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Theoretical Studies on the Hydrogen Bonding Interaction of Complexes of Formic Acid with Water

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The hydrogen bonding of the complexes formed between formic acid and water molecules (with up two water) has been completely investigated in the present study using density functional theory (DFT) and second-order Moller−Plesset perturbation (MP2) method; the large basis sets 6-311++g(d,p) and 6-311++g(2d,2p) have been employed to determine the equilibrium structure and vibrational frequencies of the interacting complexes. Twelve reasonable geometries on the potential energy hypersurface of the formic acid and water system are considered; six are with one water molecule, and six are with two water molecules. For the complexes with one water molecule, three are with the (T)-formic acid and three are with (C)-formic acid, and the most stable structure is a cyclic double-hydrogen-bonded structure. For the complexes with two water molecules, we calculated six structures, the global minimum being a cyclic double-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 vibrational frequency shifts are reported. Finally the solution phase studies are also carried out using the Onsager reaction field model in water solvent at B3LYP/6-311++g(d,p) level.

Introduction

Formic acid is a major organic constituent in cloud and fogwater, as well as in precipitation.[1] Formic acid is an oxidation product of organics both naturally and anthropogenically present, as well as being directly emitted anthropogenically. A significant amount of formic acid in the atmosphere is present in the aqueous phase. And formic acid is one of the simplest molecules usually chosen as model for studying the biological systems exhibiting the organic acidic type of bonding. The nature of hydrogen bonding between formic acid and water can explain the hydrogen-bonding mechanism expected in the hydration of organic acids. Due to the simplicity of this model, the characterization of the hydrogen-bonding interactions between water and formic acid has been of considerable interest to experimentalists and theoreticians alike. Although previous studies[2−6] have examined complexes of water and formic acid using both theoretical and experimental methods, there have no studies on this system both in the gas phase and in the solution phase.

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.[7−9] 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 formic acid−water complex as obtained by high-level ab initio calculations. We thus report geometry optimization and calculated bonding energies between formic acid and water for a variety of theoretical models and basis sets. The roles of basis set size and basis set superposition effects are analyzed in detail. The stable structure found for this complex is not entirely new, and in fact, it has been obtained previously by explicit calculations. However, in the present paper, we put forward what we believe are now the most accurate results for the hydrogen bond interaction between formic acid and water, 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 new intermolecular frequencies, 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 attention to the influence of solvent effects in both structure and stability of this hydrogen-bonded system.

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;[10,11] 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 (SCF), the second-order Moller−Plesset theory (MP2), and the hybrid density functional methods B3LYP to test the reliability of these methods to the hydrogen-bonding systems.

For hydrogen bonding, it is expected that both diffuse and polarization functions may be necessary in the basis sets, we

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TABLE 1: Structural Parameters Calculated for Formic Acid and Water

molecule	coordinate	B3LYP1[a]	B3LYP2[a]	HF[a]	MP2[a]	expt[a]
H_2O	O−H	0.962	0.961	0.941	0.959	0.957
	H−O−H	105.1	105.1	106.2	105.5	104.5
trans-HCOOH	O−H	0.971	0.969	0.947	0.969	0.972
	C═O	1.199	1.198	1.177	1.205	1.202
	C−H	1.098	1.095	1.086	1.096	1.097
	C−O	1.346	1.346	1.321	1.349	1.343
	H−O−C	108.0	107.7	109.5	106.4	106.2
	O−C═O	125.2	125.1	124.9	125.2	124.5
	H−C═O	125.3	125.2	124.6	125.3	124.8
cis-HCOOH	O−H	0.966	0.964	0.942	0.964	
	C═O	1.192	1.191	1.170	1.198	
	C−H	1.105	1.102	1.092	1.104	
	C−O	1.353	1.352	1.327	1.355	
	H−O−C	110.0	110.0	111.5	108.3	
	O−C═O	122.6	122.5	123.0	122.6	
	H−C═O	123.9	123.9	123.2	124.0	

[a] Distances in Å; angles in deg.

thus analyze the separate influence of the diffuse and polarization functions. The geometry optimization of the formic acid−water has been carried out using SCF, MP2, and B3LYP correlation methods with the 6-31g, 6-31g(d), 6-31+g(d), 6-311++g(d,p), and 6-311++g(2d,2p) basis sets, along with analytic vibrational frequency calculations.

After these optimized structures are obtained, the most reliable CCSD(T) (coupled-cluster models) single-point calculations on these geometries are used to evaluate the binding energies. Zero-point energies were computed using the harmonic vibrational frequencies at each level of theory. The interaction energy between the partners in each complex at the energetic minimum was calculated using the supermolecule method, which defines it as the difference between the electronic energy of the complex and the combined energies of the isolated molecules. The relevant energies were corrected for zero-point differences using harmonic frequencies. Since we use an incomplete basis set, the results are contaminated with basis set superposition error (BSSE).[12] Each molecule in the complex may use the basis set of the other, resulting in an overestimation of the interaction energy. The interaction energy was corrected for BSSE using the counterpoise method of Boys and Bernardi.[13] All calculations are performed using the Gaussian 98 program.[14]

Results and Discussion

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

As we all know, formic acid has two conformers: *trans*-formic acid and *cis*-formic acid, namely, (T)-formic acid and (C)-formic acid; both conformers are planer. (T)-Formic acid has the acidic hydrogen aligned toward the oxygen atom of the carbonyl group, while (C)-formic acid has the hydrogen atom away from it. And (T)-formic acid is more stable than (C)-formic acid[15] by about 4.0 kcal/mol. Our calculation of this value is in excellent agreement with this experimental number with an energy difference between the two conformations of 4.0 kcal/mol at the B3LYP/6-311++g(2d,2p)//B3LYP/6-311++g(d,p) level of theory. This corresponds to a Boltzman population ratio of about 1000 to 1 in favor of the trans conformer at room temperature.[16]

Although we have not investigated the experimental structure of (C)-formic acid, from the comparison between the calculated structure and the experimental structure of (T)-formic acid, we also can elucidate that our calculation is reliable. 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,p) basis set level reproduce the experimental values most satisfactorily for the (T)-formic acid. The HF bond distances are slightly shorter than the experimental ones. When the basis sets are enlarged to 6-311++g(2d,2p), the difference between the B3LYP calculated and experimental results may be negligible.

Formic Acid and One Water Complexes. *Geometry of the Complexes and Interaction Energies.* We have calculated six conformers of the complex between formic acid and one water molecule. Three of these are with (T)-formic acid, and three are with (C)-formic acid, and all structures are shown in Figure 1. The structural parameters are listed in Table 2.

Surveying the calculated results for the different methods at different basis set level reveals that changes in the monomer geometries upon complexation are relatively minor. The C−O bond length slightly shortened, while the C═O bond length increased a little. Other bond lengths involved in the hydrogen bonding slightly lengthen. The maximum bond length change is less than 0.019 Å at the two large basis set levels.

The most stable conformer is a cyclic complex (FAT1) with both the water and the formic acid acting as hydrogen donor and acceptor, resulting in two relatively strong hydrogen bonds. Of the six complexes of formic acid with one water, this is the only one that has been observed experimentally.[2,4] The study by Priem et al.[4] observed this complex using microwave spectroscopy. They also performed ab initio calculations at the MP2/6-311++g(3df,2p) level of theory. Both theoretical structures obtained were similarly nonplanar minima. The non-hydrogen-bonded hydrogen atom in the water molecule deviates from the COO plane about 9°. In FAT1, there are two hydrogen bonds, R1 and R2. In our work, we will designate hydrogen bonds in which the formic acid is acting as a hydrogen donor to the water as R1 and hydrogen bonds in which the water is donating a hydrogen atom to the carbonyl oxygen atom as R2. For FAT1, the R1 is 1.792, 1.789, and 1.793 Å for MP2/6-311++g(d,p), B3LYP/6-311++g(d,p), and B3LYP/6-311++g(2d,2p) levels; the R2 is 2.144, 2.066, and 2.036 Å, respectively, as Table 2 shows. The results of B3LYP/6-311++g(d,p) level are in good agreement with the structure determined by observed moments of inertia by Priem et al.[4] (1.810 and 2.201 Å) and in excellent agreement with the calculations presented both in that work (1.779 and 2.025 Å) and in the work by Rablen et al.[3] (1.775 and 2.016 Å). Moreover, our calculations are in excellent agreement with those in the work by Simone et al.[5] (1.790 and 2.056 Å). Hartree−Fock method gives a longer hydrogen bond due to its neglect of dispersion energy (1.920 and 2.291 Å).

There is a second conformer (FAT2) with the water acting as hydrogen donor to the carbonyl oxygen of formic acid. In FAT2, the water is situated on the opposite side of the carbonyl group relative to the O−H group, and there is one hydrogen bond type of R2, and it is 2.053, 2.005, and 2.011 Å for MP2/6-311++g(d,p), B3LYP/6-311++g(d,p), and B3LYP/6-311++g(2d,2p) level, which is a little shorter than that of the FAT1.

In a third conformer of (T)-formic acid with one water (FAT3), the water acts a hydrogen donor again, only this time to the oxygen bound to the acidic hydrogen on the formic acid. This is the weakest bound of the three structures of complexes

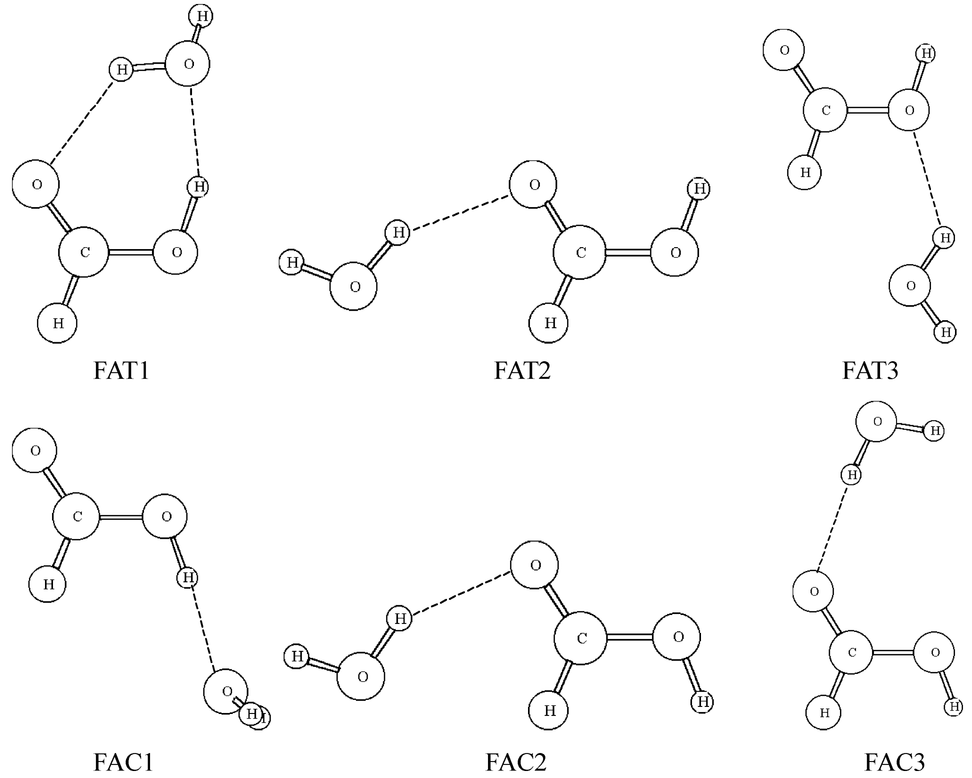


Figure 1. Formic acid complexes with one water molecule in gas phase. Dashed lines indicate hydrogen bonding.

TABLE 2: The Optimized Geometric Parameters of the Formic Acid−Water Complex Using Different Theoretical Models

		B3LYP/ 6-31g^a	B3LYP/ 6-31g(d)^a	B3LYP/ 6-31+g(d)^a	B3LYP/ 6-311++g(d,p)^a	B3LYP/ 6-311++g(2d,2p)^a	HF/ 6-311++g(d,p)^a	MP2/ 6-311++g(d,p)^a
FAT1	R1	1.605	1.737	1.779	1.789	1.793	1.920	1.792
	R2	1.934	1.961	2.042	2.066	2.036	2.291	2.144
FAT2	R2	1.998	2.023	1.988	2.005	2.011	2.141	2.053
	A1^b	96.3	96.8	102.8	103.9	102.4	103.4	99.8
	B1^c	134.4	145.8	147.9	147.9	148.6	142.2	143.3
FAT3	R3	2.022	2.157	2.180	2.189	2.225	2.375	2.204
	A2^d	148.3	151.2	148.2	147.4	147.6	147.1	147.6
	B1	134.3	134.9	128.6	129.5	131.2	123.3	128.1
FAC1	R1	1.635	1.775	1.801	1.812	1.823	1.922	1.817
	A3^e	177.2	179.2	179.5	179.0	178.7	174.8	176.5
FAC2	R2	1.992	2.016	1.998	2.018	2.006	2.159	2.060
	A1	96.6	96.7	100.7	101.3	101.1	101.4	98.8
	B1	137.7	145.4	145.0	144.6	147.6	139.0	142.0
FAC3	R2	2.147	2.114	2.042	2.051	2.044	2.156	2.167
	A1	113.8	113.4	123.9	129.8	130.2	152.9	112.7
	B1	145.6	156.7	171.9	173.4	179.0	170.3	160.6

[a] Distance in Å; angles in deg. [b] A1 is COH_W. [c] B1 is O_FHO. [d] A2 is HOH_W. [e] A3 is OHO_W.

with (T)-formic acid. As Table 2 shows, the interaction, R3, is not terribly strong, which is 2.204, 2.189 (which is the same as that presented in the in the work by Simone et al.[5]), and 2.225 Å for MP2/6-311++g(d,p), B3LYP/6-311++g(d,p), and B3LYP/6-311++g(2d,2p) level, and the MP2/6-311++g(d,p) calculations, which yield the H−O···H angle of 147.6° and O···H−O angle of 128.1°, are in good agreement with the B3LYP values of 147.4° (147.6°) and 129.5° (131.2°). (Values in parentheses are the B3LYP/6-311++g(2d,2p) results).

There are another three structures of complexes with (C)-formic acid: FAC1, FAC2, and FAC3. And all of these structures also have no negative vibrational frequencies. For FAC1, formic acid acts as a hydrogen donor to the water in a nearly linear hydrogen bond, and the O−H···O angle is 179.0°, 178.7°, and 176.5° for B3LYP/6-311++g(d,p), B3LYP/6-311++g(2d,2p), and MP2/6-311++g(d,p) level. In the structure, the hydrogen atoms of water are out-of-plane with respect to the rest of the molecule. FAC1 has an R1-type hydrogen bond with a calculated length of 1.812 Å at the B3LYP/6-311++g(d,p) level, which is in fairly good agreement with previous works[5] (1.813 Å) and similar to the analogous bond in FAT1. And the MP2/6-311++g(d,p) calculation value (1.817 Å) is in excellent agreement with the B3LYP/6-311++g(d,p) value. In FAC1, the carbonyl C=O bond is not hydrogen-bonded to the water so that coordinate is not directly affected by the water.

In FAC2, there is an R2-type hydrogen bond with a calculated length of 2.018 and 2.006 Å at the B3LYP/6-311++g(d,p) and B3LYP/6-311++g(2d,2p) level. The C=O···H and O···H−O angles are 101.3° and 144.6°, respectively, at the B3LYP/6-311++g(d,p) level. And the B3LYP/6-311++g(2d,2p) calculation values are 101.1° and 147.6°, which are in agreement with those of the B3LYP/6-311++g(d,p) level.

The third structure of complexes with (C)-formic acid is FAC3. In FAC3, water acts as a hydrogen donor to formic acid

TABLE 3: Interaction Energies (kJ/mol) of Complexes between Formic Acid and One Water Molecule

method	FAT1[a]	FAT2[a]	FAT3[a]	FAC1[a]	FAC2[a]	FAC3[a]
B3LYP/6-31g	79.6 (68.8)	32.9 (23.2)	26.0 (15.5)	65.1 (57.4)	36.7 (25.0)	28.5 (18.3)
B3LYP/6-31g(d)	63.8 (47.1)	29.3 (16.5)	20.1 (9.2)	48.1 (40.1)	31.8 (18.8)	24.0 (14.9)
B3LYP/6-31+g(d)	47.6 (42.3)	21.9 (20.0)	14.4 (12.2)	40.8 (34.9)	24.4 (22.3)	19.0 (16.6)
B3LYP/6-311++g(d,p)	43.3 (39.7)	20.3 (19.0)	13.4 (11.9)	37.9 (34.1)	22.5 (21.5)	17.6 (16.6)
B3LYP/6-311++g(2d,2p)	43.2 (38.3)	19.2 (18.2)	11.0 (10.0)	33.4 (31.5)	21.4 (20.3)	16.9 (15.8)
CCSD(T)/B3LYP	43.0 (32.5)	22.0 (17.3)	16.7 (12.7)	39.1 (30.1)	24.5 (19.6)	19.0 (15.0)
MP2/6-311++g(d,p)	43.5 (33.6)	22.1 (17.2)	17.0 (12.4)	39.8 (31.0)	24.5 (19.5)	19.7 (14.8)
HF/6-311++g(d,p)	35.3 (32.7)	18.6 (17.7)	12.3 (11.3)	34.4 (31.3)	21.0 (20.1)	16.8 (15.7)
CCSD(T)/MP2	43.2 (32.9)	22.5 (17.4)	17.3 (12.4)	39.2 (29.6)	24.7 (19.6)	20.1 (15.0)
DFT in water	42.8 (37.9)	32.2 (27.8)	21.7 (15.5)	68.2 (67.4)	35.9 (30.2)	46.3 (41.1)

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

also in a nearly linear hydrogen bond, and the O−H···O angle is 173.4° and 179.0° for B3LYP/6-311++g(d,p) and B3LYP/6-311++g(2d,2p) level. FAC3 has an R2-type hydrogen bond, and the interaction distance is 2.167, 2.051, and 2.044 Å for the MP2/6-311++g(d,p), B3LYP/6-311++g(d,p), and B3LYP/6-311++g(2d,2p) levels. Also the C═O···H angle is 129.8° at the B3LYP/6-311++g(d,p) level.

Interaction energies are calculated for the formic acid−water hydrogen bond by taking the energy difference between the fragments and the complex.

$$E_{\mathrm{int}} = E_{(\mathrm{HCOOH})} + E_{(\mathrm{H_2O})} - E_{(\mathrm{HCOOH\cdots H_2O})} \quad (1)$$

Here $E_{(\mathrm{HCOOH})}$, $E_{(\mathrm{H_2O})}$, and $E_{(\mathrm{HCOOH\cdots H_2O})}$ are the electronic energies of HCOOH, H_2O, and the complex system, respectively. To correct the basis set superposition error (BSSE), the counterpoise (CP) method[13] is employed. In this case, the corrected E_{int} is given by that used by I. Mayer,[17] which is

$$E_{\mathrm{int(cp)}} = E_{\mathrm{AB}}(\mathrm{AB}) - E_{\mathrm{A}}(E_{\mathrm{A}}) - E_{\mathrm{B}}(E_{\mathrm{A}}) - [E_{\mathrm{A}}^{0}(\mathrm{A}) - E_{\mathrm{A}}(\mathrm{A})] - [E_{\mathrm{B}}^{0}(\mathrm{B}) - E_{\mathrm{B}}(\mathrm{B})] \quad (2)$$

where $E_{\mathrm{X}}(\mathrm{Y})$ is the energy of the subsystem (fragment) X calculated in the basis of unit Y; E_{A}^{0} and E_{B}^{0} are the energies of the fragments A and B in their actual geometries within the complex; $E_{\mathrm{A}}(\mathrm{A})$ and $E_{\mathrm{B}}(\mathrm{B})$ are the energies of the free fragments in their equilibrium geometries. If zero-point vibrational energy (ZPVE) corrections are applied in the present case, the interaction energy of the complex becomes more repulsive after the correction than the uncorrected or corrected with the CP method. However, application of the ZPVE correction is known to overestimate, as pointed out by Turi and Dannerberg for the hydrogen bond interaction in the nitromethane−ammonia complex,[18] so we did not discuss this correction.

To analyze in more detail the role of basis set size effects on the binding energy between formic acid and one water molecule, we use Table 3, which 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.[13] As expected, basis set sensitivity exists. The interaction energy computed with B3LYP using the minimal basis set 6-31g is much higher. As the basis set enlarged, 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 the table we can see that the magnitude of BSSE decreases with the basis set enlarged, when the diffusion and polarization functions are considered; especially for the 6-311++g(d,p) and 6-311++g(2d,2p) basis sets using the B3LYP method, the inclusion of BSSE correction has minor importance to the binding energy. It was also true for SCF/6-311++g(d,p) level. It is very surprising that the interaction energy computed with HF method is very close to the CCSD(T) results. However, for the MP2 method at this basis set level, the BSSE correction is larger than that of SCF and B3LYP. Here we found that the most accurate values given by CCSD(T) calculations with the MP2 and B3LYP geometries are in fact nearly identical to each other. The change of geometry from MP2 to B3LYP only leads to the energy variation of about 0.9 kJ/mol. This may be also due to the extreme flatness of the formic acid−water potential surface. We also note that the CCSD(T) BSSE correction is larger for both MP2 and B3LYP geometries. It is easy to understand that the stability of FAT1 derives from the formation of a pair of hydrogen bonds between the water and formic acid (in this case, the water acts as a proton donor to the carbonyl group and as a proton acceptor from the hydroxyl group), whose interaction energy is so large as 40.4 kJ/mol at the largest basis level. For FAT2, the interaction energy is 19.2 kJ/mol. And for FAT3, it is the most weakly bound of the complexes with formic acid in the T configuration. The calculated interaction energy is only 11.0 kJ/mol. This reflects that the hydroxyl group on formic acid is a poor hydrogen acceptor. Of the complexes with the formic acid in the C configuration, FAC1, with the formic acid acting as hydrogen donor, is by far the most strongly bound. The calculated E_{int} is 33.4 kJ/mol. This large stabilization is probably due to more than just the one hydrogen bond. After all, that hydrogen bond is slightly longer than the calculated R1-type hydrogen bond in FAT1. The FAC2 and FAC3 complexes have calculated E_{int} of 21.4 and 16.3 kJ/mol, respectively, similar in magnitude to FAT2. This puts their energies very close to the energies of the isolated monomers with formic acid in the T configuration. In a word, the relative stability order of the six structures is FAT1 > FAC1 > FAC2 > FAT2 > FAC3 > FAT3, which is in agreement with previous work.[5]

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(d,p) values for both vibrational frequencies and IR intensities of the six 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 frequencies are found to reduce for all structures except the FAT3 structure considered here (44, 27, 21, 29, and 15 cm^{-1}). This is consistent 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 FAC2, there is a weak interaction between the O of H_2O and H of CHO group; the shift is 47 cm^{-1}. The O−H

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

(T)-Formic Acid

				FAT1		FAT2		FAT3	
expt	ν^a	I^b	assignment	ν^a	I^b	ν^a	I^b	ν^a	I^b
629	678	44	OCO scissors	697	38	639	52	629	35
635	630	160	COH torsion	921	159	687	171	659	165
1037	1051	2	CH rock out of plane	1067	11	1063	3	1061	3
1103	1124	279	COH−CO def	1210	246	1145	273	1103	300
1216	1293	9	CO−COH def	1381	14	1307	18	1275	2
1381	1403	2	CH wag	1451	1	1402	5	1408	9
1767	1816	398	C═O stretch	1772	366	1789	406	1819	383
2953	3058	44	C−H stretch	3055	74	3086	15	3087	10
3551	3738	62	O−H stretch	3381	601	3733	36	3792	37
			H_2O						
1649	1639	71	H_2O bending	1603	142	1619	106	1609	100
3832	3822	7	H_2O sym. stretch	3688	192	3721	256	3740	71
3942	3924	61	H_2O asym. stretch	3890	96	3899	99	3910	97

(C)-Formic Acid

				FAC1		FAC2		FAC3	
expt	ν^a	I^b	assignment	ν^a	I^b	ν^a	I^b	ν^a	I^b
503	524	99	COH torsion	298	38	541	101	532	69
661	660	10	OCO scissors	687	3	670	8	668	12
980	1035	0	CH rock out of plane	1044	0	1051	0	1039	0
1108	1098	60	COH−CO def	1152	105	1122	47	1112	42
1244	1269	322	CO−COH def	1359	306	1279	370	1272	328
1396	1420	0	CH wag	1420	5	1426	1	1419	1
1808	1862	329	C═O stretch	1841	396	1833	320	1847	356
2899	2957	84	C−H stretch	2952	85	3004	33	2989	74
3618	3800	60	O−H stretch	3564	761	3798	74	3797	74
			H_2O						
1649	1639	71	H_2O bending	1626	60	1619	106	1631	83
3832	3822	7	H_2O sym. stretch	3815	20	3718	198	3759	229
3942	3924	61	H_2O asym. stretch	3915	106	3899	96	3894	84

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

stretching of FAT1 is found to be red-shifted as much as 357 cm^{-1}, which corresponds to the strongest interaction, and that of the FAC1 is red-shifted 236 cm^{-1}; this change is a little less than that of the FAT1, which is in good agreement with the interaction energy values of theirs. The non-hydrogen-bonded C−H shows a little change, only but the CH rock of the structure FAT1 is blue-shifted by 48 cm^{-1}. In addition, it is interesting to note that the CH rock out of plane mode shows the upward shift here (16, 12, 10, 9, 16, and 4 cm^{-1}, respectively). Moreover, it is noticeable that the upward shift of the bonding mode frequency in HCOOH upon forming the hydrogen complex, which is typical for the hydrogen bond complex. For instance, the OCO scissoring, CO−CHO deformation, and CHO−CO deformation modes are almost all blue-shifted to different extent with water in different configurations. For the modes of water in the complex, like that of HCOOH, the stretching frequency associated with the hydrogen bond undergoes a shift to a lower frequency compared to the free monomer. 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 considered to be 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. From the results presented in Table 4, it can be seen that the O−H stretching intensities of the water and formic acid involved in the hydrogen bonds are enhanced largely in both hydrogen complexes. For example, the O−H stretching intensities of the water varied from 7 to 192 (198) km/mol for complex FAT1 (FAC2), approximately 28 times that of the mode in the monomer. It is remarkable that the O−H stretching intensities of the water varied from 7 to 256 (229) km/mol for complex FAT2 (FAC3), approximately 36 times that of the mode in the monomer. The OH stretching intensities of the formic acid changed from 62 (60) to 601 (761) km/mol for complex FAT1 (FAC1). For the CH 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 reduce and the related stretching frequencies are red-shifted. Moreover, the increase of the change of the vibrational dipole moments leads to the enhancement of the IR intensities.

Formic Acid and Two Water Complexes. *Geometry of the Complexes and Interaction Energies.* As mentioned earlier, (T)-formic acid is about 1000 times more abundant than (C)-formic acid at room temperature; we will focus on the T conformation of formic acid in the calculations of the complexes of formic acid and two water molecules. In addition, for simplicity, we will only discuss the results with the B3LYP/6-311++g(d,p) basis level.

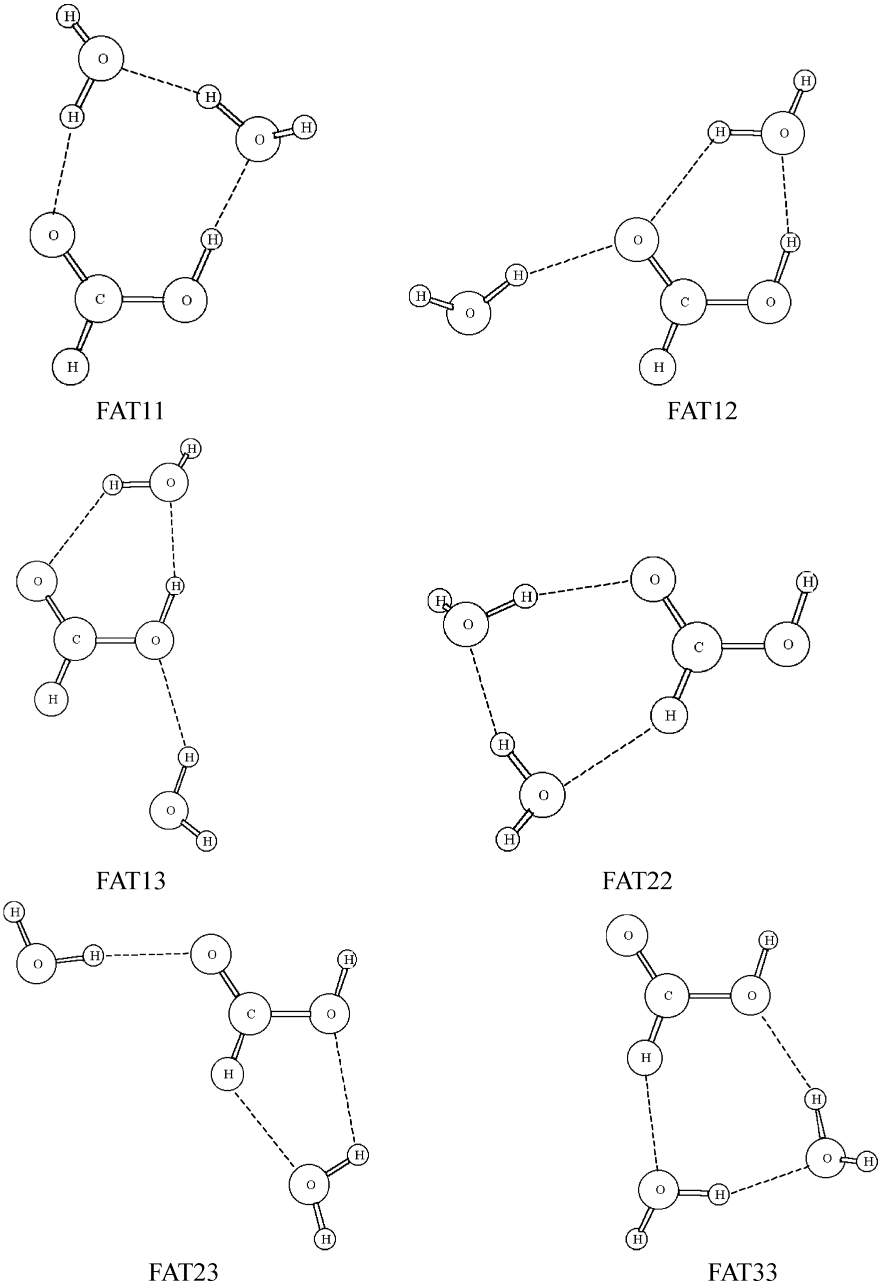
We also have calculated six conformers of the complex between formic acid and two water molecules. All of these are with formic acid in the T configuration and are shown in Figure 2. The structural parameters at the B3LYP/6-311++g(d,p) level are listed in Table 5. All of these structures have no imaginary frequencies, and this indicates that they are true local minima. Of these, FAT11 has been observed in laboratory experiments using microwave spectroscopy.[4] To the best of our knowledge, the others have not been investigated.

FAT11, which forms an eight-member ring with both the water and the formic acid acting as hydrogen donor and acceptor, resulting in two relatively strong hydrogen bonds, is the most stable structure of the six complexes, and the R1 is 1.663 Å, and the R2 is 1.843 Å, which is in fairly good agreement with previous works[5] (1.662 and 1.841 Å). Besides, the two water molecules also have formed a hydrogen bond, and the bond length is 1.758 Å. Because of the formation of the two strong hydrogen bonds, the O−H bond in formic acid is elongated as much as 0.032 Å, which is about 3% longer than that of the monomer, and the C═O bond is extended by about 1% (0.016 Å). As a result of these bonds being elongated, there is a predicted shortening of the single bond C−O, by a little over 2%.

In FAT12, there are three types of hydrogen bonds, R1, R2, and R2′, whose bond lengths are 1.761, 2.128, and 1.957 Å respectively. This is calculated to be slightly longer than that of FAT11. Again, this causes an elongation of the double bond C═O and the single bond O−H in formic acid, and both are by about 2%. In addition, the single bond C−O is shortened by 0.026 Å, about 2% shorter than that of the monomer, this is also because of the elongation of the double bond C═O and the single bond O−H.

For the third complex FAT13, there are also three types of hydrogen bonds, R1, R2, and R3, and they are 1.763, 2.086, and 2.067 Å, respectively. As a result of the formation of the three hydrogen bonds, the double bond C═O and the single bond O−H in formic acid are both elongated by 0.01 and 0.02 Å, respectively. Again, there is also a predicted shortening of the single bond C−O, but this time only by less than 1%.

FAT22 has an R2-type hydrogen bond with a calculated length of 1.897 Å, which is the same as that of the work by



FAT11 FAT12

FAT13 FAT22

FAT23 FAT33

Figure 2. Formic acid complexes with two water molecules in gas phase. Dashed lines indicate hydrogen bonding.

TABLE 5: Formic Acid Bond Distances (in Å) of Complexes between Formic Acid and Two Water Molecules

species	H−C	C═O	C−O	O−H	R1	R2	R2′	R3	R4	R_W
FAT11	1.098	1.215	1.316	1.003	1.663	1.843				1.758
FAT12	1.096	1.218	1.320	0.991	1.761	2.128	1.957			
FAT13	1.096	1.209	1.338	0.991	1.763	2.086		2.067		
FAT22	1.097	1.211	1.337	0.971		1.897			2.210	1.859
FAT23	1.094	1.205	1.347	0.971	0.971	1.973	1.973	2.450	2.359	
FAT33	1.097	1.197	1.368	0.971	0.971			1.999	2.203	1.885

Simone et al.[5] (1.897 Å) and longer than that of FAT11. As a result, the double bond C═O is elongated by about 1%, and the elongation is 0.012 Å. Here we define another type of hydrogen bond as R4, in which formic acid is offering the hydrogen atom of the CHO group to the water. There is an R4-type hydrogen bond in FAT22; its bond length is 2.210 Å, which is a little longer than the other hydrogen bonds. In addition, for FAT22, the hydrogen bond between two water molecules is in existence, with a calculated length of 1.859 Å, which is about 7% longer than that of FAT11. On all accounts, the interaction energy of FAT22 must be lower than that of FAT11.

There are three types of hydrogen bonds in FAT23, R2, R3, and R4 with the calculated bond lengths of 1.973, 2.450, and 2.359 Å, respectively, and the hydrogen bonds R3 and R4 are the longest of all of the hydrogen bonds in the same type. Of these, the R2 and R4 are both longer than those of FAT22, this time by about 4% and 6%, respectively. In a word, the interaction energy of FAT23 should be the lower than FAT22.

For the last complex between formic acid and two water molecules, FAT33, there are two types of hydrogen bonds: R3 and R4, and their bond lengths are 1.999 and 2.203 Å, respectively. In addition, it has an interaction between the two water molecules by the R_W-type hydrogen bond, whose bond length is 1.885 Å, which is 0.127 Å longer than that of FAT22, and this may indicate that interaction energy of this structure will be less than that of FAT22.

Moreover, a few additional points are worth mentioning concerning the structure of formic acid and two water molecule

TABLE 6: Interaction Energies (kJ/mol) of Complexes between Formic Acid and Two Water Molecules

method	FAT11[a]	FAT12[a]	FAT13[a]	FAT22[a]	FAT23[a]	FAT33[a]
B3LYP/6-31g	177.2 (175.3)	113.8 (98.4)	111.3 (98.4)	109.7 (88.1)	55.0 (53.2)	99.7 (81.0)
B3LYP/6-31g(d)	130.2 (118.1)	93.1 (69.5)	86.4 (61.5)	85.9 (61.3)	47.6 (33.7)	71.0 (49.5)
B3LYP/6-31+g(d)	103.5 (100.4)	69.5 (65.6)	63.4 (58.0)	67.5 (62.1)	34.8 (30.9)	55.1 (49.2)
B3LYP/6-311++g(d,p)	95.5 (95.0)	64.2 (63.2)	58.6 (55.8)	62.4 (59.6)	32.3 (30.8)	50.8 (47.9)
B3LYP/6-311++g(2d,2p)	92.1 (91.2)	59.8 (59.6)	53.2 (52.7)	56.5 (55.5)	28.5 (26.3)	43.5 (42.4)
MP2/6-311++g(d,p)	95.5 (81.3)	66.3 (55.8)	62.4 (49.2)	65.1 (51.3)	37.2 (29.4)	56.0 (43.1)
HF/6-311++g(d,p)	76.6 (74.6)	53.7 (51.8)	48.8 (46.0)	53.0 (50.6)	30.0 (28.5)	41.5 (39.1)
DFT in water	79.9 (79.2)	71.9 (70.7)	51.9 (47.9)	46.8 (40.4)	41.1 (36.1)	44.6 (38.9)

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

TABLE 7: Frequencies and IR Intensities of Monomer and Complexes at B3LYP/6-311++G(d,p) Level

			(T)-Formic Acid					
			FAT11	FAT12	FAT13	FAT22	FAT23	FAT33
ν^a	I^b	assignment	ν (I)	ν (I)	ν (I)	ν (I)	ν (I)	ν (I)
678	160	OCO scissors	711 (84)	706 (37)	698 (31)	697 (197)	641 (44)	635 (83)
630	44	COH torsion	683 (126)	549 (136)	568 (154)	638 (98)	677 (174)	651 (206)
1051	2	CH rock out of plane	1091 (51)	1078 (13)	1071 (10)	1102 (5)	1075 (4)	1075 (333)
1124	279	COH−CO def	1253 (237)	1234 (234)	1187 (264)	1150 (287)	1134 (292)	1088 (11)
1293	9	CO−COH def	1400 (7)	1392 (18)	1375 (15)	1309 (19)	1290 (7)	1271 (3)
1403	2	CH wag	1462 (7)	1453 (3)	1453 (2)	1428 (3)	1406 (20)	1433 (14)
1816	398	C═O stretch	1756 (450)	1748 (395)	1781 (355)	1759 (426)	1791 (471)	1816 (406)
3058	44	C−H stretch	3046 (289)	3080 (40)	3078 (36)	3078 (22)	3108 (6)	3071 (12)
3738	62	O−H stretch	3108 (982)	3345 (727)	3347 (744)	3728 (58)	3735 (49)	3736 (49)
			H_2O					
1639	71	H_2O bending	1653 (1627)	1623 (1599)	1620 (1603)	1648 (1629)	1626 (1603)	1638 (1621)
3822	7	H_2O sym. stretch	3586 (3448)	3718 (3698)	3771 (3694)	3632 (3580)	3808 (3725)	3722 (3626)
3924	61	H_2O asym. stretch	3889 (3883)	3894 (3891)	3903 (3889)	3893 (3889)	3917 (3894)	3892 (3890)

[a] Vibration frequencies (ν) in cm^{-1}. [b] IR intensities (I) in km/mol. Values in parentheses of the water are results of the other water molecule.

complexes, which is that the trends exhibited in the complexes of formic acid with one water molecule are typically strengthened when another water molecule is added. For instance, the FAT11 structure shows a further elongation of the O−H bond in formic acid, due to a much stronger R1-type hydrogen bond, whose bond length is 1.663 Å in FAT11, while in FAT1, it is 1.789 Å. In fact, the R1-type hydrogen bond is much stronger in all three structures that have it with two water molecules (FAT11, FAT12, and FAT13) than it is in FAT1.

Interaction energies are calculated for the formic acid and two water hydrogen bonds by taking the energy difference between the fragments and the complex.

$$E_{\mathrm{int}} = E_{(\mathrm{HCOOH})} + E_{(\mathrm{H_2O})} + E_{(\mathrm{H_2O})} - E_{(\mathrm{HCOOH\cdots H_2O\cdots H_2O})} \quad (3)$$

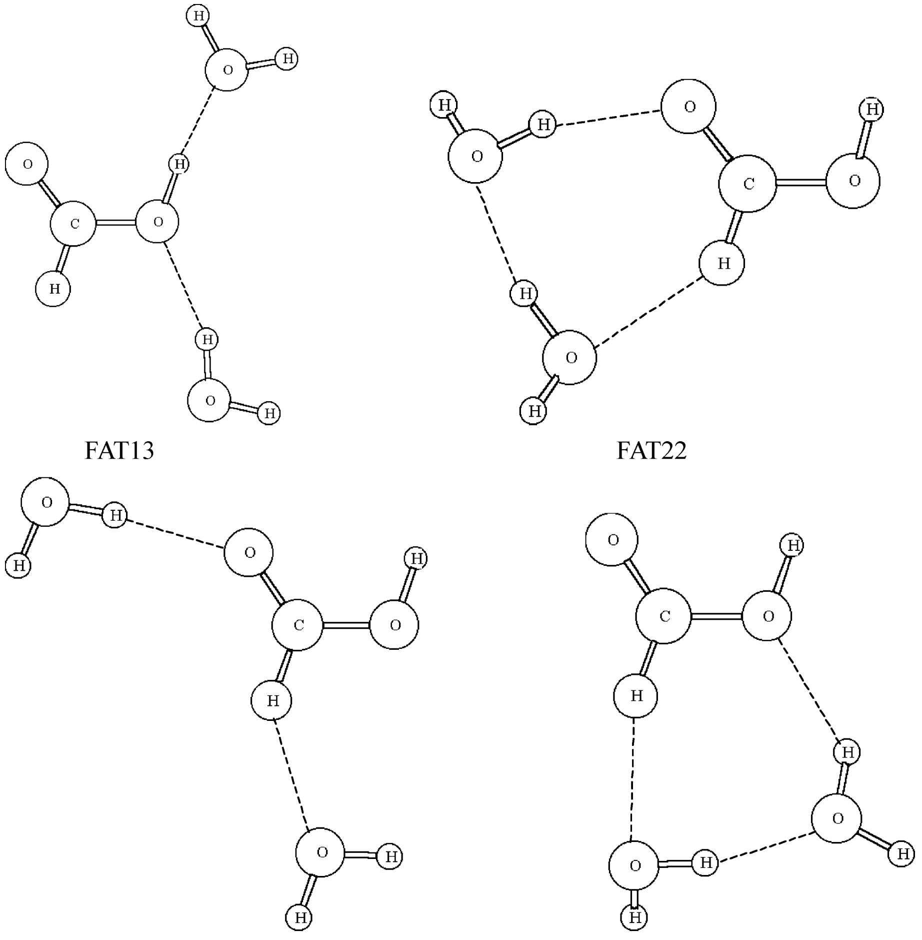
where $E_{(\mathrm{HCOOH})}$, $E_{(\mathrm{H_2O})}$, and $E_{(\mathrm{HCOOH\cdots H_2O\cdots H_2O})}$ are the electronic energies of HCOOH, H_2O, and the complex system, respectively. To correct the basis set superposition error (BSSE), the counterpoise (CP) method[13] is employed. In this case, the corrected E_{int} is given by that used by I. Mayer,[19] which is

$$\begin{aligned} E_{\mathrm{int(cp)}} = {} & E_{\mathrm{ABC}} - E_{\mathrm{AB}}(\mathrm{ABC}) + E_{\mathrm{AB}}(\mathrm{AB}) - E_{\mathrm{AC}}(\mathrm{ABC}) + \\ & E_{\mathrm{AC}}(\mathrm{AC}) - E_{\mathrm{BC}}(\mathrm{ABC}) + E_{\mathrm{BC}}(\mathrm{BC}) - E_{\mathrm{A}}(\mathrm{AB}) - \\ & E_{\mathrm{A}}(\mathrm{AC}) + E_{\mathrm{A}}(\mathrm{ABC}) - E_{\mathrm{B}}(\mathrm{AB}) - E_{\mathrm{B}}(\mathrm{BC}) + \\ & E_{\mathrm{B}}(\mathrm{ABC}) - E_{\mathrm{C}}(\mathrm{AC}) - E_{\mathrm{C}}(\mathrm{BC}) + E_{\mathrm{C}}(\mathrm{ABC}) \end{aligned} \quad (4)$$

where A, B, and C stand for HCOOH, H_2O, and H_2O. The interaction energies of complexes between formic acid and two water molecules obtained with several different theoretical models are listed in Table 6. The numbers shown in parentheses are corrected for BSSE using the counterpoise method of Boys and Bernadi.[13] As expected, basis set sensitivity exists too. Because we have already discussed the role of basis set size effects earlier, for simplicity, here we only analysize the values of the largest basis level B3LYP/6-311++g(2d,2p). From Table 6, it can be seen that FAT11 has the highest interaction energy (92.1 kJ/mol), which is the most stable structure of the complexes between formic acid and two water molecules. And there is an overall strengthening of all of the hydrogen bonds in this structure. The general importance of including BSSE corrections in calculated binding energies also has been well documented in the literature. From the Table 6, we can see that the magnitude of BSSE decreases with the basis set enlarged, when the diffusion and polarization functions are considered; especially for the 6-311++g(d,p) and 6-311++g(2d,2p) basis set using B3LYP method, the inclusion of BSSE correction has minor importance to the binding energy. It was also true for HF/6-311++g(d,p) level. However, for MP2 method at this basis set level, the BSSE correction is larger than that of HF and B3LYP.

From Table 6, we can conclude than the relative stability of the six structures is FAT11 > FAT12 > FAT22 > FAT13 > FAT33 > FAT23, which is in agreement with the previous calculations.[5] It is easy to understand that the stability of FAT11 derives from the formation a pair of hydrogen bonds between the two water molecules and formic acid, and the structure also has an added hydrogen bond of type R_W. For FAT12, the hydrogen bond length of this structure is only longer than that of the FAT11 structure and shorter than all of the others. And this is also true for the structure FAT22. For the other three structures, we can also estimate the stability by the interaction energy and the interaction distance. Furthermore, FAT23 has the lowest energy of all of the complexes.

Infrared Spectrum. In Table 7, we give the B3LYP/6-311++g(d,p) values for both vibrational frequencies and IR intensities of the six complexes. For simplicity, the experimental frequencies of the monomers have not been listed in Table 7. As mentioned earlier, since the frequency shifts are relatively



FAT13 FAT22

FAT23 FAT33

Figure 3. Formic acid complexes with one and two water molecules in solution phase.

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 7. It is noticeable that the C═O stretching frequencies are found to reduce for all structures except the FAT33 structure considered here (60, 68, 35, 57, and 25 cm^{-1}). This is consistent with the bond distance change discussed above. The reason for the significant reduction of the C═O bond in FAT12 structure is that the C═O bond of FAT12 has formed two hydrogen bonds with the water molecule, as Figure 2 shows. The C−H stretching frequency also shows a slight change in its value on hydrogen bonding. For instance, in structure FAT23, there is a weak interaction between the O of H_2O and H of CHO group; the shift is 50 cm^{-1}. The O−H stretching is found to be red-shifted, and the maximum decrease is observed for structure FAT11, which is 620 cm^{-1}, and this corresponds to the strongest interaction. It is interesting to note the upward shift of the bonding mode frequency in HCOOH upon forming the hydrogen complex, which is typical for the hydrogen bond complex. For instance, the CH rocking and wagging modes are all blue-shifted to different extents with water in different configurations. Of course, the strongest shift occurs in FAT11, which corresponds to the strongest interaction. For the modes of two water molecules in the complex, like that of HCOOH, the stretching frequency associated with the hydrogen bond undergoes a shift to a lower frequency compared to the free monomer. 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. There is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor in this system. From Table 7, it can be seen that the C═O and O−H stretching intensities involved in the hydrogen bonds are enhanced largely in both hydrogen complexes. For example, the O−H stretching intensities varied from 62 to 727 (744) km/mol for complex FAT12 (FAT13), approximately 12 times that of the mode in the monomer; especially, for complex FAT11, it is changed to 982 km/mol, which is increased about 15 times. The C═O stretching intensities changed from 398 to 426 (471) km/mol for complex FAT22 (FAT23). For the CH stretching modes, the IR intensities are similar to those of the isolated monomer except the conformer FAT11. Besides, 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 reduce and the related stretching frequencies are red-shifted.

Solution Phase Results. The interaction of water with formic acid has also been studied in 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. 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 water are presented in Figure 3. From the calculation, we can conclude that the solvent can appreciably modify the geometries of hydrogen-bonded systems. First, we discuss the complexes of formic acid and one water molecule. With respect to FAT1, the optimized geometry in solution can be compared to previous gas-phase calculations at the same level. In FAT11, the major discrepancy between the gas and solution phase is that the R2 distance increased by 0.145 Å. At the same time, the R1 distance is also changed, but it is shortened, which is only 0.041 Å. Other geometric parameters are similar to each other.

For FAT2, most dramatic changes induced by the solvent on the geometry are also observed, where the orientation of the water molecule is changed very much with respect to the gas-phase value (compare Figure 1 with Figure 3). The changes can be understood by considering the modification of the solvent energy with the complex's geometry. The dipole moments of the complex in solution and in the gas phase are 1.78 and 5.22 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 R2, it is shortening by 0.042 Å in solution compared to the gas-phase value. The angle C−O···H varied from 103.9° to 147.7°, while O···H−O changed from 147.9° to 160.9°. Differences in other bond lengths between the gas-phase and solution-phase results are less than 0.020 Å, and differences in other angles are less than 4°.

With respect to FAT3, the most notable differences between the gas and solution phase are that the R3 distance increased by as much as 0.544 Å and that the R4 hydrogen bond forms with a calculated length of 2.304 Å. At the same time, the angle H−O···H changed from 147.4° to 153.9°, and the O···H−O changed from 129.5° to 102.8°.

As to FAC1, the largest change induced by the solvent on the geometry is that the R1 bond length is reduced from 1.812 to 1.692 Å, which is shortened by 0.120 Å. Besides, the O−H···O angle varied too, which is from 179.0° to 176.3°. The other geometric parameters in solution are similar to those in the gas phase.

With respect to FAC2, most dramatic changes induced by the solvent on the geometry are also observed, where the orientation of the water molecule is inverted with respect to the gas-phase value (compare Figure 1 with Figure 3). The changes can be understood by considering the modification of the solvent energy with the complex's geometry. The dipole moments of the complex in solution and in the gas phase are 2.25 and 7.99 D, respectively. Such a large variation in the dipole moment produces a large change in the solute−solvent interaction energy favoring the aligned configuration. The C−O···H angle varied from 101.3° to 168.5°, and the O···H−O is changed from 144.6° to 151.8°. The other geometric parameters in solution are similar to those in the gas phase.

For FAC3, the major discrepancy between the gas and solution phase is that the R2 distance decreased by 0.126 Å. Differences in other bond lengths between the gas-phase and solution-phase results are less than 0.020 Å, and differences in angles are less than 5°.

Second, we will discuss the complexes between formic acid and two water molecules. As to FAT11, the differences caused by the solvent on the geometry are very little; of course, the changes exist. For example, the R1 bond length is decreased by 0.020 Å, while the R2 is increased by 0.021 Å. This little change probably may be due to the little change of the dipole moments in the gas and solution phases, which are 0.79 and 1.18 D, respectively.

With respect to FAT12, the first thing to note is that the cyclic structure disappeared when the effects of solvent are included (compare Figure 2 with Figure 3). The changes can be explained by the large variation of the dipole moments from gas phase to solution phase, which are from 2.97 to 8.92 D. From Figure 3, it can be seen that one water molecule is inverted considering the solvent modification. There is an R2-type hydrogen bond in the gas phase, but in the solution phase, it disappears. For the R1, it varied from 1.761 Å in the gas phase to 1.688 Å in the solution phase, which is shortened by 0.073 Å. At the same time, the orientation of the other water molecule is also changed, and the R2′ distance decreased by 0.073 Å, too. In addition, the C1O2H10 angle changed from 107.7° to 137.3°, which can also elucidate the diversification of the other water molecule.

For FAT13, the major discrepancy between the gas and solution phase is that the cyclic structure disappeared. In the gas phase, an R2-type hydrogen bond exists, but in the solution phase, the bond length is prolonged to 3.633 Å, which elucidates that the hydrogen bond disappears. As a result, the R1 bond length is shortened by 0.076 Å, and the O3H5O6 angle is changed from 157.0° to 173.5°. At the same time, the R3 distance is decreased by 0.061 Å.

As to FAT22, the changes between the gas and solution phase are not large. For instance, the bond length difference is only about 0.020 Å, and the angle difference is less than 4°.

With respect to FAT23, the most distinct difference induced by the solvent is that the orientation of one water molecule is inverted with respect to the gas-phase value (compare Figure 2 with Figure 3). This large discrepancy can be explained by the variation of the dipole moments, which are 4.86 and 7.78 D in the gas and solution phase, respectively. As a result, the R2-type of hydrogen bond length is shortened 0.045 Å. At the same time, the R4 bond distance is reduced by 0.155 Å. Moreover, the R3 bond is elongated to 3.217 Å, and this indicates that the R3 hydrogen bond disappears. The other geometric parameters in solution are similar to those in the gas phase.

For the last complex FAT33, the largest change caused by the solvent on the geometry is that the R3 bond distance is elongated by 0.159 Å; the other hydrogen bond lengths are also changed, and for example, the R4 distance is increased by 0.028 Å, while the R_W is decreased by 0.032 Å. Other geometric parameters are similar to each other.

A summary of the relative energies of the six complexes between formic acid and one water molecule in solution is also presented in Table 3. The energies are measured relative to the energies of separated water and formic acid in solution, and the BSSE corrections are also listed. From the table, it can be seen that a large influence of solvent polarization on hydrogen bond energies exists. The magnitude of the solvent effect is not constant across the whole potential surface and can produce a bias toward particular geometric conformations. For the (T) conformation of formic acid, the relative stability is not changed, but due to the solvent effect, the interaction energies of FAT2 and FAT3 are increased by 11.9 and 8.3 kJ/mol, respectively. However, with respect to the (C) conformation of formic acid, the relative stability is changed to FAC1 > FAC3 > FAC2, and the largest variation is in the FAC3 complex, which is from 17.6 to 46.3 kJ/mol. In a word, the relatively stability of the six complexes is FAC1 > FAC3 > FAT1 > FAC2 > FAT2 > FAT3.

The relative energies of the six complexes between (T)-formic acid and two water molecules in solution are also listed in Table 6. From Table 6, it can be seen that differences of the interaction energies between the gas phase and the solution phase are obtained. For instance, since there is an abnormal phenomena in FAT12 (one of the hydrogen bonds breaks), the relative ordering of binding energy changes as much as 7.7 kJ/mol, and this also true for complex FAT22, whose interaction energy varied from 62.4 to 46.8 kJ/mol. On all accounts, the relative stability of the six complexes is FAT11 > FAT12 > FAT13 > FAT22 > FAT33 > FAT23.

Conclusions

The hydrogen bond interaction of complexes between formic acid and water (with up to two water molecules) has been analyzed by ab initio, MP2, and B3LYP method employing different basis set levels. We calculated twelve complexes: six are with one water molecule, and six are with two water molecules. For the complexes with one water molecule, three are with (T)-formic acid and three are with (C)-formic acid, and the cyclic double-hydrogen-bonded structure (FAT1) is the most stable at all levels. From the interaction energies of the six complexes, we have defined the relative stability of them as FAT1 > FAC1 > FAC2 > FAT2 > FAC3 > FAT3. The infrared spectrum frequencies, IR intensities, and vibrational frequency shifts are reported. The frequencies of the complexes are all IR-active, and most of them have larger intensities, so one can estimate the IR spectrum for the complex by combining the observed fundamental vibrational frequency of its moieties and the frequency shift. For the six complexes of formic acid and two water molecules, we also do the same work. But in this system, we only considered the (T)-formic acid.

Finally, the study of the solvent effect on the potential energy surface of water−formic acid complex has been performed. In the description of solvent, we have employed the Onsager reaction field model. The calculations are done at B3LYP/6-311++g(d,p) level. We found that the geometry of the system is appreciable modified by the solvent, and we also found the relative stability of the complexes is changed. For the complexes with one water molecule, the order is FAC1 > FAC3 > FAT1 > FAC2 > FAT2 > FAT3, and that for the complexes with two water molecule is FAT11 > FAT12 > FAT13 > FAT22 > FAT33 > FAT23.

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