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Infrared Spectra of H_2ThS and H_2US in Noble Gas Matrices: Enhanced H-An-S Covalent Bonding

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Table S1: Calculated Frequencies for the $H_2Th(SH)_2$ (^1A) in C_s Symmetry

B3LYP			Mode
$H_2Th(SH)_2$	$D_2Th(SD)_2$	$H_2Th(^{34}SH)_2$	
2624.4 (1)	1884.2	2622.1	S-H str (sym)
2624.2 (4)	1884.0	2621.9	S-H str (asym)
1520.7 (458)	1077.4	1520.7	Th-H str (sym)
1478.2 (639)	1048.9	1478.2	Th-H str (asym)
536.5 (154)	382.1	536.4	
488.9 (16)	354.6	488.5	
451.2 (8)	352.2	449.4	
391.4 (252)	330.6	389.5	
343.0 (46)	265.6	340.8	

Table S2: Calculated Frequencies for the $H_2U(SH)_2$ (^3A) in C_s Symmetry.

B3LYP			Mode
$H_2U(SH)_2$	$D_2U(SD)_2$	$H_2U(^{34}SH)_2$	
2611.2 (0)	1874.6	2608.9	S-H str (sym)
2610.6 (3)	1874.1	2608.2	S-H str (asym)
1534.1 (506)	1087.2	1534.1	U-H str (sym)
1483.0 (623)	1052.0	1483.0	U-H str (asym)
508.3 (103)	363.9	508.2	
476.6 (5)	350.0	476.1	
432.2 (50)	348.6	430.1	
372.9 (262)	323.1	370.0	
310.1 (22)	257.4	307.3	

Table S3A. Calculated B3LYP NBO Analysis for H_2US ($^3A''$) for the Alpha Electrons.[a]

Bond	U pop %	U(%s)	U(%d)	U(%f)	H/S pop%	H/S(%s)	S(%p)
U-S π	24		67	30	76		97
U-S π	26		56	42	73%		100
U-S σ	27	18	67	15	S73	16	83
U-H σ	33	27	51	18	67	100	
U-H σ	33	27	51	18	67	100	
U *lp*	100			98			
U *lp*	100			98			

[a] natural charges U: 1.32, S: -0.66, H: -0.38

Table S3B. Calculated B3LYP NBO Analysis for H_2ThS

Bond	Th pop %	Th(%s)	Th(%d)	Th(%f)	H/S pop%	H/S(%s)	S(%p)
Th-S π	20		79	17	80		95
Th-S π	19		79	18	81		100
Th-S σ	25	19	66	14	75	16	83
Th-H σ	29	31	58	8	71	100	
Th-H σ	29	31	58	8	71	100	

Table S3C. Calculated B3LYP NBO Analysis for ^5H_2U for the Alpha Electrons.[a]

Bond	U pop %	U(%s)	U(%d)	U(%f)	H pop%	H(%s)
U-H σ	24	14	72	12	76	100
U-H σ	24	14	72	12	76	100
U *lp*	100			100		
U *lp*	100			99		
U *lp*	100	5		94		
U *lp*	100	66	25	5		

Table S3D. Calculated B3LYP NBO Analysis for H_2Th

Bond	Th pop %	Th(%s)	Th(%d)	Th(%f)	H pop%	H(%s)
Th-H σ	26	12	73	14	74	100
Th-H σ	26	12	73	14	74	100
Th *lp*	100	75	23			

Table S4. Calculated B3LYP NBO Analysis for $^4US^+$ for the Alpha Electrons[a]

Bond	U pop %	U(%s)	U(%d)	U(%f)	S pop%	S(%s)	S(%p)
U-S π	23		82	16	77		100
U-S π	23		82	16	77		100
U-S σ	26	15	56	27	74	10	90
U *lp*	100			98			
U *lp*	100			97			
U *lp*	100			97			

[a] $^4US^+$: r(U-S) =2.322 Å; freq=485.2 cm^{-1}; Natural Charges: U = 1.70e, S = -0.70e.

Table S5. Energies Used to Predict Heat of Formations Calculate using CCSD(T)/aug-TD

Molecule	Energy/ Hartrees	ZPE/ Hartrees	Thermal Correction/ kcal/mol
O	-74.978823	0.000000	1.04
S	-397.657218	0.000000	1.50
Th	-406.357642	0.000000	1.60
H2	-1.172636	0.010025	2.07
O2	-150.140967	0.003590	2.08
H_2O	-76.342326	0.011357	2.37
H_2S	-398.943621	0.010167	2.38
ThH_2	-407.584422	0.008315	2.47
UH_2	-476.747113	0.007470	2.56
ThO	-481.678614	0.002025	2.10
ThS	-804.253650	0.001089	2.23
UO	-550.81587	0.00186	2.12
US	-873.401089	0.00101	2.24
ThO_2	-556.900337	0.003955	2.86
UO_3	-701.292624	0.010291	3.30
H_2ThO	-482.873550	0.011234	3.06
H_2ThS	-805.459709	0.010690	3.11
H_2UO	-552.022479	0.010341	3.22
H_2US	-874.596262	0.007680	3.00

Table S6. Cartesian coordinates for optimized geometries using B3LYP, PW91, and CCSD(T)/aug-TD

H_2ThO

B3LYP/atz	x	y	z
Th	0.02460	-0.13783	0.00000
O	0.02460	1.72346	0.00000
H	-1.20553	-0.69157	1.61905
H	-1.20553	-0.69157	-1.61905

PW91/atz	x	y	z
Th	0.02531	-0.13902	0.00000
O	0.02531	1.72267	0.00000
H	-1.23993	-0.63480	1.59636
H	-1.23993	-0.63480	-1.59636

CCSD(T) /atz	x	y	z
Th	-0.01334	0.00000	-0.11475
O	0.04704	0.00000	1.75438
H	1.16175	1.64899	-0.71546
H	1.16175	-1.64899	-0.71546

H_2ThS

B3LYP/atz	x	y	z
Th	0.02309	-0.34622	0.00000
S	0.02309	2.04308	0.00000
H	-1.22367	-0.76491	1.59509
H	-1.22367	-0.76491	-1.59509

PW91/atz	x	y	z
Th	0.02358	-0.34580	0.00000
S	0.02358	2.03250	0.00000
H	-1.24950	-0.69887	1.57923
H	-1.24950	-0.69887	-1.57923

CCSD(T) /atz	x	y	z
Th	-0.01234	0.00000	-0.28556
S	0.01299	0.00000	2.11036
H	1.21434	1.61648	-0.69300
H	1.21434	-1.61648	-0.69300

^3H_2UO (B3LYP/ATZ)

a″	x	y	z
U	0.02166	-0.12844	0.00000
O	0.02166	1.68545	0.00000
H	-1.08283	-0.83343	1.58482
H	-1.08283	-0.83343	-1.58482

a' (a'xa')	x	y	z
U	0.02371	-0.13046	0.00000
O	0.02371	1.68378	0.00000
H	-1.18529	-0.73384	1.53742
H	-1.18529	-0.73384	-1.53742

a'(a″ x a″)	x	y	z
U	0.02086	-0.12620	0.00000
O	0.02086	1.69052	0.00000
H	-1.04321	-0.95702	1.56155
H	-1.04321	-0.95702	-1.56155

^3H_2UO (PW91/ATZ)

a″	x	y	z
U	0.02068	-0.12677	0.00000
O	0.02068	1.69227	0.00000
H	-1.03397	-0.93789	1.55899
H	-1.03397	-0.93789	-1.55899

a' (a'xa')	x	y	z
U	0.02411	-0.13057	0.00000
O	0.02411	1.68702	0.00000
H	-1.20527	-0.74177	1.50458
H	-1.20527	-0.74177	-1.50458

a'(a″ x a″)	x	y	z
U	0.01523	-0.12085	0.00000
O	0.01523	1.70217	0.00000
H	-0.76165	-1.24972	1.54738
H	-0.76165	-1.24972	-1.54738

^3H_2UO (CCSD(T)/ATZ)

a″	x	y	z
U	-0.01260	0.00000	-0.10833
O	0.04870	0.00000	1.70552
H	1.10136	1.60037	-0.74490
H	1.10136	-1.60037	-0.74490

a' (a'xa')	x	y	z
U	-0.01294	0.00000	-0.10872
O	0.04785	0.00000	1.70686
H	1.14808	1.57372	-0.70931
H	1.14808	-1.57372	-0.70931

a'(a″ x a″)	x	y	z
U	-0.01313	0.00000	-0.10812
O	0.05224	0.00000	1.70562
H	1.13571	1.56822	-0.77022
H	1.13571	-1.56822	-0.77022

^3H_2US (B3LYP/ATZ)

a″	x	y	z
U	0.02147	-0.33115	0.00000
S	0.02147	2.00374	0.00000
H	-1.15923	-0.79708	1.55916
H	-1.15923	-0.79708	-1.55916

a' (a'x a')	x	y	z
U	0.02256	-0.33258	0.00000
S	0.02256	2.00320	0.00000
H	-1.21816	-0.72696	1.52066
H	-1.21816	-0.72696	-1.52066

a'(a″ x a″)	x	y	z
U	0.02401	-0.33461	0.00000
S	0.02401	1.99107	0.00000
H	-1.29675	-0.53652	1.47763
H	-1.29675	-0.53652	-1.47763

^3H_2US (PW91/ATZ)

a″	x	y	z
U	0.02324	-0.33281	0.00000
S	0.02324	1.99373	0.00000
H	-1.25474	-0.64064	1.50124
H	-1.25474	-0.64064	-1.50124

a' (a'x a')	x	y	z
U	0.02417	-0.33238	0.00000
S	0.02417	1.98000	0.00000
H	-1.30498	-0.55040	1.46595
H	-1.30498	-0.55040	-1.46595

a'(a″ x a″)	x	y	z
U	0.02425	-0.33571	0.00000
S	0.02425	1.98220	0.00000
H	-1.30921	-0.41486	1.46800
H	-1.30921	-0.41486	-1.46800

^3H_2US (CCSD(T)/ATZ)

a″	x	y	z
U	-0.01141	0.00000	-0.27171
S	0.01355	0.00000	2.06236
H	1.13198	1.59254	-0.71597
H	1.13198	-1.59254	-0.71597

a' (a'x a')	x	y	z
U	-0.01170	0.00000	-0.27230
S	0.01178	0.00000	2.06180
H	1.19469	1.55507	-0.63818
H	1.19469	-1.55507	-0.63818

a'(a″ x a″)	x	y	z
U	-0.01195	0.00000	-0.27189
S	0.00967	0.00000	2.05362
H	1.25779	1.51874	-0.55618
H	1.25779	-1.51874	-0.55618

$^3H_2U(SH)_2$ (B3LYP)

a″	x	y	z
Th	0.01349	-0.36134	0.00000
H	-1.53316	-1.74589	0.00000
H	1.82495	-1.35870	0.00000
S	0.01349	1.09284	2.26269
H	-0.96877	0.32718	2.78294
S	0.01349	1.09284	-2.26269
H	-0.96877	0.32718	-2.78294

$^3H_2U(SH)_2$ (B3LYP)

a″	x	y	z
U	0.01686	-0.33760	0.00000
H	-1.48555	-1.66745	0.00000
H	1.73976	-1.35054	0.00000
S	0.01686	1.03399	2.23761
H	-1.17264	0.49495	2.58441
S	0.01686	1.03399	-2.23761
H	-1.17264	0.49495	-2.58441

a' (a'x a')	x	y	z
U	0.01393	-0.33707	0.00000
H	-1.53308	-1.61353	0.00000
H	1.73088	-1.35660	0.00000
S	0.01393	1.04629	2.23055
H	-0.96239	0.24963	2.71708
S	0.01393	1.04629	-2.23055
H	-0.96239	0.24963	-2.71708

a'(a″ x a″)	x	y	z
U	0.00360	-0.35103	0.00000
H	-1.44616	-1.73929	0.00000
H	1.66182	-1.47507	0.00000
S	0.00360	1.10570	2.19521
H	-0.33115	0.06320	2.98175
S	0.00360	1.10570	-2.19521
H	-0.33115	0.06320	-2.98175

Table S7. Calculated geometries and frequencies for planar C_{2v} H_2ThS and H_2US with the B3LYP Functional.

Property	B3LYP
H_2ThS ($^1A_1$)	
r(Th–S) Å	2.414
r(Th–H) Å	2.118
∠S–Th–H °	121.2
Th–H sym. str. (a_1)	1431.8 (504)
Th–H asym. str. (b_2)	1374.3 (855)
S–Th–H sym. bend (a_1)	532.3 (171)
Th–S str. + S–Th–H bend	441.1 (51)
S–Th–H asym. bend (a_1)	299.2 (38)
S–Th–H out-of-plane bend (a_1)	356*i*
H_2US ($^3A_2$)	
r(U–S) Å	2.343
r(U–H) Å	2.053
∠S–U–H °	123.3
U–H sym. str. (a_1)	1420.6 (421)
U–H asym. str. (b_2)	1396.2 (855)
S–U–H sym. bend + U–S str.	475.5 (212)
U–S str. + S–U–H bend	430.5 (1)
S–U–H asym. bend (a_1)	126.5 (153)
S–U–H out-of-plane bend (a_1)	247*i*

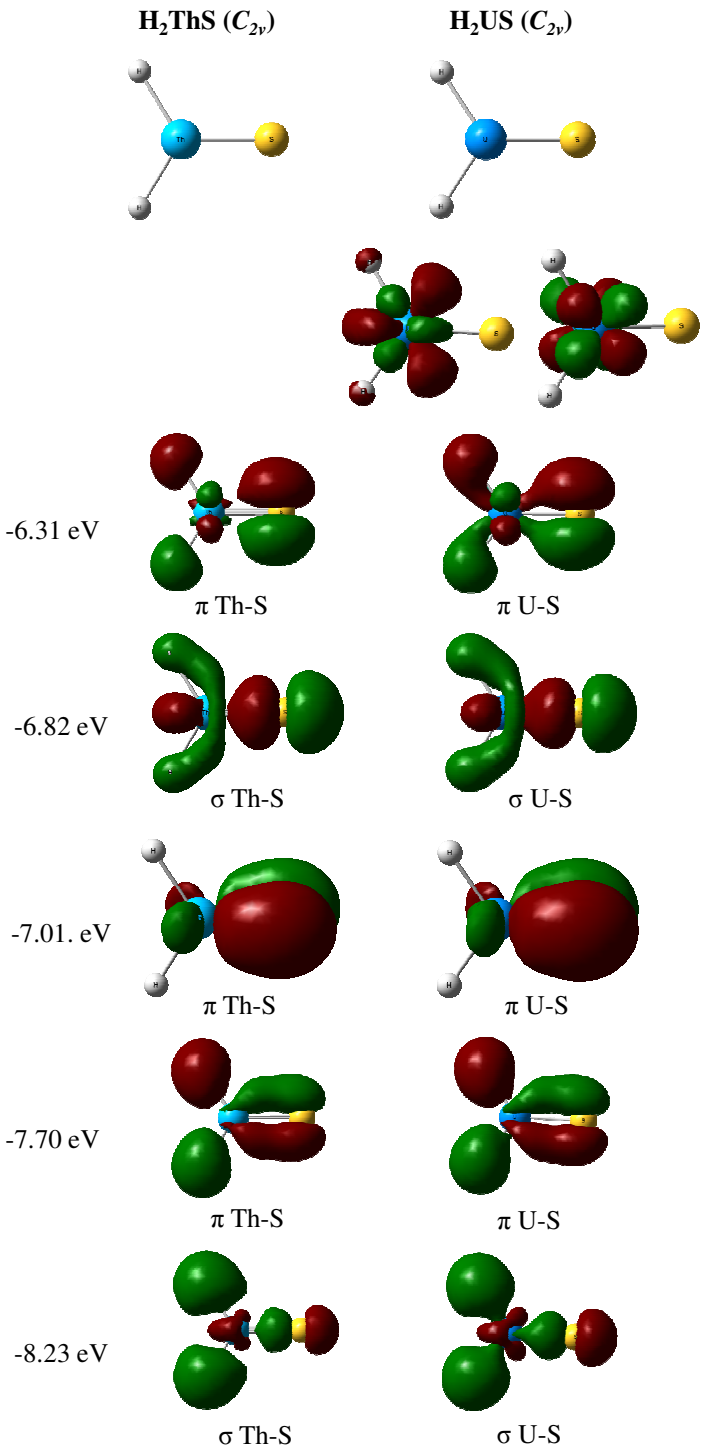

Figure S1.Comparison of structures calculated at the B3LYP level for the ground state H_2US ($^3A_2$) and H_2ThS ($^1A_1$) molecules in C_{2v} symmetry and of the high lying valence molecular orbitals (α spin for H_2US) plotted with an iso-electron density of 0.04 e/au^3. The orbital energies for closed shell H_2ThS are given. The two singly occupied orbitals for H_2US are 5*f* orbitals on U.