From Gas-Phase to Liquid Water Chemical Reactions: The $F + (H_2O)_n$, $n = 1 - 4$ Systems

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ABSTRACT: The systematic study of the growth of water clusters is of interest. The potential energy profiles for the reactions $F + (H_2O)_n$, ($n = 1 - 4$) have been investigated using the CCSD(T) method. Final energetics have been evaluated with the CCSD(T)/cc-pVQZ method. All the stationary points have been located. Structurally, the stationary points on the $F + (H_2O)_n$ potential energy surfaces are related. Energetically, the water tetramer reaction $F + (H_2O)_4$, water trimer reaction $F + (H_2O)_3$, and water dimer reaction $F + (H_2O)_2$ are barrierless, while the water monomer reaction $F + H_2O$ has a ~ 2 kcal/mol barrier.

Keywords: fluorine atom reactions, water polymers, atom-molecule reactions, potential energy profiles, CCSD(T) theory

1. Introduction

Reactions involving water are important to atmospheric, environmental, and combustion chemistry. The fluorine atom plus gas-phase water reaction $F + H_2O$ has been extensively studied both experimentally [1-3] and theoretically [4-11], following the elucidation of the prototypical $F + H_2$ reaction [12-21]. Research on small water polymer reactions establishes important steps from discrete gas-phase water species (monomer, dimer, trimer, ...) to water vapor to liquid water [22,23]. Our recent investigations of the $F + (H_2O)_2$ and $F + (H_2O)_3$ reactions continue this quest [24,25]. The primary purpose of the present research is to address the reaction between the fluorine atom and the water tetramer, $F + (H_2O)_4$. As the water tetramer has nine more degrees of freedom than the water trimer, the $F + (H_2O)_4$ potential energy surface is far more complicated, and it is challenging to study all its reaction channels. Thus, only the lower energy $F + (H_2O)_4$ channels and related complexes are considered here. Furthermore, we will gather all earlier related studies and report a comparative evaluation of the $F + (H_2O)_n$, $n = 1 - 4$ reactions.

The stationary points on the low-lying $F + (H_2O)_n$ potential energy profiles were fully optimized using initially density functional theory (DFT), the method being MPW1K [26], and then the far more reliable coupled-cluster single and double substitution method with perturbative treatment of triple excitations CCSD(T) [27-29]. The basis sets used were the Dunning correlation-consistent polarized valence basis sets cc-pVnZ ($n = D, T, Q, 5$) [30]. Harmonic vibrational frequency analyses were carried out at the same levels of theory to establish the nature of the stationary points. Intrinsic reaction coordinate (IRC) [31-33] analyses were performed with the simple MPW1K method to confirm that the transition states connect the designated entrance and exit complexes. All the MPW1K computations were carried out using the Gaussian 09 program suite [34], and all the CCSD(T) computations were undertaken with the

2. Water Monomer Reaction

Fig. 1. Stationary points on the F + H₂O monomer potential energy profile. Both geometries and energetics were determined at the CCSD(T)/cc-pV5Z level of theory. In Figs. 1 - 6, internuclear separations and energies were given in angstroms and kcal/mol, respectively.

It is undisputed that the F + H₂O reaction is among the best understood four-atom systems [1-11]. Predictions of geometries and energetics for the classical F + H₂O entrance complex, transition state, and exit complex have been carried out utilizing the CCSD(T) method in conjunction with the Dunning correlation-consistent polarized valence basis sets up to cc-pV5Z [5].

With the F atom approaching one H₂O molecule, a F $\cdots$ H₂O entrance complex formed. As shown in Fig. 1, the CCSD(T)/cc-pV5Z entrance well lies 3.4 kcal/mol below the separated reactants F + H₂O. Some earlier studies ignored this entrance complex. Following the F $\cdots$ H₂O entrance complex, a F $\cdots$ H $\cdots$ OH transition state was found. There have been disagreements concerning the height of the classical barrier of the F + H₂O $\rightarrow$ HF + OH reaction. Wang and coworkers estimated a barrier of 6 ± 1 kcal/mol in 2001 [36]. Nesbitt and coworkers suggested ~ 5 kcal/mol for the classical barrier in 2008 [2]. Guo and coworkers in 2012 reported a barrier of 3.8 kcal/mol [6-9]. Our CCSD(T)/cc-pV5Z barrier height of the F + H₂O reaction is predicted to be 2.5 kcal/mol [5], lower than the earlier predictions of 4-7 kcal/mol. Further CCSD(T)/aug-cc-pV5Z and CCSDT/cc-pVQZ computations establish even lower classical barrier of 2.1 kcal/mol [24]. Stanton and coworkers confirmed our F + H₂O barrier in 2013 [37]. There is also an exit complex FH $\cdots$ OH, which is 21.7 kcal/mol below the separated reactants F + H₂O, at the CCSD(T)/cc-pV5Z level. Compared with the separated products HF + OH, the FH $\cdots$ OH complex is bound by 5.9 kcal/mol. The F + H₂O $\rightarrow$ HF + OH reaction is predicted to be exothermic by 15.8 kcal/mol.

3. Water Dimer Reaction

The potential energy profile for the F + (H₂O)₂ $\rightarrow$ HF + (H₂O)OH reaction has been investigated using the CCSD(T) method with basis sets as large as cc-pVQZ [24]. As shown in Fig. 2, the F + (H₂O)₂ $\rightarrow$ HF + (H₂O)OH reaction has an entrance complex F $\cdots$ (H₂O)₂ looking very like the monomer complex F $\cdots$ H₂O, but attached to a second water molecule. Our CCSD(T)/cc-pVQZ computations predict that the F $\cdots$ (H₂O)₂ entrance complex lies 7.3 kcal/mol below the separated reactants F + (H₂O)₂. This is significantly more bound than the 3.4 kcal/mol noted above for the monomer complex F $\cdots$ H₂O. A barrier follows this F $\cdots$ (H₂O)₂

complex on the reaction coordinate, but lying 3.1 kcal/mol *below* the reactants $F + (H_2O)_2$. Thus the reaction of a fluorine atom with water dimer $F + (H_2O)_2$ is qualitatively different from that (+2.1 kcal/mol) with the water monomer $F + H_2O$. The second water molecule is thus a very simple catalyst, removing the barrier from the water monomer $F + H_2O$ reaction. The water dimer reaction exit complex $HF \cdots (H_2O)OH$ lies 27.2 kcal/mol below separated reactants $F + (H_2O)_2$. This $HF \cdots (H_2O)OH$ exit complex lies 11.0 kcal/mol below the separated products $HF + (H_2O)OH$, at the CCSD(T)/cc-pVQZ level, compared to 5.9 kcal/mol for the analogous water monomer system. The $F + (H_2O)_2 \rightarrow HF + (H_2O)OH$ reaction is predicted to be exothermic by 16.2 kcal/mol.

Fig. 2. Stationary points on the $F + (H_2O)_2$ potential energy surface. Geometries and energetics were obtained at the CCSD(T)/cc-pVQZ level of theory.

4. Water Trimer Reaction

Stationary points on the $F + (H_2O)_3 \rightarrow HF + (H_2O)_2OH$ potential energy profile have been fully optimized up to the CCSD(T)/cc-pVTZ level of theory with final energies obtained from the CCSD(T)/cc-pVQZ method [25]. The water trimer $(H_2O)_3$ has two important conformers: *uud*- $(H_2O)_3$ and *uuu*- $(H_2O)_3$ [38-44]. Both *uud*- $(H_2O)_3$ and *uuu*- $(H_2O)_3$ are six-membered ring structures (see Fig. 3) with each water molecule functioning as both electron donor and acceptor. The ring is formed from three OH bonds connected by three hydrogen bonds. The three out-of-ring OH bonds are in either “up-up-down” (*uud*) or “up-up-up” (*uuu*) orientations, with respect to the pseudoplanar six-membered ring. The *uud*- $(H_2O)_3$ structure is the global minimum, but the *uuu*- $(H_2O)_3$ structure lies higher by only 1.0 kcal/mol at the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ level of theory.

When an F atom attacks a $(H_2O)_3$ molecule, four $F \cdots (H_2O)_3$ entrance complexes are readily discerned: three from $F + \textit{uud}$ - $(H_2O)_3$ and one from $F + \textit{uuu}$ - $(H_2O)_3$ [25]. All of these four $F \cdots (H_2O)_3$ complexes are qualitatively similar, each having its fluorine atom bound to one H_2O molecule, with other two H_2O molecules attached. The structural differences between these four complexes involves the orientation of the three out-of-ring OH moieties, and their energetic differences are relatively small, i.e. within 1 kcal/mol. Following the four $F \cdots (H_2O)_3$ entrance complexes, four different reaction channels have been discovered. Generally speaking, the four channels have features in common, both geometrically and energetically. Thus, only the lowest energy channel of the $F + (H_2O)_3$ reaction is discussed herein. From the entrance complexes to the corresponding transition states and then to the corresponding exit complexes, the distances between the fluorine atom and the hydrogen atom being abstracted decrease, forming eight-membered ring structures. The product $(H_2O)_2OH$ radical also has two conformers,

ud-(H₂O)₂OH and *uu*-(H₂O)₂OH, differing from each other only by the orientations of the two out-of-ring OH moieties.

Fig. 3. Stationary points on the lowest energy channel of the $F + (H_2O)_3$ reaction. The geometries were fully optimized at the CCSD(T)/cc-pVTZ level of theory while the final energies are from the CCSD(T)/cc-pVQZ method.

As shown in Fig. 3, based on the lowest energy pathway for the $F + (H_2O)_3$ reaction, our CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ method predicts that the $F \cdots (H_2O)_3$ entrance complex lying 7.1 kcal/mol below the separated reactants $F + uud$ -(H₂O)₃. Compared with the entrance complex, the reaction potential barrier height predicted at the same level is 3.1 kcal/mol, but this barrier is still 4.0 kcal/mol *below* the reactants $F + uud$ -(H₂O)₃. The corresponding $HF \cdots (H_2O)_2OH$ exit complex lies 13.4 kcal/mol below the separated products $HF + (H_2O)_2OH$.

and 28.1 kcal/mol below the separated reactants $F + uud-(H_2O)_3$. The $F + uud-(H_2O)_3 \rightarrow HF + (H_2O)_2OH$ reaction is exothermic by 14.7 kcal/mol. The entrance complex wells are thus 3.4 (monomer), 7.3 (dimer), and 7.1 (trimer) kcal/mol. The energies of the transition state relative to reactants are 2.1 (monomer), -3.1 (dimer), and -4.0 (trimer) kcal/mol. Thus we see a reasonably consistent pattern of energetics.

5. Water Tetramer Reaction

The isolated water tetramer $(H_2O)_4$ system has been carefully investigated by others [44-50], and the global minimum is an eight-membered ring structure (with the rare S_4 symmetry) with each water molecule functioning as both electron donor and acceptor (see Fig. 4). The eight-membered ring is formed with four OH bonds connected by four hydrogen bonds. The four out-of-ring OH bonds are in the “up-down-up-down” (*udud*) orientation, with respect to the pseudoplanar eight-membered ring. We call this water tetramer isomer *udud*-(H_2O)₄. Changing the orientations of the out-of-ring OH bonds from *udud*-(H_2O)₄ gives two conformers: *uudd*-(H_2O)₄ and *uddd*-(H_2O)₄, which are lower in energy than *udud*-(H_2O)₄ by only ~1 kcal/mol. There are also other isomers for the water tetramer $(H_2O)_4$ in the shape of pyramid or lasso [48,49], but both pyramid and lasso isomers have higher energies (> 4 kcal/mol). Anticipating our results for $F + (H_2O)_4$, it is fair to say that the cyclic water tetramer is rather different from the trimer.

Due to the complexity of the $(H_2O)_4$ isomer structures, it is challenging to study all $F + (H_2O)_4$ reaction channels. We herein primarily consider the reaction starting from the lowest-lying reactants, i.e. the $F + udud-(H_2O)_4$ channel. Other $F + (H_2O)_4$ reaction channels should have comparable or higher energies, with respect to the $F + udud-(H_2O)_4$ channel, since

our research on the $F + (H_2O)_3$ reaction shows that all four $F + (H_2O)_3$ reaction channels are closely related, both in geometry and energetics [25]. Analogous to our previous research on the $F + (H_2O)_3$ reaction, the stationary points on the $F + udud-(H_2O)_4$ potential energy profile have been located using up to the CCSD(T)/cc-pVTZ level of theory, as shown in Fig. 5, with the final energies obtained with the CCSD(T)/cc-pVQZ method.

Fig. 4. Some low-lying isomers of the water tetramer $(H_2O)_4$. The geometries were fully optimized at the CCSD(T)/cc-pVTZ level of theory while the final energies (in parentheses) are from the CCSD(T)/cc-pVQZ method.

The $F + udud-(H_2O)_4$ reaction begins with the barrierless formation of an entrance complex $F \cdots (H_2O)_4$. All the four H_2O units of the isolated $udud-(H_2O)_4$ are equivalent. Thus, when an F atom approaches a $udud-(H_2O)_4$ molecule, only one type of the $F \cdots (H_2O)_4$ entrance complex is readily formed. We designate this $F \cdots (H_2O)_4$ complex $udud-F \cdots (H_2O)_4$. As shown in Fig. 5, this $udud-F \cdots (H_2O)_4$ entrance complex has the fluorine atom bound to one water with a water trimer attached by hydrogen bonds. With the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ method, the $udud-F \cdots (H_2O)_4$ complex is bound by 5.2 kcal/mol with respect to the separated reactants $F + udud-(H_2O)_4$. We also find other $F \cdots (H_2O)_4$ isomers having energies comparable to the above $udud-F \cdots (H_2O)_4$ structure, such as $F \cdots (H_2O)_4$ -**A** and $F \cdots (H_2O)_4$ -**B** shown in Fig. 6. In both

$F\cdots(H_2O)_4\text{-A}$ and $F\cdots(H_2O)_4\text{-B}$, the fluorine atom is connected to three waters. Thus the forward reactions from these complexes toward the departure of HF have higher barriers.

Fig. 5. Stationary points on the $F + (H_2O)_3$ potential energy surface. The geometries were fully optimized at the CCSD(T)/cc-pVTZ level of theory while the final energies are from the CCSD(T)/cc-pVQZ method.

Following the *udud*- $F\cdots(H_2O)_4$ entrance complex, we find a *udud*- $F\cdots H\cdots OH(H_2O)_3$ transition state. At this *udud*- $F\cdots H\cdots OH(H_2O)_3$ transition state, the distance between the fluorine atom and the hydrogen atom being abstracted, i.e., the $F\cdots H_{12}$ distance in Fig. 5, is ~ 1.402 Å, much shorter than the 2.070 Å found for the *udud*- $F\cdots(H_2O)_4$ entrance complex. In this way, a ten-membered ring structure is formed, as shown in the left panel of Fig. 5. The *udud*- $F\cdots H\cdots OH(H_2O)_3$

transition state structure was verified to be a first-order saddle point on the $F(H_2O)_4$ potential energy surface, as it has one imaginary vibrational frequency [$1124i\text{ cm}^{-1}$ at the CCSD(T)/cc-pVDZ level of theory]. The normal mode of the imaginary vibrational frequency shows simultaneous F–H12 bond formation and O4–H12 bond rupture as the reaction proceeds toward $HF + (H_2O)_3OH$. Energetically, this $udud-F\cdots H\cdots OH(H_2O)_3$ transition state lies 1.8 kcal/mol below the separated reactants $F + udud-(H_2O)_4$ at the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ level of theory. With respect to the $udud-F\cdots(H_2O)_4$ entrance complex the $F + udud-(H_2O)_4$ reaction barrier is predicted to be 3.4 kcal/mol by the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ method.

Fig. 6. Some low-energy structures of the $F\cdots(H_2O)_4$ complex. The geometries were fully optimized at the CCSD(T)/cc-pVTZ level of theory while the final energies [in parentheses, relative to $F + udud-(H_2O)_4$] are from the CCSD(T)/cc-pVQZ method.

The $F + udud-(H_2O)_4$ reaction proceeds to its exit complex $HF\cdots(H_2O)_3OH$, as the H–F bond is formed. The $HF\cdots(H_2O)_3OH$ exit complex has a pseudoplanar ten-membered ring structure with its three out-of-ring OH moieties in the “up-down-up” (*udu*) orientation, relative to the

pseudoplanar ten-membered ring. The chemically bound F–H distance in this *udu*-HF $\cdots$ (H₂O)₃OH exit complex is 0.953 Å, somewhat longer than the 0.917 Å for the free HF molecule. The *udu*-HF $\cdots$ (H₂O)₃OH exit complex is energetically 25.7 kcal/mol lower than the separated reactants F + *udud*-(H₂O)₄ at the same level of theory.

The release of the HF molecule from the *udu*-HF $\cdots$ (H₂O)₃OH exit complex gives the reaction products HF and (H₂O)₃OH. Analogous to the reactant (H₂O)₄, the product (H₂O)₃OH has an eight-membered ring structure with four OH bonds connected by four hydrogen bonds and three out-of-ring OH bonds in an “up-down-up” (*udu*) orientation, with respect to the pseudoplanar eight-membered ring. Compared with the separated HF + *udu*-(H₂O)₃OH products, the *udu*-HF $\cdots$ (H₂O)₃OH exit complex is bound by 11.6 kcal/mol at the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ level of theory. The HF + *udu*-(H₂O)₃OH products are predicted to lie –14.1 kcal/mol below the separated F + *udud*-(H₂O)₄ reactants. Therefore, the reaction F + (H₂O)₄ → HF + (H₂O)₃OH is significantly exothermic, consistent with the large dissociation energy of diatomic HF.

6. Comparisons

It is instructive to compare the water tetramer reaction F + *udud*-(H₂O)₄ with the water trimer reaction F + (H₂O)₃, water dimer reaction F + (H₂O)₂, and water monomer reaction F + H₂O. To be consistent, all the energies from the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ method are used in the following discussions, as shown in Fig. 7. Structurally, the entrance complexes for the water monomer reaction F + H₂O, water dimer reaction F + (H₂O)₂, water trimer reaction F + (H₂O)₃, and water tetramer reaction F + (H₂O)₄ are clearly related. All of the entrance complexes involve a most prominent F $\cdots$ H₂O fragment. The water tetramer entrance complex F $\cdots$ (H₂O)₄ looks like the water trimer entrance complex F $\cdots$ (H₂O)₃ to which has been inserted a

fourth water molecule; or the water dimer entrance complex $F\cdots(H_2O)_2$ with an $(H_2O)_2$ inserted; or the water monomer entrance complex $F\cdots H_2O$ interacting with a $(H_2O)_3$ water trimer. Energetically, the water monomer complex $F\cdots H_2O$ is predicted to be bound by 3.1 kcal/mol. The water dimer complex $F\cdots(H_2O)_2$ is bound by 7.3 kcal/mol, because of an additional $F\cdots H-O$ hydrogen bond between the fluorine atom and the second H_2O molecule. The fluorine atom in the water trimer complex $F\cdots(H_2O)_3$ has similar binding mode, i.e. a $F\cdots H_2O$ interaction plus a $F\cdots H-O$ hydrogen bond, so it has similar binding energy (7.1 kcal/mol) to that of $F\cdots(H_2O)_2$ complex. The water tetramer complex $F\cdots(H_2O)_4$ also has a similar fluorine atom bridging mode to the water dimer complex $F\cdots(H_2O)_2$ and the water trimer complex $F\cdots(H_2O)_3$. The smaller binding energy of 5.2 kcal/mol may arise from the tetramer's imperfect geometry for the hydrogen bonds. However, we do not find a series of monotonically increasing $F\cdots(H_2O)_n$ dissociation energies as a function of n . Prior to this theoretical study, such a trend was by no means obvious.

The transition states of these four reactions, the water tetramer transition state *udud*- $F\cdots H\cdots OH(H_2O)_3$, the trimer transition state $F\cdots H\cdots OH(H_2O)_2$, and the dimer transition state $F\cdots H\cdots OH(H_2O)$ are predicted to lie *below* corresponding separated reactants by 1.8, 4.0, and 3.1 kcal/mol, respectively, while the monomer transition state $F\cdots H\cdots OH$ lies *above* separated reactants $F + H_2O$ by 2.7 kcal/mol (Fig. 7). Thus, the second water molecule removes the barrier, like a catalyst, from the monomer $F + H_2O \rightarrow HF + OH$ reaction, lowering the barrier to -3.1 kcal/mol, due to an additional hydrogen bond similar to the situation for the entrance complex. The third water molecule further decreases the barrier to -4.0 kcal/mol. The surprise from $(H_2O)_3$ to $(H_2O)_4$ is that the barrier for the fluorine atom reaction *increases* to -1.8 kcal/mol. This result would not have been predicted prior to the present research. The water

dimer transition state looks like the monomer transition state attached the second water molecule; while the trimer transition state looks like the dimer transition state inserted into the ring the third water molecule; and the tetramer transition state looks like the trimer transition state with a fourth water inserted into the ring.

Fig. 7. Comparison of the potential energy profiles for the $F + (H_2O)_n$, $n=1-4$ reactions. All the energies are obtained at the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ level of theory.

The water tetramer exit complex $HF \cdots (H_2O)_3OH$ lie 25.7 kcal/mol below separated $F +$ *udud*-(H_2O)₄. Again, this exit well is somewhat shallower than those of the water trimer exit complex (28.2 kcal/mol with respect to products) and water dimer exit complex (27.2 kcal/mol with respect to products), but much deeper than that of the water monomer exit complex $HF \cdots OH$

(21.7 kcal/mol with respect to products). The water tetramer exit complex $\text{HF}\cdots(\text{H}_2\text{O})_3\text{OH}$ lies 11.6 kcal/mol below the products $\text{HF} + (\text{H}_2\text{O})_3\text{OH}$, which is less than that for the analogous water trimer exit complex [13.5 kcal/mol with respect to products $\text{HF} + (\text{H}_2\text{O})_2\text{OH}$] and about the same as the water dimer exit complex [11.0 kcal/mol with respect to products $\text{F} + (\text{H}_2\text{O})\text{OH}$], but more strongly bound than the water monomer exit complex (only 6.2 kcal/mol with respect to separated $\text{HF} + \text{OH}$).

7. Conclusions

The “Gold Standard” CCSD(T) method with Dunning correlation consistent basis sets up to cc-pVQZ has been used to predict that the potential energy profile of the fluorine atom plus the water tetramer $(\text{H}_2\text{O})_4$ reaction. Due to the abundance of possible water tetramer isomer structures, the lowest-lying $(\text{H}_2\text{O})_4$ structure, i.e. *udud*-(H_2O)₄, is mainly considered. Based on the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ results, the $\text{F} + \textit{udud}\text{-(H}_2\text{O)}_4 \rightarrow \text{HF} + (\text{H}_2\text{O})_3\text{OH}$ reaction is endothermic by 14.1 kcal/mol. The transition state *udud*- $\text{F}\cdots\text{H}\cdots\text{OH}(\text{H}_2\text{O})_3$ lies at 1.8 kcal/mol below the reactants, suggesting that the reaction is barrierless. There are an entrance complex *udud*- $\text{F}\cdots(\text{H}_2\text{O})_4$ (5.2 kcal/mol lower in energy than the reactants) and an exit complex *udu*- $\text{HF}\cdots\text{OH}(\text{H}_2\text{O})_3$ (11.5 kcal/mol below the products). Energetically, the $\text{F} + (\text{H}_2\text{O})_4 \rightarrow \text{HF} + (\text{H}_2\text{O})_3\text{OH}$ reaction is related to the water trimer reaction $\text{F} + (\text{H}_2\text{O})_3 \rightarrow \text{HF} + (\text{H}_2\text{O})_2\text{OH}$ and the water dimer reaction $\text{F} + (\text{H}_2\text{O})_2 \rightarrow \text{HF} + (\text{H}_2\text{O})\text{OH}$, but qualitatively different from the water monomer reaction $\text{F} + \text{H}_2\text{O} \rightarrow \text{HF} + \text{OH}$. This is because, structurally, the stationary points on the $\text{F} + (\text{H}_2\text{O})_4$ potential energy surface are closely related to those on the water trimer reaction $\text{F} + (\text{H}_2\text{O})_3$ and to the water dimer reaction $\text{F} + (\text{H}_2\text{O})_2$ surfaces, but different from the water monomer reaction $\text{F} + \text{H}_2\text{O}$ surfaces. There is no barrier for the water tetramer reaction $\text{F} + (\text{H}_2\text{O})_4$, the water trimer reaction $\text{F} + (\text{H}_2\text{O})_3$, or the water dimer reaction $\text{F} + (\text{H}_2\text{O})_2$, while the

water monomer reaction $F + H_2O$ has a barrier of about 2 kcal/mol, comparable to that for the prototypical $F + H_2$. Larger water polymers than $(H_2O)_4$ will be needed to obtain “converged” energetics for the $F + (H_2O)_n$ reactions.

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