



Investigation of thorium hydride fluorides by matrix-isolation spectroscopy



Thomas Vent-Schmidt^a, Jens Metzger^a, Lester Andrews^b, Sebastian Riedel^{c,*}

^a Albert-Ludwigs-Universität Freiburg, Institut für Anorganische und Analytische Chemie, D-79104 Freiburg, Germany

^b University of Virginia, Department of Chemistry, Charlottesville, VA 22904-4319, USA

^c Freie Universität Berlin, Institut für Chemie und Biochemie, Fabeckstr. 34-36, D-14195 Berlin, Germany

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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.

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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 methylenes complexes, $\text{CH}_2=\text{ThHX}$ [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 Figs. 1 and 2 while band assignment is shown in Table 1. Known bands for ThF, ThF₂, ThF₃ and ThF₄ [8,9] as well as ThOF₂ [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].

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 reformed on subsequent annealing. The Th–F stretching mode is located between the wave numbers of ThF and ThF₂ 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

* Corresponding author. Tel.: +49 030 838 59860.
E-mail address: s.riedel@fu-berlin.de (S. Riedel).

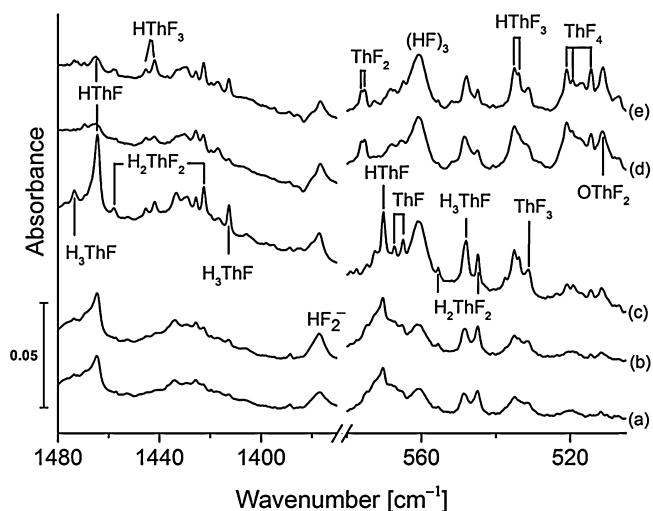


Fig. 1. IR spectra of laser ablated Th atoms with 0.2% HF in argon. (a) Deposition for 40 min. (b) Annealing to 15 K. (c) Annealing to 25 K. (d) Photolysis above 220 nm for 25 min. (e) Annealing 30 K.

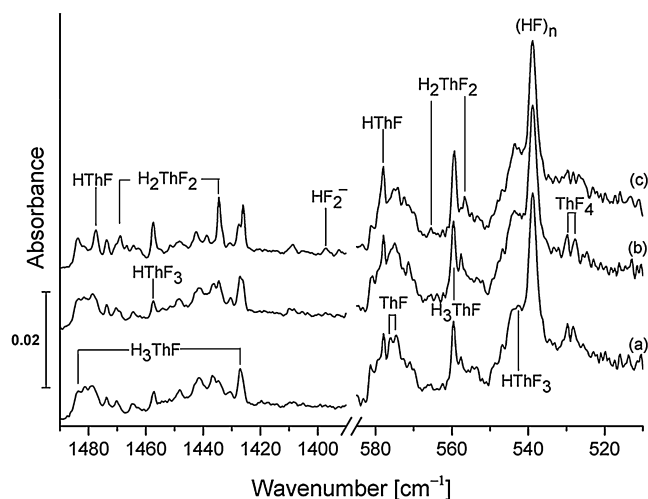


Fig. 2. IR spectra of laser ablated Th atoms with 0.15% HF in neon. (a) Deposition for 40 min. (b) Annealing to 8 K. (c) Annealing to 10 K.

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.

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. Fig. 3 shows the optimized structures of all possible hydride fluorides, cartesian coordinates are given in ESI. Similar as the previous 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 hydride fluorides. The structure of HThF₂ and H₂ThF is 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) level. 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.

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

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)	$\nu_1\text{H}_3\text{ThF}$
1477.4	1464.8	1521.8(305)	1521.4(305)	$\nu_1\text{HThF}$
1468.0	1458.1	1500.6(361)	1506.2(350)	$\nu_1\text{H}_2\text{ThF}_2$
1457.2	1441.9/1445.6	1473.6(492)	1483.1(487)	$\nu_1\text{HThF}_3$
1434.6	1422.6	1450.6(758)	1462.7(754)	$\nu_6\text{H}_2\text{ThF}_2$
1427.1	1412.7	1456.6(832)	1468.2(825)	$\nu_4\text{H}_3\text{ThF}$
–	576.0/575.4	575.1(171)	577.5(164)	$\nu_3\text{ThF}_2^c$
577.9	570.4	583.9(106)	585.6(110)	$\nu_2\text{HThF}$
576.1	567.2/565.1	585.7(78)	601.2(74)	$\nu_1\text{ThF}^c$
573.8	–	–	–	–
565.6	555.4	564.7(209)	580.1(214)	$\nu_2\text{H}_2\text{ThF}_2$
559.4	548.3	565.8(305)	582.6(321)	$\nu_2\text{H}_3\text{ThF}$
556.8	544.8	550.7(354)	565.8(359)	$\nu_8\text{H}_2\text{ThF}_2$
542.5	535.1/533.4	537.8(287)	553.3(291)	$\nu_4\text{HThF}_3$
–	531.3	533.0(191)	–	$\nu_3\text{ThF}_3^c$
–	521.2/519.2/514.3	525.3(210)	–	$\nu_3\text{ThF}_4^c$

^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 $667.2, 646.8\text{ cm}^{-1}$, ThF₂ $575.9, 575.1\text{ cm}^{-1}$ ThF₃ 531.0 cm^{-1} , ThF₄ $522.7, 521.0, 519.2, 514.5\text{ cm}^{-1}$ in argon from Ref. [8,9].

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