

## Supporting information.

### I) CH<sub>2</sub>(OH)OO<sup>•</sup> decomposition : B3LYP/cc-pVTZ

- CH<sub>2</sub>(OH)OO<sup>•</sup>\_pm

E(UB+HF-LYP) = -265.546645674 A.U.

Cartesian coordinates:

O	0.755637	0.528335	-0.303751
C	-0.608649	0.565250	0.244788
O	-1.359993	-0.500727	-0.183402
H	-1.002381	-1.302363	0.217035
O	1.375898	-0.550383	0.130359
H	-0.487470	0.611839	1.328907
H	-1.030590	1.481215	-0.160311

Rotational constants (GHz): 19.2472367 6.2785377 5.2035442

Vibrational harmonic frequencies :

110.5340	341.2555	462.2019	615.9223	816.2427	1059.3692
1135.0678	1162.3968	1273.0425	1391.6666	1421.9986	1505.2181
3040.7935	3140.3282	3786.2204			

Zero-point correction= 0.048439 (Hartree/Particle)

- CH<sub>2</sub>(OH)OO<sup>•</sup>\_pp

E(UB+HF-LYP) = -265.544332864 A.U.

Cartesian coordinates:

O	-0.709004	0.408065	-0.416867
C	0.563699	0.516905	0.290865
O	1.417816	-0.520837	-0.018120
O	-1.508038	-0.468162	0.165447
H	0.347727	0.472798	1.354197
H	0.932193	1.497317	-0.019395
H	1.731692	-0.424066	-0.923679

Rotational constants (GHz): 21.7286273 5.5467344 5.0175134

Vibrational harmonic frequencies :

109.4579	369.0796	409.2824	589.9034	854.2422	1052.4958
1113.0018	1159.4800	1278.6323	1391.3293	1417.2703	1496.7090
3040.9414	3144.9600	3803.8716			

Zero-point correction= 0.048367 (Hartree/Particle)

• **CH<sub>2</sub>(OH)OO°\_pt**

E(UB+HF-LYP) = -265.5440154 A.U.

Cartesian coordinates:

O	0.6153240518	-0.4631758539	-0.1648018261
C	-0.5008798281	0.4905799024	-0.0079229323
O	-1.6806852353	-0.2100554124	-0.0451302224
O	1.7622824458	0.1200253377	0.1112827719
H	-1.7938111151	-0.7010689822	0.7757700312
H	-0.3062951393	1.0220737954	0.9244578294
H	-0.4699848754	1.1611632013	-0.8634960542

Rotational constants (GHz): 39.05789 4.58653 4.29611

Vibrational harmonic frequencies :

58.0484	337.3384	418.8745	509.9449	893.3493	1033.2761
1168.1180	1188.6961	1224.5147	1389.0465	1414.1591	1514.5265
3049.5803	3128.9240	3804.7440			

Zero-point correction= 0.048145 (Hartree/Particle)

• **TSa**

E(UB+HF-LYP) = -265.5248061 A.U.

Cartesian coordinates:

C	-1.0659750361	0.0010274957	-0.4204601814
O	-0.9962198055	-0.0039353386	0.8427503087
O	0.8102696917	0.0036729187	-0.80466764
O	1.2746053805	-0.0008087224	0.3968416419
H	0.2567408525	-0.0036913182	0.9703894714
H	-1.2856213909	0.9286758145	-0.9598440912
H	-1.2845113789	-0.922580332	-0.9671787765

Rotational constants (GHz): 17.14734 6.97523 5.13221

Vibrational harmonic frequencies :

-774.8481	212.9095	459.8170	667.5294	734.9282	764.6736
1025.8644	1208.7161	1223.9455	1292.2516	1462.0151	1643.9195
1902.1892	2988.2840	3055.9135			

Zero-point correction= 0.042472 (Hartree/Particle)

• **c-(H<sub>2</sub>C=O---HOO<sup>o</sup>)\_Complex**

E(UB+HF-LYP) = -265.5324565 A.U.

Cartesian coordinates:

C	-1.5262674131	0.	-0.9132718962
O	-1.407049172	0.	0.2886069195
H	0.2698731173	0.	0.8973894482
O	1.2574770419	0.	0.9605799598
O	1.657342176	0.	-0.3068402783
H	-0.6494911075	0.	-1.5763885658
H	-2.5249378974	0.	-1.3801423119

Rotational constants (GHz): 19.05202 3.56180 3.00079

Vibrational harmonic frequencies :

74.2873	121.4043	186.0710	191.1693	248.3108	651.2312
1187.9014	1222.3195	1274.7858	1524.1014	1547.1827	1787.5166
2932.1038	3028.8966	3353.0488			

Zero-point correction= 0.044038 (Hartree/Particle)

• **TSb variational (300 K -600 K)**

E(UB+HF-LYP) (Hartree): -265.522456359

Cartesian coordinates (Angs):

C	-1.987458	0.486314	0.000026
O	-1.935808	-0.714664	-0.000265
H	-2.953381	1.025712	0.000157
H	-1.075848	1.108625	0.000174
H	1.438507	-1.131794	-0.000272
O	2.167632	-0.483334	0.000177
O	1.582609	0.707944	0.000061

Rotational constants (GHz): 19.3105703 2.1536975 1.9375983

Vibrational harmonic frequencies (cm-1):

-66.6127	48.8013	75.4743
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92.8552	115.7361	179.6880
1170.2270	1213.9181	1275.3782
1437.4322	1535.7823	1811.0671
2890.0096	2966.3712	3600.7776

Zero-point correction (Hartree): 0.041949

## II) CH<sub>3</sub>CH(OH)OO° decomposition: B3LYP/cc-pVTZ level

- CH<sub>3</sub>CH(OH)OO° -mp

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.884867268

Cartesian coordinates (Angs):

C	0.396736	0.089094	0.349474
O	0.308792	1.357536	-0.177370
O	-0.707831	-0.762198	-0.184576
O	-1.866076	-0.178706	0.026740
H	-0.550604	1.719716	0.074528
H	0.234680	0.074940	1.431206
C	1.678106	-0.576209	-0.068216
H	2.521138	-0.039102	0.362774
H	1.700728	-1.607784	0.279022
H	1.765923	-0.558132	-1.153431

Rotational constants (GHz): 9.1710047 4.2161397 3.1080551

Vibrational harmonic frequencies (cm-1):

93.4502	196.0049	283.2872
372.4511	453.1775	508.1195
602.1515	745.0821	917.0473
1044.4000	1109.9857	1171.1221
1208.2505	1292.4765	1353.1175
1406.2212	1472.3885	1487.5916
1490.6900	3024.6607	3054.4258
3129.0738	3129.8499	3767.0688

Zero-point correction (Hartree): 0.075891

- CH<sub>3</sub>CH(OH)OO° -pm

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.883044806

Cartesian coordinates (Angs):

O	0.919787	-0.322404	0.624547
C	-0.492563	0.143108	0.460191
O	-0.516986	1.384532	-0.131453
H	-0.122177	1.299908	-1.009669

O	1.570332	-0.218738	-0.512156
H	-0.817479	0.259190	1.492116
C	-1.257651	-0.931192	-0.281655
H	-1.207537	-1.880169	0.250951
H	-2.300333	-0.630806	-0.373845
H	-0.836244	-1.066739	-1.278272

Rotational constants (GHz): 7.2851694 4.7318293 3.6739276

Vibrational harmonic frequencies (cm-1):

109.5261	233.3594	292.6606
384.4397	401.6973	470.2176
675.3930	723.2431	904.9823
1051.2581	1086.8404	1160.2700
1170.0020	1334.8733	1351.4118
1406.8821	1434.2113	1485.4269
1492.9146	3042.4932	3100.0521
3120.1447	3122.0071	3758.6689

Zero-point correction (Hartree): 0.075893

- **CH<sub>3</sub>CH(OH)OO<sup>o</sup> -mt**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.882354605

Cartesian coordinates (Angs):

O	-0.843230	-0.447425	-0.413678
C	0.396039	-0.055095	0.317685
O	1.374485	-0.950367	-0.064330
O	-1.914558	0.048008	0.166053
H	1.168220	-1.823384	0.286922
H	0.118659	-0.130934	1.370914
C	0.789599	1.340482	-0.086140
H	-0.027586	2.028226	0.121031
H	1.669051	1.650021	0.477055
H	1.024254	1.362025	-1.149554

Rotational constants (GHz): 8.5218339 4.1168410 3.0451166

Vibrational harmonic frequencies (cm-1):

76.7964	226.8659	310.7979
386.7729	421.2298	456.6501
541.4371	807.5088	920.4570
1045.3658	1096.4335	1190.1383
1197.5361	1296.8239	1346.4435
1401.6992	1450.6076	1487.8009
1489.5495	3049.6374	3051.8135
3123.2455	3135.3220	3803.7905

Zero-point correction (Hartree): 0.075897

• **CH<sub>3</sub>CH(OH)OO<sup>o</sup> -pt**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.881267459

Cartesian coordinates (Angs):

O	-0.816878	-0.567117	-0.343302
C	0.402940	-0.058698	0.345813
O	1.411357	-0.952505	0.054866
O	-1.902931	0.016385	0.113230
H	1.746499	-0.782989	-0.832979
H	0.183301	-0.136438	1.408371
C	0.658649	1.360838	-0.101610
H	-0.207877	1.983034	0.112006
H	1.524204	1.760477	0.425412
H	0.851948	1.388974	-1.176378

Rotational constants (GHz): 8.5301598 4.1532021 3.0627407

Vibrational harmonic frequencies (cm-1):

94.7385	241.9667	298.6426
348.9909	434.3427	471.2891
524.1304	808.2220	908.0059
1066.6662	1073.8026	1178.2243
1196.9737	1331.9549	1339.2266
1404.2741	1426.6113	1482.8058
1497.3663	3034.2447	3095.9788
3114.1545	3131.8819	3790.1205

Zero-point correction (Hartree): 0.075851

• **CH<sub>3</sub>CH(OH)OO<sup>o</sup> -mm**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.881240385

Cartesian coordinates (Angs):

O	-0.794435	-0.510460	-0.385905
C	0.354716	0.074132	0.331651
O	0.520470	1.399295	-0.033345
H	0.869510	1.442184	-0.931444
O	-1.941094	-0.128828	0.140836
H	0.079921	0.070367	1.383584
C	1.528874	-0.819908	0.003847
H	2.420643	-0.441088	0.500169
H	1.343969	-1.840316	0.335590
H	1.704896	-0.836542	-1.073575

Rotational constants (GHz): 8.6529806 4.0851521 3.0544216

Vibrational harmonic frequencies (cm-1):

89.3042	223.1711	312.6073
341.4161	390.4826	518.1039
562.6363	788.7798	909.0452
1068.4939	1085.5132	1151.2195

1191.6135	1314.7826	1344.1323
1411.9597	1441.6205	1485.5242
1494.5701	3039.8673	3100.6599
3120.4083	3127.6091	3784.3647

Zero-point correction (Hartree): 0.075858

• **CH<sub>3</sub>CH(OH)OO° -pp**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.880761690

Cartesian coordinates (Angs):

O	0.977800	-0.076623	0.610407
C	-0.497387	-0.122035	0.432218
O	-0.852622	-1.173217	-0.393749
O	1.612030	0.193342	-0.512214
H	-0.808905	-0.278070	1.468661
H	-0.610937	-2.007284	0.023454
C	-1.011802	1.170336	-0.143761
H	-2.098429	1.130833	-0.197886
H	-0.716247	2.009292	0.483828
H	-0.608015	1.307412	-1.144350

Rotational constants (GHz): 7.3137525 4.6398690 3.6013305

Vibrational harmonic frequencies (cm-1):

114.6664	219.3223	298.5676
368.8992	417.3632	442.1613
685.1172	739.2698	923.6841
1039.3162	1099.5325	1146.8881
1175.2509	1291.5778	1376.8218
1401.3301	1453.9013	1484.9932
1492.2620	3034.0406	3057.5732
3127.5445	3140.6574	3802.7808

Zero-point correction (Hartree): 0.075939

• **c-(CH<sub>3</sub>CHO...HOO)-complex1**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.878340332

Cartesian coordinates (Angs):

C	-1.101095	0.170110	-0.000063
O	-0.501661	-0.885570	0.000159
H	1.237240	-0.766568	0.000004
O	2.185334	-0.471370	-0.000171
O	2.106410	0.855429	0.000126
H	-0.534312	1.115564	-0.000226
C	-2.590073	0.275957	-0.000053
H	-2.911199	0.846291	0.875668

H	-2.911271	0.847466	-0.874983
H	-3.054120	-0.707057	-0.000678

Rotational constants (GHz): 14.7341214 1.8342651 1.6476219

Vibrational harmonic frequencies (cm-1):

59.7704	69.1240	82.6179
161.1714	165.6920	242.1839
530.8388	670.2875	797.1428
900.0766	1141.5128	1151.6884
1190.2866	1383.1223	1429.5563
1458.4891	1467.8424	1563.7504
1773.9964	2968.4187	3025.5650
3076.1316	3141.4016	3290.1787

Zero-point correction (Hartree): 0.072311

- **c-(CH<sub>3</sub>CHO...HOO)-complex2**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.878797518

Cartesian coordinates (Angs):

C	-1.639170	-0.386403	0.000369
O	-0.725795	-1.184209	-0.000490
H	0.968859	-0.782324	-0.000030
O	1.926168	-0.516031	0.000051
O	1.914149	0.810765	0.000187
H	-2.676110	-0.768770	0.002406
C	-1.488173	1.096933	-0.000435
H	-1.995507	1.505759	0.878139
H	-0.440527	1.391009	-0.007590
H	-2.008836	1.506944	-0.870507

Rotational constants (GHz): 8.1001899 2.4906746 1.9273268

Vibrational harmonic frequencies (cm-1):

52.0463	114.0653	116.2575
167.0038	175.8960	247.7587
536.9917	686.4889	791.1823
900.7351	1145.9525	1156.4879
1198.0446	1387.6198	1430.0324
1463.8623	1476.8128	1566.4300
1781.0943	2928.3024	3018.0132
3069.9872	3129.6996	3284.7292

Zero-point correction (Hartree): 0.072504

- **TSa**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.865975335

Cartesian coordinates (Angs):



C	0.664364	0.252979	0.447297
O	0.137200	1.295502	-0.057596
O	-0.899069	-0.908412	0.223457
O	-1.728971	-0.056095	-0.271368
H	-0.992845	0.890903	-0.278537
H	0.655620	0.136550	1.537605
C	1.716103	-0.517781	-0.285657
H	2.681302	-0.033363	-0.111923
H	1.782654	-1.540866	0.082713
H	1.517183	-0.512378	-1.355634

Rotational constants (GHz): 8.8682683 4.0271444 3.0999201

Vibrational harmonic frequencies (cm-1):

-837.4087	131.4022	194.6579
260.0472	489.8314	507.3484
639.0539	707.2676	882.9280
943.5899	1038.0579	1128.2805
1158.5461	1286.6962	1374.2744
1399.9865	1465.3878	1475.6122
1615.4702	1883.7262	3005.0093
3028.4401	3092.7492	3132.3769

Zero-point correction (Hartree): 0.070260

- **TSb-variational**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -304.866741694

Cartesian coordinates (Angs):

C	1.358480	0.008747	-0.000027
O	1.114969	1.190683	-0.000009
H	-2.280895	1.023035	-0.000086
O	-2.925835	0.290796	0.000043
O	-2.199649	-0.820353	-0.000025
H	0.531485	-0.727931	-0.000088
C	2.742032	-0.571015	0.000026
H	2.868492	-1.212870	0.875986
H	2.868584	-1.212809	-0.875965
H	3.493383	0.215176	0.000092

Rotational constants (GHz): 11.3401152 1.3227747 1.1932486

Vibrational harmonic frequencies (cm-1):

-68.1465	39.9416	49.7320
61.5676	76.5141	163.7662
178.7534	509.8857	784.0641
887.9523	1131.0680	1145.4802
1170.2113	1379.9763	1432.7817
1438.6750	1460.7823	1470.1313
1802.9463	2905.4292	3022.7943

3074.2128          3135.0820          3600.5133  
Zero-point correction (Hartree): 0.070446

• **CH<sub>3</sub>CHO**

E(RB+HF-LYP/CC-pVTZ) (Hartree): -153.893531568

Cartesian coordinates (Angs):

C	0.233473	0.396434	-0.000002
O	1.231542	-0.275829	0.000000
H	0.304559	1.504895	0.000001
C	-1.165728	-0.148159	-0.000002
H	-1.702967	0.223765	0.876503
H	-1.703041	0.223919	-0.876395
H	-1.157355	-1.235593	-0.000091

Rotational constants (GHz): 57.4401354 10.1725371 9.1252657

Vibrational harmonic frequencies (cm-1):

160.4815	509.1232	775.9118
885.0564	1129.2854	1137.5825
1378.6988	1426.1014	1460.7506
1470.3148	1817.2308	2862.4517
3022.6314	3074.3654	3135.1356

Zero-point correction (Hartree): 0.055234

• **CH<sub>3</sub>C<sup>o</sup>HOH**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -154.446564950

Cartesian coordinates (Angs):

C	0.091401	0.525289	-0.112185
O	1.259770	-0.177566	0.047203
H	1.103574	-1.106286	-0.154604
H	0.206886	1.559428	0.179755
C	-1.208203	-0.179309	0.019543
H	-1.377059	-0.575155	1.033273
H	-2.032706	0.495299	-0.210508
H	-1.278042	-1.028635	-0.669684

Rotational constants (GHz): 44.5663000 9.4388922 8.2451064

Vibrational harmonic frequencies (cm-1):

193.7055	332.8240	407.9192
569.9588	915.2694	1019.2248
1061.4684	1200.2279	1309.1926
1401.3740	1434.8875	1467.4415
1485.9320	2927.8439	3002.1122
3093.3857	3186.2535	3800.9797

Zero-point correction (Hartree): 0.065634

### III) (CH<sub>3</sub>)<sub>2</sub>C(OH)OO° decomposition: B3LYP/cc-pVTZ level

- Acetone

E(RB+HF-LYP/CC-pVTZ) (Hartree): -193.233158042

Point group : C2V

Cartesian coordinates (Angs):

C	0.000000	0.000000	0.184854
C	0.000000	1.288132	-0.611596
C	0.000000	-1.288132	-0.611596
H	-0.876879	1.331865	-1.261519
H	0.000000	2.140866	0.061926
H	0.876879	1.331865	-1.261519
H	-0.876879	-1.331865	-1.261519
H	0.876879	-1.331865	-1.261519
H	0.000000	-2.140866	0.061926
O	0.000000	0.000000	1.394032

Rotational constants (GHz): 10.1924111 8.5207052 4.9211040

Vibrational harmonic frequencies (cm-1):

18.6455	132.8156	377.9293
489.6188	535.2587	781.7583
884.7864	885.6775	1084.3865
1120.4167	1233.8574	1386.8619
1387.5336	1460.5093	1465.9609
1470.4674	1488.1305	1794.2052
3026.0103	3033.1611	3077.9659
3085.4913	3139.1760	3140.2647

Zero-point correction (Hartree): 0.083155

- (CH<sub>3</sub>)<sub>2</sub>C°OH

E(UB+HF-LYP/CC-pVTZ) (Hartree): -193.782936571

Cartesian coordinates (Angs):

C	0.009281	0.025307	-0.219549
O	-0.051586	1.378583	0.054843
H	-0.958968	1.682822	-0.046436
C	1.362404	-0.537944	0.025673
H	1.588940	-0.614796	1.101168
H	1.449371	-1.537566	-0.399901
H	2.130494	0.096433	-0.418693
C	-1.225138	-0.770492	0.031547
H	-1.126878	-1.778904	-0.370084

H	-1.448112	-0.864820	1.107394
H	-2.101440	-0.313061	-0.438220

Rotational constants (GHz): 9.3240267 8.1307260 4.6440844

Vibrational harmonic frequencies (cm-1):

167.2616	183.4972	325.3375
359.6442	374.1079	431.5849
791.1176	955.4157	979.1733
1009.4670	1089.1501	1138.9855
1300.6606	1377.1891	1410.5646
1421.2124	1464.8870	1476.9545
1484.5406	1493.1096	2912.9354
2928.0969	3019.5566	3054.8275
3091.8041	3102.0775	3812.6790

Zero-point correction (Hartree): 0.093760

- **(CH<sub>3</sub>)<sub>2</sub>C(OH)OO°-pm**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -344.219187299

Cartesian coordinates (Angs):

O	0.813880	-0.531251	-0.687096
C	-0.380832	0.028328	0.069852
O	-0.167414	-0.157073	1.420654
H	0.690386	0.238034	1.632018
O	1.938468	-0.164382	-0.124598
C	-1.538143	-0.831160	-0.379844
H	-2.458495	-0.464462	0.072099
H	-1.639661	-0.798103	-1.463189
H	-1.376425	-1.859539	-0.063416
C	-0.478708	1.492924	-0.324298
H	-0.615438	1.601997	-1.399360
H	-1.325352	1.945993	0.189613
H	0.431614	2.017182	-0.033700

Rotational constants (GHz): 4.8191970 3.0227341 2.9280692

Vibrational harmonic frequencies (cm-1):

105.0405	192.9792	253.1851
273.4914	335.9995	365.8898
410.7800	444.3814	491.1127
589.1160	687.6566	820.4355
938.8695	1005.7206	1020.3440
1119.6312	1177.4445	1219.7976
1271.6097	1389.6954	1410.8435
1434.4992	1479.8611	1483.9912
1500.9247	1504.2965	3043.5336
3055.7784	3115.1221	3119.6505
3127.8922	3134.1202	3737.9550

Zero-point correction (Hartree): 0.103114

• **(CH<sub>3</sub>)<sub>2</sub>C(OH)OO°-pp**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -344.215493276

Cartesian coordinates (Angs):

O	-0.833499	-0.680941	-0.491989
C	0.366060	0.048547	0.053701
O	0.355879	-0.044875	1.439009
O	-1.972975	-0.166303	-0.089227
H	0.492552	-0.963372	1.698198
C	1.520775	-0.699588	-0.587870
H	1.470334	-0.638323	-1.673644
H	2.461255	-0.266419	-0.251698
H	1.496154	-1.753106	-0.304264
C	0.269861	1.510562	-0.319001
H	1.141991	2.037072	0.065012
H	0.229151	1.627135	-1.400397
H	-0.626852	1.936839	0.123480

Rotational constants (GHz): 4.7520711 3.0126189 2.8943703

Vibrational harmonic frequencies (cm-1):

111.6568	191.8010	230.2306
270.9631	321.3348	369.2837
397.7105	425.6648	479.5875
591.4177	705.2836	819.2230
939.8759	1000.0146	1016.4851
1131.3865	1165.3022	1200.4100
1267.8759	1380.3458	1416.4796
1422.8193	1480.8660	1484.1969
1496.3100	1504.3920	3041.0867
3058.4857	3108.2054	3124.4487
3130.5730	3143.7434	3790.0501

Zero-point correction (Hartree): 0.103013

• **(CH<sub>3</sub>)<sub>2</sub>C(OH)OO°-pt**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -344.216519853

Cartesian coordinates (Angs):

O	0.901327	-0.048432	-0.778640
C	-0.397597	0.007812	-0.003816
O	-1.366304	-0.055257	-0.993204
O	1.963742	0.002209	-0.009968
H	-1.395073	-0.947770	-1.356216
C	-0.419316	-1.180262	0.938421
H	0.420803	-1.135177	1.627405

H	-1.350028	-1.177385	1.503843
H	-0.351502	-2.112386	0.374263
C	-0.482286	1.359154	0.668256
H	-0.491617	2.141681	-0.088243
H	-1.400036	1.421475	1.251094
H	0.372529	1.501168	1.325184

Rotational constants (GHz): 4.7035709 2.9896674 2.9102308

Vibrational harmonic frequencies (cm-1):

128.4582	208.8704	248.3456
270.1949	347.9835	359.3436
375.3854	459.2527	488.7310
522.7822	722.5931	829.5288
942.1689	1007.7127	1018.3486
1131.9454	1154.4405	1205.6760
1287.1467	1378.3424	1412.0335
1422.4935	1478.2670	1486.2509
1499.7556	1507.0361	3039.4869
3056.1959	3107.7727	3125.9953
3136.1366	3141.9708	3792.6258

Zero-point correction (Hartree): 0.103186

- **TSa**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -344.203876616

Cartesian coordinates (Angs):

C	0.583472	0.000000	0.212002
O	-0.052606	-0.000003	1.324450
O	-1.070936	-0.000001	-0.915761
O	-1.963719	-0.000001	0.012973
H	-1.186805	-0.000001	0.961081
C	1.187977	-1.287826	-0.276311
H	1.341443	-1.280235	-1.354114
H	2.163046	-1.414650	0.203343
H	0.559708	-2.129501	0.005428
C	1.187971	1.287831	-0.276308
H	2.163035	1.414662	0.203352
H	1.341443	1.280240	-1.354110
H	0.559694	2.129501	0.005427

Rotational constants (GHz): 4.8299873 2.7898152 2.6728040

Vibrational harmonic frequencies (cm-1):

-823.5175	103.7869	162.3914
193.1894	248.9050	262.5525
377.5291	513.3507	530.4621
609.1215	731.1316	816.6673
908.9452	962.0704	1012.4806
1074.0379	1131.5936	1260.9173

1287.1943	1402.8604	1405.3401
1465.7795	1467.5959	1470.1818
1490.6109	1590.8209	1867.3646
3025.1779	3030.2830	3093.4239
3098.7809	3135.9296	3138.6675

Zero-point correction (Hartree): 0.097663

- **TSb-variational**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -344.206913108

Cartesian coordinates (Angs):

C	-1.532061	-0.137168	-0.000093
O	-0.917626	-1.181364	-0.000403
H	2.482012	-1.131720	-0.000197
O	3.300578	-0.600417	0.000284
O	2.900891	0.665175	-0.000037
C	-0.833426	1.203538	-0.000178
H	-1.134256	1.783470	0.875549
H	0.245867	1.073697	-0.000105
H	-1.134168	1.783218	-0.876100
C	-3.045476	-0.114641	0.000376
H	-3.415270	0.421720	0.877109
H	-3.415852	0.421765	-0.876098
H	-3.433304	-1.129674	0.000459

Rotational constants (GHz): 7.6173714 0.9784500 0.8763818

Vibrational harmonic frequencies (cm-1):

-63.6541	11.5321	41.4881
51.3662	71.6448	78.6657
144.0153	190.1039	383.3251
492.9538	538.6918	785.6989
887.6594	890.7181	1087.2991
1122.5355	1171.2104	1239.1329
1388.3635	1394.1119	1439.0254
1462.3032	1468.8367	1473.1295
1490.7481	1785.8011	3024.7682
3032.8096	3076.6711	3085.1849
3137.5568	3140.3749	3597.1236

Zero-point correction (Hartree): 0.098382

- **complex-cc-freq**

E(UB+HF-LYP/CC-pVTZ) (Hartree): -344.219787258

Cartesian coordinates (Angs):

C	-1.154293	-0.066269	0.007335
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O	-0.336057	-0.970369	0.018353
H	1.373182	-0.818403	0.038825
O	2.363716	-0.714839	0.040823
O	2.574152	0.590548	-0.071834
C	-0.749176	1.382232	0.040466
H	-1.068745	1.818956	0.990529
H	0.328713	1.485246	-0.061456
H	-1.262821	1.938619	-0.745853
C	-2.628313	-0.375355	-0.038226
H	-3.157834	0.160967	0.751210
H	-3.042619	-0.027031	-0.987478
H	-2.793674	-1.444721	0.058029

Rotational constants (GHz): 7.3478079 1.4993406 1.2655782

Vibrational harmonic frequencies (cm-1):

25.6461	60.5203	83.3337
106.4320	142.5274	157.3440
235.1887	396.9004	495.1591
560.2974	706.2163	799.4268
894.2572	910.5123	1097.8806
1126.6821	1199.0791	1259.5427
1394.0575	1402.0481	1461.0983
1466.7247	1473.3688	1493.0349
1574.9498	1755.6131	3024.7049
3035.3352	3080.1452	3089.0599
3132.2382	3145.1346	3240.6178

Zero-point correction (Hartree): 0.100297

#### IV) Q(OH)OO° decomposition: B3LYP/cc-pVTZ level

- **Cy<sub>-H</sub>°OH<sub>-ax</sub>**

E(UB+HF-LYP) (Hartree): -310.553597946

Cartesian coordinates (Angs):

C	0.897423	1.293079	-0.310954
C	-0.362597	1.250409	0.585810
C	-1.102918	-0.040670	0.402856
C	-0.296830	-1.289162	0.565750
C	0.966573	-1.246966	-0.325598
C	1.761634	0.044180	-0.098984
H	-0.053423	1.340506	1.631593
H	-1.010444	2.107817	0.378195
H	0.586977	1.345631	-1.358527
H	1.475043	2.197615	-0.105172



H	0.012060	-1.380957	1.611686
H	-0.907492	-2.161062	0.328632
H	1.593698	-2.119525	-0.127813
H	0.659300	-1.306656	-1.373161
H	2.156307	0.050288	0.923402
H	2.628139	0.072961	-0.763478
O	-1.990785	-0.119481	-0.657883
H	-2.393590	0.744004	-0.795574

Rotational constants (GHz): 3.7475776 2.6023802 1.8895213

Vibrational harmonic frequencies (cm-1):

112.9103	189.5600	290.0501
358.5020	394.8167	403.8363
467.6553	477.7689	631.4700
764.3708	790.1734	822.6769
858.6244	868.6736	943.9304
973.0919	1020.7658	1055.4786
1061.2997	1088.8248	1119.9851
1161.7536	1200.0630	1264.5594
1285.3612	1315.8616	1329.6369
1340.1745	1352.4943	1376.1645
1383.8596	1403.0885	1473.3525
1480.4484	1489.0967	1493.7704
1504.9827	2996.0519	3001.7269
3010.5052	3012.5173	3017.7249
3036.0268	3047.3674	3052.0738
3057.6867	3076.1042	3804.8359

Zero-point correction (Hartree): 0.160979

- **Cy<sub>H</sub>°OH<sub>eq</sub>**

E(UB+HF-LYP) (Hartree): -310.556786561

Cartesian coordinates (Angs):

C	1.105965	1.281466	-0.240324
C	-0.373588	1.273070	0.170641
C	-1.027237	-0.027231	-0.161877
C	-0.326572	-1.299692	0.165050
C	1.151100	-1.248544	-0.246562
C	1.831062	0.027630	0.256974
H	-0.444871	1.460346	1.257725
H	-0.903578	2.102144	-0.312116
H	1.173391	1.325385	-1.330819
H	1.590897	2.180763	0.144239
H	-0.391147	-1.490376	1.251017
H	-0.838399	-2.136027	-0.316100

H	1.670282	-2.130490	0.133367
H	1.221612	-1.285198	-1.337343
H	1.842365	0.025369	1.352355
H	2.874681	0.049281	-0.064318
O	-2.397173	-0.112747	-0.034827
H	-2.782225	0.760576	-0.162806

Rotational constants (GHz): 4.3113788 2.2980043 1.6148434

Vibrational harmonic frequencies (cm-1):

129.0083	217.5109	299.1800
356.9490	362.1968	366.6109
423.1233	459.7219	562.8693
754.8276	794.4952	843.1405
866.1770	907.7333	935.7608
991.0231	1035.5042	1075.2462
1098.5809	1125.1599	1129.5154
1168.5836	1208.1960	1258.8170
1281.1791	1304.9014	1343.1446
1361.9904	1374.6970	1378.3129
1396.6182	1417.2434	1473.0600
1481.6134	1489.8314	1494.6056
1505.0610	2880.4376	2895.3184
2996.6788	3001.2444	3017.7269
3021.9500	3047.2907	3053.2700
3057.4698	3061.4491	3801.2156

Zero-point correction (Hartree): 0.160625

• **Q(OH)OO°\_OHax\_mp**

E(UB+HF-LYP) = -460.992928518 A.U.

Cartesian coordinates:

C	-1.448321	1.375696	0.171118
C	-0.023418	1.198763	-0.363720
C	0.540561	-0.159082	0.051408
C	-0.339827	-1.317393	-0.375962
C	-1.773055	-1.134609	0.139289
C	-2.354427	0.222216	-0.271071
H	-0.022025	1.256159	-1.454747
H	0.642580	1.983014	0.001916
H	-1.418059	1.418316	1.262358
H	-1.849870	2.330553	-0.172511
H	-0.333895	-1.361486	-1.467375
H	0.099266	-2.242410	-0.002687
H	-2.397686	-1.946166	-0.237531
H	-1.772541	-1.217023	1.228502

H	-2.473845	0.252968	-1.359289
H	-3.352108	0.345386	0.154515
O	1.833822	-0.341797	-0.715189
O	2.817931	0.307310	-0.142840
O	0.813697	-0.251621	1.402515
H	1.545508	0.356006	1.584592

Rotational constants (GHz): 3.0857734 1.2139982 1.0826961

Vibrational harmonic frequencies :

87.7474	125.6632	201.1830	248.0261	299.6560	343.6722
359.3087	416.0502	438.9332	455.2119	497.7015	513.2645
655.8859	741.7623	791.5413	812.2899	839.6658	877.4829
912.3574	952.8048	998.8771	1034.9397	1064.1105	1078.6452
1084.8718	1153.3645	1190.1594	1199.0421	1217.7662	1282.7774
1291.6867	1318.1509	1349.8419	1369.3607	1372.7420	1381.0861
1387.7032	1437.8559	1481.3666	1490.4812	1493.4148	1497.8363
1509.7344	3004.5061	3030.3435	3030.6604	3033.0766	3041.5416
3059.4424	3065.2453	3070.6492	3076.8794	3092.7890	3725.3515

Zero-point correction= 0.169693 (Hartree/Particle)

• **Q(OH)OO°\_OHeq\_mp**

E(UB+HF-LYP) = -460.992491263 A.U.

Cartesian coordinates:

C	1.635069	0.956491	-0.681604
C	0.395654	1.429757	0.086935
C	-0.599084	0.312246	0.341219
C	0.033619	-0.953185	0.913448
C	1.275085	-1.405603	0.138291
C	2.281881	-0.262398	-0.019097
H	0.683346	1.816649	1.067061
H	-0.119318	2.235494	-0.436909
H	1.353170	0.704863	-1.706769
H	2.349241	1.778822	-0.748677
H	0.298860	-0.724474	1.948309
H	-0.725253	-1.738126	0.938847
H	1.734478	-2.251482	0.652573
H	0.976450	-1.764835	-0.849497
H	2.669617	0.019859	0.965462
H	3.138799	-0.596427	-0.606981
O	-1.648393	0.789220	1.100639
O	-1.135803	-0.044244	-1.034719
O	-2.235113	-0.751861	-0.940212

H -2.338265 0.110891 1.095765

Rotational constants (GHz): 2.5727977 1.3322964 1.2188933

Vibrational harmonic frequencies :

91.0885	133.4987	184.7564	275.6413	298.5828	329.2549
366.5289	409.3347	445.7976	457.8002	482.6814	557.4377
574.2796	701.8875	781.3272	788.5149	849.5124	886.7085
911.3265	946.8339	988.6907	1035.4387	1079.4236	1090.0665
1142.2391	1158.8734	1167.1272	1195.7223	1214.2669	1279.1256
1291.6043	1300.3817	1354.4637	1369.6656	1381.5317	1382.8912
1389.4649	1437.0272	1476.8622	1485.7984	1494.0301	1496.9056
1508.9980	3005.0478	3029.5986	3031.0035	3032.2767	3042.0549
3060.3902	3064.0280	3069.1113	3075.9634	3087.7940	3741.8571

Zero-point correction= 0.169570 (Hartree/Particle)

• **Q(OH)OO°\_OHax\_tp**

E(UB+HF-LYP) = -460.990249020 A.U.

Cartesian coordinates:

C	-1.544723	1.273011	-0.034761
C	-0.021405	1.257350	-0.207759
C	0.586166	-0.011713	0.375018
C	-0.051277	-1.283084	-0.157927
C	-1.574858	-1.254116	0.008192
C	-2.184298	0.006680	-0.611515
H	0.241511	1.297538	-1.265348
H	0.440801	2.126295	0.270052
H	-1.791719	1.351071	1.027416
H	-1.953204	2.162715	-0.517185
H	0.215570	-1.364773	-1.212330
H	0.388480	-2.131882	0.366477
H	-2.003385	-2.148381	-0.447632
H	-1.821673	-1.293701	1.071803
H	-2.035868	-0.012042	-1.696136
H	-3.262934	0.023766	-0.444216
O	2.057591	-0.029330	0.044885
O	2.306214	-0.011697	-1.243522
O	0.569692	-0.051486	1.762358
H	0.856814	0.800736	2.109847

Rotational constants (GHz): 2.5487727 1.2561591 1.2291538

Vibrational harmonic frequencies :

117.7242	125.4937	202.7906	260.3545	298.1786	303.2693
361.1581	391.1319	445.8315	467.5684	498.4663	503.8306
615.7749	729.0337	792.6861	838.8003	845.5727	884.1178
908.8454	953.4154	1002.5773	1040.4220	1061.9377	1079.5349
1084.0714	1142.2373	1188.9581	1198.6941	1206.3079	1286.0270
1289.1181	1326.7977	1348.3509	1371.1880	1377.2734	1382.8817
1391.6776	1417.5338	1484.1871	1490.0602	1492.5104	1498.4960
1509.3358	3007.4558	3019.3017	3026.5052	3030.2986	3050.3069
3059.5995	3061.3851	3068.6883	3085.1243	3097.7883	3788.3786

Zero-point correction= 0.169744 (Hartree/Particle)

• **Q(OH)OO°\_OHeq\_mm**

E(UB+HF-LYP) = -460.989282125 A.U.

Cartesian coordinates:

C	1.613775	0.877545	-0.776921
C	0.378749	1.438901	-0.063525
C	-0.630340	0.359983	0.314191
C	-0.012116	-0.826804	1.030265
C	1.225057	-1.371107	0.309803
C	2.245768	-0.267067	0.019902
H	0.673044	1.928672	0.867319
H	-0.120246	2.189452	-0.682868
H	1.327088	0.517466	-1.767405
H	2.336877	1.680254	-0.932340
H	0.253241	-0.480684	2.031480
H	-0.780632	-1.590002	1.142460
H	1.676287	-2.156284	0.918505
H	0.921826	-1.841549	-0.628602
H	2.640088	0.121442	0.964930
H	3.096823	-0.676258	-0.527633
O	-1.685509	0.833573	1.081372
O	-1.173813	-0.072355	-1.023537
O	-2.005102	-1.086156	-0.941356
H	-2.034359	1.638283	0.680030

Rotational constants (GHz): 2.4231767 1.3825532 1.2512607

Vibrational harmonic frequencies :

89.1571	149.2298	174.4534	287.7798	288.8290	322.9686
364.9318	374.7081	433.3433	457.8819	479.7474	568.9199
576.0282	703.1278	783.1359	788.1051	851.3883	894.1502
914.3266	946.0627	986.5872	1038.0211	1078.6771	1090.6295
1140.7602	1151.5330	1168.1355	1191.6749	1200.2427	1281.5919

1291.9890	1304.1927	1353.8229	1369.7194	1381.1148	1383.6432
1396.6853	1419.7719	1474.7928	1483.8684	1493.8149	1496.0385
1509.4919	3003.2164	3022.8961	3031.2955	3032.4667	3045.3738
3059.3197	3060.1353	3069.3871	3075.7502	3102.9479	3781.6611

Zero-point correction= 0.169540 (Hartree/Particle)

• **Q(OH)OO°\_OHax\_mm**

E(UB+HF-LYP) = -460.988934891 A.U.

Cartesian coordinates:

C	-1.406667	1.386405	0.216236
C	0.042101	1.205498	-0.249230
C	0.554934	-0.183244	0.095973
C	-0.339354	-1.294526	-0.442397
C	-1.787899	-1.107484	0.023293
C	-2.316809	0.284677	-0.335529
H	0.106836	1.327301	-1.332478
H	0.705746	1.938047	0.206564
H	-1.435675	1.373135	1.307910
H	-1.765890	2.368146	-0.097077
H	-0.288714	-1.278094	-1.533098
H	0.057184	-2.262431	-0.123371
H	-2.414337	-1.881896	-0.422386
H	-1.839963	-1.245308	1.106262
H	-2.381003	0.377760	-1.424834
H	-3.331752	0.407996	0.047085
O	1.860549	-0.427931	-0.596391
O	2.777378	0.462614	-0.286409
O	0.753448	-0.249485	1.470198
H	0.978727	-1.154193	1.716166

Rotational constants (GHz): 2.9762091 1.2311887 1.0934149

Vibrational harmonic frequencies :

92.6775	138.6314	199.3974	227.7737	302.8895	337.3814
363.1393	378.7847	425.9534	454.0155	491.4402	516.7041
645.6026	742.7911	794.5953	833.6536	837.1544	884.0600
913.7357	955.9400	997.8645	1039.4510	1049.4309	1078.7501
1091.1289	1144.5739	1176.5833	1189.6063	1206.2597	1287.3676
1288.1679	1317.6226	1345.4696	1372.4178	1378.7391	1381.7151
1393.6578	1416.0592	1485.9348	1490.9924	1494.0091	1499.6515
1510.8310	3005.0466	3023.7380	3028.6902	3033.7210	3045.1131
3059.4241	3060.9746	3070.4113	3075.3582	3107.4951	3785.6602

Zero-point correction= 0.169651 (Hartree/Particle)

• **Q(OH)OO°\_OHeq\_tp**

E(UB+HF-LYP) = -460.985191636 A.U.

Cartesian coordinates:

C	-1.373445	-0.593783	-1.118846
C	-0.034495	-1.226934	-0.736287
C	0.807739	-0.358936	0.189178
C	0.020216	0.266612	1.342623
C	-1.369920	0.809076	0.982016
C	-2.163303	-0.182083	0.126211
H	-0.209343	-2.161372	-0.197377
H	0.566610	-1.471974	-1.612406
H	-1.205295	0.279883	-1.751459
H	-1.944596	-1.308785	-1.713818
H	-0.088270	-0.539154	2.072958
H	0.632550	1.042612	1.808993
H	-1.909882	1.027224	1.905869
H	-1.264888	1.747744	0.441782
H	-2.399684	-1.074843	0.715577
H	-3.117964	0.261606	-0.162152
O	1.878149	-1.130014	0.630194
O	1.501575	0.697582	-0.630955
O	0.771781	1.747943	-0.932239
H	2.407963	-0.610752	1.246662

Rotational constants (GHz): 2.1977875 1.4608886 1.3622094

Vibrational harmonic frequencies (cm-1):

30.1993	127.0720	203.2773	251.9994	304.8862	335.5472
346.6629	386.8613	445.5929	460.1718	474.1425	489.9310
603.8201	695.6822	776.1998	803.1805	853.3890	890.9149
910.5350	944.4244	986.2483	1039.9347	1074.7456	1093.9818
1141.1091	1158.2682	1173.0959	1197.6481	1205.9209	1288.8065
1296.6723	1305.5198	1355.8241	1365.8845	1383.7894	1385.7183
1391.3838	1414.3746	1471.8778	1481.9438	1494.7422	1495.5397
1508.7231	3000.3253	3023.0761	3035.1120	3035.6741	3040.0836
3058.5681	3060.1898	3071.0713	3085.3111	3102.8358	3783.8873

Zero-point correction (Hartree): 0.169364

• **TSa\_ax**

E(UB+HF-LYP) = -460.976168345 A.U.

Cartesian coordinates:

C	1.733662	-1.267396	0.168435
C	0.261405	-1.269636	-0.297007
C	-0.393227	-0.000014	0.186876
C	0.261377	1.269655	-0.296923
C	1.733654	1.267410	0.168462
C	2.462347	0.000011	-0.289373
H	0.226656	-1.308679	-1.387684
H	-0.276584	-2.129139	0.099725
H	1.760415	-1.332954	1.259228
H	2.234097	-2.158383	-0.214224
H	0.226587	1.308777	-1.387596
H	-0.276607	2.129123	0.099889
H	2.234068	2.158407	-0.214200
H	1.760444	1.332955	1.259256
H	2.538059	0.000020	-1.381631
H	3.485145	0.000012	0.092552
O	-2.050819	0.000037	-0.931512
O	-2.939445	0.000012	0.002562
O	-1.021875	-0.000083	1.303377
H	-2.170473	-0.000047	0.936446

Rotational constants (GHz): 3.1974484 1.0871813 0.9863037

Vibrational harmonic frequencies :

-818.5718	87.5708	101.1335	179.4501	244.0431	251.0854
301.5089	403.5492	422.9467	502.5520	507.4772	586.9858
692.7029	766.0381	788.7195	789.4763	836.5491	884.4059
893.6063	943.7563	993.7888	1015.6036	1035.6883	1069.1675
1082.3512	1118.4302	1141.1911	1236.4760	1251.8370	1269.5146
1285.1776	1298.1320	1341.5755	1346.7240	1372.7070	1378.1509
1379.4576	1476.3439	1485.0658	1493.3322	1497.0901	1507.1538
1590.8043	1869.4978	3008.3287	3026.0946	3026.7381	3037.6762
3043.0790	3059.0381	3067.2082	3071.3294	3101.1579	3103.4064

Zero-point correction= 0.164627 (Hartree/Particle)

- **TSa\_eq**

E(UB+HF-LYP) = -460.977305347 A.U.

Cartesian coordinates:

C	1.474496	1.262441	-0.382494
C	0.311926	1.287281	0.615769



C	-0.471510	0.000420	0.680732
C	0.312027	-1.286473	0.617524
C	1.473680	-1.262864	-0.381791
C	2.326626	-0.000432	-0.230213
H	0.700200	1.439783	1.631106
H	-0.378578	2.108807	0.426016
H	1.075308	1.307514	-1.398043
H	2.086520	2.155647	-0.246641
H	0.701203	-1.437277	1.632760
H	-0.378552	-2.108365	0.429624
H	2.085280	-2.156384	-0.246076
H	1.073674	-1.308003	-1.397002
H	2.810752	-0.000379	0.752409
H	3.128217	-0.000822	-0.970993
O	-1.616049	0.000853	1.258124
O	-1.259970	-0.000824	-1.186853
O	-2.512074	-0.000422	-0.880695
H	-2.362747	0.000387	0.345079

Rotational constants (GHz): 2.5995214 1.2156656 1.1774198

Vibrational harmonic frequencies :

-783.7638	92.9450	107.5696	183.5198	239.3490	251.7923
341.1118	413.7040	444.1548	470.8868	483.9095	582.7188
608.2766	755.7373	761.2785	777.0229	848.5912	885.3787
912.0916	920.7808	999.5522	1004.8233	1036.4846	1083.9302
1090.0210	1145.1532	1157.2653	1258.2793	1267.6900	1276.2783
1288.0558	1290.9974	1354.5788	1356.8131	1375.3513	1382.1933
1388.0751	1460.2339	1466.0685	1495.3384	1496.3905	1508.8843
1580.1077	1864.9599	2990.6520	2996.2202	3002.6454	3033.1277
3034.1856	3059.9141	3067.0399	3072.0751	3082.9417	3084.4481

Zero-point correction= 0.164328 (Hartree/Particle)

• **c-(Q=O---HOO\*)\_Complex**

E(UB+HF-LYP) = -460.992629506 A.U.

Cartesian coordinates:

C	1.156765	1.545015	-0.179801
C	0.076746	0.762474	0.591649
C	0.100400	-0.705299	0.244206
C	1.453454	-1.375347	0.272860
C	2.512645	-0.561118	-0.493751
C	2.536963	0.900599	-0.042736
H	0.286067	0.836921	1.665520

H	-0.922717	1.158715	0.418759
H	0.877863	1.587861	-1.236365
H	1.173929	2.575466	0.177052
H	1.753156	-1.448117	1.324569
H	1.352078	-2.387874	-0.113778
H	3.490503	-1.025485	-0.358757
H	2.291318	-0.607667	-1.563793
H	2.864995	0.955882	1.000422
H	3.269593	1.458297	-0.628919
O	-0.905167	-1.332024	-0.048991
O	-3.420452	-0.351350	-0.236737
O	-3.294886	0.959772	-0.074258
H	-2.494565	-0.713126	-0.159380

Rotational constants (GHz): 3.0172088 0.7915228 0.6606548

Vibrational harmonic frequencies :

34.8605	42.1095	78.2844	106.3328	145.8138	191.1944
233.3451	306.0163	417.2556	423.3783	486.6111	517.7595
662.9210	717.2797	760.1783	771.2981	844.0261	881.8453
899.9271	922.0674	1001.4137	1030.7096	1070.2539	1080.3497
1139.2013	1143.8911	1199.3959	1252.3484	1259.4884	1280.4571
1302.4718	1341.3231	1350.4549	1375.8775	1381.4032	1388.8338
1469.0486	1482.0895	1496.6269	1497.8481	1510.7058	1576.5798
1748.1197	3000.3492	3006.4043	3010.3427	3023.5669	3026.3244
3062.8788	3067.8906	3072.1726	3096.9415	3100.6749	3219.3861

Zero-point correction= 0.167464 (Hartree/Particle)

- **TSb (variational)**

E(UB+HF-LYP) = -460.979307970 A.U.

Cartesian coordinates:

C	-0.926357	-1.523903	-0.141990
C	-0.096249	-0.460374	0.599568
C	-0.496630	0.947098	0.203023
C	-1.987205	1.228889	0.223673
C	-2.788558	0.141319	-0.513773
C	-2.428264	-1.260447	-0.017426
H	-0.279081	-0.556583	1.676447
H	0.972176	-0.588712	0.433014
H	-0.644919	-1.522204	-1.199020
H	-0.675002	-2.513379	0.243008
H	-2.299613	1.250121	1.274128
H	-2.159139	2.220001	-0.193051

H	-3.856607	0.330394	-0.393081
H	-2.580336	0.210053	-1.585493
H	-2.731549	-1.365599	1.029589
H	-2.987500	-2.010788	-0.579765
O	0.312985	1.793247	-0.111022
O	4.287161	0.240416	-0.248497
O	3.647871	-0.885959	0.041742
H	3.597011	0.929572	-0.282011

Rotational constants (GHz): 2.7075948 0.6197203 0.5257094

Vibrational harmonic frequencies :

-61.6437	18.3195	38.5257	40.4102	73.6193	97.0429
180.8741	204.1270	307.6099	407.8749	416.6378	482.0768
494.7454	658.7921	750.7531	763.2832	841.1375	880.4935
896.2003	920.7286	1001.4986	1028.1778	1066.4868	1079.5147
1132.8923	1140.8148	1170.8566	1245.1591	1253.8011	1276.0901
1295.1828	1338.6051	1348.0052	1373.3460	1381.3279	1385.0212
1441.0694	1466.1405	1476.5979	1495.4154	1496.4240	1510.4137
1779.4773	2999.3146	3004.5525	3007.2382	3019.1016	3022.2866
3058.6728	3061.6299	3066.1881	3096.3074	3098.5167	3597.0290

Zero-point correction= 0.165592 (Hartree/Particle)

• **Q=0**

E(RB+HF-LYP) = -310.005398486 A.U.

Cartesian coordinates:

C	1.785956	-0.000032	0.106278
C	1.013338	-1.262456	-0.280871
C	1.013401	1.262444	-0.280828
C	-0.392676	1.282440	0.344663
C	-1.156804	0.000008	0.067526
O	-2.293724	0.000011	-0.346435
C	-0.392696	-1.282420	0.344708
H	2.766347	-0.000044	-0.374132
H	1.968117	-0.000056	1.186107
H	0.919860	-1.308560	-1.369826
H	1.560938	-2.156883	0.021159
H	0.919997	1.308638	-1.369785
H	1.561017	2.156826	0.021307
H	-0.296790	1.376606	1.432554
H	-0.988009	2.122745	-0.008742
H	-0.296738	-1.376524	1.432599
H	-0.988055	-2.122741	-0.008615

Rotational constants (GHz): 4.2201075 2.4892170 1.7416233

Vibrational harmonic frequencies :

91.8170	178.3452	303.8391	404.6149	416.1052	476.6158
492.1553	656.2287	747.8202	762.1652	837.8391	879.1907
895.1523	919.6749	1001.0456	1026.4853	1064.8632	1079.9339
1131.7122	1139.6318	1242.0881	1250.7003	1273.9486	1290.9773
1336.2747	1345.6193	1373.7386	1379.0631	1382.1628	1464.6094
1472.8246	1494.2732	1495.2119	1509.7081	1789.2784	3000.8953
3004.0095	3007.7943	3018.8591	3021.4231	3058.3975	3060.0185
3064.2753	3096.1863	3097.6462			

Zero-point correction= 0.150439 (Hartree/Particle)

## V) G2M calculations

1) G2Ma = E[CCSD(T)/6-31G\*\*/B3LYP] + {E[MP2/6-311++G(3df,2p)/B3LYP] – E[MP2/6-31G\*\*/B3LYP]} + ZPE[B3LYP]

ZPE computed at the B3LYP/cc-pVTZ level

Species	ZPE	CCSD(T)/ 6-31G*	MP2/ 6-31G*	MP2/ 6-311++G(3df,2p)	G2Ma	G2Ma (kcal/mol)
O <sub>2</sub> +H <sub>2</sub> COH	0.040837	-264.6844856	-264.6436	-264.9613121	-264.9613607	<b>0.0</b>
HOO+H <sub>2</sub> C=O	0.040642	-264.7155307	-264.6645783	-264.9830694	-264.9933798	<b>-20.1</b>
CH <sub>2</sub> OHOO-mp	0.048444	-264.7446457	-264.6941647	-265.0150683	-265.0171053	<b>-35.0</b>
TSa	0.042472	-264.7132969	-264.6710958	-264.9926419	-264.992371	<b>-19.5</b>
Complex	0.044038	-264.7319363	-264.6815456	-264.997943	-265.0042957	<b>-26.9</b>
Species	ZPE	CCSD(T)/ 6-31G*	MP2/ 6-31G*	MP2/ 6-311++G(3df,2p)	G2Ma	G2Ma (kcal/mol)
O <sub>2</sub> +CH <sub>3</sub> CHOH	0.069345	-303.8735696	-303.8161656	-304.1857532	-304.1738122	<b>0.0</b>
HOO+CH <sub>3</sub> CHO	0.069348	-303.9103728	-303.8438425	-304.214994	-304.2121763	<b>-24.1</b>
CH <sub>3</sub> CHOHOO-mp	0.075891	-303.937512	-303.8712955	-304.2447676	-304.2350931	<b>-38.5</b>
TSa	0.07026	-303.9082368	-303.8503919	-304.2239965	-304.2115814	<b>-23.7</b>
Complex	0.072311	-303.9284344	-303.8624666	-304.2316909	-304.2253477	<b>-32.3</b>
Species	ZPE	CCSD(T)/ 6-31G*	MP2/ 6-31G*	MP2/ 6-311++G(3df,2p)	G2Ma	G2Ma (kcal/mol)
O <sub>2</sub> +(CH <sub>3</sub> ) <sub>2</sub> COH	0.097471	-343.0638679	-342.9903352	-343.4126114	-343.3886731	<b>0.0</b>
HOO+acetone	0.097269	-343.1031672	-343.0209243	-343.4451059	-343.4300798	<b>-26.0</b>
(CH <sub>3</sub> ) <sub>2</sub> COHOO-pm	0.103114	-343.1288047	-343.0469669	-343.4729964	-343.4517202	<b>-39.6</b>
TSa	0.097663	-343.101896	-343.028282	-343.4546115	-343.4305625	<b>-26.3</b>
Complex	0.100297	-343.1228418	-343.0411521	-343.4634104	-343.4448031	<b>-35.2</b>
Species	ZPE	CCSD(T)/ 6-31G*	MP2/ 6-31G*	MP2/ 6-311++G(3df,2p)	G2Ma	G2Ma (kcal/mol)

O <sub>2</sub> +CycOH-axi	0.16469	-459.4346116	-459.3207067	-459.8827509	-459.8319658	<b>41.7</b>
O <sub>2</sub> +CycOH-equ	0.164336	-459.4357739	-459.3218884	-459.8844111	-459.8339606	<b>40.5</b>
HOO+Cyc=O	0.164546	-459.4737162	-459.3514388	-459.9154381	-459.8731695	<b>15.9</b>
CycOHOO-mp-axi	0.169693	-459.5016203	-459.379792	-459.946234	-459.8983689	<b>0.0</b>
CycOHOO-mp-equ	0.16957	-459.5017725	-459.379949	-459.946175	-459.8984285	<b>0.0</b>
TSa-axi	0.164627	-459.4733681	-459.359518	-459.9264029	-459.875626	<b>14.3</b>
TSa-equ	0.164328	-459.4747937	-459.3610185	-459.9270896	-459.8765368	<b>13.7</b>
Complex	0.167464	-459.4941073	-459.372332	-459.934449	-459.8887598	<b>6.1</b>

$$2) \text{G2Mb} = E[\text{CCSD(T)/6-311G}^{**}/\text{B3LYP}] + \{E[\text{MP2/6-311++G(3df,2p)}/\text{B3LYP}] - E[\text{MP2/6-311G}^{**}/\text{B3LYP}]\} + \text{ZPE}[\text{B3LYP}]$$

ZPE computed at the B3LYP/cc-pVTZ level

Species	ZPE	CCSD(T)/ 6-311G <sup>**</sup>	MP2/ 6-311G <sup>**</sup>	MP2/ 6-311++G(3df,2p)	G2Mb	G2Mb (kcal/mol)
O <sub>2</sub> +H <sub>2</sub> COH	0.040837	-264.8470982	-264.8022145	-264.9613121	-264.9653588	<b>0.0</b>
HOO+H <sub>2</sub> C=O	0.040642	-264.8748629	-264.8201986	-264.9830694	-264.9970917	<b>-19.9</b>
CH <sub>2</sub> OHOO-mp	0.048444	-264.9025554	-264.8480682	-265.0150683	-265.0211115	<b>-35.0</b>
TSa	0.042472	-264.873327	-264.8251205	-264.9926419	-264.9983764	<b>-20.7</b>
Complex	0.044038	-264.8905945	-264.8360552	-264.997943	-265.0084443	<b>-27.0</b>
Species	ZPE	CCSD(T)/ 6-311G <sup>**</sup>	MP2/ 6-311G <sup>**</sup>	MP2/ 6-311++G(3df,2p)	G2Mb	G2Mb (kcal/mol)
O <sub>2</sub> +CH <sub>3</sub> CHOH	0.069345	-304.0660148	-304.0029314	-304.1857532	-304.1794916	<b>0.0</b>
HOO+CH <sub>3</sub> CHO	0.069348	-304.0996035	-304.0276309	-304.214994	-304.2176186	<b>-23.9</b>
CH <sub>3</sub> CHOHOO-mp	0.075891	-304.1251229	-304.0531616	-304.2447676	-304.2408379	<b>-38.5</b>
TSa	0.07026	-304.0984211	-304.0327234	-304.2239965	-304.2194342	<b>-25.1</b>
TSb	0.070446	-304.1051095	-304.0330776	-304.219887	-304.2214729	<b>-26.3</b>
Complex	0.072311	-304.1168472	-304.04497	-304.2316909	-304.2312571	<b>-32.5</b>
Species	ZPE	CCSD(T)/ 6-311G <sup>**</sup>	MP2/ 6-311G <sup>**</sup>	MP2/ 6-311++G(3df,2p)	G2Mb	G2Mb (kcal/mol)
O <sub>2</sub> +(CH <sub>3</sub> ) <sub>2</sub> COH	0.097471	-343.2864559	-343.2055347	-343.4126114	-343.3960616	<b>0.0</b>
HOO+acetone	0.097269	-343.3224927	-343.233014	-343.4451059	-343.4373156	<b>-25.9</b>
(CH <sub>3</sub> ) <sub>2</sub> COHOO-pm	0.103114	-343.3467417	-343.2572131	-343.4729964	-343.459411	<b>-39.8</b>
TSa	0.097663	-343.3225686	-343.2391279	-343.4546115	-343.4403892	<b>-27.8</b>
TSb	0.098382	-343.3285901	-343.238968	-343.4504843	-343.4417244	<b>-28.7</b>
Complex	0.100297	-343.3409758	-343.2515954	-343.4634104	-343.4524938	<b>-35.4</b>

$$3) \text{G2Mc} = E[\text{CCSD(T)/aug-cc-pVDZ}/\text{B3LYP}] + \{E[\text{MP2/aug-cc-pVTZ}/\text{B3LYP}] - E[\text{MP2/aug-cc-pVDZ}/\text{B3LYP}]\} + \text{ZPE}[\text{B3LYP}]$$

ZPE computed at the B3LYP/cc-pVTZ level

<b>Species</b>	<b>ZPE</b>	<b>CCSD(T)/ aug-cc-pVDZ</b>	<b>MP2/ aug-cc-pVDZ</b>	<b>MP2/ aug-cc-pVTZ</b>	<b>G2Mc</b>	<b>G2Mc (kcal/mol)</b>
O <sub>2</sub> +H <sub>2</sub> COH	0.040837	-264.8173571	-264.7676405	-264.9868251	-264.9957047	<b>0.0</b>
HOO+H <sub>2</sub> C=O	0.040642	-264.8449376	-264.7864127	-265.0084799	-265.0263628	<b>-19.2</b>
CH <sub>2</sub> OHOO-mp	0.048444	-264.8762441	-264.8175339	-265.0408637	-265.0511299	<b>-34.8</b>
TSa	0.042472	-264.8485979	-264.7973299	-265.0208905	-265.0296865	<b>-21.3</b>
Complex	0.044038	-264.8604101	-264.8018541	-265.0236317	-265.0381497	<b>-26.6</b>
<b>Species</b>	<b>ZPE</b>	<b>CCSD(T)/ aug-cc-pVDZ</b>	<b>MP2/ aug-cc-pVDZ</b>	<b>MP2/ aug-cc-pVTZ</b>	<b>G2Mc</b>	<b>G2Mc (kcal/mol)</b>
O <sub>2</sub> +CH <sub>3</sub> CHOH	0.069345	-304.0283594	-303.9598885	-304.2171469	-304.2162728	<b>0.0</b>
HOO+CH <sub>3</sub> CHO	0.069348	-304.0622473	-303.985779	-304.2464717	-304.253592	<b>-23.4</b>
CH <sub>3</sub> CHOHOO-mp	0.075891	-304.0921092	-304.0154135	-304.2761925	-304.2769972	<b>-38.1</b>
TSa	0.07026	-304.0660978	-303.9966433	-304.2579258	-304.2571203	<b>-25.6</b>
Complex	0.072311	-304.0795984	-304.0030985	-304.2633673	-304.2675562	<b>-32.2</b>