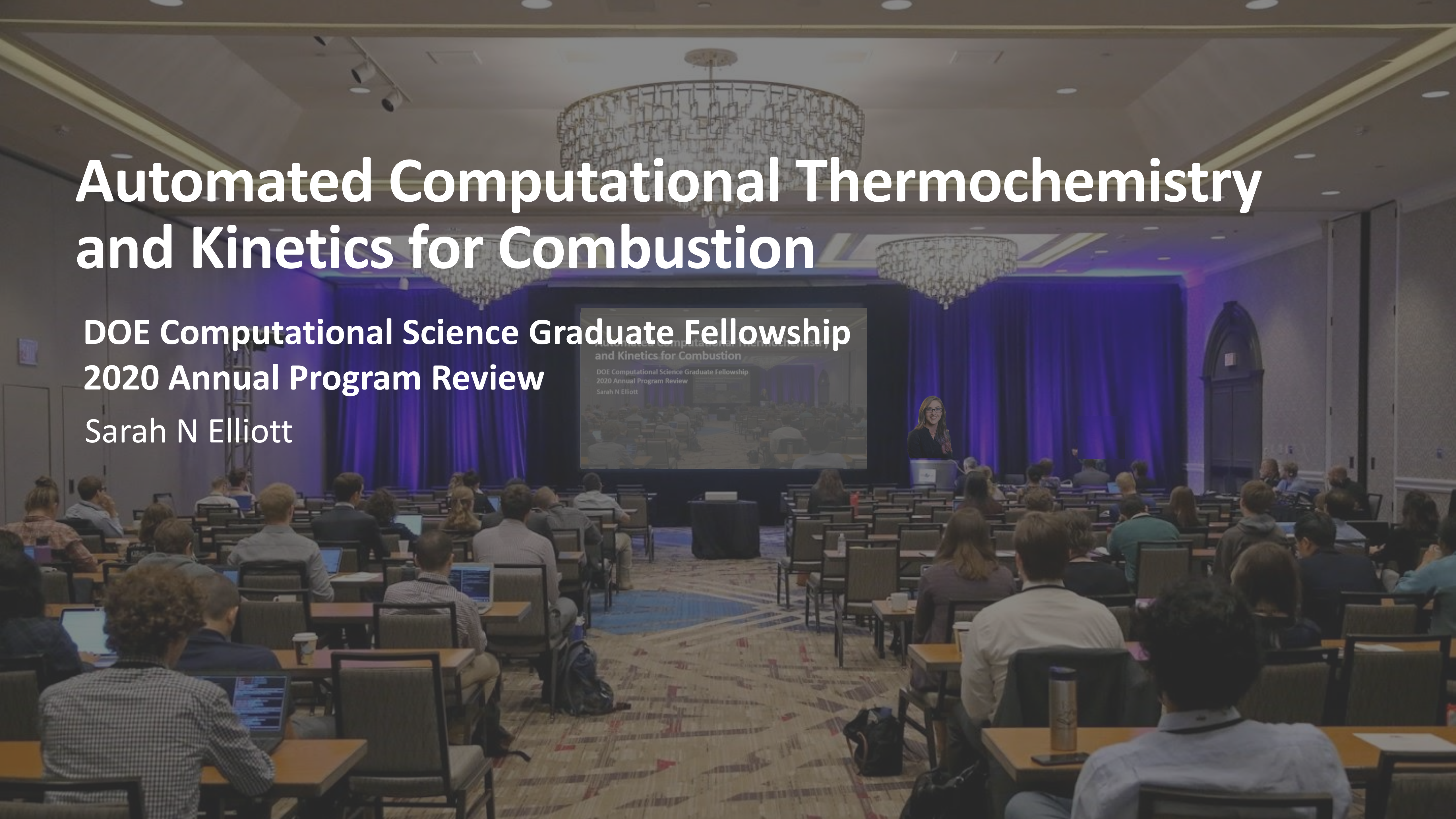

Automated Computational Thermochemistry
and Kinetics for Combustion
DOE Computational Science Graduate Fellowship
2020 Annual Program Review
Sarah N Elliott

Automated Computational Thermochemistry and Kinetics for Combustion

DOE Computational Science Graduate Fellowship 2020 Annual Program Review

Sarah N Elliott



Computational Combustion Chemistry

Quantum Chemistry
Electronic Energies
Potential Energy Surface
Stationary Points
Rotational Constants
Vibrational Frequencies

Thermochemistry
Partition Function
Enthalpy
Entropy
Heat Capacity
Gibb’s Free Energy

Kinetics
Dividing Surface
Minimum Energy Path
Rate Constant
Branching Ratios
Merging Temperatures

$$\hat{\mathrm{H}}\Psi = \mathrm{E}\Psi$$

$$\hat{\mathrm{H}} = -\sum_{i=1}^{n}\frac{h^2}{2m_i}\nabla_i^2 - \sum_{I=1}^{N}\frac{h^2}{2m_I}\nabla_I^2 + \sum_{i<j}^{n}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{I<J}^{N}\frac{Z_I Z_J e^2}{4\pi\varepsilon_0 r_{IJ}} - \sum_{I}^{N}\sum_{i}^{n}\frac{Z_I e^2}{4\pi\varepsilon_0 r_{Ii}}$$

Computational Combustion Chemistry

Quantum Chemistry
Electronic Energies
Potential Energy Surface
Stationary Points
Rotational Constants
Vibrational Frequencies

Thermochemistry
Partition Function
Enthalpy
Entropy
Heat Capacity
Gibb's Free Energy

Kinetics
Dividing Surface
Minimum Energy Path
Rate Constant
Branching Ratios
Merging Temperatures

$$Q(T) = \sum_i \exp(\frac{\epsilon_i}{k_B T})$$

$$Q = Q_T Q_R Q_V Q_E$$

Computational Combustion Chemistry

Quantum Chemistry
Electronic Energies
Potential Energy Surface
Stationary Points
Rotational Constants
Vibrational Frequencies

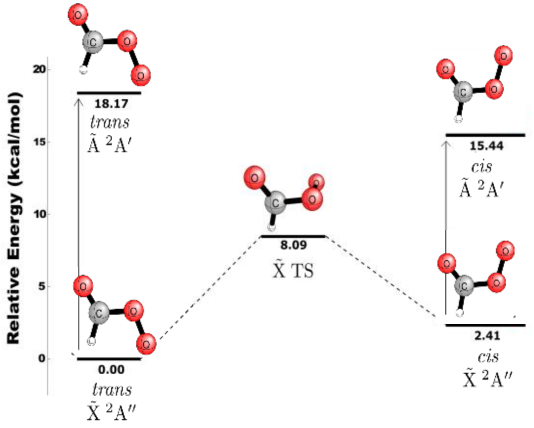
Thermochemistry
Partition Function
Enthalpy
Entropy
Heat Capacity
Gibb's Free Energy

Kinetics
Dividing Surface
Minimum Energy Path
Rate Constant
Branching Ratios
Merging Temperatures

$$k(T) = \kappa \frac{\mathrm{k_B} T}{\mathrm{h}} \frac{Q^{\dagger}}{Q_{reacs}} \exp \frac{\Delta E}{\mathrm{k_B} T}$$

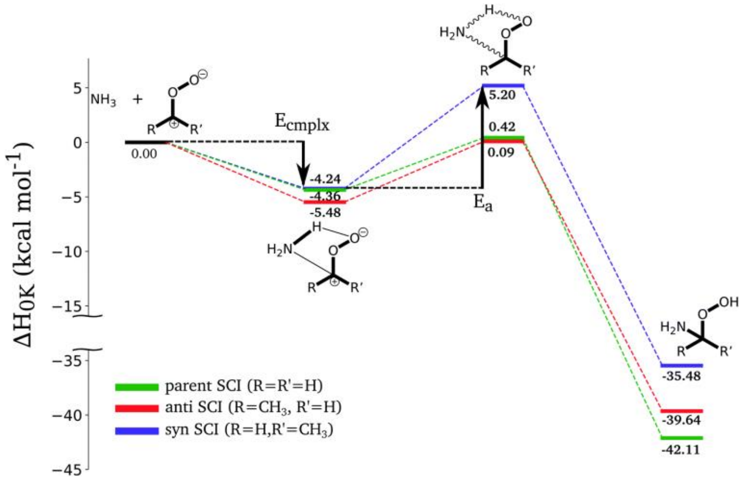
Computational Combustion Chemistry

Formylperoxy Radical



Elliott, S. N.; Turney, J. M; and Schaefer, H. F. 2015. RSC Advances, 5 (130), 107254-107265.

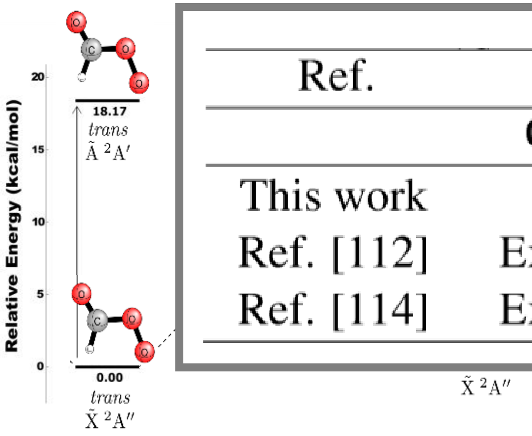
Criegee Intermediates



Misiewicz, J. P.; Elliott, S. N.; Moore, K. B.; Schaefer, H. F. *Phys. Chem. Chem. Phys.* 2018, 20, 7479–7491.

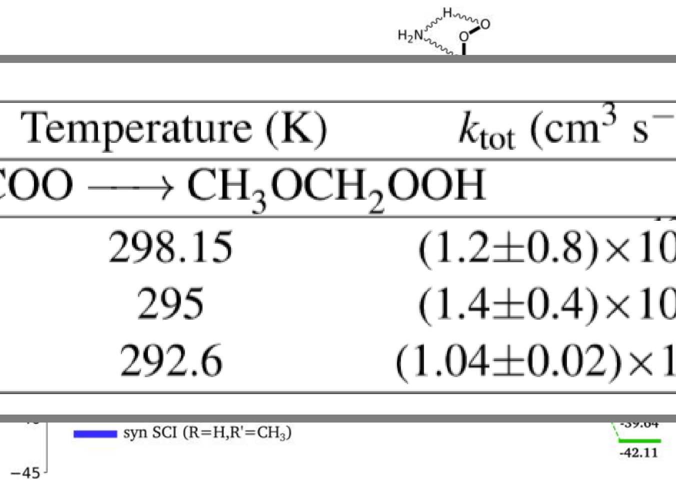
Computational Combustion Chemistry

Formylperoxy Radical



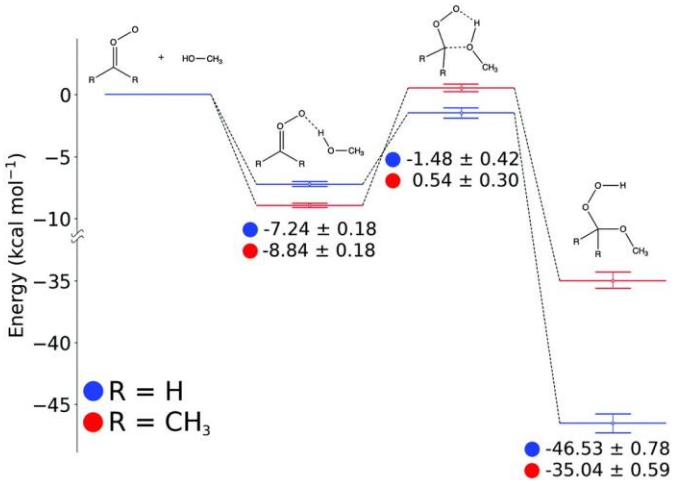
Elliott, S. N.; Turney, J. M; and Schaefer, H. F. 2015. RSC Advances, 5 (130), 107254-107265.

Criegee Intermediates

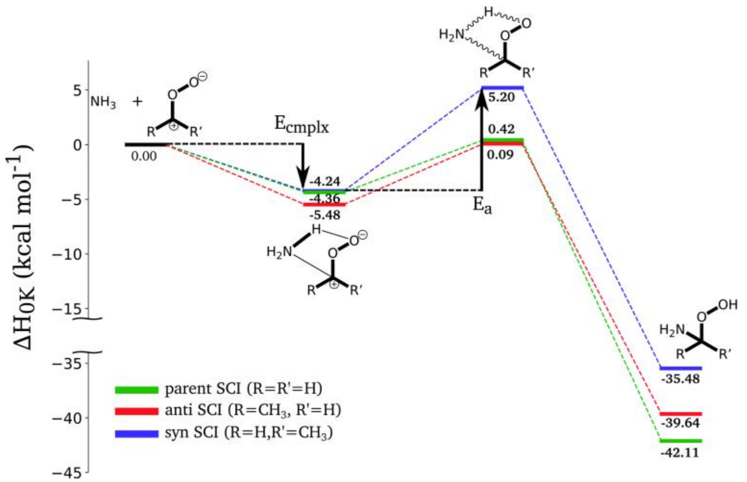


Ref.	Method	Temperature (K)	k_{tot} ($cm^3\ s^{-1}$)
$CH_3OH + H_2COO \longrightarrow CH_3OCH_2OOH$			
This work	1-D HR	298.15	$(1.2\pm0.8)\times10^{-13}$
Ref. [112]	Experimental	295	$(1.4\pm0.4)\times10^{-13}$
Ref. [114]	Experimental	292.6	$(1.04\pm0.02)\times10^{-13}$

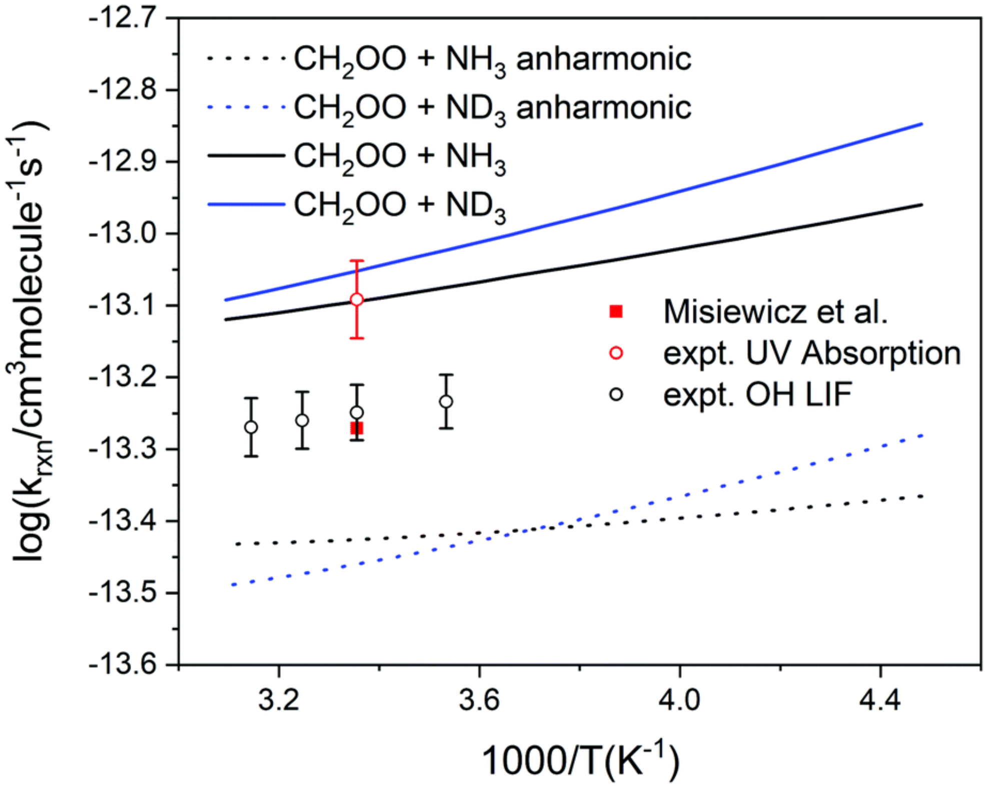
Misiewicz, J. P.; Elliott, S. N.; Moore, K. B.; Schaefer, H. F. *Phys. Chem. Chem. Phys.* 2018, 20, 7479–7491.



Aroeira, G. J. R.; Abbott, A. S.; Elliott, S. N.; Turney, J. M.; Schaefer, H. F. *Phys. Chem. Chem. Phys*. 2019, 21, 17760–17771.



Misiewicz, J. P.; Elliott, S. N.; Moore, K. B.; Schaefer, H. F. *Phys. Chem. Chem. Phys.* 2018, 20, 7479–7491.



Y. Liu, C. Yin, M. C. Smith, S. Liu, M. Chen, X. Zhou, C. Xiao, D. Dai, K. Takahashi, W. Dong, et al., *Phys. Chem. Chem. Phys.* , **2018,** 20(47), 29669–29676

Fundamental Properties

Focal Point Approach

CCSD(T)/cc-pVTZ

High-Level correction ($\Delta_{T(Q)}$)

$\Delta E_{CCSDT(Q)/cc\text{-}pVDZ} - \Delta E_{CCSD(T)/cc\text{-}pVDZ}$

Core correlation effects

CCSD(T)/cc-pCVQZ

X2C-1e scalar relativistic effects

AE-CCSD(T)/cc-pCVTZ

Non-adiabatic effects DBOC

HF/ANO0

Zero point vibrational energy

CCSD(T)/ANO1, CCSD(T)/ANO0

SCF	MP2	CCSD	CCSD(T)
cc-pVDZ	cc-pVDZ	cc-pVDZ	cc-pVDZ
cc-pVTZ	cc-pVTZ	cc-pVTZ	cc-pVTZ
cc-pVQZ	cc-pVQZ	cc-pVQZ	cc-pVQZ
CBS	CBS	CBS	CBS

Anharmonic Effects (VPT2)

CCSD(T)/ANO0

Orbit Relaxation Effects (Brueckner)

CCSD(T)/ANO0

Fermi Resonance

Nielson procedure

Partition functions

$$Q(T) = \sum_i \exp(\frac{\epsilon_i}{k_B T})$$

Rigid Rotor
Harmonic
Oscillator

$$Q = Q_T Q_R Q_V Q_E$$

$$E_n = h\nu(n + \frac{1}{2})$$

$$Q_{vib} = \prod_{i=1}^{Nvib} \frac{\exp\left(-\frac{h\nu_i}{2k_b T}\right)}{1 - \exp\left(-\frac{h\nu_i}{k_b T}\right)}$$

Partition functions

$$Q(T) = \sum_i \exp(\frac{\epsilon_i}{k_B T})$$

Rigid Rotor
Harmonic
Oscillator

$$Q = Q_T Q_R Q_V Q_E$$

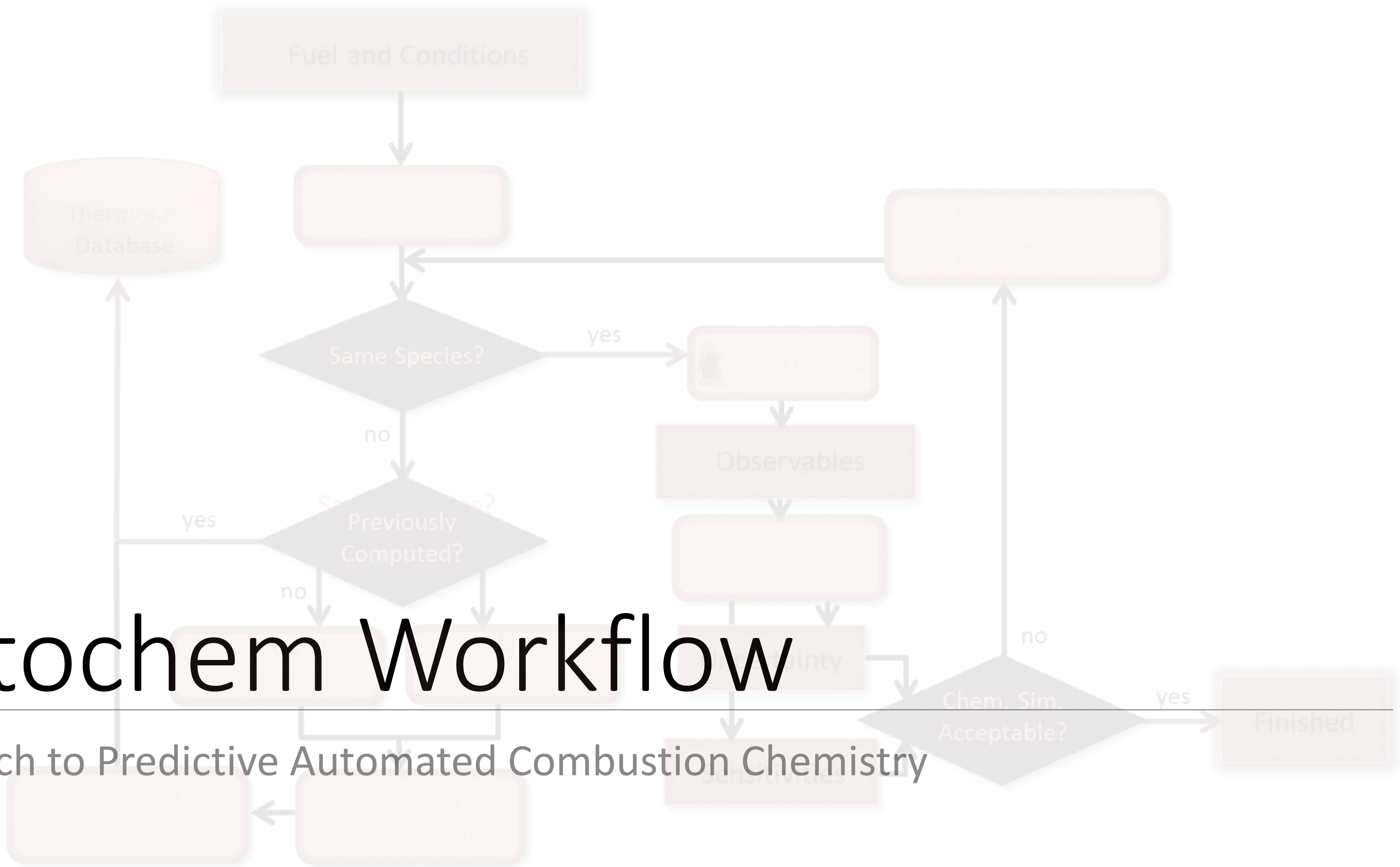
$$E_n = h\nu(n + \frac{1}{2})$$

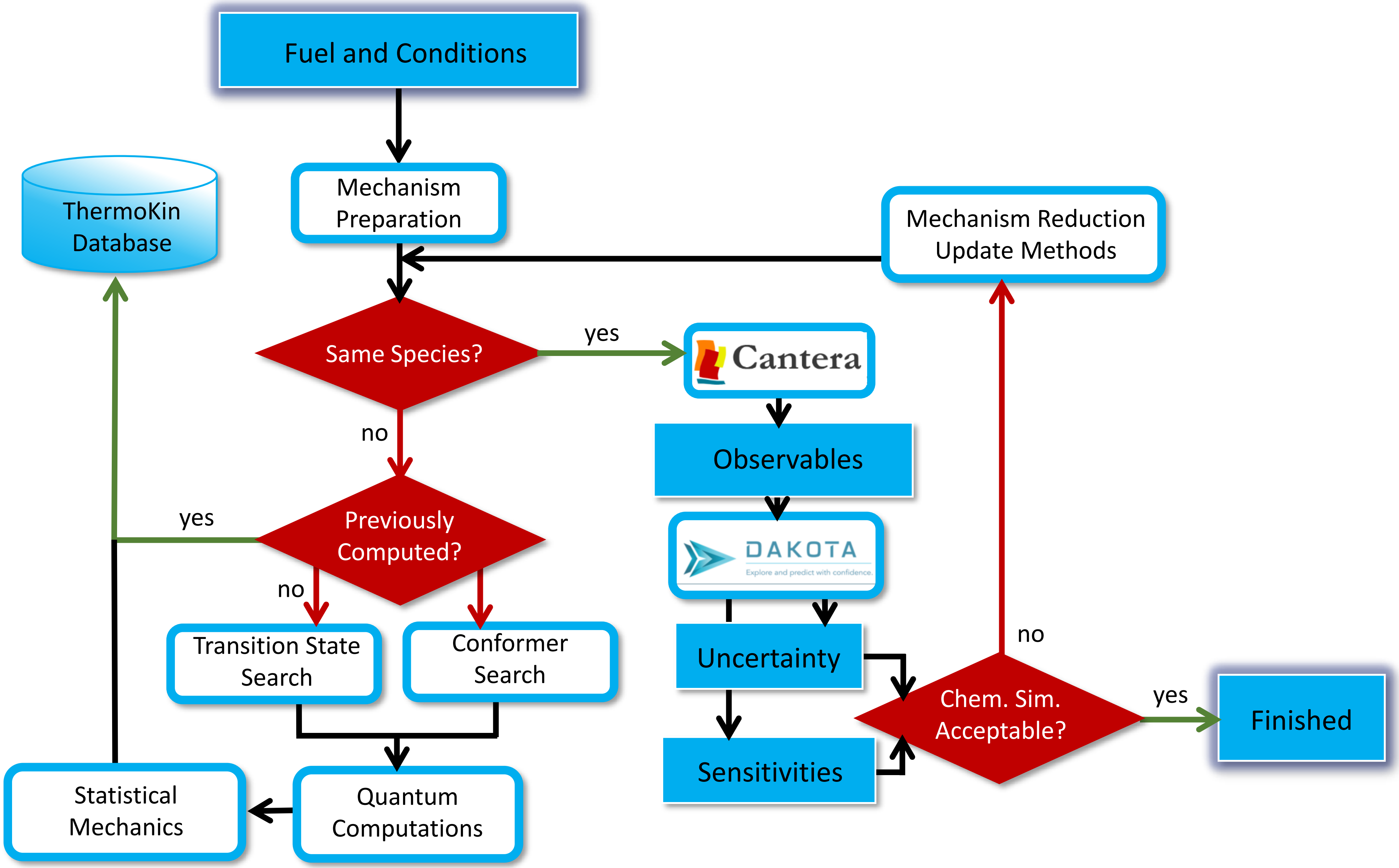
$$Q_{vib} = \prod_{i=1}^{Nvib} \frac{\exp\left(-\frac{h\nu_i}{2k_b T}\right)}{1 - \exp\left(-\frac{h\nu_i}{k_b T}\right)}$$

$$Q = \int d\phi \exp(-\frac{V(\phi)}{k_B T})$$

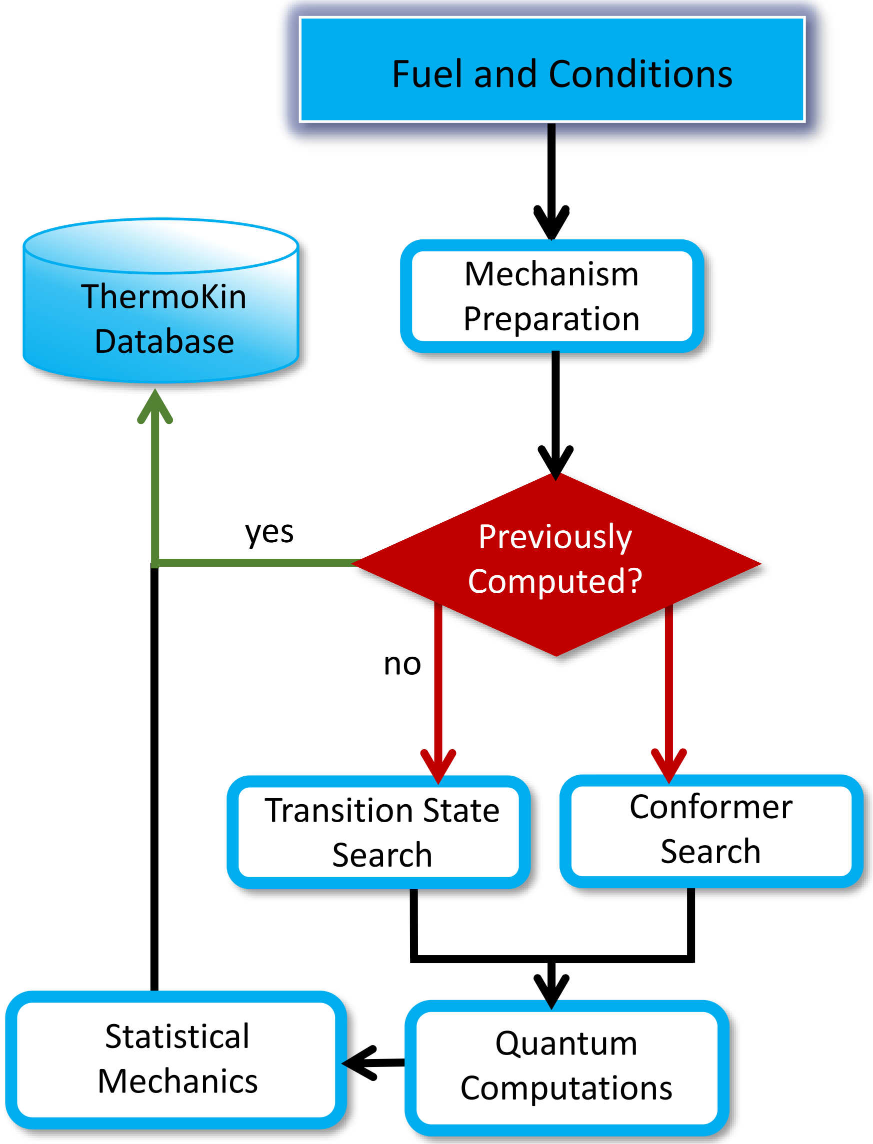
Autochem Workflow

Approach to Predictive Automated Combustion Chemistry



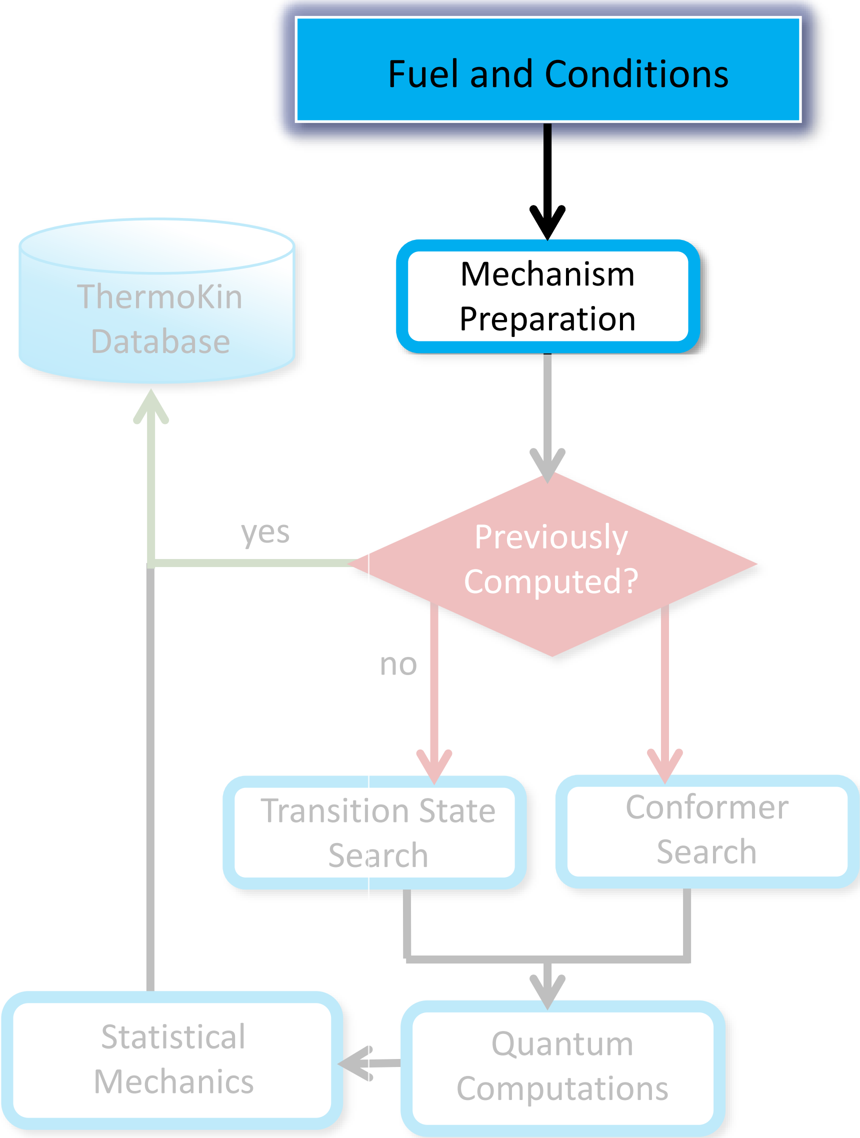


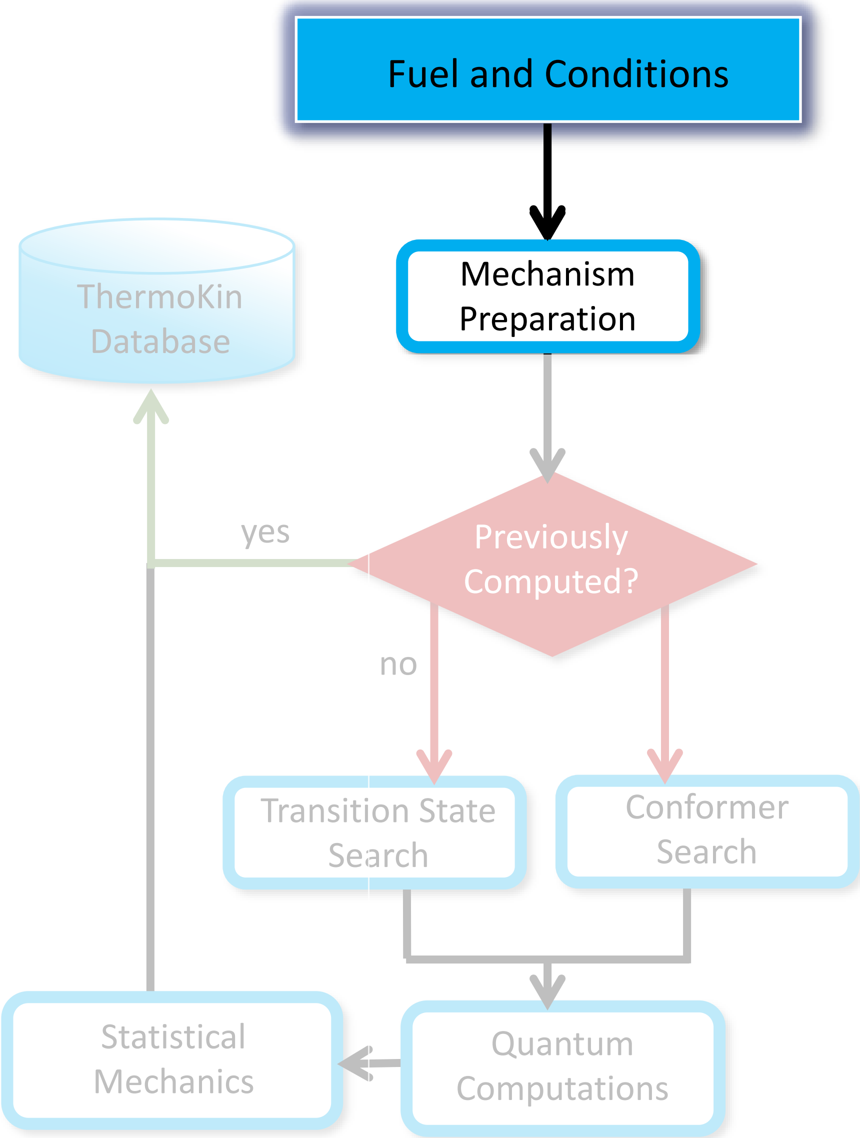
Fuel and Conditions
Mechanism Preparation
ThermoKin Database
Mechanism Reduction Update Methods
Same Species?
yes
Cantera
no
Observables
yes
Previously Computed?
DAKOTA
Explore and predict with confidence.
no
Transition State Search
Conformer Search
Uncertainty
no
Chem. Sim. Acceptable?
yes
Finished
Sensitivities
Statistical Mechanics
Quantum Computations



Overview

Identify all reactions and, for each, build partition functions for all involved species by optimizing their geometries and computing their electronic and vibrational energy levels and use the partition functions to compute thermochemical properties and rate constants


Fuel and Conditions
Mechanism Preparation
ThermoKin Database
yes
Previously Computed?
no
Transition State Search
Conformer Search
Statistical Mechanics
Quantum Computations

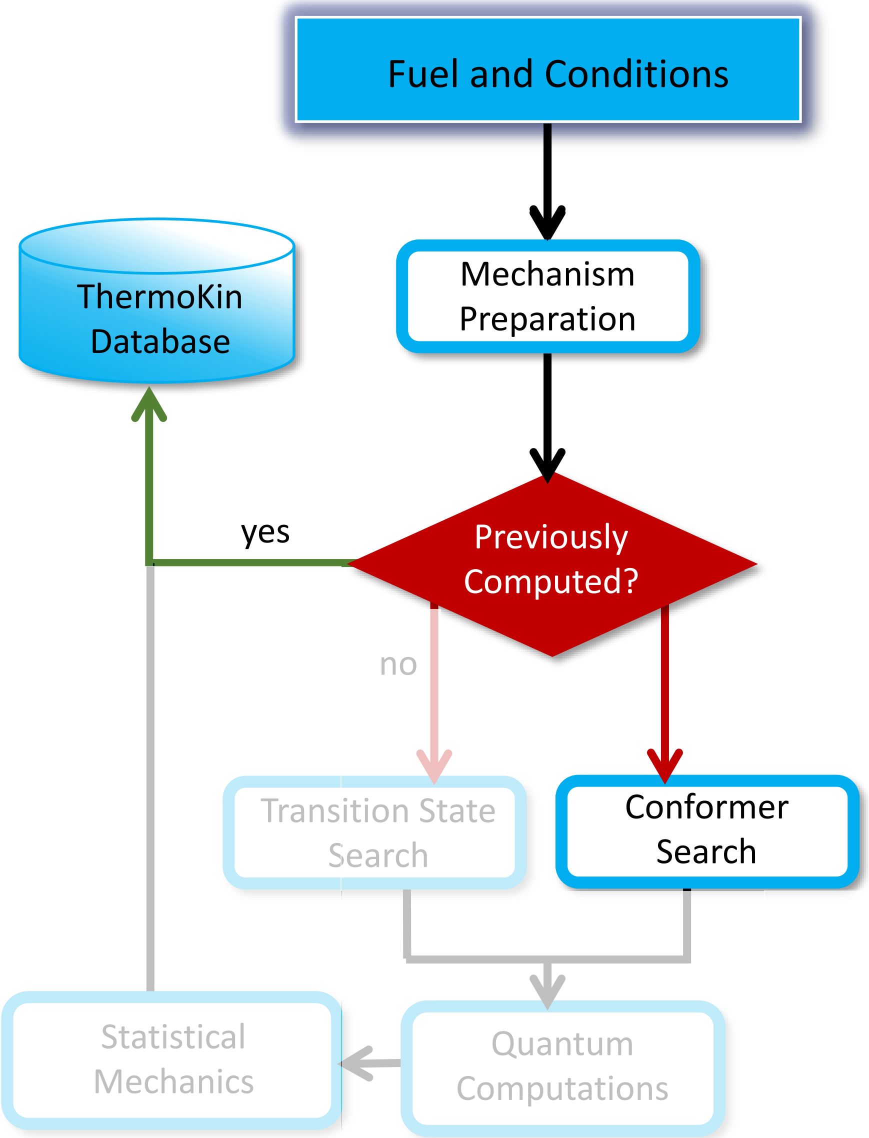


Obtaining a list of species and reactions

RMG	Full Species and Reaction list
Automol	Reaction list from species list
MechAnalyzer	Group into PES, stereochemistry

https://github.com/ReactionMechanismGenerator/RMG-Py
https://github.com/Auto-Mech/automol

Establishing preliminary geometries



OpenBabel

X2Z

Elstruct

EStokTP

Classical Force Fields

Coordinate Transformation

Monte Carlo DFT Geometry Optimization

Hindered Rotor Scan (1D or MD)

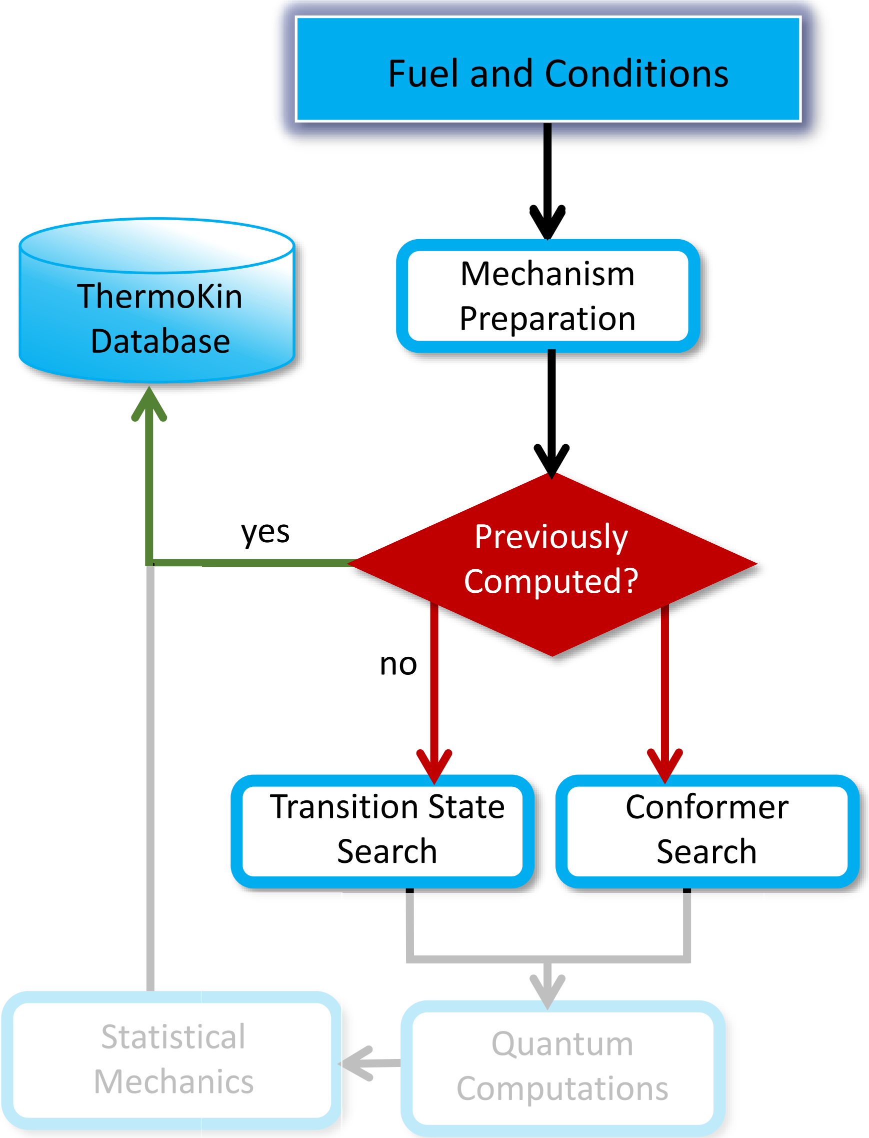
https://github.com/openbabel

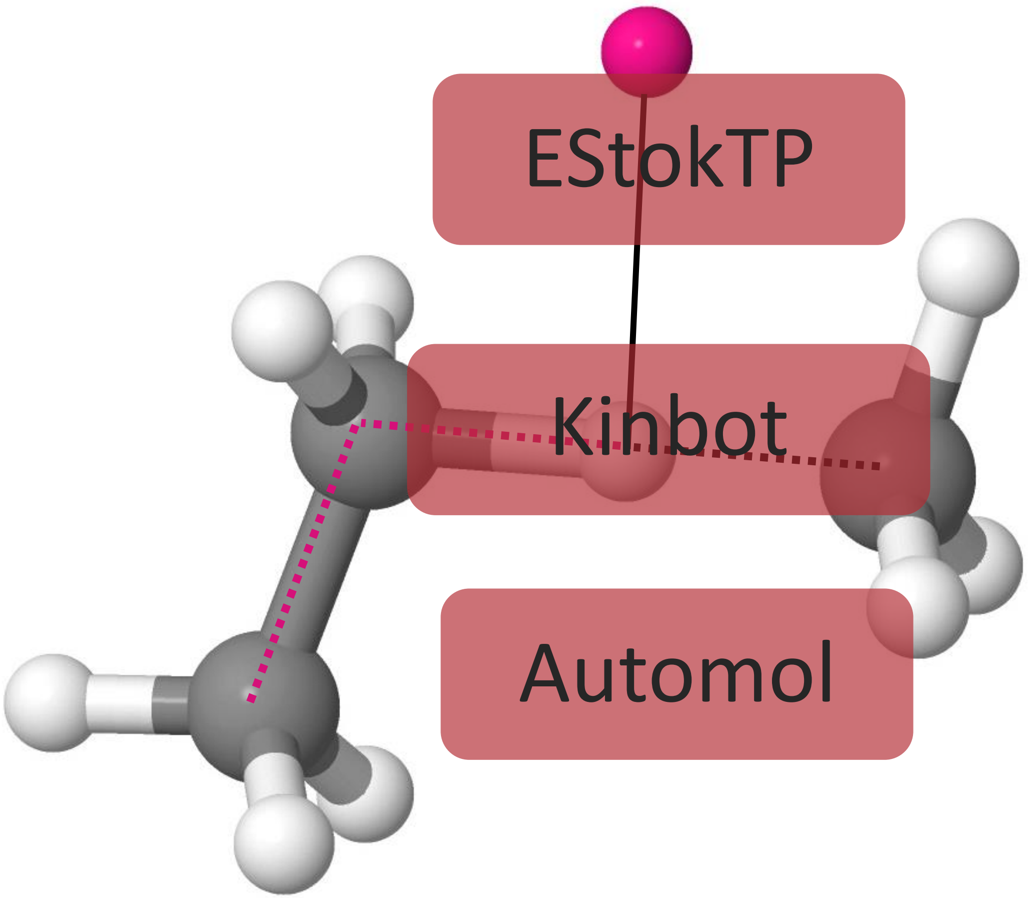
https://github.com/Auto-Mech/X2Z

https://github.com/Auto-Mech/EStokTP

https://github.com/Auto-Mech/automol

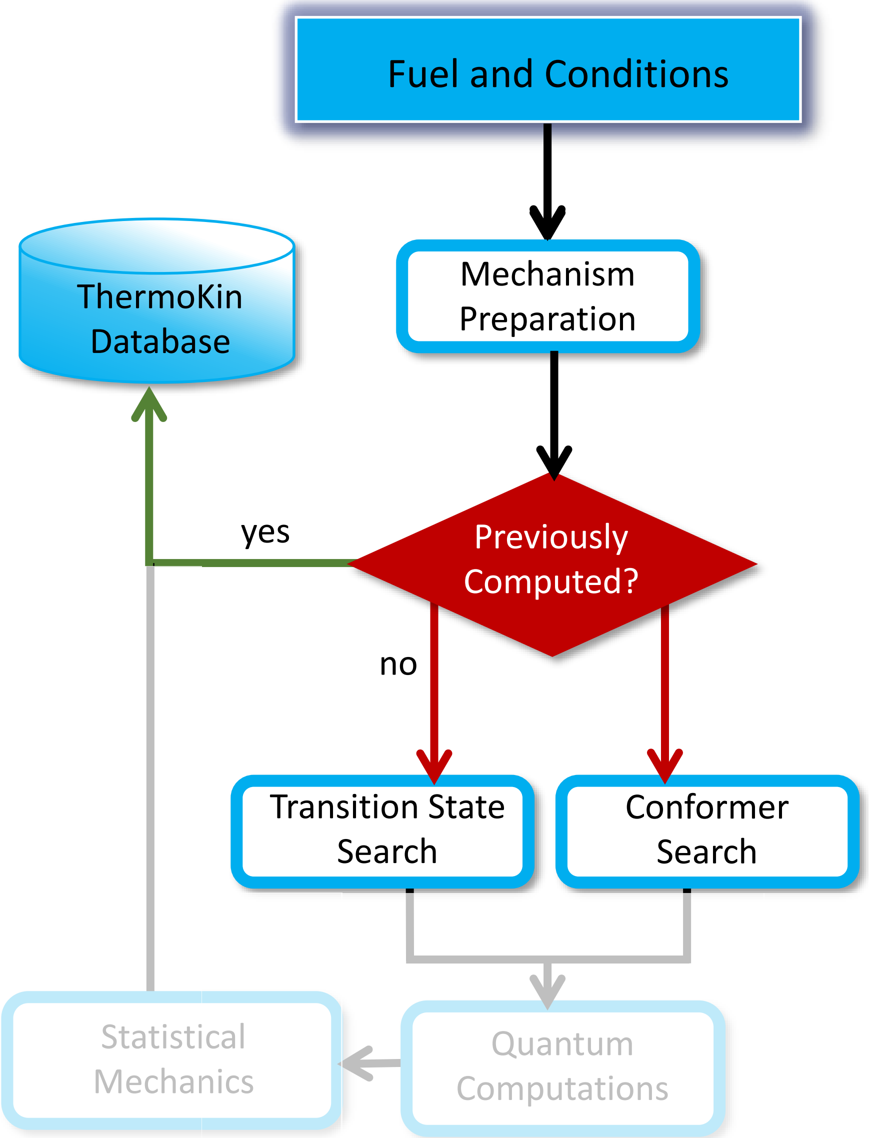
Search for Transition States





https://github.com/Auto-Mech/EStokTP

https://github.com/PACChem/KinBot



List of Species

.
.
.

HCO

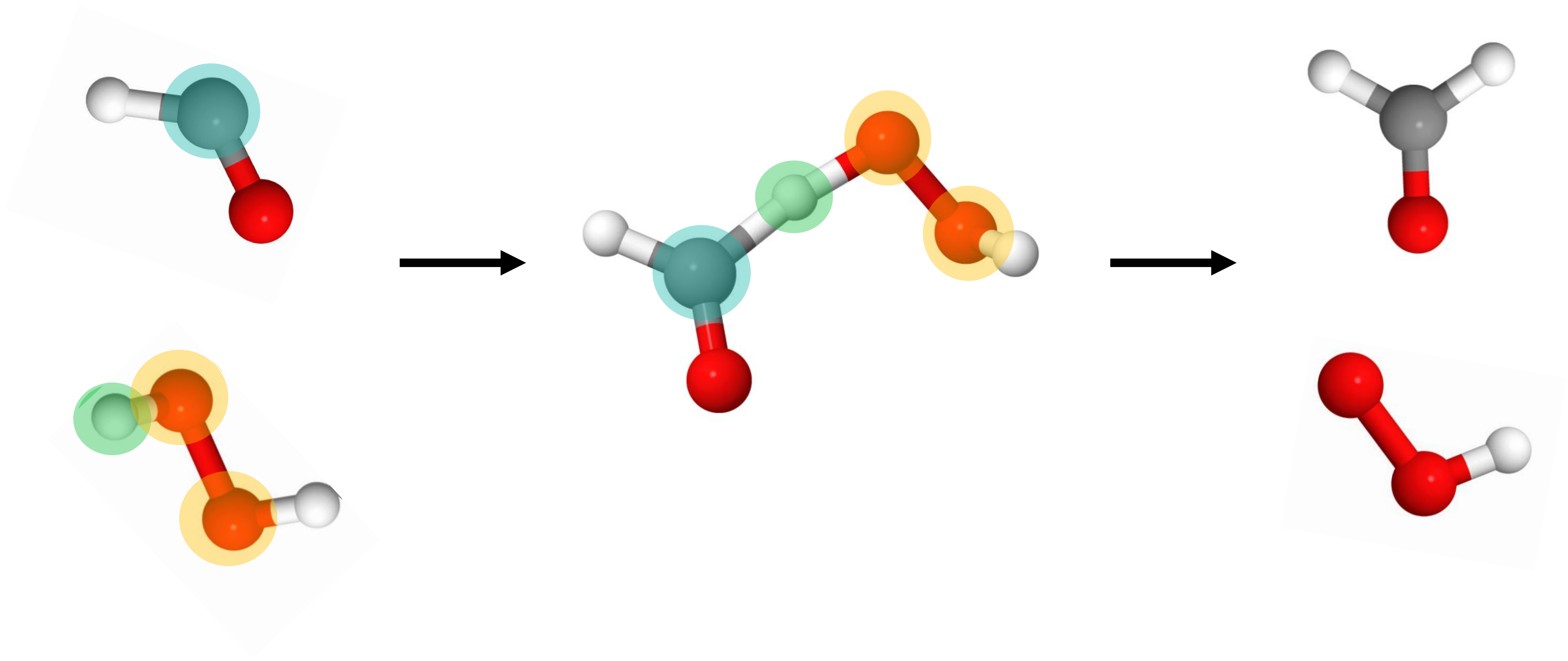
HOOH

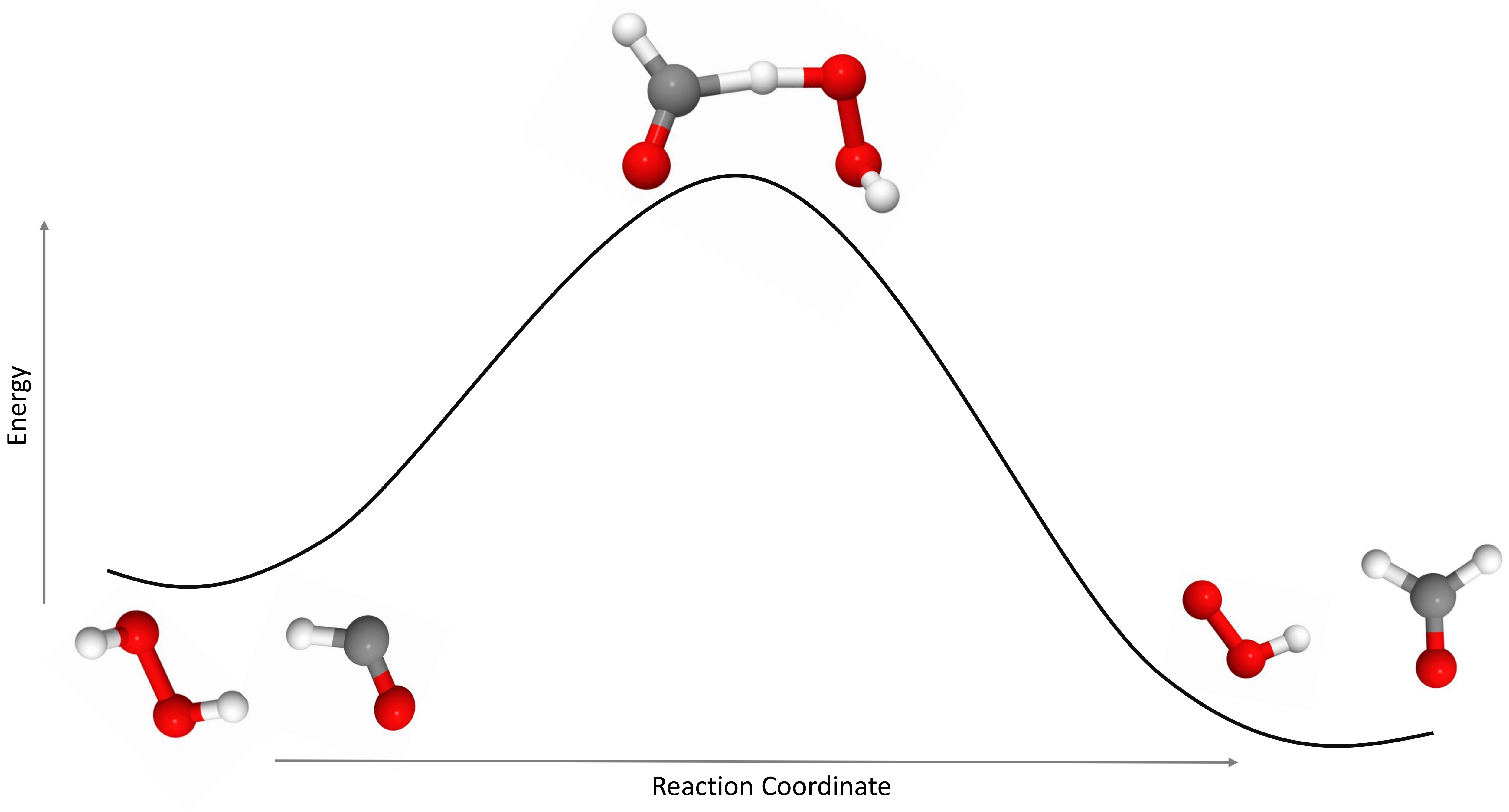
H_2CO

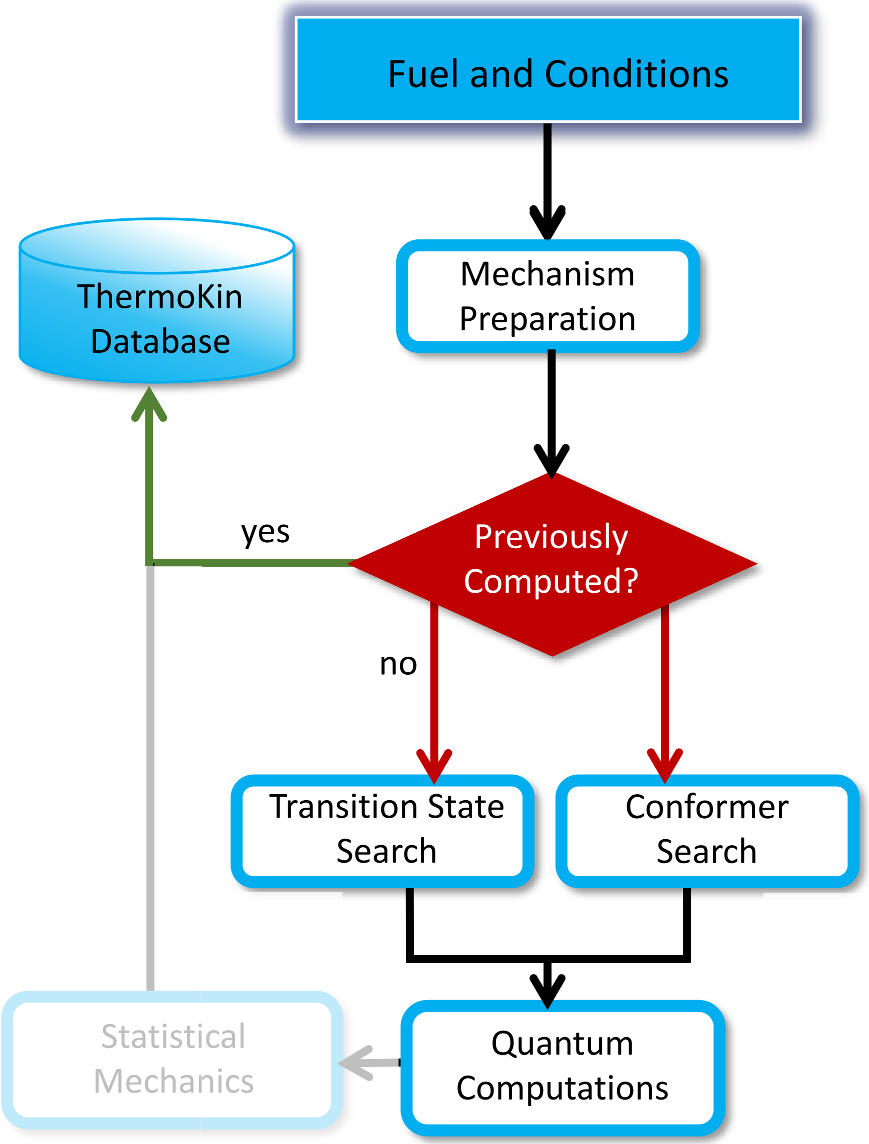
OOH

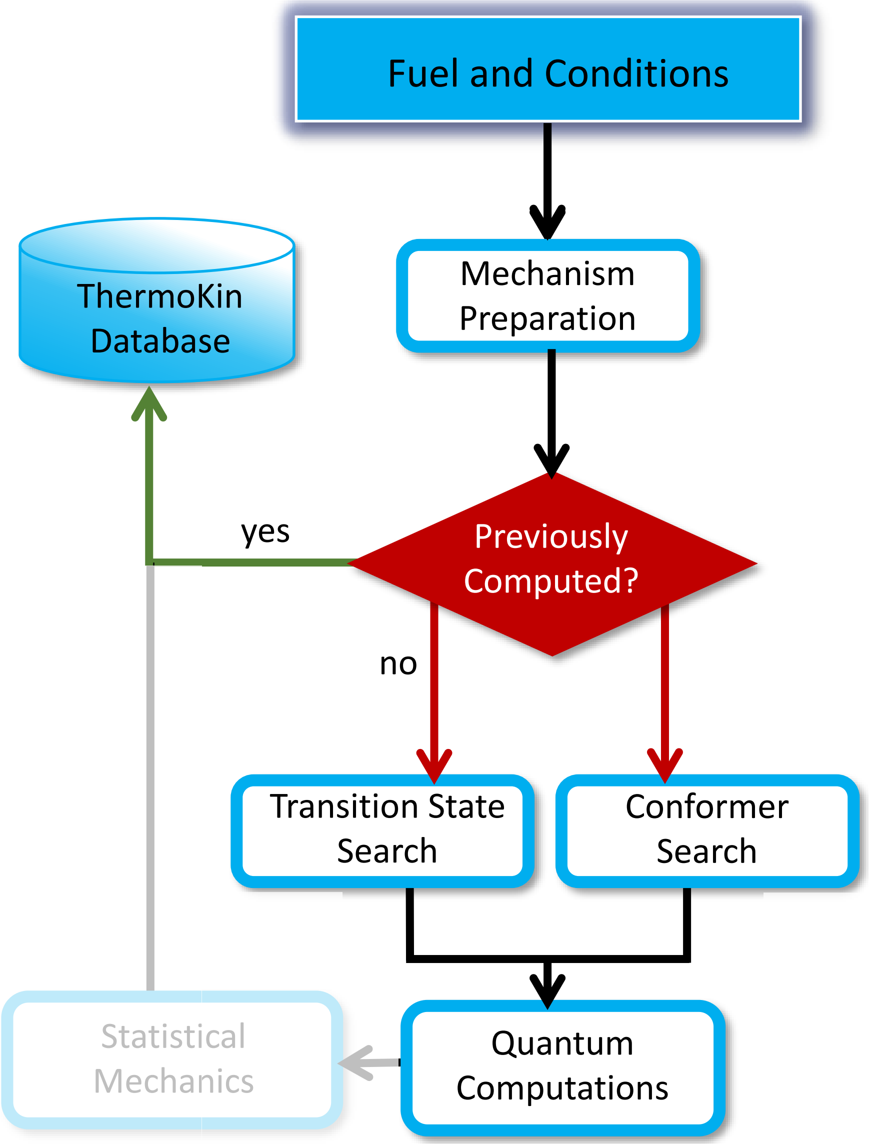
.
.
.

Reactants				**Products**
HCO				H_2CO
	$\longrightarrow$	?	$\longrightarrow$	
$HOOH$				OOH



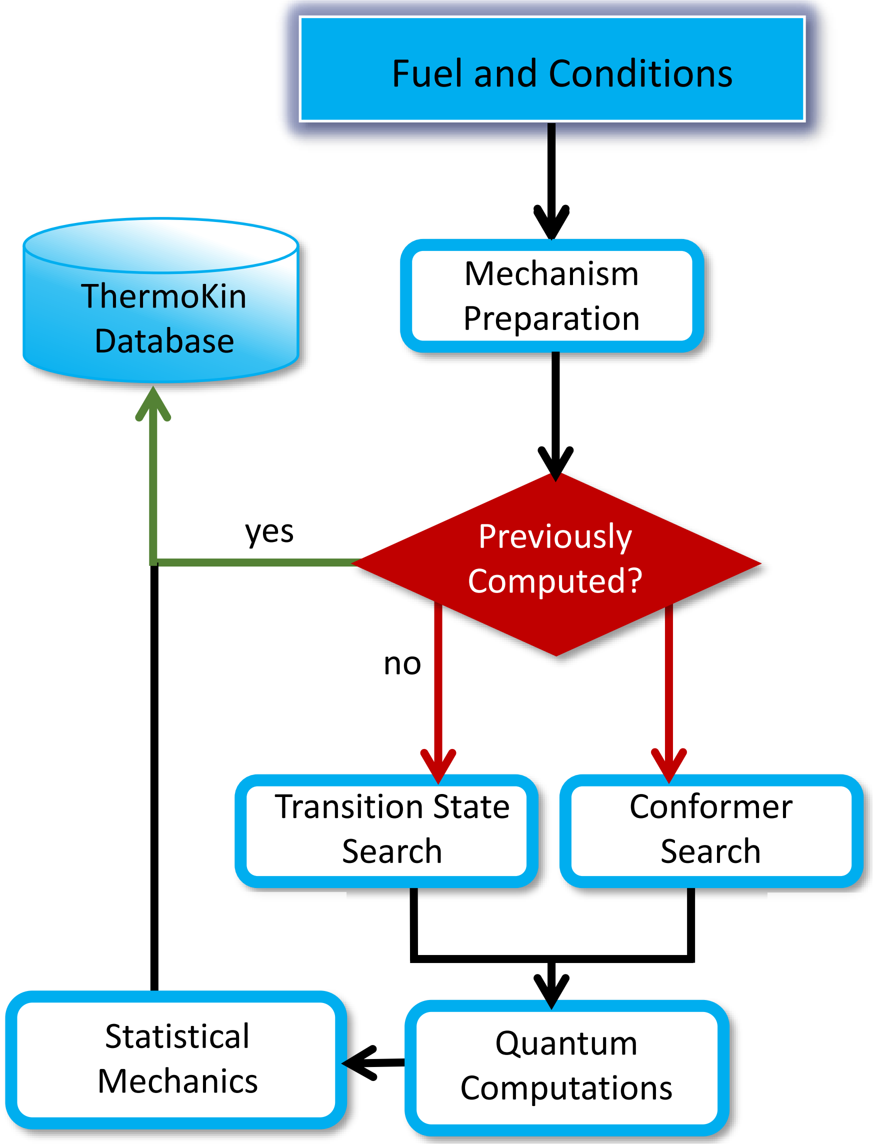

Energy
Reaction Coordinate


Fuel and Conditions
ThermoKin Database
Mechanism Preparation
yes
Previously Computed?
no
Transition State Search
Conformer Search
Statistical Mechanics
Quantum Computations



Remaining Quantum Computations

- HL Optimization and Frequencies
- Composite Energy
- Anharmonics
- HL Torsional Energy Profiles
- Failure Recovery
- Locate VDW
- IRC
- Variational TST search
- Variable Reactant Coordinate TST
- MD Tunneling



Statistical Mechanics Calculations

Thermochemistry

RRHO

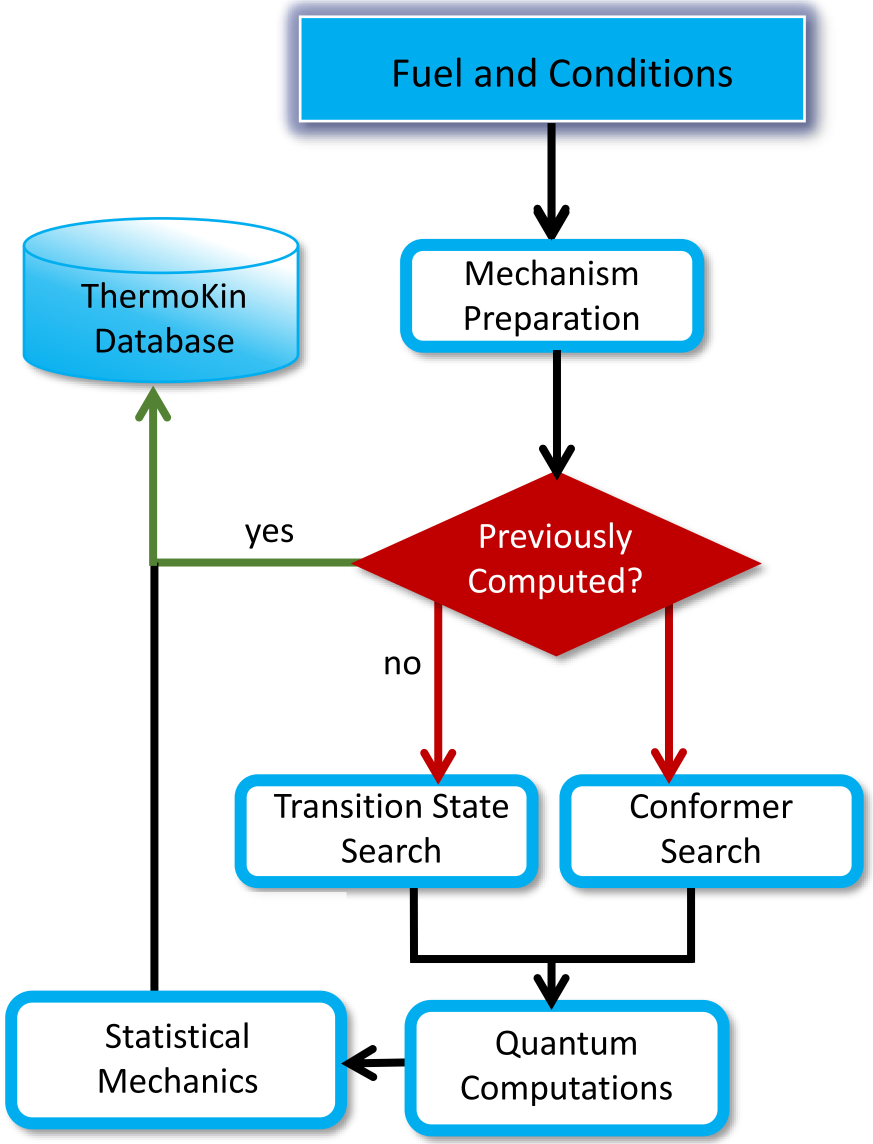
MESS

Solve PF with 1D or MD Torsions, Anharmonicities, Umbrella Modes

PAC99

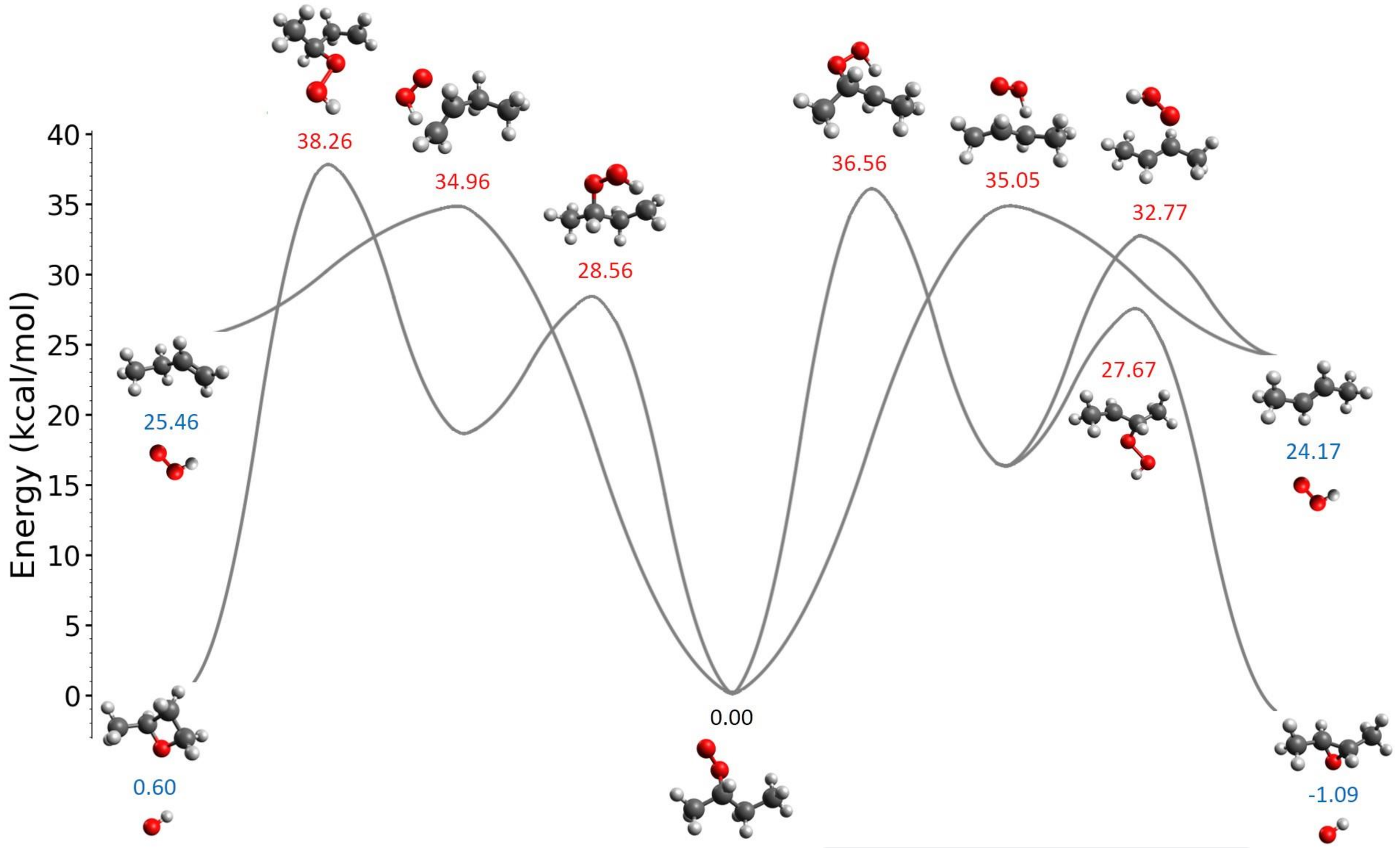
Conversion to NASA Polynomials

https://github.com/Auto-Mech/MESS

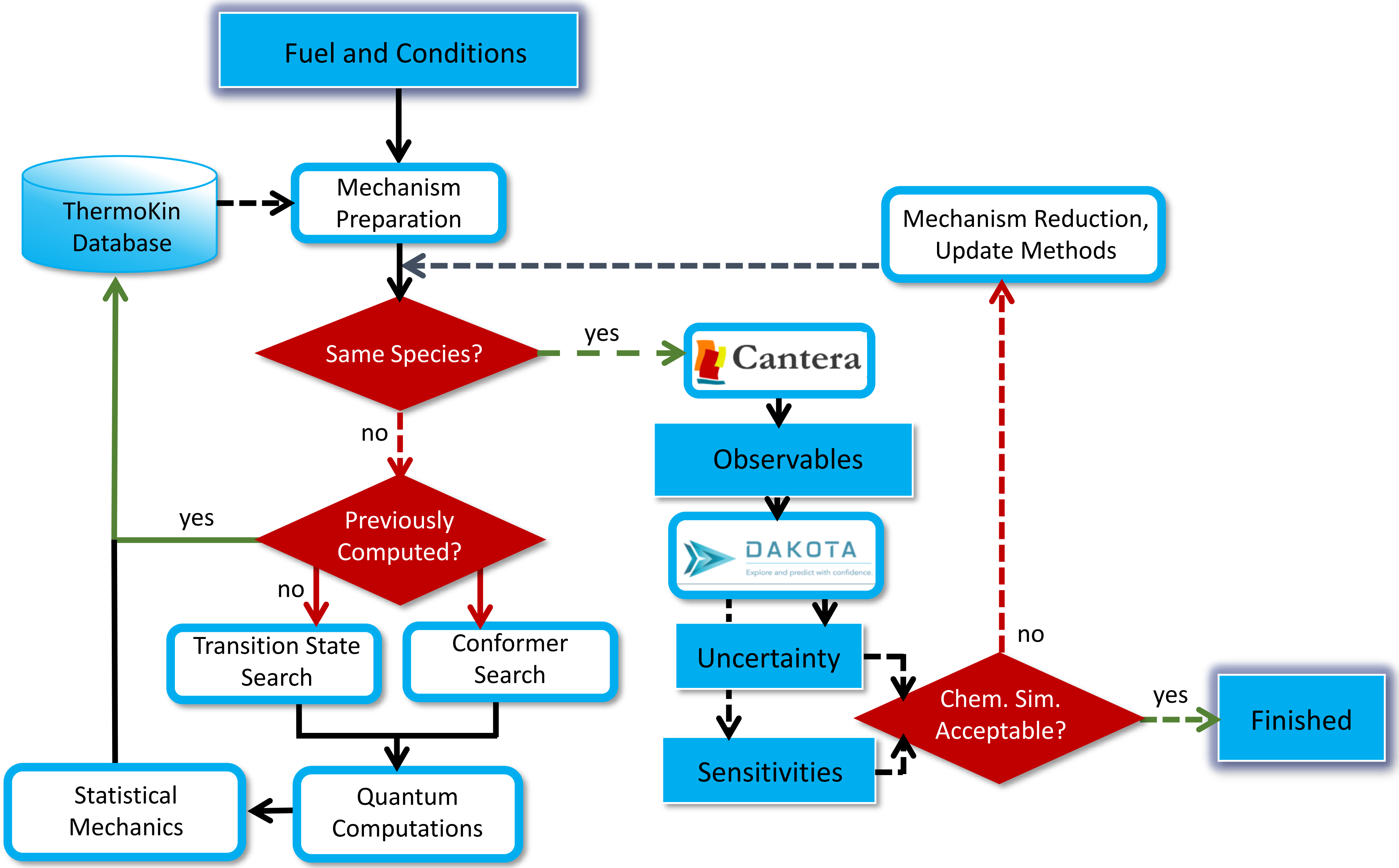


Statistical Mechanics Calculations

Kinetics

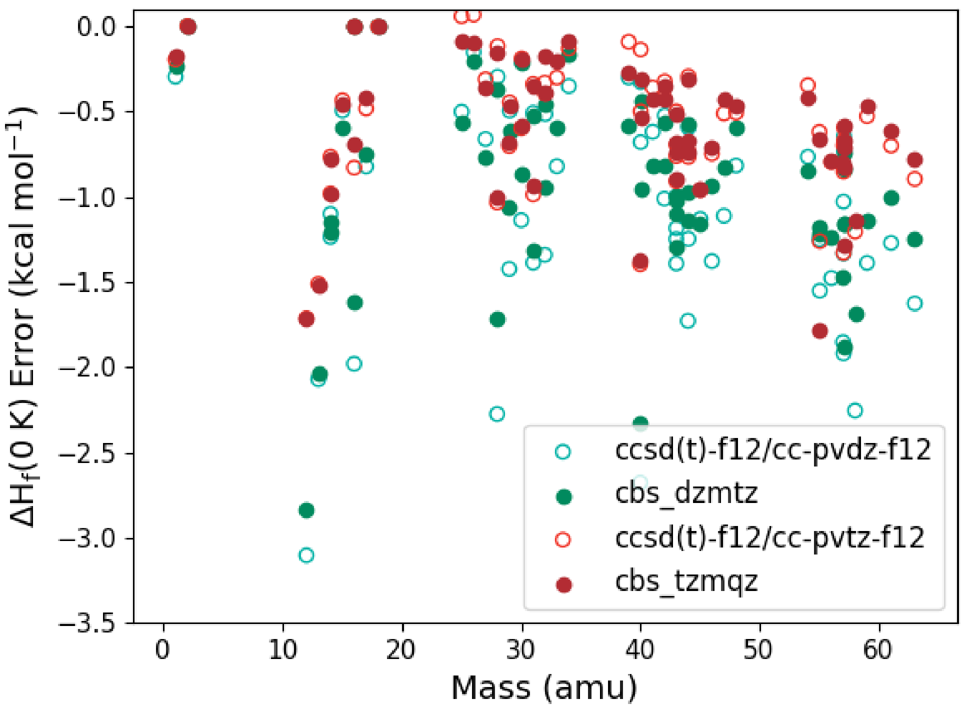


https://github.com/AutoMech/1DMin
https://github.com/AutoMech/MESS


Fuel and Conditions
ThermoKin Database
Mechanism Preparation
Mechanism Reduction, Update Methods
Same Species?
yes
Cantera
no
Observables
yes
Previously Computed?
DAKOTA
Explore and predict with confidence.
no
Transition State Search
Conformer Search
Uncertainty
no
Chem. Sim. Acceptable?
yes
Finished
Sensitivities
Statistical Mechanics
Quantum Computations

Butane Oxidation

- RMG predicted 173 relevant species
- Thermochemical information for 95% of these
- This took ~10^5 CPU hours
- Partition Functions computed with
  - MC (5 * $3^{\mathrm{Nnonmethyl}}$): ωB97X-D/6-31G*
  - 1D Hindered Rotor Scan: M06-2X/cc-pVTZ
  - Geometry: B2PLYPD3/cc-pVTZ
  - Harmonic Frequencies: B2PLYPD3/cc-pVTZ
  - Energy Schemes:



○ CCSD(T)-F12/cc-pVDZ-F12
● **cbs_dzmtz:** CCSD(T)-F12/cc-pVDZ-F12 + MP2/cc-pVTZ-F12 – MP2/cc-pVDZ-F12
○ CCSD(T)-F12/cc-pVTZ-F12
● **cbs_tzmqz:** CCSD(T)-F12/cc-pVTZ-F12 + MP2/cc-pVQZ-F12 – MP2/cc-pVTZ-F12

Keçeli, M.; Elliott, S. N.; Li, Y.-P.; Johnson, M. S.; Cavallotti, C.; Georgievskii, Y.; Green, W. H.; Pelucchi, M.; Wozniak, J. M.; Jasper, A. W., et al. Proceedings of the Combustion Institute 2018, 37, 363–371

Core Combustion Species

- Base mechanism: H_2/O_2
- Core mechanism: C3 hydrocarbons and oxygenated C2 hydrocarbons
- Nitrogen will extend applications to NOx formation

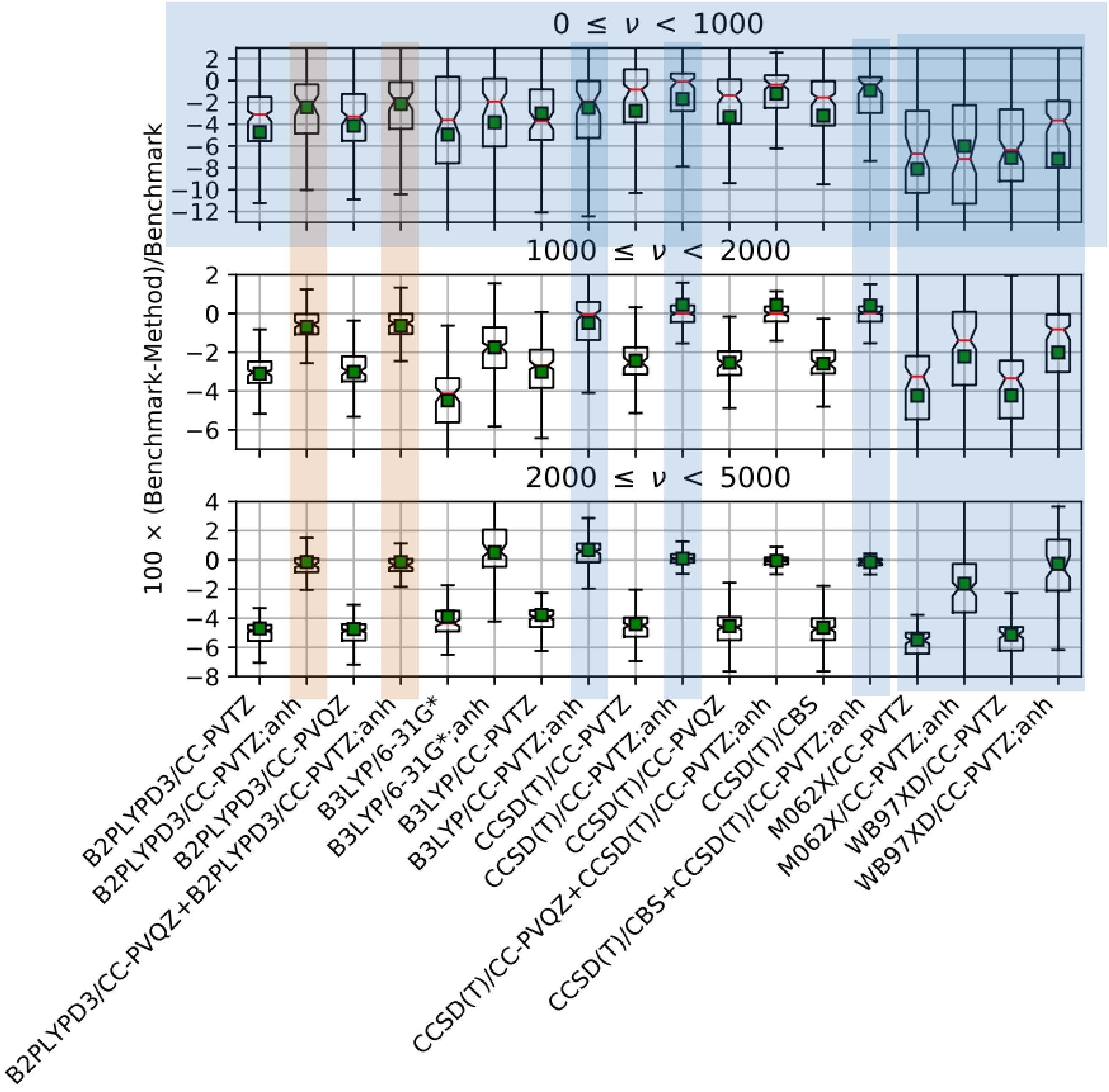
- ANL0 -- 348 species with 34 or fewer electrons with atoms C, N, O, H
- ANL1 -- 150 species with 22 or fewer electrons with atoms C, N, O, H

Sensitivity Analysis

- Geometries, harmonic, and anharmonic frequencies for ANL1 with:
  - B3LYP/6-31g*
  - B3LYP/cc-pVTZ
  - ωb97x-D/cc-pVTZ
  - M06-2X/cc-pVTZ
  - B2PLYP-D3/cc-pVTZ
  - CCSD(T)/cc-pVTZ
  - B2PLYP-D3/cc-pVQZ
  - CCSD(T)/cc-pVQZ
- Sensitivity of rotational constants, vibrational frequencies, and electronic energies

Experimental Frequencies

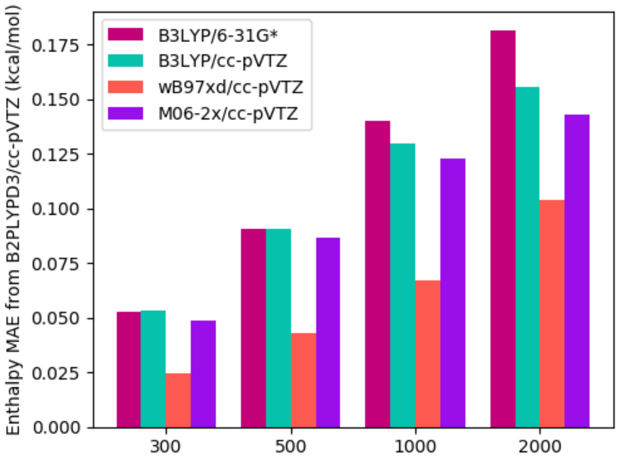
Percentage errors in harmonic and anharmonic frequencies from various methods relative to **experiment**. The red horizontal lines within each box represent the median error, the green squares represent the mean error, and the grey open circles represent outlying data points. The lower and upper edges of the box represent the 25th (Q1) and 75th (Q3) percentiles of the data. The upper and lower whiskers represent outlier rejection limits, respectively defined as Q1−1.5 ×IQR (lower limit), and Q3 + 1.5×IQR (upper limit)

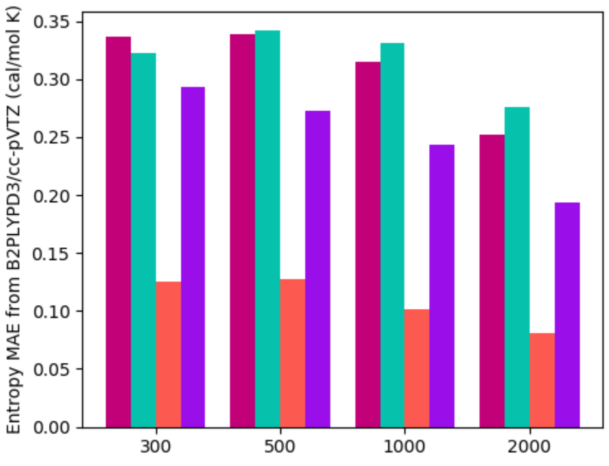


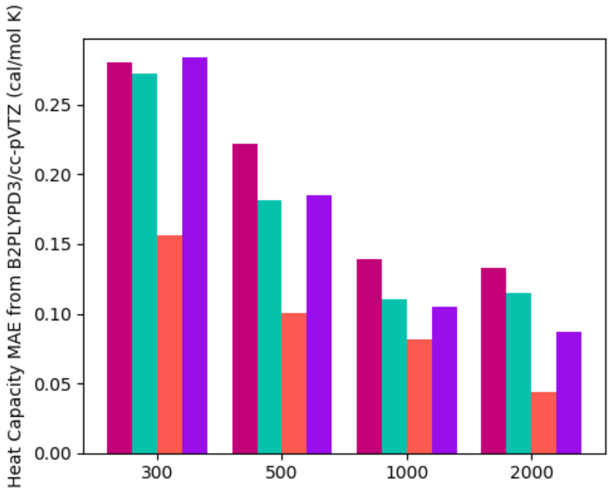
Thermochemistry

$Q_{RRHO + 1D}$

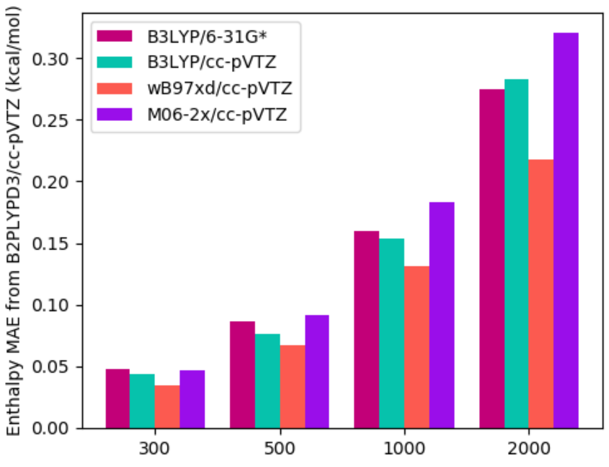
with various 1D energy profiles

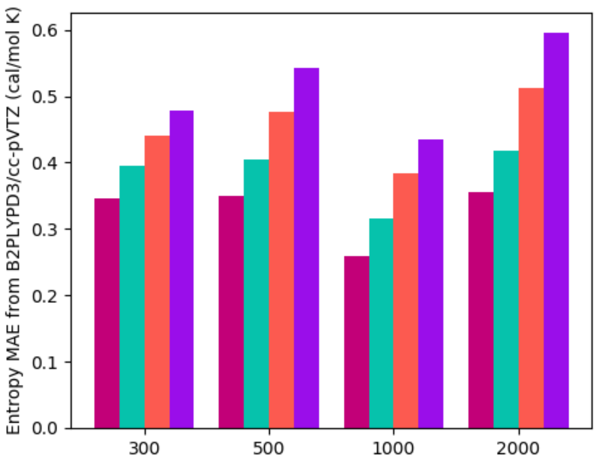


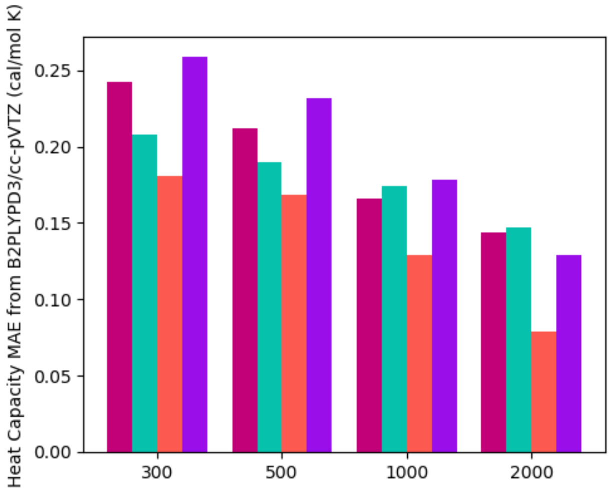




with various rotational constants, frequencies, and 1D energy profiles

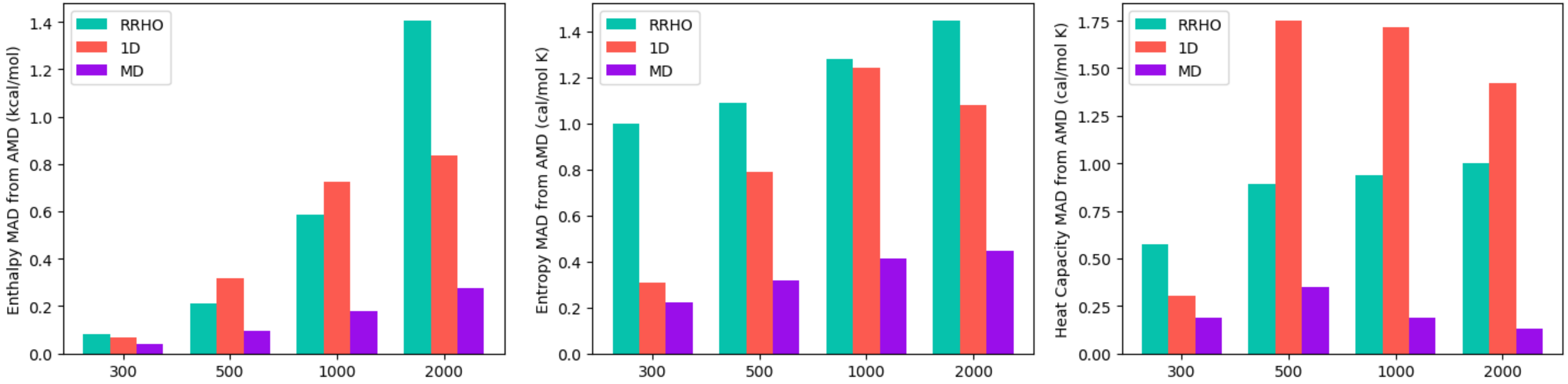




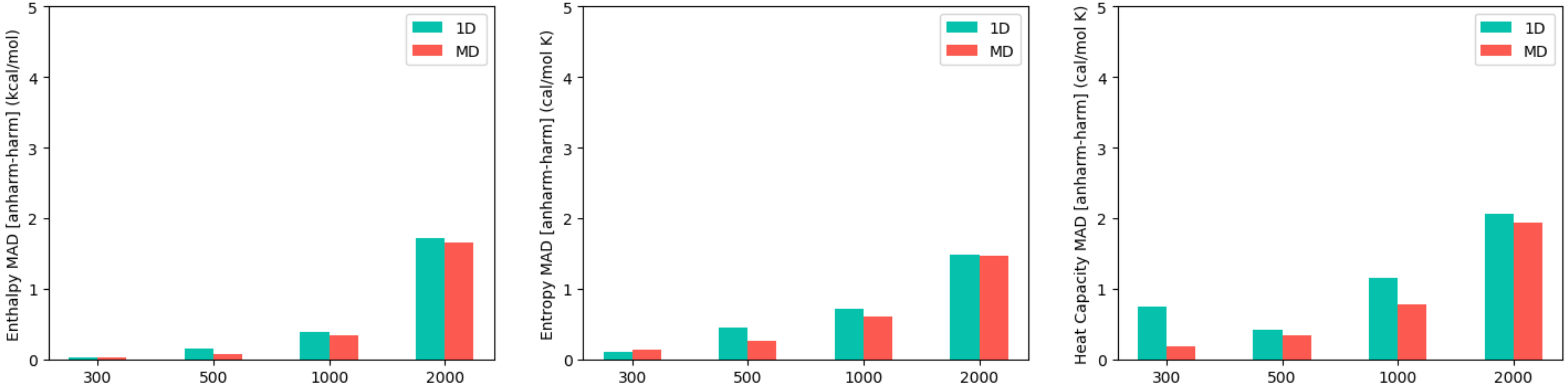


Thermochemistry

with various hindered rotor treatment

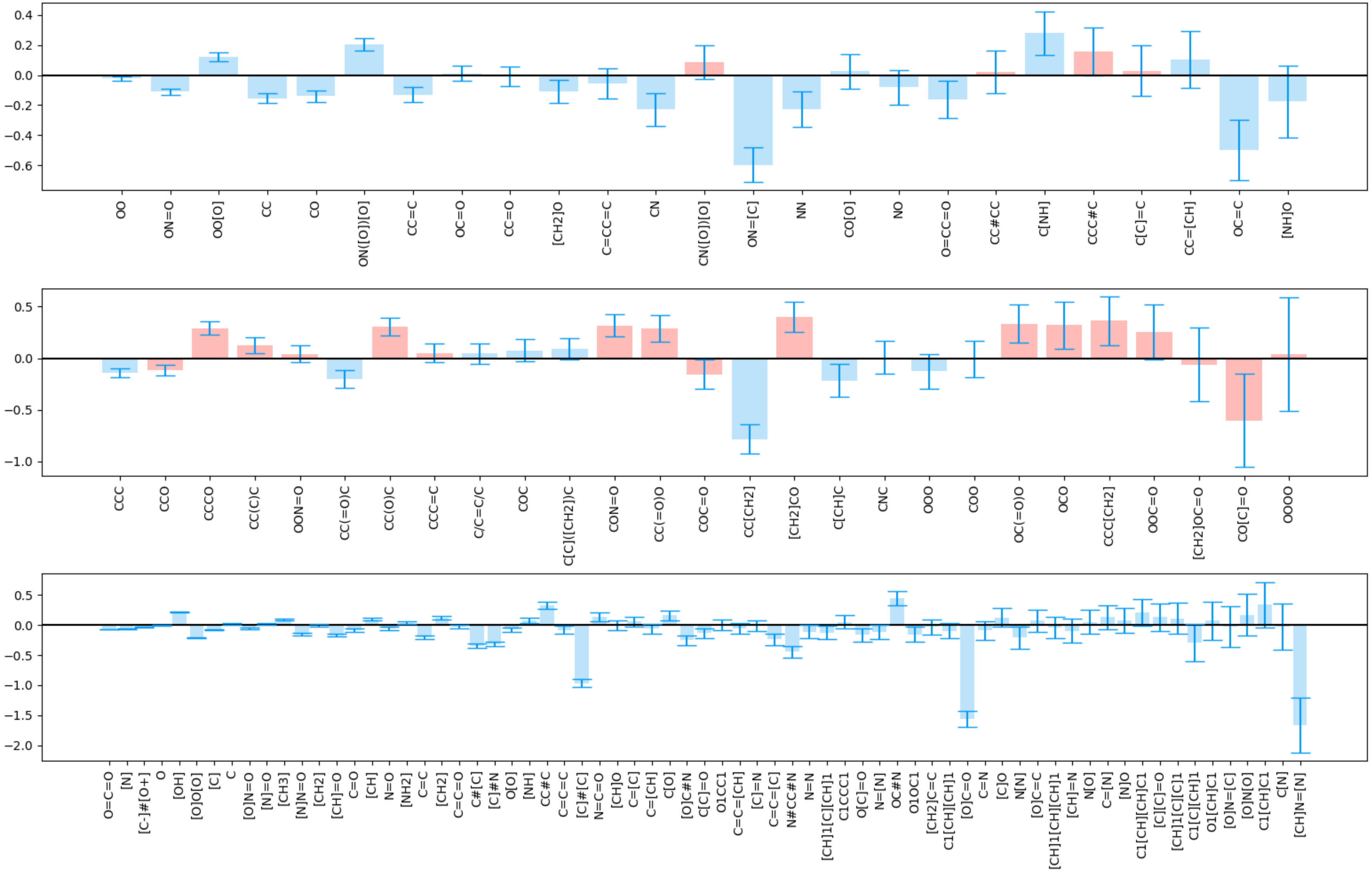


with harmonic or anharmonic treatment



Reliability

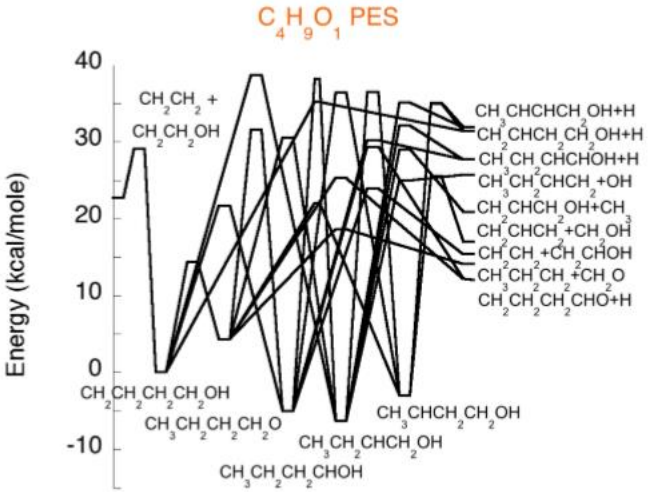
Difference in computed 298 K heats of formation and values in ATcT database

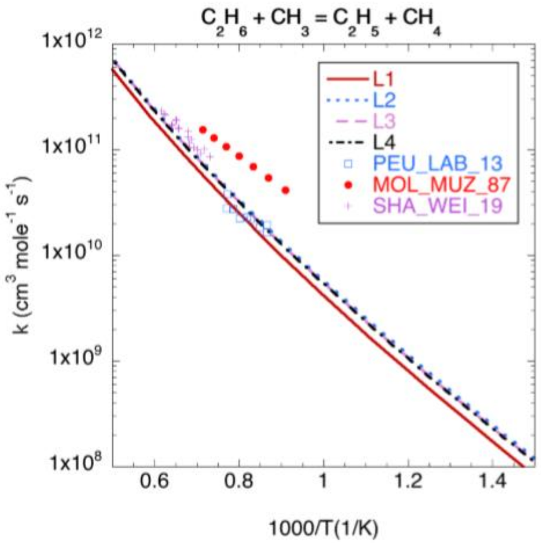


Ruscic, B.; Pinzon, R. E.; von Laszewski, G.; Kodeboyina, D.; Burcat, A.; Leahy, D.; Montoy, D.; Wagner, A. F. J. Phys.: Conference Series 2005, 16, 561–570.

Kinetics – Pyrolysis

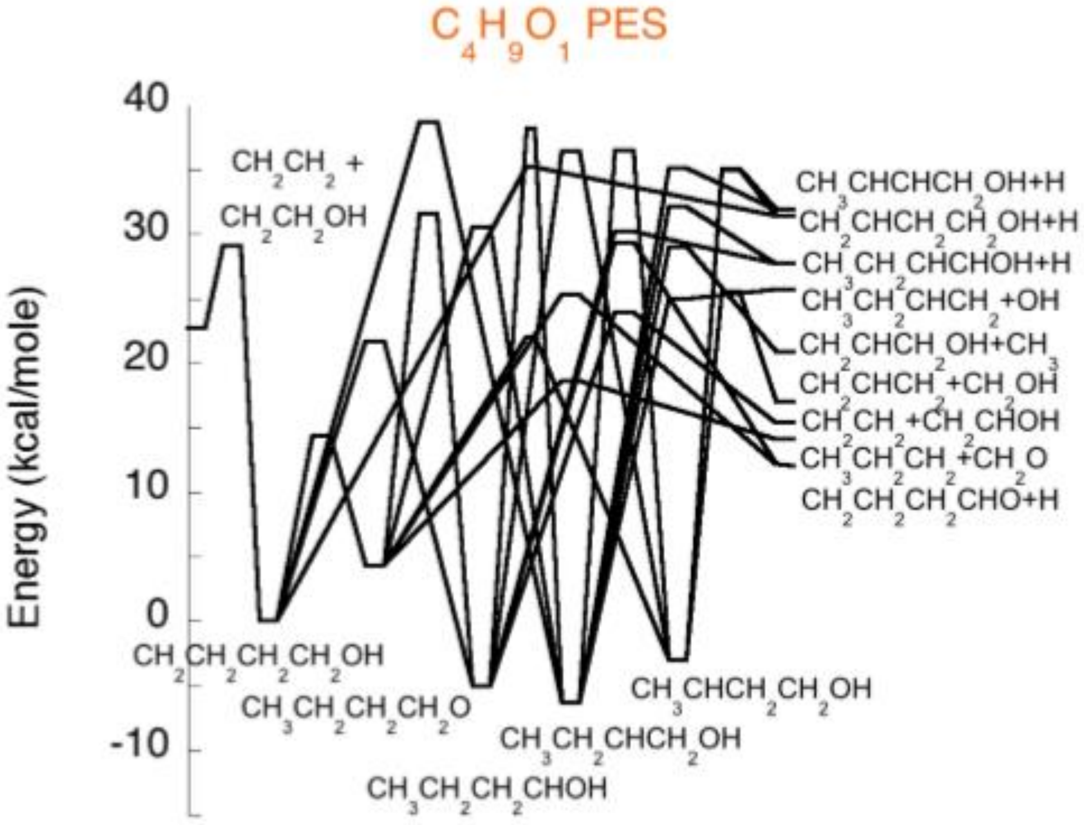
- Pyrolysis with H, CH_3, and OH as abstractors
  - Alkanes: C_2H_6, C_3H_8, n-C_4H_{10}
  - Alcohols: CH_3OH, C_2H_5OH, i-C_3H_7OH, n-C_3H_7OH, n-C_4H_9OH
  - Aldehyde/Ketone: H_2CO, CH_3CHO, and $(CH_3)_2CO$

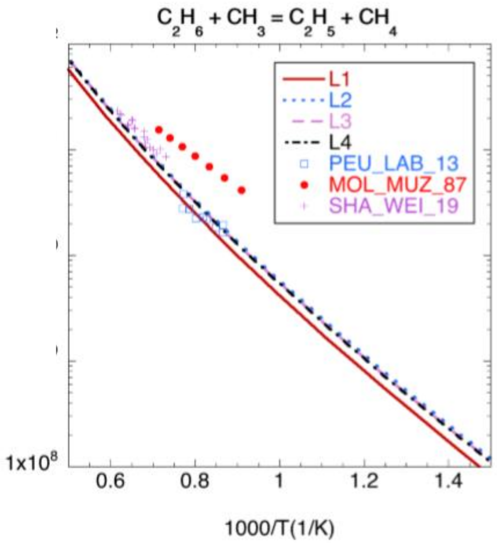




Kinetics – Pyrolysis

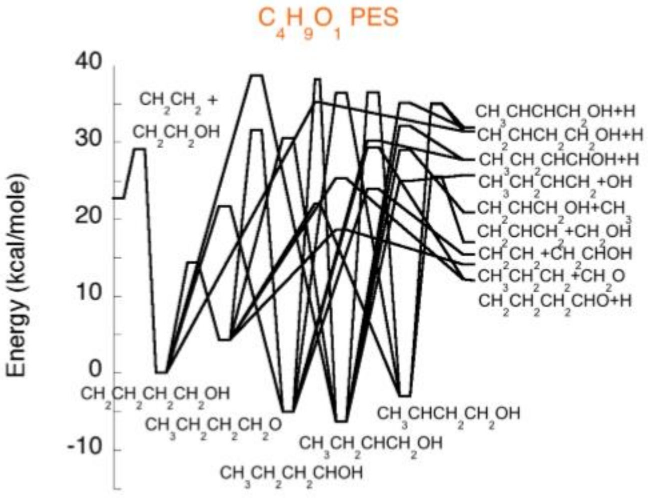
- Pyrolysis with H, CH
  - Alkanes: C_2H_6, C_3H
  - Alcohols: CH_3OH, (
  - Aldehyde/Ketone:

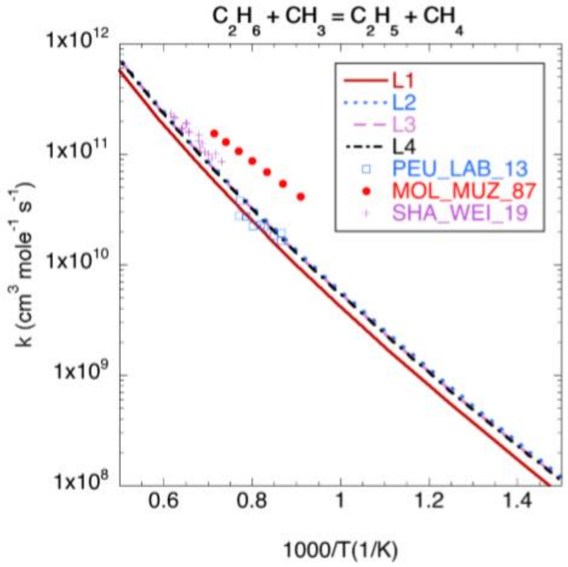




Kinetics – Pyrolysis

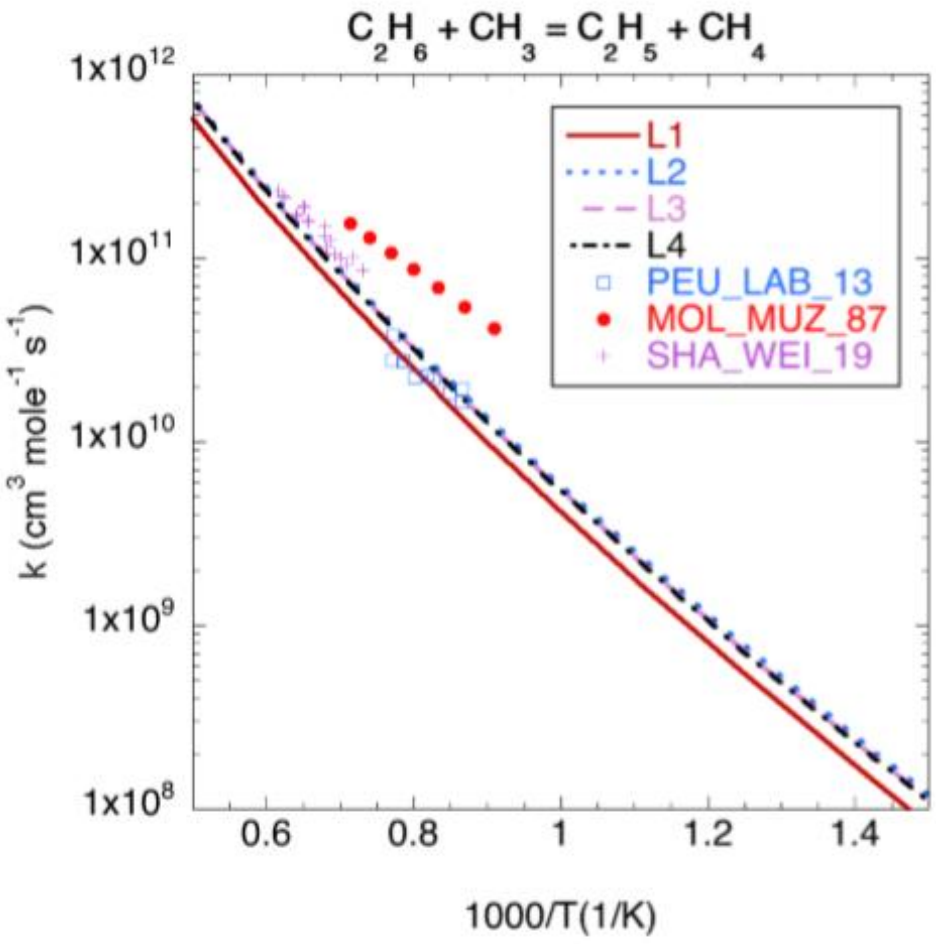
- Pyrolysis with H, CH_3, and OH as abstractors
  - Alkanes: C_2H_6, C_3H_8, n-C_4H_{10}
  - Alcohols: CH_3OH, C_2H_5OH, i-C_3H_7OH, n-C_3H_7OH, n-C_4H_9OH
  - Aldehyde/Ketone: H_2CO, CH_3CHO, and $(CH_3)_2CO$
- Multi-channel, pressure-dependent rate constants with ME using RRHO + 1D hindered rotor treatments at the following levels
  - CCSD(T)-F12/cc-pVDZ-F12//ωb97x-D/6-31G*
  - CCSD(T)-F12/ cc-pVTZ-F12//ωb97x-D/cc-pVTZ
  - CCSD(T)-F12/ cc-pVQZ-F12//B2PLYP-D3/cc-pVTZ
  - CCSD(T)-F12/ CBS(QZ,TZ)//B2PLYP-D3/cc-pVTZ
- The initial conformational sampling and symmetry factor is with ωb97x-D/6-31G*

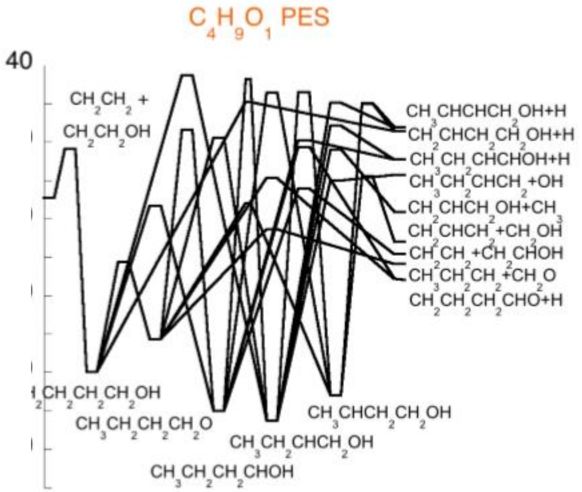




Kinetics – Pyrolysis

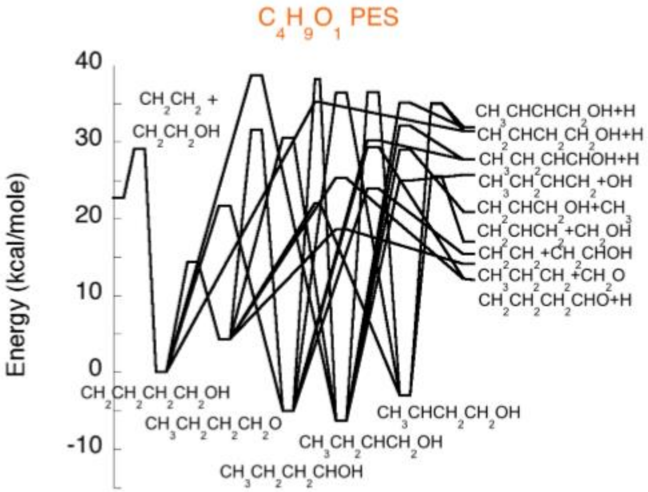
- Pyrolysis with H, CH_3,
  - Alkanes: C_2H_6, C_3H_8, r
  - Alcohols: CH_3OH, C_2H
  - Aldehyde/Ketone: H_2
- Multi-channel, pressu with ME using RRHO at the following level
  - CCSD(T)-F12/cc-pVDZ
  - CCSD(T)-F12/ cc-pVT
  - CCSD(T)-F12/ cc-pVQ
  - CCSD(T)-F12/ CBS(QZ
- The initial conformatio with ωb97x-D/6-31G*

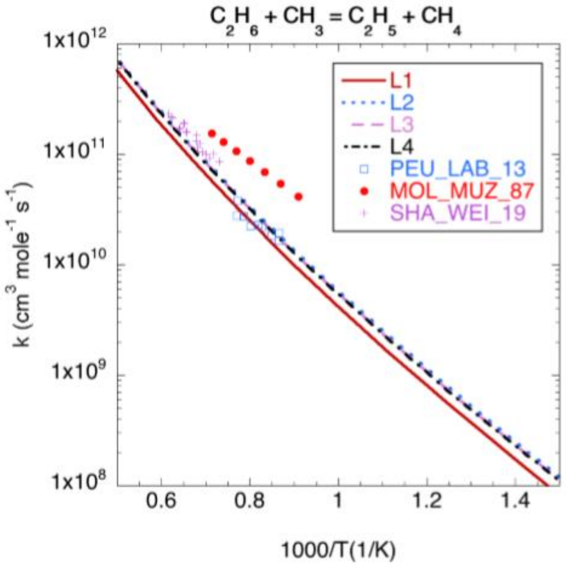




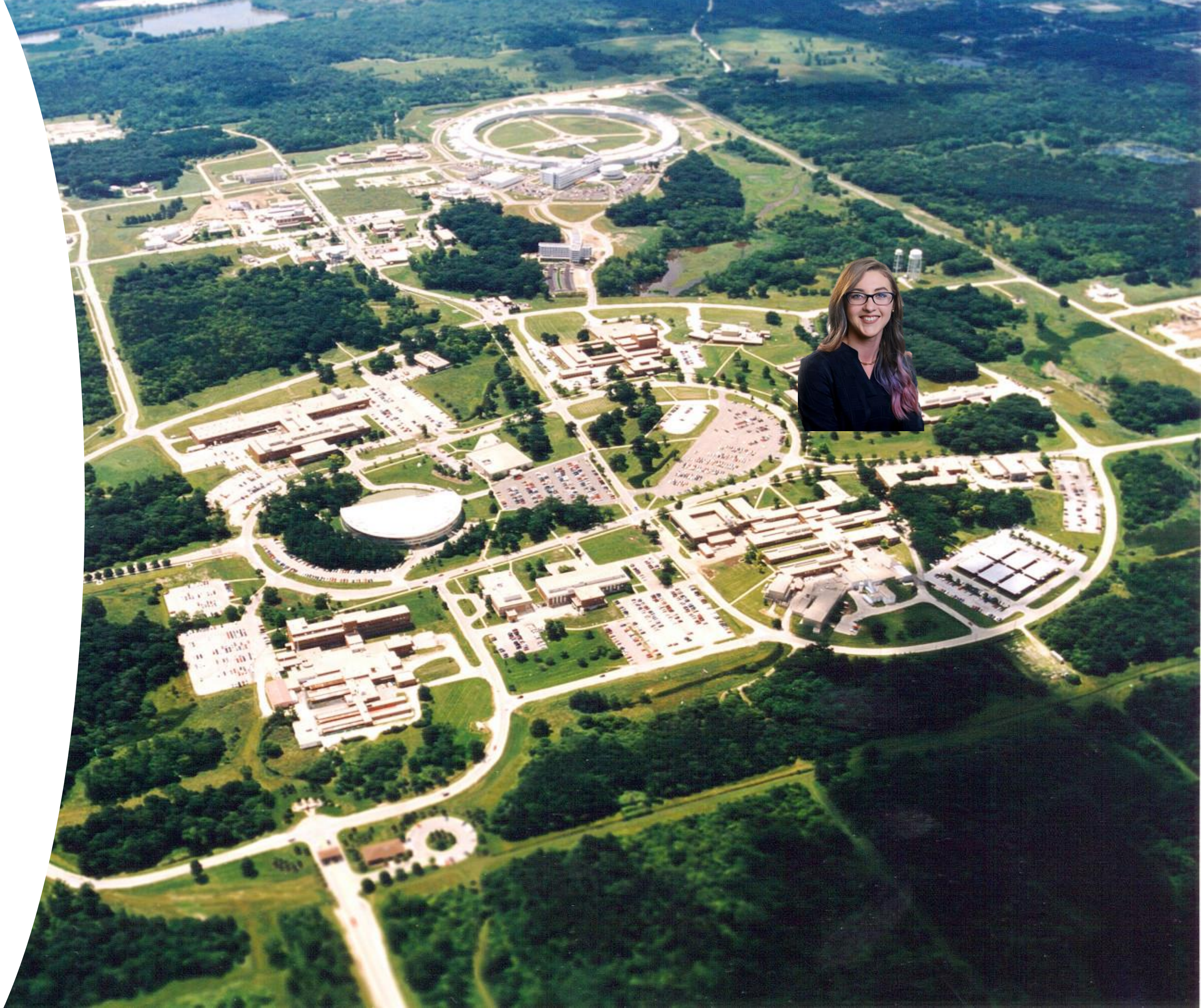
Kinetics – Pyrolysis

- Pyrolysis with H, CH_3, and OH as abstractors
  - Alkanes: C_2H_6, C_3H_8, n-C_4H_{10}
  - Alcohols: CH_3OH, C_2H_5OH, i-C_3H_7OH, n-C_3H_7OH, n-C_4H_9OH
  - Aldehyde/Ketone: H_2CO, CH_3CHO, and $(CH_3)_2CO$
- Multi-channel, pressure-dependent rate constants with ME using RRHO + 1D hindered rotor treatments at the following levels
  - L1: CCSD(T)-F12/cc-pVDZ-F12//ωb97x-D/6-31G*
  - L2: CCSD(T)-F12/ cc-pVTZ-F12//ωb97x-D/cc-pVTZ
  - L3: CCSD(T)-F12/ cc-pVQZ-F12//B2PLYP-D3/cc-pVTZ
  - L4: CCSD(T)-F12/ CBS(QZ,TZ)//B2PLYP-D3/cc-pVTZ
- The initial conformational sampling and symmetry factor is with ωb97x-D/6-31G*





Future Work



Acknowledgements

DOE CSGF UNIVERSITY OF GEORGIA ARCS CCQC ECP Argonne NATIONAL LABORATORY

Acknowledgements

University of Georgia
Jonathon Misiewicz
Gustavo Aroiera
Prof. Henry F. Schaefer III

MIT
Matt Johnson
Prof. Bill Green

Argonne National Lab
Dr. Andreas Copan
Dr. Kevin Moore III
Dr. Murat Keceli
Dr. Yuri Georgievskii
Dr. Ahren Jasper
Dr. Stephen Klippenstein

Politecnico di Milano
Prof. Carlo Cavollotti
Prof. Matteo Pelucchi

Sandia National Lab
Dr. Ruben VandeVivjer
Dr. Judit Zador

NUI Galway
Dr. Kieran Somers

DOE CSGF
UNIVERSITY OF GEORGIA
ARCS
CCQC
ECP
Argonne NATIONAL LABORATORY

Questions?