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Infrared Spectra of ThH_2, ThH_4, and the Hydride Bridging $ThH_4(H_2)_x$ ($x = 1-4$) Complexes in Solid Neon and Hydrogen

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Laser-ablated Th atoms react with molecular hydrogen to give thorium hydrides and their dihydrogen complexes during condensation in excess neon and hydrogen for characterization by matrix infrared spectroscopy. The ThH_2, ThH_4, and $ThH_4(H_2)_x$ ($x = 1-4$) product molecules have been identified through isotopic substitution (HD, D_2) and comparison to frequencies calculated by density functional theory and the coupled-cluster, singles, doubles (CCSD) method and those observed previously in solid argon. Theoretical calculations show that the Th−H bond in ThH_4 is the most polarized of group 4 and uranium metal tetrahydrides, and as a result, a strong attractive "dihydrogen" interaction was found between the oppositely charged hydride and H_2 ligands $ThH_4(H_2)_x$. This bridge-bonded dihydrogen complex structure is different from that recently computed for tungsten and uranium hydride super dihydrogen complexes but is similar to that recently called the "dihydrogen bond" (Crabtree, R. H. *Science* **1998**, *282*, 2000). Natural electron configurations show small charge flow from the Th center to the dihydrogen ligands.

Introduction

The chemistry of early actinide atoms and reactions with other elements have attracted great interest because 5f electrons are involved in bonding while 4f electrons in lanthanide metals remain in the core.[1] This is dramatically demonstrated by the involvement of 5f orbitals in the U−U multiple bonds in a variety of compounds. The U−U multiple bond in U_2 itself and in compounds $U_2@C_{60}$, U_2Ph_2 (Ph = phenyl), U_2Cl_6, $U_2Cl_8^-$, $U_2(OCHO)_4$, and $U_2(OCHO)_6$ has been investigated theoretically, and the 5f, 6d, and 7s valence orbitals of U atom are involved in bonding.[2] With 5f orbital participation, a variety of oxidation states are found for actinides, which leads to the formation of unusual compounds and complexes with other elements. For example, uranium atoms react with H_2 to give UH_4, which in solid hydrogen ultimately forms the supercomplex $UH_4(H_2)_6$.[3] This molecule has potential interest as a metal hydride with a large number of hydrogen atoms bound to uranium. In contrast, Mo and W also form tetrahydride molecules, but calculations suggest that these coordinate only four dihydrogen ligands to give $MH_4(H_2)_4$ complexes.[4−6]

The IR spectra of several thorium atom reaction products with small molecules have been investigated in solid argon in this laboratory, and several interesting reactions and products have been observed.[7] More recent investigations show that thorium atoms react with CH_4 and NH_3 to form $CH_2{=}ThH_2$ and $HN{=}ThH_2$ molecules, which reveal multiple bonding for thorium with significant 5f orbital participation.[8,9] Laser-ablated thorium atom reactions with H_2 have been studied in solid argon, and the major ThH_2 and ThH_4 molecular species were identified.[10] In the pure solid state, such thorium hydride compounds as Th_4H_{15}, for example, form and behave as weak coupling semiconductors.[11]

We report here the further investigation of thorium metal atom reactions with molecular hydrogen in solid neon and pure hydrogen during condensation at 4 K. The ThH_2 and ThH_4 hydrides and the super dihydrogen thorium hydride complexes $ThH_4(H_2)_x$ ($x = 1-4$) are identified through infrared spectroscopy and quantum chemical calculations. Owing to the unique chemistry of thorium, the structure of this complex is computed to be different from the uranium and tungsten analogues.[3,6]

Experimental and Computational Methods

The experiment for investigating reactions of laser-ablated thorium atoms with hydrogen has been described in detail previously.[7,12] The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused onto a rotating thorium target (Oak Ridge National Laboratory). Laser-ablated metal atoms were codeposited with pure hydrogen or hydrogen (0.3−4%) in excess neon onto a 4 K CsI cryogenic window at 3 mmol/h for 30 min (for pure H_2) and 60 min (for neon). Deuterium gas and HD (Cambridge Isotopic Laboratories) and selected mixtures were used in different experiments. The laser energy was varied from 10 to 20 mJ/pulse. Reducing radiation from the ablation plume as low as possible makes solid H_2 easier to form and minimizes its evaporation. Fourier transform infrared (FTIR) spectra were recorded at 0.5 cm^{-1} resolution on Nicolet 750 with 0.1 cm^{-1} accuracy in the 4500−400 region using an HgCdTe range B detector. Matrix samples were annealed at different temperatures and were subjected to broad-band irradiation using a medium-pressure mercury arc lamp (Philips, 175W) with the outer globe removed.

Density functional theory calculations of thorium hydrides and dihydrogen complexes are given for comparison. The Gaussian 03 program[13] was employed to calculate the structures and frequencies of expected product molecules. All geometrical parameters were fully optimized with the B3LYP functional.[14] The 6-311++G(3df,3pd) basis set for hydrogen atom and SDD pseudopotential for thorium atom were used.[15,16] Analytical vibrational frequencies were obtained at the optimized structures. Single-point energies of optimized complex species were

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TABLE 1: Infrared Absorptions (cm^{-1}) Observed from Reaction of Thorium and Isotopic Dihydrogen in Solid Neon and Hydrogen

neon			hydrogen			identification
H_2	HD	D_2	H_2	HD	D_2	
1511.0		1078.3				ThH/ThD
1476.0	1475.5		1478.4			ThH_2
	1496.8, 1062sh					ThHD
	1055.0	1054.5			1053.9	ThD_2
1455.7			1453.1			ThH_4
	1496.2, 1454.9					ThH_2D_2
	1063.9, 1041.1					ThH_2D_2
		1040.1			1029.9	ThD_4
1393.1			1389.3			$ThH_4(H_2)_x$
1377.7			1374.3			$ThH_4(H_2)_x$
	1372.3			1412, 1366		$ThH_2D_2(HD)_x$
	991.3			1008, 988		$ThH_2D_2(HD)_x$
		992.2			991.8	$ThD_4(D_2)_x$
		982.4			979.6	$ThD_4(D_2)_x$
1345.8						?
	1340.2, 959.2					?
		959.2				?

calculated with coupled-cluster CCSD(T) methods.[17a] Natural charges were calculated by means of natural bond orbital (NBO)[17b] using built-in subroutines in the Gaussian 03 program, and B3LYP and BPW91 functionals with larger (6-311++G-(3df,3pd) and smaller (6-311++G(d,p) basis sets for hydrogen atom were used.

Multiconfigurational complete active space (CASSCF)[18] calculations followed by second-order perturbation theory (CASPT2)[19] were performed on $ThH_4(H_2)_4$ and $UH_4(H_2)_6$ complexes to understand the differences in the electronic structure between these systems. The tetrahydride molecules ThH_4 and UH_4 were also investigated at the same level of theory. Single-point energy calculations were perfomed at the density functional theory (DFT) optimized geometries.

Scalar relativistic effects were included using a Douglas−Kroll−Hess Hamiltonian and relativistic ANO-RCC basis set (2s1p for hydrogen and 9s8p6d5f2g1h for uranium and thorium).[20] In the CASSCF calculations, the orbitals formed by linear combinations of 7s, 6d, and 5f orbitals of uranium/thorium with 1s orbitals of the hydrogens were included in the active space, resulting in active spaces formed of 12 electrons in 12 orbitals (12/12) up to 16 electrons in 16 orbitals (16/16). In the following CASPT2 calculations, all orbitals up to and including 5d orbitals of uranium/thorium were kept frozen. This method has proven successful for the study of actinide chemistry.[21,22]

Results

Infrared spectra are presented for Th atom reactions with H_2 in excess neon and hydrogen, and the absorptions of reaction products are listed in Table 1. Absorptions common to pure hydrogen experiments, namely, $H(H_2)_n$, $D(D_2)_n$, $H^-(H_2)_n$, $D^-(D_2)_n$, and $D_3^+(D_2)_n$, have been reported previously[23,24] and are not discussed again here. Trace impurity absorptions for CO_2, CO, H_2O, and CH_4 appeared in all spectra, but no reaction products were observed with these molecules. Theoretical calculations are used to support the product identifications.

In Solid Neon. Infrared spectra for the Th−H and Th−D stretching regions are illustrated in Figures 1 and 2 for laser-ablated thorium atoms codeposited with H_2, HD, and D_2 in neon using 1−4% samples. In the Th−H stretching region, strong absorptions at 1455.7 and 1476.0 cm^{-1} and a weaker band at 1511.0 cm^{-1} appeared on deposition. The 1455.7 cm^{-1} band increased on >380 nm, >290 nm irradiation and annealing while the 1476.0 cm^{-1} band decreased on irradiation but increased on annealing. Two broad bands centered at 1393.1 and 1377.7 cm^{-1} appeared on deposition and increased markedly on later annealing and irradiation while a 1435 cm^{-1} band decreased. With D_2/Ne, the upper bands shift to the Th−D stretching region at 1078.3, 1054.5, 1040.1, 992.2, and 982.4 cm^{-1}. The HD/Ne experiments gave sharp bands at 1496.8, 1475.6, and 1454.9 cm^{-1} in the Th−H stretching region and at 1064.0, 1055.2, and 1041.1 cm^{-1} in the Th−D stretching region and gave broad bands centered at 1411.8, 1371.0, 1006.1 and 988.4 cm^{-1}.

Spectra from a more dilute 0.3% sample show weak, sharp 1511.0, 1476.0, and 1455.7 cm^{-1} bands and weak, broad bands at 1393 and 1378 cm^{-1}. Annealing to 8 K slightly increased the sharp bands with little effect elsewhere, but >320 nm and then 240−380 nm irradiations decreased the 1476.0 and increased the 1455.7 cm^{-1} band and increased broad features at 1435, 1421, 1393, and 1377 cm^{-1}. Subsequent annealings to 10 and 12 K increased both sharp bands and markedly increased the upper broad bands and destroyed the lower broad bands.

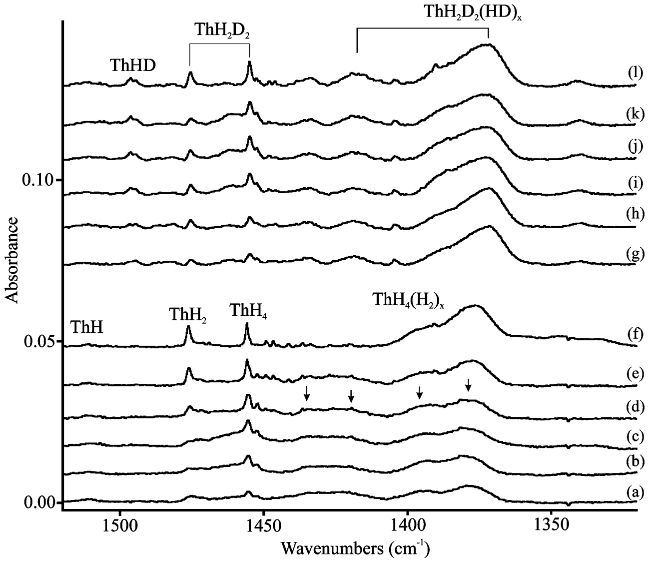

Figure 1. Infrared spectra for the thorium atom and H_2 reaction products in neon at 4 K. (a) Th + H_2 (1%) deposition for 60 min, (b) after annealing to 7 K, (c) after 240−380 nm irradiation, (d) after annealing to 8 K, (e) after annealing to 10 K, and (f) after annealing to 12 K. (g) Th + HD (4%) deposition for 60 min, (h) after annealing to 8 K, (i) after >320 nm irradiation, (j) after 240−380 nm irradiation, (k) after >220 nm irradiation, and (l) after annealing to 11 K. Arrows denote $ThH_4(H_2)_x$ complex absorptions.

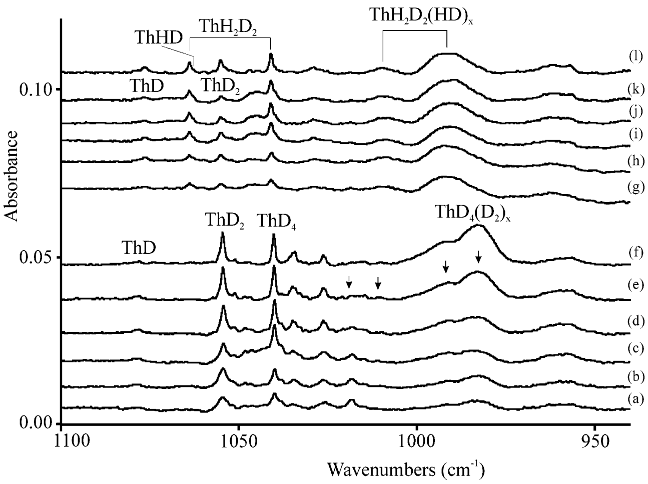

Figure 2. Infrared spectra for the thorium atom and D_2 reaction products in neon at 4 K. (a) Th + D_2 (2%) deposition for 60 min, (b) after annealing to 7 K, (c) after 240−380 nm irradiation, (d) after annealing to 8 K, (e) after annealing to 10 K, and (f) after annealing to 12 K. (g) Th + HD (4%) deposition for 60 min, (h) after annealing to 8 K, (i) after >320 nm irradiation, (j) after 240−380 nm irradiation, (k) after >220 nm irradiation, and (l) after annealing to 11 K.

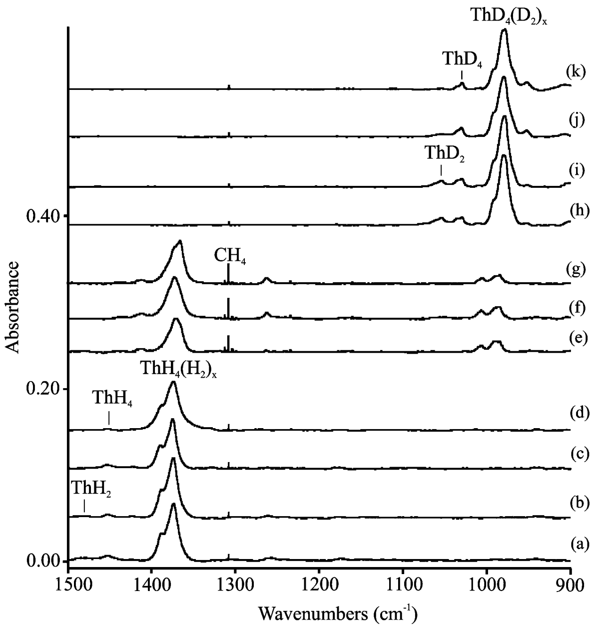

Figure 3. Infrared spectra for the thorium atom reaction with H_2, HD, and D_2 in solid hydrogen, deuterium hydride, and deuterium at 4 K. (a) Th + H_2 deposition for 25 min, (b) after >380 nm irradiation, (c) after >220 nm irradiation, and (d) after annealing to 6.4 K. (e) Th + HD deposition for 30 min, (f) after >320 nm irradiation, and (g) after annealing to 9 K. (h) Th + D_2 deposition for 25 min, (i) after >380 nm irradiation, (j) after >220 nm irradiation, and (k) after annealing to 8 K.

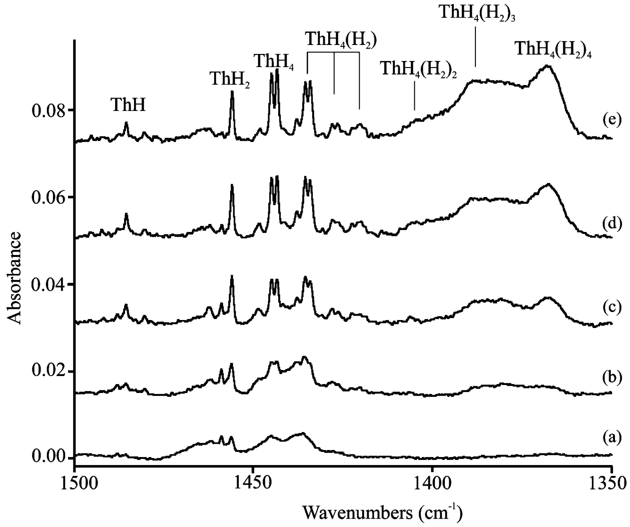

Figure 4. Infrared spectra for the thorium atom reaction with H_2 in solid argon at 4 K. (a) Th + H_2 (0.5%) deposition for 60 min, (b) annealing to 30 K, (c) after annealing to 35 K, (d) after annealing to 40 K, and (e) after annealing to 45 K.

Final annealings to 13 and 14 K decreased the sharp bands and increased the broad absorptions.

In Solid Hydrogen. Laser-ablated Th atom reactions with H_2 in solid hydrogen gave a very strong band at 1374.3 cm^{-1} with a shoulder at 1389.3 cm^{-1}. Two very weak bands were also observed at 1453.1 and 1478.4 cm^{-1}. In solid D_2, the counterpart bands appeared at 979.6 and 991.8 cm^{-1} (broad) with two weak bands at 1029.9 and 1053.9 cm^{-1}, respectively. Pure HD and Th gave a strong 1366.0 cm^{-1} band with a 1372.8 cm^{-1} shoulder and weaker bands at 1006.9, 989.9, and 984.8 cm^{-1}. These spectra are compared in Figure 4.

In Solid Argon. The Th + H_2 reactions in solid argon were done again using 4 K temperature to trap reactive species more efficiently, although spectra of Th + H_2 in argon at 8 K have been published. The initial ThH, ThH_2, and ThH_4 species are the same as we have assigned in our earlier paper,[10] but on annealing, several broad bands centered at 1405, 1382, and 1367 cm^{-1} appeared. With deuterium, these bands shifted to 1006, 993, and 978 cm^{-1}.

Discussion

Infrared spectra of thorium hydrides and their dihydrogen complexes will be assigned on the basis of isotopic shifts and correlation with density functional frequency calculations.

ThH. The ThH diatomic molecule was observed at 1485.2 cm^{-1} in solid argon with ThD counterpart at 1060.2 cm^{-1} (H/D ratio 1.4009).[10] The weak neon matrix band at 1511.0 cm^{-1} increases slightly on near-UV irradiation and annealing and is appropriate for assignment to ThH. The same absorption was weak in the HD experiments. A band with analogous behavior at 1078.3 cm^{-1} (H/D ratio 1.4013) in deuterium experiments is assigned to ThD. The B3LYP harmonic frequency of 1493.9 cm^{-1} suggests a repulsive interaction and blue shift in the neon matrix cage. The largest neon-to-argon shift observed here (25.8 cm^{-1}) is for ThH, which has more of the Th center exposed for matrix interaction than any of the higher hydrides. In this regard, then, we are considering here a $(Ng)_x$ThH complex. We expect that ThH will have a gas-phase fundamental near 1500 cm^{-1}.

ThH$_2$. Infrared spectra of ThH_2 have been reported in our earlier Th atom investigation with H_2 in solid argon.[10] In solid neon, the Th−H stretching mode of ThH_2 was found at 1476.0 cm^{-1}, which is 20 cm^{-1} higher than the same mode in solid argon. The slightly higher frequency suggests a weaker binding interaction of neon with Th than of argon. Such noble gas actinide binding interactions have been discussed in earlier papers.[25] The Th−D stretching mode in solid neon was observed at 1054.5, giving a 1.3998 H/D isotopic frequency ratio, which is appropriate for the Th−H stretching mode. With HD in neon, a new weak band at 1494.5 cm^{-1} (Th−H stretching region) and a 1062 cm^{-1} shoulder (Th−D stretching region) were observed. These bands are assigned to the appropriate stretching modes of HThD, and their appearance is 18.5 and 8 cm^{-1} higher than the antisymmetric stretching modes of ThH_2 and ThD_2, respectively, meaning that the symmetric stretching modes are at the same separation and higher still, namely, at 1518 and 1070 cm^{-1}. Our calculation (Table 2) predicts slightly larger (49 and 32 cm^{-1}) mode separations and symmetric stretching modes only 15% as intense, which are not observed here. Although the ThH and ThD bands are close to these positions, they do not track with the stronger ThH_2 and ThD_2 bands on irradiation and annealing. In solid hydrogen, a very weak absorption at 1478.4 cm^{-1} can be assigned to the ThH_2 molecule adsorbed on the matrix surface. However, any ThH_2 in the bulk hydrogen matrix will react with H_2 to give ThH_4 spontaneously. With solid deuterium, a weak ThD_2 band was observed at 1053.9 cm^{-1}.

The appearance of ThH_2 at 1475.5 cm^{-1} in the neon experiment with HD, along with ThD_2 at 1055.0 cm^{-1} and the former appearing 0.5 cm^{-1} lower and the latter 0.5 cm^{-1} higher than for the H_2 and D_2 reagents, respectively, suggests that some weak reagent association occurs with the ThH_2 product in the neon matrix and, more importantly, that most of the ThH_2 product is formed by combination of ThH and H atoms rather than by insertion into the hydrogen reagent.

ThH_4. In solid neon, a sharp band at 1455.7 cm^{-1} is appropriate for the Th−H stretching mode of ThH_4. The deuterium counterpart band at 1040.1 cm^{-1} showed the same annealing and irradiation behavior. The 1455.7 and 1040.1 cm^{-1} bands define a heavy metal hydride H/D ratio of 1.3996 and can be assigned to antisymmetric Th−H and Th−D stretching fundamentals of the tetrahydride on the basis of the following evidence. With HD, the above bands split to 1496.2 and 1454.8 cm^{-1} and to 1063.9 and 1041.0 cm^{-1}, respectively, which are due to symmetric and antisymmetric ThH_2 and ThD_2 stretching fundamentals in ThH_2D_2. This pattern of four Th−H(D) stretching modes identifies a metal tetrahydride molecule as described for MH_4^- (M = Sc, Y, La),[26] ZrH_4, and HfH_4.[27] Notice that the symmetric−antisymmetric mode separation for ThH_2D_2 is less, namely, 41.4 and 22.9 cm^{-1}, and that the H−Th−H bond angle, which affects stretch−stretch interaction, is also less than with ThH_2. Our calculations predict this mode separation to be 50.6 and 27.7 cm^{-1}, which is in very good agreement with the observed separations. In solid argon,[10] the absorptions of ThH_4 and ThD_4 were found at 1443.3 cm^{-1} and 1031.1 cm^{-1}, respectively, and the mode separations for ThH_2D_2 are 43.4 and 23.6 cm^{-1}, which are very close to the present neon matrix values.

In solid hydrogen, a weak band at 1453.1 cm^{-1} is appropriate for ThH_4. This band is located slightly lower than found for ThH_4 in neon but higher than in argon. This neon−hydrogen−argon absorption shift is found in many metal hydrides.[12] The weak band survives on deposition but disappears on annealing, suggesting that ThH_4 is trapped on the surface, and reacts with H_2 to give higher order complexes with the hydrides. With solid D_2, the absorption of ThD_4 was observed at 1029.9 cm^{-1}.

The strong degenerate ν_3 (t_2) mode calculated using the B3LYP method for ThH_4 at 1448.7 cm^{-1} and ThD_4 at 1028.1 cm^{-1} (H/D = 1.4091) is in excellent agreement with experimental values. The Th−H and Th−D symmetric and antisymmetric stretching mode splittings calculated for ThH_2D_2 are only 17% larger than the observed separations.

$ThH_4(H_2)$. In solid argon, strong doublet bands appeared at 1435.5 and 1434.1 cm^{-1} on deposition and increased greatly on annealing following Th atom reactions with H_2, which track two weak doublets at 1428.1, 1426.4 cm^{-1} and 1420.3, 1418.8 cm^{-1} (Figure 4). These bands are located slightly lower than the Th−H stretching vibration of ThH_4, and they show very similar band contours and annealing behaviors. With D_2, the strong doublets shift to 1028.9 and 1024.9 cm^{-1}, and two weak doublets shift to 1020.8 and 1019.6 cm^{-1} and to 1017.9 and 1017.0 cm^{-1}, revealing a very similar H/D ratio as for ThH_4. The counterpart bands in solid neon at 1435 cm^{-1} are weak, and no counterparts are observed in solid hydrogen, suggesting that this species is very reactive and can only be efficiently trapped in the more polarizable argon matrix. A H_2 complex with the ThH_4 core, $ThH_4(H_2)$, is suggested for these bands.

The HD substituted spectra strongly support this $ThH_4(H_2)$ assignment. There are six new doublets found in both Th−H and Th−D stretching regions, respectively, in Th atom reactions with HD in argon. First of all, the above strong doublet bands split into several new bands on symmetry lowering, which are due to symmetric and antisymmetric ThH_2 and ThD_2 stretching fundamentals perturbed by HD subunit in ThH_2D_2(HD). There are totally three isotopomers for ThH_2D_2(HD), and all of the isotopomers have the similar splitting pattern but different wavenumber shifts. Three bands for $ThH_4(H_2)$ at 1435.5, 1428.1, and 1420.3 cm^{-1} in Th−H stretching region split to three pairs at 1434.9 and 1470.3 cm^{-1}, 1427.8 and 1452.7 cm^{-1}, and 1421.6 and 1442.9 cm^{-1}, and three bands for $ThD_4(D_2)$ at 1025.9, 1020.8, and 1017.9 cm^{-1} in Th−D stretching region split to another three pairs at 1026.4 and 1056.8 cm^{-1}, 1020.9 and 1047.6 cm^{-1}, and 1018.2 and 1036.8 cm^{-1}, which are assigned to three different ThH_2D_2(HD) isotopomers. Theoretical frequency calculations match the observed values very well as listed in Table 3.

The 1435.5 cm^{-1} band was assigned to ThH_3 in our earlier paper because early theoretical calculations did not give isotopic frequencies, and the complicated HD isotopic shifts were misleading. We do not have a definitive assignment for the trihydride.

$ThH_4(H_2)_{2,3,4}$. A major broad band was observed at 1377.7 cm^{-1} with a shoulder at 1393.1 cm^{-1} in Th atom reactions with H_2 in solid neon, which appeared on deposition and which increased on annealing. These bands are still due to the Th−H stretching vibrations, but they are much lower than the same modes for ThH_2 and ThH_4. The deuterium counterparts in neon are at 992.2 and 982.4 cm^{-1}. With HD in neon, two broad bands were observed in Th−H stretching region at 1371.0 and 1411.8 cm^{-1} and in Th−D stretching region at 1007.7 and 988.4 cm^{-1}. This isotopic pattern suggests a metal tetrahydride structure for this molecule, so a series of thorium tetrahydride super dihydrogen complexes, $ThH_4(H_2)_x$, is proposed. Arrows denote $ThH_4(H_2)_x$ complex absorptions leading to the final, strongest broad band.

Theoretical calculations were performed at the CCSD(T) level with one to six H_2 molecules attached to ThH_4, and the energy profile is illustrated in Figure 6 and the Th−H stretching vibrations are listed in Table 2. First, as shown in Figure 6, this reaction is exothermic when one to four H_2 molecules are coordinated to ThH_4, but it is endothermic when more H_2 molecules are added, so the stable molecule in solid hydrogen is most likely due to the ThH_4 $(H_2)_x$ complex with $x = 4$. Second, our frequency calculations show that the Th−H stretching mode of $ThH_4(H_2)_4$ supercomplex reaches maximum red shift about 50 cm^{-1} from that of ThH_4 itself, which is close to the observed shift of about 70 cm^{-1}. As five and six H_2 molecules are added to ThH_4, the Th−H vibrations return to the Th−H stretching region of ThH_4 itself as the ligands are less strongly associated. Third, the calculated Th−H and Th−D splittings in $ThH_2D_2(HD)_4$ molecule match experimental values very well. The calculated antisymmetric−symmetric Th−H and

TABLE 2: Calculated and Observed Th−H Stretching Modes for Thorium Hydrides

species	calculated	observed		
		Ne	Ar	H_2
ThH	1493.9 (276)	1511.0	1485.2	
ThD	1059.0 (139)	1078.3	1060.2	
ThH_2 ($^1A_1$)	1539.5 (84,ν_1)		1480.1	
	1490.8 (538, ν_3)	1476.0	1455.6	1478.4
ThD_2	1090.2 (42)		1055.6	
	1058.1 (271)	1054.5	1040.3	1053.9
ThHD	1515.9(295)	1494.5	1467.7	
	1073.6(173)	1062	1048.6	
ThH_4 (^1A)	1542.5 (0)			
	1448.7 (8543)	1455.7	1435.4 (1434.1)[a]	1453.1
ThD_4	1091.0 (0)			
	1028.1 (3433)	1040.1	1025.9 (1024.8)[a]	1029.9
ThH_2D_2	1499.0(369)	1475.6	1487.3	
	1448.4(841)	1454.9	1443.9	
	1056.3(277)	1055.2	1056.6	
	1928.6(451)	1041.1	1033.0	
$ThH_4(H_2)$	1442.2(846)			
	1428.6(731)		1435.5 (1434.1)[a]	
	1420.5(767)		1428.1 (1426.4)[a]	
			1420.3 (1418.8)[a]	
$ThD_4(D_2)$	1075.3 (22)			
	1023.5 (430)		1025.9 (1024.9)[a]	
	1013.6 (372)		1020.8 (1019.6)[a]	
	1008.2 (390)		1017.9 (1017.0)[a]	
$ThH_4(H_2)_2$	1420.2(7602)		1405	
	1416.5(666)			
$ThD_4(D_2)_2$	1008.1(3862)			
	1004.8(340)			
$ThH_4(H_2)_3$	1415.7(767)		1382	1390
	1407.1(669)			
	1403.5(634)			
$ThD_4(D_2)_3$	1005.1(391)			
	998.5(339)			
	995.8(321)			
$ThH_4(H_2)_4$	1408.4(780)	1378	1367	1374
	1390.3(5822)			
$ThD_4(D_2)_4$	1000.3(395)	982		980
	987.0(2972)			
$ThH_2D_2(HD)_4$	1434.8(251)			1412
	1399.1(665)	1372		1366
	1013.2(201)			1008
	995.8(374)	992		988

[a] Matrix site splitting for observed band.

TABLE 3: Calculated and Observed Th−H and Th−D Stretching Modes for ThH_4, ThD_4, and Mixed ThH_2D_2 Isotopomers in the $ThH_4(HH)$ Complexes[a]

calcd	exptl	calcd	exptl	calcd	exptl
$H_2ThH_2(H_2)$		HDThHD(H D)		$H_2ThD_2(HD)$	
1520.0(41)		1480.3(402)	1452.7	1488.6(416)	1470.3
1442.2(846)	1435.5	1427.5(717)	1427.8	1442.0(837)	1434.9
1428.6(731)	1428.1	1044.5(283)	1047.6	1033.6(208)	1033.6
1420.5(767)	1420.3	1014.9(406)	1020.9	1008.9(404)	1018.2
$D_2ThH_2(HD)$		$D_2ThD_2(D_2)$			
1466.0(254)	1442.9	1075.3(22))			
1420.1(752)	1420.6	1023.5(430)	1025.9		
1050.1(296)	1056.8	1013.6(372)	1020.8		
1023.8(440)	1026.4	1008.2(390)	1017.9		

[a] B3LYP/6-311++G(3df,3pd)/SDD.

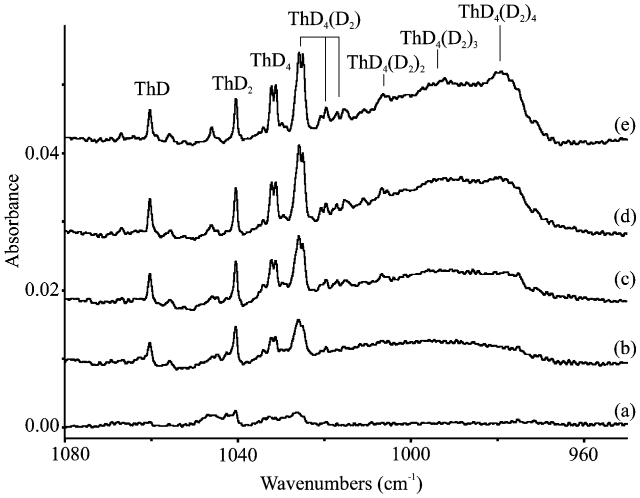

Figure 5. Infrared spectra for the thorium atom reaction with D_2 in solid argon at 4 K. (a) Th + D_2 (0.5%) deposition for 60 min, (b) annealing to 30 K, (c) after annealing to 35 K, (d) after annealing to 40 K, and (e) after annealing to 45 K.

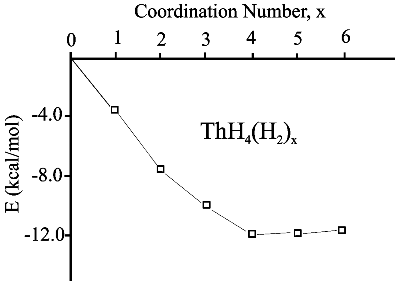

Figure 6. Total binding energy curves calculated for $ThH_4(H_2)_x$ complexes using the CCSD(T) method at the B3LYP converged minimum energy structures.

Th−D mode separations are 35.7 and 17.4 cm^{-1}, respectively, and the observed band separations are 46 and 20 cm^{-1} in solid hydrogen, which represents the maximum coordination of dihydrogen possible.

The solid hydrogen spectra strongly support the $ThH_4(H_2)_4$ assignment. After deposition, a very strong band at 1374.3 cm^{-1} with a shoulder at 1389.3 cm^{-1} was observed, which shows no further change on annealing. This suggests that the final reaction product is observed in solid hydrogen. In solid deuterium, these bands shift to 979.6 and 991.8 cm^{-1} as shown in Figure 3. The H/D ratio, 1.4029, is virtually the same as found for the broad band in solid neon, 1.4024, and for the sharp ThH_4 absorption in solid neon, 1.3996. The two absorptions are due to antisymmetric Th−H(D) stretching modes split by symmetry lowering from isolated tetrahedral ThH_4 to $ThH_4(H_2)_4$ in C_{2v} symmetry. Our calculation predicts this splitting to be 16 cm^{-1}, and we observe it to be 15 cm^{-1}.

Absorptions for $ThH_4(H_2)_2$ and $ThH_4(H_2)_3$ were observed at 1404 and 1388 cm^{-1}, respectively, in the argon matrix, which shift to 1006 and 994 cm^{-1} with deuterium. However, these bands are weak in solid neon and hydrogen.

The absorptions of $ThH_4(H_2)_4$ were observed at 1368.1 and 1385.8 cm^{-1} in solid argon as shown in Figure 4. Because of the more rigid argon matrix environment, these bands were not observed on deposition but appeared on annealing and maximized on higher annealing. This gives a clear mechanism that H_2 molecules are added to ThH_4 to form a super dihydrogen complex.

Search for HThThH. In view of our observation of $(UH)_2$ in analogous matrix isolation experiments,[3,28] we have searched diligently for evidence of the analogous interesting dithorium counterpart molecule.[29] If the ground-state molecule is linear, a terminal Th−H stretching modes is expected in the 1350 cm^{-1} region. Unfortunately, the weak 1346 cm^{-1} band does not show the computed HThThD isotopic shift for this identification. If

TABLE 4: Natural Charges and Electron Configurations Calculated for Metal Tetrahydrides and the $ThH_4(H_2)_4$ Complex[a]

	M	H	M−H bond length (Å)	natural electron configuration
ThH_4[c]	+2.631	−0.658	2.071	Th: [core] $7s^{0.49}\,5f^{0.16}\,6d^{0.74}$ H: $1s^{1.65}$
UH_4[c]	+2.458	−0.615	2.011	U: [core] $7s^{0.48}\,5f^{2.39}\,6d^{0.70}$ H: $1s^{1.60}$
HfH_4	+1.822	−0.455	1.854	Hf: [core] $6s^{0.73}\,5d^{1.44}$ H: $1s^{1.45}$
ZrH_4	+1.647	−0.416	1.851	Zr: [core] $5s^{0.65}\,4d^{1.70}$ H: $1s^{1.40}$
TiH_4	+1.297	−0.324	1.689	Ti: [core] $4s^{0.67}\,3d^{2.0}$ H: $1s^{1.31}$
$ThH_4(H_2)_4$	+2.678	−0.619 −0.025[b]	2.085	Th: [core] $7s^{0.38}\,5f^{0.24}\,6d^{0.71}$ H: $1s^{1.60}$ H[b]: $1s^{1.02}$

[a] B3LYP/6-311++G(3df,3pd)/SDD. [b] H atom from hydrogen molecule. [c] With BPW91/6-311++G(3df,3pd)/SDD, natural charges of Th and H for ThH_4 are +1.759 and −0.440; natural charges of U and H for UH_4 are +1.640 and −0.410. With B3LYP/6-311++G(d,p)/SDD, natural charges for Th and H are +1.873 and −0.468, and U and H are +1.757 and −0.439.

the ground-state molecule is bridged, new bands are expected in the 800−1100 cm^{-1} region where none are found. We believe that the very small yield of ThH in these experiments, which would dimerize to form HThThH, is the likely justification for its absence from our spectra. In contrast, UH is produced in higher yield, and its rhombic dimer is observed.[3,28] CASPT2 calculations indicate that HThThH has a rhombic structure and a $^1A_{1g}$ ground state, while DFT predicts a linear ^3A_g ground state.[29]

Bonding. The 5f orbital participation in the bonding for thorium and uranium has been discussed extensively.[1] Recently, we reported the evidence for six hydrogen molecules bound to the uranium tetrahydride center.[3] The 5f orbitals must play a very important role in bonding the dihydrogen ligands. A different complex $ThH_4(H_2)_4$ and structure are found for the thorium case, in which H_2 ligands are bridging the hydride centers suggesting a different bonding mechanism within the Th species. The U−H bond is computed to be 2.01 Å and the Th−H bond is computed to be 2.07 Å in the tetrahydrides, which is a difference typical of these metals. However, the U−H(H_2) distance of 2.38 Å is much shorter than the corresponding Th−H(H_2) distance of 2.53 Å. The average H_2 submolecule binding energies (2 kcal/mol for the six H_2 in the UH_4 complex[3] and 4 kcal/mol for the four in the present ThH_4 complex), however, suggest a stronger interaction in the ThH_4 complex.

To understand the bonding, we have calculated natural charges and natural electron configurations using NBO[17b] for the group 4 metal tetrahydrides, ThH_4, and UH_4, and the results are listed in Table 4. We have found the Th−H bond in ThH_4 to be the most polarized using both B3LYP and BPW91 density functionals and different basis sets, which results in strong intermolecular hydrogen bonding when a H_2 molecule is coordinated to ThH_4. On the other hand, the hydride in ThH_4 is the most electronegative in these metal tetrahydrides, which also interacts with H_2 giving additional stabilization energy. Our calculation for $ThH_4(H_2)$ gave a 1.949 Å distance between H(Th) and H(H_2) (as shown in Figure 7), which is much shorter than the normal H....H contact (2.4 Å),[25] and this unusually short distance suggests an attractive interaction between nonequivalent hydrogen atoms in the $ThH_4(H_2)$ complex. In fact, the coplanar bridge-bonded structure of the dihydrogen molecule and of the two hydride centers demonstrates an attractive interaction; otherwise, the dihydrogen molecule would torque out of this plane, as in other such complexes,[3,6] which are dominated by dihydrogen interaction with the metal centers. This attractive interaction with short H...H distance between oppositely charged hydrogen centers has been defined as a new type of hydrogen bond,[30] and several dihydrogen-bonded molecules with this type of bonding interaction have been found.[31]

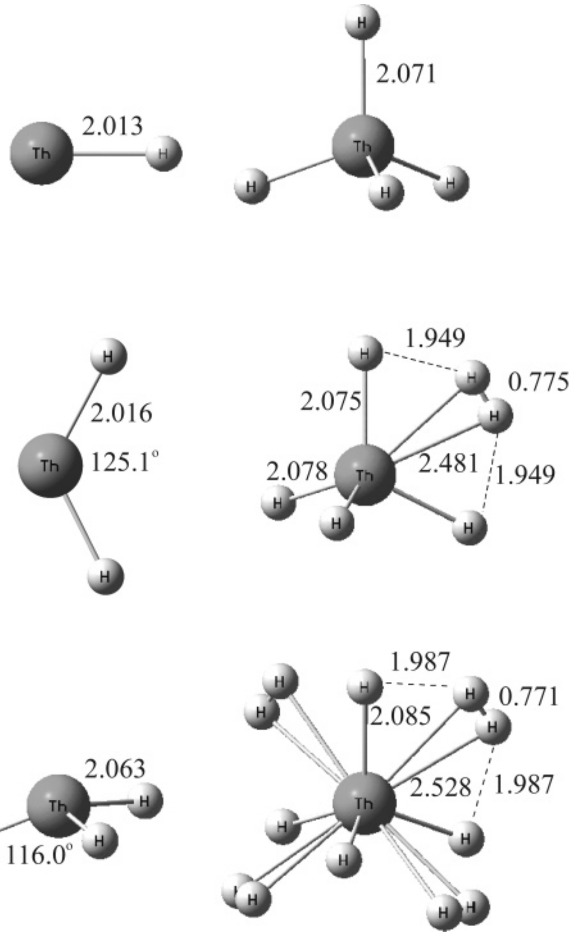

Figure 7. Structures for thorium hydrides calculated at the B3LYP/SDD/6-311++G(3df,3pd) level of theory.

The nature of this interaction is revealed by comparison of the natural charges for ThH_4 and the $ThH_4(H_2)_4$ complex (Table 4). The addition of the four dihydrogen ligands slightly elongates the Th−H bonds and increases the positive charge at the thorium center, and part of the negative hydride charge is shared with the dihydrogen ligands. The 7s character in the configuration decreases while the 5f character increases. The CASSCF electron density plots in Figure 8 further show evolution of the interaction. The smallest iso density (0.02) reveals a weak interaction with the metal center, but as the iso density increases, interaction with the H's is also apparent.

The uranium tetrahydride has similar properties, but the U−H bond polarization is less than the Th−H bond on the basis of the natural charge calculation. As a result, the attractive interaction in $UH_4(H_2)_6$ depends on interaction with the uranium metal center. The M−H bond polarization for d-type metal tetrahydrides (TiH_4, ZrH_4, and HfH_4) is much less, and weak attractive interactions are expected in these molecules.

Inspection of the CASSCF wave function for both the U and Th complexes shows that the ground state is a singlet in both ThH_4 and $ThH_4(H_2)_4$, while it is a triplet in both UH_4 and $UH_4(H_2)_6$. There is not a change in the ground state in going from the actinide-tetrahydride to the supersystem, unlike the more

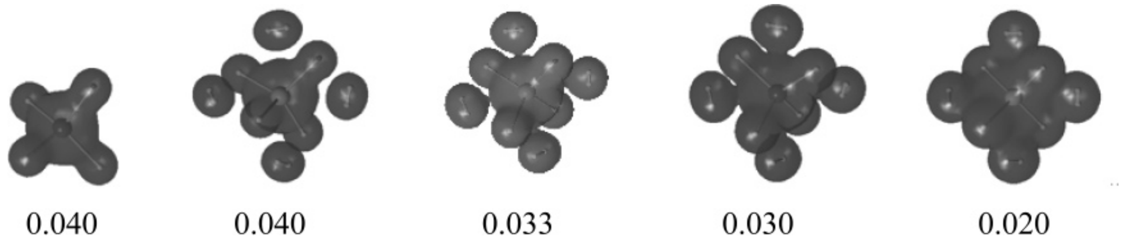

Figure 8. Electron density plots for thorium tetrahydride and the tetradyhydrogen complex calculated at the CASSCF level of theory. Iso density values given below.

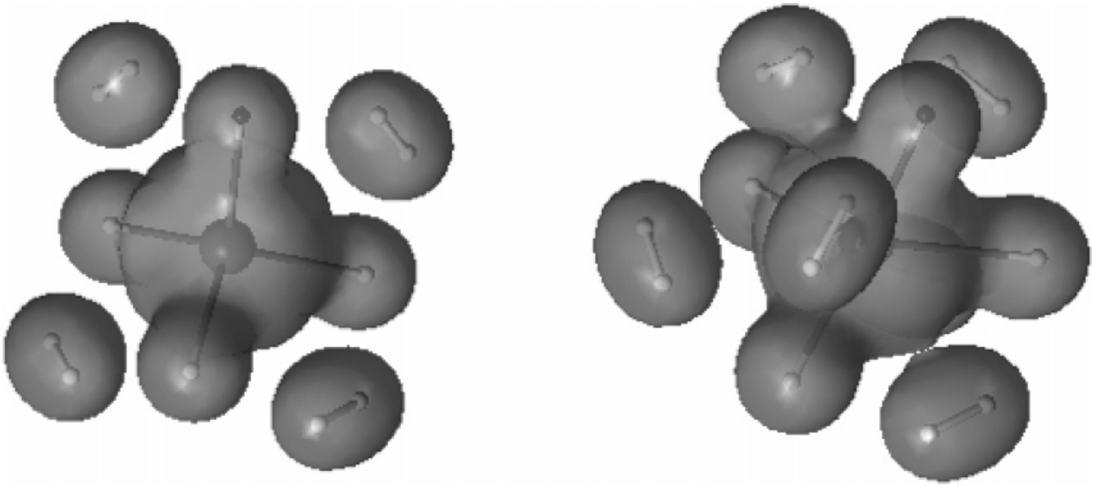

Figure 9. Electron density plots for thorium tetrahydride tetradihydrogen (left) and uranium tetrahydride hexadihydrogen (right) complexes calculated at the CASSCF level of theory. (The sixth dihydrogen is directly behind the U center.) Iso density 0.04 e/au^3.

strongly bound WH_4 case currently under investigation.[6b] In the Th case, the bonding orbitals between Th and H(hydrides) are mainly 6d on the Th, while in the U case there is a significant 5f U component. The interaction between Th/U and the H_2 moieties seems slightly different for the two actinides: in the Th case, all the $H(H_2)$ bear a partial charge of about +0.02, while in the U case the $H(H_2)$ bear a partial charge that varies from −0.03 to +0.04. Overall, they are more polarized. The comparison of the total electronic densities at the same 0.04 isovalues shows that the electronic density delocalizes the bond region more in the U case than in the Th case (Figure 9).

Conclusions

Laser-ablated thorium atoms react with dihydrogen molecules in excess neon or pure hydrogen to form thorium hydrides and dihydrogen complexes. The ThH_2, ThH_4, and $ThH_4(H_2)_x$ ($x = 1-4$) major product molecules have been identified through matrix IR spectra, isotopic substitution (HD, D_2), and comparison to frequencies calculated by density functional theory and the CCSD method. Theoretical calculations show that the Th−H bond in ThH_4 is the most polarized of group 4 and uranium metal tetrahydrides, and as a result, a strong attractive electrostatic dihydrogen interaction[30] was found between the oppositely charged hydride and H_2 ligands $ThH_4(H_2)_x$. This bridge-bonded dihydrogen complex structure is different from that recently computed for super dihydrogen complexes for tungsten and uranium hydrides.[3,6] Natural charges reveal an increased charge flow from the metal center in tetrahydride complex relative to the isolated tetrahydride.

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