Supporting Information for: "Theoretical investigation of uranium hexafluoride hydrolysis: Initiation mechanism and vibrational spectroscopy"

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Table 1 Measured IR frequencies from Shimanouchi et al.[1], the computed harmonic modes used to generate the statistical analysis in the main text.

Exp.	PBE	PBE0	LCCD	CCSD(T)
142	137.18	135.5	145.48	139.15
142	143.25	138.79	145.71	139.15
142	144.63	141.29	145.72	139.22
186	188.86	181.47	191.44	186.21
186	193.35	183.73	191.65	186.21
186	194.05	184.7	191.70	186.26
202	262.50	201.42	207.70	202.14
202	267.00	204.99	207.71	202.14
202	267.74	205.59	207.71	202.15
533	525.74	547.04	549.38	540.57
533	525.99	547.19	549.44	540.59
667	639.42	634.73	648.58	632.3
667	714.38	634.90	648.59	632.3
667	720.63	635.11	648.69	632.31
667	746.09	691.33	707.50	685.3

Table 2 Optimized interatomic distances between U and other atoms in the $UF_6\cdots H_2O$ adduct. Triple-ζ basis sets were used, as described in the main text. Taking the LCCD values as reference, mean unsigned errors (MUEs) and mean signed errors (MSE) are also given to facilitate comparison with past studies.

UF6-H2O	Bond lengths (Å)							Stats (pm)	
Methods	O-U	U-F	U-F	U-F	U-F	U-F	U-F	MUE	MSE
LCCD	2.7159	1.9997	2.0295	2.0290	2.0016	2.0015	1.9986	—	—
PBE0+D3BJ	2.7853	1.9861	2.0113	2.0110	1.9872	1.9872	1.9855	14.9	-0.31
PBE+D3BJ	2.8293	2.0141	2.0415	2.0412	2.0148	2.0150	2.0136	18.1	2.77
Hu et al.	2.8971	2.0233	2.0468	2.0470	2.0243	2.0239	2.0231	28.9	4.42
Garrison and Becnel	2.85	2.04	2.04	2.04	2.04	2.04	2.04	27.9	4.49

Part I
Supplementary benchmark studies

This section describes benchmarking methods and data referenced without explanation in the main text.

1 Benchmark analysis of the vibrational frequencies of UF_6 and $UF_6\cdots H_2O$

In this section we discuss benchmark studies referenced in Section 4.1.1 of the main text. The objective is an evaluation of the performance of the dispersion-corrected density functional theory (DFT) methods for generating accurate geometrical parameters for UF_6 and the $UF_6\cdots H_2O$ adduct. Table 1 tabulates experimental and calculated IR frequencies for UF_6, while Table 2 collects intra- and intermolecular bond lengths predicted by two levels of density functional theory and linearized coupled-cluster doubles (LCCD) with the cc-pVTZ basis set. Comparisons are made with geometrical parameters reported previously by Hu et al.[2] and by Garrison and Becnel.[3]

Bond distances in the $UF_6\cdots H_2O$ adduct generally contract with increasing level of theory. PBE-level optimizations overestimate the intermolecular U-O distance by 5–10% for both our calculations and the calculations of Hu et al. In addition to considering the intermolecular distance, all of the U-F bonds in UF_6 are distorted by the non-bonding interaction with H_2O. For all bond lengths considered, our PBE0-based approach outperforms PBE-based approaches using LCCD-level parameters as the reference.

Table 2 collects mean signed errors (MSE) and mean unsigned errors (MUE), with LCCD-optimized parameters used as reference for the seven bond lengths discussed above. Comparing MUEs between our dispersion-corrected calculations and the results of Hu et al., the D3BJ correction accounts for an improvement of about 10 pm. The MUE for PBE0+D3BJ further improves the PBE+D3BJ MUE by 3 pm. The advantage of PBE0+D3BJ is apparent from the MSEs, where PBE0+D3BJ returns -0.3 pm compared to the PBE-level MSEs of 2.8 or 4.4 pm. We conclude that PBE0+D3BJ is a very reliable method for predicting geometrical parameters of U-containing H-bonded adducts.

2 Estimation of the Hartree-Fock extrapolation error for the UF_6+H_2O barrier height

In this section we examine consider the error associated with extrapolation of the Hartree-Fock (HF) energy to the complete basis set limit (CBS). Many extrapolation formulae exist for approximation of the CBS-limit value. Below are listed the methods employed here:

1. The exponential extrapolation scheme[4]

Extrapolation formula	$E^{HF}[UF_6]$ (hartree)	$E^{HF}[H_2O]$ (hartree)	$E^{HF}[UF_6\cdots H_2O]^{\ddagger}$ (hartree)	E_a (kcal/mol)
Exponential extrapolation scheme	-1131.458402	-76.38407349	-1207.820482	13.800
Power function extrapolation scheme	-1131.489589	-76.38736511	-1207.854274	14.232
A Mixed Gaussian/Exponential Extrapolation Scheme	-1131.468157	-76.38561315	-1207.831206	14.159
Equation 11 from [8]	-1131.483116	-76.38669314	-1207.847265	14.147
Three parameters expression with integer exponents	-1131.473947	-76.38620763	-1207.837481	14.228
Two parameters expression with integer exponent 4	-1131.469611	-76.38590830	-1207.832818	14.245
Two parameters expression with integer exponent 3	-1131.478952	-76.38707748	-1207.842994	14.455
Average and standard deviation	—	—	—	14.181±0.169

Table 3 Complete-basis-limit HF energies for the separated UF_6+H_2O reactants, the $[UF_6\cdots H_2O]^{\ddagger}$ transition state structure, and the associated barrier height (E_a^{HF}).

2. The power function extrapolation scheme (Ref.[5])
3. A Mixed Gaussian/Exponential Extrapolation Scheme (Ref.[6–8])
4. Extrapolation using Equation 11 from Ref.[9]
5. Three-parameter expression with integer exponents (Ref.[9])
6. Two-parameter expression with integer exponent 4 (Ref.[9])
7. Two-parameter expression with integer exponent 3 (Ref.[5])

These were computed using the web interface created by Vasilyev.[10] While many studies exist evaluating the accuracy of CBS extrapolation formulae for main-group phenomena, it is unclear which approach works best for actinides. Such an analysis is best left to a separate study.

Seeking a rough estimate of the error introduced by CBS extrapolation of the HF energy, we gathered values produced by various extrapolation formulae and computed the standard deviation. A sample size of seven is quite small, far fewer than the rule-of-thumb for a lower bound on the sample size (i.e., 30), so we anticipate obtaining an order-of-magnitude estimate.

Table 3 collects CBS-extrapolated HF energies of individual species and the barrier height corresponding to the $[UF_6\cdots H_2O]^{\ddagger}$ structure. Averaging over the barrier heights produced by all extrapolation formulae, 14.181 ± 0.169 kcal/mol is obtained. Of particular interest to the present study is the standard deviation, from which the 95% confidence interval is found to be 0.338 kcal/mol. In most cases this is much smaller than spin-orbit or zero-point vibrational energy corrections.

3 A comparison of initiation-step barrier heights produced by various methods

In this section we compile energy differences associated with several potential initiation steps, as predicted by several electronic structure methods. These are the barriers used in the statistical analysis described in Section 4.1.2 and Table 4 of the main text.

Two classes of energy differences are considered. The first is the what is conventionally referred to as the activation energy, i.e., the energy difference between the transition state and the separated reactants. An example of this is the energy difference formed by E($[UF_6\cdots H_2O]^{\ddagger}$) - E($UF_6$+$H_2O$). The second is the difference between the the transition state and the pre-reactive van der Walls (vdW) energy minimum, for which both forward and reverse reactions are considered. Here an example is E($[UF_6\cdots H_2O]^{\ddagger}$) - E($UF_6\cdots H_2O$), with emphasis on both terms containing center dots, meaning they are both clusters. Barriers taken with respect to separated species vs vdW clusters represent cases where dispersion is effectively turned off and on. This adds diversity to the barrier height set used in the statistcal analysis.

Table 4 collects barrier heights associated with UF_6:H_2O ratios of 1:1 and 1:2. Literature data by Hu et al. was computed using PBE0 and a triple-ζ basis set of Slater-type orbitals. The DFT computations performed as part of this study used the Gaussian-based triple-ζ basis set described in Section 3 of the main text. As a reminder, each of the DFT methods empoyed here included empirical corrections for two-body (D3BJ) and three-body (ABC) intermolecular interactions. Meanwhile, the DLPNO-CCSD(T) and CCSD(T) methods represent composite schemes, also described in Section 3 the main text. For further discussion of the relative performance of these methods for generating barrier heights, see Section 4.1.2 of the main text.

Table 4 Forward and reverse barrier heights for several potential hydrolysis initiation steps. Reactions are labeled by their stoichiometric ratios whether the energy difference is taken with respect to separated reactants or the well structure.

Method	$E([UF_6\cdots H_2O]^{\ddagger})$ - $E(UF_6 + H2O)$	$E([UF_6\cdots 2H_2O]^{\ddagger}_a)$ - $E(UF_6 + 2H2O)$	$E([UF_6\cdots 2H_2O]^{\ddagger}_b)$ - $E(UF_6 + 2H2O)$	$E([UF_6\cdots H_2O]^{\ddagger})$ - $E(UF_6\cdots H_2O)$	$E([UF_6\cdots H_2O]^{\ddagger})$ - $E(UF_5OH\cdots HF)$	$E([UF_6\cdots 2H_2O]^{\ddagger}_a)$ - $E(UF_6\cdots 2H_2O)$	$E([UF_6\cdots 2H_2O]^{\ddagger}_b)$ - $E(UF_6\cdots 2H_2O)$	$E([UF_6\cdots 2H_2O]^{\ddagger}_a)$ - $E(UF_5OH\cdots H_2O\cdots HF)$	$E([UF_6\cdots 2H_2O]^{\ddagger}_b)$ - $E(UF_5OH\cdots HF\cdots H_2O)$
Hu et al.	18.39	13.41	10.43	18.59	11.38	17.3	14.32	13.59	3.91
PBE0	13.94	2.18	-1.72	18.91	14.9	15.61	11.71	19.66	9.75
B97M	12.53	3.01	-0.38	19.19	12.46	19.24	15.84	15.15	7.41
B2PLYP	14.43	4.41	0.57	18.54	14.63	17.83	13.99	19.65	10.09
DSD-BLYP	14.29	4.57	0.83	18.61	15.00	17.98	14.24	19.83	10.51
DSD-PBEB95	15.24	6.11	2.71	19.46	15.15	18.82	15.42	19.45	10.88
DSD-PBEP86	14.33	4.60	0.87	18.40	14.82	17.75	14.03	19.72	10.53
PBE0-DH	15.75	6.56	2.44	18.61	14.70	17.90	13.78	20.10	10.40
PBE-QIDH	15.26	5.92	1.81	18.56	14.93	17.92	13.81	20.23	10.59
PWB95	14.90	5.79	2.34	19.26	14.30	18.53	15.08	18.70	10.13
DLPNO-CCSD(T)	14.54	5.70	2.42	18.70	16.12	17.95	14.66	19.39	11.29
CCSD(T)	13.80	5.18	1.90	17.62	15.41	19.96	14.08	22.46	11.44

Part II

Computed PBE0-level molecular geometries, energies, and properties

This section collects geometries, energies, and properties of individual species, van der Waals clusters, and transition state structures.

4 Pre-reaction dimer and trimer formation

This section tabulates PBE0-level total energies (hartree), dipole moments (debye), zero-point energies (hartree), and atomic positions (angstroms) for each molecular species.

4.1 $H_2O+H_2O \rightarrow H_2O\cdots H_2O$

3
H2O E = -76.488010445886 Dipole = 2.06452 ZPE = 0.02147735

H	-3.070831	0.042655	1.154238
H	-3.250390	0.292340	-0.336747
O	-2.797779	0.624004	0.441509

6
H2O-H2O E = -152.985599508232 Dipole = 2.73228 ZPE

O	-2.464929	-0.980943
O	-4.190234	1.336355
H	-3.106514	-0.256160
H	-2.765117	-1.567196
H	-3.558151	2.034161
H	-4.525054	1.529782

4.2 $H_2O\cdots H_2O+H_2O \rightarrow H_2O\cdots H_2O\cdots H_2O$

9
H2O-H2O-H2O E = -229.494872384260 Dipole = 1.22166 ZPE = 0.07362531

O	-2.543640	-0.965215	-1.079284
O	-4.792523	0.285970	-0.089917
H	-2.411638	-1.169099	-2.006986
H	-3.030272	-1.723712	-0.703673
H	-3.949095	0.135831	-0.558310
H	-4.624530	0.986295	0.542762
O	-4.491532	-2.444433	0.178240
H	-4.844251	-1.541889	0.293127
H	-4.455289	-2.835367	1.052721

4.3 $UF_6+UF_6 \rightarrow UF_6\cdots UF_6$

7
UF6 E = -30408.579376006292 Dipole = 0.000000 ZPE = 0.01200091

U	0.000000	0.000000	-0.000000
F	-1.419399	-0.699589	1.197986
F	1.419399	0.699589	-1.197986
F	-0.483946	1.856133	0.509822
F	0.483946	-1.856132	-0.509822
F	1.300394	-0.072402	1.497670
F	-1.300394	0.072403	-1.497670

14

UF6-UF6 E = -60817.163090674308 Dipole = 0.01896 ZPE = 0.02436804

U	-0.067314	0.215948	-0.916715
F	-1.449216	-1.083467	-0.334524
F	1.307836	1.522203	-1.504497
F	-1.414847	1.669847	-0.854287
F	1.269376	-1.246000	-0.982606
F	0.396757	0.569916	0.985018
F	-0.537378	-0.137150	-2.812240
U	3.814981	2.189130	1.710755
F	2.814339	1.338758	3.195689
F	4.824578	3.039506	0.230500
F	4.228523	3.737973	2.880696
F	3.408289	0.634815	0.537293
F	5.474969	1.287610	2.317806
F	2.159381	3.099020	1.101203

5 Elementary step 1: UF_6OH to UF_5OH

5.1 $\mathbf{UF_6 \cdots H_2O} \xrightarrow{[UF_6-H_2O]^{\ddagger}} \mathbf{UF_5OH \cdots HF}$

10

UF6-H2O E = -30485.075971586088 Dipole = 3.83971 ZPE = 0.03674404

U	-0.024766	0.000418	0.003039
F	1.169534	0.703078	-1.421242
F	-1.276459	-0.375693	-1.525752
F	0.686810	-1.811809	-0.386334
F	1.494801	0.251517	1.258703
F	-0.424817	1.909923	0.375209
F	-0.903662	-0.895994	1.574362
H	-3.067173	0.067863	1.167241
H	-3.248290	0.316672	-0.343172
O	-2.719978	0.565025	0.420946

10

UF6-H2O-TS E = -30485.043946645150 Dipole = 2.81669 ZPE = 0.03331745

U	-0.005798	0.001842	-0.005452
O	-1.052442	1.963080	0.339769
F	1.132672	2.119345	0.270443
F	-1.905896	-0.273329	-0.538503
F	-0.419653	-0.381342	1.888514
F	0.108495	-1.947644	-0.402136
F	0.379565	0.411298	-1.900266
F	1.904116	-0.256932	0.444860
H	-1.837234	2.265808	-0.122705
H	0.075175	2.435876	0.290476

10

UF5OH-HF E = -30485.067699861014 Dipole = 1.15521 ZPE = 0.03485172

H	-0.600632	-0.226744	0.507143
O	-2.372159	-0.137242	2.685227
H	-1.646912	-0.689099	2.326078
F	-0.393819	-0.979689	1.019547
F	-1.855862	2.641734	2.853163
U	-3.129621	1.486720	1.843845
F	-1.701586	1.225803	0.393874
F	-4.482267	1.648988	3.301151
F	-4.378530	0.374862	0.757571
F	-3.851993	3.108665	0.960528

5.2 $\mathbf{UF_6 \cdots H_2O \cdots UF_6} \xrightarrow{[UF_6-H_2O-UF_6]^{\ddagger}} \mathbf{UF_5OH \cdots HF \cdots UF_6}$

17

UF6-H2O-UF6 E = -60893.662392400962 Dipole = 3.61959 ZPE = 0.04949497

U	2.197373	-0.574463	-1.121183
F	2.841719	-0.205170	0.718522
F	1.773170	-1.018779	-3.024536
F	3.343406	-2.197774	-1.141592
F	0.872809	-1.809005	-0.271751
F	3.797952	0.359789	-1.837442
F	1.438767	1.280795	-1.077971
O	-0.517323	-0.217276	-1.770839
H	-0.953178	-0.966266	-2.188306
H	-0.684098	0.546395	-2.331751
F	-2.511371	-1.139022	0.204167
F	-0.301785	0.436366	1.202758
U	-2.283416	0.538217	1.246933
F	-2.347365	1.655841	-0.400565
F	-2.274831	-0.534725	2.913920
F	-4.259424	0.673895	1.364573
F	-2.133353	2.195032	2.325183

17

UF6-H2O-UF6-TS E = -60893.629419908983 Dipole = 2.67313 ZPE = 0.04603016

U	2.171773	-1.620206	-0.834283
F	3.969527	-2.384155	-0.476702
F	0.378384	-0.859759	-1.264614
F	1.550970	-3.393161	-1.472449
F	1.626332	-2.117587	0.999737
F	2.752971	-1.181161	-2.679915
F	2.828504	0.158289	-0.242325
O	-0.454727	2.143184	-0.131539
H	0.269532	1.492285	0.586103
H	-0.499549	3.102502	-0.114190
F	0.294739	0.571549	1.220960
F	-2.958852	2.560690	0.380610
U	-2.079059	0.799417	0.669593
F	-2.360437	0.336055	-1.226587
F	-1.951255	1.328750	2.567046
F	-1.614121	-1.102428	0.958800
F	-3.924735	0.165737	1.059754

17

UF5OH-HF-UF6 E = -60893.653551555755 Dipole = 0.86097 ZPE = 0.04729485

U	-1.590438	-2.242163	-2.320288
F	-1.708309	-4.016284	-1.469733
F	-1.418308	-0.512297	-3.261910
F	-2.474077	-2.999596	-3.927261
F	-3.361362	-1.655564	-1.664826
F	0.165291	-2.775875	-3.061354
F	-0.595477	-1.410281	-0.757247
O	-0.884849	0.089657	1.529173
H	-3.122485	-2.032975	1.257514
H	-0.604806	-0.507323	0.808717
F	-2.585711	-2.690191	0.869301
F	-1.393553	2.894866	1.496459
U	-2.489238	1.234479	1.668997
F	-2.676076	1.118374	-0.316547
F	-2.291495	1.287531	3.648060
F	-3.631831	-0.463140	1.800439
F	-4.128007	2.340312	1.811476

5.3 $\mathbf{UF_6 \cdots H_2O \cdots H_2O} \xrightarrow{[UF_6-H_2O-H_2O]^{\ddagger}_{a}} \mathbf{UF_5OH \cdots H_2O \cdots HF}$

13

UF6-H2O-H2O E = -30561.58303010532 Dipole = 4.47158 ZPE = 0.06244973

U	-0.083513	0.084713	-0.011949
F	1.798614	0.330762	0.580559
F	-1.979139	0.307024	-0.597090
F	-0.395720	-0.431533	1.928596
F	0.721346	-1.543396	-0.880263
F	-0.376749	1.924823	0.695229
F	0.354853	0.927724	-1.759771
O	-1.482142	-2.081194	0.165215
O	-2.801874	-1.897289	2.490411
H	-2.051611	-2.127234	0.968009
H	-0.954411	-2.882975	0.129395
H	-2.175601	-1.280119	2.885886
H	-3.656819	-1.459647	2.507789

13

UF6-H2O-H2O-TSa E = -30561.551306999030 Dipole = 5.25006 ZPE = 0.05792905

U	-0.012501	0.026300	0.007447
F	1.995169	0.215551	-0.131094
F	-0.210933	0.251416	-1.951221
F	0.426695	-1.901672	-0.255513
F	0.260735	-0.223640	1.951854
F	-1.866394	-0.682468	0.000598
O	0.370961	2.186178	0.034568
H	1.252746	2.573715	0.274062
F	-1.565511	1.641381	0.912568
O	2.843547	2.879486	0.598898
H	-0.676727	2.265627	0.621705
H	3.256251	2.027704	0.417792
H	3.313961	3.527421	0.068337

13

UF5OH-H2O-HF E = -30561.574967880275 Dipole = 3.76393 ZPE = 0.05976097

U	0.149886	-0.613518	-0.818394
F	2.031443	-1.072625	-1.320928
F	-0.043007	0.360126	-2.557336
F	-0.541663	-2.266731	-1.683025
F	0.355248	-1.619472	0.896520
F	-1.709049	-0.090569	-0.300163
O	0.826366	1.052181	0.040481
H	1.734963	1.515581	0.058099
F	0.362413	3.420106	1.161102
O	2.873659	2.525953	0.283479
H	0.174788	2.557854	0.845867
H	3.301818	2.893052	-0.494696
H	2.371203	3.244521	0.694062

5.4 $\mathbf{UF_6 \cdots H_2O \cdots H_2O} \xrightarrow{[UF_6-H_2O-H_2O]^{\ddagger}_{b}} \mathbf{UF_5OH \cdots HF \cdots H_2O}$

13

UF6-H2O-H2O-TSb E = -30561.558782938060 Dipole = 5.98002 ZPE = 0.05901169

U	0.019008	0.057329	0.057857
F	-0.301526	-0.250542	2.002739
F	1.867377	0.444680	0.689068
F	0.388583	-1.903789	0.152883
F	-1.705870	-0.488073	-0.762181
F	0.776127	-0.169327	-1.789739
O	0.253669	2.100230	-0.768370
H	0.851723	2.143767	-1.520446
F	-1.562318	1.539340	0.883554
O	-1.465963	3.636498	-0.073309
H	-1.677103	2.675584	0.486449
H	-0.613366	3.184765	-0.511163
H	-1.193341	4.329535	0.536659

13

UF5OH-HF-H2O E = -30561.584690838819 Dipole = 4.00201 ZPE = 0.06029468

U	0.324492	0.178999	-0.010162
F	0.402619	1.057310	1.788294
F	1.806336	1.334443	-0.699603
F	1.660847	-1.157978	0.601418
F	-1.214805	-0.982991	0.718277
F	0.212417	-0.783102	-1.758884
O	-1.011818	1.465983	-0.597232
H	-1.975018	1.691288	-0.404210
F	-3.433826	1.790270	-0.009554
H	-3.669977	0.965006	0.479830
O	-3.837824	-0.317922	1.147273
H	-4.073916	-0.291069	2.078072
H	-2.992527	-0.792237	1.080481

5.5 $UF_6 \cdots H_2O \cdots H_2O \cdots H_2O \xrightarrow{[UF_6-H_2O-H_2O-H_2O]^{\ddagger}_{a}} UF_5OH \cdots H_2O \cdots HF \cdots H_2O$

16

UF6-H2O-H2O-H2Oa E = -30638.088924426531 Dipole = 4.68072 ZPE = 0.08728389

U	-0.017653	0.077394	0.065366
F	0.091561	-0.161401	2.033957
F	-0.096839	0.174582	-1.926230
F	1.527432	1.382146	0.369724
F	-1.969357	0.543548	0.458827
F	1.586047	-1.085799	-0.204839
F	-0.930405	-1.690671	-0.131789
O	1.550934	3.933553	-0.834058
O	-0.583888	2.389896	-0.401834
H	2.077270	3.304462	-0.325493
H	1.976706	3.999774	-1.692279
O	-3.202586	2.769820	-0.760629
H	0.091592	3.054857	-0.664586
H	-1.497348	2.666364	-0.639724
H	-3.364125	1.980116	-0.229867
H	-3.635340	2.613360	-1.603545

16

UF6-H2O-H2O-H2O-TSa E = -30638.067043347441 Dipole = 5.19377 ZPE = 0.08383441

U	0.054550	0.093601	0.107981
F	-0.608264	-0.471065	1.906970
F	1.810217	0.252118	1.115632
F	0.488846	-1.848435	-0.042801
F	-1.244972	-0.399845	-1.327544
F	1.234778	0.437475	-1.490147
O	0.297326	2.226504	0.241224
O	-1.736641	3.422553	0.647864
O	2.888401	2.673284	-0.137362
H	1.231544	2.531707	0.090083
F	-1.964800	1.122262	0.509196
H	-0.715092	3.116272	0.482290
H	-1.834338	3.776087	1.538010
H	3.181473	1.948350	0.427695
H	3.057506	2.367975	-1.034675
H	-2.054533	2.365156	0.623579

16

UF5OH-H2O-HF-H2O E = -30638.089318740618 Dipole = 6.80138 ZPE = 0.08569936

U	0.200951	-0.409569	-0.148954
F	-1.833483	-0.906264	0.227088
F	0.461392	-0.142045	1.840782
F	0.703350	-2.317353	0.047205
F	-0.170075	-0.716893	-2.113429
F	2.133638	0.065348	-0.511488
F	-0.991220	3.392734	1.169454
O	-0.351036	1.369777	-0.313804
O	-2.603671	2.461175	-0.718500
O	-3.927965	0.550722	0.015233
H	-1.697776	2.001954	-0.800792
H	-0.481602	2.681116	0.805409
H	-3.266964	1.683080	-0.353013
H	-2.418097	3.106260	-0.005973
H	-4.472360	0.564159	0.806509
H	-3.233301	-0.145765	0.133473

5.6 $\mathbf{UF_6\cdots H_2O\cdots H_2O\cdots H_2O} \xrightarrow{[UF_6-H_2O-H_2O-H_2O]^{\ddagger}_{b}} \mathbf{UF_5OH\cdots H_2O\cdots H_2O\cdots HF}$

16

UF6-H2O-H2O-H2Ob E = -30638.09076027500 Dipole = 3.47887 ZPE = 0.08771438

U	-0.004464	0.094823	0.091446
F	1.714527	1.065675	0.611265
F	-0.137957	0.632505	-1.838529
F	1.359677	-1.188996	-0.597620
F	0.204720	-0.730318	1.886901
F	-1.300711	-1.329733	-0.421047
F	-1.674125	0.860330	0.912052
O	-0.186841	2.588914	-0.058734
O	1.320801	3.543302	-1.939859
O	3.567694	2.785672	-0.643547
H	0.343954	3.023436	-0.791799
H	-1.082078	2.935826	-0.075481
H	2.225207	3.356320	-1.605848
H	1.216920	3.019717	-2.738550
H	4.396351	2.403155	-0.938204
H	3.170324	2.146370	-0.037449

16

UF6-H2O-H2O-H2O-TSb E = -30638.058707888929 Dipole = 6.00106 ZPE = 0.08240399

U	-0.894600	-1.569809	0.482625
F	1.020666	-0.929656	0.174149
F	-1.100849	-1.836673	-1.472917
F	0.093950	-3.300495	0.634220
F	-0.690926	-1.269750	2.429993
F	-2.426456	-2.792372	0.817718
F	-3.001986	-0.386921	0.533988
O	-1.057735	0.549350	0.176950
O	0.412876	2.405825	-0.688175
O	2.758426	1.216237	-0.231021
H	-0.484601	1.316609	-0.181304
H	-2.243030	0.416114	0.317046
H	1.344885	2.097429	-0.598888
H	0.281346	2.646674	-1.607860
H	3.559003	1.109464	-0.747935
H	2.429033	0.327977	-0.038589

16

UF5OH-H2O-H2O-HF E = -30638.099935908340 Dipole = 4.92164 ZPE = 0.08591264

U	-0.832380	0.168583	-0.914635
F	1.049564	-0.239915	-0.008928
F	1.917496	3.141314	1.741781
F	-0.211229	-0.662052	-2.658635
F	-1.463646	-1.591625	-0.291058
F	-2.700295	0.554988	-1.605900
O	-0.244100	1.811602	-1.347045
O	-0.358824	3.308458	0.936330
O	2.903226	1.074983	1.177822
H	3.671358	1.120586	0.602659
F	-1.338943	1.089211	1.000842
H	-0.266907	3.278069	-0.038009
H	0.603389	3.254998	1.329478
H	2.385761	2.235799	1.499058
H	2.234727	0.490538	0.738861
H	-0.834854	2.408633	1.123906

6 Elementary step 2: UF_5OH to UOF_4

6.1 $UF_5OH\cdots H_2O \xrightarrow{[UF_5OH-H_2O]^{\ddagger}} UOF_4\cdots H_2O\cdots HF$

11

UF5OH-H2O E = -30460.989106307330 Dipole = 4.64971 ZPE = 0.04733355

U	-1.165650	-0.573939	-0.232941
F	0.723087	-1.018052	-0.848110
F	-1.521464	0.309359	-1.996040
F	-1.892996	-2.269796	-0.973039
F	-0.769512	-1.528458	1.488317
F	-2.983801	-0.056178	0.427040
O	-0.392659	1.079622	0.487314
H	0.598942	1.267101	0.496310
O	2.186368	1.252872	0.319112
H	2.725557	1.179929	1.111194
H	2.355163	0.458688	-0.201669

11

UF5OH-H2O-TS E = -30460.978853813249 Dipole = 6.12975 ZPE = 0.04665395

U	-1.111581	-0.484557	-0.189386
F	0.992308	-0.808182	-0.762200
F	-1.427870	0.374475	-1.989022
F	-1.695969	-2.212896	-0.954807
F	-0.645111	-1.443173	1.533839
F	-2.992517	-0.086340	0.437582
O	-0.412843	1.087726	0.490801
H	0.982194	1.313394	0.459910
O	2.004000	1.111460	0.219160
H	2.505075	0.942931	1.026618
H	1.802315	0.205160	-0.272495

11

UOF4-H2O-HF E = -30460.982090859481 Dipole = 5.85146 ZPE = 0.04790079

U	-1.214095	-0.460455	-0.197753
F	1.075595	-0.725737	-0.813838
F	-1.532271	0.320408	-2.040092
F	-1.676972	-2.233688	-0.927423
F	-0.607785	-1.375107	1.515557
F	-3.123361	-0.193505	0.432474
O	-0.604974	1.108665	0.416131
H	1.351090	1.525779	0.571528
O	2.159006	1.070048	0.274221
H	2.664869	0.837640	1.059854
H	1.647207	0.025375	-0.367955

6.2 $UF_5OH\cdots HF \xrightarrow{[UF_5OH-HF]^{\ddagger}} UOF_4\cdots HF\cdots HF$

10

UF5OH-HF E = -30485.067699861014 Dipole = 1.15521 ZPE = 0.03485172

H	-0.600632	-0.226744	0.507143
O	-2.372159	-0.137242	2.685227
H	-1.646912	-0.689099	2.326078
F	-0.393819	-0.979689	1.019547
F	-1.855862	2.641734	2.853163
U	-3.129621	1.486720	1.843845
F	-1.701586	1.225803	0.393874
F	-4.482267	1.648988	3.301151
F	-4.378530	0.374862	0.757571
F	-3.851993	3.108665	0.960528

10

UF5OH-HF-TS E = -30485.049889228958 Dipole = ZPE = 0.03099894

H	1.505061	-0.795103	-1.001375
O	0.073655	-0.952835	0.935546
H	1.022265	-1.511321	0.361686
F	1.816263	-1.715269	-0.399452
F	0.645456	1.739251	1.171462
U	-0.685700	0.590779	0.212090
F	0.942989	0.152090	-1.323025
F	-2.052715	0.792958	1.670721
F	-1.922122	-0.504993	-0.920032
F	-1.345152	2.204444	-0.707622

10

UOF4-HF-HF E = -30485.055098031884 Dipole = 2.24988 ZPE = 0.03530459

H	-0.289039	0.073521	0.277664
O	-1.940699	-0.147988	2.278421
H	-0.626013	-0.983245	1.728774
F	0.077299	-1.091796	1.086680
F	-1.283205	2.491799	2.485419
U	-2.620811	1.337656	1.512480
F	-0.767395	0.868811	-0.028645
F	-4.099819	1.605875	2.859317
F	-3.733964	0.222082	0.254066
F	-3.193783	2.936177	0.517302

6.3 $UF_5OH\cdots UF_6 \xrightarrow{[UF_5OH-UF_6]^{\ddagger}} U_2OF_{10}\cdots HF$

15

UF5OH-UF6 E = -60793.067030528102 Dipole = 2.77804 ZPE = 0.03522433

U	5.071680	3.229292	1.366290
F	5.778763	1.769369	2.500623
F	6.006115	2.453278	-0.195560
F	3.465330	2.077304	0.946394
F	4.382065	4.681918	0.221495
O	0.724587	1.983775	0.171206
F	6.670992	4.325018	1.785030
F	4.140045	3.982158	2.937573
H	1.593389	1.670717	0.467755
U	0.260398	3.855025	-0.346668
F	-1.308331	3.834173	0.887319
F	1.459672	4.507629	1.126380
F	1.856702	3.889810	-1.553496
F	-0.188995	5.723552	-0.856033
F	-0.895864	3.178469	-1.826159

15

UF5OH-UF6-TS E = -60793.037497033336 Dipole = 0.59794 ZPE = 0.03305340

U	1.742018	-0.354004	0.988973
F	2.933418	-1.901723	1.256753
F	2.669351	0.087663	-0.689434
F	0.841781	-2.248571	-0.045225
F	0.951645	1.460207	1.043630
O	-0.291355	-0.359130	-0.265279
F	3.146578	0.543191	2.070266
F	0.717147	-0.838028	2.597287
H	0.046599	-1.503850	-0.346576
U	-1.870639	0.691860	-0.982330
F	-2.190694	1.460763	0.825618
F	-0.670468	2.214685	-1.430341
F	-1.547115	-0.101571	-2.780771
F	-3.426430	1.700949	-1.693377
F	-3.052137	-0.852641	-0.549297

6.4 $U_2OF_{10} \xrightarrow{[U_2OF_{10}]^{\ddagger}} UOF_4\cdots UF_6$

13

U2OF10 E = -60692.480884608129 Dipole = 0.01430 ZPE = 0.02338850

U	1.070778	0.702706	-0.966528
F	2.075084	0.580978	0.743371
F	2.729477	1.271853	-1.900350
F	1.488023	-1.198094	-1.361058
F	0.061406	0.847820	-2.671659
O	0.640057	2.650747	-0.565304
F	-0.592759	0.156925	-0.027368
U	0.166871	4.594045	-0.189909
F	0.158028	4.202869	1.757944
F	2.101527	5.035477	-0.093157
F	0.180962	4.961603	-2.142399
F	-0.296180	6.489567	0.178065
F	-1.761942	4.128739	-0.292708

13
U2OF10-TS E = -60692.453857894776 Dipole = 2.72023 ZPE = 0.02346348

U	0.718891	-1.909911	0.021642
F	1.957044	-3.104009	1.082620
F	2.099769	-1.251073	-1.303459
F	0.304230	-3.373154	-1.228961
F	-0.655304	-0.199847	-0.960270
O	0.951553	-0.444425	1.033489
F	-0.974532	-2.373330	1.028653
U	-0.649951	1.730531	-0.018867
F	-0.987249	1.283871	1.864337
F	1.270036	2.113484	0.144247
F	-0.486605	2.341748	-1.880290
F	-0.955574	3.619496	0.491385
F	-2.592309	1.566620	-0.274526

13
UOF4-UF6 E = -60692.456621165198 Dipole = 4.72671 ZPE = 0.02294324

U	1.576227	0.089920	-0.799449
F	2.558210	-1.638879	-0.394395
F	2.788355	0.859947	-2.243565
F	0.575796	-0.815655	-2.232418
F	0.396494	2.284951	-1.207105
O	2.381309	1.050182	0.443229
F	-0.062044	-0.151071	0.387385
U	0.314914	4.209550	-0.423329
F	0.286497	3.482313	1.400626
F	2.276822	4.298464	-0.389725
F	0.323964	4.922253	-2.258214
F	0.208295	6.050414	0.298489
F	-1.650001	4.112421	-0.485277

7 Elementary step 3: UOF_4 to $UF_4(OH)_2$

7.1 $\mathbf{UOF_4 \cdots H_2O} \xrightarrow{[UOF_4 \cdots H_2O]^{\ddagger}} \mathbf{UO_2F_3H \cdots HF}$

9
UOF4-H2O E = -30360.370565959769 Dipole = 4.85971 ZPE = 0.03506597

U	0.643526	-0.467096	-0.549439
F	-0.884615	-1.314758	-1.626746
F	1.434556	-0.344224	1.341269
F	1.778412	-2.102669	-0.899573
F	-0.648585	1.006067	-0.023217
O	1.594960	0.576799	-1.634236
H	-1.615761	-1.989119	0.687789
O	-0.702368	-1.833950	0.952397
H	-0.668755	-1.597287	1.885876

9
UOF4-H2O-TS E = -30360.346901426405 Dipole = 2.66093 ZPE = 0.03117955

U	0.368331	0.314065	-0.608089
F	-0.950739	-0.365869	-1.984867
F	0.919686	0.271575	1.696738
F	1.583304	-1.261720	-0.908957
F	-0.919261	1.802860	-0.160490
O	1.488082	1.413068	-1.417678
H	-1.724980	-0.868402	0.943933
O	-0.772194	-0.922049	0.820510
H	0.007769	-0.383528	1.618901

9

UO2F3H-HF E = -30360.357745848592 Dipole = 2.91203 ZPE = 0.03292477

U	0.999645	-0.310459	0.000324
F	0.248111	-0.912278	-1.795619
F	2.132423	-0.073789	2.317009
F	2.355283	-1.816141	0.589405
F	-0.159000	1.330362	0.380398
O	2.309983	0.630158	-0.687388
H	-1.352793	-1.189824	0.955829
O	-0.404880	-1.367406	0.914290
H	2.586216	-0.873593	2.105330

7.2 $UOF_4 \cdots H_2O \cdots HF \xrightarrow{[UOF_4 \cdots H_2O \cdots HF]^{\ddagger}} UF_4(OH)_2 \cdots HF$

11

UOF4-HF-H2O E = -30460.984679957695 Dipole = 3.10951 ZPE = 0.04834211

U	1.268395	0.635551	-0.793919
F	0.812062	-0.027061	1.172698
F	3.295755	0.542851	-0.818749
F	1.223977	-1.242492	-1.352503
F	0.813062	1.156911	-2.711457
O	1.226752	2.309732	-0.265292
H	-0.625827	0.087153	1.823691
F	-1.562394	0.253978	1.820996
H	-1.690573	1.184720	-1.299005
O	-1.174071	0.594415	-0.743516
H	-1.583638	0.535114	0.147506

11

UOF4-HF-H2O-TS E = -30460.961284151697 Dipole = 3.14649 ZPE = 0.04210179

U	0.944905	-0.396689	0.031614
F	0.676481	-0.971769	1.932774
F	2.908012	-0.121215	0.360166
F	1.167270	-2.307376	-0.452427
F	1.174561	0.053471	-1.908307
O	0.453892	1.389678	0.445046
H	-0.623107	1.720822	0.374170
F	-1.850414	1.697343	0.189892
H	-1.831747	-1.186272	-0.605713
O	-1.260008	-0.484098	-0.287264
H	-1.759845	0.606108	-0.079950

11

UF4OH2-HF-HF E = -30460.969619378302 Dipole = 2.65650 ZPE = 0.04584230

U	1.026307	0.705822	-0.877053
F	0.742804	0.193245	1.036224
F	2.977250	0.960634	-0.532725
F	1.272793	-1.221387	-1.319824
F	1.312639	1.121846	-2.813313
O	0.651401	2.608022	-0.465434
H	-0.243079	3.007102	-0.400036
F	-2.029696	2.807580	-0.614505
H	-1.506181	-0.229770	-1.588010
O	-1.030180	0.521388	-1.219127
H	-1.880137	1.907680	-0.879306

7.3 $\mathbf{UOF_4\cdots HF\cdots H_2O\cdots HF} \xrightarrow{[UOF_4\cdots HF\cdots H_2O\cdots HF]^{\ddagger}} \mathbf{UF_4(OH)_2\cdots HF\cdots HF}$

13

UOF4-HF-H2O-HF E = -30561.569540591183 Dipole = 2.41344 ZPE = 0.06017701

O	-1.012388	0.440292	0.178573
H	-0.522177	-0.367491	0.418631
H	-1.095003	3.186666	-0.601060
H	-0.485345	1.052397	-0.362520
O	-2.528074	-0.375673	2.427082
H	-1.210923	-1.524560	2.045286
F	-0.468936	-1.781424	1.526680
F	-1.140473	1.955984	2.795640
U	-2.674340	1.254997	1.685145
F	-0.368294	2.766635	-1.008707
F	-4.051631	2.061155	2.927747
F	-4.086655	0.630168	0.389565
F	-2.509089	2.953524	0.583578

13

UOF4-HF-H2O-HF-TS E = -30561.547644365986 Dipole = 1.67853 ZPE = 0.05452205

O	-0.998944	0.510983	0.521369
H	-0.716985	-0.639047	0.817442
H	-1.211599	3.152167	-0.725768
H	-0.572245	0.988807	-0.206458
O	-2.447348	-0.443692	2.483228
H	-1.672789	-1.161726	2.059873
F	-0.764117	-1.619952	1.367139
F	-1.287792	2.052259	3.043417
U	-2.625578	1.302209	1.758027
F	-0.555484	2.660208	-1.164961
F	-4.119688	1.916781	2.947764
F	-3.956711	0.682054	0.398290
F	-2.485771	3.037349	0.713706

13

UF4OH2-HF-HF E = -30561.553683036913 Dipole = 1.68596 ZPE = 0.05765706

O	-2.247091	2.609187	0.589965
H	-1.489765	2.950615	0.072330
H	0.133210	1.616742	-0.552419
H	-0.256515	-1.471959	0.520823
O	-2.105955	-0.824799	2.549712
H	-1.654342	-1.617717	2.195043
F	-0.437350	-2.287942	0.940331
F	-0.854390	1.693555	2.841007
U	-2.221033	0.910046	1.604599
F	-0.602678	0.271643	0.369841
F	-3.738320	1.511783	2.766511
F	-3.465647	0.079485	0.273923
F	0.126994	2.523481	-0.780285

8 Elementary step 4: dimerization of $UF_4(OH)_2$

8.1 $UO_2F_3H\cdots H_2O \xrightarrow{[UO_2F_3H\cdots H_2O]^{\ddagger}} UO_2F_2\cdots HF\cdots H_2O$

10
UO2F3H-H2O E = -30336.275185663613 Dipole = 4.50916 ZPE = 0.04632069

O	-1.515192	1.640920	0.312924
O	-2.514117	-0.069062	3.409729
F	-0.531736	1.813139	2.861653
U	-2.004082	0.859185	1.800991
F	-3.897200	1.642607	1.688675
F	-1.767012	-1.091258	1.037198
H	-2.610242	-1.086936	3.463692
O	-2.565189	-2.599174	3.180035
H	-2.243512	-2.560490	2.265427
H	-3.398518	-3.077241	3.162958

10
UO2F3H-H2O-TS E = -30336.270564166593 Dipole = 5.94842 ZPE = 0.04463766

O	0.901432	1.974890	-1.940607
O	-0.442904	0.404474	1.002830
F	1.840576	1.918987	0.649854
U	0.243201	1.271021	-0.480912
F	-1.504582	2.346048	-0.657899
F	0.345755	-0.825009	-1.225762
H	-0.596128	-0.881135	1.019933
O	-0.604590	-1.958277	0.672878
H	-0.171139	-1.745333	-0.239593
H	-0.011621	-2.505665	1.199277

10
UO2F2-HF-H2O E = -30336.275529902432 Dipole = 6.49130 ZPE = 0.04666526

O	-1.341293	1.214168	0.304435
O	-2.726769	-0.148535	3.250460
F	-0.463940	1.371884	2.918207
U	-2.033320	0.629171	1.801338
F	-3.741949	1.756954	1.547054
F	-1.867917	-1.694002	1.116563
H	-2.946468	-2.013393	3.493563
O	-2.791652	-2.829062	2.976182
H	-2.234583	-2.297810	1.876552
H	-2.234119	-3.412986	3.498927

8.2 $UO_2F_3H\cdots HF\cdots H_2O \xrightarrow{[UO_2F_3H\cdots HF\cdots H_2O]^{\ddagger}} UF_4(OH)_2\cdots H_2O$

12

UO2F3H-HF-H2O E = -30436.881527516900 Dipole = 4.74304 ZPE = 0.05807114

O	-1.755055	2.455576	0.463566
H	-0.661896	2.803715	-1.108501
O	-1.641743	-0.934655	2.142872
H	-2.315367	-1.624194	2.101185
F	-0.329642	1.506518	2.605914
U	-1.779752	0.880879	1.323256
F	-0.022619	0.391066	-0.250807
F	-3.369436	1.317200	2.525682
F	-2.981285	0.043736	-0.108897
O	-0.011864	2.310242	-1.643565
H	-0.391115	2.198599	-2.520994
H	0.058693	1.172049	-0.923953

12

UO2F3H-HF-H2O-TS E = -30436.877641888681 Dipole = 4.73482 ZPE = 0.05660904

O	-0.520577	1.352123	-0.117528
H	0.366337	1.586474	-1.150265
O	-0.245576	-2.026191	1.717169
H	-0.910811	-2.722905	1.766547
F	0.900704	0.525760	2.112706
U	-0.453816	-0.248424	0.818738
F	1.204134	-0.638370	-0.602274
F	-2.048824	0.187117	2.003642
F	-1.689626	-1.155940	-0.523983
O	1.179987	1.391642	-1.837800
H	0.840030	1.316471	-2.737100
H	1.378037	0.432242	-1.449850

12

UF4(OH)2-H2O E = -30436.877641888681 Dipole = 4.73482 ZPE = 0.05660904

O	-0.520577	1.352123	-0.117528
H	0.366337	1.586474	-1.150265
O	-0.245576	-2.026191	1.717169
H	-0.910811	-2.722905	1.766547
F	0.900704	0.525760	2.112706
U	-0.453816	-0.248424	0.818738
F	1.204134	-0.638370	-0.602274
F	-2.048824	0.187117	2.003642
F	-1.689626	-1.155940	-0.523983
O	1.179987	1.391642	-1.837800
H	0.840030	1.316471	-2.737100
H	1.378037	0.432242	-1.449850

8.3 $\mathbf{UF_4(OH)_2 \cdots UF_4(OH)_2} \xrightarrow{[UF_4(OH)_2 \cdots UF_4(OH)_2]^{\ddagger}} \mathbf{U_2O_4F_7H_3 \cdots HF}$

18

UF4(OH)2-UF4(OH)2 E = -60720.778809611264 Dipole = 0.05373 ZPE = 0.06637691

O	-2.115789	2.395600	0.400382
H	-1.469631	3.117285	0.219521
O	-1.941326	-0.930579	2.561527
H	-2.544229	-1.675940	2.662577
F	-1.128289	1.770124	2.939266
U	-2.051735	0.753732	1.483332
F	-0.173663	0.386819	0.670778
F	-3.869520	1.116374	2.262851
F	-2.934842	-0.298801	0.022800
O	2.182381	5.800722	-0.131287
H	2.647335	6.455499	-0.664524
O	1.580833	1.901593	-0.576732
H	1.017042	1.240678	-0.111797
F	3.886505	3.592974	-0.602905
U	1.905013	3.829638	-0.356025
F	1.736205	4.130547	-2.331306
F	2.033461	3.568023	1.623860
F	-0.145539	4.064572	-0.108560

18

UF4(OH)2-UF4(OH)2-TS E = -60720.752833734041 Dipole = 2.37884 ZPE = 0.06476997

O	-0.554837	0.187007	0.220521
H	-0.706240	1.353448	0.103531
O	-2.365701	-3.063673	1.568388
H	-3.055530	-3.617228	1.184118
F	-0.756818	-1.064861	2.730537
U	-1.498863	-1.387796	0.897909
F	0.240165	-2.415845	0.374889
F	-3.126453	-0.276363	1.308405
F	-2.265536	-1.795642	-0.913472
O	1.838128	3.169250	-1.267490
H	1.148488	3.822578	-1.087647
O	1.891019	-0.687486	-0.610165
H	1.374695	-1.455319	-0.256529
F	3.502863	1.176921	-1.613983
U	1.654270	1.230863	-0.850708
F	0.748400	0.907212	-2.600343
F	2.258022	1.540787	1.026309
F	-0.326070	2.376145	-0.214270

18
U2O4F7H3-HF E = -60720.779537985160 Dipole = 3.16220 ZPE = 0.06689956

O	-0.078647	2.003567	0.572989
H	-2.298760	4.312958	0.795260
O	-3.219966	0.173562	2.092790
H	-3.772484	-0.544282	1.762150
F	-1.055699	1.641419	3.156785
U	-1.609916	1.071174	1.318573
F	-0.554406	-0.639270	1.462870
F	-2.683880	2.868609	1.121396
F	-2.230285	0.504556	-0.503330
O	0.626192	4.742677	0.342096
H	-0.329803	5.006294	0.424056
O	2.441674	1.439323	-0.858069
H	3.269767	1.019340	-0.597739
F	3.070269	4.213472	-1.028275
U	1.553573	3.133149	-0.269661
F	0.519897	3.186010	-1.983218
F	2.556357	2.974377	1.458874
F	-1.912282	5.150605	0.549301

9 Additional isolated species

8
UF5OH E = -30384.479964320766 Dipole = 2.65581 ZPE = 0.02156594

U	-0.045751	0.033464	0.087695
F	-1.737442	-0.590552	-0.755663
O	1.653586	0.658521	0.944125
F	-1.050215	1.531950	0.941511
F	0.939885	-1.453961	-0.808825
F	-0.412607	-1.125757	1.667498
F	0.356952	1.198407	-1.484495
H	2.459590	1.107929	0.669154

6
UOF4a E = -30283.862190650711 Dipole = 0.30551 ZPE = 0.01031687

U	-1.299506	-0.021546	-0.066351
F	0.396007	0.951072	-0.014463
O	-2.817890	-0.891759	-0.112344
F	-2.232341	1.784625	-0.122964
F	-0.652368	-0.885125	-1.790099
F	-0.785253	-0.836976	1.724341

6
UOF4e E = -30283.862190506432 Dipole = 0.31209 ZPE = 0.01031745

U	-1.298888	-0.021165	-0.066011
F	0.396798	0.951358	-0.013619
O	-2.817290	-0.891343	-0.111886
F	-2.232945	1.784245	-0.124296
F	-0.653420	-0.884882	-1.790181
F	-0.785605	-0.837923	1.724113

7
UO2F3H E = -30259.762802825077 Dipole = 2.60576 ZPE = 0.02053645

O	-1.423707	1.639097	0.345794
O	-2.956022	-0.117319	3.258621
F	-0.534735	1.228001	2.947041
U	-2.111939	0.790905	1.716253
F	-3.832047	1.885733	1.581064
F	-1.851827	-1.055299	0.870631
H	-2.614505	-0.810756	3.836505

5
UO2F2 E = -30159.151037568681 Dipole = 4.32494 ZPE = 0.00926553

U	0.004539	-0.021874	-0.019828
O	1.646500	0.392481	0.428631
O	-1.605348	-0.208243	-0.684984
F	-0.704217	0.290174	1.879249
F	0.479336	-1.990739	-0.342178

9
UF4(OH)2 E = -30360.379413667819 Dipole = 0.01762 ZPE = 0.03191386

O	-2.134953	2.530841	0.584321
H	-1.473510	3.199136	0.375627
O	-1.927246	-1.052319	2.397350
H	-2.590613	-1.715528	2.615914
F	-0.798187	1.540867	2.857093
U	-2.030887	0.739130	1.490522
F	-0.418602	0.304300	0.376393
F	-3.642984	1.172761	2.605580
F	-3.263938	-0.061208	0.123520

Part III

Supplementary figures

This section collects visualizations of the molecular species optimized using the PBE0 functional and a mixed triple-ζ basis set, as described in the main text. For reference, level diagrams are also provided as constructed using an alternate double hybrid density functional method, DSD-BLYP.

10 Isolated and pre-reactive species

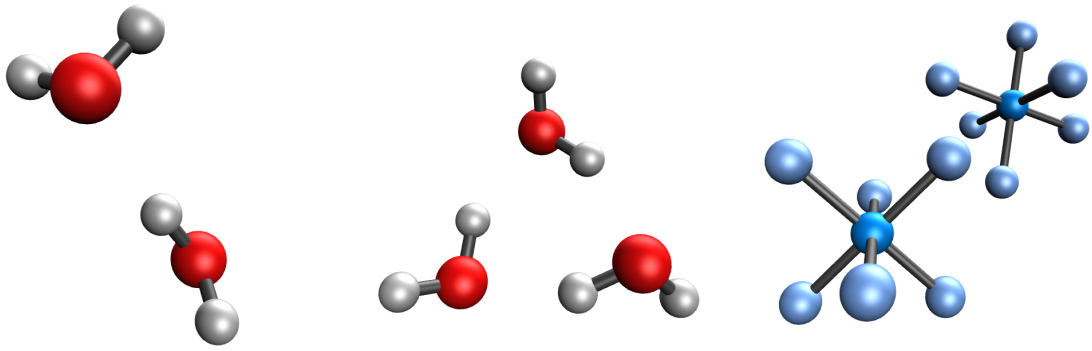


Figure 1 Geometries of pre-reactive species

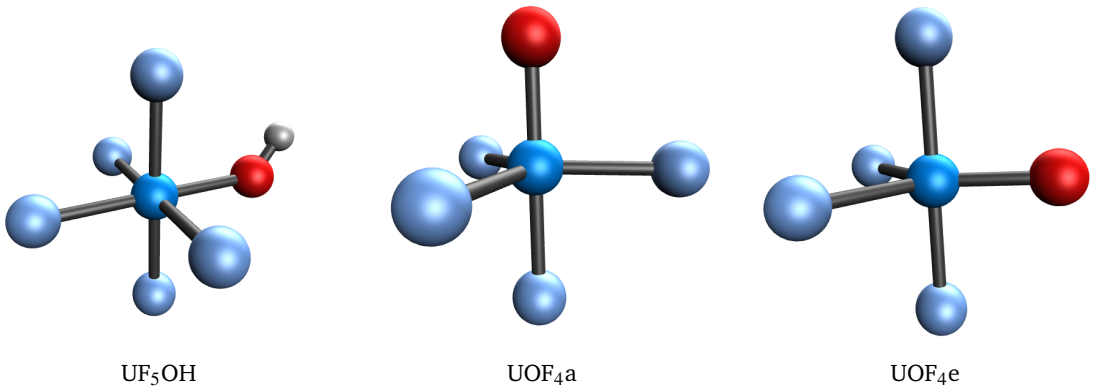


Figure 2 Geometries of early isolated species

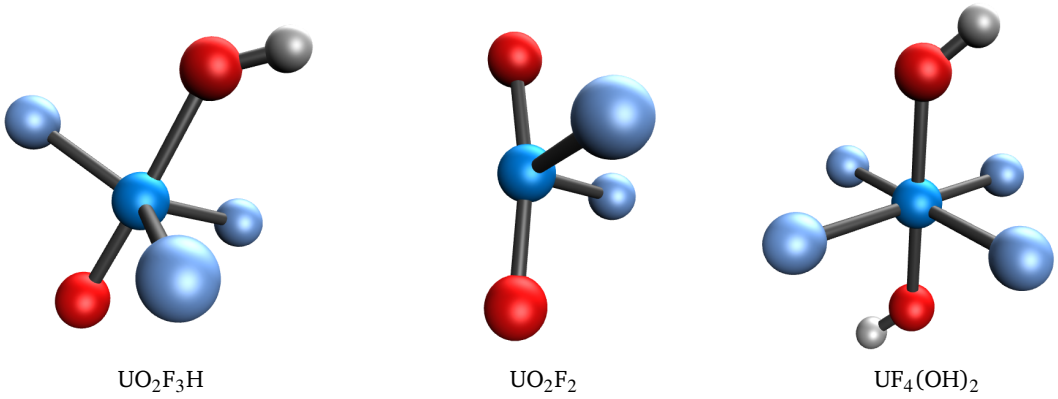


Figure 3 Geometries of late isolated species

11 Elementary step 1, from UF_6 to UF_5OH: DSD-BLYP level diagrams and PBE0 geometrical structures

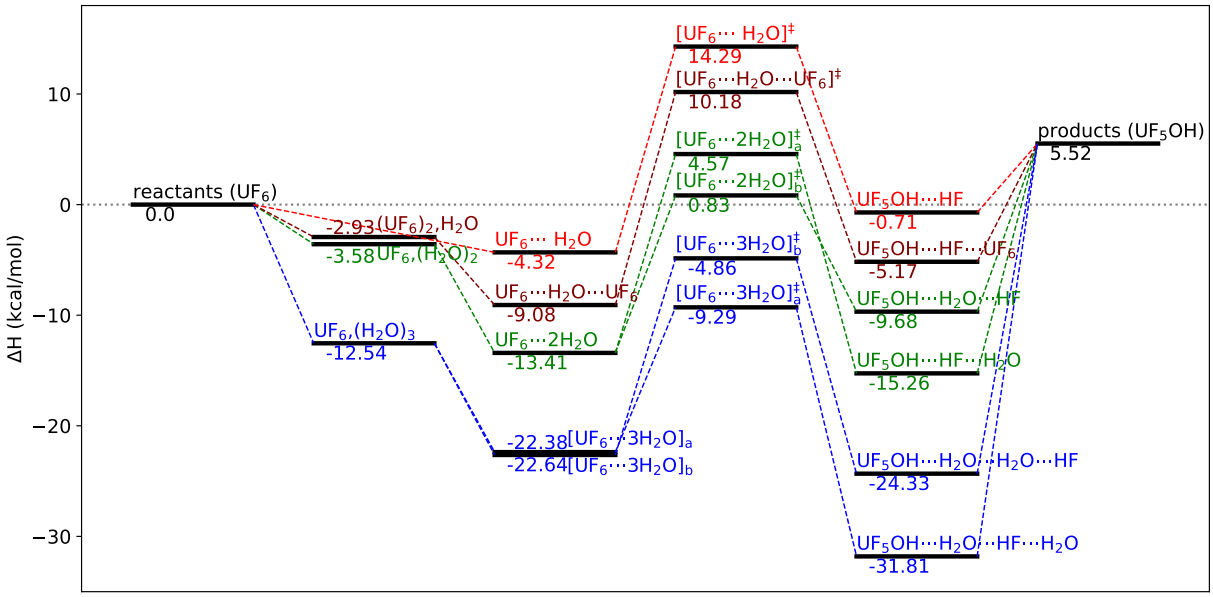
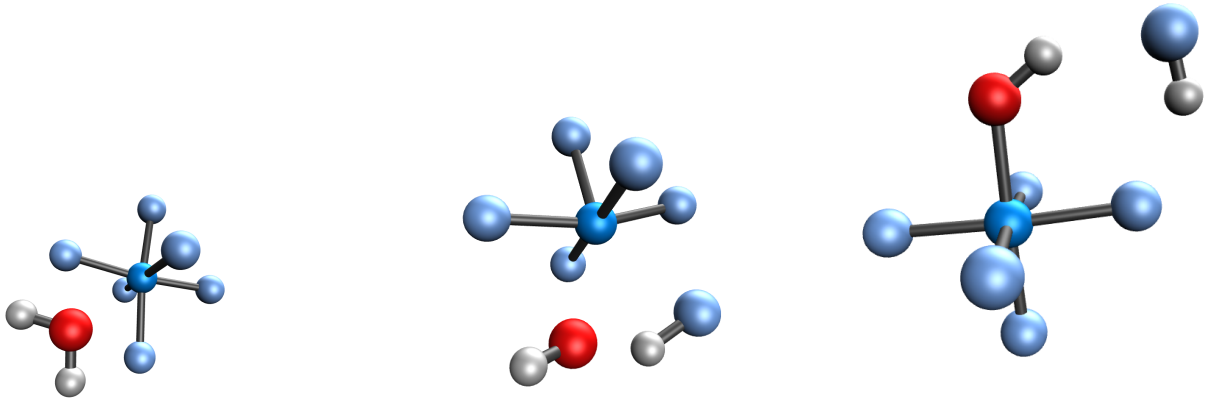
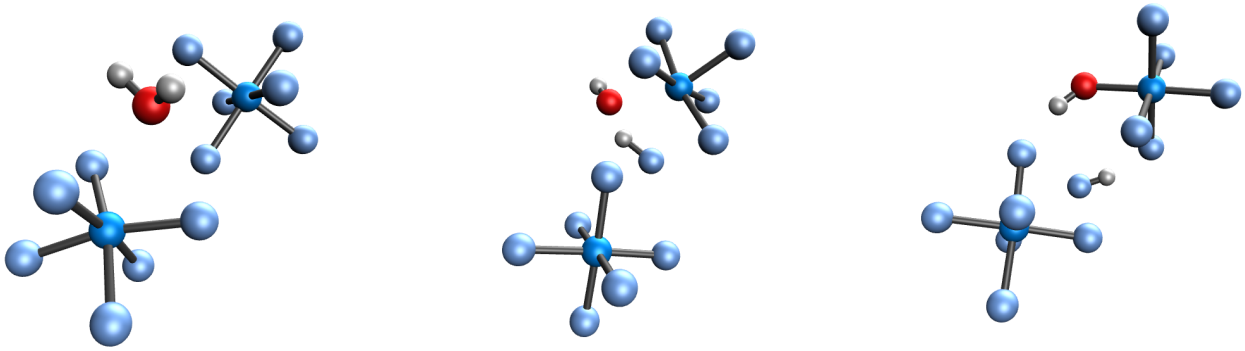


Figure 4 DSD-BLYP energy level diagram for possible elementary steps connecting UF_6 and UF_5OH.



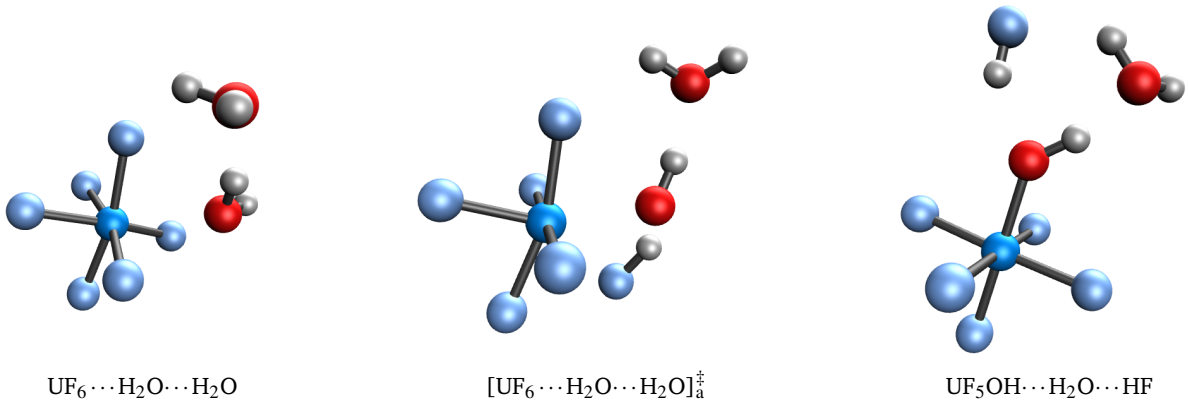
$UF_6 \cdots H_2O$ $[UF_6 \cdots H_2O]^{\ddagger}$ $UF_5OH \cdots HF$

Figure 5 $UF_6 \cdots H_2O \xrightarrow{[UF_6-H_2O]^{\ddagger}} UF_5OH \cdots HF$; visualizations of PBE0-level stataionary points



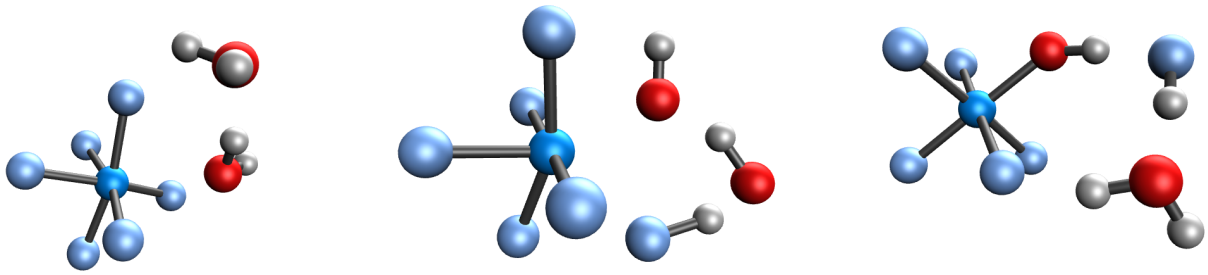
$UF_6 \cdots H_2O \cdots UF_6$ $[UF_6 \cdots H_2O \cdots UF_6]^{\ddagger}$ $UF_5OH \cdots HF \cdots UF_6$

Figure 6 $UF_6 \cdots H_2O \cdots UF_6 \xrightarrow{[UF_6-H_2O-UF_6]^{\ddagger}} UF_5OH \cdots HF \cdots UF_6$; visualizations of PBE0-level stationary points.



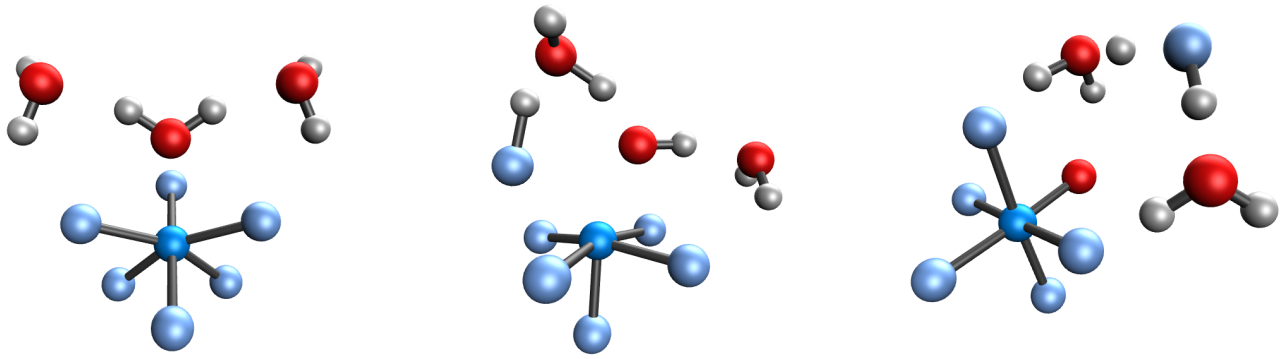
$UF_6 \cdots H_2O \cdots H_2O$ $[UF_6 \cdots H_2O \cdots H_2O]^{\ddagger}_{a}$ $UF_5OH \cdots H_2O \cdots HF$

Figure 7 $UF_6 \cdots H_2O \cdots H_2O \xrightarrow{[UF_6-H_2O-H_2O]^{\ddagger}_{a}} UF_5OH \cdots H_2O \cdots HF$; visualizations of the PBE0-level stationary points



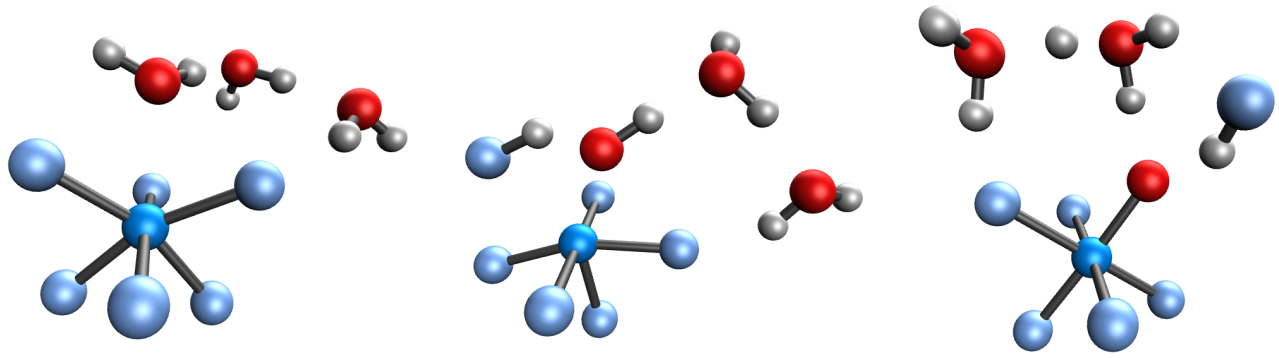
$UF_6\cdots H_2O\cdots H_2O$ $UF_6\cdots H_2O\cdots H_2O]_b^{\ddagger}$ $UF_5OH\cdots HF\cdots H_2O$

Figure 8 $UF_6\cdots H_2O\cdots H_2O \xrightarrow{[UF_6-H_2O-H_2O]_b^{\ddagger}} UF_5OH\cdots HF\cdots H_2O$; visualizations of the PBE0-level stationary points



$UF_6\cdots H_2O\cdots H_2O\cdots H_2O(a)$ $UF_6\cdots H_2O\cdots H_2O\cdots H_2O]_a^{\ddagger}$ $UF_5OH\cdots H_2O\cdots HF\cdots H_2O$

Figure 9 $UF_6\cdots H_2O(a)\cdots H_2O\cdots H_2O \xrightarrow{[UF_6-H_2O-H_2O-H_2O]_a^{\ddagger}} UF_5OH\cdots H_2O\cdots HF\cdots H_2O$; visualizations of the PBE0-level stationary points



$UF_6\cdots H_2O\cdots H_2O\cdots H_2O(b)$ $UF_6\cdots H_2O\cdots H_2O\cdots H_2O]_b^{\ddagger}$ $UF_5OH\cdots H_2O\cdots H_2O\cdots HF$

Figure 10 $UF_6\cdots H_2O\cdots H_2O\cdots H_2O(b) \xrightarrow{[UF_6-H_2O-H_2O-H_2O]_b^{\ddagger}} UF_5OH\cdots H_2O\cdots H_2O\cdots HF$; visualizations of the PBE0-level stationary points

12 Elementary step 2, from UF_5OH to UOF_4: DSD-BLYP level diagrams and PBE0 geometrical structures

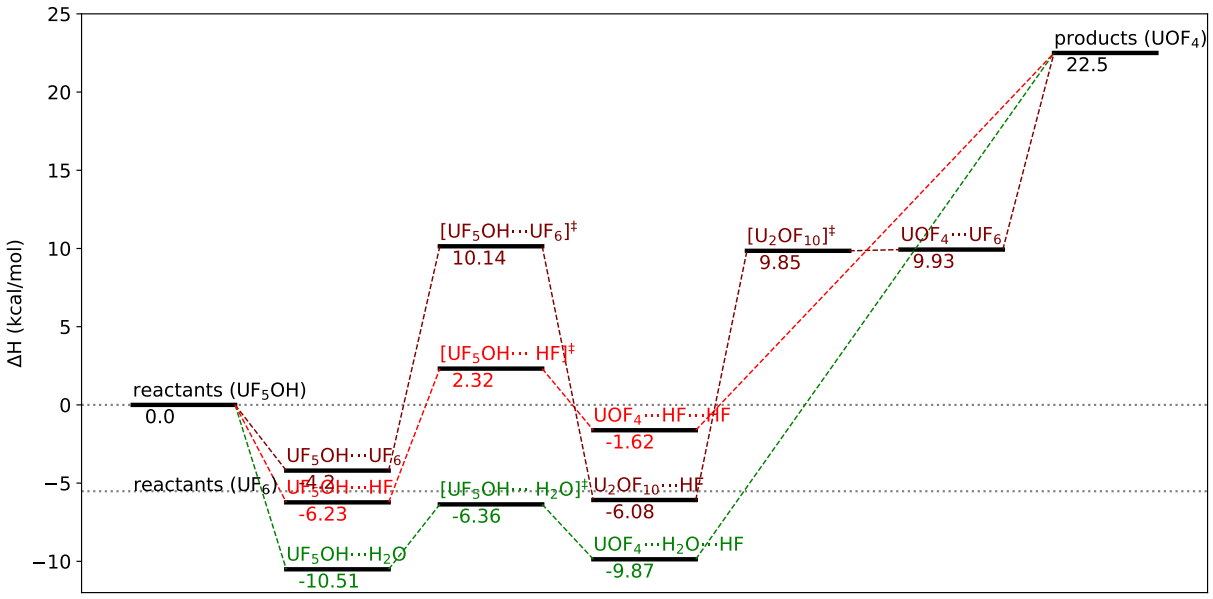
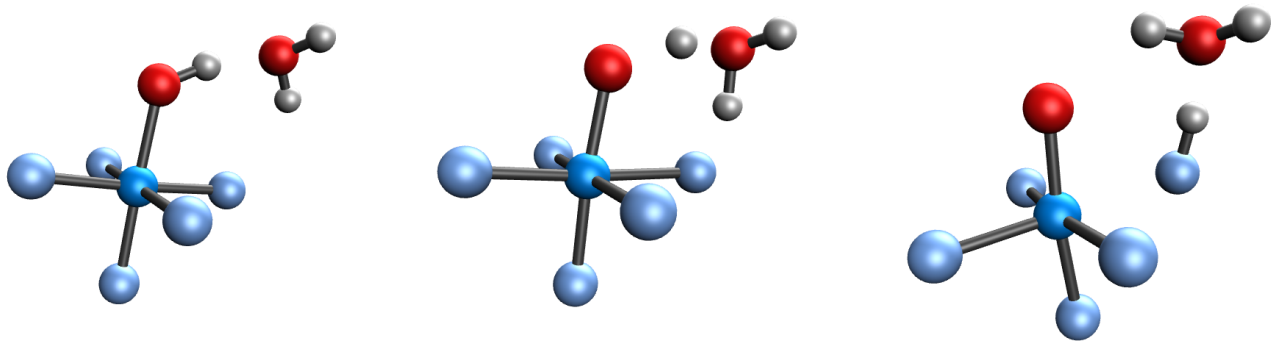


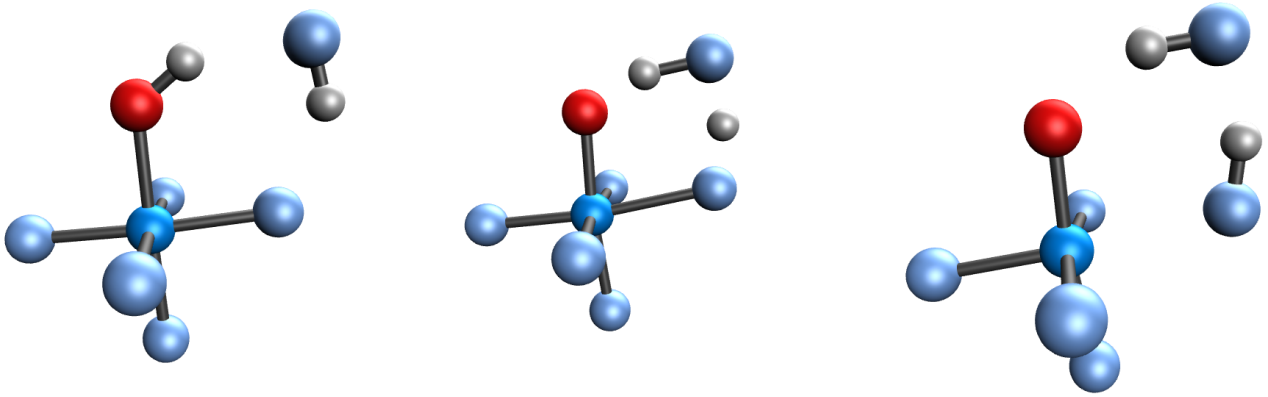
Figure 11 DSD-BLYP level diagram for elementary steps linking UF_5OH and UOF_4



$UF_5OH\cdots H_2O$ $[UF_5OH\cdots H_2O]^{\ddagger}$ $UOF_4\cdots H_2O\cdots HF$

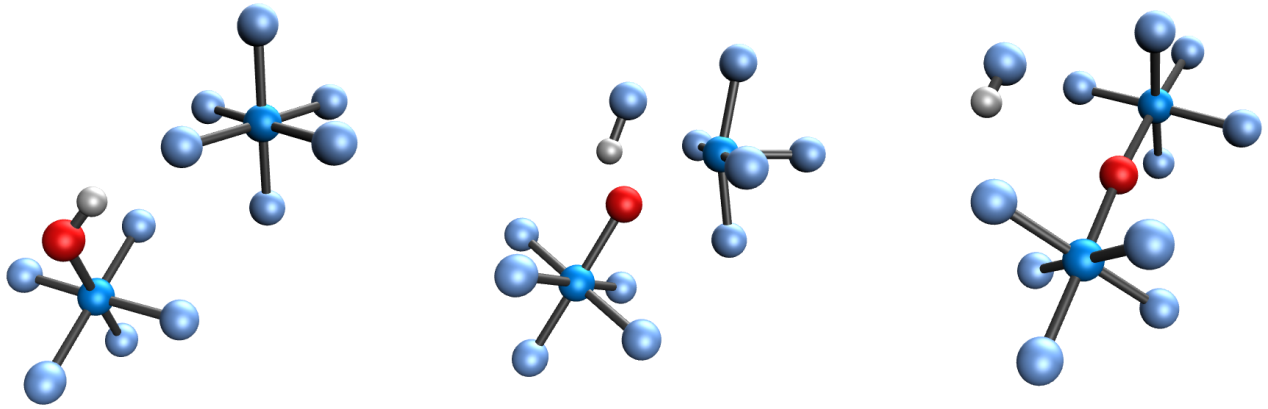
Figure 12 $UF_5OH\cdots H_2O \xrightarrow{[UF_5OH-H_2O]^{\ddagger}} UOF_4\cdots H_2O\cdots HF$; visualizations of the PBE0-level stationary points

13 Elementary step 3, from UOF_4 to $UF_4(OH)_2$: DSD-BLYP level diagrams and PBE0 geometrical structures



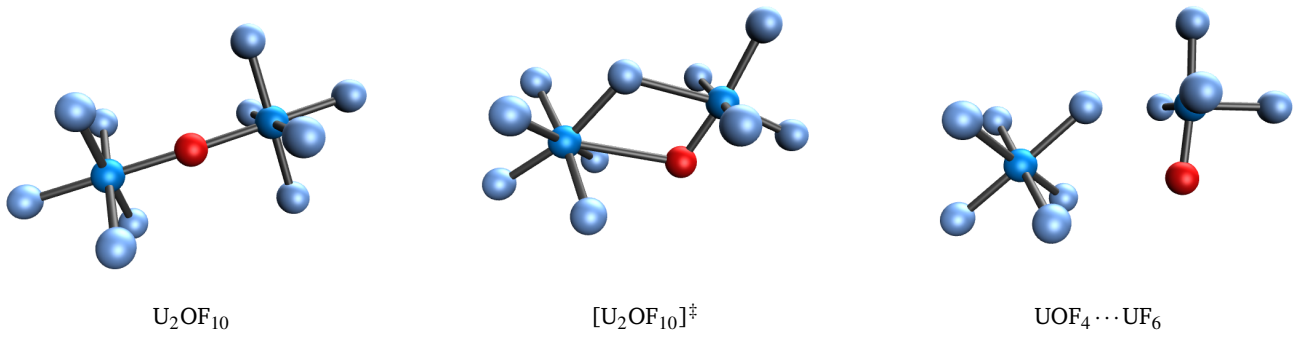
$UF_5OH\cdots HF$ $UF_5OH\cdots HF]^{\ddagger}$ $UOF_4\cdots HF\cdots HF$

Figure 13 $UF_5OH\cdots HF \xrightarrow{[UF_5OH-HF]^{\ddagger}} UOF_4\cdots HF\cdots HF$; visualizations of the PBE0-level stationary points



$UF_5OH\cdots UF_6$ $[UF_5OH\cdots UF_6]^{\ddagger}$ $U_2OF_{10}\cdots HF$

Figure 14 $UF_5OH\cdots UF_6 \xrightarrow{[UF_5OH-UF_6]^{\ddagger}} U_2OF_{10}\cdots HF$; visualizations of the PBE0-level stationary points



U_2OF_{10} $[U_2OF_{10}]^{\ddagger}$ $UOF_4\cdots UF_6$

Figure 15 $U_2OF_{10} \xrightarrow{[U_2OF_{10}]^{\ddagger}} UOF_4\cdots UF_6$; visualization of the PBE0-level stationary points

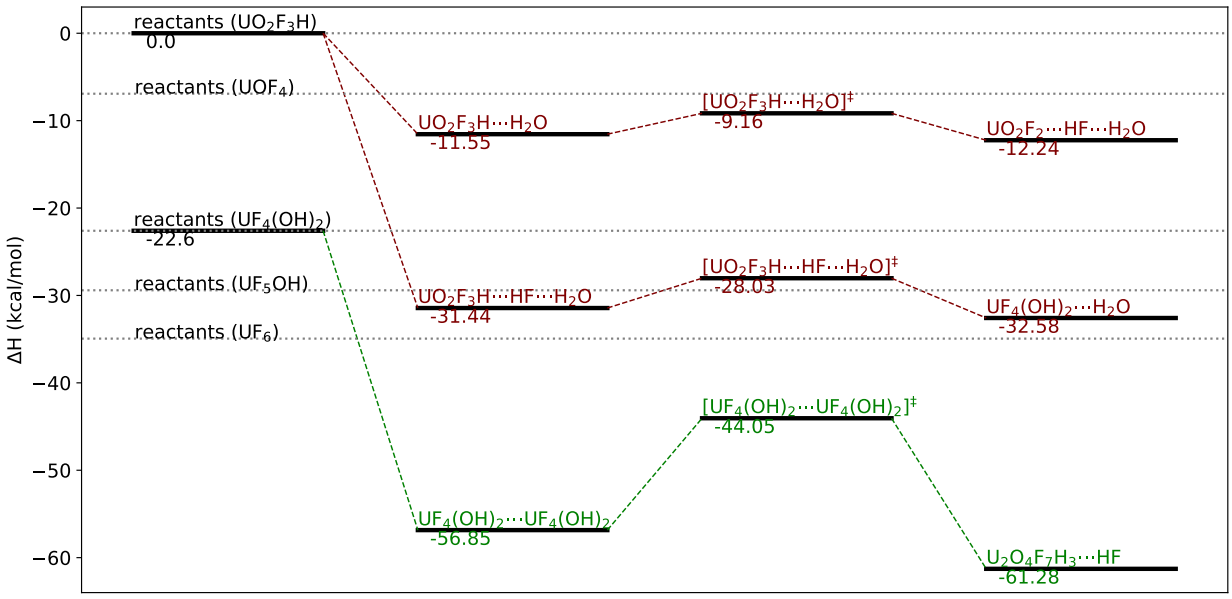
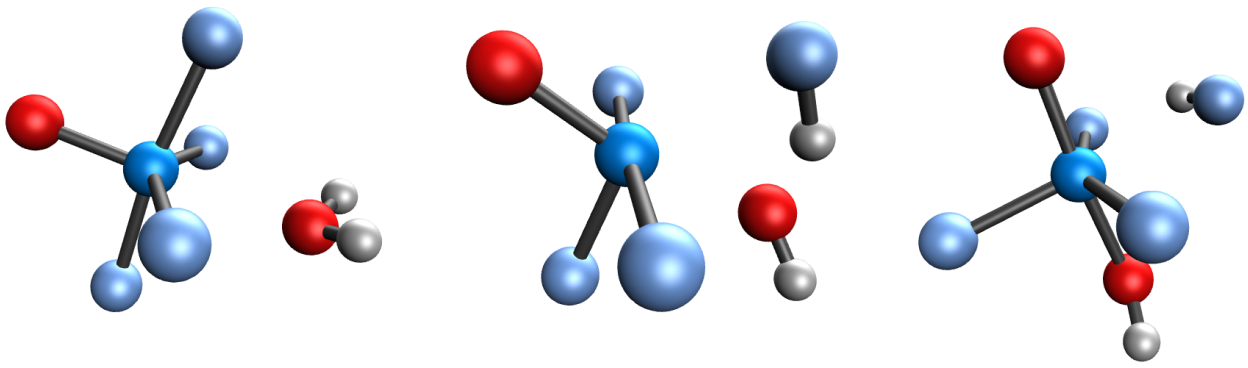


Figure 16 DSD-BLYP level diagram for elementary steps linking UOF_4 and $UF_4(OH)_2$



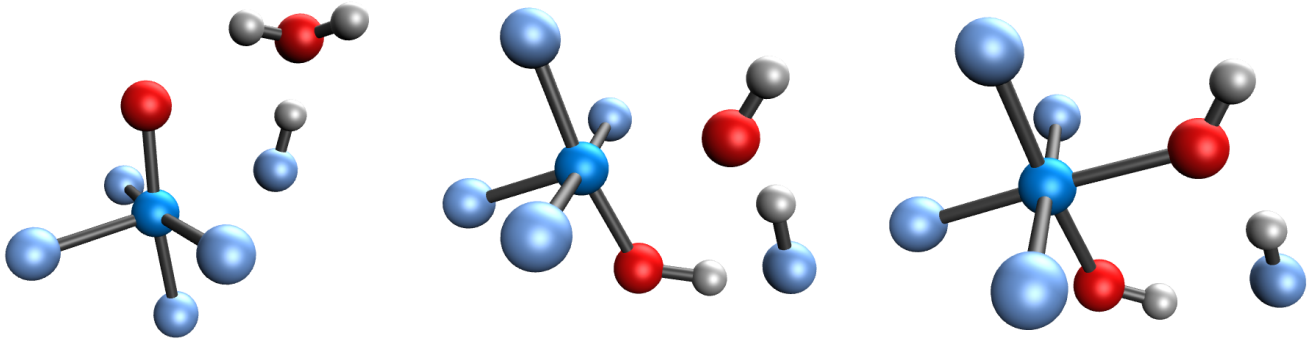
$UOF_4\cdots H_2O$ $[UOF_4\cdots H_2O]^‡$ $UO_2F_3H\cdots HF$

Figure 17 $UOF_4\cdots H_2O \xrightarrow{[UOF_4\cdots H_2O]^‡} UO_2F_3H\cdots HF$; visualizations of the PBE0-level stationary points

14 Elementary step 4, dimerization of $UF_4(OH)_2$: DSD-BLYP level diagrams and PBE0 geometrical structures

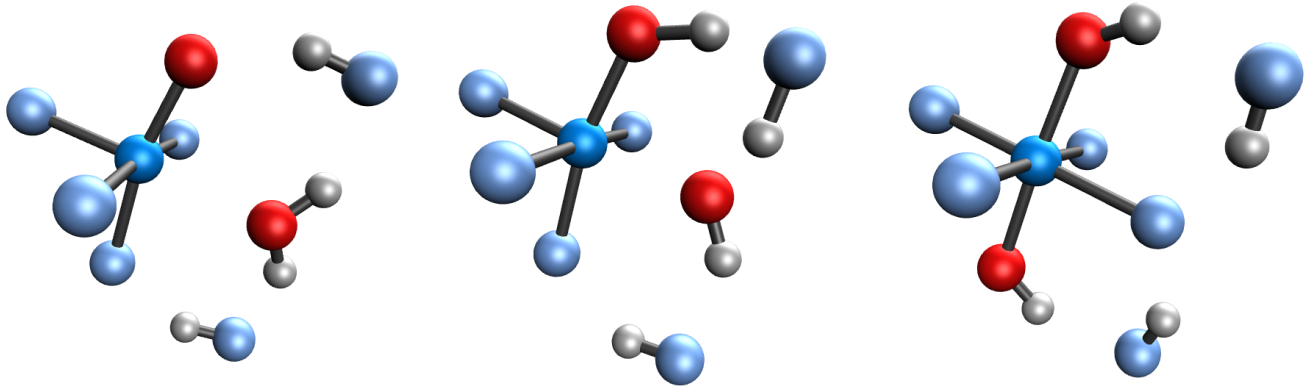
Part IV
Supplementary files

Optimized Cartesian coordinates and computed harmonic vibrational frequencies are provided in the accompanying folder `PBE0`$_g$*eoms*$_f$*reqs*.



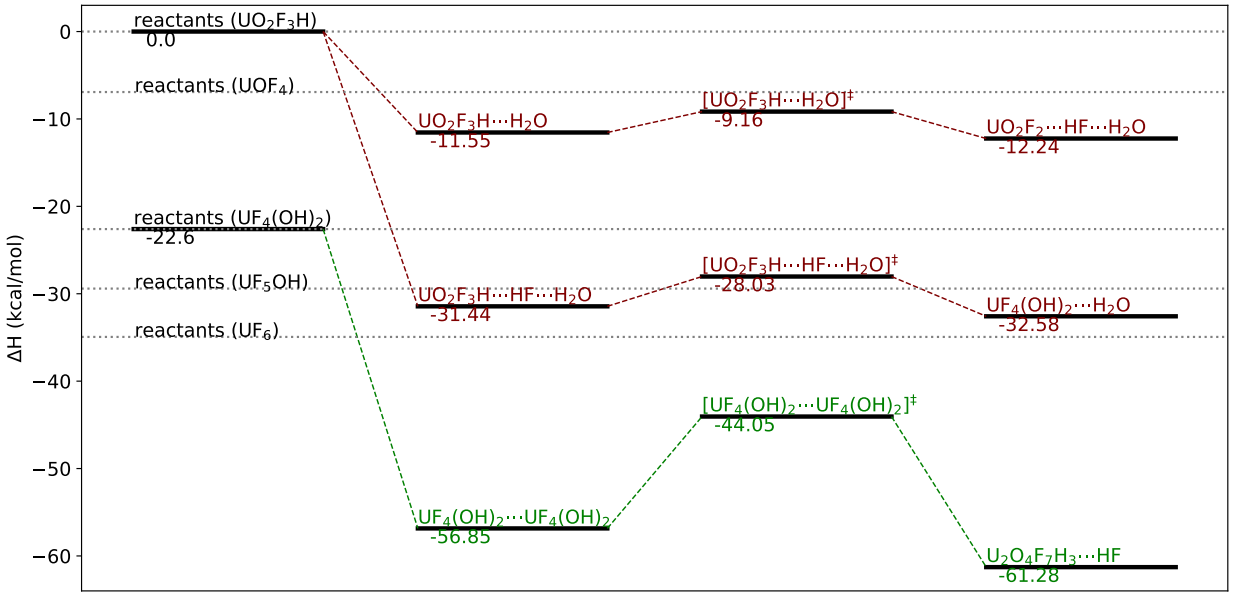
$UOF_4 \cdots H_2O \cdots HF$ $[UOF_4 \cdots H_2O \cdots HF]^{\ddagger}$ $UF_4(OH)_2 \cdots HF$

Figure 18 $UOF_4 \cdots H_2O \cdots HF \xrightarrow{[UOF_4 \cdots H_2O \cdots HF]^{\ddagger}} UF_4(OH)_2 \cdots HF$; visualizations of the PBE0-level stationary points



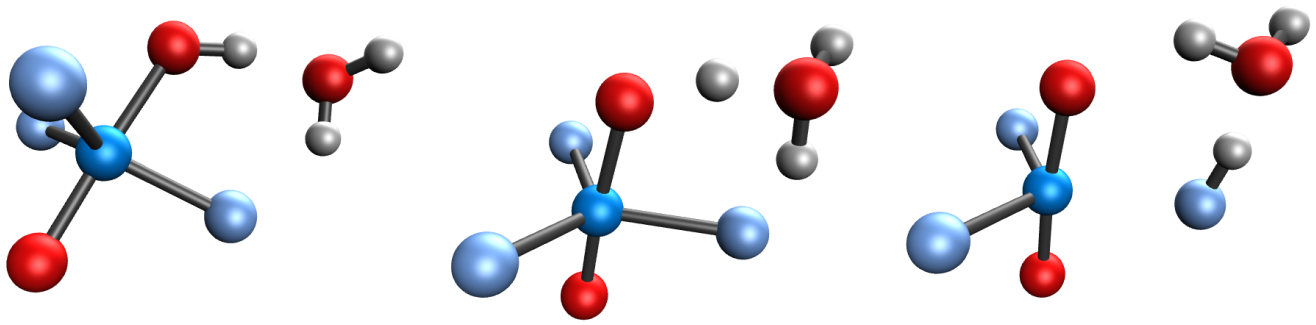
$UOF_4 \cdots HF \cdots H_2O \cdots HF$ $[UOF_4 \cdots HF \cdots H_2O \cdots HF]^{\ddagger}$ $UF_4(OH)_2 \cdots HF \cdots HF$

Figure 19 $UOF_4 \cdots HF \cdots H_2O \cdots HF \xrightarrow{[UOF_4 \cdots HF \cdots H_2O \cdots HF]^{\ddagger}} UF_4(OH)_2 \cdots HF \cdots HF$; visualizations of the PBE0-level stationary points



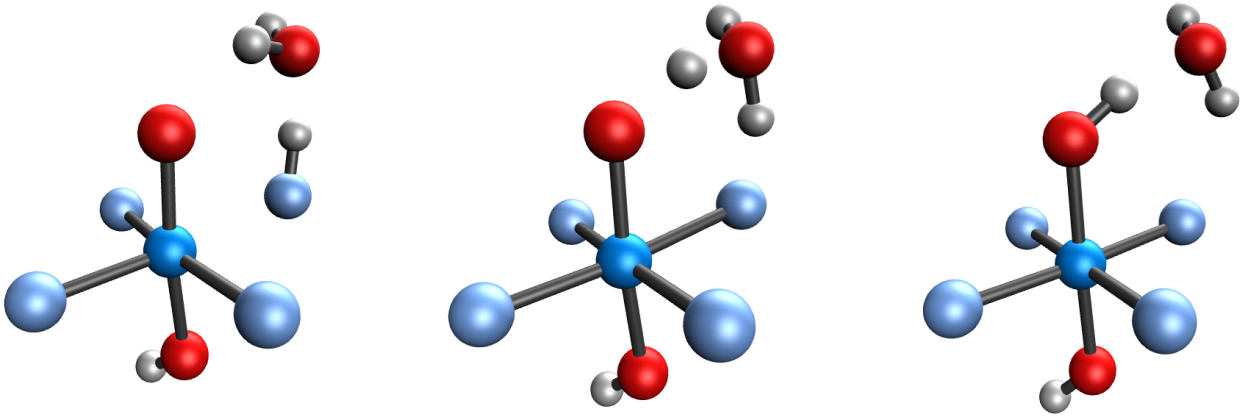
tabular

Figure 20 DSD-BLYP energy level diagram for possible elementary steps connecting $UF4(OH)_2$, UO_2F_2, and the $UF4(OH)_2$ dimer.



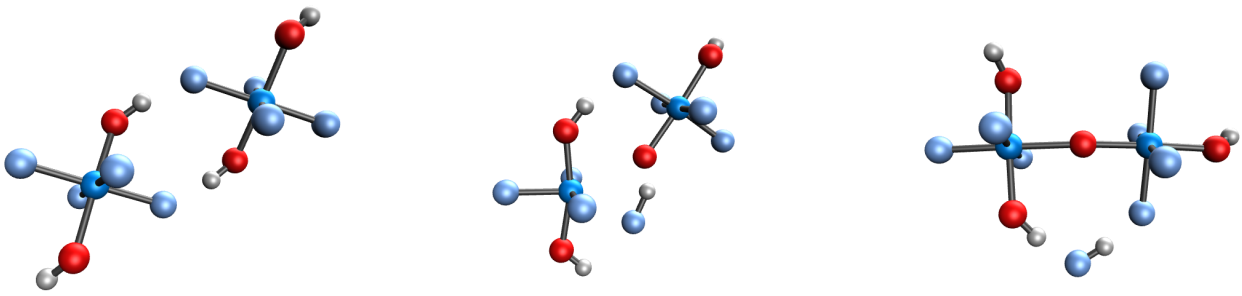
$UO_2F_3H\cdots H_2O$ $[UO_2F_3H\cdots H_2O]^{\ddagger}$ $UO_2F_2\cdots HF\cdots H_2O$

Figure 21 $UO_2F_3H\cdots H_2O \xrightarrow{[UO_2F_3H\cdots H_2O]^{\ddagger}} UO_2F_2\cdots HF\cdots H_2O$; visualizations of the PBE0-level stationary points



$UO_2F_3H\cdots HF\cdots H_2O$ $[UO_2F_3H\cdots HF\cdots H_2O]^{\ddagger}$ $UF_4(OH)_2\cdots H_2O$

Figure 22 $UO_2F_3H\cdots HF\cdots H_2O \xrightarrow{[UO_2F_3H\cdots HF\cdots H_2O]^{\ddagger}} UF_4(OH)_2\cdots H_2O$; visualizations of the PBE0-level stationary points



$UF_4(OH)_2\cdots UF_4(OH)_2$ $[UF_4(OH)_2\cdots UF_4(OH)_2]^{\ddagger}$ $U_2O_4F_7H_3\cdots HF$

Figure 23 $UF_4(OH)_2\cdots UF_4(OH)_2 \xrightarrow{[UF_4(OH)_2\cdots UF_4(OH)_2]^{\ddagger}} U_2O_4F_7H_3\cdots HF$; visualizations of the PBE0-level stationary points

Part V
References

15 Full form of references abbreviated in the main document

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16 Supporting Information bibliography

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