$CH_2 + O_2$: Reaction mechanism, biradical and zwitterionic character, and formation of CH_2OO, the simplest Criegee Intermediate

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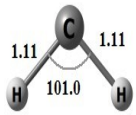

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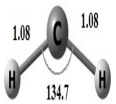

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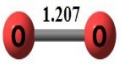

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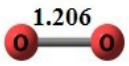

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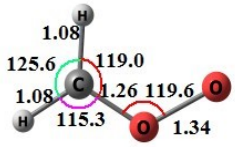

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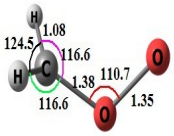

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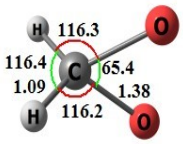

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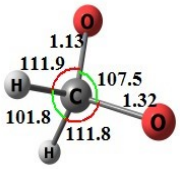

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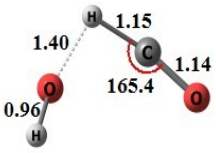

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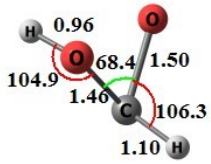

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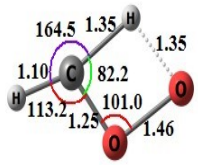

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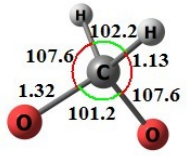

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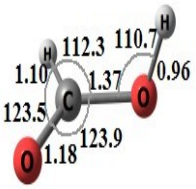

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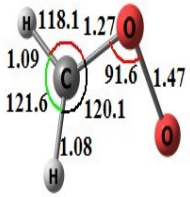

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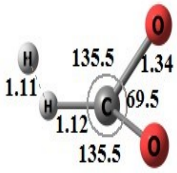

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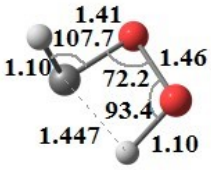

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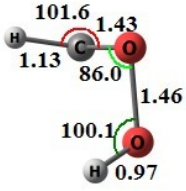

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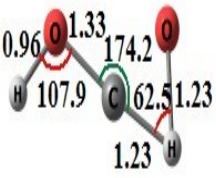

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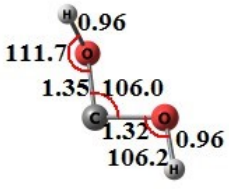

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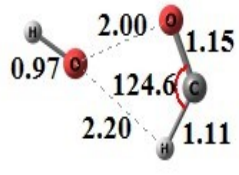
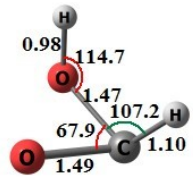


$^1TS12$

Figure1: continued



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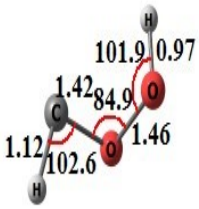

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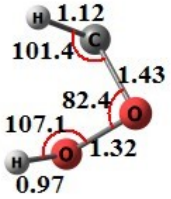

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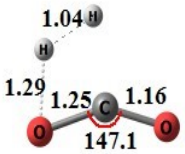

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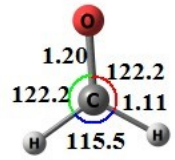

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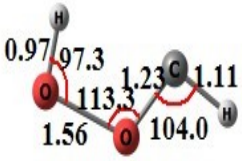
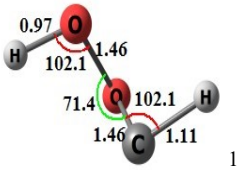


^{1}t,c-HCOOH



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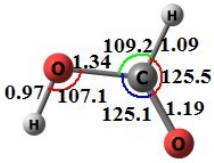

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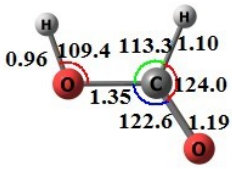

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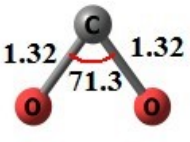

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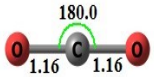

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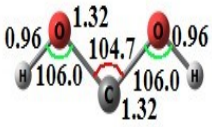

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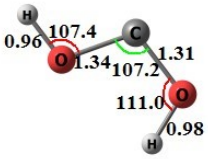
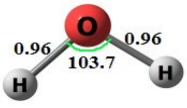
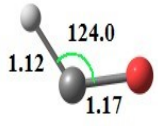


^{1}S-DHC

^{1}CO



H_2O



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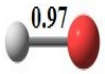

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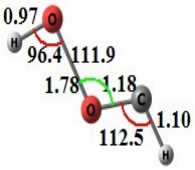

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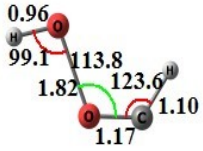

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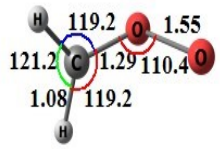

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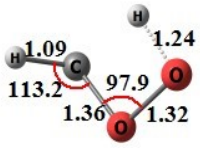

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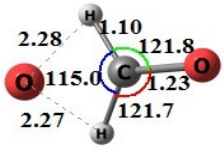

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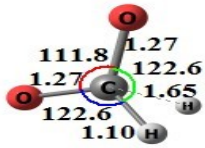

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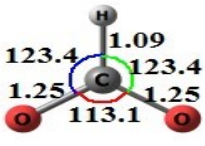

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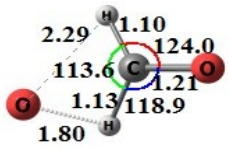

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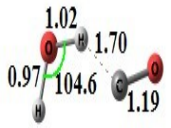

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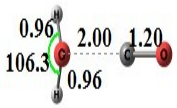

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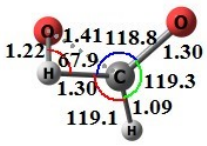

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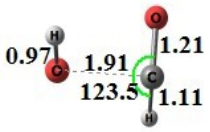

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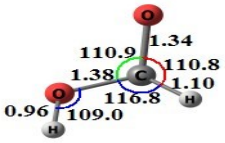

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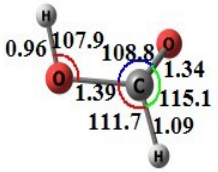

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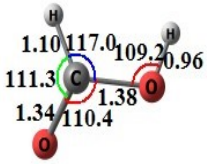

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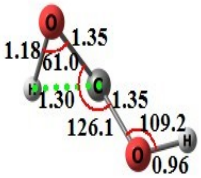

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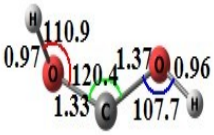

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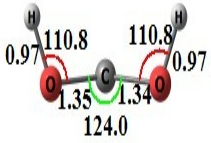

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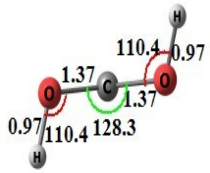

^{3}S-DHC

^{3}CO

Figure 1S: Optimized geometries of the stationary points for title reaction on singlet and triplet PES at B3LYP/CBSB7 level of theory.

Table 1S. Vibrational term values and moments of inertia of the stationary points for title reaction at the B3LYP/CBSB7 level of theory.

Specie	Vibrational term values (cm^{-1})	I_i (amu. $Å^2$)
$^1CH_2$	1404.6, 2885.3, 2947.0	0.9,1.5,2.4
$^3CH_2$	1056.3,3116.6,3357.3	0.3,2.0,2.3
$^1O_2$	1626.6	11.6
$^3O_2$	1641.2	11.6
$^1CH_2O_2$	807.6,896.3,1024.5,1182.0,1252.6,1313.6,1550.6,3050.8,3144.4	17.5,19.7,33.8
$^1CH_2OO$	534.5,674.7,909.7,933.1,1241.0,1397.2,1527.3,3120.2,3277.0	6.2,40.7,48.0
^{1}TS1	1640.3i,319.8,399.4,579.3,784.9,1049.8,1949.9,2594.8,3763.7	6.1,61.3,66.4
^{1}TS2	1224.1i,586.3,846.0,981.0,1113.1,1152.8,1323.1,2959.1,3765.1	17.0,24.8,38.4
^{1}TS3	1781.2i,673.1,720.2,892.8,1147.8,1273.6,1528.7,2090.9,3020.7	8.5,35.7,44.2
^{1}TS4	1326.7i,816.8,834.5,1098.2,1180.3,1207.1,1317.3,2609.1,2656.7	11.1,35.2,43.2
^{1}TS5	637.7i,679.2,905.3,1081.9,1192.2,1398.5,1849.5,2977.7,3824.4	6.3,44.2,49.0
^{1}TS6	696.9i,739.8,776.9,1014.4,1199.9,1406.7,1555.8,3051.7,3210.2	11.5,32.9,42.5
^{1}TS7	1613.2i,653.6,682.5,799.2,840.5,1100.4,1318.6,1585.5,2870.8	18.0,20.9,34.8
^{1}TS8	1250.7i,523.2,838.3,942.0,1081.1,1247.8,1388.6,2389.8,2987.0	16.3,23.5,36.6
^{1}TS9	787.6i,435.5,528.1,897.9,998.1,1335.6,1371.6,2699.5,3732.3	13.4,32.7,42.4
^{1}TS10	1962.4i,460.4,605.9,638.2,1136.9,1228.9,1554.6,2605.0,3814.6	5.4,43.8,49.3
^{1}TS11	836.4i,651.9,751.2,950.1,1081.5,1225.8,1356.5,3783.8,3814.7	6.7,42.8,48.0
^{1}TS12	383.1i,253.9,426.1,790.9,840.0,888.6,1977.9,2855.9,3747.4	10.4,50.6,61.0
^{1}TS13	1234.6i,579.1,889.8,969.5,1045.1,1142.7,1253.8,2895.5,3495.0	17.0,24.9,38.5
^{1}TS14	689.6i,455.3,648.1,907.5,1016.8,1349.2,1356.7,2792.9,3654.4	13.6,31.6,41.6
^{1}TS15	343.5i,598.5,778.2,966.5,1321.2,1401.0,1462.3,2719.7,3548.3	13.5,26.8,36.7

^{1}TS16	2248.4i,606.9,733.1,865.2,1074.9,1339.2,1729.2,2029.7,2136.6	5.1,44.3,49.5
^{1}trans-HC(O)OH	632.9,702.5,1057.9,1131.8,1310.2,1411.2,1836.9,3043.4,3735.5	6.5,41.9,48.4
^{1}cis-HC(O)OH	528.0,663.3,1041.4,1108.3,1276.9,1426.3,1881.7,2939.3,3801.1	5.8,43.3,49.1
^{1}CO	2219.8	8.7,8.7
Cyc-CO_2	618.1,841.7,1487.1	10.1,19.0,29.1
CO_2	666.6,666.6,1375.3,2435.6	43.1
H_2	4417.8	0.3
H_2O	1638.2, 3813.3,3910.1	0.6,1.2,1.82
^{2}HCO	1111.2,1941.2,2619.3	0.7,11.2,12.0
^{2}OH	3706.2	0.9
$^{3}CH_2OO$	166.3,356.3,576.1,951.6,1054.8, 1105.0,1444.0,3125.6,3280.0	8.8,41.5,46.6
$^{3}CH_2O_2$	559.1,569.1,1037.8,1084.7,1118.8,1243.5,1283.9,2609.7,2666.6	10.1,38.2,45.2
^{3}TS1	812.4i,177.7,333.6,813.4,1171.9,1223.7,1501.6,3062.2,3189.8	9.3,45.7,51.3
^{3}TS2	2271.1i,578.0,671.9, 881.6,995.1,117.9,1245.4,1997.3,3022.6	10.3,31.8,40.4
^{3}TS3	402.0i,246.4,503.1,1103.6,1211.3,1467.1,1594.4,2899.3,2943.7	13.0,49.3,58.8
^{3}TS4	937.8i,411.0,558.4,635.2,1025.1,1039.1,1260.2,1407.6,2973.2	10.4,37.7,43.6
^{3}TS5	476.9i,228.9,688.4,1000.1,1127.8,1372.6,1623.9,2609.0,2951.9	8.7,59.1,64.8
^{3}TS6	436.6i,106.1,326.1,372.7,645.5,1473.7,1841.2,2594.5,3763.8	2.5,92.2,93.6
^{3}TS7	1878.2i,392.9,792.4,887.5,996.4,1191.9,1281.8,2163.6,3021.9	9.3,40.4,47.2
^{3}TS8	286.3i,359.7,847.2,1081.4,1101.8,1150.3,1349.1,2939.3,3820.7	8.0,44.3,50.7
^{3}TS9	386.2i,237.1,331.3,742.4, 823.8,1095.5,1674.1,2808.9,3733.3	11.7,48.4,57.7
^{3}TS10	2009.2i,299.0,529.5,635.6,1052.8,1157.4,1310.6,2346.5,3731.9	5.0,51.8,53.7
^{3}TS11	231.3i,469.3,527.1,1029.4,1164.3,1206.0,1387.4,3553.7,3841.0	5.0.50.8,54.3

$^1CH_2O$	1202.1,1270.1,1539.0,1826.8,2869.8,2919.1	1.8,12.9,14.7
^{1}HOOCH	393.2,654.4,790.6,966.3,1014.2,1295.8,1374.7,2879.4,3715.8	16.7,24.6,37.5
t,t-^{1}HCOOH	84.6,261.0,434.4,743.0,961.1,1045.0,1739.8,2943.6,3760.2	6.3,53.6,59.9
c,t-^{1}HCOOH	168.6,330.4,428.9,824.0,917.6,1034.0,1824.4,2987.8,3780.3	8.1,52.0,60.1
t,c-^{1}HCOOH	307.5,344.8,565.1,832.2,1211.2,1332.4,1484.0,2917.3,3644.7	6.8,44.6,51.4
^{1}U-DHC	647.3,664.7,736.3,1139.8,1145.1,1346.9,1435.3,3842.2,3847.8	5.9,42.1,48.1
^{1}S-DHC	637.9,656.8,796.1,1119.9,1165.4,1341.3,1417.9,3500.8,3832.4	6.8,40.5,47.3

Table 2S. Comparison of the forward and reverse barrier heights ($V_f^{\#}$ and $V_r^{\#}$) of various reactions at two Different Levels of Theory with reported data by Chen et al. in kJ mol^{-1}.

Species	$V_r^{\#}$(CASPT2/6-31+G(D,P))[a]	$V_r^{\#}$(CASPT2/6-31+G(D,P))[a]	$V_f^{\#}$(CASPT2/avtz[a]	$V_r^{\#}$(CASPT2/avtz[a]	$V_f^{\#b}$	$V_r^{\#b}$
$^3CH_2(X^3B_1)+^3O_2$	0.0	0.0	0.0	0.0	0.0	0.0
^{1}TS1	297.8	258.9	287.7	247.1	273.4	255.0
^{1}TS2	56.2	780.0	56.3	773.9		
^{1}TS3	149.2	104.6	138.8	92.1	135.8	101.2
^{1}TS4	66.5	455.9	86.8	474.9		
^{1}TS5	57.3	35.7	54.1	36.4		
^{1}TS6	100.8	219.8	101.3	225.8	79.9	192.7
^{1}TS7	430.6	220.4	411.3	184.3		
^{1}TS8	360.9	28.5	352.6	24.2		
^{1}TS9	323.4	250.0	319.8	246.3		
^{1}TS10	311.9	156.2	309.4	142.6		
^{1}TS11	76.6	71.3	75.8	69.9		
^{1}TS12	379.1	8.1	384.8	4.8		
^{1}TS13	74.8	777.0	72.3	772.7		
^{1}TS14	184.4	15.6	183.8	26.6		
^{1}TS15	57.6	348.5	56.4	333.4		
^{1}TS16	322.0	302.4	304.9	288.3		
^{1}Imts4	77.6	66.6	94.0	63.4	77.3	62.3

[a] this work

[b] Chen et al.(2002)