

## Master Equation Simulations of Competing Unimolecular and Bimolecular Reactions: Application to OH Production in the Reaction of Acetyl Radical with O<sub>2</sub>.

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### Supplementary Information

**Table S-1. Molecule and transition State Properties.**

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Free Radical + O <sub>2</sub> :	
frequencies /cm <sup>-1</sup>	132.5, 186.3, 319.9, 345.9, 488.9, 558.2, 609.2, 777.0, 842.9, 955.9, 1014.4, 1258.3, 1402.1, 1448.6,
product of adiabatic moments of inertia /amu A <sup>2</sup>	133.8; 11.6
moment of inertia: active external rotor /amu A <sup>2</sup>	48.7
collisions: (σ/A <sup>2</sup> , ε/K)	1.00; 404
collider (O <sub>2</sub> ) (σ/A <sup>2</sup> , ε/K, <ΔE> <sub>d</sub> /cm <sup>-1</sup> )	3.48; 103; 160
Transition State:	
frequencies /cm <sup>-1</sup>	56.2, 94.3, 109.0, 165.4, 270.5, 313.1, 365.8, 482.3, 552.7, 569.5, 665.8, 835.2, 847.3, 958.6, 1009.0, 1246.0, 1408.2, 1440.8, 1509.7, 1747.7, 3185.3,
product of adiabatic moments of inertia /amu A <sup>2</sup>	270.0
moment of inertia: active external rotor /amu A <sup>2</sup>	151.7

**Table S-2. Calculated Molecular Properties**

OH

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
O	0.000000	0.000000	0.000000	
H	0.000000	0.000000	0.900000	

Energy (Hartree): -75.756457  
Energy+ZPE (Hartree): -75.748016  
Enthalpy (Hartree): -75.744712  
Free Energy (Hartree): -75.764943  
Frequencies (cm-1): 3705.0406  
Product of Adiabatic Moments of Inertia (amu A\*\*2): 0.768  
Moment of inertia: Active External Rotor (amu A\*\*2): 0.000

O<sub>2</sub>

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
O	0.000000	0.000000	0.000000	
O	0.000000	0.000000	1.214500	

Energy (Hartree): -150.372863  
Energy+ZPE (Hartree): -150.369112  
Enthalpy (Hartree): -150.365805  
Free Energy (Hartree): -150.389076  
Frequencies (cm-1): 1646.5035  
Product of Adiabatic Moments of Inertia (amu A\*\*2): 11.800  
Moment of inertia: Active External Rotor (amu A\*\*2): 0.000

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Acetyl radical

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.516474	
O	0.938078	0.000000	2.247484	
H	-0.546068	0.881267	-0.352671	
H	1.019852	-0.001157	-0.403418	
H	-0.546731	-0.880756	-0.352804	

Energy (Hartree): -153.234349  
Energy+ZPE (Hartree): -153.191370  
Enthalpy (Hartree): -153.186479  
Free Energy (Hartree): -153.216942

Frequencies (cm-1): 117.0937 467.5424 844.8802 953.1939 1046.7833 1354.9094  
1453.823 1457.7959 1934.3639 3016.807 3106.4855 3111.713

Product of Adiabatic Moments of Inertia (amu A\*\*2): 52.500  
Moment of inertia: Active External Rotor (amu A\*\*2): 6.100

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A1

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.499400	
O	0.927238	0.000000	2.251005	
O	-1.297763	-0.003214	2.129625	
O	-2.311562	-0.001356	1.270759	
H	-0.514314	-0.885645	-0.383789	
H	1.037728	0.010844	-0.334300	
H	-0.534590	0.872221	-0.385963	

Energy (Hartree): -303.662241

Energy+ZPE (Hartree): -303.610004

Enthalpy (Hartree): -303.603742

Free Energy (Hartree): -303.639042

Frequencies (cm-1): 141.8453 163.6481 328.9528 505.904 547.2 555.659  
741.8141 984.557 1049.5733 1136.6121 1197.2245 1399.3618 1460.5202 1466.6425  
1901.6775 3063.0254 3122.446 3162.8135

Product of Adiabatic Moments of Inertia (amu A\*\*2): 128.331

Moment of inertia: Active External Rotor (amu A\*\*2): 54.714

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TS-A1-A2

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.506100	
O	0.960183	0.000000	2.225523	
O	-1.278225	0.007771	1.992321	
O	-2.191514	-0.006238	0.881539	
H	-1.350079	-0.016483	0.018024	
H	0.393394	-0.901126	-0.469512	
H	0.347022	0.924168	-0.462392	

Energy (Hartree): -303.611236  
Energy+ZPE (Hartree): -303.565174  
Enthalpy (Hartree): -303.559389  
Free Energy (Hartree): -303.593617

Frequencies (cm-1): -1693.3233 148.5268 288.4783 490.308 547.0884 605.7824  
686.6766 844.4526 951.6433 1035.1315 1035.6045 1102.8837 1152.9301 1423.0583  
1725.8073 1875.7104 3111.5508 3193.4097

Product of Adiabatic Moments of Inertia (amu A\*\*2): 125.394  
Moment of inertia: Active External Rotor (amu A\*\*2): 49.571

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A2

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.439800	
O	0.998017	0.000000	2.138874	
O	-1.201695	0.007576	2.129754	
O	-2.350624	0.033297	1.232661	
H	-2.849143	-0.714639	1.609377	
H	-0.906363	0.009707	-0.587390	
H	0.970771	-0.002325	-0.479188	

Energy (Hartree): -303.643984

Energy+ZPE (Hartree): -303.593209

Enthalpy (Hartree): -303.586582

Free Energy (Hartree): -303.622413

Frequencies (cm-1): 132.5148 186.3335 319.8944 345.9181 488.8667 558.214  
609.1769 776.9909 842.9467 955.9167 1014.3519 1258.2962 1402.1153 1448.5973  
1689.3725 3182.3823 3302.4153 3773.2889

Product of Adiabatic Moments of Inertia (amu A\*\*2): 134.666

Moment of inertia: Active External Rotor (amu A\*\*2): 49.130

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TS-A2-A2'

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.429900	
O	0.990934	0.000000	2.140868	
O	-1.289262	0.053470	2.014208	
O	-1.713683	-1.342195	2.109802	
H	-1.405338	-1.547818	3.013454	
H	-0.930105	-0.021664	-0.554369	
H	0.947995	0.011826	-0.525361	

Energy (Hartree): -303.631463  
Energy+ZPE (Hartree): -303.581113  
Enthalpy (Hartree): -303.57526  
Free Energy (Hartree): -303.609481

Frequencies (cm-1): -139.2791 246.2702 320.2693 347.5147 439.2967 579.5188  
666.8683 801.4073 856.4531 937.4664 1023.8435 1229.2807 1373.9652 1461.1864  
1636.9647 3162.9066 3279.7103 3738.1045

Product of Adiabatic Moments of Inertia (amu A\*\*2): 126.722  
Moment of inertia: Active External Rotor (amu A\*\*2): 57.635

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A2'

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.437900	
O	1.276107	0.000000	1.932764	
O	1.259837	-0.000066	3.367772	
O	-0.973986	-0.000131	2.182499	
H	0.280423	0.000188	3.529644	
H	0.928105	0.000683	-0.557937	
H	-0.953281	-0.000646	-0.512261	

Energy (Hartree): -303.653671

Energy+ZPE (Hartree): -303.602085

Enthalpy (Hartree): -303.595974

Free Energy (Hartree): -303.630554

Frequencies (cm-1): 203.4386 324.3489 341.0624 427.1731 491.3802 636.3293  
685.4267 764.0328 877.5476 1011.056 1030.1034 1250.897 1450.0928 1513.1864  
1718.4424 3171.8546 3290.4824 3456.6401

Product of Adiabatic Moments of Inertia (amu A\*\*2): 131.615

Moment of inertia: Active External Rotor (amu A\*\*2): 45.274



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TS-A2'-C3

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.467800	
O	0.791231	0.000000	2.376501	
O	-1.312470	0.002998	1.438517	
O	-1.947258	0.008423	3.163091	
H	-1.048127	0.017016	3.561786	
H	-0.059035	0.935444	-0.545328	
H	-0.066817	-0.934232	-0.546308	

Energy (Hartree): -303.613645

Energy+ZPE (Hartree): -303.565738

Enthalpy (Hartree): -303.559107

Free Energy (Hartree): -303.595006

Frequencies (cm-1): -673.1921 154.4395 194.3514 282.8 328.01 388.0285  
617.2525 640.7974 814.5226 980.2912 1009.8401 1012.6962 1188.8228 1434.962  
1877.8271 3160.2918 3278.2244 3665.7244

Product of Adiabatic Moments of Inertia (amu A\*\*2): 141.044

Moment of inertia: Active External Rotor (amu A\*\*2): 54.406

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C3

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
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C	0.049632	0.000000	0.021493	
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O	-0.154792	0.000000	1.196571	
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C	0.884749	0.000000	-1.168206	
---	----------	----------	-----------	--

H	1.306730	0.924978	-1.554485	
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H	1.306730	-0.924978	-1.554485	
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O	-0.641252	0.000000	-1.121100	
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Energy (Hartree): -227.883638

Energy+ZPE (Hartree): -227.845107

Enthalpy (Hartree): -227.840646

Free Energy (Hartree): -227.870592

Frequencies (cm-1): 497.5964 537.0204 723.2399 944.2939 999.243

1065.6451 1122.9864 1195.9179 1485.4433 2016.784 3113.7095 3211.4758

Product of Adiabatic Moments of Inertia (amu A\*\*2): 71.023

Moment of inertia: Active External Rotor (amu A\*\*2): 20.132

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TS-A2' -Ketene

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.349227	
O	0.489713	0.000000	2.404560	
H	0.932077	-0.237168	-0.494605	
H	-0.890298	0.209916	-0.561920	
O	-1.870304	-0.406869	1.603154	
O	-2.224365	-0.704824	2.892513	
H	-1.383883	-0.627759	3.372690	

Energy (Hartree): -303.617608

Energy+ZPE (Hartree): -303.568104

Enthalpy (Hartree): -303.562033

Free Energy (Hartree): -303.596869

Frequencies (cm-1): -369.1213 147.2892 265.583 407.8372 480.1669

561.416 597.2728 678.776 778.9463 987.181 1131.5847 1183.4868

1440.5002 1518.3469 2012.5656 3076.4931 3175.9588 3286.1602

Product of Adiabatic Moments of Inertia (amu A\*\*2): 154.115

Moment of inertia: Active External Rotor (amu A\*\*2): 52.580

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ketene  
Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.314816	
O	0.004089	0.000000	2.486212	
H	0.939204	0.000000	-0.538628	
H	-0.936067	0.000000	-0.544061	

Energy (Hartree): -152.656092  
Energy+ZPE (Hartree): -152.624528  
Enthalpy (Hartree): -152.620071  
Free Energy (Hartree): -152.648113  
Frequencies (cm-1): 446.7219 555.5558 593.5215 992.3063 1173.7169 1416.3561  
2229.0263 3178.8907 3268.8683  
Product of Adiabatic Moments of Inertia (amu A\*\*2): 50.526  
Moment of inertia: Active External Rotor (amu A\*\*2): 1.772

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TS-A2-B1

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.452200	
H	0.912860	0.000000	-0.576950	
H	-0.944097	-0.240481	-0.472323	
O	-0.210440	2.305212	-0.269215	
O	0.603624	2.992961	0.336092	
O	-0.954804	-0.283730	2.145680	
O	1.151738	0.365101	2.124966	
O	2.251558	0.665365	1.221423	
H	2.264036	1.638507	1.297612	

Energy (Hartree): -454.017368  
Energy+ZPE (Hartree): -453.960684  
Enthalpy (Hartree): -453.951821  
Free Energy (Hartree): -453.994444  
Frequencies (cm-1): -200.5149 56.1938 94.2686 109.0348 165.4327  
270.5135 313.1211 365.8184 482.2592 552.6903 569.4685 665.8397  
835.1705 847.2665 958.5526 1009.0051 1245.982 1408.1666 1440.8294 1509.7196  
1747.6753 3185.3391 3305.4625 3743.6716  
Product of Adiabatic Moments of Inertia (amu A\*\*2): 276.330  
Moment of inertia: Active External Rotor (amu A\*\*2): 152.206

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TS-A2'-B1  
Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.445604	
O	1.277818	0.000000	1.926161	
O	1.280433	0.043903	3.361260	
O	-0.968738	0.037871	2.191756	
O	0.276467	2.188837	-0.316361	
O	1.179604	2.692500	0.339750	
H	0.908944	-0.221559	-0.544473	
H	-0.956835	-0.058064	-0.502221	
H	0.304117	0.072438	3.536070	

Energy (Hartree): -454.025673  
Energy+ZPE (Hartree): -453.968376  
Enthalpy (Hartree): -453.959754  
Free Energy (Hartree): -454.002441

Frequencies (cm-1): -240.5152 42.71 61.6792 102.4763 217.6015 300.369  
333.2452 427.3626 487.2219 617.5607 688.6438 709.1657 828.129 883.6783  
1014.2165 1030.1259 1255.6734 1449.5068 1500.9684 1517.9104 1744.7595  
3177.0148 3292.9908 3467.6773

Product of Adiabatic Moments of Inertia (amu A\*\*2): 315.266  
Moment of inertia: Active External Rotor (amu A\*\*2): 127.139

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B1

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.529900	
H	1.003573	0.000000	-0.425372	
H	-0.590288	-0.849159	-0.341509	
O	-0.729628	1.156825	-0.524162	
O	-0.200607	2.318660	-0.184580	
O	-0.786783	-0.621288	2.192876	
O	0.920923	0.778662	2.169711	
O	1.914831	1.348587	1.280335	
H	1.386337	2.073268	0.873201	

Energy (Hartree): -454.054389  
Energy+ZPE (Hartree): -453.992473  
Enthalpy (Hartree): -453.984597  
Free Energy (Hartree): -454.02445

Frequencies (cm-1): 85.7563 151.3802 181.8697 250.6923 315.3326  
470.6418 502.9802 539.873 563.5123 718.3903 848.6056 887.6519 975.3958  
997.7553 1158.6499 1215.1838 1288.4527 1362.1436 1466.031 1476.344 1849.4524  
3102.4384 3175.4788 3594.0129

Product of Adiabatic Moments of Inertia (amu A\*\*2): 166.251  
Moment of inertia: Active External Rotor (amu A\*\*2): 285.991

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TS-B1-B2

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
O	0.000000	0.000000	1.438373	
O	1.285917	0.000000	1.947971	
C	-0.015824	-1.452870	-0.478270	
O	1.045706	-2.248762	-0.053563	
O	2.165624	-1.541547	0.365405	
O	-0.893794	-1.969926	-1.105852	
H	0.854216	0.566827	-0.380559	
H	-0.943807	0.458458	-0.297249	
H	1.811018	-0.721222	1.251988	

Energy (Hartree): -454.026376  
Energy+ZPE (Hartree): -453.970053  
Enthalpy (Hartree): -453.962886  
Free Energy (Hartree): -454.001231  
Frequencies (cm-1): -1763.0109 87.748 203.8615 269.1262 321.9887  
418.8419 509.6673 575.8499 660.9574 714.3952 796.154 925.1942 969.4396  
1037.3927 1078.9012 1102.4102 1140.2301 1278.219 1341.9533 1456.7146 1742.7767  
1870.3956 3069.7617 3151.1492  
Product of Adiabatic Moments of Inertia (amu A\*\*2): 244.290  
Moment of inertia: Active External Rotor (amu A\*\*2): 118.246



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B2

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.525200	
H	1.023583	0.000000	-0.385302	
H	-0.494794	-0.933376	-0.287738	
O	-0.728199	1.085916	-0.548334	
O	0.183722	1.962173	-1.248985	
O	-0.341893	-0.895714	2.233822	
O	0.455886	1.180291	2.216271	
O	0.999110	2.112565	1.445868	
H	0.488830	2.521251	-0.506677	

Energy (Hartree): -454.042214  
Energy+ZPE (Hartree): -453.981451  
Enthalpy (Hartree): -453.973143  
Free Energy (Hartree): -454.014227

Frequencies (cm-1): 61.6818 127.1059 139.8698 222.1278 293.5994  
414.1725 430.9151 487.5017 559.4689 650.4167 741.5427 898.2661  
1018.1532 1056.1329 1103.8754 1193.7781 1273.4744 1358.373 1419.8828  
1454.0813 1894.857 3054.922 3111.2739 3706.536

Product of Adiabatic Moments of Inertia (amu A\*\*2): 275.348  
Moment of inertia: Active External Rotor (amu A\*\*2): 116.243

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TS-B2-B3

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.525188	
H	1.300000	0.000000	0.000000	
H	-0.494797	-0.933366	-0.287732	
O	-0.728207	1.085937	-0.548332	
O	0.183713	1.962181	-1.248982	
O	-0.956606	-0.064292	2.233834	
O	1.389761	0.087875	1.898317	
O	2.156612	-0.040819	0.824443	
H	0.488833	2.521238	-0.506696	

Energy (Hartree): -454.011121

Energy+ZPE (Hartree): -453.955507

Enthalpy (Hartree): -453.947692

Free Energy (Hartree): -453.987537

Frequencies (cm-1): -1463.5604 72.4617 152.8042 193.6296 282.6553 306.6242  
451.0504 503.1015 554.5551 658.498 699.8822 856.0881 892.051 956.2307 1001.596  
1131.616 1179.4385 1246.1865 1378.6508 1420.4077 1773.4165 1889.4911 3107.2446  
3704.0064

Product of Adiabatic Moments of Inertia (amu A\*\*2): 277.706

Moment of inertia: Active External Rotor (amu A\*\*2): 132.224

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B3

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.443900	
H	0.955928	0.000000	-0.507091	
O	-1.099980	-0.133118	-0.759105	
O	-0.687487	-0.802928	-2.008844	
O	1.038359	-0.064178	2.076161	
O	-1.173020	0.042348	2.176983	
O	-2.285922	0.547716	1.395584	
H	-2.779977	-0.277035	1.230369	
H	-1.225467	-0.281721	-2.634853	

Energy (Hartree): -454.044445  
Energy+ZPE (Hartree): -453.985110  
Enthalpy (Hartree): -453.976075  
Free Energy (Hartree): -454.018596  
Frequencies (cm-1): 64.7067 114.5201 157.7793 197.7637 215.3356  
273.8965 312.4471 400.0261 519.9338 586.2357 637.5033 702.7075  
843.3149 890.1956 970.5308 1178.2132 1291.4088 1392.6258 1405.7833 1427.1834  
1711.7126 3231.9459 3758.0721 3761.0498  
Product of Adiabatic Moments of Inertia (amu A\*\*2): 312.548  
Moment of inertia: Active External Rotor (amu A\*\*2): 119.459

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TS-B3-B4

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
O	0.000000	0.000000	1.308100	
O	1.494473	0.000000	1.791147	
C	-0.767512	0.943145	-0.816547	
O	-1.754425	1.726820	-0.257378	
O	-2.290960	1.151716	0.960176	
O	-0.534688	1.089728	-1.997216	
H	0.717226	-0.624955	-0.524260	
H	-1.785287	1.639500	1.637339	
H	1.378251	-0.623211	2.534405	

Energy (Hartree): -454.043517

Energy+ZPE (Hartree): -453.985745

Enthalpy (Hartree): -453.977135

Free Energy (Hartree): -454.018487

Frequencies (cm-1): -426.2363 108.5393 127.2336 155.8191 222.9685 256.4413  
292.238 343.4174 439.2902 512.909 652.1251 667.0339 778.5326 857.512 972.6553  
1189.6641 1271.5088 1285.458 1377.1814 1407.6326 1750.9344 3178.4972 3753.5443  
3757.9283

Product of Adiabatic Moments of Inertia (amu A\*\*2): 308.296

Moment of inertia: Active External Rotor (amu A\*\*2): 124.156

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B4

Optimized Geometry DFT(B3LYP)/6-311G(2df,p)

Atom	x	y	z	(Angstrom)
C	0.000000	0.000000	0.000000	
C	0.000000	0.000000	1.532800	
H	1.017717	0.000000	-0.430181	
O	-1.002408	-0.140358	-0.663553	
O	0.907869	-0.523778	2.126509	
O	-1.100569	0.430677	2.200280	
O	-1.905898	1.343353	1.404563	
H	-2.313599	0.728029	0.759775	

Energy (Hartree): -378.317949

Energy+ZPE (Hartree): -378.271980

Enthalpy (Hartree): -378.264952

Free Energy (Hartree): -378.301781

Frequencies (cm-1): 117.1784 162.1257 249.252 325.2812 381.0034

460.3368 571.4595 703.392 825.0892 970.4071 1005.4663 1276.7915

1379.6629 1448.0412 1804.2056 1828.4554 2970.0286 3699.8738

Product of Adiabatic Moments of Inertia (amu A\*\*2): 114.320

Moment of inertia: Active External Rotor (amu A\*\*2): 219.659

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