Lanthanoids Lectures
03

Value of L

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H I K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

$4f^2$

$\ell_1 = 3;\ \ell_2 = 3$ $\qquad$ $s_1 = ½;\ s_2 = ½$

$L = \ell_1+\ell_2;\ \ell_1+\ell_2-1;\ldots;|\ell_1-\ell_2|$ $\qquad$ $S = s_1+s_2;\ s_1+s_2-1;\ldots;|s_1-s_2|$

$L = 6, 5, 4, 3, 2, 1, 0$ $\qquad$ $S = 1, 0$

I, H, G, F, D, P, S

$$\frac{[2(2\ell+1)]!}{[2(2\ell+1)-n]!\times n!}$$

$$\binom{14}{2} = \frac{14!}{12!\times 2!} = \frac{13\times 14}{2} = 91$$

$M_L \backslash M_S$	1	0	-1
6		$(3^+,3^-)$	
5	$(3^+,2^+)$	$(3^+,2^-)$ $(3^-,2^+)$	$(3^-,2^-)$
4	$(3^+,1^+)$	$(3^+,1^-)$ $(3^-,1^+)$ $(2^+,2^-)$	$(3^-,1^-)$
3	$(3^+,0^+)(2^+,1^+)$	$(3^+,0^-)$ $(3^-,0^+)$ $(2^+,1^-)$ $(2^-,1^+)$	$(3^-,0^-)$ $(2^-,1^-)$
2	$(3^+,-1^+)(2^+,0^+)$	$(3^+,-1^-)$ $(3^-,-1^+)$ $(2^+,0^-)$ $(2^-,0^+)$ $(1^+,1^-)$	$(3^-,-1^-)(2^-,0^-)$
1	$(3^+,\underline{2}^+)(2^+,\underline{1}^+)$ $(1^+,0^+)$	$(3^+,\underline{2}^-)$ $(3^-,\underline{2}^+)$ $(2^+,\underline{1}^-)$ $(2^-,\underline{1}^+)$ $(1^+,0^-)$ $(1^-,0^+)$	$(3^-,\underline{2}^-)$ $(2^-,\underline{1}^-)$ $(1^-,0^-)$
0	$(3^+,\underline{3}^+)(2^+,\underline{2}^+)$ $(1^+,\underline{1}^+)$	$(3^+,\underline{3}^-)$ $(3^-,\underline{3}^+)$ $(2^+,\underline{2}^-)$ $(2^-,\underline{2}^+)$ $(1^+,\underline{1}^-)$ $(1^-,\underline{1}^+)$ $(0^+,0^-)$	$(3^-,\underline{3}^-)$ $(2^-,\underline{2}^-)$ $(1^-,\underline{1}^-)$

^{1}I, ^{3}**H**, ^{1}G, ^{3}F, ^{1}D, ^{3}P, ^{1}S

Value of L

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H I K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

$M_L \setminus M_S$	1	0	-1
6		$(3^+,3^-)$	
5	$(3^+,2^+)$	$(3^+,2^-)$ $(3^-,2^+)$	$(3^-,2^-)$
4	$(3^+,1^+)$	$(3^+,1^-)$ $(3^-,1^+)$ $(2^+,2^-)$	$(3^-,1^-)$
3	$(3^+,0^+)(2^+,1^+)$	$(3^+,0^-)$ $(3^-,0^+)$ $(2^+,1^-)$ $(2^-,1^+)$	$(3^-,0^-)$ $(2^-,1^-)$
2	$(3^+,-1^+)(2^+,0^+)$	$(3^+,-1^-)$ $(3^-,-1^+)$ $(2^+,0^-)$ $(2^-,0^+)$ $(1^+,1^-)$	$(3^-,-1^-)(2^-,0^-)$
1	$(3^+,\underline{2}^+)(2^+,\underline{1}^+)$ $(1^+,0^+)$	$(3^+,\underline{2}^-)$ $(3^-,\underline{2}^+)$ $(2^+,\underline{1}^-)$ $(2^-,\underline{1}^+)$ $(1^+,0^-)$ $(1^-,0^+)$	$(3^-,\underline{2}^-)$ $(2^-,\underline{1}^-)$ $(1^-,0^-)$
0	$(3^+,\underline{3}^+)(2^+,\underline{2}^+)$ $(1^+,\underline{1}^+)$	$(3^+,\underline{3}^-)$ $(3^-,\underline{3}^+)$ $(2^+,\underline{2}^-)$ $(2^-,\underline{2}^+)$ $(1^+,\underline{1}^-)$ $(1^-,\underline{1}^+)$ $(0^+,0^-)$	$(3^-,\underline{3}^-)$ $(2^-,\underline{2}^-)$ $(1^-,\underline{1}^-)$

^{1}I, ^{3}**H**, ^{1}G, ^{3}F, ^{1}D, ^{3}P, ^{1}S

$$E(^3H) = F_0 - 25F_2 - 51F_4 - 13F_6$$
$$E(^3F) = F_0 - 10F_2 - 33F_4 - 286F_6$$
$$E(^1G) = F_0 - 30F_2 + 97F_4 + 78F_6$$
$$E(^1D) = F_0 + 19F_2 - 99F_4 + 715F_6$$
$$E(^1I) = F_0 + 25F_2 + 9F_4 + F_6$$
$$E(^3P) = F_0 + 45F_2 + 33F_4 - 1287F_6$$
$$E(^1S) = F_0 + 60F_2 + 198F_4 + 1716F_6$$

F_2	F_4	F_6	$2L+1$	$F_2 \times (2L+1)$	$F_4 \times (2L+1)$	$F_6 \times (2L+1)$
-25	-51	-13	11 (*H*)	-275	-561	-143
-10	-33	-286	7 (*F*)	-70	-231	-2002
-30	97	78	9 (*G*)	-270	873	702
19	-99	715	5 (*D*)	95	-495	3575
25	9	1	13 (*I*)	325	117	13
45	33	-1287	3 (*P*)	135	99	-3861
60	198	1716	1 (*S*)	60	198	1716
				0	0	0

$s_1 = ½; s_2 = ½$
$S = s_1+s_2; s_1+s_2-1;\ldots; |s_1-s_2|$
$S = 1, 0$

$\ell_1 = 3; \ell_2 = 3$
$L = \ell_1+\ell_2; \ell_1+\ell_2-1;\ldots; |\ell_1-\ell_2|$
$L = 6, 5, 4, 3, 2, 1, 0$
I, H, G, F, D, P, S

$M_L \backslash M_S$	1	0	-1
6		$(3^+,3^-)$	
5	$(3^+,2^+)$	$(3^+,2^-)$ $(3^-,2^+)$	$(3^-,2^-)$
4	$(3^+,1^+)$	$(3^+,1^-)$ $(3^-,1^+)$ $(2^+,2^-)$	$(3^-,1^-)$
3	$(3^+,0^+)(2^+,1^+)$	$(3^+,0^-)$ $(3^-,0^+)$ $(2^+,1^-)$ $(2^-,1^+)$	$(3^-,0^-)$ $(2^-,1^-)$
2	$(3^+,-1^+)(2^+,0^+)$	$(3^+,-1^-)$ $(3^-,-1^+)$ $(2^+,0^-)$ $(2^-,0^+)$ $(1^+,1^-)$	$(3^-,-1^-)(2^-,0^-)$
1	$(3^+,\underline{2}^+)(2^+,\underline{1}^+)$ $(1^+,0^+)$	$(3^+,\underline{2}^-)$ $(3^-,\underline{2}^+)$ $(2^+,\underline{1}^-)$ $(2^-,\underline{1}^+)$ $(1^+,0^-)$ $(1^-,0^+)$	$(3^-,\underline{2}^-)$ $(2^-,\underline{1}^-)$ $(1^-,0^-)$
0	$(3^+,\underline{3}^+)(2^+,\underline{2}^+)$ $(1^+,\underline{1}^+)$	$(3^+,\underline{3}^-)$ $(3^-,\underline{3}^+)$ $(2^+,\underline{2}^-)$ $(2^-,\underline{2}^+)$ $(1^+,\underline{1}^-)$ $(1^-,\underline{1}^+)$ $(0^+,0^-)$	$(3^-,\underline{3}^-)$ $(2^-,\underline{2}^-)$ $(1^-,\underline{1}^-)$

^{1}I, ^{3}**H**, ^{1}G, ^{3}F, ^{1}D, ^{3}P, ^{1}S

$\ell_1 = 2; \ell_2 = 2$
$L = \ell_1+\ell_2; \ell_1+\ell_2-1;\ldots; |\ell_1-\ell_2|$
$L = 4, 3, 2, 1, 0$
G, F, D, P, S

$M_L \backslash M_S$	1	0	-1
4		$(2^+,2^-)$	
3	$(2^+,1^+)$	$(2^+,1^-)$ $(2^-,1^+)$	$(2^-,1^-)$
2	$(2^+,0^+)$	$(2^+,0^-)$ $(2^-,0^+)$ $(1^+,1^-)$	$(2^-,0^-)$
1	$(2^+,\underline{1}^+)(1^+,0^+)$	$(2^+,\underline{1}^-)$ $(2^-,\underline{1}^+)$ $(1^+,0^-)$ $(1^-,0^+)$	$(2^-,\underline{1}^-)$ $(1^-,0^-)$
0	$(2^+,\underline{2}^+)$ $(1^+,\underline{1}^+)$	$(2^+,\underline{2}^-)$ $(2^-,\underline{2}^+)$ $(1^+,\underline{1}^-)$ $(1^-,\underline{1}^+)$ $(0^+,0^-)$	$(2^-,\underline{2}^-)$ $(1^-,\underline{1}^-)$

^{1}G, ^{3}**F**, ^{1}D, ^{3}P, ^{1}S

Value of L

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H I K L M N O Q R T U V W X Y Z

f^3, f^{11}

S. No.	L	Label	S	Multiplicity (2S + 1)	Term symbol	Total values of J	Several possible terms	Array	Micro states
1	8	L	1/2	2	^2L	J = 2	$^2L_{17/2}$, $^2L_{15/2}$	17 x 2	34
2	7	K	1/2	2	^2K	J = 2	$^2K_{15/2}$, $^2K_{13/2}$	15 x 2	30
3	6	I	3/2	4	^4I	J = 3	$^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$ $^4I_{9/2}$	13 x 4	52
			1/2	2	^2I	J = 2	$^2I_{13/2}$, $^2I_{11/2}$	13 x 2	26
4	5	H	1/2	2	^2H	J = 2	$^2H_{11/2}$, $^2H_{9/2}$	11 x 2	22
			1/2	2	^2H	J = 2	$^2H_{11/2}$, $^2H_{9/2}$	11 x 2	22
5	4	G	3/2	4	^4G	J = 4	$^4G_{11/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$	9 x 4	36
			1/2	2	^2G	J = 2	$^2G_{9/2}$, $^2G_{7/2}$	9 x 2	18
			1/2	2	^2G	J = 2	$^2G_{9/2}$, $^2G_{7/2}$	9 x 2	18
6	3	F	3/2	4	^4F	J = 4	$^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$	7 x 4	28
			1/2	2	^2F	J = 2	$^2F_{7/2}$, $^2F_{5/2}$	7 x 2	14
			1/2	2	^2F	J = 2	$^2F_{7/2}$, $^2F_{5/2}$	7 x 2	14
7	2	D	3/2	4	^4D	J = 4	$^4D_{7/2}$, $^4D_{5/2}$, $^4D_{3/2}$, $^4D_{1/2}$	5 x 4	20
			1/2	2	^2D	J = 2	$^2D_{5/2}$, $^2D_{3/2}$	5 x 2	10
			1/2	2	^2D	J = 1	$^2D_{5/2}$, $^2D_{3/2}$	5 x 2	10
8	1	P	1/2	2	^2P	J = 2	$^2P_{3/2}$, $^2P_{1/2}$	3 x 2	6
9	0	S	3/2	4	^4S	J = 1	$^4S_{1/2}$	1 x 4	4

$$\frac{\left[2(2\ell+1)\right]!}{\left[2(2\ell+1)-n\right]!\times n!}$$

$$\binom{14}{3} = \frac{14!}{11!\times 3!} = \frac{12\times 13\times 14}{2\times 3} = 364$$

364

Value of L

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H I K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

Value of L

0 1 2 **3** 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D **F** G H I K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	**3**	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

Value of L

0 1 2 3 4 **5** 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G **H** I K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	**5**	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

Value of L

0 1 2 3 4 5 **6** 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H **I** K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	**6**	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

Value of L

0 1 2 3 4 5 **6** 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H **I** K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	**6**	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

Value of L

0 1 2 3 4 **5** 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G **H** I K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	**5**	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

Value of L

0 1 2 **3** 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D **F** G H I K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	**3**	**^7F**
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

Value of L

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H I K L M N O Q R T U V W X Y Z

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	**0**	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

Value of L

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H I K L M N O Q R T U V W X Y Z

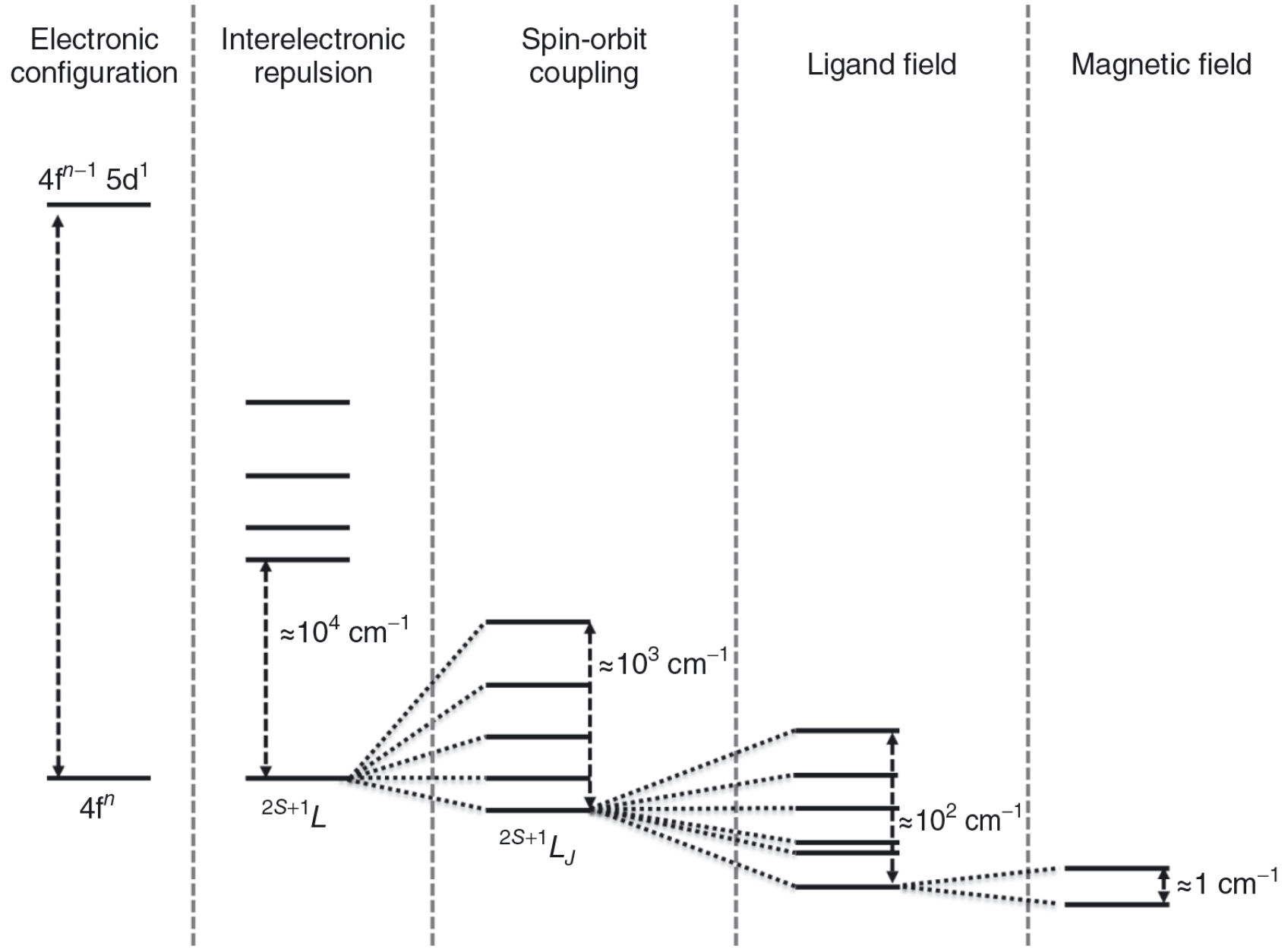
Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state
La^{III}	f^0	none	0	^1S
Ce^{III}	f^1	3	3	^2F
Pr^{III}	f^2	3, 2	5	^3H
Nd^{III}	f^3	3, 2, 1	6	^4I
Pm^{III}	f^4	3, 2, 1, 0	6	^5I
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S
Tb^{III}	f^8	3[a]	3	^7F
Dy^{III}	f^9	3, 2	5	^6H
Ho^{III}	f^{10}	3, 2, 1	6	^5I
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

d electron config.	Angular momentum relevant orbitals	Total orbital angular momentum	GS term
d^0	none	0	^{1}S
d^1	2	2	^{2}D
d^2	2, 1	3	^{3}F
d^3	2, 1, 0	3	^{4}F
d^4	2, 1, 0, -1	2	^{5}D
d^5	2, 1, 0, -1, -2	0	^{6}S

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state	
La^{III}	f^0	none	0	^1S (1)	1
Ce^{III}	f^1	3	3	^2F (14)	14
Pr^{III}	f^2	3, 2	5	^3H (33)	91
Nd^{III}	f^3	3, 2, 1	6	^4I (52)	364
Pm^{III}	f^4	3, 2, 1, 0	6	^5I (65)	1001
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H (66)	2002
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F (21)	3003
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S (8)	3432
Tb^{III}	f^8	3[a]	3	^7F	
Dy^{III}	f^9	3, 2	5	^6H	
Ho^{III}	f^{10}	3, 2, 1	6	^5I	
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I	
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H	
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F	
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S	

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.


Electronic configuration
Interelectronic repulsion
Spin-orbit coupling
Ligand field
Magnetic field
$4f^{n-1}\,5d^1$
$4f^n$
$\approx 10^4$ cm^{-1}
^{2S+1}L
$\approx 10^3$ cm^{-1}
$^{2S+1}L_J$
$\approx 10^2$ cm^{-1}
≈ 1 cm^{-1}

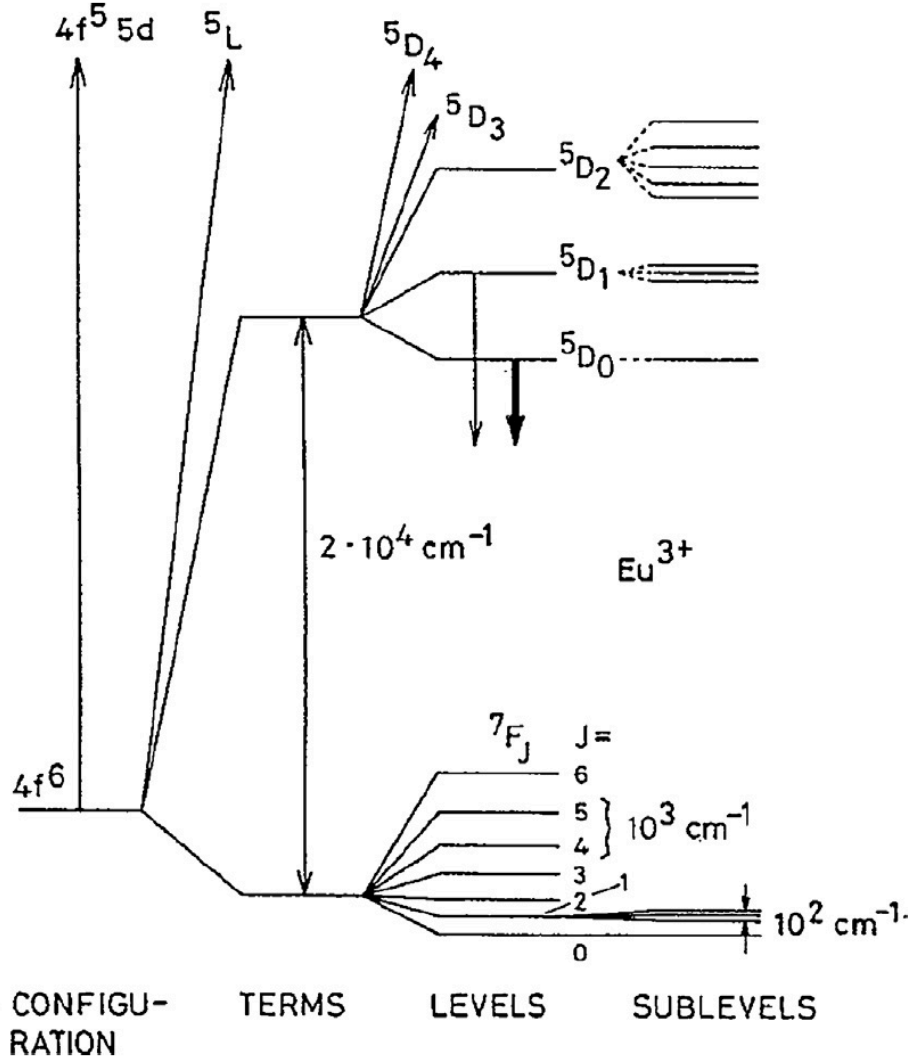
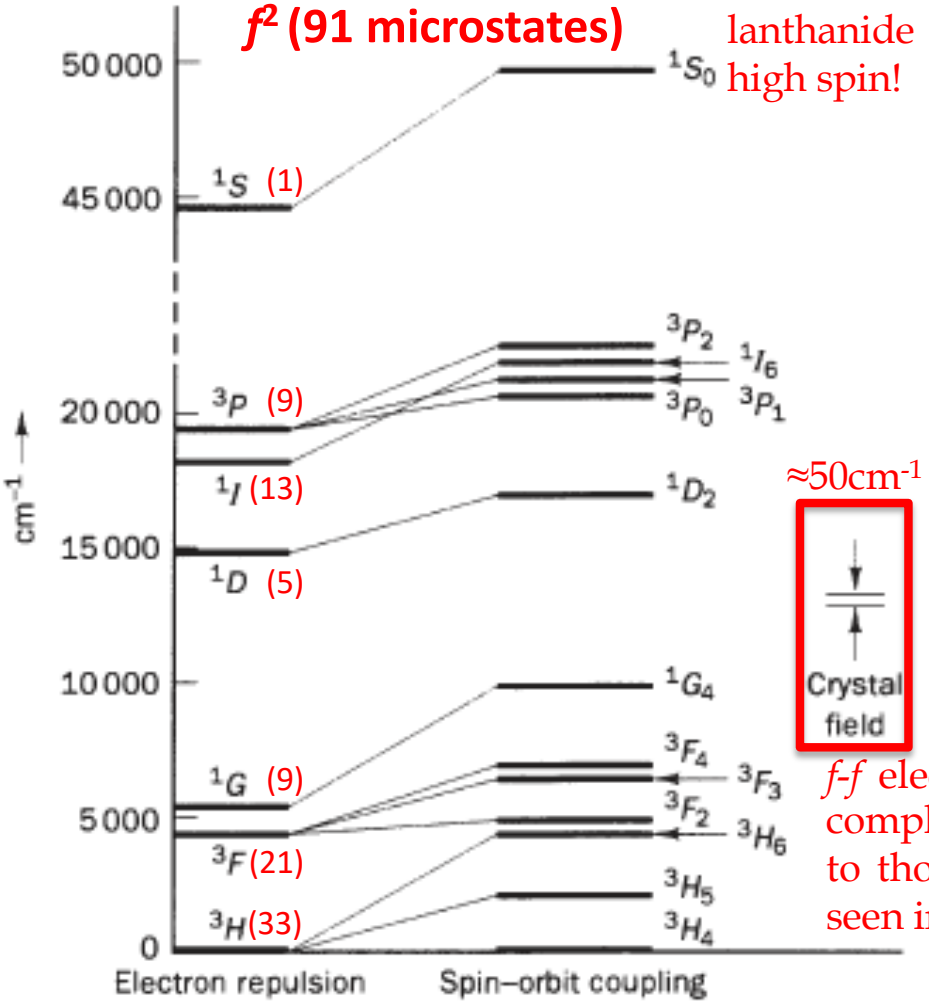


Fig. 2. Partial energy diagram of Eu^{3+} ($4f^6$) showing the relative magnitude of the interelectronic repulsion (terms), spin–orbit coupling (levels) and crystal-field effects (sublevels). The downward arrows indicate the excited states $^5D_0$ and $^5D_1$ from which luminescence occurs.

K. Binnemans
Coord. Chem. Rev. 2015, **295**, 1-45



in the language of crystal field theory, all lanthanide and actinide complexes are weak field, high spin!

Terms arising from the f^2 configurations (left-hand column) and state consequently resulting from SO coupling

Russel-Saunders term	**Spin-Orbit states**
^1S	$^1S_0$
^3P	$^3P_0\ ^3P_1\ ^3P_2$
^1D	$^1D_2$
^3F	$^3F_2\ ^3F_3\ ^3F_4$
^1G	$^1G_4$
^3H	$^3H_4\ ^3H_5\ ^3H_6$
^1I	$^1I_6$

$s_1 = ½;\ s_2 = ½$

$S = s_1 + s_2 = 1;\ S = s_1 - s_2 = 0$

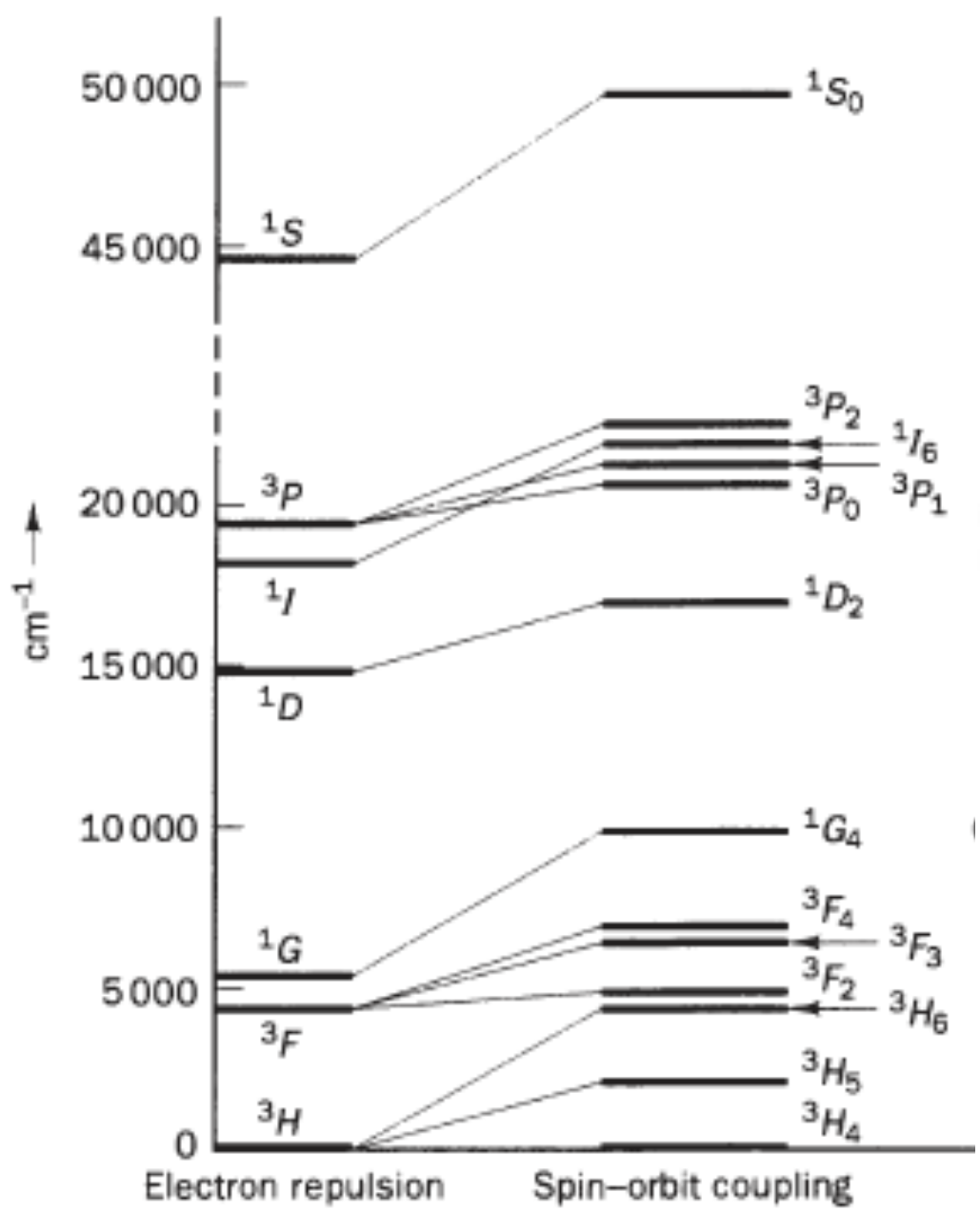
$\ell_1 = 3;\ \ell_2 = 3$

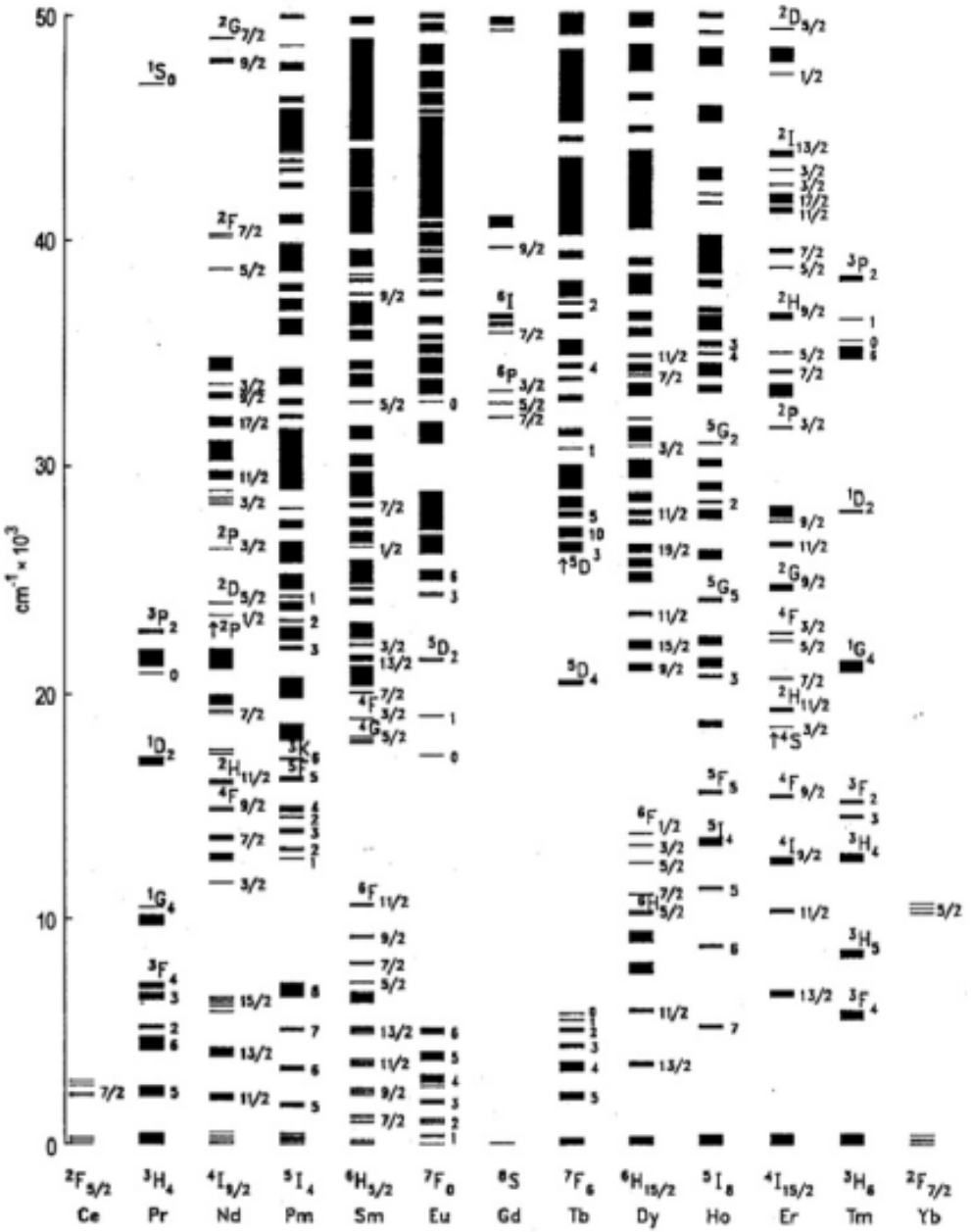
$L = \ell_1+\ell_2;\ \ell_1+\ell_2-1;\ldots;|\ell_1-\ell_2|$

$J = L + S;\ L + S - 1;\ldots;|L - S|$

f-f electronic spectra of the complexes are very similar to those of the free ions as seen in arc spectra!

The Pr^{3+} ($4f^2$) electronic energy level diagram. A typical crystal field splitting is shown at the right; its effects are much smaller than those of spin-orbit coupling. As with Tanabe-Sugano diagrams, the horizontal axis is taken as the ground state ($^3H_4$). This enables the effects of interactions between levels with the same total angular momentum to be more clearly seen. Note, for instance, the relative upward displacements of levels with the J quantum number 4 ($^3F_4$, $^1G_4$).


50 000
45 000
20 000
15 000
10 000
5000
0
cm⁻¹
^1S
^3P
^1I
^1D
^1G
^3F
^3H
$^1S_0$
$^3P_2$
$^1I_6$
$^3P_0$
$^3P_1$
$^1D_2$
$^1G_4$
$^3F_4$
$^3F_3$
$^3F_2$
$^3H_6$
$^3H_5$
$^3H_4$
Electron repulsion
Spin–orbit coupling


cm⁻¹ × 10³
50
40
30
20
10
0
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb

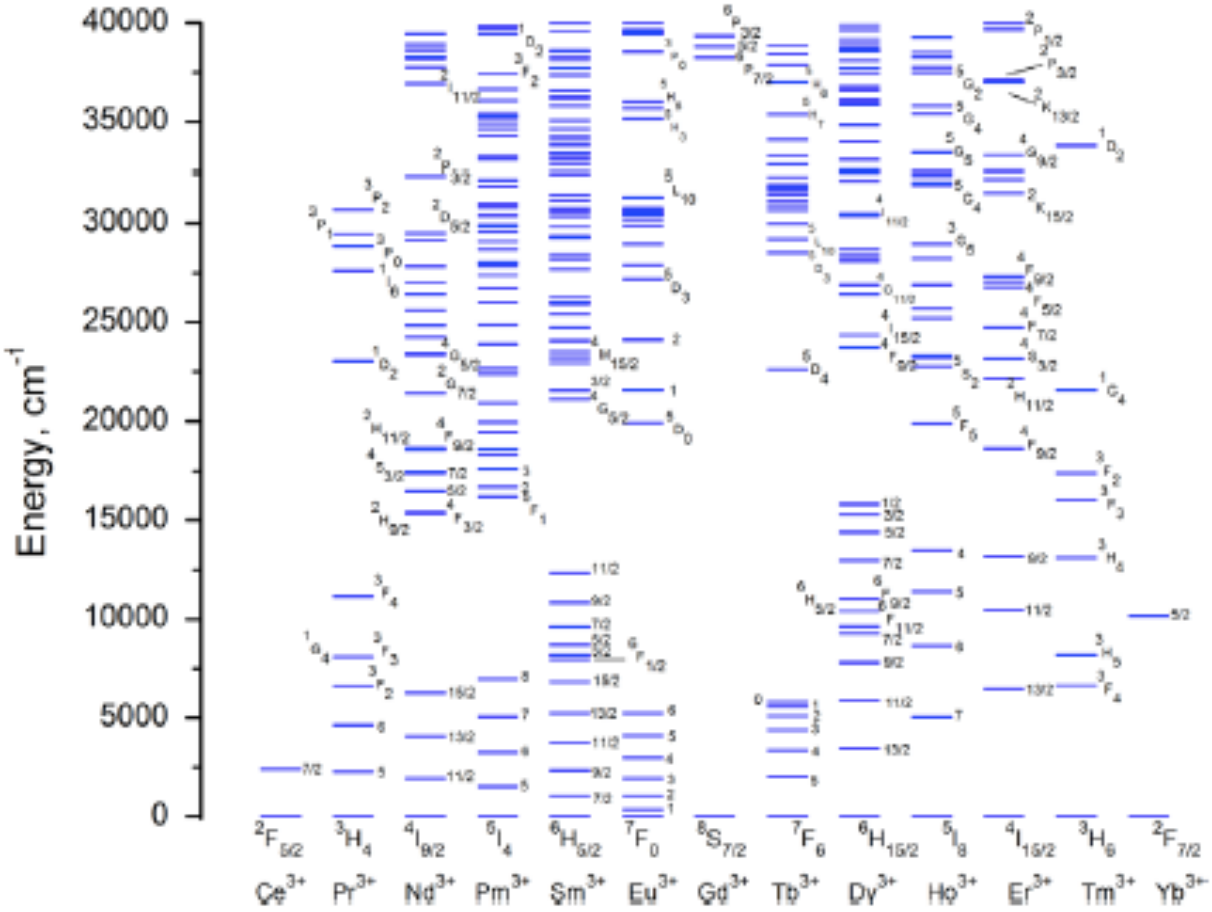
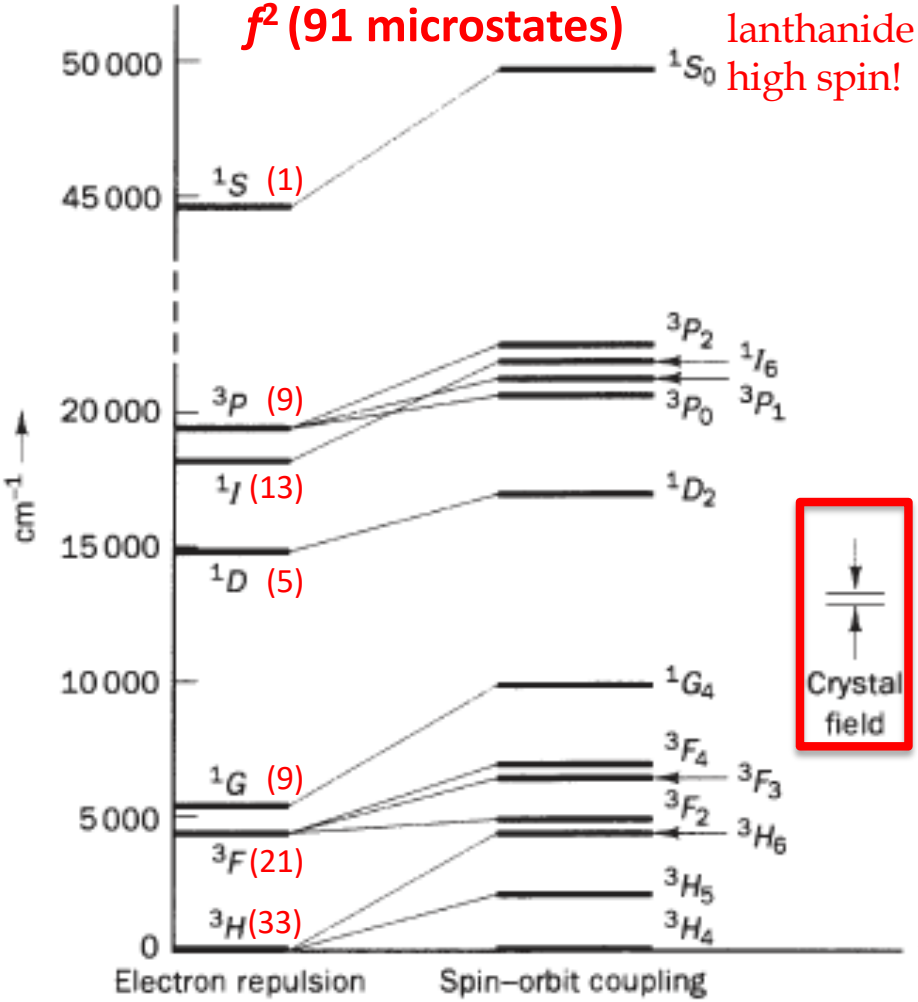


Fig. 2. Calculated energy levels of trivalent lanthanides in the energy range up to 40,000 cm^{-1}.

Ma *et al.*, Journal of Luminescence 2016, **170**, 369



in the language of crystal field theory, all lanthanide and actinide complexes are weak field, high spin!

Terms arising from the f^2 configurations (left-hand column) and state consequently resulting from SO coupling

Russel-Saunders (RS) term	**Spin-Orbit states**
^1S	$^1S_0$
^3P	$^3P_0$ $^3P_1$ $^3P_2$
^1D	$^1D_2$
^3F	$^3F_2$ $^3F_3$ $^3F_4$
^1G	$^1G_4$
^3H	$^3H_4$ $^3H_5$ $^3H_6$
^1I	$^1I_6$

Terms arising from the f^2 configurations (left-hand column) and state consequently resulting from SO coupling

RS term	**Degeneracy**	
^1S	$1(^1S_0)$	1
^3P	$1(^3P_0)$ $3(^3P_1)$ $5(^3P_2)$	
	9	
^1D	$5(^1D_2)$	5
^3F	$5(^3F_2)$ $7(^3F_3)$ $9(^3F_4)$	21
^1G	$9(^1G_4)$	9
^3H	$9(^3H_4)$ $11(^3H_5)$ 13 $(^3H_6)$	33
^1I	$13(I_6)$	13

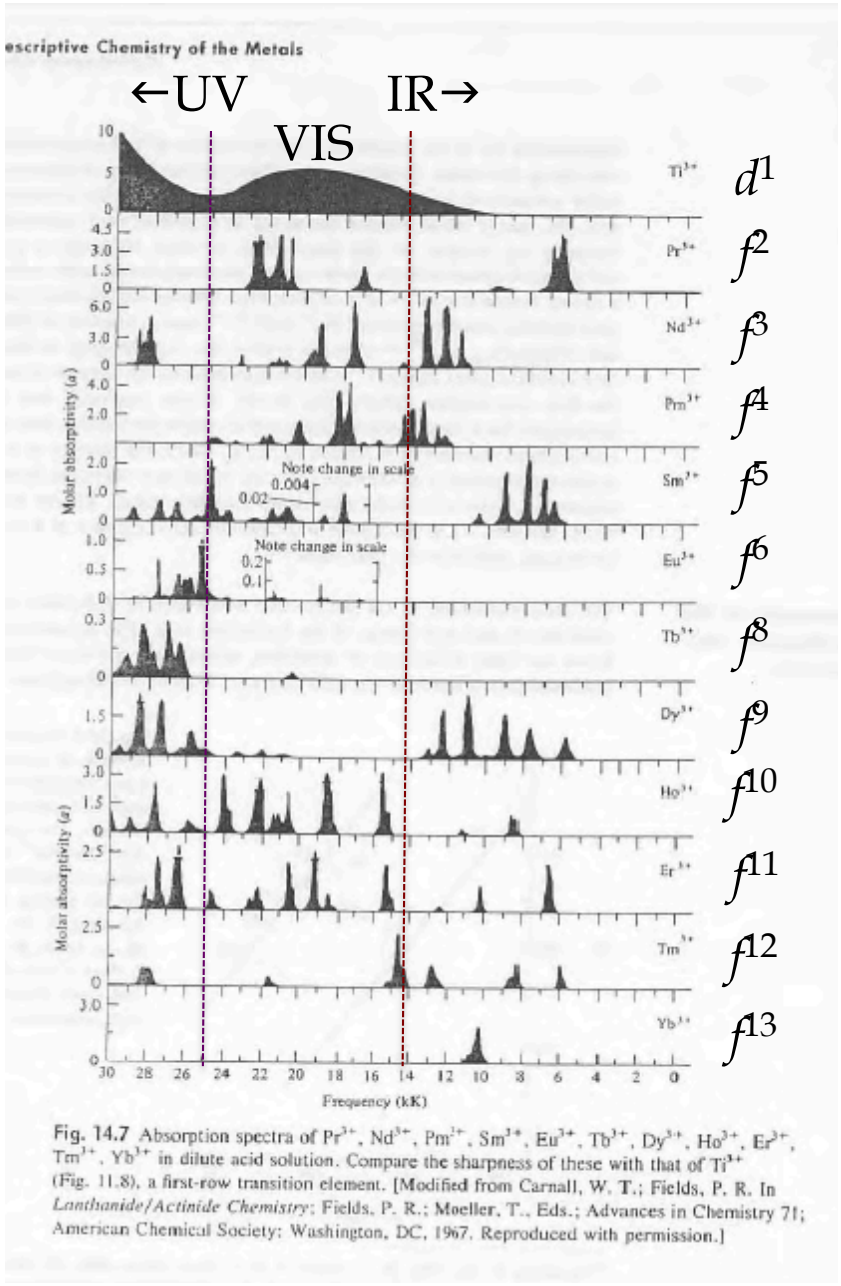


Fig. 14.7 Absorption spectra of Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} in dilute acid solution. Compare the sharpness of these with that of Ti^{3+} (Fig. 11.8), a first-row transition element. [Modified from Carnall, W. T.; Fields, P. R. In *Lanthanide/Actinide Chemistry*; Fields, P. R.; Moeller, T., Eds.; Advances in Chemistry 71; American Chemical Society: Washington, DC, 1967. Reproduced with permission.]

$$\left|n,\ell,m_\ell\right\rangle = R_{n,\ell}P_\ell^{|m_\ell|}\left(\cos\theta\right)\frac{e^{im_\ell\varphi}}{\sqrt{2\pi}}$$

If we carry a rotation of Φ around z

$$\varphi \rightarrow \varphi + \Phi$$

$$R_{n,\ell}P_\ell^{|m_\ell|}\left(\cos\theta\right)\frac{e^{im_\ell\varphi}}{\sqrt{2\pi}} \rightarrow R_{n,\ell}P_\ell^{|m_\ell|}\left(\cos\theta\right)\frac{e^{im_\ell\left(\varphi+\Phi\right)}}{\sqrt{2\pi}}$$

The rotation is thus given by the matrix

$$\begin{pmatrix} e^{i\ell\Phi} & 0 & \cdots & 0 \\ 0 & e^{i(\ell-1)\Phi} & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & e^{-i\ell\Phi} \end{pmatrix}$$

$$\chi\left(\Phi\right) = e^{i\ell\Phi} + e^{i(\ell-1)\Phi} + \ldots + e^{-i\ell\Phi} = e^{-i\ell\Phi}\sum_{n=0}^{2\ell}\left(e^{i\Phi}\right)^n = \frac{\sin\left(\ell+\frac{1}{2}\right)\Phi}{\sin\frac{\Phi}{2}}$$

$$\chi(\Phi) = e^{i\ell\Phi} + e^{i(\ell-1)\Phi} + \ldots + e^{-i\ell\Phi} = e^{-i\ell\Phi}\sum_{n=0}^{2\ell}\left(e^{i\Phi}\right)^n = \frac{\sin\left(\ell+\frac{1}{2}\right)\Phi}{\sin\frac{\Phi}{2}}$$

Geometrical series from $e^{-i\ell\Phi}$ to $e^{i\ell\Phi}$ having path $e^{i\Phi}$

$$a + ar + ar^2 + \ldots + ar^{n-1} + ar^n = a\frac{r^{n+1}-1}{r-1}$$

$$a = e^{-i\ell\Phi}; \quad r = e^{i\Phi}; \quad n = 2\ell$$

$$e^{-i\ell\Phi}\frac{\left(e^{i\Phi}\right)^{2\ell+1}-1}{e^{i\Phi}-1} = e^{-i\ell\Phi}\frac{e^{i(2\ell+1)\Phi}-1}{e^{i\Phi}-1} =$$

$$\frac{e^{i\ell\Phi}e^{i\Phi}-e^{-i\ell\Phi}}{e^{i\Phi}-1} = \frac{e^{i(\ell+1)\Phi}-e^{-i\ell\Phi}}{e^{i\Phi}-1} =$$

$$\frac{\sin\left(\ell+\frac{1}{2}\right)\Phi}{\sin\frac{\Phi}{2}}$$

$$\cos\theta = \frac{e^{i\theta}+e^{-i\theta}}{2}; \qquad \sin\theta = \frac{e^{i\theta}-e^{-i\theta}}{2i}$$

$$\cos 2\theta = \frac{e^{i2\theta}+e^{-i2\theta}}{2}; \quad \sin\theta = \frac{e^{i2\theta}-e^{-i2\theta}}{2i}$$

$$e^{i(\ell+1)\Phi} - e^{-i\ell\Phi} = e^{i\left(\ell+\frac{1}{2}\right)\Phi}e^{i\frac{1}{2}\Phi} - e^{-i\left(\ell+\frac{1}{2}\right)\Phi}e^{i\frac{1}{2}\Phi} =$$

$$2ie^{i\frac{1}{2}\Phi}\sin\left(\ell+\frac{1}{2}\right)\Phi$$

$$e^{i\Phi}-1 = e^{i\frac{1}{2}\Phi}\left(e^{i\frac{1}{2}\Phi}-e^{-i\frac{1}{2}\Phi}\right) = 2ie^{i\frac{1}{2}\Phi}\sin\frac{\Phi}{2}$$

$$\chi(\Phi) = \frac{\sin\left(\ell + \frac{1}{2}\right)\Phi}{\sin\frac{\Phi}{2}}$$

$$\Phi = \pi \qquad \chi(C_2) = \frac{\sin\left(\ell + \frac{1}{2}\right)\Phi}{1} = (-1)^{\ell}$$

$$\Phi = \frac{\pi}{2} \qquad \chi(C_4) = \begin{cases} 1 & \ell = 0,1,4,5\ldots \\ -1 & \ell = 2,3,6,7\ldots \end{cases}$$

The characters of the reducible representation Γ spanned by the five d orbitals ($\ell = 2$) in the point group D_{4h} (we limit our attention to the pure rotational group D_4)

E	$2C_4$	C_2	$2C_2'$	$2C_2''$
5	−1	1	1	1

The irreducible components of Γ are

$$\underbrace{n(a_1) = 1}_{d_{z^2}}; \quad n(a_2) = 0; \quad \underbrace{n(b_1) = 1}_{d_{x^2-y^2}}; \quad \underbrace{n(b_2) = 1}_{d_{xy}}; \quad \underbrace{n(e) = 1}_{d_{xz},d_{yz}}$$

Atomic wave functions are in general made up by both an orbital (ℓ) and a spin part (s). Whereas the orbital part is always characterized by having integer values of ℓ, this is not so for the spin part. In a state system characterized by the quantum number J we have

$$\vec{J} = \vec{L} + \vec{S}$$

J will be always half-integer in systems with an odd number of electrons

$$\chi(\Phi) = \frac{\sin\left(j+\frac{1}{2}\right)\Phi}{\sin\frac{\Phi}{2}}$$

For ***J*** integer $$\chi\left(\Phi+2\pi\right) = \frac{\sin\left(j+\frac{1}{2}\right)\left(\Phi+2\pi\right)}{\sin\frac{\left(\Phi+2\pi\right)}{2}} = \frac{\sin\left[\left(j+\frac{1}{2}\right)\Phi+\pi\right]}{\sin\left(\frac{\Phi}{2}+\pi\right)} = \frac{-\sin\left(j+\frac{1}{2}\right)\Phi}{-\sin\frac{\Phi}{2}} = \chi\left(\Phi\right)$$

For ***J*** half-integer $$\chi\left(\Phi+2\pi\right) = \frac{\sin\left(j+\frac{1}{2}\right)\left(\Phi+2\pi\right)}{\sin\frac{\left(\Phi+2\pi\right)}{2}} = \frac{\sin\left[\left(j+\frac{1}{2}\right)\Phi+2\pi\right]}{\sin\left(\frac{\Phi}{2}+\pi\right)} = \frac{\sin\left(j+\frac{1}{2}\right)\Phi}{-\sin\frac{\Phi}{2}} = -\chi\left(\Phi\right)$$

$$\chi(\Phi) = \frac{\sin\left(j+\frac{1}{2}\right)\Phi}{\sin\frac{\Phi}{2}}$$

$$\textit{Hospital's rule}\begin{cases}\chi(0) = \dfrac{\left(j+\frac{1}{2}\right)\cos\left(j+\frac{1}{2}\right)0}{\frac{1}{2}\cos\frac{1}{2}0} = 2j+1 \\ \chi(2\pi) = \dfrac{\left(j+\frac{1}{2}\right)\cos\left(j+\frac{1}{2}\right)2\pi}{\frac{1}{2}\cos\frac{1}{2}2\pi} = \begin{cases} 2j+1 & j \text{ integer} \\ -(2j+1) & j \text{ half-integer} \end{cases}\end{cases}$$

For half integer values of J

$$\chi(\Phi+2\pi) = -\chi(\Phi)$$

$$\chi\left(RC_n\right) = -\chi\left(C_n\right)$$

RC_n and C_n must be in different classes

A new group element (R), corresponding to a 2π rotation, is introduced. It implies a double number of elements but not a twice number of classes (irreducible representations); rotations by π are in fact unique!

O	E	$8C_3$	$3C_2$	$6C_2'$	$6C_4$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	-1	1
T_2	3	0	-1	1	-1

$h = 24$
$\Gamma = 5$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2'$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1

$h = 48$
$\Gamma = 10$

For half integer values of J

$$\chi(\Phi + 2\pi) = -\chi(\Phi)$$

$$\chi(RC_n) = -\chi(C_n)$$

RC_n and C_n must be in different classes

$$\chi(\pi) = \frac{\sin\left(j+\frac{1}{2}\right)\pi}{\sin\frac{\pi}{2}} = \frac{\sin\left(j+\frac{1}{2}\right)\pi}{1} = 0$$

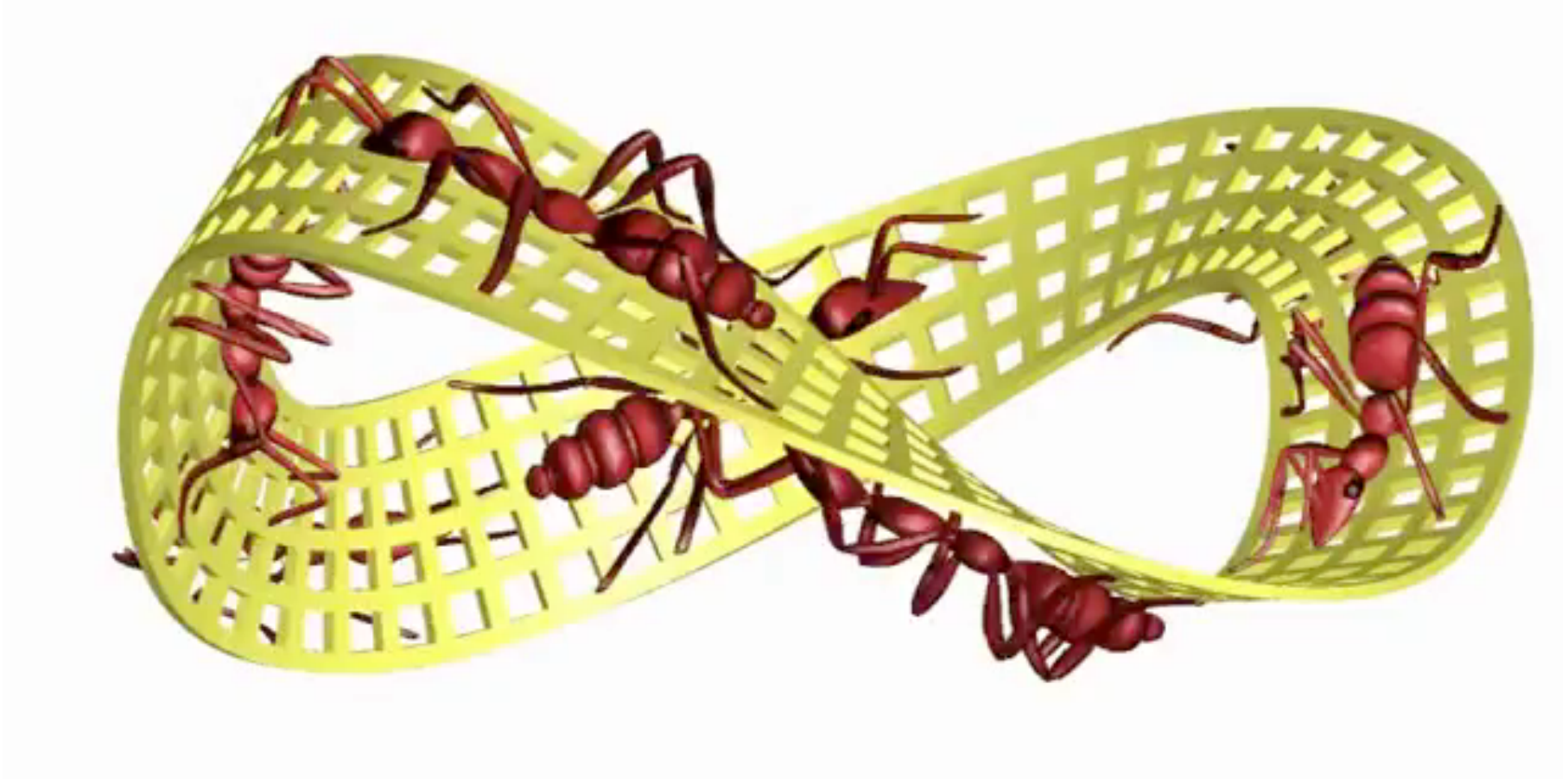
$$\chi(\pi + 2\pi) = \frac{\sin\left(j+\frac{1}{2}\right)(\pi + 2\pi)}{\sin\frac{(\pi + 2\pi)}{2}} = \frac{\sin\left[\left(j+\frac{1}{2}\right)\pi + 2\pi\right]}{-1} = 0$$

except

$$\chi(RC_2) = \chi(C_2) = 0$$

Moebius strip

$$\chi(\Phi + 2\pi) = -\chi(\Phi)$$



On the other hand a rotation by 4π is equivalent to the $\hat{E}$ operator. Moreover, the only character with a unique value is the character for a rotation of π for j half-integer

$$\chi(\pi) = \frac{\sin\left(j+\frac{1}{2}\right)\pi}{\sin\frac{1}{2}\pi} = 0 = \chi(3\pi) = \frac{\sin\left(j+\frac{1}{2}\right)3\pi}{\sin\frac{3}{2}\pi}$$

The introduction of a new group element (R), corresponding to a 2π rotation, implies a double number of elements but not a twice number of classes (irreducible representations); rotations by π are in fact unique!

Complete Character Table for Point Group D_{4h}

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2iC_4$	iC_2	$2iC_2'$	$2iC_2''$
a_{1g}	1	1	1	1	1	1	1	1	1	1
a_{2g}	1	1	1	−1	−1	1	1	1	−1	−1
b_{1g}	1	−1	1	1	−1	1	−1	1	1	−1
b_{2g}	1	−1	1	−1	1	1	−1	1	−1	1
e_g	2	0	−2	0	0	2	0	−2	0	0
a_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
a_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
b_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1
b_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1
e_u	2	0	−2	0	0	−2	0	2	0	0

The tables of characters of D_4 and D'_4 symmetry point groups are then

D_4	E	$2C_4$	$C_2(=C_4^2)$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	−1	−1	z, R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

D'_4		E	R	C_4 C_4^3R	C_4^3 C_4R	C_2 C_2R	$2C_2'$ $2C_2'R$	$2C_2''$ $2C_2''R$
Γ_1	A_1'	1	1	1	1	1	1	1
Γ_2	A_2'	1	1	1	1	1	−1	−1
Γ_3	B_1'	1	1	−1	−1	1	1	−1
Γ_4	B_2'	1	1	−1	−1	1	−1	1
Γ_5	E_1'	2	2	0	0	−2	0	0
Γ_6	E_2'	2	−2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
Γ_7	E_3'	2	−2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0

Classes containing rotations by π correspond to one class each of the double group, whereas all others correspond to two classes each.

The tables of characters of *O* and *O′* symmetry point groups are then

O	E	$8C_3$	$3C_2(=C_4^2)$	$6C_4$	$6C_2$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1	−1	$(R_x, R_y, R_z); (x, y, z)$	
T_2	3	0	−1	−1	1		(xy, xz, yz)

O'		E	R	$4C_3$ $4C_3^2R$	$4C_3^2$ $4C_3R$	$3C_2$ $3C_2R$	$3C_4$ $3C_4^3R$	$3C_4^3$ $3C_4R$	$6C_2'$ $6C_2'R$
Γ_1	A_1'	1	1	1	1	1	1	1	1
Γ_2	A_2'	1	1	1	1	1	−1	−1	−1
Γ_3	E_1'	2	2	−1	−1	2	0	0	0
Γ_4	T_1'	3	3	0	0	−1	1	1	−1
Γ_5	T_2'	3	3	0	0	−1	−1	−1	1
Γ_6	E_2'	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7	E_3'	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8	G'	4	−4	−1	1	0	0	0	0

O'		E	R	$4C_3$ $4C_3^2R$	$4C_3^2$ $4C_3R$	$3C_2$ $3C_2R$	$3C_4$ $3C_4^3R$	$3C_4^3$ $3C_4R$	$6C_2'$ $6C_2'R$
Γ_1	A_1'	1	1	1	1	1	1	1	1
Γ_2	A_2'	1	1	1	1	1	−1	−1	−1
Γ_3	E_1'	2	2	−1	−1	2	0	0	0
Γ_4	T_1'	3	3	0	0	−1	1	1	−1
Γ_5	T_2'	3	3	0	0	−1	−1	−1	1
Γ_6	E_2'	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7	E_3'	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8	G'	4	−4	−1	1	0	0	0	0

A point to note is that the double-valued representations all are of even dimension. All levels having half-integer values of j are therefore at least twofold degenerate. This result has been shown by **Kramers** to be true in general for all half-integer values of j in any symmetry, provided that no magnetic field is present. Such a degeneracy is accordingly called a **Kramers degeneracy**.

O'		E	R	$4C_3$ $4C_3^2R$	$4C_3^2$ $4C_3R$	$3C_2$ $3C_2R$	$3C_4$ $3C_4^3R$	$3C_4^3$ $3C_4R$	$6C_2'$ $6C_2'R$
Γ_1	A_1'	1	1	1	1	1	1	1	1
Γ_2	A_2'	1	1	1	1	1	−1	−1	−1
Γ_3	E_1'	2	2	−1	−1	2	0	0	0
Γ_4	T_1'	3	3	0	0	−1	1	1	−1
Γ_5	T_2'	3	3	0	0	−1	−1	−1	1
Γ_6	E_2'	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7	E_3'	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8	G'	4	−4	−1	1	0	0	0	0

$$\chi(\Phi)=\frac{\sin\left(j+\frac{1}{2}\right)\Phi}{\sin\frac{\Phi}{2}}$$

$j = \ell = 2$

	E	$8C_3$	$3C_2$	$6C_4$	$6C'_2$
χ	5	-1	1	-1	1

$$\Gamma_{\ell=2}=e+t_2=\Gamma_3+\Gamma_5$$

Hospital's rule

$$\begin{cases}\chi(0)=\dfrac{\left(\ell+\frac{1}{2}\right)\cos\left(\ell+\frac{1}{2}\right)0}{\frac{1}{2}\cos\frac{1}{2}0}=2\ell+1\\ \chi(2\pi)=\dfrac{\left(\ell+\frac{1}{2}\right)\cos\left(\ell+\frac{1}{2}\right)2\pi}{\frac{1}{2}\cos\frac{1}{2}2\pi}=\begin{cases}2\ell+1 & \ell \text{ integer}\\ -(2j+1) & j \text{ half-integer}\end{cases}\end{cases}$$

$$\chi(0)=\frac{\left(\ell+\frac{1}{2}\right)\cos\left(\ell+\frac{1}{2}\right)0}{\frac{1}{2}\cos\frac{1}{2}0}=2\ell+1$$

$$\chi\left(\frac{2\pi}{3}\right)=\frac{\sin\left(\ell+\frac{1}{2}\right)\left(\frac{2\pi}{3}\right)}{\sin\left(\frac{2\pi}{6}\right)}=-1$$

$$\chi(\pi)=\frac{\sin\left(\ell+\frac{1}{2}\right)(\pi)}{\sin\left(\frac{\pi}{2}\right)}=1$$

$$\chi\left(\frac{2\pi}{4}\right)=\frac{\sin\left(\ell+\frac{1}{2}\right)\left(\frac{2\pi}{4}\right)}{\sin\left(\frac{\pi}{4}\right)}=-1$$

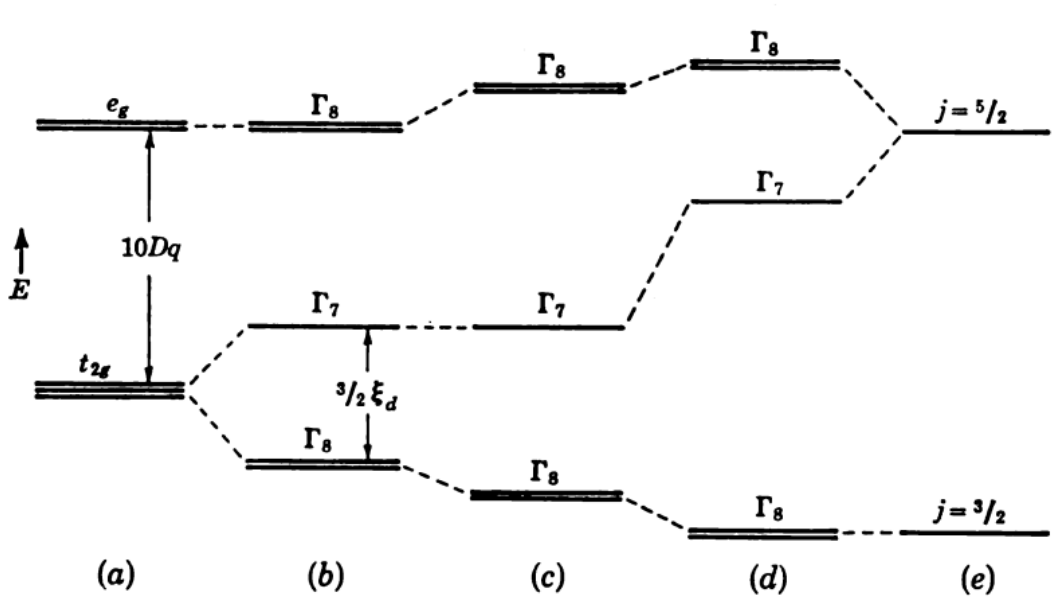


FIG. 6-1. Term splittings for a single *d* electron. (*a*) Levels in a strong octahedral field; (*b*) levels with weak spin-orbit coupling; (*c*) levels with intermediate spin-orbit coupling; (*d*) levels with strong spin-orbit coupling; (*e*) levels for the free ion in *jj* coupling.

O'		E	R	$4C_3$ $4C_3^2R$	$4C_3^2$ $4C_3R$	$3C_2$ $3C_2R$	$3C_4$ $3C_4^3R$	$3C_4^3$ $3C_4R$	$6C_2'$ $6C_2'R$
Γ_1	A_1'	1	1	1	1	1	1	1	1
Γ_2	A_2'	1	1	1	1	1	−1	−1	−1
Γ_3	E_1'	2	2	−1	−1	2	0	0	0
Γ_4	T_1'	3	3	0	0	−1	1	1	−1
Γ_5	T_2'	3	3	0	0	−1	−1	−1	1
Γ_6	E_2'	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7	E_3'	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8	G'	4	−4	−1	1	0	0	0	0

$$\chi(\Phi)=\frac{\sin\left(j+\frac{1}{2}\right)\Phi}{\sin\frac{\Phi}{2}}$$

$$J = s = 1/2$$

j = ½

	E	R	C_3	C_3R	C_2	C_4	C_4R	C'_2
χ	2	-2	1	-1	0	$(2)^{1/2}$	$-(2)^{1/2}$	0

$\Gamma_{j=1/2} = \Gamma_6$

$$\Gamma_{\ell=2} = e + t_2 = \Gamma_3 + \Gamma_5$$

$$\Gamma_{s=1/2} \otimes \Gamma_{\ell=2} = \left(\Gamma_3 + \Gamma_5\right) \otimes \Gamma_6$$

$$\chi(0)=\frac{\left(j+\frac{1}{2}\right)\cos\left(j+\frac{1}{2}\right)0}{\frac{1}{2}\cos\frac{1}{2}0}=2j+1 \qquad \chi(2\pi)=\frac{\left(j+\frac{1}{2}\right)\cos\left(j+\frac{1}{2}\right)2\pi}{\frac{1}{2}\cos\frac{1}{2}2\pi}=-(2j+1)$$ j half-integer

$$\chi\left(\frac{2\pi}{3}\right)=\frac{\sin\left(j+\frac{1}{2}\right)\left(\frac{2\pi}{3}\right)}{\sin\left(\frac{2\pi}{6}\right)}=1 \qquad \chi\left(\frac{2\pi}{4}\right)=\frac{\sin\left(j+\frac{1}{2}\right)\left(\frac{2\pi}{4}\right)}{\sin\left(\frac{2\pi}{8}\right)}=(2)^{\frac{1}{2}}$$

For half integer values of J

$$\chi(\Phi+2\pi)=-\chi(\Phi)$$

$$\chi(RC_n)=-\chi(C_n)$$

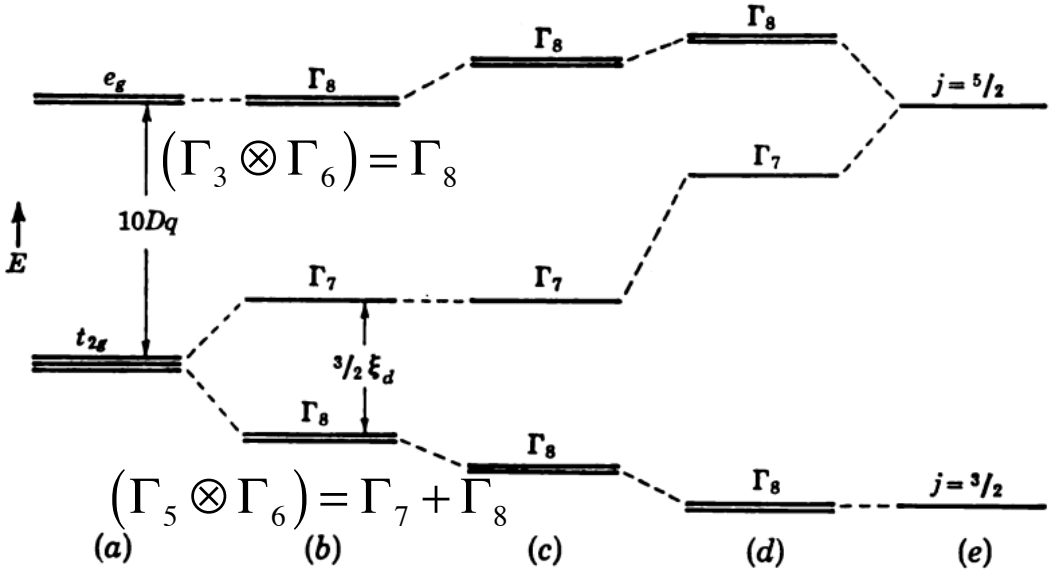
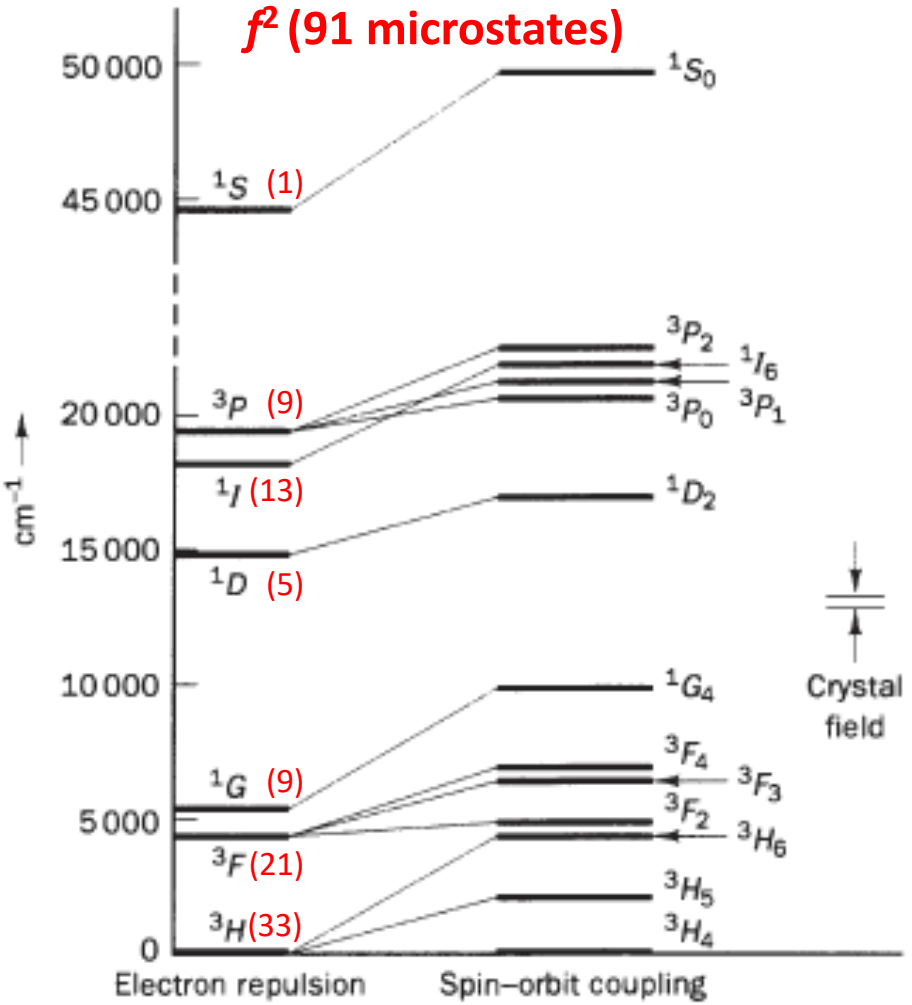


FIG. 6-1. Term splittings for a single d electron. (a) Levels in a strong octahedral field; (b) levels with weak spin-orbit coupling; (c) levels with intermediate spin-orbit coupling; (d) levels with strong spin-orbit coupling; (e) levels for the free ion in jj coupling.



$$F^k = e^2 \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+1}} \left[R_{4f}(r_i) R_{4f}(r_j) \right]^2 dr_i dr_j$$

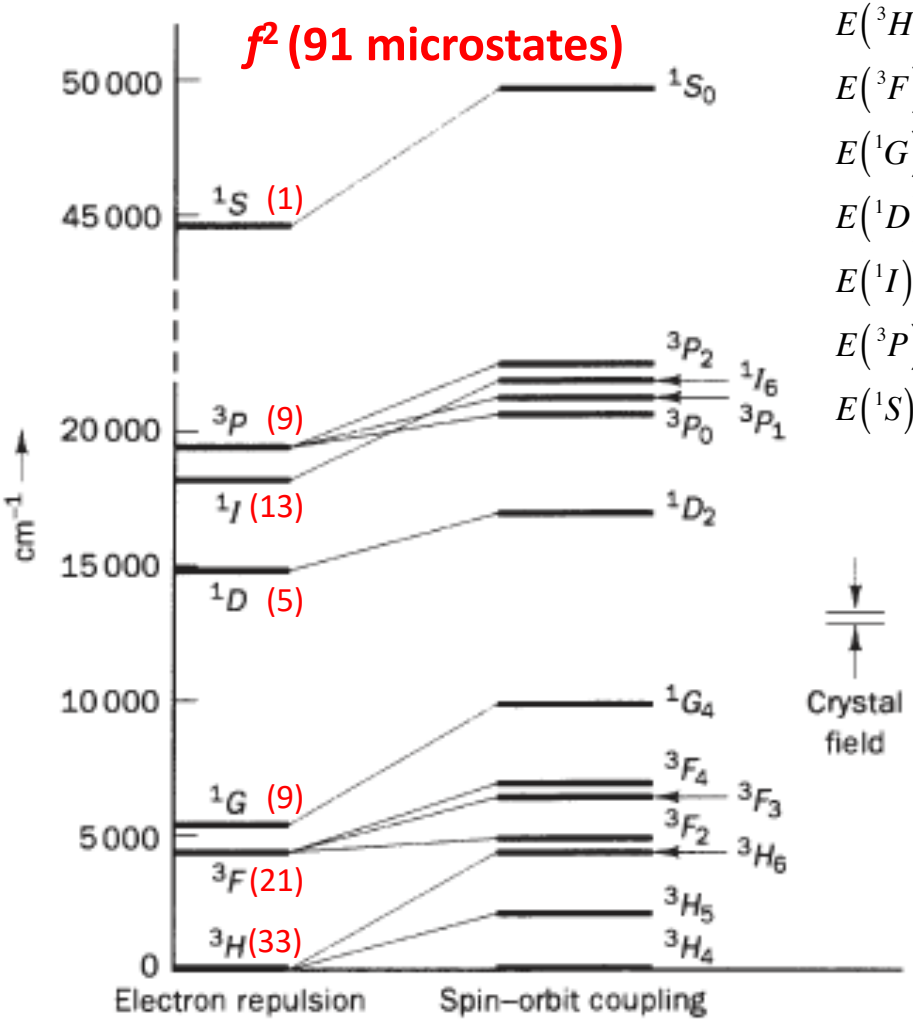
$$F_0 = F^0; \quad F_2 = \frac{F^2}{225}; \quad F_4 = \frac{F^4}{1089}; \quad F_6 = \frac{25F^6}{184041}$$

$$\frac{F_4}{F_2} = \frac{41}{297} = 0.138$$

$$\frac{F_6}{F_2} = \frac{175}{11583} = 0.0151$$

$$E(^3H) = F_0 - 25F_2 - 51F_4 - 13F_6$$
$$E(^3F) = F_0 - 10F_2 - 33F_4 - 286F_6$$
$$E(^1G) = F_0 - 30F_2 + 97F_4 + 78F_6$$
$$E(^1D) = F_0 + 19F_2 - 99F_4 + 715F_6$$
$$E(^1I) = F_0 + 25F_2 + 9F_4 + F_6$$
$$E(^3P) = F_0 + 45F_2 + 33F_4 - 1287F_6$$
$$E(^1S) = F_0 + 60F_2 + 198F_4 + 1716F_6$$

The Pr^{3+} ($4f^2$) electronic energy level diagram. A typical crystal field splitting is shown at the right; its effects are much smaller than those of spin-orbit coupling. As with Tanabe-Sugano diagrams, the horizontal axis is taken as the ground state ($^3H_4$). This enables the effects of interactions between levels with the same total angular momentum to be more clearly seen. Note, for instance, the relative upward displacements of levels with the J quantum number 4 ($^3F_4$, $^1G_4$).



$$E(^3H) = F_0 - 25F_2 - 51F_4 - 13F_6$$
$$E(^3F) = F_0 - 10F_2 - 33F_4 - 286F_6$$
$$E(^1G) = F_0 - 30F_2 + 97F_4 + 78F_6$$
$$E(^1D) = F_0 + 19F_2 - 99F_4 + 715F_6$$
$$E(^1I) = F_0 + 25F_2 + 9F_4 + F_6$$
$$E(^3P) = F_0 + 45F_2 + 33F_4 - 1287F_6$$
$$E(^1S) = F_0 + 60F_2 + 198F_4 + 1716F_6$$

Spin-Orbit states

$^1S_0$
$^3P_0\ ^3P_1\ ^3P_2$
$^1D_2$
$^3F_2\ ^3F_3\ ^3F_4$
$^1G_4$
$^3H_4\ ^3H_5\ ^3H_6$
$^1I_6$

Notice that there is no spin-orbit coupling between the $^3F_3$ level and any other levels, and hence there are no intermediate coupling corrections to be included in this case. In this sense $^3F_3$ is a pure state, similarly as the excited states $^3P_1$ and $^3H_5$.

$$\begin{array}{c} \\ ^3P_0 \\ ^1S_0 \end{array}\begin{array}{c} \begin{array}{cc} ^3P_0 & ^1S_0 \end{array} \\ \begin{pmatrix} -1 & -2\sqrt{3} \\ -2\sqrt{3} & 0 \end{pmatrix} \end{array} \qquad \begin{array}{c} ^3P_1 \\ ^3P_1\ \left(-\frac{1}{2}\right) \end{array} \qquad \begin{array}{c} \\ ^3P_2 \\ ^1D_2 \\ ^3F_2 \end{array}\begin{array}{c} \begin{array}{ccc} ^3P_2 & ^1D_2 & ^3F_2 \end{array} \\ \begin{pmatrix} \frac{1}{2} & \frac{3}{2}\sqrt{2} & 0 \\ \frac{3}{2}\sqrt{2} & 0 & -\sqrt{6} \\ 0 & -\sqrt{6} & -2 \end{pmatrix} \end{array}$$

$$\begin{array}{c} ^3F_3 \\ ^3F_3\ \left(-\frac{1}{2}\right) \end{array} \qquad \begin{array}{c} \\ ^3F_4 \\ ^1G_4 \\ ^3H_4 \end{array}\begin{array}{c} \begin{array}{ccc} ^3F_4 & ^1G_4 & ^3H_4 \end{array} \\ \begin{pmatrix} \frac{3}{2} & \frac{\sqrt{33}}{3} & 0 \\ \frac{\sqrt{33}}{3} & 0 & -\frac{\sqrt{30}}{3} \\ 0 & -\frac{\sqrt{30}}{3} & -3 \end{pmatrix} \end{array} \qquad \begin{array}{c} ^3H_5 \\ ^3H_5\ \left(-\frac{1}{2}\right) \end{array} \qquad \begin{array}{c} \\ ^3H_6 \\ ^1I_6 \end{array}\begin{array}{c} \begin{array}{cc} ^3H_6 & ^1I_6 \end{array} \\ \begin{pmatrix} \frac{5}{2} & \frac{\sqrt{6}}{2} \\ \frac{\sqrt{6}}{2} & 0 \end{pmatrix} \end{array}$$

Ion	f electron configuration	Angular momentum of relevant orbitals	Total orbital angular momentum	Term associated with the ground state		
La^{III}	f^0	none	0	^1S	1	$^1S_{1/2}$
Ce^{III}	f^1	3	3	^2F	14	$^2F_{5/2,7/2}$
Pr^{III}	f^2	3, 2	5	^3H	33	$^3H_{4,5,6}$
Nd^{III}	f^3	3, 2, 1	6	^4I	52	$^4I_{9/2,11/2,13/2,15/2}$
Pm^{III}	f^4	3, 2, 1, 0	6	^5I	65	$^5I_{4,5,6,7,8}$
Sm^{III}	f^5	3, 2, 1, 0, −1	5	^6H	66	$^6H_{5/2,7/2,9/2,11/2,13/2,15/}$
Eu^{III}	f^6	3, 2, 1, 0, −1, −2	3	^7F	21	^{2}
Gd^{III}	f^7	3, 2, 1, 0, −1, −2, −3	0	^8S	8	$^5F_{0,1,2,3,4,5,6}$ $^1S_{7/2}$
Tb^{III}	f^8	3[a]	3	^7F		
Dy^{III}	f^9	3, 2	5	^6H		
Ho^{III}	f^{10}	3, 2, 1	6	^5I		
Er^{III}	f^{11}	3, 2, 1, 0	6	^4I		
Tm^{III}	f^{12}	3, 2, 1, 0, −1	5	^3H		
Yb^{III}	f^{13}	3, 2, 1, 0, −1, −2	3	^2F		
Lu^{III}	f^{14}	3, 2, 1, 0, −1, −2, −3	0	^1S		

[a] From Tb^{III} onwards, for simplicity, the half-filled shell that is also present is not detailed.

Value of L

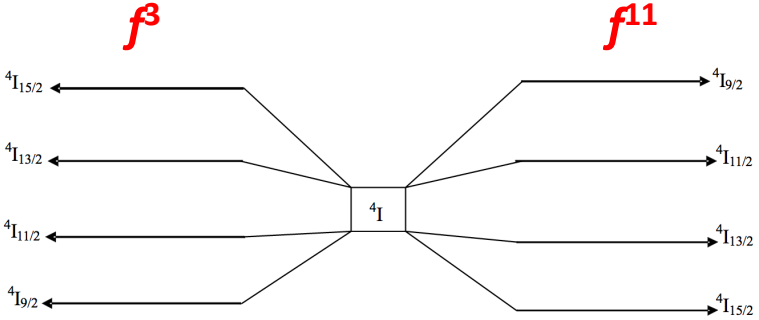
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Symbol of L

S P D F G H I K L M N O Q R T U V W X Y Z

f^3, f^{11}

S. No.	L	Label	S	Multiplicity (2S + 1)	Term symbol	Total values of J	Several possible terms	Array	Micro states
1	8	L	1/2	2	^2L	J = 2	$^2L_{17/2}$, $^2L_{15/2}$	17 x 2	34
2	7	K	1/2	2	^2K	J = 2	$^2K_{15/2}$, $^2K_{13/2}$	15 x 2	30
3	6	I	3/2	4	^4I	J = 3	$^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$ $^4I_{9/2}$	13 x 4	52
			1/2	2	^2I	J = 2	$^2I_{13/2}$, $^2I_{11/2}$	13 x 2	26
4	5	H	1/2	2	^2H	J = 2	$^2H_{11/2}$, $^2H_{9/2}$	11 x 2	22
			1/2	2	^2H	J = 2	$^2H_{11/2}$, $^2H_{9/2}$	11 x 2	22
5	4	G	3/2	4	^4G	J = 4	$^4G_{11/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$	9 x 4	36
			1/2	2	^2G	J = 2	$^2G_{9/2}$, $^2G_{7/2}$	9 x 2	18
			1/2	2	^2G	J = 2	$^2G_{9/2}$, $^2G_{7/2}$	9 x 2	18
6	3	F	3/2	4	^4F	J = 4	$^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$	7 x 4	28
			1/2	2	^2F	J = 2	$^2F_{7/2}$, $^2F_{5/2}$	7 x 2	14
			1/2	2	^2F	J = 2	$^2F_{7/2}$, $^2F_{5/2}$	7 x 2	14
7	2	D	3/2	4	^4D	J = 4	$^4D_{7/2}$, $^4D_{5/2}$, $^4D_{3/2}$, $^4D_{1/2}$	5 x 4	20
			1/2	2	^2D	J = 2	$^2D_{5/2}$, $^2D_{3/2}$	5 x 2	10
			1/2	2	^2D	J = 1	$^2D_{5/2}$, $^2D_{3/2}$	5 x 2	10
8	1	P	1/2	2	^2P	J = 2	$^2P_{3/2}$, $^2P_{1/2}$	3 x 2	6
9	0	S	3/2	4	^4S	J = 1	$^4S_{1/2}$	1 x 4	4



f^3, f^{11}

S. No.	L	Label	S	Multiplicity (2S + 1)	Term symbol	Total values of J	Several possible terms	Array	Micro states
1	8	L	1/2	2	^2L	J = 2	$^2L_{17/2}$, $^2L_{15/2}$	17 x 2	34
2	7	K	1/2	2	^2K	J = 2	$^2K_{15/2}$, $^2K_{13/2}$	15 x 2	30
3	6	I	3/2	4	^4I	J = 3	$^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$ $^4I_{9/2}$	13 x 4	52
			1/2	2	^2I	J = 2	$^2I_{13/2}$, $^2I_{11/2}$	13 x 2	26
4	5	H	1/2	2	^2H	J = 2	$^2H_{11/2}$, $^2H_{9/2}$	11 x 2	22
			1/2	2	^2H	J = 2	$^2H_{11/2}$, $^2H_{9/2}$	11 x 2	22
5	4	G	3/2	4	^4G	J = 4	$^4G_{11/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$	9 x 4	36
			1/2	2	^2G	J = 2	$^2G_{9/2}$, $^2G_{7/2}$	9 x 2	18
			1/2	2	^2G	J = 2	$^2G_{9/2}$, $^2G_{7/2}$	9 x 2	18
6	3	F	3/2	4	^4F	J = 4	$^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$	7 x 4	28
			1/2	2	^2F	J = 2	$^2F_{7/2}$, $^2F_{5/2}$	7 x 2	14
			1/2	2	^2F	J = 2	$^2F_{7/2}$, $^2F_{5/2}$	7 x 2	14
7	2	D	3/2	4	^4D	J = 4	$^4D_{7/2}$, $^4D_{5/2}$, $^4D_{3/2}$, $^4D_{1/2}$	5 x 4	20
			1/2	2	^2D	J = 2	$^2D_{5/2}$, $^2D_{3/2}$	5 x 2	10
			1/2	2	^2D	J = 1	$^2D_{5/2}$, $^2D_{3/2}$	5 x 2	10
8	1	P	1/2	2	^2P	J = 2	$^2P_{3/2}$, $^2P_{1/2}$	3 x 2	6
9	0	S	3/2	4	^4S	J = 1	$^4S_{1/2}$	1 x 4	4

^4S		$^4S_{3/2}$												
^2P	$^2P_{1/2}$	$^2P_{3/2}$												
^2D		$^2D_{3/2}$	$^2D_{5/2}$											
^2D		$^2D_{3/2}$	$^2D_{5/2}$											
^4D	$^4D_{1/2}$	$^4D_{3/2}$	$^4D_{5/2}$	$^4D_{7/2}$										
^2F			$^2F_{5/2}$	$^2F_{7/2}$										
^2F			$^2F_{5/2}$	$^2F_{7/2}$										
^4F		$^4F_{3/2}$	$^4F_{5/2}$	$^4F_{7/2}$	$^4F_{9/2}$									
^2G				$^2G_{7/2}$	$^2G_{9/2}$									
^2G				$^2G_{7/2}$	$^2G_{9/2}$									
^4G			$^4G_{5/2}$	$^4G_{7/2}$	$^4G_{9/2}$	$^4G_{11/2}$								
^2H					$^2H_{9/2}$	$^2H_{11/2}$								
^2H					$^2H_{9/2}$	$^2H_{11/2}$								
^2I						$^2I_{11/2}$	$^2I_{13/2}$							
^4I					$^4I_{9/2}$	$^4I_{11/2}$	$^4I_{13/2}$	$^4I_{15/2}$						
^2K							$^2K_{13/2}$	$^2K_{15/2}$						
^2L								$^2L_{15/2}$	$^2L_{17/2}$					

f electron configuration	Number of functions listed	Total number of functions	Terms arising
f^1, f^{13}	14	14	^2F
f^2, f^{12}	91	91	$^3H + {}^3F + {}^1G + {}^1D + {}^3P + {}^1I + {}^1S$
f^3, f^{11}	294	364	$^4I + {}^4F + {}^4S + {}^2H + {}^2G + {}^2K + {}^4G + {}^2D + {}^2P + {}^2I + {}^2J + {}^4D$
f^4, f^{10}	394	1001	$^5I + {}^5F + {}^5S + {}^3K + {}^5G + {}^3H + {}^3G + {}^3J + {}^3D + {}^3P + {}^3I + {}^5D$
f^5, f^9	238	2002	$^6H + {}^6F + {}^4H + {}^4D + {}^6P + {}^4I + {}^4S$
f^6, f^8	49	3003	^7F
f^7	478	3432	$^8S + {}^6P + {}^6I + {}^4S + {}^4D + {}^4H + {}^4I + {}^4K + {}^6D + {}^6G + {}^6F + {}^6H$

For f^n, $3 < n < 11$, only a selection of terms is given, listed in approximate energy sequence (lowest first). A limited number is given because mixing of the type shown in Fig. 8.16 occurs and particularly complicates the more highly excited states of those configurations for which the total number of functions is large.

f electron configuration	Relevant ions	Ground state	Low-lying excited levels
f^0	La^{III}, Ac^{III}	$^1S_0$	–
f^1	Ce^{III}, Th^{III}	$^2F_{5/2}$	$^2F_{7/2}$
f^2	Pr^{III}, Pa^{III}	$^3H_4$	$^3H_5$, $^3H_6$
f^3	Nd^{III}, U^{III}	$^4I_{9/2}$	$^4I_{11/2}$, $^4I_{13/2}$, $^4I_{15/2}$
f^4	Pm^{III}, Np^{III}	$^5I_4$	$^5I_5$, $^5I_6$, $^5I_7$, $^5I_8$
f^5	Sm^{III}, Pu^{III}	$^6H_{5/2}$	$^6H_{7/2}$, $^6H_{9/2}$, $^6H_{11/2}$, $^6H_{13/2}$, $^6H_{15/2}$
f^6	Eu^{III}, Am^{III}	$^7F_0$	$^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$, $^7F_5$, $^7F_6$
f^7	Gd^{III}, Cm^{III}	$^8S_{7/2}$	–
f^8	Tb^{III}, Bk^{III}	$^7F_6$	$^7F_5$, $^7F_4$, $^7F_3$, $^7F_2$, $^7F_1$, $^7F_0$
f^9	Dy^{III}, Cf^{III}	$^6H_{15/2}$	$^6H_{13/2}$, $^6H_{11/2}$, $^6H_{9/2}$, $^6H_{7/2}$, $^6H_{5/2}$
f^{10}	Ho^{III}, Es^{III}	$^5I_8$	$^5I_7$, $^5I_6$, $^5I_5$, $^5I_4$
f^{11}	Er^{III}, Fm^{III}	$^4I_{15/2}$	$^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$
f^{12}	Tm^{III}, Md^{III}	$^3H_6$	$^3H_5$, $^3H_4$
f^{13}	Yb^{III}, No^{III}	$^2F_{7/2}$	$^2F_{5/2}$
f^{14}	Lu^{III}, Lr^{III}	$^1S_0$	–

Note the symmetry in this table (compare the first level listed for an f^n ion with the last listed for the f^{14-n}). This symmetry is detailed in the text.

- When *d* electron systems were considered it was found that a detailed study of the d^1 and d^2 configurations could easily be extended to cover all the low-lying excited states of the same spin multiplicity as the ground state for all d^n configurations.

- Even if spin-orbit coupling could be ignored, the *f* electron case is more complicated. Not only f^1 and f^2 but also f^3 configurations would have to be included before all the possible ground terms *F*, *H* and *I*, had been covered.

- But spin-orbit coupling cannot be ignored and this means that we cannot even talk about spin allowed and spin forbidden transitions and thus restrict the discussion to terms with the same spin multiplicity.

f electron configuration	Relevant ions	Ground state	Low-lying excited levels
f^0	La^{III}, Ac^{III}	$^1S_0$	–
f^1	Ce^{III}, Th^{III}	$^2F_{5/2}$	$^2F_{7/2}$
f^2	Pr^{III}, Pa^{III}	$^3H_4$	$^3H_5$, $^3H_6$
f^3	Nd^{III}, U^{III}	$^4I_{9/2}$	$^4I_{11/2}$, $^4I_{13/2}$, $^4I_{15/2}$
f^4	Pm^{III}, Np^{III}	$^5I_4$	$^5I_5$, $^5I_6$, $^5I_7$, $^5I_8$
f^5	Sm^{III}, Pu^{III}	$^6H_{5/2}$	$^6H_{7/2}$, $^6H_{9/2}$, $^6H_{11/2}$, $^6H_{13/2}$, $^6H_{15/2}$
f^6	Eu^{III}, Am^{III}	$^7F_0$	$^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$, $^7F_5$, $^7F_6$
f^7	Gd^{III}, Cm^{III}	$^8S_{7/2}$	–
f^8	Tb^{III}, Bk^{III}	$^7F_6$	$^7F_5$, $^7F_4$, $^7F_3$, $^7F_2$, $^7F_1$, $^7F_0$
f^9	Dy^{III}, Cf^{III}	$^6H_{15/2}$	$^6H_{13/2}$, $^6H_{11/2}$, $^6H_{9/2}$, $^6H_{7/2}$, $^6H_{5/2}$
f^{10}	Ho^{III}, Es^{III}	$^5I_8$	$^5I_7$, $^5I_6$, $^5I_5$, $^5I_4$
f^{11}	Er^{III}, Fm^{III}	$^4I_{15/2}$	$^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$
f^{12}	Tm^{III}, Md^{III}	$^3H_6$	$^3H_5$, $^3H_4$
f^{13}	Yb^{III}, No^{III}	$^2F_{7/2}$	$^2F_{5/2}$
f^{14}	Lu^{III}, Lr^{III}	$^1S_0$	–

Note the symmetry in this table (compare the first level listed for an f^n ion with the last listed for the f^{14-n}). This symmetry is detailed in the text.

$$V_O^f = \frac{1}{4\pi\varepsilon_0}\left\{\frac{7Ze^2\left\langle r^4\right\rangle\sqrt{\pi}}{3a^5}\left[\mathrm{Y}_4^0+\sqrt{\frac{5}{14}}\left(\mathrm{Y}_4^4+\mathrm{Y}_4^{-4}\right)\right]+\frac{3Ze^2\left\langle r^6\right\rangle\sqrt{\pi}}{2\sqrt{13}a^7}\left[Y_6^0-\sqrt{\frac{7}{2}}\left(Y_6^4+Y_6^{-4}\right)\right]\right\}$$

$$Dq' = \frac{2}{165}\left(\frac{Ze^2\overline{r}^4}{a^5}\right);\quad Fr = \left(\frac{5}{572}\right)^{\frac{1}{2}}\left(\frac{Ze^2\overline{r}^6}{a^7}\right)$$

$$\hat{\mathcal{V}}_O^d = \frac{1}{4\pi\varepsilon_0}\left\{\frac{7Ze^2\left\langle r^4\right\rangle\sqrt{\pi}}{3a^5}\left[\mathrm{Y}_4^0+\sqrt{\frac{5}{14}}\left(\mathrm{Y}_4^4+\mathrm{Y}_4^{-4}\right)\right]\right\}\quad D=\frac{35Ze^2}{4a^5};\, q=\frac{2}{105}\int_0^\infty R_{n\ell}^2\left(r\right)r^4r^2\,dr=\frac{2}{105}\left\langle r^4\right\rangle$$

$$\left\langle\left(2,m_\ell\right)\middle|V_o^d\middle|\left(2,m'_\ell\right)\right\rangle=\alpha Dq$$

$$\left\langle d_{m=0}\middle|V_o^d\middle|d_{m=0}\right\rangle=6Dq$$
$$\left\langle d_{m=\pm1}\middle|V_o^d\middle|d_{m=\pm1}\right\rangle=-4Dq$$
$$\left\langle d_{m=\pm2}\middle|V_o^d\middle|d_{m=\pm2}\right\rangle=Dq$$
$$\left\langle d_{m=\pm2}\middle|V_o^d\middle|d_{m=\mp2}\right\rangle=5Dq$$

$$\left\langle\left(3,m_\ell\right)\middle|V_o^f\middle|\left(3,m'_\ell\right)\right\rangle=\alpha Dq'+\beta Fr$$

$$\left\langle f_{m=0}\middle|V_o^f\middle|f_{m=0}\right\rangle=6Dq'+20Fr$$
$$\left\langle f_{m=\pm1}\middle|V_o^f\middle|f_{m=\pm1}\right\rangle=Dq'-15Fr$$
$$\left\langle f_{m=\pm2}\middle|V_o^f\middle|f_{m=\pm2}\right\rangle=-7Dq'+6Fr$$
$$\left\langle f_{m=\pm3}\middle|V_o^f\middle|f_{m=\pm3}\right\rangle=3Dq'-Fr$$
$$\left\langle f_{m=\pm1}\middle|V_o^f\middle|f_{m=\mp3}\right\rangle=15^{\frac{1}{2}}Dq'+735^{\frac{1}{2}}Fr$$
$$\left\langle f_{m=\pm2}\middle|V_o^f\middle|f_{m=\mp2}\right\rangle=5Dq'-42Fr$$

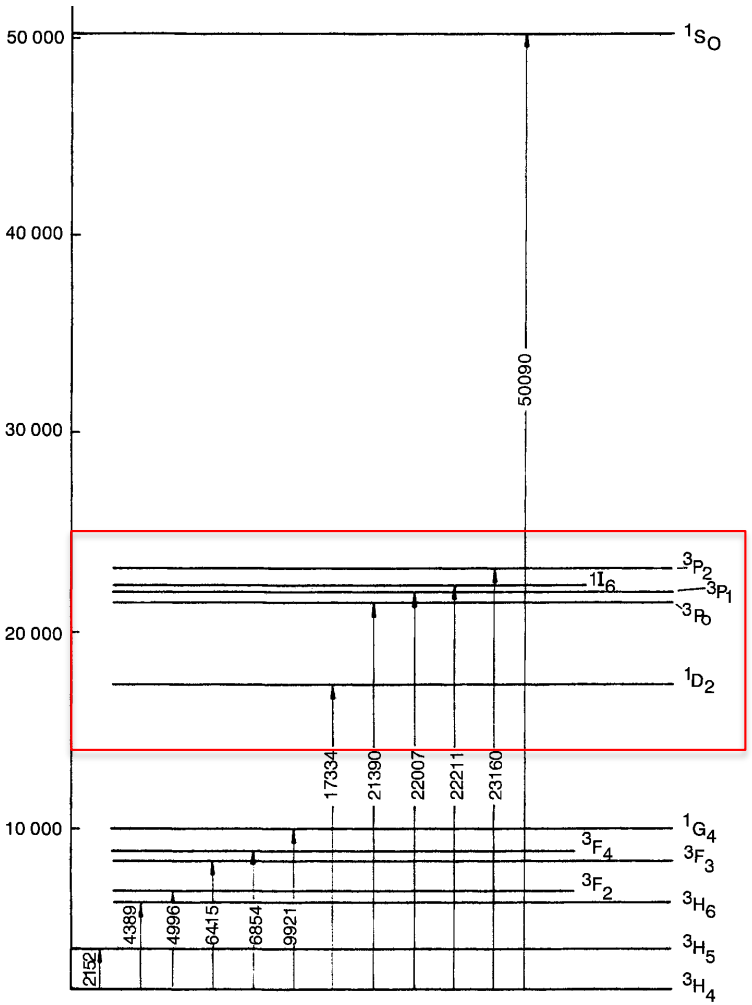


Fig. 8.16. Energy-level diagram for Pr^{3+} free ion [154].

- The transition to the highest $^1S_0$ level lying in the UV region cannot be observed since it is masked by the $4f \rightarrow 5d$ transition.
- For two pairs of levels $^1I_6$ – $^3P_1$ and $^3F_4$ – $^3F_3$ the split components may overlap.
- The absorption spectra of Pr(III) in solutions in the **visible region** have four bands due to the transitions from the ground state to $^3P_2$, $^3P_1 + {}^1I_6$, $^3P_0$ and $^1D_2$ levels.

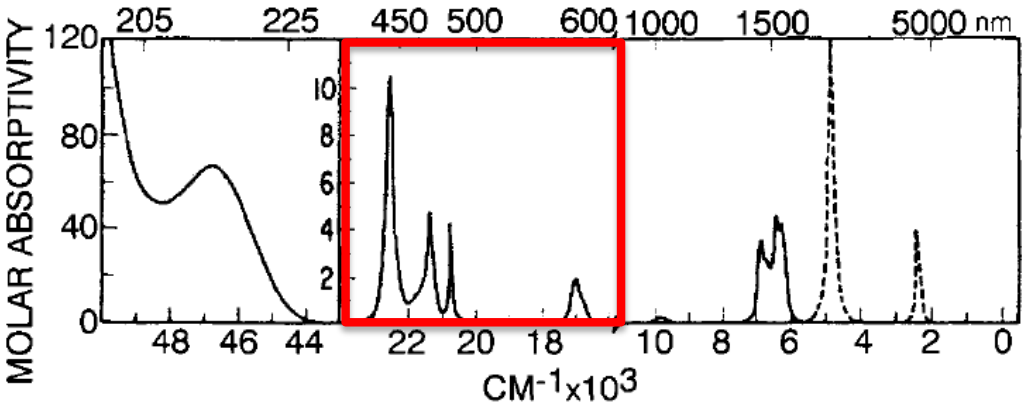


Fig. 8.17. Solution absorption spectrum of Pr^{3+} (aquo). Dashed lines indicate calculated curves.

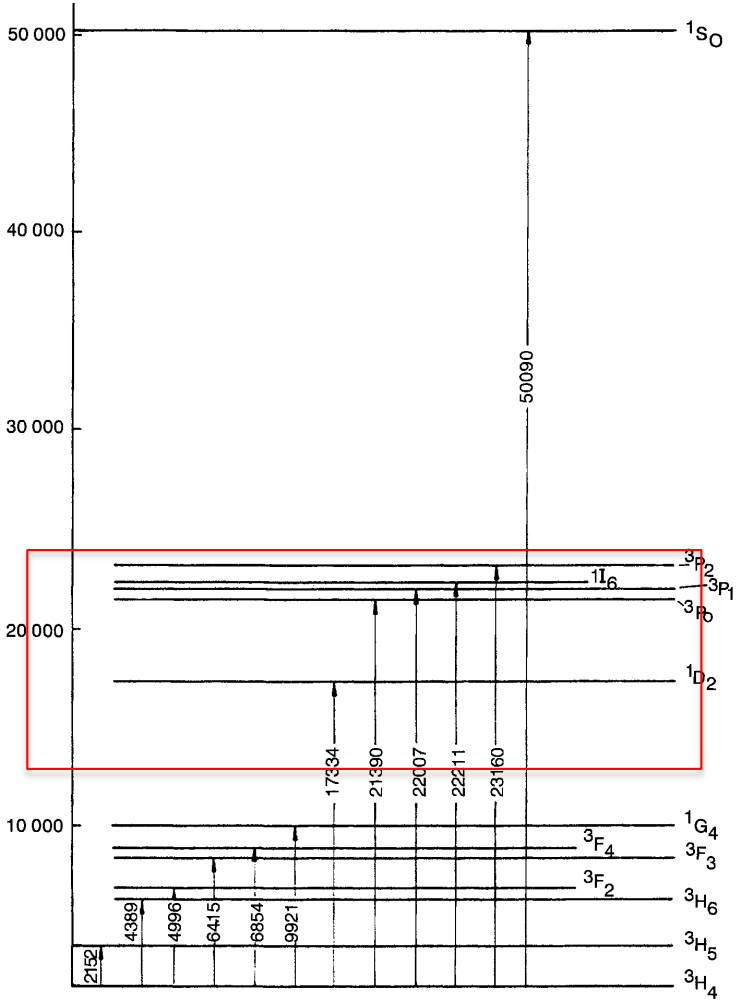
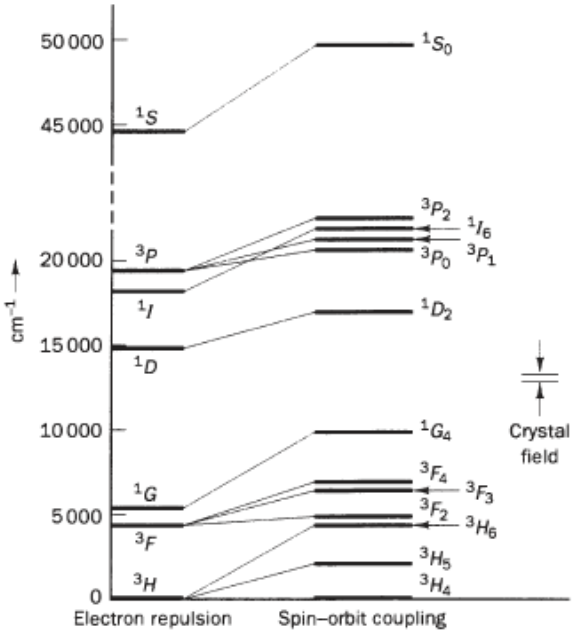


Fig. 8.16. Energy-level diagram for Pr^{3+} free ion [154].

Table 3. Selection rules for intra-configurational f-f transitions

Operator	Parity	ΔS	ΔL	ΔJ [a]
ED	opposite	0	≤ 6	≤ 6 (2, 4, 6 if J or J'=0)
MD	same	0	0	0, ±1
EQ	same	0	0, ±1, ±2	0, ±1, ±2

[a] J=0 to J'=0 transitions are always forbidden



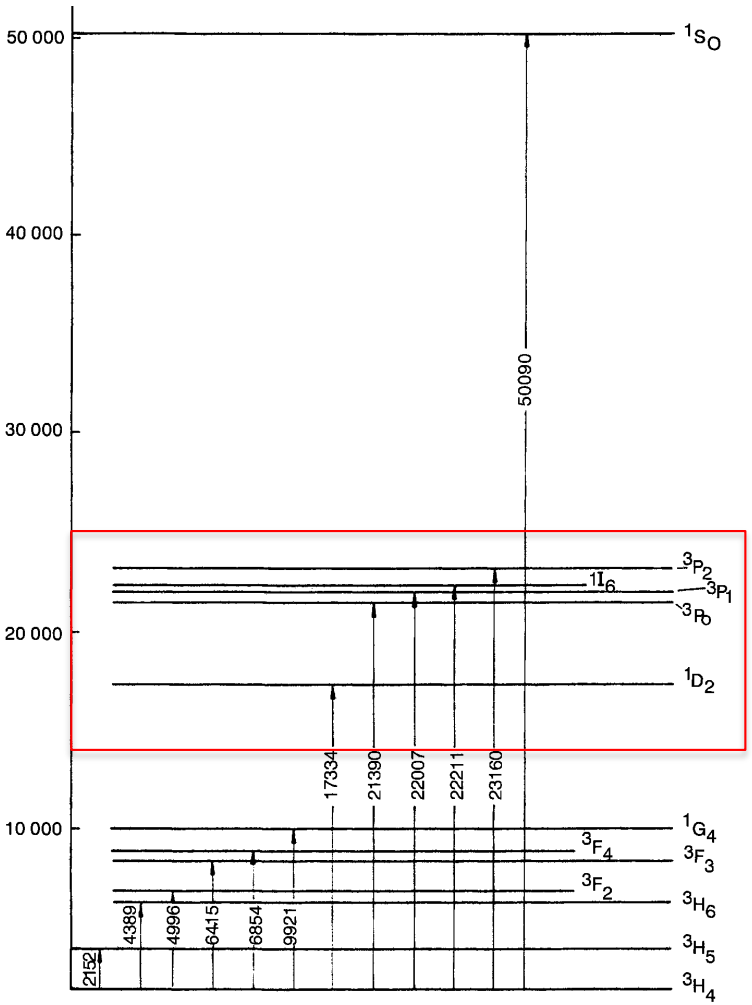


Fig. 8.16. Energy-level diagram for Pr^{3+} free ion [154].

- The transition to the highest $^1S_0$ level lying in the UV region cannot be observed since it is masked by the $4f \rightarrow 5d$ transition.
- For two pairs of levels $^1I_6$ – $^3P_1$ and $^3F_4$ – $^3F_3$ the split components may overlap.
- The absorption spectra of Pr(III) in solutions in the **visible region** have four bands due to the transitions from the ground state to $^3P_2$, $^3P_1 + {}^1I_6$, $^3P_0$ and $^1D_2$ levels.

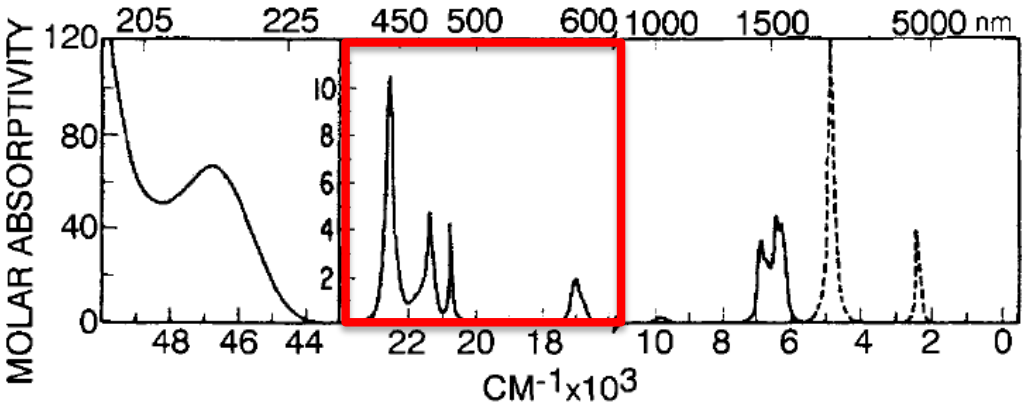
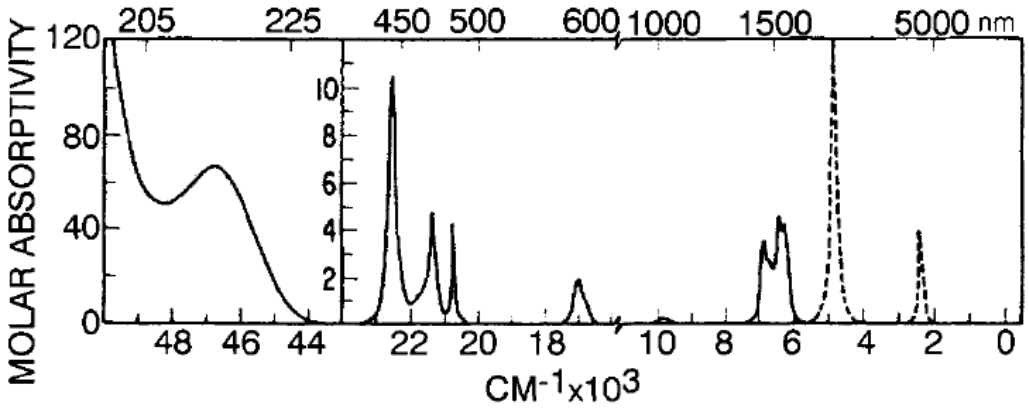


Fig. 8.17. Solution absorption spectrum of Pr^{3+} (aquo). Dashed lines indicate calculated curves.



17. Solution absorption spectrum of Pr^{3+} (aquo). Dashed lines indicate calculated curves.

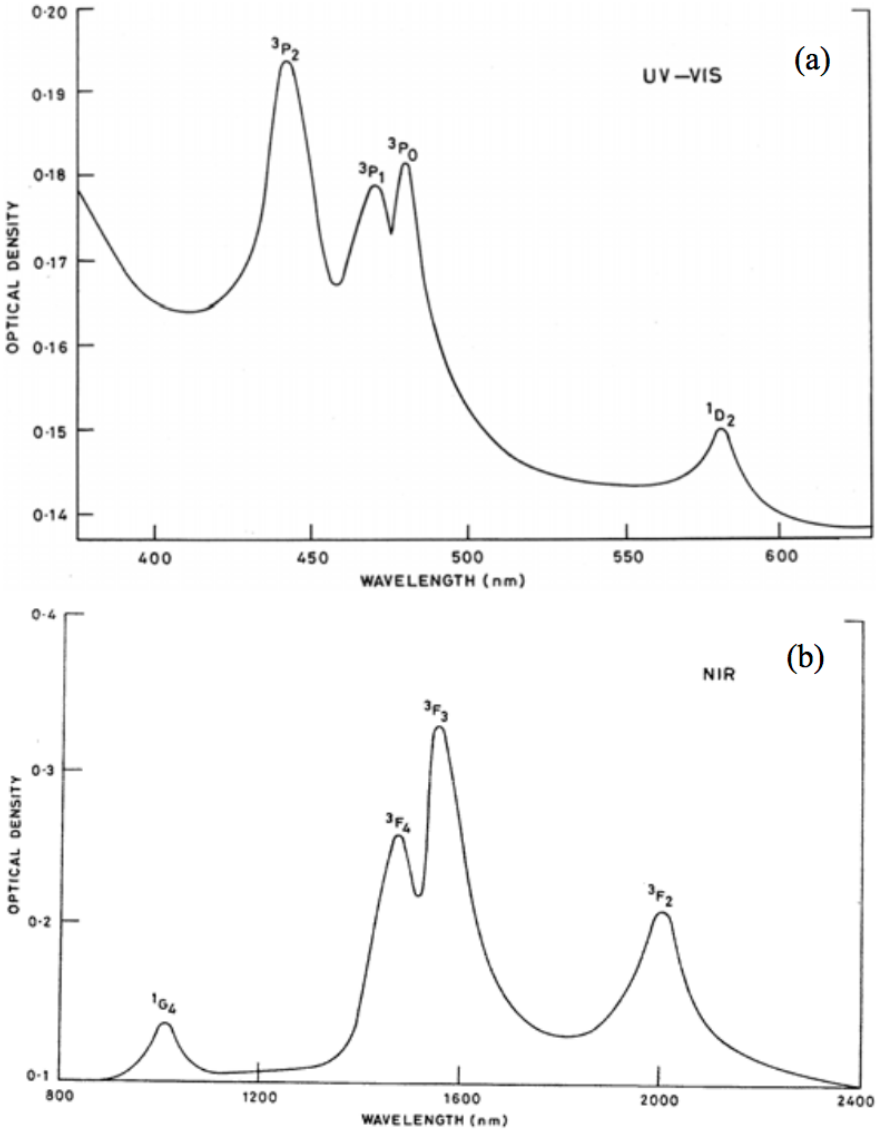


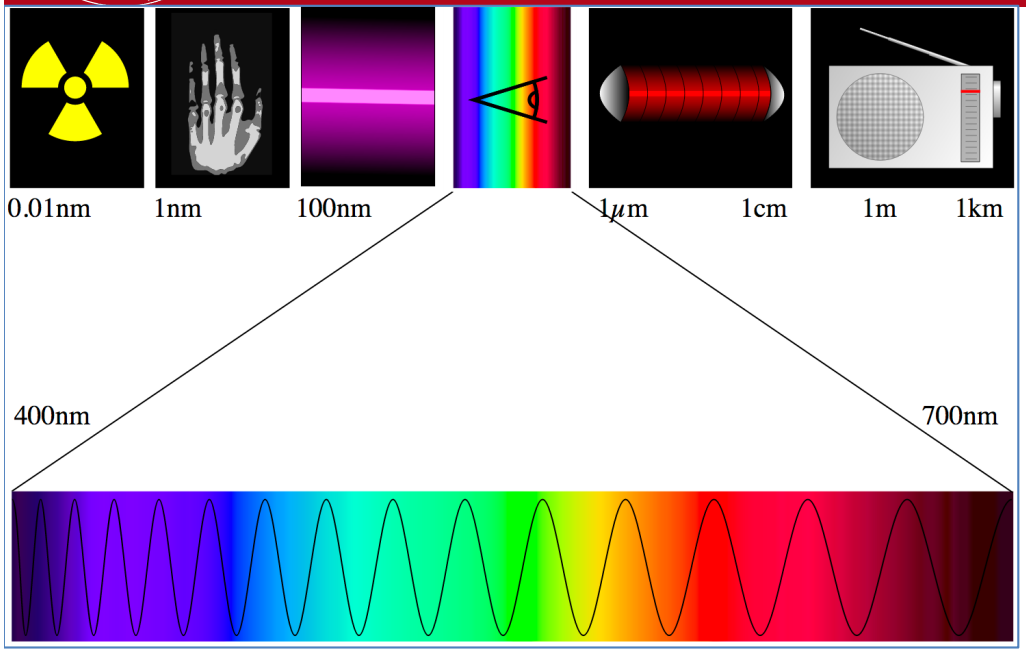
Fig. 1 — Absorption spectrum of Pr^{3+} (0.5 wt %) doped borosilicate glass (A) in the (a) visible region; (b) NIR region

The actual absorption bands that occur in the spectra of the lanthanides are associated with electronic transitions can be divided into three types:

- $f \rightarrow f$ **transitions:** localized entirely within the f shell and so, like $d \rightarrow d$ transitions, formally forbidden. However, like $d \rightarrow d$, they actually occur and give rise to a large number of weak, sharp bands from the IR to the VIS region. Absorption band patterns obtained from species in solution are closely related to the emission spectrum of the corresponding ion.

- $nf \rightarrow (n + 1)d$ **transitions.** Here, the n and $(n + 1)$ are principal quantum numbers so these are allowed bands in which a $4f$ electron is promoted to a $5d$ orbital. They give rise to quite intense and broad bands, lowered by ca. 15 000 cm^{-1} in solution compared to the gaseous ion.

- **LMCT transition.** These are usually intense, broad bands which lie in the UV region.



Configuration	Ion	Colour	Configuration	Ion	Colour
Aqueous ions					
f^1	Ce^{III}	colourless	f^{13}	Yb^{III}	colourless
f^2	Pr^{III}	yellow–green	f^{12}	Tm^{III}	light green
f^3	Nd^{III}	red–violet	f^{11}	Er^{III}	lilac
f^4	Pm^{III}	pink	f^{10}	Ho^{III}	yellow
f^5	Sm^{III}	yellow	f^9	Dy^{III}	yellow–green
f^6	Eu^{III}	pale pink	f^8	Tb^{III}	pale pink
f^7	Gd^{III}	colourless			
Lanthanide tricyclopentadiene complexes[a]					
f^1	Ce^{III}	orange	f^{13}	Yb^{III}	dark green
f^2	Pr^{III}	greenish	f^{12}	Tm^{III}	yellow–green
f^3	Nd^{III}	blue	f^{11}	Er^{III}	pink
f^4	Pm^{III}	yellow–orange	f^{10}	Ho^{III}	yellow
f^5	Sm^{III}	orange	f^9	Dy^{III}	yellow
f^6	Eu^{III}	brown	f^8	Tb^{III}	colourless
f^7	Gd^{III}	yellowish			

[a] The crystal structures of these complexes show three cyclopentadiene rings η^5-coordinated to each lanthanide, one of these rings additionally being bonded in η^1 or η^2 fashion to an adjacent lanthanide.

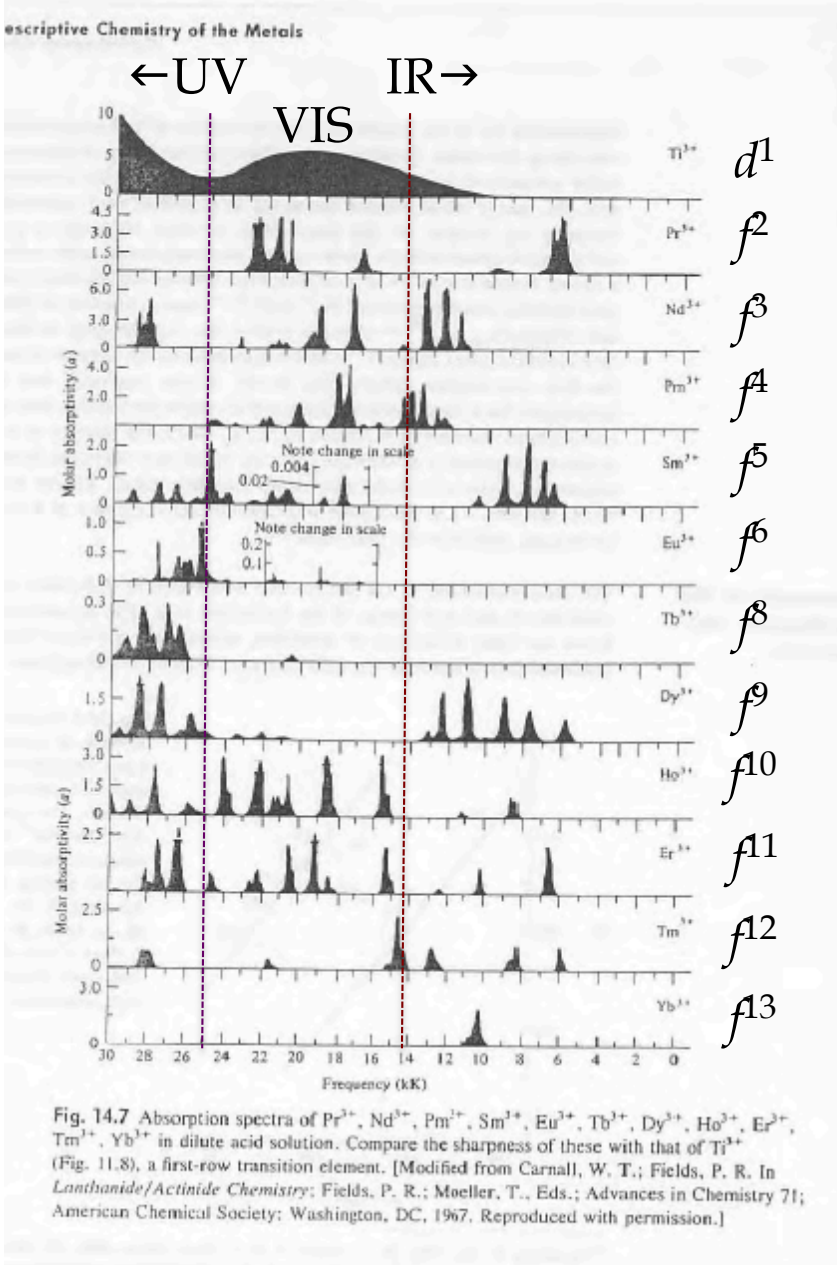


Fig. 14.7 Absorption spectra of Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} in dilute acid solution. Compare the sharpness of these with that of Ti^{3+} (Fig. 11.8), a first-row transition element. [Modified from Carnall, W. T.; Fields, P. R. In *Lanthanide/Actinide Chemistry*; Fields, P. R.; Moeller, T., Eds.; Advances in Chemistry 71; American Chemical Society: Washington, DC, 1967. Reproduced with permission.]

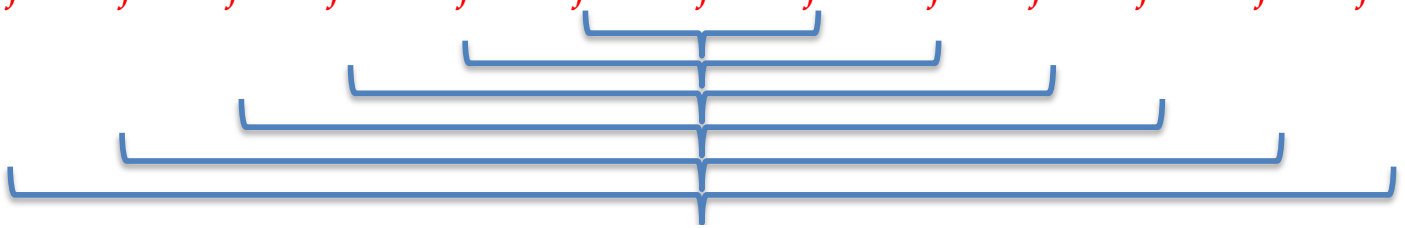
Configuration	Ion	Colour	Configuration	Ion	Colour
Aqueous ions					
f^1	Ce^{III}	colourless	f^{13}	Yb^{III}	colourless
f^2	Pr^{III}	yellow–green	f^{12}	Tm^{III}	light green
f^3	Nd^{III}	red–violet	f^{11}	Er^{III}	lilac
f^4	Pm^{III}	pink	f^{10}	Ho^{III}	yellow
f^5	Sm^{III}	yellow	f^9	Dy^{III}	yellow–green
f^6	Eu^{III}	pale pink	f^8	Tb^{III}	pale pink
f^7	Gd^{III}	colourless			
Lanthanide tricyclopentadiene complexes[a]					
f^1	Ce^{III}	orange	f^{13}	Yb^{III}	dark green
f^2	Pr^{III}	greenish	f^{12}	Tm^{III}	yellow–green
f^3	Nd^{III}	blue	f^{11}	Er^{III}	pink
f^4	Pm^{III}	yellow–orange	f^{10}	Ho^{III}	yellow
f^5	Sm^{III}	orange	f^9	Dy^{III}	yellow
f^6	Eu^{III}	brown	f^8	Tb^{III}	colourless
f^7	Gd^{III}	yellowish			

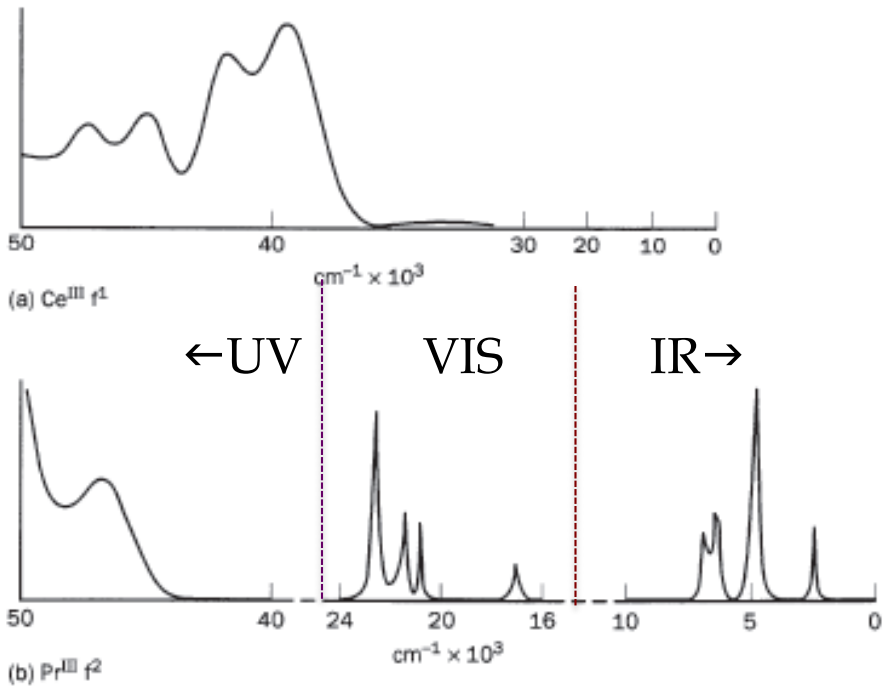
[a] The crystal structures of these complexes show three cyclopentadiene rings η^5-coordinated to each lanthanide, one of these rings additionally being bonded in η^1 or η^2 fashion to an adjacent lanthanide.

Approximate colors of lanthanide ions in aqueous solution[5][12][13]

Oxidation state	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
+2						Sm^{2+}	Eu^{2+}						Tm^{2+}	Yb^{2+}	
+3	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
+4		Ce^{4+}	Pr^{4+}	Nd^{4+}					Tb^{4+}	Dy^{4+}					

f^1 f^2 f^3 f^4 f^5 f^6 f^7 f^8 f^9 f^{10} f^{11} f^{12} f^{13}





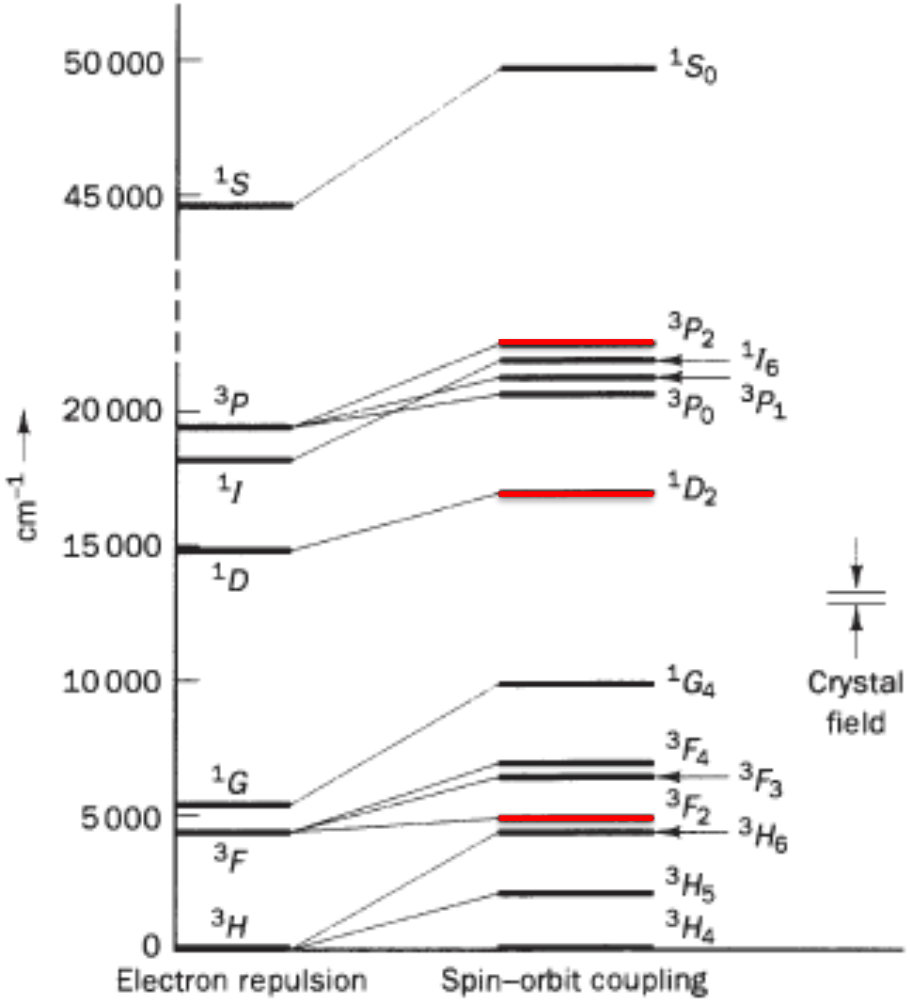
Transition type	μ transforms as	note
Electric dipole	x, y, z	Optical spectra
Electric quadrupole	x^2, y^2, z^2, xy, xz, yz	Constraint $x^2 + y^2 + z^2 = 0$
Electric polarizability	x^2, y^2, z^2, xy, xz, yz	Raman spectra
Magnetic dipole	R_x, R_y, R_z	Optical spectra (weak)

J. Van Vleck, *J. Chem. Phys.* 1937, **11**, 67

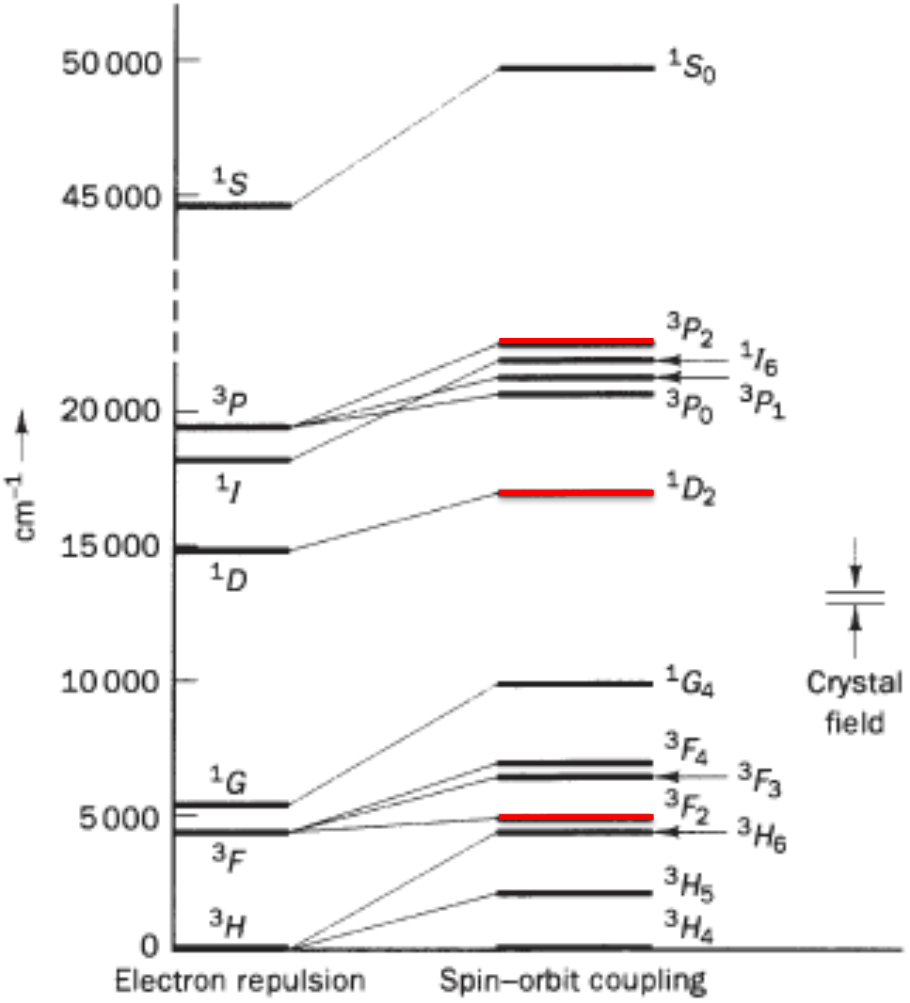
(a) The electronic spectrum of Ce^{III} (f^1) is dominated by LMCT bands. The f – f spectrum will consist of a single transition between the two spin-orbit levels $^2F_{5/2}$ and $^2F_{7/2}$ (ΔJ = 1). This transition will be both weak and in the infrared-towards the right-hand side of the spectrum where it is lost somewhere in the forest of vibrational bands that occur in this spectral region.

(a) The electronic spectrum of Pr^{III} , a f^2 ion, is more characteristic of Ln, showing both LMCT and f – f transitions (sharp). The involvement of f – f electron repulsion moves some of these transitions into the visible region of the spectrum.

The optical properties of intra-$4f^n$ transitions (f–f transitions) in lanthanide compounds are usually insensitive to the surrounding environment due to the shielding effect of the outer 5s and 5p electrons. However, there are exceptional transitions, the so-called **hypersensitive transitions**, whose oscillator strengths change sensitively to a small change of the surrounding environment.



Excited state levels of hypersensitive transitions for Pr(III)



Excited state levels of hypersensitive transitions for Pr(III)

Selection Rules

Table 3. Selection rules for intra-configurational f-f transitions

Operator	Parity	ΔS	ΔL	ΔJ [a]
ED	opposite	0	≤ 6	≤ 6 (2, 4, 6 if J or J'=0)
MD	same	0	0	0, ±1
EQ	same	0	0, ±1, ±2	0, ±1, ±2

[a] J=0 to J'=0 transitions are always forbidden

- When the lanthanide ion is at the center of symmetry, the intensity of the hypersensitive transitions is zero (Ln in ClO_4^- aqueous solution).
- The intensities of hypersensitive transitions can be as large as 200 times the value of the aquo ions.
- The intensity seems to be in the order I^- >> Br^- > Cl~ > H_2O > F^-.
- Hypersensitivity has been found to be proportional to the degree of involvement of 4*f* orbital in bonding.
- The intensities of the hypersensitive transitions can be correlated with the pK_a of the ligands.
- In the presence of some ligands, the hypersensitivity can be found in some transitions which are not usually hypersensitive. For example, $^3H_4 \rightarrow {}^3P_2$ and $^3H_4 \rightarrow {}^1D_2$ in Pr(III); $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$; $^4I_{9/2} \rightarrow {}^4F_{5/2}$, and $^4I_{9/2} \rightarrow {}^4F_{3/2}$, in Nd(III).
- These transitions are known as ligand mediated pseudohypersensitive transitions.

Ion	Ground state term	Excited state levels of hypersensitive transitions
La^{III}	$^1S_0$	none
Ce^{III}	$^2F_{5/2}$	none
Pr^{III}	$^3H_4$	$^3H_5$, $^3F_2$
Nd^{III}	$^4I_{9/2}$	$^4G_{5/2}$, $^4G_{7/2}$, $^2G_{7/2}$, $^2K_{13/2}$
Pm^{III}	$^5I_4$	$^5G_2$, $^5G_3$
Sm^{III}	$^6H_{5/2}$	$^6F_{1/2}$, $^6F_{3/2}$, $^4H_{7/2}$
Eu^{III}	$^7F_0(^7F_1)$	$^7F_2$
Gd^{III}	$^8S_{7/2}$	none
Tb^{III}	$^7F_6$	$^7F_5$
Dy^{III}	$^6H_{15/2}$	$^6H_{13/2}$, $^6H_{11/2}$, $^6F_{11/2}$
Ho^{III}	$^5I_8$	$^5G_6$, $^3H_6$
Er^{III}	$^4I_{15/2}$	$^2H_{11/2}$, $^4G_{11/2}$
Tm^{III}	$^3H_6$	$^3H_5$, $^3H_4$, $^3F_4$
Yb^{III}	$^2F_{7/2}$	none

Selection Rules

Electric quadrupole (E2)	Magnetic quadrupole (M2)
$\Delta J = 0, \pm 1, \pm 2$ ($J = 0 \nleftrightarrow 0, 1;\ \frac{1}{2} \nleftrightarrow \frac{1}{2}$)	
$\Delta M_J = 0, \pm 1, \pm 2$	

Here has been recognized that the Eu^{III} $^7F_1$ state is low lying and thermally populated at room temperature so that the hypersensitive transition could involve it as the ground state.

Physical Inorganic Chemistry, A Coordination Chemistry Approach
by
S. F. A. Kettle
1996, Springer-Verlag Berlin Heidelberg GmbH

Modern Aspects of Rare Earths and Their Complexes
by
V. S. Sastri, J.-C. Bunzli, V. Ramachandra Rao, G. V. S. Rayudu & J. R. Perumareddi
2003, ELSEVIER B.V., The Netherlands

Lanthanide and Actinide Chemistry
by
S. Cotton
2006, John Wiley & Sons Ltd

Optical Spectroscopy of Lanthanides, Magnetic and Hyperfine Interaction
by
L. Smentek, B. G. Wybourne
2007, CRC Press, Boca Raton

"The Lanthanons: These elements perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us mocking, mystifying, and murmuring strange revelations and possibilities"

Sir William Crookes addressing the Royal Institution in 1887