Investigation of Thorium Hydride Fluorides by Matrix-Isolation Spectroscopy

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Abstract: Following the successful preparation of HUF through the reaction of laser ablated uranium atoms with HF in excess noble gases, we continue the investigation of actinide atom reactions with HF. Herein we report the reaction products of laser ablated thorium atoms with HF as well as supporting quantum chemical calculations and a discussion of the bonding in HThF and higher oxidation state molecules. The results of this study are compared to previous results obtained in similar uranium reactions.

1 Introduction: The chemistry of early actinides is of special interest due to the involvement of the 5f electrons in the chemical bond. While much is known about the chemistry of uranium due to its applications in the nuclear fuel cycle, investigations on thorium are much less prominent. Reintroducing the concept of the molten salt reactor where thorium is the nuclear fuel, the chemistry of thorium has gained importance.[1, 2] The laser ablation technique combined with matrix-isolation spectroscopy provides a straightforward means to investigate new reactive thorium molecular species. Following this method investigations on thorium hydrides[3, 4] and nitrides[5], thorium methylenide complexes, $\text{CH}_2=\text{ThHX}_2$ [6, 7] and more recently on thorium fluorides including the novel trigonal bipyramidal $[\text{ThF}_5]^-$ anion[8, 9] have been reported. However, to the best of our knowledge no mixed thorium hydride fluorides are known. Recently we have shown that the reaction of hydrogen fluoride with uranium atoms forms HUF as the major product[10]. In this work we continue the investigation of the reaction of hydrogen fluoride with laser ablated metal atoms in order to gain more information about the chemical bonding in actinide metal hydride fluorides.

2 Results and Discussion: The reaction of laser-ablated thorium atoms together with hydrogen fluoride in excess of rare gas yields several product absorptions which could not be found in similar experiments using hydrogen and fluorine reagents separately. Spectra obtained in neon and argon are shown in Figures 1 and 2 while band assignment is shown in Table 1. Known bands for

ThF, ThF_2 , ThF_3 and ThF_4 [8, 9] as well as ThOF_2 [11] were assigned by comparison with data reported earlier. Further impurities like HF oligomers and $[\text{HF}_2]^-$ were also assigned by comparison with literature.[12-15]

Figure 1. IR spectra of laser ablated Th atoms with 0.2% HF in argon a.) Deposition for 40min b.) Annealing to 15K c.) Annealing to 25K d.) photolysis above 220nm for 25min e.) Annealing 30K.

After deposition intense bands for the expected major product of the reaction, HThF, based on our recent observation of the related HUF molecule, were found at 1464.8 and 570.4 cm^{-1} . Annealing to 15 and 25 K increased the yield of HThF and sharpened the band while photolysis with a medium pressure mercury arc destroyed the compound. However, the compound is partially re-formed on subsequent annealing. The Th–F stretching mode is located between the wave numbers of ThF and ThF_2 indicating an electronic situation on thorium between a mono- and a divalent

compound. The calculated NPA charge for Th in this compound of +1.36 at B3LYP level supports this thesis. The Th–H stretching mode also falls between values observed for ThH₂ and ThH₄ at 1480.1 and 1444.8 cm⁻¹, respectively[4]. In neon the HThF bands are not that prominent as in argon. We assigned bands at 1477.4 and 577.9 cm⁻¹ to this molecule. These wavenumbers account for a neon shift of 12.6 cm⁻¹ for the Th–H stretch and a somewhat smaller shift of 7.5 cm⁻¹ for the Th–F stretch, which are typical values for neon shifts.

Figure 2. IR spectra of laser ablated Th atoms with 0.15% HF in neon. a.) Deposition for 40min b.) Annealing to 8K c.) Annealing to 10K.

Table 1. Observed and calculated frequencies for the reaction products of laser-ablated thorium with HF in argon and neon.

Neon	Argon	B3LYP ^[a,b]	CCSD(T) ^[a,b]	Assignment
1483.8	1473.6	1527.6(178)	1530.2(168)	ν_1 H ₃ ThF
1477.4	1464.8	1521.8(305)	1521.4(305)	ν_1 HThF
1468.0	1458.1	1500.6(361)	1506.2(350)	ν_1 H ₂ ThF ₂
1457.2	1441.9/ 1445.6	1473.6(492)	1483.1(487)	ν_1 HThF ₃
1434.6	1422.6	1450.6(758)	1462.7(754)	ν_6 H ₂ ThF ₂
1427.1	1412.7	1456.6(832)	1468.2(825)	ν_4 H ₃ ThF
–	576.0/ 575.4	575.1(171)	577.5(164)	ν_3 ThF ₂ ^[c]
577.9	570.4	583.9(106)	585.6(110)	ν_2 HThF
576.1	567.2/ 565.1	585.7(78)	601.2(74)	ν_1 ThF ^[c]
565.6	555.4	564.7(209)	580.1(214)	ν_2 H ₂ ThF ₂
559.4	548.3	565.8(305)	582.6(321)	ν_2 H ₃ ThF
556.8	544.8	550.7(354)	565.8(359)	ν_8 H ₂ ThF ₂
542.5	535.1/ 533.4	537.8(287)	553.3(291)	ν_4 HThF ₃
–	531.3	533.0(191)	–	ν_3 ThF ₃ ^[c]
–	521.2/ 519.2/ 514.3	525.3(210)	–	ν_3 ThF ₄ ^[c]

[a] Th:Stuttgart RSC 1997 ECP H,F: aug-cc-pVTZ [b] Frequencies in cm⁻¹ and calculated intensities in parenthesis in km mol⁻¹. [c] Lit. bands: ThF 667.2, 646.8 cm⁻¹, ThF₂ 575.9, 575.1 cm⁻¹, ThF₃ 531.0 cm⁻¹, ThF₄ 522.7, 521.0, 519.2, 514.5 cm⁻¹ in argon from ref 8 and 9.

The following assignments are strongly related to the calculated frequencies; therefore a short discussion of the structures of possible hydride fluorides should be given first. A complete list of frequencies for all species in question is given in table S1 in ESI. Figure 3 shows the optimized structures of all possible hydride fluorides, cartesian coordinates are given in ESI. Similar as the previously synthesized HUF molecule HThF is also bent which indicates the participation of the 5d orbitals in covalent bonding. NBO analysis shows that the Th contribution to the Th–H bond is 26.6% and only 7.6% for the Th–F bond. The 5d orbital contribution to the Th participation is 68% for the Th–H bond and 65% for the Th–F bond. The 5d orbital contribution for the Th–H bond is comparable to the corresponding bond in HUF, however for U–F no bonding orbital was found, which indicates that the U–F bond is more ionic than the Th–F bond. We found a ¹A' ground state for HThF. The triplet ³A'' state is higher in energy by 46.2 kJ mol⁻¹, note also table S2 for total energies of all possible spin states of all thorium hydrides. The structure of HThF₂ and H₂ThF are deduced from the structure of ThH₃ which is C_{3v} symmetric. In contrast to the planar D_{3h} symmetric structure of ThF₃, HThF₂ is non planar which indicates the less ionic character of the thorium hydrogen bond. However the difference in energy between the planar and non planar structure of HThF₂ is quite small and accounts for only 2 kJ mol⁻¹ at CCSD(T). At DFT level the planar C_{2v} symmetric structure is found to be the minimum. The structures of the Th(IV) hydride fluorides are all deduced from the tetrahedral structure of ThF₄ or ThH₄ and are C_{3v} symmetric for HThF₃ and FThH₃ and C_{2v} symmetric for H₂ThF₂ with only small structural changes compared to ThF₄ or ThH₄.

Figure 3. Optimized structures of thorium hydride fluorides at different level of theory. Bond lengths in pm and angles in degree. S abbreviates the total spin of the molecules ground state.

The calculated frequencies for HThF are 1521.8 and 583.9 cm^{-1} at the DFT level resulting in a shift between calculated and observed argon matrix frequencies of 54.0 cm^{-1} for the Th–H stretch and 13.5 cm^{-1} for the Th–F stretch at DFT level and of 56.6 and 15.2 cm^{-1} at CCSD(T) level. For HThF, anharmonic frequencies at B3LYP level have been calculated predicting frequencies at 1519.7 and 578.0 cm^{-1} and thus improving our results slightly. However, the observed neon matrix frequencies are higher than the argon matrix values and thus closer to the computed values, shifted only 44.4 and 6.0 cm^{-1} for B3LYP harmonic frequencies, respectively. The shift for the anharmonic Th–H stretching frequency is only 35.9 cm^{-1} and a perfect agreement of calculated anharmonic frequency and observed neon value could be obtained for the Th–F stretching mode.

The assignment of higher thorium hydride fluorides is more difficult and not straightforward because the chemical behaviour on annealing and photolysis of these compounds is quite similar. Therefore the band assignment has been made by taking three major points into account. First the relative behaviour of the intensities of bands which might belong to the same compound, second, the shifts between calculated and observed frequencies should be about the same as for HThF and third the calculated gap between two bands of the same molecule should be about the same as in the experiment. Although usually the CCSD(T) results are more reliable than DFT results, our DFT values are closer to the experimental values. Therefore we used only the harmonic frequencies calculated at B3LYP level for the following assignment. However a similar analysis with slightly higher shifts but the same trends could be done using the CCSD(T) values as pointed out in table 1. Starting with these assumptions the highest calculated frequency in the Th–H region of the spectra is the one of FThH₃, which is found at 1473.6 cm^{-1} in the argon matrix spectra. The shift to the calculated value is 54 cm^{-1} which is about right compared to the shift for HThF. The calculated shift to the second band in this area is 71 cm^{-1} . We assign the band at 1412.7 cm^{-1} to FThH₃ because of the same behaviour as the upper band on photolysis. Also the relation between experimental values and calculated frequencies are about right. The calculated shift between the Th–F stretch of HThF and FThH₃ is 18.1 cm^{-1} . Therefore we assigned the band at 548.3 cm^{-1} to FThH₃. The next molecule in the calculated order is H₂ThF₂. We assign the bands at 1458.1 cm^{-1} and 1422.6 cm^{-1} to this molecule. The upper band is in line with our assumed relationships; however, the lower one is not. The calculated order would predict the band to come at lower wave numbers than the one of FThH₃. Also the shift between the calculated and the experimental value of only 28 cm^{-1} seems a little bit too small. The band at 1412.7 cm^{-1} which we assigned to FThH₃ would fit better, however the correlation with the upper band of FThH₃ on photolysis clearly indicates that these two bands belong to the same molecule. In the Th–F region we assign the bands at 555.4 and 544.8 cm^{-1} to H₂ThF₂. Again the band of FThH₃ is higher than the lower band of H₂ThF₂ in contrast to the order suggested by the calculated frequencies.

The assignment of HThF₃ to the bands at 535.1 and 533.4 cm^{-1} in the Th–F stretching region is quite straightforward. Being the most stable of all hydride fluorides the band should grow on annealing, which could also be found in experiment. The assignment of the Th–H stretching mode in argon is somewhat more difficult. However the band seems to be much more prominent in neon experiments. The typical neon shift observed in these experiments for all hydride fluorides is between 8 and 15 cm^{-1} . Assuming that the shift for HThF₃ is within these boundaries the only bands which could be assigned to this molecule in argon are the band at 1441.9 and 1445.6 cm^{-1} . The upper band might be a

second stable site of the compound. This band shows also the same behaviour on annealing and photolysis than the band assigned to the Th–F mode. The deviation between calculated and observed frequency for the Th–F mode of only 3.7 cm^{-1} seems to be a little bit too small compared to the shifts of other compounds but is in line with the likewise small shift for ThF₄. Therefore the smaller shift for the Th–H mode seems not to be out of order. Having no clear experimental evidence, further assignment of H₂ThF and HThF₂ based on our calculations seems to be too tentative. However there are a few bands which could not be assigned yet and which might belong to one of these compounds. Some bands might also result from HF complexes of the species of interest which can not totally be excluded. However experiments using different concentrations of HF show no clear evidence for the presence of such complexes.

Figure 4. IR spectra of laser ablated Th atoms with 0.5% DF/HF (enrichment 70%) in argon a.) Deposition for 50 min b.) Annealing to 23 K c.) Annealing to 29 K d.) Photolysis above 220 nm for 20 min e.) Annealing to 33 K. Atmospheric water bands are marked with asterisks.

Additional experiments have been performed with DF/HF mixtures made through the reaction of F₂ with D₂, shown in Figure 4. Thus, spectra obtained in these experiments contain the standard impurities in commercial F₂ which are not present in the studies with pure HF. The deuterium counterpart to HThF is assigned to the band at 1046.0 cm^{-1} in argon. This gives a shift of 427.6 cm^{-1} which is in good agreement with the calculated value of 442.8 cm^{-1} and is comparable to the deviation found for the deuterium shift of HUF. The H/D frequency ratio is 1.4003, which is in good agreement with the ratio observed for HUF. The thorium fluorine stretch shows only a small deuterium shift of 2.2 cm^{-1} , which is in good agreement with the calculated value and probably due to small coupling with the lower frequency bending mode. Assignments for other deuterium counterparts are shown in Table 2. The H/D ratios for all compounds is about 1.4.

Table 2. Calculated and observed frequencies for deuterium compounds compared to their hydrogen counterparts.

Molecule	Neon	Argon	B3LYP ^[a,b]	CCSD(T) ^[a,b]
HThF	1483.8	1473.6	1527.6(178)	1530.2(168)
	577.9	570.4	583.9(106)	585.6(110)
DThF	1058.0	1046.0	1079.0(151)	1078.7

	576.0	568.0	582.7(102)	583.4
H ₂ ThF ₂	1468.0	1458.1	1500.6(361)	1506.2(350)
	1434.6	1422.6	1450.6(758)	1462.7(754)
	556.8	544.8	550.7(354)	565.8(359)
D ₂ ThF ₂	–	1040.4	1029.4(387)	1038.3
	–	1016.7	543.7(255)	557.8
HThF ₃	1457.2	1441.9/1 445.6	1473.6(492)	1483.1(487)
	542.5	535.1/ 533.4	537.8(287)	553.3(291)
DThF ₃	–	1030.5	1045.6(245)	–
	–	530.8	533.5(233)	–
H ₃ ThF	1427.1	1412.7	1456.6(832)	1468.2(825)
	559.4	548.3	565.8(305)	582.6(321)
D ₃ ThF	–	1010.5	1033.8(424)	–
	–	539.2	558.2(200)	–

[a] Th:Stuttgart RSC 1997 ECP H,F: aug-cc-pVTZ [b] Frequencies in cm⁻¹ and calculated intensities in parenthesis in km mol⁻¹.

With these assignments we generate a consistent set of relations between experimental values and calculated frequencies. Further evidence for these assignments is given by the thermochemistry data, shown in Table 3. The formation of HThF is calculated to be highly exothermic, and possible decompositions to ThH or ThF are endothermic. However HThF is not stable against reaction with additional HF, H₂ and F₂, which will be present in the system due to the photochemistry of HF during the laser ablation process. These three reactions show that the +IV oxidation state is more stable than the +II state and also that the +IV state is even more favored with more fluorine in the molecule. Therefore HThF₃ is the most stable hydride fluoride in the system, which is also demonstrated by the exothermic reaction of H₂ThF₂ with HF to form HThF₃ and fluorine. However, HThF₃ is still less stable than the tetrafluoride. In addition, the +III oxidation state is more stable than the +II state. The hydride fluorides HThF₂ and H₂ThF are accessible through the reaction of HThF and ThH₂ with HF but these reactions are in competition with the formation of the thorium(IV) hydride fluorides and the energies of reaction are much lower. They might also be formed by reaction of HThF with hydrogen or fluorine atoms or through photolysis reaction of any higher hydride fluoride. However, although the reactions with HF to form higher thorium hydride fluorides are highly exothermic there might be a high activation barrier due to the high dissociation energy of HF and the observed higher compounds might result from the reaction of HThF with H₂ or F₂. In contrast, the insertion of ground state thorium atoms in HF seems to be spontaneous as the increase of the HThF bands after annealing shows.

Table 3. Calculated reaction energies of thorium hydride fluorides. Values in kJ mol⁻¹ and ZPE corrected.

Reaction	B3LYP ^[a]	CCSD(T) ^[a]
HThF → Th + HF	408.6	405.9
HThF → ThH + F	677.9	691.1
HThF → ThF + H	280.6	285.7
HThF + HF → H ₂ ThF ₂	-416.3	-404.3
HThF + HF → HThF ₂ + H	-113.5	-95.6

HThF + HF → H ₂ ThF + F	263.9	286.6
HThF + H ₂ → H ₃ ThF	-169.4	-162.6
HThF + F ₂ → HThF ₃	-1190.5	-1185.3
H ₂ ThF ₂ → ThF ₂ + H ₂	143.5	137.3
H ₂ ThF ₂ → ThH ₂ + F ₂	1211.7	1201.3
H ₂ ThF ₂ + HF → HThF ₃ + H ₂	-242.2	-236.7
H ₂ ThF ₂ + HF → FThH ₃ + F ₂	778.8	785.9
HThF ₃ + HF → ThF ₄ + H ₂	-233.6	-228.5

[a] Th:Stuttgart RSC 1997 ECP H,F: aug-cc-pVTZ. Calculated at 0K in the gas phase. Di- and tetravalent compounds have a singlet ground state while trivalent species have a duplet ground state. The electronic state of the thorium atom is a triplet.

Contrary to similar experiments with laser ablated uranium atoms and HF where only weak bands were observed for possible higher hydride fluorides in addition to the major HUF product, the experiments using thorium yield several higher hydride fluorides. The comparison of some reactions leading to higher hydride fluorides, as shown in figure 4, clearly shows that the thorium energies of reaction are much higher than the corresponding uranium reactions. This shows that the thorium hydrogen as well as the thorium fluorine bonds are stronger than their uranium counterparts. An explanation for that might be given by comparison of HThF and HUF. Interestingly the Th–F of 205.6 pm as well as the Th–H bonds of 202.6 pm calculated at B3LYP level are shorter than their uranium counterparts (205.6 pm for U–H and 206.3 pm for U–F) although uranium is smaller than thorium by 5 pm according to calculated covalence radii of Pyykkö et al.[16] In this context the angle opening of 20° in HThF compared to HUF seems plausible. But there is another inconsistency in the NPA charges. The charges for HThF as aforementioned are +1.16 for Th, -0.48 for H and -0.68 for F and are therefore lower than in HUF (1.24 for U, -0.53 for H and -0.71 for F) which is unexpected because U is more electronegative than Th. Hence due to the lower charges and shorter bonds the Mayer Bond orders are slightly higher for HThF than for HUF and therefore the bonds in the thorium compounds are expected to be slightly more covalent. The inconsistency of the charges and the bond lengths can be explained by looking at the electronic state. HUF has a ⁵A₂ ground state and thus four unpaired electrons while HThF is a ¹A₁ state with only one free electron pair. Therefore the longer bonds and the lower charges in HUF can be explained by the steric requirements of the unpaired electrons. Note that the same holds for the comparison of UH₂ and ThH₂ where uranium also forms longer bonds and a smaller bending angle.[3, 17] CASPT2 calculations show that the free electron pair in HThF is located in the 7s orbital while the occupation of HUF is 7s¹5f³ which is in line with an +II oxidation state of uranium and recently found by Heaven et al.[18] However the electrons in the f-orbitals are distributed over all seven 5f orbitals resulting in a ground state with multireference character. These present results are more accurate than the CASPT2 results from our previous communication due to the correlated 7s orbital.[10] The correlation of this orbital leads to a multireference character of the wave function while the freezing of the occupation leads to a single reference wave function with a 5f³ configuration. The multireference character of the wave function is expected not to affect the results using single reference methods too much because only the non-bonding unpaired electrons are distributed however the steric requirement of the unpaired electrons is expected to be bigger than for localized electrons. With increasing oxidation state of

uranium there are less unpaired electrons – which might also be more localized – and therefore steric requirements become a minor effect and the bond length and charges follow the expected trend. This can be seen by comparison of HThF₃ and HUF₃ where the uranium compound has bond lengths of 203.1 pm for the U–H bond and 206.1 pm for the U–F bonds which is shorter than the bonds in HThF₃ as shown in figure 3. Looking at the bonding in HThF₃ the NPA charges calculated at B3LYP level are +2.46 for thorium, –0.49 for hydrogen and –0.66 for fluorine and the Mayer Bond order is calculated to be 0.64 for the thorium fluorine bond and 0.74 for the thorium hydrogen bond. In the uranium counterpart the charges are +2.22 for uranium, –0.44 for hydrogen and –0.59 for fluorine and the bond orders are 0.81 for U–H and 0.74 for fluorine. Due to the higher charges and lower bond orders the thorium hydrogen bonds are expected to be more ionic. In HUF the hydrogen NPA charge is –0.53 while in the unstable HUF₅ molecule the charge is zero. The bond order is 0.73 in HUF and 0.92 in the unstable HUF₅ molecule, respectively. This shows that with increasing oxidation state of uranium the uranium hydrogen bond gets more covalent which is not the case for thorium. This might be another reason for the instability of higher uranium hydride fluorides, especially the ones higher than the +IV oxidation state. However the reactions forming uranium(IV) hydride fluorides are still highly exothermic and should take place.

Figure 4. Comparison of several reactions of thorium and uranium hydride fluorides calculated at B3LYP level. Values in bold belong to uranium reactions. All values in kJ mol^{–1} and ZPE corrected.

To get further insights in the differences between HUF and HThF we also investigated relativistic effects. In table 4 the structural parameters of these two compounds are listed using different methods and relativistic corrections.

Table 4. Calculated structural parameters for HThF and HUF applying different relativistic corrections. Bond lengths in pm and angles in degree.^[a]

Parameter	BP86 ^[b]	BP86 ^[b]	BP86 ^[b]	CCSD(T) ^[c]
	Non-rel.	scalar-rel.	Spin-orbit	scalar-rel.
U–H	210.7	204.2	203.7	203.1
U–F	212.2	205.2	204.4	204.3
∠HUF	114.6	99.2	98.1	96.1
Th–H	211.2	202.7	202.4	204.2
Th–F	209.9	205.0	204.7	206.4

∠HThF 109.4 120.3 119.0 122.6

[a] Values of HUF computed at CASPT2 level: U–H 202.1 pm, U–F 204.2 pm, ∠HUF 99.5° [b] Using TZ2P basis sets as implemented in ADF. [c] Th, U: Stuttgart RSC 1997 ECP H, F: aug-cc-pVTZ.

The calculated parameters show that spin-orbit effects are of minor importance in these systems and that the bent structures of the HAnF compounds are due to covalent bonding and not an artefact from neglecting spin-orbit coupling. The major part of relativistic effects can be described by including scalar relativistic corrections. Ignoring scalar relativistic effects leads to a dramatic underestimation of the bonding caused by the s-orbitals being too high in energy while d- and f-orbitals being too low in energy. Due to the high 7s orbital in HUF the occupation of the four unpaired electrons changes from 7s¹5f³ to 5f⁴ and the 7s orbital contribution to the UH bond is significantly reduced. In HThF the occupation of the free electron pair mainly consisting of the 7s orbital changes in the non relativistic calculation to a 5f² occupation with the two electrons distributed over all seven f-orbitals. The decrease in the bonding angle in this case might be due to the bigger steric requirements of the distributed f-electrons and gives further evidence for the much bigger bonding angle in HThF than in HUF.

In this study we have reported the reaction products of thorium atoms with HF as well as HF/DF mixtures. Our assignments are supported by quantum-chemical descriptions of the thorium hydride fluoride molecules in question. The experiments show that HThF is the major reaction product although the +IV oxidation state on thorium is favoured in the presence of more reagent molecules. However, the role of matrix isolation is to minimize additional reactions, and this has happened again here in order to trap the initial HThF reaction product. While the assignment of HThF is consistent with calculated frequencies, matrix shifts and deuterium shifts the assignment of higher oxidized thorium hydride fluorides must be regarded as tentative. Our observations are supported by thermochemistry analysis at state-of-the-art quantum-chemical calculations. Moreover, the thermochemistry data is compared to similar uranium hydride fluoride reactions showing that the thorium compounds are much more stable and the Th–F and Th–H bonds are stronger.

3. Experimental Section

3.1 Matrix-isolation experiments: HF (99.8%, Solvay) was premixed with neon (99.999%, Air Liquide) argon (99.999%, Sauerstoffwerk Friedrichshafen) in a stainless steel cylinder. The mixing vessel was connected to a self-made matrix chamber by a stainless steel capillary. The reactants were condensed onto a CsI window cooled to 4 K using a closed-cycle helium cryostat (Sumitomo Heavy Industries, RDK-205D) inside the vacuum chamber. For the laser-ablation experiments, the 1064 nm fundamental of a Nd:YAG laser (Continuum, Minilite II, 10 Hz repetition rate and 6 ns pulse width, laser energy about 25–40 mJ/pulse) was used which was focused onto a rotating thorium target through a hole in the cold window. Infrared spectra were recorded on a Bruker Vertex 70 spectrometer purged with dry air at 0.5 cm^{–1} resolution in the region between 4000 and 420 cm^{–1} using liquid nitrogen cooled MCT detector. The matrix samples were irradiated by a mercury arc street lamp (Osram HQL 250) with the outer globe removed. Additional experiments with a similar matrix setup for laser ablated Th reacting with HF/DF mixtures were done in

Virginia using a Nicolet 750 FTIR instrument with MCT range B detector.[4-6]

3.2 Quantum-chemical calculations: The structures of all molecules have been fully optimized (by relaxing all parameters) at density functional theory using the B3LYP[19-21] hybrid functional and Dunning's correlation consistent triple- ζ basis set (denoted as aVTZ) for fluorine and hydrogen[22] as well as the 28 electron core SDD pseudopotential (denoted as SDD) for thorium[23]. All possible spin multiplicities have been considered. Structure optimizations at Coupled-Cluster (CCSD(T)) level have been performed for the ground states of all molecules within the restrictions of their respective point groups. Structure optimizations as well as harmonic frequency calculations were carried out with Gaussian09[20] at DFT level and with the CFOUR program package[24] for coupled-cluster calculations. Bond analysis and the calculation of Mayer bond orders [25, 26] was carried out with the NBO 3.1 program package implemented in Gaussian09. CASPT2 calculations were executed with the MOLPRO 2006.1 program using the same basis sets as mentioned above.[27] The 7s and the seven 5f orbitals of uranium and thorium were chosen as active space. For HUF the MCSCF wave function consists of the three lowest states whereas for HThF only one state was used. Relativistic corrections have been investigated with the ADF 2014 program using the TZ2P basis sets for all atoms as implemented in the program[28-30].

ASSOCIATED CONTENT

Supporting Information

Complete list of calculated harm. frequencies and intensities for all species in question; Total Energies of all possible spin states and cartesian coordinates for all species.

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Notes

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SYNOPSIS TOC