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ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE THEOCHEM · NOVEMBER 2005

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Study of the hydrogen bonding interaction of 1:1 complexes of serine with formamide using density functional theory

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Received 31 March 2005; revised 16 May 2005; accepted 23 May 2005

Available online 15 November 2005

Abstract

The hydrogen bonding of 1:1 complexes formed between formamide and serine molecules 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(d,p). Fifteen reasonable geometries on the potential energy hypersurface of formamide and serine system are considered with the global minimum, 13 of them are cyclic double-hydrogen bonded structures and the other two are one-hydrogen bonded structures. 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.

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Keywords: Density functional theory; Hydrogen bonding; Formamide; Serine

1. Introduction

One of the fundamental issues of chemistry is the relationship between the reactivity of a molecule and its structure. Chemists have long sought the principle governing this fundamental relation with impressive successes in a wide range of chemical problems. This close relationship between the reaction and molecular structure is especially important for biomolecules. Indeed, the structure of a biomolecule may be considered as the blueprint interplay between the reactivity and the structure of biomolecules is the underlying mechanism of life itself. 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 the model for studying biological systems exhibiting the peptide type of bonding and DNA structures. And serine is a chiral amino acid out of the roughly 21 amino acids common in nature. A significant amount of serine is present in the aqueous phase. Serine has been studied by a few of groups [1–5]. Its Raman and IR spectra and their assignments have been reported in a number of papers [6–8]. The crystal structures of L- and D-serine were studied by X-ray diffraction [9] and neutron diffraction [10] methods. All of them indicate that L-serine occurs in crystals in the dipolar ion (zwitterion) form and the hydrogen atoms in amino and hydroxyl group participate in a three-dimensional network of hydrogen bonds. 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 [11–17]. The characterization of the hydrogen bonding interaction between formamide and water has been well studied by a lot of theoretical calculations [11–17] while in the case of formamide–serine complex, there are few investigations. In addition, serine is one of the important amino acids; therefore, investigation of the hydrogen bonding interaction between formamide and serine must

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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 [18–20]. 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–serine complex as obtained by high level ab initio calculations. We thus report geometry optimization and calculate bonding energies between formamide and serine for a variety of theoretical models and basis sets. The roles of basis set size and basis set superposition effects are analyzed in details. In the present paper, we put forward what we believe are now the most accurate results for the hydrogen bond interaction between formamide and serine, as got from high-level calculations and systematic analysis of the theoretical results obtained.

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

2. Computational methods

It is well known that in the SCF model, the electrostatic exchange and some induction–polarization effects are included. In more recent years, it has been learnt that the induced–induced dispersion interaction may be of great importance [21,22], 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 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 to the hydrogen bonding systems.

The geometry optimization of the monomers (formamide and serine) has been carried out using HF, MP2 and B3LYP correlation methods with the 6-31G, 6-31 + G, 6-31 + G(d), 6-31 + +G(d) and 6-311 + +G(d,p) basis sets. For the geometry of the complexes of formamide and serine, we only utilize the B3LYP method with the 6-31G, 6-31 + G, 6-31 + G(d), 6-31 + +G(d), 6-311 + +G(d,p) 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) [23]. This is done using the counterpoise method [24]. All calculations are performed using the GAUSSIAN 98 program [25].

3. Results and discussion

3.1. Structure of formamide and serine monomers

The structures of the super molecules will depend on the structures calculated from the formamide and serine monomers. Despite the large number of experimental [26] and theoretical studies [27,28] of formamide, its structure has been controversial. The peptide moiety was assumed from the early work of Pauling and Coorey to be planar, and more recently, however, the planarity of the peptide moiety has been questioned. Two early microwave studies [29,30] 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 symmetries. 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 surfaces.

It is interesting to note the difference between the B3LYP, HF and MP2 predictions about the NH_2 moiety in the formamide molecule. B3LYP and SCF methods at all basis set levels indicate formamide to be planar (in C_s symmetry), MP2/6-31G level supports this view, while at other basis set levels we have mentioned, MP2 predicts formamide to be nonplanar (in C_s constrained symmetry case, 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 that the planar structure of formamide is not a local minimum on the MP2 electronic energy surface. So all of the results we examined are in C_1 symmetry.

In our work, we calculated nine possible conformations of serine by using B3LYP method from 6-31G level to 6-311 + +G(d,p) level. The energies of all the nine conformers calculated by different methods at different basis levels are listed in Table 1 and the structures of them are shown in Fig. 1. For comparison we also calculated these conformations by using HF and MP2 methods at 6-31 + G level. The results show that Ser2 is more stable than others.

The calculated structures of formamide and serine using DFT method at 6-311 + +G(d) and 6-31 + G basis sets are presented in Table 2. For comparison, results of MP2, HF at 6-31 + G level and the experimentally determined structures are also given in Table 2. 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

Table 1
Relative energies of the nine configurations of serine monomer (kJ/mol)

	B3LYP ^a	B3LYP ^a	HF/6-31G	MP2/6-31G
Ser. 1	6.58 (6.59)	6.24 (6.23)	5.63 (5.51)	4.53 (4.38)
Ser. 2	0 (0)	0 (0)	0 (0)	0 (0)
Ser. 3	18.96 (16.97)	19.41 (17.43)	13.72 (12.12)	15.54 (13.45)
Ser. 4	12.12 (10.94)	12.41 (11.30)	7.49 (6.64)	8.91 (7.94)
Ser. 5	13.04 (13.26)	11.40 (10.85)	3.40 (2.69)	8.69 (8.28)
Ser. 6	18.95 (17.13)	19.48 (17.66)	8.64 (6.65)	12.04 (10.04)
Ser. 7	6.58 (6.59)	6.24 (6.24)	5.63 (5.50)	4.53 (4.38)
Ser. 8	17.00 (15.86)	18.33 (17.12)	3.40 (2.70)	18.04 (15.25)
Ser. 9	10.82 (10.11)	12.49 (11.73)	12.52 (13.18)	8.51 (9.02)

Values in parenthesis are the relative zero-point vibrational energy (ZPVE) corrections.

^a Represent 6-311++G(d,p) and 6-311++G(d) basis sets, respectively.

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 models 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 6-311++G(d) basis set level reproduce the experimental values most satisfactorily for the formamide.

3.2. Geometry of the formamide–serine complex and interaction energies

We have calculated 15 conformations of the complex between formamide and serine monomers. Thirteen of them are cyclic double-hydrogen bonded structures and the other two are one-hydrogen bonded structures. The structures of the formamide–serine dimer are shown in Fig. 2 and the most interesting geometrical parameters are listed in Table 3 (We included in these work optimizations with unconstrained formamide with all methods).

Surveying the calculated results using B3LYP method at different basis set levels shows that changes in the monomer geometries upon complexation are relatively minor. For formamide monomer, 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 large basis set levels. As to serine monomer, due to the formation of the hydrogen bonding, the C=O bond, C–O bond, C–N bond as well as

the O–H bond are all prolonged, of course, other bond lengths in the hydrogen bonding also slightly lengthen.

FS1 exhibits a cyclic conformation, with formamide accepting a proton from the hydroxyl group of serine while donating a proton to the hydroxyl group. $R_{\text{OF-HS}}$ (the hydrogen bond distance between the oxygen of formamide and hydrogen of serine) is 2.121 Å at the 6-311++G(d,p) level and the $R_{\text{OS-HF}}$ is 2.022 Å which indicates that the interaction between the hydroxyl group and the formamide is a little strong. Furthermore, the cyclic arrangement results in more bent hydrogen bonds, the deformation from linearity is 38.8° for the $\text{NH}\cdots\text{O}_\text{S}$ hydrogen bond and 46° for the $\text{OH}\cdots\text{O}_\text{F}$ one at the 6-311++G(d,p) level.

In FS2, formamide bonded to the hydroxyl group, all the results indicate the tendency of the oxygen of formamide to interact with the H of the COOH of serine, and the interaction distance is 1.773 Å at the 6-311++G(d,p) level, shorter than that of the structure FG1. Therefore, the interaction energy of this structure will be larger than that of the complex FS1. In addition, formamide offers the proton of the NH_2 group to the carbonyl group of serine. Moreover, the cyclic arrangement results in more bent hydrogen bonds.

For structure FS3, it is a cyclic configuration, too. Formamide accepts the H proton from the amino group of serine and offers H of amino group to amino group of serine. The cyclic arrangement results in more bent hydrogen bonds, the deformation from linearity are 37.3° for the $\text{NH}\cdots\text{N}_\text{S}$ hydrogen bond and 27.2° for the $\text{NH}\cdots\text{O}_\text{F}$ one at the 6-311++G(d,p) level.

For structure FS4, formamide offers the H proton to the hydroxyl group of serine and this is the same as the configuration FS1, however, unlike FS1, formamide accepts the H proton from the amino group not the hydroxyl group. The 6-311++G(d,p) basis set level calculations yield the $R_{\text{OF-HS}}$ of 2.310 Å and $R_{\text{OS-HF}}$ of 1.957 Å and the departures of the $\text{NH}\cdots\text{O}_\text{S}$ angles from the linearity is 9.9°.

For structure FS5, formamide accepts the H proton from the amino group of serine and offers the H proton to the carbonyl group of the serine. Moreover, in this structure, the hydrogen bond is quasi-linear. The departure of the $\text{NH}\cdots\text{O}_\text{F}$ angle from the linearity is 13.8° at the 6-311++G(d,p) level, while the $\text{NH}\cdots\text{O}_\text{S}$ angles is 9.4°.

FS6 also shows a cyclic structure, in which serine bonded to the carbonyl group, all the results indicate the tendency of the hydrogen of hydroxyl group to interact with the O of formamide, and the interaction distance is 1.663 Å at the 6-311++G(d,p) level. In addition, in FS6, formamide offers the proton of the amino group to the carbonyl group and $R_{\text{OS-HF}}$ is 1.910 Å. From all the values (in Table 3) of the hydrogen-bond distances, we can see the values of FS6 are the minimal, which indicates that the hydrogen bonds are very strong, therefore, the interaction energy must be the largest and this structure is the most stable.

With respect to structure FS7, it is also a cyclic structure and turns out a six-member ring. In this configuration, the COOH of serine and the NH of

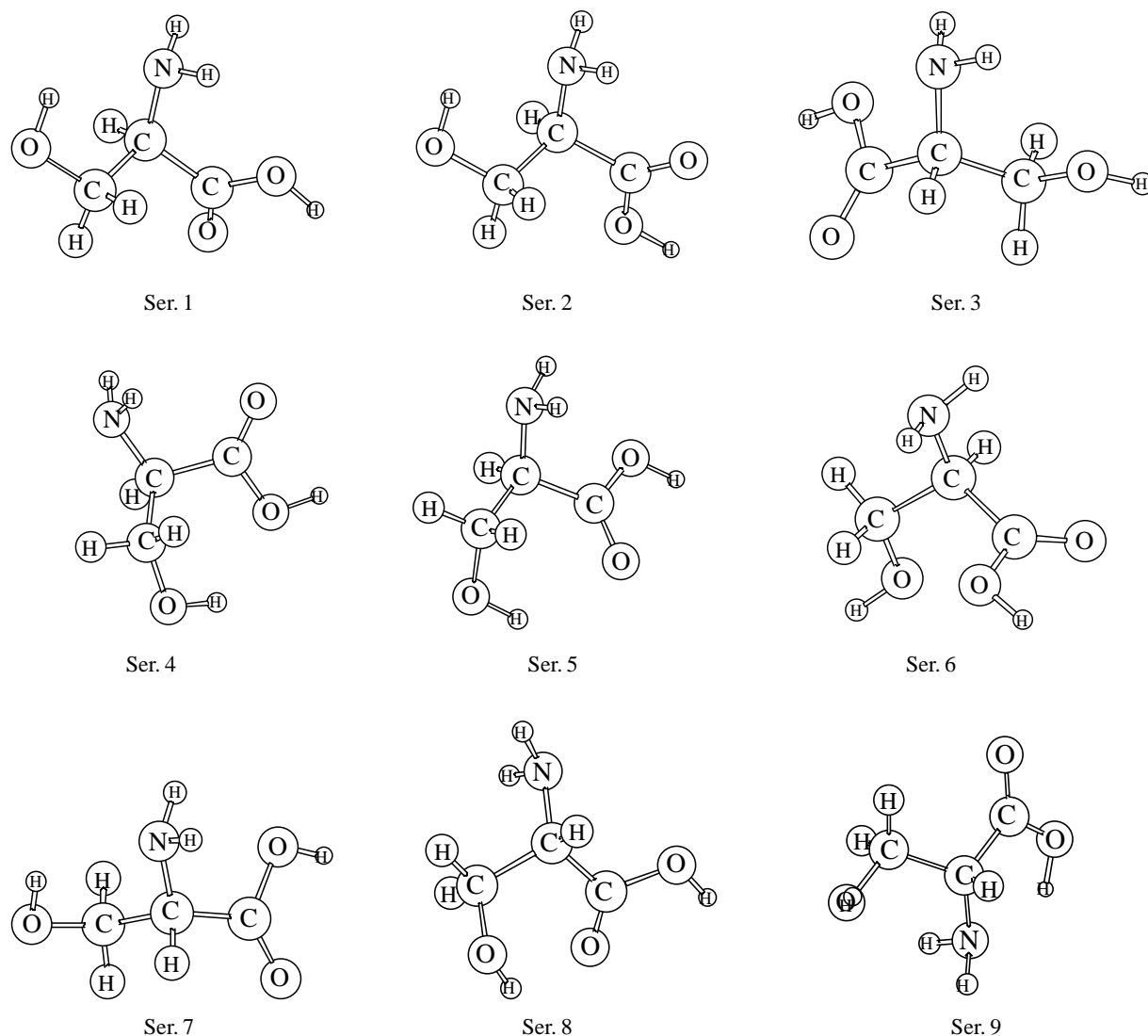


Fig. 1. Nine possible conformers of serine in gas phase at B3LYP/6-311++G(d,p) level.

formamide are the hydrogen acceptor as well as the hydrogen donor; formamide offers the H proton of the amino group to the carbonyl group. Furthermore, the cyclic arrangement results in more bent hydrogen bonds, the deformation from linearity is 40.6° for the $\text{NH}\cdots\text{O}_\text{S}$ hydrogen bond at the 6-311++G(d,p) level.

FS8 is also a cyclic structure with formamide accepting a proton from the hydroxyl group while donating a proton to the amino group. In this structure, the hydrogen bond is quasi-linear. The departure of the $\text{NF}\cdots\text{HS}$ angle from the linearity is 17.9° at the 6-311++G(d,p) level, while the $\text{NS}\cdots\text{HF}$ angle is 13.5° .

For structure FS9, formamide offered the H proton to the carbonyl group of serine and this is the same as the configuration FS7, however, unlike FS7, formamide accept the H proton from the amino group not the hydroxyl group. The 6-31++G(d,p) basis set level calculation the $R_{\text{NF}\cdots\text{HS}}$ of 2.865 Å and $R_{\text{OS}\cdots\text{HF}}$ of 2.042 Å. Moreover, The departure

of the $\text{OS}\cdots\text{H}_\text{F}$ angle from the linearity is 11.9° at 6-311++G(d,p) level.

For structure FS10, it is a cyclic configuration, too. Formamide accepts the H proton from the amino group of serine and this is the same as the configuration FS4, however, unlike FS4, the H proton that formamide offers to serine is not from the amino group but the CHO group.

In FS11, there also is a cyclic structure, in which formamide bonded to the hydroxyl group, all the results indicate the tendency of the oxygen of formamide to interact with the H of serine and this is the same as the configuration FS6, and in this structure H proton that formamide offers to serine is not from the amino group but the CHO group, and $R_{\text{OS}\cdots\text{HF}}$ is 2.384 Å, slightly longer than that of the structure FS6. Therefore, the interaction energy of this structure will be smaller than that of the complex FS6. Also this structure is the most stable. Moreover, the departure of the $\text{OF}\cdots\text{H}_\text{S}$ angle from the linearity is 1.2° at 6-311++G(d,p) level.

Table 2
The structural parameters calculated for formamide and serine

Parameters	B3LYP ^{a,b}	B3LYP ^{a,b}	HF ^b	MP2 ^b	Expt ^b
<i>Formamide</i>					
R _{N-C}	1.360	1.364	1.349	1.377	1.352
R _{CH}	1.106	1.100	1.081	1.100	1.098
R _{C=O}	1.212	1.245	1.189	1.263	1.219
∠NCH	112.5	113.7	114.4	114.0	112.7
∠NCO	125.1	124.4	124.2	124.3	124.7
<i>Serine</i>					
R _{O1C2}	1.409	1.446	1.422	1.466	1.433
R _{O1H8}	0.971	0.986	0.954	0.988	0.88
R _{C2C3}	1.548	1.555	1.538	1.554	1.510
R _{C3N4}	1.460	1.461	1.446	1.475	1.485
R _{C3C5}	1.523	1.517	1.510	1.523	1.527
R _{C5=O6}	1.206	1.234	1.211	1.251	1.247
R _{C5O7}	1.352	1.378	1.349	1.399	1.240
R _{O7H14}	0.971	0.982	0.955	0.987	
∠C3C2O1	109.9	108.9	109.5	109.0	110.0
∠O1C2H10	111.0	110.6	110.4	110.5	109.6
∠C3C2H10	109.1	109.7	109.9	109.5	107.6
∠N4C3C2	108.1	108.8	109.5	108.7	109.7
∠C5C3C2	110.3	110.6	110.5	110.8	112.6
∠N4C3C5	113.5	113.0	112.9	112.9	110.8
∠C3C5O6	125.2	125.9	125.8	126.3	116.3
∠C3C5O7	111.8	111.6	112.0	110.9	118.4
∠C5O7H14	108.1	111.5	114.7	110.9	

^a Represent 6-311++G(d,p) and 6-311++G(d) basis sets, respectively.

^b Distances in Å, angles in degree.

For structure FS12, formamide is not only the hydrogen acceptor but also the hydrogen donor; it accepts the H proton from the amino group of serine offers the H proton the CHO group. The R_{OF-HS} is 2.067 Å and R_{OS-HF} is 2.410 Å at the 6-311++G(d,p) level. The departure of the NH...O_F angle from the linearity is 3.6°.

FS13 exhibits a cyclic conformation, too, which is similar to the FS12 structure, the only difference is that formamide offers the H proton to the hydroxyl group not to the carbonyl group. R_{OF-HS} is 2.214 Å at the 6-311++G(d,p) longer than that of structure FS12, hence, the interaction energy must be smaller than FS12. In addition, the CH...O_S angle is 135.9° and the CH...O_F is 120.7°, which are largely beyond the linearity.

As to the configuration FS14, unlike all the structures discussed above, it is not a cyclic structure; there is only one hydrogen bond between the amino group of formamide and the hydroxyl group of serine. The interaction distance is 1.970 Å for the 6-311++G(d,p) level. Furthermore, the NH...O_G angle is 178.0° which is almost close to linearity.

With respect to the last structure FS15, there is only one hydrogen bond too and the serine bonded to the carbonyl, all the results indicate the tendency of the hydrogen of formamide to interact with the oxygen of serine, the interaction distance is 2.172 Å at the 6-311++G(d,p) level. The departure of OH...O_F angle from the linearity is 8.4°.

Finally, one additional point is worth mentioning concerning the structure of formamide–serine complexes.

We have found 15 structures, 13 of which are being cyclic structures; the other two are not. As we all know, hydrogen bond can be formed between H atom and O, F, N atoms, and so on. Therefore, in this paper, there are four types of structures, one type is that two hydrogen bonds are located between H atom and O atom and the structures are being cyclic, such as FS1, FS2, FS4, etc.; the second one is that one hydrogen bond is between H atom and O atom but the other is between H atom and N atom and the structures are also being cyclic, such as FS3, FS7, FS9; the third one is that two hydrogen bonds are between H atom and N atom and the structures are being cyclic, such as FS8; the fourth one is that there is only one hydrogen bond between H atom and O atom or N atom, such as FS14 and FS15.

Interaction energies are calculated for the formamide–serine hydrogen bond by taking the energy difference between the fragments and the complex:

$$E_{\text{int}} = E_{\text{FS}} - E_{\text{formamide}} - E_{\text{serine}} \quad (1)$$

where E_{FS} , $E_{\text{formamide}}$ and E_{serine} are the electronic energies of the complex system, formamide and serine, respectively. 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 [29] is employed. In this case, the corrected E_{int} is given by

$$E_{\text{int}(\text{cp})} = E_{\text{FS}} - E_{\text{formamide}(\text{cp})} - E_{\text{serine}} \quad (2)$$

where $E_{\text{formamide}(\text{cp})}$ and $E_{\text{serine}(\text{cp})}$ are computed with the basis set of the complex FS.

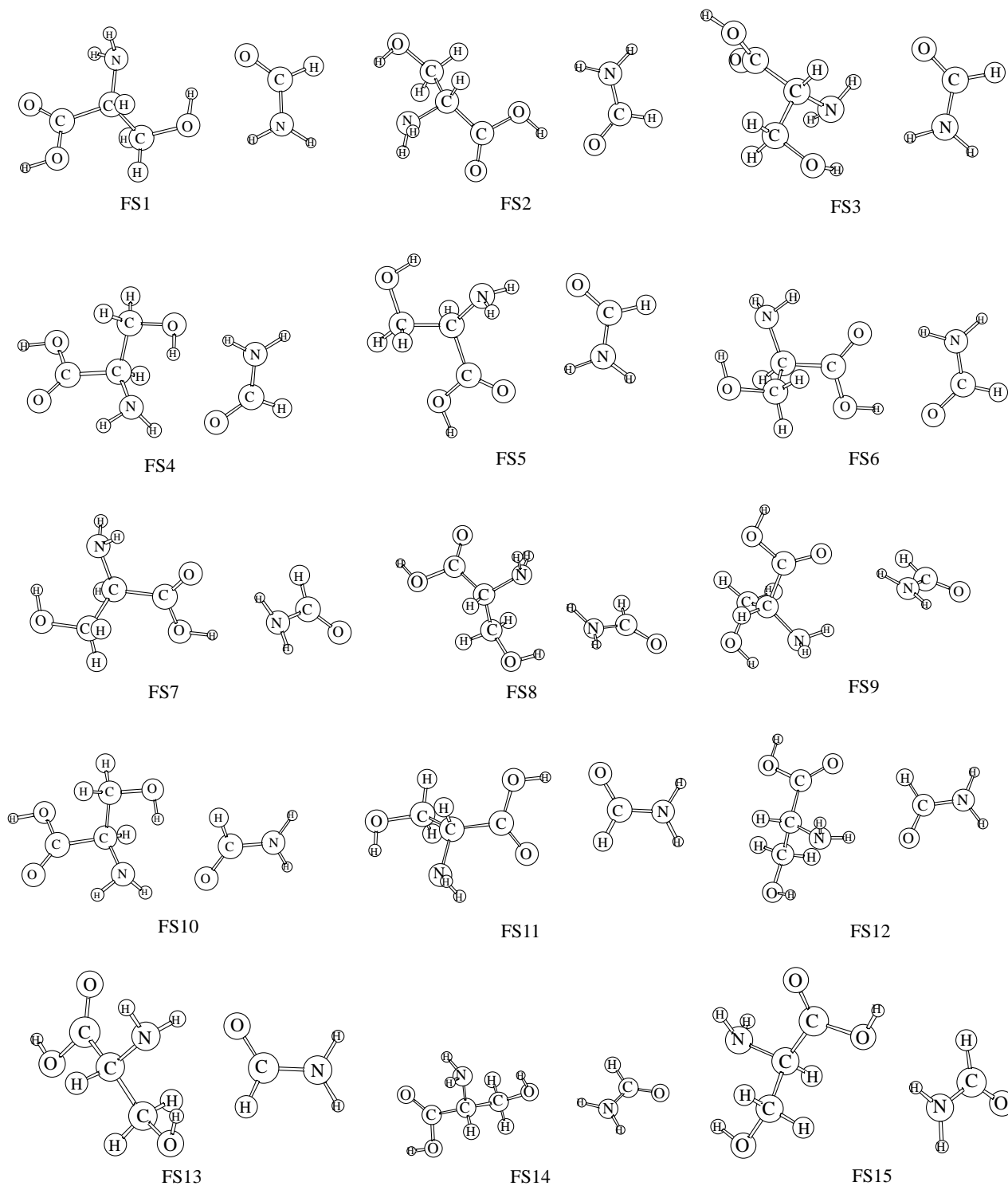


Fig. 2. The optimized structure of formamide-serine complexes at B3LYP/6-311++G(d,p) level.

To analyze in more details the role of basis set size effects on the binding energy between formamide and serine, we use Table 4, which gives a detailed analysis of the interaction zero-point vibrational energy (ZPVE) obtained with several different theoretical models. The numbers shown in the parenthesis are corrected for BSSE using the counterpoise method of Boys and Bernadi [29]. As

expected, basis set sensitivity exists. The interaction energy computed using the minimal basis set 6-31G is much higher. As the basis set enlarges, the computed values decrease and converge smoothly. The general importance of including BSSE corrections in calculated binding energies has been well documented in the literature. From Table 4 we can see that the magnitudes of BSSE are decreasing with the basis

Table 3

The optimized geometric parameters of the formamide–serine complex using B3LYP method at different basis set levels

Species		6-31G ^a	6-31+G ^a	6-31+G(d) ^a	6-31++G(d) ^a	6-311++G(d,p) ^a
FS1	R _{OF-HSS}	1.988	2.208	2.088	2.081	2.121
	R _{OS-HF}	1.878	1.898	2.012	2.012	2.022
FS2	R _{OF-HS}	1.678	1.692	1.780	1.780	1.773
	R _{OS-HF}	2.139	2.211	2.349	2.345	2.370
FS3	R _{OF-HS}	2.000	2.165	2.113	2.113	2.128
	R _{NS-HF}	2.212	2.219	2.275	2.273	2.291
FS4	R _{OF-HS}	2.065	2.220	2.268	2.269	2.310
	R _{OS-HF}	1.823	1.839	1.936	1.935	1.957
FS5	R _{OF-HS}	1.951	2.001	2.082	2.070	2.084
	R _{OS-HF}	1.926	1.942	2.000	1.998	2.008
FS6	R _{OF-HS}	1.574	1.595	1.687	1.686	1.663
	R _{OS-HF}	1.829	1.865	1.910	1.992	1.910
FS7	R _{NF-HS}	2.022	2.067	2.032	2.031	2.087
	R _{OS-HF}	2.036	1.972	2.170	2.169	2.160
FS8	R _{NF-HS}	2.101	2.156	2.142	2.141	2.204
	R _{NS-HF}	1.915	1.966	2.035	2.035	2.058
FS9	R _{NF-HS}	2.575	3.073	2.850	2.859	2.865
	R _{OS-HF}	1.953	1.982	2.035	2.035	2.042
FS10	R _{OF-HS}	2.083	2.175	2.252	2.252	2.274
	R _{OS-HF}	2.296	2.384	2.613	2.610	2.598
FS11	R _{OF-HS}	1.601	1.618	1.715	1.703	1.685
	R _{OS-HF}	2.261	2.337	2.389	2.387	2.384
FS12	R _{OF-HS}	1.946	1.974	2.057	2.057	2.067
	R _{OS-HF}	2.265	2.316	2.412	2.410	2.410
FS13	R _{OF-HS}	2.033	2.126	2.179	2.204	2.214
	R _{OS-HF}	2.292	2.203	2.616	2.618	2.659
FS14	R _{OS-HF}	1.832	1.848	1.964	1.964	1.970
	R _{OS-HF}	2.004	2.034	2.156	2.152	2.172

^a Distances in Å, angles in degree.

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

From the values of Table 4, we can see that the relative stability order of the 15 structures is FS6>FS11>FS4>FS2>FS5>FS1>FS10>FS14>FS3>FS7>FS12>FS13>FS8>FS9>FS15. 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 that the stability of FS6 derives from the formation of a pair of hydrogen bonds between the serine and formamide due to the strongest interaction (the shortest hydrogen bond distance). At the

Table 4

Interaction energies (kJ/mol) of formamide–serine complex

	6-31G ^a	6-31+G ^a	6-31+G(d) ^a	6-31++G(d) ^a	6-311++G(d,p) ^a
FS1	45.3 (40.5)	35.7 (39.5)	23.0(28.8)	23.0 (28.9)	22.1 (28.3)
FS2	55.5(54.7)	44.2(51.6)	31.6(38.0)	31.7(37.7)	30.2(37.6)
FS3	34.7(30.5)	44.4(51.9)	19.2(25.0)	19.2(24.8)	17.9(23.6)
FS4	59.8(59.8)	44.4(57.8)	30.4(41.8)	30.4(41.7)	28.9(40.8)
FS5	47.4(44.4)	35.4(42.8)	27.2(34.2)	27.2(33.9)	26.3(33.9)
FS6	86.8(89.1)	70.8 (84.9)	55.9(68.1)	56.1(68.2)	54.5(68.4)
FS7	30.3(31.2)	19.9(26.8)	18.2(25.0)	18.5(25.0)	16.1(24.2)
FS8	23.6(35.2)	13.5(28.5)	12.4(25.4)	12.5(25.2)	10.6(24.0)
FS9	23.7(21.4)	17.8(20.3)	12.6(14.2)	12.8(16.5)	12.2(16.8)
FS10	35.5(35.6)	30.7(34.3)	20.8(25.0)	20.8(24.8)	19.9(24.7)
FS11	67.1(67.4)	55.9(65.8)	43.1(51.7)	43.2(51.7)	41.8(51.6)
FS12	32.4(28.6)	25.0(29.5)	16.4(21.9)	16.5(21.5)	16.1(21.9)
FS13	29.0 (28.9)	15.0(17.7)	10.3(19.5)	10.5(18.7)	9.8(18.4)
FS14	35.5(35.6)	30.6(34.6)	20.8(24.8)	20.8(24.7)	19.9(24.5)
FS15	18.9(15.7)	10.9(11.8)	5.8(7.6)	5.8(7.2)	5.3(8.1)

^a Values are corrected for zero-point vibrational energy and values in the parentheses are results with correction for basis set superposition.

Table 5

Frequencies (in cm^{-1}), infrared (km/mol, in parentheses), and assignments for monomer and complexes at B3LYP/6-311 + +G(d,p) level

		FS1	FS2	FS3	FS4	FS5	FS6	FS7	FS8	FS9	FS10	FS11	FS12	FS13	FS14	FS15
v(I)	Assign- ment	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)	v(I)
<i>Formamide</i>																
568 (11)	NCO scissors	608 (9)	601 (13)	606 (79)	604 (2)	597 (14)	616 (6)	573 (20)	594 (34)	583 (12)	571 (29)	592 (42)	571 (48)	570 (42)	587 (11)	579 (21)
636 (18)	NH ₂ wag	659 (101)	674 (14)	737 (40)	831 (6)	752 (56)	817 (32)	655 (190)	634							
(160)	708 (24)	649 (26)	664 (20)	648 (16)	648 (21)	759 (5)	695 (1)									
1262	CN	1310	1302	1308	1308	1302	1340	1249	1265	1270	1273	1289	1269 (5)	1273	1279	1269
(117)	stretch	(109)	(88)	(102)	(87)	(115)	(158)	(127)	(138)	(122)	(148)	(72)		(136)	(113)	(119)
1790	C=O	1768	1755	1765	1765	1760	1722 (8)	1799	1787	1779	1763	1726	1758	1767	1777	1787
(465)	stretch	(450)	(659)	(419)	(430)	(195)		(472)	(525)	(861)	(460)	(224)	(407)	(485)	(563)	(579)
2943	CH	2957	3003	2968	2953	2961	3003	2960	2938	2941	2986	3039	2973	2979	2938	2935
(104)	stretch	(137)	(113)	(123)	(141)	(133)	(267)	(71)	(86)	(96)	(24)	(44)	(49)	(34)	(105)	(104)
3579	NH ₂	3475	3554	3486	3380	3482	3384	3469	3344	3520	3577	3578	3578	3578	3487	3552
(36)	stretch	(213)	(98)	(260)	(446)	(388)	(739)	(33)	(556)	(247)	(58)	(51)	(51)	(48)	(485)	(130)
3716	NH ₂	3690	3701	3688	3615	3683	3677	3615	3615	3664	3714	3713	3715	3714	3661	3687
(45)	astretch	(113)	(105)	(111)	(110)	(112)	(118)	(93)	(79)	(145)	(49)	(58)	(48)	(49)	(166)	(139)
1019 (2)	NH ₂ rocking	1090 (151)	1022 (4)	1027 (75)	1054 (10)	1019 (2)	1023 (6)	1018 (2)	1027 (89)	1011 (1)	1045 (1)	1024 (6)	1021 (5)	1017 (11)	1021 (5)	1015 (5)
<i>Serine</i>																
1121	CN	1160	1133	1127	1126	1134	1136	1133	1127	1127	1124	1179	1120	1117	1123	1111
(149)	stretch	(48)	(75)	(135)	(164)	(188)	(18)	(43)	(110)	(131)	(174)	(12)	(232)	(237)	(142)	(216)
1183	NH wag	1254	1195	1188	1198	1189	1178	1204	1182	1184	1194	1227	1189	1199	1186	1180
(54)		(11)	(379)	(10)	(58)	(55)	(12)	(171)	(55)	(86)	(49)	(117)	(35)	(24)	(67)	(42)
1257 (8)	OH wag	1296 (56)	1270 (183)	1264 (4)	1246 (12)	1267 (3)	1303 (120)	1249 (127)	1255 (7)	1260 (9)	1250 (18)	1301 (287)	1272 (165)		1278 (5)	1261 (12)
1433	OH	1417	1433	1426	1445	1437	1430	1435	1424	1431	1439	1370 (2)	1437	1448	1439	1428
(66)	bending	(125)	(53)	(45)	(70)	(88)	(68)	(21)	(24)	(62)	(49)		(76)	(66)	(82)	(69)
1670	NH ₂	1671	1670	1684	1640	1695	1669	1669	1671	1672	1645	1513 (2)	1692	1675	1670	1669
(35)	bending	(37)	(36)	(32)	(98)	(36)	(34)	(35)	(33)	(41)	(109)		(30)	(42)	(38)	(36)
1806	CO	1806	1798	1808	1808	1783	1761	1799	1804	1790	1806	1669	1799	1817	1811	1821
(313)	stretch	(309)	(177)	(306)	(320)	(659)	(834)	(472)	(315)	(96)	(315)	(35)	(470)	(320)	(305)	(282)
3503 (7)	NH ₂ syn- stretch	3511 (5)	3497 (7)	3419 (101)	3504 (25)	3456 (105)	3501 (6)	3469 (33)	3473 (5)	3506 (7)	3502 (24)	3497 (6)	3427 (255)	3464 (94)	3502 (6)	3505 (8)
3584	NH ₂	3584	3579	3520	3587	3549	3582	3528	3544	3593	3584	3580	3581	3586	3585	3587
(13)	asyn- stretch	(11)	(12)	(50)	(83)	(59)	(12)	(799)	(11)	(23)	(75)	(11)	(21)	(25)	(16)	(14)
3726	OH	3622	3719	3766	3615	3703	3720	3615	3734	3737	3664	3717	3712	3655	3679	3734
(74)	stretch	(246)	(74)	(52)	(110)	(89)	(74)	(93)	(383)	(72)	(81)	(76)	(80)	(108)	(85)	(74)
3750	OH	3749	3319	3750	3755	3749	3104	3727	3748	3745	3754	3182	3753	3754	3748	3740
(68)	stretch	(63)	(1089)	(70)	(75)	(67)	(1330)	(71)	(67)	(72)	(71)	(1743)	(59)	(65)	(77)	(71)

same time, the instability of FS15 is by reason of the weakest interaction, it is one hydrogen bond structure. For the other structures, we can also estimate the stability by the interaction energy and the interaction distance.

3.3. 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. And the elucidation of reaction mechanisms via vibrational mode analysis gets more and more attentions from our laboratory [31–34]. In Table 5, we give the B3LYP/6-311++G(d,p) values for both vibrational frequencies and IR intensities of the 15 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 5. The C=O stretching frequencies are found to reduce for all structures but structure FS7 (which is increased by 9 cm^{-1}) considered here (22, 35, 25, 25, 30, 68, 3, 11, 27, 64, 32, 23, 13, 3 cm^{-1} , respectively). This is in consistent with the bond distance change discussed above. The C–H stretching frequencies also show slight changes in their values on hydrogen bonding. For instance, in structures FS8, FS9, FS14, FS15, the C–H stretching frequencies are red-shifted by 5, 2, 5 and 8 cm^{-1} , respectively, and in structures FS1, FS2, FS3, FS4, FS5, FS6, FS7, FS10, FS11, FS12, FS13, the C–H stretching frequencies are blue-shifted by 14, 60, 25, 10, 18, 60, 17, 43, 96, 30 and 36 cm^{-1} , respectively. The C–N stretching is found to be blue shifted except FS7 (red-shifted by 13 cm^{-1}) and the maximum increase is observed for structure FS6 (78 cm^{-1}). At the same time, the NCO scissoring frequencies are also found to be blue shifted for all structures considered here (40, 33, 38, 36, 29, 48, 5, 26, 15, 3, 24, 3, 2, 19 and 11 cm^{-1} , respectively.) It is interesting to note the upward shift of the bonding mode frequency in formamide 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 serine in different configurations. For the modes of serine in the complex, the stretching frequencies associated with the hydrogen bond undergo shifts to lower frequencies compared with the free monomer. For example, the O–H stretching modes are red-shifted by 104, 111, 71 and 365 cm^{-1} for structures FS1, FS4, FS7, FS13, 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 predict that IR spectral characteristics might be of great interest in the analysis of the experimental spectral features. It is considered more difficult to predict accurate shifts in

absorption intensities, which is unfortunate. For this system, there is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor of the types NH–O, OH–O, and NH–H. From the results presented in Table 5, we can see that 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 68 to 1089, 1330, 1743 km/mol for complex FS2, FS6, FS11, respectively, which are approximately 16, 20 and 26 times as large as that of the mode in the monomer. The N–H stretching intensities change from 36 to 213, 260, 446, 388, 556, 247, 485 km/mol for complex FS1, FS3, FS4, FS5, FS8, FS9, FS14, respectively. Of course, the largest change occurs in FS6 (up to 739 km/mol , approximately 21 times as large as 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.

4. Conclusions

The hydrogen bond interaction of 1:1 complex between formamide and serine has been analyzed using density functional theory (DFT) method at varied basis set levels from 6-31G to 6-311++G(d,p). Fifteen structures are considered: 13 of them are cyclic double-hydrogen bonded structure and the other two are one-hydrogen bonded structure. Among them the cyclic double hydrogen bonded structure (FS6) is the most stable at all levels; another cyclic structure FS15 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 serine. Moreover, the infrared spectrum frequencies, IR intensities and the vibrational frequency shifts are reported. We found that the stretching frequencies associated with the hydrogen bond undergo shifts to lower frequencies compared with the free monomer and there is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor of the types NH–O, OH–O, and NH–H.

Acknowledgements

This work is supported by the Natural Science Foundation of Shandong Province (Z2002F01), the State Key Laboratory Foundation of Crystal Material and the National Natural Science Foundation of China (2967305).

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