Supplementary Material

Photoelectron spectrum and breakdown diagram of ethanolamine: conformers, excited states, and thermochemistry

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Figure S1: Low lying ethanolamine neutral structures as calculated at the CCSD(T)-F12/cc-pVDZ-F12 level.

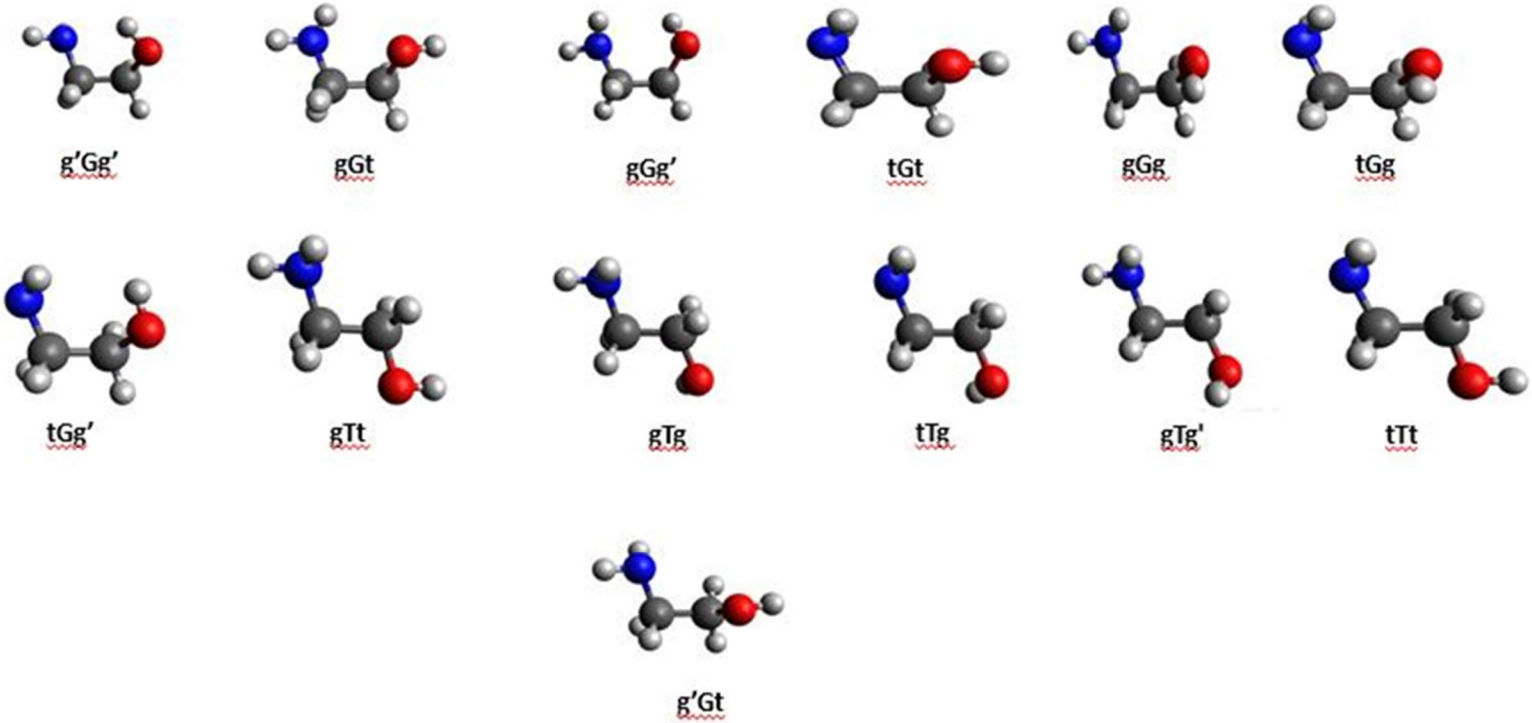


Figure S2: Numbering of atoms of ethanolamine.

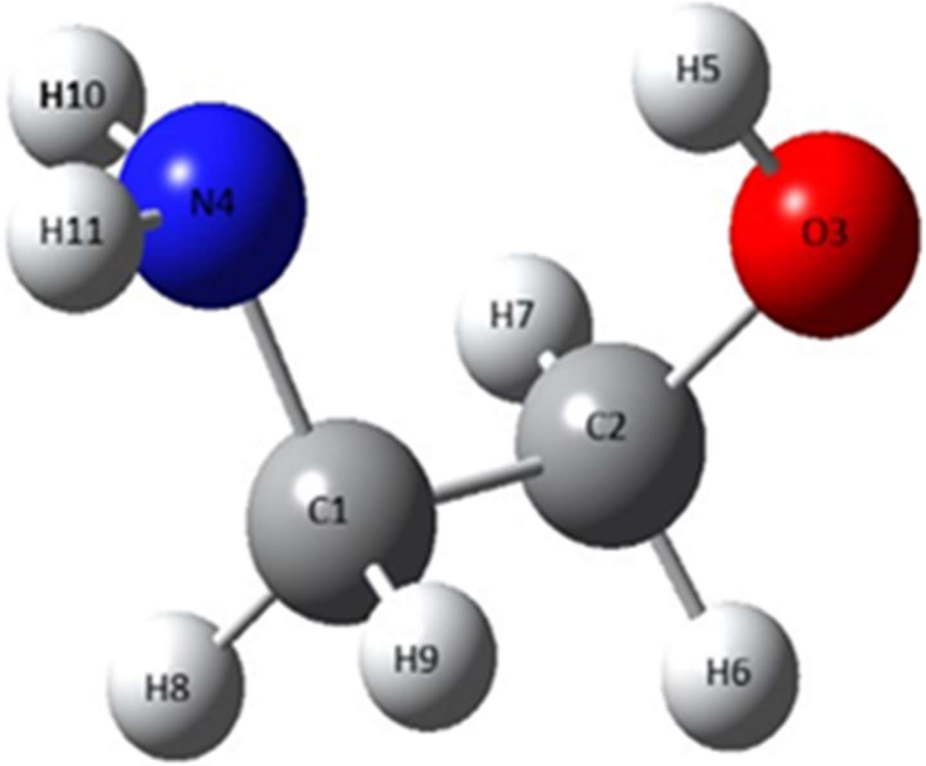
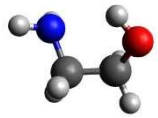
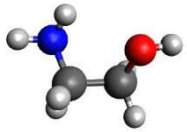
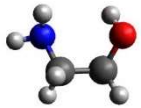
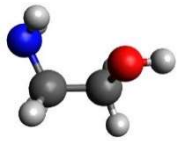
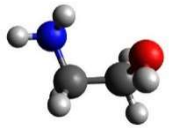
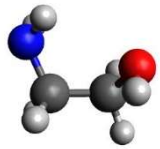
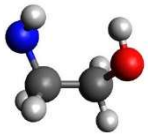
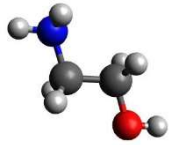


Table S1: Total energies (in Hartree) of ethanolamine. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. respectively PBE0 and CCSD(T)-F12 computations correspond to optimization and the other computations are single point computations.

	g'Gg'	**gGt**	**gGg'**	**tGt**
				
ZPVE/ PBE0/aug-cc-pVDZ	255.57	254.27	251.58	254.11
(R)CCSD(T)-F12/cc-pVDZ-F12 (opt)	-210.12270758	-210.12004863	-210.12009434	-210.11966974
(R)CCSD(T,fc)/cc-pwCVTZ	-210.27785399	-210.27482940	-210.27500355	-210.27456167
(R)CCSD(T,full)/cc-pwCVTZ	-210.07709168	-210.07412080	-210.07430168	-210.07386645
(R)CCSD(T)/cc-pVTZ	-210.06477529	-210.06184915	-210.06196197	-210.06155775
(R)CCSD(T)cc-pVTZ-DK	-210.05665429	-210.05371743	-210.05382531	-210.05342354
	gGg	**tGg**	**tGg'**	**gTt**
				
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	254.398	254.273	253.633	253.830
(R)CCSD(T)-F12/cc-pVDZ-F12(opt)	-210.11938247	-210.11935552	-210.11865107	-210.11757480
(R)CCSD(T,fc)/cc-pwCVTZ	-210.27441875	-210.27459518	-210.27361161	-210.27232322
(R)CCSD(T,full)/cc-pwCVTZ	-210.07372343	-210.07391597	-210.07291927	-210.07162591
(R)CCSD(T)/cc-pVTZ	-210.06141445	-210.06155775	-210.06055637	-210.05935476

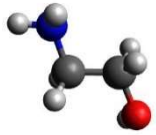
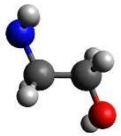
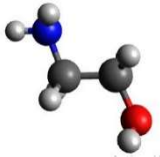
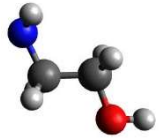
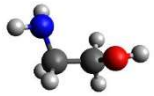
(R)CCSD(T)cc-pVTZ-DK	-210.05328252	-210.05344511	-210.05242176	-210.05122048
	gTg	**tTg**	**gTg'**	**tTt**
				
ZPVE/ PBE0/aug-cc-pVDZ	253.974	253.341	253.511	253.438
(R)CCSD(T)-F12/cc-pVDZ-F12(opt)	-210.11763143	-210.11786516	-210.11751911	-210.11777099
(R)CCSD(T,fc)/cc-pwCVTZ	-210.27246932	-210.27290691	-210.27231952	-210.27259414
(R)CCSD(T,full)/cc-pwCVTZ	-210.07178449	-210.07223397	-210.07163455	-210.07190694
(R)CCSD(T)/cc-pVTZ	-210.05947930	-210.05989634	-210.05931584	-210.05961248
(R)CCSD(T)cc-pVTZ-DK	-210.05134551	-210.05176426	-210.05118174	-210.05148037
	g'Gt			
				
ZPVE/ PBE0/aug-cc-pVDZ	252.29			
(R)CCSD(T)-F12/cc-pVDZ-F12(opt)	-210.11494020			
(R)CCSD(T,fc)/cc-pwCVTZ	-210.26938334			
(R)CCSD(T,full)/cc-pwCVTZ	-210.06869892			
(R)CCSD(T)/cc-pVTZ	-210.05640091			
(R)CCSD(T)cc-pVTZ-DK	-210.04827060			

Table S2: Geometrical parameters (distances are in Å and angles in degree) of the 13 low lying neutral conformers of ethanolamine in their ground state as computed at the CCSD(T)-F12/cc-pVDZ-F12 level. See Figure S2 for the numbering of the atoms.

Parameters	**g′Gg′**	**tGt**	**gGt**	**tGg**	**tGg′**	**gGg**	**gGg′**	**tTg**	**gTg**	**tTt**	**gTt**	**gTg′**	**g′Gt**	**Experiment [a] (g′Gg′)**	**Theory [b] (g′Gg′)**
		Distances													
C1C2	1.516	1.514	1.507	1.518	1.518	1.516	1.519	1.521	1.521	1.521	1.511	1.521	1.516	1.526±0.016	1.522
C1N4	1.458	1.450	1.452	1.450	1.451	1.426	1.469	1.451	1.464	1.460	1.454	1.463	1.463	1.475±0.023	1.459
C2O3	1.405	1.416	1.418	1.416	1.413	1.460	1.421	1.412	1.421	1.422	1.414	1.420	1.419	1.396±0.01	1.395
O3H5	0.964	0.956	0.956	0.958	0.958	0.96	0.961	0.958	0.959	0.958	0.956	0.959	0.958	1.139±0.001	0.950
C2H6	1.095	1.101	1.1	1.101	1.096	1.095	1.091	1.103	1.094	1.097	1.099	1.089	1.096		1.083
C2H7	1.104	1.102	1.099	1.096	1.103	1.090	1.095	1.096	1.092	1.097	1.102	1.097	1.097		1.091
C1H8	1.101	1097	1.097	1.098	1.098	1.093	1.092	1.096	1.096	1.091	1.101	1.1	1.098		1.084
C1H9	1.096	1.097	1.103	1.10	1.096	1.101	1.095	1.099	1.094	1.091	1.096	1.091	1.092		1.091
N4H10	1.013	1.014	1012	1.014	1.013	1.012	1.011	1.013	1.013	1.013	1.013	1.013	1.013	1.017±0.005	1.001
N4H11	1.011	1.014	1.013	1.014	1.012	1.013	1.012	1.013	1.012	1.013	1.011	1.011	1.012	1.017±0.003	1.002
		Angles													
C1C2O3	110.8	107.6	107.4	112.1	112.9	111.6	111.3	112.9	112.3	107.7	107.8	112.2	108.7	112.1±0.1	108.9
N4C1C2	108.3	115.3	109.7	115.2	115.8	109.3	109.2	114.8	109.2		109.5	109.3	111.1	108.1±2.0	111.2
H5O3C2	105.0	109.2	109.1	108.4	108.2	107.8	106.2	108.6	108.0	108.6	108.9	108.1	108.4	103.7±0.2	106.2
H6C2C1	110.4	109.7	109.8	110.2	109.2	110.3	110.5	109.7	109.5	109.6	109.2	109.5	109.1		110.3

H7C2C1	109.5	109.8	109.2	110.1	109.9	109.5	109.5	109.8	109.8	109.5	109.5	109.7	109.3		109.5
H8C1C2	109.8	108.8	108.3	109.0	108.5	108.8	108.8	109.0	108.6	108.8	108.4	108.9	108.0		108.6
H9C1C2	108.7	108.4	108.2	108.9	109.0	108.5	109.4	109.3	109.1	108.8	108.5	108.7	107.9	110.4±0.8	109.9
H10N4C1	110.9	110.3	110.8	110.1	111.8	110.8	110.6	110.8	110.1	110.5	110.6	110.3	110.1	111.3±0.8	111.4
H11N4C1	111.6	109.1	109.0	109.1	111.6	108.9	109.8	111.0	110.4	110.5	110.7	110.5	110.4		111.0
H8C1N4	107.9	109.0	108.9	109.0	108.5	109.0	108.9	110.8	114.5	108.8	114.5	113.9	113.7		107.9
H9C1N4	114.2	108.1	114.0	108.2	107.8	113.9	112.7	111.0	108.5	108.8	108.6	108.7	108.3		113.6
H6C2O3	107.8	110.9	110.7	111.0	106.0	110.8	106.5	111.1	111.7	111.0	111.7	106.5	110.7		107.5
H7C2O3	110.7	110.6	110.7	105.0	110.6	105.7	110.4	105.8	105.8	111.0	110.8	111.0	110.9		110.8
		Dihedral angles													
O3C2C1N4	55.0	60.6	64.7	58.3	61.1	62.7	55.1	178.4	177.6	180.0	177.9	-179.6	72.7	55.4± 2	57.4
H5O3C2C1	-39.3	-177.0	-170.4	69.1	-67.4	70.3	-68.6	62.4	68.1	-180.0	176.9	-63.7	-170.4	28.3± 2	-43.3
H6C2C1N4	174.4	-178.7	-55.4	-177.5	179.1	-173.6	173.3	-57.0	-57.7	-59.2	-60.6	-61.5	-166.6	40.7± 1	176.6
H7C2C1N4	-67.3	-59.8	-176.5	-58.8	-62.9	-54.0	-96.1	60.6	60.3	59.1	57.3	56.5	-48.6		-65.4
H8C1C2O3	-179.7	-176.6	-176.5	-178.9	-176.8	-178.4	173.8	56.1	52.2	58.1	52.4	55.4	-162.0		-60.0
H9C1C2O3	-61.9	-60.8	-60.2	-63.4	-60.6	-62.0	-68.6	-59.8	-64.6	-58.2	-63.7	-61.2	-46.0		-177.6
H11N4C1C2	-163.2	-53.9	-59.4	-49.4	-66.5	-55.1	-88.6	57.6	172.1	58.9	169.5	171.3	-169.0	-78.2±2	-163.0
H10N4C1C2	77.5	62.6	-176.8	66.5	54.6	-172.7	154.5	-60.8	-70.9	-58.9	-72.8	-71.1	73.7	159.5±1	77.7

a) Geometry parameters were determined by microwave spectroscopy (Penn et al; 1971).

b) Geometry parameters were optimized at the MP2/6-31G* level (Vanquickenborne et al; 1988).

Table S3: Relative energies (E_r, eV) of ethanolamine with respect to the **g'Gg'** conformer ground state. ΔZPVE (in eV) is evaluated at the PBE0/aug-cc-pVDZ using the corresponding anharmonic frequencies (Table S4). ΔCV, ΔSR are the core-valence and scalar relativistic corrections, respectively. The room-temperature abundances are calculated assuming conformer independent thermal internal energies and entropies.

	g'Gg'	**gGt**	**gGg'**	**tGt**
E_r @CCSD(T)-F12/cc-pVDZ-F12(opt)	0	0.072	0.071	0.083
ΔCV	0	-0.00146152	-0.00164466	-0.00182561
ΔSR	0	0.000291706	0.000426131	0.000359463
ΔZPVE	0	-0.013	-0.0399	-0.0146
E_r @CCSD(T)-F12/cc-pVDZ-F12(opt) + ΔCV + ΔSR + ΔZPVE	0	0.058	0.030	0.066
Approx. abundance at room temperature	55%	6%	17%	4%
	gGg	**tGg**	**tGg'**	**gTt**
E_r @CCSD(T)-F12/cc-pVDZ-F12(opt)	0.090	0.091	0.110	0.140
ΔCV	-0.00182289	-0.00226127	-0.00190398	-0.00176874
ΔSR	0.000297421	-0.00022749	0.000370347	0.000361367
ΔZPVE	-0.01172	-0.01297	-0.01937	-0.0174
E_r @CCSD(T)-F12/cc-pVDZ-F12(opt) + ΔCV + ΔSR + ΔZPVE	0.077	0.076	0.089	0.121
Approx. abundance at room temperature	3%	3%	2%	0%
	gTg	**tTg**	**gTg'**	**tTt**
E_r @CCSD(T)-F12/cc-pVDZ-F12(opt)	0.066	0.132	0.141	0.134
ΔCV	-0.00210834	-0.00243188	-0.00210453	-0.00204385
ΔSR	0.000348034	0.000301502	0.000356469	0.000302319
ΔZPVE	-0.01596	-0.02229	-0.02059	-0.02132

E_r @CCSD(T)-F12/cc-pVDZ-F12(opt) + ΔCV + ΔSR + ΔZPVE	0.048	0.107	0.119	0.111
Approx. abundance at room temperature	8%	1%	1%	1%
	g'Gt			
E_r @CCSD(T)-F12/cc-pVDZ-F12(opt)	0.211			
ΔCV	-0.0021195			
ΔSR	0.000253338			
ΔZPVE	-0.0328			
E_r @CCSD(T)-F12/cc-pVDZ-F12(opt) + ΔCV + ΔSR + ΔZPVE	0.177			
Approx. abundance at room temperature	0%			

Table S4: Anrhamonic frequencies (ν_i in cm^{-1}) as computed at the CCSD(T)-F12/cc-pVDZ-F12//PBE0/aug-cc-pVDZ level for the low-lying conformers of ethanolamine.

	g'Gg'	tGt	gGt	tGg	tGg'	gGg	tTg	gTg	tTt	gTt	gTg'	g'Gt	Theo [a]	Exp [a]
ν_1	3567	3696	3682	3668	3663	3669	3659	3683	3689	3732	3646	3665	3575	3567.8
ν_2	3403	3405	3421	3398	3412	3412	3407	3421	3409	3413	3416	3419	3432	3430
ν_3	3334	3334	3352	3331	3335	3339	3339	3352	3341	3341	3343	3345	3357	
ν_4	2934	2947	2936	2949	2966	2967	2962	2951	2960	2914	2973	2943	2959	
ν_5	2946	2923	2920	2926	2939	2922	2937	2924	2940	2880	2947	2887	2950	
ν_6	2866	2886	2845	2894	2916	2913	2903	2866	2880	2792	2840	2922	2844	
ν_7	2865	2842	2834	2898	2896	2802	2841	2838	2848	2810	2813	2825	2835	
ν_8	1512	1591	1579	1594	1633	1626	1637	1650	1636	1662	1646	1649	1622	1625
ν_9	1485	1480	1479	1472	1471	1471	1484	1492	1494	1502	1503	1476	1469	
ν_{10}	1468	1452	1469	1453	1453	1470	1461	1469	1462	1485	1461	1462	1457	1463
ν_{11}	1414	1420	1428	1399	1408	1406	1414	1412	1430	1433	1413	1424	1403	1397
ν_{12}	1381	1368	1388	1366	1342	1383	1356	1362	1350	1379	1354	1393	1373	1376
ν_{13}	1342	1361	1313	1355	1354	1344	1342	1328	1332	1320	1339	1316	1341	1343
ν_{14}	1300	1282	1253	1334	1332	1307	1309	1289	1288	1280	1298	1293	1293	1280
ν_{15}	1228	1222	1226	1234	1223	1179	1266	1255	1210	1221	1242	1230	1236	1232
ν_{16}	1162	1144	1159	1129	1144	1162	1124	1123	1184	1181	1141	1146	1166	1165
ν_{17}	1099	1101	1094	1094	1101	1105	1078	1091	1085	1105	1086	1092	1098	1093
ν_{18}	1048	1062	1065	1068	1050	1038	1060	1061	1048	1085	1057	1058	1045	1049
ν_{19}	989	1001	1023	982	986	1030	1022	1037	1003	1055	1037	976	986	
ν_{20}	905	889	888	873	862	885	969	954	984	962	960	910	901	901
ν_{21}	869	835	858	855	851	850	773	812	771	838	805	861	869	880
ν_{22}	786	811	823	808	727	796	774	778	783	781	773	753	787	774
ν_{23}	390	499	499	508	501	501	461	468	461	474	470	488	497	463
ν_4	592	324	411	458	359	492	251	455	347	327	478	314	495	530
ν_{25}	321	394	267	133	295	203	336	72	280	223	13	60	318	
ν_{26}	235	61	72	249	179	157	125	221	86	99	186	202	237	210
ν_{27}	174	159	169	176	167	168	146	137	138	113	139	48	175	

a) Theoretical and experimental IR spectroscopic study. Ref. (Asselin et al; 2016).

Table S5: Geometrical parameters of the 4 low-lying isomers of the ethanolamine cations as computed at the RCCSD(T)-F12/cc-pVDZ-f12 level. Distances are in Å and angles in degrees. See Figure S2 for the numbering of the atoms.

Structures	**EtA1$^+$**	**EtA2$^+$**	**EtA3$^+$**	**EtA4$^+$**
Distances				
C1C2	1.531	1.808	1.531	1.789
C1N4	1.424	1.351	1.424	1.354
C2O3	1.414	1.339	1.414	1.342
O3H5	0.961	0.964	0.961	0.964
C2H6	1.090	1.088	1.090	1.087
C2H7	1.093	1.088	1.093	1.086
C1H8	1.090	1.087	1.090	1.088
C1H9	1.109	1.086	1.109	1.088
N4H10	1.017	1.010	1.017	1.010
N4H11	1.024	1.010	1.024	1.010
Angles				
C1C2O3	104.1	110.0	104.1	110.0
N4C1C2	109.2	111.5	109.2	111.4
H5O3C2	110.8	111.9	110.8	111.8
H6C2C1	108.9	96.9	108.9	100.0
H7C2C1	109.8	103.5	109.8	99.1
H8C1C2	115.4	99.2	115.4	104.0
H9C1C2	109.0	98.2	109.0	97.3
H10N4C1	122.9	121.5	122.9	121.2
H11N4C1	116.9	121.2	116.9	121.4
H8C1N4	110.5	114.2	104.5	114.0
H9C1N4	104.5	114.3	110.5	114.1
H6C2O3	112.8	111.6	112.8	111.4
H7C2O3	111.8	117.0	111.8	117.0
Dihedral angles				
O3C2C1N4	38.6	67.9	38.6	-69
H5O3C2C1	173.2	-99.1	173.2	100
H6C2C1N4	159.1	-176.1	159.2	175

H7C2C1N4	-81.1	-57.8	-81.1	57
H8C1C2O3	163.9	-171.3	163.9	170
H9C1C2O3	-75.0	-52.3	-75.0	52
H11N4C1C2	-26.7	89.0	-26.7	-89
H10N4C1C2	158.7	-87.0	158.8	87

Table S6: Total energies (in Hartree) of low-lying forms of the ethanolamine cation. ZPE (in kJ/mol) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies respectively PBE0 and CCSD(T)-F12/cc-pVDZ-F12 computations correspond to optimization and the other computations are single point computations.

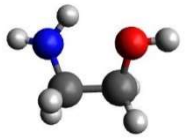
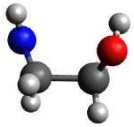
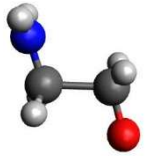
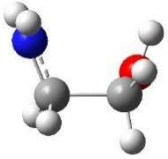
	EtA1$^+$	**EtA2$^+$**	**EtA3$^+$**	**EtA4$^+$**
				
ZPVE/ PBE0/aug-cc-pVDZ (kJ/mol)	248.151	251.671	252.001	251.465
(R)CCSD(T)-F12/cc-pVDZ-F12(opt)	-209.79684731	-209.79348114	-209.79343227	-209.79412874
(R)CCSD(T,fc)/cc-pwCVTZ	-209.95719056	-209.95391877	-209.95409055	-209.95392140
(R)CCSD(T,full)/cc-pwCVTZ	-209.75646365	-209.75335792	-209.75354931	-209.75336136
(R)CCSD(T)/cc-pVTZ	-209.74435627	-209.74106572	-209.74127728	-209.74107010
(R)CCSD(T)cc-pVTZ-DK	-209.73624397	-209.73296428	-209.73317679	-209.73296865

Table S7: Harmonic frequencies (in cm^{-1}) evaluated at the CCSD(T)-F12/cc-pVDZ-F12 level of the four lowest conformers of the ethanolamine cation.

Structures	**EtA1$^+$**	**EtA2$^+$**	**EtA3$^+$**	**EtA4$^+$**
ω_1	3851	3794	3784	3799
ω_2	3570	3664	3660	3671
ω_3	3408	3547	3544	3553
ω_4	3121	3209	3219	3214
ω_5	3119	3191	3200	3183
ω_6	3056	3101	3108	3103
ω_7	2892	3084	3091	3086
ω_8	1563	1690	1682	1690
ω_9	1539	1551	1538	1549
ω_{10}	1441	1516	1511	1513
ω_{11}	1410	1430	1406	1427
ω_{12}	1384	1399	1396	1404
ω_{13}	1277	1355	1343	1353
ω_{14}	1251	1300	1283	1298
ω_{15}	1206	1255	1271	1260
ω_{16}	1122	1240	1219	1226
ω_{17}	1083	1152	1159	1168
ω_{18}	1062	1068	1068	1069
ω_{19}	1010	905	902	893
ω_{20}	890	855	829	857
ω_{21}	790	653	682	636
ω_{22}	710	596	605	597
ω_{23}	536	494	495	495
ω_{24}	335	438	413	414
ω_{25}	318	383	337	396
ω_{26}	249	246	266	243
ω_{27}	153	137	79	134

Table S8: Anharmonic frequencies (in cm^{-1}) evaluated at the PBE0/aug-cc-pVDZ level of the four lowest isomers of the ethanolamine cation.

Structures	EtA1$^+$	EtA2$^+$	EtA3$^+$	EtA4$^+$
ν_1	3791	3780	3727	3780
ν_2	3540	3623	3597	3632
ν_3	3348	3519	3495	3527
ν_4	3088	3190	3177	3198
ν_5	3026	3182	3154	3172
ν_6	2810	3099	3091	3118
ν_7	1630	3088	3069	3086
ν_8	1551	1756	1729	1757
ν_9	1485	1589	1565	1591
ν_{10}	1434	1572	1542	1568
ν_{11}	1410	1492	1456	1488
ν_{12}	1333	1453	1412	1461
ν_{13}	1314	1430	1369	1428
ν_{14}	1247	1370	1359	1371
ν_{15}	1214	1355	1307	1362
ν_{16}	1174	1296	1256	1289
ν_{17}	1127	1216	1216	1235
ν_{18}	1127	1179	1163	1177
ν_{19}	971	1050	1004	1044
ν_{20}	874	980	929	989
ν_{21}	794	665	759	801
ν_{22}	676	590	640	667
ν_{23}	453	563	551	574
ν_4	444	457	472	551
ν_{25}	316	387	428	475
ν_{26}	205	287	402	377
ν_{27}	113	144	214	291

Table S9: Relative energies (E_r, eV) of ethanolamine cation most stable forms with respect to the **EtA1$^+$** conformer ground state. ΔZPVE (in eV) is evaluated at the PBE0/aug-cc-pVDZ using the corresponding anharmonic frequencies (Table S8). ΔCV, ΔSR are the core valence and scalar relativistic corrections, respectively.

	EtA1$^+$	**EtA4$^+$**	**EtA2$^+$**	**EtA3$^+$**
E_r @RCCSD(T)-F12/cc-pVDZ-F12(opt)	0.000	0.074	0.092	0.093
ΔCV	0.000	-0.00454077	-0.00451873	-0.00505234
ΔSR	0.000	-0.00029524	-0.00029552	-0.00032137
ΔZPVE	0.000	0.03314	0.0352	0.0385
E_r @RCCSD(T)-F12/cc-pVDZ-F12(opt) + ΔCV + ΔSR + ΔZPVE	0.000	0.102	0.122	0.126

Table S10: (R)CCSD(T)-F12/cc-pVDZ-F12 + ΔCV + ΔSR + ΔZPVE level ionization energies in eV for transitions from the **g'Gg'**, **gGt**, **gGg'** neutral structures to the five cationic structures.

AIE	EtA1$^+$	EtA2$^+$	EtA3$^+$	EtA4$^+$
g'Gg'	8.940	9.062	9.066	9.042
gGt	8.882	9.004	9.008	8.984
gGg'	8.910	9.032	9.036	9.012
gTg	8.892	9.014	9.018	8.994