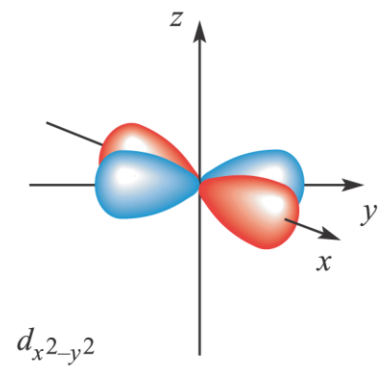
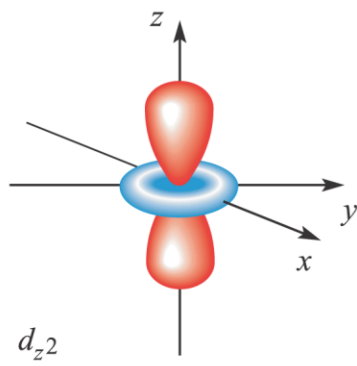
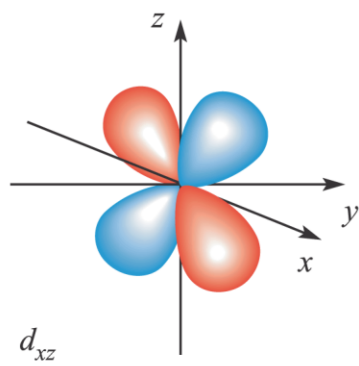
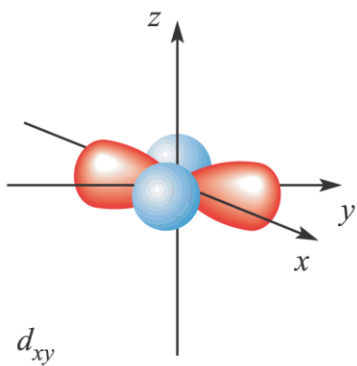
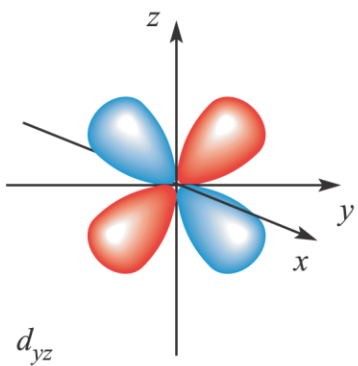
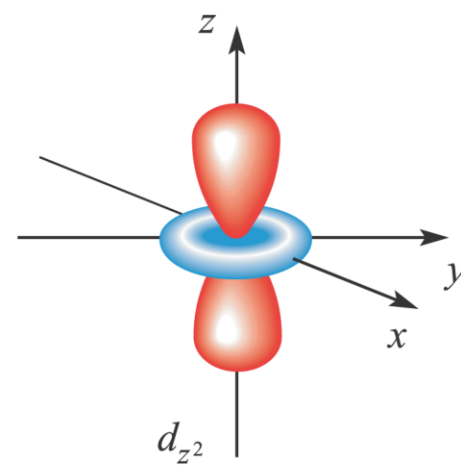
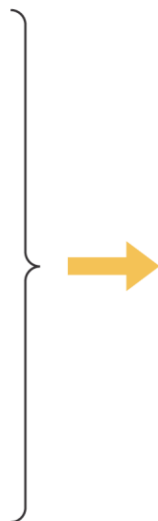
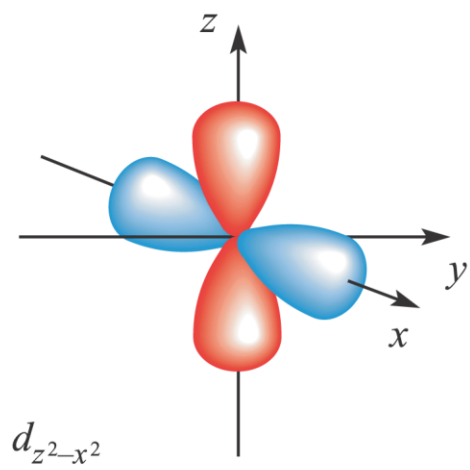
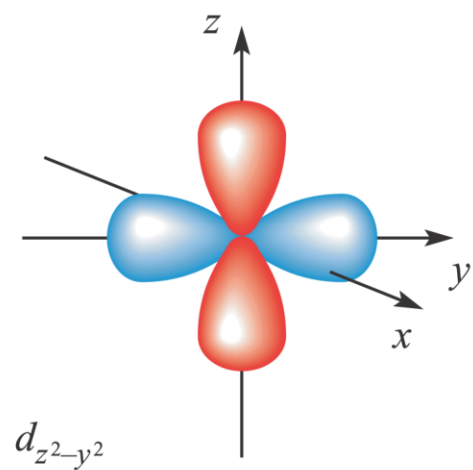


(a)

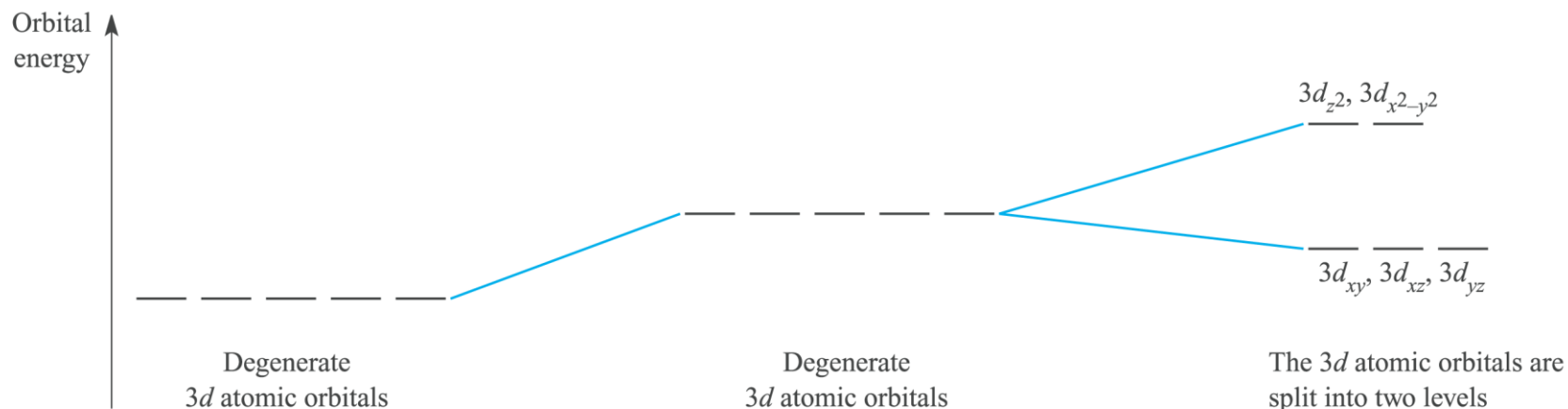


(b)

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



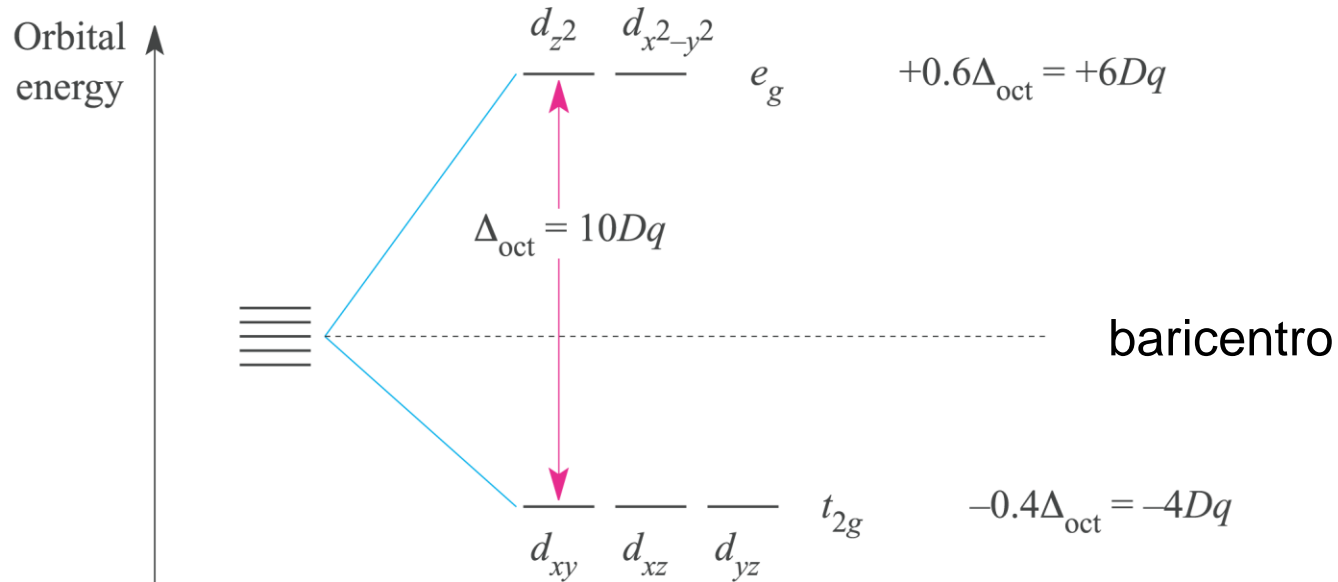
If the electrostatic field created by the point charge ligands is *spherical*, the energies of the electrons in the  $3d$  orbitals are raised uniformly



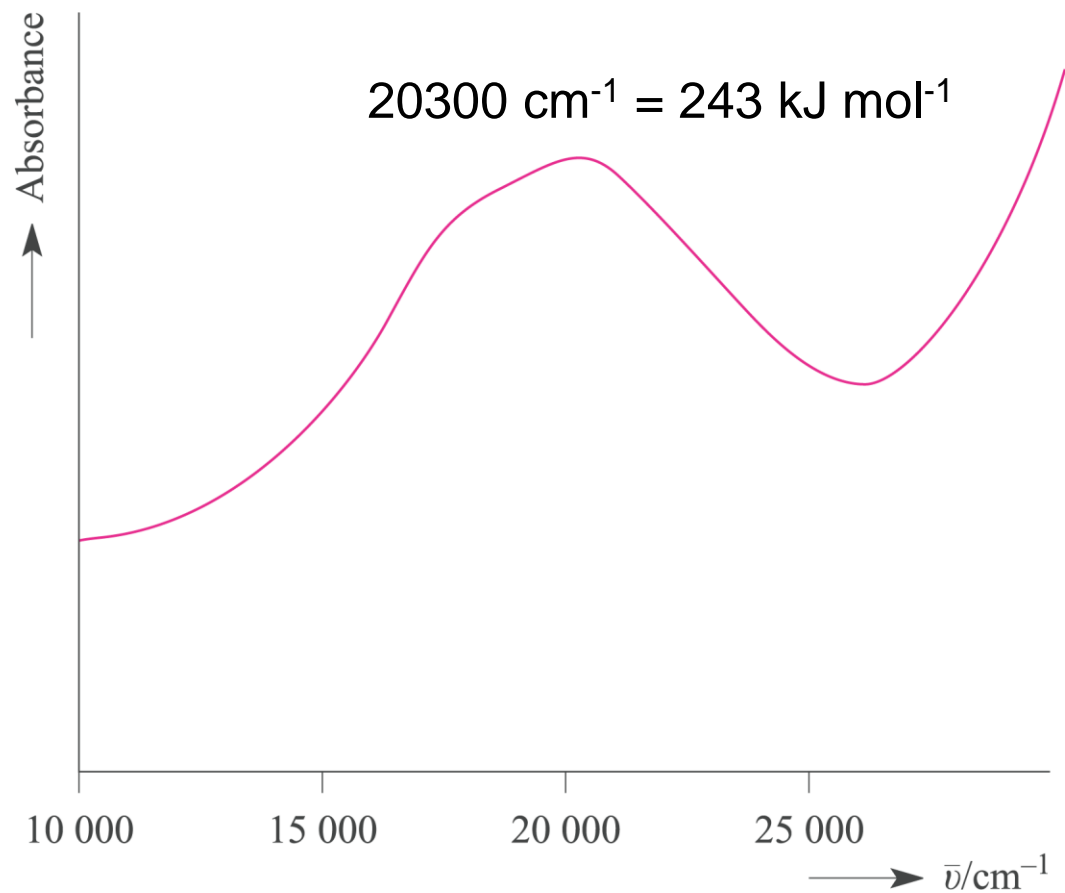
If the electrostatic field created by the point charge ligands is *octahedral*, the energy of the electrons in the  $3d$  orbitals that point *directly* at the ligands is raised with respect to that in the spherical field, while the energy of the electrons in the orbitals that point *between* the ligands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

| $O_h$<br>( $m\bar{3}m$ ) | $E$ | $8C_3$ | $6C_2$ | $6C_4$ | $3C_2$<br>( $=C_4^2$ ) | $i$ | $6S_4$ | $8S_6$ | $3\sigma_h$ | $6\sigma_d$ |   |
|--------------------------|-----|--------|--------|--------|------------------------|-----|--------|--------|-------------|-------------|---|
| $A_{1g}$                 | 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

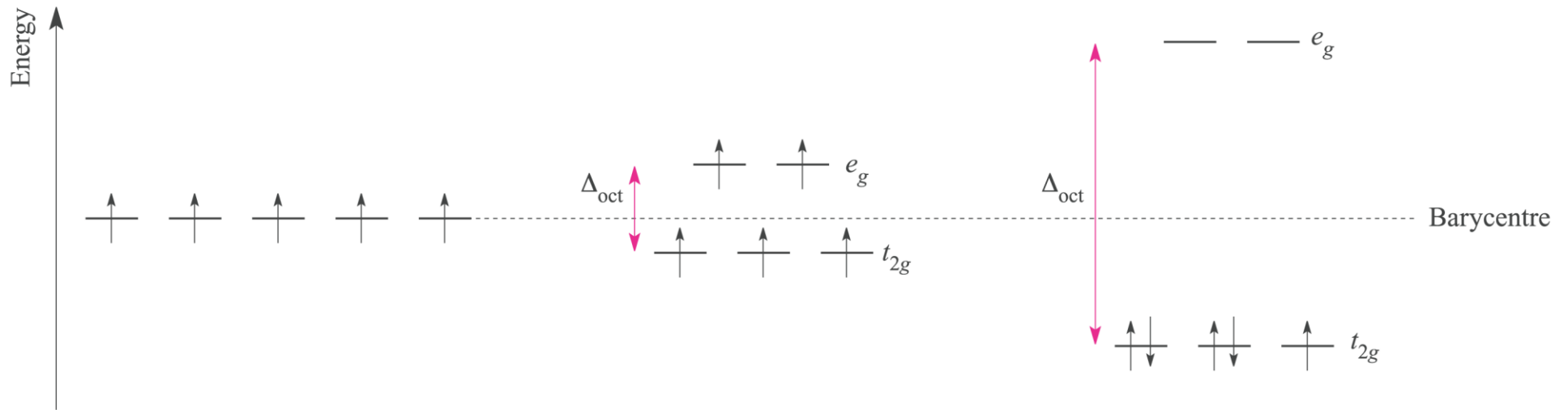


# Spettro di assorbimento elettronico del complesso $d^1$ $[\text{Ti}(\text{OH}_2)_6]^{3+}$



*i  $\Delta_o$  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                         |

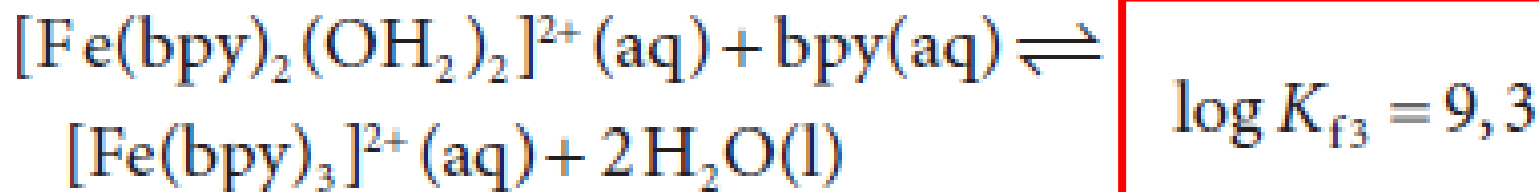
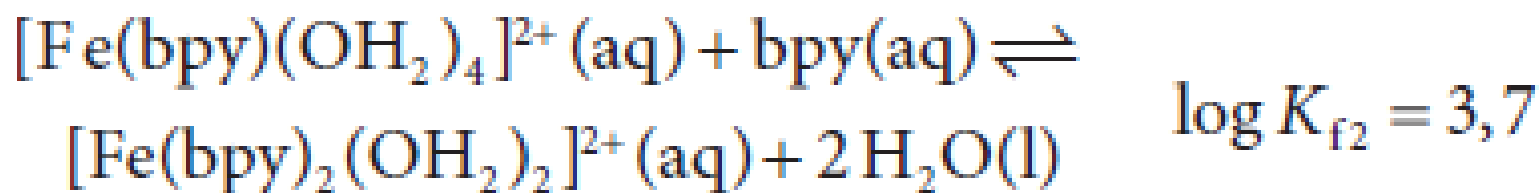
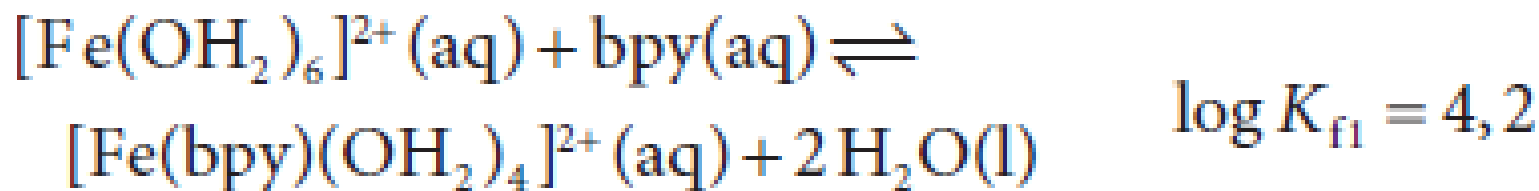


$$\Delta_o > P$$

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

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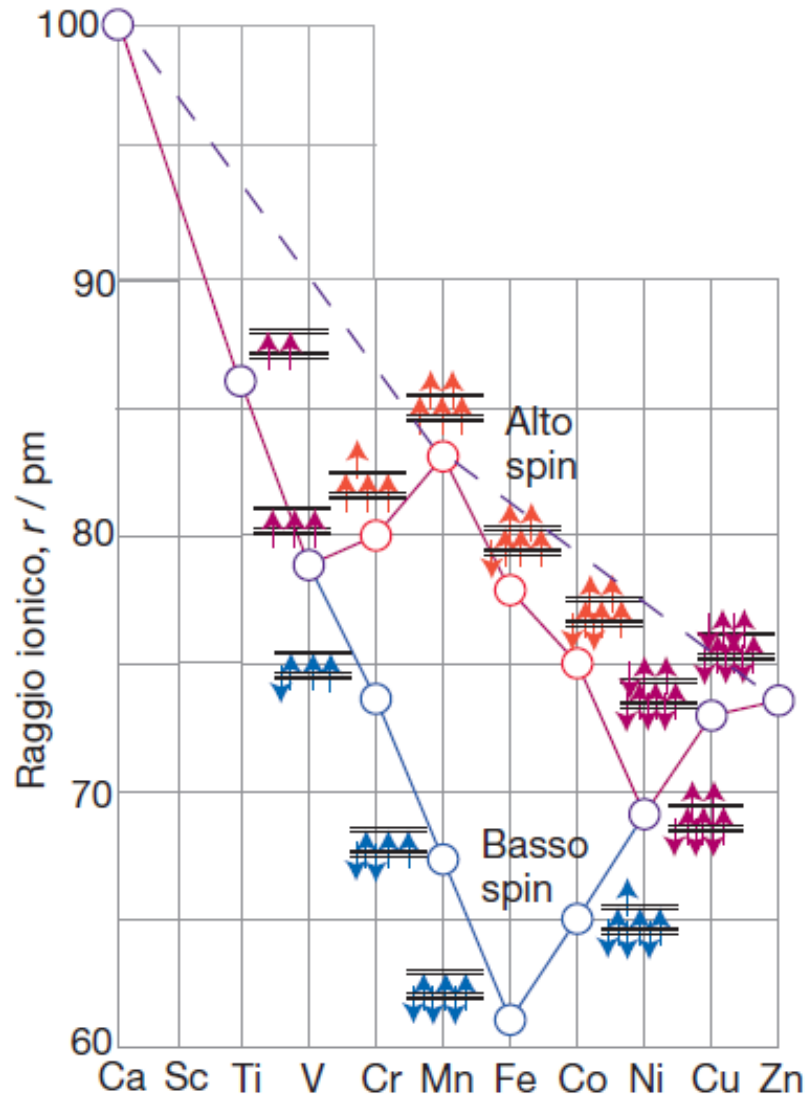
Un'inversione nell'andamento  $Kf_n > Kf_{n+1}$  è normalmente un'indicazione di una grande variazione nella struttura elettronica del complesso



*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

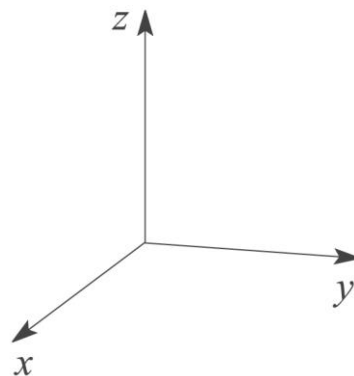
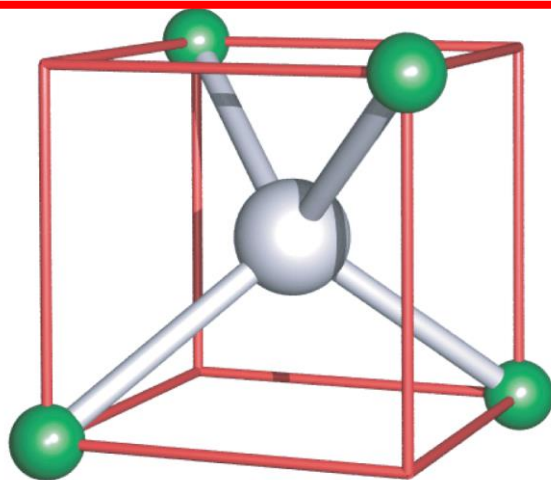
# Andamento dei raggi degli ioni $M^{2+}$ dei metalli 3d in complessi ottaedrici

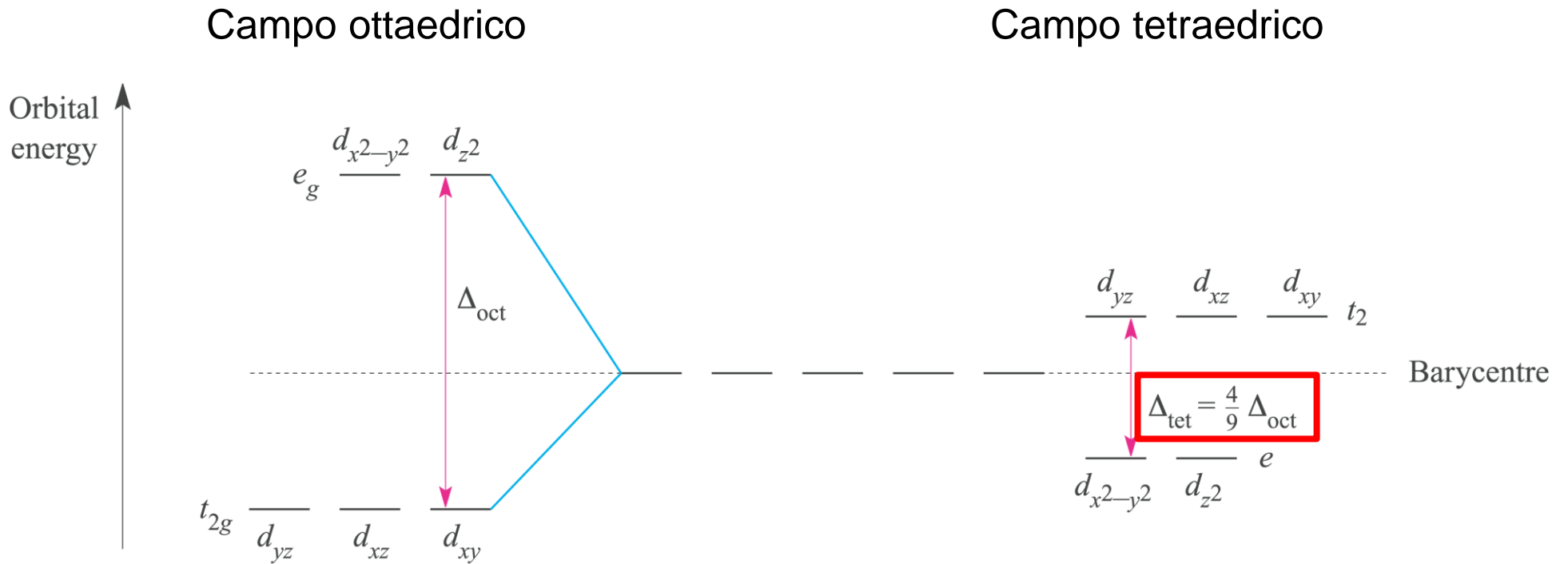


*La linea tratteggiata indica i valori attesi tenendo conto soltanto dell'aumento di carica nucleare effettiva*

# Splitting degli orbitali d in campo tetraedrico

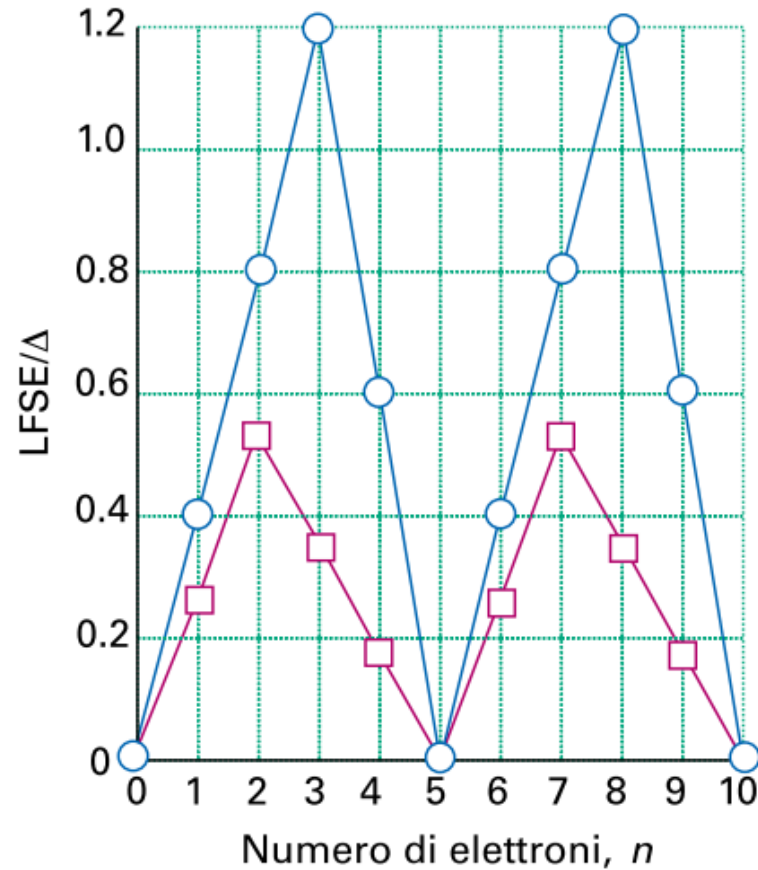
|       | E | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ | linear,<br>rotations | quadratic                 |
|-------|---|--------|--------|--------|-------------|----------------------|---------------------------|
| $A_1$ | 1 | 1      | 1      | 1      | 1           |                      | $x^2+y^2+z^2$             |
| $A_2$ | 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           | $(x, y, z)$          | $(xy, xz, yz)$            |



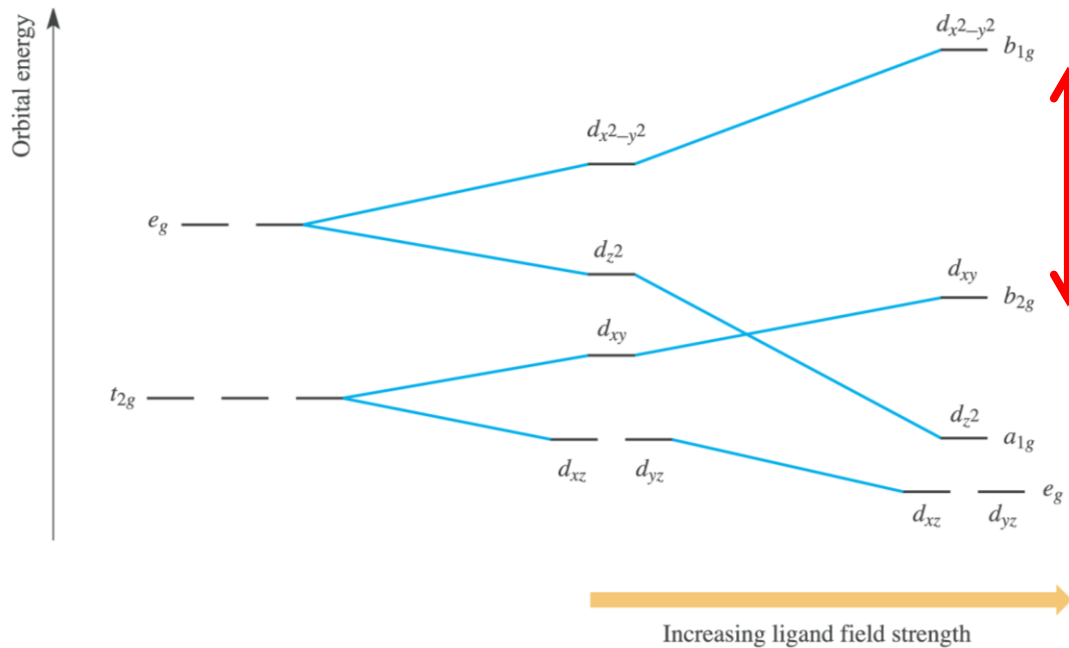
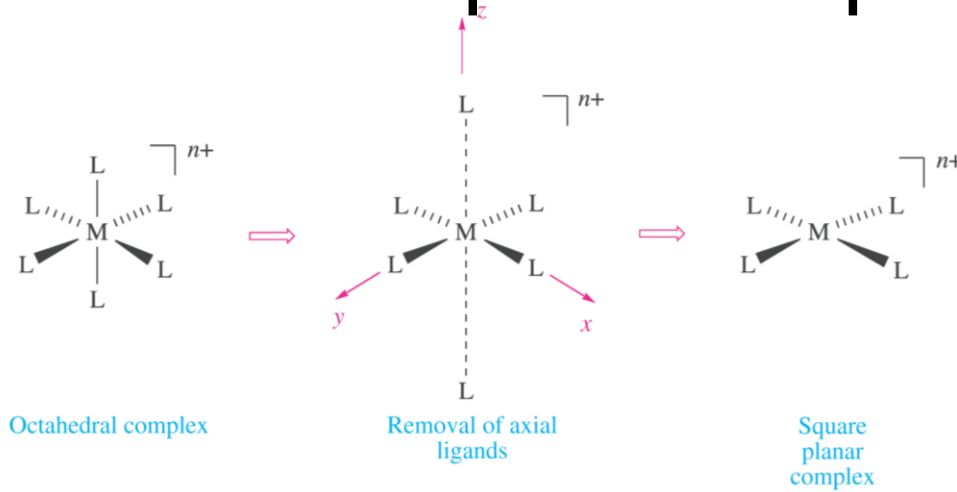


*I complessi tetraedrici sono sempre ad alto spin ( $\Delta_t < P$ )*

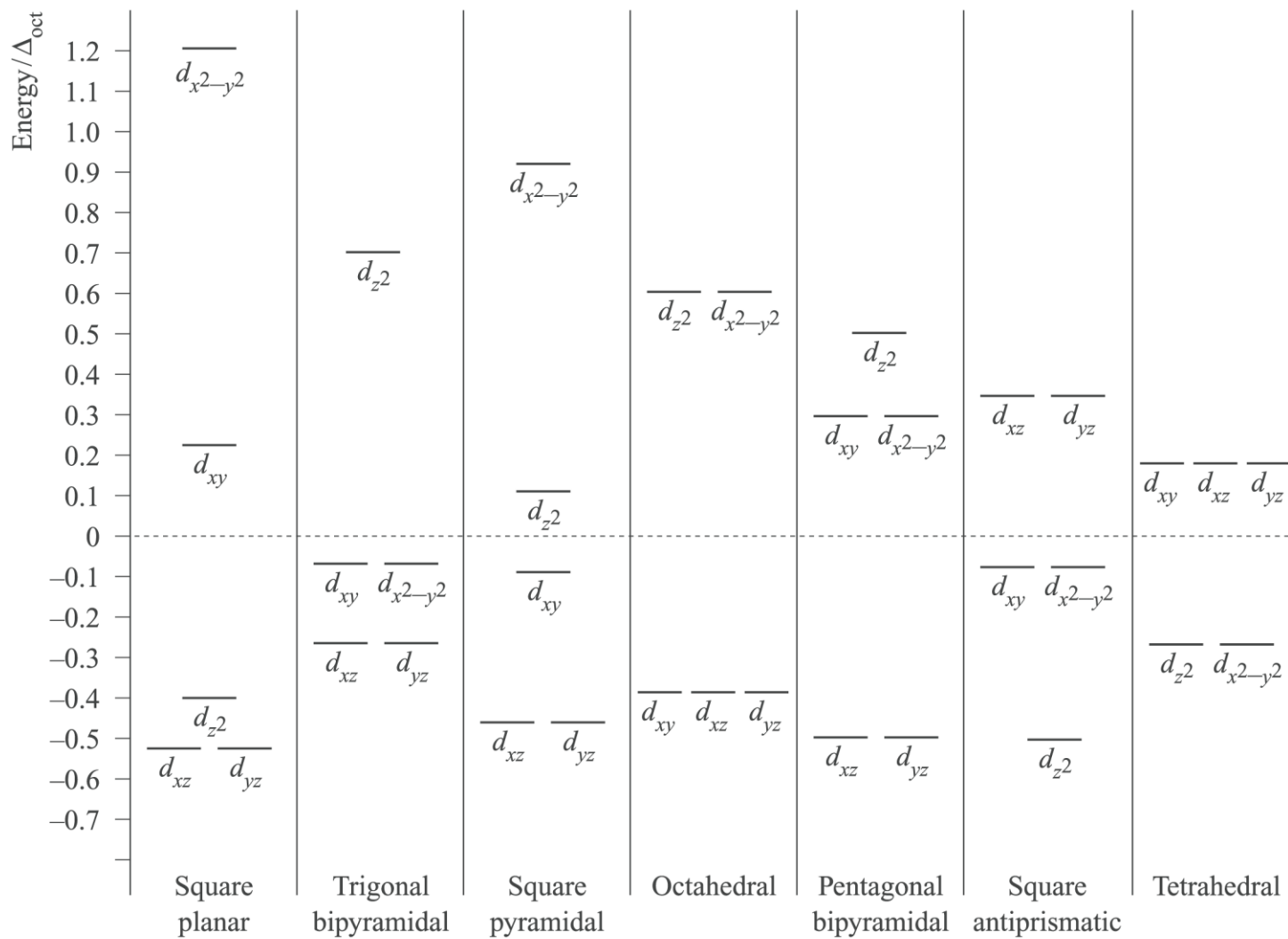
# LFSE per complessi ottaedrici (alto spin) e tetraedrici



# Splitting degli orbitali d in campo planare quadrato



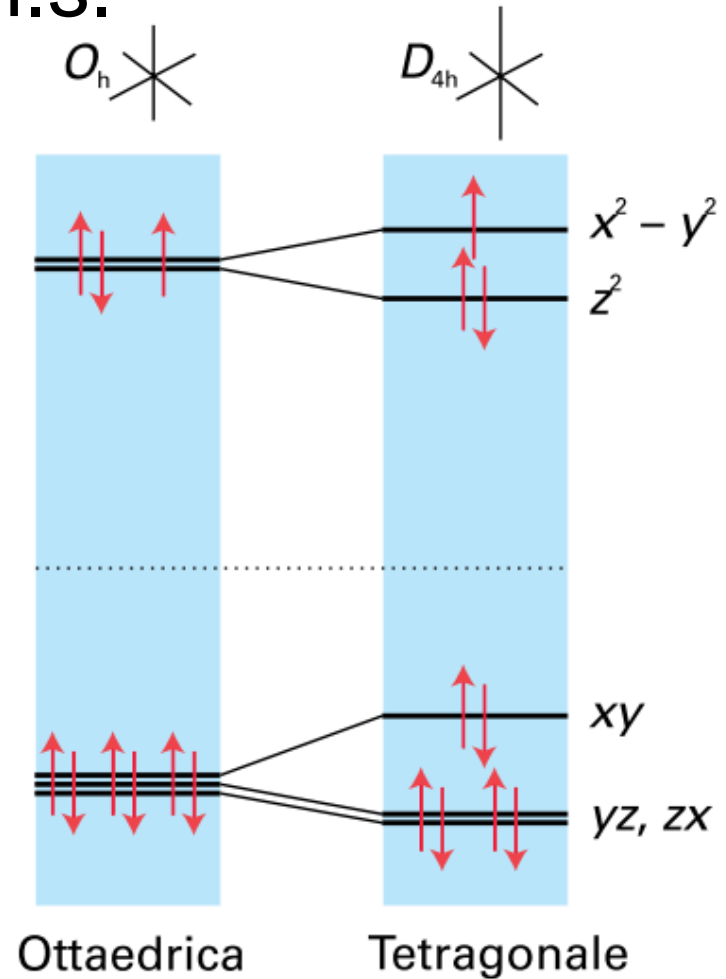
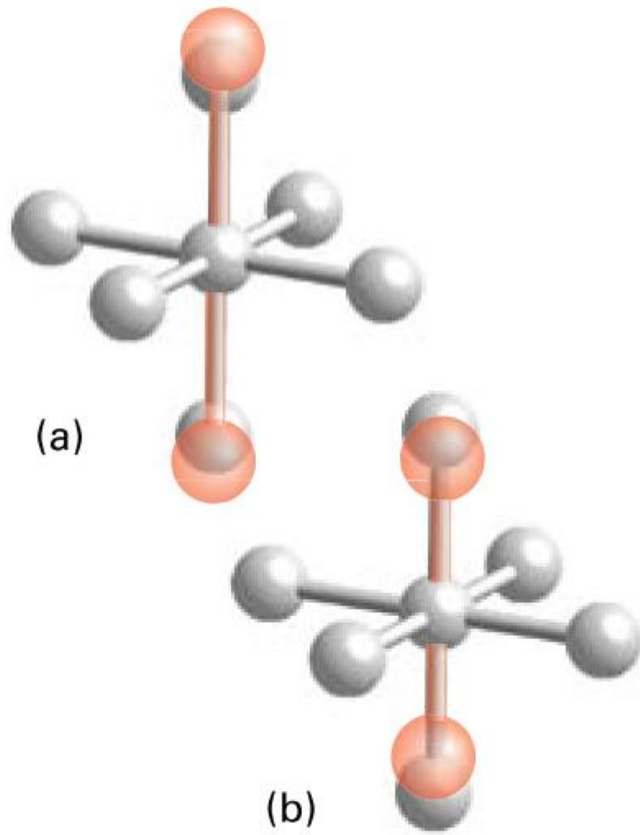
*I complessi planari quadrati sono particolarmente comuni per gli ioni con configurazione elettronica  $d^8$ : Ni(II), Pd(II), Pt(II), Rh(I), Ir(I), Au(III)*





# Effetto Jahn – Teller

$d^9$ ,  $d^4$  h.s.

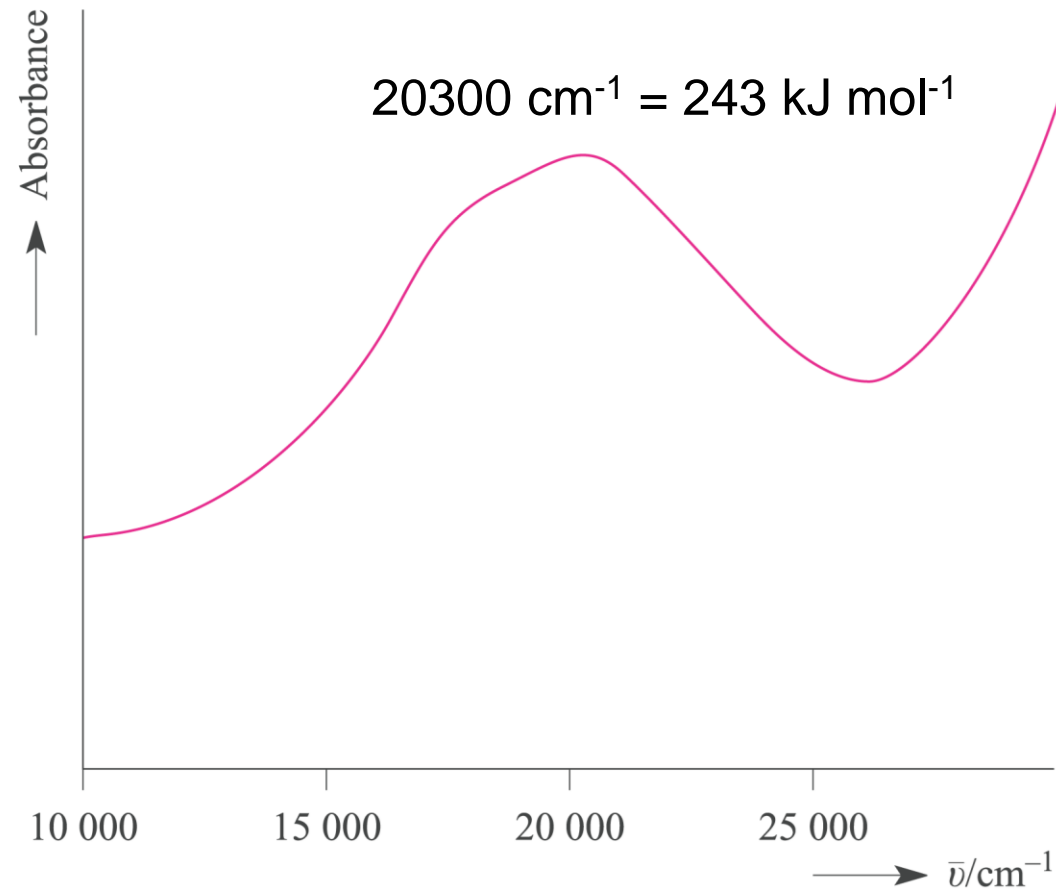


# Teorema di Jahn-Teller

(da Hermann A. Jahn ed Edward Teller)

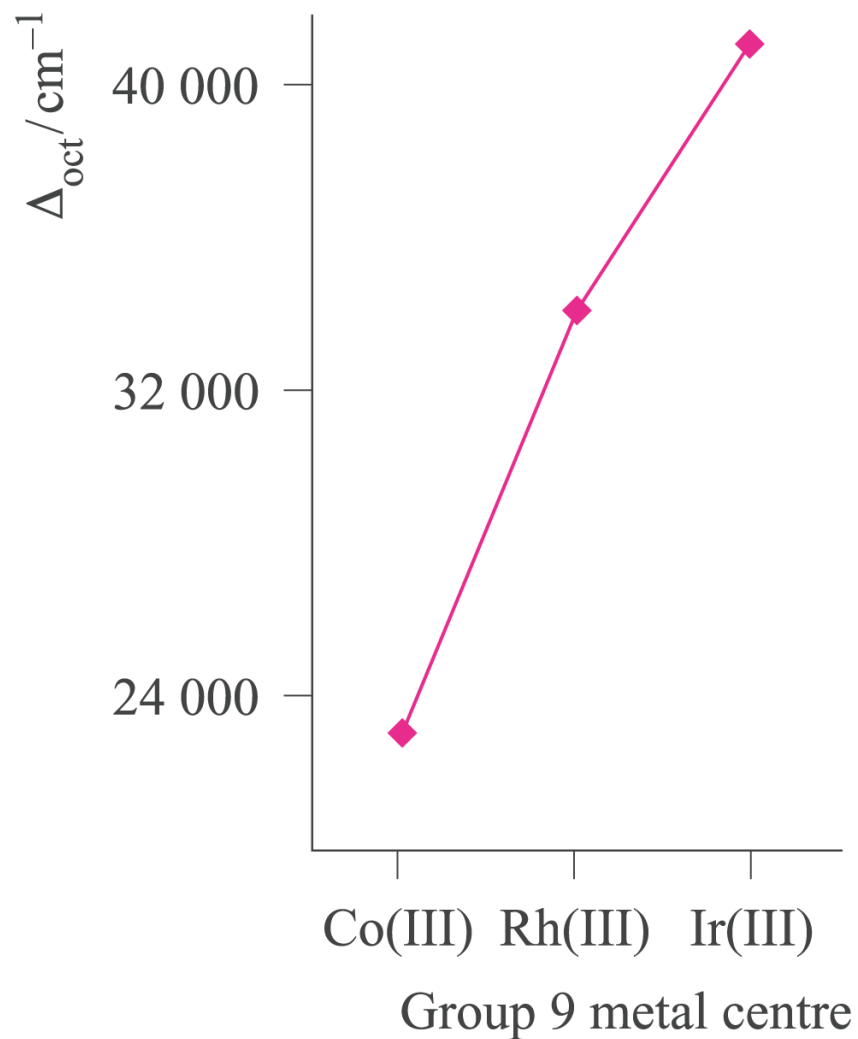
*ogni sistema molecolare **non lineare** che abbia uno **stato elettronico degenere** è instabile e subirà distorsioni per generare un sistema a più bassa simmetria e più bassa energia, rimuovendo in questo modo la degenerazione.*

# Effetto Jahn – Teller nello stato eccitato



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

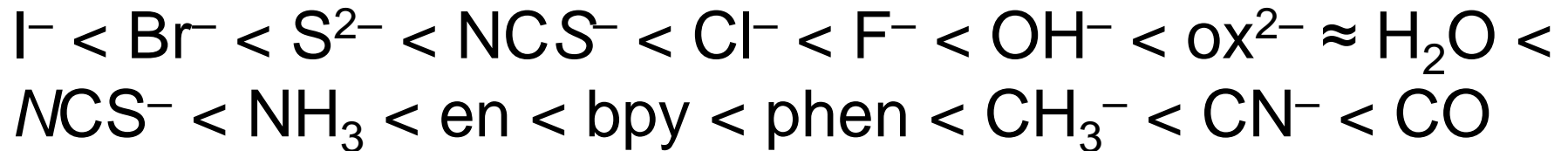
# Fattori che influenzano la grandezza dello splitting ( $\Delta$ )



# Natura e stato di ossidazione del metallo

| Complex                           | $\Delta / \text{cm}^{-1}$ | Complex                           | $\Delta / \text{cm}^{-1}$ |
|-----------------------------------|---------------------------|-----------------------------------|---------------------------|
| $[\text{TiF}_6]^{3-}$             | 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 <sup>-</sup>   | 2.3 |
| Rh(III)   | 0.28 | 6 Cl <sup>-</sup>   | 2.0 |
| Co(II)    | 0.24 | 6 [CN] <sup>-</sup> | 2.0 |
| Fe(III)   | 0.24 | 3 en                | 1.5 |
| Cr(III)   | 0.21 | 6 NH <sub>3</sub>   | 1.4 |
| Ni(II)    | 0.12 | 6 H <sub>2</sub> O  | 1.0 |
| Mn(II)    | 0.07 | 6 F <sup>-</sup>    | 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*