Supplementary Information for

Ab Initio Dynamics of Hydrogen Abstraction from N_2H_4 by OH radical: An RRKM-based Master Equation Study

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Table S1: Optimized geometries, electronic energies at 0 K ($E_{elec}^{0\,K}$), zero-point energy (ZPE) corrections and harmonic wavenumbers of the species involved with the lowest-energy conformer of a given species, calculated at CCSD(T)/CBS//M06-2X/6-311++G(3df,2p) level of theory for the title reaction.

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
N_2H_4 (C_2)	N	0.000000000	0.711888000	-0.073931000	-111.762113	0.053935	456.4792	837.1659	983.8477
	H	0.233290000	1.096273000	0.834599000			1149.7730	1306.6103	1337.6895
	H	-0.930617000	1.022768000	-0.317081000			1677.7693	1691.5919	3503.0561
	N	0.000000000	-0.711888000	-0.073931000			3510.1914	3607.0977	3613.3481
	H	0.930617000	-1.022768000	-0.317081000			(376.7 [1]; 780.0 [2]; 966.0 [2]; 1076.0 [3]; 1275.0 [2]; 1275.0 [2]; 1628.0 [2]; 1642.0 [3]; 3314.0 [2]; 3329.0 [3]; 3350.0 [2]; 3398.0 [3])		
	H	-0.233290000	-1.096273000	0.834599000					
OH ($C_{\infty v}$)	O	0.000000000	0.000000000	0.107841000	-75.678298	0.008594	3772.3906 (3737.8) [4]		
	H	0.000000000	0.000000000	-0.862726000					
RC (C_1)	N	-1.064489000	-0.680233000	-0.120152000	-187.452865	0.066121	116.3421	208.4956	232.3586
	H	-1.883948000	-0.925235000	0.422726000			380.6348	610.5391	756.1863
	H	-0.276263000	-1.217132000	0.222525000			872.0995	1020.5025	1146.4034
	N	-0.737053000	0.701372000	0.006621000			1307.9600	1352.5886	1673.6136
	H	-1.213040000	1.208917000	-0.727602000			1694.4290	3431.7873	3503.6922
	H	-1.022877000	1.090031000	0.899147000			3509.0255	3600.5952	3606.4644
	O	1.984011000	-0.088668000	0.008667000					
	H	1.134829000	0.404792000	-0.091415000					
TS1 (C_1)	N	0.589520000	0.749524000	0.093541000	-187.443994	0.063863	-383.6143	156.2509	198.1793
	H	0.404735000	1.189851000	-0.797535000			227.2116	522.8449	580.3970
	H	-0.283472000	0.667925000	0.640861000			762.3747	928.4211	1138.9856
	N	1.232769000	-0.480389000	-0.125426000			1252.3314	1373.7288	1640.2053
	H	0.559538000	-1.190992000	-0.401215000			1679.6876	3093.1859	3464.4702
	H	1.656874000	-0.768123000	0.746543000			3589.4573	3606.2092	3818.6515
	O	-1.618484000	-0.266870000	0.062220000					
	H	-2.145823000	0.352361000	-0.463216000					
TS2 (C_1)	N	0.057363000	-0.209252000	-0.000158000	-187.411713	0.064993	-941.8708	247.4297	273.3997
	H	0.061751000	-0.818205000	-0.811063000			291.6127	462.4152	522.7916
	H	0.061880000	-0.819173000	0.810014000			915.3303	932.3138	1095.9160

Species	Cartesian coordinate (Å)				$E_{elec}^{0\ K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
	N	-1.728024000	0.022278000	0.000150000			1280.0681	1332.2917	1530.0342
	H	-1.830119000	0.644204000	0.802502000			1576.9499	3441.6309	3532.6439
	H	-1.830236000	0.645499000	-0.801177000			3543.8248	3636.0377	3914.0022
	O	1.690849000	0.077314000	-0.000020000					
	H	1.704556000	1.037978000	-0.000065000					
PC	N	0.904003000	0.721684000	0.012156000	-187.511373	0.065660	179.8924	192.8272	230.2471
(C_1)	H	1.829884000	1.130671000	-0.101748000			265.9670	375.6061	546.0712
	H	-1.066959000	0.601893000	-0.054005000			670.2131	742.3608	1162.7291
	N	1.052648000	-0.602612000	0.078820000			1321.4940	1484.2178	1640.1259
	H	1.879490000	-1.052686000	-0.286891000			1655.2801	3510.4701	3516.3821
	H	0.180833000	-1.113116000	0.018694000			3650.2560	3703.9865	3973.2157
	O	-1.768382000	-0.066848000	-0.103089000					
	H	-2.372755000	0.134514000	0.611828000					
N_2H_3	N	-0.590674000	0.024445000	-0.066851000	-111.119005	0.039822	524.7286	707.2286	1145.4111
(C_1)	H	-1.017418000	0.904360000	0.189425000			1293.0997	1486.1696	1660.6973
	H	-1.133753000	-0.796292000	0.149147000			3452.2059	3531.6000	3678.6318
	N	0.733970000	-0.151406000	0.021782000					
	H	1.148106000	0.780661000	-0.023083000					
H_2O	O	0.000000000	0.000000000	0.116269000	-76.379099	0.021678	1619.8405	3895.1601	4000.3510
(C_{2v})	H	0.000000000	0.761709000	-0.465075000			(1595.0; 3657.0 [5]; 3756.0 [4])		
	H	0.000000000	-0.761709000	-0.465075000					
NH_2OH	N	-0.009699000	0.693817000	0.000000000	-131.612501	0.041192	433.5638	1014.1868	1164.3672
(C_s)	H	0.543784000	0.950235000	0.811953000			1361.9311	1421.3981	1685.3473
	H	0.543784000	0.950235000	-0.811953000			3504.8465	3586.1126	3909.5418
	O	-0.009699000	-0.725969000	0.000000000			(386.0 [5]; 895.2 [6]; 1115.5 [6]; 1294.5 [6]; 1353.3 [6]; 1604.5 [6]; 3294.3 [6]; 3358.8 [6]; 3649.9 [6])		
	H	-0.942085000	-0.949438000	0.000000000					
NH_2	N	0.000000000	0.000000000	0.141114000	-55.822746	0.019237	1527.3038	3412.5353	3504.0696
(C_{2v})	H	0.000000000	0.804394000	-0.493899000			(1497.3 [7]; 3219.4 [7]; 3301.1 [4])		
	H	0.000000000	-0.804394000	-0.493899000					

Frequencies in the parentheses ("( )") are taken from experimental studies.

Table S2: T1 diagnostics and spin contaminant for the open shell species involved in N_2H_4 + OH reaction computed at UCCSD(T)/aug-cc-pV(T,Q)Z based on the M06-2X/6-311++G(3df,2p) geometries. "aTZ" and "aQZ" denote for aug-cc-pVTZ & aug-cc-pVQZ, respectively.

Species	T1 diagnostics		Spin contaminant	
	UCCSD(T)/aTZ	UCCSD(T)/aQZ	UCCSD(T)/aTZ	UCCSD(T)/aQZ
OH	0.01001371	0.00949501	0.7500	0.7500
RC	0.01008440	0.00971666	0.7500	0.7500
TS1	0.03103722	0.03071951	0.7501	0.7501
TS2	0.03325900	0.03314802	0.7571	0.7572
PC	0.01779455	0.01748602	0.7502	0.7502
NH_2	0.01021578	0.01014355	0.7501	0.7501
N_2H_3	0.02078132	0.02057907	0.7502	0.7502

Table S3: Calculated overall rate constants, k_{tot}, of the N_2H_4 + OH → products over the range of temperature 200 – 3000 K at P = 760 Torr with and without HIR treatments based on CCSD(T)/CBS//M06-2X/6-311++G(3df,2p) level of theory. Units are in cm^3/molecule/s.

T (K)	N_2H_4 + OH → products ($k_{\_tot}$)	
	With HIR	Without HIR
200	6.26E-11	4.87E-11
250	4.75E-11	3.50E-11
300	3.91E-11	2.71E-11
400	3.11E-11	1.88E-11
500	2.97E-11	1.43E-11
600	3.13E-11	1.18E-11
700	3.45E-11	1.07E-11
800	3.86E-11	1.05E-11
900	4.31E-11	1.13E-11
1000	4.78E-11	1.35E-11
1100	5.26E-11	1.65E-11
1200	5.76E-11	2.02E-11
1300	6.32E-11	2.45E-11
1400	6.88E-11	2.96E-11
1500	7.44E-11	3.44E-11
1600	8.07E-11	3.96E-11
1700	8.61E-11	4.45E-11
1800	9.21E-11	4.95E-11
1900	9.73E-11	5.47E-11
2000	1.03E-10	5.96E-11
2100	1.09E-10	6.45E-11
2200	1.15E-10	6.89E-11
2300	1.20E-10	7.41E-11
2400	1.26E-10	7.83E-11
2500	1.31E-10	8.30E-11
2600	1.37E-10	8.70E-11
2700	1.42E-10	9.11E-11

2800	1.47E-10	9.62E-11
2900	1.53E-10	9.87E-11
3000	1.58E-10	1.02E-10

Table S4: Calculated overall rate constants, k_{tot}, of the N_2H_4 + OH → products over the range of temperature 200 – 3000 K at the different pressures (i.e., 1, 760 and 7600 Torr) with HIR treatments and tunneling effects based on CCSD(T)/CBS//M06-2X/6-311++G(3df,2p) level of theory. Units are in cm^3/molecule/s.

T (K)	N_2H_4 + OH → products (k_{tot})		
	1 Torr	760 Torr	7600 Torr
200	5.50E-11	6.26E-11	7.59E-11
250	4.38E-11	4.75E-11	5.27E-11
300	3.66E-11	3.91E-11	4.10E-11
400	3.03E-11	3.11E-11	3.17E-11
500	2.99E-11	2.97E-11	2.99E-11
600	3.15E-11	3.13E-11	3.13E-11
700	3.45E-11	3.45E-11	3.46E-11
800	3.83E-11	3.86E-11	3.85E-11
900	4.31E-11	4.31E-11	4.31E-11
1000	4.80E-11	4.78E-11	4.78E-11
1100	5.32E-11	5.26E-11	5.31E-11
1200	5.82E-11	5.76E-11	5.81E-11
1300	6.36E-11	6.32E-11	6.37E-11
1400	6.91E-11	6.88E-11	6.94E-11
1500	7.45E-11	7.44E-11	7.49E-11
1600	8.03E-11	8.07E-11	8.02E-11
1700	8.59E-11	8.61E-11	8.59E-11
1800	9.15E-11	9.21E-11	9.15E-11
1900	9.70E-11	9.73E-11	9.72E-11
2000	1.03E-10	1.03E-10	1.03E-10
2100	1.08E-10	1.09E-10	1.09E-10
2200	1.14E-10	1.15E-10	1.14E-10
2300	1.20E-10	1.20E-10	1.20E-10
2400	1.26E-10	1.26E-10	1.25E-10
2500	1.32E-10	1.31E-10	1.31E-10
2600	1.37E-10	1.37E-10	1.36E-10
2700	1.42E-10	1.42E-10	1.42E-10
2800	1.48E-10	1.47E-10	1.48E-10
2900	1.53E-10	1.53E-10	1.53E-10
3000	1.58E-10	1.58E-10	1.57E-10

Table S5: Calculated thermodynamic data of the species involved in NASA format for the title reaction.

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oh                O   1H   1         G   300.000  2500.000 1500.000     1
1.88516486E+001-3.73201434E-0022.90412010E-005-9.92871903E-0091.25881490E-012    2
1.94245122E+003-9.56227412E+0011.00185370E+0004.21481574E-004-8.15743202E-007    3
6.42588641E-010-1.75428999E-0138.64874073E+0031.81777404E+000                    4
n2h4              N   2H   4         G   300.000  2500.000 1500.000     1
-1.29683914E+0013.36676575E-002-2.49543300E-0058.11533829E-009-9.81263451E-013    2
2.09660713E+0041.06576921E+0023.88053887E+000-3.95409504E-0041.07098586E-006    3
-1.16316747E-0093.95477771E-0131.43988653E+0041.38769619E+001                    4
rc                N   2H   5O   1    G   300.000  2500.000 1500.000     1
3.41926984E+002-6.82507788E-0015.12334095E-004-1.68733462E-0072.05602514E-011    2
-1.08778060E+005-1.82306756E+0034.81941265E+0001.83109033E-003-2.04872777E-006    3
2.31314398E-0103.95254256E-0132.24861985E+0042.98973578E+001                     4
n2h3              N   2H   3         G   300.000  2500.000 1500.000     1
4.69592525E+001-8.59741271E-0026.29330850E-005-2.04291558E-0082.48298743E-012    2
3.54028491E+002-2.29409770E+0022.86835431E+0001.14996484E-003-1.93590678E-006    3
1.30408866E-009-2.94570928E-0131.81526390E+0041.43847547E+001                    4
h2o               O   1H   2         G   300.000  2500.000 1500.000     1
8.38585854E-0014.38564923E-003-5.45642149E-0062.55538513E-009-4.09438468E-013    2
3.92614166E+0026.84952831E+0001.73761726E+000-3.41305469E-0046.07497735E-007    3
-4.41071214E-0101.13126948E-0135.41127220E+0023.25445581E+000                    4
nh2oh             N   1H   3O   1    G   300.000  2500.000 1500.000     1
7.82454297E+001-1.50985539E-0011.12269192E-004-3.65984149E-0084.41006260E-012    2
-1.72268051E+004-4.03429158E+0021.81822022E+0007.02147432E-003-1.27228159E-005    3
9.64977082E-009-2.60141336E-0121.23893056E+0041.59508220E+001                    4
nh2               N   1H   2         G   300.000  2500.000 1500.000     1
-2.68484151E+0008.08121962E-003-5.71254714E-0061.85313714E-009-2.35614906E-013    2
1.29357799E+0042.81804795E+0011.67304818E+0008.45484781E-005-3.79559026E-007    3
4.77299297E-010-1.83127885E-0131.10516209E+0043.78343009E+000                    4
```

Table S6: Comparison of the relative energies (0 K) obtained from CCSD(T)/CBS//M06-2X/6-311++G(3df,2p) and CCSD(T)/CBS//M06-2X/aug-cc-pVTZ levels, including ZPE corrections. Units are in kcal/mol.

Species	CCSD(T)/CBS//M06-2X/6-311++G(3df,2p)	CCSD(T)/CBS//M06-2X/aug-cc-pVTZ
RC	-5.6	-5.6
TS1	-1.4	-1.5
TS2	19.5	19.4
PC	-42.6	-42.7
P1	-36.9	-36.8
P2	1.9	1.9
Mean absolute deviation (MAD) = 0.06 (kcal/mol)		

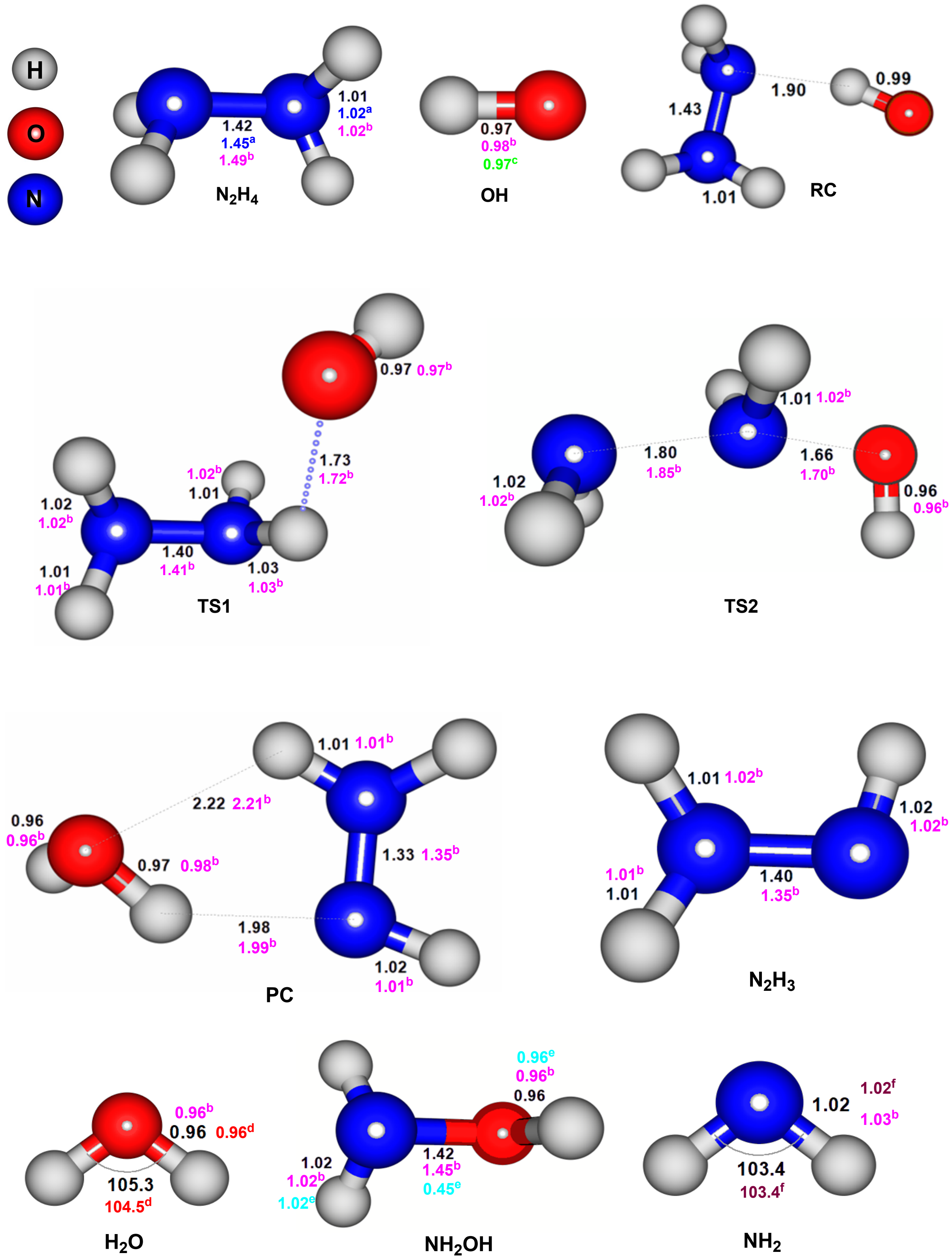
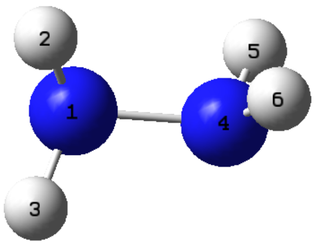
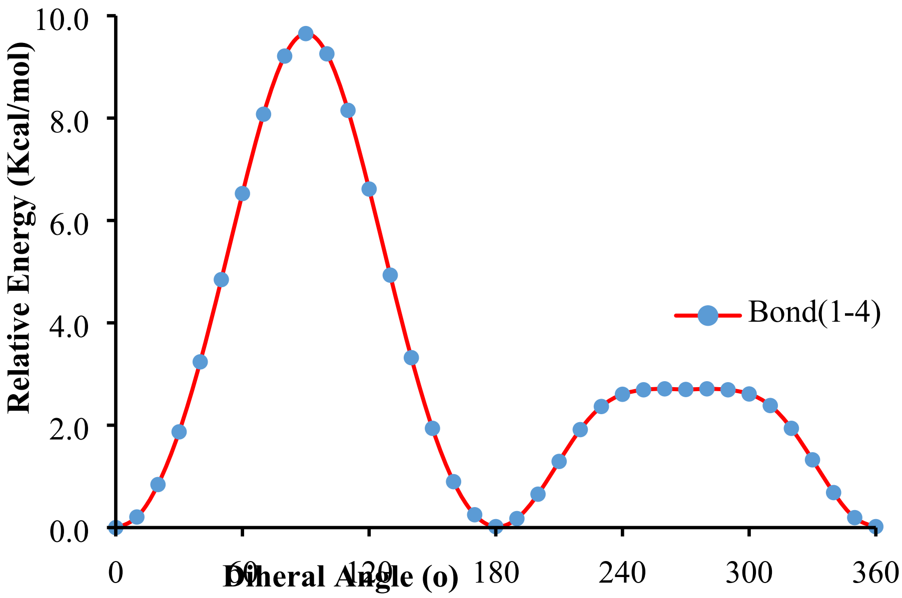
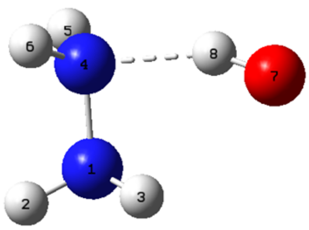
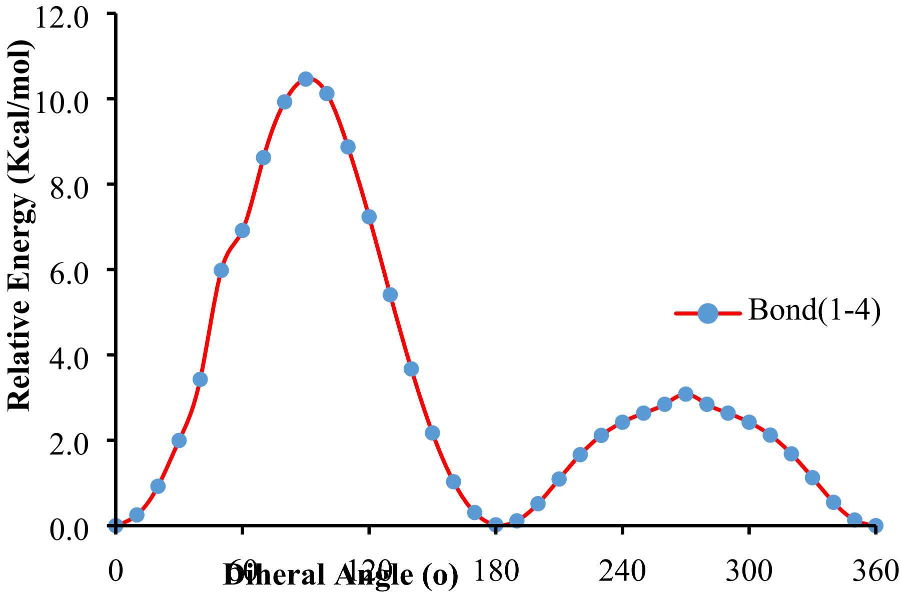
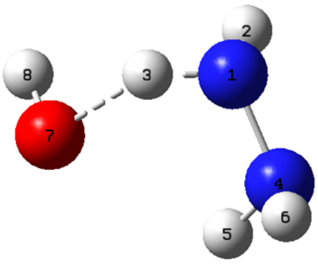
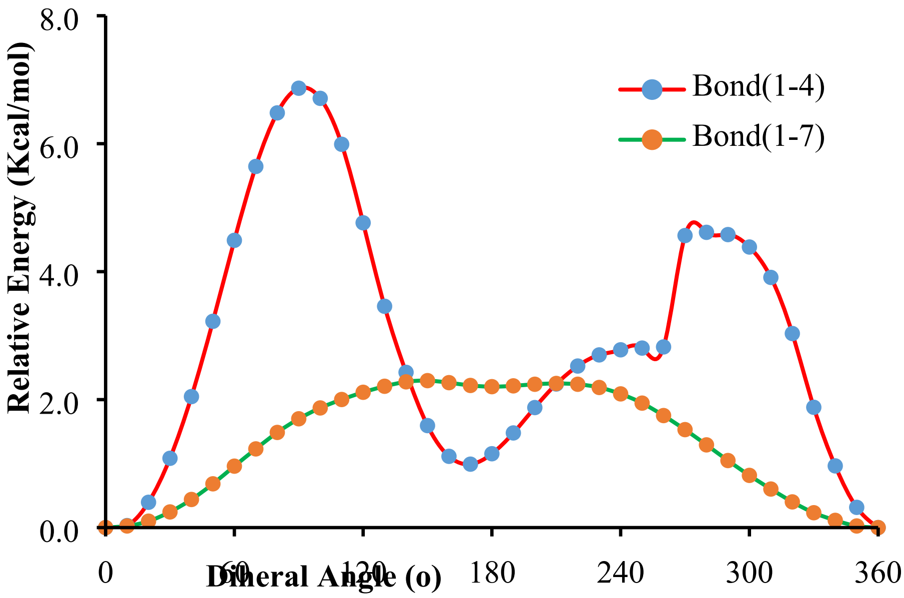
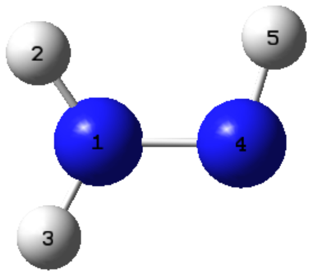
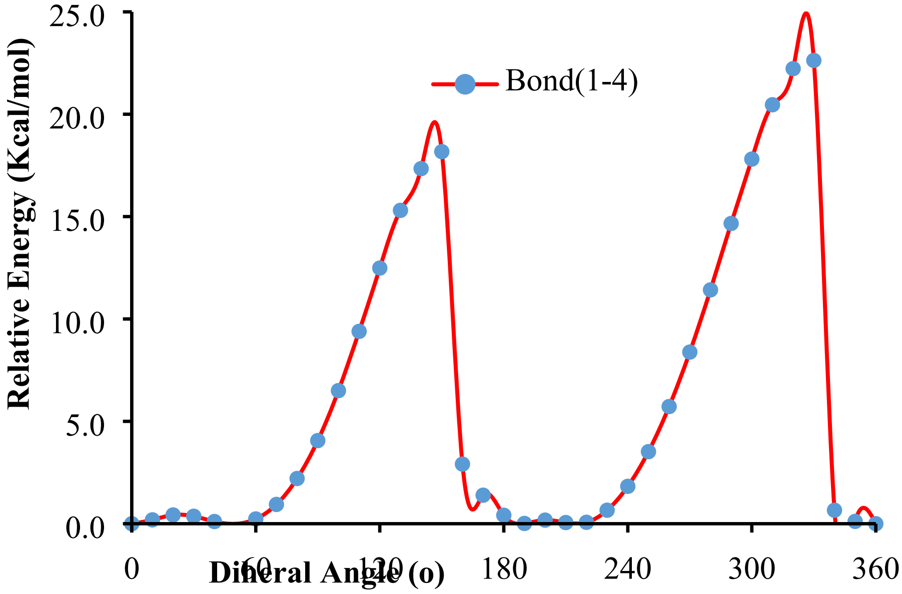


Figure S1: M06-2X/6-311++G(3df,2p) optimized geometries for the species involved in the N_2H_4 + OH reaction. All structures were obtained for the lowest-energy conformer of a given species. Bond lengths and bond angles are in Å and degree (°), respectively. [a, b, c, d, e, f] obtained from Tsuboi *et al*. [8], Tang *et al*. [9], Huber *et al*. [4], Hoy *et al*. [10], Gurvich *et al*. [2] and Herzberg [11], respectively.

Species	Potential energy surfaces for the internal rotations

Species	Potential energy surfaces for the internal rotations
 IM1	
 RC	

Species	Potential energy surfaces for the internal rotations
 **TS1**	
 **N_2H_3**	

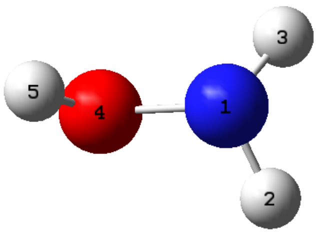
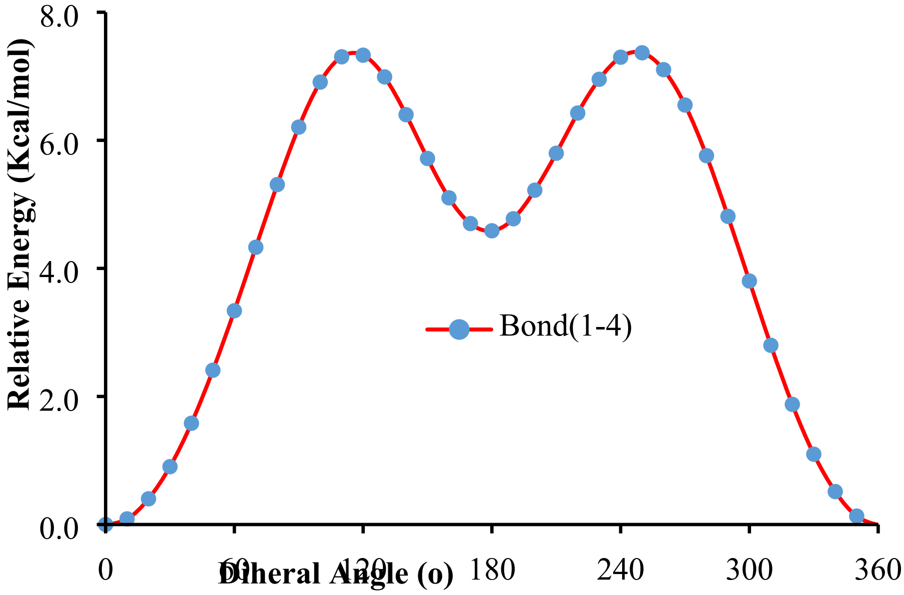
Species	Potential energy surfaces for the internal rotations
 **NH_2OH**	

Figure S2: Hindrance potentials for the species involved in the N_2H_4 + OH reaction, calculated at M06-2X/6-311G(d,p) level of theory.

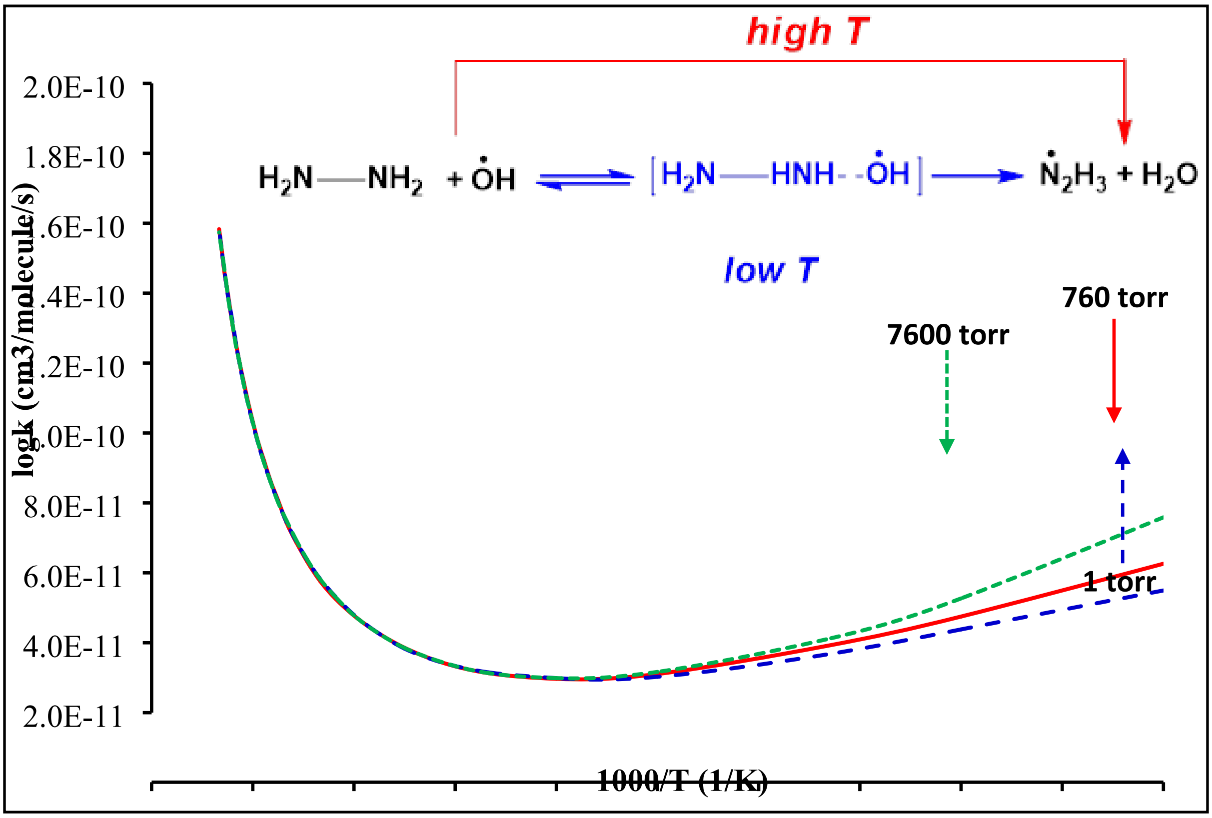


Figure S3: Calculated rate coefficients of N_2H_4 + OH → products as a function of temperature at the different pressures (i.e., 1, 760 and 7600 Torr).

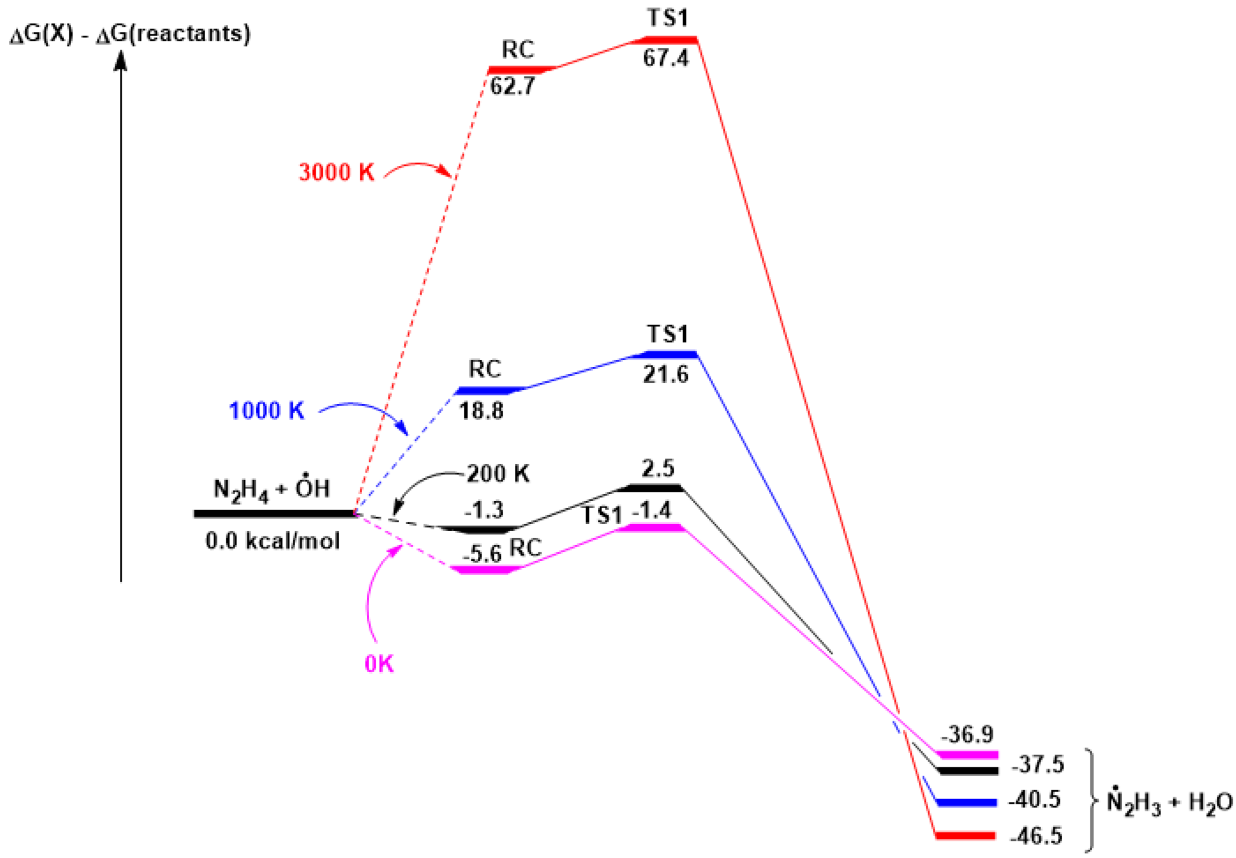


Figure S4: Plot of the relative Gibbs free energy ΔG(X) (X = RC, TS1 and N_2H_3 + H_2O (P1)) calculated at different temperatures (i.e., 0, 200, 1000 and 3000 K).

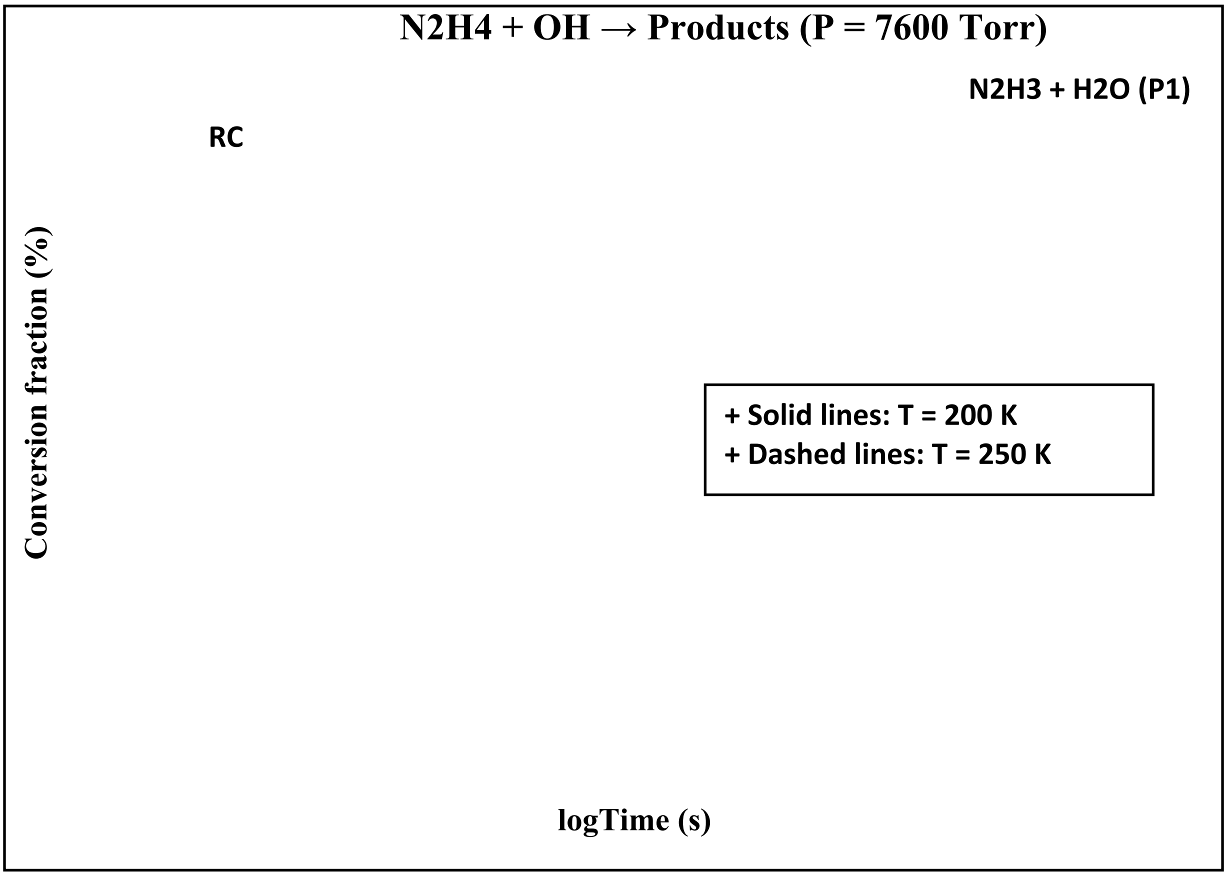


Figure S5: Flux conversion as a function of time at different temperatures and P = 7600 torr for N_2H_4 + OH → products.

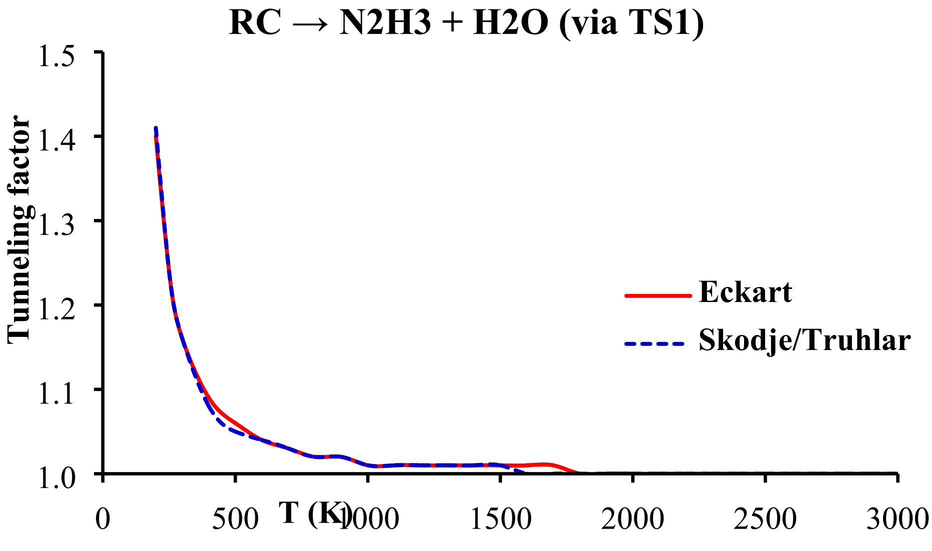


Figure S6: Tunneling factor as a function of temperature for RC → N_2H_3 + H_2O (via TS1), calculated using the 1-D asymmetrical Eckart [12] (solid line) and Skodje/Truhlar [13] (dashed line) potentials.

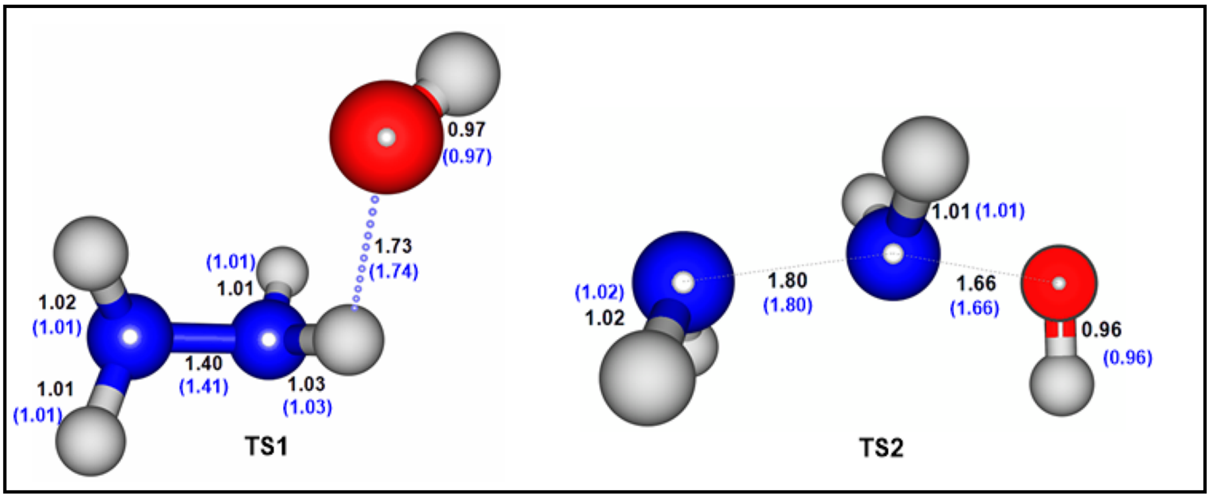


Figure S7: M06-2X/6-311++G(3df,2p) and M06-2X/aug-cc-pVTZ (values in parentheses) optimized geometries for the TS1 and TS2. Bond lengths are in Å.

References:

[1] Yamaguchi A, Ichishima I, Shimanouchi T, Mizushima S-I. Far infra-red spectrum of hydrazine. Spectrochimica Acta 1960;16(11-12):1471-85.

[2] Gurvich LV, Veyts IV, Alcock CB. Thermodynamic Properties of Individual Substances. 4th ed. New York: Hemisphere; 1989.

[3] Durig JR, Griffin MG, Macnamee RW. Raman spectra of gases. XV: Hydrazine and hydrazine-d4. Journal of Raman Spectroscopy 1975;3(2-3):133-41.

[4] Huber KP, Herzberg G. Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules. Van Nostrand Reinhold Co; 1979.

[5] Shimanouchi T. Tables of Molecular Vibrational Frequencies, Consolidated Volume 1, NSRDS NBS-39.

[6] Luckhaus D. The rovibrational spectrum of hydroxylamine: A combined high resolution experimental and theoretical study. The Journal of Chemical Physics 1997;106(20):8409-26.

[7] Jacox ME. Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules. J Phys ChemRef Data 1994;Monograph 3

[8] Tsuboi M, Overend J. Amino wagging and inversion in hydrazines. Journal of Molecular Spectroscopy 1974;52(2):256-68.

[9] Tang Y, Sun J, Jia X, Sun H, Pan X, Wang R. Mechanistic and kinetic investigations of N2H4 + OH reaction. J Comput Chem 2010;31(7):1520-7.

[10] Hoy AR, Bunker PR. A precise solution of the rotation bending Schrödinger equation for a triatomic molecule with application to the water molecule. Journal of Molecular Spectroscopy 1979;74(1):1-8.

[11] Herzberg G. Electronic spectra and electronic structure of polyatomic molecules. New York: Van Nostrand; 1966.

[12] Eckart C. The Penetration of a Potential Barrier by Electrons. Phys Rev 1930;35(11):1303-9.

[13] Skodje RT, Truhlar DG. Parabolic tunneling calculations. J Phys Chem 1981;85(6):624-8.