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Density Functional Theory Study of the Hydrogen-Bonding Interaction of 1:1 Complexes of Alanine with Water

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The hydrogen bonding of 1:1 complexes formed between alanine and water molecules has been completely investigated in the present study using density functional theory, method B3LYP at varied basis set levels from 6-31G to 6-311++G(d,p) and the second-order Møller−Plesset perturbation method at the 6-31++G(d,p) level. Eight reasonable geometries on the potential energy hypersurface of the alanine and water system are considered with the global minimum. The optimized geometric parameters and interaction energies for various isomers at different levels are estimated. The infrared spectrum frequencies, IR intensities, and vibrational frequency shifts are reported. Finally, the solvent effects on the geometries of the alanine−water complexes have also been investigated using self-consistent reaction-field calculations at the B3LYP/6-311++G(d,p) level. The results indicate that the polarity of the solvent plays an important role in determining the structures and relative stabilities of different isomers.

1. Introduction

Amino acids are the building blocks of proteins, and alanine is the smallest chiral amino acid of the roughly 21 amino acids common in nature. A significant amount of alanine in the atmosphere is present in the aqueous phase. Alanine is simply an amino group and a carboxyl group separated by a chiral carbon, which is usually chosen as a good model for studying biological systems exhibiting the amino acid type of bonding and DNA structures. The nature of the hydrogen bonding between alanine and water can explain the hydrogen-bonding mechanism expected in the hydration of amino acids. For this system, there would exist distinctness caused by the chirality of alanine compared with those systems without chirality. Therefore, investigation of the hydrogen-bonding interaction between alanine and water molecules must be very significant. This work is a foundation for further research work on the hydration of alanine, which is a very interesting subject for fundamental research.

Recently, density functional theory (DFT) has been accepted by the ab initio quantum chemistry community as a cost-effective approach for the computation of molecular structure, vibrational frequencies, and energies of chemical reactions. Many studies have shown that molecular structures and vibrational frequencies calculated by DFT methods are more reliable than those calculated by MP2 methods.[1−4] While there is sufficient evidence that DFT provides an accurate description of the electronic and structural properties of solids, interfaces, and small molecules, relatively little is known about the systematic performance of DFT applications to molecular associates. To further assess the reliability of DFT methods applied to this field of chemistry, in this paper we discuss the structure and bonding of the alanine−water complex as obtained by high-level ab initio calculations. We thus report geometry optimization and calculated bonding energies between alanine and water for a variety of theoretical models and basis sets. The effects of basis set size and basis set superposition are analyzed in detail. Moreover, zero-point vibrational energy (ZPVE) corrections are also applied in the present case.

In addition, the vibrational frequencies of the monomer and the stationary complexes are calculated; the intramolecular frequencies and their shifts due to the complex formation are analyzed.

In the second part, as compared to the isolated gas-phase results, we pay some attentions to the influence of solvent effects on both the structure and the stability of these hydrogen-bonded systems.

2. Computational Methods

It is well known that in the SCF model, electrostatic, exchange, and some induction−polarization effects are included. In more recent years, it has been learned that the dispersion interaction may be of great importance.[5,6] It is therefore necessary to go beyond the SCF model and include some of the correlation effects. So, in the present paper, a variety of theoretical methods have been used, including Hartree−Fock (HF) and second-order Møller−Plesset theory (MP2) as well as the hybrid density functional methods B3LYP, in order to test the reliability of these methods for the hydrogen-bonding systems. For hydrogen bonding, it is expected that both diffuse and polarization functions may be necessary in the basis sets;[7] we thus analyze the separate influence of the diffuse and polarization functions.

The geometry optimization of alanine−water has been carried out using the B3LYP method with the 6-31G, 6-31G(d), 6-31+G(d), 6-31++G(d,p), and 6-311++G(d,p) basis sets along with analytic vibrational frequency calculations. To confirm the superiority of the DFT method, we simultaneously adopted HF and MP2 methods at the 6-31++G(d,p) level. In

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TABLE 1: Energies of the 13 Configurations of Alanine Monomer (hartrees)

	B3LYP/ 6-31G	B3LYP/ 6-31G(d)	B3LYP/ 6-31+G(d)	B3LYP/ 6-31++G(d,p)	B3LYP/ 6-311++G(d,p)	B3LYP/ 6-311++G(2d,2p)	HF/ 6-31++G(d,p)	MP2/ 6-31++G(d,p)
Alan1	−323.6349235	−323.73964	−323.7589117	−323.7765225	−323.8560796	−323.8671902	−323.8983775	−322.9888669
	−323.527139	−323.631197	−323.650810	−323.668624	−323.748488	−323.759414	−323.782171	
Alan2	−323.6329104	−323.7373311	−323.757175	−323.7747864	−323.8543781	−323.8543781	−323.8964564	
	−323.525131	−323.628874	−323.649020	−323.666831	−323.746685	−323.746685	−323.780216	
Alan3							−323.8959808	
							−323.779810	
Alan4	−323.636721	−323.7395049	−323.7588107	−323.7765343	−323.8560581	−323.8668957	−323.8945342	−322.9881152
	−323.528216	−323.630529	−323.650209	−323.668183	−323.747950	−323.758628	−323.777813	
Alan5		−323.7965064	−323.7581007	−323.7765353	−323.856035	−323.8669854	−323.7395064	−322.9886024
		−323.630513	−323.650294	−323.668172	−323.747940	−323.758700	−323.630513	
Alan6	−323.6323688	−323.7365545	−323.7562787	−323.7740972	−323.8537624	−323.8644812	−323.8957109	−322.9865437
	−323.525049	−323.628267	−323.648364	−323.666399	−323.746365	−323.757372	−323.779632	
Alan7	−323.6325985	−323.7370904	−323.7566147	−323.774321	−323.8539962	−323.8652425	−323.9684557	−322.9869542
	−323.525146	−323.628671	−323.648642	−323.666565	−323.746487	−323.757520	−323.852804	
Alan8	−323.6238674	−323.7303403	−323.7493885	−323.7671501	−323.849574	−323.8588571	−323.8872365	−322.9796562
	−323.516566	−323.622256	−323.641673	−323.659686	−323.739812	−323.751415	−323.771348	
Alan9	−323.6220422	−323.7278749	−323.7471795	−323.7651095	−323.8405327	−323.8405327	−323.8511095	−322.9778271
	−323.515163	−323.619833	−323.639549	−323.657696	−323.737911	−323.737911	−323.749683	
Alan10	−323.6219307	−323.7247063	−323.746965	−323.7650515	−323.845018	−323.8568983	−323.9573117	−322.973361
	−323.515181	−323.619391	−323.639246	−323.657564	−323.737801	−323.749494	−323.841990	
Alan11	−323.6314454	−323.7351032	−323.755207	−323.77307	−323.8529239	−323.8639455	−323.8954625	−322. 986055
	−323.523834	−323.627406	−323.647243	−323.665568	−323.745474	−323.756306	−323.779337	
Alan12	−323.6309753	−323. 735488	−323.7552094	−323.7229085	−323.8524942	−323.8634944	−323.9674427	−322.9856551
	−323.523402	−323.626886	−323.647252	−323.665155	−323.745012	−323.755802	−323.857790	
Alan13		−323.7289525					−323.8854514	−323.8465838
		−323.626840					−323.769989	

addition, the calculated binding energies and the ZPVE corrections obtained with both B3LYP and HF methods and all theoretical procedures are then corrected for the basis set superposition error (BSSE).[8] This is done using the counterpoise method.[9] All calculations are performed using the Gaussian98 program.

3. Results and Discussion

3.1. Structure of Alanine and Water Monomers. The structures of the supermolecule will depend on the structures calculated for the alanine and water monomers. In the crystal, alanine exists as zwitterions.[10−13] In structural studies of alanine in the gas phase, low-resolution photoelectron spectroscopy[14,15] did not yield any conformational information. An electron diffraction study[16] indicated that there was only one conformer present. However, only the heavy-atom positions were established in this study, the electron diffraction patterns being too insensitive to hydrogen positions to enable the hydrogen to be located. Therefore, reliance was placed on molecular orbital calculations to decide the nature of the conformer.

The conformers of alanine acid arise from rotations about the C2−C3 and C3−O2 bonds. It is reported that the lowest energy conformer of alanine has the amine and carbonyl groups oriented such that a bifurcated intramolecular hydrogen bond is formed between the hydrogen of the amine and the carbonyl oxygen.[17,18]

Godfrey et al.[19] had observed the rotational spectrum of alanine using their Stark-modulated free-expansion jet spectrometer, and they estimated that the relative abundances in the expanding plume were about 8:1 in favor of conformer 1 over conformer 5. They also calculated six configurations of alanine by using the HF method at the 6-31G(d,p) level. Ming Cao et al.[20] have calculated 13 possible configurations by using HF and MP2 method, and all their calculations show that the most energetically stable conformation is conformer 1. However, to the best of our knowledge, until now there have been no DFT calculations at large basis set levels of the 13 conformers of alanine. In the first part of our work, we calculated the 13 possible conformations by using B3LYP methods from the 6-31G level to the 6-311++G(2d,2p) level; for comparison we also calculated these conformations by using HF and MP2 methods at the 6-31++G(d,p) level. The results show that Alan1 is more stable than other conformations.

The energies of all 13 conformers calculated by different methods at different basis levels are listed in Table 1, and the structures are shown in Figure 1.

Surveying all the numerical values listed in Table 1, it is easy to find that the computational models play a very important role in determining the configurations of alanine. For Alan2 and Alan3, neither of the possible conformations can be found by using the MP2 method at the 6-31++G(d,p) level, and for Alan3 even the B3LYP method employed here cannot get the configuration achieved at the HF/6-31++G(d,p) level. Moreover, the basis set has a significant influence on some conformers of alanine: with the inclusion of the diffuse functions and the polarization functions, we cannot get the same configurations of some conformers as those achieved at low basis levels. For instance, without the diffuse function and the polarization function, the B3LYP method cannot yield the configuration of Alan5. It is interesting to note that we can get the desirable conformer of Alan13 by using the B3LYP method at the 6-31G(d) level.

The calculated parameters of structures of the Alan1 monomer and H_2O using the B3LYP method at 6-31++G(d,p), 6-311++G(d,p), and 6-311++G(2d,2p) basis set are presented in Table 2. For comparison, results of MP2 and HF methods at the 6-31++G(d,p) level are also given in Table 2. For simplicity, the results with 6-31G, 6-31G(d), 6-31+G(d) are not listed.

Considering all geometric parameters obtained with different theoretical models at various basis sets, as expected, 6-31G predicted the bond length in relatively poor agreement with the values calculated at high levels. For the B3LYP results, when the polarization and diffuse functions are included, the results are improved. The HF bond distances are slightly shorter than the MP2 ones. As we can see from Table 2, at the 6-31++G(d,p) level the difference between the B3LYP calculated and MP2

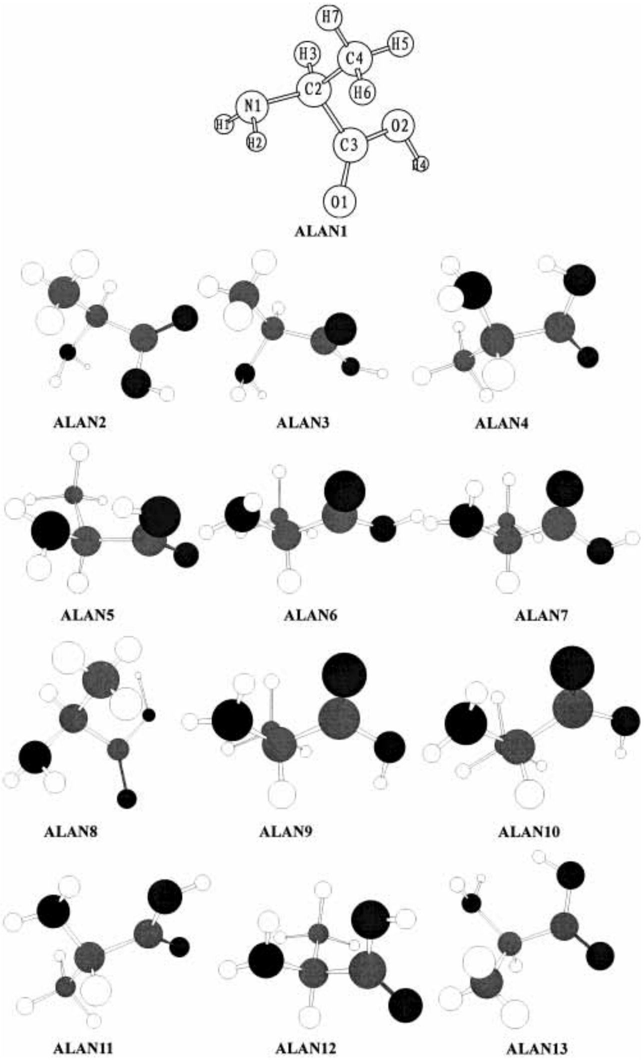

Figure 1. The 13 possible conformers of alanine.

results may be negligible. Of course, what we have discussed above is also true for the H_2O monomer.

3.2. Geometry of the Alanine−Water Complex. By using the ab initio method and density functional theory (B3LYP), we have calculated eight conformers of the complex formed between alanine and water monomers. It is very interesting to find that the diffuse functions and the polarization functions have significant effects on the results: we cannot get the same configurations for some complexes as those achieved at low basis levels. For Alan5, we cannot even get the configuration by using the ab initio method. The structures of the alanine−water dimers are shown in Figure 2, and the most interesting geometrical parameters are listed in Tables 3−6.

Surveying the results calculated for the different methods at different basis set levels, we find that changes in the monomer geometries upon complexation are relatively minor. Complex formation induces a small elongation of the C3−O2 bond and very small elongations of the O2−H4 and C3−O1 bonds. Other bond lengths involved in the hydrogen bonding are slightly lengthened. The maximum bond length change is less than 0.018 Å at the two large basis set levels.

AW1 is a cyclic structure in which water is bonded to the carbonyl. All the results indicate the tendency of the hydrogen of water to interact with the O of the carbonyl group; the interaction distance is 1.781 and 1.805 Å at the B3LYP/6-31++G(d,p) and MP2/6-31++G(d,p) basis set levels, respectively. As we can see from Table 3, the MP2 result is in good agreement with that calculated at B3LYP/6-311++G(d,p) (1.797 Å). The R_{OA-HW} is 1.939 and 1.980 Å at the B3LYP/6-311++G(d,p) and B3LYP/6-31++G(d,p) levels, respectively, which are both shorter than the MP2/6-31++G(d,p) level result (2.049 Å). The inclusion of the polarization functions and diffusion functions has a significant influence on the B3LYP results: R_{OW-HA} and R_{OA-HW} are increased by about 0.18 and 0.051 Å from the 6-31G level to the 6-311++G(d,p) level. From Tables 3−6, it also can be found that the interaction distance of this structure is the shortest of all the eight structures; therefore, the interaction energy of this structure should be the highest (as Table 7 shows). The departure of the $O_WH_W\cdots O_A$ angle from linearity is 23.8° and 22.6° at the B3LYP/6-311++G(d,p) and MP2/6-31++G(d,p) levels, respectively; in addition, the bond angle $O_AH_A\cdots O_W$ is 134.7° and 132.3° at the two basis levels.

As to AW2, alanine forms a hydrogen bond with one hydrogen atom of a water molecule. The B3LYP/6-311++G(d,p) calculations, which yield the H⋯N bond distance of 1.939 Å and OH⋯N angle 164.2°, are in good agreement with the MP2/6-31++G(d,p) values of 1.931 Å and 163.6°, while the difference in the length of the H⋯N bond between the 6-311++G(d,p) and 6-31++G(d,p) levels is obvious. The length of R_{OW-HA} calculated at the MP2/6-31++G(d,p) level (2.572 Å) is much shorter than that achieved using the B3LYP method at the 6-31++G(d,p) level (2.676 Å). In addition, it is very interesting to note that the interaction distances between O of water molecule and the H atom of the methyl group are almost the same: 2.676 and 2.677 Å for the B3LYP/6-31++G-(d,p) and B3LYP/6-311++G(d,p) levels. For A1, except for the results at the 6-31G and 6-31G(d) levels, we almost get the same value, which should be attributed to the lack of polarization and diffuse functions at the two basis levels. As we can see from Table 3, the differences between A1 and A2 brought by the variation of methods are negligible, especially for those at high basis levels.

AW3, which is very similar to AW4, exhibits a cyclic conformation, in which water forms a hydrogen bond to the carbonyl oxygen and receives a hydrogen bond from the amide hydrogen. For AW3, the length of R_{OA-HW} (the hydrogen bond between the oxygen of alanine and a hydrogen of water) is 1.935, 1.944, and 1.950 Å at the B3LYP/6-31+G(d), B3LYP/6-31++G(d,p), and B3LYP/6-311++G(d,p) levels, but at the 6-31++G(d,p) level the MP2 method yields a longer bond distance (2.035 Å). The R_{OW-HA} is 2.282, 2.282, and 2.283 Å, respectively, by the B3LYP method at those three basis sets motioned above, which are all longer than the result of the MP2 method (2.200 Å). The Hartree−Fock method gives longer hydrogen bonds of 2.060 and 2.478 Å. Furthermore, the cyclic arrangement results in more bent hydrogen bonds, the deformation from linearity being 22.5° (30.4°) for the OH⋯O hydrogen bond and 40.8° (35.6°) for the NH⋯O one at the B3LYP/6-31++G(d,p) (MP2/6-31++G(d,p)) level.

In AW4, R_{OA-HW} (the hydrogen bond distance between the oxygen of alanine and a hydrogen of water) is 1.916, 1.917, and 1.825 Å for the B3LYP/6-31+G(d), B3LYP/6-31++G(d,p), and B3LYP/6-311++G(d,p) levels; the R_{OW-HA} is 2.157, 2.183, and 2.187 Å, respectively. While at the MP2/6-31++G(d,p) level the lengths of the two bonds are 2.035 and 2.171 Å, respectively, the Hartree−Fock method gives longer hydrogen bonds of 2.059 and 2.341 Å. The reason the Hartree−Fock method gives longer hydrogen bonds is that it neglects dispersion energy. Furthermore, the cyclic arrangement results in more bent

TABLE 2: Structural Parameters Calculated for Alanine and Water Monomers (Distances in Angstroms, Angles in Degrees)

parameters	B3LYP/ 6-311++G(2d,2p)	B3LYP/ 6-311++G(d,p)	B3LYP/ 6-31++G(d,p)	HF/ 6-31++G(d,p)	MP2/ 6-31++G(d,p)
			Alanine		
R_{N-C1}	1.454	1.454	1.455	1.440	1.453
R_{NH1}	1.012	1.015	1.016	1.001	1.016
R_{NH2}	1.013	1.015	1.017	1.001	1.017
R_{C1C2}	1.528	1.531	1.532	1.523	1.532
R_{C1C3}	1.535	1.537	1.538	1.533	1.532
R_{CH3}	1.091	1.094	1.096	1.087	1.095
$R_{O1=C2}$	1.205	1.205	1.213	1.189	1.211
$R_{O2=C2}$	1.356	1.356	1.356	1.330	1.358
R_{CH4}	1.089	1.091	1.093	1.084	1.091
R_{CH5}	1.091	1.094	1.096	1.087	1.095
R_{CH6}	1.088	1.091	1.092	1.082	1.091
R_{O-H7}	0.968	0.969	0.972	0.949	0.968
∠H1NC1	110.7	110.9	110.9	111.5	110.2
∠H2NC1	110.0	110.2	110.0	111.0	109.1
∠C1C2N	113.5	113.6	113.5	113.3	113.7
∠C3C1N	110.2	110.2	110.2	110.2	109.6
∠H3C1N1	108.4	108.3	108.3	108.5	108.6
∠O1C2C1	125.4	125.5	125.5	125.4	125.4
∠O2C2C1	112.0	111.8	112.1	112.3	111.4
∠H4C3C1	111.3	111.3	111.3	111.3	111.1
∠H5C3C1	110.0	110.4	110.5	110.6	110.0
∠H6C3C1	109.1	109.1	109.0	108.9	109.0
∠H7O3C1	107.1	107.4	107.4	109.1	106.1
$D_{H2NC1H1}$	116.8	117.5	117.5	119.1	115.9
$D_{C2C1NH1}$	−61.6	−61.1	−61.3	−61.1	−57.9
$D_{C3C1NC2}$	−122.8	−122.9	−123.0	−123.2	−121.4
$D_{H3C1NC2}$	118.7	118.6	118.5	118.2	119.6
$D_{O1C2C1N}$	−20.3	−18.6	−18.8.	−14.4	−20.1
$D_{O2C2C1O1}$	−179.2	−179.1	−179.2	−179.5	−178.3
$D_{H4C3C1N}$	−178.1	−177.5	−177.5	−178.4	−176.8
$D_{H5C3C4H4}$	−120.5	−120.5	−120.5	−120.7	−120.4
$D_{H6C3C1H4}$	120.6	120.6	120.6	120.3	120.7
$D_{H7O2C2C1}$	178.1	178.1	178.2	178.8	177.0
			Water		
R_{O-H}	0.961	0.962	0.965	0.943	0.963
∠HOH	105.1	105.1	105.1	105.1	105.1

hydrogen bonds again, the deformationa from linearity being 28.2° and 27.3° for the OH···O hydrogen bond, while they are 28.4° and 32.9° for the NH···O bond at the B3LYP/6-311++G(d,p) and MP2/6-31++G(d,p) levels, respectively.

The main difference between AW5 and AW6 is the direction of the O−H bond in the water molecule. AW5 also shows a cyclic conformation, water accepting a proton from the methyl group while donating a proton to the hydroxyl group. We cannot get this conformation by using HF and MP2 methods, while in both calculations the same configuration as that of AW7 is achieved. In AW5, the B3LYP/6-311++G(d,p) calculations, which yield the O_W-H_A bond distance of 2.650 Å and O_A-H_W distance of 2.019 Å, are in excellent agreement with the values (2.643 and 2.021 Å) at the B3LYP/6-31++G(d,p) level. The bond angle of $O_WH_WO_A$ is 164.0° and 147.1°, while $O_WH_WO_A$ is 149.2° and 163.2°, respectively. For AW6, we can get this conformation only at the B3LYP/6-31G and B3LYP/6-31G(d) levels, and at other basis levels we get the same configuration as that of AW5.

The main difference between AW7 and AW8 is the direction of the O−H bond in the water molecule, which is very similar to that in AW6: for AW8 we can get this conformation only at the B3LYP/6-31G and B3LYP/6-31G(d) levels, and at other basis levels the same configurations as that of AW7 are achieved. In AW7, the alanine accepts a proton from one hydrogen atom of a water molecule. It is very interesting to note that the B3LYP/6-311++G(d,p) calculations, which yield the O_W-H_A bond length of 2.561 Å and the O_A-H_W bond length of 2.049 Å, are in good agreement with the B3LYP/6-31+G(d) values of 2.570 and 2.030 Å. But for the two bonds, the MP2 method yields longer lengths: 2.690 and 2.201 Å. As we can see from Table 6, for the B3LYP method at the 6-311++G(d,p), 6-31++G(d,p), and 6-31+G(d) levels, there exists little difference among the values of the $C_AH_AO_W$ and $O_WH_WO_A$. And as expected, the HF method does not yield desirable results compared with MP2 method results.

3.3. Interaction Energies. Interaction energies are calculated for the alanine−water hydrogen bond by taking the energy difference between the fragments and the complex:

$$E_{\text{int}} = E_{\text{alanine-water}} - E_{\text{alanine}} - E_{\text{water}} \qquad (1)$$

where E_{alanine}, E_{water}, and $E_{\text{alanine-water}}$ are the electronic energies of alanine, water, and the complex system, respectively. To correct for the BSSE, the counterpoise (CP) method[8] is employed. In this case, the corrected E_{int} is given by

$$E_{\text{int(cp)}} = E_{\text{alanine-water}} - E_{\text{alanine(cp)}} - E_{\text{water(cp)}} \qquad (2)$$

where $E_{\text{alanine(cp)}}$ and $E_{\text{water(cp)}}$ are computed with the basis set of the complex alanine−water. Moreover, the ZPVE corrections are also applied in the present case.

To analyze in more detail the role of basis set size effects on the binding energy between alanine and water, Table 7 gives a detailed analysis of the binding energy obtained with several different theoretical models. The numbers shown in parentheses are corrected for BSSE using the counterpoise method of Boys and Bernadi.[8] As expected, basis set sensitivity exists. The

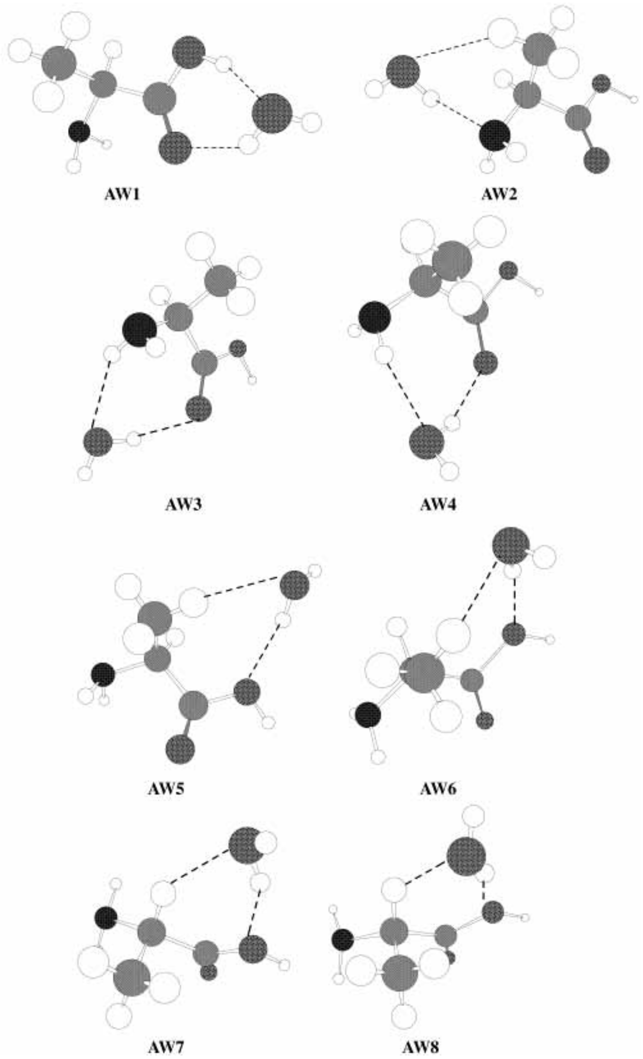

Figure 2. Optimized alanine−water complexes in the gas phase.

interaction energy computed with B3LYP using the minimal basis set 6-31G is much higher. As the basis set is enlarged, the computed values decrease and converge smoothly. Most of the ZPVE corrected energies are smaller than the uncorrected and the BSSE-corrected ones at the same level of the theory. This is because the interaction energy of the complex becomes more repulsive after the correction than the uncorrected or corrected with the CP method. Moreover, the ZPVE correction is not sensitive to the basis sets. The general importance of including BSSE corrections in calculated binding energies has been well documented in the literature. From the Table 7 it can be seen that the magnitude of BSSE decreases as the basis set is enlarged, when the diffusion and polarization functions are considered: especially for the 6-311++G(d,p) and 6-31++G(d,p) basis sets using the B3LYP method, the inclusion of BSSE correction has minor importance to the binding energy. This was also true for the MP2 and HF/6-31++G(d,p) levels.

From the values in Table 7, it can be seen that the relative stability order of the eight structures is AW1 > AW2 > AW4 > AW3 > AW7 > AW5 > AW6 > AW8. However, it is very surprising that the stability of AW2 and AW4 is reversed at the two little basis set levels of the DFT method and the HF method. It is hard to find the reason for this result, and this may be due to fortune. Here, we focus on the results of the large basis sets. It is easy to understand the stability of AW1, which derives from the formation of a pair of hydrogen bonds between the alanine and water molecules, due to the strongest interaction (the shortest hydrogen bond distance). For the same reason, the instability of AW8 is linked to the weakest interaction, though it is also a cyclic structure. For other structures, we can also estimate the stability relative to the interaction energy and the interaction distance.

The interaction energies calculated by using the MP2 method are higher than those obtained by the B3LYP method in all the complexes. And it is very interesting to find that the energy difference maybe determined by the relative stability of the complexes. For example, for AW1, which is the most stable complex among AW1, AW2, AW3, AW4, and AW7, the difference in the interaction energies found by the two different theoretical models using the same basis set (6-31++G(d,p)) is only about 2.4 kJ/mol. For AW7, which is the most unstable of the five complexes, the difference is about 6.7 kJ/mol.

Finally, one additional point is worthy of being mentioned concerning the ZPVE corrections of water−alanine complexes. Due to the restriction of the EMS memory of our computers, the ZPVE corrections of the MP2 method cannot be carried out.

3.4. Infrared Spectrum. Vibrational spectroscopy is one of the most useful experimental tools to study of the H-bonded clusters, so the information on calculated harmonic vibrational frequencies can be useful. In Table 8, we give the B3LYP/6-311++G(d,p) values for both vibrational frequencies and IR intensities of the six complexes (values of AW6 and AW8 are not listed in it) and monomers. Since the frequency shifts are relatively stable with respect to theoretical methods, we can estimate the IR spectrum for the complex by combining the observed fundamental vibrational frequency of its moieties and the frequency shift in Table 8.

The O2−H4 stretch frequencies are found to decrease for all structures except AW1 considered here (255, 252, 246, 245, and 243 cm^{-1}, respectively), which is mainly because of the formation of the cyclic structure of AW1. But the stretch frequencies of the NH_2 symmetrical stretch mode and the NH_2 asymmetrical stretch mode in all six complexes are decreased. The CCO bend in-plane mode frequency also shows a slight change in its value on hydrogen bonding. For instance, in AW1, there is a weak interaction between the H of H_2O and O of the carbonyl group—the shift is 158 cm^{-1}, but in other complexes there does not exist such a shift. The O−H4 rock in-plane frequency is found to be blue-shifted, and the maximum increase is observed for AW1 (45 cm^{-1}), corresponding to the strongest interaction. It is noteworthy that the C3−O1 stretch stretching frequency is red-shifted due to formation of the hydrogen bond, which weakens the C═O bond. For example, in AW1, AW3, and AW4, because the hydrogen bond between H of H_2O and O of the carbonyl group forms, the C═O stretching frequency is red-shifted by 38, 20, and 19 cm^{-1}, respectively. For the modes of water in the complex, like that of alanine, the stretching frequency associated with the hydrogen bond undergoes a shift to a lower frequency compared to the free monomer. For instance, it is very similar to the NH_2 stretch mode in that the frequencies of the H_2O symmetrical stretch mode and H_2O asymmetrical stretch mode are all decreased in all structures. This may be due to formation of the hydrogen bond weakening the O−H bond.

With respect to IR intensities, these complexes are all IR-active and most of them have large intensities. These predicted IR spectral characteristics might be of great interest in the analysis of the experimental spectral features. It is considerably more difficult to predict accurate shifts in absorption intensities, which is unfortunate. For in this system, there is an extremely

TABLE 3: Optimized Geometric Parameters of AW1 and AW2 Using Different Theoretical Models (Distances in Angstroms, Angles in Degrees)[a]

		B3LYP/ 6-31G	B3LYP/ 6-31G(d)	B3LYP/ 6-31+G(d)	B3LYP/ 6-31++G(d,p)	B3LYP/ 6-311++G(d,p)	MP2/ 6-31++G(d,p)	HF/ 6-31++G(d,p)
AW1	R_{OW-HA}	1.619	1.744	1.787	1.781	1.799	1.805	1.931
	R_{OA-HW}	1.882	1.923	1.980	1.980	1.939	2.049	2.181
	A1	157.6	152.1	156.3	156.2	156.2	157.4	156.6
	A2	140.5	134.3	136.0	135.6	134.7	132.3	128.6
AW2	R_{HW-NA}	1.825	1.944	1.919	1.913	1.939	1.931	2.094
	R_{OW-HA}	2.482	2.411	2.698	2.676	2.677	2.572	2.874
	A1	136.4	133.8	130.7	130.5	131.1	131.4	131.6
	A2	165.3	165.5	165.2	164.3	164.2	163.6	165.5

[a] OW−HA means O of water hydrogen-bonded to H of alanine, and OA−HW means O of alanine hydrogen-bonded to H of water. In AW1, A1 is $O_WH_WO_A$, and A2 is $O_AH_AO_W$. In AW2, A1 is $C_AH_AO_W$, and A2 is $O_WH_WN_A$.

TABLE 4: Optimized Geometric Parameters of AW3 and AW4 Using Different Theoretical Models (Distance in Angstroms, Angles in Degrees)[a]

		B3LYP/ 6-31G	B3LYP/ 6-31G(d)	B3LYP/ 6-31+G(d)	B3LYP/ 6-31++G(d,p)	B3LYP/ 6-311++G(d,p)	MP2/ 6-31++G(d,p)	HF/ 6-31++G(d,p)
AW3	R_{OW-HA}	1.937	2.131	2.282	2.280	2.283	2.200	2.478
	R_{OA-HW}	1.862	1.948	1.935	1.944	1.950	2.035	2.060
	A1	146.3	152.0	135.5	137.2	138.2	144.4	134.4
	A2	156.4	157.3	158.9	158.5	158.5	149.6	157.0
AW4	R_{OW-HA}	2.082	1.962	2.157	2.183	2.187	2.171	2.341
	R_{OA-HW}	1.914	1.838	1.916	1.917	1.825	1.990	2.059
	A1	159.0	147.9	151.0	153.8	151.8	152.7	151.0
	A2	160.3	156.9	158.6	156.2	151.6	147.1	158.6

[a] OW−HA means O of water hydrogen-bonded to H of alanine, and OA−HW means O of alanine hydrogen-bonded to H of water. A1 is $N_AH_AO_W$, and A2 is $O_WH_WO_A$.

TABLE 5: Optimized Geometric Parameters of AW5 and AW6 Using Different Theoretical Models (Distances in Angstroms, Angles in Degrees)[a]

		B3LYP/ 6-31G	B3LYP/ 6-31G(d)	B3LYP/ 6-31+G(d)	B3LYP/ 6-31++G(d,p)	B3LYP/ 6-311++G(d,p)
AW5	R_{OW-HA}	2.384	2.462	2.707	2.643	2.650
	R_{OA-HW}	1.893	2.029	2.001	2.021	2.019
	A1	160.4	157.8	145.3	147.1	149.2
	A2	169.6	170.6	166.0	163.2	164.0
AW6	R_{HW-NA}	2.402	2.458			
	R_{OW-HA}	1.906	2.044			
	A1	156.0	170.3			
	A2	167.6	165.9			

[a] OW−HA means O of water hydrogen-bonded to H of alanine, and OA−HW means O of alanine hydrogen-bonded to H of water. A1 is $O_WH_WO_A$, and A2 is $C_AH_AO_W$. MP2 and HF methods were not used.

TABLE 6: Optimized Geometric Parameters of AW7 and AW8 Using Different Theoretical Models (Distances in Angstroms, Angles in Degrees)[a]

		B3LYP/ 6-31G	B3LYP/ 6-31G(d)	B3LYP/ 6-31+G(d)	B3LYP/ 6-31++G(d,p)	B3LYP/ 6-311++G(d,p)	MP2/ 6-31++G(d,p)	HF/ 6-31++G(d,p)
AW7	R_{OW-HA}	2.364	2.460	2.570	2.531	2.561	2.412	2.690
	R_{OA-HW}	1.902	2.047	2.030	2.057	2.049	2.062	2.201
	A1	143.6	137.5	142.2	142.3	142.2	142.6	138.8
	A2	156.8	157.6	153.6	153.4	153.6	147.5	151.1
AW8	R_{HW-NA}	2.536	2.506					
	R_{OW-HA}	1.886	2.046					
	A1	123.1	135.6					
	A2	158.9	155.4					

[a] OW−HA means O of water hydrogen-bonded to H of alanine, and OA−HW means O of alanine hydrogen-bonded to H of water. A1 is $C_AH_AO_W$, and A2 is $O_WH_WO_A$.

large increase in the intensity of the stretching vibration of the hydrogen donor. From the results presented in Table 8, it can be seen that the N−H and O−H stretching intensities involved in the hydrogen bonds are enhanced largely in both hydrogen complexes. For example, the OH stretching intensities of alanine monomer varied from 2 to 647 km/mol for AW1, approximately 324 times that of the mode in the monomer. Moreover, for water monomer, it is noteworthy that the intensities of the H_2O symmetrical stretch changed from 9 to 313, 653, 294, 335, 162, and 112 km/mol for complexes AW1, AW2, AW3, AW4, AW5, and AW7, at least 10 times that of the mode in the monomer. The NH_2 symmetrical stretch intensities changed from 4 to 34, 23, and 40 km/mol for AW2, AW3, and AW4, respectively. For the CC, CN, and CO stretching modes, the IR intensities are similar to those of the isolated monomer. For the other bending modes, most of them are slightly enhanced. In a word, owing to the formation of the hydrogen bond, the force constants involved in the hydrogen bonding is reduced and the related

TABLE 7: Interaction Energies of Alanine−Water Complexes Using Different Theoretical Models (kJ/mol)[a]

method	AW1	AW2	AW3	AW4	AW5	AW6	AW7	AW8
B3LYP/6-31G	−78.3	−49.2	−47.2	−52.3	−30.9	31.9	−31.9	−30.4
	(−69.9)	(−38.1)	(−14.9)	(−40.6)	(−18.5)	(19.5)	(−19.5)	(−18.3)
ZPVE corrected	−45.9	−37.7	−37.0	−41.3	−22.3	23.8	−23.8	−22.9
B3LYP/6-31G(d)	−63.3	−40.1	−36.6	−40.1	−22.9	23.3	−23.3	−21.9
	(−49.4)	(−28.1)	(−23.7)	(−26.7)	(−10.9)	(11.5)	(−11.5)	(−10.1)
ZPVE corrected	−51.7	−29.7	−27.0	−29.7	−15.4	16.0	−16.0	−15.1
B3LYP/6-31+G(d)	−46.6	−33.1	−26.8	−29.8	−14.6		−15.2	
	(−43.9)	(−30.2)	(−25.2)	(−28.1)	(−12.3)		(−12.7)	
ZPVE corrected	−28.3	−24.1	−18.8	−20.7	−8.6		−9.2	
B3LYP/6-31++G(d,p)	−44.	−32.1	−25.8	−28.7	−13.7		−14.5	
	(−43.6)	(−30.1)	(−25.1)	(−28.0)	(−12.3)		(−12.3)	
ZPVE corrected	−34.5	−23.1	−18.1	−19.8	−7.7		−8.5	
B3LYP/6-311++G(d,p)	−42.9	−30.4	−24.8	−27.3	−13.7		−14.4	
	(−13.9)	(−29.1)	(−24.6)	(−27.1)	(−12.6)		(−13.1)	
ZPVE corrected	−33.1	−21.6	−17.2	−19.0	−7.6		−8.29	
HF/6-31++G(d,p)	−36.4	−23.7	−22.6	−24.1			−11.	
	(−39.1)	(−28.6)	(−22.8)	(−13.1)			(−25.0)	
ZPVE corrected	−27.3	−15.2	−5.9	−16.3			−5.8	
MP2/6-31++G(d,p)	−46.9	−36.8	−30.3	−33.8			−21.2	
	(−35.7)	(−28.6)	(−21.2)	(−23.4)			(−8.5)	

[a] Values in parentheses are results with correction for basis set superposition error.

TABLE 8: Frequencies and IR Intensities of Monomers and Complexes at the B3LYP/6-311++G(d,p) Level (Vibrational Frequencies (v) in cm^{-1}, IR Intensities (I) in km/mol)

	B3LYP/ 6-311++G(d,p)		AW1		AW2		AW3		AW4		AW5		AW7		
exptl[21]	v	I	v	I	v	I	v	I	v	I	v	I	v	I	assignment
no	48	2	42	1	44	2	50	2	39	2	46	12	32	1	COO bend out of plane
no	215	41	210	57	251	10	272	50	295	47	224	37	219	36	NH_2 bend out of plane
no	228	3	233	33	233	0	223	0	228	2	232	9	232	11	CH_3 rock in plane
no	239	2	266	9	317	2	255	8	233	1	237	21	238	5	CCC bend in plane
no	301	8	389	18	391	7	313	8	304	16	299	11	302	26	CCN bend out of plane
no	377	14	514	15	501	11	402	36	370	27	376	6	376	15	CCN bend in plane
493	495	17	653	18	no	no	495	20	504	21	529	69	501	29	CCO bend in plane
580	594	102	no	no	595	87	587	95	610	112	605	109	596	146	C−H4 rock out of plane
623	635	12	745	6	750	9	636	30	656	16	638	16	634	10	OCO bend in plane
741	752	32	no	no	802	28	742	36	765	37	753	30	754	34	OCO bend out of plane
805	788	35	812	44	no	no	793	34	789	29	785	36	784	28	CH_2 bend out of plane
852	884	146	882	138	960	142	890	35	883	172	877	149	872	152	NH_2 rock out of plane
925	923	1	926	2	924	1	929	14	922	5	925	1	921	1	C1−C2 stretch
1037	1018	2	1016	1	1026	3	1021	2	1025	7	1020	3	1021	3	CH_3 rock out of plane
1064	1082	28	1084	31	1096	39	1078	28	1080	29	1080	37	1082	68	CH_3 rock out of plane
1117	1126	293	1156	48	1129	268	1139	265	1140	264	1165	11	1166	9	C1−N stretch
1153	1168	20	1217	217	1171	50	1217	24	1171	38	1110	366	1107	304	C3−O2 stretch
1215	1274	1	1278	12	1274	2	1274	1	1281	1	1274	2	1274	2	NH_2 bend out of plane
no	1291	2	1329	30	1295	5	1300	6	1295	1	1291	1	1295	1	C2−H3 rock in plane
1368	1351	18	1396	1	1357	19	1350	14	1358	14	1344	11	1349	11	O2−H4 rock in plane
1386	1399	2	1404	2	1421	8	1394	1	1399	3	1402	1	1404	4	CH_3 bend out of plane
1408	1416	8	1444	5	1403	1	1413	6	1419	11	1419	9	1428	7	C2−H3 bend out of plane
1454	1494	8	1495	10	1499	5	1495	8	1492	7	1498	5	1494	7	CH_3 bend in plane
1460	1500	8	1500	9	1504	10	1502	8	1501	9	1501	9	1500	9	CH_3 bend in plane
1642	1674	27	1671	25	1668	27	1681	29	1683	29	1671	29	1671	29	NH_2 bend in plane
1774	1800	316	1762	281	1806	319	1780	390	1781	369	1820	320	1820	318	C3−O1 stretch
no	3033	13	3033	13	3032	13	3035	25	3036	13	3034	10	3034	17	CH_3 sym stretch
2886	3052	13	3052	13	3056	8	3024	5	3052	14	3051	18	3067	1	C1−H3 stretch
2940	3104	22	3104	22	3107	15	3105	20	3107	22	3107	15	3104	19	CH_3 asym stretch
2999	3125	12	3126	13	3132	4	3133	11	3122	12	3130	5	3125	12	H5−C3−H7 asym stretch
no	3498	2	3406	647	3753	68	3750	58	3744	55	3743	80	3745	81	O2−H4 stretch
no	3572	4	3497	1	3486	34	3502	23	3488	40	3500	2	3501	2	NH_2 sym stretch
3560	3751	58	3570	4	3556	7	3575	21	3577	21	3575	5	3577	5	NH_2 asym stretch
Water															
1649	1603	66	1602	147	1643	46	1615	75	1612	76	1606	43	1610	58	H_2O bend in plane
3832	3816	9	3656	313	3515	653	3704	294	3682	335	3764	162	3765	112	H_2O sym stretch
3942	3921	56	3889	98	3887	63	3895	94	3895	89	3898	129	3901	119	H_2O asym stretch

stretching frequencies are red-shifted. At the same time, increasing the vibrational dipole moments results in the enhancement of the IR intensities.

3.5. Solution Phase Results. The interaction of water with alanine has also been studied in the solution phase using density functional theory. All calculations for the solution phase work have been carried out at the B3LYP/6-311++G(d,p) level of theory. The Onsager reaction field model has been used to treat solvent effects. We have investigated the effect of varying the dielectric constant on the energies and geometries of the

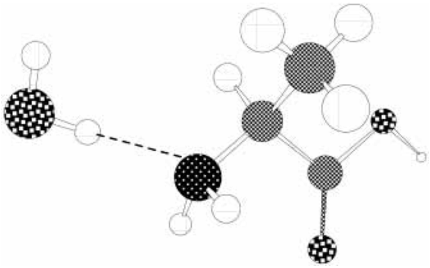

Figure 3. Optimized conformation of AW2 in acetone, dimethyl sulfoxide, and water.

TABLE 9: Optimized Geometric Parameters of AW1, AW2, AW3, AW4, AW5, and AW7 in Solutions Calculated at the B3LYP/6-311++G(d,p) Level (Distances in Angstroms, Angles in Degrees)[a]

complex		in gas	in cyclohexane (2.023)	in acetone (20.7)	in dimethyl sulfoxide (46.7)	in water (78.39)
AW1	R_{OW-HA}	1.799	1.790	1.768	1.766	1.772
	R_{OA-HW}	1.939	2.021	2.077	2.084	2.064
	A1	156.2	156.6	157.6	157.8	157.5
	A2	134.7	133.3	129.9	129.4	130.6
AW2	R_{HW-NA}	1.939	1.932	1.926	1.924	1.923
	R_{OW-HA}	2.677	2.709			
	A1	131.1	131.4			
	A2	164.2	167.3	175.0	175.3	175.3
AW3	R_{OW-HA}	2.283	2.320	2.380	2.386	2.388
	R_{OA-HW}	1.950	1.932	1.913	1.912	1.911
	A1	138.2	137.8	138.5	138.3	138.3
	A2	158.5	161.8	164.2	164.3	164.4
AW4	R_{OW-HA}	2.187	2.215	2.278	2.285	2.286
	R_{HW-OA}	1.825	1.918	1.898	1.898	1.896
	A1	151.8	151.0	149.5	149.4	149.4
	A2	151.6	158.6	164.6	164.9	165.0
AW5	R_{OW-HA}	2.650	2.649			
	R_{OA-HW}	2.019	2.028			
	A1	149.2	138.7			
	A2	164.0	160.9			
AW7	R_{OW-HA}	2.561	2.518	2.462	2.458	2.436
	R_{OA-HW}	2.049	2.069	2.104	2.107	2.064
	A1	142.2	142.9	144.4	144.5	144.5
	A2	153.6	150.6	146.6	146.2	146.1

[a] OW−HA means O of water hydrogen-bonded to H of alanine, and OA−HW means O of alanine hydrogen-bonded to H of water. A1 and A2 in all the complexes are the same as those in the gas phase.

alanine−water interaction. In this work, we focus on results obtained using water as the solvent, with a dielectric constant of 78.39.

The optimized structures of complexes in the solution phase are very similar to those in the gas phase, except for AW2 and AW5. In our optimization, we cannot achieve the same configuration of AW5 as that in gas phase. And it seems that in the liquid phase AW7 is more stable than AW5. Except in cyclohexane, we get the same configuration as that of AW7. The structure of AW2 in water is presented in Figure 3. The most interesting geometrical parameters of all the structures optimized in solution are listed in Table 9, and for comparison the values calculated at the B3LYP/6-311++G(d,p) level are also presented. From the calculations it can be concluded that the solvent can appreciably modify the geometries of hydrogen-bonded systems.

With respect to AW1, the first thing to note is the change of the length of the R_{OW-HA} bond (gas phase, 1.799 Å; solution phase, 1.790, 1.768, 1.766, and 1.772 Å), and it is obvious that with the increment of the dielectric constant, the length of this bond is decreased. However, another hydrogen bond, R_{OA-HW}, is elongated (gas phase, 1.939 Å; solution phase, 2.021, 2.077, 2.084, and 2.064 Å). There is little difference between the values of the bond angle of $C_AH_AO_W$ in the gas phase and in solutions.

TABLE 10: Interaction Energies of Alanine−Water Complexes in Solutions (kJ/mol)[a]

solvent	ϵ	AW1	AW2	AW3	AW4	AW5	AW7
in gas		−42.9	−30.4	−24.8	−27.3	−27.3	−14.4
		(−13.9)	(−29.1)	(−24.6)	(−27.1)	(−27.1)	(−13.1)
		−33.1	−21.6	−17.2	−19.0	−19.0	−8.29
cyclohexane	(2.023)	−40.0	−27.6	−23.1	−25.6	−25.6	−12.3
		(−39.7)	(−26.5)	(−23.0)	(−25.3)	(−25.3)	(−11.1)
		−30.4	−19.1	−15.2	−17.2	−17.2	−6.1
acetone	(20.7)	−36.2	−27.2	−21.3	−23.8		−9.4
		(−36.4)	(−28.2)	(−21.4)	(−24.5)		(−8.7)
		−26.8	−18.8	−13.2	−15.3		−3.3
dimethyl sulfoxide	(46.7)	−36.0	−27.5	−21.3	−23.8		−9.4
		(−36.2)	(−28.5)	(−21.3)	(−23.5)		(−8.5)
		−26.6	−18.9	−13.1	−15.2		−3.1
water	(78.39)	−35.6	−27.5	−21.2	−23.8		−9.3
		(−35.7)	(−28.7)	(−21.3)	(−23.4)		(−8.5)
		−26.1	−18.9	−13.0	−15.1		−3.0

[a] Values in parentheses are results with correction for basis set superposition error.

For AW2, the most dramatic changes induced by the solvent on the geometry are observed: in acetone, dimethyl sulfoxide, and water AW2 is transformed to a single hydrogen bond structure, while in cyclohexane it still exists as in the gas phase. In AW2, the orientation of the water molecule is inverted (compare Figure 1 with Figure 3). In solution, the water dipole moment points in the same direction as the C−N bond, while in the gas phase, the dipole moment points in the opposite direction. The changes can be understood by considering the modification of the solvation energy with the complex's geometry. The dipole moments of the complex in water solution and in the gas phase are 5.4923 and 1.708 D, respectively. Such a large variation in the dipole moment produces a large change in the solute−solvent interaction energy that favors the aligned configuration. For the bond length R_{HW-NA} and the bond angle $O_WH_WN_A$, in the three solutions almost the same values are observed, and obviously there is little effect caused by the variations of the dielectric.

With respect to AW3, the major discrepancy between the gas and water phases is that the R_{OW-HA} distance has been increased by 0.104 Å. At the same time, R_{OA-HW} is decreased from 1.950 to 1.911 Å. Other geometric parameters are similar to each other.

For AW4, R_{HW-OA} is increased by 0.071 Å in water solution compared to the gas-phase value. Moreover, the angle $O_WH_WO_A$ varies from 151.6° to 165.0°. But the change of R_{OW-HA} and the angle of $N_AH_AO_W$ are not obvious.

As we have discussed before, for AW5 we get the same configuration as that of AW7 in all solutions except in cyclohexane. And for this structure, comparing the parameters in cyclohexane with those in the gas phase, it can be found that the differences are negligible, so we will not discuss it any more.

For AW7, the most distinct change is the shortening of the bond length R_{OW-HA} from 2.561 Å in the gas phase to 2.436 Å in water solution. But for another hydrogen bond, there is no obvious change; it is very similar to other complexes. The changes of the bond angle are also negligible.

A summary of the relative energies of the four structures in solution is presented in Table 10. The energies are measured relative to the energies of separated alanine and water in solution and including BSSE corrections. Moreover, the ZPVE corrections are also applied in Table 10.

The binding energies in various solvents of AW1, AW2, AW3, AW4, AW5, and AW7 as a function of dielectric constant

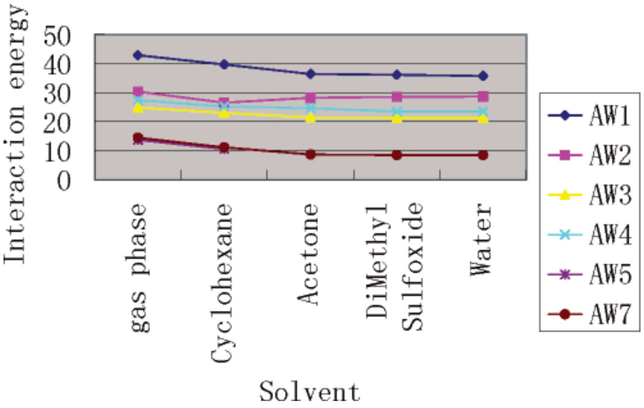

Figure 4. Variation of the interaction energies of AW1, AW2, AW3, AW4, AW5, and AW7 with dielectric constant.

are shown in Figure 4. From Figure 4, it can be seen that the general trend is that the binding energies decreases as the polarity of the solvent increases. And we can see from Figure 4 that in all the solvents considered here, AW1 is more stable than the others.

From Table 10 it can be found that an obvious influence of solvent polarization on interaction energies is observed. The magnitude of the solvent effect is not constant across the whole potential surface and can produce a bias for particular geometric conformations. This fact can modify for instance, the relative ability of the carbonyl vs the amide group to hydrogen bond to alanine. However, it appears certain that the solvent effect did not change the relative ability of the carbonyl vs the amide group to hydrogen bond to alanine. The energy difference between AW1 and AW2 in water solution is still about 8.1 kJ/mol, which indicates that bonding to the carbonyl group is still a little energetically favorable over binding to the amide group in solution. In addition, from the values of Table 10 it can be seen that the BSSE energies are very near to the uncorrected energies. Moreover, the stability order of different conformations does not change compared with that in the gas phase, even if the ZPVE corrections are considered.

4. Conclusions

The hydrogen-bonding interaction of the 1:1 complex between alanine and water has been analyzed by ab initio, MP2, and B3LYP methods employing different basis set levels. Eight structures are considered, and six of them are discussed in detail. In all of the eight structures, AW1 is the most stable at all levels, and AW8 is the most unstable due to its having the weakest interaction. For the other complexes, their stabilities depend on the interaction distance between alanine and water. Moreover, the infrared spectrum frequencies, IR intensities, and vibrational frequency shifts are reported. We found that the stretching frequency associated with the hydrogen bond undergoes a shift to a lower frequency compared to that for the free monomer, and there is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor.

Finally, a study of the solvent effect on the potential energy surface of the water−alanine complex has been performed. In the description of solvent we have employed the Onsager reaction field model. The calculations are done at the B3LYP/6-311++G(d,p) level. We found that the geometry of the system is appreciably modified by the solvent.

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