

Supporting Information

Actinide–Silicon Multiradical Bonding: Infrared Spectra and Electronic Structures of the $\text{Si}(\mu\text{-X})\text{AnF}_3$ (An = Th, U; X = H, F) Molecules

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Table S1. Relative B3LYP DFT energies for the optimized $\text{Si}(\mu\text{-X})\text{UF}_3$ (X = H, F) isomers ^a

	Molecule	X=H	X=F
D _T	$\text{Si}(\mu\text{-X})\text{UF}_3$	14.59 ($\sigma_s^2\sigma_{ }^2\pi_{\perp}^1f^1$)	3.29 ($\sigma_s^2\sigma_{ }^2\pi_{\perp}^0f^2$)
D _Q	$\text{Si}(\mu\text{-X})\text{UF}_3$	0.00 ($\sigma_s^2\sigma_{ }^1\pi_{\perp}^1f^2$)	0.00 ($\sigma_s^2\sigma_{ }^1\pi_{\perp}^1f^2$)

^a All relative energies are in kcal/mol.

Table S2. Natural charges from natural population analysis (NPA), compositions of natural localized molecular orbitals (NLMO), and Wiberg bond orders (BO_w) from NBO analysis of $\text{Si}(\mu\text{-H})\text{UF}_3$ ^a

	q _{NPA}	NLMO	Occ.	BO _w
Si-U	Si(-0.04), U(2.66)	80% Si($s^{0.06}p$) + 20% U($sp^{0.06}d^{1.56}f^{1.89}$)	α 0.99	0.47
Si-U	Si(-0.04), U(2.66)	73% Si(p) + 27% U($p^{0.03}d^{0.25}f$)	α 1.00	
H-Si	H(-0.40), Si(-0.04)	73% H(s) + 27% Si($s^{0.07}p$)	α 0.95	0.71
H-Si	H(-0.40), Si(-0.04)	73% H(s) + 27% Si($s^{0.08}p$)	β 0.95	
Si (LP)		100% Si($sp^{0.13}$)	α 0.99	
Si (LP)		100% Si($sp^{0.08}$)	β 0.98	
U (LP)		100% U(f)	α 1.00	
U (LP)		100% U(f)	α 1.00	

^aAll the data are calculated with optimized B3LYP geometry of quintet $\text{Si}(\mu\text{-H})\text{UF}_3$. LP denotes lone pair.

Table S3. Observed and calculated vibrational frequencies for $\text{Si}(\mu\text{-X})\text{UF}_3$ (X = H, D) molecules ^a

Mode	Obs. ^b	Calc.	Obs. ^b	Calc.
		$\text{Si}(\mu\text{-H})\text{UF}_3(^5\text{A})$	$\text{Si}(\mu\text{-D})\text{UF}_3(^5\text{A})$	
Si-H str		1601(248), 820(23)	1080(Ar)	1151(127), 588(55)
U-F sy str	588.6 (Ne) 578.6 (Ar)	579(199)	577(Ar)	566(157)
U-F as str	550.1 (Ne) 537.5 (Ar)	543(144), 542(145)	537(Ar)	542(143), 540(140)

^a Vibrational frequencies (cm⁻¹) and intensities (km/mol, in parenthesis) are calculated using PBE/TZ2P (see text), with seven low-frequency bending modes omitted. ^b Absorptions observed in neon (in bold face) and argon matrix.

Table S4. Optimized total energies and geometries for various states of Si(μ -X)UF₃ molecules calculated using CASPT2 method with CASSCF(6e,11o) and Basis-II

Molecule (State)	Geometry & Energy (Hartrees)			
Si(μ -H)UF ₃ (¹ A'')	ENERGY=-1064.34969			
Si	0.0000000000	0.2101894196	-2.7880183798	
U	0.0000000000	0.0146878823	0.1331226129	
H	0.0000000000	1.3438915663	-1.6541954796	
F	0.0000000000	-2.0300994214	0.3260699709	
F	1.6494768125	0.7320265148	1.1076821083	
F	-1.6494768125	0.7320265148	1.1076821083	
Si(μ -H)UF ₃ (³ A')	ENERGY=-1064.35590			
Si	0.0000000000	0.0200858745	-2.7610024985	
U	0.0000000000	0.0303613985	0.1340437579	
H	0.0000000000	1.2569381917	-1.7336538808	
F	0.0000000000	-1.9499843872	0.6292800351	
F	1.7514927256	0.7366055670	0.9324455014	
F	-1.7514927256	0.7366055670	0.9324455014	
Si(μ -H)UF ₃ (³ A'')	ENERGY=-1064.34287			
Si	0.0000000000	-0.4416767416	-2.7460814296	
U	0.0000000000	0.0424173783	0.1711264304	
H	0.0000000000	0.9888880343	-2.0599218344	
F	0.0000000000	-1.5733594507	1.4360300587	
F	1.9006427555	0.8211934268	0.2943940559	
F	-1.9006427555	0.8211934268	0.2943940559	
Si(μ -H)UF ₃ (⁵ A')	ENERGY=-1064.35792			
Si	0.0000000000	0.1027438112	-2.7493706656	
U	0.0000000000	0.0001297805	0.1316086797	
H	0.0000000000	1.3138823840	-1.7016193844	
F	0.0000000000	-1.9997103179	0.5851051589	
F	1.6522991697	0.8882453193	0.9603398564	
F	-1.6522991697	0.8882453193	0.9603398564	
Si(μ -F)UF ₃ (¹ A')	ENERGY=-1163.45814			
Si	0.0000000000	-0.5602906110	-2.7443518340	
U	0.0000000000	0.0105511777	0.2199972275	
F	0.0000000000	1.1309028335	-1.7342639773	
F	0.0000000000	-1.8913991914	0.9738630131	
F	1.7382357462	0.7282920836	1.0305392337	
F	-1.7382357462	0.7282920836	1.0305392337	

Si(μ -F)UF ₃ (³ A'')		ENERGY=-1163.46078		
Si	0.0000000000	-0.5616963844	-2.7753233017	
U	0.0000000000	-0.0105999225	0.2173094806	
F	0.0000000000	1.1069766462	-1.7589052606	
F	0.0000000000	-1.8527417793	1.1121407591	
F	1.6804357983	0.8544654577	1.0134509363	
F	-1.6804357983	0.8544654577	1.0134509363	
Si(μ -F)UF ₃ (⁵ A')		ENERGY=-1163.45967		
Si	0.0000000000	-0.5860876222	-2.7679890806	
U	0.0000000000	0.0057981388	0.2273474154	
F	0.0000000000	1.0907367657	-1.7694618597	
F	0.0000000000	-1.8549943295	1.0751301742	
F	1.7493811795	0.7790158072	0.9689313176	
F	-1.7493811795	0.7790158072	0.9689313176	
Si(μ -F)UF ₃ (⁵ A'')		ENERGY=-1163.46384		
Si	0.0000000000	-0.5778032540	-2.7485249435	
U	0.0000000000	-0.0105231163	0.2188067442	
F	0.0000000000	1.0944748146	-1.7817871976	
F	0.0000000000	-1.8460106313	1.1290130546	
F	1.6871429758	0.8687751126	0.9872681116	
F	-1.6871429758	0.8687751126	0.9872681116	

Table S5. Optimized total energies and geometries for various states of XSiThF_3 and $\text{Si}(\mu\text{-X})\text{ThF}_3$
(X=H, F) isomers calculated using CASPT2 method with CASSCF(4e,11o) and Basis-II

Molecule_State	Geometry & Energy (Hartrees)			
$\text{HSiThF}_3(^1\text{A}'')$	ENERGY=-995.20508			
Th	-0.0000000000	0.0000000000	-0.1336288706	
Si	-0.0000000000	0.0000000000	2.7642877097	
F	1.9517539099	0.0000000000	-0.8933010823	
F	-0.9758769550	1.6902684679	-0.8933010823	
F	-0.9758769550	-1.6902684679	-0.8933010823	
H	-0.0000000000	0.0000000000	4.2507179429	
$\text{HSiThF}_3(^3\text{A}'')$	ENERGY=-995.23193			
Th	-0.0000000000	0.0000000000	-0.1349230688	
Si	-0.0000000000	0.0000000000	2.7619926576	
F	1.9517349949	0.0000000000	-0.8868553179	
F	-0.9758674974	1.6902520870	-0.8868553179	
F	-0.9758674974	-1.6902520870	-0.8868553179	
H	-0.0000000000	0.0000000000	4.2481218635	
$\text{SiHThF}_3(^1\text{A}'')$	ENERGY=-995.20856			
Si	0.0000000000	0.0437408129	-2.8666982293	
Th	0.0000000000	0.0089935914	0.1390850083	
H	0.0000000000	1.2665614438	-1.8473875164	
F	0.0000000000	-2.0094303760	0.7039232572	
F	1.7152194228	0.8838640719	0.9666146706	
F	-1.7152194228	0.8838640719	0.9666146706	
$\text{SiHThF}_3(^3\text{A}'')$	ENERGY=-995.23695			
Si	0.0000000000	0.0484284748	-2.8516510788	
Th	0.0000000000	0.0096039157	0.1370085567	
H	0.0000000000	1.2898385466	-1.8452609286	
F	0.0000000000	-2.0106545045	0.6927454847	
F	1.7131656994	0.8766666447	0.9737054107	
F	-1.7131656994	0.8766666447	0.9737054107	
$\text{FSiThF}_3(^1\text{A}'')$	ENERGY=-1094.28870			
Th	-0.0000000000	0.0000000000	-0.3580296253	
Si	-0.0000000000	0.0000000000	2.5056484883	
F	1.9340284911	0.0000000000	-1.1635658987	
F	-0.9670142455	1.6749178049	-1.1635658987	
F	-0.9670142455	-1.6749178049	-1.1635658987	
F	-0.0000000000	0.0000000000	4.1593919742	

FSiThF ₃ (³ A'')		ENERGY=-1094.31280		
	Th	-0.0000000000	0.0000000000	-0.3570738744
	Si	-0.0000000000	0.0000000000	2.4910008920
	F	1.9338014230	0.0000000000	-1.1562979557
	F	-0.9669007115	1.6747211582	-1.1562979557
	F	-0.9669007115	-1.6747211582	-1.1562979557
	F	-0.0000000000	0.0000000000	4.1475686918
SiFThF ₃ (¹ A'')		ENERGY=-1094.31188		
	Si	0.0000000000	-0.5228921569	-2.8844988470
	Th	0.0000000000	-0.0034428373	0.2424920976
	F	0.0000000000	1.0916900571	-1.8307143176
	F	0.0000000000	-1.9496612754	1.0199974535
	F	1.7389506195	0.8365082074	1.0566022965
	F	-1.7389506195	0.8365082074	1.0566022965
SiFThF ₃ (³ A'')		ENERGY=-1094.34212		
	Si	0.0000000000	-0.4680333126	-2.8790361207
	Th	0.0000000000	-0.0028538942	0.2372326706
	F	0.0000000000	1.1561770555	-1.7694582298
	F	0.0000000000	-2.0040984578	0.8600584583
	F	1.7206765612	0.7873376066	1.1340241115
	F	-1.7206765612	0.7873376066	1.1340241115

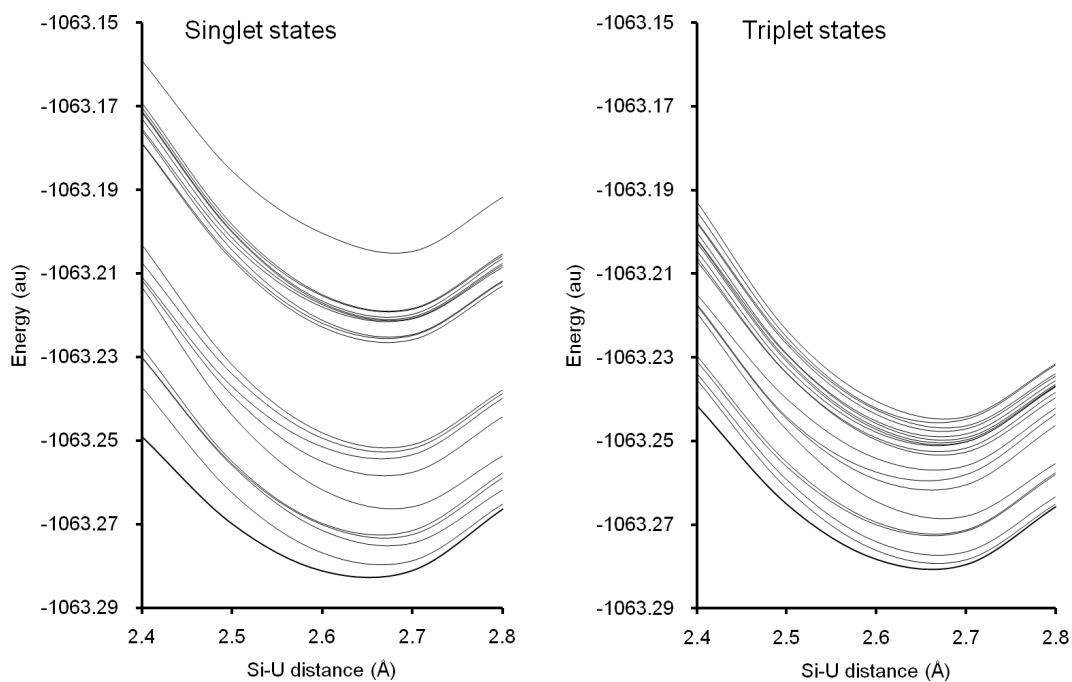
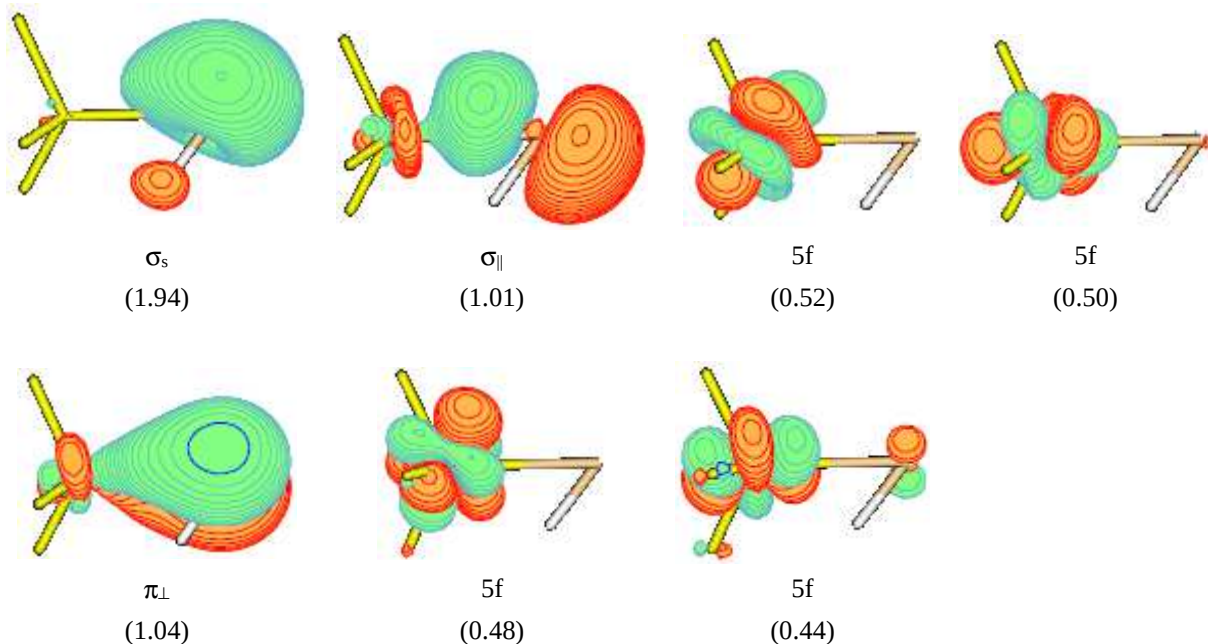


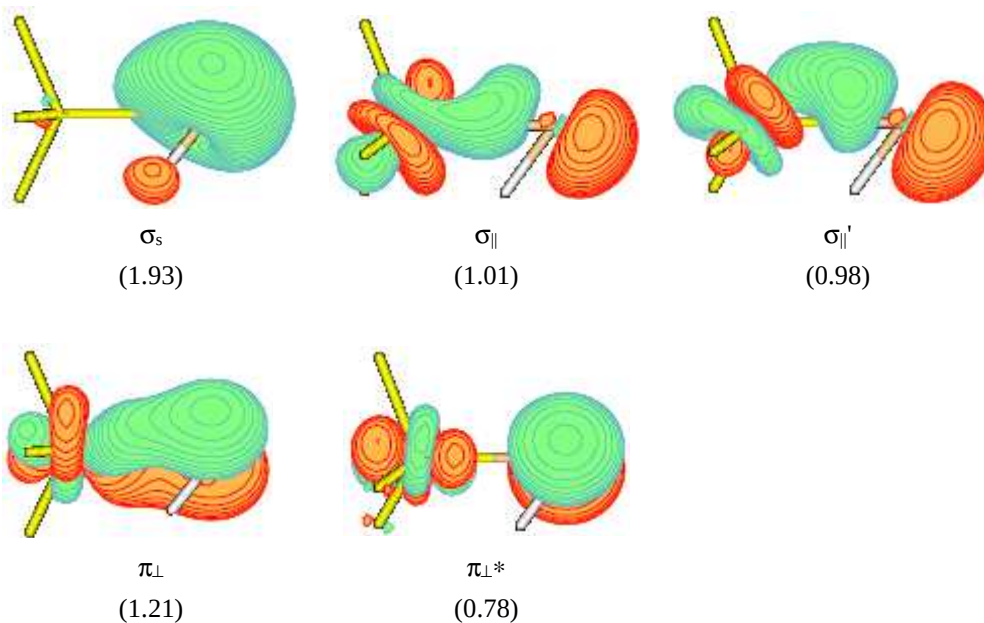
Figure S1. Energy curves of 20 low-lying singlet states (left) and triplet states (right) of HSiUF₃ (C_{3v}) along the Si-U stretching path obtained from CASPT2(6e,11o) calculations.

The natural orbital contours, character, and occupation numbers (NOON) and CASSCF wavefunctions of SiHUF₃ (Table 3), XSiThF₃ and Si(μ-X)ThF₃ (X = H, F; Table 6) are shown below in Figs.S2-S13.



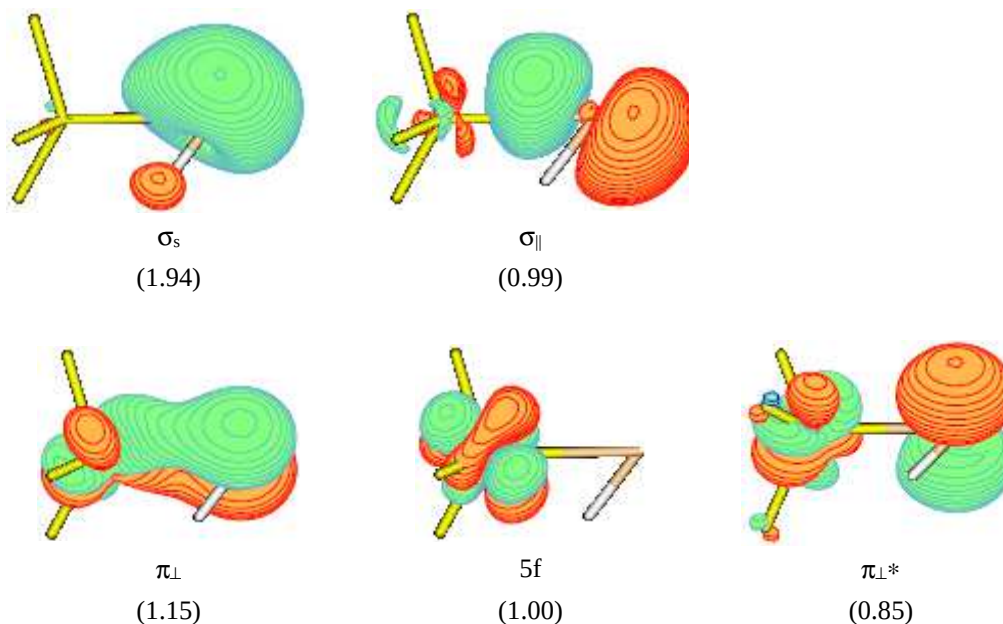
$$\Psi(^1A'')=0.38(\sigma_s^2\sigma_{\parallel}^1\pi_{\perp}^1f^1f^1)+0.38(\sigma_s^2\sigma_{\parallel}^1\pi_{\perp}^1f^1f^1)+0.33(\sigma_s^2\sigma_{\parallel}^1\pi_{\perp}^1f^1f^1)+0.33(\sigma_s^2\sigma_{\parallel}^1\pi_{\perp}^1f^1f^1)+0.22(\sigma_s^2\sigma_{\parallel}^1\pi_{\perp}^2f^1)-0.22(\sigma_s^2\sigma_{\parallel}^1\pi_{\perp}^2f^1)+...$$

Figure S2. Natural valence orbitals contours (cutoff=0.05au) of the ¹A'' Si(μ-H)UF₃ molecule from CASSCF(6e, 11o) at CASPT2 optimized geometry.



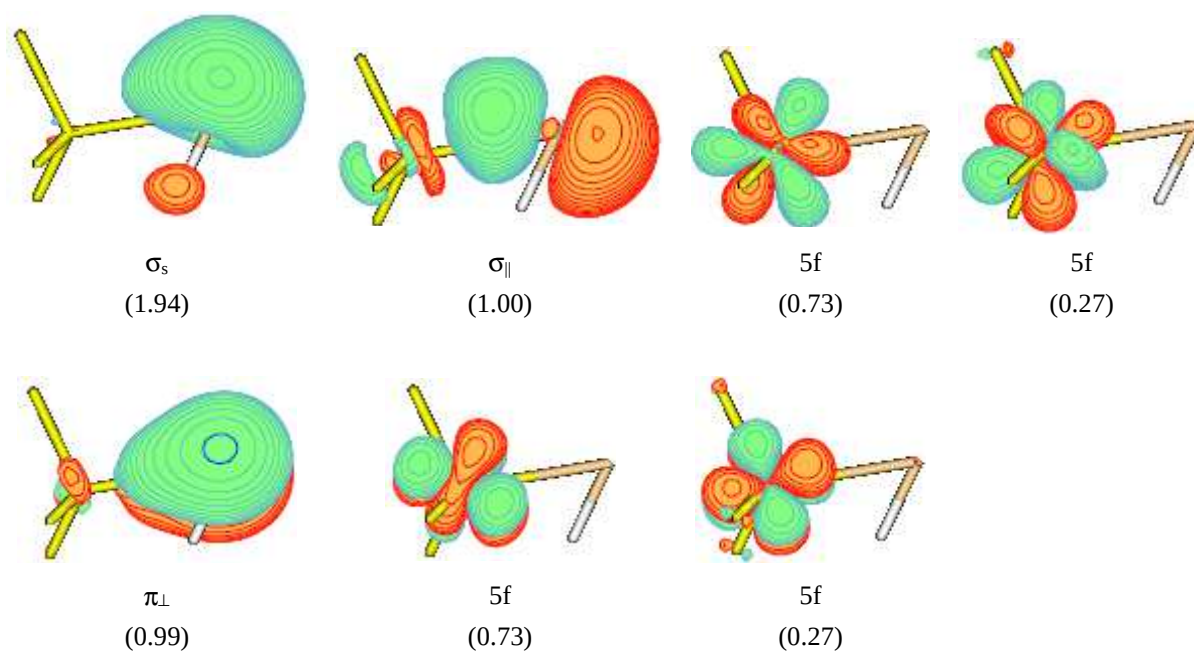
$$\Psi(^3A') = 0.64(\sigma_s^2 \sigma_{||}^{\uparrow} \pi_{\perp}^2 \sigma_{||}^{\uparrow}) - 0.45(\sigma_s^2 \sigma_{||}^{\uparrow} \pi_{\perp}^* \sigma_{||}^{\uparrow}) + 0.40(\sigma_s^2 \sigma_{||}^2 \pi_{\perp}^{\uparrow} \pi_{\perp}^{*\uparrow}) - 0.39(\sigma_s^2 \sigma_{||}^2 \pi_{\perp}^{\uparrow} \pi_{\perp}^{*\uparrow}) \dots$$

Figure S3. Natural valence orbitals contours (cutoff=0.05au) of the $^3A'$ Si(μ -H)UF₃ molecule from CASSCF(6e, 11o) at CASPT2 optimized geometry.



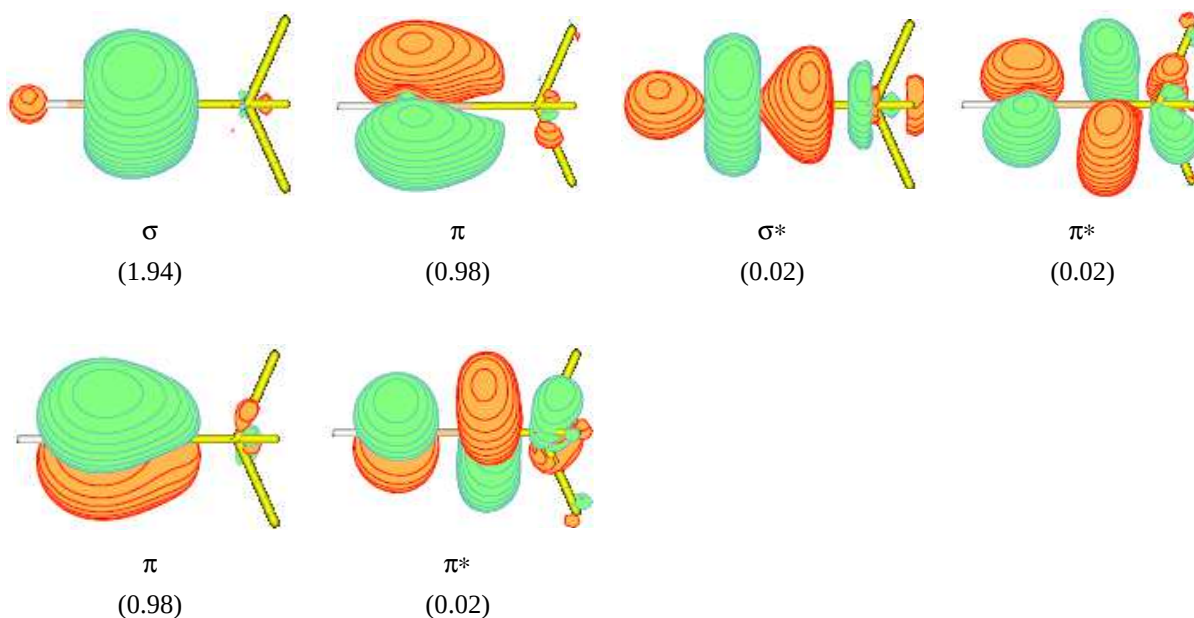
$$\Psi(^3A'') = 0.59(\sigma_s^2 \sigma_{||}^{\uparrow} \pi_{\perp}^2 f^{\uparrow}) - 0.46(\sigma_s^2 \sigma_{||}^{\uparrow} \pi_{\perp}^{\uparrow} f^{\uparrow} 3p\pi^{*\uparrow}) - 0.46(\sigma_s^2 \sigma_{||}^{\uparrow} f^{\uparrow} \pi_{\perp}^{*2}) + 0.41(\sigma_s^2 \sigma_{||}^{\uparrow} \pi_{\perp}^{\uparrow} f^{\uparrow} \pi_{\perp}^{*\uparrow}) \dots$$

Figure S4. Natural valence orbitals contours (cutoff=0.05au) of the $^3A''$ Si(μ -H)UF₃ molecule from CASSCF(6e, 11o) at CASPT2 optimized geometry.



$$\Psi(^5A') = 0.83(\sigma_s^2 \sigma_{||}^{\uparrow} f^{\uparrow} \pi_{\perp}^{\uparrow} f^{\uparrow}) + 0.51(\sigma_s^2 \sigma_{||}^{\uparrow} f^{\uparrow} \pi_{\perp}^{\uparrow} f^{\uparrow}) + \dots$$

Figure S5. Natural valence orbitals contours (cutoff=0.05au) of the $^5A'$ Si(μ -H)UF₃ molecule from CASSCF(6e, 11o) at CASPT2 optimized geometry.



$$\Psi(^1A'') = -0.69(\sigma^2 \pi^{\uparrow} \pi^{\downarrow}) + 0.69(\sigma^2 \pi^{\downarrow} \pi^{\uparrow}) + \dots$$

Figure S6. Natural valence orbitals contours (cutoff=0.05au) of the $^1A''$ HSiThF₃ molecule from CASSCF(4e, 11o) at CASPT2 optimized geometry.

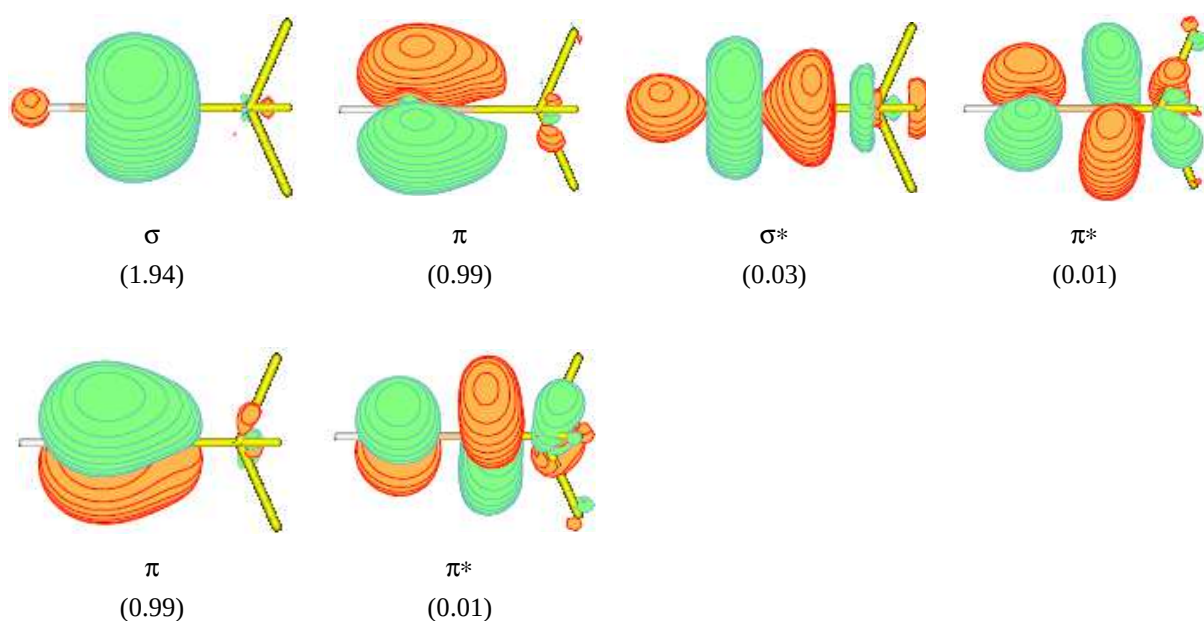


Figure S7. Natural valence orbitals contours (cutoff=0.05au) of the $^3A''$ HSiThF₃ molecule from CASSCF(4e, 11o) at CASPT2 optimized geometry.

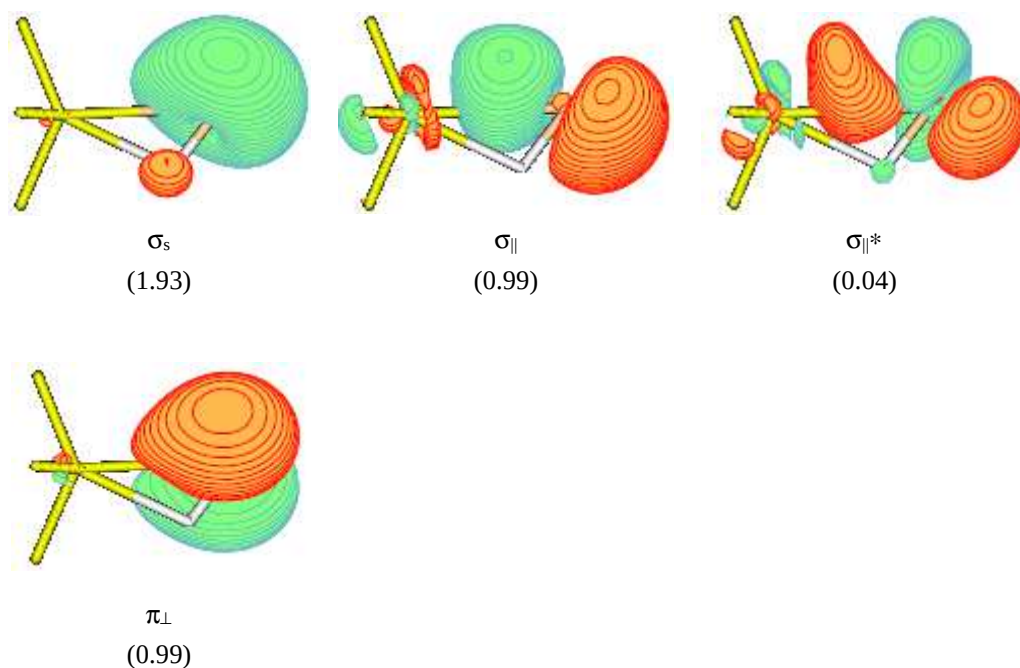
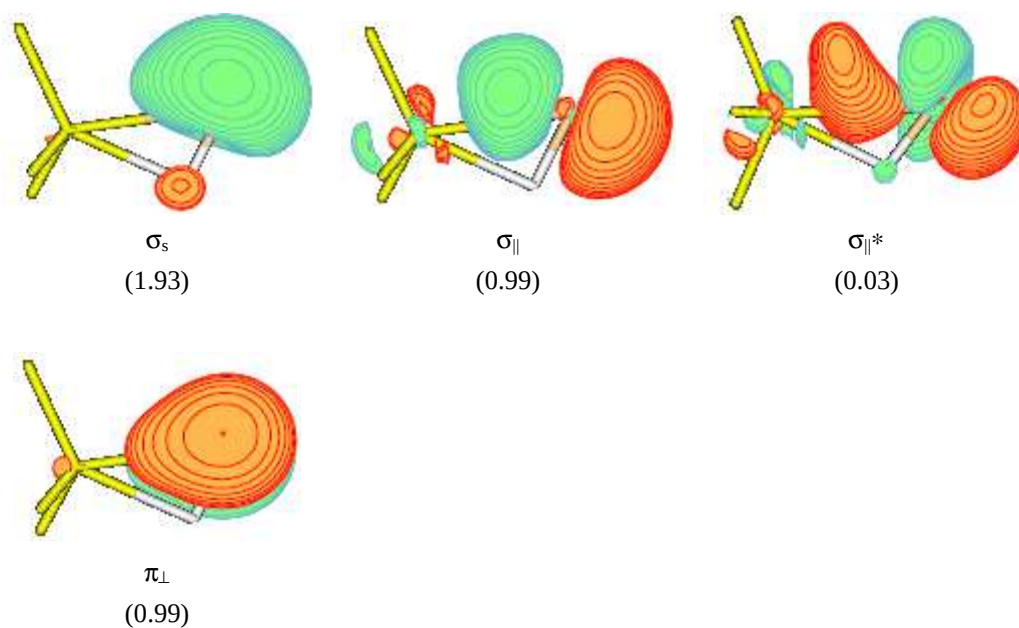
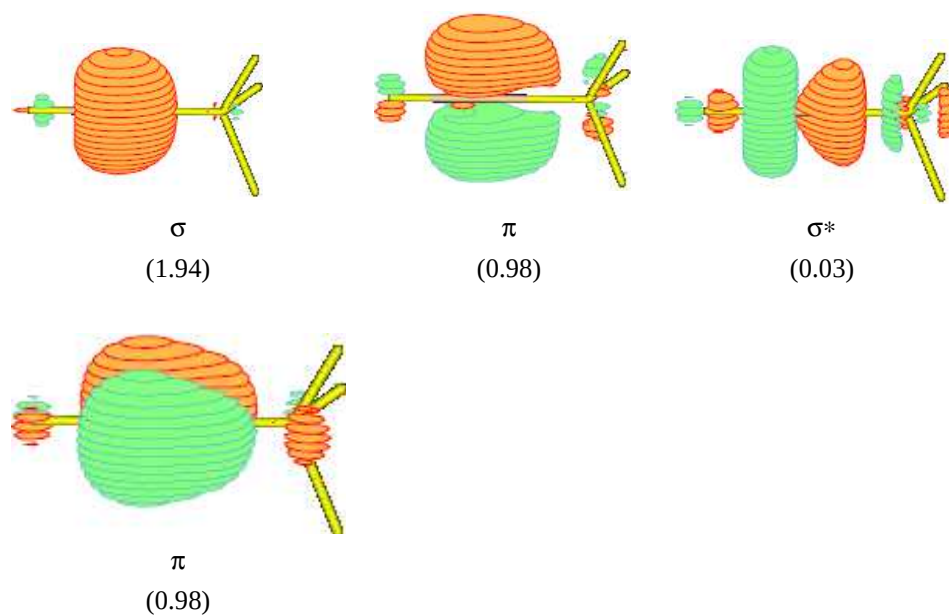


Figure S8. Natural valence orbitals contours (cutoff=0.05au) of the $^1A''$ Si(μ -H)ThF₃ molecule from CASSCF(4e, 11o) at CASPT2 optimized geometry.



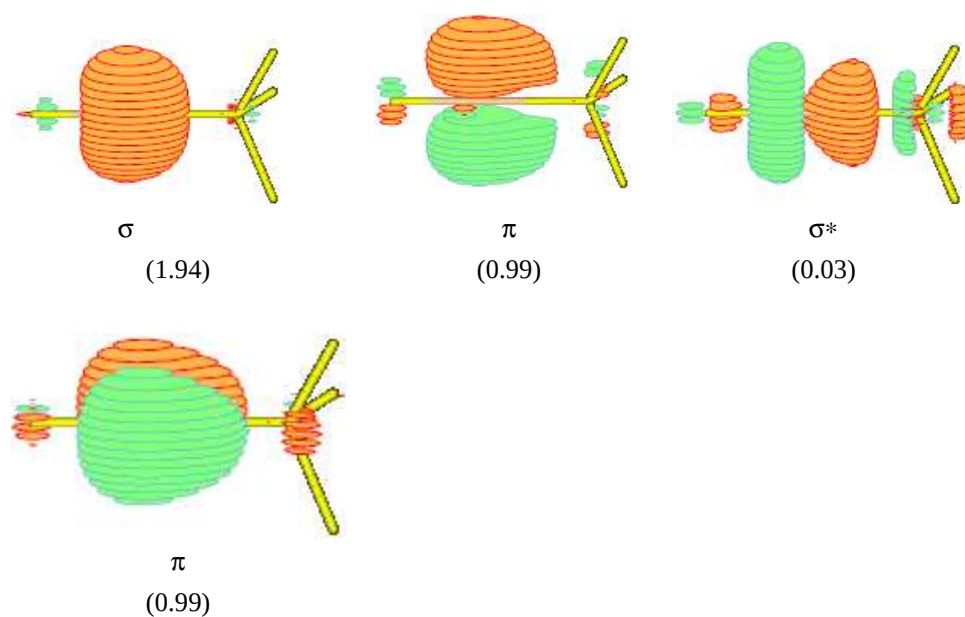
$$\Psi(^3A'')=0.97(\sigma_s^2\sigma_{\parallel}^{\uparrow}\pi_{\perp}^{\uparrow})+\dots$$

Figure S9. Natural valence orbitals contours (cutoff=0.05au) of the $^3A''$ Si(μ -H)ThF₃ molecule from CASSCF(4e, 11o) at CASPT2 optimized geometry.



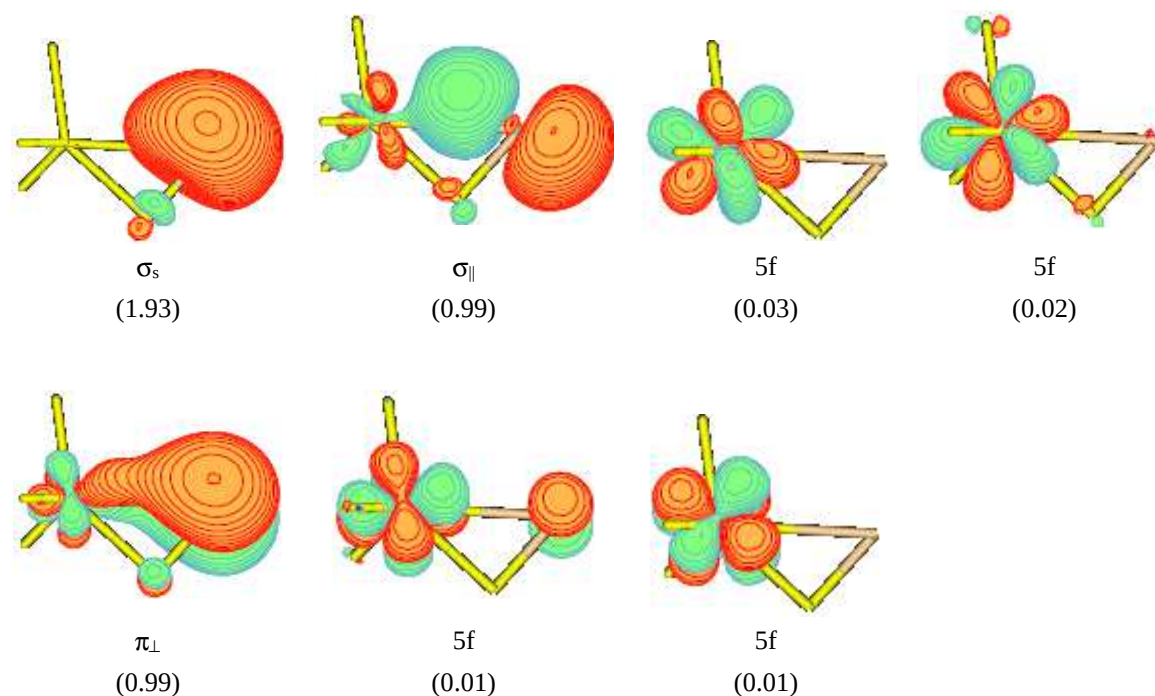
$$\Psi(^1A'')=-0.69(\sigma^2\pi^{\uparrow}\pi^{\downarrow})+0.69(\sigma^2\pi^{\downarrow}\pi^{\uparrow})+\dots$$

Figure S10. Natural valence orbitals contours (cutoff=0.05au) of the $^1A''$ FSiThF₃ molecule from CASSCF(6e, 11o) at CASPT2 optimized geometry.



$$\Psi(^3A'')=0.97(\sigma^2\pi^\uparrow\pi^\uparrow)+\dots$$

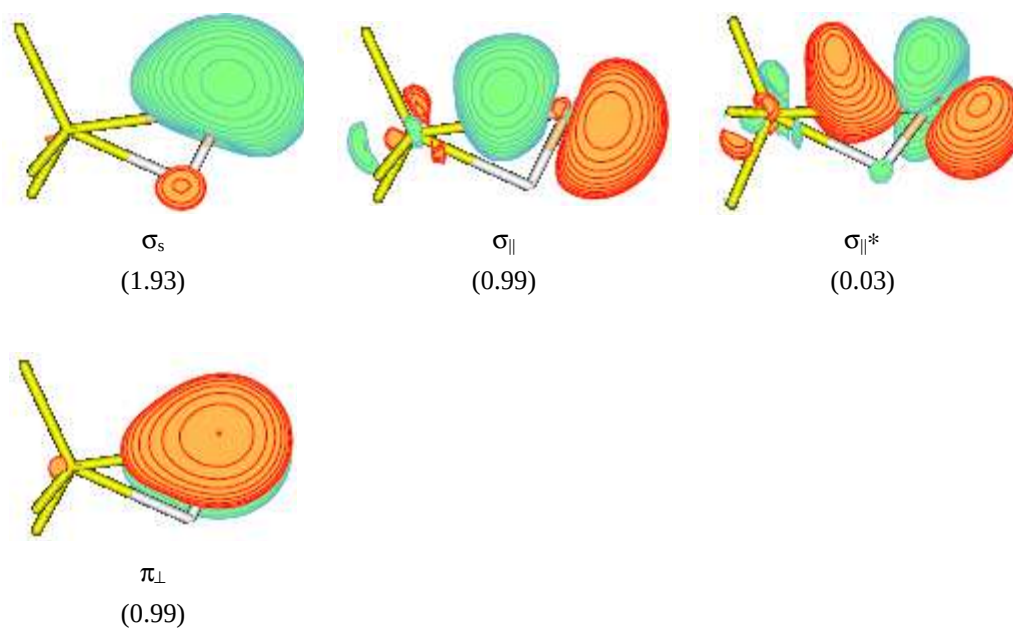
Figure S11. Natural valence orbitals contours (cutoff=0.05au) of the $^3A''$ FSiThF₃ molecule from CASSCF(4e, 11o) at CASPT2 optimized geometry.



$$\Psi(^1A'')=-0.68 (\sigma_s^2\sigma_{\parallel}^\uparrow\pi_{\perp}^\downarrow) + 0.68 (\sigma_s^2\sigma_{\parallel}^\downarrow\pi_{\perp}^\uparrow) + \dots$$

Figure S12. Natural valence orbitals contours (cutoff=0.05au) of the $^1A''$ Si(μ -F)ThF₃ molecule from

CASSCF(6e, 11o) at CASPT2 optimized geometry.



$$\Psi(^3A'')=0.97 (\sigma_s^2 \sigma_{||}^1 \pi_{\perp}^1) + \dots$$

Figure S13. Natural valence orbitals contours (cutoff=0.05au) of the $^3A''$ $\text{Si}(\mu\text{-F})\text{ThF}_3$ molecule from CASSCF(6e, 11o) at CASPT2 optimized geometry.

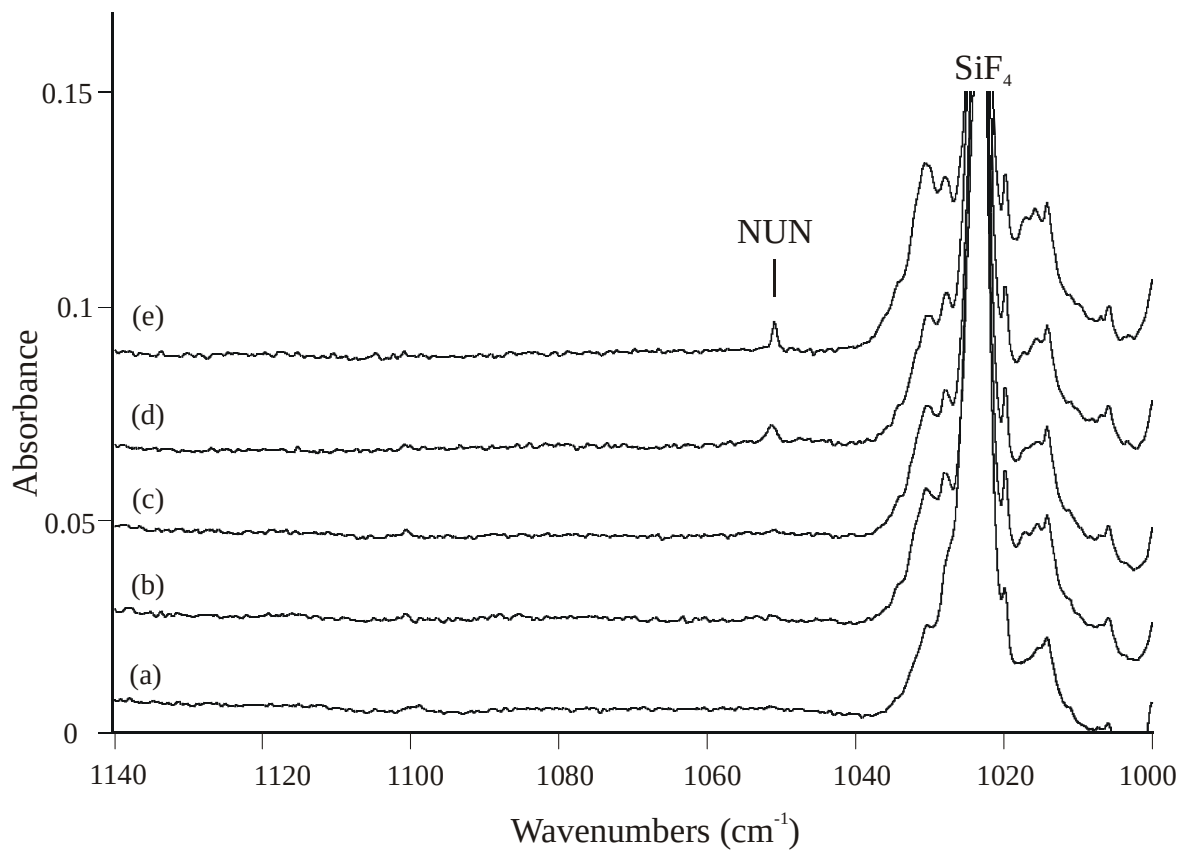


Figure S14. Infrared spectra from the 1140-1000 cm^{-1} region for the same samples and treatments as in the argon matrix spectra shown in Figure 3 from our paper. Note the weak 1051 cm^{-1} band for NUN, which shows that the U atom small molecule reaction is working in this experiment, even with trace N_2 impurity.