Supporting Information for

An Efficient Route to Glyceraldehyde ($HOCH_2CH(OH)CHO$) — the Simplest Aldose — via Reactions of Carbon-Centered Radicals in Deep Space

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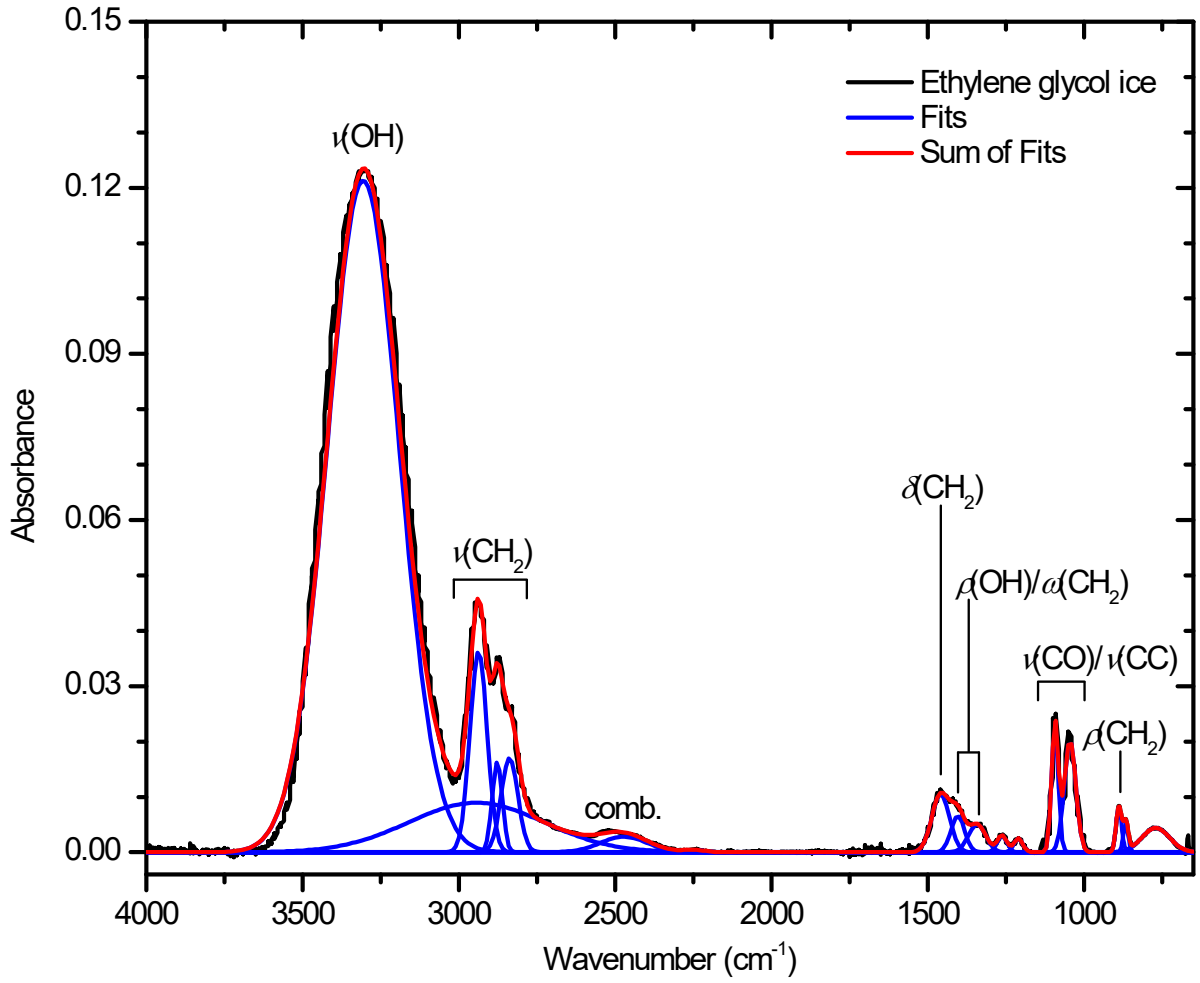


Figure S1. Infrared spectrum of pure 1,2-ethanediol ice. Absorption bands are deconvoluted using a minimal number of gaussian functions (blue) which sum to give good agreement with the observed spectrum (red).[9] Assignments are given as stretching (ν), in-plane scissoring (δ), in-plane bending (ρ), and out-of-plane wagging (ω).

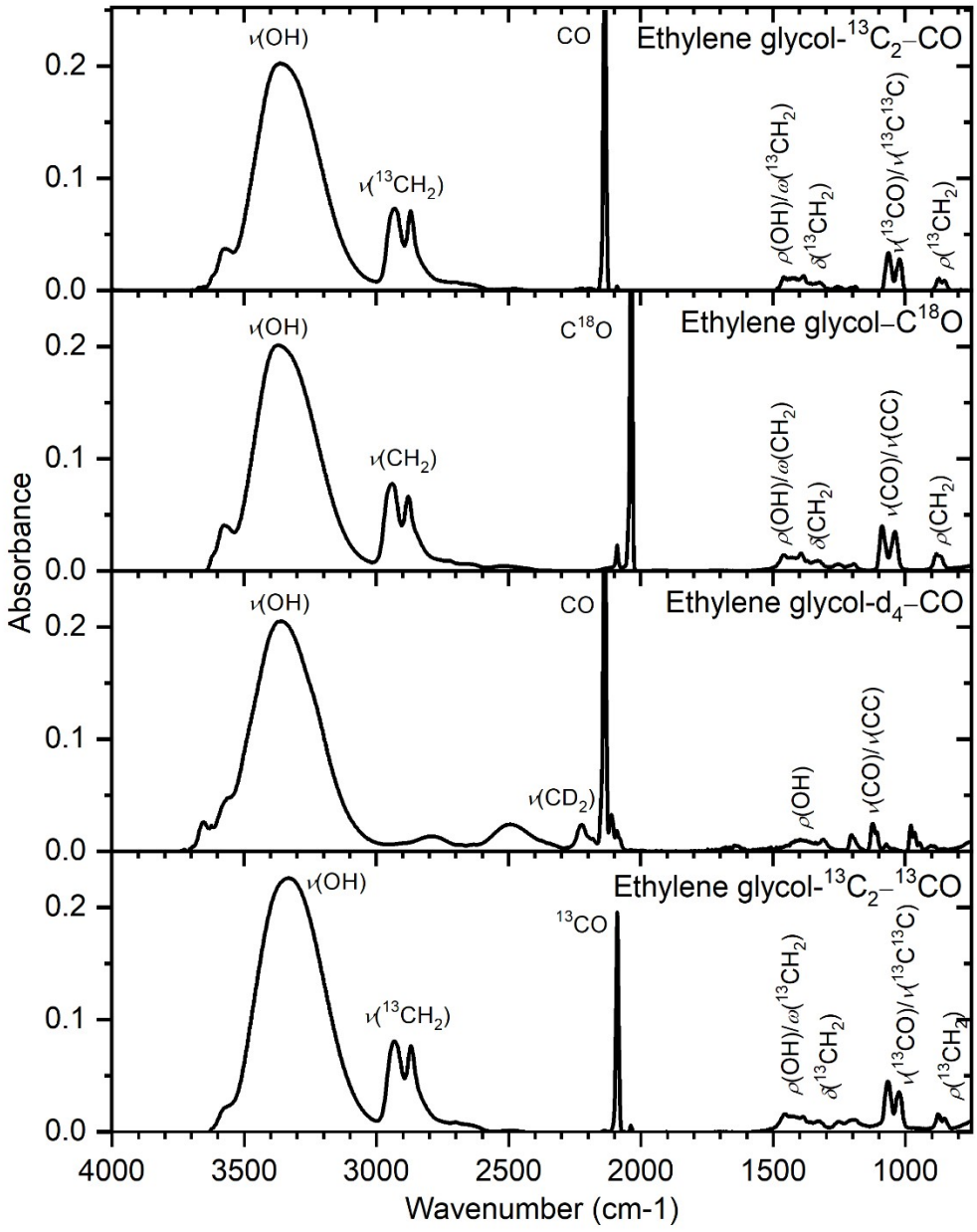


Figure S2. Infrared spectra of isotopically labelled ices studied in these experiments. Tentative assignments are given as stretching (ν), in-plane scissoring (δ), in-plane bending (ρ), and out-of-plane wagging (ω).

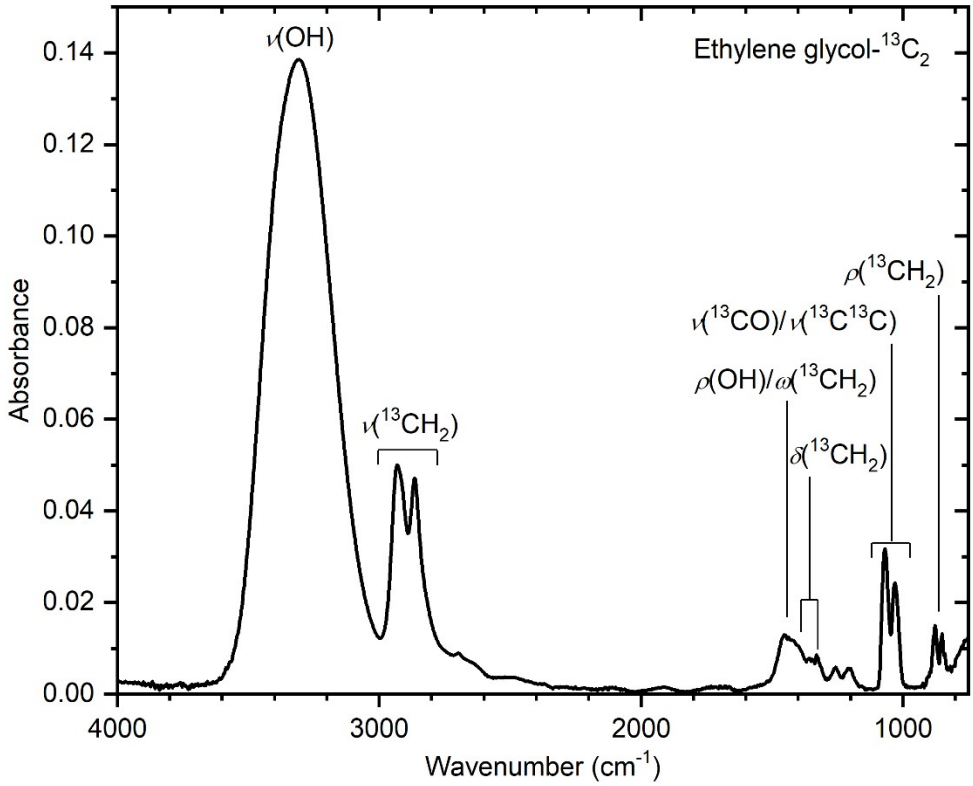


Figure S3. Infrared spectrum of pure ethylene glycol-$^{13}C_2$ ice.

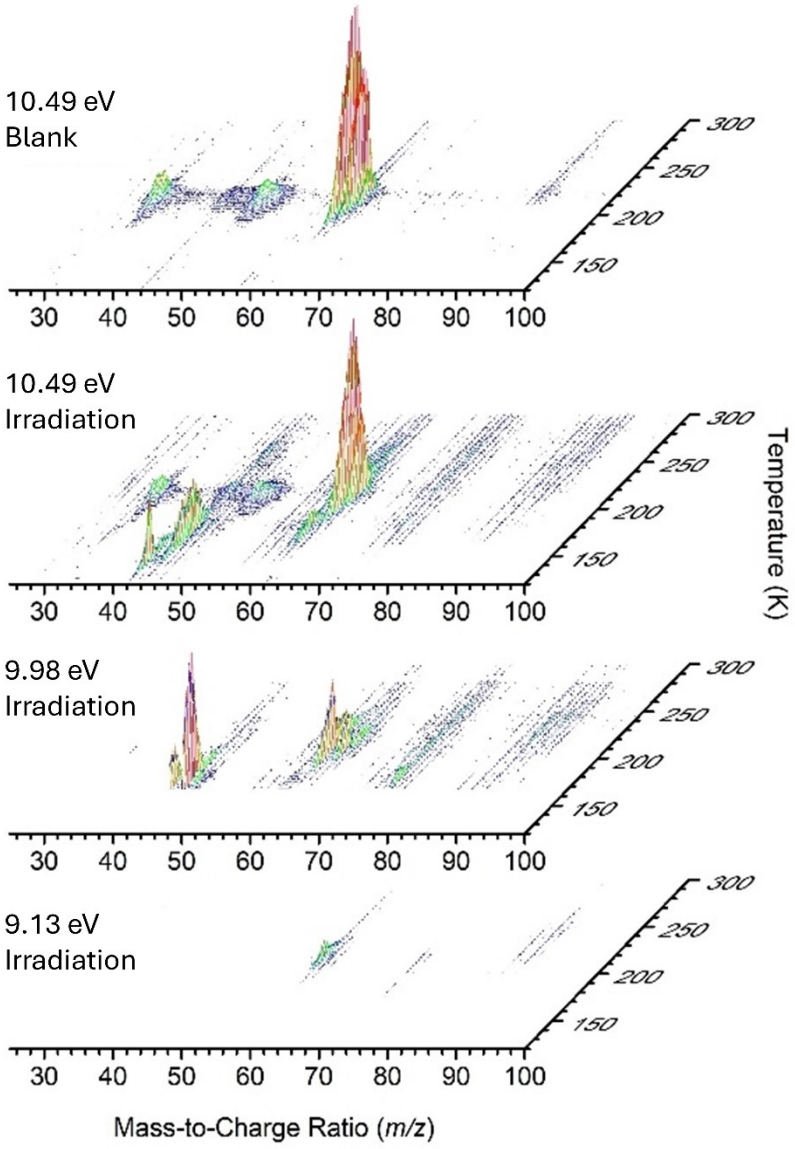


Figure S4. Photoionization Reflectron Time-of-Flight Mass Spectrometry (PI-ReToF-MS) measures the mass-to-charge ratios (*m/z*) for all ions produced during the photoionization of sublimed molecules in the temperature-programmed desorption (TPD) of blank (unirradiated) and irradiated ethylene glycol–CO ices.

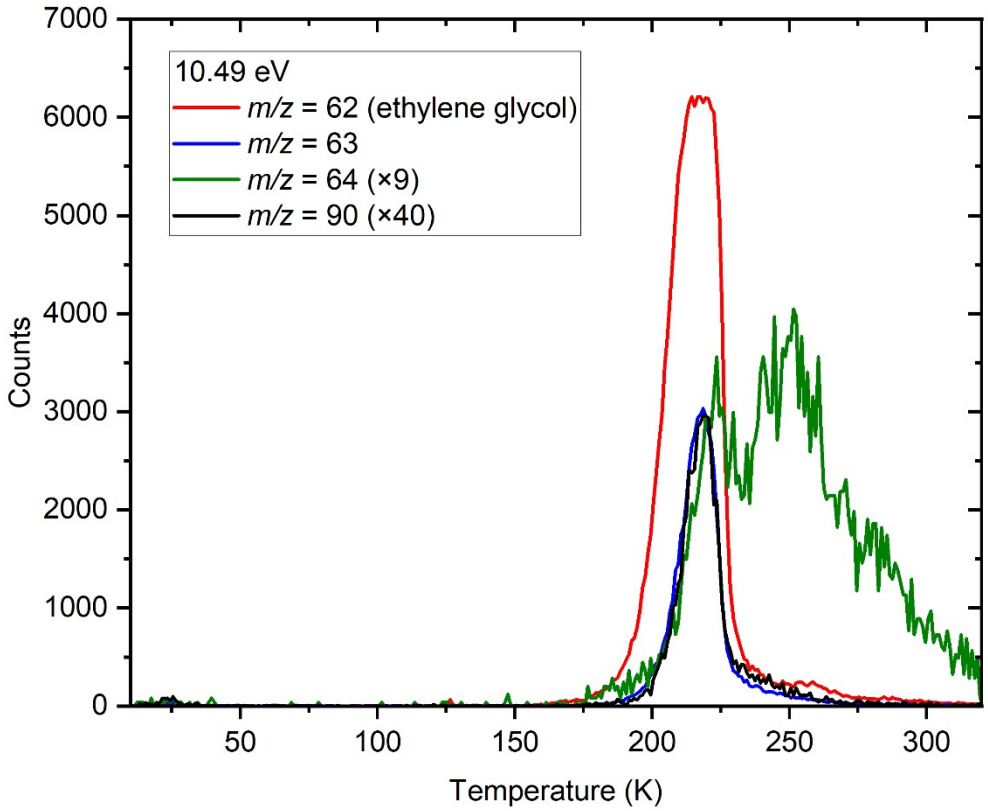


Figure S5. Sublimation of ethylene glycol (*m/z* = 62) saturates the detector due to its ready photoionization, but its naturally occurring isotopomer at *m/z* = 63 and 64 which respectively account for 2.3% and 0.4% of the sample given natural isotopic abundance.

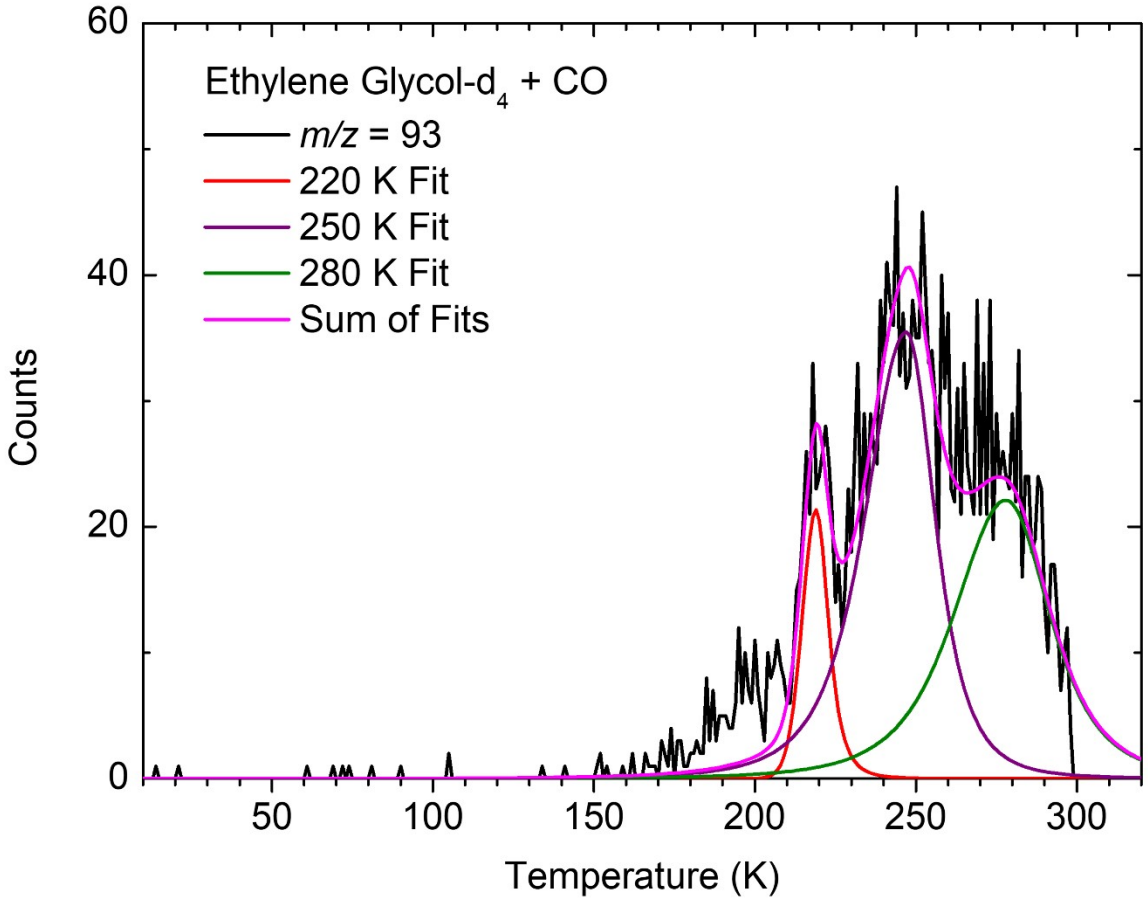


Figure S6. TPD profile of *m/z* = 93 measured with 10.49 eV photons during TPD of irradiated ethylene glycol-d_4–carbon monoxide ice.

Table S1. Experiments conducted in support of this research.

Experiment	Composition	Ratio	Thickness (nm)	Photon energy (eV)	Irradiation Time (s)	Irradiation Current (nA)
1	Ethylene glycol–CO	(3 ± 1):1	750 ± 50	10.49	–	–
2	Ethylene glycol–CO	(3 ± 1):1	750 ± 50	9.98	–	–
3	Ethylene glycol–CO	(3 ± 1):1	750 ± 50	9.13	–	–
4	Ethylene glycol–CO	(3 ± 1):1	750 ± 50	10.49	600	10
5	Ethylene glycol–CO	(3 ± 1):1	750 ± 50	10.49	3600	30
6	Ethylene glycol–CO	(3 ± 1):1	750 ± 50	9.98	3600	30
7	Ethylene glycol–CO	(3 ± 1):1	750 ± 50	9.98	3600	30
8	Ethylene glycol–CO	(3 ± 1):1	750 ± 50	9.13	3600	30
9	Ethylene glycol–CO	(3 ± 1):1	750 ± 50	7.45	3600	30
10	Ethylene glycol–$C^{18}O$	(3 ± 1):1	750 ± 50	10.49	3600	30
11	Ethylene glycol-d_4–CO	(3 ± 1):1	750 ± 50	10.49	3600	30
12	Ethylene glycol–^{13}CO	(3 ± 1):1	750 ± 50	10.49	3600	30
13	Ethylene glycol-$^{13}C_2$–CO	(3 ± 1):1	750 ± 50	10.49	3600	30
14	Ethylene glycol-$^{13}C_2$–^{13}CO	(3 ± 1):1	750 ± 50	10.49	3600	30

Table S2. Parameters Used in Irradiation Dose Calculation and Resulting Doses

Irradiated area	1.6 ± 0.1 cm^2
Initial kinetic energy of e^-	5.000 keV
Irradiation current	30 nA
Total number of e^-	$(6.7 \pm 0.1) \times 10^{14}$
Total molecules irradiated	$(6.3 \pm .5) \times 10^{17}$

	$HOCH_2CH_2OH$ CO	$HO^{13}CH_2{}^{13}CH_2OH$ CO	$HO^{13}CH_2{}^{13}CH_2OH$ ^{13}CO	$HOCD_2CD_2OH$ CO	$HOCH_2CH_2OH$ $C^{18}O$
Approximate density of mixed ice*	1.048 g cm^{-1}	1.077 g cm^{-1}	1.082 g cm^{-1}	1.105 g cm^{-1}	1.059 g cm^{-1}
Average Penetration depth	277 ± 10 nm	270 ± 10 nm	268 ± 10 nm	263 ± 10 nm	274 ± 10 nm
Fraction of backscattered e^-	0.352	0.355	0.356	0.354	0.354
Average energy of backscattered e^-	1.170 keV	1.175 keV	1.178 keV	1.176 keV	1.177 keV
Fraction of Transmitted e^-	0.000	0.000	0.000	0.000	0.000
Average energy of transmitted e^-	0.000 keV	0.000 keV	0.000 keV	0.000 keV	0.000 keV
Dose per molecule of ethylene glycol	5.6 ± 0.5 eV	5.8 ± 0.6 eV	5.9 ± 0.6 eV	6.0 ± 0.6 eV	5.7 ± 0.6 eV
Dose per molecule of carbon monoxide	2.6 ± 0.3 eV	2.6 ± 0.3 eV	2.7 ± 0.3 eV	2.7 ± 0.3 eV	2.7 ± 0.3 eV

*average density with 0.80 g cm^{-3} for CO and 1.11 g cm^{-3} for ethylene glycol, with corrections applied for isotopic labelling

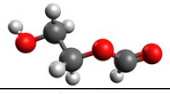
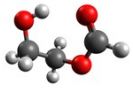
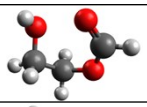
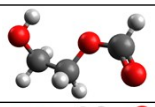
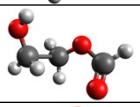
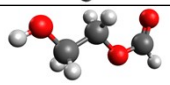
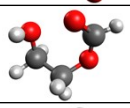
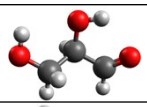
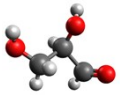
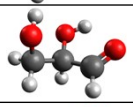
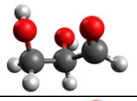
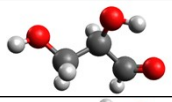
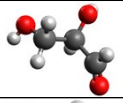
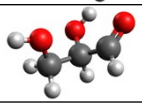
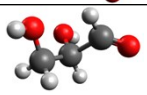
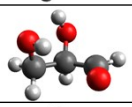
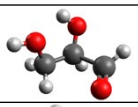
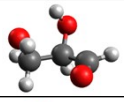
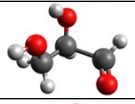
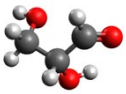
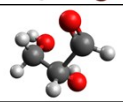
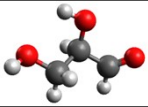
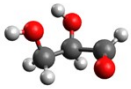
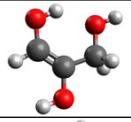
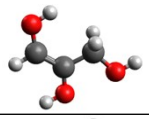
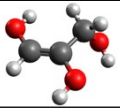
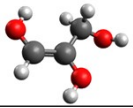
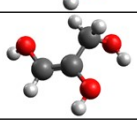
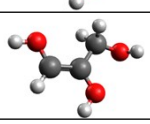
Table S3. Position, absorbance coefficients (A, cm molecule^{-1}), and assignments for vibrational bands observed with Fourier transform infrared (FTIR) spectra of ice composed of 1,2-ethanediol.[9] Absorption coefficients are calculated from the area of the deconvoluted peaks shown in Figure S1. Assignments are given as stretching (ν), in-plane scissoring (δ), in-plane bending (ρ), and out-of-plane wagging (ω).

Position (cm^{-1})	Absorbance (A) (10^{-18} cm molecule^{-1})	Assignment
3306	70.6	ν(OH)
2942	9.82	ν(OH)/ν(CH_2)
2937	5.06	ν(CH_2)
2877	1.34	ν(CH_2)
2838	2.33	ν(CH_2)
2473	1.06	comb.
1460	1.50	δ(CH_2)
1403	0.727	ρ(OH)/ρ(CH_2)
1341	0.703	ρ(OH)/ρ(CH_2)
1262	0.233	
1209	0.179	
1093	1.26	ν(CO)/ν(CC)
1042	1.90	ν(CO)/ν(CC)
889	0.370	ρ(CH_2)
866	0.203	ρ(CH_2)
771	0.988	

Table S4. Four-wave mixing (FWM) schemes employed for experiments listed in Table S1. These non-linear processes represent the generation of the ninth harmonic of an Nd:YAG laser (10.49 eV; $\omega_{VUV} = 3\omega_1$) or difference frequency generation (9.98, 9.13, & 7.45 eV; $\omega_{VUV} = 2\omega_1 - \omega_2$).

Experiments	Photon Energy (eV)	Nonlinear Medium	ω_1 (nm)	ω_1 Dye	ω_2 (nm)	ω_2 Dye
1, 4, 5, 12–16	10.49	Xe	355	(Nd:YAG)	–	–
2, 6, 7	9.98	Xe	222.566	Coumarin 450	1064	(Nd:YAG)
3, 8	9.13	Xe	222.566	Coumarin 450	616.439	Rhodamine 640/610
9	7.45	Xe	248.446	Coumarin 503	496.892	Coumarin 503

Table S5. Calculated relative energy (ΔE) and adiabatic ionization energy (IE) of all structural and conformational isomers of $C_3H_6O_3$ accessible *via* the reaction scheme proposed in Figure 1a. These values are computed at the CCSD(T)-F12b/cc-pVTZ-F12//B3LYP/aug-cc-pVTZ level of theory.

Isomer	Neutral structure	ΔE (kJ/mol)	IE (eV)	Ionic structure
2a		24.2	11.39	
2b		1	10.16	
2c		0	10.12	
2d		7.2	10.11	
1a		36.6	9.89	
1b		32.2	9.88	
1c		48.6	9.74	
1d		42.4	9.62	
1e		40.7	9.48	
1f		40.7	9.48	
1g		42.4	9.47	
1h		57.1	9.31	
3a		81.2	8.34	
3b		87.8	8.28	
3c		86.7	8.13	

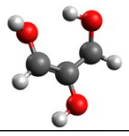
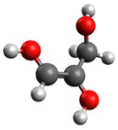
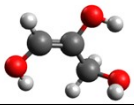
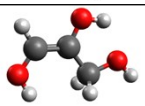
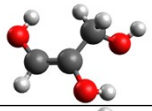
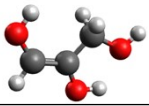
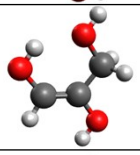
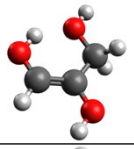
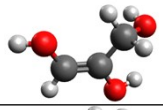
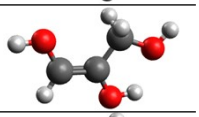
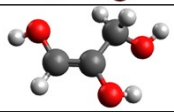
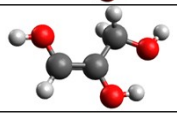
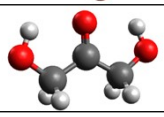
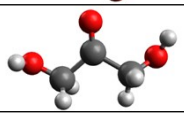
3d		90.6	8.11	
3e		85.8	7.89	
3f		87.9	7.87	
3g		81.2	7.85	
3h		79.9	7.73	
3i		82	7.71	
4		20.6	9.71	

Table S6. Cartesian coordinates (Å) and vibrational frequencies (cm^{-1}) of all identified 2-hydroxyethyl formate (**2**) conformational isomers (**2a**–**2d**) and their corresponding cations after adiabatic ionization.

2a			
C	-0.112967	-0.009056	-0.066612
O	0.017407	0.205944	1.333426
H	0.936267	0.391999	1.543618
C	-1.564536	-0.383327	-0.309908
O	-1.756967	-0.674515	-1.701329
C	-2.490942	0.179978	-2.438955
H	-2.900856	1.018102	-1.850061
O	-2.676069	0.030214	-3.608185
H	-1.823682	-1.281373	0.247916
H	-2.224259	0.426251	0.010029
H	0.135496	0.893973	-0.634749
H	0.534168	-0.820134	-0.412670
Frequencies			
42.7713	90.5435	149.9840	
219.8233	294.6091	379.4558	
405.7423	685.5406	816.0280	
1017.6643	1031.0663	1038.3433	
1064.9793	1119.6608	1185.4858	
1241.0686	1266.7844	1321.2754	
1374.1076	1411.9203	1459.6078	
1509.6763	1527.7895	1828.4208	
2951.4930	2994.3903	3030.8502	
3042.6075	3105.5252	3834.0036	
2a^{+}			
C	-0.050960	-0.105210	0.014312
O	0.129949	0.101857	1.379465
H	1.057422	0.289216	1.595200
C	-1.532051	0.059985	-0.303681
O	-1.576352	0.398909	-1.719908
C	-2.611450	0.041883	-2.436823
H	-3.389281	-0.582569	-1.964947
O	-2.744116	0.369746	-3.596727
H	-2.114522	-0.842182	-0.118474
H	-1.943629	0.894609	0.260628
H	0.558683	0.585178	-0.588360
H	0.293710	-1.119288	-0.261512
Frequencies			
10.1571	87.0255	155.2172	
185.5395	267.2920	382.2553	
387.2605	589.9923	739.7701	
933.8771	998.3140	1008.4191	

1043.3436	1069.9149	1127.0707	
1191.4124	1225.8100	1261.4489	
1291.2642	1359.0680	1383.7347	
1429.4542	1498.4219	1583.0428	
2883.9157	2950.6411	2955.1425	
3062.6618	3129.3120	3716.3518	
2b			
C	-0.151200	-0.165664	-0.178060
O	-0.218320	-0.682974	1.133576
H	0.529465	-0.324722	1.633422
C	0.102257	1.334177	-0.258302
O	1.511612	1.713602	-0.328608
C	2.284607	1.529086	0.735565
H	3.278796	1.947156	0.541660
O	1.974135	0.988528	1.767955
H	-0.299123	1.738310	-1.184177
H	-0.353310	1.843264	0.590921
H	0.600867	-0.685944	-0.785334
H	-1.124531	-0.360985	-0.631911
Frequencies			
76.6125	175.2123	230.3701	
288.0909	383.2714	498.7950	
552.9071	765.5354	779.7693	
919.3889	999.8949	1047.5237	
1087.5431	1111.1778	1209.2472	
1244.0700	1301.3187	1384.5817	
1397.2287	1405.6845	1453.2513	
1481.2226	1496.2331	1762.1047	
2978.0923	3048.9685	3056.4417	
3069.1279	3126.2276	3698.4464	
2b$^+$			
C	-0.098164	-0.064396	-0.102846
O	0.077786	-0.240693	1.310574
H	0.527865	-1.074584	1.529948
C	0.065429	1.412262	-0.386688
O	1.444328	1.884967	-0.254067
C	2.213659	1.550464	0.729831
H	3.188333	2.049688	0.719064
O	1.976236	0.746823	1.636752
H	-0.180145	1.631999	-1.421175
H	-0.546523	2.013786	0.282970
H	0.593847	-0.685371	-0.669742
H	-1.127397	-0.351113	-0.337913
Frequencies			
94.2055	235.2627	308.9167	
337.8486	391.4231	518.5415	

536.4328	748.2776	779.0547	
896.1300	988.8838	996.8611	
1027.1097	1047.0052	1201.2677	
1233.9693	1257.9569	1311.5174	
1346.6818	1393.0617	1420.5765	
1473.0722	1481.9317	1578.0012	
3032.7925	3069.5920	3090.5006	
3112.5472	3161.8070	3695.1664	
2c			
C	0.073949	0.100207	0.056274
O	-0.327207	-0.648401	1.193462
H	0.239313	-0.405267	1.932659
C	1.491584	-0.196998	-0.374363
O	2.364442	0.251108	0.694518
C	3.681606	0.102161	0.496153
H	4.222859	0.468600	1.377090
O	4.197186	-0.354426	-0.485376
H	1.645664	-1.264378	-0.527886
H	1.748281	0.333748	-1.291596
H	-0.601590	-0.182637	-0.751226
H	-0.042236	1.175151	0.231765
Frequencies			
76.6125	175.2123	230.3701	
288.0909	383.2714	498.7950	
552.9071	765.5354	779.7693	
919.3889	999.8949	1047.5237	
1087.5431	1111.1778	1209.2472	
1244.0700	1301.3187	1384.5817	
1397.2287	1405.6845	1453.2513	
1481.2226	1496.2331	1762.1047	
2978.0923	3048.9685	3056.4417	
3069.1279	3126.2276	3698.4464	
2c$^+$			
C	0.176128	-0.270156	0.130411
O	-0.401520	0.385732	1.120954
H	-0.109778	0.103561	2.003604
C	1.716625	0.660521	-0.417172
O	2.662959	0.577284	0.519389
C	3.534804	-0.562949	0.483874
H	4.349721	-0.384085	1.186202
O	3.314417	-1.492694	-0.203951
H	1.895268	0.099288	-1.332269
H	1.297838	1.658583	-0.481635
H	0.626262	-1.237078	0.345097
H	-0.368875	-0.159139	-0.803029
Frequencies			

60.1463	106.9659	167.0927	
236.3500	328.1966	371.5893	
431.5771	494.2969	661.8643	
835.1783	867.6101	912.7868	
1018.9793	1114.3170	1121.9589	
1200.4744	1238.9436	1253.3930	
1285.9957	1365.2895	1382.1821	
1470.0784	1511.0026	1858.1273	
3063.9209	3074.7298	3131.8725	
3182.8648	3202.3895	3701.9117	
2d			
C	0.001952	0.000000	0.003932
O	0.004857	0.000000	1.427203
H	0.912319	0.000000	1.742386
C	-1.452216	0.000000	-0.419532
O	-1.462029	0.000000	-1.864273
C	-2.665350	0.000000	-2.451338
H	-2.533779	0.000000	-3.540151
O	-3.724390	0.000000	-1.888274
H	-1.970819	-0.883456	-0.049868
H	-1.970819	0.883456	-0.049868
H	0.502655	0.887056	-0.396381
H	0.502655	-0.887056	-0.396381
Frequencies			
55.9227	103.2543	159.4073	
219.0613	325.9673	337.8543	
434.1975	787.8716	821.6812	
957.5905	1039.3178	1043.5422	
1069.0226	1155.2049	1206.3571	
1231.4538	1244.7933	1302.5493	
1372.6510	1397.5158	1464.3257	
1512.3253	1530.0164	1787.9783	
2998.1359	3030.4543	3035.3459	
3064.3338	3113.4984	3835.5275	
2d$^+$			
C	-0.246569	0.145577	-0.018136
O	0.286356	-1.171762	0.083151
H	-0.037161	-1.645584	0.869897
C	-1.687665	0.106093	-0.528860
O	-1.790226	-0.477067	-1.851919
C	-1.484276	-1.731101	-2.032042
H	-1.717114	-2.108609	-3.031685
O	-0.978844	-2.469221	-1.188340
H	-2.332514	-0.459362	0.143498
H	-2.056124	1.120104	-0.653664
H	-0.241277	0.630196	0.960918

H	0.401896	0.676230	-0.710841
Frequencies			
100.9369	239.0188	290.9455	
310.7744	403.7163	507.4075	
556.8140	734.9559	801.6621	
900.4938	938.1612	988.4941	
1032.1808	1046.7929	1167.2634	
1191.9598	1298.5049	1321.3183	
1340.4603	1376.4113	1398.2767	
1478.5072	1484.7259	1575.1699	
3046.8974	3073.4445	3087.9392	
3136.4400	3157.2002	3678.3577	

Table S7. Cartesian coordinates (Å) and vibrational frequencies (cm^{-1}) of all identified glyceraldehyde (**1**) conformational isomers. (**1a**–**1h**) and their corresponding cations after adiabatic ionization.

1a			
C	0.045352	0.045326	0.005812
O	0.045453	0.000989	1.417957
H	0.904708	-0.334728	1.699174
C	1.237828	0.858196	-0.517912
H	1.142923	1.880838	-0.125886
O	2.439204	0.286679	-0.053812
H	2.963735	0.053661	-0.835295
C	1.220797	0.946579	-2.022331
H	0.329740	1.413486	-2.479151
O	2.127633	0.527385	-2.699389
H	0.086373	-0.963554	-0.420910
H	-0.893914	0.511844	-0.293792
Frequencies			
95.6828	133.5329	254.4282	
293.6075	385.0980	402.5706	
444.9142	497.3054	743.8351	
832.8094	901.9129	963.2423	
1065.9292	1097.4363	1147.1655	
1227.1130	1245.3070	1310.4208	
1378.2353	1386.1320	1417.5984	
1422.0968	1496.0966	1784.5578	
2931.0701	2971.8574	2994.1711	
3075.5993	3688.9395	3782.8123	
1a^{+}			
C	0.099386	0.013547	-0.037554
O	0.077567	0.204716	1.331189
H	0.550715	-0.498178	1.800068
C	1.408702	0.750824	-0.557045
H	1.468110	1.767618	-0.158304
O	2.506390	-0.000282	-0.368409
H	3.273541	0.505627	-0.062407
C	1.050735	0.949395	-2.160633
H	0.298140	1.748473	-2.299772
O	1.539447	0.306683	-3.005471
H	0.152370	-1.030588	-0.346966
H	-0.775271	0.508867	-0.460230
Frequencies			
46.9963	112.2825	243.4815	
270.4367	319.1798	350.4996	
457.1400	465.8988	570.5104	
652.2695	762.1422	899.8368	

955.3482	1103.6200	1119.6931	
1155.9949	1198.3570	1237.8026	
1284.5559	1356.7847	1390.9694	
1433.1244	1488.0995	1890.7793	
2916.4388	3045.8928	3053.1039	
3117.1865	3734.5782	3742.6674	
1b			
C	0.0294501	-0.0515584	0.0560527
O	0.0901327	0.0129846	1.4677140
H	0.9141810	0.4539334	1.7041450
C	1.2538540	-0.7506146	-0.5360921
H	1.1186114	-0.7951385	-1.6295356
O	2.4166551	-0.0264311	-0.2084190
H	3.0634587	-0.6697282	0.1208548
C	1.3686939	-2.1834997	-0.0655139
H	0.4771421	-2.8197023	-0.2101953
O	2.3823237	-2.6176215	0.4215598
H	-0.8764205	-0.6033664	-0.1991650
H	-0.0446516	0.9463150	-0.3873395
Frequencies			
105.6675	139.7505	248.7020	
281.1664	342.7512	407.1855	
496.3849	638.9229	705.2774	
823.7536	897.8142	943.8038	
1048.4125	1076.5781	1142.0841	
1224.4944	1248.3171	1323.6718	
1367.1659	1386.2458	1411.3585	
1427.7566	1499.0559	1790.8296	
2927.9866	2941.9781	3012.8224	
3075.4465	3682.9540	3787.4828	
1b$^+$			
C	0.085912	-0.050552	0.173339
O	0.158779	-0.167474	1.550458
H	0.921971	0.309837	1.914102
C	1.263173	-0.761007	-0.551795
H	1.111371	-0.787580	-1.631537
O	2.477870	-0.242838	-0.169723
H	3.083872	-0.112046	-0.912192
C	1.250596	-2.264623	0.021749
H	1.508176	-3.048707	-0.714429
O	1.037450	-2.496206	1.158772
H	-0.861149	-0.478757	-0.149273
H	0.155408	0.995525	-0.155405
Frequencies			
114.3487	126.9286	205.8205	
280.1939	329.8743	383.1017	

485.0650	511.7542	658.3185	
757.6307	794.6785	932.2341	
956.2181	1062.1019	1107.8958	
1165.7338	1189.2032	1212.8415	
1249.4545	1310.9368	1386.6198	
1419.2186	1468.2960	1816.0103	
2923.2419	2977.7308	3083.9097	
3119.2421	3707.4652	3757.4788	
1c			
C	-0.0073801	0.0156460	-0.0235748
O	0.0082108	-0.1864455	1.3824332
H	0.8591934	0.0878314	1.7342515
C	-1.4613842	-0.0069638	-0.4874946
H	-1.9286717	-0.8829888	-0.0078219
O	-2.1434788	1.1634722	-0.1229104
H	-2.5618477	1.5068866	-0.9268423
C	-1.5540936	-0.2512110	-1.9767111
H	-1.0403175	-1.1512688	-2.3606085
O	-2.1707938	0.4804138	-2.7105629
H	0.4280300	0.9814943	-0.2945671
H	0.5527863	-0.7799544	-0.5311270
Frequencies			
93.7179	125.4095	159.5607	
280.2869	293.1794	397.7113	
410.4805	482.2541	739.0214	
829.3982	919.2274	977.2613	
1069.0132	1075.3742	1166.4988	
1216.5136	1260.9843	1285.4209	
1339.4241	1386.7688	1413.6530	
1449.7486	1499.6424	1789.1321	
2923.7981	2942.2410	2973.9590	
3036.8020	3694.5761	3832.5450	
1c$^+$			
C	0.0331733	0.4770666	-0.1812851
O	0.1627931	0.4950934	1.1925482
H	0.6794806	-0.2539191	1.5219044
C	-1.4365981	-0.0824950	-0.4677985
H	-1.6093152	-1.0236239	0.0531087
O	-2.3820420	0.8639638	-0.2746058
H	-3.1182143	0.5653783	0.2804365
C	-1.3910392	-0.3997379	-2.0687256
H	-1.3849679	0.5021698	-2.7042166
O	-1.3924261	-1.5163884	-2.4305423
H	0.0500678	1.4990503	-0.5608089
H	0.7693413	-0.1496459	-0.6855511
Frequencies			

68.8974	108.0063	225.6504	
284.2244	302.5090	380.6199	
403.7147	443.6972	513.3401	
668.2887	813.6216	931.7533	
961.5918	1111.6611	1164.2050	
1176.2463	1201.2986	1219.5780	
1273.4799	1352.0974	1380.8520	
1422.5752	1491.0595	1867.2967	
2962.7621	3046.1497	3099.2850	
3119.2458	3732.5265	3750.2655	
1d			
C	-0.0116341	0.0358489	-0.0075886
O	-0.0701845	0.0996220	1.4109264
H	0.7537127	-0.2203312	1.7861312
C	-1.4357520	0.0015946	-0.5567375
H	-1.3610833	0.1990610	-1.6384860
O	-2.0553926	-1.2372829	-0.3421475
H	-2.8629076	-1.0656248	0.1655577
C	-2.2620693	1.1332641	0.0199477
H	-1.8361373	2.1481621	-0.0758306
O	-3.3320362	0.9434602	0.5394209
H	0.5090054	0.9106828	-0.4165479
H	0.5024266	-0.8647543	-0.3505797
Frequencies			
104.3412	117.4554	137.6762	
262.6408	289.2873	355.3173	
412.0644	612.4673	711.7231	
824.1096	912.4394	951.2744	
1032.7135	1092.9847	1161.6007	
1198.4535	1268.3387	1295.6461	
1341.7023	1391.2660	1424.1688	
1433.6172	1502.7313	1795.5717	
2928.3084	2943.4899	2983.4793	
3050.9254	3694.9960	3841.5154	
1d$^+$			
C	-0.043098	0.033887	-0.096236
O	0.045662	0.105066	1.297004
H	0.886409	0.487817	1.577785
C	-1.507271	-0.153591	-0.482415
H	-1.695196	-0.096661	-1.553724
O	-2.102276	-1.182070	0.165922
H	-2.827577	-1.577628	-0.341619
C	-2.221963	1.223344	0.206619
H	-1.836352	1.325048	1.242984
O	-2.987892	1.869804	-0.386014
H	0.366694	0.911294	-0.604371

H	0.460807	-0.862607	-0.491868
Frequencies			
95.3207	123.3157	208.9687	
277.5389	315.3437	341.8644	
403.3347	484.7021	536.6989	
704.3414	841.2463	923.3795	
952.9692	1077.0130	1122.0311	
1153.5354	1175.2749	1218.7993	
1239.3038	1271.5098	1401.5468	
1440.7442	1470.8487	1910.2209	
2878.7036	2945.0561	3049.1308	
3106.1219	3726.4225	3781.3143	
1e			
C	0.063106	0.086124	0.071581
O	-0.033138	0.347026	1.469627
H	0.675630	-0.138395	1.906976
C	1.193899	0.894390	-0.549991
H	1.191680	0.757556	-1.636969
O	1.045722	2.289214	-0.315266
H	0.739095	2.386761	0.596287
C	2.565682	0.473246	-0.032865
H	3.387241	1.156880	-0.319362
O	2.765075	-0.489168	0.666644
H	0.207945	-0.978047	-0.126219
H	-0.883206	0.398653	-0.367194
Frequencies			
78.4578	128.0227	211.2717	
305.3644	387.4928	424.6808	
501.9022	536.4935	715.0394	
807.8473	927.1658	936.8790	
1053.4594	1068.4165	1112.4473	
1202.4988	1247.8344	1344.8673	
1381.5723	1387.0298	1401.7342	
1421.5479	1490.1050	1789.0066	
2917.6815	3014.8245	3041.0963	
3099.4696	3745.9107	3788.2548	
1e$^+$			
C	0.187479	0.011812	0.188823
O	0.124082	0.537579	1.496055
H	-0.552834	0.102041	2.026256
C	1.076439	0.965485	-0.568285
H	1.170038	0.843973	-1.648478
O	1.024785	2.230527	-0.190248
H	0.638170	2.270671	0.713274
C	2.866003	0.465298	-0.212676
H	3.497341	1.359673	-0.341111

O	3.104710	-0.628993	0.066943
H	0.569816	-1.009378	0.150776
H	-0.787298	0.035550	-0.318082
Frequencies			
42.2407	96.7658	199.4172	
246.5801	255.6674	291.6462	
404.1019	467.7865	659.7077	
753.3460	829.8236	876.0112	
988.1615	1051.6116	1092.8335	
1141.6370	1179.2651	1212.4232	
1239.8577	1369.3143	1420.3379	
1452.0284	1489.9639	1966.2011	
2970.2878	2980.9575	3076.5608	
3088.2018	3501.4636	3807.2056	
1f			
C	0.019927	0.005067	0.050656
O	-0.125502	0.261327	1.444967
H	0.601712	-0.177680	1.900671
C	1.110622	0.883202	-0.547261
H	1.141300	0.745364	-1.633688
O	0.869102	2.265941	-0.318706
H	0.534217	2.343908	0.584752
C	2.494535	0.550748	0.001273
H	3.276879	1.285362	-0.268213
O	2.739352	-0.396563	0.706983
H	0.237696	-1.047824	-0.140804
H	-0.934114	0.255017	-0.410941
Frequencies			
78.0235	127.7661	211.2408	
305.2514	387.4570	424.0148	
501.8207	536.3570	714.9626	
807.8662	927.2582	937.0988	
1053.8591	1068.4703	1112.7917	
1202.5238	1247.8775	1344.8796	
1381.7675	1387.0727	1401.8202	
1421.5857	1490.1980	1788.8932	
2917.8984	3014.7200	3040.7640	
3099.1851	3745.8610	3788.4446	
1f^{+}			
C	0.147431	-0.063165	0.172270
O	0.022299	0.459323	1.476438
H	-0.634085	-0.020246	1.994308
C	0.987088	0.946087	-0.568888
H	1.111356	0.829224	-1.646503
O	0.843725	2.205594	-0.195975
H	0.436453	2.221631	0.699184

C	2.797571	0.566162	-0.173853
H	3.370572	1.500509	-0.290647
O	3.102289	-0.509731	0.112906
H	0.597122	-1.056886	0.145070
H	-0.816094	-0.104635	-0.354622
Frequencies			
42.2986	96.7188	199.6554	
246.7111	255.5566	291.6979	
404.1868	467.9070	659.5868	
753.3162	829.8332	876.0682	
988.1878	1051.5795	1092.6973	
1141.6566	1179.1949	1212.4644	
1239.7632	1369.3136	1420.3161	
1452.0261	1489.9682	1966.2117	
2970.3479	2980.9169	3076.6442	
3088.1656	3501.5243	3807.2633	
1g			
C	0.100198	0.079325	-0.008191
O	0.119176	0.195749	1.408162
H	0.985977	-0.045315	1.743645
C	-1.346385	-0.084685	-0.467874
H	-1.350298	0.073932	-1.558520
O	-1.854050	-1.357276	-0.171750
H	-2.641525	-1.226764	0.378033
C	-2.223540	1.003488	0.117409
H	-1.884392	2.043043	-0.040320
O	-3.243442	0.754315	0.707704
H	0.526334	0.973866	-0.479099
H	0.662067	-0.792943	-0.349365
Frequencies			
105.2426	118.5286	137.7579	
262.7012	289.3228	355.3125	
412.8681	612.4679	711.7323	
824.0988	912.4152	951.1774	
1032.7384	1092.8020	1161.5681	
1198.4526	1268.3723	1295.6050	
1341.6788	1391.2763	1424.2599	
1433.5454	1502.6463	1795.5056	
2928.4787	2943.7326	2983.8399	
3051.1614	3694.2887	3841.1703	
1g^{+}			
C	0.0472736	0.0339488	0.1921087
O	-0.2578791	-0.6053990	1.4118285
H	0.5310586	-0.7610067	1.9432324
C	-1.2230091	-0.0493797	-0.6157099
H	-1.1968175	0.2618935	-1.6610585

O	-1.9716775	-1.1185908	-0.4104687
H	-1.7132244	-1.5200122	0.4494941
C	-2.3299958	1.3835518	-0.0670827
H	-3.3755435	1.0948552	-0.2631595
O	-1.8487030	2.3381192	0.3685219
H	0.3775862	1.0665100	0.3151818
H	0.8110515	-0.5077551	-0.3830545
Frequencies			
42.1936	96.7304	199.4380	
246.6550	255.9701	291.6690	
404.0872	467.8171	659.6267	
753.5646	829.7369	875.9521	
988.1991	1051.4727	1092.6006	
1141.4770	1179.3245	1212.4346	
1239.7782	1369.3807	1420.2667	
1452.0504	1489.9528	1966.2975	
2970.3932	2981.3452	3076.6929	
3088.3057	3501.2056	3807.1777	
1h			
C	0.022977	-0.035386	-0.055043
O	0.001157	0.044955	1.369699
H	0.885652	0.231988	1.695471
C	-1.434817	0.023916	-0.508228
H	-1.948157	-0.845554	-0.063192
O	-2.050937	1.224715	-0.125455
H	-1.856138	1.358048	0.809415
C	-1.524178	-0.172468	-2.007048
H	-1.103502	-1.143018	-2.347124
O	-2.000637	0.605119	-2.785730
H	0.567471	0.810279	-0.485047
H	0.487670	-0.969332	-0.386934
Frequencies			
88.4514	130.2601	242.2968	
260.4635	266.7728	392.7779	
402.9881	484.5618	722.0614	
824.9404	919.3664	953.9746	
1061.9250	1080.1177	1168.3460	
1217.3290	1243.3670	1269.2865	
1327.2312	1415.1040	1425.2662	
1436.0329	1506.5870	1822.9481	
2857.6259	2926.8219	2998.5028	
3043.1377	3786.9908	3831.2525	
1h$^+$			
C	0.015835	-0.182934	0.183405
O	-0.108170	1.119519	0.710481
H	0.645632	1.357269	1.262095

C	-1.336862	-0.490702	-0.407076
H	-1.532564	-1.504276	-0.760208
O	-2.373714	0.056479	0.202406
H	-2.052548	0.806599	0.751662
C	-1.379873	0.274517	-2.136472
H	-2.433504	0.478520	-2.387905
O	-0.392135	0.429000	-2.713640
H	0.808857	-0.275500	-0.560220
H	0.185606	-0.935231	0.966257
Frequencies			
42.0810	96.7329	199.6302	
246.7364	255.8454	291.7169	
404.1521	467.9096	659.6647	
753.6327	829.8535	875.9548	
988.2371	1051.5814	1092.6646	
1141.5903	1179.3119	1212.4144	
1239.7896	1369.3312	1420.2614	
1452.0096	1489.9548	1966.2499	
2970.3453	2981.2676	3076.7213	
3088.2519	3500.9567	3807.2160	

Table S8. Cartesian coordinates (Å) and vibrational frequencies (cm^{-1}) of all identified 1,2,3-propenetriol (**3**) conformational isomers (**3a**–**3i**) and their corresponding cations after adiabatic ionization.

3a			
C	-0.338861	-0.389457	0.096499
C	0.011255	-0.299242	1.549873
C	0.955850	0.445993	2.124868
O	1.831756	1.300687	1.517711
H	1.616049	1.327398	0.573265
H	1.099857	0.414140	3.198409
O	-0.819135	-1.149861	2.263696
H	-0.549090	-1.169151	3.186993
O	0.349223	0.626254	-0.641192
H	0.258768	0.454278	-1.581486
H	-0.073977	-1.384458	-0.279944
H	-1.422833	-0.273569	-0.010684
Frequencies			
52.5190	183.9090	229.7228	
260.1771	325.7663	368.4680	
423.3489	443.9545	586.2709	
624.3272	839.3822	858.8925	
1039.7908	1051.9609	1148.6625	
1160.5478	1222.9858	1247.5201	
1257.9118	1366.5443	1447.9794	
1477.1855	1511.6333	1752.2051	
2983.2496	3009.4654	3156.9544	
3684.2169	3815.6335	3842.9974	
3a^{+}			
C	-0.051729	-0.011488	-0.021955
C	-0.030249	-0.007825	1.474855
C	1.157099	-0.001357	2.228490
O	2.369845	0.001743	1.745979
H	2.438014	-0.001222	0.777920
H	1.130498	0.001743	3.312498
O	-1.191537	-0.010762	2.061876
H	-1.159015	-0.008290	3.033550
O	-1.367042	-0.021356	-0.464427
H	-1.399549	-0.021198	-1.427963
H	0.505343	0.877910	-0.363358
H	0.517184	-0.894885	-0.359458
Frequencies			
54.8773	199.4551	207.5616	
256.9650	323.2486	411.8820	
519.2395	556.0094	616.2982	
618.2700	807.8249	894.1475	

979.5270	1122.8712	1147.2787	
1210.9146	1217.9995	1255.3183	
1357.6293	1396.7152	1435.1330	
1453.3148	1515.2726	1615.6908	
2922.2362	2933.9010	3175.7295	
3688.8487	3713.1196	3802.2460	
3b			
C	-0.087416	-0.283501	0.050266
C	0.056736	-0.235098	1.535024
C	1.142533	0.113844	2.224475
O	2.344329	0.543973	1.724399
H	2.267222	0.736297	0.784404
H	1.163096	0.076294	3.306407
O	-1.131460	-0.605943	2.147662
H	-1.086229	-0.438350	3.094357
O	-0.942400	0.736441	-0.468698
H	-1.785622	0.677379	-0.007409
H	0.872930	-0.150975	-0.446530
H	-0.463182	-1.273768	-0.232040
Frequencies			
54.5240	217.0411	237.0132	
261.3775	283.6274	336.2752	
367.8405	430.6937	575.4211	
622.8355	836.9218	858.3129	
969.2017	1022.9995	1127.2956	
1151.8541	1223.0185	1234.8214	
1334.6604	1357.8826	1397.4297	
1439.3165	1502.7086	1742.7344	
2995.3003	3082.5157	3169.1027	
3804.8353	3807.3842	3810.5152	
3b$^+$			
C	-0.124170	-0.055136	0.065186
C	-0.002243	-0.009931	1.569982
C	1.216964	0.059154	2.269576
O	2.400937	0.127468	1.729989
H	2.419097	0.153097	0.759174
H	1.244249	0.054441	3.354243
O	-1.133132	-0.060027	2.215857
H	-1.059126	-0.029190	3.184801
O	-1.340695	0.429126	-0.396875
H	-2.016975	-0.257275	-0.415673
H	0.659355	0.573030	-0.373113
H	0.086277	-1.088164	-0.250831
Frequencies			
46.3435	193.6052	202.7725	
212.4261	304.1045	414.4045	

525.0807	568.3260	605.5545	
626.6050	810.5312	900.5551	
951.4356	1116.5140	1133.6456	
1203.0778	1216.8056	1337.5432	
1381.3827	1399.9400	1427.7591	
1438.2355	1475.7606	1617.3278	
2961.2637	3020.1642	3167.9860	
3687.0435	3701.2542	3801.6853	
3c			
C	-0.033876	-0.181789	0.075923
C	0.043305	-0.194980	1.568928
C	1.143533	-0.005431	2.293499
O	2.381150	0.160121	1.702952
H	2.880193	0.827800	2.182371
H	1.128143	-0.051285	3.378745
O	-1.190047	-0.458462	2.128439
H	-1.147634	-0.390044	3.087795
O	-0.967913	0.781509	-0.409196
H	-1.812254	0.620809	0.024666
H	0.935204	0.080345	-0.337539
H	-0.302958	-1.184132	-0.279524
Frequencies			
86.0535	203.8260	224.0984	
257.9498	280.0930	332.7434	
353.7555	430.5329	574.4175	
633.4126	813.7156	842.6241	
986.3868	1033.6831	1133.4965	
1155.0686	1208.3655	1243.5633	
1310.8458	1352.4896	1396.4464	
1446.2707	1496.1106	1755.9328	
2983.4618	3118.3484	3133.3308	
3804.2608	3805.9335	3812.5670	
3c$^+$			
C	-0.085436	0.027056	0.111751
C	-0.029057	0.035603	1.616732
C	1.182502	0.015447	2.333147
O	2.297630	-0.004049	1.647455
H	3.094089	-0.014667	2.201699
H	1.213689	0.014273	3.418323
O	-1.174456	0.058845	2.232823
H	-1.123029	0.073337	3.203193
O	-1.328080	0.385301	-0.391954
H	-1.915203	-0.373606	-0.477597
H	0.656208	0.745151	-0.252158
H	0.267991	-0.958232	-0.226357
Frequencies			

71.8069	185.8191	202.0328	
216.2344	310.5642	431.4345	
532.5582	557.9135	611.6380	
625.5829	814.2118	839.3153	
940.8489	1122.5478	1127.0873	
1205.6625	1229.0164	1312.8325	
1352.4127	1375.3545	1414.3017	
1446.2276	1485.5003	1630.9944	
2970.8210	3040.3012	3152.5194	
3691.8778	3723.6746	3805.9271	
3d			
C	0.044398	-0.079276	0.046082
C	0.044430	-0.018988	1.551038
C	1.111122	0.032877	2.346374
O	2.397899	0.159249	1.829871
H	2.988344	-0.449494	2.284989
H	1.024602	0.069436	3.427323
O	-1.240440	0.023958	2.035459
H	-1.235050	0.214461	2.979693
O	1.169210	-0.714716	-0.528235
H	1.955555	-0.387442	-0.075022
H	-0.835163	-0.646216	-0.260363
H	-0.079862	0.939582	-0.346301
Frequencies			
74.7754	230.6976	276.7858	
286.5136	351.6746	372.1197	
417.4800	464.8496	508.6851	
621.5231	787.6731	850.4446	
1002.2763	1074.7201	1130.6828	
1158.8042	1232.5125	1244.0663	
1295.2697	1357.9517	1414.9327	
1457.9392	1497.0217	1747.2411	
2962.2163	3073.2320	3132.5463	
3756.4042	3795.6299	3797.0772	
3d$^+$			
C	0.154109	-0.024371	0.074962
C	0.044012	-0.028645	1.568863
C	1.132591	-0.001543	2.461276
O	2.342434	0.146380	2.004258
H	3.018050	0.150243	2.701416
H	0.971987	-0.087923	3.532468
O	-1.180341	-0.048536	2.026761
H	-1.263483	0.012903	2.993180
O	1.155385	-0.932735	-0.301834
H	1.418780	-0.776453	-1.215304
H	-0.830138	-0.276226	-0.330903

H	0.381659	1.010335	-0.224233
Frequencies			
37.7144	188.0667	200.7789	
217.4957	312.8094	439.2069	
483.1515	569.3090	619.1672	
646.0867	808.8696	878.3171	
985.9515	1099.8404	1143.9491	
1209.1431	1236.3356	1267.1086	
1338.2583	1411.2612	1427.6779	
1468.7399	1496.6507	1646.3884	
2959.6362	3041.4254	3141.5518	
3689.5387	3716.7331	3808.4541	
3e			
C	-0.080114	-0.034920	-0.007799
C	0.008311	-0.114148	1.481673
C	1.107878	0.002078	2.227874
O	2.398533	0.162683	1.796866
H	2.443582	0.142564	0.836022
H	1.049573	-0.054408	3.304818
O	-1.193331	-0.367491	2.117187
H	-1.893961	0.029047	1.584844
O	-1.091295	0.900310	-0.416262
H	-0.820509	1.782961	-0.139963
H	0.882110	0.217555	-0.464250
H	-0.404202	-0.990144	-0.424690
Frequencies			
93.9422	230.6102	245.2306	
262.9493	340.3245	363.5310	
426.4701	478.4616	563.9421	
622.7843	833.6963	893.0017	
961.1381	1012.4081	1122.9070	
1177.4197	1207.7165	1270.1151	
1324.9436	1353.2310	1391.7895	
1418.9944	1492.2905	1753.4813	
3003.5566	3061.8563	3207.5614	
3763.3131	3787.9646	3810.6094	
3e$^+$			
C	-0.028716	0.322163	0.079715
C	0.044898	0.085982	1.563412
C	1.195444	-0.255584	2.290040
O	2.390464	-0.423370	1.794701
H	2.474722	-0.296669	0.836700
H	1.131880	-0.403035	3.360767
O	-1.048664	0.204586	2.253286
H	-1.786727	0.444655	1.646981
O	-1.372925	0.634530	-0.175919

H	-1.539860	0.803562	-1.109858
H	0.648992	1.142501	-0.193257
H	0.297069	-0.583234	-0.450249
Frequencies			
27.2091	172.5991	195.7333	
223.1498	348.4189	416.2608	
527.0098	582.1377	634.3429	
759.6939	811.9309	921.2756	
1005.5396	1101.1668	1148.3149	
1191.3893	1235.0634	1246.0096	
1374.2066	1411.5664	1433.0246	
1470.4082	1497.3047	1648.5978	
2971.3808	2998.5845	3200.8006	
3484.1041	3718.4683	3811.1568	
3f			
C	0.006159	-0.046169	-0.066215
C	0.026149	-0.074157	1.425461
C	1.101033	-0.010318	2.210798
O	2.413469	0.072724	1.830816
H	2.486688	0.150983	0.874437
H	0.995688	-0.054113	3.284573
O	-1.213440	-0.244472	2.014408
H	-1.844185	0.285588	1.511507
O	-0.950714	0.947746	-0.467357
H	-1.221239	0.778450	-1.374128
H	0.991953	0.191212	-0.480112
H	-0.296451	-1.026349	-0.451932
Frequencies			
88.0024	232.0002	242.6610	
260.8931	275.1706	375.1145	
412.5978	445.9788	560.8493	
620.6580	824.1321	895.4552	
999.4268	1017.0275	1129.3079	
1180.7162	1214.3115	1265.1270	
1289.2587	1323.2075	1393.6835	
1441.1128	1499.0100	1758.3282	
2982.0739	3011.5673	3210.3933	
3763.0625	3805.8444	3824.6387	
3f^{+}			
C	0.028990	0.141844	-0.079389
C	0.020029	0.094828	1.424042
C	1.132351	-0.122314	2.251093
O	2.357348	-0.319260	1.848430
H	2.495023	-0.312279	0.888257
H	1.008907	-0.135706	3.326656
O	-1.114291	0.269389	2.031255

H	-1.819936	0.411689	1.359070
O	-1.304356	0.379700	-0.447275
H	-1.417978	0.434121	-1.402677
H	0.703178	0.941508	-0.415160
H	0.405844	-0.812394	-0.472045
Frequencies			
25.2540	172.1684	195.7067	
223.1737	348.3702	416.2767	
527.0271	582.2006	634.3329	
759.8466	811.9237	921.2906	
1005.5200	1101.2591	1148.4195	
1191.3907	1235.1624	1246.0587	
1374.2434	1411.6103	1433.0618	
1470.4684	1497.3317	1648.6322	
2971.3798	2998.5416	3200.7346	
3483.7840	3718.3580	3811.2799	
3g			
C	-0.050169	-0.096290	0.002026
C	0.056997	-0.013055	1.493513
C	1.154424	-0.097149	2.246389
O	2.442948	-0.275339	1.829194
H	2.431208	-0.392570	0.867223
H	1.085099	-0.020419	3.325069
O	-1.209370	0.184329	2.022776
H	-1.146807	0.325964	2.972391
O	1.199204	-0.510375	-0.560700
H	1.176330	-0.389025	-1.512811
H	-0.841118	-0.809830	-0.253228
H	-0.346259	0.881412	-0.395961
Frequencies			
51.9781	181.2192	229.0426	
260.1672	325.6544	368.4335	
423.3480	443.9329	586.8834	
624.3538	839.4260	858.9135	
1039.6276	1052.1954	1148.7891	
1160.5729	1222.6693	1247.5567	
1258.0944	1366.6336	1448.0655	
1477.1528	1511.6818	1752.2650	
2983.0965	3009.4129	3156.9341	
3683.7503	3815.8452	3844.0251	
3g$^+$			
C	-0.045988	-0.072973	-0.011909
C	0.013710	0.019786	1.481304
C	1.173645	-0.136694	2.263399
O	2.347520	-0.383134	1.784540
H	2.305969	-0.444403	0.790816

H	1.127377	-0.053304	3.345232
O	-1.150342	0.269161	2.028604
H	-1.141208	0.334621	2.997480
O	1.254870	-0.342885	-0.505919
H	1.268334	-0.412651	-1.466904
H	-0.758057	-0.863587	-0.275111
H	-0.443344	0.873716	-0.395652

Frequencies		
46.2151	183.9642	247.8443
314.3832	389.0325	455.4094
457.4579	552.3416	637.6624
804.6696	813.1055	989.9491
991.2901	1086.5968	1166.8168
1220.6823	1249.1237	1293.2982
1396.0938	1406.2106	1456.6231
1472.0722	1523.4325	1629.6435
3000.5974	3034.5015	3152.2686
3232.6435	3704.0756	3808.4919

3h

C	-0.078880	-0.085107	0.049902
C	-0.018857	-0.187897	1.541707
C	1.082946	-0.061249	2.277873
O	2.321896	0.105183	1.690643
H	2.926804	0.485351	2.332002
H	1.052087	-0.160086	3.355278
O	-1.211571	-0.487233	2.160020
H	-1.916847	-0.185337	1.572819
O	-1.206981	0.710201	-0.357089
H	-1.018346	1.632211	-0.152927
H	0.856913	0.306655	-0.346786
H	-0.258006	-1.066928	-0.392612

Frequencies		
92.3649	189.2598	219.6722
268.5882	313.1333	335.5377
435.5077	504.5139	565.7946
627.6391	836.6820	848.7737
967.7978	1015.7432	1122.3882
1184.1662	1190.8996	1265.2235
1318.4951	1353.8424	1386.0091
1424.5854	1495.8506	1777.1211
3041.1564	3093.1691	3170.9137
3749.3316	3798.0727	3843.3791

3h^{+}

C	-0.067329	0.234742	0.139270
C	-0.007983	0.039287	1.623851
C	1.172784	-0.147031	2.355706

O	2.305616	-0.150941	1.698234
H	3.078612	-0.284671	2.268566
H	1.146822	-0.283214	3.430394
O	-1.119026	0.040378	2.290827
H	-1.864022	0.179559	1.660525
O	-1.434297	0.379512	-0.154726
H	-1.593473	0.512335	-1.095341
H	0.525160	1.117523	-0.130821
H	0.388296	-0.631714	-0.355653
Frequencies			
54.3830	166.2093	198.1291	
240.7088	342.9188	440.5450	
535.9035	585.7846	634.8060	
772.4953	822.3528	867.6665	
999.3535	1100.7190	1152.2035	
1191.0586	1233.5515	1247.5112	
1314.3062	1413.7513	1444.3076	
1471.9097	1499.7051	1667.0374	
2993.1685	3020.8931	3183.5630	
3470.3938	3729.8028	3817.7674	
3i			
C	-0.024968	-0.116166	-0.046427
C	0.033356	-0.084953	1.447626
C	1.129538	0.165266	2.158289
O	2.353385	0.348920	1.544220
H	2.912960	0.887053	2.109782
H	1.111044	0.150989	3.240326
O	-1.133658	-0.415224	2.094147
H	-1.857820	-0.156023	1.509134
O	-1.259079	0.516455	-0.431761
H	-1.471202	0.267855	-1.335006
H	0.836242	0.403247	-0.466407
H	-0.018994	-1.153901	-0.399690
Frequencies			
95.0962	204.0867	220.9829	
243.0051	285.7453	315.4741	
431.5786	479.9351	559.9627	
628.6571	830.3731	840.3345	
1008.7538	1029.3151	1126.4526	
1175.9295	1216.8824	1245.3886	
1277.4917	1328.4358	1392.1692	
1444.1678	1505.8525	1782.0097	
2986.9253	3076.4475	3172.0440	
3746.9381	3834.3462	3836.7360	
3i^{+}			
C	-0.045980	0.039749	-0.067719

C	-0.008127	0.052394	1.430221
C	1.161435	0.150061	2.196253
O	2.303509	0.235251	1.560594
H	3.067886	0.299770	2.154108
H	1.119907	0.154706	3.279025
O	-1.128385	-0.032398	2.076047
H	-1.863898	-0.095156	1.422888
O	-1.407845	-0.074258	-0.396751
H	-1.554372	-0.078147	-1.348718
H	0.411087	0.962240	-0.446377
H	0.555587	-0.800694	-0.435338
Frequencies			
54.7999	166.0912	198.1326	
240.6708	342.9575	440.5322	
535.9247	585.8286	634.8591	
772.0732	822.5033	867.6581	
999.3255	1100.7885	1152.2479	
1191.1173	1233.6010	1247.5015	
1314.3053	1413.7772	1444.3351	
1471.9149	1499.7831	1667.2571	
2993.0462	3020.7234	3183.6974	
3471.2416	3729.7514	3817.8145	

Table S9. Cartesian coordinates (Å) and vibrational frequencies (cm^{-1}) of the only dihydroxyacetone (**4**) structure identified and its corresponding cation after adiabatic ionization.

4			
C	-0.010607	0.000000	0.006043
C	-0.004386	0.000000	1.518771
C	1.318199	0.000000	2.253039
O	1.148869	0.000000	3.644502
H	0.194327	0.000000	3.811078
H	1.891423	-0.880173	1.935986
H	1.891423	0.880173	1.935986
O	-1.049440	0.000000	2.136784
O	-1.311510	0.000000	-0.515968
H	-1.917367	0.000000	0.240230
H	0.543395	0.880173	-0.343512
H	0.543395	-0.880173	-0.343512
Frequencies			
62.1927	99.2254	215.3045	
341.3890	357.4180	382.9438	
415.9178	480.8016	687.3803	
844.3662	879.8292	1031.5704	
1075.0716	1122.3698	1152.8258	
1234.3889	1283.1762	1299.7323	
1301.0259	1434.4536	1439.7661	

1476.6430	1485.4094	1763.1351	
2981.8314	2994.2921	2995.9580	
3010.7349	3696.2538	3703.0490	
4^{+}			
C	0.062116	0.251948	-0.031719
C	0.006908	-0.088553	1.562574
C	1.552256	-0.219262	2.181840
O	1.655170	0.407793	3.369981
H	1.357831	-0.134281	4.116347
H	1.682788	-1.306015	2.196070
H	2.187024	0.273192	1.447855
O	-0.947773	-0.234507	2.210068
O	-1.161958	0.311472	-0.595283
H	-1.472946	-0.542606	-0.928010
H	0.522681	1.243310	-0.033466
H	0.743623	-0.503134	-0.436581
Frequencies			
22.2913	102.0791	201.5623	
274.3595	307.6176	356.6723	
451.5312	469.3014	509.6788	
602.8849	611.7418	888.9741	
968.3665	1156.0347	1184.2317	
1199.9090	1219.0315	1293.9588	
1313.7138	1382.9606	1391.1155	
1470.8087	1485.5274	1942.0126	
3014.0166	3021.7269	3086.1517	
3128.6461	3729.4329	3746.9854	