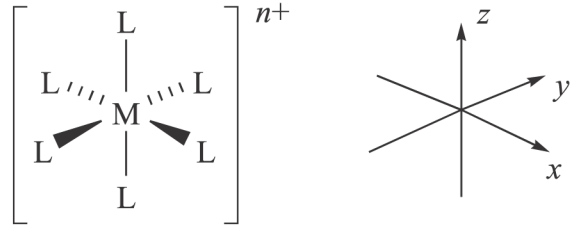
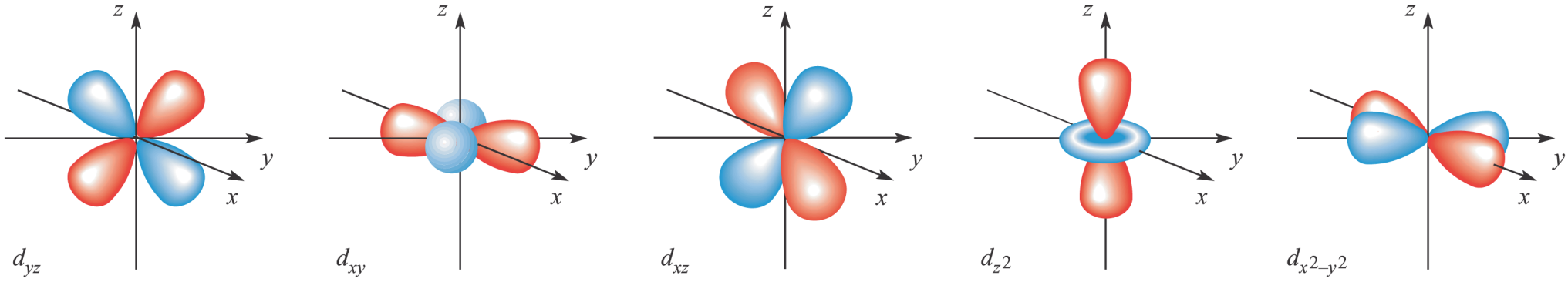
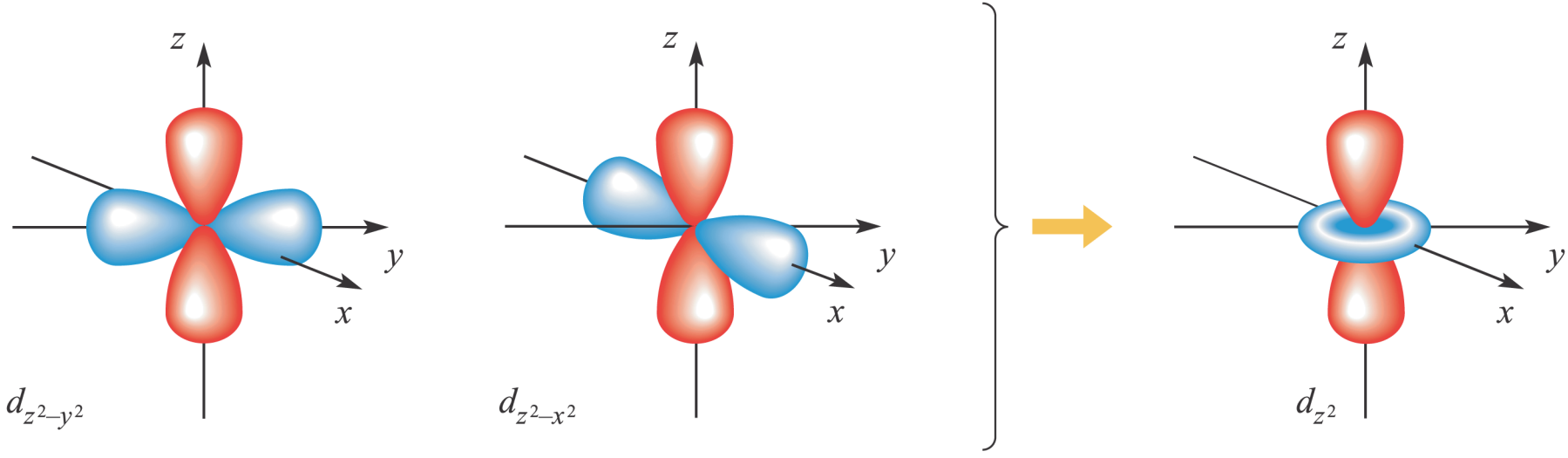


(a)

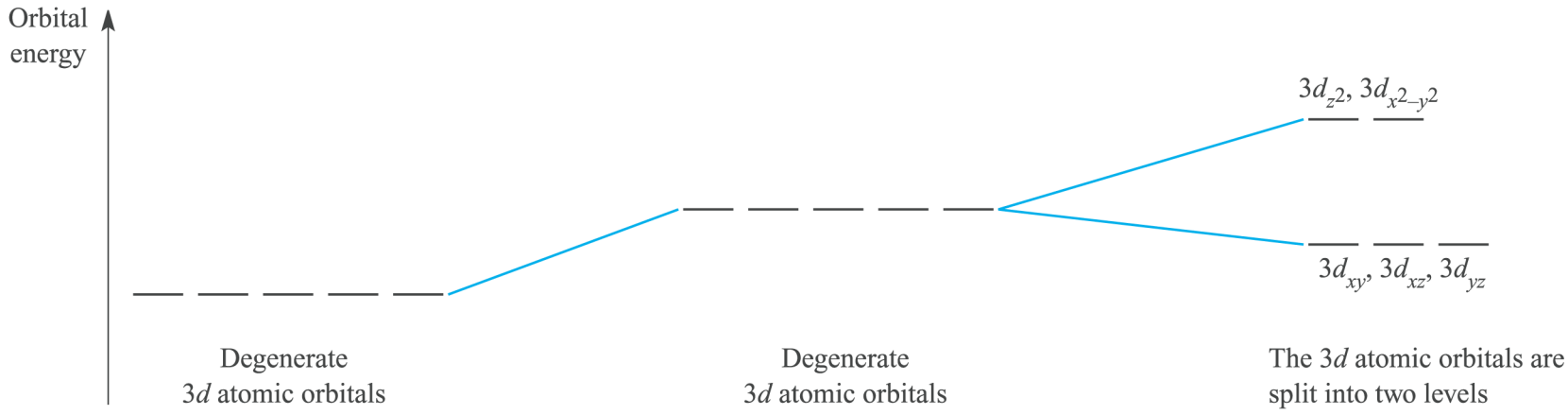


(b)

Formazione di un orbitale d_{z^2} da una combinazione lineare di $d_{z^2-y^2}$ e $d_{z^2-x^2}$



Teoria del Campo Cristallino



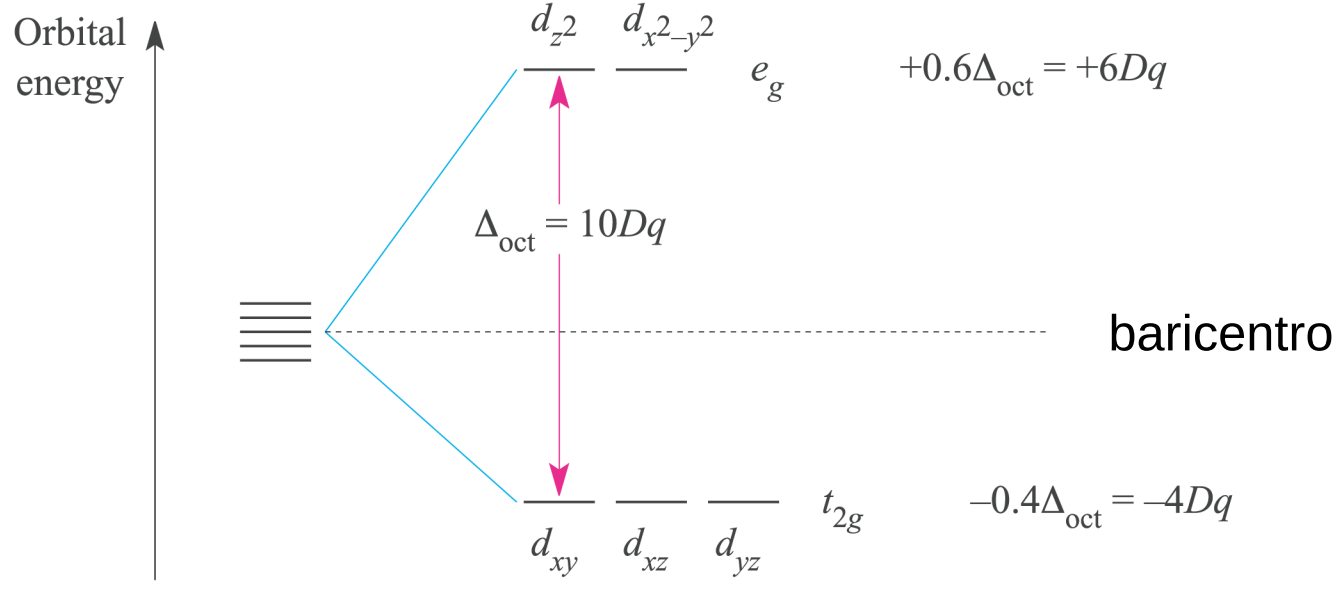
Metal ion M^{n+} and six ligands L at an infinite distance away

If the electrostatic field created by the point charge ligands is *spherical*, the energies of the electrons in the 3*d* orbitals are raised uniformly

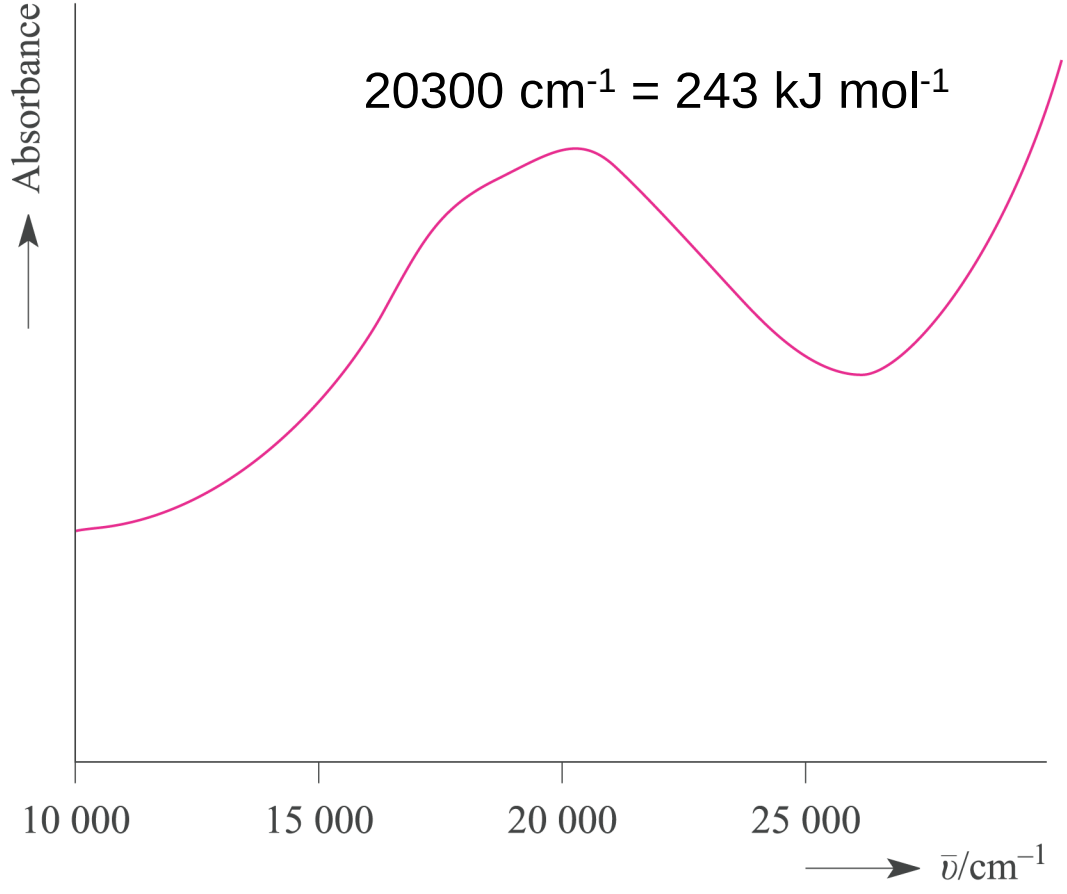
If the electrostatic field created by the point charge ligands is *octahedral*, the energy of the electrons in the 3*d* orbitals that point *directly* at the ligands is raised with respect to that in the spherical field, while the energy of the electrons in the orbitals that point *between* the ligands is lowered with respect to the spherical field

O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2,$ $\sqrt{3}\,(x^2-y^2))$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
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	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

Separazione degli orbitali d in un campo cristallino ottaedrico

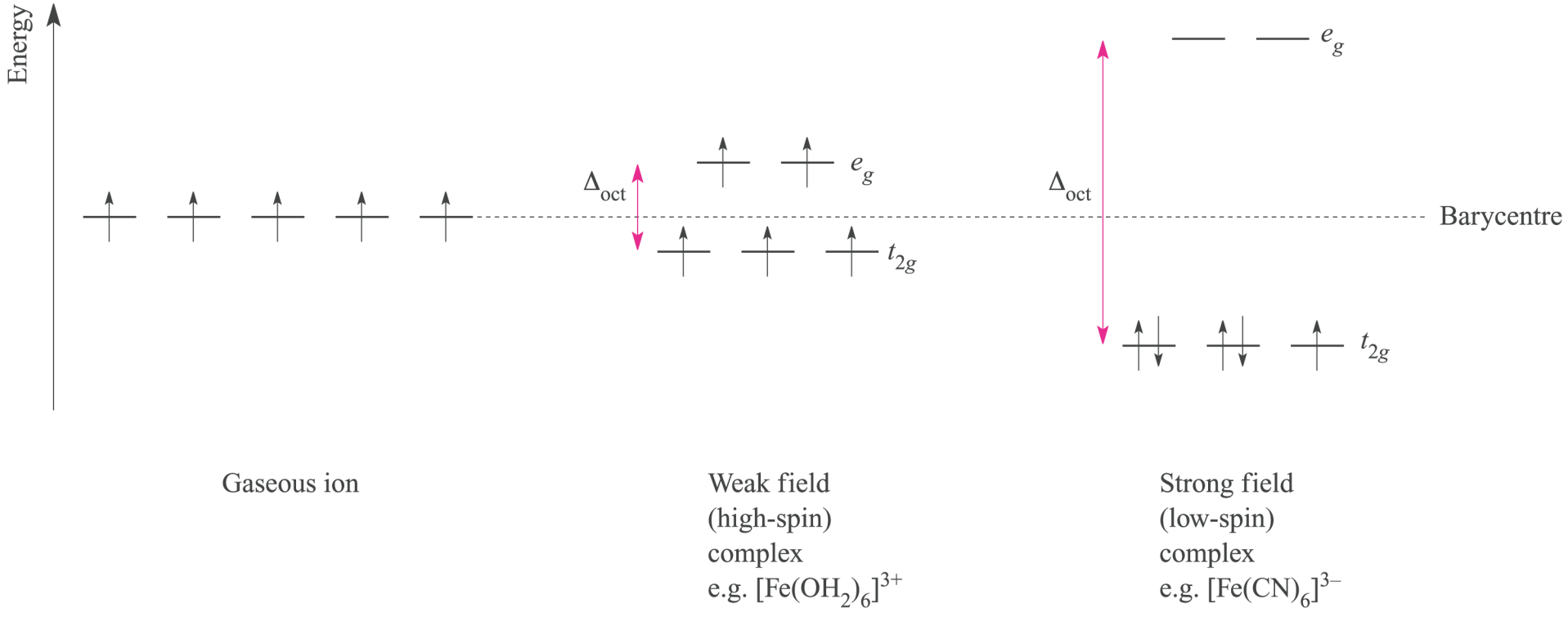


Spettro di assorbimento elettronico del complesso d^1 $[Ti(OH_2)_6]^{3+}$



i Δ_o hanno grandezze tipiche confrontabili con quelle dei legami chimici

Ligand Field Stabilization Energy (LFSE)



$\Delta_o < P$ $\Delta_o > P$

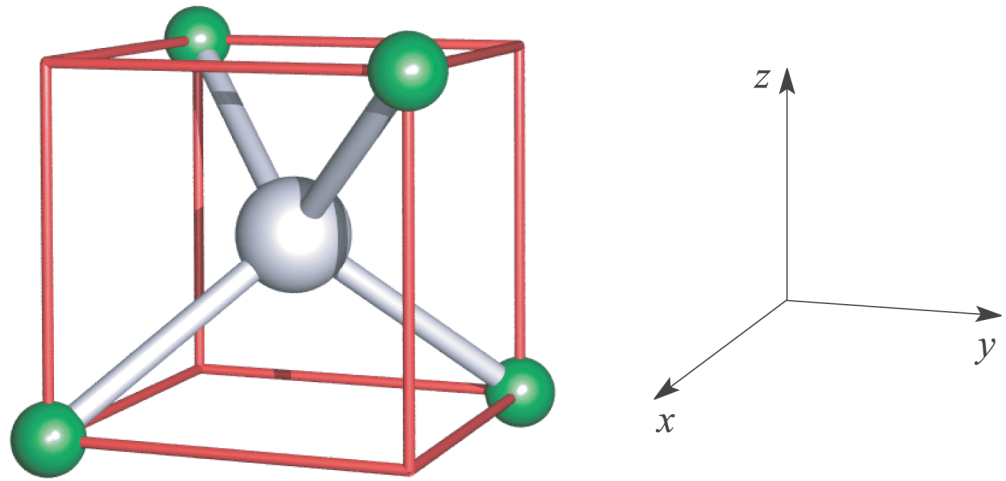
P =180 – 300 kJmol^{-1}

$\Delta_o < P$

d^n	High-spin = weak field	
	Electronic configuration	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_{oct}$
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_{oct}$
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_{oct}$
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_{oct}$
d^5	$t_{2g}^3 e_g^2$	0
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_{oct}$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_{oct}$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_{oct}$
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_{oct}$
d^{10}	$t_{2g}^6 e_g^4$	0

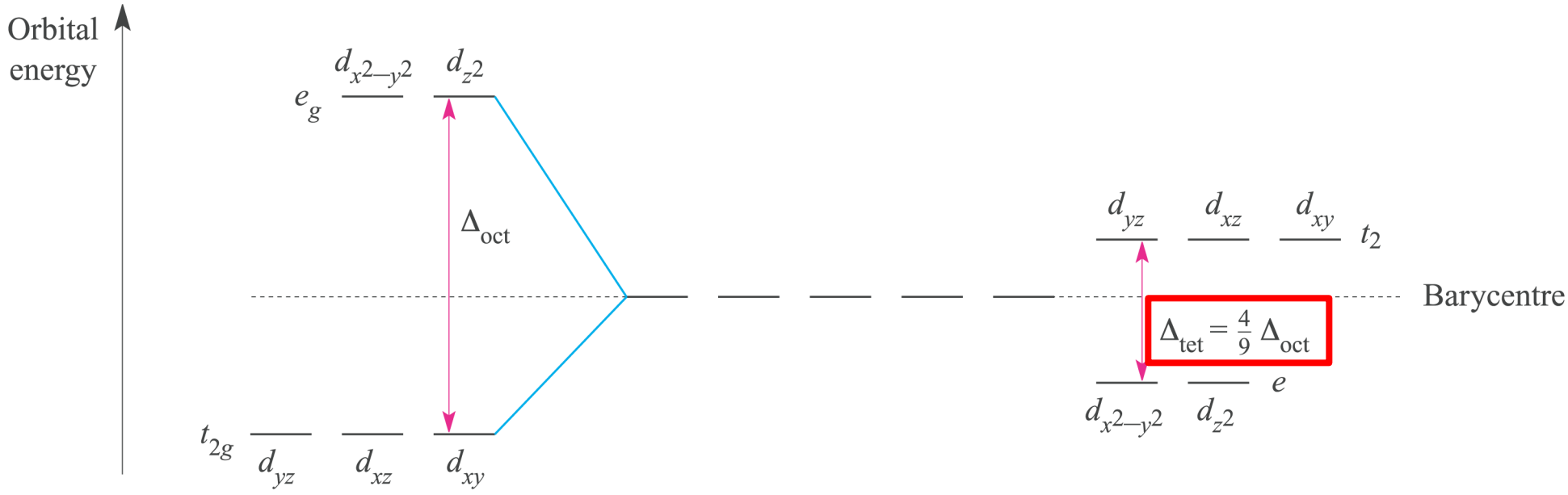
$\Delta_o > P$

d^n	Low-spin = strong field	
	Electronic configuration	CFSE
d^1		
d^2		
d^3		
d^4	$t_{2g}^4 e_g^0$	$-1.6\Delta_{oct} + P$
d^5	$t_{2g}^5 e_g^0$	$-2.0\Delta_{oct} + 2P$
d^6	$t_{2g}^6 e_g^0$	$-2.4\Delta_{oct} + 2P$
d^7	$t_{2g}^6 e_g^1$	$-1.8\Delta_{oct} + P$
d^8		
d^9		
d^{10}		

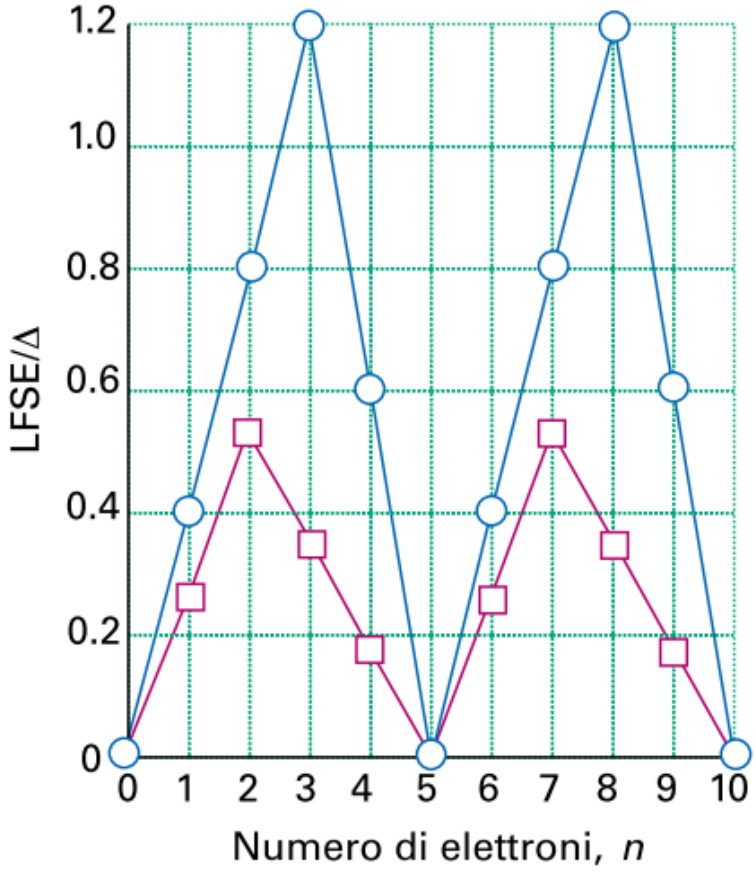

z
y
x

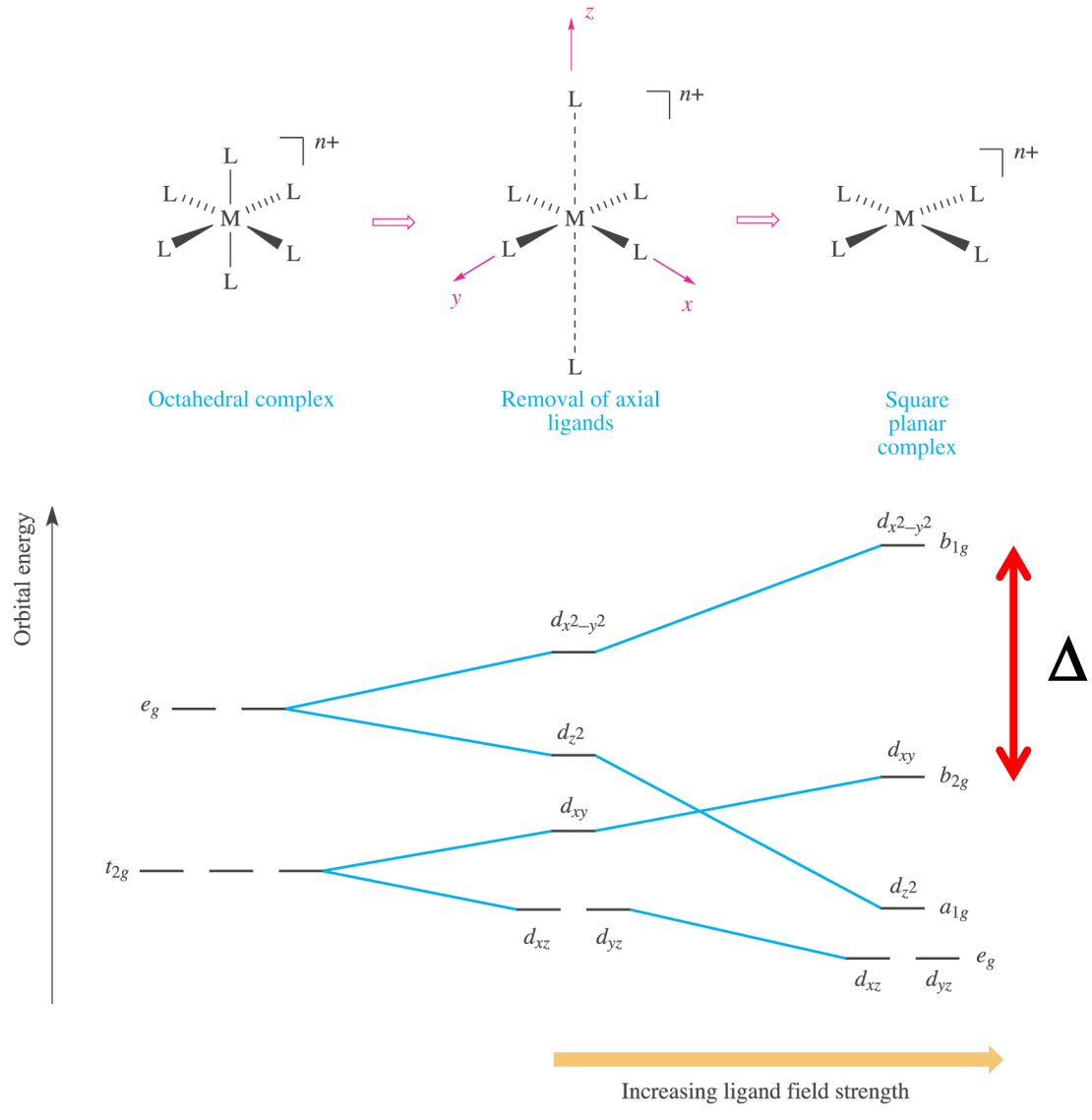
Campo ottaedrico

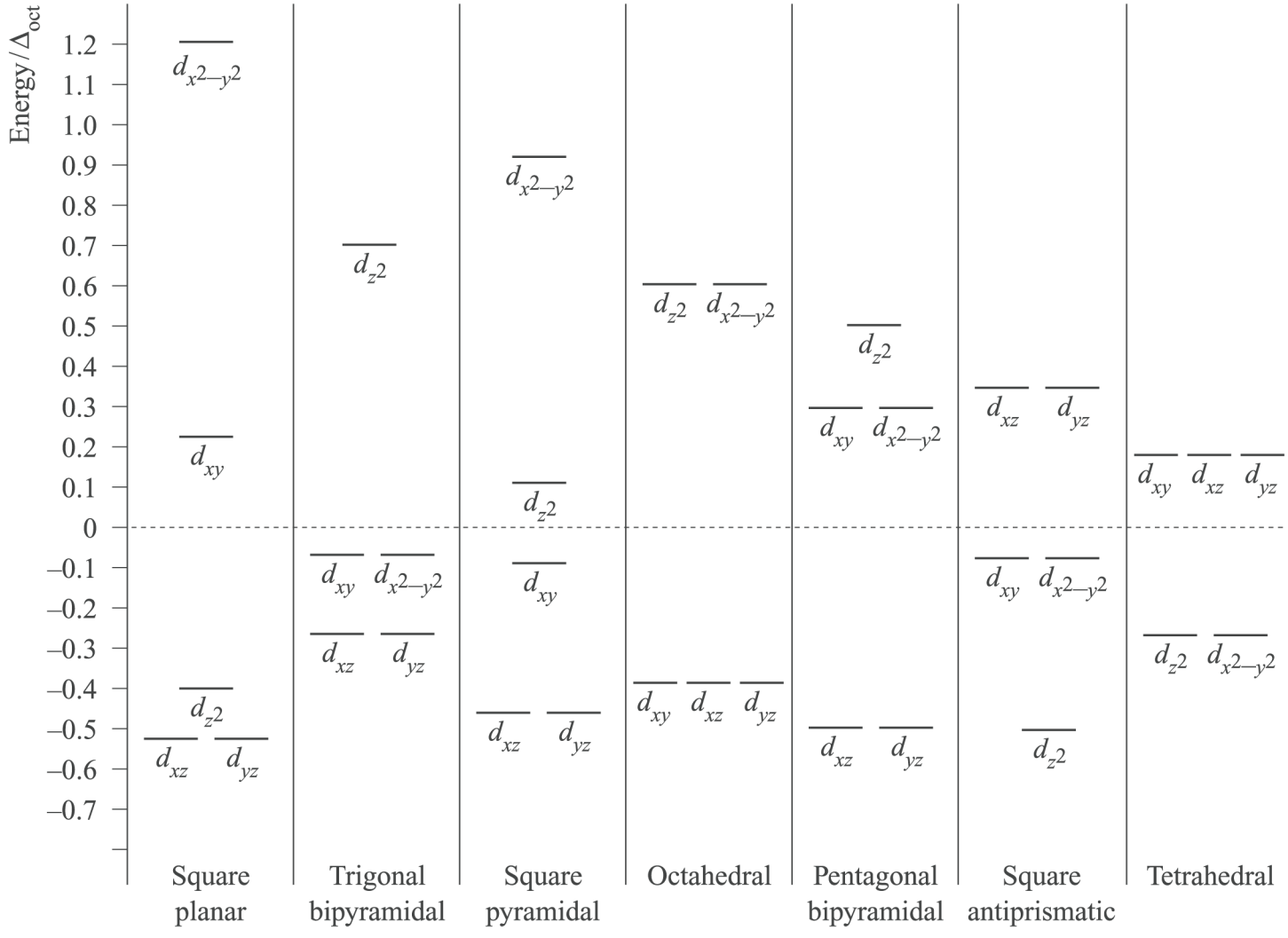
Campo tetraedrico



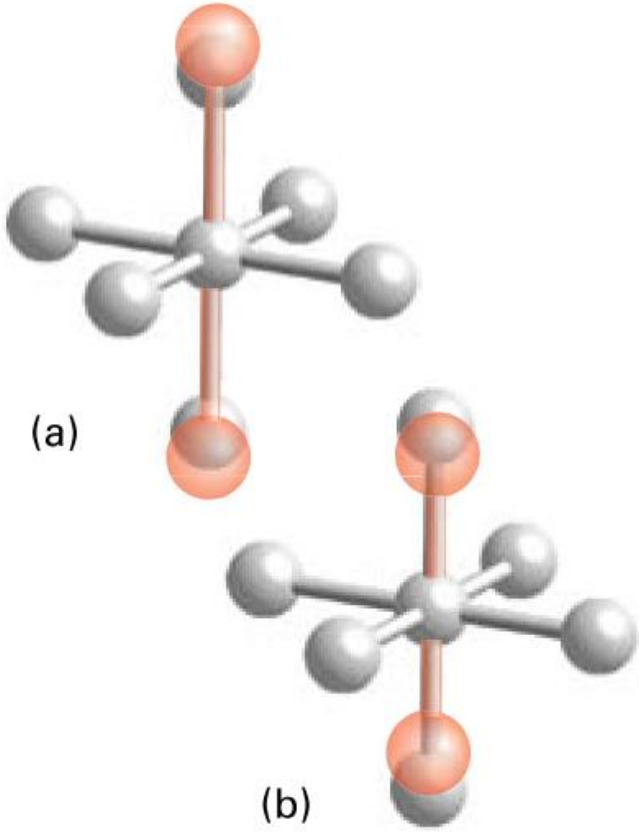
LFSE per complessi ottaedrici (alto spin) e tetraedrici

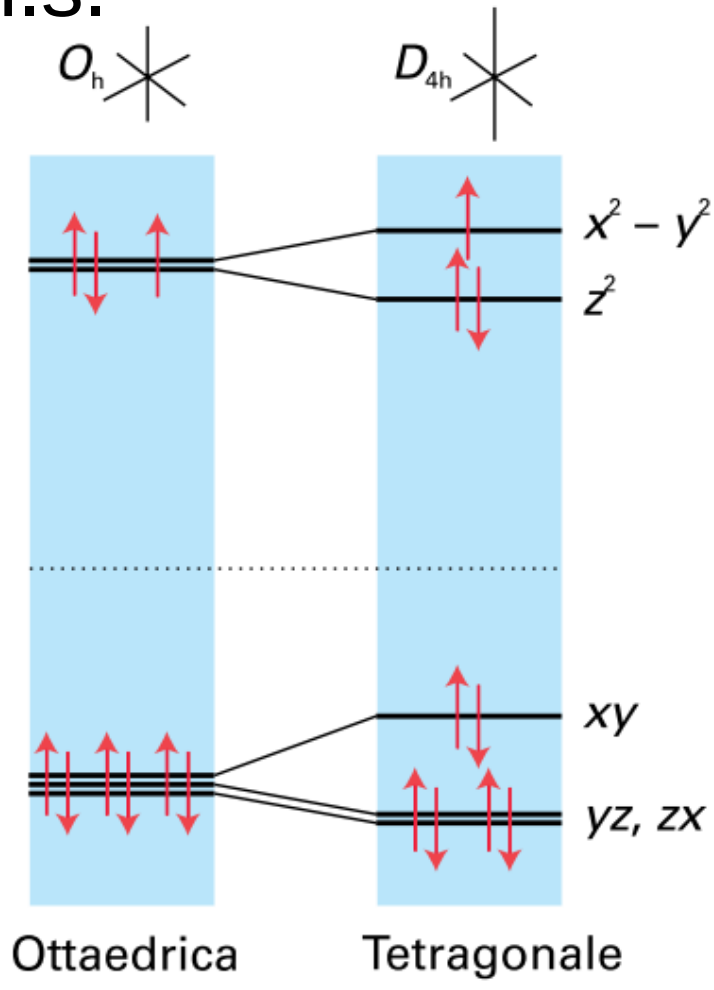



z
L
n+
L
L
M
L
L
L
L
L
L
L
L
L
L
L
y
x
L
Octahedral complex
Removal of axial ligands
Square planar complex
Orbital energy
$d_{x^2-y^2}$
b_{1g}
$d_{x^2-y^2}$
e_g
d_{z^2}
d_{xy}
b_{2g}
d_{xy}
t_{2g}
d_{z^2}
a_{1g}
d_{xz}
d_{yz}
d_{xz}
d_{yz}
e_g
Δ
Increasing ligand field strength


Energy/Δ_{oct}
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
–0.1
–0.2
–0.3
–0.4
–0.5
–0.6
–0.7
$d_{x^2-y^2}$
d_{xy}
d_{z^2}
d_{xz} d_{yz}
Square planar
d_{z^2}
d_{xy} $d_{x^2-y^2}$
d_{xz} d_{yz}
Trigonal bipyramidal
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
d_{xz} d_{yz}
Square pyramidal
d_{z^2} $d_{x^2-y^2}$
d_{xy} d_{xz} d_{yz}
Octahedral
d_{z^2}
d_{xy} $d_{x^2-y^2}$
d_{xz} d_{yz}
Pentagonal bipyramidal
d_{xz} d_{yz}
d_{xy} $d_{x^2-y^2}$
d_{z^2}
Square antiprismatic
d_{xy} d_{xz} d_{yz}
d_{z^2} $d_{x^2-y^2}$
Tetrahedral

Effetto Jahn – Teller
d^9, d^4 h.s.

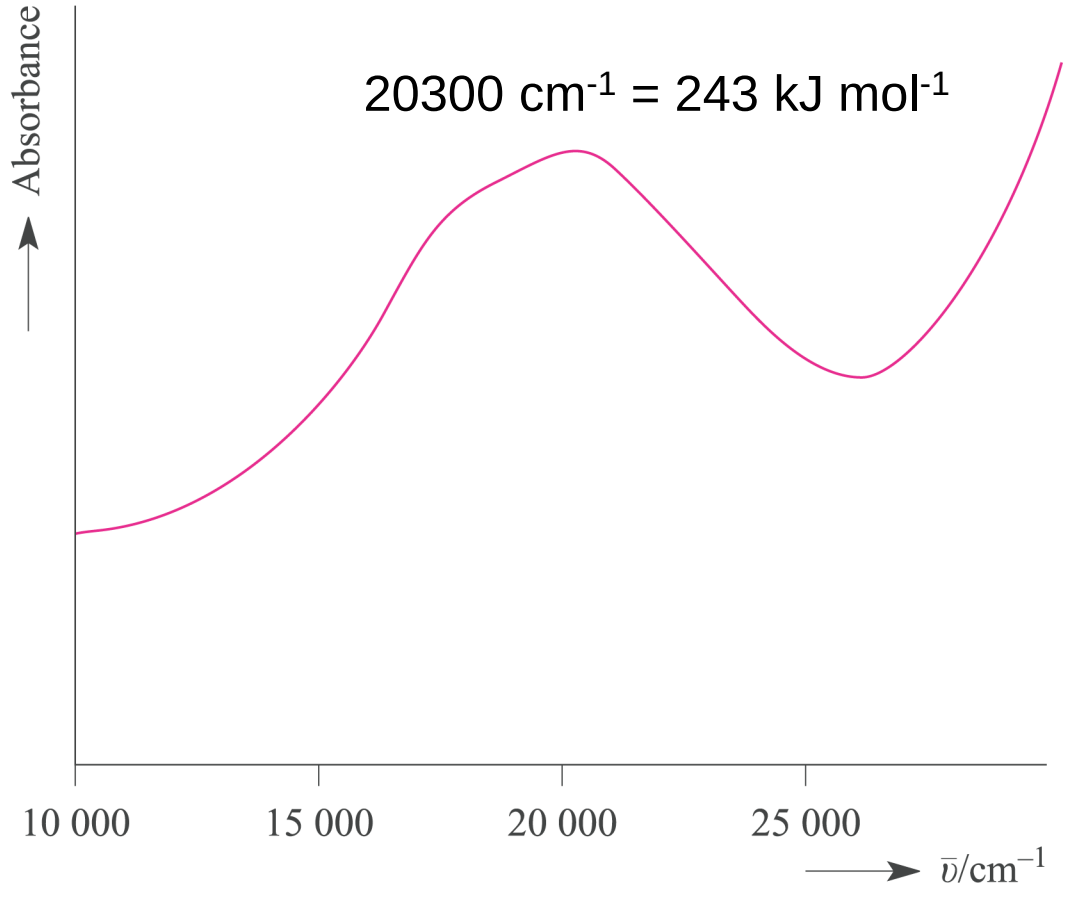




Teorema di Jahn-Teller

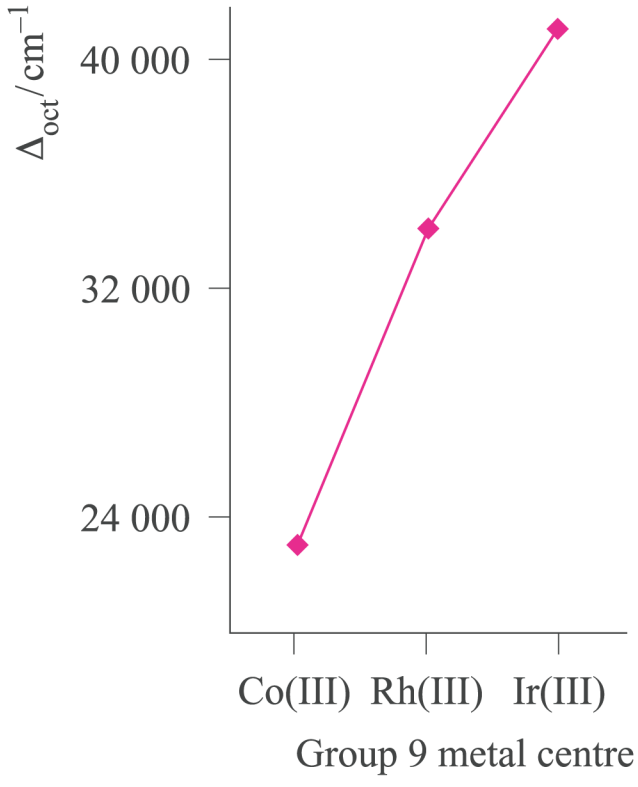
ogni sistema molecolare non lineare che abbia uno stato elettronico degenere è instabile e subirà distorsioni per generare un sistema a più bassa simmetria e più bassa energia, rimuovendo in questo modo la degenerazione.

Effetto Jahn – Teller nello stato eccitato



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

Fattori che influenzano la grandezza dello splitting (Δ)



Natura e stato di ossidazione del metallo

Complex	Δ / cm^{-1}	Complex	Δ / cm^{-1}
$[TiF_6]^{3-}$	17 000	$[Fe(ox)_3]^{3-}$	14 100
$[Ti(OH_2)_6]^{3+}$	20 300	$[Fe(CN)_6]^{3-}$	35 000
$[V(OH_2)_6]^{3+}$	17 850	$[Fe(CN)_6]^{4-}$	33 800
$[V(OH_2)_6]^{2+}$	12 400	$[CoF_6]^{3-}$	13 100
$[CrF_6]^{3-}$	15 000	$[Co(NH_3)_6]^{3+}$	22 900
$[Cr(OH_2)_6]^{3+}$	17 400	$[Co(NH_3)_6]^{2+}$	10 200
$[Cr(OH_2)_6]^{2+}$	14 100	$[Co(en)_3]^{3+}$	24 000
$[Cr(NH_3)_6]^{3+}$	21 600	$[Co(OH_2)_6]^{3+}$	18 200
$[Cr(CN)_6]^{3-}$	26 600	$[Co(OH_2)_6]^{2+}$	9 300
$[MnF_6]^{2-}$	21 800	$[Ni(OH_2)_6]^{2+}$	8 500
$[Fe(OH_2)_6]^{3+}$	13 700	$[Ni(NH_3)_6]^{2+}$	10 800
$[Fe(OH_2)_6]^{2+}$	9 400	$[Ni(en)_3]^{2+}$	11 500

Serie spettrochimica dei leganti

$I^- < Br^- < S^{2-} < NCS^- < Cl^- < F^- < OH^- < ox^{2-} \approx H_2O <$
$NCS^- < NH_3 < en < bpy < phen < CH_3^- < CN^- < CO$

Campo debole **Campo forte**

Effetto nefelauxetico

l'energia di accoppiamento di elettroni P è inferiore nei complessi che nei corrispondenti ioni in fase gassosa

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

è necessario sviluppare una teoria che descriva i legami di coordinazione anche in termini covalenti e non solo elettrostatici