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Hydration and Dissociation of Hydrogen Fluoric Acid (HF)

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The hydration and dissociation phenomena of $HF(H_2O)_n$ ($n \leq 10$) clusters have been studied by using both the density functional theory with the 6-311++G**[sp] basis set and the Møller−Plesset second-order perturbation theory with the aug-cc-pVDZ+(2s2p/2s) basis set. The structures for $n \geq 8$ are first reported here. The dissociated form of the hydrogen-fluoric acid in $HF(H_2O)_n$ clusters is found to be less stable at 0 K than the undissociated form until $n = 10$. HF may not be dissociated at 0 K solely by water molecules because the HF H bond is stronger than the OH H bond, against the expectation that the dissociated $HF(H_2O)_n$ would be more stable than the undissociated one in the presence of a number of water molecules. The dissociation would be possible for only a fraction of a number of hydrated HF clusters by the Boltzmann distribution at finite temperatures. This is in sharp contrast to other hydrogen halide acids (HCl, HBr, HI) showing the dissociation phenomena at 0 K for $n \geq 4$. The IR spectra of dissociated and undissociated structures of $HF(H_2O)_n$ are compared. The structures and binding energies of $HF(H_2O)_n$ are found to be similar to those of $(H_2O)_{n+1}$. It is interesting that $HF(H_2O)_{n=5,6,10}$ are slightly less stable compared with other sizes of clusters, just like the fact that $(H_2O)_{n=6,7,11}$ are slightly less stable. The present study would be useful for the experimental/spectroscopic investigation of not only the dissociation phenomena of HF but also the similarity of the HF−water clusters to the water clusters.

I. Introduction

Acid dissociation is one of the most fundamental chemical reactions. It is also of fundamental importance in atmospheric and biological science.[1] A number of studies on hydration- and photoinduced dissociation of acids have been reported.[2] Among many acids, HF is a weak acid, while the HF hydrogen bond is very strong. Thus, its dissolution and reactivity have been interesting subjects because of its anomalous properties among acids. The strong bases can dissolve the HF acid in aqueous solution. Hydration and photolysis of HF with other solutes in the presence of water vapor upon ultraviolet radiation may lead to the formation and accumulation of atomic F and/or inorganic fluoric compounds. Because of its high reactivity, F can react with ozone and cause decay of the ozone layer. Another important point is the relevance in the design of novel receptors for the fluoride anion.[3] The study of the interaction of a single HF acid molecule with water molecules[4−7] helps illuminate some of the basic structural features that are required to allow proton transfer. The hydration of a fluoride anion and a proton[8,9] is closely related to the dissociation phenomena of HF. It should be noted that the F atom is more electronegative than the O atom, and the number of lone pairs of electrons of HF is three, while that of water is two.

In our previous study of $HF(H_2O)_{1-6}$,[5] we did not find any dissociation phenomena in contrast to other hydrogen halide acids HX (X = Cl/Br/I). The energy difference between undissociated and dissociated structures is getting smaller with the increasing number of water molecules. Therefore, it is of importance to investigate the possible dissociation of HF in the presence of more water molecules. Indeed, there have been a few studies on the dissociation/undissociation of $HF((H_2O)_7$.[6,7] Thus, here we have extended our study for the neutral clusters of $HF(H_2O)_{7-10}$ using density functional theory (DFT) and ab initio calculations. We have investigated diverse structures including the conformers that are not available in the literature. The comparison between $HF(H_2O)_{n=1-10}$ and $(H_2O)_{n=2-11}$ is also a very interesting subject.

II. Calculation Methods

Numerous structures of neutral clusters of $[HF(H_2O)_{7-10}]$ were examined using density functional theory (DFT) with Becke's three parameter exchange potential and the Lee, Yang, and Parr correlation functional (B3LYP) with the 6-311++G**[sp] basis set where [sp] are the extra diffuse functions for the fluorine atom. Then, the lowest-energy clusters obtained from the B3LYP results were further optimized at the Møller−Plesset second-order perturbation (MP2) theory with the aug-cc-pVDZ+(2s2p/2s) basis set. The [sp] and (2s2p/2s) diffuse functions were added to describe the dissociation phenomena properly.[5] The B3LYP and MP2 interaction energy differences between the most stable undissociated and dissociated forms are consistent. Vibrational frequency analysis was made to assess the nature of the stationary points and to obtain zero-point vibrational and free energies (ZPE and G) at the B3LYP level of theory. Calculations were performed using the

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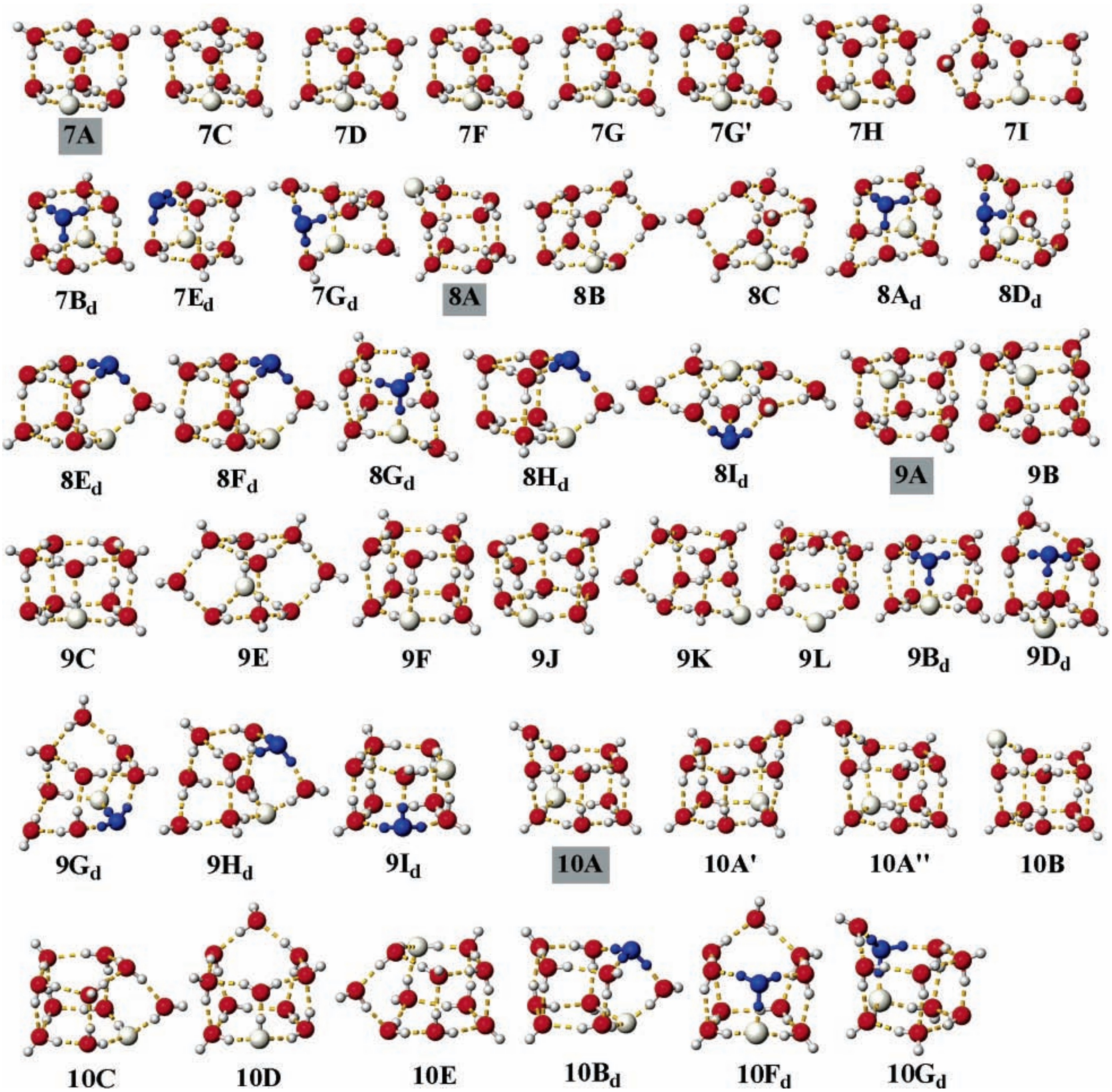

Figure 1. Low-energy structures of $HF(H_2O)_{n=7-10}$.

Gaussian suite of programs.[11] Most of the figures presented here were drawn using the Pohang Sci-Tech Molecular Modeling (POSMOL).[12]

III. Results and Discussions

A. Hydration Structures and Energetics. We have searched for various conformers of neutral $HF(H_2O)_{7-10}$ clusters at the B3LYP/6-311++G**[sp] level by investigating its possible topological structures (Figure 1). In order not to miss low-energy structures, not only the structures of neutral water clusters and electron-bound water clusters[13,14] but also the structures of hydrated cation clusters and hydrated halide clusters[9,15,16] were used to build the hydrated HF structures. The geometrical parameters (such as F−H distance and its dissolution or partial ionization phenomena with increasing number of water molecules) depend highly on the coordination number of the halogen atom and hydrogen-bonding interactions. The lowest-energy $HF(H_2O)_{7-10}$ clusters were analyzed by considering (a) the coordination number of hydrogen halide, (b) H-bonding energy gain against strain, and (c) minimized H···H repulsions between two neighboring H atoms with alternating up−down H orientations. Among the many structures investigated, only low-lying energy structures are discussed in this work. Further, the lowest-energy clusters or the nearly isoenergetic clusters for the undissociated and dissociated cases are calculated at the MP2/aug-cc-pVDZ+(2s2p/2s) level. The dissociated structures are denoted by subscript "d" in the notation of structure. The lowest-energy clusters of $HF(H_2O)_{1-6}$ are reported in our earlier work. The successive binding energies from mono- to hexahydrated HF systems are estimated as 6.3, 7.0, 10.0, 7.7, 7.6, and 8.2 kcal/mol based on the ZPE-corrected interaction energies ($-\Delta E_0$) at the MP2/aug-cc-pVDZ+(2s2p/2s) level. The numbers of their H bonds for $n = 1-6$ are 1, 3, 4, 5, 7, and 8, respectively. The small hydrated hydrogen-fluoroic acids (for $n = 1-4$) have structures similar to the neutral water clusters (for $n = 2-5$). The successive binding energy of trihydrated hydrogen-fluoric acid [3R4] is considerably large because of the effective H-bond interactions of cyclic tetramer. The pentahydrated HF has a book-like structure, which is one of the low-energy neutral water hexamers. However, the hexahydrated HF has a fused 4- and 5-ring structure, which is different

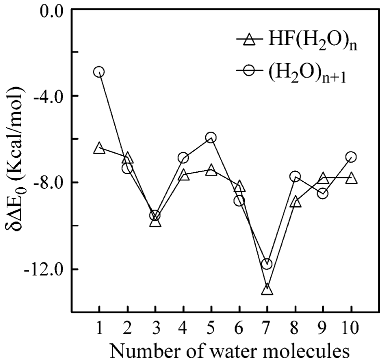

Figure 2. Successive binding energies ($\delta\Delta E_0$) of $HF(H_2O)_n$ and $(H_2O)_{n+1}$. where each structure is chosen with the lowest energy confomer. The successive binding energies of $(H_2O)_n$ are at the MP2/TZ2P++ level with the B3LYP-ZPE correction (ref 13).

from the lowest-energy structure of neutral water heptamer. This reflects the fact that the water hexamer and heptamer are less stable compared with other sizes of clusters and are susceptible to undergoing conformational transformation from two-dimensional to three-dimensional structures.

The interaction energies of HF with water molecules are larger than those of water molecules in neutral water clusters. The successive binding energies ($-\Delta E_0$) of neutral water clusters for $n = 2-11$ (which have 1, 3, 4, 5, 8, 10, 12, 13, 15, and 17 H bonds) are reported as 2.9, 7.4, 9.5, 6.9, 6.0, 8.9, 11.8, 7.8, 8.5, and 6.9 kcal/mol at the MP2/TZ2P++ level.[13] The successive binding energies of HF with water molecules are compared with those of H_2O with water molecules (Figure 2). It is interesting to note a similar trend between them.

For $HF(H_2O)_7$, Figure 1 shows 11 structures among which 9 structures are in cubic form with different hydrogen-bonding orientations and different dangling H-atom arrangements and the remaining two structures are in cyclic form (7I, $7G_d$). Owing to the structural similarity of $HF(H_2O)_n$ to $(H_2O)_{n+1}$, the cubical structures $HF(H_2O)_7$ are particularly stable as those of $(H_2O)_8$. The hydrogen fluoride directly coordinated to double-donor-single-acceptor (DDA)-type water molecule is found to be more stable than that coordinated to a single-donor-double-acceptor (DAA)-type water molecule (7G′). Their interaction energies are reported in Table 1. On the basis of the F−H distance and stretch mode, we note that 7G, 7C, and 7D are only partially ionized structures, in which the F−H distances are found to be 1.14−1.22 Å. Cyclic structures (7I, $7G_d$) with 10 hydrogen bonds are found to be less stable than the cubic forms (12 hydrogen bonds). The lowest-energy structure 7A is found to be undissociated with 3.90 (3.19) kcal/mol lower in energy than the dissociated structure $7B_d$ (reported in a previous work[7]) at the B3LYP (MP2) level. Partially ionized structure 7G is still 0.63 (0.31) kcal/mol higher in energy than the undissociated form 7A. Among all possible hydrogen-bonded isomers of cubic $HF(H_2O)_7$, the lowest-energy conformer is undissociated structure 7A, followed by structure 7G.

The undissociated structures of $HF(H_2O)_8$ are derived by adding an additional water monomer unit (single-donor-single-acceptor; DA) to $HF(H_2O)_7$. Among the nine possible isomers, hydrogen fluoride directly connected to the DDA-type water molecule (8A) is found to be ∼4.6 kcal/mol more stable than that connected to the DAA-type water molecule (8B and 8C). For $HF(H_2O)_9$, the lowest-energy structure 9A is undissociated, 2.63 kcal/mol lower in energy than the dissociated form $9D_d$. For $HF(H_2O)_{10}$, the lowest-energy undissociated structure 10A (followed by 10B and 10A″) is 3.05 kcal/mol lower in energy than the dissociated structure $10B_d$. In the case of the lowest-energy undissociated structures of $HF(H_2O)_{9-10}$, the hydrogen fluoride is directly coordinated to the DDA-type water molecule.

On the basis of MP2/aug-cc-pVDZ+(2s2p/2s), the lowest-energy undissociated and dissociated structures of $HF(H_2O)_n$ are 7A and $7B_d$ for $n = 7$; 8A and $8H_d$ for $n = 8$; 9A and $9H_d$ for $n = 9$; and 10A and $10B_d$ for $n = 10$. The lowest-energy undissociated structures of $HF(H_2O)_{7-10}$ (7A, 8A, 9A, and 10A) are almost similar to those of $(H_2O)_{7-10}$ structures. The very strong hydrogen bonding between hydrogen fluoride and water costs a lot of energy to break, in contrast to other hydrogen halides.[4−6] This is the reason that HF is a very weak acid. In Table 1 and Figure 3, the interaction energy difference between the undissociated and dissociated forms $HF(H_2O)_n$ for $n = 4-10$ decreases with the successive addition of water molecules. To compare the relative stabilities of undissociated and dissociated

TABLE 1: Interaction Energies of $HF(H_2O)_{7-10}$ Clusters at B3LYP/6-311++G[sp] and [MP2-aug-cc-pVDZ+(2s2p/2s)] Levels**

B3LYP/6-311++G**[sp] and [MP2-aug-cc-pVDZ+(2s2p/2s)]											
n	conf	no. HB/CN	$-\Delta E_e$	$-\Delta E_0$	$-\Delta G_{100}$	*n*	conf	no. HB/CN	$-\Delta E_e$	$-\Delta E_0$	$-\Delta G_{100}$
7	**7A**	12/3	80.56[79.74]	59.92[59.14]	42.18[42.02]	9	**9A**	15/3	104.15[101.71]	78.21[75.82]	54.90[52.45]
	7G	12/3	79.21[78.70]	59.29[58.82]	41.50[40.32]		**9B**	15/3	102.82		
	7H	12/3	80.49	59.78	42.12		**9C**	15/3	99.45		
	7C	12/3	77.70				**9E**	14/3	101.91		
	7D	12/3	75.77				**9F**	15/3	99.37		
	7F	12/3	74.22				**9J**	15/3	99.31		
	7G′	12/3	75.93				**9K**	14/2	101.09		
	7I	10/3	73.37				**9L**	14/2	102.79		
	$7B_d$	12/3	76.92[76.55]	56.02[55.70]	38.15[37.78]		**$9B_d$**	15/3	102.43[100.38]	76.36[74.36]	52.97[50.92]
	$7E_d$	12/3	73.07				**$9D_d$**	14/3	100.95[98.06]	75.58[72.75]	52.31[49.42]
	$7G_d$	10/3	73.07				**$9G_d$**	14/3	98.08	73.89	50.82
							$9H_d$	14/3	99.92	74.65	51.40
							$9I_d$	15/3	91.62		
8	**8A**	13/2	93.01[91.42]	69.70[68.03]	49.23[47.64]	10	**10A**	16/3	114.91[111.56]	86.91[83.62]	60.92[57.57]
	8B	13/3	91.29[89.62]	68.39[66.77]	48.00[46.33]		**10A′**	16/3	113.13	84.90	58.99
	8C	13/3	85.86	63.80	43.52		**10A″**	16/3	114.51[111.29]	86.34[83.41]	60.39[57.14]
	$8A_d$	13/3	88.70	65.54	44.97		**10B**	16/2	115.28[112.32]	86.35[83.45]	60.36[57.39]
	$8D_d$	12/3	80.35				**10C**	16/3	112.53	84.38	58.44
	$8E_d$	13/3	86.42				**10D**	16/3	110.73		
	$8F_d$	13/3	84.38				**10E**	16/3	110.52		
	$8G_d$	13/3	87.54				**$10B_d$**	16/3	111.89[108.81]	83.60[80.57]	57.39[54.30]
	$8H_d$	13/3	89.81[88.08]	66.71[65.02]	46.12[44.38]		**$10F_d$**	16/3	111.52		
	$8I_d$	13/4	79.82				**$10G_d$**	16/3	113.34[110.14]	85.10[81.96]	59.03[55.84]

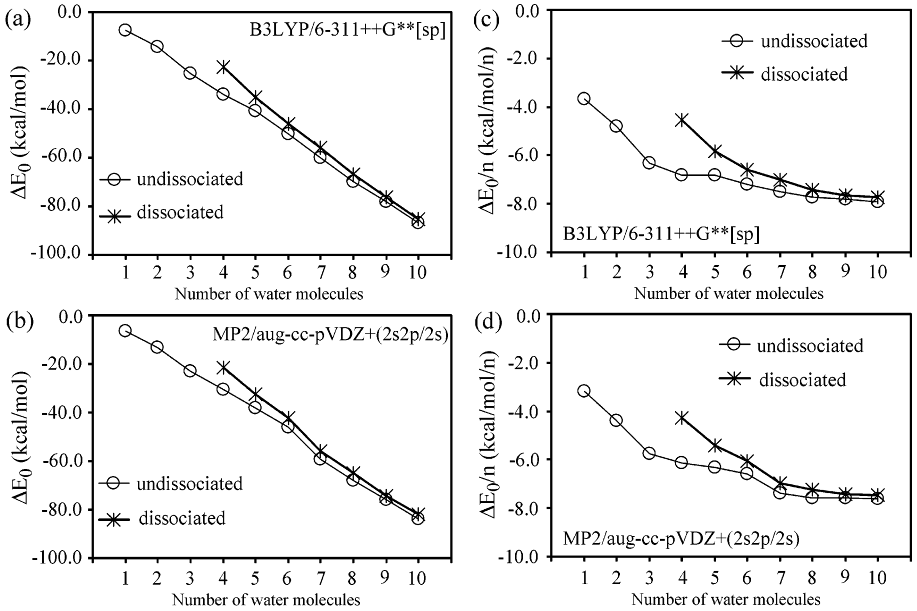

Figure 3. Hydration energies (a and b) and interaction energies per monomer (c and d) of undissociated and dissociated $HF(H_2O)_{n=1-10}$ clusters at the B3LYP/6-311++G**[sp] and MP2/aug-cc-pVDZ+(2s2p/2s) levels of theory.

TABLE 2: MP2/aug-cc-pVDZ+(2s2p/2s) Conformational Characteristics, Geometric Parameters, and Electronic Properties [Distances (r/Å), HOMO−LUMO Energy Gap (δE_g/eV), Dipole Moment (μ/Debye) and Koopman's Ionization Potential (IP_K/eV)] for the Low-Energy Clusters $HX(H_2O)_{7-10}$[a]

conf		B3LYP/6-311++G**[sp]				MP2/aug-cc-pVDZ+(2s2p/2s)				
$HF(H_2O)_{1-6}$	no. $^{HB/co/Hd}$	r_{FH}	r_{FH1}	r_{FO1}	δE_g	r_{FH}	r_{FH1}	r_{FO1}	μ	IP_K
7A	12/3/3	0.998	1.66	2.45	7.96	0.995	1.64	2.46	2.71	13.78
7G	12/3/3	1.20	1.53	2.35	7.92	1.27	1.49	2.37	2.60	13.77
$7B_d$	12/3/3		1.54	2.53	7.94		1.53	2.52	2.26	13.87
8A	13/2/4	1.001	1.35	2.43	7.89	0.995	1.34	2.45	2.35	13.65
$8H_d$	13/3/4		1.53	2.50	7.92		1.52	2.49	1.10	13.61
9A	15/3/4	1.021	1.62	2.41	7.46	1.002	1.65	2.43	2.23	13.30
$9B_d$	15/3/4		1.51	2.40	7.48		1.50	2.36	4.39	13.39
10A	16/3/5	1.067	1.56	2.36	7.71	1.034	1.58	2.39	1.07	13.43
10B	16/2/5	0.984	1.39	2.47	7.61	0.975	1.39	2.48	4.10	13.54
$10G_d$	16/3/5		1.51	2.39	7.31		1.50	2.36	3.54	13.16

[a] no. $^{HB/co/Hd}$ are the numbers of H bonds/halide−water coordination/dangling hydrogen atoms. r_{FO1} is the smallest fluorine−oxygen distance in the primary hydration shell. For the water molecules in all clusters, r_{OHn}= 0.969 ± (0.004 Å), where Hn denotes the non-hydrogen-bonded H atom, and r_{OHw} = 0.98−1.03 Å.

forms of hydrated hydrogen fluorides, their ZPE-corrected interaction energies at the B3LYP and MP2 levels of theory are shown in Figure 3. Because of the weak acidity and high dissociation energy, the hydrated hydrogen fluoride prefers to be in the undissociated form until $n = 10$. Against the possible expectation[7] that HF would dissociate in the presence of a number of water molecules (because HCl/HBr/HI dissociates easily for $n \geq 4$), it is likely that HF would not be dissociated at 0 K because the HF H bond is stronger than the OH H bond, while the dissociation would occur probabilistically according to the Boltzmann distribution at finite temperatures. At 100 K, the free energy differences between the undissociated and dissociated states for $n = 7$, 8, 9, and 10 are 4.03, 3.11, 1.93, and 1.89 kcal/mol. In the case of $n = 10$, the population of dissociated structure would be ~0.01% at 100 K.

The interaction energies per monomer (Figure 3c and 3d) reflect the effect of the structure ($n = 1$: linear, $n = 2-4$: monoring, $n = 5-6$: 2D fused rings, and $n = 7-10$: 3D structures) on the stabilization by the H-bond interactions. Similar to the neutral water clusters, the cyclic tetramer or pentamer ring structures are highly effective for the stable H-bond interaction. The B3LYP results are overall similar to the MP2 results in the dissociation/undissociation trend. The MP2 hydration energies are slightly smaller than those of B3LYP, and the MP2 calculation results also show a smaller energy difference between dissociated and undissociated structures than the B3LYP results.

B. Structural and Electronic Properties. Table 2 lists the conformational characteristics, geometrical parameters, and electronic properties of the lowest-energy undissociated and dissociated $HF(H_2O)_n$ clusters at the B3LYP/6-311++G**[sp] and MP2/aug-cc-pVDZ+(2s2p/2s) levels. The coordination numbers (no. co) of undissociated $HF(H_2O)_n$ for $n = 2-10$ are two or three, while the dissociated structures $HF(H_2O)_n$ for $n = 4-10$ are tricoordinated. Tetracoordinated conformations such as $8I_d$ are less favorable, which is contrasted to other acid halides HX (X = Cl, Br, and I) (hexahydrated chloride, tetrahydrated bromide, and tetrahydrated iodide).

Figure 4 and Table 2 show the changes of F−H and F−O distances for the undissociated and dissociated forms of $HF(H_2O)_n$ upon the successive addition of n water molecules to the parent hydrogen fluoride. The F−H distances of undissociated $HF(H_2O)_n$ for $n = 1-10$ are 1L: 0.941 (0.943) Å; 2R3: 0.957 (0.957) Å; 3R4: 0.974 (0.972) Å; 4R5: 0.980 (0.976) Å; 5R44: 1.058 (1.038) Å; 6R54: 1.091 (1.066) Å; 7A: 0.998 (0.995)Å; 8A: 1.001 (0.995) Å, 9A: 1.021 (1.002) Å; 10A: 1.067 (1.003) Å at the B3LYP (MP2) level, respectively. The F−H distance of undissociated hydrated hydrogen

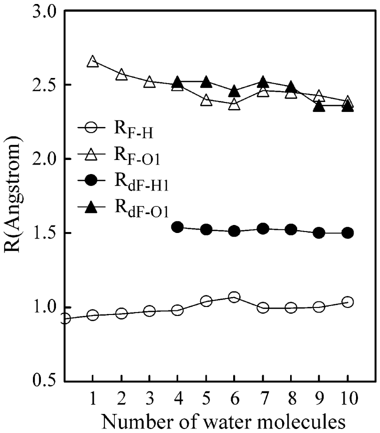

Figure 4. H−F (R_{F-H} and R_{dF-H1}) and F−O1 (R_{F-O1} and R_{dF-O1}) distances of undissociated and dissociated $HF(H_2O)_n$, where "d" denotes the dissociated state.

halides increases slightly with the increase of water molecules. $HF(H_2O)_{5,6,10}$ show tricoordination with strong H-bond interactions between HF and water molecules. Thus, these H−F distances are enhanced slightly. The structures of $n = 5$, 6, and 10 correspond to those of water clusters $(H_2O)_{n=6,7,11}$, which are relatively less stable than other size of clusters.[13] Thus, this phenomenon is caused by the less stable structural effect. Generally, the average F−H distances of hydrated hydrogen halides tend to increase with the increase of cluster size and coordination number. The increase in H−X distance with the increase in number of water molecules for X = F is very small compared to X = Cl, Br, and I, which ensures the weak acidity of HF acid. The F−O distance decreases gradually as the number of water molecules increases, but the F−O distances of dissociated cases are generally shorter than those of undissociated cases at the MP2 level. The dissociated cases have a charged fluoride anion, which involves stronger $F^- \cdots HO$ interactions. The ionization potential (IP_K) decreases with the increasing number of water molecules because of the hydration effect.

C. IR spectra of $HF(H_2O)_n$. The B3LYP/6-311++G**[sp] vibrational frequencies for X−H and O−H stretching modes for hydrated hydrogen halides for dissociated/undissociated structures are in Table 3 and Figure 5. From our previous calculations,[5] the stretching frequencies (ω_h) are generally overestimated in comparison with the experimental data. The calculated frequencies were scaled (ω_s) with the scale factor 0.96. An $HF(H_2O)_n$ cluster in the undissociated form has one F−H and 2*n* O−H stretch modes that typically fall in the 2600−4000 cm^{-1} range. The dissociated form $H_3O^+ \cdots F^- \cdots (H_2O)_{n-1}$ has three O−H stretch modes corresponding to the hydronium moiety as a characteristic peak for the H−F dissociation, and $n - 1$ OH stretch modes. Experimentally, the pure F−H stretch was observed around 3959 cm^{-1},[17] and the scaled (ω_s) frequency for F−H mode is 3936 cm^{-1}. The undissociated hydrogen halides bound to water clusters show strongly red shifted F−H stretch peaks (Figure 5). For the dissociated hydrated hydrogen fluorides, the O−H stretch peaks show those of hydronium moiety.

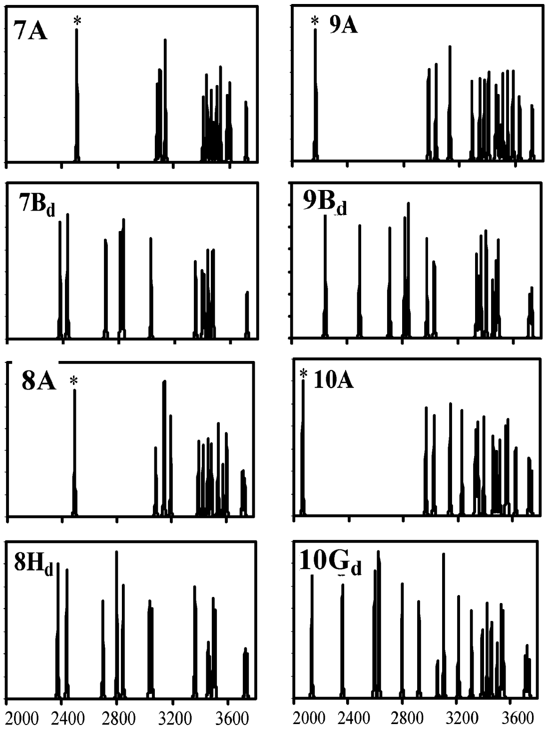

Figure 5. IR spectra for the O−H and F−H stretching modes of $HF(H_2O)_{n=7-10}$ (B3LYP/6-311++G**[sp]; harmonic frequencies scaled by 0.96).

TABLE 3: Scaled (Scale Factor: 0.96) Frequencies (ω_s in cm^{-1}) and Intensities (10 km/mol in Subscript) of $HF(H_2O)_{7-10}$ Conformers at B3LYP/6-311++G[sp]**

$HF(H_2O)_n$											
7A	2506_{169}	3081_{36}	3103_{94}	3141_{145}	3413_{29}	3439_{57}	3468_{41}	3488_{8}	3508_{35}	3535_{75}	3584_{22}
	3603_{45}	3721_{9}	3721_{8}	3722_{4}							
7G	1221_{2519}	2957_{1061}	3043_{677}	3114_{926}	3238_{619}	3315_{651}	3468_{266}	3483_{411}	3488_{125}	3516_{83}	3547_{765}
	3549_{705}	3721_{67}	3724_{98}	3725_{45}							
8A	2465_{204}	$3070_{0.5}$	3076_{59}	3144_{242}	3334_{75}	3393_{46}	3409_{45}	3467_{46}	3487_{6}	3493_{17}	$3498_{0.1}$
	3543_{75}	3545_{109}	3720_{8}	3721_{12}	3721_{2}	3725_{6}					
9A	2168_{214}	2979_{91}	3031_{88}	3131_{179}	3290_{62}	3344_{44}	3377_{49}	3408_{70}	3461_{36}	3474_{35}	3492_{4}
	3511_{53}	3545_{59}	3583_{58}	3630_{21}	3719_{7}	3719_{8}	3722_{6}	3723_{8}			
10A	1701_{136}	3037_{94}	3082_{45}	3096_{41}	3143_{236}	3198_{99}	3346_{90}	3372_{65}	3445_{35}	3461_{45}	3481_{2}
	3488_{18}	3504_{10}	3535_{58}	3550_{89}	3566_{60}	3716_{7}	3721_{7}	3722_{8}	3722_{4}	3736_{7}	
10B	2737_{1798}	2967_{535}	3049_{499}	3070_{927}	3124_{2780}	3265_{1025}	3404_{377}	3438_{524}	3449_{26}	3473_{124}	3477_{294}
	3482_{170}	3483_{371}	3535_{794}	3538_{779}	3557_{802}	3714_{58}	3719_{101}	3719_{75}	3720_{45}	3723_{64}	
$F^-H_3O^+(H_2O)_{n-1}$											
7Bd	2378_{169}	2432_{160}	2707_{101}	2815_{139}	2831_{135}	3033_{72}	3353_{53}	3403_{34}	3417_{32}	3443_{55}	3472_{64}
	3479_{70}	3721_{7}	3724_{8}	3725_{3}							
8Hd	2372_{192}	2437_{153}	2699_{101}	2799_{260}	2843_{138}	3033_{81}	3051_{71}	$3354_{0.9}$	3364_{117}	3457_{20}	3467_{8}
	3493_{87}	3507_{72}	3722_{7}	3723_{7}	3725_{4}	3738_{7}					
9Bd	1983_{1957}	2626_{1728}	2854_{861}	3024_{1433}	3084_{923}	3180_{599}	3259_{432}	3309_{1108}	3435_{458}	3453_{214}	3497_{175}
	3503_{422}	3523_{730}	3544_{258}	3571_{664}	3719_{67}	3720_{63}	3722_{91}	3724_{53}			
10Gd	1969_{218}	2709_{216}	2841_{74}	3005_{113}	3030_{175}	3090_{88}	3194_{63}	3300_{21}	3333_{116}	3421_{51}	3460_{20}
	3499_{23}	3511_{43}	3524_{58}	3538_{40}	3582_{57}	3714_{6}	3720_{5}	3724_{7}	3724_{7}	3736_{7}	

The small undissociated $HF(H_2O)_n$ clusters are cyclic with the coordination number of two, and show monotonically increased red-shifted X−H stretch frequencies with the increased number of water molecules. More red-shifted F−H stretch frequency indicates a lower energy barrier for the proton transfer toward the dissociation structure. The F−H stretch modes of $HF(H_2O)_n$ clusters for $n = 1-4$ with monocyclic rings show high frequencies because of the low coordination number. For clusters $n = 5-6$ with tricoordination, the F−H stretch modes show large red-shifts. The undissociated forms of $HF(H_2O)_7$ are cubic with tricoordination and show the F−H stretch mode at 2506 cm^{-1}. In the case of $HF(H_2O)_8$, the undissociated form 8C with bicoordination shows a very strong F−H stretch mode at 2465 cm^{-1}. The undissociated forms of $HF(H_2O)_{9-10}$ with tricoordination show large red-shifts in the F−H stretch mode. The lowest energy undissociated forms of $HF(H_2O)_{7-10}$ (7A, 8A, 9A, and 10A) have the F−H stretch frequencies of 2506, 2465, 2168, and 1701 cm^{-1}, respectively. All of the dissociated $HF(H_2O)_{4-10}$ clusters ($4_d'$R44, $5_d'$R54, $6_d'$R55, $7B_d$, $8H_d$, $9B_d$, and $10G_d$) are tricoordinated, showing three strong red-shifted O−H stretch modes ensuring the hydronium moiety (2414, 2526, 2778 cm^{-1} for $n = 4$; 1969, 2709, 2841 cm^{-1} for $n = 10$). The hydronium moiety of the $4_d'$R44, $5_d'$R54, $6_d'$R55, $7B_d$, $8H_d$ clusters are slightly different from the $9B_d$ and $10G_d$. In the cases of $9B_d$ and $10G_d$, the hydronium moiety directly interacts with the fluoride, whereas in the other cases ($n = 4-8$), the hydronium moiety is separated from the fluoride.

IV. Concluding Remarks

The structures of $HF(H_2O)_{7-10}$ were investigated with B3LYP/6-311++G**[sp] and MP2/aug-cc-pVDZ+(2s2p/2s) calculations. The undissociated structures are found to be more stable than the dissociated structures (zwitter-ionic form) until $n = 10$ because of the weak acidity and strong binding energy of HF. Against the possible expectation that HF would dissociate in the presence of a number of water molecules (because HCl/HBr/HI dissociates easily for $n \geq 4$), it is likely that HF would not be dissociated at 0 K because the HF H bond is stronger than the OH H bond, while the dissociation would occur probabilistically according to the Boltzmann distribution at finite temperatures. The coordination number (no. co) for F in hydrated hydrogen fluoride clusters changes from two (for $n < 4$) to three at the pentahydrated case. Mono- to tetrahydrated systems have monocyclic ring structures, whereas cagelike structures are formed from the heptahydrated cases, similar to the neutral water clusters [$(H_2O)_n$]. Their interaction energies are slightly larger but similar to those of neutral water clusters. The penta- and hexahydrated undissociated HF acids have double cyclic-ring structures, which are different from the cage structures of $(H_2O)_{n=6,7}$, and they have relatively longer H−F distances with respect to other clusters because of the effective H-bond interaction with water molecules. Nevertheless, the overall stability of $HF(H_2O)_n$ is similar to that of $(H_2O)_{n+1}$. It is interesting to find that the slightly less stable behavior of $(H_2O)_{n=6,7,11}$ is also noted for the cases of $HF(H_2O)_{n=5,6,10}$.

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Supporting Information Available: The basis sets used at B3LYP and MP2 calculations and the structures and *xyz* coordinations are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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