Actinides

Infrared Spectra of the HAnX and H_2AnX_2 Molecules (An = Th and U, X = Cl and Br) in Argon Matrices Supported by Electronic Structure Calculations

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Abstract: Uranium and thorium hydrides are known as functional groups for ligand stabilized complexes and as isolated molecules under matrix isolation conditions. Here, the new molecular products of the reactions of laser-ablated U and Th atoms with HCl and with HBr, namely HUCl, HUBr and HThCl, HThBr, based on their mid and far infrared spectra in solid argon, are reported. The assignment of these species is based on the close agreement between observed and calculated vibrational frequencies. The H–U and U–³⁵Cl stretching modes of HUCl were observed at 1404.6 and 323.8 cm⁻¹, respectively. Using DCl instead to form DUCl gives absorption bands at 1003.1 and 314.7 cm⁻¹. The corresponding bands of HThCl are 1483.8 (H–Th) and 1058.0 (D–Th), as well as

Introduction

Early actinide metal atoms and their reactions with small molecules have attracted great interest in part because 5f electrons are involved in their bonding whereas 4f electrons remain in the core for lanthanide metals.^[1] It is also of interest to compare the relative participation of 5f electrons in the bonding for analogous molecules bearing Th and U atoms. The dioxides are a good case in point. A linear configuration for ThO₂ would have strong Th 6d-O 2p bonds. However, ThO₂ is bent because the 5f is higher in energy than the 6d so that 5f–6d hybridization provides for lowering the energy on bending.^[2] In UO₂, there is increasing difference between the sizes and energies

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340.3 and 335.8 cm⁻¹ (Th–³⁵Cl), respectively. HUBr is observed at 1410.6 cm⁻¹ and the BP86 computed shift from HUCl is 6.2 cm⁻¹ in excellent agreement. The U–H stretching frequency increases from 1383.1 (HUF), 1404.6 (HUCl), 1410.6 (HUBr) to 1423.6 cm⁻¹ (UH) as less electronic charge is removed from the U–H bond by the less electronegative substituent. These U–H stretching frequencies follow the Mayer bond orders calculated for the three HUX molecules. A similar trend is found for the Th counterparts. Additional absorptions are assigned to the H₂AnX₂ molecules (An=U, Th, X= Cl, Br) formed by the exothermic reaction of a second HX molecule with the above primary products.

of the 5f and 6d orbitals, which makes the former hybridization unfavorable on bending, and thus UO₂ is a linear molecule.^[2] Uranium dioxide UO₂ has a ${}^{3}\Phi_{2,u}$ ground state made up of the (7s)¹(5f(ϕ))¹ configuration.^[3,4]

Uranium reacts with hydrogen to form the UH₃ solid, which is a useful reagent for the synthesis of uranium compounds.^[5,6] Thorium is quite electropositive and it oxidizes readily in air.^[5] Uranium and thorium hydrides are known as functional groups for ligated complexes^[5] and as isolated molecules under matrix isolation conditions.^[7–9] Simple binary uranium and thorium hydride molecules were first prepared by reaction of the laser-ablated metal atoms with H₂ diluted in argon with condensation at 7 K. Matrix infrared spectra were obtained for isolated UH_x, and ThH_x (x = 1-4) molecules, and a hydrogen-bridge-bonded molecule identified as U₂H₂ was reported in 1997.^[7–9] Later work using hydrogen as the matrix and reagent also produced uranium and thorium hydride complexes involving side-bound dihydrogen molecules.^[9, 10]

The first monomeric monohydride complexes for thorium and uranium, HTh[N(SiMe_3)_2]_3 and HU[N(SiMe_3)_2]_3 metal(IV) state compounds, were communicated in 1979 by Turner, Simpson and Andersen.^[11] These workers next discovered a novel H–D exchange process for the uranium derivative by stirring a pentane solution under D₂ gas which gave complete exchange for D and was reversible with H₂ gas over pressure.^[12] The thorium hydride compound was also found to undergo complete and reversible exchange under similar conditions.^[12] In addition to their importance for the synthesis of novel Th and U complexes, these monomeric monohydrides reveal

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good vibrational spectra for comparison to the HTh-Cl, HU-Cl, HTh-Br and HU-Br, which are subjects of this paper. The HTh[N(SiMe₃)₂]₃ compound revealed a Th-H stretching mode at 1480 cm^{-1} and the DTh[N(SiCD₃)₂]₃ isotope Th–D stretching mode shifted to 1060 cm⁻¹. Their ratio 1480:1060 = 1.396 confirmed these absorptions as heavy metal hydride and deuteride stretching modes. Likewise for the HU[N(SiMe₃)₂]₃ derivative the U–H stretching mode was assigned as 1430 cm⁻¹ and the deuterated material gave U-D modes at 1020 and 1027 cm⁻¹ in the two communications.[11,12] Taking the average to calculate the U-H/U-D frequency ratio, 1430:1023 = 1398, which is again characteristic of a heavy metal hydride vibrational mode, and a verification of their vibrational assignments. Our first adventure into hydrogen halide reactions with these early actinide atoms gave H–UF and D–UF absorption bands at 1383.1 and 988.3 cm⁻¹ and a 1.399 frequency ratio.^[13,14] Likewise for H-ThF and D-ThF with frequencies 1464.8 and 1046.0 cm⁻¹ the same frequency ratio (1.400) for these heavy metal hydrides was obtained.^[15]

A few more examples of Th and U hydride complexes will be summarized here. The synthesis and molecular structure of a novel uranium(III) bisphosphine hydride have been reported. Of particular interest here is the very strong infrared absorption (1219 cm^{-1}) for the hydride, which shifted (870 cm^{-1}) in the analogue prepared with D₂.^{(16]} Although these absorptions are substantially lower (211 and 150 cm⁻¹) than found for the above metal(IV) complexes, the H/D frequency ratio (1.40) verifies that they are mechanically due to a relatively pure U and H vibration. Thus, there must be some interaction within this complex that reduces the U–H bond stretching force constant (and likely also the bond energy) relative to those for the above metal(IV) complexes.

Another terminal monomeric U–H complex has been prepared by reacting [U(COT^{TIPS2})Cp*R] (COT^{TIPS2} = $C_8H_6(Si'Pr_3-1,4)_2$) with H₂. This uranium(IV) hydrido complex, [HU(COT^{TIPS2})Cp*], is special for its instability with respect to hydrogen loss.^[17] In order to find out if tris(pentamethyl cyclopentadienyl) chemistry would be possible with thorium, the (C_5Me_5)₃ThH complex was prepared.^[18] Again Th and U analogues have been synthesized this time for [(C_5Me_5)₂MH₂]₂).^[19] In this case the trivalent monohydride exists as an equilibrium mixture with the tetravalent dihydride. A thorium(III) monohydride complex has even been prepared in a bimetallic system.^[20] Only recently isolable crystalline molecular complexes of U^{II} have been reported.^[21] The scarce nature of ligated U^{II} complexes makes our matrix isolated HAnX molecules (An = Th, U; X = F, Cl, Br) an even more important contribution to early actinide metal chemistry.

Experimental and Theoretical Methods

Laser-ablated U and Th atoms were reacted with the HCl and HBr gases (Linde AG) in argon host gas during their deposition at 12 K using a closed-cycle helium refrigerator (Sumitomo Heavy Industries, RDK-205D) inside of a self-made vacuum chamber, which has been described in more detail in our previous works.^[14, 15, 22] Early experiments with U and HCl were also done with 5 and 15 K substrates, but 12 K gave a higher prod-

uct yield and better signal-to-noise spectra. The 1064 nm fundamental of a Nd:YAG laser (10 Hz repetition rate with 10 ns pulse width, and a pulse energy up to 55 mJ) was focused onto the rotating metal targets. Infrared (IR) spectra were recorded at a resolution of 0.5 cm⁻¹ on a FTIR vacuum spectrometer (Bruker Vertex 80v) equipped with a transfer optic, Mid-IR MCT detector (4000–450 cm⁻¹) or liquid helium cooled FIR bolometer (680–180 cm⁻¹). Matrix samples were annealed at different temperatures, and selected samples were irradiated by 455 or 365 nm LED light. DCl for these experiments was synthesized by reacting D₂O with SiCl₄: D₂O (0.2 mL) was slowly added to SiCl₄ (3 mL) at -78 °C using a dry ice/ethanol bath. The bath was removed and the system slowly warmed back to room temperature. The DCI gas was passed through a trap cooled to -120°C and collected by two -196°C liquid nitrogen traps.^[23]

Preliminary calculations at the density functional theory (DFT)^[24] level using the Turbomole V7.1 program^[25] were performed with the GGA BP86^[26-28] exchange-correlation or the B3LYP^[29] hybrid exchange-correlation functionals. Since both methods produced structures and vibrational frequencies in good agreement with our CCSD(T) values of HThX, the faster and simpler BP86 GGA functional combined with the triple- ζ basis set def-TZVP^[30,31] for all elements was finally used for all calculations. Scalar relativistic effects were included by employing effective core potentials (def-ECP)^[31] with 60 electrons at U and Th. Spin-orbit coupling effects were not incorporated. For the HAnX (An = U, Th and X = Cl and Br) species calculations were supplemented by single point calculations at the CCSD(T) level with the augmented triple- ζ basis set aug-cc-pVTZ^[32] on H, Cl and Br, and the cc-pVTZ-PP^[33] basis set on U and Th employing the small-core pseudo potential ECP60MDF.[34] All CCSD(T) calculations for HThX species were performed using the CFOUR V1 program,^[35] whereas Molpro 2015.1^[36] was used for all HUX species. The 2, 10, 18, 8 and 8 inner electrons on F, Cl, Br, Th and U were excluded from the correlation treatment in CFOUR, while the default settings were used in Molpro. All obtained electronic ground state configurations obeyed the "Aufbau principle" with positive HOMO-LUMO gaps. The vibrational analyses were carried out in the harmonic approximation for all molecules and isotopologues. In order to estimate the amount of the anharmonic correction to the vibrational frequencies of the ^{1,2}HAnX molecules, additional anharmonic corrections were calculated at the CCSD(T) level for ^{1,2}HThCl using vibrational second-order perturbation theory^[37,38] (VPT2). Calculations of AIM charges,^[39] electron densities at the bond critical point^[39] (ρ_b) and Mayer Bond Orders^[40] were carried out using Multifwn 3.5^[41] on the basis of the BP86 wave functions.

Computational Results

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All possible spin states have been considered for the HAnX and H_2AnX_2 (An = U, Th and X = Cl and Br) species. Table 1 lists fully optimized structures obtained at the DFT BP86 level for all HAnX species and zero-point-energy (ZPE) corrected DFT relative energies for their low-lying electronic states including the configuration of the lowest four MOs, as well as CCSD(T)

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Table 1. Calculated structures and ZPE corrected relative energies of low-lying electronic states of HAnX molecules (X=CI, Br; An=Th, U) at theBP86 (normal font) and CCSD(T) (italic font) level.

	Bond length [Å]		Angle [°]	E _{rel} [kJ mol ⁻¹		
Electronic state	H–An	An–X	HAnX	CCSD(T) ^[a]	DFT	
HThCl						
X ¹ A' (16a' ² 6a'' ² 17a' ² 18a' ²)	2.021	2.509	126.7	0	0	
	2.035	2.536	129.5			
A ³ A'' (6a'' ² 17a' ² 18a' ¹ 7a'' ¹)	2.060	2.549	115.5	33	5	
<i>B</i> ³ A' (6a'' ² 17a' ² 18a' ¹ 19a' ¹)	2.071	2.559	125.2	39	11	
HThBr						
X ¹ A' (22a' ² 9a'' ² 23a' ² 24a' ²)	2.021	2.673	129.4	0	0	
	2.034	2.696	131.3			
A ³ A'' (9a'' ² 23a' ² 24a' ¹ 10a'' ¹)	2.058	2.714	116.7	33	3	
<i>B</i> ³ A' (9a'' ² 23a' ² 24a' ¹ 25a' ¹)	2.068	2.723	126.4	35	8	
HUCI						
X ⁵ A' (18a' ¹ 7a'' ¹ 8a'' ¹ 19a' ¹)	2.037	2.527	104.1	0	0	
A ⁵ A' (18a' ¹ 19a' ¹ 20a' ¹ 21a' ¹)	2.036	2.522	101.3	0	5	
<i>B</i> ⁵ A'' (18a' ¹ 19a' ¹ 7a'' ¹ 20a' ¹)	2.034	2.523	101.7	2	0	
³ A' (17a' ² 18a' ² 7a'' ¹ 8a'' ¹)	2.025	2.505	106.2	-	30	
HUBr						
X ⁵ A' (10a'' ¹ 24a' ¹ 11a'' ¹ 25a' ¹)	2.032	2.695	105.7	0	2	
A ⁵ A' (24a' ¹ 25a' ¹ 26a' ¹ 27a' ¹)	2.032	2.695	105.7	0	4	
<i>B</i> ⁵ A'' (24a' ¹ 25a' ¹ 10a'' ¹ 26a' ¹)	2.032	2.690	102.9	3	0	
³ A' (23a' ² 24a' ² 10a'' ¹ 11a'' ¹)	2.025	2.671	106.4	-	31	
[2] CCSD(T) relative energies (F) based on CCSD(T) single point energies						

at BP86 minimum structures. A plot of selected frontier orbitals is shown in Figure S2.

single point relative energies. For the HUX species the electronic ground state energies were obtained at the CCSD(T) level by single point calculations at fully DFT optimized structures, while for the HThX species CCSD(T) optimized electronic ground state structures are given. Since structure relaxations only accounted for 0.6 and 0.4 kJ mol⁻¹ energy difference for HThCl and HThBr, it can be assumed the error of the ZPE corrected relative CCSD(T) energies is well below 1 kJ mol⁻¹ due to error cancelation. Table 2 contains electronic configurations and structures of the H₂AnX₂ species, as well as relative energies of low-lying electronic states of the H₂UX₂ species. The

electronic energies obtained by the DFT calculations predict several low-lying excited electronic states for both, the HUX and H₂UX₂ species due to the presence of partially filled neardegenerate metal centered d- and f-type orbitals. Uraniumcentered spin densities for HUF, HUCI and HUBr are depicted in Figure S1. Although due to their multi-reference nature the electronic configuration of the HUX molecules cannot unambiguously be evaluated at the DFT level, the valence molecular orbital Scheme of HUX shown in Figure 1 reveals that the singly occupied valence molecular orbitals are energetically well separated from the binding H–U and X–U MOs, suggesting that the strong static correlated electrons have little influence on the molecular structure (see Table 1). As shown in Table 3 for two selected low-lying electronic states of the HUX molecules the different HUX states have very similar computed vibrational frequencies. While our computed frequencies can be safely assigned to a given matrix-isolated HUX species (see below), neither our experimental frequencies nor the DFT re-



Figure 1. Valence molecular orbital diagram of HUF and HUBr calculated at the RO-BP86 level of theory. Atomic orbital energies of s(H) and p(F/Br) are adjusted to meaningful positions. Atomic orbital participations have been indicated with full lines (>10%), dashed lines (3–10%) and dotted lines (1–3%).

Table 2. Calculated structures and ZPE corrected relative energies of lowest and low-lying electronic states of H₂ThX₂ and H₂UX₂ molecules (X=Cl, Br) at the BP86 level.

	Bond lengt	h [Å]	A	ngle [°]		E _{rel}
Electronic state (configuration) [Point group]	H–An	M–An	HAnX	HAnH	XAnX	$[kJ mol^{-1}]$
H ₂ ThCl ₂						
${}^{1}A_{1}(C_{2\nu})$	2.067	2.567	107.8	107.2	118.2	-
H ₂ ThBr ₂						
$^{1}A_{1}(C_{2\nu})$	2.062	2.721	107.8	107.2	117.9	-
H ₂ UCl ₂						
X ³ B (17a ² 16b ² 18a ¹ 17b ¹) [C ₂]	1.998	2.514	101.7, 107.9	109.8	127.5	0
A ³ A' (19a' ² 20a' ² 21a' ¹ 22a' ¹) [C _s]	1.994, 1.997	2.512	105.9, 107.9	108.1	120.7	1
$B^{3}B_{2} (14a_{1}^{2} 6b_{1}^{2} 11b_{2}^{1} 15a_{1}^{1}) [C_{2\nu}]$	2.005	2.515	110.6	104.0	110.2	3
$C^{3}A_{2} (14a_{1}^{2} 6b_{1}^{2} 11b_{2}^{1} 7b_{1}^{1}) [C_{2\nu}]$	2.006	2.512	101.7	114.7	136.0	7
H ₂ UBr ₂						
X ³ A'' (28a' ² 29a' ² 23a'' ¹ 30a' ¹) [C _s]	1.986, 1.990	2.678	105.7, 100.5	105.3	135.8	0
A ³ A' (28a' ² 29a' ² 30a' ¹ 31a' ¹) [C _s]	1.995, 1.990	2.672	108.6, 105.3	107.3	121.0	0
<i>B</i> ³ A'' (36a' ² 15a'' ² 37a' ¹ 16a'' ¹) [C _s]	1.992	2.678, 2.666	104.5, 108.3	107.5	122.9	0
$C^{3}A_{2} (20a_{1}^{2} 9b_{1}^{2} 7a_{2}^{1} 21a_{1}^{1}) [C_{2\nu}]$	1.993	2.678	102.4	106.6	138.1	10

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at the BP8	86/def-TZVP le	vel.									
	$ ilde{ u}$ (H-An) [cm $^{-1}$]				AIM charge			Mayer B.O.		$ ho_{\sf b}$ [au]	
	State	Obs. (Ar)	calcd	н	М	Х	H–M	X—M	H–M	X—M	
HUF	X⁵A′	1202.1	1407.8	-0.553	1.240	-0.687	0.926	1.095	0.0879	0.1346	
	<i>B</i> ⁵A′′	1383.1	1403.9	-0.555	1.241	-0.685	0.928	1.100	0.0879	0.1360	
HUCI	<i>X</i> ⁵A′	1404 6	1425.7	-0.549	1.190	-0.640	0.936	1.233	0.0904	0.0836	
	<i>B</i> ⁵A″	1404.6	1428.5	-0.548	1.184	-0.637	0.937	1.238	0.0907	0.0834	
HUBr	<i>X</i> ⁵A′	1410 6	1432.0	-0.551	1.167	-0.618	0.939	1.213	0.0906	0.0694	
	<i>B</i> ⁵ A′′	1410.0	1427.8	-0.549	1.162	-0.613	0.939	1.216	0.0912	0.0704	
HU		1423.6									
HThF	<i>X</i> ¹ A′	1464.8	1507.2	-0.544	1.237	-0.693	0.934	1.259	0.1047	0.1421	
HThCl	<i>X</i> ¹ A′	1483.8	1515.5	-0.543	1.156	-0.613	0.940	1.416	0.1060	0.0944	
HThBr	$X^{1}A'$	1485.4	1518.2	-0.545	1.112	-0.575	0.940	1.415	0.1062	0.0807	
HTh		1485.2									

Table 3. HAnX molecules (X = F, Cl, Br; An = Th, U): AIM charges, Mayer bond orders (B.O.) and electron densities at the bond critical points ($\rho_{\rm b}$) obtained

sults allow an unambiguous conclusion on the electronic ground states of the observed species. Our preliminary DFT calculation yield singlet and quintet ground state spin multiplicities for the HThX and HUX species, respectively, with their lowest triplet states between 30 and 39 kJ mol⁻¹ above the ground state (Table 1).

Table S1 contains calculated vibrational frequencies and intensities employing a harmonic approximation at both, the DFT BP86/def-TZVP (all HAnX species, X = Cl, Br) and CCSD(T) (only HThX) levels for all H/D, $^{35/37}\text{CI}$ and $^{79/81}\text{Br}$ isotopologues. Additional anharmonic vibrational analysis were performed for ^{1,2}HThCl at the CCSD(T) level using vibrational second-order perturbation theory^[37, 38] (VPT2). The anharmonic corrections to the H-Th and D-Th stretching modes amounts to -39 and -20 cm^{-1} , respectively, and it can be assumed that these anharmonic corrections can approximately be applied to other computed harmonic ^{1,2}H-An vibrational stretching frequencies as well. We note that our calculated H–U stretching frequencies of the HUX molecules at the BP86/def-TZVP level increases from 1407.8 (HUF), 1425.7 (HUCl) to 1427.8 cm⁻¹ (HUBr), which suggests an increasing strength of the corresponding H–U bond. This conclusion is supported by the Mayer Bond $\mathsf{Order}^{^{[40]}}$ which increases from 0.926 (HUF), 0.936 (HUCI) to 0.939 (HUBr), as well as by an increasing electron density at the bond critical point $(\rho_{\rm b})^{\rm [39]}$ between U and H in the different species (Table 3). It rises from 0.0879 (HUF), 0.0904 (HUCI) to 0.0906 (HUBr) as less electronic charge is removed from the U-H bond by the less electronegative substituent. The same effect is observed for the HThX species, with a less pronounced impact on the Mayer Bond Order. Based on a Mulliken partition analysis we also found an increasing f-orbital participation in the H–An bonds of the HAnX molecules, with X =F < CI < Br, while the opposite is true for the An–X bond, which decreases going from F to Br (Table 4). The f-orbital participation is found to be larger for the Th species.

The lowest electronic states for the H_2AnX_2 species have been found to be singlet and triplet states for thorium and uranium, respectively (Table 2, Table S2). No convergence was reached for singlet states of H_2UX_2 species. All vibrational frequencies of the H_2An_2X species and their H/D substituted iso
 Table 4. Percentage of f-orbital participations in the H–An and X–An bonds obtain by orbital composition analysis with Mulliken partition.

Bond	HUF	HUCI	HUBr	HThF	HThCl	HThBr
H—An	2.88	2.95	3.12	5.51	7.11	7.97
X—An	3.13	2.11	1.97	4.34	3.29	2.85

topologues are listed in Table S3. The H₃UX₃ species converged to singlet ¹A₁ ground states in the $C_{2\nu}$ point group, which is favored by 17 and 16 kJ mol⁻¹ for H₃UCl₃ and H₃UBr₃ over the $C_{3\nu}$ isomer (Table S4). No other spin states of the H₃UX₃ species were considered. Calculated ground state vibrational frequencies and intensities of the H₃UX₃ species are listed in Table S5. The optimized ground state structures for the HAnX, H₂AnX₂ und H₃AnH₃ species are depicted in Figure 2 and listed in Table S6.

Experimental Results

Figure 3 illustrates IR spectra for the major products from the reactions of laser ablated U atoms with HCl and with HBr in excess argon. The strongest bands are the HCl₂⁻ features at 697.0 and 956.2 cm⁻¹ and the HBr₂⁻ bands at 728.3, 892.6 and 1054.7 cm⁻¹, which were also observed with Th.^[42-45] The laser ablation process generates vacuum-UV, UV and visible light, which irradiates the condensing sample, and metal cations and electrons in addition to the major flux of metal atoms that emanate from the laser focal point. The first strong bands are due to the HCl_2^- anion made by reaction of Cl^- with HCl where chloride anion arises from the Cl atom photolysis product after electron capture.^[42] The HBr2⁻ anion is formed likewise.^[43,44] The DCl_2^- counterparts are observed in Figure 4(c) at 463.9 and 729.1 cm^{-1} . Other bands at 775.5 and 1051.0 cm^{-1} are due to $UO_2^{[46]}$ and $UN_2^{[47]}$ from the U atom reaction with trace air impurity in our vacuum system. The weak 819.5 band is due to UO.^[46] The sought reaction product at 1404.6, labeled HUCI in Figure 3, exhibits shoulder satellite absorptions at 1422.4 and 1388.8 cm⁻¹, and the HUBr counterpart at 1410.6 cm⁻¹ shows side bands at 1425.6, 1389.7 and also 1388.8 cm⁻¹. The blue-

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Figure 2. Structures calculated for HAnX, H_2AnX_2 and H_3UX_3 molecules (An = Th, U; X = Cl, Br) using BP86/def-TZVP.

shifted shoulder band for HUCl appears to be a matrix site as it is removed by annealing to 25 K, while the sharp 1404.6 band increases slightly (Figure 4(b)). The latter sharp 1388.8 band for HO₂ and the sharp 952.1 band for UO₂⁺ are resolved in the HBr experiment.^[46,48] Other features at 1569.8 and 1531.4 cm⁻¹ for HCl and 1553.1 and 1532.9 for HBr will be discussed later. From Figure 4(b), the annealing difference spectrum also shows that the sharp bands for HCl₂⁻ increase, but the broad blue wing on the 697.0 band decreases. The UO₂ absorption also increases slightly as this U atom reaction with O₂ is spontaneous.^[3,46]

Figure S3 shows annealing spectra from the U and HBr experiment. The very strong 728.3, 892.6 and 1054.7 cm⁻¹ bands are due to the HBr_2^- anion^[43] where a second combination band is also observed: these absorptions increase on annealing



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Figure 3. Infrared spectra of the reaction products of laser-ablated U with HCI (top) and HBr (bottom) (0.5%) each seeded in excess Ar and co-deposited for 150 min at 12 K. The 1023.1 band is due to an impurity in the HBr sample.

Wavenumber/ cm⁻



Figure 4. Infrared spectra of the reaction products of laser-ablated U with HCl and with a DCl/ HCl mixture seeded in excess Ar and co-deposited for 150 min at 12 K: (a) U + HCl (0.5%) in Ar, (b) difference spectrum after annealing to 25 K, (c) U + DCl/HCl approximately 1:1 (0.5%) mixture at 12 K in Ar, (d) difference spectrum after annealing to 35 K.

to 20 K, and they decrease upon exposure to 455 nm light for 15 min, but they increase a little on annealing to 25 K and a lot more on final annealing to 35 K. The new band at 1410.6 (HUBr) has satellites at 1425.6, 1389.7 and 1388.8 cm⁻¹, and thus it appears much like the HUCI band at 1404.6 in the top spectrum of Figure 3.

The lower two scans in Figure 4 were taken from the highest DCI enrichment used with U. The two product bands labeled HUCI at 1404.6 and DUCI at 1003.1 cm⁻¹ have almost equal experimental intensities (5/4) but the infrared intensity of the HUCI mode is calculated to be double that of DUCI, so this means that the DCI enrichment is 8/5 over HCI. Annealing difference spectra show that both HUCI and DUCI increase slightly on annealing, but there is no effect from 455 nm LED photolysis. The very sharp shoulder at 952.1 cm⁻¹, resolved from the 956.2 cm⁻¹ band of the HCl₂⁻ anion, is due to UO₂⁺,^[3,46] which is shown more clearly in the Figure 3 bottom spectrum.

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Figure 5. IR spectra of the reaction products of laser-ablated U with HCI/DCI seeded in excess of Ar co-deposited for 150 min at 12 K: (a) U + HCI (0.5%) co-deposited in Ar, (b) difference spectrum after annealing to 25 K. (c) U + DCI/HCI (0.5%) co-deposited in Ar, (d) difference spectrum after annealing to 25 K. Noise spikes of the bolometer are marked by an asterisk.

Spectra were recorded in the far IR region using the bolometer detector and plotted for U and HCl in the 260–360 cm⁻¹ region, Figure 5. It is clearly more difficult to obtain good spectra of matrix isolated species in this region. The deposited sample revealed absorptions in the 320 cm⁻¹ region, which increased and sharpened after annealing to 25 K. The band at 323.8 cm⁻¹ exhibited the same behavior on annealing as the 1404.6 cm⁻¹ band labeled HUCl in Figure 3. The band at 313.3 cm⁻¹ is assigned to UCl₂ based on agreement with a 312 cm⁻¹ band assigned to UCl₂ from the U+Cl₂ reaction, and the 296 cm⁻¹ nitrogen matrix band assigned to UCl₂ using two different methods of production.^[49] The 15 cm⁻¹ red matrix shift for PbCl₂ in this region allows a prediction of 311 cm⁻¹ for UCl₂ in solid argon with the reasonable assumption of the same N₂ to Ar matrix shift for PbCl₂ and UCl₂. Blue photolysis at 455 nm (Figure S4) appeared to increase both bands. The UCl₄ band at 345 cm⁻¹ is not observed.^[50] Similar experiments were done with HCI/DCI samples and the spectra are shown in Figure 5(c),(d). Unfortunately, our BP86 calculation predicts a 9 cm^{-1} red shift for DUCI which puts this band near UCl₂. The 25 K annealing difference spectrum shows increases in the 323.8, 314.7 and UCI_2 bands.

Figure 6 compares products from the laser-ablated Th atom reaction with HCl and HBr. Again, the hydrogen dihalide anions were observed like in the U atom reaction spectra as they were made from the common reagents with photons and electrons added in the ablation process. These bands increased on sample annealing. Sharp bands at 735.0 and 787.5 cm⁻¹ are due to ThO₂ and the band at 876.7 cm⁻¹ arises from ThO.^(8,51) The ThO₂ bands increase slightly on annealing as the Th reaction with O₂ is a spontaneous process. The important new band using HCl appears at 1483.8 with clear satellites lower at 1436.8, 1446.3, and 1463.0 cm⁻¹: the latter bands increase very slightly on annealing to 20 K. The new band is at 1485.6 with satellite at 1464.3 cm⁻¹ using HBr. Both spectra contained the 1388.8 spike for HO₂.^[48]



Figure 6. Infrared spectra of the reaction products of laser-ablated Th with HCI (top spectrum) and HBr (bottom spectrum) (0.5%) each seeded in argon at 12 K and co-deposited for 150 min.



Figure 7. IR spectra of the reaction products of laser-ablated Th with DCl/ HCl at 3:1 in excess Ar. (a) Th + DCl/ HCl (0.5%) in Ar co-deposited for 180 min at 12 K, (b) difference spectrum after annealing to 30 K.

Figure 7 illustrates the spectra from laser ablated Th reactions with a DCI/HCl 3:1 mixture and with DCl. The same strong HCl_2^- and DCl_2^- anion bands were observed (not shown). The primary new product feature labeled HThCl at 1483.8 cm⁻¹ exhibited a series of satellites beginning at 1463.0 and the DThCl counterpart at 1058.0 with a sharp well-resolved satellite at 1044.4 and a 1067.4 cm⁻¹ shoulder. The HThCl/ DThCl frequency ratio, 1.4024, is appropriate for a heavy metal hydride stretching mode. Unlike the uranium counterparts, there are no significant bands to higher wavenumbers of the main bands. Annealing to 20 K increased the primary feature slightly (not shown), but annealing to 30 K decreased the 1483.8 band and increased the 1454.5 absorption in the Th-H stretching region and decreased the 1058.0 band and increased the 1044.4 band in the Th-D region. Figure S5 shows annealing spectra from the Th and HBr experiment.

Far IR spectra were recorded in several experiments with thorium in different samples. The top two spectra in Figure 8 are for the $Th + Cl_2$ reaction with product absorptions at 340.5 and 330.5 cm⁻¹. The higher band is in good agreement with

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Figure 8. IR spectra of the reaction products of laser-ablated Th with CI_2 or HCI seeded in excess of Ar co-deposited at 12 K: (a) Th + CI_2 (0.5%) in Ar, (b) difference spectrum after annealing to 30 K, (c) Th + HCI (0.5%) in Ar, (d) difference spectrum after annealing to 20 K. Noise spikes of the bolometer are marked by an asterisk.

the Beattie observation of bands at 340.4 and 342.7 cm⁻¹ for ThCl₄ in solid argon.^[50] We are not aware of any spectra for ThCl₂ so our 330.5 cm⁻¹ absorption is a good bet for ThCl₂ in solid argon. Our BP86 calculations predicted the strongest band for $ThCl_2$ to be 20 cm⁻¹ lower than that for $ThCl_4$ and our bands are 10 cm⁻¹ apart. Annealing to 30 K decreased the lower band with little effect on the higher absorption. The next two spectra come from an experiment with Th and HCI and the higher band is stronger than the lower band (Figure 8(c),(d)), the reverse of the top scan using Cl_2 . This opens the possibility that something else like HThCl could be on top of a weak ThCl_4 band. Annealing to 20 K decreased both bands, but ThCl₄ did not decrease in scan (b) so HThCl might be sharing the absorption at 340.3 cm⁻¹. Two spectra from an experiment with Th and HCI/DCI are shown in Figure 9. The first thing to notice is a new band at 335.8 cm⁻¹ and the 330.5 band is as strong as the ThCl₂ band. Thus, assignment of the new band at 335.8 cm⁻¹ to DThCl is straightforward and guite



Figure 9. IR spectra of the reaction products of laser-ablated Th with HCI/ DCI at 2/1 in excess Ar co-deposited at 12 K: (a) Th + DCI/HCI (0.5%) in Ar, (b) Th + DCI/HCI (0.5%) difference spectrum after annealing to 20 K. Noise spikes of the bolometer are marked by an asterisk.

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likely HThCl also absorbs at 340.3 cm⁻¹. Annealing to 25 K does increase the 335.8 band and decrease ThCl₂ as before, but judgment on the 340.3 band is not clear.

Discussion

The new metal bearing product absorptions will be assigned and compared with computed frequencies and energies for their formation. Tables 5 and 6 list the observed and computed frequencies for the major product HAnX molecules (An=Th, U; X=Cl, Br). Bonding trends in these chemical series will be considered.

HUCI: The major new product absorption with uranium and hydrogen chloride appears at 1404.6 cm⁻¹ upon sample co-deposition. Annealing to 25 K resulted in a 20% increase in

	Exptl (argon)	Calcd BP86/def-TZVP
HU³⁵CI	1404.6	1425.79 (326)
	323.8	328.66 (89)
HU ³⁷ CI	1404.65	1425.79 (326)
	-	322.70 (90)
DU ³⁵ CI	1003.1	1010.79 (164)
	314.7	319.62 (54)
DU ³⁷ CI	1003.1	1010.79 (164)
	-	312.32 (53)
HU ⁷⁹ Br	1410.6	1432.02 (340)
	-	282.78 (87)
HU ⁸¹ Br	1410.6	1432.02 (340)
	-	282.57 (86)

Table 6. Comparison of observed and computed harmonic vibrational frequencies (in $\rm cm^{-1})$ for the HThCl, DThCl and HThBr molecules. $^{[a]}$

	Exptl (argon)	(Calcd					
		BP86/def-TZVP	CCSD(T)/aVTZ(-PP)					
HTh³⁵Cl	1483.8	1515.61 (363)	1541.19 (384)					
			1502.24 (379)					
	340.3	349.92 (66)	352.53 (55)					
			346.15 (57)					
HTh ³⁷ Cl	1483.8	1515.60 (363)	1541.19 (384)					
	-	342.27 (65)	346.51 (50)					
DTh³5Cl	1058.0	1074.39 (183)	1092.54 (193)					
			1072.83 (191)					
	335.8	346.35 (51)	342.71 (49)					
			338.7 (49)					
DTh ³⁷ Cl	1058.0	1074.38 (183)	1092.53 (53)					
	-	338.29 (49)	334.85 (47)					
HTh ⁷⁹ Br	1485.4	1518.33 (305)	1543.80 (416)					
	-	270.08 (27)	309.00 (16)					
HTh ⁸¹ Br	1485.4	1518.32 (305)	1543.80(416)					
	-	269.71 (27)	308.85(15)					
[a] A comm	[2] A complete list of the computed harmonic frequencies is given in							

[a] A complete list of the computed harmonic frequencies is given in Table S1. Computed intensities are given in parentheses (km mol⁻¹). Anharmonic frequencies are indicated in italics.

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this band, which is illustrated in Figure 4. The DUCI counterpart shows the same band profile and growth on annealing at 1003.1 cm⁻¹. The high HUCI/DUCI frequency ratio 1406.6/ 1003.1 = 1.4002 is characteristic of a very heavy metal hydride vibration. (The H/D frequency ratio for the vibration of a hydrogen atom against a baseball would be 1.4142). The DFT calculated values using the BP86^[26-28] exchange-correlation functional for the U-H/D stretching mode in the harmonic approximation given in Table 5 are 1425.8 and 1010.8 cm⁻¹, respectively, which are 1.5 and 0.8% higher than the observed values, and in very good agreement for this level of theory especially for a uranium hydride vibration. The 1134.0 cm⁻¹ absorption exhibits the same band contour as the above strong HUCI band, but we cannot match it with any of the other vibrational modes for HUCI, nor can we find a deuterium or HBr counterpart. This band also appears with Zr ablation and HCl, so it is most likely due to an impurity in our HCl gas sample.

Far IR spectra in Figure 5 reveal the most obvious new band at 323.8 cm⁻¹ which increases on annealing like the stronger counterpart at 1404.6 cm⁻¹. Our DFT BP86 calculations find the two lowest modes to be mixed U-Cl stretch and H-U-Cl bend, and the stronger of these two bands to be at 328.7 cm⁻¹ which is just above the new band we observed so it is the best assignment we have for this mode of HUCI. The analogous mode for DUCI shifts down into the region for UCI₂, but fortunately a shoulder absorption at 314.7 increases on annealing and is appropriate for the DUCI counterpart. Obviously, our confidence in these far-IR assignments is not up to the higher level we have for the mid-IR absorptions of HUCI and DUCI. The increase for the above 1404.6 and 1003.1 cm⁻¹ bands on annealing the solid matrix to 25 or 35 K shows that their formation reactions are spontaneous. Reaction (1) is 322 kJ mol⁻¹ exothermic at the (ZPE corrected) BP86 level of theory.

$$U + HCI \rightarrow HUCI \ \Delta H = -322 \, kJ \, mol^{-1} \tag{1}$$

HUBr

The HBr experiments were performed for a chemical comparison with HCl. First, the strong HBr product band at 1410.6 cm⁻¹ in Figure 3 has the same profile as the HUCI counterpart, and the new band increases about 30% on annealing to 20 K (see Figure S3), but irradiation at 455 nm results in a slight decrease for this new absorption. Annealing to 25 and 30 K continues substantial increases, but final annealing to 35 K decreases the 1410.6 cm⁻¹ band. The HUBr band at 1410.6 has almost the same annealing behavior as HBr₂⁻ since both require the HBr reagent. First annealing to 15 or 20 K also decreases the HCI and HBr Q branch bands. The 6.0 cm⁻¹ blue shift for the major 1410.6 band from HUCl at 1404.6 is matched by a 6.2 cm⁻¹ blue shift in the BP86 frequency calculation for HUBr. This agreement shows that the approximations in each calculation are nearly the same. The calculated harmonic U–H frequency for HUBr at 1432.0 cm⁻¹ is 1.5% higher than the observed value, which is appropriate. The reaction to form HUBr is almost as exothermic as the chlorine counterpart [reaction (2)]:

$$U + HBr \rightarrow HUBr \ \Delta H = -301 \text{ kJ mol}^{-1}$$
⁽²⁾

H₂UCl₂ and H₂UBr₂

The strong bands for HUCl and for HUBr have no major lower frequency satellites, but weaker bands appear at 1569.8 and 1531.4 cm⁻¹ above HUCl and at 1553.1 and 1532.9 cm⁻¹ above HUBr (Figure 3). Our DCl experiment revealed a 1094 counterpart for the strongest 1531.4 band with a 1.400 H/D frequency ratio for this U–H stretching mode. Our BP86 calculations predict the strongest two U–H stretching modes for H₂UCl₂ (Table 7) to be 67 and 93 cm⁻¹ higher than computed for the U–H mode discussed above for HUCl, and likewise for H₂UBr₂

Table 7. Comparison of observed and computed harmonic vibrational frequencies (in cm^{-1}) for the H ₂ AnCl ₂ and H ₂ AnBr ₂ molecules.					
	Exptl (argon)	Calcd ^[a] BP86/def-TZVP			
H ₂ UCl ₂	1569.8	1518.77 (347)			
	1531.4	1492.42 (565)			
D_2UCI_2	1094	1076.00 (176)			
		1059.01 (288)			
H_2UBr_2	1553.1	1531.12 (331)			
	1532.9	1504.01 (488)			
H_2 ThCl ₂	1463.2	1506.22 (401)			
		1468.91 (575)			
D_2 ThCl ₂	1044.4	1067.12 (203)			
		1042.32 (294)			
H_2 ThBr ₂	1464.3	1511.63 (439)			
		1476.80 (545)			
[a] A complete list of the computed frequencies is given in Table S3. Computed intensities are given in parentheses (km mol ⁻¹).					

to be 72 and 99 cm⁻¹ higher than the calculated U–H mode for HUBr (Table 5). Now we turn to the two observed bands listed above for the product of reaction (3) to be 127 and 165 cm⁻¹ higher than HUCl and those above for the product of reaction (4) at 122 and 143 cm⁻¹ higher than HUBr. However, the computed U–H modes for H₂UCl₂ are 39 and 51 cm⁻¹ lower (about 3%) than the observed value and 22 and 29 cm⁻¹ lower (less than 2% of the observed value) than the observed bands for the dibromide. It is also possible for matrix site splittings to be involved with these absorptions. We assign the above pairs of new absorptions to the dihalides H₂UCl₂ and H₂UBr₂ whose energies of formation are also exothermic.

$$HUCI + HCI \rightarrow H_2UCI_2 \ \Delta H = -255 \text{ kJ mol}^{-1}$$
(3)

$$HUBr + HBr \rightarrow H_2 UBr_2 \ \Delta H = -251 \text{ kJ mol}^{-1}$$
(4)

H₃UCl₃ and H₃UBr₃

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We computed these molecules (Table S4 and S5) with hopes of finding them in our spectra, but there were no absorptions in the region about 40 cm^{-1} above $H_2\text{UCl}_2$ and $H_2\text{UBr}_2$ where the

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strongest absorptions for H₃UCl₃ and H₃UBr₃ are predicted to occur. These molecules converged to singlet ¹A₁ ground states (Table S4), with the *mer*-isomers ($C_{2\nu}$) 17 and 16 kJ mol⁻¹ lower in energy for X=Cl and Br, respectively, compared to the *fac*-isomer ($C_{3\nu}$). The calculated structures are shown in Figure 2. Their formations are exothermic [reactions (5) and (6)], but much less so than reactions (3) and (4).

 $H_2UCI_2 + HCI \rightarrow H_3UCI_3 \ \Delta H = -54 \text{ kJ mol}^{-1}$ (5)

 $H_2 UBr_2 + HCI \rightarrow H_3 UBr_3 \ \Delta H = -59 \text{ kJ mol}^{-1}$ (6)

HThCl and HThBr

The strong product band in the thorium atom reaction with HCl appeared at 1483.8 cm⁻¹, which is 79 cm⁻¹ above the uranium counterpart. This band increased slightly on annealing to 20 K along with the 1463.2 cm^{-1} satellite band (see Figure S6). The DThCl counterpart at 1058.0 had a sharp well resolved satellite at 1044.4 and a 1067.4 cm⁻¹ shoulder. Annealing to 30 K in this HCI/DCI experiment decreased the 1483.8 cm⁻¹ band and increased the satellite band at 1454.5 while the 1058.0 cm⁻¹ DThCl counterpart also decreased and the 1044.4 satellite increased (Figure 7). The same strong HCl₂⁻ and DCl₂⁻ anion bands were observed as in Figure 4. The HThCl/DThCl frequency ratio, 1483.8/1058.0=1.4024, is also indicative of a heavy metal hydride vibration. Unlike the uranium counterparts, no significant absorption bands were observed above the main bands. Our anharmonic vibrational analysis at the CCSD(T) level (Table 6) predicted this HThCl frequency 18.5 cm⁻¹ or 1.2% higher than the observed value. Also, the harmonic BP86 wavenumber, which is 31.8 cm⁻¹ higher than the observed value, is in very good agreement considering an anharmonic correction of -39 cm^{-1} . We must remember here that a red matrix shift on the order of ten wavenumbers is also expected for the observed frequencies, but since no AnH molecules have been observed in the gas phase this is an estimate. The corresponding frequency observed for HThBr 1485.4 cm⁻¹ is 1.6 cm⁻¹ higher than the frequency observed for HThCl and our BP86 calculation predicted a 2.7 cm⁻¹ difference, again showing that the errors in each calculation are almost the same. The BP86 frequency for HThBr is 32.9 cm⁻¹ or 2.2% higher than observed, which is certainly very good agreement for this harmonic frequency calculation. Finally, the ThH diatomic molecule absorption at 1485.2 cm⁻¹ in solid argon is within experimental error of the HThBr band at 1485.4 cm⁻¹ but not with HThCl at 1483.8 cm⁻¹. However the band profiles are very different: ThH exhibits a sharp symmetrical band.^[8] The broader bands with site splittings assigned here to HThCl and HThBr are not due to ThH.

The thorium reactions with HCl and HBr are even more exothermic than their uranium counterparts. The slight growth of HThCl and HThBr on annealing to 20 K shows that reactions (7) and (8) are also spontaneous.

 $Th + HCI \rightarrow HThCl \ \Delta H = -419 \, kJ \, mol^{-1}$ (7)

 $Th + HBr \rightarrow HThBr \ \Delta H = -410 \text{ kJ mol}^{-1}$ (8)

Spectra for the Th and HCl reaction products in the far-IR region are complicated by the presence of ThCl₄ and ThCl₂ in the same 10 cm^{-1} space. The top two spectra in Figure 8 examine the $Th + Cl_2$ reaction and give product absorptions at 340.5 and 330.5 cm⁻¹ for ThCl₄ and ThCl₂.^[50] Annealing to 30 K decreased the lower band with little effect on the higher absorption. The next two spectra come from an experiment with Th and HCl and the higher band is stronger than the lower band, the reverse of the top scan using Cl₂. This suggests that HThCl could be on top of a weak ThCl₄ band. Annealing to 20 K decreased both bands. Two scans from an experiment with Th and HCI/DCI are shown in Figure 9. The new band at 335.8 cm⁻¹ has got to come from DCl, and the 340.3 band is in the right place for the HCl counterpart. Thus, assignment of the new band at 335.8 cm⁻¹ to DThCl follows and probably HThCl also absorbs near 340.3 cm⁻¹ based on the DFT frequency calculations in Table 6.

Finally, we note that the computed increase in the H–An stretching frequencies in the series HAnF < HAnCI < HAnBr < HAn (An = U, Th, X = F, Cl, Br) is nicely confirmed by the experimental spectra (see Table 8).

H₂ThCl₂ and H₂ThBr₂

DFT calculations find the strong thorium dichloride and dibromide Th-H frequencies just below the strong HThCl and HThBr bands, in contrast to their uranium counterparts. Figures 6 and 7 show the spectra. Take the first band at 1463.2 cm⁻¹ below the strong 1483.8 band for HThCl and its deuterium counterpart at 1044.4 and their ratio is 1.4010, which is perfect for a Th-H stretching mode (Figure S7 and S9). The sharp bands that increase on 30 K annealing at 1446.3, 1454.5 and at 1034.2, 1039.8 are matrix sites for H₂ThCl₂ and D₂ThCl₂. Their H/D frequency ratios are 1.3985 and 1.3988 (Figure 7). The HBr counterpart at 1464.3 is 21.1 cm⁻¹ below the strong HThBr band and the first satellite band on the HThCl band is 20.6 cm⁻¹ lower than the strong band. The near agreement of these frequency differences and the only 1.6 cm⁻¹ difference between the main HThCl and HThBr bands tells us that we are dealing with halogen counterparts of the same product molecules. Again, their exothermicities are nearly the same. The annealing spectra (Figure 7) reveal decreases in the HThCl and DThCl bands and increases in the H₂ThCl₂ and D₂ThCl₂ absorptions on annealing to 30 K, which supports the participation of reactions (9) and (10). The differences between the H₂ThCl₂ band at 1463.2 and the H₂ThBr₂ band at 1464.3 cm⁻¹ is just 1.1 cm⁻¹ (see Table 7), a small difference near that has also been indicated above between the main HThCl and HThBr bands.

 $HThCI + HCI \rightarrow H_2 ThCl_2 \ \Delta H = -404 \text{ kJ mol}^{-1}$ (9)

$$HThBr + HBr \rightarrow H_2 ThBr_2 \ \Delta H = -401 \text{ kJ mol}^{-1}$$
(10)

Conclusions

Laser-ablated U and Th atoms react by insertion with HCl and with HBr to form the metal (II) state HUCl, HUBr and HThCl,

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HThBr molecules with considerable exothermicity, which are identified by their mid and far infrared spectra in solid argon. Our assignment of these reaction products is based on the close agreement between observed and calculated vibrational frequencies and with frequency differences between these molecules. The most interesting trend observed here is the increase in U-H stretching frequencies from 1383.1 (HUF), 1404.6 (HUCI), 1410.6 (HUBr) to 1423.6 cm⁻¹ (UH) as less electronic charge is removed from the U-H bond by the less electronegative substituent (Table 8). An analogous trend is observed for the Th-H stretching modes of the thorium counterparts 1464.8 (HThF), 1483.8 (HThCl), 1485.4 (HThBr) to 1485.2 cm⁻¹ (ThH).^[8] It is important to notice that the computed increase in the H–An stretching frequencies in the HAnF <HAnCI < HAnBr < HAn (An = U, Th, X = F, Cl, Br) series are in very good agreement with these trends in the experimental spectra (see Table 8).

Table 8. Observed (argon matrix) and computed U–H stretching frequencies (in cm^{-1}) for the HUX and HThX molecules.							
них	U—H Freq	Calcd	Ref.	HThX	Th—H Freq	Calcd	Ref.
HU HU ⁷⁹ Br HU ³⁵ Cl HUF	1423.6 1410.6 1404.6 1383.1	1466.7 ^[a] 1432.02 ^[b] 1425.79 ^[b] 1426.4 ^[a]	[7, 9, 14] this work this work [13, 14]	HTh HTh ⁷⁹ Br HTh ³⁵ Cl HThF	1485.2 1485.4 1483.8 1464.8	1493.9 ^[d] 1518.33 ^[c] 1515.61 ^[c] 1527.6 ^[e]	[8, 10] this work this work [15]
[a] Calculated at the DFT B3LYP/aug-cc-pVTZ (H,F) level using the SDD pseudopotential for U. [b,c] DFT BP86/def-TZVP (def-ECP with 60 electrons at U and Th) level. [d] B3LYP/6-311 + +G(3df, 3pd)/ SDD. [e] B3LYP/ aug-cc-pVTZ (H,F), Th: Stuttgart RSC 1997 ECP.							

This observation is consistent with an increase in the computed Mayer bond orders as well as in the corresponding densities at the bond critical point ((ρ_b) see Table 3) and indicates an increase in the H–U bond strength going down the halogen families of HAnX molecules. Additional absorptions are assigned to the H₂AnX₂ molecules formed by the exothermic reaction of a second HX molecule with the above primary HAnX products. DFT BP86 calculations also show that the H₃UX₃ molecules are stable, but unfortunately, they were not observed here.

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Conflict of interest

The authors declare no conflict of interest.

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FULL PAPER

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Infrared Spectra of the HAnX and H₂AnX₂ Molecules (An = Th and U, X = Cl and Br) in Argon Matrices Supported by Electronic Structure Calculations



Uranium and thorium hydrides are known as functional groups for ligand stabilized complexes and as isolated molecules under matrix isolation conditions. Here, the new molecular products of the reactions of laser-ablated U and Th atoms with HCl and with HBr, namely HUCl, HUBr and HThCl, HThBr, based on their mid and far infrared spectra in solid argon, is reported.