Structure and Stability of Glycine–$(H_2O)_3$ Cluster and Anion: Zwitterion vs. Canonical Glycine

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ABSTRACT: Calculations are presented for the glycine–$(H_2O)_3^-$ cluster anion, with glycine in canonical or zwitterionic form. The zwitterionic anions are predicted to be considerably lower in energy than the canonical anions, and the latter forms are found to be prone to isomerization to the zwitterionic anions. Therefore, we predict that the zwitterionic anions would be observed predominantly in the gas phase at low temperature. In contrast, calculated stability of neutral glycine–$(H_2O)_3$ clusters indicates that only the canonical forms of the anions would be observed in photoelectron experiments, if anions are produced from preformed neutrals. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 107: 1316–1327, 2007

Key words: glycine; water; zwitterion

Introduction

Amino acids [1–8] are ideal systems in which to study the effects of solvation on the biochemical activity due to their moderate size. The structures and stability of canonical [9–13] and zwitterionic [11, 14–20] amino acids in the presence of solvent molecules are of fundamental interest. It is

well known that amino acids exist in canonical (nonzwitterionic) form in the gas phase, whereas zwitterionic conformer is the predominant form in aqueous solution [19, 21–24]. The cluster model [1–7, 25–30] has proved very useful to study the structures and reactions of amino acid–solvent system, by which the effects of microsolvation on the thermodynamic and kinetic properties of the resulting amino acid are monitored as a function of the number of solvent molecules. This approach may also give invaluable information for the configuration of solvent molecules around the amino acid in the solution phase. The magnitude of barrier and

TABLE I

Energy (hartree), ZPE (kcal/mol), relative energy ΔE (kcal/mol), and relative Gibbs function at 5 K ΔG_{5K} (kcal/mol), and vertical detachment energy (eV) of Gly–(H$_2$O)$_3^-$ anion with zwitterionic and canonical Gly core.

Conformer	E	ZPE	ΔE	ΔG_{5K}	VDE
Zwitterionic					
a-zw-1	−513.95475	95.8	0	0	2.89
a-zw-2	−513.95553	96.7	0.37	0.08	2.88
a-zw-3	−513.95506	96.6	0.64	0.27	2.86
a-zw-4	−513.95245	95.4	1.05	1.35	2.94
a-zw-5	−513.95239	95.4	1.06	1.36	3.02
a-zw-6	−513.95207	95.4	1.27	1.57	2.99
a-zw-7	−513.95062	95.1	1.84	2.38	2.99
a-zw-8	−513.95019	95.6	2.71	2.59	3.47
a-zw-9	−513.95094	96.1	2.72	2.80	3.14
a-zw-10	−513.94967	95.8	3.18	3.26	3.14
a-zw-11	−513.94943	95.7	3.19	3.39	2.86
a-zw-12	−513.94397	94.9	5.91	6.20	2.97
Canonical					
a-c-1	−513.95014	94.8	0[a] (1.89)[b]	0 (2.54)	3.38
a-c-2	−513.94851	95.2	1.43 (3.32)	0.92 (3.40)	3.56
a-c-3	−513.94555	94.2	2.32 (4.17)	2.69 (5.29)	3.61
a-c-4	−513.94605	94.7	2.46 (4.36)	2.53 (5.05)	3.62
a-c-5	−513.94407	94.2	3.17 (5.10)	3.63 (6.25)	3.56
a-c-6	−513.94435	94.5	3.34 (5.23)	3.50 (6.03)	3.59

[a] Relative energy and Gibbs function with respect to (a-c-1).
[b] Relative energy and Gibbs function with respect to (a-zw-1).

dynamic paths of transformation between the two forms of amino acid–solvent clusters are also of fundamental importance along with the thermodynamic stability, since these properties describe the ease with which they may transform to the other form in low-temperature gas phase environments.

Examining the stability of amino acid with an excess electron [26, 31–34] is interesting, because the excess electron may stabilize the amino acid zwitterion relative to the canonical form [35]. It is also important concerning the experimental detection of zwitterionic neutral amino acid by the photodetachment technique, which proved very successful for elucidating the structures of glycine (Gly)–water clusters [35, 36]. In these experiments, a Gly–water cluster anion is produced, and the excess electron is subsequently detached by a photon. Two such experimental studies are notable: Bowen and colleagues [35] prepared the Gly–(H$_2$O)$_n^-$ anion clusters within a supersonic ion source, in which anions are produced by 3-body collisions between thermalized electrons, Gly–water clusters and argon atoms. These investigators observed Gly–(H$_2$O)$_n^-$ anion clusters only

for $n \geq 5$ and they assigned them to zwitterionic core anions. In the experiments by Johnson and colleagues [36], the Gly–(H$_2$O)$_n^-$ anions ($n = 0$–2) are produced by collision between Gly and water dimer cluster anion and were found to possess canonical Gly cores.

In the present work, we examine the Gly–(H$_2$O)$_3^-$ cluster anion, with the amino acid in canonical or in zwitterionic form. Three zwitterionic conformers are of very similar energy with a canonical structure. Since these thermodynamically stable conformers would not isomerize to the other form, we suggest that both the zwitterionic and the canonical forms of the Gly–(H$_2$O)$_3^-$ cluster anion should be observed in the gas phase at low temperature. In contrast, the zwitterionic conformers of neutral Gly–(H$_2$O)$_3$ are calculated to be much higher in energy than the canonical clusters, isomerizing to the latter forms via very small barrier. We therefore predict that, if anions are produced from low-energy conformers of preformed neutral clusters, only the canonical conformers of Gly–(H$_2$O)$_3^-$ would be observed in experiments.
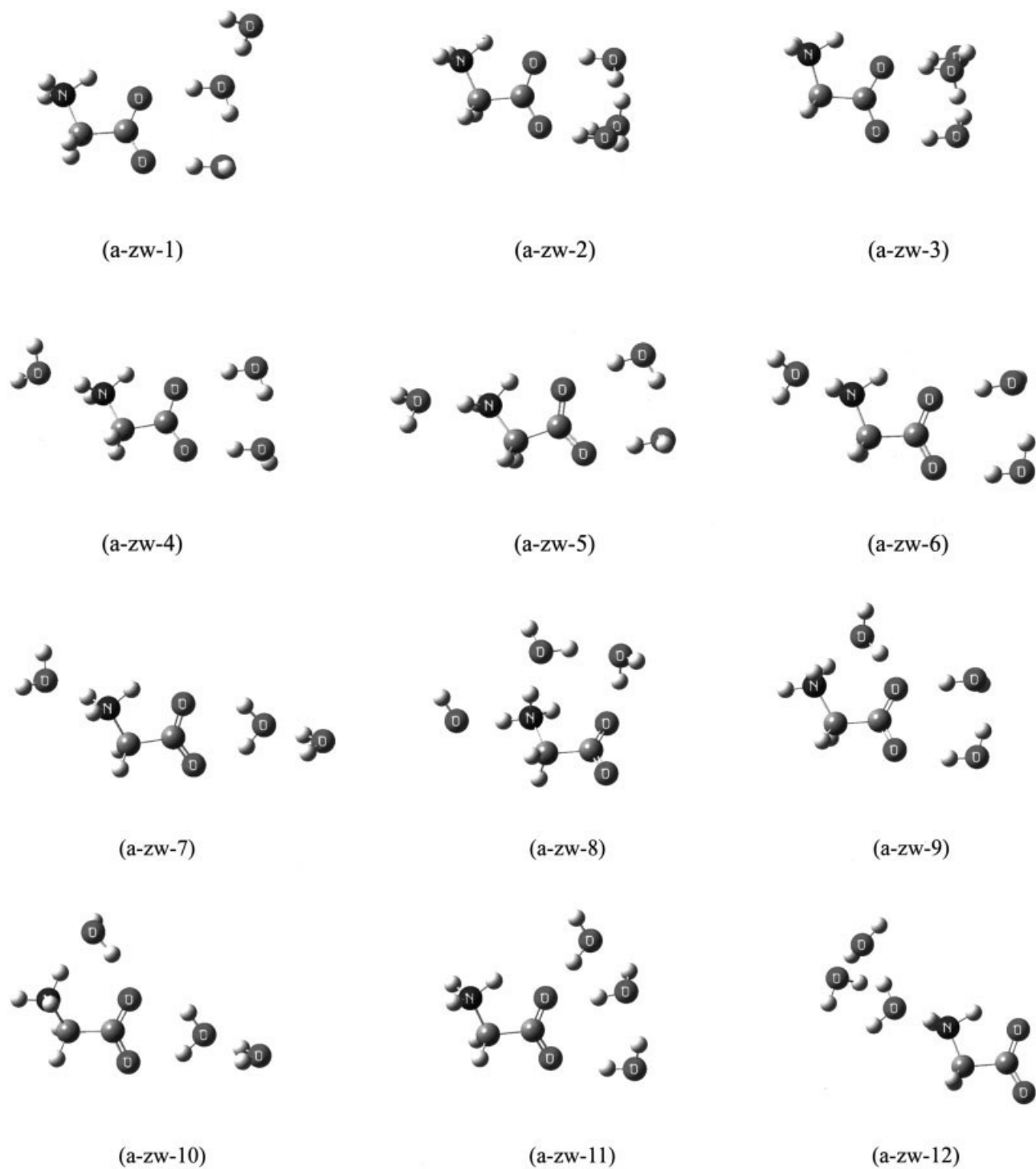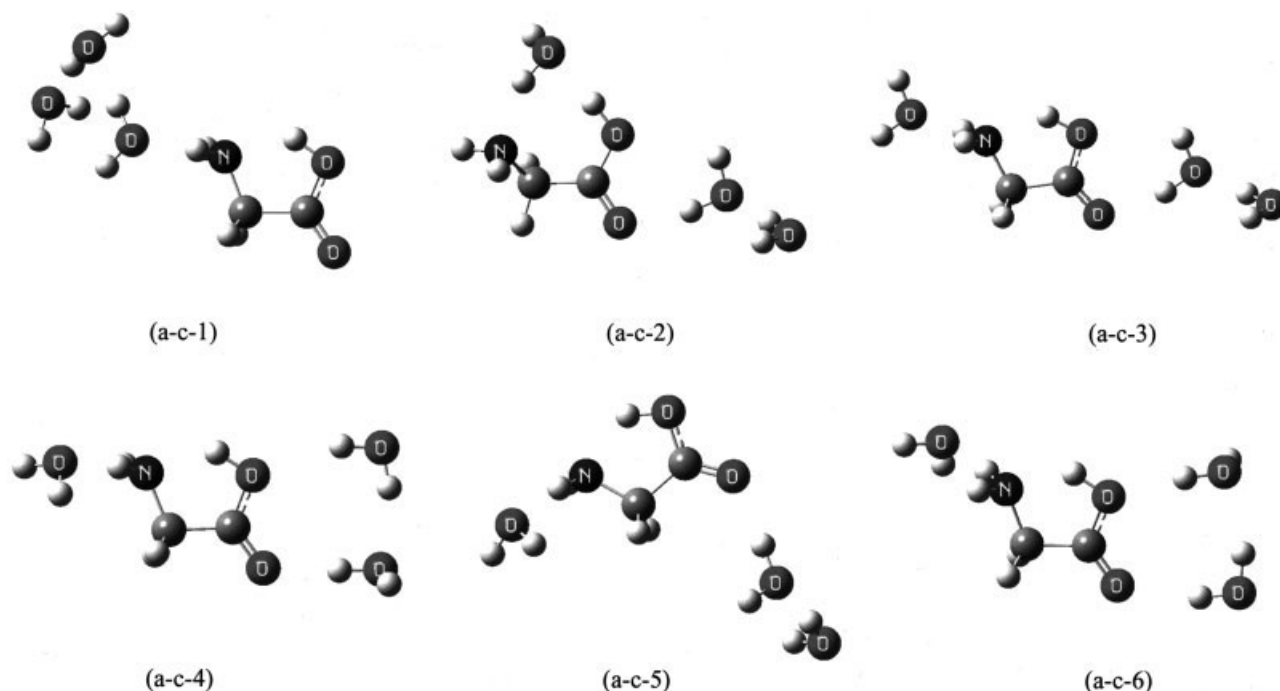
FIGURE 1. Structures of the low-energy conformers of zwitterionic Gly–$(H_2O)_3^-$ anion.

COMPUTATIONAL METHODS

We employ the density functional theory methods (B3LYP) [37,38] with the 6-311++G** basis set.

Intrinsic reaction coordinate (IRC) analysis is carried out to obtain the reaction path and to identify the transition state for given dynamic path. All

FIGURE 2. Structures of the low-energy conformers of canonical Gly- $(H_2O)_3^-$ anion.

calculations are carried out with the Gaussian 03 set of programs [39]. Default criteria are employed for all optimizations. Calculations for the structures of glycine–$(H_2O)_3$ clusters and anions proceeded by adding a water molecule to the glycine–$(H_2O)_2$ clusters and anions obtained in Ref. [34] in a variety of configurations.

Results

GLY–$(H_2O)_3^-$ ANION

The dipole bound excess electron in amino acid or amino acid–solvent cluster is known to stabilize the zwitterionic form of the amino acid relative to the canonical form. Bowen and coworkers [40] recently observed that arginine plus an excess electron exists as a zwitterion in low-temperature gas phase environment, as predicted by Gutowski and coworkers [32a]. Table I lists the calculated electronic energy, relative energy, and relative Gibbs function of the Gly–$(H_2O)_3^-$ cluster anions with zwitterionic and canonical Gly. Three zwitterionic conformers (a-zw-1), (a-zw-2), and (a-zw-3) presented in Figure 1 are calculated to be of lowest energy, indicating that an excess electron may in-

deed stabilize the zwitterion relative to the canonical form, in contrast with Gly–$(H_2O)_n^-$ ($n \leq 2$) for which the canonical forms have been predicted [35] to be thermodynamically much more stable. The energies of these three conformers are very close (within 1 kcal/mol). Three water molecules are clustered in the vicinity of the carboxylate group, indicating that interactions between the water molecules are stronger than those with the functional groups in the Gly moiety. In the fourth lowest-energy conformer (a-zw-4), a water molecule interacts with the ammonium group, while the other two water molecules bind to the carboxylate side. This structural feature of (a-zw-4) gives notable differences in the infrared (IR) spectra as discussed below. The lowest-energy Gly–$(H_2O)_3^-$ conformer with canonical Gly is (a-c-1) [Fig. 2(a)], and it is calculated to be 1.89 kcal/mol higher in energy than the lowest-energy zwitterionic conformer (a-zw-1). In this conformer, three water molecules form a ring, interacting with the amino group. In other conformers, at least a water molecule forms hydrogen bond with the carboxyl group. Although the structure (a-c-1) is much lower (by >1.5 kcal/mol) in energy than other anionic canonical conformers, it lies considerably higher in energy than

the low-energy zwitterionic ones. Estimating that the relative energies calculated by the B3LYP/6-311++G** method to be accurate to within 1 kcal/mol, we predict that the three zwitterionic conformers (a-zw-1), (a-zw-2) and (a-zw-3) would be predominantly observed, although small amount of the lowest-energy canonical conformer (a-c-1) (note the kinetic stability of the latter conformer discussed below) may also be present in low-temperature experiments.

Calculated vertical detachment energies (VDEs) are given in Table I. Since the VDE (3.4 eV) of the lowest-energy canonical conformer (a-c-1) is somewhat larger than those ($\sim$2.9 eV) of the three lowest-energy zwitterionic conformers, measuring this property may help distinguish the two forms. Because of the very similar VDEs of the three zwitterionic conformers, however, it would be rather difficult to identify them. Differences in the IR frequencies of these conformers may be useful in this regard. Figure 3 presents the calculated IR spectra (calculated frequencies are scaled by a factor of 0.9613) of the five (four zwitterionic and one canonical) lowest-energy conformers listed in Table I. For the low-energy zwitterionic anions, the features below 2000 cm^{-1} are quite similar, but some differences are to be noted for strong bands near or above 3000 cm^{-1}, most of which represent the OH and NH stretch modes. The intense bands at 2910–2925 cm^{-1} representing the antisymmetric stretch of the ammonium group are shared among the conformers (a-zw-1), (a-zw-2), and (a-zw-3). In the IR spectra of (a-zw-4), however, this band is absent, and a strong band at 2994 cm^{-1} is obtained instead due to the interactions of the ammonium group with a water molecule. An intense band at 3218 cm^{-1}, representing the symmetric stretch mode of the ammonium, is also a feature of the IR spectra of this zwitterionic anion. The conformer (a-zw-1) is characterized by a strong band at 3317 cm^{-1} (OH stretch mode of the water molecule binding to the carboxylate). As expected, the IR spectrum for the canonical conformer (a-c-1) is very different, with an intense band at $\sim$3070 cm^{-1} (stretch of OH in the carboxyl group) and two close lying strong bands (OH stretching of water in the vicinity of the amino group) in the high-frequency region (3600–3650 cm^{-1}).

Figure 4 depicts the isomerization (zwitterionic $\leftarrow \rightarrow$ canonical) by proton transfer processes of Gly–(H$_2$O)$_3^-$ cluster anions. Many of them isomerize either by barrierless process or via very

small barrier. In some higher-lying conformers of Gly–(H$_2$O)$_3^-$ the proton transfer is more difficult. For example, the zwitterionic (a-zw-10), and the canonical conformer (a-c-2) are separated by a barrier of $\sim$4 kcal/mol due to the bridging water molecule, with the isomerization occurring by a double proton transfer process via the water molecule [Fig. 4(a)] bridging the amino and the carboxyl groups. This multiple proton transfer pathway is similar to that for the zwitterionic $\leftarrow \rightarrow$ canonical transformation in the alanine–water clusters [8a,b]. Other conformers are found to isomerize almost spontaneously to the other form. Figure 4(b)–(e) depict the calculated isomerization processes of the three canonical [(a-c-4), (a-c-6), and (a-c-3)] and a zwitterionic (a-zw-12) anion. Isomerizations from (a-c-4) and (a-c-3) proceed by direct (single) proton transfer from the carboxyl to the amino group via very small ZPE-corrected barrier (0.25 and 0.56 kcal/mol, respectively). The conformers (a-c-6) and (a-zw-12) are predicted to isomerize without any barrier, because the transition state is calculated to be lower in energy than these structures. Therefore, these Gly–(H$_2$O)$_3^-$ cluster anions are unstable, and will not be observed in experiments. These low barriers of isomerization are to be understood by the fact that the water molecules do not bridge the amino and the carboxyl groups in these clusters, allowing the proton to transfer almost freely. The barrierless isomerization of the high-energy zwitterionic anion (a-zw-12) to the canonical one (a-c-1) described in Figure 4(e) is important, with regard to the stability of the latter conformer. Since the zwitterionic conformer (a-zw-12) is higher in energy than (a-c-1), the canonical conformer is stable against the isomerization, once it is formed in experiments. Combined with the fact that the energy of the canonical conformer (a-c-1) is higher than the lower-energy zwitterionic conformers, we thus predict that it may exist in small amount in gas phase at low temperature.
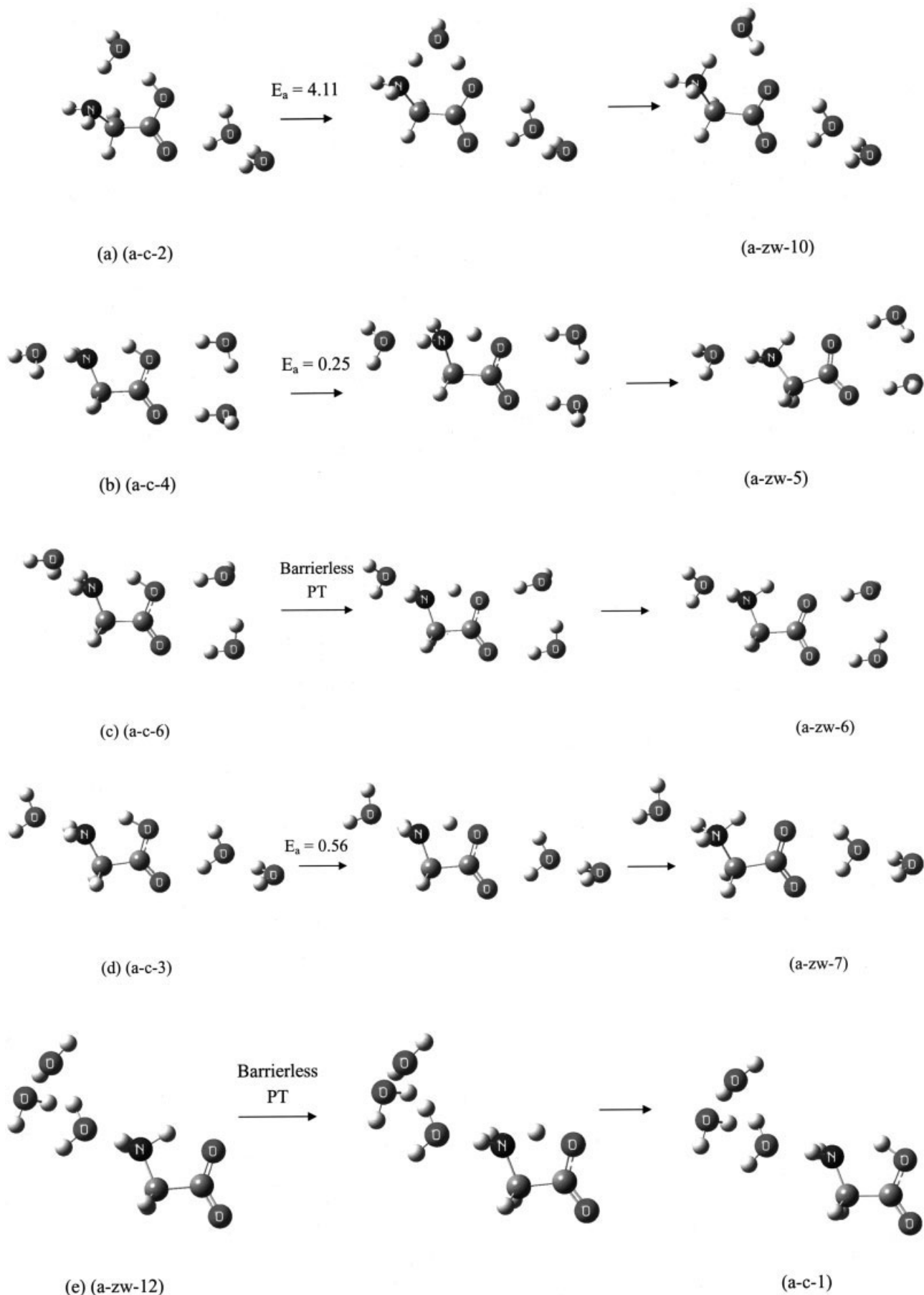
NEUTRAL GLY–(H$_2$O)$_3$ CLUSTER

In photoelectron spectroscopy experiments, the excess electron is detached to give the neutral species. For the Gly–water clusters studied in this work, the neutral Gly–(H$_2$O)$_3$ cluster [28] is produced with Gly either in zwitterionic or canonical form, depending on several factors. If the incumbent cluster anion Gly–(H$_2$O)$_3^-$ is zwitterionic (ca-
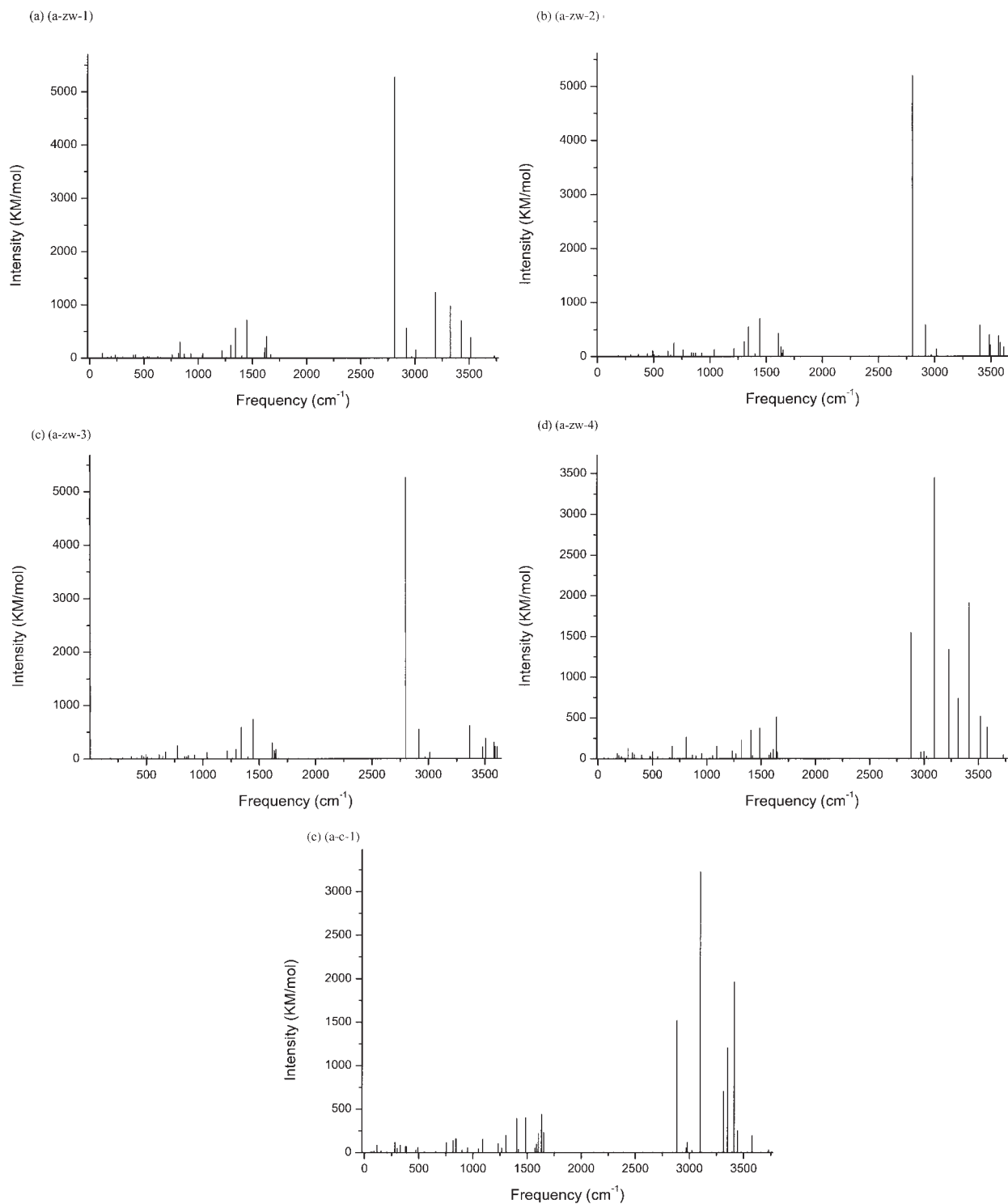
FIGURE 3. IR spectra of the four lowest-energy conformers of Gly–$(H_2O)_3^-$ anion (scaling factor of 0.9613 is employed).

FIGURE 4. Isomerization of some higher-energy conformers of Gly–$(H_2O)_3^-$ anion (barrier in kcal/mol).

TABLE II

Energy (hartree), ZPE (kcal/mol), relative energy ΔE (kcal/mol), and relative Gibbs function at 5 K ΔG_{5K} (kcal/mol) of neutral Gly–$(H_2O)_3$ with canonical and zwitterionic Gly core.

| Conformer	E	ZPE	ΔE	ΔG_{5K}
Canonical				
n-c-1	−513.95680	97.1	0	0
n-c-2	−513.95302	97.3	2.57	2.47
n-c-3	−513.95207	97.4	3.27	3021
n-c-4	−513.95151	97.3	3.52	3.52
n-c-5	−513.95158	97.4	3.58	3.52
n-c-6	−513.95188	97.7	3.69	3.28
n-c-7	−513.95085	97.2	3.83	3.91
n-c-8	−513.94995	97.2	4.40	4.48
Zwitterionic				
n-zw-1	−513.94335	98.2	0[a] (9.54)[b]	0.04 (8.76)
n-zw-2	−513.94194	97.6	0.28 (9.82)	0.48 (9.20)
n-zw-3	−513.94288	98.2	0.29 (9.83)	0 (8.73)
n-zw-4	−513.94178	97.5	0.29 (9.83)	0.62 (9.35)
n-zw-5	−513.94279	98.2	0.35 (9.89)	0.44 (9.16)
n-zw-6	−513.94258	98.1	0.38 (9.92)	0.46 (9.18)
n-zw-7	−513.94117	97.3	0.47 (10.01)	0.88 (9.61)
n-zw-8	−513.94091	97.4	0.73 (10.27)	1.09 (9.82)
n-zw-9	−513.94199	98.2	0.85 (10.39)	0.90 (9.62)
n-zw-10	−513.94199	98.2	0.85 (10.39)	0.86 (9.59)
n-zw-11	−513.94145	98.2	1.19 (10.73)	1.27 (10.00)

[a] Relative energy and Gibbs function with respect to (n-zw-1).
[b] Relative energy and Gibbs function with respect to (n-c-1).

nonical), the neutral cluster formed would also be zwitterionic (canonical), because the photodetachment processes do not induce much change in the nuclear configuration. The neutral species thus formed may subsequently survive long enough for experimental detection, or may evolve to the other form by zwitterion ← → canonical transformation. Both the thermodynamic (relative Gibbs function) and the kinetic (magnitude of barrier) factors should be considered to determine which forms (zwitterionic or canonical) would be more stable. Table II presents the electronic energy, relative energy and relative Gibbs function, and Figures 5 and 6 depict the structures of the neutral Gly–$(H_2O)_3$ cluster. Several observations are to be noted. First, the energy and the Gibbs function of the conformers with zwitterionic Gly are much higher (by >9 kcal/mol) than those with canonical Gly. This is high, in contrast with the case of the Gly–$(H_2O)_3^-$ anion presented in Table I, for which the reverse is true. Therefore, once the neutral zwitterionic Gly–$(H_2O)_3$ cluster is produced by photodetaching the

stable zwitterionic cluster anion given in Table I, it may isomerize to the canonical form, unless the barrier is sufficiently high. Second, one of the canonical conformers, (n-c-1), is much lower in energy than the others. In this lowest-energy neutral canonical conformer depicted in Figure 5, three water molecules bridge the carboxyl group, whereas in all the other conformers three water molecules form a chain connecting the amino and the carboxyl group. In the second lowest-energy conformer (n-c-2), a water molecule interacts with the hydrogen atom in the OH group of the Gly moiety, whereas in other conformers [with the exception of (n-c-6)] it forms a hydrogen bond either with the carbonyl oxygen or with the oxygen atom in the OH group of the amino acid. In all the Gly–$(H_2O)_3$ conformers with zwitterionic Gly presented in Figure 6, water molecules connect the ammonium and the carboxylate group. When the three water molecules form a chain in the conformer, the ammonium group is close to the carboxylate. In contrast, these two functional groups are bridged by water molecule(s) in some
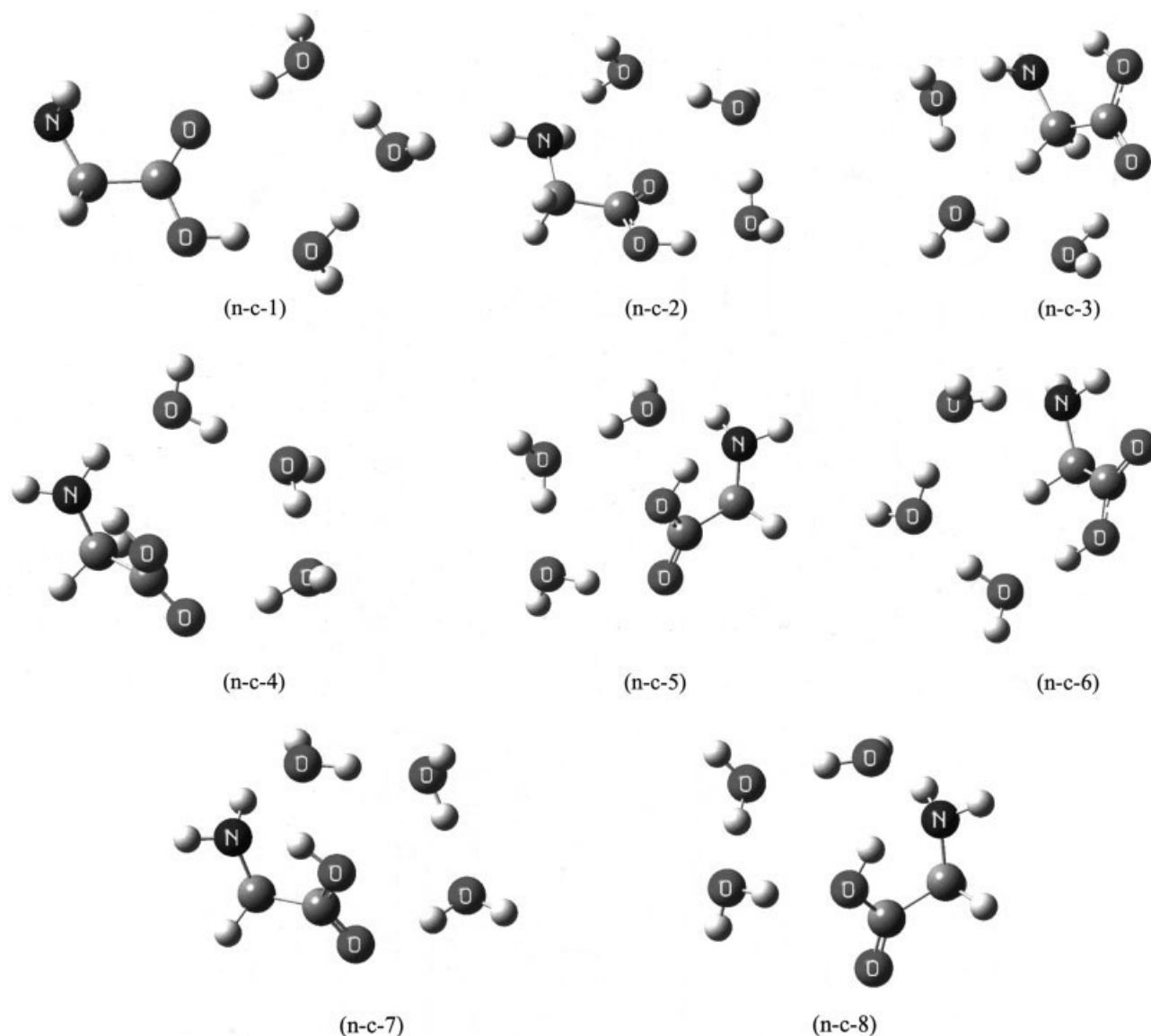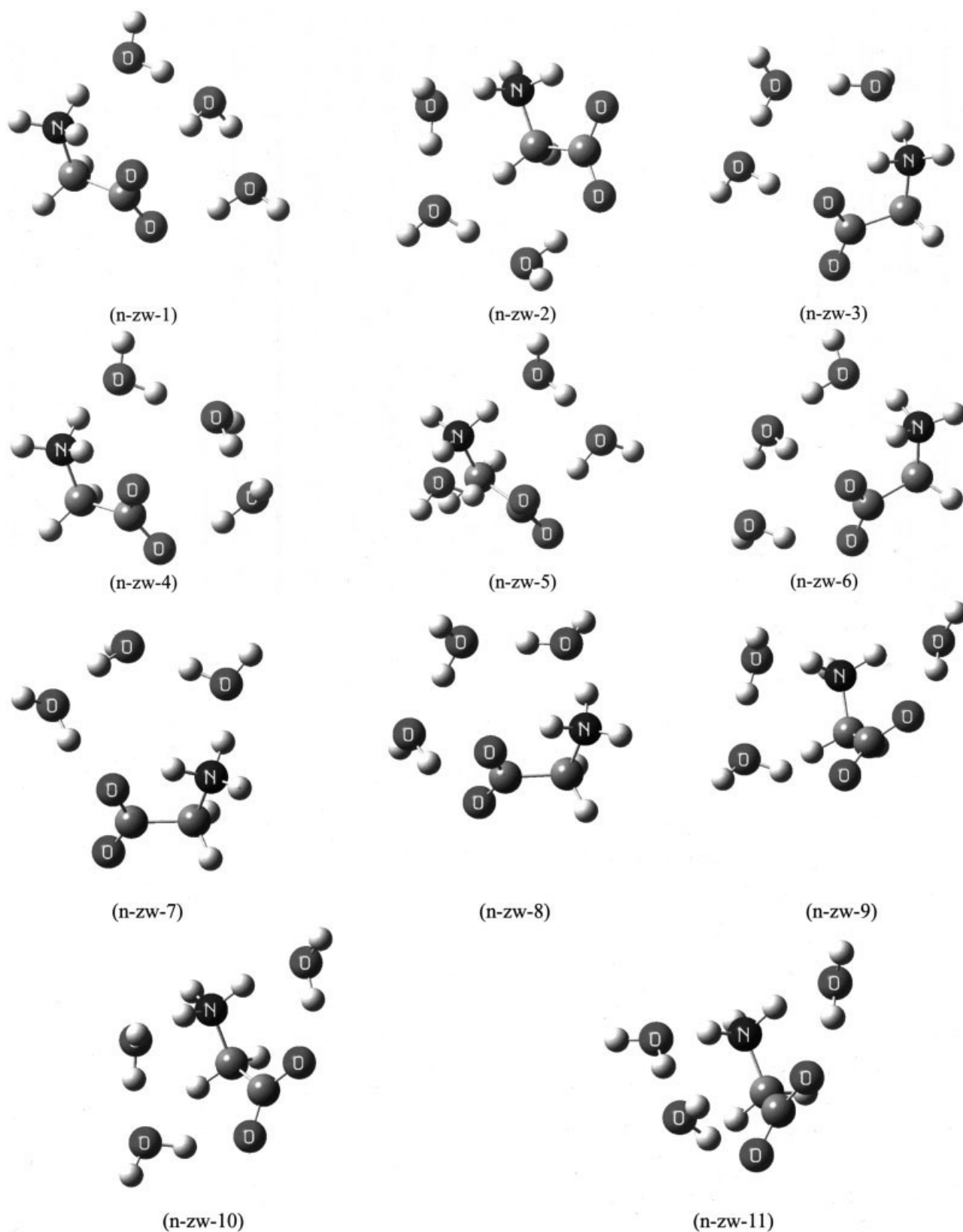
FIGURE 5. Structures of the low-energy conformers of neutral canonical Gly–$(H_2O)_3$.

conformers [(n-zw-5), (n-zw-9), (n-zw-10), and (n-zw-11)].

Figure 7 describes the calculated dynamic paths of zwitterionic $\leftarrow \rightarrow$ canonical transformation of Gly–$(H_2O)_3$. Since the transition states for isomerization from (n-zw-1), (n-zw-3), and (n-zw-4) lie lower in ZPE-corrected energy than the zwitterionic conformers, we predict that they will transform to the canonical conformers [(n-zw-1), (n-zw-3), and (n-zw-4), respectively] by a barrierless single proton transfer. The zwitterionic conformer (n-zw-2) may isomerize to the canonical form (n-c-6) by a triple proton transfer pathway with the barrier of 8.7 kcal/mol, or to (n-c-3) by a single proton trans-

fer process. Since the latter pathway is barrierless, the conformer (n-zw-2) is also considered unstable. Therefore, these lower-energy conformers of neutral zwitterionic Gly–$(H_2O)_3$ cluster, which lie much higher in energy than the neutral canonical clusters, may not be observed in the gas phase at low temperature. We find that the barriers of isomerization from some higher-energy neutral zwitterionic conformers may be large enough to exhibit some degree of kinetic stability. The zwitterionic neutral conformer (n-zw-5), for example, may transform to the canonical forms via two competing pathways with the barrier of 3.6 and 7.6 kcal/mol by the concerted double and triple proton transfer process,

FIGURE 6. Structures of the low-energy conformers of neutral zwitterionic Gly–(H₂O)₃.
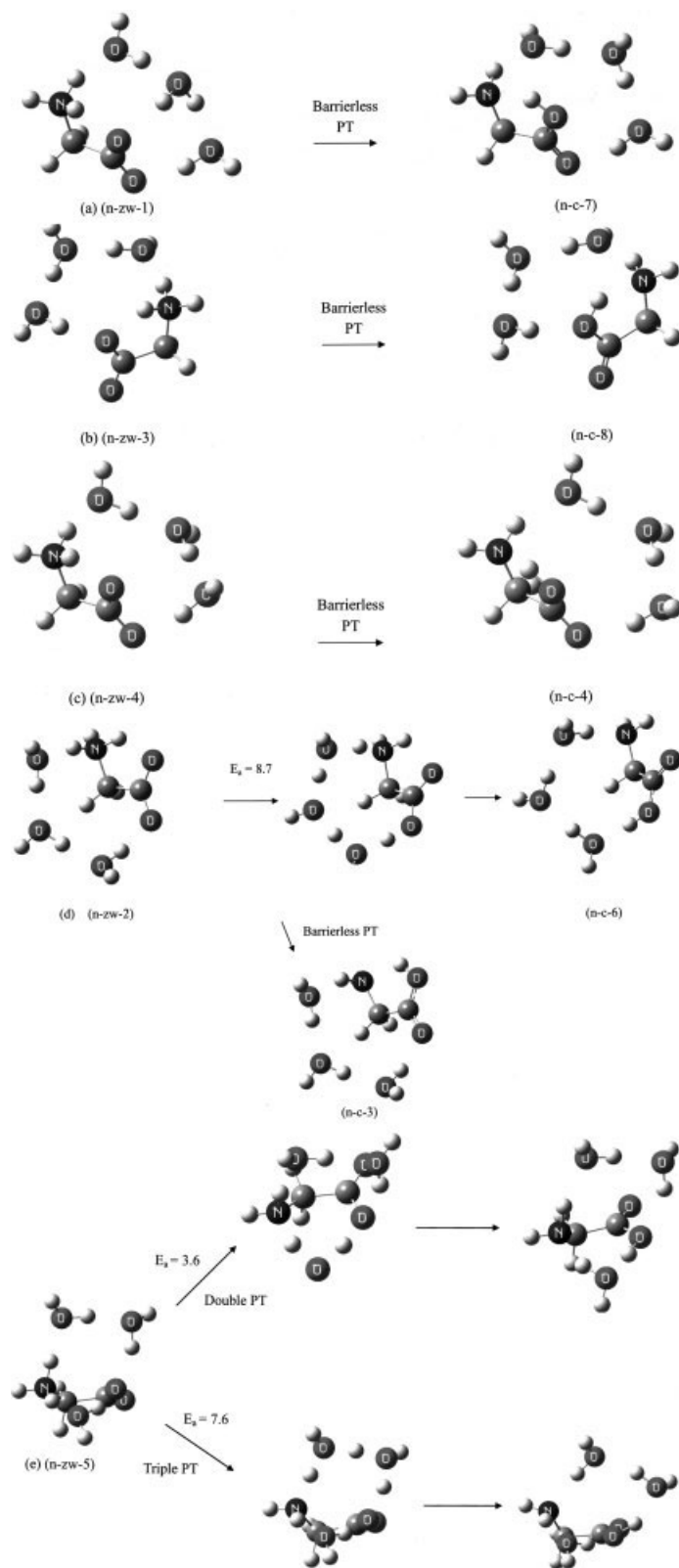
FIGURE 7. Isomerization from the low-energy conformers of zwitterionic forms of neutral Gly–$(H_2O)_3$ to canonical forms (barrier in kcal/mol).

respectively. Due to the high relative energy, they may be present in the low-temperature gas phase as a nascent species, if they are produced by photodetaching a zwitterionic anion.

Our calculated results suggest that the zwitterionic Gly–(H$_2$O)$_3^-$ anion is predicted to be the most stable anionic form of the Gly–(H$_2$O)$_3$ system in the gas phase; however, the canonical rather than the zwitterionic Gly–(H$_2$O)$_3$ neutral form is predicted to be its most stable neutral form. If zwitterionic Gly–(H$_2$O)$_3^-$ anions are dipole bound, then they would almost have to be made by electron attachment to their corresponding neutral. Since that neutral is not a zwitterion, forming dipole bound zwitterionic Gly–(H$_2$O)$_3^-$ anions in this way is unlikely, and thus, this may not be the mechanism of zwitterionic Gly–(H$_2$O)$_3^-$ anion formation. Microsolvation by three water molecules is not sufficient to stabilize the zwitterionic form of neutral Gly. In glycine/water clusters with even more water molecules [35], neutral Gly–(H$_2$O)$_3$ may well be zwitterionic, making the formation of dipole bound, zwitterionic Gly–(H$_2$O)$_3^-$ anions feasible.

References

1. Desfrançois, C.; Carles, S.; Schermann, J. P. Chem Rev 2000, 100, 3943.

2. Zwier, T. S. J. Phys Chem A 2001, 105, 8827.

3. Rizzo, T. R.; Park, Y. D.; Levy, D. H. J Chem Phys 1986, 85, 6945.

4. Snoek, L. C.; Robertson, E. G.; Kroemer, R. T.; Simons, J. P. Chem Phys Lett 2000, 321, 49.

5. Compagnon, I.; Hagemeister, F. C.; Antoine, R.; Rayane, D.; Broyer, M.; Dugourd, P.; Hudgins, R. R.; Jarrold, M. F. J Am Chem Soc 2001, 123, 8440.

6. Kim, N. J.; Kang, H.; Jeong, G.; Kim, Y. S.; Lee, K. T.; Kim, S. K. J Phys Chem A 2001, 104, 6552.

7. Schutz, M.; Burgi, T.; Leutwyler, S.; Fischer, T. J Chem Phys 1993, 98, 3763.

8. (a) Ahn, D.-S.; Park, S.-W.; Jeon, I.-S.; Lee, M.-K.; Kim, N.-H.; Han Y.-H.; Lee, S. J Phys Chem B 2003, 107, 14109.; (b) Park, S.-W.; Ahn, D.-S.; Lee, S. Chem Phys Lett 2003, 371, 74; (c) Jeon, I.-S.; Ahn, D.-S.; Park, S.-W.; Lee, S., Kim, B. Int J Quantum Chem 2005, 101, 55; (d) Lee, K.-M.; Park, S.-W.; Jeon, I.-S.; Lee, B.-R.; Ahn, D.-S.; Lee, S. Bull Korean Chem Soc 2005, 909, 26.

9. Csaszar, A. G.; Perczel, A. Prog Biophys Mol Biol 1999, 71, 243.

10. Tajkhorshid, E.; Jalkanen, K. J.; Suhai, S. J Phys Chem B 1998, 102, 5899.

11. Snoek, L. C.; Kroemer, R. T.; Hockridge, M. R.; Simons, J. P. Phys Chem Chem Phys 2001, 3, 1819; Snoek, L. C.; Kroemer, R. T.; Simons, J. Phys Chem Chem Phys 2001, 4, 2130.

12. Godfrey, P. D.; Firth, S.; Heatherley, L. D.; Brown, R. D.; Pierlot, A. P. J Am Chem Soc 1993, 115, 9687.

13. Spinor, J.; Sulkes, M. J Chem Phys 1993, 98, 9389.

14. Gao, X.; Fischer, G. J Phys Chem A 1999, 103, 4404; Gao, X.; Fischer, G. Spectrochim Acta 1999, 55, 2329.

15. Fernandez-Ramos, A.; Smedarchina, Z.; Siebrand, W.; Zgierski, M. Z. J Chem Phys 2000, 113, 9714.

16. Lemoff, A. S.; Bush, M. F.; Williams, E. R. J Phys Chem A 2005, 109, 1903.

17. Hu, C. H.; Shen, M.; Schafer, H. F., III. J Am Chem Soc 1993, 115, 2923.

18. Bandyopadhyay, P.; Gordon, M. S.; Mennucci, B.; Tomasi, J. J Chem Phys 2002, 116, 5023.

19. Julian, R. R.; Jarrold, M. F. J Phys Chem A 2004, 108, 10861.

20. Jensen, J. H.; Gordon, M. S. J Am Chem Soc 1995, 117, 8159.

21. Albrecht, G.; Corey, R. B. J Am Chem Soc 1939, 61, 1087.

22. Ding, Y.; Krogh-Jespersen, K. Chem Phys Lett 1992, 199, 261.

23. Jonsson, P. G.; Kvick, A. Acta Crystallogr B 1972, 28, 1827.

24. Tortonda, F. R.; Pascual-Ahuir, J. L.; Silla, E.; Tunon, I. Chem Phys Lett 1996, 260, 21.

25. Castleman, A. W., Jr.; Bowen, K. T. J Phys Chem 1996, 100, 10911.

26. Gutowski, M.; Skurski, P.; Simon, J. J Am Chem Soc 2000, 122, 10159.

27. Robertson, W. H.; Johnson, M. A. Annu Rev Phys Chem 2003, 54, 173.

28. Chaudhari, A.; Lee, S.-L. Chem Phys 2005, 310, 281.

29. Robertson, W. H.; Diken, E. G.; Price, E. A.; Shin, J.-W.; Johnson, M. A. Science 2003, 299, 1367.

30. Lyapustina, S. A.; Xu, S.-J.; Nilles, J. M.; Bowen, K. H. J Chem Phys 2000, 112, 6643.

31. Gutowski, M.; Dabkowska, I.; Rak, J.; Xu, S.-J.; Nilles, J. M.; Radisic, D.; Bowen, K. H. Eur Phys J 2002, D 20, 431; Rak, J.; Skurski, P.; Gutowski, M. J Chem Phys 2000, 114, 10673.

32. (a) Rak, J.; Skurski, P.; Simons, J.; Gutowski, M. J Am Chem Soc 2001, 123, 11695; (b) Skurski, P.; Rak, J.; Simons, J.; Gutowski, M. J Am Chem Soc 2001, 123, 11073.

33. Desfrançois, C.; Abdoul-Carime, H.; Schermann, J. P. J Chem Phys 1996, 104, 7792; Carles, S.; Desfrançois, C.; Schermann, J. P.; Smith, D. M. A.; Adamowicz, L. J Chem Phys 2000, 112, 3726.

34. Ahn, D.-S.; Kang, A.-R.; Lee, S.; Kim, B.; Kim, S. K.; Neuhauser, D. J Chem Phys 2005, 122, 084310.

35. Xu, S.; Nilles, J. M.; Bowen, K. H., Jr. J Chem Phys 2003, 119, 10696.

36. Diken, E. G.; Hammer, N. I.; Johnson, M. A. J Chem Phys 2004, 120, 9902.

37. Lee, C.; Yang, W.; Parr, R. P. Phys Rev B 1988, 37, 785.

38. Becke, A. D. J Chem Phys 1993, 98, 5648.

39. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A., Jr.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M; Gonzalez, C.; J. A. Pople, J. A. Gaussian: Pittsburgh, PA, 2003.

40. Xu, S.; Zheng, W.; Radisic, D.; Bowen, K. T. J Chem Phys 2005, 122, 091103.