Argonne NATIONAL LABORATORY

Theory of Low Temperature Reactions

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Motivation

Predict Rate Constants for Interstellar Chemistry

- Temperature ~ 5 to 100 K
- Barrierless Reactions
  1. Ion-Molecule
  2. Radical-Radical
  3. Radical-Molecule
- Long-Range Potential – Smallest n's in R^{-n} Dominate
  1. Ion-Dipole ~ R^{-2}
  2. Ion-Quadrupole ~ R^{-3}
  3. Ion-Induced Dipole ~ R^{-4}
  4. Dipole-Dipole ~ R^{-3}
  5. Dipole-Quadrupole ~ R^{-4}
  6. Quadrupole-Quadrupole ~ R^{-5}
  7. Dipole-Induced Dipole ~ R^{-6}
  8. Dispersion ~ R^{-6}

Long-Range Transition State Theory

Low Temperature =>

Transition State at Large Separations =>

Orbital Rot. Const. << Fragment Rot. Const.

Chemical Forces are not important

High Temperature =>

kT > B => Classical Rotations

For Single Long-Range Term in V Results are “Analytic”

$$V = V_0 \frac{f(\Omega)}{R^n}$$

$$k(T) = C\mu^{-1/2} V_0^{2/n} T^{1/2-2/n}$$

$$C = \sqrt{8\pi}\min\left\{ \tilde{R}^2 \left\langle e^{-f(\Omega)/\tilde{R}^n} \right\rangle_\Omega ; \tilde{R} \right\}; \tilde{R} = R(T/V_0)^{1/n}$$

Multiple Terms in V Require Evaluation of C for Sum Potential

Analytic Results

Ion Induced-Dipole; Langevin $k(T) = k_L \equiv 2\pi q\sqrt{\alpha/\mu}.$

Ion Dipole $k = C^{(\pm)}\mu^{-1/2}|qQ|^{2/3}T^{-1/6}.$

Ion Quadrupole $k(T) = \sqrt{2\pi}qd\mu^{-1/2}T^{-1/2}.$

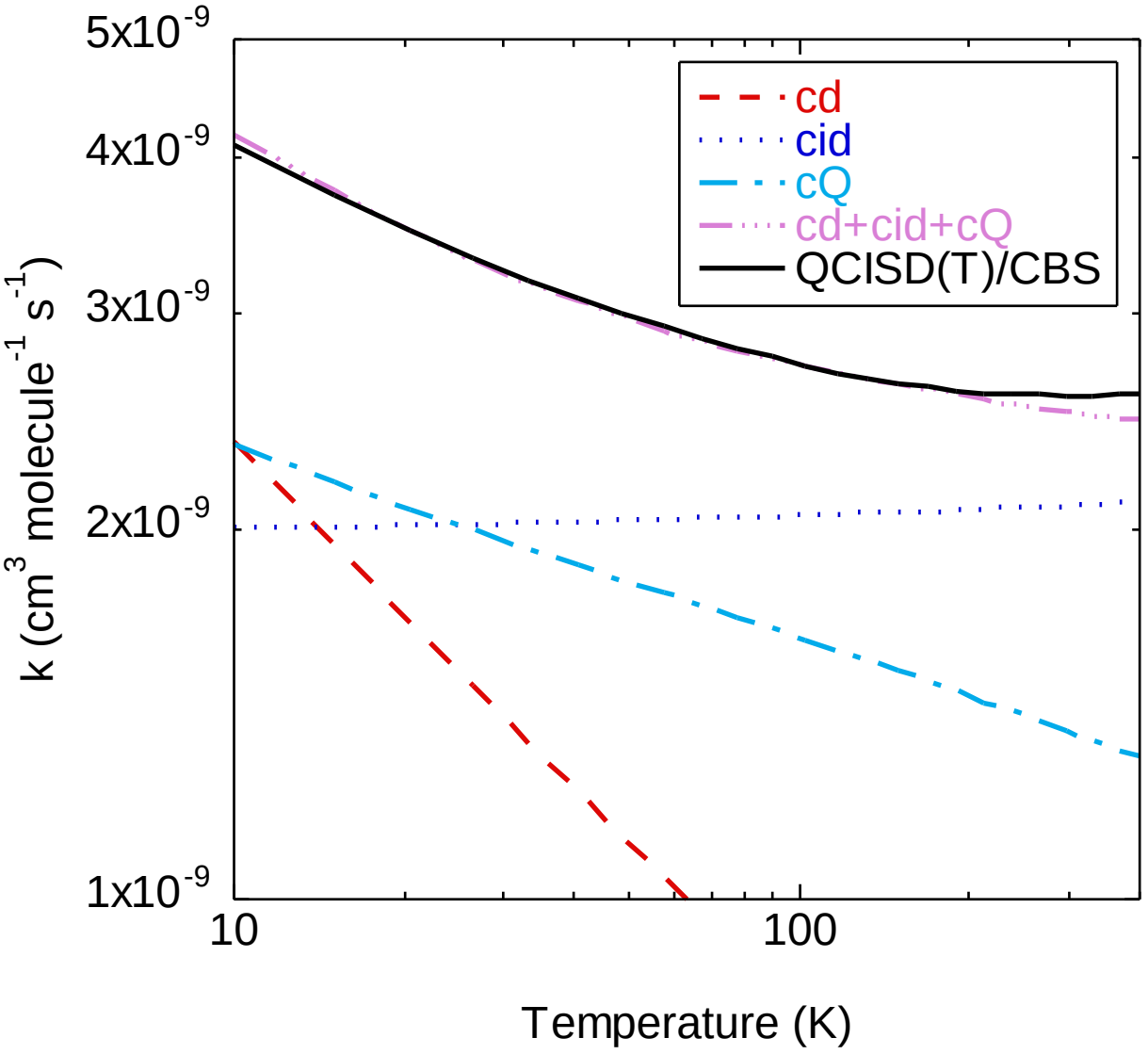
Dipole Dipole $k = C\mu^{-1/2}(d_1 d_2)^{2/3}T^{-1/6}.$

Dipole Quadrupole $k = C\mu^{-1/2}|dQ|^{1/2}$

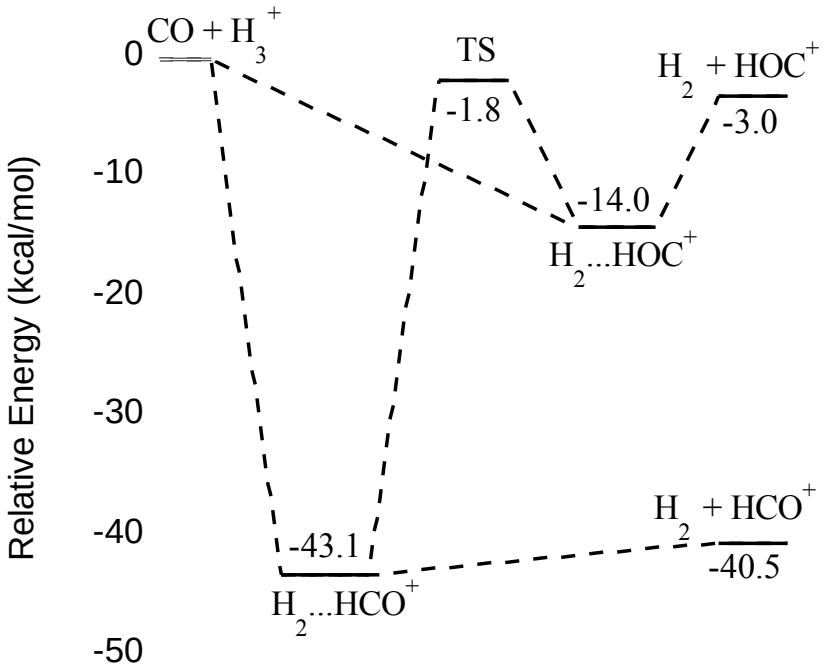
Dipole Induced-Dipole $k = C\mu^{-1/2}(d^2\alpha)^{1/3}T^{1/6}.$

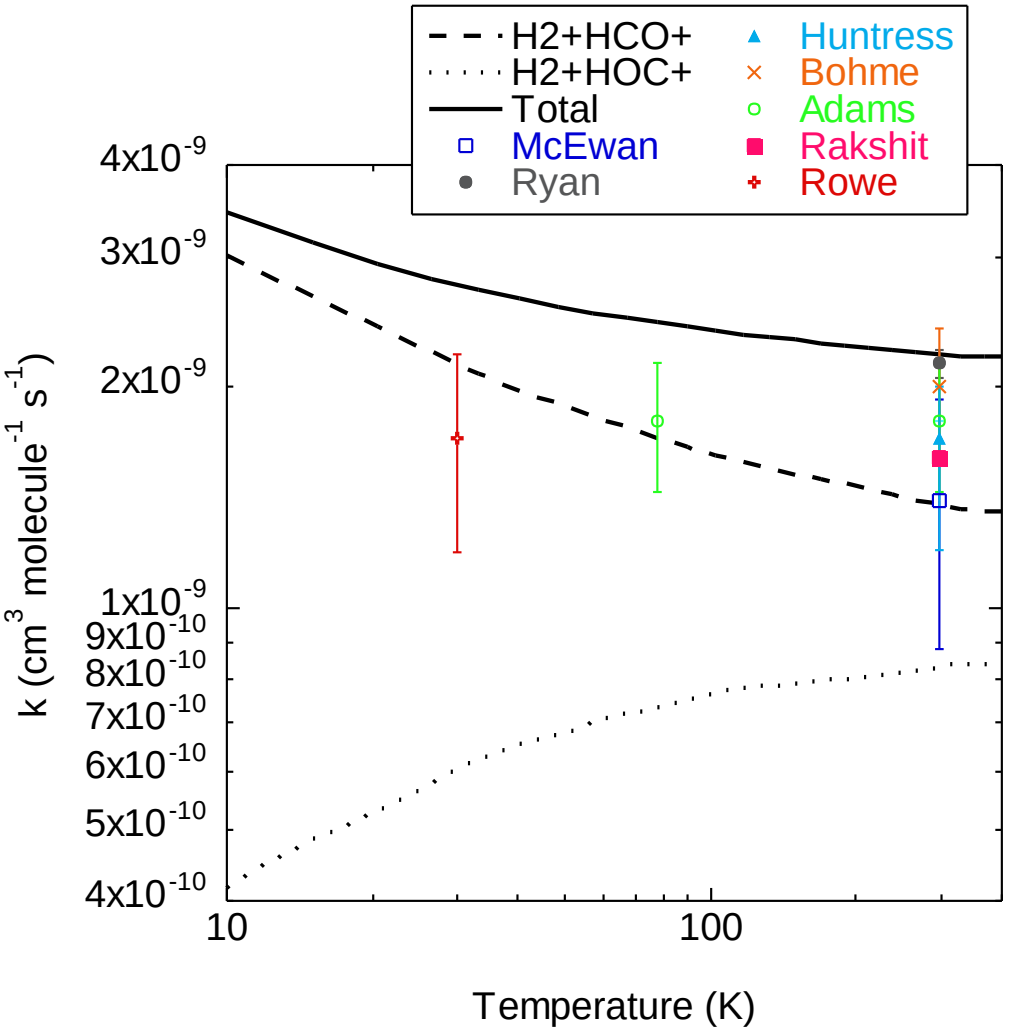
Dispersion $k(T) = 8.55\mu^{-1/2}C_6^{1/3}T^{1/6}.$

$H_3^+ + CO$: Capture Rate



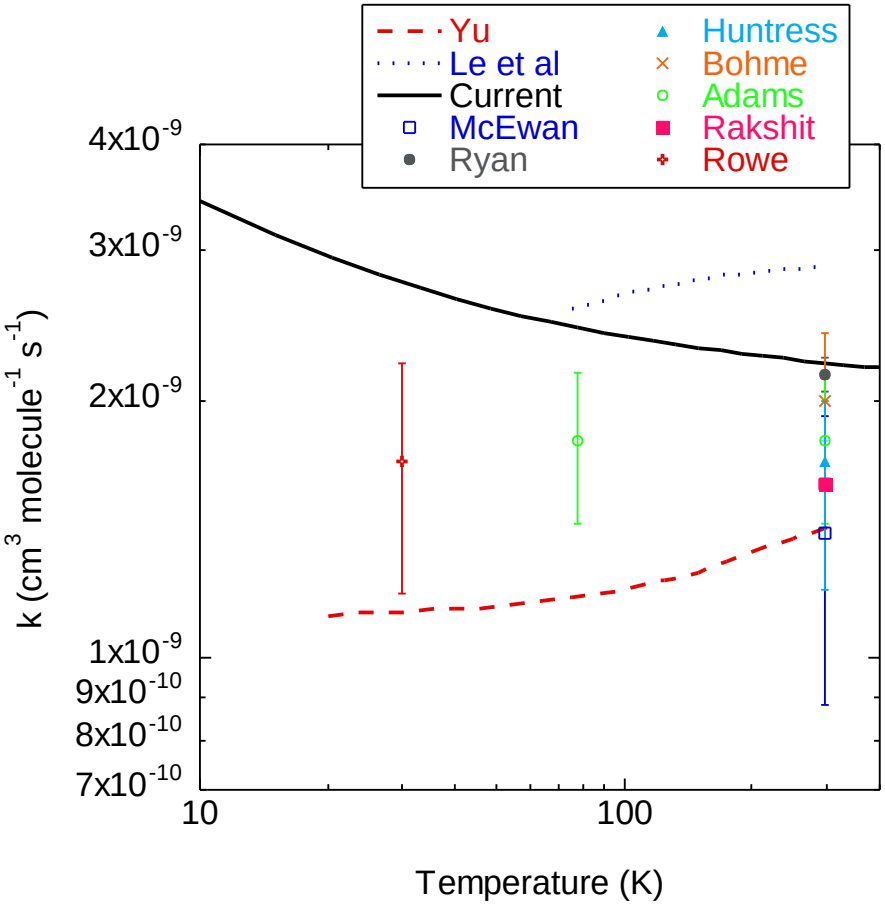
$H_3^+ + CO$: Comparison with Experiment



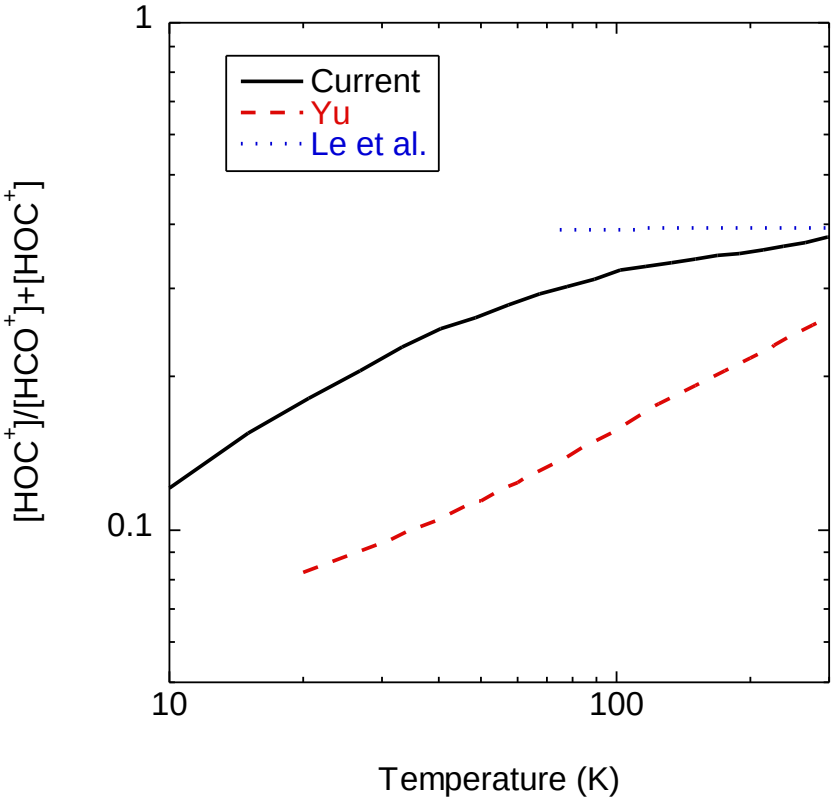


$H_3^+ + CO$: Other Theory

Le et al: CCSD/aug-cc-pVDZ
Grow PES



Yu: SAC-MP2/cc-pVTZ
Direct Dynamics



Limitations in Classical Long-Range Transition State Theory

Spin-Orbit ($kT \sim E_{SO}$)

Atomic Quadrupoles – Electronic Only

Important Reactions:

McCall: $O(^3P) + H_3^+$

Wakelam et al. ; Space Sci. Rev. 2010,156: 13-72.

$C(^3P) + NH_2$

$C(^3P) + C_3O$

$O(^3P) + CN$

$O(^3P) + C_2H$

$O(^3P) + HNO$

Quantum rotations of the fragments can be important at T > 5 K

$H_2+H_2^+$

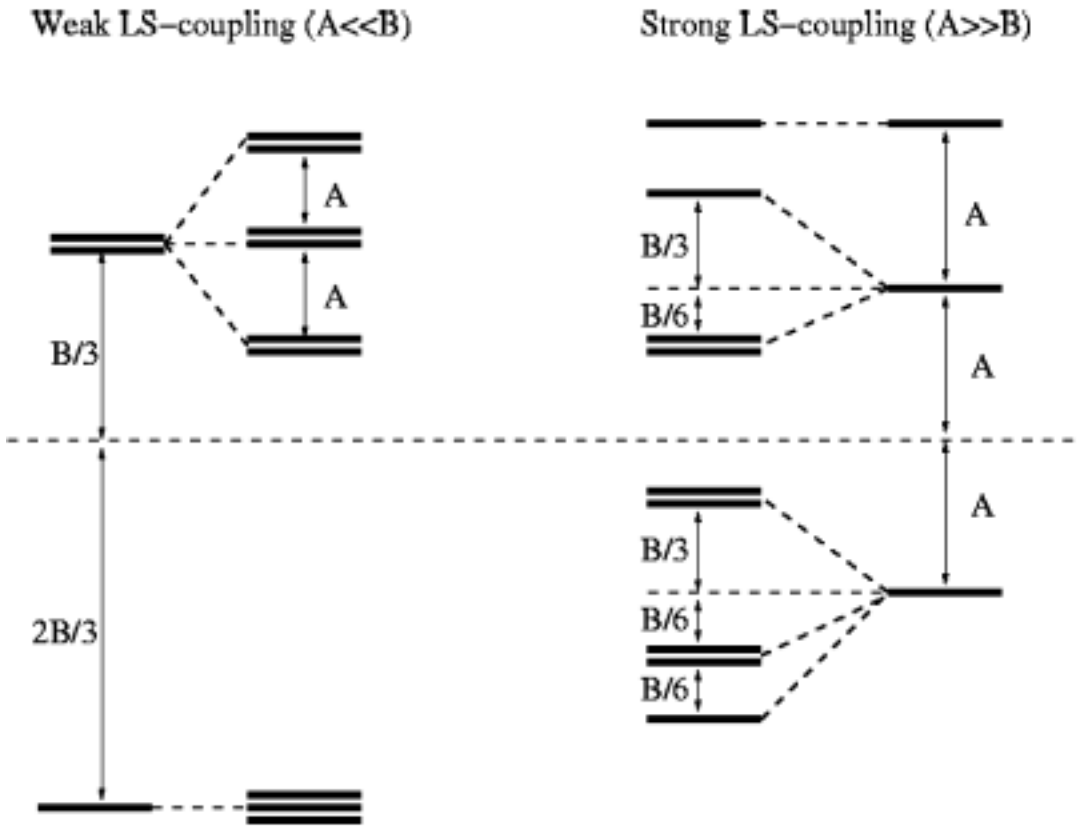
Coupling of Ion-Quadrupole and Spin-Orbit Interactions for (^{3}P) States

$$\hat{V} = B\left(\hat{L}_z^2 - \frac{1}{3}\hat{L}^2\right) - A\hat{S}\cdot\hat{L}$$

$$B = 3Qq/(2R^3I(2I-1))$$

$$E_0 = -\sqrt{\frac{(B+A)^2}{4} + 2A^2} - \frac{B}{6} + \frac{A}{2}$$

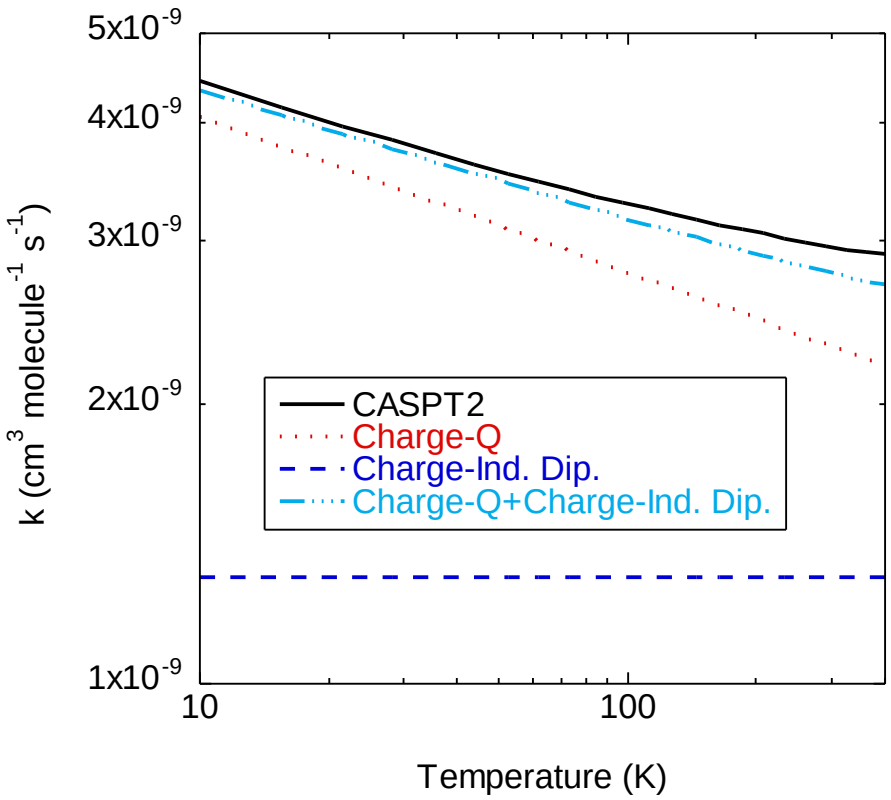
$$E_{1,2} = -\sqrt{\frac{B^2}{4} + A^2} - \frac{B}{6}$$



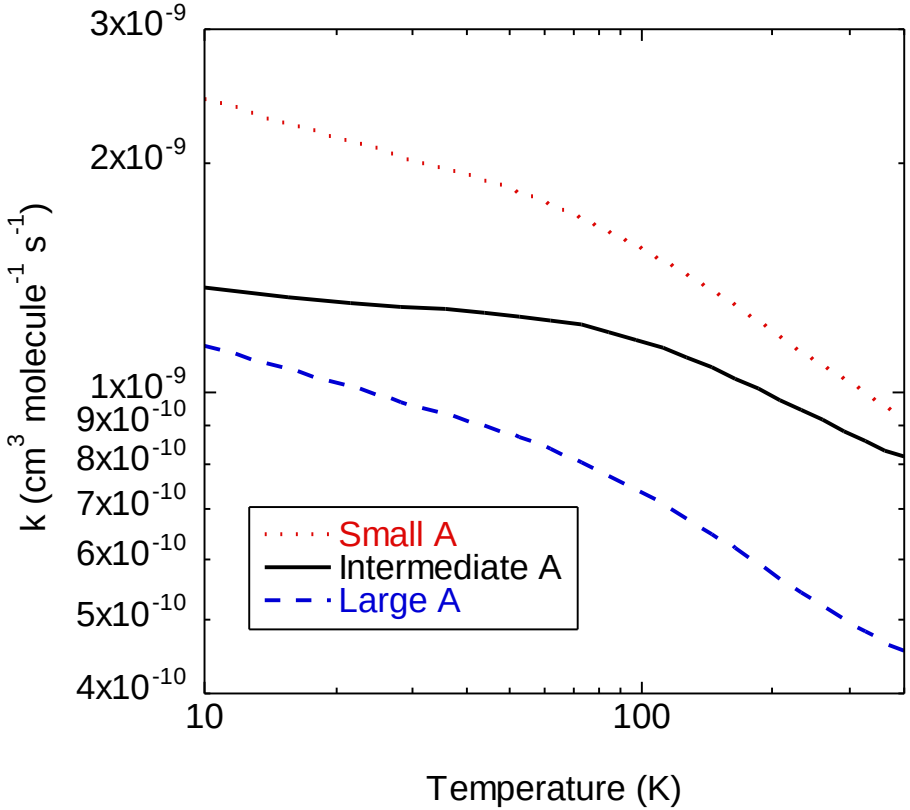
Gentry and Giese, J. Chem. Phys. 67, 2355 (1977)
Talbi, DeFrees, Egolf, Herbst, Astrophys. J. 374, 390 (1991)

$O(^3P) + H_3^+$: Temperature Dependence

Test of Long-Range Expansion

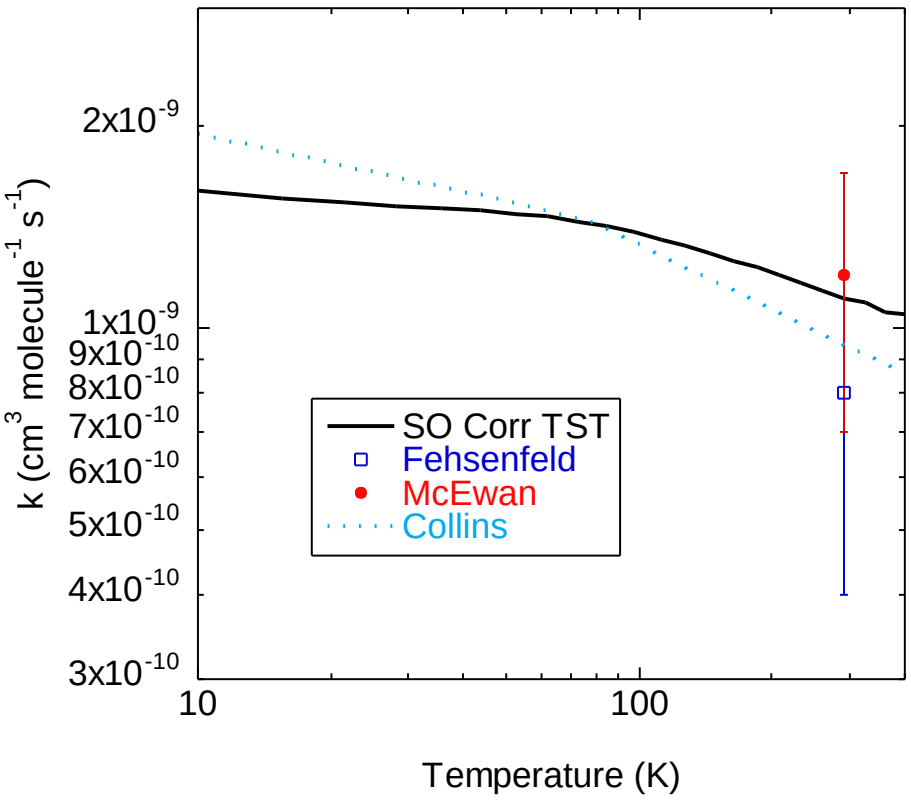


Variation between Spin-Orbit Limits

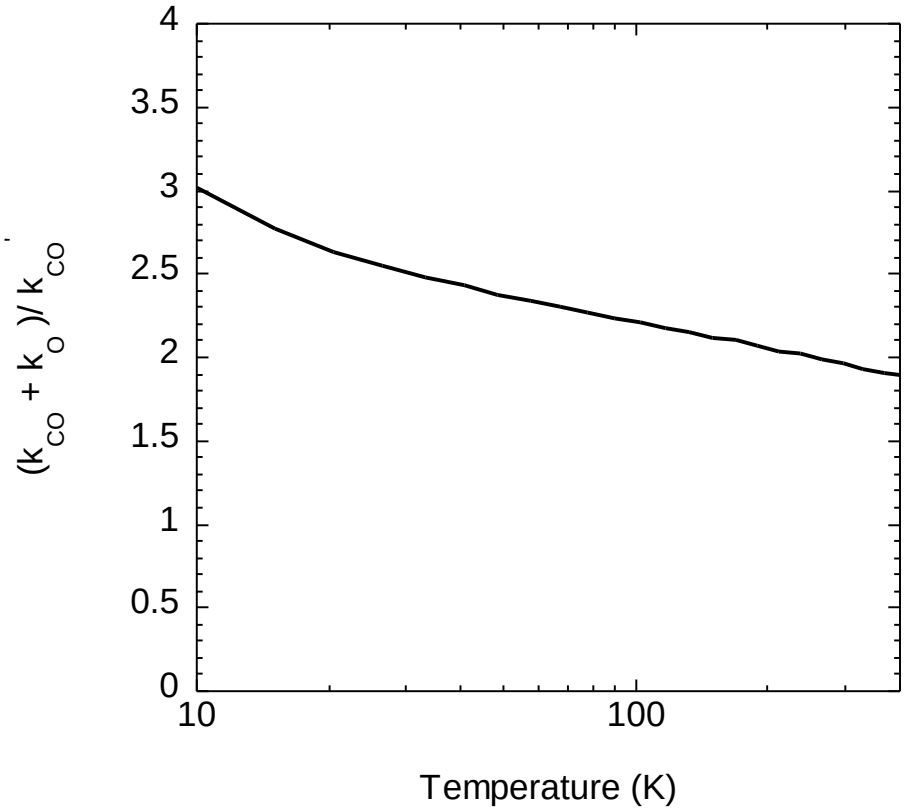


$O(^3P) + H_3^+$: Temperature Dependence

Comparison With Experiment



Effect on H_3^+ Destruction Rates



McCall, Geballe, Hinkle, Oka, Astrophys. J. 522, 338 (1999)

Electronic Contribution

Adiabatic

$$k = \sum_i k_i \frac{g_i}{Q_{electronic}}$$

Statistical

$$k = \min\left(\sum_i k_i(R) \frac{g_i}{Q_{electronic}}; R \right)$$

Ab Initio Electronic Structure

CASPT2 for TST Direct Sampling

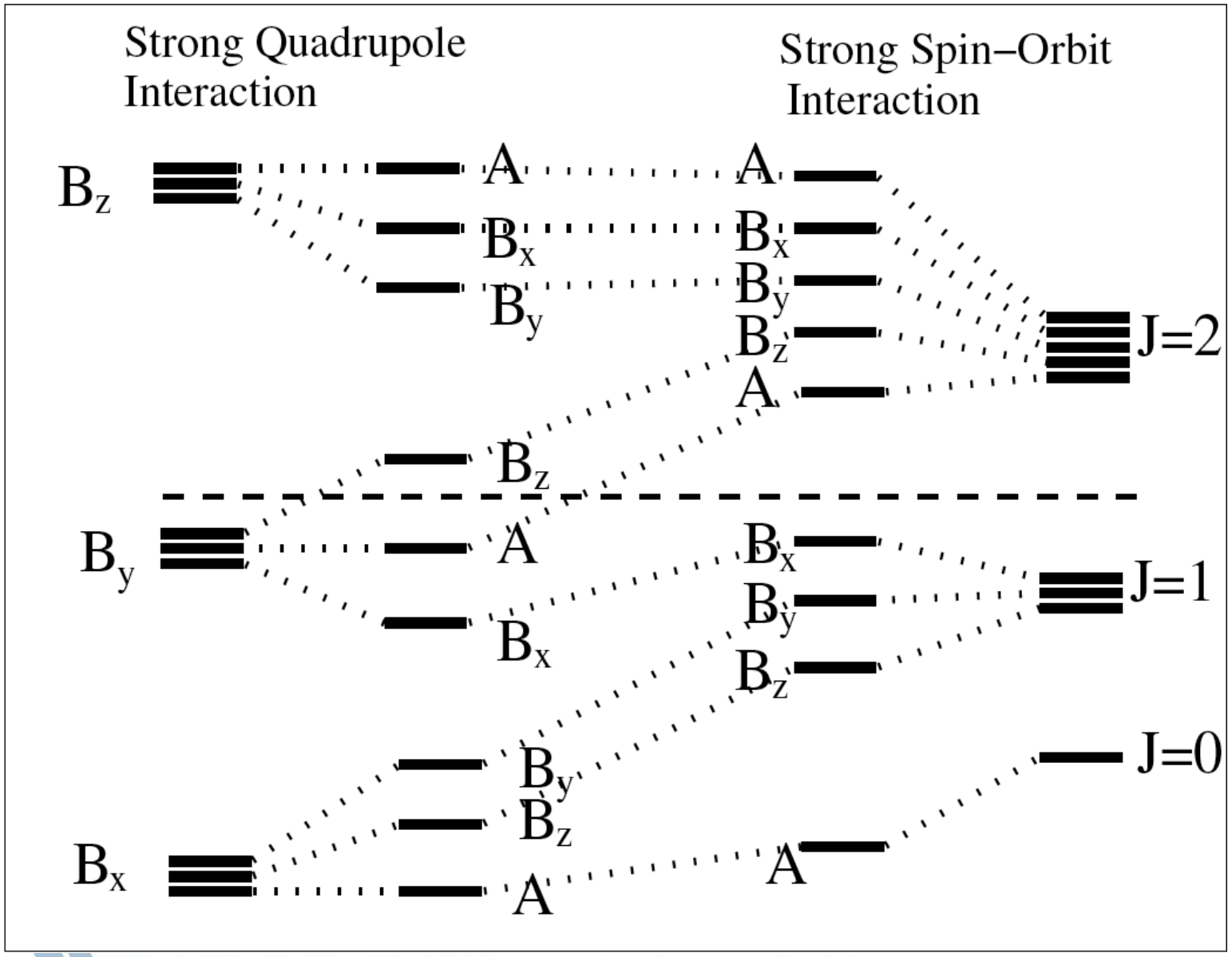
QCISD(T)/CBS for Stationary Points

Coupling of Quadrupolar and Spin-Orbit Interactions for (^{3}P) States

$$\hat{H} = \hat{V}_{dQ} - A\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}.$$

R	dQ − limit	T	SL − limit	T
A	$-3Qp_x + \frac{A^2}{3Q}(\frac{1}{p_y-p_x} + \frac{1}{p_z-p_x})$	R	$2A$	?
	$-3Qp_y + \frac{A^2}{3Q}(\frac{1}{p_x-p_y} + \frac{1}{p_z-p_y})$	A	$-A + \sqrt{\frac{3}{2}}Q\sqrt{p_x^2+p_y^2+p_z^2}$	R
	$-3Qp_z + \frac{A^2}{3Q}(\frac{1}{p_x-p_z} + \frac{1}{p_y-p_z})$	A	$-A - \sqrt{\frac{3}{2}}Q\sqrt{p_x^2+p_y^2+p_z^2}$	A
B_x	$-3Qp_y + \frac{A^2}{3Q}\frac{1}{p_z-p_y}$	A	$A + \frac{3}{2}Qp_x$	A
	$-3Qp_z + \frac{A^2}{3Q}\frac{1}{p_y-p_z}$	A	$-A + \frac{3}{2}Qp_x$	A
B_y	$-3Qp_x + \frac{A^2}{3Q}\frac{1}{p_z-p_x}$	R	$A + \frac{3}{2}Qp_y$	A
	$-3Qp_z + \frac{A^2}{3Q}\frac{1}{p_x-p_z}$	A	$-A + \frac{3}{2}Qp_y$	A
B_z	$-3Qp_x + \frac{A^2}{3Q}\frac{1}{p_y-p_x}$	R	$A + \frac{3}{2}Qp_z$	R
	$-3Qp_y + \frac{A^2}{3Q}\frac{1}{p_x-p_y}$	A	$-A + \frac{3}{2}Qp_z$	R

Correlation Diagram



$C(^3P)$

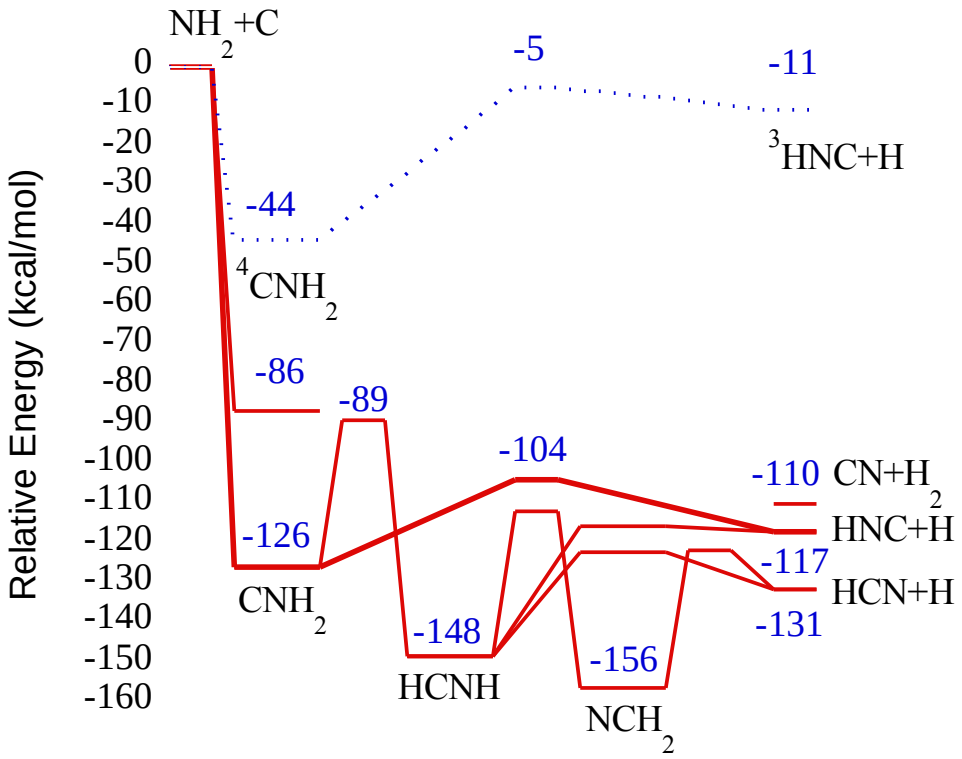
E = 20.8

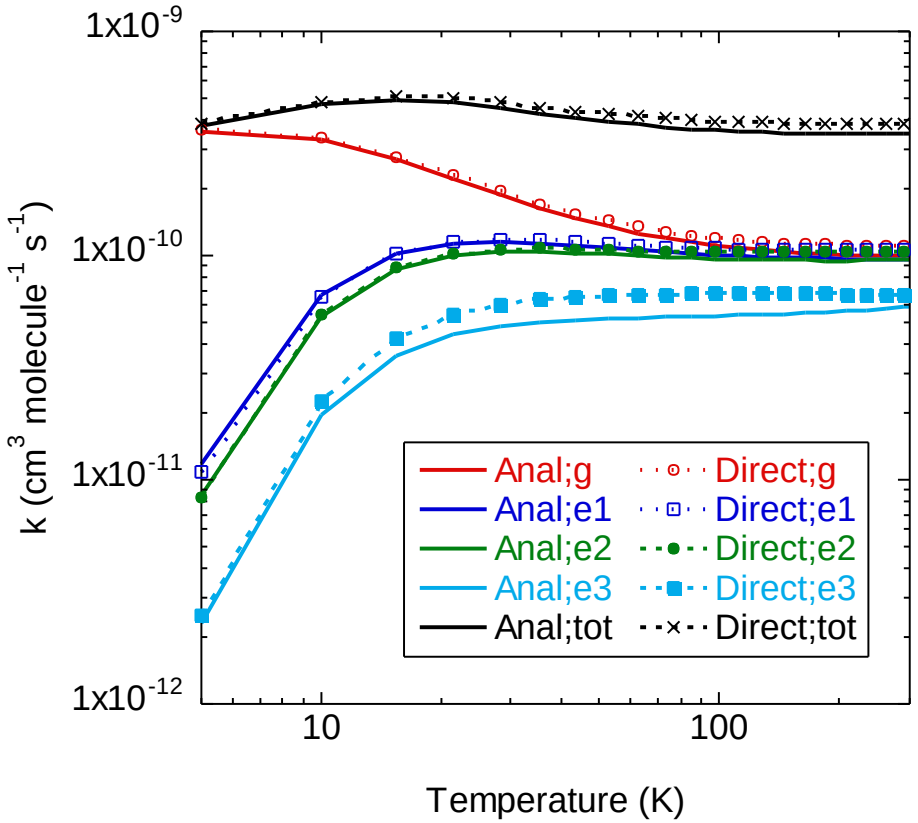
E = 0

E = -20.8

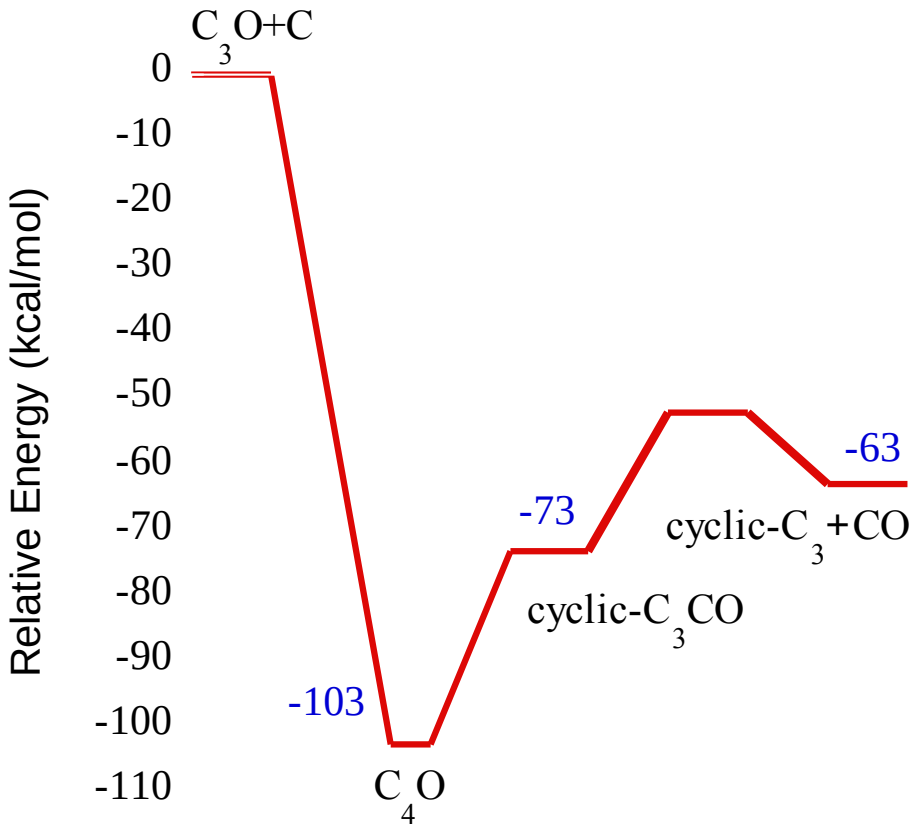
E = -41.6

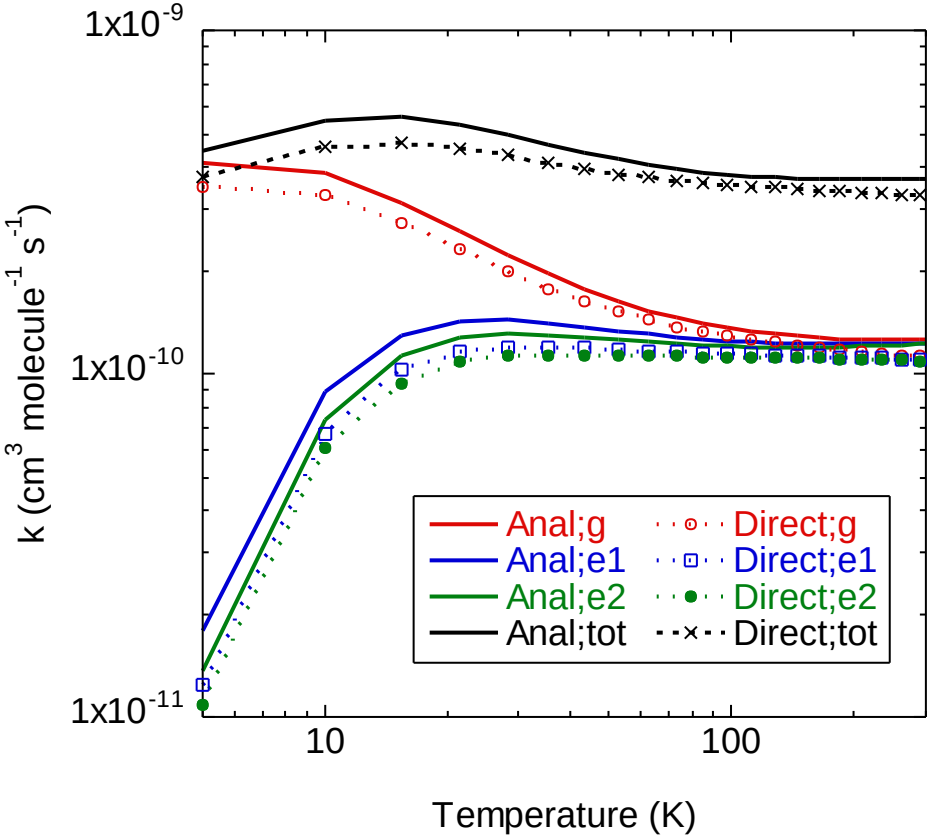
$C(^3P) + NH_2$


NH2+C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
Relative Energy (kcal/mol)
-5
-11
3HNC+H
-44
4CNH2
-86
-89
-104
-110
CN+H2
HNC+H
-126
-117
HCN+H
CNH2
-148
-131
HCNH
-156
NCH2

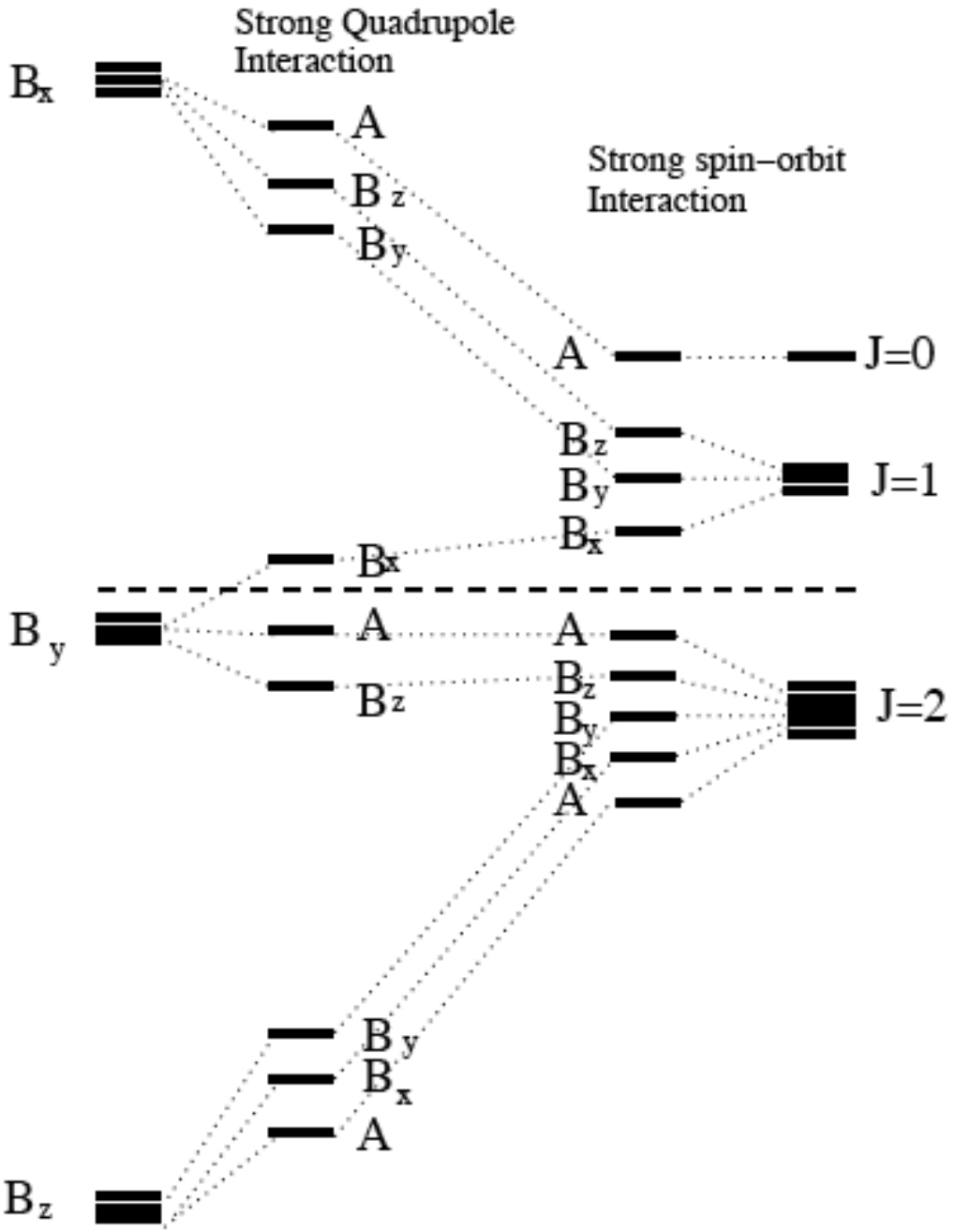

1x10-9
1x10-10
1x10-11
1x10-12
k (cm3 molecule-1 s-1)
10
100
Temperature (K)
Anal;g
Direct;g
Anal;e1
Direct;e1
Anal;e2
Direct;e2
Anal;e3
Direct;e3
Anal;tot
Direct;tot

$C(^3P) + C_3O$


C3O+C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
Relative Energy (kcal/mol)
-103
C4O
-73
cyclic-C3CO
-63
cyclic-C3+CO


1x10-9
1x10-10
1x10-11
k (cm3 molecule-1 s-1)
10
100
Temperature (K)
Anal;g
Anal;e1
Anal;e2
Anal;tot
Direct;g
Direct;e1
Direct;e2
Direct;tot

Correlation Diagram



$O(^3P)$

E = 230

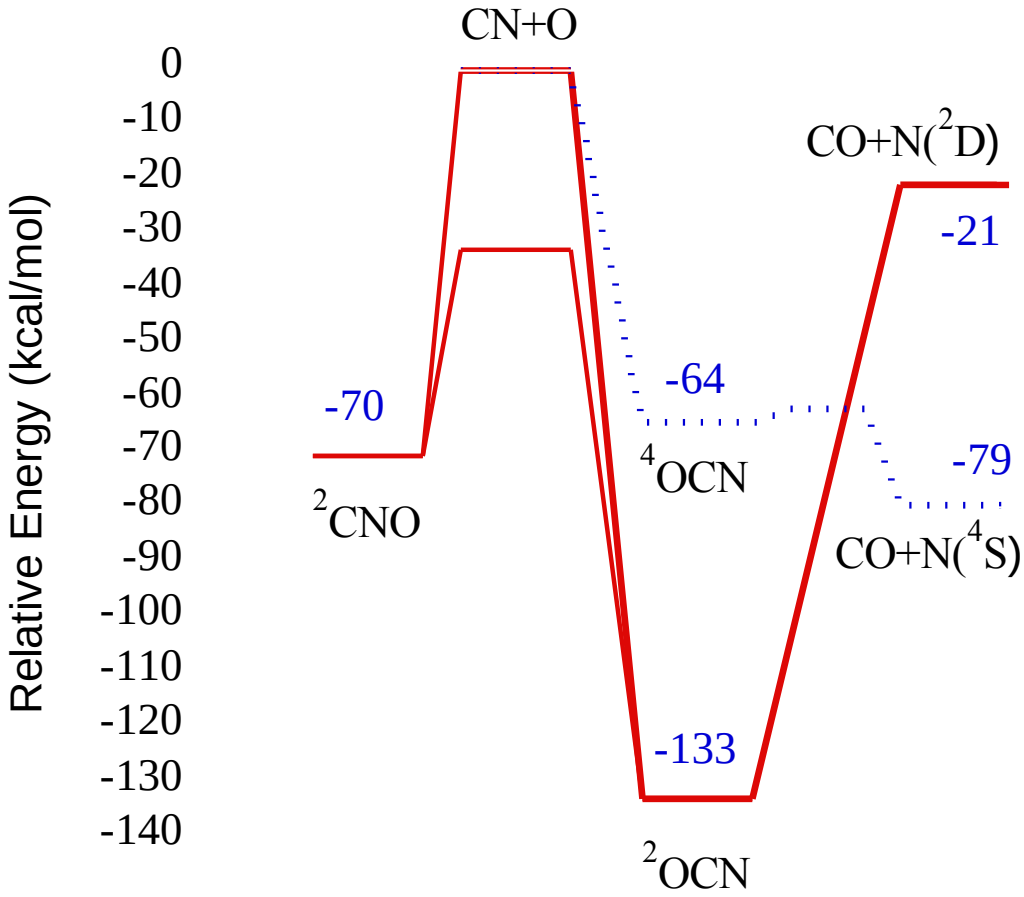
E = 115

E = 0

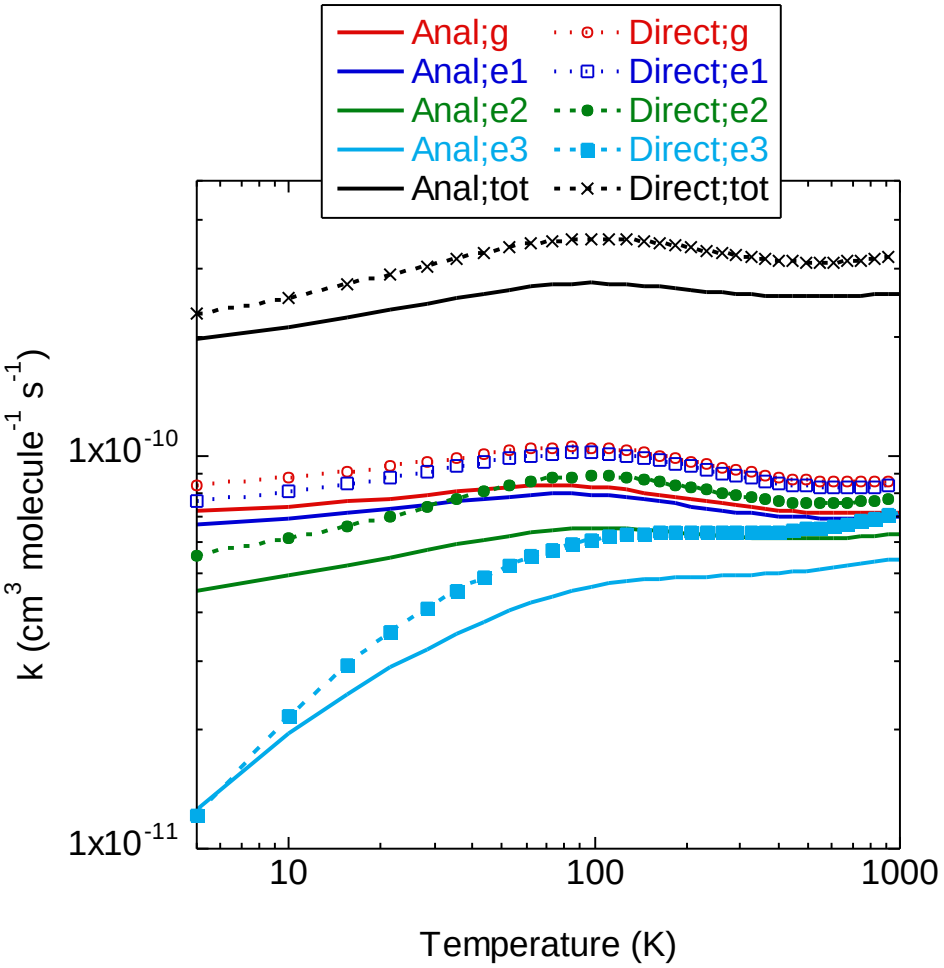
E = -115

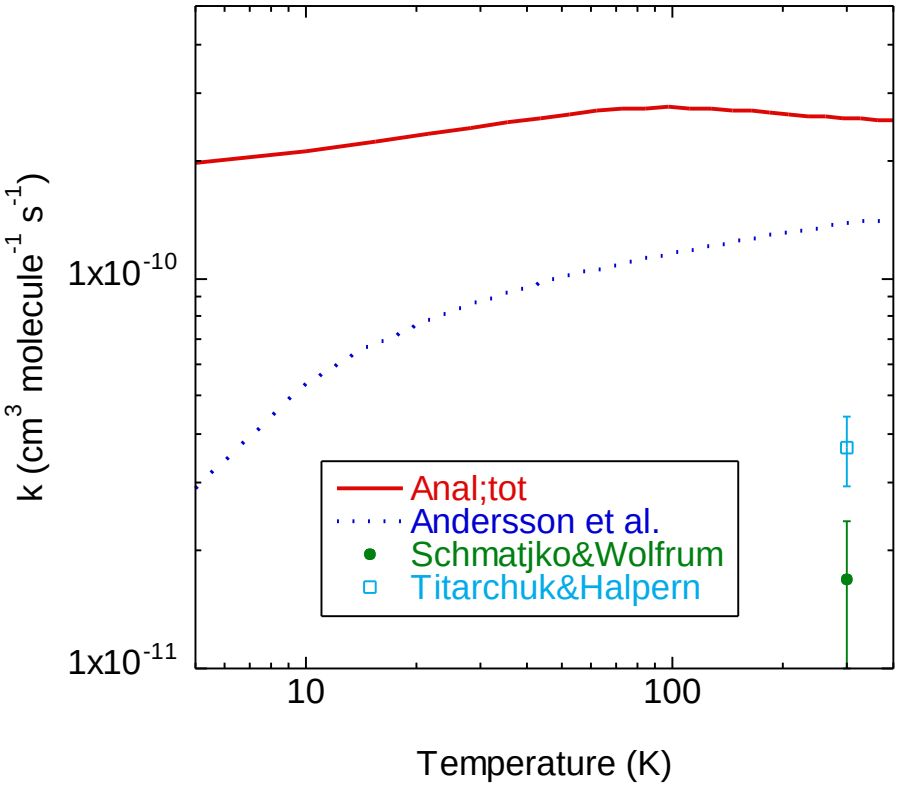
$O(^3P) + CN$

Andersson, Markovic, Nyman
Phys. Chem. Chem. Phys. 2, 613 (2000)
Andersson, Markovic, Nyman
J. Phys. Chem. A, 107, 5439 (2003)
Abrahamsson, Andersson, Markovic, Nyman
Phys. Chem. Chem. Phys. 10, 4400, (2008)

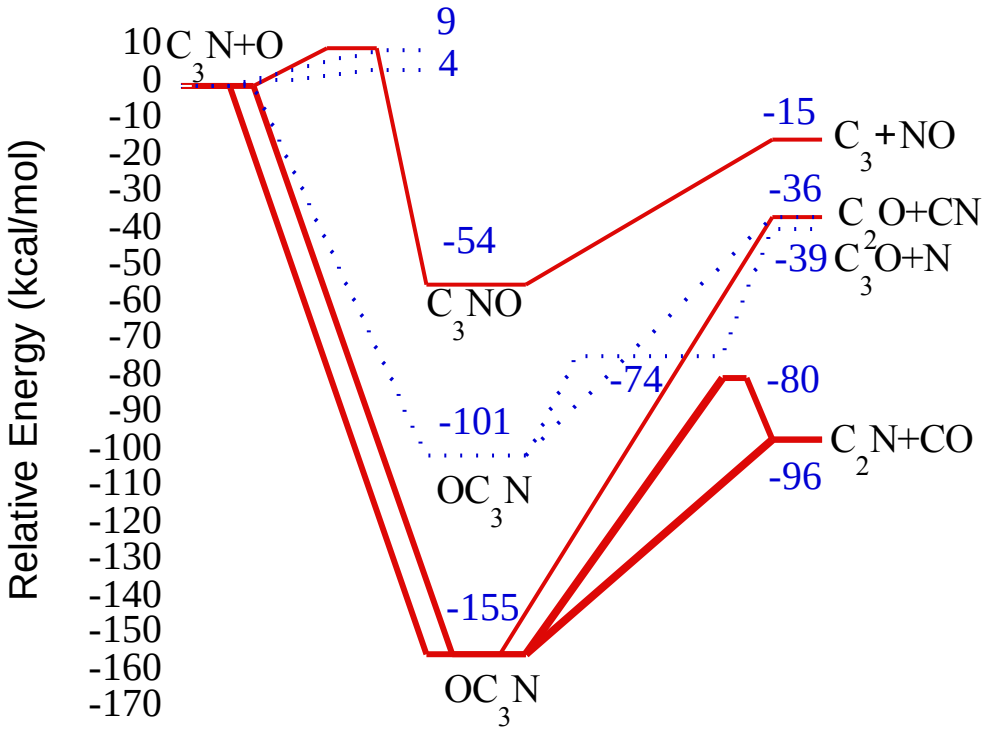


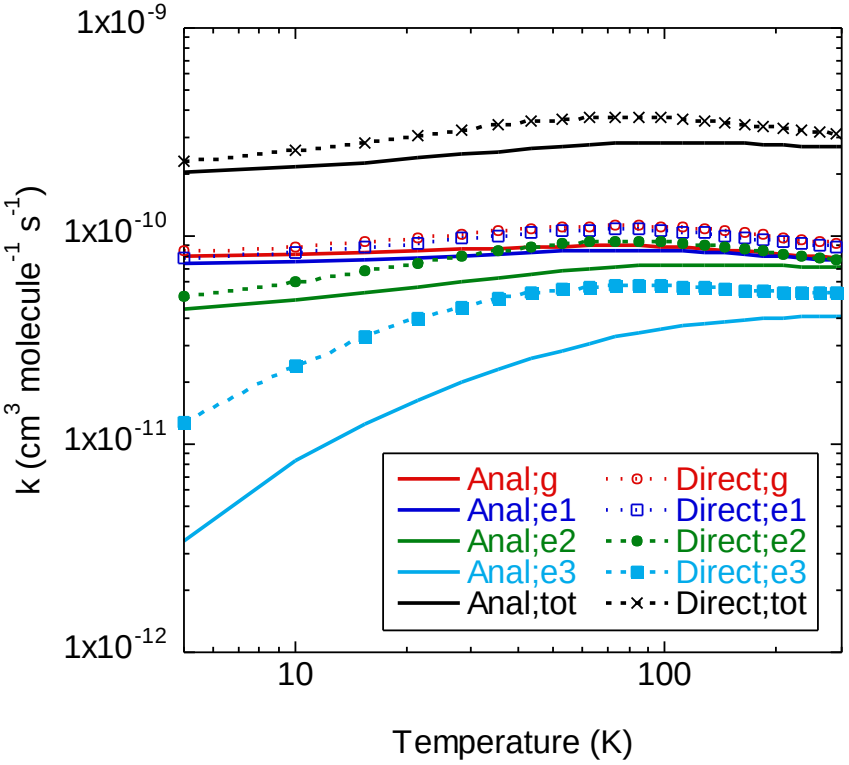
O(^{3}P) + CN


Anal;g
Anal;e1
Anal;e2
Anal;e3
Anal;tot
Direct;g
Direct;e1
Direct;e2
Direct;e3
Direct;tot
k (cm^3 molecule^{-1} s^{-1})
1x10^{-10}
1x10^{-11}
10
100
1000
Temperature (K)

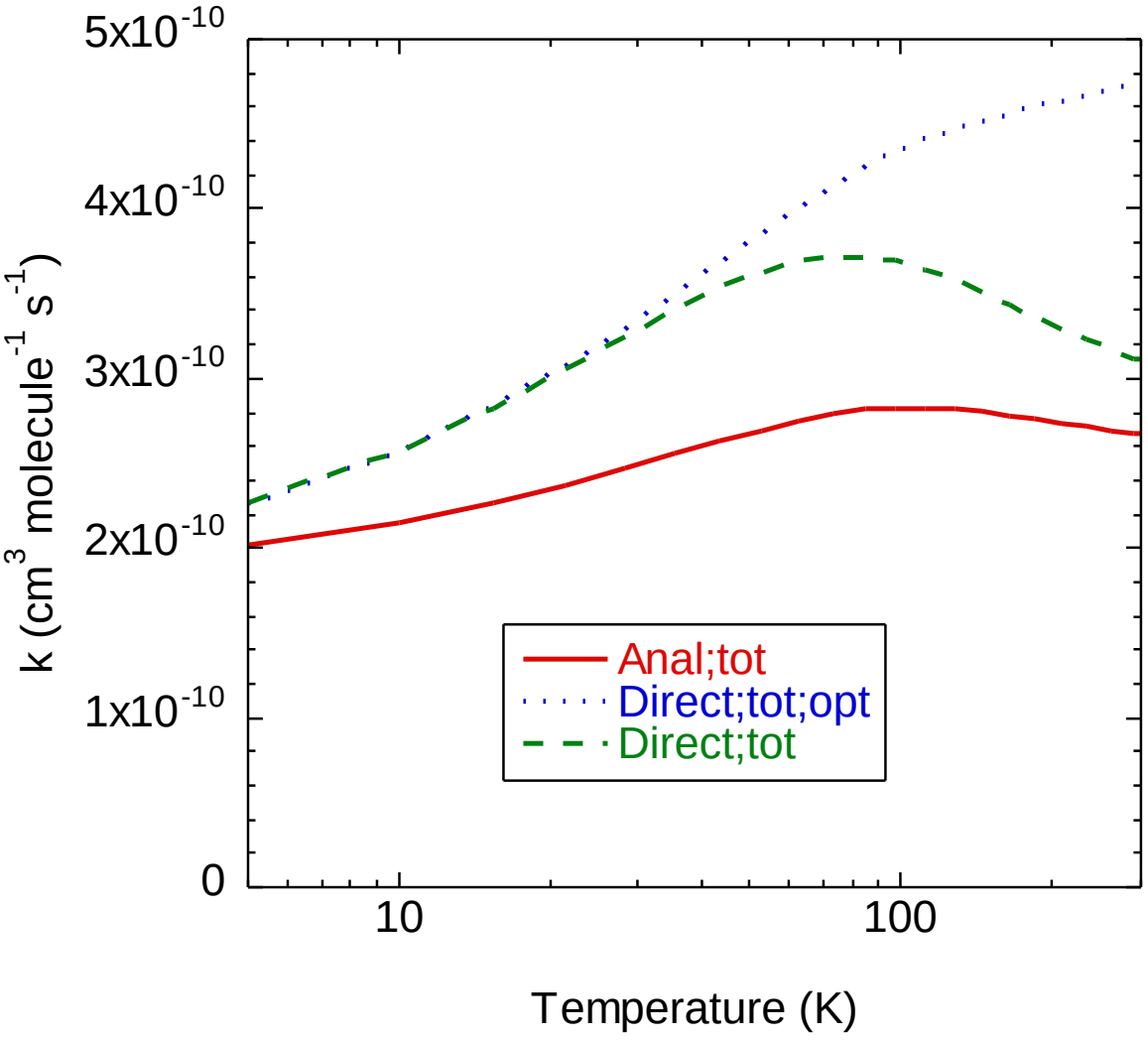

k (cm^3 molecule^{-1} s^{-1})
1x10^{-10}
1x10^{-11}
Anal;tot
Andersson et al.
Schmatjko&Wolfrum
Titarchuk&Halpern
10
100
Temperature (K)

$O(^3P) + C_3N$

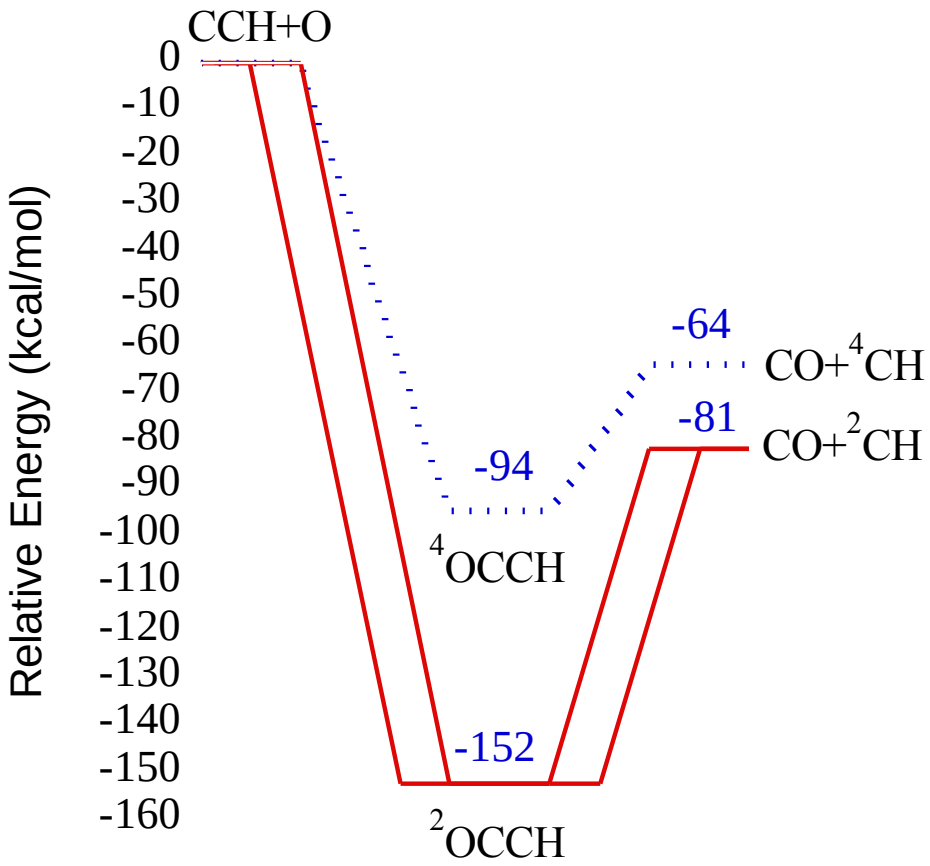

Relative Energy (kcal/mol)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
C3N+O
9
4
-15
C3+NO
-36
C2O+CN
-54
-39
C3O+N
C3NO
-74
-80
-101
C2N+CO
-96
OC3N
-155
OC3N

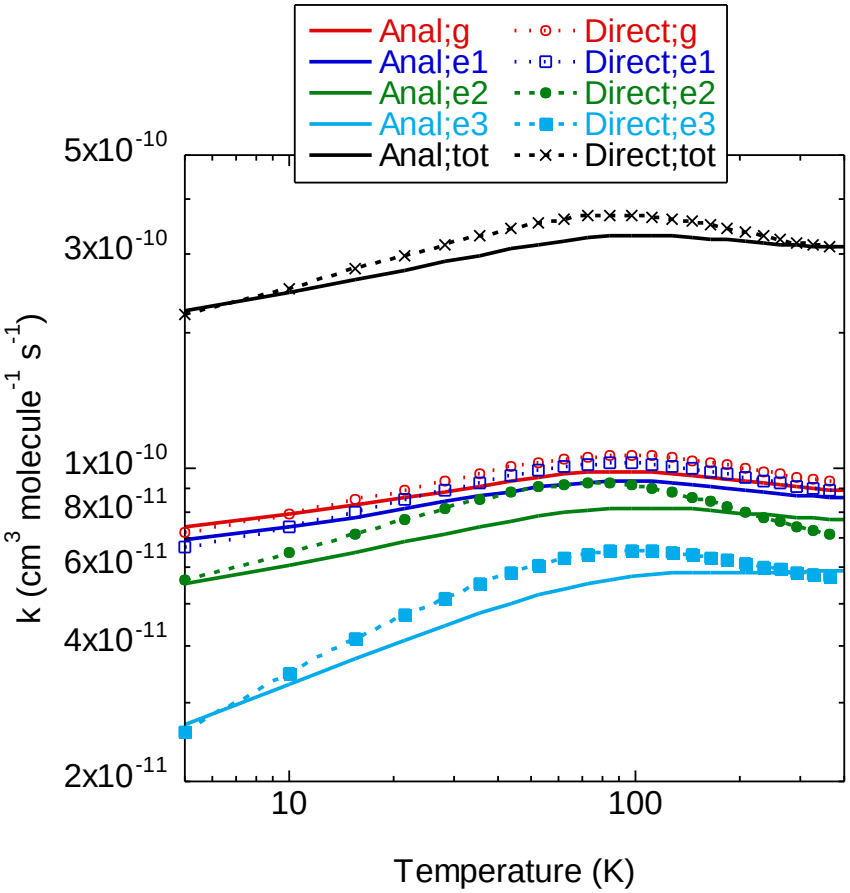

1x10-9
1x10-10
1x10-11
1x10-12
k (cm3 molecule-1 s-1)
10
100
Temperature (K)
Anal;g
Anal;e1
Anal;e2
Anal;e3
Anal;tot
Direct;g
Direct;e1
Direct;e2
Direct;e3
Direct;tot

$O(^3P) + C_3N$

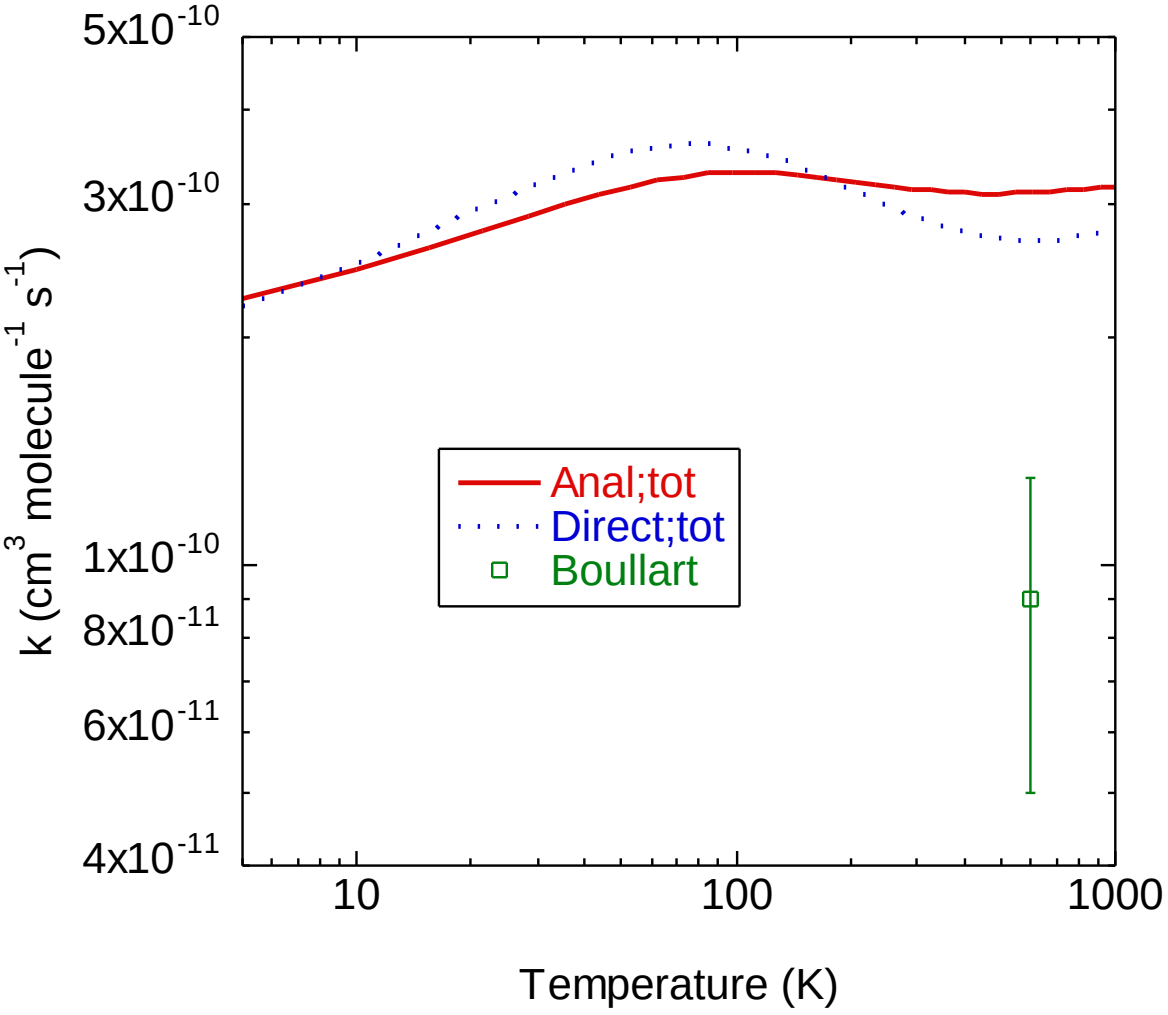

5x10-10
4x10-10
3x10-10
2x10-10
1x10-10
0
k (cm3 molecule-1 s-1)
10
100
Temperature (K)
Anal;tot
Direct;tot;opt
Direct;tot

$O(^3P) + C_2H$

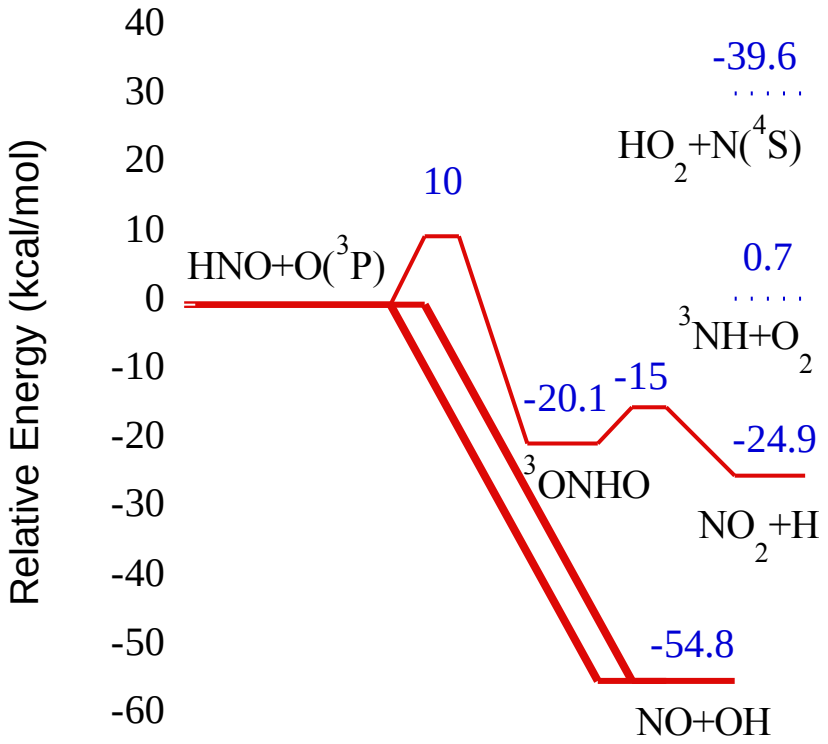

CCH+O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
Relative Energy (kcal/mol)
-64
CO+4CH
-81
CO+2CH
-94
4OCCH
-152
2OCCH

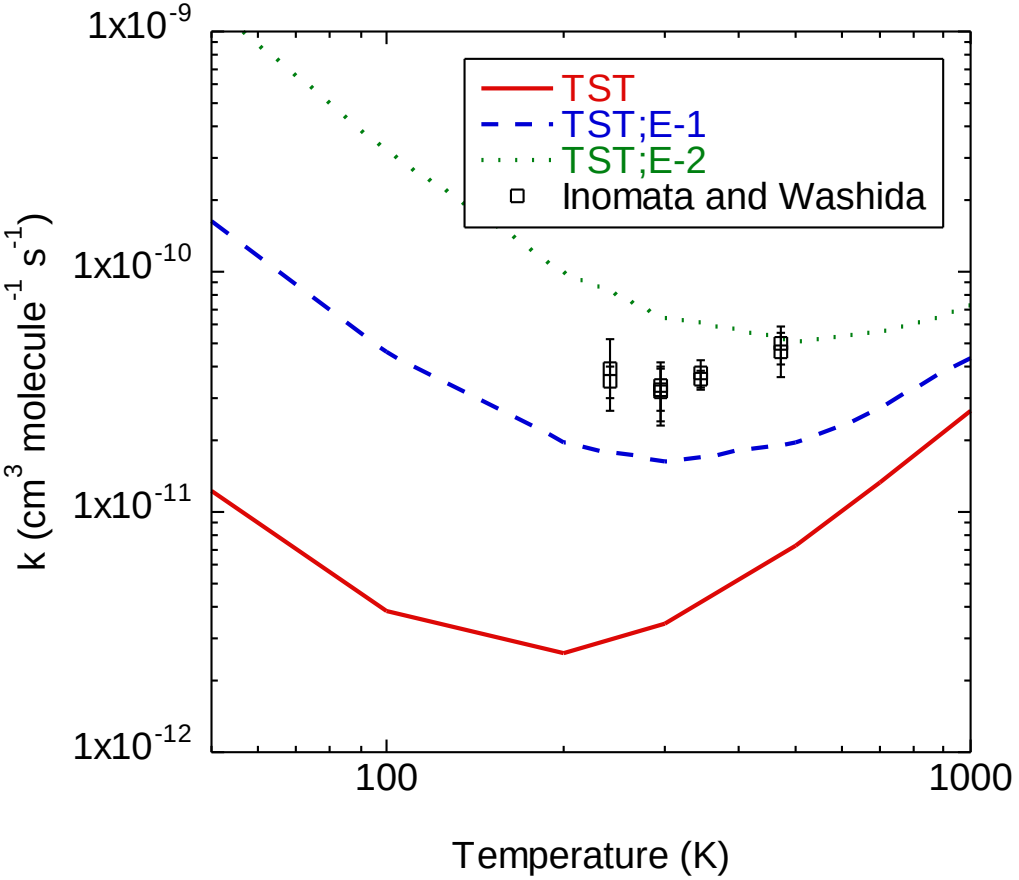

Anal;g
Anal;e1
Anal;e2
Anal;e3
Anal;tot
Direct;g
Direct;e1
Direct;e2
Direct;e3
Direct;tot
5x10-10
3x10-10
1x10-10
8x10-11
6x10-11
4x10-11
2x10-11
k (cm3 molecule-1 s-1)
10
100
Temperature (K)

$O(^3P) + C_2H$


5x10-10
3x10-10
1x10-10
8x10-11
6x10-11
4x10-11
k (cm3 molecule-1 s-1)
10
100
1000
Temperature (K)
Anal;tot
Direct;tot
Boullart

O(^{3}P) + HNO


Relative Energy (kcal/mol)
40
30
20
10
0
-10
-20
-30
-40
-50
-60
HNO+O(3P)
10
-20.1
-15
-24.9
-54.8
-39.6
0.7
HO2+N(4S)
3NH+O2
3ONHO
NO2+H
NO+OH


k (cm3 molecule-1 s-1)
1x10-9
1x10-10
1x10-11
1x10-12
100
1000
Temperature (K)
TST
TST;E-1
TST;E-2
Inomata and Washida

Low-Temperature Quantum Corrections

At low temperatures fragment rotations are no longer classical

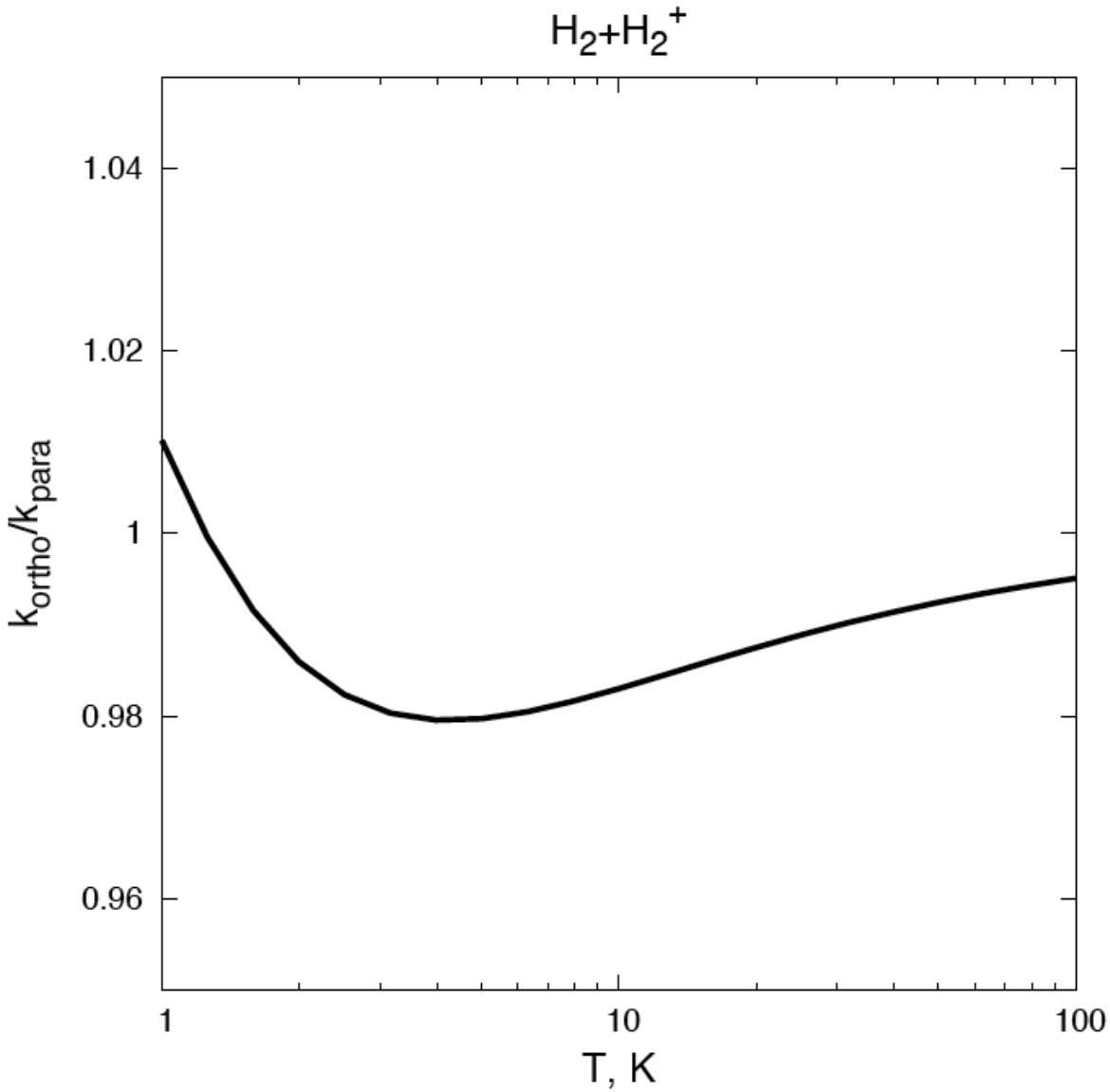
But orbital motions are still classical

$$N(E,J|R) = 2JN_{bf}\left(E - \frac{J^2}{2\mu R^2}|R\right)$$

Rate constant can be written in terms of sums over only fragment rotational states

Low T limit => just consider ground fragment rot. State

$H_2^+ + H_2$



Funding:

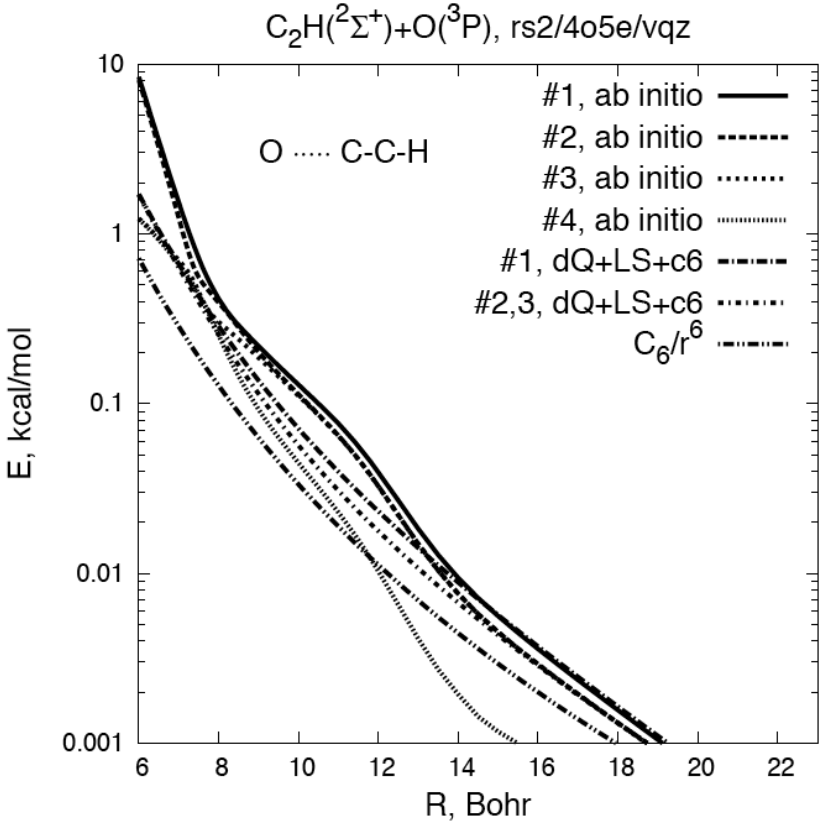
NASA (PATM)

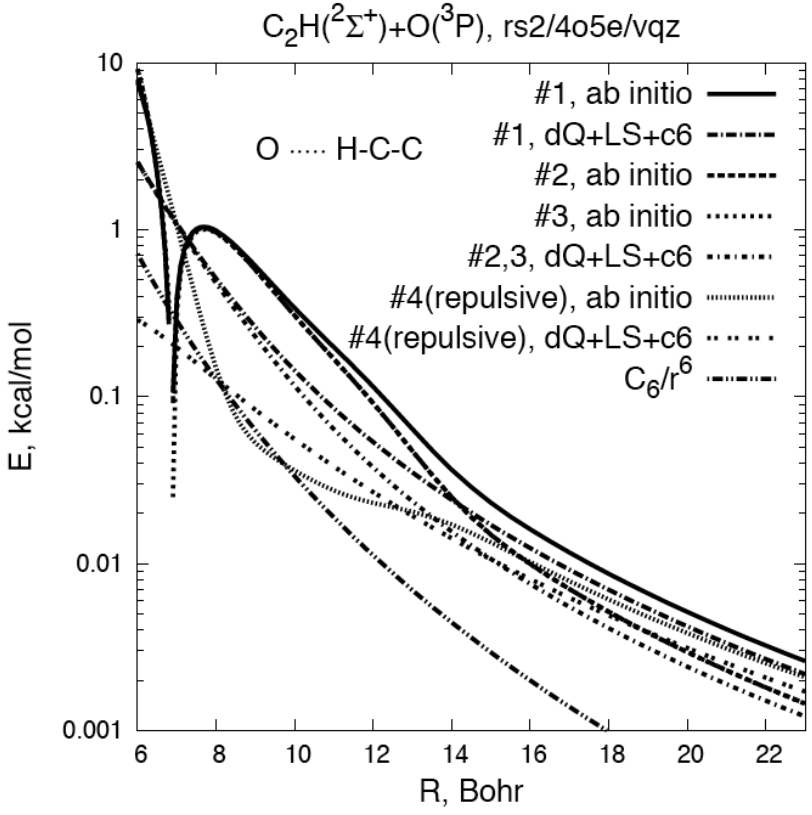
DOE – Computational Resources

Summary:

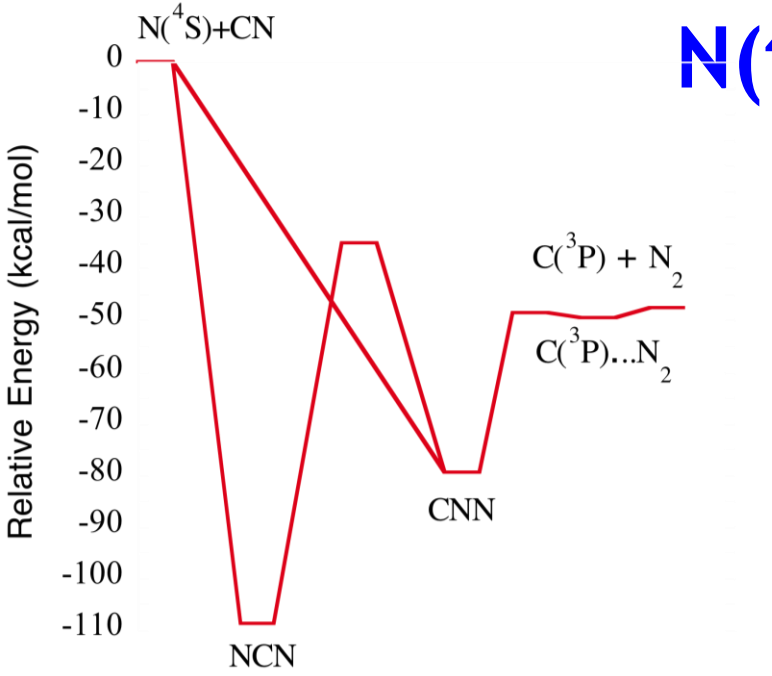
1. Long-range TST extended
2. Important to consider potential carefully
3. Analytic and direct sampling yield consistent results (within 10%)
4. Discrepancies between theory and experiment are not understood

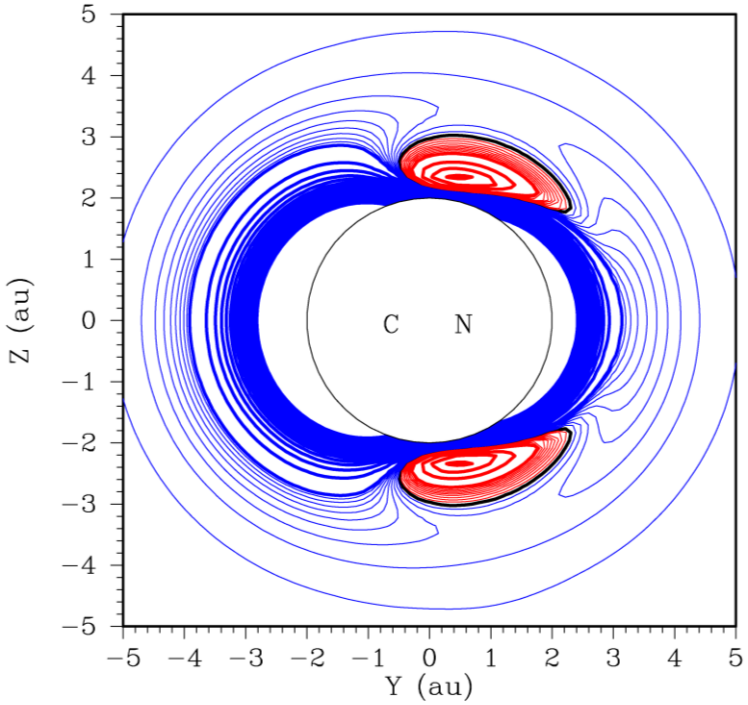
$O(^3P) + C_2H$

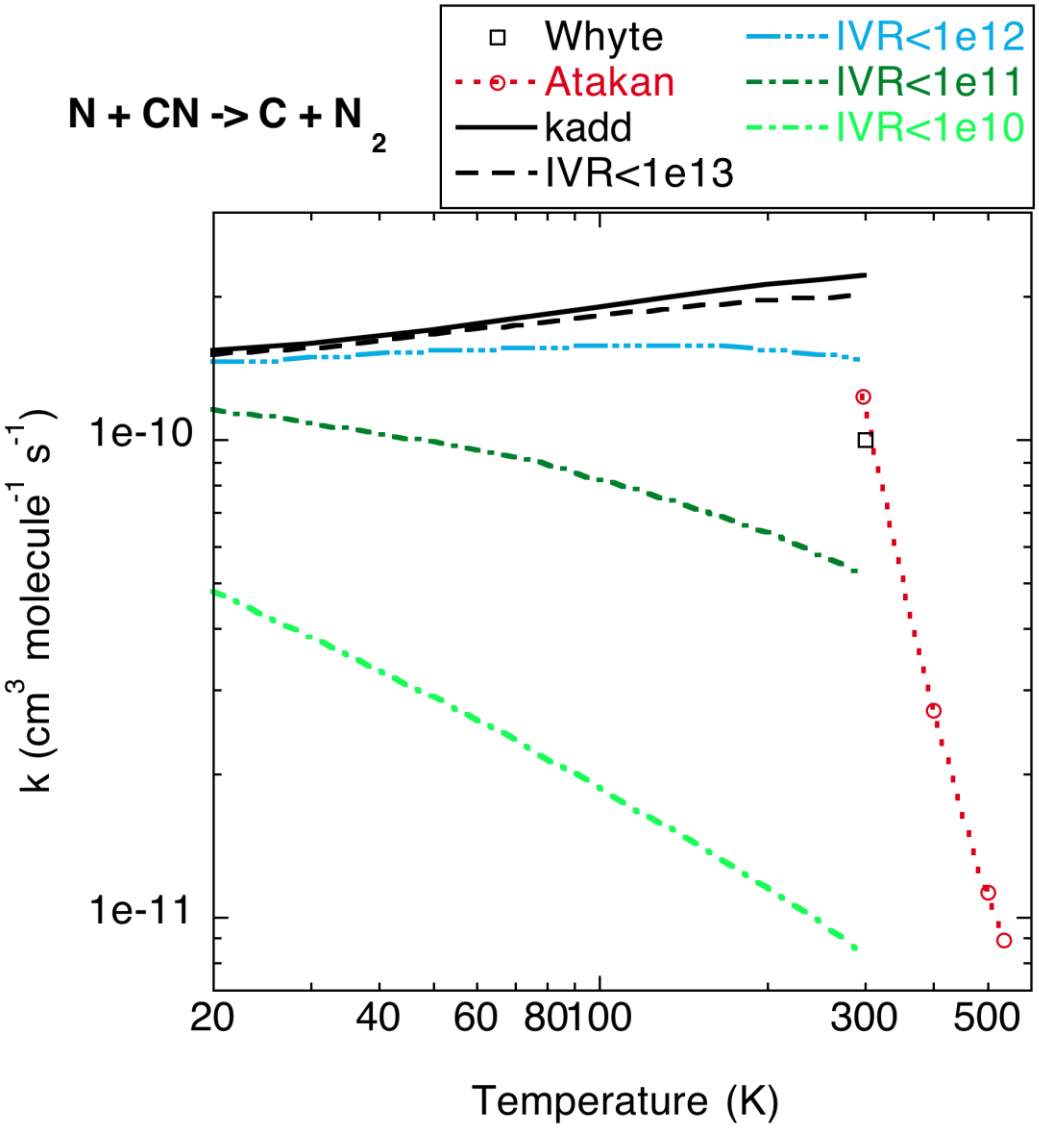

C2H(2Σ+)+O(3P), rs2/4o5e/vqz
O ····· C-C-H
#1, ab initio
#2, ab initio
#3, ab initio
#4, ab initio
#1, dQ+LS+c6
#2,3, dQ+LS+c6
C6/r6
E, kcal/mol
R, Bohr
10
1
0.1
0.01
0.001
6
8
10
12
14
16
18
20
22


C2H(2Σ+)+O(3P), rs2/4o5e/vqz
O ····· H-C-C
#1, ab initio
#1, dQ+LS+c6
#2, ab initio
#3, ab initio
#2,3, dQ+LS+c6
#4(repulsive), ab initio
#4(repulsive), dQ+LS+c6
C6/r6
E, kcal/mol
R, Bohr
10
1
0.1
0.01
0.001
6
8
10
12
14
16
18
20
22

N(4S) + CN


N(4S)+CN
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
Relative Energy (kcal/mol)
C(3P) + N2
C(3P)...N2
CNN
NCN


5
4
3
2
1
0
−1
−2
−3
−4
−5
Z (au)
C
N
−5 −4 −3 −2 −1 0 1 2 3 4 5
Y (au)


N + CN -> C + N2
Whyte
Atakan
kadd
IVR<1e13
IVR<1e12
IVR<1e11
IVR<1e10
k (cm3 molecule-1 s-1)
1e-10
1e-11
20
40
60
80
100
300
500
Temperature (K)