# Theoretical Determinations of Ionization Potential and Electron Affinity of Glycinamide Using Density Functional Theory

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Accurate vertical (adiabatic) ionization potential (IP) and valence electron affinity (EA) of glycinamide, including its possible conformers, have been determined employing density functional theory (B3LYP) with 6-311++G** and 6-311G** basis sets, respectively. The calculated adiabatic IPs are 8.60, 8.57, 8.52, and 8.49 eV for conformer IA, IIA, IIIA, and IV, respectively, decreasing gradually with the decreasing of their relative stabilities. Comparisons with glycine indicate that the substitute of $-NH_2$ for $-OH$ in glycine decreases its ionization potential. In various solutions, IPs decrease apparently with respect to those in the gas phase. All electron affinities of glycinamide conformers are negative values in the gas phase, indicating that the anionic states are unstable with respect to electron autodetachment vertically and adiabatically. On the contrary, all of the adiabatic EAs in solution possess positive values and become larger and larger with the increasing of dielectric constants. Additionally, the IPs and EAs for hydrated glycinamide with one, two, and three water molecules have been explored. Finally, all kinds of chemical quantities associated with the IP and EA, such as electronegativity, chemical potential, chemical hardness, and chemical softness, have also been determined.

## 1. Introduction

Glycinamide ($H_2NCH_2CONH_2$), being the simple derivative of glycine, is of great importance in the interstellar studies and biochemistry since amide derivatives may also serve as simple models for N-terminal amino acids in peptides.[1] Some related studies have been reported in the past.[2−9] For example, the formations of the peptide bond in glycinamide uncatalyzed or catalyzed by the metal cations or ammonia had been extensively studied.[2−5] Klassen et al. reported the collision-induced dissociation threshold energies of protonated glycinamide determined with a modified triple quadrupole mass spectrometer.[6] The unimolecular chemistry of protonated glycinamide and its proton affinity determined by mass spectrometric experiments and theoretical model had been reported by Kinser et al.[7] The interrelationship between conformations and theoretical chemical shift had been investigated by Sulzbach et al.,[8] in which some useful conformational information had been mentioned at restricted Hartree-Fock (RHF) theory and 6-31G* basis set. Ramek et al. discussed the basis-set influence on the nature of the conformations of glycinamide (minimum or saddle point) in ab initio self-consistent field (SCF) calculations.[9] Recently,[10,11] we investigated the possible conformers of glycinamide in the gas phase and in solution, in which three pairs of mirror-image conformers and one $C_s$ conformer had been found on the global potential energy surface (PES) of glycinamide (see Figure 1) at the B3LYP/6-311++G**level of theory. The calculated proton affinity,[12] 216.81 kcal/mol, for the global minimum is well consistent with the experimental value 217.23 kcal/mol.[7] The reliability of the DFT(B3LYP) method has also been verified through comparisons with higher-level calculations including MP2, MP3, MP4(SDQ), and CCSD(T) levels.[10−12] As an important supplement in property for glycinamide, IP and EA are not only fundamental in assessing the electron donating and accepting ability but also play a key role in electron-transfer process occurring in the gas phase or in the condensed phase.[13,14] However, to our best knowledge, these two quantities have not been determined by theoretical and experimental methods despite of the fact that some experimental measurements, such as molecular beams, low-energy electron transmission spectroscopy (ETS), electron spin resonance (ESR), photoelectron spectroscopy, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR), and so forth, can provide useful information about the IPs and EAs. As an alternative approach, the reliability and validity of theoretical investigations have also been confirmed by lots of studies,[14−29] though the theoretical study of molecular negative ions associated with EAs involves complications not encountered in analogous studies of neural or cationic species.[30] Generally, upon the formation of anions, two states may result. One is the valence-bound (conventional) anion, where the excess electron fills the unoccupied valence molecular orbital. Another is the dipole-bound anion, which may be formed when the excess electron is weakly bounded to the molecules through long-range interaction, i.e., the electron interacts with the positive side of the molecular dipole moments. Another feature of the dipole-bound anion is that it has a very diffuse state of the excess electron, viz. the excess electron localizes outside of the molecular framework and the average separation between the loosely bound electron and the neutral polar molecule is large (typically 10∼100 Å).[31] Obviously, the dipole-bound anions are fragile species since the binding energies of the excess electron in these systems lie in the thermal and subthermal domains, typically below 100 meV.[32,33] It has been known that, within the Born−Oppenheimer approximation, molecules with dipole

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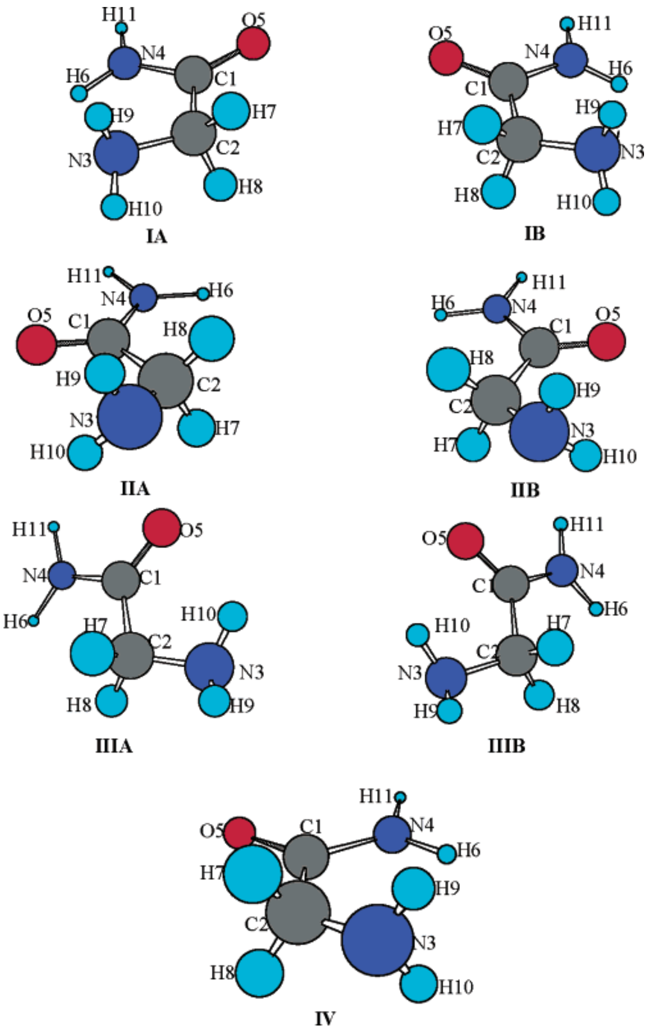

**Figure 1.** Seven conformers of gas-phase glycinamide obtained at the B3LYP/6-311++G* level of theory.

moments greater than 1.625 D can bind an excess electron to give so-called dipole-bound anions.[34,35] Recently, Desfrançois et al. report another a critical value of about 2.5 D.[32] Usually, the excess electron in valence-bound anions causes significant structural changes, whereas in dipole-bound anions, it is too distant to influence the structure. Theoretically, as mentioned above, the calculations of dipole-bound anions are more complicated with respect to the neutral or cationic states due to the fact that the proper descriptions of the spatial expansion of electron density for the dipole-bound anionic states need very diffuse functions. In most cases, both states should coexist, interplay, and even interconvert each other due to environmental (solvation) effects.[36] Strictly speaking, there is only a single "true" adiabatic EA, i.e., the difference in energy between the most stable forms of the anion and neutral.[22] Desfrançois et al. also concluded that valence or dipole binding of electrons can be favored and thus lead to results that are only apparently different and represent two complementary aspects of reality.[37]

As for the calculations of EA, there are two approaches presently used widely. One is the use of small basis sets that confine the electron to the molecular framework and produce reasonable estimates of the valence electron affinities.[26,38] Another is the stabilization method proposed by Falcetta et al.[39,40] More recently, a Drude model has been developed by Jordan et al. to treat dipole-bound anions.[41−43] In the present study, the first approach has been adopted for the calculations of the valence EA based on the choice of a suitable basis set that can avoid the mixing of dipole-bound with valence-bound anionic states found with larger basis sets containing diffuse functions. Further investigations of the dipole-bound EAs are in progress in our group.

As an expansion of our previous studies,[10] in this work, we calculate the IPs and EAs for glycinamide to gain insights into its chemical reactivity with respect to electron detachment or attachment in the gas phase and in various solutions quantitatively. Naturally, relevant chemical quantities, such as chemical potential ($\mu$), electronegativity ($\chi$), chemical hardness ($\eta$), and chemical softness ($s$), can be obtained on the basis of the calculated IPs and EAs. All these quantities should be helpful to the experimentalists who specialize in this area.

## 2. Computational Details

On the basis of the available gas-phase glycinamide conformers studied previously,[10] the cationic and anionic species are fully optimized without any symmetry constraints employing B3LYP method with 6-311++G** and 6-311G** basis sets, respectively. Every conformer is further characterized by the harmonic vibrational frequencies using the analytical second derivative method, and none of these frequencies are scaled due to the ability of DFT calculations to predict them accurately as proposed by Johnson.[44] As a result, two and four stable stationary points have been found for cationic and anionic states, respectively.

For the following chemical process

$$M \rightarrow M^+ + e \tag{1}$$

$$M^- \rightarrow M + e \tag{2}$$

The IP and EA can be calculated as[45]

$$\begin{aligned}\mathrm{IP(EA)} = \Delta E_{\mathrm{elec}} + \Delta(\mathrm{PV}) + \Delta(\mathrm{ZPVE}) + \Delta E_{\mathrm{vib(298)}} + \\ \Delta E_{\mathrm{rot(298)}} + \Delta E_{\mathrm{trans(298)}} = \Delta E_{\mathrm{elec}} + \Delta E_{\mathrm{therm(298)}}\end{aligned} \tag{3}$$

where $\Delta E_{\mathrm{elec}}$ is the variation in internal energy obtained from the corresponding level of theory; $\Delta(\mathrm{PV}) = 0$; $\Delta E_{\mathrm{therm(298)}}$, the variation in thermal energy at 298.15 K, is derived from the calculated harmonic vibrational frequencies, in which the vibrational, rotational, and translational corrections have been included. For simplicity, the zero-point vibrational energies (ZPVE) corrections are also included in $\Delta E_{\mathrm{therm(298)}}$ term. In both cases, the neutral and charged states correspond to the optimized geometries and consequently the calculated IP and EA refer to the adiabatic ionization potential (AIP) and adiabatic electron affinity (AEA). Similarly, the vertical ionization potential (VIP) corresponds to the energy difference between the cationic state in the geometry of neutral state and the optimized neutral state, whereas the vertical electron affinity (VEA) refers to the energy difference between the optimized neutral state and the anionic state in the geometry of neutral state. Therefore, a positive EA implies that the anion is lower in energy than its corresponding neutral parent molecule and hence stable, whereas a negative value means that the anion is unstable with respect to electron detachment.

Other relevant quantities are defined as follows:

(a) Vertical electron attachment energy (VEAE) is the energy difference between the neutral state in the geometry of its cationic state and the optimized cationic state.

(b) Vertical electron detachment energy (VEDE) is the energy required to remove an electron from the optimized anion without causing geometry changes, viz. the energy difference between the neutral state in the geometry of its anionic state and the optimized anionic state.

(c) Reorganization energy (RE) is the energy difference between the charged state in the geometry of its neutral state and the optimized charged state, which can be used to evaluate the structural changes for the charged state in the geometry of neutral state upon nuclear relaxation.

(d) Deformation energy (DE) is the energy difference between the neutral state in the geometry of its optimized charged state and the optimized neutral state, which can be used to assess the structural changes for neutral state upon electron detachment or attachment qualitatively.

On the basis of the calculated VIP (AIP) and VEA (AEA), some useful chemical quantities can be derived from them, namely[46−48]

$$\text{chemical potential } \mu = -(\text{IP} + \text{EA})/2, \quad \text{electronegativity } \chi = (\text{IP} + \text{EA})/2$$

$$\text{chemical hardness } \eta = (\text{IP} - \text{EA})/2, \quad \text{chemical softness s} = 1/(\text{IP} - \text{EA}) = 1/(2\eta)$$

As mentioned above, the density functional method adopted here is B3LYP, i.e., Becke's three-parameter hybrid functional using the Lee−Yang−Parr correlation function.[49,50] To further verify the density functional results, single-point energy calculations have been performed employing the higher-level calculations including second-, third-, and fourth-order Møller−Plesset theory (abbreviated as MP2, MP3, and MP4(SDQ)) and the coupled cluster method (CCSD(T)) including the single, double, and perturbative triple excitation. The standard basis sets, 6-311++G** and 6-311G**, are used throughout to calculate the IP and EA, respectively. All electrons have been considered in the higher-level wave function-correlated calculations mentioned above.

To investigate how the presence of solvent molecules affects the relevant energy quantities mentioned above qualitatively, especially on EA, the isodensity surface polarized continuum model (IPCM),[51−53] which has been successful in the descriptions of several chemical systems in solution,[38,54−56] has been employed. These calculations are performed on the optimized gas-phase structures employing a series of solutions, such as chloroform, dichloroethane, acetone, nitromethane, and water (the dielectric constants $\epsilon = 4.9$, 10.36, 20.7, 38.2, and 78.39, respectively). Additionally, the specific interactions between conformer IA and explicit water molecules (from one to three) have also been studied for the further examination of solvent effect.

All of the computations were performed using the Gaussian 98 program and the SCF convergence criteria *Tight* have been used throughout.[57]

## 3. Results and Discussions

First, the calculated AIP and AEA in the gas phase are summarized in Table 1 together with the higher-level computational results. Table 2 presents the calculated IP and EA in solution performed using the IPCM model. The differences in ZPVE correction between the optimized neutral and anionic glycinamide conformers at the B3LYP level with different basis sets are listed in Table 3. Neutral glycinamide conformers obtained at the B3LYP/6-311++G** level of theory are displayed in Figure 1. The highest occupied molecular orbital (HOMO) and spin density contour plots for the neutral, cationic, and anionic glycinamide conformers are depicted in Figures 2−4, respectively. Figure 5 shows the diagrams of HOMO and spin density distributions for glycinamide complexes with one, two, and three water molecules. Finally, Figure 6 displays the dependences of the calculated chemical potential and chemical hardness on dielectric constants ranging from 1.0 to 78.39. In the Supporting Information, Tables S1 and S2 list the selected structural parameters, dipole moments, and rotational constants for the neutral and charged glycinamide conformers, respectively. Total energies, relative energies, and ZPVEs for the neutral, cationic, and anionic glycinamide conformers are summarized in Table S3. Table S4 gives the calculated spin densities on every atom for charged glycinamide conformers. Other relevant chemical quantities, such as chemical potential, chemical hardness, and chemical softness are presented in Table S5.

For the sake of simplicity, the notations of IA−e or IA+e are employed to stand for the optimized structures that IA loses

**TABLE 1: Calculated Adiabatic Ionization Potential (AIP) and Electron Affinity (AEA) in Parentheses in the Gas Phase at Various Levels**[a]

| levels | IA | IIA | IIIA | IV |
|---|---|---|---|---|
| B3LYP | 8.60(−1.55) | 8.57(−1.42) | 8.52(−1.35) | 8.49(−1.38) |
| MP2 | 8.66(−2.50) | 8.68(−2.10) | 8.65(−2.04) | 8.50(−2.06) |
| MP3 | 8.88(−2.46) | 8.83(−2.07) | 8.79(−2.00) | 8.72(−2.02) |
| MP4(SDQ) | 8.90(−2.48) | 8.91(−2.08) | 8.87(−2.02) | 8.74(−2.04) |
| CCSD(T) | 8.78(−2.37) | 8.73(−2.02) | 8.69(−1.95) | 8.62(−1.98) |

[a] All of the units are in eV.

**TABLE 2: Calculated Vertical and Adiabatic Ionization Potential, Electron Affinity, Reorganization Energy (RE), and Vertical Electron Attachment/Detachment (VEAE/VEDE) Using the IPCM Model**

| | $\epsilon$[a] | VIP(VEA) | AIP(AEA) | RE [b] | VEAE(VEDE) |
|---|---|---|---|---|---|
| IA | 1.0 | 9.25(−2.34) | 8.60(−1.55) | 0.65(0.79) | −8.04(0.86) |
| | 4.90 | 7.33(−0.69) | 6.64(0.06) | 0.70(0.74) | −6.07(0.90) |
| | 10.36 | 7.06(−0.47) | 6.35(0.33) | 0.71(0.79) | −5.79(1.16) |
| | 20.70 | 6.93(−0.37) | 6.21(0.45) | 0.72(0.82) | −5.66(1.28) |
| | 38.20 | 6.87(−0.32) | 6.15(0.51) | 0.72(0.83) | −5.62(1.34) |
| | 78.39 | 6.83(−0.30) | 6.11(0.54) | 0.72(0.84) | −5.57(1.37) |
| IIA | 1.0 | 9.29(−2.46) | 8.57(−1.42) | 0.72(1.04) | −7.91(1.48) |
| | 4.90 | 7.35(−0.87) | 6.62(0.20) | 0.72(1.06) | −5.94(1.70) |
| | 10.36 | 7.08(−0.67) | 6.34(0.44) | 0.74(1.11) | −5.66(1.95) |
| | 20.70 | 6.96(−0.59) | 6.21(0.55) | 0.74(1.14) | −5.54(2.06) |
| | 38.20 | 6.90(−0.56) | 6.15(0.60) | 0.75(1.16) | −5.48(2.11) |
| | 78.39 | 6.87(−0.54) | 6.12(0.63) | 0.75(1.17) | −5.44(2.14) |
| IIIA | 1.0 | 9.27(−2.49) | 8.52(−1.35) | 0.75(1.14) | −7.91(1.41) |
| | 4.90 | 7.28(−0.72) | 6.58(0.27) | 0.71(0.99) | −5.94(1.70) |
| | 10.36 | 7.00(−0.47) | 6.30(0.51) | 0.70(0.98) | −5.66(1.95) |
| | 20.70 | 6.87(−0.35) | 6.17(0.62) | 0.70(0.97) | −5.54(2.06) |
| | 38.20 | 6.81(−0.30) | 6.11(0.67) | 0.70(0.97) | −5.48(2.11) |
| | 78.39 | 6.77(−0.27) | 6.07(0.70) | 0.70(0.97) | −5.44(2.14) |
| IV | 1.0 | 8.98(−2.22) | 8.49(−1.38) | 0.49(0.84) | −8.04(1.41) |
| | 4.90 | 7.01(−0.66) | 6.57(0.20) | 0.44(0.86) | −6.07(1.68) |
| | 10.36 | 6.72(−0.47) | 6.29(0.44) | 0.43(0.91) | −5.79(1.93) |
| | 20.70 | 6.59(−0.39) | 6.17(0.54) | 0.43(0.93) | −5.66(2.04) |
| | 38.20 | 6.53(−0.36) | 6.11(0.59) | 0.43(0.94) | −5.60(2.09) |
| | 78.39 | 6.49(−0.34) | 6.07(0.62) | 0.42(0.95) | −5.57(2.12) |

[a] All of the units are in eV, and $\epsilon = 1.0$ refers to the results in the gas-phase quantitatively. [b] The data in parentheses refer to those in the process of electron attachment.

**TABLE 3: Differences in ZPVE Correction (in kcal/mol) between the Optimized Neutral and Anionic Glycinamide Conformers at the B3LYP Level with Different Basis Sets**

| conformers | 6-31+G* | 6-311+G* | 6-311++G** | 6-311G** |
|---|---|---|---|---|
| IA | 1.70 | 1.44 | 0.77 | 3.82 |
| IIA | 0.62 | 0.73 | 0.29 | 2.51 |
| IIIA | 1.24 | 0.97 | 0.42 | 2.57 |
| IV | 1.09 | 0.71 | 0.27 | 2.80 |

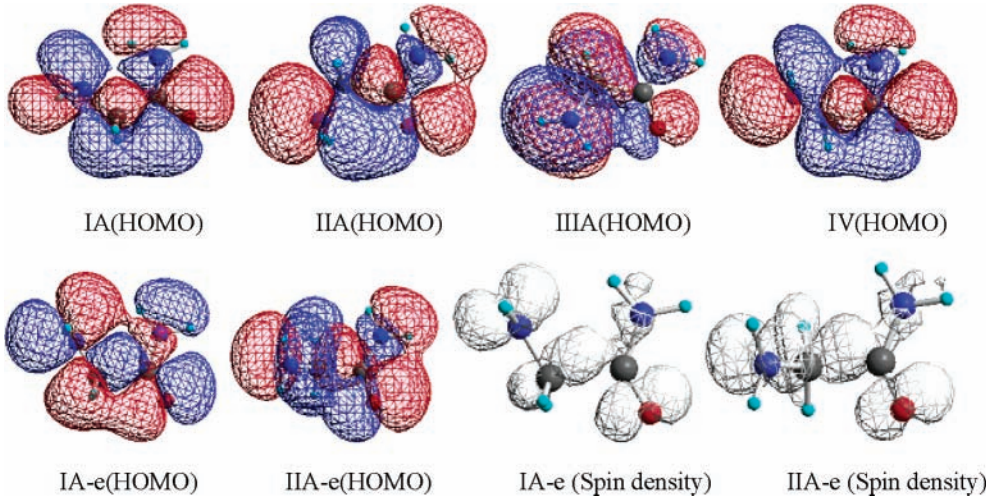

**Figure 2.** Digrams of HOMO and spin density distributions for neutral and cationic conformers of glycinamide. Isocontour values of 0.01 and 0.002 are used for the HOMO and spin density distributions, respectively.

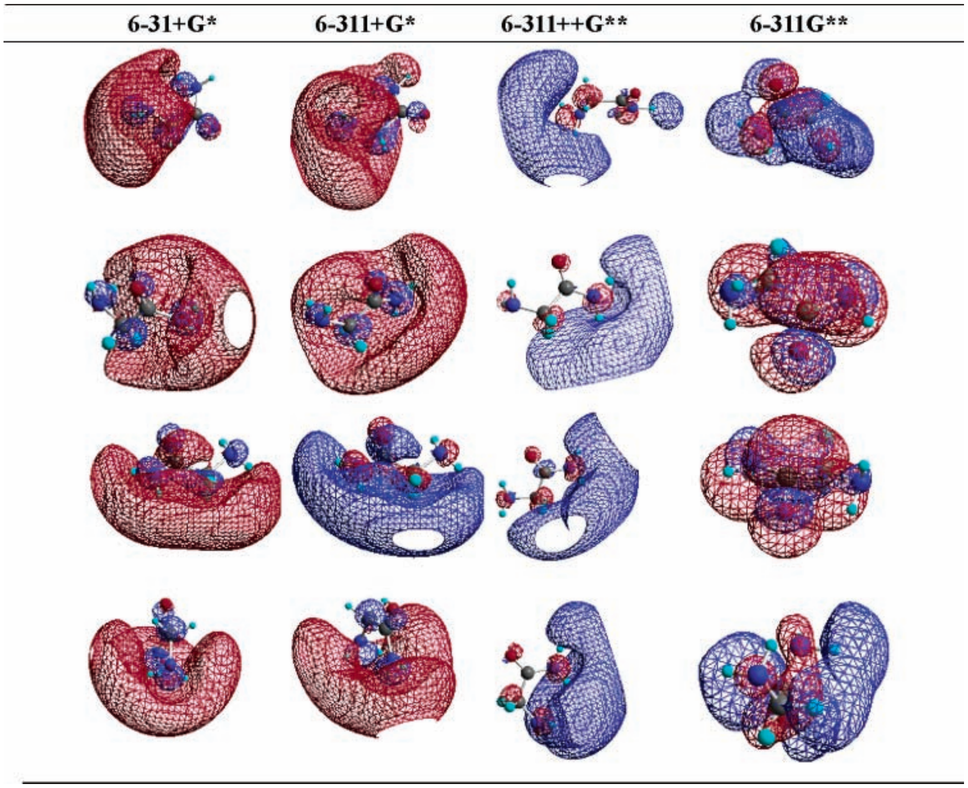

**Figure 3.** Digrams of HOMO for anionic conformers of glycinamide employing the B3LYP method with different basis sets. Isocontour values of 0.02 are used.

or gains an electron. Similarly, the same holds for other conformers. Here, only IA, IIA, IIIA, and IV are discussed since the mirror-image conformers are identical to each other in energy and in structural parameters except for the dihedral angles.

**3.1. IP.** As mentioned above, two stable conformers have been found in the ionization process of glycinamide. Comparisons with neutral glycinamide show that the ionization process results in significant structural rearrangements, which can be further verified by the calculated deformation energies (DE) (ranging from 11.1 to 14.9 kcal/mol) as listed in Table S3. First, the most apparent changes in bond length are the elongation of the C1−C2 bond by about 0.18 Å among all of the bonds, which may be derived from the fact that the HOMO from which the electron is removed in neutral state possesses important bonding character between C1 and C2 atoms as displayed in Figure 2. Furthermore, this phenomenon can be also reflected from the charge distributions. Comparing the charge distributions before and after ionization, one can see that the positive charge at C1 site increases while the negative charge at C2 site decreases. The net contributions result in a smaller product ($Q_{C1}Q_{C2}$) of both charges at C1 and C2 site than those of the neutral state. According to the Coulomb's law, the electrostatic interaction between C1 and C2 should decrease. Thus, the elongation of C1−C2 bond is reasonable. More importantly, two moieties separated by C1 and C2 atoms should be observed easily experimentally. As expected, other bond lengths between non-hydrogen atoms in two moieties decrease slightly. Second, all of the main molecular skeletons have been distorted significantly except for the $C_s$ symmetry conformer IV. For example, the dihedral angles $D(4,1,2,3)$ have been changed about 13.81,

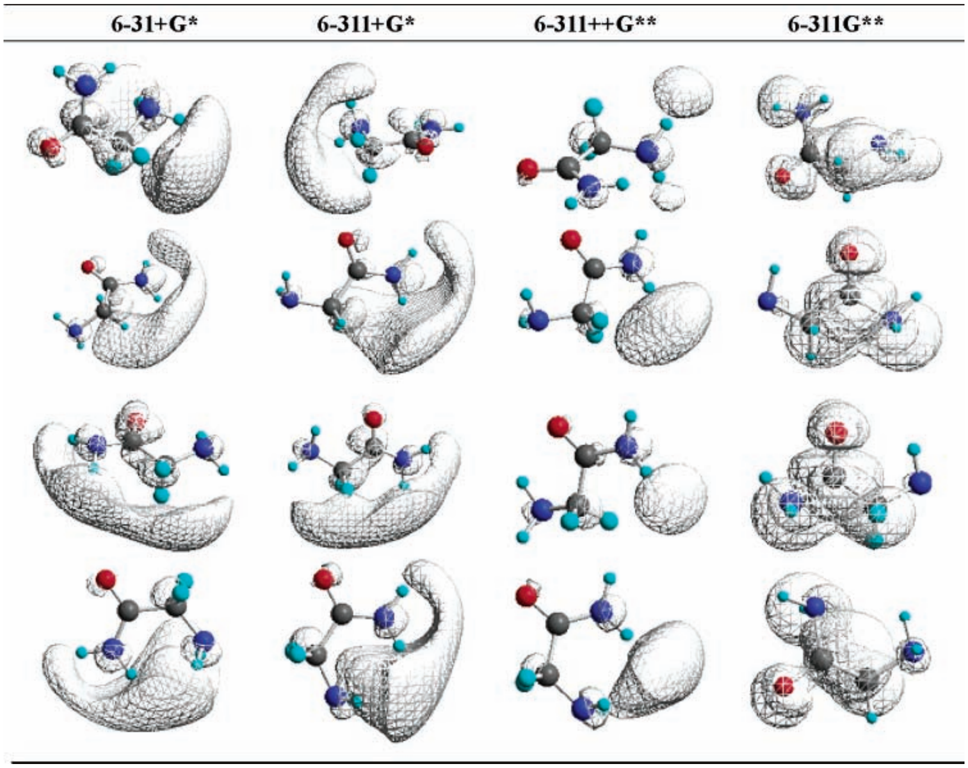

**Figure 4.** Digrams of spin density distributions for anionic conformers of glycinamide employing the B3LYP method with different basis sets. Isocontour values of 0.002 are used.

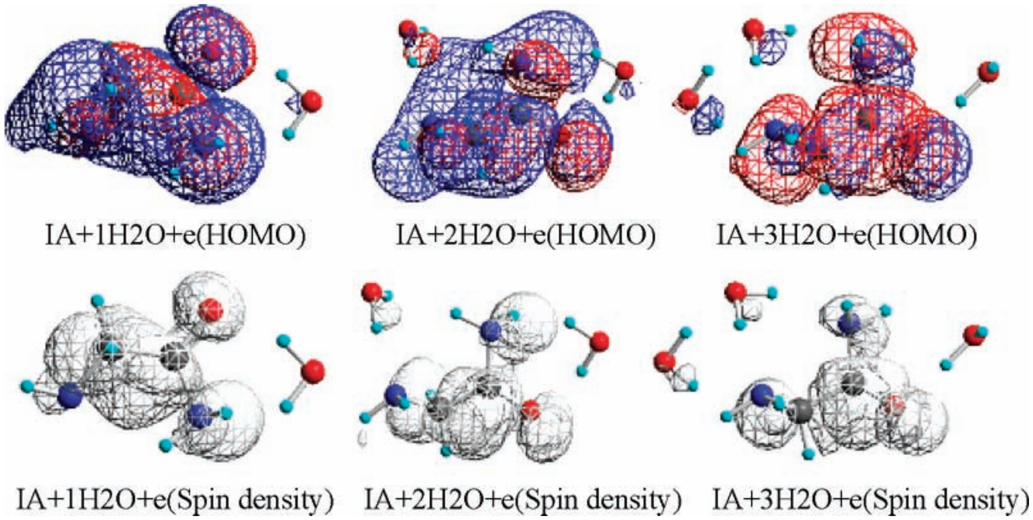

**Figure 5.** Digrams of HOMO and spin density distributions for glycinamide complexes with one, two, and three water molecules. Isocontour values of 0.02 and 0.001 are used for the HOMO and spin density distributions, respectively.

75.86, and 58.46° for conformer IA, IIA, and IIIA, respectively. However, the planarity of the peptide bond (C1−N4) is still kept as these of the neutral states; that is, it cannot be affected significantly for glycinamide upon ionization.

As listed in Table S3, the relative stabilities between two cationic states may be determined at the B3LYP/6-311++G** level of theory compared with those higher-level calculations, i.e., IA+e > IIA+e. From the AIPs listed in Table 1, the agreement can be observed between the DFT(B3LYP) level and the higher-level calculations though some gaps exist between them due to the lack of ZPVE corrections for the latter partly. Obviously, the calculated AIPs decrease with the decreasing of their relative stabilities. Moreover, the larger difference between the VIP and AIP (i.e., RE) indicates that the significant nuclear relaxation should occur for glycinamide upon ionization. Inspections of the HOMO and spin density distributions displayed in Figure 2 indicate that the single electron distributes evenly over the entire molecular framework. As expected, the dipole moments increase by about 1.0 D for neutral glycinamide conformers upon ionization.

Compared with glycine,[58,59] the substitute of amide $-NH_2$ for $-OH$ decreases the IP apparently, where the IP of glycine is 8.8∼8.9 eV theoretically and experimentally.[58,59] This phenomenon should be applied to similar compounds, namely, the IPs of the acylamine and alkylamine are smaller than those of the corresponding carboxylic acid and alcohol.

As displayed in Table 2, inclusion of solvation effects through the IPCM model leads to a reduction in both the VIP and AIP by 1.9∼2.5 eV and all of the IPs decrease with the increasing of dielectric constants ($\epsilon$), indicating that it is much easier to

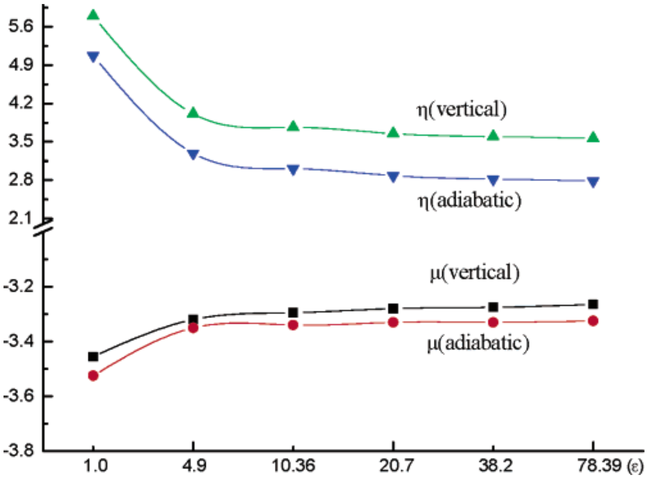

**Figure 6.** Dependences of the chemical potential ($\mu$) and chemical hardness ($\eta$) on dielectric constants for conformer IA and the same holds for other conformers. The notations in parentheses refer to that they are obtained from vertical or adiabatic IP or EA.

remove an electron from glycinamide in polar solution than in the gas phase. From the calculated REs, one can see that the existences of solvents change the nuclear relaxation in magnitude more or less. In more detail, REs increase for conformers IA and IIA whereas they decrease for IIIA and IV, indicating that the existences of solvents have different influences on different conformers. On the other hand, all of the VEAEs are greater than those in the gas phase but still remain negative values, implying that all of the cationic states are unstable with respect to electron attachment vertically. Additionally, as discussed below, the glycinamide complexes with water molecules (from one to three) have been discussed. The calculated AIPs (REs) are 8.31 (1.04), 7.89 (1.76), and 7.54 eV (1.78 eV) for glycinamide IA complexes with one, two, and three water molecules, respectively. Further combinations of the IPCM model in aqueous solution with monohydrated glycinamide show that the AIP and RE are 6.06 and 0.88 eV, which are well consistent with the results obtained employing the IPCM model.

**3.2. EA.** *3.2.1. Choice of the Basis Sets.* As for the basis sets used to calculate EA, it has been reported that expansion in basis set size provides a more accurate estimate for valence-bound EA values to a point at which further expansion leads to mixing of dipole-bound states and questionable values for valence EA.[24] Thus, it is very necessary to determine an appropriate basis set which can exclude the contaminations of the dipole-bound state.

First, Figures 3 and 4 display the HOMO and spin density plots for four anionic glycinamide conformers using different basis sets ranging from 6-31+G* to 6-311++G**. As mentioned above, the diffuse functions are important for the proper descriptions of dipole-bound anions. To a good approximation, all of the HOMOs obtained from the basis sets containing diffuse functions appear to be a diffuse sp hybrid oriented along the positive direction of the dipole moment in every anion, assuming the characters of the dipole-bound anionic state. Similarly, the corresponding spin densities of the single electron mostly reside in a diffuse orbital and locate entirely outside of the molecular framework. All of these HOMOs and spin density distributions suggest that the dipole-bound states have mixed with the valence-bound states even though only a single diffuse function is considered. On the other hand, all of the HOMOs and spin density distributions obtained with 6-311G** basis set assume the valence-bound anion characters, namely, the excess electron distributes almost in the molecular framework.

Second, the differences in ZPVE corrections between the optimized anion and neutral species can be used as a measure of electron location to the molecular framework.[26] Generally, the differences for valence-bound anions are greater than those of the dipole-bound anions. As shown in Table 3, the ZPVE differences are largest for those obtained with the 6-311G** basis set. At the 6-311++G** basis set, the values are smallest among those calculated with the basis sets containing diffuse functions, indicating a rather diffuse spacial distribution of the excess electron. These analyses are well consistent with the above-mentioned dipole-bound anion characters at the basis sets containing diffuse functions.

Additionally, at the 6-311G** basis set, all of the dipole moments of neutral states at the geometry of optimized anionic forms are smaller than those of the optimized neutral states, which are completely opposite to the characters of the dipole-bound anions.[60] In fact, all of the dipole moments for optimized anions (ranging from 0.96∼2.92 D) are significantly smaller than those of the neutral states (ranging from 3.44∼4.18 D). Hence, the 6-311G** basis set should be appropriate to estimate the valence EAs for glycinamide because no significant dipole contributions are found for those anionic states at this basis set.

*3.2.2. Calculations of EA.* As displayed in Figure 3, four anionic glycinamide conformers have been found employing the B3LYP/6-311G** level of theory, where IIA+e and IIIA+e are mirror-image conformers judging from their structural and energetic characters. Like those in the ionization process, the geometrical changes upon electron attachment are relatively larger, which can be further verified by the larger deformation energies (DE) listed in Table S3. Obviously, the strengths of the C1═O5 and the peptide bond (C1−N4) are weakened relative to those in neutral states, where the increments in bond length are ∼0.06 and ∼0.1 Å for the former and the latter, respectively. More importantly, the planarity of the peptide bond in all of the anions has been destroyed compared with those neutral and cationic states; for example, the dihedral angles of *D*(5,1,4,6) (*D*(5,1,4,11)) for IA+e, IIA+e, IIIA+e, and IV+e are 162.03(42.70), 79.17(−29.44), −79.17(29.44), and −74.73°(34.01°), respectively. Here, note also that the structural differences for neutral glycinamide obtained at the 6-311++G** and 6-311G** basis set are small, where the largest deviations in bond length and bond angles are not more than 0.001 Å and 2°, respectively.

As can be seen from Table S3, the relative stabilities among all anions are (IIA+e) = (IIIA+e) > (IV+e) > (IA+e), which is changed compared with that of neutral states.[10] Comparisons with those higher-level computations suggest that the B3LYP method can yield accurate relative stabilities among the available anionic states. As a consequence, in the mixture of glycinamide anions in the gas phase, one should be able to notice some presence of IV+e anion if the thermodynamics governs the equilibrium of the anionic mixture.

As displayed in Table 1, all of the EAs are negative in the gas phase, indicating the anionic states are unstable with respect to electron detachment vertically and adiabatically. At the same time, the relative order in magnitude for EA among four conformers is well reproduced by the higher-level calculations though these EAs are smaller by around 0.7 eV than those at the DFT(B3LYP) level. Certainly, these results should be further improved if considering ZPVE corrections. Unlike those in the ionization process, the ZPVE corrections account for 10.7, 7.6, 8.2, and 8.8% in total AEAs for conformers IA, IIA, IIIA, and IV, respectively, indicating the importance of considering ZPVE corrections in determining EA. Additionally, for the analogous compound glycine, its valence-bound anion is also unstable with respect to electron detachment in the gas phase,[61] where the energy of 1.93 eV is required to attach an electron into the lowest unoccupied molecular orbital (LUMO) of glycine.[62] On the other hand, a neutral conformer with an appreciable dipole moment of about 5.7 D is predicted to form a dipole-bound state with an adiabatic electron affinity of 279 $\text{cm}^{-1}$.[61] Recalling that all of the dipole moments for neutral glycinamide conformers, ranging from 3.44 to 4.18 D, are greater than the critical value (~2.5 D) as mentioned above, the probability of the formation of dipole-bound anions for glycinamide should be worthy of further investigating in future studies.

As displayed in Table 2, all of the AEAs in solution shift into positive values, indicating that the anionic states are stable with respect to electron detachment adiabatically. In other words, the existence of solvents stabilizes sufficiently glycinamide anions to prevent autodetachment of the excess electron. On the other hand, all of the VEAs are still negative in solution, suggesting that the anionic states are unstable with respect to electron detachment vertically. Additionally, all of the VEAs and AEAs increase gradually with the increasing of dielectric constants, which should be due to the larger solvation energies for anions (about 50~65 kcal/mol) with respect to those neutral states (about 6~12 kcal/mol). Of course, the IPCM model adopted here does not represent the realistic situation in the biological medium due to the lack of considering geometric optimization and short-range interaction with solvent molecules. As a preliminary study, the interactions between glycinamide IA and water molecules, i.e., the glycinamide complexes with one, two, and three water molecules named IA+1$H_2O$, IA+2$H_2O$, and IA+3$H_2O$, respectively, have been investigated in the gas phase employing the B3LYP/6-311G** level of theory. Once again, all of the optimized anions still assume the valence-bound characters as displayed in Figure 5. Here, only representative hydrated complexes have been considered though many conformations may exist for the IA complex with water molecules (from one to three). For IA+1$H_2O$, this complex should correspond to the lowest-energy conformer among the monohydrated glycinamide conformers. It has a network of intermolecular hydrogen bonds formed from the amide to water and from water to the carbonyl oxygen, which is well consistent with the analogous complexes of alaninamide and formamide with one water molecule.[63−65] On the basis of the geometry of IA+1$H_2O$, another double hydrogen bonds formed from the amide to water and from water to the amino nitrogen have been found in IA+2$H_2O$. Only an additional single hydrogen bond formed from the amino to water has been found in IA+3$H_2O$. Computational results show that the VEA(AEA) of IA+1$H_2O$, IA+2$H_2O$, and IA+3$H_2O$ are −2.23(−1.17), −1.77(−0.87), and −1.51 eV (−0.51 eV), respectively, which are greater than those of the isolated gas-phase glycinamide. Moreover, all of them increase gradually with the increasing of water molecule numbers though they are still negative. Additionally, combinations of the IPCM model with hydrated glycinamide complexes show that all of the VEAs and AEAs are greater than those of the isolated glycinamide conformers calculated with IPCM model in aqueous solution, where only the results of monohydrated glycinamide surrounded by the continuous solvents are presented (VIP = −0.29 eV, AIP = 0.72 eV) in our computational ability. Thus, in solution, the anionic state of glycinamide should be stable with respect to electron detachment adiabatically, implying that the observation of solvated glycinamide anion should be possible experimentally.

**3.3. Other Chemical Quantities.** On the basis of the calculated vertical and adiabatic IP and EA, other relevant chemical quantities, such as chemical potential ($\mu$), electronegativity ($\chi$), chemical hardness ($\eta$), and chemical softness ($s$), can be obtained quantitatively. Considering that their definitions use vertical IP and EA, it may be interesting to check how far those values, using calculated adiabatic IP and EA, match the future experimental results.[66] As displayed in Figure 6, in solution, the chemical potential increases, whereas the chemical hardness decreases versus dielectric constants ranging from 1.0 to 78.39, which is well consistent with the findings of Pearson.[67] Overall, the calculated chemical hardness in magnitude among four conformers are consistent with the maximum hardness principle (MHP);[68] that is, “there seems to be a rule of nature that molecules tend to arrange themselves so as to be as hard as possible”. These quantities should offer some conveniences for theorists and experimentalists who are accustomed to using the chemical potential or electronegativity to assess the chemical properties for the selected species.

## 4. Conclusions

In the present study, the IP and EA of glycinamide have been calculated employing DFT(B3LYP) method with 6-311++G** and 6-311G** basis sets, respectively. Higher-level calculations including MP2, MP3, MP4(SDQ), and CCSD(T) have also been performed on the basis of the optimized gas-phase geometries to further improve the energy quantities. The accurate AIPs are calculated to be 8.60, 8.57, 8.52, and 8.49 eV for IA, IIA, IIIA, and IV, decreasing with the decreasing of their relative stabilities. Two fragments separated by two carbon atoms should be observed easily because the ionization process results in significant elongation of the C1−C2 bond. As for the valence EA, all of the negative values have been found at the B3LYP/6-311G** level of theory even at higher levels, indicating that glycinamide anion is unstable with respect to electron detachment in the gas phase. However, all of the AEAs turn out to be positive values in solution and increase when the dielectric constants increase. This means that solvents can stabilize sufficiently the anions to prevent the excess electron autodetachment from glycinamide adiabatically. Moreover, for the global minimum IA, the IP and EA of its complexes formed with one, two, and three water molecules have also been studied. The positive sign of the EA in solution implies that the observation of solvated glycinamide anion should be possible experimentally. Finally, other relevant chemical quantities derived from the IP and EA, such as electronegativity, chemical potential, chemical hardness, and chemical softness, should fill a void in the available data for glycinamide.

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**Supporting Information Available:** Tables S1 and S2 list the selected structural parameters, dipole moments, and rotational constants for the neutral and charged glycinamide conformers, respectively. Total energies, relative energies, and ZPVEs for the neutral, cationic, and anionic glycinamide conformers are summarized in Table S3. Table S4 gives the calculated spin densities on every atom for charged glycinamide conformers. Other relevant chemical quantities, such as chemical potential, chemical hardness, and chemical softness are presented in Table S5. This material is available free of charge via the Internet at http://pubs.acs.org.

**Note Added after ASAP Posting.** This article was posted ASAP on 01/09/2004. A label in Figure 5 has been changed. The correct version was posted on 01/21/2004.

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