Supplementary Information for

Ab Initio Kinetics of the $CH_3NH + NO_2$ Reaction: Formation of Nitramines and *N*-Alkyl Nitroxides

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Contents

Table S1: The optimized geometries, electronic energies at 0 K ($E_{elec}^{0\,K}$), zero-point energy (ZPE) corrections (without scaling factor), harmonic wavenumbers of the species involved, calculated at W1U level of theory for the title reaction.

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
CH_3NH	7	-0.801905000	0.152653000	-0.000002000	-95.220370	0.048581	252.6533	949.3536	1006.9376
(C_s)	1	-1.209113000	-0.788345000	0.000006000			1041.5963	1339.1806	1392.9122
	6	0.626711000	-0.012084000	-0.000003000			1476.8046	1485.6711	2944.5395
	1	0.968370000	-0.582305000	-0.876219000			2974.7192	3082.6076	3377.7554
	1	1.125442000	0.956762000	-0.000059000					
	1	0.968367000	-0.582179000	0.876299000					
NO_2	7	0.000000000	0.000000000	0.321408000	-205.194993	0.008783	766.6921	1391.8445	1696.6674
(C_{2v})	8	0.000000000	1.098754000	-0.140616000			(750^1; 1318^1; 1618^2)		
	8	0.000000000	-1.098754000	-0.140616000					
I1	6	-1.813257000	0.021736000	0.082443000	-300.505393	0.067100	138.0721	178.4764	303.0174
(C_1)	1	-1.948113000	0.842071000	-0.616390000			526.3556	585.6371	747.3428
	1	-1.865742000	0.412718000	1.100902000			793.9449	945.8673	1109.2837
	1	-2.605638000	-0.708047000	-0.069828000			1146.5185	1202.0121	1355.2583
	7	-0.558458000	-0.656404000	-0.192063000			1423.1319	1462.1558	1481.9700
	1	-0.422324000	-1.603531000	0.127847000			1517.1696	1654.4160	3030.5238
	7	0.613645000	0.049398000	-0.020471000			3109.7747	3143.8128	3598.9523
	8	1.630892000	-0.619615000	0.081950000					
	8	0.535989000	1.266542000	-0.025631000					
I2	6	1.833839000	-0.110459000	0.000284000	-300.493827	0.066188	154.3161	250.2920	310.9255
(C_s)	1	1.964609000	0.522138000	0.881745000			467.3456	541.8352	647.5326
	1	1.964877000	0.522025000	-0.881220000			739.6108	933.7899	1031.4883
	1	2.575910000	-0.902662000	0.000447000			1108.6982	1185.5651	1308.6083
	7	0.523232000	-0.744425000	0.000125000			1346.9343	1437.3246	1479.1448
	1	-1.486020000	-1.440972000	-0.000136000			1483.0849	1687.4339	3016.6878
	7	-0.413191000	0.091835000	-0.000069000			3066.8814	3143.8099	3711.6839
	8	-1.688601000	-0.491007000	-0.000224000					
	8	-0.410485000	1.307300000	-0.000142000					
I3	6	-1.801755000	0.003566000	-0.000002000	-300.488677	0.065821	155.4429	242.5498	332.4570
(C_s)	1	-1.861967000	0.640741000	-0.884102000			457.3105	562.2277	620.7980
	1	-1.861970000	0.640699000	0.884128000			710.8906	752.3310	1052.2292
	1	-2.635247000	-0.692228000	-0.000020000			1102.5953	1143.8537	1285.8856

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
	7	-0.587781000	-0.799710000	-0.000019000			1335.8594	1441.3640	1486.3943
	1	1.379487000	1.466778000	0.000038000			1493.6191	1732.5026	3026.6720
	7	0.492132000	-0.191061000	-0.000003000			3082.3462	3138.8270	3735.8537
	8	1.624006000	-0.646870000	-0.000013000					
	8	0.433465000	1.254121000	0.000029000					
I4 (C_1)	6	1.817991000	-0.308253000	-0.340699000	-300.469573	0.064550	41.2356	211.4670	304.5276
	1	2.361519000	0.579213000	-0.656982000			362.6805	487.9637	603.6424
	1	1.401068000	-0.808130000	-1.219654000			778.3168	855.4736	990.4554
	1	2.515461000	-0.981055000	0.158803000			1019.5498	1158.2394	1242.6588
	7	0.811245000	0.074270000	0.652518000			1442.3505	1478.8039	1495.8993
	1	0.283070000	-0.750015000	0.937917000			1520.9702	1686.7613	3010.1087
	7	-1.405468000	0.328528000	-0.298043000			3088.1140	3121.5747	3433.4967
	8	-0.144214000	0.919962000	0.017707000					
	8	-1.519474000	-0.796221000	0.025140000					
I5 (C_1)	6	2.034811000	-0.468953000	-0.023959000	-300.468648	0.064447	91.4384	189.7544	217.1731
	1	1.741328000	-1.374219000	-0.552523000			366.1232	413.0034	545.8714
	1	2.206159000	-0.709394000	1.029908000			709.9643	935.2627	982.4874
	1	2.962507000	-0.100466000	-0.463371000			1059.9938	1167.3505	1220.3868
	7	1.020058000	0.558901000	-0.232144000			1444.4426	1476.5269	1485.4411
	1	1.306838000	1.423042000	0.216277000			1518.8394	1781.0692	3003.5214
	7	-1.238918000	0.033307000	-0.461740000			3080.2383	3111.9039	3488.0653
	8	-0.146932000	0.190745000	0.501229000					
	8	-2.214777000	-0.262082000	0.095102000					
PC1 (C_s)	6	2.099504000	0.569343000	0.000037000	-300.511381	0.062636	67.5933	110.6307	161.5135
	1	-0.126475000	-0.855904000	-0.000028000			194.6588	229.3748	274.3572
	1	1.397572000	1.399750000	0.000023000			707.5268	989.6424	1016.0589
	1	3.164728000	0.803583000	0.000087000			1081.0765	1123.8887	1153.3468
	7	1.637704000	-0.607370000	-0.000006000			1383.7772	1471.0896	1484.1776
	1	2.363055000	-1.322394000	0.000010000			1655.1694	1717.6843	3000.8914
	7	-1.818627000	0.094815000	-0.000016000			3051.9749	3153.6364	3465.8161
	8	-1.151632000	1.082978000	0.000018000					
	8	-1.114549000	-1.064629000	-0.000038000					
PC2 (C_1)	6	-0.478164000	1.545086000	-0.259554000	-300.507656	0.060126	45.8825	101.3148	115.9203
	1	1.724992000	-0.502876000	0.629597000			134.0171	185.4964	233.9317

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
	7	-1.095044000	0.619055000	0.339175000			353.4693	411.1460	528.4905
	1	2.675154000	-0.719279000	-0.541086000			734.9168	925.4886	1074.8206
	1	-0.899721000	2.543268000	-0.220175000			1193.1122	1488.5410	1606.3307
	7	-0.552495000	-0.648069000	0.393918000			1649.5468	1708.1530	3079.8624
	8	2.333464000	-0.036257000	0.043649000			3188.4679	3761.4513	3871.9762
	1	0.457880000	1.377489000	-0.788029000					
	8	-1.028032000	-1.434495000	-0.375478000					
TS1 (C_s)	6	-1.848773000	-0.031497000	-0.000001000	-300.444098	0.061550	-1892.6632	47.6517	161.6616
	1	-2.572424000	-0.841309000	-0.000002000			287.5551	630.2198	730.3719
	1	-1.999775000	0.587422000	-0.887267000			731.1629	931.9566	1023.9090
	1	-1.999776000	0.587420000	0.887267000			1129.2240	1180.6365	1222.4633
	7	-0.531120000	-0.629419000	-0.000001000			1375.4190	1447.8530	1477.3559
	1	0.450704000	-1.473901000	-0.000002000			1494.2476	1609.5008	2301.8468
	7	0.529847000	0.131784000	0.000000000			3019.1489	3072.2891	3142.9724
	8	1.531411000	-0.730738000	-0.000001000					
	8	0.621441000	1.332337000	0.000002000					
TS2 (C_1)	7	1.111205000	-0.923977000	-0.150837000	-300.419250	0.059724	-1459.9558	190.6577	282.2249
	1	0.931816000	-1.410915000	0.725735000			376.6272	524.1662	538.7866
	6	1.816291000	0.202649000	0.020877000			628.7931	831.9012	980.2415
	1	2.342596000	0.558943000	-0.863496000			1060.8424	1072.5391	1268.7387
	1	0.750400000	1.004315000	0.013981000			1285.7081	1332.8299	1375.9120
	1	2.275818000	0.435663000	0.982666000			1529.4277	1558.4087	1760.6987
	7	-0.790074000	-0.070631000	0.019089000			3027.0492	3119.3203	3471.0380
	8	-0.533407000	1.157980000	0.003077000					
	8	-1.897380000	-0.513185000	-0.010816000					
TS3 (C_1)	6	-2.219091000	-0.395242000	0.215907000	-300.366594	0.057394	-366.6136	73.4353	154.4933
	1	-2.856975000	0.483423000	-0.191725000			199.5416	271.3846	309.9706
	1	-2.310490000	-0.386548000	1.316750000			395.1998	689.2550	856.8197
	1	-2.627140000	-1.312835000	-0.242668000			913.2361	1034.8205	1166.6846
	7	-1.317793000	0.355642000	-0.431280000			1242.6074	1340.3249	1417.2663
	1	0.199459000	1.407577000	0.095716000			1551.9544	1757.5110	2611.5313
	7	0.890445000	-0.246307000	-0.043967000			2881.4008	2918.0639	3407.4203
	8	1.132048000	1.090644000	0.163428000					
	8	1.855593000	-0.913832000	-0.031776000					

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
TS4	6	1.851527000	0.068704000	-0.000006000	-300.447877	0.061656	-1855.4543	82.5600	260.0775
(C_s)	1	1.877718000	0.709134000	0.883465000			297.9440	607.1480	668.4966
	1	1.877710000	0.709202000	-0.883426000			796.8801	983.7930	1072.9294
	1	2.708847000	-0.596226000	-0.000035000			1077.3535	1106.5360	1167.2248
	7	0.654508000	-0.768231000	-0.000033000			1319.2950	1432.7629	1479.1754
	1	-1.743352000	0.647569000	0.000033000			1489.6482	1632.9284	2322.4302
	7	-0.395817000	-0.133043000	-0.000003000			3029.3943	3086.4960	3150.7302
	8	-1.610020000	-0.628509000	-0.000017000					
	8	-0.595095000	1.181886000	0.000048000					
TS5	6	1.965321000	-0.081268000	0.208911000	-300.436308	0.064317	-376.1551	127.0454	196.1793
(C_1)	1	2.028810000	-1.009714000	0.783383000			472.2292	499.2629	541.4050
	1	2.116876000	0.777215000	0.869884000			710.3742	772.3399	953.6421
	1	2.756868000	-0.085106000	-0.535292000			1085.6131	1141.3616	1237.5456
	7	0.707798000	0.018714000	-0.492359000			1384.8872	1446.0313	1487.5674
	1	-2.081984000	-0.770856000	0.307118000			1497.1142	1780.2182	2993.7101
	7	-0.428531000	0.156622000	-0.091611000			3047.2853	3128.0354	3729.9955
	8	-1.203616000	-1.097785000	0.057810000					
	8	-1.117306000	1.141374000	0.118344000					
TS6	6	-1.612379000	-0.512075000	0.005618000	-300.415333	0.057666	-1527.0879	171.1138	213.3385
(C_1)	1	-1.198006000	0.783858000	0.031585000			308.8569	408.1669	470.1734
	7	-0.282007000	-1.002062000	0.015792000			560.6707	613.0817	677.0925
	1	-0.000760000	1.929905000	0.768627000			781.7161	970.6639	1018.4264
	1	-2.162626000	-0.898243000	0.860872000			1147.6666	1358.9937	1475.1012
	7	0.683359000	-0.307853000	0.013068000			1534.9643	1624.3747	1962.1554
	8	-0.317855000	1.659308000	-0.100841000			3072.3508	3138.5645	3804.8021
	1	-2.099870000	-0.770858000	-0.932886000					
	8	1.858613000	-0.259658000	-0.019650000					
TS7	6	-1.934184000	-0.194353000	-0.343388000	-300.373713	0.060634	-904.1806	91.7438	163.1137
(C_1)	1	-1.781993000	-0.961243000	-1.097878000			215.4695	245.3370	397.2903
	1	-2.038889000	0.788516000	-0.804669000			730.5741	868.0701	942.5240
	1	-2.872503000	-0.408426000	0.197096000			999.1949	1049.0903	1105.9337
	7	-0.924511000	-0.278442000	0.666264000			1319.9850	1380.1445	1418.6109
	1	-0.990132000	0.539306000	1.277565000			1510.3243	1619.8116	2940.1489
	7	0.871171000	-0.164859000	-0.313030000			3057.4221	3134.2539	3426.3156

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
	8	0.510724000	1.060912000	-0.038241000					
	8	1.947026000	-0.522028000	0.040187000					
TS8	7	-1.527136000	0.596185000	-0.135701000	-300.408879	0.060950	-478.6243	173.7925	277.2430
(C_1)	1	-1.580811000	1.074200000	0.761922000			334.4568	484.7625	538.6410
	6	-1.631680000	-0.767592000	0.020089000			782.8549	860.6205	928.2080
	1	-2.002729000	-1.142772000	0.976257000			1099.5812	1157.9449	1216.3371
	1	-2.072431000	-1.255726000	-0.849286000			1299.5464	1357.1100	1402.3260
	1	-0.507057000	-1.102231000	-0.007281000			1508.5969	1579.6876	2149.8594
	7	0.918970000	-0.199451000	-0.011220000			3022.3235	3102.6777	3477.1694
	8	2.111423000	-0.396068000	0.014968000					
	8	0.414861000	0.927935000	-0.011681000					
TS9	6	1.470984000	-0.638445000	0.100455000	-300.387072	0.058311	-1291.3849	58.3863	272.6942
(C_1)	1	0.343085000	-1.056278000	-0.107395000			417.7606	442.4808	526.5532
	1	1.700583000	-0.947109000	1.120646000			666.3620	824.6513	940.5302
	1	2.012342000	-1.156151000	-0.693423000			1070.5982	1117.7012	1218.7666
	7	1.271370000	0.681501000	-0.169013000			1244.9025	1302.3048	1325.1804
	1	1.229681000	1.240605000	0.682078000			1421.4693	1508.7731	1626.6035
	7	-1.323297000	0.101900000	0.343929000			3022.2787	3114.3371	3473.3377
	8	-0.646585000	1.049931000	-0.159106000					
	8	-1.071928000	-1.016707000	-0.194526000					
TS10	6	-1.816844000	0.568828000	0.101057000	-300.451281	0.063251	-261.7171	106.2161	201.5860
(C_1)	1	-1.321282000	1.522433000	0.272592000			301.9898	365.2865	462.8744
	1	-2.252529000	0.222736000	1.044106000			720.6882	797.8277	961.3273
	1	-2.613608000	0.720034000	-0.629387000			1053.5971	1161.2177	1210.1118
	7	-0.866358000	-0.376777000	-0.471484000			1441.9172	1471.2610	1475.7506
	1	-1.327713000	-1.245968000	-0.716603000			1516.4083	1849.9976	2997.1281
	7	1.466972000	-0.327876000	-0.181118000			3072.2561	3109.9857	3486.4734
	8	0.087734000	-0.742993000	0.509230000					
	8	1.688754000	0.780540000	-0.010333000					
CH_2=NH	6	0.055963000	0.582385000	0.000000000	-94.664232	0.039785	1074.3843	1101.5529	1169.2041
(C_s)	1	-0.840330000	1.209840000	0.000000000			1372.3390	1492.8378	1713.1064
	1	1.009846000	1.109427000	0.000000000			3010.5207	3104.0728	3425.7671
	7	0.055963000	-0.680883000	0.000000000			(1058; 1061; 1127; 1344; 1452; 1638; 2914; 3024; 3263)[3]		
	1	-0.897036000	-1.047398000	0.000000000					

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
HONO (*cis*)	7	-0.171354000	-0.519439000	-0.000077000	-205.830337	0.020156	631.1661	702.5896	878.8425
(C_s)	8	1.089362000	0.067553000	0.000037000			1336.9617	1714.2846	3583.4347
	1	0.934015000	1.033966000	0.000152000			(543[1]; 596[3]; 790[3]; 1263[3]; 1700[3]; 359[3])		
	8	-1.056180000	0.257711000	0.000011000					
CH_2=N-NO	6	1.040657000	-1.219867000	0.000000000	-224.019303	0.036238	83.1868	399.1837	538.5469
(C_s)	1	1.922918000	-0.576372000	0.000000000			701.0159	810.5176	1107.7043
	1	1.173956000	-2.296723000	0.000000000			1195.2813	1438.7415	1667.3048
	7	-0.135712000	-0.745503000	0.000000000			1747.3616	3045.6742	3172.2790
	7	0.000000000	0.744519000	0.000000000					
	8	-1.048854000	1.274899000	0.000000000					
H_2O	8	0.000000000	0.000000000	0.117686000	-76.483030	0.021279	1639.4030	3800.3529	3900.7184
(C_{2v})	1	0.000000000	0.760236000	-0.470746000			(1595[1]; 3657[1]; 3756[4])		
	1	0.000000000	-0.760236000	-0.470746000					
CH_3NNO (*trans*)	6	-1.673287000	0.149494000	0.000002000	-224.624471	0.048858	121.3550	344.7110	347.1287
(C_s)	1	-1.590055000	1.235940000	0.000001000			660.4835	996.1279	1122.7354
	1	-2.224545000	-0.177452000	0.881334000			1135.8183	1374.4655	1436.8226
	1	-2.224550000	-0.177454000	-0.881326000			1479.3916	1501.4367	1680.4903
	7	-0.369196000	-0.514361000	0.000001000			3032.5543	3100.5697	3112.1887
	7	0.610512000	0.232155000	0.000001000					
	8	1.798708000	0.024681000	-0.000004000					
OH	8	0.000000000	0.000000000	0.108292000	-75.782257	0.008425	3698.2530 (3738)[4]		
(C_∞)	1	0.000000000	0.000000000	-0.866334000					
CH_3NNO (*cis*)	6	1.376586000	-0.408293000	-0.000115000	-224.619274	0.048549	38.0957	260.5562	517.7341
(C_s)	1	1.193619000	-1.017447000	-0.887491000			785.0130	896.3255	1058.3773
	1	1.194362000	-1.016931000	0.887767000			1122.9139	1297.3767	1403.6263
	1	2.395732000	-0.038295000	-0.000626000			1469.9696	1483.9767	1704.4243
	7	0.463987000	0.758246000	-0.000047000			3024.4666	3087.3616	3160.4760
	7	-0.720612000	0.484991000	0.000062000					
	8	-1.405856000	-0.522528000	0.000117000					
HNO_2	7	0.000000000	0.000000000	0.308076000	-205.818974	0.021858	796.5383	1060.5053	1405.0737
(C_{2v})	8	0.000000000	1.092629000	-0.219140000			1517.9654	1659.3744	3154.8788
	1	0.000000000	0.000000000	1.349716000					
	8	0.000000000	-1.092629000	-0.219140000					
CH_3NHO	7	0.177988000	0.425710000	-0.057006000	-170.481181	0.055170	148.6300	356.9578	511.0034

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies [a] (cm^{-1})		
(C_1)	1	0.277701000	1.414666000	0.161390000			956.1754	1109.9093	1182.7104
	6	-1.143596000	-0.170434000	0.009303000			1389.0299	1444.1976	1469.6452
	1	-1.888999000	0.581749000	-0.247412000			1485.9229	1523.3014	3008.1934
	1	-1.190987000	-0.991819000	-0.703689000			3082.0345	3121.0555	3428.2267
	1	-1.352352000	-0.560448000	1.009870000					
	8	1.221286000	-0.300190000	0.015383000					
NO (C_∞)	7	0.000000000	0.000000000	-0.611196000	-129.965112	0.004503	1976.5303 (1904)[1]		
	8	0.000000000	0.000000000	0.534796000					

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

Table S2: High-pressure rate constants for the $CH_3NH + NO_2$ system calculated at W1U method[a].

No.	Reaction	$k^\infty(T) = A\times T^n\times\exp(-E_a/RT)$			$k^\infty(T)$ at 298 K [b]
		A [b]	n	E_a/R (K)	
1	$CH_3NH + NO_2 \rightarrow CH_3NHNO_2$ (**I1**)[c]	8.768E-012	-3.419E-002	-3.144E+002	2.073E-011
	(reverse reaction)	9.580E+023	-2.128E+000	2.620E+004	3.516E-020
2	$CH_3NH + NO_2 \rightarrow CH_3NH$-ONO_cis (**I4**)[c]	4.055E-013	1.888E-001	-7.851E+002	1.657E-011
	(reverse reaction)	1.517E+023	-2.463E+000	1.517E+004	9.844E-006
3	$CH_3NH + NO_2 \rightarrow CH_3NH$-ONO_trans (**I5**)[c]	4.055E-013	1.888E-001	-7.851E+002	1.657E-011
	(reverse reaction)	1.512E+023	-2.494E+000	1.478E+004	2.999E-005
4	CH_3NH-ONO_cis (**I4**) $\rightarrow CH_3NHO + NO$ (**P6**)[c]	1.607E+018	-1.052E+000	5.999E+003	7.360E+006
	(reverse reaction)	3.490E-017	1.382E+000	-8.241E+002	1.460E-012
5	CH_3NH-ONO_trans (**I5**) $\rightarrow CH_3NHO + NO$ (**P6**)[c]	1.601E+018	-1.083E+000	5.610E+003	2.242E+007
	(reverse reaction)	3.490E-017	1.382E+000	-8.241E+002	1.460E-012
6	CH_3N-N(O)OH_trans (**I2**) $\rightarrow CH_3N$-NO_cis + OH (**P4**)[c]	5.073E+020	-1.608E+000	2.725E+004	1.062E-023
	(reverse reaction)	2.047E-012	1.065E-001	-8.977E+001	5.077E-012
7	CH_3N-N(O)OH_cis (**I3**) $\rightarrow CH_3N$-NO_trans + OH (**P3**)[c]	1.744E+022	-2.019E+000	2.436E+004	5.852E-019

	(reverse reaction)	2.087E-012	1.206E-001	-1.458E+002	6.764E-012
8	**PC1** → CH_2=NH + HO-NO (**P1**)[c]	4.647E+024	-2.912E+000	5.122E+003	1.010E+010
	(reverse reaction)	1.046E-009	-1.682E-001	8.545E-001	4.000E-010
9	**PC2** → CH_2=NNO + H_2O (**P2**)[c]	4.537E+023	-3.113E+000	1.473E+003	6.442E+013
	(reverse reaction)	1.046E-009	-1.682E-001	8.545E-001	4.000E-010
10	CH_3NHNO_2 (**I1**) → CH_3N-N(O)OH_trans (**I2**) (via **TS1**)	1.126E-005	5.340E+000	1.192E+004	1.269E-009
	(reverse reaction)	1.811E-005	5.044E+000	8.572E+003	2.861E-005
11	CH_3NHNO_2 (**I1**) → **PC1** (via **TS2**)	1.496E+000	3.949E+000	2.163E+004	3.613E-022
	(reverse reaction)	2.677E+000	3.048E+000	2.462E+004	1.644E-028
12	CH_3N-N(O)OH_trans (**I2**) → **PC1** (via **TS3**)	3.489E+010	1.297E+000	3.767E+004	7.298E-042
	(reverse reaction)	3.883E+010	6.915E-001	4.401E+004	1.473E-052
13	CH_3N-N(O)OH_trans (**I2**) → CH_3N-N(O)OH_cis (**I3**) (via **TS4**)	1.398E-001	3.868E+000	8.608E+003	2.082E-004
	(reverse reaction)	6.106E+000	3.447E+000	7.256E+003	7.808E-002
14	CH_3N-N(O)OH_trans (**I2**) → CH_3N-N(O)OH_cis (**I3**) (via **TS5**)	8.689E+011	3.827E-001	1.771E+004	2.405E-026
	(reverse reaction)	2.252E+013	2.868E-002	1.631E+004	1.104E-022
15	CH_3N-N(O)OH_cis (**I3**) → **PC2** (via **TS6**)	8.929E-001	4.099E+000	1.723E+004	1.403E-015
	(reverse reaction)	3.656E-003	3.498E+000	2.401E+004	2.301E-029
16	CH_3NHNO_2 (**I1**) → CH_3NH-ONO_trans (**I5**) (via **TS7**)	2.004E+009	1.631E+000	3.926E+004	1.391E-044
	(reverse reaction)	6.837E+009	1.042E+000	2.831E+004	1.484E-029
17	CH_3NH-ONO_trans (**I5**) → CH_2=NH + H-NO_2 (**P5**) (via **TS8**)	2.037E+010	6.091E-001	1.736E+004	3.235E-014
	(reverse reaction)	5.622E-025	3.450E+000	2.206E+004	1.347E-048
18	CH_3NH-ONO_cis (**I4**) → **PC1** (via **TS9**)	5.117E+004	2.421E+000	2.207E+004	3.926E-022
	(reverse reaction)	2.675E+004	2.077E+000	3.563E+004	5.101E-043
19	CH_3NH-ONO_cis (**I4**) → CH_3NH-ONO_trans (**I5**) (via **TS10**)	5.463E+011	5.513E-001	5.476E+003	1.342E+005
	(reverse reaction)	5.445E+011	5.199E-001	5.087E+003	4.090E+005

[a] Rate constants are valid for 298−2000 K. [b] Units of [s^{-1}] for first-order reactions and [cm^3 $molecule^{-1}$ s^{-1}] for second-order reactions. This work calculated at the composite W1U method including asymmetric Eckart tunneling, HIR treatments and symmetry reactions. [c] Barrierless channels, see the main text for details.

Table S3: $k(T, P)_{\_tot}$ (overall rate constants) for the $CH_3NH + NO_2 \rightarrow$ products, calculated at different pressures.

T (K)	$k(T, P)_{\_tot}$ (cm^3/molecule/s)					
	0.76 torr	7.6 torr	76 torr	760 torr	7600 torr	76000 torr
298	4.52E-11	5.17E-11	5.29E-11	5.33E-11	5.37E-11	5.38E-11
300	4.45E-11	5.10E-11	5.22E-11	5.26E-11	5.30E-11	5.32E-11
400	2.25E-11	3.00E-11	3.27E-11	3.32E-11	3.34E-11	3.35E-11
500	1.42E-11	1.99E-11	2.45E-11	2.55E-11	2.57E-11	2.59E-11
600	1.05E-11	1.37E-11	1.93E-11	2.14E-11	2.18E-11	2.19E-11
700	8.69E-12	1.01E-11	1.49E-11	1.86E-11	1.94E-11	1.95E-11
800	7.66E-12	8.23E-12	1.13E-11	1.60E-11	1.76E-11	1.79E-11
900	6.99E-12	7.22E-12	8.80E-12	1.33E-11	1.62E-11	1.67E-11
1000	6.54E-12	6.63E-12	7.33E-12	1.06E-11	1.47E-11	1.58E-11
1100	6.21E-12	6.25E-12	6.54E-12	8.40E-12	1.28E-11	1.50E-11
1200	5.96E-12	5.97E-12	6.08E-12	6.97E-12	1.06E-11	1.40E-11
1300	5.75E-12	5.75E-12	5.79E-12	6.16E-12	8.48E-12	1.28E-11
1400	5.58E-12	5.57E-12	5.59E-12	5.72E-12	6.87E-12	1.11E-11
1500	5.42E-12	5.41E-12	5.42E-12	5.46E-12	5.93E-12	8.97E-12
1600	5.27E-12	5.26E-12	5.27E-12	5.28E-12	5.44E-12	7.07E-12
1700	5.14E-12	5.14E-12	5.13E-12	5.14E-12	5.18E-12	5.86E-12
1800	5.02E-12	5.02E-12	5.02E-12	5.03E-12	5.04E-12	5.27E-12
1900	4.94E-12	4.95E-12	4.95E-12	4.95E-12	4.95E-12	5.03E-12
2000	4.89E-12	4.89E-12	4.89E-12	4.89E-12	4.90E-12	4.93E-12

Table S4: T1 diagnostics for the species involved in $CH_3NH + NO_2$ reaction computed at CCSD(T)/cc-pVQZ based on the B3LYP/cc-pVTZ+d and M06-2X/cc-pVTZ+d geometries.

No.	Species	T1 diagnostics	
		B3LYP/cc-pVTZ+d	M06-2X/cc-pVTZ+d
1	CH_3NH	0.01335086	0.01327600
2	NO_2	0.02375747	0.02303088
3	**I1**	0.01653630	0.01610682
4	**I2**	0.01580088	0.01537740
5	**I3**	0.01720916	0.01647766
6	**I4**	**0.02218522**	0.01989297
7	**I5**	0.01918596	0.01806648
8	**TS1**	0.01801579	0.01745645
9	**TS2**	**0.02619867**	**0.02402151**
10	**TS3**	**0.02078098**	**0.02077468**
11	**TS4**	0.01789687	0.01734725
12	**TS5**	0.01837344	0.01734336
13	**TS6**	**0.02182776**	**0.02127202**
14	**TS7**	**0.05081448**	**0.05146866**
15	**TS8**	**0.03569021**	**0.03172304**
16	**TS9**	**0.02743051**	**0.02285567**
17	**TS10**	0.01672695	0.01587366
18	**PC1**	0.01823907	0.01770982
19	**PC2**	0.01666078	0.01639753
20	CH_2=NH	0.01199711	0.01191721
21	HO-NO	0.02083094	0.02003886
22	CH_2=NNO	0.01694887	0.01648308
23	H_2O	0.00740894	0.00736938
24	CH_2N-NO (*trans*)	**0.04787236**	**0.04538593**
25	OH	0.00803902	0.00799882
26	CH_2N-NO (*cis*)	0.04237074	0.04121106
27	H-NO_2	0.01970569	0.01918845
28	CH_3NHO	0.02006362	0.01936007
29	NO	0.02475097	0.02166677

Numbers in bold type are greater than the critical value.

Table S5: Detailed kinetic submechanism in NASA format for the reaction $CH_3NH + NO_2$.

ch3nh N 1H 4C 1 G 300.000 2500.000 1500.000 1
2.36094664E+001-3.71092656E-0022.53992603E-005-7.54974081E-0098.21570071E-013 2
-3.63128071E+003-9.56573966E+0013.64703306E+0004.64647258E-004-9.51964453E-007 3
7.89581153E-010-2.26233476E-0134.74614762E+0031.55757677E+001 4
no2 N 1O 2 G 300.000 2500.000 1500.000 1
-5.88599089E+0011.23621161E-001-9.36405727E-0053.11761251E-008-3.84976273E-012 2
2.42265809E+0043.38016068E+0021.76010733E+000-2.85565278E-0045.36983231E-008 3
3.64188179E-010-2.18943331E-0137.50711074E+0025.19962282E+000 4
i1 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
-3.92405559E+0028.13960917E-001-6.17205852E-0042.05791015E-007-2.54594826E-011 2
1.53740901E+0052.21685994E+0034.22553242E+0009.70356752E-003-1.85390982E-005 3
1.40028702E-008-3.67474521E-012-3.38607675E+0023.72407915E+001 4
i2 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
1.03397417E+002-2.15869573E-0011.76293076E-004-6.30414463E-0088.33661059E-012 2
-3.44135271E+004-4.99963486E+0025.67980938E+0001.25027446E-003-1.79918236E-006 3
5.50244420E-0109.63041046E-0142.35832717E+0022.81949400E+001 4
i3 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
1.37943692E+002-2.88744451E-0012.32666275E-004-8.18076531E-0081.05909370E-011 2
-4.69019690E+004-6.88530352E+0025.18209331E+0003.58806690E-003-6.96858913E-006 3
6.28410125E-009-2.01876737E-0126.79397377E+0023.03733180E+001 4
i4 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
-7.68397949E+0021.54441780E+000-1.14102085E-0033.70105295E-007-4.44745617E-011 2
3.08695818E+0054.30001822E+0032.88905943E+0002.21221254E-002-5.22851196E-005 3
4.76540168E-008-1.47532211E-0112.27924060E+0034.30515549E+001 4
i5 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
-3.31904046E+0027.00446400E-001-5.39775247E-0041.83195567E-007-2.31110343E-011 2
1.31231227E+0051.87777571E+0035.08742168E+0006.64249269E-003-1.48925879E-005 3
1.26874381E-008-3.67971850E-0122.06602778E+0033.07229972E+001 4
pc1 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
1.24512701E+003-2.60118239E+0002.02460947E-003-6.92741918E-0078.79453679E-011 2
-4.68119240E+005-6.73626727E+0033.00658883E+0002.18581717E-002-5.11761432E-005 3
4.62529304E-008-1.40426980E-011-1.06515150E+0034.59926020E+001 4
pc2 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
-7.56023010E+0021.51860504E+000-1.12114138E-0033.62735550E-007-4.33370667E-011 2
3.01455561E+0054.23493499E+003-1.91266493E-0013.69463585E-002-7.44742502E-005 3
6.04674673E-008-1.71462906E-011-4.93303429E+0025.90302789E+001 4
ts1 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
2.46499559E+002-5.26032086E-0014.26480342E-004-1.52023359E-0072.00945884E-011 2
-8.38091354E+004-1.27798001E+0033.59831735E+0001.17295228E-002-2.30535248E-005 3
1.81874407E-008-4.95208027E-0123.91519165E+0033.77144509E+001 4
ts2 N 2H 4C 1O 2G 300.000 2500.000 1500.000 1
-1.70342718E+0023.51107362E-001-2.59829345E-0048.45654171E-008-1.02157468E-011 2
7.53280081E+0041.00222841E+0034.35028250E+0007.71090005E-003-1.50197973E-005 3
1.20770782E-008-3.42640788E-0125.58178283E+0033.72681668E+001 4
ts3 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
-2.50349909E+0017.96080172E-002-7.78724227E-0053.32413224E-008-5.17833066E-012 2
1.93035353E+0041.94581960E+0023.96458189E+0001.04311371E-002-2.32345421E-005 3
2.24230884E-008-7.60189881E-0129.42349940E+0033.99627062E+001 4

ts4 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
-1.17943288E+002 2.35153479E-001 -1.64371087E-004 5.00469022E-008 -5.60269919E-012 2
5.42166910E+004 7.15268896E+002 5.15658690E+000 2.44878166E-003 -4.52674219E-006 3
3.91320340E-009 -1.25619528E-012 3.43053227E+003 7.07161884E+001 4
ts5 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
1.71662281E+002 -3.33450141E-001 2.49052509E-004 -8.21235329E-008 1.00907164E-011 2
-6.09679342E+004 -8.88676197E+002 7.26883553E+000 -8.89637369E-003 1.65695047E-005 3
-1.26432280E-008 3.36065769E-012 4.22500668E+003 1.85657172E+001 4
ts6 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
2.05461380E+002 -4.33048877E-001 3.49805963E-004 -1.24742465E-007 1.65509478E-011 2
-6.75953739E+004 -1.05355188E+003 3.86616246E+001 4.14707795E-002 -2.39748645E-005 3
1.98747348E-008 -5.69766979E-012 5.77777221E+003 3.98156026E+001 4
ts7 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
-3.80105133E+002 7.80160390E-001 -5.83028755E-004 1.90983910E-007 -2.31664729E-011 2
1.59295704E+005 2.15049103E+003 8.35816410E+000 -1.65389172E-002 3.55152199E-005 3
-3.04101118E-008 8.84118856E-012 8.56915377E+003 1.72892020E+001 4
ts8 N 2H 4C 1O 2G 300.000 2500.000 1500.000 1
1.22002187E+002 -2.39075891E-001 1.80139299E-004 -5.89780455E-008 7.08462373E-012 2
-3.79291996E+004 -6.05900299E+002 4.78018258E+000 5.79818282E-003 -1.24953899E-005 3
1.13390760E-008 -3.64302792E-012 6.38395187E+003 3.52115641E+001 4
ts9 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
7.37170807E+002 -1.50376242E+000 1.14699550E-003 -3.84897490E-007 4.79528743E-011 2
-2.73624500E+005 -3.98002346E+003 6.55922740E+000 -5.07280497E-003 1.05964428E-005 3
-9.24862083E-009 2.83403898E-012 7.62669899E+003 2.78899244E+001 4
ts10 C 1H 4N 2O 2G 300.000 2500.000 1500.000 1
1.05881016E+002 -1.98095417E-001 1.47961565E-004 -4.95711427E-008 6.28666710E-012 2
-3.74652081E+004 -5.28216821E+002 8.82346780E+000 -1.88277633E-002 4.02633918E-005 3
-3.51657050E-008 1.06277475E-011 2.80384522E+003 1.21612584E+001 4
ch2nh C 1H 3N 1 G 300.000 2500.000 1500.000 1
-9.39305603E+001 2.04797018E-001 -1.60299404E-004 5.51750869E-008 -7.04974199E-012 2
3.86014208E+004 5.42313103E+002 2.55197751E+003 1.10135710E-003 -5.83869579E-006 3
4.37884517E-009 -1.12374682E-012 2.31322254E+003 1.51409611E+001 4
hono N 1O 2H 1 G 300.000 2500.000 1500.000 1
-4.12055066E+001 9.44174575E-002 -7.54330867E-005 2.63008249E-008 -3.37385755E-012 2
1.33721119E+004 2.46691256E+002 1.49659531E+003 5.24363477E-003 -1.03999459E-005 3
8.39277637E-009 -2.35708515E-012 -2.40307944E+003 1.38585878E+001 4
ch2n-no C 1H 2N 2O 1G 300.000 2500.000 1500.000 1
-1.71806191E+002 3.71430681E-001 -2.91701906E-004 1.00730689E-007 -1.29032475E-011 2
7.20343238E+004 9.74844337E+002 3.73450234E+000 -3.31372516E-004 1.29233738E-006 3
-1.28513614E-009 3.91595288E-013 6.29797341E+003 1.70677551E+001 4
h2o O 1H 2 G 300.000 2500.000 1500.000 1
1.43097202E+001 -2.52600145E-002 1.87552529E-005 -6.12899109E-009 7.44981245E-013 2
-1.23306984E+004 -6.61253037E+001 1.68470636E+000 -9.87178121E-005 2.93621280E-007 3
-3.70788066E-010 1.54189401E-013 -7.31059079E+003 3.50817262E+000 4
ch3nno_trans C 1H 3N 2O 1G 300.000 2500.000 1500.000 1
-7.18734362E+001 1.62893716E-001 -1.30123553E-004 4.59657270E-008 -6.04419540E-012 2
3.39843701E+004 4.37193889E+002 3.72595479E+003 4.70056406E-003 -1.00350195E-005 3
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oh O 1H 1 G 300.000 2500.000 1500.000 1

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1.63324390E+002-3.26013269E-0012.49731299E-004-8.46764898E-0081.07221657E-011 2
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hno2 N 1O 2H 1 G 300.000 2500.000 1500.000 1
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1.16888356E-008-3.23627891E-0121.07004536E+0032.57469255E+001 4
no N 1O 1 G 300.000 2500.000 1500.000 1
-5.23681623E+0001.44898609E-002-1.21967302E-0054.46719534E-009-6.01398112E-013 2
4.56534583E+0033.63068566E+0011.13853730E+000-4.08437247E-0048.39997620E-007 3
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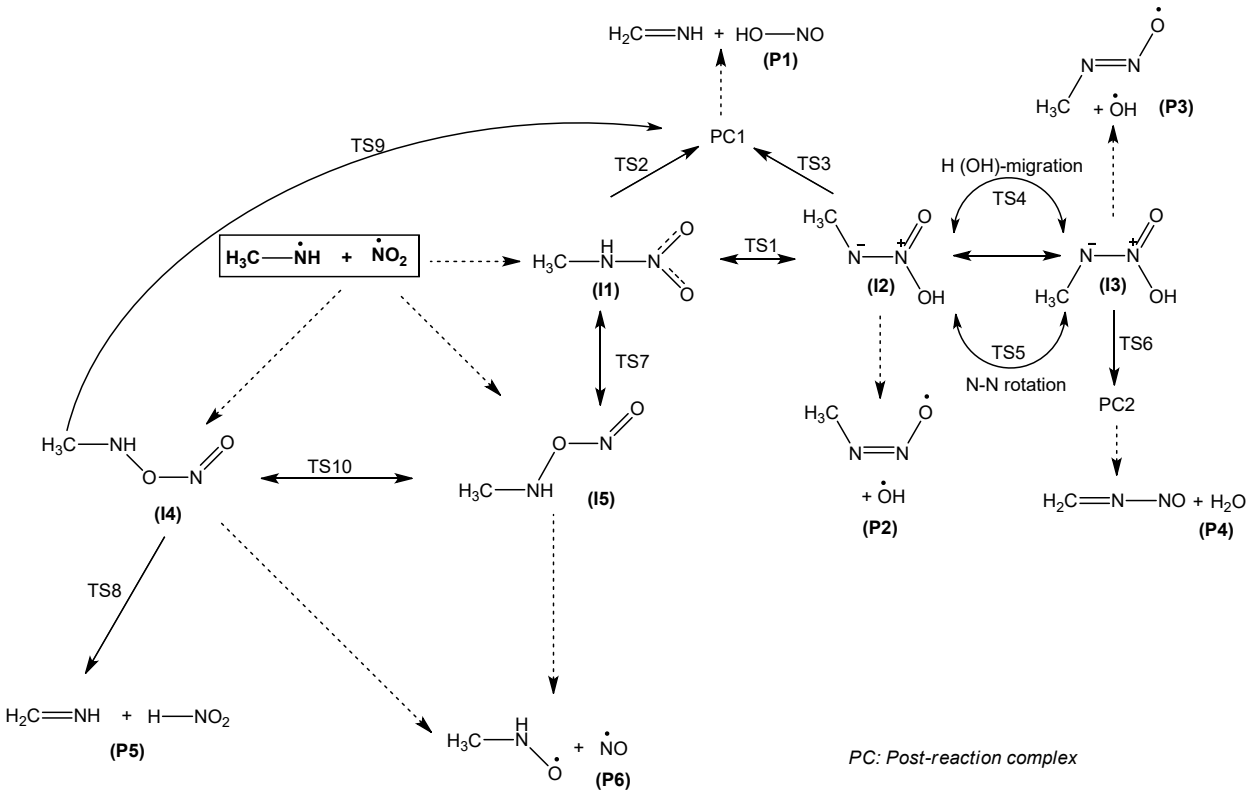
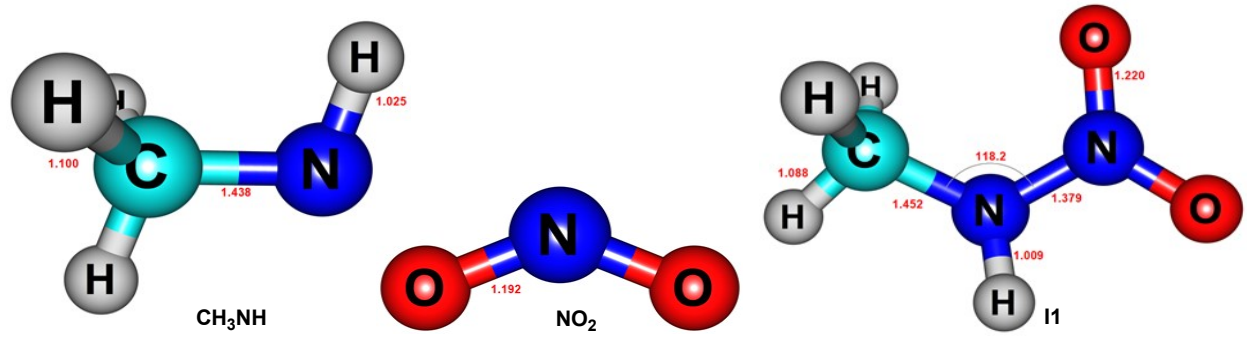
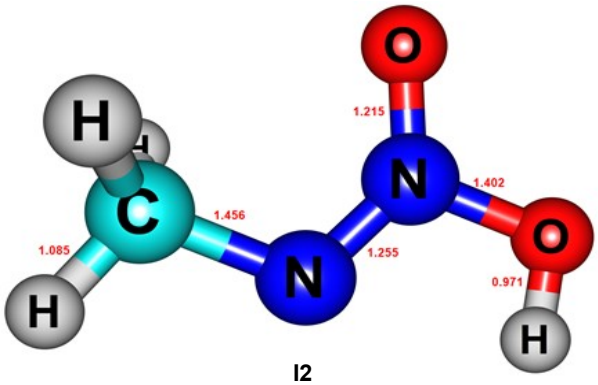


Figure S1: Reaction pathway scheme of the $CH_3NH + NO_2$ reaction. Dashed arrows present the reactions without tight transition states.





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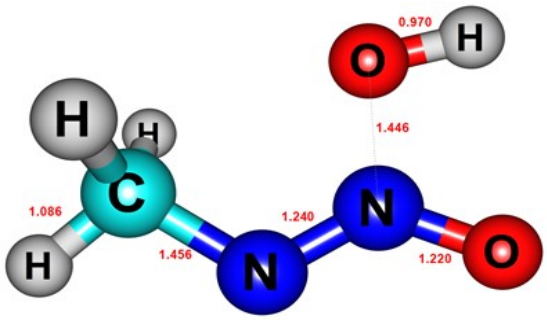

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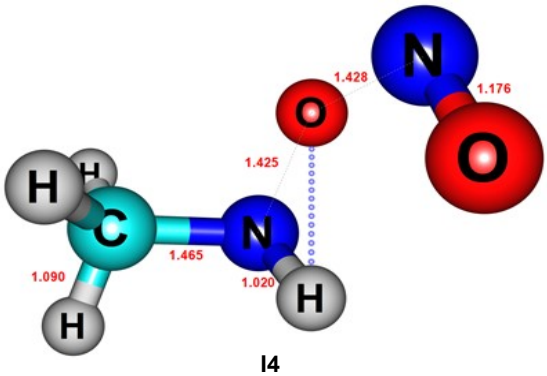

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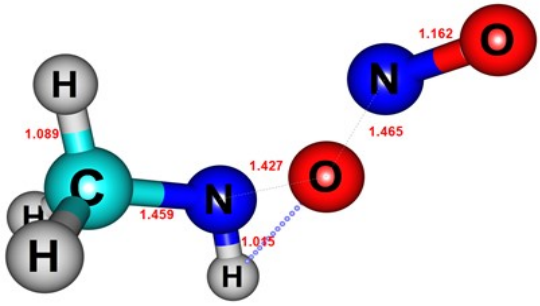

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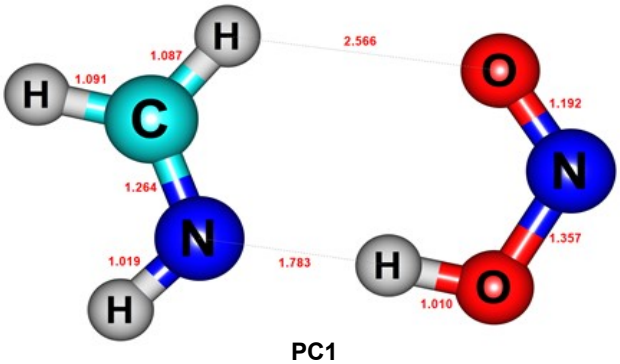

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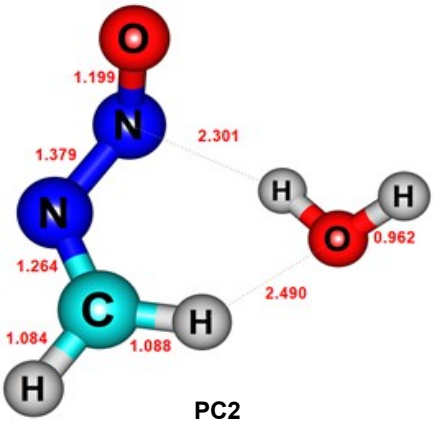
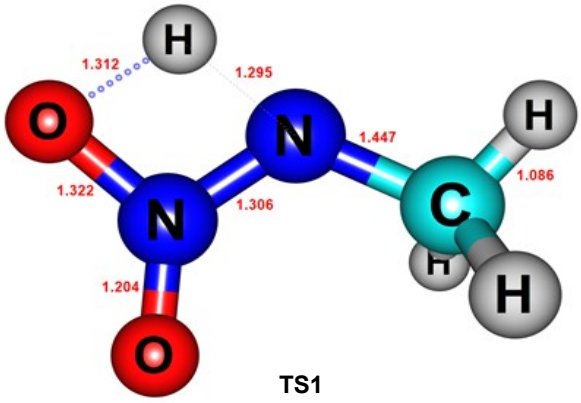


PC2



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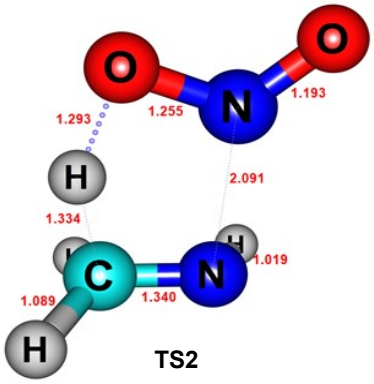

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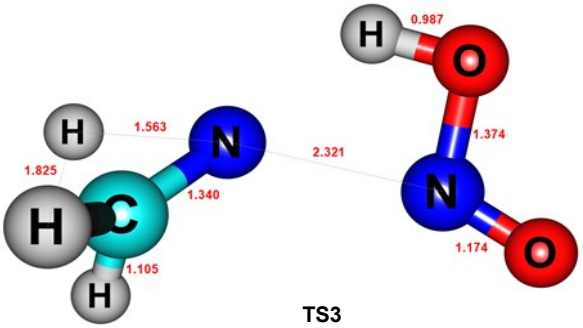

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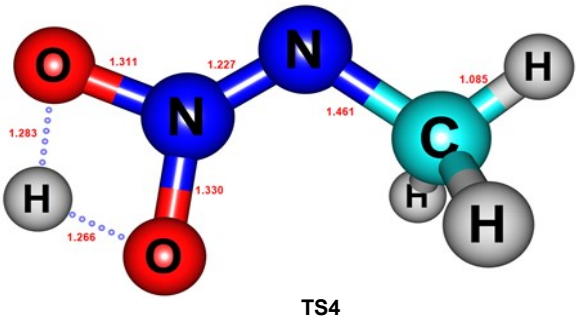

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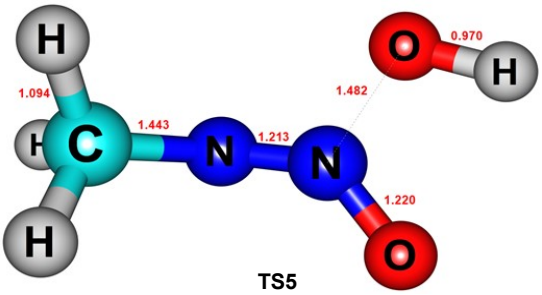

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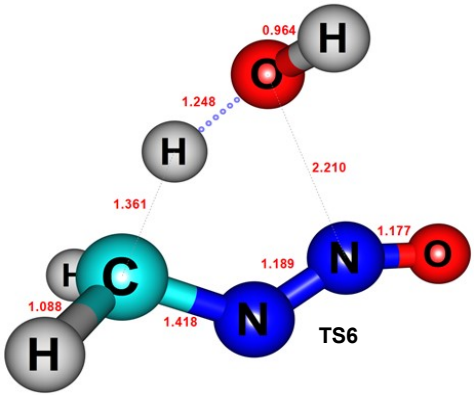

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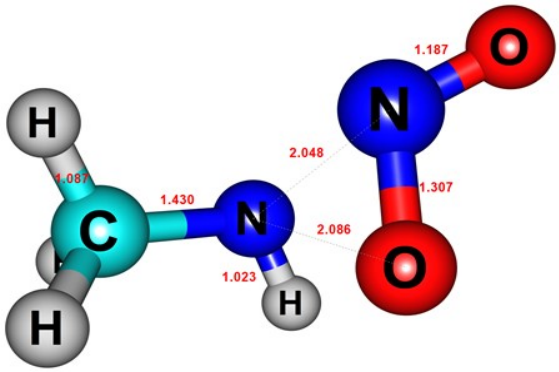
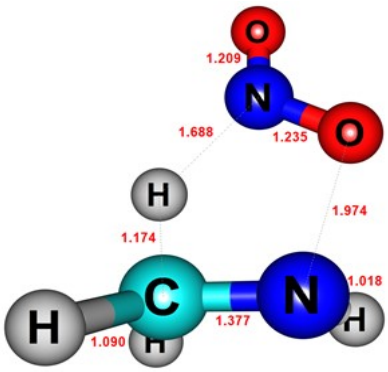
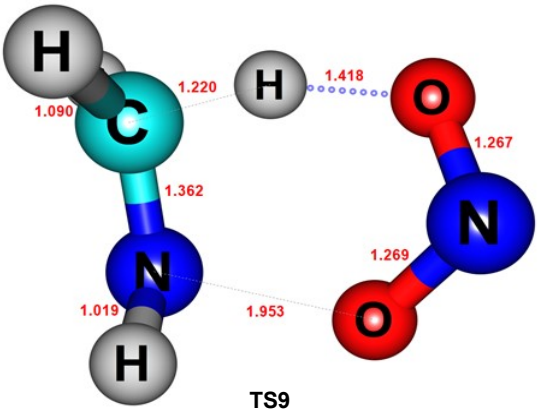


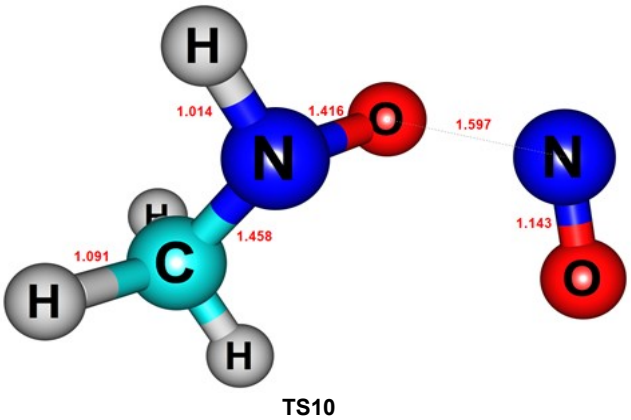
TS7



TS8



TS9



TS10

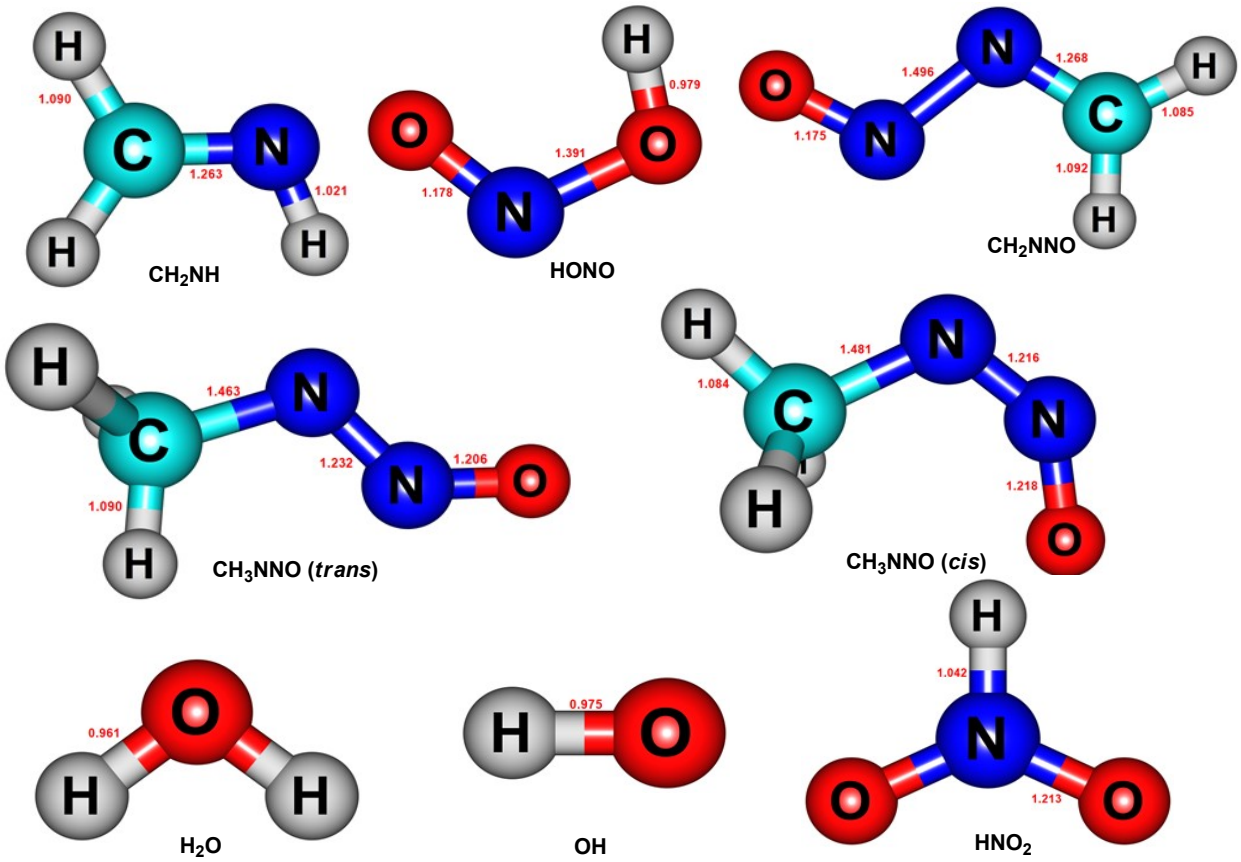
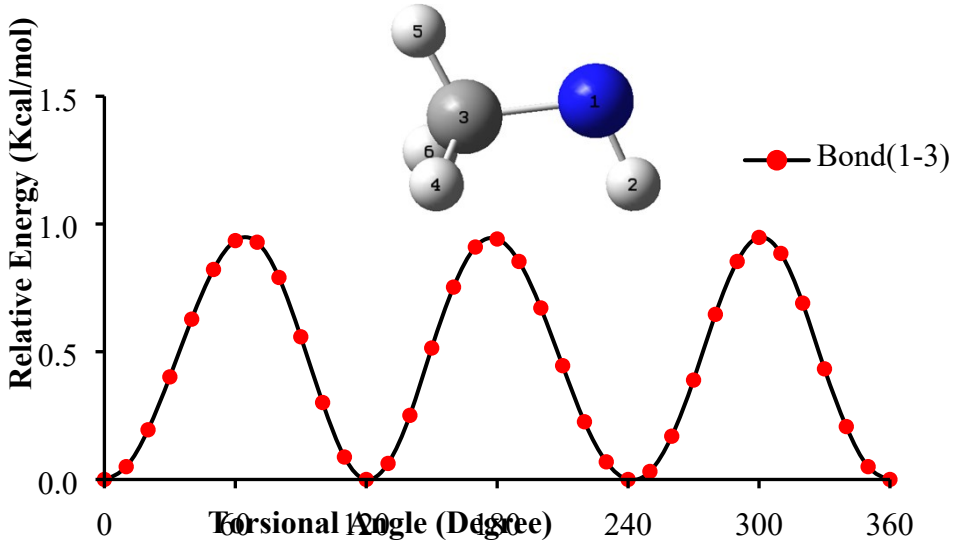
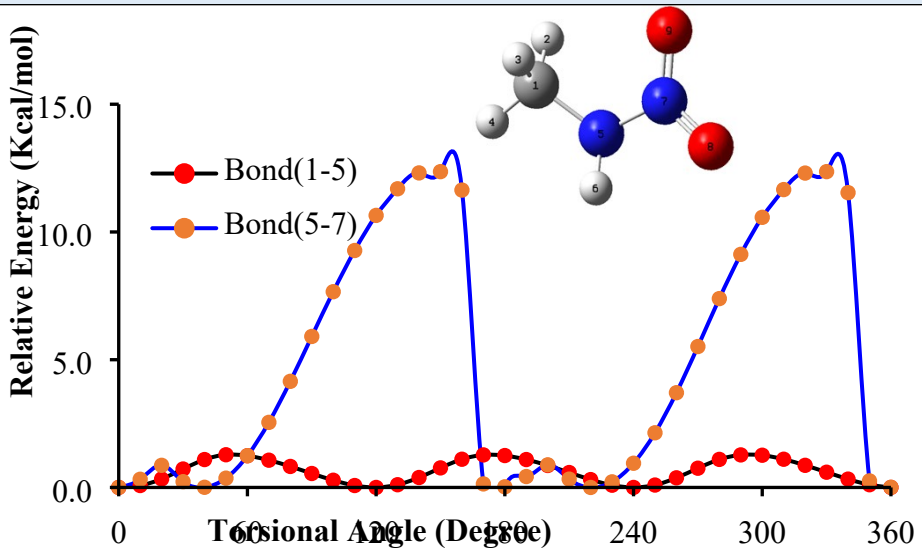
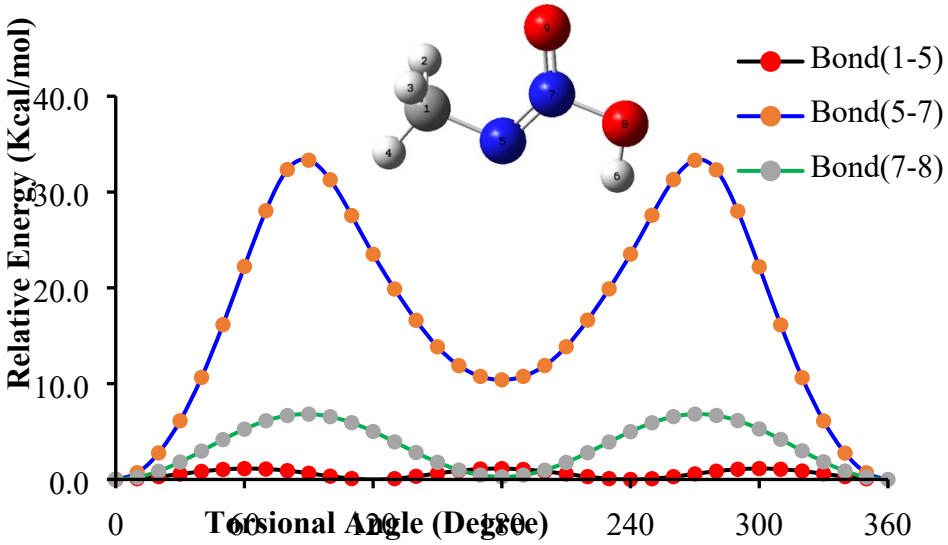
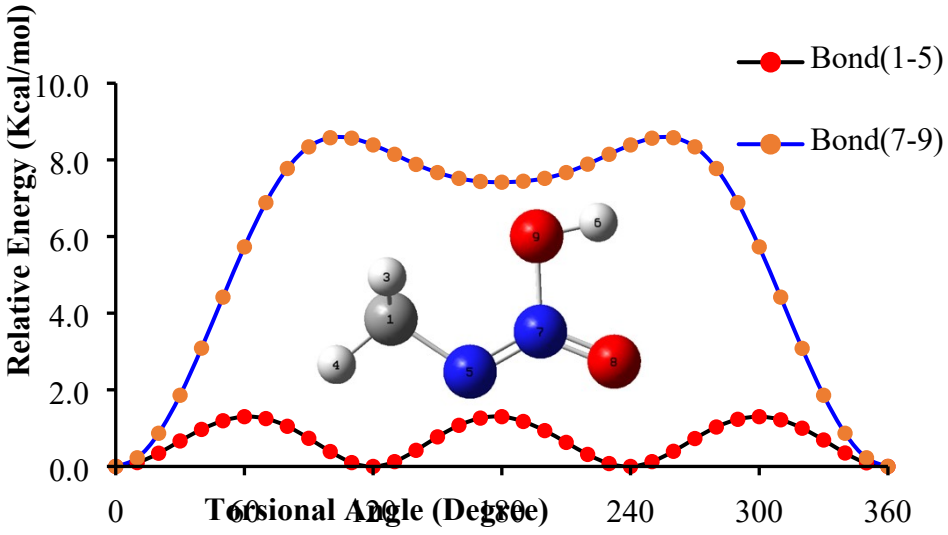
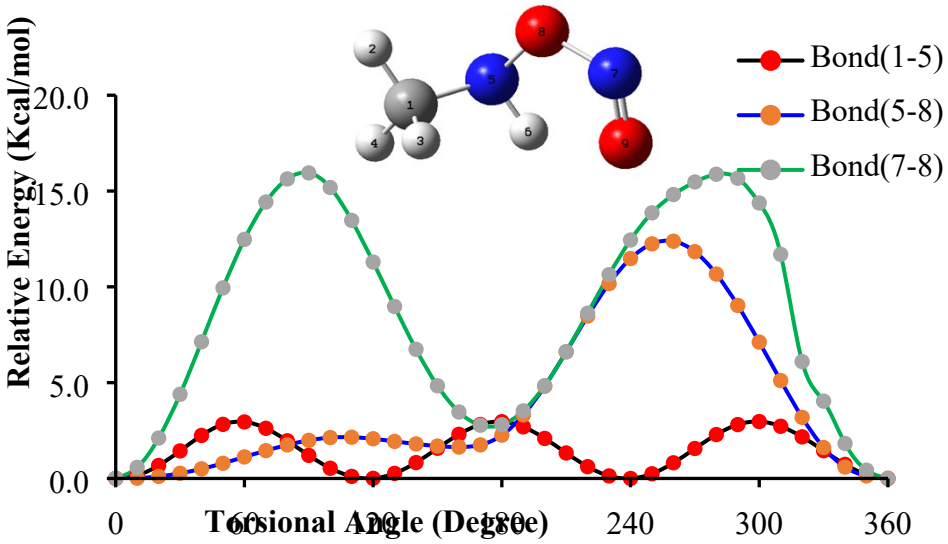
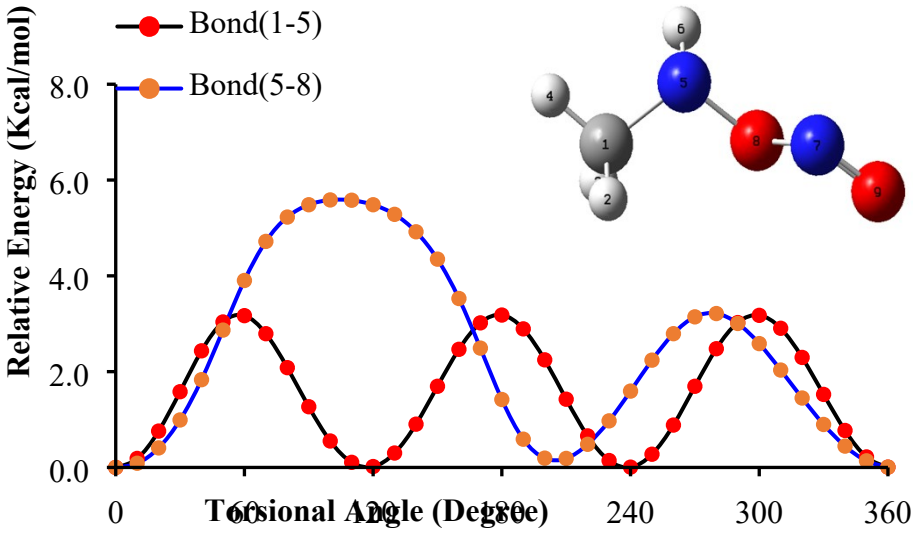
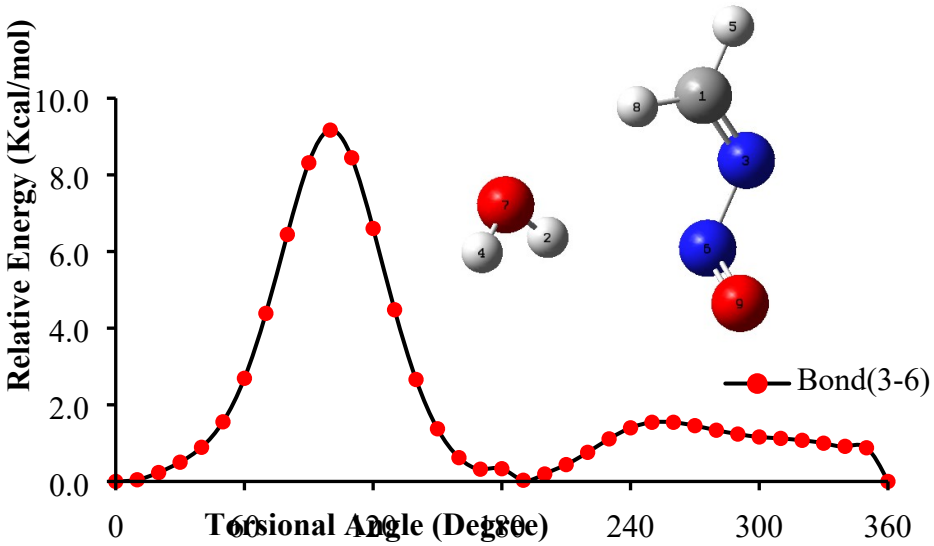
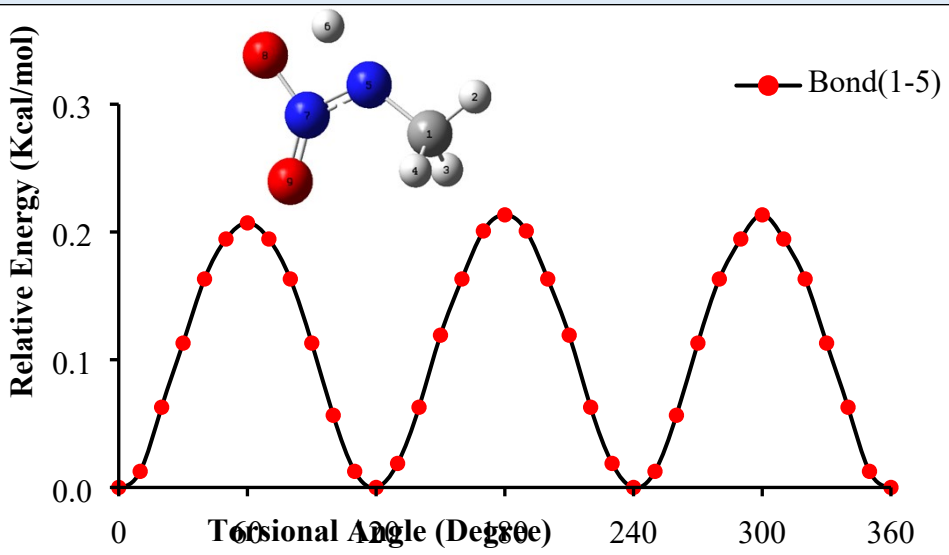
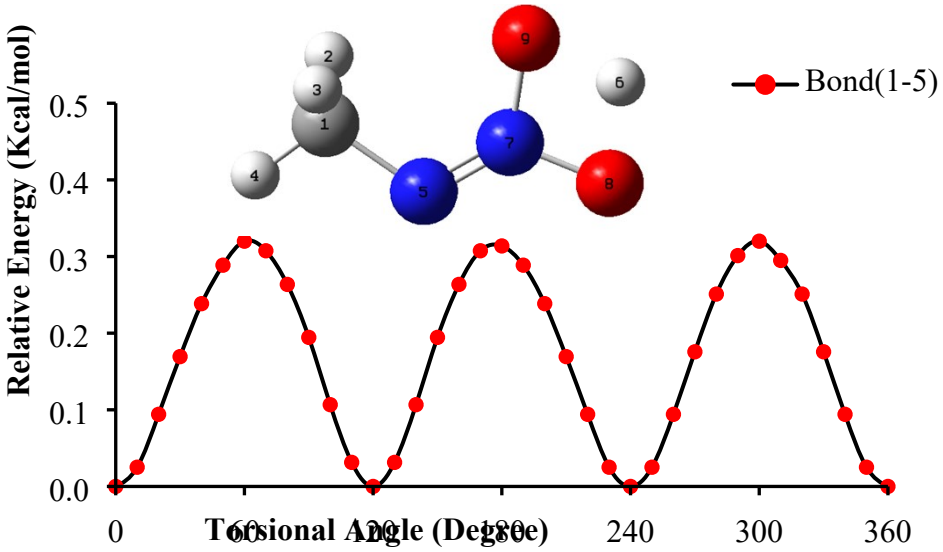
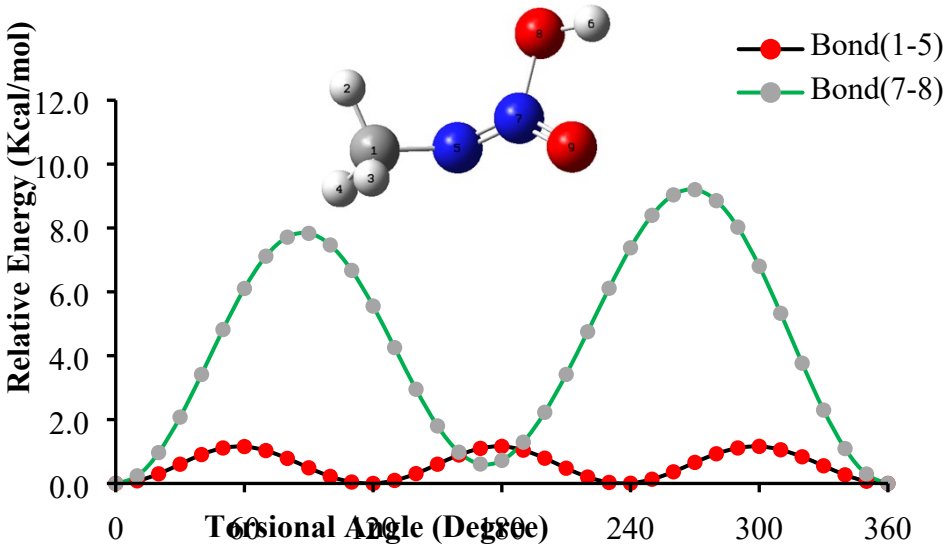


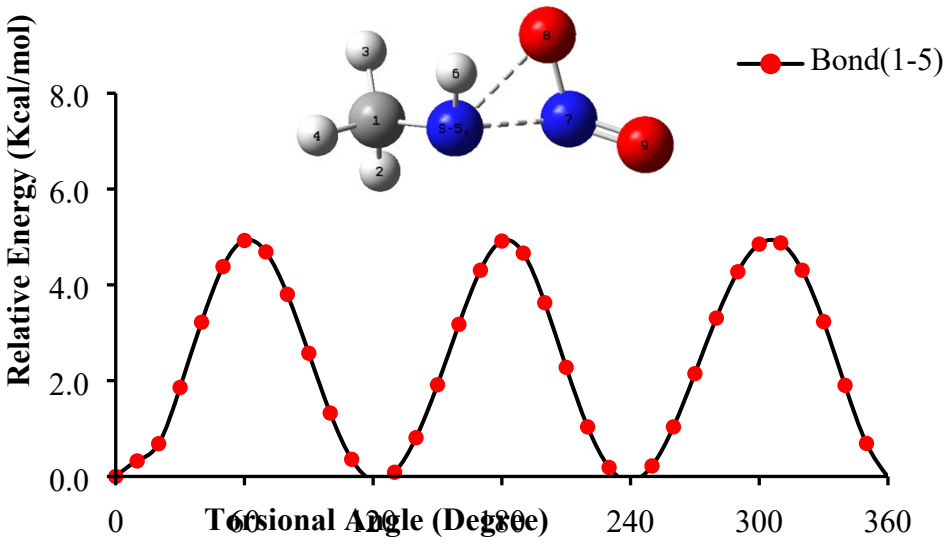
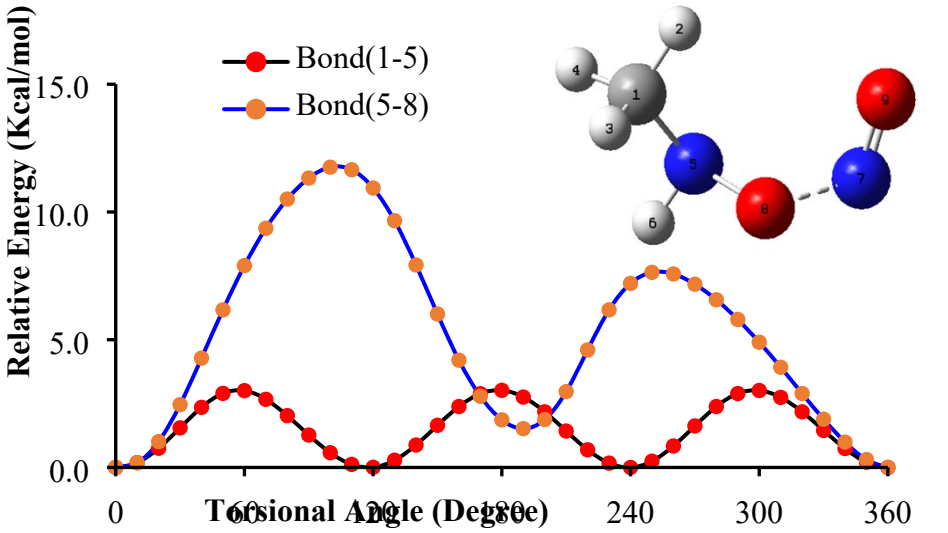
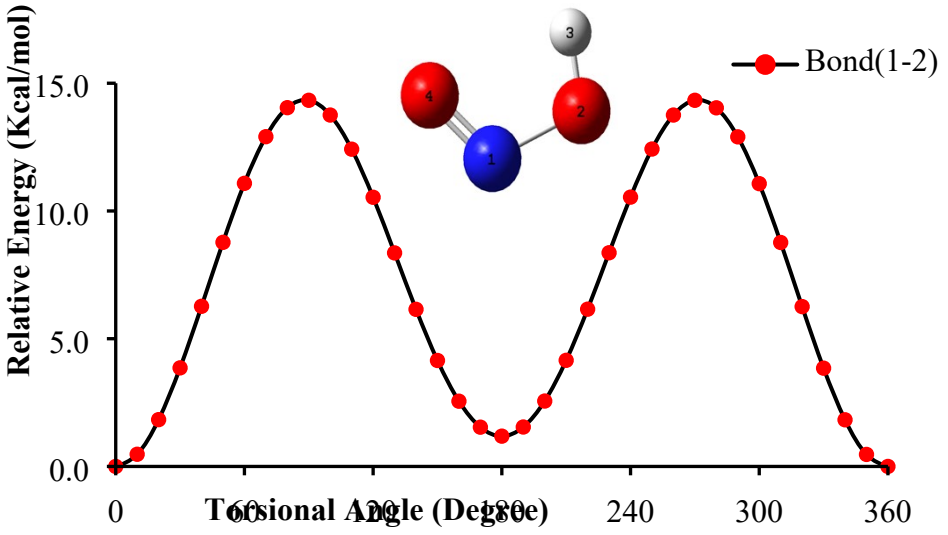
Figure S2: B3LYP/cc-pVTZ+d optimized geometries for the species involved in the CH_3NH + NO_2 reaction. All structures were obtained for the lowest-energy conformer of a given species. Bond lengths are in Å.

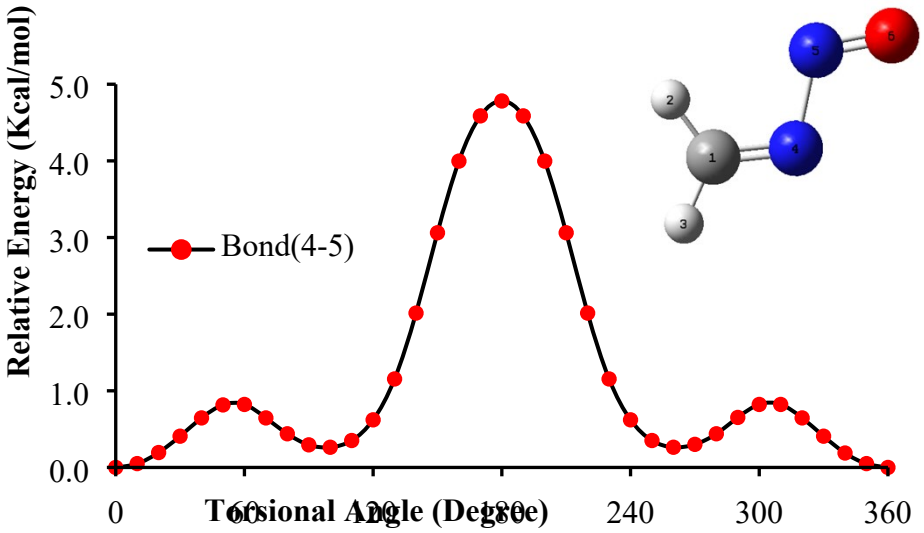
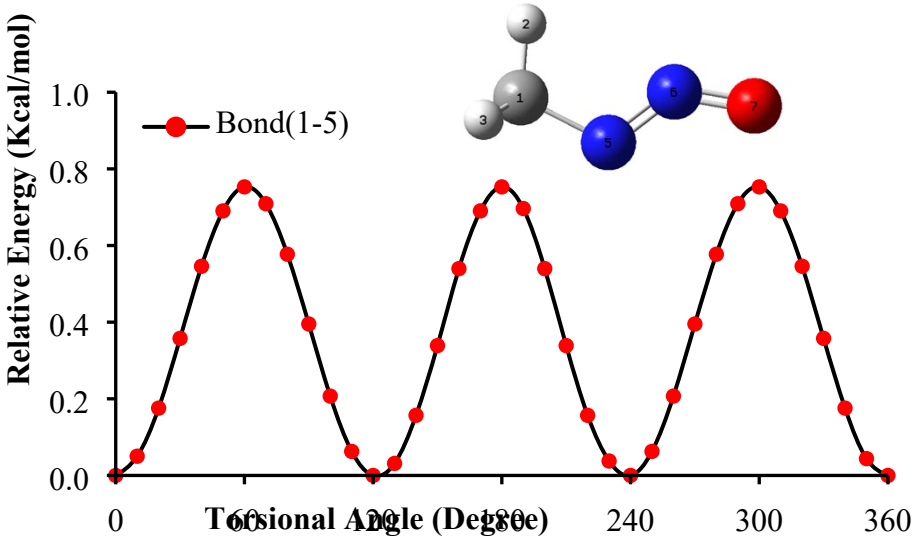
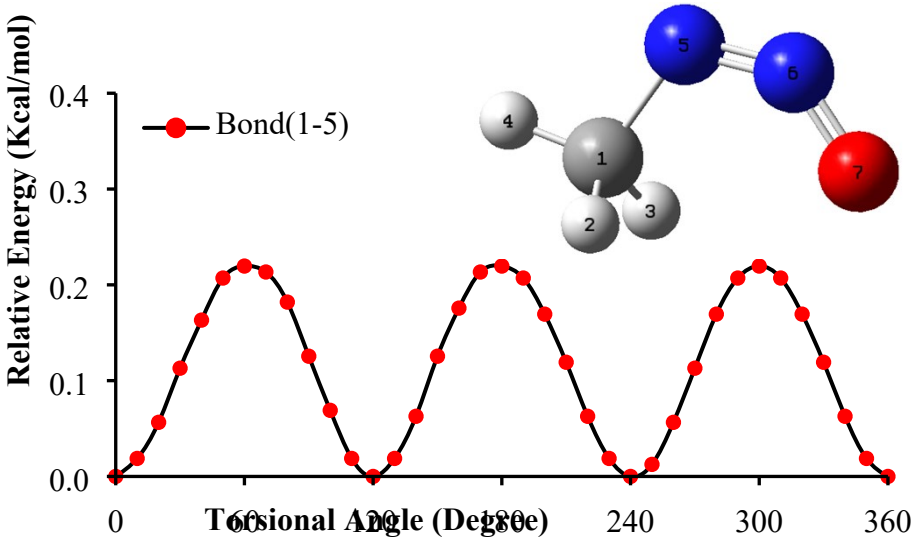
Species	Potential energy surfaces for the internal rotations
CH_3NH	

Species	Potential energy surfaces for the internal rotations
I1	
I2	
I3	

Species	Potential energy surfaces for the internal rotations
I4	
I5	
PC2	

Species	Potential energy surfaces for the internal rotations
TS1	
TS4	
TS5	

Species	Potential energy surfaces for the internal rotations
TS7	
TS10	
HONO	

Species	Potential energy surfaces for the internal rotations
CH_2N-NO	
CH_3N-NO (*trans*)	
CH_3N-NO (*cis*)	

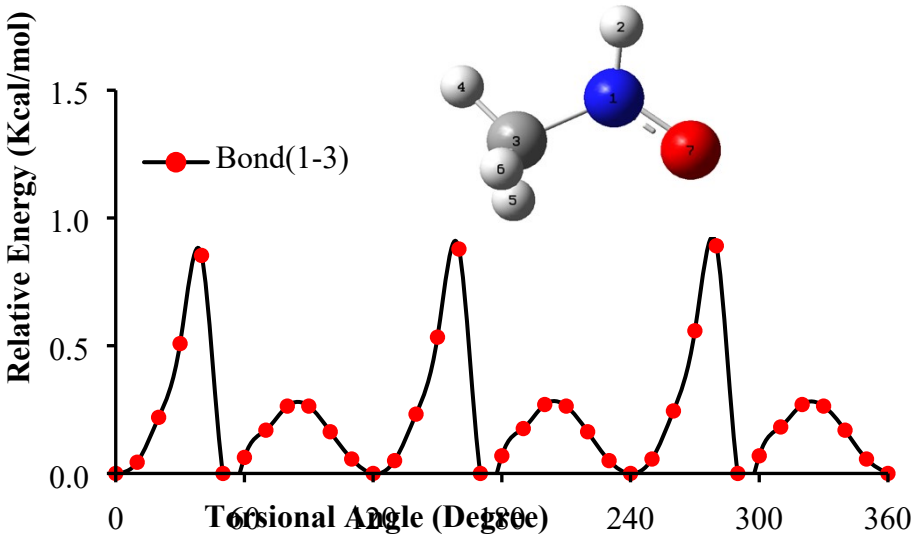
Species	Potential energy surfaces for the internal rotations
CH_3NHO	

Figure S3: Hindrance potentials for the species involved in the $CH_3NH + NO_2$ reaction, calculated at B3LYP/cc-pVDZ level of theory.

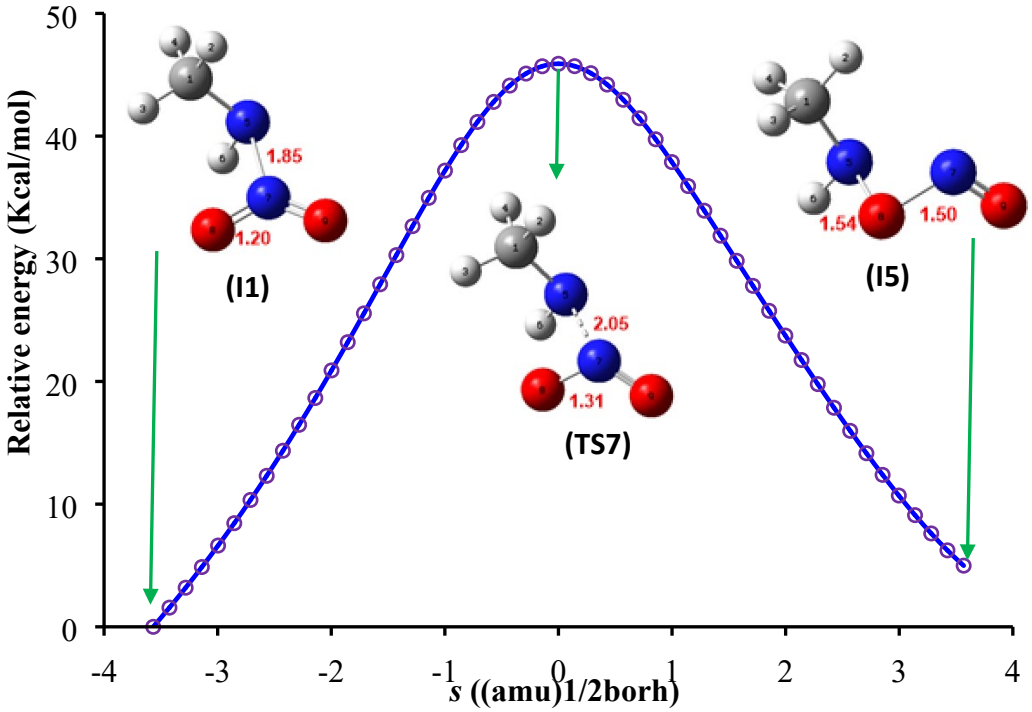


Figure S4: IRC plot for the conversion between **I1** and **I5** (via **TS7**) calculated at B3LYP/cc-pVTZ+d level of theory. Distances are in Å.

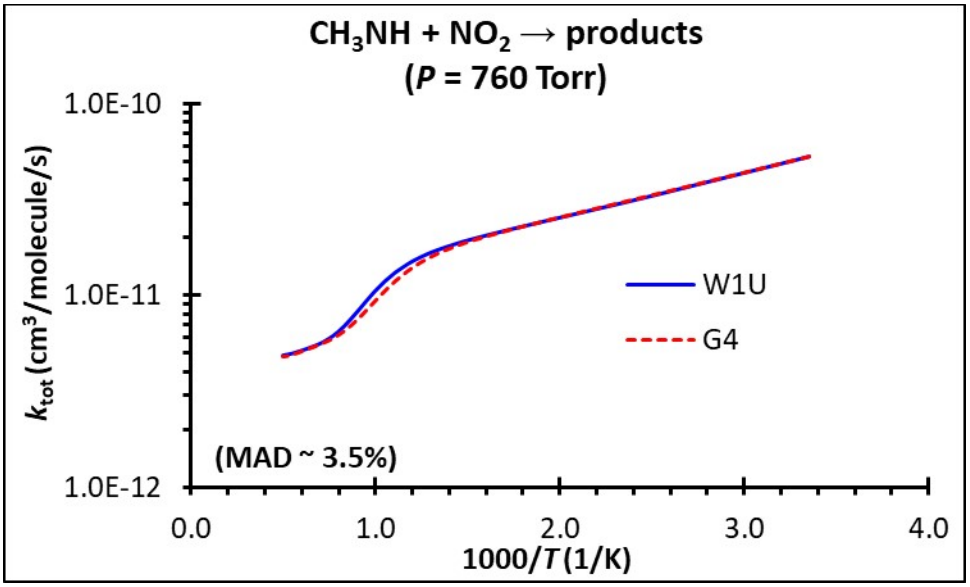


Figure S5: Calculated overall rate constant, k_{tot}, for the reaction between CH_3NH and NO_2 using the PES characterized at W1U and G4 levels of theory at P = 760 Torr.

References

1. T. Shimanouchi, *Tables of Molecular Vibrational Frequencies, Consolidated Volume 1, NSRDS NBS-39*.
2. L. M. Sverdlov, M. A. Kovner and E. P. Krainov, *Vibrational Spectra of Polyatomic Molecules*, Wiley, New York, 1974.
3. M. E. Jacox, *J. Phys. Chem.Ref. Data*, 1994, **Monograph 3**
4. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Co, 1979.