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Experimental and Theoretical Evidence for the Isolation of Thorium Hydride Molecules in Argon Matrices

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The primary reaction products of laser-ablated thorium atoms with dihydrogen, ThH, ThH_2, ThH_3, and ThH_4 have been isolated for the first time in an argon matrix and identified by the effects of isotopic substitution on their infrared spectra. DFT calculations provide firm theoretical support for the spectral assignments.

Introduction

Thorium metal reacts with dihydrogen to give ThH_2(s) or Th_4H_{15}(s) or mixtures of the two, depending upon the conditions used.[1] The crystal structures,[2−4] thermodynamic,[5] and physical properties, especially superconductivity[6−10] and nuclear magnetic resonance,[11,12] have been extensively studied for both compounds.

Theoretical calculations on the thorium hydrides ThH_4[13−15] and $HThCl_3$[16] have been performed, and the importance of relativistic effects in these compounds has been established. Pulsed-laser evaporation of metals has been demonstrated to be an effective way to produce metal atoms, for reaction with small molecules,[17−23] especially dihydrogen,[24−28] on condensation in excess argon at low temperatures. Here we report the matrix infrared spectra of several novel thorium hydride molecules and DFT-based theoretical calculations to support our spectral assignments.

Experimental Section

The technique used for matrix investigation of the reactions of pulsed-laser-ablated metal atoms has been detailed previously.[18−20] FTIR spectra were recorded on a Nicolet 550 at 0.5 cm^{-1} resolution and ± 0.1 cm^{-1} accuracy. Typically mixtures of between 0.5% and 2% dihydrogen in argon were deposited at a rate of ca. 3 mmol/h for 2 h onto a CsI window held at 6−7 K while the thorium metal target (Oak Ridge National Laboratory) was ablated using 35−50 mJ pulses from a Nd:YAG laser 1064 nm fundamental focused onto the target. In some experiments the argon/dihydrogen mixture was discharged in a 6 mm o.d. quartz tube using a microwave source at relatively low powers of ca. 30 W to provide a source of H atoms. Variation of the laser power used also gave rise to different relative intensities of the product bands. After deposition the samples were annealed to 20 K, photolyzed using a 175-W mercury street lamp (Philips H39KB) with the globe removed and then further annealed, typically to 30, 35, and 40 K.

Theoretical Section

The Amsterdam Density Functional code (ADF 2.0.1) developed by Baerends and colleagues was used to carry out all the calculations.[29] These DFT calculations employed the Vosko−Wilk−Nusair potential in the context of the local density approximation (LDA), along with the Becke (B) and Perdew (P) gradient corrections to the exchange and correlation energies. Nonlocal gradient corrections were explicitly accounted for in each SCF cycle. ADF employs a series of Slater basis functions and the adjustable parameter controlling the accuracy of the numerical integration was set at a value of 6.0.[30] A triple-ζ basis set was used for thorium and a triple-ζ basis set with polarization was used for hydrogen; the core electrons in thorium were frozen up to the 5d level to treat relativistic core effects. Quasirelativistic corrections were employed using the Pauli formalism with corrected core potentials. The quasi relativistic frozen core shells were generated using the auxiliary program Dirac. The resultant approach has been shown to improve results considerably over first-order treatments.[31−33]

Results and Discussion

Figures 1 and 2 show the spectra of the matrix-isolated products from the reactions of Th with H_2 and D_2, respectively, and the effects of annealing and photolysis upon these deposits. Figures 3 and 4 show the spectra of the matrix-isolated products from the reactions of Th with H_2, HD, H_2/D_2, and D_2, as well as the effect of using higher laser power in the reaction between Th and H_2 or D_2. The frequencies of the observed bands together with their proposed assignments are presented in Table 1. Below 900 cm^{-1}, bands attributable to ThO (880 cm^{-1})[34] and ThO_2 (787, 736 cm^{-1})[34] were present but very weak, indicating minimal atmospheric contamination. The discharge experiments, as expected, increased the yield of products and enhanced the relative yields of ThH and ThH_3. Using higher laser powers had much the same effect, probably as a result of the large excess energy imparted to the thorium atoms,[35,36] leading to dissociation of some of the dihydrogen reagent. For all quoted hydride frequencies in the ensuing discussion, numbers in parentheses refer to the corresponding deuteride counterpart.

ThH. The band at 1485.2 (1060.2) cm^{-1} is assigned to the diatomic ThH (ThD) molecule. The H/D isotopic ratio of 1.4009 is slightly below the harmonic diatomic value, 1.4106, as a result of anharmonicity. This product was favored at low concentrations of dihydrogen, by using high laser powers and also in the discharge experiments, especially upon annealing, owing to larger numbers of H atoms present in the matrix. The band was invariant with respect to isotopic mixtures. The band at 1495.4 (1067.1) cm^{-1} appears to be either a site or a dihydrogen complex of ThH. Both bands grow upon annealing

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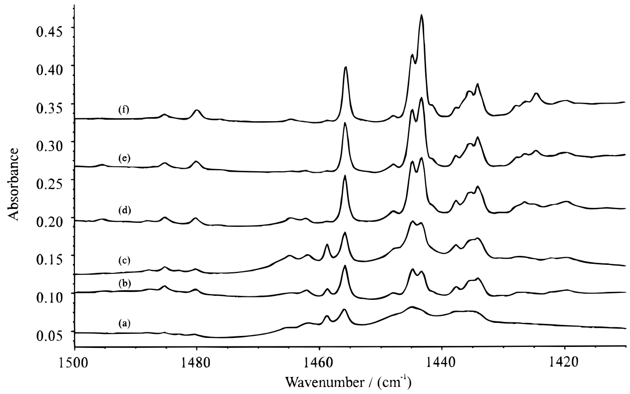

Figure 1. Infrared spectra in the region 1500−1410 cm^{-1} for samples from the reactions of Th atoms with 1% H_2 in argon during condensation at 6−7 K: (a) 1 h deposition; (b) annealed to 20 K; (c) broad-band photolysis; (d) annealed to 30 K; (e) annealed to 35 K; (f) annealed to 40 K.

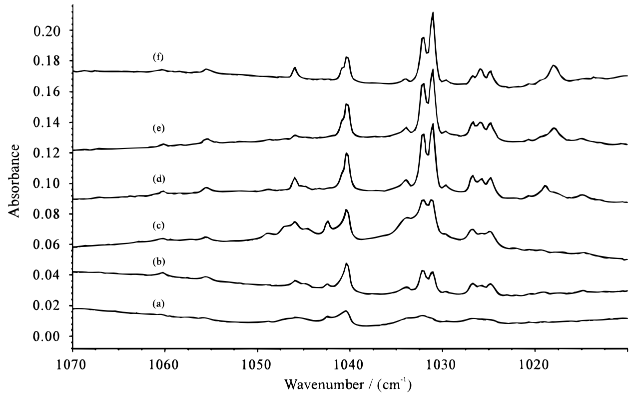

Figure 2. Infrared spectra in the region 1070−1010 cm^{-1} for samples from the reactions of Th atoms with 1% D_2 in argon during condensation at 6−7 K: (a) 1 h deposition; (b) annealed to 20 K; (c) broad-band photolysis; (d) annealed to 30 K; (e) annealed to 35 K; (f) annealed to 40 K.

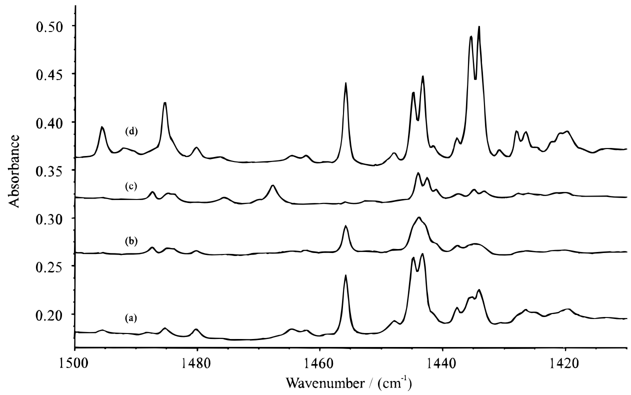

Figure 3. Infrared spectra in the region 1500−1410 cm^{-1} for samples from the reactions of Th atoms with 1% reagent mixtures in argon during condensation at 6−7 K: (a) H_2, (b) H_2/D_2, (c) HD, and (d) H_2 using higher laser power, after annealing to 20 K followed by broad-band UV photolysis and further annealing to 30 K.

and decrease slightly upon photolysis, possibly due to the reaction $ThH + H_2 \rightarrow ThH_3$. DFT calculations, as detailed in Table 2 and Figure 5, predict a doublet ground state for ThH with its vibrational mode occurring at 1496 cm^{-1} with an intensity of 162 km/mol, in excellent agreement with the observed frequency value.

ThH_2. Bands at 1480.1 (1055.6) and 1455.6 (1040.3) cm^{-1} correspond to the ν_1 and ν_3 modes, respectively, of a bent ThH_2 (ThD_2) molecule. The H/D frequency ratios, 1.4021 and 1.3992, are also slightly below the harmonic diatomic value. The lower H/D ratio for the antisymmetric stretch helps confirm the assignment, as examination of the Wilson **G** matrix reveals a greater contribution to this stretching mode from the thorium, resulting in a slight lowering in the H/D ratio, as expected for an MH_2 molecule with a bond angle greater than 90°. The ThH_2 is formed predominantly by direct insertion of thorium into a dihydrogen molecule as testified by the fact that only HThH and DThD are observed in the reaction between thorium and a H_2/D_2 mix, whereas the reaction with HD at low laser powers gave almost no HThH nor DThD, but new bands at 1467.7 and 1048.6 cm^{-1}, corresponding to the Th−H and Th−D stretching modes of the HThD molecule. At higher laser powers, the major dihydride is still HThD, but there is also a little ThH_2 and ThD_2 present. The large kinetic energies of the thorium atoms in the higher laser power experiments facilitate a dissociative reaction to give ThH and H, and ThH_2 (ThD_2) are then formed by reactions involving hydrogen(deuterium) atoms, as shall be discussed later. The Th−H (Th−D) stretch of the HThD molecule is observed at an energy almost exactly halfway between the ν_1 and ν_3 modes of HThH (DThD) and this provides further proof of the validity of these assignments. Annealing of the matrix causes the yield of ThH_2 to increase, but broad-band UV photolysis decreases the intensity of the ThH_2 bands presumably due to photoinduced reaction of ThH_2 with H_2. DFT calculations predict ThH_2 to have a triplet ground state with ν_1 occurring at 1454 cm^{-1} and ν_3 at 1399 cm^{-1}, with intensities of 190 and 624 km/mol, respectively. The observed bands at 1480.1 and 1455.6 cm^{-1}, with relative intensities of approximately 1:5.5 are in excellent agreement with the calculations.

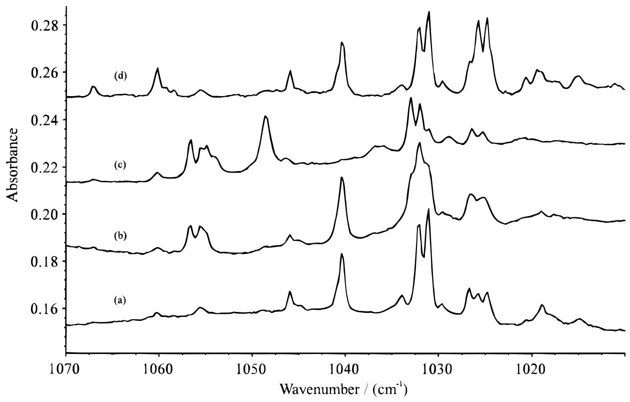

Figure 4. Infrared spectra in the region 1070−1010 cm^{-1} for samples from the reactions of Th atoms with 1% reagent mixtures in argon during condensation at 6−7 K: (a) D_2, (b) H_2/D_2, (c) HD, and (d) D_2 using higher laser power, after annealing to 20 K followed by broad-band UV-photolysis and further annealing to 30 K.

A set of bands at 1482.7 (1057.5) and 1458.7 (1042.4) cm^{-1} are assigned to the ν_1 and ν_3 modes of the dihydride ThH_2 (ThD_2) present in a different matrix site. The bands are observed to grow on photolysis, presumably as a result of photoinsertion of Th atoms into H_2, but disappear completely upon annealing as the more thermodynamically favored site is preferred. The two bands exhibit approximately a 1:5.5 relative intensity pattern and display isotopic ratios (1.4021 and 1.3994, respectively) consistent with their assignment to the symmetric and antisymmetric modes of ThH_2 (ThD_2). A similar pair of bands is observed at 1471.9 and 1049.7 cm^{-1}, also with relative intensities of approximately 1:5.5, and an isotopic ratio of 1.4022, in the HD experiment. These bands are not present in the H_2/D_2 experiment confirming that they are due to the HThD molecule formed by direct insertion of Th into HD.

TABLE 1: Observed Infrared Absorptions (cm^{-1}) of the Dominant Products in the Reaction of Laser-Ablated Thorium Atoms with H_2, D_2, and HD Trapped in an Argon Matrix at 6−7 K

Th + H_2	Th + D_2	Th + HD	assignment
1485.2	1060.2	1485.2, 1060.2	ThH/ThD
1495.4	1067.1	1495.4, 1067.1	site/H_2 complex of ThH/ThD
1480.1	1055.6		ν_1(ThH_2/ThD_2)
		1467.7	Th−H stretch of HThD
		1048.6	Th-D stretch of HThD
1455.6	1040.3		ν_3 (ThH_2/ThD_2)
1435.4, 1434.1	1025.9, 1024.8		e mode of ThH_3/ThD_3
		1434.9, 1433.2	b_2 mode of ThH_2D
		1026.4, 1025.3	b_2 mode of $ThHD_2$
1444.8, 1443.3	1032.1, 1031.1		as. mode of ThH_4/ThD_4[a]
		1487.3, 1484.5	Th−H ss. mode of ThH_2D_2[b]
		1443.9, 1441.1	Th−H as. mode of ThH_2D_2[a]
		1056.6, 1054.9	Th−D ss. mode of ThH_2D_2[b]
		1033.0, 1031.0	Th−D as. mode of ThH_2D_2[a]

[a] as. = antisymmetric stretching. [b] ss. = symmetric stretching.

TABLE 2: Results of DFT Calculations on Thorium Hydrides

		DFT (LDA + BP)		
molecule and symmetry	multiplicity of ground state	stretching frequencies (cm^{-1})	intensities (km/mol)	molecular parameters
ThH ($C_{\infty v}$)	doublet	1496	162	r(Th−H) = 1.99 Å
ThH_2 (C_{2v})	triplet	ν_1 1454 (a_1)	190	r(Th−H) = 2.04 Å
		ν_3 1399 (b_2)	624	ϕ(HThH) = 114°
ThH_3 (C_{3v})	doublet	ν_1 1475 (a_1)	61	r(Th−H) = 2.05 Å
		ν_3 1409 (e)	1600	ϕ(HThH) = 114°
ThH_4 (T_d)	singlet	ν_1 1504 (a_1)	0	r(Th−H) = 2.06 Å
		ν_3 1413 (t_2)	2359	ϕ(HThH) = 109°

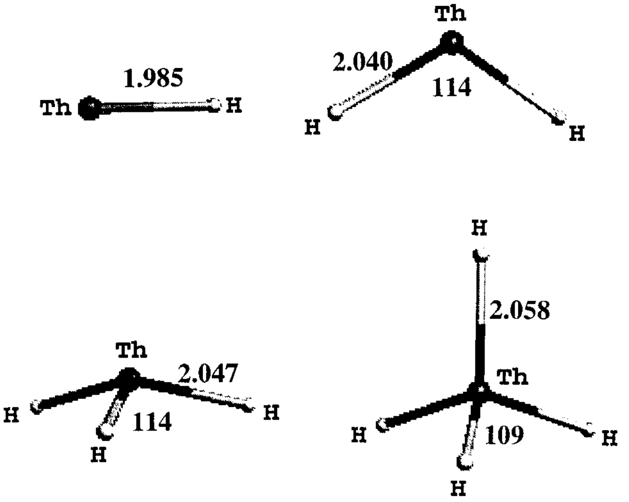

Figure 5. Thorium hydride structures calculated by ADFT; bond distances in angstroms and bond angles in degrees.

ThH_3. The bands at 1435.4 (1025.9) and 1434.1 (1024.8) cm^{-1} are assigned to the antisymmetric stretch of a pyramidal ThH_3 molecule present in two different matrix sites. The relative intensity of the band increases in the discharge experiments and when higher laser powers are used, giving a strong indication that this absorption is indeed due to a species containing an odd number of hydrogens. The Th−H antisymmetric stretch broadens and shifts to ca. 1435, 1434.1, 1433.5 cm^{-1} in the H_2/D_2 experiments and to ca. 1434.9, 1433.2 cm^{-1} in the HD experiments, while the Th−D antisymmetric stretch broadens and shifts up to ca. 1026.6, 1025.0 and 1026.4, 1025.3 cm^{-1} in the H_2/D_2 and HD experiments, respectively. These shifts are due to the presence of ThH_2D and $ThHD_2$ whose antisymmetric stretches are expected to be very close to the e-mode of ThH_3, as indeed is observed for similar MH_3 molecules.[27,37,38] DFT calculations predict ThH_3 to have C_{3v} symmetry and a doublet ground state with the a_1 stretching mode occurring at 1474.9 cm^{-1} and the e stretching mode at 1409 cm^{-1}, with intensities of 61 and 1600 km/mol. These calculated intensities are consistent with the inability to observe the a_1 mode of ThH_3 experimentally. ThH_3 increases in intensity upon both photolysis and initial annealing, but at higher temperatures its intensity decreases as a result of polymerization, as evidenced by the growth of very broad features at ca. 1386 (992) and 1368 (978) cm^{-1}.

ThH_4. The sharp bands at 1444.8 and 1443.3 cm^{-1} in the H_2 experiments and 1032.1 and 1031.1 cm^{-1} in the D_2 experiments are assigned to the antisymmetric stretch of the ThH_4 and ThD_4 molecules, respectively, present in two different matrix sites. In the reaction with HD, bands occur at 1487.3 (1056.6) cm^{-1} and 1484.5 (1054.9) cm^{-1} due to the symmetric Th−H (Th−D) stretch of the ThH_2D_2 molecule and at 1443.9 (1033.0) and 1441.1 (1031.0) cm^{-1} due to the antisymmetric Th−H (Th−D) stretch of ThH_2D_2, also present in two different matrix sites. The relative intensities and change in profile of these two sets of bands mirror each other on both annealing and photolysis, confirming that they are vibrations of the same molecule present in two different matrix environments. The observation of four distinct absorptions due to the four stretching modes of the ThH_2D_2 molecule confirms the identification of thorium tetrahydride. Similar evidence has been found for other metal tetrahydride molecules.[21,26−28] For a tetrahedral or near-tetrahedral MH_4 molecule, isotopic substitution of one hydrogen for a deuterium lowers the symmetry to C_{3v}, and three bands are expected for the vibrational stretching mode, namely, M−H stretches with a_1 and e symmetry and an M−D stretch of a_1 symmetry. Experiments with HD/H_2 mixtures showed new bands corresponding to the Th−H and Th−D stretches of ThH_3D, while experiments with HD/D_2 mixtures showed new bands corresponding to the Th−H and Th−D stretches of $ThHD_3$. ThH_3D occurs in two different sites and shows a Th−D stretch at 1044.7, 1043.6 cm^{-1}, a symmetric Th−H stretch at 1505.6, 1503.8 cm^{-1}, and an antisymmetric Th−H stretch at 1444.2, 1443.0 cm^{-1}. $ThHD_3$ also occurs in two sites and shows a Th−H stretch at 1465.6, 1464.1 cm^{-1}, a symmetric Th−D stretch at 1070.1, 1068.6 cm^{-1}, and an antisymmetric Th−D

TABLE 3: Selected Infrared Absorptions (cm^{-1}) for the Hydrides of Ti, Zr, Hf, Th, and U in Solid Argon

metal, M	MH	MH_2	MH_3	MH_4	ref
Ti	1385.3	1435.5 (ν_3)	1580.6	1663.8	21
Zr	1540.8(?)	1518.6 (ν_3)	1545.3	1623.6	26, 39
Hf	1637.8	1622.4 (ν_3)	1646	1683.2	26, 39
Th	1485.2	1480.1 (ν_1), 1455.6 (ν_3)	1435.4, 1434.1[a]	1444.9, 1443.2[a]	this work
U	1423.6	1406.1 (ν_1), 1370.7 (ν_3)[b]	1346.8	1483.6, 1481.7[a]	27, 28

[a] Present in two different sites. [b] Present in different sites (only the highest energy absorption is listed).

stretch at 1032.2, 1031.5 cm^{-1}. ThH_2D_2 was present in both these experiments while ThH_4 appeared only in the HD/H_2 experiment and ThD_4 only in the HD/D_2 experiment. These observations together with the fact that neither $ThHD_3$ nor ThH_3D were seen in experiments run with HD or H_2/D_2 shows that the formation of ThH_4 occurs primarily by stepwise addition of two dihydrogen units, not via reactions involving hydrogen atoms. The observation of one band for ThH_4, three bands for ThH_3D and four bands for ThH_2D_2 implies that the ThH_4 molecule has tetrahedral or near-tetrahedral symmetry. The bands due to these molecules increase markedly in intensity upon both photolysis and initial annealings but, at higher temperatures, decrease due to polymerization.

DFT calculations predict that the ThH_4 molecule is almost tetrahedral (the geometry optimized to lowest energy using no symmetry, but the bond lengths and angles are extremely close to those needed for tetrahedral symmetry, and this deviation from tetrahedral symmetry is well within the error margin of the calculation). The frequency calculation was performed assuming no symmetry, owing to technical difficulties in applying the code when using tetrahedral symmetry. Assuming tetrahedral symmetry, the a_1 mode is predicted to occur at 1504 cm^{-1} and the t_2 mode at ca. 1413 cm^{-1} (value obtained by averaging the three modes, 1418, 1412, and 1410 cm^{-1}, obtained using no symmetry). The value predicted for the t_2 stretching mode, 1413 cm^{-1}, is in excellent agreement with the bands at 1444.8 and 1443.3 cm^{-1} observed for the two sites of ThH_4. That the a_1 mode is predicted to be higher in energy is in pleasing agreement with the experimental observation of the a_1 modes of ThH_3D, ThH_2D_2, and $ThHD_3$ at higher energy than the antisymmetric stretches.

Other Bands. Broad bands are observed to grow upon annealing deposits to 30 K or higher at ca. 1427 (1019) and 1420 (1015) cm^{-1} in the reactions of Th with H_2 (D_2). These bands shift to 1426 (1019) and 1420 (1015) cm^{-1} in the reaction with HD and 1427 (1020) and 1422 (1018) cm^{-1} in the reaction with an H_2/D_2 mixture. These broad bands may be due to terminal Th−H (Th−D) stretching modes of higher oligomers of the type $[ThH_x]_y$.

Other extremely broad bands, that also grow upon annealing to higher temperatures, at ca. 1386 (992) and 1368 (978) cm^{-1} can be assigned to polymeric $[ThH_x]_n$.

Reaction Mechanisms

The mechanisms of product formation and their energies of reaction, based on DFT calculations, are presented below.

$$\mathrm{Th} + \mathrm{H_2} \rightarrow \mathrm{ThH} + \mathrm{H} \qquad \Delta E = +144\ \mathrm{kJ\ mol^{-1}} \tag{1}$$

$$\mathrm{Th} + \mathrm{H_2} \rightarrow \mathrm{ThH_2} \qquad \Delta E = -185\ \mathrm{kJ\ mol^{-1}} \tag{2}$$

$$\mathrm{ThH} + \mathrm{H_2} \rightarrow \mathrm{ThH_2} + \mathrm{H} \qquad \Delta E = +136\ \mathrm{kJ\ mol^{-1}} \tag{3}$$

$$\mathrm{ThH} + \mathrm{H} \rightarrow \mathrm{ThH_2} \qquad \Delta E = -330\ \mathrm{kJ\ mol^{-1}} \tag{4}$$

$$\mathrm{ThH} + \mathrm{H_2} \rightarrow \mathrm{ThH_3} \qquad \Delta E = -194\ \mathrm{kJ\ mol^{-1}} \tag{5}$$

$$\mathrm{ThH_2} + \mathrm{H_2} \rightarrow \mathrm{ThH_3} + \mathrm{H} \qquad \Delta E = +135\ \mathrm{kJ\ mol^{-1}} \tag{6}$$

$$\mathrm{ThH_2} + \mathrm{H_2} \rightarrow \mathrm{ThH_4} \qquad \Delta E = -195\ \mathrm{kJ\ mol^{-1}} \tag{7}$$

$$\mathrm{H_2} \rightarrow 2\mathrm{H} \qquad \Delta E = +466\ \mathrm{kJ\ mol^{-1}} \tag{8}$$

As can be seen, the excess energy imparted to the thorium atoms during ablation is necessary for the formation of ThH. The high kinetic energies of pulsed laser-ablated metals are well-known and have been documented for aluminum and nickel.[35,36] Whether it is this excess kinetic energy, the excess electronic energy or the presence of highly reactive cations which subsequently recapture electrons after reaction that permits this endothermic process to occur cannot be determined by these experiments. Given the energetics indicated above (reactions 3 and 4), the small quantities of ThH_2 and ThD_2 present in the reaction of Th with HD at higher laser powers, especially upon annealing, must be formed via addition of H atoms to ThH, not via H abstraction from HD, unless the ThH is in an excited state. The energies indicated by reactions 5 and 6 show that ThH_3 is generated from the reactions of ThH with H_2 and ThH_2 with H, not from ThH_2 and H_2. The large exothermicity of reaction 5 may be part of the reason for the low yield of ThH. The experimentally observed products from the reactions of Th with H_2, D_2, HD, HD/H_2, H_2/D_2, and HD/D_2 indicate that reaction 7 is the predominant means by which ThH_4 is formed, rather than reactions involving H atoms. The analogous reaction is dominant in the Zr/H_2 and Hf/H_2 systems[39] as has been shown by high-level ab initio calculations which included electron correlation effects.[40] The values obtained for the Th−H bond energies are in excellent agreement with those calculated[16] (318 kJ mol^{-1}) for $HThCl_3$ and observed (ca. 335 kJ mol^{-1}) for $HTh(Cl)(C_5H_5)_2$.[41]

Conclusions

The molecules ThH, ThH_2, ThH_3, and ThH_4 have been isolated for the first time in solid argon from the reaction of laser-ablated Th atoms and H_2 molecules. Although vibrational frequencies cannot be directly related to bond energies, for heavy atoms the correlation between the two parameters is reasonably good as the reduced mass, μ, which is so heavily dependent upon the light atom, in this case hydrogen, hardly varies with the heavy metal present. The hydrides of titanium,[21] zirconium, and hafnium[26,39] have been characterized, and a comparison of their M−H stretching frequencies with those of thorium is presented in Table 3.

These data indicate that both zirconium and hafnium form stronger bonds with hydrogen than does thorium. No data are available for cerium, but uranium[27,28] does form stronger bonds with hydrogen than neodymium[42] and one might reasonably expect this trend to continue. Upon descending the triad of group 4, it can be seen that the bond strengths clearly increase owing to the better overlap of the 5d than the 4d than the 3d orbitals with hydrogen. Calculations confirm that the greater strength of the Hf−H bond than the Zr−H bond is mainly due to relativistic effects.[14,15,39] It is interesting to note that the observed stretching frequencies for ThH_2 occur at higher energy than those for UH_2, whereas for the tetrahydrides the pattern is reversed. For Ti, Zr, and Hf, the tetrahydrides all have higher stretching frequencies than the dihydrides, also in contrast to the order observed for thorium. Calculations by Pyykkö and Desclaux[14] have shown that by removing the 7p atomic orbitals from thorium, the 5f contribution to the bonding can be artificially enhanced and that, as a result, the Th−H bond length, R_e, for ThH_4 shortens markedly. The increased 5f orbital participation in the bonding for uranium has been used to explain the stability of UO_2^{2+} and can also be used to explain the greater U−H bond strength in UH_4 relative to the Th−H bond in ThH_4. The reaction of uranium with hydrogen under similar conditions[27,28] gave $U(\mu\text{-}H)_2U$ as a major product, but intriguingly no evidence could be found for such a product here. Whether this is a kinetic effect, due to the faster reaction between ThH and H_2 than between UH and H_2, resulting in greater concentrations of UH than ThH being available to dimerize is unclear. Energy calculations on the rhombic dimer Th_2H_2 predict a quintet ground state with a Th−Th bond length of 2.81 Å, considerably longer than the 2.18 Å of the U−U bond in U_2H_2, due in part to less 5f orbital contribution to the bonding. The singlet linear HThThH isomer is calculated to have an energy within 0.001 eV of that of the rhombic dimer. Within the accuracy of these calculations determining which is the preferred isomer is clearly not possible, but if the linear isomer were the lower in energy, this would provide an explanation for the lack of bands in the Th−H bridging region. The dimerization of ThH is still calculated to be highly exothermic, but there is little ThH present in the matrix, so it is perhaps not that surprising that its dimer has proved elusive.

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