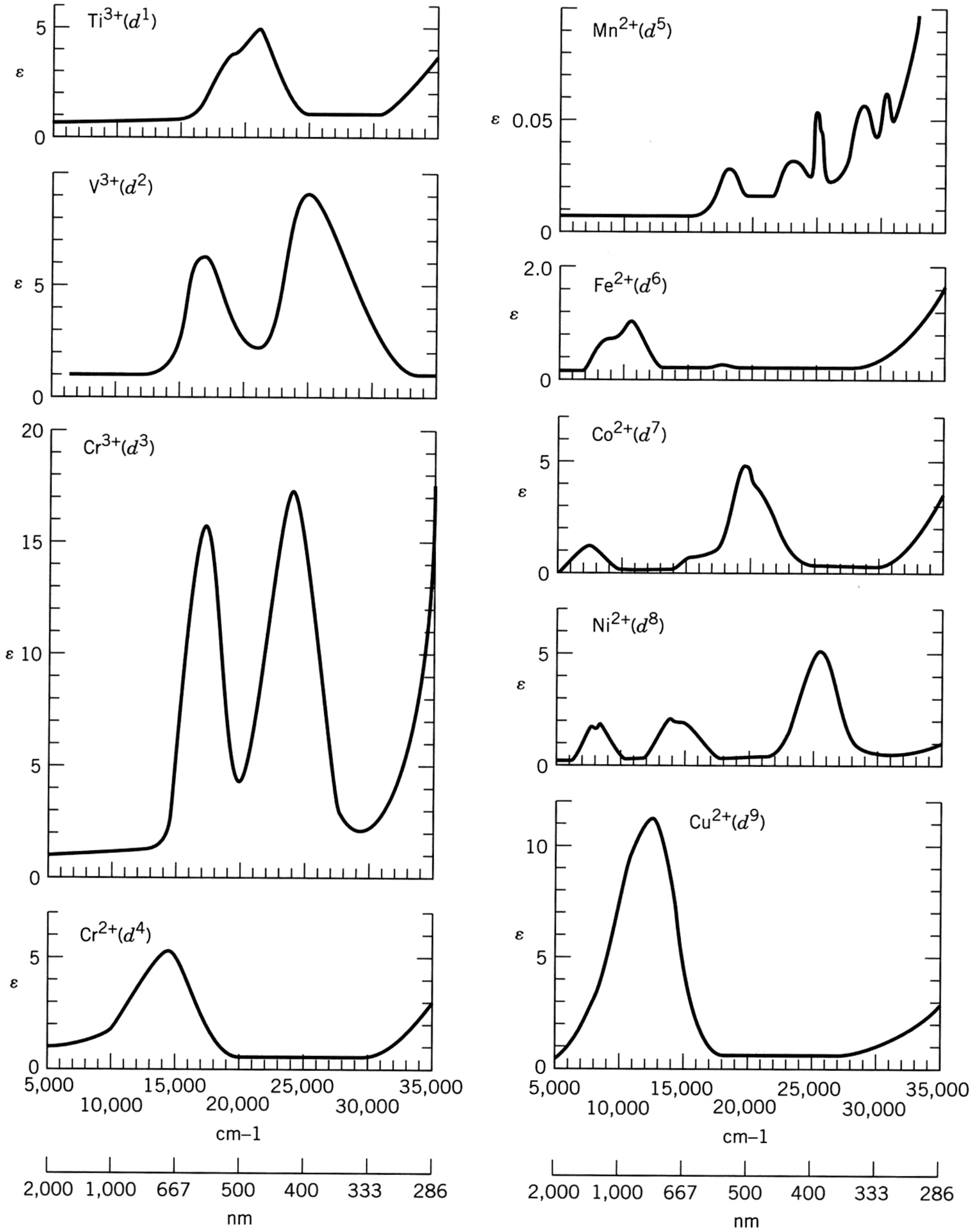
Absorption Spectra

- 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 ~500 nm = ~20,000 cm^{-1}.

Beer-Lambert Law

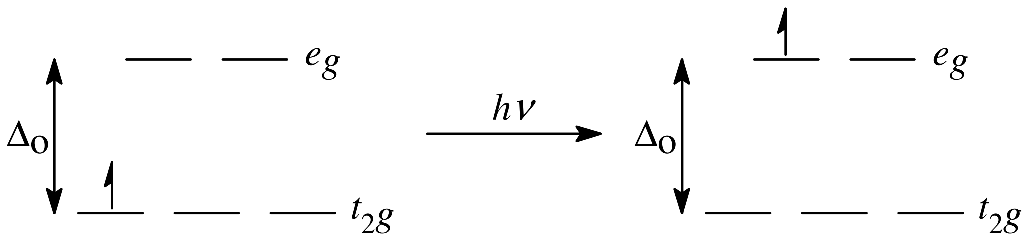
- The absorption at any wavelength obeys the Beer-Lambert Law:

$$A = \log(I_o/\mathrm{I}) = \varepsilon c b$$

where A = absorbance
I_o = incident light intensity
I = transmitted light intensity
ε = 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 $Ti(H_2O)_6^{3+}$ (d^1) the absorption causes the configuration to change from $t_{2g}^1e_g^0$ to $t_{2g}^0e_g^1$.



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

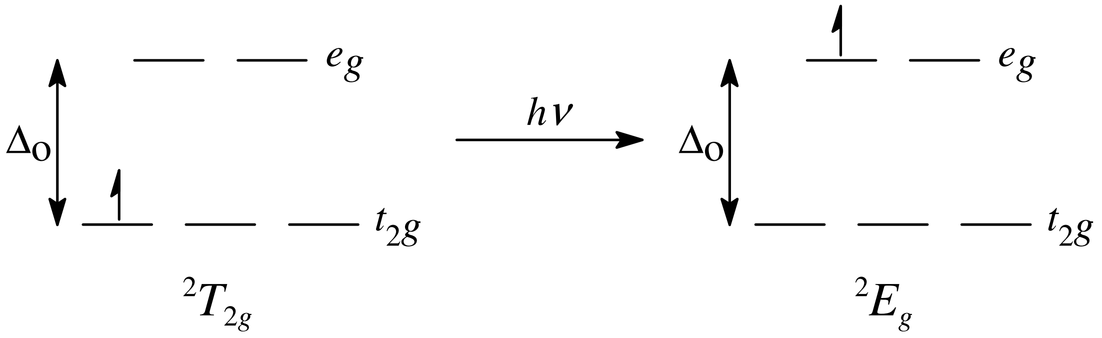
$$t_{2g}^1e_g^0 \Rightarrow d_{xy}^1 = d_{yz}^1 = d_{xz}^1$$

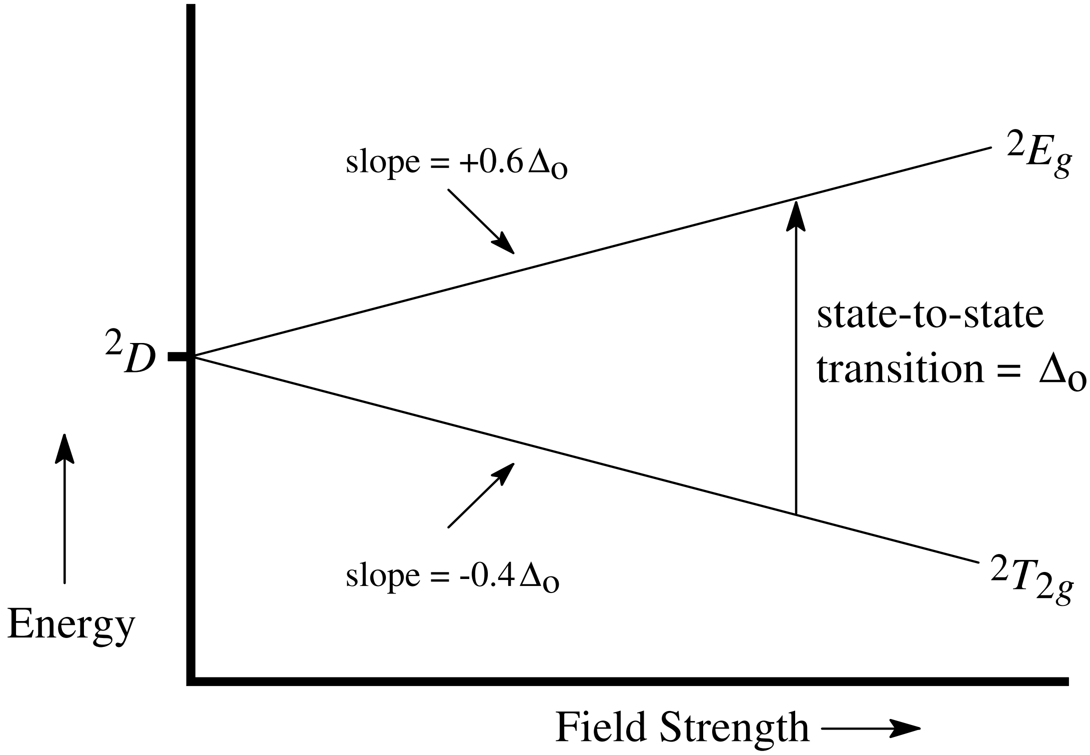
  - The excited state is doubly degenerate, corresponding to the two microstates represented by $t_{2g}^0e_g^1$.

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

- 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 $\Delta_o = 10Dq$, which is energetically equivalent to the frequency of the absorption, for $[Ti(H_2O)_6]^{3+}$~20,000 cm^{-1}.
  - Breadth of the observed band is in part a result of the oscillation of the strength of Δ_o as the complex vibrates.

- The state notation for the absorption transition is

$$^2T_{2g} \rightarrow {}^2E_g$$

Free-Ion Terms for $d^{1\text{-}10}$ 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

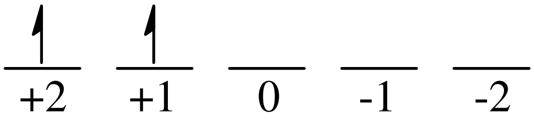
① Write out the configuration so as to maximize the total orbital angular momentum and total spin (Hund's Rule).

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

L	0	1	2	3	4	...
Term	S	P	D	F	G	...

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

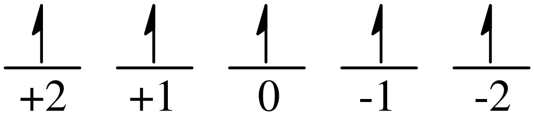
d^2



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

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

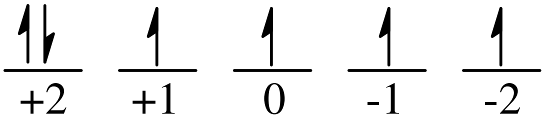
d^5



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

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

d^6



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

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

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
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
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.[1]

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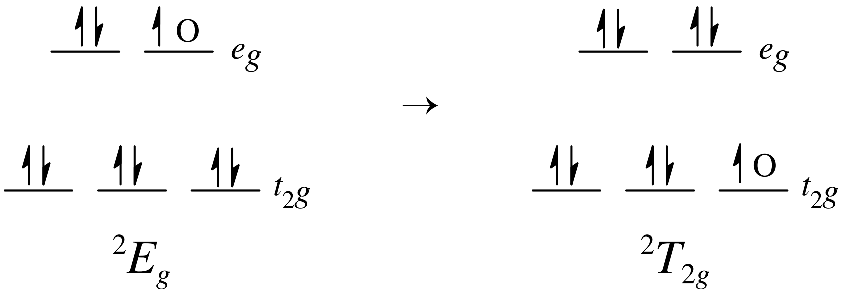
[1] Cf. R. L. Carter, *Molecular Symmetry and Group Theory,* Wiley, NY 1998, p. 205 & 233-236.

Electronic Transitions for d^9 O_h

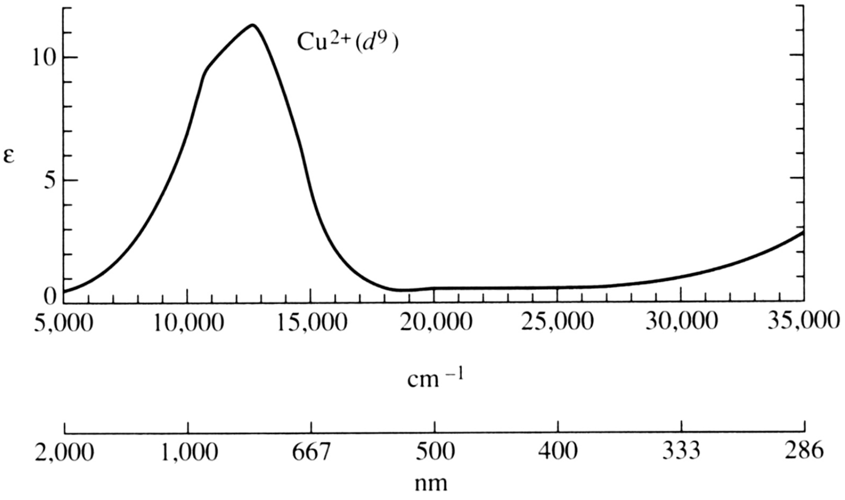
- For d^1 there is only one state-to-state transition, $^2T_{2g} \rightarrow {}^2E_g$.

- 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.

- $Cu(H_2O)_6^{2+}$ has a blue color due to the single $^2E_g \rightarrow {}^2T_{2g}$ electronic transition at ~800 nm.



- The state notation for this transition is

$$^2E_g \rightarrow {}^2T_{\mathbf{2g}}$$

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 ($\varepsilon >> 10^3$).
  - 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 ($\varepsilon \approx 5 - 100$).
  - *d-d* transitions between states with different spin multiplicities typically have very low molar absorptivities ($\varepsilon < < 1$).

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* → *g*, *u* → *u*) are forbidden, but transitions between states of different inversion symmetry (*g* → *u*, *u* → *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., $\mathrm{Co(en)_3}^{2+}$ – D_3).

- Either vibronic or static distortion results in a small departure from centrosymmetry, so the molar absorptivities are typically $\varepsilon \approx 5 - 50$.

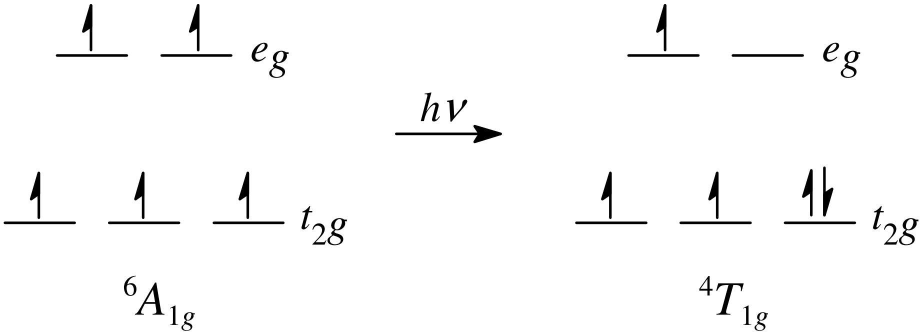
- Tetrahedral $\mathrm{ML_4}$ complexes (T_d) have no inversion symmetry.
  - *d-d* transitions for tetrahedral complexes are *Laporte allowed*.
  - Because they are allowed, these transitions have higher molar absorptivities ($\varepsilon \approx 100 - 1000$).

- CT transitions are $g \leftrightarrow u$, allowed by the Laporte Rule, and so have very high molar absorptivities ($\varepsilon >> 10^3$).

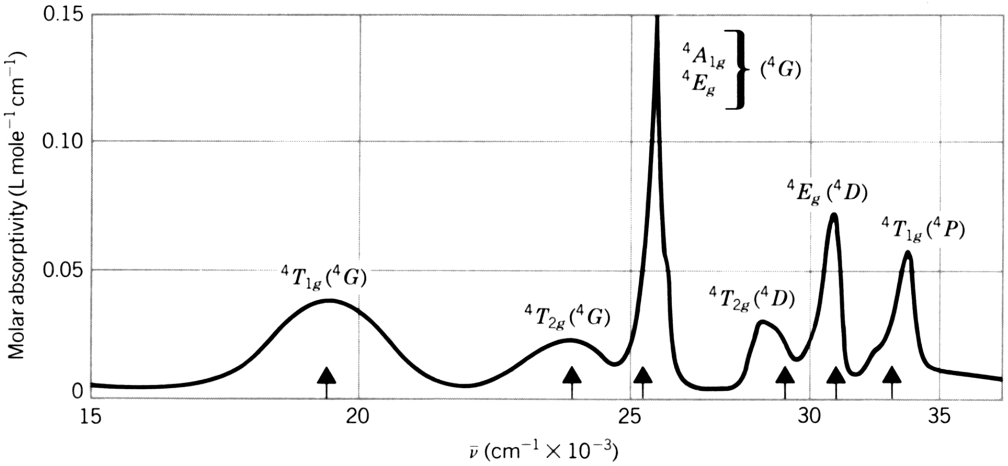
Violations of the Spin Multiplicity Rule

- 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:



- $Mn(H_2O)_6^{2+}$ is a d^5 high-spin octahedral complex with a very pale pink color, owing to a series of weak spin-forbidden transitions.



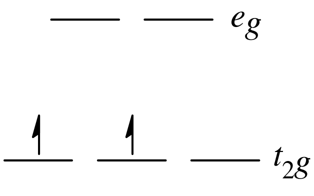
  - Note that for all absorptions $\varepsilon < 0.15$.

☛ We will be most concerned with *d-d* transitions that are spin allowed (i.e., Laporte forbidden but vibronically allowed same-spin transitions).

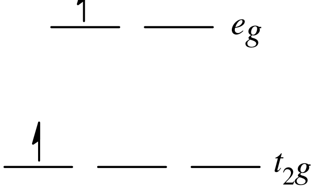
Triplet Terms for d^2 O_h

- 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.

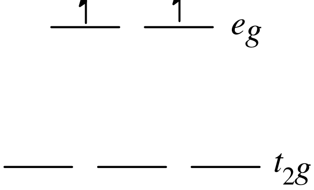
- The triplet terms of d^2 in O_h arise from the following configurations:



$t_{2g}{}^2 \Rightarrow {}^3T_{1g}(F)$



$t_{2g}{}^1 e_g{}^1 \Rightarrow {}^3T_{1g}(P) + {}^3T_{2g}$



$e_g{}^2 \Rightarrow {}^3A_{2g}$

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 ${}^{3}T_{2g}$ the two electrons are placed in *d* orbitals that are geometrically orthogonal to each other:

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

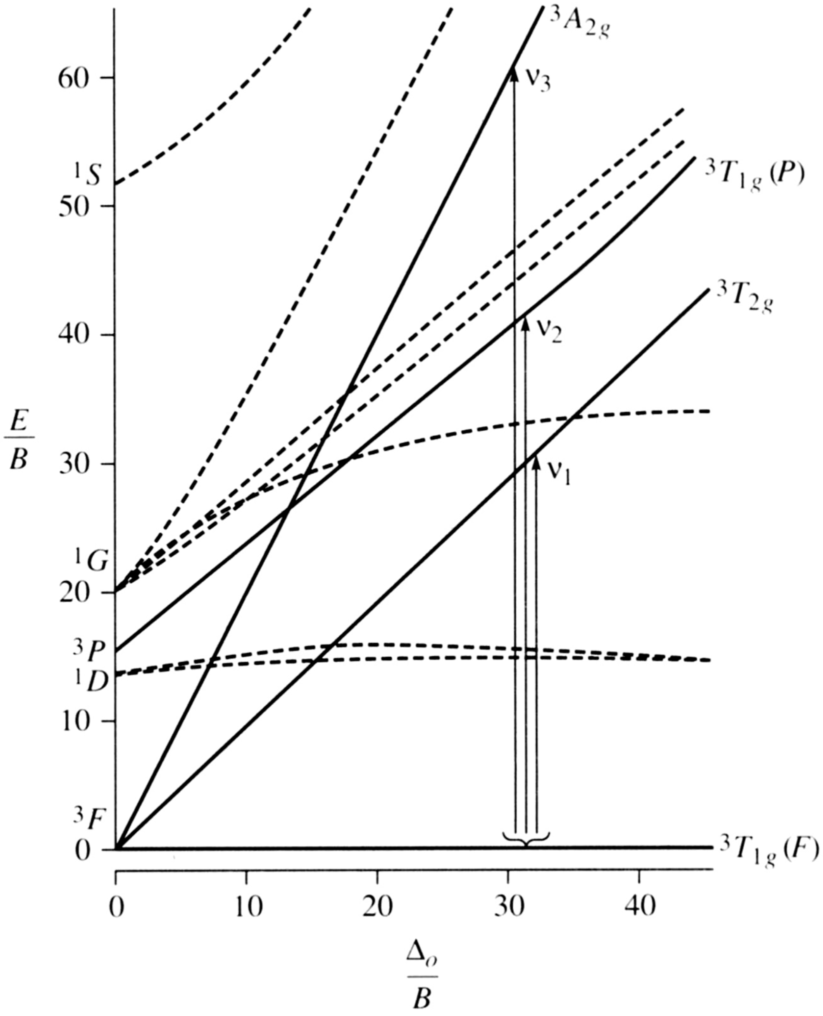
- In all three microstates of ${}^{3}T_{1g}(P)$ the two electrons are placed in *d* orbitals that lie in the same plane:

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

- Electron-electron repulsions are less in the microstates of ${}^{3}T_{2g}$ than they are in the microstates of ${}^{3}T_{1g}(P)$, so the energy of the ${}^{3}T_{2g}$ 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[2], shows the free-ion states, the octahedral states arising from them, and the energy separations between states as a function of Δ_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.

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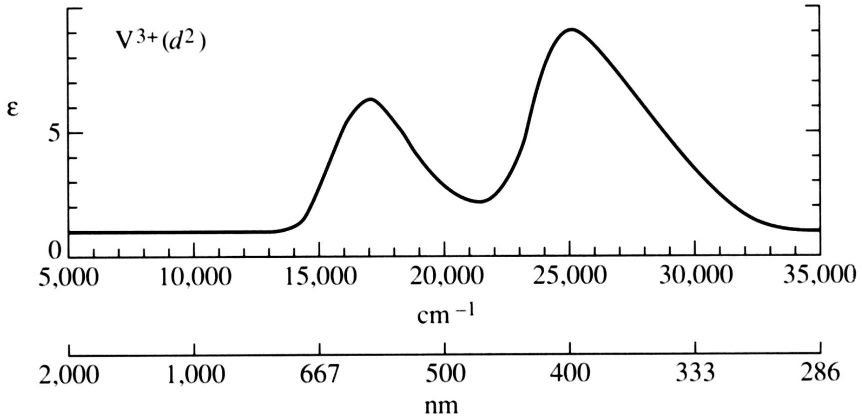
[2] T. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **1954**, *9*, 766.

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

Complex	${}^3T_{1g}(F) \rightarrow {}^3T_{2g}$ (cm^{-1})	${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ (cm^{-1})	${}^3T_{1g}(F) \rightarrow {}^3A_{2g}$ (cm^{-1})	Δ_o (cm^{-1})
$[V(H_2O)_6]^{3+}$	17,200	25,000	38,000	21,500
$[V(ox)_3]^{3-}$	17,000	24,000	—	17,800

Uv-vis spectrum of $[V(H_2O)_6]^{3+}$



- ν_1 [${}^3T_{1g}(F) \rightarrow {}^3T_{2g}$] and ν_2 [${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$] are shown.
- ν_3 [${}^3T_{1g}(F) \rightarrow {}^3A_{2g}$] at 38,000 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.[3]
  - These plot energy (E) above the ground state as Δ_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 Δ_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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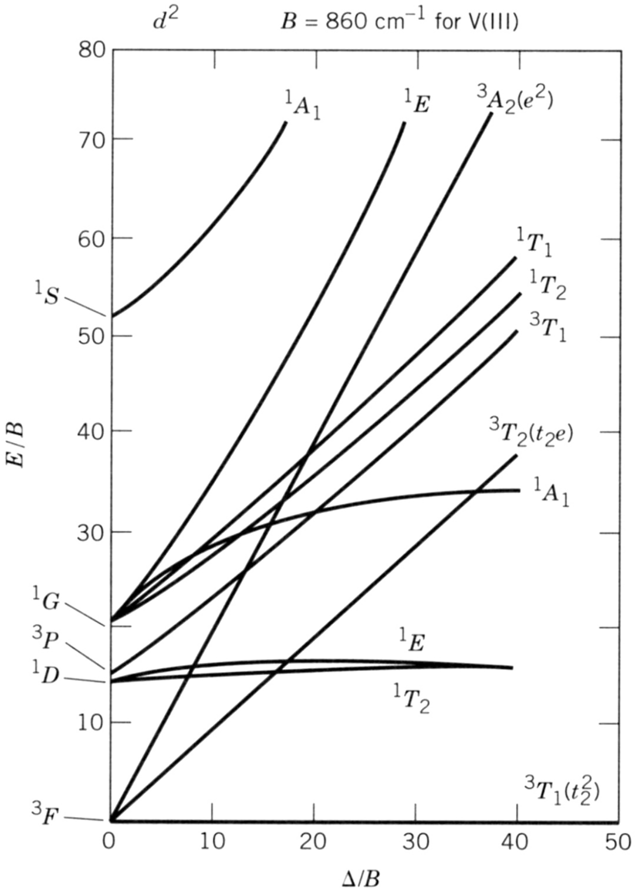
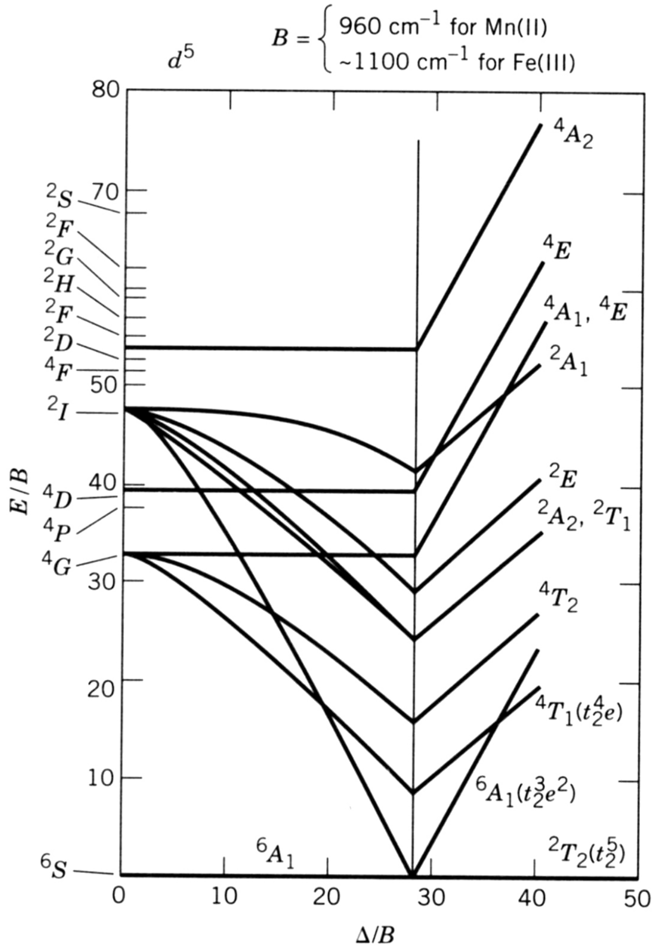
[3] Simplified diagrams are shown as Figure 11.7 in G. L. Miessler and D. A. Tarr, *Inorganic Chemistry*, 4th ed., Prentice Hall, NY, p. 427; more complete diagrams are shown in Appendix D in R. L. Carter, *Molecular Symmetry and Group Theory*, Wiley, NY, 1998, pp. 289-292.

Complete d^2 Tanabe-Sugano Diagram

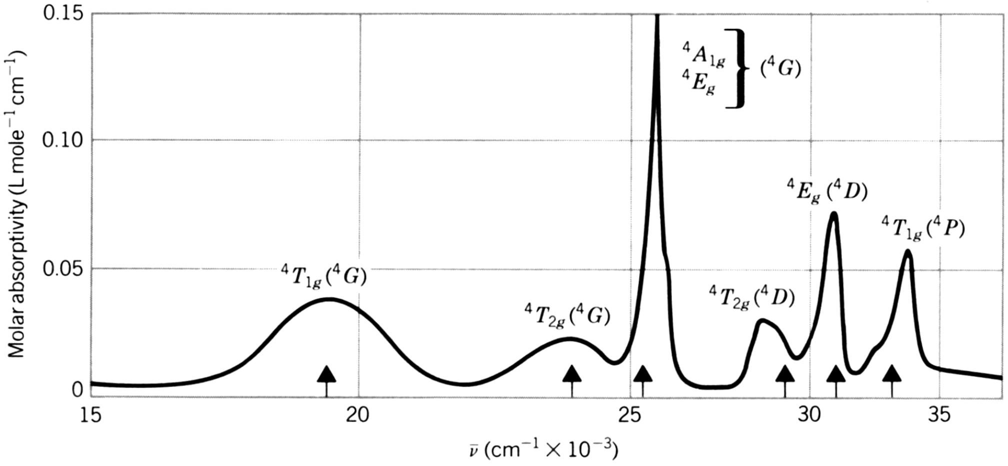


- In addition to the three possible spin-allowed transitions (cf. previous diagram), there are seven singlet states that suggest there could be as many as seven multiplicity (spin) forbidden transitions.
  - Transitions from the $^3T_{1g}$ ground state to any of the singlet states would have extremely low ε 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.

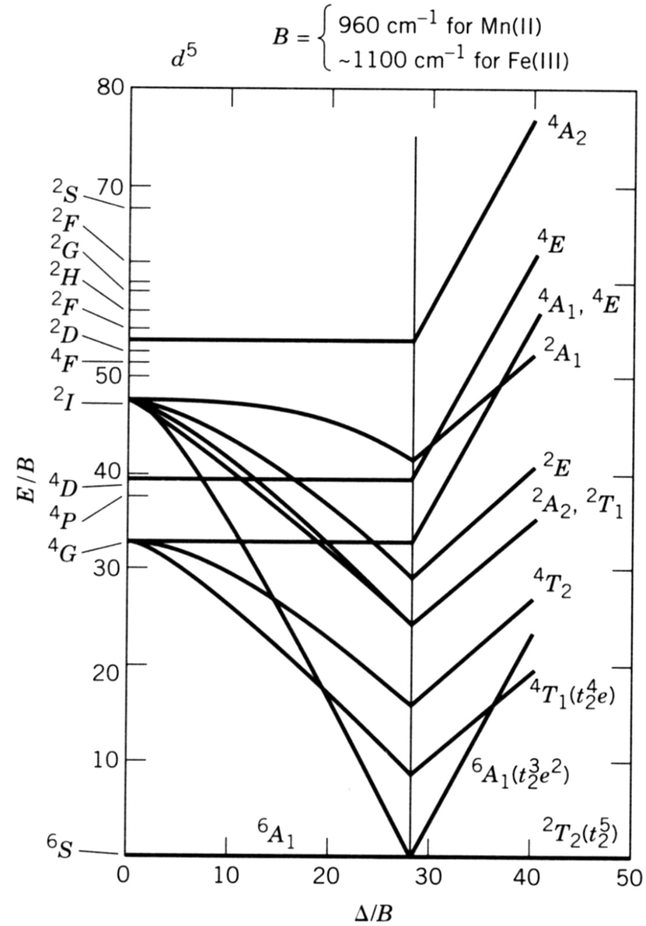
d^5 Tanabe-Sugano Diagram – High-Spin Side ($t_{2g}^3e_g^2$)



- 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 $[Mn(H_2O)_6]^{2+}$ 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[4] 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 $d^{n\pm5}$ have the same diagram.
  ② d^n (T_d) and $d^{n\pm5}$ have the same diagram.
  ③ d^n, $d^{n\pm5}$ (O_h) is the reverse of d^n, $d^{n\pm5}$ (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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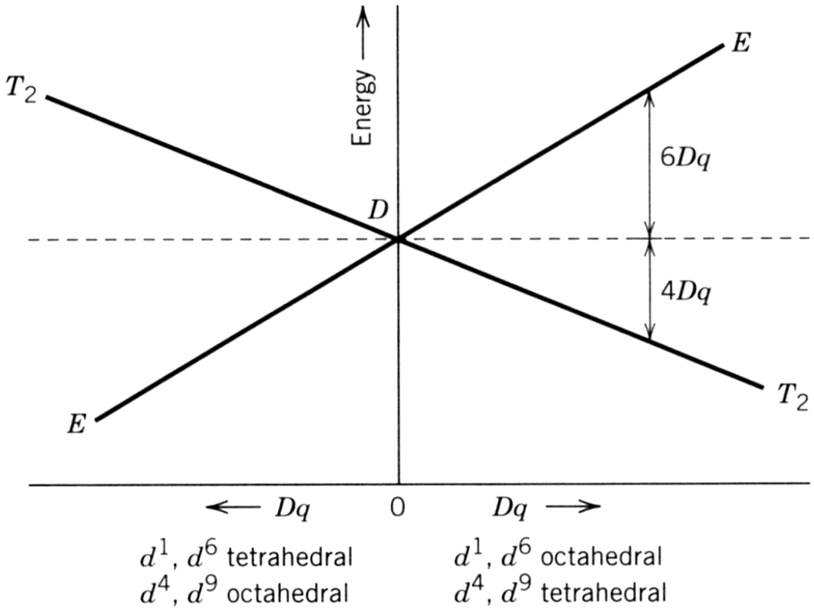
[4] L. E. Orgel, *J. Chem. Phys.,* **1955**, *23*, 1004.

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

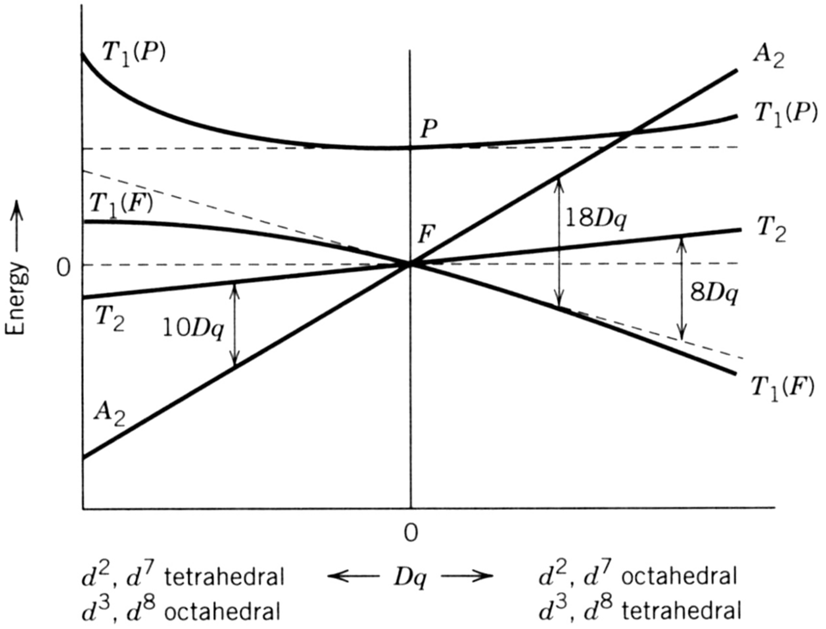
- This diagram can be easily remembered by starting with the d^1 case, where a free-ion D state is split into a T_2 ground state and a E excited state.
  - The rest of the diagram is generated by extrapolating the lines to the left side and invoking the relationships previously noted.



- 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 spitting 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 Δ_o from Spectra

- Relationship between Δ_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 Δ_o.

$Cu(H_2O)_6^{2+}$: $\nu = 12{,}500\ \mathrm{cm}^{-1} = \Delta_o$

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, ν_1 ($A_{2g} \rightarrow T_{2g}$), is Δ_o.

$Cr(NH_3)_6^{3+}$: $\nu_1 = 21{,}500\ \mathrm{cm}^{-1} = \Delta_o$

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 Δ_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 Δ_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 ν_3 is often not observed, only the first relationship is generally usable.

$V(H_2O)_6^{3+}$: $\nu_1 = 17{,}200\ \mathrm{cm}^{-1}$

$\Delta_o \approx 17{,}200\ \mathrm{cm}^{-1}/0.8 \approx 21{,}500\ \mathrm{cm}^{-1}$

- 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 $t_{2g}{}^6 e_g{}^3$:

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

✓ 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.

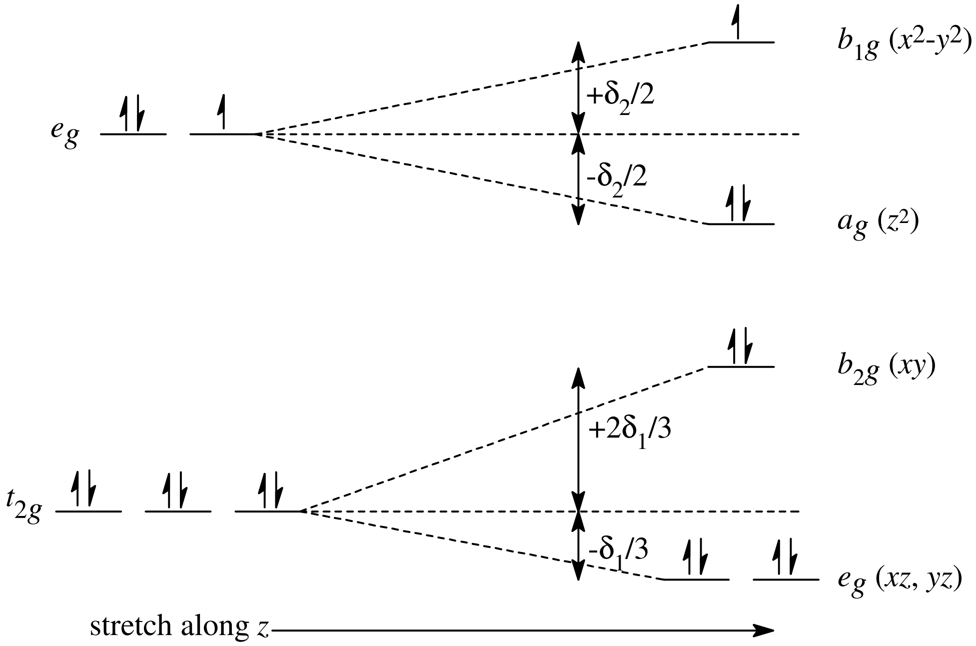
☛ Jahn-Teller Corollary: If the system is centrosymmetric, the distorted configuration will also be centrosymmetric.

- 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:

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

  - 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}.

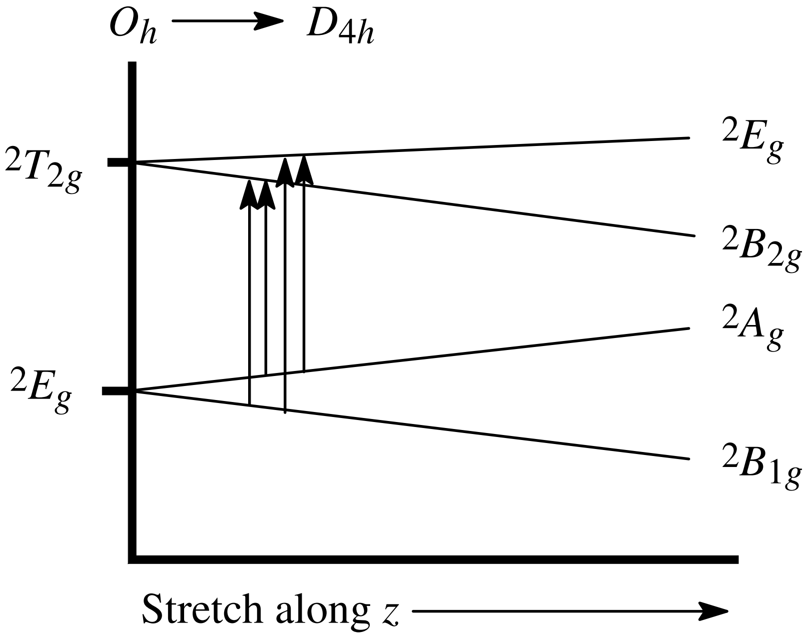
Strong and Weak Jahn-Teller Distortion

- 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.

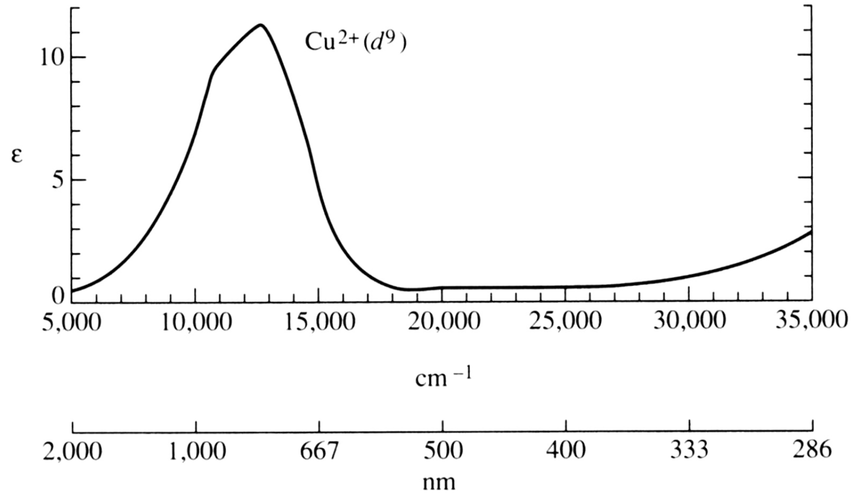


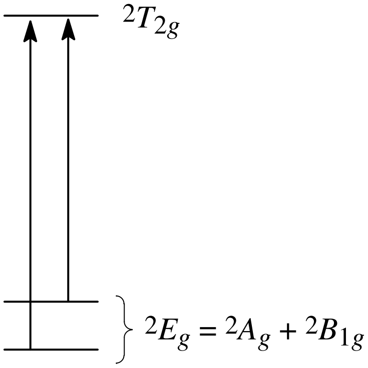
- Because both ground- and excited-state terms are split, additional transitions are possible, which contribute to band broadening.

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.

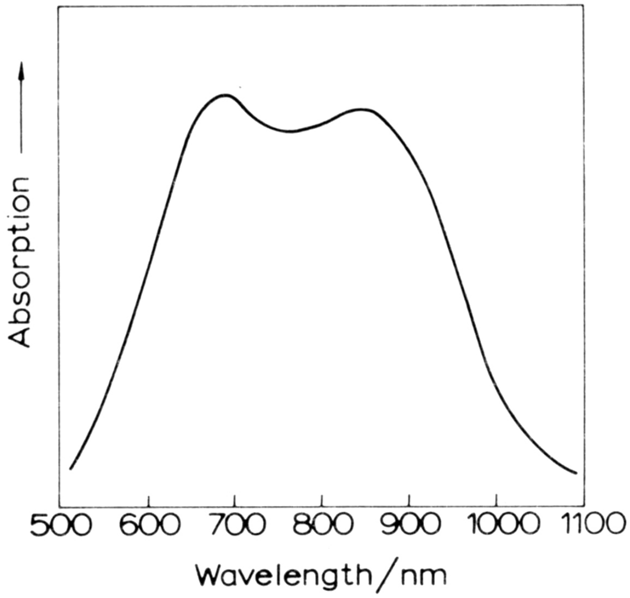
- The shoulder in the single band for $Cu(H_2O)_6^{2+}$ results from splitting of the ^2E_g ground state into two distinct states with two transition energies to the slightly split $^2T_{2g}$ excited state.



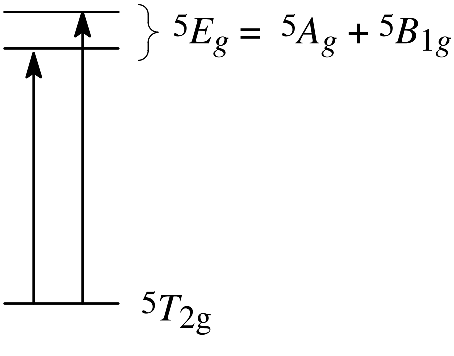


Spectroscopic Evidence of Jahn-Teller Distortions
Splitting of the Excited State

- The uv-vis spectrum of CoF_6^{3-}, a d^6 high-spin case,[5] 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 spit 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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[5] CoF_6^{3-} is an exception to the tendency for Co^{3+} ML_6 complexes to be d^6 low-spin.