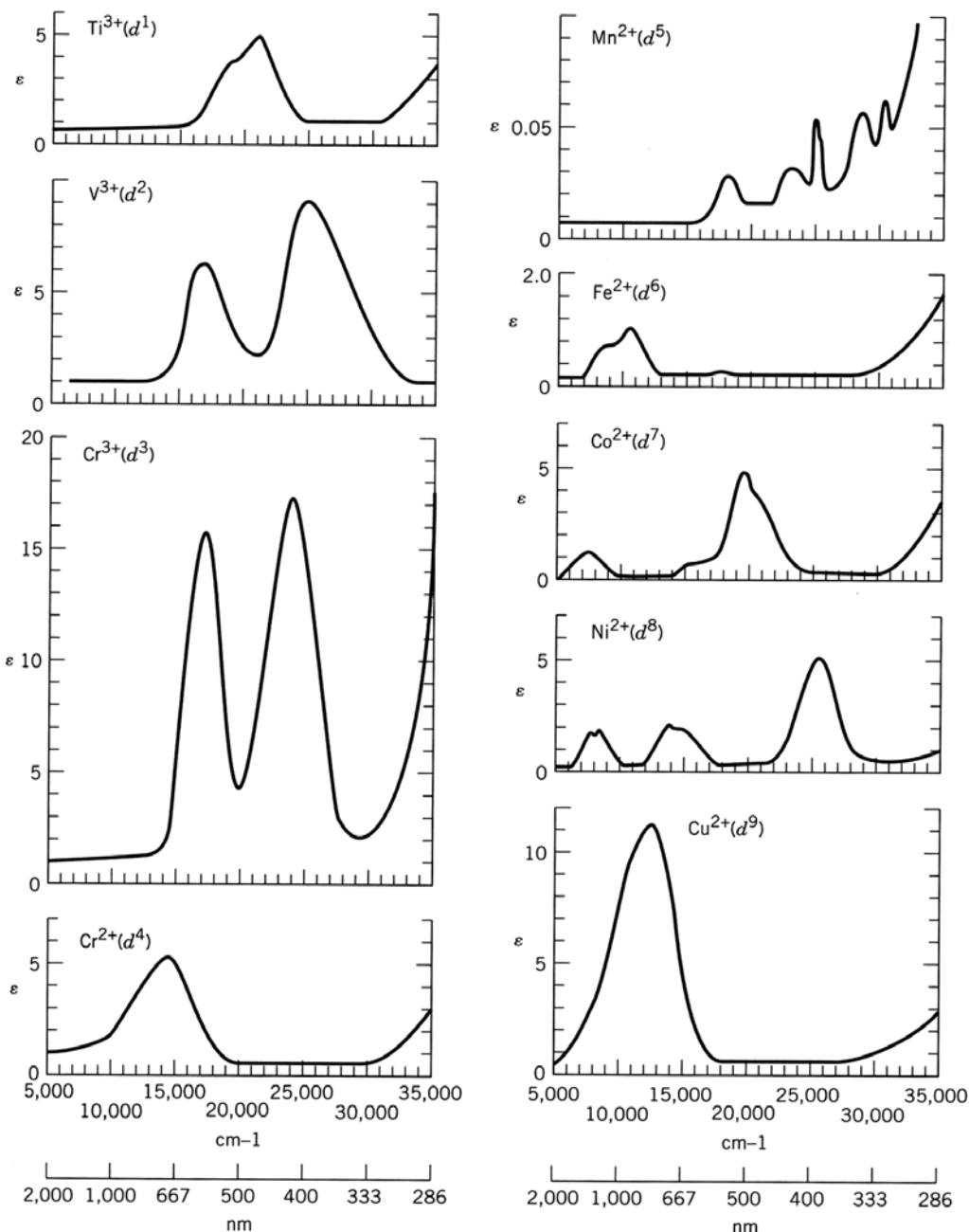


## Absorption Spectra

- Colors of transition metal complexes result from absorption of a small portion of the visible spectrum with transmission of the unabsorbed frequencies.

### Visible Spectra of $[M(H_2O)_6]^{n+}$ Complexes



- $Ti(H_2O)_6^{3+}$  appears purple (red + blue) because it absorbs green light at  $\sim 500\text{ nm} = \sim 20,000\text{ cm}^{-1}$ .

## Beer-Lambert Law

- The absorption at any wavelength obeys the Beer-Lambert Law:

$$A = \log(I_0/I) = \epsilon cb$$

where  $A$  = absorbance

$I_0$  = incident light intensity

$I$  = transmitted light intensity

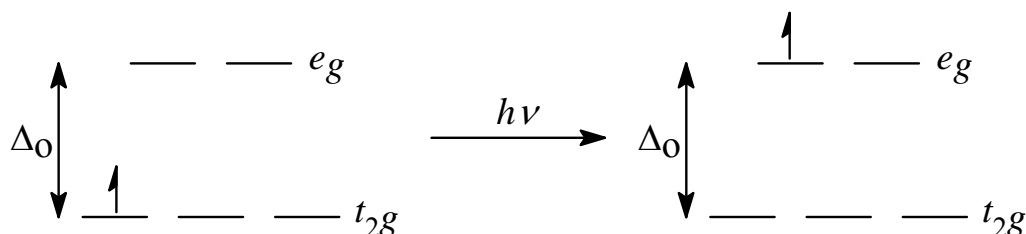
$\epsilon$  = molar absorptivity at a particular wavelength

$c$  = molar concentration

$b$  = path length through the absorbing medium

## Electronic Transitions

- In the CFT model, absorption causes electrons from lower lying  $d$  orbitals to be promoted to higher levels.
  - For  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  ( $d^1$ ) the absorption causes the configuration to change from  $t_{2g}^1 e_g^0$  to  $t_{2g}^0 e_g^1$ .



- The change in configuration causes a change in the term state of the system.
- For a free  $d^1$  ion, the ground state term is  ${}^2D$ , a five-fold degenerate term arising from the five possible ways of placing the one electron in the five degenerate  $d$  orbitals.

$$d_{xy}^1 = d_{yz}^1 = d_{xz}^1 = d_{x^2-y^2}^1 = d_{z^2}^1$$

- In an octahedral field this term is split into a new ground state term, corresponding to the configuration  $t_{2g}^1 e_g^0$ , and a new excited state term, corresponding to the configuration  $t_{2g}^0 e_g^1$ .

- The ground state term is triply degenerate, corresponding to the three equivalent microstates represented by  $t_{2g}^1 e_g^0$ .

$$t_{2g}^1 e_g^0 \Rightarrow d_{xy}^1 = d_{yz}^1 = d_{xz}^1$$

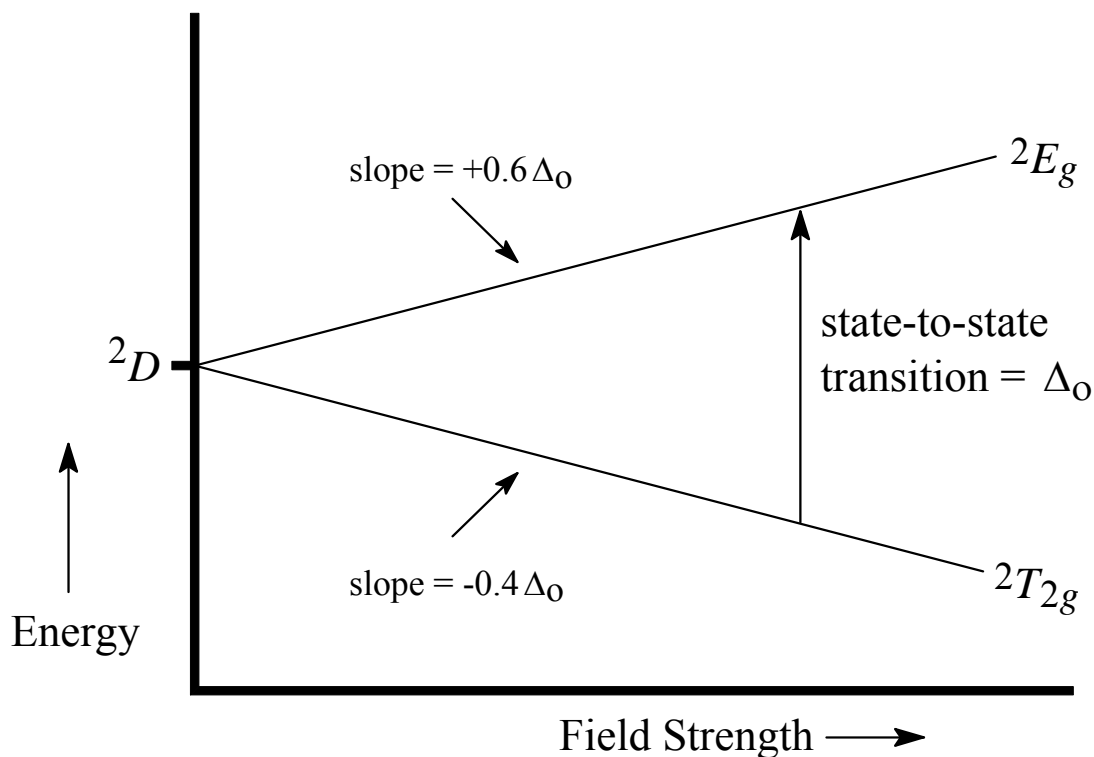
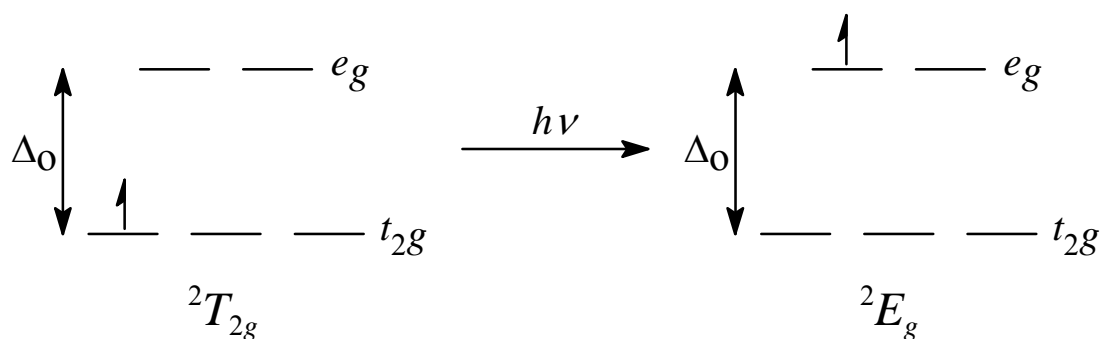
- The excited state is doubly degenerate, corresponding to the two microstates represented by  $t_{2g}^0 e_g^1$ .

$$t_{2g}^0 e_g^1 \Rightarrow d_{x^2-y^2}^1 = d_{z^2}^1$$

- The new ground state term is designated  ${}^2T_{2g}$ , and the new excited state term is designated  ${}^2E_g$ .

- Both terms are doublets, because the spin multiplicity is  $2S + 1 = (2)(\frac{1}{2}) + 1 = 2$ .

## Term Splitting Diagram for $d^1(O_h)$



- The energy difference between the two states is  $\Delta_0 = 10Dq$ , which is energetically equivalent to the frequency of the absorption, for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} \sim 20,000 \text{ cm}^{-1}$ .
  - Breadth of the observed band is in part a result of the oscillation of the strength of  $\Delta_0$  as the complex vibrates.

## Free-Ion Terms for $d^{1-10}$ Configurations

- Transition metal ions with configurations  $d^2 - d^8$  have more than one free-ion term.

$d^n$	Free-Ion Term
$d^0, d^{10}$	$^1S$
$d^1, d^9$	$^2D$
$d^2, d^8$	$^1S, ^1D, ^1G, ^3P, ^3F$
$d^3, d^7$	$^2P, ^2D(2), ^2F, ^2G, ^2H, ^4P, ^4F$
$d^4, d^6$	$^1S(2), ^1D(2), ^1F, ^1G(2), ^1I, ^3P(2), ^3D, ^3F(2), ^3G, ^3H, ^5D$
$d^5$	$^2S, ^2P, ^2D(3), ^2F(2), ^2G(2), ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$

- Terms for  $d^n$  are the same as for  $d^{10-n}$ .

## Determining the Ground State Free-Ion Term

① Write out the configuration so as to maximize the total orbital angular momentum and total spin (Hund's Rule).

② Determine the orbital term from  $L = |\Sigma M_L|$ , where

$L$	0	1	2	3	4	...
Term	<i>S</i>	<i>P</i>	<i>D</i>	<i>F</i>	<i>G</i>	...

③ Determine the spin multiplicity as  $2S + 1$ , where  $S = |\Sigma m_s|$ .

$$d^2 \quad \begin{array}{ccccc} \uparrow & \uparrow & & & \\ \hline +2 & +1 & 0 & -1 & -2 \end{array}$$

$$L = 2 + 1 = 3 \Rightarrow F$$

$$S = (2)(\frac{1}{2}) = 1 \Rightarrow 2S + 1 = 3 \Rightarrow {}^3F$$

$$d^5 \quad \begin{array}{ccccc} \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline +2 & +1 & 0 & -1 & -2 \end{array}$$

$$L = 2 + 1 + 0 - 1 - 2 = 0 \Rightarrow S$$

$$S = (5)(\frac{1}{2}) = 5/2 \Rightarrow 2S + 1 = 6 \Rightarrow {}^6S$$

$$d^6 \quad \begin{array}{ccccc} \uparrow\downarrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline +2 & +1 & 0 & -1 & -2 \end{array}$$

$$L = (2)(2) + 1 + 0 - 1 - 2 = 2 \Rightarrow D$$

$$S = (5)(\frac{1}{2}) + (1)(-\frac{1}{2}) = 2 \Rightarrow 2S + 1 = 5 \Rightarrow {}^5D$$

## Splitting of Free-Ion Terms in Various Fields

- Splitting diagrams for any  $d^1 - d^9$  configuration can be constructed.
- The terms into which free-ion terms are split depend upon the symmetry of the complex.
- Splitting of free-ion terms for  $O_h$  is shown below.

Free-ion Term	Terms in $O_h$
<i>S</i>	$A_{1g}$
<i>P</i>	$T_{1g}$
<i>D</i>	$E_g + T_{2g}$
<i>F</i>	$A_{2g} + T_{1g} + T_{2g}$
<i>G</i>	$A_{1g} + E_g + T_{1g} + T_{2g}$
<i>H</i>	$E_g + 2T_{1g} + T_{2g}$
<i>I</i>	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

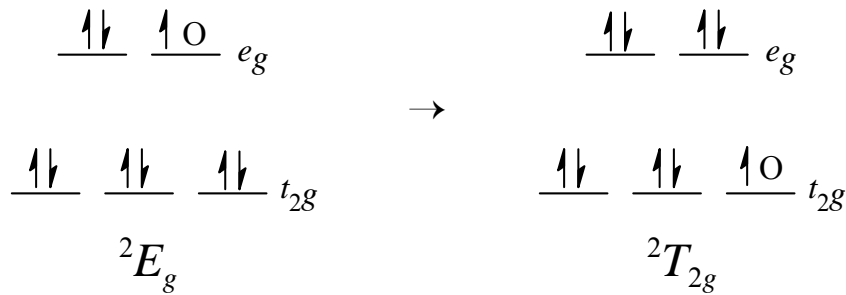
- Term splitting in fields of other symmetry can be deduced either by descent in symmetry from  $O_h$ , or by constructing the reducible representation for the free-ion term in the appropriate point group and reducing it into its component irreducible representations.<sup>1</sup>

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<sup>1</sup>Cf. R. L. Carter, *Molecular Symmetry and Group Theory*, Wiley, NY 1998, p. 205 & 233-236.

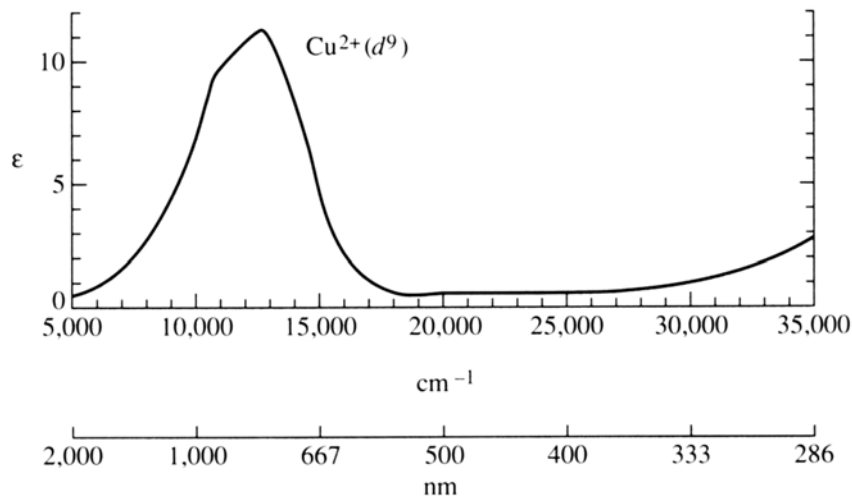
## Electronic Transitions for $d^9 O_h$

- For  $d^1$  there is only one state-to-state transition,  ${}^2T_{2g} \rightarrow {}^2E_g$ .
- For  $d^9$  there is also one state-to-state transition, but it is  ${}^2E_g \rightarrow {}^2T_{2g}$ .
  - For  $d^9 O_h$  the transition can be seen as demotion of a “hole” (i.e., electron vacancy).



- ☛ This is an example of a general “hole formalism”, whereby terms for a  $d^n$  configuration are the same as those for  $d^{10-n}$ , but the order of same-spin terms is reversed.

- $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  has a blue color due to the single  ${}^2E_g \rightarrow {}^2T_{2g}$  electronic transition at  $\sim 800$  nm.





## Electronic Transitions for Other Configurations in $O_h$

- Other  $d^n$  cases ( $n = 2-8$ ) have more than one possible  $d-d$  transition because there are more possible states.
  - Multiple electron promotions and electron demotions can occur.
  - Non-equivalent arrangements for the same  $t_{2g}^n e_g^m$  configuration may be possible.
  - States with spin multiplicities different from the ground state may exist.
  - Both high- and low-spin ground state configurations may be possible.
- The types of transitions possible for transition metal complexes are
  - ① Transitions between the ground state and excited states with the same spin.
  - ② Transitions between the ground state and excited states with different spin.
  - ③ Transitions involving electron transfer between the metal and ligand (charge transfer).
- Only charge transfer (CT) transitions are quantum mechanically allowed.
  - CT transitions result in absorption bands with high molar absorptivity ( $\epsilon \gg 10^3$ ).
  - CT transitions typically fall in the u.v.
- Color in transition metal complexes arises from  $d-d$  transitions in the visible region.
  - These arise from breakdown of quantum mechanical selection rules.
  - $d-d$  transitions between same-spin states typically have low molar absorptivities ( $\epsilon \approx 5 - 100$ ).
  - $d-d$  transitions between states with different spin multiplicities typically have very low molar absorptivities ( $\epsilon \ll 1$ ).

## Selection Rules

- *d-d* transitions in the visible region occur as a result of a breakdown in either or both of the following selection rules.
  - ① *Laporte's Rule*. If a system is centrosymmetric, transitions between states with the same inversion symmetry ( $g \rightarrow g, u \rightarrow u$ ) are forbidden, but transitions between states of different inversion symmetry ( $g \rightarrow u, u \rightarrow g$ ) are allowed.
  - ② *Spin Multiplicity Rule*. Transitions between states with different spin multiplicities are forbidden.

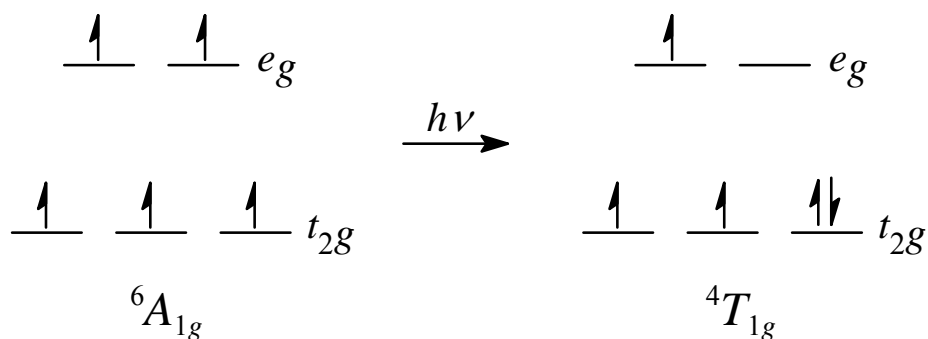
## Breakdown of the Laporte Rule

- In  $O_h$  and  $D_{4h}$ , all  $d$  orbitals are *gerade* and so too are the states arising from their  $d$  configurations.
  - Thus, all transitions of octahedral and square planar complexes are *Laporte forbidden*.
- Laporte forbidden transitions occur as a result of distortions from centrosymmetry that occur continuously as the complex vibrates.
  - These distortions cause  $d$ - $p$  mixing ( $p$  orbitals are *ungerade*) and set up transitions between states with varying amounts of  $p$  character.
  - The vibration-induced breakdown of the Laporte Rule makes the  $d$ - $d$  transitions *vibronically allowed*.
- Static loss of centrosymmetry has the same effect (e.g.,  $\text{Co(en)}_3^{2+} - D_3$ ).
- Either vibronic or static distortion results in a small departure from centrosymmetry, so the molar absorptivities are typically  $\epsilon \approx 5 - 50$ .
- Tetrahedral  $\text{ML}_4$  complexes ( $T_d$ ) have no inversion symmetry.
  - $d$ - $d$  transitions for tetrahedral complexes are *Laporte allowed*.
  - Because they are allowed, these transitions have higher molar absorptivities ( $\epsilon \approx 100 - 1000$ ).
- CT transitions are  $g \leftrightarrow u$ , allowed by the Laporte Rule, and so have very high molar absorptivities ( $\epsilon \gg 10^3$ ).

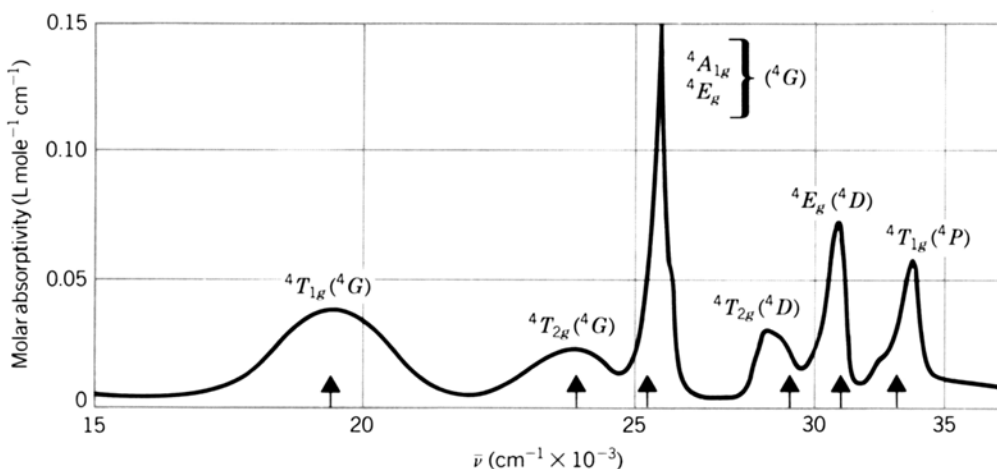
## Violations of the Spin Multiplicity Rule

- Transitions to excited states with different spin multiplicities lead to even weaker bands.
  - In complexes with vibronically allowed same-spin transitions, any spin forbidden transitions are likely to be too weak to be observed.
  - Octahedral  $d^5$  high-spin complexes, which have no same-spin transitions, show only very weak bands from spin-forbidden transitions.

Example of a spin-forbidden transition:



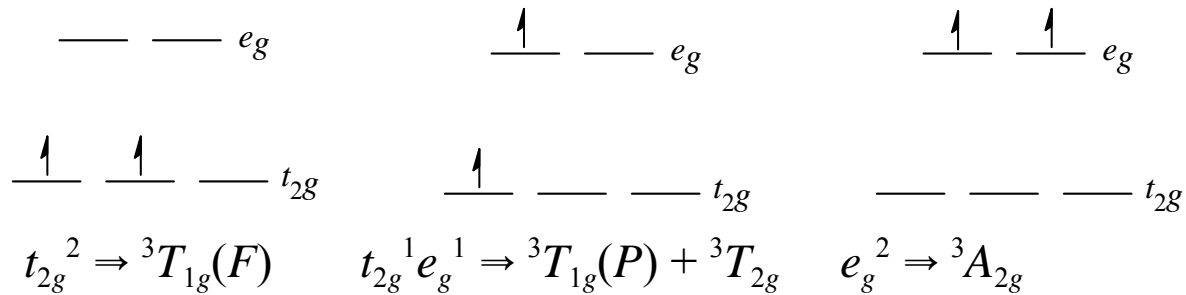
- $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  is a  $d^5$  high-spin octahedral complex with a very pale pink color, owing to a series of weak spin-forbidden transitions.



- Note that for all absorptions  $\epsilon < 0.15$ .
- ☛ We will be most concerned with  $d-d$  transitions that are spin allowed (i.e., Laporte forbidden but vibronically allowed same-spin transitions).

## Triplet Terms for $d^2 O_h$

- For free-ion  $d^2$ , the triplet states are  ${}^3F$  and  ${}^3P$ .
  - Both terms split or change their identities in  $O_h$ .
 
$${}^3F \Rightarrow {}^3A_{2g} + {}^3T_{1g} + {}^3T_{2g} \qquad {}^3P \Rightarrow {}^3T_{1g}$$
  - The two  ${}^3T_{1g}$  terms are labeled  ${}^3T_{1g}(F)$  and  ${}^3T_{1g}(P)$  to indicate the free-ion term from which each arises.
  
- The triplet terms of  $d^2$  in  $O_h$  arise from the following configurations:



### Triplet States for $d^2 O_h$ in Order of Increasing Energy

Term	Configuration	Specific Degenerate Configurations
${}^3T_{1g}(F)$	$t_{2g}^2$	$(d_{xy})^1 (d_{xz})^1 (d_{yz})^0$
		$(d_{xy})^1 (d_{xz})^0 (d_{yz})^1$
		$(d_{xy})^0 (d_{xz})^1 (d_{yz})^1$
${}^3T_{2g}$	$t_{2g}^1 e_g^1$	$(d_{xy})^1 (d_z^2)^1$
		$(d_{xz})^1 (d_{x^2-y^2})^1$
		$(d_{yz})^1 (d_{x^2-y^2})^1$
${}^3T_{1g}(P)$	$t_{2g}^1 e_g^1$	$(d_{xy})^1 (d_{x^2-y^2})^1$
		$(d_{xz})^1 (d_z^2)^1$
		$(d_{yz})^1 (d_z^2)^1$
${}^3A_{2g}$	$e_g^2$	$(d_{x^2-y^2})^1 (d_z^2)^1$

## Why Are There Two Different-Energy Triply Degenerate States for the Configuration $t_{2g}^1 e_g^1$ ?

- In all three microstates of  ${}^3T_{2g}$  the two electrons are placed in  $d$  orbitals that are geometrically orthogonal to each other:

$$(d_{xy})^1 (d_{z^2})^1 \quad (d_{xz})^1 (d_{x^2-y^2})^1 \quad (d_{yz})^1 (d_{x^2-y^2})^1$$

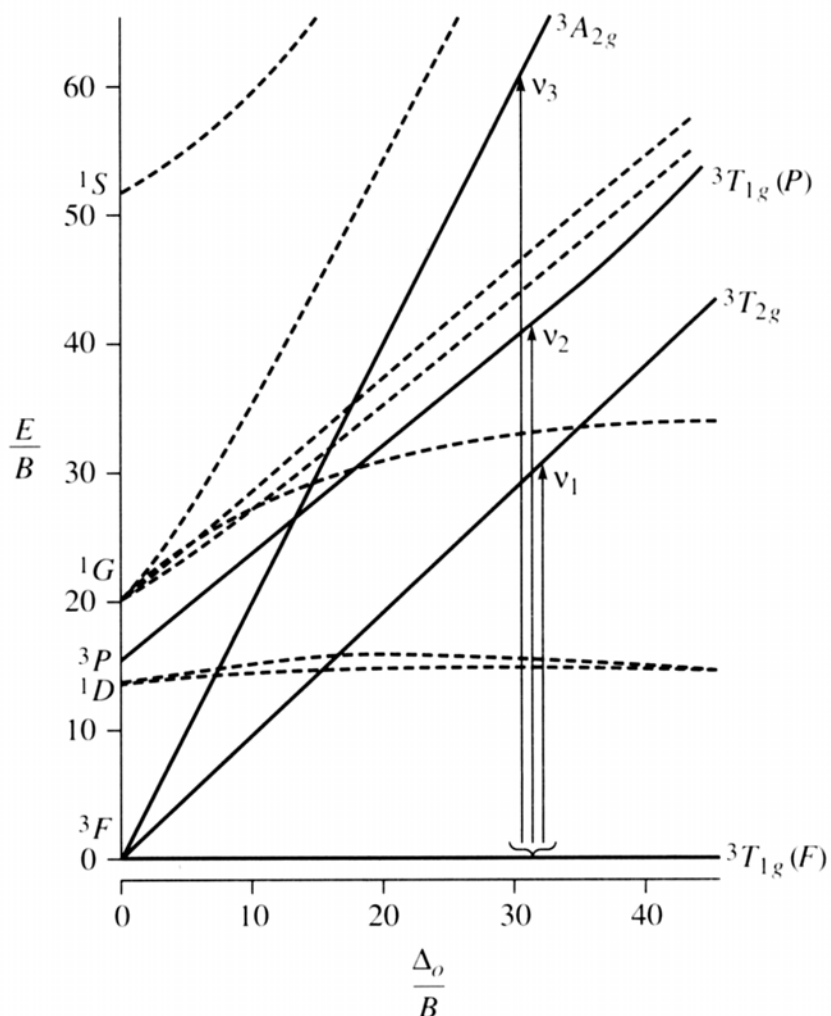
- In all three microstates of  ${}^3T_{1g}(P)$  the two electrons are placed in  $d$  orbitals that lie in the same plane:

$$(d_{xy})^1 (d_{x^2-y^2})^1 \quad (d_{xz})^1 (d_z)^1 \quad (d_{yz})^1 (d_z)^1$$

- Electron-electron repulsions are less in the microstates of  ${}^3T_{2g}$  than they are in the microstates of  ${}^3T_{1g}(P)$ , so the energy of the  ${}^3T_{2g}$  state is lower.

## Splitting Diagram for $d^2 O_h$

- There are many other states for  $d^2$  that are not triplets, shown in the following diagram, but only transitions from the triplet ground state to triplet excited states are spin allowed.
  - This diagram, originally published by Tanabe and Sugano<sup>2</sup>, shows the free-ion states, the octahedral states arising from them, and the energy separations between states as a function of  $\Delta_o$ .



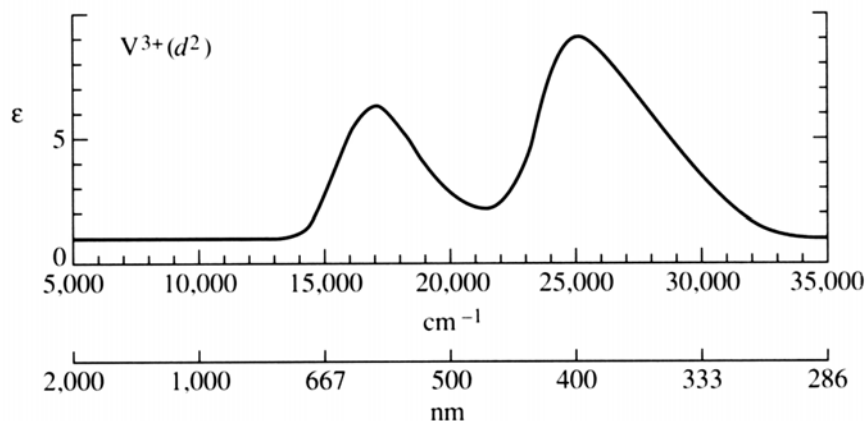
- Possible spin-allowed transitions giving rise to visible absorption bands:  ${}^3T_{1g}(F) \rightarrow {}^3T_{2g}$ ;  ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ ;  ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}$ .
  - The  ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}$  transition, which simultaneously promotes two electrons, is unlikely, and its band is often weak or unobserved.

<sup>2</sup>T. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **1954**, 9, 766.

## Transitions for $V^{3+} (d^2) O_h$ Complexes

Complex	${}^3T_{1g}(F) \rightarrow {}^3T_{2g}$ ( $\text{cm}^{-1}$ )	${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ ( $\text{cm}^{-1}$ )	${}^3T_{1g}(F) \rightarrow {}^3A_{2g}$ ( $\text{cm}^{-1}$ )	$\Delta_o$ ( $\text{cm}^{-1}$ )
$[V(\text{H}_2\text{O})_6]^{3+}$	17,200	25,000	38,000	21,500
$[V(\text{ox})_3]^{3-}$	17,000	24,000	—	17,800

Uv-vis spectrum of  $[V(\text{H}_2\text{O})_6]^{3+}$



- $\nu_1 [{}^3T_{1g}(F) \rightarrow {}^3T_{2g}]$  and  $\nu_2 [{}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)]$  are shown.
- $\nu_3 [{}^3T_{1g}(F) \rightarrow {}^3A_{2g}]$  at  $38,000 \text{ cm}^{-1}$  falls in the uv and is not shown.



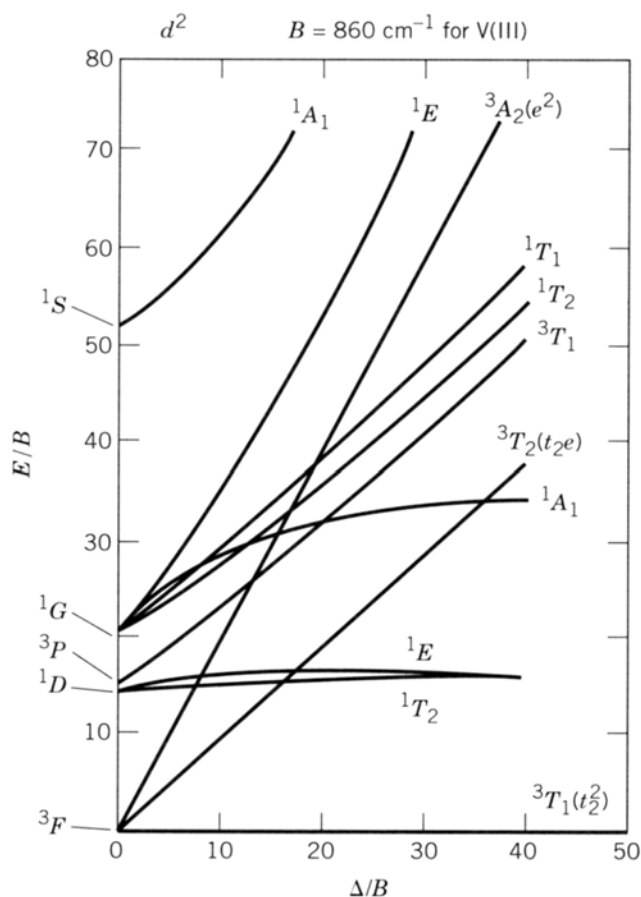
## Tanabe-Sugano Diagrams

- Tanabe-Sugano diagrams for configurations  $d^2 - d^8$  are published in most advanced inorganic chemistry and group theory texts.<sup>3</sup>
  - These plot energy ( $E$ ) above the ground state as  $\Delta_o$  changes.
  - $B$  is the Racah parameter, which is a measure of repulsion between terms of the same multiplicity.
  - The ordinate is  $E/B$  and the abscissa is  $\Delta_o/B$ .
  - Although they can be used quantitatively, most often Tanabe-Sugano diagrams are used qualitatively.
  - State notations usually do not show the subscript  $g$  notation, which should be added when discussing transitions of  $O_h$  complexes.
- Tanabe-Sugano diagrams for  $d^4, d^5, d^6, d^7$  have a vertical line down the middle, separating high-spin (low field) cases on the left, and low-spin (high field) cases on the right.

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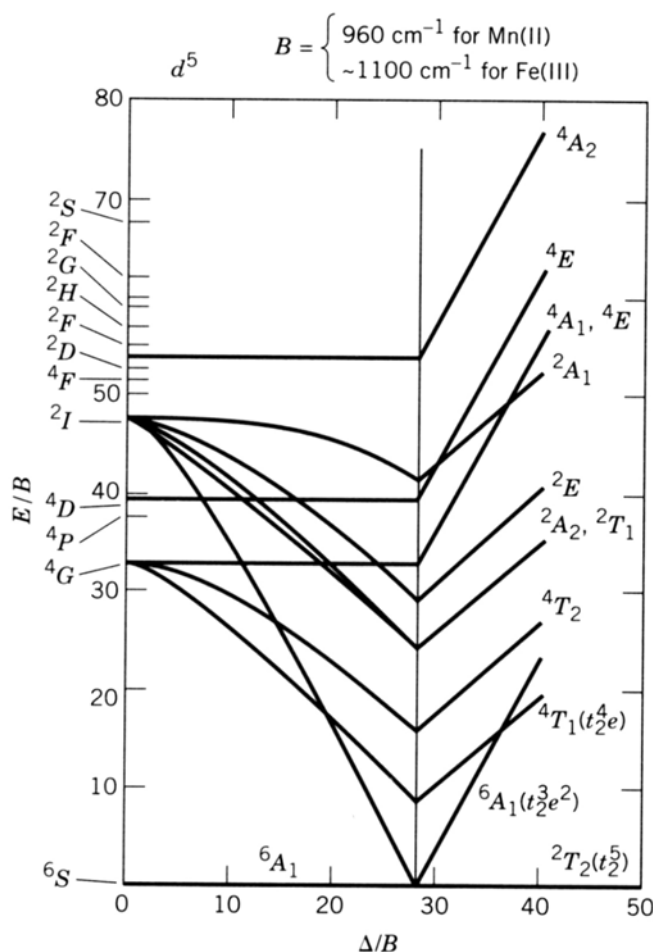
<sup>3</sup>Simplified diagrams are shown as Figure 11.7 in G. L. Miessler and D. A. Tarr, *Inorganic Chemistry*, 4th ed., Prentice Hall, NY, p. 427; more complete diagrams are shown in Appendix D in R. L. Carter, *Molecular Symmetry and Group Theory*, Wiley, NY, 1998, pp. 289-292.

## Complete $d^2$ Tanabe-Sugano Diagram

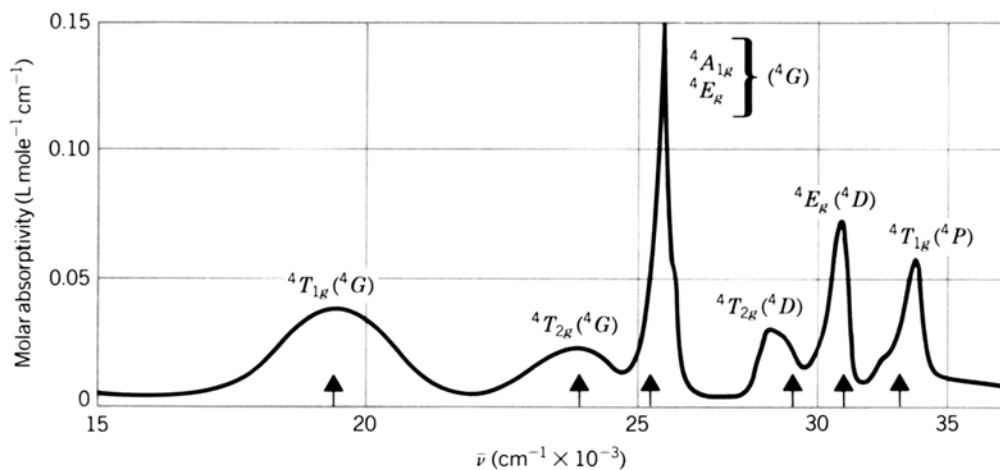


- In addition to the three possible spin-allowed transitions (cf. previous diagram), there are seven singlet states that suggest there could be as many as seven multiplicity (spin) forbidden transitions.
  - Transitions from the  $3T_{1g}$  ground state to any of the singlet states would have extremely low  $\epsilon$  values and are seldom observed in routine work.
  - Some singlet states (e.g.,  $1A_{1g}$ ,  $1E_g$ ) are so high in energy that transitions to them would fall in the uv, where they would likely be obscured by the intense CT band.

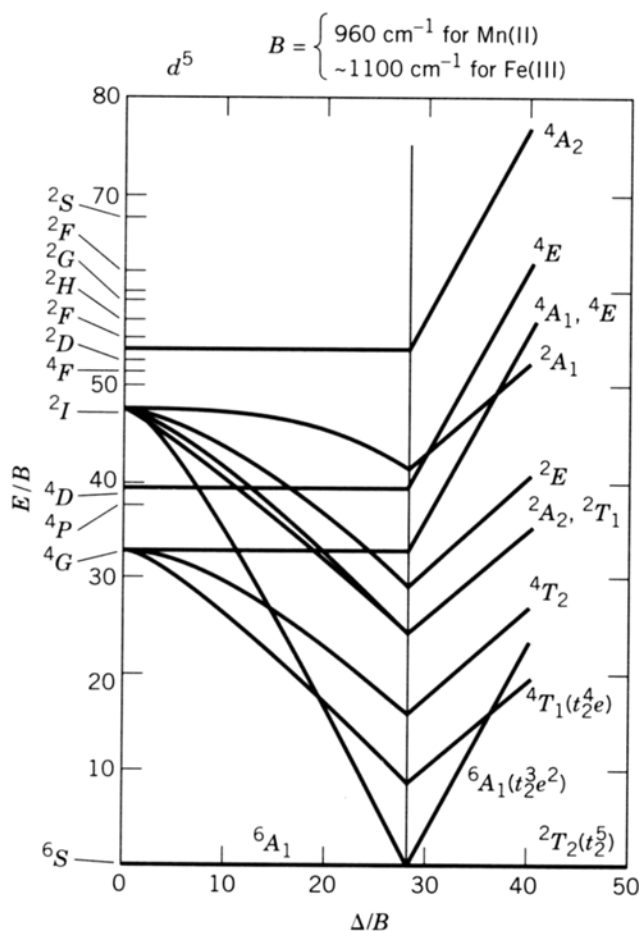
## $d^5$ Tanabe-Sugano Diagram – High-Spin Side ( $t_{2g}^3 e_g^2$ )



- High-spin side (left) has no sextuplet excited states, so all transitions from the  $6A_{1g}$  ground state are spin forbidden, as previously noted.
  - Spectrum of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  shows only very weak absorptions.



## $d^5$ Tanabe-Sugano Diagram – Low-Spin Side ( $t_{2g}^5$ )



- As field strength increases on the high-spin side, the  ${}^2T_{2g}$  state, emanating from the  ${}^2I$  free-ion term, descends in energy and becomes the ground state at the cross-over point to low-spin cases (right).
  - At the cross-over point to low-spin cases the former  ${}^6A_{1g}$  ground state of high-spin cases ascends rapidly.
- On the low-spin side, there are potentially three spin-allowed transitions:
 
$${}^2T_{2g} \rightarrow ({}^2A_{2g}, {}^2T_{1g}) \quad {}^2T_{2g} \rightarrow {}^2E_g \quad {}^2T_{2g} \rightarrow {}^2A_{1g}$$
  - Spectra of  $d^5$  low-spin octahedral complexes are expected to show three bands, although the band from  ${}^2T_{2g} \rightarrow {}^2A_{1g}$  might fall in the uv.
  - The  ${}^2A_{2g}$  and  ${}^2T_{1g}$  states are accidentally degenerate (i.e., not fundamentally degenerate by symmetry), and only one band is expected from transitions to both states.

## Orgel Diagrams - Principles

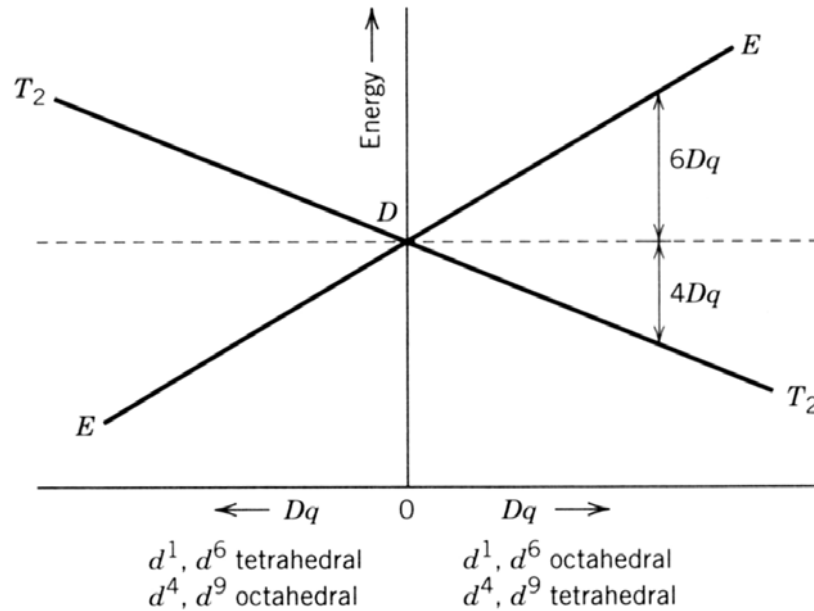
- In 1955 L. E. Orgel<sup>4</sup> published a set of two diagrams, which are easily memorized, to account qualitatively for the spectra of all  $d^1$ – $d^9$  high-spin cases of both octahedral ( $O_h$ ) and tetrahedral ( $T_d$ ) complexes.
- Orgel diagrams are based on the following relationships:
  - ①  $d^n (O_h)$  and  $d^{n\pm 5}$  have the same diagram.
  - ②  $d^n (T_d)$  and  $d^{n\pm 5}$  have the same diagram.
  - ③  $d^n, d^{n\pm 5} (O_h)$  is the reverse of  $d^n, d^{n\pm 5} (T_d)$ .
  - ④  $d^n (O_h)$  is the reverse of  $d^{10-n} (O_h)$ , and  $d^n (T_d)$  is the reverse of  $d^{10-n} (T_d)$ .
- Labels on Orgel diagrams do not include spin multiplicity designations or  $g$  subscripts for octahedral cases.
  - Multiplicities must be added when discussing specific transitions.
  - Subscript  $g$  should be added to all states when discussing octahedral complexes with centrosymmetry (true  $O_h$ ).
- ☛ Orgel diagrams only cover high-spin cases.
- ☛ Orgel diagrams only account for spin-allowed transitions.
- ☛ Orgel diagrams are for qualitative purposes only.
- ☛ Tanabe-Sugano diagrams must be used for low-spin cases and any spin-forbidden transitions (high-spin or low-spin).

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<sup>4</sup>L. E. Orgel, *J. Chem. Phys.*, **1955**, 23, 1004.

## Orgel Diagram for $d^1$ ( $O_h$ ) and Related Cases

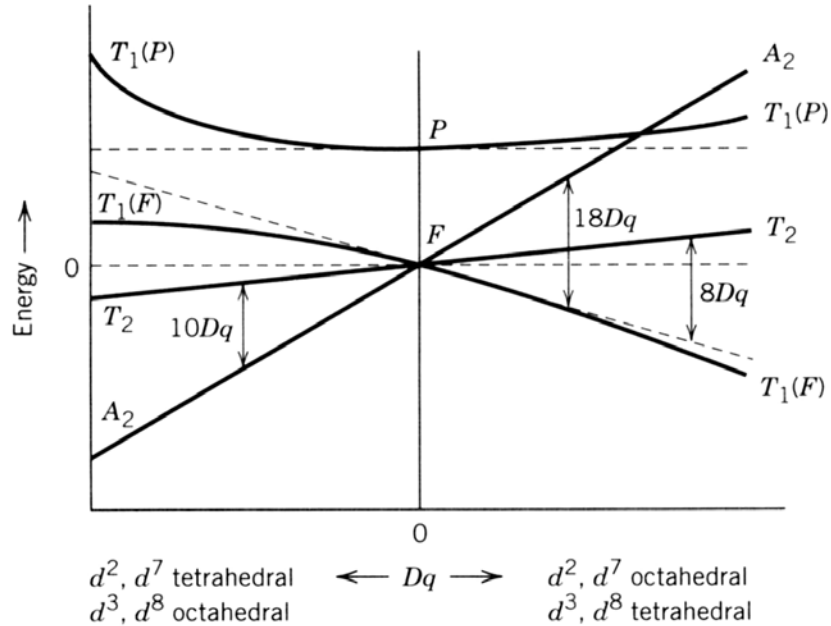
- This diagram can be easily remembered by starting with the  $d^1$  case, where a free-ion  $D$  state is split into a  $T_2$  ground state and a  $E$  excited state.
- The rest of the diagram is generated by extrapolating the lines to the left side and invoking the relationships previously noted.



- One visible absorption band is expected for all cases covered by this diagram, either  $T_2 \rightarrow E$  or  $E \rightarrow T_2$ .

## Orgel Diagram for $d^2 (O_h)$ and Related Cases

- This somewhat more complicated diagram can be remembered by knowing the splitting for  $d^2 (O_h)$ , extrapolating the lines to the left side, and invoking the relationships previously noted.



- The  $T_1(F)$  and  $T_1(P)$ , being same symmetry, curve away from each other as a result of the quantum mechanical non-crossing rule.
- Three visible absorption bands are expected for all cases covered by this diagram, either from a  $T_1(F)$  or  $A_2$  ground state.

## Estimating $\Delta_o$ from Spectra

- Relationship between  $\Delta_o$  and observed spectral band frequencies depends upon the  $d^n$  configuration.
  - The following guidelines apply only to those octahedral ( $O_h$ ) cases covered by the Orgel diagrams.
  
- ① For cases related to the  $d^1$  ( $O_h$ ) diagram, the frequency of the single band ( $T_{2g} \rightarrow E_g$  or  $E_g \rightarrow T_{2g}$ ) is  $\Delta_o$ .  
 $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ :  $\nu = 12,500 \text{ cm}^{-1} = \Delta_o$
  
- ② For  $d^3$  and  $d^8$  (left side of the  $d^2$  Orgel diagram), the ground state is  $A_{2g}$  and the frequency of the first band,  $\nu_1$  ( $A_{2g} \rightarrow T_{2g}$ ), is  $\Delta_o$ .  
 $\text{Cr}(\text{NH}_3)_6^{3+}$ :  $\nu_1 = 21,500 \text{ cm}^{-1} = \Delta_o$
  
- ③ For  $d^2$  and  $d^7$  high-spin, the ground state  $T_{1g}(F)$  is repelled by the excited state  $T_{1g}(P)$ .
  - Relationship between the ground state and any excited state is not fixed in terms of  $\Delta_o$ .
  - For exact work, the Racah parameter,  $B$ , must be used to correct for the repulsions between the  $T_{1g}$  states.
  - For an *approximate* value of  $\Delta_o$  the following relationships can be used.
    - $\Delta_o \approx \nu_1 [T_{1g}(F) \rightarrow T_{2g}]/0.8$
    - $\Delta_o \approx \nu_3 [T_{1g}(F) \rightarrow A_{2g}]/1.8$
    - $\Delta_o \approx \nu_3 [T_{1g}(F) \rightarrow A_{2g}] - \nu_1 [T_{1g}(F) \rightarrow T_{2g}]$
  - Inasmuch as  $\nu_3$  is often not observed, only the first relationship is generally usable.
    - $\text{V}(\text{H}_2\text{O})_6^{3+}$ :  $\nu_1 = 17,200 \text{ cm}^{-1}$
    - $\Delta_o \approx 17,200 \text{ cm}^{-1}/0.8 \approx 21,500 \text{ cm}^{-1}$
  
- For cases not covered by the Orgel diagrams, a quantitative Tanabe-Sugano diagram and estimation of the Racah parameter are required.



## Jahn-Teller Effect

☛ Jahn-Teller Theorem: For any nonlinear system in a degenerate state, a distortion will occur that will lift the degeneracy.

● For octahedral complexes, only five ground-state configurations are immune from Jahn-Teller distortion:

$d^3$  ( ${}^4A_{2g}$ ),  $d^5$  high-spin ( ${}^6A_{1g}$ ),  $d^6$  low-spin ( ${}^1A_{1g}$ ),  $d^8$  ( ${}^3A_{2g}$ ),  $d^{10}$  ( ${}^1A_{1g}$ )

● All other configurations have a degenerate ground state ( $E$  or  $T$ ).

● The strongest distortions result from a  ${}^2E_g$  term arising from configurations  $t_{2g}^n e_g^1$  and  $t_{2g}^n e_g^3$ , which have unequal distribution of electrons in orbitals pointing at ligands.

• Consider the two microstates of  $t_{2g}^6 e_g^3$ :

$$t_{2g}^6(d_{x^2-y^2})^2(d_{z^2})^1 \qquad t_{2g}^6(d_{x^2-y^2})^1(d_{z^2})^2$$

✓ With  $t_{2g}^6(d_{x^2-y^2})^2(d_{z^2})^1$ , ligands in the  $xy$  plane are more shielded from the nuclear charge than those along  $z$ .

✓ With  $t_{2g}^6(d_{x^2-y^2})^1(d_{z^2})^2$ , ligands along  $z$  are more shielded from the nuclear charge than those in the  $xy$  plane.

☛ Either microstate results in inequality among M–L distances, producing a distortion from perfect  $O_h$  symmetry.

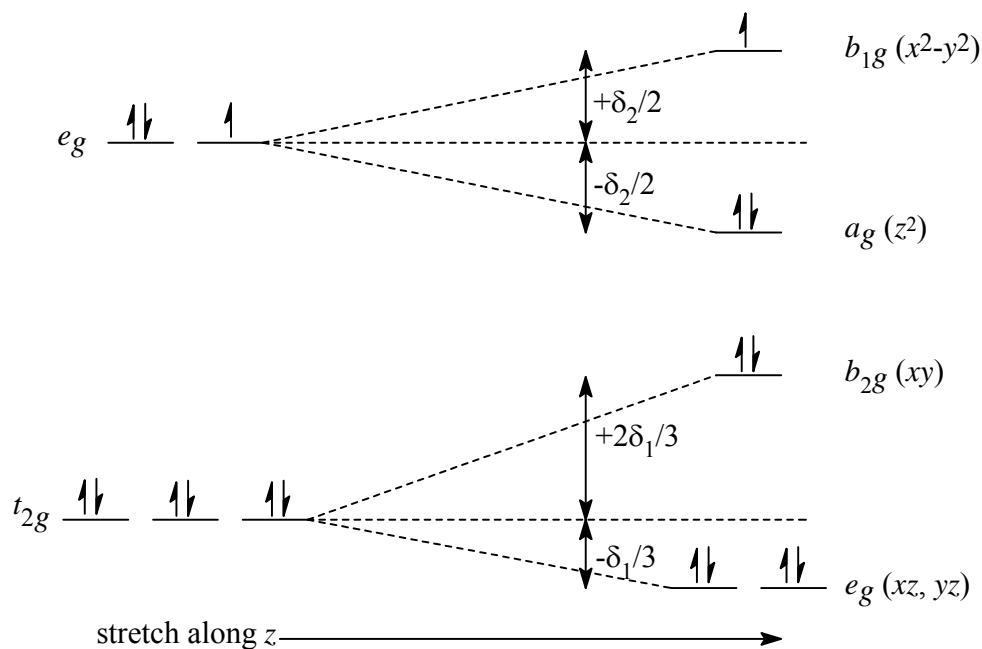
● The Jahn-Teller theorem does not predict the exact distortion, but the following corollary is observed.

☛ Jahn-Teller Corollary: If the system is centrosymmetric, the distorted configuration will also be centrosymmetric.

● For  $O_h$  complexes, the distortion will cause a descent in symmetry to a centrosymmetric subgroup.

## Tetragonal Distortion of Octahedral $ML_6$

- For  $ML_6$  complexes, a tetragonal distortion  $O_h \rightarrow D_{4h}$  is the most probable result of the Jahn-Teller effect.
  - Either equal stretching or compression of two *trans*-related positions would result in this kind of distortion.
  - Jahn-Teller theorem cannot predict the distortion and either or both may occur.
- Suppose a  $d^9$   $ML_6$  complex undergoes equal stretching of the *trans*-related positions along  $z$ .



- The distortion results in a Jahn-Teller stabilization energy:

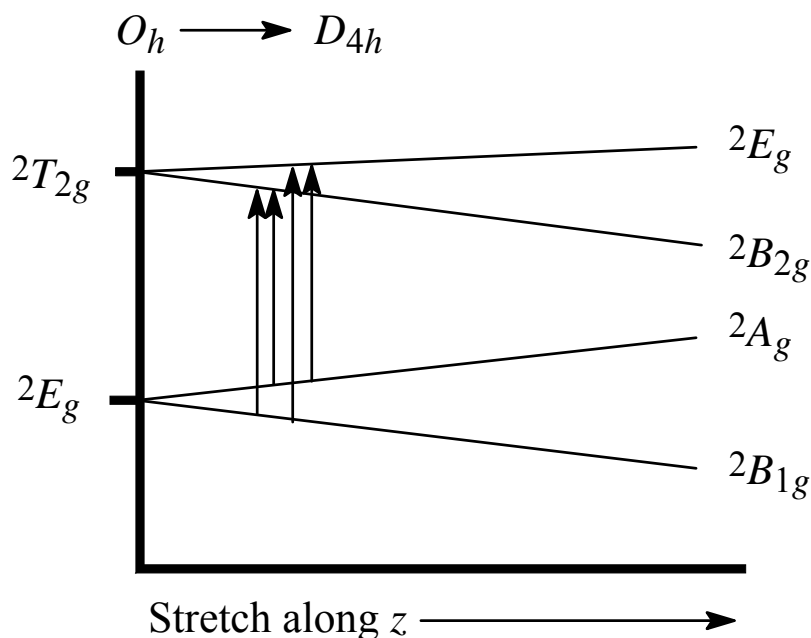
$$\Delta E_{JT} = -2(\delta_2/2) + \delta_2/2 = -\delta_2/2$$

- The new state is non-degenerate  ${}^2B_{1g}$  in  $D_{4h}$ , because there is only one microstate for the configuration of lowest energy.
- The stabilization energy achieved drives the distortion.
- Compression along  $z$  would give the opposite splitting but the same stabilization energy.
  - The new state would be non-degenerate  ${}^2A_g$  in  $D_{4h}$ .

## Strong and Weak Jahn-Teller Distortion

- Configurations with  $e_g^1$  or  $e_g^3$  show pronounced Jahn-Teller distortions, because the orbitals are directed at ligands.
  - These configurations correspond to  $E_g$  terms.
- Configurations with  $t_{2g}^1$ ,  $t_{2g}^2$ ,  $t_{2g}^4$ ,  $t_{2g}^5$  have weaker Jahn-Teller distortions, because these orbitals lie between ligands.
  - These configurations correspond to  $T_{1g}$  or  $T_{2g}$  states.
- Jahn-Teller distortion causes splitting of  $E$  and  $T$  terms, whether ground- or excited-state.
  - Energy split for any  $E$  term is greater than the energy split for  $T$  terms of the same complex.

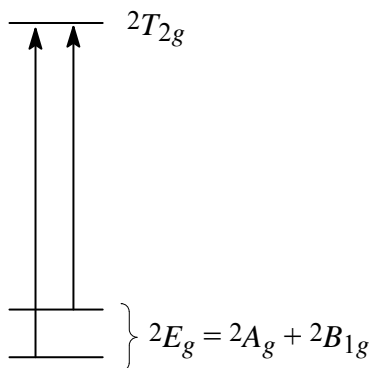
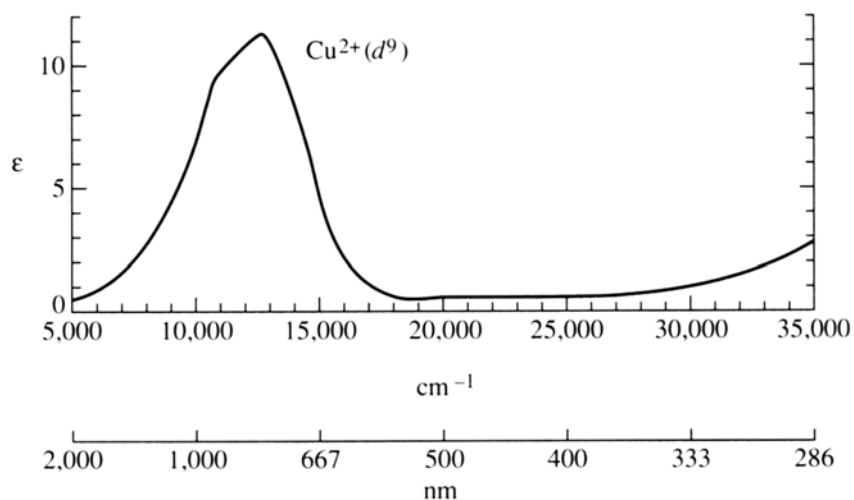
Example: Assuming a stretching tetragonal distortion, the two terms of an octahedral  $d^9 ML_6$  complex would split as shown in the following diagram.



- Because both ground- and excited-state terms are split, additional transitions are possible, which contribute to band broadening.

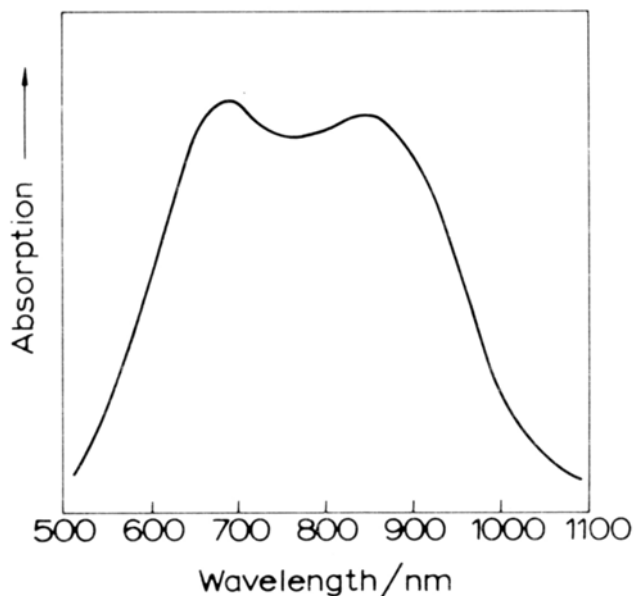
## Spectroscopic Evidence of Jahn-Teller Distortions Splitting of the Ground State

- In some cases the larger split of an  $E$  state results in two partially resolved bands.
- The shoulder in the single band for  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  results from splitting of the  ${}^2E_g$  ground state into two distinct states with two transition energies to the slightly split  ${}^2T_{2g}$  excited state.

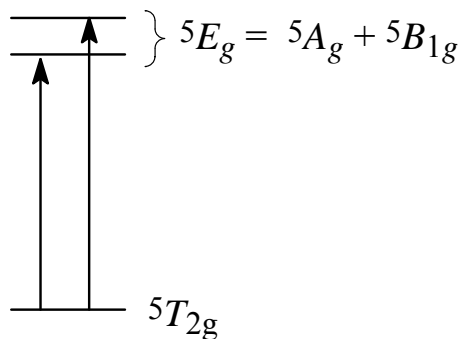


## Spectroscopic Evidence of Jahn-Teller Distortions Splitting of the Excited State

- The uv-vis spectrum of  $\text{CoF}_6^{3-}$ , a  $d^6$  high-spin case,<sup>5</sup> shows two distinct bands, although only one is expected from  ${}^5T_{2g} \rightarrow {}^5E_g$ .



- The ground state ( ${}^5T_{2g}$ ) is only slightly distorted, but the excited state ( ${}^5E_g$ ) is strongly distorted.
- The  ${}^5E_g$  state is split into two distinct states ( ${}^5A_g + {}^5B_{1g}$  in  $D_{4h}$ ), whose different energies give rise to two different transition energies, and hence two bands.




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<sup>5</sup> $\text{CoF}_6^{3-}$  is an exception to the tendency for  $\text{Co}^{3+} \text{ML}_6$  complexes to be  $d^6$  low-spin.