Supporting Information for:
Methanetriol — Formation of an Impossible Molecule

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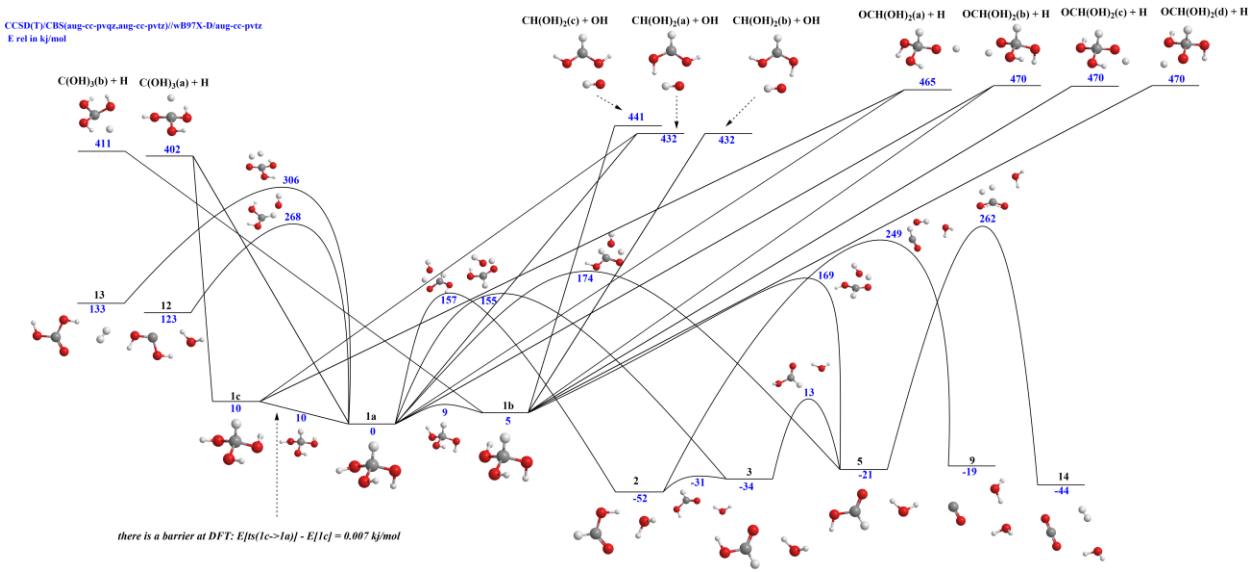


Figure S1. Potential energy surface exploring the conformational structure of methanetriol (**1**, $CH(OH)_3$) and its decomposition pathways.

Table S1. Calculated structures for all minimum energy conformers of neutral and radical cationic methanetriol (**1**, $CH(OH)_3$), hydroxyperoxymethane (**2**, CH_3OOOH), and hydroperoxymethanol (**3**, $CH_2(OH)OOH$) in Cartesian coordinates (Å) with energetics, vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}).

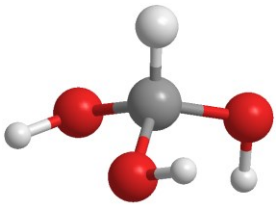
ωB97X-D/aug-cc-pVTZ optimization and CCSD(T)/aug-cc-pV(Q+T)Z single-point energy refinement

$CH(OH)_3$ (1)

Neutral and cation $CH(OH)_3$ molecule correspondence table

Neutral	Cation
1a	**$1a^{\bullet+}$/$1b^{\bullet+}$**
1b	**$1b^{\bullet+}$**
1c	**$1a^{\bullet+}$**

1a



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.8586495 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.9298637 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.9792699 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.87696 kcal/mol

Cartesian coordinates

C	0.024344	0.001271	0.354546
O	-0.603189	1.154193	-0.087821
O	-0.700927	-1.072658	-0.181367
O	1.341142	0.013376	-0.046569
H	0.049558	-0.058402	1.448231
H	-1.534411	0.953540	-0.196837
H	-0.304326	-1.886879	0.132222
H	1.346906	0.224834	-0.984834

Vibrational frequencies

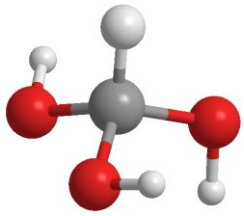
186.0174	287.6654	330.5702
511.3889	549.9037	662.3049
1007.3642	1065.7814	1115.2251
1243.2970	1299.7410	1360.6770
1418.2897	1470.5149	3042.2809
3848.8726	3894.5161	3900.4214

IR intensities

130.8766	71.3553	95.1454

20.3820	43.2075	34.4329
34.9044	220.5300	260.7211
46.8775	89.5503	50.3774
65.8920	129.2279	61.9726
42.7931	51.5138	58.1660

1b



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.8572505 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.9284232 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.9778007 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 39.11257 kcal/mol

Cartesian coordinates

C	0.000002	-0.018126	0.344556
O	-1.091686	-0.705923	-0.160060
O	1.091808	-0.705707	-0.160099
O	-0.000133	1.324374	-0.032677
H	0.000020	-0.001339	1.440384
H	-1.884263	-0.268871	0.154813
H	1.884326	-0.268748	0.155034
H	-0.000004	1.345765	-0.994886

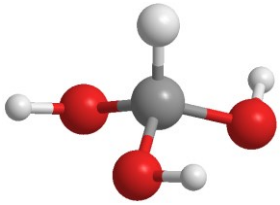
Vibrational frequencies

190.8675	366.3088	403.4998
516.8111	569.9034	657.0318
1009.3756	1071.2058	1095.8079
1253.0150	1300.5950	1346.2232
1446.8442	1447.6118	3038.0051
3838.4985	3903.9836	3904.0497

IR intensities

26.9282	212.6640	35.0128
20.6374	74.9541	36.2781
38.0791	202.3036	366.2631
0.0738	1.7206	122.7186
141.8562	23.1489	62.8689
38.3679	30.0229	85.8718

1c



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.8536347 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.9248772 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.9743031 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.18702 kcal/mol

Cartesian coordinates

C	0.002004	-0.000548	0.328767
O	-0.377880	1.245246	-0.145563
O	-0.890038	-0.946889	-0.150117
O	1.267336	-0.295123	-0.153311
H	0.005102	-0.003317	1.430540
H	-1.309367	1.373051	0.043768
H	-0.560252	-1.819331	0.073549
H	1.857144	0.427011	0.071464

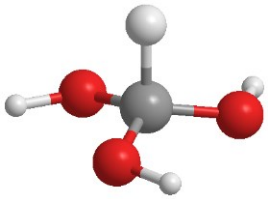
Vibrational frequencies

101.3872	136.4022	190.8415
501.4294	502.0359	697.5278
1055.2320	1070.5812	1072.3148
1258.5764	1297.8106	1301.2277
1447.0592	1450.5856	2956.3450
3889.7131	3891.0786	3892.0579

IR intensities

82.5869	79.4460	219.8974
5.0781	5.2900	4.3536
19.3576	205.2706	206.3839
79.6693	93.6281	94.4956
95.9581	94.8663	105.6092
38.3309	61.2929	61.6375

1a$^{\bullet+}$



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.4577676 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.5277866 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.5763637 Hartree

Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 35.48788 kcal/mol

Cartesian coordinates

C	-0.000039	-0.000024	0.166080
O	-0.775523	-1.052745	-0.085482
O	1.299514	-0.145229	-0.085530
O	-0.524002	1.197991	-0.085396
H	0.000458	0.000107	1.400286
H	-0.275493	-1.883823	-0.114833
H	1.769094	0.703431	-0.115224
H	-1.493734	1.180283	-0.115451

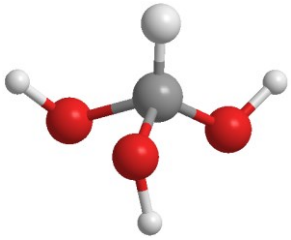
Vibrational frequencies

345.9340	421.9106	426.4778
525.0813	528.5023	737.1865
738.2031	738.8241	903.5575
1145.8479	1149.0589	1197.6617
1483.4682	1485.2112	1752.0843
3742.3304	3743.2146	3759.5794

IR intensities

392.2822	26.4466	26.4376
5.8644	5.8807	23.5185
106.7350	106.8235	1.0021
247.2820	247.1521	16.2793
187.9914	187.4067	75.9047
483.3157	482.7526	9.6196

1b$^{\bullet+}$



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.4575415 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.5263634 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.57411 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.11163 kcal/mol

Cartesian coordinates

C	-0.145797	-0.036157	0.396583
O	-1.300492	-0.084145	-0.239962
O	0.784077	-0.931701	-0.225334
O	0.652124	1.069492	0.011083
H	-0.153558	-0.109256	1.481805

H	-2.054600	-0.245133	0.336636
H	1.534365	-1.146682	0.360601
H	0.462901	1.288846	-0.924834

Vibrational frequencies

199.8368	445.9188	479.7661
512.8748	626.7224	647.9027
705.1196	997.1912	1115.0916
1168.5388	1272.5556	1305.9261
1365.4350	1490.3258	3161.2076
3628.7692	3687.6330	3848.6551

IR intensities

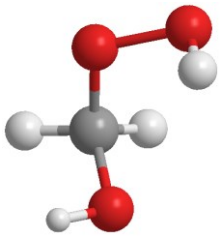
122.5978	21.4910	69.0798
10.9943	44.3453	123.6521
10.2626	128.5760	203.6289
71.2128	28.1257	37.9694
143.4335	73.0744	0.2339
408.1228	234.1454	242.2292

$CH_2(OH)OOH$ (2)

Neutral and cation $CH_2(OH)OOH$ molecule correspondence table

Neutral	Cation
2a	**2a**$^{\bullet+}$
2b	**2b**$^{\bullet+}$
2c	**2b**$^{\bullet+}$
2d	**2b**$^{\bullet+}$
2e	**2c**$^{\bullet+}$
2f	**2c**$^{\bullet+}$

2a



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.7493029 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.8190162 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.8673812 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.63843 kcal/mol

Cartesian coordinates

C	-0.024867	-0.002403	0.355575

O	0.683526	1.084793	-0.178345
O	-1.341010	-0.035108	-0.047842
O	0.624514	-1.144568	-0.085342
H	-0.050702	0.054945	1.448628
H	0.265051	1.894778	0.118164
H	-1.349038	-0.252186	-0.984956
H	1.547644	-0.924062	-0.223051

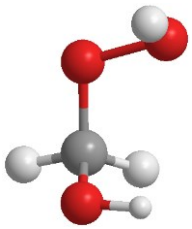
Vibrational frequencies

177.4630	281.9756	334.9831
510.5253	547.7915	661.5397
1005.0589	1065.0734	1112.4481
1241.3322	1299.6508	1355.3727
1415.5131	1468.0871	3049.8476
3847.1595	3892.6496	3896.2906

IR intensities

141.8181	66.2521	90.8498
20.9583	42.8167	32.7156
35.4030	221.7146	258.1905
47.4645	85.1011	55.2376
67.0553	129.3402	60.9121
43.4002	44.8023	66.9310

2b



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.7489051 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.8186433 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.8670256 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.54608 kcal/mol

Cartesian coordinates

C	-0.024847	0.002402	0.355569
O	0.683413	-1.084877	-0.178359
O	0.624599	1.144504	-0.085400
O	-1.340996	0.035242	-0.047813
H	-0.050649	-0.054931	1.448626
H	0.264820	-1.894806	0.118144
H	1.547809	0.924074	-0.222681
H	-1.349018	0.252297	-0.984933

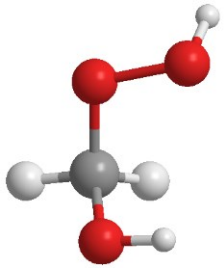
Vibrational frequencies

177.4525	281.9396	335.0022
510.5251	547.7916	661.5457
1005.0770	1065.0616	1112.4480
1241.3320	1299.6082	1355.4060
1415.4975	1468.0871	3049.8288
3847.1463	3892.6308	3896.2681

IR intensities

141.7229	66.3370	90.8971
20.9458	42.8180	32.7202
35.3969	221.6692	258.1921
47.4783	85.1895	55.1864
67.0204	129.3521	60.9190
43.4015	44.7944	66.9214

2c



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.7479032 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.817676 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.8660822 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.5062 kcal/mol

Cartesian coordinates

C	0.024840	0.002383	0.355562
O	-0.624203	1.144705	-0.085425
O	-0.683755	-1.084666	-0.178396
O	1.341002	0.034821	-0.047795
H	0.050608	-0.054989	1.448619
H	-1.547553	0.924680	-0.222413
H	-0.265550	-1.894732	0.118276
H	1.349100	0.251852	-0.984922

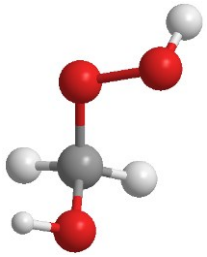
Vibrational frequencies

177.5687	282.0346	335.0044
510.5203	547.8045	661.5498
1005.0801	1065.0456	1112.4631
1241.3231	1299.5846	1355.4261
1415.5061	1468.0826	3049.8115
3847.1362	3892.6201	3896.2701

IR intensities

141.6017	66.4200	90.9457
20.9409	42.8185	32.7317
35.3909	221.6371	258.2242
47.4741	85.2554	55.1461
66.9890	129.3588	60.9236
43.4022	44.8980	66.8018

2d



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.7467519 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.8164751 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.8648469 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.37899 kcal/mol

Cartesian coordinates

C	-0.614395	0.521940	-0.291307
O	0.600639	0.531228	0.407509
O	1.409624	-0.535553	-0.090928
O	-1.428755	-0.559099	0.009419
H	-0.439539	0.488491	-1.366572
H	-1.059578	1.478620	0.002210
H	2.156193	-0.041772	-0.444313
H	-1.622774	-0.549582	0.948520

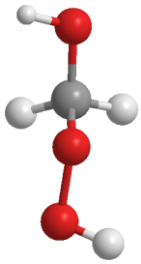
Vibrational frequencies

170.6401	222.3170	342.1523
414.9567	616.2100	924.8382
1044.6620	1084.6172	1130.7174
1292.6200	1382.5910	1408.5167
1442.9984	1496.3590	3035.0930
3116.3448	3837.7690	3883.0620

IR intensities

7.6171	118.2870	99.6186
18.5004	44.0817	38.4153
27.8488	66.8311	146.2756
21.4352	10.9700	41.2864
57.5544	4.4041	44.0203
23.6460	43.0304	42.6250

2e



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.7434442 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.8131931 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.8615827 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.33593 kcal/mol

Cartesian coordinates

C	-0.024871	0.002399	0.355572
O	-1.341017	0.034987	-0.047840
O	0.683625	-1.084726	-0.178357
O	0.624407	1.144625	-0.085341
H	-0.050695	-0.054955	1.448626
H	-1.349066	0.252028	-0.984963
H	0.265301	-1.894758	0.118237
H	1.547561	0.924206	-0.223027

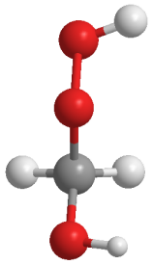
Vibrational frequencies

177.4738	282.0315	334.9753
510.5257	547.7951	661.5393
1005.0560	1065.0710	1112.4554
1241.3280	1299.6550	1355.3720
1415.5171	1468.0839	3049.8443
3847.1576	3892.6374	3896.2862

IR intensities

141.7733	66.2892	90.8545
20.9584	42.8170	32.7188
35.3990	221.7102	258.2077
47.4609	85.1101	55.2289
67.0523	129.3397	60.9122
43.3999	44.8589	66.8719

2f



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.74258 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.8123327 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.860725 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.37528 kcal/mol

Cartesian coordinates

C	0.024868	-0.002393	0.355568
O	1.341018	-0.034878	-0.047829
O	-0.683713	1.084671	-0.178372
O	-0.624299	-1.144676	-0.085360
H	0.050673	0.054969	1.448622
H	1.349092	-0.251892	-0.984958
H	-0.265508	1.894741	0.118290
H	-1.547511	-0.924394	-0.222873

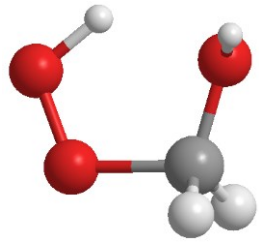
Vibrational frequencies

177.5303	282.0710	334.9740
510.5259	547.7988	661.5411
1005.0590	1065.0643	1112.4616
1241.3245	1299.6416	1355.3844
1415.5171	1468.0815	3049.8353
3847.1541	3892.6296	3896.2813

IR intensities

141.7121	66.3355	90.8789
20.9547	42.8173	32.7238
35.3944	221.6910	258.2234
47.4603	85.1477	55.2056
67.0375	129.3431	60.9148
43.4003	44.8865	66.8352

2a$^{\bullet+}$



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.3895904 Hartree

Total electronic energy CCSD(T)/aug-cc-pVQZ -265.4577077 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.5049655 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.49164 kcal/mol

Cartesian coordinates

C	0.758677	0.645435	0.057750
O	-0.799937	0.642365	-0.090565
O	1.164394	-0.633613	0.069110
H	0.866505	1.129819	1.027650
H	1.062908	1.261767	-0.785993
H	1.580646	-0.906420	-0.758206
O	-1.307011	-0.534165	0.026191
H	-0.521688	-1.154476	0.132156

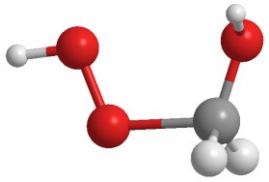
Vibrational frequencies

194.8607	322.4063	495.6151
596.8166	690.6485	849.4633
1029.3211	1183.4240	1222.5780
1298.7937	1369.0099	1398.2036
1496.0443	1528.4891	3090.4892
3171.2874	3186.4387	3801.4029

IR intensities

15.1510	19.9309	4.5693
177.5610	11.3276	119.6902
27.8561	12.9046	125.5598
14.4639	18.5246	10.4272
43.3555	113.1844	19.2297
214.2799	10.6451	205.2081

2b$^{\bullet+}$



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.3885305 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.4565571 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.503752 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.0473 kcal/mol

Cartesian coordinates

C	0.894531	0.595944	-0.009060
O	-0.830442	0.644516	-0.022430
O	-1.297753	-0.560987	0.008422
O	1.304395	-0.627290	0.115214

H	1.003765	1.189061	0.894319
H	1.032678	1.115781	-0.955316
H	-2.272564	-0.453559	0.030328
H	1.459338	-1.076862	-0.724613

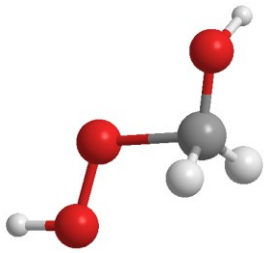
Vibrational frequencies

65.6836	212.0004	311.1524
512.0955	568.8735	638.2888
1013.3572	1170.5767	1275.2200
1331.9551	1356.7715	1408.3988
1470.1310	1553.7505	3104.0442
3213.6294	3604.0950	3804.4592

IR intensities

6.6455	38.4635	94.9997
132.2764	17.4936	174.6652
25.7509	61.7787	43.9008
110.2234	69.7310	7.7483
71.2644	35.1106	14.3954
5.7696	307.0418	183.4860

2c$^{\bullet+}$



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.3876796 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.4556433 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.5027945 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 37.96285 kcal/mol

Cartesian coordinates

C	0.728254	0.541429	0.046702
O	1.749407	-0.230159	-0.146158
H	0.564690	0.980236	1.029171
H	0.468023	1.145287	-0.817348
H	2.134811	-0.582577	0.665539
O	-0.650574	-0.512064	0.024151
O	-1.732440	0.199389	-0.017042
H	-2.468194	-0.448844	-0.045185

Vibrational frequencies

54.7817	227.0295	258.1018
495.4250	541.5322	639.1823
1014.5519	1171.0842	1306.3699
1315.9980	1354.9243	1414.2081
1474.1403	1556.8403	3104.8785
3220.1775	3602.2198	3803.9516

IR intensities

2.8243	107.3473	10.9535
140.3470	29.5594	190.9987
25.4311	73.8289	1.3010
199.9704	113.9330	11.5331
69.4088	34.6234	13.6759
3.5714	305.3832	208.8586

CH_3OOOH (3)

Neutral and cation CH_3OOOH molecule correspondence table

Neutral	Cation
3a	**3a$^{\bullet+}$**
3b	**3a$^{\bullet+}$**

3a

Total electronic energy CCSD(T)/aug-cc-pVTZ -265.6604795 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.7289101 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.7763852 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 37.25871 kcal/mol

Cartesian coordinates

O	0.542597	-0.562389	-0.391601
O	-0.611215	-0.524634	0.406962
O	-1.424234	0.526567	-0.059066
C	1.454770	0.407749	0.094562
H	-1.878266	0.115857	-0.804770
H	1.040567	1.411670	-0.002981
H	2.332083	0.308124	-0.541925
H	1.719804	0.201501	1.131952

Vibrational frequencies

156.2417	208.6106	386.4227
455.2105	586.5762	857.9897
962.8816	1053.7134	1182.3437
1222.6104	1421.7766	1456.1667
1478.4298	1512.4577	3045.8388
3127.7815	3152.7816	3795.0088

IR intensities

9.1989	3.9984	106.8079
7.1269	8.6897	52.8949
26.0530	25.0169	1.5453
4.9514	41.5274	0.1205
10.6360	10.6549	31.8227
22.0212	9.8662	37.5076

3b

Total electronic energy CCSD(T)/aug-cc-pVTZ -265.65662 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.7250836 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.7725816 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 37.21365 kcal/mol

Cartesian coordinates

O	0.564318	-0.588985	-0.35770
O	-0.619500	-0.536139	0.39183
C	1.436157	0.428689	0.09284
H	1.047938	1.420941	-0.15045
H	2.362719	0.268391	-0.45486
H	1.619104	0.338264	1.16461
O	-1.482287	0.401480	-0.21430
H	-1.346951	1.189419	0.32503

Vibrational frequencies

135.6033	234.3172	371.2695
466.0617	568.2317	862.7535
962.8616	1061.5568	1177.8101
1223.3060	1404.7974	1459.7141
1489.8534	1507.0000	3036.0909
3111.3730	3156.7738	3801.9511

IR intensities

4.5029	2.5102	64.7205
30.9652	1.9107	64.8933
23.0849	21.1276	0.8791
3.4342	39.2754	2.0636
11.1804	9.8396	33.5057
30.0050	8.4836	23.9588

3a$^{\bullet+}$

Total electronic energy CCSD(T)/aug-cc-pVTZ -265.2968275 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.3641558 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.4108662 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 37.14846 kcal/mol

Cartesian coordinates

O	0.572136	-0.732111	0.000000
O	-0.735357	-0.642129	0.000000
O	-1.156217	0.649818	0.000000
C	1.347633	0.503291	0.000000
H	-2.127977	0.533258	0.000001
H	1.118260	1.064160	-0.905045
H	2.361161	0.114040	0.000000
H	1.118260	1.064161	0.905044

Vibrational frequencies

210.6266	241.2203	352.5814
358.5699	631.1912	838.0121
1022.1494	1089.2702	1115.8241
1191.8778	1439.5383	1453.2823
1457.1859	1502.1904	3058.8692
3168.2160	3205.5248	3649.5847

IR intensities

8.7814	28.1344	7.9138
120.3713	11.3330	19.9597
140.4205	13.6991	0.3502
4.9167	3.6411	27.4267
8.9026	77.9705	22.5575
6.8551	10.3387	413.7004

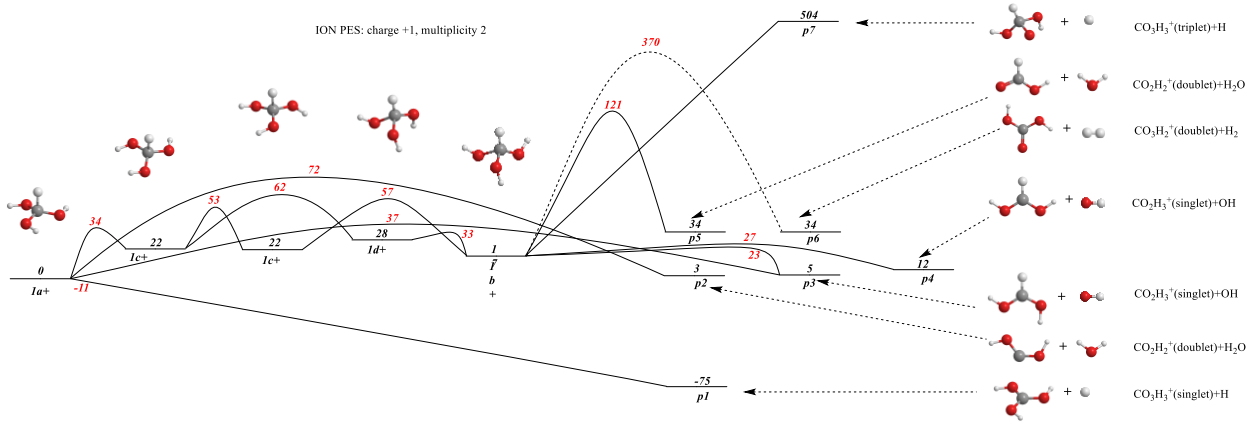
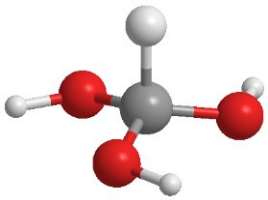


Figure S2. Full potential energy diagram calculated for **1**$^{\bullet+}$. Figure 2 is derived from this data by exclusion of reaction pathways not accessible with relevant photon energies. Relative energies are shown in kJ mol^{-1}.

Table S2. Calculated structures for all structures used in Figure 4 in Cartesian coordinates (Å) with energetics, vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}).

ωB97X-D/aug-cc-pVTZ optimization and CCSD(T)/aug-cc-pV(Q+T)Z single-point energy refinement

$1a^{\bullet+}$



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.4577676 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.5277866 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.5763637 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 35.48788 kcal/mol

Cartesian coordinates

C	-0.000039	-0.000024	0.166080
O	-0.775523	-1.052745	-0.085482
O	1.299514	-0.145229	-0.085530
O	-0.524002	1.197991	-0.085396
H	0.000458	0.000107	1.400286
H	-0.275493	-1.883823	-0.114833
H	1.769094	0.703431	-0.115224
H	-1.493734	1.180283	-0.115451

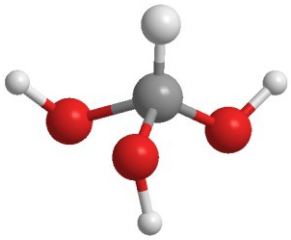
Vibrational frequencies

345.9340	421.9106	426.4778
525.0813	528.5023	737.1865
738.2031	738.8241	903.5575
1145.8479	1149.0589	1197.6617
1483.4682	1485.2112	1752.0843
3742.3304	3743.2146	3759.5794

IR intensities

392.2822	26.4466	26.4376
5.8644	5.8807	23.5185
106.7350	106.8235	1.0021
247.2820	247.1521	16.2793
187.9914	187.4067	75.9047
483.3157	482.7526	9.6196

$1b^{\bullet+}$



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.4575415 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.5263634 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.57411 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.11163 kcal/mol

Cartesian coordinates

C	-0.145797	-0.036157	0.396583
O	-1.300492	-0.084145	-0.239962
O	0.784077	-0.931701	-0.225334
O	0.652124	1.069492	0.011083
H	-0.153558	-0.109256	1.481805
H	-2.054600	-0.245133	0.336636
H	1.534365	-1.146682	0.360601
H	0.462901	1.288846	-0.924834

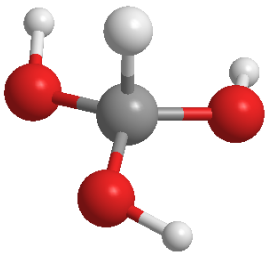
Vibrational frequencies

199.8368	445.9188	479.7661
512.8748	626.7224	647.9027
705.1196	997.1912	1115.0916
1168.5388	1272.5556	1305.9261
1365.4350	1490.3258	3161.2076
3628.7692	3687.6330	3848.6551

IR intensities

122.5978	21.4910	69.0798
10.9943	44.3453	123.6521
10.2626	128.5760	203.6289
71.2128	28.1257	37.9694
143.4335	73.0744	0.2339
408.1228	234.1454	242.2292

1c$^{\bullet+}$



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.44932 Hartree

Total electronic energy CCSD(T)/aug-cc-pVQZ -265.51922 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.56772 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 35.41862 kcal/mol

Cartesian coordinates

C	-0.004731	-0.016315	0.171144
O	1.081483	-0.748119	-0.070538
O	0.134074	1.295539	-0.067610
O	-1.118079	-0.689253	-0.136302
H	0.007781	-0.078626	1.389334
H	1.872112	-0.196820	-0.192066
H	-0.695013	1.777573	-0.191737
H	-1.936310	-0.269571	0.163203

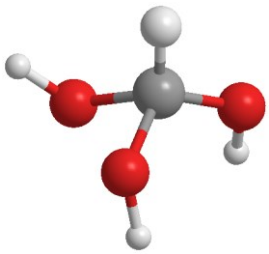
Vibrational frequencies

135.2510	380.8314	473.3246
510.6292	535.9086	713.0169
763.9920	787.4153	919.2250
1140.8158	1150.7044	1172.8693
1409.4217	1489.0558	1876.8027
3734.1315	3782.4690	3799.8204

IR intensities

94.3361	85.9866	198.9271
34.1301	56.9059	24.5872
68.6651	107.7934	5.2636
344.2338	197.9218	29.4608
267.8757	46.5810	94.3431
443.1370	128.8627	373.8154

1d$^{\bullet+}$



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.45323 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.52198 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.56967 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 38.03991 kcal/mol

Cartesian coordinates

C	-0.144833	-0.018148	0.411906
O	-1.373454	0.033147	-0.049018
O	0.655253	-0.998060	-0.220422

O	0.773358	1.016040	-0.027233
H	-0.113981	-0.026514	1.497505
H	-1.465617	-0.221818	-0.976909
H	1.387847	-1.303900	0.345505
H	0.619499	1.252105	-0.964164

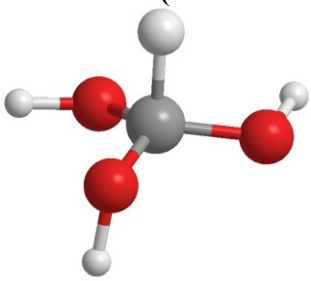
Vibrational frequencies

342.9979	425.9950	453.2616
509.3668	588.4033	620.7370
661.6816	989.3739	1119.2969
1145.1018	1216.5496	1326.1743
1414.1013	1474.3003	3186.7172
3649.4910	3696.8060	3788.9520

IR intensities

45.7183	2.5864	25.9418
91.3351	63.2175	101.2374
43.3031	38.2516	102.3290
123.2169	291.1878	24.0751
12.9360	106.9598	1.9012
390.8822	239.7628	159.0452

$1a^{\bullet+} \rightarrow 1c^{\bullet+}$ (Transition State)



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.44508 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.51491 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.56335 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 35.43709 kcal/mol

Cartesian coordinates

C	0.007410	0.016829	0.182917
O	-1.155675	0.637779	-0.112356
O	0.024785	-1.296868	-0.110333
O	1.097488	0.751674	0.030464
H	-0.165203	-0.003215	1.378292
H	-1.918862	0.032483	-0.079544
H	0.904866	-1.681955	0.028015
H	1.401950	0.811037	-0.886469

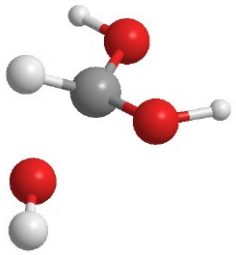
Vibrational frequencies

-439.5370	440.6736	473.8734
514.1912	583.7065	653.3533
679.9557	877.9783	1033.9202
1115.5813	1150.3563	1219.3967
1352.7232	1464.4732	2023.9272
3691.0404	3743.8956	3769.5567

IR intensities

97.9312	130.0901	11.3889
118.9647	48.7237	131.3254
123.9997	24.2986	34.4144
249.6608	129.9688	147.3143
107.1448	186.1145	177.3409
413.4642	298.3289	234.9150

$1a^{\bullet+}$ → $CO_2H_3^+$(*cis-trans*) + $^{\bullet}OH$ (Transition State)



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.44688 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.51577 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.56356 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 36.34225 kcal/mol

Cartesian coordinates

C	-0.143642	0.003398	0.288331
O	-0.826509	-1.010520	-0.143839
O	1.461990	-0.170387	-0.148823
O	-0.577344	1.184703	-0.013409
H	-0.520075	-1.870029	0.175496
H	1.900762	0.705922	-0.108119
H	-1.297986	1.164994	-0.662757
H	0.314053	-0.051642	1.313956

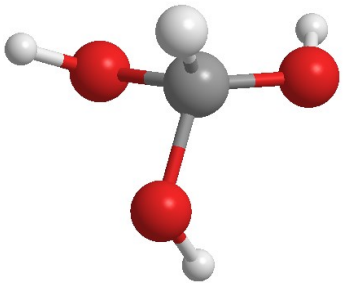
Vibrational frequencies

-508.2198	302.0904	421.0514
449.6723	488.7117	602.0283
629.7966	922.4784	1083.6771
1171.2185	1180.5179	1259.8121
1404.9365	1567.6707	2762.7082
3638.5612	3745.3026	3791.5402

IR intensities

4.1465	26.5325	131.9063
91.8678	121.2745	106.8831
31.2191	175.1136	104.2208
92.3874	76.7538	101.2828
209.8345	219.9366	156.9900
280.9131	288.6893	243.4755

$1b^{\bullet+} \rightarrow 1d^{\bullet+}$ (Transition State)



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.45088 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.51961 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.56729 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 37.59518 kcal/mol

Cartesian coordinates

C	0.121528	0.019711	0.422077
O	1.340801	-0.065761	-0.092450
O	-0.677114	0.989103	-0.223449
O	-0.729459	-1.034946	-0.044607
H	0.055908	0.038693	1.509319
H	1.647225	0.743055	-0.519861
H	-1.437186	1.260235	0.324283
H	-0.468931	-1.267419	-0.962149

Vibrational frequencies

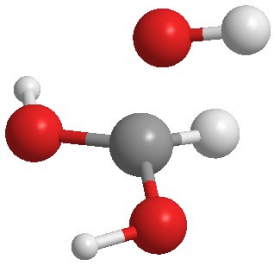
-376.2622	437.2463	472.2006
504.1141	627.8968	642.1009
696.0173	1017.2008	1135.4152
1158.3217	1207.1024	1317.4331
1351.2903	1464.9088	3149.2129
3606.4902	3689.0984	3822.1619

IR intensities

146.1234	4.8541	14.2944
49.1813	89.4995	76.6017
60.6921	62.5415	35.6161
324.5812	113.0752	30.7795

5.4772	114.3694	2.4898
392.9596	261.4490	208.4816

1b$^{\bullet+}$ → $CO_2H_3^+$(*gauche-trans*) + $^{\bullet}OH$ (Transition State)



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.45433 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.52284 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.57036 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 37.30037 kcal/mol

Cartesian coordinates

C	-0.226767	0.056045	0.416116
O	-1.270221	-0.347477	-0.234632
O	1.102719	-0.815142	-0.200752
O	0.335487	1.174797	-0.020367
H	-0.150030	-0.089660	1.489291
H	-1.790305	-1.017738	0.226082
H	1.894371	-0.706736	0.366446
H	0.062679	1.380437	-0.932511

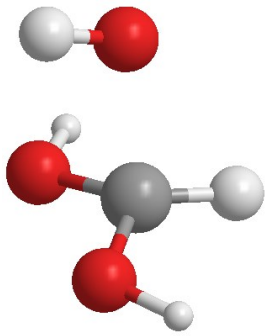
Vibrational frequencies

-393.1862	357.6493	434.3780
462.3520	502.9440	613.2432
666.1711	910.9236	1115.3035
1188.0209	1207.4501	1324.5317
1405.1314	1553.7103	3188.3276
3650.8282	3697.8366	3813.1849

IR intensities

25.7311	39.2152	76.7519
82.8525	91.4014	48.8994
134.2363	130.0077	103.3846
80.6983	53.8979	87.4839
117.6484	186.5084	1.4530
286.0280	243.1041	250.6375

1b$^{\bullet+}$ → $CO_2H_3^+$ (*trans-trans*) + $^{\bullet}OH$ (Transition State)



Total electronic energy CCSD(T)/aug-cc-pVTZ -265.45299 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.52146 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.56896 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 37.32711 kcal/mol

Cartesian coordinates

C	-0.240065	-0.122956	0.392683
O	-1.296480	0.269382	-0.239701
O	0.373946	-1.121862	-0.225694
O	1.099907	0.904931	0.025118
H	-0.189406	-0.055565	1.476730
H	-1.873341	0.834671	0.288894
H	1.025733	-1.569434	0.334478
H	1.058420	1.108461	-0.933987

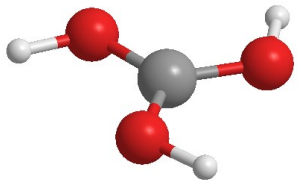
Vibrational frequencies

-387.9181	323.5199	431.5201
512.3354	535.8041	589.8768
632.0720	901.4325	1138.2943
1173.0561	1202.4682	1313.0378
1391.2611	1576.6148	3170.7558
3634.8801	3769.2617	3814.5043

IR intensities

23.1993	3.8470	78.9537
187.6872	11.6277	96.3022
145.5771	36.0245	84.1328
163.2585	74.6272	60.7619
154.2835	145.3976	0.9124
214.8429	321.3006	234.5217

$CO_3H_3^+$



Total electronic energy CCSD(T)/aug-cc-pVTZ -264.98142 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -265.05194 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -265.10086 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 33.02151 kcal/mol

Cartesian coordinates

C	0.000189	0.000057	0.000000
O	-0.709024	-1.059799	0.000000
O	1.272641	-0.084036	0.000000
O	-0.563645	1.143891	0.000000
H	-0.188841	-1.879382	0.000000
H	1.721458	0.776704	0.000000
H	-1.533527	1.101894	0.000000

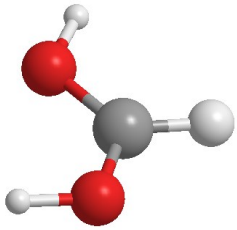
Vibrational frequencies

548.5261	561.3777	563.3336
637.0359	641.4008	793.7696
1076.6379	1197.8460	1201.1629
1214.5150	1713.1466	1714.3346
3739.2240	3741.1719	3755.3970

IR intensities

447.4642	31.9019	31.3549
0.0007	0.5106	28.9729
0.0003	231.2358	216.8927
14.3876	412.6308	412.5796
432.0344	428.0167	4.6780

$CO_2H_3^+$ (*cis-trans*)



Total electronic energy CCSD(T)/aug-cc-pVTZ -189.81157 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -189.86163 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -189.89636 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 29.67746 kcal/mol

Cartesian coordinates

C	-0.003929	0.424292	0.000000
O	-1.041431	-0.302056	0.000000
O	1.141453	-0.094540	0.000000
H	-0.044107	1.512090	0.000000
H	-1.881163	0.184801	0.000000
H	1.148665	-1.069875	0.000000

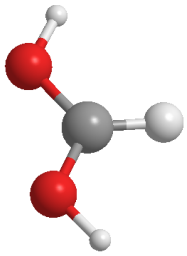
Vibrational frequencies

616.7192	669.3787	788.4130
1090.2243	1182.5585	1205.8680
1371.1239	1486.8109	1729.6667
3191.7771	3681.0684	3746.0739

IR intensities

46.0981	227.4068	91.2219
7.0425	80.7069	139.7489
109.3808	118.8580	330.0518
10.1332	289.7585	301.2327

$CO_2H_3^+$ (*trans-trans*)



Total electronic energy CCSD(T)/aug-cc-pVTZ -189.80892Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -189.85898 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -189.89371 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 29.66159 kcal/mol

Cartesian coordinates

C	-0.000002	0.393674	0.000000
O	-1.070567	-0.273037	0.000000
O	1.070574	-0.273034	0.000000
H	-0.000006	1.484668	0.000000
H	-1.880161	0.260927	0.000000
H	1.880121	0.260934	0.000000

Vibrational frequencies

634.0464	650.0609	734.2336
1084.4265	1165.9819	1208.7187
1372.1567	1478.9024	1749.7648
3155.4039	3750.4645	3764.4252

IR intensities

0.0007	3.7855	222.8641
1.1527	261.1838	58.3199
87.1281	145.0828	272.8373
3.5539	627.5643	48.7257

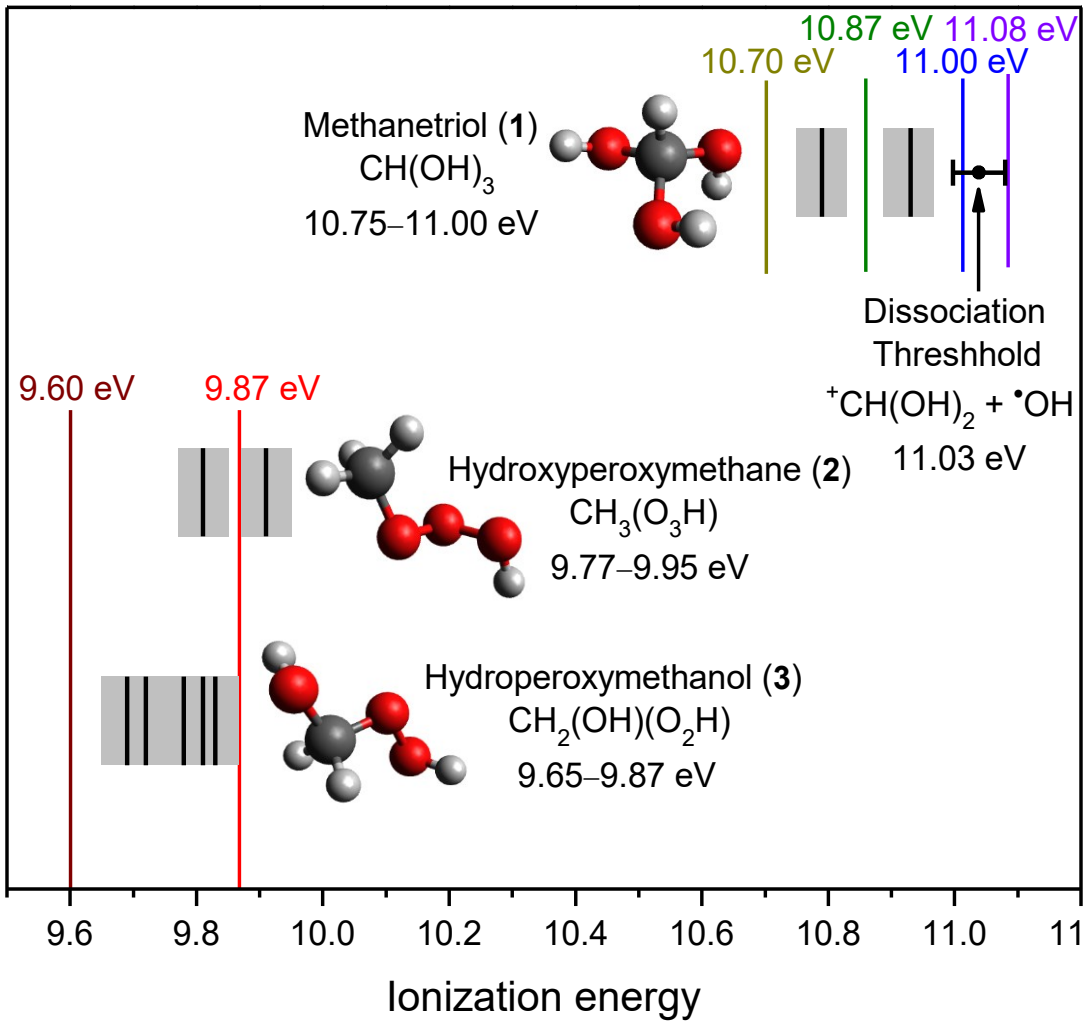


Figure S3. Calculated ionization energies for conformational and structural isomers of CH_4O_3. Black lines represent conformer specific calculated adiabatic ionization energies of each structural isomer after correction (–0.03 eV) to account for thermal and Stark effects, gray rectangles represent an error of ±4 kJ mol^{-1}.

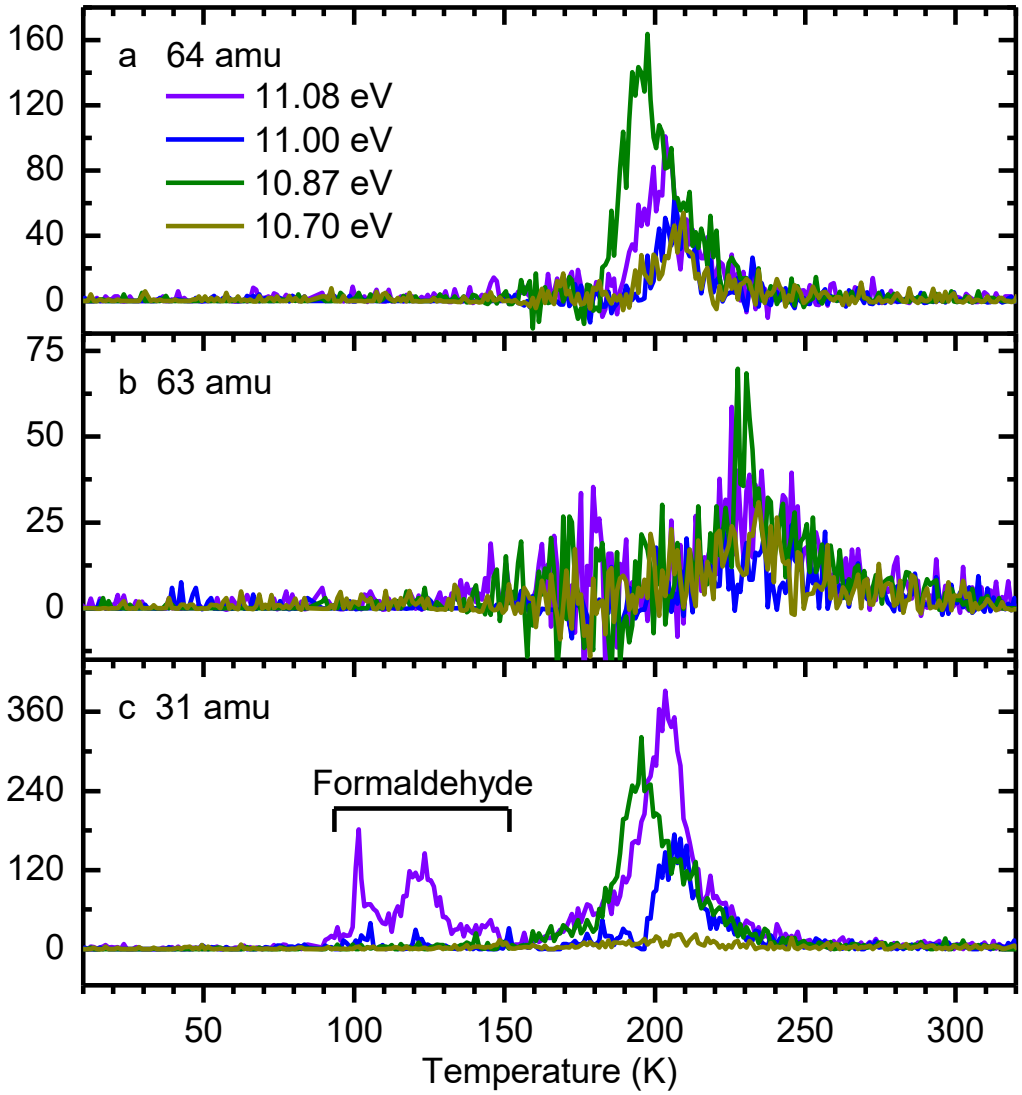


Figure S4. TPD profiles observed during SVUV-PI-ReToF-MS experiments with CH_3OH–O_2 ices after background subtraction (Figures S9–S12).

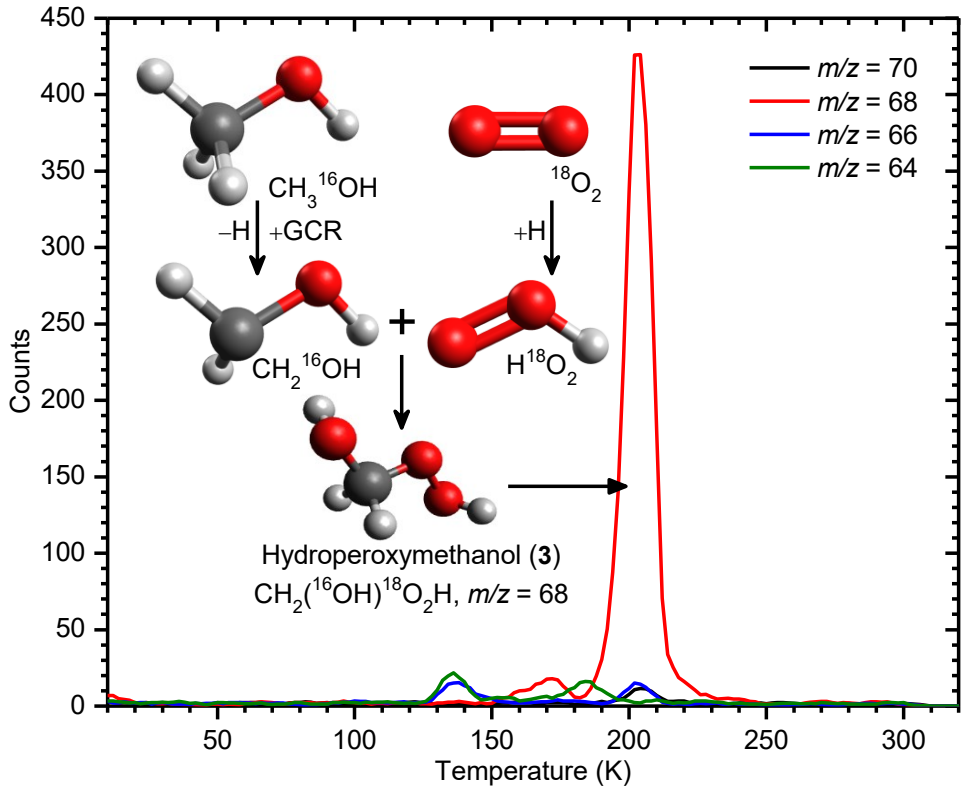


Figure S5. Molecule **3** is only observed as in intact molecular radical cation at *m/z* = 68 in CH_3OH–$^{18}O_2$ ice.

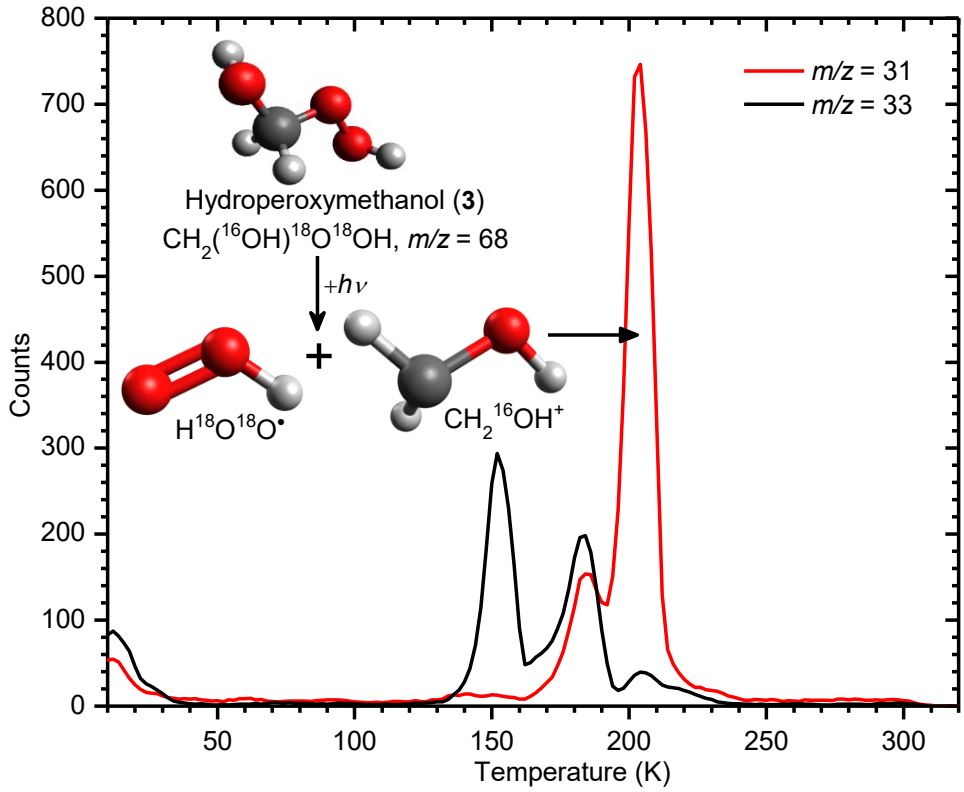


Figure S6. The OH fragment of **3** is observed at *m/z* = 31 in CH_3OH–$^{18}O_2$ ice.

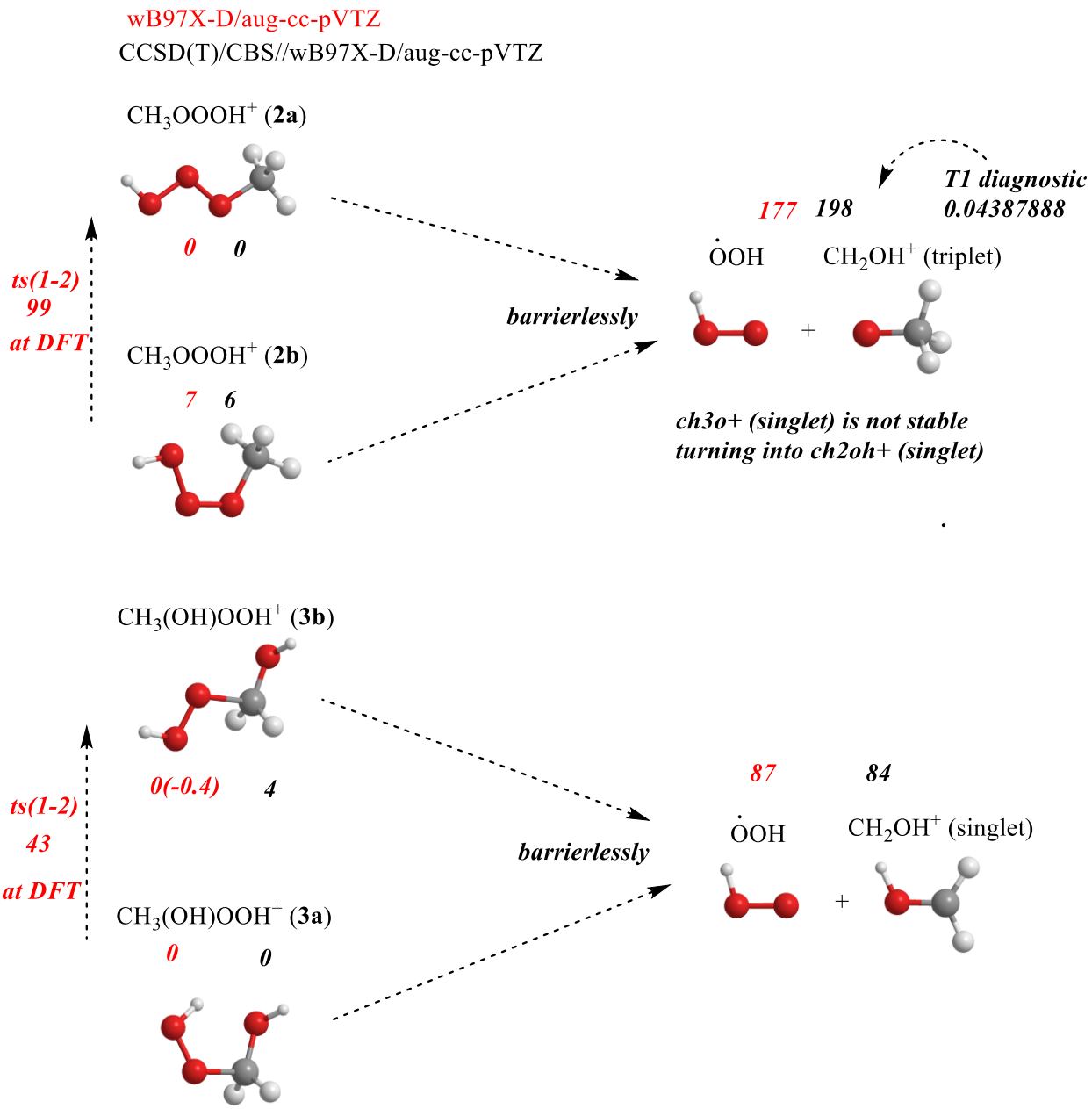


Figure S7. Calculated enthalpies of reaction (kJ mol^{-1}) for unimolecular dissociation of **2** and **3** radical cations.

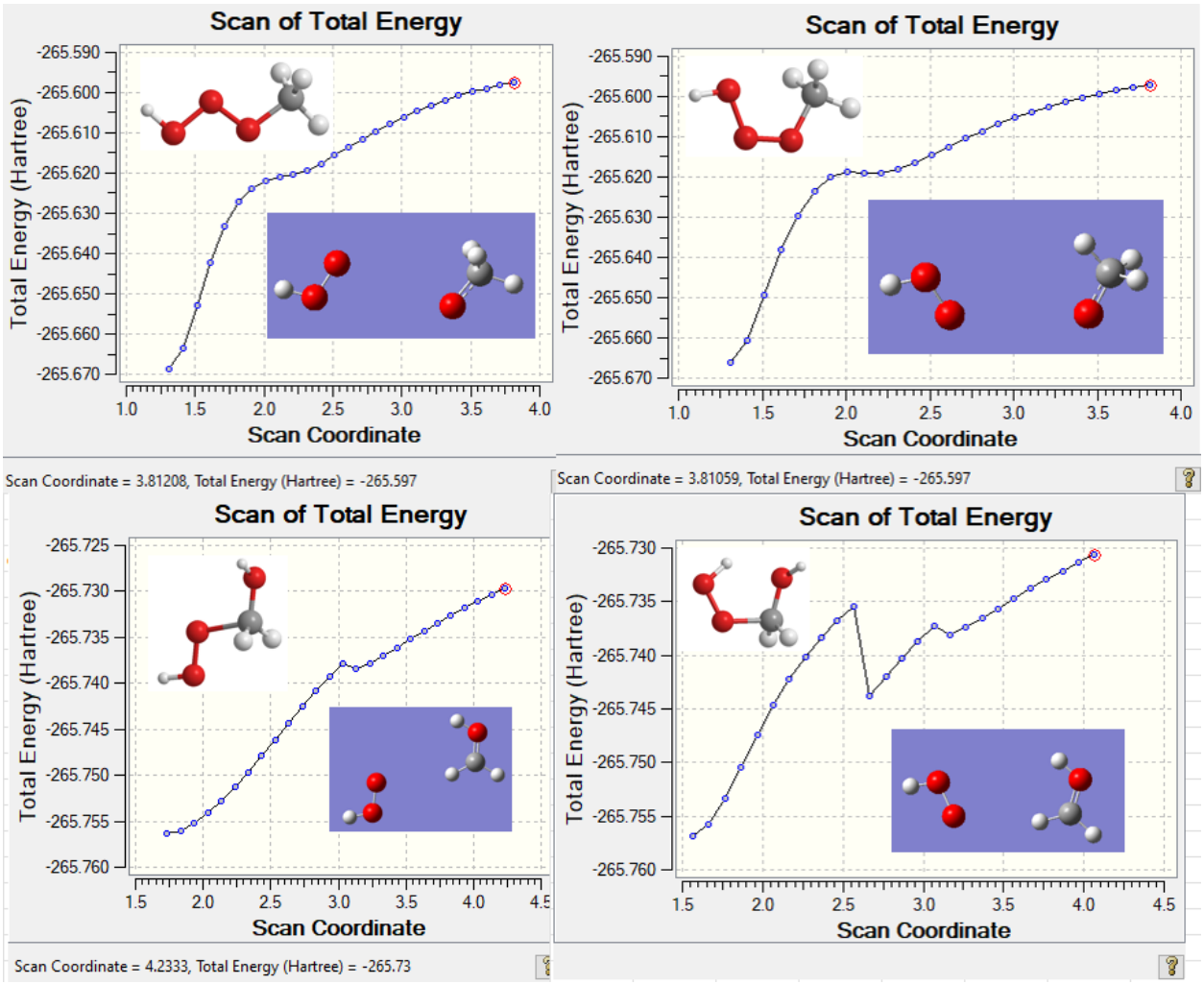


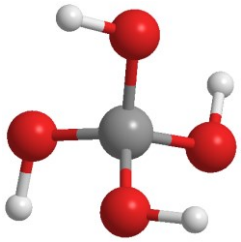
Figure S8. Scans along the reaction coordinate (the breaking bond distance in Å) for investigated channels of unimolecular dissociation of the $\mathbf{2}^{+}$ and $\mathbf{3}^{+}$ radical cations.

Table S3. Calculated conformers of methanetetrol (**4**, $C(OH)_4$) with Cartesian coordinates (Å), energetics, vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}).

Neutral and cation $C(OH)_4$ molecule correspondence table

Neutral	Cation
4a	**4a**$^+$
4b	**4b**$^+$
4c	**4c**$^+$

4a



Total electronic energy CCSD(T)/aug-cc-pVTZ -341.0142177 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -341.1056313 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -341.1690513 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 41.67905 kcal/mol

Cartesian coordinates

C	0.000066	-0.000096	-0.000089
O	-0.107760	-1.154254	0.755043
O	1.154618	-0.106018	-0.755173
O	-1.152562	0.107716	-0.757656
O	0.105853	1.152668	0.757681
H	0.756955	-1.340698	1.127421
H	1.340947	0.759712	-1.125201
H	-1.339344	-0.757621	-1.128459
H	-0.760144	1.338281	1.127617

Vibrational frequencies

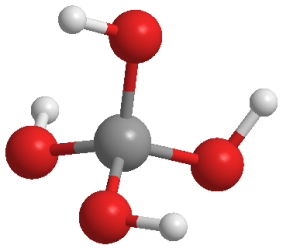
254.3659	318.0202	318.6812
336.4093	472.0474	487.3487
598.2872	598.3857	623.7500
893.7786	1053.2428	1053.3664
1165.4348	1242.3422	1329.6548
1434.6355	1434.7867	3883.6451
3883.9876	3885.5051	3887.2428

IR intensities

0.0126	73.1748	73.3920
230.5764	0.0002	14.3339
23.3065	23.3220	48.6247

0.0002	208.5001	208.3306
426.7613	0.0006	0.1967
276.5910	276.7123	93.1319
94.5416	3.3683	54.0028

4b



Total electronic energy CCSD(T)/aug-cc-pVTZ -341.0100746 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -341.1014236 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -341.1647988 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 41.33085 kcal/mol

Cartesian coordinates

C	-0.030131	-0.002448	-0.025965
O	0.569809	0.108019	1.238319
O	1.021238	0.030060	-0.932033
O	-0.773237	-1.154361	-0.145398
O	-0.933744	1.007835	-0.257524
H	-0.129691	0.056751	1.893212
H	1.835908	0.086021	-0.428978
H	-0.159133	-1.887135	-0.213965
H	-0.438828	1.826626	-0.321389

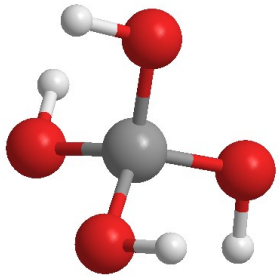
Vibrational frequencies

88.5383	195.9188	330.9558
356.5840	458.7774	488.6144
599.6219	604.6234	610.8578
890.0907	1033.9027	1076.2919
1112.5879	1274.5594	1347.0745
1402.1735	1458.9655	3886.1521
3892.8151	3898.7659	3903.4762

IR intensities

20.6513	124.9995	200.0186
7.0515	6.0053	37.1268
38.9388	30.3091	0.8857
3.9248	132.9415	229.6618
418.3671	65.0262	202.6601
35.0171	317.4728	56.5004
74.3034	75.8186	47.7827

4c



Total electronic energy CCSD(T)/aug-cc-pVTZ -341.0116948 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -341.1029803 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -341.1663114 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 42.06959 kcal/mol

Cartesian coordinates

C	0.000011	0.000098	-0.000008
O	0.807912	0.730379	0.855719
O	-0.730207	0.807681	-0.856116
O	0.729903	-0.808035	-0.855825
O	-0.808045	-0.729585	0.856217
H	1.386021	1.260326	0.302781
H	-1.263521	1.383128	-0.303458
H	1.263338	-1.383231	-0.303006
H	-1.382399	-1.264326	0.303775

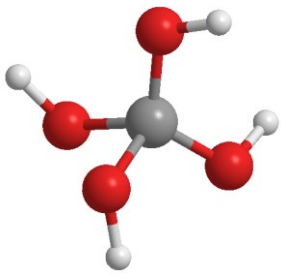
Vibrational frequencies

165.6371	353.3359	444.0346
445.1013	450.8050	549.4664
602.7085	605.5072	605.5748
892.1585	1036.6806	1095.2266
1095.5678	1302.6161	1395.0579
1395.4906	1440.1602	3886.0930
3887.4429	3888.1667	3891.2776

IR intensities

0.0037	0.0205	180.1127
179.7773	0.2102	0.0552
16.3077	69.4187	69.6002
0.0001	30.5225	428.6288
428.6867	0.0011	24.1048
24.1704	427.9923	22.2095
117.5697	104.6326	5.2061

4a^{+}



Total electronic energy CCSD(T)/aug-cc-pVTZ -340.6097973 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -340.6988196 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -340.7605805 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 40.59458 kcal/mol

Cartesian coordinates

C	0.124488	-0.000016	0.000013
O	0.787489	1.116013	0.280110
O	-0.879269	-0.294443	0.968920
O	-0.879431	0.294366	-0.968849
O	0.787534	-1.115955	-0.280262
H	1.524262	0.968696	0.886232
H	-1.163156	-1.226742	0.878550
H	-1.163356	1.226653	-0.878427
H	1.524745	-0.968365	-0.885782

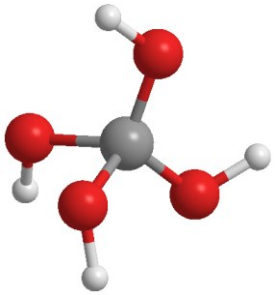
Vibrational frequencies

264.9343	380.2543	403.2648
463.2202	485.4933	549.1358
557.2576	590.5619	678.2141
680.1626	893.0150	1108.7090
1114.7559	1170.3615	1248.5427
1386.7305	1486.7211	3639.1495
3665.0524	3811.5756	3819.2117

IR intensities

149.1980	8.7446	1.2427
126.0316	40.4667	7.9705
6.1054	46.1154	50.4907
124.6388	25.2887	288.5694
132.6045	86.9130	185.9035
87.1200	325.1486	578.3800
85.7095	153.4231	246.4113

4b^{+}



Total electronic energy CCSD(T)/aug-cc-pVTZ -340.6087898 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -340.6978735 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -340.759677 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 40.1732 kcal/mol

Cartesian coordinates

C	0.129572	-0.003300	0.000346
O	1.076652	0.909718	-0.002562
O	0.569675	-1.255022	0.000778
O	-0.859579	0.221616	1.015615
O	-0.862119	0.218295	-1.014966
H	0.745059	1.817069	-0.000646
H	1.534804	-1.293283	0.002607
H	-1.225372	-0.628135	1.330906
H	-1.228954	-0.632701	-1.325866

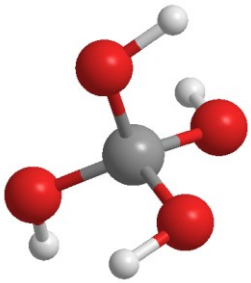
Vibrational frequencies

229.1276	292.4825	395.3978
423.4975	482.3854	544.6198
546.4837	605.9160	609.6634
672.7050	869.2186	1098.3967
1117.0351	1117.8507	1207.8287
1401.5717	1546.7816	3648.1412
3678.2232	3805.0669	3809.1692

IR intensities

125.9287	48.2624	6.0773
33.1685	128.5539	12.4484
6.2582	35.2103	56.2831
17.6253	36.5697	127.4728
154.5214	212.3027	57.5175
271.2622	261.0098	400.0295
286.1094	262.6994	163.5878

4c$^+$



Total electronic energy CCSD(T)/aug-cc-pVTZ -340.6077432 Hartree
Total electronic energy CCSD(T)/aug-cc-pVQZ -340.6967101 Hartree
Total electronic energy CCSD(T)/CBS(aug-cc-pVQZ, aug-cc-pVTZ) -340.7584326 Hartree
Zero-point vibrational energy ωB97X-D/aug-cc-pVTZ 40.8331 kcal/mol

Cartesian coordinates

C	0.126519	0.000000	0.000000
O	0.789924	-1.125839	-0.239595
O	-0.883910	-0.091435	1.007088
O	0.789924	1.125839	0.239595
O	-0.883910	0.091435	-1.007088
H	1.585050	-1.201364	0.302020
H	-1.212715	-1.011043	1.046905
H	1.585050	1.201364	-0.302020
H	-1.212716	1.011043	-1.046905

Vibrational frequencies

309.9726	383.5389	421.3418
471.3126	496.7507	572.2230
574.3520	586.0824	672.4268
688.9481	889.7482	1089.3838
1114.2133	1187.8846	1235.0273
1405.0630	1490.0177	3655.5776
3679.9434	3815.3320	3824.0234

IR intensities

128.6482	8.5398	17.3704
112.9472	31.5818	9.9617
22.2587	119.5949	21.2939
96.6968	24.9306	321.6313
115.7520	43.5222	181.5496
81.7308	312.0763	531.2545
113.0084	119.4096	274.2664

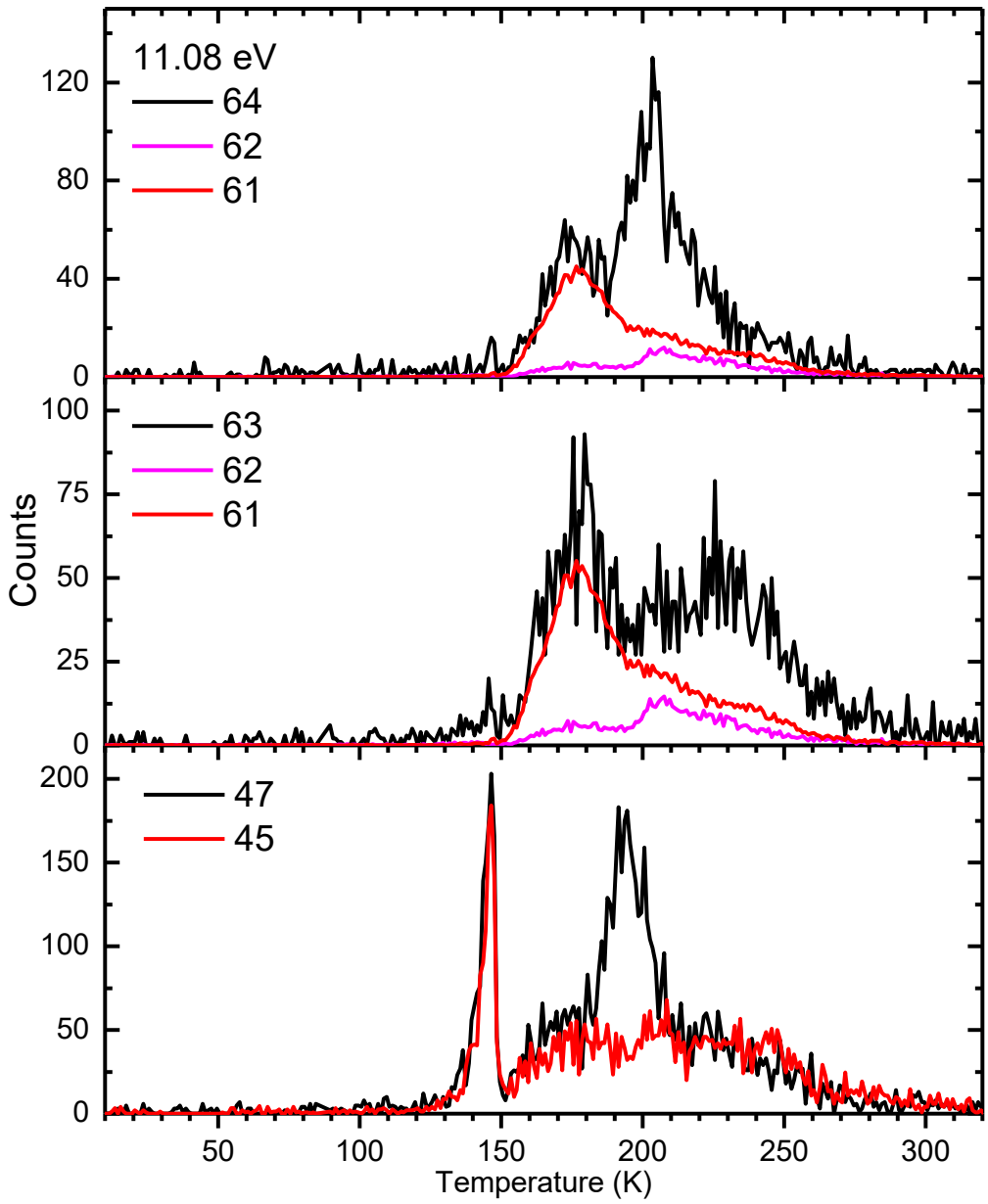


Figure S9. The interface of a quasi-continuous light source to a pulsed mass spectrometer means that during extraction ions are produced continuously, but not effectively mass-analyzed. The temporal width of the extraction (typically 2.5 μs) results in background from ions produced during extraction with flight times approaching 2 μs greater than expected for an ion of that mass. Subsequently, peaks in the TPD profile of an ion of m/z = X must be corrected for any major peaks occurring with m/z = X–1, X–2, X–3. This figure shows the signal observed at 11.08 eV (black) and the scaled signal at lower mass (red, magenta) that was subtracted as part of the background.

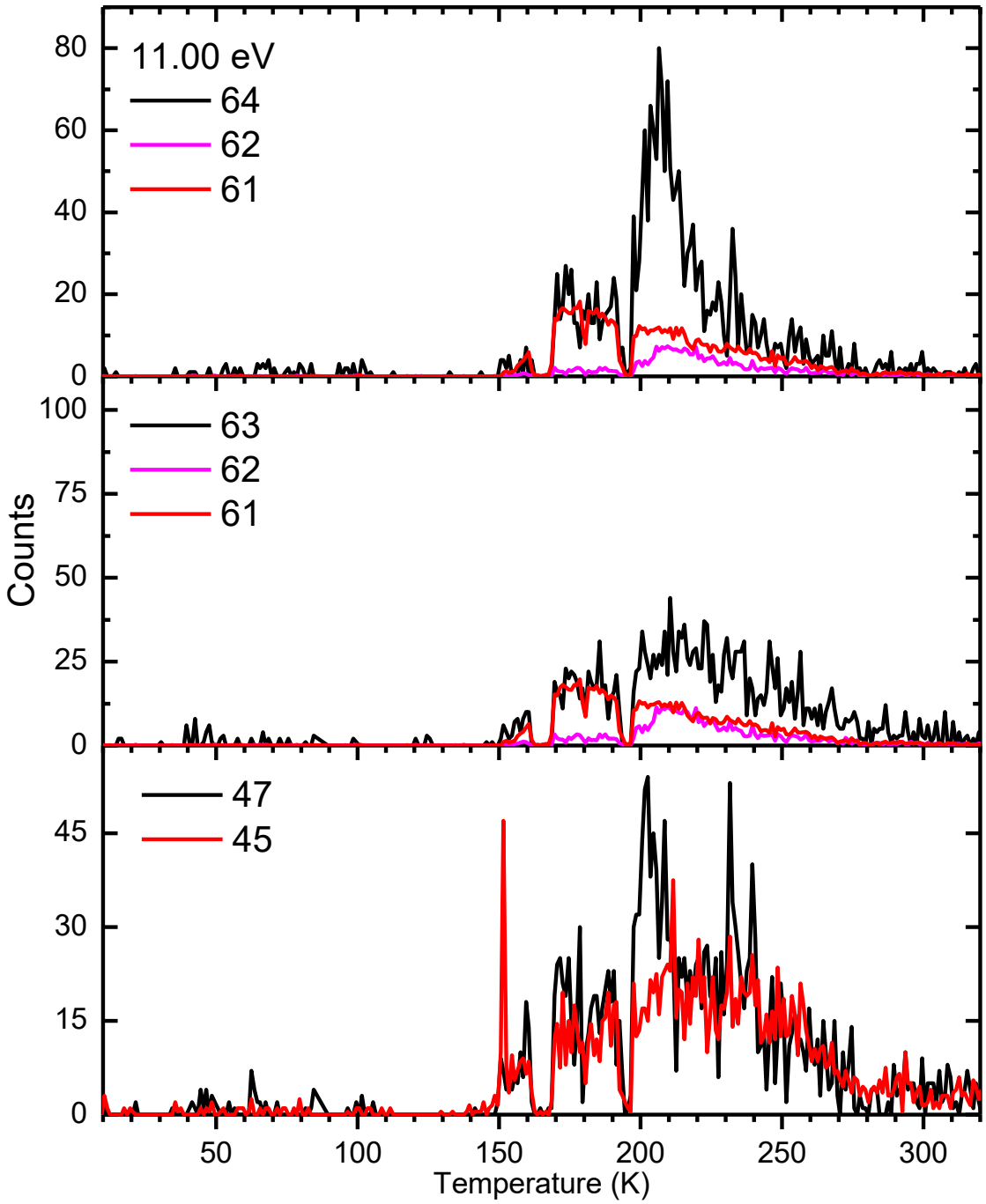


Figure S10. The interface of a quasi-continuous light source to a pulsed mass spectrometer means that during extraction ions are produced continuously, but not effectively mass-analyzed. The temporal width of the extraction (typically 2.5 μs) results in background from ions produced during extraction with flight times approaching 2 μs greater than expected for an ion of that mass. Subsequently, peaks in the TPD profile of an ion of m/z = X must be corrected for any major peaks occurring with m/z = X–1, X–2, X–3. This figure shows the signal observed at 11.00 eV (black) and the scaled signal at lower mass (red, magenta) that was subtracted as part of the background.

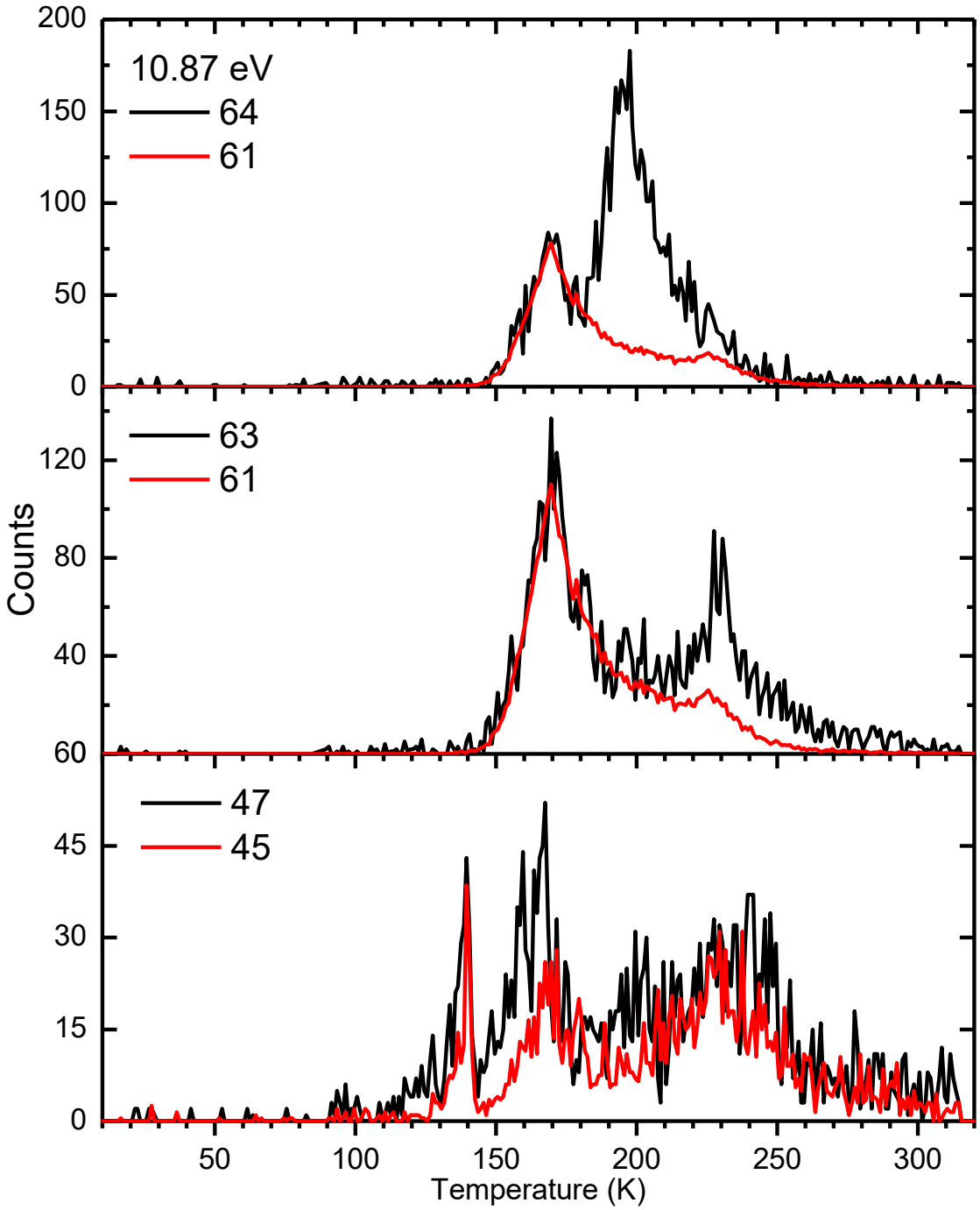


Figure S11. The interface of a quasi-continuous light source to a pulsed mass spectrometer means that during extraction ions are produced continuously, but not effectively mass-analyzed. The temporal width of the extraction (typically 2.5 μs) results in background from ions produced during extraction with flight times approaching 2 μs greater than expected for an ion of that mass. Subsequently, peaks in the TPD profile of an ion of m/z = X must be corrected for any major peaks occurring with m/z = X–1, X–2, X–3. This figure shows the signal observed at 10.87 eV (black) and the scaled signal at lower mass (red, magenta) that was subtracted as part of the background.

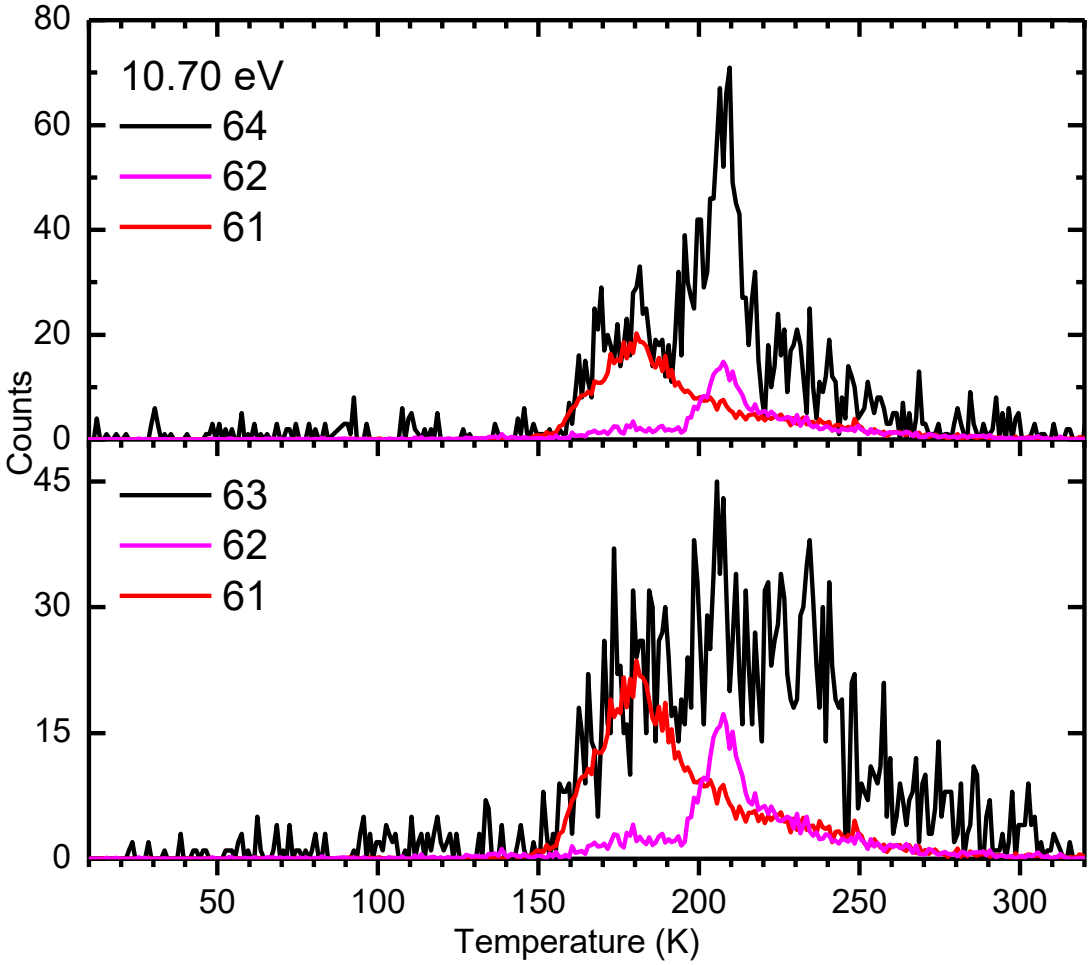


Figure S12. The interface of a quasi-continuous light source to a pulsed mass spectrometer means that during extraction ions are produced continuously, but not effectively mass-analyzed. The temporal width of the extraction (typically 2.5 μs) results in background from ions produced during extraction with flight times approaching 2 μs greater than expected for an ion of that mass. Subsequently, peaks in the TPD profile of an ion of m/z = X must be corrected for any major peaks occurring with m/z = X–1, X–2, X–3. This figure shows the signal observed at 10.70 eV (black) and the scaled signal at lower mass (red, magenta) that was subtracted as part of the background.

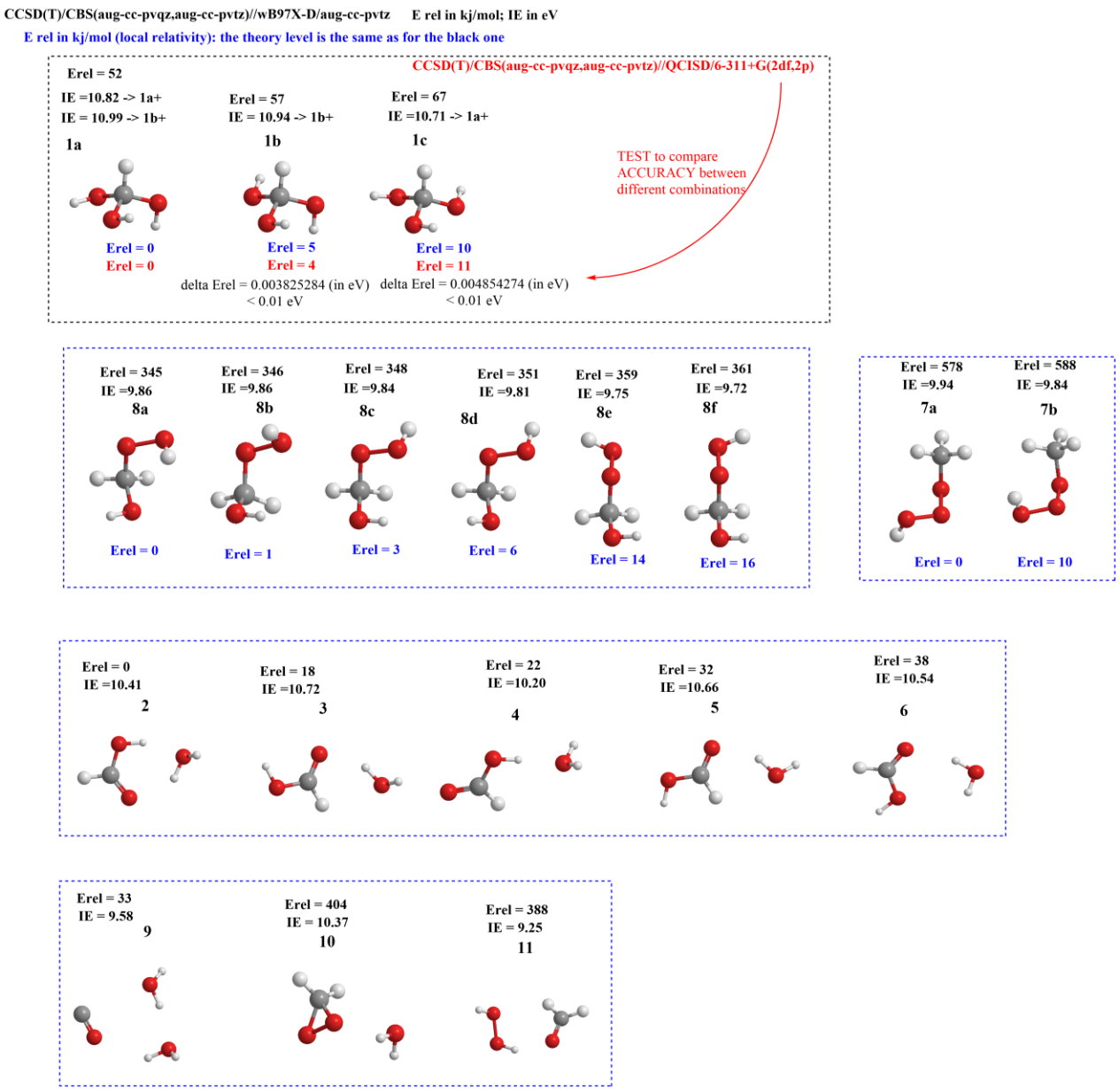


Figure S13. All computed local minima configurations of CH_4O_3.