Supplementary Material

The $CH(X^2\Pi) + H_2O$ Reaction: Two Transition State Kinetics

Thanh Lam Nguyen[1]* and Jozef Peeters[2]*

[1]*Quantum Theory Project, Department of Chemistry and Physics, University of Florida, Gainesville, FL. 32611, USA.*

[2]*Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium.*

*Corresponding authors: tlam.nguyen@chem.ufl.edu and jozef.peeters@kuleuven.be

Table of contents:

Geometries and ro-vibrational parameters for various relevant species (optimized at fc-CCSD(T)/aug-cc-pVTZ)

PRC (C_1, X^2A)

CH_H2O
C
H 1 B1*
O 1 B2* 2 A1*
H 3 B3* 1 A2* 2 D1*
H 3 B4* 1 A3* 2 D2*

B1 = 1.115370714217354
B2 = 1.839497439991700
A1 = 91.116842944595064
B3 = 0.965394362954735
A2 = 96.563008220913886
D1 = -172.739909509340208
B4 = 0.966897794432377
A3 = 103.814717130473156
D2 = 79.766818377709370

Harmonic vibrational frequencies (cm-1) calculated with CCSD(T)/aVTZ

151.3961
341.2384
584.6504
622.1406
1136.924
1639.5719
2877.6137
3757.7486
3859.8917

External rotational constants (cm-1)

A =5.87548
B =0.62166
C =0.59166

Anharmonic constants (cm-1) at CCSD(T)/aVDZ

-82.2157								
-12.8706	-7.4088							
-4.1176	-18.2309	-12.1112						

-27.3888	-22.1073	-35.0092	-19.9396					
-77.075	-34.0612	-26.5325	-38.9710	-34.0593				
10.13	0.8005	7.2362	17.3444	1.0456	-13.1257			
27.5698	0.9636	1.2643	3.0212	-6.5597	-2.2912	-72.3865		
-1.6357	1.5280	-8.1791	-3.6946	1.2622	-20.4693	-0.5628	-46.2510	
-13.6121	1.4105	-5.3222	-8.2782	-2.9764	-25.8975	1.7975	-168.8253	-51.6533

TS1 (C_1, X^2A)

TS1
C
H 1 B1*
O 1 B2* 2 A1*
H 3 B3* 1 A2* 2 D1*
H 3 B4* 1 A3* 2 D2*

B1 = 1.096554067566681
B2 = 1.785805772565297
A1 = 97.752426758281459
B3 = 0.969520779015062
A2 = 100.625344863703319
D1 = -129.230939433929933
B4 = 1.141932165401778
A3 = 47.452978263753600
D2 = 136.524882512374290

Harmonic vibrational frequencies (cm^{-1})

1503.2756i
(331.3324)
506.7877
800.9299
1071.714
1365.8921
2244.2936
3068.8453
3761.5708

Note: Eigenvalues of the 1D Hindered Rotation mode (see Fig. S3) replace the torsional frequency of 331 cm-1

External rotational constants (cm^{-1})

A =6.38022
B =0.66967
C =0.64616

Anharmonic constants (cm^{-1}) calculated with fc-CCSD(T)/aVTZ level of theory

-153.2556								
-40.3636i	17.4747							
11.3649i	-64.9378	16.0387						
16.4897i	0.9410	5.1708	-5.9393					
-0.6400i	-16.4235	-6.9867	-15.5287	-13.9594				
-35.2254i	-37.4949	-38.3725	-25.7937	-28.8313	-23.6153			
-227.1695i	-9.5050	13.1666	-13.3263	-8.1187	-18.2011	-34.0760		
22.9666i	3.7938	9.9473	5.0673	-8.0479	5.3454	-4.5517	-64.2620	
-6.0473i	-2.0579	-3.3073	-18.0450	-1.9272	-15.1733	1.2328	-1.4341	-81.7572

CH_2O (C_{2v}, X^1A_1)

CH2O
O
C 1 R1*
H 2 R2* 1 A1*
H 2 R2* 1 A1* 3 T180

R1 = 1.211515087382290
R2 = 1.103061904375071
A1 = 121.714028216910862
T180 = 180.000000000000000

Harmonic vibrational frequencies (cm^{-1})

1181.2346
1261.8602
1529.5951
1765.3231
2932.2521
3000.2530

Rotational constants (cm-1)

A =9.49832
B =1.28627

C =1.13286

Anharmonic constants (cm^{-1})

-2.2616					
6.9695	-1.8298				
0.3649	-18.2100	0.5245			
-7.1521	94.5140	-7.3284	-9.5293		
-7.6579	-8.1305	-31.9415	-2.3062	-31.6632	
-19.2336	-110.0806	-12.9343	-102.2618	-130.4032	-36.3678

H_2O (C_{2v},X^1A_1)

H2O
O
H 1 R1*
H 1 R1* 2 A1*

R1 = 0.961579640410436
A1 = 104.179636130297880

Harmonic vibrational frequencies (cm^{-1})

1645.9102
3810.8181
3919.9216

Rotational constants (cm^{-1})

A =26.97851
B =14.53063
C =9.44406

Anharmonic constants (cm^{-1})

-16.2447		
-15.2627	-41.9580	
-19.9830	-162.0977	-47.7829

CH ($C_{\infty v}$,$X^2\Pi$)

C
H 1 B1

B1 = 1.121937531368334

Spectroscopic parameters

Theory/Exptl	B(2D) / cm^{-1}	freq (cm^{-1})	Xii (cm^{-1})
CCSD(T)/aVTZ	14.40448	2843.3353	-62.6919
Exptl. (NIST)	14.457	2858.5	-63.02

and $\Delta E_{AO}(CH) = 28\ cm^{-1}$

Table S1: Selected ceiling energy, angular momentum, and collisional parameters of van der Waals Complex of CH and H_2O (PRC) with the bath gas, Air.

Molecule / Parameter	Values
Complex (PRC): H_2O---CH	mass = 31.0 g/mol, σ = 3.63 Å, and ε/k_B = 481.0 K[1, 2]
Air	mass = 28.8 g/mol, σ = 3.688 Å, and ε/k_B = 86.2 K[3]
E_{max}: maximum energy	from 10,000 to 30,000 cm^{-1}
ΔE: energy grain	from 1 to 10 cm^{-1}
J_{max}: maximum angular momentum	from 100 to 200
ΔJ: step size of angular momentum	from 1 to 5
$\langle \Delta E \rangle_d$ in cm^{-1}: average amount of energy transferred per collision in a downward direction[1, 2]	$\langle \Delta E \rangle_d = 1.2 \times \left(\frac{T}{300}\right)^{0.76}$ $\langle \Delta E \rangle_d = 4.0 \times \left(\frac{T}{300}\right)^{0.76}$

1. E. E. Dames and D. M. Golden, *J Phys Chem A*, 2013, **117**, 7686-7696.
2. H. Hippler, F. Striebel and B. Viskolcz, *Phys Chem Chem Phys*, 2001, **3**, 2450-2458.
3. J. R. Barker, T. L. Nguyen, J. F. Stanton, C. Aieta, M. Ceotto, F. Gabas, T. J. D. Kumar, C. G. L. Li, L. L. Lohr, A. Maranzana, N. F. Ortiz, J. M. Preses, J. M. Simmie, J. A. Sonk and P. J. Stimac, *Multiwell software package*, Jan. 2021.

Table S2: Calculated rate constants (cm^3/s) from first-principles for a wide temperature range between 50 K and 3500 K

T (K)	1000/T (1/K)	k(T,P=0) / cm^3/s
50	20	1.91498E-10
52	19.23076923	1.85527E-10
54	18.51851852	1.79759E-10
56	17.85714286	1.74192E-10
58	17.24137931	1.68825E-10
60	16.66666667	1.63655E-10
62	16.12903226	1.58678E-10
64	15.625	1.53888E-10
66	15.15151515	1.49281E-10
68	14.70588235	1.4485E-10
70	14.28571429	1.4059E-10
72	13.88888889	1.36492E-10
74	13.51351351	1.32554E-10
76	13.15789474	1.28767E-10
78	12.82051282	1.25127E-10
80	12.5	1.21626E-10
82	12.19512195	1.1826E-10
84	11.9047619	1.15021E-10
86	11.62790698	1.11905E-10
88	11.36363636	1.08907E-10
90	11.11111111	1.06021E-10
92	10.86956522	1.03244E-10
94	10.63829787	1.00569E-10
96	10.41666667	9.79931E-11
98	10.20408163	9.55109E-11
100	10	9.31195E-11
105	9.523809524	8.75088E-11
110	9.090909091	8.23809E-11
115	8.695652174	7.76869E-11
120	8.333333333	7.33812E-11
125	8	6.94252E-11
130	7.692307692	6.57839E-11
135	7.407407407	6.24263E-11
140	7.142857143	5.93251E-11

145	6.896551724	5.64559E-11
150	6.666666667	5.37974E-11
155	6.451612903	5.133E-11
160	6.25	4.90367E-11
165	6.060606061	4.6902E-11
170	5.882352941	4.49118E-11
175	5.714285714	4.30544E-11
180	5.555555556	4.13182E-11
185	5.405405405	3.96935E-11
190	5.263157895	3.8171E-11
195	5.128205128	3.67426E-11
200	5	3.54011E-11
205	4.87804878	3.41397E-11
210	4.761904762	3.29523E-11
215	4.651162791	3.18336E-11
220	4.545454545	3.07784E-11
225	4.444444444	2.9782E-11
230	4.347826087	2.88404E-11
235	4.255319149	2.79498E-11
240	4.166666667	2.71067E-11
245	4.081632653	2.63077E-11
250	4	2.55502E-11
255	3.921568627	2.48311E-11
260	3.846153846	2.41482E-11
265	3.773584906	2.3499E-11
270	3.703703704	2.28814E-11
275	3.636363636	2.22937E-11
280	3.571428571	2.17338E-11
285	3.50877193	2.12E-11
290	3.448275862	2.0691E-11
295	3.389830508	2.02052E-11
300	3.333333333	1.97412E-11
325	3.076923077	1.77112E-11
350	2.857142857	1.60521E-11
375	2.666666667	1.47007E-11
400	2.5	1.35886E-11
425	2.352941176	1.26658E-11
450	2.222222222	1.18945E-11
475	2.105263158	1.12463E-11

500	2	1.06989E-11
525	1.904761905	1.02354E-11
550	1.818181818	9.84197E-12
575	1.739130435	9.50796E-12
600	1.666666667	9.22458E-12
625	1.6	8.98475E-12
650	1.538461538	8.78266E-12
675	1.481481481	8.61355E-12
700	1.428571429	8.47348E-12
725	1.379310345	8.35909E-12
750	1.333333333	8.26757E-12
775	1.290322581	8.19657E-12
800	1.25	8.14411E-12
825	1.212121212	8.1084E-12
850	1.176470588	8.08804E-12
875	1.142857143	8.08173E-12
900	1.111111111	8.08838E-12
925	1.081081081	8.10701E-12
950	1.052631579	8.13682E-12
975	1.025641026	8.17709E-12
1000	1	8.22718E-12
1025	0.975609756	8.28653E-12
1050	0.952380952	8.35471E-12
1075	0.930232558	8.43121E-12
1100	0.909090909	8.51574E-12
1125	0.888888889	8.60788E-12
1150	0.869565217	8.70744E-12
1175	0.85106383	8.81407E-12
1200	0.833333333	8.92763E-12
1225	0.816326531	9.04786E-12
1250	0.8	9.17464E-12
1275	0.784313725	9.30779E-12
1300	0.769230769	9.44719E-12
1325	0.754716981	9.59273E-12
1350	0.740740741	9.74422E-12
1375	0.727272727	9.90182E-12
1400	0.714285714	1.00652E-11
1425	0.701754386	1.02345E-11
1450	0.689655172	1.04095E-11

1475	0.677966102	1.05904E-11
1500	0.666666667	1.07769E-11
1525	0.655737705	1.09691E-11
1550	0.64516129	1.11671E-11
1575	0.634920635	1.13709E-11
1600	0.625	1.15803E-11
1625	0.615384615	1.17955E-11
1650	0.606060606	1.20165E-11
1675	0.597014925	1.22433E-11
1700	0.588235294	1.24758E-11
1725	0.579710145	1.27143E-11
1750	0.571428571	1.29587E-11
1775	0.563380282	1.3209E-11
1800	0.555555556	1.34655E-11
1825	0.547945205	1.37279E-11
1850	0.540540541	1.39966E-11
1875	0.533333333	1.42714E-11
1900	0.526315789	1.45525E-11
1925	0.519480519	1.484E-11
1950	0.512820513	1.51339E-11
1975	0.506329114	1.54343E-11
2000	0.5	1.57414E-11
2025	0.49382716	1.60552E-11
2050	0.487804878	1.63757E-11
2075	0.481927711	1.67031E-11
2100	0.476190476	1.70375E-11
2125	0.470588235	1.7379E-11
2150	0.465116279	1.77276E-11
2175	0.459770115	1.80835E-11
2200	0.454545455	1.84468E-11
2225	0.449438202	1.88174E-11
2250	0.444444444	1.91957E-11
2275	0.43956044	1.95817E-11
2300	0.434782609	1.99753E-11
2325	0.430107527	2.03769E-11
2350	0.425531915	2.07864E-11
2375	0.421052632	2.1204E-11
2400	0.416666667	2.16298E-11
2425	0.412371134	2.20638E-11

2450	0.408163265	2.2506E-11
2475	0.404040404	2.29569E-11
2500	0.4	2.34163E-11
2525	0.396039604	2.38843E-11
2550	0.392156863	2.43611E-11
2575	0.388349515	2.48466E-11
2600	0.384615385	2.5341E-11
2650	0.377358491	2.63569E-11
2700	0.37037037	2.74093E-11
2750	0.363636364	2.84987E-11
2800	0.357142857	2.96256E-11
2850	0.350877193	3.07904E-11
2900	0.344827586	3.19935E-11
2950	0.338983051	3.32349E-11
3000	0.333333333	3.4515E-11
3050	0.327868852	3.58336E-11
3100	0.322580645	3.71908E-11
3150	0.317460317	3.85861E-11
3200	0.3125	4.00196E-11
3250	0.307692308	4.14905E-11
3300	0.303030303	4.29986E-11
3350	0.298507463	4.45429E-11
3400	0.294117647	4.61229E-11
3450	0.289855072	4.77373E-11
3500	0.285714286	4.93853E-11

Table S3: Energy levels for the coupling of the 2D rotation and the electronic motion in CH, calculated using Hill and Van Vleck's formalism.

Rotational Zero-Energy Level= 5.45831 (cm^{-1})

Index	n_{F1}	F_1(J=K+1/2)	n_{F2}	F_2(J=K-1/2)
1	8	0.00000	4	22.99135
2	12	60.32298	8	75.76140
3	16	148.37087	12	159.79816
4	20	264.58740	16	273.61033
5	24	409.07123	20	416.51054
6	28	581.76426	24	588.08697
7	32	782.51999	28	788.01488
8	36	1011.13098	32	1015.98841
9	40	1267.34120	36	1271.69297
10	44	1550.85196	40	1554.79300
11	48	1861.32509	44	1864.92599
12	52	2198.38467	48	2201.69930
13	56	2561.61806	52	2564.68847
14	60	2950.57650	56	2953.43614
15	64	3364.77555	60	3367.45145
16	68	3803.69534	64	3806.20964
17	72	4266.78072	68	4269.15180
18	76	4753.44140	72	4755.68467
19	80	5263.05202	76	5265.18055
20	84	5794.95224	80	5796.97717
21	88	6348.44676	84	6350.37770
22	92	6922.80535	88	6924.65064
23	96	7517.26290	92	7519.02980
24	100	8131.01940	96	8132.71430
25	104	8763.24001	100	8764.86854
26	108	9413.05502	104	9414.62218
27	112	10079.55988	108	10081.07012
28	116	10761.81520	112	10763.27252
29	120	11458.84678	116	11460.25474
30	124	12169.64557	120	12171.00742
31	128	12893.16772	124	12894.48638
32	132	13628.33455	128	13629.61268
33	136	14374.03259	132	14375.27259
34	140	15129.11352	136	15130.31761
35	144	15892.39423	140	15893.56443
36	148	16662.65681	144	16663.79496
37	152	17438.64851	148	17439.75634
38	156	18219.08181	152	18220.16088
39	160	19002.63436	156	19003.68613
40	164	19787.94902	160	19788.97483
41	168	20573.63382	164	20574.63493
42	172	21358.26201	168	21359.23958
43	176	22140.37203	172	22141.32714

44	180	22918.46751	176	22919.40117
45	184	23691.01729	180	23691.93043
46	188	24456.45539	184	24457.34891
47	192	25213.18104	188	25214.05575
48	196	25959.55867	192	25960.41535
49	200	26693.91789	196	26694.75728
50	204	27414.55353	200	27415.37630

Table S4: Ro-vibrational parameters for grid points calculated along the reaction coordinate of the barrier-less association of CH and H_2O.

HC--OH_2=3 Å	3.1 Å	3.2 Å	3.3 Å	3.4 Å	3.5 Å	3.6 Å	3.7 Å	3.8 Å	3.9 Å
76.7504	74.1245	70.8000	70.2423	76.4689	73.6544	66.7191	67.7378	66.6701	65.1468
161.0056	141.9389	125.3327	111.0430	97.9966	84.6367	76.2831	67.8510	71.7809	71.2491
173.4826	158.9712	147.3800	135.6529	126.9398	118.5733	110.4205	105.8534	119.7897	119.0828
338.6108	304.7243	274.2258	246.4668	220.4794	194.9028	166.4939	218.9887	212.9114	206.0997
1647.6367	1647.3546	1646.8299	1646.0359	1644.8510	1643.0791	1640.1110	1618.5004	1618.3952	1618.4787
2863.1967	2860.4219	2857.6940	2854.8834	2851.7550	2847.9275	2842.2585	2803.1407	2794.8878	2789.0779
3800.1104	3801.6735	3802.7737	3803.3623	3803.3646	3802.5779	3800.4301	3780.4169	3780.8345	3781.2149
3906.8261	3908.9948	3910.8707	3912.5522	3913.9925	3915.2119	3916.3501	3917.9586	3918.4311	3918.6898
A= 5.78096	5.81787	5.87470	5.96008	6.09121	6.30445	6.71907	14.49973	14.50304	14.50839
B=0.24470	0.22933	0.21529	0.20247	0.19075	0.18000	0.17011	0.16204	0.15372	0.14602
C=0.24261	0.22754	0.21379	0.20124	0.18979	0.17933	0.16979	0.16025	0.15211	0.14456

Continued

4.0 Å	4.5 Å	5.0 Å	5.5 Å	6.0 Å	6.5 Å	7.0 Å	7.5 Å	8.0 Å	8.5 Å
57.8479	51.9207	50.5289	46.8134	40.4720	35.2596	31.1672	28.0342	25.1329	22.8139
71.9842	63.2478	54.5334	47.3388	42.3497	37.3431	32.8901	29.2341	26.6537	24.6526
122.6404	104.1179	84.0054	70.0782	60.6149	54.2085	49.1758	45.1478	41.8225	38.9474
199.2420	158.6000	126.9869	104.1054	87.2590	74.5536	64.7586	57.0770	50.9205	45.8812
1618.2132	1618.0406	1618.1760	1618.1209	1617.9995	1617.8822	1617.7924	1617.7156	1617.6384	1617.5725
2791.1023	2784.6341	2784.1677	2783.7995	2783.2137	2782.6045	2782.0345	2781.5440	2781.1045	2780.7282
3781.3866	3781.7191	3781.6483	3781.5699	3781.5330	3781.5180	3781.5090	3781.5030	3781.4986	3781.4969
3919.0140	3919.3830	3919.3919	3919.4073	3919.4513	3919.4995	3919.5437	3919.5876	3919.6250	3919.6593
A=14.50899	14.52034	14.52697	14.53010	14.53156	14.53221	14.53251	14.53258	14.53251	14.53240
B=0.13888	0.10994	0.08917	0.07376	0.06202	0.05287	0.04560	0.03973	0.03493	0.03094
C=0.13756	0.10912	0.08863	0.07339	0.06175	0.05268	0.04546	0.03962	0.03484	0.03088

Continued

9.0 Å	9.5 Å	10.0 Å	10.5 Å	11.0 Å	11.5 Å	12.0 Å
21.0163	19.3548	17.9569	16.6897	15.6091	14.6412	13.7678
22.9963	21.5819	20.1755	20.4564	19.4853	18.6863	18.0512
36.4079	34.2157	32.0580	30.6490	29.0082	27.5309	25.9788
41.6897	38.0844	34.9707	32.2579	29.9003	27.8203	26.2588
1617.5180	1617.4755	1617.4335	1617.3998	1617.3727	1617.3497	1617.3300
2780.4116	2780.1494	2779.9324	2779.7505	2779.6002	2779.4720	2779.3639
3781.4962	3781.4977	3781.4986	3781.5004	3781.5026	3781.5044	3781.5060
3919.6900	3919.7138	3919.7384	3919.7590	3919.7758	3919.7906	3919.8034
14.53227	14.53221	14.53201	14.53189	14.53178	14.53168	14.53159
0.02760	0.02477	0.02236	0.02028	0.01848	0.01691	0.01553
0.02755	0.02473	0.02232	0.02025	0.01846	0.01689	0.01551

Continued

12.5 Å	13.0 Å	13.5 Å	14.0 Å	14.5 Å	15.0 Å
12.9875	12.3678	11.3420	10.7400	10.2035	9.8966
17.3889	16.8174	16.3426	15.8934	15.4455	15.0075
24.3275	22.8854	21.5011	20.2912	19.2001	18.2546
25.0529	23.9926	23.0745	22.2611	21.5175	20.8390
1617.3133	1617.2991	1617.2855	1617.2744	1617.2646	1617.2560
2779.2707	2779.1913	2779.1219	2779.0620	2779.0107	2778.9648
3781.5073	3781.5085	3781.5088	3781.5099	3781.5109	3781.5119
3919.8146	3919.8243	3919.8303	3919.8382	3919.8451	3919.8526
14.53152	14.53144	14.53138	14.53132	14.53127	14.53122
0.01431	0.01323	0.01227	0.01141	0.01063	0.00994
0.01430	0.01322	0.01226	0.01140	0.01063	0.00993

Table S5: Calculated energies of grid points (relative to PRC) on the minimum energy path for the association of CH and H_2O

HC-------OH_2 (Å)	Energy (in kcal/mol) relative to PRC
3	6.3559
3.1	6.7072
3.2	7.0082
3.3	7.2634
3.4	7.4881
3.5	7.6527
3.6	7.7716
3.7	7.8115
3.8	7.8930
3.9	7.9663
4	8.0349
4.5	8.3936
5	8.6237
5.5	8.7526
6	8.8240
6.5	8.8656
7	8.8906
7.5	8.9065
8	8.9167
8.5	8.9232
9	8.9275
9.5	8.9296
10	8.9300
10.5	8.9325
11	8.9318
11.5	8.9309
12	8.9298
12.5	8.9284
13	8.9271
13.5	8.9251
14	8.9237
14.5	8.9222
15	8.9210

Table S6: Calculated relative energies (kcal/mol) and ro-vibrational parameters on the reaction coordinate via TS1

	F-100	F-90	F-80	F-70	F-60	F-50	F-45
Vib (cm-1)	149.8397	163.3432	178.7122	195.3851	215.7027	240.4922	253.8537
Vib	376.7852	378.0980	381.6681	386.7910	395.0044	407.5858	416.3058
Vib	659.1747	669.7250	681.2971	693.4032	706.2745	719.9529	727.0538
Vib	1072.5006	1073.2611	1074.3833	1075.4895	1076.9048	1078.9249	1080.0282
Vib	1624.1259	1617.1754	1608.6763	1598.5956	1586.3979	1571.6085	1562.9715
Vib	2886.9282	2895.6453	2905.2873	2915.9095	2927.5613	2940.3031	2946.9396
Vib	3668.0773	3604.0961	3520.6628	3416.3608	3287.1265	3128.8019	3039.2177
Vib	3840.6780	3836.2339	3832.3909	3828.8290	3825.3220	3821.8145	3820.0980
A (cm-1)	5.9293	5.9805	6.0371	6.0980	6.1613	6.2242	6.2544
B	0.6275	0.6321	0.6369	0.6419	0.6471	0.6524	0.6551
C	0.6109	0.6146	0.6186	0.6227	0.6269	0.6313	0.6334
Va + 8.93 kcal/mol	1.1416	1.7813	2.4722	3.2015	3.9588	4.7268	5.1084

F-40	F-35	F-30	F-25	F-20	F-15	F-10	F-9	F-8
267.4910	281.6948	296.4842	311.8277	328.1213	345.4524	363.0429	366.4472	369.8289
426.8468	438.9117	451.6051	464.3693	477.8658	491.8026	504.3934	506.6178	508.7459
734.4063	742.0227	749.9690	758.3476	767.2446	776.6266	786.4887	788.5265	790.6572
1081.2391	1082.6636	1084.3088	1086.0524	1087.7612	1089.2658	1090.3082	1090.4405	1090.5467
1553.1761	1541.9201	1528.8241	1513.5164	1495.8070	1475.4989	1452.2436	1447.2289	1442.1139
2938.0298	2838.7280	2731.8276	2623.7766	2520.9315	2429.3625	2353.1256	2339.9476	2327.4754
2958.9115	2963.3611	2971.2300	2979.5809	2988.2242	2997.0973	3006.1248	3007.9422	3009.7634
3818.4029	3816.7325	3815.1159	3813.5705	3812.1189	3810.8179	3809.6275	3809.3802	3808.9689
6.2830	6.3091	6.3318	6.3505	6.3644	6.3732	6.3768	6.3770	6.3768
0.6578	0.6605	0.6631	0.6656	0.6680	0.6703	0.6724	0.6729	0.6733
0.6356	0.6378	0.6399	0.6420	0.6440	0.6459	0.6477	0.6480	0.6483
5.4836	5.8481	6.1954	6.5199	6.8189	7.0850	7.3010	7.3363	7.3683

F-7	F-6	F-5	F-4	F-3	F-2	F-1	TS1	R-1
372.7481	376.0881	378.9019	381.7904	384.4255	387.0088	389.3451	391.7986	394.0069
510.7337	512.7063	514.5586	516.3733	518.1172	519.8192	521.4401	523.1010	524.6255
792.3735	794.7569	796.6808	798.8537	800.7847	803.2171	805.0505	807.5044	809.7040

1090.6152	1090.6806	1090.7030	1090.7065	1090.7309	1090.5753	1090.5459	1090.4891	1090.3228
1436.8246	1431.5403	1426.0743	1420.5502	1414.8938	1409.2145	1403.3795	1397.1307	1390.6986
2316.1363	2305.2429	2295.4158	2286.0868	2277.7173	2268.9423	2262.9737	2256.5399	2250.8664
3011.5925	3013.4170	3015.2510	3017.0777	3018.6192	3020.6769	3022.5275	3024.5229	3026.4748
3809.2934	3808.5790	3808.7111	3808.3956	3808.2827	3807.3832	3807.9627	3807.8228	3807.6318
6.3769	6.3763	6.3759	6.3751	6.3742	6.3727	6.3718	6.3702	6.3685
0.6737	0.6741	0.6745	0.6749	0.6753	0.6756	0.6760	0.6764	0.6768
0.6487	0.6490	0.6493	0.6497	0.6500	0.6503	0.6506	0.6509	0.6513
7.3976	7.4234	7.4461	7.4647	7.4793	7.4880	7.4968	7.5000	7.4969

R-2	**R-3**	**R-4**	**R-5**	**R-6**	**R-7**	**R-8**	**R-9**	**R-10**
395.9948	397.7741	399.5502	401.1415	402.8174	404.2613	406.0476	407.5184	409.5171
525.9291	527.0606	528.0409	528.8560	529.5638	530.1781	530.8458	531.5223	532.4186
812.1763	814.0825	816.4338	818.5756	820.8561	822.9154	825.3075	827.2975	829.7621
1090.1488	1090.0692	1089.8121	1089.5531	1089.2623	1088.9195	1088.5779	1088.1820	1087.8037
1384.7525	1378.6229	1372.4865	1366.2361	1359.9509	1353.5745	1347.2410	1340.8195	1334.5153
2245.6666	2242.8222	2239.6752	2237.3066	2235.4031	2234.2430	2233.6249	2233.6098	2234.1412
3028.2994	3029.9058	3031.9650	3033.7989	3035.6013	3037.4434	3039.2349	3041.0628	3042.8661
3806.8570	3807.3846	3807.1570	3807.1216	3806.8277	3806.9801	3806.4864	3806.8317	3806.2331
6.3665	6.3649	6.3628	6.3607	6.3582	6.3559	6.3532	6.3506	6.3477
0.6771	0.6775	0.6778	0.6782	0.6785	0.6788	0.6792	0.6795	0.6798
0.6516	0.6519	0.6521	0.6524	0.6527	0.6530	0.6533	0.6535	0.6538
7.4880	7.4776	7.4605	7.4379	7.4096	7.3763	7.3377	7.2939	7.2450

R-15	**R20**	**R-25**	**R-30**	**R-35**	**R-40**	**R-45**	**R-50**	**R-60**
419.7329	428.8663	431.9983	429.5998	425.9008	419.8549	408.4611	391.6051	343.1087
539.9182	549.7501	554.6494	555.9468	561.9881	572.3964	583.0158	593.7885	612.3726
840.8897	852.0153	862.6944	873.0107	882.9040	891.8986	899.4455	905.1475	911.1235
1085.7754	1083.4506	1080.2297	1076.7279	1073.9538	1071.1998	1068.1472	1065.9866	1064.7557
1303.6473	1274.4406	1245.4549	1217.1442	1192.0939	1171.9303	1155.8883	1142.0178	1118.1997
2244.4311	2265.3479	2294.2175	2330.5520	2373.7252	2421.1126	2471.0378	2522.9223	2627.4724
3051.9043	3060.9600	3069.9960	3079.0628	3088.1816	3097.3462	3106.5326	3115.7762	3134.4162
3806.0476	3805.7342	3805.5225	3805.4234	3805.4008	3805.4634	3805.5857	3805.7466	3806.3472
6.3321	6.3141	6.2941	6.2725	6.2496	6.2254	6.2002	6.1741	6.1199

0.6813	0.6828	0.6842	0.6855	0.6868	0.6881	0.6894	0.6906	0.6932
0.6551	0.6563	0.6574	0.6586	0.6597	0.6607	0.6618	0.6628	0.6650
6.9221	6.4487	5.8120	5.1455	4.3271	3.3463	2.2045	0.9149	-2.0610

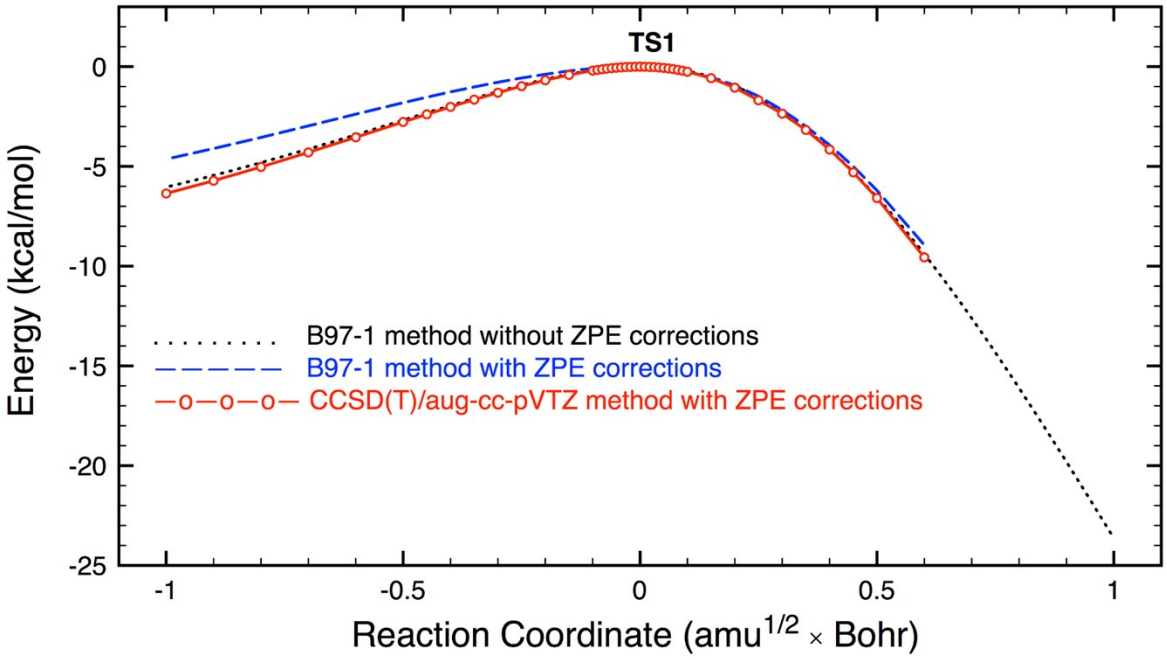

Figure S1: IRC calculations via TS1 using B97-1/6-311G(d,p) and CCSD(T)/aug-cc-pVTZ level of theory.

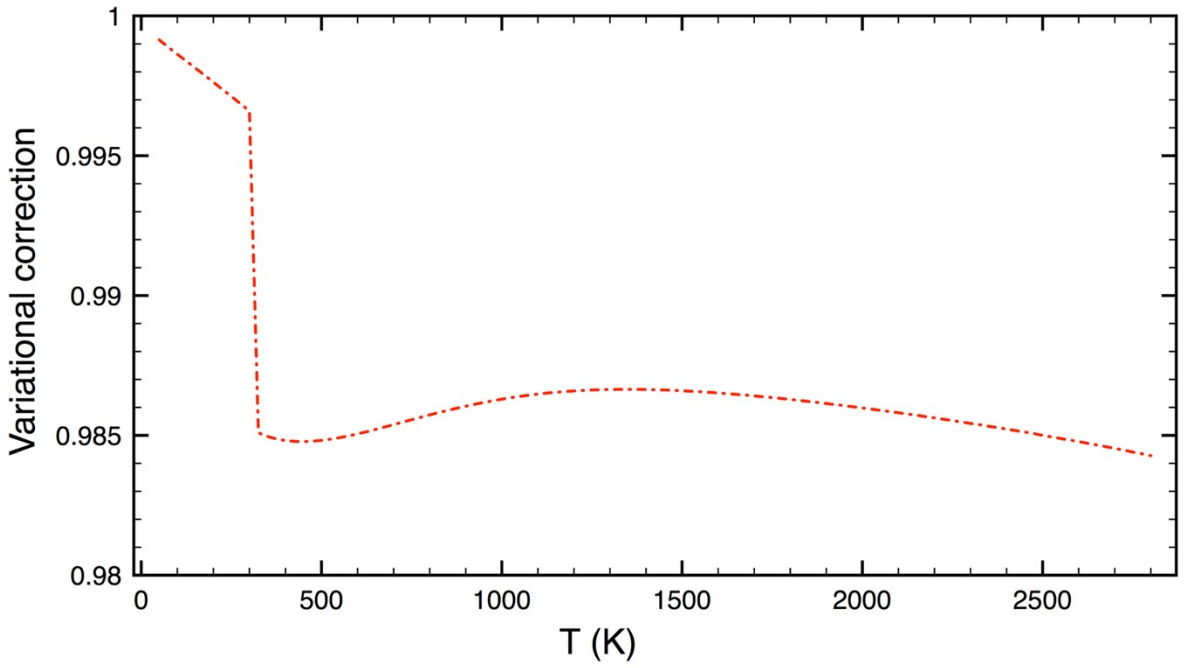

Figure S2: Calculated variational correction that is defined as a ratio of rate constants with and without variational treatments.

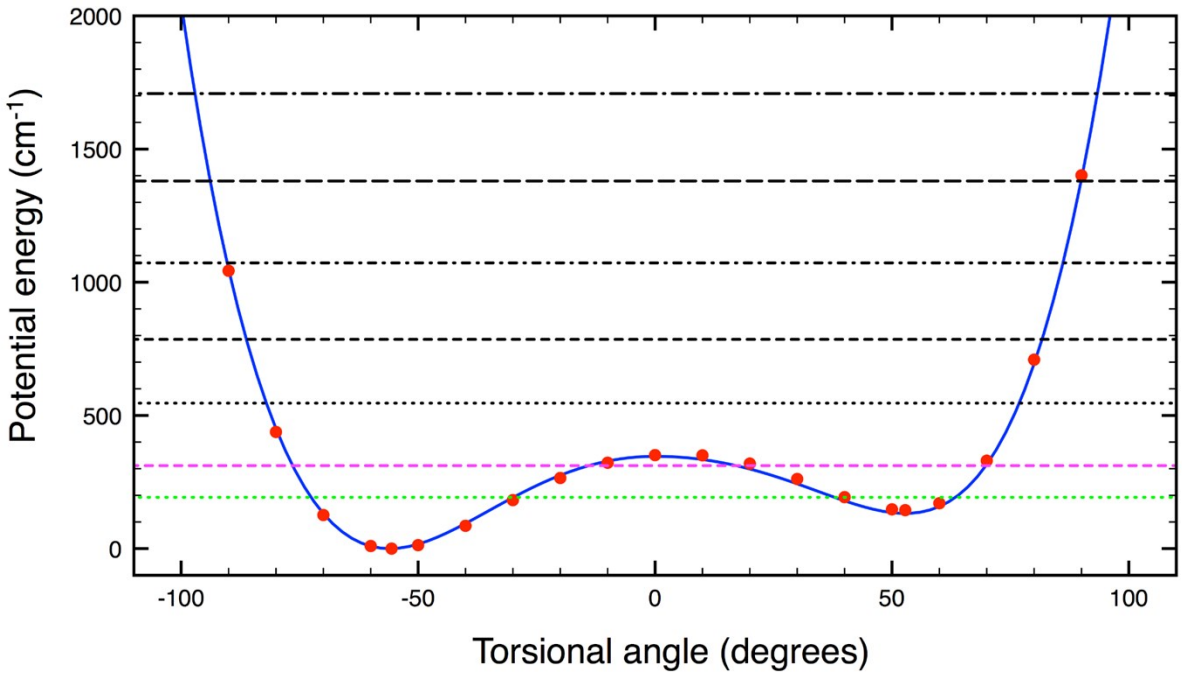

Figure S3: Calculated hindered internal rotation (1DHR) potential in TS1 using CCSD(T)/aug-cc-pVTZ level of theory. Dash- and dotted-lines are low-lying eigenvalues.

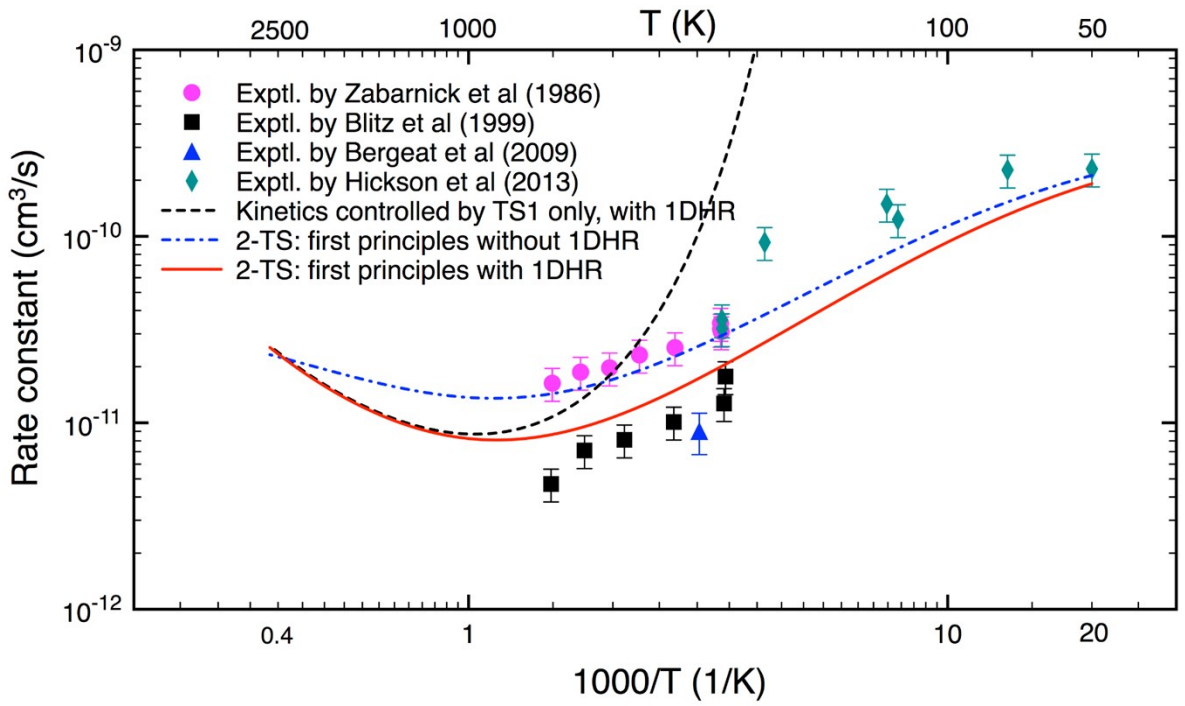

Figure S4: Calculated rate constants (cm^3/s) at the Low-Pressure Limit, k(T,P=0), using three different kinetics models, namely: (1) Hypothetical kinetics controlled by TS1 only, with 1DHR; (2) two-TS kinetics model without 1DHR treatment (i.e. the two minima of the 1DHR potential for TS1 are considered as separated transition state conformers); (3) two-TS kinetics model with 1DHR treatment.