

# Ionization Dynamics of trans-Formanilide–H<sub>2</sub>O Complexes: A Direct ab Initio Dynamics Study

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Ionization dynamics of trans-formanilide-water 1:1 complexes FA(H<sub>2</sub>O) have been investigated by means of direct ab initio trajectory method. From the static ab initio calculations, three conformers of the FA(H<sub>2</sub>O) complexes were obtained as stable structures: namely, these are the N–H site, the C=O carbonyl site and the bridge site, which are different in the positions of H<sub>2</sub>O around FA. In the N–H and C=O sites, a water molecule binds to the hydrogen and oxygen atoms of the peptide (–NH–CO), respectively. In the bridge site, the hydrogen and oxygen atoms of H<sub>2</sub>O bind to the C=O carbonyl and a hydrogen of benzene ring (*o*-position) of FA, respectively. The trajectories from the vertical ionization points of these three structures were calculated by means of full dimensional direct ab initio trajectory method. It was found that the H<sub>2</sub>O molecule in the N–H site is still remained in its site after ionization, i.e., the strong complex cation where H<sub>2</sub>O binds to the N–H site of FA<sup>+</sup> is directly formed. On the other hand, in the cases of the ionization from both CO and bridge sites, the water molecule was moved easily around both the benzene ring and the C=O carbonyl group. The mechanism of the ionization of FA(H<sub>2</sub>O) was discussed on theoretical results.

## 1. Introduction

Trans-formanilide (FA) is one of the model compounds of peptide in proteins because the molecule has a planar –NH–CO– bond.<sup>1,2</sup> Therefore, FA has been widely used as a model molecule for the study of proteins.<sup>3–6</sup> In particular, a complex of FA with water molecule is utilized as a simple model for elucidating the interaction between protein and H<sub>2</sub>O.<sup>7–16</sup>

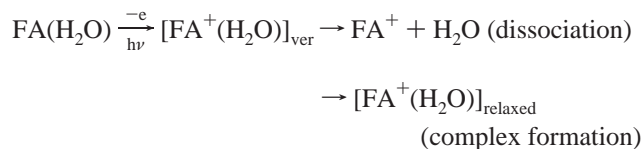
For the formanilide–water complex (FA–H<sub>2</sub>O), the most important conclusions obtained by experiments and theoretical calculations can be summarized as follows:<sup>7–16</sup> (a) only trans-FA is found in the case of the FA–water complex, although both *cis*- (1–4%) and *trans*-(96–99%) isomers of FA are observed in the gas phase; (b) two-types of trans-FA(H<sub>2</sub>O) complexes are found by ion-dip experiment<sup>10</sup> and ab initio calculations.<sup>7,8,10</sup> One is a complex where H<sub>2</sub>O acts as a proton donor by connecting to the C=O site of amide group (referred hereafter as [FA(H<sub>2</sub>O)]<sub>CO</sub>) and the other one is that H<sub>2</sub>O acts as the hydrogen acceptor by connecting to the N–H site (referred by [FA(H<sub>2</sub>O)]<sub>NH</sub>). In addition to above two isomers, the other site, where H<sub>2</sub>O connects to both the C=O carbonyl and the hydrogen of benzene ring, is found by the ab initio calculations.<sup>14</sup> The H<sub>2</sub>O molecule plays as a bridge molecule between the O and H atoms (referred by [FA(H<sub>2</sub>O)]<sub>bridge</sub>). However, this form was not detected experimentally.<sup>7</sup> (c) The ab initio calculations also predicted that the [FA(H<sub>2</sub>O)]<sub>NH</sub> complex is the most stable in energy at the ground state.

Recently, ionic states of FA(H<sub>2</sub>O) have investigated by means of two-color (1+1') resonance enhanced multiphoton ionization (REMPI) and zero electron kinetic energy (ZEKE) spectroscopy.

The binding energies of H<sub>2</sub>O to FA<sup>+</sup> are measured to be 5158±105 cm<sup>-1</sup> for [FA<sup>+</sup>(H<sub>2</sub>O)]<sub>NH</sub> and 5064±97 cm<sup>-1</sup> for [FA<sup>+</sup>(H<sub>2</sub>O)]<sub>CO</sub>. Ab initio calculations indicated that the positive charge in the cationic complex is delocalized over benzene ring and amide group.<sup>6,12,13</sup> In the [FA<sup>+</sup>(H<sub>2</sub>O)]<sub>NH</sub> complex, the O–H distance between the oxygen of H<sub>2</sub>O and the hydrogen atoms of NH is shorter than that of the neutral complex.

Thus, the ionic states of the FA(H<sub>2</sub>O) complex have been investigated from both experiments and theoretical calculations, and the structures and the energetics have been revealed. However, the ionization dynamics of FA(H<sub>2</sub>O) is not clearly understood. In particular, microscopic feature for molecular dynamics after the ionization is scarcely known.

In the present study, the ionization dynamics of trans-formanilide–water 1:1 complexes (referred by FA(H<sub>2</sub>O)) have been investigated by means of full dimensional direct ab initio trajectory method.<sup>17–21</sup> For the ionization of FA(H<sub>2</sub>O), two reaction channels would be competitive each other.<sup>16</sup> The reactions would be expressed as follows

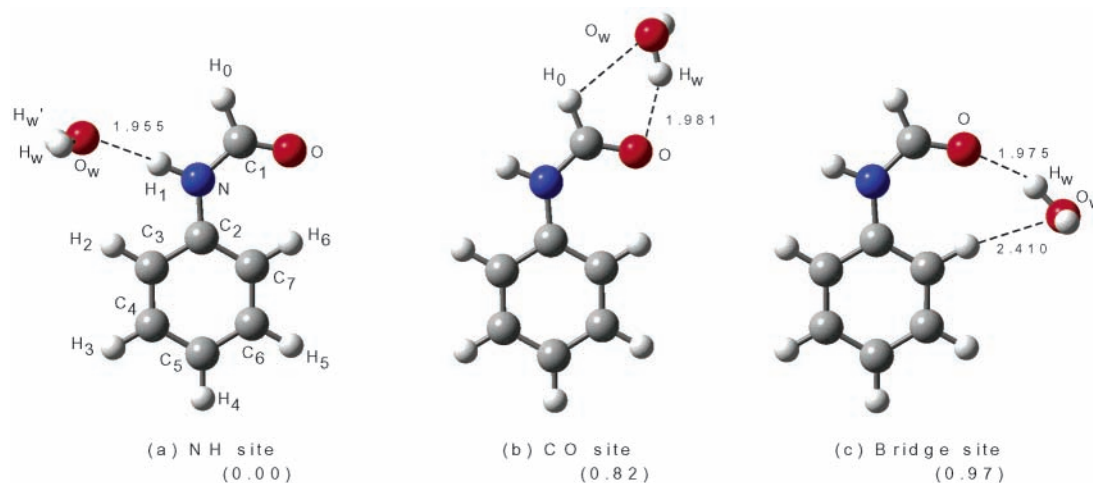


By the ionization of FA(H<sub>2</sub>O), the vertical ionic state expressed by [FA<sup>+</sup>(H<sub>2</sub>O)]<sub>ver</sub> is formed. As relaxation processes of [FA<sup>+</sup>(H<sub>2</sub>O)]<sub>ver</sub>, dissociation and complex formation channels would be competitive. Here, [FA<sup>+</sup>(H<sub>2</sub>O)]<sub>relaxed</sub> means an energetically relaxed state for the cationic state. The solvent reorientation may be occurred. The purpose of this study is to qualitatively elucidate the ionization dynamics of FA(H<sub>2</sub>O) from theoretical point of view. In particular, we focus our attention on site dependence on the product reaction channels.

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**Figure 1.** Optimized structures of neutral complexes trans-FA(H<sub>2</sub>O) calculated at the B3LYP/6-311G(d,p) level. (a) NH site, (b) CO site, and (c) bridge site. The relative energies (in kcal/mol) calculated at the B3LYP/6-311G(d,p) level are given in parentheses. The intermolecular distances are in Å.

**TABLE 1: Total Energies (in a.u) and Selected Structural Parameters of Neutral Complexes FA(H<sub>2</sub>O) Calculated at the Several Levels of Theory (Bond lengths and angles are in Å and Degrees, Respectively)**

	NH site			CO site			bridge site		
	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)
energy	-471.86201	-475.90481	-477.51194	-471.85765	-475.90426	-477.51062	-471.85873	-475.90308	-477.51040
C <sub>1</sub> -N	1.353	1.366	1.367	1.351	1.362	1.362	1.349	1.363	1.363
C <sub>2</sub> -N	1.406	1.409	1.409	1.413	1.414	1.414	1.417	1.417	1.417
C <sub>1</sub> -O	1.218	1.230	1.213	1.225	1.235	1.220	1.218	1.230	1.215
N-H <sub>1</sub>	1.009	1.021	1.017	0.999	1.015	1.010	0.999	1.015	1.010
C <sub>1</sub> -H <sub>0</sub>	1.084	1.105	1.107	1.078	1.101	1.102	1.083	1.104	1.105
C <sub>1</sub> -N-C <sub>2</sub>	127.4	128.2	128.6	128.3	129.2	129.6	129.4	129.5	130.4
N-C <sub>1</sub> -O	127.4	127.2	127.4	126.2	126.1	126.4	127.3	127.0	127.4
H <sub>1</sub> -O <sub>w</sub>	1.851	1.969	1.955						
H <sub>1</sub> -O <sub>w</sub> -H <sub>w</sub>	124.8	122.3	120.9						
O-H <sub>w</sub>				1.932	1.975	1.981	1.829	1.982	1.975
O-O <sub>w</sub> -H <sub>w</sub>				27.0	19.3	21.1	15.0	13.7	16.4
H <sub>6</sub> -O <sub>w</sub>							2.201	2.425	2.410

**TABLE 2: Binding Energies of H<sub>2</sub>O to Three Binding Sites of FA Calculated at Several Levels of Theory (in kcal/mol)**

	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)
FA + H <sub>2</sub> O	0.0	0.0	0.0
FA(H <sub>2</sub> O) <sub>NH</sub>	13.8	8.9	9.0
FA(H <sub>2</sub> O) <sub>CO</sub>	11.1	8.5	8.2
FA(H <sub>2</sub> O) <sub>bridge</sub>	11.8	7.8	8.1

## 2. Computational Methods

In general, a classical trajectory calculation has been made on an analytically fitted potential energy surface (PES). However, it is not appropriate to predetermine the reaction surfaces of the present systems due to the large number of degrees of freedom ( $3N - 6 = 51$ , where  $N$  is number of atoms in the system). Therefore, in the present study, we applied the direct ab initio trajectory calculation<sup>17-21</sup> with all degrees of freedom to the ionization dynamics of FA(H<sub>2</sub>O) system.

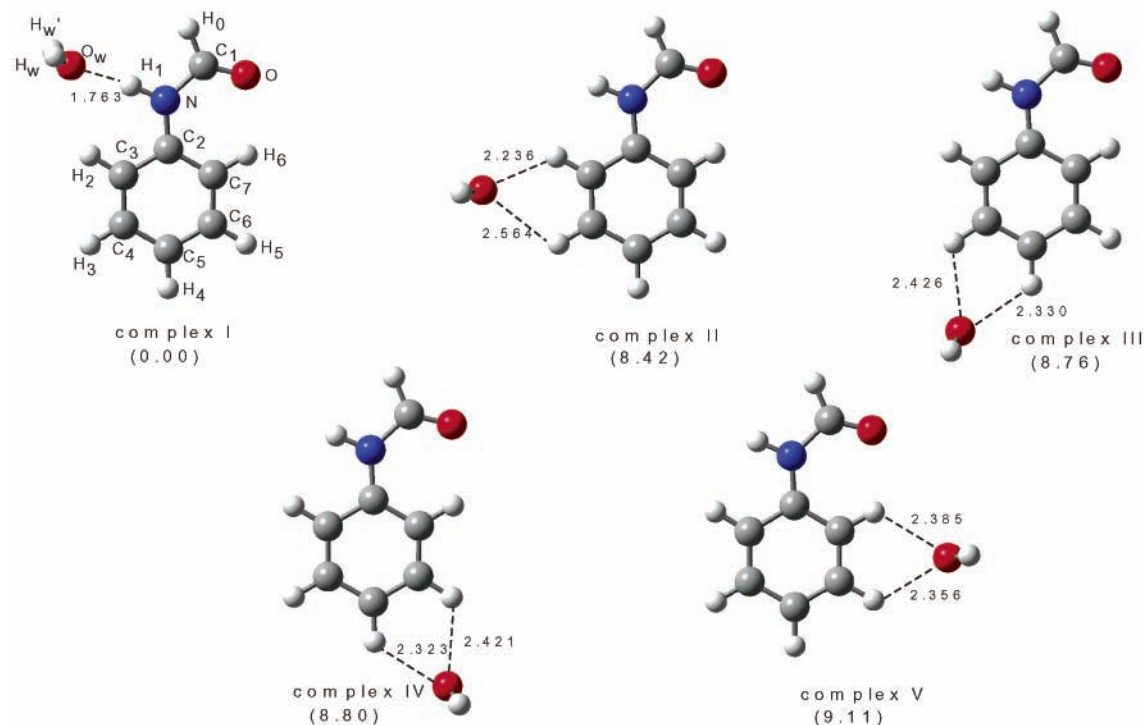
The direct ab initio trajectory calculations were carried out at the HF/3-21G(d) level of theory throughout. First, the neutral complexes FA(H<sub>2</sub>O) for three conformers were fully optimized by the energy gradient method. Next, trajectories for FA<sup>+</sup>(H<sub>2</sub>O) were run from the optimized points. The velocities of atoms at the starting point were assumed to zero (i.e., momentum vector

of each atom is zero). The equations of motion for  $n$  atoms in a molecule are given by

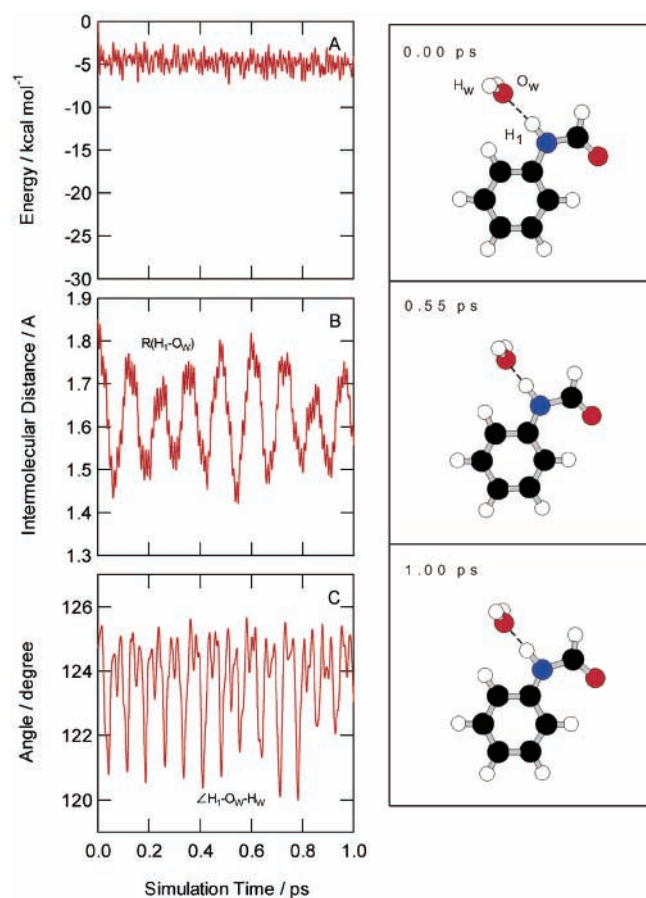
$$\frac{dQ_j}{dt} = \frac{\partial H}{\partial P_j}$$

$$\frac{\partial P_j}{\partial t} = -\frac{\partial H}{\partial Q_j} = -\frac{\partial U}{\partial Q_j}$$

where  $j = 1 - 3N$ ,  $H$  is classical Hamiltonian,  $Q_j$  is Cartesian coordinate of  $j$ -th mode and  $P_j$  is conjugated momentum. These equations were numerically solved by the Runge-Kutta method. No symmetry restriction was applied to the calculation of the energy gradients. The time step size was chosen by 0.10 fs, and a total of 10 000 or 20 000 steps were calculated for each dynamics calculation. The drift of the total energy is confirmed to be less than  $1 \times 10^{-3}$  % throughout at all steps in the trajectory. The momentum of the center of mass and the angular momentum are assumed to zero. Static ab initio MO calculations were carried out using Gaussian 98.<sup>22</sup> The structures and energetics of neutral and cationic complexes FA(H<sub>2</sub>O) and FA<sup>+</sup>(H<sub>2</sub>O) were obtained at the B3LYP/6-311G(d,p) and MP2/6-31G(d) levels of theory.



**Figure 2.** Optimized structures of cation complexes trans-FA<sup>+</sup>(H<sub>2</sub>O) calculated at the B3LYP/6-311G(d,p) level. The relative energies (in kcal/mol) calculated at the B3LYP/6-311G(d,p) are given in parentheses. The intermolecular distances are in Å.



**Figure 3.** Trajectory for FA<sup>+</sup>(H<sub>2</sub>O) from the NH site. The dynamics calculation was carried out at the HF/3-21(d) level. (A) potential energy of the reaction system, (B) intermolecular distance between FA<sup>+</sup> and H<sub>2</sub>O, denoted by R(H<sub>1</sub>-O<sub>w</sub>), and (C) angle of <math>\angle H\_1-O\_w-H\_w</math>. Snapshots of the structure of FA<sup>+</sup>(H<sub>2</sub>O) after the ionization are illustrated in right panels.

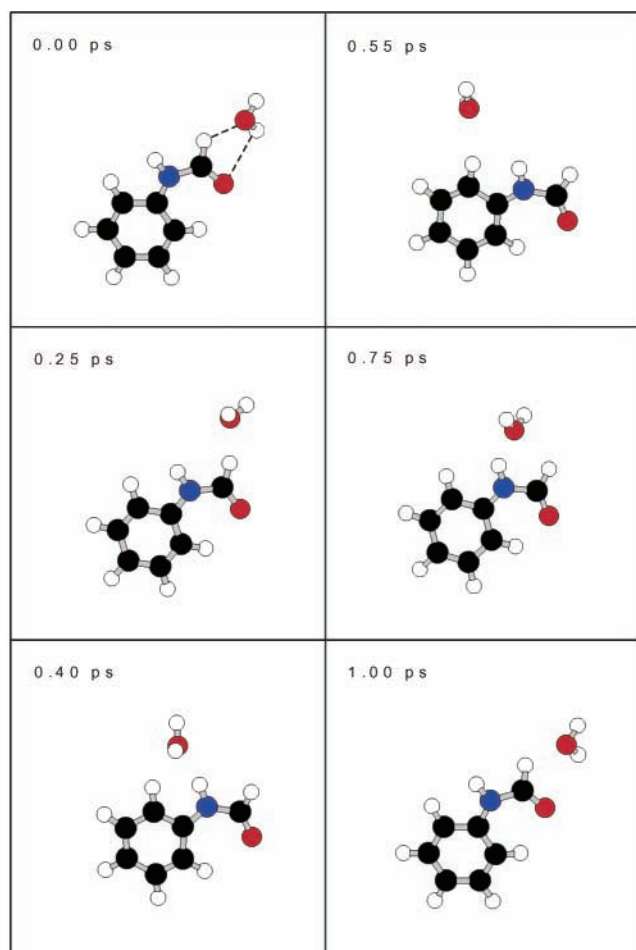
### 3. Results

**A. Structures of FA(H<sub>2</sub>O) Neutral Complexes.** First, the neutral structures of FA(H<sub>2</sub>O) were fully optimized at the HF/3-21G(d), MP2/6-31G(d) and B3LYP/6-311G(d,p) levels of theory. The geometrical parameters and schematic illustrations of the optimized structures are given in Table 1 and Figure 1, respectively. The binding energies of H<sub>2</sub>O to the neutral FA are summarized in Table 2. We will discuss here the structures and energetics of FA(H<sub>2</sub>O) using the results of the B3LYP/6-311G(d,p) calculations.

As pointed out by previous work,<sup>14</sup> the neutral FA(H<sub>2</sub>O) has three conformers which are distinguished by the different positions of H<sub>2</sub>O around FA. These are denoted by NH, CO, and bridge sites. The present calculations also gave the similar results for the structures and energetics for the neutral system. The most stable form is of the NH site [FA(H<sub>2</sub>O)]<sub>NH</sub> where H<sub>2</sub>O binds to the NH of the amide by a hydrogen bond (Figure 1a) and the oxygen of H<sub>2</sub>O acts as proton acceptor. The O-H distance of the hydrogen bond  $r(O_w-H_1)$  is calculated to be 1.955 Å, and the binding energy is 9.0 kcal/mol at the B3LYP/6-311G(d,p) level. The nonbonding orbital of H<sub>2</sub>O orients toward the hydrogen of the NH site.

Figure 1b shows the structure of the complex where the hydrogen of H<sub>2</sub>O binds to the oxygen atom of C=O carbonyl in peptide moiety of FA (namely, -NH-CO-). The hydrogen of -NH-CO- group interacts weakly with the oxygen of H<sub>2</sub>O. This structure is referred hereafter by CO site, [FA(H<sub>2</sub>O)]<sub>CO</sub>. The binding energy was calculated to be 8.2 kcal/mol, which is 0.8 kcal/mol less stable than that of [FA(H<sub>2</sub>O)]<sub>NH</sub>.

As be shown in Figure 1c, the H<sub>2</sub>O molecule behaves as both hydrogen-donor and acceptor to FA. In this complex, the water molecule is bound to two sites of FA, the oxygen atom of NH-CO and a hydrogen atom of benzene group. The distances of the hydrogen bonds for  $r(H_w-O)$  and  $r(O_w-H)$  are calculated to be 1.975 Å and 2.410 Å, respectively. This binding structure is referred hereafter by [FA(H<sub>2</sub>O)]<sub>bridge</sub>. The H<sub>2</sub>O molecule binds to FA by 8.1 kcal/mol. The relative energies calculated at the



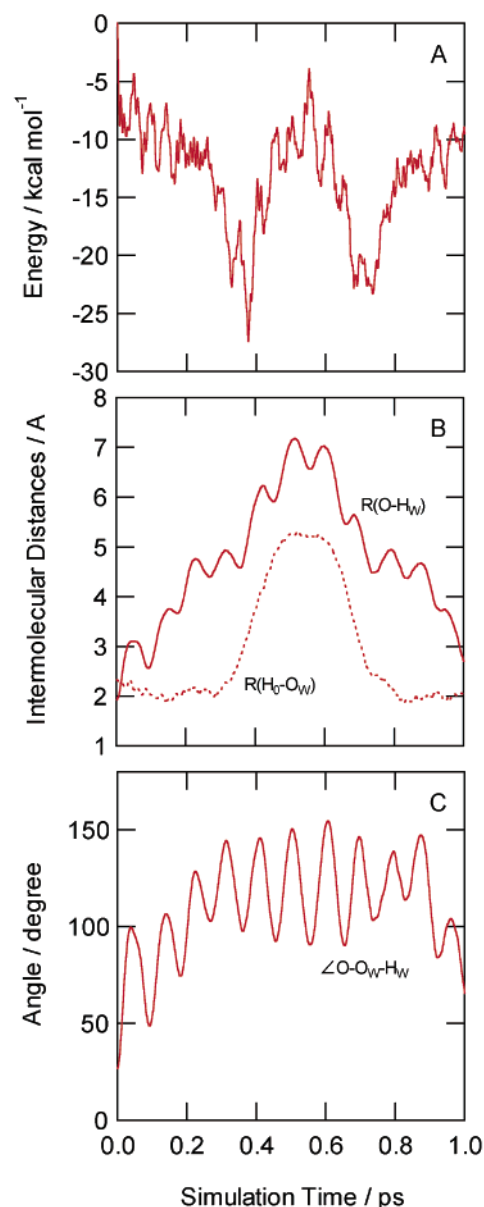
**Figure 4.** Snapshots of the structure of  $\text{FA}^+(\text{H}_2\text{O})$  after the ionization from the CO site. The dynamics calculation was carried out at the HF/3-21(d) level.

B3LYP/6-311G(d,p) level are given in parentheses of Figure 1. The binding energies of  $\text{H}_2\text{O}$  to the NH, CO and bridge sites are calculated to be 9.0, 8.2 and 8.1 kcal/mol, respectively. After the correction of basis set superposition error (BSSE) by counterpoise method, the binding energies are changed to 5.6 kcal/mol (N–H site), 4.8 kcal/mol (CO site) and 4.2 kcal/mol (bridge site), but the relative stability is not changed. These results imply that the most stable structure is the NH site bonded  $[\text{FA}(\text{H}_2\text{O})]_{\text{NH}}$ .

These structural and energetic features are also obtained by HF/3-21G(d) level, which is utilized in the direct ab initio trajectory calculations. As clearly shown in Table 1, the HF/3-21G(d) calculations gave reasonable structures of the complexes and energetics for the present system. Details of the difference of the energetics between HF/3-21G(d) and B3LYP/6-311G(d,p) calculations will be discussed in latter section.

**B. Structures of the Cationic Complexes  $\text{FA}^+(\text{H}_2\text{O})$ .** Next, the structures for cationic states were fully optimized at the same levels of theory. Several initial points were examined as starting point in the geometry optimizations. Consequently, the static ab initio calculations gave five stable structures as the cationic complexes  $\text{FA}^+(\text{H}_2\text{O})$ . The optimized structures thus obtained are referred hereafter by complexes I–V and are illustrated in Figure 2. Total energies and structural parameters are given in Table 3.

In complex I, the water molecule binds to the hydrogen of –NH–CO– peptide site. This structure is very resemble to that of neutral complex  $[\text{FA}(\text{H}_2\text{O})]_{\text{NH}}$ . However, the bond distance



**Figure 5.** Trajectory for  $\text{FA}^+(\text{H}_2\text{O})$  from the CO site. The dynamics calculation was carried out at the HF/3-21(d) level. (A) potential energy of the reaction system, (B) intermolecular distance between  $\text{FA}^+$  and  $\text{H}_2\text{O}$ , denoted by  $R(\text{H}_1-\text{O}_w)$ , and (C) angle of  $\angle \text{H}_1-\text{O}_w-\text{H}_w$ . Snapshots of the structure of  $\text{FA}^+(\text{H}_2\text{O})$  after the ionization are illustrated in Figure 4.

of NH–OH<sub>2</sub>,  $r(\text{O}_w-\text{H}_1)$ , in  $\text{FA}^+(\text{H}_2\text{O})$  is shorter than that of neutral  $\text{FA}(\text{H}_2\text{O})$  complex (1.763 vs 1.955 Å). This is due to that fact that the interaction between  $\text{H}_2\text{O}$  and the peptide site is changed from a hydrogen bonding to Coulomb interaction by the ionization, and then the bond becomes stronger. This feature is already pointed out by Müller–Dethlefs and co-workers:<sup>14,15</sup> namely, the positive charge on the  $\text{FA}^+(\text{H}_2\text{O})$  complex is somewhat localized on the peptide site and is largest in the N atom of –NH–CO– peptide bond, so that  $\text{H}_2\text{O}$  interacts strongly with the NH site at the cationic state. The present calculations strongly support their interpretation.

In the other complexes II–V,  $\text{H}_2\text{O}$  interacts with bay-arias of benzene ring of  $\text{FA}^+$ . This feature is very similar to that of a cation complex composed of benzene cation and  $\text{H}_2\text{O}$ .<sup>24,25</sup> The binding energies of  $\text{H}_2\text{O}$  to several sites of  $\text{FA}^+$  are given in Table 4. The complex I is 8.4–9.1 kcal/mol more stable in energy than the other complexes II–V at the B3LYP/6-311G(d,p) level.

**TABLE 3: Total Energies (in a.u.) and Key Structural Parameters of Cation Complexes FA<sup>+</sup>(H<sub>2</sub>O) Calculated at the Several Levels of Theory (bond lengths and angles are in Å and degrees, respectively)**

	complex I			complex II		
	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)
energy	-471.63348	-475.61036	-477.23125	-471.60997	-475.59928	-477.21783
C <sub>1</sub> –N	1.410	1.422	1.427	1.424	1.423	1.433
C <sub>2</sub> –N	1.331	1.365	1.352	1.328	1.373	1.356
C <sub>1</sub> –O	1.228	1.195	1.195	1.211	1.198	1.192
N–H <sub>1</sub>	1.046	1.032	1.037	1.009	1.019	1.017
C <sub>1</sub> –H <sub>0</sub>	1.072	1.103	1.099	1.074	1.102	1.099
C <sub>1</sub> –N–C <sub>2</sub>	129.5	126.5	128.8	129.7	127.6	129.6
N–C <sub>1</sub> –O	123.5	125.5	124.6	123.1	124.7	123.9
C <sub>2</sub> –C <sub>3</sub>	1.436	1.437	1.439	1.436	1.431	1.436
C <sub>3</sub> –C <sub>4</sub>	1.375	1.341	1.370	1.369	1.343	1.369
C <sub>4</sub> –C <sub>5</sub>	1.408	1.415	1.412	1.409	1.414	1.412
C <sub>5</sub> –C <sub>6</sub>	1.407	1.412	1.412	1.412	1.417	1.415
C <sub>6</sub> –C <sub>7</sub>	1.377	1.346	1.373	1.370	1.345	1.371
C <sub>7</sub> –C <sub>2</sub>	1.433	1.433	1.435	1.440	1.431	1.436
H <sub>1</sub> –Ow	1.603	1.841	1.763			
H <sub>1</sub> –Ow–Hw	124.7	122.8	125.3			
H <sub>2</sub> –Ow				2.152	2.254	2.236
C <sub>3</sub> –H <sub>2</sub> –Ow				127.9	127.1	128.0
H <sub>3</sub> –Ow				2.483	2.553	2.564
C <sub>4</sub> –H <sub>3</sub> –Ow				114.6	114.3	114.8
H <sub>4</sub> –Ow						
C <sub>5</sub> –H <sub>4</sub> –Ow						
H <sub>5</sub> –Ow						
C <sub>6</sub> –H <sub>5</sub> –Ow						
H <sub>6</sub> –Ow						
C <sub>7</sub> –H <sub>6</sub> –Ow						

	complex III			complex IV		
	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)
energy	-471.60846	-475.60086	-477.21729	-471.60831	-475.60060	-477.21723
C <sub>1</sub> –N	1.425	1.419	1.433	1.425	1.422	1.433
C <sub>2</sub> –N	1.328	1.376	1.356	1.328	1.375	1.357
C <sub>1</sub> –O	1.209	1.201	1.192	1.209	1.200	1.192
N–H <sub>1</sub>	1.008	1.019	1.016	1.008	1.019	1.016
C <sub>1</sub> –H <sub>0</sub>	1.074	1.102	1.099	1.074	1.102	1.099
C <sub>1</sub> –N–C <sub>2</sub>	129.6	127.9	129.6	129.5	127.6	129.5
N–C <sub>1</sub> –O	123.3	124.9	124.0	123.3	124.8	124.0
C <sub>2</sub> –C <sub>3</sub>	1.439	1.423	1.436	1.443	1.430	1.438
C <sub>3</sub> –C <sub>4</sub>	1.362	1.342	1.367	1.367	1.341	1.368
C <sub>4</sub> –C <sub>5</sub>	1.415	1.431	1.412	1.410	1.420	1.415
C <sub>5</sub> –C <sub>6</sub>	1.409	1.405	1.413	1.414	1.416	1.415
C <sub>6</sub> –C <sub>7</sub>	1.370	1.350	1.372	1.366	1.347	1.371
C <sub>7</sub> –C <sub>2</sub>	1.440	1.436	1.436	1.436	1.430	1.434

	complex III			complex IV		
	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)	HF/ 3-21G(d)	MP2/ 6-31G(d)	B3LYP/ 6-311G(d,p)
H <sub>1</sub> –Ow						
H <sub>1</sub> –Ow–Hw						
H <sub>2</sub> –Ow						
C <sub>3</sub> –H <sub>2</sub> –Ow						
H <sub>3</sub> –Ow	2.292	2.361	2.426			
C <sub>4</sub> –H <sub>3</sub> –Ow	121.5	120.8	119.5			
H <sub>4</sub> –Ow	2.315	2.326	2.330	2.297	2.315	2.232
C <sub>5</sub> –H <sub>4</sub> –Ow	120.5	122.0	123.6	121.2	123.4	123.6
H <sub>5</sub> –Ow				2.307	2.419	2.421
C <sub>6</sub> –H <sub>5</sub> –Ow				121.0	119.7	119.7
H <sub>6</sub> –Ow						
C <sub>7</sub> –H <sub>6</sub> –Ow						

TABLE 3 (Continued)

	complex V		
	HF/3-21G(d)	MP2/6-31G(d)	B3LYP/6-311G(d,p)
energy	-471.60884	-475.59849	-477.21673
C <sub>1</sub> -N	1.425	1.424	1.433
C <sub>2</sub> -N	1.328	1.373	1.356
C <sub>1</sub> -O	1.210	1.197	1.192
N-H <sub>1</sub>	1.008	1.019	1.016
C <sub>1</sub> -H <sub>0</sub>	1.074	1.102	1.099
C <sub>1</sub> -N-C <sub>2</sub>	129.5	127.8	129.6
N-C <sub>1</sub> -O	123.3	124.9	124.1
C <sub>2</sub> -C <sub>3</sub>	1.444	1.427	1.438
C <sub>3</sub> -C <sub>4</sub>	1.366	1.338	1.367
C <sub>4</sub> -C <sub>5</sub>	1.413	1.429	1.417
C <sub>5</sub> -C <sub>6</sub>	1.408	1.402	1.410
C <sub>6</sub> -C <sub>7</sub>	1.373	1.352	1.374
C <sub>7</sub> -C <sub>2</sub>	1.433	1.435	1.434
H <sub>1</sub> -O <sub>w</sub>			
H <sub>1</sub> -O <sub>w</sub> -H <sub>w</sub>			
H <sub>2</sub> -O <sub>w</sub>			
C <sub>3</sub> -H <sub>2</sub> -O <sub>w</sub>			
H <sub>3</sub> -O <sub>w</sub>			
C <sub>4</sub> -H <sub>3</sub> -O <sub>w</sub>			
H <sub>4</sub> -O <sub>w</sub>			
C <sub>5</sub> -H <sub>4</sub> -O <sub>w</sub>			
H <sub>5</sub> -O <sub>w</sub>	2.347	2.404	2.356
C <sub>6</sub> -H <sub>5</sub> -O <sub>w</sub>	118.6	118.4	121.7
H <sub>6</sub> -O <sub>w</sub>	2.224	2.321	2.385
c <sub>7</sub> -H <sub>6</sub> -O <sub>w</sub>	122.5	121.5	119.6
H <sub>1</sub> -O <sub>w</sub>			
H <sub>1</sub> -O <sub>w</sub> -H <sub>w</sub>			
H <sub>2</sub> -O <sub>w</sub>			
C <sub>3</sub> -H <sub>2</sub> -O <sub>w</sub>			

**TABLE 4: Binding Energies of H<sub>2</sub>O to Five Binding Sites of Cationic FA<sup>+</sup> Calculated at Several Levels of Theory (in kcal/mol) and the Relative Energies of FA<sup>+</sup>(H<sub>2</sub>O) at the Vertical Ionization Points from Three Binding Sites of FA(H<sub>2</sub>O) Relative to the Dissociation Limit (FA<sup>+</sup> + H<sub>2</sub>O)**

	HF/3-21G(d)	MP2/6-31G(d)	B3LYP/6-311G(d,p)
FA <sup>+</sup> + H <sub>2</sub> O	0.0	0.0	0.0
complex I	30.2	18.8	20.0
complex II	15.4	11.9	11.6
complex III	14.5	12.9	11.3
complex IV	14.4	12.7	11.2
complex V	14.7	11.4	10.9
FA <sup>+</sup> (H <sub>2</sub> O) <sub>NH-ver</sub>	21.3	2.0	13.3
FA <sup>+</sup> (H <sub>2</sub> O) <sub>CO-ver</sub>	-0.6	-3.3	-0.5
FA <sup>+</sup> (H <sub>2</sub> O) <sub>bridge-ver</sub>	-1.3	-2.2	-0.2

**C. Ionization Process in the FA(H<sub>2</sub>O) Complexes.** As be shown in previous sections, the static ab initio calculations indicated that the FA(H<sub>2</sub>O) complexes have three stable isomers, [FA(H<sub>2</sub>O)]<sub>NH</sub>, [FA(H<sub>2</sub>O)]<sub>CO</sub>, and [FA(H<sub>2</sub>O)]<sub>bridge</sub>. Hence, we investigate the ionization processes from the three complexes by means of direct ab initio trajectory method. The trajectory calculation for the ionization process of FA(H<sub>2</sub>O) needs a long CPU time, so that we have chosen the HF/3-21G(d) level of theory throughout in the dynamics calculations. Note that the HF/3-21G(d) level represents reasonably the structures calculated by the B3LYP/6-311G(d,p) level as described in previous section.

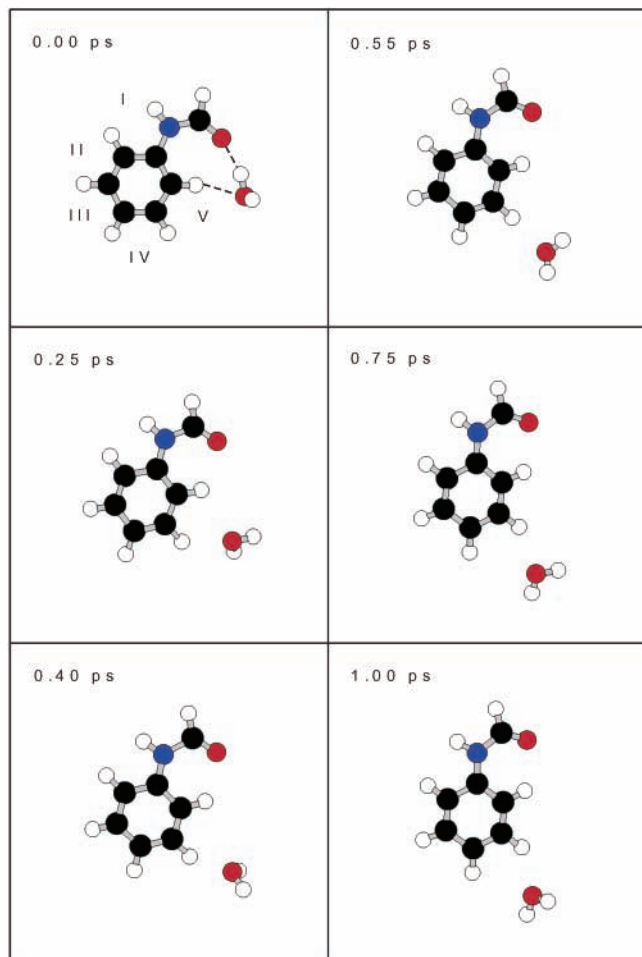
*Trajectory from the NH Site of FA(H<sub>2</sub>O).* First, we will show the results of the dynamics calculation from the NH site. Snapshots for the geometrical conformations calculated for [FA<sup>+</sup>(H<sub>2</sub>O)]<sub>NH</sub>, following the vertical ionization of [FA(H<sub>2</sub>O)]<sub>NH</sub>, are given in Figure 3(right). At time zero, the

H<sub>2</sub>O molecule is bound to the N-H site of FA. After the vertical ionization of the complex, the water molecule approached to the N-H and was vibrated periodically around its equilibrium distance for the [FA<sup>+</sup>(H<sub>2</sub>O)]<sub>NH</sub> complex. The H<sub>2</sub>O molecule was still remained and was bound to the NH site. The dissociation of H<sub>2</sub>O from FA<sup>+</sup> did not occur in this trajectory.

Potential energy of the system, intermolecular distances and angle are plotted as a function of time in Figure 3 (left). First, the energy decreased rapidly after the ionization of FA(H<sub>2</sub>O). This energy-lowering was caused by the rapid structural deformation of the FA moiety of the complex. Namely, the structure of FA is deformed by removing an electron. Before the ionization, the intermolecular distance R(H<sub>1</sub>-O<sub>w</sub>) is calculated to be 1.85 Å. After the ionization, it decreased suddenly up to 1.43 Å at 0.05 ps, and vibrated periodically in the range 1.43–1.81 Å. The change of the angle <H<sub>1</sub>-O<sub>w</sub>-H<sub>w</sub> plotted as function of time (Figure 3C) means that the bending mode of H<sub>2</sub>O relative to N-H is slightly excited after the ionization.

*Trajectory from the CO Site of FA(H<sub>2</sub>O).* Snapshots for the geometrical conformations of FA<sup>+</sup>(H<sub>2</sub>O) ionized from the CO site are given in Figure 4. At time zero, the hydrogen of H<sub>2</sub>O orients toward the oxygen atom of CO and the bonding is constructed by a hydrogen bond. After the ionization, a hole is mainly localized on the oxygen and nitrogen atoms in -NH-CO- site, so that the water molecule leaves quickly from the CO carbonyl because of repulsive interaction between the hydrogen of H<sub>2</sub>O and a positive charge on the -NH-CO- site.

After the ionization, the water molecule left-turned around FA<sup>+</sup> as be indicated by the arrows in Figure 4. At time = 0.25 ps, the water molecule passes near the hydrogen connecting to the C=O carbonyl, and it approached to the N-H site at time



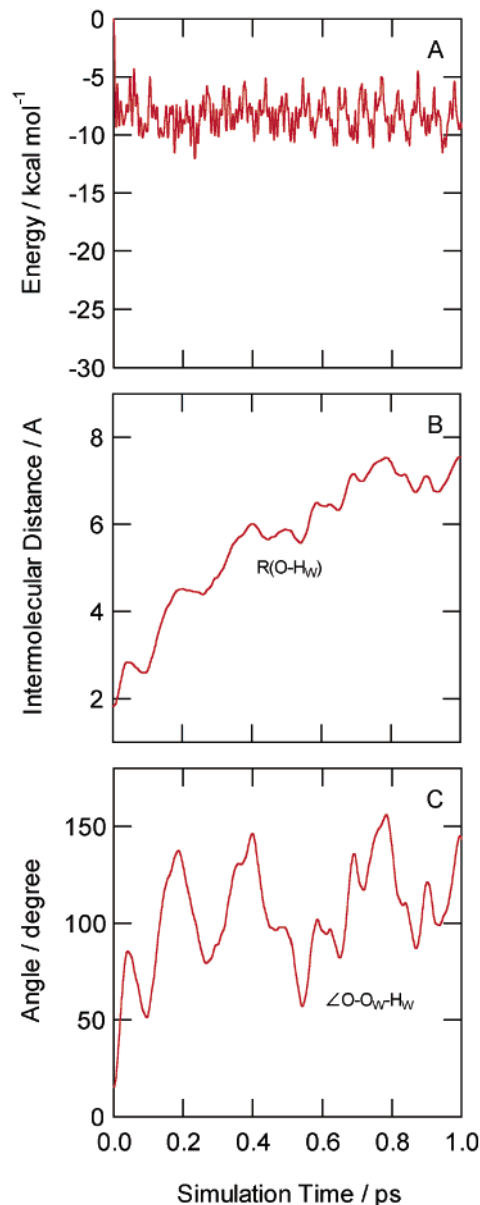
**Figure 6.** Snapshots of the structure of FA<sup>+</sup>(H<sub>2</sub>O) after the ionization from the bridge site. The dynamics calculation was carried out at the HF/3-21(d) level.

= 0.38–0.40 ps. At time = 0.55 ps, the water molecule was rebound near the hydrogen of benzene ring (o-position), and it reached the N–H site and the hydrogen of H<sub>2</sub>O connected to the carbonyl. At 1.00 ps, the water molecule returned again in the carbonyl group. Thus, it is concluded that the water molecule travels around the amide group and the benzene ring of FA<sup>+</sup> after the ionization of [FA(H<sub>2</sub>O)]<sub>CO</sub>, and it moves easily around FA<sup>+</sup>. This feature is much different from that of [FA(H<sub>2</sub>O)]<sub>NH</sub>.

The energy of the reaction system, distances R(O–H<sub>W</sub>) and R(H<sub>1</sub>–O<sub>W</sub>), and angle <O–O<sub>W</sub>–H<sub>W</sub> are plotted as a function of time in Figure 5. After the ionization, the energy was suddenly down to –9.0 kcal/mol at time = 15 fs, and then it decreased gradually with vibration. At time = 0.3 ps, the energy further decreased at time = 0.3 ps, and it reached the lowest energy point (–27.5 kcal/mol at 0.39 ps). This lowest energy point corresponds to the position that H<sub>2</sub>O passes the N–H site. After that, the energy increased again and reached the top of energy point (–3.9 kcal/mol at time = 0.55 ps).

The intermolecular distance between H<sub>2</sub>O and the carbonyl oxygen, R(O–H<sub>W</sub>), increased gradually and reached at time = 0.52 ps to the longest distance of R(O–H<sub>W</sub>) = 7.2 Å, and then it decreased again, indicating that H<sub>2</sub>O leaves from the carbonyl after the ionization, and then it returns again near the carbonyl within about 1.0 ps.

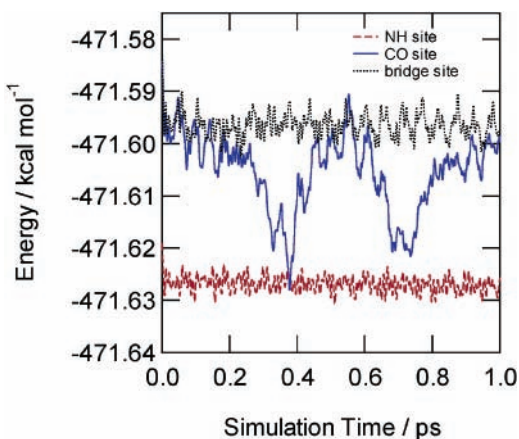
*Trajectory from the Bridge Site of FA(H<sub>2</sub>O).* The results of the trajectory calculation for the ionization from the bridge site are given in Figures 6 and 7. The snapshots of the conformations for [FA<sup>+</sup>(H<sub>2</sub>O)] after the ionization are given in Figure 6. Roman



**Figure 7.** Trajectory for FA<sup>+</sup>(H<sub>2</sub>O) from the bridge site. The dynamics calculation was carried out at the HF/3-21(d) level. (A) potential energy of the reaction system, (B) intermolecular distance between FA<sup>+</sup> and H<sub>2</sub>O, denoted by R(H<sub>1</sub>–O<sub>w</sub>), and (C) angle of <H<sub>1</sub>–O<sub>w</sub>–H<sub>w</sub>. Snapshots of the structure of FA<sup>+</sup>(H<sub>2</sub>O) after the ionization are illustrated in Figure 6.

numbers in Figure 6, I–V, mean the positions of H<sub>2</sub>O for the formation of the cationic complexes (I–V). First, the H<sub>2</sub>O molecule is located in the bridge site. After the ionization, H<sub>2</sub>O right-turned around FA<sup>+</sup> as be indicated by the arrows in Figure 6. At time = 0.25 ps, the water molecule passed on the region of the complex V, and it is remained very short time. The water molecule further moves for the region of IV at 0.75 ps. The complex IV was still formed at time 1.0 ps. From the trajectory calculation, it is concluded that the H<sub>2</sub>O molecule moves along the edge of benzene ring after the ionization and it stays short time in each complex region.

Figure 7 shows change of the energy of the system, intermolecular distance R(O–H<sub>W</sub>) and angle <O–O<sub>W</sub>–H<sub>W</sub> plotted as a function of time. As well as in the trajectories for the N–H and CO sites, the energy of the system was suddenly down to –9.0 kcal/mol after the ionization. This is caused by the structural deformation of FA<sup>+</sup>. And then, the energy vibrated periodically during the simulation. From change of the distance



**Figure 8.** Potential energies of the system (total energies) for all trajectories calculated at the HF/3-21G(d) level.

and angle plotted as a function of time, it was found that the H<sub>2</sub>O molecule leaves slowly from the amide group.

**D. Comparison of the Dynamics for Three Channels.** As be above-mentioned, the ionization from each site differs greatly each other. To compare the energetics for three trajectories, total energies of the reaction systems are monitored as a function of time. The results are given in Figure 8. At time zero, the total energies for FA<sup>+</sup>(H<sub>2</sub>O) at the NH, CO and bridge sites are calculated to be  $-471.6192$ ,  $-471.5843$ , and  $-471.5833$  au, respectively. After the ionization, both energies are suddenly dropped by about 9.0 kcal/mol. It seems that amplitude of vibration of the energy for the NH site is slightly smaller than that of the bridge site, although the global feature is the similar to each other. Time-profile of the energy for the trajectory from the CO site is much different from the others: namely, the energy decreased gradually as a function of time, and it reaches the lowest energy points at time = 0.4 and 0.7 ps. These are the points that H<sub>2</sub>O approaches the N–H site of FA<sup>+</sup>. The water molecule passing in the vicinity of the N–H site has an efficient excess energy enough to exceed the potential well. Hence, the trajectory is not stabilized in this well and it moves freely along the edge of benzene ring.

#### 4. Discussion

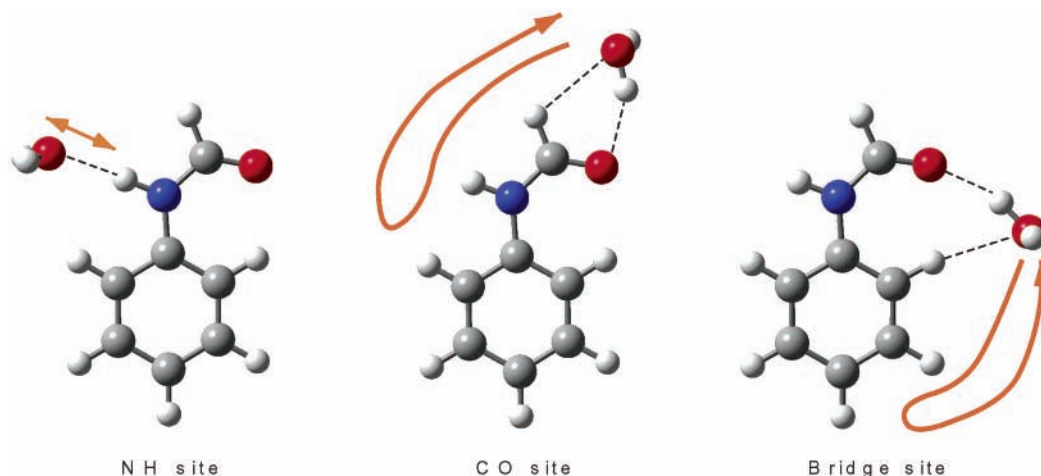
**A. Summary of the Present Study.** In the present study, we investigated the ionization dynamics of water–formanilide 1:1 complexes by means of full dimensional direct ab initio trajectory method. For neutral state, three conformers of the

FA(H<sub>2</sub>O) complexes were found: the N–H site, the C=O carbonyl site and the bridge site, which are distinguished by the positions of H<sub>2</sub>O around FA. Next, we calculated the ionization processes from these sites by means of the direct ab initio trajectory method. In the ionization from the N–H site, a water molecule still binds to the hydrogen of the N–H group and the water molecule cannot be dissociated from the N–H site. On the other hand, in the cases of the ionization from the CO and bridge sites, the water molecule was moved easily around both the benzene ring and the C=O carbonyl group.

Schematic illustrations for the trajectory passed for each channel are shown in Figure 9. The trajectory for FA<sup>+</sup>(H<sub>2</sub>O) ionized from the N–H site is illustrated in Figure 9(a). After the ionization, H<sub>2</sub>O molecule is still bound to the N–H group and it vibrates periodically in the site. On the other hand, the water molecule from the CO site moves largely around the NH–CO– amino group, as shown in Figure 9(b). The trajectory for the ionization of FA(H<sub>2</sub>O) from the bridge site indicated the round trip around the benzene ring. Thus, the trajectories obtained from three binding sites give each other typical feature for ionization dynamics.

In the case of the ionization from the latter two sites, large amplitude motions of H<sub>2</sub>O around FA<sup>+</sup> were found. However, a dissociation channel of water molecule from FA<sup>+</sup> was not found. This is due to the fact that the excess energy of FA(H<sub>2</sub>O) is assumed to zero in the dynamics calculations. Also, the HF/3-21G(d) calculation gave an overestimation of binding energy of H<sub>2</sub>O to FA<sup>+</sup>. The binding energies calculated by HF/3-21G(d) are 15.4 kcal/mol (complex II), 14.5 kcal/mol (III), 14.1 kcal/mol (IV) and 14.7 kcal/mol (V). These energies are 3–5 kcal/mol overestimated compared with those of B3LYP/6-311G(d,p) calculations (10.9–11.6 kcal/mol). If we use B3LYP/6-311G(d,p) level of theory for the dynamics calculations, then the dissociation channel of H<sub>2</sub>O molecule would be found. Such calculations may be possible after the development of high performance CPU computer.

**B. Comparison with Previous Studies.** Mons et al. observed the products after the ionization of two FA(H<sub>2</sub>O) complexes where a water molecule binds to the CO or NH site using a supersonic beam and tunable lasers combined to reflectron type time-of-flight (TOF) mass spectrometer.<sup>16</sup> They found that two kinds of ions, a parent ion FA<sup>+</sup>(H<sub>2</sub>O) and daughter ion FA<sup>+</sup> are observed after the ionization. In the ionization of [FA(H<sub>2</sub>O)]<sub>NH</sub>, the main product is the parent ion FA<sup>+</sup>(H<sub>2</sub>O). On the other hand, in the ionization of [FA(H<sub>2</sub>O)]<sub>CO</sub>, the daughter ion is also observed as well as the parent ion. These



**Figure 9.** Schematic illustrations for the trajectories after the ionization from three binding sites (a) N–H site, (b) C–O site, and (c) bridge site.



results indicate that the water molecule is strongly bound to the N–H site at the ionized state, and dissociation of the water molecule from the N–H site is difficult, whereas the water molecule binding to the CO site can move easily at the ionized state. The present calculations indicate that the H<sub>2</sub>O molecule in the N–H site is strongly bound to the site after the ionization, whereas the water molecule in the CO site moves largely around the benzene ring at the ionized state. This result strongly suggests that the water molecule formed by the ionization of CO site can easily dissociate from FA<sup>+</sup>. Thus, the present model can explain reasonably these dynamics features of FA<sup>+</sup>(H<sub>2</sub>O).

For the cation structures of FA<sup>+</sup>(H<sub>2</sub>O), Müller–Dethlefs and co-workers showed on the basis of ab initio calculations that the water molecule can bind strongly to the N–H site at the ionized D<sub>0</sub> state.<sup>14,15</sup> In the present study, in addition to the cation complex in the N–H site, four new structures were found for the binding sites of H<sub>2</sub>O around FA<sup>+</sup>, as described for the cation complexes I–V.

**C. Additional Comments.** In the present study, several approximations have been employed in the calculations of the potential energy surface and the reaction dynamics. First, we have assumed that FA<sup>+</sup>(H<sub>2</sub>O) has no excess energy at the initial step of the trajectory calculation (time = 0.0 ps). Also, we neglected zero-point vibrational energies (ZPEs) in the dynamics calculation because the ZPEs for neutral and ionic states were close each other in the case of the present system (difference was less than 4 kcal/mol). Therefore, this approximation was enough to describe the dynamics of the present system. Inclusion of these effects on the dynamics calculations may cause a slight change of lifetime and energy distribution of the products. In the case of higher excess energy, the dissociation product from the FA<sup>+</sup>(H<sub>2</sub>O) may be observed as product channel. However, these effects were not considered in the present calculations. It should be noted therefore that the present model is limited in the case of no excess energy and no-ZPE.

Last, we assumed HF/3-21G(d) multidimensional potential energy surface in the trajectory calculations throughout. In previous papers, we investigated ionization dynamics of BzNH<sub>3</sub> and BzH<sub>2</sub>O at the HF/3-21G(d) level of theory.<sup>23,25</sup> The results obtained at the HF/3-21G(d) calculations would give a reasonable feature of the ionization dynamics of the complexes. Therefore, the level of theory used in the present calculation (HF/3-21G(d)) would be adequate to discuss qualitatively the ionization dynamics of FA(H<sub>2</sub>O). However, more accurate wave functions may provide deeper insight in the dynamics. Such calculation will be possible after development of high-speed CPU in near future. Despite the several assumptions introduced here, the results enable us to obtain valuable information on the mechanism of the ionization of FA(H<sub>2</sub>O).

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