

On the stability of glycine-water clusters with excess electron: Implications for photoelectron spectroscopy

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Calculations are presented for the glycine-(H₂O)_n⁻ ($n=0-2$) anionic clusters with excess electron, with the glycine core in the canonical or zwitterion form. A variety of conformers are predicted, and their relative energy is examined to estimate thermodynamic stability. The dynamic (proton transfer) pathways between the anionic clusters with the canonical and the zwitterion glycine core are examined. Small barrier heights for isomerization from the zwitterion glycine-(H₂O)₂⁻ anion to those with canonical glycine core suggest that the former conformers may be kinetically unstable and unfavorable for detection of *neutral* glycine zwitterion-(H₂O)_n ($n=1,2$) clusters by photodetachment, in accordance with the photoelectron spectroscopic experiments by Bowen and co-workers [Xu *et al.*, J. Chem. Phys. **119**, 10696 (2003)]. The calculated stability of the glycine-(H₂O)_n⁻ anion clusters with canonical glycine core relative to those with zwitterion core indicates that the observation of the *anionic* conformers with the *canonical* glycine core would be much more feasible, as revealed by Johnson and co-workers [Diken *et al.* J. Chem. Phys. **120**, 9902 (2004)].

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I. INTRODUCTION

Biomolecules clustered with solvent molecules¹⁻⁸ have received a lot of attention, since they are intermediary structures lying between isolated molecules and fully solvated molecules in solution phase. Many biomolecules may exist in clusters as a number of conformers of close energies. Amino acids, which are the building blocks of protein, are ideal system to study the effects of solvation on the biochemical activity due to their moderate size. The structures of canonical amino acids⁸⁻¹³ and the corresponding zwitterion^{11,14-20} in clusters and in solution are of fundamental interest. It is well known that amino acids exist in the canonical (i.e., nonzwitterionic) form in the gas phase, whereas in aqueous solution the zwitterionic conformer is the predominant form.^{19,21-24} Thus, a fundamental question concerning the solvation of zwitterion is how many solvent molecules would stabilize the zwitterion. The cluster approach^{1-7,25-31} has proved quite useful in addressing this intriguing question, in which the effects of microsolvation on the thermodynamic and kinetic properties of the resulting amino acid-solvent clusters are monitored as a function of the number of solvent molecules. This approach may also give invaluable (although indirect) information for the configuration of solvent molecules near the canonical and zwitterionic

amino acids in aqueous solution. The magnitude of barrier and the dynamic paths of transformation between these two forms of amino acid clusters are also of fundamental importance in relation to the mechanism of chemical reactions in clusters. The transformation between the two forms of amino acid clusters may be studied as a prototype of chemical reactions in cluster. There has been a paucity of systematic studies on this extremely interesting subject, however, probably due to the difficulty of locating the transition states and of carrying out the rigorous intrinsic reaction coordinate (IRC) analysis.

The stability of the amino acid with an excess electron^{26,32-34} (with the canonical or the zwitterion amino acid core) is very interesting in several respects. It has been known that the dipole-binding electron may stabilize the amino acid zwitterion relative to the canonical form, although not experimentally observed yet. The stability of zwitterionic amino acid anion with excess electron is also concerned with the experimental detection of zwitterionic amino acid by the photoelectron spectroscopic technique, which seems to be the most successful of the recent experimental studies for elucidating the structures of glycine (Gly)-water clusters. In these experiments, a Gly-(H₂O)_n⁻ ($n=0-2$) cluster anion with excess electron is produced, with the core Gly either in the canonical or in the zwitterion form, and the excess electron is detached by interacting with a photon. Two experimental studies are notable: Xu *et al.*³⁵

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prepared the Gly-(H₂O)_n⁻ anion clusters with zwitterionic Gly core, and observed the corresponding Gly zwitterion-(H₂O)_n neutral clusters only for $n \geq 5$, whereas several theoretical studies indicate that there may exist stationary structures of the clusters with $n \geq 2$. This apparent inconsistency has baffled investigators, but no reasonable explanations have been given yet. On the other hand, in the experiments by Diken *et al.*,³⁶ the Gly-(H₂O)_n⁻ anion clusters produced by collision between Gly and water dimer anion were found to possess the *canonical* Gly core.

We believe that examining the stability (thermodynamic and kinetic) of the Gly-(H₂O)_n⁻ anion clusters, either with the zwitterionic or canonical Gly core, may shed considerable light into resolving the ambiguity described above. The thermodynamic stability of the conformers may be probed by comparing the relative energy and Gibbs function (at 5 K, which is the typical temperature at which the clusters studied in this work are to be observed, these two thermodynamic functions are almost identical). The kinetic stability^{7,37} (the facileness of transformation from the given species to other), on the other hand, has rarely been assessed in theoretical studies, probably due to the difficulty of obtaining the reaction pathways along with the transition states by carrying out the IRC analysis. Some species may be calculated to be stationary (with real frequencies for all vibrational modes), but still kinetically unstable (changing to other forms without reaction barrier) when the zero point energy (ZPE)-corrected energy of the transition state is lower than that of the reactant(s), as we demonstrated in previous works.^{7,37} Our basic supposition is that the Gly-water cluster anion with excess electron should be stable (both thermodynamically and kinetically) to exist sufficiently long to undergo the process of photodetachment, for the neutral species to be detected in the experiments. To estimate the kinetic stability of these cluster anions, calculations must be carried out for the reaction barriers to isomerization to the canonical form. In this paper, we present calculations for the Gly-(H₂O)_n⁻ ($n=0-2$) with excess electron, with the core Gly in the canonical or zwitterion form. A variety of conformers are predicted, and their relative energies are compared to estimate their thermodynamic stability. Detailed analysis is presented on the dynamic (proton transfer) pathways between the anion with canonical Gly core to that with the Gly zwitterion. The barrier heights are calculated to estimate the kinetic stability of the zwitterionic Gly-water neutral clusters with excess electron for detection of the zwitterionic Gly-water cluster in photodetachment experiments. The relative energies of Gly-(H₂O)_n⁻ with canonical and zwitterionic Gly core are also examined to explain the observation of canonical Gly⁻ anion in the photoelectron experiments by Diken *et al.*³⁶

II. COMPUTATIONAL METHODS

Electron correlation is known to be very important in studying the dipole bound anion. We have carried out calculations with high-level correlated *ab initio* methods, MP2, CCSD, and also density functional theory methods (B3LYP^{38,39} and MPW1K⁴⁰). We employ the aug-cc-pVDZ basis set supplemented with additional diffuse functions on

TABLE I. ZPE-corrected relative energies (kcal/mol) of bare Gly⁻ anion.

Basis sets	ANO	ATS0	AZ0
6-31++G(<i>d,p</i>)	0 ^a (0) ^b	+3.08(+2.67)	+3.41(+2.81)
6-311++G(<i>d,p</i>)	0(0)	+3.85(+3.83)	+3.85(+4.84)
aug-cc-pVDZ	0(0)	+3.78(+2.96)	+4.42(+3.80)
aug-cc-pVDZ+diffuse function on N	0(0)	+5.06(+4.67)	+6.19(+5.99)
	[0] ^c	[7.79]	[+8.49]
aug-cc-pVDZ+diffuse function on N, H	0(0)	+6.18	+7.35
aug-cc-pVDZ+diffuse function on N, O	0	+5.06	+6.19

^aUB3LYP.

^bUMP2.

^cCCSD corrected with MP2 zero point energy.

the nitrogen atom.⁴¹ The effects of adding diffuse functions on O and H atoms for the loosely bound excess electron are also monitored. We find that the value of $\langle S^2 \rangle$ never exceed 0.7501 when aug-cc-pVDZ basis sets are used with augmented diffuse function on N. The IRC analysis is carried out to obtain the reaction path and to identify the transition state(s) for given dynamic path. All calculations are implemented with GAUSSIAN03 and GAUSSIAN98W set of programs,⁴² and default criteria are employed for all the optimization.

III. RESULTS

A. Bare Gly⁻ anion with an excess electron

It is well known that Gly zwitterion is not a minimum energy stationary structure in the ground state potential energy surface. The Gly⁻ anion with an excess electron, however, has been predicted to exhibit stationary structure with the zwitterionic core by Gutowski *et al.*²⁶ They calculated that the zwitterionic Gly⁻ anion lies about 10 kcal/mole above that with the canonical Gly⁻, predicting that the former form of the Gly⁻ anion may not be observed due to the extremely small barrier along the proton transfer path to the canonical Gly⁻.

To confirm this prediction and to check the validity of the various methods and basis sets employed in this work, we calculate the structures of zwitterionic or canonical Gly⁻. The results are presented in Tables I, Table II, and Fig. 1. By

TABLE II. Vertical detachment energy and harmonic frequencies (unscaled) of CO, OH, and NH₂ stretching modes.

	Vertical detachment energy (eV)	ν_{CO} (cm ⁻¹)	ν_{OH} (cm ⁻¹)	ν_{NH_2}	
				sym.	antisym.
ANO	0.10 ^a	1803.4	3227.3	3415.4	3485.3
AN1-1	0.26	1782.5	3137.0	3399.9	3465.5
AN1-2	0.23	1759.2	3305.0	3358.4	3454.8
AN1-3	0.30	1804.9	3158.2	3380.7	3510.2
AN2-1	0.44	1783.3	3038.5	3357.2	3496.9
AN2-2	0.38	1773.6	3092.3	3386.6	3454.1
AN2-3	0.36	1775.1	3066.3	3380.2	3447.6
AN2-4	0.39	1717.2	3142.7	3337.4	3445.3
AN2-5	0.41	1799.7	3020.0	3381.8	3449.8
AN2-6	0.03	1805.1	3074.0	3425.3	3511.1

^aB3LYP/aug-cc-pVDZ plus diffuse function on N atom.

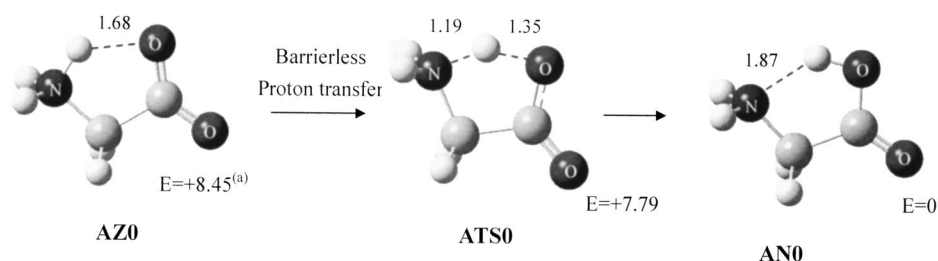


FIG. 1. Structure and isomerization of Gly⁻. (a) CCSD with aug-cc-pvdz basis set augmented by diffuse function on N (corrected for ZPE calculated by the MP2 method with same basis set).

employing the MP2 method with the aug-cc-pVDZ basis sets augmented with the diffuse function on nitrogen, we find the two minimum energy structures, AZO and ANO, along with the transition state linking them on the anionic potential energy surface. Because the zwitterionic Gly⁻ anion is calculated to be higher in ZPE-corrected energy than the canonical Gly⁻, this form of the Gly⁻ anion is thermodynamically unstable. We also find that the ZPE-corrected energy of zwitterionic Gly⁻ is higher than the transition state TS0, indicating that the conformer is kinetically unstable. Thus, AZO may spontaneously isomerize to ANO without barrier, and may not be observed experimentally. The magnitude of the barrier for the reverse process (from canonical to zwitterionic Gly⁻) is calculated to be 4.7 kcal/mole. We also perform CCSD calculations to further check this latter finding,⁴³ and obtained similar conclusion. Thus, we have corroborated the prediction²⁶ of Gutowski *et al.* by carrying out the rigorous IRC analysis. The magnitude of barrier from ANO to AZO is found to depend quite sensitively on the level of approximation, increasing to 7.8 kcal/mol when the CCSD method is employed.

Since the relative energy of the conformers may depend considerably^{43,44} on the basis set, we carry out calculations by employing other basis sets. The results are presented in Table I. The ZPE-corrected energy difference between AZO and ANO varied 3–7 kcal/mol. Dunning's basis sets produce larger energy difference than the valence type basis sets 6-31++G(*d,p*) and 6-31++G(*d,p*). Adding the diffuse functions on N atom only or both on N and H also tends to

increase the energy difference. This finding shows that the aug-cc-pVDZ basis set with additional diffuse functions on N and H may be appropriate for predicting the relative energy for the conformers of Gly⁻ binding with the water molecules to be discussed below.

B. Gly-(H₂O)₁⁻ complex with an excess electron

It will be interesting to see whether the excess electron may stabilize the Gly zwitterion relative to the canonical form when a water molecule interacts by hydrogen bonding. The structures of the canonical and zwitterion Gly-(H₂O)⁻ anion complex are presented in Figs. 2 and 3, respectively, and the vertical detachment energies and the harmonic frequencies of the canonical conformers are given in Table II. All structures are found to be dipole bound anions, as seen in the contour map of the excess electron in Fig. 4. The singly occupied electron is mainly located on the outside of nitrogen atom. A water molecule may affect the location of excess electron. For example, water molecule in AN1-2 and AN1-3 is bound close to the excess electron, whereas in AN1-1 water is located far from it. The singly occupied molecular orbital (MO) in AN1-2 and AN1-3 covers more volume than in AN1-1, exhibiting the diffuseness of the excess electron. The global minimum structure with the canonical Gly core is AN1-1, in which two hydrogen atoms in water molecule bind to the carboxyl group of Gly. Hydrogen bond lengths are 3.05 and 1.91 Å, respectively. This structure does not correspond to the global minimum energy structure of the

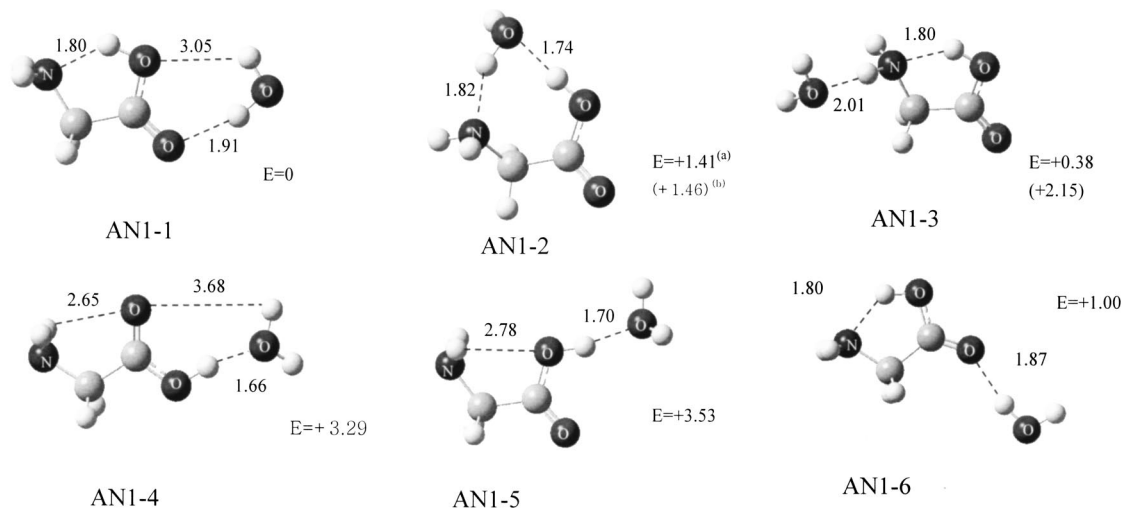


FIG. 2. Structures, relative energies (kcal/mol), and vertical detachment energy (VDE in eV) Gly-(H₂O)₁⁻ cluster anion with canonical Gly core. (a) B3LYP (aug-cc-pvdz with augmented diffuse function on N); (b) B3LYP (aug-cc-pvdz with augmented diffuse function both on N and H).

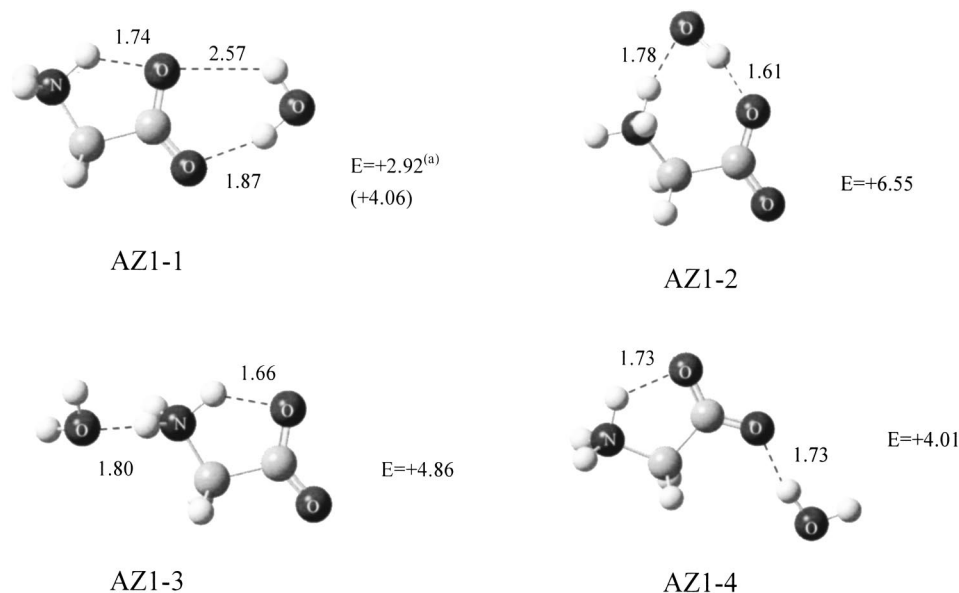


FIG. 3. Structures and relative energies (kcal/mol) of Gly-(H₂O)₁⁻ anion complexes with zwitterionic Gly core. (a) Relative energy compared to global minimum energy structure AN1-1 with the canonical Gly core.

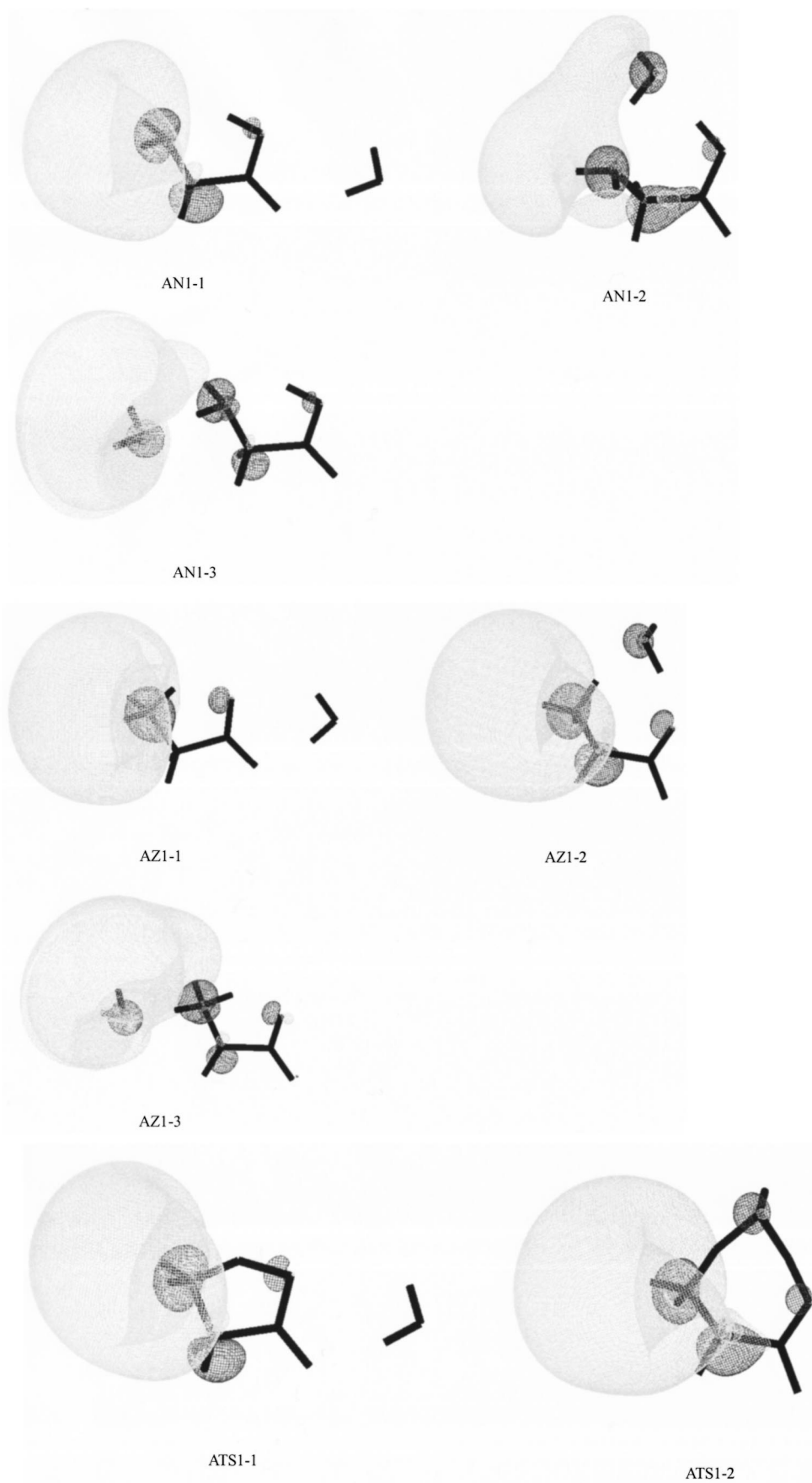
neutral complex (N1c in Ref. 20), but is similar to N1g whose energy is quite higher than the global minimum energy of the neutral complex by approximately 5 kcal/mole (see Table IV in Ref. 20). This finding indicates that the ordering of the thermodynamic stability of the Gly-water complex is profoundly affected under the influence of an excess electron. The influence of an excess electron may also be noted in the structure of AN1-4. This conformer is similar to the global minimum energy structure of the neutral Gly-(H₂O) complex (N1c in Ref. 21), but the hydrogen bond lengths are quite different: One hydrogen bond (3.68 Å) is lengthened by about 1.48 Å, whereas the other hydrogen bond (1.66 Å) is shortened by about 0.27 Å compared to corresponding neutral complex N1c. In AN1-4, the oxygen atom in water molecule binds to the O-H bond of carboxyl group. The carbonyl group does not form direct hydrogen bond with water, in contrast with the neutral Gly-(H₂O) complex.²⁰ The second lowest energy conformer is AN1-3, in which the water molecule binds to the amino group. This conformer is calculated to be lying only 0.38 kcal/mole in energy above AN1-1. When the diffuse functions are augmented on H, however, the energy difference becomes larger (2.15 kcal/mole), and AN1-2 becomes the second lowest energy conformer. Interestingly, these anion complexes with canonical Gly are calculated to possess larger dipole moments (>8 D) than those (3.7–7.8 D) with the Gly zwitterion core presented in Fig. 3.

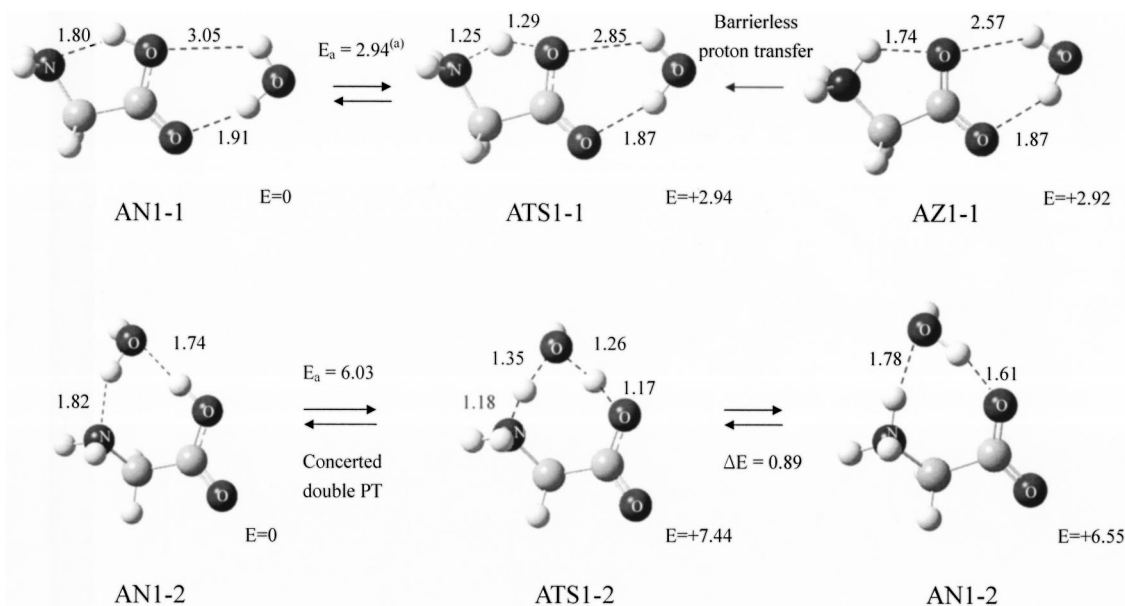
The conformer AZI-1 with Gly zwitterion core is of the lowest energy, isomerizing to AN1-1 with the canonical Gly core by proton transfer via the transition state ATS1-1. The zwitterionic Gly-(H₂O)⁻ anion AZI-1 is calculated to be higher (by 3–4 kcal/mol) in ZPE-corrected energy than the canonical conformer AN1-1 and thus thermodynamically unstable. It is also predicted to be kinetically unstable, because the ZPE-corrected energy is higher than that of the transition state ATS1-1, producing the cluster anion aN1-1 with the canonical Gly core by barrierless proton transfer. Therefore, it may not be detected experimentally. We also find that another Gly-(H₂O)⁻ anion complexes of higher energy with the

zwitterionic Gly core may exhibit a finite but very small barrier as depicted in Fig. 5. The anion complex AZI-2, for example, is calculated to isomerize to that with the canonical Gly core with low reaction barrier (0.89 kcal/mol) by concerted double proton transfer mechanism. The barrier is so small that it seems that the isomerization would occur too fast for the experimental detection of AZI-2.

C. Gly-(H₂O)₂⁻ cluster with an excess electron

The structures of the Gly-(H₂O)₂⁻ cluster anion would be determined by a complicated interplay of factors such as the hydrogen bond among Gly and two water molecules, the electrostatic interaction with the excess electron, the stability of chain formation of the two water molecules, and so on. We obtain a number of minimum energy structures within 1 kcal/mole energy, as shown in Figs. 6 and 7. The vertical detachment energies and the harmonic frequencies of the canonical conformers are given in Table II. All the conformers exhibit the character of dipole bound anion, with the excess electron located near the amino group as shown in Fig. 8. The global minimum structure with the canonical Gly core is calculated to be AN2-1, in which one of the two water molecules binds to the carboxyl group and the other binds to the amino group. This observation is in contrast with the global minimum energy conformer of the neutral Gly-(H₂O)₂ cluster, in which the water dimer is directly linked toward the carboxyl group of the global minimum of neutral bare Gly.²⁰ Thus, it seems that the excess electron tends to decrease the stabilization caused by the hydrogen bonding between the water dimer and Gly, rendering the conformers AN2-2 and AN2-3 to be slightly higher in energy, as presented in Fig. 6. It seems that the interactions between the amino group and a water molecule is greatly affected by the excess electron for Gly-(H₂O)_n⁻ (*n*=1,2) cluster anion: When a water molecule is interacting with this site, outside of amino group depicted in Fig. 8, the hydrogen bond between water and the amino group is enhanced by the flexibility of loosely bound excess electron. The contour map for Gly-(H₂O)₂⁻ clusters in Fig. 8

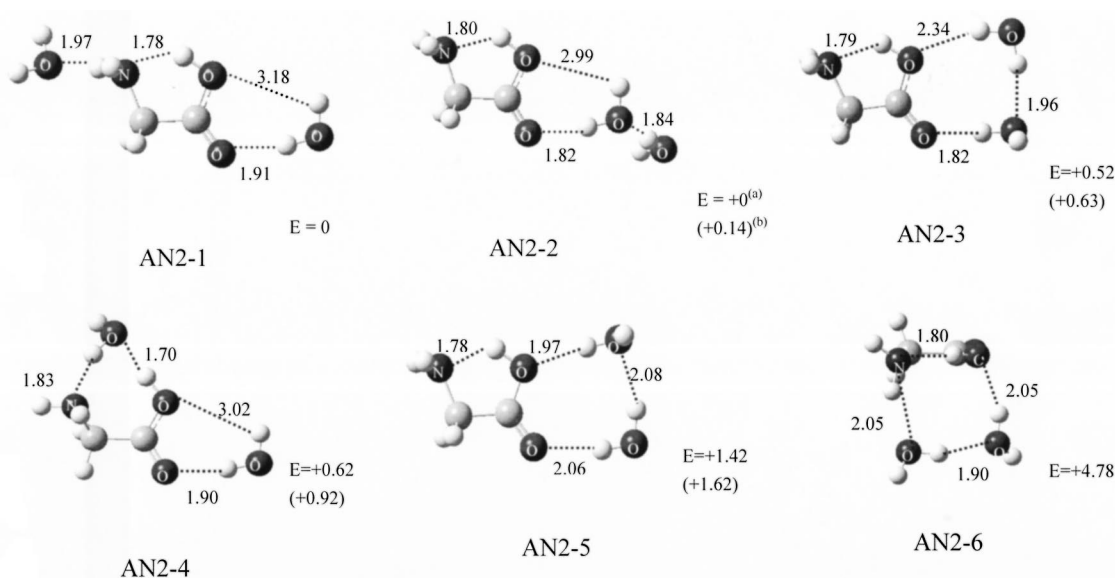
FIG. 4. Contour map of the singly occupied molecular orbital at the Gly-(H₂O)⁻ complexes.

FIG. 5. Single and double proton transfer in Gly-(H₂O)₁⁻ anion complexes.

may also confirm this prediction: In AN2-1, the singly occupied MO extends to the outside of amino group and water is bound on amino group, whereas the excess electron is more or less localized on the amino group in AN2-2 and AN2-3. It is also useful to note that the lower energy conformers of Gly-(H₂O)₂⁻ cluster anion are based on the Gly-(H₂O)₂⁻ anion AN1-1 with minor changes in the structure of the Gly moiety. The exception is the conformer AN2-6 of considerably higher energy. These structures of Gly-(H₂O)₂⁻ cluster anion with the canonical Gly core may bear importance as regards the photoelectron experiments by Diken *et al.*,³⁶ in which the Gly-(H₂O)_n⁻ ($n=0-2$) anion clusters are produced by collision between Gly and water dimer anion. Since the water anion is formed first, the conformers AN2-2, AN2-3, AN2-5, or AN2-6 with explicit hydrogen bonding between

the linking two water molecules may be formed and observed with higher probability than AN2-1 or AN2-4 in which the two water molecules are more or less separate. Experimental verification of these lower energy structures of Gly-(H₂O)₂⁻ anion with the water dimer moiety would be highly interesting.

All the zwitterionic Gly-(H₂O)₂⁻ cluster anions with the zwitterionic Gly core presented in Fig. 7 are calculated to be higher (by 1–4 kcal/mol) in ZPE-corrected energy than the conformers with canonical Gly core in Fig. 6, indicating that the latter canonical anionic conformers would be thermodynamically more stable. The most stable one is predicted to be AZ2-5, which may be produced by proton transfer from AN2-5. This cluster anion with the zwitterionic Gly core lies 0.8–1.9 kcal/mol higher (depending on the basis set used) in

FIG. 6. Structures, relative energies (kcal/mol), and vertical detachment energy (VDE in eV) of Gly-(H₂O)₂⁻ cluster anion with canonical Gly core. (a) B3LYP (aug-cc-pvdz with augmented diffuse function on N); (b) B3LYP (aug-cc-pvdz with augmented diffuse function both on N and H).

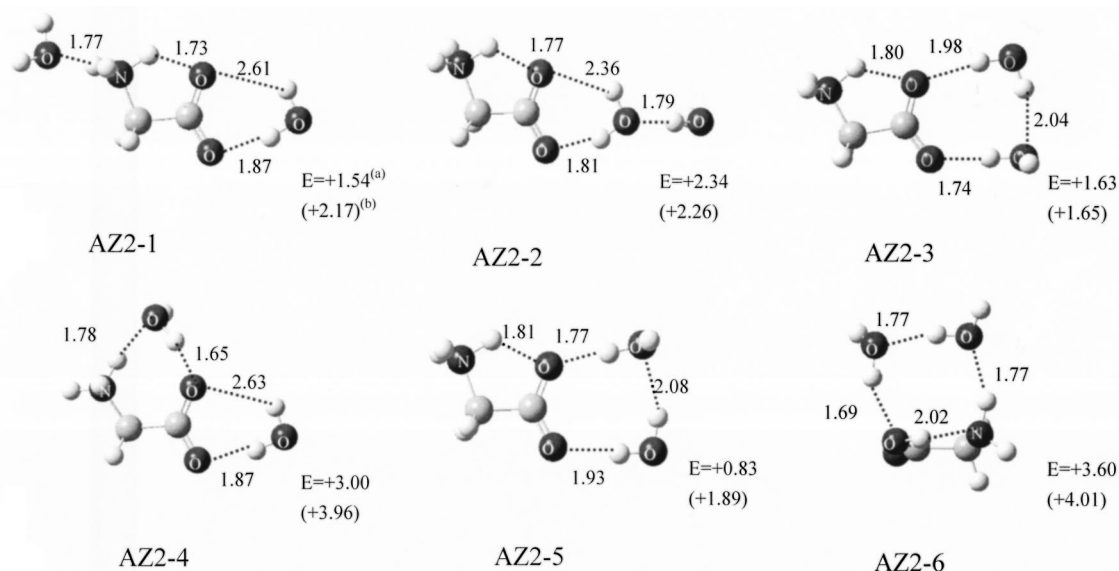


FIG. 7. Structures and relative energies (kcal/mol) of Gly-(H₂O)₂⁻ anion clusters with zwitterionic Gly core. (a) B3LYP (aug-cc-pvdz with augmented diffuse function on N); (b) B3LYP (aug-cc-pvdz with augmented diffuse function both on N and H).

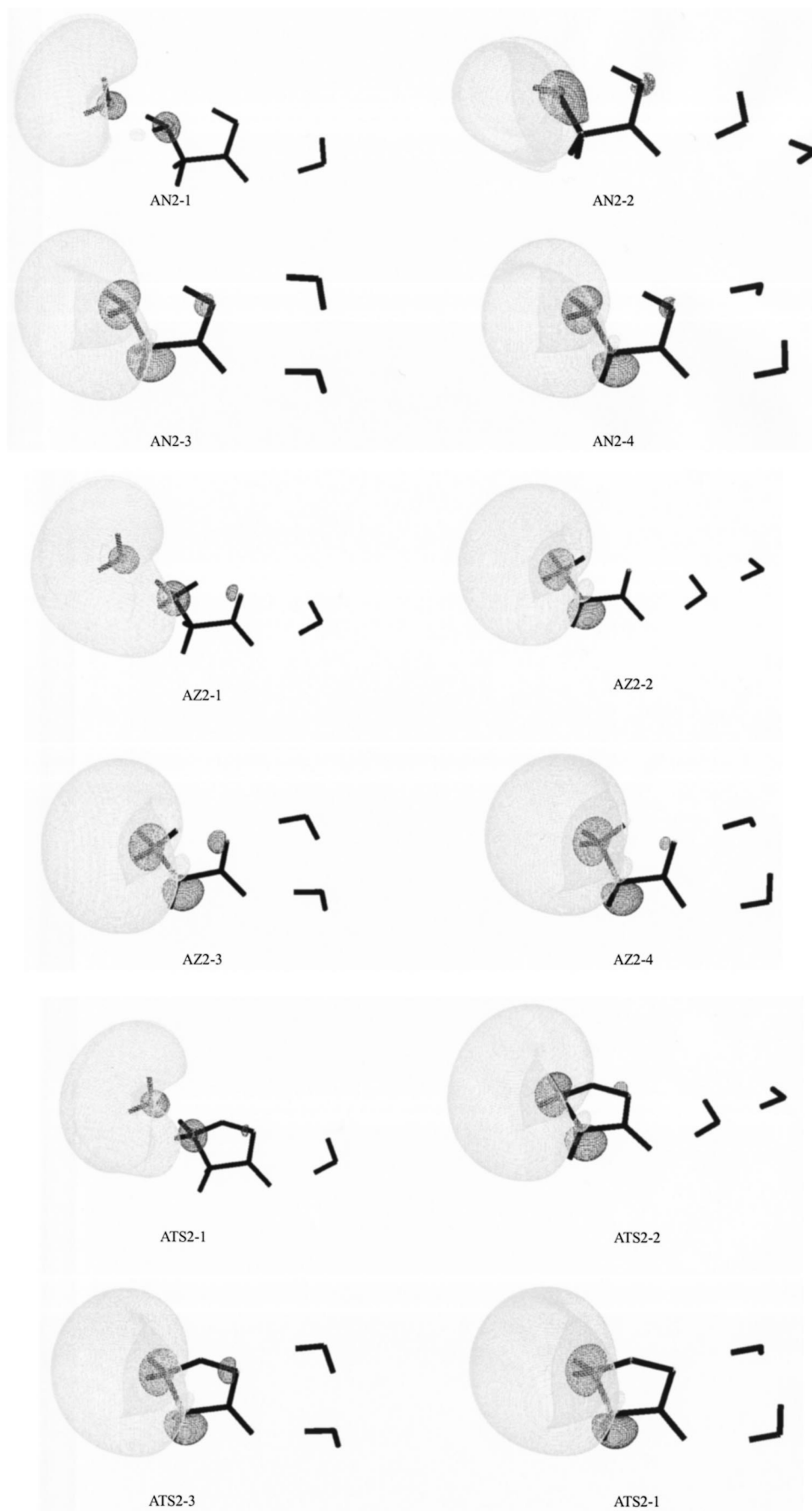
energy above the most stable conformer AN2-1 of Gly-(H₂O)₂⁻ cluster anion with canonical Gly core. The relative energies of AZ2-5 and AN2-5 somewhat vary depending on the basis set: AZ2-5 (+0.83 kcal/mole relative to AN1-1) is predicted to be more stable than AN2-5 (+1.42 kcal/mole) by employing the aug-cc-pVDZ basis set augmented with diffuse functions on N. However, calculations using the aug-cc-pVDZ set with diffuse functions on N and H predict that AN2-5 (+1.62 kcal/mole) is a bit more stable than AZ2-5 (+1.89 kcal/mole).

The kinetic stability of the Gly-(H₂O)₂⁻ anion clusters with zwitterionic Gly core depicted in Fig. 7 is extremely important as regards the photoelectron experiments by Xu *et al.*,³⁵ in which the zwitterionic Gly-(H₂O)_n neutral clusters are to be detected by photodetaching the Gly-(H₂O)_n⁻ anion clusters with Gly zwitterion. We have carried out extensive IRC analysis for the isomerization between the Gly-(H₂O)₂⁻ anionic clusters with canonical and zwitterionic Gly core to identify the transition state and to calculate the magnitude of barrier, and the results are presented in Fig. 9. The activation barrier from the lowest energy conformer AZ2-5 is calculated to be small (1.5–1.9 kcal/mole), and even smaller for other conformers (0.62–1.23 kcal for AZ2-3, and 0.04 kcal/mol for AZ2-1 by B3LYP/aug-cc-pVDZ plus diffuse function both on N and H). Since the magnitude of the barrier is of critical importance for determining the stability of the Gly-(H₂O)₂⁻ anionic clusters with Gly zwitterion core, we carry out calculations employing the MPW1K⁴⁰ method that is known to give more accurate energy of the transition states. The activation barrier for AZ2-5 now decreases to 0.65 kcal/mole with the basis set aug-cc-pVDZ plus diffuse function on N. The barrier for isomerization from AZ2-3 is calculated to be only 0.36 kcal/mole, and AZ2-1 and AZ2-2 are predicted to isomerize by barrierless proton transfer processes. It seems that these barriers are too small for the clusters to be stable even in a low temperature gas phase environment.

Since the Gly-(H₂O)₂⁻ anion clusters with zwitterionic Gly core presented in Fig. 7 are thermodynamically less stable than those with neutral Gly core, and since they are predicted to be kinetically not stable, they may easily isomerize to those with the neutral Gly core in photoelectron experiments. These results may help understand the two excellent experiments by Diken *et al.*³⁶ and by Xu *et al.*³⁵ Once formed in the photoelectron experiments, the Gly-(H₂O)₂⁻ anion clusters with zwitterionic Gly core may transform to those with canonical Gly core too rapidly to survive sufficiently long for photodetachment, forbidding the experimental detection of the Gly-(H₂O)₂ neutral clusters with Gly zwitterion core (i.e., zwitterionic Gly-(H₂O)₂ clusters). On the other hand, the stability of the bare Gly⁻ and the Gly-(H₂O)₂⁻ anion clusters with canonical Gly core relative to those with zwitterionic core may nicely explain the observation of the anionic canonical conformers of bare Gly⁻ in the photoelectron spectroscopic experiments by Diken *et al.*³⁶

IV. CONCLUSION

Our present study has shown that a loosely bound excess electron may profoundly affect the structures and reactions of Gly-(H₂O)_n ($n \leq 2$) clusters. The calculated results clearly predict that detection of the canonical bare Gly⁻ and Gly-(H₂O)_n⁻ are much more favorable than that for the zwitterion Gly-(H₂O)_n⁻ in the photoelectron spectroscopic experiments at least for $n \leq 2$, in agreement with the experimental observations by Xu *et al.*,³⁵ and by Diken *et al.*³⁶ On the other hand, experimental detection by Xu *et al.* of Gly zwitterion-(H₂O)_n clusters with larger number of the water molecules ($n \geq 5$) indicates that the corresponding zwitterion Gly-(H₂O)_n⁻ cluster anions are stable enough for photodetachment. Theoretical analysis of the stability of these zwitterionic clusters and the mechanism of isomerization would be highly interesting. Further work is in progress.

FIG. 8. Contour map of the singly occupied molecular orbital at the Gly-(H₂O)₂⁻ clusters.

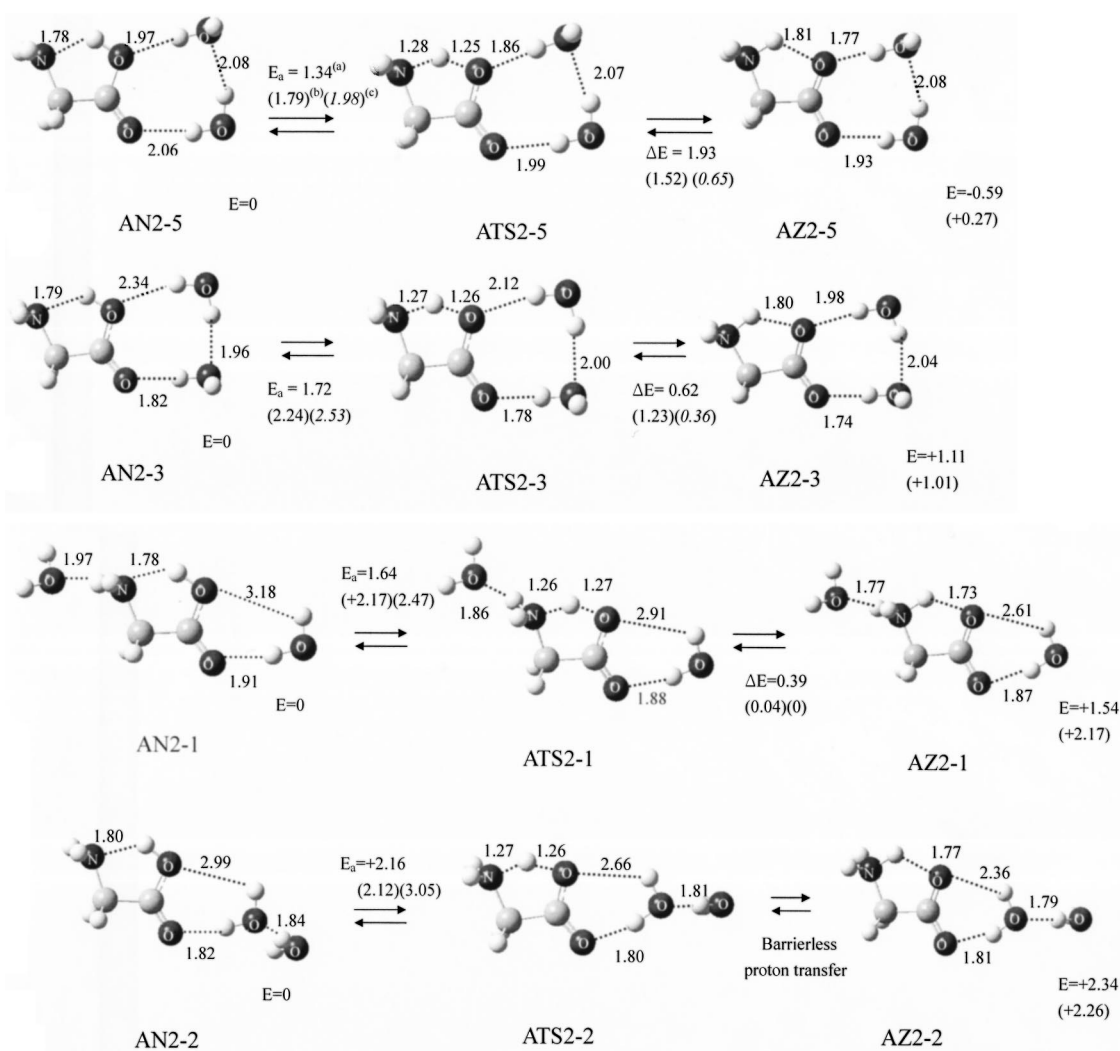


FIG. 9. Proton transfer in Gly-(H₂O)₂⁻ anion clusters. (a) B3LYP (aug-cc-pvdz with augmented diffuse function on N); (b) B3LYP (aug-cc-pvdz with augmented diffuse function both on N and H); (c) MPW1K (aug-cc-pvdz with augmented diffuse function on N).

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