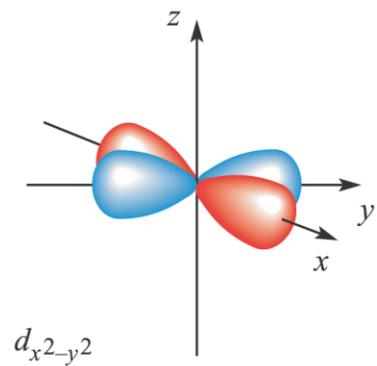
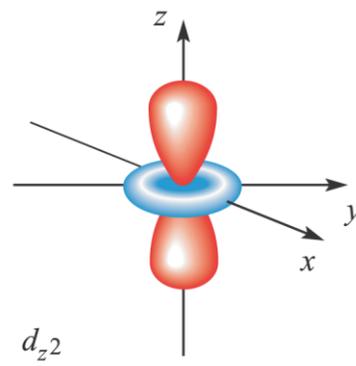
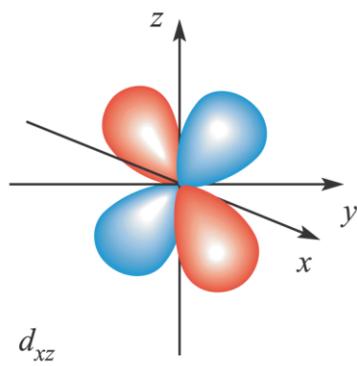
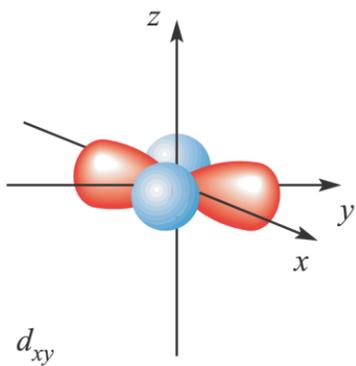
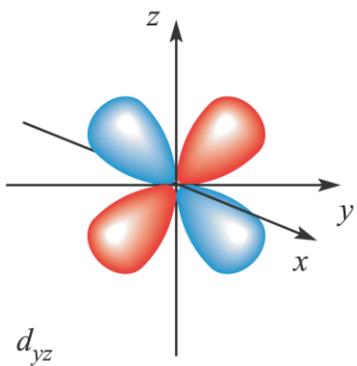
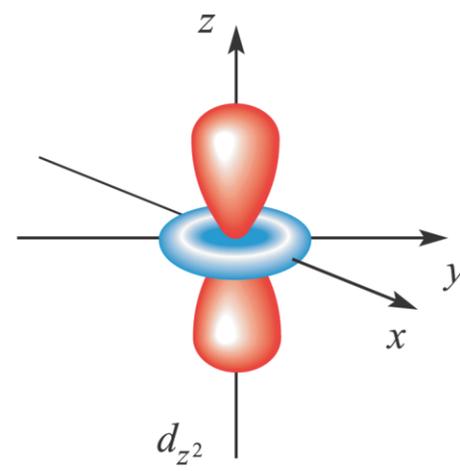
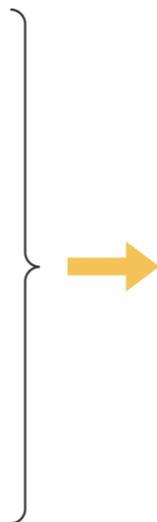
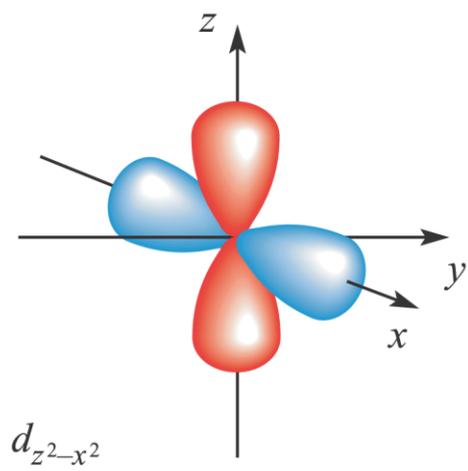
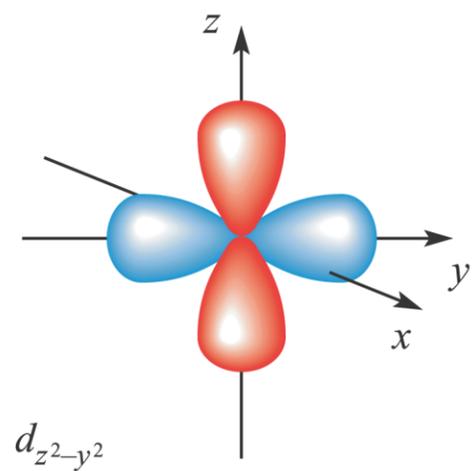


(a)

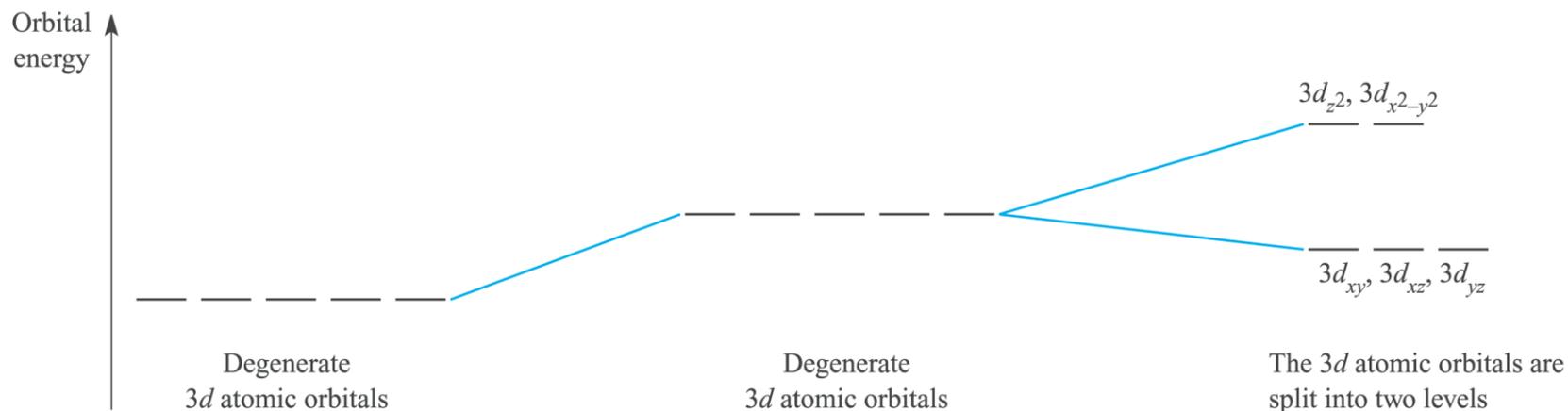


(b)

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



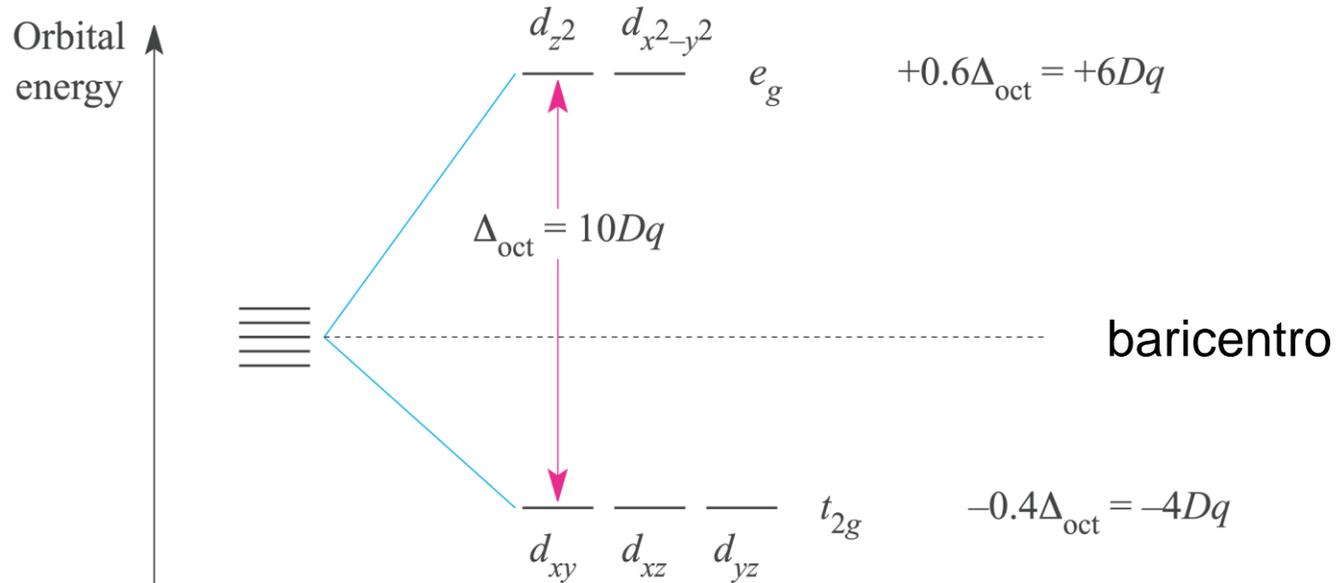
If the electrostatic field created by the point charge ligands is *spherical*, the energies of the electrons in the $3d$ orbitals are raised uniformly



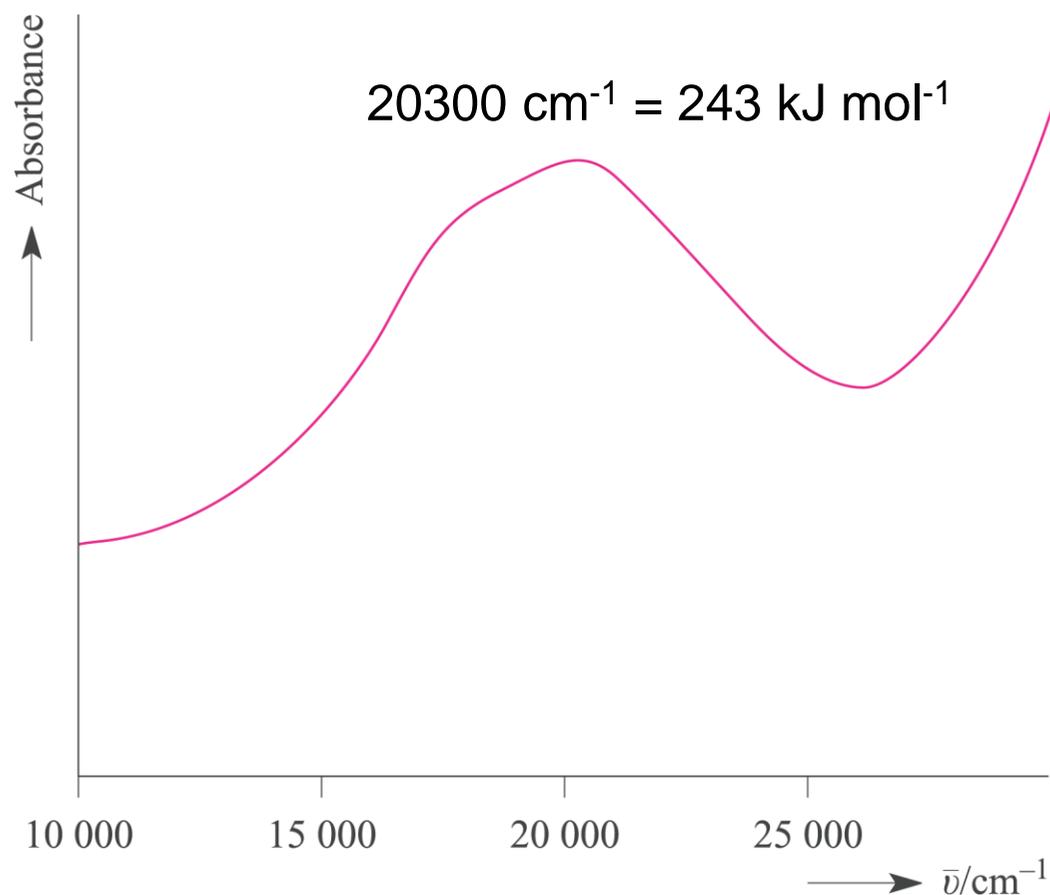
If the electrostatic field created by the point charge ligands is *octahedral*, the energy of the electrons in the $3d$ orbitals that point *directly* at the ligands is raised with respect to that in the spherical field, while the energy of the electrons in the orbitals that point *between* the ligands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

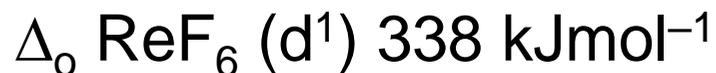
Separazione energetica (*splitting*) degli orbitali d in un campo cristallino ottaedrico



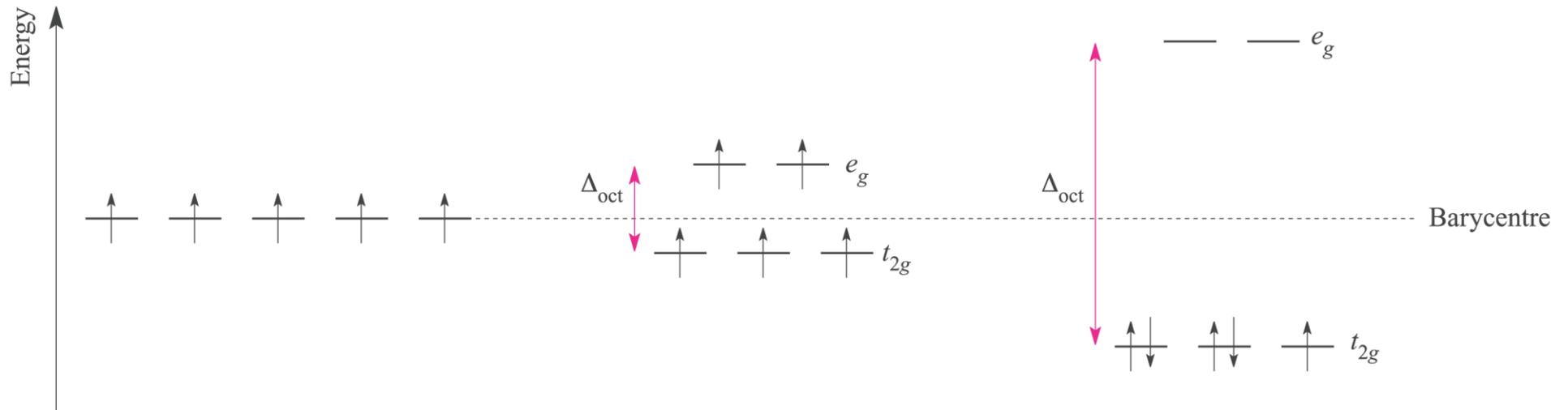
Spettro di assorbimento elettronico del complesso d^1 $[\text{Ti}(\text{OH}_2)_6]^{3+}$



i Δ_o hanno grandezze tipiche confrontabili con quelle dei legami chimici



Ligand Field Stabilization Energy (LFSE)



Gaseous ion

Weak field
(high-spin)
complex
e.g. $[\text{Fe}(\text{OH}_2)_6]^{3+}$

Strong field
(low-spin)
complex
e.g. $[\text{Fe}(\text{CN})_6]^{3-}$

$$\Delta_o < P$$

$$\Delta_o > P$$

$$P = 180 - 300 \text{ kJmol}^{-1}$$

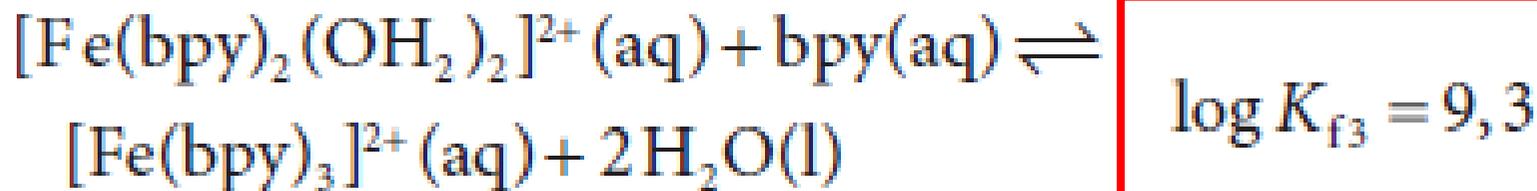
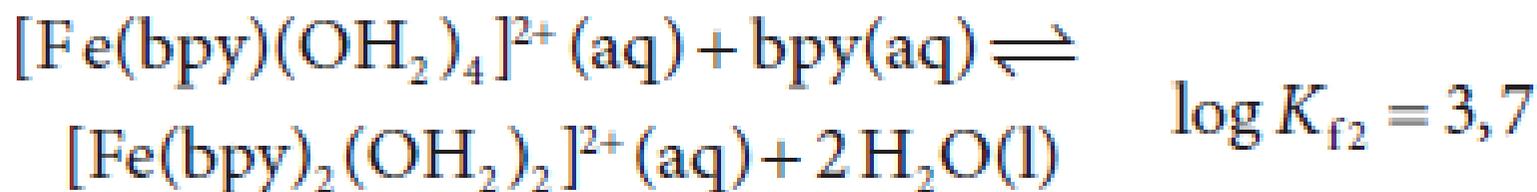
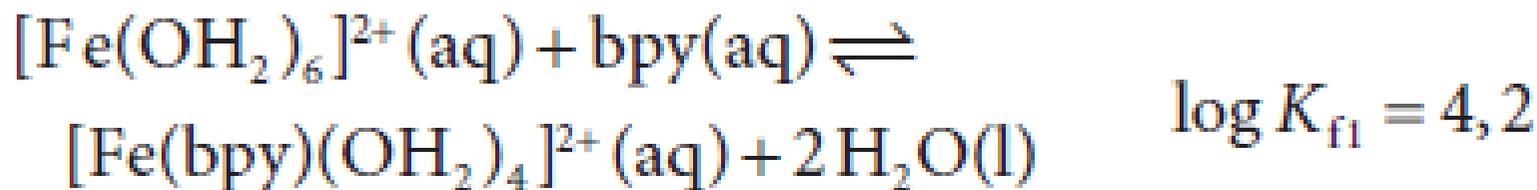
$$\Delta_o < P$$

d^n	High-spin = weak field	
	Electronic configuration	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_{\text{oct}}$
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_{\text{oct}}$
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_{\text{oct}}$
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_{\text{oct}}$
d^5	$t_{2g}^3 e_g^2$	0
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_{\text{oct}}$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_{\text{oct}}$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_{\text{oct}}$
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_{\text{oct}}$
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	$t_{2g}^4 e_g^0$	$-1.6\Delta_{\text{oct}} + P$
d^5	$t_{2g}^5 e_g^0$	$-2.0\Delta_{\text{oct}} + 2P$
d^6	$t_{2g}^6 e_g^0$	$-2.4\Delta_{\text{oct}} + 2P$
d^7	$t_{2g}^6 e_g^1$	$-1.8\Delta_{\text{oct}} + P$
d^8		
d^9		
d^{10}		

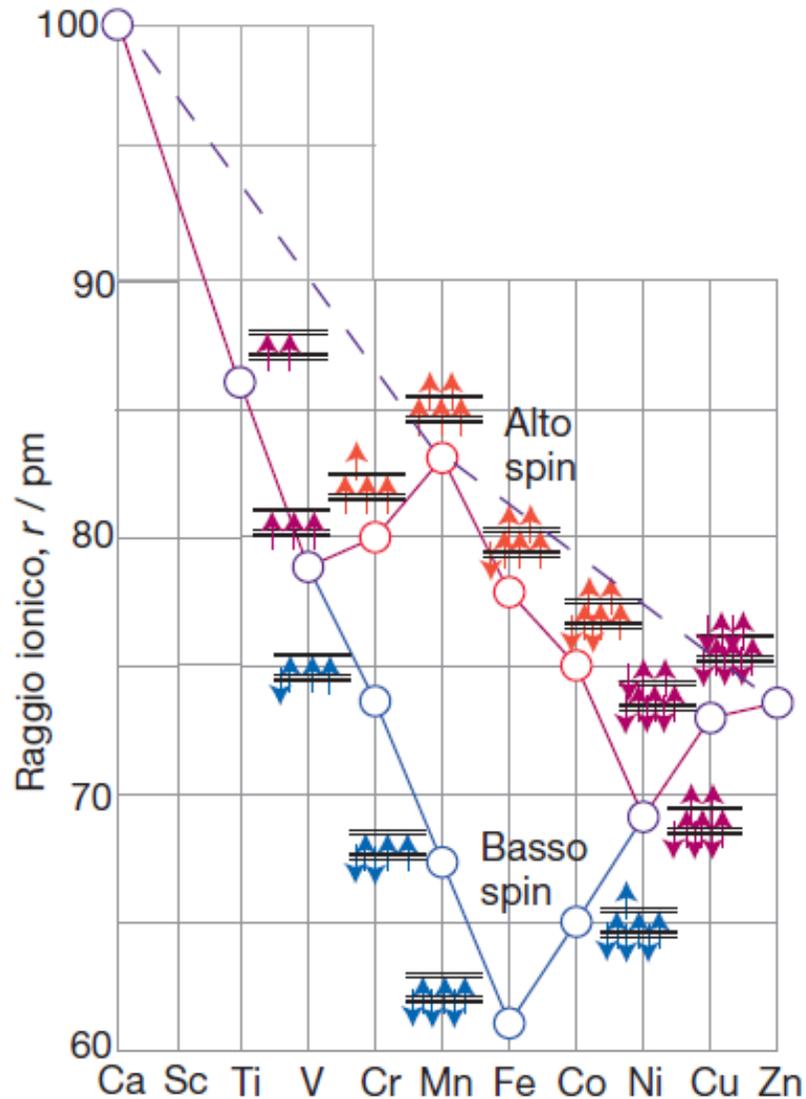
Un'inversione nell'andamento $Kf_n > Kf_{n+1}$ è normalmente un'indicazione di una grande variazione nella struttura elettronica del complesso



Transizione alto-spin – basso-spin, aumento LFSE

Fe(II) d^6 LFSE l.s. = $2.4\Delta_o - 2P$, h.s. = $0.4\Delta_o$
 differenza LFSE (l.s. – h.s.) = $2\Delta_o - 2P$, cioè $\Delta_o - P$ per spin elettronico

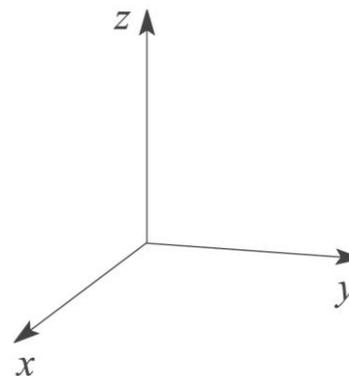
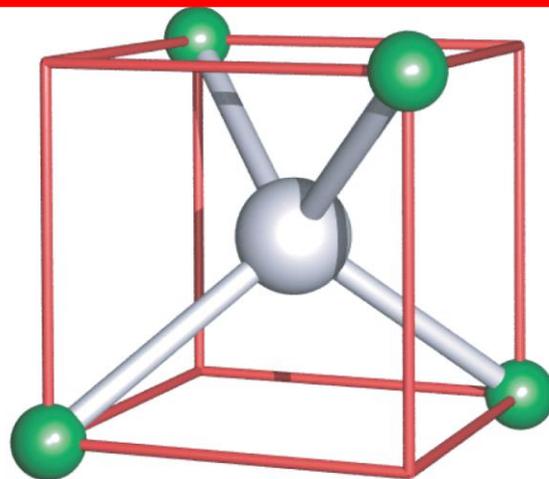
Andamento dei raggi degli ioni M^{2+} dei metalli 3d in complessi ottaedrici

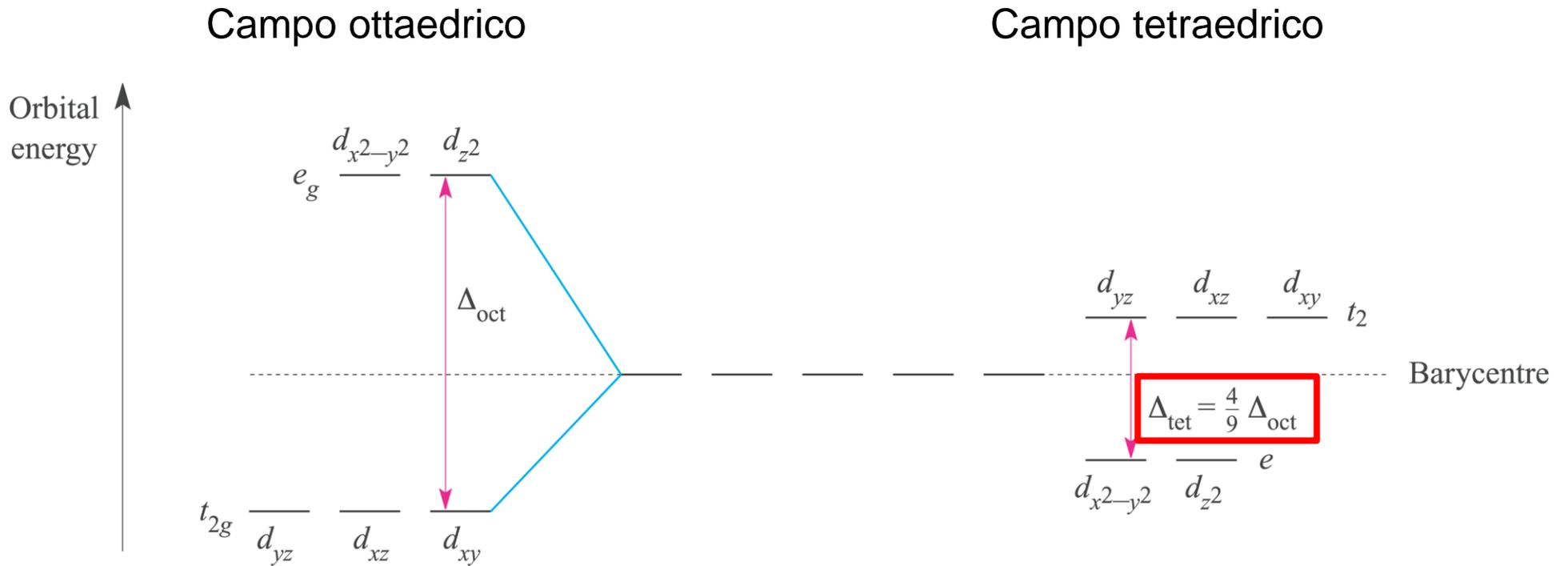


La linea tratteggiata indica i valori attesi tenendo conto soltanto dell'aumento di carica nucleare effettiva

Splitting degli orbitali d in campo tetraedrico

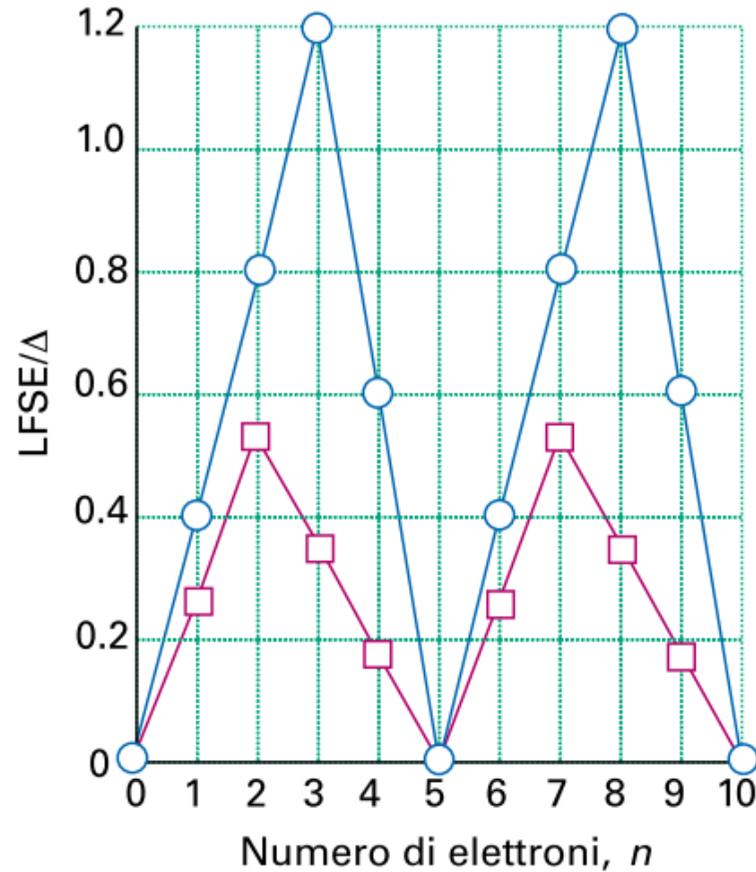
	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)



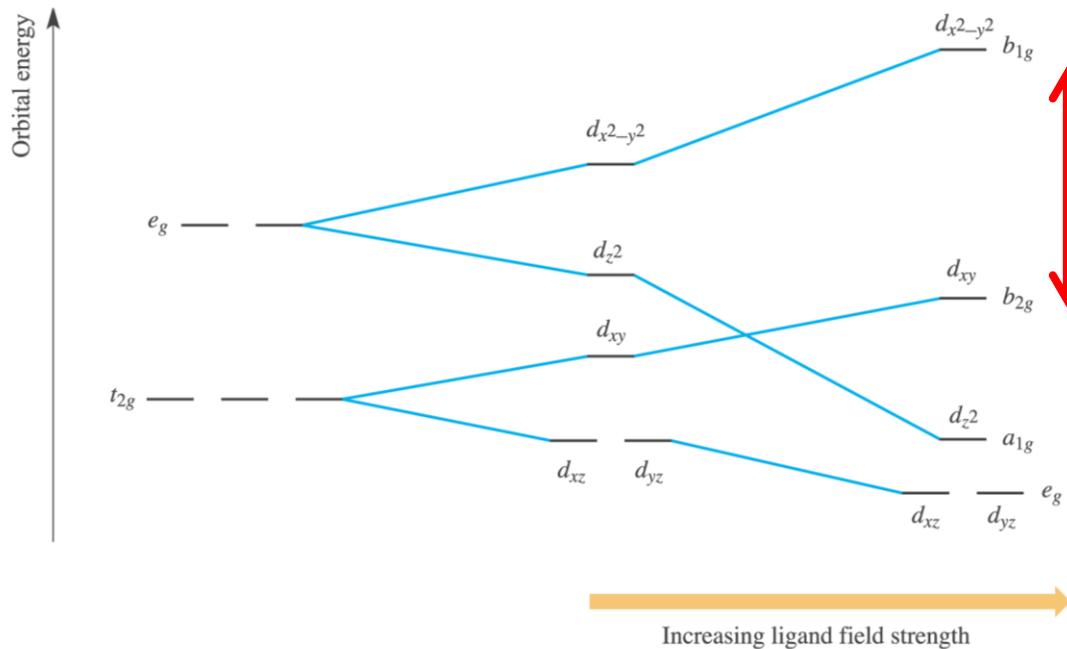
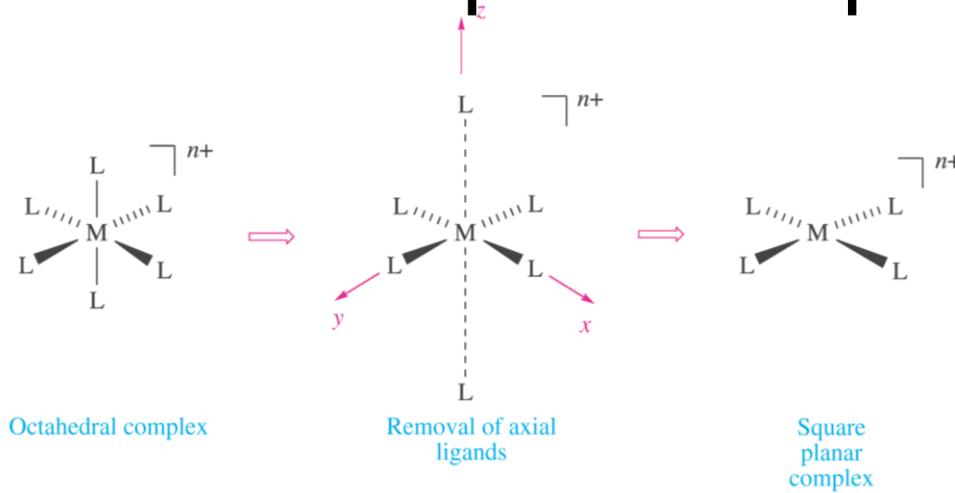


I complessi tetraedrici sono sempre ad alto spin ($\Delta_t < P$)

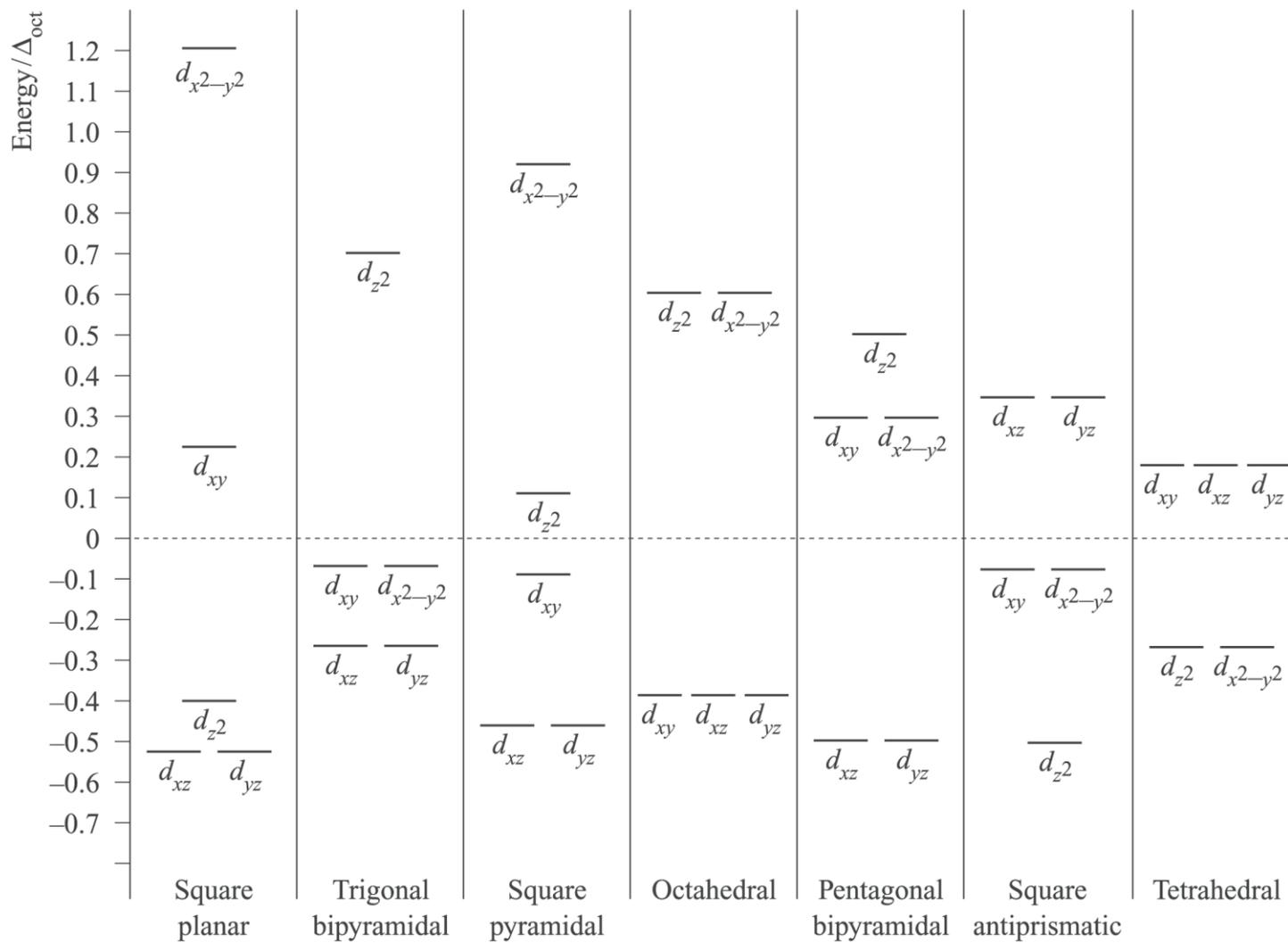
LFSE per complessi ottaedrici (alto spin) e tetraedrici



Splitting degli orbitali d in campo planare quadrato

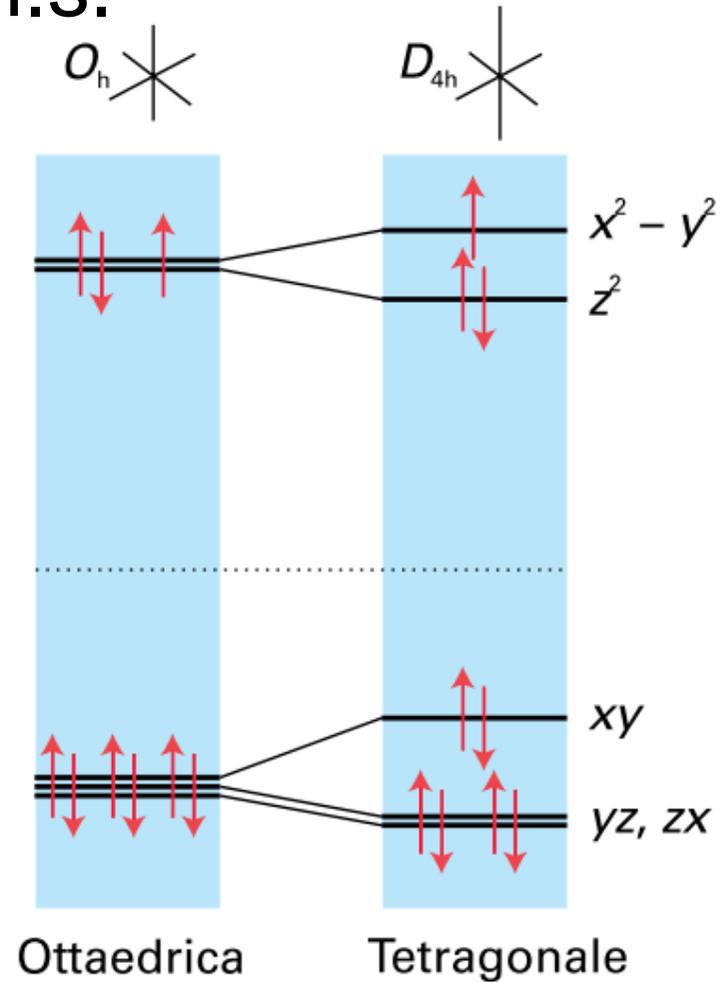
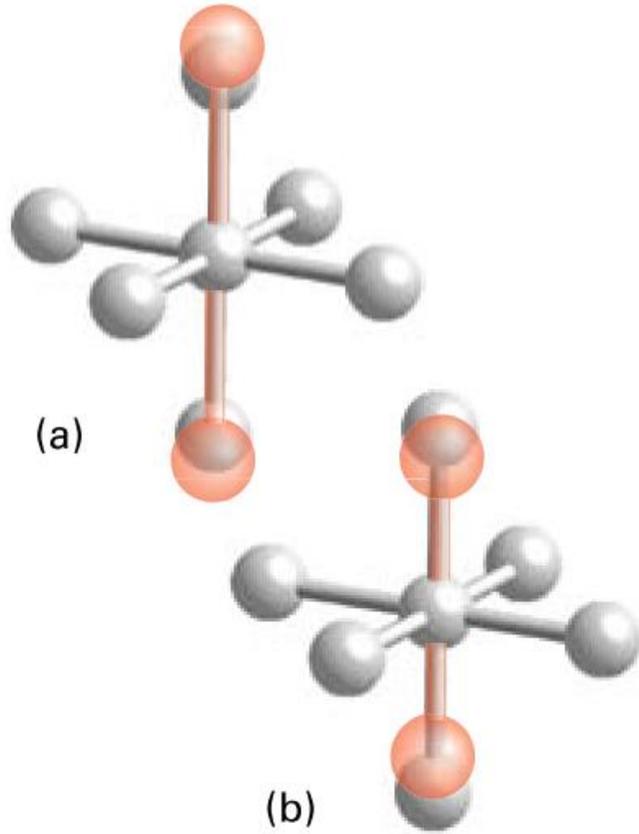


I complessi planari quadrati sono particolarmente comuni per gli ioni con configurazione elettronica d^8 : Ni(II), Pd(II), Pt(II), Rh(I), Ir(I), Au(III)



Effetto Jahn – Teller

d^9 , d^4 h.s.

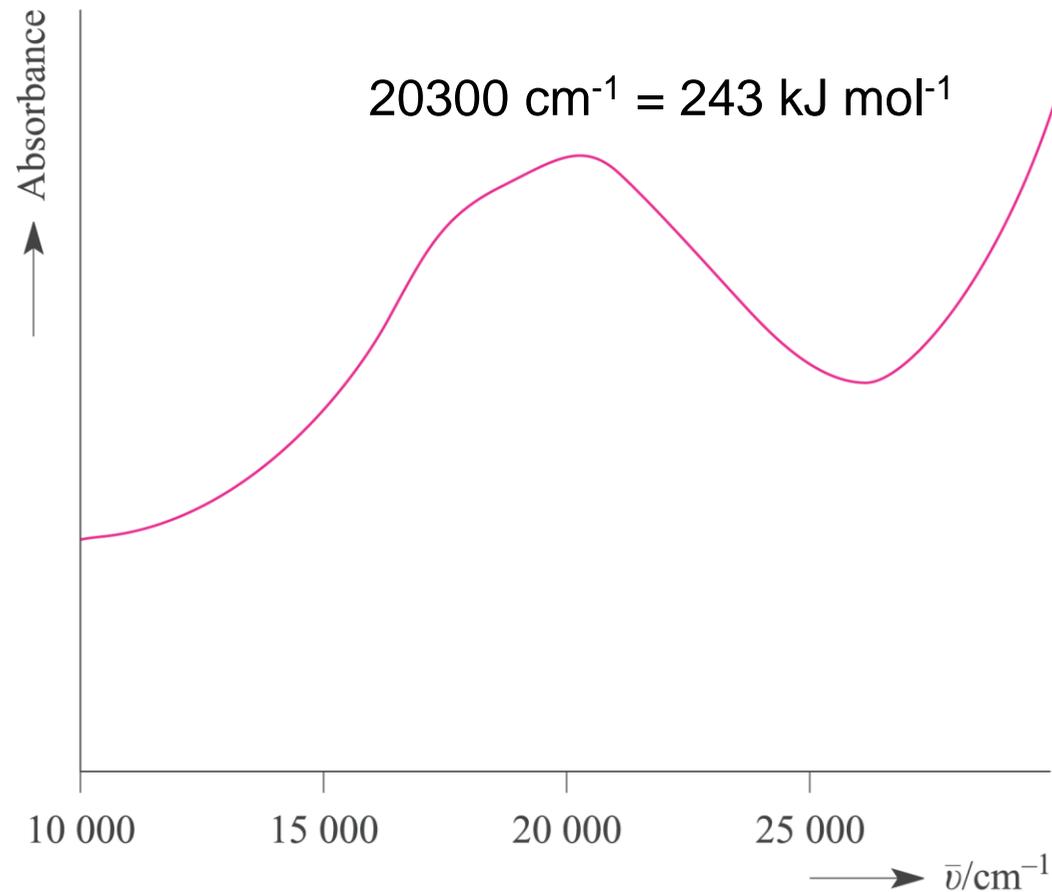


Teorema di Jahn-Teller

(da Hermann A. Jahn ed Edward Teller)

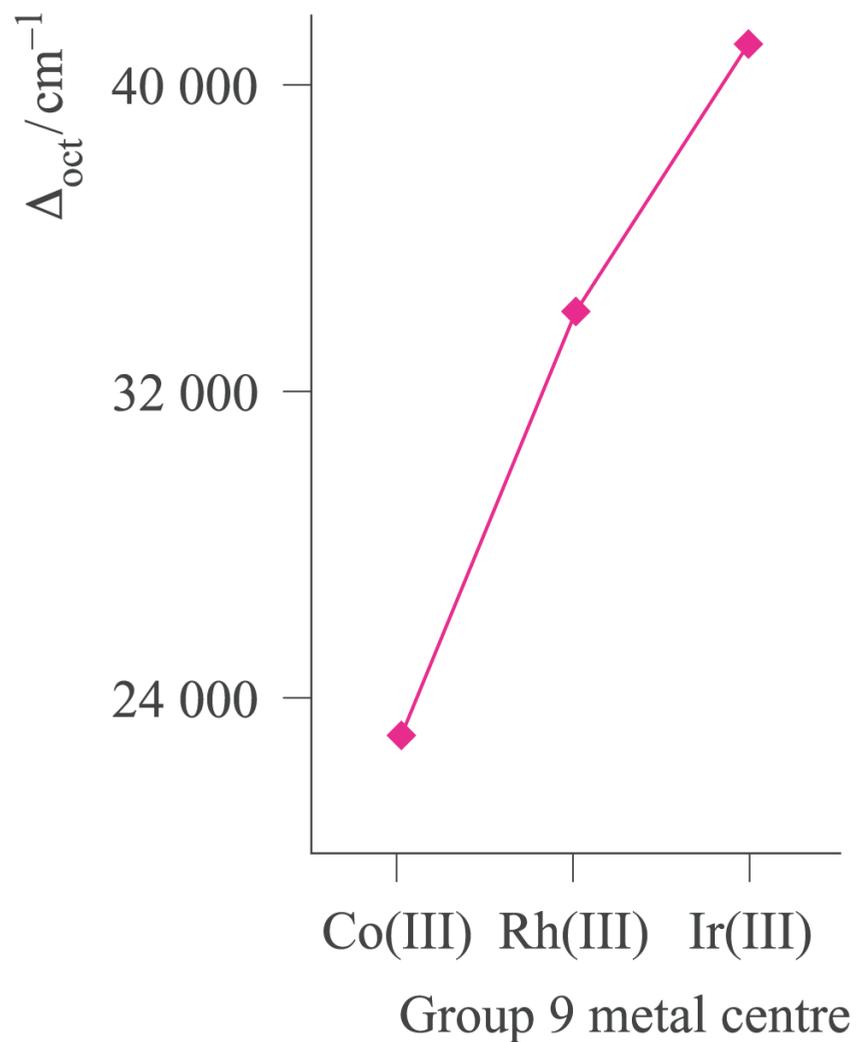
*ogni sistema molecolare **non lineare** che abbia uno **stato elettronico degenere** è instabile e subirà distorsioni per generare un sistema a più bassa simmetria e più bassa energia, rimuovendo in questo modo la degenerazione.*

Effetto Jahn – Teller nello stato eccitato



Spettro di assorbimento elettronico del complesso d^1 $[\text{Ti}(\text{OH}_2)_6]^{3+}$

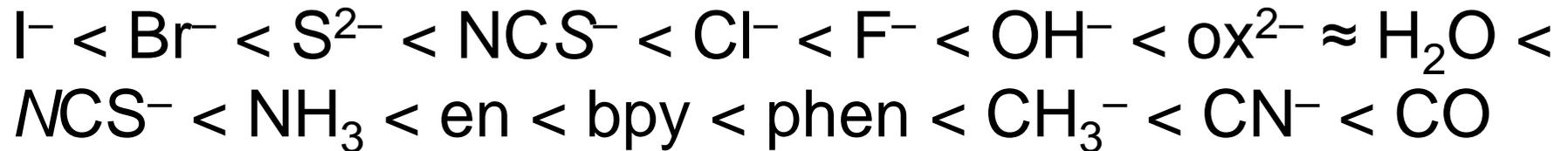
Fattori che influenzano la grandezza dello splitting (Δ)



Natura e stato di ossidazione del metallo

Complex	Δ / cm^{-1}	Complex	Δ / cm^{-1}
$[\text{TiF}_6]^{3-}$	17 000	$[\text{Fe}(\text{ox})_3]^{3-}$	14 100
$[\text{Ti}(\text{OH}_2)_6]^{3+}$	20 300	$[\text{Fe}(\text{CN})_6]^{3-}$	35 000
$[\text{V}(\text{OH}_2)_6]^{3+}$	17 850	$[\text{Fe}(\text{CN})_6]^{4-}$	33 800
$[\text{V}(\text{OH}_2)_6]^{2+}$	12 400	$[\text{CoF}_6]^{3-}$	13 100
$[\text{CrF}_6]^{3-}$	15 000	$[\text{Co}(\text{NH}_3)_6]^{3+}$	22 900
$[\text{Cr}(\text{OH}_2)_6]^{3+}$	17 400	$[\text{Co}(\text{NH}_3)_6]^{2+}$	10 200
$[\text{Cr}(\text{OH}_2)_6]^{2+}$	14 100	$[\text{Co}(\text{en})_3]^{3+}$	24 000
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21 600	$[\text{Co}(\text{OH}_2)_6]^{3+}$	18 200
$[\text{Cr}(\text{CN})_6]^{3-}$	26 600	$[\text{Co}(\text{OH}_2)_6]^{2+}$	9 300
$[\text{MnF}_6]^{2-}$	21 800	$[\text{Ni}(\text{OH}_2)_6]^{2+}$	8 500
$[\text{Fe}(\text{OH}_2)_6]^{3+}$	13 700	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	10 800
$[\text{Fe}(\text{OH}_2)_6]^{2+}$	9 400	$[\text{Ni}(\text{en})_3]^{2+}$	11 500

Serie spettrochimica dei leganti



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 ₂ O	1.0
Mn(II)	0.07	6 F ⁻	0.8

$$\text{Effetto nefelauxetico} = k \times h$$

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