

*Aspetti chimico-fisici microscopici
che sono dietro ai colori :
il colore dei sali metallici*

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Università di Pavia*

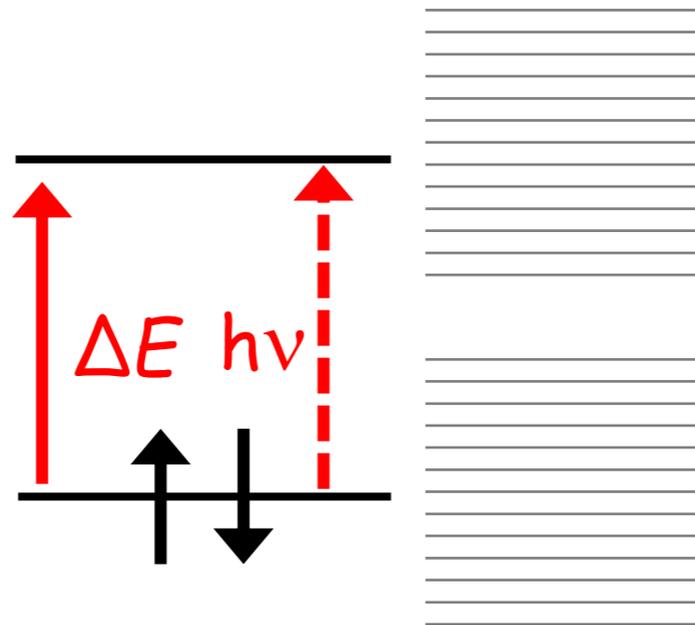
L'interazione tra la luce e le molecole

Lowest Unoccupied
Molecular Orbital

Highest Occupied
Molecular Orbital

LUMO

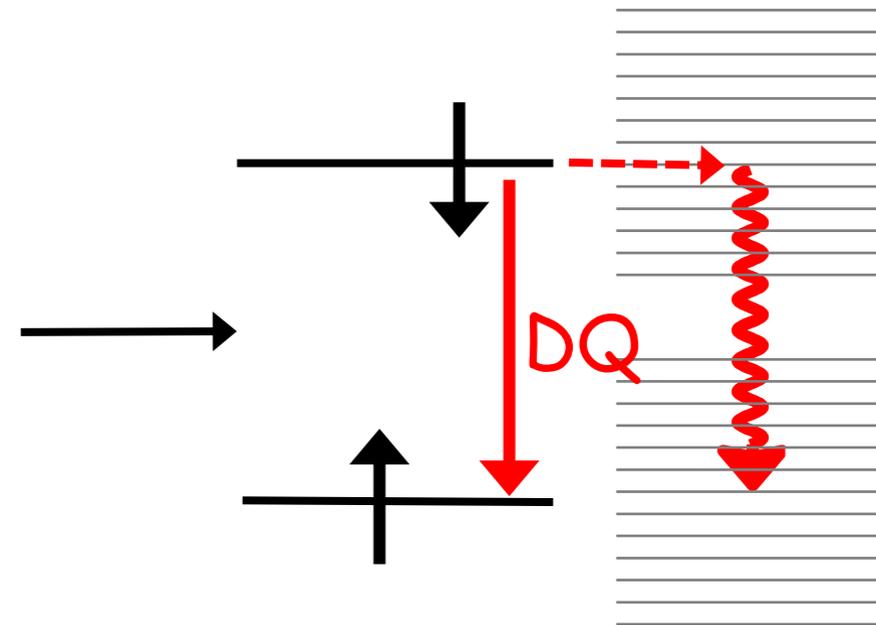
HOMO



stato
fondamentale

$$- \Delta E = h\nu$$

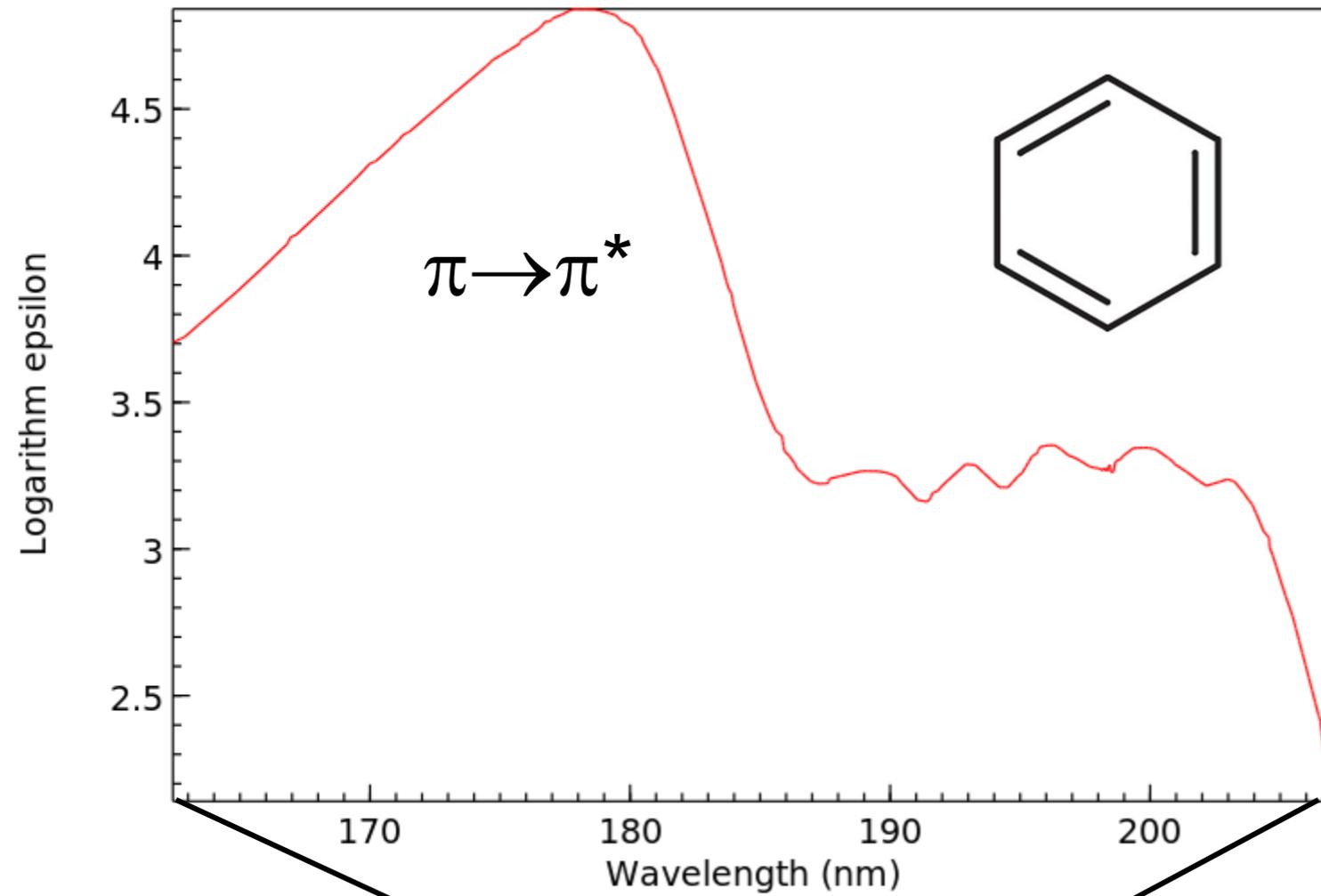
*viene assorbita l'energia ΔE di
una radiazione elettromagnetica
di frequenza ν*



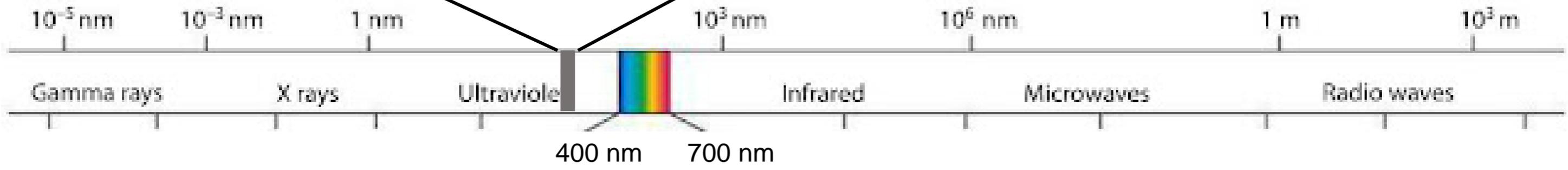
stato
eccitato

$$\Delta E = DQ$$

*L'energia ΔE viene restituita
attraverso il rilascio di una
minuscola quantità di calore DQ*

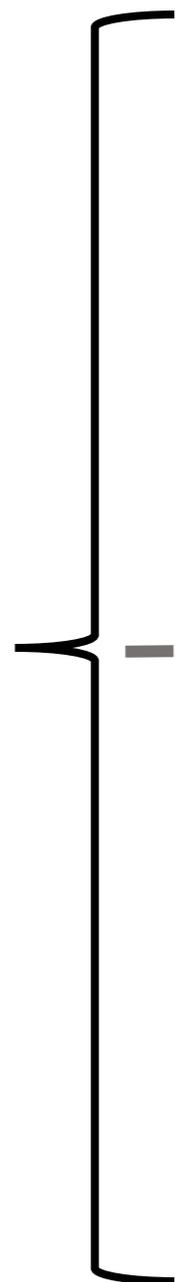
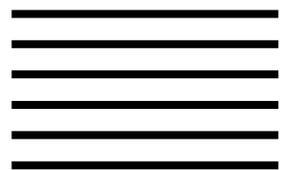


Il benzene è un liquido incolore

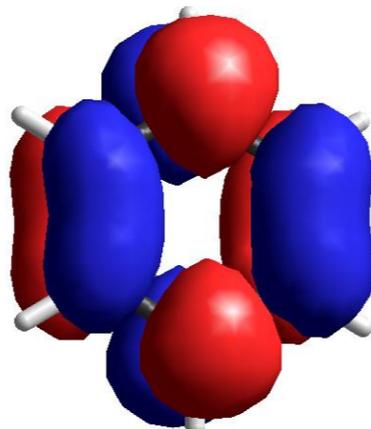




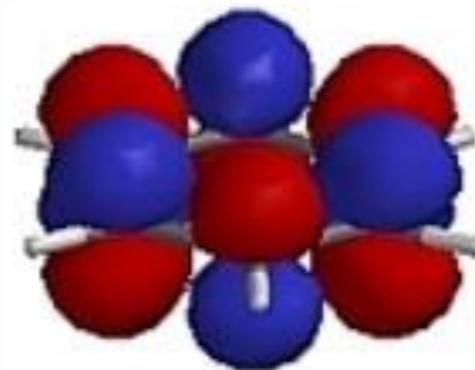
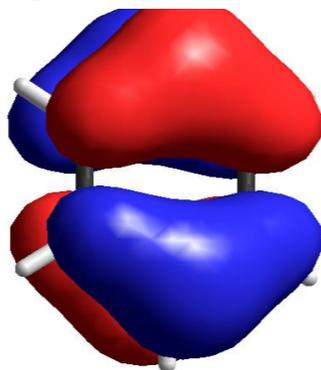
6 x 2p_z



π_4^*



π_2

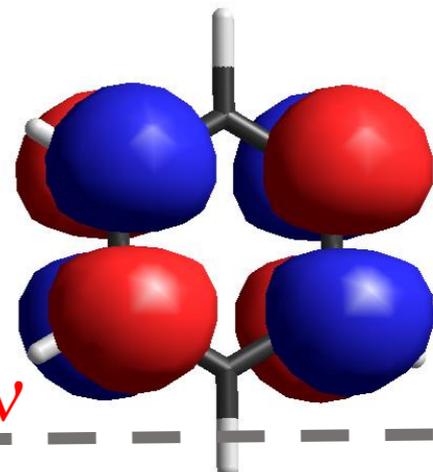


LUMO

π_6^*

$\pi_3 \rightarrow \pi_5^*$

$E = h\nu$

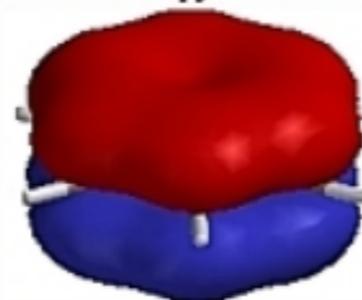
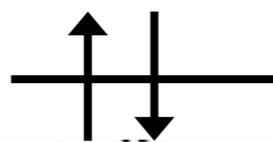


π_5^*



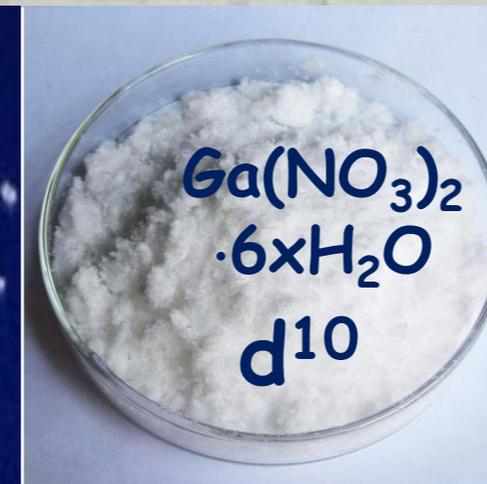
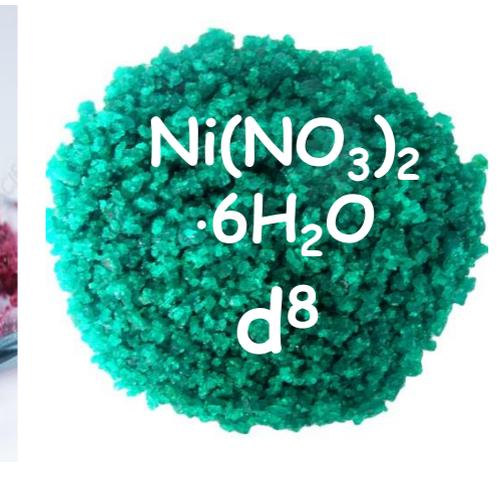
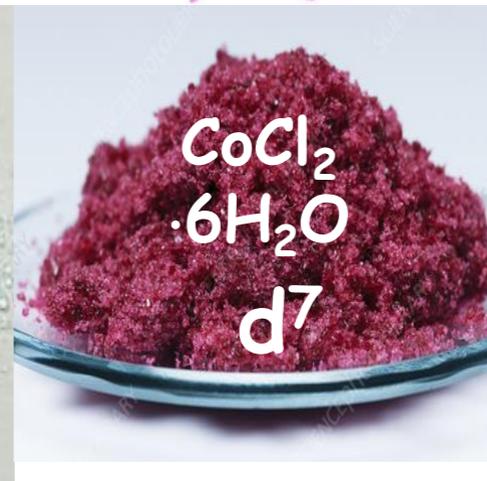
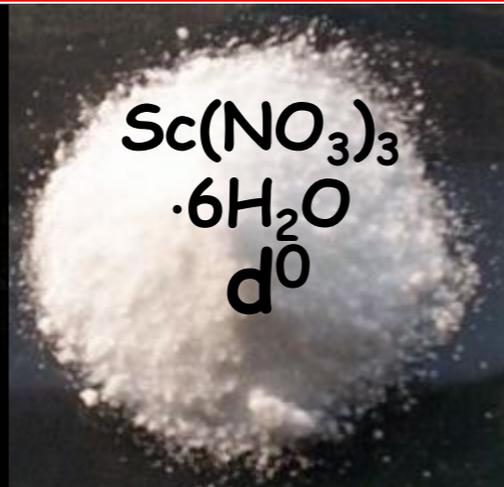
HOMO

π_3

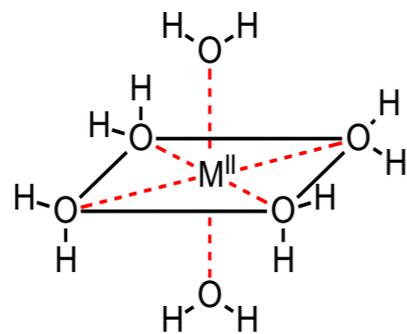
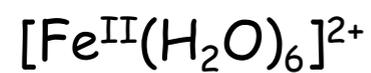
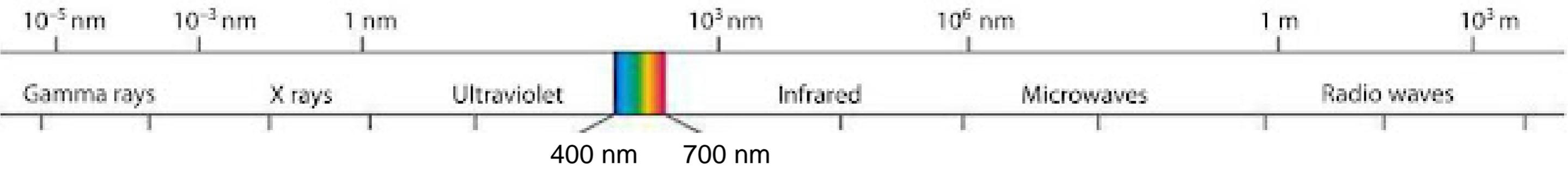


π_1

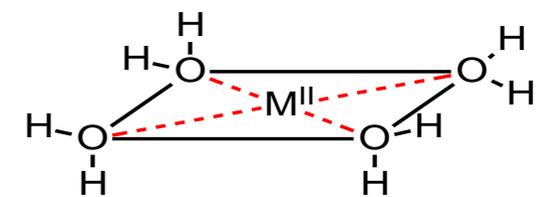
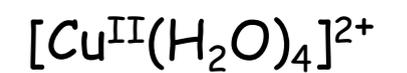
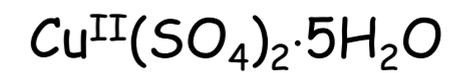
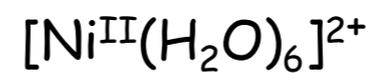
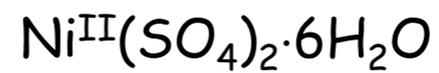
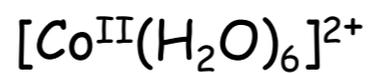
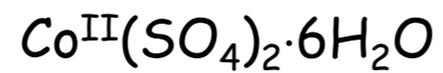
19 K potassium 39.098 ±0.001	20 Ca calcium 40.078 ±0.004	21 Sc scandium 44.956 ±0.001	22 Ti titanium 47.867 ±0.001	23 V vanadium 50.942 ±0.001	24 Cr chromium 51.996 ±0.001	25 Mn manganese 54.938 ±0.001	26 Fe iron 55.845 ±0.002	27 Co cobalt 58.933 ±0.001	28 Ni nickel 58.693 ±0.001	29 Cu copper 63.546 ±0.003	30 Zn zinc 65.38 ±0.02	31 Ga gallium 68.723 ±0.001	32 Ge germanium 72.630 ±0.008	33 As arsenic 74.922 ±0.001	34 Se selenium 78.971 ±0.008	35 Br bromine 79.904 ±0.003	36 Kr krypton 83.798 ±0.002
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Sono colorati i sali di quegli ioni metallici nei quali si vanno riempiendo gli orbitali d
(config. elettronica d¹-d⁹)



geometria ottaedrica



geometria quadrata

La Teoria del Campo Cristallino (Crystal Field Theory - CFT)

«Come cambia l'energia degli orbitali atomici in un campo di cariche elettriche negative di una data geometria».

ANNALEN DER PHYSIK

5. F O L G E , 1 9 2 9 , B A N D 3 , H E F T 2

Termaufspaltung in Kristallen

Von H. Bethe

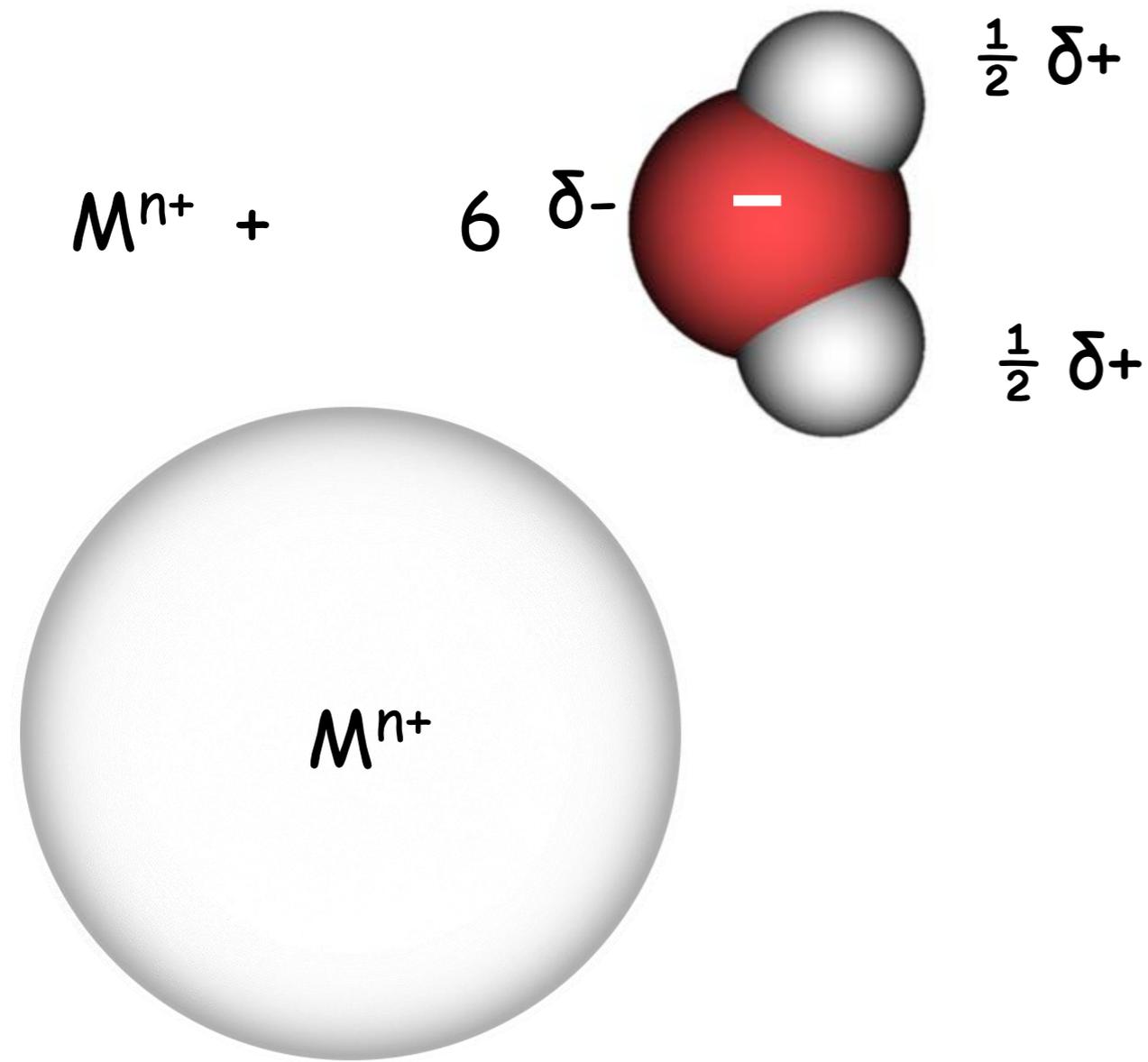
(Mit 8 Figuren)

Der Einfluß eines elektrischen Feldes von vorgegebener Symmetrie (Kristallfeld) auf ein Atom wird wellenmechanisch behandelt. Die Terme des Atoms spalten auf in einer Weise, die von der Symmetrie des Feldes und vom Drehimpuls l (bzw. j) des Atoms abhängt. s -Terme spalten allgemein, p -Terme in Feldern von kubischer Symmetrie *nicht* auf. Für den Fall, daß die einzelnen Elektronen des Atoms separat behandelt werden dürfen (aufgehobene Wechselwirkung im Atom), werden zu jedem Term im Kristall die Eigenfunktionen nullter Näherung angegeben; aus diesen ergibt sich eine für den Term charakteristische Gruppierung der Elektronendichte nach den Symmetrieachsen des Kristalls. — Die Größe der Termaufspaltung bewegt sich in der Ordnung einiger hundert cm^{-1} . — Bei tetragonaler Symmetrie kann ein quantitatives Maß für die Abweichung von der kubischen Symmetrie definiert werden, welches eindeutig die stabilste Elektronenanordnung im Kristall bestimmt.



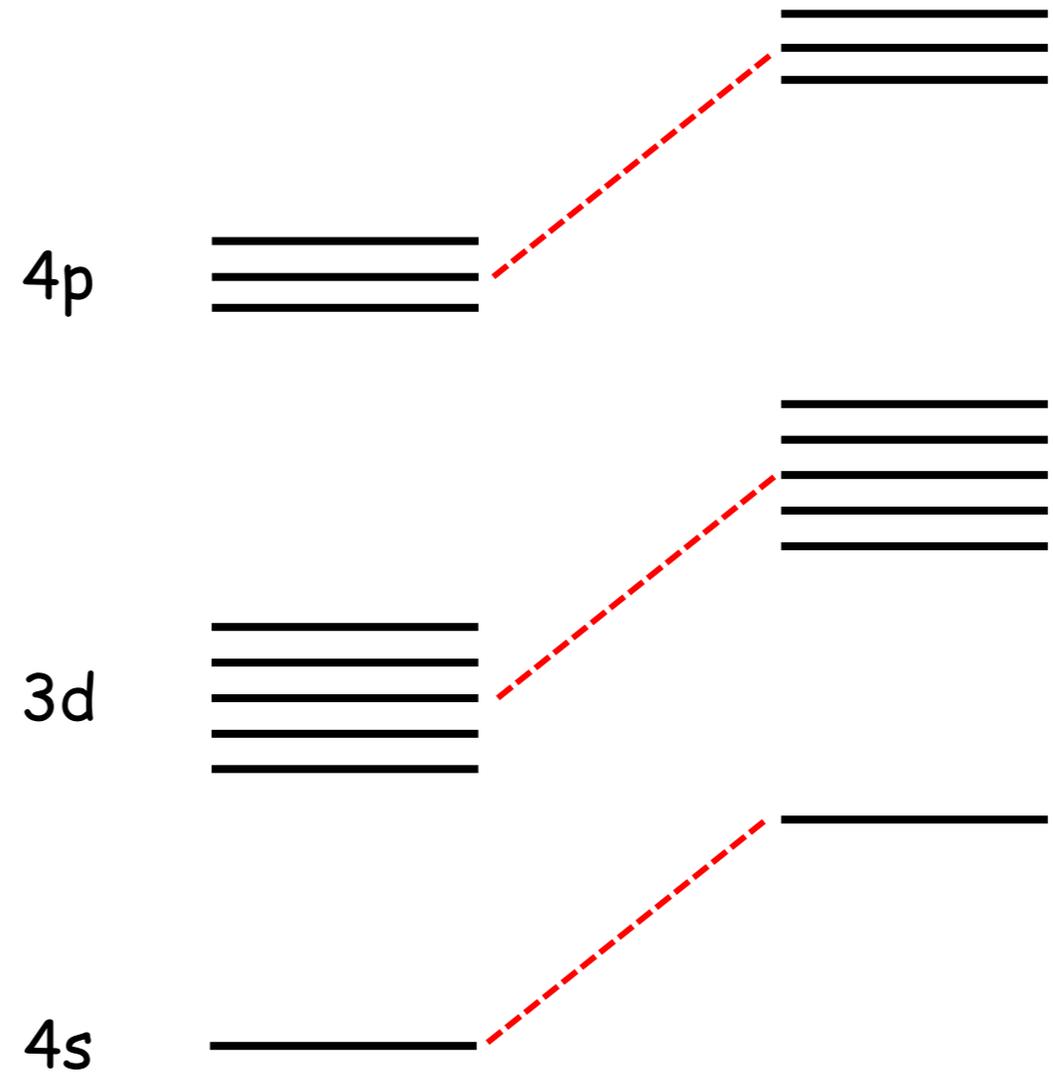
Hans Bethe
(1906-2005)

L'influenza di un campo elettrico di una determinata simmetria (campo cristallino) su un atomo viene trattata in termini di meccanica ondulatoria.

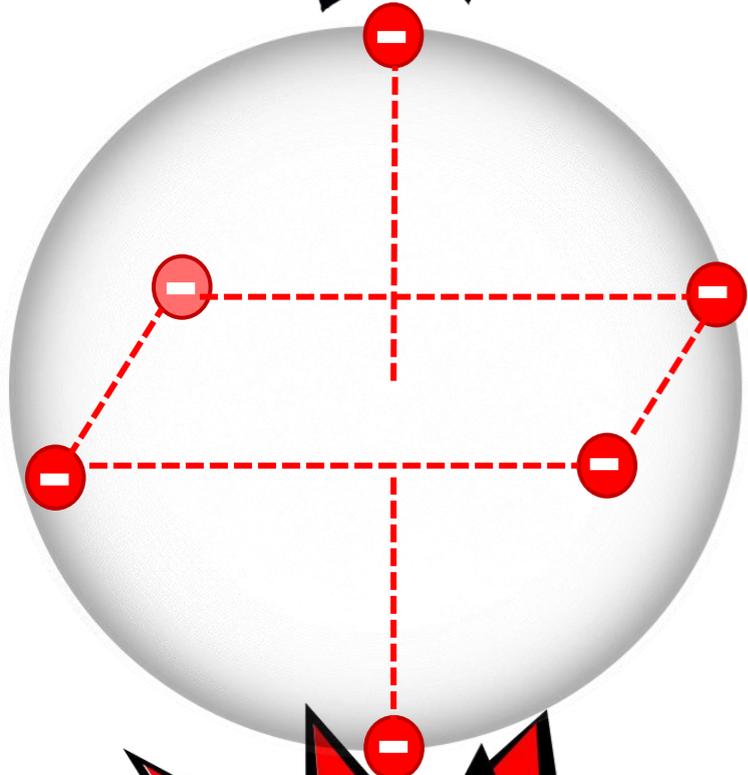


le 6 cariche negative dei leganti sono 'spalmate' sulla superficie della sfera che include l'aquaione

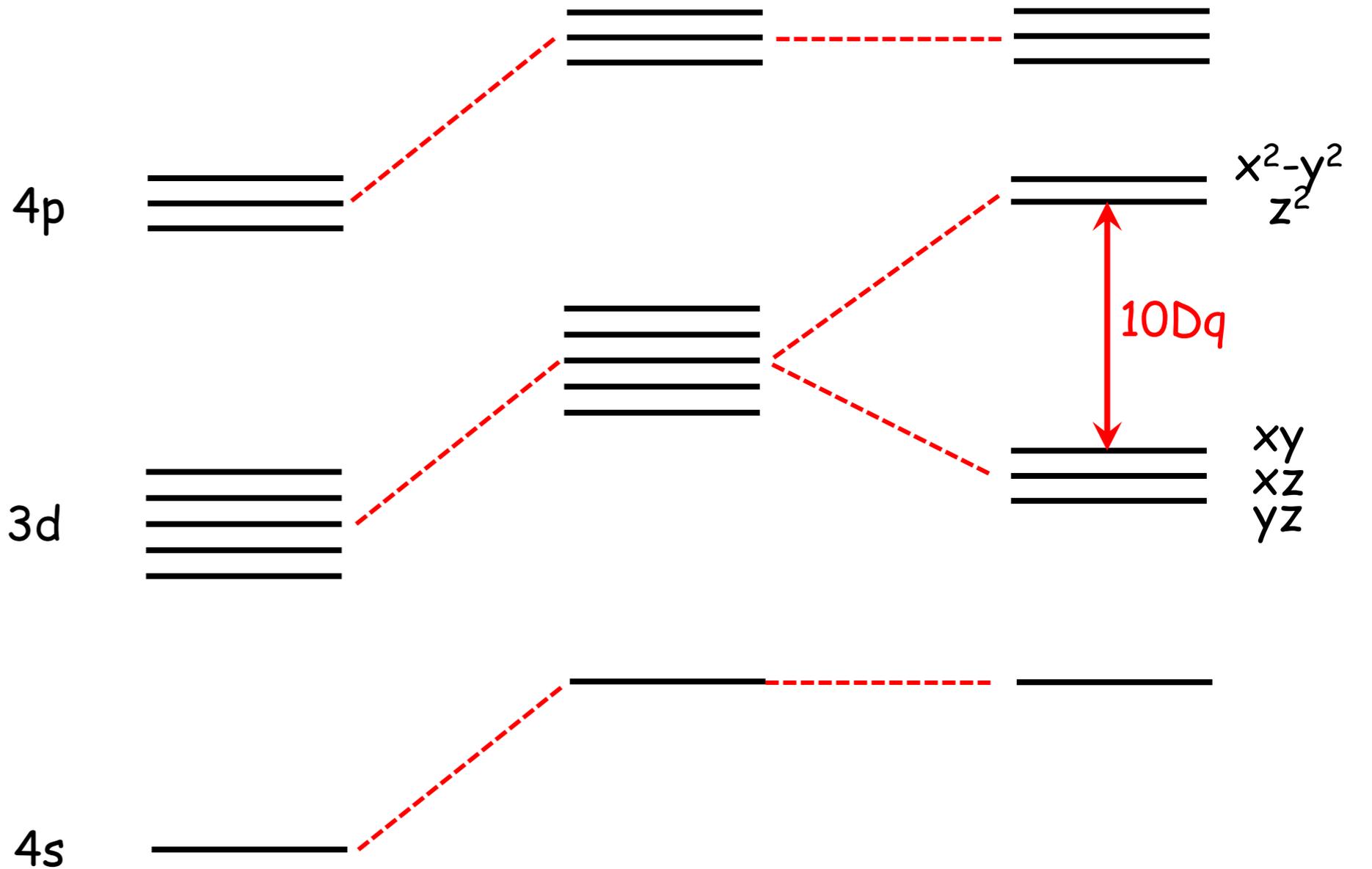
cosa succede all'energia degli orbitali esterni dell'aquaione



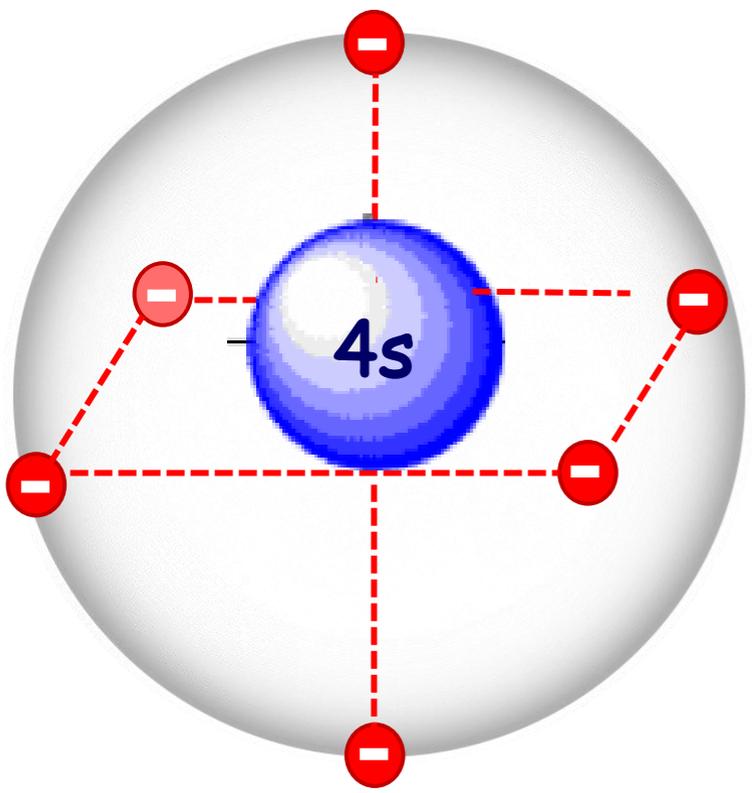
SNAP!



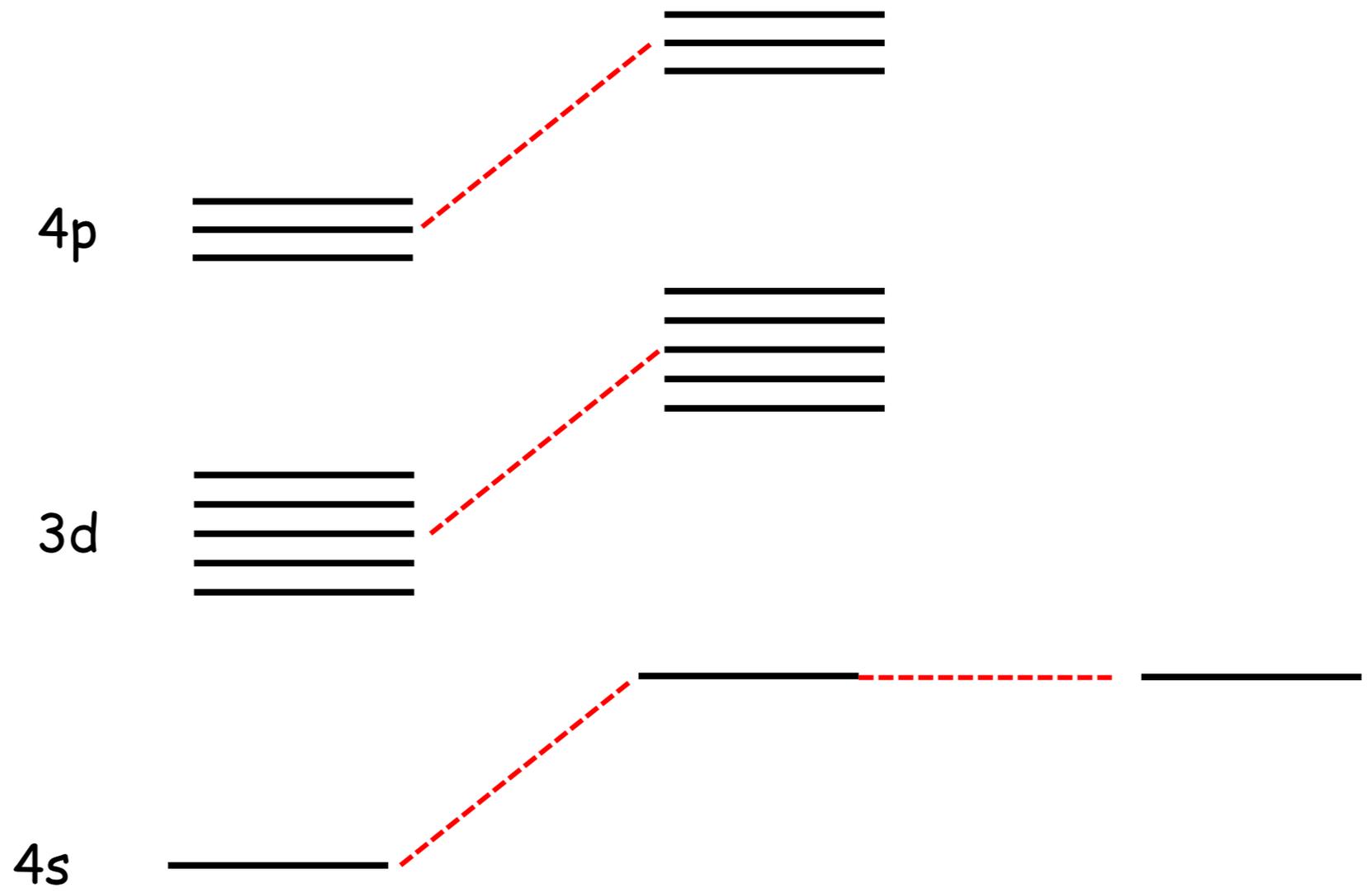
le 6 cariche
negative si dispongono
ciascuna ai vertici di un
ottaedro



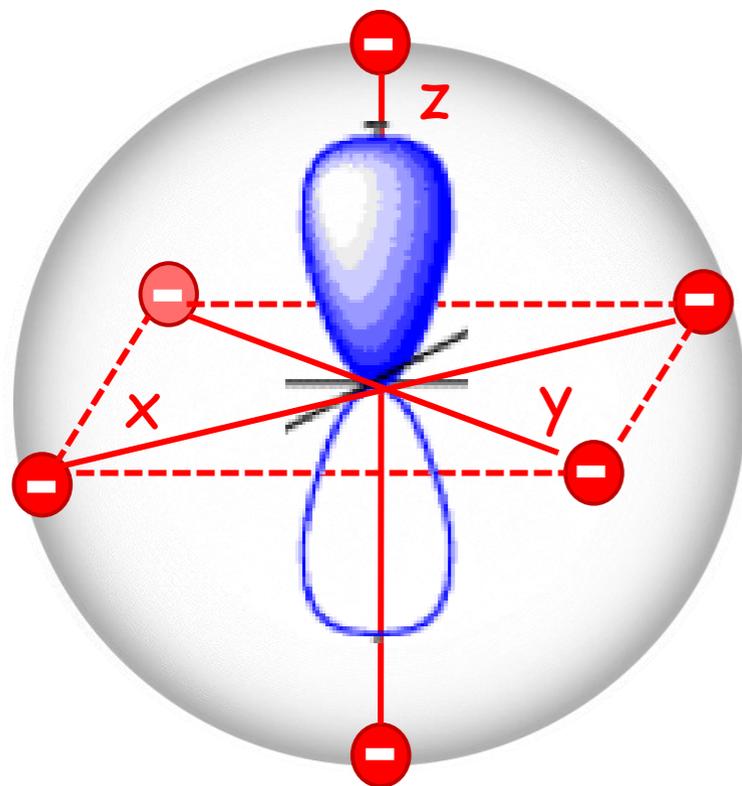
cosa succede
all'orbitale 4s



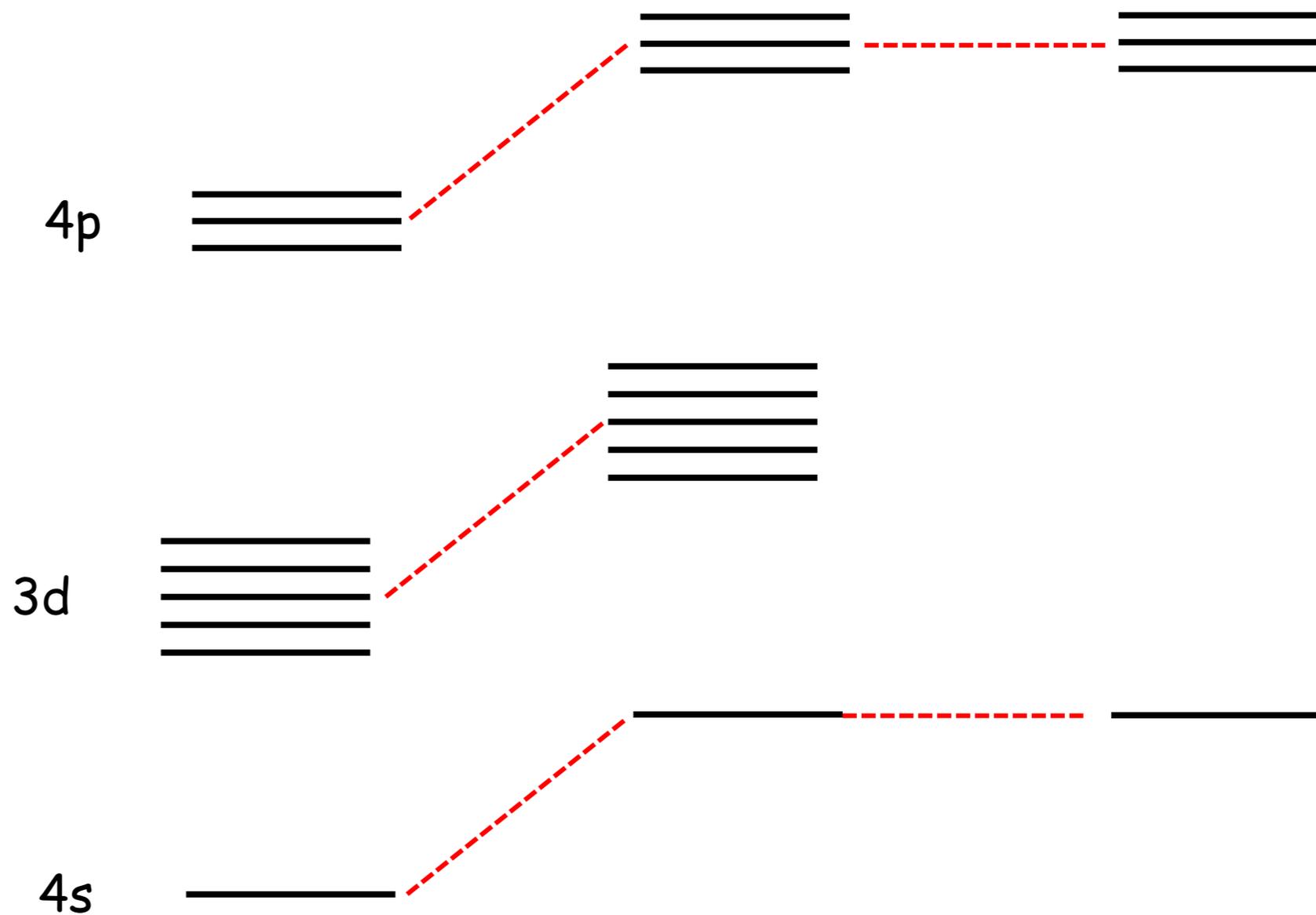
le 6 cariche negative
sono disposte
ciascuna ai vertici di
un ottaedro



cosa succede ai
3 orbitali $4p_x$, $4p_y$, $4p_z$

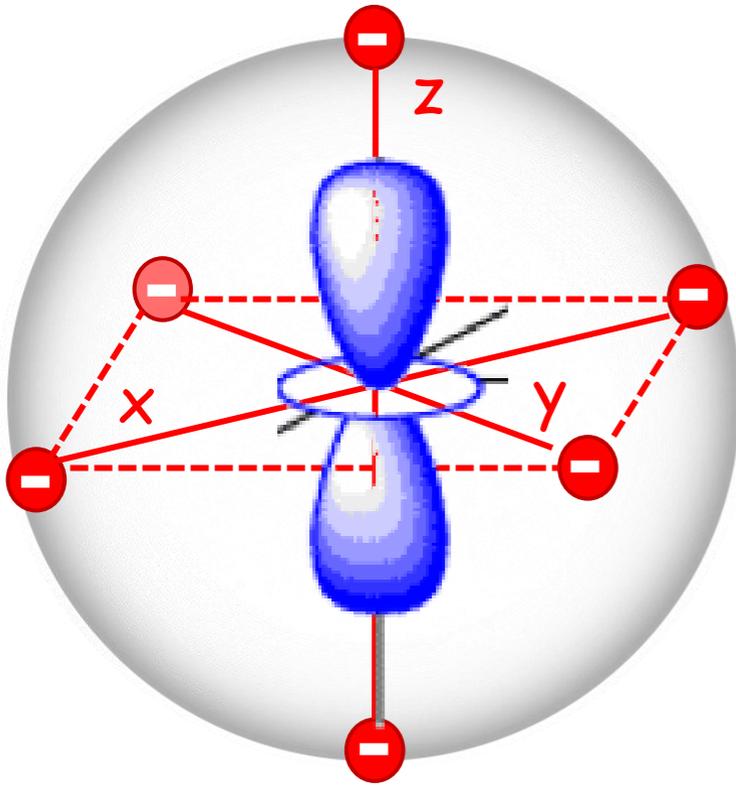


le 6 cariche negative
sono disposte
ciascuna ai vertici di
un ottaedro

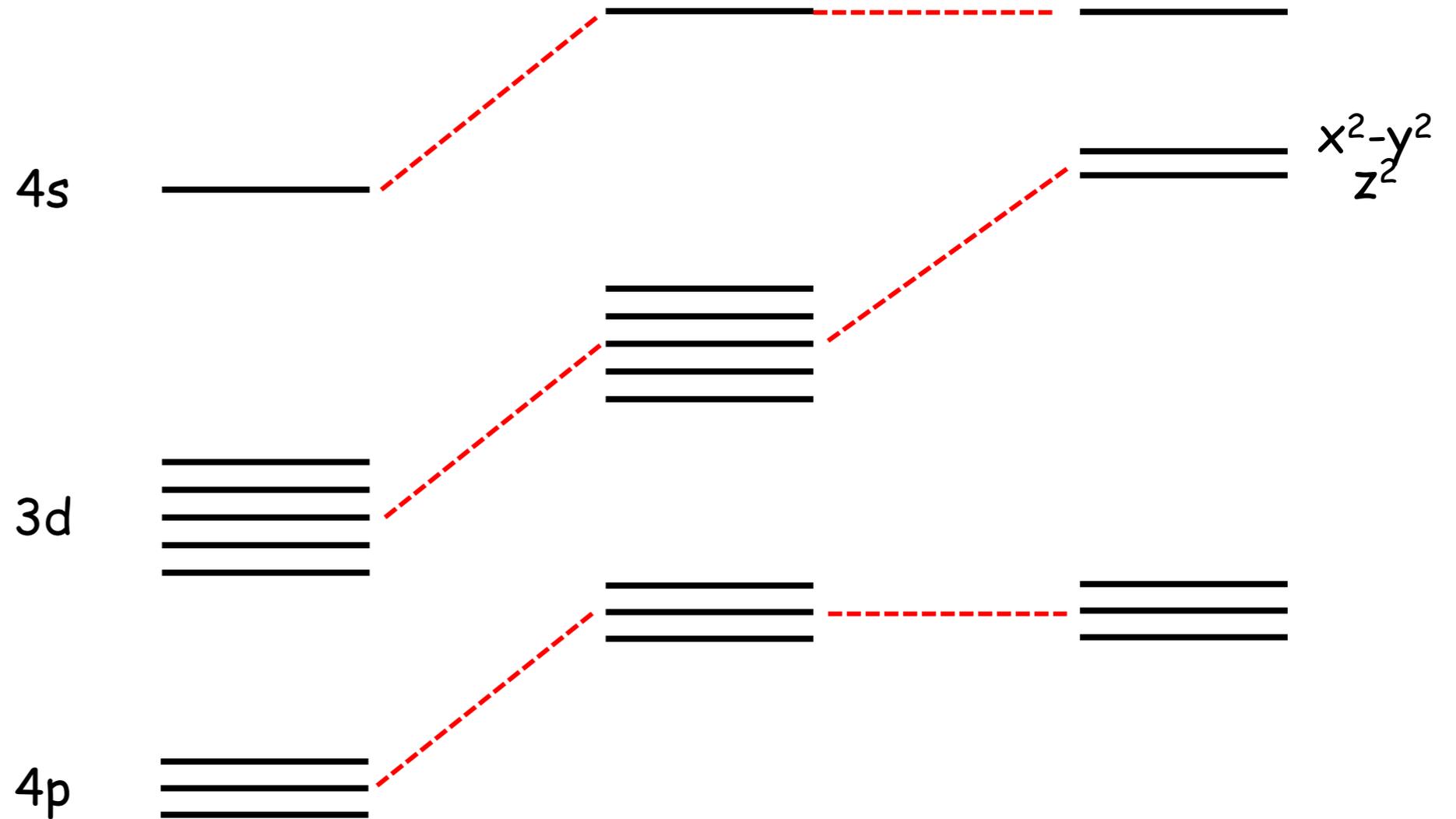


e gli orbitali 3d?

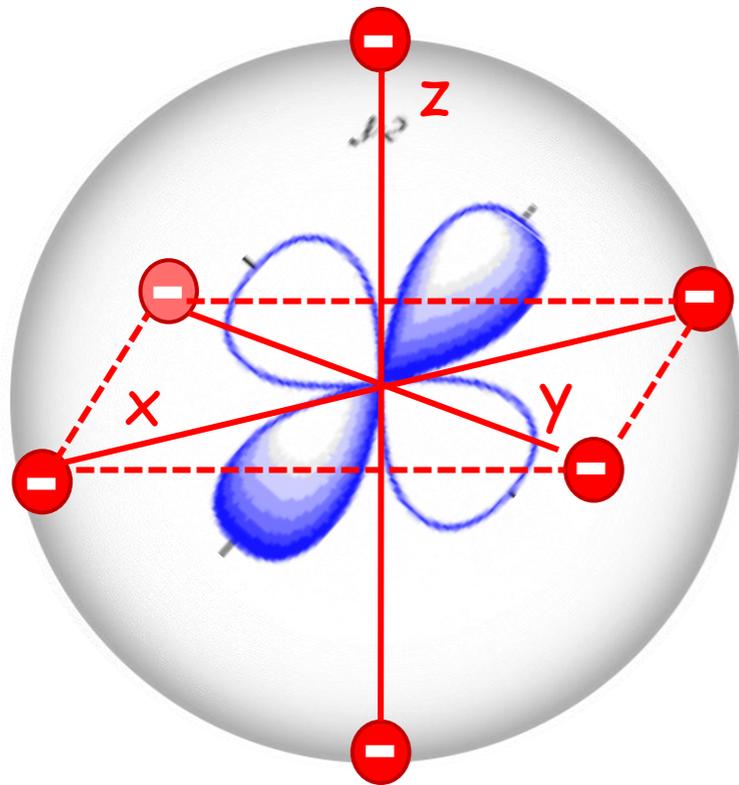
z^2 x^2-y^2



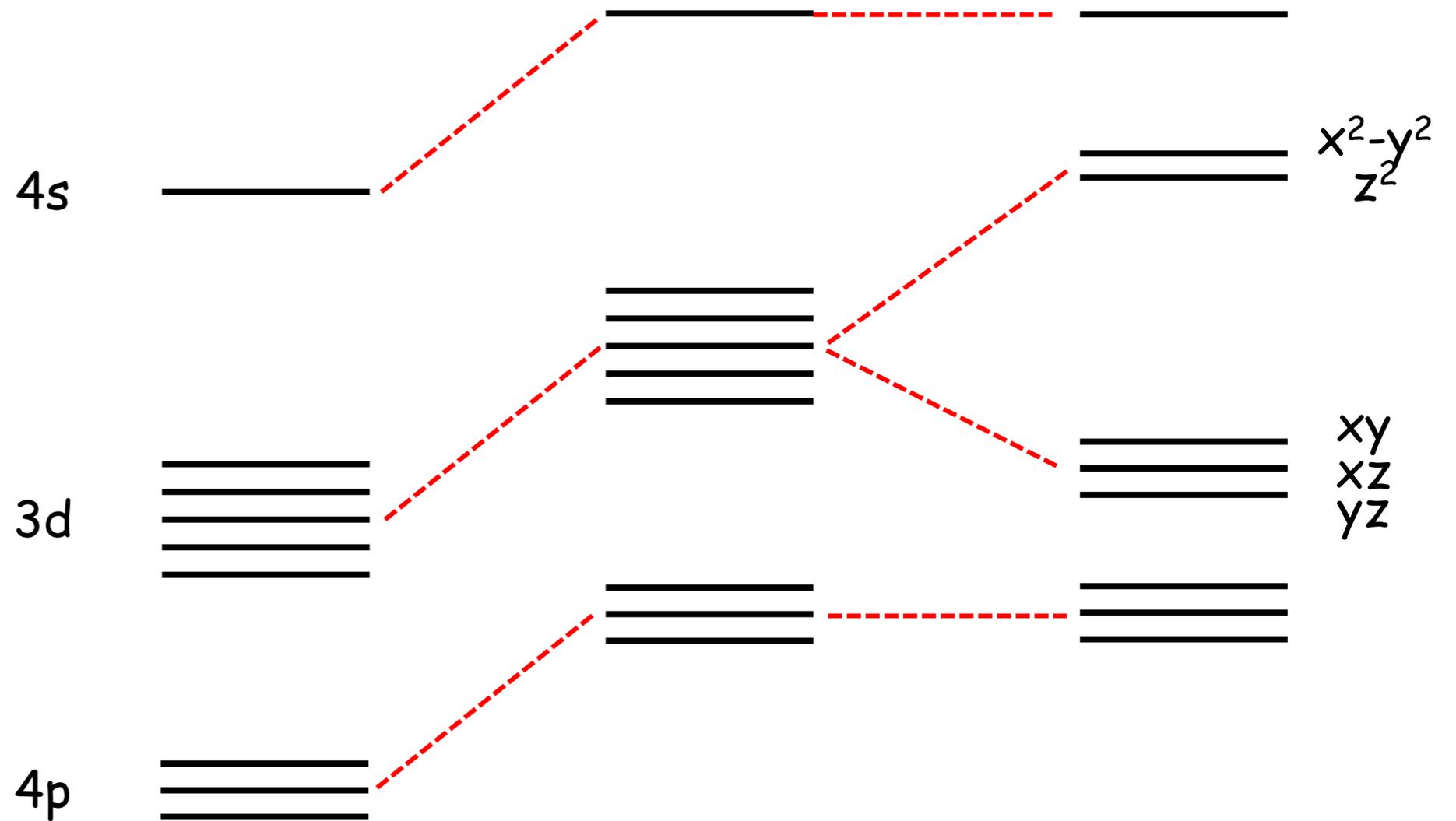
le 6 cariche negative
sono disposte
ciascuna ai vertici di
un ottaedro

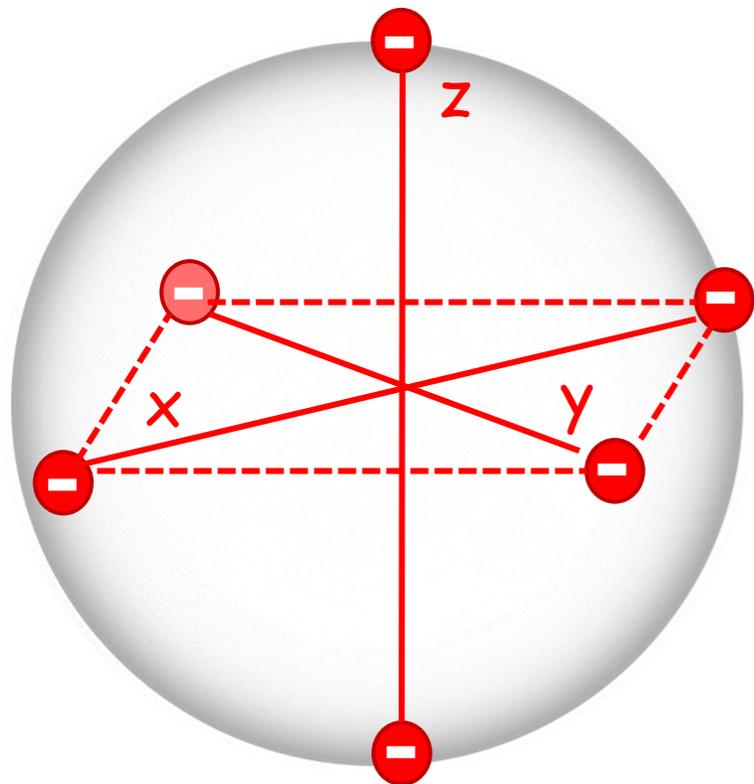


xz yz xy

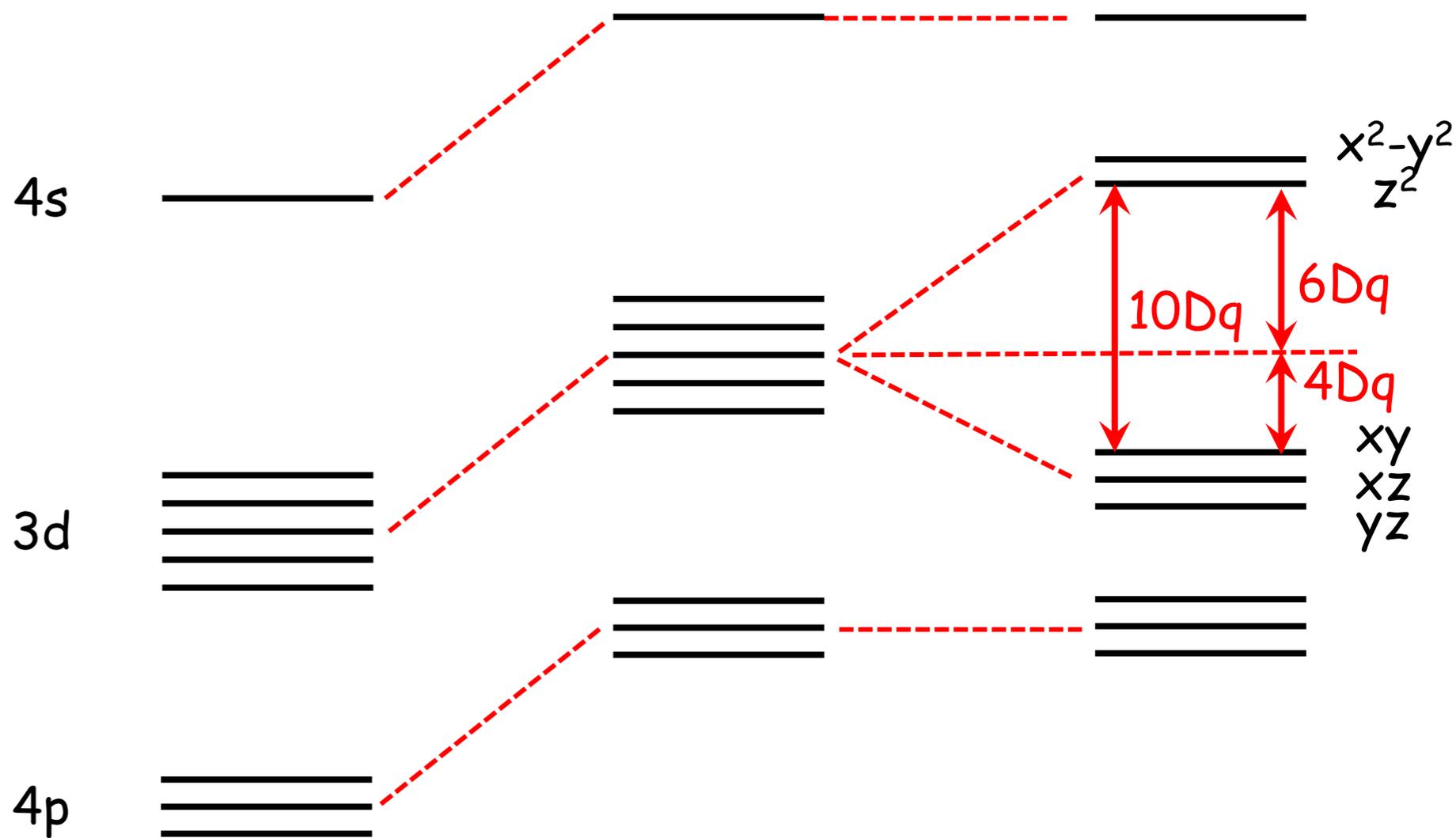


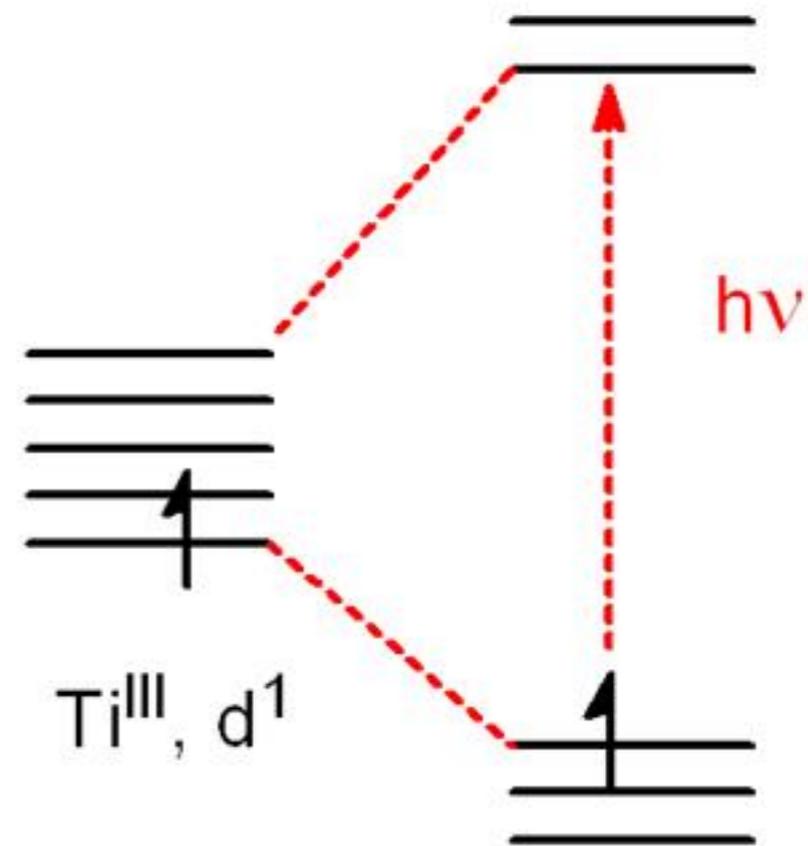
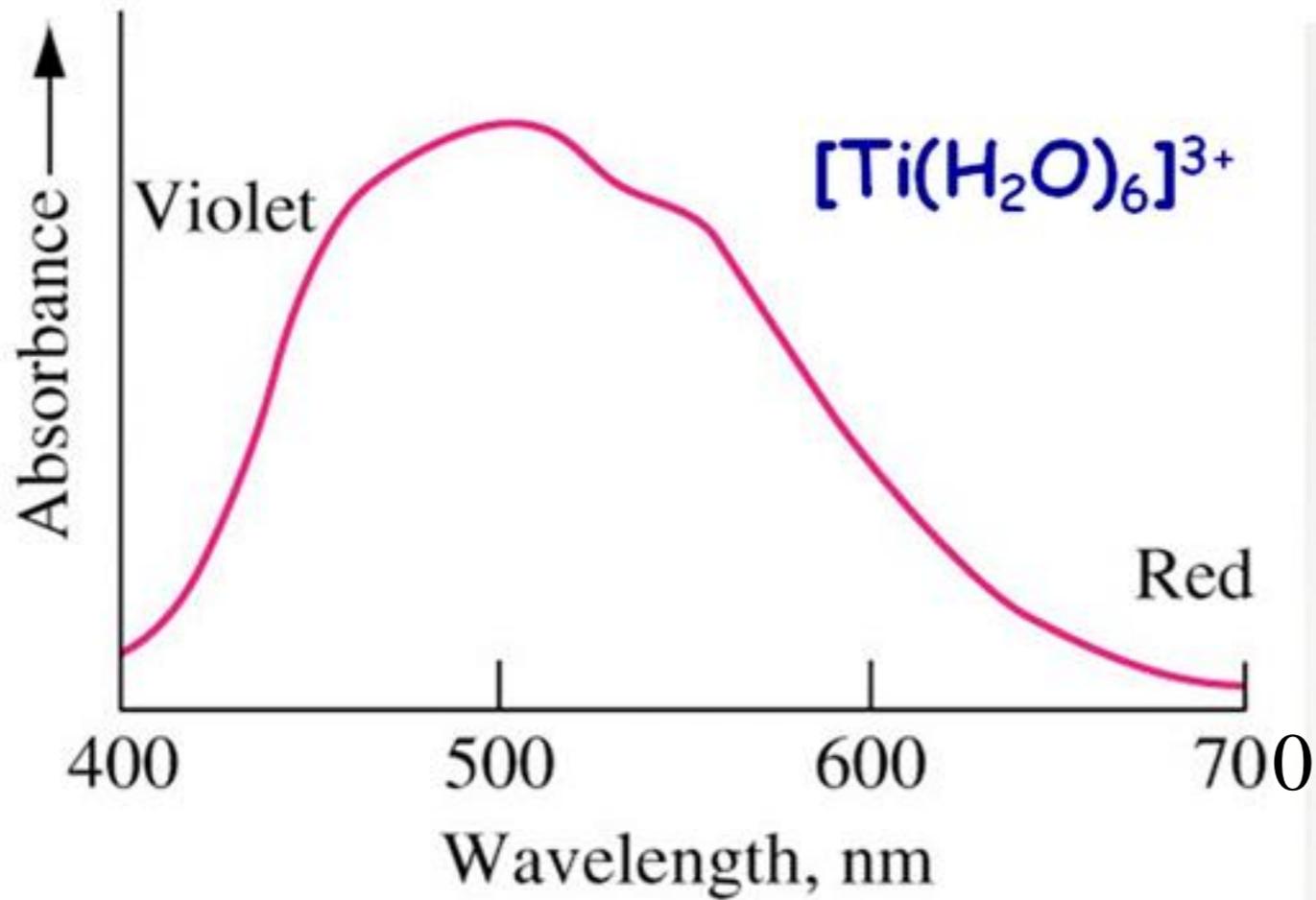
le 6 cariche negative
si dispongono
ciascuna ai vertici di
un ottaedro

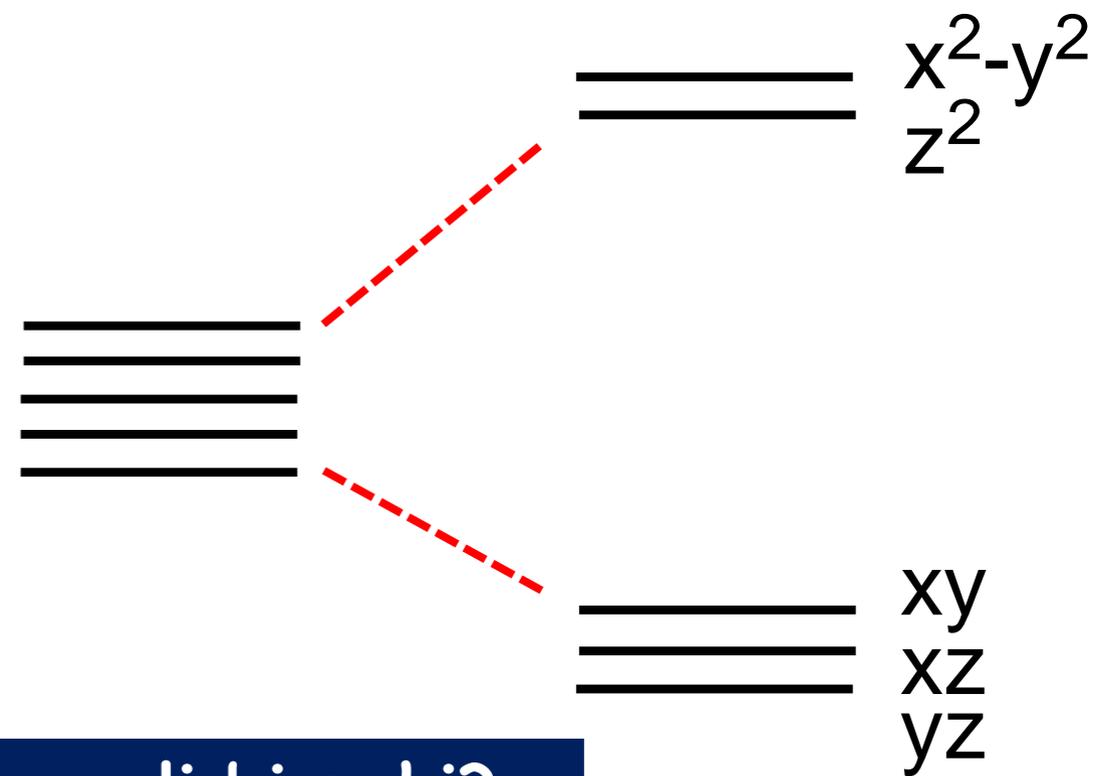




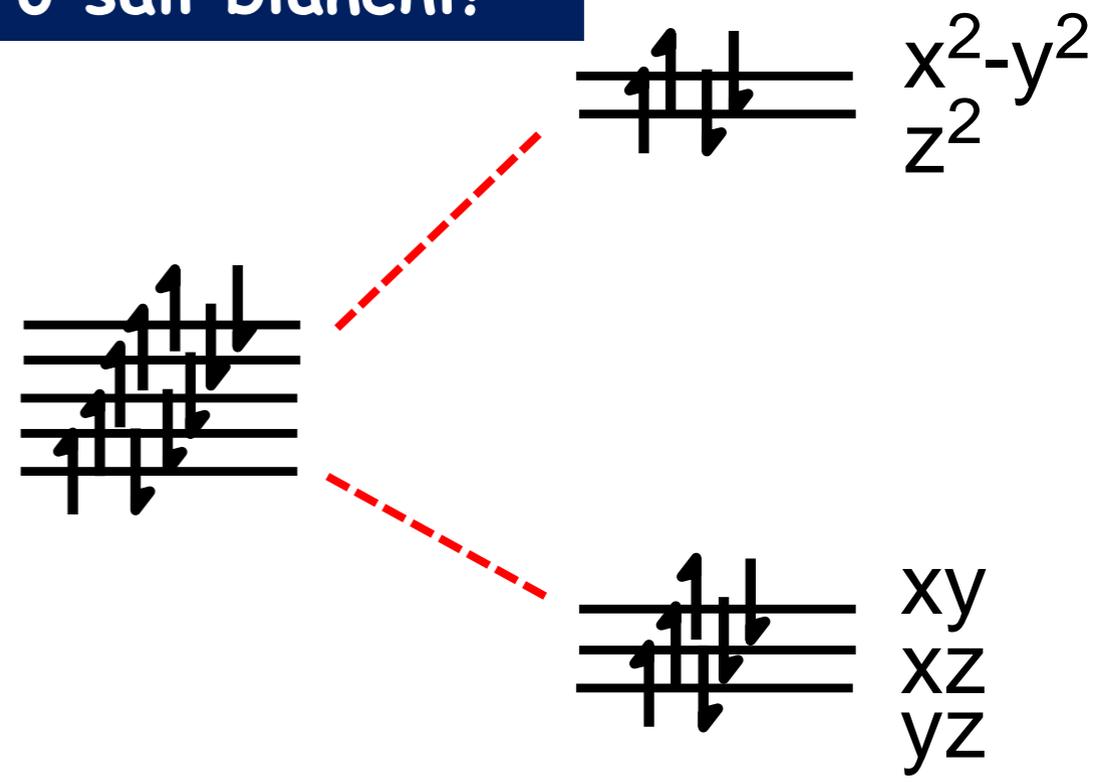
le 6 cariche negative
si dispongono
ciascuna ai vertici di
un ottaedro



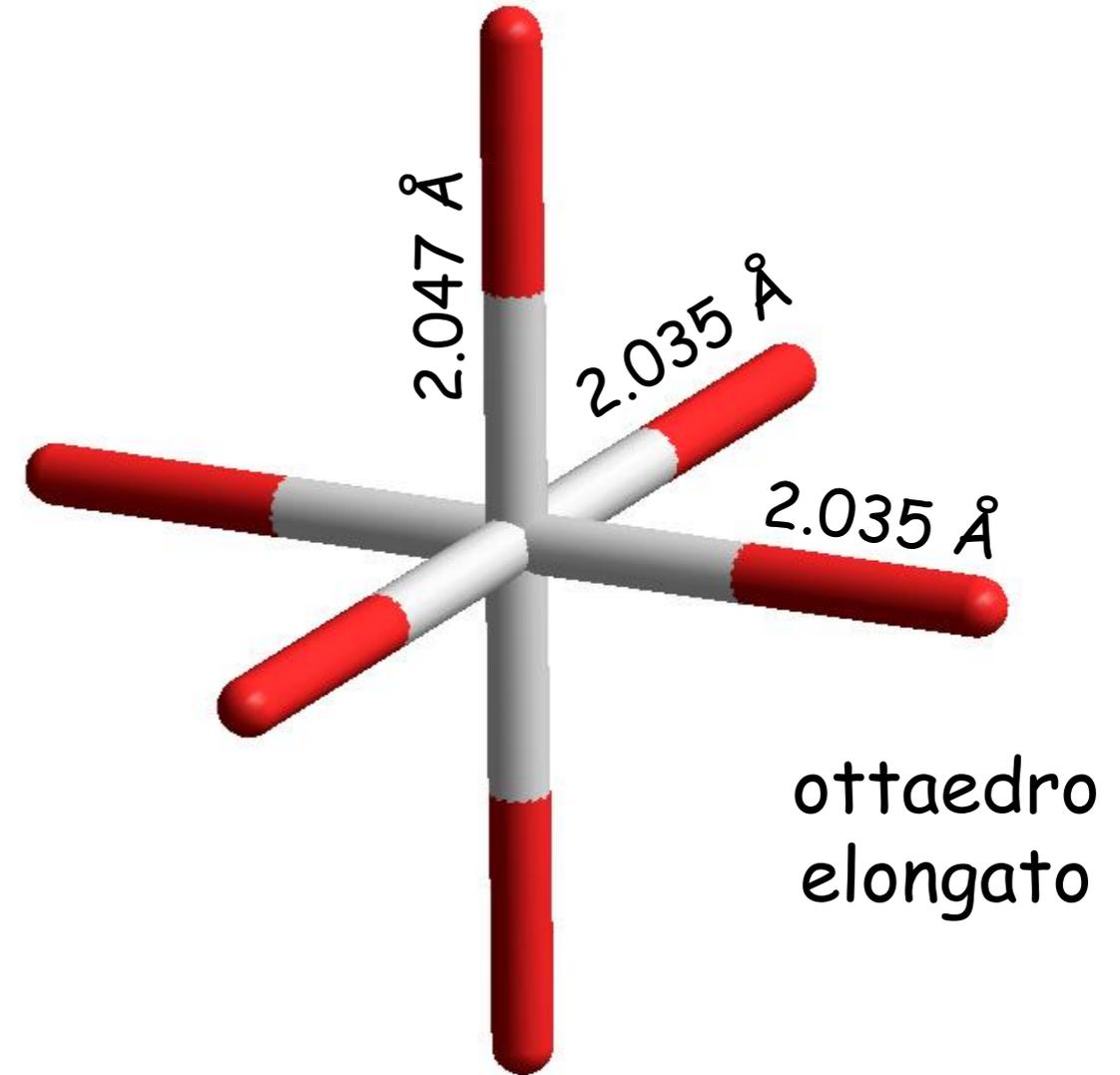
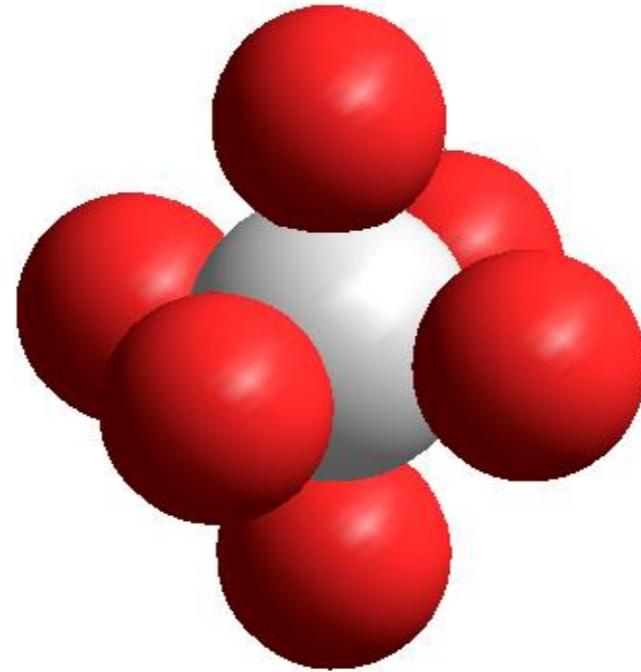




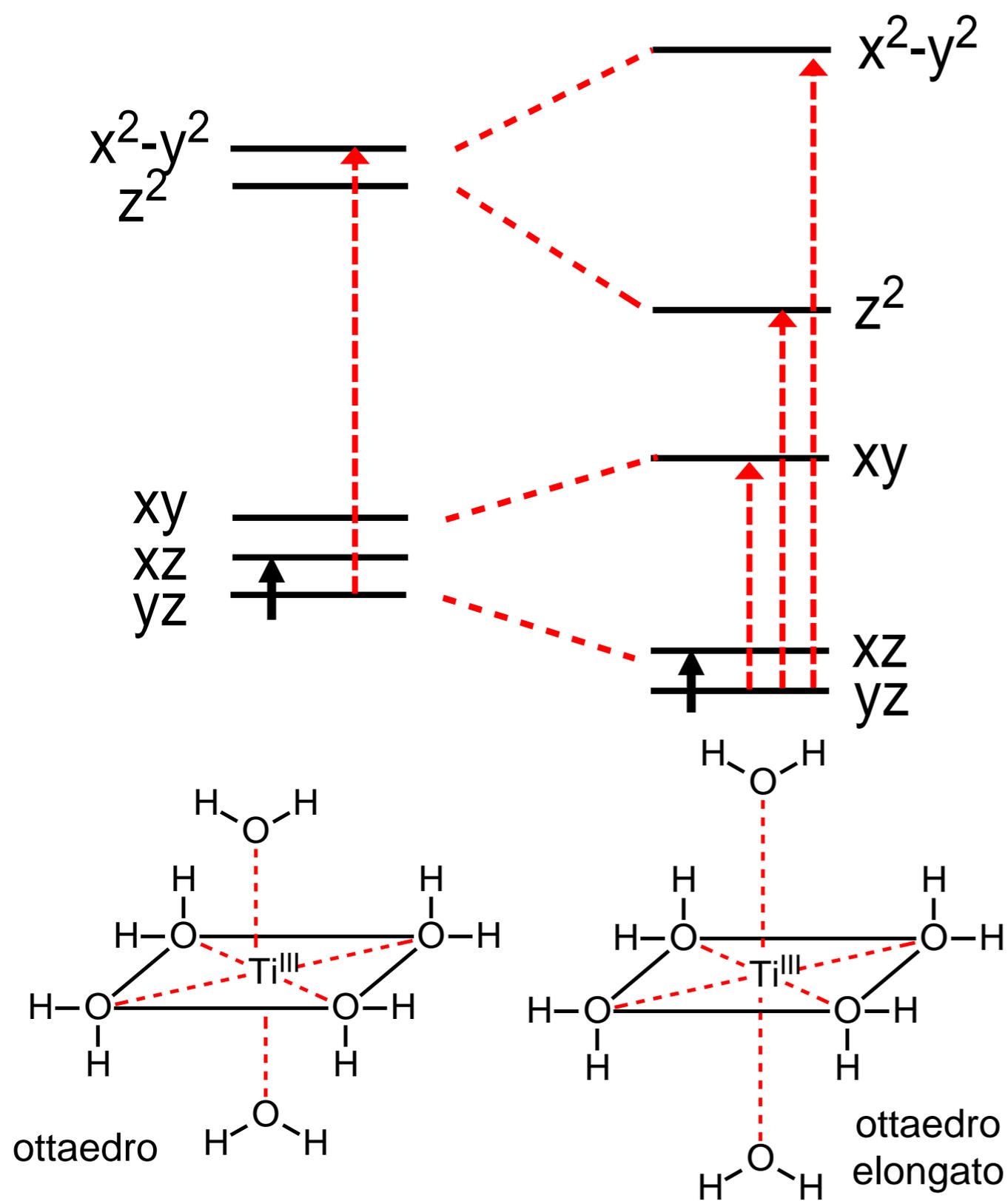
Perché gli ioni metallici d^0 e d^{10} sono incolori e i loro sali bianchi?



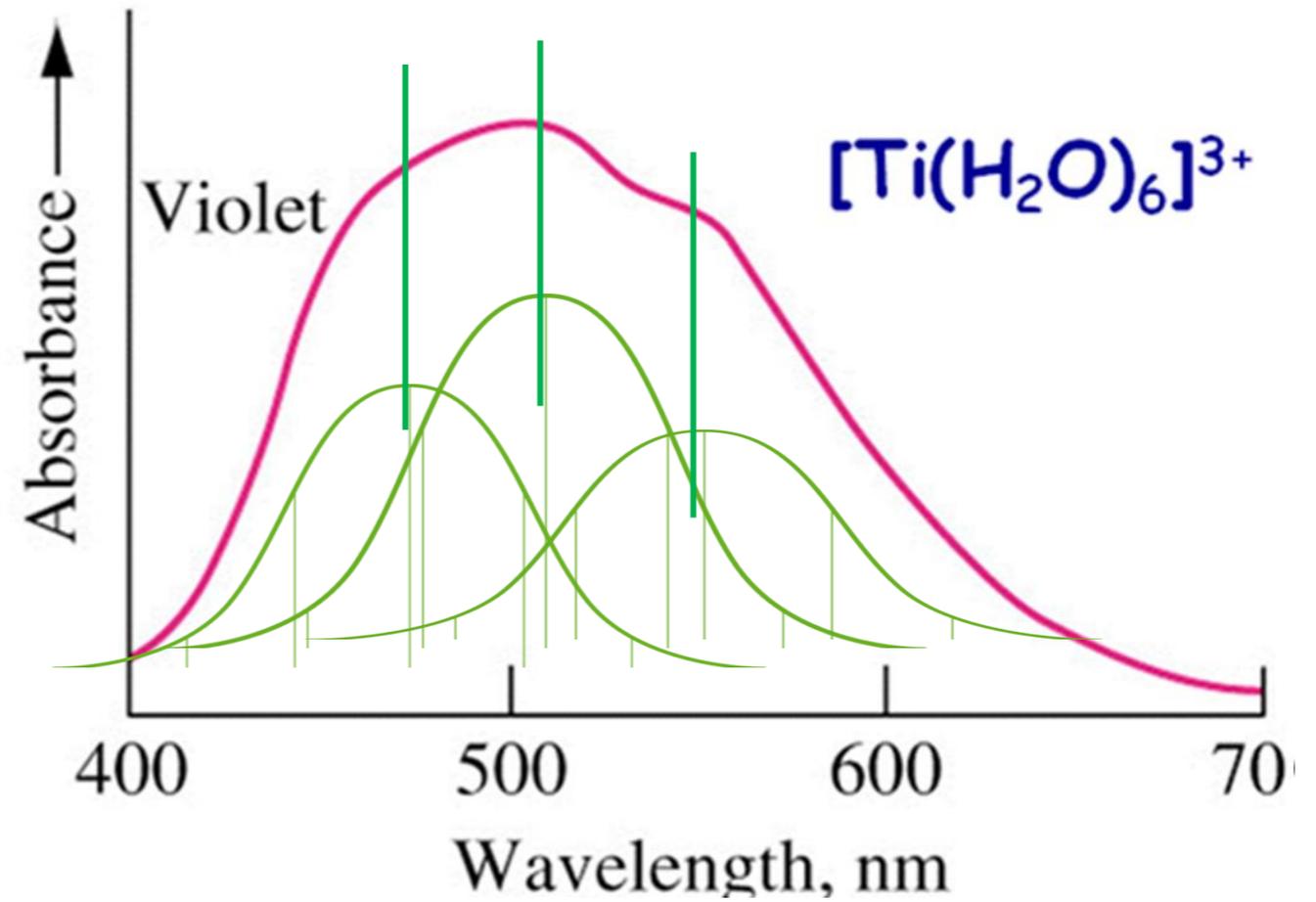
La struttura cristallina dell'aqua-ione $[\text{Ti}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$



M. A. S. Aquino, W. Clegg, Q.-T. Liu and A. G. Sykes , Hexaaquatitanium(III) Tris(*p*-Toluenesulfonate) Trihydrate, *Acta Cryst.* **1995**, C51, 560–562.



Lo spettro può essere deconvoluto in 3 bande, corrispondenti alle 3 transizioni

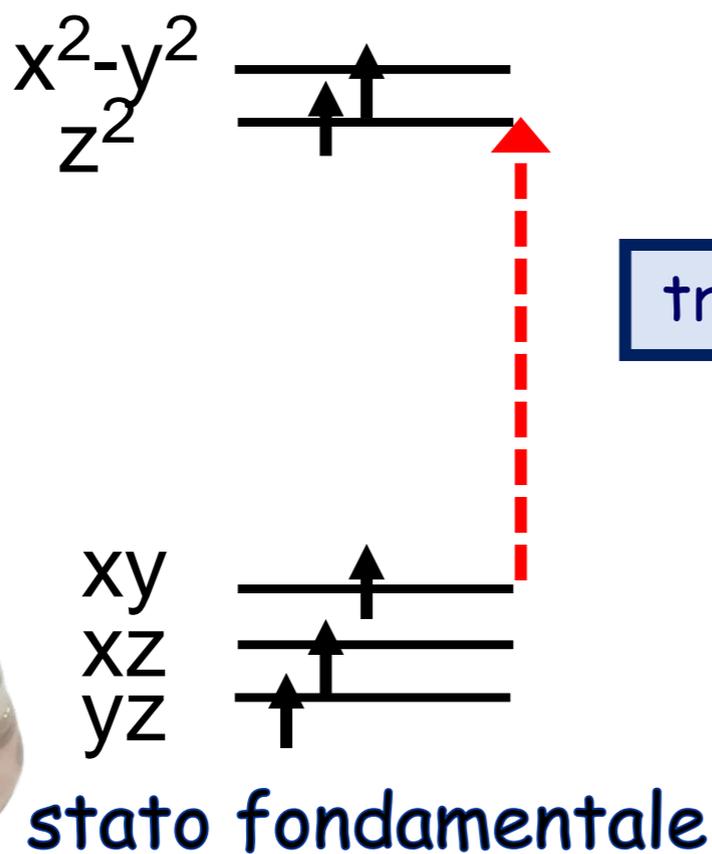
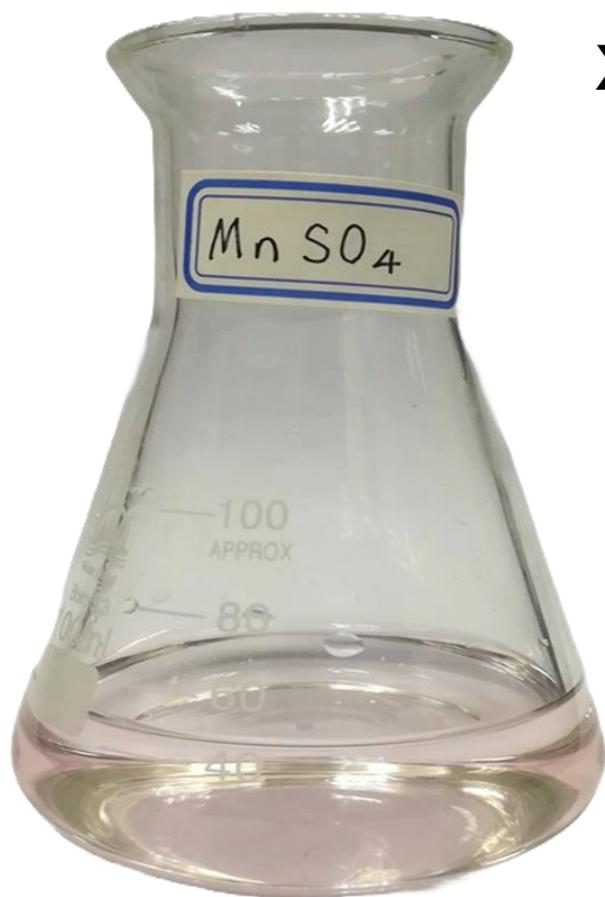


L'intensità del colore e le regole di selezione

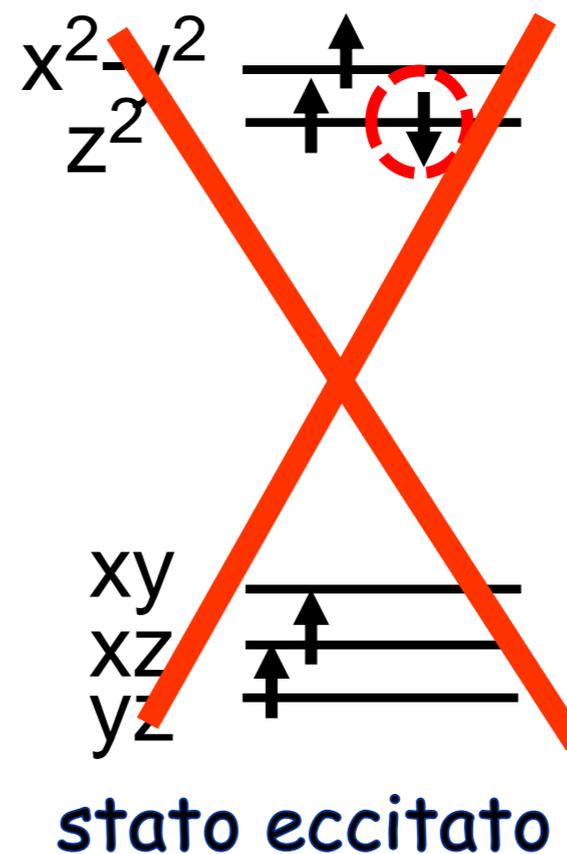
1. Stato fondamentale e stato eccitato devono avere la stessa molteplicità di spin ($\Delta S = 0$). Se c'è variazione di spin la transizione è vietata (*spin forbidden*).



Perché l'aquaione $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ($3d^5$) è praticamente incolore?



transition



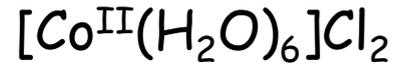


BLU COBALTO

Pierre-Auguste Renoir,
La Yole (1875),
huile sur toile, 71 cm x 92 cm
The National Gallery,
Londres

*(En yole sur la Seine, à
Chatou, une journée
ensoleillée).*

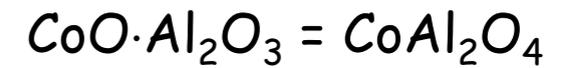
La sintesi del blu cobalto



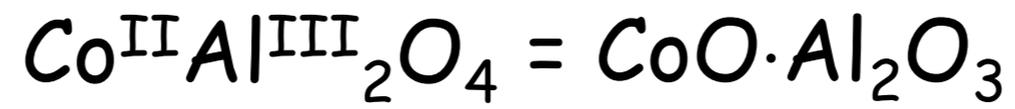
+



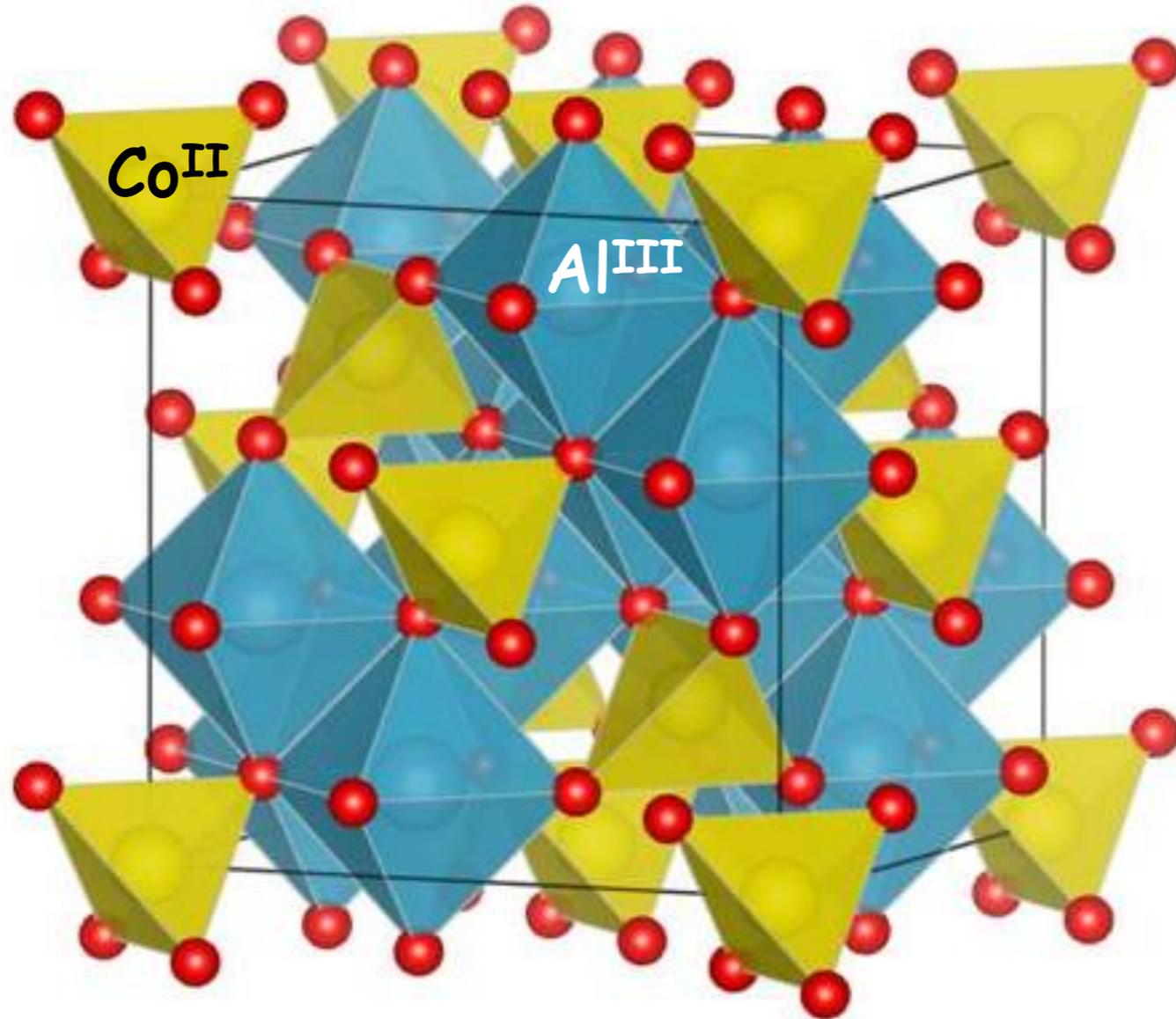
1200 °C
→



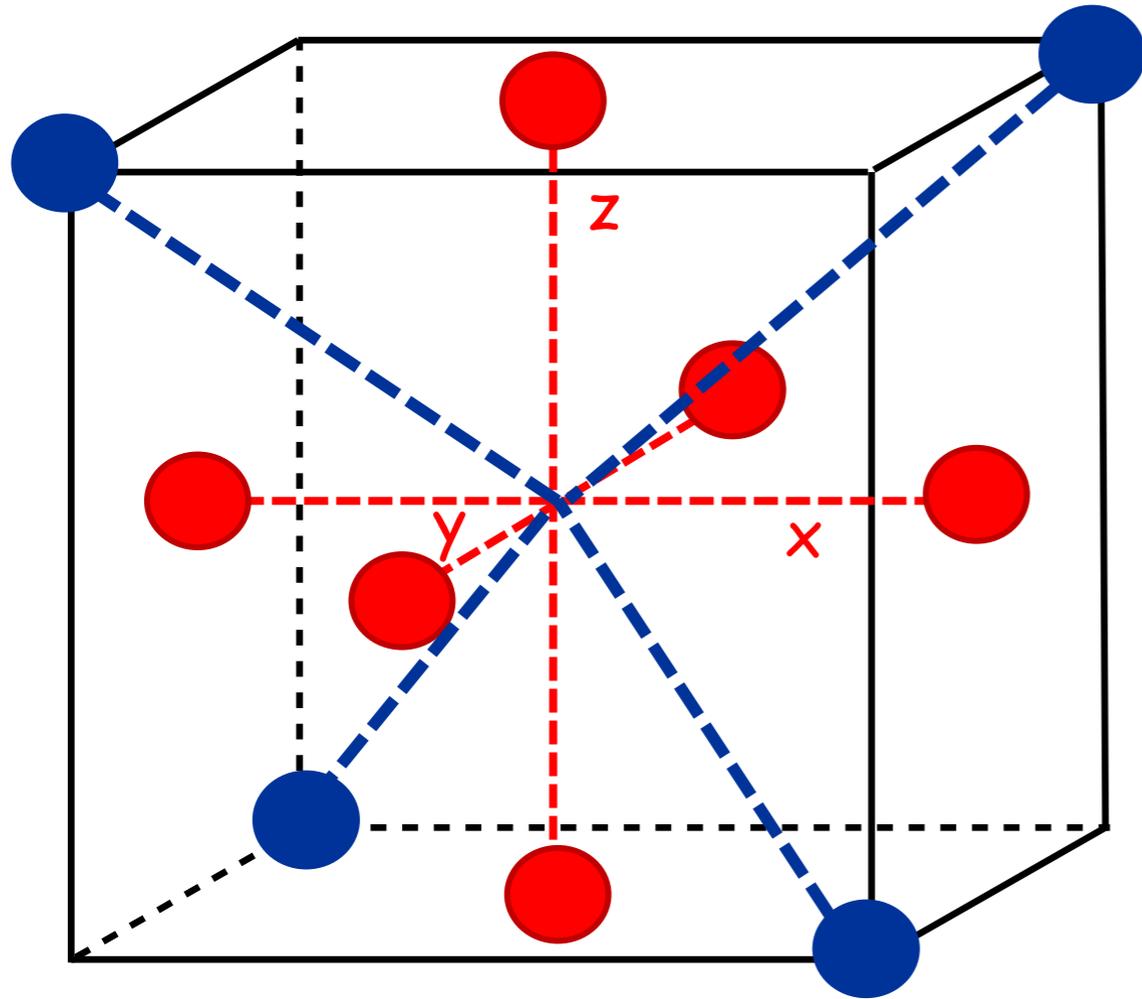
L. J. Thénard, *Considérations générales sur les couleurs, suivies d'un procédé pour préparer une couleur bleue aussi belle que l'outremer*, *Journal des Mines*, **1803**, 86, 128–136 (arseniate de cobalt + alumine).



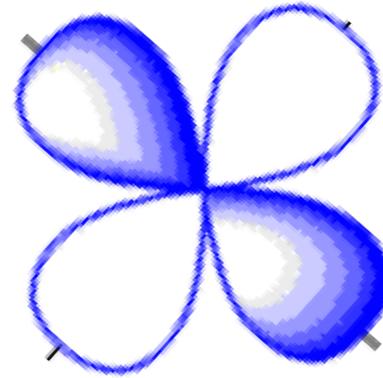
spinello: $\text{M}^{\text{II}}\text{O}_4(\text{tetraedrico}) \cdot \text{M}^{\text{III}}\text{O}_6(\text{ottaedrico})$



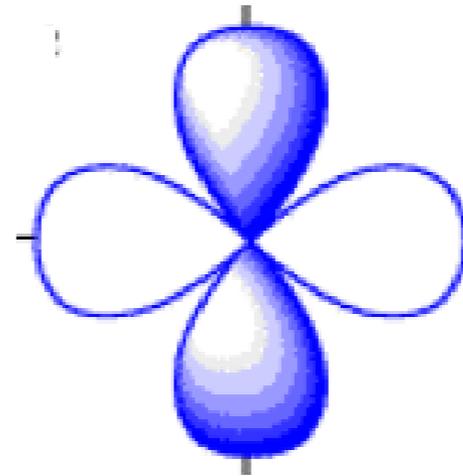
Il comportamento degli orbitali d in un campo di cariche tetraedrico



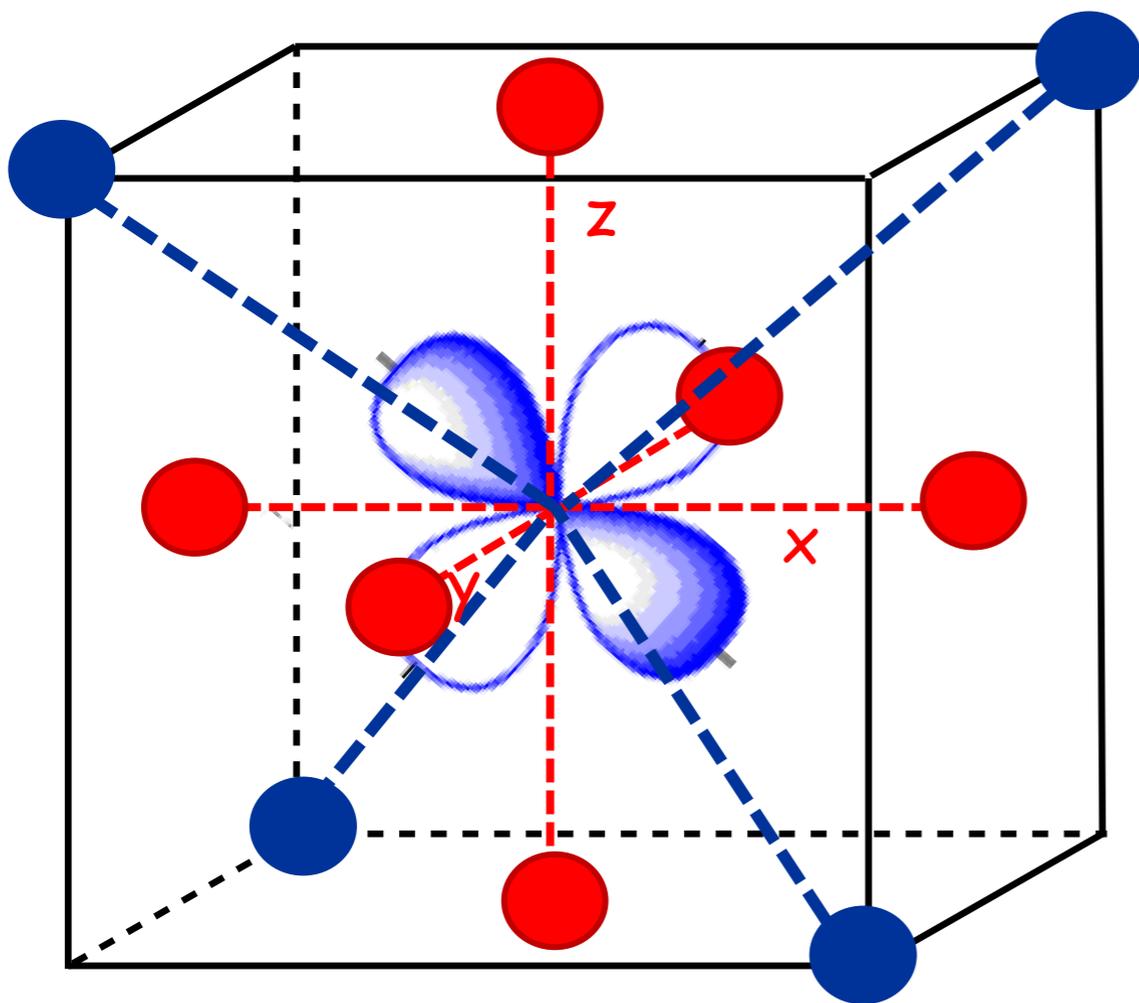
ottaedro
tetraedro



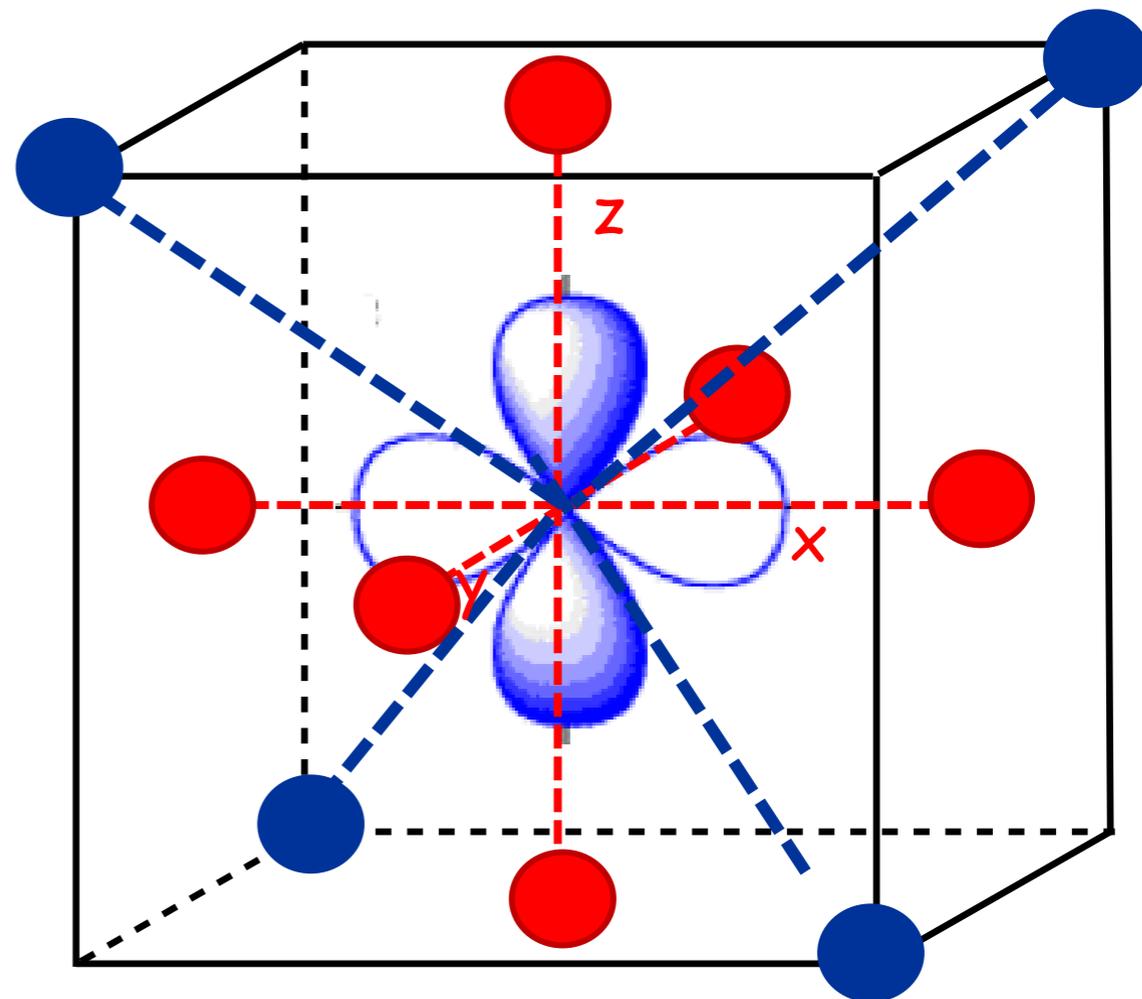
xz si destabilizza



x^2-y^2 si stabilizza



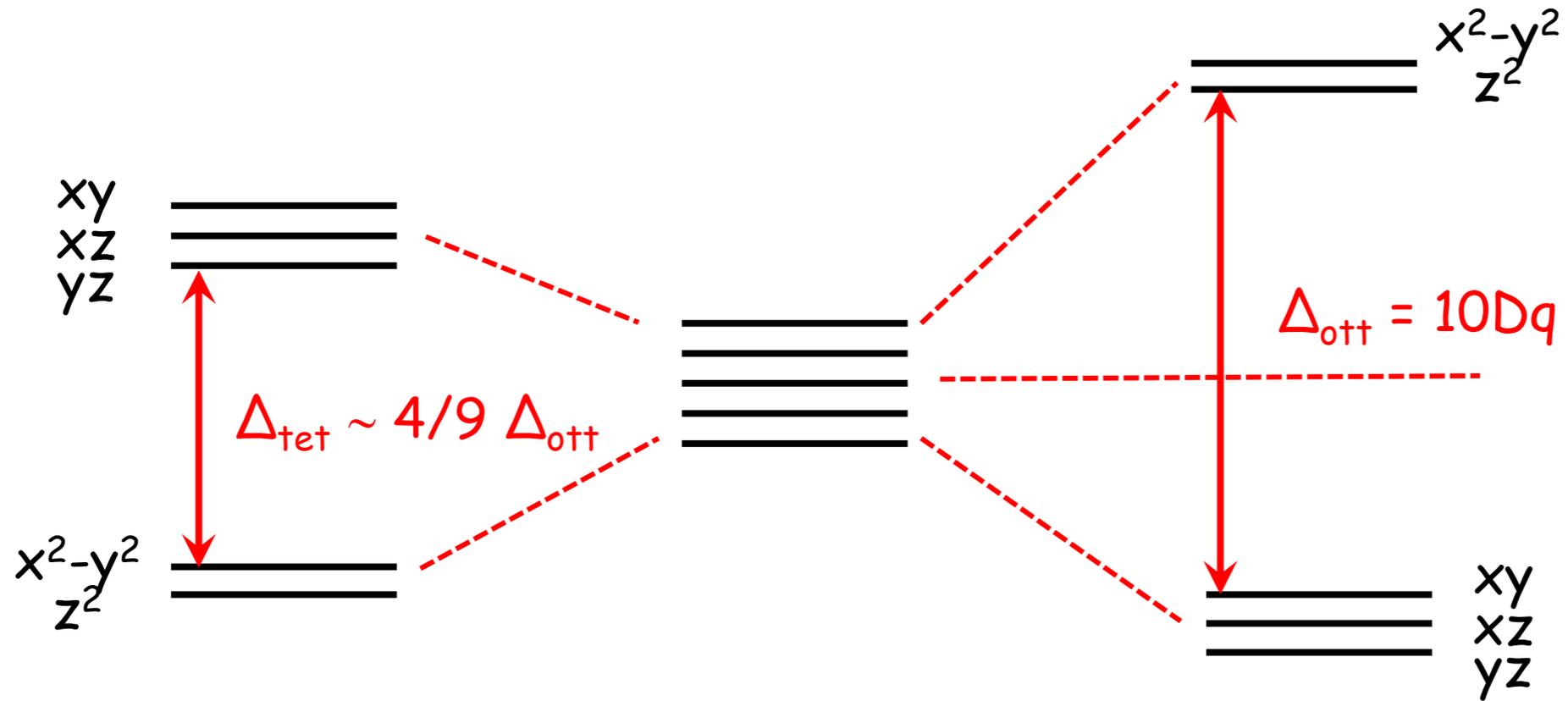
xz si destabilizza



x^2-y^2 si stabilizza

tetraedro

ottaedro



Dai valori delle energie (in unità Dq) riportate in tabella si può disegnare lo schema energetico degli orbitali d per complessi metallici di diverse geometrie.

C.N.	Structure	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
1	Linear ^c	5.14	-3.14	-3.14	0.57	0.57
2	Linear ^c	10.28	-6.28	-6.28	1.14	1.14
3	Trigonal ^d	-3.21	5.46	5.46	-3.86	-3.86
4	Tetrahedral	-2.67	-2.67	1.78	1.78	1.78
4	Square planar ^d	-4.28	12.28	2.28	-5.14	-5.14
5	Trigonal bipyramidal ^e	7.07	-0.82	-0.82	-2.72	-2.72
5	Square pyramidal ^e	0.86	9.14	-0.86	-4.57	-4.57
6	Octahedral	6.00	6.00	-4.00	-4.00	-4.00
6	Trigonal prismatic	0.96	-5.84	-5.84	5.36	5.36
7	Pentagonal bipyramidal	4.93	2.82	2.82	-5.28	-5.28
8	Cubic	-5.34	-5.34	3.56	3.56	3.56
8	Square antiprismatic	-5.34	-0.89	-0.89	3.56	3.56
9	$[\text{ReH}_9]^{2-}$ structure (see Fig. 12.40)	-2.25	-0.38	-0.38	1.51	1.51
12	Icosahedral	0.00	0.00	0.00	0.00	0.00

^a Zuckerman, J. J. *J. Chem. Educ.* **1965**, *42*, 315. Krishnamurthy, R.; Schaap, W. B. *J. Chem. Educ.* **1969**, *46*, 799. Used with permission.

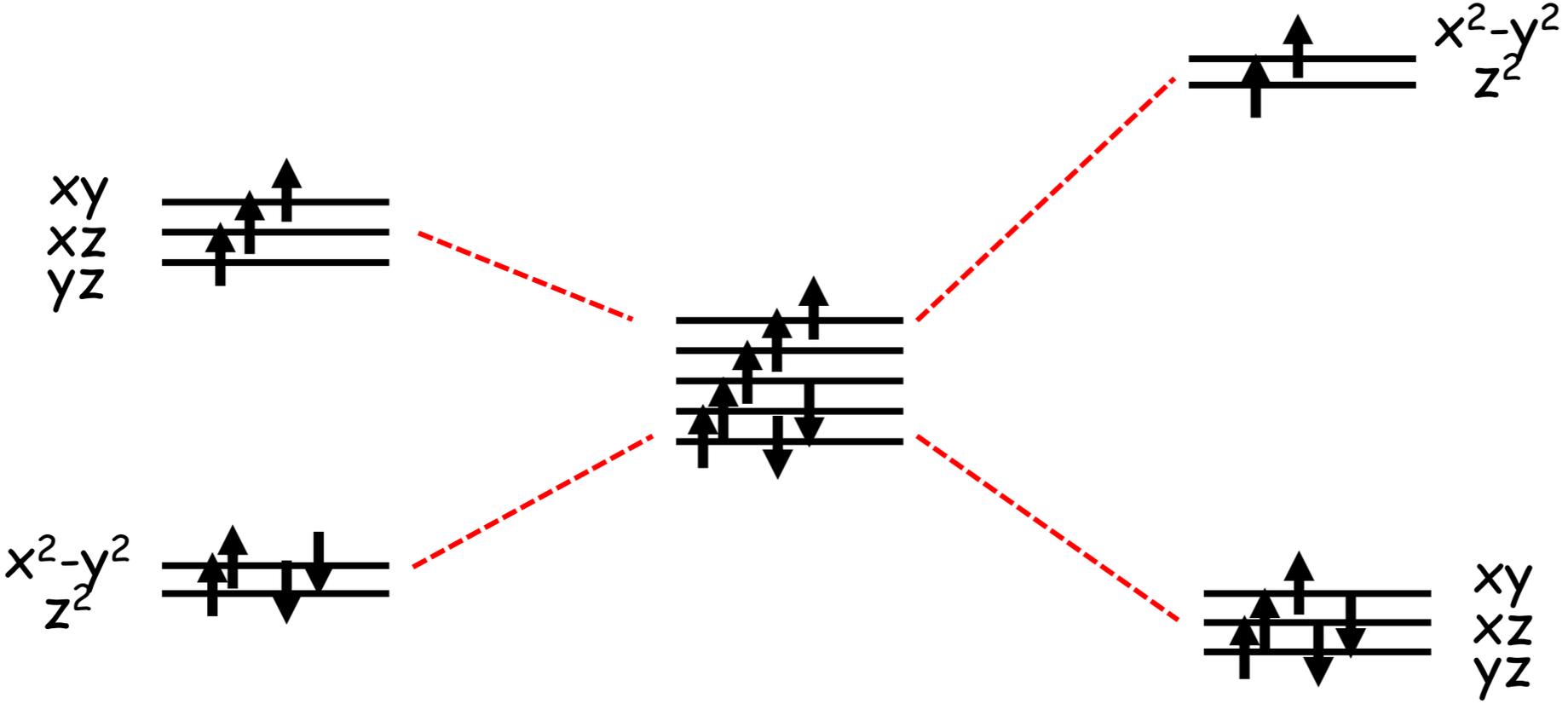
^b All energies are in Dq units; $10Dq = \Delta_o$.

Il rapporto $\Delta_t/\Delta_o = 4.45/10 = 0.445 \cong 0.444 = 4/9$ ($\Delta_t = \Delta$ in un campo tetraedrico). La serie

Co^{II}, d⁷

tetraedro

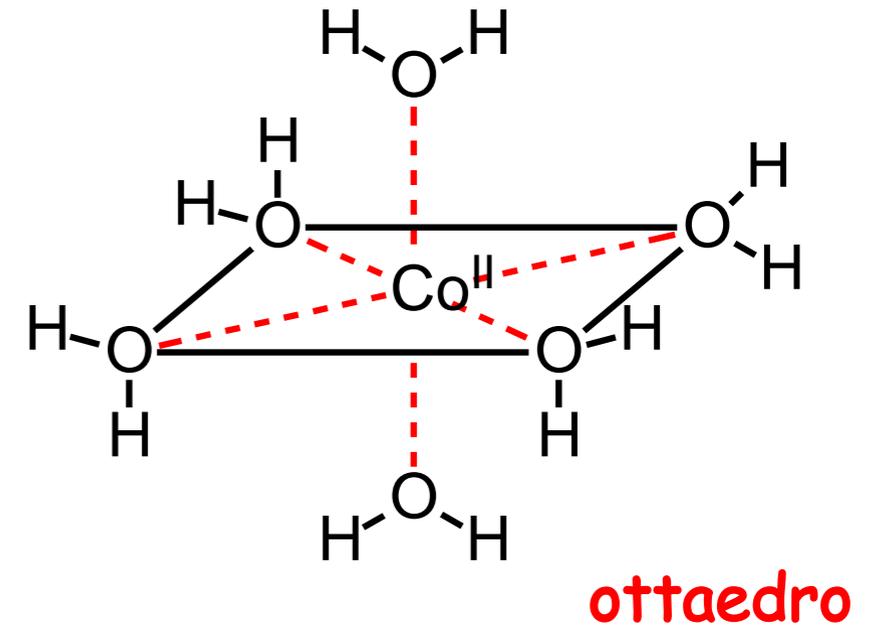
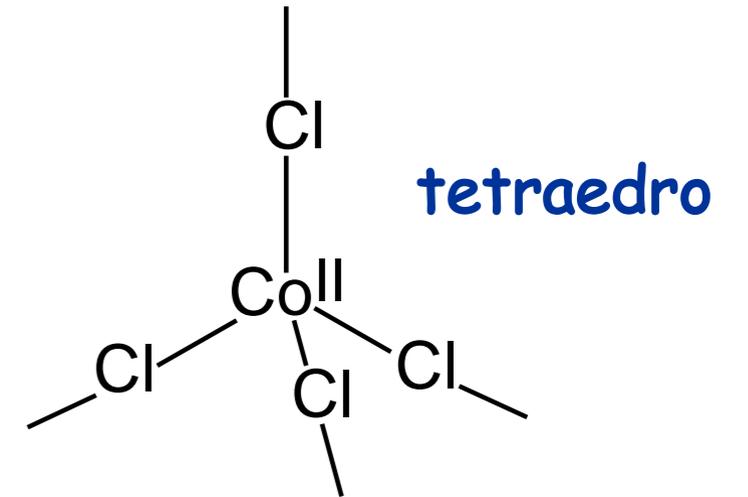
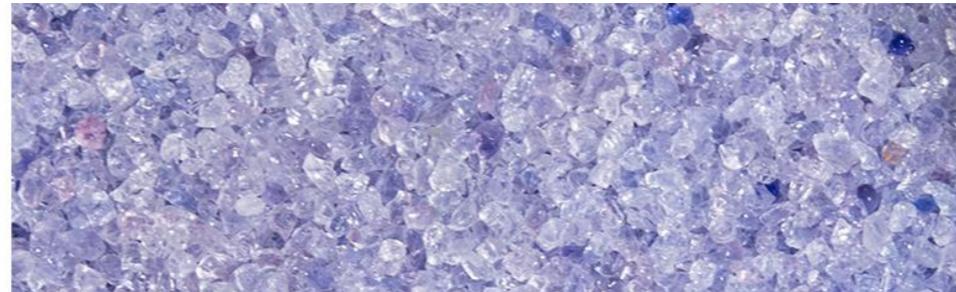
ottaedro

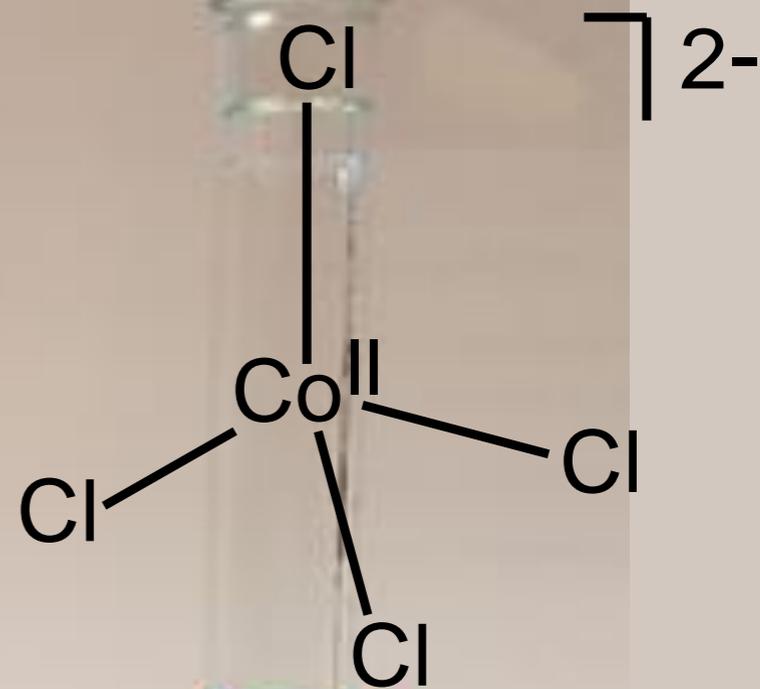
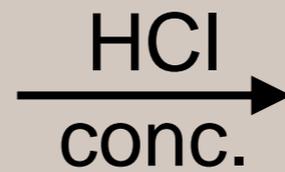
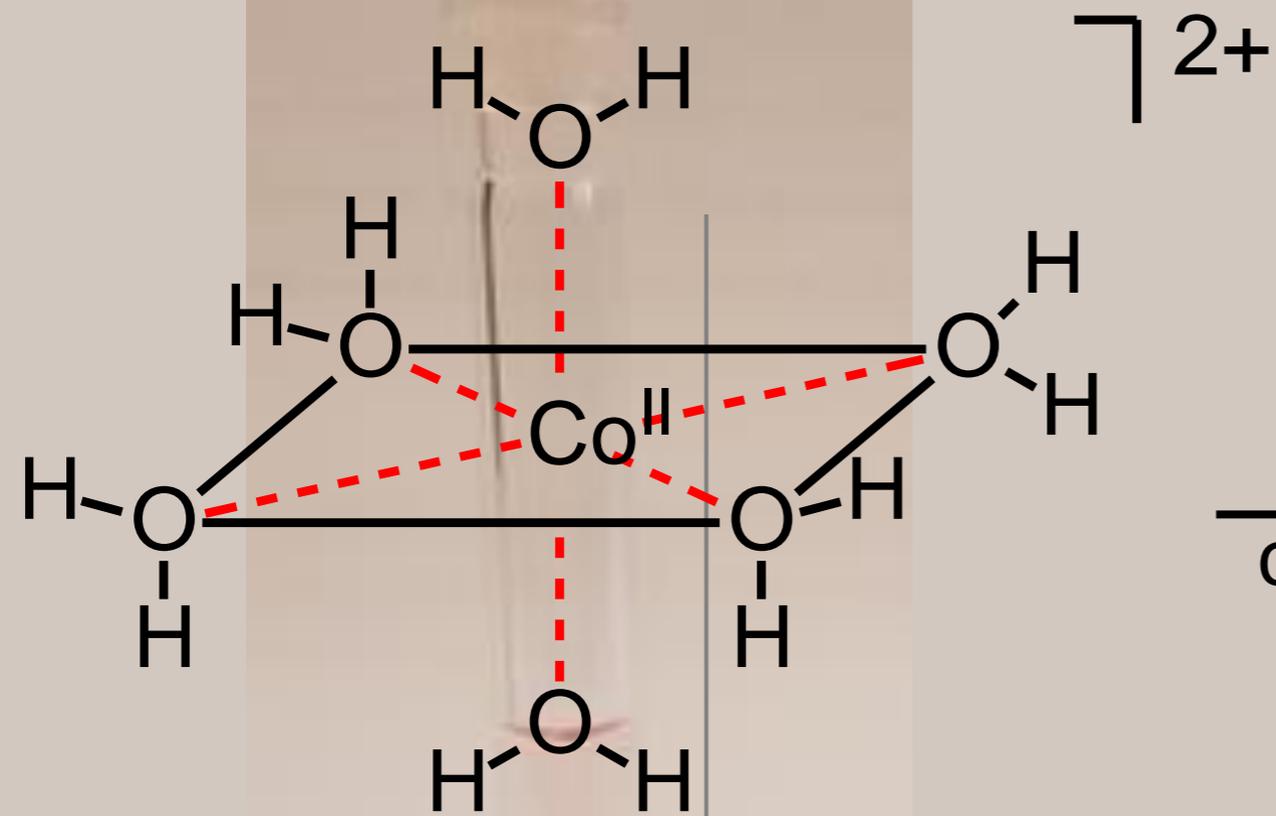




gel di silice

indicatore:
 $\text{CoCl}_2/\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$





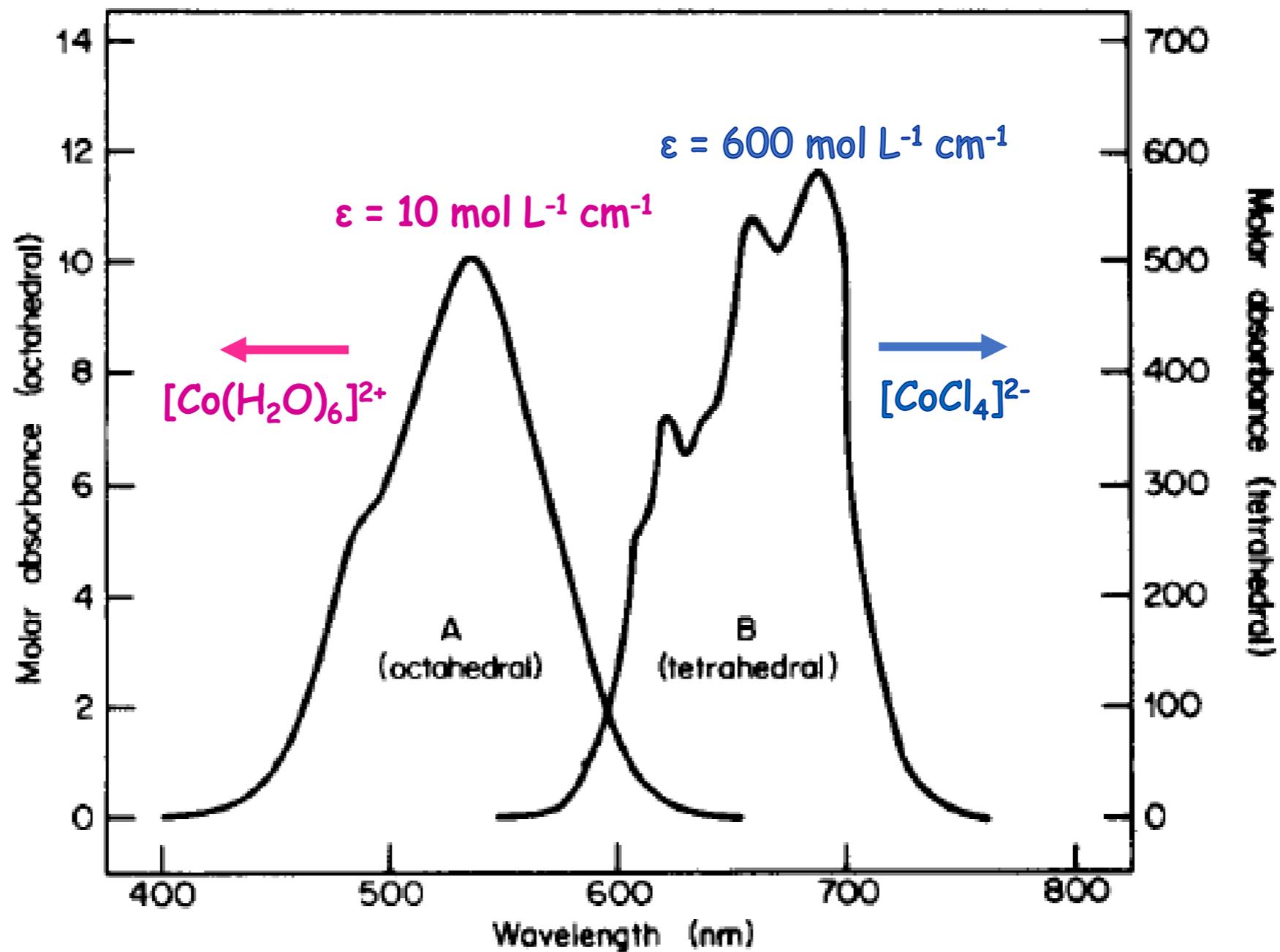
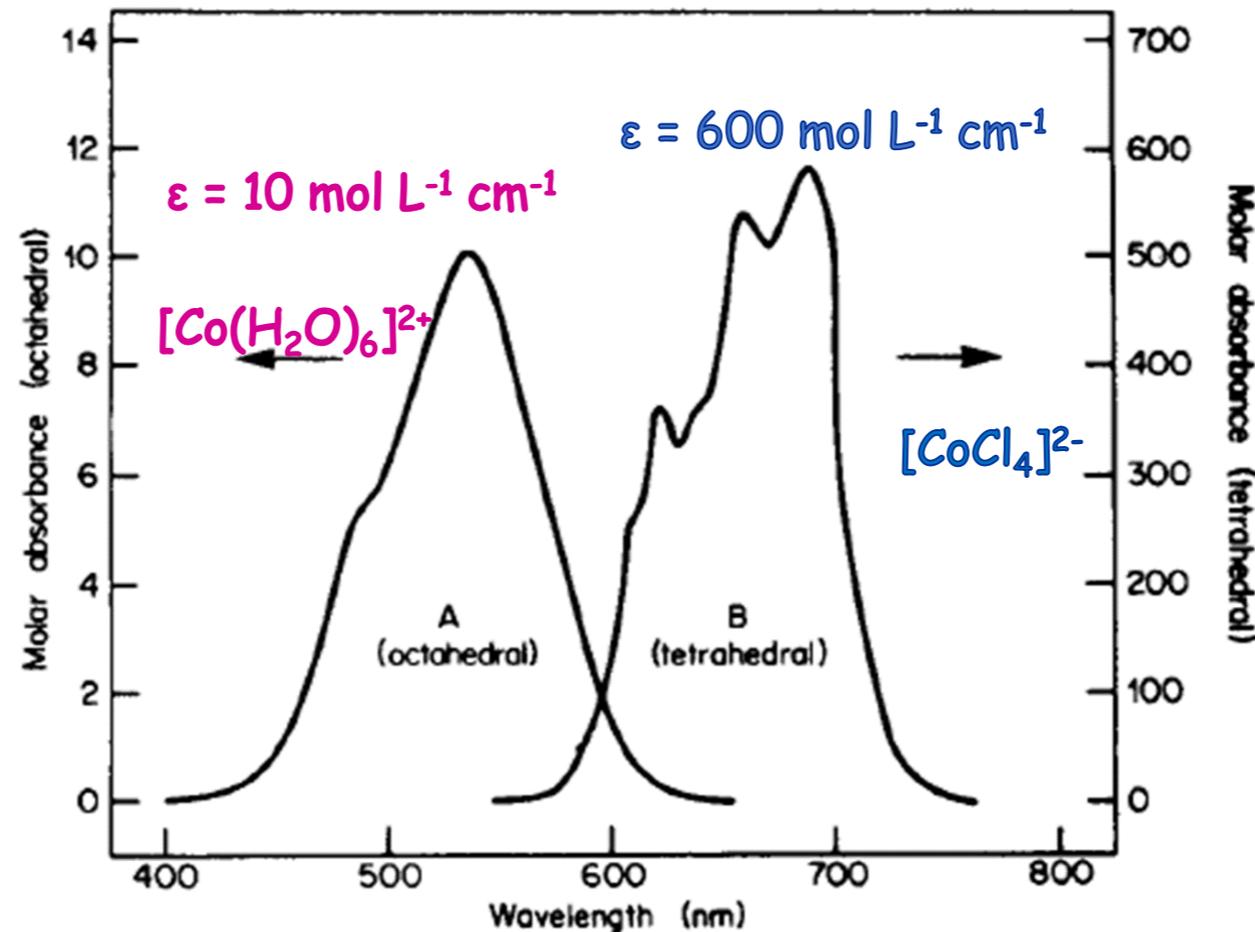


Fig. 21-F-3. The visible spectra of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (curve A) and $[\text{CoCl}_4]^{2-}$ (curve B).

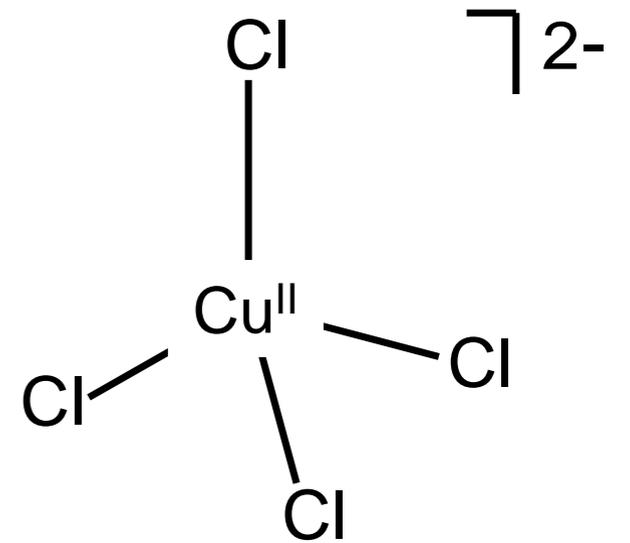
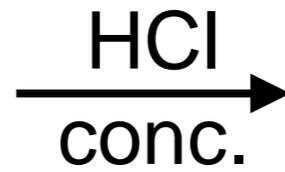
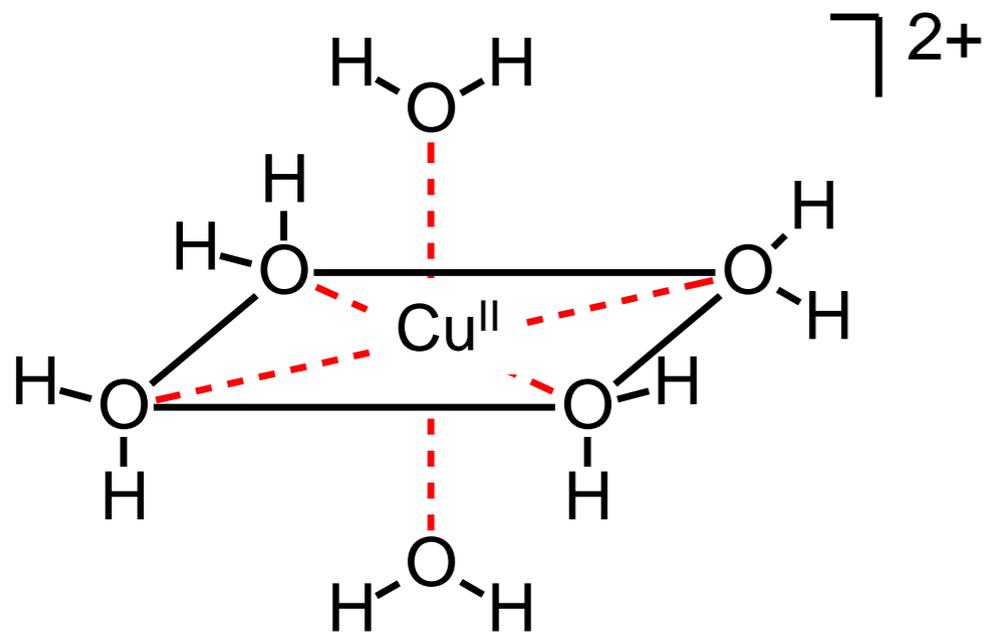
L'intensità del colore e le regole di selezione

2. **La regola di Laporte.** Le transizioni $s \rightarrow s$, $p \rightarrow p$, $d \rightarrow d$ e $f \rightarrow f$ sono formalmente vietate se il complesso metallico ha un centro di simmetria (*Laporte forbidden*). Sono permesse se il complesso non è centrosimmetrico.

l'ottaedro ha un centro di simmetria, il tetraedro no: per questo $[\text{CoCl}_4]^{2-}$ ha un colore molto più intenso di $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$



Cu^{2+} ha un comportamento simile:

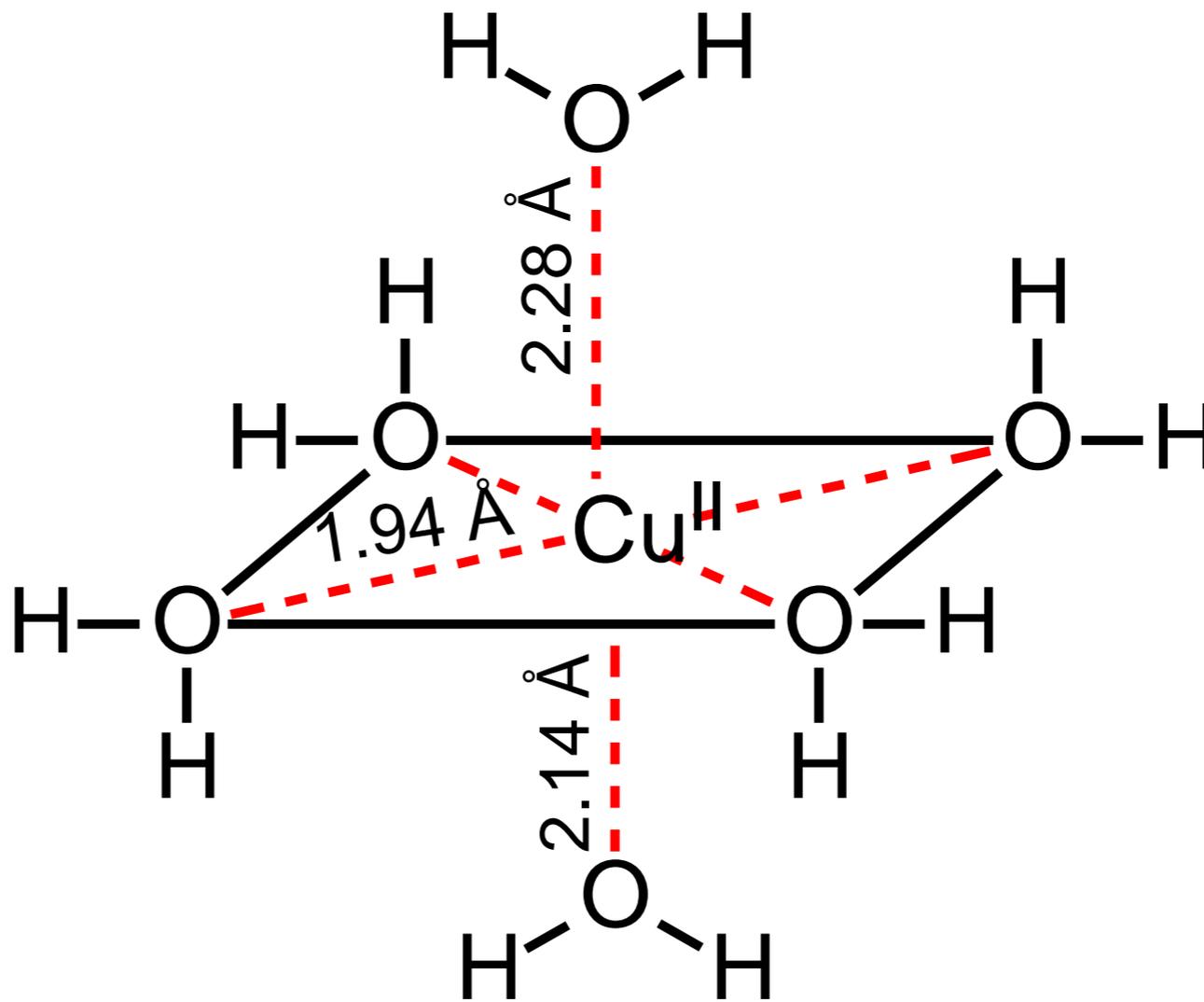




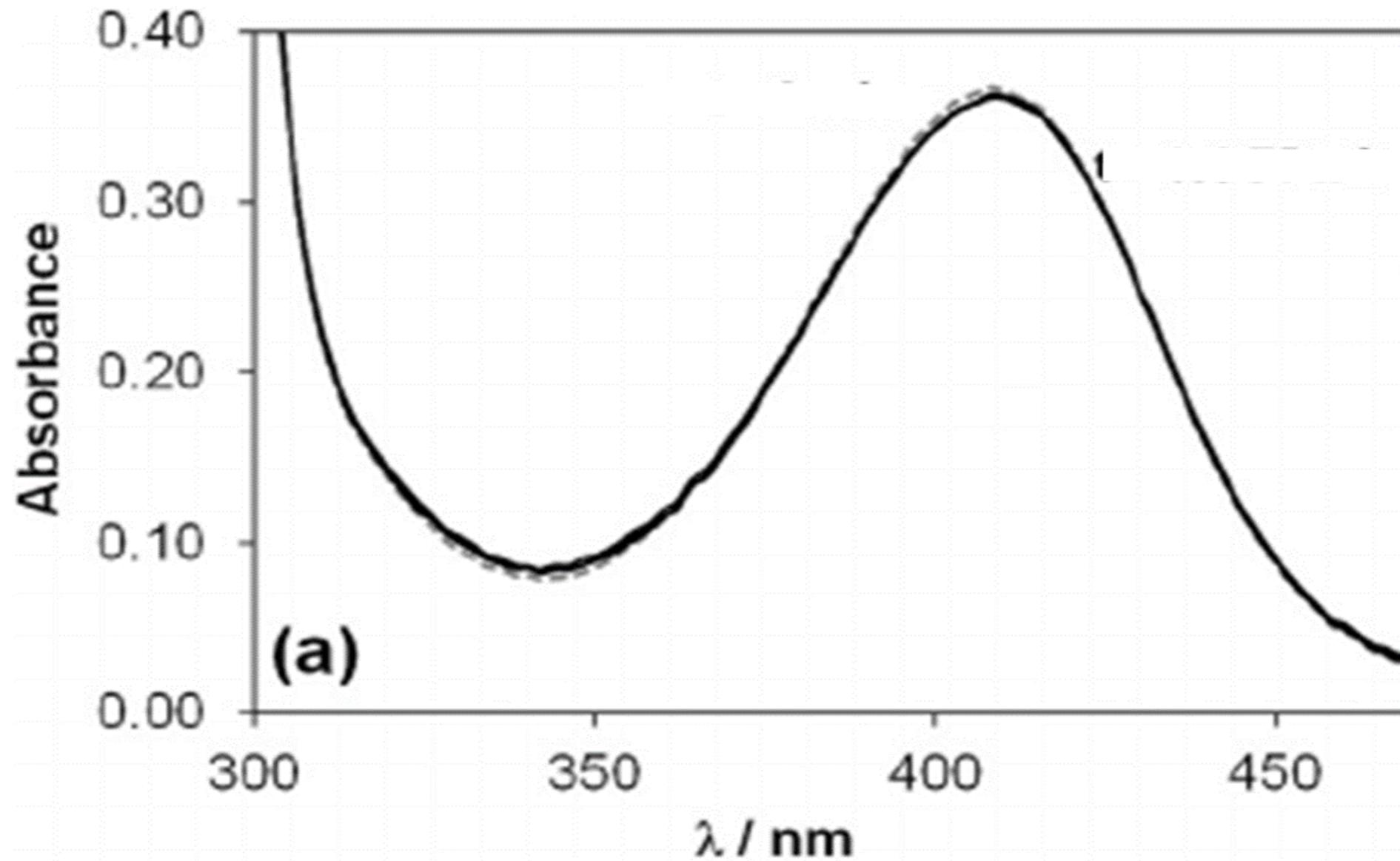
Otto Laporte
(1902-1971)

La presenza di bande d-d, quantunque deboli, anche in complessi metallici centro-simmetrici deriva dal fatto che il centro di simmetria di questi cromofori è perturbato per vari motivi. Per esempio dalle vibrazioni termiche. I complessi quindi non sono sempre perfettamente simmetrici. Le transizioni che si verificano come risultato di una vibrazione asimmetrica sono chiamate **transizioni vibroniche** (= **vibrazionali + elettroniche**).

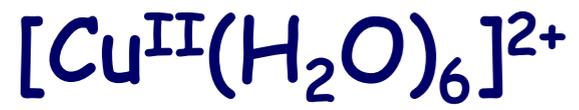
Anche l'aquaione Cu^{2+} ha una struttura ottaedrica distorta



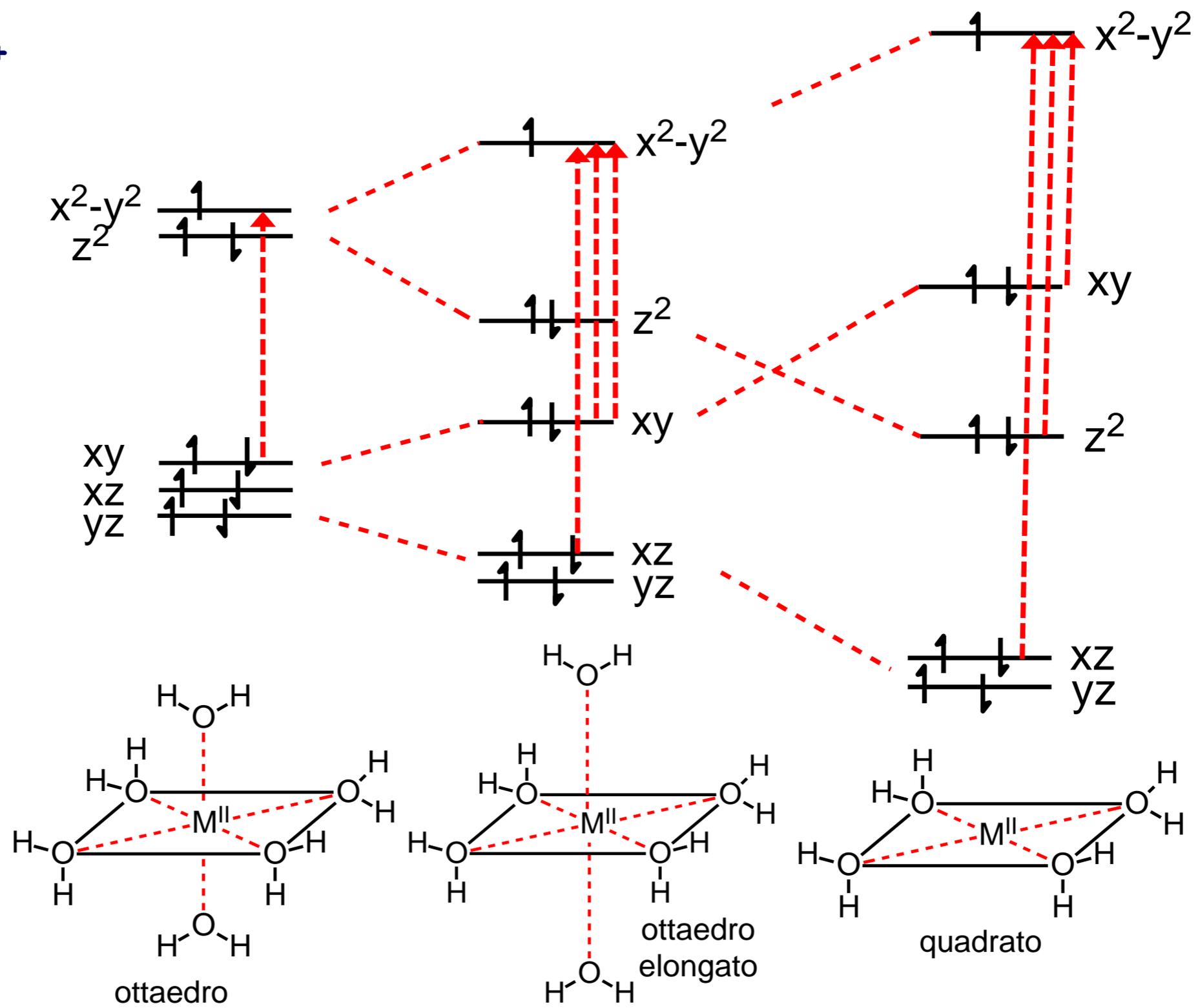
P. Frank, M. Benfatto, M. Qayyum, $[\text{Cu}(\text{aq})]^{2+}$ is structurally plastic and the axially elongated octahedron goes missing, *J. Chem. Phys.* **2018**, *148*, 204302.



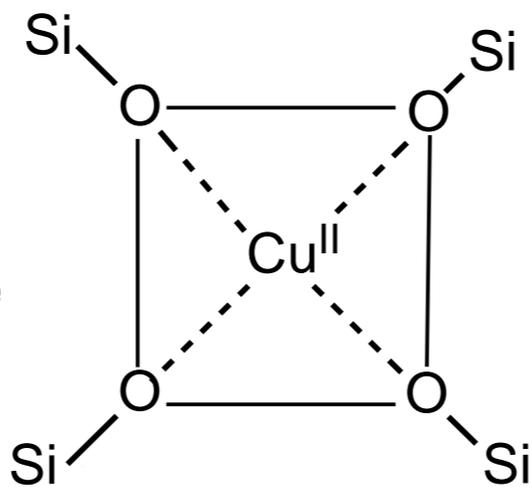
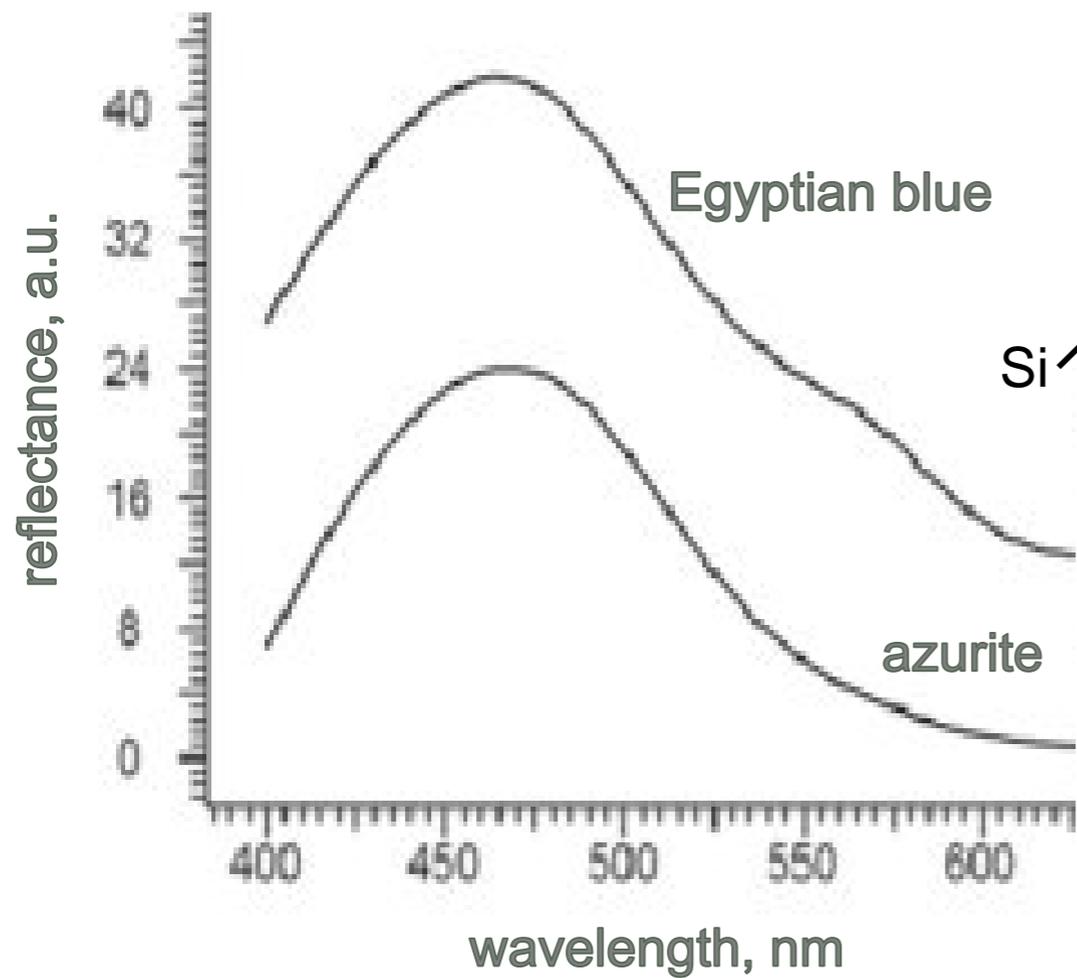
La banda di assorbimento centrata a 405 nm è l'involuppo di 3 distinte transizioni



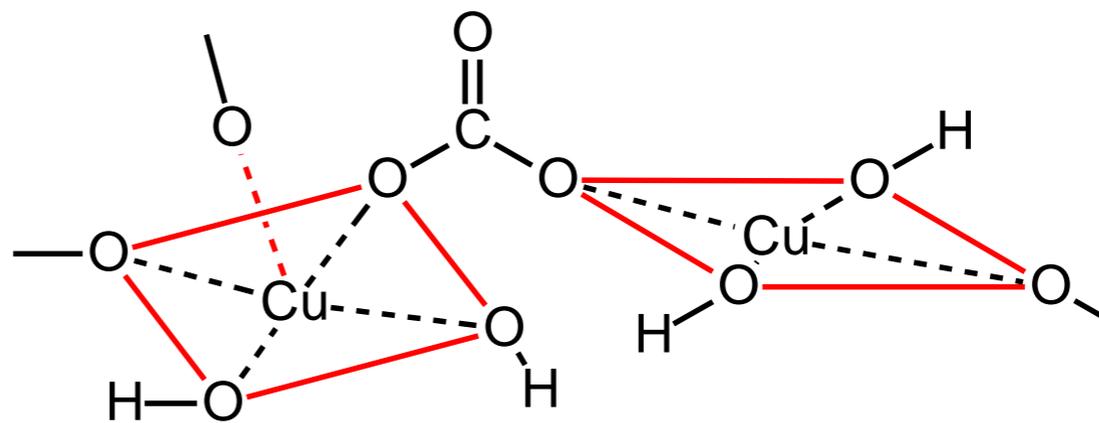
ottaedro
 elongato



Variazioni della geometria di coordinazione (ottaedrica, piramidale quadrata, quadrata) e degli atomi donatori (ossigeni di Si-O, C-O, OH) determinano apprezzabili variazioni del colore.



quadrata



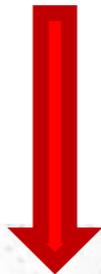
piramidale
quadrata

quadrata





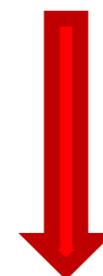
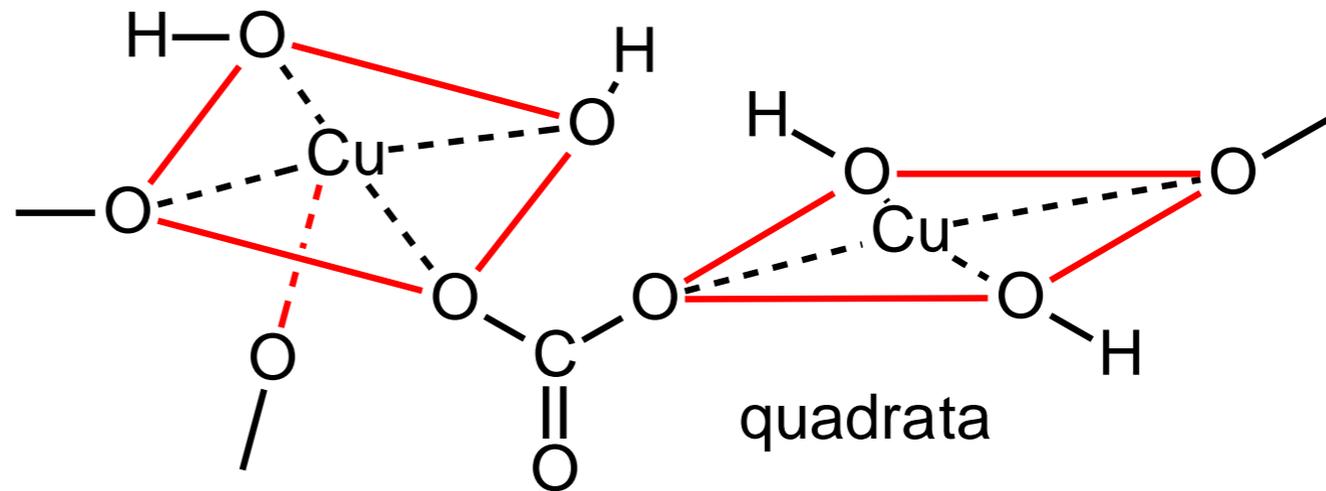
azzurrite



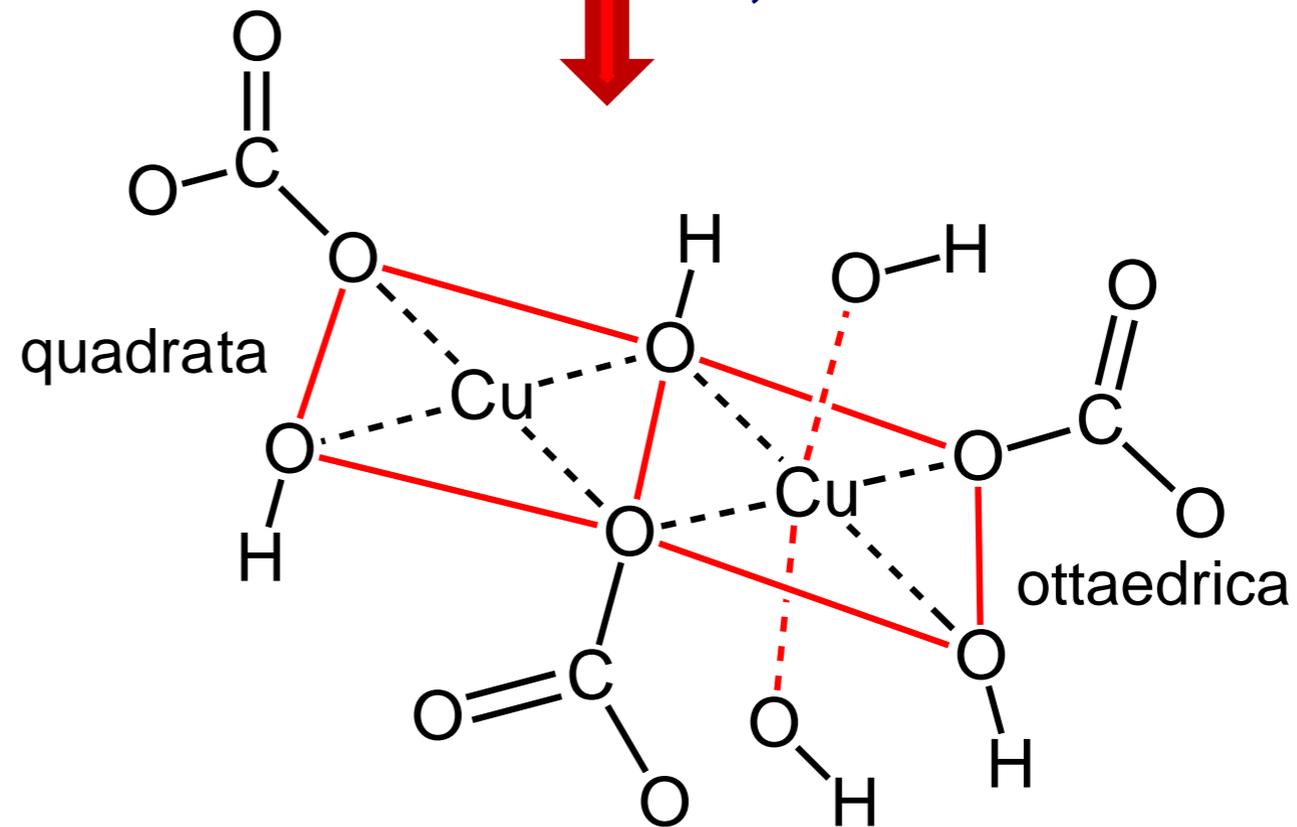
$\Delta T, h\nu$

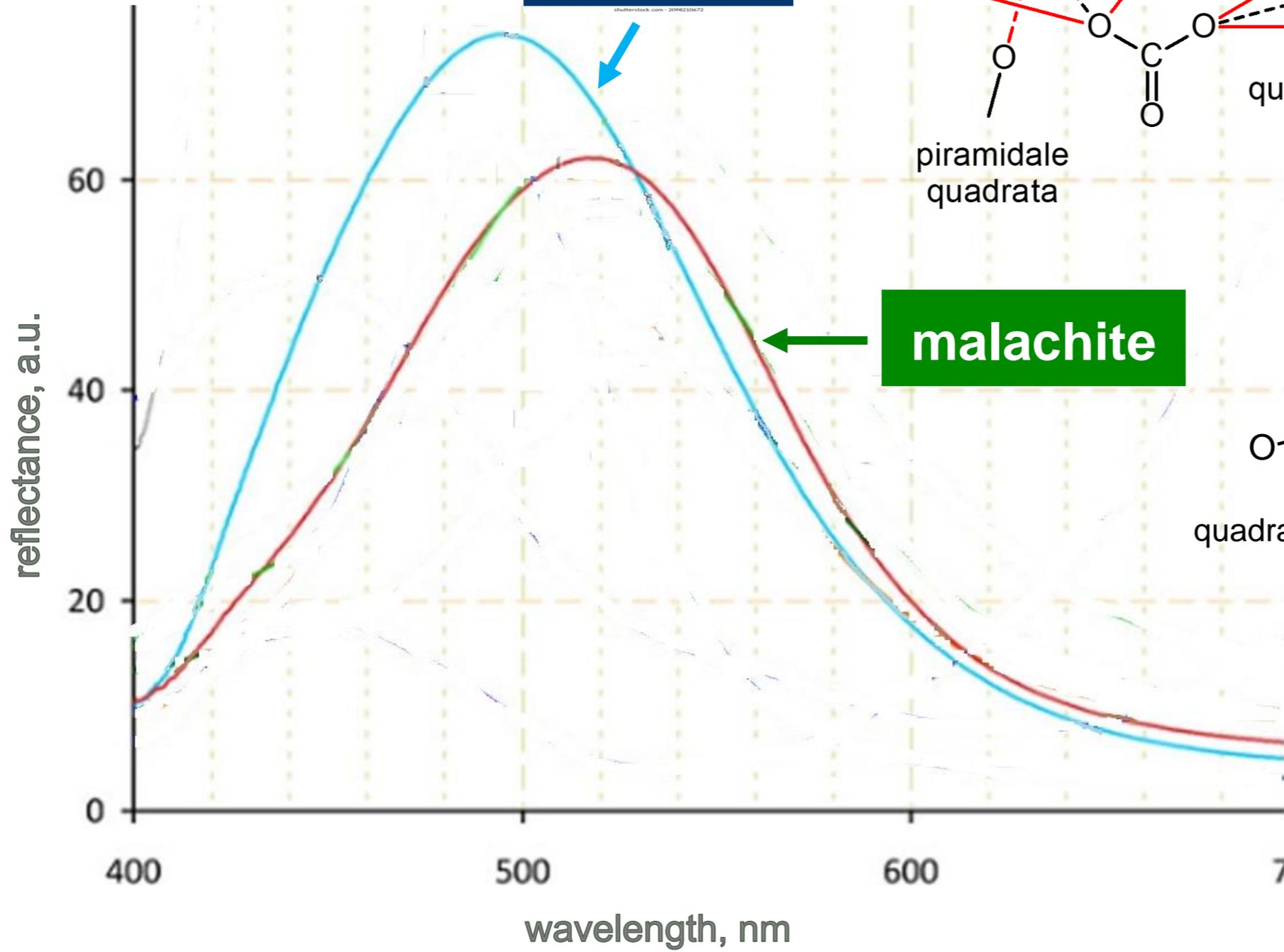


malachite

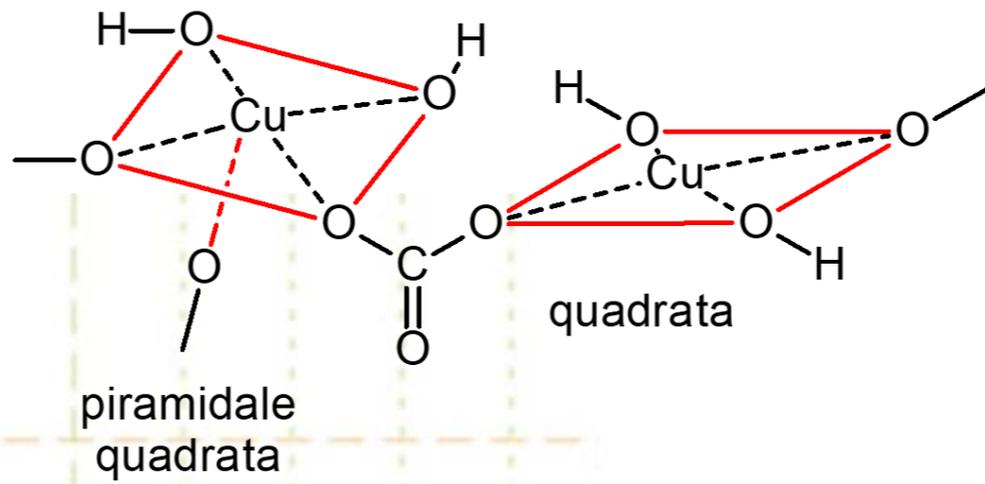


$\Delta T, h\nu$

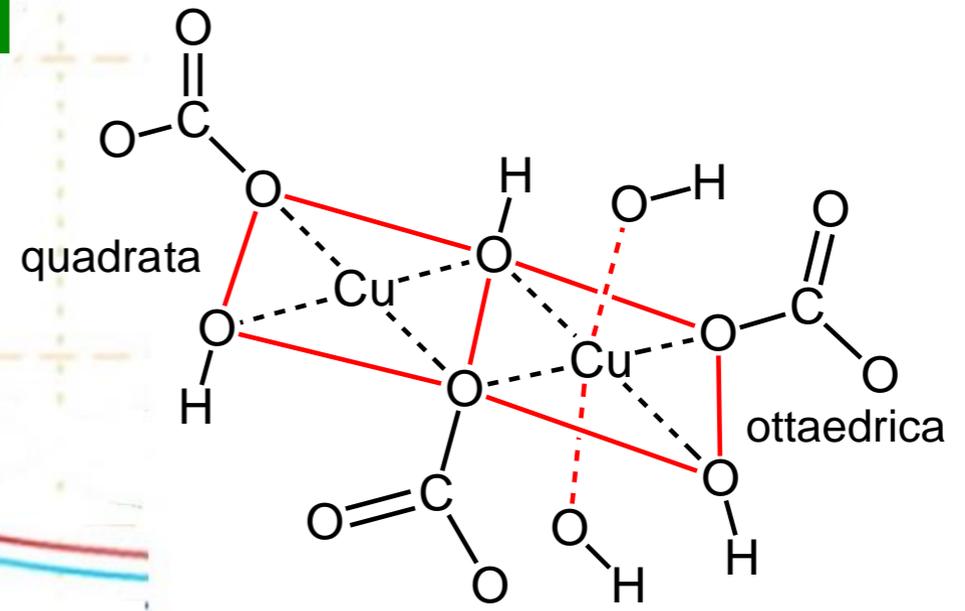




azzurrite



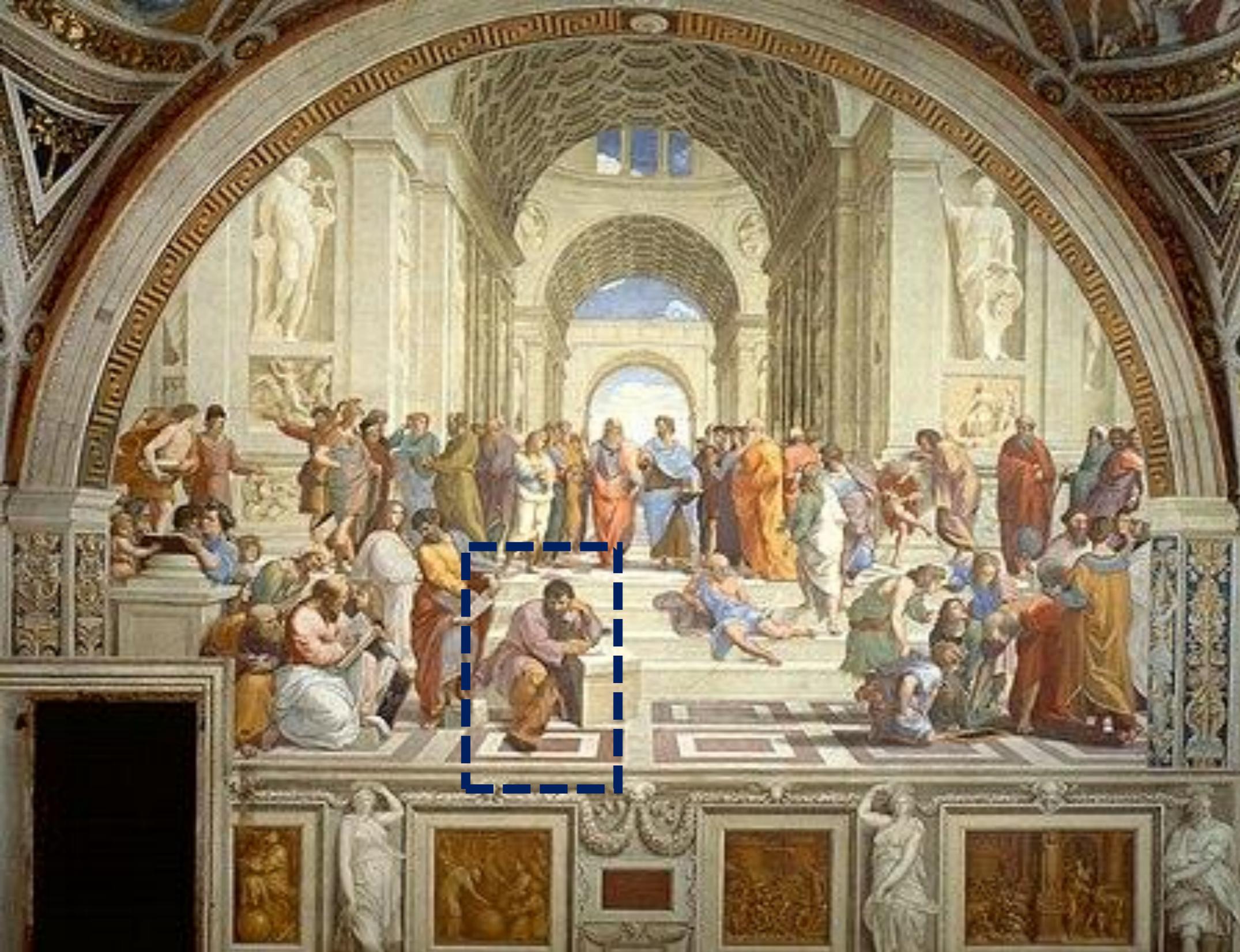
malachite





Ah, se la chimica
avesse seguito il
progresso della
pittura...

Giorgio Vasari (1511-1574)



Raffaello Sanzio,
La Scuola di Atene (1509-1511)
affresco, 5,0 × 7,7 m,
Musei Vaticani, Città del
Vaticano



ORA VADO IN LABORATORIO E
SINTETIZZO UN COMPLESSO DI
RAME(II) COMPLETAMENTE PRIVO DI
SIMMETRIA, SAI CHE BLU BRILLANTE...
ALTRO CHE OLTREMARE!

Michelangelo

Raffaello Sanzio, La Scuola di Atene (1509-1511),
particolare: Eraclito (ispirato a Michelangelo Buonarroti).