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 $CH_3 + OH$

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

$A + B \rightarrow AB(E)$ $\quad k_f(E) \quad [k(T) = \int k(E)\, P(E)]$

But, E is above dissociation threshold so AB just redissociates

$AB(E) \rightarrow A + B$ $\quad k_d(E)$

Need some process to take away energy and stabilize AB

Collisions with bath gas M (or photon emission)

$AB(E) + M \rightarrow AB(E') + M'$ $\quad k_c \times P(E \rightarrow E')$

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

$A + B \rightarrow AB^*$ $k_f(T)$

$AB^* \rightarrow A + B$ $k_d(T)$

$AB^* + M \rightarrow AB + M'$ k_c

Steady state for [AB*] =>

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

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

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

$k_{eff} = k_f$

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

$k_{eff} = k_f k_c / k_d$

Not accurate but good for qualitative thought

Simple Models RRKM Theory

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

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

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

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

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

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

$$k_{eff}^{\infty} = \frac{1}{hQ_AQ_B}\int dE N^{\pm}(E)\exp(-\beta E) = \frac{k_BT}{hQ_AQ_B}\int dE \rho^{\pm}(E)\exp(-\beta E)$$

$$k_{eff}^{\infty} = \frac{k_BT}{h}\frac{Q^{\pm}}{Q_AQ_B}$$

Simple Models Modified Strong Collider

Assume only a fraction β_c of collisions lead to stabilization

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

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

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

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

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

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

Replace n(E,t) with normalized population x(E,t) = n(E,t)/ ∫ dE n(E,t)

Steady state for x =>

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

Master equation Reversible Formulation

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

$$k_f(E)\frac{\rho_{reac\tan t}(E)\exp(-\beta E)}{Q_A Q_B}n_A n_B$$

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 => Matrix inversion

Master Equation Problems at high T

Dissociation occurs on same time scale as energy relaxation

Nonequilibrium factor f_{ne}

$$f_{ne} = \frac{\left(\int dE c(E)\right)^2}{\left(\int dE \frac{c^2(E)}{F(E)}\right)^2}$$

c(E) = 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 CH_4

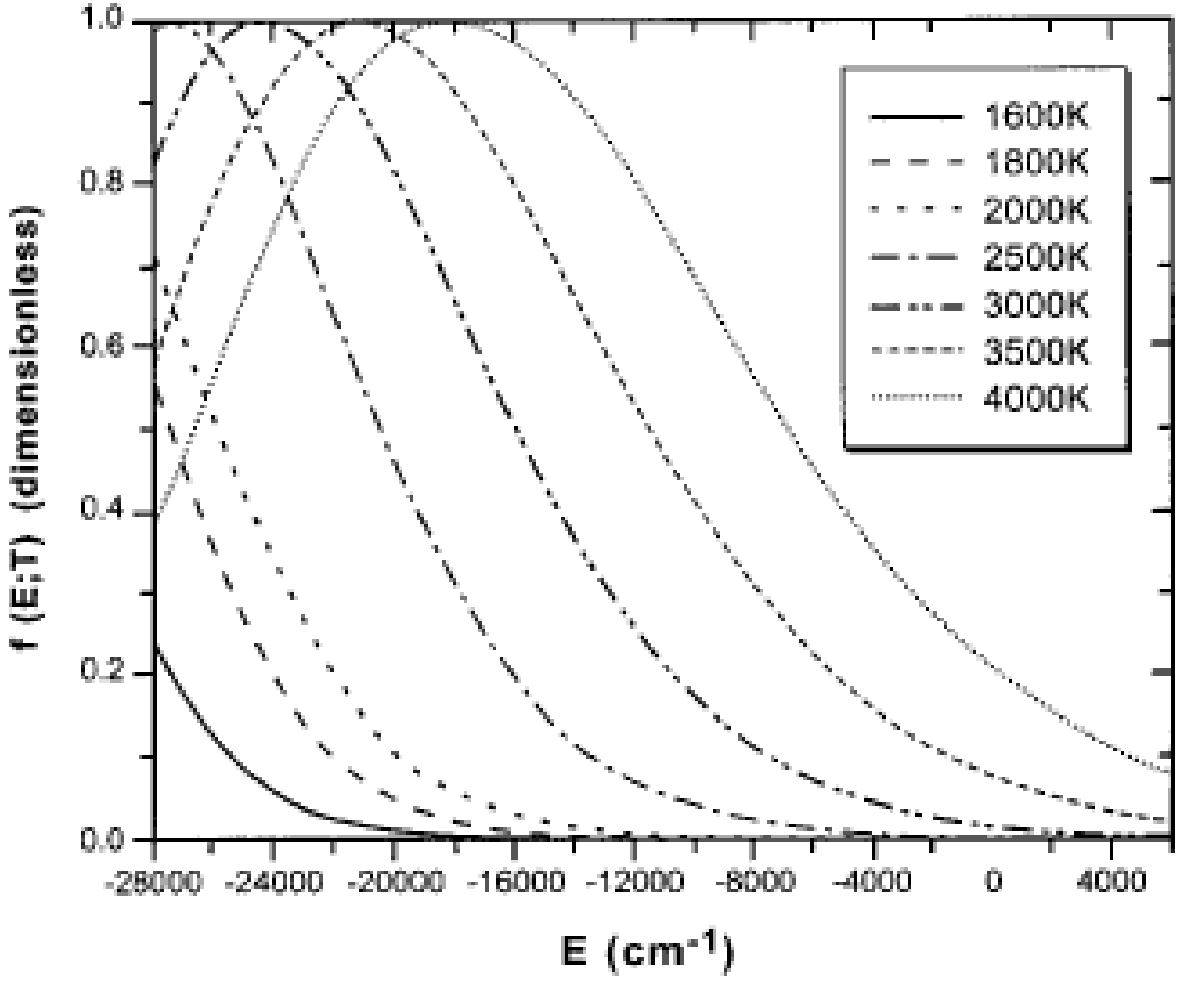
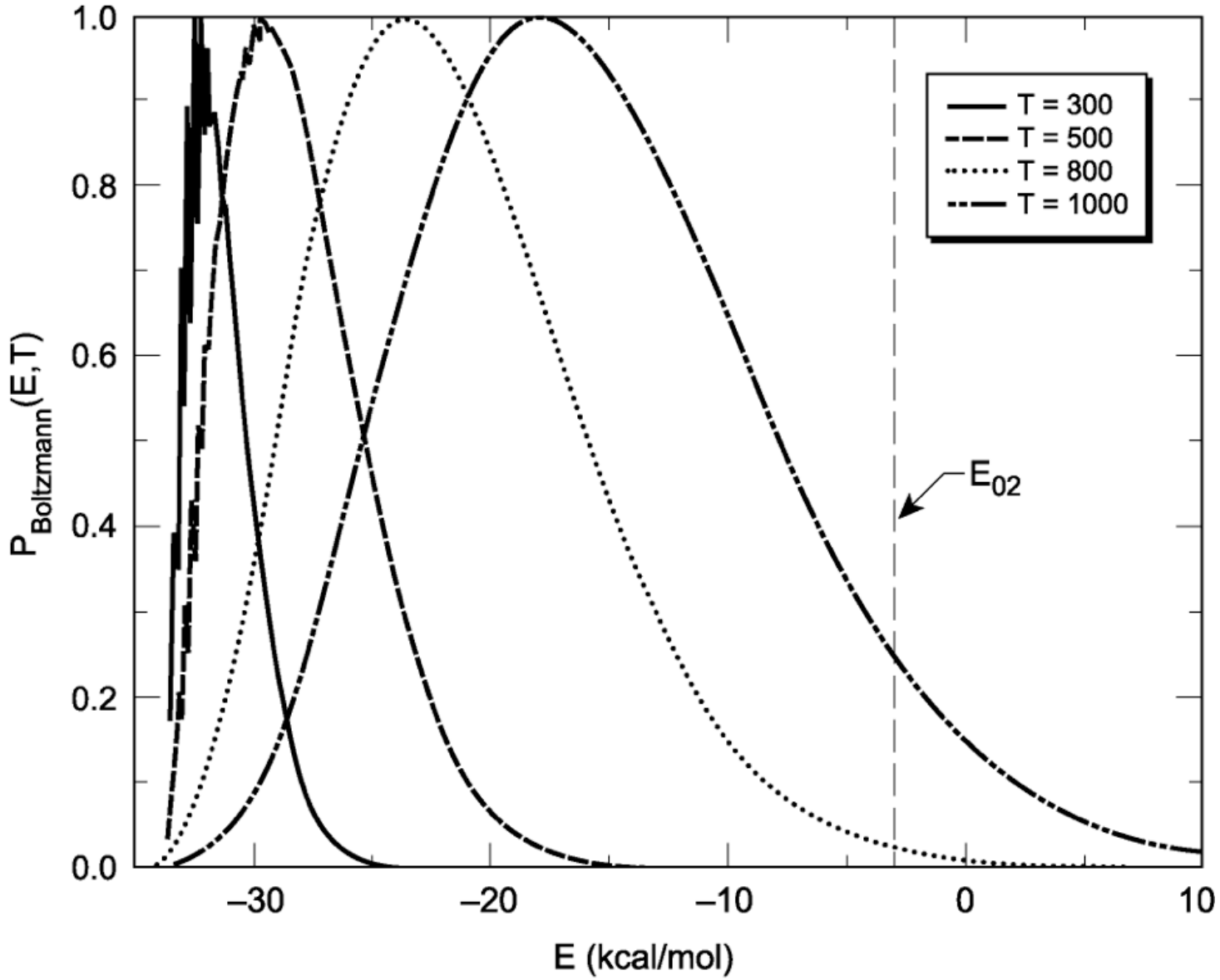
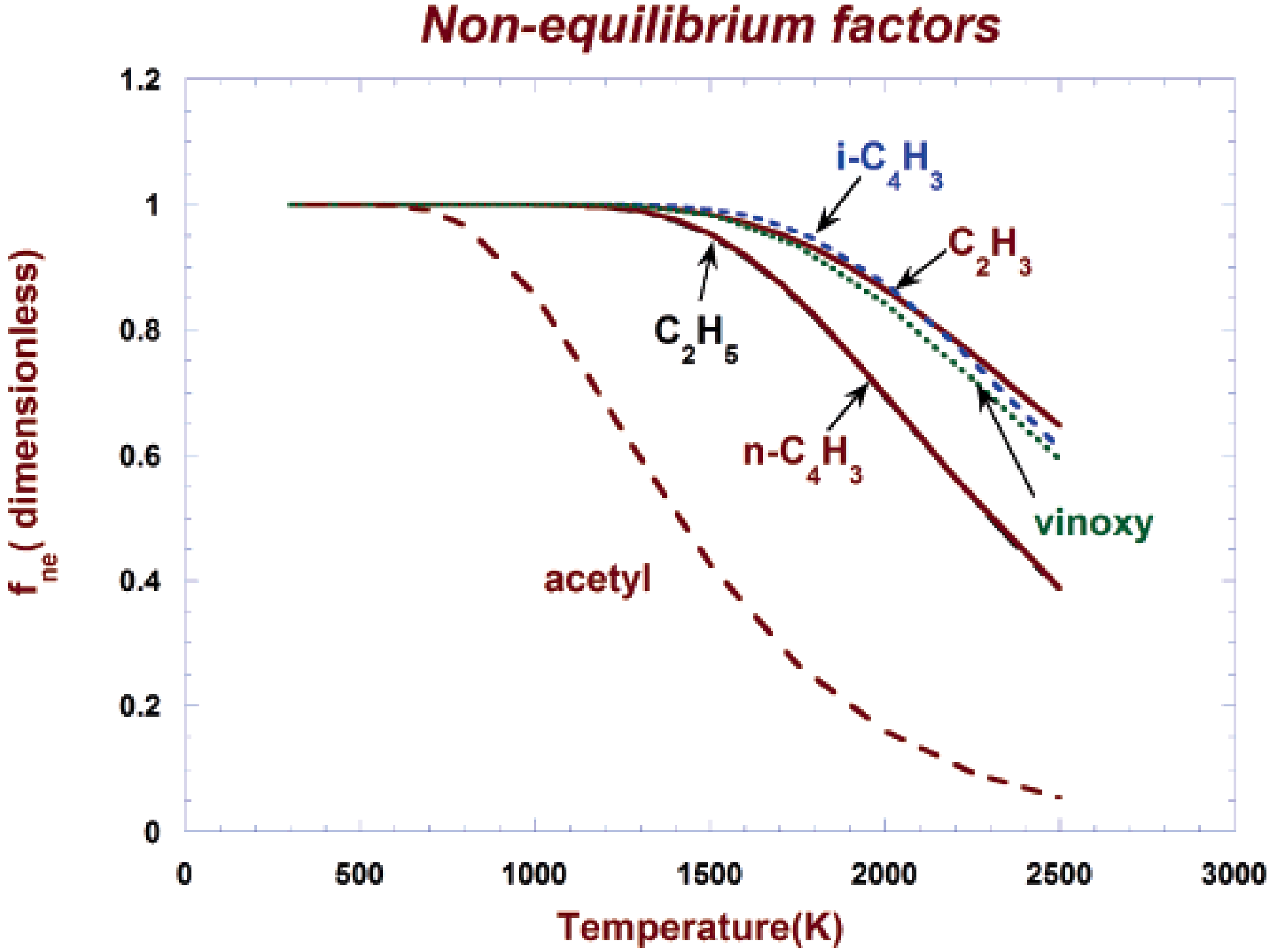


Figure 8. Relative values of $f(E;T)$. The functions are normalized so that the peak is always unity.

Boltzmann Distributions $C_2H_5O_2$




Non-equilibrium factors
1.2
1
0.8
0.6
0.4
0.2
0
f ne (dimensionless)
0
500
1000
1500
2000
2500
3000
Temperature(K)
i-C4H3
C2H3
C2H5
n-C4H3
vinoxy
acetyl

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

Approximate Reduction from 2D to 1D

E model

$P(E,J,E',J') = P(E,E')\,\varphi(E,J)$

Rotational energy transfer like vibrational

J distribution given by phase space volume

$\varphi(E,J)=(2J+1)\,\rho(E,J) / \rho(E)$

$\rho(E) = \sum_J (2J+1)\,\rho(E,J)$

$k(E) = \sum_J (2J+1)\,N^{\ddagger}(E,J) / h\rho(E)$

Use k(E) and P(E,E') in 1D Master Eqn

Does not resolve J dependent thresholds

All rotational degrees of freedom are active

Incorrect low pressure limit

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

$\varepsilon = E - E_J$

$E_J = BJ(J+1)$

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

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

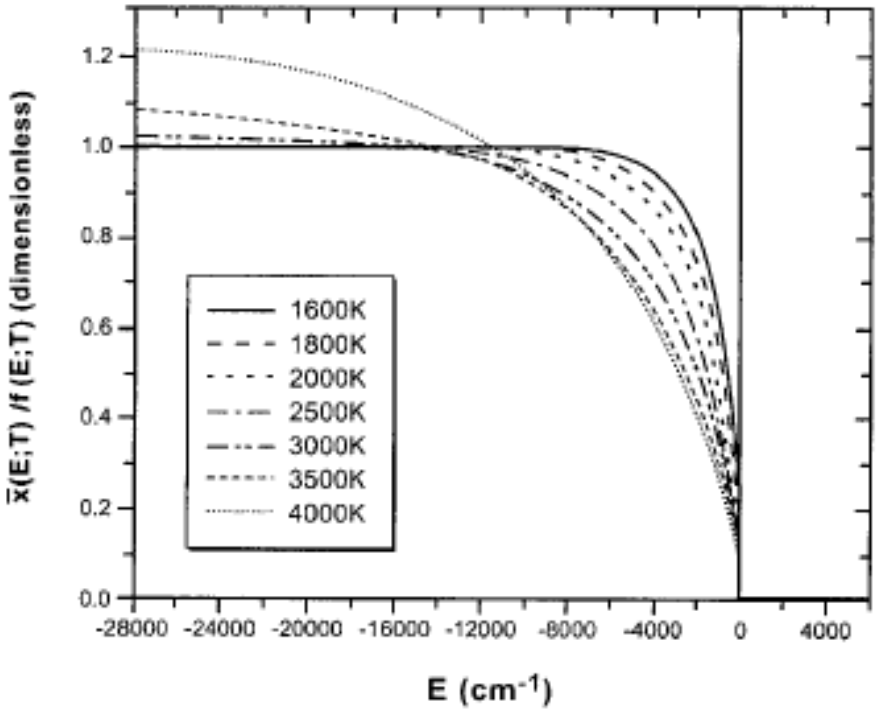
$\rho(\varepsilon,J)$ = density of states for active degrees of freedom

Thermally equilibrated J distribution

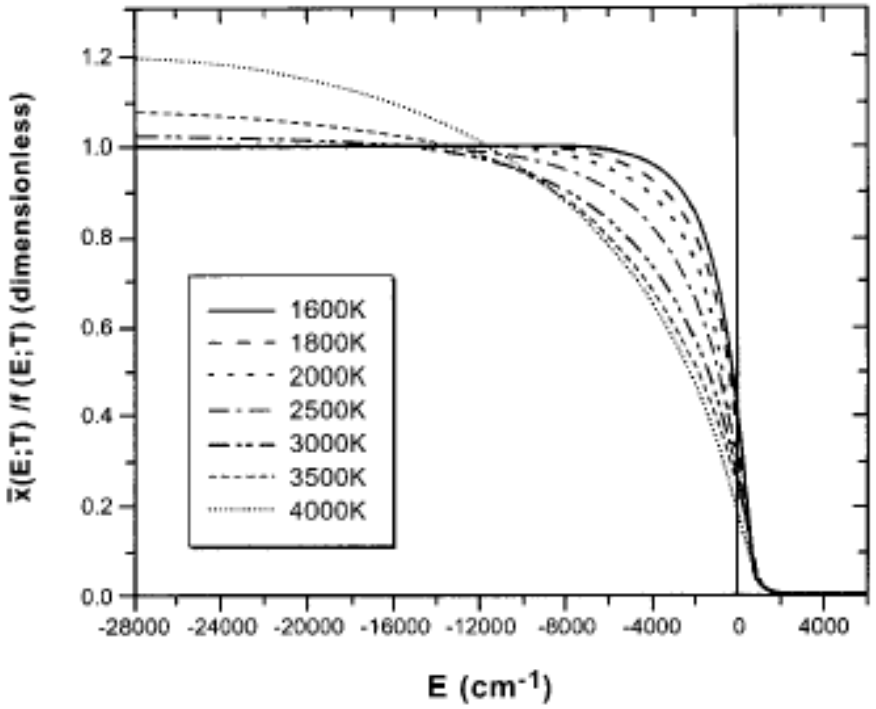
Satisfies Detailed balance

Steady State Distribution CH_4

E model



E,J model



Low Pressure Limit CH_4

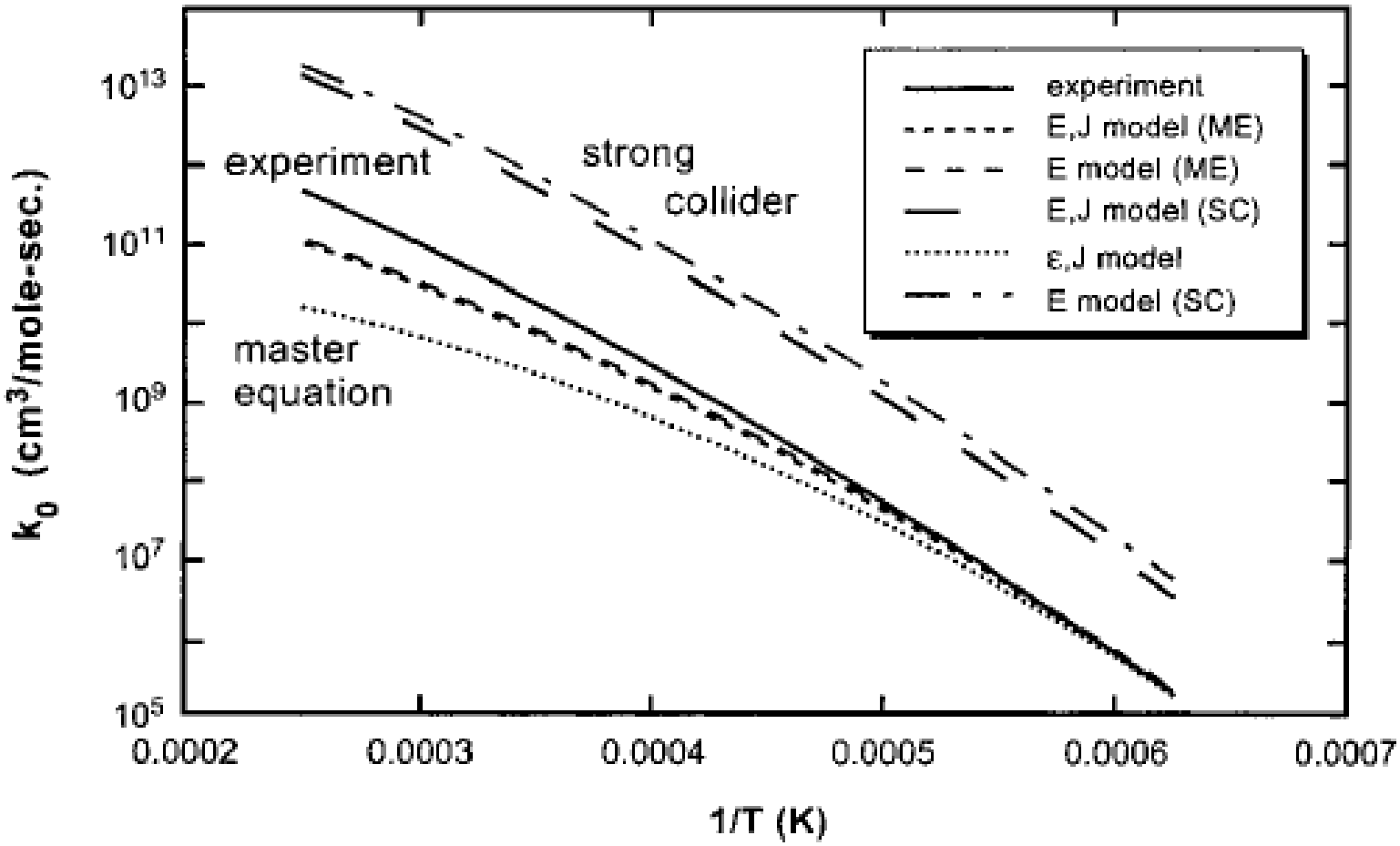
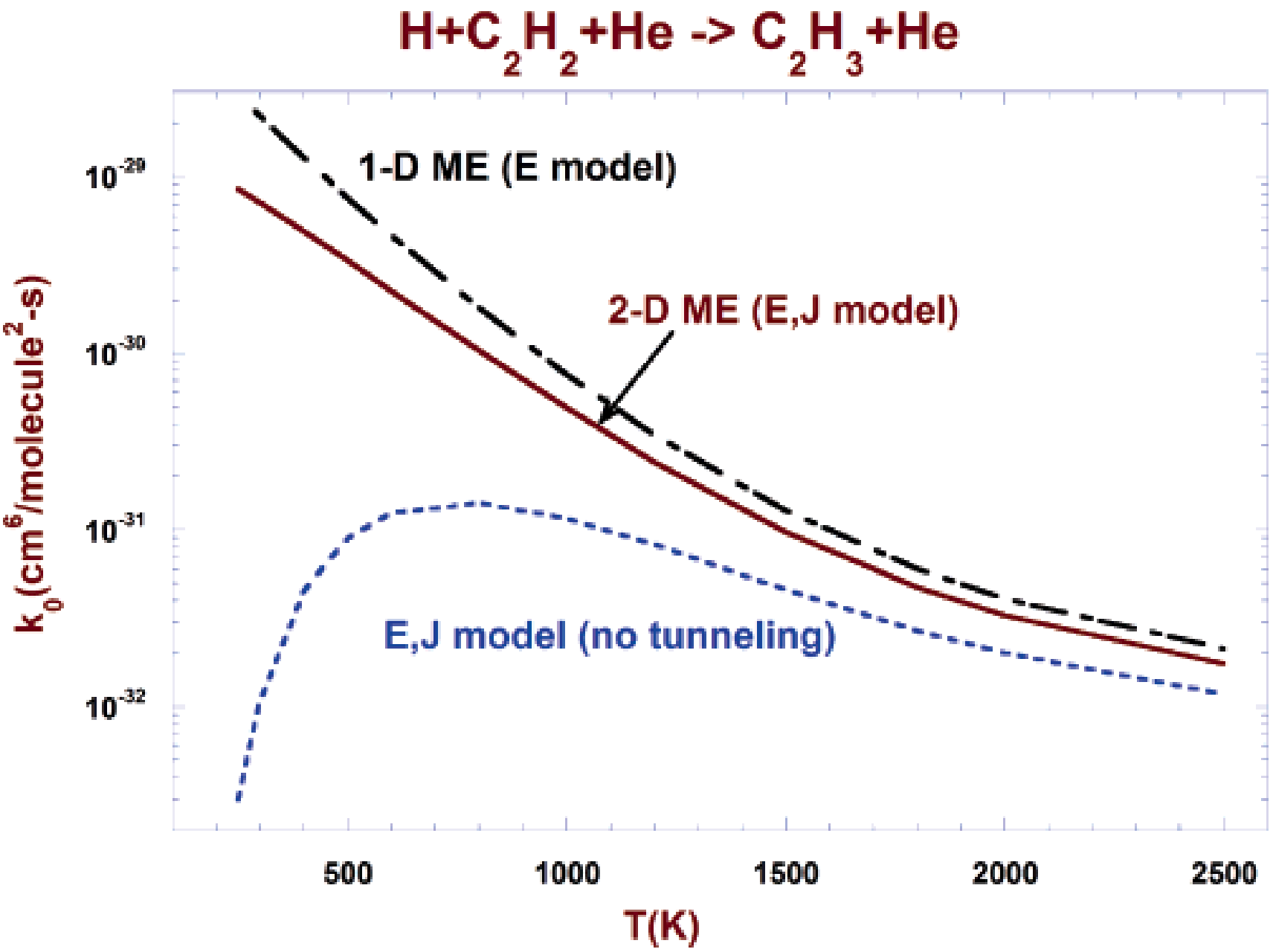
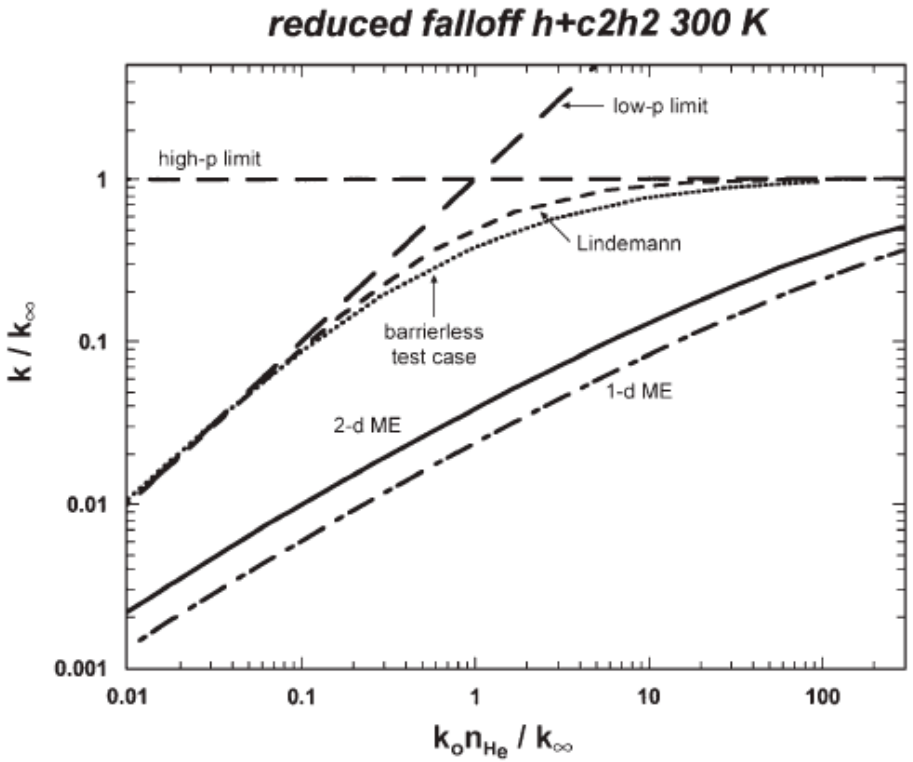


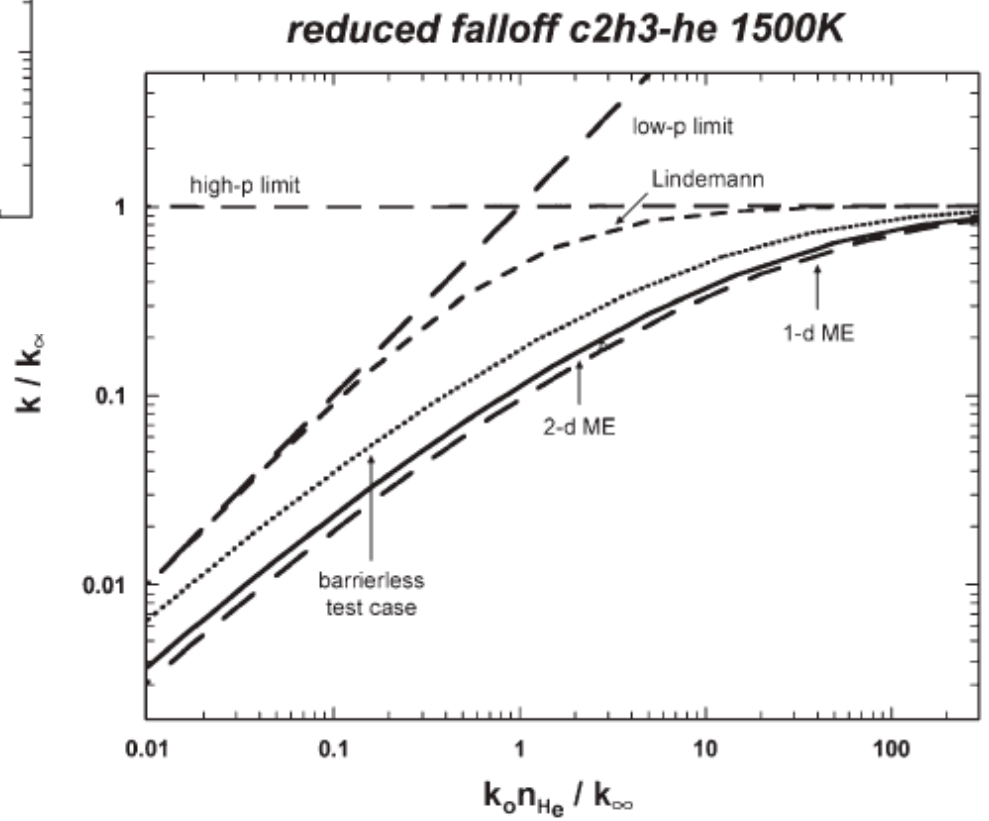
Figure 1. High-temperature rate coefficients. The master-equation calculations were done with $\langle \Delta E_d \rangle = 410$ cm^{-1}, independent of T, for the E,J and E models. A constant value of $\langle \Delta \epsilon_d \rangle = 35$ cm^{-1} was assumed for the ϵ,J ME calculations.

Low Pressure Limit



Reduced Falloff Curves





Collision Rates

Hard Sphere

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

Lennard-Jones

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

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

Underestimates collision rate

Correct with larger average energy transferred

Dipole Corrections

Energy Transfer Forms

Exponential Down

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

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

α_0 ~ 50-400 cm^{-1}

n ~ 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

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

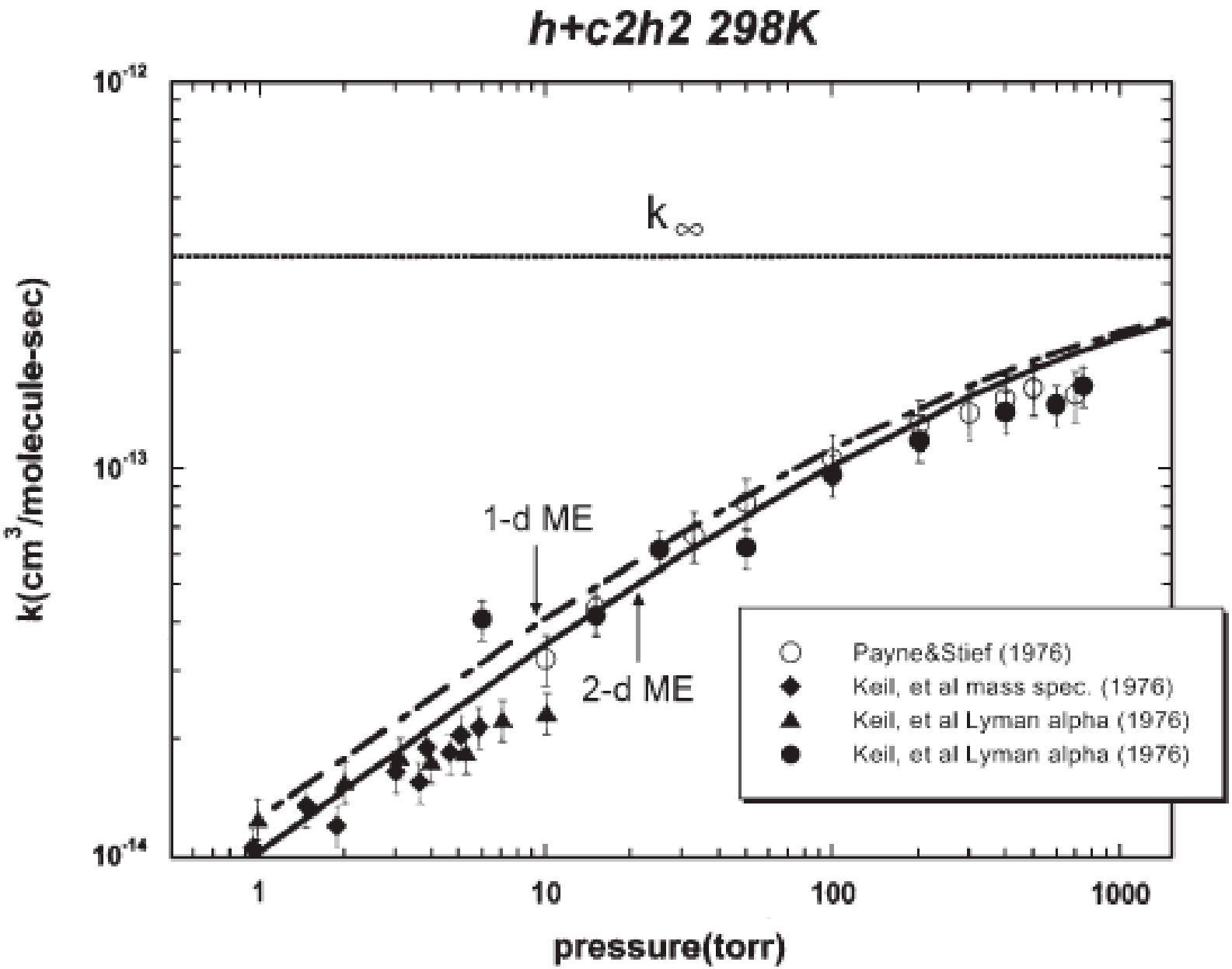
$\langle \Delta E_d \rangle \approx \alpha$ for exponential down

Average squared energy transfer

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

Fits to Experiment

H + C_2H_2 Addition



Fits to Experiment C_2H_3 Dissociation

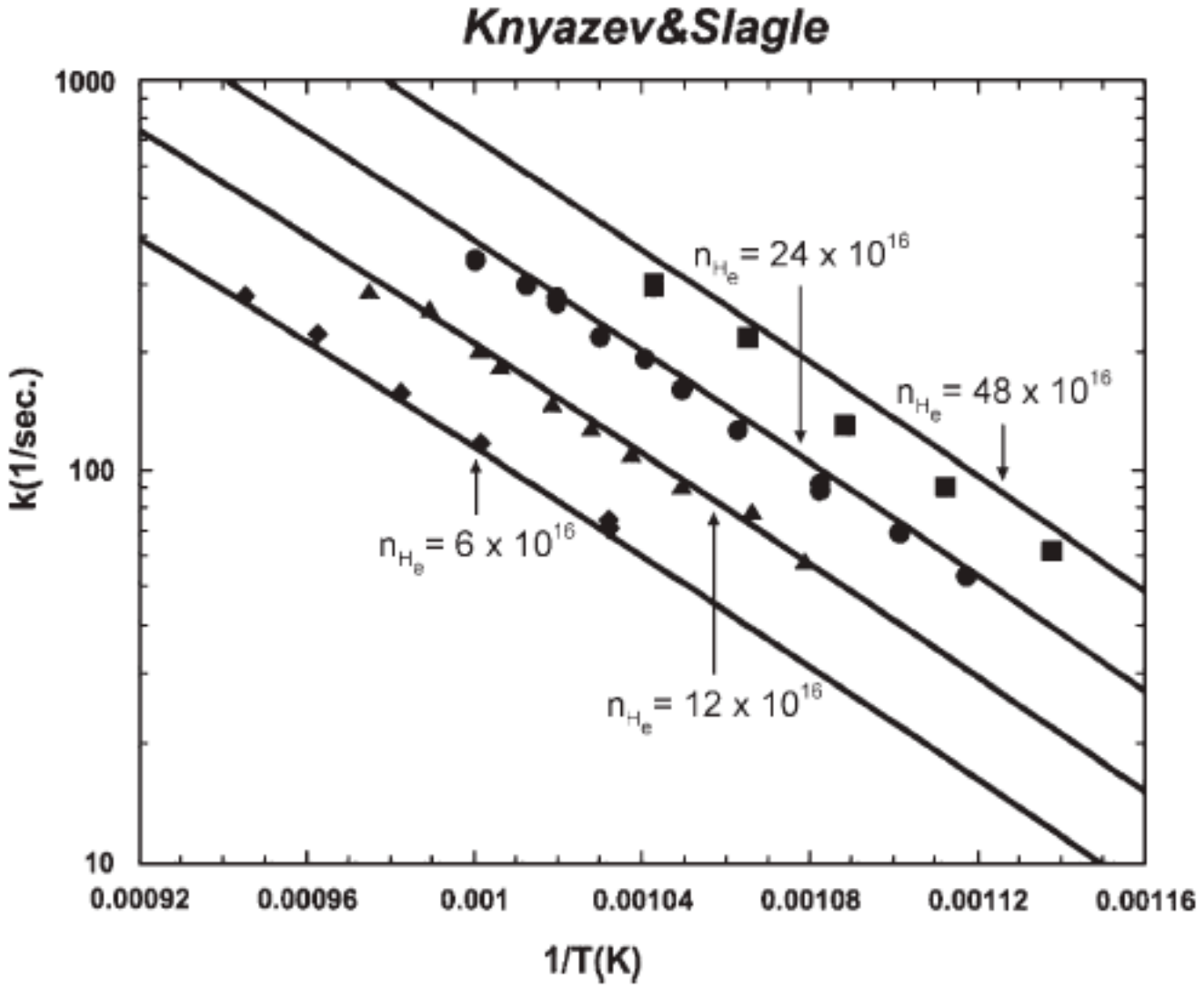


Fig. 5 Comparison of the theoretical results for $k_{-1}(T,p)$ ($C_2H_3 \rightarrow C_2H_2 + H$) with the experiments of Knyazev and Slagle.[21] The units of n_{He} are molecule cm^{-3}.

Fits to Experiment

T dependent ΔE_d

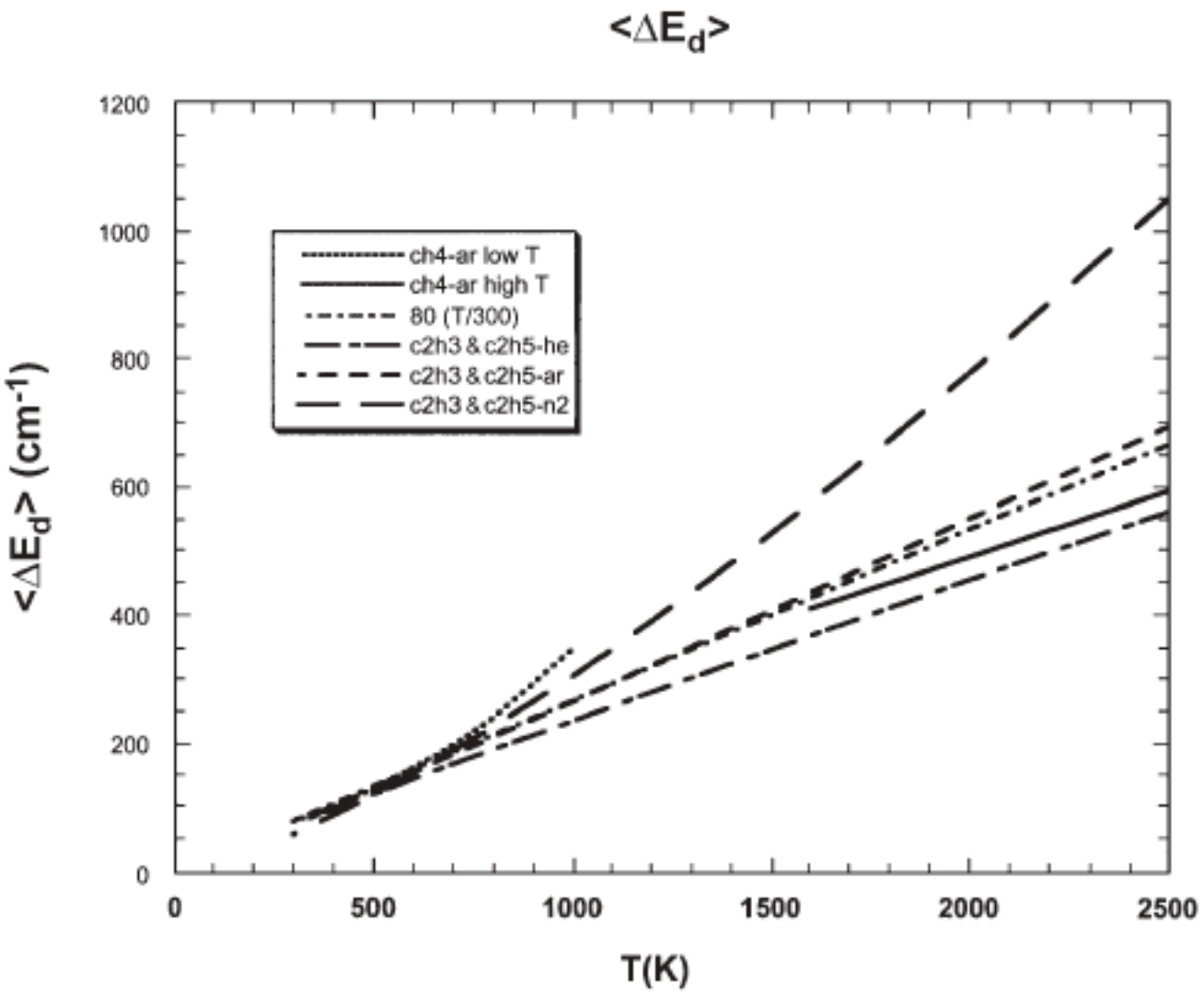


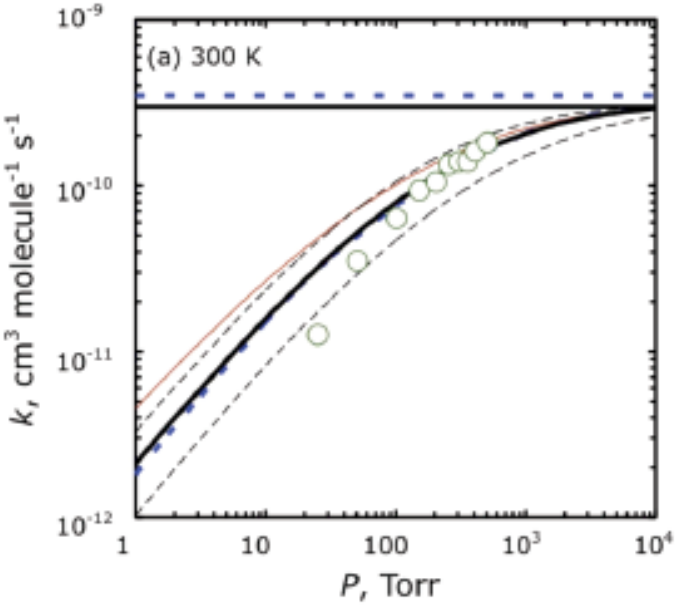
Fig. 8 Values of $\langle \Delta E_d \rangle$ as a function of temperature for several molecules and collision partners.

Energy Transfer from Trajectories

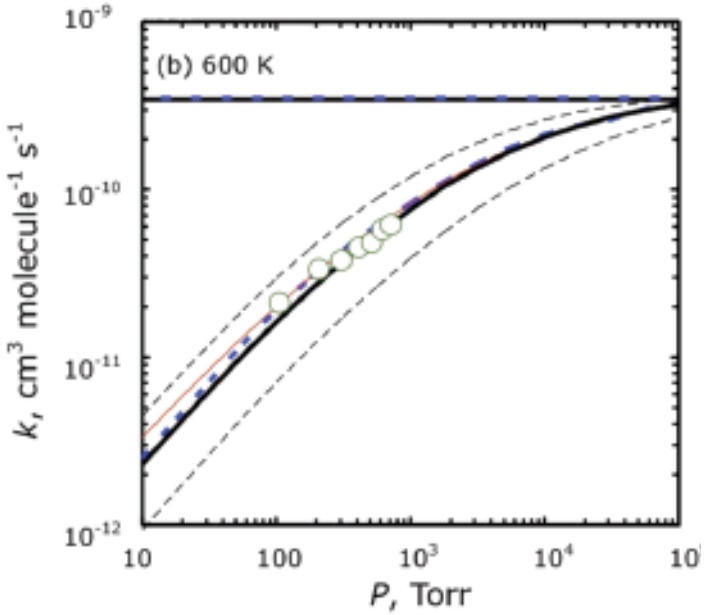
Collisional energy transfer in unimolecular reactions: Direct classical trajectories for CH_4=CH_3+H in Helium

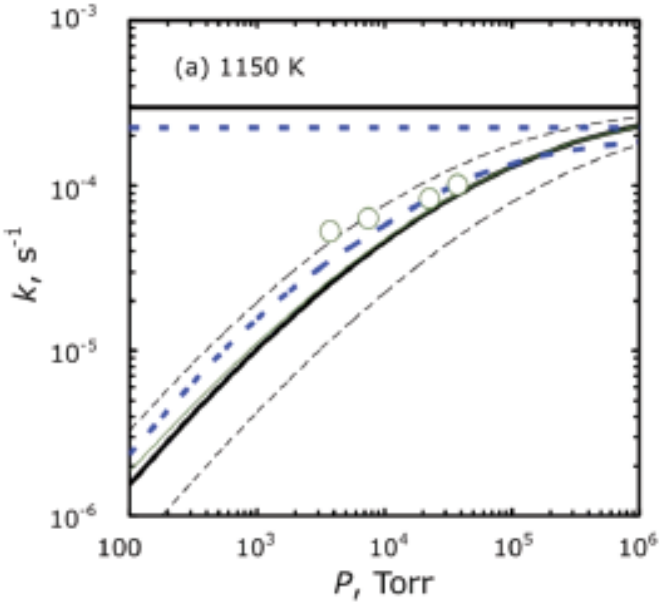
A. W. Jasper, J. A. Miller, J. Phys. Chem. A 113, 5612 (2009).

α_0=110 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

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

$$p^* = k_0[M]/k^{\infty} \qquad d = 0.14$$

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

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

Fit F_{cent} to:

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

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)

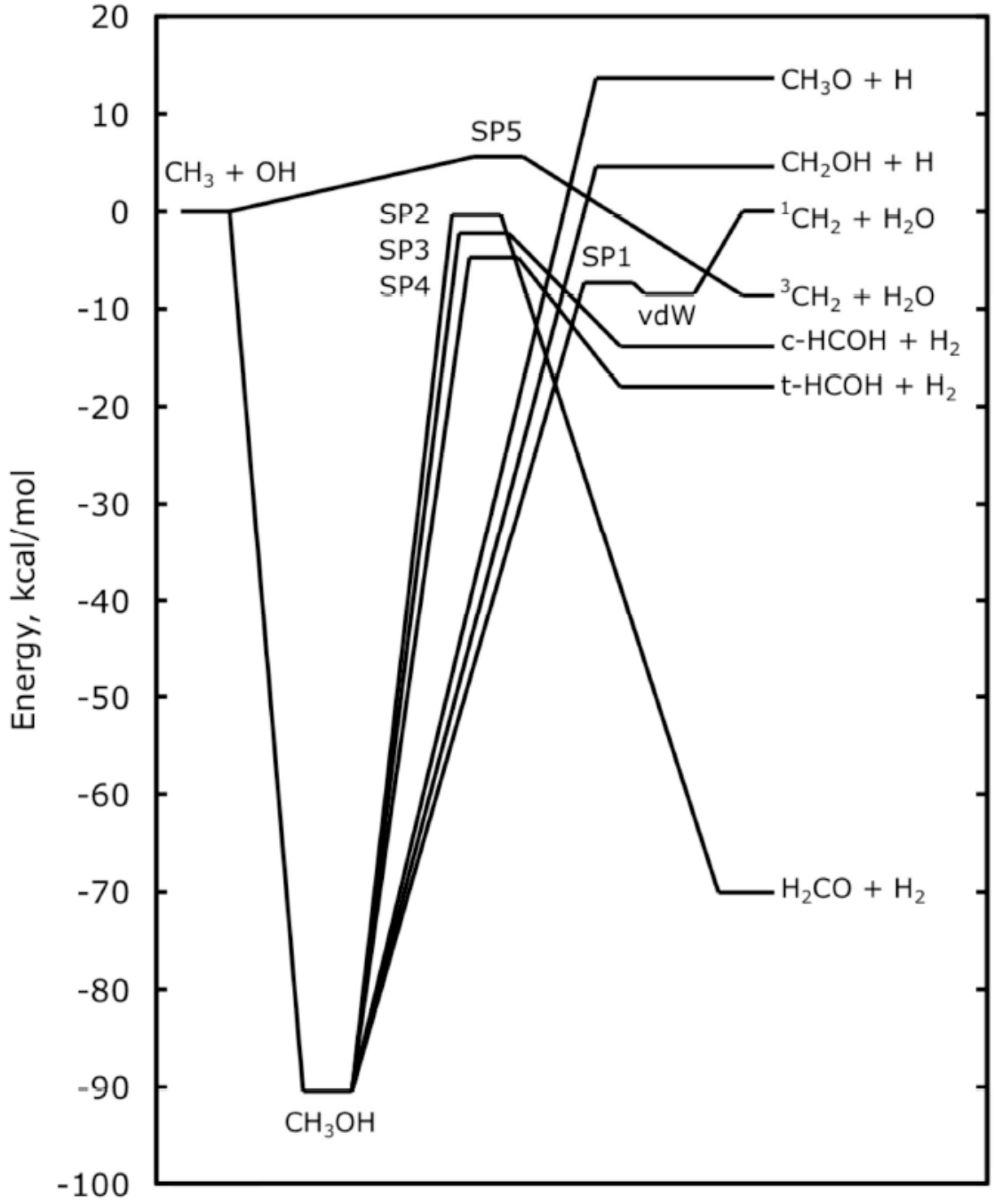
Still problems for tunneling

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

Use Log Interpolation

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

Part of Current ChemKin



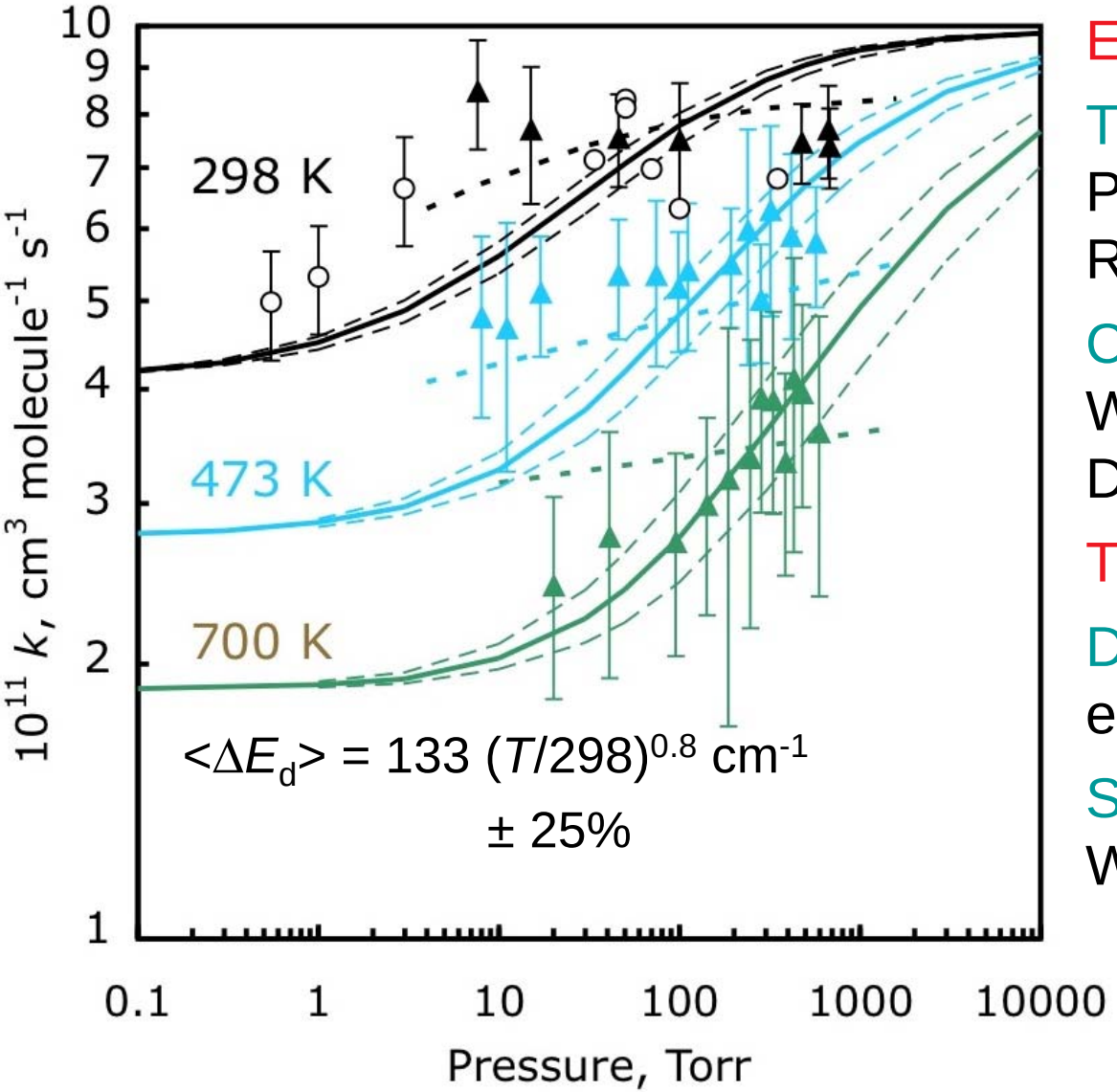
$CH_3 + OH$

Potential Energy Surface

QCISD(T)/CBS G2M MRCI//CAS

Stationary point	ATcT[a]	Present[b]	Ref. 29[c]	Ref. 51[d]
$CH_3 + OH$	0.0	0.0	0.0	0.0
CH_3OH	–90.25 ± 0.05	–90.4	–91.9	–87.6
CH_3OH[e]		–89.8		–87.0
$^1CH_2 + H_2O$	0.58 ± 0.07	0.03	–1.6	0.5
$H_2 + H_2CO$	–69.92 ± 0.06	–70.0	–73.8	–68.2
H_2 + *cis*-HCOH	–13.13 ± 0.32	–13.8	–17.1	–12.3
H_2 + *trans*-HCOH	–17.77 ± 0.29	–18.0	–21.4	–16.4
$H + CH_2OH$	4.30 ± 0.09	4.6	4.3	7.5
$H + CH_3O$	13.75 ± 0.10	13.7	13.0	15.6
$^3CH_2 + H_2O$	–8.42 ± 0.06	–8.7	–11.2	
$CH_2 \cdots H_2O$ (vdW)		–8.5	–9.2	–4.8
$[^1CH_2 + H_2O \Leftrightarrow CH_3OH]^{\ddagger}$ (SP1)		–7.3	–7.8	–4.6
$[H_2 + H_2CO \Leftrightarrow CH_3OH]^{\ddagger}$ (SP2)		–0.3	–1.3	1.7
$[H_2$ + *cis*-HCOH $\Leftrightarrow CH_3OH]^{\ddagger}$ (SP3)		–2.2	–3.8	–0.6
$[H_2$ + *trans*-HCOH $\Leftrightarrow CH_3OH]^{\ddagger}$ (SP4)		–4.8	–6.4	–2.2
$[CH_3 + OH \Leftrightarrow {}^3CH_2 + H_2O]^{\ddagger}$ (SP5)		5.6	6.7	15.8

Reactions with Products: $CH_3 + OH$



Experiment:

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

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

Theory: Master Equations

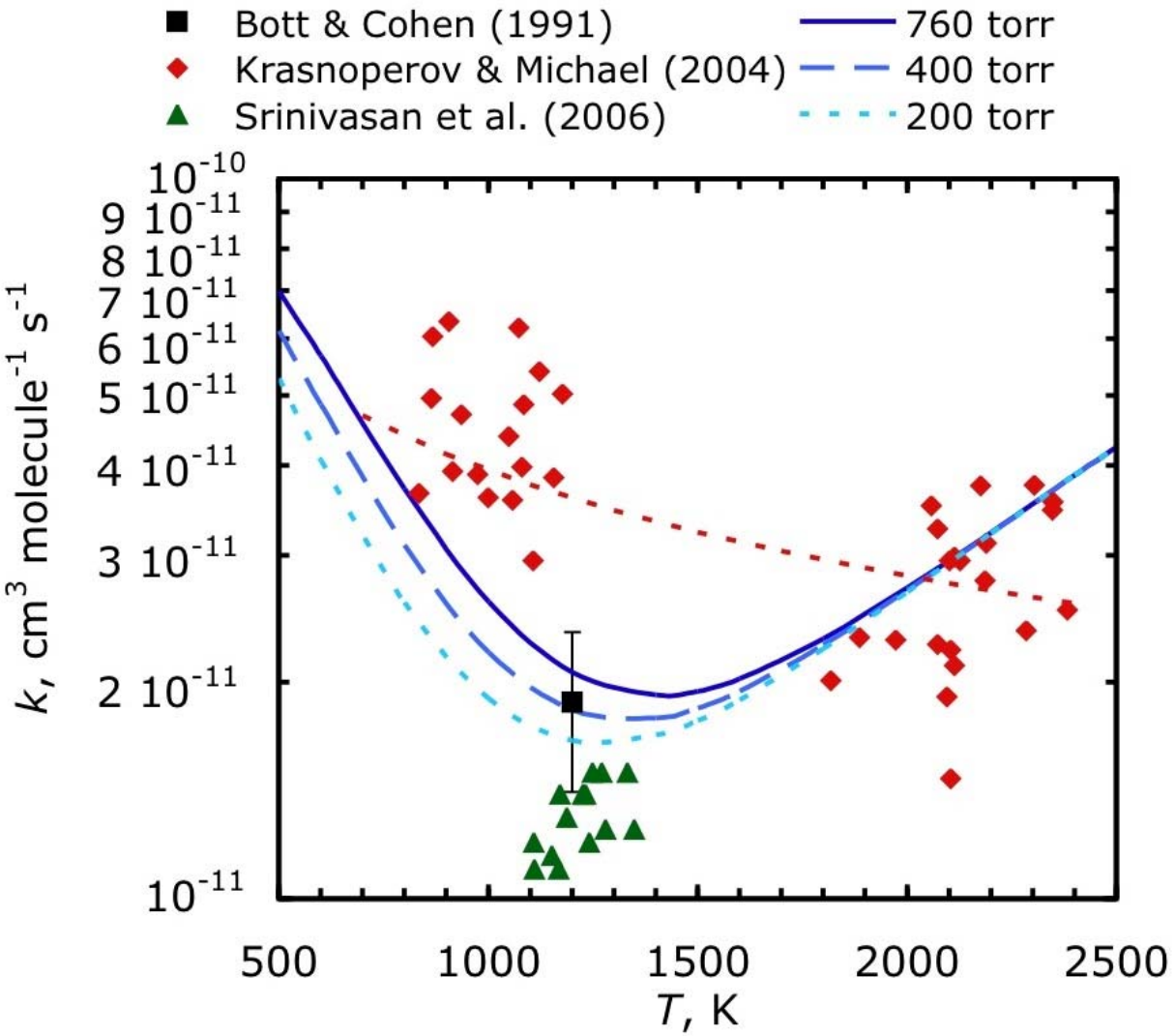
Dotted - De Avillez Pereira et al.

Solid & Dashed - Present Work

CH_3 + 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% CH_3 + OH

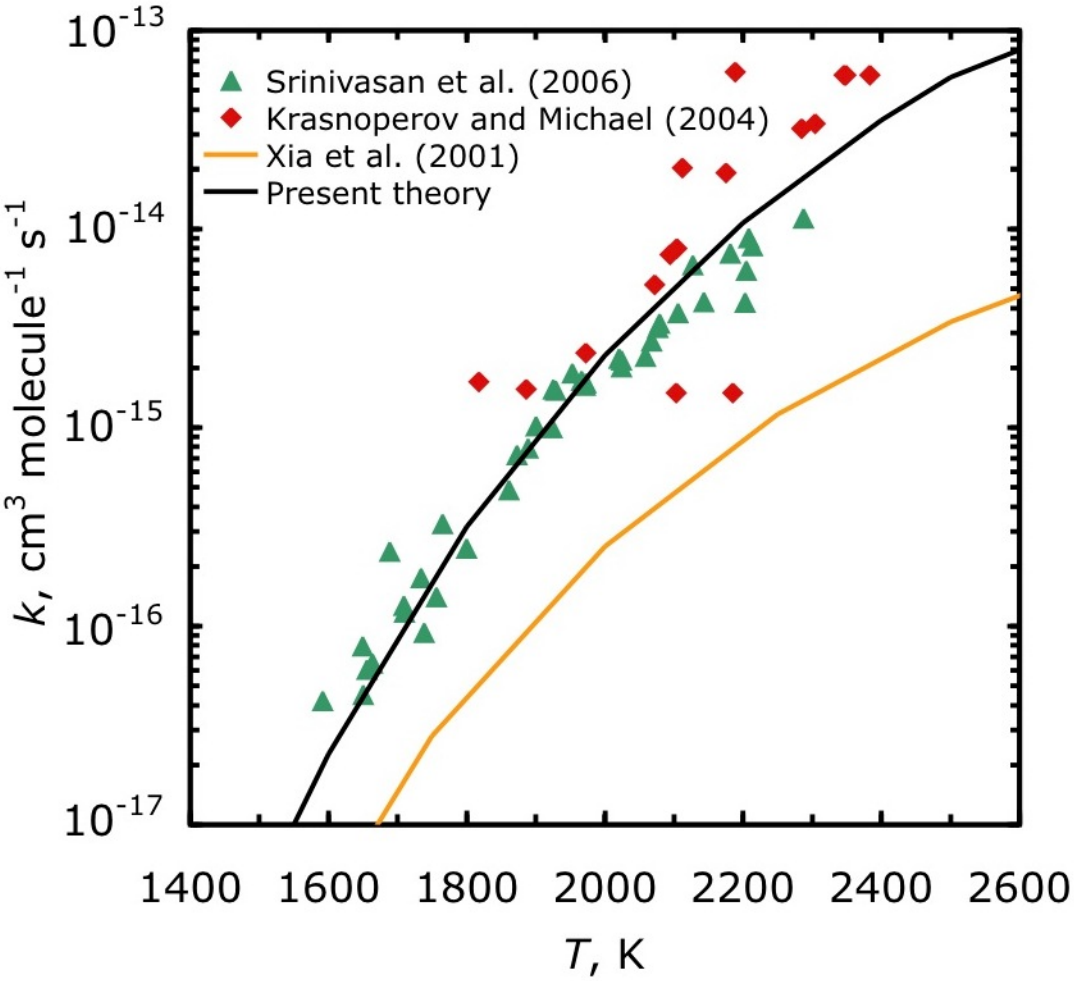
Previous theory

- 2001, Xia, Zhu, Lin, and Mebel (shown at 1 atm)
- Falloff below 1 atm
- ~33% CH_3 + OH
  ~52% CH_2 + H_2O
  ~15% H_2 + HCOH

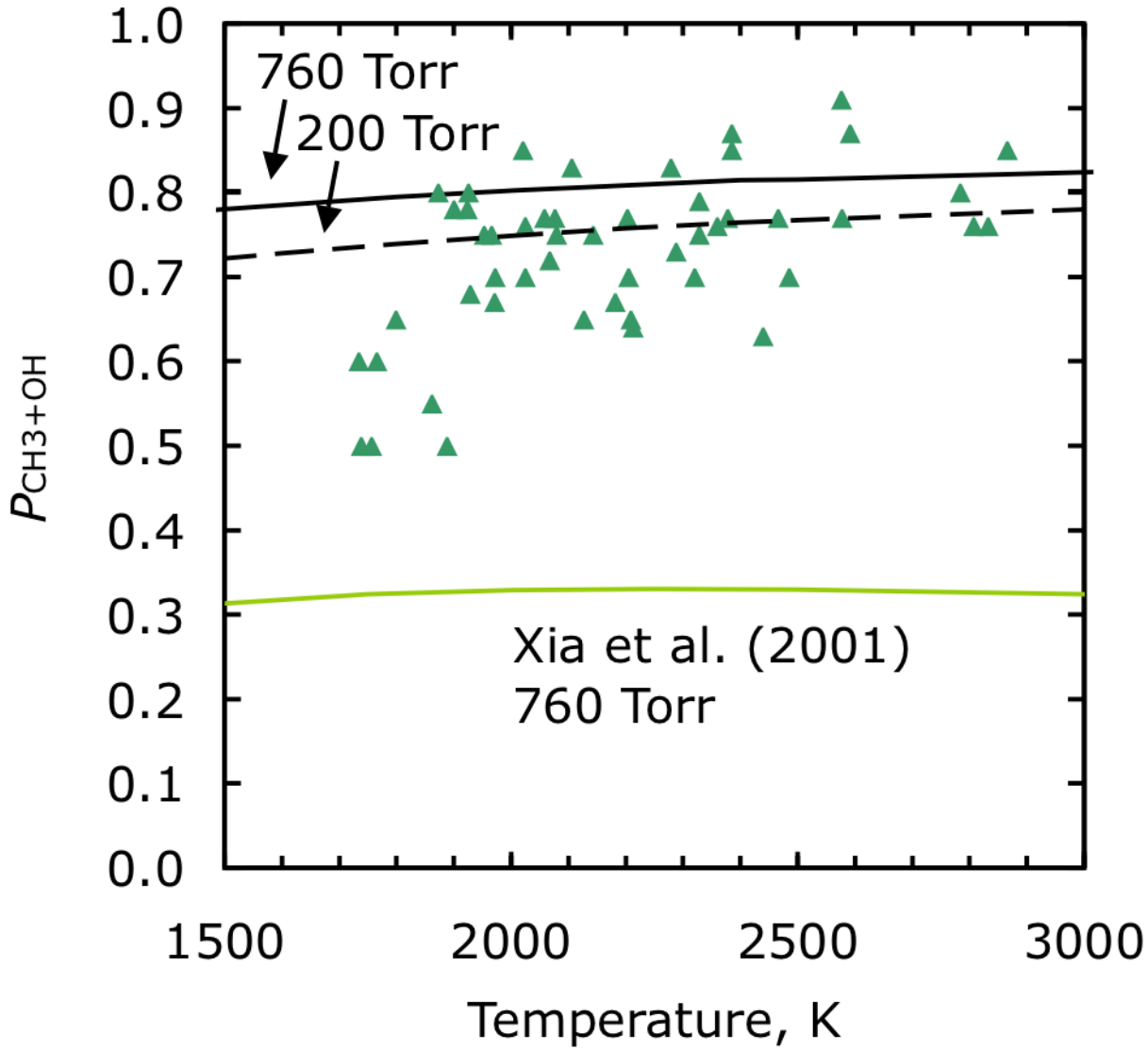
Present theory

- Low-*P* limit at 1 atm
- ~75% CH_3 + OH
  ~20% CH_2 + H_2O
  < 5% H_2 + HCOH

$CH_3OH \rightarrow CH_3 + OH$



Methanol decomposition: Product branching



Secondary kinetics of methanol decomposition

Well characterized

$OH + OH \rightarrow O + H_2O$

$H + OH \rightarrow O + H_2$

Not well characterized

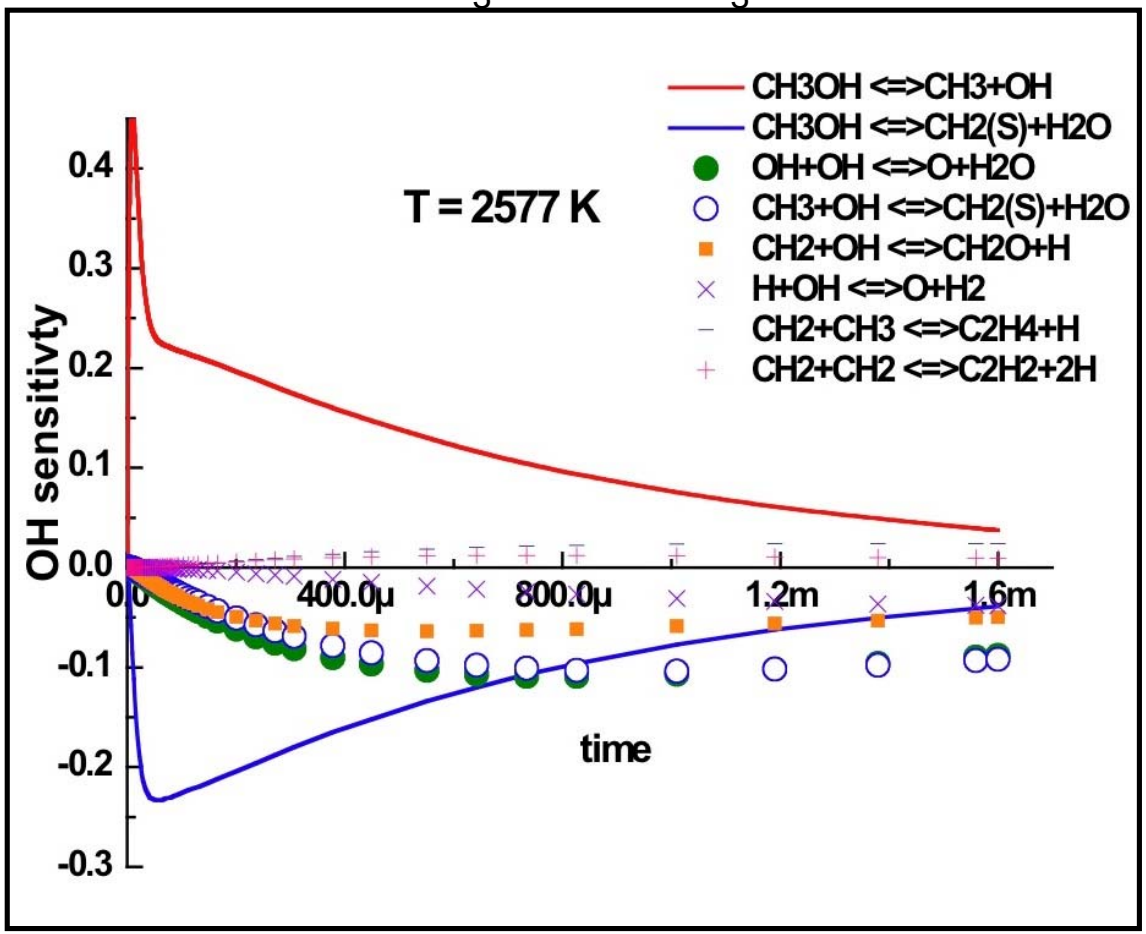
$^3CH_2 + OH \rightarrow CH_2O + H$

Ambiguous experiments

$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + 2H$

$CH_3 + {}^3CH_2 \rightarrow C_2H_4 + H$

Shock tube OH absorption profile sensitivities for $CH_3OH \rightarrow CH_3 + OH$



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

Secondary kinetics: OH Time Traces

Michael et al.

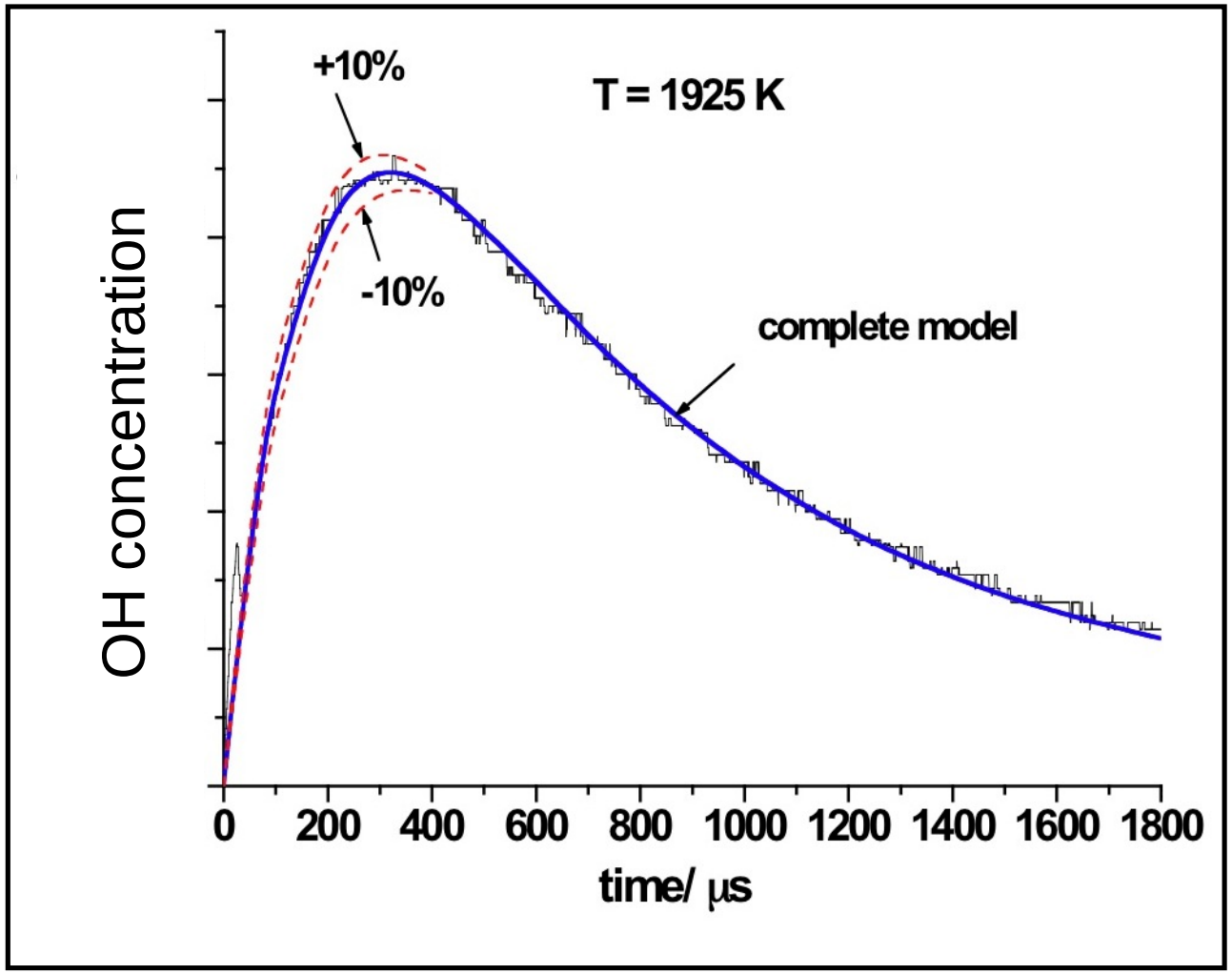
Good agreement at long times using our predicted rates for

$^3CH_2 + OH$

$^3CH_2 + {}^3CH_2$

$CH_3 + {}^3CH_2$

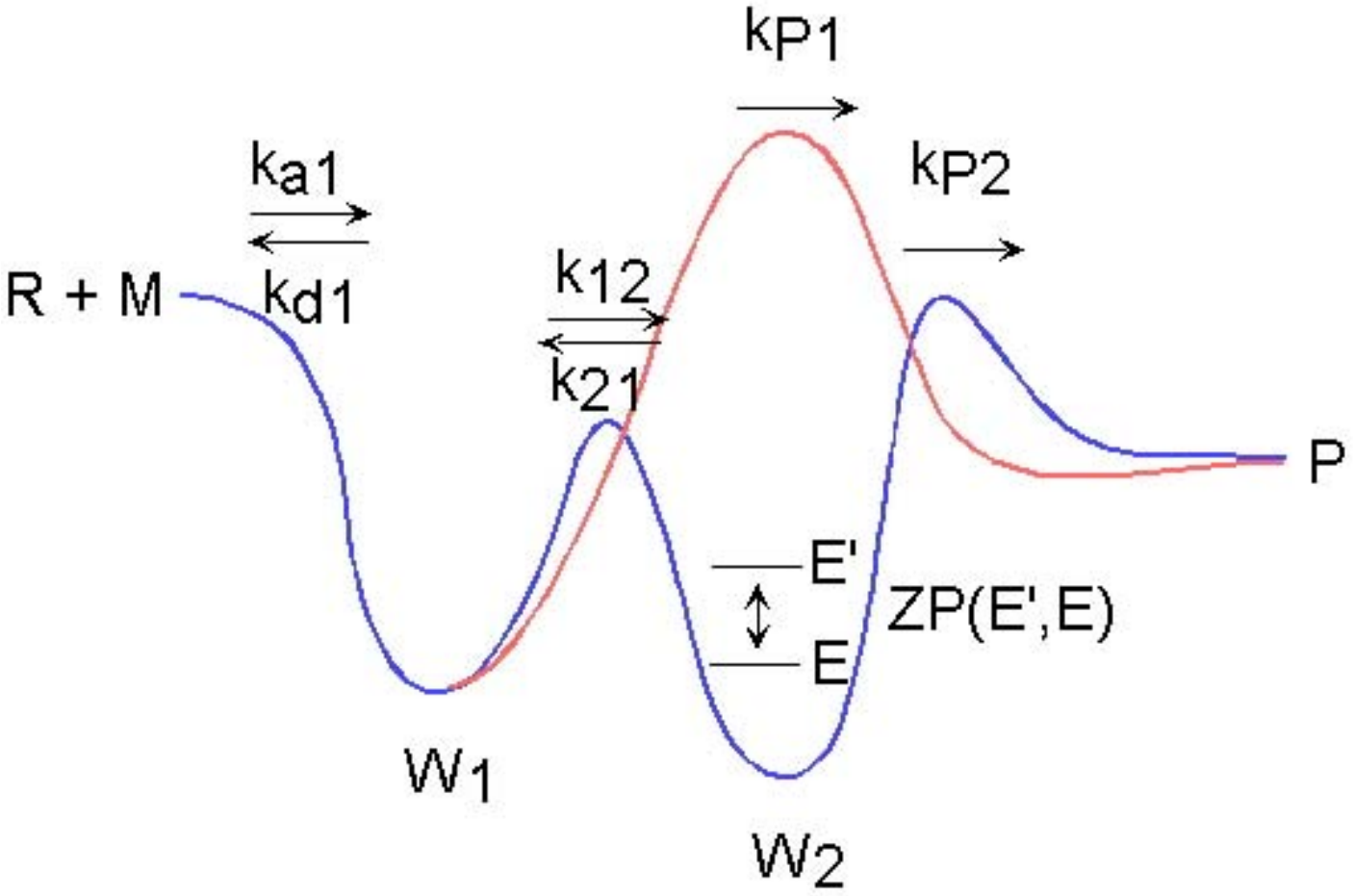
$CH_3 + OH$



Multiple-Well Multiple-Channel Time Dependent Master Equation

1. The Kinetic Model
2. Collisionless Limit
3. $CH + N_2$
4. Time Dependent Populations
5. Kinetic Phenomenology
6. $C_2H_5 + O_2$
7. Reduction in Species at High Pressure
8. $C_3H_3 + H$
9. Radical Oxidation
10. $C_3H_3+C_3H_3$

The Kinetic Model



Phenomenology

$k_{R+M \rightleftarrows P}$

$k_{R+M \rightleftarrows W1}$

$k_{R+M \rightleftarrows W2}$

$k_{W1 \rightleftarrows W2}$

$k_{W1 \rightleftarrows P}$

$k_{W2 \rightleftarrows P}$

RRKM Theory

k_{d1}

k_{a1}

k_{12}

k_{21}

k_{p1}

k_{p2}

Energy Transfer

Bath Gas B; [B] >> [M] >> [R]

Z; Lennard Jones

P(E',E); Exponential Down

Multiple-Well Multiple-Channel Master Equation

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

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

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

M Wells N_p Products

M+1 Chemical Species

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

Linear Master Equation

Collisionless Limit

Consider Z$\rightarrow$ 0

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

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

Steady State for n(E,J)

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

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

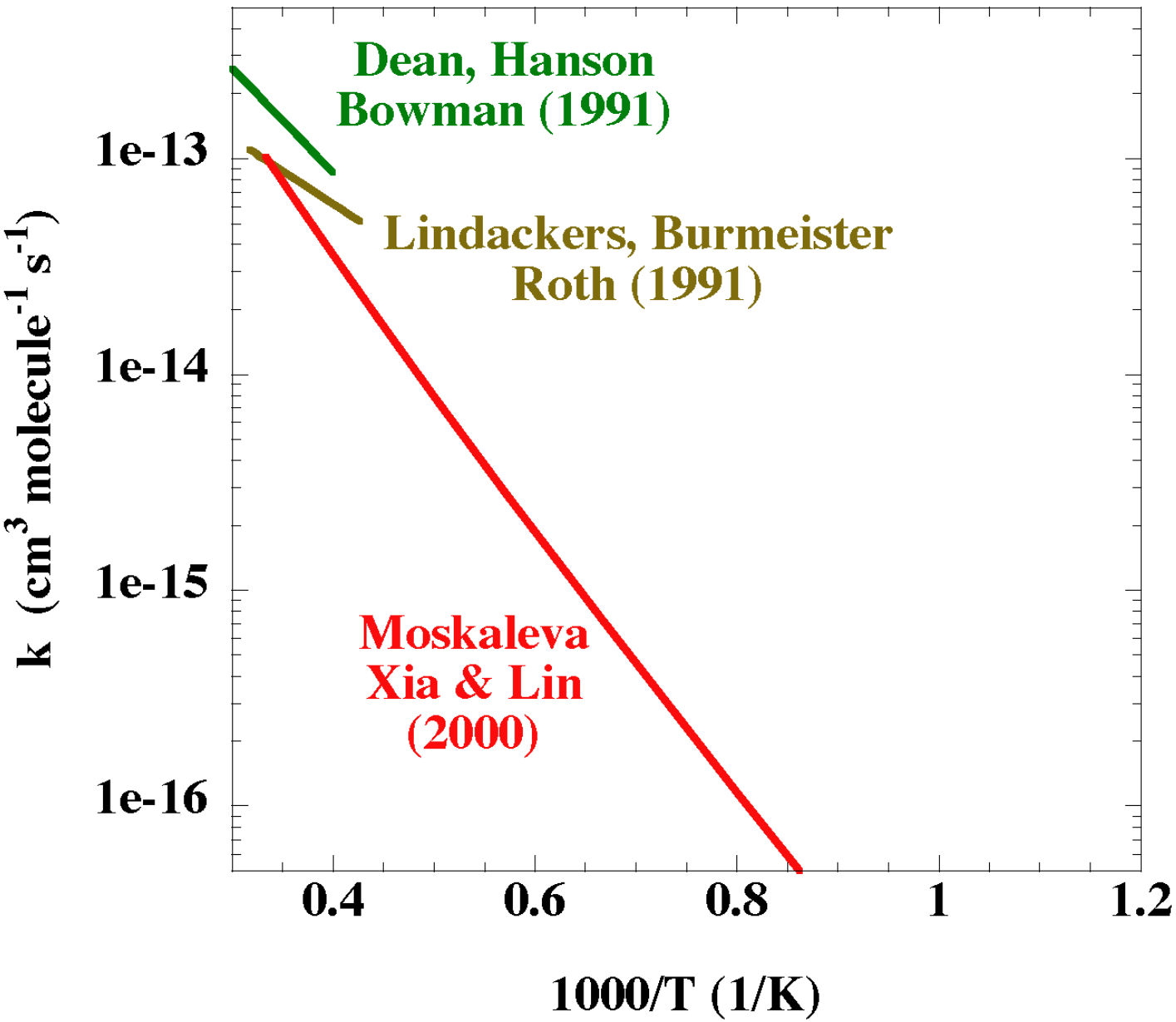
Flux coefficients

$CH + N_2$ Prompt NO

- **1971 Fenimore** $^2CH + N_2 \rightarrow HCN + {}^4N$
- **1991 Dean, Hanson & Bowman -- shock tube measurements of rate for** $^2CH + N_2 \rightarrow$ **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,**

$$^2CH + N_2 \rightarrow HNCN \rightarrow {}^2H + {}^3NCN$$

- **2007 Szpunar, Faulhaber, Kautzman, Crider & Neumark -- observed the photodissociation of DNCN to CD+N_2 and D+NCN with 1:1 branching ratio**


Dean, Hanson
Bowman (1991)
Lindackers, Burmeister
Roth (1991)
Moskaleva
Xia & Lin
(2000)
1e-13
1e-14
1e-15
1e-16
k (cm3 molecule-1 s-1)
0.4
0.6
0.8
1
1.2
1000/T (1/K)

Recent Modeling

- Williams, Fleming

  Proc. Comb. Inst. 31, 1109-1117, 2007

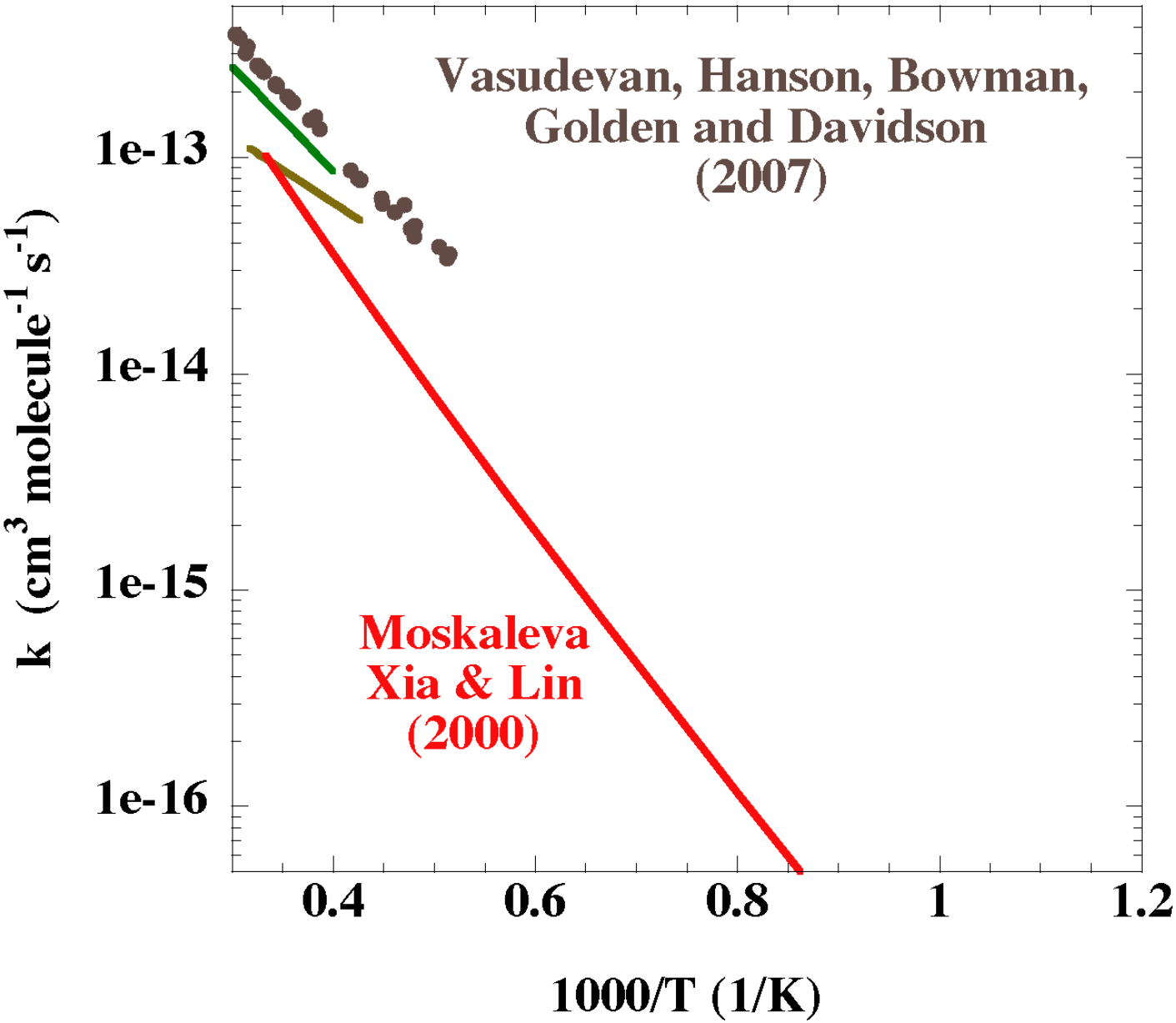
  NO severely underpredicted in CH_4 and C_3H_8 flames

- El Bakali, Pillier, Desgroux, Lefort, Gasnot, Pauwels, da Costa,
  Fuel 85, 896, 2006
  Increasing CH + N_2 rate by 1-2 orders of magnitude over the 1000 to 1500 K range yields good predictions for NO in natural gas flames

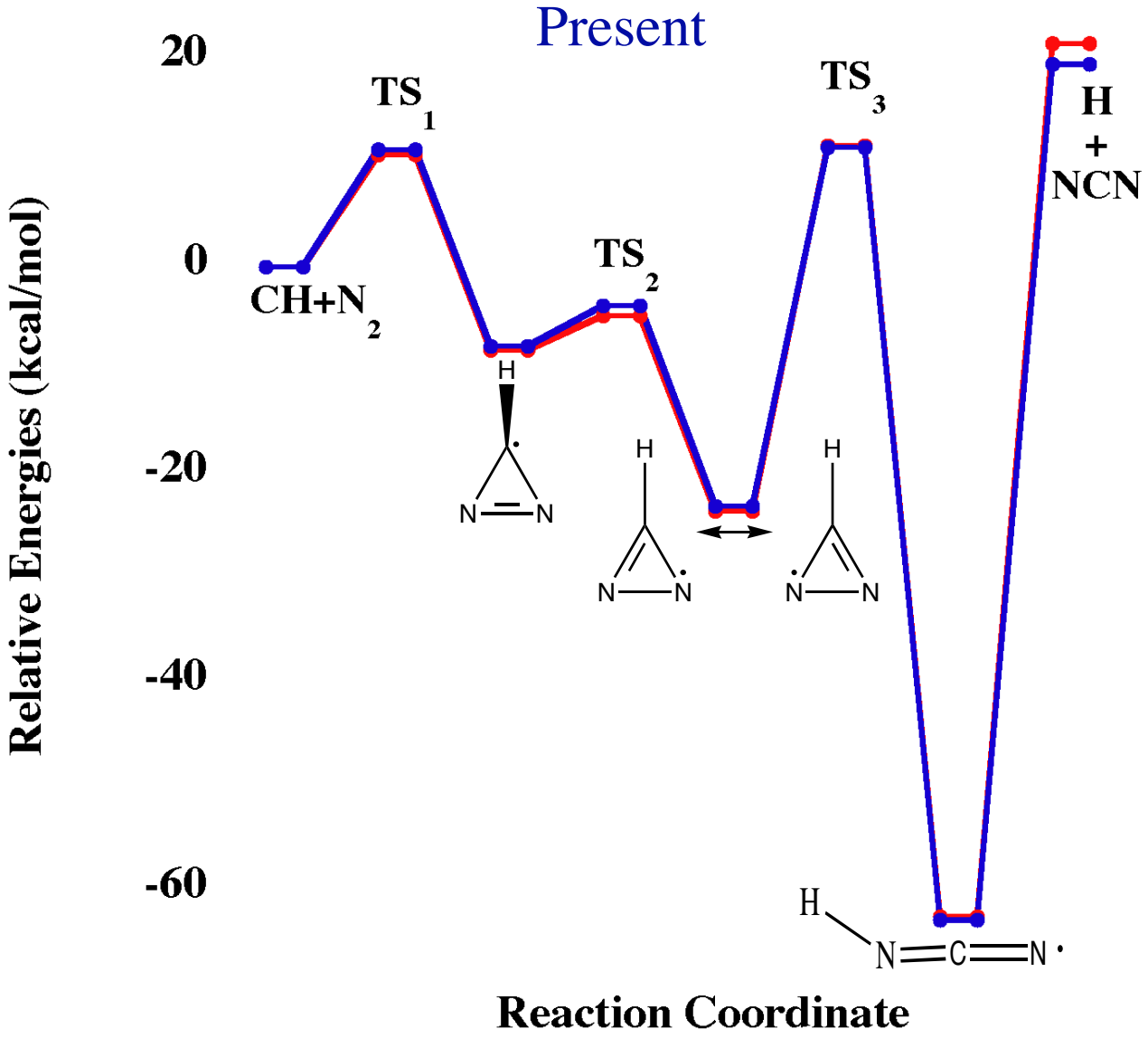
- Sutton, Williams, Fleming,

  Comb. Flame, 2008, in press.

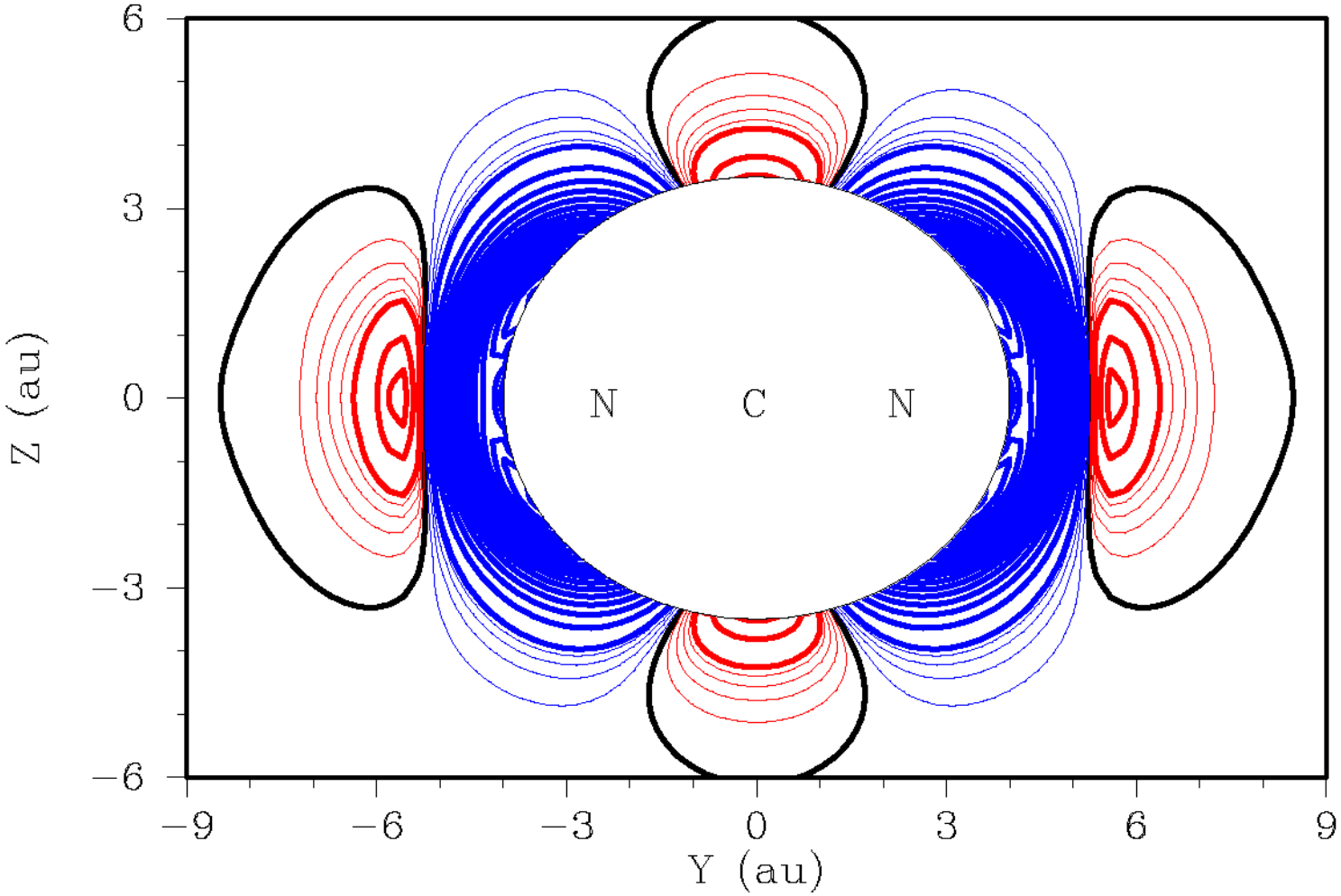
  Improved modeling for CH4/O2/N2 flames with rates of El Bakali et al.


Vasudevan, Hanson, Bowman,
Golden and Davidson
(2007)
Moskaleva
Xia & Lin
(2000)
k (cm3 molecule-1 s-1)
1e-13
1e-14
1e-15
1e-16
0.4
0.6
0.8
1
1.2
1000/T (1/K)

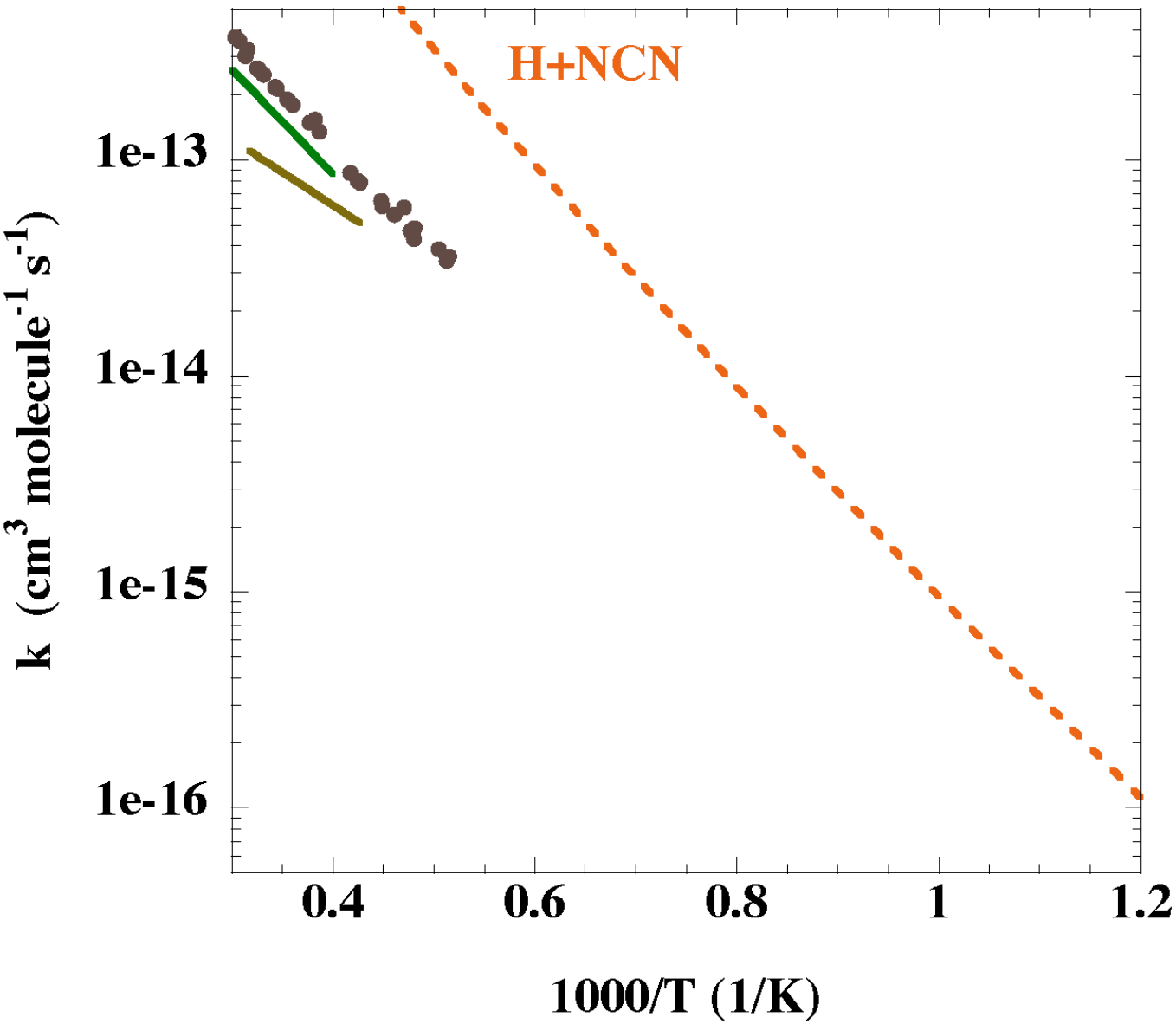
Moskaleva, Xia and Lin (2000)



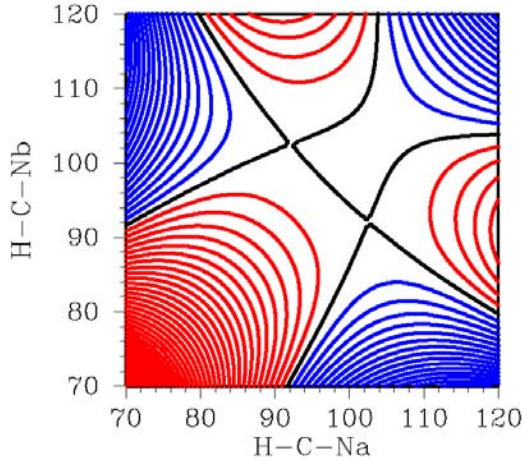
CAS+1+2+QC/aug-cc-pvtz



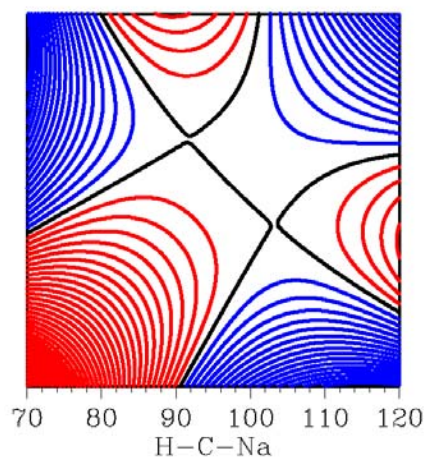
Contour Increments: Thick- 5 kcal/mol, Thin- 1 kcal/mol


H+NCN
1e-13
1e-14
1e-15
1e-16
k (cm3 molecule-1 s-1)
0.4
0.6
0.8
1
1.2
1000/T (1/K)

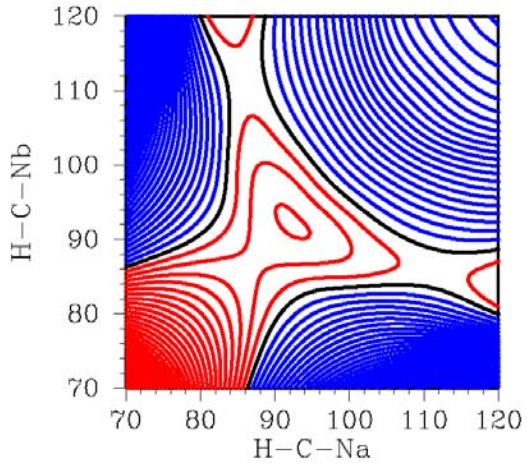
CASPT2



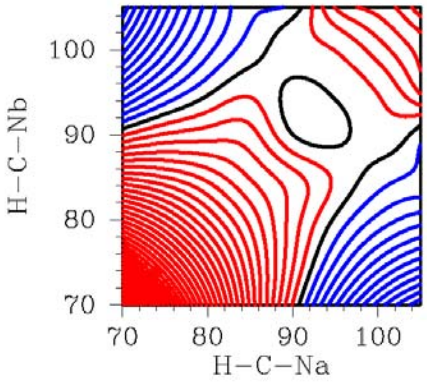
CAS+1+2+QC

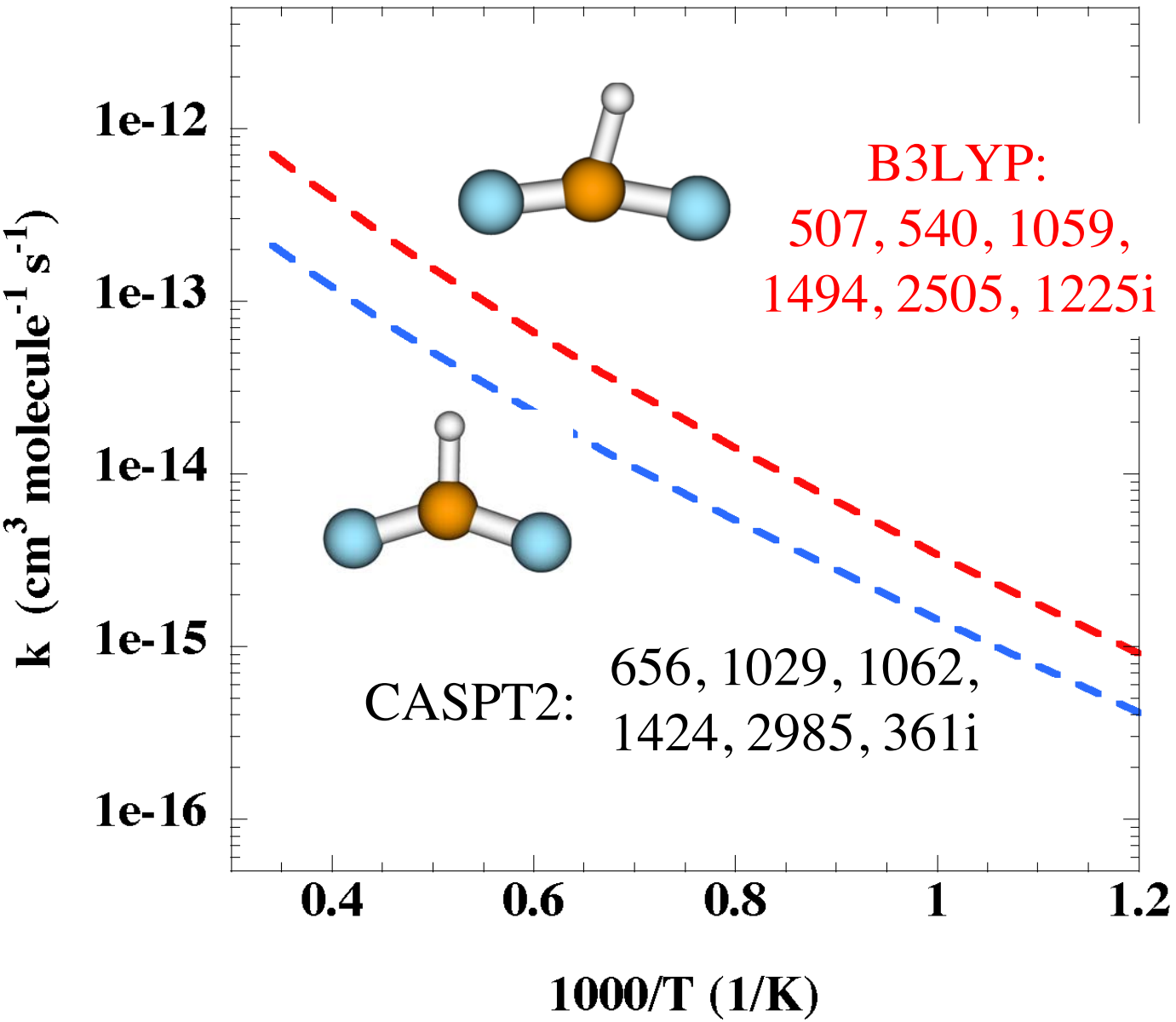


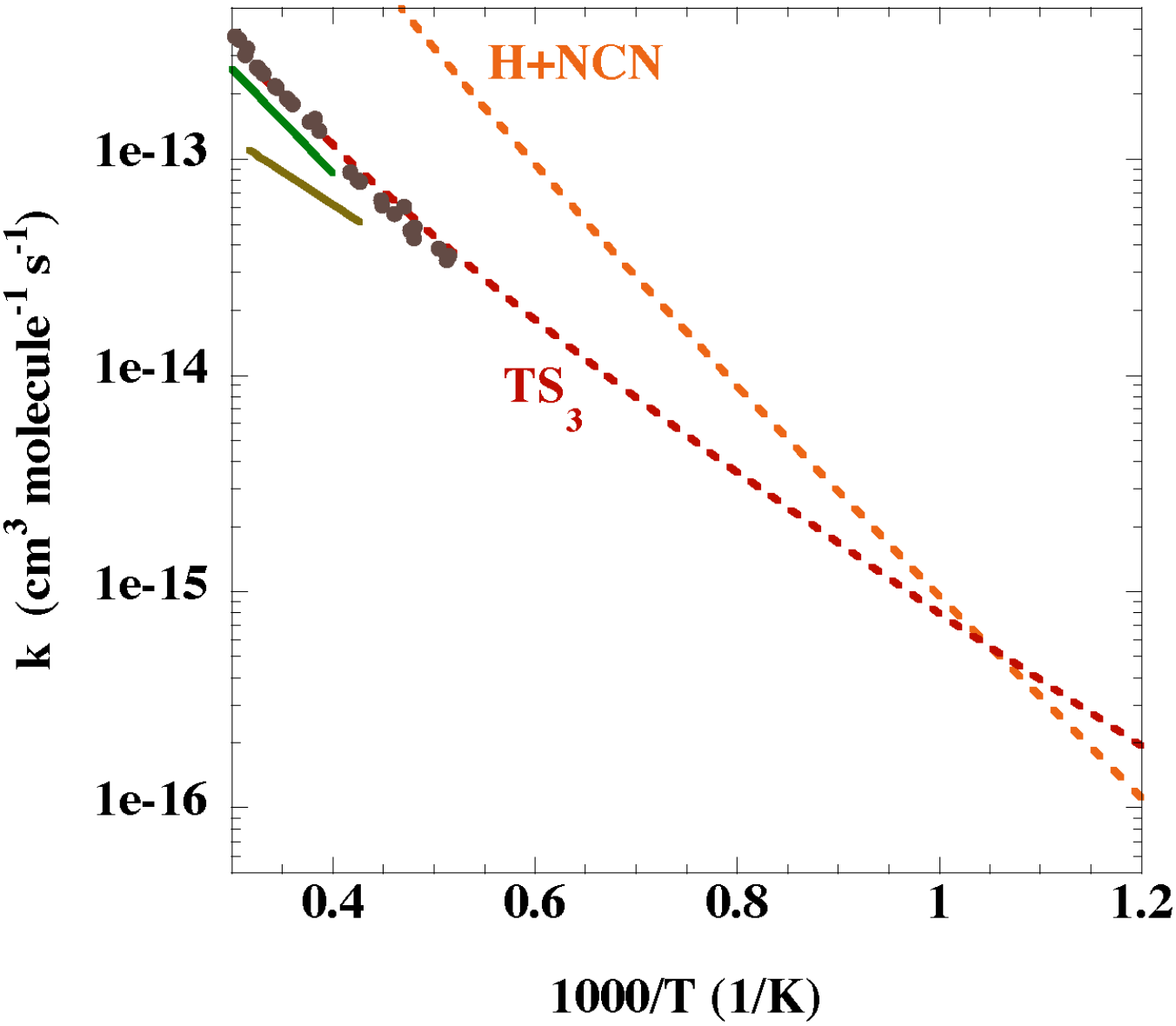
B3LYP

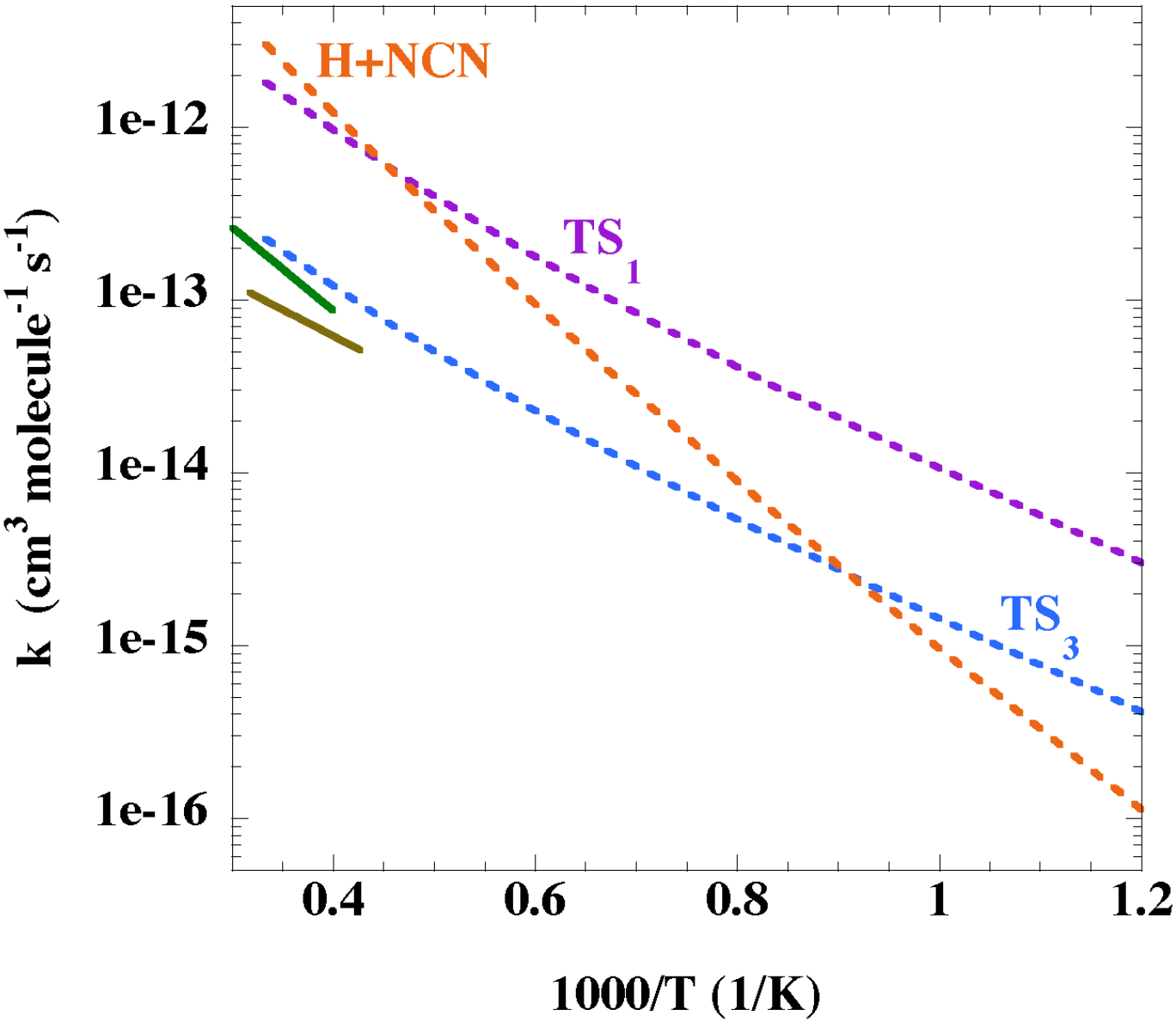


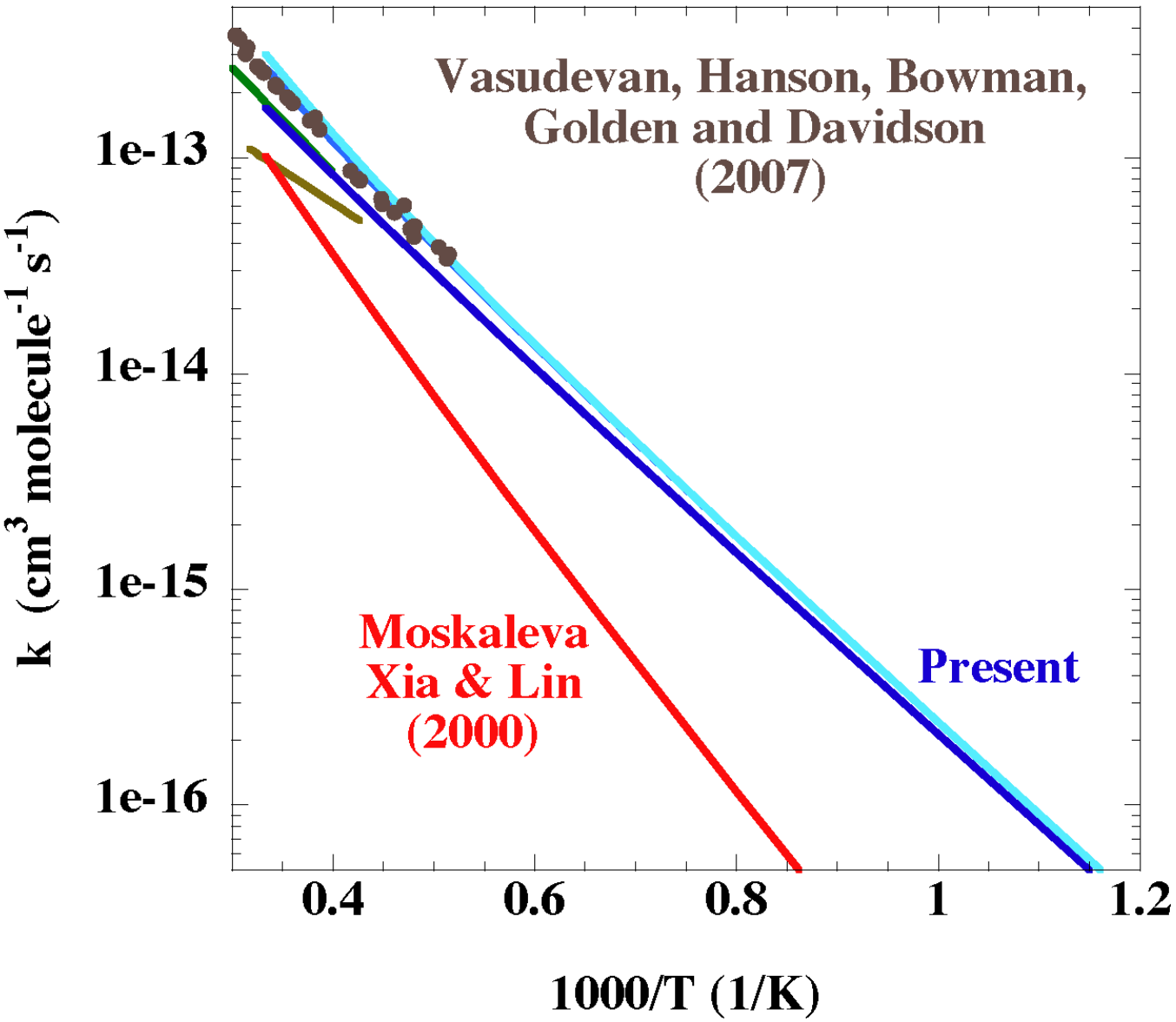
CCSD(T)




1e-12
1e-13
1e-14
1e-15
1e-16
k (cm3 molecule-1 s-1)
0.4
0.6
0.8
1
1.2
1000/T (1/K)
B3LYP:
507, 540, 1059,
1494, 2505, 1225i
CASPT2:
656, 1029, 1062,
1424, 2985, 361i


H+NCN
TS3
1e-13
1e-14
1e-15
1e-16
k (cm3 molecule-1 s-1)
0.4
0.6
0.8
1
1.2
1000/T (1/K)


H+NCN
TS1
TS3
1e-12
1e-13
1e-14
1e-15
1e-16
k (cm3 molecule-1 s-1)
0.4
0.6
0.8
1
1.2
1000/T (1/K)


Vasudevan, Hanson, Bowman,
Golden and Davidson
(2007)
Moskaleva
Xia & Lin
(2000)
Present
k (cm3 molecule-1 s-1)
1e-13
1e-14
1e-15
1e-16
0.4
0.6
0.8
1
1.2
1000/T (1/K)

Time-Dependent Populations

- Discretize Energy Levels
- Transition Matrix; Renormalize → real, symmetric; G
- $\frac{d}{dt}\left|w(t)\right\rangle = G\left|w(t)\right\rangle \qquad y_i(E,t) = x_i(E,t)/f_i(E)$
- $\left|w(t)\right\rangle = \left[y_I(E_{0_I}),\cdots,y_I(E_{\max}),\cdots,y_i(E_{0_i}),\cdots,y_i(E_{\max}),\cdots,\left(\frac{n_m}{QR_m\delta E}\right)^{1/2} X_R,\cdots \right]^T$
- Diagonalize
- $\left|w(t)\right\rangle = \sum_{j=1}^{N_I+\ldots N_M+1} e^{\lambda_j t}\left|g_j\right\rangle\left\langle g_j\middle|w(0)\right\rangle$

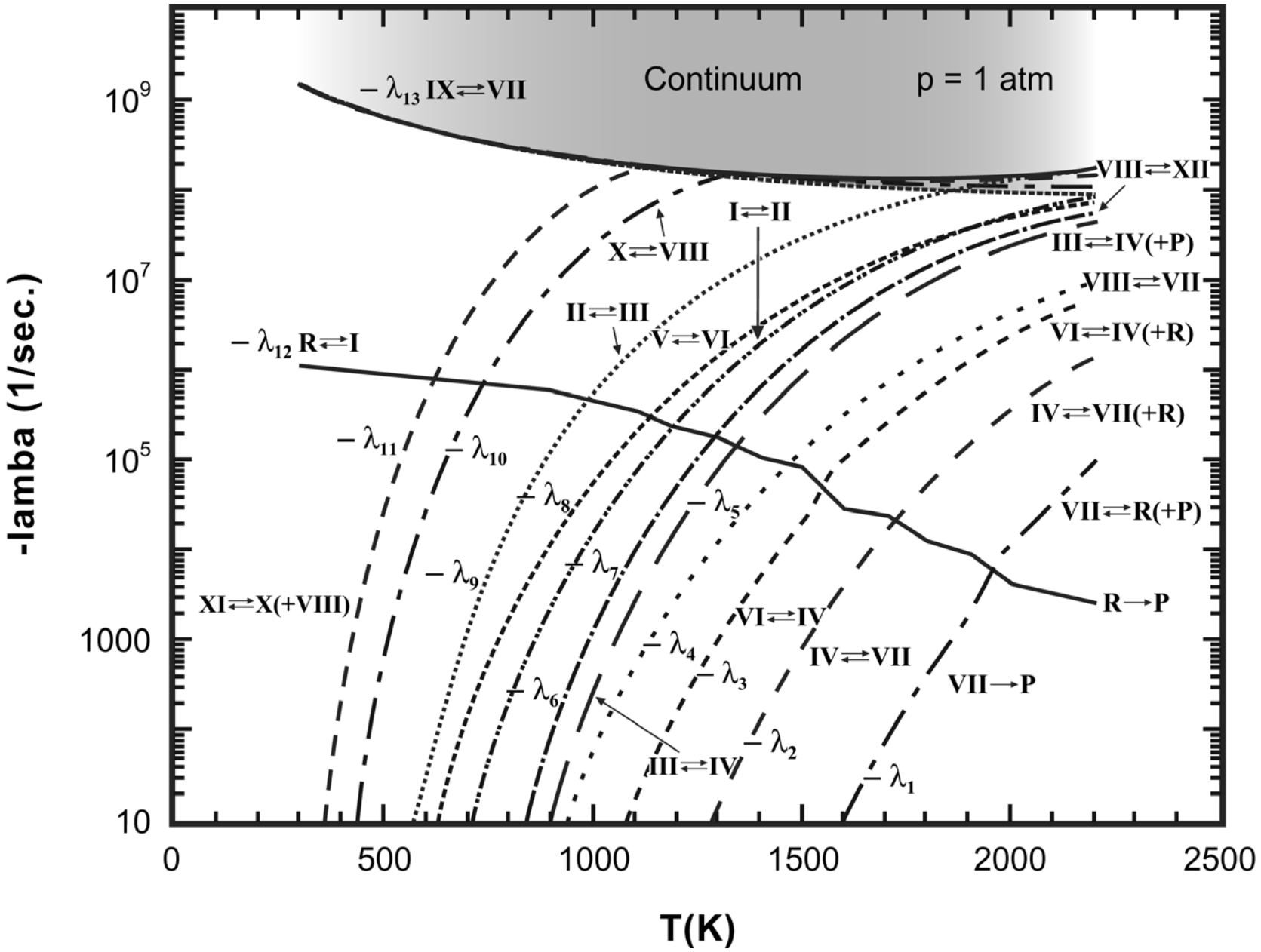
Kinetic Phenomenology
Experimental Viewpoint

- **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 $C_3H_3 + C_3H_3$



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**

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

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

- **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$_i$/dt* implies**

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

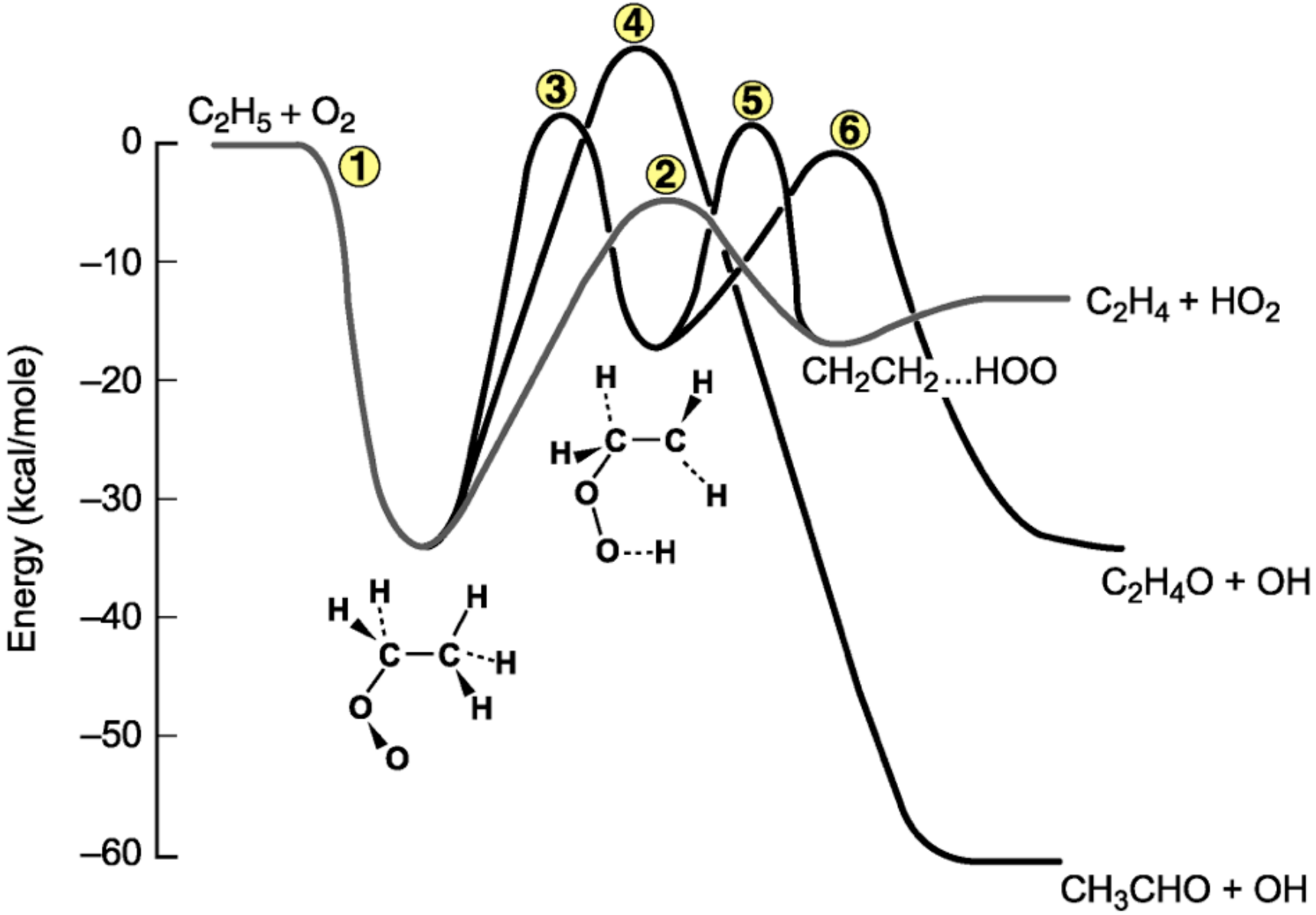
- $$k_{AR} = -\sum_{j=1}^{M+1} \lambda_j \Delta X_{Rj}^{(A)}; \quad \Delta X_{Rj} = -\left(\frac{Q_{Rm}\delta E}{n_m}\right)^{1/2} g_{j\ell} \left\langle g_j \middle| w_A(0) \right\rangle$$

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

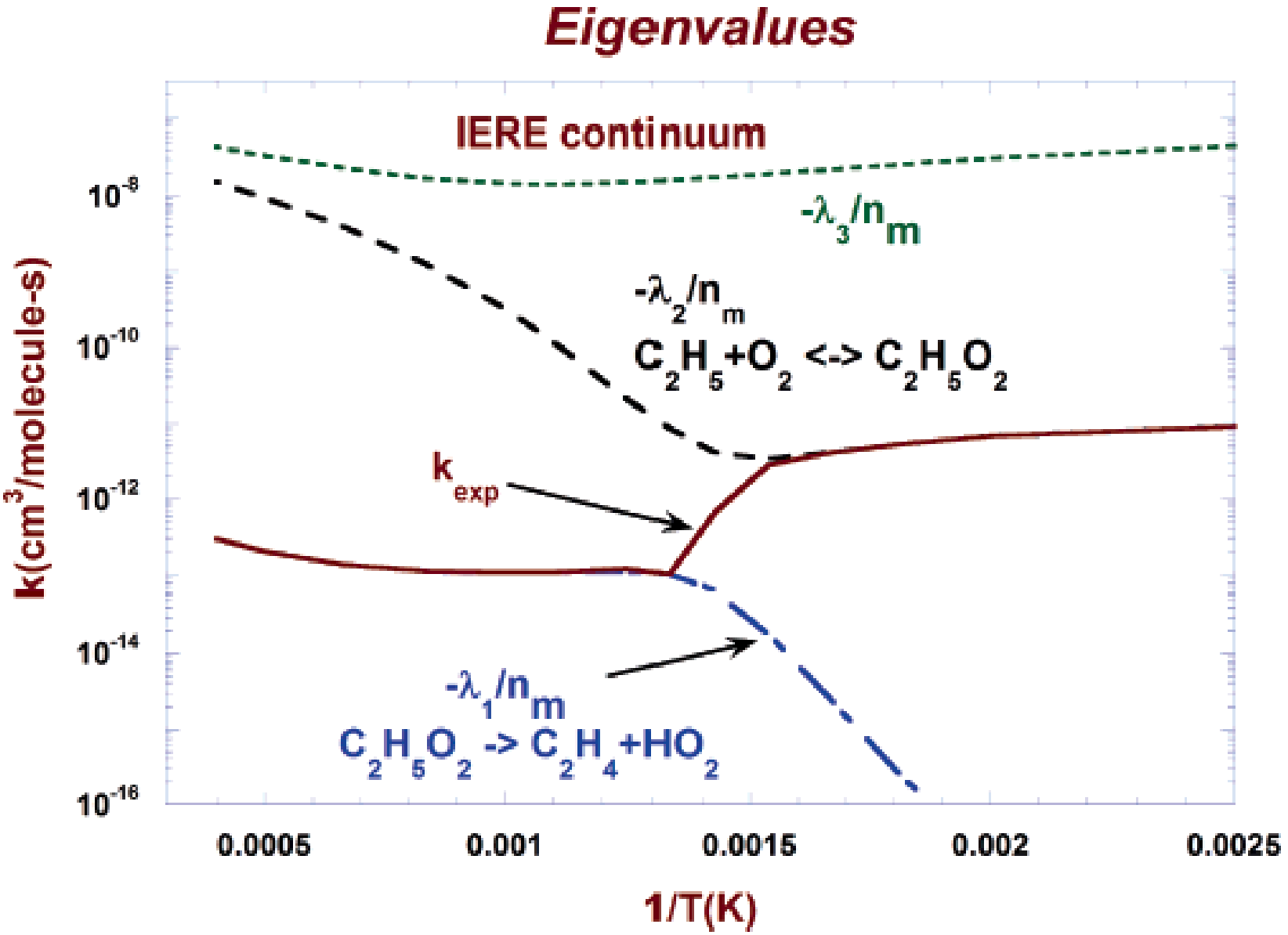
Method 2 Long time limit

- $X_i(t) = \sum_{j=0}^{M+1} a_{ij} e^{\lambda_j t} \equiv \sum_{j=0}^{M+1} a_{ij} v_j \qquad |X\rangle = A|v\rangle \qquad |v\rangle = B|X\rangle$
- $\frac{dX_i}{dt} = \sum_{j=0}^{M+1} \sum_{\ell=1}^{M+2} \lambda_j a_{ij} b_{j\ell} X_\ell$
- $\frac{dX_i}{dt} = \sum_{\ell \neq i} k_{\ell i} X_\ell - \sum_{\ell \neq i} k_{i\ell} X_i$
- $k_{\ell i} = \sum_{j=0}^{M+1} \lambda_j a_{ij} b_{j\ell} \qquad \ell \neq i$

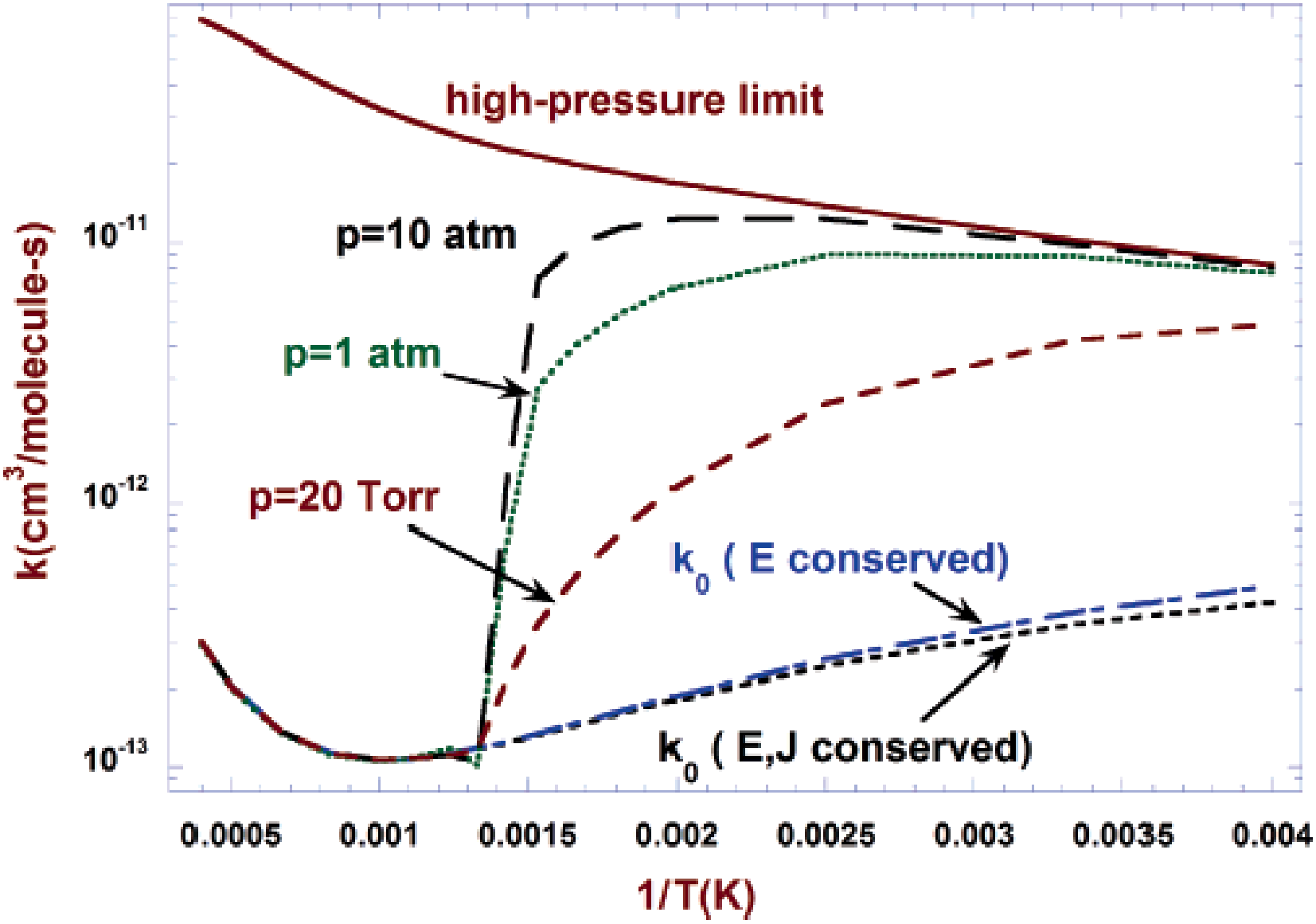
$C_2H_5 + O_2$ Potential Energy Surface



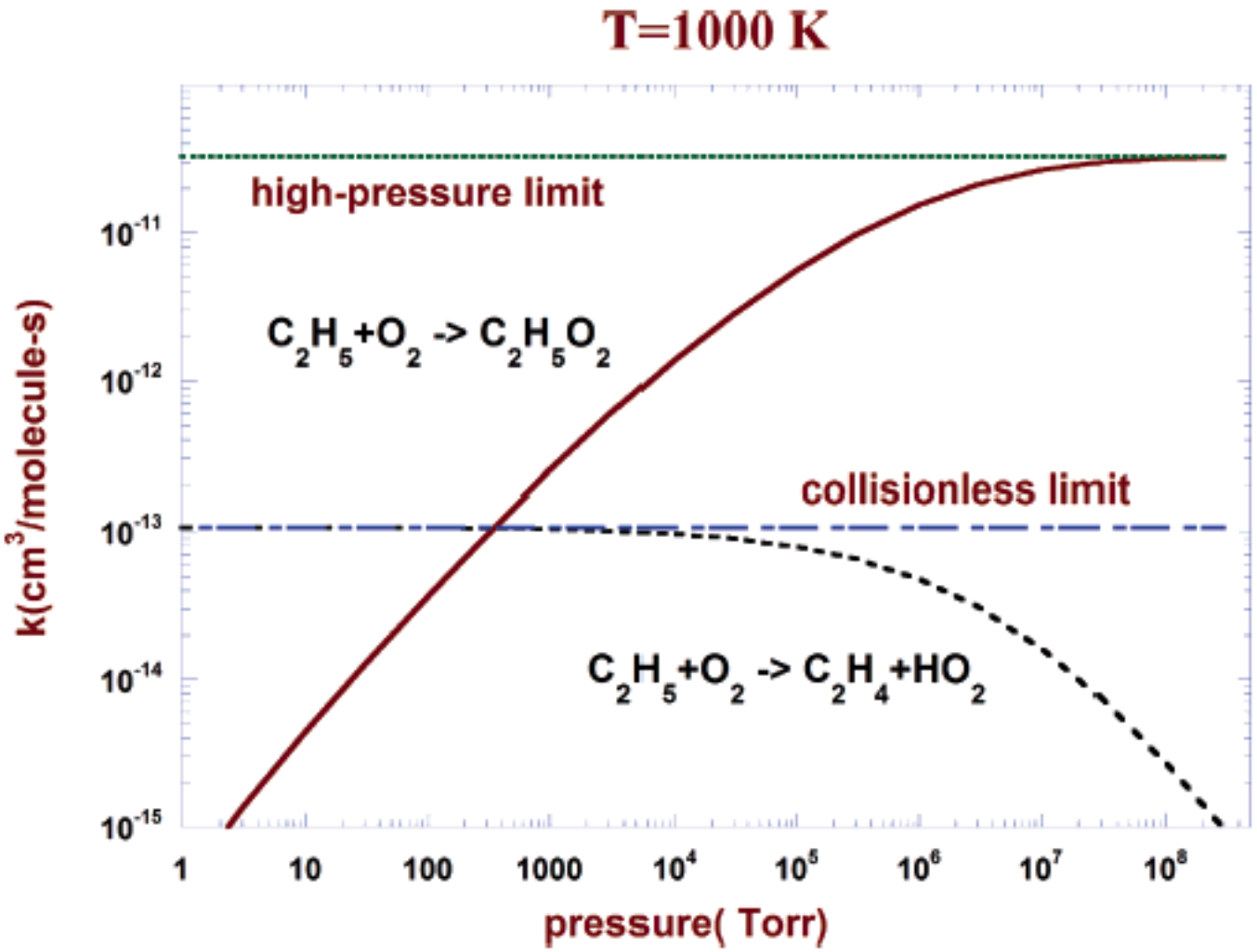
$C_2H_5 + O_2$


Eigenvalues
IERE continuum
-λ3/nm
-λ2/nm
C2H5+O2 <-> C2H5O2
kexp
-λ1/nm
C2H5O2 -> C2H4+HO2
k(cm3/molecule-s)
10-8
10-10
10-12
10-14
10-16
0.0005
0.001
0.0015
0.002
0.0025
1/T(K)

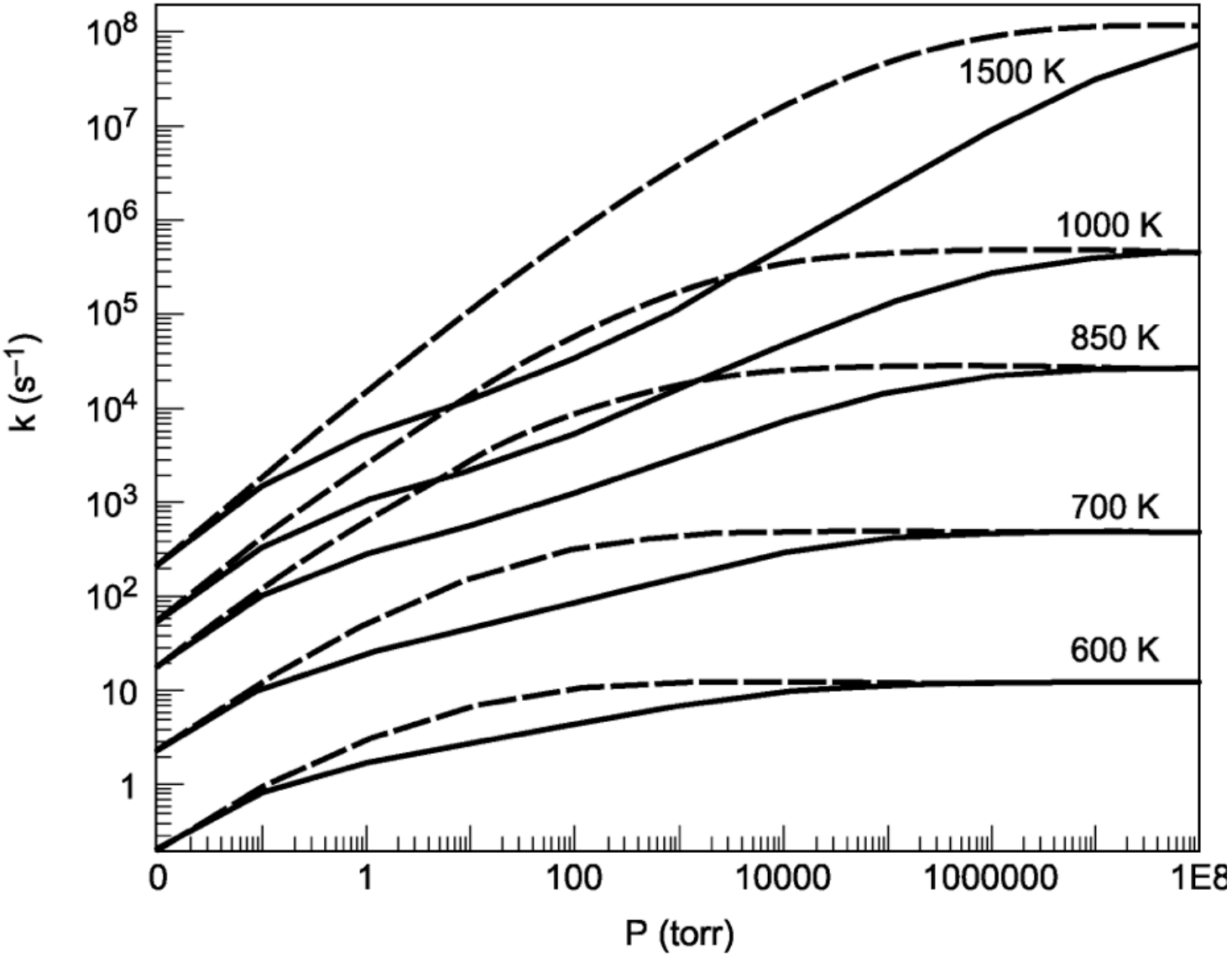
$C_2H_5 + O_2$ T Dependent Rate Coefficients



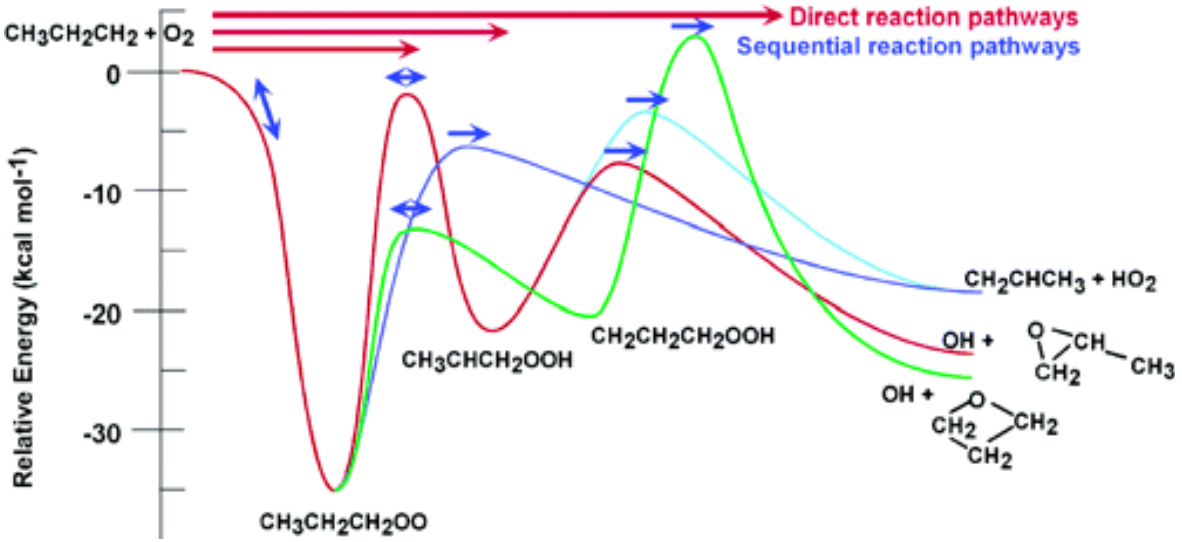
$C_2H_5 + O_2$ P Dependent Rate Coefficients

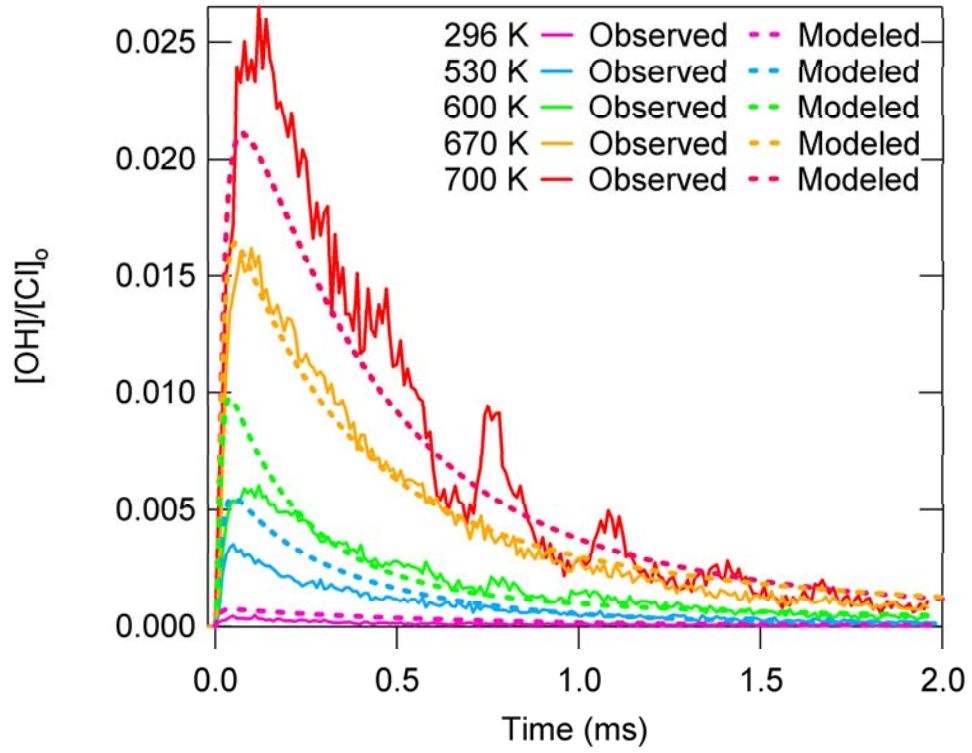


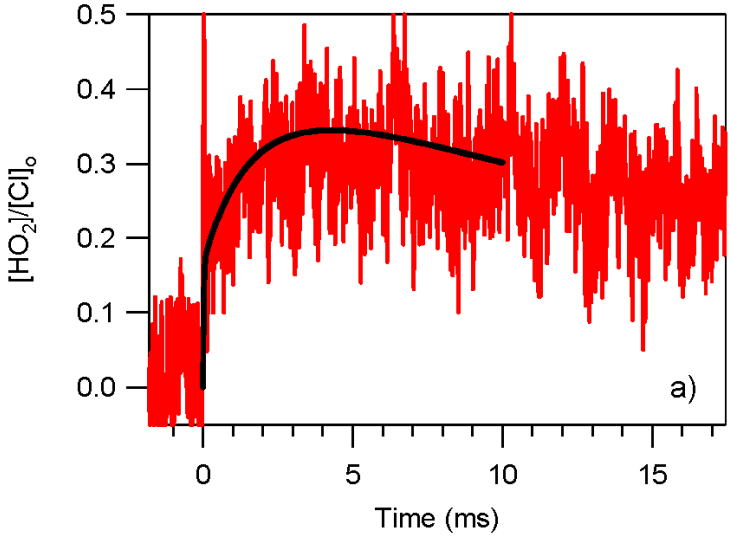
$C_2H_5O_2 \rightarrow C_2H_4 + HO_2$ P Dependent Rate Coefficients

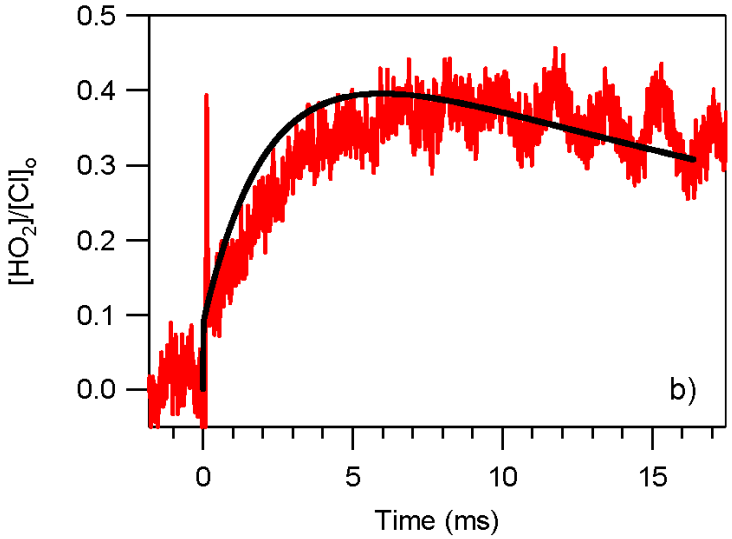


$C_3H_7 + O_2$ Formally Direct Pathways; QOOH

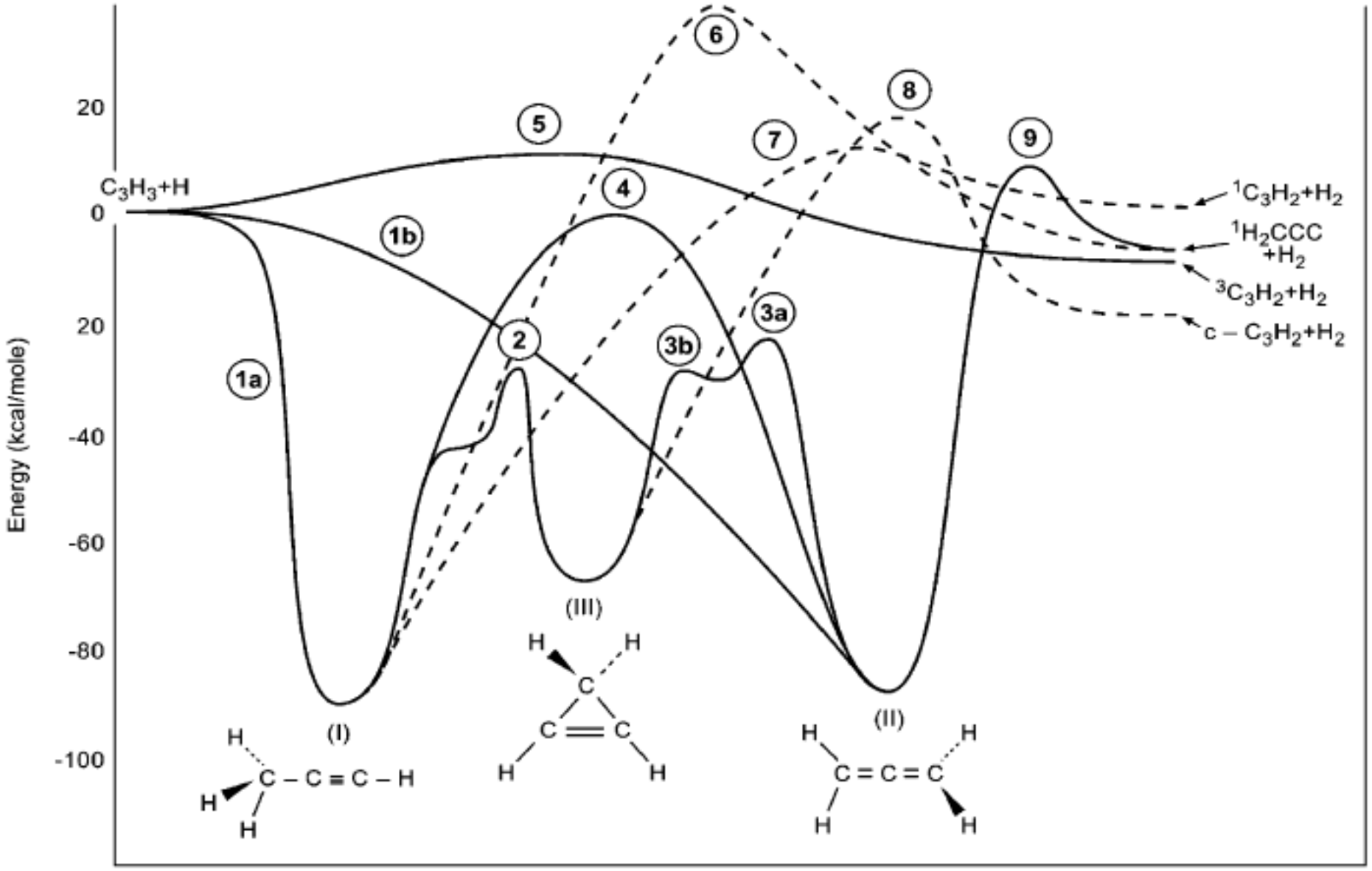


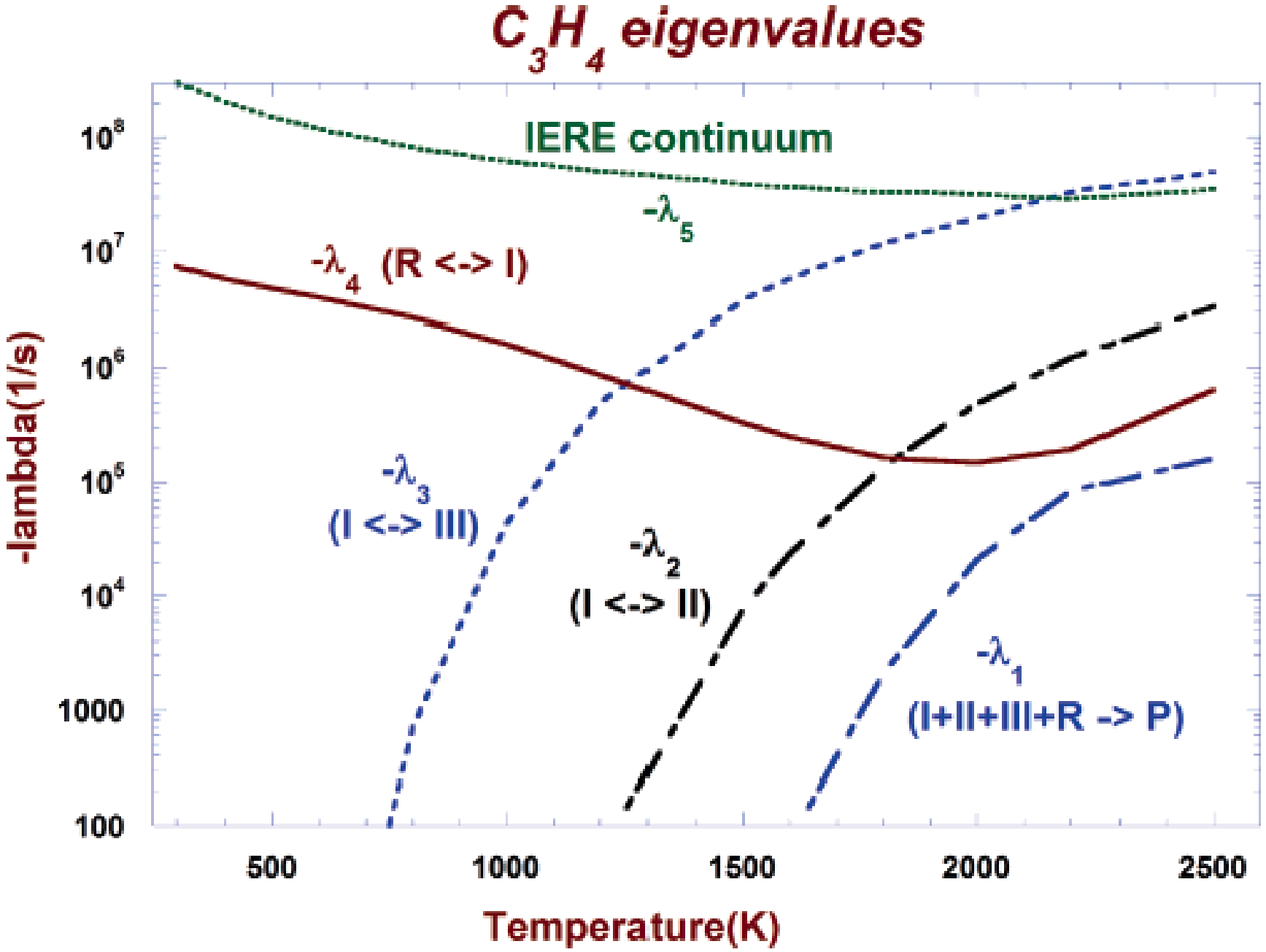




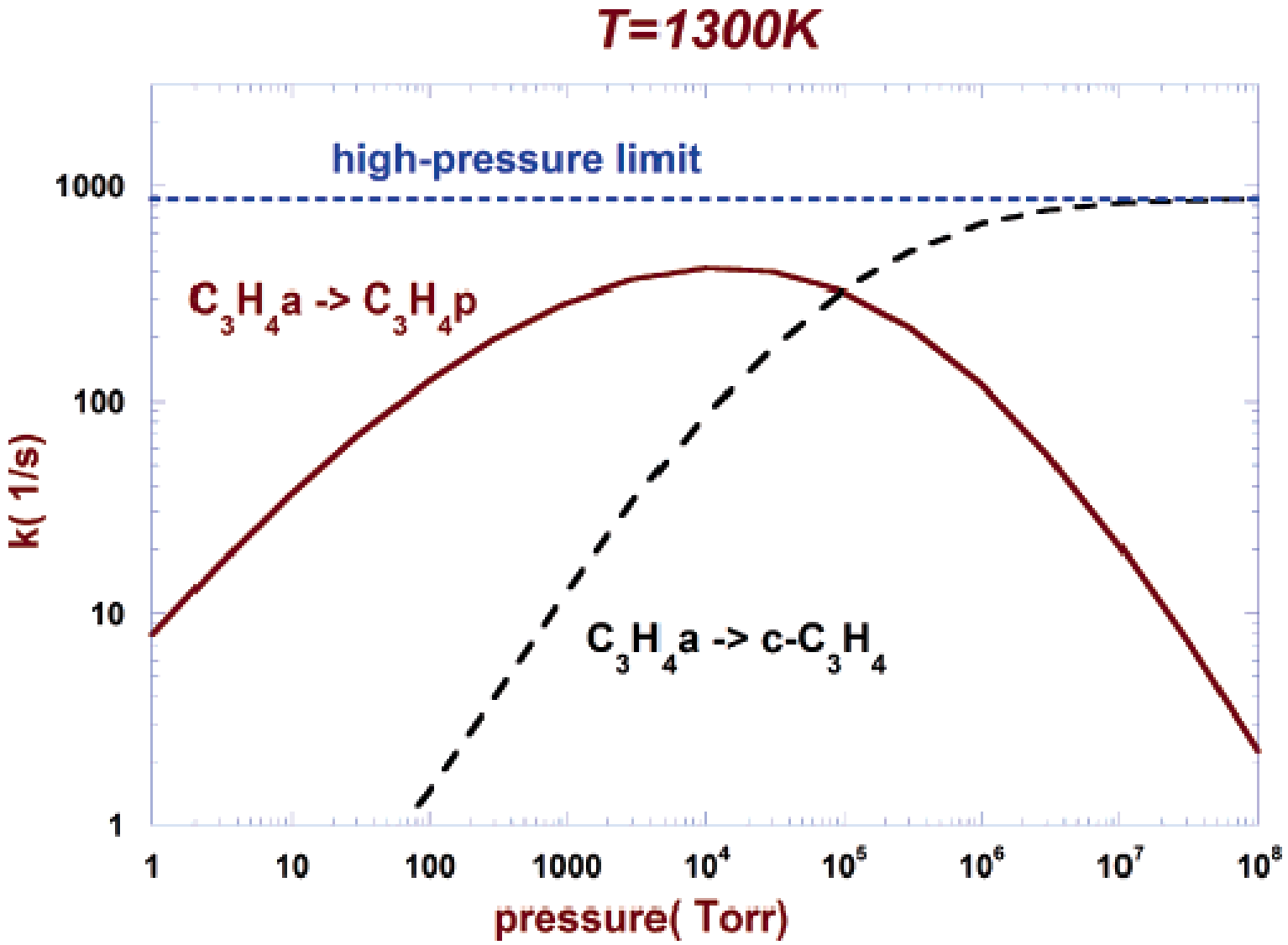


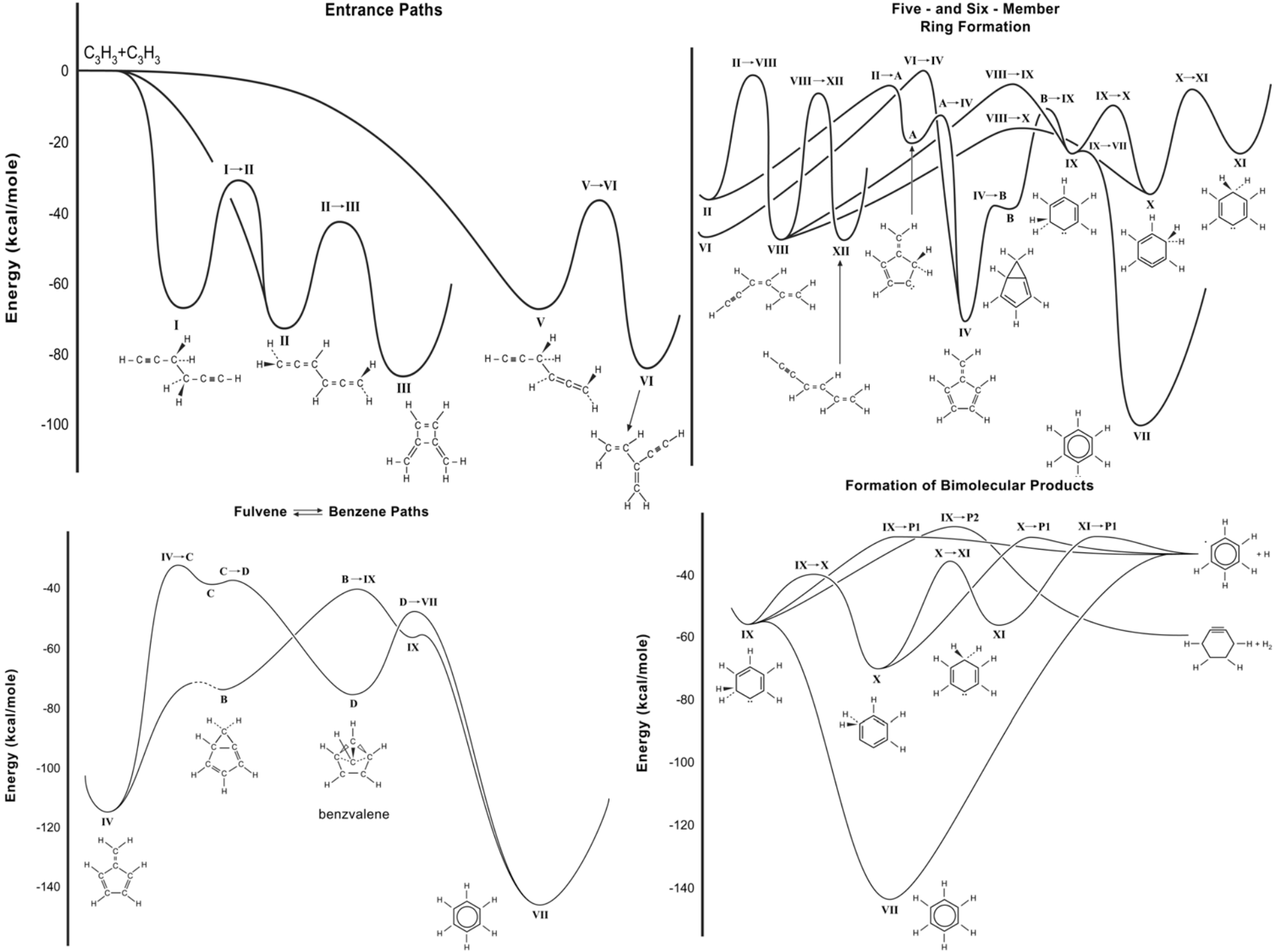
C_3H_4 Potential Energy Surface



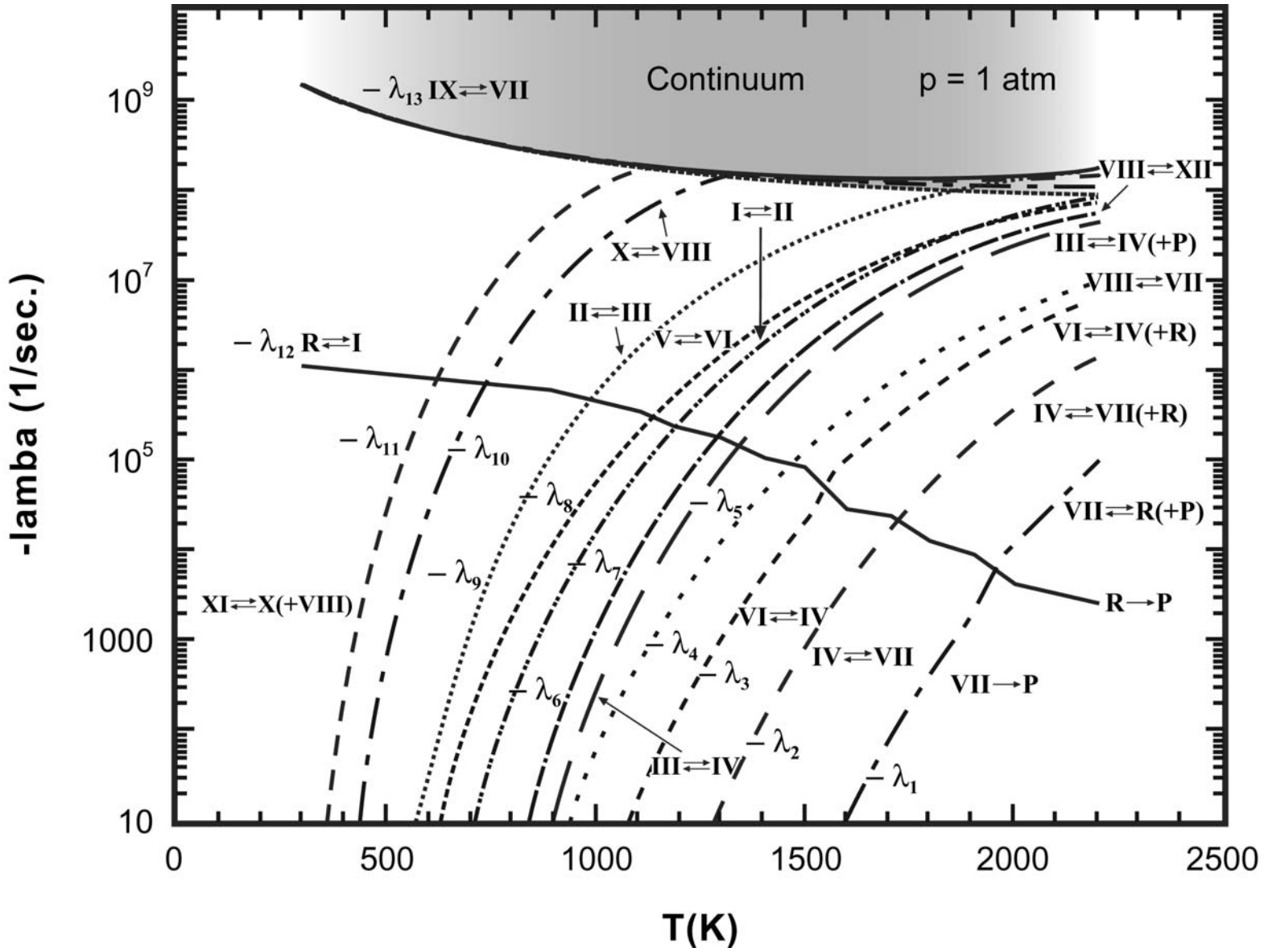

C3H4 eigenvalues
IERE continuum
-λ5
-λ4 (R <-> I)
-λ3
(I <-> III)
-λ2
(I <-> II)
-λ1
(I+II+III+R -> P)
-lambda(1/s)
10^8
10^7
10^6
10^5
10^4
1000
100
500
1000
1500
2000
2500
Temperature(K)

C_3H_4 Rate Coefficients

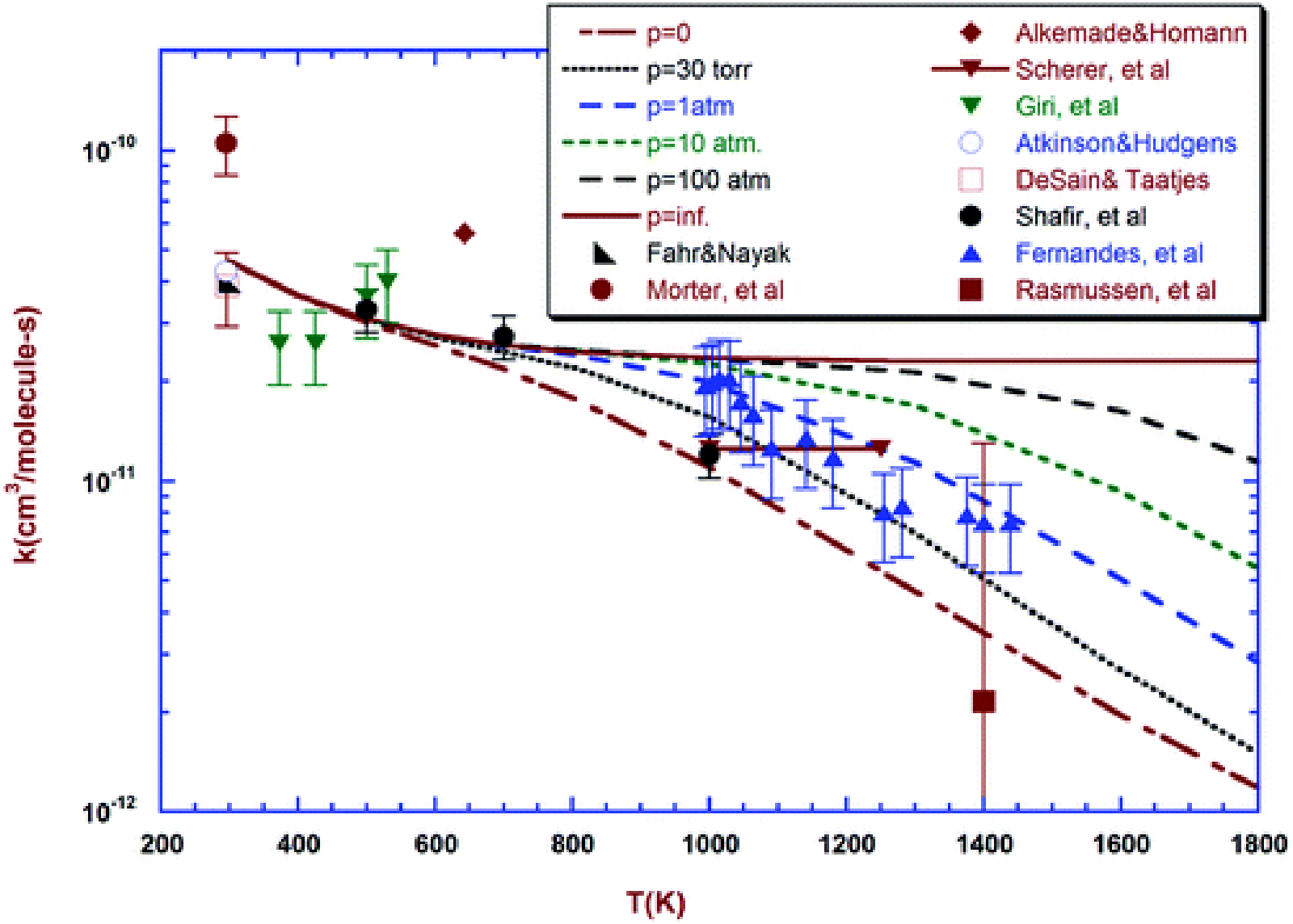



Entrance Paths
Energy (kcal/mole)
$C_3H_3+C_3H_3$
0
-20
-40
-60
-80
-100
I→II
II→III
V→VI
I
II
III
V
VI
Five - and Six - Member
Ring Formation
II→VIII
VIII→XII
II→A
VI→IV
A→IV
VIII→IX
B→IX
IX→X
X→XI
VIII→X
IX→VII
IV→B
II
VI
VIII
XII
A
B
IV
IX
X
XI
VII
Fulvene ⇌ Benzene Paths
Energy (kcal/mole)
-40
-60
-80
-100
-120
-140
IV→C
C→D
B→IX
D→VII
C
B
D
IX
IV
benzvalene
VII
Formation of Bimolecular Products
Energy (kcal/mole)
IX→P1
IX→P2
X→P1
XI→P1
IX→X
X→XI
IX
X
XI
VII
+ H
+ H2

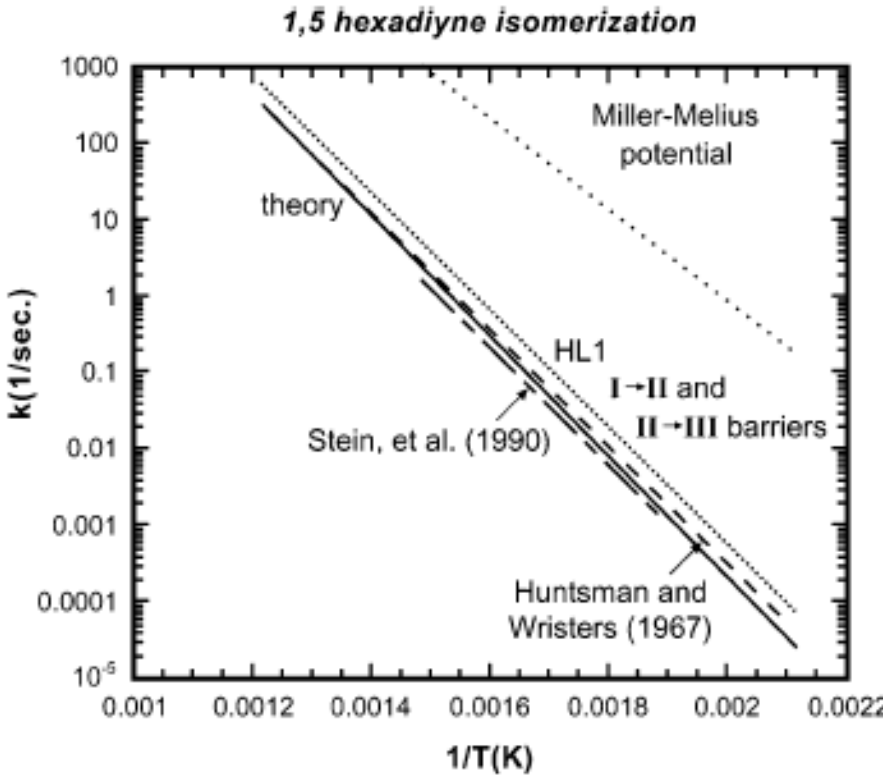
$C_3H_3 + C_3H_3$ Eigenvalues

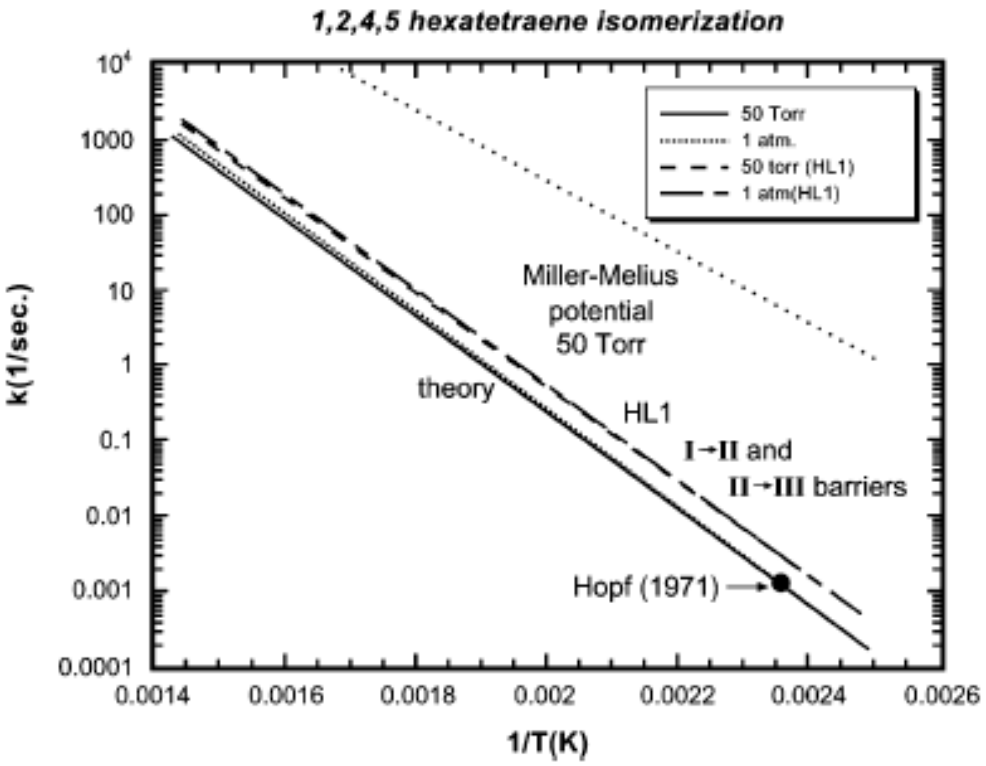


$C_3H_3 + C_3H_3$ Rate Coefficients

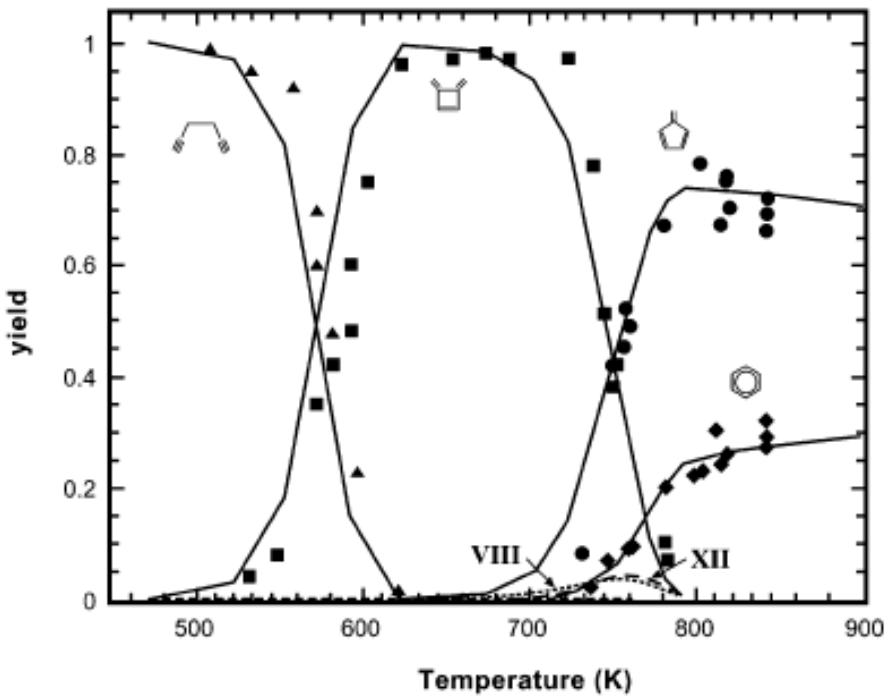


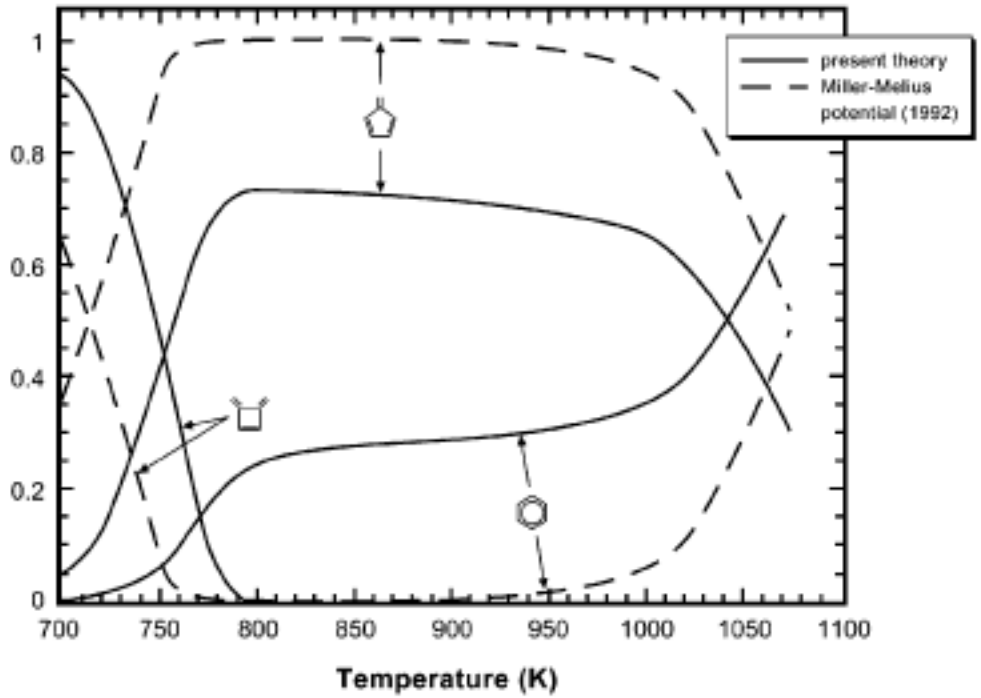
$C_3H_3 + C_3H_3$ Isomerization Rate Coefficients

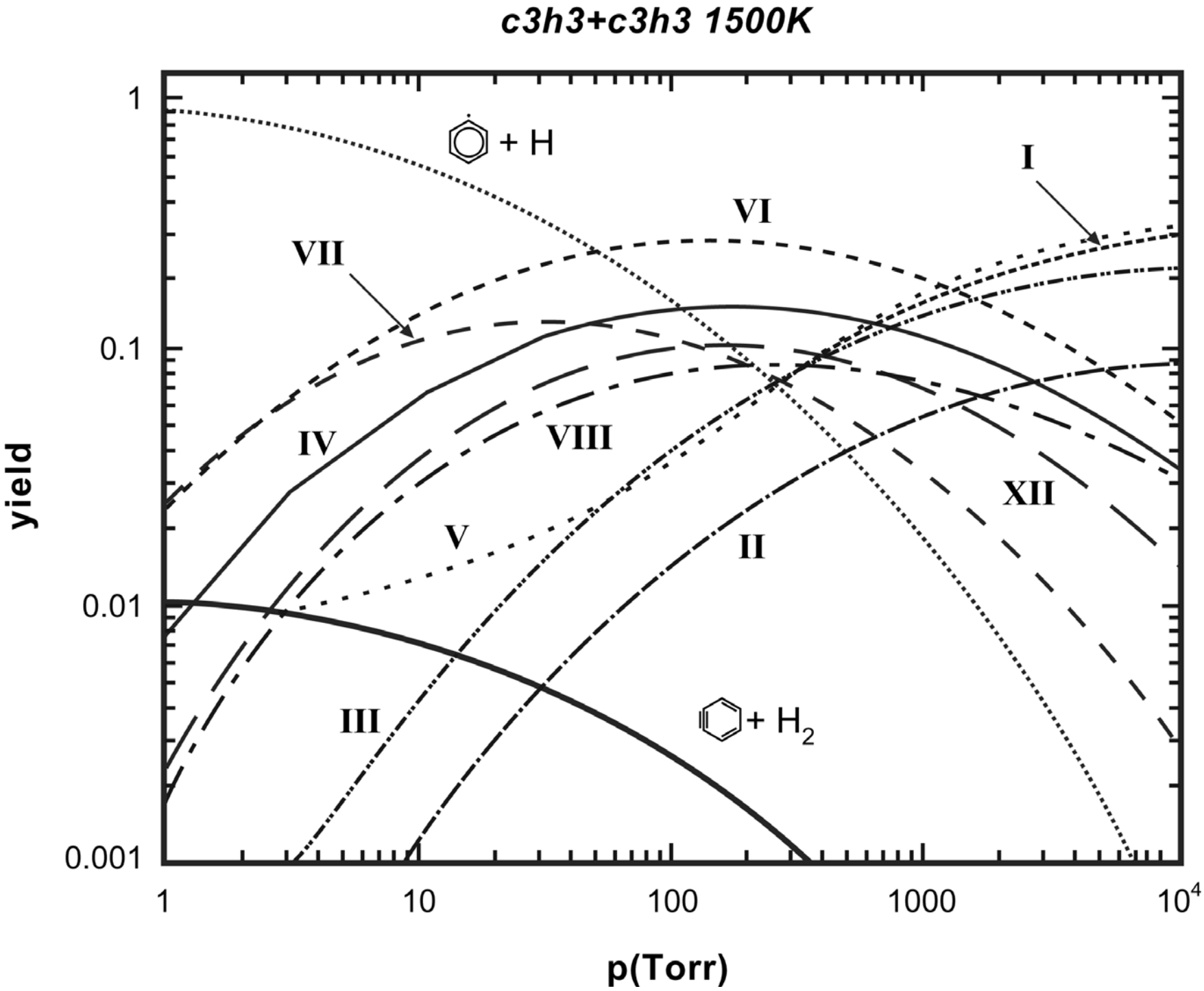




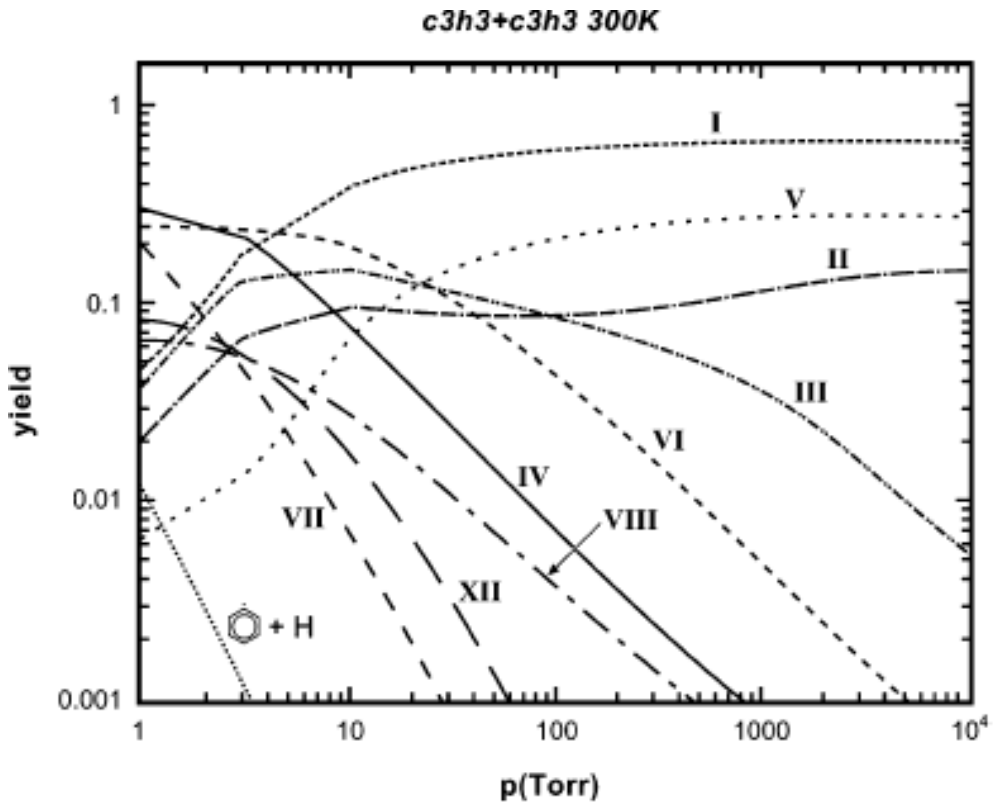
$C_3H_3 + C_3H_3$
Product Branching in 1,5-Hexadiyne Pyrolysis

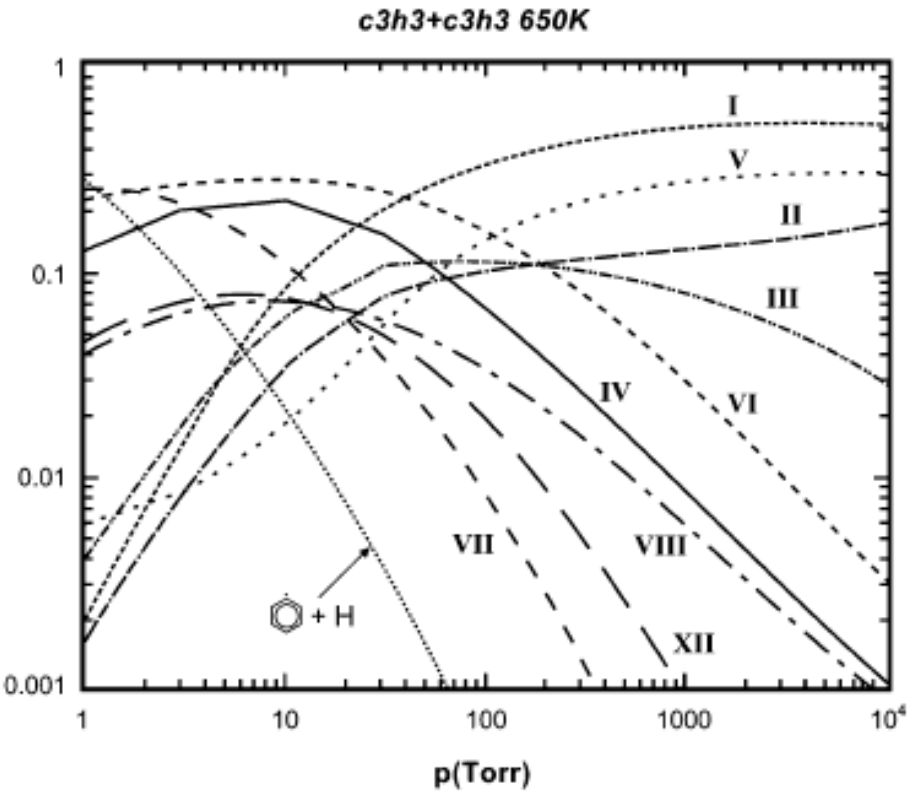




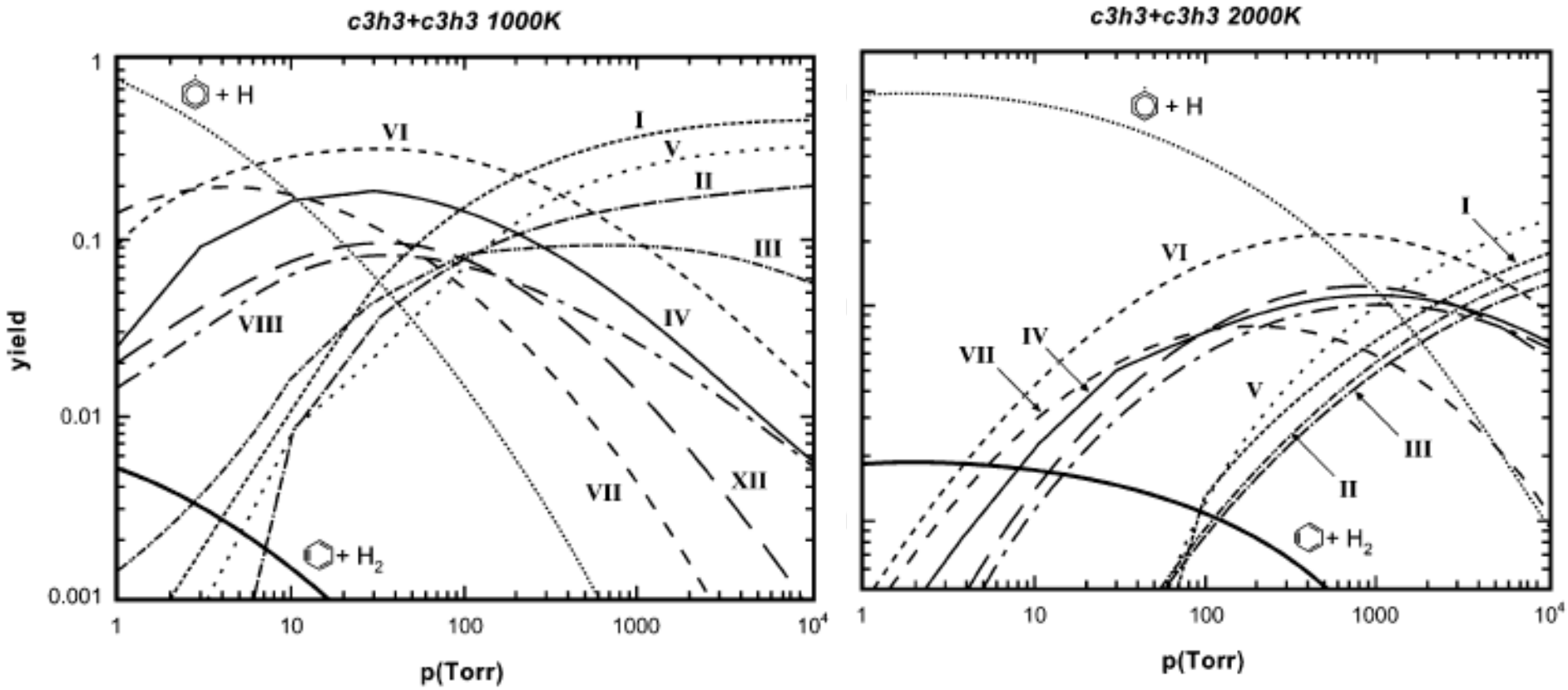

c3h3+c3h3 1500K
yield
p(Torr)
1
0.1
0.01
0.001
1
10
100
1000
10^4
+ H
+ H2
I
II
III
IV
V
VI
VII
VIII
XII

$C_3H_3 + C_3H_3$ Product Branching

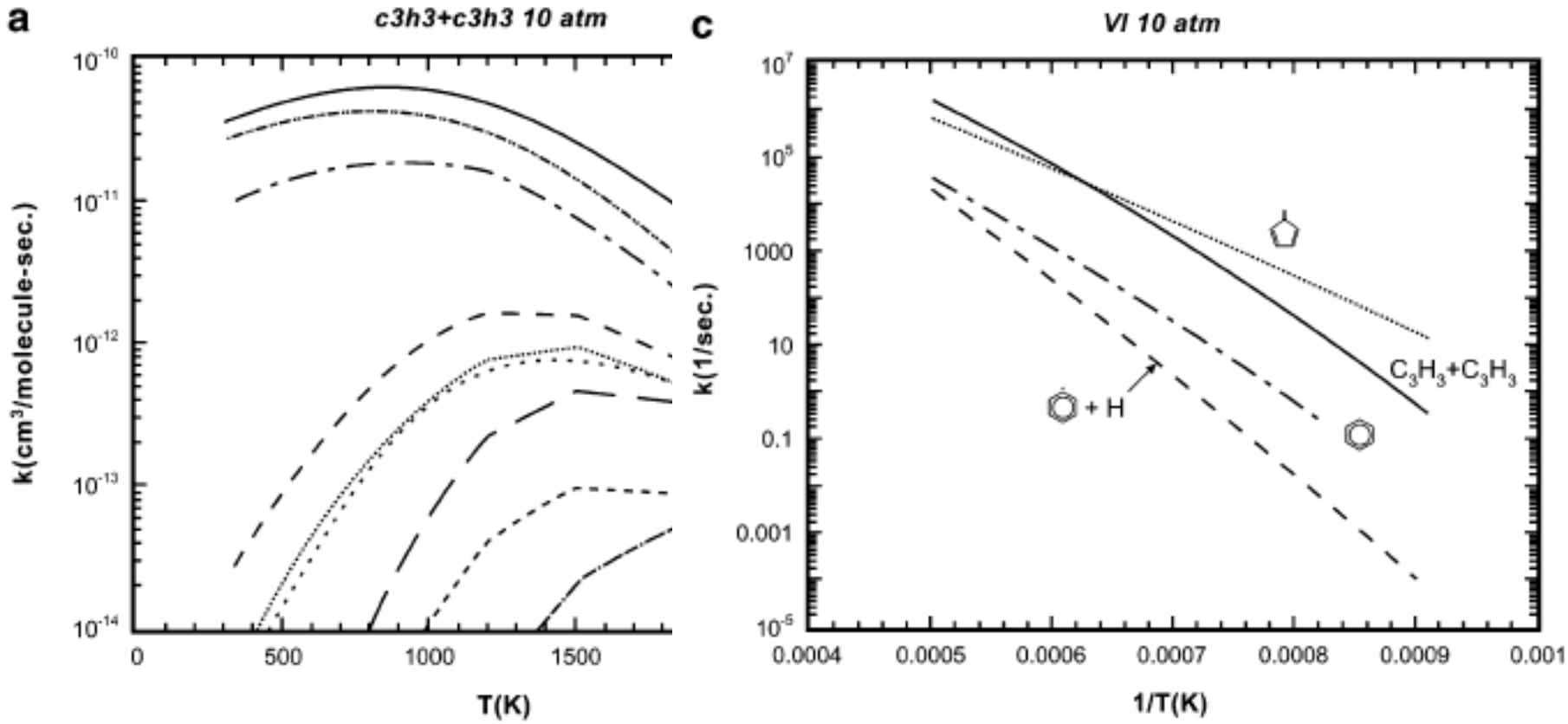




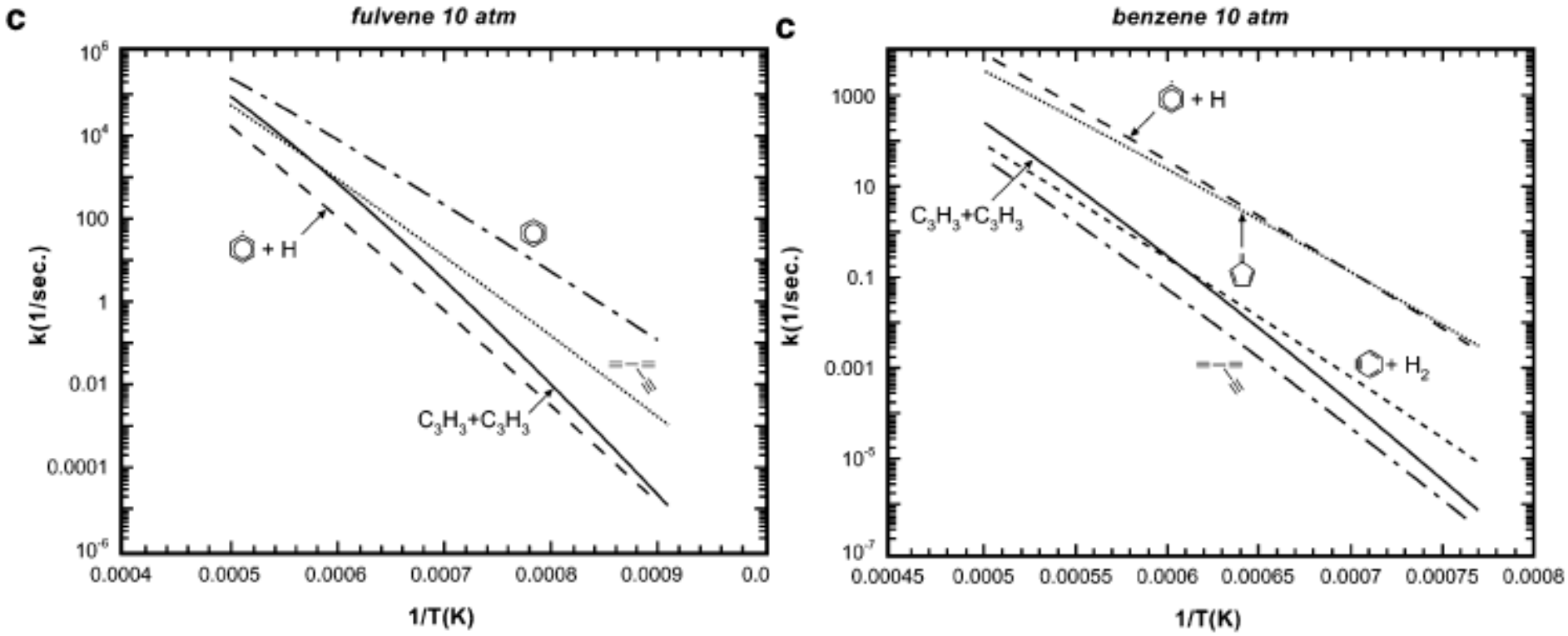
$C_3H_3 + C_3H_3$ Product Branching



$C_3H_3 + C_3H_3$ Rate Coefficients



C_6H_6 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