The Color of Transition Metal Complexes

- Color results when a complex absorbs frequencies in the visible region of the spectrum, causing transitions from the ground electronic state to certain of the excited states of the configuration.

- The electronic states arise from *d*-electron configurations on the metal ion, so the absorptions are said to result from *d-d transitions*.

- The unabsorbed portion of the spectrum is transmitted, and results in the perceived color.

  Example: $[\mathrm{Ti(H_2O)_6}]^{3+}$ – d^1 (O_h)

  $$\tilde{\nu}_{\mathrm{max}} = 20{,}000\ \mathrm{cm}^{-1} \Rightarrow \lambda_{\mathrm{max}} = 5{,}000\ \text{Å} \Rightarrow \text{absorbs green}$$

  $$\therefore \text{transmits red + blue = purple}$$

- The absorption of a complex ion at a given wavelength follows the Beer-Lambert law

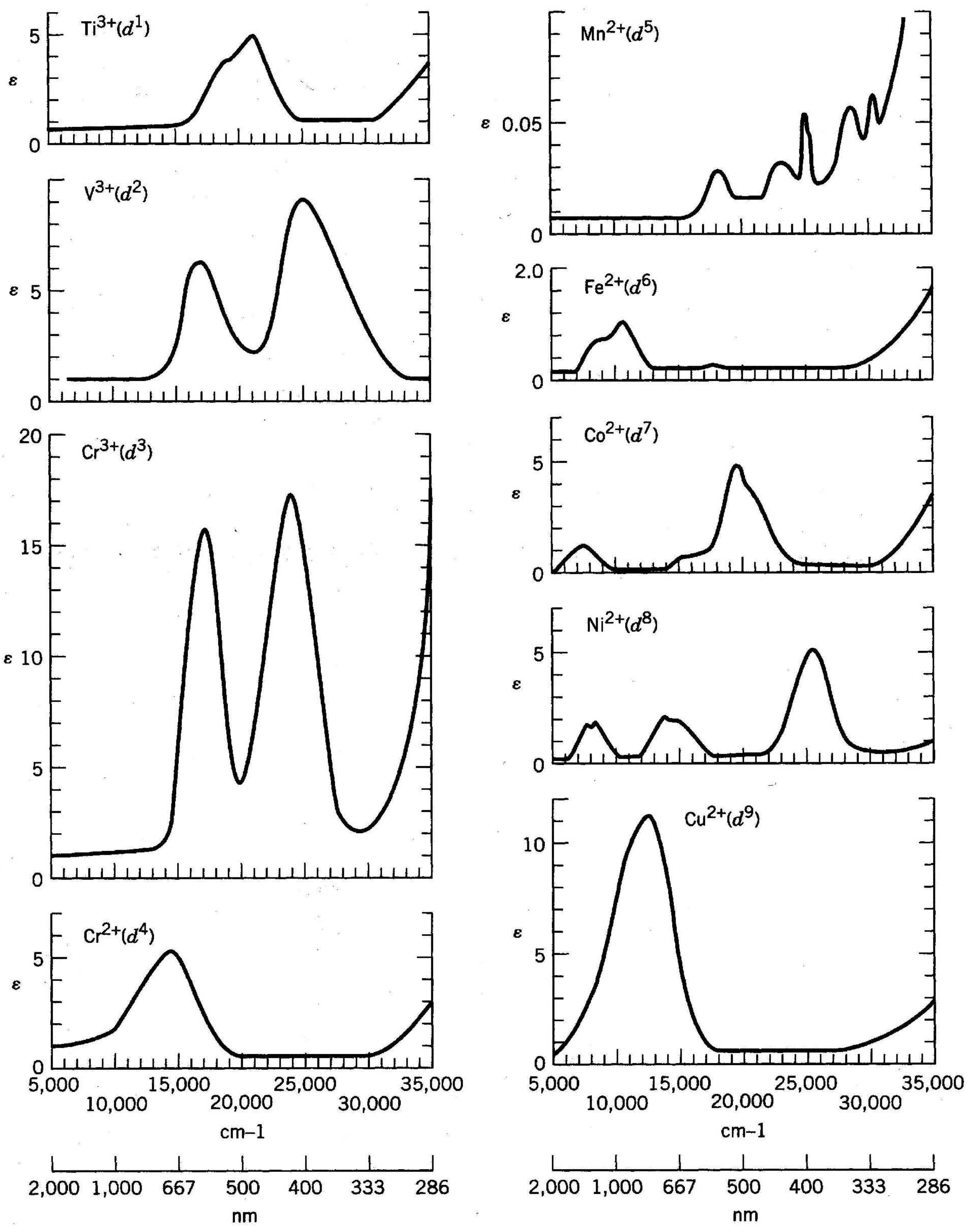
  $$A = -\log(I/I_o) = \varepsilon c b$$

  where

  A = absorbance
  I_o = intensity of the incident radiation
  I = transmitted intensity
  ε = molar absorptivity
  c = molar concentration
  b = path length of the light through the sample

  ○ With constant concentration and fixed path length it is customary to plot the spectra as absorptivity (ε) versus frequency or wavelength.

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



Molar Absorptivities of Complexes at λ_{max} in the Visible Region

- Molar absorptivities at the maximum absorbing frequencies in the ***visible region*** are relatively low for *d-d* transitions of octahedral complexes (e.g., $\varepsilon \approx 5 - 100$).

- In addition to *d-d* transitions, transition metal complexes typically have ***charge transfer transitions*** between the metal ion and the ligands ($M \rightarrow L$ or $M \leftarrow L$), which have very high molar absorptivities in the ***ultraviolet region***.

- By contrast, other systems, such as organic dyes, show values of molar absorptivities that are often $\geq 10^4$.

Why are ε_{max} Values So Low for *d*-*d* Transitions?

- The ε values are low for visible absorptions of complex ions because the electronic transitions are actually forbidden by either or both of the following two quantum mechanical selection rules:

    - *LaPorte's rule* - If the 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 symmetries ($g \rightarrow u$, $u \rightarrow g$) are allowed.

    - *Spin multiplicity rule* - Transitions between states with different spin multiplicities are forbidden.

- These selection rules, which would seem to preclude any visible absorption spectra for octahedral complexes, are clearly violated routinely, as evidenced by the colors that are so characteristic of transition metal compounds.

    - We can understand the mechanisms by which these rules break down by considering the symmetry of the transition moments.

Basis for the Quantum Mechanical Selection Rules

- For purposes of molecular spectroscopy we routinely assume that the internal energy of the system can be expressed as the sum of rotational, vibrational, and electronic contributions,

$$E_{\text{int}} = E_r + E_v + E_e$$

  - This implies that the overall wave function is

$$\Psi = \psi_r \psi_v \psi_e$$

    for which the individual energies are given by separate Schrödinger equations of the form $\mathcal{H}\psi = \mathrm{E}\psi$.

  - By this model, the absorption spectra of metal complexes involve one or more transitions between an electronic ground state ψ_e and some excited state ψ_e'.

    - The transition will be observable as a band in the absorption spectrum if there is a nonzero *transition moment* of the form

$$M_e = \int \psi_e \, \mu \psi_e' d\tau$$

      in which μ is the electronic dipole moment operator, whose components resolve as $\mu = \mu_x + \mu_y + \mu_z$.

    - M_e will be nonzero if the symmetry of the transition belongs to the totally symmetric representation, which for O_h this is A_{1g}.

    - The product $\psi_e \, \mu \psi_e'$ can be totally symmetric only if the product of two of the terms is the same symmetry species as the third.

Why *d-d* Transitions Should be Forbidden

- In O_h the vectors x, y, z transform as T_{1u}, which is then the symmetry of the electric dipole moment operator, $\boldsymbol{\mu}$.

- All the ψ_e's are *gerade* for an octahedral complex.

  - ☞ The product $\psi_e\, \mu \psi_e'$ must be *ungerade* ($g \times u \times g = u$) and cannot be totally symmetric.

    - ☞ In principle, the equation for the transition moment must always be zero for an octahedral complex, as stipulated by LaPorte's rule.

How the LaPorte Rule Breaks Down

- Transitions do occur because the electronic wave functions are not fully independent of the vibrational functions.
  - This means that the appropriate integral has a form such as

    $$\int(\psi_e\psi_v)\mu(\psi_e'\psi_v')d\tau$$

    - This *vib*rational-elect*ronic* interaction is called ***vibronic coupling***.
- The vibrational ground state is totally symmetric, so $\psi_e\psi_v$ has the same symmetry as ψ_e alone.
  - Inclusion of ψ_v does not affect the symmetry of the transition from what we had previously.
  - However, ψ_v' may have the symmetry of any of the normal modes of the complex.
  - Regardless of the vibrational spectroscopic activity, if any normal mode has the appropriate symmetry so that the direct product $\psi_e\mu\psi_e'\psi_v'$ contains the totally symmetric representation, the integral will not vanish and the transition will be allowed.
  - Regardless of the electronic terms involved, $\psi_e\mu\psi_e'$ is *ungerade*, so ψ_v' must have an identical *ungerade* symmetry in order for the entire product $\psi_e\mu\psi_e'\psi_v'$ to contain the totally symmetric representation.

Example: The $^2T_{2g} \rightarrow {}^2E_g$ Transition of d^1 O_h Complexes

- In the case of a d^1 ion in an octahedral field like $[\mathrm{Ti(H_2O)_6}]^{3+}$ the only possible electronic transition is from the $^2T_{2g}$ ground state to the ^2E_g excited state: $^2T_{2g} \rightarrow {}^2E_g$

- The symmetry of $\psi_e\mu\psi_e'$ is given by the direct product $T_{2g} \times T_{1u} \times E_g$.
  - ○ Multiplying the characters of these irreducible representations gives the reducible representation

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_e	18	0	0	0	2	-18	0	0	-2	0

$$\Rightarrow \Gamma_e = A_{1u} + A_{2u} + 2E_u + 2T_{1u} + 2T_{2u}$$

    - As expected, all species are *ungerade*.
    - If any one of these matches with the symmetry of a normal mode, then the direct product for $\psi_e\mu\psi_e'\psi_v'$ will contain the totally symmetric representation, and the integral for the transition moment will not vanish.

- The normal modes of an octahedral $\mathrm{ML_6}$ complex are

$$\Gamma_{3n\text{-}6} = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$$

  - ○ Comparing , Γ_e and $\Gamma_{3n\text{-}6}$, there are matches of T_{1u} and T_{2u}.

☞ The $^2T_{2g} \rightarrow {}^2E_g$ transition is *vibronically allowed* through possible coupling with the normal modes ν_3 (T_{1u}), ν_4 (T_{1u}), and ν_6 (T_{2u}).

General Vibronic Coupling

- It can be shown that the possible electronic transitions for any octahedral complex will be vibronically allowed.

- Note that the normal modes responsible for the break down of the LaPorte rule are those in which the vibration destroys the center of symmetry.

  - Static loss of centrosymmetry would have the same result, as in the D_3 complex $[Co(en)_3]^{2+}$.

  - Whether static or dynamic, these perturbations from ideal centrosymmetry are minor, and the resulting molar absorptivities are small.

- By contrast, the LaPorte rule ***does not*** apply to tetrahedral, trigonal bipyramidal, and other noncentrosymmetric complexes.

  - Non-centrosymmetric species tend to have higher molar absorptivities ($\varepsilon \approx 100 - 200$), but not as high as LaPorte-allowed transitions.

- All complex ions show very high absorbance at higher frequencies, usually in the ultraviolet region, due to metal-ligand ***charge transfer transitions***.

  - These are $g \leftrightarrow u$, allowed by the LaPorte rule, and accordingly have very high molar absorptivities ($\varepsilon \approx 10{,}000$).

Spin Multiplicity Selection Rule

- We can understand the origin of the spin multiplicity selection rule if we recognize that ψ_e consists of both ***orbital*** and ***spin*** contributions; i.e., $\psi_e = \psi_o\psi_s$.
  - On this basis we might rewrite the transition moment integral as

$$\int(\psi_o\psi_s\psi_v)\mu(\psi_o{}'\psi_s{}'\psi_v{}')d\tau$$

    - Building on our previous analysis of the LaPorte rule, this can only be nonvanishing if $\psi_s = \psi_s{}'$, which means the two wave functions have the same overall spin quantum number, S.
    - Otherwise, the symmetry of the transition, which is totally symmetric on the basis of the orbital and vibrational terms, would change and not be totally symmetric.

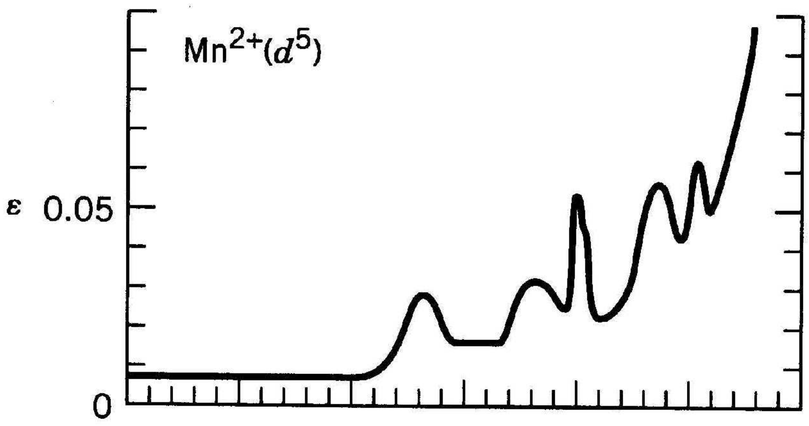
Spin-Forbidden Transitions Do Occur

- Despite the spin multiplicity rule, transitions between different spin states do occur, although with molar absorptivities that are even smaller than those for LaPorte-forbidden transitions.

- In a spectrum with bands from vibronically-allowed transitions with the same multiplicity, spin-forbidden transitions are likely to be too weak to be observed.

- In d^5 high-spin complexes, the only conceivable *d-d* transitions are spin forbidden and give rise to bands with molar absorptivities typically 0.01 - 1.

Example: The visible spectrum of $[Mn(H_2O)_6]^{2+}$ has many weak bands with $\varepsilon \leq 0.4$, which account for the barely perceptible faint pink color of this complex in solution.



Why Spin-Forbidden Transitions Occur

- Spin forbidden transitions occur because of spin-orbital coupling.

- The Russell-Saunders coupling scheme, which assumes separately definable *L* and *S* values, is only an approximation, which becomes less valid with the heavier transition metals.

  - ☞ As a result, spin-forbidden transitions are more common among second and third series transition metal complexes.

Assigning Visible Spectra With Tanabe-Sugano Diagrams

- The observed spectra of octahedral transition metal complexes can be assigned on the basis of the Tanabe and Sugano diagrams.
  - ○ All transitions are presumed to originate from the ground state term to the various upper state terms.
  - ○ The absorption spectra of most transition metal complexes, except as noted, consist principally of bands arising from transitions that are **LaPorte forbidden** (***vibronically allowed***) and ***spin allowed***.
    - ☞ The most intense bands arise from transitions to excited states with the same spin multiplicity as the ground state term.

Example: For a d^7 high-spin octahedral complex, the Tanabe and Sugano diagram predicts three spin-allowed transitions:

$$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$$
$$^4T_{1g}(F) \rightarrow {}^4A_{2g}$$
$$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$$

For $[Co(H_2O)_6]^{2+}$:

$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	8,000 cm^{-1}
$^4T_{1g}(F) \rightarrow {}^4A_{2g}$	19,600 cm^{-1}
$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	21,600 cm^{-1}

Orgel Diagrams

- Recall that
  - the term splittings are reversed for d^n and d^{10-n} configurations of the same symmetry
  - the term splittings are reversed for $d^n(O_h)$ and $d^n(T_d)$ cases.
- These relationships are used to advantage in an abbreviated set of correlation diagrams, originally devised by Orgel, which may be used to predict the spin-allowed transitions of octahedral and tetrahedral ***high-spin*** complexes.
  - Since the Orgel diagrams are only intended for use with spin-allowed transitions, no correlations are shown for states with different spin multiplicities from that of the ground state term.
    - Consequently, there is no Orgel diagram for d^5, since only spin-forbidden transitions are possible for the high-spin case.
  - Orgel diagrams cannot be used to interpret the spectra of low-spin complexes.
- These restrictions allow the Orgel diagrams to take advantage of yet another relationship between correlation diagrams, which can be verified by inspecting the Tanabe and Sugano diagrams:

  In the same ligand field (O_h or T_d), the terms with the same spin multiplicity as the ground state and their splitting patterns are identical for d^n and $d^{n\pm5}$ configurations.

Relationship Between Orgel Diagrams

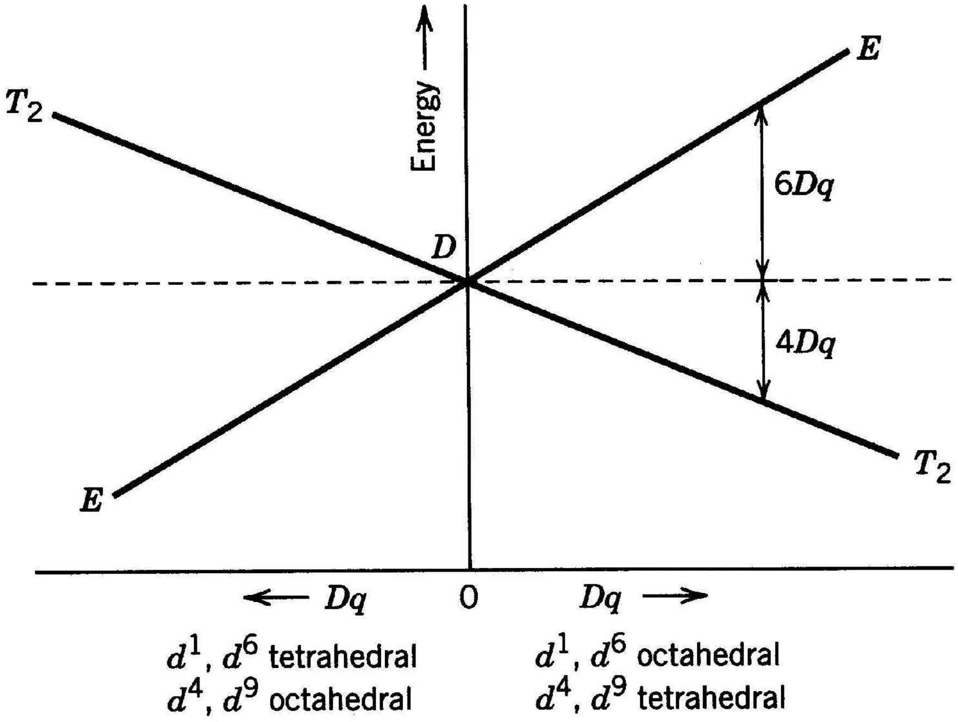
The Orgel diagrams are related to each other as follows:

1. d^n (O_h) and $d^{n\pm5}$ (O_h) have the same diagram
2. d^n (T_d) and $d^{n\pm5}$ (T_d) have the same diagram
3. d^n, $d^{n\pm5}$ (O_h) is the reverse of d^n, $d^{n\pm5}$ (T_d), and vice versa
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)

- As a result, we need only two diagrams, both of which are easily committed to memory.

Orgel Diagram Based on d^1 (O_h)

- The simpler of the two Orgel diagrams can be generated by extrapolating the lines for the term splitting scheme for the d^1 octahedral case to the left side of the diagram.



  - ○ The right side is the diagram for d^1 and d^6 octahedral and d^4 and d^9 tetrahedral complexes.

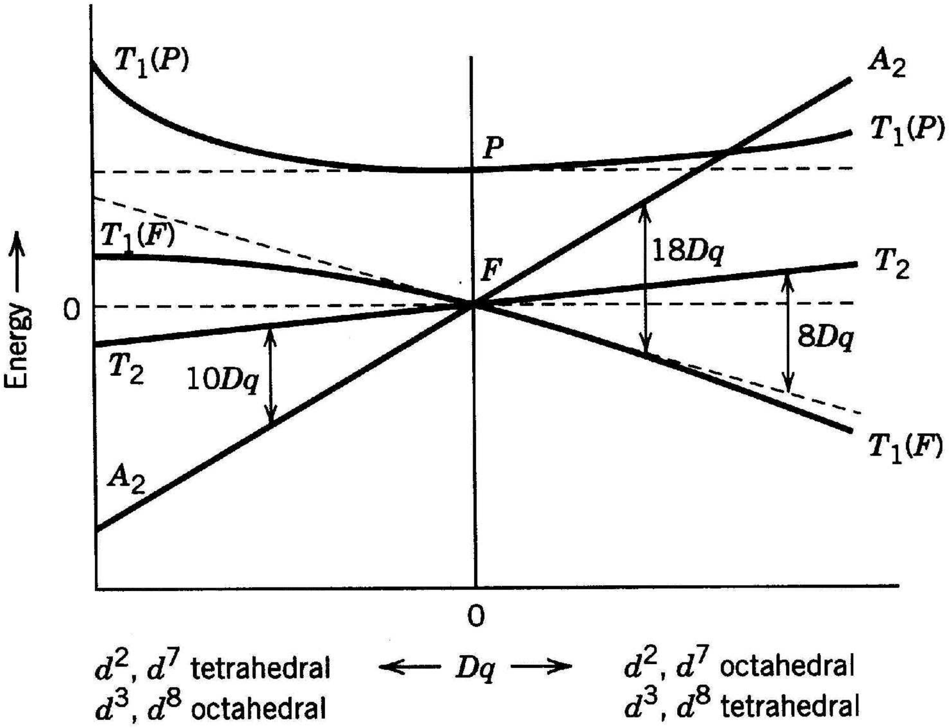
  - ○ The left side is the diagram for d^4 and d^9 octahedral and d^1 and d^6 tetrahedral complexes.

  - ○ For these cases, the spectrum is expected to show a single band ($T_2 \rightarrow E$ or $E \rightarrow T_2$).

    - The separation between the two states is Δ_o or Δ_t, as the case may be, so the observed frequency corresponds to the crystal field splitting energy.

Orgel Diagram Based on d^2 (O_h)

- The diagram generated from the d^2 octahedral case is more complex but its construction employs the same principles.
    - The right side is the diagram for d^2 and d^7 octahedral and d^3 and d^8 tetrahedral complexes.
    - The left side is the diagram for d^3 an d^8 octahedral and d^2 and d^7 tetrahedral complexes on the left.



Notes on the Orgel Diagram Based on d^2 (O_h)

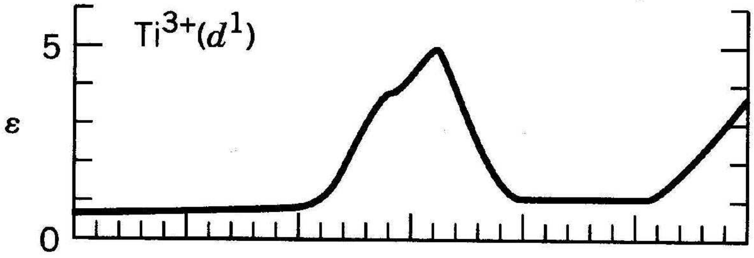
- The correlation lines for the $T_1(F)$ and $T_1(P)$ states curve away from each other as a consequence of the noncrossing rule.
  - The straight-line projections for these terms (without mutual repulsions) are shown as dotted lines.
- Three absorption bands are expected for complexes covered by this diagram.
  - For complexes treated by the left side of the diagram, the crystal field splitting energy (Δ_o or Δ_t) can be obtained directly from the lowest frequency band in the visible absorption spectrum (assigned as ν_1).
  - For complexes treated by the right side of the diagram the crystal field splitting cannot be obtained directly, owing to the mutual repulsion of the two T_1 states.
    - In these cases it is necessary to carry out a calculation involving estimation of the Racah parameter.
    - Details of this process are given in some advanced inorganic chemistry texts.

Comparing Predictions to Real Spectra
Jahn-Teller Splitting

- The Orgel diagrams (and also the corresponding Tanabe and Sugano diagrams) predict either one or three bands for the absorption spectra of octahedral complexes.

  ○ Actual spectra do not always show this ideal behavior.

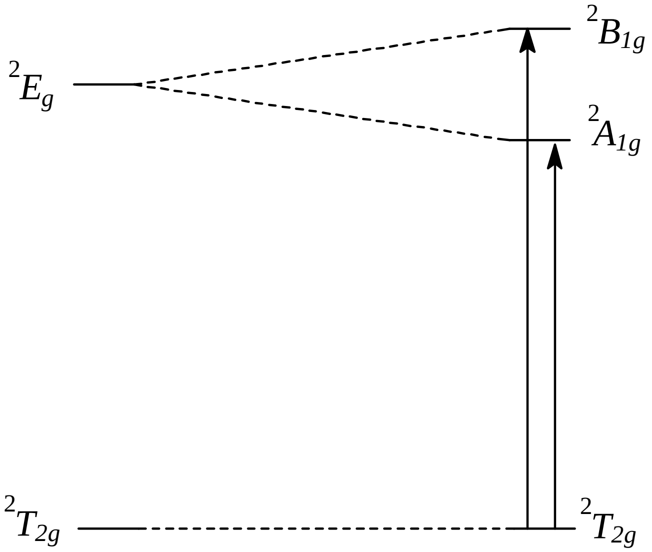
- Example: The spectrum of $[Ti(H_2O)_6]^{3+}$ shows evidence of two bands, rather than the expected one band from a $^2T_{2g} \rightarrow {}^2E_g$ transition. This is the consequence of the Jahn-Teller effect.



○ Both the ground state and excited state terms are subject to distortion, but the doubly degenerate ^2E_g excited state term is expected to experience the more pronounced distortion.

Effect of a Tetragonal Distortion on The Spectrum of a d^1 O_h Complex

- If we assume a tetragonal distortion leading to D_{4h}, the excited state will be split into two new terms, $^2A_{1g}$ and $^2B_{1g}$.
  - The relative energy ordering of these new terms cannot be predicted, since it will depend on the nature of the distortion (e.g., $^2A_{1g} < {}^2B_{1g}$ for a stretching distortion along z, as shown here).



  - Ignoring any splitting of the ground state term, the splitting of the excited state gives rise to two possible transitions, which account for the band shape in the spectrum of $[Ti(H_2O)_6]^{3+}$.
- Similar evidence of band splitting from Jahn-Teller distortions, either in the ground state or an excited state, can be found in some of the other spectra of $[M(H_2O)_6]^{n+}$ complexes, previously shown.

Spectra With Fewer Bands Than Predicted

- Some spectra, such as that of $[V(H_2O)_6]^{3+}$, have only two bands when three are expected from the Orgel diagram.
  - In these cases the highest energy band (ν_3) either falls in the ultraviolet, beyond the region shown, or is obscured by the tail of the very strong LaPorte-allowed charge-transfer band in the ultraviolet.

Example: $[V(H_2O)_6]^{3+}$

- The missing band, which corresponds to a ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}$ transition, is estimated to lie at about 36,000 cm^{-1}.
- This transition corresponds to the simultaneous excitation of two electrons, so the band is expected to have an extremely low molar absorptivity (ε).
- This prevents it from being observed in a region where the charge transfer bands are beginning to rise in intensity.