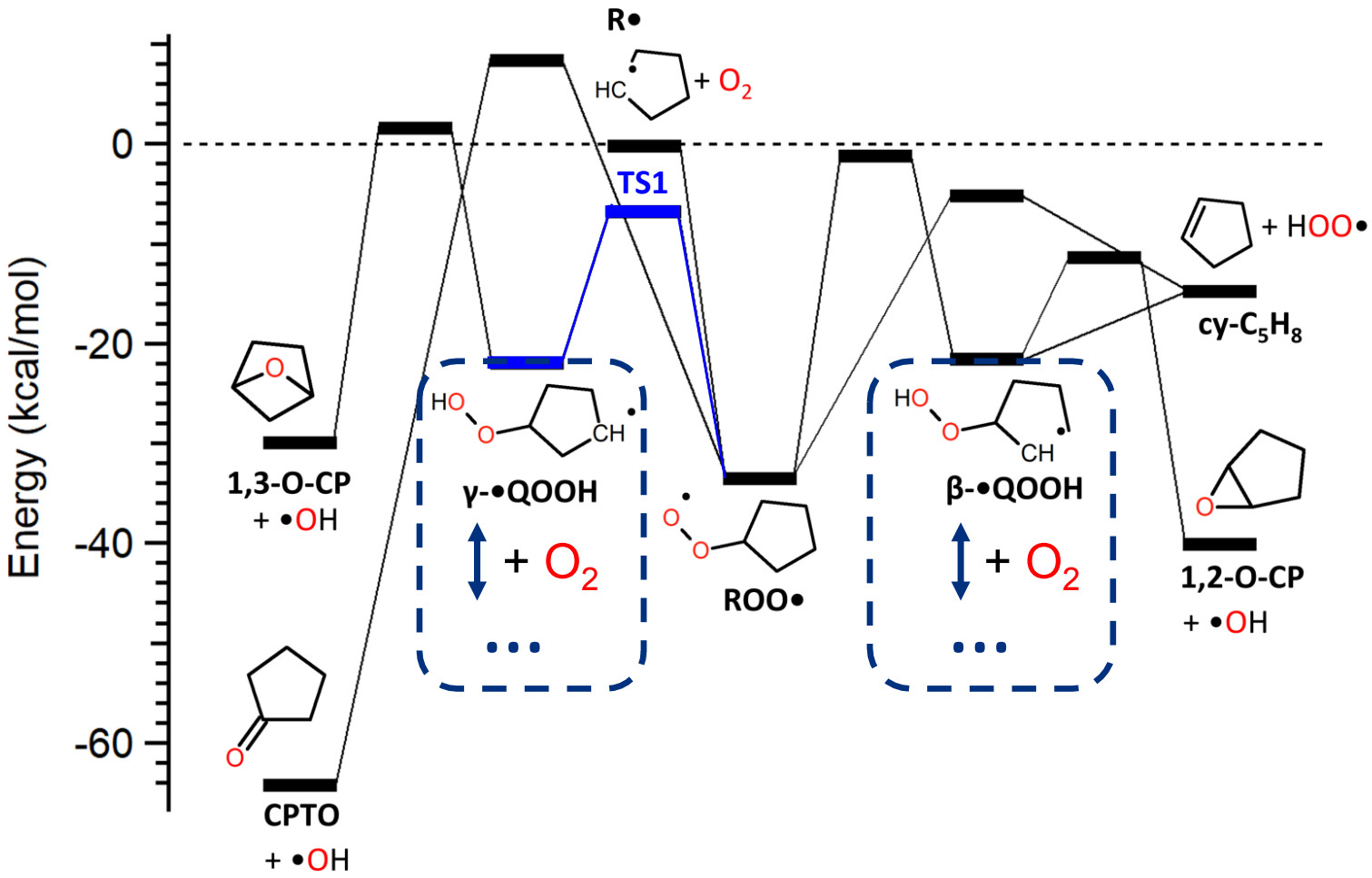


Barrier energy ± 1 kcal/mol



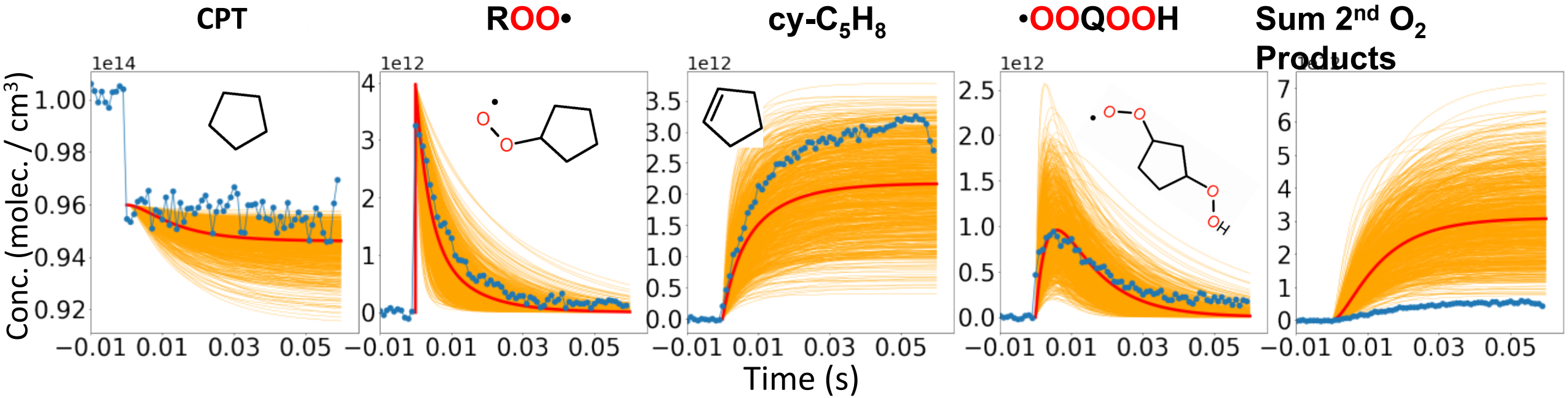
1st O_2 Addition PES:

CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/6-311++G**



Global Sensitivity Analysis

Effect of random perturbation to the 223 parameters on species concentration profiles from 1000 models at 575 K and 7500 Torr.



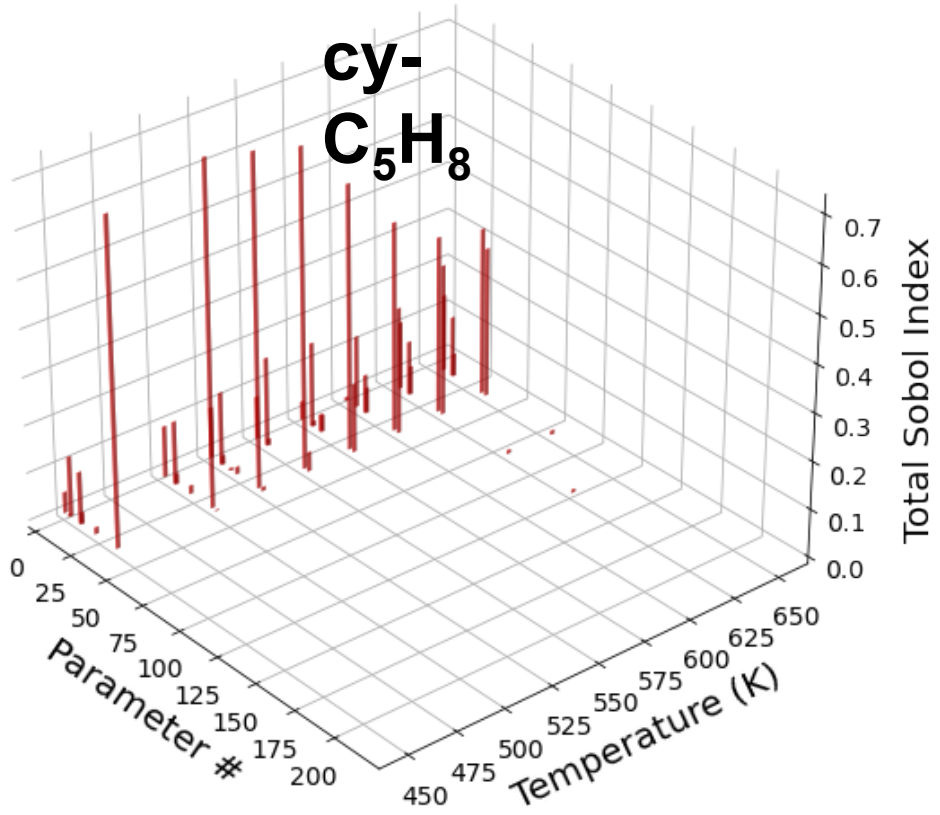
Experiment; **Perturbed Models**; **Original Model**

Global Sensitivity Analysis

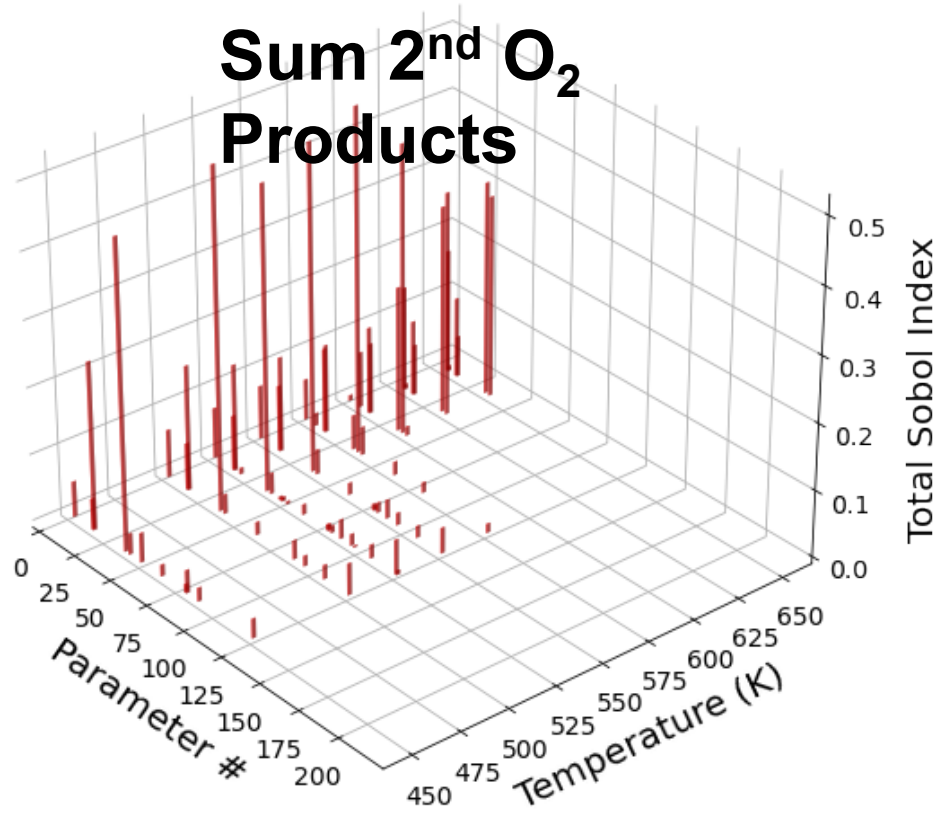
James Oreluk

- Determine most sensitive parameters from global sensitivity analysis.
- Parameter sensitivity from total Sobol index for species concentrations at 10 ms shown.
- Mainly same 6 of 223 parameters influence modeled species concentrations.

1st O_2:



2nd O_2:



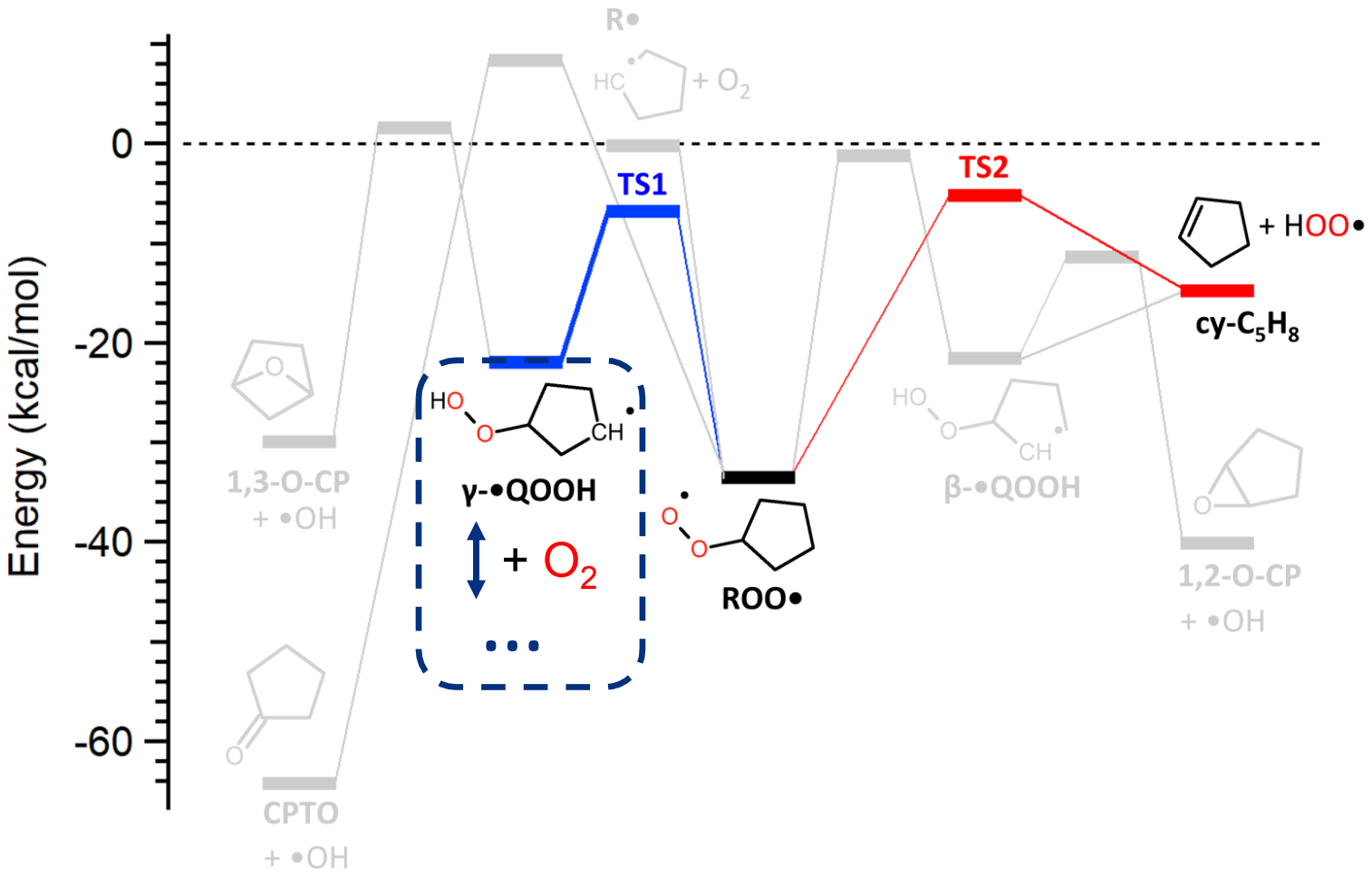
Global Sensitivity Analysis

1st O_2 Addition PES:

CCSD(T)-F12a/cc-pVTZ-F12//M06-2X/6-311++G**

6 most sensitive parameters:

1) Barrier energy for TS1.
2) Barrier energy for TS2.
3) Imaginary frequency, TS1.
4) Frequencies of TS2.
5) Frequencies of ROO•.
6) Frequencies of TS1.



Global Sensitivity Analysis

6 most sensitive parameters:

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4) Frequencies of TS2.
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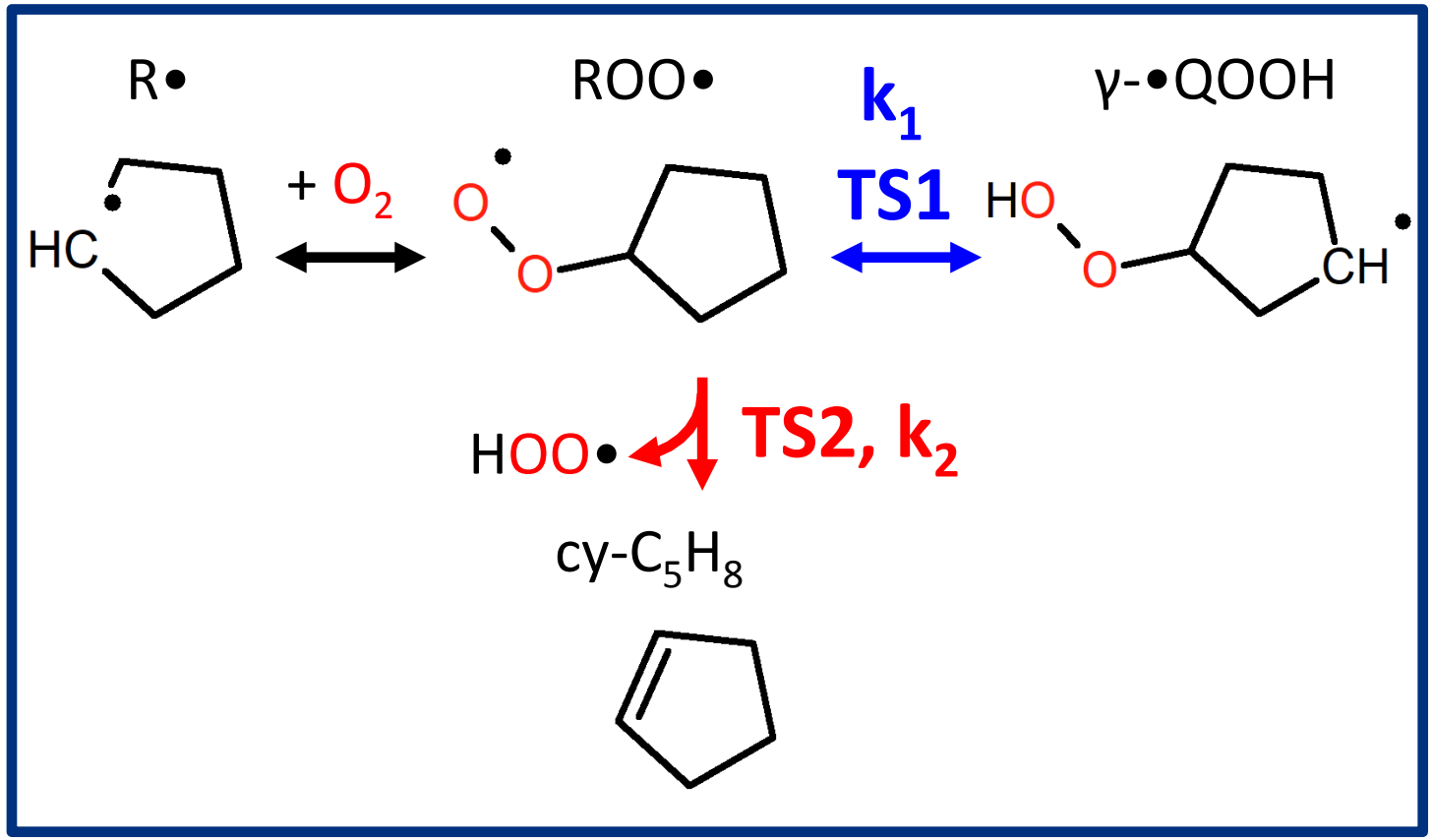
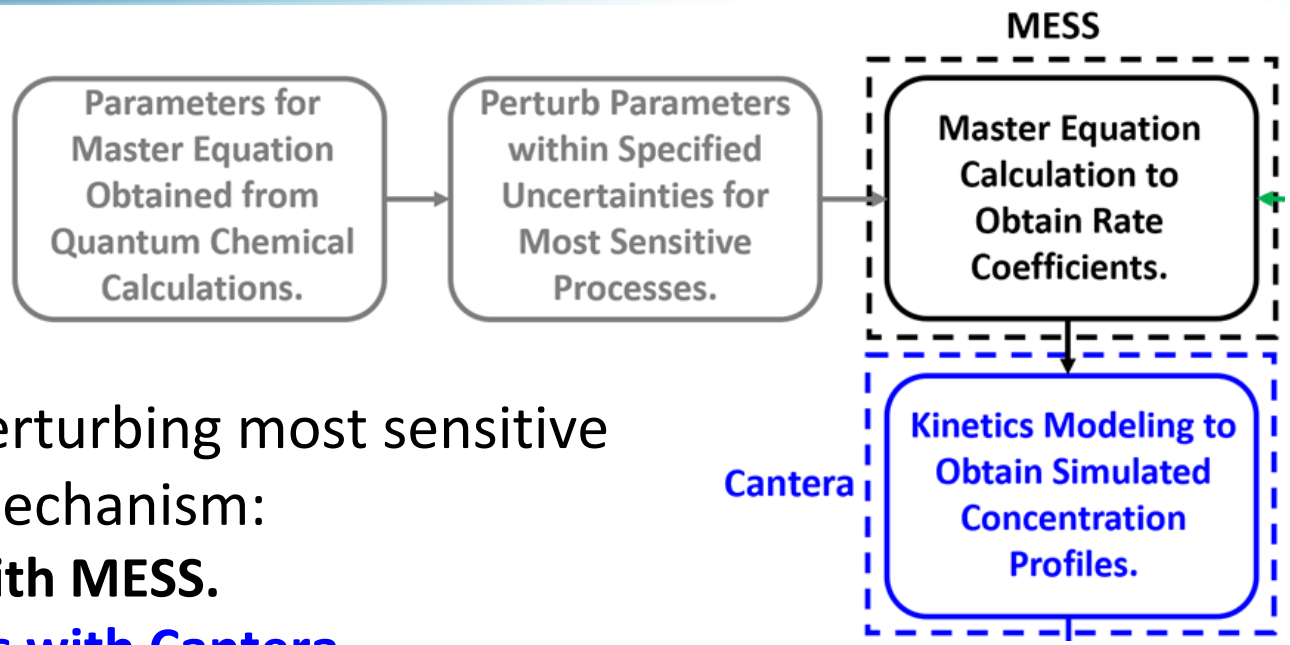
1st O_2 Addition



Most sensitive parameters impact two rate coefficients.

Optimization Workflow:



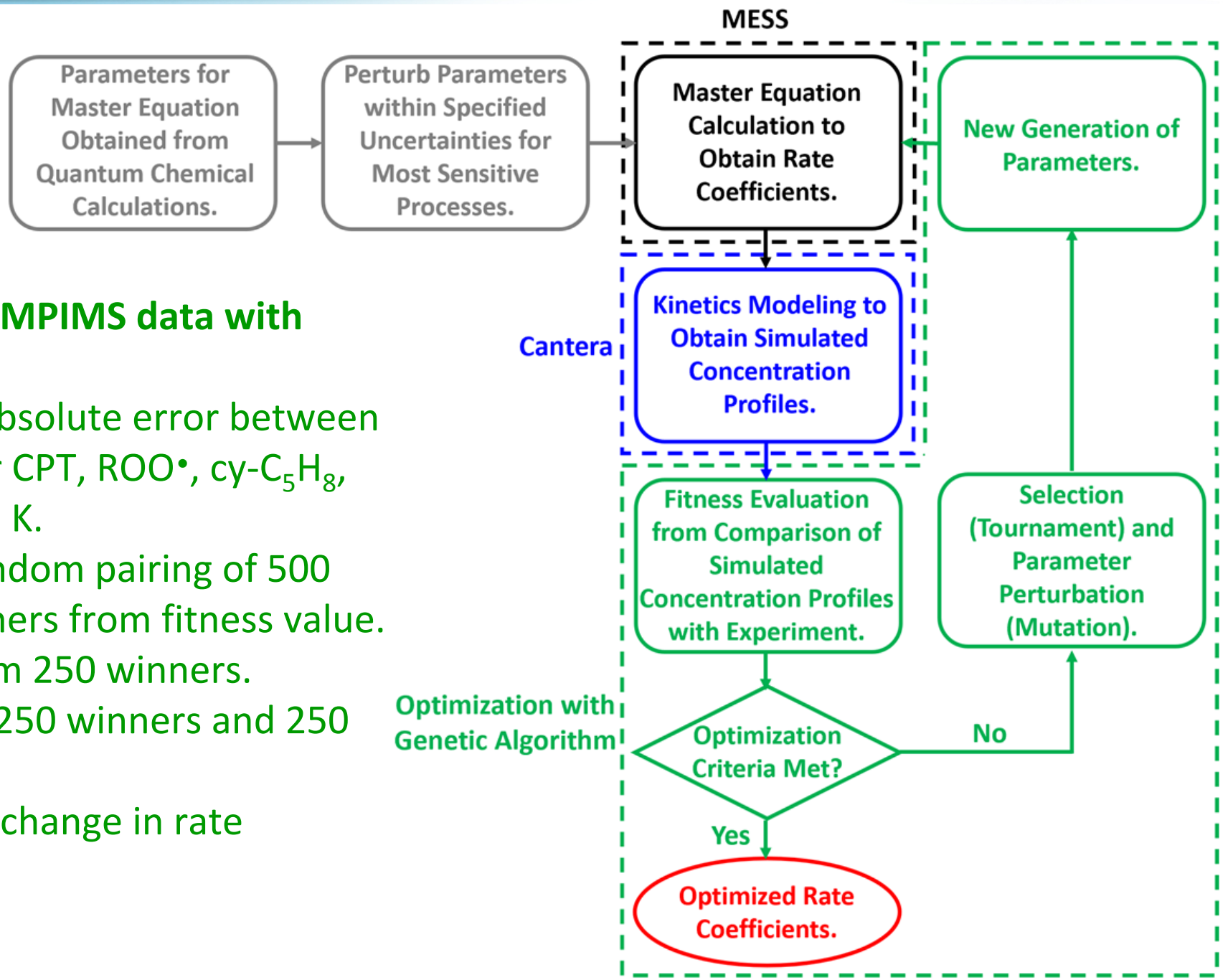
Create 500 initial models by perturbing most sensitive parameters (16 total) in sub-mechanism:

1) **Calculate rate coefficients with MESS.**
2) **Model concentration profiles with Cantera.**

Optimization Workflow:

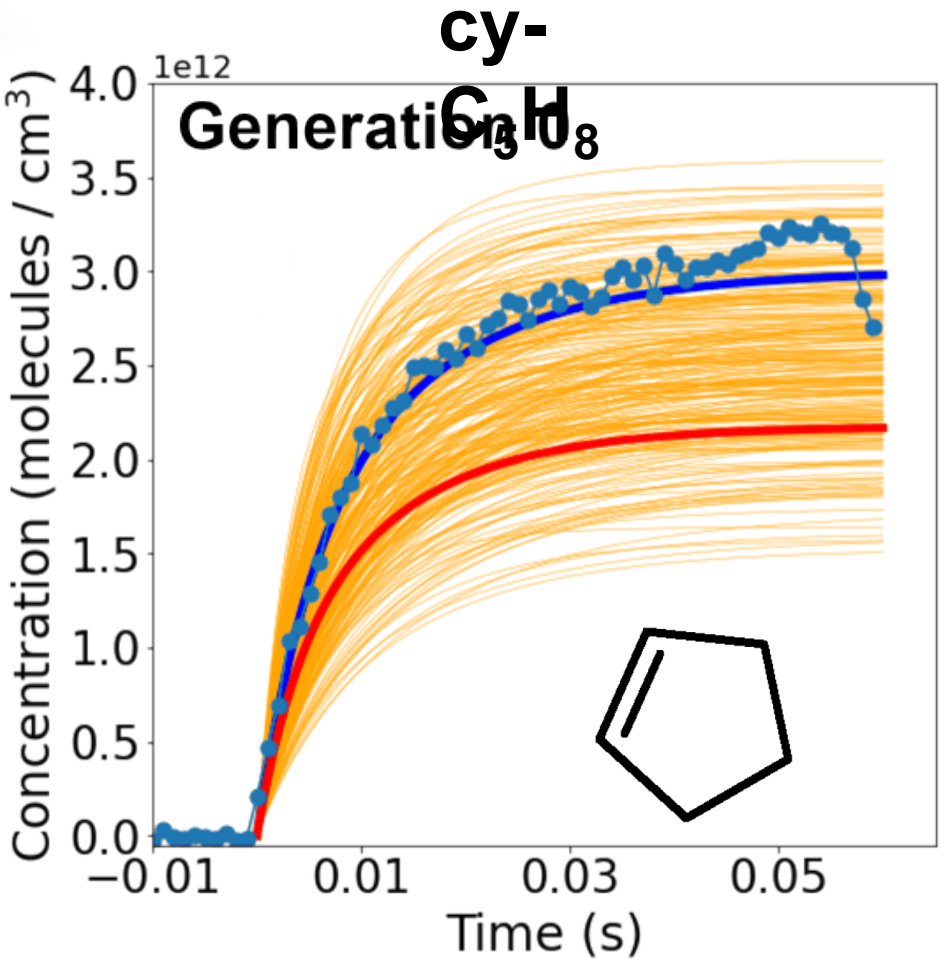
3) Optimize parameters against MPIMS data with genetic algorithm:

1) Fitness value: combined absolute error between model and experiment for CPT, ROO•, cy-C_5H_8, and •OOQOOH at 450-575 K.
2) Tournament selection: random pairing of 500 models and selecting winners from fitness value.
3) New models spawned from 250 winners.
4) Population replaced with 250 winners and 250 new models.
5) Process repeated until no change in rate coefficients.

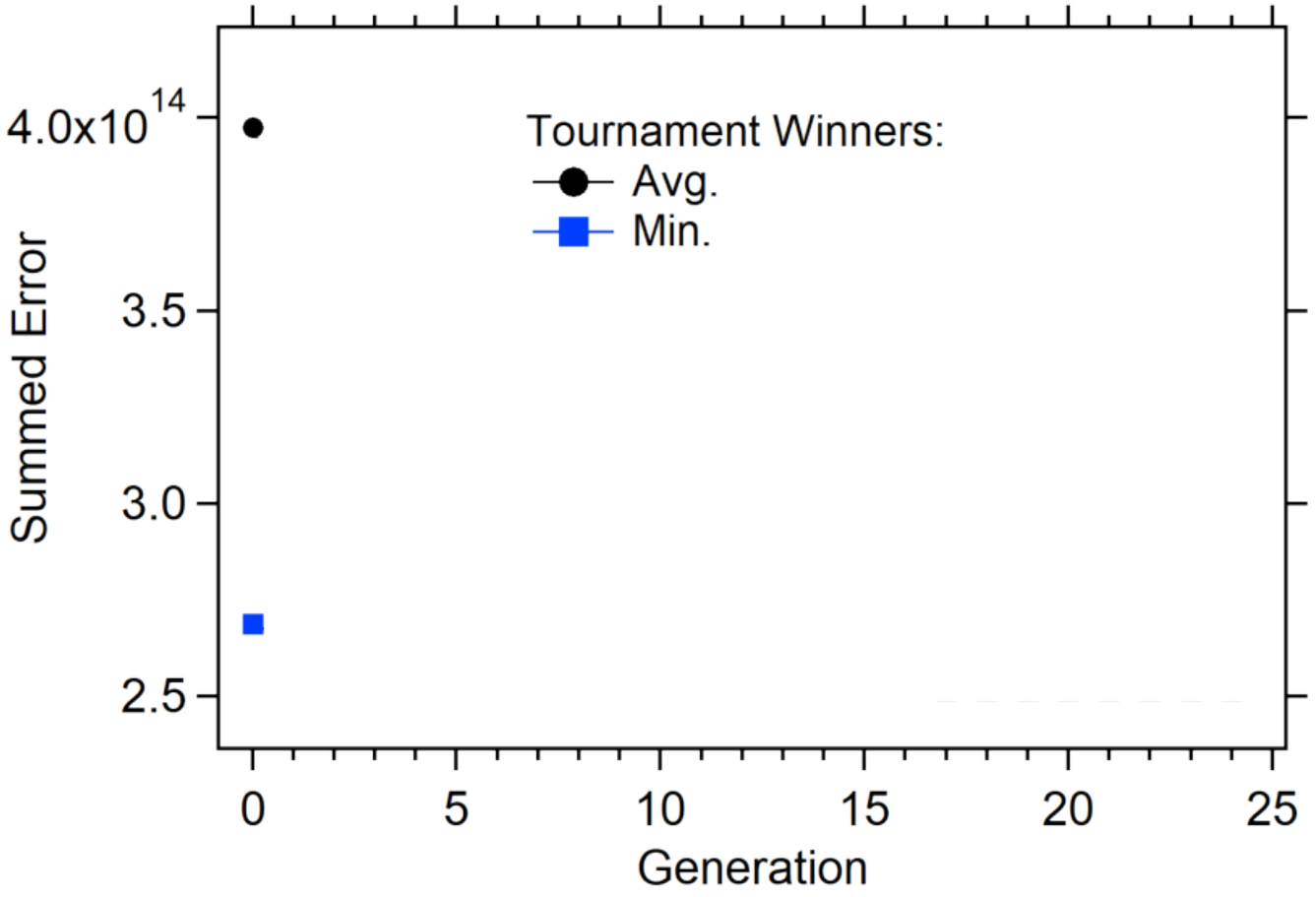


Genetic Algorithm Optimization

Illustration of optimization for top 250 fits of cy-C_5H_8 at 575 K, 7500 Torr:



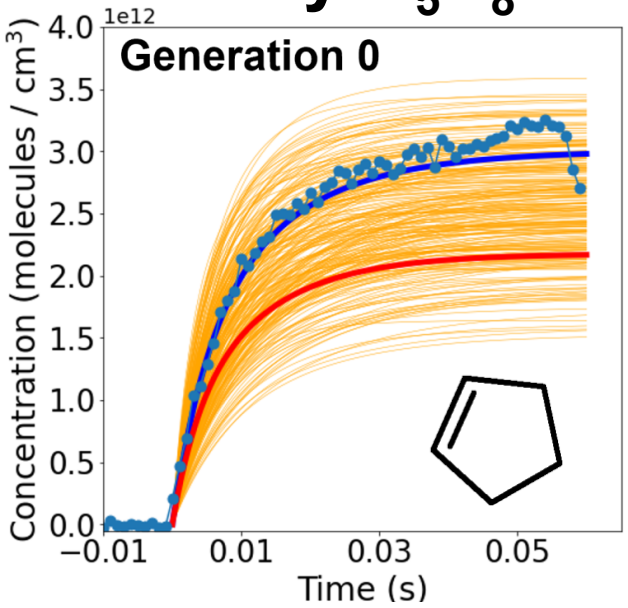
Simultaneous fitting to CPT, ROO•, cy-C_5H_8 and •OOQOOH at 450, 500, 525, 550, 575 K:

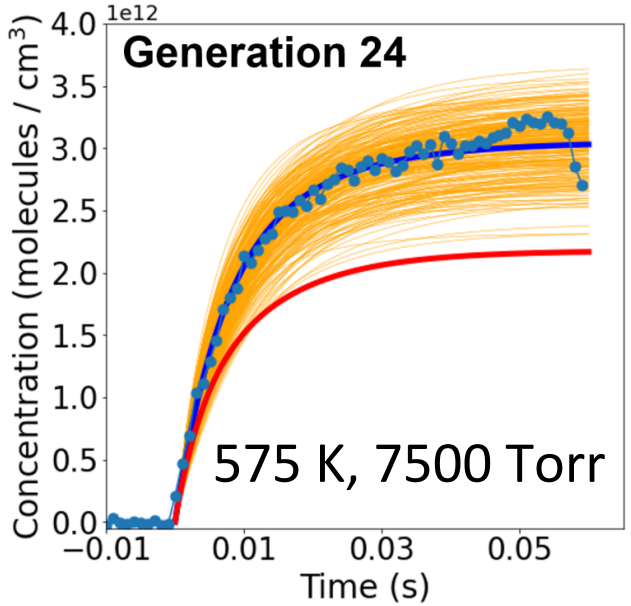


Experiment; **Perturbed Models**; **Original Model**; **Best Fit Model**

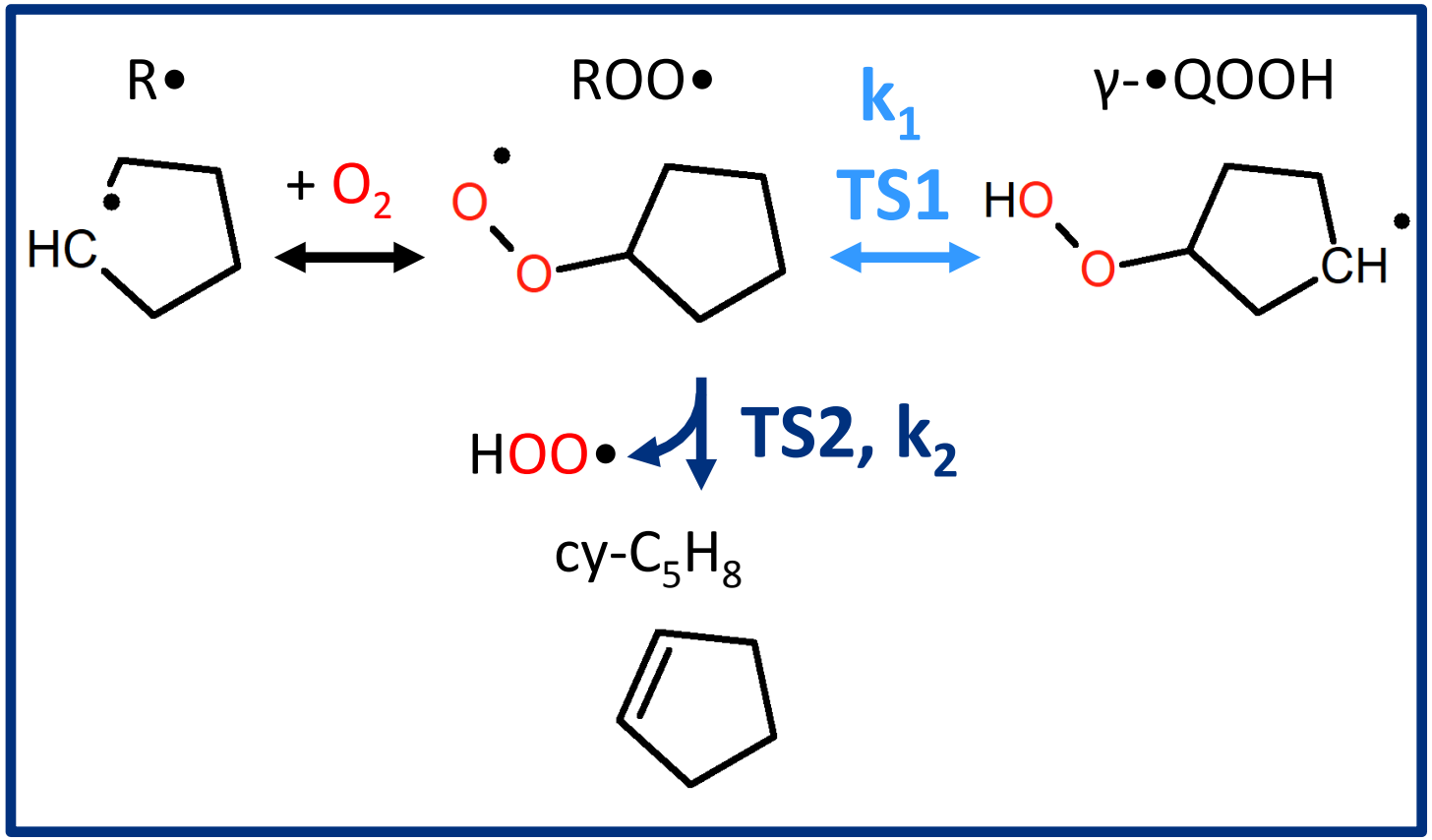
Genetic Algorithm Optimization

cy-C_5H_8





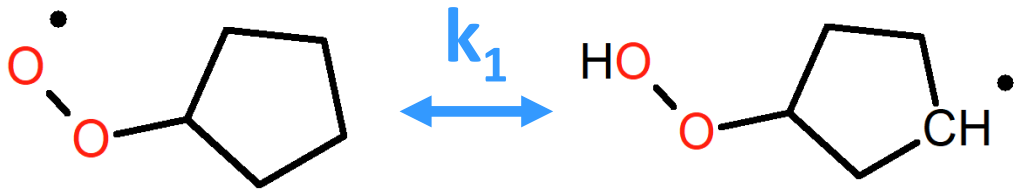
1st O_2 Addition



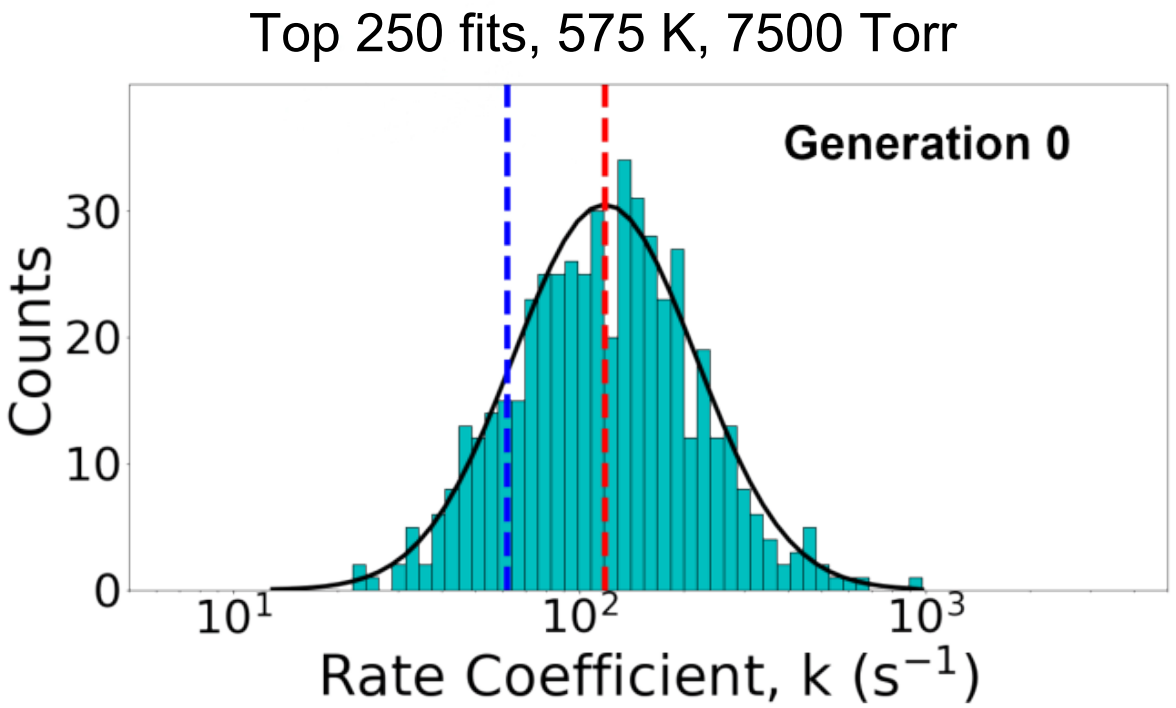
Optimization alters k_1 (isomerization) and k_2 (HO_2 elimination) to yield higher cy-C_5H_8 concentration.

Experiment; Perturbed Models; Original Model; Best Fit Model

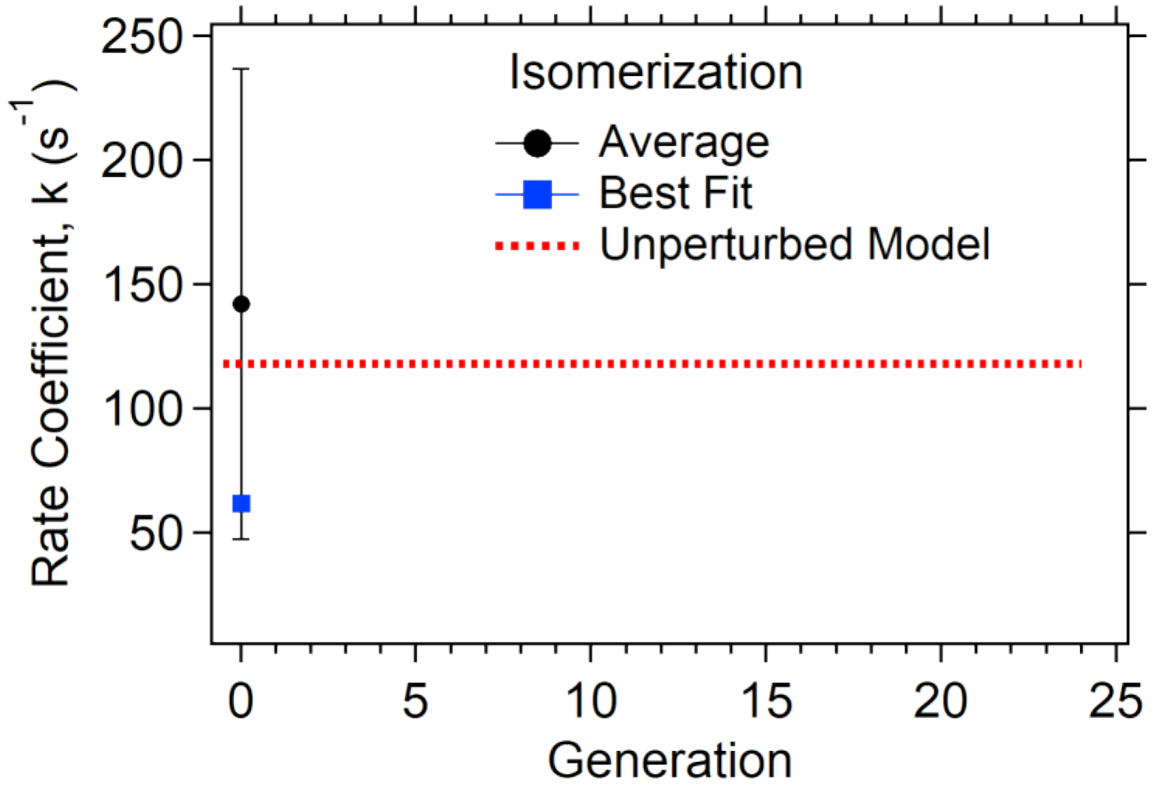
Genetic Algorithm Optimization: Isomerization Reaction



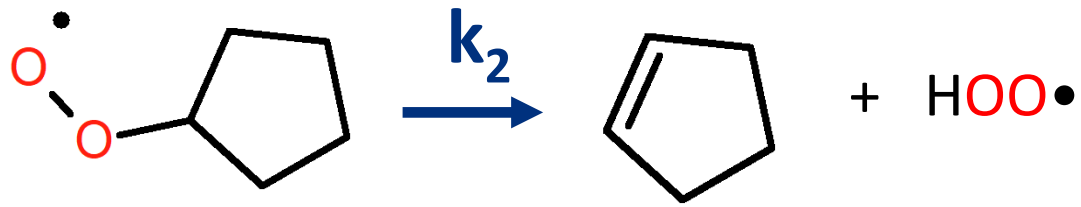
Optimization reduces k_1 by a factor of ~2 compared with the original model.



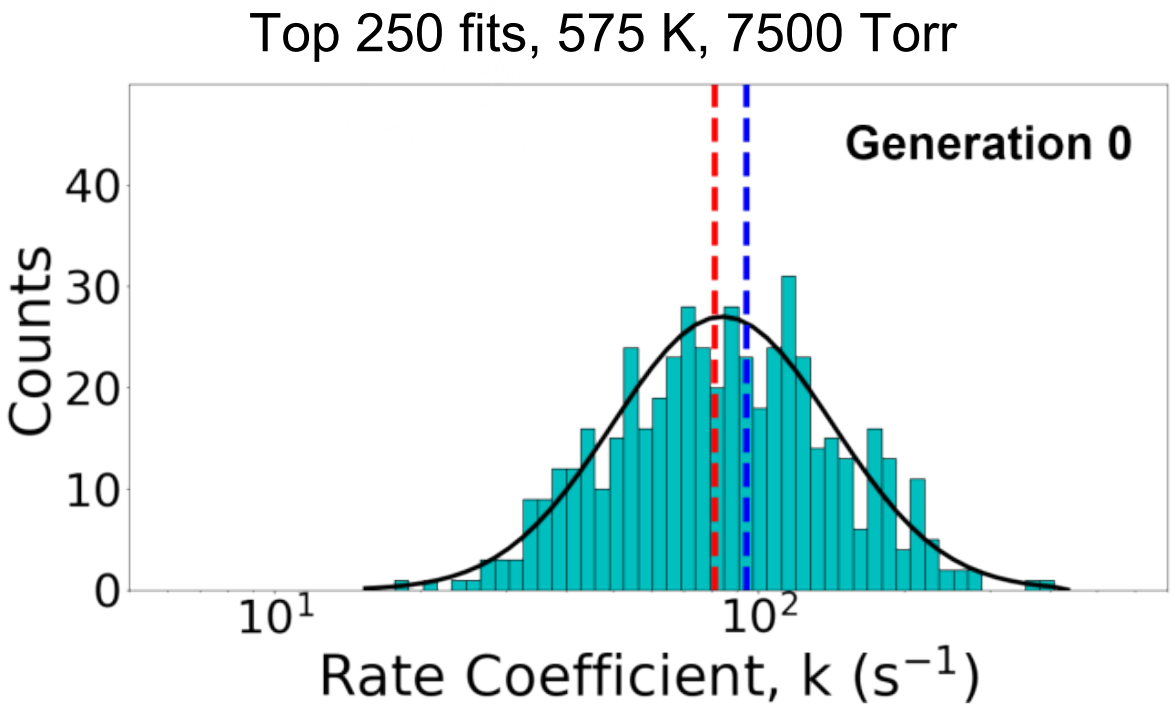
Best fit; **original, unperturbed model**



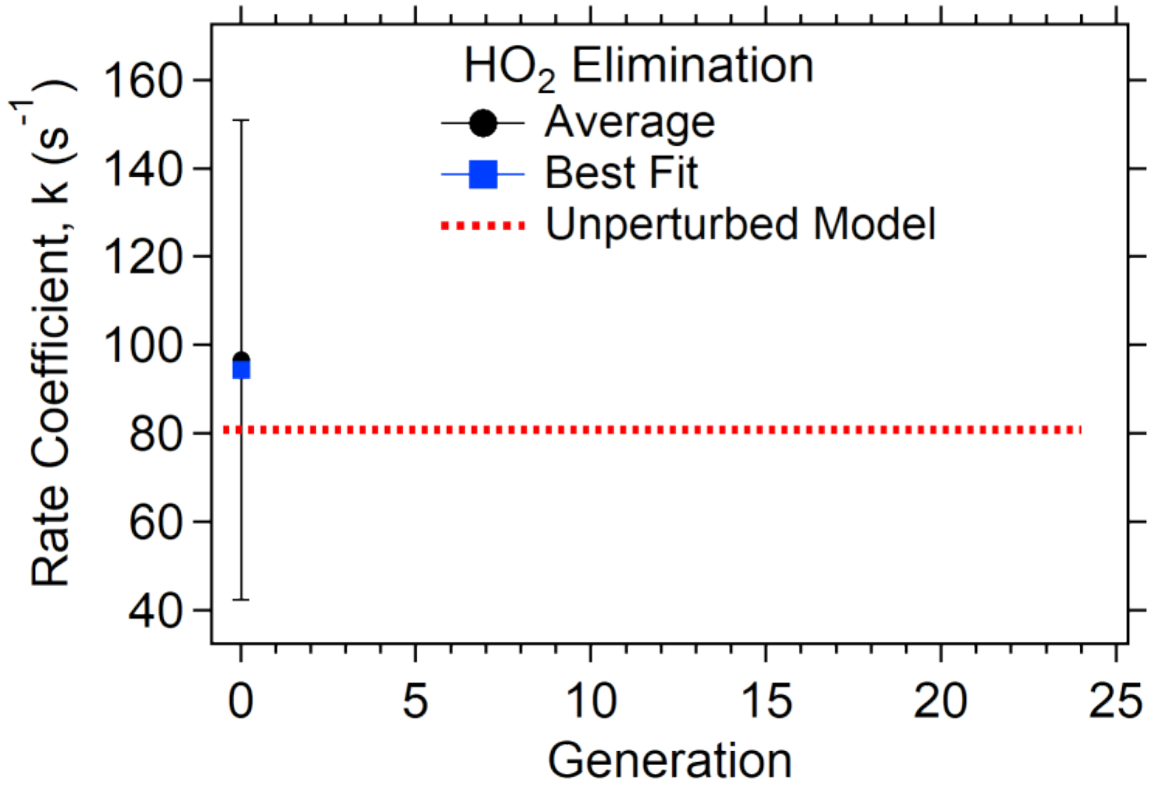
Genetic Algorithm Optimization: HO_2 Elimination Reaction



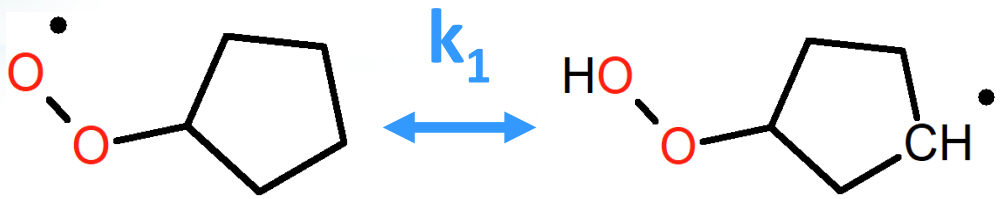
Optimization yields slightly larger k_2 compared with the original model.

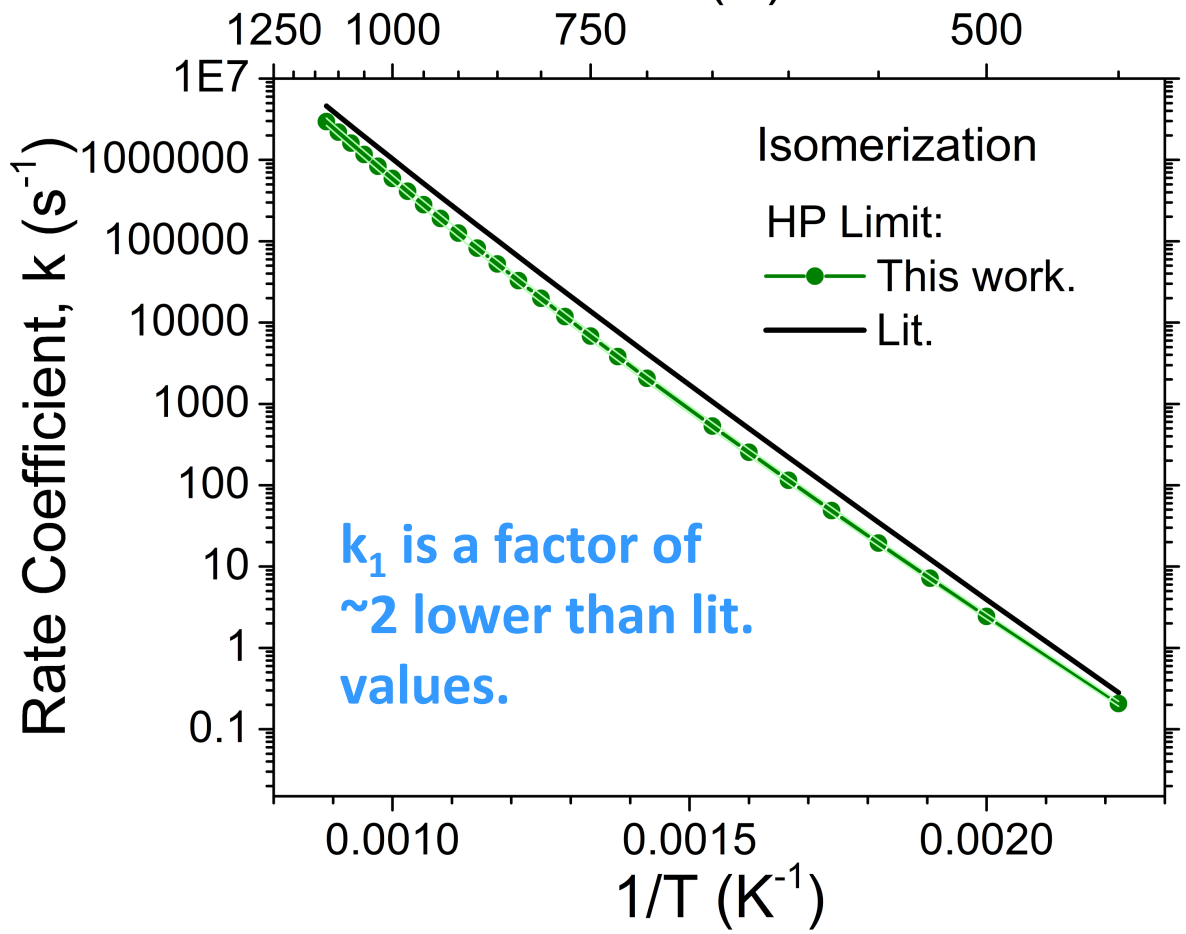


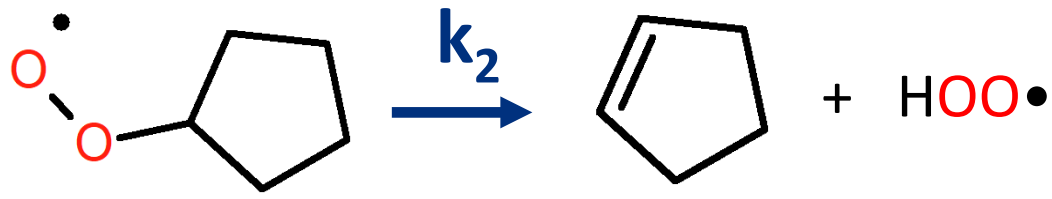
Best fit; **original, unperturbed model**

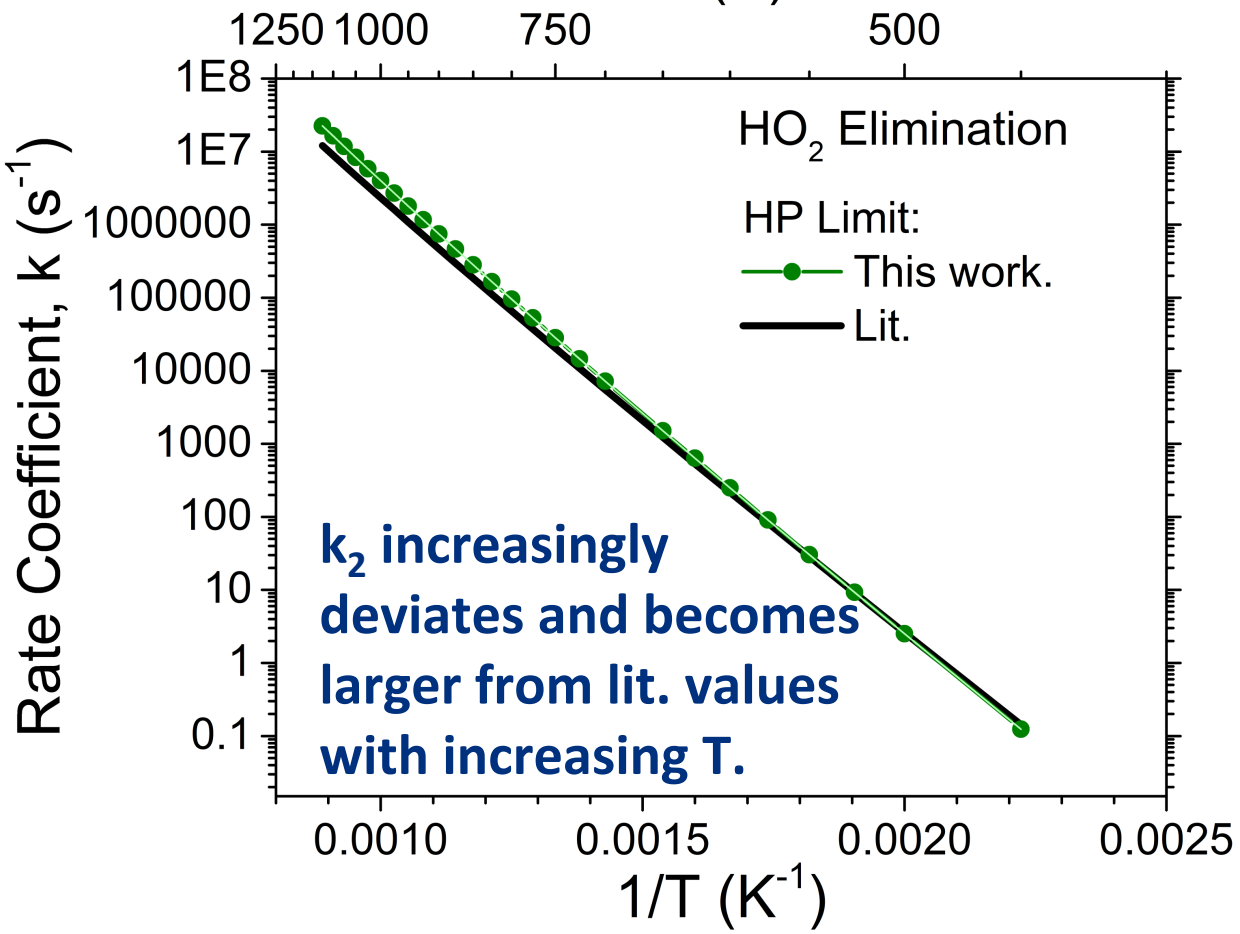


Temperature Dependent Rate Coefficients



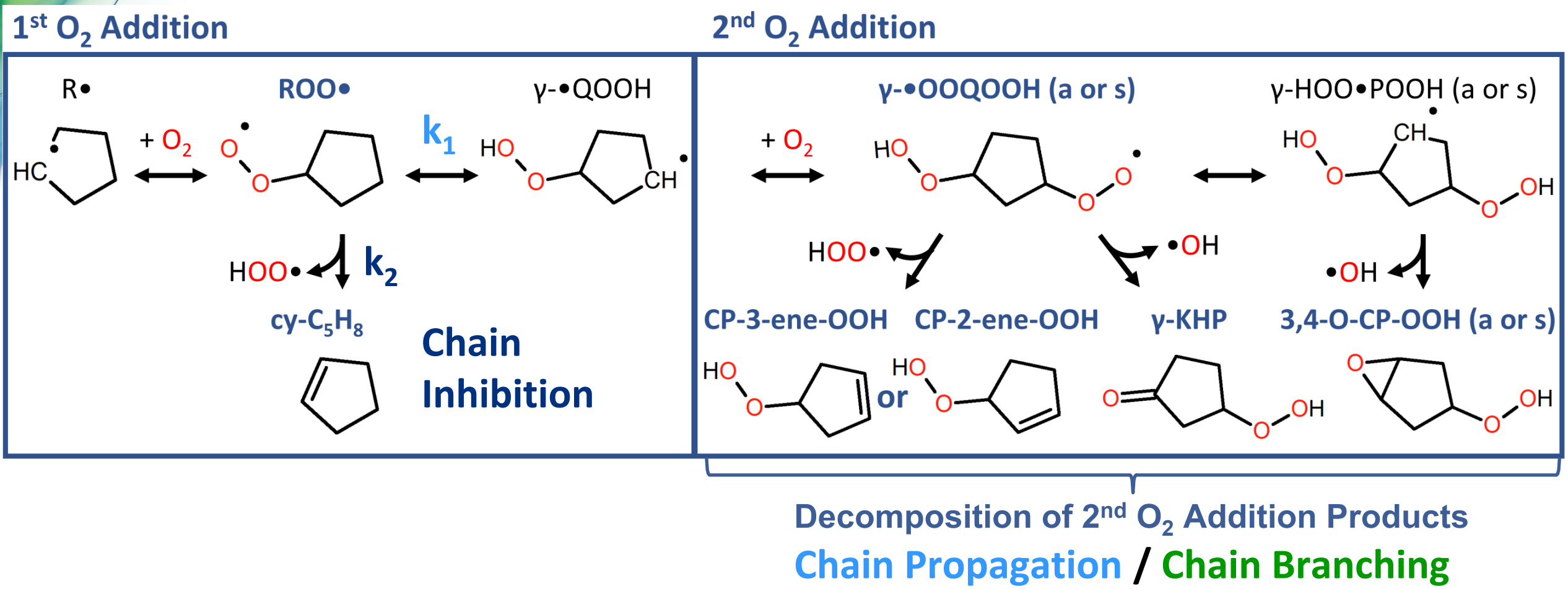






Lokachari, Wagnon, Kukkadapu, Pitz, Curran *Combust. Flame* **2021**, *225*, 255.

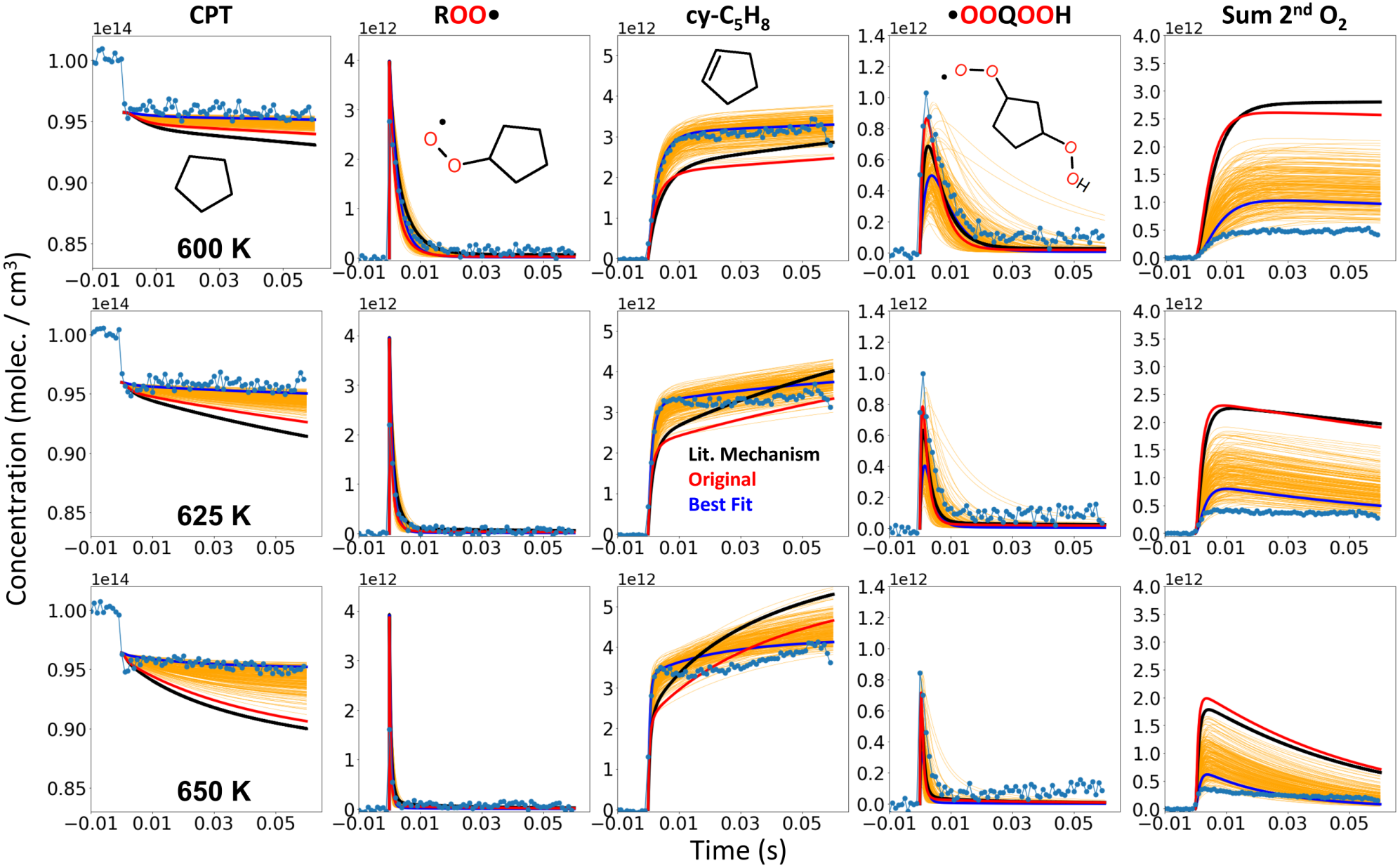
CPT Low-Temperature Reactivity



Compared to lit. and original models, optimization yields:

- Smaller k_1; reduces flux into chain propagating and branching pathways.
- Larger k_2 at high T; further increases flux into chain inhibiting pathway.

Evaluation Against High Temperature MPIMS Data

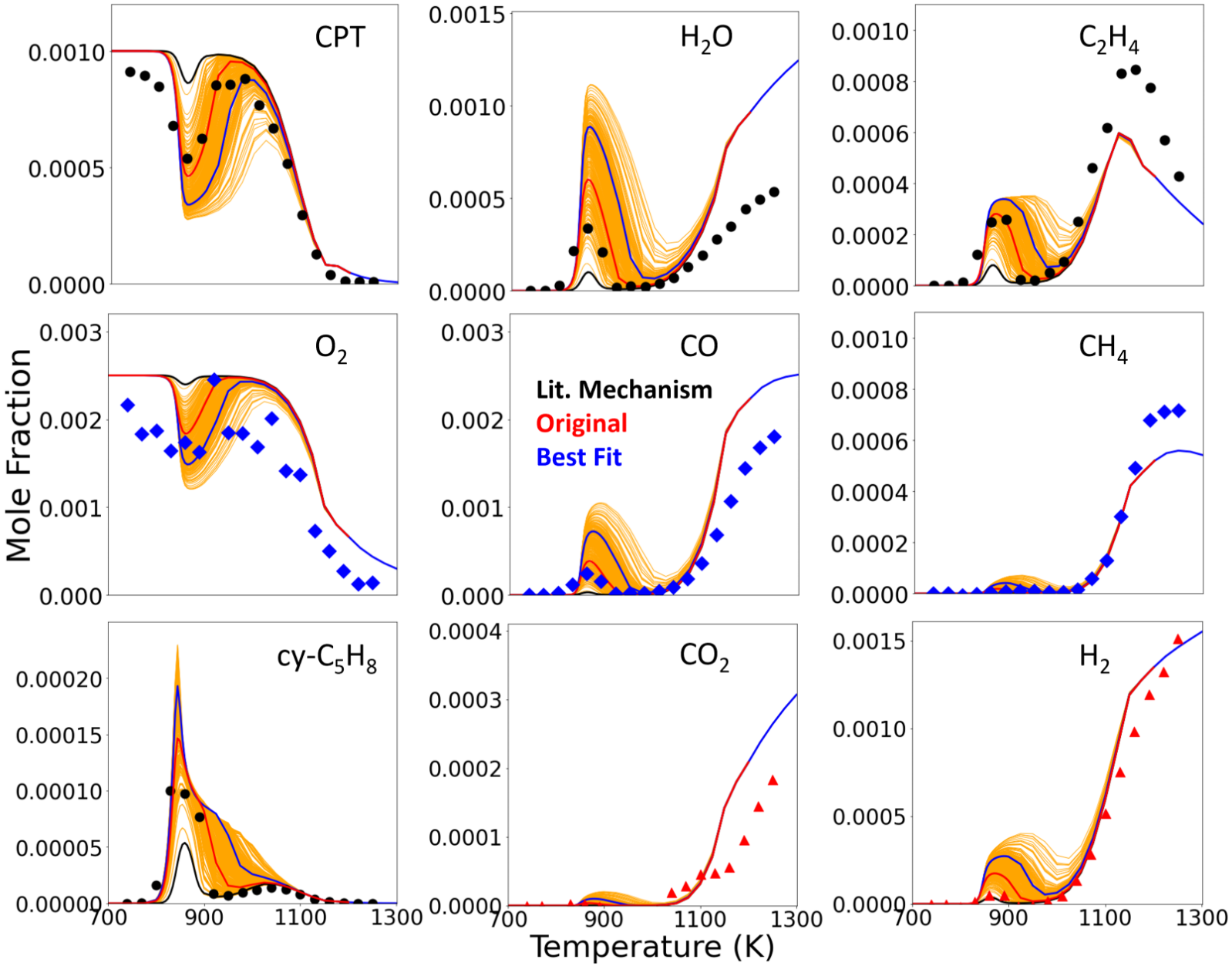


Top 250 optimized models:

- Reproduce cy-C_5H_8 concentration significantly better compared with lit. and original models.
- Perform better than lit. and original models in capturing 2nd O_2 addition products and CPT consumption.

Lit. Mechanism: Lokachari, Wagnon, Kukkadapu, Pitz, Curran *Combust. Flame* **2021**, *225*, 255.

Evaluation Against High Temperature Jet-Stirred Reactor Data



Experimental data from: Al Rashidi et al. *Proc. Combust. Inst.*, **2017**, *36*, 469.

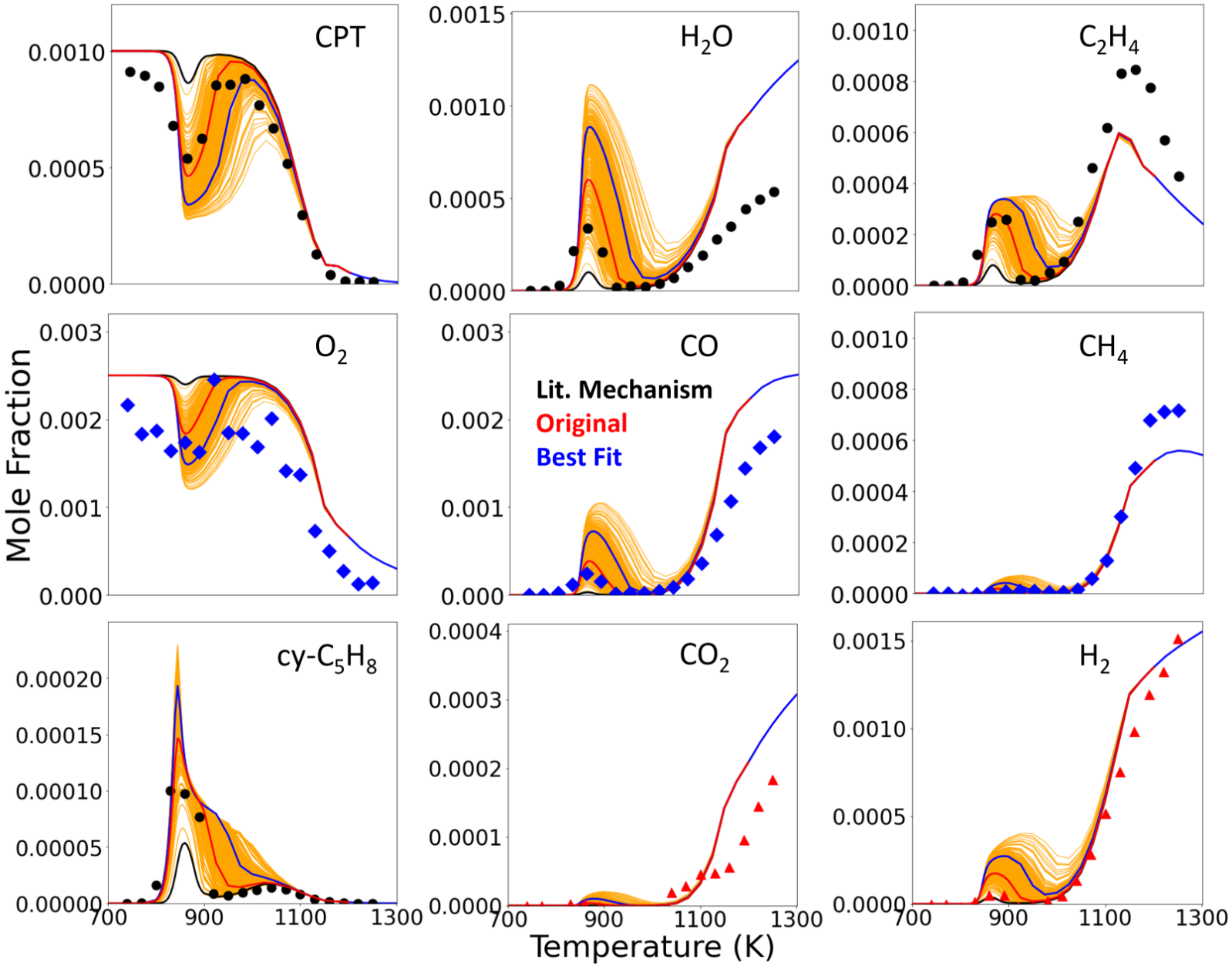
Fuel/air equivalence ratio = 3.

Pressure: 10 atm

- Inhibition in CPT reactivity at 850 – 1000 K.
- Models exhibit a wide range of behavior, but generally do better than lit. mechanism.

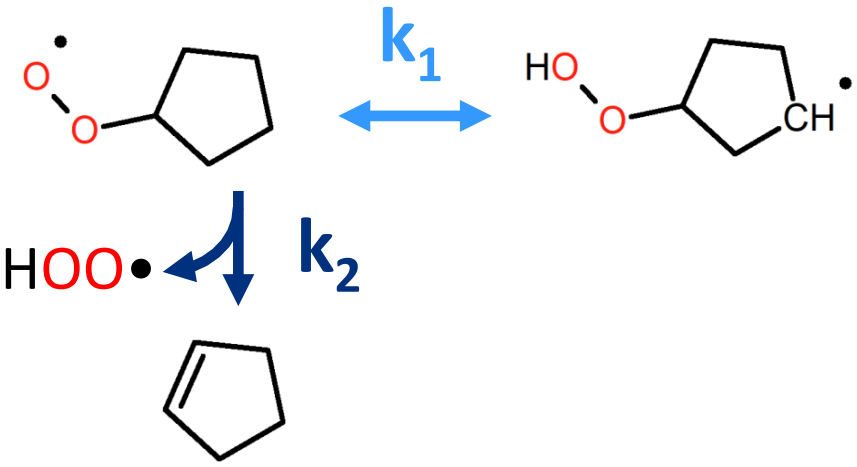
Lit. Mechanism:
Lokachari, Wagnon, Kukkadapu, Pitz, Curran *Combust. Flame* **2021**, *225*, 255.

Evaluation Against High Temperature Jet-Stirred Reactor Data



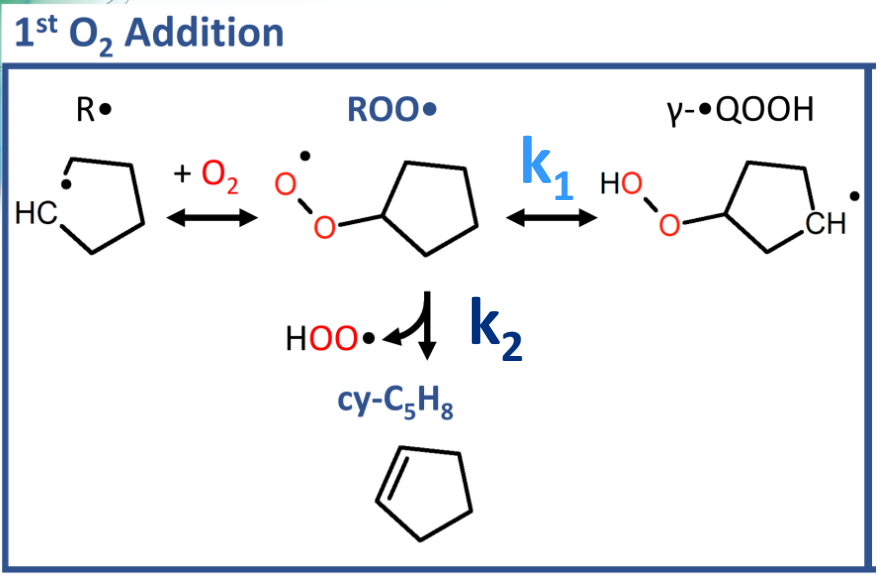
Experimental data from: Al Rashidi et al. *Proc. Combust. Inst.*, **2017**, *36*, 469.

- At fuel rich conditions, not much HO_2 produced.
- At high T, HO_2 reacts with allyl in OH producing pathways, which increases CPT reactivity.

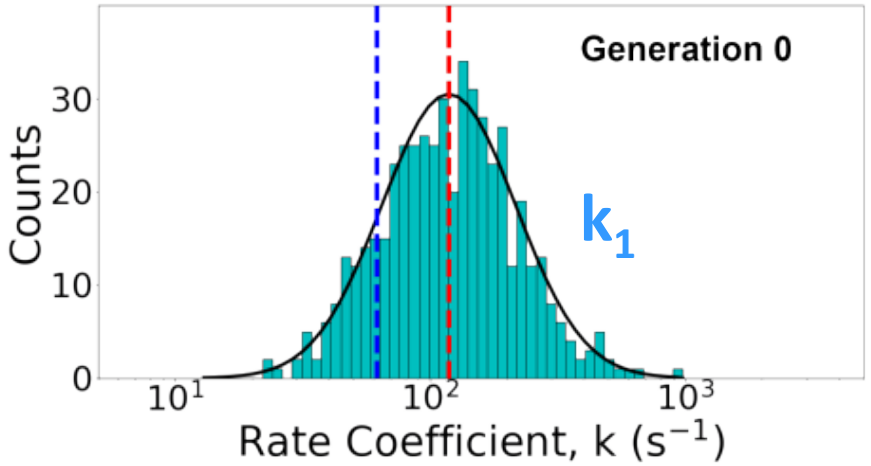


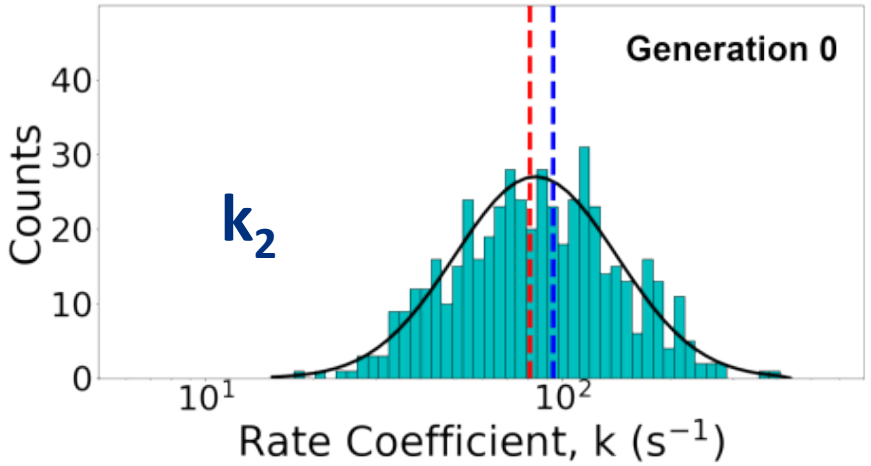
Lit. Mechanism:
Lokachari, Wagnon, Kukkadapu, Pitz, Curran *Combust. Flame* **2021**, *225*, 255.

Conclusions



- Unique approach using genetic algorithm to optimize most sensitive quantum chemistry parameters within expected uncertainties against time-resolved data.
  - Self-consistent perturbation, allows for model extrapolation beyond experimental conditions.
- Rate coefficients for two key reactions constrained improving model accuracy and agreement with experiment.





- Effects of parameter uncertainties on model outcomes illustrated.

Acknowledgements

My co-authors:

- James Oreluk
- Amanda Dewyer
- Judit Zádor
- Leonid Sheps

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Thank you.