

# The Reaction of Fluorine Atoms with Methanol: Yield of CH<sub>3</sub>O / CH<sub>2</sub>OH and Rate Constant of the Reactions CH<sub>3</sub>O + CH<sub>3</sub>O and CH<sub>3</sub>O + HO<sub>2</sub> - Supporting information -

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## FRAGMENTS

### CH3O2

E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -189.96049733  
E (CCSD/Aug-CC-pVTZ) (Hartree): -189.93414093  
T1 diagnostic: 0.027847  
E (MP2/Aug-CC-pVTZ) (Hartree): -189.90702947  
E (MP3/Aug-CC-pVTZ) (Hartree): -189.92274648  
E (PMP2/Aug-CC-pVTZ) (Hartree): -189.91015752  
E (PMP3/Aug-CC-pVTZ) (Hartree): -189.92458433  
E (PUHF/Aug-CC-pVTZ) (Hartree): -189.28655267  
E (UHF/Aug-CC-pVTZ) (Hartree): -189.28145234  
E (UM062X/Aug-CC-pVTZ) (Hartree): -190.20981111  
Point group : CS  
Electronic state : 2-A"  
Cartesian coordinates (Angs):  
C -0.987497 -0.480576 0.000000  
O 0.000000 0.561551 0.000000  
O 1.199179 0.067204 0.000000  
H -0.859473 -1.084492 0.894432  
H -0.859473 -1.084492 -0.894432  
H -1.949500 0.022404 0.000000  
Rotational constants (GHz): 53.5982700 11.5647700 10.1270600  
Vibrational harmonic frequencies (cm-1):  
131.9535 ( A") 512.7257 ( A') 979.3410 ( A')  
1146.3196 ( A") 1201.5411 ( A') 1294.9751 ( A')  
1458.0924 ( A') 1485.2020 ( A") 1494.9065 ( A')  
3087.8938 ( A') 3178.9210 ( A") 3195.3532 ( A')  
Zero-point correction (Hartree): 0.043666

### OH

E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -75.64558463  
E (CCSD/Aug-CC-pVTZ) (Hartree): -75.63969595  
T1 diagnostic: 0.010032  
E (MP2/Aug-CC-pVTZ) (Hartree): -75.62633139  
E (MP3/Aug-CC-pVTZ) (Hartree): -75.63789655  
E (PMP2/Aug-CC-pVTZ) (Hartree): -75.62832196  
E (PMP3/Aug-CC-pVTZ) (Hartree): -75.63903953  
E (PUHF/Aug-CC-pVTZ) (Hartree): -75.42491177  
E (UHF/Aug-CC-pVTZ) (Hartree): -75.42155904  
E (UM062X/Aug-CC-pVTZ) (Hartree): -75.73381017  
Point group : C\*v  
Cartesian coordinates (Angs):

O 0.000000 0.000000 0.107996  
 H 0.000000 0.000000 -0.863971  
 Rotational constants (GHz): 0.000000 564.2418254 564.2418254  
 Vibrational harmonic frequencies (cm-1):  
 3769.1136 ( SG)  
 Zero-point correction (Hartree): 0.008587

CH3O

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 E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -114.88503865  
 E (CCSD/Aug-CC-pVTZ) (Hartree): -114.87138374  
 T1 diagnostic: 0.018331  
 E (MP2/Aug-CC-pVTZ) (Hartree): -114.84389597  
 E (MP3/Aug-CC-pVTZ) (Hartree): -114.86669911  
 E (PMP2/Aug-CC-pVTZ) (Hartree): -114.84635299  
 E (PMP3/Aug-CC-pVTZ) (Hartree): -114.86816675  
 E (PUHF/Aug-CC-pVTZ) (Hartree): -114.47242060  
 E (UHF/Aug-CC-pVTZ) (Hartree): -114.46839717  
 E (UM062X/Aug-CC-pVTZ) (Hartree): -115.04237469  
 Electronic state : 2-A  
 Cartesian coordinates (Angs):  
 C -0.576758 0.000000 -0.012094  
 O 0.790789 0.000000 -0.007227  
 H -0.997749 0.905435 -0.460177  
 H -0.997749 -0.905435 -0.460177  
 H -0.870264 -0.000000 1.050731  
 Rotational constants (GHz): 158.2267200 28.0055000 27.8344500  
 Vibrational harmonic frequencies (cm-1):  
 405.1819 969.5691 1136.5838  
 1385.0820 1386.8381 1519.1092  
 2963.4431 3036.9864 3077.7963  
 Zero-point correction (Hartree): 0.036179

HO2

-----  
 E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -150.72604292  
 E (CCSD/Aug-CC-pVTZ) (Hartree): -150.70776038  
 T1 diagnostic: 0.028799  
 E (MP2/Aug-CC-pVTZ) (Hartree): -150.69255912  
 E (MP3/Aug-CC-pVTZ) (Hartree): -150.69874647  
 E (PMP2/Aug-CC-pVTZ) (Hartree): -150.69557501  
 E (PMP3/Aug-CC-pVTZ) (Hartree): -150.70048285  
 E (PUHF/Aug-CC-pVTZ) (Hartree): -150.24520737  
 E (UHF/Aug-CC-pVTZ) (Hartree): -150.24028066  
 E (UM062X/Aug-CC-pVTZ) (Hartree): -150.90809462  
 Point group : CS  
 Electronic state : 2-A"  
 Cartesian coordinates (Angs):  
 O 0.055022 0.708334 0.000000  
 O 0.055022 -0.599994 0.000000  
 H -0.880350 -0.866714 0.000000  
 Rotational constants (GHz): 629.2136600 34.6871500 32.8748300  
 Vibrational harmonic frequencies (cm-1):  
 1252.3111 ( A') 1458.2887 ( A') 3687.4120 ( A')  
 Zero-point correction (Hartree): 0.014576

H2O

-----  
 E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -76.34229141  
 E (CCSD/Aug-CC-pVTZ) (Hartree): -76.33365041  
 T1 diagnostic: 0.010015  
 E (MP2/Aug-CC-pVTZ) (Hartree): -76.32895633  
 E (MP3/Aug-CC-pVTZ) (Hartree): -76.33161406  
 E (RHF/Aug-CC-pVTZ) (Hartree): -76.06049554  
 E (RM062X/Aug-CC-pVTZ) (Hartree): -76.43010673  
 Point group : C2V  
 Electronic state : 1-A1  
 Cartesian coordinates (Angs):  
 O 0.000000 -0.000000 0.116425  
 H -0.000000 0.762551 -0.465701  
 H -0.000000 -0.762551 -0.465701  
 Rotational constants (GHz): 833.1294600 431.1858700 284.1329600  
 Vibrational harmonic frequencies (cm-1):  
 1620.0733 3867.4456 3970.2989  
 Zero-point correction (Hartree): 0.021546

HOOH

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-----
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -151.37359886
E (CCSD/Aug-CC-pVTZ) (Hartree): -151.35395722
  T1 diagnostic: 0.012184
E (MP2/Aug-CC-pVTZ) (Hartree): -151.34746342
E (MP3/Aug-CC-pVTZ) (Hartree): -151.34969243
E (RHF/Aug-CC-pVTZ) (Hartree): -150.84121855
E (RM062X/Aug-CC-pVTZ) (Hartree): -151.55365119
Point group : C2
Electronic state : 1-A
Cartesian coordinates (Angs):
  H      0.782073      0.904027      0.470608
  O      0.000000      0.711507     -0.058826
  O     -0.000000     -0.711507     -0.058826
  H     -0.782073     -0.904027      0.470608
Rotational constants (GHz): 307.6033400  27.3254400  26.4946200
Vibrational harmonic frequencies (cm-1):
  374.6713 ( A)      1043.0598 ( A)      1356.2611 ( B)
  1462.7232 ( A)      3837.7760 ( B)      3839.1361 ( A)
Zero-point correction (Hartree): 0.027141

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CH2O

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E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -114.34257083
E (CCSD/Aug-CC-pVTZ) (Hartree): -114.32534887
  T1 diagnostic: 0.015268
E (MP2/Aug-CC-pVTZ) (Hartree): -114.31598800
E (MP3/Aug-CC-pVTZ) (Hartree): -114.32041897
E (RHF/Aug-CC-pVTZ) (Hartree): -113.91459703
E (RM062X/Aug-CC-pVTZ) (Hartree): -114.49897017
Point group : C2V
Electronic state : 1-A1
Cartesian coordinates (Angs):
  C     -0.000000     -0.000000     -0.525642
  O      0.000000      0.000000      0.670496
  H     -0.000000      0.938500     -1.105059
  H     -0.000000     -0.938500     -1.105059
Rotational constants (GHz): 284.6644600  39.4579200  34.6544000
Vibrational harmonic frequencies (cm-1):
  1212.9431      1273.4284      1539.4444
  1868.4043      2946.9453      3017.7464
Zero-point correction (Hartree): 0.027017

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HCOOH

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-----
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -189.51743914
E (CCSD/Aug-CC-pVTZ) (Hartree): -189.48985644
  T1 diagnostic: 0.016332
E (MP2/Aug-CC-pVTZ) (Hartree): -189.48638235
E (MP3/Aug-CC-pVTZ) (Hartree): -189.48384009
E (RHF/Aug-CC-pVTZ) (Hartree): -188.84523309
E (RM062X/Aug-CC-pVTZ) (Hartree): -189.76956659
Electronic state : 1-A
Cartesian coordinates (Angs):
  C      0.135051      0.398947     -0.000006
  H      0.112180      1.493403      0.000042
  O      1.126440     -0.265039     -0.000060
  O     -1.110574     -0.088952      0.000055
  H     -1.049413     -1.055164      0.000041
Rotational constants (GHz): 77.9838300  12.2098800  10.5569800
Vibrational harmonic frequencies (cm-1):
  644.6502      673.5968      1075.1559
  1161.5868      1317.5241      1414.2985
  1868.8096      3101.8095      3792.1421
Zero-point correction (Hartree): 0.034285

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O2\_3P

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E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -150.14024314
E (CCSD/Aug-CC-pVTZ) (Hartree): -150.12181932
  T1 diagnostic: 0.017116
E (MP2/Aug-CC-pVTZ) (Hartree): -150.11943111
E (MP3/Aug-CC-pVTZ) (Hartree): -150.11498886
E (PMP2/Aug-CC-pVTZ) (Hartree): -150.12651233
E (PMP3/Aug-CC-pVTZ) (Hartree): -150.11820853
E (PUHF/Aug-CC-pVTZ) (Hartree): -149.69199085
E (UHF/Aug-CC-pVTZ) (Hartree): -149.68070842

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E(UM062X/Aug-CC-pVTZ) (Hartree): -150.32479537  
Point group : D\*H  
Electronic state : 3-SGG  
Cartesian coordinates (Angs):  
O 0.000000 0.000000 0.594897  
O 0.000000 0.000000 -0.594897  
Rotational constants (GHz): 0.0000000 44.6397461 44.6397461  
Vibrational harmonic frequencies (cm-1):  
1754.7928 ( SGG)  
Zero-point correction (Hartree): 0.003998

#### O2\_1D

-----  
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -150.09179386  
E(CCSD/Aug-CC-pVTZ) (Hartree): -150.06905130  
T1 diagnostic: 0.014676  
E(MP2/Aug-CC-pVTZ) (Hartree): -150.07079799  
E(MP3/Aug-CC-pVTZ) (Hartree): -150.06086620  
E(RHF/Aug-CC-pVTZ) (Hartree): -149.59505420  
E(RM062X/Aug-CC-pVTZ) (Hartree): -150.26570478  
Point group : D\*H  
Cartesian coordinates (Angs):  
O 0.000000 0.000000 0.594062  
O 0.000000 0.000000 -0.594062  
Rotational constants (GHz): 0.0000000 44.7653142 44.7653142  
Vibrational harmonic frequencies (cm-1):  
1748.4400 ( SGG)  
Zero-point correction (Hartree): 0.003983

#### CH3OH

-----  
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -115.56228300  
E(CCSD/Aug-CC-pVTZ) (Hartree): -115.54648707  
T1 diagnostic: 0.009878  
E(MP2/Aug-CC-pVTZ) (Hartree): -115.52894040  
E(MP3/Aug-CC-pVTZ) (Hartree): -115.54321816  
E(RHF/Aug-CC-pVTZ) (Hartree): -115.09240265  
E(RM062X/Aug-CC-pVTZ) (Hartree): -115.71780209  
Electronic state : 1-A  
Cartesian coordinates (Angs):  
C -0.663403 -0.020645 0.000003  
O 0.744504 0.122294 0.000004  
H -1.020127 -0.543450 0.890281  
H -1.083236 0.982067 -0.001343  
H -1.019920 -0.545725 -0.889006  
H 1.147669 -0.747376 0.000019  
Rotational constants (GHz): 129.0773300 24.9389100 24.0778700  
Vibrational harmonic frequencies (cm-1):  
303.4402 1069.5054 1109.1150  
1180.7230 1369.6254 1485.3421  
1510.5915 1519.2002 3039.9509  
3093.0885 3150.9694 3900.4280  
Zero-point correction (Hartree): 0.051787

#### CH4

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E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -40.44090721  
E(CCSD/Aug-CC-pVTZ) (Hartree): -40.43436815  
T1 diagnostic: 0.007510  
E(MP2/Aug-CC-pVTZ) (Hartree): -40.41445787  
E(MP3/Aug-CC-pVTZ) (Hartree): -40.43256467  
E(RHF/Aug-CC-pVTZ) (Hartree): -40.21364109  
E(RM062X/Aug-CC-pVTZ) (Hartree): -40.50173480  
Electronic state : 1-A  
Cartesian coordinates (Angs):  
C -0.000002 -0.000002 -0.000012  
H -0.155588 0.585018 0.902701  
H 0.276427 -1.015910 0.269842  
H -0.916932 -0.016813 -0.583330  
H 0.796105 0.447719 -0.589138  
Rotational constants (GHz): 159.1872900 159.1816700 159.1809700  
Vibrational harmonic frequencies (cm-1):  
1338.6335 1339.2763 1339.7530  
1564.1779 1564.3042 3064.6806  
3176.5210 3177.1443 3177.6693  
Zero-point correction (Hartree): 0.044976

O3

-----  
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -225.14982225  
E(CCSD/Aug-CC-pVTZ) (Hartree): -225.10450671  
T1 diagnostic: 0.024552  
E(MP2/Aug-CC-pVTZ) (Hartree): -225.13390915  
E(MP3/Aug-CC-pVTZ) (Hartree): -225.09295699  
E(RHF/Aug-CC-pVTZ) (Hartree): -224.35734389  
E(RM062X/Aug-CC-pVTZ) (Hartree): -225.40549226  
Point group : C2V  
Electronic state : 1-A1  
Cartesian coordinates (Angs):  
O -0.000000 0.000000 0.420819  
O 0.000000 1.057274 -0.210410  
O -0.000000 -1.057274 -0.210410  
Rotational constants (GHz): 118.9469400 14.1328500 12.6319700  
Vibrational harmonic frequencies (cm-1):  
791.3126 1358.1285 1365.7811  
Zero-point correction (Hartree): 0.008008

H2O0

-----  
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -151.3006254  
E(CCSD/Aug-CC-pVTZ) (Hartree): -151.28079211  
T1 diagnostic: 0.018302  
E(MP2/Aug-CC-pVTZ) (Hartree): -151.26821617  
E(MP3/Aug-CC-pVTZ) (Hartree): -151.27438412  
E(RHF/Aug-CC-pVTZ) (Hartree): -150.77689079  
E(RM062X/Aug-CC-pVTZ) (Hartree): -151.48060932  
Electronic state : 1-A  
Cartesian coordinates (Angs):  
O -0.858129 -0.000034 0.017368  
H 0.899359 0.782681 0.388787  
O 0.633214 0.000001 -0.114580  
H 0.899959 -0.782423 0.388907  
Rotational constants (GHz): 295.8088600 24.9796100 24.0749300  
Vibrational harmonic frequencies (cm-1):  
768.0519 936.5586 942.1577  
1595.8428 3747.4484 3841.8760  
Zero-point correction (Hartree): 0.026955

CH2OH

-----  
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -114.89877167  
E(CCSD/Aug-CC-pVTZ) (Hartree): -114.88372521  
T1 diagnostic: 0.016039  
E(MP2/Aug-CC-pVTZ) (Hartree): -114.86627621  
E(MP3/Aug-CC-pVTZ) (Hartree): -114.87928443  
E(PMP2/Aug-CC-pVTZ) (Hartree): -114.86830704  
E(PMP3/Aug-CC-pVTZ) (Hartree): -114.88045849  
E(PUHF/Aug-CC-pVTZ) (Hartree): -114.46901400  
E(UHF/Aug-CC-pVTZ) (Hartree): -114.46575173  
E(UM062X/Aug-CC-pVTZ) (Hartree): -115.05612487  
Electronic state : 2-A  
Cartesian coordinates (Angs):  
C 0.681987 0.028055 -0.063593  
O -0.666745 -0.125682 0.021263  
H 1.110427 0.992427 0.165462  
H 1.233812 -0.881149 0.102992  
H -1.102200 0.725845 -0.057001  
Rotational constants (GHz): 194.8391600 30.1188800 26.3229200  
Vibrational harmonic frequencies (cm-1):  
407.1124 575.1984 1062.7828  
1235.0205 1358.7326 1493.7157  
3163.7755 3302.1084 3895.8079  
Zero-point correction (Hartree): 0.037577

H2

-----  
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -1.17262518  
E(CCSD/Aug-CC-pVTZ) (Hartree): -1.17262524  
T1 diagnostic: 0.005299  
E(MP2/Aug-CC-pVTZ) (Hartree): -1.16502134  
E(MP3/Aug-CC-pVTZ) (Hartree): -1.17056565  
E(RHF/Aug-CC-pVTZ) (Hartree): -1.13304095  
E(RM062X/Aug-CC-pVTZ) (Hartree): -1.16888309  
Point group : D\*H

Electronic state : 1-SGG  
 Cartesian coordinates (Angs):  
 H 0.000000 0.000000 0.369512  
 H 0.000000 0.000000 -0.369512  
 Rotational constants (GHz): 0.0000000 1836.3065507 1836.3065507  
 Vibrational harmonic frequencies (cm-1):  
 4467.0849 ( SGG)  
 Zero-point correction (Hartree): 0.010177

TRIPLET SURFACE CH3O + HO2  
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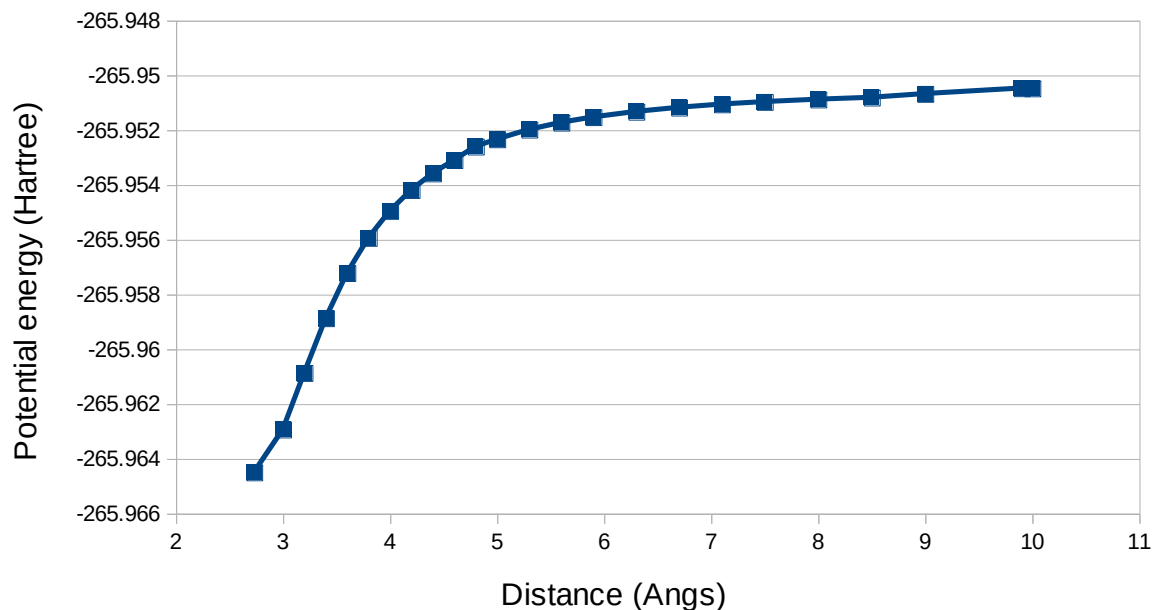
CH3O..HO2  
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E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.62480276  
 E (CCSD/Aug-CC-pVTZ) (Hartree): -265.59147768  
 T1 diagnostic: 0.025755  
 E (MP2/Aug-CC-pVTZ) (Hartree): -265.54956199  
 E (MP3/Aug-CC-pVTZ) (Hartree): -265.57740374  
 E (PMP2/Aug-CC-pVTZ) (Hartree): -265.55382509  
 E (PMP3/Aug-CC-pVTZ) (Hartree): -265.57991097  
 E (PUHF/Aug-CC-pVTZ) (Hartree): -264.72007096  
 E (UHF/Aug-CC-pVTZ) (Hartree): -264.71314453  
 E (UM062X/Aug-CC-pVTZ) (Hartree): -265.96449039  
 Electronic state : 3-A  
 Cartesian coordinates (Angs):  
 C 1.634940 0.479270 0.131999  
 O 1.168575 -0.768211 -0.189140  
 H 1.286990 1.133119 -0.686484  
 H 1.151135 0.871328 1.032497  
 H 2.724095 0.519658 0.185354  
 H -0.609247 -0.871612 0.080569  
 O -1.528523 -0.528900 0.175564  
 O -1.435379 0.731097 -0.161915  
 Rotational constants (GHz): 16.1154700 3.6555800 3.0992600  
 Vibrational harmonic frequencies (cm-1):  
 47.7305 117.5180 133.2963  
 150.5990 242.7421 560.7099  
 843.4809 1027.2911 1146.7106  
 1277.8174 1361.3725 1394.6830  
 1509.5027 1540.0016 2953.4805  
 3038.5412 3109.3543 3433.0675  
 Zero-point correction (Hartree): 0.054421

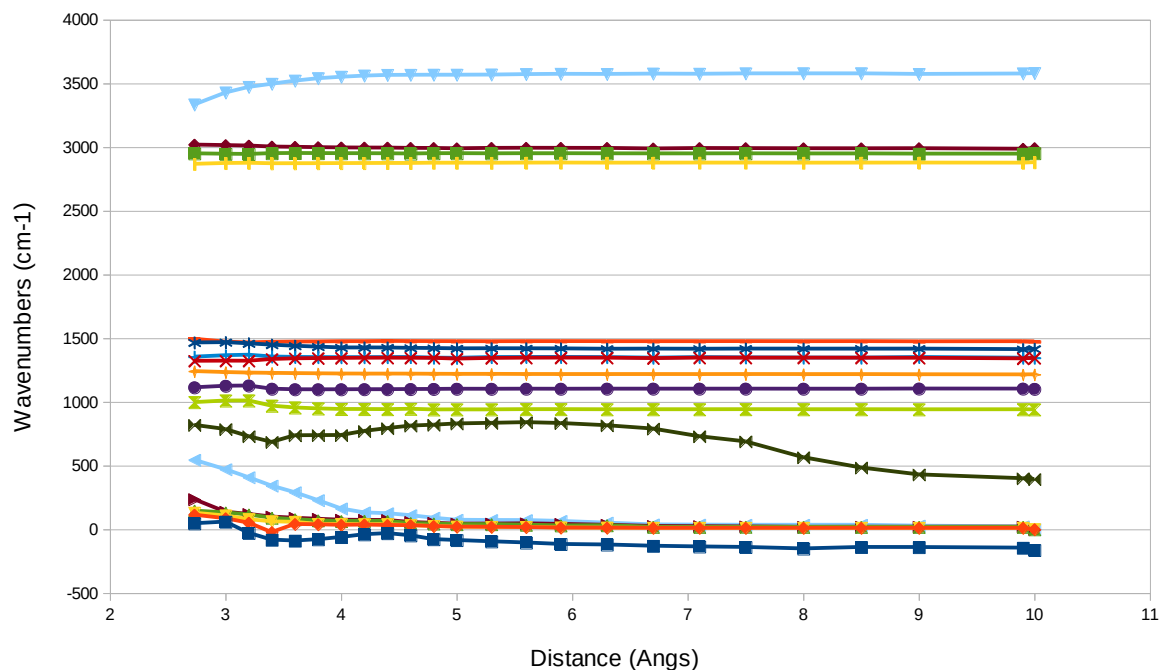
Complexation CH3O+HO2 -> CH3O..HO2  
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Barrierless reaction.

Energy Profile:



Vibrational wavenumbers:



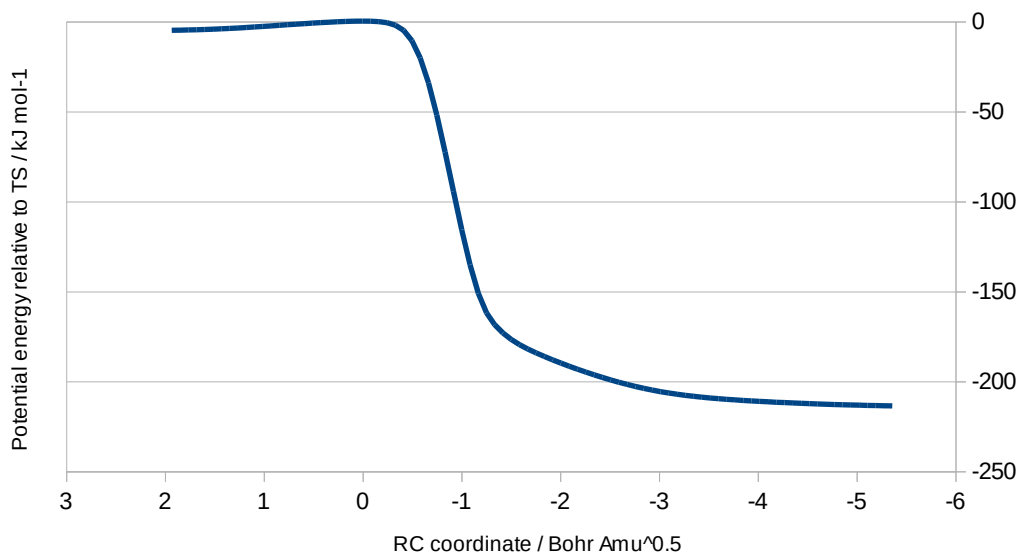
TS.CH3O..HO2.CH3OH+O2 (TS1)

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-----
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.62094031
E (CCSD/Aug-CC-pVTZ) (Hartree): -265.58565819
  T1 diagnostic: 0.047404
E (MP2/Aug-CC-pVTZ) (Hartree): -265.54330796
E (MP3/Aug-CC-pVTZ) (Hartree): -265.56952035
E (PMP2/Aug-CC-pVTZ) (Hartree): -265.54777992
E (PMP3/Aug-CC-pVTZ) (Hartree): -265.57214920
E (PUHF/Aug-CC-pVTZ) (Hartree): -264.70666771
E (UHF/Aug-CC-pVTZ) (Hartree): -264.69941913
E (UM062X/Aug-CC-pVTZ) (Hartree): -265.96218163
Electronic state : 3-A
Cartesian coordinates (Angs):
  C      1.549164      0.514948      0.052459
  O      1.133791     -0.769544     -0.084982
  H      0.657885      1.130385     -0.227200
  H      1.750948      0.783361      1.095923
  H      2.370725      0.775798     -0.618052
  H     -0.394553     -0.808035      0.095103
  O     -1.383388     -0.566338      0.072651
  O     -1.460402      0.714482     -0.070234
Rotational constants (GHz):  16.3922600   4.0331900   3.3204100
Vibrational harmonic frequencies (cm-1):
  i424.5340      94.3399      161.3161
  247.4175      264.0910      689.2329
  864.8316      1012.4508     1155.8347
  1263.1935     1342.7900     1359.3135
  1513.5801     1584.6786     2462.4977
  2800.4375     3017.6612     3096.2723
Zero-point correction (Hartree): 0.052238
IRC Pathway available

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IRC Plot:



CH300\_OH.Habstr (TS2)

-----  
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.59602878  
E (CCSD/Aug-CC-pVTZ) (Hartree): -265.55897152  
T1 diagnostic: 0.028887  
E (MP2/Aug-CC-pVTZ) (Hartree): -265.52056737  
E (MP3/Aug-CC-pVTZ) (Hartree): -265.54226373  
E (PMP2/Aug-CC-pVTZ) (Hartree): -265.52744925  
E (PMP3/Aug-CC-pVTZ) (Hartree): -265.54627484  
E (PUHF/Aug-CC-pVTZ) (Hartree): -264.66934776  
E (UHF/Aug-CC-pVTZ) (Hartree): -264.65889952  
E (UM062X/Aug-CC-pVTZ) (Hartree): -265.93560435  
Electronic state : 3-A  
Cartesian coordinates (Angs):  
C -0.193269 1.097019 0.069993  
O -1.201290 0.113097 -0.126471  
O -0.805411 -1.108101 0.069468  
H 0.908194 0.568825 -0.031449  
H -0.266999 1.512242 1.072004  
H -0.273625 1.832150 -0.725005  
O 1.924154 -0.188132 -0.043540  
H 1.452422 -1.030244 0.068829  
Rotational constants (GHz): 11.5216900 5.1385800 3.6624700  
Vibrational harmonic frequencies (cm-1):  
i1609.8106 45.2256 175.9535  
276.4640 360.6593 475.2585  
711.7844 822.1453 987.5693  
1096.6613 1183.1505 1242.4963  
1297.3385 1460.5832 1471.9333  
3109.6881 3205.8670 3768.3856  
Zero-point correction (Hartree): 0.049416  
IRC Pathway available

TS\_SN2subst (TS3)

-----  
E (UM062X/Aug-CC-pVTZ) (Hartree): -265.91369955  
Electronic state : 3-A  
Cartesian coordinates (Angs):  
C -0.404346 0.165162 -0.048648  
H -0.451031 -0.308642 0.917679  
H -0.404430 -0.462872 -0.922142  
H -0.726010 1.187521 -0.157467  
O -2.429685 -0.217616 -0.066494  
H -2.725724 0.228835 0.740473  
O 1.287492 0.516663 -0.008588  
O 1.983851 -0.503523 0.039250  
Rotational constants (GHz): 37.2574600 2.5737000 2.4632700  
Vibrational harmonic frequencies (cm-1):  
i1475.9937 100.7859 152.4120



175.4545	224.7631	271.8633
468.8106	713.3243	1081.0079
1087.9902	1169.9987	1396.9630
1421.8326	1426.2979	3140.6994
3308.4143	3323.1856	3799.8492

Zero-point correction (Hartree): 0.052999  
IRC Pathway available

TS\_Oshift (TS4)

-----  
E(UM062X/Aug-CC-pVTZ) (Hartree): -265.89398876  
Electronic state : 3-A  
Cartesian coordinates (Angs):

C	-1.487453	0.593679	-0.000000
O	-0.935055	-0.699011	-0.000001
O	0.616463	-0.582874	-0.000000
H	-1.190586	1.142938	-0.895983
H	-1.190587	1.142936	0.895984
H	-2.570041	0.469419	-0.000001
O	1.869487	0.339524	0.000001
H	1.468778	1.221524	0.000002

Rotational constants (GHz): 20.2170500 4.3681700 3.6766300  
Vibrational harmonic frequencies (cm-1):

i1153.3790	148.3971	166.1960
265.2132	429.3319	485.8952
675.0046	1066.4583	1119.8441
1163.8693	1172.1499	1448.8682
1484.0536	1499.6153	3037.9877
3107.8401	3135.6774	3792.2440

Zero-point correction (Hartree): 0.055129  
IRC Pathway available

SINGLET SURFACE CH3O + HO2

-----  
CH3O3H.pm

-----  
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.65639308  
E(CCSD/Aug-CC-pVTZ) (Hartree): -265.61614825  
T1 diagnostic: 0.015600  
E(MP2/Aug-CC-pVTZ) (Hartree): -265.59879511  
E(MP3/Aug-CC-pVTZ) (Hartree): -265.60786538  
E(RHF/Aug-CC-pVTZ) (Hartree): -264.67604045  
E(RM062X/Aug-CC-pVTZ) (Hartree): -265.99436741  
Electronic state : 1-A  
Cartesian coordinates (Angs):

C	1.417296	0.435932	0.093778
O	0.563997	-0.599676	-0.352220
O	-0.622205	-0.545458	0.386560
H	1.597776	0.350830	1.165589
H	1.005062	1.416026	-0.154059
H	2.346114	0.293674	-0.453965
O	-1.456362	0.412365	-0.217923
H	-1.336170	1.186035	0.348425

Rotational constants (GHz): 19.4957000 5.8088600 5.1012700  
Vibrational harmonic frequencies (cm-1):

133.0320	223.0946	349.1003
460.2741	579.1151	916.9424
984.0423	1087.8873	1178.9588
1225.8594	1406.6724	1455.7268
1487.9440	1511.8069	3051.3216
3124.2306	3162.7394	3800.7144

Zero-point correction (Hartree): 0.059550

-----  
CH3O3H.tt

-----  
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.66030787  
E(CCSD/Aug-CC-pVTZ) (Hartree): -265.62018160  
T1 diagnostic: 0.015465  
E(MP2/Aug-CC-pVTZ) (Hartree): -265.60296296  
E(MP3/Aug-CC-pVTZ) (Hartree): -265.61184836  
E(RHF/Aug-CC-pVTZ) (Hartree): -264.68052779  
E(RM062X/Aug-CC-pVTZ) (Hartree): -265.99831713  
Electronic state : 1-A  
Cartesian coordinates (Angs):

C	1.438401	0.412968	0.096476
O	0.539538	-0.569901	-0.391756
O	-0.611871	-0.532285	0.404661

H	1.706272	0.200282	1.130774	
H	0.998644	1.405738	0.009165	
H	2.314647	0.336095	-0.543397	
O	-1.403210	0.532026	-0.056943	
H	-1.845620	0.141359	-0.823088	
Rotational constants (GHz):	19.6255300	5.7970100	5.1543400	
Vibrational harmonic frequencies (cm-1):				
159.5129	210.9690		375.7800	
453.9830	595.6650		913.8459	
986.1249	1078.4809		1183.0752	
1227.0947	1422.2572		1454.2339	
1480.9376	1515.6300		3065.6310	
3145.3208	3165.1073		3789.9507	
Zero-point correction (Hartree):	0.059742			

CH30..HO2

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-----
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.62493320
E (CCSD/Aug-CC-pVTZ) (Hartree): -265.59158404
  T1 diagnostic: 0.027878
E (MP2/Aug-CC-pVTZ) (Hartree): -265.54964854
E (MP3/Aug-CC-pVTZ) (Hartree): -265.57746649
E (PMP2/Aug-CC-pVTZ) (Hartree): -265.57780054
E (PMP3/Aug-CC-pVTZ) (Hartree): -265.60545521
E (PUHF/Aug-CC-pVTZ) (Hartree): -264.74153875
E (UHF/Aug-CC-pVTZ) (Hartree): -264.71314345
E (UM062X/Aug-CC-pVTZ) (Hartree): -265.96458779
Electronic state : 1-A
Cartesian coordinates (Angs):
  C      1.639985      0.487015      0.085413
  O      1.171374     -0.784116     -0.116954
  O     -1.430803      0.746811     -0.101596
  H      2.727607      0.531291      0.156394
  H      1.139758      0.958035      0.938789
  H      1.299129      1.070011     -0.786929
  O     -1.539676     -0.538924      0.109660
  H     -0.613558     -0.871595      0.050385
Rotational constants (GHz): 16.1268100      3.6661800      3.0668400
Vibrational harmonic frequencies (cm-1):
  48.4959      115.2099      136.4351
  163.3406      242.2590      546.3395
  824.2458      1034.8543      1167.9825
  1279.8216      1356.1132      1407.2181
  1502.6229      1542.4650      2957.7770
  3032.7669      3112.7020      3429.4152
Zero-point correction (Hartree): 0.054448

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CH300..OH.a

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-----
E (UM062X/Aug-CC-pVTZ) (Hartree): -265.94925809
Electronic state : 1-A
Cartesian coordinates (Angs):
  C      0.476016      1.153761     -0.000006
  O      0.425386     -0.282177     -0.000990
  O      1.604314     -0.799047      0.000769
  H      0.996402      1.483585     -0.895233
  H      0.995088      1.482372      0.896422
  H     -0.560090      1.483049     -0.000586
  H     -1.607602     -0.843324     -0.005254
  O     -2.364686     -0.234808      0.000807
Rotational constants (GHz): 13.6534300      3.5373600      2.8609300
Vibrational harmonic frequencies (cm-1):
  i102.0328      i45.0294      127.4581
  142.2948      232.1595      294.6208
  513.9448      978.4641      1149.1455
  1209.3013      1330.3246      1462.4874
  1478.0923      1495.0556      3083.6666
  3181.3324      3186.5839      3770.6708
Zero-point correction (Hartree): 0.053846

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CH300..OH.c

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-----
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.61342724
E (CCSD/Aug-CC-pVTZ) (Hartree): -265.58019171
  T1 diagnostic: 0.025372
E (MP2/Aug-CC-pVTZ) (Hartree): -265.54033934
E (MP3/Aug-CC-pVTZ) (Hartree): -265.56694685

```

E (PMP2/Aug-CC-pVTZ) (Hartree): -265.56662804  
 E (PMP3/Aug-CC-pVTZ) (Hartree): -265.59310142  
 E (PUHF/Aug-CC-pVTZ) (Hartree): -264.72990001  
 E (UHF/Aug-CC-pVTZ) (Hartree): -264.70340540  
 E (UM062X/Aug-CC-pVTZ) (Hartree): -265.95280344  
 Electronic state : 1-A  
 Cartesian coordinates (Angs):  
 C 0.596170 1.094861 0.000412  
 O 1.283421 -0.169990 -0.000898  
 O 0.460766 -1.169267 0.000557  
 H -0.017786 1.160416 0.896307  
 H -0.018878 1.161659 -0.894657  
 H 1.375956 1.849983 0.000437  
 H -1.523497 -0.655655 0.000250  
 O -2.168288 0.078561 -0.000261  
 Rotational constants (GHz): 11.3136000 4.3854200 3.2255900  
 Vibrational harmonic frequencies (cm-1):  
 38.4741 121.4661 166.1426  
 179.9576 407.4745 416.5788  
 522.6672 969.1177 1137.0425  
 1201.4897 1314.3733 1459.3471  
 1483.6088 1491.3222 3079.6742  
 3165.9696 3194.3804 3675.3282  
 Zero-point correction (Hartree): 0.054732

CH300..OH.e

-----  
 E (UM062X/Aug-CC-pVTZ) (Hartree): -265.95038179  
 Electronic state : 1-A  
 Cartesian coordinates (Angs):  
 C -0.572759 1.159945 -0.097345  
 O -0.450484 -0.167644 0.445671  
 O -1.161427 -1.020132 -0.223458  
 H -1.613454 1.465640 -0.025922  
 H -0.235677 1.142536 -1.129894  
 H 0.072803 1.784912 0.511901  
 H 1.867816 -1.012949 0.210039  
 O 2.030045 -0.104700 -0.094969  
 Rotational constants (GHz): 10.8745200 4.7230500 3.5625000  
 Vibrational harmonic frequencies (cm-1):  
 59.6627 129.0171 138.5680  
 153.5010 179.1608 337.2983  
 512.7332 972.2251 1149.0531  
 1202.2660 1298.5550 1457.7615  
 1481.2313 1490.7185 3088.3523  
 3183.5134 3197.5649 3774.0153  
 Zero-point correction (Hartree): 0.054232

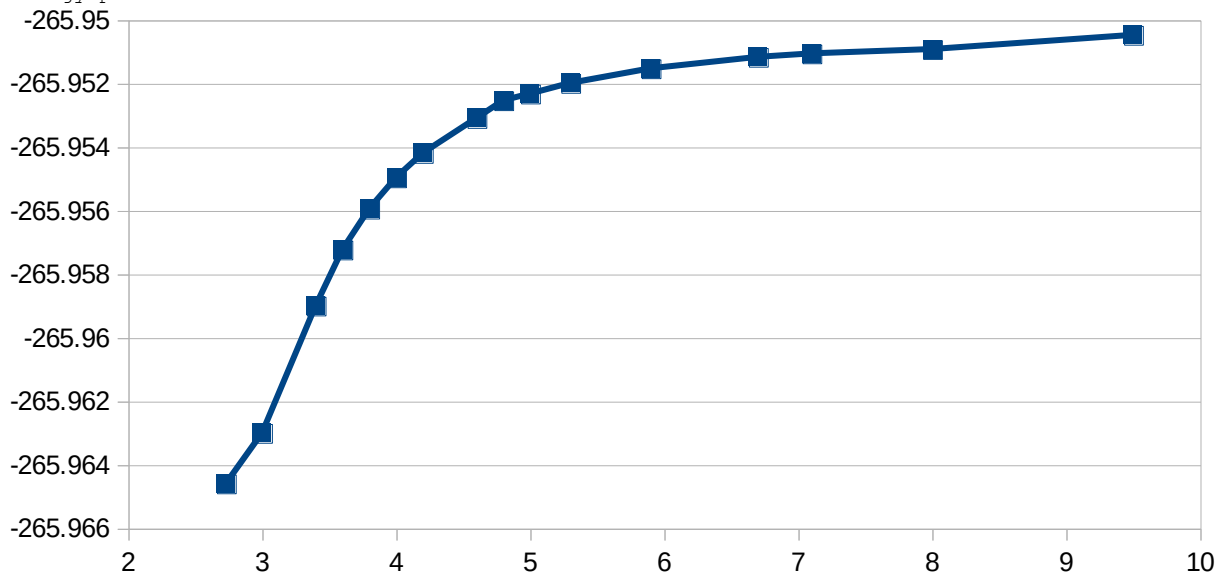
CH300HO

-----  
 E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.59744212  
 E (CCSD/Aug-CC-pVTZ) (Hartree): -265.55533136  
 T1 diagnostic: 0.021368  
 E (MP2/Aug-CC-pVTZ) (Hartree): -265.53672786  
 E (MP3/Aug-CC-pVTZ) (Hartree): -265.54390998  
 E (RHF/Aug-CC-pVTZ) (Hartree): -264.61421455  
 E (RM062X/Aug-CC-pVTZ) (Hartree): -265.93295357  
 Electronic state : 1-A  
 Cartesian coordinates (Angs):  
 C -1.304027 0.209198 0.128962  
 O 0.012080 -0.060839 -0.420575  
 O 0.502037 -1.251958 0.112077  
 H -1.219451 0.142417 1.208402  
 H -1.930344 -0.574560 -0.280776  
 H -1.588097 1.197308 -0.217806  
 H 1.495097 0.421659 0.526546  
 O 0.869253 1.007546 0.057230  
 Rotational constants (GHz): 10.3295600 9.7930300 5.5989300  
 Vibrational harmonic frequencies (cm-1):  
 258.0306 327.4957 414.6166  
 438.0688 498.6111 764.4800  
 858.4017 1016.5049 1197.2733  
 1209.2367 1447.6746 1464.7034  
 1478.5987 1485.9911 3104.9619  
 3215.7710 3224.5085 3655.1946  
 Zero-point correction (Hartree): 0.059369

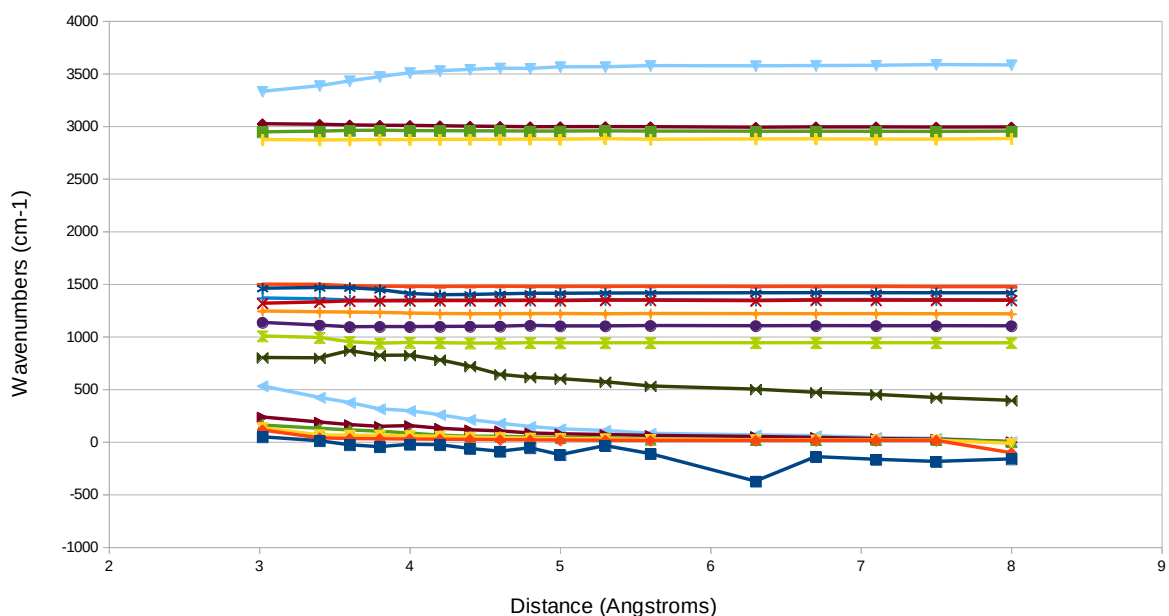
TS Complexation CH3O+HO2 -> CH3O..HO2

Barrierless reaction

Energy profile:



Vibrational wavenumbers:



TS.CH3O..HO2.CH3OH+O2 (TS5)

E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.61656432

E (CCSD/Aug-CC-pVTZ) (Hartree): -265.57882685

T1 diagnostic: 0.082129

E (MP2/Aug-CC-pVTZ) (Hartree): -265.53485903

E (MP3/Aug-CC-pVTZ) (Hartree): -265.55980132

E (PMP2/Aug-CC-pVTZ) (Hartree): -265.56412507

E (PMP3/Aug-CC-pVTZ) (Hartree): -265.58887703

E (PUHF/Aug-CC-pVTZ) (Hartree): -264.71560569

E (UHF/Aug-CC-pVTZ) (Hartree): -264.68607395

E (UM062X/Aug-CC-pVTZ) (Hartree): -265.95833962

Electronic state : 1-A

Cartesian coordinates (Angs):

C	1.506760	0.518385	0.011593
O	1.084970	-0.769973	-0.020595
O	-1.434803	0.707342	-0.016289
H	2.234906	0.748772	-0.769856
H	1.839840	0.831804	1.007611
H	0.591162	1.136377	-0.186551
O	-1.325989	-0.565611	0.010203
H	-0.299883	-0.801325	0.092682

Rotational constants (GHz): 16.5933800 4.2973800 3.4925600

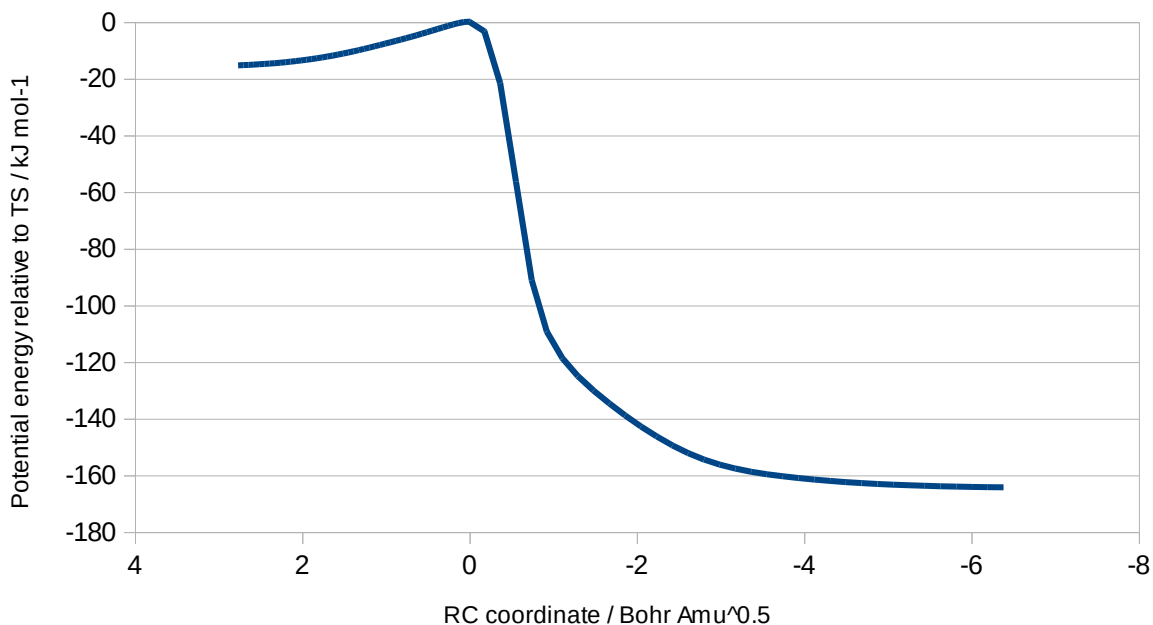
Vibrational harmonic frequencies (cm-1):

i1008.3726	94.0508	165.2588
237.2938	329.4784	571.0753
960.1721	998.8104	1159.2927
1178.2869	1341.3748	1362.4117
1511.8535	1552.9932	1731.0094
2737.1011	3016.8800	3089.6308

Zero-point correction (Hartree): 0.050204

IRC Pathway available.

IRC Plot:



TS.CH3OOH.CH3O..HO2 (TS6)

-----

E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.61776235

E (CCSD/Aug-CC-pVTZ) (Hartree): -265.58045567

T1 diagnostic: 0.033493

E (MP2/Aug-CC-pVTZ) (Hartree): -265.53453914

E (MP3/Aug-CC-pVTZ) (Hartree): -265.56228366

E (PMP2/Aug-CC-pVTZ) (Hartree): -265.57312747

E (PMP3/Aug-CC-pVTZ) (Hartree): -265.59975623

E (PUHF/Aug-CC-pVTZ) (Hartree): -264.73289859

E (UHF/Aug-CC-pVTZ) (Hartree): -264.69354755

E (UM062X/Aug-CC-pVTZ) (Hartree): -265.95334359

Electronic state : 1-A

Cartesian coordinates (Angs):

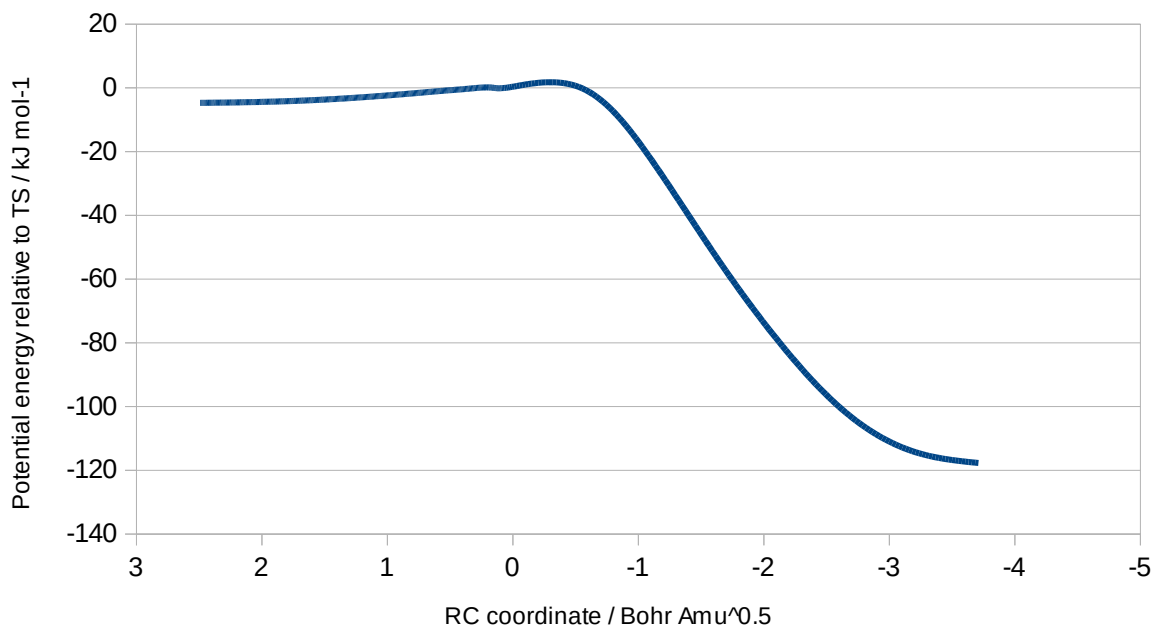
C	-1.518965	0.452467	0.144476
O	-0.874196	-0.646930	-0.389002
O	0.910661	-0.497488	0.454180
H	-2.479628	0.496696	-0.386562
H	-0.983276	1.383485	-0.061917
H	-1.717744	0.344450	1.212877
O	1.507510	0.512104	-0.153191
H	1.942641	0.119072	-0.927152

Rotational constants (GHz): 17.9305800 4.5014500 4.1111000

Vibrational harmonic frequencies (cm-1):

i379.8618	87.5330	173.7134
229.8219	294.0874	494.5760
1008.4048	1143.5557	1159.9997
1169.6838	1413.3662	1432.5101

1459.8591                      1518.4158                      2999.0601  
 3063.8208                      3101.2559                      3716.8020  
 Zero-point correction (Hartree): 0.055739  
 IRC Pathway available  
 IRC plot:



TS.CH3O..HO2.CH2O+HOOH (TS7)

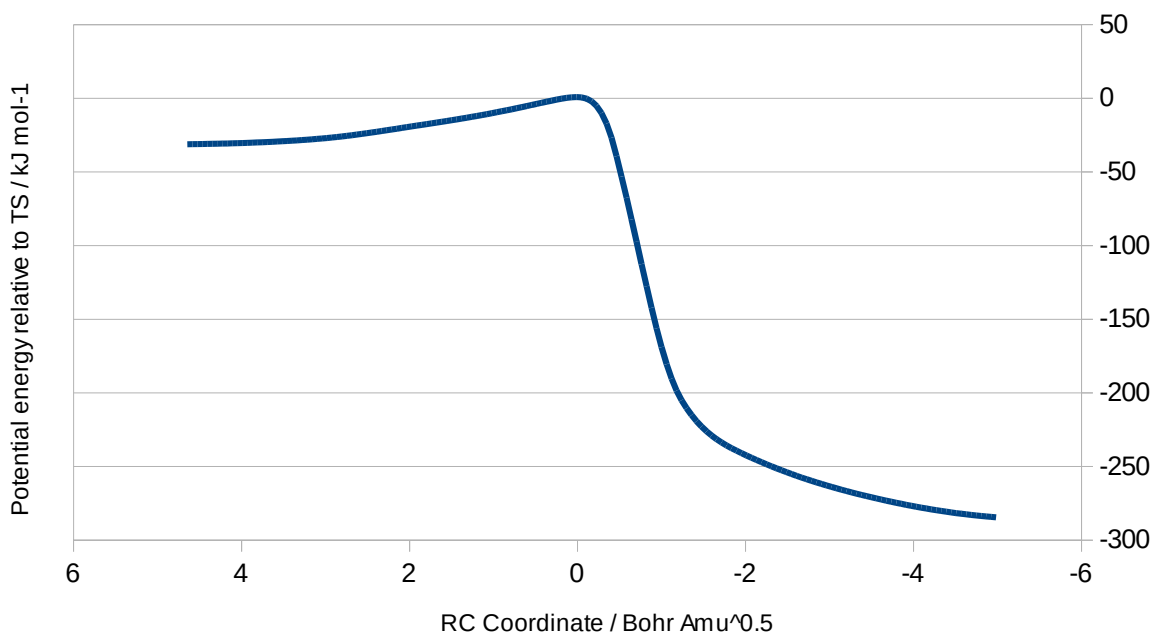
-----  
 E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.61178970  
 E (CCSD/Aug-CC-pVTZ) (Hartree): -265.57358173  
 T1 diagnostic: 0.038594  
 E (MP2/Aug-CC-pVTZ) (Hartree): -265.52895294  
 E (MP3/Aug-CC-pVTZ) (Hartree): -265.55398533  
 E (PMP2/Aug-CC-pVTZ) (Hartree): -265.56844289  
 E (PMP3/Aug-CC-pVTZ) (Hartree): -265.59254886  
 E (PUHF/Aug-CC-pVTZ) (Hartree): -264.71787589  
 E (UHF/Aug-CC-pVTZ) (Hartree): -264.67770549  
 E (UM062X/Aug-CC-pVTZ) (Hartree): -265.95225945  
 Electronic state : 1-A  
 Cartesian coordinates (Angs):  

C	-1.390043	0.502497	0.065406
O	-1.166307	-0.781391	-0.078458
O	1.242242	0.731057	-0.102692
H	-1.887323	0.807628	0.992931
H	-1.745270	1.025120	-0.833488
H	-0.291298	0.942727	0.134784
O	1.348944	-0.546664	0.163514
H	0.865120	-1.014475	-0.545580

 Rotational constants (GHz): 15.6896800 4.6325100 3.7204400  
 Vibrational harmonic frequencies (cm-1):  

i1036.0131	148.4217	205.7127
244.4277	347.6130	399.0646
677.3780	1041.6699	1216.1512
1225.5587	1269.2892	1320.2471
1488.8392	1522.0553	1750.8974
2980.0655	3068.5432	3626.9718

 Zero-point correction (Hartree): 0.051334  
 IRC Pathway available  
 IRC plot:



TS.CH3OOH.CH3OH+O2 (TS8)

-----

E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.58690101  
 E (CCSD/Aug-CC-pVTZ) (Hartree): -265.53999558  
 T1 diagnostic: 0.025283  
 E (MP2/Aug-CC-pVTZ) (Hartree): -265.52712712  
 E (MP3/Aug-CC-pVTZ) (Hartree): -265.52625031  
 E (RHF/Aug-CC-pVTZ) (Hartree): -264.58220713  
 E (RM062X/Aug-CC-pVTZ) (Hartree): -265.91812475  
 Electronic state : 1-A  
 Cartesian coordinates (Angs):  
 C 1.517388 -0.165219 -0.293355  
 O 0.458757 0.136191 0.625752  
 O -0.768025 0.662239 -0.202544  
 H 1.934388 0.778405 -0.628685  
 H 1.112168 -0.741361 -1.122828  
 H 2.263498 -0.731782 0.259869  
 O -1.459981 -0.502700 -0.101242  
 H -0.260385 -0.679784 0.676042  
 Rotational constants (GHz): 21.0098100 5.3378000 5.1420400  
 Vibrational harmonic frequencies (cm<sup>-1</sup>):  
 i1336.0552 147.9497 219.9953  
 367.3372 594.7242 819.9999  
 1029.5135 1102.8074 1136.0842  
 1193.9551 1304.8421 1458.0771  
 1487.4351 1502.0959 2245.1340  
 3081.8312 3170.7783 3195.7850  
 Zero-point correction (Hartree): 0.054809  
 IRC Pathway available

TS\_SN2subst (TS9)

-----

E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.56986438  
 E (CCSD/Aug-CC-pVTZ) (Hartree): -265.52795914  
 T1 diagnostic: 0.046421  
 E (MP2/Aug-CC-pVTZ) (Hartree): -265.48412748  
 E (MP3/Aug-CC-pVTZ) (Hartree): -265.50546665  
 E (PMP2/Aug-CC-pVTZ) (Hartree): -265.53410852  
 E (PMP3/Aug-CC-pVTZ) (Hartree): -265.55476710  
 E (PUHF/Aug-CC-pVTZ) (Hartree): -264.67774165  
 E (UHF/Aug-CC-pVTZ) (Hartree): -264.62711605  
 E (UM062X/Aug-CC-pVTZ) (Hartree): -265.90374673  
 Electronic state : 1-A  
 Cartesian coordinates (Angs):  
 C -0.437847 0.164193 -0.059272  
 H -0.454085 -0.299283 0.913354  
 H -0.398227 -0.464772 -0.930869  
 H -0.726487 1.195268 -0.177129

O	-2.383149	-0.219444	-0.061983	
H	-2.687418	0.213359	0.748986	
O	1.275590	0.518904	-0.001012	
O	1.969221	-0.503176	0.038156	
Rotational constants (GHz):	37.0430600	2.6386200	2.5224500	
Vibrational harmonic frequencies (cm-1):				
i1513.0935		96.4151		146.5238
188.0928		229.3692		290.0204
470.0589		766.8263		1104.4969
1117.4041		1183.7545		1389.6995
1411.8960		1420.3880		3135.9052
3301.8415		3324.2695		3804.0171
Zero-point correction (Hartree):	0.053266			
Partial IRC Pathway available				

TS.CH300OH.CH2O\_H2OO (TS10)

```

-----
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.60132390
E (CCSD/Aug-CC-pVTZ) (Hartree): -265.54771045
  T1 diagnostic: 0.023744
E (MP2/Aug-CC-pVTZ) (Hartree): -265.55750173
E (MP3/Aug-CC-pVTZ) (Hartree): -265.53949749
E (RHF/Aug-CC-pVTZ) (Hartree): -264.56750856
E (RM062X/Aug-CC-pVTZ) (Hartree): -265.92936200
Electronic state : 1-A
Cartesian coordinates (Angs):
  C      1.302350      -0.481546      -0.023859
  O      0.951279       0.732280       0.063047
  O     -1.005765       0.714116      -0.035767
  H      1.691780      -0.847630      -0.982678
  H      0.067256      -0.990184      -0.110522
  H      1.651471      -0.992535       0.883097
  O     -1.169905      -0.620741      -0.085067
  H     -1.429481      -0.885621       0.815545
Rotational constants (GHz): 16.0402500    6.0714100    4.6136700
Vibrational harmonic frequencies (cm-1):
i1200.2267          205.6238          507.5552
 516.3337          582.4680          653.8444
 849.4603         1089.7121         1181.3268
1214.6818         1310.8685         1351.0256
1450.3218         1522.9731         1609.5940
2973.6211         3062.3147         3680.9734
Zero-point correction (Hartree): 0.054135
IRC Pathway available

```

TS.CH300OH.CH2O+H2+O2 (TS11)

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-----
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -265.55588604
E (CCSD/Aug-CC-pVTZ) (Hartree): -265.50303797
  T1 diagnostic: 0.023043
E (MP2/Aug-CC-pVTZ) (Hartree): -265.50913248
E (MP3/Aug-CC-pVTZ) (Hartree): -265.49003591
E (RHF/Aug-CC-pVTZ) (Hartree): -264.53162070
E (RM062X/Aug-CC-pVTZ) (Hartree): -265.88547942
Electronic state : 1-A
Cartesian coordinates (Angs):
  C      1.406843       0.371417       0.117840
  O      0.898315      -0.718635      -0.208355
  O     -0.997129      -0.615507       0.192611
  H      1.597167       0.607045       1.171328
  H      0.440898       1.490264      -0.109669
  H      2.011960       0.910276      -0.625062
  O     -1.411192       0.512897      -0.131975
  H     -0.411033       1.333873       0.038121
Rotational constants (GHz): 17.7324600    5.3256600    4.3430900
Vibrational harmonic frequencies (cm-1):
i1302.5786          153.2697          269.9352
 424.9890          486.0658          541.5202
 852.9018          945.1350         1071.1988
1209.6252         1240.6160         1285.1098
1455.6740         1464.3107         1607.2635
2335.6190         2991.0454         3077.0524
Zero-point correction (Hartree): 0.048779

```