

Pressure Dependent Kinetics: Single Well Reactions

Simple Models

- Lindemann-Hinshelwood
- RRKM Theory
- Modified Strong Collider

The Master Equation

- 1-dimensional (E)
- 2d Master Equation (E,J)
- Energy Transfer
- Troe Fitting
- Product Channels $\text{CH}_3 + \text{OH}$

Theory of Unimolecular and Recombination Reactions, R. G. Gilbert and S. C. Smith, Blackwell, 1990

Unimolecular Reactions, K. A. Holbrook, M. J. Pilling, S. H. Robertson, Wiley, 1996

Recombination Kinetics

Recombination is a Multistep Process - not single elementary step



But, E is above dissociation threshold so AB just redissociates



Need some process to take away energy and stabilize AB
Collisions with bath gas M (or photon emission)



Effective rate constant is some mix of $k_f(E)$, $k_d(E)$, k_c , and $P(E \rightarrow E')$
Dissociation is related to recombination through equilibrium constant

Simple Models

Lindemann-Hinshelwood

Assume every collision leads to stabilization

Treat association and dissociation on canonical level



Steady state for $[AB^*] \Rightarrow$

$$d[AB]/dt = k_{\text{eff}} [A] [B]$$

$$k_{\text{eff}} = k_f k_c [M] / (k_d + k_c [M]) = k_f P_{\text{stabilization}}$$

High Pressure limit ($[M] \rightarrow \infty$)

$$k_{\text{eff}} = k_f$$

Low Pressure limit ($[M] \rightarrow 0$)

$$k_{\text{eff}} = k_f k_c / k_d$$

Not accurate but good for qualitative thought

Simple Models

RRKM Theory

Treat energy dependence of association and dissociation rate constants $k_f(E)$ and $k_d(E)$

$$k_{\text{eff}}(T,P) = \int dE k_{\text{eff}}(E) P(E) = \int dE k_f(E) P(E) P_{\text{stabilization}}(E,P)$$

Use transition state theory with quantum state counting to evaluate k_f , k_d

$$k_{\text{eff}} = \int dE \frac{N^\pm(E)}{h\rho_{\text{reactant}}(E)} \frac{\rho_{\text{transition}}(E) \exp(-\beta E)}{Q_A Q_B} \frac{k_c[M]}{k_d(E) + k_c[M]}$$

$$k_{\text{eff}} = \frac{1}{hQ_A Q_B} \int dE N^\pm(E) \exp(-\beta E) \frac{k_c[M]}{k_d(E) + k_c[M]}$$

Consider High Pressure Limit; $[M] \rightarrow \infty$

$$k_{\text{eff}}^\infty = \frac{1}{hQ_A Q_B} \int dE N^\pm(E) \exp(-\beta E) = \frac{k_B T}{hQ_A Q_B} \int dE \rho^\pm(E) \exp(-\beta E)$$

$$k_{\text{eff}}^\infty = \frac{k_B T}{h} \frac{Q^\pm}{Q_A Q_B}$$

Simple Models

Modified Strong Collider

Assume only a fraction β_c of collisions lead to stabilization

$$k_{eff} = \frac{1}{hQ_A Q_B} \int dE N^\pm(E) \exp(-\beta E) \frac{\beta_c k_c [M]}{k_d(E) + \beta_c k_c [M]}$$

Consider low pressure limit; $[M] \rightarrow 0$

$$k_{eff}^0 = \frac{1}{hQ_A Q_B} \int dE N^\pm(E) \exp(-\beta E) \frac{\beta_c k_c [M]}{k_d(E)}$$

$$k_{eff}^0 = \frac{\beta_c k_c [M]}{Q_A Q_B} \int_0^\infty dE \rho_{AB}(E) \exp(-\beta E)$$

k_{eff}^0 does not depend on transition state! Only the threshold E matters

β_c is a fitting parameter -typical value ~ 0.1

Master Equation

Consider $n(E,t)$ = time-dependent population of AB molecule at energy E

Master equation Irreversible Formulation

$$\frac{dn(E)}{dt} = k_c[M] \int dE' [P(E,E')n(E',t) - P(E',E)n(E,t)] - k_d(E)n(E,t)$$

Replace $n(E,t)$ with normalized population $x(E,t) = n(E,t) / \int dE n(E,t)$

Steady state for $x \Rightarrow$

$$-k(T,p)x(E) = k_c[M] \int dE' P(E,E')x(E') - k_c[M]x(E) - k_d(E)x(E)$$

Master equation Reversible Formulation

$$\frac{dn(E)}{dt} = k_c[M] \int dE' [P(E,E')n(E',t) - P(E',E)n(E,t)] - k_d(E)n(E,t) +$$

$$k_f(E) \frac{\rho_{\text{reactant}}(E) \exp(-\beta E)}{Q_A Q_B} n_A n_B$$

Master Equation

Symmetrized Form

$$f^2(E) = \rho(E) \exp(-\beta E) = F(E)Q(T)$$

$$y(E) = x(E)/f(E)$$

Discretize master equation

$$\frac{d|y\rangle}{dt} = G'|y\rangle$$
$$G'_{ij} = k_c[M]P(E_i, E_j) \frac{f(E_j)}{f(E_i)} \delta E - \left[1 + \frac{k_d(E)}{k_c[M]} \right] \delta_{ij}$$

Diagonalize

$$|y(t)\rangle = \sum_{j=1}^N \exp(\xi_j t) |g'_j\rangle \langle g'_j|y(0)\rangle$$

Eigenvalues are all negative

One with smallest magnitude defines the rate coefficient

$$k(T, p) = -\xi_1$$

Others are related to rate of energy transfer - form continuum

Master Equation

Problems at Low T

numerical difficulties with diagonalization due to large dynamic range

Various Solutions

1. Integrate in time
2. Quadruple Precision
3. Reformulate with sink for complex \Rightarrow Matrix inversion

Master Equation

Problems at high T

Dissociation occurs on same time scale as energy relaxation

Nonequilibrium factor f_{ne}

$$f_{ne} = \frac{\left(\int dE c(E)\right)^2}{\left(\int dE \frac{c^2(E)}{F(E)}\right)^2} \quad c(E) = \text{steady state distribution}$$

Deviation of f_{ne} from unity indicates how much dissociation happens before relaxation

Detailed balance is still satisfied for fraction that happens after relaxation

Boltzmann Distributions

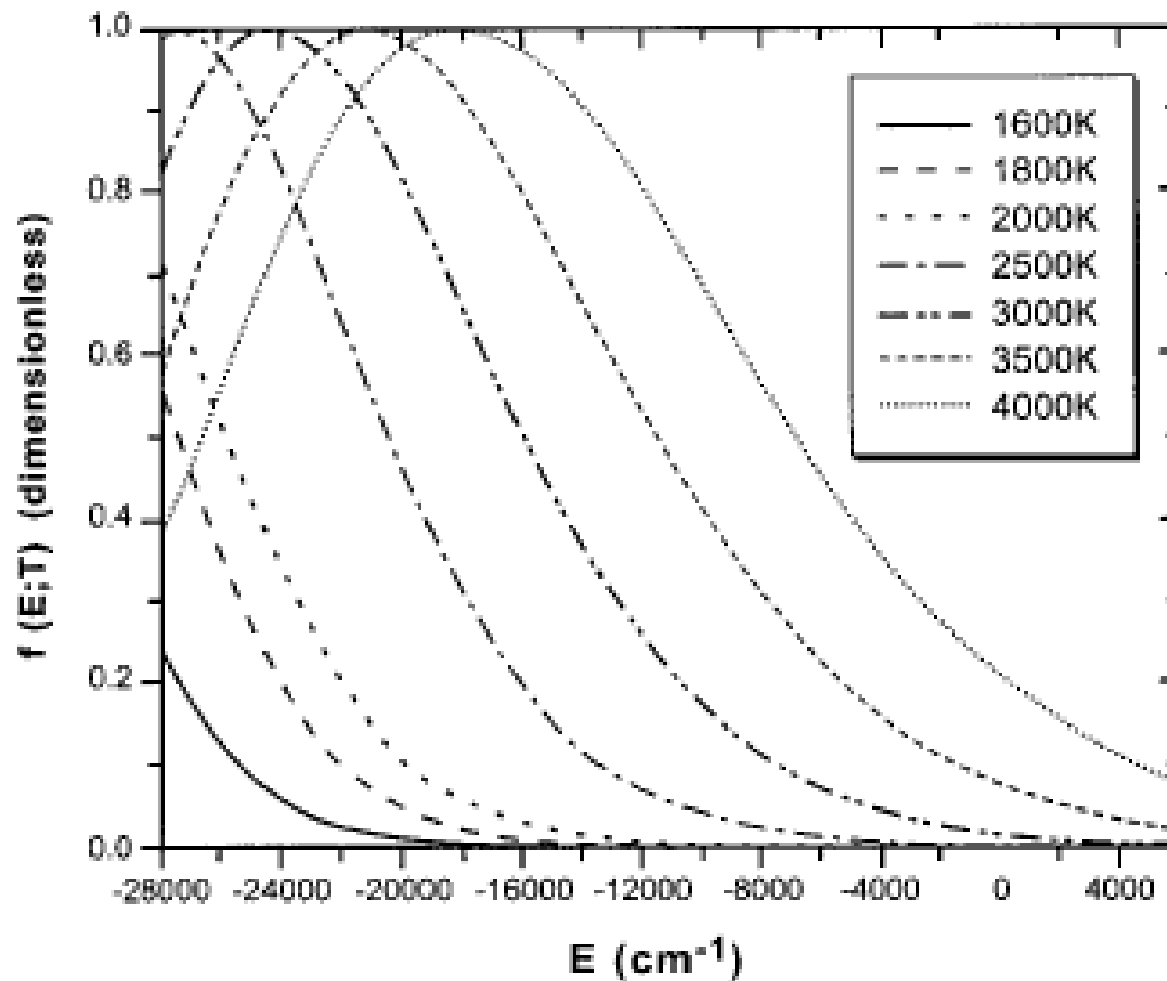
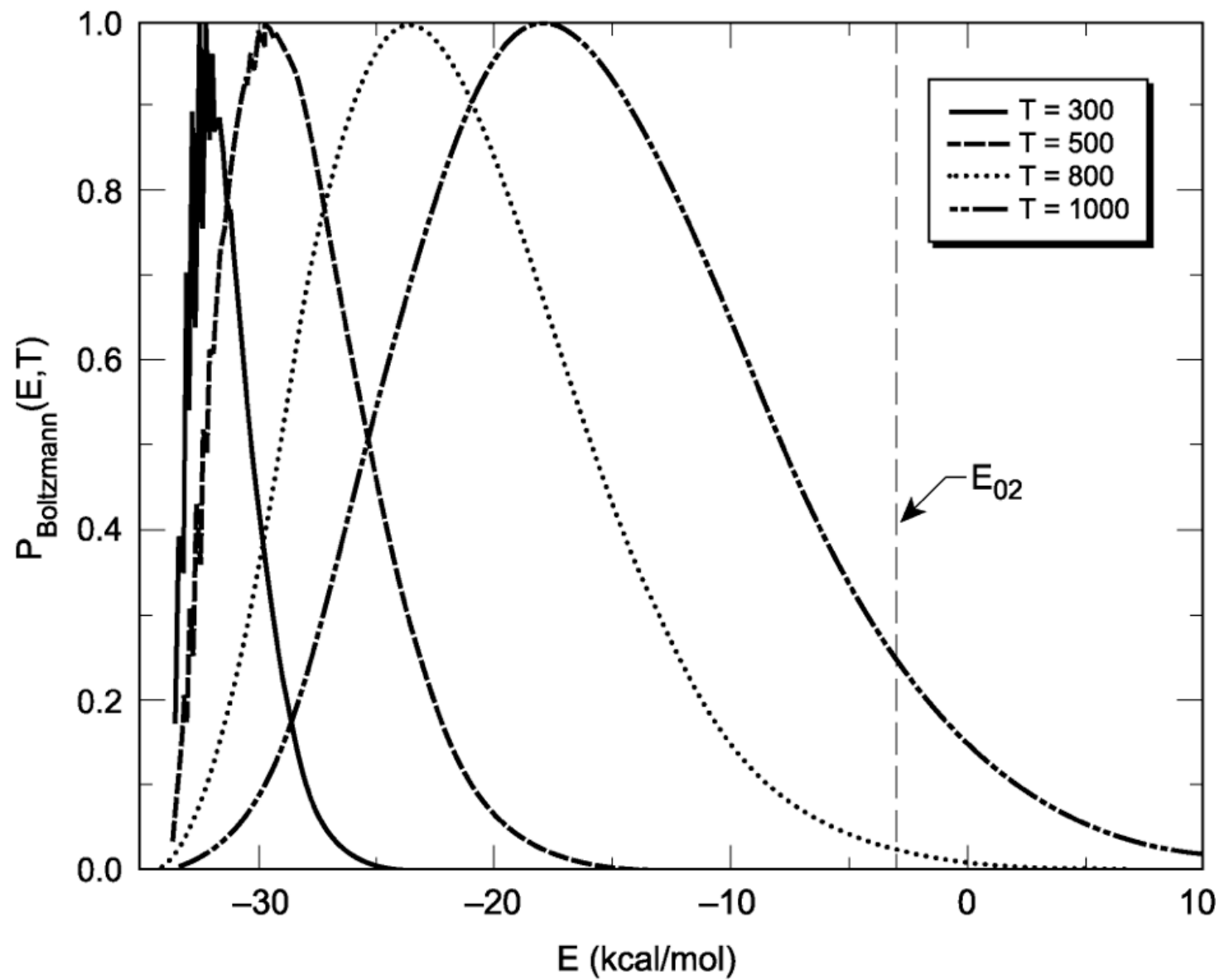
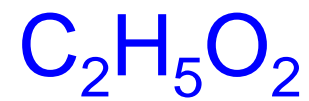


Figure 8. Relative values of $f(E;T)$. The functions are normalized so that the peak is always unity.

Boltzmann Distributions



Master Equation

2-Dimensional

Total Angular Momentum J - conserved between collisions

Master equation in E and J

$n(E, J, t)$

or

$x(E, J, t)$

$P(E, J, E', J')$

$k(E, J)$

Numerical solution timeconsuming

Need more information on energy transfer than we have

2D Master Equation

E,J Model

E,J model

like E model, but treat $k(E,J)$ properly

$$k(E) = \sum_J k(E,J) y(E,J) / \sum_J y(E,J)$$

$$y(E,J) = \varphi(E,J) / \{ k_c[M] + k(E,J) \}$$

$$x(E) = \sum_J x(E,J)$$

$$x(E,J) = \frac{k_c[M]\varphi(E,J)}{Z + k(E,J)} \int dE' P(E,E') x(E')$$

Proper treatment of J dependent thresholds

Proper zero-pressure limit

Proper high-pressure limit

Consistent with detailed balance

2D Master Equation

ε, J Model

ε, J model

Active energy - does not include overall rotation

$$\varepsilon = E - E_J$$

$$E_J = BJ(J+1)$$

$$P(\varepsilon, J, \varepsilon', J') = P(\varepsilon, \varepsilon')\Phi(\varepsilon, J)$$

$$\Phi(\varepsilon, J) = (2J+1)\rho(\varepsilon, J)\exp(-\beta E_J) / \sum_J (2J+1)\rho(\varepsilon, J)\exp(-\beta E_J)$$

$\rho(\varepsilon, J)$ = density of states for active degrees of freedom

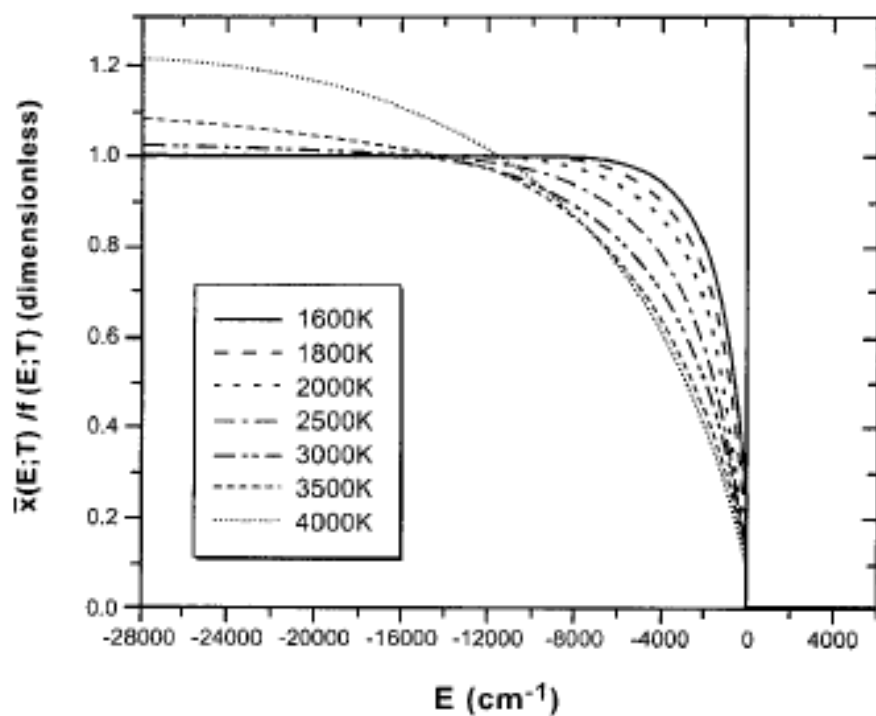
Thermally equilibrated J distribution

Satisfies Detailed balance

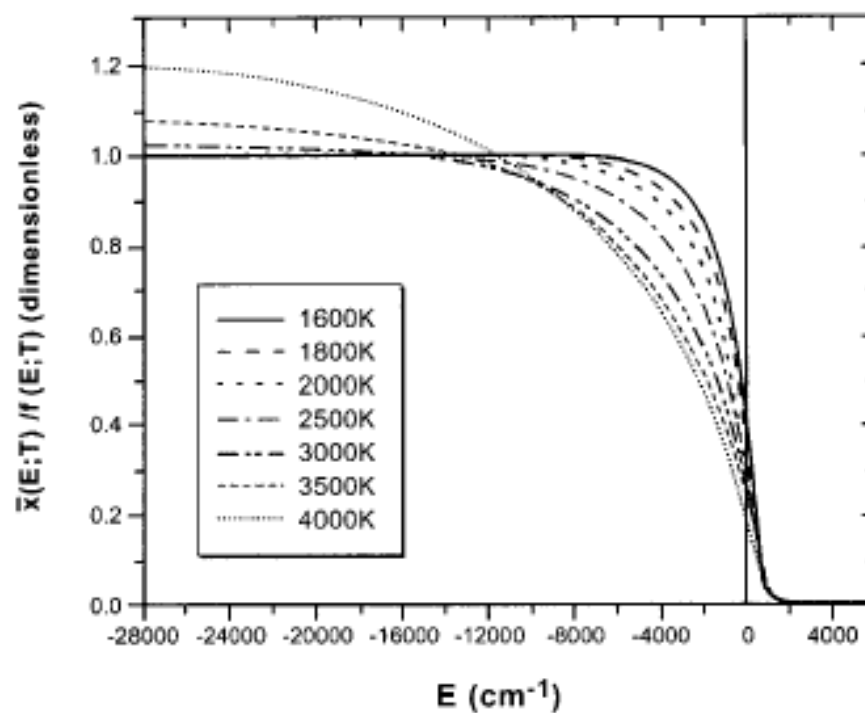
Steady State Distribution



E model



E,J model



Low Pressure Limit CH_4

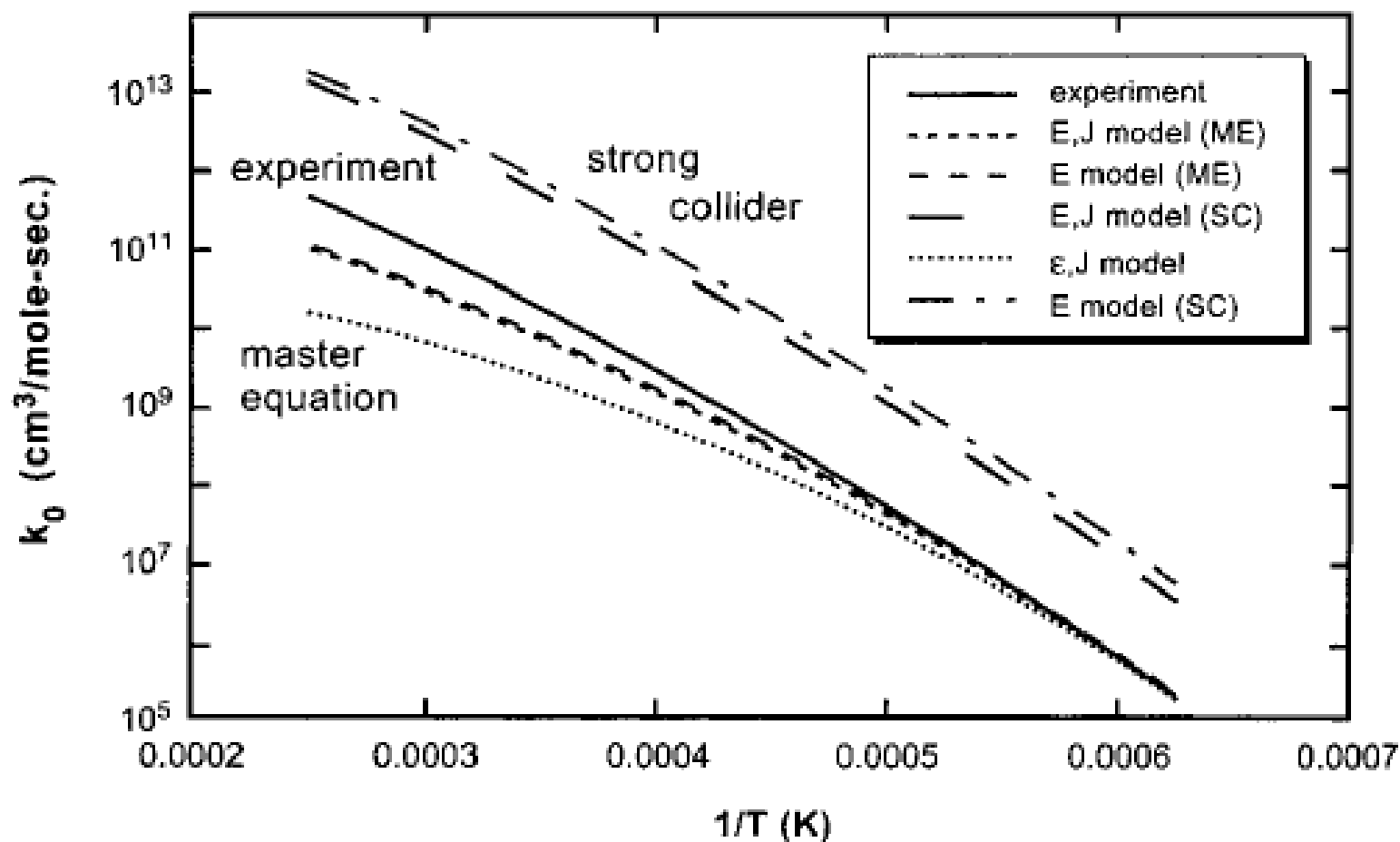
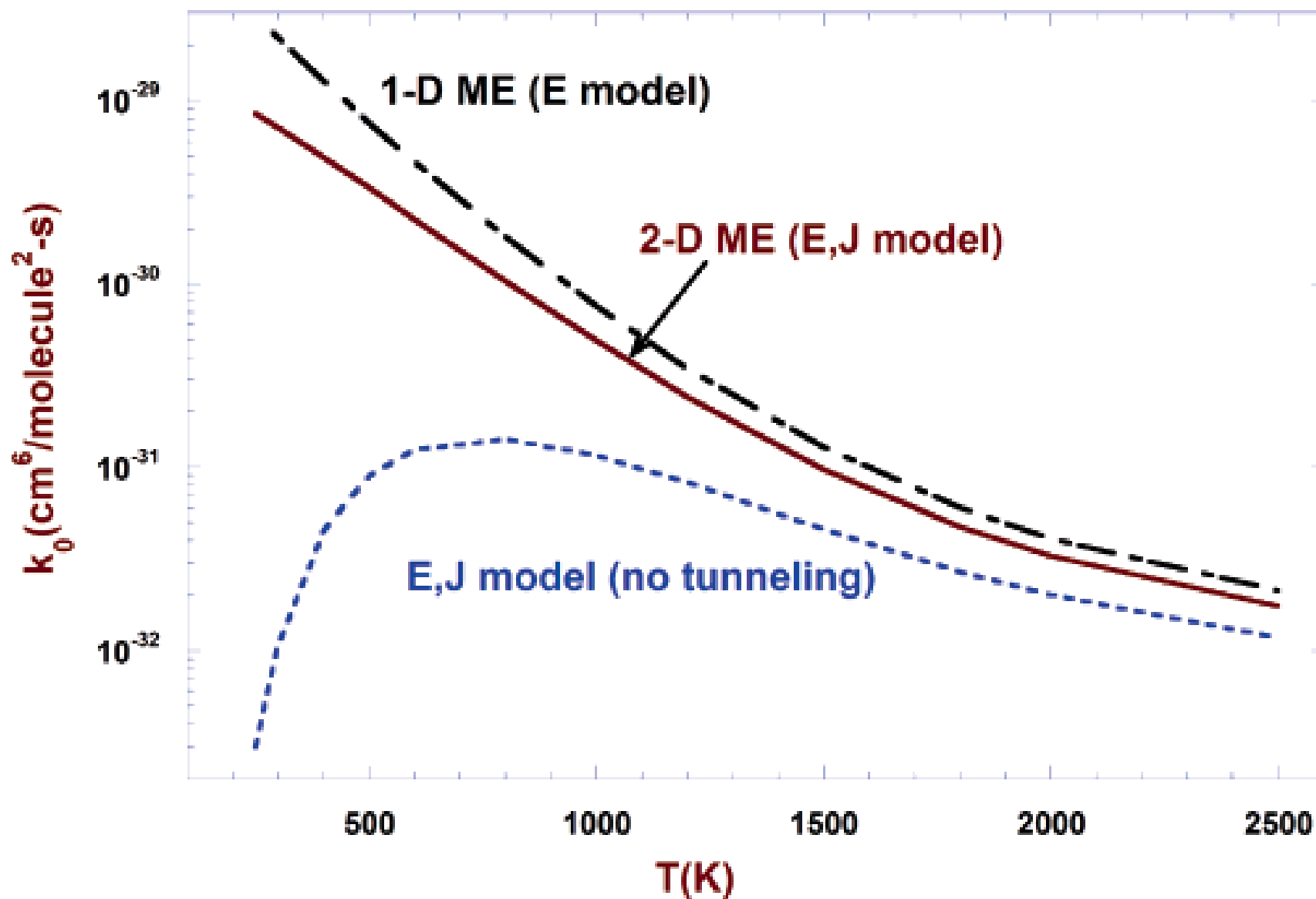
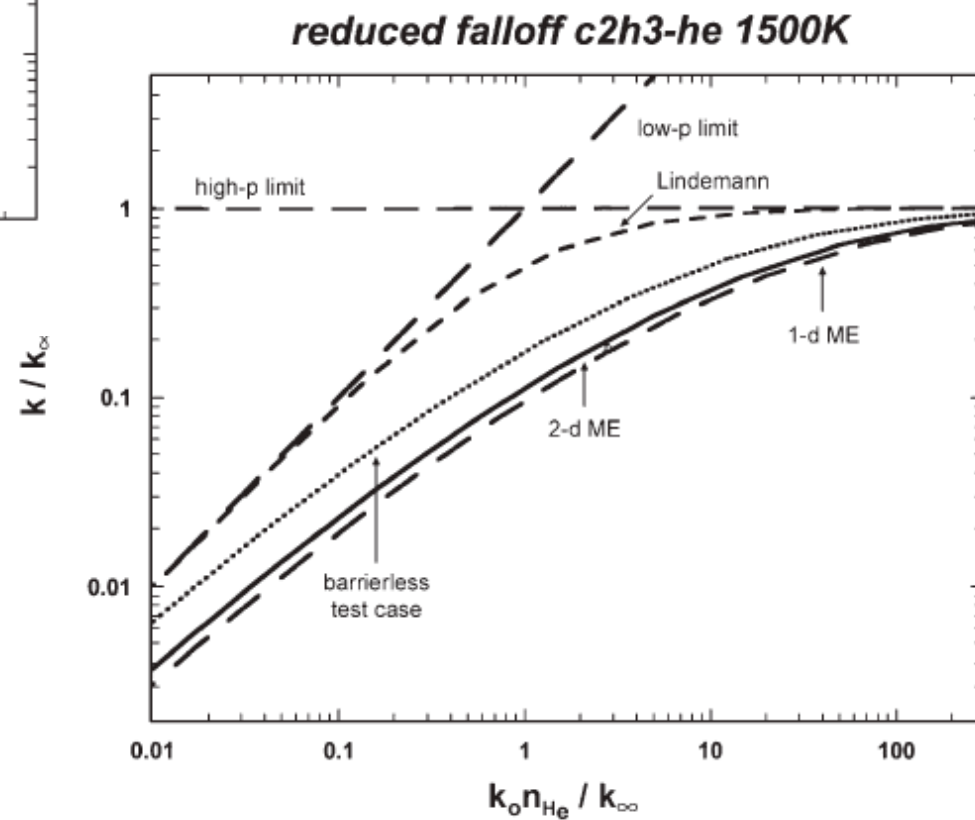
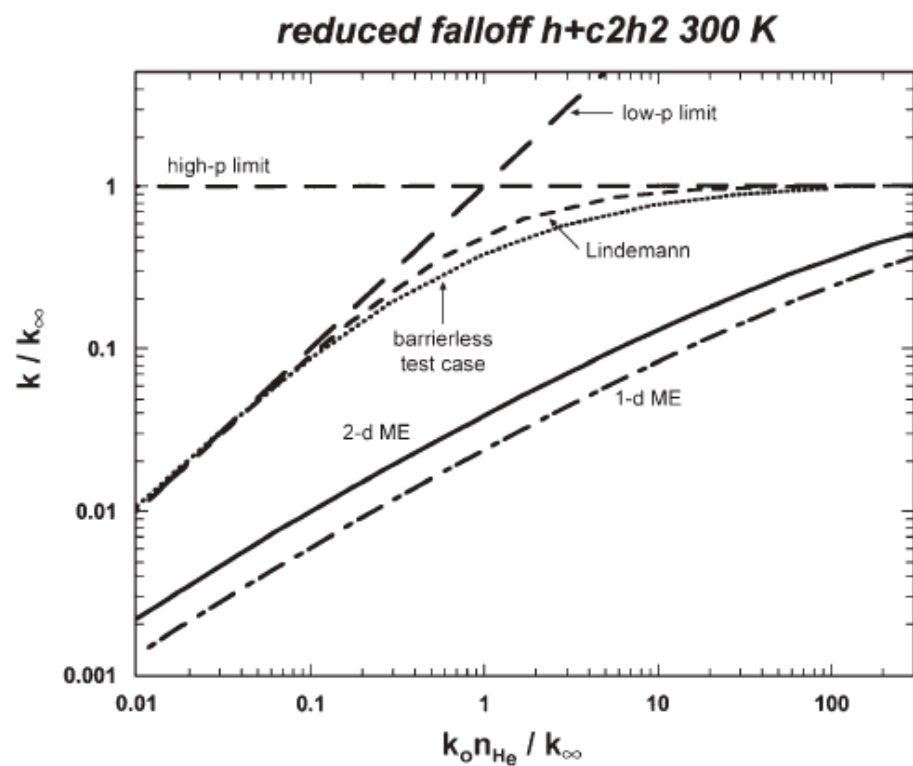


Figure 1. High-temperature rate coefficients. The master-equation calculations were done with $\langle \Delta E_d \rangle = 410 \text{ cm}^{-1}$, independent of T , for the EJ and E models. A constant value of $\langle \Delta \epsilon_d \rangle = 35 \text{ cm}^{-1}$ was assumed for the ϵJ ME calculations.

Low Pressure Limit



Reduced Falloff Curves



Collision Rates

Hard Sphere

$$k_c^{HS} = \sqrt{\frac{8kBT}{\pi\mu}} \pi d^2$$

Lennard-Jones

$$k_c^{LJ} = k_c^{HS} \Omega_{2,2}^*$$

$$\Omega_{2,2}^* = \frac{1.16145}{(T^*)^{0.14874}} + \frac{0.52487}{\exp(0.7732T^*)} + \frac{2.16178}{\exp(2.437887T^*)} \quad T^* = k_B T / \epsilon$$

Underestimates collision rate

Correct with larger average energy transferred

Dipole Corrections

Energy Transfer Forms

Exponential Down

$$P(E, E') = \frac{1}{C_N(E')} \exp(-\Delta E / \alpha)$$

$$\alpha = \alpha_0 (T / 298)^n$$

$$\alpha_0 \sim 50-400 \text{ cm}^{-1}$$

$$n \sim 0.85$$

Fit to experiment

Gaussian Down

$$P(E, E') = \frac{1}{C_N(E')} \exp\left[-(\Delta E / \alpha)^2\right]$$

Double Exponential Down

$$P(E, E') = \frac{1}{C_N(E')} \left[(1-f) \exp(-\Delta E / \alpha_1) + f \exp(-\Delta E / \alpha_2) \right]$$

Energy Transfer Moments

Average Energy Transferred

$$\langle \Delta E \rangle = \int dE (E' - E) P(E, E')$$

Average Downwards Energy Transferred

$$\langle \Delta E_d \rangle = \int_0^{E'} dE' (E' - E) P(E, E') / \int_0^{E'} dE' P(E, E')$$

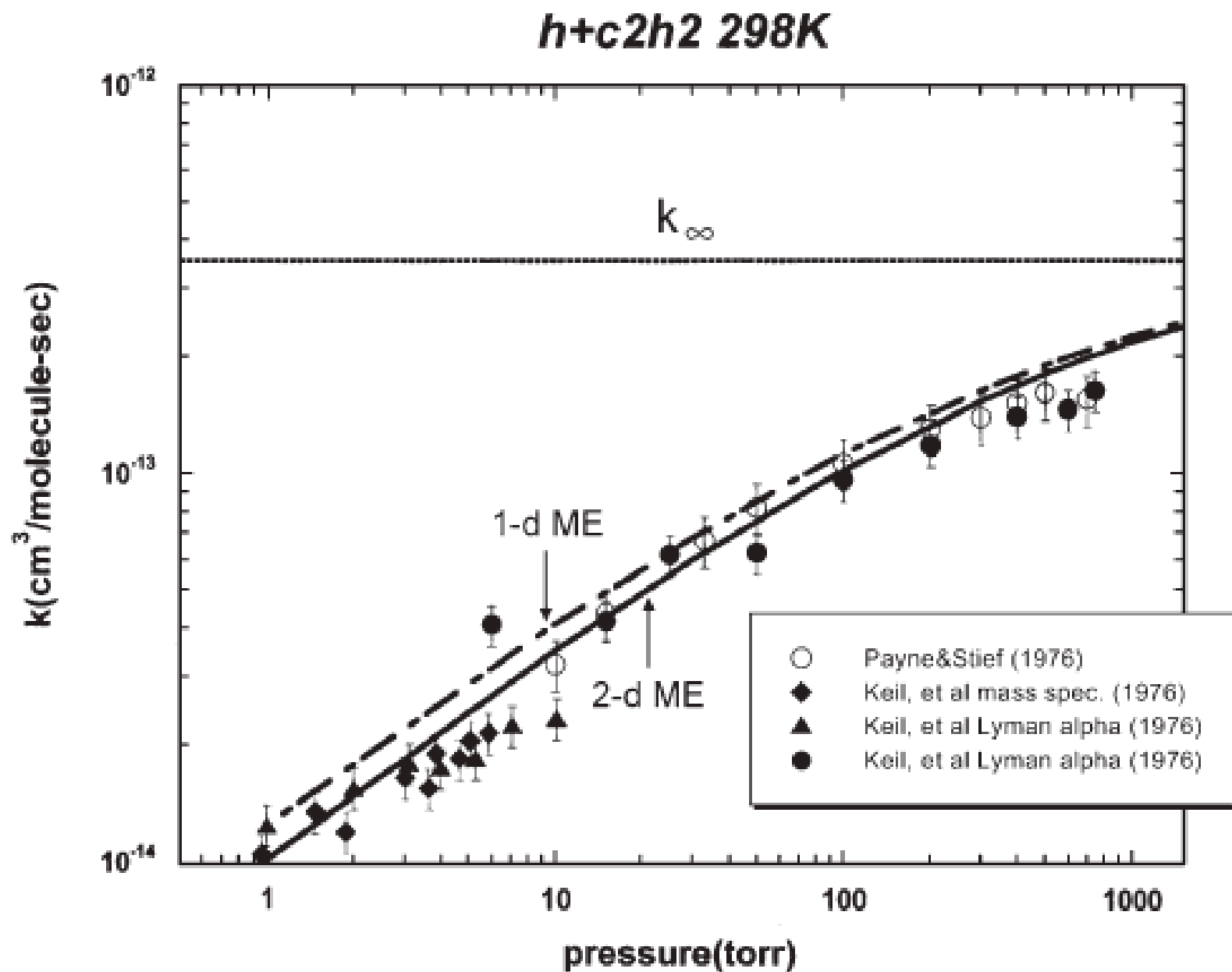
$$\langle \Delta E_d \rangle \approx \alpha \quad \text{for exponential down}$$

Average squared energy transfer

$$\langle \Delta E^2 \rangle = \int dE (E - E')^2 P(E, E')$$

Fits to Experiment

H + C₂H₂ Addition



Fits to Experiment

C₂H₃ Dissociation

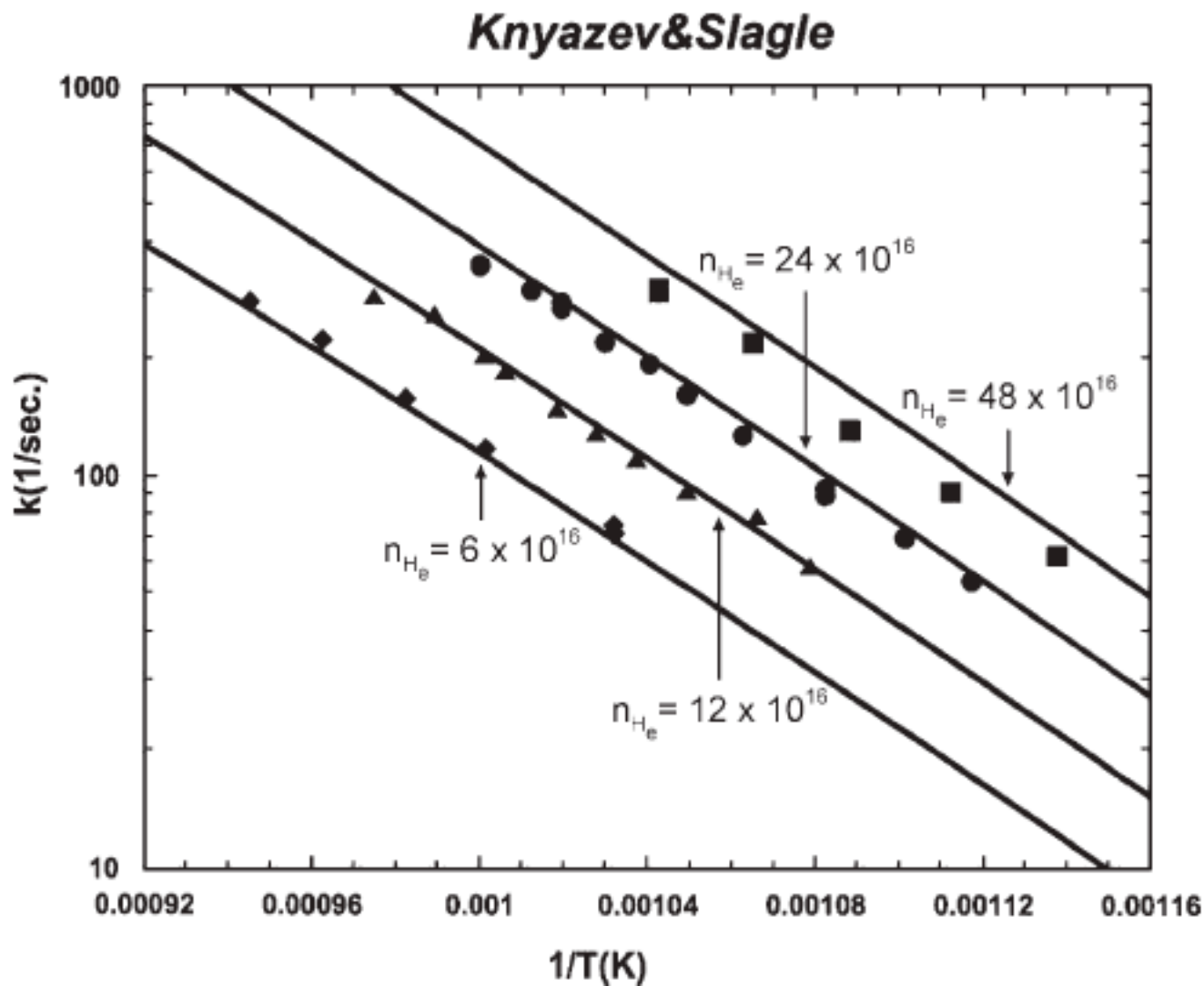


Fig. 5 Comparison of the theoretical results for $k_{-1}(T,p)$ ($\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}$) with the experiments of Knyazev and Slagle.²¹ The units of n_{He} are molecule cm^{-3} .

Fits to Experiment

T dependent ΔE_d

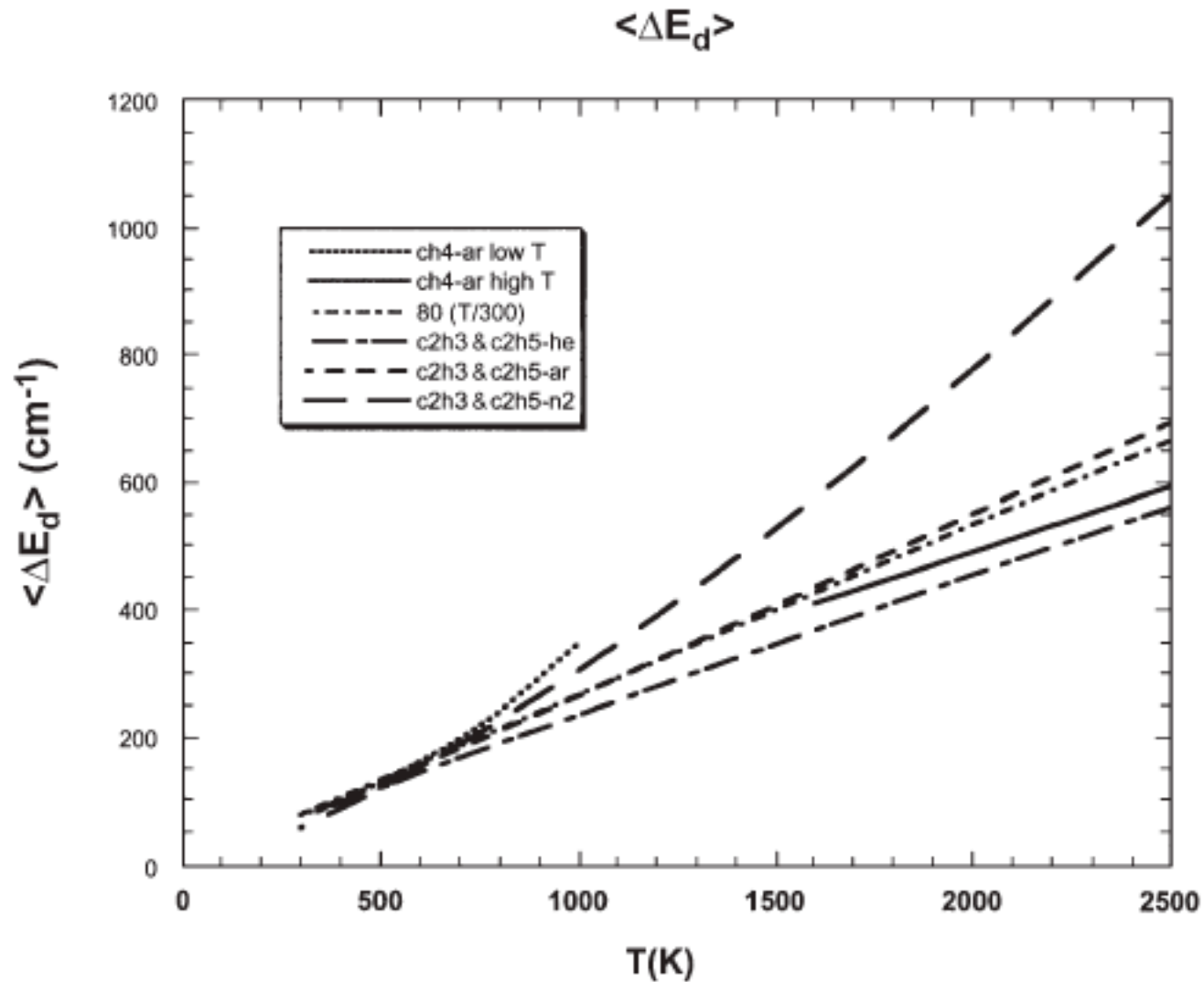


Fig. 8 Values of $\langle \Delta E_d \rangle$ as a function of temperature for several molecules and collision partners.

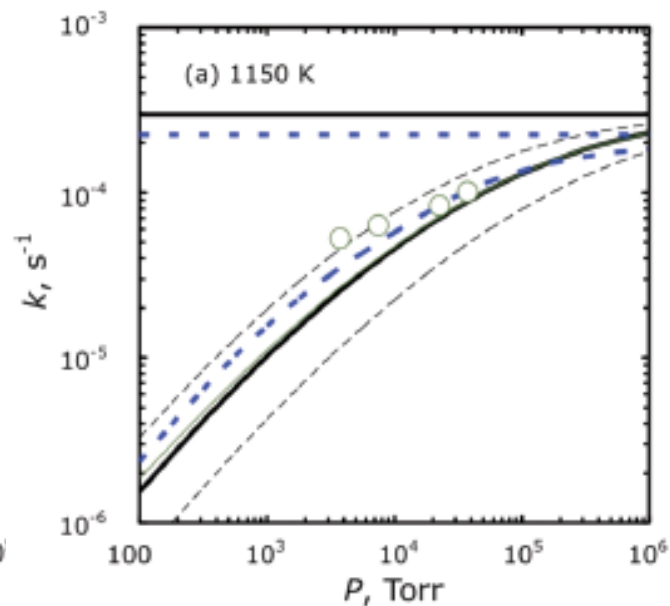
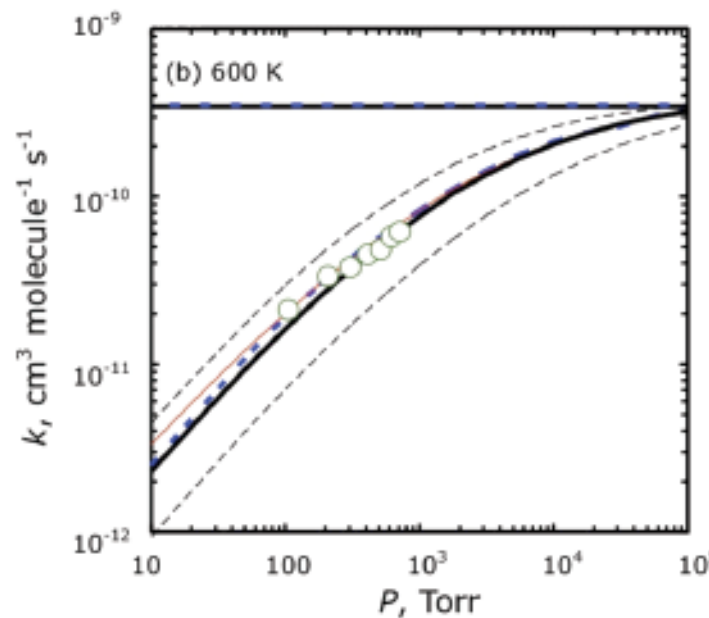
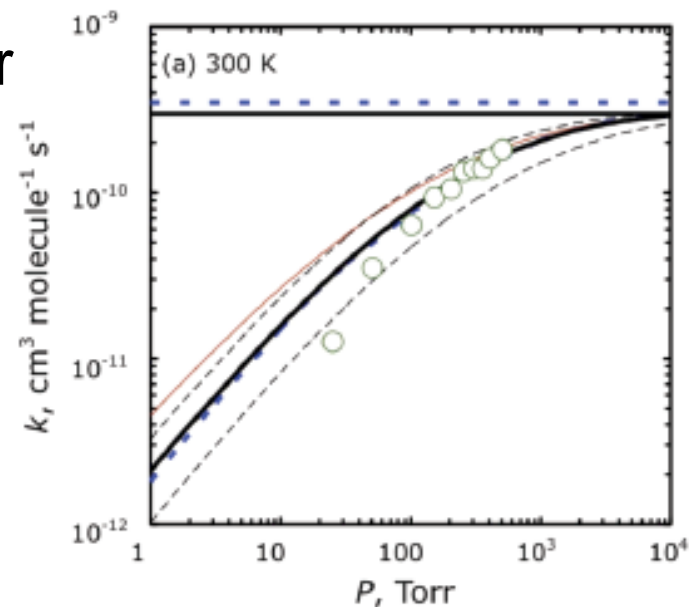
Energy Transfer from Trajectories

Collisional energy transfer in unimolecular reactions: Direct classical trajectories for $\text{CH}_4=\text{CH}_3+\text{H}$ in Helium

A. W. Jasper, J. A. Miller, *J. Phys. Chem. A* 113, 5612 (2009).

$\alpha_0=110 \text{ cm}^{-1}$ $n=0.81$

Barker is studying $P(E, J, E', J')$



Troe Fitting

Need to represent $k(T,P)$ for Global Models

Standard is Troe Fitting

$$k(T,p) = \frac{k_0[M]k^\infty}{k^\infty + k_0[M]} F \quad \log_{10} F = \frac{\log_{10} F_{cent}}{1 + \left[\frac{\log_{10}(p^*) + c}{N - d(\log_{10}(p^*) + c)} \right]^2}$$

$$p^* = k_0[M]/k^\infty \quad d = 0.14$$

$$c = -0.4 - 0.67 \log_{10} F_{cent} \quad N = 0.75 - 1.27 \log_{10} F_{cent}$$

Fit k_0 & k^∞ to modified Arrhenius $k_0 = A_0 T^{n_0} \exp(-E_0/T)$

Fit F_{cent} to:

$$F_{cent} = (1 - a) \exp(-T/T^{***}) + a \exp(-T/T^*) + \exp(-T^{**}/T)$$

Troe Fitting Problems

Limited Accuracy

Typical Errors ~ 10 to 20%

Improved Fitting Formulas

A Fitting Formula for the Falloff Curves of Unimolecular Reactions, P. Zhang, C. K. Law, Int. J. Chem. Kinet. 41, 727 (2009)

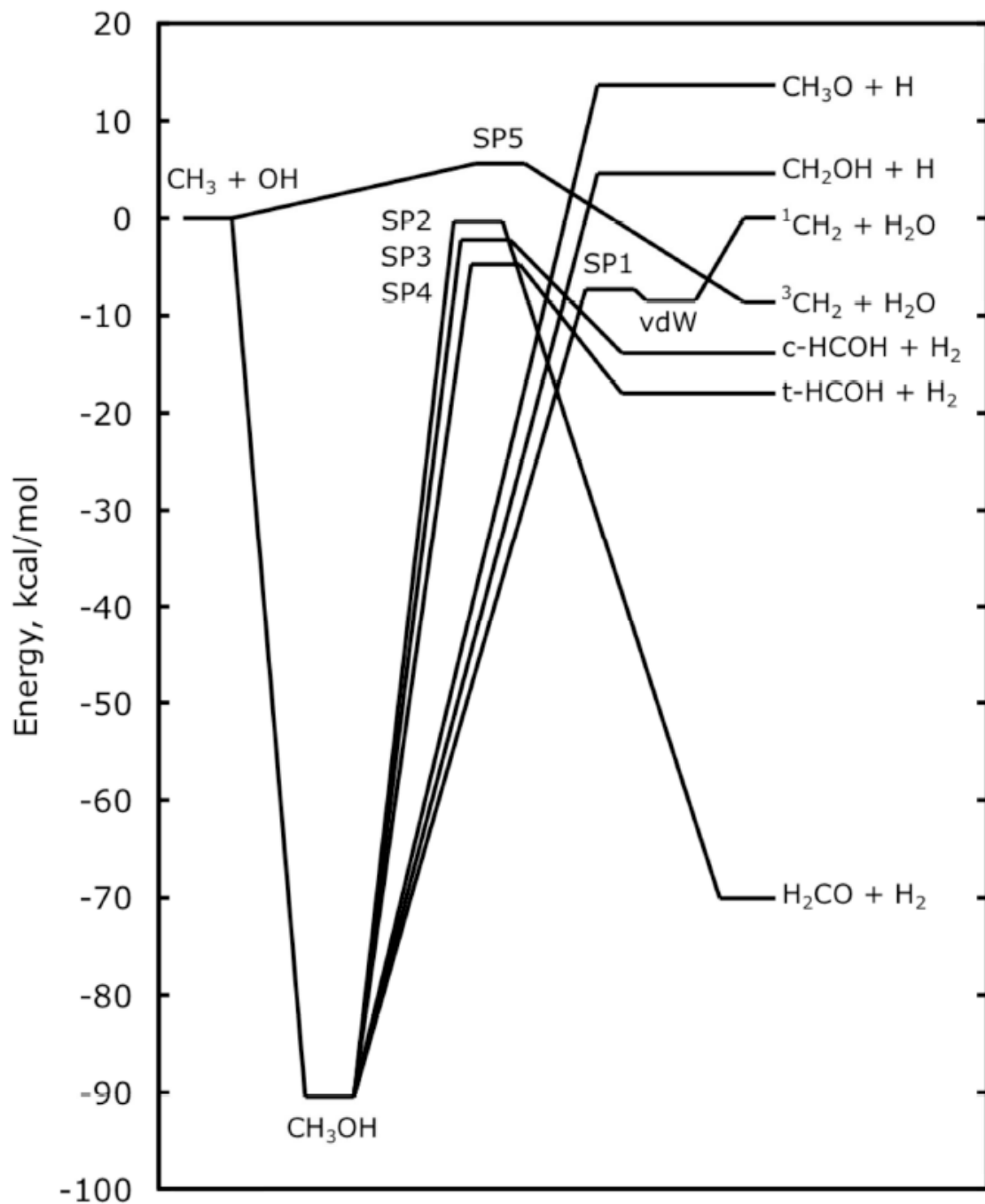
Still problems for tunneling

Multiple channels - actual P dependence is dramatically different from Troe Form

Use Log Interpolation

$$\log k = \log k_i + (\log k_{i+1} - \log k_i) \frac{(\log p - \log p_i)}{(\log p_{i+1} - \log p_i)}$$

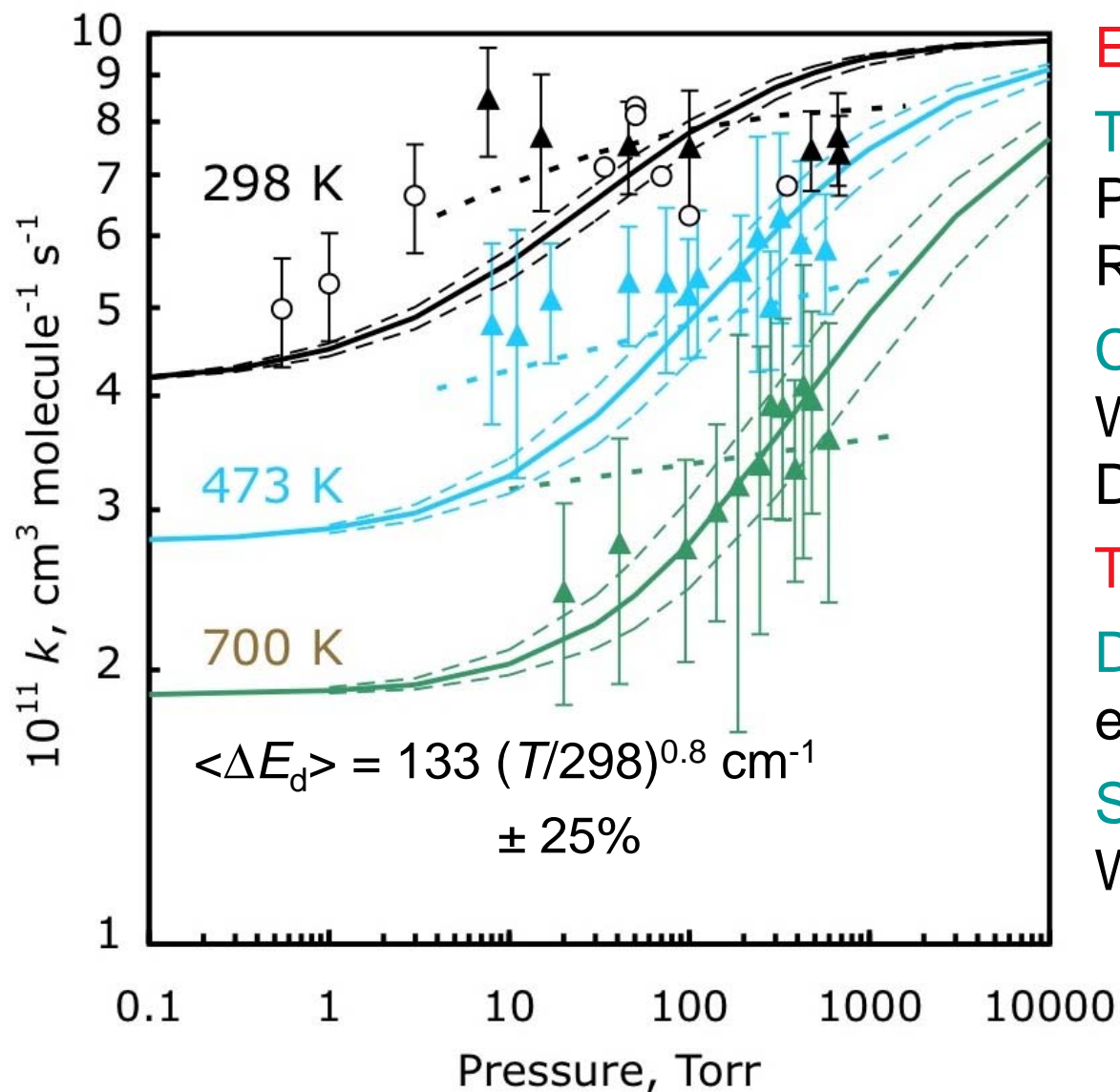
Part of Current ChemKin



Potential Energy
Surface

Stationary point	ATcT ^a	Present ^b	Ref. 29 ^c	Ref. 51 ^d
CH ₃ + OH	0.0	0.0	0.0	0.0
CH ₃ OH	-90.25 ± 0.05	-90.4	-91.9	-87.6
CH ₃ OH ^e		-89.8		-87.0
¹ CH ₂ + H ₂ O	0.58 ± 0.07	0.03	-1.6	0.5
H ₂ + H ₂ CO	-69.92 ± 0.06	-70.0	-73.8	-68.2
H ₂ + <i>cis</i> -HCOH	-13.13 ± 0.32	-13.8	-17.1	-12.3
H ₂ + <i>trans</i> -HCOH	-17.77 ± 0.29	-18.0	-21.4	-16.4
H + CH ₂ OH	4.30 ± 0.09	4.6	4.3	7.5
H + CH ₃ O	13.75 ± 0.10	13.7	13.0	15.6
³ CH ₂ + H ₂ O	-8.42 ± 0.06	-8.7	-11.2	
CH ₂ ···H ₂ O (vdW)		-8.5	-9.2	-4.8
[¹ CH ₂ + H ₂ O ⇌ CH ₃ OH] [‡] (SP1)		-7.3	-7.8	-4.6
[H ₂ + H ₂ CO ⇌ CH ₃ OH] [‡] (SP2)		-0.3	-1.3	1.7
[H ₂ + <i>cis</i> -HCOH ⇌ CH ₃ OH] [‡] (SP3)		-2.2	-3.8	-0.6
[H ₂ + <i>trans</i> -HCOH ⇌ CH ₃ OH] [‡] (SP4)		-4.8	-6.4	-2.2
[CH ₃ + OH ⇌ ³ CH ₂ + H ₂ O] [‡] (SP5)		5.6	6.7	15.8

Reactions with Products:



Experiment:

Triangles - De Avillez Pereira, Baulch, Pilling, Robertson, and Zeng, **1997**

Circles - Deters, Otting, Wagner, Temps, László, Dóbé, Bérces, **1998**

Theory: Master Equations

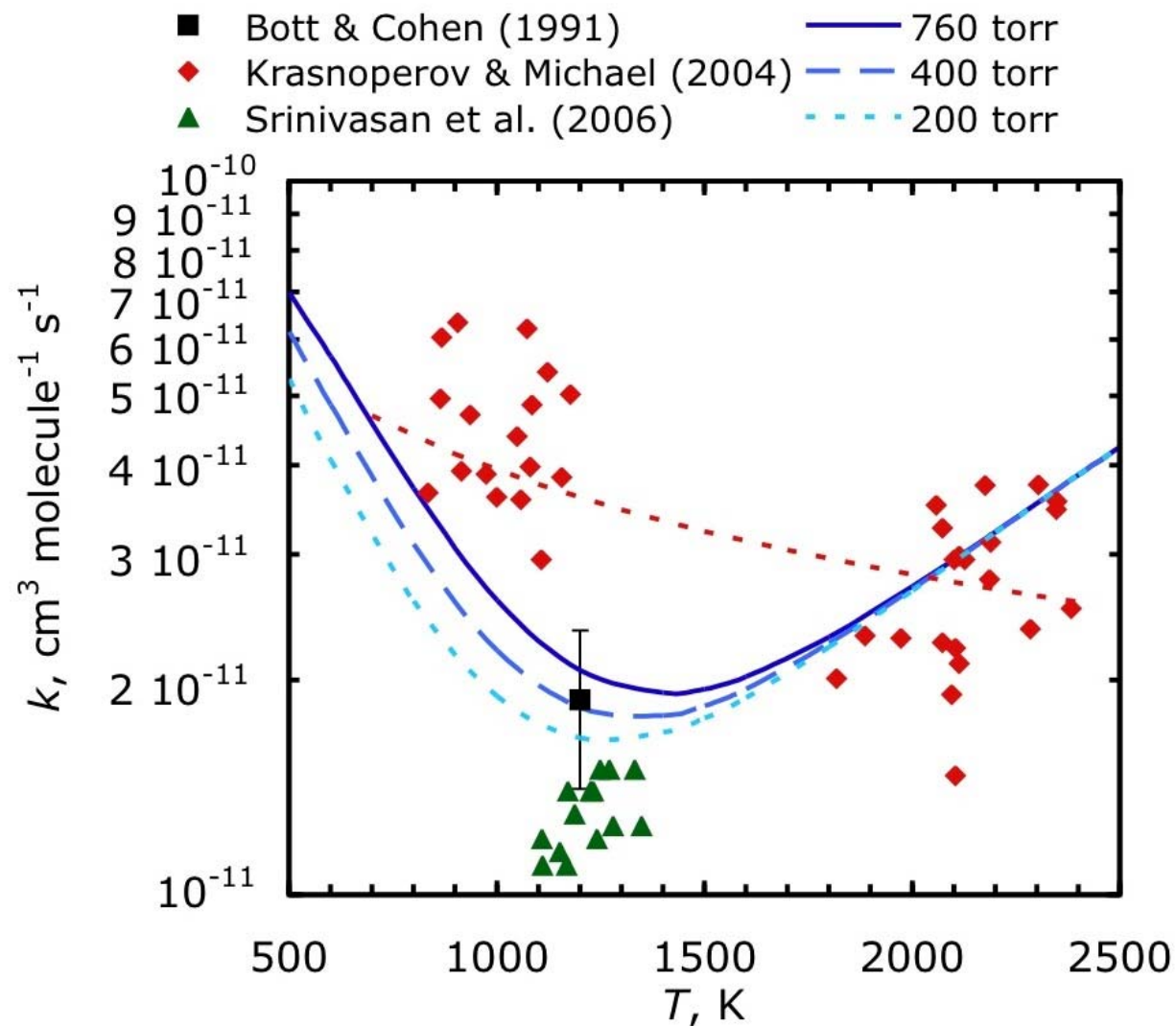
Dotted - De Avillez Pereira et al.

Solid & Dashed - Present Work

CH₃ + OH: Higher T and P ~1 atm

Shock tube studies

- 1991, Bott and Cohen (1 atm)
- 2004, Krasnoperov and Michael (100–1100 torr)
- 2006, Srinivasan, Su, and Michael (200–750 torr)



Methanol decomposition: Low pressure limit

Experimental

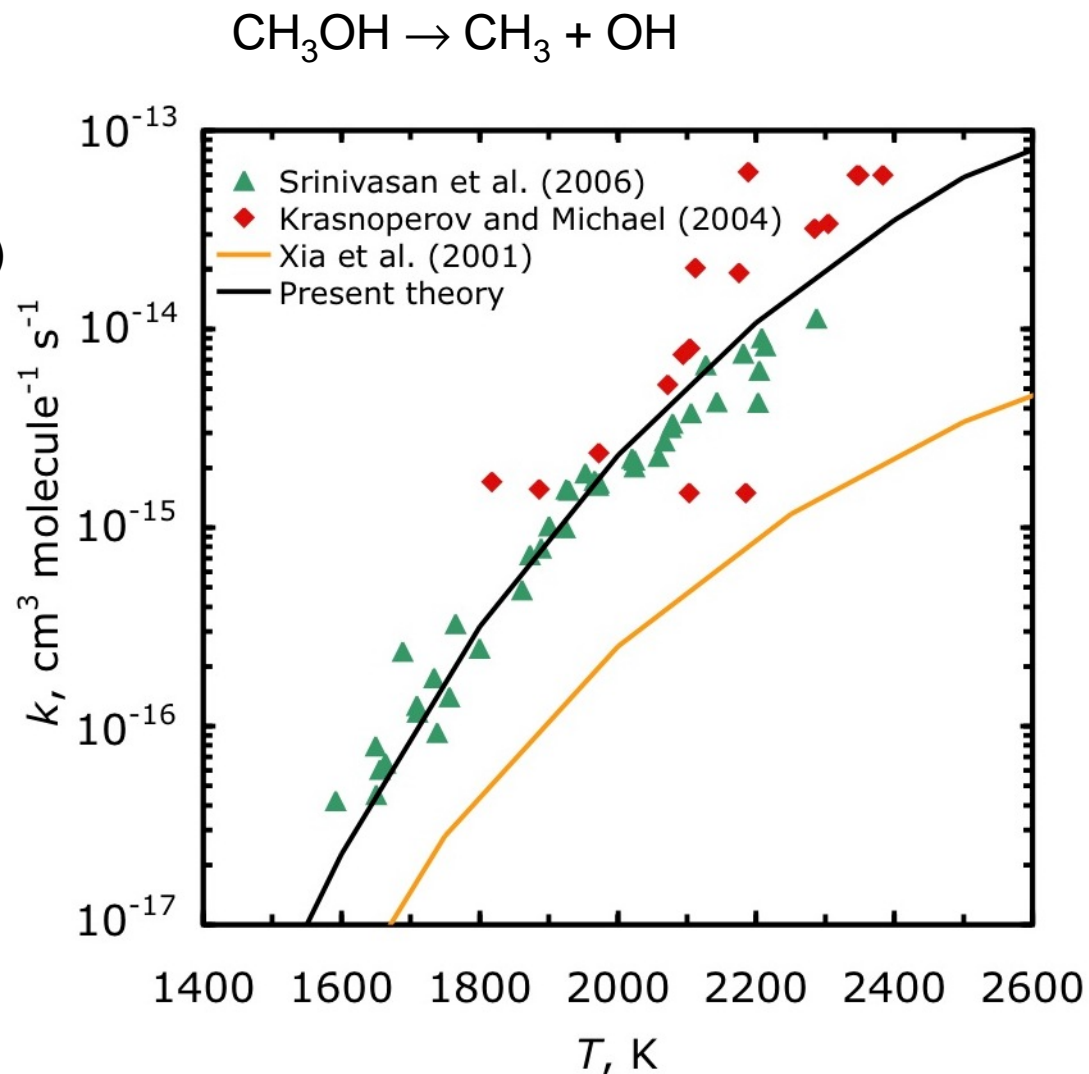
- 2004, Krasnoperov and Michael
- 2006, Srinivasan, Su, and Michael
- 1981–2000, Many others
- k independent of P (100–1000 torr)
- 60–90% $\text{CH}_3 + \text{OH}$

Previous theory

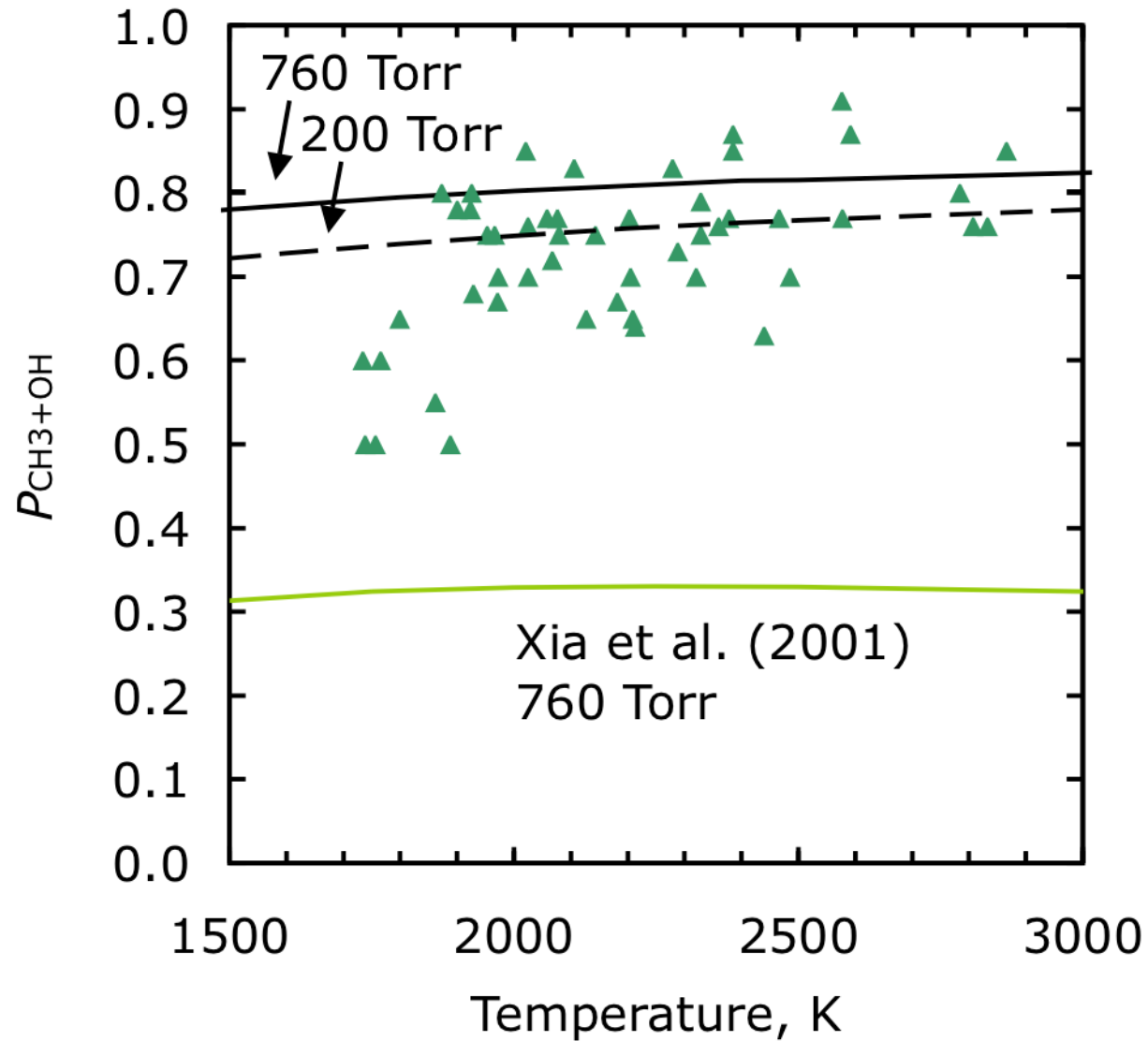
- 2001, Xia, Zhu, Lin, and Mebel (shown at 1 atm)
- Falloff below 1 atm
- ~33% $\text{CH}_3 + \text{OH}$
- ~52% $\text{CH}_2 + \text{H}_2\text{O}$
- ~15% $\text{H}_2 + \text{HCOH}$

Present theory

- Low- P limit at 1 atm
- ~75% $\text{CH}_3 + \text{OH}$
- ~20% $\text{CH}_2 + \text{H}_2\text{O}$
- < 5% $\text{H}_2 + \text{HCOH}$



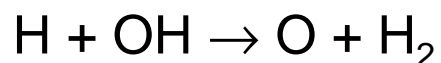
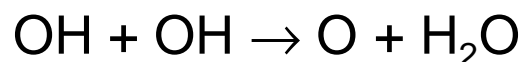
Methanol decomposition: Product branching



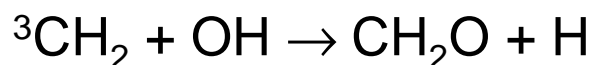
Secondary kinetics of methanol decomposition

Shock tube OH absorption profile sensitivities for $\text{CH}_3\text{OH} \rightarrow \text{CH}_3 + \text{OH}$

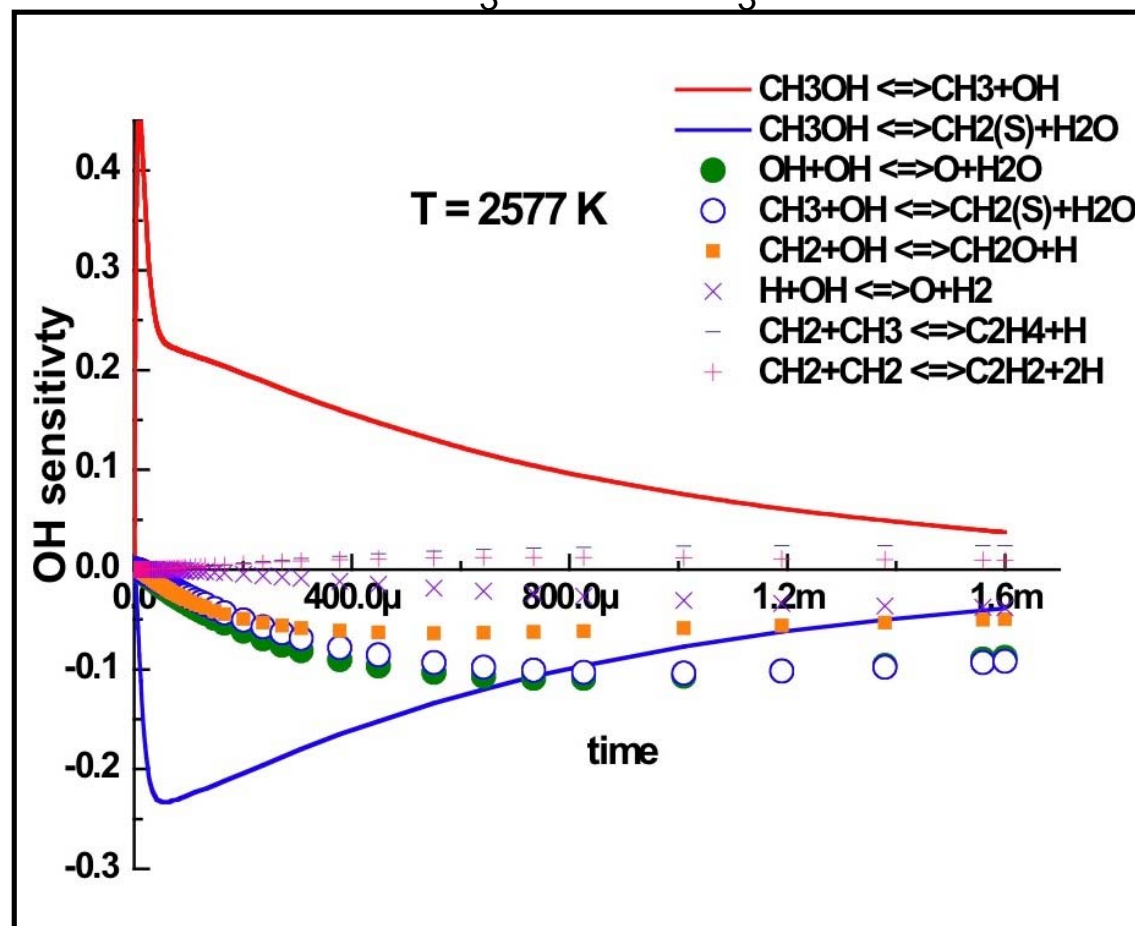
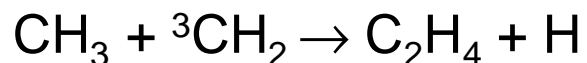
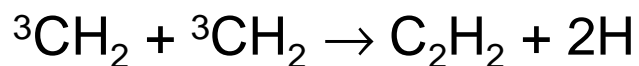
Well characterized



Not well characterized



Ambiguous experiments

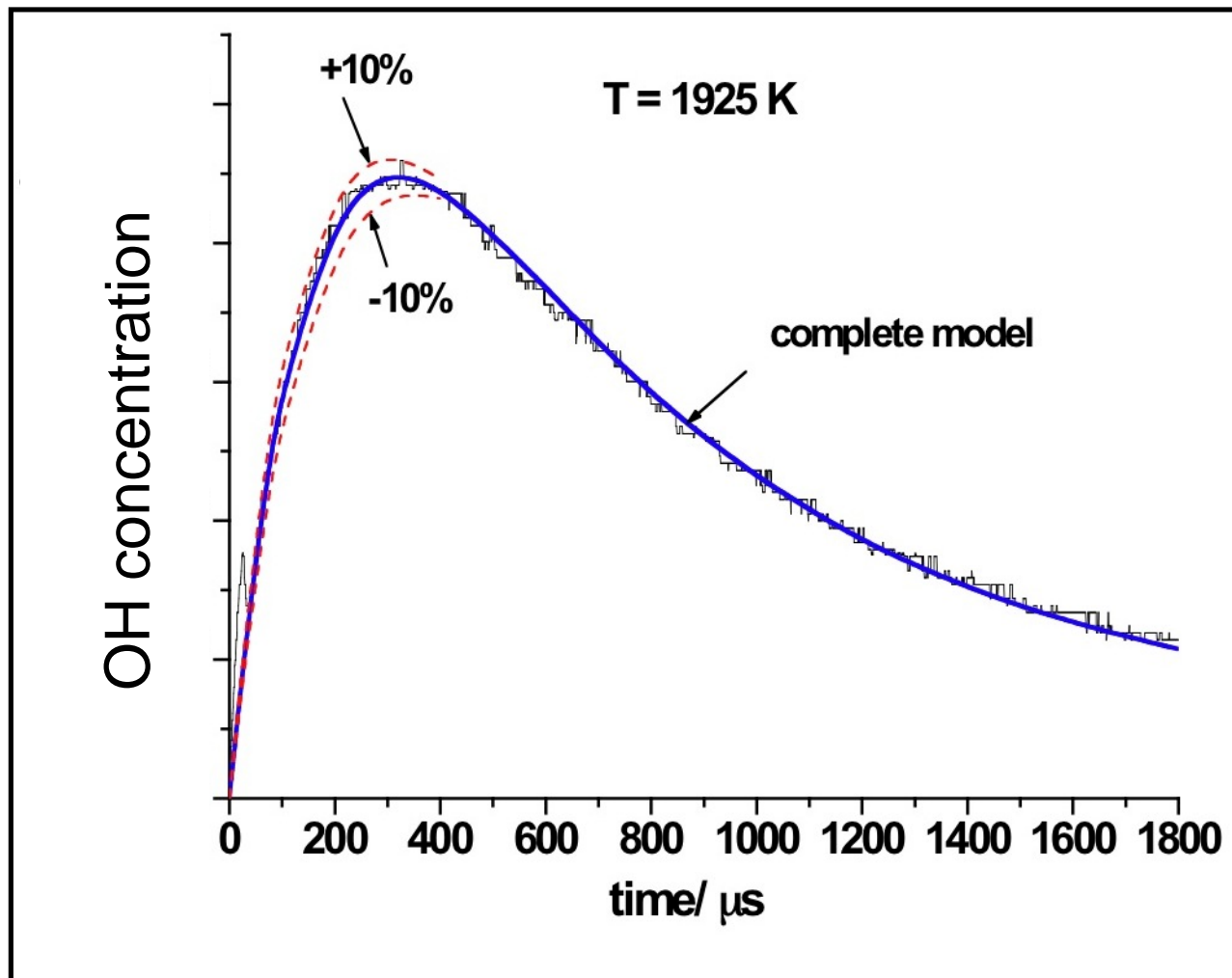
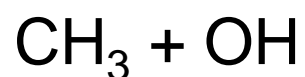
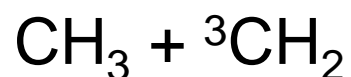
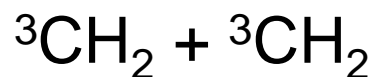
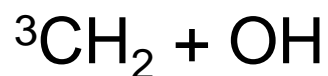


Srinivasan, Su, and Michael, *JPCA*, 2007

Secondary kinetics: OH Time Traces

Michael et al.

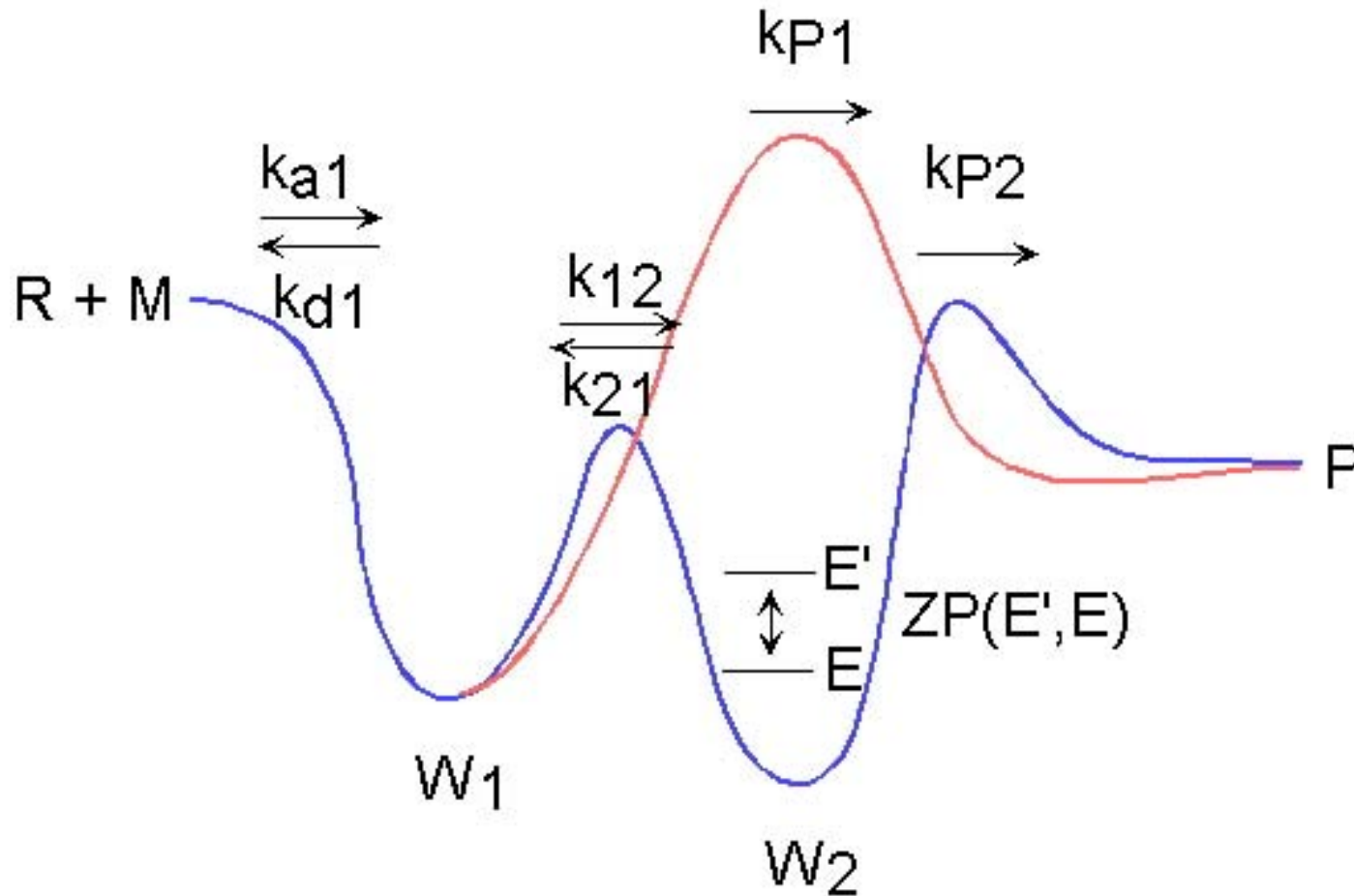
*Good agreement
at long times
using our
predicted rates
for*



Multiple-Well Multiple-Channel Time Dependent Master Equation

1. The Kinetic Model
2. Collisionless Limit
3. $\text{CH} + \text{N}_2$
4. Time Dependent Populations
5. Kinetic Phenomenology
6. $\text{C}_2\text{H}_5 + \text{O}_2$
7. Reduction in Species at High Pressure
8. $\text{C}_3\text{H}_3 + \text{H}$
9. Radical Oxidation
10. $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$

The Kinetic Model



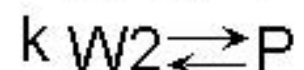
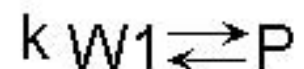
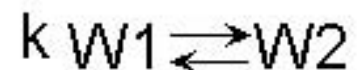
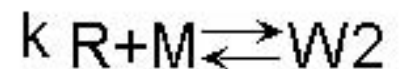
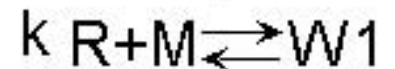
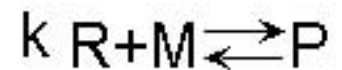
Energy Transfer

Bath Gas B; $[B] \gg [M] \gg [R]$

Z; Lennard Jones

$P(E', E)$; Exponential Down

Phenomenology



RRKM Theory

k_{d1}

k_{a1}

k_{12}

k_{21}

k_{p1}

k_{p2}

Multiple-Well Multiple-Channel Master Equation

$$\frac{dn_i(E)}{dt} = k_c n_B \int dE' P_i(E, E') n_i(E') - k_c n_B n_i(E) - k_{d_i}(E) n_i(E) - \sum_{p=1}^{N_p} k_{p_i}(E) n_i(E) -$$

$$\sum_{j \neq i}^M k_{ji}^{isom}(E) n_j(E) + \sum_{j \neq i}^M k_{ij}^{isom}(E) n_i(E) + K_{eq_i} k_{d_i}(E) F_i(E) n_R n_m$$

$$\frac{dn_R}{dt} = \sum_{i=1}^M \int dE k_{d_i}(E) n_i(E) - n_R n_m \sum_{i=1}^M K_{eq_i} \int dE k_{d_i}(E) F_i(E)$$

M Wells N_p Products

M+1 Chemical Species

$n_B \gg n_m \gg n_R$ B=Bath, m=Molecule, R=Radical

Linear Master Equation

Collisionless Limit

Consider $Z \rightarrow 0$

$$\frac{d|n(E,J)\rangle}{dt} = -K(E,J)|n(E,J)\rangle + n_R n_m |b(E,J)\rangle \rho_{Rm}(E,J) \exp(-\beta E) / Q_{Rm}$$

$$\frac{d|P(E,J)\rangle}{dt} = D(E,J)|n(E,J)\rangle$$

Steady State for $n(E,J)$

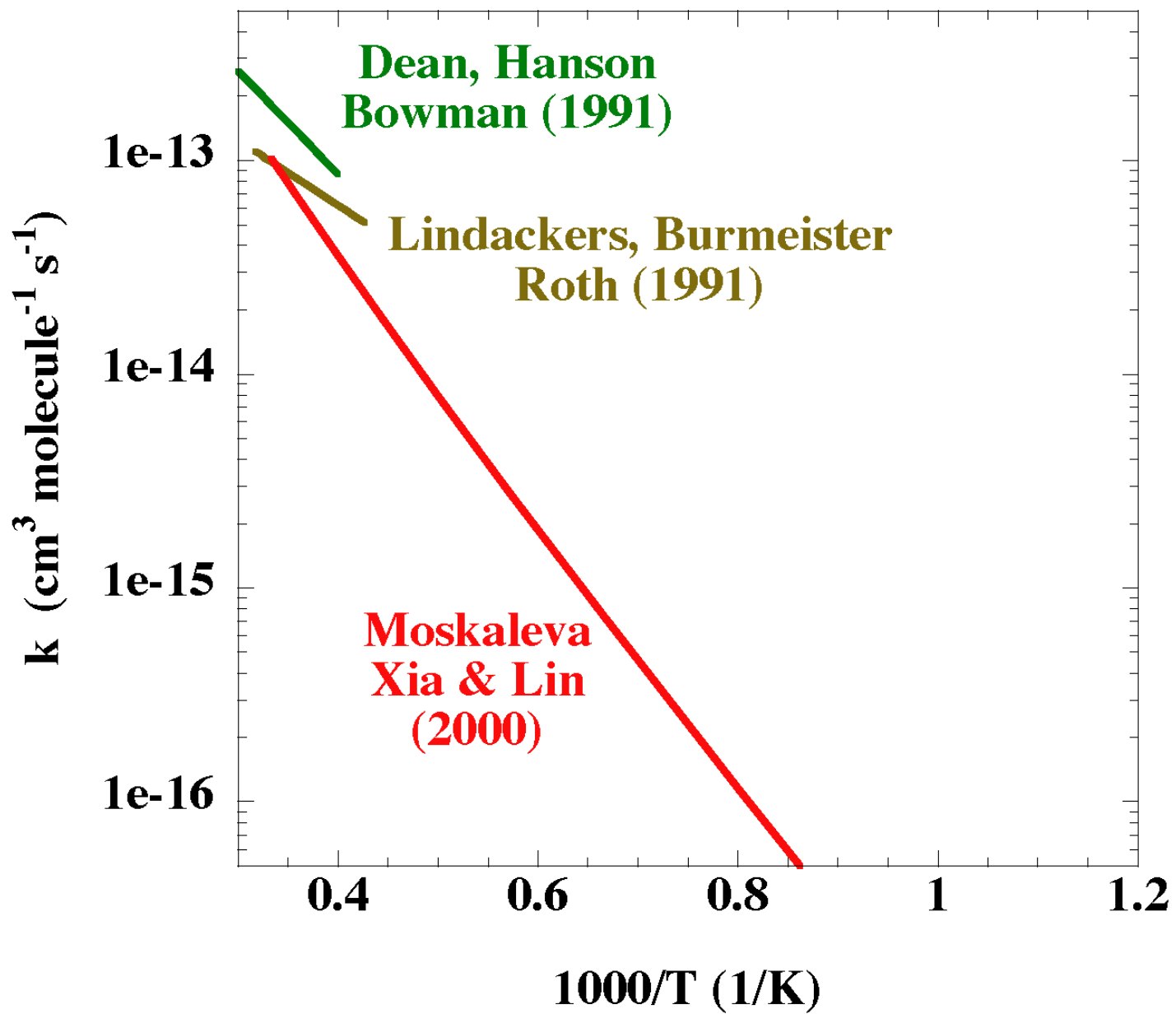
$$\frac{d|P(E,J)\rangle}{dt} = D(E,J)K^{-1}(E,J)|b(E,J)\rangle n_R n_m \rho_{Rm}(E,J) \exp(-\beta E) / Q_{Rm}(T)$$

$$|k_0(T)\rangle = \frac{1}{Q_{Rm}(T)} \sum_J (2J+1) \int dE D(E,J)K^{-1}(E,J)|b(E,J)\rangle \rho_{Rm}(E,J) \exp(-\beta E)$$

Flux coefficients

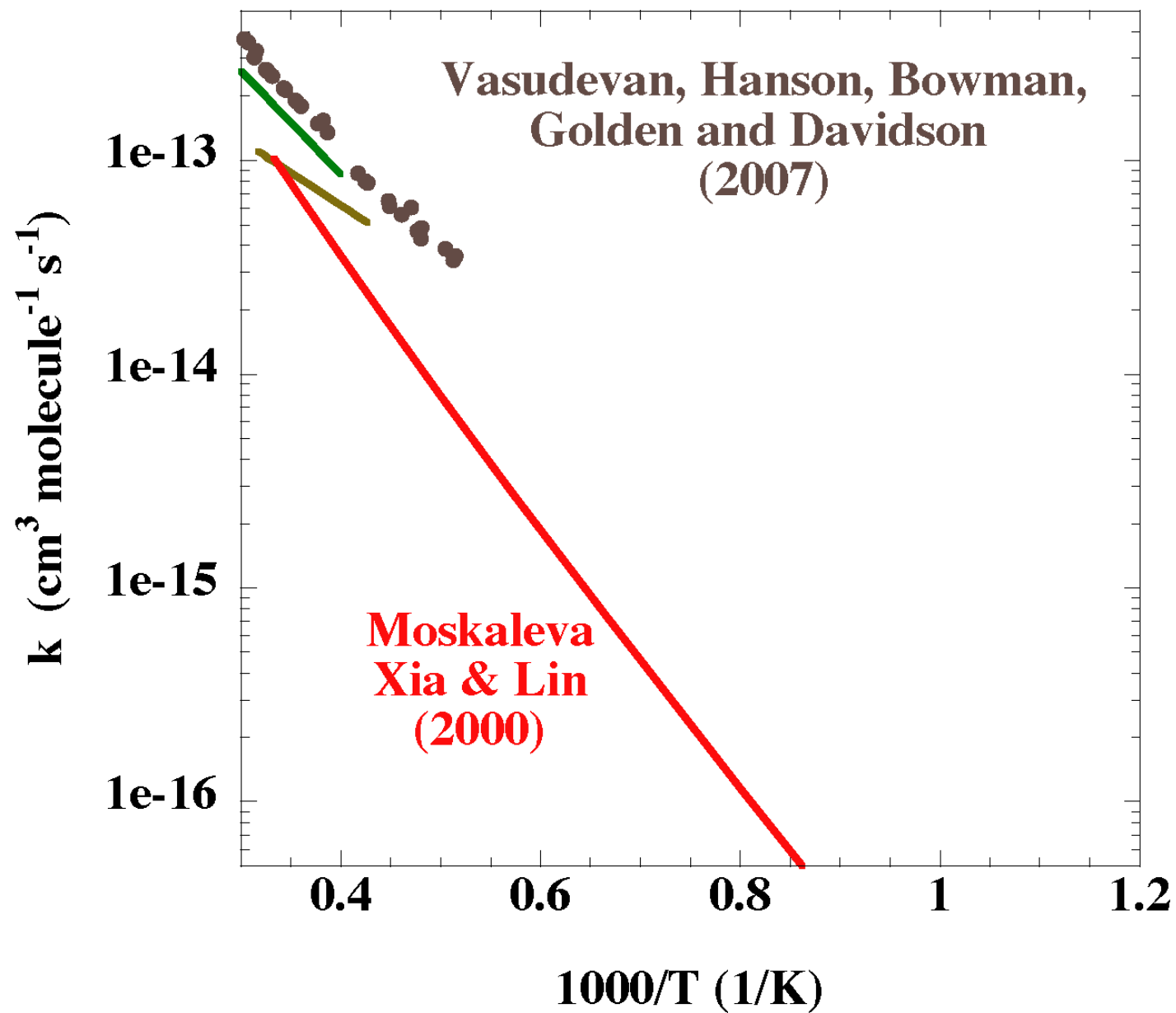
CH + N₂ Prompt NO

- 1971 **Fenimore** $^2\text{CH} + \text{N}_2 \rightarrow \text{HCN} + ^4\text{N}$
- 1991 **Dean, Hanson & Bowman** -- shock tube measurements of rate for $^2\text{CH} + \text{N}_2 \rightarrow \text{Products}$
- 1991 **Manaa & Yarkony** -- located minimum crossing point for doublet to quartet transition
- 1996 **Miller & Walch** -- found maximum on spin forbidden path corresponds to dissociation of the quartet complex; not the doublet-quartet crossing; presume rapid ISC and fit experimental data
- 1999 **Qui, Morokuma, Bowman & Klippenstein** -- predicted spin-forbidden reaction to be less than observed rate by at least 10^2
- 2000 **Moskaleva, Xia & Lin** -- predicted new spin allowed mechanism,
$$^2\text{CH} + \text{N}_2 \rightarrow \text{HNCN} \rightarrow ^2\text{H} + ^3\text{NCN}$$
- 2007 **Szpunar, Faulhaber, Kautzman, Crider & Neumark** -- observed the photodissociation of DNCN to CD+N₂ and D+NCN with 1:1 branching ratio

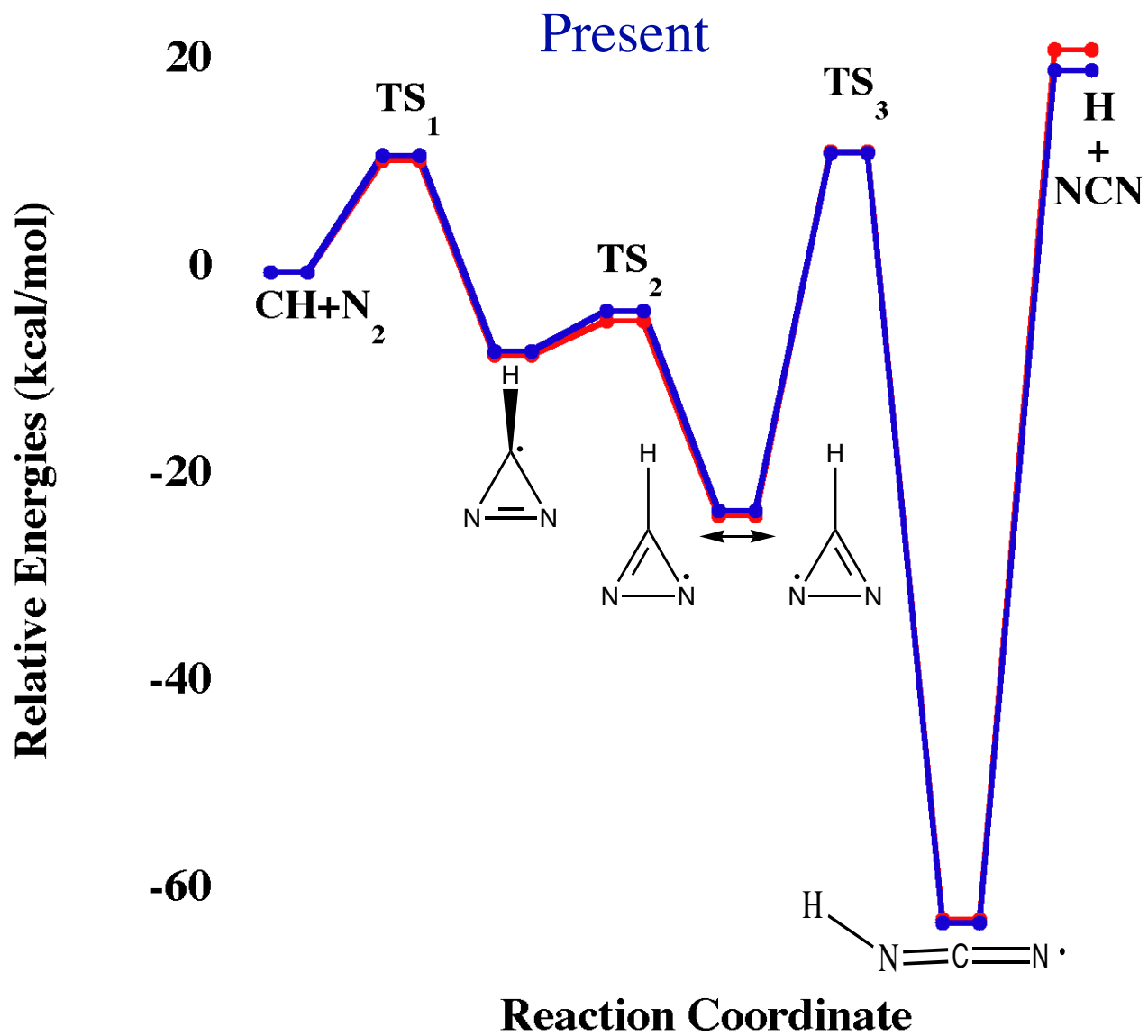


Recent Modeling

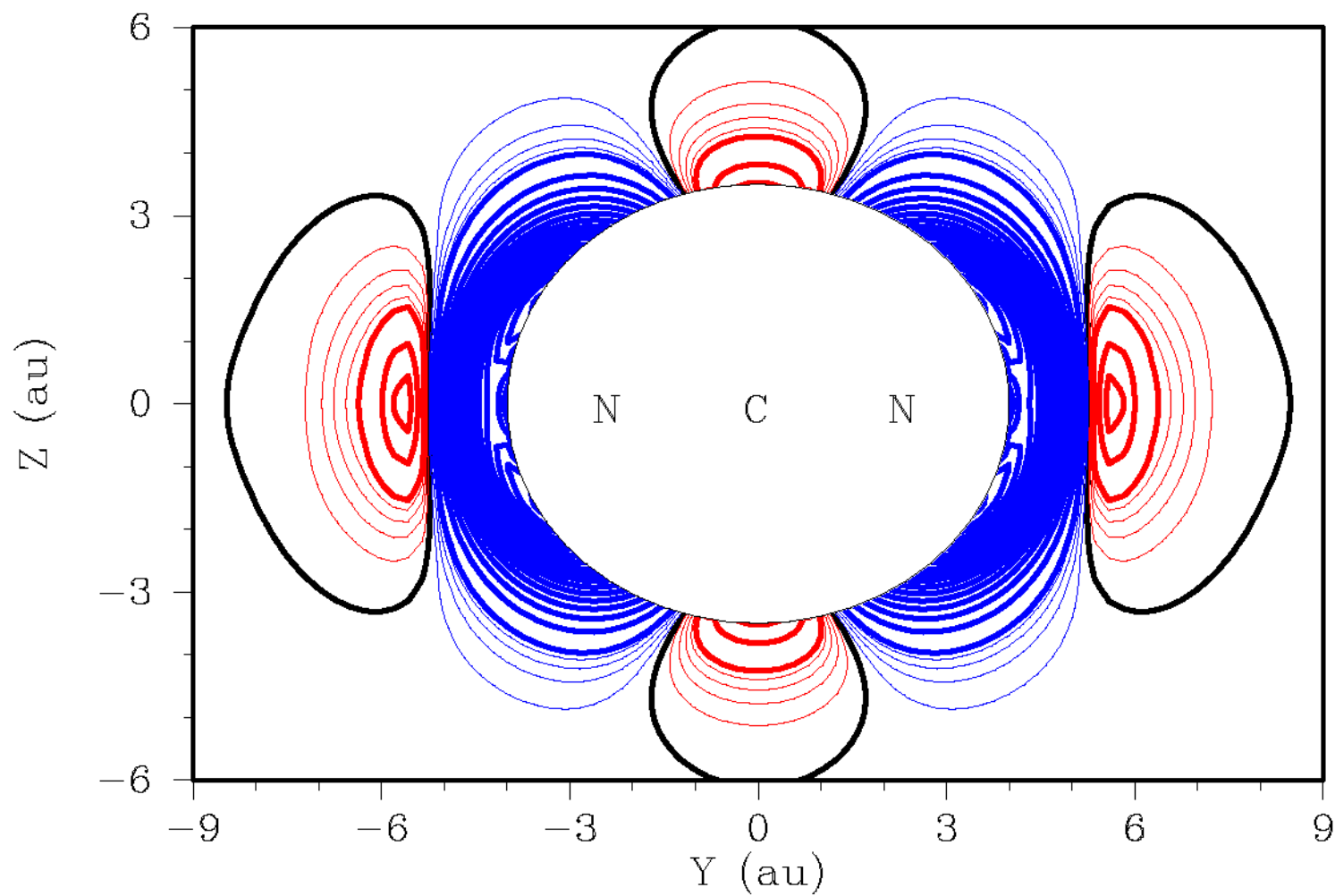
- Williams, Fleming
Proc. Comb. Inst. 31, 1109-1117, 2007
NO severely underpredicted in CH₄ and C₃H₈ flames
- El Bakali, Pillier, Desgroux, Lefort, Gasnot, Pauwels, da Costa,
Fuel 85, 896, 2006
Increasing CH + N₂ rate by 1-2 orders of magnitude over the
1000 to 1500 K range yields good predictions for NO in natural
gas flames
- Sutton, Williams, Fleming,
Comb. Flame, 2008, in press.
Improved modeling for CH₄/O₂/N₂ flames with rates of El
Bakali et al.



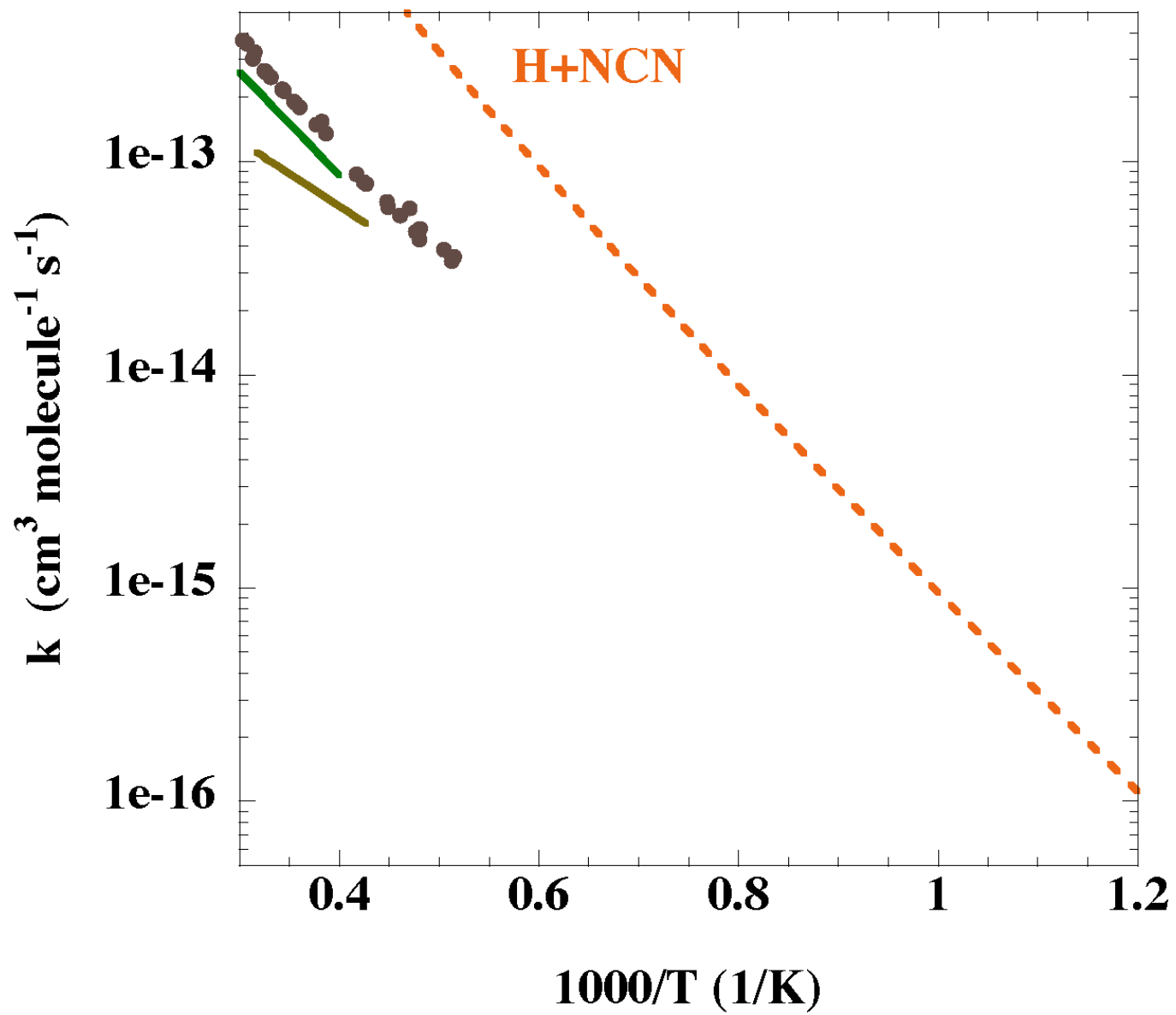
Moskaleva, Xia and Lin (2000)



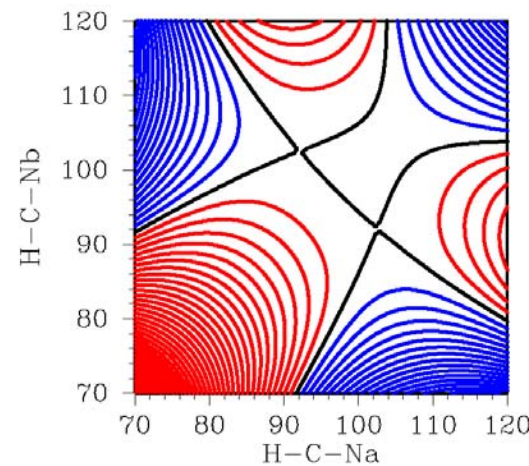
CAS+1+2+QC/aug-cc-pvtz



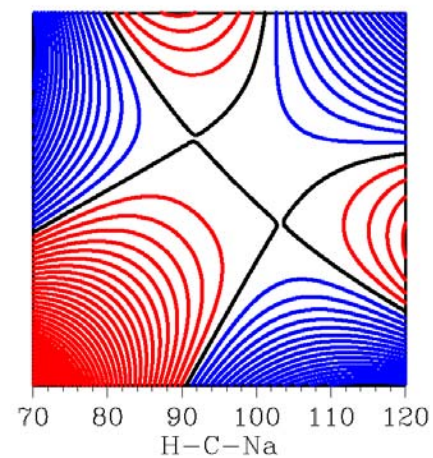
Contour Increments: Thick- 5 kcal/mol, Thin- 1 kcal/mol



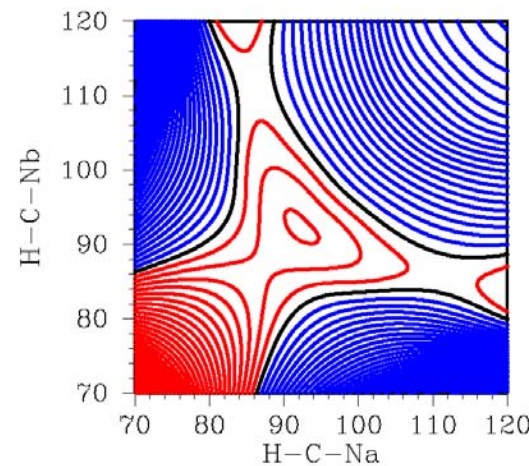
CASPT2



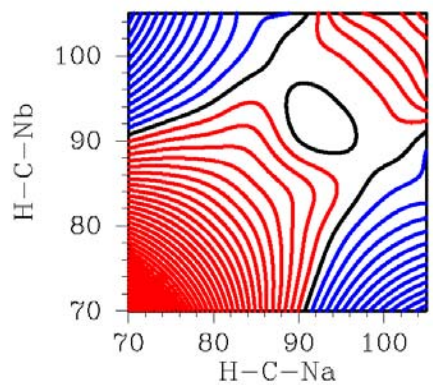
CAS+1+2+QC

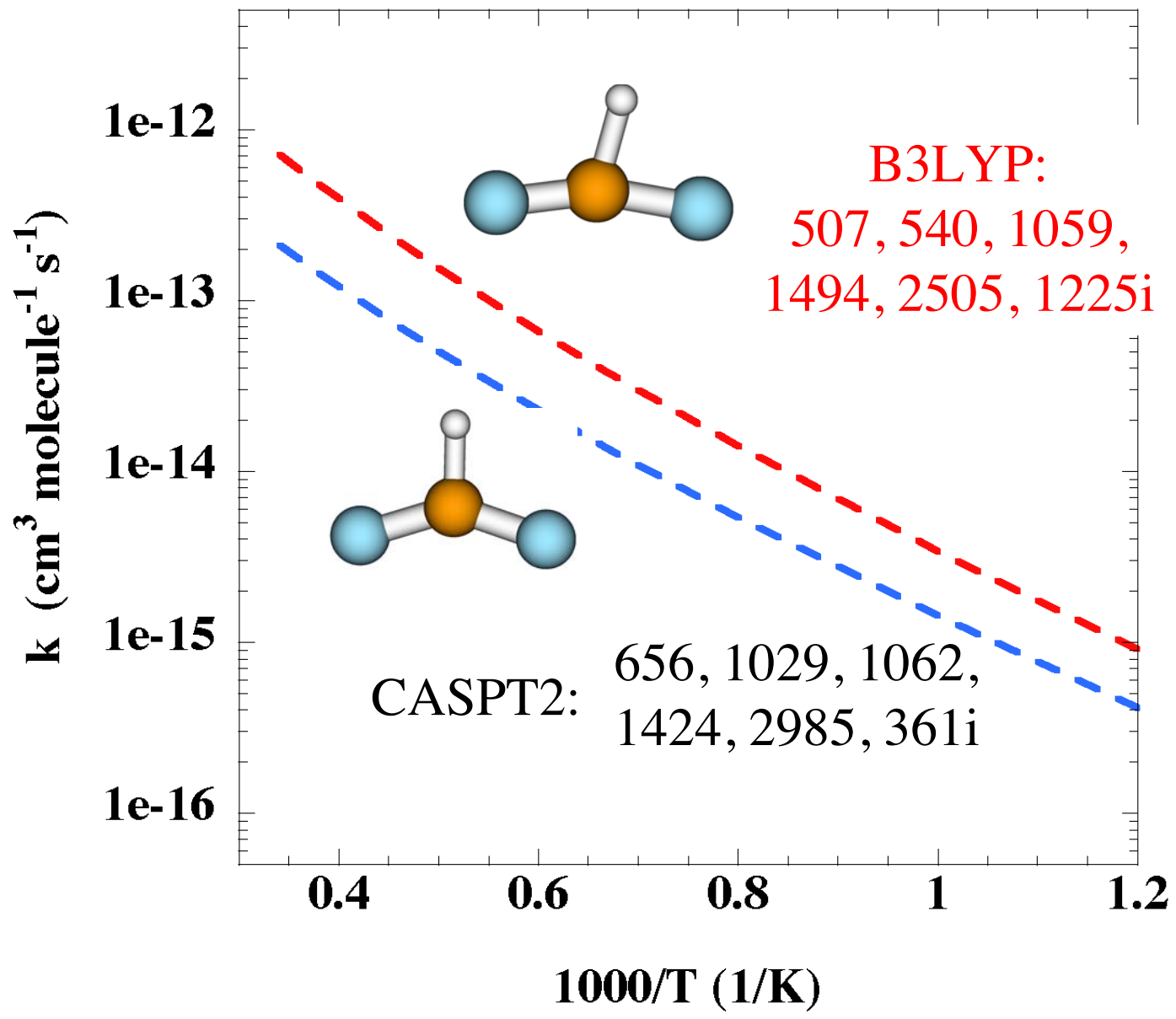


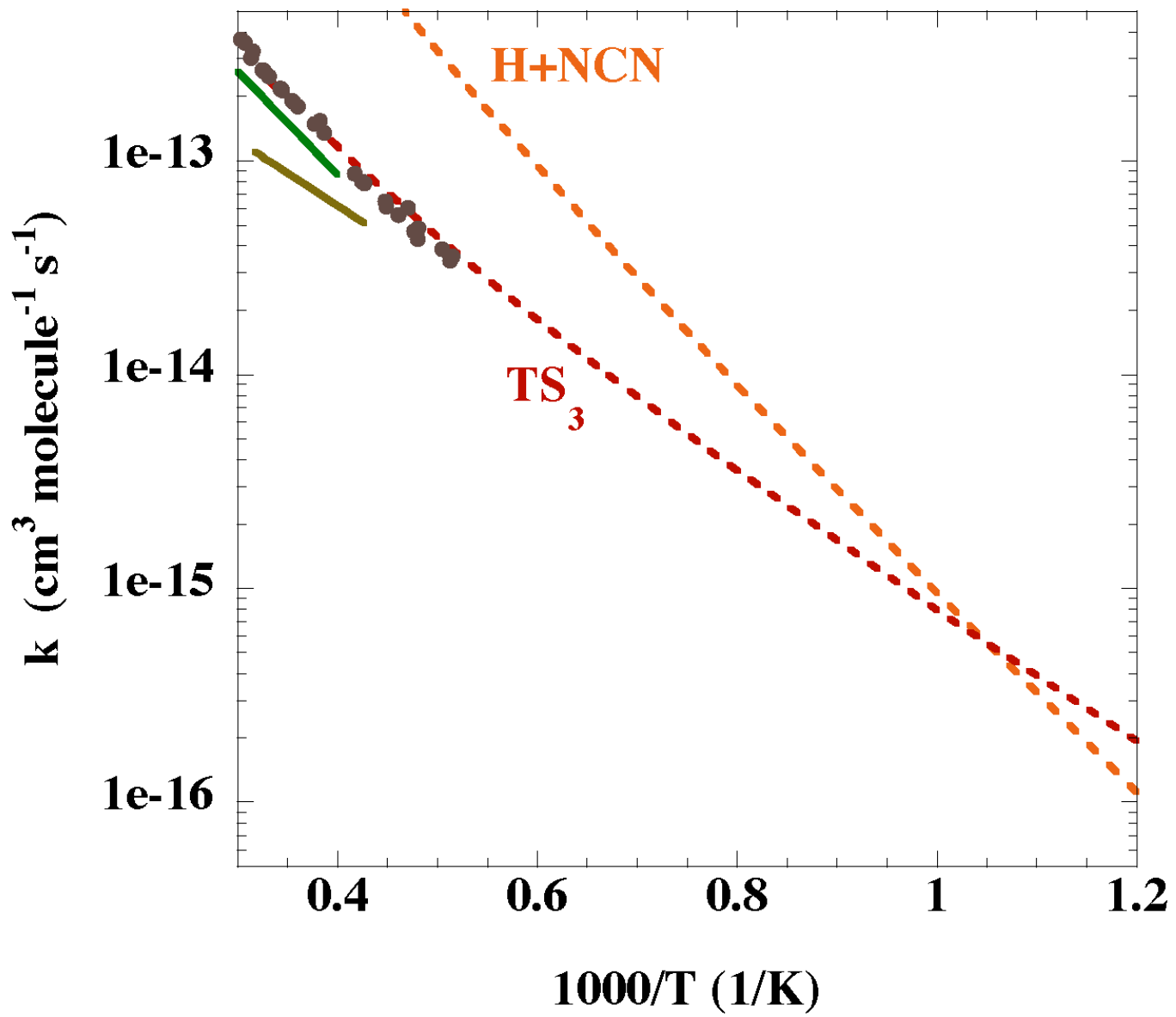
B3LYP

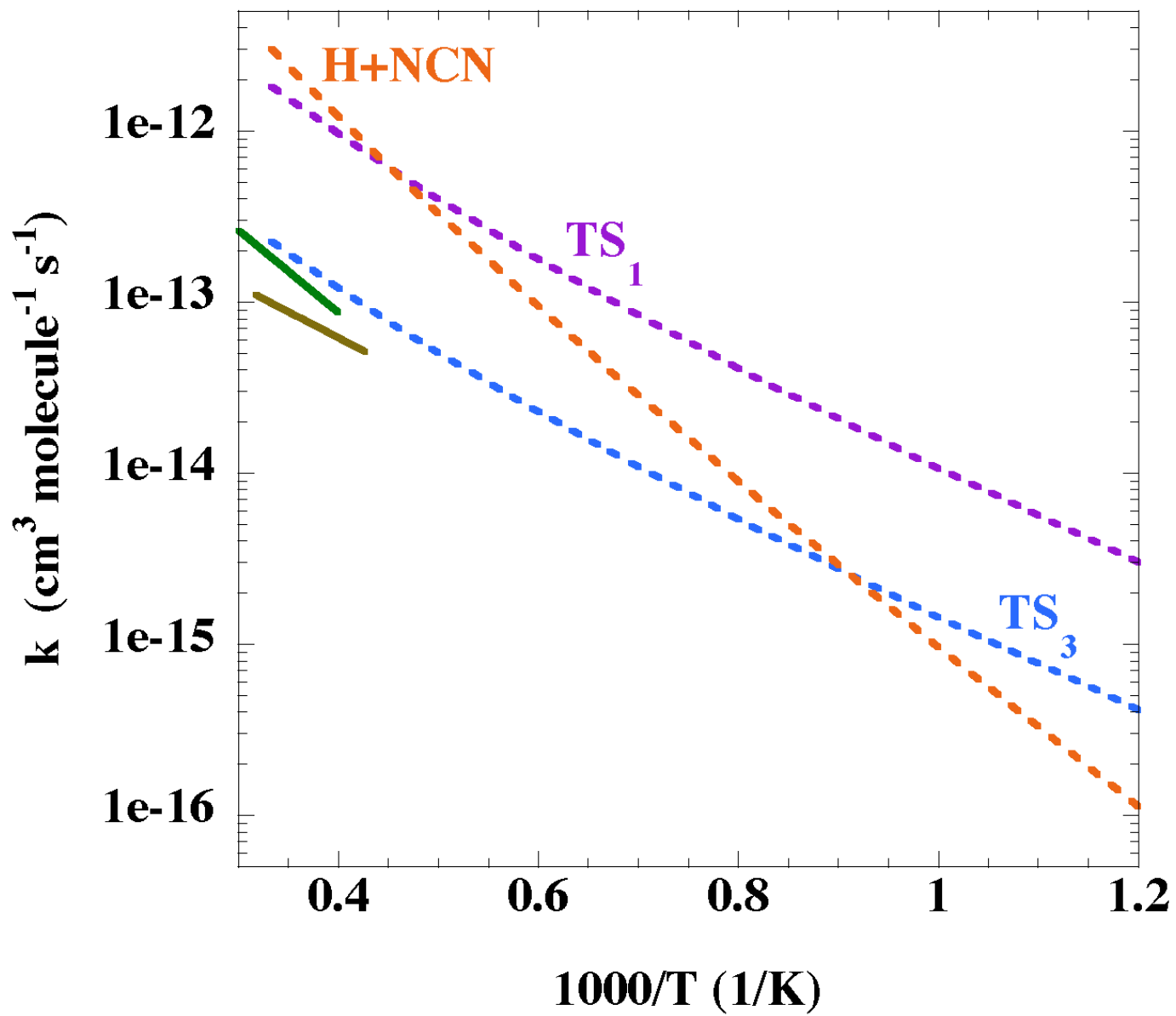


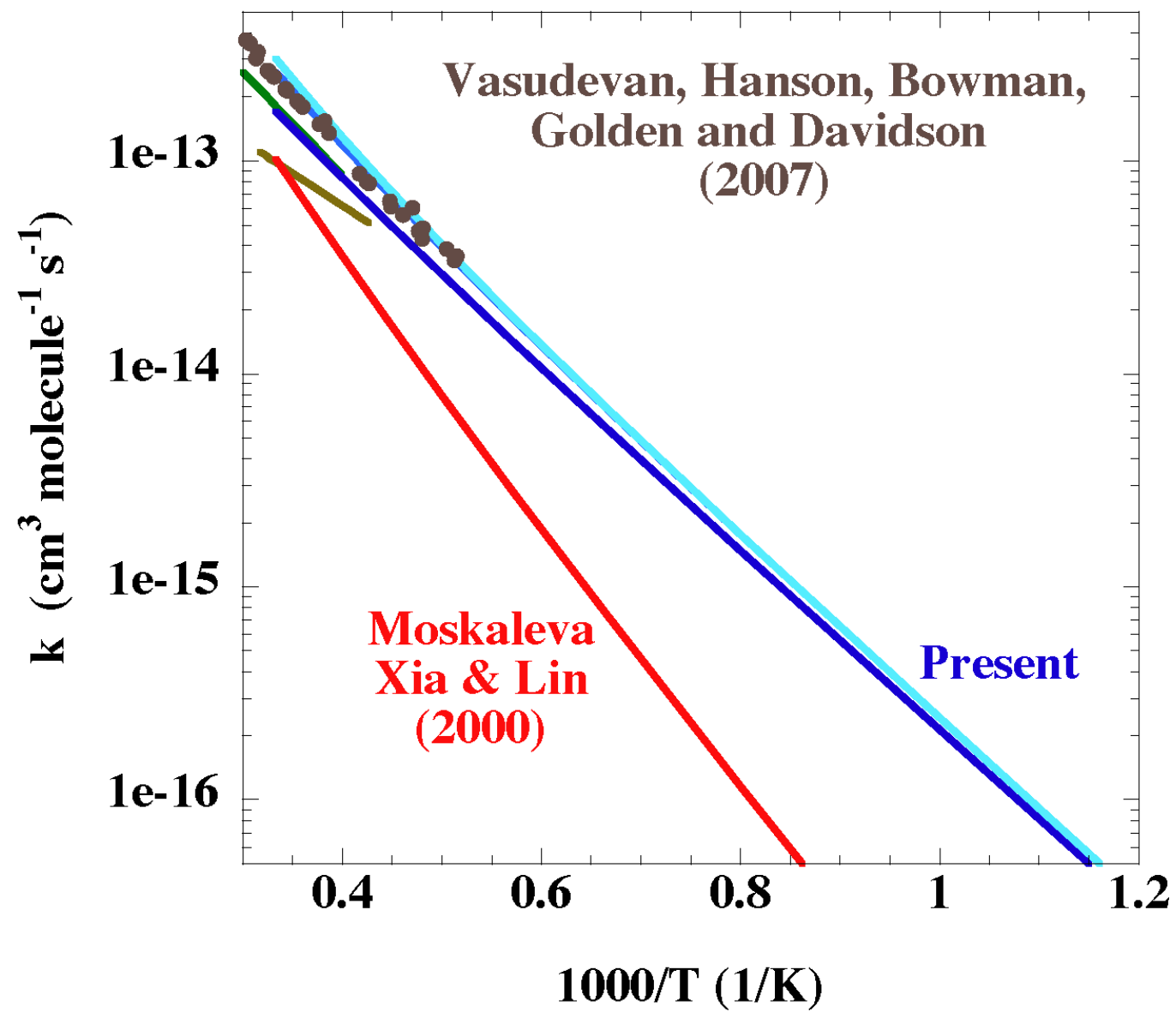
CCSD(T)











Time-Dependent Populations

- Discretize Energy Levels
- Transition Matrix; Renormalize \rightarrow real, symmetric; **G**

- $\frac{d}{dt} |w(t)\rangle = G |w(t)\rangle \quad y_i(E, t) = x_i(E, t) / f_i(E)$

- $|w(t)\rangle = \left[y_I(E_{0_I}), \dots, y_I(E_{\max}), \dots, y_i(E_{0_i}), \dots, y_i(E_{\max}), \dots, \left(\frac{n_m}{QR_m \delta E} \right)^{1/2} X_R, \dots \right]^T$

- Diagonalize

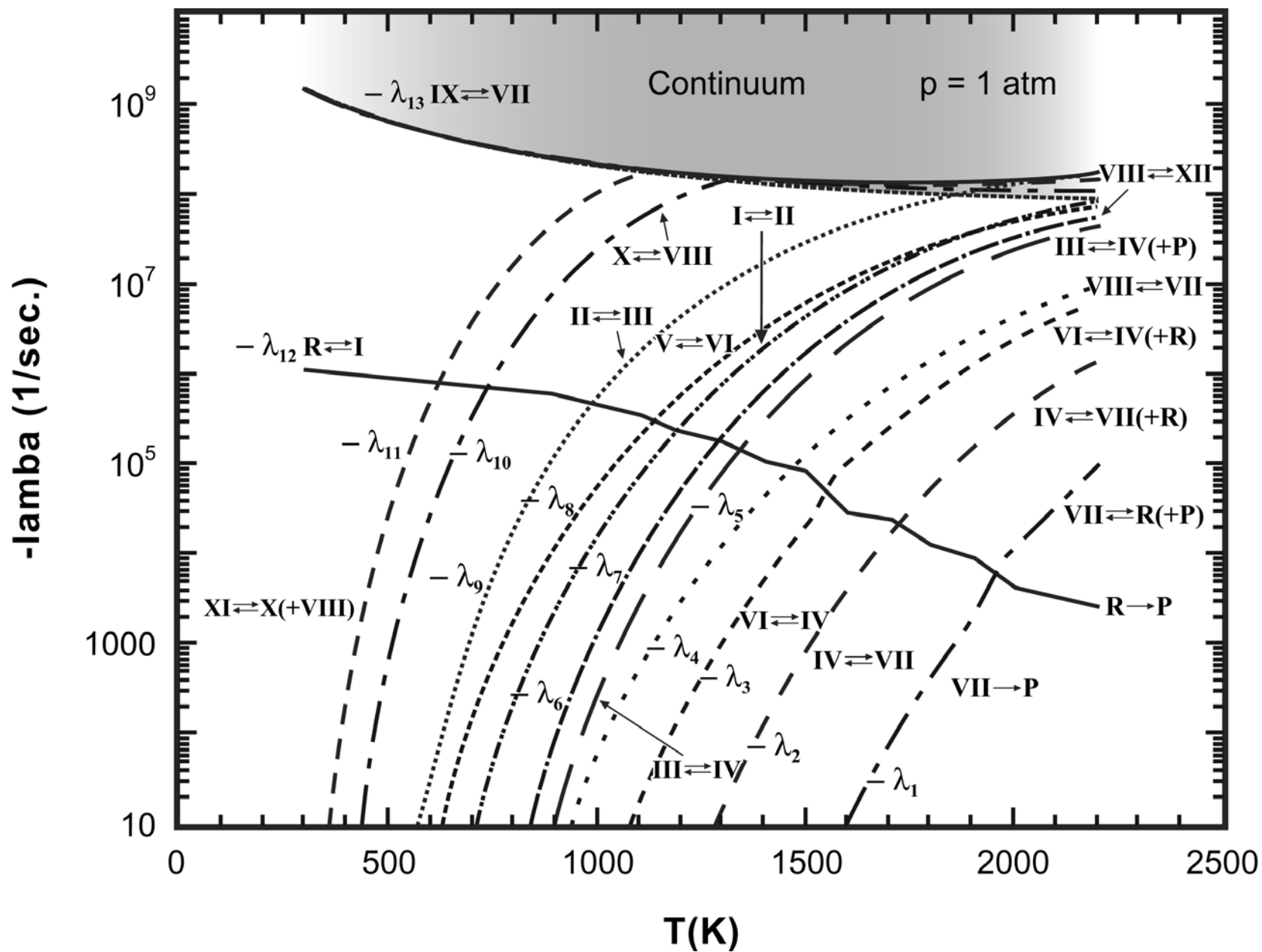
- $|w(t)\rangle = \sum_{j=1}^{N_I + \dots + N_M + 1} e^{\lambda_j t} |g_j\rangle \langle g_j | w(0)\rangle$

Kinetic Phenomenology

Experimental Viewpoint

- **Find regimes of single exponential decay (λ)**
 - λ implies total rate coefficient
 - Eigenvector corresponding to λ implies branching
 - Branching implies individual rate coefficient (k_{tot})
- **When is decay close enough to single exponential?**
 - Suppose 2nd eigenvector contributes to only 1% of the initial decay but that $\lambda_2/\lambda_1 = 100$
 - Rate coefficient will differ by a factor of two from apparent exponential decay
 - Branching similarly incorrect
- **Difficult to find single exponential decay regimes in multiple well situations**

Eigenvalues



A Simple Solution: Separation of Timescales

- **M+1 modes corresponding to chemical change have least negative eigenvalues.**
- λ 's for **chemical modes** well separated from remaining λ 's for **energy transfer**
- **After energy relaxation can treat populations as**

- $$w_\ell(t) = \sum_{j=1}^{M+1} e^{\lambda_j t} g_{j\ell} \langle g_j | w_A(0) \rangle$$

- $$\frac{dX_i}{dt} = - \sum_{j=1}^{M+1} \lambda_j e^{\lambda_j t} \Delta X_{ij}^{(A)}; \quad \Delta X_{ij}^{(A)} = - \langle g_j | w_A(0) \rangle \delta E \sum_{\ell \in i} f_i(E_\ell) g_{j\ell}$$

- **Eigenpairs $(\lambda_i, \Delta X_i)$ correspond to Normal modes of chemical relaxation**

Method 1 $t=0$ Limit and Start in Well A

- **Phenomenology**

$$\frac{dX_A}{dt}(0) = -k_{TA} X_A(0)$$

- **Master Equation**

$$\frac{dX_A}{dt}(0) = - \sum_{j=1}^{M+1} \lambda_j \Delta X_{Aj}^{(A)}$$

- $k_{TA} = \sum_{j=1}^{M+1} \lambda_j \Delta X_{Aj}^{(A)}$

- **Similarly, consider dX_j/dt implies**

$$k_{Ai} = - \sum_{j=1}^{M+1} \lambda_j \Delta X_{ij}^{(A)}$$

- $k_{AR} = - \sum_{j=1}^{M+1} \lambda_j \Delta X_{Rj}^{(A)}$; $\Delta X_{Rj} = - \left(\frac{Q_{Rm} \delta E}{n_m} \right)^{1/2} g_{j\ell} \langle g_j | w_A(0) \rangle$

- $k_{Ap} = - \sum_{j=1}^{M+1} \lambda_j \Delta X_{pj}^{(A)}$; $\left(\Delta X_R + \Delta X_p + \sum_{i=1}^M \Delta X_i \right)_j = 0$

Method 2

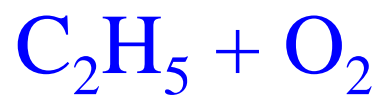
Long time limit

- $X_i(t) = \sum_{j=0}^{M+1} a_{ij} e^{\lambda_j t} \equiv \sum_{j=0}^{M+1} a_{ij} v_j$ $|X\rangle = A|v\rangle$ $|v\rangle = B|X\rangle$

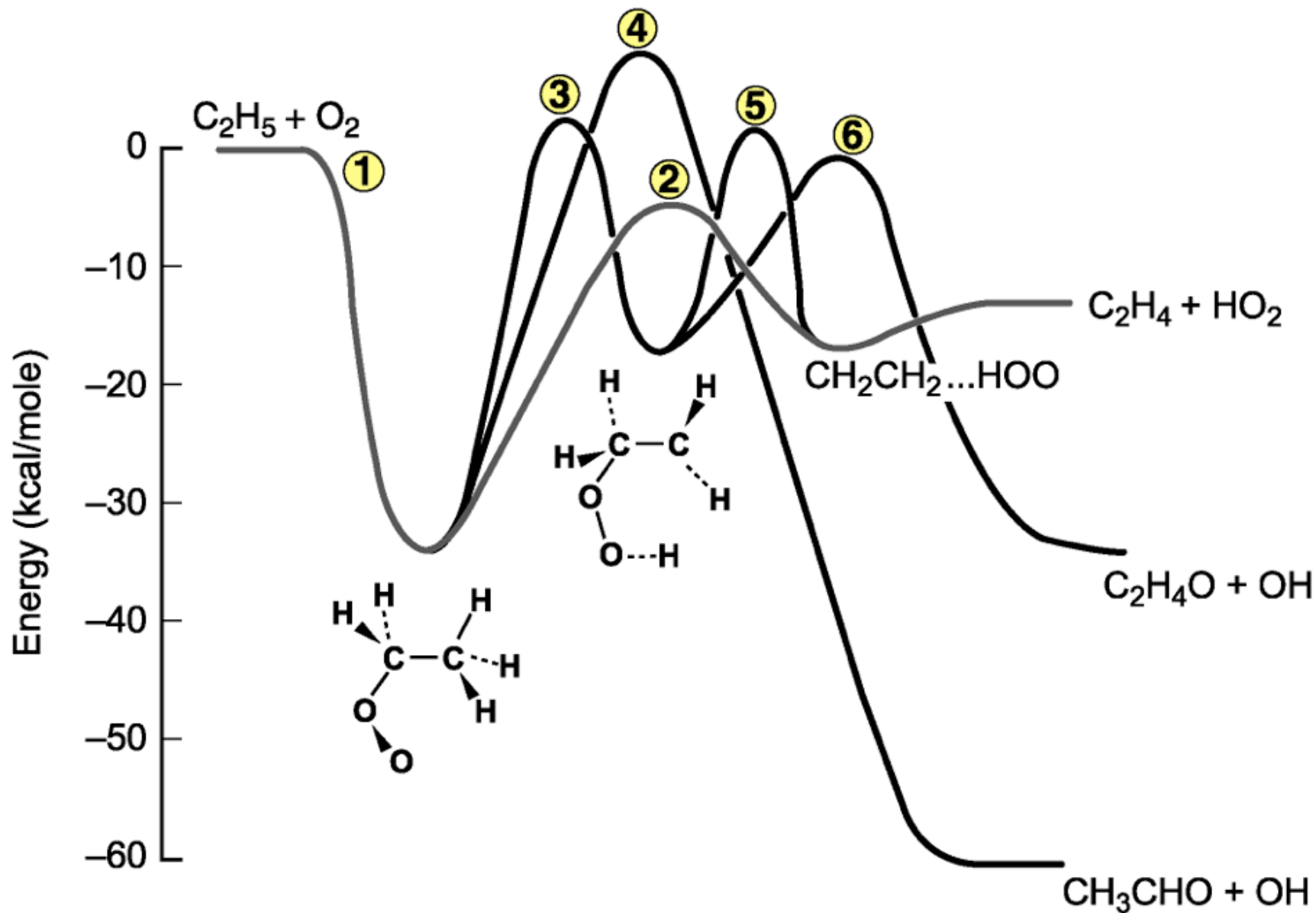
- $\frac{dX_i}{dt} = \sum_{j=0}^{M+1} \sum_{\ell=1}^{M+2} \lambda_j a_{ij} b_{j\ell} X_\ell$

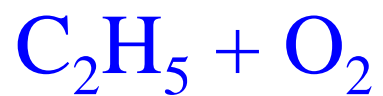
- $\frac{dX_i}{dt} = \sum_{\ell \neq i} k_{li} X_\ell - \sum_{\ell \neq i} k_{il} X_i$

- $k_{li} = \sum_{j=0}^{M+1} \lambda_j a_{ij} b_{j\ell} \quad \ell \neq i$

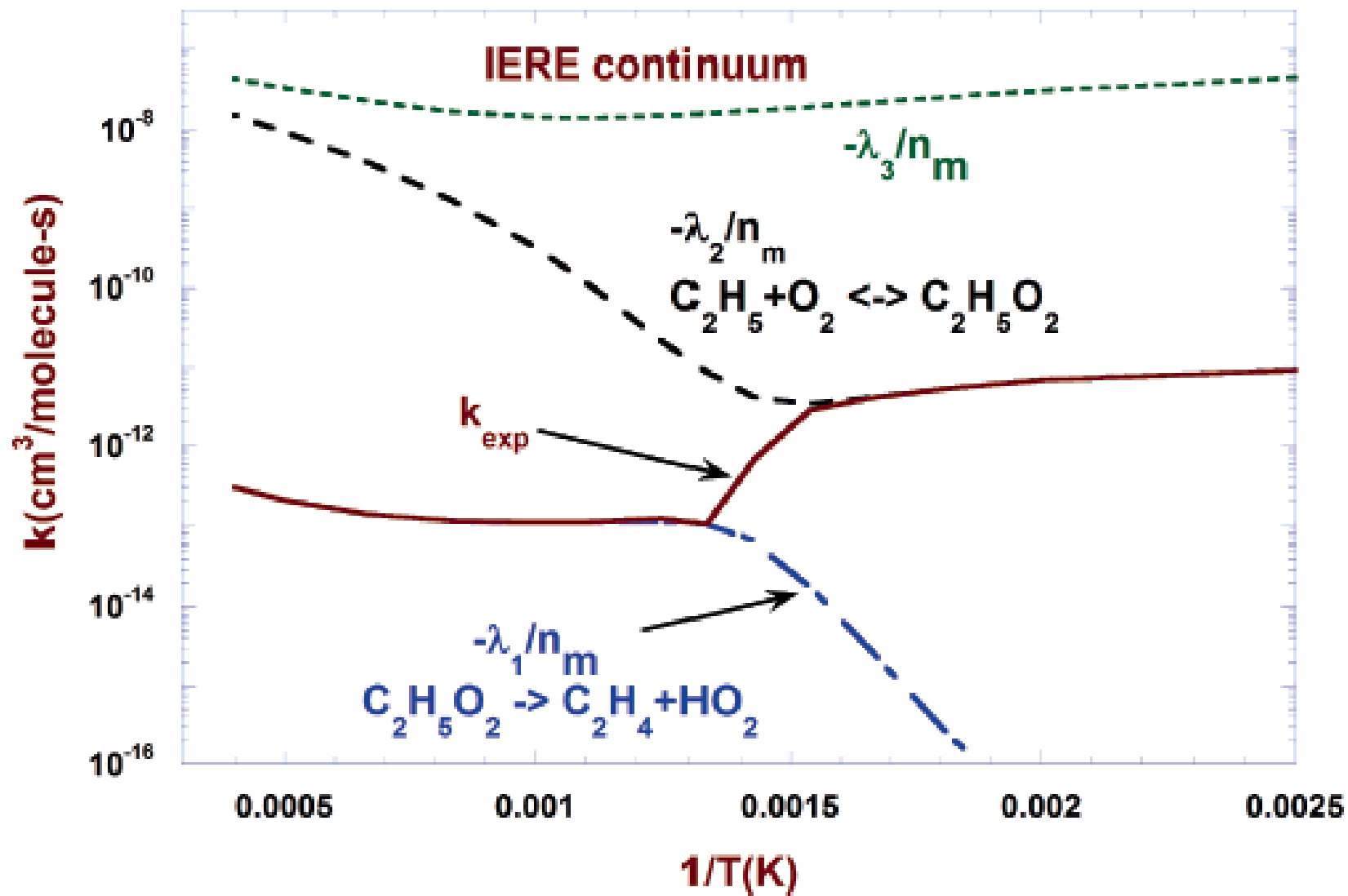


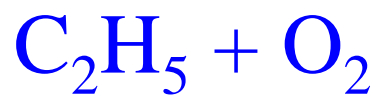
Potential Energy Surface



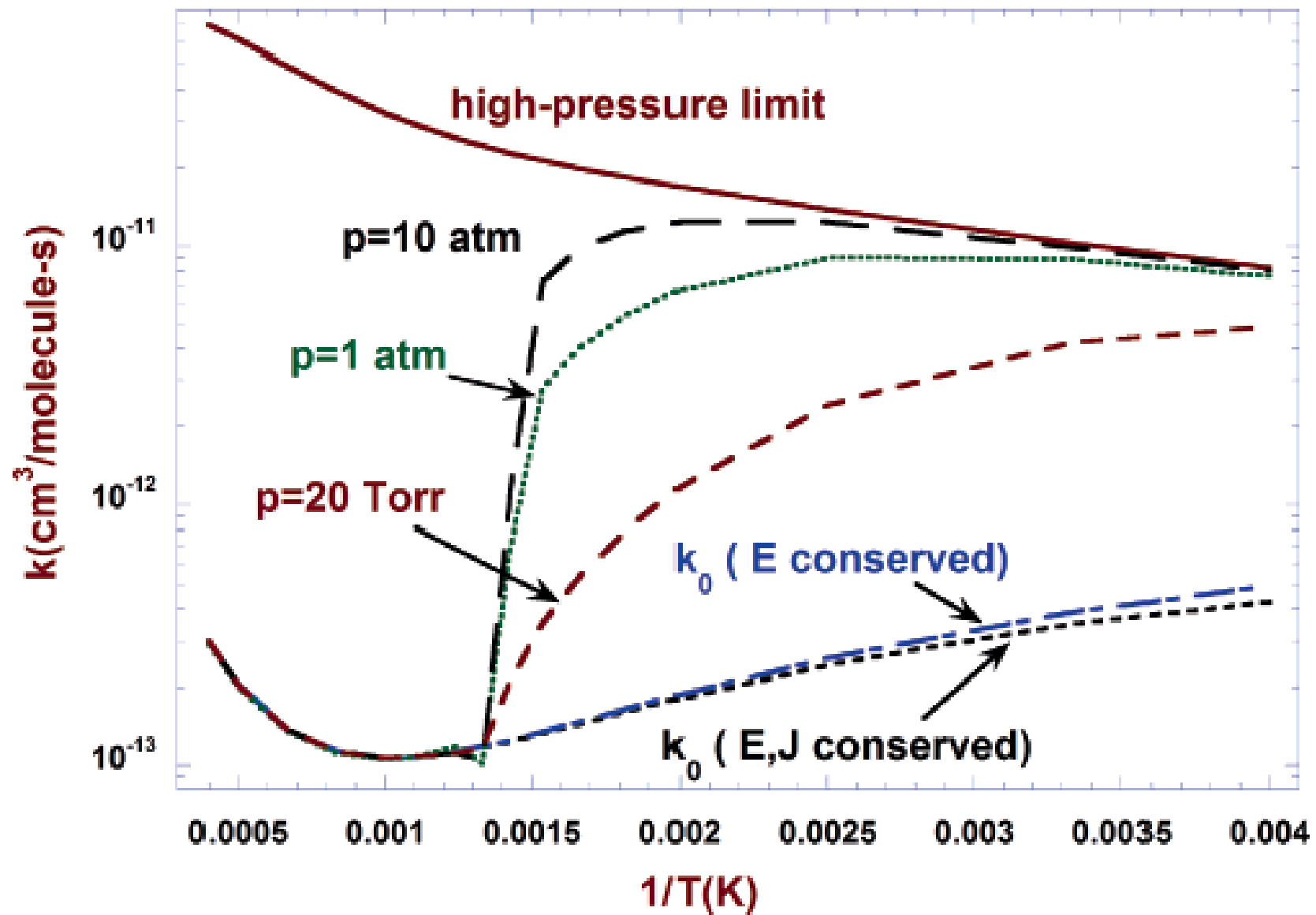


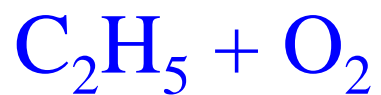
Eigenvalues





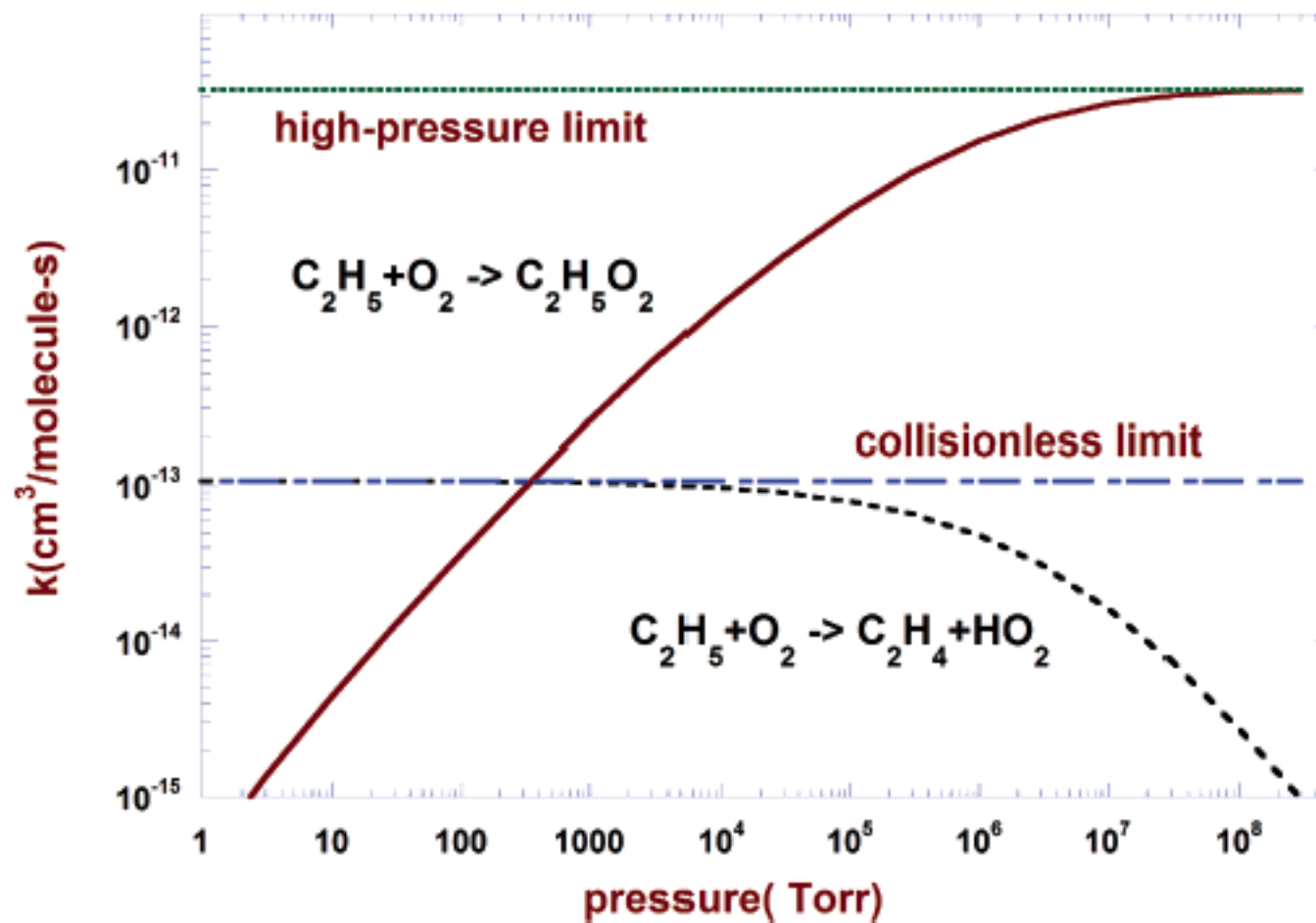
T Dependent Rate Coefficients

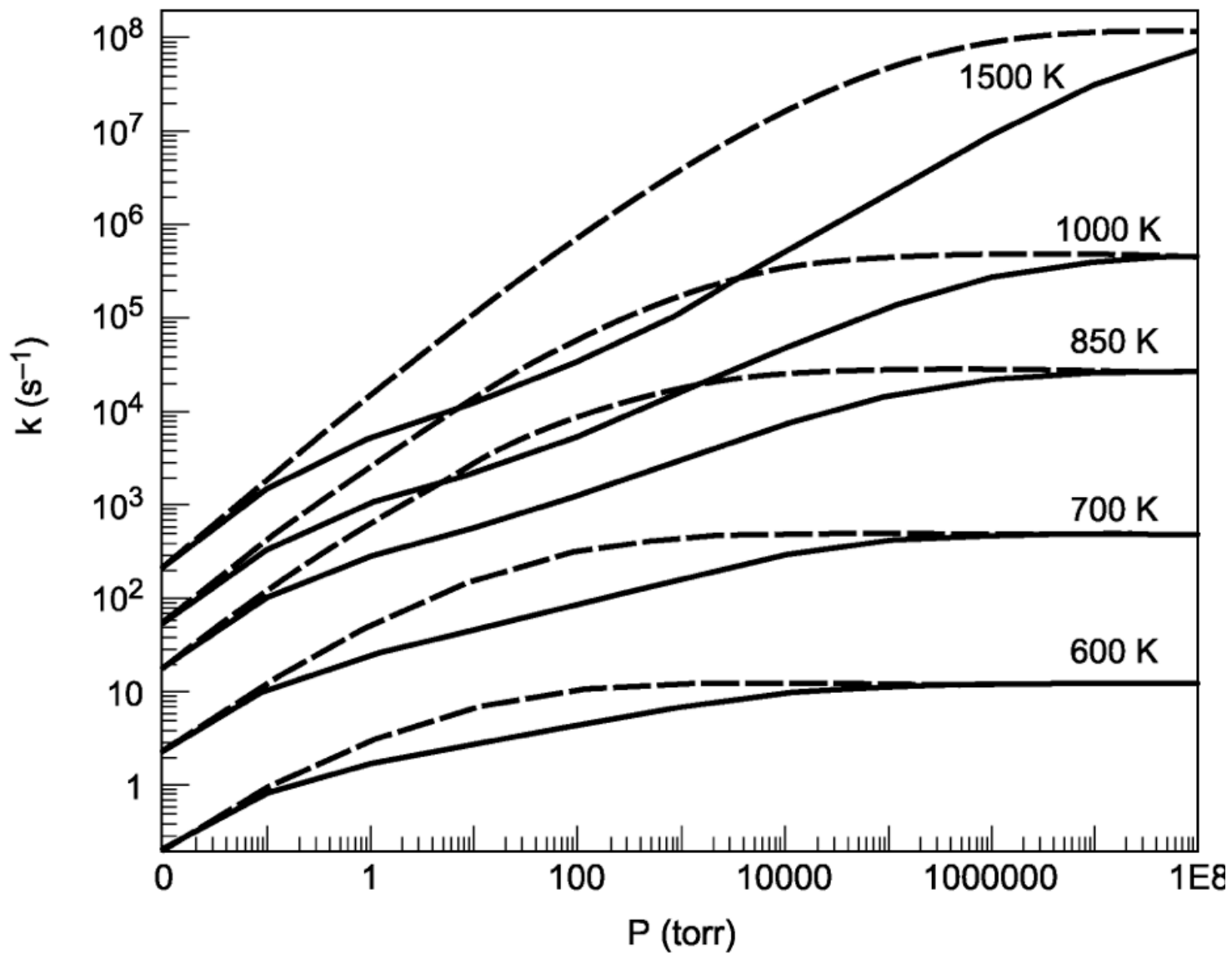




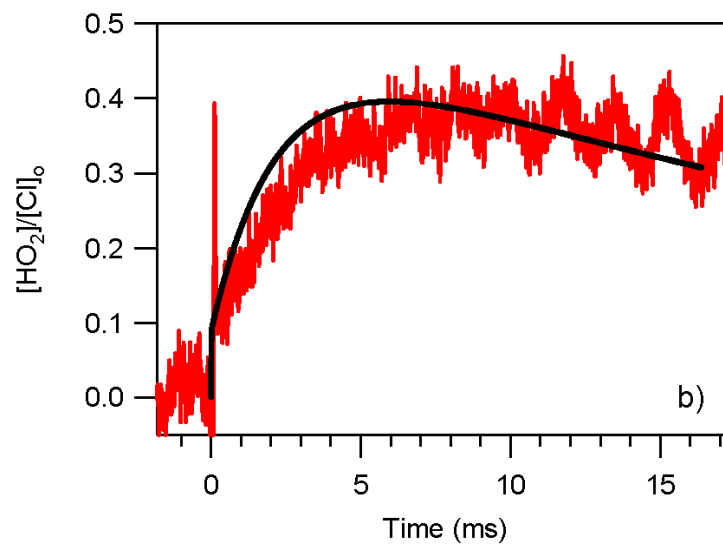
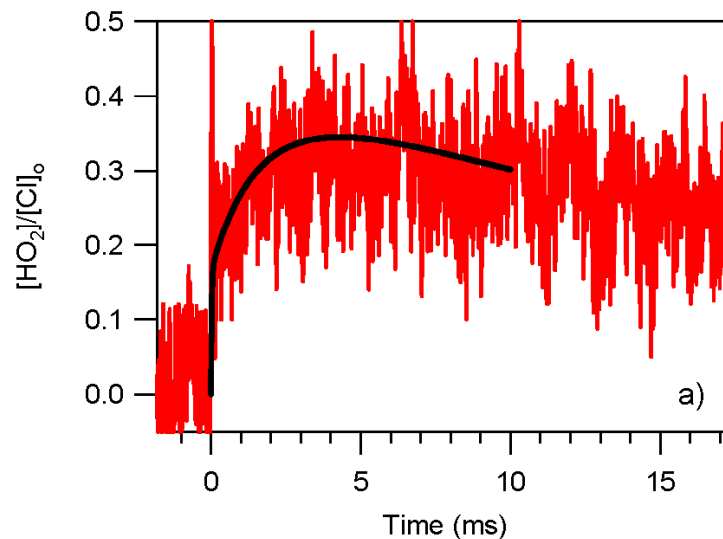
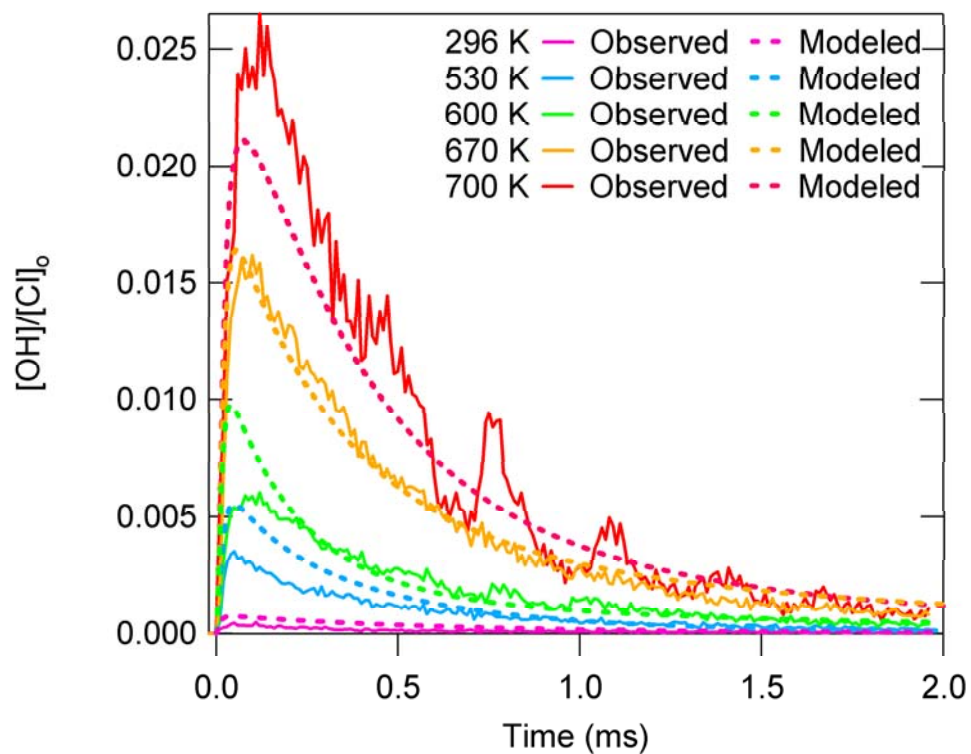
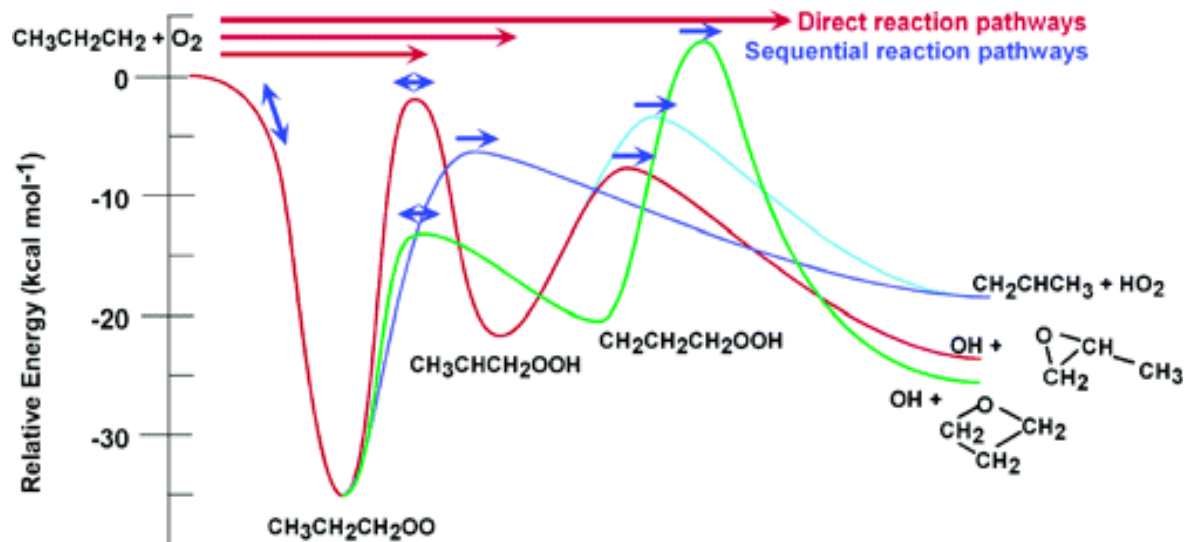
P Dependent Rate Coefficients

T=1000 K



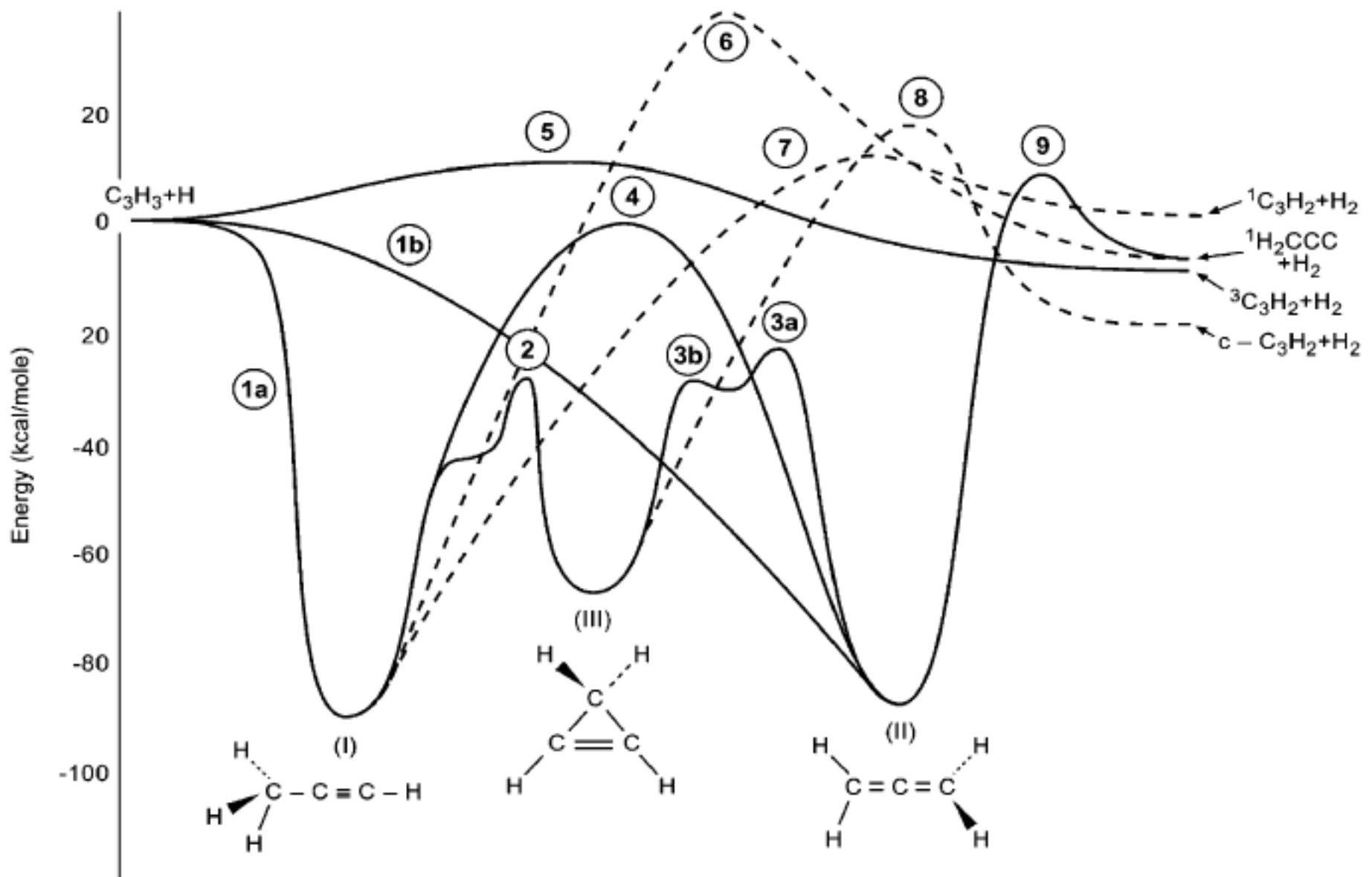


$C_3H_7 + O_2$ Formally Direct Pathways; QOOH

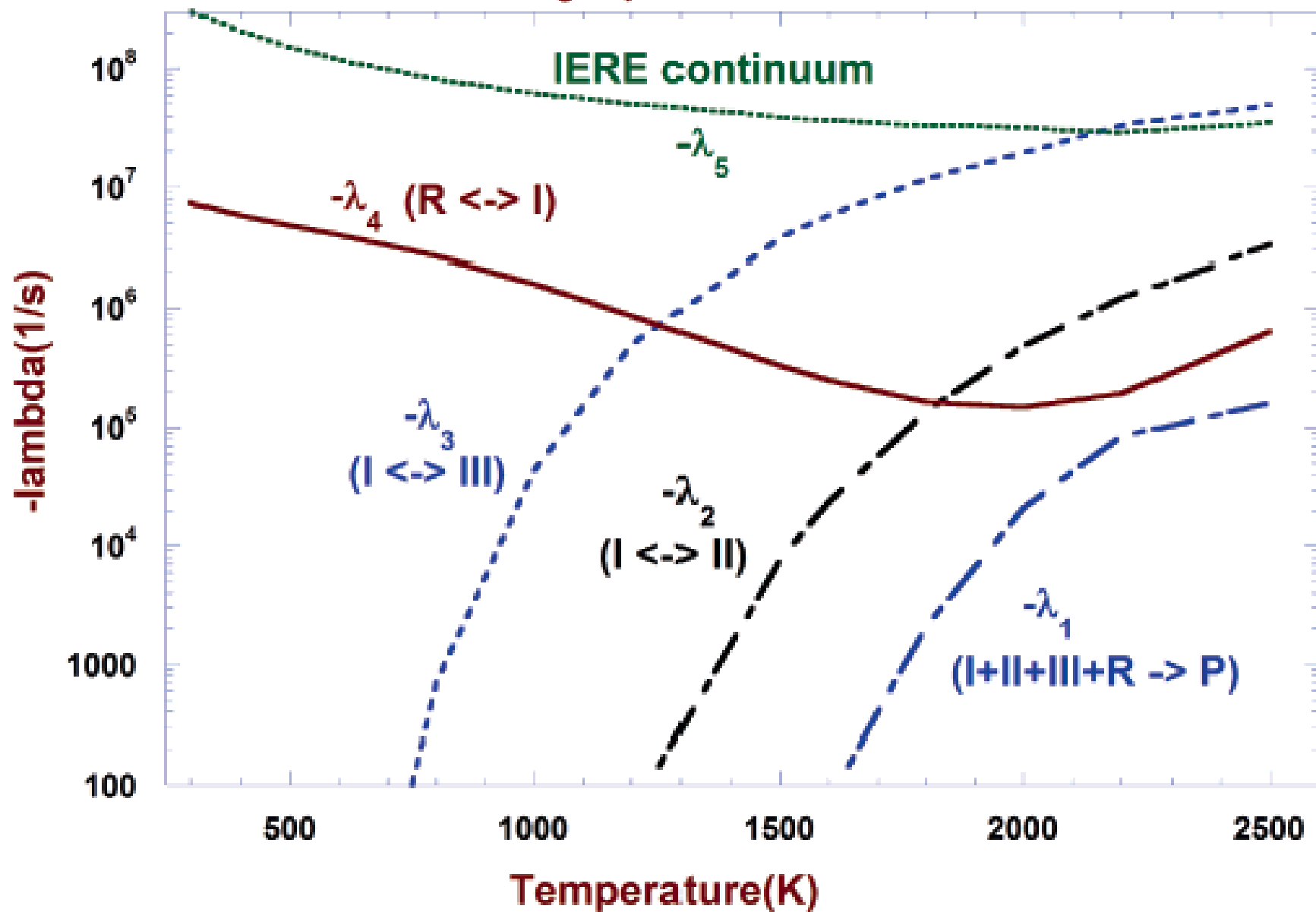




Potential Energy Surface

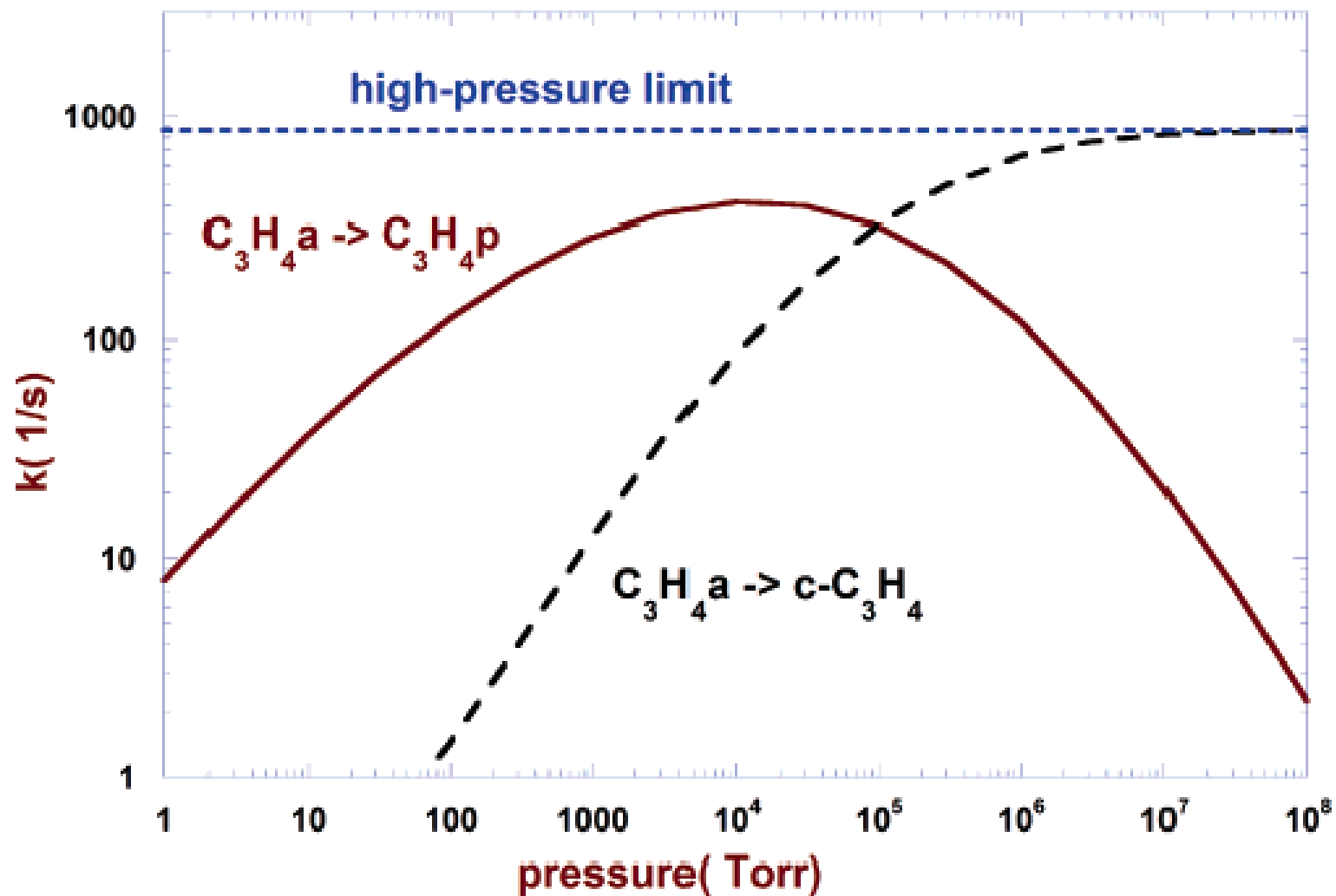


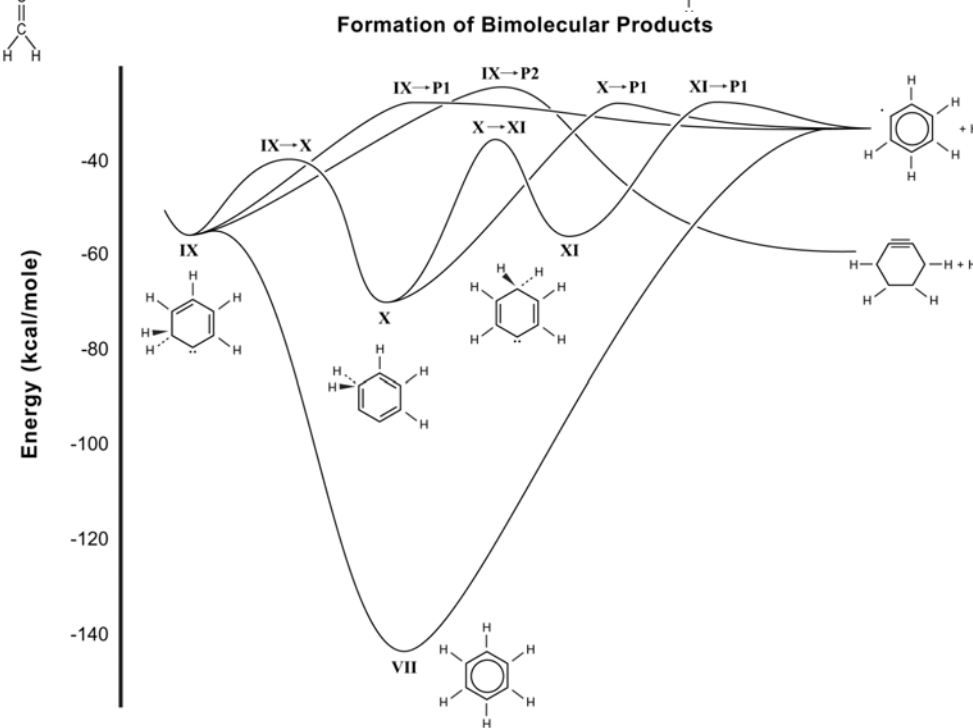
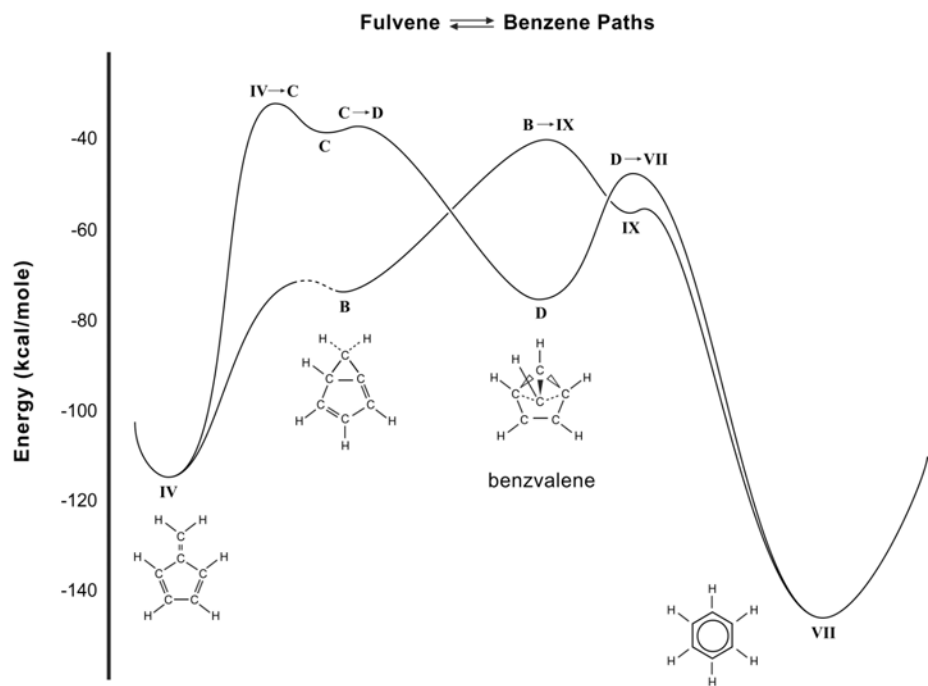
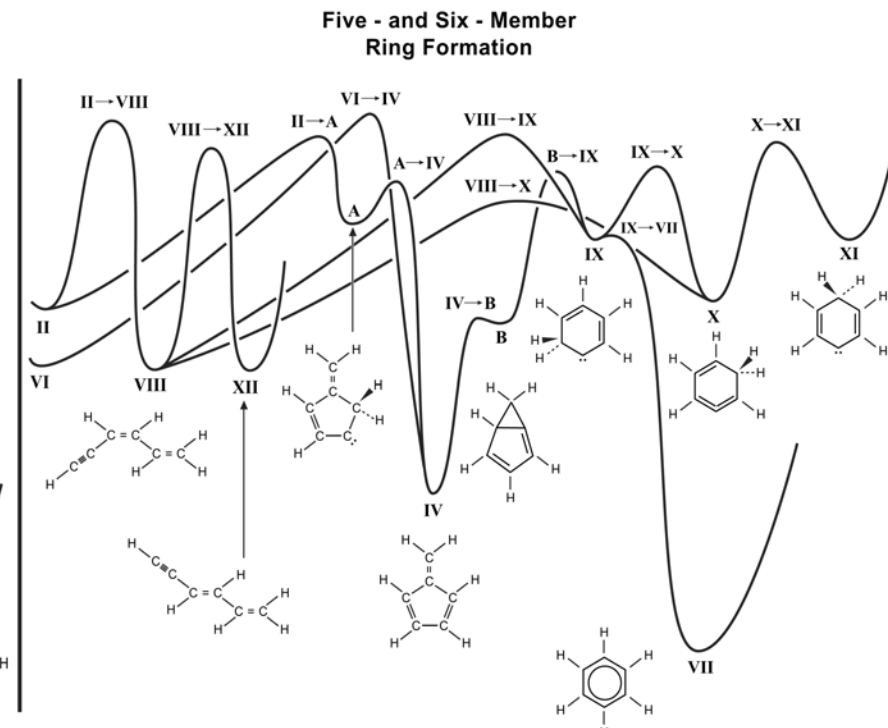
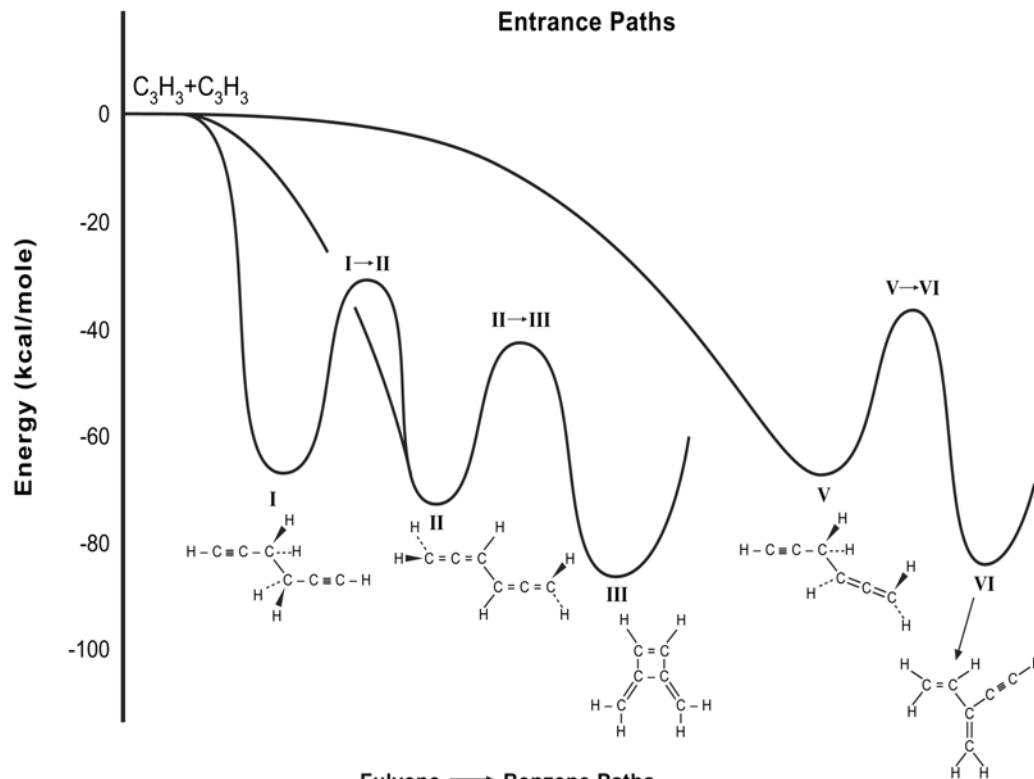
C_3H_4 eigenvalues

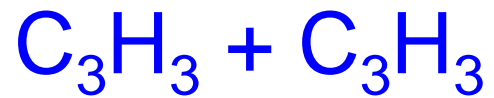




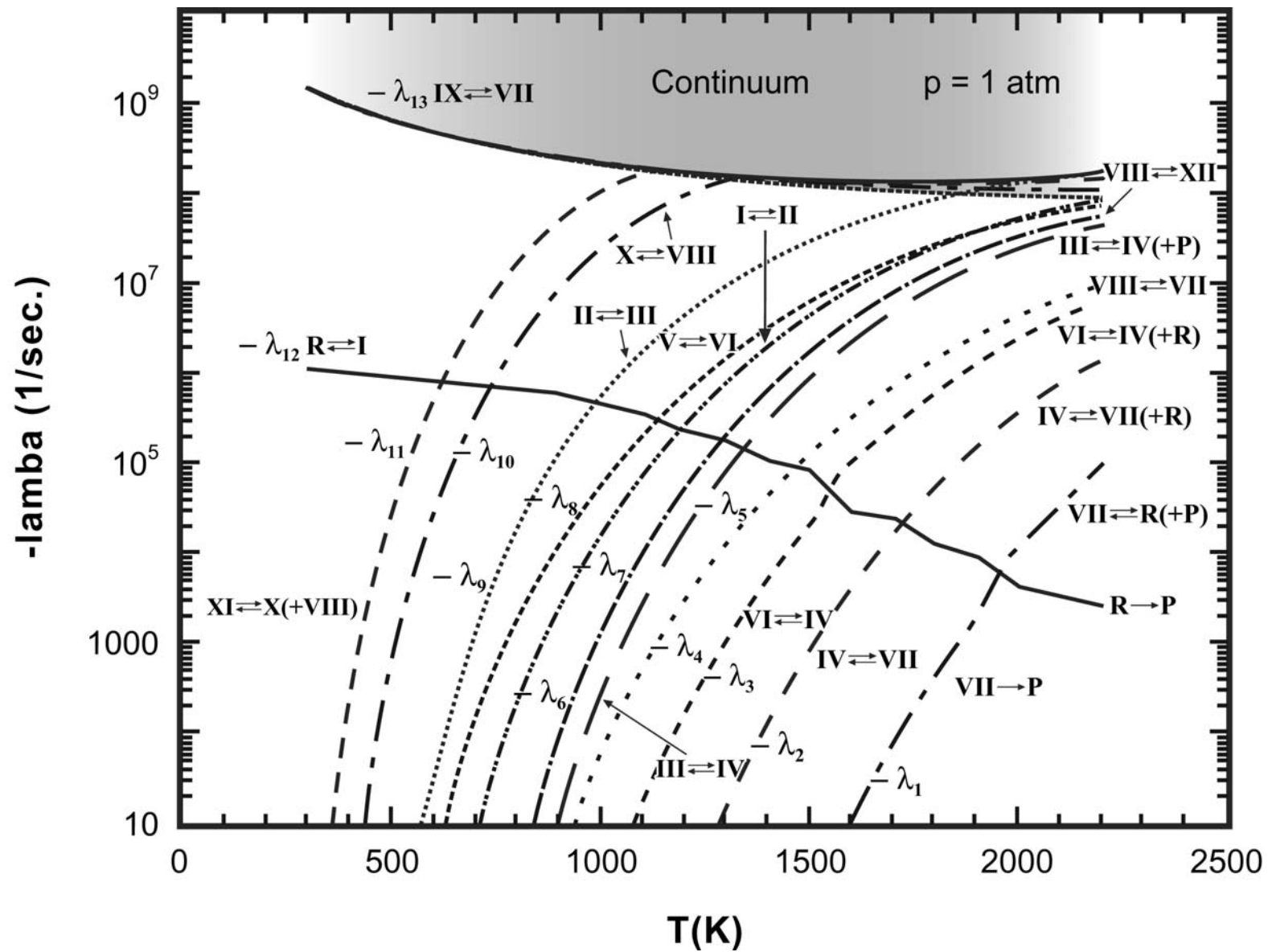
Rate Coefficients

 $T=1300K$ 



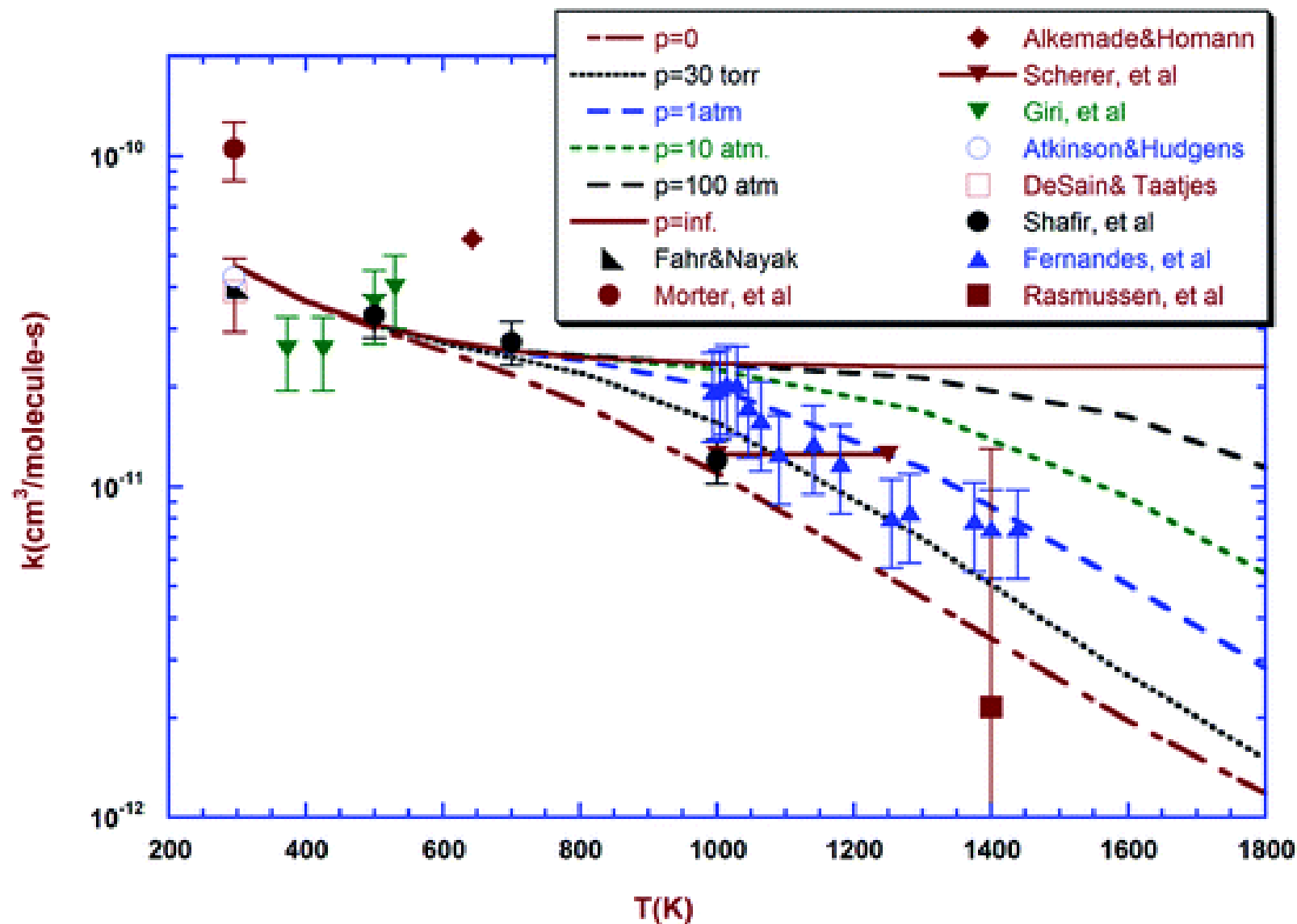


Eigenvalues

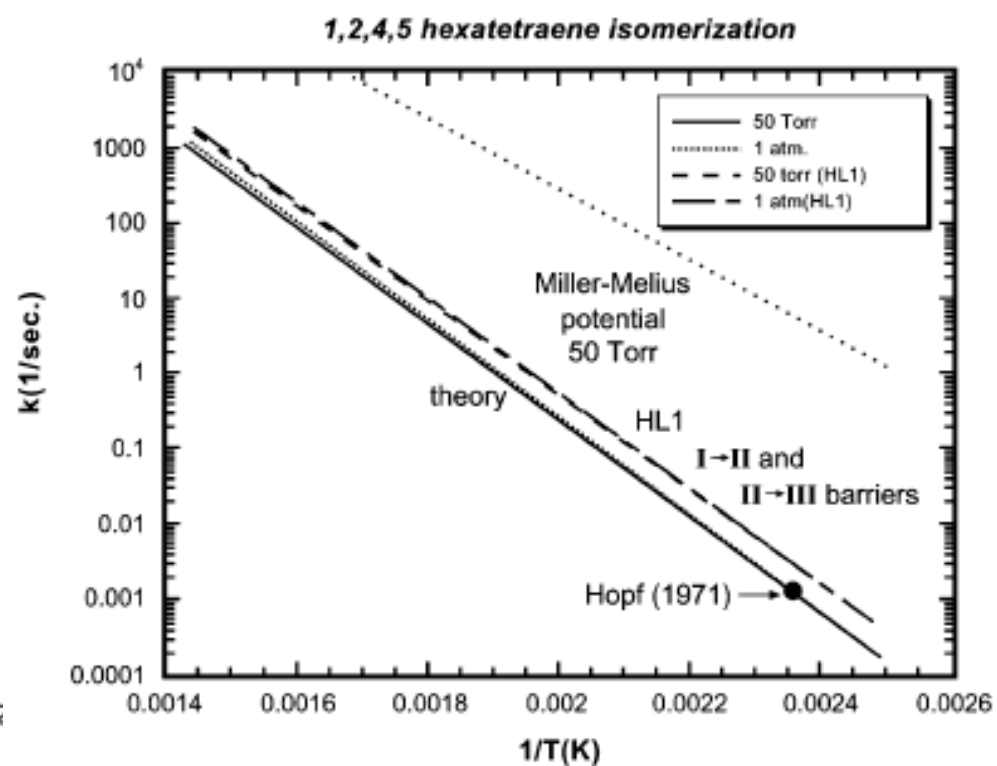
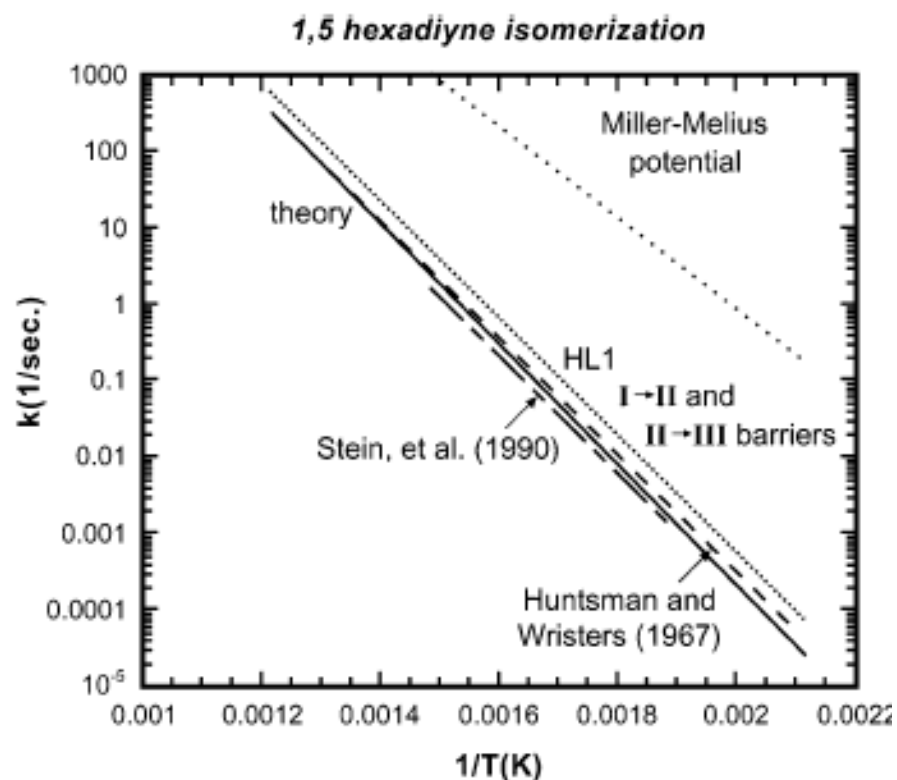




Rate Coefficients

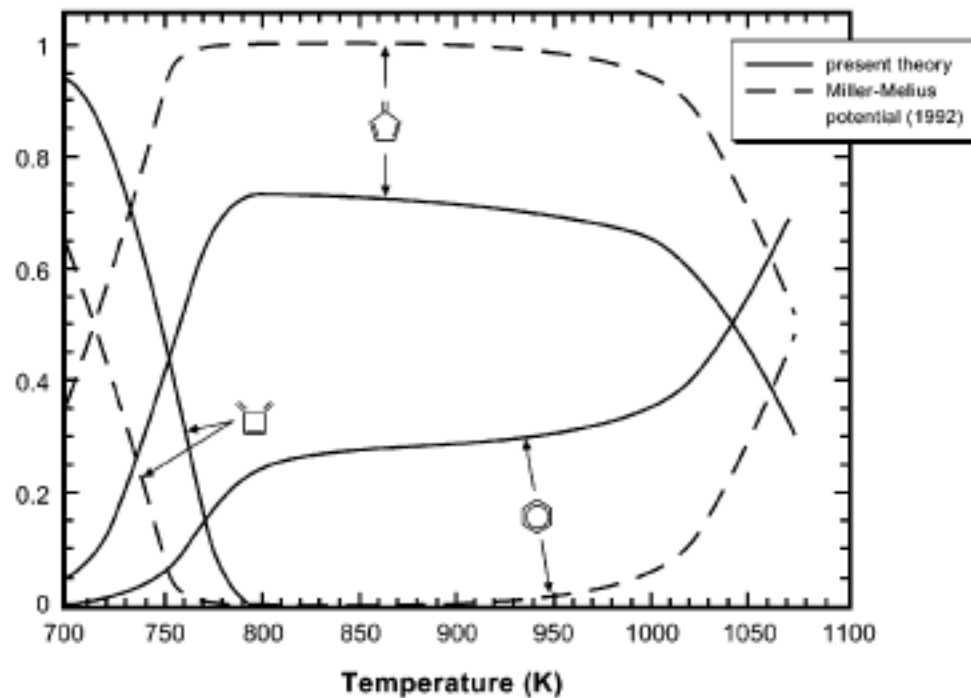
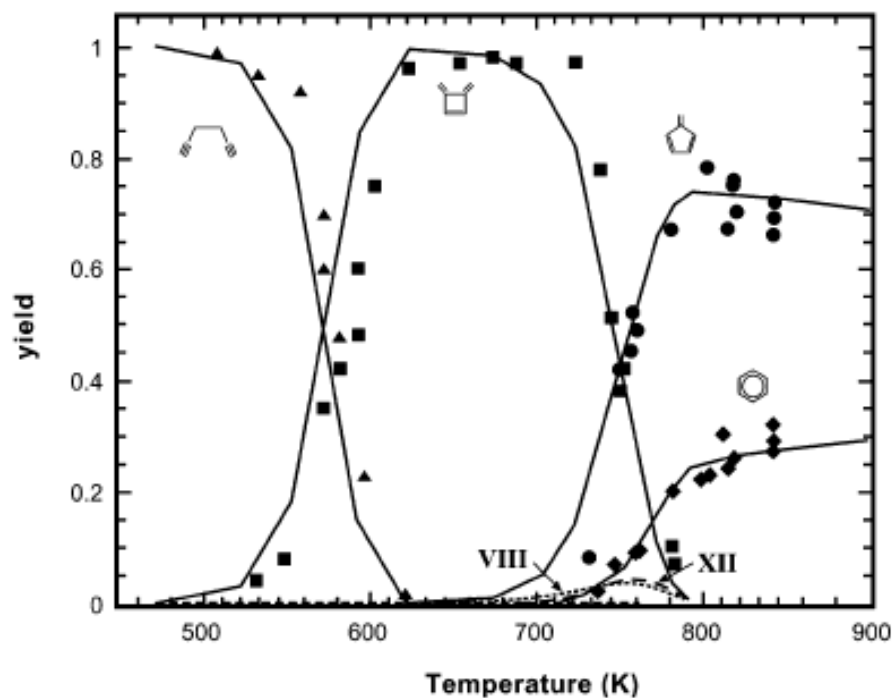


$C_3H_3 + C_3H_3$ Isomerization Rate Coefficients

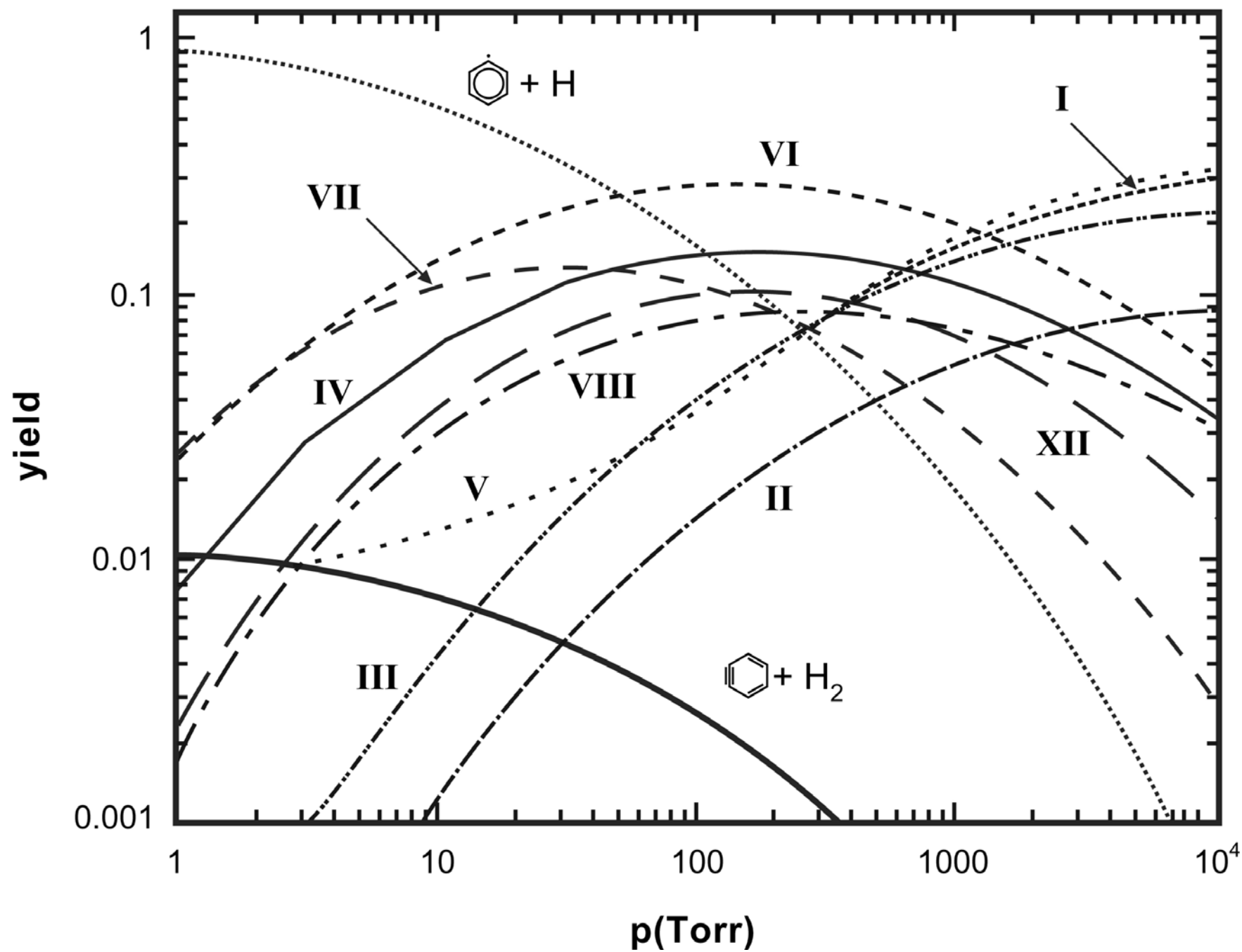




Product Branching in 1,5-Hexadiyne Pyrolysis

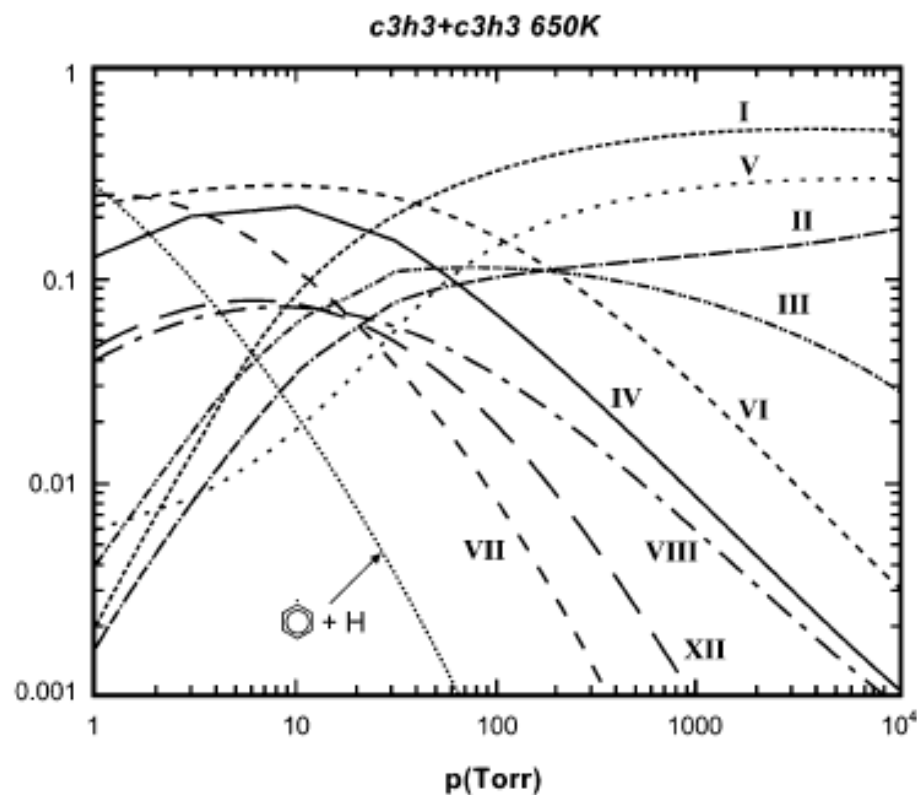
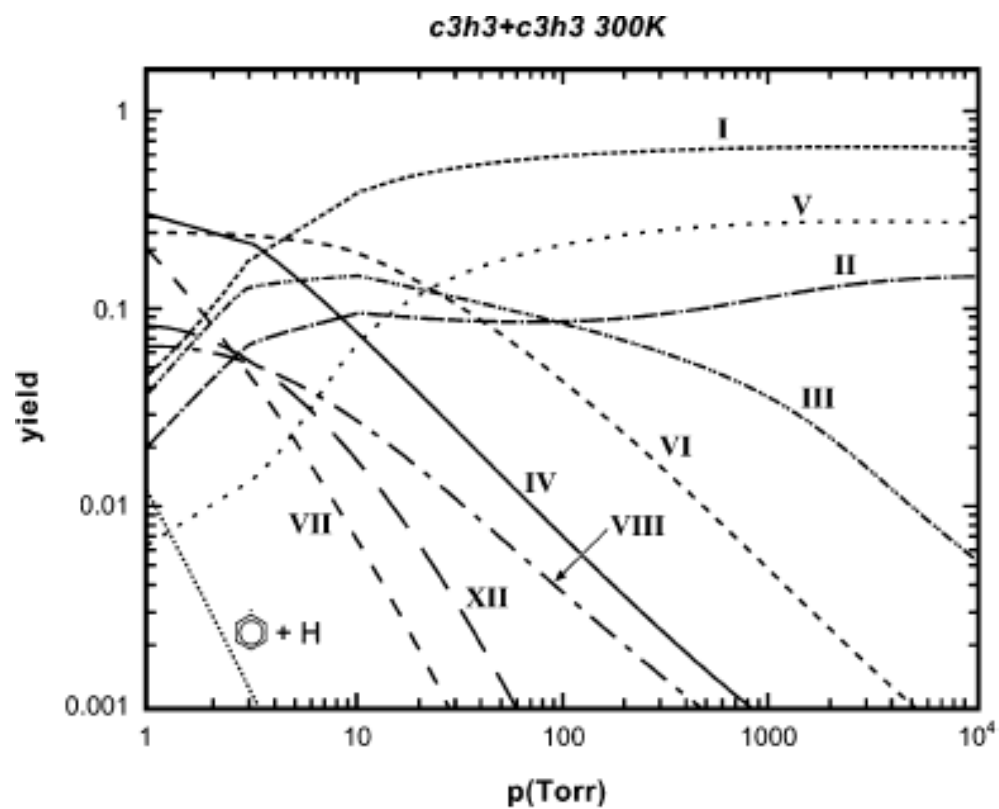


c3h3+c3h3 1500K



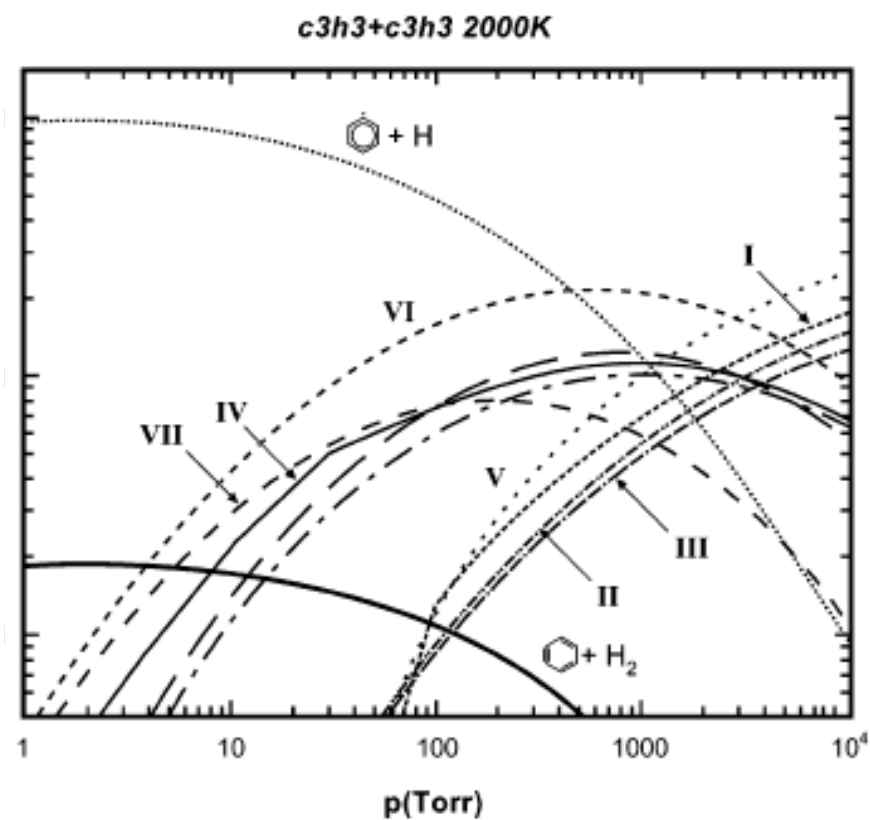
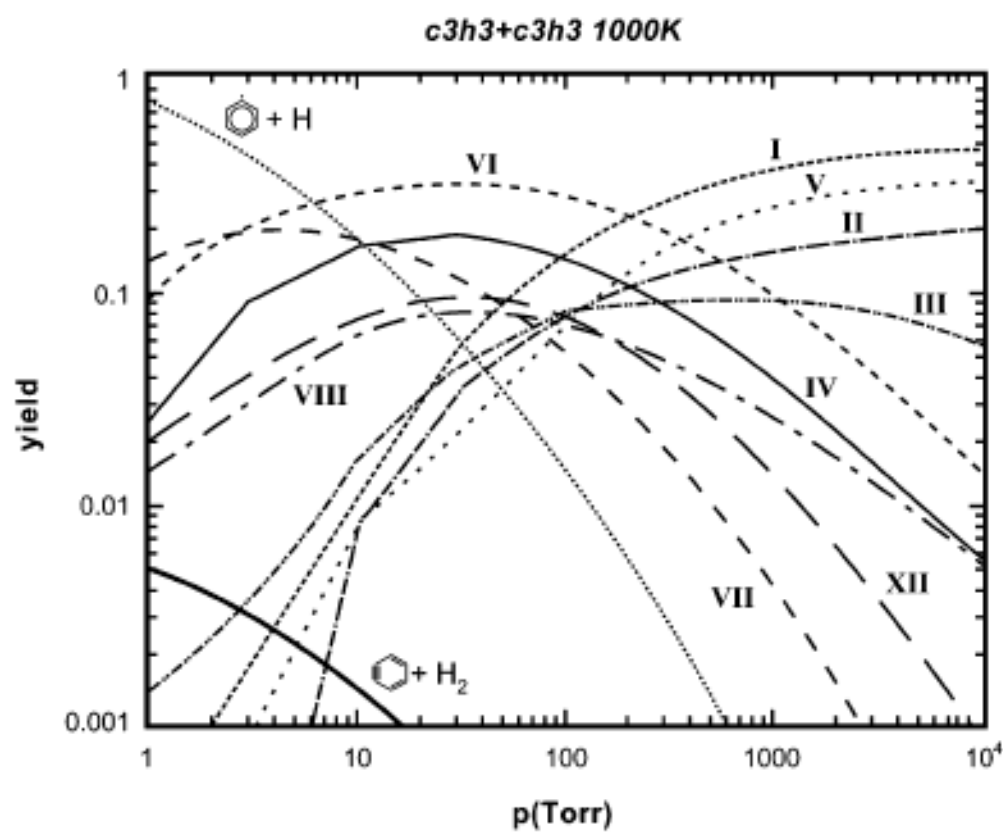


Product Branching



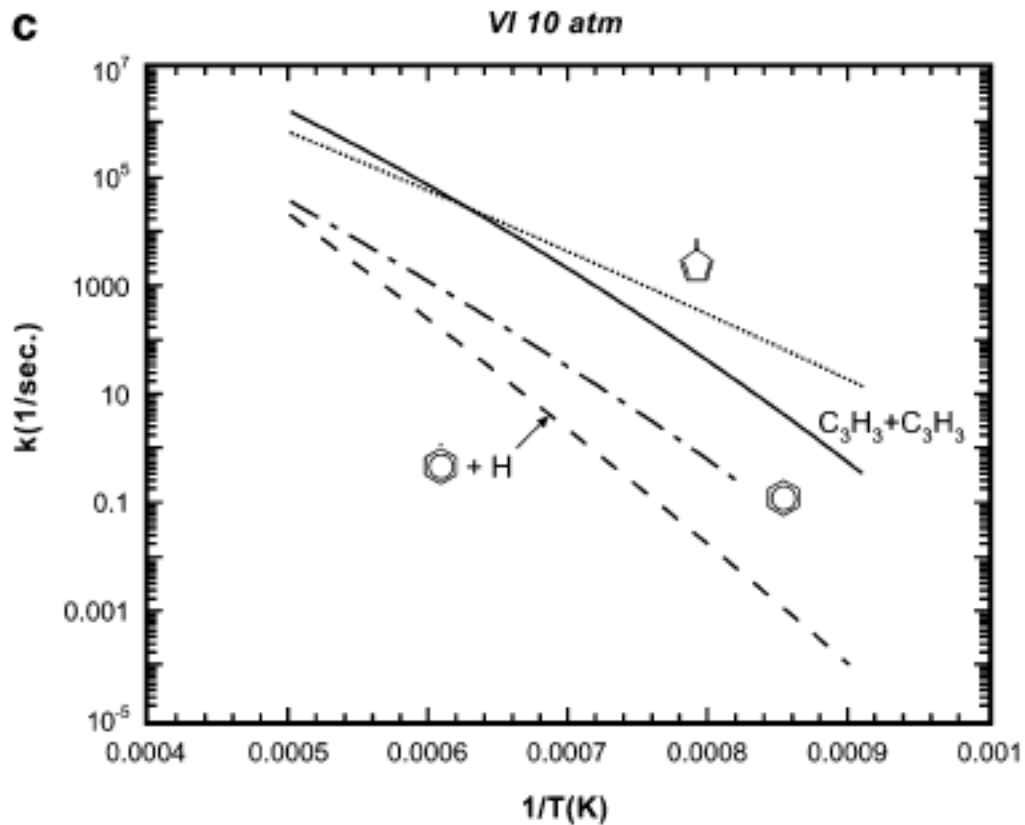
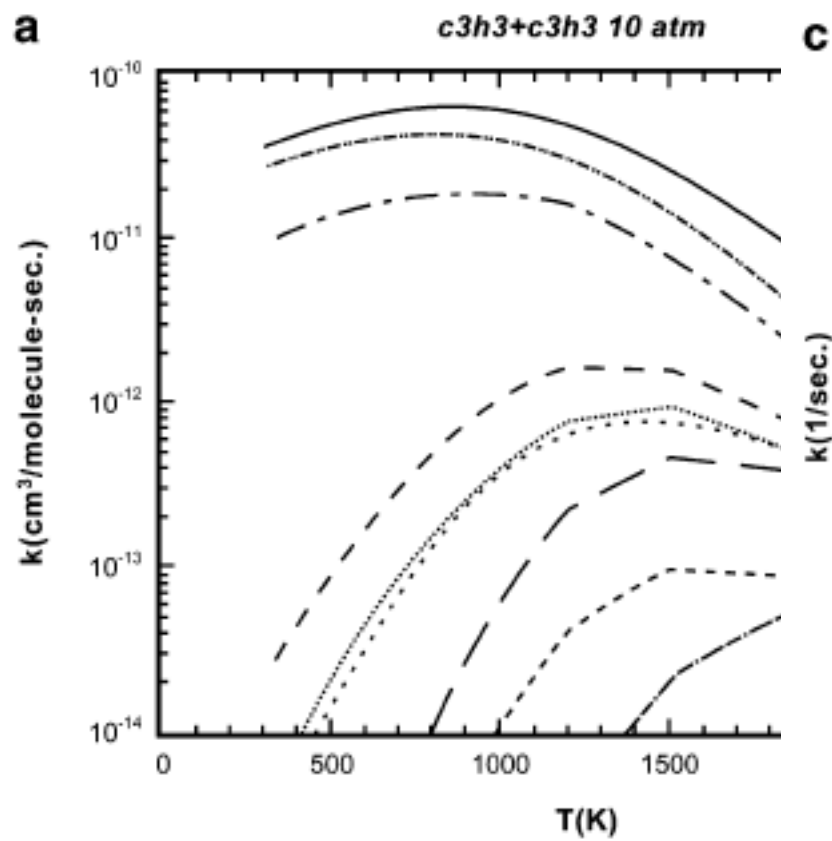


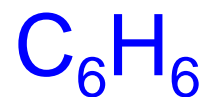
Product Branching



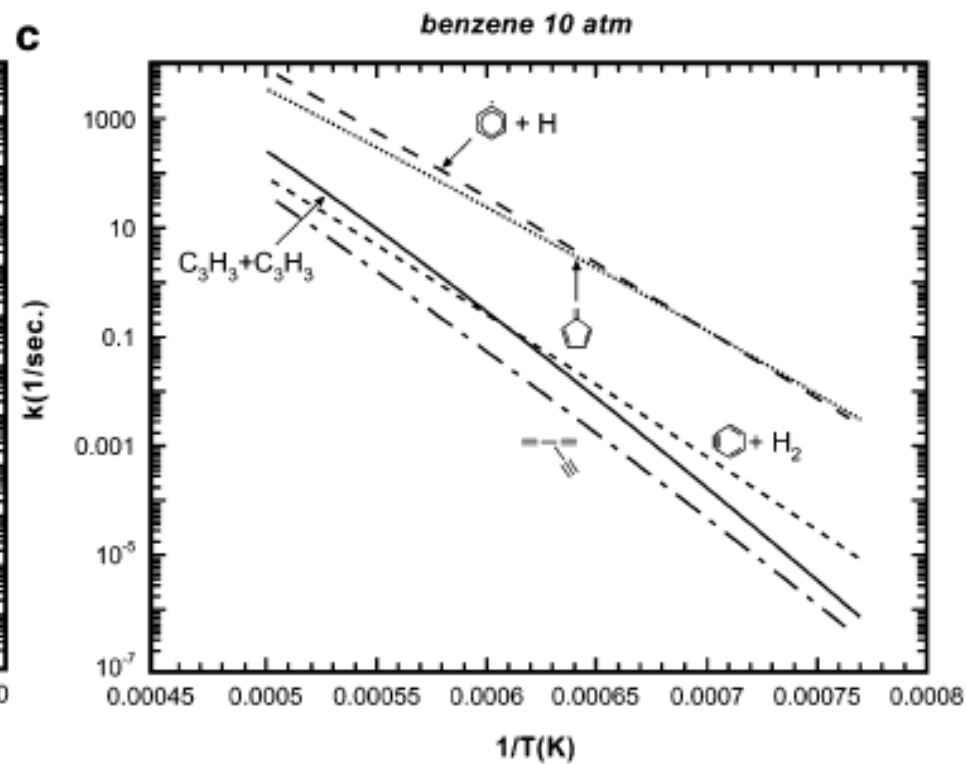
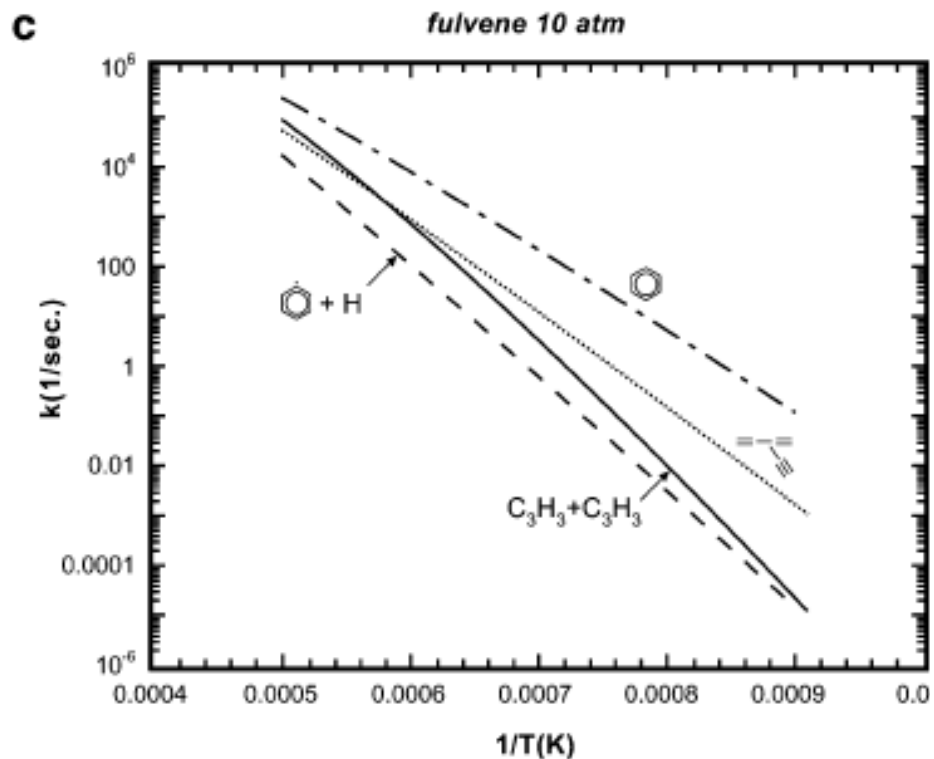


Rate Coefficients





Dissociation Rates



Master Equation Codes

Eigenvalue Eigenvector Methods

VariFlex

Klippenstein

Research Code - Not usable without personal training

MESMER

Pilling (Leeds)

<http://sourceforge.net/projects/mesmer/>

Stochastic Master Equation Solvers

Experimental Perspective only

Multiwell

Barker (Michigan)

<http://esse.engin.umich.edu/multiwell/MultiWell/MultiWell%20Home/MultiWell%20Home.html>

Vereecken and Peeters (Leuven)

Steady State Solvers

ChemRate

Tsang (NIST)

<http://www.mokrushin.com/ChemRate/chemrate.html>