Electronic Supplementary Material (ESI) for Faraday Discussions.

Supplementary Material

Probing the dynamics of the photo-induced decarboxylation of neutral and ionic pyruvic acid

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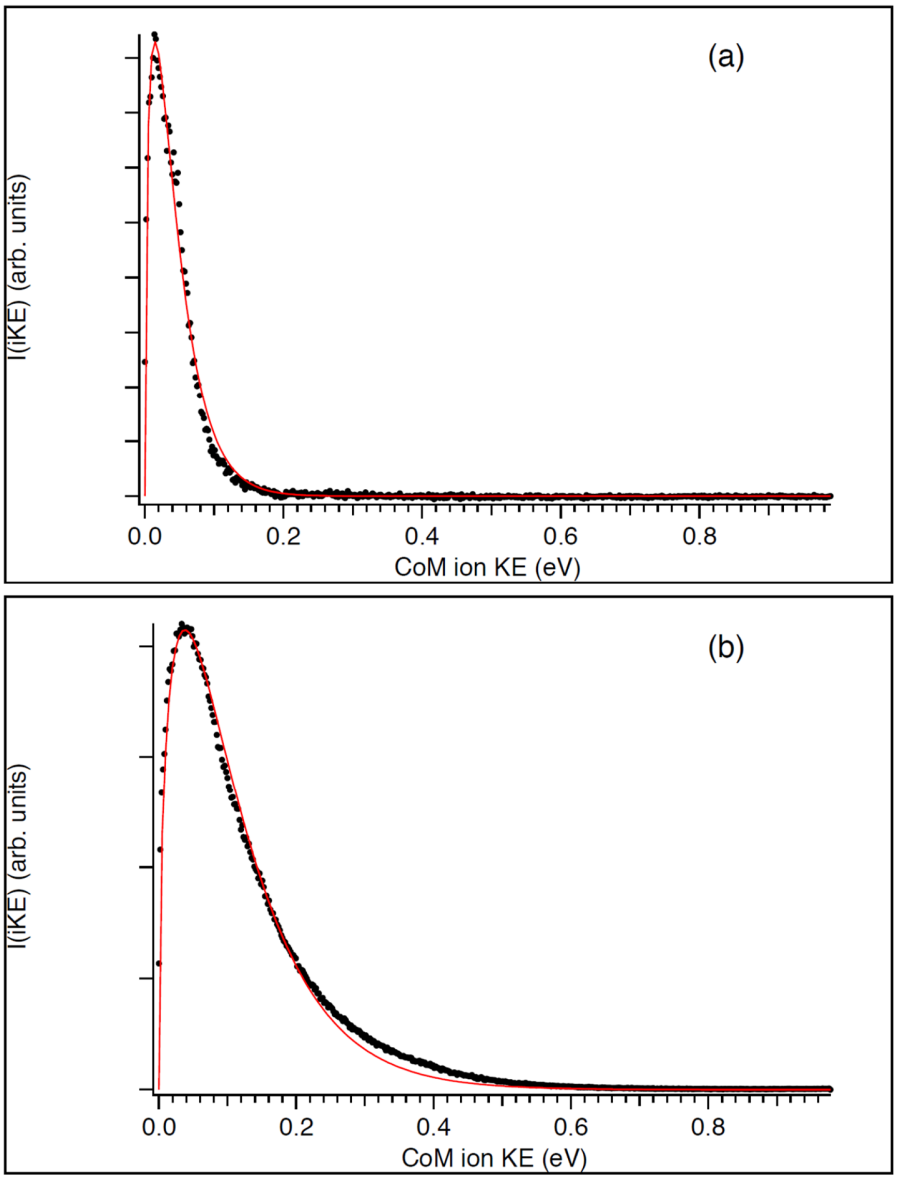


Figure S1: Ion kinetic energy distributions for fragments m/z 87 (a) and m/z 43 (b). The energy axis is given in center of mass assuming parent masses of m/z 176 (PA dimer) and m/z 88 for (a) and (b) respectively. The black points represent the experimental data while the red curves are the result of a fit assuming a Boltzmann distribution with translational temperatures of 330K and 876K for (a) and (b). The good agreement with a Boltzmann distribution points to a statistical fragmentation as opposed to a direct dissociation from a repulsive state. Note that a bad fitting is obtained for m/z = 87 fragment is coming from PA^+ monomer. CoM is for center of mass.

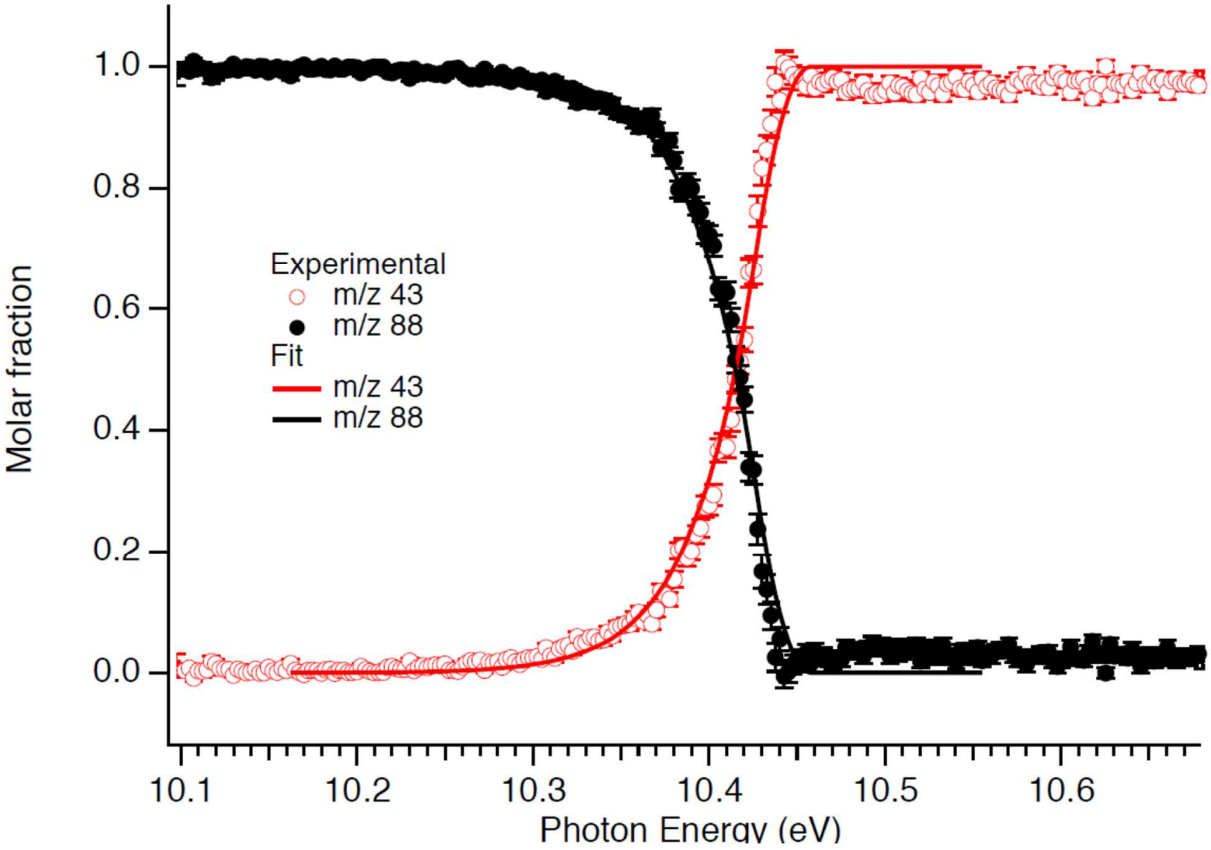


Figure S2: Breakdown diagram showing the branching ratio of parent (m/z 88) and fragment (m/z 43) ions as a function of photon energy. Because the ratios are obtained from the mass selected TPES curves, the photoelectron takes no energy and the photon energy equals the energy deposited into the molecule. The solid and open circles represent the experimental data while the solid lines are the result of a statistical model which considers the initial thermal energy of the molecule (see main text for details). The temperature defining this thermal energy, as well as the appearance energy of the m/z 43 fragment at 0K are varied and extracted using a least squared fit to the data.

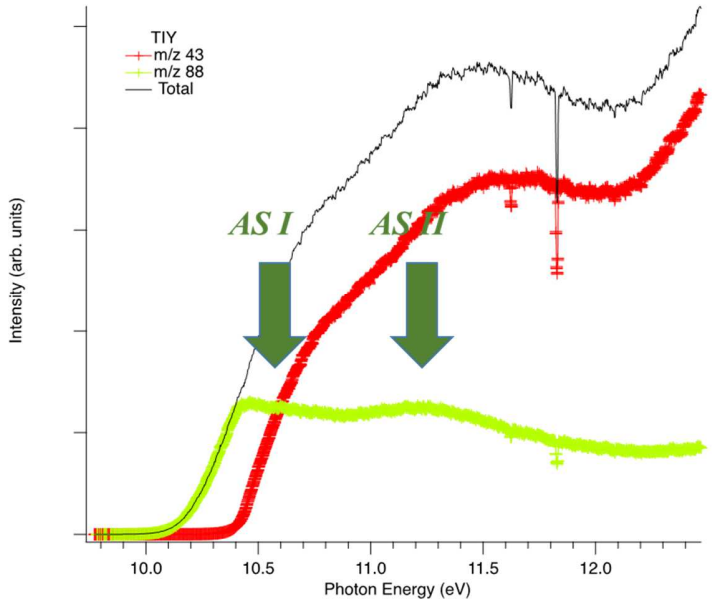
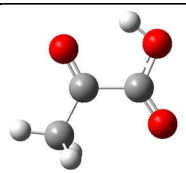
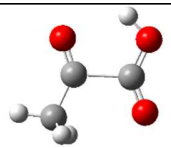
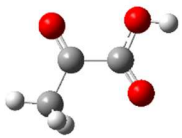
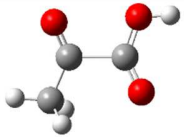
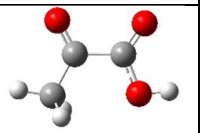
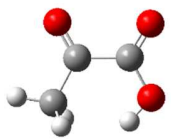
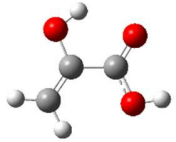
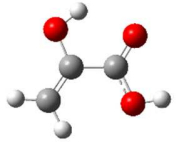
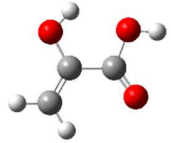
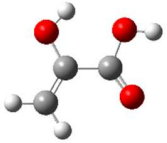


Figure S3: Total ion yield (TIY) of Tc pyruvic acid isomer and ion yield of m/z 43 and 88.

Table S1: Total energies (in Hartree) of Pyruvic acid and the resulting cation. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. PBE0 computations correspond to optimization and the other computations are single point computations. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S18 and S20, respectively.

	Tc	Tc^+	Tt	Tt^+	Ct
					
PBE0/aug-cc-pVDZ	-342.086476504	-341.724768314	-342.081324740	-341.726522737	-342.078476602
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	185.84	178.80	185.10	178.97	184.87
(R)CCSD(T)-F12/cc-pVTZ-F12	-342.04898277	-341.67769851	-342.04462661	-341.67835633	-342.04202977
(R)CCSD(T,fc)/cc-pwCVTZ	-342.23182247	-341.86720520	-342.22750924	-341.86783717	-342.22480717
(R)CCSD(T,full)/cc-pwCVTZ	-341.92772794	-341.56323818	-341.92344888	-341.56412647	-341.92075582
(R)CCSD(T)/cc-pVTZ	-341.90541494	-341.54117241	-341.90119356	-341.54187799	-341.89850796
(R)CCSD(T)cc-pVTZ-DK	-341.88955326	-341.52529570	-341.88532564	-341.52601634	-341.88263860
	Cc	enolPACc	$enolPACc^+$	enolPATc	$enolPATc^+$
					
PBE0/aug-cc-pVDZ	342.068238100	-342.077856035	-341.741445179	-342.072898088	-341.737598714
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	183.06	189.06	185.93	187.96	185.70
(R)CCSD(T)-F12/cc-pVTZ-F12	-342.03191335	-342.03974625	-341.69296111	-342.03539086	-341.68952301
(R)CCSD(T,fc)/cc-pwCVTZ	-342.21449512	-342.22162304	-341.88096760	-342.21739421	-341.87737596

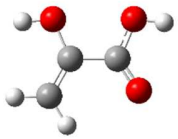
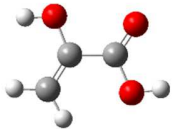
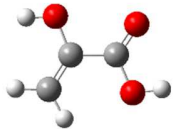
(R)CCSD(T,full)/cc-pwCVTZ	-341.91046303	-341.91730928	-341.57717551	-341.91309781	-341.57358080
(R)CCSD(T)/cc-pVTZ	-341.88813825	-341.89520339	-341.55533006	-341.89097460	-341.55172501
(R)CCSD(T)cc-pVTZ-DK	-341.87227606	-341.87934374	-341.53950723	-341.87511680	-341.53590112
	enolPATt	enolPACt	enolPACt $^{+}$		
					
PBE0/aug-cc-pVDZ	-342.068778205	-342.068291547	-341.726442871		
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	187.89	187.71	184.81		
(R)CCSD(T)-F12/cc-pVTZ-F12	-342.03142836	-342.03110252	-341.67886667		
(R)CCSD(T,fc)/cc-pwCVTZ	-342.21348412	-342.21298144	-341.86663954		
(R)CCSD(T,full)/cc-pwCVTZ	-341.90921906	-341.90870646	-341.56290703		
(R)CCSD(T)/cc-pVTZ	-341.88712025	-341.88661792	-341.54108116		
(R)CCSD(T)cc-pVTZ-DK	-341.87125975	-341.87076084	-341.52525843		

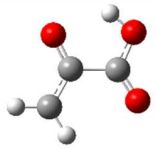
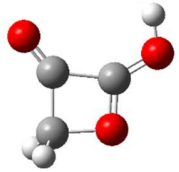
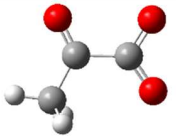
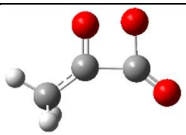
Table S2: relative energies (E_r, eV) of Pyruvic acid with respect to the Tc isomer ground state. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. ΔCV and ΔSR are for core valence and scalar relativistic effects.

	Tc	Tt	Ct	Cc	enolPACc	enolPATc	enolPATt	enolPACt
E_r(PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12)	0	0.119	0.189	0.464	0.251	0.370	0.478	0.487
ΔCV	0	-0.000929814	-0.001174988	-0.0017	0.005965555	0.005493165	0.00464036	0.004910297
ΔSR	0	0.000169799	0.000208984	0.0000139	-0.0000552391	-0.00010558	-0.0000321095	-0.000125172
ΔZPVE	0	-0.00766956	-0.0100533	-0.0288127	0.033373	0.021972	0.021247	0.019381
E_r (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12/cc-pVTZ-F12 +ΔCV+ΔSR+ΔZPVE (SP))	0	0.110	0.178	0.434	0.291	0.397	0.504	0.511

Table S3: Relative energies (Er, eV) of Pyruvic acid cation with respect to the Tc^+ isomer ground state. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. ΔCV and ΔSR are for core valence and scalar relativistic effects.

	Tc^+	Tt^+	enolPACc$^+$	enolPATc$^+$	enolPACt$^+$
E_r(PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12)	0	-0.018	-0.415	-0.322	-0.032
ΔCV	0	-0.006974826	-0.00476009	-0.004676551	-0.006381345
ΔSR	0	-0.000409804	-0.00146615	-0.001437306	-0.001468871
ΔZPVE	0	0.0017619	0.073897	0.07151	0.062289
E_r (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12 +ΔCV+ΔSR+ΔZPVE (SP))	0	-0.024	-0.348	-0.256	0.023

Table S4: Total energies (in Hartree) of the $(H + X)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. PBE0 computations correspond to optimization and the other computations are single point computations. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

	H	CH_2-CO-CO_2H	CH_2-CO-CO_2H^+	CH_3-CO-CO_2	CH_3-CO-CO_2^+
					
PBE0/aug-cc-pVDZ	-0.5006506	-341.432017372	-341.125342721	-341.400558850	-341.013858913
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	0	153.01	161.11	146.96	151.73
(R)CCSD(T)-F12/cc-pVTZ-F12	-0.49994621	-341.38664607	-341.08018252	-341.30942010	-340.96849445
(R)CCSD(T,fc)/cc-pwCVTZ	-0.49980981	-341.57067566	-341.27001292	-341.49427191	-341.15919882
(R)CCSD(T,full)/cc-pwCVTZ	-0.49980981	-341.26681262	-340.96652100	-341.18861941	-340.85601276
(R)CCSD(T)/cc-pVTZ	-0.49980981	-341.24457512	-340.94435547	-341.16691727	-340.83369349
(R)CCSD(T)cc-pVTZ-DK	-0.49980981	-341.22871105	-340.92856221	-341.15166991	-340.81780522
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	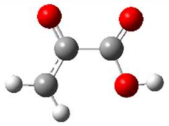		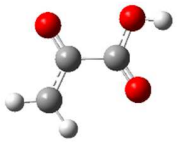		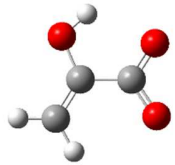
PBE0/aug-cc-pVDZ	-341.423995565		-341.426983789	-341.124678769	-341.395330417
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	151.45		151.94	160.62	150.55

(R)CCSD(T)-F12/cc-pVTZ-F12	-341.37950804		-341.38216726	-341.07974919	-341.29231408
(R)CCSD(T,fc)/cc-pwCVTZ	-341.56344112		-341.56625806	-341.26979519	-341.47212923
(R)CCSD(T,full)/cc-pwCVTZ	-341.25961196		-341.26242668	-340.96630798	-341.16802682
(R)CCSD(T)/cc-pVTZ	-341.23746689		-341.24024583	-340.94421458	-341.14545029
(R)CCSD(T)cc-pVTZ-DK	-341.22159699		-341.22437580	-340.92841929	-341.12953002
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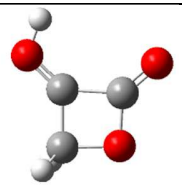
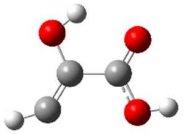
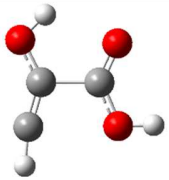
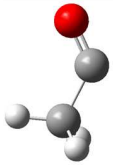
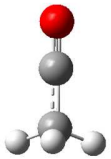
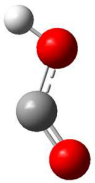
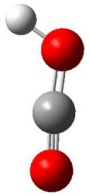
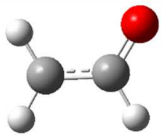
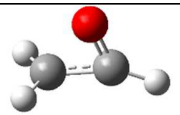
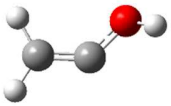
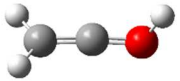
					
PBE0/aug-cc-pVDZ	-341.104348534	-341.388420234	-341.058548012		
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	159.38	153.52	150.29		
(R)CCSD(T)-F12/cc-pVTZ-F12	-341.05663689	-341.34397590	-341.01497221		
(R)CCSD(T,fc)/cc-pwCVTZ	-341.24591947	-341.52741355	-341.20310189		
(R)CCSD(T,full)/cc-pwCVTZ	-340.94240928	-341.22342643	-340.89942164		
(R)CCSD(T)/cc-pVTZ	-340.92028867	-341.20129760	-340.87713063		
(R)CCSD(T)cc-pVTZ-DK	-340.90448484	-341.18541638	-340.86128181		

Table S5: Calculated and measured appearance energies (AEs in eV) of the $(H + X)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. ΔCV and ΔSR are for core-valence and scalar relativistic effects. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

m/z	87					1					
	CH_2-CO-CO_2H^+ + H	CH_2-CO-CO_2H-2 $^+$ + H	CH_2-COH-CO_2^+ + H	CH-COH-CO_2H^+ + H	CH_3-CO-CO_2^+ + H	CH_2-CO-CO_2H + H^+	CH_2-COH-CO_2 + H^+	CH_3-CO-CO_2 + H^+	CH-COH-CO_2H + H^+	CH_2-CO-CO_2H-1 + H^+	CH_2-CO-CO_2H-2 + H^+
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 / cc-pVTZ-F12)	12.758	12.770	13.399	14.533	15.797	18.023	19.184	20.124	19.184	18.217	18.145
ΔCV	-0.016397862	-0.016526027	-0.0159	-0.011273139	-0.02472	-0.0063	-0.00292	0.042395	-0.002922776	-0.007221089	-0.00716068
ΔSR	-0.001861804	-0.001806565	-0.00157	-0.000349939	0.000724	6.5E-05	0.000532	-0.01672	0.000531711	0.000223678	0.000227215
ΔZPVE	-0.256308	-0.2613869	-0.2742386	-0.3684499	-0.3535253	-0.3402591	-0.3349733	-0.4029629	-0.3349733	-0.3564273	-0.351349
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12 + ΔCV + ΔSR + ΔZPVE (SP))	12.484	12.490	13.107	14.153	15.420	17.677	18.847	19.747	18.847	17.854	17.787

Table S6: Total energies (in Hartree) of the $(CH_3CO + HOCO)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. PBE0 computations correspond to optimization and the other computations are single point computations. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

	CH_3CO	CH_3CO^+	HOCO	$HOCO^+$
				
PBE0/aug-cc-pVDZ	-153.025794052	-152.766167246	-188.928465476	-188.625909802
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	111.61	115.17	54.951	56.319
(R)CCSD(T)-F12/cc-pVTZ-F12	-152.99792146	-152.74339388	-188.91661008	-188.61952009
(R)CCSD(T,fc)/cc-pwCVTZ	-153.09510820	-152.84551662	-189.00324885	-188.71221011
(R)CCSD(T,full)/cc-pwCVTZ	-152.94555926	-152.69588137	-188.84925360	-188.55795002
(R)CCSD(T)/cc-pVTZ	-152.93574208	-152.68578339	-188.83641046	-188.54499963
(R)CCSD(T)cc-pVTZ-DK	-152.92958433	-152.67969359	-188.82656346	-188.53527196
	CH_2COH	$C_2H_3O^+$	$CH_2C\text{-}OH$	$CH_2C\text{-}OH^+$
				
PBE0/aug-cc-pVDZ	-153.017159781	-152.680884388	-152.979195667	-152.7039209
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	110.31	116.49	111.28	111.94

(R)CCSD(T)-F12/cc-pVTZ-F12	-152.98678057	-152.65528742	-152.94945039	-152.41276303
(R)CCSD(T,fc)/cc-pwCVTZ	-153.08384131	-152.75603239	-153.04603888	-152.51136496
(R)CCSD(T,full)/cc-pwCVTZ	-152.93431005	-152.60692325	-152.89630230	-152.36154767
(R)CCSD(T)/cc-pVTZ	-152.92480241	-152.59744500	-152.88674741	-152.35125870
(R)CCSD(T)cc-pVTZ-DK	-152.91868223	-152.59133340	-152.88062093	-152.41276303

Table S7: Calculated and measured appearance energies (AEs in eV) of the $(CH_3CO + HOCO)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. ΔCV and ΔSR are for core valence and scalar relativistic effects. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

m/z	43			45		
	CH_3CO^++ HOCO	$C_2H_3O^+$+ HOCO	$CH_2C\text{-}OH^+$+ HOCO	CH_3CO + $HOCO^+$	CH_2COH + $HOCO^+$	$CH_2C\text{-}OH$ + $HOCO^+$
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12)	10.585	12.982	19.582	11.743	12.046	13.062
ΔCV	-0.01263	-0.026943096	-0.007673343	-0.00777	-0.008249952	-0.002662908
ΔSR	0.002044	0.002637329	-1.837286789	0.000646	-0.000376334	-0.000204902
ΔZPVE	-0.162916	-0.14923516	-0.1963926	-0.18563448	-0.19910804	-0.18905469
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12 +ΔCV+ΔSR+ΔZPVE (SP))	10.411	12.809	17.540	11.550	11.838	12.870

Table S8: Total energies (in Hartree) of the $(CH_3 + COCOOH)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. PBE0 computations correspond to optimization and the other computations are single point computations. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

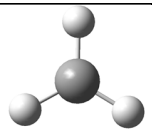
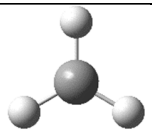
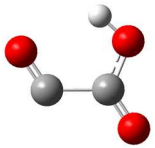
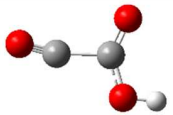
	CH_3	CH_3^+	COCOOH	$COCOOH^+$
				
PBE0/aug-cc-pVDZ	-39.7868782203	-39.4220439689	-302.142986372	-301.848106430
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	77.089	82.270	79.128	82.215
(R)CCSD(T)-F12/cc-pVTZ-F12	-39.77543764	-39.41641199	-302.08231892	-301.82859162
(R)CCSD(T,fc)/cc-pwCVTZ	-39.81103253	-39.45360820	-302.23031931	-301.98463815
(R)CCSD(T,full)/cc-pwCVTZ	-39.76275605	-39.40604667	-301.97450691	-301.72957640
(R)CCSD(T)/cc-pVTZ	-39.76080467	-39.40419450	-301.95331057	-301.70883029
(R)CCSD(T)cc-pVTZ-DK	-39.75999697	-39.40338213	-301.93823489	-301.69376183

Table S9: Calculated and measured appearance energies (AEs in eV) of the $(CH_3 + COCOOH)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. ΔCV and ΔSR are for core valence and scalar relativistic effects. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

m/z	73	15
	$CH_3 + COCOOH^+$	$CH_3^+ + COCOOH$
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12)	12.108	14.973
ΔCV	-0.02058	-0.01961
ΔSR	0.000394	0.000718
ΔZPVE	-0.27502633	-0.25332354
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12 +ΔCV+ΔSR+ΔZPVE (SP))	11.813	14.701

Table S10: Total energies (in Hartree) of the (OH + CH_3-CO-CO)$^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. PBE0 computations correspond to optimization and the other computations are single point computations. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

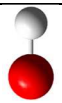
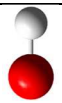
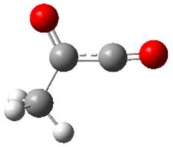
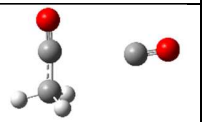
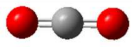
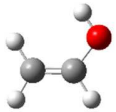
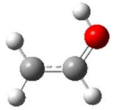
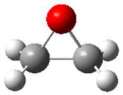
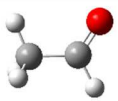
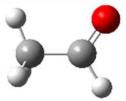
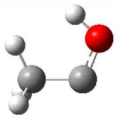
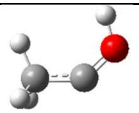
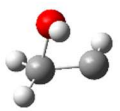
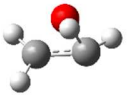
	OH	OH^+	CH_3-CO-CO	CH_3-CO-CO^+
				
PBE0/aug-cc-pVDZ	-75.6673072792	-75.1891550277	-266.246018965	-265.975308104
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	21.47	17.40	137.15	132.03
(R)CCSD(T)-F12/cc-pVTZ-F12	-75.67033505	-75.19212473	-266.19661144	-265.95209795
(R)CCSD(T,fc)/cc-pwCVTZ	-75.69523600	-75.22593813	-266.35617899	-266.11899158
(R)CCSD(T,full)/cc-pwCVTZ	-75.64248265	-75.17358117	-266.10515783	-265.86867635
(R)CCSD(T)/cc-pVTZ	-75.63765847	-75.16906305	-266.08766511	-265.85035505
(R)CCSD(T)cc-pVTZ-DK	-75.63304823	-75.16451897	-266.07626114	-265.83890404

Table S11: Calculated and measured appearance energies (AEs in eV) of the $(OH + CH_3\text{-}CO\text{-}CO)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. ΔCV and ΔSR are for core valence and scalar relativistic effects. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

m/z	71	17
	$CH_3\text{-}CO\text{-}CO^+ + OH$	$CH_3\text{-}CO\text{-}CO + OH^+$
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12)	11.607	17.966
ΔCV	-0.02792	-0.01949
ΔSR	0.005431	0.00235
ΔZPVE	-0.33516	-0.32428
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12 +ΔCV+ΔSR+ΔZPVE (SP))	11.249	17.625

Table S12: Total energies (in Hartree) of the $(CO_2 + X)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. PBE0 computations correspond to optimization and the other computations are single point computations. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

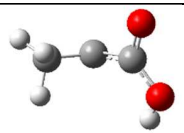
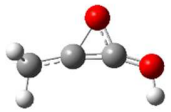
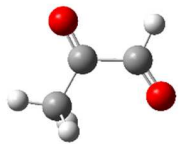
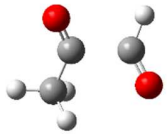
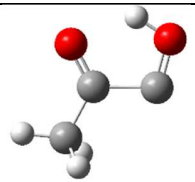
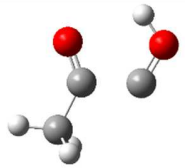
	CO_2	CO_2^+	CH_2-CH-OH	CH_2-CH-OH^+	CH_2-OCH_2	CH_2-OCH_2^+
						
PBE0/aug-cc-pVDZ	-188.414157458	-187.909219161	-153.657329474	-153.325148015	-153.634153504	-153.252816012
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	30.86	24.51	147.09	146.23	149.34	140.56
(R)CCSD(T)-F12/cc-pVTZ-F12	-188.40586081	-187.89564368	-153.63453086	-153.29211150	-153.60780562	-153.21572392
(R)CCSD(T,fc)/cc-pwCVTZ	-188.49484433	-187.99187430	-153.72966261	-153.39211567	-153.70239134	-153.31693194
(R)CCSD(T,full)/cc-pwCVTZ	-188.34054828	-187.83821391	-153.57970301	-153.24272138	-153.55272689	-153.16773485
(R)CCSD(T)/cc-pVTZ	-188.32719079	-187.82532512	-153.57044196	-153.23352843	-153.54346032	-153.15873467
(R)CCSD(T)cc-pVTZ-DK	-188.31738266	-187.81554969	-153.56413281	-153.22745570	-153.53733301	-153.15261041
	CH_3-CH-O	CH_3-CH-O^+	CH_3-C-O-H	CH_3-C-O-H^+	CH- CH_2-OH	CH- CH_2-OH^+
						
PBE0/aug-cc-pVDZ	-153.672427821	-153.304140477	-153.586719850	-153.294615393	-153.523765978	-153.247881834
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	143.46	137.15	139.70	139.60	143.13	144.45

(R)CCSD(T)-F12/cc-pVTZ-F12	-153.64953585	-153.26990680	-153.56321018	-153.26089944	-153.50022622	-153.21563131
(R)CCSD(T,fc)/cc-pwCVTZ	-153.74544265	-153.37135943	-153.65864490	-153.36100916	-153.59492362	-153.31535212
(R)CCSD(T,full)/cc-pwCVTZ	-153.59568130	-153.22194056	-153.50943806	-153.21152149	-153.44610643	-153.16621022
(R)CCSD(T)/cc-pVTZ	-153.58610501	-153.21262205	-153.50001688	-153.20220369	-153.43695504	-153.15724598
(R)CCSD(T)cc-pVTZ-DK	-153.57999295	-153.20651803	-153.49389388	-153.19612142	-153.43084580	-153.15116518

Table S13: Calculated and measured appearance energies (AEs in eV) of the $(CO_2 + X)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. ΔCV and ΔSR are for core valence and scalar relativistic effects. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

m/z	44					44				
	CH_2-CH-$OH^+ + CO_2$	CH_3-CH-$O^+ + CO_2$	CH_3-C-O-$H^+ + CO_2$	CH- CH_2-$OH^+ + CO_2$	CH_2-$OCH_2^+ + CO_2$	CH_3-CH-O + CO_2^+	CH_2-CH-OH + CO_2^+	CH_2-OCH_2 + CO_2^+	CH_3-C-O-H + CO_2^+	CH- CH_2-OH + CO_2^+
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12)	9.551	10.156	10.401	11.633	11.630	13.709	14.118	14.845	16.058	17.772
ΔCV	-0.011	-0.01033	-0.00846	-0.01787	-0.01636	-0.01831	-0.01291	-0.02094	-0.0334	-0.044
ΔSR	0.000522	0.001373	0.000782	0.000742	0.001924	0.000702	0.006065	0.001117	0.001	0.000626
ΔZPVE	-0.0906874	-0.184795	-0.1594025	-0.1091358	-0.1494528	-0.1852095	-0.1475872	-0.1242676	-0.2241792	-0.18863
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12 +ΔCV+ΔSR+ΔZPVE (SP))	9.450	9.962	10.234	11.506	11.466	13.506	13.963	14.701	15.802	17.540

Table S14: Total energies (in Hartree) of the $(O + X)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. PBE0 computations correspond to optimization and the other computations are single point computations. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

	O	O^+	CH_3-C-CO_2H	CH_3-C-CO_2H^+
				
PBE0/aug-cc-pVDZ	-75.0002110695	-74.4911691344	-266.796422782	-266.507836191
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	0	0	164.30	167.96
(R)CCSD(T)-F12/cc-pVTZ-F12	-75.00069988	-74.50232615	-266.75291927	-266.45328204
(R)CCSD(T,fc)/cc-pwCVTZ	-75.03119932	-74.54085749	-266.90921306	-266.61635367
(R)CCSD(T,full)/cc-pwCVTZ	-74.97865207	-74.48877120	-266.65861371	-266.36544495
(R)CCSD(T)/cc-pVTZ	-74.97382933	-74.48437583	-266.64152965	-266.34850672
(R)CCSD(T)cc-pVTZ-DK	-74.96911772	-74.47975951	-266.63010453	-266.33712177
	CH_3-CO-CHO	CH_3-CO-CHO^+	CH_3-CO-COH	CH_3-CO-COH^+
				
PBE0/aug-cc-pVDZ	-266.887311061	-266.538886226	-266.808614389	-266.498889227

ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	168.79	162.11	167.65	164.12
(R)CCSD(T)-F12/cc-pVTZ-F12	-266.85019955	-266.49336390	-266.77078825	-266.45150303
(R)CCSD(T,fc)/cc-pwCVTZ	-267.00855861	-266.65760146	-266.92901488	-266.61442512
(R)CCSD(T,full)/cc-pwCVTZ	-266.75755826	-266.40704750	-266.67861817	-266.36413980
(R)CCSD(T)/cc-pVTZ	-266.74045013	-266.38982830	-266.66165740	-266.34714014
(R)CCSD(T)cc-pVTZ-DK	-266.72905291	-266.37842741	-266.65024884	-266.33575280

Table S15: Calculated and measured appearance energies (AEs in eV) of the $(O + X)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. ΔCV and ΔSR are for core valence and scalar relativistic effects. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

m/z	72			16		
	CH_3-CO-CHO^+ + O	CH_3-C-CO_2H^+ + O	CH_3-CO-COH^+ + O	CH_3-CO-CHO + O^+	CH_3-CO-COH + O^+	CH_3-C-CO_2H + O^+
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12)	15.100	16.191	16.239	18.952	21.112	21.599
ΔCV	-0.02703	-0.01738	-0.03434	-0.02743	-0.04385	-0.03834
ΔSR	0.006825	0.006391	0.006456	0.004132	0.004441	0.004892
ΔZPVE	-0.2459442	-0.1853132	-0.225112	-0.1767108	-0.1885261	-0.2232464
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12 +ΔCV+ΔSR+ΔZPVE (SP))	14.834	15.995	15.986	18.752	20.885	21.342

Table S16: Total energies (in Hartree) of the $(H_2C_2O + H_2CO_2)^+$ and $(H_2C_2O + CO_2 + H_2)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. PBE0 computations correspond to optimization and the other computations are single point computations. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

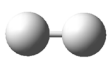
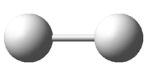
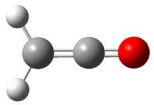
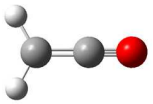
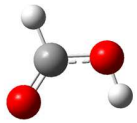
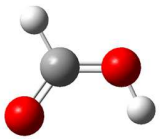
	H_2	H_2^+	H_2C_2O	$H_2C_2O^+$	H_2CO_2	$H_2CO_2^+$
						
PBE0/aug-cc-pVDZ	-1.16388851188	-0.608136156337	-152.446776790	-152.096384536	-189.590222020	-189.182538255
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	24.836	11.571	82.141	81.232	88.093	83.710
(R)CCSD(T)-F12/cc-pVTZ-F12	-1.17380645	-0.60203438	-152.41949304	-152.06697548	-189.58350208	-189.16609480
(R)CCSD(T,fc)/cc-pwCVTZ	-1.17212023	-0.60171636	-152.51832795	-152.17065574	-189.66854677	-189.25866463
(R)CCSD(T,full)/cc-pwCVTZ	-1.17212023	-0.60171636	-152.36838624	-152.02127530	-189.51434060	-189.10480058
(R)CCSD(T)/cc-pVTZ	-1.17212023	-0.60171636	-152.35825095	-152.01129805	-189.50182263	-189.09259871
(R)CCSD(T)cc-pVTZ-DK	-1.17212099	-0.60171626	-152.35215229	-152.00520404	-189.49201998	-189.08282581

Table S17: Calculated and measured appearance energies of the $(H_2C_2O + H_2CO_2)^+$ and $(H_2C_2O + CO_2 + H_2)^+$ fragmentation pathways of the resulting cation of Pyruvic acid. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. ΔCV and ΔSR are for core valence and scalar relativistic effects. The corresponding Cartesian coordinates and the harmonic frequencies are given in Tables S19 and S20, respectively.

m/z	42		46	44	2
	$H_2C_2O^+ + H_2CO_2$	$H_2C_2O^+ + CO_2 + H_2$	$H_2C_2O + H_2CO_2^+$	$H_2C_2O + CO_2^+ + H_2$	$H_2C_2O + CO_2 + H_2^+$
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12)	10.844	10.948	12.610	15.239	16.914
ΔCV	-0.01382	-0.011375454	-0.00786	-0.01339971	0.003897
ΔSR	0.000952	0.001080293	0.000269	0.000317013	0.00123
ΔZPVE	-0.17116596	-0.50693729	-0.20717144	-0.56332929	-0.63499824
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12/ cc-pVTZ-F12 +ΔCV+ΔSR+ΔZPVE (SP))	10.660	10.431	12.395	14.663	16.285

Table S18: Harmonic frequencies (ω_i, cm^{-1}) of pyruvic acid and its ions as computed at the PBE0/aug-cc-pVDZ level of theory.

Species	**Tc**	**Tc^+**	**Tt**	**Tt^+**	**Ct**
ω_1	3633.630	3667.388	3790.605	3682.547	3781.720
ω_2	3202.461	3197.582	3201.152	3209.910	3195.701
ω_3	3066.777	3049.810	3142.526	3132.050	3140.533
ω_4	1871.802	1977.364	3066.876	3047.504	3063.504
ω_5	1810.092	1903.255	1839.738	1921.024	1866.967
ω_6	1431.359	1401.974	1828.853	1866.336	1845.480
ω_7	1420.811	1327.888	1429.602	1406.827	1434.562
ω_8	1367.310	1281.127	1425.343	1391.867	1429.093
ω_9	1261.380	1210.429	1418.757	1323.646	1374.391
ω_{10}	1174.468	1028.689	1361.614	1317.563	1354.929
ω_{11}	978.888	945.326	1237.055	1184.477	1204.462
ω_{12}	784.317	592.532	1158.523	1021.005	1158.435
ω_{13}	612.152	494.660	1024.244	1001.748	1026.702
ω_{14}	530.300	372.099	972.614	948.433	977.462
ω_{15}	392.372	295.092	756.895	697.620	747.830
ω_{16}	250.264	227.426	734.972	599.687	736.980
ω_{17}	3141.106	3136.144	634.695	595.187	628.598
ω_{18}	1426.077	1390.887	595.202	492.822	614.160
ω_{19}	1022.984	1007.509	518.900	451.819	485.054
ω_{20}	759.801	672.146	388.318	344.557	399.797
ω_{21}	714.311	565.575	384.061	332.740	387.797
ω_{22}	398.426	389.591	245.248	232.341	252.705
ω_{23}	126.252	127.989	130.495	123.200	157.695
ω_{24}	94.579	57.522	37.997	15.000	22.659
	Cc	**enolPACc**	**$enolPACc^+$**	**enolPATc**	**$enolPATc^+$**
ω_1	3842.626	3802.668	3729.470	3836.296	3745.984
ω_2	3187.798	3715.621	3348.481	3810.869	3603.442
ω_3	3114.420	3318.702	3309.481	3319.828	3311.229
ω_4	3037.630	3203.956	3174.033	3204.038	3174.503
ω_5	1888.766	1798.288	1859.838	1845.238	1863.844

ω_6	1850.048	1751.195	1615.288	1745.344	1610.636
ω_7	1450.071	1476.553	1525.989	1414.493	1510.564
ω_8	1439.578	1412.744	1445.526	1404.132	1412.676
ω_9	1359.717	1358.249	1379.946	1343.979	1357.171
ω_{10}	1325.075	1245.001	1211.139	1211.955	1178.976
ω_{11}	1198.727	1195.099	1187.865	1152.900	1175.460
ω_{12}	1136.943	985.815	1012.337	976.558	1006.196
ω_{13}	1017.602	903.963	965.404	912.956	973.892
ω_{14}	965.861	824.777	916.737	810.839	813.447
ω_{15}	759.558	808.031	785.132	794.129	781.453
ω_{16}	711.397	738.199	773.587	738.513	723.374
ω_{17}	615.807	615.092	651.675	613.376	617.486
ω_{18}	503.687	599.753	606.842	578.043	575.518
ω_{19}	480.504	568.121	508.739	540.936	532.031
ω_{20}	403.413	515.301	439.738	411.008	463.841
ω_{21}	376.252	402.005	379.864	402.079	379.095
ω_{22}	258.495	397.133	340.584	398.581	356.686
ω_{23}	187.144	275.264	235.391	277.882	238.194
ω_{24}	4.252	109.209	116.817	90.661	75.647
	enolPATt	**enolPACt**	**enolPACt$^+$**		
ω_1	3859.754	3867.354	3746.336		
ω_2	3800.348	3809.430	3698.273		
ω_3	3304.871	3307.515	3299.076		
ω_4	3187.878	3185.062	3163.324		
ω_5	1828.241	1843.410	1885.031		
ω_6	1728.118	1720.379	1582.123		
ω_7	1463.870	1459.195	1496.314		
ω_8	1407.140	1417.279	1438.485		
ω_9	1328.016	1341.946	1344.695		
ω_{10}	1198.212	1219.673	1195.504		
ω_{11}	1174.544	1148.927	1153.259		
ω_{12}	972.265	982.831	1000.326		
ω_{13}	894.508	888.491	950.981		

ω_{14}	815.332	820.682	797.343		
ω_{15}	802.889	800.004	774.411		
ω_{16}	727.571	724.297	689.222		
ω_{17}	651.658	600.488	640.845		
ω_{18}	580.371	600.090	591.119		
ω_{19}	527.607	509.091	503.996		
ω_{20}	432.918	430.825	410.415		
ω_{21}	404.839	414.747	398.493		
ω_{22}	384.753	391.244	268.263		
ω_{23}	272.691	278.170	260.605		
ω_{24}	67.699	63.927	43.355		

Table S19: Harmonic frequencies (in cm^{-1}) of all fragments, in their electronic ground state, treated in this study as computed at the PBE0/aug-cc-pVDZ level of theory. See Figure ??FRAGMENTS for the denomination of the molecular species.

Species	OH	OH^+	H_2	H_2^+	CO_2	CO_2^+	CH_3	CH_3^+	HOCO	$HOCO^+$	H_2C_2O	$H_2C_2O^+$
ω_1	3744.700	3081.923	4369.570	2090.547	1379.954	1317.058	3122.767	3243.802	3837.598	3546.571	3321.490	3256.767
ω_2					2438.578	1421.399	542.183	3243.801	1928.759	2498.180	3211.821	3121.421
ω_3					679.992	477.132	3320.658	1423.198	1257.646	1277.831	2246.129	2308.411
ω_4					679.992	477.132	3320.658	1385.714	1117.672	1053.895	1395.528	1359.150
ω_5							1378.610	1385.713	620.644	602.187	1175.587	1066.536
ω_6							1378.610	3029.885	554.038	549.907	971.085	1000.104
ω_7											437.776	408.407
ω_8											595.004	757.356
ω_9											544.733	461.424
	H_2CO_2	$H_2CO_2^+$	COCOOH	$COCOOH^+$	CH_3CO	CH_3CO^+	CH_2COH	$C_2H_3O^+$	CH_2C-OH	CH_2C-OH^+	CH_2-CH-OH	CH_2-CH-OH^+
ω_1	3767.075	3631.707	3750.335	3667.893	3158.379	3123.776	3293.790	3202.453	3842.232	3548.574	3842.319	3675.624
ω_2	3082.823	3027.368	1944.974	2373.416	3152.658	3122.796	3166.316	3146.061	3269.501	3218.148	3285.555	3292.252
ω_3	1841.989	1588.217	1892.899	1988.850	3041.907	3018.045	2981.420	1697.092	3132.764	3119.092	3222.207	3213.952
ω_4	1390.463	1383.498	1330.747	1304.408	1949.421	2396.044	1578.189	1438.455	1749.006	2154.979	3173.191	3161.019
ω_5	1312.139	1220.959	1170.990	1178.612	1419.610	1362.462	1461.836	1355.477	1390.098	1329.583	1723.025	1608.688
ω_6	1152.920	1173.806	778.533	723.628	1416.702	1362.349	1383.305	1129.391	1239.707	1208.476	1431.058	1469.324
ω_7	1058.118	1008.762	657.426	668.294	1323.504	1330.645	1171.553	1013.792	1133.533	1128.942	1354.131	1413.078
ω_8	690.301	713.300	646.341	600.717	1043.732	1000.247	977.474	578.748	955.174	880.387	1318.267	1296.983
ω_9	629.483	481.080	549.735	558.613	933.359	999.864	974.612	3286.522	825.615	837.252	1134.149	1157.673
ω_{10}			488.896	415.837	892.789	940.483	767.184	1081.522	620.810	813.477	995.870	1048.214
ω_{11}			265.085	260.278	465.497	415.867	499.567	1017.391	441.972	380.382	957.407	980.378

ω_{12}			26.677	167.414	120.270	415.796	438.528	785.785	316.917	373.966	841.728	932.099
ω_{13}											715.023	684.506
ω_{14}											485.690	484.785
ω_{15}											465.565	389.136
Species	CH_2-OCH_2	CH_2-OCH_2^+	CH_3-CH-O	CH_3-CH-O^+	CH_3-C-O-H	CH_3-C-O-H^+	CH-CH_2-OH	CH-CH_2-OH^+	CH_3-CO-CO	CH_3-CO-CO^+	CH_2-CO-CO_2H	CH_2-CO-CO_2H^+
ω_1	3222.382	3193.072	3183.728	3218.113	3400.051	3455.230	3844.242	3639.516	3154.276	3137.092	3633.421	3696.662
ω_2	3207.620	3174.758	3123.953	3111.323	3127.761	3124.062	3162.051	3257.787	3145.517	3133.421	3319.453	3222.012
ω_3	3121.913	3095.674	3048.650	3029.015	3097.983	3087.108	3085.798	3250.474	3054.285	3027.483	3185.997	3126.560
ω_4	3113.705	3059.203	2912.024	2867.543	2925.582	3004.662	3016.999	3136.317	2172.742	2392.149	1867.237	2000.173
ω_5	1533.068	1432.995	1836.754	1642.252	1440.139	1743.088	1512.648	1462.672	1545.854	2268.619	1575.133	1732.403
ω_6	1483.564	1391.763	1435.906	1393.419	1391.799	1381.517	1307.649	1334.404	1451.914	1366.947	1477.702	1490.232
ω_7	1324.133	1289.356	1427.030	1392.186	1365.482	1343.945	1268.624	1184.961	1431.802	1364.629	1411.805	1441.630
ω_8	1162.302	1154.828	1409.774	1277.874	1343.918	1309.541	1246.350	1136.386	1369.891	1333.900	1299.377	1266.772
ω_9	1159.422	1151.334	1349.624	1149.421	1319.362	1193.215	1136.949	1094.304	1237.981	1006.298	1194.083	1152.108
ω_{10}	1148.749	1138.228	1127.817	1028.968	1054.023	1025.134	1042.914	1081.073	997.802	993.663	1007.888	1126.441
ω_{11}	1148.677	1010.253	1122.236	986.829	962.815	959.049	1012.473	961.485	984.940	938.082	873.562	994.965
ω_{12}	1039.590	868.460	901.409	877.262	920.868	910.318	916.701	873.200	763.953	416.801	795.778	993.635
ω_{13}	921.517	785.329	762.787	752.338	730.834	606.805	893.992	829.502	653.431	395.554	774.149	885.058
ω_{14}	884.737	564.595	504.254	374.902	523.446	423.508	554.110	708.147	437.861	151.420	739.515	773.995
ω_{15}	811.186	560.367	164.126	164.156	139.588	141.346	344.339	587.149	399.531	126.006	608.787	731.079
ω_{16}									166.669	102.520	536.323	673.991
ω_{17}									155.827	98.751	453.235	627.151
ω_{18}									104.723	78.523	393.239	551.346
ω_{19}											387.934	321.441
ω_{20}											261.852	250.214

ω_{21}											105.089	201.470
	CH_3-CO-CO_2	CH_3-CO-CO_2^+	CH_3-C-CO_2H	CH_3-C-CO_2H^+	CH_3-CO-CHO	CH_3-CO-CHO^+	CH_3-CO-COH	CH_3-CO-COH^+	CH_2-CO-CO_2H-1		CH_2-CO-CO_2H-2	CH_2-CO-CO_2H-2^+
ω_1	3197.131	3185.440	3811.398	3718.319	3198.930	3191.706	3195.019	3335.795	3786.937		3792.999	3632.499
ω_2	3057.189	3050.798	3141.717	3170.142	3064.114	3139.758	3087.583	3202.326	3316.425		3319.270	3226.074
ω_3	1838.724	2997.617	3059.370	3119.295	2973.444	3049.075	3051.930	3040.885	3184.876		3186.438	3128.959
ω_4	1603.899	2050.791	2947.302	3037.202	1827.417	3017.889	1797.818	1916.529	1867.304		1825.888	2003.218
ω_5	1420.515	1601.365	1732.835	2040.258	1814.256	1995.119	1449.990	1693.278	1555.890		1566.087	1736.088
ω_6	1370.747	1395.981	1478.140	1434.622	1423.093	1947.772	1438.554	1409.081	1455.641		1470.178	1483.471
ω_7	1219.013	1382.842	1473.496	1396.838	1374.755	1406.682	1414.669	1354.214	1380.849		1404.589	1439.518
ω_8	1070.073	1361.360	1350.425	1380.644	1343.310	1391.065	1369.384	1130.964	1250.819		1272.090	1261.027
ω_9	962.327	1261.950	1289.846	1367.975	1261.101	1328.768	1220.181	1079.619	1172.848		1178.555	1152.110
ω_{10}	757.336	1027.420	1227.691	1298.333	1001.962	1120.352	987.347	978.157	1012.712		1006.866	1122.890
ω_{11}	589.279	960.479	1136.660	1127.844	805.536	1015.737	759.257	606.453	865.763		869.265	992.907
ω_{12}	504.359	957.247	1054.889	992.570	573.359	1011.163	654.562	507.275	768.310		768.935	992.084
ω_{13}	352.789	824.883	868.217	965.703	482.394	929.330	442.085	366.573	757.553		764.470	859.996
ω_{14}	179.749	737.470	785.711	782.436	245.027	834.992	304.450	241.695	633.153		652.475	762.161
ω_{15}	3132.092	712.917	653.069	547.968	3138.828	560.248	3121.632	3113.416	610.672		587.757	732.659
ω_{16}	1427.899	693.487	529.490	524.474	1429.062	454.414	1421.556	1401.656	492.411		525.386	710.417
ω_{17}	1020.271	503.272	469.465	506.390	1070.655	410.383	1080.425	1011.714	429.033		433.370	625.933
ω_{18}	680.798	321.788	326.802	502.734	892.460	308.411	925.692	742.370	410.700		395.374	542.474
ω_{19}	372.268	263.684	240.122	258.021	468.322	227.198	459.960	456.520	371.841		381.201	317.854
ω_{20}	113.816	240.332	166.197	194.006	126.679	123.760	153.244	159.841	269.300		258.637	263.620
ω_{21}	63.841	128.251	143.396	115.441	85.894	20.350	110.882	108.722	40.183		50.997	199.155

	CH_2-COH-CO_2	CH_2-COH-CO_2^+	CH-COH-CO_2H^+	CH-COH-CO_2H^+								
ω_1	3738.442	3578.466	3797.710	3694.553								
ω_2	3305.322	3139.862	3687.688	3639.033								
ω_3	3195.310	3067.786	3317.175	3349.355								
ω_4	1755.281	1976.521	1799.475	1944.336								
ω_5	1591.909	1765.945	1714.739	1887.309								
ω_6	1416.721	1412.788	1444.228	1334.437								
ω_7	1378.748	1361.557	1335.788	1304.584								
ω_8	1274.336	1298.850	1230.055	1223.958								
ω_9	1164.291	1119.652	1183.862	1173.801								
ω_{10}	975.335	1095.508	883.651	908.308								
ω_{11}	907.775	1018.485	806.402	735.193								
ω_{12}	786.066	973.926	757.127	698.645								
ω_{13}	772.184	961.442	657.733	605.046								
ω_{14}	712.350	830.885	604.420	596.570								
ω_{15}	588.719	804.980	598.813	568.431								
ω_{16}	478.623	697.264	549.843	440.697								
ω_{17}	447.616	614.072	509.574	398.121								
ω_{18}	378.453	562.062	398.970	324.486								
ω_{19}	353.191	305.551	379.808	309.064								
ω_{20}	224.380	253.859	260.564	227.374								
ω_{21}	87.321	147.036	110.046	90.778								

Table S20: Cartesian coordinates (in Å) of pyruvic acid, ionized pyruvic acid and its fragments as obtained after geometry optimizations at the PBE0/aug-cc-pVDZ level of theory. All species are taken in their electronic ground state.

Tc	**Tc$^+$**
O 1.06946700 1.30464200 0.00000000	O 1.08467200 1.31302000 0.00000000
C 0.00000000 0.72818200 0.00000000	C 0.00000000 0.86640500 0.00000000
C 0.03051300 -0.81407300 0.00000000	C 0.07446600 -0.91584200 0.00000000
C -1.33449600 1.38528600 0.00000000	C -1.37282000 1.40313800 0.00000000
O -0.96416000 -1.49105900 0.00000000	O -0.98551900 -1.43579300 0.00000000
O 1.26940200 -1.29500600 0.00000000	O 1.27047700 -1.37361400 0.00000000
H 1.85840700 -0.51499100 0.00000000	H 1.94614500 -0.66779200 0.00000000
H -1.22105800 2.47267500 0.00000000	H -1.32767000 2.49756900 0.00000000
H -1.90556200 1.04867000 0.87679600	H -1.89269700 1.00955400 0.88720400
H -1.90556200 1.04867000 -0.87679600	H -1.89269700 1.00955400 -0.88720400
Tt	**Tt$^+$**
C 1.75394600 0.77395700 0.00024500	O 0.82509500 -1.48203300 -0.22541100
H 1.62254100 1.42193600 0.87807200	C 0.76937200 -0.32254800 -0.02691200
H 1.62337900 1.42136200 -0.87811800	C -0.82257200 0.25701300 -0.01718200
H 2.74668300 0.31570600 0.00078200	C 1.80718400 0.71367300 0.18743900
C 0.70978200 -0.29727100 0.00000600	O -0.96017000 1.41384300 -0.23086900
C -0.74419500 0.21499900 -0.00002700	O -1.62066100 -0.72930000 0.22841800
O -1.63583100 -0.77613200 0.00028300	H -2.55273200 -0.43496200 0.24371100
H -2.51248000 -0.36347600 0.00026200	H 2.80099100 0.26124100 0.12023900
O -1.02364000 1.39027500 -0.00029400	H 1.63003800 1.17208900 1.17301300
O 0.93480600 -1.48234700 -0.00028200	H 1.64368600 1.49272700 -0.57414000
Ct	**Cc**
C 1.60162400 0.96285200 0.00002100	O 0.90413200 1.55152200 0.00000000
H 1.37670000 1.58205200 0.87982100	C 0.00000000 0.75876700 0.00000000
H 1.37671600 1.58207200 -0.87976700	C 0.35302700 -0.75642800 0.00000000
H 2.65386100 0.66410200 0.00003600	C -1.45134200 1.16674200 0.00000000
C 0.73748600 -0.26122100 -0.00000300	O 1.48182600 -1.14728100 0.00000000
C -0.79803900 -0.06555900 0.00000200	O -0.68971000 -1.61546600 0.00000000
O -1.13484700 1.23991800 -0.00002600	H -1.52820300 -1.13911500 0.00000000
H -2.10330700 1.27889900 -0.00002500	H -1.51729100 2.25879200 0.00000000
O -1.59135300 -0.96527200 0.00003000	H -1.96729900 0.77782500 0.89250800
O 1.15740100 -1.39009200 -0.00002700	H -1.96729900 0.77782500 -0.89250800
enolPACc	**enolPACc$^+$**
O 1.39603000 -1.11883200 -0.00041400	O 1.25952800 -1.16928800 0.00006900
C 0.75465100 0.06767400 0.00013900	C 0.73571800 -0.00263200 0.00002400
C -0.72344500 -0.08092200 -0.00005600	C -0.78712200 -0.03372200 -0.00007900
C 1.38291900 1.24968400 0.00031900	C 1.55693700 1.14095000 0.00010500
O -1.41747400 1.06164100 -0.00054800	O -1.32929200 1.15930200 0.00010100
O -1.24196100 -1.18085900 0.00071600	O -1.30372600 -1.12127400 -0.00025600
H 0.80325700 2.16742400 0.00009500	H 1.10124300 2.13097700 0.00007900
H 2.46982300 1.30312400 0.00021400	H 2.64276700 1.02761900 0.00019900
H 0.70309400 -1.80017100 -0.00051800	H 0.51181300 -1.82960600 0.00005300
H -2.35368100 0.81541000 -0.00024100	H -2.30110200 1.09351400 0.00005400
enolPATc	**enolPATc$^+$**

O 1.20240400 -1.28508400 0.00000000	O 1.12472400 -1.30047100 0.00000400
C 0.75618100 -0.00410600 -0.00017700	C 0.72321700 -0.07886400 -0.00004800
C -0.71738800 0.21322400 -0.00000100	C -0.76048800 0.23440500 -0.00055100
C 1.58567300 1.04508400 0.00004200	C 1.67517800 0.95807800 0.00025500
O -1.37985300 -0.97141900 0.00006400	O -1.44625500 -0.90314100 0.00022000
O -1.28421500 1.27709800 -0.00004800	O -1.16014600 1.36166100 -0.00010300
H 1.16666000 2.04702100 0.00024400	H 1.32505000 1.99077400 0.00016300
H 2.66448400 0.90496900 0.00029900	H 2.74010400 0.71947100 0.00056400
H 0.44047000 -1.87668500 -0.00005300	H 0.36502400 -1.92249600 -0.00029100
H -2.32509100 -0.76528600 0.00019400	H -2.40420000 -0.73384800 0.00066100
enolPATt	
O -1.16172500 -1.27475900 -0.00018400	
C -0.73697300 0.01335800 -0.00001000	
C 0.75037100 0.15604900 -0.00000300	
C -1.50837000 1.10686200 0.00015400	
O 1.38256500 -1.02766300 0.00020300	
O 1.32879200 1.21775900 -0.00019400	
H -1.03476900 2.08464800 0.00026700	
H -2.59657200 1.04431600 0.00018400	
H -2.12478000 -1.28631900 0.00000200	
H 2.32890400 -0.82295500 0.00009900	
enolPACt	**enolPACt^{+}**
O -1.38004900 -1.12405100 -0.00010900	O -1.29014500 -1.15475900 0.00000500
C -0.73042600 0.06262000 -0.00010600	C -0.71470400 -0.00843200 -0.00003400
C 0.74880000 -0.14018700 -0.00005300	C 0.81050500 -0.11732400 -0.00020000
C -1.29925400 1.27568400 0.00013500	C -1.41473200 1.22075200 0.00006100
O 1.43227500 1.02236700 -0.00010100	O 1.34105500 1.09888100 -0.00002900
O 1.28635400 -1.21938700 0.00014800	O 1.35232200 -1.17955300 0.00009900
H -0.67928800 2.16662100 -0.00014100	H -0.85060400 2.15338500 -0.00010400
H -2.38311300 1.39764400 0.00039900	H -2.50764600 1.25093700 0.00030300
H -2.32894700 -0.96065300 0.00017200	H -2.26539800 -1.12055400 0.00008700
H 2.36799200 0.77624500 0.00021400	H 2.31138100 1.02970600 0.00014800
CH3CO	**CH3CO^{+}**
C 1.16474000 -0.09877600 -0.00011800	C 1.21123400 -0.00010400 -0.00001600
H 1.68309500 0.29972000 -0.88205000	H 1.55350900 -1.04833000 -0.04706800
H 1.18259800 -1.19871600 -0.00109400	H 1.55294000 0.48391500 0.93131100
H 1.68166300 0.29734800 0.88387300	H 1.55299200 0.56557100 -0.88409400
C -0.23990800 0.42568700 0.00004600	C -0.21282200 -0.00017700 -0.00001700
O -1.26204400 -0.16997700 -0.00003800	O -1.33123900 0.00006600 0.00000600
HOCO	**HOCO^{+}**
H 1.74804100 0.47074800 0.00003000	H 1.66801400 0.70109100 0.00000600
C -0.12835900 0.38636900 -0.00000600	C -0.10865500 0.01159600 -0.00001600
O -1.18798100 -0.13572000 0.00000400	O -1.23480800 0.01644100 0.00000600
O 1.06574500 -0.21290100 -0.00000300	O 1.10779800 -0.11277500 0.00000500
CH_3	**CH_3^{+}**
C 0.00000000 0.00000000 0.00001300	C 0.00000000 0.00000000 -0.00000300
H 0.00000000 1.08758900 -0.00002500	H 0.00000000 1.10089700 0.00000600
H 0.94188000 -0.54379400 -0.00002500	H 0.95340500 -0.55044900 0.00000600
H -0.94188000 -0.54379400 -0.00002500	H -0.95340500 -0.55044900 0.00000600
COCOOH	**COCOOH^{+}**

O 2.07202600 -0.09738500 -0.00009400	O 2.07202600 -0.09738500 -0.00009400
C 0.95862200 -0.15959600 0.00011800	C 0.95862200 -0.15959600 0.00011800
C -0.59912900 0.12107000 0.00017900	C -0.59912900 0.12107000 0.00017900
O -1.19669900 -1.02396700 -0.00001100	O -1.19669900 -1.02396700 -0.00001100
O -0.87357100 1.26614500 -0.00006000	O -0.87357100 1.26614500 -0.00006000
H -2.17100900 -0.92719100 -0.00045900	H -2.17100900 -0.92719100 -0.00045900
OH	**OH^+**
O 0.00000000 0.00000000 0.10840100	O 0.00000000 0.00000000 0.11516900
H 0.00000000 0.00000000 -0.86720700	H 0.00000000 0.00000000 -0.92134800
CH_3-CO-CO	**CH_3-CO-CO^+**
O -0.75247000 1.39157500 -0.00004300	O -1.28446900 1.35842400 -0.00004900
C -0.44315800 0.17848800 0.00002900	C -1.33098800 0.24047500 0.00013300
C 0.92631900 -0.10654300 0.00029300	C 1.62671300 -0.09324400 0.00004700
C -1.41360500 -0.96743500 -0.00003500	C -1.48804700 -1.17584800 -0.00003600
O 2.07697600 -0.25306000 -0.00014400	O 2.75008800 -0.01972100 -0.00002600
H -0.90592900 -1.94109700 0.00004100	H -1.00088800 -1.57312900 0.90515100
H -2.05360200 -0.89703000 -0.89003300	H -1.00041900 -1.57286100 -0.90508800
H -2.05385900 -0.89705700 0.88976700	H -2.56971600 -1.39193200 -0.00032400
CH_2-CH-OH	**CH_2-CH-OH^+**
C -1.20143500 -0.20561100 0.00001700	C -1.21946600 -0.19794600 -0.00004500
H -2.12898400 0.36177900 -0.00013300	H -2.13276900 0.39902500 0.00045000
H -1.26673600 -1.29525000 0.00028600	H -1.29603500 -1.28881800 -0.00024900
C -0.03251500 0.43932600 -0.00004600	C 0.03099000 0.45723100 -0.00000100
H 0.03304600 1.52817100 -0.00008600	H 0.11356000 1.54880200 -0.00021600
O 1.20556200 -0.11516200 0.00010500	O 1.16605800 -0.13761300 0.00001400
H 1.12188200 -1.07569600 -0.00073400	H 1.11763500 -1.11381500 0.00018000
CH_2-OCH_2	**CH_2-OCH_2^+**
C 0.73226900 -0.37113900 0.00001100	C 0.73103400 -0.40188800 0.00002500
H 1.27032800 -0.58842600 -0.92620700	H 1.30449600 -0.51580400 -0.92985900
H 1.27034800 -0.58826800 0.92625700	H 1.30474400 -0.51544800 0.92979800
O -0.00025700 0.85128000 -0.00002800	O 0.00053200 0.85997100 -0.00004200
C -0.73200400 -0.37158300 0.00001200	C -0.73163000 -0.40142800 0.00003300
H -1.27012800 -0.58853100 0.92624500	H -1.30498800 -0.51426300 0.93004400
H -1.27008200 -0.58868400 -0.92621400	H -1.30493300 -0.51436200 -0.92999500
CH_3-CH-O	**CH_3-CH-O^+**
C 1.16353800 -0.15032400 0.00003200	C 1.16966900 -0.15324100 0.00004600
H 1.15433400 -1.24545500 -0.00069600	H 1.16986600 -1.24675500 -0.00048400
H 1.70263100 0.22877500 -0.88164500	H 1.65864400 0.27616900 -0.89171500
H 1.70231500 0.22800500 0.88217300	H 1.65861900 0.27546400 0.89207600
C -0.22936500 0.39702200 0.00002100	C -0.22269900 0.39065100 -0.00011700
H -0.30439400 1.51228900 -0.00020600	H -0.38993200 1.50098400 0.00022200
O -1.23249100 -0.27547500 0.00000700	O -1.22237700 -0.27879000 0.00004100
CH_3-C-O-H	**CH_3-C-O-H^+**
C -1.13277500 0.14649000 0.00000500	C -1.22706000 0.11805700 0.00003000
H -1.72534100 -0.15980200 -0.87583000	H -1.75124000 -0.30098100 -0.87850000
H -1.72537800 -0.15946700 0.87591700	H -1.75040800 -0.29978100 0.87961200
H -0.99913900 1.25106700 -0.00020000	H -1.24964600 1.22001800 -0.00089500
C 0.12936200 -0.64206800 0.00001300	C 0.10826100 -0.41789500 -0.00011800
O 1.18699100 0.11978700 -0.00000100	O 1.25969800 0.02205300 0.00003300
H 0.97440900 1.08336900 0.00001600	H 1.38650400 1.00335000 0.00004800

CH- CH_2-OH	**CH- CH_2-OH^+**
C -0.93697300 0.46963600 -0.20001000	C 0.22991900 0.83130600 -0.17806100
H -1.25778900 0.78112900 0.81620600	H 0.69860900 1.64549600 0.37596700
C -0.11937300 -0.75287500 -0.00523900	C -0.86097000 -0.08151100 0.00304800
H -0.09227000 -1.31782000 0.93481600	H -1.35726100 -0.17738400 0.97321900
O 0.81113500 0.37132000 0.13754900	O 0.60812100 -0.55126500 0.15041300
H 1.08965500 0.64545200 -0.74537000	H 0.93650400 -1.04145200 -0.63242400
H 0.10940200 -1.37988600 -0.87455200	H -1.35651400 -0.51530800 -0.86999100
CO_2	**CO_2^+**
C 0.00000000 0.00000000 0.00000000	C 0.00000000 0.00000000 0.00000000
O 0.00000000 0.00000000 1.16366000	O 0.00000000 0.00000000 1.17476600
O 0.00000000 0.00000000 -1.16366000	O 0.00000000 0.00000000 -1.17476600
CH_2-CO-CO_2H	**CH_2-CO-CO_2H^+**
O 1.01728500 -1.36603600 -0.00008800	O 1.49446600 -1.33590100 0.00004600
C 0.73667100 -0.15830700 -0.00005500	C 0.82884300 -0.36853300 -0.00016200
C -0.74749500 0.22806000 -0.00001000	C -0.70991200 -0.06987900 -0.00006000
C 1.69807800 0.88635000 0.00012200	C 0.95145600 1.15584300 0.00004700
O -1.13646500 1.36742400 -0.00010700	O -0.55409700 1.20303400 -0.00003100
O -1.54352800 -0.83614700 0.00011300	O -1.85017700 -0.61122800 0.00004200
H -0.95154100 -1.61382800 0.00011300	H -1.81249600 -1.58728200 0.00007100
H 2.75631900 0.63020300 -0.00005700	H 1.33451400 1.61797600 -0.91634300
H 1.37336500 1.92508200 0.00025800	H 1.33412400 1.61748700 0.91686500
CH_3-CO-CO_2	**CH_3-CO-CO_2^+**
O 1.00929400 1.41736300 0.00000000	O -0.41385600 1.23929400 0.00016100
C 0.00000000 0.75605800 0.00000000	C -0.67523200 -0.00774900 -0.00006800
C 0.16938800 -0.76670600 0.00000000	C 0.82590400 -0.34328400 -0.00007300
C -1.39737600 1.27439700 0.00000000	C -1.96629400 -0.63176800 -0.00005400
O -0.75383800 -1.59306300 0.00000000	O 1.57186100 -1.23608600 0.00009700
O 1.32272200 -1.29060900 0.00000000	O 1.05475000 1.04969500 -0.00012500
H -1.39268100 2.36812400 0.00000000	H -2.78893500 0.09188900 -0.00001500
H -1.93241000 0.88992500 0.88100500	H -2.00966600 -1.30902500 0.87621600
H -1.93241000 0.88992500 -0.88100500	H -2.00970900 -1.30928700 -0.87608900
CH_3-C-CO_2H	**CH_3-C-CO_2H^+**
C -0.73036600 -0.16209700 -0.65357700	C -0.62074300 -0.09563000 0.00036400
C 0.54463700 0.09634900 -0.07357900	C 0.71391000 -0.06307000 0.00009700
C -1.89437600 -0.13800600 0.22453500	C -2.03713900 -0.38073000 -0.00017200
O 0.76180400 1.29126200 0.05844100	O 0.17158400 1.15896000 -0.00007200
O 1.47703100 -0.83703500 0.16455300	O 1.92873300 -0.41400900 -0.00004100
H 1.15383700 -1.69849000 -0.13292100	H 2.05450200 -1.38109200 -0.00045800
H -2.83358800 0.10455300 -0.28746500	H -2.50295200 0.06335700 -0.89439300
H -1.78267700 0.40603200 1.17619100	H -2.50327500 0.06232900 0.89447500
H -1.96761900 -1.22338400 0.47596700	H -2.18698400 -1.46762500 -0.00045700
CH_3-CO-CHO	**CH_3-CO-CHO^+**
O 0.60250700 1.60264600 0.00000000	O -1.24142000 -1.17352300 -0.13378400
C 0.00000000 0.55036900 0.00000000	C -0.64608700 -0.18021100 0.01824300
C 0.83219200 -0.73402600 0.00000000	C 1.10301700 -0.49711700 0.20334500
C -1.48759700 0.41038800 0.00000000	C -0.95458000 1.26615100 0.06558700
O 0.34318700 -1.83567100 0.00000000	O 1.83325800 0.31548100 -0.19409300
H -1.95673200 1.39821600 0.00000000	H -0.34802200 1.76683200 -0.70453900

H -1.80378700 -0.17041300 0.87820700	H -0.64839600 1.65911300 1.04724600
H -1.80378700 -0.17041300 -0.87820700	H -2.02926100 1.39949700 -0.10308300
H 1.93118800 -0.55358200 0.00000000	H 1.27687600 -1.49403900 0.66034500
CH_3-CO-COH	**CH_3-CO-COH$^+$**
O 1.21788500 0.46172200 0.00000000	
C 0.00000000 0.43924600 0.00000000	O 1.18661800 0.59595000 0.00000000
C -0.71111500 -0.98465200 0.00000000	C 0.00000000 0.56290100 0.00000000
C -0.87875400 1.63171300 0.00000000	C -0.49988200 -1.00995800 0.00000000
O 0.25827600 -1.82585100 0.00000000	C -1.06044100 1.57462700 0.00000000
H 1.12727800 -1.31434600 0.00000000	O 0.32717500 -1.91445500 0.00000000
H -0.30907100 2.56540400 0.00000000	H 1.28085300 -1.62218600 0.00000000
H -1.54414100 1.57206600 0.87501200	H -0.62833600 2.57993600 0.00000000
H -1.54414100 1.57206600 -0.87501200	H -1.70046300 1.41243500 0.88295900
	H -1.70046300 1.41243500 -0.88295900
H_2	**H_2^+**
H 0.00000000 0.00000000 0.38053400	H 0.00000000 0.00000000 0.55643600
H 0.00000000 0.00000000 -0.38053400	H 0.00000000 0.00000000 -0.55643600
H_2C_2O	**$H_2C_2O^+$**
C 0.00031300 1.21222200 0.00000000	C 0.00176500 1.24269100 0.00000000
C 0.00000000 -0.10347600 0.00000000	C 0.00000000 -0.14037100 0.00000000
O -0.00028900 -1.26773400 0.00000000	O -0.00186800 -1.26799700 0.00000000
H 0.94692100 1.74492400 0.00000000	H 0.96537000 1.76442500 0.00000000
H -0.94648400 1.74447100 0.00000000	H -0.96101600 1.76563300 0.00000000
H_2CO_2	**$H_2CO_2^+$**
C -0.13183300 0.39960700 0.00019400	C -0.08366600 0.39748200 0.00001300
H -0.10130500 1.50351100 0.00022100	H -0.20963100 1.50065300 0.00005200
O 1.11544700 -0.09181400 -0.00021000	O 1.09191800 -0.08394500 -0.00002500
H 1.03988300 -1.05941000 0.00109800	H 1.14248100 -1.06417500 0.00013500
O -1.13389500 -0.26340400 -0.00010000	O -1.14577500 -0.26872700 -0.00000800
CH_2-CO-CO_2H-1	
O 1.34319500 -1.23162200 -0.00000500	
C 0.78527200 -0.13201700 -0.00007000	
C -0.74976900 -0.10446900 -0.00021600	
C 1.50794100 1.09406000 0.00007000	
O -1.23801600 1.15390000 -0.00027300	
O -1.43760600 -1.08748600 0.00041500	
H 1.00636200 2.05917100 -0.00000400	
H 2.59607200 1.04218900 0.00026500	
H -2.20369300 1.07485600 -0.00006200	
CH_2-CO-CO_2H-2	**CH_2-CO-CO_2H-2$^+$**
O 1.12687800 -1.36491800 -0.00009700	O 1.56589900 -1.27065400 0.00011200
C 0.76885400 -0.18449700 0.00003600	C 0.84709200 -0.34334100 -0.00008900
C -0.71879300 0.18130200 0.00000500	C -0.69561600 -0.11847900 0.00009800
C 1.67591600 0.91182100 0.00008700	C 0.90432100 1.18790100 -0.00033200
O -1.50463400 -0.89549100 0.00001900	O -1.74255900 -0.81709200 -0.00015300
O -1.12155900 1.32117100 -0.00004100	O -0.60819000 1.16427700 0.00045900
H 1.31342800 1.93781800 0.00015500	H 1.26224400 1.66801200 0.91666900
H 2.74341300 0.69737000 0.00004900	H 1.26095000 1.66859500 -0.91757000
H -2.41817200 -0.57303300 -0.00001300	H -2.57917900 -0.30534300 -0.00051200
CH_2-COH-CO_2	**CH_2-COH-CO_2^+**

O -1.26098600 -1.21799500 0.00053300	O -1.72724100 -0.88477700 -0.00006600
C -0.73983200 0.02609000 0.00005000	C -0.73007300 -0.13988000 0.00010100
C 0.73634100 0.05101000 0.00000100	C 0.81015400 -0.26145600 0.00009600
C -1.46339600 1.15022200 -0.00041600	C -0.55196000 1.32868200 -0.00006400
O 1.44380400 1.11249000 0.00051400	O 0.89743000 1.09452700 0.00001500
O 1.42079500 -0.98841300 -0.00055100	O 1.59615100 -1.13602200 -0.00007100
H -0.95072200 2.10972900 -0.00066700	H -0.89504800 1.84564200 -0.90940800
H -2.55121100 1.12865600 -0.00051600	H -0.89513900 1.84543000 0.90941400
H -0.52564700 -1.85096800 -0.00060100	H -1.50925600 -1.84497800 0.00017200
CH-COH-CO_2H	**CH-COH-CO_2H^+**
O -1.47872300 -1.00758800 0.00007200	O -1.78519900 -0.54918900 0.00014000
C -0.77142300 0.14886600 -0.00008200	C -0.81662600 0.31284500 -0.00016700
C 0.69921300 -0.07743100 -0.00003800	C 0.66770400 -0.28725400 -0.00001000
C -1.30116300 1.36260500 -0.00012000	C -0.67808300 1.58930300 0.00003200
O 1.44460600 1.02824800 0.00003700	O 1.59624000 0.63347100 0.00016700
O 1.15360900 -1.20458400 0.00004900	O 0.71976500 -1.47212200 -0.00014600
H -2.27228200 1.84354600 -0.00009900	H -0.36321500 2.62705900 -0.00064700
H -0.81313100 -1.71816000 0.00015600	H -1.41108200 -1.45346000 0.00018600
H 2.36971900 0.74176500 0.00012500	H 2.48987900 0.23975900 0.00003500
CH_2COH	**$C_2H_3O^+$**
C 1.16782100 -0.17184500 -0.00000500	C -0.74601500 -0.483041000.00000000
C -0.133874000.40798300 -0.00000200	C 0.000000000.737767000.00000000
O -1.16760900 -0.266270000.00000000	O 0.81428200 -0.192981000.00000000
H 2.061567000.453055000.00000300	H -1.07815200 -0.906799000.95049900
H 1.26898000 -1.257620000.00002400	H -1.07815200 -0.90679900 -0.95049900
H -0.193352001.517893000.00001800	H 0.118141001.829093000.00000000
CH_2C-OH	**CH_2C-OH^+**
C -1.245228000.101566000.01641200	C -1.28657500 -0.00001400 0.00990600
C -0.02454100 -0.40439200 -0.01114800	C -0.00740000 -0.00035400 0.01294500
O 1.166341000.18737400 -0.07004900	O 1.21234400 0.00003000 -0.11333300
H -2.11113900 -0.55032000 -0.07227600	H -1.83349000 -0.95084000 0.02170400
H -1.403949001.177558000.14398200	H -1.83048300 0.95271200 0.02165000
H 1.80297200 -0.309272000.45710100	H 1.72907100 0.00009200 0.72620400