Predictive Theoretical Elementary Reaction Kinetics and its Role in Combustion Modeling

Stephen J. Klippenstein

Theoretical Elementary Reaction Kinetics

Potential Energy Surface Exploration

       Ab Initio Electronic Structure Theory

       Stationary Points – Minima and Transition States

       Evaluate Energies and Rovibrational Properties

Predict Rate Constants for Individual Dynamical Steps

       Transition State Theory (TST)

       Evaluate Partition Functions

       Tunneling, Hindered Rotors, Variational Effects

Predict Collision Induced Energy Transfer Rates

       Collision Rate

       Energy Transfer Distribution

       Usually Empirical

Predict/Model Pressure Dependence

       Master Equation -> Population vs. Time

       Represent with Kinetic Phenomenology

Team Effort

How to Calculate Rate Constants Accurately and Efficiently?

Ab Initio   **Transition State Theory**   **Master Equation**

Lawrence B. Harding   Yuri Georgievskii   James A. Miller

AITSTME Coding Team

Energy Transfer

Applications

Ahren Jasper

Judit Zador

Outline

1. **Theoretical Studies Motivated by Modeling**
   - $CO + HO_2$, $H + HO_2$, $CH_3OH + HO_2$
   - NNH Chemistry
   - $CH_2 + O_2$
   - $C_3H_6OOH + O_2$
   - C_4H_9OH, C_4H_9O, $C_4H_9O + O_2$

2. **Uncertainties**
   - Electronic Energies
   - Vibrational Frequencies
   - Torsional Modes
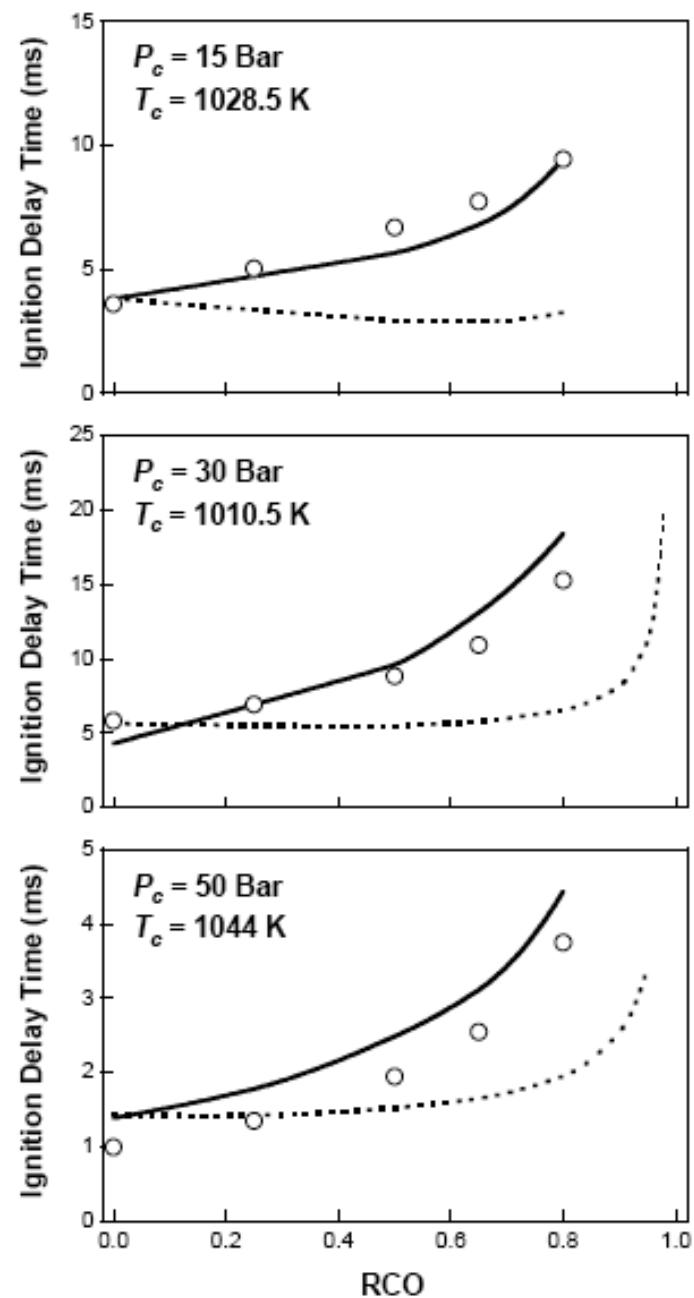   - Energy Transfer
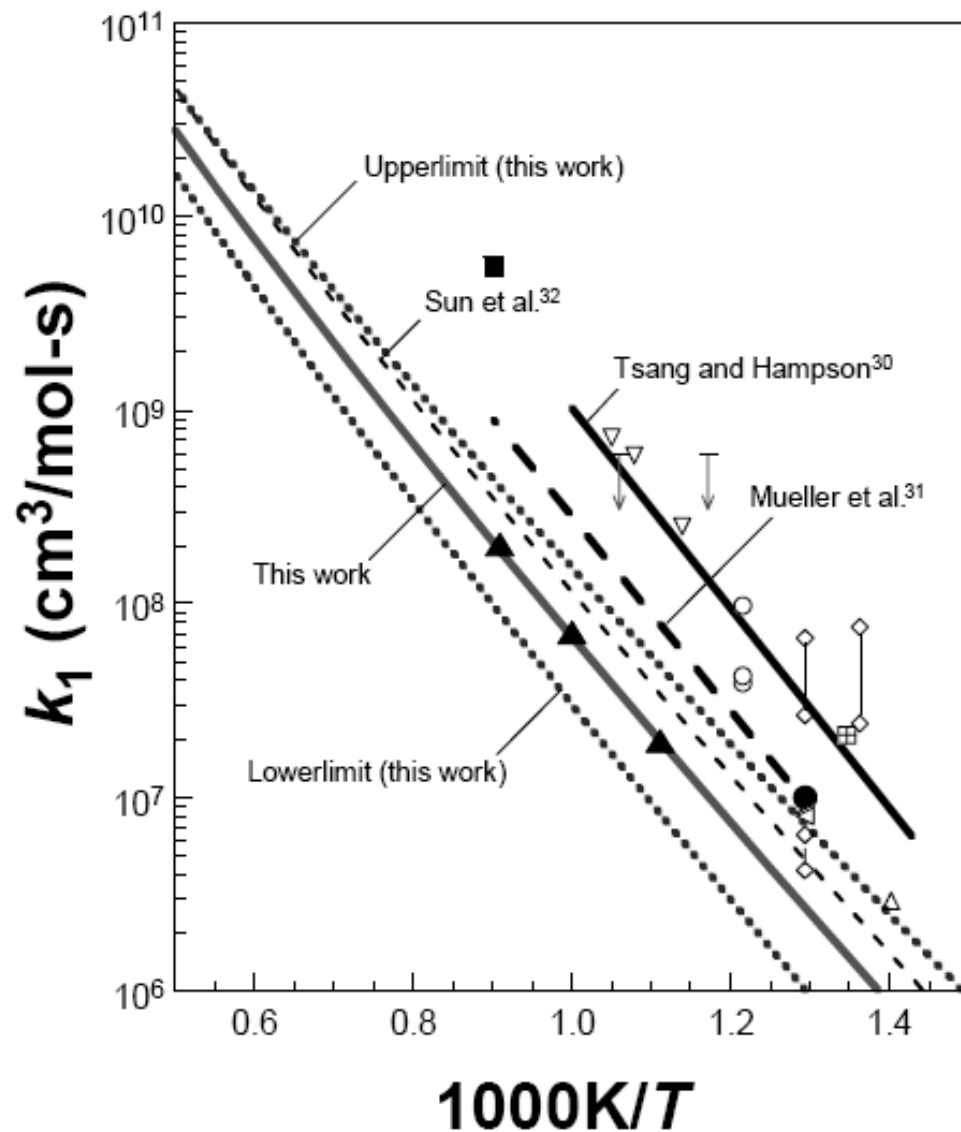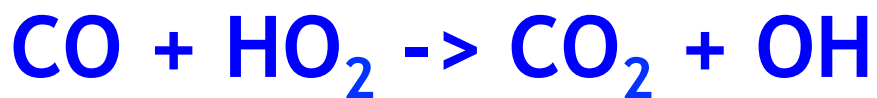   - Coupling of TST and Energy Transfer

CO/H$_2$/O$_2$ Oxidation: Ignition Delays in RCM
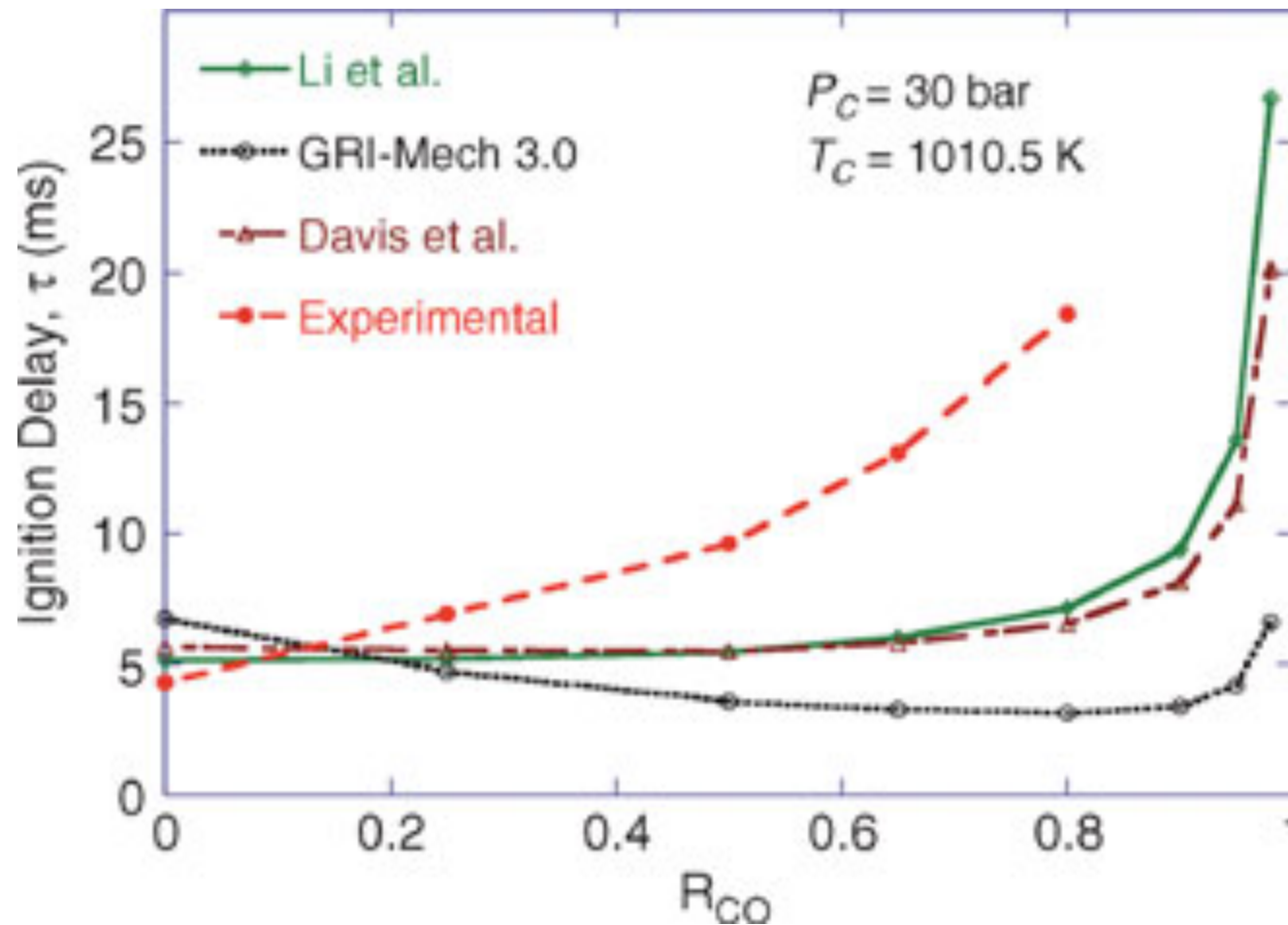
G. Mittal, C. J. Sung, R. A. Yetter, Int. J. Chem. Kinet. 38, 516 (2006).

Uncertainty Analysis Highlighted Sensitivity to CO + HO$_2$
G. Mittal, C. J. Sung, M. Fairweather, A. S. Tomlin, J. F. Griffiths, K. J. Hughes, Proc. Comb. Inst. 31, 419 (2007).
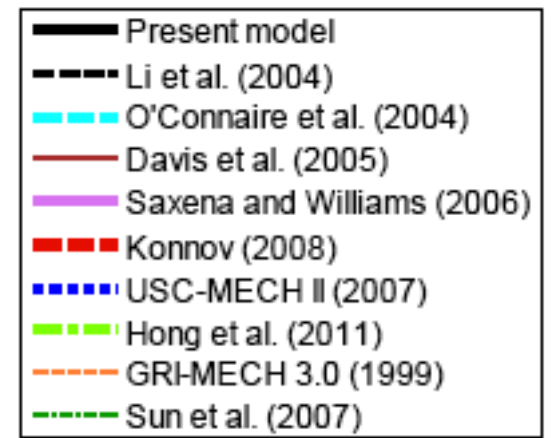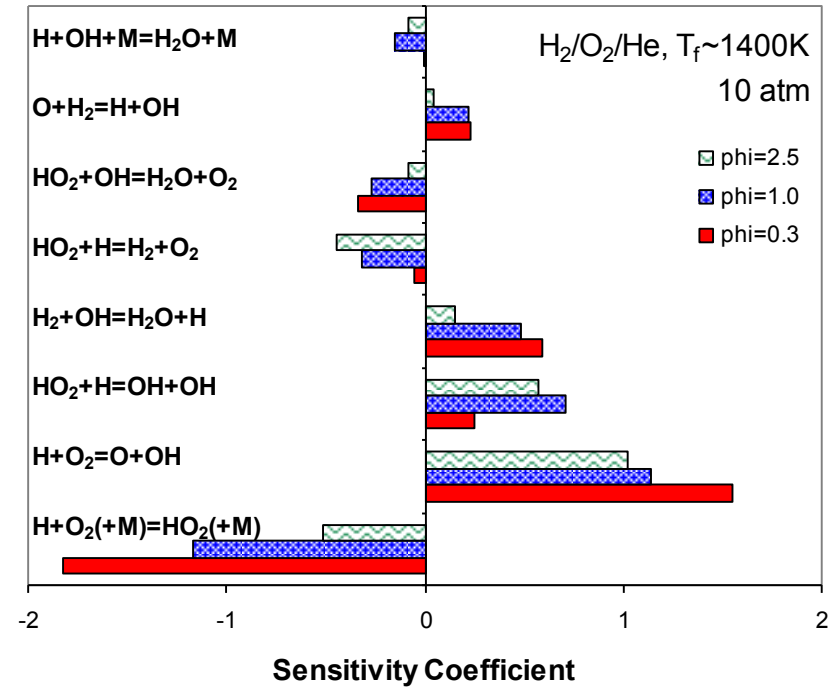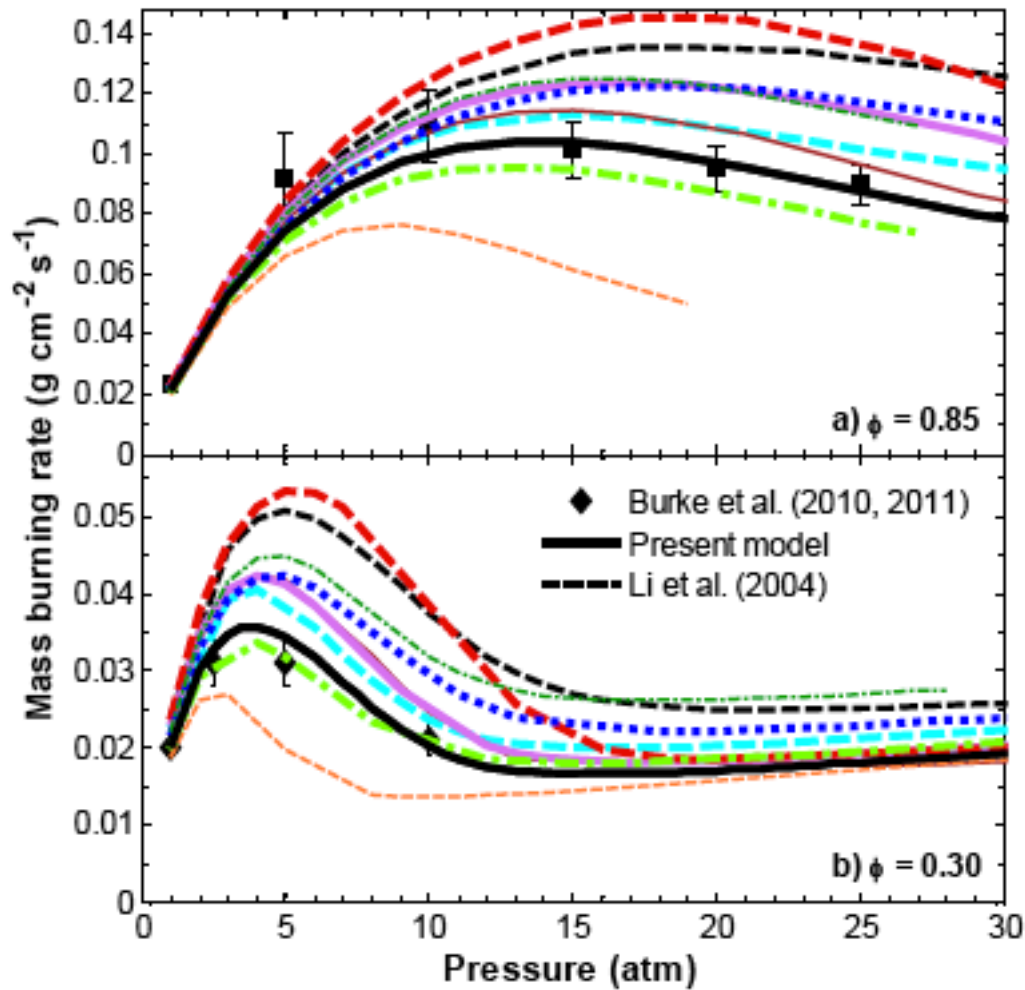
CO + HO$_2$ -> CO$_2$ + OH

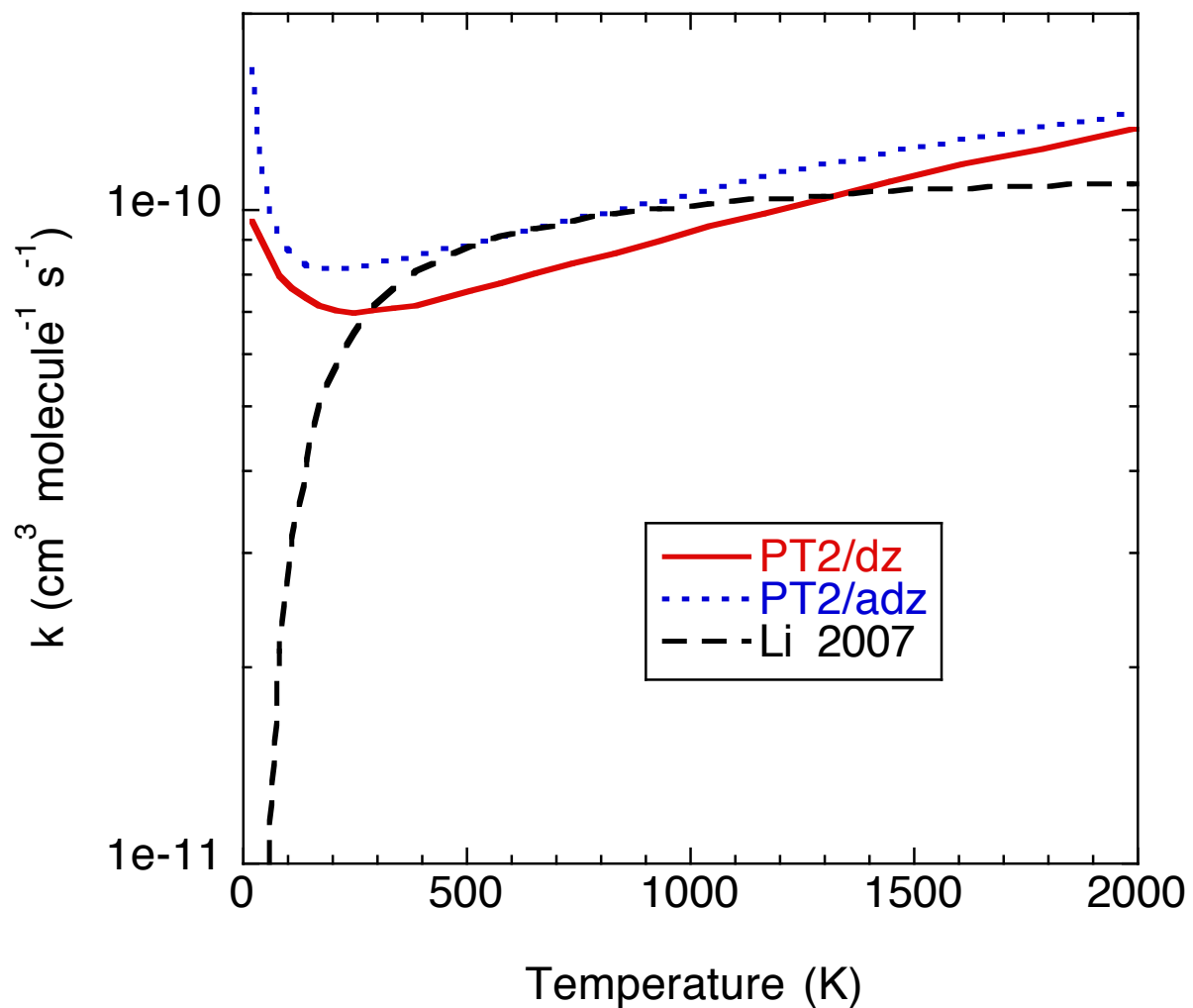You, Wang, Goos, Sung, Klippenstein, J. Phys. Chem. A, 111, 4031 (2007)

H$_2$/O$_2$ at High Pressure

Burke, Chaos, Ju, Dryer, Klippenstein, Int. J. Chem. Kinet. 44, 444 (2012).

H + HO$_2$ Recombination

Direct CASPT2 Variable Reaction Coordinate TST Calculations

~ 20% Uncertainty

Validate Modeling Determined Rate

The Role of NNH in NO Formation and Control

NNH Lifetime – Discrepancy between value required for modeling and value predicted by theory

NNH Mechanism for NO_x Formation – Possibly important at low temperatures

1. $NNH + O_2$
2. $NNH + O$; $NH + NO$, $H + N_2O$
3. $NH_2 + O_2 -> H_2NO + O$
4. Literature Review of NNH Lifetime and Thermochemistry
5. More accurate branching ratios for $NH_2 + NO$

S. J. Klippenstein, L. B. Harding, P. Glarborg, and J. A. Miller, Comb. Flame, 158, 774 (2011).

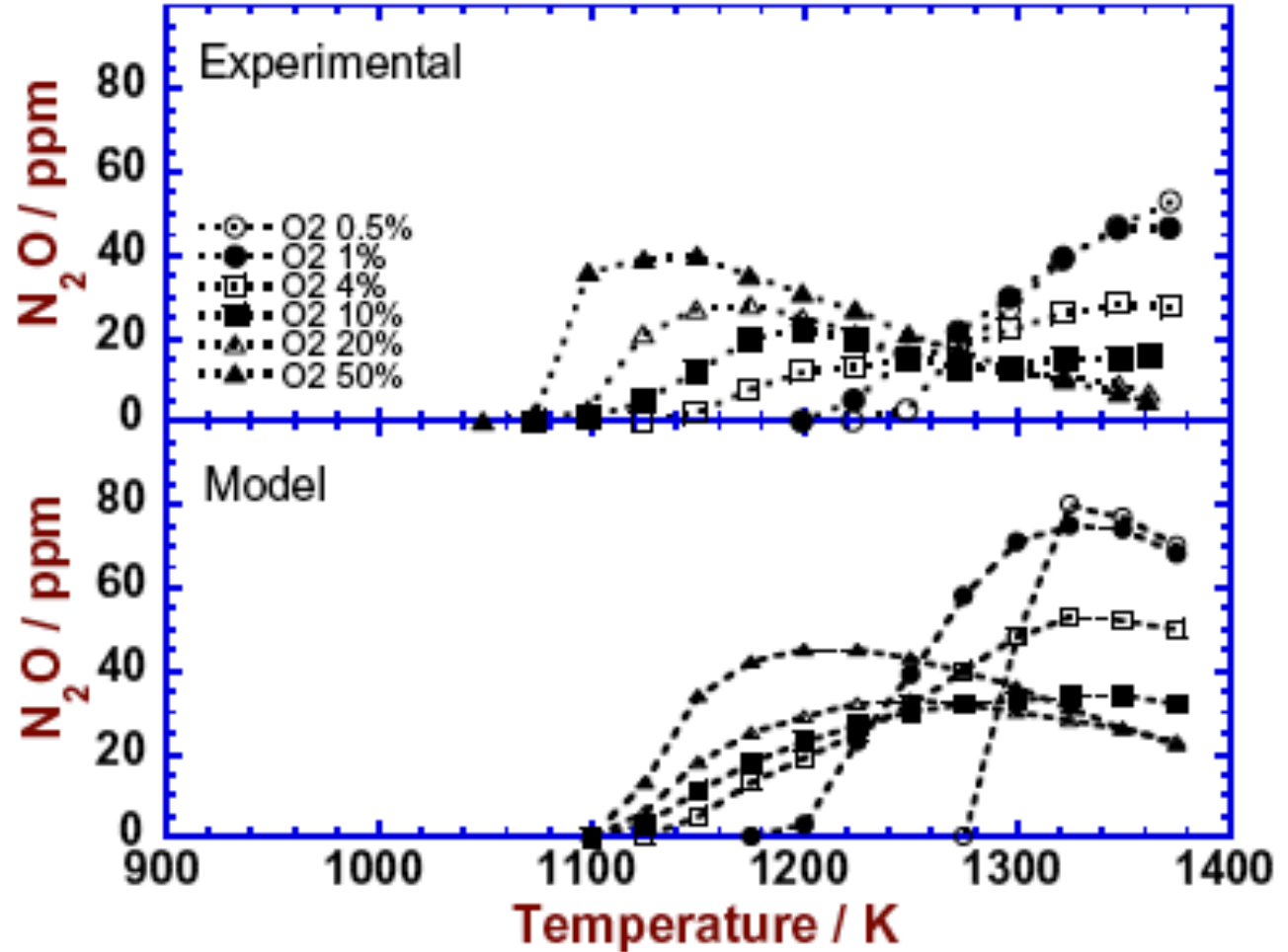# Modeling vs Expt   NO   O$_2$ and T Dependence
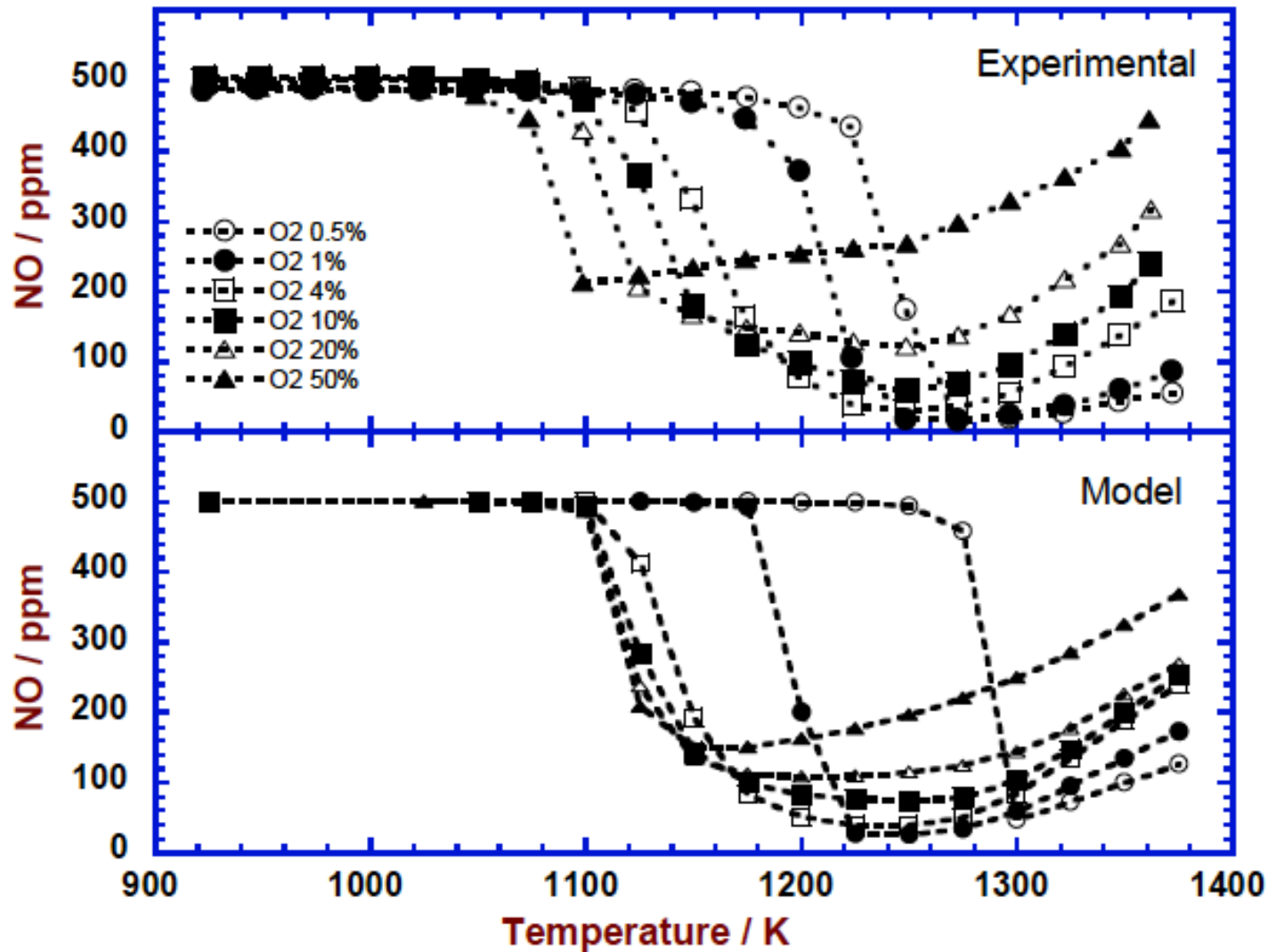
Experiments:
F. Kasuya, P. Glarborg, K. Dam-Johansen, Chem. Eng. Sci. 50 (1995) 1455-1466.

Modeling vs Expt   N₂O   O₂ and T Dependence

Inlet concentrations:
NO = 500 +/- 30 ppm
NH₃ = 1000 +/- 60 ppm
H₂O = 5%
balance N₂

F. Kasuya, P. Glarborg, K. Dam-Johansen, Chem. Eng. Sci. 50 (1995) 1455-1466.

Modeling vs Expt   NO₂ O₂ and T Dependence

Inlet concentrations:
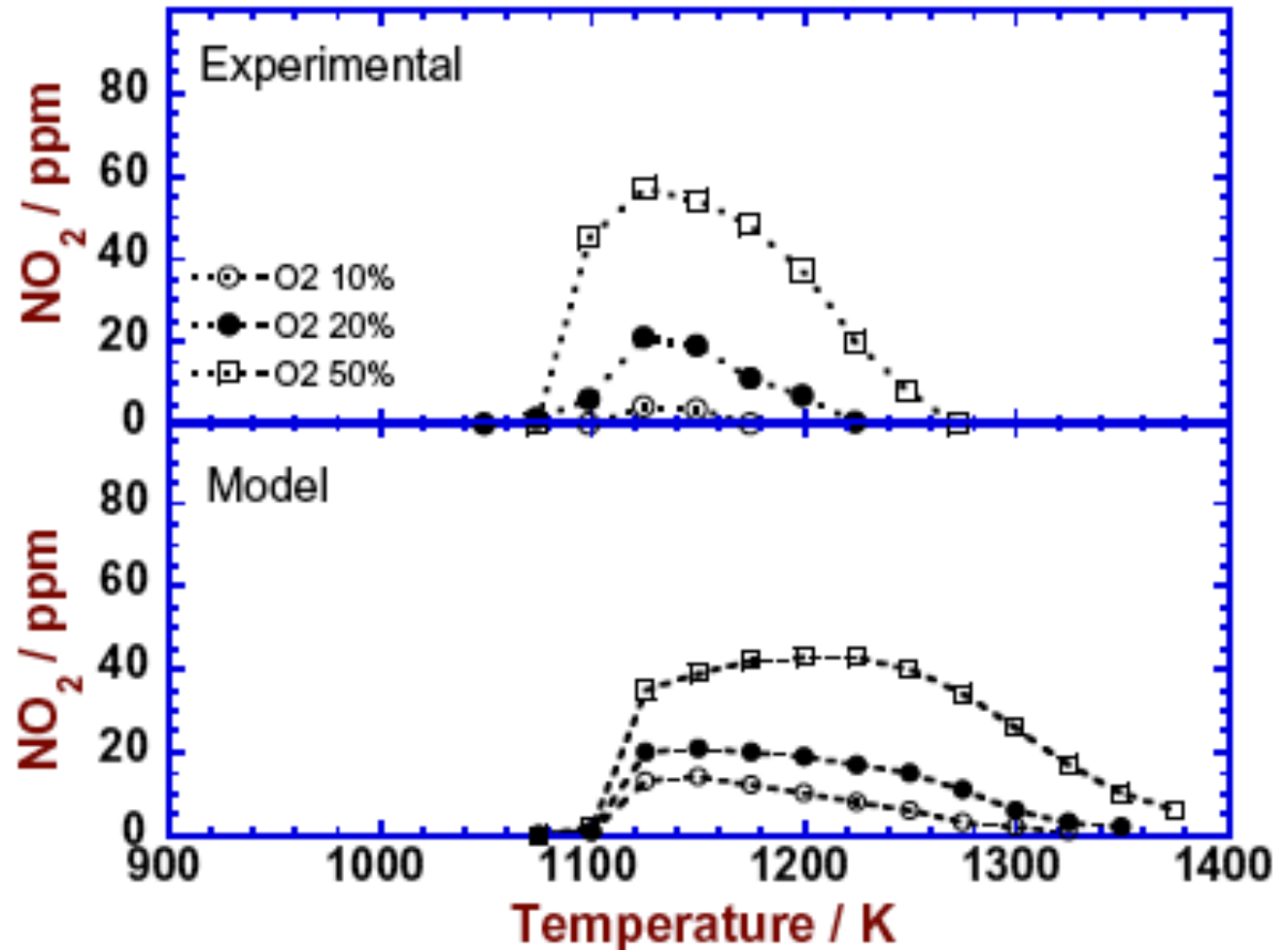NO = 500 +/- 30 ppm
NH₃ = 1000 +/- 60 ppm
H₂O = 5%
balance N₂

F. Kasuya, P. Glarborg, K. Dam-Johansen, Chem. Eng. Sci. 50 (1995) 1455-1466.

Modeling vs Expt   NO H_2 and T Dependence

Inlet concentrations:
NO = 500 +/- 30 ppm
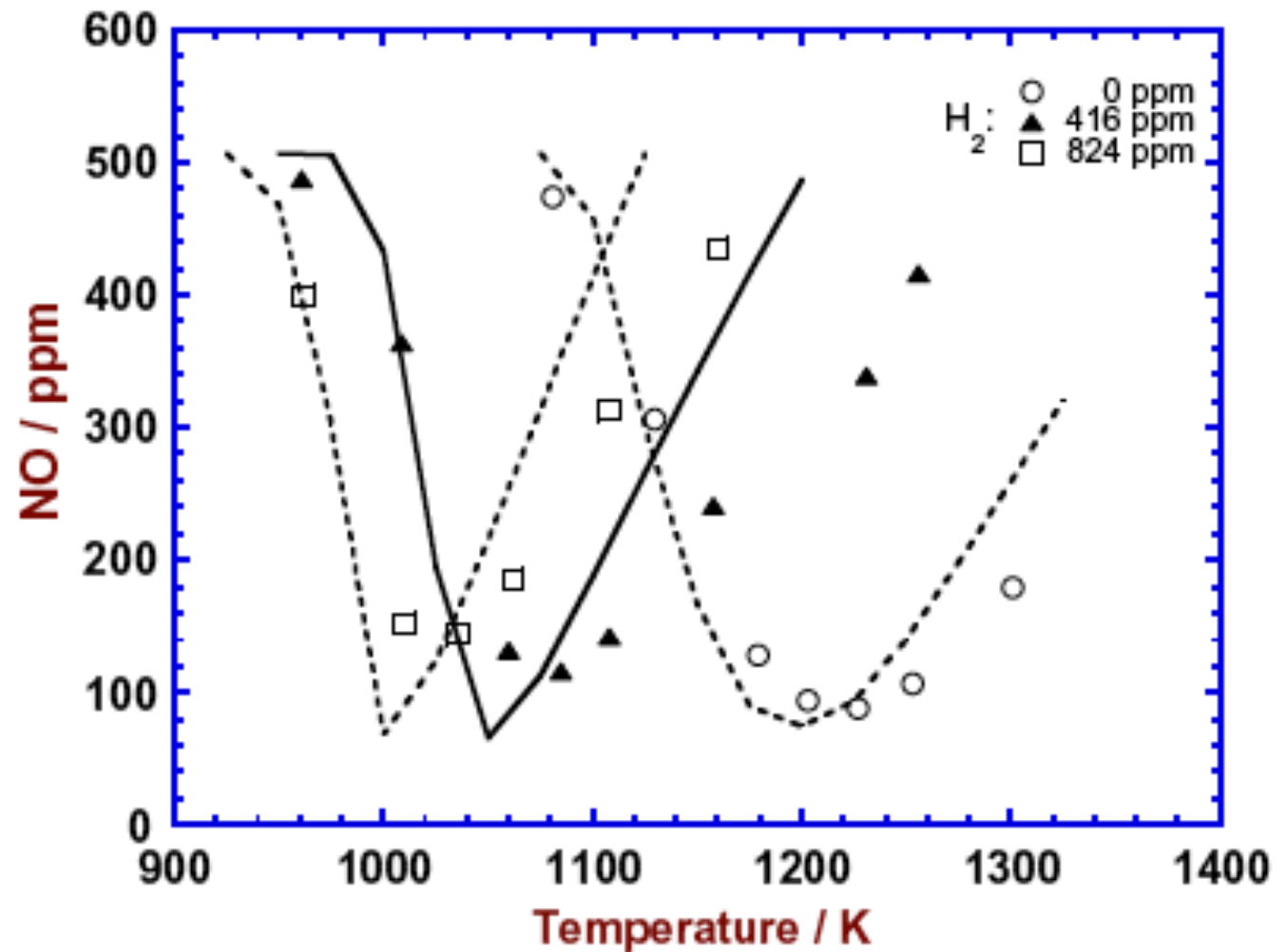NH_3 = 1000 +/- 60 ppm
H_2O = 5%
balance N_2

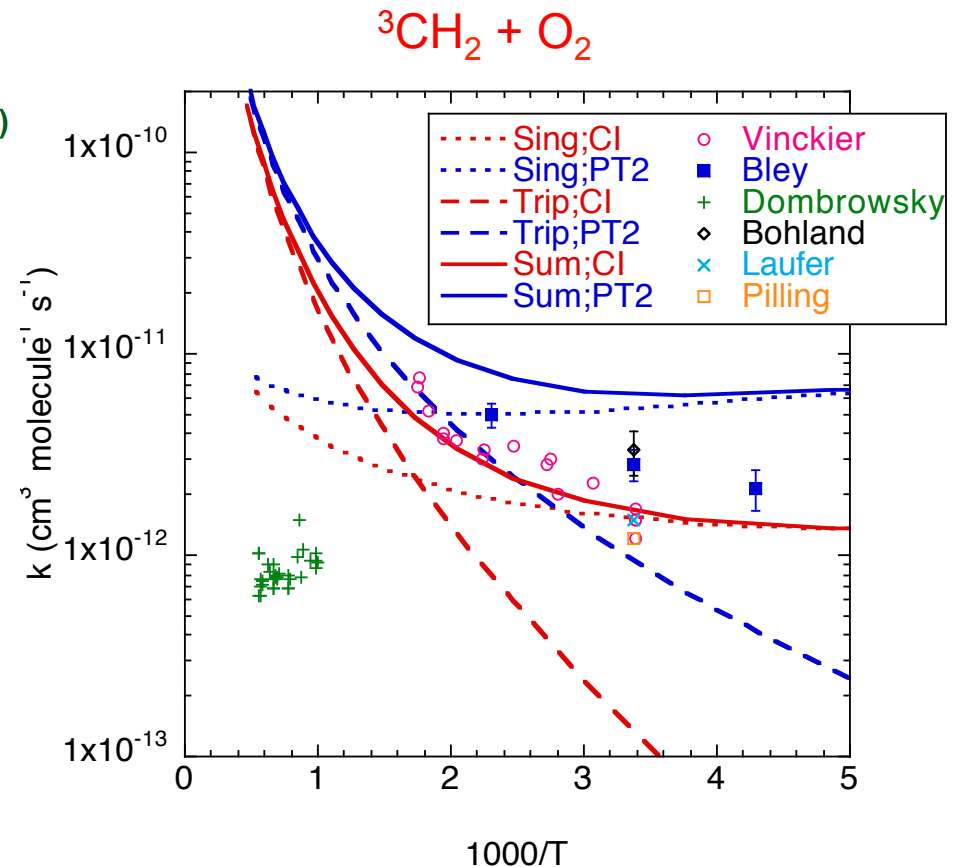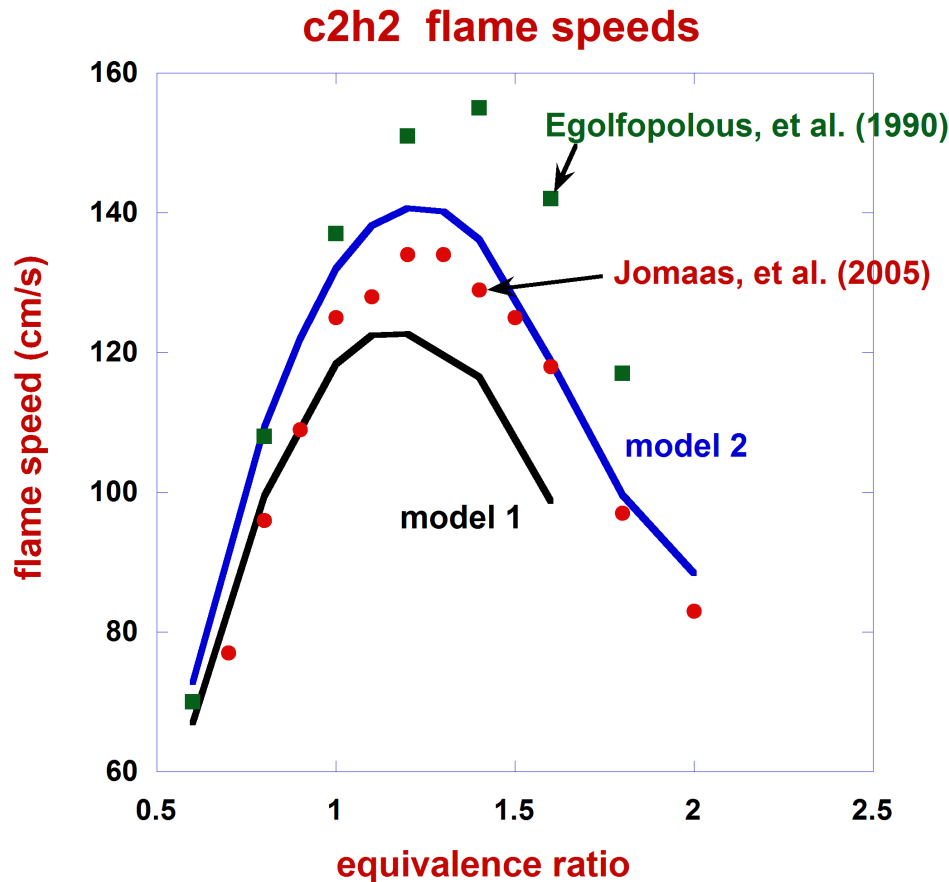W. Duo, K. DamJohansen, K. Ostergaard, Can. J. Chem. Eng. 70 (1992) 1014-1020.

Mechanism Development   C0-C3 Core Mechanism

Large scale update of Miller mechanism
Include Pressure Dependent Rate Coefficients

c2h2 flame speeds

Egolfopolous, et al. (1990)

Jomaas, et al. (2005)

model 2

model 1

flame speed (cm/s)

equivalence ratio

$^3CH_2 + O_2$

- ...... Sing;CI   ○ Vinckier
- ...... Sing;PT2   ■ Bley
- ----- Trip;CI   + Dombrowsky
- ----- Trip;PT2   ◇ Bohland
- —— Sum;CI   × Laufer
- —— Sum;PT2   □ Pilling

k (cm^3 molecule^{-1} s^{-1})

1000/T

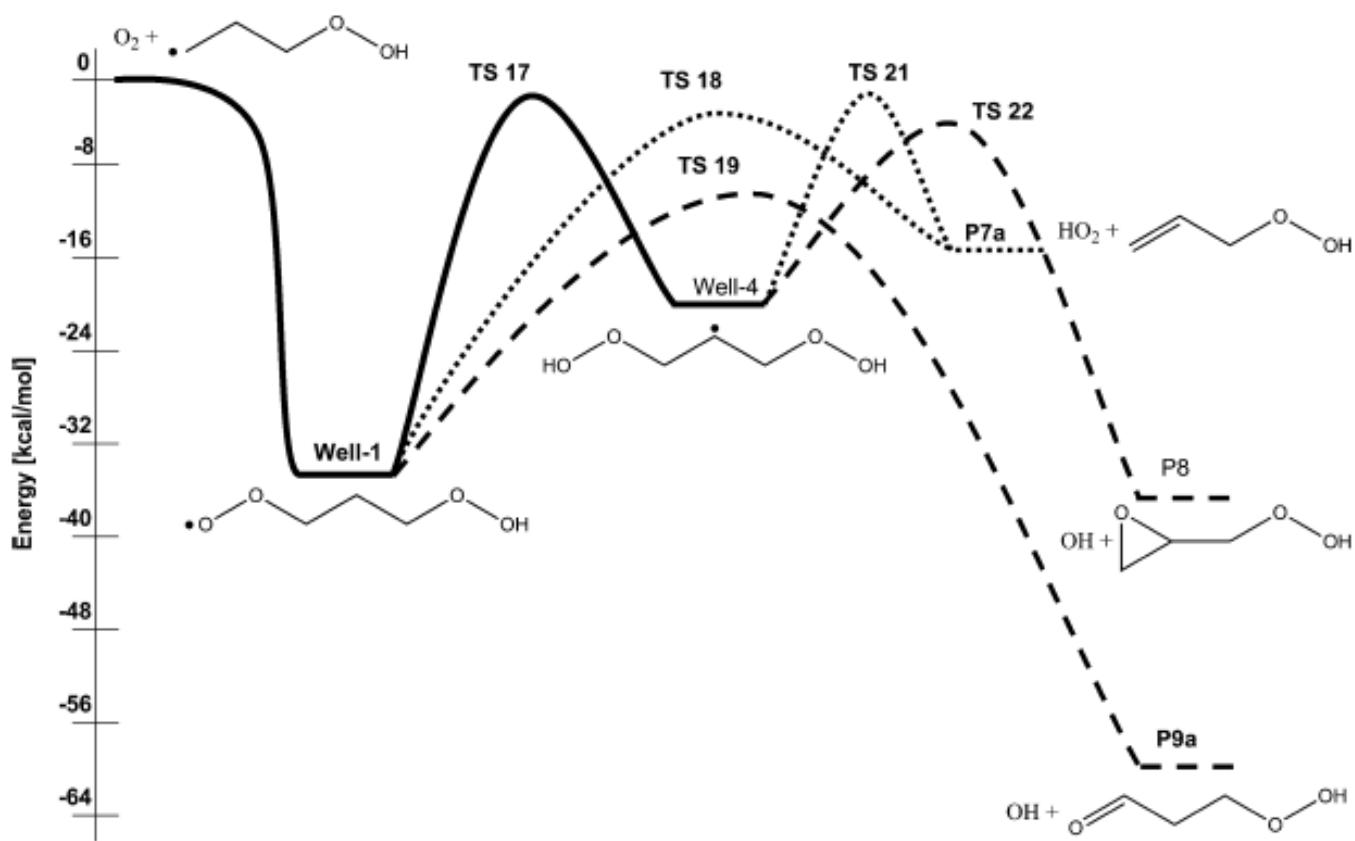Miller, Klippenstein, and Glarborg, work in progress

Pressure Dependent Reactions   QOOH + O₂

Modeling indicates QOOH + O$_2$ Central to Low Temperature Chain Branching but essentially no Elementary Kinetics Studies

C$_3$H$_6$OOH + O$_2$ Smallest Prototype

Goldsmith, Green, Klippenstein, J. Phys. Chem. A, 116, 3325 (2012)

Butanol Chemistry

CEFRC Developing Mechanism for Butanol Combustion

Sensitivity Analyses Suggest Need for Further Study of a Few Key Reactions

C_4H_9OH Decomposition - Isobutanol
    C. W. Zhou, S. J. Klippenstein, J. M. Simmie, H. J. Curran, Proc. Comb. Inst. in press (2012); Paper 4D05

C_4H_9O Decomposition (α, β, γ, δ, and O radicals)
    P. Zhang, C. K. Law, S. J. Klippenstein, (2012).

$C_4H_9O + O_2$ (α, β, γ, and δ radicals)
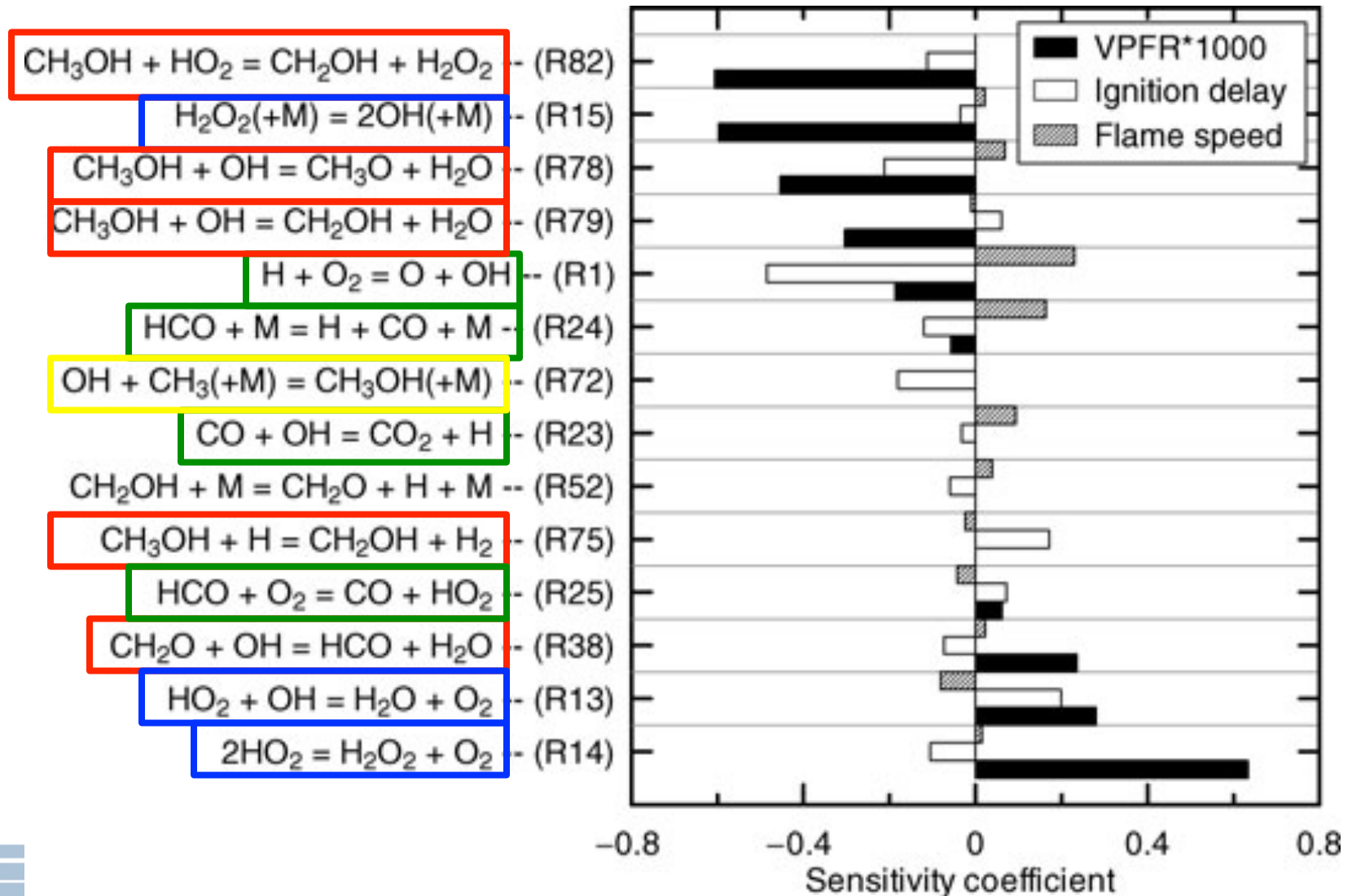   O. Welz, J. Zador, S. J. Klippenstein, in progress (2012).

Sensitivity for Methanol (CH_3OH) Combustion

Li, Zhao, Kazakov, Chaos, Dryer, Scire, IJCK, 39, 109 (2007)

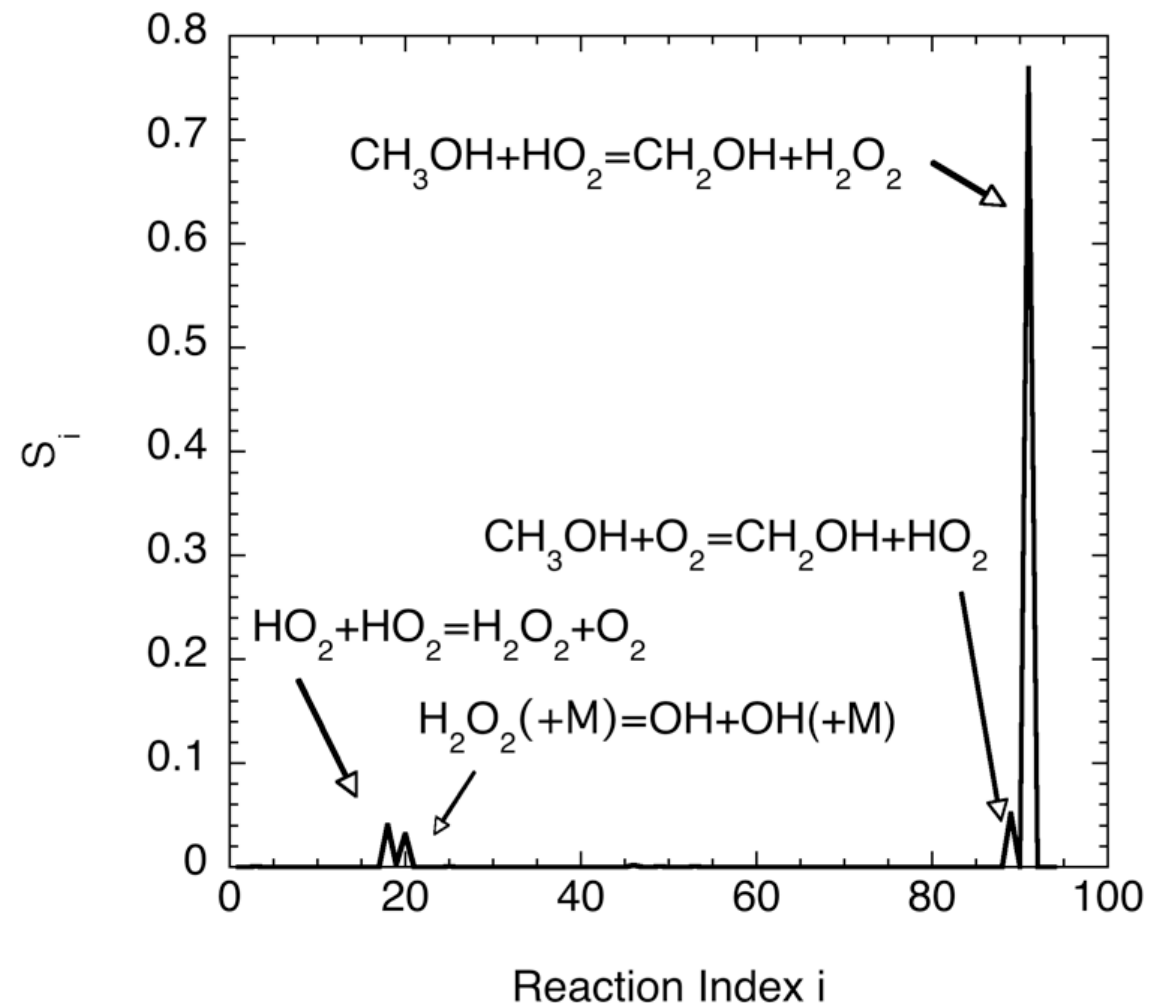### Validated Against Ignition Delays, Flame Speeds, Species Profiles

How to Improve for Engine Conditions - High Pressures/Non-Dilute?

Global uncertainty analysis

- Indicates reaction with dominant contribution to overall uncertainty
- Theoretical predictions of selected rate coefficients
- How accurate?

Klippenstein, Harding, Davis, Tomlin, Skodje Proc. Comb. Inst. 33, 351 (2011).

Variance Analysis for the Ignition Delay

$CH_3OH+HO_2=CH_2OH+H_2O_2$

$CH_3OH+O_2=CH_2OH+HO_2$

$HO_2+HO_2=H_2O_2+O_2$
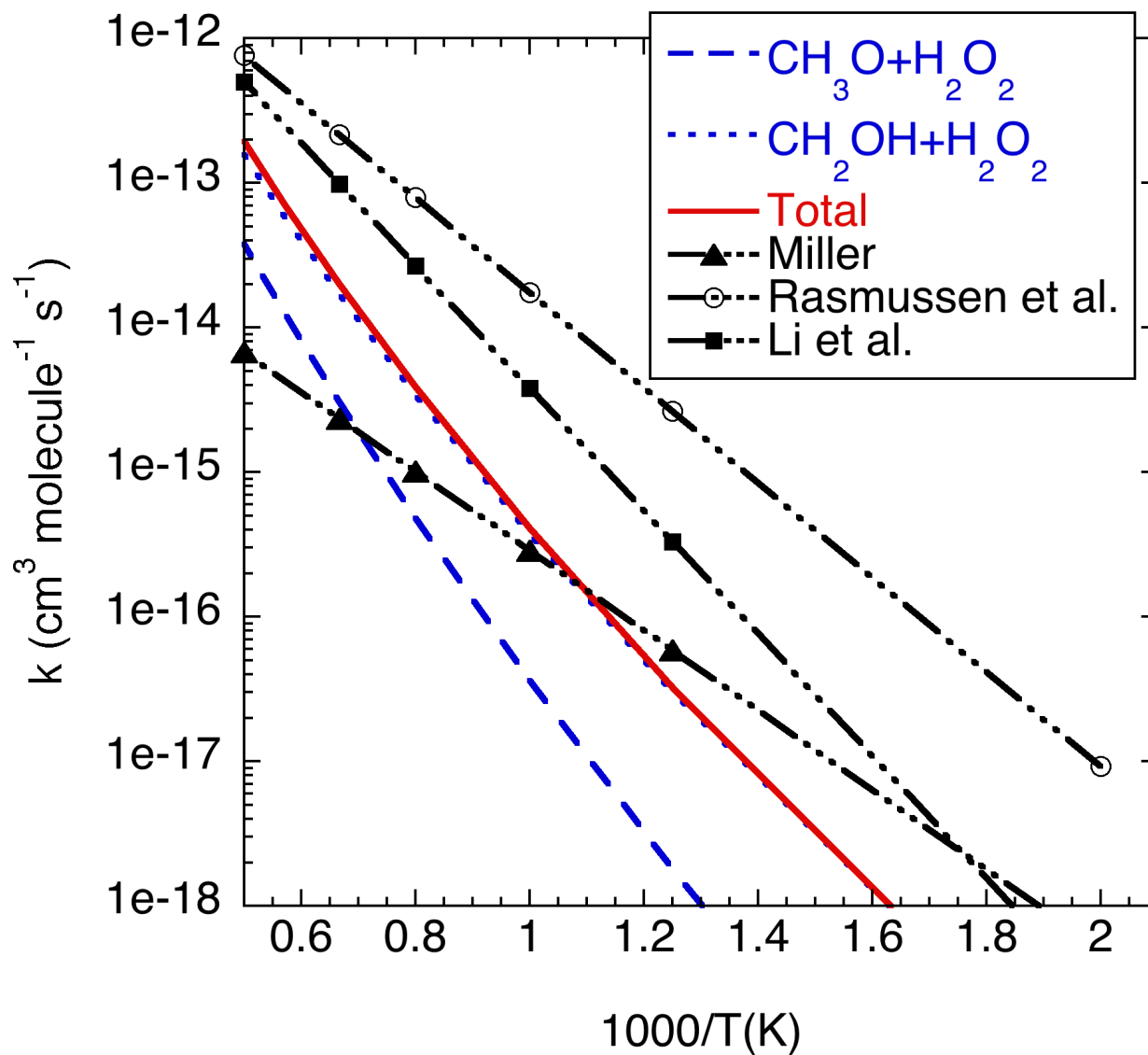
$H_2O_2(+M)=OH+OH(+M)$

Reaction Index i

Transition State Theory

Complete torsional sampling to find torsional minima

Torsional modes treated as uncoupled 1-dimensional hindered rotors
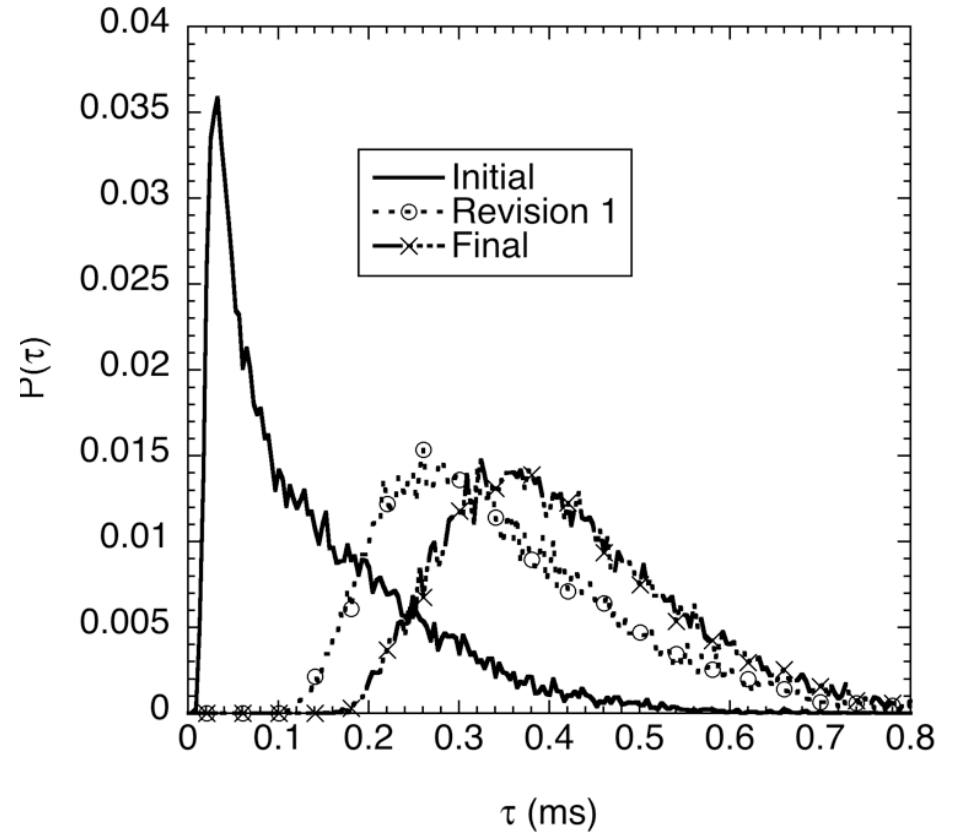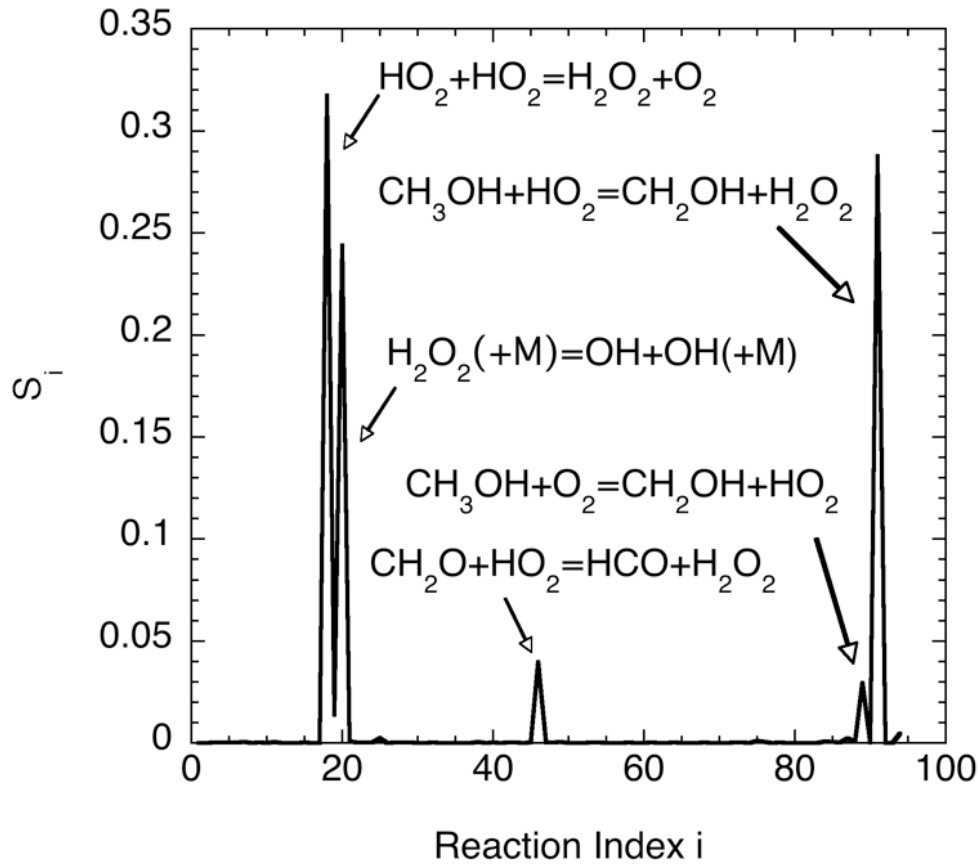
Asymmetric Eckart Tunneling

Other modes – harmonic oscillators and rigid rotors

$CH_3OH + HO_2$

Legend:
- $CH_3O + H_2O_2$
- $CH_2OH + H_2O_2$
- Total
- Miller
- Rasmussen et al.
- Li et al.

y-axis: k (cm^3 molecule^{-1} s^{-1})

x-axis: 1000/T(K)

Change in ignition characteristics

Predicted Ignition Delays

Final Uncertainty Analysis

$HO_2+HO_2=H_2O_2+O_2$

$CH_3OH+HO_2=CH_2OH+H_2O_2$

$H_2O_2(+M)=OH+OH(+M)$

$CH_3OH+O_2=CH_2OH+HO_2$

$CH_2O+HO_2=HCO+H_2O_2$

| $\langle\tau\rangle$		Width/$\langle\tau\rangle$	
Initial	0.11	Initial	2.0
Final	0.40	Final	0.70

How Accurate are our Predictions?

- Currently a Factor of 2-3 Uncertainty

- Compare with Experiments
  - Experience from many comparisons

- Analysis of uncertainty for underlying factors in theoretical analysis
  - Barrier Height Uncertainties
  - Vibrational Frequency Uncertainties
  - Anharmonicity Corrections

- Do Mechanisms Improve?

- Trying to reduce uncertainties to about 1.2-1.3

Reactions with Barriers

Boltzmann Factors for Given Errors (kcal/mol)
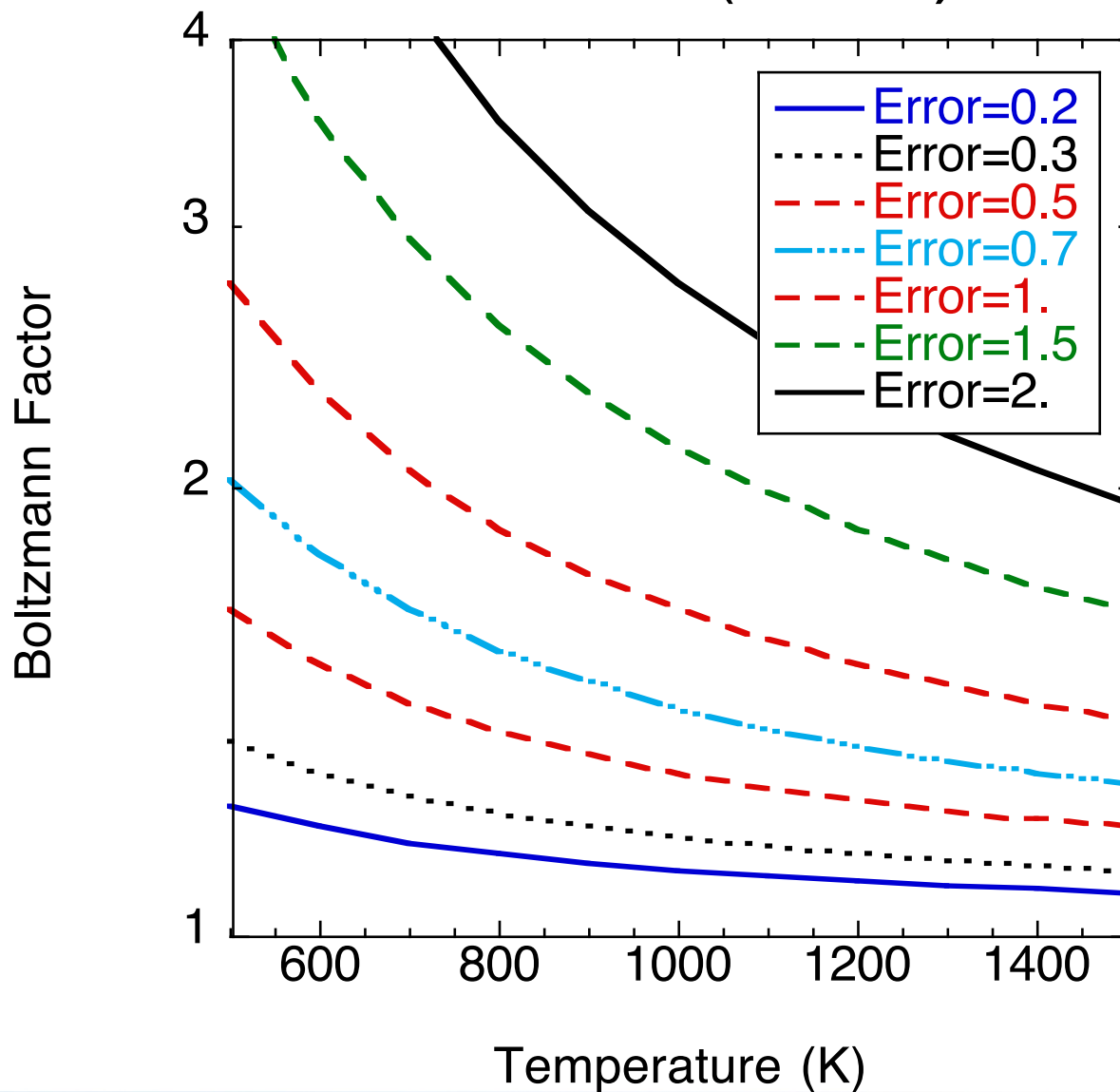
Combustion Thermochemistry Database

HEAT (Stanton and coworkers); Wn (Martin and coworkers); Focal Point (Allen and coworkers)

CCSD(T)/TZ optimizations and Frequencies

CCSD(T)/CBS from CCSD(T)/AQZ',A5Z'

CCSDT(Q)/DZ

Core-Valence CCSD(T)/CBS; TZ and QZ

Relativistic from DKH with CI/TZ

DBOC from HF/cc-pVTZ

Anharmonic corrections from B3LYP/6-311++G**
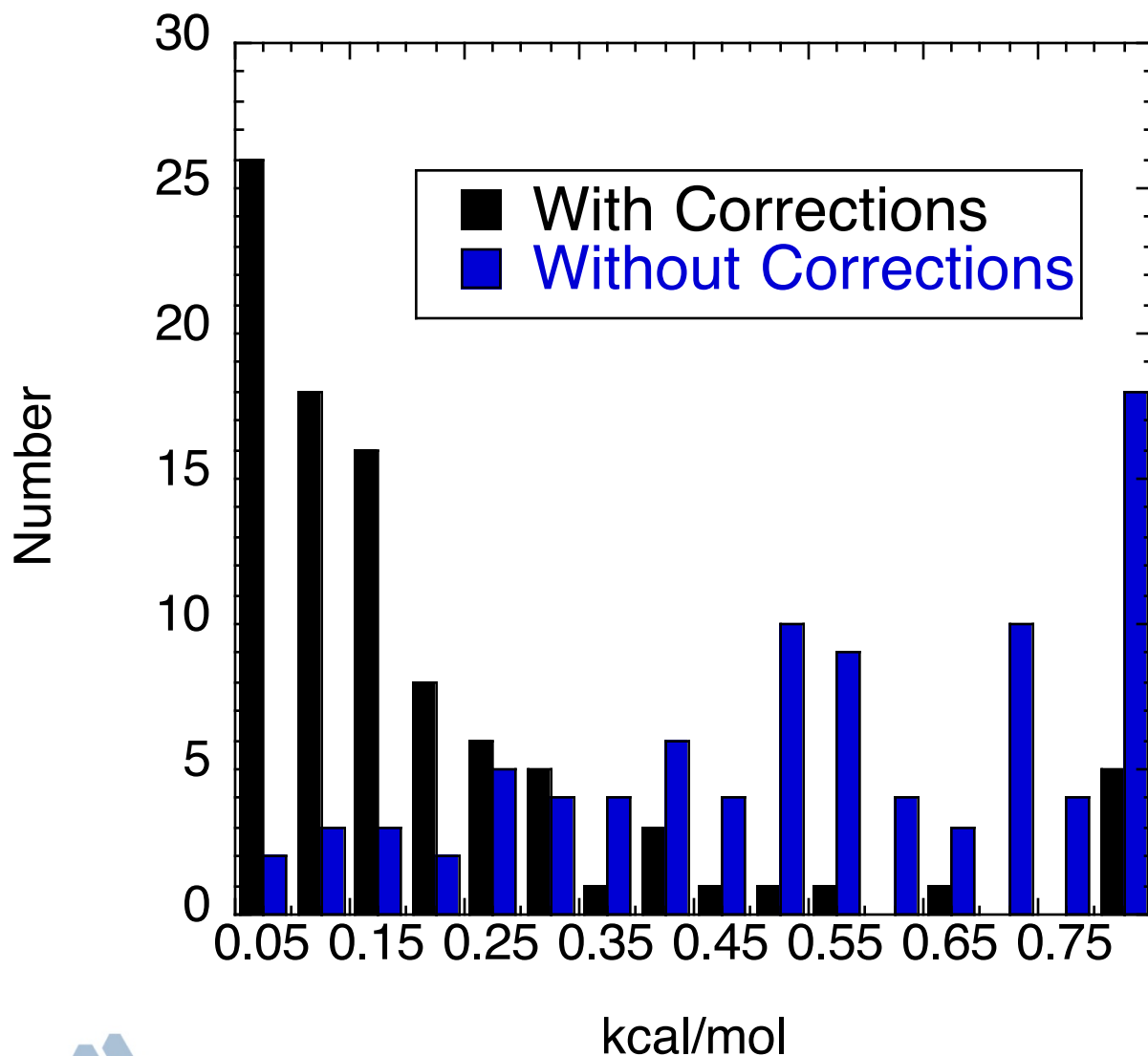
Heats of formation relative to H_2, CH_4, H_2O, NH_3

5 Heavy Atoms

Size of Individual Corrections

	Mean	MAD	RMSD	Variance
CCSDT(Q)	-0.36	0.42	0.62	0.46
Core-Valence	0.54	0.54	0.60	0.28
Anharmonicity	0.47	0.49	0.59	0.32
Relativistic	-0.16	0.16	0.20	0.11
DBOC	0.10	0.11	0.14	0.09

Accuracy vs ATcT from Ruscic

Heat of Formation Errors

H, O, OH, O2, HO2, H2O2, O3, C, CH, CH2, 1CH2, CH3, CO, HCO, COH, CH2O, HCOH, CH2OH, CH3O, CO2, HOCO, HCO2, OCHOH, CH3O2, CH3OOH, C2, C2H2, H2CC, C2H3, CCH3, C2H4, CHCH3, C2H5, C2H6, CCO, 1CCO, HCCO, CH2CO, HCCOH, CH3CO, CH3CHO, CH2CHOH, CH3CHOH, C2H4OH, CH3CH2O, C2H5OH, CH3OCH3, OCHCHO, CH3C(O)OH, CH2CCH, CH3CCH, CH2CCH2, -CH2CHCH-, CH3CHCH2, CH3CH2CH3, N, NNH, NHNH, H2NN, NHNH2, NH2NH2, NO, HNO, NOH, H2NO, HNOH, H2NOH, N2O, NO2, NO3, CN, HCN, CNH, H2CN, HCNH, CH3N, CH2NH, CH3NH, CH2NH2, CH3NH2, NCO, HNCO, HCNO, NCOH
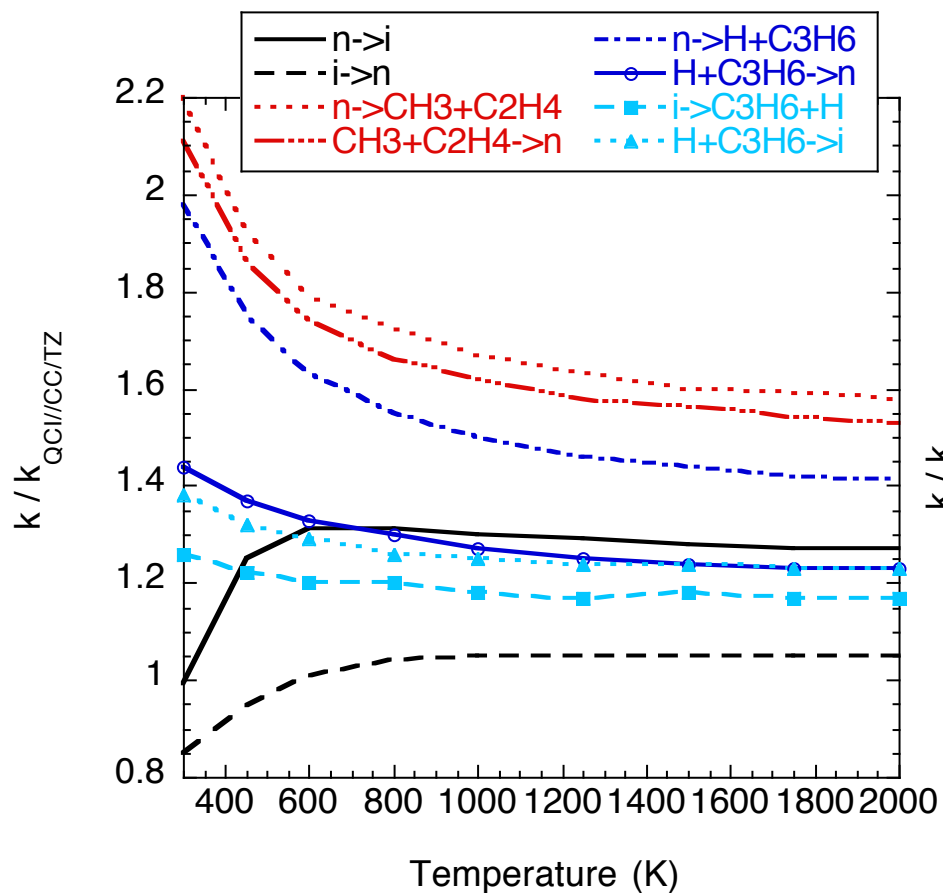
Rovibrational Properties Reactions on C_3H_7 PES

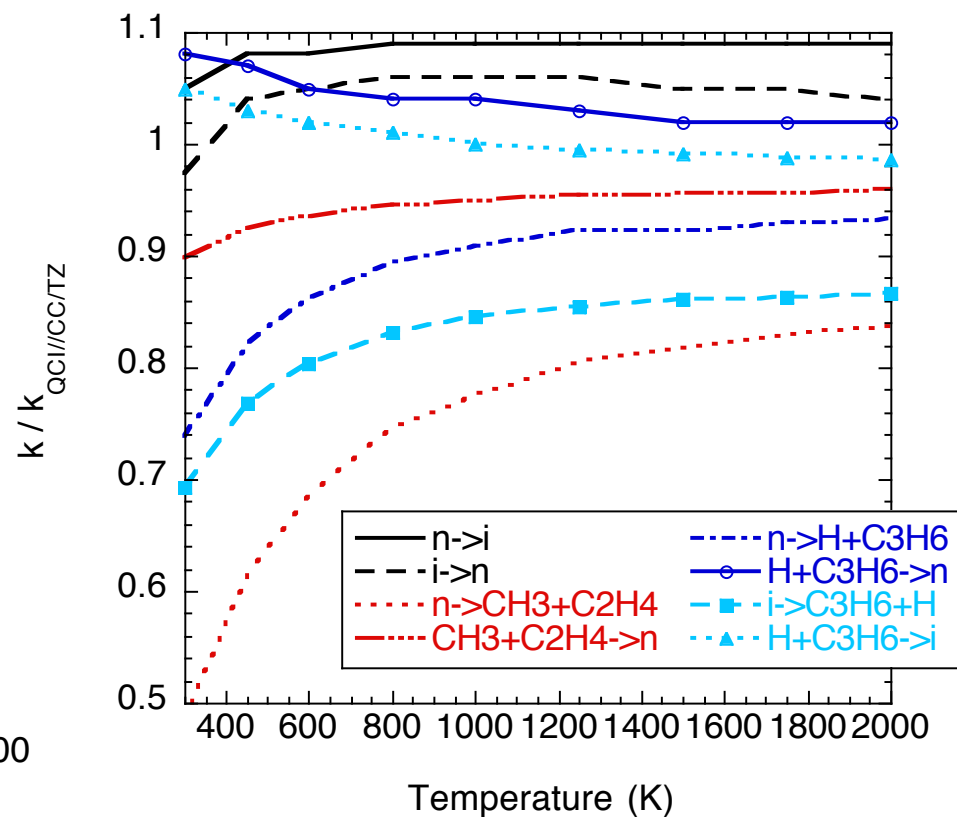QCISD(T)/CBS//B3LYP/6-311++G(d,p)

QCISD(T)/CBS//M06-2X//6-311++G(d,p)
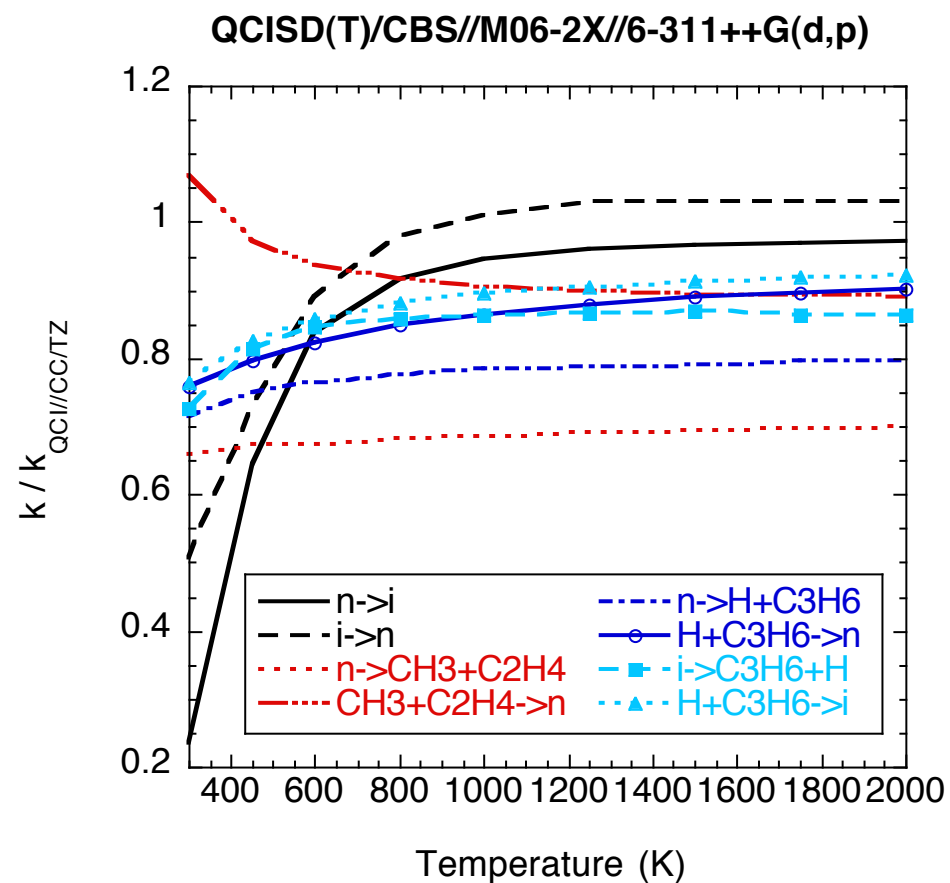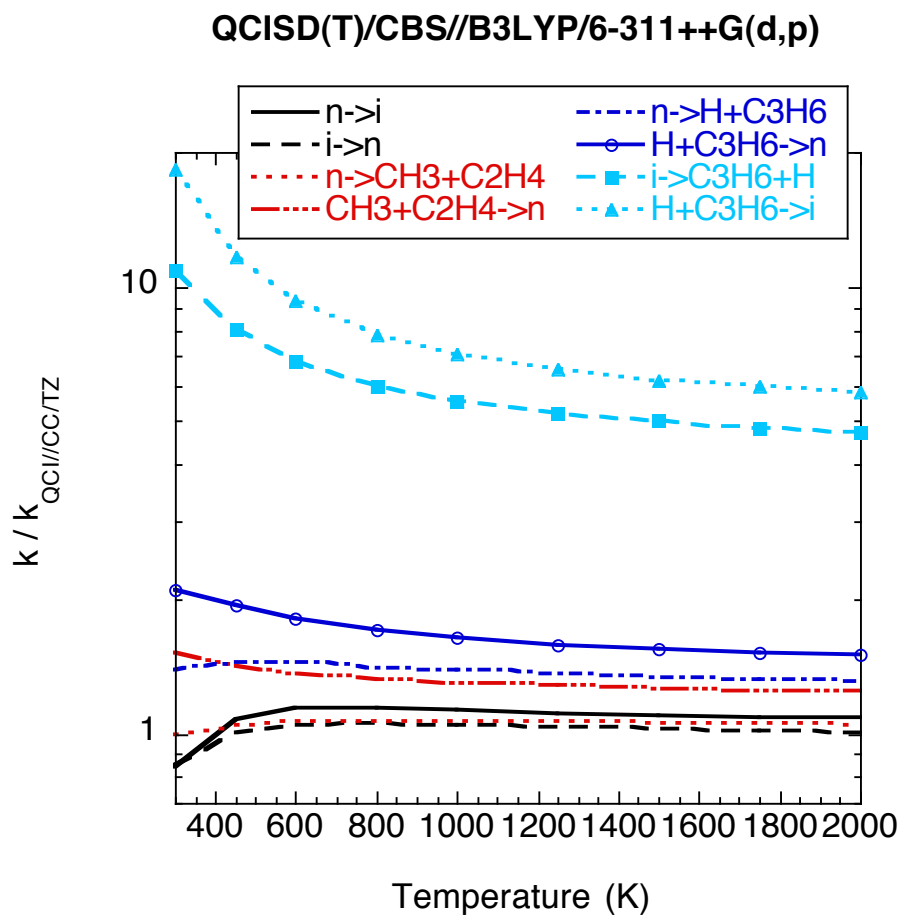
Rovibrational Properties

QCISD(T)/CBS//PT2/TZ

QCISD(T)/CBS//CCSD(T)/ADZ

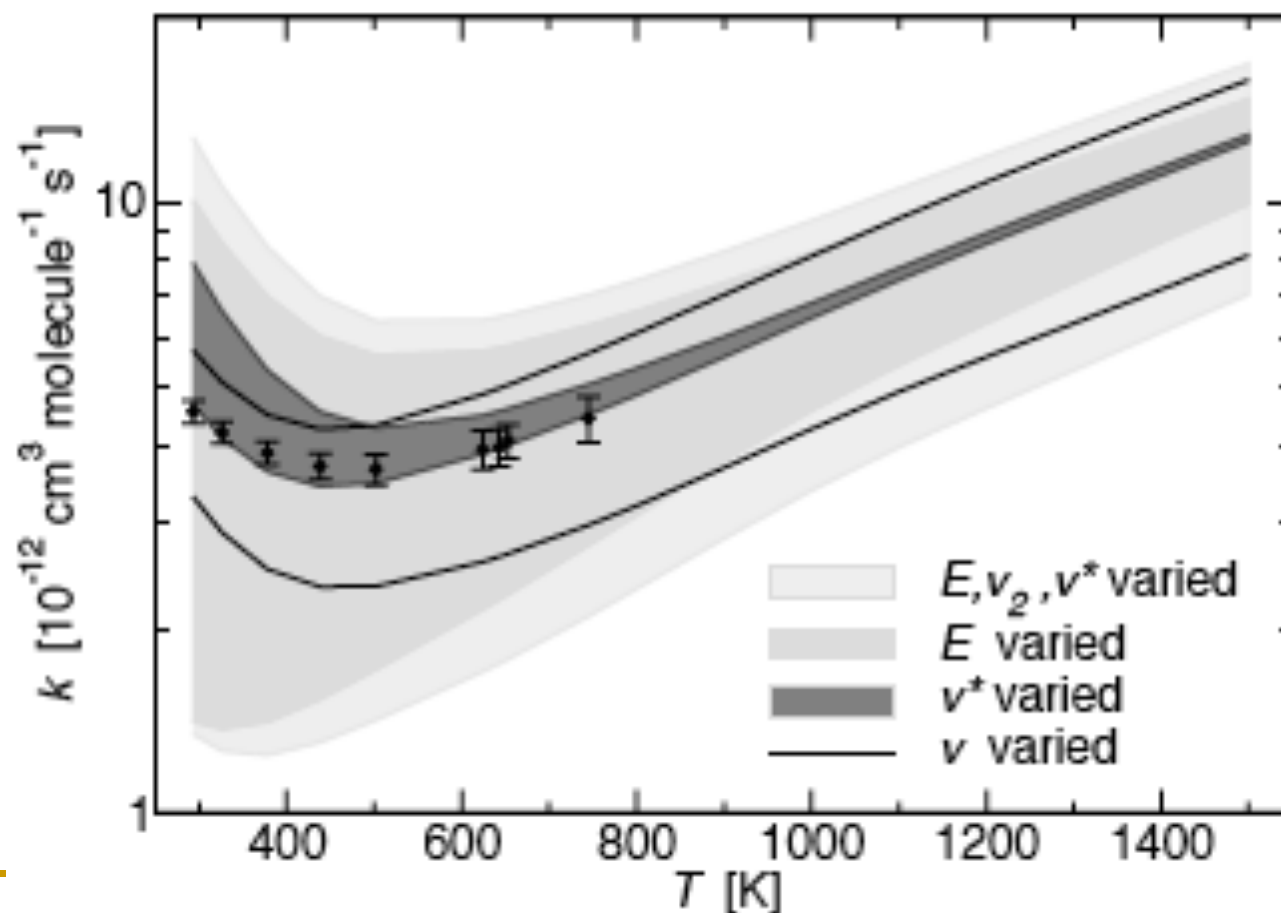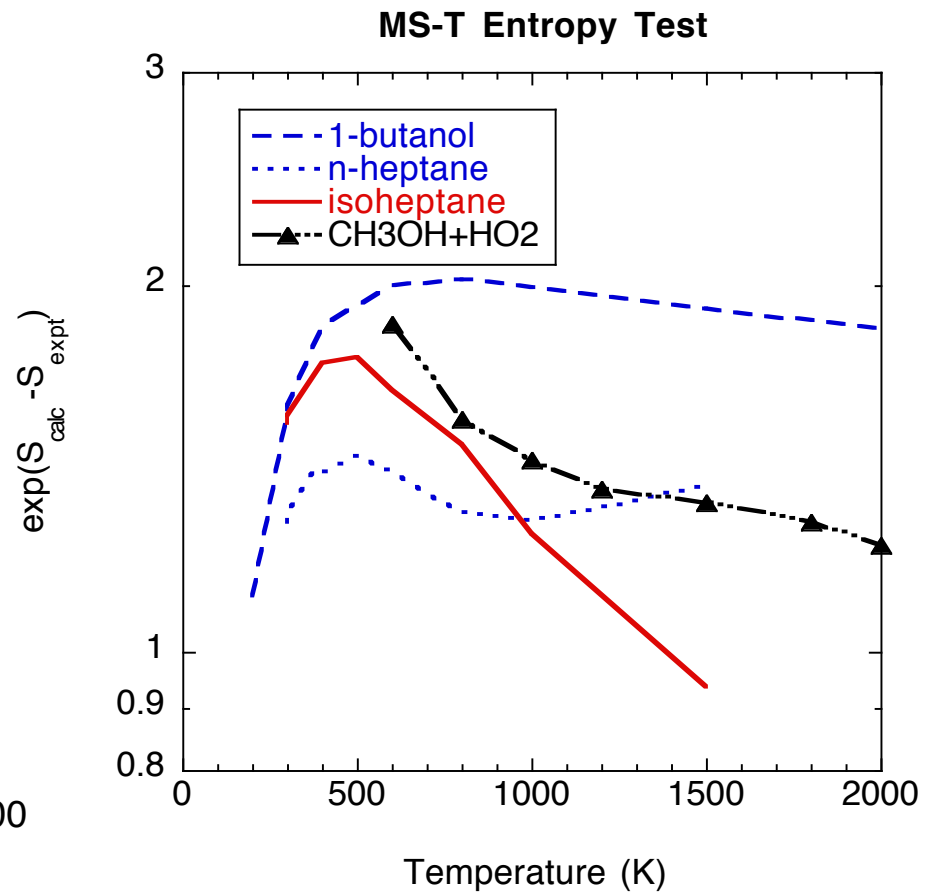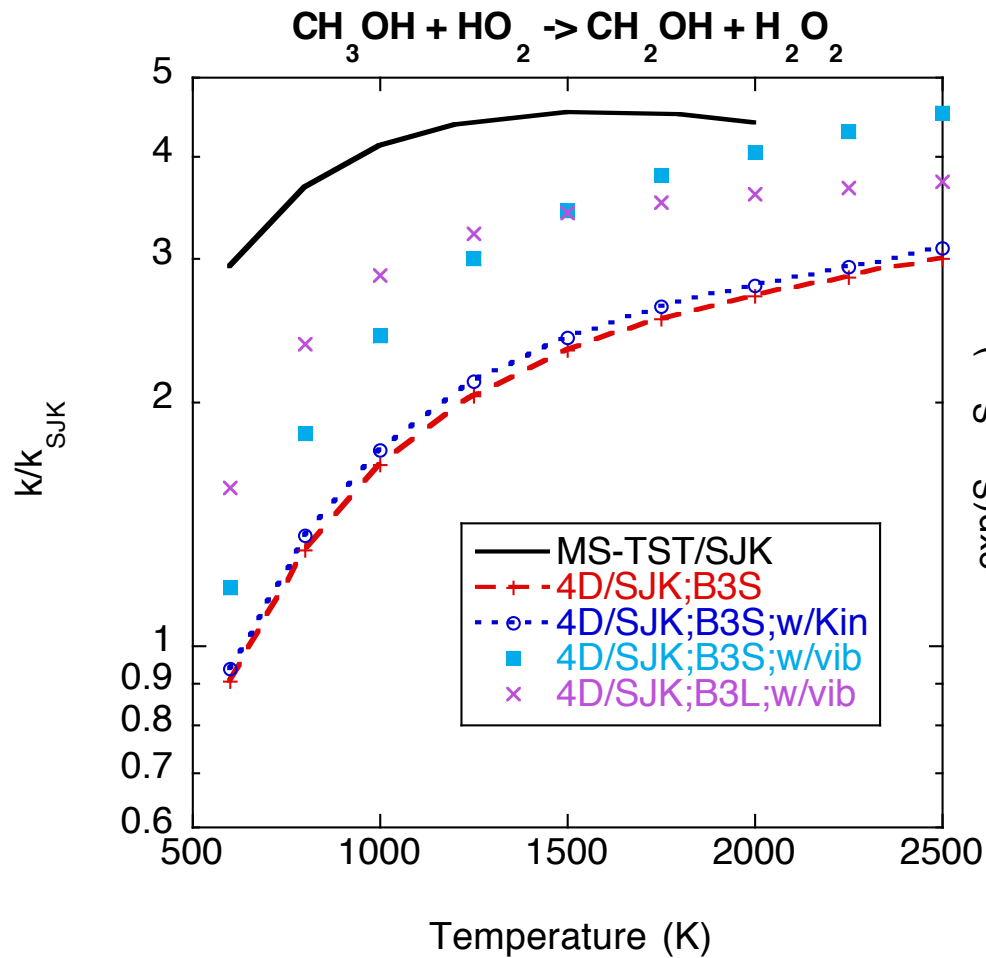# Coupling of Uncertainties

ΔE = ±1.0 kcal/mol

Δv = 1.5 factor

$v^{\neq}$ = (50,850) cm^{-1}

J. Prager, H. N. Najm, J. Zador Proc. Comb. Inst. In press (2012) Paper 5D03

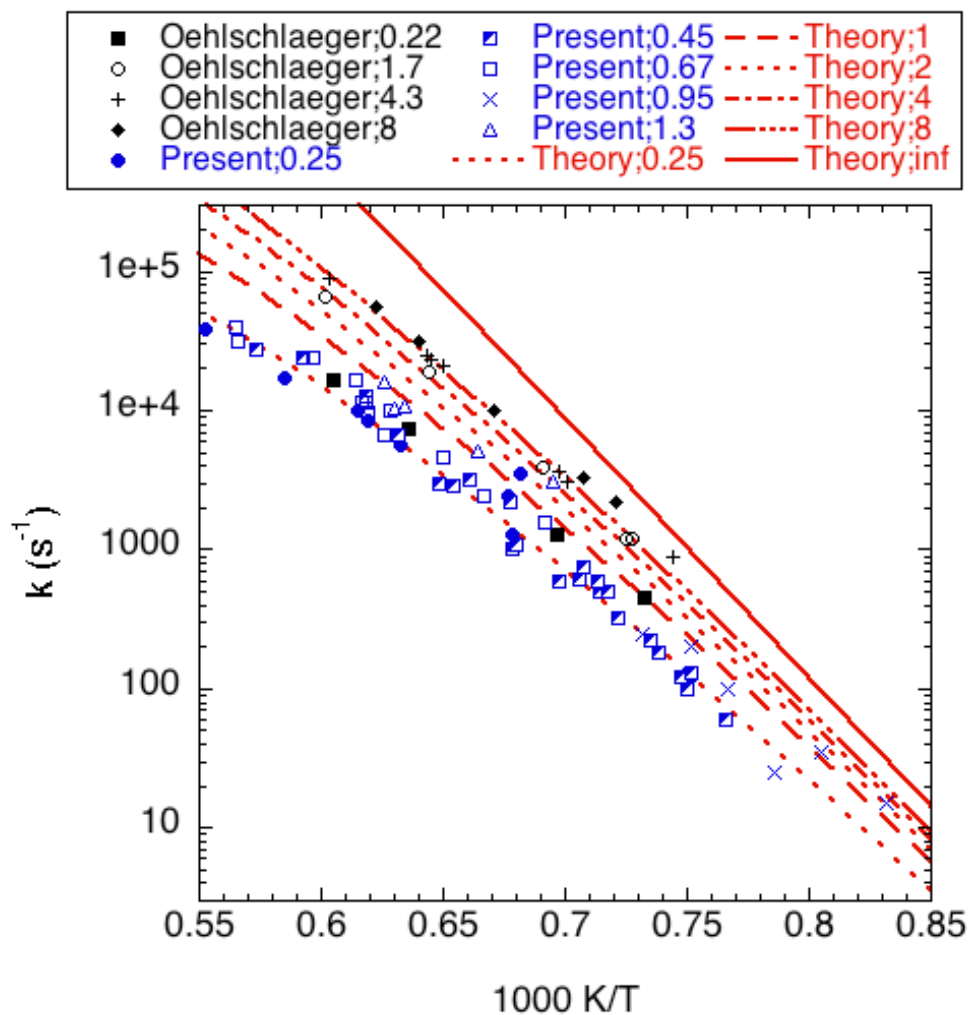$$CH_3CH(OH)CH_3 + OH \rightarrow CH_3C^{\cdot}(OH)CH_3 + H_2O$$
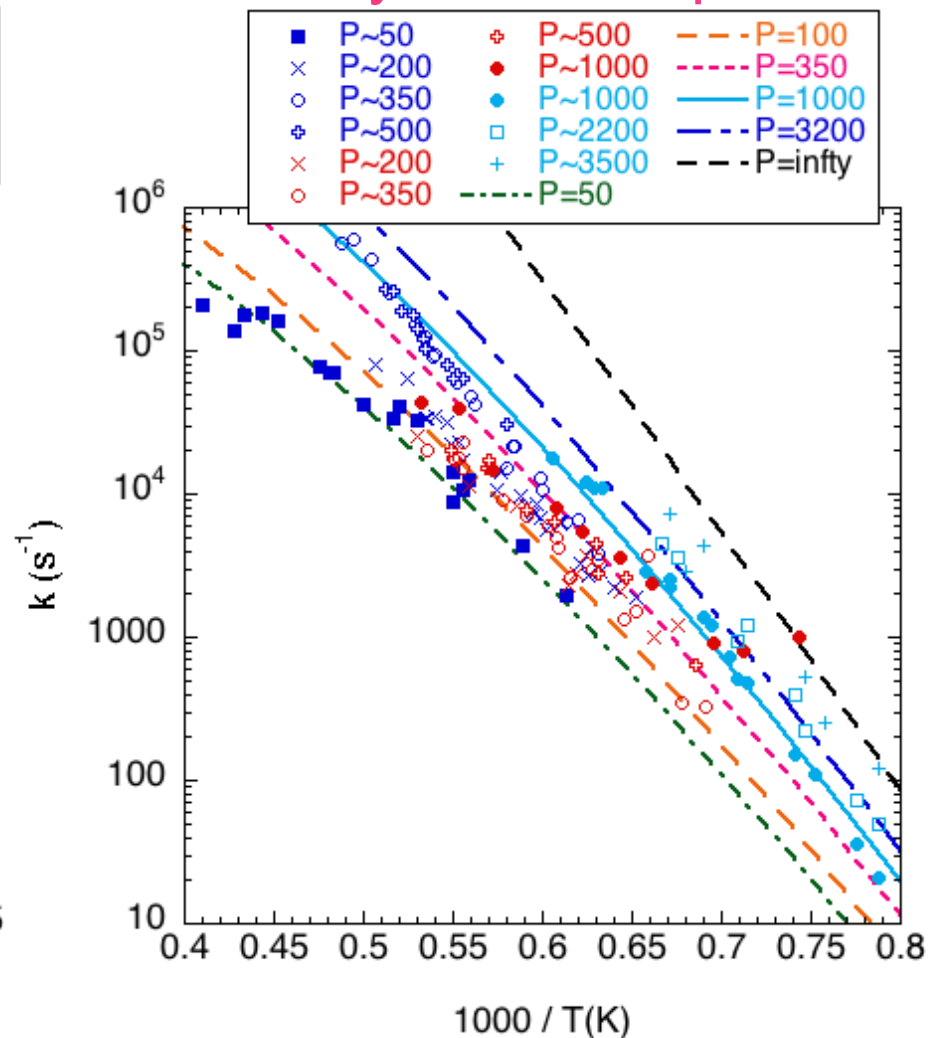
Direct Sampling of Torsions

Pressure Dependence: Comparison with Expt

Propane Decomposition

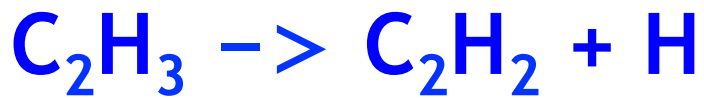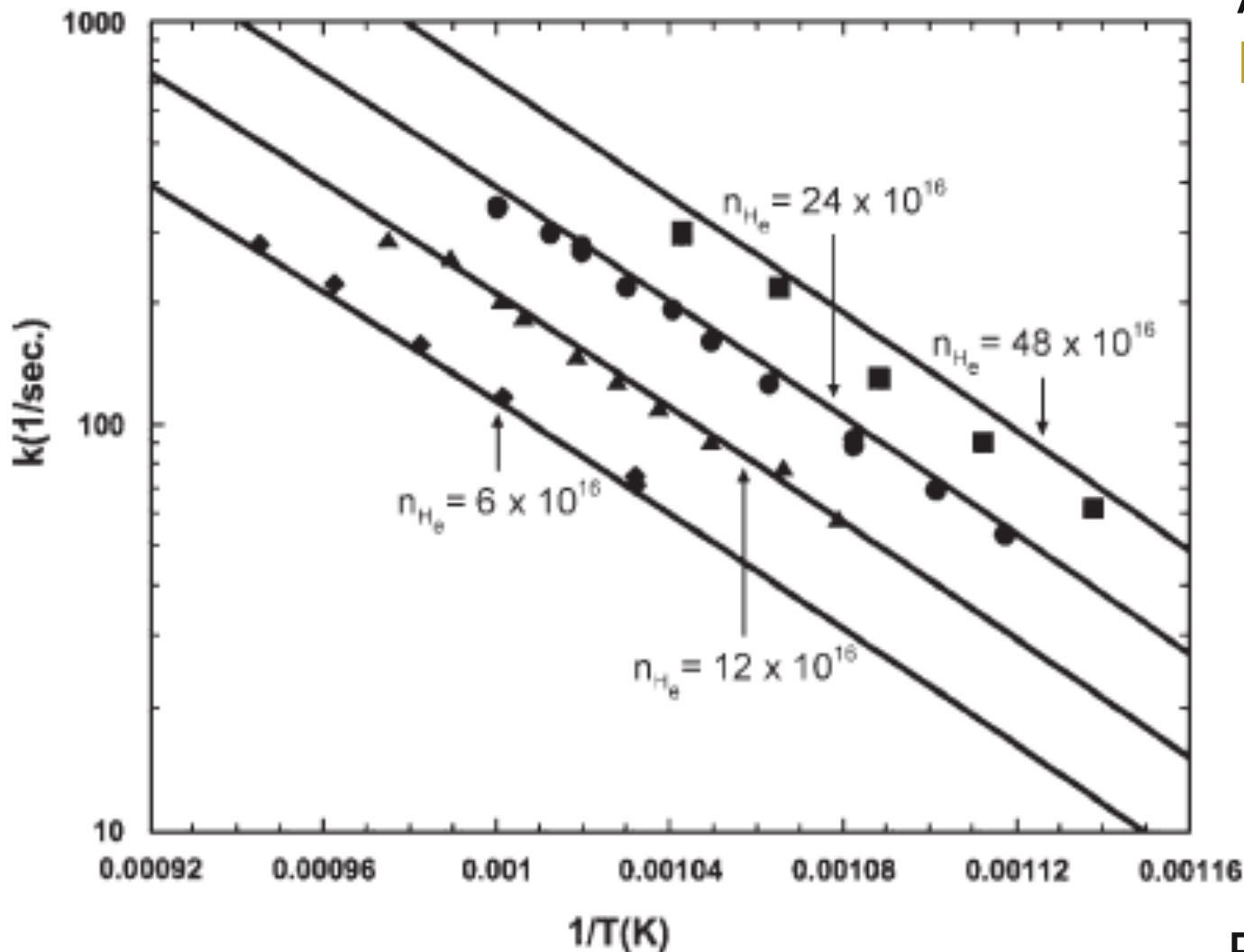## Acetaldehyde Decomposition

$$\langle \Delta E_{down} \rangle = 100 \, (T/300)^{0.85} \, cm^{-1}$$

$$\langle \Delta E_{down} \rangle = 150 \, (T/300)^{0.85} \, cm^{-1}$$

$C_2H_3 \rightarrow C_2H_2 + H$

Energy Transfer
Jasper & Oana
AITSTME
Pelzer, Miller, SJK

Delta E_{down}

Fit
237 cm^{-1}

Trajectory
470 cm^{-1}

Experiment
Knyazev & Slagle

A Priori Predictions of Pressure Dependence

Trajectory Simulations of Energy Transfer
A Priori P(E'-> E)
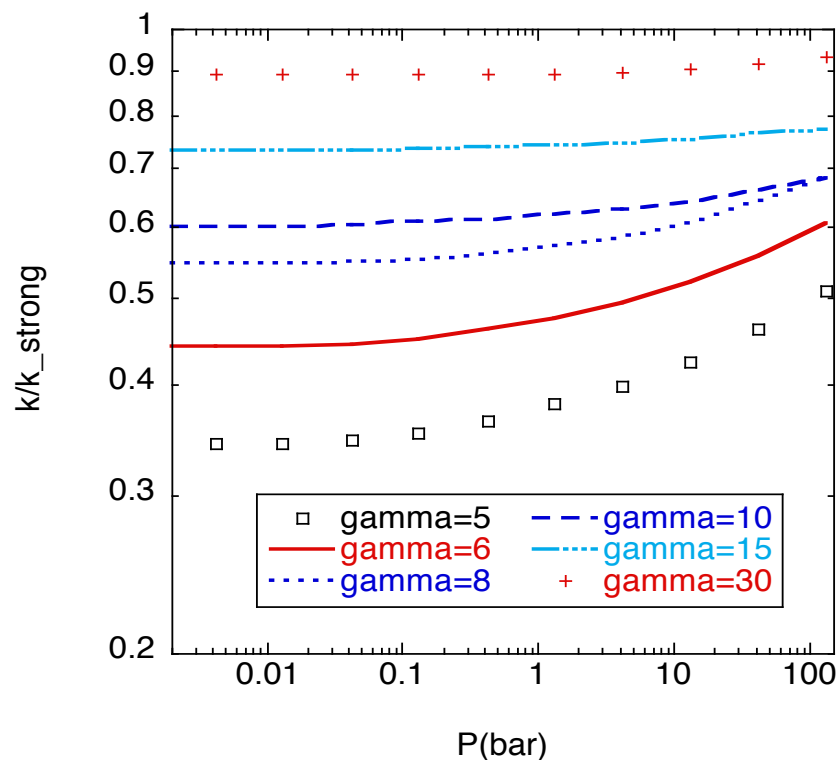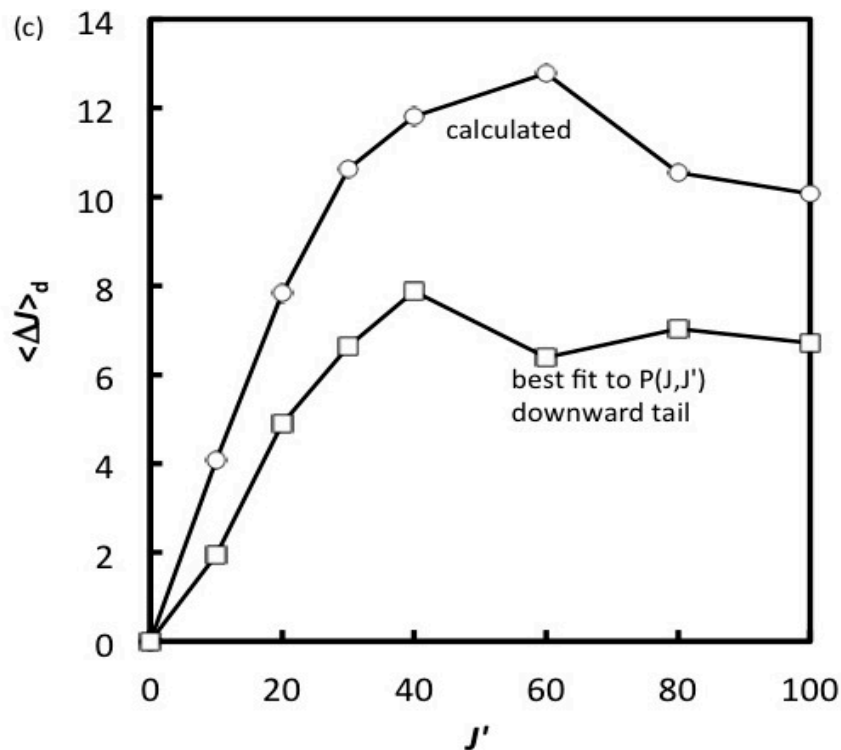1D Master Equation Assumes Strong Collider in J – Not Valid
P(E',J'->E,J) ΔE_{down} ΔJ_{down}
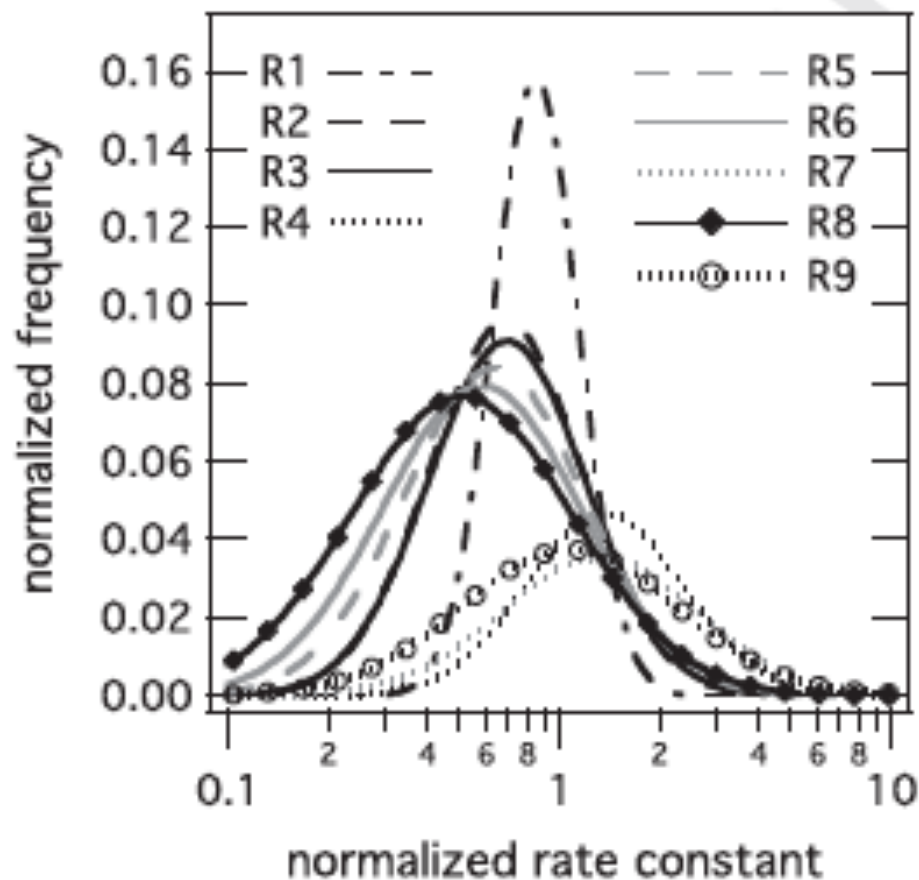2-Dimensional Master Equation (E,J)

Coupling of Uncertainties: n-propyl + O₂
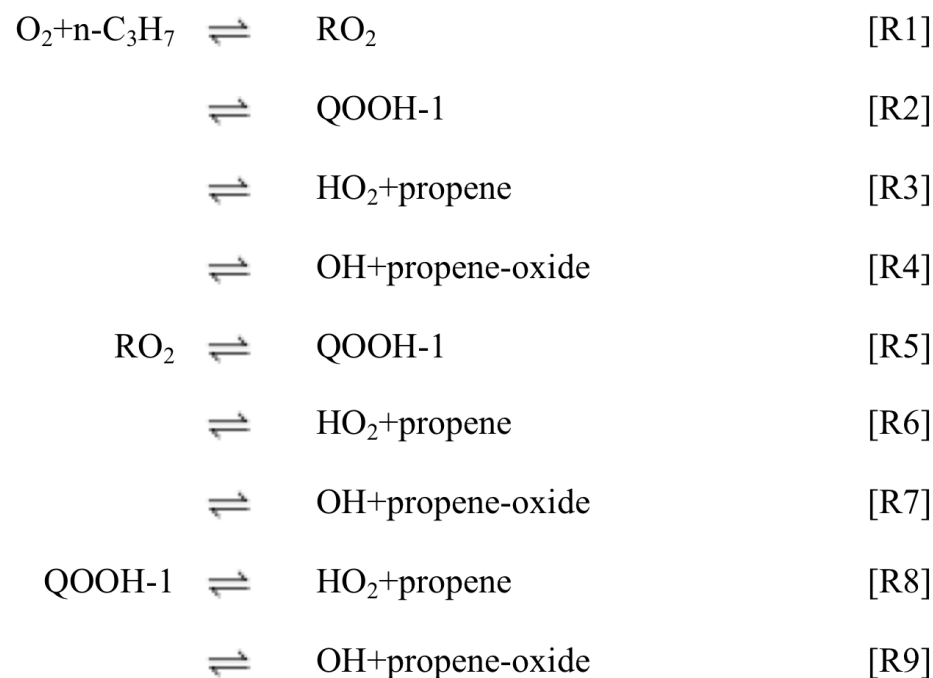
$O_2 + n\text{-}C_3H_7 \rightleftharpoons$	RO_2	[R1]
$\rightleftharpoons$	QOOH-1	[R2]
$\rightleftharpoons$	HO_2+propene	[R3]
$\rightleftharpoons$	OH+propene-oxide	[R4]
$RO_2 \rightleftharpoons$	QOOH-1	[R5]
$\rightleftharpoons$	HO_2+propene	[R6]
$\rightleftharpoons$	OH+propene-oxide	[R7]
QOOH-1 $\rightleftharpoons$	HO_2+propene	[R8]
$\rightleftharpoons$	OH+propene-oxide	[R9]

Funding

US-Department Of Energy

1. Chemical-Physics Program – Chemical Dynamics in the Gas Phase

2. Argonne-Sandia Consortium on High Pressure Combustion Chemistry

3. Combustion Energy Frontier Research Center

4. An Expert Ab Initio Transition-State-Theory-Based Master Equation Code