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Theoretical Mechanism Study of UF_6 Hydrolysis in the Gas Phase (II)

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In our previous work (*J. Phys. Chem. A* **2008**, *112*, 8877.), we found theoretical evidence indicating UF_5OH is an intermediate produced in the first step of UF_6 hydrolysis. In this work, we explored the probable reaction channels starting from $UF_5OH + UF_6$ and $UF_5OH + UF_5OH$ systems using relativistic density functional theory calculations. Initially, the two uranium containing species associate to form complex $UF_6 \cdot UF_5OH$ or dimer $(UF_5OH)_2$ through hydrogen bonding. The energy released is 12−16 kcal/mol, which may promote further reactions. After H_2O or HF are eliminated from the complex or dimer, compounds containing U−O−U bond are produced. These compounds are potentially feasible to associate into larger clusters or solidify. Relative to the isolated initial species, the energies of the final products are −6 to −13 kcal/mol lower, indicating that the reactions may spontaneously proceed. The calculated IR spectra features can be used to indicate the formation and interaction type of the intermediates and products.

I. Introduction

Gas-phase hydrolysis of uranium hexafluoride (UF_6) plays a crucial role in the nuclear fuel industry and of fundamental interest in actinide chemistry.[1,2] The mechanism of this reaction remains unclear. According to the few published works focused on this issue,[3,4] the major controversy can be summarized in two points. First, although UOF_4 is proposed to be an intermediate in this reaction,[5] the compound, synthesized using different methods,[6] has never been obtained or detected directly during the gas phase hydrolysis. Instead, besides the desired product, uranyl fluoride (UO_2F_2), a few other kinds of solid uranium oxofluorides have been obtained.[4] Second, the gas-phase reaction, performed at certain experimental conditions, can proceed to form solid products spontaneously even at ambient temperature. On the basis of theoretical calculation, however, the pure gas-phase reaction

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$$

is endothermic.[7] Although the solid formation and surface reaction may substantially lower the system's energy, it is not clear when and how the reaction turns from the gas phase to the solid state, while this information is helpful in manipulating the morphology of the solid products.[8]

To our knowledge, several computational works focus on relevant reactants or probable products of UF_6 hydrolysis.[9] In a recent computational work,[10] Garrison et al. found that the first rate-limiting step of UF_6 hydrolysis is the formation of UF_5OH. Almost at the same time, we studied the mechanism of the initial few steps of the hydrolysis using density functional theory calculations.[11] Besides the first step, which is essentially identical with Garrison's work, we found that the isolated intermediate UF_5OH may further convert to $UOF_4 \cdot HF$ by hydrogen transfer from OH group to an adjacent F atom. However, the second HF eliminating process is more energy demanding. Catalysis with another H_2O or HF lowers the reaction barrier but the total process is still endothermic. In order to simulate the real hydrolysis reaction, the gas−solid conversion should be considered. The first step to realize the conversion may be the combination of two uranium containing species in the gas phase. The interactions between two UF_6 molecules are very weak,[12] accounting for its usual gaseous state. Once UF_5OH forms, it has several choices for further reactions, besides self-dissociation and react with small molecules H_2O or HF, it may also react with UF_6 or another UF_5OH. In this work, therefore, we studied the probable interactions and reactions of UF_5OH/UF_6 and UF_5OH/UF_5OH systems using the same relativistic density functional theory methods as we previously used.

II. Methods and Calculations

The method choice was based on former theoretical works.[9] More details of the calculations have been described in our previous work.[11] Briefly, the geometry structures of all stationary points were fully optimized using the density functional with general gradient approximation (GGA) methods incorporated with all-electron TZ2P basis set. The relativistic effect was evaluated using scalar zero order regular approximation (ZORA). Analytical frequency calculations using the same GGA method were performed to characterize their nature as well as to provide zero point vibration energy (ZPE) and infrared (IR) spectra data. Intrinsic reaction coordinate (IRC) calculations were performed for each transition state to ensure the correct connections between relevant reactant and product. Using each GGA optimized structure, single point calculation using hybrid density functional PBE0 incorporated with all-electron TZ2P basis set and scalar relativistic ZORA was performed. The final energies reported were at the hybrid PBE0 level with GGA calculated ZPE corrections. The relative energies calculated using the two methods were listed comparatively in Table 1.

The interaction energy of molecular fragments in complexes was calculated and corrected by basis set superposition error (BSSE) and ZPE. This was referred to as binding energy (E_{bi}, Table 2). For all of the energy items, the hybrid density

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TABLE 1: Relative Energies and Dipole Moments of the Species

species	sym[a]	E_GGA[b]	E_Z[c]	E_PBE0[d]	E_PBE0 + E_Z	dipole[e]
			$U_2OF_{11}H$			
$UF_6 \cdot UF_5OH$ (**1**)	$C_1(0)$	0.00	0.00	0.00	0.00	4.059
TS1	$C_1(1)$	16.67	−1.22	19.83	18.60	0.488
$(UF_5)_2O \cdot HF$ (**6**)	$C_1(0)$	3.91	−0.20	3.98	3.78	2.949
			$U_2O_2F_{10}H_2$			
$(UF_5OH)_2$ (**2**)	$C_1(0)$	0.00	0.00	0.00	0.00	0.041
$(UF_5OH)_2$ (**3**)	$C_1(0)$	1.95	0.14	2.76	2.91	0.877
$(UF_5OH)_2$ (**4**)	$C_1(0)$	4.03	−0.90	4.52	3.63	5.533
$(UF_5OH)_2$ (**5**)	$C_1(0)$	4.27	−0.88	5.08	4.20	6.816
TS2	$C_1(1)$	16.09	−1.03	18.24	17.20	0.410
TS3	$C_1(1)$	18.57	−1.54	21.30	19.76	2.625
TS4	$C_1(1)$	20.01	−1.81	22.97	22.17	3.250
TS5	$C_1(1)$	20.43	−1.82	24.10	22.29	3.539
TS6	$C_1(1)$	16.06	−1.58	19.54	17.97	3.997
TS7	$C_1(1)$	15.64	−0.94	19.61	18.67	1.784
TS8	$C_1(1)$	11.20	−2.16	13.03	10.87	4.308
TS9	$C_1(1)$	14.33	−2.29	15.47	13.46	1.298
$U_2O_2F_9H \cdot HF$ (**8**)	$C_1(0)$	7.81	−0.71	7.49	6.78	3.686
$UOF_4 \cdot UF_5OH \cdot HF$ (**17**)	$C_1(0)$	10.38	−0.16	9.42	9.27	3.728
$(UF_5)_2O \cdot H_2O$ (**15**)	$C_1(0)$	−1.83	1.64	−1.23	0.41	2.611
$U_2O_2F_9H \cdot HF$ (**16**)	$C_s(0)$	7.08	0.04	7.56	7.60	3.299
$U_2O_2F_9H \cdot HF$ (**10**)	$C_1(0)$	0.48	0.18	0.86	1.04	1.267
$U_2O_2F_9H \cdot HF$ (**11**)	$C_1(0)$	8.33	−1.18	8.87	7.69	4.040
$U_2O_2F_9H \cdot HF$ (**13**)	$C_s(0)$	4.69	0.09	4.80	4.90	1.003
$U_2O_2F_8 \cdot 2HF$ (**18**)	$C_s(0)$	13.52	−0.07	12.43	12.36	2.025
			$U_2O_2F_9H$			
$U_2F_9O_2H$ (**9**)	$C_1(0)$	0.00	0.00	0.00	0.00	1.068
$U_2O_2F_9H$ (**12**)	$C_1(0)$	0.81	−0.60	1.59	0.99	2.730
$U_2O_2F_9H$ (**14**)	$C_s(0)$	1.14	−0.72	1.78	1.06	3.230

[a] Point group of the species, number of imaginary frequency is in parentheses. [b] Relative energy (kcal/mol) of GGA calculation. [c] Relative ZPE (kcal/mol) of GGA calculation. [d] Relative energy (kcal/mol) of hybrid PBE0 calculation. [e] Dipole moments are in Debye, hybrid PBE0 calculation.

TABLE 2: Binding Energies of Molecular Fragments in Complexes

associations	ΔE[a]	ΔE[b]	BSSE[b]	ΔE_z[a]	E_{bi}[c]
	$UF_6 + UF_5OH \rightarrow$				
$UF_6 \cdot UF_5OH$ (**1**)	−8.00	−11.87	−0.52	0.47	−10.88
	$2UF_5OH \rightarrow$				
$(UF_5OH)_2$ (**2**)	−14.37	−18.52	−1.02	1.25	−16.25
$(UF_5OH)_2$ (**3**)	−12.43	−15.76	−0.97	1.39	−13.39
$(UF_5OH)_2$ (**4**)	−10.35	−14.00	−0.53	0.35	−13.12
$(UF_5OH)_2$ (**5**)	−10.11	−13.44	−0.57	0.37	−12.50
	$(UF_5)_2O(7) + HF \rightarrow$				
$(UF_5)_2O \cdot HF$ (**6**)	−2.68	−3.60	−0.39	1.16	−2.04
	$U_2O_2F_9H$ (**9**) $+ HF \rightarrow$				
$U_2O_2F_9H \cdot HF$ (**8**)	−2.99	−4.01	−0.41	0.91	−2.70
	$(UF_5)_2O$ (**7**) $+ H_2O \rightarrow$				
$(UF_5)_2O \cdot H_2O$ (**15**)	−4.26	−5.66	−0.99	2.46	−2.21
	$U_2O_2F_9H$ (**9**) $+ HF \rightarrow$				
$U_2O_2F_9H \cdot HF$ (**16**)	−3.73	−3.94	−0.54	1.66	−1.75
	$U_2O_2F_9H$ (**12**) $+ HF \rightarrow$				
$U_2O_2F_9H \cdot HF$ (**11**)	−3.28	−4.22	−0.40	1.04	−2.78
	$U_2O_2F_9H$ (**14**) $+ HF \rightarrow$				
$U_2O_2F_9H \cdot HF$ (**13**)	−7.26	−8.48	−0.59	2.43	−5.45

[a] Energies (kcal/mol) of GGA calculations. [b] Energies (kcal/mol) of hybrid PBE0 calculations. [c] Binding energies of hybrid PBE0 calculation. See section II for definition.

functional PBE0 calculated results were used except for ZPE, for which the GGA calculated results were used.

ADF2007 program package[13] was employed. The accuracy criterion of 6.5 was used for all the numerical integration, which is a rough indication of the number of significant digits.

III. Results and Discussion

We have previously discussed the accuracy of our calculation results.[11] In this work, the same calculation methods were used for larger systems, which essentially has no effect on the accuracy. Therefore, no more discussions about this issue are necessary.

This section consists of four parts. In part I, we discuss the formation probability of a complex $UF_6 \cdot UF_5OH$ and several conformers of dimer $(UF_5OH)_2$. In part II, we discuss the HF and H_2O elimination from the complex and the dimers. In part III, total reaction pathways are overviewed. In part IV, we show the calculated IR spectra features of the species.

Each minimum structure of the complexes is named according to its structure and numbered as it appears in the discussion. Symbols "TS" plus a number is used to name each transition state.

Part I: Formation of $UF_6 \cdot UF_5OH$ Complex and $(UF_5OH)_2$ Dimers. In our previous work, we showed that UF_6 forms a complex with H_2O, $UF_6 \cdot H_2O$. Over an energy barrier of about 19 kcal/mol, one of the hydrogen atoms of H_2O transfers to a fluorine ligand, resulting in UF_5OH and HF. Unlike the original F ligand, which can only act as a hydrogen bonding acceptor, the newly formed OH group is also a hydrogen-bonding donor. Therefore, besides H_2O, UF_5OH may also associate with UF_6 or other UF_5OH molecules. Considering all of the probable orientations, we found one $UF_6 \cdot UF_5OH$ complex **1** and four $(UF_5OH)_2$ dimers **2**, **3**, **4**, **5**. (Figure 1). The binding energy of UF_6 and UF_5OH in **1** is −10.88 kcal/mol. Compared with the binding energy of UF_6 and H_2O (−0.14 kcal/mol), we can see that UF_5OH is a much stronger hydrogen-bonding donor than H_2O. The formation probability of **1** is, therefore, significant if the concentration of UF_5OH and H_2O is comparable at this stage of the reaction. When two UF_5OH molecules approach to each other, there are four kinds of probable dimerizations. In dimer **2**, two UF_5OH molecular fragments play the same role as

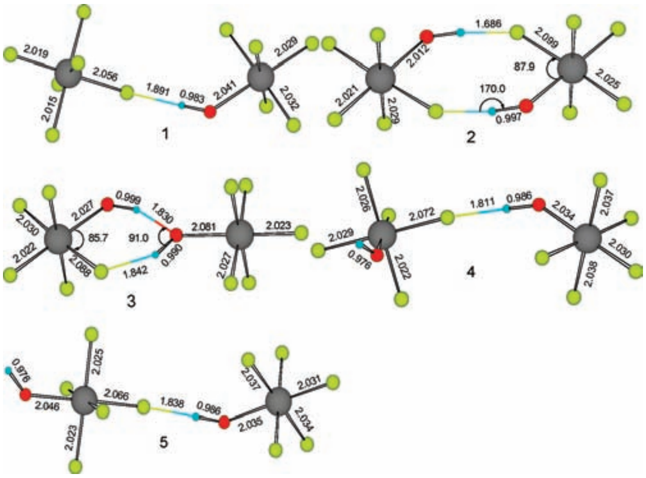

Figure 1. Structures of $UF_6 \cdot UF_5OH$ and $(UF_5OH)_2$; bond lengths are in Å; angles are in degrees.

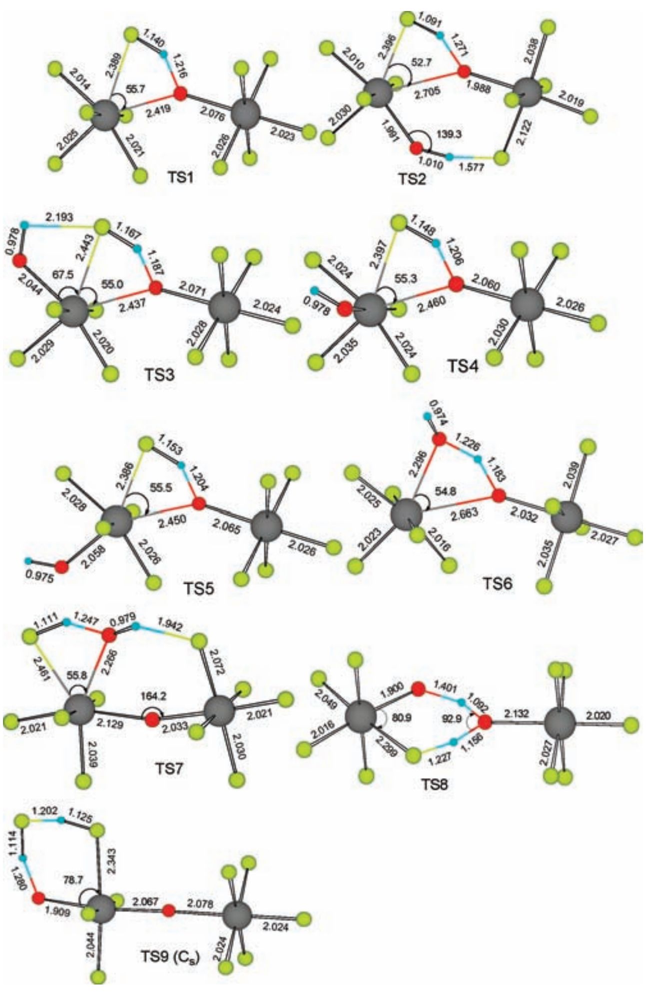

Figure 2. Structures of transition state species involved in the initial reactions between UF_6 and UF_5OH, and two UF_5OH molecules; bond lengths are in Å; angles are in degrees; and the symmetry of the species is indicated in parentheses except for C_1.

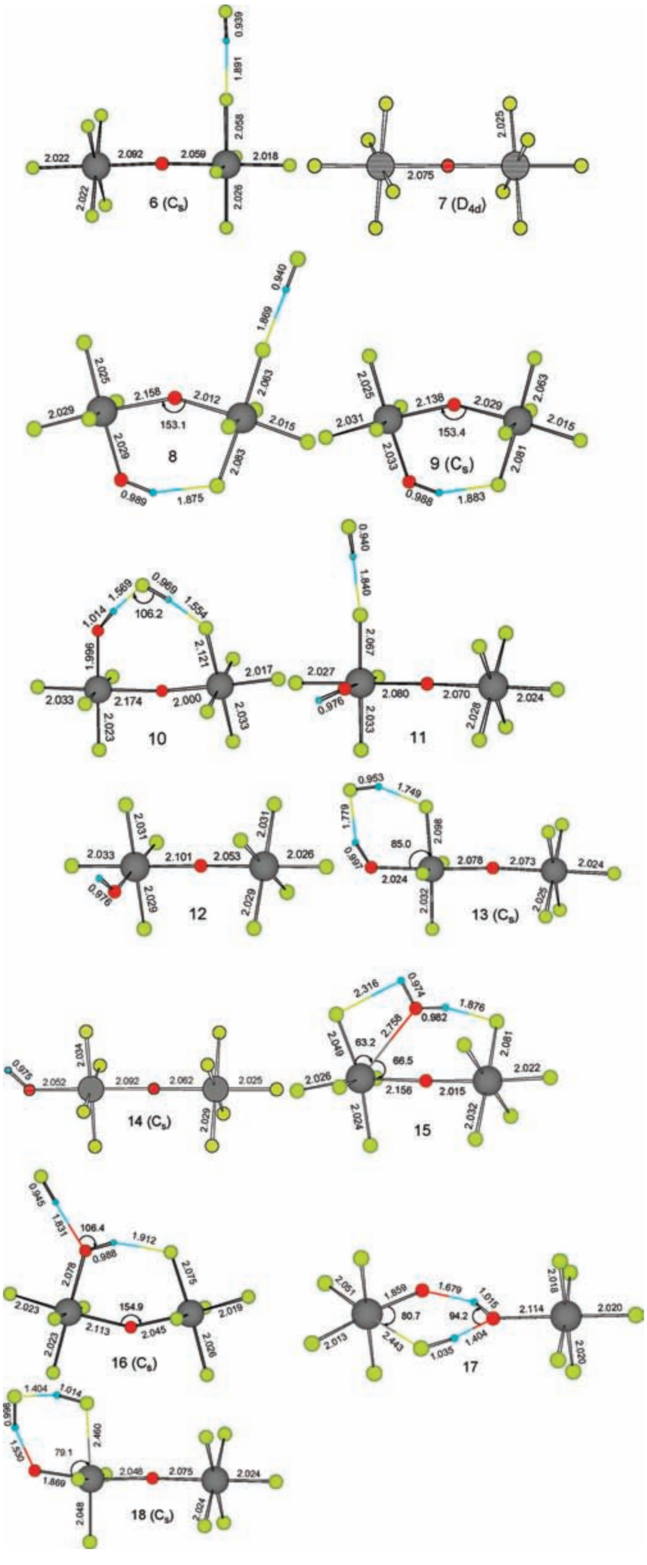

Figure 3. Structures of intermediates produced in the initial reactions between UF_6 and UF_5OH, and two UF_5OH molecules; bond lengths are in Å; angles are in degrees; and the symmetry of the species is indicated in parentheses except for C_1.

hydrogen bonding donor and acceptor, forming a stable eight-member ring structure. In dimer **3**, the OH group of one UF_5OH acts as both hydrogen bonding donor and acceptor, forming a six-member ring structure. Dimers **4** and **5** are single hydrogen bonded species. The free OH group in **4** and **5** makes the two dimers potentially feasible to associate with other molecules just like a single UF_5OH. As indicated in Table 2, the binding energy of two UF_5OH fragments in **2**, **3**, **4**, and **5** is −16.25, −13.39, −13.12, and −12.50 kcal/mol, respectively, also much stronger than that of $UF_5OH \cdot H_2O$ complex. Considering the strong bonding of the species and their potential ability to acts either as single UF_6 or as UF_5OH, we can infer that larger clusters may also form at this stage.

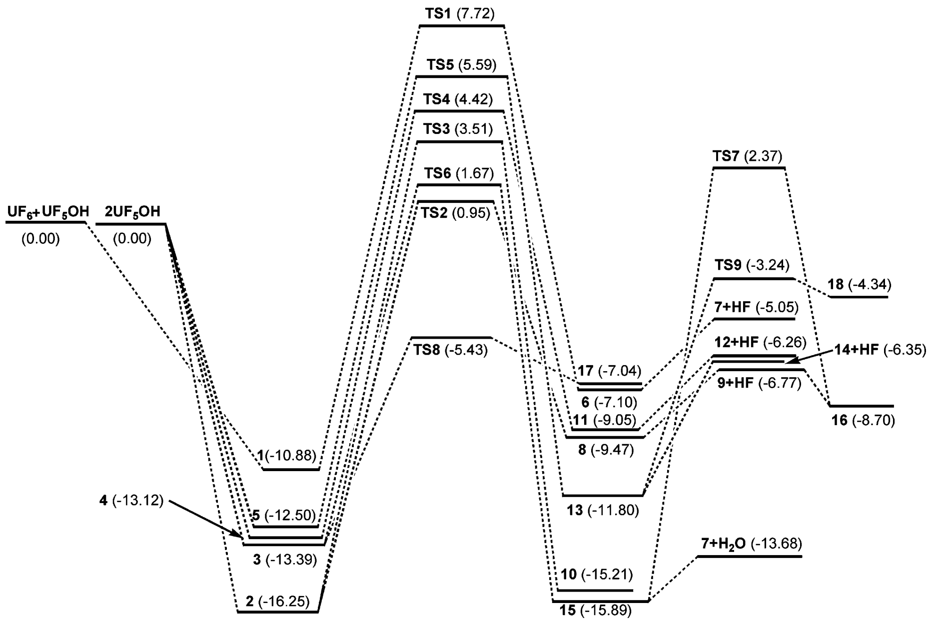

Figure 4. The pathways of the reactions $UF_6 + UF_5OH$ and $UF_5OH + UF_5OH$; the relative energies (in parentheses) calculated at the PBE0 level with the GGA ZPE corrections are in kcal/mol.

Part II. Elimination of HF or H_2O from $UF_6 \cdot UF_5OH$ and $(UF_5OH)_2$. Starting from $UF_6 \cdot UF_5OH$ (**1**), HF elimination happens through transition state TS1 (Figure 2). This transition state is similar to that forms between UF_6 and H_2O. UF_5OH plays the role of H_2O, transferring its hydrogen atom to UF_6, resulting in $(UF_5)_2O \cdot HF$ (**6**) (Figure 3), which is a compound $(UF_5)_2O$ (**7**) hydrogen bonded by the eliminated HF. Relative to **1**, the energies of TS1 and **6** is 18.60 and 5.82 kcal/mol, respectively. The binding energy of **7** and HF in **6** is −2.04 kcal/mol. Compound **7** belongs to point group D_{4d}, two symmetric UF_5 groups are connected through a linear U−O−U bond.

For the $(UF_5OH)_2$ dimers, HF elimination can happen in a similar way. One UF_5OH fragment transfers its hydrogen atom to another UF_5OH. Due to the existence of the additional OH group, however, the transition states and products are quite different in both geometry and energy.

Starting from **2**, one of the transition states of HF elimination is TS2. The product is $U_2O_2F_9H \cdot HF$ (**8**), which is $U_2O_2F_9H$ (**9**) hydrogen bonded by the eliminated HF. Relative to **2**, the energies of TS2 and **8** are 17.20 and 9.48, respectively. The binding energy of **9** and HF in **8** is weak (−2.70 kcal/mol). It is clear that the hydrogen bonding donated by the OH group in the species lowers the energy barrier of the HF elimination process slightly. Furthermore, the product **9** belongs to C_s point group and its U−O−U bond becomes bent in favor of the hydrogen bonded ring structure.

Alternatively, dimer **2** converts to $U_2O_2F_9H \cdot HF$ (**10**) via transition state TS3. Hydrogen bonding is weak in TS3 but stronger in **10**. The eliminated HF is actually part of the eight-member ring structure and makes **10** more stable than **8**. Relative to **2**, the energies of TS3 and **10** are 19.76 and 1.04 kcal/mol.

Starting from the simple hydrogen bonded dimers **4** and **5**, HF elimination proceeds through transition states TS4 and TS5, resulting in $U_2O_2F_9H \cdot HF$ (**11**) and $U_2O_2F_9H \cdot HF$ (**13**), which are $U_2O_2F_9H$ (**12**) and $U_2O_2F_9H$ (**14**) hydrogen bonded by the eliminated HF. Relative to **4**, the energies of TS4 and **11** are 17.54 and 6.85 kcal/mol respectively. The binding of **12** and HF in **11** is weak (−2.78 kcal/mol). In both **11** and **12**, an OH group is free. Relative to **5**, the energies of TS5 and **13** are 18.09 and 6.15 kcal/mol, respectively. The binding energy of **14** and HF in **13** is −5.45 kcal/mol. The free OH group in these reactants and the products makes them potentially feasible to associate with other species through hydrogen bond.

Besides several HF eliminating channels, an energetically favored pathway of H_2O elimination exists. Starting from dimer **2**, H_2O elimination happens via transition state TS6, one OH group transfer a H atom to another OH group, resulting in $(UF_5)_2O \cdot H_2O$(**15**), which is **7** weakly associated with the eliminated H_2O. Although TS6 is structurally similar to the transition states of HF elimination, its energy is considerable lower. Relative to **3**, the energies of TS6 and **15** are 15.06 and −2.50 kcal/mol, respectively. The binding of **7** and H_2O in **15** is weak (−2.21 kcal/mol) but further reactions may start from this association. Over a barrier of 18.26 kcal/mol (TS7), H_2O may transfer one of its H atom to an adjacent F ligand, resulting in **16**, a weak hydrogen bonded complex of **9** and HF. The energy of **16** is close to that of **8**. Structurally, the two species are both complexes formed between **9** and HF, albeit they provide different atoms to bond the HF.

In our previous work, we have discussed the probability of forming UOF_4 from UF_5OH. This process can be realized with H_2O or HF as catalyst at quite low energy barriers. The product UOF_4, however, can hardly exist in isolated form. It binds tightly with the eliminated HF and the ambient H_2O or HF. In this work, we found UF_5OH itself can also play a role as such a catalyst. Starting from dimer **3**, HF may partially form via transition state TS8, resulting in $UOF_4 \cdot UF_5OH \cdot HF$ (**17**), a hydrogen bonded association of UOF_4, HF, and UF_5OH. Relative to **3**, the energies of TS8 and **17** are 7.96 and 6.35 kcal/mol, respectively. Although the barrier is low, the relatively high energy of the product makes the reverse reaction much easier. Similarly, starting from **13**, second HF elimination possibly proceeds via transition state TS9, hydrogen atom transfers from oxygen to fluorine with HF as a catalyst, resulting in $U_2O_2F_8 \cdot 2HF$ (**18**), which can be seen as a hydrogen bonded association of $U_2O_2F_8$ and two HF molecules. Relative to **13**, the energies of TS9 and **18** are 8.56 and 7.46 kcal/mol, respectively. Therefore, the two species containing a *U*=O bond

TABLE 3: Specific Vibration Frequencies of the Species[a]

species	calculated[b]			
	O(F)−H	U−O−U	H−O−H	U=O
H_2O	3758(49)[c]		1596(73)[c]	
$UF_6 \cdot H_2O$			1586(77)[c]	
HF	3951(101)[c]			
UF_5OH	3656(244)[c]			
$UF_6 \cdot UF_5OH$ (**1**)	3527(1279)			
$(UF_5OH)_2$ (**2**)	3211(670), 3310(3226)			
$(UF_5OH)_2$ (**3**)	3244(1380), 3415(1487)		852(83)	
$(UF_5OH)_2$ (**4**)	3508(1676), 3697(294)			
$(UF_5OH)_2$ (**5**)	3537(1628), 3708(311)			
$(UF_5)_2O \cdot HF$ (**6**)	3826(628)	704(444)		
$(UF_5)_2O$ (**7**)		714(499)		
$U_2O_2F_9H \cdot HF$ (**8**)	3426(339), 3812(739)	696(380)		
$U_2O_2F_9H$ (**9**)	3437(322)	694(363)		
$U_2O_2F_9H \cdot HF$ (**10**)	2947(1289), 3301(1324)	706(167)		
$U_2O_2F_9H \cdot HF$ (**11**)	3702(357), 3758(753)	714(505)		
$U_2O_2F_9H$ (**12**)	3675(290)	701(432)		
$U_2O_2F_9H \cdot HF$ (**13**)	3283(885), 3583(865)	697(482)	844(53)	
$U_2O_2F_9H$ (**14**)	3682(376)	700(470)		
$(UF_5)_2O \cdot H_2O$ (**15**)	3531(163), 3721(126)	692(413)	1584(55)	
$U_2O_2F_9H \cdot HF$ (**16**)	3441(277),3672(277)	691(356)	786(127)	
$UOF_4 \cdot UF_5OH \cdot HF$ (**17**)	2171(2763),2978(3158)	754(459)		853(308)
$U_2O_2F_8 \cdot 2HF$ (**18**)	2435(428), 2883(2883)	689(781)	747(162)	887(279)

[a] Frequencies are in cm^{-1}; intensities (in parentheses) are in km/mol. [b] Results of GGA calculations in this work. [c] Results of GGA calculations in reference.[11]

may be too transient to be detected. It seems quite unlikely that the reaction will proceed via these intermediates.

Part III. Overview of the Reaction Channels. The pathways of the reactions $UF_6 + UF_5OH$ and $UF_5OH + UF_5OH$ are drawn schematically in Figure 4. From these theoretical results, we can see several features of the total reaction of UF_6 hydrolysis at this stage.

According to our previous work, the initial steps of UF_6 hydrolysis are endothermic, assuming the reaction system is composed of isolated uranium containing molecules and H_2O or HF. The evidence we provided in this work shows that once the first probable intermediate UF_5OH forms, association of two uranium containing species and the following steps are exothermic. The association of UF_5OH with each other or with UF_6 lowers the energy of the system significantly. Although the following steps of HF and H_2O elimination require activation energies, the final products containing the U−O−U bond are all stable than the initially isolated single UF_6 and UF_5OH molecular systems.

Because the formation of either $UF_6 \cdot UF_5OH$ or $(UF_5OH)_2$ requires collision between two uranium containing species, the association and subsequent reactions may not happen if initial concentration of UF_6 is very low. If the H_2O/UF_6 ratio is small, then part of the UF_6 may remain after the first step of hydrolysis. The probabilities of forming $UF_6 \cdot UF_5OH$ and produce $(UF_5)_2O$ (**7**) are relative large. Otherwise, the formation of several kinds of $(UF_5OH)_2$ dimer are energetically favored.

If large amount of UF_5OH produced at the initial stage, then dimerization dominates. $(UF_5OH)_2$ (**2**) is the most stable dimer. The energy released through dimerization is almost sufficient to activate further reactions. The two most probable reaction channels are **2** → TS2 → **8** → **9** + HF and **2** → TS6 → **15** → **7** + H_2O. Their activation energies are competitive. The products of H_2O elimination, $(UF_5)_2O$ (**7**) + H_2O, are more stable than those of HF elimination, $U_2O_2F_9H$ (**9**) + HF. At elevated temperature, however, HF elimination after H_2O elimination is probable. The system then may either stay as the stable product **7** + H_2O, or go forward along the channel **15** → TS7 → **16** → **9** + HF.

In summary, at relatively low temperature and high UF_6 concentration, UF_6 may hydrolyze in the gas phase along the following initial steps.

$$UF_6 + H_2O \rightarrow UF_5OH + HF$$

$$UF_5OH + UF_6 \rightarrow UF_6 \cdot UF_5OH$$

$$2UF_5OH \rightarrow (UF_5OH)_2$$

$$UF_6 \cdot UF_5OH \rightarrow (UF_5)_2O + HF$$

$$(UF_5OH)_2 \rightarrow (UF_5)_2O + H_2O$$

$$(UF_5OH)_2 \rightarrow U_2O_2F_9H + HF$$

$$(UF_5)_2O + H_2O \rightarrow U_2O_2F_9H + HF$$

Part IV. Vibration Frequency Spectra of the Species. Several IR spectra absorption bands of the species are chosen to list in Table 3. For comparison, the corresponding absorption features of H_2O, $UF_6 \cdot H_2O$, HF, and UF_5OH are also listed.

When $UF_6 \cdot UF_5OH$ forms, the O−H vibration band of OH group in UF_5OH, which appears at 3656 cm^{-1}, red shifts and intensifies due to hydrogen bonding. When $(UF_5OH)_2$ forms, the band at this region doubles and further red shifts and intensifies due to double hydrogen bonding. Because forming the complex and dimers stabilizes the system significantly, this spectra feature may be observed at certain stage of UF_6 hydrolysis.

It should be mentioned, however, after HF elimination, the F−H vibration band appears at the same region with slightly higher frequency than that of O−H vibration. The band also red shifts due to hydrogen bonding and makes it undistinguishable with the band of O−H vibration. Therefore, the fact that double bands appearing at this region alone can hardly tell whether HF elimination happens or not.

Because a U−O−U bond forms while HF or H_2O eliminates from $UF_6 \cdot UF_5OH$ or $(UF_5OH)_2$, the products may be detected via the unique U−O−U vibration band appears around 700 cm^{-1}. Compound **7** has a typical symmetric U−O−U bond, which vibrates at 714 cm^{-1}. The band red shifts when the species involved in hydrogen bonding. For the H_2O eliminated product $(UF_5)_2O \cdot H_2O$ (**15**), the leaving H_2O coordinates to uranium as a Lewis base, like the complex $UF_6 \cdot H_2O$, the H−O−H absorption band at 1584 cm^{-1} is a specific signal to indicate this kind of interaction.[4] In addition, the U−O−U vibration red shifts to 692 cm^{-1} due to such interaction.

The spectral band appearing around 850 cm^{-1} is a signal of *U*═O bond vibration, which has been used to indicate the formation of UOF_4.[4] According to our work, isolated UOF_4 is hardly formed in the gas phase due to its unstable nature. Likewise, the species containing the *U*═O bond usually involve in hydrogen bonding. The actual vibration band caused by partially formed *U*═O bond red shifts in species $UOF_4 \cdot UF_5OH \cdot HF$ (**17**) and $U_2O_2F_8 \cdot 2HF$ (**18**). For the two species as well as dimer **3**, the band appearing at the 800 to 900 cm^{-1} region is also caused by hydrogen bonding, O···H−O.

IV. Conclusions

According to our previous mechanism study, UF_5OH is a key intermediate produced in the initial step of the UF_6 hydrolysis. In this work, we studied the UF_6/UF_5OH and UF_5OH/UF_5OH systems with the assumption that the solid products should form via association of two uranium containing species. Starting from UF_5OH, several reaction channels exist, including association into a complex and some dimers and subsequent HF and H_2O elimination. Unlike the endothermic reaction $UF_5OH \rightarrow UOF_4 + HF$ with substantial activation energy barrier, the reactions $UF_6 + UF_5OH \rightarrow (UF_5)_2O + HF$ and $2UF_5OH \rightarrow U_2O_2F_9H + HF$ are exothermic over relatively low energy barriers. Because the products are potentially feasible to react with other uranium containing species in a similar way, the processes studied in this work can be extended to larger systems. This information is helpful to explain how and when gas−solid conversion takes place during the hydrolysis.

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