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On Structure and Bonding of Lanthanoid Trifluorides LnF_3 (Ln = La to Lu)

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Contents

TABLE S1. Valence Basis Functions for Ln Atoms:
ADF-provided a) and here added exponents.

Ln	Provided 6s exponents	Provided 6p exponent, here split	Provided or added(→) 5f exponent a)
La	1.95,1.25, 0.82	1.25 →1.60, 1.035	÷ → 1.65
Ce	1.95, 1.25, 0.82	1.25 →1.60, 1.035	÷ → 1.65
Pr	2.00, 1.30, 0.86	1.30 →1.65, 1.08	÷ → 1.65
Nd	2.00, 1.30, 0.87	1.30 →1.65, 1.085	÷ → 1.65
Pm	2.10, 1.35, 0.88	1.35 →1.725, 1.115	÷ → 1.65
Sm	2.15, 1.35, 0.89	1.35 →1.75, 1.12	÷ → 1.65
Eu	2.15, 1.40, 0.90	1.40 →1.775, 1.15	÷ → 1.65
Gd	2.20, 1.40, 0.92	1.40 →1.80, 1.16	÷ → 1.65
Tb	2.25, 1.40, 0.92	1.40 →1.825, 1.16	1.65
Dy	2.30, 1.45, 0.94	1.45 →1.875, 1.18	1.65
Ho	2.30, 1.45, 0.95	1.45 →1.875, 1.20	1.65
Er	2.35, 1.50, 0.96	1.45 →1.90, 1.23	1.65
Tm	2.40, 1.50, 0.97	1.45 →1.95, 1.235	1.65
Yb	2.40, 1.50, 0.97	1.45 →1.95, 1.235	1.65
Lu	2.45, 1.55, 1.00	1.55 →2.00, 1.275	1.65

a) E. Van Lenthe and E. J. Baerends; *J. Comput. Chem.* **2003**, *24*, 1142; [65]

TABLE S2. Valence MO bands of HoF_3 (C_{3v}, SR): Alpha orbital energies ε_i (in eV), orbital symmetries, occupation numbers, and % contributions [a)] of Ho and F valence AOs.

E_i	Sym.	Occ.	Ho(4f)	Ho(5d)	Ho(6s)	Ho(5p)	F(2s)	F(2p)
-8.56	$2A_2$	1	33					**67**
-8.74	7E	2	16			2		**82**
-8.87	$7A_1$	1	42	1	1	1		55
-9.02	$6A_1$	1	40	2	1	1		56
-9.16	6E	2	38	5				57
-9.56	5E	2	32	7				61
-9.90	$5A_1$	1	**79**	1				20
-9.93	$1A_2$	1	**69**					31
-9.93	4E	2	**70**	1				29
-10.09	3E	2	45	4		1	1	49
-10.46	$4A_1$	1	38	2	1		1	58

[a)] MOs dominated by Ho or by F AOs are bold face underlined

TABLE S3. Geometry optimization of LnF_3 (Ln = La to Lu) at scalar (SR) and spin-orbit coupled (SOC) relativistic ECP-DFT levels. Bond lengths R_{LnX} in pm, bond angles θ_{XLnX} for C_{3v} in degree (for D_{3h} θ= 120°).

Ln	Sym-metry	SR		SOC		R_{Recom} [a)]	θ_{Recom} [a)]	R_{Exp} [b)] R_e,R_g	θ_{Exp} [b)]
		R	θ	R	θ				
La	C_{3v}	211.7	113.3	211.7	113.3	207.7	109.0		
	D_{3h}	212.8		212.5					
Ce	C_{3v}	209.0	110.3	208.9	111.8	206.8	109.5		
	D_{3h}	210.6		210.3					
Pr	C_{3v}	208.8	114.6	208.2	113.8	205.8	110.0	205.6(5),209.1(3)	105.(2)
	D_{3h}	209.4		209.1					
Nd	C_{3v}	207.6	113.6	207.0	113.6	204.9	110.5		
	D_{3h}	208.3		207.9					
Pm	C_{3v}	207.0	115.8	206.3	115.0	203.9	111.0		
	D_{3h}	207.5		206.8					
Sm	C_{3v}	206.6	116.2	205.6	115.7	202.9	111.5		
	D_{3h}	207.1		206.0					
Eu	C_{3v}	206.1	116.7	204.8	116.2	202.0	112.0		
	D_{3h}	206.6		206.6					
Gd	C_{3v}	204.1	116.4	204.1	116.8	201.0	112.5	201.6(6),205.3(3)	110.(2)
	D_{3h}	204.4		204.4					
Tb	C_{3v}	202.7	114.1	203.4	117.4	200.1	113.0		
	D_{3h}	203.3		203.6					
Dy	C_{3v}	202.3	117.1	202.9	117.6	199.1	113.5		
	D_{3h}	202.4		203.1					
Ho	C_{3v}	201.3	117.5	202.2	117.7	198.1	114.0	198.(1),200.7(3)	108.(3)
	D_{3h}	201.6		202.4					
Er	C_{3v}	200.8	117.7	202.4	120.0	197.2	114.5		
	D_{3h}	201.1		202.0					
Tm	C_{3v}	200.5	118.0	201.4	118.4	196.2	115.0		
	D_{3h}	200.6		201.4					
Yb	C_{3v}	200.5	119.9	201.3	117.5	195.3	115.5		
	D_{3h}	200.1		200.8					
Lu	C_{3v}	197.7	117.4	197.6	117.4	194.3	116.0		
	D_{3h}	197.8		197.6					

[a)] Recommended Bond Lengths from Table 5 in Kovács and Konings' review.[2] [b)] Experimental bond lengths R_e for the lowest point of potential energy surface and R_g for the distance averaged over molecular vibrations and bond angles from Kovács and Konings' review,[2] and Hargittai.[3]

Table S4. Vibrational harmonic normal frequencies (in cm^{-1}) of LnF3 at the SR level.

Z.Ln	A1 invers	E bend	A1 stretch,sym	E stretch,asym
57.La	74	114	527	498
58.Ce	92	113	537	501
59.Pr	63	116	527	510
60.Nd	60	115	532	517
61.Pm	49	116	527	516
62.Sm	43	116	521	512
63.Eu	39	118	511	505
64.Gd	48	126	549	533
65.Tb	77	129	555	534
66.Dy	45	128	552	538
67.Ho	41	129	552	541
68.Er	38	129	545	539
69.Tm	41	131	532	531
70.Yb	21	128	515	521
71.Lu	49	141	571	567

Table S5. Change of geometry of LnF3 upon basis set extentsion (table S1):
Ln-F bond length *R* in pm, F-Ln-F bond angle *θ* in degree.

Ln		ADF-TZ2P	extended basis	Rec.[a)]	Exp.[b)] R_e,R_g
La	*R*	212.0	211.7	207.7	
	θ	113.4	113.3	109.0	
Ce	*R*	209.2	209.0	206.8	
	θ	110.4	110.3	110.0	
Pr	*R*	208.4	208.8	205.8	205.6(5),209.1(3)
	θ	112.8	114.6	110.0	
Nd	*R*	207.4	207.6	204.9	
	θ	113.7	113.6	110.5	
Pm	*R*	206. 5	207.0	203.9	
	θ	114.2	115.8	111.0	
Sm	*R*	206.4	206.6	202.9	
	θ	115.5	116.2	111.5	
Eu	*R*	205.8	206.1	202.0	
	θ	116.1	116.7	112.0	
Gd	*R*	203.6	204.1	201.0	201.6(6),205.3(3)
	θ	115.3	116.4	112.5	
Tb	*R*	202.2	202.7	200.1	
	θ	113.2	114.1	113.0	
Dy	*R*	201.9	202.3	199.1	
	θ	116.0	117.1	113.5	
Ho	*R*	201.1	201.3	198.1	198.(1),200.7(3)
	θ	116.3	117.5	114.0	
Er	*R*	200.8	200.8	197.2	
	θ	118.1	117.7	114.5	
Tm	*R*	200.3	200.5	196.2	
	θ	118.4	118.0	115.0	
Yb	*R*	200.3	200.5	195.3	
	θ	118.4	119.9	115.5	
Lu	*R*	197.7	197.7	194.3	
	θ	118.5	117.5	116.0	

[a)] Recommended Bond Lengths from Table 5 in Kovács and Konings' review.[2] [b)] Experimental bond lengths R_e for the lowest point of potential energy surface and R_g for the distance averaged over molecular vibrations from Kovács and Konings' review,[2] and Hargittai.[3]

FIGURE S1. Valence MO envelop diagram of GdF_3 (D_{3h}, SR, PW91-DF) showing from which Gd-4f AO the MOs of Gd(4f)-F(2p) mixed type originate.