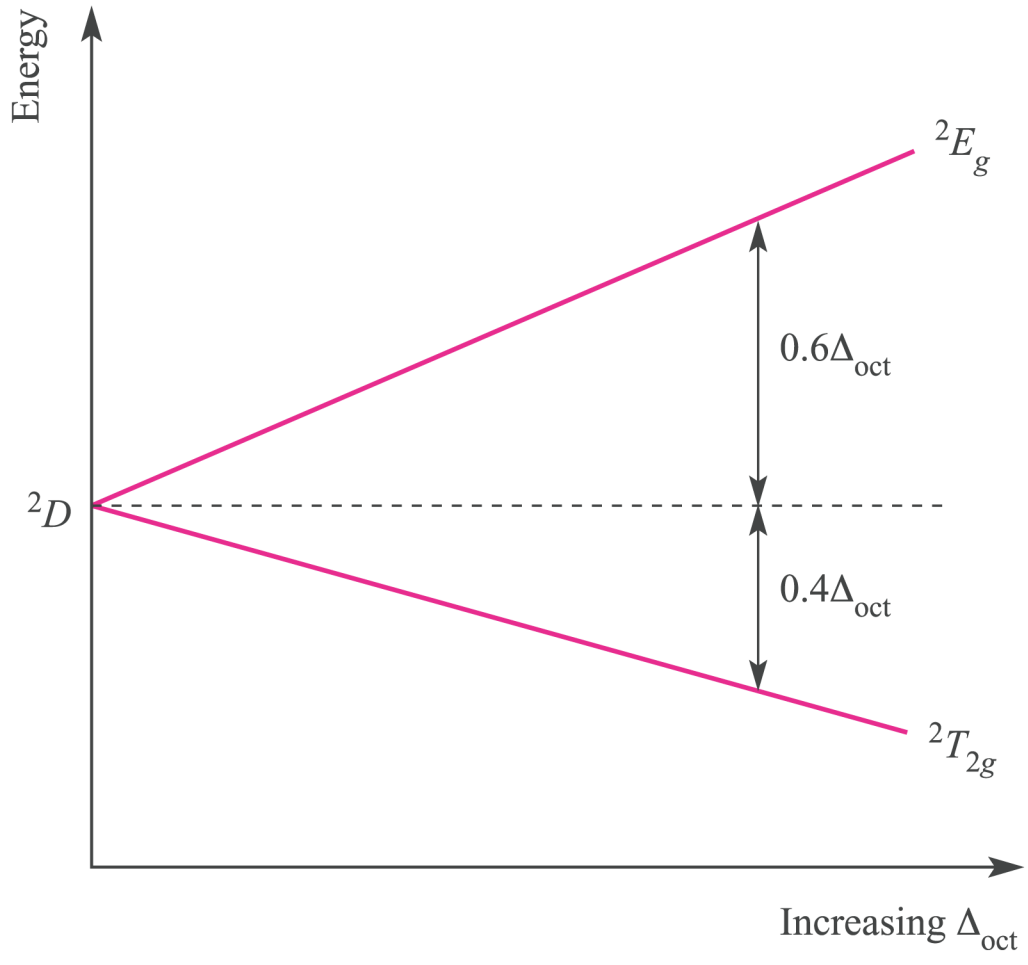
Table 19.7 The correlation of spectroscopic terms for *d* electrons in O_h complexes

Atomic term	Number of states	Terms in O_h symmetry
S	1	A_{1g}
P	3	T_{1g}
D	5	$T_{2g} + E_g$
F	7	$T_{1g} + T_{2g} + A_{2g}$
G	9	$A_{1g} + E_g + T_{1g} + T_{2g}$

Diagramma dei livelli di energia per uno ione d^1 in campo ottaedrico



Spettro di assorbimento elettronico del complesso d^1 $[Ti(OH_2)_6]^{3+}$

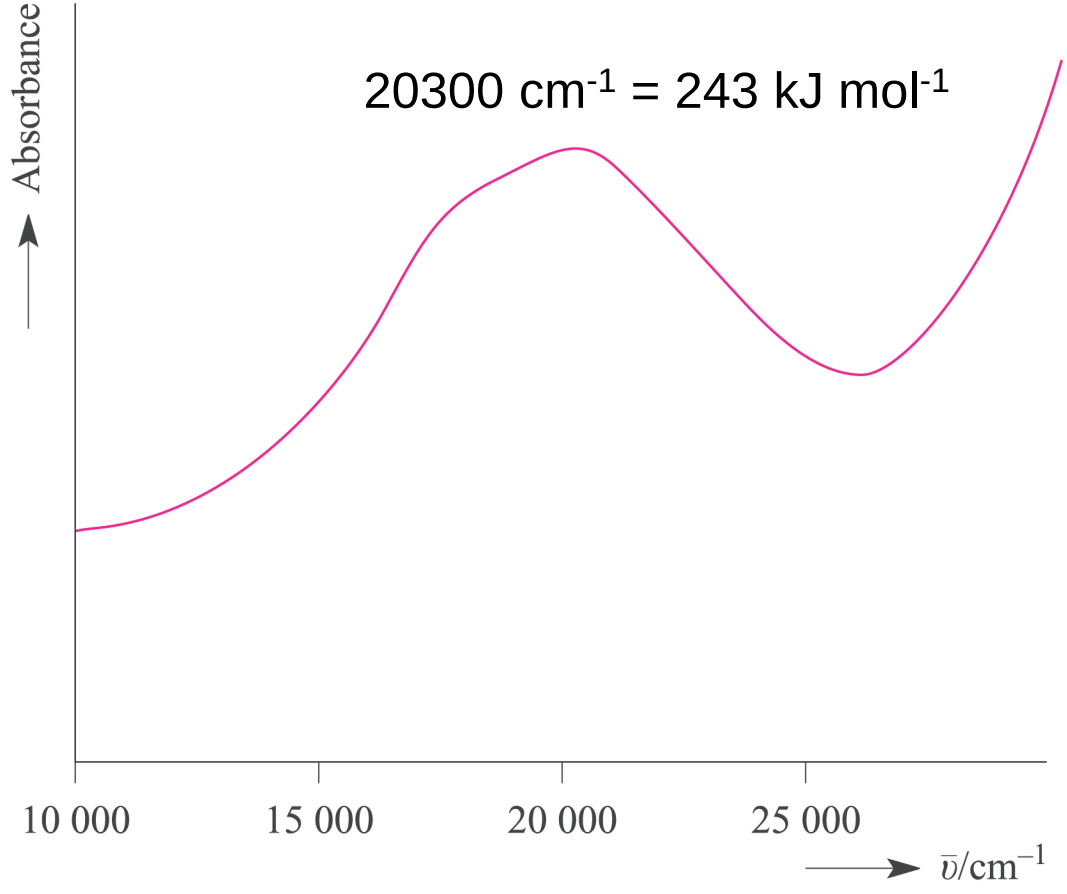
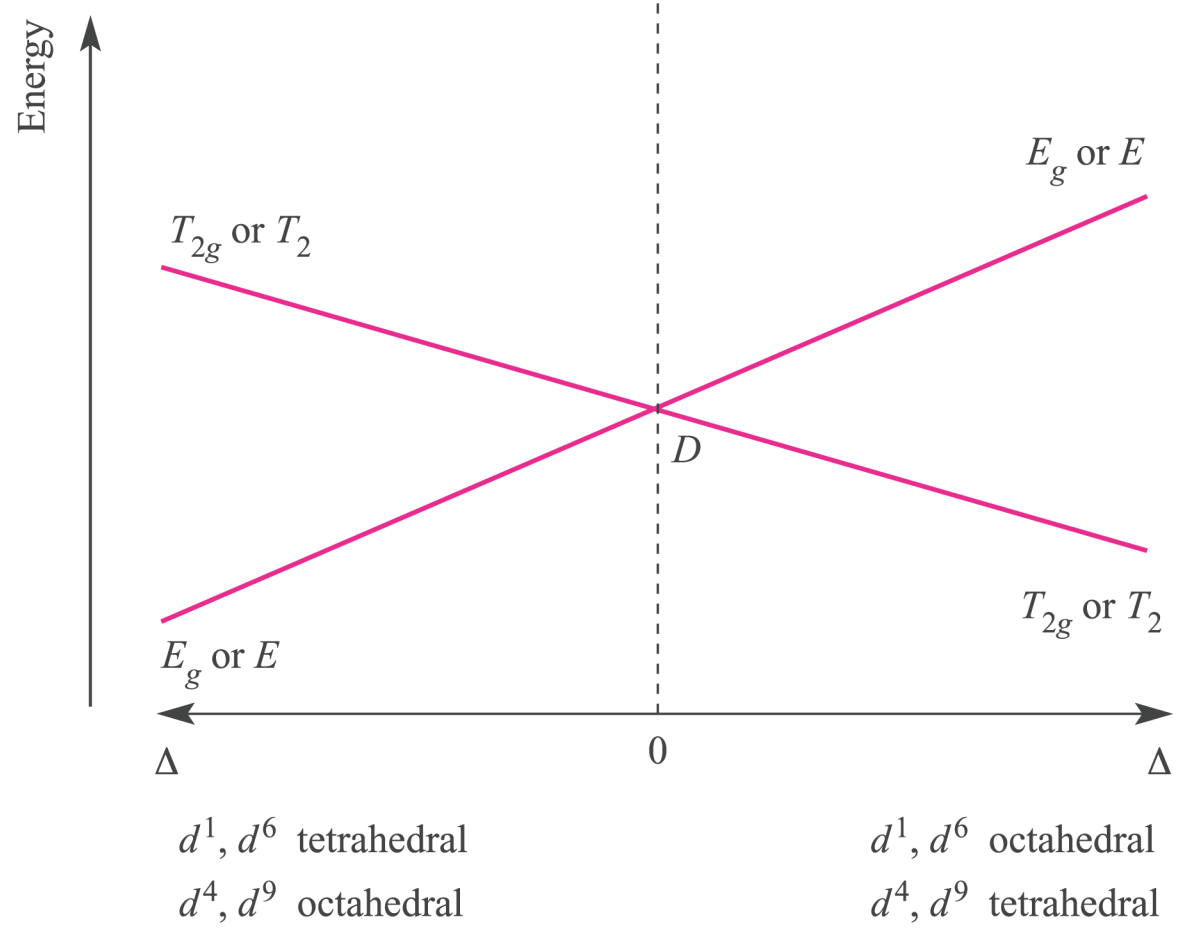


Diagramma di correlazione di Orgel per ioni d^1, d^4 (h.s.), d^6 (h.s.) e d^9 in campo ottaedrico (debole) e tetraedrico



La molteplicità di spin dipende dalla configurazione elettronica

Parametri di Racah

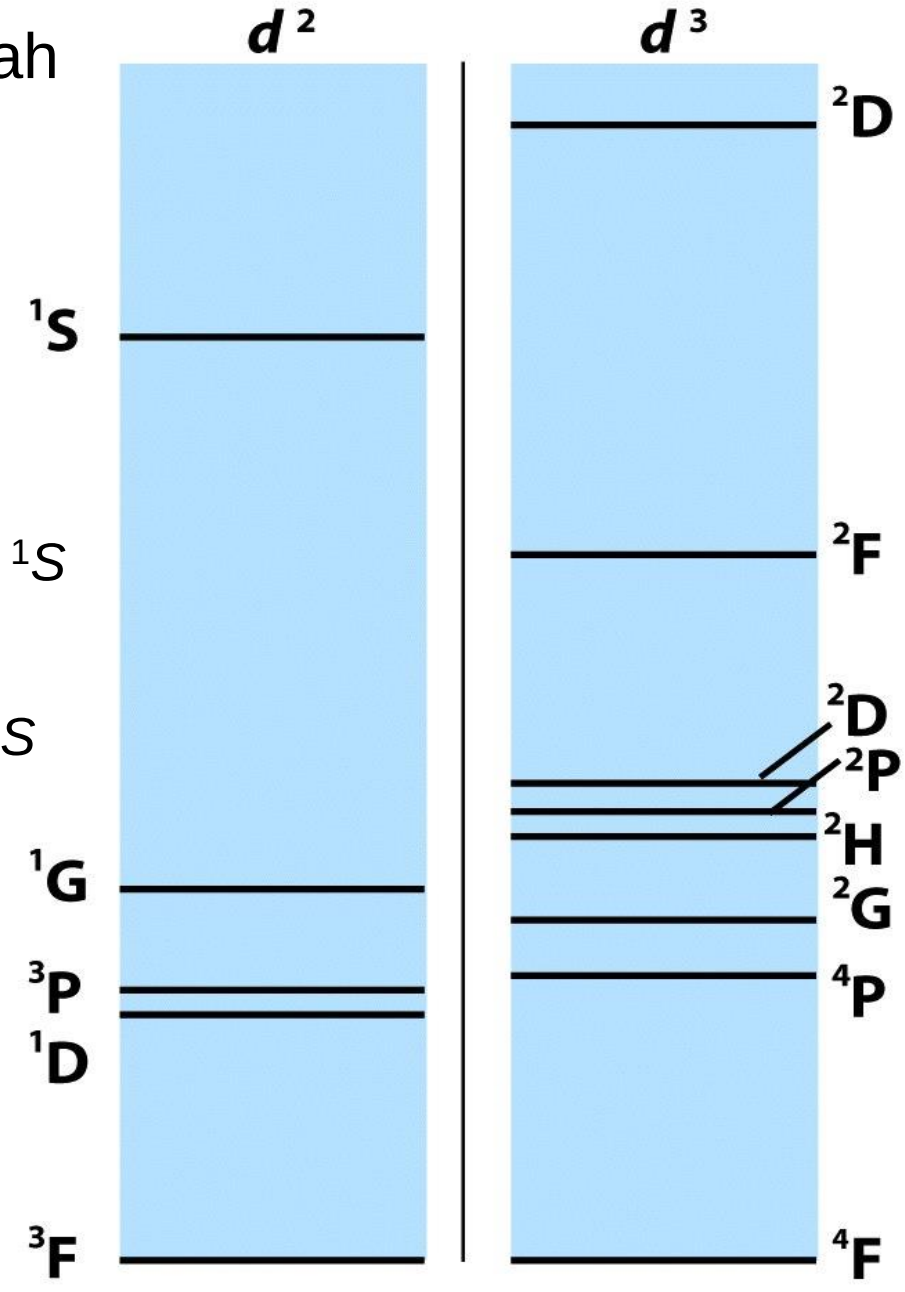
$E(^1S) = A + 14B + 7C$
$E(^1G) = A + 4B + 2C$
$E(^1D) = A - 3B + 2C$
$E(^3P) = A + 7B$
$E(^3F) = A - 8B$

$C > 5B$

$^3F < {}^3P < {}^1D < {}^1G < {}^1S$

$C < 5B$

$^3F < {}^1D < {}^3P < {}^1G < {}^1S$



Ti^{2+}

Table 19.7 The correlation of spectroscopic terms for *d* electrons in O_h complexes

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S	1	A_{1g}
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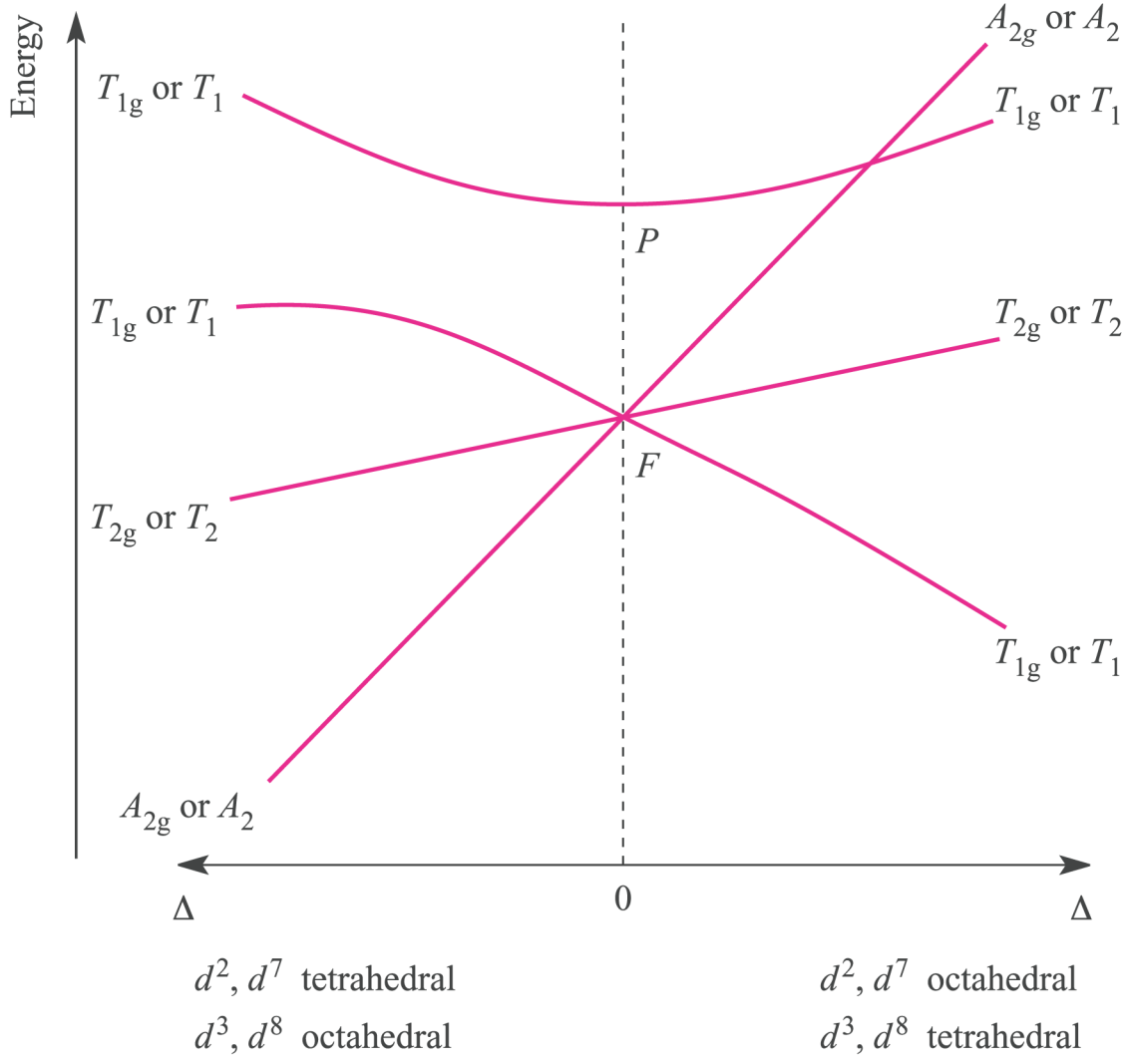
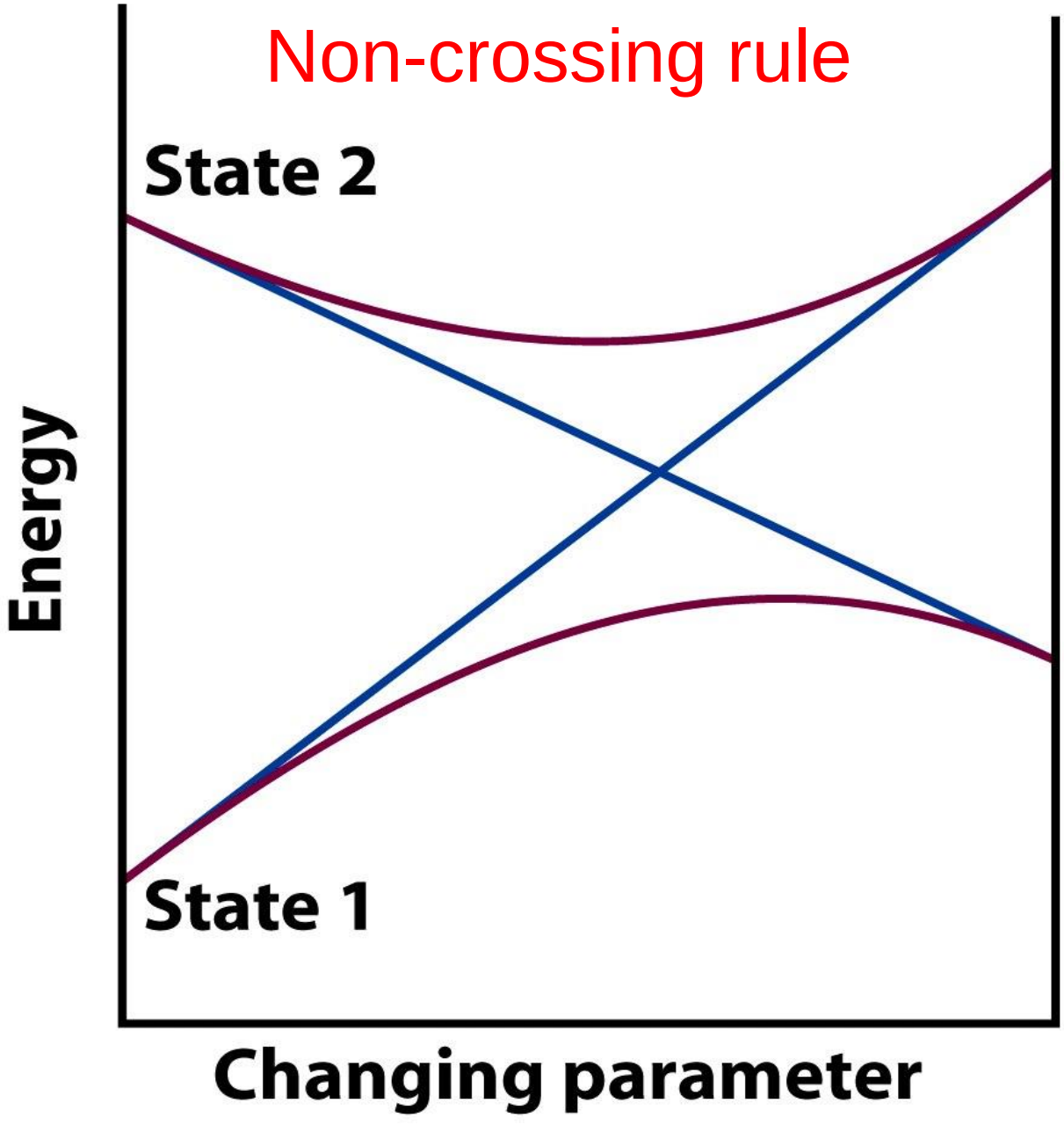
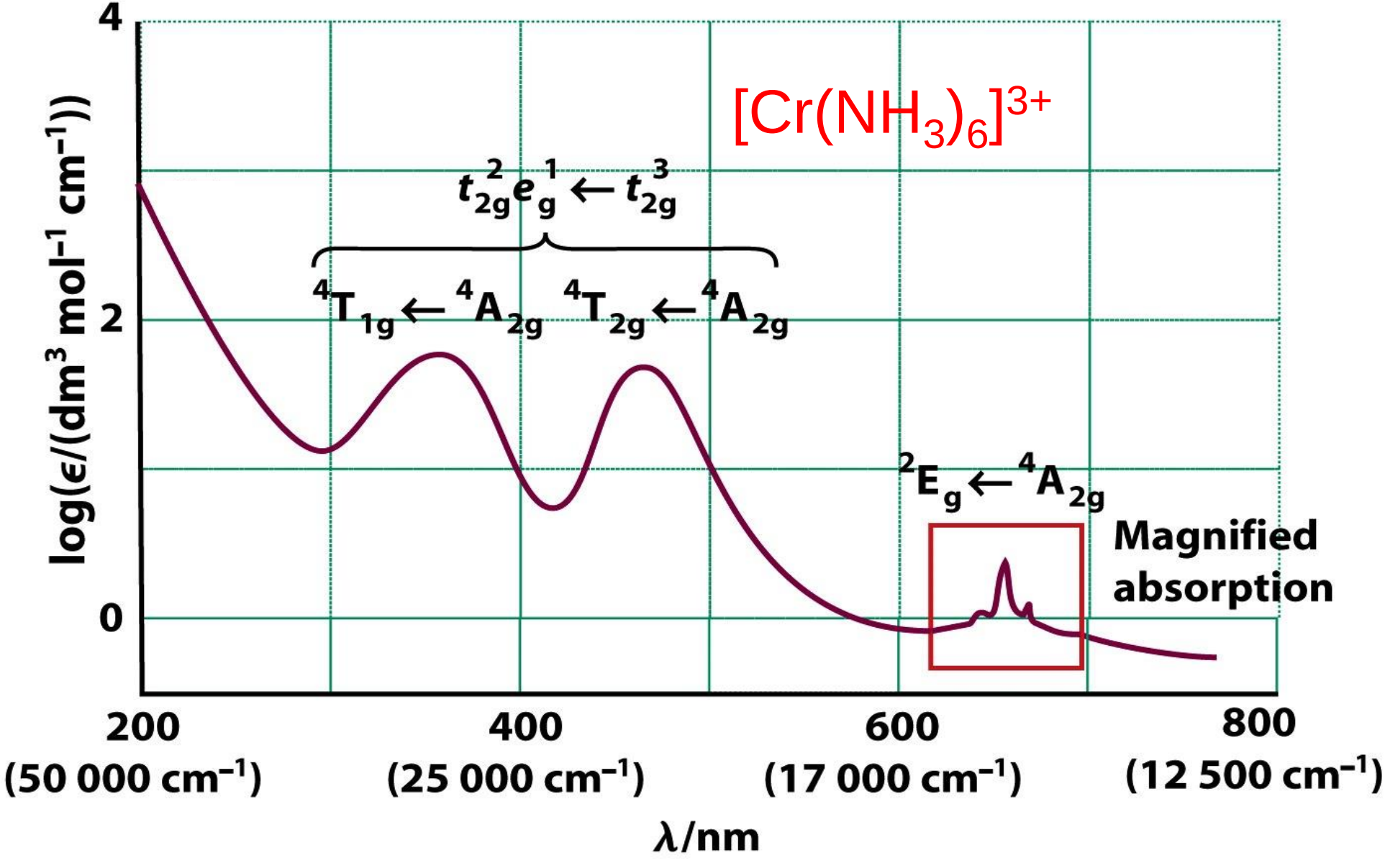
Diagramma di correlazione di Orgel per ioni d^2, d^3, d^7 e d^8 (tutti h.s.) in campo ottaedrico e tetraedrico



La molteplicità di spin dipende dalla configurazione elettronica

Non-crossing rule




[Cr(NH3)6]3+
t2g2eg1 ← t2g3
4T1g ← 4A2g
4T2g ← 4A2g
2Eg ← 4A2g
Magnified absorption
log(ε/(dm3 mol-1 cm-1))
4
2
0
200
(50 000 cm-1)
400
(25 000 cm-1)
600
(17 000 cm-1)
800
(12 500 cm-1)
λ/nm

Le 3 bande di assorbimento per complessi d^8 h.s.

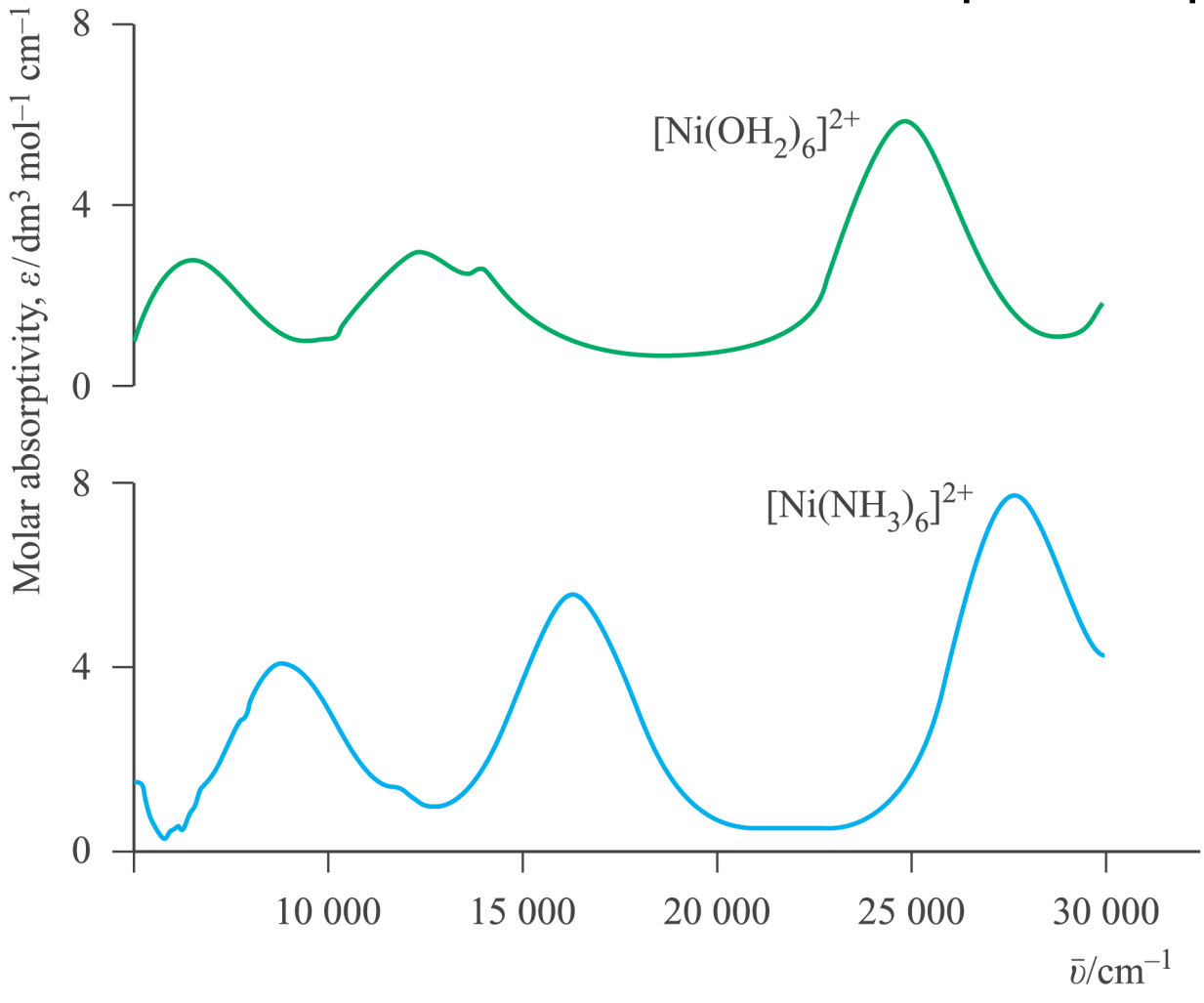
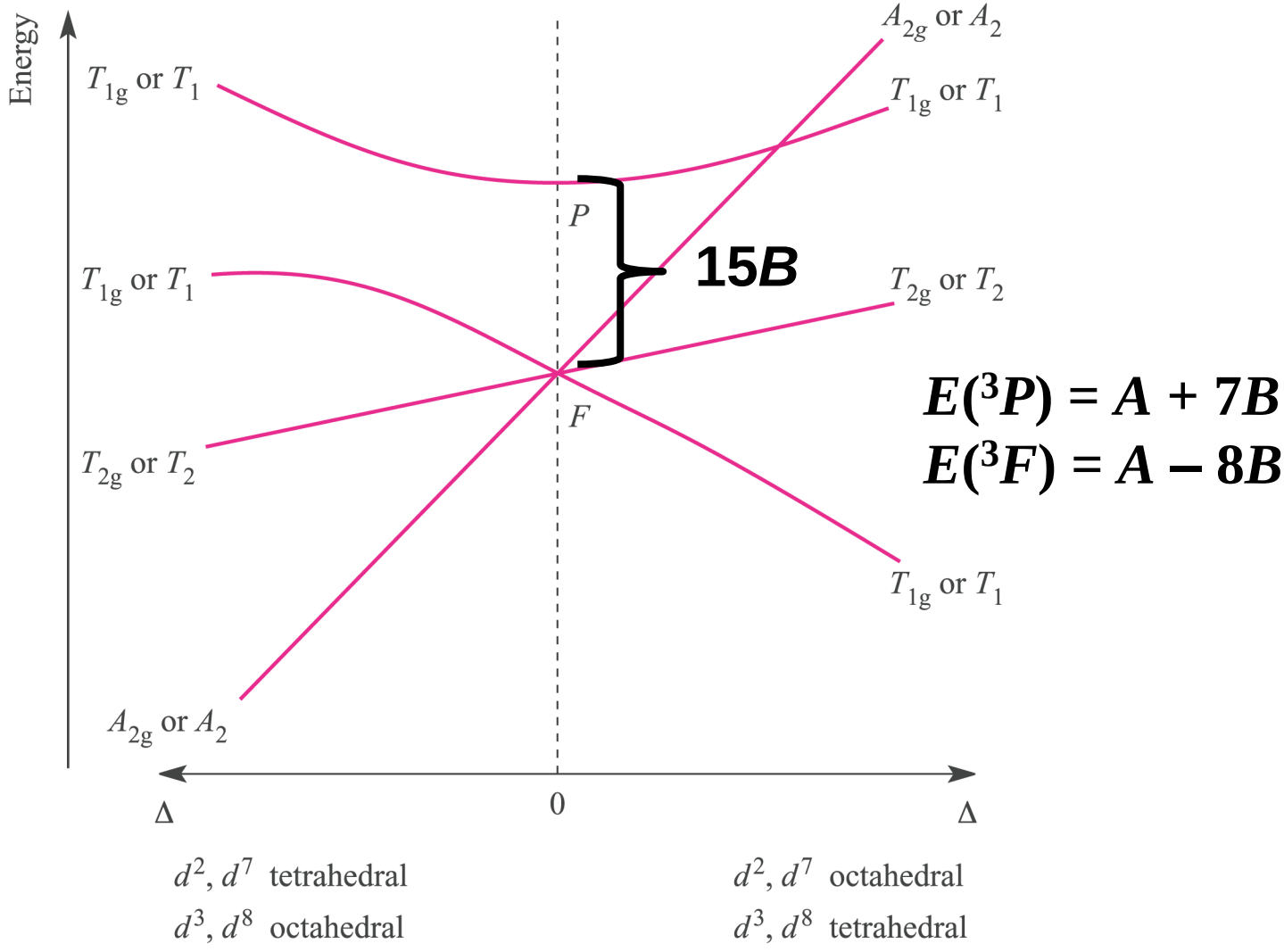


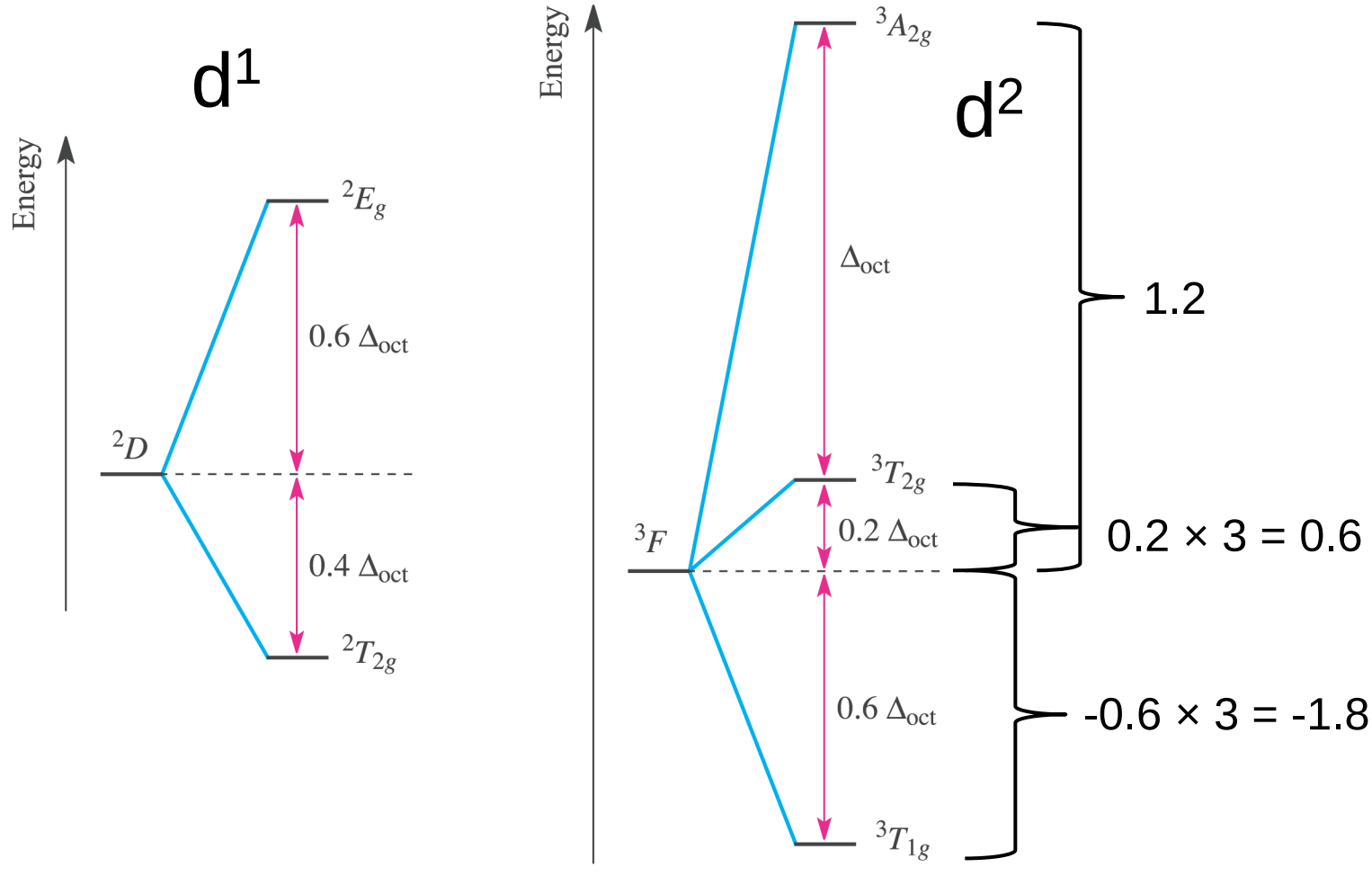
Diagramma di correlazione di Orgel per ioni d^2, d^3, d^7 e d^8 (tutti h.s.) in campo ottaedrico e tetraedrico



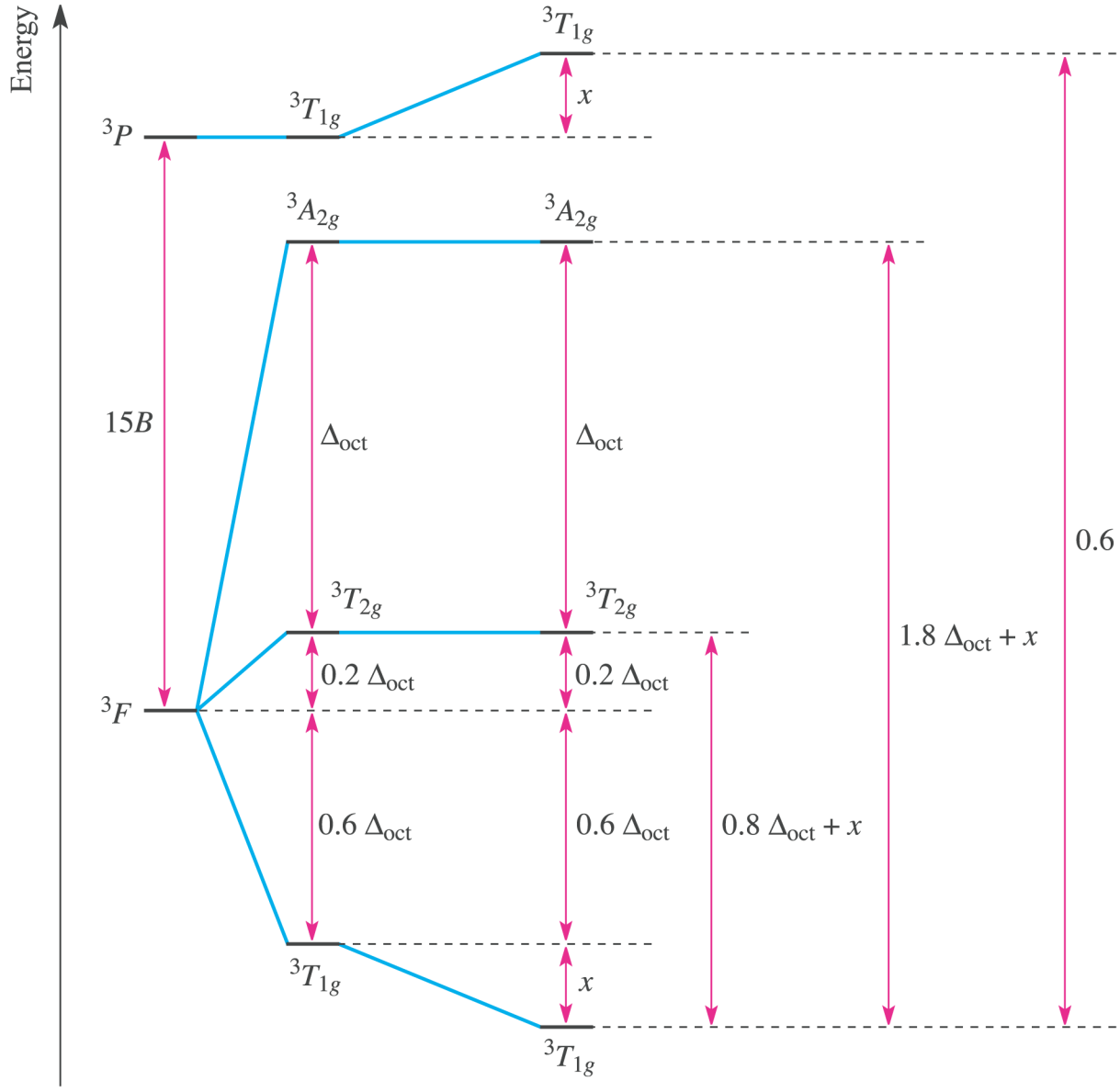
$$E(^3P) = A + 7B$$
$$E(^3F) = A - 8B$$

La molteplicità di spin dipende dalla configurazione elettronica

Dipendenza della separazione di energia fra i termini in funzione di Δ_O



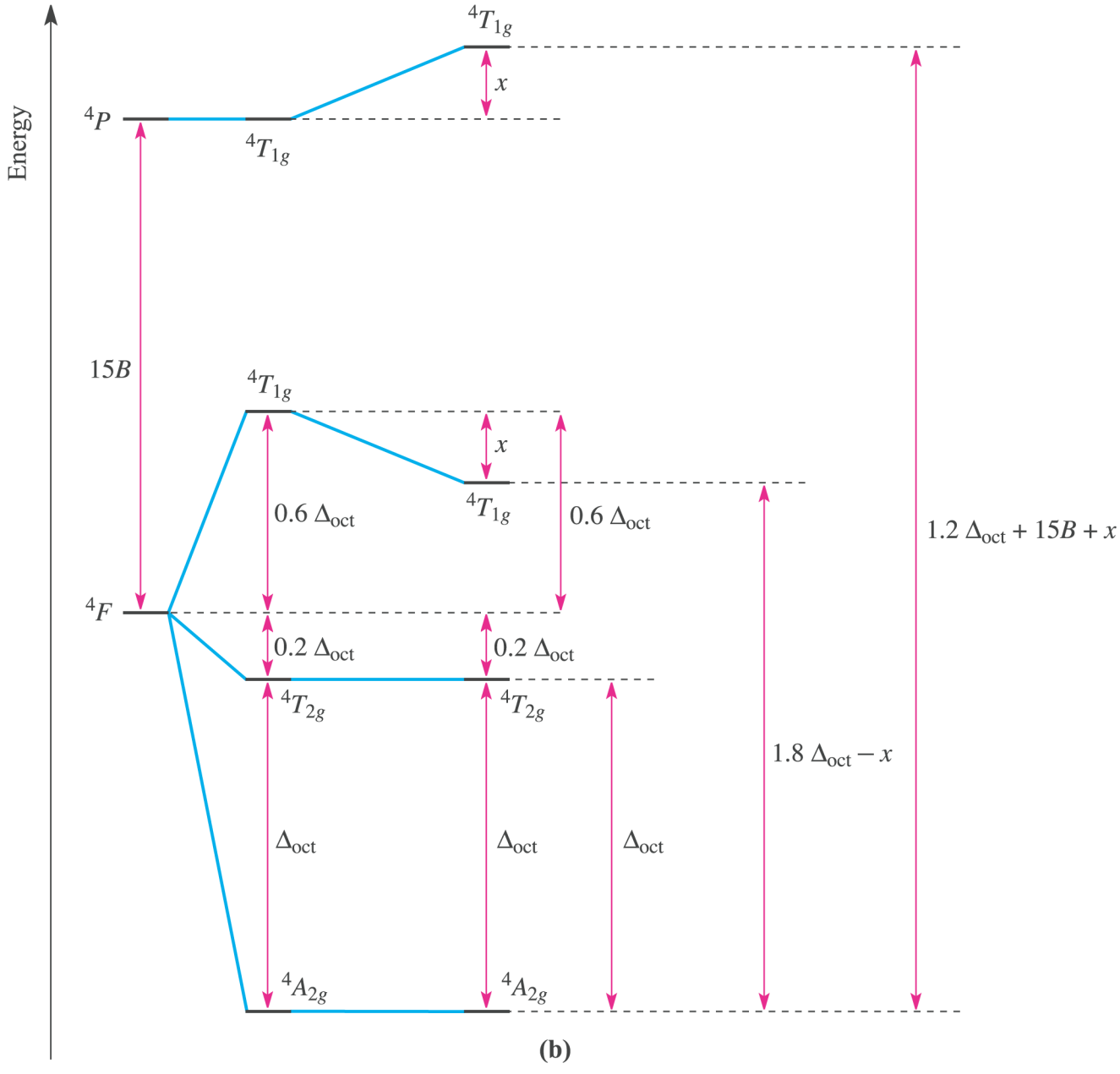
d^2, d^7



x = fattore di perturbazione dovuto al parziale mescolamento fra i termini di uguale simmetria

$$\Delta_o = 1.8\Delta_o + x - (0.8\Delta_o + x)$$

d^3, d^8


Energy
$^4T_{1g}$
x
^4P
$^4T_{1g}$
$15B$
$^4T_{1g}$
x
$0.6\ \Delta_{oct}$
$^4T_{1g}$
$0.6\ \Delta_{oct}$
$1.2\ \Delta_{oct} + 15B + x$
^4F
$0.2\ \Delta_{oct}$
$0.2\ \Delta_{oct}$
$^4T_{2g}$
$^4T_{2g}$
$1.8\ \Delta_{oct} - x$
Δ_{oct}
Δ_{oct}
Δ_{oct}
$^4A_{2g}$
$^4A_{2g}$

(b)

Diagramma di Tanabe-Sugano per la configurazione d^2 in campo ottaedrico

$C \approx 4B$

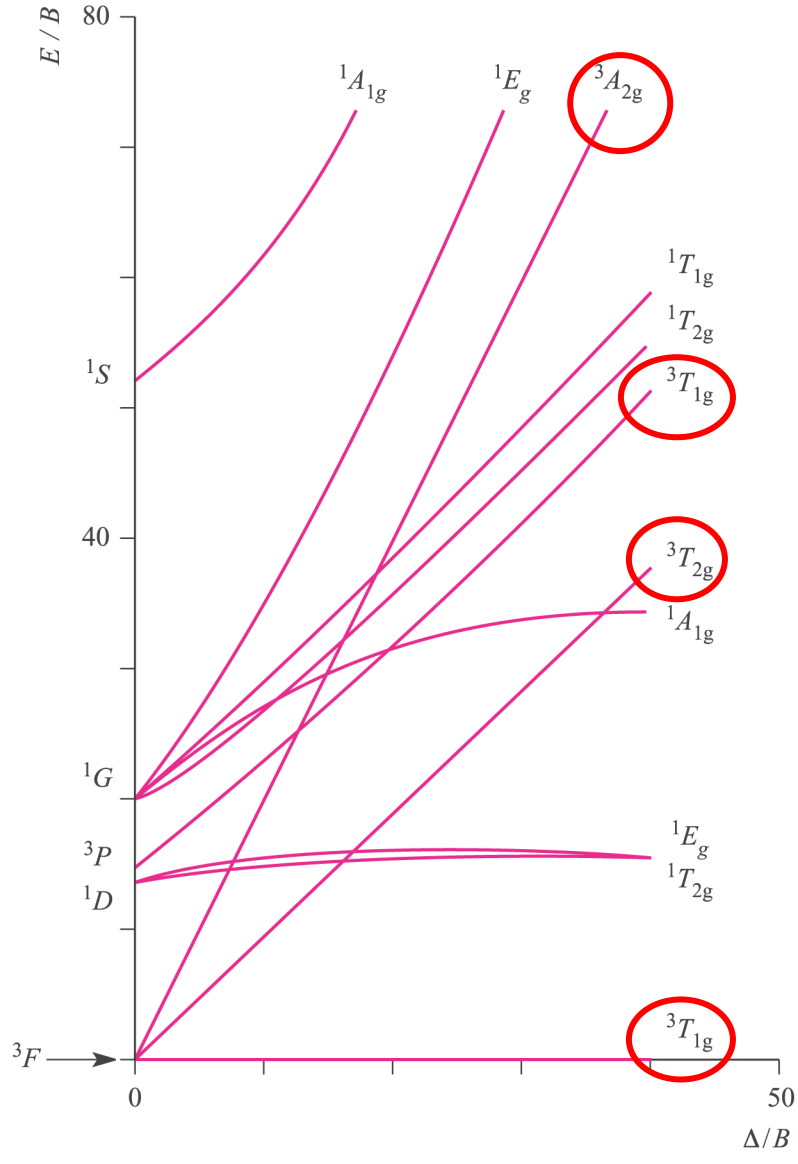
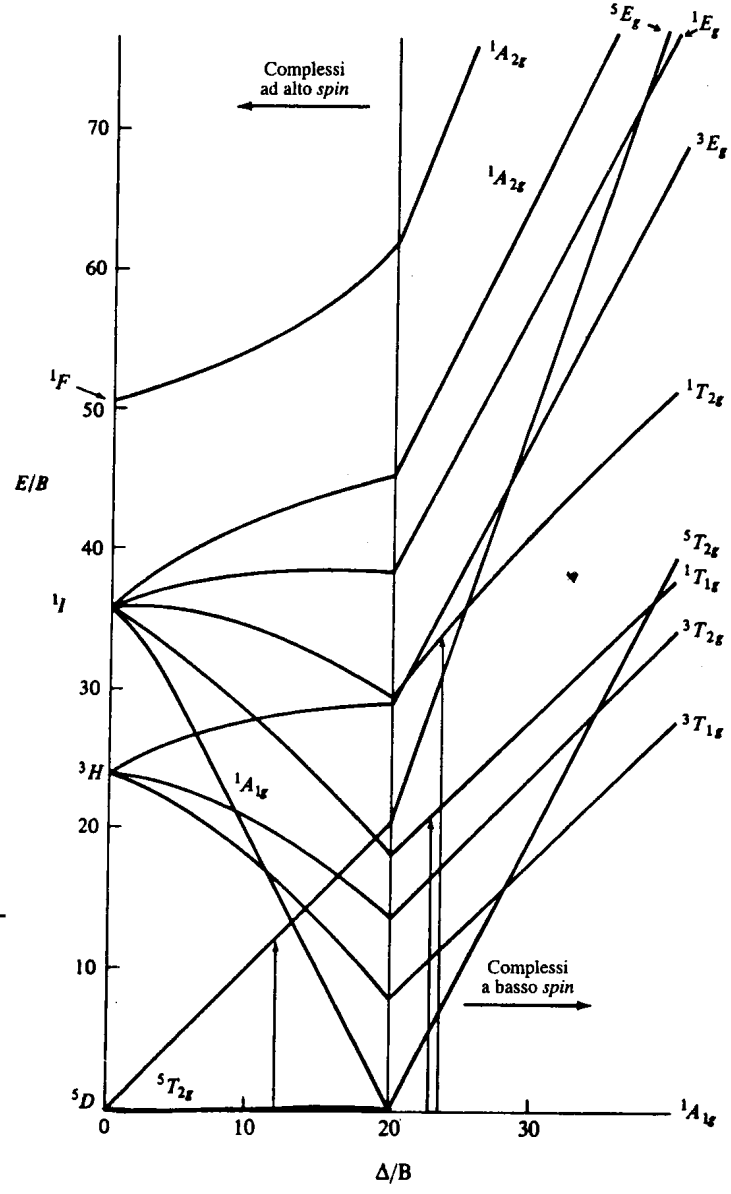
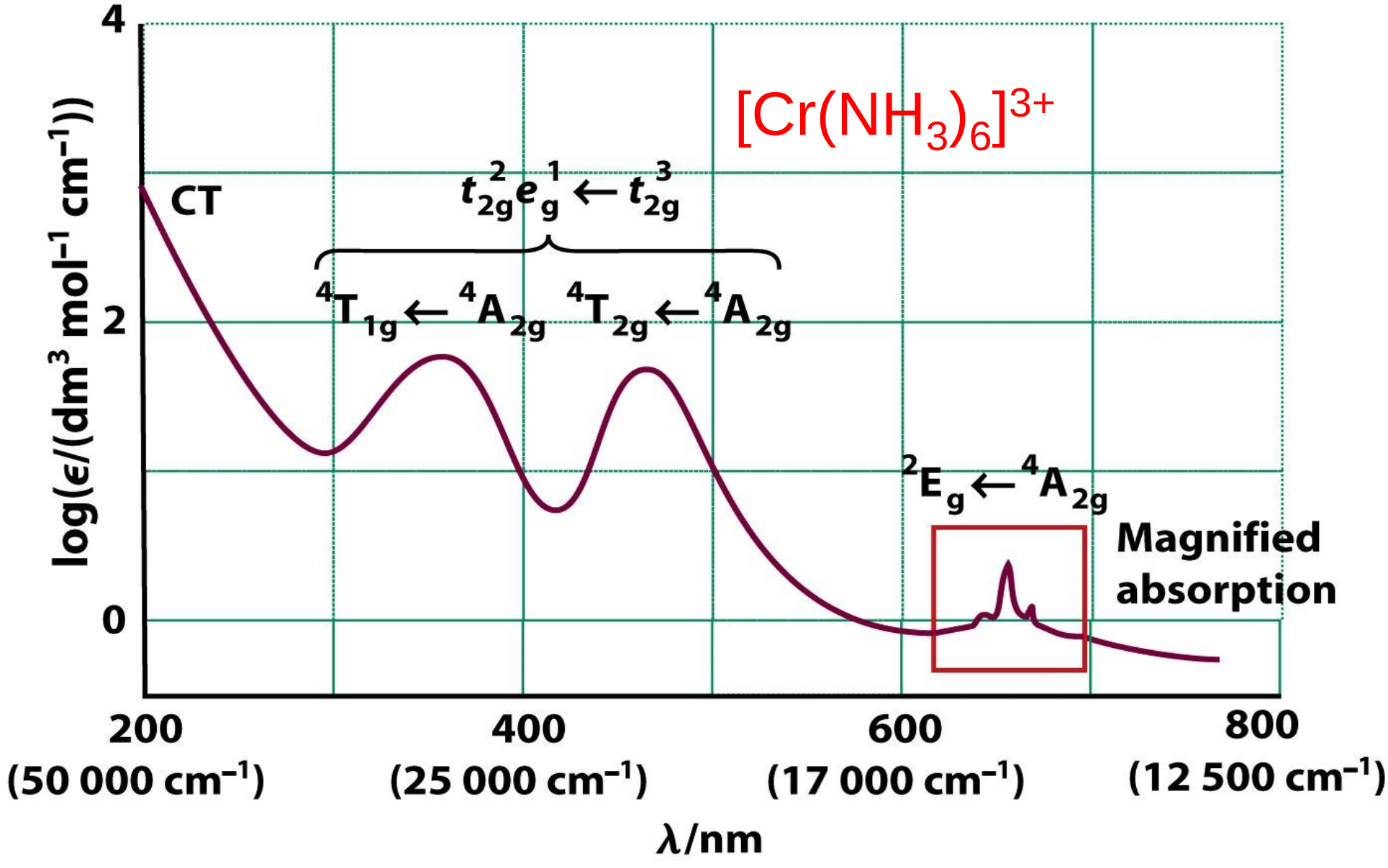


Diagramma di Tanabe-Sugano per la configurazione d^6 in campo ottaedrico

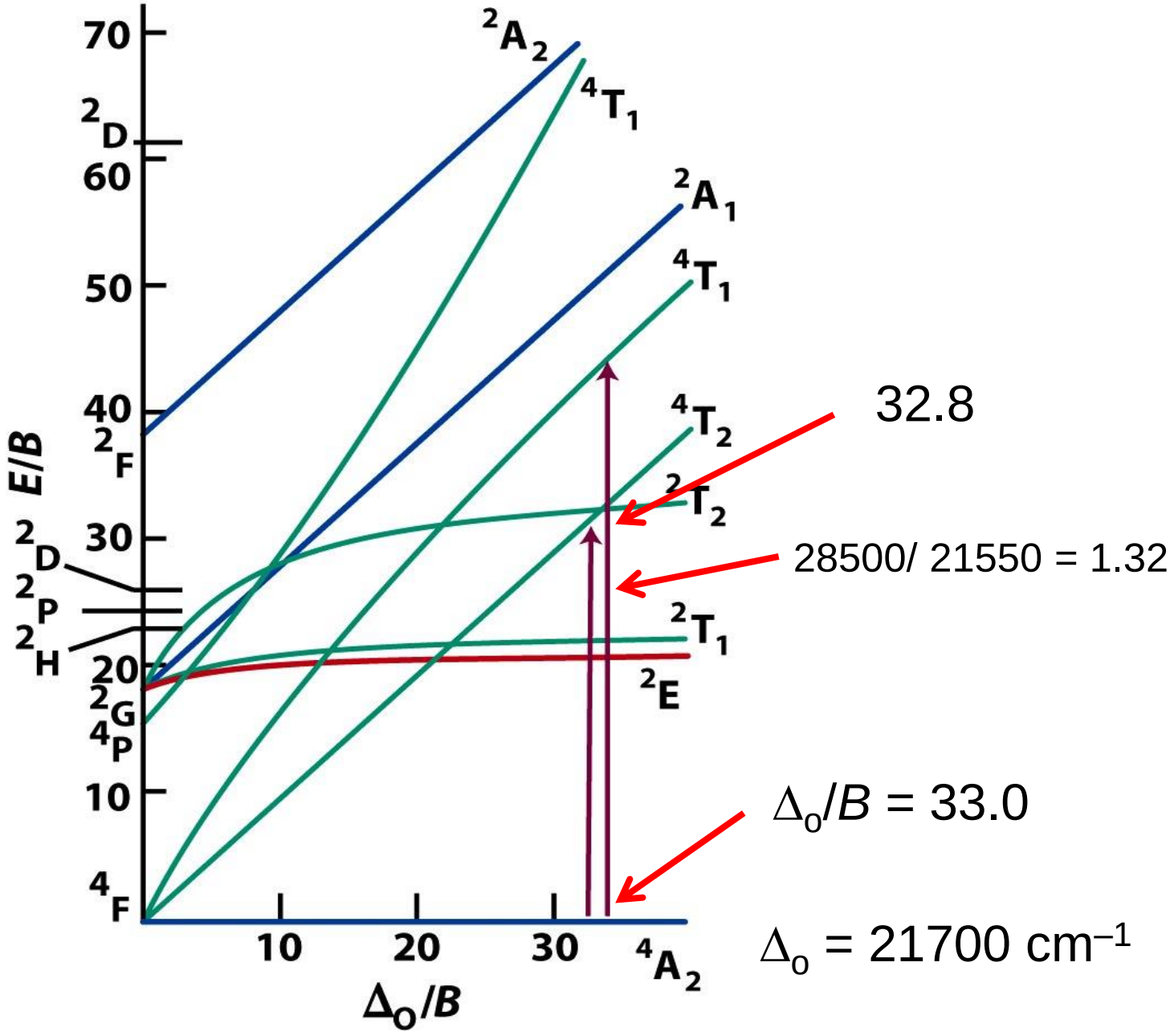
$[CoF_6]^{3-}$



$[Co(en)_3]^{3+}$



21550 e 28500 cm^{-1}



32.8 = 21550/*B* cm^{-1}

B = 657 cm^{-1}

Diagramma di Tanabe-Sugano per la configurazione d^3 in campo ottaedrico

Effetto nefelauxetico

Metal ion	k	Ligands	h
Co(III)	0.35	6 Br^-	2.3
Rh(III)	0.28	6 Cl^-	2.0
Co(II)	0.24	6 $[CN]^-$	2.0
Fe(III)	0.24	3 en	1.5
Cr(III)	0.21	6 NH_3	1.4
Ni(II)	0.12	6 H_2O	1.0
Mn(II)	0.07	6 F^-	0.8

$\beta = \frac{B}{B°}$ rapporto nefelauxetico (< 1)