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Enhanced Stability of Non-Proton-Transferred Clusters of Hydrated Hydrogen Fluoride $HF(H_2O)_n$ ($n = 1-7$): A Molecular Orbital Study

Suyong Re*

Department of Chemistry, Faculty of Science, Rikkyo University,
3−34−1 Nishi-ikebukuro, Toshima-ku, Tokyo 171-8501, Japan

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The results of a molecular orbital study on structures and stabilities are presented for the hydrated clusters of the hydrogen fluoride (HF) molecule, $HF(H_2O)_n$ ($n = 1-7$). For each cluster system, the most stable structure is found to be the non-proton-transferred type, but not the ion-pair form. The computational results are quite consistent with the weak acidity of the HF in water. The differences between $HF(H_2O)_n$ and $HCl(H_2O)_n$ cluster systems are further discussed for the structure and stability depending on the cluster size. The calculated IR spectra of the stable $HF(H_2O)_n$ clusters predict large red-shifts of H−F and hydrogen-bonded O−H stretching frequencies.

I. Introduction

Hydrated clusters of an acid are of interest in conjunction with chemistry in aqueous solution. This cluster system is the simplest model of acid−water interaction via hydrogen bonds in aqueous solution. The proton transfer in the cluster system is especially important to explore, at molecular level, the mechanism of the acid dissociation in water. Our previous computational study on the hydrated clusters of the strong acid, HCl, showed the occurrence of complete proton transfer at a certain cluster size.[1] Analogous investigation into the $HF(H_2O)_n$ clusters enables systematic comparison between two systems, and provides the microscopic insight into what governs the acidic behavior of the molecules in water.

Hydrogen fluoride is well-known to behave as a weak acid in water in contrast to the three other hydrogen halides:[2,3]

$$HF + H_2O \rightarrow H_3O^+ + F^-$$

$$K_{25°} = 7.2 \times 10^{-5}$$

This characteristic has been customarily attributed to the enhanced strength of the H−F bond as well as to the ability to form a strong hydrogen bond with a water molecule.[3,4] Spectroscopic studies[5] offer an alternative explanation that the weakness of HF acid is ascribed to the presence of a proton-transferred contact $F^-\cdots H_3O^+$ ion pair and its unfavorable separation. Recently, this fundamental issue is being reconsidered from a theoretical point of view.[6−8] Ando and Hynes examined the acid dissociation of HF in water by using the electronic structure-Monte Carlo method and have shown the activation barrier and positive reaction free energy for the formation of the contact ion-pair.[7] Hirata and Sato have reported from their RISM-SCF/MCSCF study that the hydration structure around the HF is qualitatively different from those of the other three hydrogen halides and that the stability of nondissociated HF is enhanced due to hydrogen bonding.[8] Their results suggest that the contact ion-pair is unlikely to be formed in HF acid. However, the microscopic mechanisms behind the dissociation process and the origin of the weakness of HF as an acid do not yet appear to be fully unveiled.

There have been a number of studies into solute-water cluster systems. Not only experimental studies,[9−12] but a large number of ab initio molecular orbital studies[13] have been devoted to understanding the interaction between HF and one or two water molecules. However, there is only limited information on the structure and stability of larger clusters. If the contact ion-pair does exist in HF acid, it is necessary to have large numbers of water molecules so that the ion-pair structure is sufficiently stabilized.

In this work, we have performed calculations on the $HF(H_2O)_n$ clusters with systematic extension to larger cluster sizes up to the $n = 7$ by using the Density Functional Theory (DFT) method. The aims in this study are (i) to explore whether the proton transfer does occur, and (ii) to seek the origin of the weakness of the HF acid. The structures and stabilities are elucidated for the hydrogen-bonded clusters as well as the proton transferred ion-pair clusters through the range of cluster sizes. These are also discussed in connection with the results[1] obtained for the $HCl(H_2O)_n$ clusters. Since the HF acid has weak acidity, a large number of water molecules is required for the proton transfer compared to that in the $HCl(H_2O)_n$ cluster system. This is shown in the following sections.

II. Theoretical Calculations

In the present calculations, we have employed the DFT method together with the Hartree−Fock method as a reference. Recent publications have shown that the DFT methods provide quantitative descriptions of structure and vibrational frequency for the hydrogen-bonded system.[14] We applied the DFT methods for the hydrated clusters of the strong acids, and successfully gained a microscopic insight into the acid dissociation process.[1,15] We adapted the B3LYP method which is the Becke's three-parameter hybrid method using the Lee−Yang−Parr (LYP) local and non-local-exchange functional.[16] The ab initio correlated MP2 method is also applied for the small systems ($n = 1-3$) for comparison. To describe reasonably the hydrogen-bonded system, we employ the relatively large basis

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* To whom correspondence should be addressed. E-mail: lee@chem.rikkyo.ac.jp.

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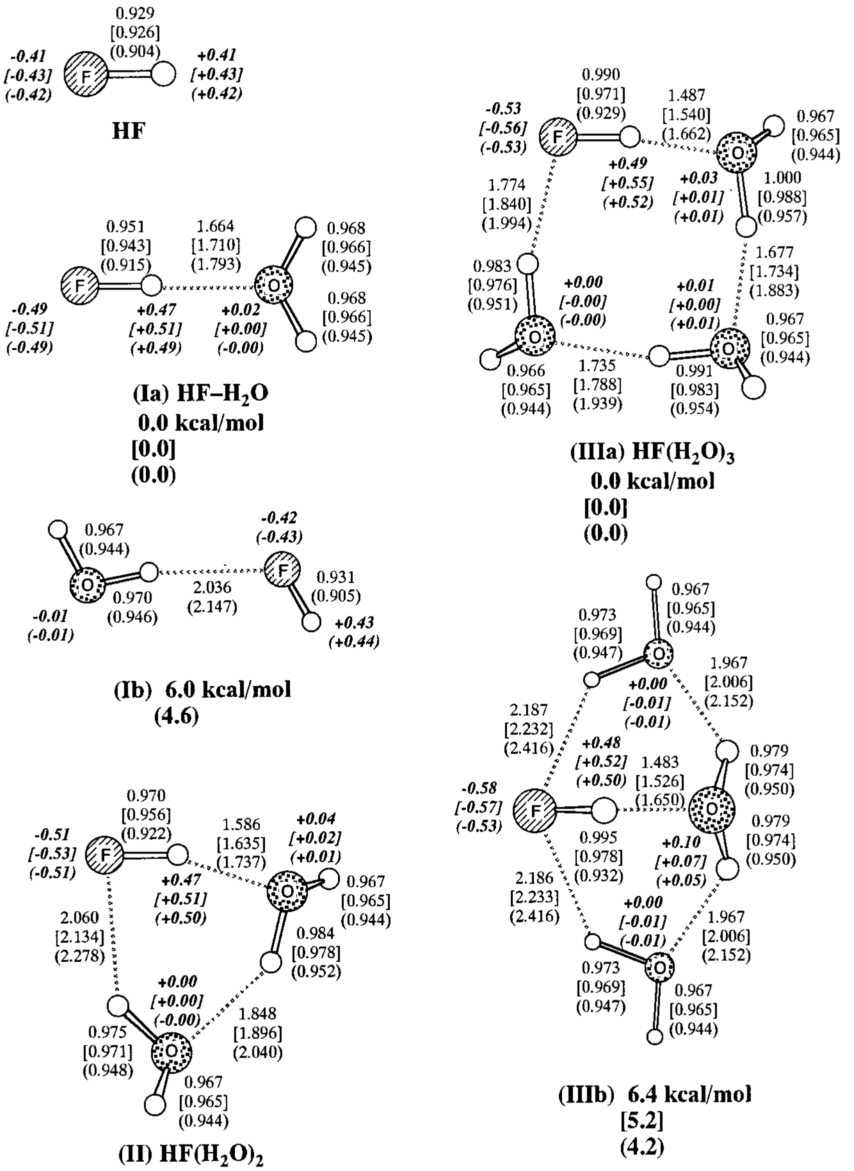


(Ia) HF–H_2O
0.0 kcal/mol
[0.0]
(0.0)

(Ib) 6.0 kcal/mol
(4.6)

(II) $HF(H_2O)_2$

(IIIa) $HF(H_2O)_3$
0.0 kcal/mol
[0.0]
(0.0)

(IIIb) 6.4 kcal/mol
[5.2]
(4.2)

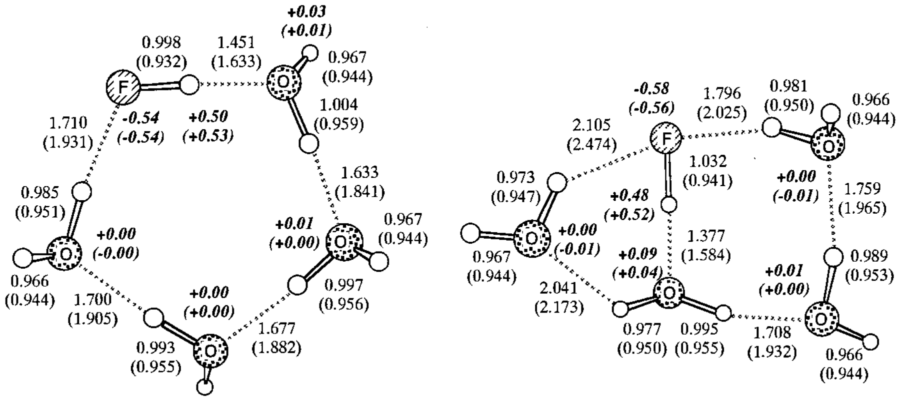
Figure 1. Optimized structures of the $HF(H_2O)_n$ clusters for $n = 0$ to 3, determined with the B3LYP/D95++(p,d), [MP2/D95++(p,d)], and (HF/D95++(p,d)) methods. The bond lengths are shown in Å. Relative stabilities of the isomers are shown with respect to the most stable structures at each cluster size. Electronic charge of each monomeric moiety is indicated as the value in bold italics.

set, the Huzinage–Dunning double-ζ plus polarization with additional diffuse functions (D95++(p,d)).[17] Although the employed basis set involves enough flexibility, the effect of the basis set superposition error (BSSE)[18] is also examined for the small size clusters ($n = 1-3$). The evaluated values of BSSE are less than 3 kcal/mol for the system, and do not significantly affect the overall trend in the structures and stabilities of the clusters. The discussion in the text is, thus, based on the energies without the BSSE correction. The geometries of the $HF(H_2O)_n$ ($n = 1-7$) clusters have been optimized using the above methods. To avoid missing the isomers, the starting geometries are systematically constructed in a way that a water molecule is added to the previously sized clusters. To search the ion-pair structures, the starting geometries are also constructed by forcing the several optimized neutral clusters to have ion-pair form. The vibrational analyses have also been carried out using the analytical second derivative method for the most stable species. The relative energies and the stabilization energies are all stated with correction for zero-point vibrational energies. All calculations have been carried out with the GAUSSIAN 94 program package.[19]

III. Results and Discussion

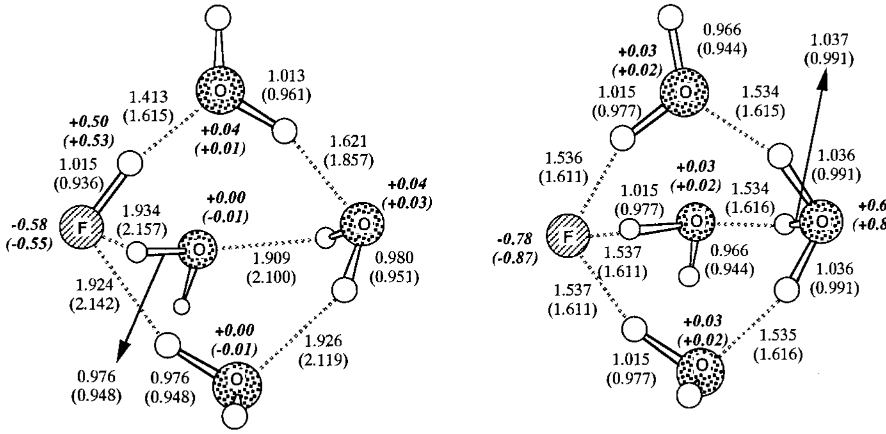
A. Structure and Stability of $HF(H_2O)_n$ Clusters. $HF(H_2O)_n$ ($n = 1-3$) Clusters. Figure 1 shows optimized structures of the HF molecule itself and the $HF(H_2O)_n$ ($n = 1-3$) clusters by using the B3LYP method with D95++(p,d) basis set in addition to the Hartree–Fock method as a reference. Those at the MP2 level are also shown in the same figure for comparison. Although the hydrogen bond distances are slightly shorter (ca. 0.05 Å) at the B3LYP level than those at MP2, the B3LYP procedure gives geometries and relative stabilities in good agreement with those obtained from the MP2 calculation. Note that we could not obtain the structure (Ib) with the MP2 method possibly because of the exaggerated correction for the electron correlation effect in the MP2 level of theory.

The H–F bond length in HF is calculated, at the B3LYP level, to be approximately 0.012 Å longer than the corresponding experimental value.[20] Two energy minima, (Ia) and (Ib), are obtained for the $n = 1$ system. Structure (Ia), in which HF acts as a proton donor, is 6.0 kcal/mol more stable than structure (Ib), in which HF acts as a proton acceptor. The potential surface



(IVa) $HF(H_2O)_4$
0.0 kcal/mol
(0.0)

(IVb) 4.4 kcal/mol
(3.4)



(IVc) 4.6 kcal/mol
(3.6)

(IVd) 9.6 kcal/mol
(25.4)

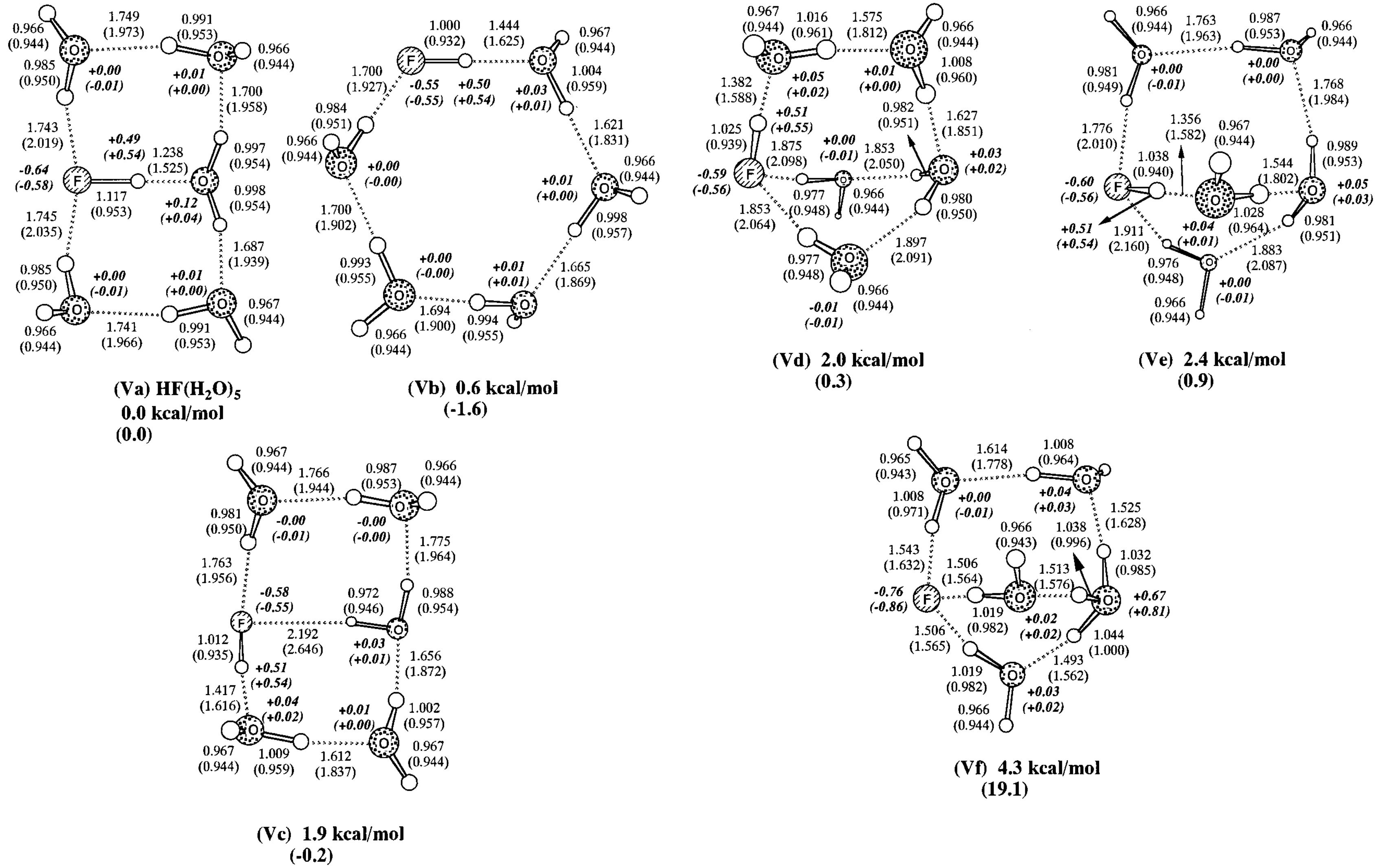
Figure 2. Structures of the four possible isomers of $HF(H_2O)_4$. For detail, see Figure 1.

around structure (Ib) is so flat that the transition state is hard to obtain at this level of theory. In contrast to the other hydrogen halides, the stability of structure (Ib) is intrinsic to HF, although it is energetically less favorable than structure (Ia). This intrinsic feature of the HF could be responsible for the qualitatively different hydration structure of the HF compared to those of the other three hydrogen halides as reported by Hirata and Sato.[8]

In the most stable structure, (Ia), the hydrogen bonding with a water molecule induces the elongation of the H−F bond length (by 0.02 Å) compared to the isolated HF. The stabilization energy of the system resulting from the hydrogen bonding is 7.6 kcal/mol, which is in reasonable agreement with an experimentally estimated value of 8.2 kcal/mol.[12] Note that the stabilization energy is approximately 3 kcal/mol larger for the $HF\cdots H_2O$ complex than the $HCl\cdots H_2O$ complex.[1] The O···F distance is calculated to be 2.614 Å at the B3LYP/D95++-(*p*,*d*) level. This value is also in reasonable agreement with the corresponding experimental one, 2.66 Å.[10] The F−H···O part in structure (Ia) is almost linear ($\angle F-H\cdots O = 177.2°$), the same as in the case of the $HCl\cdots H_2O$. The hydrogen-bond length of structure (Ia), 1.664 Å, is shown to be 0.156 Å shorter than that of the $HCl\cdots H_2O$ and 0.244 Å shorter than that of the H_2O dimer. The hydrogen bond length of the meta-stable structure (Ib) is much longer (2.036 Å), and the H−F bond length (0.931 Å) is almost unchanged by complexation.

There is only one stable structure for the $n = 2$ cluster size, where the HF and two water molecules form a hydrogen bond ring without proton transfer from the HF to a water molecule. The H−F bond length (0.970 Å) turns out to be 0.02 Å longer than the corresponding value in structure (Ia). In contrast, the hydrogen-bond length between HF molecule and one of the water molecules (1.586 Å) becomes 0.08 Å shorter than that in structure (Ia).

The right side of Figure 1 illustrates the optimized structures for two possible isomers at the $n = 3$ cluster size. Both of the isomers obtained are non-proton-transferred types. Structure (IIIa) is the most stable, where HF and three water molecules are connected through a single ring of hydrogen bonds. On the other hand, structure (IIIb) is highly distorted resulting from the bicyclic hydrogen bonding, which makes structure (IIIb) 6.4 kcal/mol less stable than structure (IIIa). Note that this energy difference, 6.4 kcal/mol, at the B3LYP level is in reasonable correspondence with that derived from the MP2 calculation, 5.2 kcal/mol. For these clusters, the optimizations converge to non-proton-transferred forms even when the initial geometries are chosen to be proton-transferred ones. The calculated charge densities of each moiety in clusters are shown with bold italic numbers in Figure 1, indicating that all these clusters are hydrogen-bonded systems among electronically neutral species. The HF molecule forms a strong hydrogen bond with a water molecule, $FH\cdots OH_2$, similar to the case of the



(Va) $HF(H_2O)_5$
0.0 kcal/mol
(0.0)

(Vb) 0.6 kcal/mol
(-1.6)

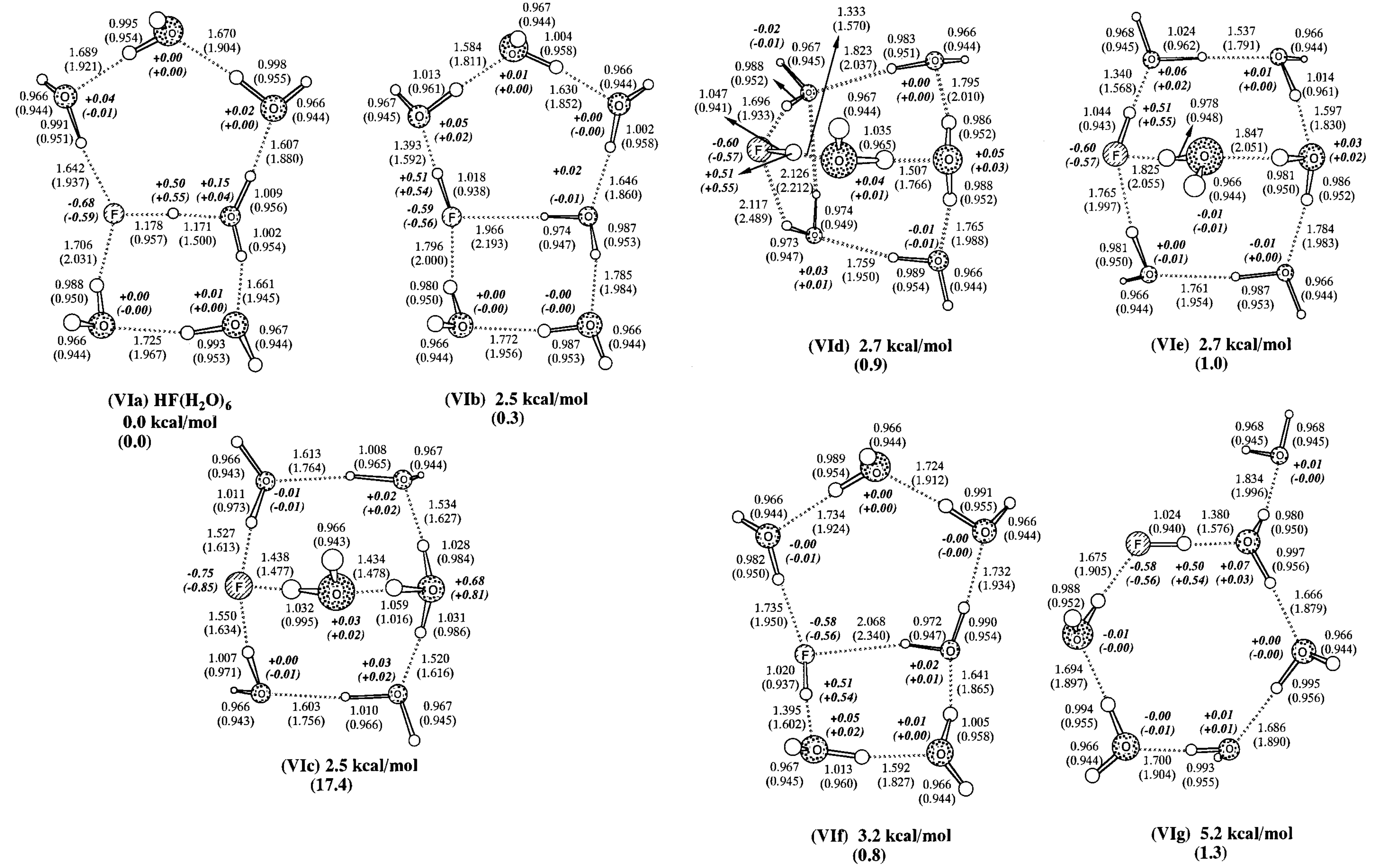
(Vd) 2.0 kcal/mol
(0.3)

(Ve) 2.4 kcal/mol
(0.9)

(Vc) 1.9 kcal/mol
(-0.2)

(Vf) 4.3 kcal/mol
(19.1)

Figure 3. Structures of several isomers of $HF(H_2O)_5$. For detail, see Figure 1.



(VIa) $HF(H_2O)_6$
0.0 kcal/mol
(0.0)

(VIb) 2.5 kcal/mol
(0.3)

(VId) 2.7 kcal/mol
(0.9)

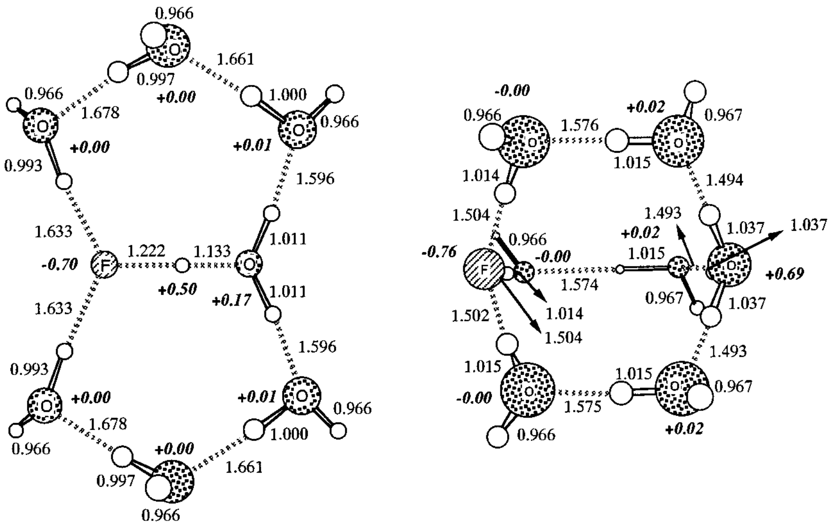
(VIe) 2.7 kcal/mol
(1.0)

(VIc) 2.5 kcal/mol
(17.4)

(VIf) 3.2 kcal/mol
(0.8)

(VIg) 5.2 kcal/mol
(1.3)

Figure 4. Structures of several isomers of $HF(H_2O)_6$. For detail, see Figure 1.



(VIIa) 0.0 kcal/mol **(VIIb) 3.3 kcal/mol**

Figure 5. Structures of two possible isomers of $HF(H_2O)_7$. For detail, see Figure 1.

TABLE 1: Stabilization Energies with (ΔE_{czpv}) and without (ΔE) Zero-Point Vibrational Correction for $HF(H_2O)_n$ ($n = 1-7$) Clusters[a]

			HF D95++(*p*,*d*) (kcal/mol)		MP2 D95++(*p*,*d*) (kcal/mol)		B3LYP D95 ++(*p* ,*d*) (kcal /mol)	
			ΔE	ΔE_{czpv}	ΔE	ΔE_{czpv}	ΔE	ΔE_{czpv}
$HF+H_2O$	→$HF\bullet H_2O$	(Ia)	8.6	6.0	10.3	7.4	10.5	7.6
	→$HF\bullet H_2O$	(Ib)	2.6	1.4	–	–	3.0	1.6
$HF\bullet H_2O+H_2O$	→$HF(H_2O)_2$	(II)	7.6	4.9	10.6	7.8	10.4	7.4
$HF(H_2O)_2+H_2O$	→$HF(H_2O)_3$	(IIIa)	10.6	7.8	14.4	11.3	14.6	11.7
	→$HF(H_2O)_3$	(IIIb)	5.3	3.6	7.9	6.1	7.1	5.3
$HF(H_2O)_3+H_2O$	→$HF(H_2O)_4$	(IVa)	8.9	6.6	–	–	11.7	9.5
	→$HF(H_2O)_4$	(IVb)	4.9	3.2	–	–	6.9	5.1
	→$HF(H_2O)_4$	(IVc)	5.0	3.0	–	–	6.9	4.9
	→$HF(H_2O)_4$	(IVd)	−14.2	−18.8	–	–	2.7	−0.1
$HF(H_2O)_4+H_2O$	→$HF(H_2O)_5$	(Va)	5.9	3.8	–	–	9.7	7.6
	→$HF(H_2O)_5$	(Vb)	7.2	5.4	–	–	9.0	7.0
	→$HF(H_2O)_5$	(Vc)	6.1	4.0	–	–	8.3	5.7
	→$HF(H_2O)_5$	(Vd)	5.5	3.5	–	–	7.8	5.6
	→$HF(H_2O)_5$	(Ve)	4.9	2.9	–	–	7.3	5.2
	→$HF(H_2O)_5$	(Vf)	−11.0	−15.3	–	–	6.2	3.3
$HF(H_2O)_5+H_2O$	→$HF(H_2O)_6$	(VIa)	9.1	6.6	–	–	12.3	9.8
	→$HF(H_2O)_6$	(VIb)	8.8	6.3	–	–	10.1	7.3
	→$HF(H_2O)_6$	(VIc)	−6.3	−10.8	–	–	10.2	7.3
	→$HF(H_2O)_6$	(VId)	8.5	5.7	–	–	9.9	7.1
	→$HF(H_2O)_6$	(VIe)	7.9	5.6	–	–	9.5	7.1
	→$HF(H_2O)_6$	(VIf)	8.3	5.8	–	–	9.5	6.6
	→$HF(H_2O)_6$	(VIg)	6.5	5.3	–	–	6.4	4.6
$HF(H_2O)_6+H_2O$	→$HF(H_2O)_7$	(VIIa)	–	–	–	–	11.9	9.4
	→$HF(H_2O)_7$	(VIIb)	–	–	–	–	9.0	6.1

[a] Energies were calculated by the HF, MP2, and B3LYP methods with the D95++(*p*,*d*) basis set. The relative energies of $n = 4$, $n = 5$, and $n = 6$ clusters were evaluated using the energy of (IIIa), (IVa), and (Va) clusters, respectively.

$HCl(H_2O)_n$ system. However, in the $HF(H_2O)_3$ system, a strong hydrogen bond (1.774 Å) is also formed between the F atom of HF and one of the water molecules as shown in structure (IIIa). This is approximately 0.6 Å shorter than the corresponding distance in the $HCl(H_2O)_3$ cluster.

$HF(H_2O)_4$ Cluster. The optimized structures for the four stable isomers of the $HF(H_2O)_4$ cluster are depicted in Figure 2. Structures (IVa), (IVb), and (IVc) are non-proton-transferred forms, while structure (IVd) is a proton-transferred form. The single-ringed structure (IVa) is the most stable in the $n = 4$ cluster size. Compared with the geometry of (IIIa) at $n = 3$, the H−F bond length is approximately 0.01 Å longer and the hydrogen bond distance, $FH\cdots OH_2$, is approximately 0.04 Å shorter. The proton of the HF molecule is, however, still strongly attracted to the fluorine. The multi-cyclic structures of (IVb) and (IVc) are similar in stability and are approximately 4 kcal/mol less stable than the monocyclic structure (IVa). The H−F bond lengths are relatively longer for both structures (IVb) and (IVc) than structure (IVa). This is consistent with the fact that the HF molecule in the multi-cyclic structures (IVb) and (IVc) acts as a double-proton acceptor, compared to the monocyclic structure (IVa) in which the HF acts as a single-proton acceptor.

Differing from the smaller $n = 3$ cluster size, a proton-transferred ion-pair structure (IVd) was found for the $n = 4$ species. The structure (IVd) has an ion-pair structure in which the negative charge (−0.78) is located on the F^- ion and positive charge (+0.67) is located on the H_3O^+ moiety. In this separated ion-pair structure, F^- and H_3O^+ ions interact indirectly through

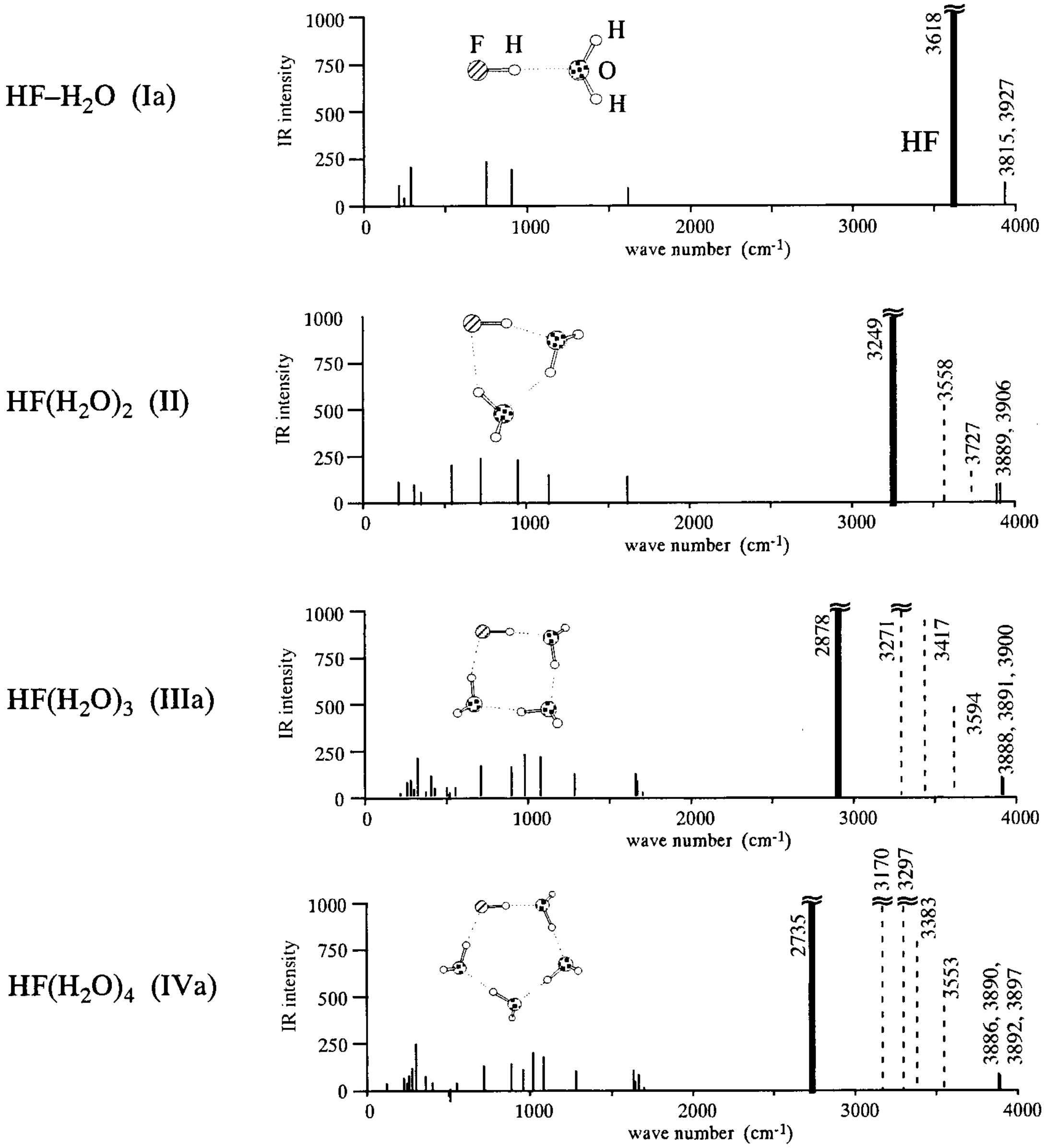


Figure 6. Predicted IR spectra of the $HF(H_2O)_n$ clusters (for $n = 1-4$) determined with the B3LYP/D95++(*p*,*d*) method. In all spectra, bold lines correspond to the H−F stretching and dotted lines correspond to hydrogen-bonded O−H stretching of the water molecules. The O−H stretching frequencies of the free O−H bonds of the water molecules appear in the region of 3800 to 3900 cm^{-1}.

the water molecules. Structure (IVd) is 9.6 kcal/mol less stable than the non-proton-transferred structure (IVa). The potential energy surface around structure (IVd) appears to be very flat. The energy barrier was calculated to be only 0.7 kcal/mol for isomerization from (IVd) to (IVc). In addition, this energy barrier disappears through the correction of zero-point vibrational energies by the B3LYP/D95++(*p*,*d*) method. It should be mentioned from these results that the complexes of HF with four water molecules tend to have non-proton-transferred structures. The relative energy of the proton-transferred structure (IVd) with respect to structure (IVa) obtained at the HF/D95++(*p*,*d*) level is much higher than those predicted at the B3LYP/D95++(*p*,*d*) level because of the lack of electron correlation effect.

$HF(H_2O)_5$ Cluster. We also optimized several possible isomers of the $n = 5$ clusters, $HF(H_2O)_5$, which are illustrated in Figure 3. Five structures, (Va) to (Ve), had non-proton-transferred forms, but only one structure, (Vf), had a proton-transferred form. The bicyclic structure (Va) and the monocyclic one (Vb) have almost similar stability at the $n = 5$ clusters, in contrast to the smaller cluster sizes ($n = 2-4$) in which the most stable structure was of monocyclic rather than multi-cyclic structure. In structure (Va), the H−F bond length is 0.12 Å longer than the corresponding value in structure (IVa). Because the hydrogen bond length of 1.238 Å is shorter (0.21 Å), the interaction in structure (Va) is stronger than in structure (IVa). The proton of HF is still attached to the F atom and is not transferred to the water site. The other nonionic isomers, (Vc) to (Ve), are approximately 1~2 kcal/mol less stable than the most stable structure, (Va).

Similar to the case of $n = 4$, one separated ion-pair structure (Vf), $H_3O^+(H_2O)_4F^-$, is obtained for the $n = 5$ cluster size. Structure (Vf) was calculated to be 4.3 kcal/mol less stable than the non-proton-transferred structure (Va). Note that the energy difference between the non-proton-transferred (Va) and the proton transferred (Vf) is 5.3 kcal/mol smaller than that of the $n = 4$ cluster size (9.6 kcal/mol), although (Vf) is still energetically less favorable than (Va). At the noncorrelated HF level of theory, the stability of the proton-transferred structure

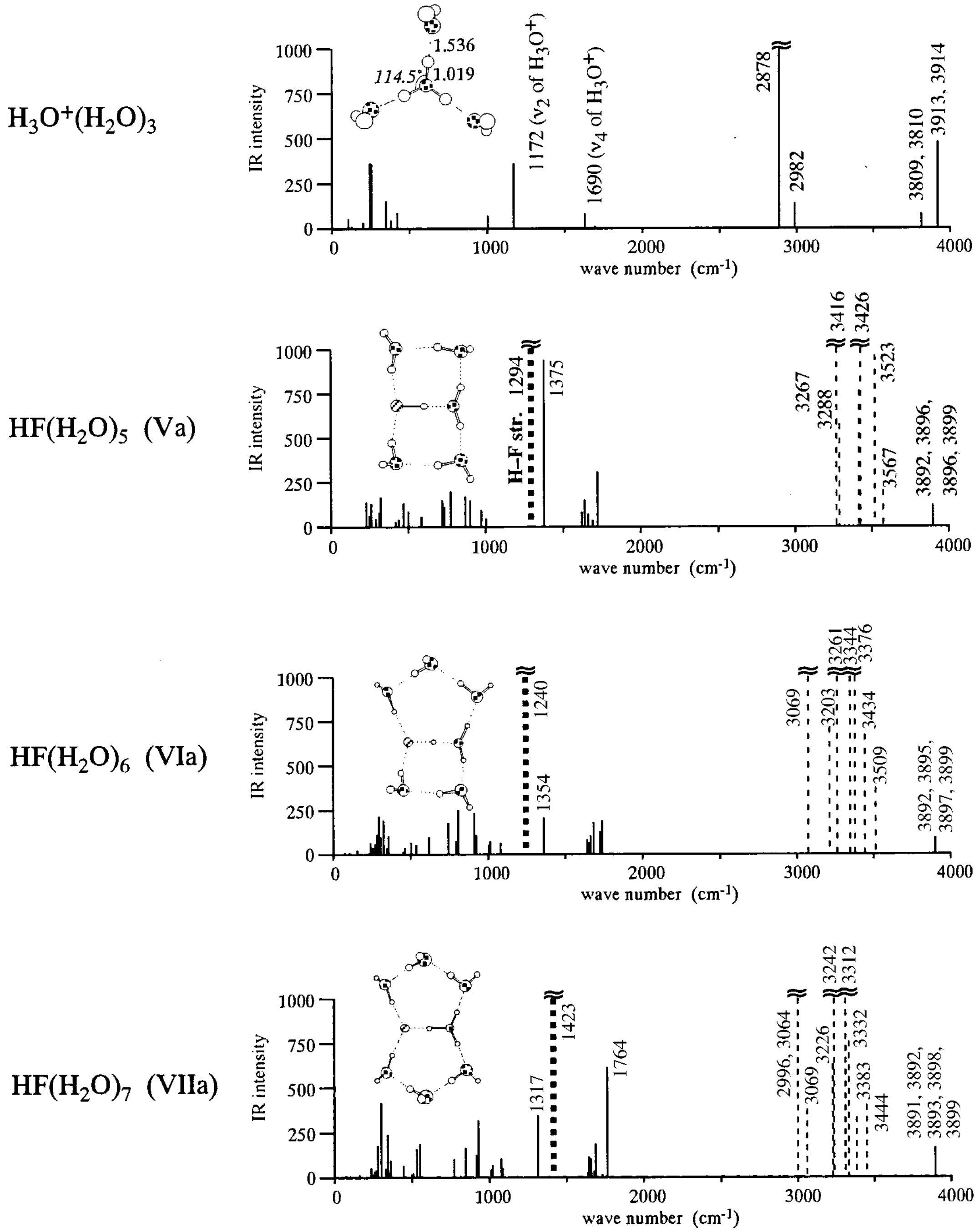


Figure 7. Predicted IR spectra of the bicyclic $HF(H_2O)_n$ clusters (for $n = 5-7$) together with the $H_3O^+(H_2O)_3$ complex determined with the B3LYP/D95++(*p*,*d*) method. In all spectra, dotted bold lines correspond to the $FH\cdots OH_2$ interaction and dotted lines correspond to the hydrogen-bonded O–H stretching of the water molecules.

(~20 kcal/mol) decreases compared to the values obtained with the density functional B3LYP method.

$HF(H_2O)_6$ Cluster. The optimized structures for several possible isomers at $n = 6$ are illustrated in Figure 4. The lowest energy configuration has a bicyclic form as shown in structure (VIa). The energy of the monocyclic form (VIg) was found to be 5.2 kcal/mol higher than that of structure (VIa). The monocyclic form consisting of the HF and six water molecules is not located at the energy minimum at the B3LYP/D95++(*p*,*d*) level of calculation. In the most stable structure (VIa), the H–F bond length (1.178 Å) and the $FH\cdots OH_2$ distance (1.171 Å) are almost the same. The separated ion-pair structure (VIc) is 2.5 kcal/mol less stable than the most stable non-proton-transferred form (VIa). The energy difference between the (VIa) and the (VIc) structures is half of the value observed at the $n =$ 5, although (VIc) is still less stable than (VIa). There are several non-proton-transferred isomers, which have similar stabilities. Consequently, the HF molecule favors forming a hydrogen bond complex, $HF\cdots(H_2O)_n$, rather than a separated ion-pair, $F^-(H_2O)_nH_3O^+$, even in interactions with six water molecules.

$HF(H_2O)_7$ Cluster. Because of the computational expense, only two isomers were examined for the $n = 7$ cluster size (Figure 5). The structures, (VIIa) and (VIIb), are obtained when we add a water molecule to the structures, (VIa) and (VIc), at the $n = 6$ cluster size. In structure (VIIa), the proton is more attracted toward the water site, but it does not completely transfer to a fully ionic structure. Structure (VIIa) is 3.3 kcal/mol more stable than the separated ion-pair, (VIIb). Note that structure (VIIa) could be responsible for the presence of contact ion-pairs, $F^-\cdots H_3O^+$, in aqueous systems, which has been

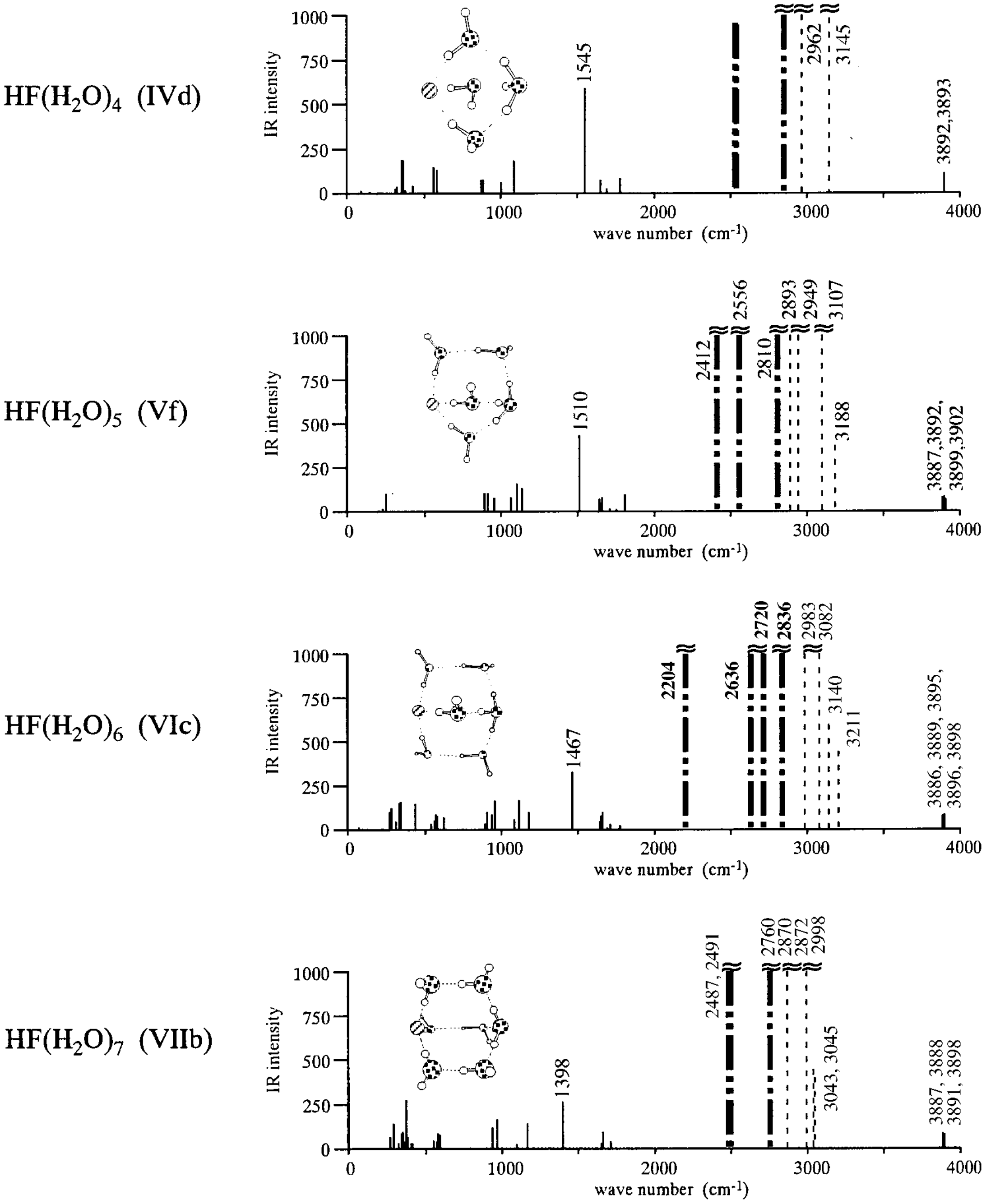


Figure 8. Predicted IR spectra of the ionic $HF(H_2O)_n$ clusters (for $n = 4-7$) determined with the B3LYP/D95++(*p*,*d*) method. In all spectra, partially dotted bold lines correspond to the O−H stretching of the H_3O^+ moiety and dotted lines correspond to the hydrogen-bonded O−H stretching of the water molecules.

suggested by experiment.[5] It is interesting to see that all the ionic structures found in this work commonly contain the three-hydrated structure of the $H_3O^+(H_2O)_3$ form. This is consistent with its importance emphasized in the previous studies.[21]

B. Stabilization Energy. The stabilization energies for the $HF(H_2O)_n$ ($n = 1-7$) clusters relative to the smaller clusters, $HF(H_2O)_{n-1} + H_2O \rightarrow HF(H_2O)_n$ are summarized in Table 1. One can find close agreement of the values between the B3LYP and the MP2 results for the small clusters ($n = 1-3$). In all complexes, the stabilization energies are reduced by 1 to 4 kcal/mol after the zero-point vibrational correction; however, the relative energies of the isomers in each cluster size do not change at the B3LYP/D95++(*p*,*d*) level of calculations. In comparison with the density functional B3LYP results, the noncorrelated HF methods predict a somewhat different energetic relationship for (Va) and (Vb) isomers in the $n = 5$ cluster size, although the energy difference between them is very small. The electron correlation effect is important to properly describe the structures and stabilities of the hydrated clusters of an acid.

C. Vibrational Analyses. The predicted IR spectra for the most stable species of $HF(H_2O)_n$ ($n = 1-4$) clusters at the B3LYP/D95++(*p*,*d*) level are summarized in Figure 6. The calculated stretching frequency of the free HF molecule (4090 cm^{-1}) is in good agreement with the experimentally observed harmonic vibrational frequency of 4138 cm^{-1}.[20]

The H−F stretching frequency for the $n = 1$ cluster (Ia) appears at 3618 cm^{-1} as depicted in the IR spectrum of the complex (Ia). This H−F stretching frequency of the (Ia) cluster reasonably reproduces the experimental frequency (3554 cm^{-1}).[11] When the HF molecule forms a hydrogen-bonded complex with

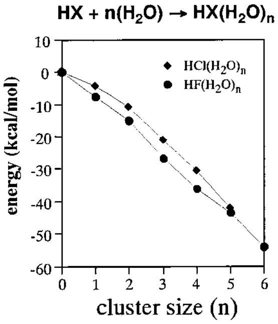


Figure 9. Stabilization energies (ΔE_{zpvc}, kcal/mol) for $HF(H_2O)_n$ and $HCl(H_2O)_n$ systems depending on the cluster size. Obtained with the B3LYP/D95++(*p*,*d*) method.

water molecules, the H−F stretching frequency exhibits a remarkable red shift (Figure 6). The red shift is shown to be 472 cm^{-1} from that of the isolated HF molecule (4090 cm^{-1}), which is larger than that in the case of HCl (313 cm^{-1}). The larger red shift in the present system results from the formation of a much stronger hydrogen bond between the HF and a water molecule, when compared to that between HCl and a water molecule. In the reverse complex (Ib), where the HF acts as a proton acceptor, the theoretical stretching frequency of HF (4067 cm^{-1}) is approximately 151 cm^{-1} higher than the corresponding experimental value (3916 cm^{-1}).[11]

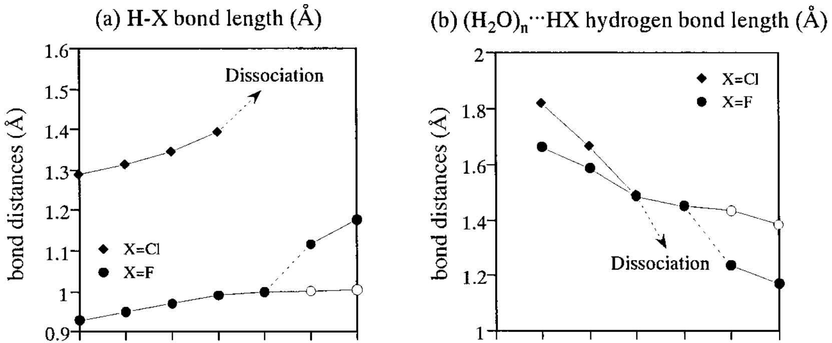
The theoretically predicted H−F stretching is 3249 cm^{-1} for the $n = 2$ cluster (II) and 2878 cm^{-1} for the $n = 3$ cluster (IIIa). The amount of shift decreases by approximately 100 cm^{-1} as cluster size increases. In the case of the $n = 4$ system, the H−F stretching is 2735 cm^{-1} with a red shift of 143 cm^{-1} from that of complex (IIIa). This trend is in contrast to that in the $HCl(H_2O)_n$ clusters[1], where the red shift of the H−Cl stretching increases as the cluster size increases.

Figure 7 shows the predicted IR spectra for the bicyclic structures, (Va), (VIa), and (VIIa), together with the $H_3O^+(H_2O)_3$ complex for comparison. The specific feature of the bicyclic structures—the strongly elongated H−F bond—can be seen in the IR spectra. In the spectrum for the $n = 5$ cluster (Va), the band corresponding to the $FH\cdots OH_2$ interaction appears at 1294 cm^{-1}, instead of the peak corresponding to the H−F stretching frequency. The strong peak at 1375 cm^{-1} is similar to the ν_2 band of the H_3O^+ ion, which appears at 1172 cm^{-1} in the IR spectrum of the $H_3O^+(H_2O)_3$ complex. The relatively strong peaks around the 1700 cm^{-1} region correspond to the ν_4 band of the H_3O^+ ion. Similar IR spectra were obtained for the most stable structures, (VIa) and (VIIa), at the $n = 6$ and $n = 7$ cluster sizes. It is noteworthy that the O−H stretching of water molecules appears at two distinct regions: The O−H stretching frequency for the hydrogen-bonded O−H bond in H_2O falls to the region of between 3100 and 3500 cm^{-1}, while that for the dangling O−H remains in the region of between 3800 and 3900 cm^{-1}.

The predicted IR spectra of the proton-transferred isomers are shown in Figure 8, although these isomers are found to be less stable species. The peak corresponding to the H−F stretching frequency disappears in all spectra. At the same time, the band corresponding to the H_3O^+ ion appears in the 2200 to 2900 cm^{-1} region.

D. Weak Acidic Nature of $HF(H_2O)_n$. The hydration energies (ΔE_{zpvc}) of two systems, $HF(H_2O)_n$ and $HCl(H_2O)_n$, are illustrated in Figure 9. As the cluster size increases, each system stabilizes by 5 to 10 kcal/mol. The stabilization energy for the $HF(H_2O)_n$ system is 2 to 6 kcal/mol larger than that for the $HCl(H_2O)_n$ system. This is consistent with the fact that the dipole moment of the HF molecule is much larger (1.99 D at the B3LYP/D95++(*p*,*d*) level; experimental value, 1.83 D[22]) than that of the HCl molecule (1.43 D at the B3LYP/D95++(*p*,*d*) level; experimental value, 1.09 D[23]).

The H−X (X = F, Cl) bond lengths and the $XH\cdots OH_2$ bond distances of $HX(H_2O)_n$ clusters obtained at the B3LYP/D95++(*p*,*d*) level were plotted against the cluster size (Figure 10). Although the H−X bond of both systems (X = F, Cl) gradually lengthens as the cluster size increases (Figure 10a), the tendency is small when X = F. A similar propensity can be found for the hydrogen bond distances (Figure 10b). Increasing the cluster size from $n = 1$ to $n = 3$, shortens the hydrogen bond distances in the $HCl(H_2O)_n$ system. The tendency of the distance to decrease is less marked for the $HF(H_2O)_n$ system. It should be noted that a significant difference between the two hydrated species is clearly found for the $n = 4$ cluster size: the proton-transferred form is the most stable in the $HCl(H_2O)_4$ cluster, while the non-proton-transferred cluster of the HF, (IVa), is still 9.6 kcal/mol more stable than the separated ion-pair structure (IVd). These facts result in the disappearance of the H−Cl bond for the $HCl(H_2O)_4$ system in Figure 10. In contrast, the gradual elongation of the H−F bond length and the shortening of the hydrogen bond length are still observed for cluster sizes of $n \geq 4$ in the $HF(H_2O)_n$ system. The binding energy was calculated to be 131.7 kcal/mol for HF and 98.5 kcal/mol for HCl molecules, respectively. This difference in binding energy between HF and HCl is reflected by the difference mentioned above. The present work provides insight at the molecular level


(a) H-X bond length (Å)

(b) $(H_2O)_n\cdots HX$ hydrogen bond length (Å)

Figure 10. Size dependency of (a) H−X bond and (b) $(H_2O)_n\cdots HX$ hydrogen bond distances for the X = F, Cl systems obtained with the B3LYP/D95++(*p*,*d*) method. The distances are plotted as black circles for the most stable species, and as white circles for the meta-stable monocyclic structures.

into the current belief that the weakness of hydrogen fluoride arises from the enhanced strength of the H−F bond as well as the large hydration energy of the HF.

IV. Concluding Remarks

We elucidated the significant differences between the $HF(H_2O)_n$ and the $HCl(H_2O)_n$ cluster systems based on our computational work. We obtained the following two results:

(i) In the $HF(H_2O)_n$ ($n = 1-7$) cluster system, the hydrogen fluoride molecule is difficult to dissociate.

Throughout the range of cluster sizes examined, the most stable structures were found as non-proton-transferred types. Only one separated ion-pair structure could be found for each cluster size at $n \geq 4$, where F^- and H_3O^+ ions indirectly interact through the water molecules. However, in all systems, these proton-transferred ionic forms were shown to be less stable than the non-proton-transferred forms. Several non-proton-transferred structures were found throughout the range of cluster sizes. In the most stable structures, the HF and water molecules favored formation of monocyclic structures at $n = 2-4$ clusters and tended to form bicyclic structures at larger clusters. We observed significant lengthening of the H−F bond and shortening of the hydrogen bond, $FH\cdots OH_2$, in the bicyclic structures at $n = 5-7$ clusters. The HF was shown to form very strong hydrogen bonds with water molecules as both donor and acceptor in all of the non-proton-transferred clusters. It should be noted that in the $HF(H_2O)_n$ system, non-proton-transferred clusters, rather than ion-pair structures, have enhanced stability.

(ii) The enhanced stability of the non-proton-transferred forms is responsible for the weakness of HF as an acid in water.

We draw this conclusion based on the comparison with the results obtained for the $HCl(H_2O)_n$ cluster system. The stability of the non-proton-transferred $HF(H_2O)_n$ clusters can be rationalized by the strong H−F bond as well as the high ability to form hydrogen bonds as both as donor and acceptor.

The theoretical IR spectra indicate a significant red shift in the H−F stretching frequencies and the hydrogen-bonded O−H stretching frequencies of the water molecules. This significant change suggested in the IR spectra reflects the change from monocyclic to bicyclic structures as the cluster size increases.

The examined cluster models already involve the essential interactions governing the behavior of molecules in water, and motivate us to further extend the study.

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