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Density Functional Theory Study of the Hydrogen Bonding Interaction of 1:1 Complexes of Formamide with Glycine

Yun Shi, Zheng-yu Zhou,* and Hai-tao Zhang

Department of Chemistry, Qufu Normal University, Qufu 273165, P. R. China, and
State Key Laboratory Crystal Materials, Shandong University, Jinan 250100, P. R. China

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The hydrogen bonding of 1:1 complexes formed between formamide and glycine molecule has been completely investigated in the present study using density functional theory (DFT) method at varied basis set levels from 6-31G to 6-311++G(2d,2p). Twelve reasonable geometries on the potential energy hypersurface of formamide and glycine system are considered with the global minimum, 10 of which have a cyclic double-hydrogen-bonded structure and the other two have a one-hydrogen-bonded structure. The optimized geometric parameters and interaction energies for various isomers at different levels are estimated. The infrared spectrum frequencies, IR intensities and the vibrational frequency shifts are reported.

I. Introduction

The importance of the amide functional group is demonstrated by the fact that the amide peptide bond is the basic linkage in peptides and proteins. The geometric constraints of the amide bond, such as the nearly planar structure around the C−N bond because of its partial double-bond character, define the conformational freedom of motion for many small molecules as well as for peptides and proteins. Formamide is one of the simplest molecules usually chosen as a model for studying biological systems exhibiting the peptide type of bonding and DNA structures. Since formamide complexes such as formamide−water and formamide−methanol can serve as model systems for protein−water and protein−solvent interactions, numerous experimental and theoretical studies have been reported.[1−12] The characterization of the hydrogen-bonding interaction between formamide and water has been well studied by many theoretical calculations,[1−12] while in the case of formamide−glycine complex there are few investigations. In addition, glycine is the simplest amino acid; therefore, investigation of the hydrogen-bonding interaction between formamide and glycine must be very useful to study biological systems exhibiting the peptide type of bonding and DNA structures.

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 MP2 methods.[13−15] 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 access the reliability of DFT methods applied to this field of chemistry, in this paper, we discuss the structure and bonding of the formamide−glycine complex as obtained by high-level ab initio calculations. We thus report geometry optimization and calculated bonding energies between formamide and glycine for a variety of theoretical models and basis sets. The roles of basis set size and basis set superposition effects are analyzed in detail. In the present paper, we put forward what we believe are now the most accurate results for the hydrogen-bond interaction between formamide and glycine, as obtained from high-level calculations and systematic analysis of the theoretical results obtained.

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.

II. Computational Methods

It is well-known in the SCF model that the electrostatic, exchange, and some induction−polarization effects are included. In more recent years, it has been learned that the induced−induced dispersion interaction may be of great importance,[16,17] and it is therefore necessary to go beyond the SCF model and include some of the correlation effects. Thus, in the present paper, a variety of theoretical methods have been used in the research, including the Hartree−Fock (HF), the second-order Moller−Plesset theory (MP2), as well as the hybrid density functional methods B3LYP, in order to test the reliability of these methods in the study of the hydrogen-bonding systems.

The geometry optimization of the monomers (formamide and glycine) has been carried out using HF, MP2, and B3LYP correlation methods with the 6-31G, 6-31+G, 6-31+G(d), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets. For the geometry of the complexes of formamide and glycine, we only utilize the B3LYP method with the 6-31G, 6-31+G, 6-31+G(d), 6-311++G(d,p), and 6-311++G(2d,2p) basis sets along with analytic vibrational frequency calculations. In addition, the calculated binding energies and the zero-point vibrational energy (ZPVE) corrections obtained with all the above theoretical procedures are then corrected for the basis set superposition error (BSSE).[18] This is done using the counterpoise method.[19] All calculations are performed using the Gaussian 98 program.[20]

III. Results and Discussion

Structure of Formamide and Glycine Monomers. The structures of the super molecule will depend on the structures

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TABLE 1: Structural Parameters Calculated for Formamide and Glycine

parameters	B3LYP1[a]	B3LYP2[a]	HF[a]	MP2[a]	expt[a]
formamide					
R_{N-C}	1.361	1.358	1.349	1.364	1.352
R_{NH1}	1.007	1.004	0.991	1.006	1.002
R_{NH2}	1.009	1.006	0.994	1.009	1.002
R_{CH}	1.106	1.103	1.093	1.105	1.098
$R_{C=O}$	1.212	1.211	1.189	1.217	1.219
∠H1NC	119.4	119.4	119.4	119.2	118.5
∠H2NC	121.4	121.3	121.3	121.2	119.9
∠NCH	112.4	112.5	112.8	112.3	112.7
∠NCO	124.9	124.8	125.0	124.8	124.7
glycine					
R_{N-C}	1.448	1.448	1.437	1.449	1.469
R_{NH1}	1.014	1.013	1.010	1.015	1.014
R_{NH2}	1.014	1.013	1.010	1.015	1.014
R_{CC}	1.524	1.522	1.516	1.521	1.532
R_{CH1}	1.095	1.092	1.092	1.095	1.096
R_{CH2}	1.095	1.092	1.092	1.095	1.096
$R_{C=O}$	1.205	1.203	1.203	1.210	1.207
R_{C-O}	1.355	1.355	1.355	1.357	1.357
R_{O-H}	0.969	0.968	0.968	0.968	0.974

[a] Distances in angstroms; angles in degrees.

calculated for the formamide and glycine monomers. Despite the large number of experimental[21] and theoretical studies[22,23] of formamide, its structure has been controversial. The peptide moiety was assumed from the early work of Pauling and Corey to be planar, and more recently, however, the planarity of the peptide moiety has been questioned. Two early microwave studies[24,25] of formamide have reached different conclusions on the planarity of the peptide moiety. Since it is still unresolved whether formamide is planar, the potential energy surfaces of formamide are examined both in C_1 and C_s symmetry. Full geometry optimizations have been performed along with analytic vibrational frequency calculations in order to characterize the structures obtained as minima on the potential energy surface.

It is interesting to note the difference between the B3LYP, HF, and MP2 predictions about the NH_2 moiety in formamide molecule. B3LYP and SCF methods at all basis set levels indicate formamide to be planar (in C_s symmetry), and MP2/6-31G level support this view, while at other basis set levels we have mentioned, MP2 predict formamide to be nonplanar (in the case of C_s constrained symmetry, an imaginary vibrational frequency corresponding to NH_2 out-of-plane motion provides a signature that the species has a nonplanar equilibrium geometry). These results clearly indicate the planar structure of formamide is not a local minimum on the MP2 electronic energy surface. Thus, all of the results we examined have C_1 symmetry.

The calculated structures of formamide and glycine using the DFT method at 6-311++G(d,p) and 6-311++G(2d,2p) basis sets are presented in Table 1. For comparison, the results of MP2 and HF at 6-311++G(d,p) level and the experimentally determined structures are also given in Table 1. For simplicity, the results with 6-31G, 6-31G(d), and 6-31+G(d) are not listed.

A general observation from comparing the calculated and the experimental structural parameters is that all HF bond distances are slightly shorter than the experimental results. This may be due to the result of the neglect of the electron correlation by HF theory and of the influence of zero-point vibrational effects (which are neglected in the calculations) and possible packing effects in the experimental results (if they come from crystal structure data). Considering all geometric parameters obtained with different theoretical model at varied basis sets, as expected, the 6-31G predicted the bond length in relatively poorly agreement with the experimental values. When polarization and diffuse functions are added, the results are improved. MP2 and B3LYP at the 6-311++G(d,p) basis set level reproduce the experimental values most satisfactorily for the formamide. When the basis sets are enlarged to 6-311++G(2d,2p), the difference between the B3LYP calculated and experimental results may be negligible.

Geometry of the Formamide−Glycine Complex and Interaction Energies. We have calculated 12 conformations of the complex between formamide and glycine monomers. Ten of these are cyclic double-hydrogen-bonded structure and the other two are one-hydrogen-bonded structure. The structures of the formamide−glycine dimer are shown in Figure 1, and the most interesting geometrical parameters are listed in Table 2 (we included in these work optimizations with unconstrained formamide with all methods).

Surveying the calculated results using the B3LYP method at different basis set levels is that changes in the monomer geometries upon complexation are relatively minor. For the monomer formamide, complex formation induces a small elongation of the C=O bond and a very small contraction of the C−N bond. Other bond lengths involved in the hydrogen bonding slightly lengthen. The maximum bond length change is less than 0.021 Å at the two large basis set levels. As to glycine monomer, due to the formation of the hydrogen bonding, the C=O bond, C−O bond, and the O−H bond are all prolonged; of course, other bond lengths in the hydrogen bonding also slightly lengthen. Of those, the largest elongation is the O−H bond length, which is 0.031 Å; other bond length changes are less than 0.017 Å.

FG1 exhibits a cyclic conformation, with formamide accepting a proton from the methylene group while donating a proton to the hydroxyl group. R_{OF-HG} (the hydrogen bond distance between the oxygen of formamide and hydrogen of glycine) is 2.353 and 2.363 Å at the two large basis set levels, and the R_{OG-HF} is 2.749 and 2.811 Å, respectively, which indicates the interaction between CHO group and hydroxyl group is relatively weak. Furthermore, the cyclic arrangement results in more bent hydrogen bonds, the deformation from linearity being 50.9° (61.3°) for the CO···H_F hydrogen bond and 65.9° (66.6°) for the CO···H_G one at the two large basis set levels.

In FG2, there is also a cyclic structure in which formamide bonded to the hydroxyl group, and all the results indicate the tendency of the oxygen of formamide to interact with the H of glycine. The the interaction distance is 1.705 Å and 1.693 Å at the two large basis set levels. In addition, in this structure, formamide offers the proton of the CHO group to the carbonyl group of glycine; R_{OG-HF} is 2.365 and 2.351 Å, respectively, slightly shorter than that of the structure FG1. Therefore, the interaction energy of this structure will be larger than that of the complex FG1. Moreover, the formation of the hydrogen bond leads to the change of bond angle; for example, the OH···O_F is 178.4° at the 6-311++G(d,p) level, while the 6-311++G(2d,2p) calculations suggest the hydrogen bond is linear (180.0°).

For structure FG3, it is a cyclic configuration too. Formamide is not only the hydrogen acceptor but also the hydrogen donor; which accepts the H proton from the amino group of glycine and offers the H proton to the carbonyl group, respectively. The 6-311++G(d,p) basis set level calculations which yield the R_{OF-HG} of 2.133 Å and R_{OG-HF} of 2.410 Å are in good agreement with the 6-311++G(2d,2p) values of 2.143 and 2.418 Å. The departure of the NH···O_F angle from the linearity is

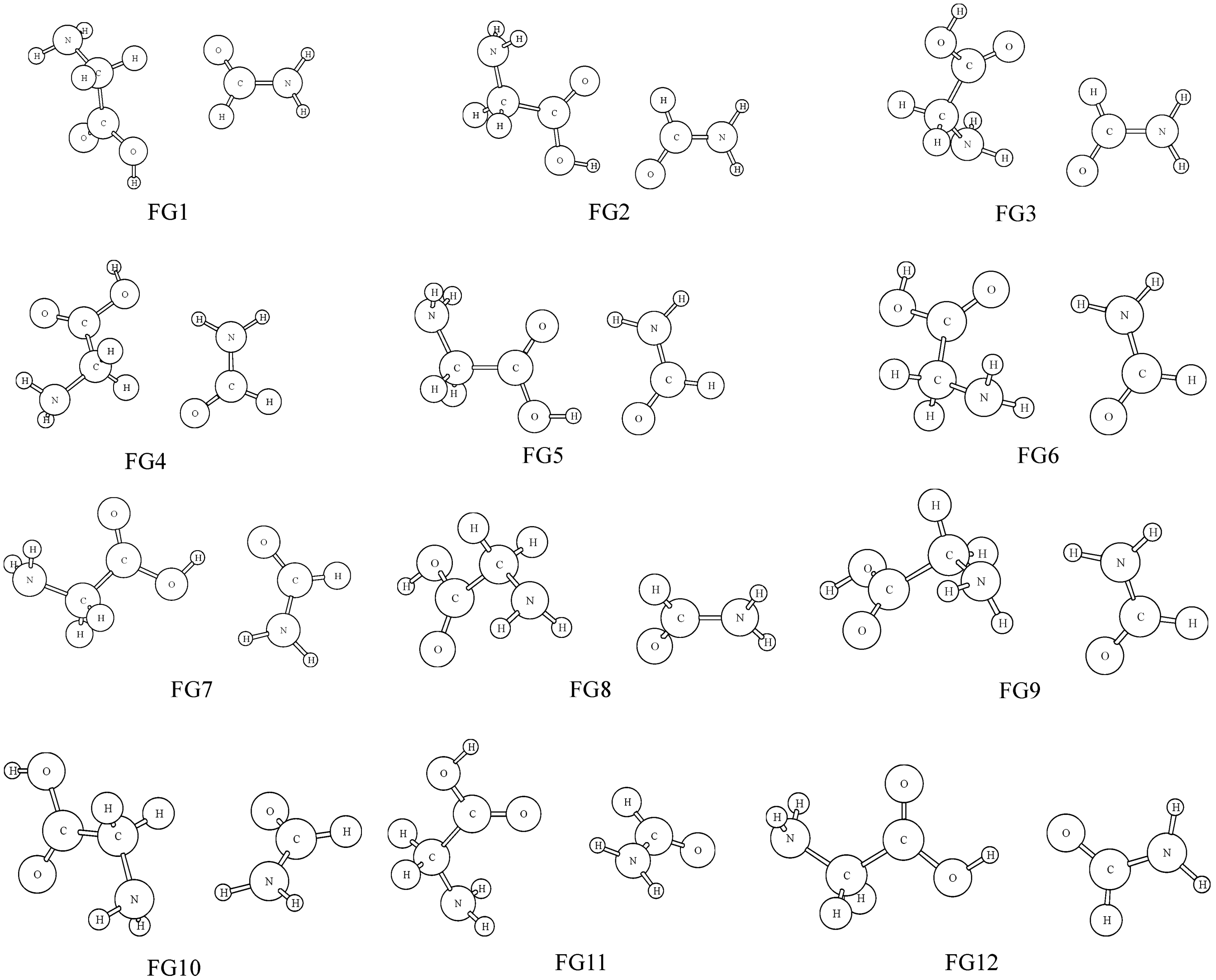

Figure 1. Optimized structure of formamide−glycine complexes at the B3LYP/6-311++G(d,p) level.

TABLE 2: Optimized Geometric Parameters of the Formamide−Glycine Complex Using the B3LYP Method at Different Basis Set Levels

species		6-31G^a	6-31+G^a	6-31+G(d)^a	6-311++G(d,p)^a	6-311++G(2d,2p)^a
FG1	$R_{\mathrm{OF-HG}}$	2.234	2.264	2.369	2.353	2.363
	$R_{\mathrm{OG-HF}}$	2.503	2.536	2.793	2.749	2.811
FG2	$R_{\mathrm{OF-HG}}$	1.625	1.641	1.720	1.705	1.693
	$R_{\mathrm{OG-HF}}$	2.233	2.308	2.370	2.365	2.351
FG3	$R_{\mathrm{OF-HG}}$	2.016	2.051	2.123	2.133	2.143
	$R_{\mathrm{OG-HF}}$	2.260	2.297	2.413	2.410	2.418
FG4	$R_{\mathrm{OF-HG}}$	2.205	2.255	2.364	2.351	2.363
	$R_{\mathrm{OG-HF}}$	1.971	1.981	2.111	2.126	2.159
FG5	$R_{\mathrm{OF-HG}}$	1.598	1.617	1.704	1.681	1.669
	$R_{\mathrm{OG-HF}}$	1.813	1.849	1.898	1.897	1.879
FG6	$R_{\mathrm{OF-HG}}$	1.992	2.027	2.104	2.111	2.119
	$R_{\mathrm{OG-HF}}$	1.900	1.917	1.974	1.977	1.984
FG7	$R_{\mathrm{OF-HG}}$	1.715	1.725	1.806	1.804	1.794
	$R_{\mathrm{OG-HF}}$	2.080	2.143	2.297	2.311	2.323
FG8	$R_{\mathrm{OF-HG}}$	2.047	2.085	2.132	2.163	2.174
	$R_{\mathrm{NG-HF}}$	2.658	2.813	2.865	2.876	2.866
FG9	$R_{\mathrm{OF-HG}}$	2.078	2.208	2.299	2.302	2.288
	$R_{\mathrm{NG-HF}}$	1.986	2.000	2.048	2.069	2.086
FG10	$R_{\mathrm{OF-HG}}$	2.191	2.286	2.399	2.386	2.395
	$R_{\mathrm{NG-HF}}$	1.893	1.931	2.000	2.022	2.032
FG11	$R_{\mathrm{OG-HF}}$	1.948	1.969	2.034	2.042	2.052
	$\angle\mathrm{NHO_G}$	174.2	179.2	176.3	176.5	176.9
FG12	$R_{\mathrm{OF-HG}}$		1.699	1.790	1.787	1.776
	$\angle\mathrm{OHO_F}$		167.9	164.3	164.4	163.5

^{a} Distance in angstroms; angles in degrees.

10.7° and 10.4° at the two large basis set levels, respectively, while the $CH\cdots O_G$ angle is 41.0° and 39.7°.

FG4 minimum is also a cyclic structure, in this structure, although formamide is also accepting a proton from the methylene group of glycine, but it is donating the H proton of the amino group to the hydroxyl group, which is different from the FG1 structure. R_{OF-HG} is 2.351 and 2.363 Å for the two large basis set levels, and the R_{OG-HF} is 2.126 and 2.159 Å, respectively, which is a little shorter than that of the complex FG1. Hence, the interaction energy of this configuration should be larger than FG1. On the other hand, the $NH\cdots O_G$ angle and the $CH\cdots O_F$ are 169.2° and 165.6° at the 6-311++G(d,p) level, respectively, which are near linearity.

FG5 also shows a cyclic structure in which glycine bonded to the carbonyl group, and all the results indicate the tendency of the hydrogen of hydroxyl group to interact with the O of formamide and the interaction distance is 1.681 and 1.669 Å at the two large basis set levels. In addition, unlike FG2, in FG5, formamide offers the proton of the amino group to the carbonyl group; R_{OG-HF} is 1.879 Å at the 6-311++G(d,p) level. From all the values (in Table 2) of the hydrogen bond distances, we can see the values of FG5 are the minimal, which indicates that the hydrogen bonds are very strong; therefore, the interaction energy should be the largest and this structure is the most stable.

For structure FG6, it is a cyclic configuration too. Formamide is not only the hydrogen acceptor but also the hydrogen donor, which accepts the H proton from the amino group of glycine, and this is the same as the configuration FG3; however, unlike FG3, the H proton formamide offered to the carbonyl group is that of the amino group not the CHO group. The 6-311++G(d,p) basis set level calculations which yield the R_{OF-HG} of 2.111 Å and R_{OG-HF} of 1.977 Å are in excellent agreement with the 6-311++G(2d,2p) values of 2.119 and 1.984 Å. Moreover, in this structure, the hydrogen bond is quasilinear. The departure of the $NH\cdots O_F$ angle from the linearity is 7.6° and 6.4° at the two large basis set levels, while the $NH\cdots O_G$ angle is 8.5° and 7.7°, respectively.

With respect to structure FG7, it is also a cyclic structure and turns out to be a six-membered ring. In this configuration, the hydroxyl of glycine is the hydrogen acceptor as well as the hydrogen donor, and formamide offers the H proton of the amino group to the hydroxyl group. R_{OF-HG} is 1.804 and 1.794 Å, and R_{OG-HF} is 2.311 and 2.323 Å at the two largest basis sets, respectively. Furthermore, the cyclic arrangement results in more bent hydrogen bonds, the deformation from linearity being 65.6° (66.0°) for the $CO\cdots H_G$ hydrogen bond and 49.6° (49.7°) for the $NH\cdots O_G$ one at the two large basis set levels, respectively.

As to the configuration FG8, it is different from all the structures mentioned above, although it also turns out to be a cyclic structure, but in this one, the amino group ofglycine is not only the hydrogen acceptor but also the hydrogen donor; namely, the amino group donates one of its H atom to the carbonyl group and formamide provides the H proton of the CHO group to the N atom of the amino group, so that the hydrogen bonds form. Furthermore, the R_{OF-HG} bond distance is 2.163 and 2.174 Å at the two large basis set levels and R_{NG-HF} is 2.876 and 2.866 Å, respectively; the latter bond distance is much longer, which means that the interaction energy of this structure should be very small.

FG9 exhibits a cyclic conformation too, which is similar to FG8 structure; the only difference is that formamide provides the H proton of the amino group not of the CHO group. R_{OF-HG} is 2.302 Å at the 6-311++G(d,p) level and the R_{NG-HF} is 2.069 Å, slightly shorter than that of structure FG8; hence, the interaction energy should be larger than FG8. In addition, the $NH\cdots N_G$ angle is 148.4° at the 6-311++G(d,p) level, while the $CO\cdots H_G$ is 106.0°, which is largely beyond the linearity.

The FG10 minimum is also a cyclic structure, formamide accepting a proton from the methylene group while donating a proton to the amino group. The hydrogen bond distance between O atom of carbonyl group and H atom of methylene group is 2.386 and 2.395 Å at the two large basis set levels. The R_{NG-HF} is 2.022 and 2.032 Å, respectively, slightly shorter than that of FG8; therefore, the interaction energy of this structure should be larger than FG8. The departure of the $NH\cdots N_G$ angle from the linearity is 15.8° and 15.1° at two large basis set levels, respectively, while the $CO\cdots H_G$ angle is 64.0° and 64.3°.

As to the configuration FG11, unlike all the structures discussed above, it is not a cyclic structure; there is only one hydrogen bond between the amino group and the carbonyl group. The interaction distance is 2.042 and 2.052 Å for the two large basis sets. Furthermore, the 6-311++G(d,p) calculation which produces the $NH\cdots O_G$ angle of 176.5° is in good agreement with the 6-311++G(2d,2p) value of 176.9°, which is almost to linearity.

With respect to the last structure FG12, there is only one hydrogen bond too, glycine bonded to the carbonyl, all the results indicate the tendency of the hydrogen of glycine to interact with the O of formamide, the interaction distance is 1.787 Å and 1.776 Å at the two large basis set levels. The departure of $OH\cdots O_F$ angle from the linearity is 15.6° and 16.5°, respectively. Moreover, there is one thing should be pointed out: we have not found FG12 structure at the 6-31G level.

Finally, one additional point is worth mentioning concerning the structure of formamide−glycine complexes. We have found 12 structures, 10 of which are cyclic structures; the other two are not. As we all know, a hydrogen bond can form between the H atom and O, F, N atoms, and so on. Therefore, in our paper, there are three types of structures, one type is that two hydrogen bonds between an H atom and an O atom with the structures being cyclic, such as FG1, FG2, etc.; the second type is one hydrogen bond between the H atom and the O atom but the other bond is between the H atom and the N atom and the structures are also cyclic, such as FG8, FG9, and FG10; the third type is that there is only one hydrogen bond between the H atom and the O atom or N atom, such as FG11 and FG12.

Interaction energies are calculated for the formamide−glycine hydrogen bond by taking the energy difference between the fragments and the complex. The zero-point vibrational energy (ZPVE) corrections are applied in the present case. To correct the basis set superposition error (BSSE), the counterpoise (CP) method[19] is employed.

To analyze in more detail the role of basis set size effects on the binding energy between formamide and glycine, we use Table 3, which gives a detailed analysis of the binding energy obtained with several different theoretical models. The numbers shown in the first set of parentheses are corrected for zero-point vibrational energy (ZPVE) and in the second set of parentheses they are corrected for BSSE using the counterpoise method of Boys and Bernadi.[19] As expected, basis set sensitivity exists. The interaction energy computed using the minimal basis set 6-31G is much higher. As the basis set is enlarged, the computed values decreases and converge smoothly. The general importance of including BSSE corrections in calculated binding energies has been well documented in the literature. From Table 3 we can see the magnitude of BSSE are decreasing with the basis set enlarged, when the diffusion and polarization functions

TABLE 3: Interaction Energies (kJ/mol) of Formamide−Glycine Complexes

	6-31G[a]	6-31+G[a]	6-31+G(d)[a]	6-311++G(d,p)[a]	6-311++G(2d,2p)[a]
FG1	19.8 (16.5) (11.8)	13.9 (11.0) (13.3)	9.7 (6.9) (9.3)	9.5 (6.8) (9.7)	8.7 (6.1) (9.2)
FG2	70.6 (63.5) (62.9)	59.0 (52.2) (60.6)	47.6 (40.8) (49.4)	45.8 (39.4) (45.4)	45.0 (38.2) (45.2)
FG3	35.3 (29.8) (24.6)	27.0 (21.9) (25.8)	20.0 (15.2) (19.5)	19.7 (15.1) (19.7)	18.9 (14.2) (19.0)
FG4	34.7 (29.6) (25.8)	26.2 (21.3) (24.2)	17.1 (12.4) (16.3)	17.0 (12.5) (17.0)	15.2 (10.8) (15.8)
FG5	92.7 (84.8) (86.4)	76.4 (68.5) (80.8)	63.2 (54.6) (67.3)	60.8 (53.1) (60.4)	60.1 (51.9) (60.1)
FG6	54.3 (47.3) (43.3)	42.9 (36.2) (42.0)	33.2 (26.3) (32.8)	32.4 (25.9) (33.0)	31.0 (24.3) (32.0)
FG7	58.6 (52.3) (50.8)	46.9 (40.7) (47.4)	35.3 (29.3) (35.5)	33.2 (27.9) (33.0)	31.9 (26.3) (33.0)
FG8	27.2 (21.4) (19.1)	19.7 (14.7) (19.2)	15.8 (11.2) (15.9)	15.0 (10.7) (15.6)	14.4 (10.0) (15.2)
FG9	50.4 (42.3) (41.5)	37.6 (30.2) (37.3)	32.2 (25.1) (31.8)	30.0 (23.2) (30.0)	28.0 (21.2) (29.3)
FG10	50.9 (43.0) (43.8)	39.2 (31.8) (38.5)	33.5 (26.4) (32.3)	31.5 (24.9) (31.5)	29.2 (22.5) (30.3)
FG11	30.9 (26.9) (23.7)	24.7 (21.2) (23.8)	19.1 (15.0) (18.3)	18.5 (14.9) (18.5)	17.5 (13.7) (17.7)
FG12		41.4 (36.5) (41.3)	33.7 (27.8) (32.7)	31.8 (26.7) (31.6)	29.8 (25.3) (31.2)

[a] Values in the first parentheses are corrected for zero-point vibrational energy and in the second parentheses are results with correction for basis set superposition.

are considered, especially for the 6-311++G(d,p) and 6-311++G(2d,2p) basis set, the inclusion of BSSE correction has minor importance to the binding energy.

From the values of Table 3, we can see the relative stability order of the 12 structures is FG5 > FG2> FG7 > FG6 > FG12 > FG10 > FG9 > FG3 > FG11 > FG4 > FG8 > FG1. The inclusion of ZPVE correction is relatively more important to the binding energy than BSSE at large basis set levels. However, the correction is not sensitive to the basis sets. Even if it is considered, the stability order of different conformations does not change. It is easy to understand the stability of FG5 derives from the formation of a pair of hydrogen bonds between the glycine and formamide due to the strongest interaction (the shortest hydrogen bond distance). At the same time, the instability of FG1 is by reason of the weakest interaction, though it is also a cyclic structure. For the other structures, we can also estimate the stability by the interaction energy and the interaction distance.

Infrared Spectrum. Vibrational spectroscopy is one of the most useful experimental tools for study of the H-bonded clusters, so the information on calculated harmonic vibrational frequencies can be useful. In Table 4, we give the B3LYP/6-311++G(2d,2p) values for both vibrational frequencies and IR intensities of the twelve complexes and monomers. Since the frequency shifts are relatively stable with respect to theoretical methods, one can estimate the IR spectrum for the complex by combining the observed fundamental vibrational frequency of its moieties and the frequency shift in Table 4. The C═O stretching frequency are found to reduce for all structures but structure FG12 (which is increased by 8 cm^{-1}) considered here (14, 61, 30, 14, 63, 28, 32, 21, 23, 22, and 12 cm^{-1}, respectively). This is inconsistent with the bond distance change discussed above. The C−H stretching frequency also shows a slight change in its value on hydrogen bonding. For instance, in structure FG1, there is a weak interaction between the O of glycine and the H of the CHO group—the shift is 29 cm^{-1}; for another example, in configuration FG2, there is an interaction between the O of carbonyl group and H of CHO group—the C−H stretching frequency is blue-shifted by 93 cm^{-1}. In addition, in the configurations FG5 and FG7, there is an interaction between the H of the hydroxyl group and the O of the carbonyl group, which weakens the C═O bond of the CHO group as well as strengthens the C−H bond, so the C−H stretching frequencies are blue-shifted by 54 and 52 cm^{-1}, respectively. The C−N stretching is found to be blue shifted and the maximum increase is observed for structure FG5 (78 cm^{-1}). At the same time, the NCO scissoring frequency is also found to be blue shifted for all structures considered here (4, 22, 6, 23, 51, 33, 35, 6, 44, 48, 16, and 22 cm^{-1}, respectively). It is interesting to note the upward shift of the bonding mode frequency in NH_2CHO upon forming the hydrogen complex, which is typical for the hydrogen bond complex. For instance, the NH_2 scissoring, rocking, twisting, and wagging modes are all blue shifted to different extent with glycine in different configurations. Of course, the strongest shifts occur in FG5, such as the NH_2 twisting frequency increased by 296 cm^{-1} and those of other structures are less than 296 cm^{-1}, which is corresponding to the strongest interaction. For the modes of glycine in the complex, the stretching frequency associated with the hydrogen bond undergoes a shift to a lower frequency compared to the free monomer. For example, the O−H stretching mode is red-shifted by 556, 644, 404, and 365 cm^{-1} for structure FG2, FG5, FG7,and FG12, respectively. This occurs also because formation of the hydrogen bond weakens the O−H bond.

With respect to IR intensities, they 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. In this system, there is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor of the type NH−O, OH−O, and NH−H. From the results presented in Table 4, we can see the N−H and O−H stretching intensities involved in the hydrogen bonds are enhanced largely in both hydrogen complexes. For instance, the O−H stretching intensities varied from 60 km/mol to 1603, 1269, 976, and 1372 km/mol for complexes FG2, FG5, FG7, and FG12, respectively, which are approximately 27, 21, 16, and 23 times that of the mode in the monomer. The N−H stretching intensities changed from 35 to 504(625) km/mol for complex FG6 (FG10); of course, the largest change occurs in FG5 (to 888 km/mol, approximately 26 times that of the mode in the monomer), which is due to the strongest interaction. For the CH, 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 a strong hydrogen bond, the force constants of the bond involved in the hydrogen-bonding reduce and the frequencies are red-shifted. At the same time, the increasing of the change of the vibrational dipole moments results in the enhancement of the IR intensities.

IV. Conclusions

The hydrogen-bond interaction of the 1:1 complex between formamide and glycine has been analyzed using density functional theory (DFT) method at varied basis set levels from

TABLE 4: Frequencies and IR Intensities of Monomer and Complexes at the B3LYP/6-311++G(2d,2p) Level[a]

		FG1	FG2	FG3	FG4	FG5	FG6	FG7	FG8	FG9	FG10	FG11	FG12
$v(I)$	assignment	$v(I)$	$v(I)$	$v(I)$	$v(I)$	$v(I)$	$v(I)$	$v(I)$	$v(I)$	$v(I)$	$v(I)$	$v(I)$	$v(I)$
formamide													
167(208)	$\tau(\mathrm{NH_2})$	202(205)	304(201)	221(195)	319(112)	463(116)	404(104)	335(162)	219(194)	393(72)	282(3)	424(229)	279(199)
569(11)	$\delta(\mathrm{NCO})$	573(18)	591(39)	575(25)	592(9)	620(6)	602(9)	604(12)	575(18)	613(6)	617(4)	585(15)	591(32)
637(14)	$\omega(\mathrm{NH_2})$	643(11)	662(14)	648(10)	714(32)	833(27)	752(36)	679(7)	645(13)	800(21)	435(102)	703(4)	655(16)
1038(3)	$\gamma(\mathrm{CH})$	1050(4)	1085(2)	1063(8)	1045(3)	1062(22)	1049(3)	1047(6)	1058(4)	1049(9)	1051(7)	1042(2)	1050(2)
1055(6)	$r(\mathrm{NH_2})$	1060(6)	1077(2)	1067(4)	1073(6)	1104(0)	1084(1)	1078(12)	1063(3)	1089(3)	1092(2)	1083(6)	1074(2)
1265(115)	$\nu(\mathrm{CN})$	1271(145)	1292(195)	1273(157)	1291(109)	1343(102)	1307(111)	1303(91)	1275(133)	1314(126)	1312(118)	1279(117)	1295(83)
1419(7)	$\omega(\mathrm{CH})$	1425(9)	1425(26)	1433(17)	1421(10)	1422(32)	1422(15)	1422(15)	1423(9)	1420(2)	1420(20)	1418(11)	1423(6)
1623(58)	$\delta(\mathrm{NH_2})$	1625(55)	1628(30)	1624(54)	1638(28)	1624(11)	1646(16)	1637(39)	1625(51)	1625(13)	1647(5)	1645(36)	1629(41)
1783(440)	$\nu(\mathrm{C{=}O})$	1769(491)	1722(233)	1753(340)	1769(424)	1720(13)	1755(239)	1751(611)	1762(460)	1760(393)	1761(408)	1771(732)	1791(217)
2951(94)	$\nu(\mathrm{CH})$	2980(50)	3044(39)	3014(22)	2960(114)	3005(228)	2962(124)	3003(101)	2989(41)	2958(124)	2949(140)	2945(96)	2997(53)
3587(35)	$\nu_s(\mathrm{NH_2})$	3586(42)	3586(46)	3587(37)	3533(167)	3356(888)	3478(504)	3560(104)	3588(41)	3382(414)	3318(625)	3537(262)	3586(48)
3725(45)	$\nu_{as}(\mathrm{NH_2})$	3724(47)	3723(58)	3724(48)	3702(106)	3683(107)	3692(104)	3710(104)	3725(49)	3687(87)	3678(73)	3682(159)	3722(58)
glycine													
64(6)	$\tau(\mathrm{CCN})$	100(0)	174(29)	134(5)	116(13)	121(2)	156(30)	183(42)	138(14)	121(15)	149(32)	76(8)	84(4)
200(44)	$\tau(\mathrm{NH_2})$	205(42)	212(50)	363(34)	207(47)	218(42)	371(52)	203(44)	255(19)	274(8)	305(20)	221(44)	193(48)
257(10)	$\delta(\mathrm{CCN})$	260(11)	285(35)	256(17)	260(17)	306(63)	258(13)	276(34)	372(69)	420(75)	468(31)	258(7)	274(29)
462(290	$\delta(\mathrm{CCO})$	463(28)	496(7)	465(26)	465(26)	502(8)	469(31)	497(6)	462(28)	469(23)	519(39)	467(33)	492(8)
508(36)	$\tau(\mathrm{CCO})$	513(39)	567(0)	508(39)	510(43)	569(0)	511(39)	557(0)	511(41)	513(39)	638(28)	511(33)	560(0)
635(6)	$\delta(\mathrm{COO}) + \delta(\mathrm{CCN})$	635(7)	658(8)	639(9)	634(8)	664(9)	643(11)	650(9)	636(38)	637(41)	655(76)	637(5)	648(10)
647(89)	$\gamma(\mathrm{OH})$	652(89)	981(91)	649(90)	645(74)	1009(81)	655(87)	905(95)	656(63)	656(65)	822(32)	654(90)	837(141)
817(84)	$\nu_s(\mathrm{CCN})$	817(76)	849(101)	822(52)	814(72)	851(121)	823(64)	837(137)	827(60)	845(48)	857(42)	811(122)	903(87)
913(119)	$\nu_{as}(\mathrm{CCN})$	908(120)	934(118)	915(71)	900(124)	929(100)	898(89)	921(7)	934(44)	995(217)	932(3)	888(79)	921(9)
918(3)	$\gamma(\mathrm{CH_2}) + \gamma(\mathrm{NH_2})$	933(6)	923(1)	940(77)	932(5)	922(2)	934(30)	931(109)	959(160)	940(8)	982(152)	917(3)	935(107)
1119(210)	$\nu(\mathrm{CO}) + \nu(\mathrm{CN})$	1112(229)	1135(24)	1123(277)	1103(272)	1137(19)	1133(244)	1134(99)	1121(234)	1123(161)	1115(91)	1130(174)	1133(59)
1158(105)	$\nu(\mathrm{CO}) + \nu(\mathrm{CN})$	1153(61)	1243(243)	1165(59)	1151(33)	1193(1)	1171(81)	1187(516)	1157(86)	1158(149)	1158(199)	1169(147)	1188(1)
1192(1)	$\tau(\mathrm{NH_2}) + \tau(\mathrm{CH_2})$	1205(5)	1191(1)	1208(1)	1206(3)	1262(219)	1209(1)	1188(1)	1210(12)	1209(13)	1197(15)	1193(1)	1200(525)
1313(11)	$\omega(\mathrm{CCO})$	1316(5)	1377(25)	1312(11)	1314(7)	1380(40)	1317(12)	1351(62)	1314(12)	1317(18)	1321(17)	1319(15)	1355(21)
1389(0)	$\omega(\mathrm{CH_2}) + \omega(\mathrm{NH_2})$	1381(2)	1390(0)	1393(7)	1380(1)	1390(0)	1395(2)	1390(0)	1382(6)	1384(6)	1397(4)	1386(0)	1390(0)
1399(12)	$\nu(\mathrm{CC})$	1419(10)	1468(12)	1404(4)	1418(7)	1475(4)	1404(10)	1411(4)	1414(12)	1418(25)	1414(22)	1406(17)	1420(11)
1463(17)	$\delta(\mathrm{CH_2})$	1477(16)	1464(12)	1458(18)	1478(19)	1462(16)	1457(20)	1465(13)	1466(14)	1468(14)	1477(20)	1460(21)	1466(14)
1684(20)	$\delta(\mathrm{NH_2})$	1682(22)	1684(19)	1701(12)	1682(23)	1684(17)	1702(19)	1684(18)	1692(28)	1684(45)	1678(22)	1681(28)	1684(17)
1808(304)	$\nu(\mathrm{C{=}O})$	1806(307)	1768(593)	1795(434)	1818(329)	1759(786)	1784(572)	1800(202)	1808(297)	1809(300)	1802(317)	1790(203)	1756(740)
3052(17)	$\nu_s(\mathrm{CH_2})$	3034(21)	3050(21)	3037(26)	3031(16)	3050(24)	3039(24)	3045(23)	3025(27)	3036(22)	3045(39)	3050(16)	3048(22)
3082(6)	$\nu_{as}(\mathrm{CH_2})$	3080(22)	3080(8)	3074(6)	3073(21)	3081(6)	3071(5)	3076(9)	3090(6)	2095(4)	3090(7)	3080(4)	3078(10)
3516(3)	$\nu_s(\mathrm{NH_2})$	3515(2)	3512(1)	3469(151)	3518(2)	3514(1)	3464(18)	3512(8)	3473(102)	3461(91)	3500(3)	3524(1)	3509(1)
3582(7)	$\nu_{as}(\mathrm{NH_2})$	3584(7)	3576(4)	3570(39)	3587(8)	3580(5)	3577(38)	3576(6)	3562(43)	3553(29)	3563(9)	3596(7)	3572(5)
3758(60)	$\nu(\mathrm{OH})$	3756(54)	3204(1603)	3759(53)	3750(59)	3114(1269)	3755(59)	3354(976)	3757(58)	3757(65)	3759(68)	3752(68)	3393(1372)

[a] Vibrational frequencies (ν) in $\mathrm{cm^{-1}}$; IR intensities (I) in km/mol.

6-31G to 6-311++G(2d,2p). Twelve structures are considered, 10 of which are cyclic double-hydrogen-bonded structure and the other two are one-hydrogen-bonded structure. Of them the cyclic double-hydrogen-bonded structure (FG5) is the most stable at all levels; another cyclic structure, FG1, is the most unstable due to the weakest interaction. For the other complexes, their stabilities depend on the values of the interactions between formamide and glycine. Moreover, the infrared spectrum frequencies, IR intensities and the 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 the free monomer and there is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor of the type NH−O, OH−O, and NH−H.

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