

Theoretical studies on ethanolamine in gas phase and solution: Conformations, frequencies and basicities

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Abstract

The conformational stability, intramolecular H-bond strength, energy barriers, vibrational frequencies and gas-phase basicities of fourteen most stable conformers of ethanolamine in gas phase and in aqueous and carbon tetrachloride solutions have been investigated at B3LYP and MP2 level with 6-311+G(d,p) basis set. In gas phase, the results of two methods suggest that G⁺1 and G⁺2 conformers, which possess intramolecular H-bonds, are the two most stable conformers. The population ratios of T-, G⁻ and G⁺-type conformers are about 2.2%:48.9%:48.9% (B3LYP), 1.2%:49.4%:49.4% (MP2). The energy barrier of interconversions G⁺5 → T1 is obviously larger than that of T2 → T3. In aqueous solution (SCRF-PCM method), the calculations indicate that the stabilizations of ethanolamine conformations are determined by the combination of intramolecular hydrogen bonds and intermolecular solvation of hydroxyl groups. The normal mode analysis for vibrational frequencies shows that the C-O-H bending and the C-O stretching frequencies of the conformers from high energy to low energy are blue-shifted, the O-H stretching frequency is red-shifted conversely. The computed vibrational frequencies in carbon tetrachloride solution are in good agreement with the experimental data. The calculated results of gas-phase basicities of different ethanolamine conformers suggest that the GBs of G⁺-type conformers are higher than that of T-type conformers.

1. Introduction

Alkanolamines have been widely used in the petroleum and natural gas industry for the removal of acid gas impurities such as CO₂

and H₂S from gas mixtures [1,2], since Bottoms[3] introduced the use of triethanolamine for the regenerative removal of CO₂ from natural gas streams. In these alkanolamines, ethanolamine and diethano-

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amine are particularly used as CO₂ removal and sorbent regeneration because of their efficacy in removing CO₂. On the other hand, ethanolamine metabolized to ethanal and ammonium by ethanolamine ammonia lyase is an important reaction in a living system [4, 5]. So ethanolamine is an important compound in biochemistry and industry. However, the study on ethanolamine is still deficient. Both from theoretical and experimental point of view, ethanolamine is a suitable model for investigation of alkanolamine.

Ethanolamine has several low energy conformations due to the rotations of C-C, C-O, O-H, C-N, N-H bonds. Furthermore, the conformational behavior of ethanolamine in solution may be different from that in the gas phase. So, the effect of water on the conformational energy and intramolecular H-bond strength are necessary to be studied. In this work, we will focus on the conformers, energy barriers, intramolecular H-bond strength and gas-phase basicity of ethanolamine in the gas phase and in aqueous and carbon tetrachloride solutions.

In the present context, the conformational study of ethanolamine, including optimized geometry, population distribution, energy order and energy barriers in the gas phase and in aqueous solution is reported firstly. Then, the vibrational frequency is calculated and analyzed. Additionally, the gas-phase basicity of ethanolamine is reported at the end of the context.

2. Theoretical Methods

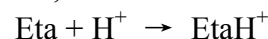
The relative population of ethanolamine conformations based on Gibbs free energy is determined by the following equation [6]:

$$p(i) = \frac{\exp(-\Delta G(i) / RT)}{\sum_i \exp(-\Delta G(i) / RT)}$$

Here, $\Delta G(i)$ is the difference of Gibbs free

energy between the conformation i and the most stable conformation. R is the ideal gas constant and T is 298.15K

The Gibbs free energy change (ΔG) for the protonation reaction of ethanolamine (Eta) at 298.15K and 1 atm,



is calculated by the following equation:

$$\Delta G = G(\text{EtaH}^+) - G(\text{Eta})$$

Here, we take no account of the Gibbs free energy of H^+ , since it does not change the order of gas-phase basicity (GB). The GB is defined as the negative of the Gibbs free energy change: $\text{GB} = -\Delta G$.

The optimized geometries, energies, frequencies, Gibbs free energies and enthalpies of all the conformations studied are computed at MP2 and B3LYP levels of theory with 6-311+G(d,p) basis set using Gaussian03 package[7].

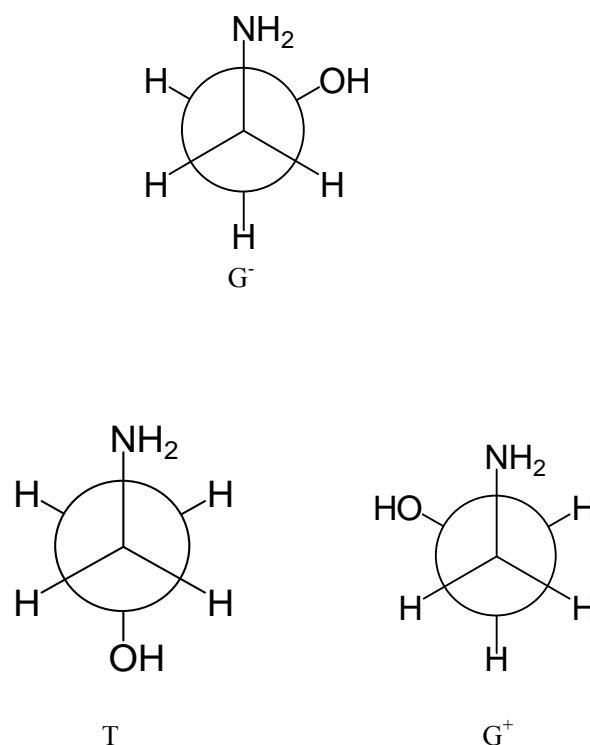


Figure 1. The backbones of ethanolamine.

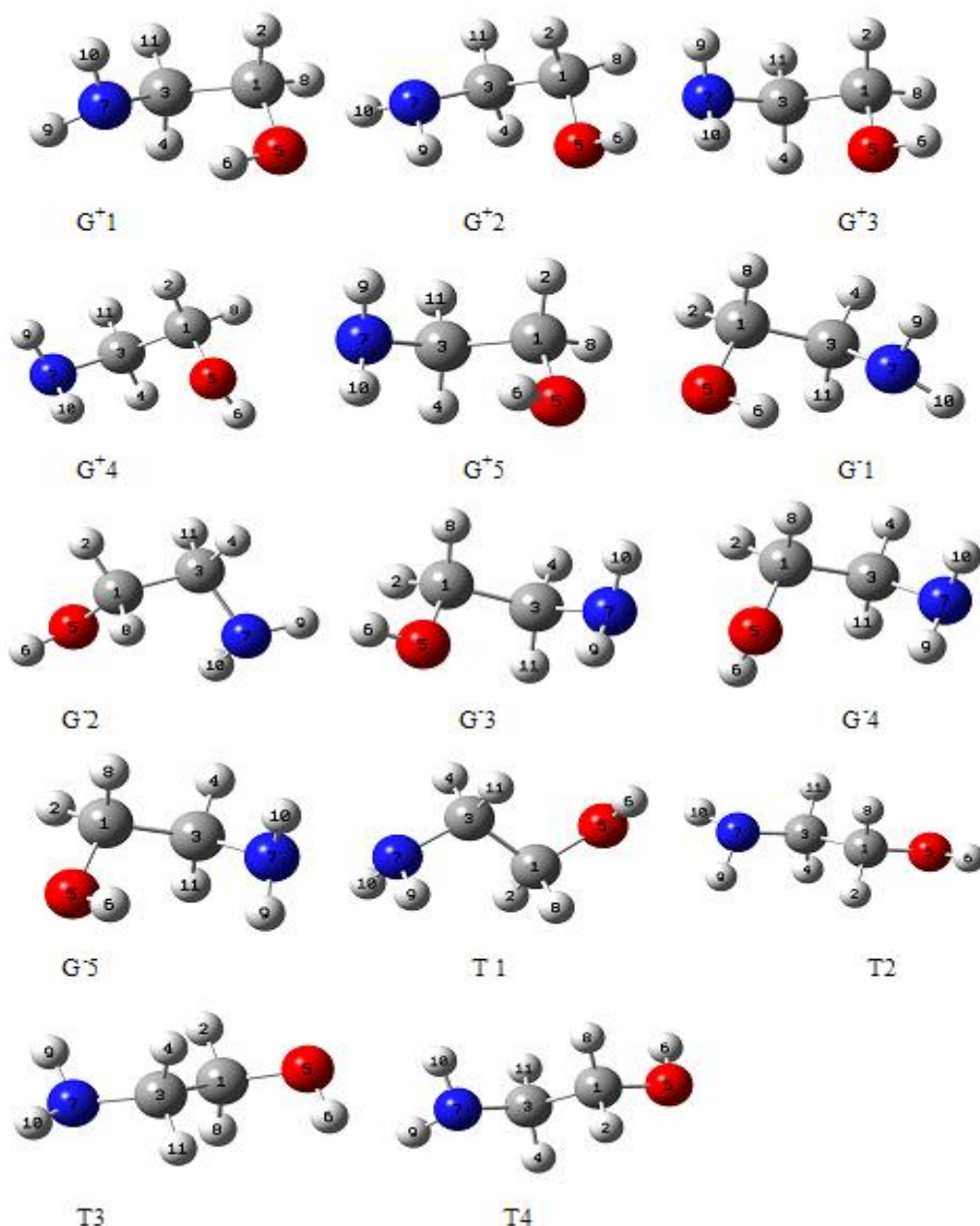


Figure 2. Fourteen possible rotameric conformations of ethanolamine optimized at B3LYP/6-311+G(d,p) level. Carbon atoms are indicated as black circles, oxygen atoms as red circles, hydrogen atoms as gray circles and nitrogen atoms as blue circles.

3. Results and discussions

3.1 Equilibrium geometries and relative energies

Three backbones, differing in the dihedral angle N-C-C-O, of ethanolamine are shown in Figure 1. There are fourteen possible rotameric

conformations of ethanolamine optimized at B3LYP and MP2 levels of theory using 6-311+G(d,p) basis set, of which five are G⁻-type conformers and five are G⁺-type conformers and four are T-type conformers, shown in Figure 2. These conformers were labeled with a capital letter that identifies the backbone conformation followed by an Arabian number in order of increasing energy. For the

fourteen conformations, the dihedral angle of N-C-C-O in the G⁻-type conformer is about -60° and that in G⁺-type about 60°, in T-type about 180°. The relative electronic energies, enthalpies, Gibbs free energies and population based on Gibbs free energy of different ethanolamine conformers, calculated at B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) levels, are listed in Table 1. An analysis of the harmonic vibrational frequencies of the optimized species reveals that all the fourteen structures are minima, qualified by the absence of imaginary normal mode frequencies. As shown in Figure 2, it is interesting that the five

G⁻-type conformers are respectively the mirror images of the five G⁺-type conformers, namely G⁻1 conformer is the mirror image of G⁺1 conformer, and G⁻2 is that of G⁺2, etc. Ethanolamine is not chiral since it contains no asymmetric carbons. Furthermore, Table 1 indicates that the energy, enthalpy and Gibbs free energy of G⁻-type conformer is equal to that of the corresponding G⁺-type conformer. To investigate the conformational structures, energy barriers, gas-phase basicities and the solvent effects, we report the calculated results of G⁺-type and T-type conformers only.

Table 1 Relative electronic energies (ΔE), relative enthalpies (ΔH), relative Gibbs free energies (ΔG) in kcal/mol and population (Pop.) in % based on Gibbs free energy of ethanolamine conformers, calculated at different levels of theory using 6-311+G(d,p) basis set

Conformer	B3LYP				MP2			
	ΔE	ΔH	ΔG	Pop.	ΔE	ΔH	ΔG	Pop.
G ⁻ 1	0.0	0.0	0.004	37.4	0.0	0.0	0.0	39.5
G ⁻ 2	1.775	1.625	1.291	4.3	1.817	1.621	1.237	4.9
G ⁻ 3	2.005	1.794	1.381	3.7	2.338	2.048	1.482	3.2
G ⁻ 4	2.230	2.045	1.696	2.2	2.589	2.383	2.081	1.2
G ⁻ 5	2.673	2.412	2.009	1.3	3.267	2.952	2.536	0.6
T1	3.081	2.912	2.422	0.7	3.605	3.421	2.963	0.3
T2	3.172	2.998	2.288	0.8	3.629	3.394	2.601	0.4
T3	3.228	3.107	2.535	0.4	3.672	3.527	2.971	0.3
T4	3.341	3.164	2.610	0.3	3.815	3.626	3.078	0.2
G ⁺ 1	0.0	0.001	0.0	37.6	0.0	0.0	0.0	39.5
G ⁺ 2	1.775	1.625	1.295	4.2	1.817	1.621	1.237	4.9
G ⁺ 3	2.005	1.792	1.377	3.7	2.338	2.048	1.483	3.2
G ⁺ 4	2.230	2.046	1.697	2.1	2.589	2.383	2.081	1.2
G ⁺ 5	2.673	2.412	2.010	1.3	3.267	2.952	2.536	0.6

As shown in Table 1, the results of both B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) suggest that G⁺1 (G⁻1) conformer is the most stable conformer, followed by G⁺2 (G⁻2) conformer. The optimized geometries, rotational constants and dipole moments for G⁺- and T-type conformers are listed in Table 2. It is found that the distance between H6 and N7 in conformer G⁺1 is about 2.27Å (B3LYP) and 2.23Å (MP2), and the distance between H9 and

O5 in conformer G⁺2 is 2.52Å (B3LYP) and 2.46Å (MP2), respectively. Obviously, G⁺1 and G⁺2 conformers are stabilized by the intramolecular hydrogen bonds formed by the OH group and NH group, respectively. In other conformations there is no intramolecular hydrogen bond. This suggests that intramolecular H-bond is an important driving factor for energy stabilization [8]. There are some other differences between conformers of

ethanolamine. Thus the C-N bond is longer in G⁺1 than in others, but the C-O bond in G⁺1 is shorter. These differences and those in other bonds and angles are also due at least in part to

the O-H...N intramolecular H-bond in G⁺1. The strength of the intramolecular H-bond N-H...O in conformer G⁺2 is too weak to cause significant differences.

Table 2 B3LYP/6-311+G(d,p) and MP2/6-311+G(d) optimized geometries, rotational constants and dipole moments for G⁺ and T conformers

Parameter	G ⁺ 1	G ⁺ 2	G ⁺ 3	G ⁺ 4	G ⁺ 5	T1	T2	T3	T4
B3LYP									
r(N7-H9)	1.013	1.015	1.015	1.015	1.014	1.015	1.015	1.015	1.013
r(N7-H10)	1.015	1.014	1.015	1.016	1.013	1.015	1.013	1.013	1.015
r(N7-C3)	1.471	1.465	1.461	1.461	1.462	1.462	1.467	1.467	1.465
r(C3-C1)	1.527	1.517	1.526	1.531	1.531	1.534	1.523	1.523	1.523
r(C1-O5)	1.418	1.433	1.430	1.430	1.427	1.427	1.429	1.427	1.426
r(O5-H6)	0.968	0.961	0.961	0.963	0.962	0.963	0.961	0.962	0.962
r(H6...N7)	2.272	3.653	3.798	3.394	2.806	4.036	4.392	4.023	3.994
r(H9...O5)	3.628	2.523	3.350	3.421	3.369	4.099	4.039	4.052	4.493
r(H10...O5)	3.360	3.773	2.601	2.645	2.881	4.089	4.428	4.499	4.086
∠(N7C3C1)	108.9	110.2	116.0	115.8	116.4	115.3	109.8	109.9	110.1
∠(C3C1O5)	111.2	107.6	107.8	112.4	113.2	112.9	107.7	112.5	112.5
∠(C1O5H6)	105.4	109.2	109.3	108.6	108.4	108.8	108.9	108.7	108.8
τ(N7C3C1O5)	55.6	65.4	61.3	58.9	62.1	177.8	177.7	177.3	178.9
τ(C3C1O5H6)	-41.2	-167.8	-175.5	70.5	-68.6	63.6	175.9	68.7	64.1
A	14.461	15.156	15.013	14.893	14.889	27.865	28.870	28.394	28.385
B	5.540	5.337	5.224	5.126	5.116	3.784	3.877	3.829	3.829
C	4.553	4.459	4.401	4.362	4.301	3.571	3.616	3.590	3.595
μ	3.298	1.046	2.899	1.441	1.693	1.670	1.160	1.815	2.983
MP2									
r(N7-H9)	1.014	1.016	1.016	1.016	1.015	1.015	1.015	1.015	1.014
r(N7-H10)	1.016	1.015	1.015	1.016	1.014	1.015	1.014	1.014	1.015
r(N7-C3)	1.469	1.463	1.460	1.460	1.461	1.461	1.466	1.465	1.463
r(C3-C1)	1.522	1.514	1.522	1.525	1.526	1.528	1.518	1.524	1.523
r(C1-O5)	1.416	1.430	1.427	1.427	1.423	1.423	1.426	1.424	1.423
r(O5-H6)	0.967	0.960	0.960	0.962	0.961	0.961	0.960	0.961	0.961
r(H6...N7)	2.232	3.589	3.752	3.301	2.731	3.972	4.356	3.954	3.931
r(H9...O5)	3.618	2.463	3.287	3.379	3.308	4.063	3.989	4.016	4.476
r(H10...O5)	3.338	3.727	2.537	2.594	2.847	4.054	4.413	4.481	4.046
∠(N7C3C1)	108.1	109.3	115.2	115.2	115.9	115.0	109.1	109.4	109.6
∠(C3C1O5)	110.5	107.0	107.2	111.8	112.7	112.5	107.5	112.2	112.1
∠(C1O5H6)	104.1	107.8	107.9	106.9	106.9	107.2	107.6	107.1	107.2
τ(N7C3C1O5)	56.9	65.1	60.8	59.2	62.1	177.8	176.2	177.8	178.8
τ(C3C1O5H6)	-42.2	-165.3	-174.8	65.7	-65.9	59.1	168.2	63.3	59.2
A	14.499	15.043	14.911	14.839	14.866	27.767	28.715	28.293	28.279
B	5.606	5.455	5.337	5.221	5.198	3.829	3.917	3.875	3.875
C	4.617	4.538	4.475	4.435	4.361	3.606	3.651	3.626	3.631
μ	3.349	1.053	3.020	1.459	1.615	1.594	0.835	1.883	3.046

Bond length in Å, bond angle in degrees, rotational constant (A,B,C) in GHz, dipole moment (μ) in debye

The energies of T-type conformations are integrally larger than those of G⁻- and G⁺-type conformations. As it seen from Table 1, the calculated population ratio based on Gibbs free energy of T-, G⁻, and G⁺-type conformations is 2.2%:48.9%:48.9% (B3LYP), 1.2%:49.4%:49.4% (MP2). The abundance of gauche conformations (G⁺ and G⁻) is predominantly higher than that of trans conformations (T). It is consistent with the prediction of the gauche effect [9], which was originally defined as the tendency for a molecule to adopt the gauche structure in a molecular fragment X-C-C-Y, where X and Y are two electronegative substituents. In ethanolamine, N7-C3-C1-O5 is such a fragment, and for ethanolamine the gauche effect means it prefers gauche (G⁺ or G⁻) conformation, rather than trans (T) conformation.

Table 3 Energy barriers (kcal/mol) of interconversions for ethanolamine conformers in gas phase, calculated at B3LYP and MP2 level with 6-311+G(d,p) basis set.

Interconversion	B3LYP	MP2
G ⁺ 1 → G ⁺ 2	2.373	2.572
G ⁺ 2 → G ⁺ 3	2.992	3.425
G ⁺ 3 → G ⁺ 4	0.936	1.043
G ⁺ 4 → G ⁺ 5	2.639	3.111
G ⁺ 5 → T1	4.182	4.833
T1 → T2	2.501	3.060
T2 → T3	0.699	0.789
T3 → T4	0.932	1.041

We also calculate the energy barriers of interconversions for ethanolamine conformers in the gas phase at B3LYP and MP2 level with 6-311+G(d,p) basis set. The transition states are specified by QST2 technique. For every transition state, exact one imaginary frequency is obtained to make sure these structures are at the first-order saddle point. The energy barriers for the mentioned interconversions are calculated by comparing the energies of the local minima and the corresponding transition

state. The relative energies of the nine conformers (G⁺- and T-type) and the eight transition states are listed in Table 3. The results of MP2 method are all slightly larger than those of B3LYP method, but they have the same order. The highest-energy barrier is obtained for G⁺5 → T1 interconversion, about 4.18 kcal/mol (B3LYP) and 4.83 kcal/mol (MP2), followed by the energy barrier G⁺2 → G⁺3, about 2.99 kcal/mol (B3LYP) and 3.43 kcal/mol (MP2). The lowest-energy barrier is for interconversion T2 → T3, about 0.70 kcal/mol (B3LYP) and 0.79 kcal/mol (MP2), followed by T3 → T4, about 0.93 kcal/mol (B3LYP) and 1.04 kcal/mol (MP2). This indicates that T2 → T3 and T3 → T4 interconversions could occur more easily than interconversions G⁺5 → T1 and G⁺2 → G⁺3.

Table 4 Relative electronic energies (ΔE), enthalpies (ΔH) and Gibbs Free energies (ΔG) in kcal/mol of ethanolamine conformers in aqueous solution (PCM method), calculated at B3LYP/6-311+G(d,p) level

Con- former	B3LYP		MP2	
	ΔE^a	ΔE^b	ΔE^a	ΔE^b
G ⁺ 1	0.008	0.019	0.785	0.124
G ⁺ 2	0.203	0.141	0.293	0.043
G ⁺ 3	0.060	0.057	0.0	0.0
G ⁺ 4	0.0	0.0	0.214	0.181
G ⁺ 5	0.272	0.158	0.582	0.364
T1	0.115	0.122	0.090	0.171
T2	0.713	0.705	0.304	0.215
T3	0.514	0.526	0.232	0.267
T4	0.531	0.538	0.235	0.283

^a Relative PCM energies (total free energy in solution), calculated for gas-phase optimized geometries.

^b Relative PCM energies (total free energy in solution), obtained for optimized geometry in solution.

In order to determine the effects of solvent on the conformer stability, the conformational behavior of ethanolamine is studied further in aqueous solution at B3LYP and MP2 level with 6-311+G (d,p) basis set using PCM[10-12]

approach in Gaussian03. Table 4 collects the relative PCM energies of the single point PCM calculation and optimization in solution. When solvation is included, conformation G⁺4 and G⁺3 is the lowest energy conformer calculated at B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) level, respectively. In aqueous solution, conformation G⁺1 which is the global minimum at two levels in the gas phase is now 0.019 (B3LYP) and 0.124 kcal/mol (MP2) higher in

energy than the global minimum with solvation, respectively. The possible reason is that the OH group in G⁺1 conformer is involved in an intramolecular H-bonding and is unavailable to interact with the solvent. Furthermore, the relative energies become lower in aqueous solution comparing to the corresponding results in gas phase. In other words, the relative energy

Table 5 Calculated wavenumbers (cm⁻¹), infrared intensities (km/mol) and Raman activities (Å⁴/amu) for the G⁺1 conformer at B3LYP and MP2 level with 6-311+G(d,p) basis set.

Vib. No.	Description	B3LYP			MP2		
		wave-number	IR int.	Raman act.	wave-number	IR int.	Raman act.
1	C1C3 asymmetric torsion	173	6.2	0.2	188	5.9	0.1
2	N7H9H10 bend	261	9.5	0.4	267	12.7	0.3
3	C1C3 symmetric torsion	322	0.6	0.3	332	0.8	0.3
4	C3H4H11 bend	524	40.4	1.3	540	11.3	0.7
5	C1O5H6 bend	553	108.8	0.5	585	136.7	0.7
6	N7H9H10 rock	806	104.7	2.3	844	84.3	2.2
7	C1C3 stretch	873	16.0	8.9	904	16.1	9.1
8	C3H4H11 rock	915	56.4	1.4	948	66.5	1.0
9	C1H2H8 rock, N7H9H10 rock	999	6.4	0.8	1018	7.5	1.2
10	C3N7 stretch	1057	47.4	4.5	1088	42.2	4.4
11	C1O5 stretch	1099	47.5	4.5	1136	45.6	5.6
12	C1H2H8 rock, C1O5H6 bend	1183	10.0	2.5	1206	7.3	2.6
13	C3H4H11 rock	1248	26.3	3.4	1271	21.9	3.4
14	C1H2H8 rock	1323	3.6	5.4	1342	3.3	5.1
15	C1O5H6 bend, C1H2H8 rock	1365	5.5	8.2	1394	3.3	7.3
16	C3H4H11 rock	1403	11.3	1.7	1423	15.1	2.3
17	C1O5H6 scissor	1434	54.9	5.7	1462	49.2	4.5
18	C3H4H11 scissor	1496	5.1	8.3	1514	4.1	7.6
19	C1H2H8 scissor	1508	1.3	7.2	1529	1.5	6.6
20	N7H9H10 scissor	1658	33.4	3.4	1652	33.5	3.3
21	C1H2 stretch	2953	62.3	111.6	3028	55.8	99.4
22	C3H11 stretch	2975	85.6	175.9	3048	64.4	155.9
23	C3H4H11 asymmetric stretch	3066	29.3	70.5	3139	23.8	72.1
24	C1H8 stretch	3077	42.6	99.7	3148	34.6	73.0
25	N7H9H10 symmetric stretch	3511	0.4	119.3	3547	0.8	116.2
26	N7H9H10 asymmetric stretch	3594	5.4	62.5	3647	7.9	52.2
27	O5H6 stretch	3783	68.5	48.9	3798	74.7	44.6

range is quite compressed. Generally, the changes of the relative energies in solution can be explained by two contributions: the geometry relaxation in solution and the polarization induced by the solution. The geometry effects are estimated by comparing the calculations at the geometries optimized in gas phase with that in solution adding solvent

effect. The polarization effects can be determined by comparing the relative energies in gas phase and that in solution at a fixed geometry. In addition, these results also suggest that a combination of intramolecular hydrogen bonds and intermolecular solvation of hydroxyl groups stabilizes ethanolamine in aqueous solution.

Table 6 Comparison of predicted and observed wavenumbers (cm^{-1}) for ethanolamine in carbon tetrachloride solution.

Con- former	νOH^{a}		$\nu\text{NH}(\text{as.})^{\text{b}}$		$\nu\text{NH}(\text{s.})^{\text{c}}$	
	Calc. ^d	Pred. ^e	Calc. ^d	Pred. ^e	Calc. ^d	Pred. ^e
G ⁺ 1	3701	3571	3546	3422	3467	3346
G ⁺ 2	3735	3604	3543	3419	3457	3336
G ⁺ 3	3735	3604	3541	3417	3467	3346
G ⁺ 4	3736	3605	3543	3419	3458	3337
G ⁺ 5	3712	3582	3529	3405	3455	3334
T1	3716	3586	3543	3419	3466	3345
T2	3710	3580	3534	3410	3457	3336
T3	3737	3606	3542	3418	3465	3344
T4	3717	3587	3539	3415	3463	3342
Exptl. ^f	3620 (3517) ^g		3412		3340	

^a the frequency of OH stretch; ^b the frequency of NH antisymmetric stretch; ^c the frequency of NH symmetric stretch; ^d calculated at B3LYP/6-311+G(d,p) level; ^e ab initio frequencies scaled with 0.965; ^f from reference 15; ^g the 3517 cm^{-1} band is assigned to the OH group engaged in the hydrogen bond with the nitrogen atom.

3.2 Vibrational frequencies

The ab initio vibrational frequencies, infrared (IR) intensities and Raman activities for ethanolamine in the gas phase and carbon tetrachloride solvent are calculated at MP2/6-311+G(d,p) and B3LYP/6-311+G(d,p) level. On the basis of our normal coordinate calculations, we give the vibrational modes of the fundamental harmonic frequencies, IR intensities and Raman activities for G⁺1 conformer at B3LYP/6-311+G(d,p) level in Table 5. The harmonic vibrational IR spectra of the nine conformers are displayed in Figure 3. The intramolecular hydrogen bonding in conformer G⁺1 induces the C-O-H bending and C-O stretching vibrations shift to higher frequencies, since the force constants upon

hydrogen bonding might be changed by the interaction between the donor and acceptor[13,14]. As shown in Figure 3 the C-O-H bending frequency of conformer T4, T3, T2, T1, G⁺5, G⁺4, G⁺3, and G⁺2 (in which there is no intramolecular H-bond formed by OH group) is 317, 309, 227, 312, 239, 287, 238, and 224 cm^{-1} , respectively. The corresponding frequency of conformer G⁺1, which possess intramolecular hydrogen-bonding interaction as noted previously, rises to 553 cm^{-1} . Simultaneously, the C-O stretching frequency of conformers from T4 to G⁺1 rises from 1061 to 1099 cm^{-1} . We also note that the O-H stretching frequency of the conformers from higher energy to lower energy is red-shifted. As shown in Figure 3, The O-H stretching

frequencies of the conformers without intramolecular H-bond concentrate on 3830 cm^{-1} , however, the corresponding frequencies of G^+1 red-shift to about 3780 cm^{-1} . It may also be induced by the intramolecular H-bond (O5-H6...N7). The similarity is got when considering the G^+2 conformer with intramolecular H-bonding formed by NH group. However, the magnitude of the corresponding vibrational frequencies is too little to be found in Figure 3.

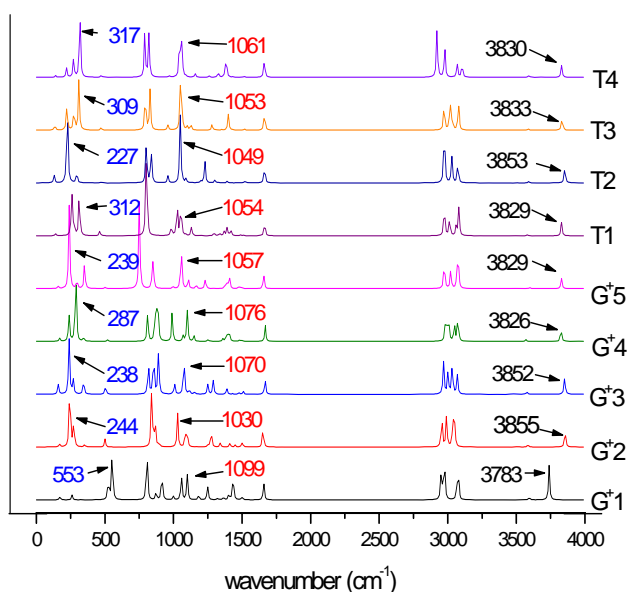


Figure 3. Ab initio vibrational absorption spectra for nine conformers of ethanolamine obtained at B3LYP/6-311+G(d,p) level. The red numbers denote the C-O stretching frequencies, the blue numbers denote the C-O-H bending frequencies and the black

numbers denote the O-H stretching frequencies.

To compare with the experimental results of K. Erbel and R. Mierzecki[15], the PCM calculations are performed on ethanolamine at B3LYP/6-311+G(d,p) level with optimized geometries in carbon tetrachloride solution. The calculated, predicted and experimental frequencies of O-H stretch, N-H symmetric and antisymmetric stretch are listed in Table 6. Since the ab initio calculated frequencies are higher than the experimental results, the ab initio frequencies are multiplied by 0.965[16]. The predicted frequencies of NH antisymmetric stretching, ranging from 3405 to 3422 cm^{-1} , and symmetric stretching, ranging from 3334 to 3346 cm^{-1} , match the experimental data very well, since the experiment reported the corresponding bands were 3412 and 3340 cm^{-1} . The predicted frequency of OH stretching in conformer G^+1 , about 3571 cm^{-1} , is slightly higher than the experimental result, 3517 cm^{-1} , which is assigned to the OH group engaged in the hydrogen bond with the nitrogen atom, as in conformer G^+1 . The predicted frequency of OH stretching in other conformers, ranging from 3580 to 3606 cm^{-1} , are slightly lower than the experimental data, 3620 cm^{-1} . In general, B3LYP/6-311+G (d,p) is an accurate method to study the properties of ethanolamine.

Table 7 Enthalpy and Gibbs free energy changes (kcal/mol) associated with the protonation reaction of ethanolamine calculated at B3LYP and MP2 level with 6-311++G(d,p) basis set at 298.15K

Conformer	B3LYP		MP2	
	$-\Delta H_{298}$	$-\Delta G_{298}$	$-\Delta H_{298}$	$-\Delta G_{298}$
G^+1	218.57	218.84	218.87	219.27
G^+2	220.36	220.22	220.49	220.50
G^+3	220.19	220.14	220.91	220.75
G^+4	220.98	220.85	221.25	221.35
G^+5	220.61	220.54	221.82	221.80
T1	213.12	213.65	213.42	214.51
T2	213.23	213.75	213.39	214.14
T3	213.29	213.84	213.53	214.55
T4	213.04	213.50	213.62	214.63

3.3 Gas-phase basicities

The gas-phase basicities (GB) of the nine conformations are investigated through the protonation reactions of ethanolamine. The enthalpy and Gibbs free energy differences associated to the protonation reactions are calculated with B3LYP and MP2 theory using 6-311++G(d,p) basis set. We did not succeed in optimizing the geometry of the O-protonated form of G⁺-type conformers, due to spontaneous proton-transfer from O5 to N7 atom during the optimization. The spontaneous proton transfer can be understood considering the atomic partial charge: the average natural charges of O5 and N7 are -0.74 and -0.86. The optimization of the O-protonated form of T-type conformers causes the cleavage of ethanolamine. The calculated results of the N-protonated form are listed in Table 7. At B3LYP level, the energetically easiest process is the protonation of G⁺4 conformer with the enthalpy and Gibbs free energy changes, 220.98 and 220.85 kcal/mol. At MP2 level, the energetically easiest process is the protonation of G⁺5 conformer with the enthalpy and Gibbs free energy changes, 221.82 and 221.80 kcal/mol. Furthermore, the GBs of T-type conformers are obviously lower than that of G⁺-type. This suggests that the basicities of T-type conformers are weaker than that of G⁺-type conformers. However, we might be more interested in the differences enthalpy and Gibbs free energy changes of the most stable conformers since it can have physical meaning and can be compared with experiments. As shown in Table 7, the enthalpy and Gibbs free energy changes associated with the protonation reactions of the most stable conformer G⁺1 conformer are 218.57 and 218.84 kcal/mol (B3LYP), 218.87 and 219.27 kcal/mol (MP2). The enthalpy and Gibbs free energy changes associated with the protonation reactions of the other G⁺-type conformers are slightly larger than these values, about 220 kcal/mol.

4. Conclusions

B3LYP functionals and highly correlated MP2 calculations are performed on ethanolamine to study the conformations, energy barrier of interconversion, intramolecular hydrogen bonding strength, vibrational frequency and gas-phase basicity of it in gas phase and in aqueous and carbon tetrachloride solution. The results of calculations suggest that in gas phase, G⁺1 and G⁺2 conformers are the two most stable conformers, and the calculated population ratio based on Gibbs free energy of T-, G⁻-, and G⁺-type conformations is 2.2%:48.9%:48.9% (B3LYP), 1.2%:49.4%:49.4% (MP2), which is consistent with the prediction of Gauche effect. In aqueous solution, the different relative energy order and the compressed relative energy range, comparing with that in gas phase are due to the interaction ethanolamine with water. That the frequencies of the C-O-H bending and C-O stretching vibrations of G⁺1 conformer blue-shift, and the O-H stretching frequencies red-shift, comparing with that of other conformers, is correlated with the intramolecular H-bond in G⁺1. The calculated results of gas-phase basicities of different ethanolamine conformers suggest that the GBs of G⁺-type conformers are about 220 kcal/mol and slightly higher than that of T-type conformers.

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