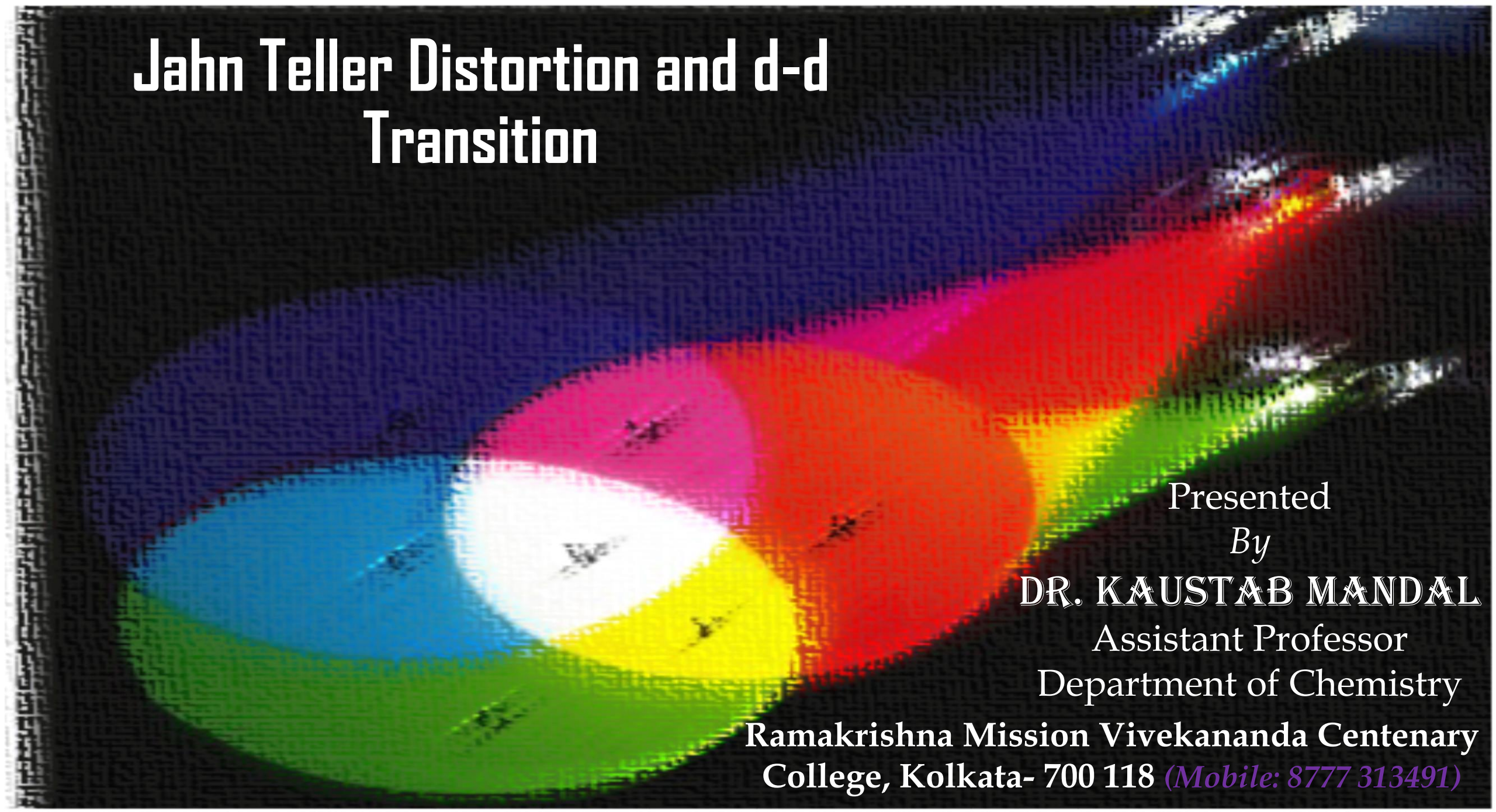
Jahn Teller Distortion and d-d Transition



Presented
By
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Assistant Professor
Department of Chemistry
Ramakrishna Mission Vivekananda Centenary College, Kolkata- 700 118 *(Mobile: 8777 313491)*

PREVIOUS CLASSES ON BONDING OF COORDINATION COMPOUNDS.

Class 1:

Coordination Compound in the Light of Valence Bond Theory.

Class 2:

Coordination Compound in the Light of Crystal Field Theory.

Present Class:

Jahn Teller Distortion and d-d Transition.

JAHN-TELLER THEOREM

Hermann Arthur Jahn
(31.05.1907 to 24.10.1979)

FIRST REPORTED IN 1937.

Edward Teller
(15.01.1908 to 09.09.2003)

JAHN-TELLER THEOREM

Hermann Arthur Jahn
(31.05.1907 to 24.10.1979)

Hermann Arthur Jahn received Bachelor of Science degree in Chemistry at University College, London in 1928. He received PhD in 1935 under the supervision of **Werner Heisenberg** at the University of Leipzig.

JAHN-TELLER THEOREM

Edward Teller is known colloquially as "**the father of the hydrogen bomb**". He made numerous contributions to nuclear and molecular physics, spectroscopy and surface physics. In chemistry, he is associated with **Jahn–Teller** effect and the Brunauer–Emmett–Teller (**BET**) theory.

Edward Teller
(15.01.1908 to 09.09.2003)

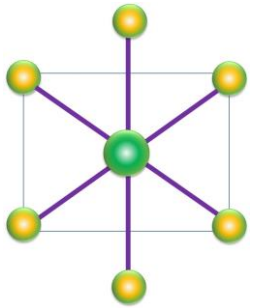
JAHN-TELLER THEOREM

John Hasbrouck Van Vleck
(3.03.1899–27.10.1980)

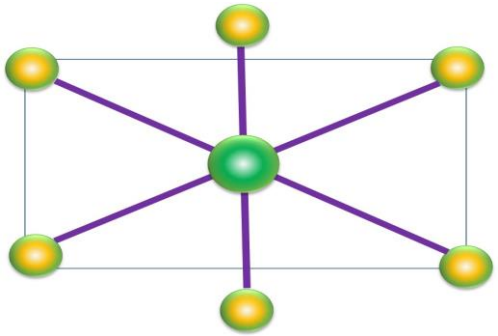
John Hasbrouck Van Vleck extended the Jahn–Teller theorem to complex ions in crystals in 1939.

DISTORTION IN OCTAHEDRAL COMPLEXES: TETRAGONAL DISTORTION

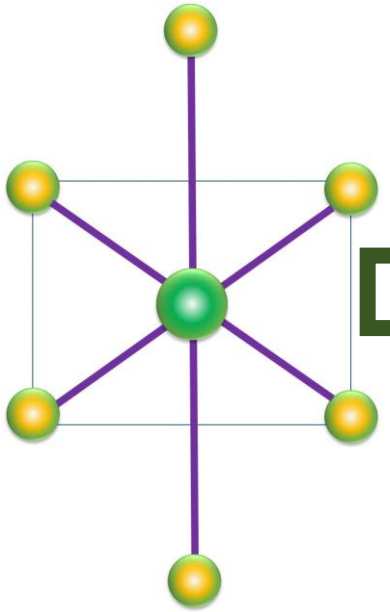
- Symmetrical octahedral field: All metal-ligand bond distances are equal.



- Non-symmetrical octahedral field: All metal-ligand bond distances are not equal.



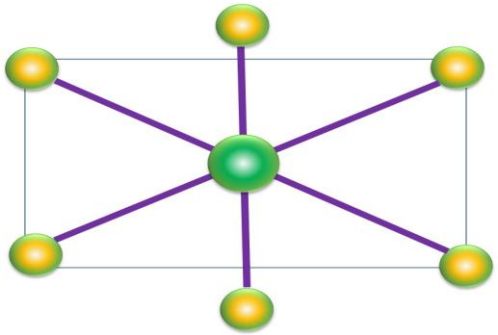
Tetragonal Compression (Z-in situation)



Tetragonal Elongation (Z-out situation)

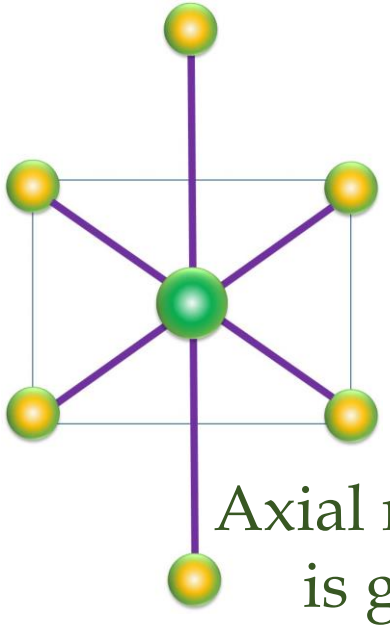
DISTORTION OF OCTAHEDRAL COMPLEXES: TETRAGONAL DISTORTION

- Non-symmetrical octahedral field: All metal-ligand bond distances are not equal.



Tetragonal Compression (Z-in situation)

Axial metal-ligand bond length is less than equatorial metal-ligand bond length.

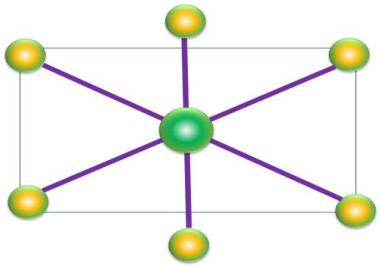


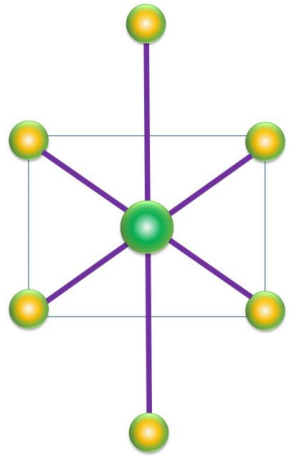
Tetragonal Elongation (Z-out situation)

Axial metal-ligand bond length is greater than equatorial metal-ligand bond length.

Octahedral complexes which are not perfect octahedron, are considered as tetragonally distorted.

SPLITTING OF d ORBITALS IN TETRAGONAL DISTORTION





d_{z^2} $+\frac{1}{2}\delta_2$ $-\frac{1}{2}\delta_2$ $d_{(x^2-y^2)}$ δ_2

e_g

d_{z^2} , $d_{(x^2-y^2)}$

$d_{(x^2-y^2)}$ $+\frac{1}{2}\delta_2$ $-\frac{1}{2}\delta_2$ d_{z^2} δ_2

d_{yz}, d_{xz} $+1/3\,\delta_1$ $-\frac{2}{3}\delta_1$ d_{xy} δ_1

t_{2g}

d_{yz}, d_{xy}, d_{xz}

d_{xy} $+\frac{2}{3}\delta_1$ $-1/3\,\delta_1$ d_{yz}, d_{xz} δ_1

Tetragonal Compression | Perfect Octahedral | Tetragonal Elongation

δ_2 is very much greater than δ_1

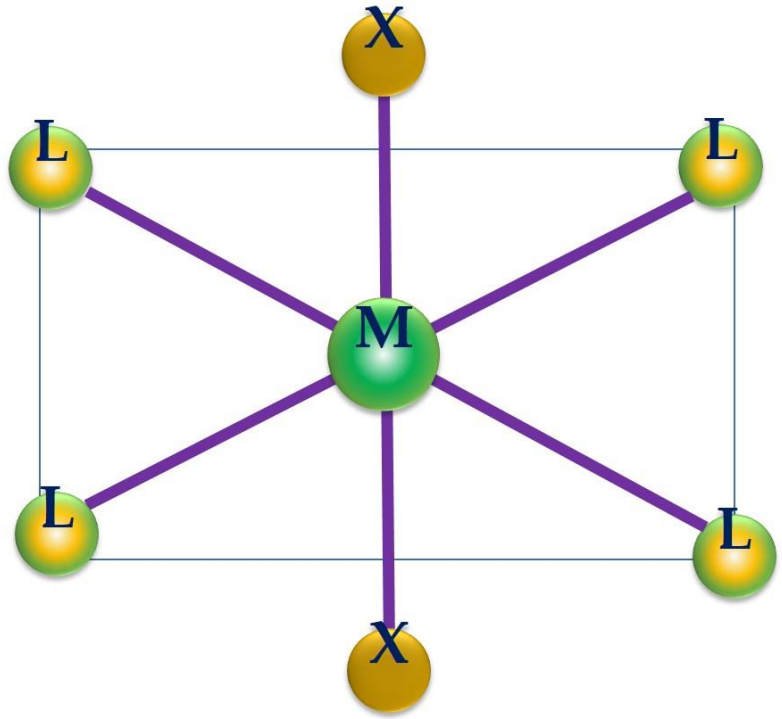
WHY TETRAGONAL DISTORTION?

Case I : X is stronger ligand than L.

Axial M-X bond lengths are less than equatorial M-L bond lengths. It causes **Tetragonal Compression.**

Case II : X is weaker ligand than L.

Axial M-X bond lengths are higher than equatorial M-L bond lengths. It causes **Tetragonal Elongation.**



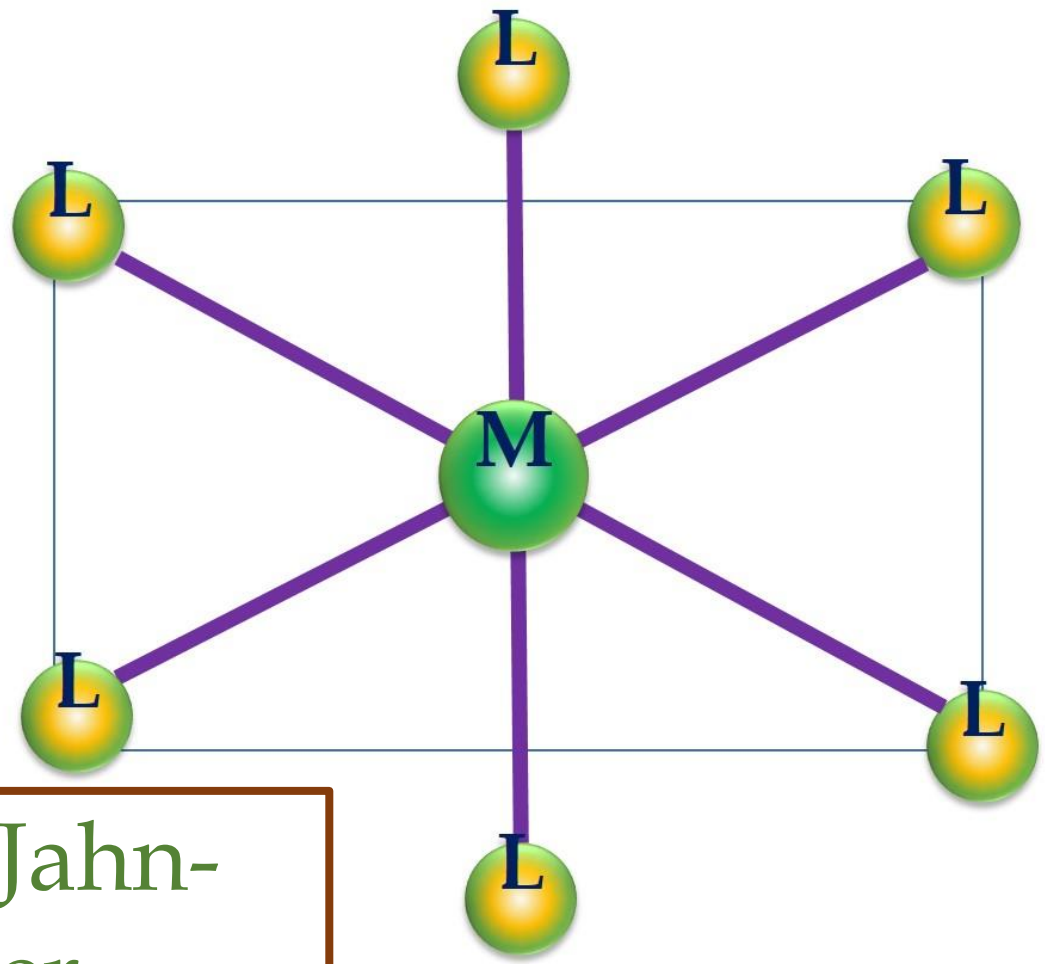
ML_4X_2 type octahedral complex

WHY TETRAGONAL DISTORTION?

DKM

Case III: All the six ligands are equivalent.

Tetragonal Compression and Tetragonal Elongation occur due to **Jahn-Teller distortion.**

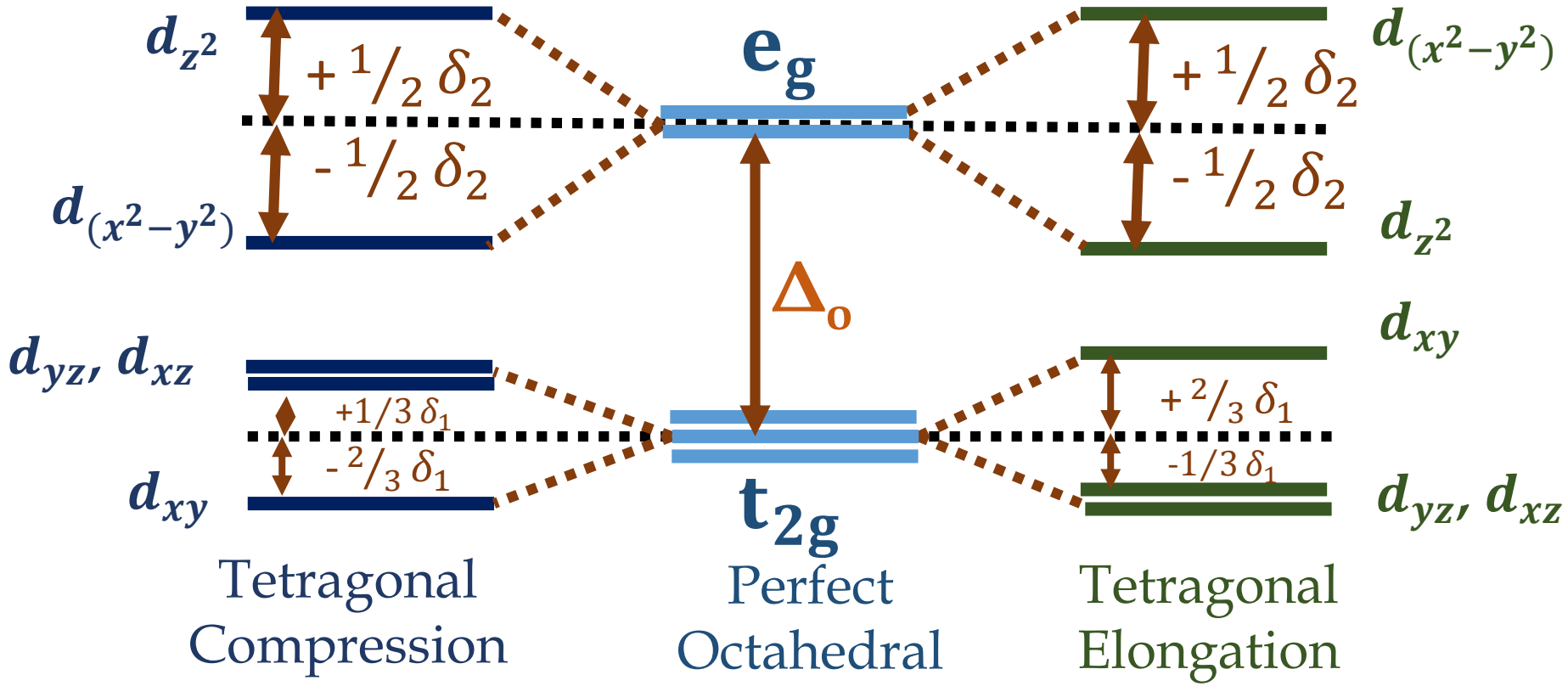


ML_6 type octahedral complex

All tetragonal distortions are not Jahn-Teller distortion, but all Jahn-Teller distortions are tetragonal distortion.

JAHN-TELLER THEOREM

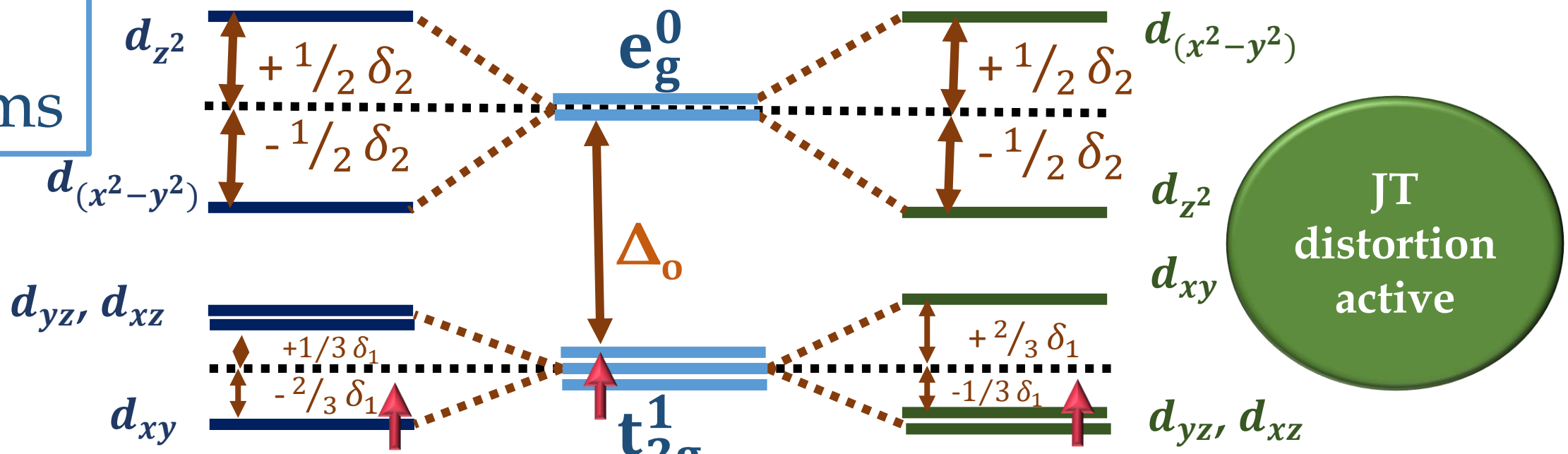
Any non-linear molecule in degenerate electronic configuration undergoes distortion to remove degeneracy and attain low energy.



JAHN-TELLER DISTORTION

DKM

d^1 Systems



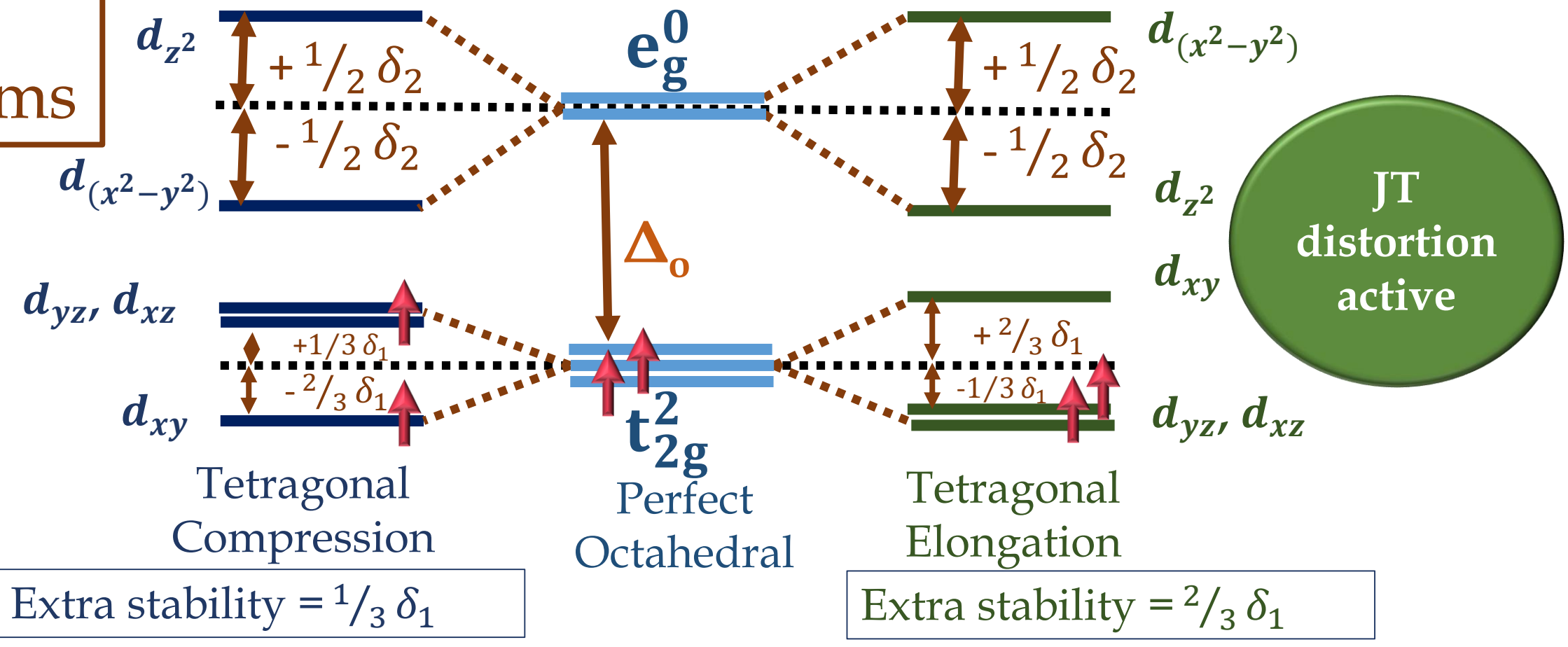
Extra stability = $^2/_3\,\delta_1$

Extra stability = $^1/_3\,\delta_1$

Tetragonal compression is favorable. δ_2 is very much greater than δ_1. The Jahn-Teller distortion due to uneven fill of t_{2g} orbitals is **weak tetragonal distortion**.

JAHN-TELLER DISTORTION

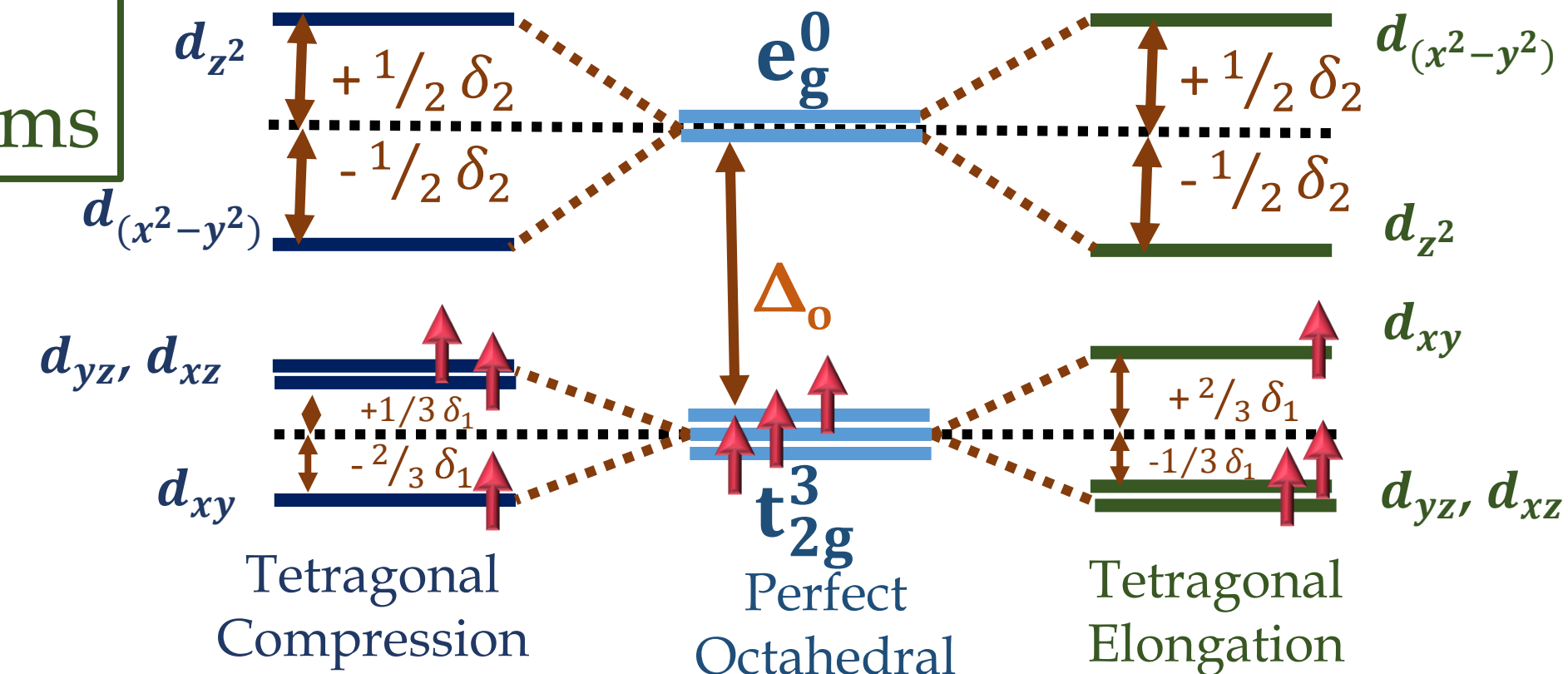
d^2 Systems



Tetragonal elongation is favorable and it is **weak tetragonal distortion**.

JAHN-TELLER DISTORTION

d^3 Systems



Tetragonal Compression

Perfect Octahedral

Tetragonal Elongation

Extra stability =0

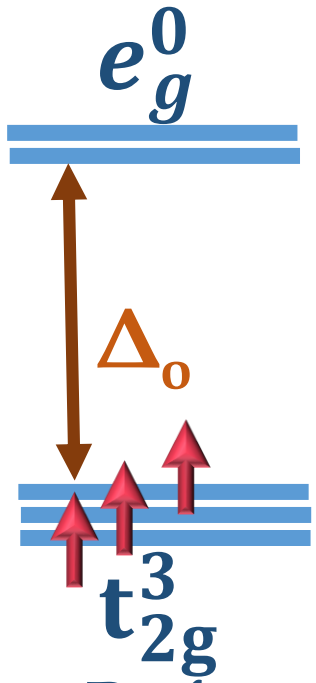
Extra stability =0

No Jahn-Teller distortion.

JAHN-TELLER DISTORTION

d^3 Systems

No further splitting of e_g and t_{2g}



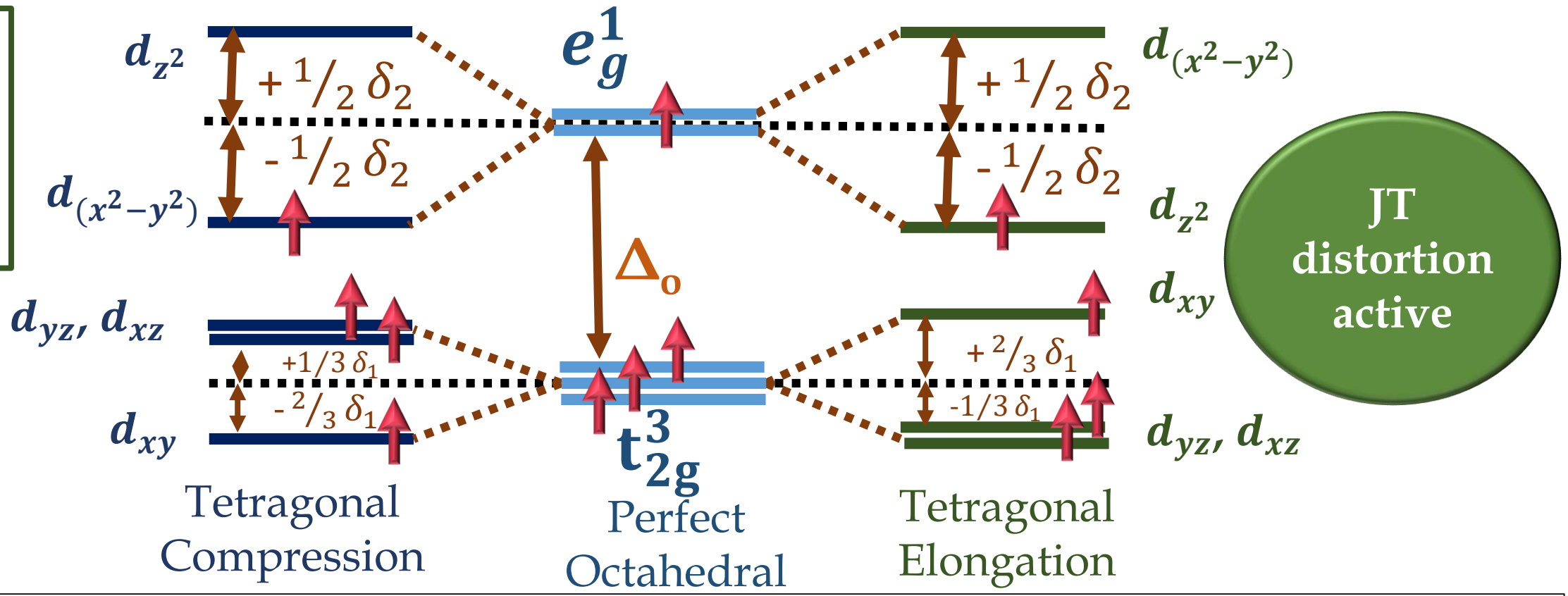
Perfect Octahedral

JT distortion inactive

No Jahn-Teller distortion.

JAHN-TELLER DISTORTION

High spin d^4

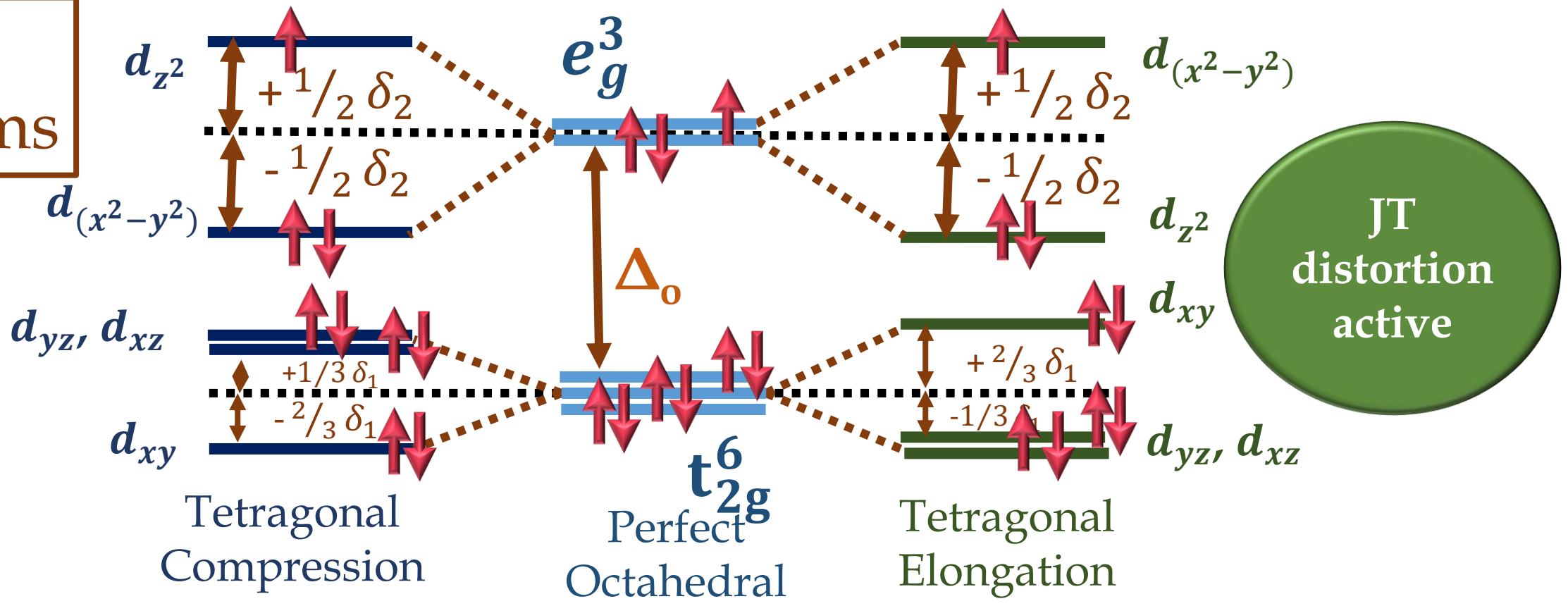


Extra stabilities ($ {}^1/_2\,\delta_2$) are same for both cases. So, tetragonal compression or tetragonal elongation is not certain.

δ_2 is very much greater than δ_1. The Jahn-Teller distortion due to uneven fill of e_g orbitals is called **strong tetragonal distortion**.

JAHN-TELLER DISTORTION

d^9 Systems



Tetragonal compression or tetragonal elongation may occur and it is strong tetragonal distortion.

DKM

Summary:

- t_{2g}^1, t_{2g}^2, t_{2g}^4 and t_{2g}^5 give **weak** Jahn-Teller distortion.
- e_g^1 and e_g^3 give **strong** Jahn-Teller distortion.
- Half filled or full filled t_{2g} (t_{2g}^3 and t_{2g}^6) and e_g (e_g^2 and e_g^4) give **no** Jahn-Teller distortion.

High spin d^4, low spin d^7 and d^9 systems give **strong JT** distortion.

Effect of JT distortion…

SPECTRA OF COMPLEXES

The plot of absorbance *vs* the wavelength (or wave number) of light that absorbed is called spectrum.

Spectrum of a complex arises due to the transition of electron from one energy level to another energy level. The electronic transitions are guided by selection rule.

Selection rules for centro-symmetric molecule:
(a)$\Delta l = \pm 1$ (Laporte selection rule)
(b)$\Delta s = 0$ (Spin selection rule)

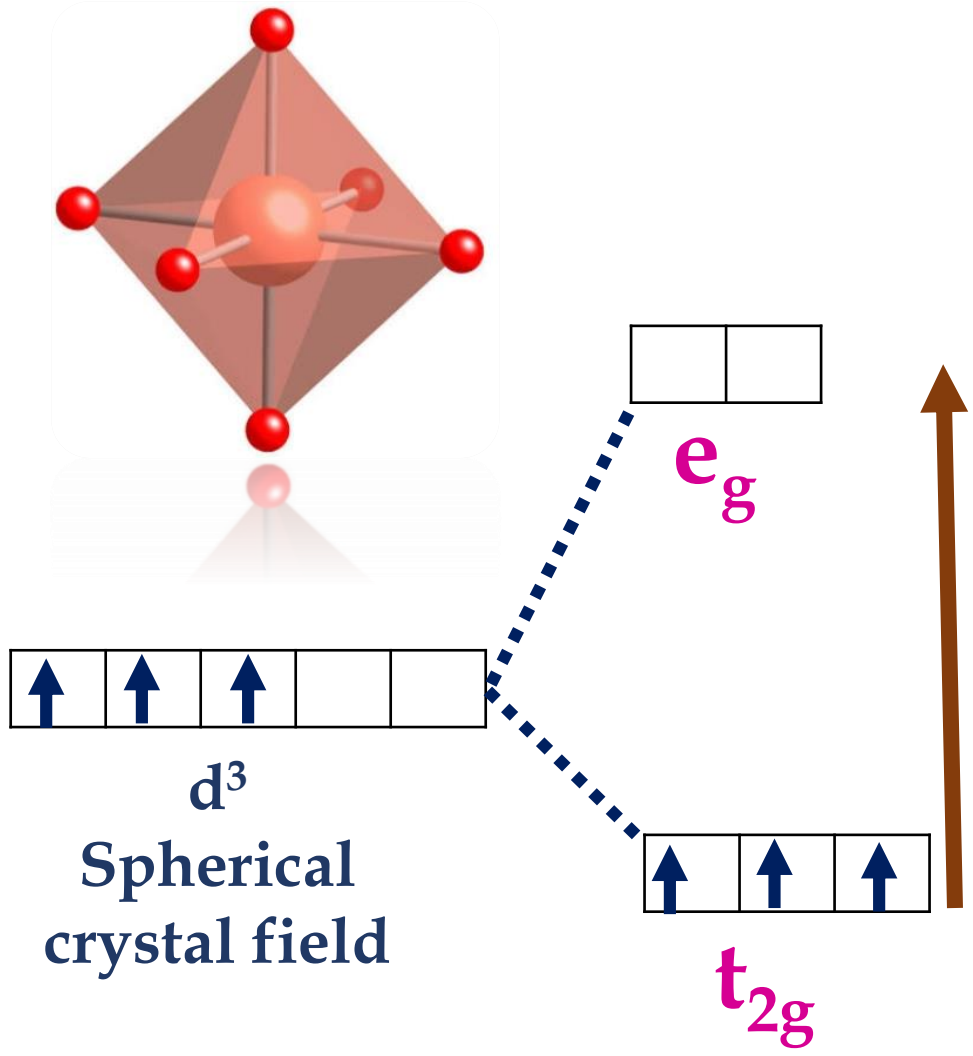
The transition which obeys both selection rules has higher intensity than the transition which does not obey all selection rules.

SPECTRA OF COMPLEXES

Regular octahedral complexes are centro-symmetric molecules.

In octahedral complex (d-d transition), first selection rule (Laporte selection rule) is not obeyed. So, to give spectrum second selection rule ($\Delta s = 0$) must be obeyed.

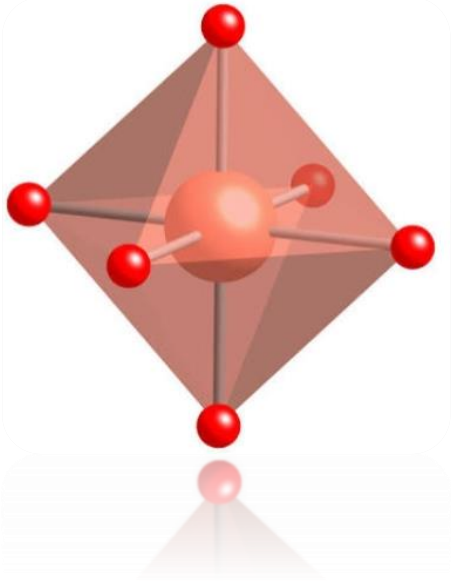
The intensity of the spectrum of octahedral complex is very low.

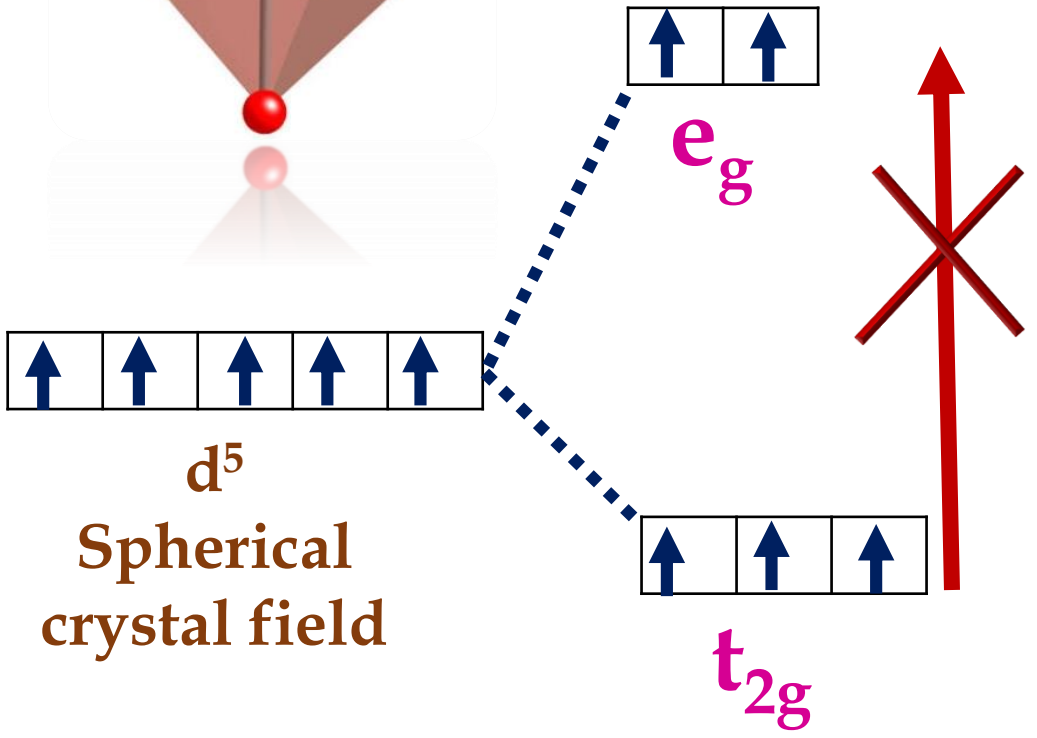


SPECTRA OF COMPLEXES

Regular octahedral complexes are centro-symmetric molecules.

High spin d^5 complexes are expected to be colorless compound.



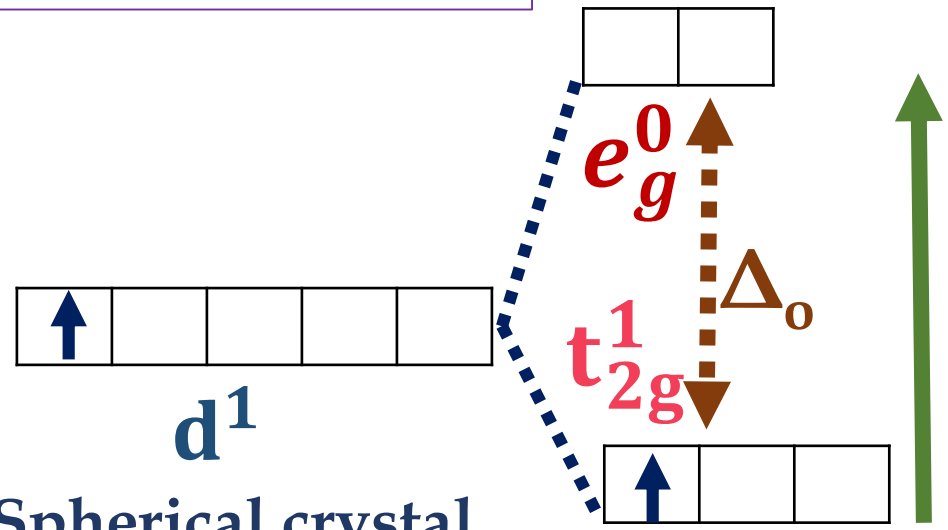


High spin complex

SPECTRA OF COMPLEXES

Spectrum of $[Ti(H_2O)_6]^{3+}$ complex ion with out considering JT distortion

Ti^{3+} (d^1 system)



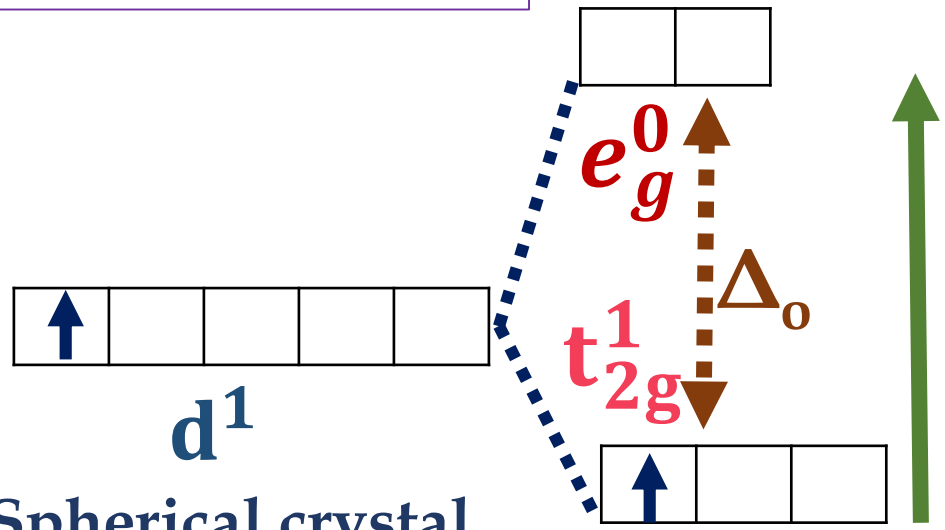
- Only one electronic transition: t_{2g} to e_g
- Energy of transition: Δ_o
- If Δ_o is in the visible range, then the compound is colored, otherwise the compound is colorless.
- By measuring the spectrum of complex, crystal field splitting energy (Δ_o) can be measure.

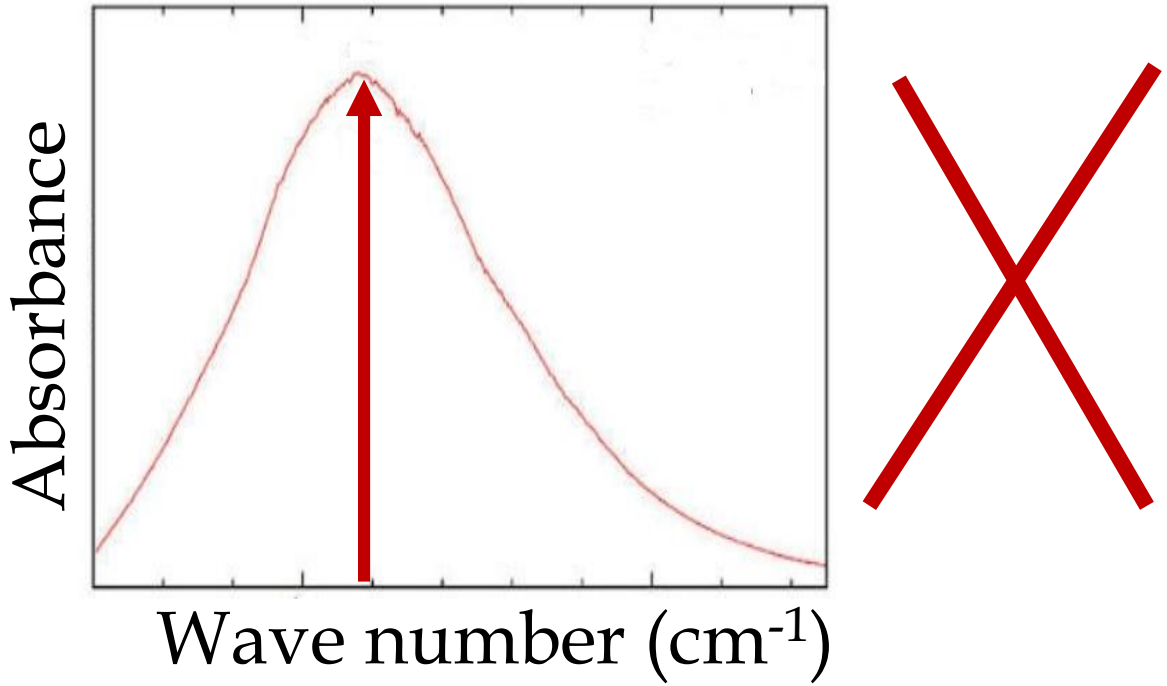
(a) $\Delta l \neq \pm 1$ Forbidden transition.
(b) $\Delta s = 0$ Allowed transition.

SPECTRA OF COMPLEXES

Spectrum of $[Ti(H_2O)_6]^{3+}$ complex ion with out considering JT distortion

Ti^{3+} (d^1 system)





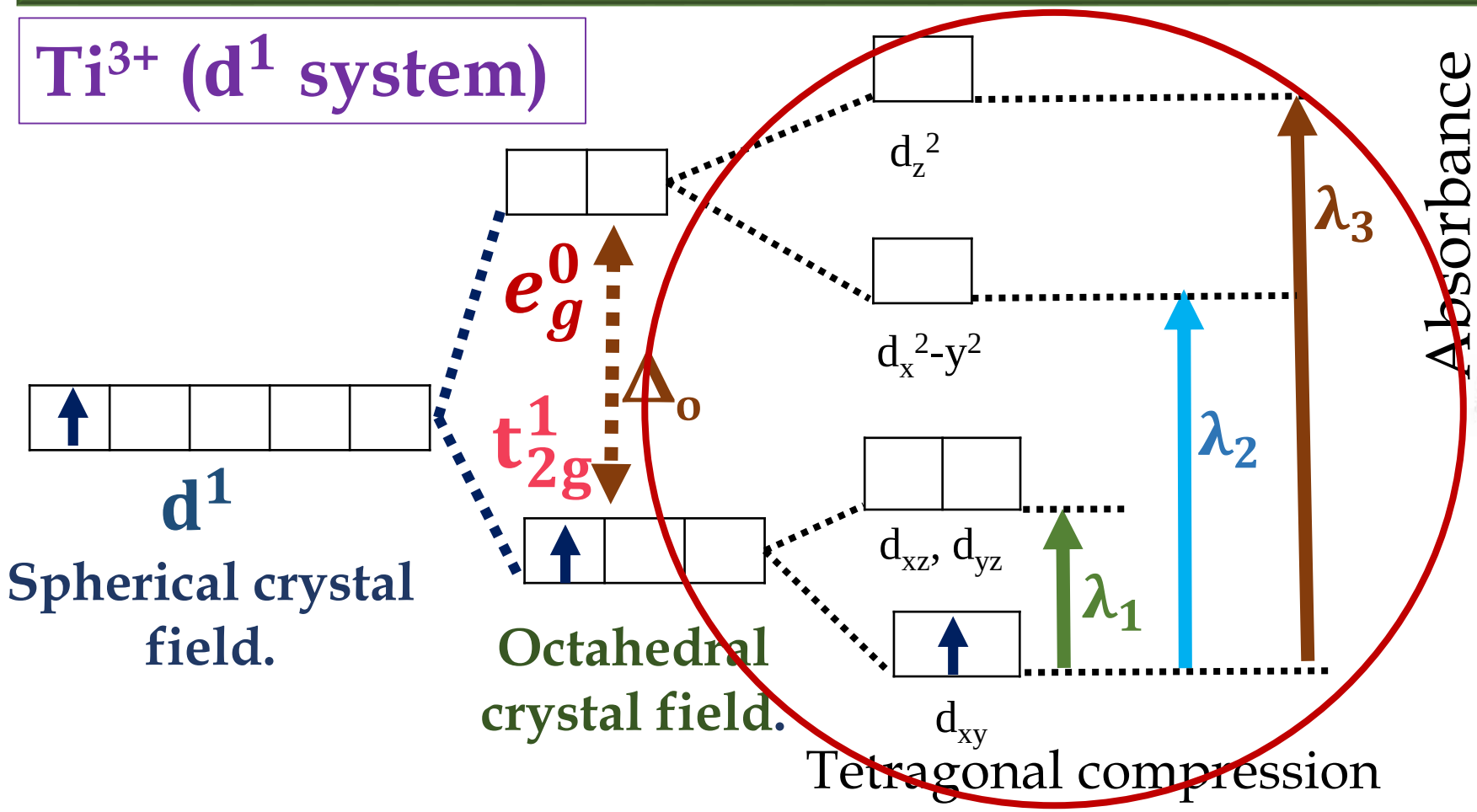
Expected spectrum **of** $[Ti(H_2O)_6]^{3+}$

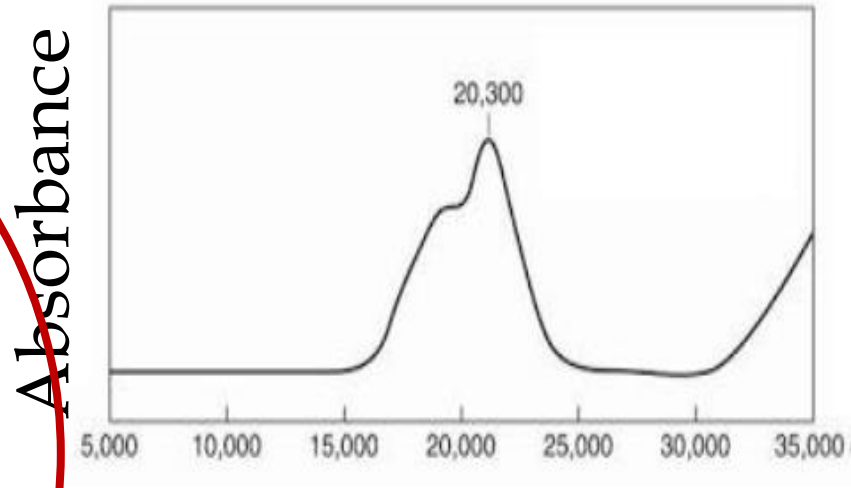
(a) $\Delta l \neq \pm 1$ Forbidden transition.
(b) $\Delta s = 0$ Allowed transition.

SPECTRA OF COMPLEXES

Spectrum of $[Ti(H_2O)_6]^{3+}$ complex ion by considering JT distortion

Ti^{3+} (d^1 system)

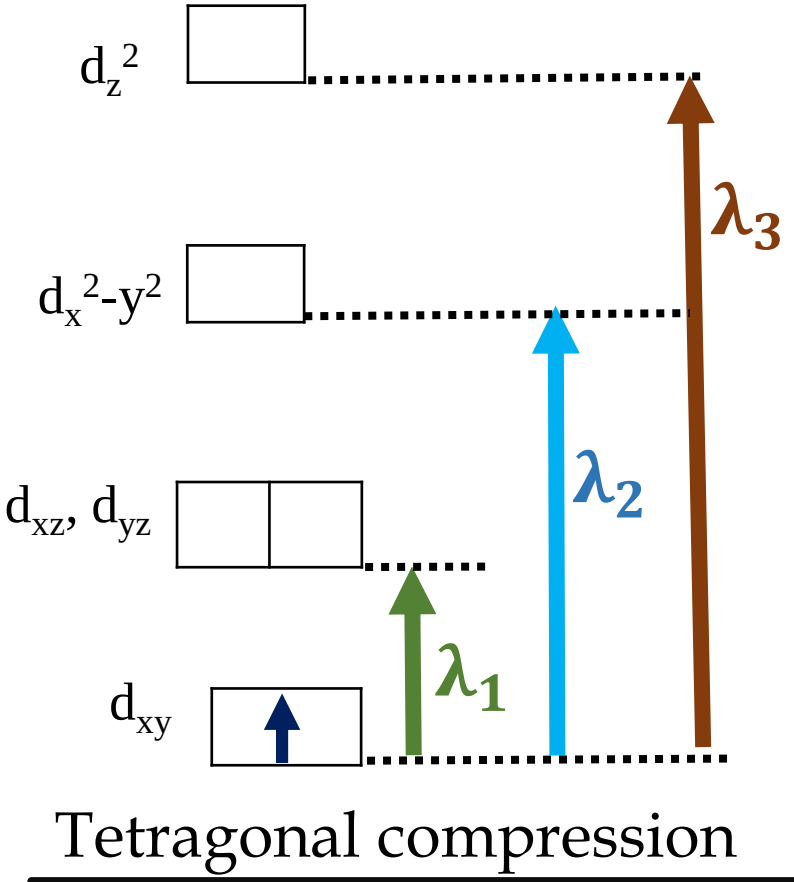




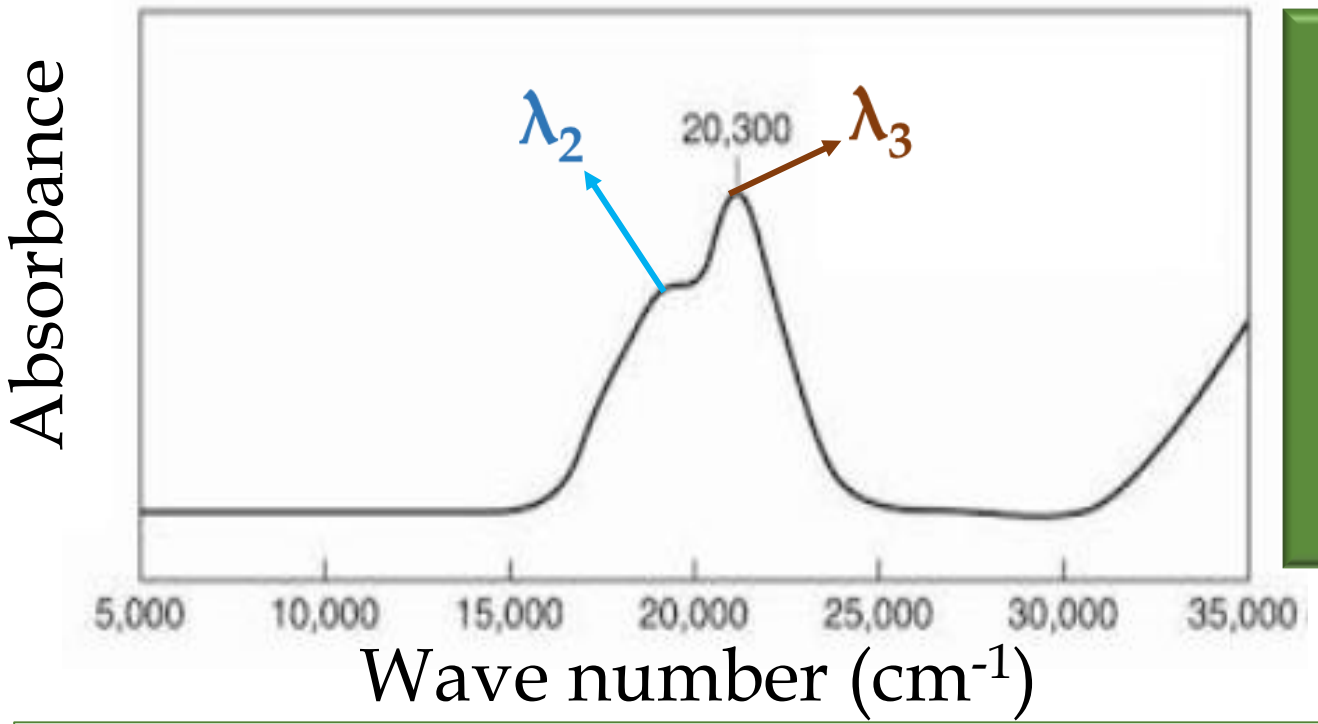
Actual spectrum of $[Ti(H_2O)_6]^{3+}$

SPECTRA OF COMPLEXES

Spectrum of $[Ti(H_2O)_6]^{3+}$ complex ion considering JT distortion



Tetragonal compression



Weak JT distortion causes low energy separation.

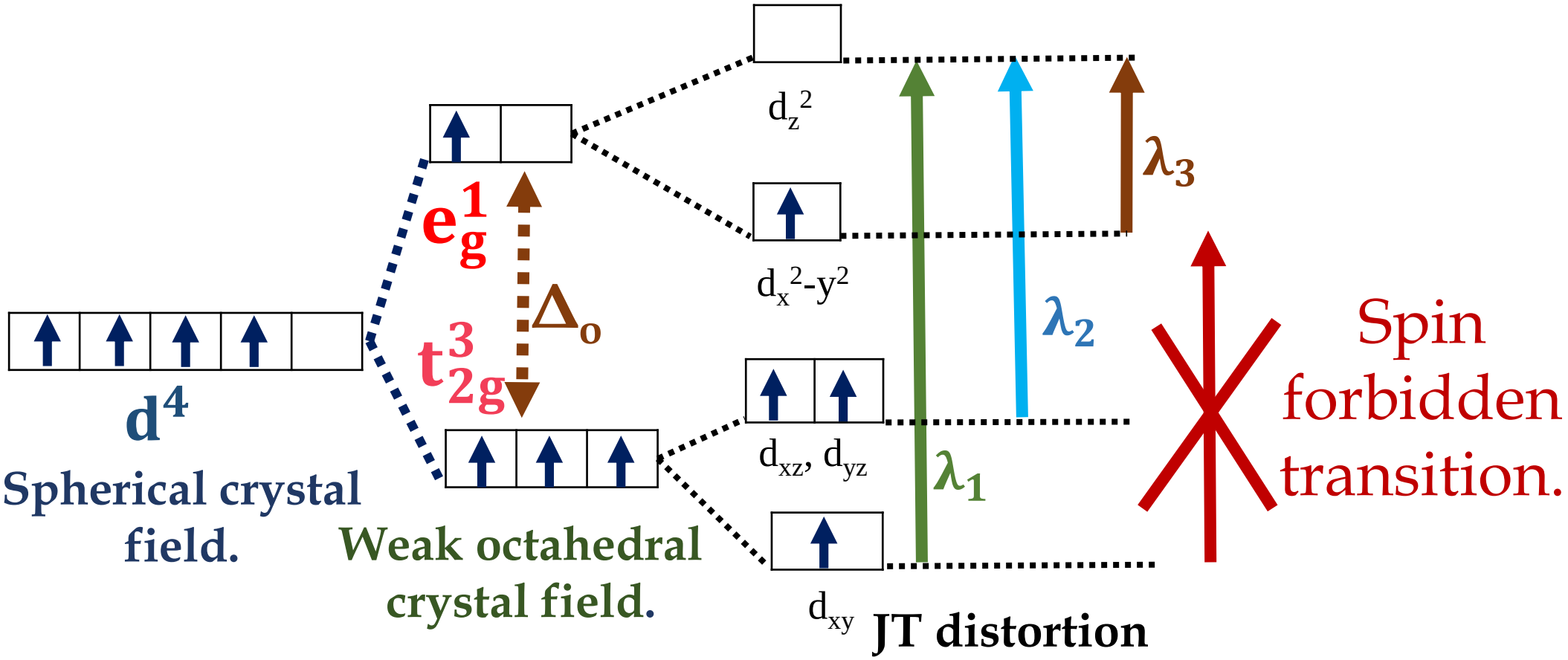
Actual spectrum of $[Ti(H_2O)_6]^{3+}$ (visible range)

$\lambda_1 > \lambda_2 > \lambda_3$

The λ_1 is in IR region and, λ_2 and λ_3 are in visible region.

SPECTRA OF COMPLEXES

Spectrum of weak field Mn^{3+} octahedral complex(d^4 system)



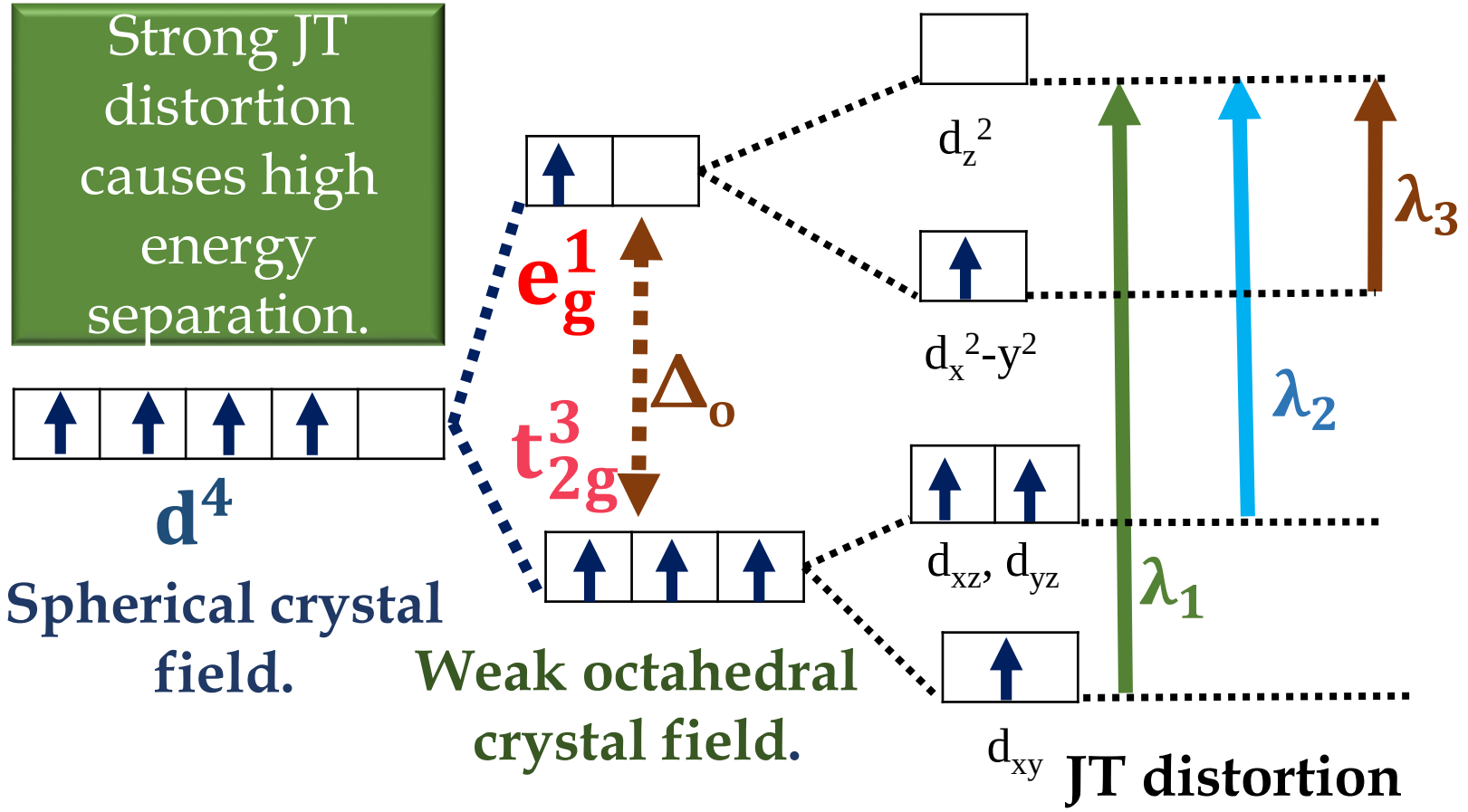
$\lambda_3 > \lambda_2 > \lambda_1$

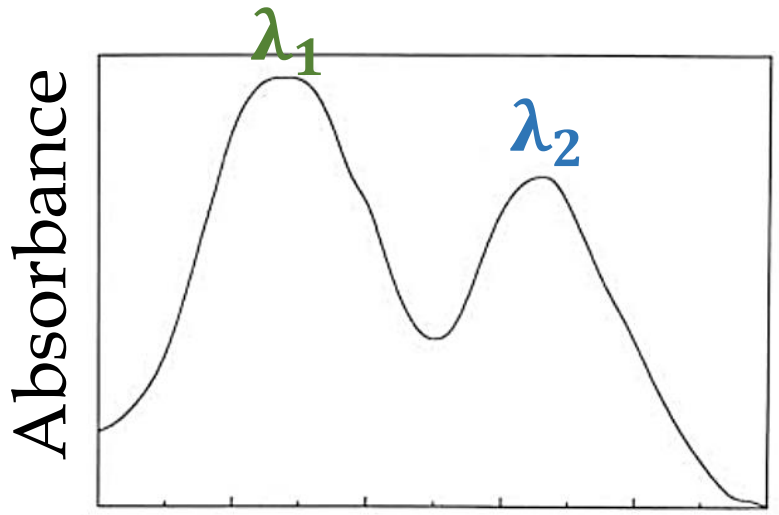
The λ_3 is in IR region and, λ_2 and λ_1 are in visible region.

SPECTRA OF COMPLEXES

Spectrum of weak field Mn^{3+} octahedral complex(d^4 system)

Strong JT distortion causes high energy separation.





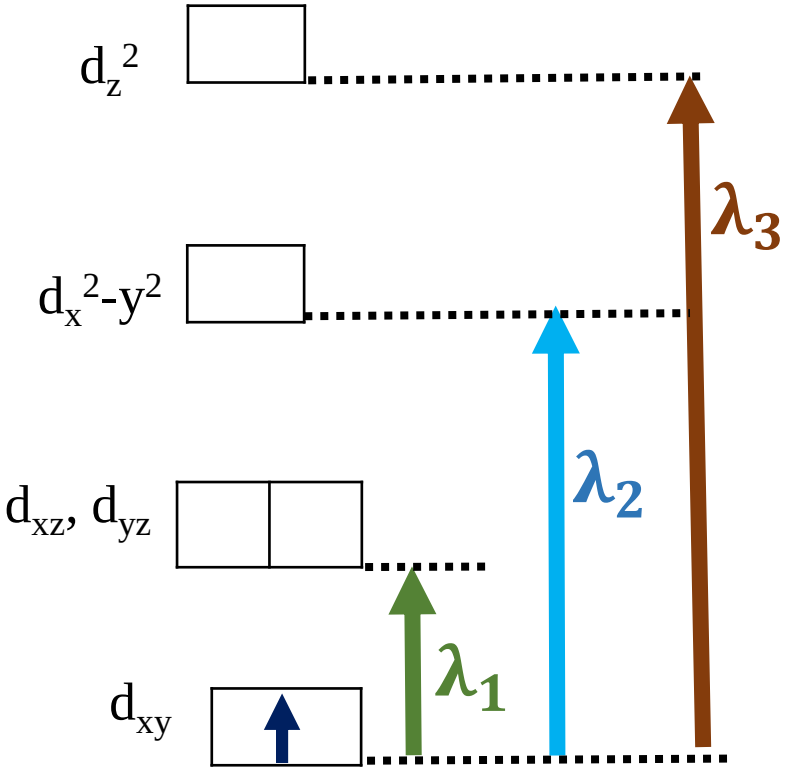
Spectrum of weak field Mn^{3+} octahedral complex (Visible range)

$\lambda_3 > \lambda_2 > \lambda_1$

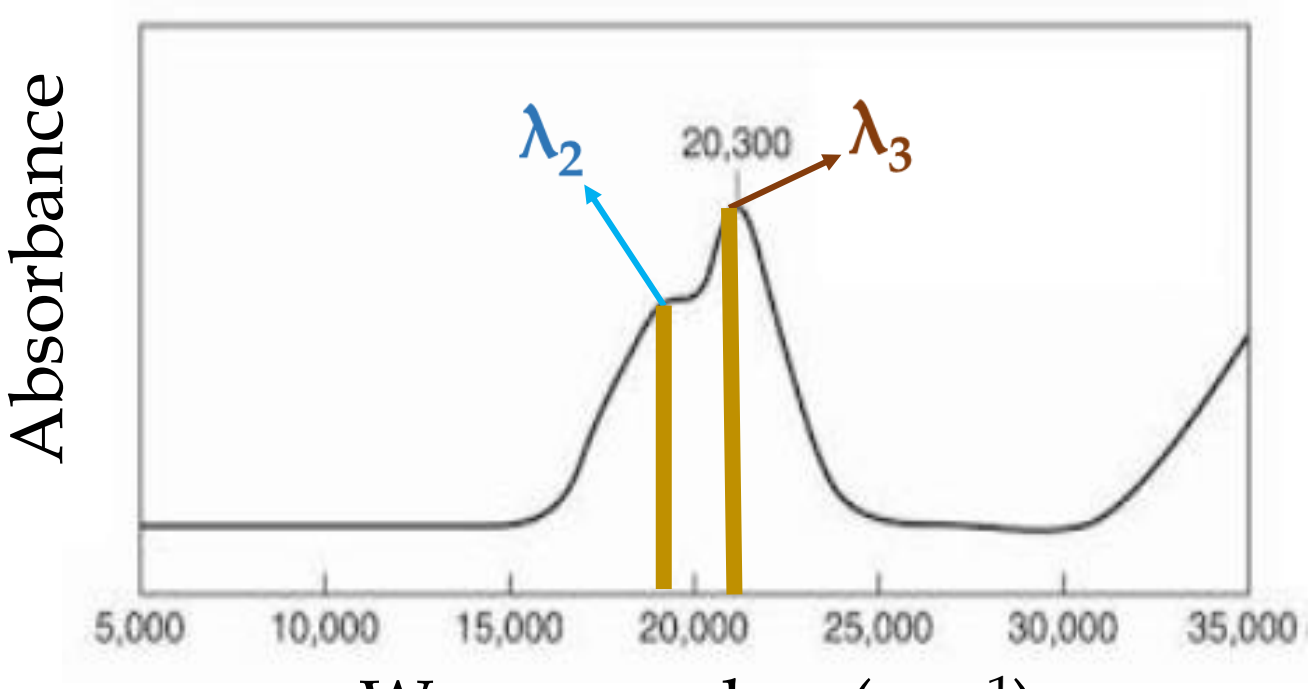
The λ_3 is in IR region and, λ_2 and λ_1 are in visible region.

SPECTRA OF COMPLEXES

Instead of line spectrum why continuous spectrum?



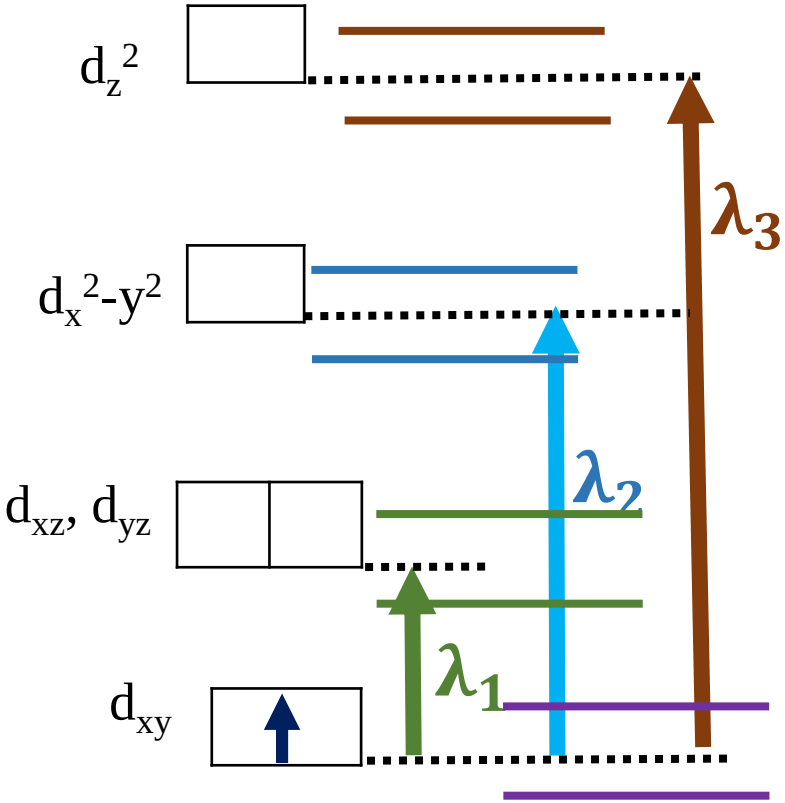
Tetragonal compression



Spectrum of $[Ti(H_2O)_6]^{3+}$

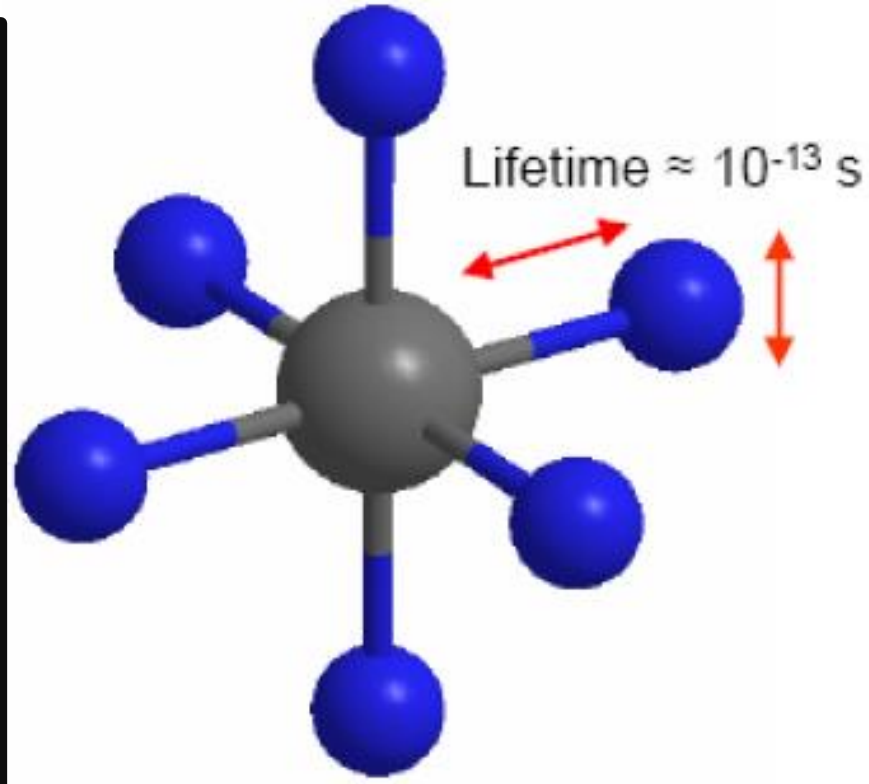
SPECTRA OF COMPLEXES

Instead of line spectrum why continuous spectrum?



Tetragonal compression

Continuous variation of metal-ligand bond distance causes continuous variation of energy of different d orbitals in a certain range. Hence, continuous spectrum of complex results.



Metal-ligand bond vibration

SPECTRA OF COMPLEXES

DKM

How can you differentiate between octahedral and tetrahedral complex by seeing their color?

d-d transition in **octahedral complex (centro-symmetric)**	d-d transition in **tetrahedral complex** (no centre of symmetry)
(i) Laporte forbidden (ii) Spin allowed	(i) Laporte rule is relaxed. (ii) Spin allowed

The color intensity of tetrahedral complex is very much higher than that of octahedral complex. In general, molar extinction coefficient of tetrahedral complex is 100 times greater than that of octahedral complex.

Example: $[Cu(H_2O)_6]^{2+}$ is a pale blue color *vs* $[Cu(NH_3)_4]^{2+}$ which is an intense dark blue.

SPECTRA OF COMPLEXES

Color of Complex

Colour of light absorbed	Approx. λ ranges / nm	Colour of light transmitted
Red	700-620	Green
Orange	620-580	Blue
Yellow	580-560	Violet
Green	560-490	Red
Blue	490-430	Orange
Violet	430-380	Yellow

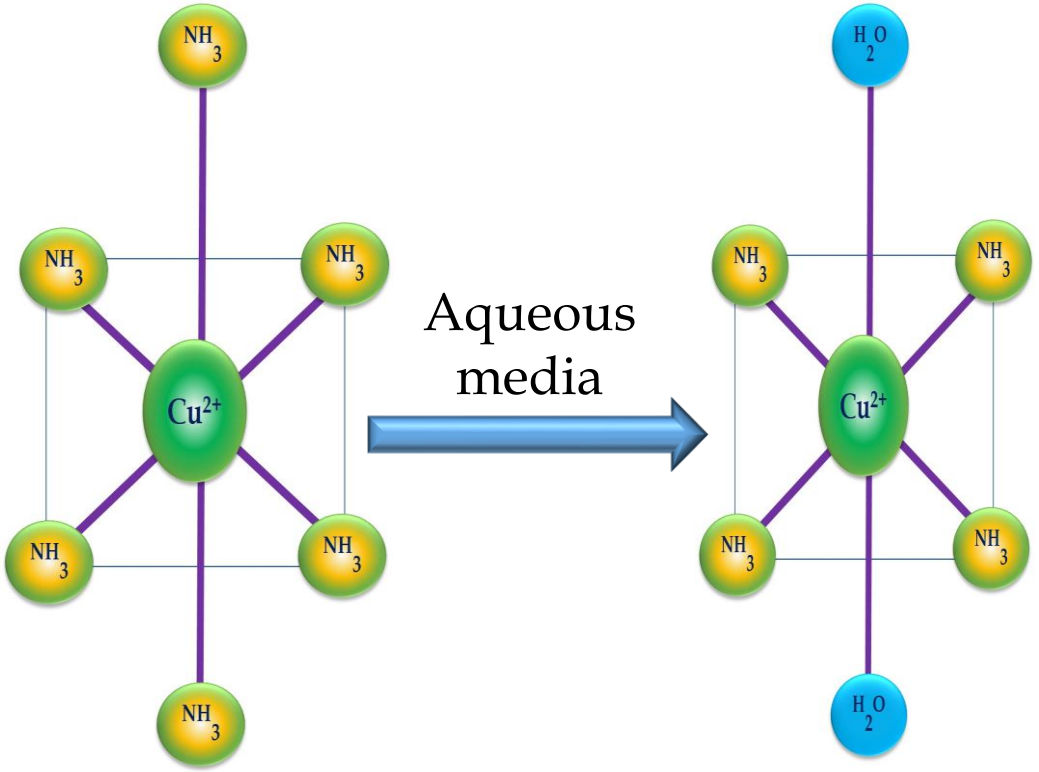
No scope of d-d transition in the complexes having d^0 and d^{10} electronic configurations. These complexes are expected to be white compound.

OTHER EFFECTS OF JAHN-TELLER DISTORTION

$[Cu(NH_3)_6]^{2+}$ does not exist in aqueous medium.

- Cu^{2+} is a d^9 system.
- It may form tetragonally elongated or compressed complex.
- Experimentally it is seen that axial bond distance is greater than equatorial bond distance in $[Cu(NH_3)_6]^{2+}$.

In $[Cu(NH_3)_6]^{2+}$, the axial NH_3 ligands are labile. In aqueous media, the axial NH_3 ligands are replaced by the H_2O molecules.

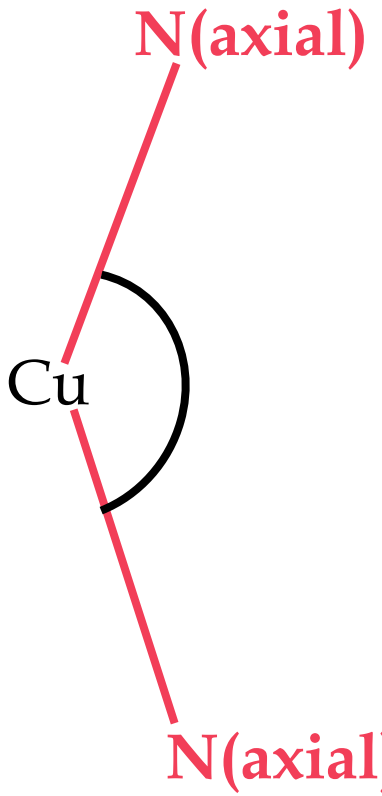


Tetragonally elongated complex

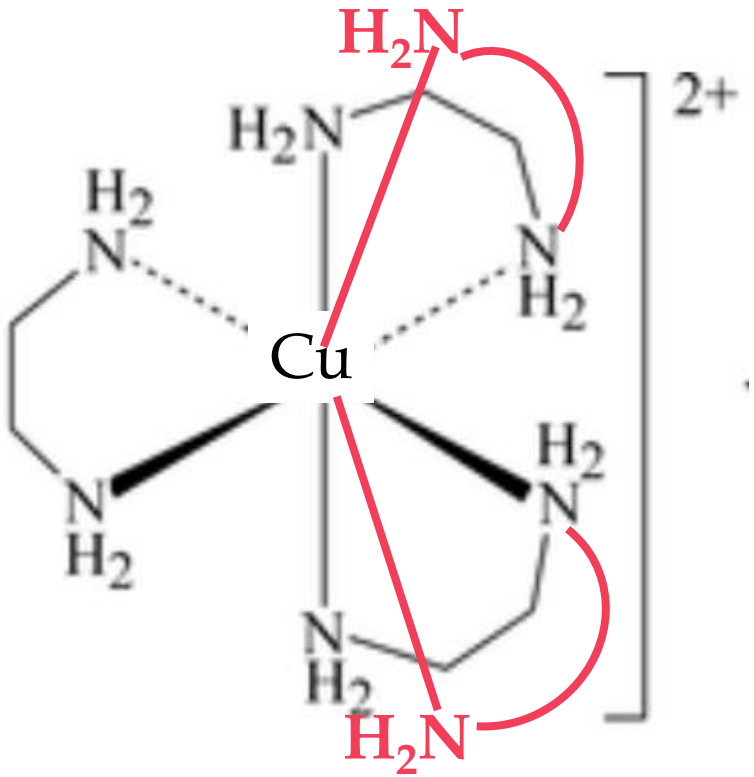
OTHER EFFECTS OF JAHN-TELLER DISTORTION

JT distortion in $[Cu(en)_3]^{2+}$ complex ion.

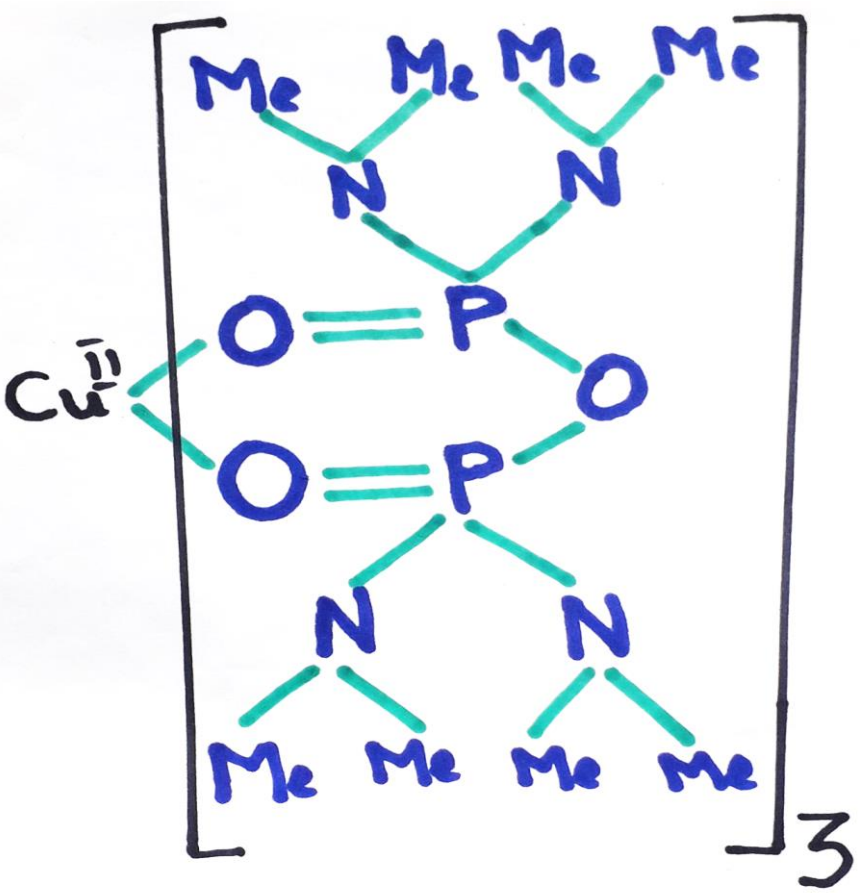
- $[Cu(en)_3]^{2+}$ is a **tetragonally elongated** complex. Axial bonds are longer than equatorial bonds.



N(axial)-Cu-N(axial) bond angle is less than 180°.



OTHER EFFECTS OF JAHN-TELLER DISTORTION



JT distortion will happen or not?

Two factors control the JT distortion:

(i) Stability gained from JT distortion.

(ii) Energy required to break the strain of chelating ligand.

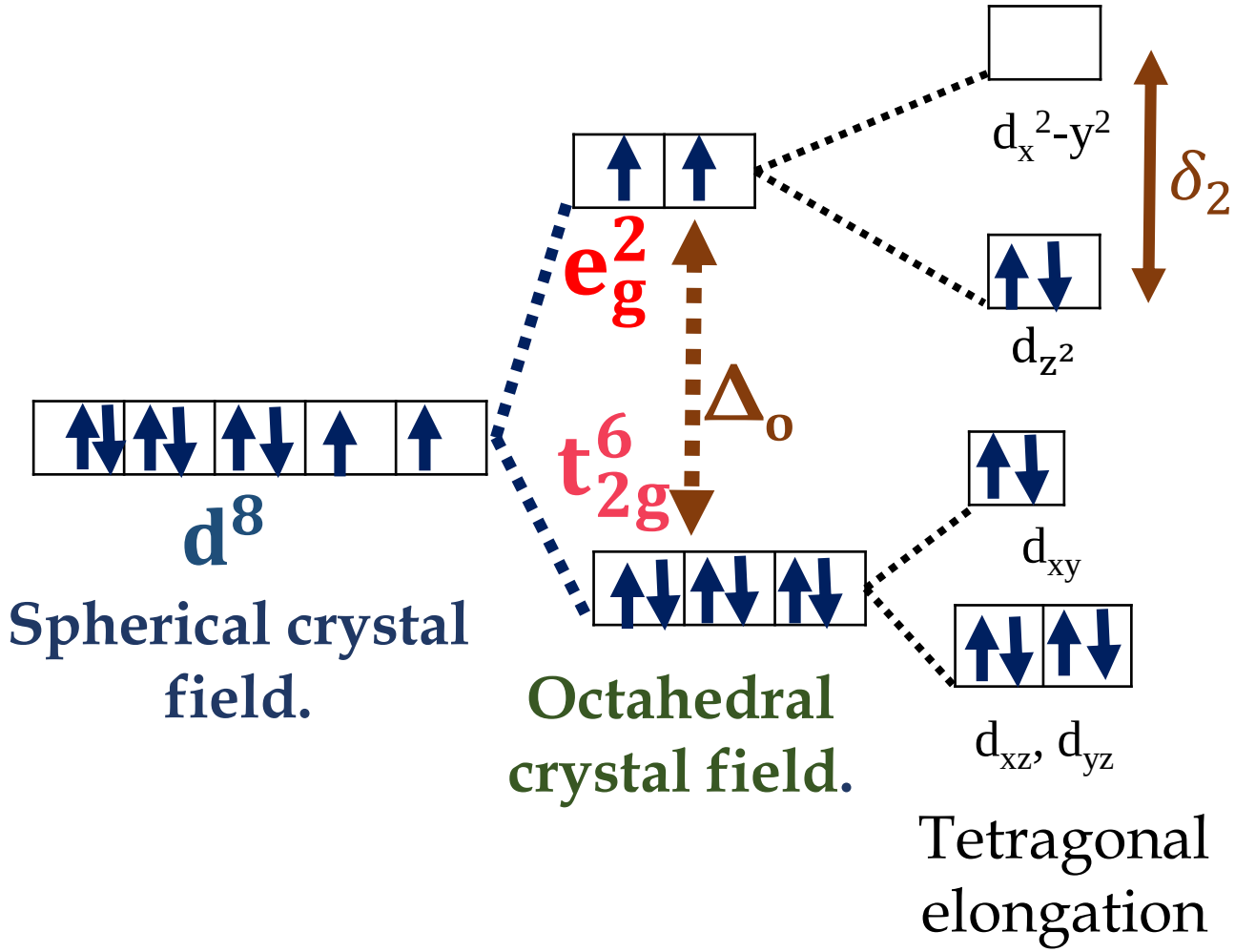
- If **(i)** is greater than **(ii)**, then JT distortion occurs.
- If **(ii)** is greater than **(i)**, then no JT distortion.

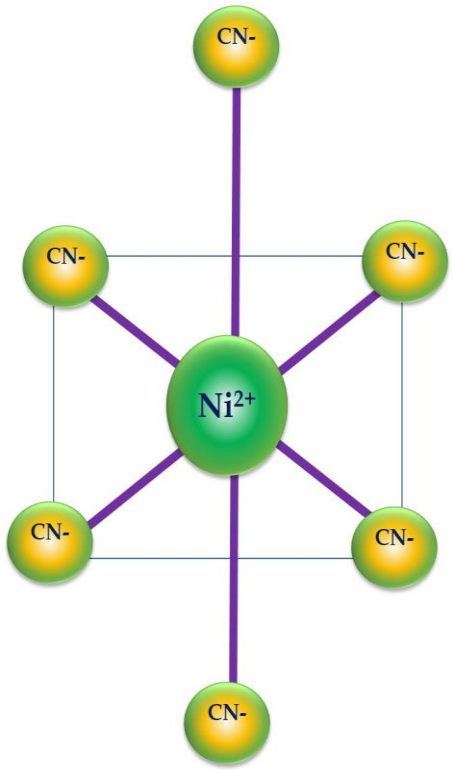
In this case, **(ii)** is greater than **(i)**, so **no JT distortion** in this complex.

EXCEPTIONAL JAHN-TELLER DISTORTION

$[Ni(CN)_6]^{4-}$ complex (d^8 system)

- CN^- is a very strong field ligand.
- δ_2 is greater than pairing energy (P).
- Pairing of electrons in to d_{z^2} orbital gives higher stabilization energy.





Elongated Tetragonal Complex

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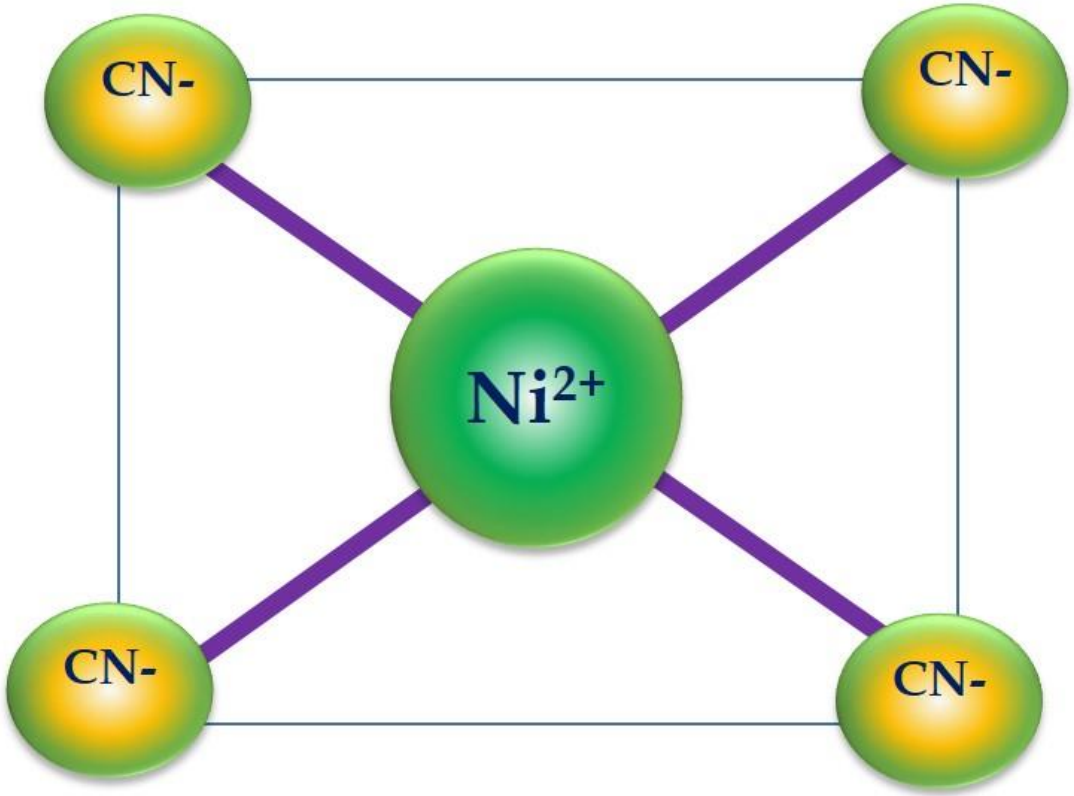
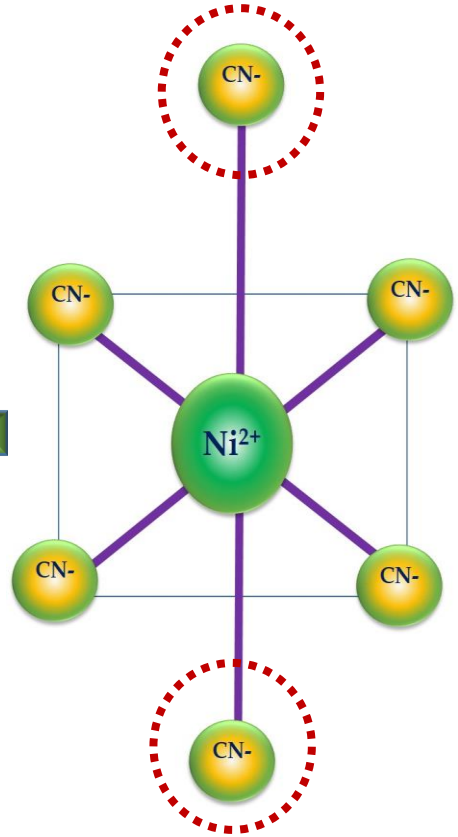


Square Planar Complex



Elongated Tetragonal Complex

TYPES OF JAHN-TELLER DISTORTION

JOHN-TELLER DISTORTION

Static JT distortion

Static JT distortion is independent of temperature.
Example: $K_2Ba[Cu(NO_2)_6]$.

Dynamic JT distortion

Dynamic JT distortion is temperature dependent distortion.
Example: $K_2Pb[Cu(NO_2)_6]$

Elongated form ⟷ Compressed form


NEXT
CLASS...
Preferred Geometry of
Coordination Compounds.

Static JT

(Permanent JT, which does not depend on Temperature)

Dynamic JT

(Temporary J.T., which depends on Temperature)

Elongated form $\rightleftharpoons$ Contracted form

Eg. – At room temp. $\Rightarrow$ Very rapid conversion $\Rightarrow$ All bonds have equal lengths (time average)

At very low temp $\Rightarrow$ Rate of conversion is low $\Rightarrow$ Axial & equatorial bonds have different lengths

Eg. —

(i) $K_2Ba[Cu(NO_2)_6]$ $\Rightarrow$ elongated octahedral at R.T. (crystallographic measurement)