

Effect of microsolvation on zwitterionic glycine: an ab initio and density functional theory study

Prabhat K. Sahu · Shyi-Long Lee

Received: 17 October 2007 / Accepted: 29 January 2008 / Published online: 11 March 2008
© Springer-Verlag 2008

Abstract The effect of microsolvation on zwitterionic glycine, considering both ($-\text{NH}_3^+$) as proton donor and ($-\text{COO}^-$) as proton acceptor at correlated ab initio (MP2) level and density functional methods (B3LYP, PW91, MPW1PW91 and PBE) using 6-311++G** basis set has been reported. DFT methods have been employed so as to compare the performance/quality of different gradient-corrected correlation functionals (PW91, PBE), hybrid functionals (B3LYP, MPW1PW91) and to predict the near quantitative structural and vibrational properties, at reduced computational cost. B3LYP method outperforms among the different DFT methods for the computed hydrogen bond distances and found closer to the value obtained by correlated MP2 level, whereas MPW1PW91 and PBE methods shows very similar values but ~ 0.03 Å less, compared to B3LYP method. MP2 calculation and single point CCSD(T)/MP2 calculation have been considered to decompose the interaction energy, including corrections for basis set superposition error (BSSE). Moreover, charge distribution analysis has also been carried out to understand the long raised questions, how and why the two body energies have significant contribution to the total binding energy.

Keywords Ab initio · Density functional theory · Microsolvation · Zwitterionic glycine

Introduction

The effects of solvation represent a challenging research area due to its significant applicability in many chemical and biological processes [1]. Aqueous solutions are perplexing since they adopt some of the eccentric behavior of water. The interactions between the solvent and the various constituent groups of a protein, such as the amino acid side-chains and the backbone peptide group, play a crucial role in the structure and function of proteins in aqueous solutions. Because of the complexity of these interactions in the intact macromolecule, one approach to characterize the thermodynamic and hydration behavior of the various constituent groups of proteins is to study low molar mass compounds chosen to model specific structural features of a protein. These compounds are referred to as model compounds. This approach has received a lot of attention in recent years. In view of the role of water in the structural and functional properties of macromolecules and their interactions, much attention has been paid to the properties of water in aqueous biomolecular system [2]. Several theoretical studies on environmental effects on the molecular structure of amino acids have been performed [3–12].

The amino acids are known to exist in solution and in crystalline phase as zwitterions [13–15]. However, neutral molecules have been isolated in gas phase [13, 15–19]. Study of interaction of water with amino acid is important for the ultimate understanding of protein hydration and the role of water in biological systems. There are various investigations reporting structure, stability and bulk solvent effect on amino acid [3–6, 10–30]. It has also been shown that both, bulk and microscopic solvent effect, changes the molecular properties in the same way [31, 32]. However, in microscopic solvent effect we get additional information on how different many-body interaction energies contribute to the

P. K. Sahu · S.-L. Lee (✉)
Department of Chemistry and Biochemistry,
National Chung Cheng University,
Chia-Yi 621, Taiwan
e-mail: chesll@ccu.edu.tw

binding energy and also on hydrogen bonding and it is also insightful since it provides a fundamental understanding of solvent-solute interactions at the molecular level [3–6, 33–35].

The experimental matrix IR spectroscopic results for the glycine-water complex in isolated condition have also been reported [11]. Very recently; the rotational spectra of glycine-water complex have been reported [36] by using laser-ablation devices in combination with molecular beam Fourier-transform microwave spectroscopy [LA-MB-FTMW].

Earlier, we have reported [5] the density functional theory study of zwitterionic glycine-(water)₃ complex, taking the (-NH₃⁺) group as proton donor into account. Chaudhari et al. [6], have later reported cyclic zwitterionic glycine-(water)₃ stable structure, resulted by considering (-COO⁻) as proton acceptor. We would like to report the effect of microsolvation on zwitterionic glycine, considering both (-NH₃⁺) as proton donor and (-COO⁻) as proton acceptor using co-related ab initio (MP2) level and density functional methods (B3LYP, PW91, MPW1PW91 and PBE) using 6-311++G** basis set. DFT methods have been employed so as to compare the performance/quality of different gradient-corrected correlation functionals (PW91, PBE), hybrid functionals (B3LYP, MPW1PW91). The present work will be interesting especially from the perspective of the previous reports [5, 6] in order to provide complete and benchmark study for the effect of microsolvation on zwitterionic glycine-(water)₃ complex. However, trihydrated zwitterionic glycines have also been of interest to other researchers [11, 23, 25, 37]. The optimized geometries, vibrational frequencies and interaction energies of the stable conformers have been investigated. The decomposition of the interaction energies of these stable conformers has also been carried out. It is believed that the computed interaction energy for the zwitterionic glycine with three water molecules will be of interest, since previous theoretical studies in the gas phase has predicted that zwitterionic glycine is not stable [18]. Moreover, charge distribution analysis has also been carried out to understand the long raised questions, how and why the two body energies have significant contribution to the total binding energy.

The paper is structured as follows. In Sect. 2, the computational details are given. Section 3 gives the brief summary of the energy decomposition scheme including correction for basis set superposition error (BSSE) by using function counterpoise and its generalized version [38–40]. Results are presented in Sect. 4. Final conclusions are summarized in Sect. 5.

Computational details

Quantum chemical calculations, using correlated ab initio (MP2) [41–43] and density functional methods (B3LYP

[44–46], PW91 [47], MPW1PW91 [48] and PBE [49]) for the different stable conformers of glycine-(water)₃ complex, considering both (-NH₃⁺) as proton donor and (-COO⁻) as proton acceptor have been carried out. The optimized geometries, vibrational frequencies and interaction energies of the stable conformers have been investigated. DFT methods have been employed so as to compare the performance/quality of different gradient-corrected correlation functionals (PW91, PBE), hybrid functionals (B3LYP, MPW1PW91) and to predict the near quantitative structural, vibrational and energetic properties, at reduced computational cost. Although the performance of DFT method has been generally credited to give very good geometries and vibrational frequencies with the experimental ones, we note that improved calculations, using higher level theory are needed to achieve satisfactory accuracy and reliability for electronic energies at an economical computational cost. The second-order Møller-Plesset (MP2) method has been employed in our calculation so as to include electron correlation explicitly in order to obtain good representations of dispersion and electrostatic forces that are responsible for the binding of the species. Valence triple-zeta basis set with diffuse and polarization function, 6-311++G** has been used in the overall calculations, since for hydrogen bonded systems, it is expected that both diffuse and polarization function may be necessary in the basis set. A quantitative account of the cooperative effect has been achieved by decomposing the interaction energy at MP2 level and single point CCSD(T)/MP2, using counterpoise and generalized counterpoise methods [38–40]. All such calculations have been performed using GAUSSIAN 03 program [50].

Energy decomposition

The two, three and four body contributions to the total binding energy are calculated using many body analysis. The decomposition of the total energy of the complex can be written as

$$\begin{aligned}\Delta E &= E(1234) - \{E_{Gly} + 3E_W\} \\ &= \sum_{i=1}^4 E(i) - \{E_{Gly} + 3E_W\} \text{ (relaxation energy)} \\ &\quad + \sum_{i=1}^3 \sum_{j>i}^4 \Delta^2(ij) \text{ (Two body energy)} \\ &\quad + \sum_{i=1}^2 \sum_{j>i}^3 \sum_{k>j}^4 \Delta^3E(ijk) \text{ (Three body energy)} \\ &\quad + \Delta^4E(1234) \text{ (Four body energy)}\end{aligned}$$

where $E(i)$, $E(ij)$, $E(ijk)$, $E(1234)$ are the energies of the various monomers, dimers, trimers, and tetramer in the complex and E_{Gly} , E_W are the energies of isolated glycine and water molecules, respectively. The pairwise additive two-body interaction energies and higher three-body and four-body nonadditive interaction energies are defined as the following equations.

$$\Delta^2 E(ij) = E(ij) - \{E(i) + E(j)\}$$

$$\begin{aligned} \Delta^4 E(1234) = & E(1234) - \{E(1) + E(2) + E(3) + E(4)\} \\ & - \{\Delta^2 E(12) + \Delta^2 E(13) + \Delta^2 E(14) + \Delta^2 E(23) + \Delta^2 E(24) + \Delta^2 E(34)\} \\ & - \{\Delta^3 E(123) + \Delta^3 E(124) + \Delta^3 E(134) + \Delta^3 E(234)\} \end{aligned}$$

The BSSE-corrected energy of a subsystem (ijk) is evaluated in the full basis of a larger system (1234), and denoted by the term $E(ijk|1234)$. Accordingly, the n -body terms are substituted with the BSSE-corrected ones:

$$\Delta^2 E_C(ij) = E(ij|1234) - \{E(i|1234) + E(j|1234)\}$$

$$\begin{aligned} \Delta^4 E_C(1234) = & E(1234) - \{E(1|1234) + E(2|1234) + E(3|1234) + E(4|1234)\} \\ & - \{\Delta^2 E(12|1234) + \Delta^2 E(13|1234) + \Delta^2 E(14|1234) + \Delta^2 E(23|1234) + \Delta^2 E(24|1234) + \Delta^2 E(34|1234)\} \\ & - \{\Delta^3 E(123|1234) + \Delta^3 E(124|1234) + \Delta^3 E(134|1234) + \Delta^3 E(234|1234)\}. \end{aligned}$$

The BSSE corrected total binding energy is calculated as suggested by Valiron and Mayer [39].

Results and discussion

Geometry

Figure 1a and b show the vibrationally stable structure of two different conformers out of several different optimized glycine-(water)₃ complexes, considering both ($-\text{NH}_3^+$) as proton donor and ($-\text{COO}^-$) as proton acceptor, at MP2/6-311++G** level. The selected geometries parameters for these two different conformers at correlated ab initio (MP2) and density functional methods (B3LYP, PW91, MPW1PW91 and PBE) are listed in Tables 1 and 2.

Table 1 depicts the hydrogen bond distances between zwitterionic glycine(G) and three water molecules (W1, W2 and W3) for complex-I, where the zwitterionic glycine acts as hydrogen bond donor through ($-\text{NH}_3^+$) to W3, W2 and hydrogen bond acceptor through ($-\text{COO}^-$) to W1 and the

$$\begin{aligned} \Delta^3 E(ijk) = & E(ijk) - \{E(i) + E(j) + E(k)\} \\ & - \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(jk)\}, \end{aligned}$$

$$\begin{aligned} \Delta^3 E_C(ijk) = & E(ijk|1234) - \{E(i|1234) + E(j|1234) + E(k|1234)\} \\ & - \{\Delta^2 E(ij|1234) + \Delta^2 E(ik|1234) + \Delta^2 E(jk|1234)\} \end{aligned}$$

three water molecules take part as both hydrogen bond donor and acceptor simultaneously in the cyclic structure. The computed hydrogen bond distances between zwitterionic glycine(G) and three water molecules (W1, W2 and W3) for complex-II can be observed from Table 2, in which the zwitterionic glycine simultaneously act as hydrogen bond donor through ($-\text{NH}_3^+$) to all the three water molecules, W1, W2, W3 and hydrogen bond acceptor through ($-\text{COO}^-$) to W1 and W3. Thereby, G interacts with each of W1 and W3 via two hydrogen bonds and with W2 through single hydrogen bond.

It is worthy to note here that both in Tables 1 and 2, B3LYP method outperforms among the different DFT methods for the computed hydrogen bond distances and is found closer to the value obtained by correlated MP2 level, whereas MPW1PW91 and PBE methods shows very similar values but ~ 0.03 Å less, compared to B3LYP method. The van der Waals distances between heavy atoms (O7–O12, O12–O15, O15–O18, O15–N1, O18–N1) for complex-I and (O7–O18, O8–O12, O12–N1, O15–N1, O18–N1) for complex-II are found to be less than 3 Å. The O–H bonds of water molecules, involved in hydrogen

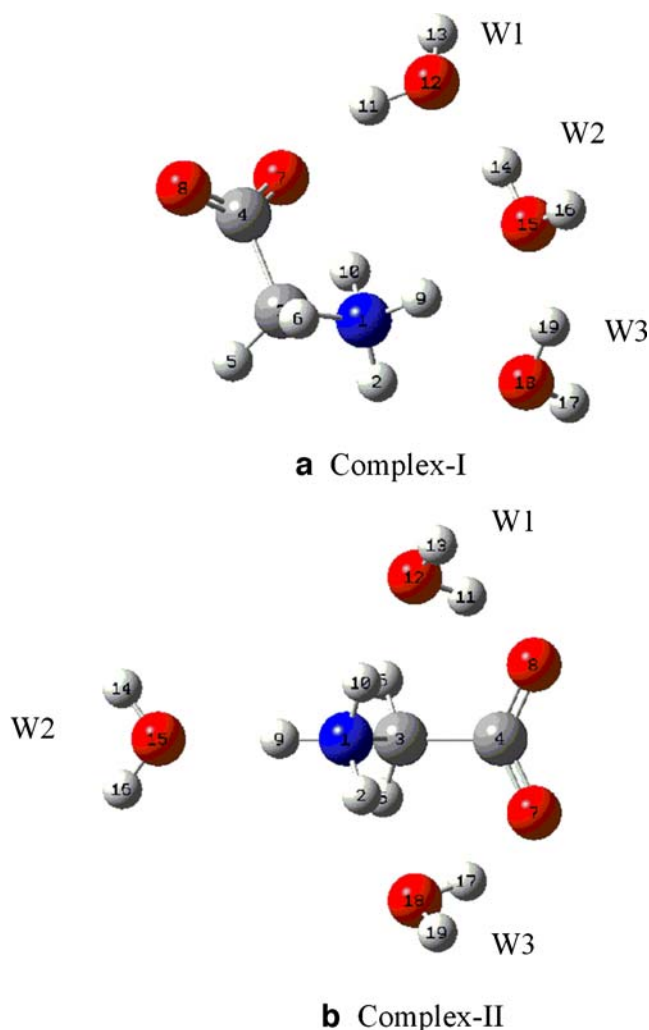


Fig. 1 The optimized vibrationally stable conformers of zwitterionic glycine-(water)₃ complexes

bonding are found to be increased as compared to those which are not involved.

Energetics and charge distributions

The total energies, zeropoint vibrational energies and dipole moment for the complexes I and II using 6-311++G** at correlated ab initio (MP2) and density functional methods (B3LYP, PW91, MPW1PW91 and PBE) are listed in Table 3. It can be observed from Table 3 that the complex-I is more stable compared to complex-II, with regard to the calculated total energy. It is interesting to note here that the most stable complex-I is similar to the lowest energy structure predicted by Ramaekers et al. [11]. We also note that although the performance of DFT method, B3LYP in particular has been generally credited to give very good geometries and vibrational frequencies with the experimental ones, the calculated total energies and dipole moment at MP2 level, which include electron correlation explicitly in order to obtain good representations of dispersion and

electrostatic forces that are responsible for the binding of the species, can provide better values. It is found to be fact that all the DFT methods employed here overestimate the total energies, however, PBE method proved to be better compared to other DFT methods. For the calculated dipole moment values, both PBE and MPW1PW91 shows approximate values closer to those obtained by MP2 level.

The ChelpG charges and dipole moments calculated at MP2/6-311++G** level for the complex-I and II are given in Table 4. Since it is believed that, the hydrogen-bond strengths correlate strongly with the charge separations, a more detailed description will be discussed later in energy decomposition.

Vibrational frequencies

Table 5 shows the calculated frequencies for the two different stable complex-I and II at correlated ab initio (MP2) and density functional methods (B3LYP, PW91, MPW1PW91 and PBE). Since it lacks any experimental evidence for the vibrational spectra, presently, we believe that these values may be helpful in providing future

Table 1 Selected optimized geometries for glycine-(water)₃ complex-I at ab initio and DFT methods using 6-311++G**

Parameters	B3LYP	PW91	MPW1PW91	PBE	MP2
N1-H2	1.019	1.025	1.016	1.017	1.017
N1-H9	1.031	1.040	1.028	1.029	1.028
N1-H10	1.053	1.082	1.061	1.063	1.059
C4-O7	1.279	1.296	1.277	1.277	1.285
C4-O8	1.219	1.226	1.214	1.215	1.225
O7-H11	1.704	1.664	1.686	1.684	1.710
O12-H14	1.691	1.632	1.666	1.662	1.698
O15-H19	1.951	1.895	1.927	1.920	1.962
O15-H9	1.945	1.908	1.926	1.922	1.938
O18-H9	2.539	2.517	2.512	2.505	2.487
O18-H2	2.326	2.333	2.309	2.297	2.402
O12-H11	0.991	1.005	0.988	0.989	0.985
O12-H13	0.961	0.968	0.957	0.957	0.959
O15-H14	0.994	1.012	0.992	0.993	0.987
O15-H16	0.962	0.969	0.958	0.959	0.960
O18-H19	0.973	0.983	0.969	0.970	0.968
O18-H17	0.961	0.968	0.957	0.957	0.959
O7-O12	2.661	2.639	2.641	2.639	2.652
O12 O15	2.666	2.629	2.641	2.638	2.672
O15 O18	2.819	2.785	2.797	2.792	2.818
O15 N1	2.882	2.849	2.860	2.856	2.877
O18 N1	2.815	2.810	2.797	2.787	2.799
C3 C4 O7	112.18	111.68	111.86	111.84	111.63
C3 N1 H2	118.19	118.90	118.49	118.59	118.04
C3 N1 H9	113.09	113.44	113.34	113.37	112.50
C3 N1 H10	100.37	97.86	98.97	98.84	98.98
H11 O12 H13	107.36	106.53	107.13	107.08	105.55
H14 O15-H16	106.44	106.37	106.41	106.37	104.58
H17-O18-H19	106.88	106.27	106.72	106.67	105.16

Table 2 Selected optimized geometries for glycine-(water)₃ complex-II at ab initio and DFT methods using 6-311++G**

Parameters	B3LYP	PW91	MPW1PW91	PBE	MP2
N1-H2	1.041	1.056	1.041	1.043	1.038
N1-H9	1.028	1.037	1.026	1.027	1.027
N1-H10	1.041	1.056	1.041	1.043	1.038
C4-O7	1.251	1.261	1.246	1.247	1.255
C4-O8	1.251	1.261	1.246	1.247	1.255
O7-H17	1.693	1.634	1.659	1.655	1.682
O8-H11	1.693	1.634	1.659	1.655	1.682
O12-H10	1.804	1.754	1.769	1.764	1.784
O18-H2	1.804	1.754	1.769	1.764	1.784
O15-H9	1.893	1.856	1.873	1.864	1.884
O12-H11	0.997	1.016	0.996	0.998	0.992
O12-H13	0.961	0.968	0.957	0.958	0.959
O15-H14	0.963	0.969	0.958	0.959	0.961
O15-H16	0.963	0.969	0.958	0.959	0.961
O18-H17	0.997	1.016	0.996	0.998	0.992
O18-H19	0.961	0.968	0.957	0.958	0.959
O7-O18	2.646	2.614	2.616	2.612	2.634
O8-O12	2.646	2.614	2.616	2.612	2.634
O12-N1	2.763	2.725	2.729	2.724	2.734
O15-N1	2.921	2.896	2.899	2.892	2.909
O18-N1	2.763	2.725	2.729	2.724	2.734
C3-C4-O7	115.48	115.82	115.55	115.58	115.25
C3-C4-O8	115.48	115.82	115.55	115.58	115.25
C3-N1-H2	108.21	107.37	107.96	107.88	108.18
C3-N1-H9	111.46	111.56	111.56	111.39	110.82
C3-N1-H10	108.21	107.37	107.96	107.88	108.18
H11-O12-H13	106.91	106.19	106.66	106.67	105.35
H14-O15-H16	106.32	105.88	106.32	106.24	104.68
H17-O18-H19	106.91	106.19	106.66	106.67	105.35

experimental work. Although B3LYP currently provides the best values nearly approaching to experiment, it will be interesting to compare the different computed vibrational frequency stretching mode at different DFT methods. For complex-I, it has been observed that the highest intensity peaks at B3LYP level are approximately the same, 3319.47 cm⁻¹ (935.43) for O-Hstr. and N-Hstr between G and water molecules and 3341.5 cm⁻¹ (917.14) for O-Hstr between water molecules. Similar kinds of peaks are

not observed in other DFT methods, where three peaks are observed for the same with different intensity. However, at the correlated MP2 level, similar kind of peaks to those obtained at B3LYP level are observed for complex-I, 3411.96 cm⁻¹ (930.38) for O-Hstr. and N-Hstr between G and water molecules and 3462.76 cm⁻¹ (988.55). For complex-II, three different high intensity peaks are observed for all calculations at different DFT as well as MP2 levels and are analyzed to be resulted from O-Hstr. and N-Hstr(asym), O-Hstr. and N-Hstr(sym) and N-Hstr. The pair, O-Hstr. and N-Hstr(asym), O-Hstr. and N-Hstr(sym) mode are observed between G and each of W1, W3 whereas, the N-Hstr is observed between G and W2. The B3LYP computed values for the same are, 3210.88 cm⁻¹ (1479.45), 3228.63 cm⁻¹ (1090.8) and 3350.94 cm⁻¹ (529.95), respectively as compared to those obtained by correlated MP2 level, 3308.15 cm⁻¹ (1547.4), 3323.96 cm⁻¹ (1110.2) and 3421.07 cm⁻¹ (515.35).

Energy decomposition

A quantitative account on the roles of hydrogen bond cooperativity on the two different stable structures has been analyzed through energy decomposition scheme, as mentioned in Sect. 3. Although the DFT methods, B3LYP in particular provides more accurate descriptions for the geometry and vibrational frequencies, closer to the experimental findings, an accurate treatment of dispersive force may be critical to describe the binding in these stable complexes-I and II and hence MP2 calculation is considered better to decompose the interaction energy. Single-point CCSD(T)//MP2 calculation has also been carried out to better estimate the decomposed interaction energy. For calculating the many body interaction energies, the stable complexes are divided into two body, three body, four body interaction terms. The interaction energies for two body, three body, four body and BSSE corrected total binding energy, are listed in Table 6. It can be observed from Table 6 that the BSSE corrected total binding energy for the two different stable complex-I and II at CCSD(T)/6-311++G**//MP2/6-311++G** are

Table 3 Total energies (Hartree), zeropoint vibrational energies (kcal mol⁻¹) and dipole moment (Debye) for the glycine-(water)₃ complexes I and II using 6-311++G**

	B3LYP	PW91	MPW1PW91	PBE	MP2
Complex-I					
Total energy	-513.93553	-513.76912	-513.78501	-513.36190	-512.64627
ZPVE	97.40	94.48	98.42	98.29	98.84
μ	8.18	7.42	7.97	7.96	7.86
Complex-II					
Total energy	-513.93308	-513.76643	-513.78263	-513.35919	-512.64426
ZPVE	97.37	94.50	98.44	98.29	98.85
μ	9.71	9.18	9.60	9.56	9.31

Table 4 ChelpG charges calculated at MP2/6-311++G** level

	Complex-I	Complex-II
N1	−0.3376	−0.374
H2	0.3281	0.2448
C3	−0.1915	−0.1623
C4	0.8726	0.9144
H5	0.1025	0.077
H6	0.0727	0.0772
O7	−0.7788	−0.7467
O8	−0.6648	−0.7473
H9	0.3774	0.5067
H10	0.2813	0.2444
H11	0.4389	0.4244
O12	−0.8744	−0.8194
H13	0.4208	0.3996
H14	0.4416	0.4584
O15	−0.84	−0.96
H16	0.4167	0.4583
H17	0.4361	0.424
O18	−0.8698	−0.8191
H19	0.3679	0.3994
$\mu(D)$	7.787	9.209

19.64 kcal mol^{−1} and 18.38 kcal mol^{−1}, respectively, as compared to 21.29 kcal mol^{−1} and 20.03 kcal mol^{−1} at MP2/6-311++G**. Complex-I has highest BSSE corrected total binding energy, which was also observed to be most stable during total energy calculations. The two-body interaction energies contribute more to the total binding energy than the three-body and four-body interaction energies. For both these structures, the two-body interaction energies are found to be attractive, except for contribution from W1–W3 in complex-I (almost zero) and W1–W2, W1–W3 and W2–W3 in complex-II, in which W1, W2 and W3 are beyond the van der Waals interaction distance. For complex-I, the two body attractive interaction energy contribution from G and W2 is largest, 10.14 kcal mol^{−1} at CCSD(T)/MP2 and 10.27 kcal mol^{−1} at MP2/6-311++G** level. Hereafter,

CCSD(T)/MP2 results will be discussed and the bracketed values will be assigned for MP2 results. In complex-II, the largest two body contribution is obtained from G–W1 and G–W3 [21.27 kcal mol^{−1} (21.67 kcal mol^{−1})]. As it can be observed from ChelpG charge distribution analysis (Table 4), in complex-I, the atomic charge on O15 (−0.84) of W2 is more negative than O18 (−0.87) of W3 and the atomic charge on H9 (0.38) is more positive than H2 (0.33) at NH₃⁺ proton donor in G, which supports the hydrogen bonding strength for G–W2 is more than G–W3, though both the water molecules, W2 and W3 remain within van der Waal's interaction distance (<3 Å). On the other hand, looking to the −COO[−] as proton acceptor in G attached to W1, the atomic charge on O8 (−0.66) is more negative than O7 (−0.78), where O7 is hydrogen bonded to W1 through H11 and the atomic charge on H11 (0.44) is more positive than non-bonded H13 (0.42). The interaction energy between G and W1 is found to be 7.93 kcal mol^{−1} (8.10 kcal mol^{−1}). The attractive interaction energy between W1–W2 and W2–W3 are observed to be very similar (around 0.2 kcal mol^{−1} difference), 2.64 kcal mol^{−1} (2.89 kcal mol^{−1}) and 2.89 kcal mol^{−1} (3.01 kcal mol^{−1}), respectively. Similarly, for complex-II, it can also be observed that the largest interaction energy (21.27 kcal mol^{−1}) contribution is from both G–W1 and G–W3, for which we have already observed the same hydrogen bond distances; O₇–H₁₇ between G and W3 and O₈–H₁₁ between G and W1 (resulted from G as hydrogen bond acceptor through (−COO[−])) and O₁₂–H₁₀ between G and W1 and O₁₈–H₂ between G and W3 (resulted from G as hydrogen bond donor through (−NH₃⁺)). From Table 4, it can also be observed that the ChelpG charge distribution analysis in complex-II, indicates that both O7 and O8 in G have similar negative atomic charge values (−0.74), O12 of W1 and O18 of W3 have also similar negative atomic charge values (−0.82), H11 of W1 and H17 of W2 have similar positive atomic charge values (0.42) and H10 and H2 of G have also similar positive atomic charge values (0.24), which support the similar interaction energies and hydrogen bond length between G and each of W1 and W3,

Table 5 Vibrational frequencies (cm^{−1}) and peak intensity as bracketed values for complexes I and II using 6-311++G** basis set

B3LYP	PW91	MPW1PW91	PBE	MP2	
Complex-I					
O-Hstr. and N-Hstr	3319.47 (935.43)	3188.79 (547.541)	3353.07 (857.12)	3348.34 (848.69)	3411.96 (930.38)
O-Hstr	3341.5 (917.14)	3125.66 (1253.59)	3370.1 (974.63)	3363 (976.97)	3462.76 (988.55)
	2957.73 (1131.9)	3248.5 (752.29)	3238.4 (781.59)		
Complex-II					
O-Hstr. and N-Hstr(asym)	3210.88 (1479.45)	2984.98 (1895.73)	3210.63 (1585.84)	3197.02 (1570.63)	3308.15 (1547.4)
O-Hstr. and N-Hstr(sym)	3228.63 (1090.8)	2985.22 (910.31)	3226.86 (1153.74)	3210.66 (1145.02)	3323.96 (1110.2)
N-Hstr	3350.94 (529.95)	3238.63 (598.68)	3380.99 (560.36)	3373.38 (575.34)	3421.07 (515.35)

Table 6 Decomposition of interaction energies (two, three and four body) for the Glycine-(Water)₃ complex-I and II at MP2/6-311++G** level and CCSD(T)/6-311++G** //MP2/6-311++G**

Complex	I	II
Two body		
G-W ₁	-8.10 (-7.93)	-21.67 (-21.27)
G-W ₂	-10.27 (-10.14)	-10.27 (-10.16)
G-W ₃	-4.16 (-4.23)	-21.67 (-21.27)
W ₁ -W ₂	-2.89 (-2.64)	0.56 (0.54)
W ₁ -W ₃	-0.75 (-0.74)	0.62 (0.59)
W ₂ -W ₃	-3.01 (-2.89)	0.56 (0.54)
Total 2B	-29.19 (-28.59)	-51.87 (-51.04)
Three Body		
G-W ₁ -W ₂	-4.86 (-4.90)	0.66 (0.66)
G-W ₁ -W ₃	-0.49 (-0.52)	2.59 (2.56)
G-W ₂ -W ₃	0.19 (0.23)	0.66 (0.66)
W ₁ -W ₂ -W ₃	-0.92 (-0.92)	-0.02 (-0.01)
Total 3B	-6.08 (-6.10)	3.89 (3.88)
Four body		
G-W ₁ -W ₂ -W ₃	-0.09 (-0.02)	-0.07 (-0.04)
BE	-21.29 (-19.64)	-20.03 (-18.38)

G is glycine and W_i denotes *i*th water molecule in a complex according to Fig. 1

The bracketed values are computed at CCSD(T)/6-311++G** //MP2/6-311++G**

All energies are in kcal mol⁻¹ and BSSE corrected.

within van der Waal's interaction distance. The attractive interaction energy between G and W₂ is found to be 10.16 kcal mol⁻¹, which is hydrogen bonded through H₉-O₁₅ to W₂. From the ChelpG charge distribution analysis, the positive atomic charge value obtained for H₉ (0.50) is more than those obtained for H₂ and H₁₀ at NH₃⁺ as proton donor in G. Table 6 also depicts the three body interaction energy for complex-I and II. For complex-I, the attractive three body interaction energy contribution from G-W₁-W₂ is largest 4.90 kcal mol⁻¹ (4.86 kcal mol⁻¹), where as no such significant contribution is observed for complex-II. However, the total three-body interaction energy for complex-I is found to be attractive 6.10 kcal mol⁻¹ (6.08 kcal mol⁻¹) compared to the repulsive total three-body interaction energy of complex-II 3.88 kcal mol⁻¹ (3.89 kcal mol⁻¹). The four body interaction energies are found to be negligible as compared to two-body and three-body interaction energies contribution to total binding energy for both complex-I and II.

Experimental people have also started work [12, 36] on these areas of microsolvation, however only one water or two water molecules have been considered so far. It would also be interesting for the theoreticians that Mark Gordon et al. [12] have considered up to eight water molecule with glycine, though these are yet to be experimentally accessible. The methods used earlier only reported the total

energies or relative energy ordering. As it has been pointed out, recently [12] that the zwitterionic glycine is not a minimum [18] in the gas phase, we consider this hierarchical counterpoise scheme [39, 40] is the appropriate and adequate method to calculate the binding energy for the microhydrated zwitterionic glycine. The treatment of BSSE in N-body cluster has been reviewed very deliberately [51] and mentioned to be more correct [52], though the number of calculations required for the CP treatment increases with increasing cluster size.

Conclusions

Structural properties, energetics and vibrational frequencies for the optimized stable structures of glycine-(water)₃ complex are analyzed at the correlated ab initio (MP2) and density functional methods (B3LYP, PW91, MPW1PW91 and PBE) using 6-311++G** basis set. In this study, both (-NH₃⁺) as proton donor and (COO⁻) as proton acceptor have been considered for the effect of microsolvation on zwitterionic glycine. DFT methods have been employed so as to compare the performance/quality of different gradient-corrected correlation functionals (PW91, PBE), hybrid functionals (B3LYP, MPW1PW91) and to predict the near quantitative structural, vibrational and energetic properties, at reduced computational cost. It is worthy to note here that the B3LYP method outperforms among the different DFT methods for the computed hydrogen bond distances and is found closer to the value obtained by correlated MP2 level, whereas MPW1PW91 and PBE methods show very similar values but ~0.03 Å less, compared to the B3LYP method. For complex-I, the highest intensity peaks at B3LYP level are approximately same, (3319.47 cm⁻¹) for O-Hstr. and N-Hstr between G and water molecules and (3341.5 cm⁻¹) for O-Hstr. between water molecules. The B3LYP computed values for the three different high intensity peaks in complex-II, are analyzed to be resulted from O-Hstr. and N-Hstr(asym) (3210.88 cm⁻¹), O-Hstr. and N-Hstr(sym) (3228.63 cm⁻¹) between G and each of W₁, W₃ whereas, the N-Hstr is observed between G and W₂ (3350.94 cm⁻¹). MP2 calculation is considered to decompose the interaction energy. Single-point CCSD(T)//MP2 calculation has also been carried out to better estimate the decomposed interaction energy. Contributions of two- through four-body terms to each of these stable conformer for their interaction energies, including corrections for basis set superposition error (BSSE) are investigated by using function counterpoise and its generalized version. The BSSE corrected total binding energy for the most stable complex-I is found to be 19.64 kcal mol⁻¹ at CCSD(T)/6-311++G**//MP2/6-311++G**.

Acknowledgements We acknowledge National Science Council, Taiwan for the financial support and NCHC, Hsin-Chu for providing partial computational resources.

References

- Robinson GW, Zhu S-B, Singh S, Evans MW (1996) Water in biology, chemistry and physics: experimental overviews and computational methodologies. World Scientific, Singapore
- Kaatze U (1990) *Phy Med Bio* 35:1663–1681
- Jensen JH, Gordon MS (1995) *J Am Chem Soc* 117:8159–8170
- Ahn D-S, Park S-W, Jeon I-S, Lee M-K, Kim N-H, Han Y-H, Lee S (2003) *J Phys Chem B* 107:14109–14118
- Chaudhari A, Sahu PK, Lee S-L (2004) *J Chem Phys* 120:170–174
- Chaudhari A, Lee S-L (2005) *Chem Phys* 310:281–285
- Hall NE, Smith BJ (1998) *J Phys Chem A* 102:3985–3990
- Nagaoka M, Yoshida NO, Yamabe T (1998) *J Phys Chem A* 102:8202–8208
- Kushwaha PS, Mishra PC (2001) *J Mol Struct Theochem* 549:229–242
- Wang W, Pu X, Zheng W, Wong N, Tian A (2003) *J Mol Struct Theochem* 626:127–132
- Ramaekers R, Pajak J, Lambie B, Maes G (2004) *J Chem Phys* 120:4182–4193
- Aikens CM, Gordon MS (2006) *J Am Chem Soc* 128:12835–12850
- Mcgilvbery RW, Glodstein G (1979) *Biochemistry-A functional approach*. Saunders, USA
- Jeffrey GA, Saenger W (1991) *Hydrogen bonding in biological structures*. Springer, New York, USA
- Geoffrey L (1984) *Biochemistry*. Addison-Wesley, Boston
- Bonaccorsi R, Palla P, Tomasi J (1984) *J Am Chem Soc* 106:1945–1950
- Lehninger AL (1987) *Principles of biochemistry*. CBS, New Delhi, p 97
- Ding Y, Krogh-Jespersen K (1992) *Chem Phys Lett* 199:261–266
- Trotonda FR, Pascual-Ahuir JL, Silla E, Tunon I (1996) *Chem Phys Lett* 260:21–26
- Gaffney JS, Pierce RC, Friedman L (1977) *J Am Chem Soc* 99:4293–4298
- Albrecht G, Corey RB (1939) *J Am Chem Soc* 61:1087–1103
- Gontrani L, Mennucci B, Tomasi J (2000) *J Mol Struct Theochem* 500:113–127
- Watanabe T, Hashimoto K, Takase H, Kikuchi O (1997) *J Mol Struct Theochem* 397:113–119
- Balta B, Aviyente V (2003) *J Comput Chem* 24:1789–1802
- Kassab E, Langlet J, Evleth E, Akacem Y (2001) *J Mol Struct Theochem* 531:267–282
- Bandopadhyay P, Gordon MS (2000) *J Chem Phys* 113:1104–1109
- Bandopadhyay P, Gordon MS, Menucci B, Tomasi J (2002) *J Chem Phys* 116:5023–5032
- Truong TN, Stefanovich EV (1995) *J Chem Phys* 103:3709–3717
- Gordon MS, Jensen JH (1996) *Acc Chem Res* 29:536–543
- Ellzy MW, Jensen JO, Hameka HF, Kay JG (2003) *Spectrochim Acta A* 59:2619–2633
- Shukla MK, Mishra PC (1998) *Chem Phys* 230:187–200
- Shukla MK, Mishra SK, Kumar A, Mishra PC (2000) *J Comput Chem* 21:826–846
- Gregory JK, Clary DC, Liu K, Brown MG, Saykally RJ (1997) *Science* 275:814–817
- Gruenloh CJ, Carney JR, Arrington CA, Zwier TS, Fredericks SY, Jordan KD (1997) *Science* 276:1678–1681
- Ayotte P, Weddle GH, Johnson MA (1999) *J Chem Phys* 110:7129–7132
- Alonso JL, Cocinero EJ, Lesarri A, Eugenia sanz M, Lopez JC (2006) *Angew Chem Int Ed* 45:3471–3474
- Adamovic I, Freitag AM, Gordon MS (2003) *J Chem Phys* 118:6725–6732
- Boys SF, Bernardi F (1970) *Mol Phys* 19:553–556
- Valiron P, Mayer I (1997) *Chem Phys Lett* 275:46–55
- White JC, Davidson ER (1990) *J Chem Phys* 93:8029–8035
- Head-Gordon M, Pople JA, Frisch MJ (1988) *Chem Phys Lett* 153:503–506
- Frisch MJ, Pople JA, Head-Gordon MJ (1990) *Chem Phys Lett* 166:275–280
- Frisch MJ, Pople JA, Head-Gordon MJ (1990) *Chem Phys Lett* 166:281–289
- Becke AD (1988) *Phys Rev A* 38:3098–3100
- Becke AD (1993) *J Chem Phys* 98:5648–5652
- Becke AD (1997) *J Chem Phys* 107:8554–8560
- Perdew JP, Wang Y (1992) *Phys Rev B* 45:13244–13249
- Adamo C, Barone VJ (1998) *J Chem Phys* 108:664–675
- Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77:3865–3868
- Frisch MJ, Trucks GW, Schlegel HB, et al (2003) *GAUSSIAN 03; Rev. B.03*. Pittsburgh, PA, Gaussian, Inc.
- Mierzwicki K, Latajka Z (2003) *Chem Phys Lett* 380:654–664
- Salvador P, Meyer I (2004) *J Chem Phys* 120:5882–5889