Supplementary Information

DFT study of Atmospheric characteristics of CF_3SO_2F: The fungibility of the insulation gas of SF_6

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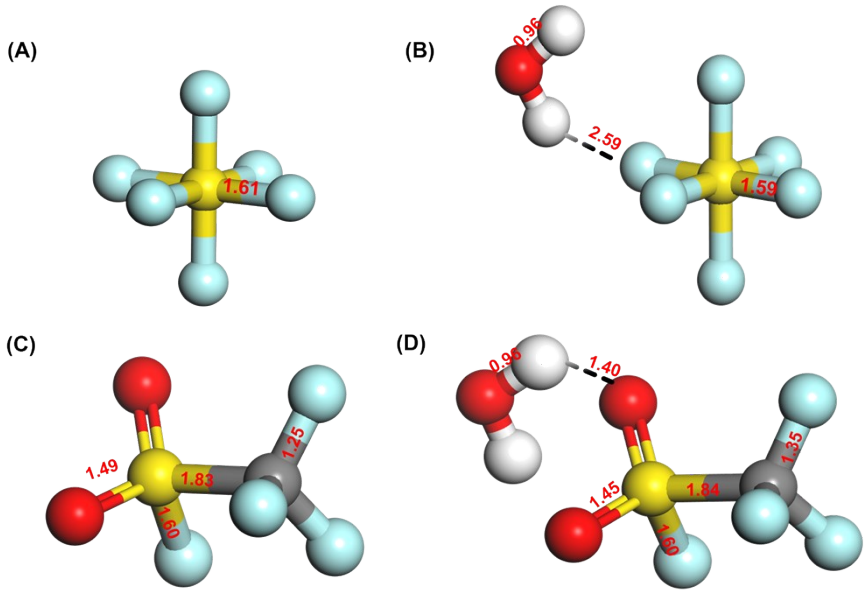


Fig. S1 The optimized structures of (A) SF_6, (B) SF_6-H_2O, (C) CF_3SO_2F, and (D) CF_3SO_2F-H_2O for preparing the motion groups in the Polymorph code (Red: O, Blue: F, Yellow: S, White: H, Grey: C).

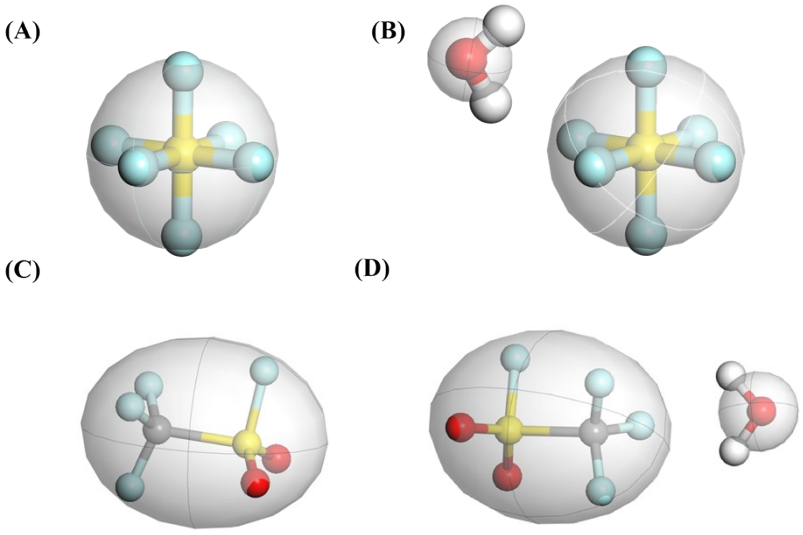
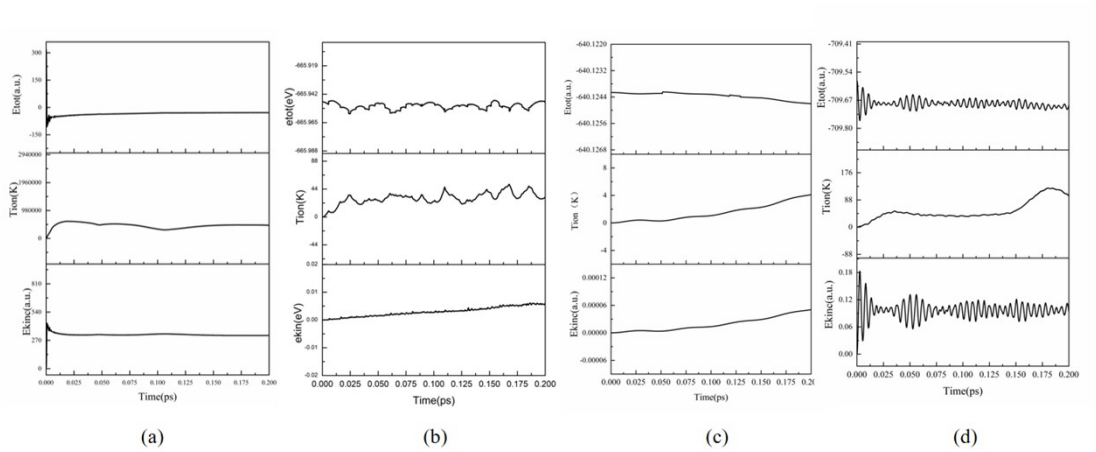


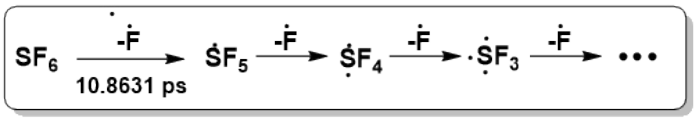
Fig. S2 Pure (A) SF_6, (B) SF_6-H_2O, (C) CF_3SO_2F, and (D) CF_3SO_2F-H_2O crystals dispensed prior to packing. (Red: O, Blue: F, Yellow: S, White: H, Grey: C).



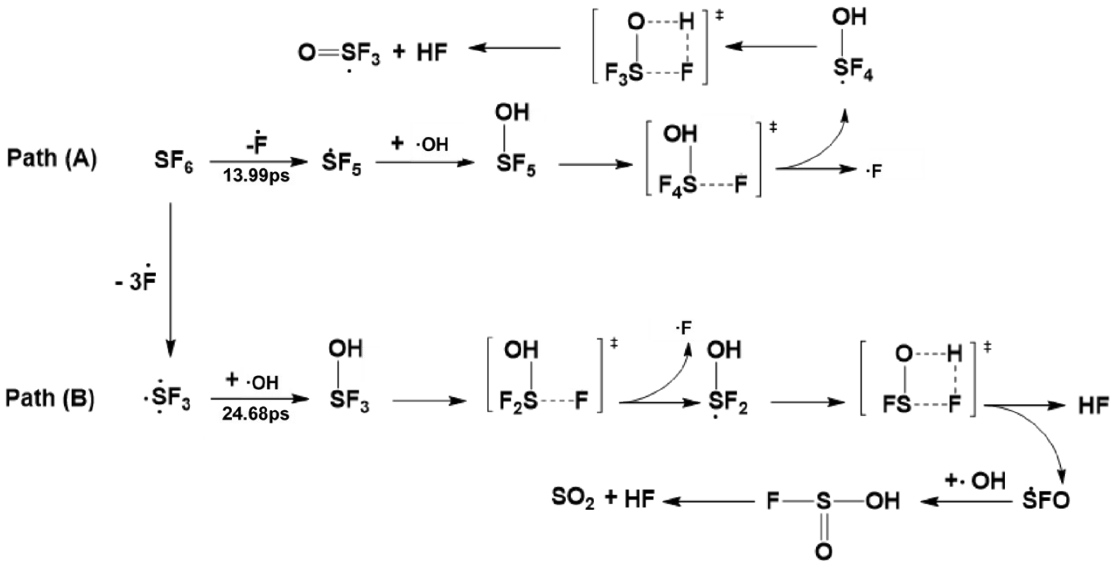
(a) (b) (c) (d)

Fig. S3 The convergence statement for the ion temperature (K), fictitious electronic kinetic energy (a.u.), and electronic total energy (a.u.) in the equilibration stage (2000 steps, 0.20 ps), (a) CF_3SO_2F, (b) CF_3SO_2F-H_2O, (c) SF_6, (d) SF_6-H_2O.

Scheme S1 The decomposition pathway of pure SF_6 at 3000 K with the initial time of 10.8631 ps.



Scheme S2 Oxygen radical initiated SF_6 dissociation with initial decomposition times of 12.9877 ps and 24.6732 ps for path (A) and path (B), respectively.



Scheme S3 The reaction between CF_3SO_2F and H_2O with lowest energy barrier.

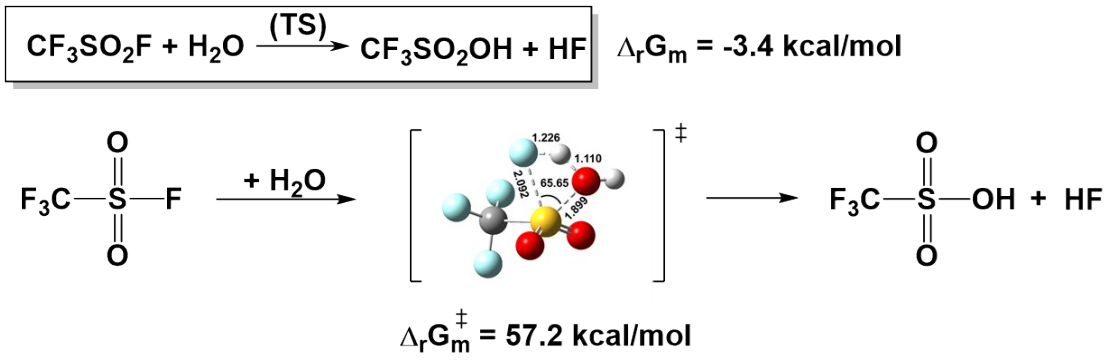


Table S1 The atomic coordinates of the original molecular structure.

Species	Coordinates (x, y, z in Å)			
CF_3SO_2F	C	-0.01581663	0.68426054	0.03910000
	S	0.49752046	1.41022300	1.58113228
	O	1.96502684	1.40720071	1.65949075
	O	0.00562136	2.79283941	1.65943486
	F	-0.09947279	0.56607487	2.78906978
	F	-1.36389339	0.68703687	-0.03288145
	F	0.49106443	1.40099008	-0.98650731
	F	0.43605039	-0.58583483	-0.03283011
SF_6	S	2.25503367	-0.58389261	0.00000000
	F	2.25503367	1.00610739	0.00000000
	F	0.66503367	-0.58389261	0.00000000
	F	2.25503367	-2.17389261	0.00000000
	F	2.25503367	-0.58389261	1.59000000
	F	3.84503367	-0.58389261	0.00000000
	F	2.25503367	-0.58389261	-1.59000000
H_2O	O	3.39243390	1.11237181	0.00000000
	H	4.35243387	1.11261291	0.00000000
	H	3.07220660	2.01738809	0.00000000

Table S2 The atomic coordinates of the optimized molecular structure.

Species	Coordinates (x, y, z in Å)			
CF_3SO_2F	C	0.43871100	0.88149000	0.00000000
	S	-0.24527300	-0.82925500	0.00000000
	O	0.03365100	-1.42495100	-1.24557400
	O	0.03365100	-1.42495100	1.24557400
	F	-1.73710800	-0.41010200	0.00000000
	F	0.03365100	1.52095900	1.07805900
	F	1.75354900	0.78800200	0.00000000
	F	0.03365100	1.52095900	-1.07805900
SF_6	C	0.43871100	0.88149000	0.00000000
	S	-0.24527300	-0.82925500	0.00000000
	O	0.03365100	-1.42495100	-1.24557400
	O	0.03365100	-1.42495100	1.24557400
	F	-1.73710800	-0.41010200	0.00000000
	F	0.03365100	1.52095900	1.07805900
	F	1.75354900	0.78800200	0.00000000
	F	0.03365100	1.52095900	-1.07805900
H_2O	O	0.00000000	0.00000000	0.11617200
	H	0.00000000	0.76427800	-0.46468900
	H	0.00000000	-0.76427800	-0.46468900

Table S3 The atomic coordinates of the optimized crystal structure.

Species	Coordinates (x, y, z in Å)			
CF_3SO_2F	F	-2.22000000	2.93060000	-1.12020000
	F	-2.67990000	1.11600000	-0.02150000
	F	-0.68280000	1.42790000	-0.81460000
	C	-1.72940000	2.04450000	-0.23420000
	S	-1.24830000	2.86970000	1.33020000
	O	-1.29620000	4.31580000	1.24450000
	O	-1.82250000	2.23880000	2.50190000
	F	0.29560000	2.45880000	1.29770000
CF_3SO_2F-H_2O	F	-0.46920000	4.00680000	-0.18580000
	F	-2.49090000	4.21390000	-0.93510000
	F	-1.60940000	2.23590000	-0.69380000
	C	-1.70270000	3.46180000	-0.14320000
	S	-2.33120000	3.39120000	1.58110000
	O	-3.42670000	4.30780000	

			1.84370000	
	O	-2.40460000	2.04640000	2.12310000
	F	-1.04590000	4.05690000	2.26200000
	O	-4.53590000	2.22460000	-0.08240000
	H	-4.65110000	1.39070000	-0.54390000
	H	-5.41780000	2.60400000	-0.07810000
SF_6	S	-2.82330000	1.90850000	0.00000000
	F	-2.82330000	0.30160000	0.00000000
	F	-1.21630000	1.90850000	0.00000000
	F	-2.82330000	1.90850000	-1.60690000
	F	-2.82330000	1.90850000	1.60700000
	F	-4.43020000	1.90850000	0.00000000
	F	-2.82330000	3.51550000	0.00000000
SF_6-H_2O	S	-2.28780000	2.09490000	-0.07440000
	F	-1.92520000	0.67230000	-0.73180000

	F -1.02430000 1.95870000 0.91170000 F -1.35820000 2.83170000 -1.16070000 F -3.20790000 1.35000000 1.01310000 F -3.54250000 2.22700000 -1.06770000 F -2.63830000 3.51800000 0.58170000 O -5.73030000 3.09040000 1.03360000 H -6.38830000 3.76520000 0.86630000 H -6.13050000 2.52560000 1.69500000

Table S4 The lowest total energy (kcal/mol), Van der Waals (vDW) energy (kcal/mol), the number of predicted structures, and crystal parameters of the CF_3SO_2F, CF_3SO_2F-H_2O, SF_6, and SF_6-H_2O by applying Monte-Carlo methods.

CF_3SO_2F				
Space group	total energy (kcal/mol)	Van der Waals energy (kcal/mol)	Number of predicted structures	Crystal parameters
C2/c	98.35	-0.61	1228	a=23.57, b=17.15, c=59.59; α=90.00, β=107.44, γ=90.00.
P1	97.54	-0.61	1484	a=28.84, b=15.34, c=15.39; α=79.08, β=97.34, γ=104.66.
P21	97.33	-0.60	1688	a=15.39, b=25.92, c=18.54; α=90.00, β=100.61, γ=90.00.
P21/c	97.46	-0.61	1320	a=15.40, b=57.94, c=17.13; α=90.00, β=123.83, γ=90.00.
P212121	98.18	-0.60	1789	a=35.87, b=17.17, c=25.77;

				α=90.00, β=90.00, γ=90.00.
CF_3SO_2F-H_2O				
Space group	total energy (kcal/mol)	Van der Waals energy (kcal/mol)	Number of predicted structures	Crystal parameters
C2/c	11.44	-9.94	1260	a=23.71, b=4.74, c=12.20; α=90.00, β=55.33, γ=90.00.
P1	11.46	-9.51	1655	a=4.81, b=9.94, c=6.17; α=95.20, β=89.55, γ=76.60.
P21	11.60	-9.38	861	a=7.19, b=8.45, c=4.94; α=90.00, β=73.58, γ=90.00.
P21/c	11.46	-9.59	1050	a=8.40, b=18.10, c=4.72; α=90.00, β=104.63, γ=90.00.
P212121	11.39	-9.31	1314	a=23.45, b=4.77, c=5.15;

				α=90.00, β=90.00, γ=90.00.

SF_6				
Space group	total energy (kcal/mol)	Van der Waals energy (kcal/mol)	Number of predicted structures	Crystal parameters
C2/c	-8.61785897	-7.62	764	a=4.68, b=7.98, c=19.95; α=90.00, β=121.57, γ=90.00.
P1	-8.75550527	-7.67	2134	a=4.64, b=6.83, c=5.00; α=84.24, β=90.01, γ=90.00.
P21	-8.77	-7.66	1471	a=4.60, b=4.44, c=7.26; α=90.00, β=90, γ=90.00.
P21/c	-8.86	-7.62	1529	a=4.59, b=8.69, c=9.12; α=90.00, β=120.18, γ=90.00.
P212121	-8.86	-7.62	1909	a=8.69, b=4.59, c=7.89;

				α=90.00, β=90.00, γ=90.00.
SF_6-H_2O				
Space group	total energy (kcal/mol)	Van der Waals energy (kcal/mol)	Number of predicted structures	Crystal parameters
C2/c	-18.52	-4.49	2959	a=7.74, b=5.17, c=23.62; α=90.00, β=118.82, γ=90.00.0
P1	-15.40	-5.30	4140	a=11.26, b=4.68, c=10.74; α=106.48, β=152.20, γ=89.91.
P21	-16.38	-4.01	3491	a=6.26, b=5.30, c=7.34; α=90.00, β=64.73, γ=90.00.
P21/c	-18.86	-4.28	3452	a=31.88, b=4.88, c=8.22; α=90.00, β=160.61, γ=90.00.
P212121	-17.88	-4.70	3603	a=20.52, b=4.59, c=4.45;

α=90.00,

β=90.00,

γ=90.00.

Table S5 The convergence tests of k points and cut-off Energy of CF_3SO_2F, CF_3SO_2F-H_2O, SF_6, and SF_6-H_2O.

CF_3SO_2F	k=1×1×1	k=2×1×2
Cutoff Energy(eV)	Energy(eV)	Energy(eV)
200	-7831.55065	-7831.32901
300	-7903.500047	-7903.518066
400	-7906.502112	-7906.502265
500	-7906.772452	-7906.773236
600	-7907.069649	-7907.069542
700	-7907.142213	-7907.142231
800	-7907.170459	-7907.170397

CF_3SO_2F-H_2O	k=1×1×1	k=1×2×2	k=1×3×2
Cutoff Energy(eV)	Energy(eV)	Energy(eV)	Energy(eV)
300	-17682.50224	-17682.29637	-17682.36324
400	-17689.5097	-17689.46289	-17689.4571
500	-17690.13975	-17690.08705	-17690.08264
600	-17690.86205	-17690.8172	-17690.81295
700	-17691.07433	-17691.02787	-17690.81295
800	-17691.1602	-17691.11628	-17691.11181

SF_6	k=1×1×1	k=3×1×1	k=4×2×2
Cutoff Energy(eV)	Energy(ev)	Energy(ev)	Energy(ev)
300	-16990.95245	-16991.39535	-16991.41479
400	-16996.08887	-16996.54329	-16996.56988
500	-16996.57205	-16997.02983	-16997.05595

600	-16997.06999	-16997.5222	-16997.54754
700	-16997.13843	-16997.59007	-16997.61637
800	-16997.209	-16997.66102	-16997.6882

SF_6-H_2O	k=1×1×1	k=1×2×1	k=1×3×5
Cutoff Energy(eV)	Energy(ev)	Energy(ev)	Energy(ev)
300	-37728.49974	-37732.79516	-37733.04996
400	-37741.28974	-37745.52796	-37745.57323
500	-37742.42328	-37746.64131	-37746.6824
600	-37743.67017	-37747.89545	-37747.9375
700	-37743.94098	-37748.16789	-37748.21123
800	-37744.14283	-37748.37169	-37748.41597

Table S6 The final test of the atomic force field in three dimensions.

CF_3SO_2F			
atom	x	y	z
C	0.7442	0.00371	0.62585
C	0.2558	0.50371	0.37415
O	0.83651	0.00662	0.76494
O	0.69213	-0.04243	0.7417
O	0.16349	0.50662	0.23506
O	0.30787	0.45757	0.2583
F	0.78587	0.04676	0.60989
F	0.78613	-0.0383	0.60607
F	0.65991	0.00423	0.58959
F	0.69514	0.05162	0.73432
F	0.21413	0.54676	0.39011
F	0.21387	0.4617	0.39393
F	0.34009	0.50423	0.41041
F	0.30486	0.55162	0.26568
S	0.74755	-0.00081	0.72776
S	0.25245	0.49919	0.27224
CF_3SO_2F-H_2O			
atom	x	y	z
H	0.02423	0.58484	-0.01592
H	-0.00138	0.76978	0.20921
H	0.47577	0.41516	0.48408
H	0.50138	0.23022	0.70921
H	0.97577	0.08484	0.51592
H	1.00138	0.26978	0.29079
H	0.52423	0.91516	1.01592
H	0.49862	0.73022	0.79079

C	0.18062	0.74436	0.83685
C	0.31938	0.25564	0.33685
C	0.81938	0.24436	0.66315
C	0.68062	0.75564	0.16315
O	0.14429	1.07459	0.44801
O	0.0861	1.06165	0.86025
O	-0.00392	0.5815	0.12314
O	0.35571	-0.07459	-0.05199
O	0.4139	-0.06165	0.36025
O	0.50392	0.4185	0.62314
O	0.85571	0.57459	1.05199
O	0.9139	0.56165	0.63975
O	1.00392	0.0815	0.37686
O	0.64429	0.42541	0.55199
O	0.5861	0.43835	0.13975
O	0.49608	0.9185	0.87686
F	0.21129	0.59523	0.6636
F	0.21433	0.93902	0.94832
F	0.15962	0.57129	1.01961
F	0.08939	0.65938	0.56971
F	0.28871	0.40477	0.1636
F	0.28567	0.06098	0.44832

SF_6

atom	x	y	z
F	0.86524	0.02993	0.60567
F	0.58913	0.00259	0.75005
F	1.15388	0.02991	0.89454
F	0.5387	0.22154	0.60623

F	0.82628	0.22159	0.89388
F	1.103	0.247	0.75011
F	0.13476	0.52993	0.89433
F	0.41087	0.50259	0.74995
F	-0.15388	0.52991	0.60546
F	0.4613	0.72154	0.89377
F	0.17372	0.72159	0.60612
F	-0.103	0.747	0.74989
F	0.13476	0.97007	0.39433
F	0.41087	0.99741	0.24995
F	-0.15388	0.97009	0.10546
F	0.4613	0.77846	0.39377
F	0.17372	0.77841	0.10612
F	-0.103	0.753	0.24989
F	0.86524	0.47007	0.10567
F	0.58913	0.49741	0.25005
F	1.15388	0.47009	0.39454
F	0.5387	0.27846	0.10623
F	0.82628	0.27841	0.39388
F	1.103	0.253	0.25011
S	0.84575	0.12531	0.75008
S	0.15425	0.62531	0.74992
S	0.15425	0.87469	0.24992
S	0.84575	0.37469	0.25008

SF_6-H_2O

atom	x	y	z
H	-0.06827	0.59801	0.75057
H	0.19995	0.50451	0.71814
H	0.40199	1.06827	0.74943

H	0.49549	0.80005	0.78186
H	1.06827	0.40199	0.24943
H	0.80005	0.49549	0.28186
H	0.59801	-0.06827	0.25057
H	0.50451	0.19995	0.21814
O	0.15682	0.45856	0.75032
O	0.54144	0.84318	0.74968
O	0.84318	0.54144	0.24968
O	0.45856	0.15682	0.25032
F	0.91687	0.79008	0.65242
F	0.47201	1.21343	0.64849
F	0.81896	1.11911	0.59495
F	0.42074	0.70253	0.59708
F	0.32175	1.0332	0.53986
F	0.77103	0.60867	0.5438
F	0.20992	0.08313	0.84758
F	-0.21343	0.52799	0.85151
F	-0.11911	0.18104	0.90505
F	0.29747	0.57926	0.90292
F	-0.0332	0.67825	0.96014
F	0.39133	0.22897	0.9562
F	0.08313	0.20992	0.34758
F	0.52799	-0.21343	0.35151
F	0.18104	-0.11911	0.40505
F	0.57926	0.29747	0.40292
F	0.67825	-0.0332	0.46014
F	0.22897	0.39133	0.4562
F	0.79008	0.91687	0.15242
F	1.21343	0.47201	0.14849

F	1.11911	0.81896	0.09495
F	0.70253	0.42074	0.09708
F	1.0332	0.32175	0.03986
F	0.60867	0.77103	0.0438
S	0.61984	0.91059	0.59599
S	0.08941	0.38016	0.90401
S	0.38016	0.08941	0.40401
S	0.91059	0.61984	0.09599

Table S7 M06-2X/def2tzvp optimized the Cartesian coordinates of substances involved in the hydrolysis of CF_3SO_2F.

Species	Coordinates (x, y, z in Å)			Energies (in Hartree)
CF_3SO_2F	F	-0.03365100	1.52095900	1.07805900	-986.13
	F	-1.75354900	0.78800200	0.00000000	
	F	-0.03365100	1.52095900	-1.07805900	
	C	-0.43871100	0.88149000	0.00000000	
	S	0.24527300	-0.82925500	0.00000000	
	O	-0.03365100	-1.42495100	1.24557400	
	O	-0.03365100	-1.42495100	-1.24557400	
	F	1.73710800	-0.41010200	0.00000000	
·OH	O	0.00000000	0.00000000	0.10812600	-75.74
	H	0.00000000	0.00000000	-0.86500900	
CF_3SO_2OH	F	0.06178300	1.53673700	-1.07815400	-962.13
	F	0.06178300	1.53673700	1.07815400	
	C	0.44666500	0.88184100	0.00000000	
	S	-0.26066000	-0.81890600	0.00000000	
	O	0.06178300	-1.43120500	-1.23766400	
	O	0.06178300	-1.43120500	1.23766400	
	F	1.76150200	0.76094100	0.00000000	
	O	-1.76176900	-0.33808300	0.00000000	

	H -2.36940500 -1.09434600 0.00000000	
·F	F 0.00000000 0.00000000 0.00000000	-99.73
CF_2OHSO_2F	C -0.97985000 0.00332200 0.01684500 S 0.85654500 -0.04803000 0.11953700 O 1.29222500 0.82718700 1.13445200 O 1.27012900 -1.39126600 0.00989900 F -1.44014400 -0.63113700 1.10253400 F -1.36466800 -0.70820600 -1.04857700 O -1.36639500 1.28072800 -0.04450700 H -2.33190700 1.33210300 -0.09799200 F 1.13132600 0.63748200 -1.24444800	-962.12
$\cdot CF_3$	C 0.00000000 0.00000000 0.32462100 F 0.00000000 1.25003700 -0.07213800 F -1.08256400 -0.62501900 -0.07213800 F 1.08256400 -0.62501900 -0.07213800	-337.60
FSO_2OH	S 0.08779400 -0.12537200 0.00000000 O 0.48662400 -0.68035100 1.23294000 O 0.48662400 -0.68035100 -1.23294000 F 0.48662400 1.35747300 0.00000000 O -1.45296900 0.16755200 0.00000000 H -1.94653700 -0.66610600 0.00000000	-724.32
$\cdot SO_2F$	S 0.18791947 -1.81879192 0.00000000	-648.43

	O1.58382847	-1.81879192	0.00000000	
	O -0.50153953	-0.60502892	0.00000000	
	F -0.35859572	-2.75777382	1.16091952	
CF_3OH	C -0.00425800	-0.02234300	0.00000000	-413.52
	F 0.80882200	-1.06065200	-0.00000200	
	F 0.26573400	0.73016700	-1.07168400	
	F 0.26573600	0.73016500	1.07168400	
	O -1.27040200	-0.46844600	0.00000100	
	H-1.87387100	0.28450800	0.00000100	
TS-a	S -0.85668500	0.15165300	0.16318100	-1061.79
	O-1.00670500	0.19889200	1.76682000	
	F-0.74622498	-1.37057227	-0.33828791	
	O -0.48073700	1.59641800	-0.73266600	
	H-2.43281469	-0.83431223	-0.45404401	
	O-2.16079269	0.11631477	-0.41235801	
	C 1.34167600	-0.02345000	-0.04714800	
	F 1.64251900	-1.10939900	0.70372300	
	F 1.62824000	-0.22131800	-1.35364400	
	F 1.93467600	1.08628800	0.45285100	
TS-b	C-1.16528452	0.17493960	0.73590054	-1061.70
	F-2.43844117	0.34187218	1.15268065	
	F-1.03572882	-1.03936677	0.16042217	

	F-0.38824540	1.14461729	1.26357031	
	S-0.98907454	1.20703312	-1.20407889	
	O-1.45018636	2.48703318	-0.89176869	
	O0.23069006	1.05602096	-1.86585225	
	F-2.12406725	0.38557006	-1.95580356	
	O-1.17618637	-0.59220016	2.32242859	
	H-0.47093945	-0.30795717	2.90845991	
TS-c	F 0.70423431	0.84450164	0.88718428	-1061.81
	F 1.46184100	0.73759300	-0.51178900	
	F 1.31721641	-0.41275639	-0.72901201	
	O -0.64112300	-1.23966400	0.55304100	
	H -0.58524500	-1.97721600	-0.06740600	
	C 0.35053000	0.34305700	-0.24313300	
	S 0.10843897	1.18470658	-1.79278390	
	O -0.92431508	0.57975780	-2.51112781	
	O 0.09099982	2.56585750	-1.59106044	
	F 1.51706905	0.73555549	-2.37769808	
TS-d	S 0.31703738	-1.88896489	-0.86737753	-1061.76
	C 0.74294238	-0.07443589	-0.61585153	
	F 0.18966538	0.38290511	0.47964347	
	F 2.06009638	-0.05234889	-0.48644453	
	F 0.39530938	0.63504411	-1.65613953	

	F	-1.56315500	-0.87609400	-0.99217200	
	O	0.74577638	-2.44581789	0.37032147	
	O	0.80266238	-2.15825689	-2.16654353	
	O	-0.98957055	-2.89126250	-0.98277196	
	H	-1.06103755	-3.34942850	-0.13435196	

Table S8. The reaction Gibbs free energies (Δ_rG/ kcal· mol^{-1}), energy barriers ($\Delta_rG_m^{\neq}$/ kcal· mol^{-1}), rate constants ($k_{\cdot OH}$/mol^{-1}· cm^3· s^{-1}) and lifetime (τ/year) of SF_6 at 298 K.

Pathways	Δ_rG_m	$\Delta_rG_m^{\neq}$		$k_{\cdot OH}$	τ
		TS1	TS2		
Pathway (a)	-0.5	12.3	21.3	$1.4x10^{-3}$	$4.83x10^{-11}$
Pathway (b)	-18.1	15.6	40.1	$2.0x10^{-17}$	3296

Table S9 The correlation energy of path (c) calculated under M062X/def2tzvp and MP2/def2tzvp theory level.

Species	Relative Energy （kcal/mol)	
	M062X/def2tzvp	MP2/def2tzvp
$CF_3SO_2F + \cdot OH$	0.0	0.0
$CF_3SO_2OH + \cdot F$	13.2	14.8
TS-c	37.6	42.5