Microstates and term symbols

Microstates – the electronic states that are possible for a given electronic configuration.

•no two electrons may have the same set of quantum numbers (Pauli exclusion principle)

•only *unique* microstates may be included

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ns^2 configuration

Cannot physically distinguish between the electrons, so must use sets of quantum numbers to decide if the microstates (rows in the table) are the same or different.

First microstate: $l = 0$, $m_l = 0$, $m_s = +1/2$; $l = 0$, $m_l = 0$, $m_s = -1/2$
Second microstate: $l = 0$, $m_l = 0$, $m_s = -1/2$; $l = 0$, $m_l = 0$, $m_s = +1/2$

First electron: $m_l = 0$	Second electron: $m_l = 0$	$M_L = \Sigma m_l$	$M_S = \Sigma m_s$	
↑ ~~↓~~	↓ ~~↑~~	0	0	$L = 0, S = 0$

Term Symbol

Multiplicity of the term

$$^{(2S+1)}L \leftarrow \left\{ \begin{array}{ll} L = 0 & \text{S term} \\ L = 1 & \text{P term} \\ L = 2 & \text{D term} \\ L = 3 & \text{F term} \\ L = 4 & \text{G term} \end{array} \right.$$

Term Symbol

- Spectroscopic states of Ti^{3+}, V^{4+}
- Electronic configuration in ground state = d^1; 1 u.e.
- Spin of the metal ion due to unpaired electron (S) = ½
- Multiplicity of Ground state = 2S+1 = 2 × ½ +1 = 2 (doublet)
- Electronic ground state ^{2S+1}L
- $m_l = 2$, Therefore L = 2 = D [$L = l_1 + l_2 + l_3 = l_n$, L =0 is S, L =1 is P, L = 2 is D, L= 3 is F]
- Spectroscopic ground state term symbol of Ti^{3+} = ^2D

- Links to [microstates and spectroscopic term symbol determination]().

- **Problem**

1. Find the number of microstates possible for Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+} and Mn^{2+} ions in the gaseous state. Also determine the ground state term symbol for each. [**Hint**: Ground state is the one with largest spin and orbital multiplicity]
2. A solution of a copper complex absorbs at λ_{max} 540nm. If the concentration of the sample is 5×10^{-4} M and the molar extinction coefficient is 3200 l/mol/cm, calculate the percentage transmittance of the sample.

Term Symbol

- Spectroscopic states of V^{3+}, Cr^{4+}
- Electronic configuration in ground state = d^2; 2 u.e.
- Spin of the metal ion due to unpaired electron (S) = 1
- Multiplicity of Ground state = 2S+1 = 2 × 1 +1 = 3 (triplet)
- Electronic ground state ^{2S+1}L
- m_l = +2, +1, Therefore L = 2 +1 = 3 =F [L = $l_1 + l_2 + l_3 + l_n$, L = 0 is S, L =1 is P, L = 2 is D]
- Spectroscopic ground state term symbol of V^{3+} = ^3F

- Link to determination of spectroscopic states from various microstates possible in d^2.

Term Symbol

- Spectroscopic states of V^{2+}, Cr^{3+}
- Electronic configuration in ground state = d^3; 3 u.e.
- Spin of the metal ion due to unpaired electron (S) = 3/2
- Multiplicity of Ground state = 2S+1 = 2 × 3/2 +1 = 4 (quartet)
- Electronic ground state ^{2S+1}L (Term symbol of spectroscopic state)
- m_l = +2, +1, 0. Therefore, L = 2 +1+0 = 3 = F [L = $l_1 + l_2 + l_3 + l_n$, L = 0 is S, L =1 is P, L = 2 is D]
- Spectroscopic ground state term symbol of V^{2+} = ^4F

- **Problems**

1. Determine the ground state term symbol for high spin d^6, low spin and high spin d^7 and d^9.
2. Show spectroscopic transition in for d^7 (low-spin) and d^9 systems in an octahedral field.
3. What will be the spectroscopic transition for a d^6 and d^8 tetrahedral systems?

Effect of a crystal field on the free ion term of a d[1] complex

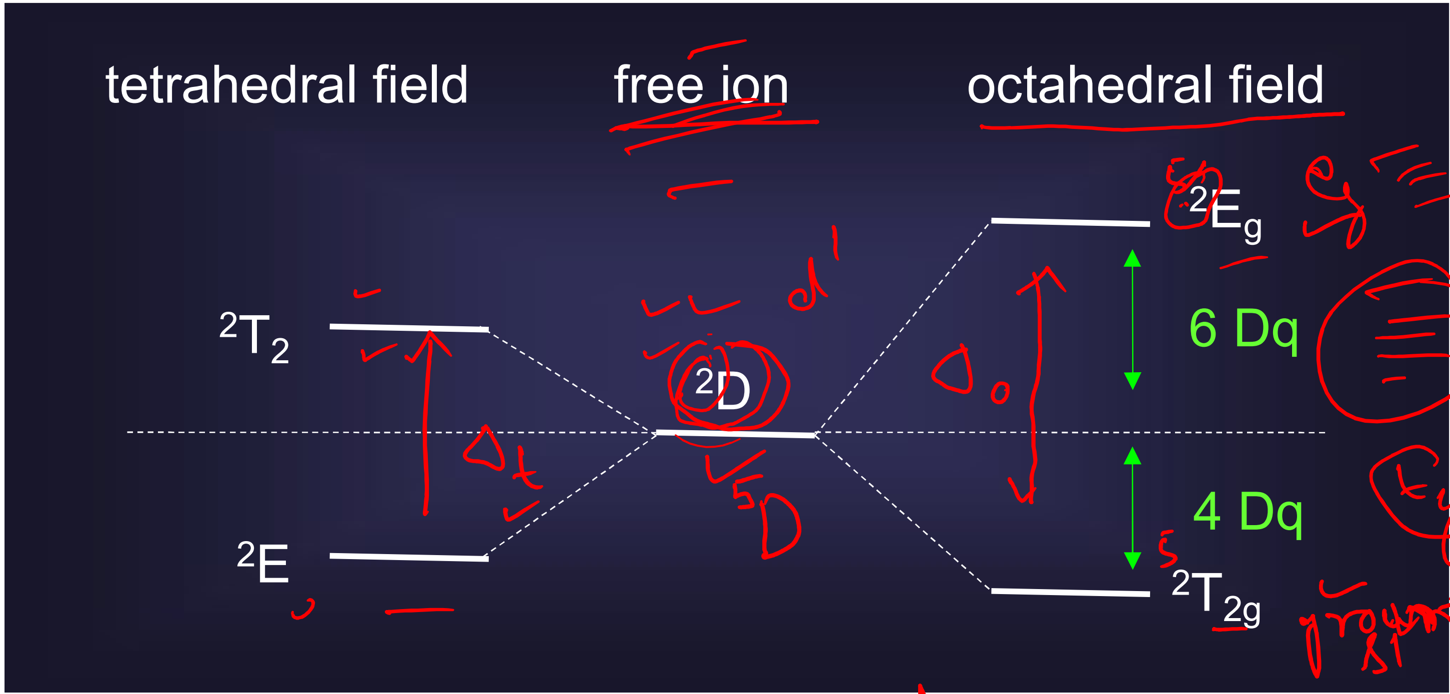
$[Ti(H_2O)_6]^{3+}$

$d^1 \equiv \cancel{d^6}$

ground state Term symbol free Metal ion ^2D

$Ti^{3+} \rightarrow d^1$

d^1



d → oct
e_g
t_{2g}
orbital

200 — 800 nm

ground st

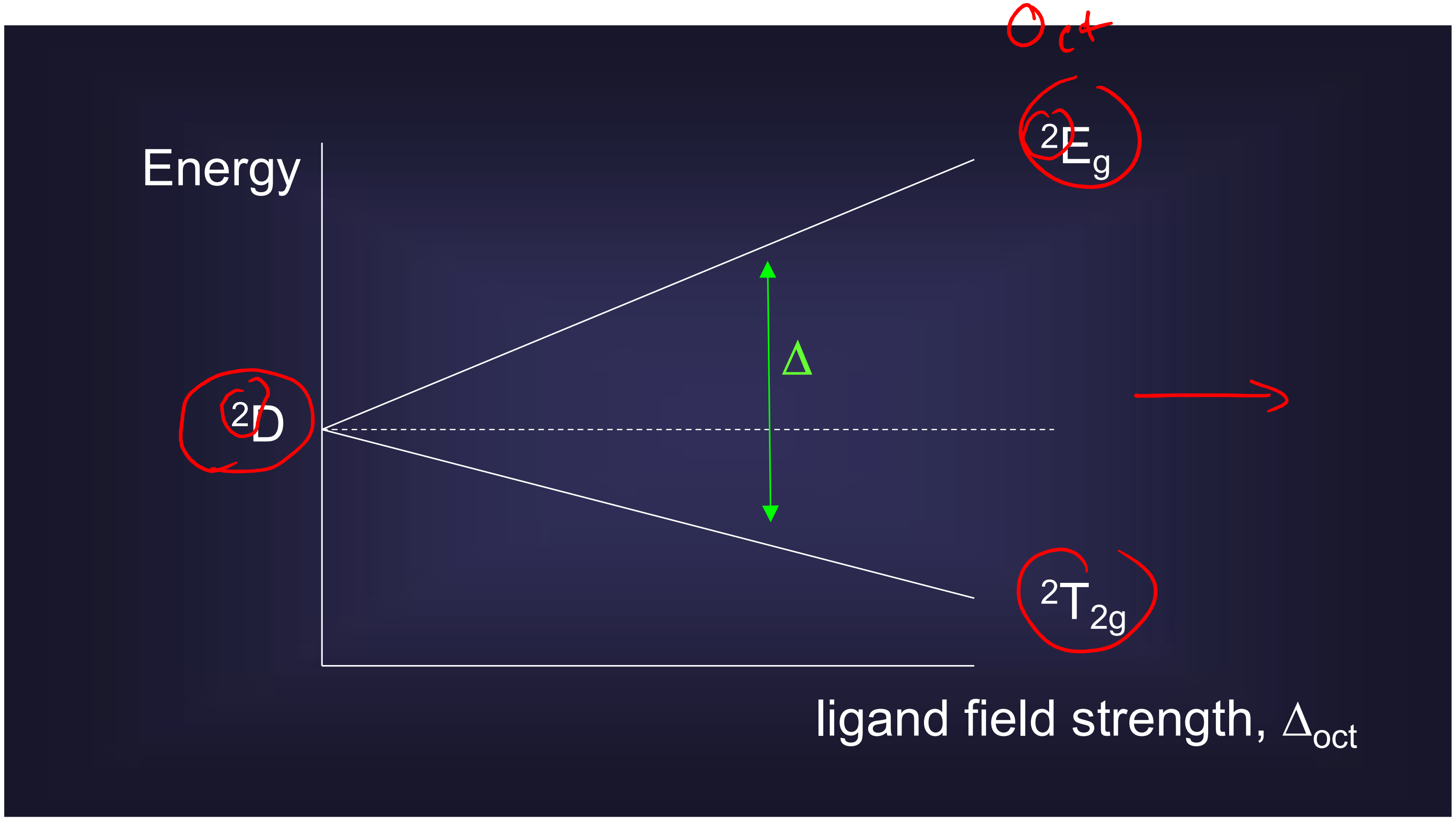
$d^6 \equiv {}^5D$

orgel diagram

+2 +1 0 −1 −2

$L = 2$

Energy level diagram for d^1 ions in an O_h field

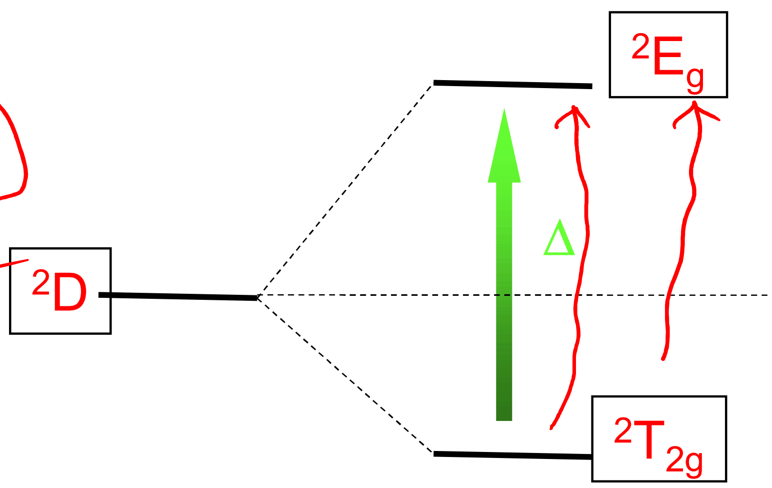


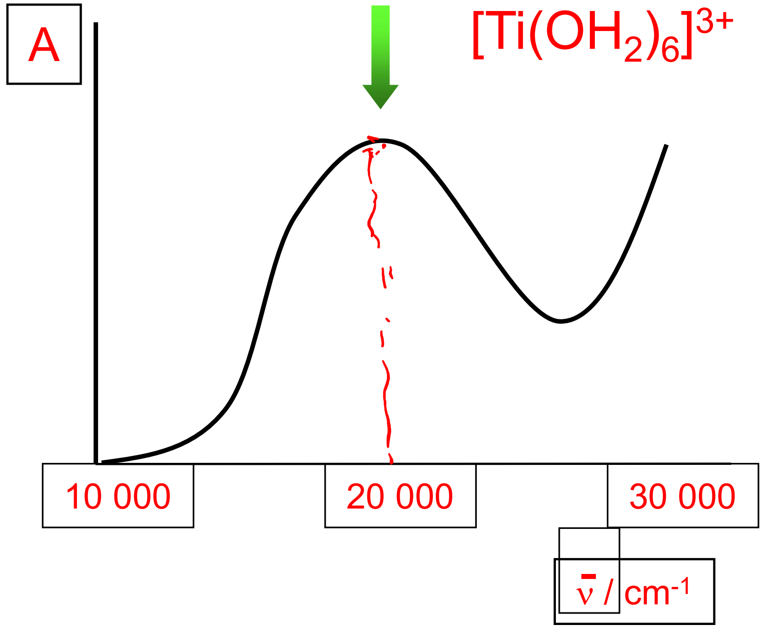
For d^6 ions in an O_h field, the splitting is the same, but the multiplicity of the states is 5,

ie ^5E_g and $^5T_{2g}$

d^1 oct

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





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

❖ A 0.01 M solution of a compound transmits 20% of the radiation in a container with a path length equal to 1.5 cm. Calculate molar extinction coefficient of the compound.

Here $\frac{I}{I_0} = \frac{20}{100} = 0.2$

Again $A = \log \frac{I_0}{I} = \epsilon c l$

or $A = -\log \frac{I}{I_0} = -\log(0.2)$

$\therefore \epsilon = \frac{-\log(0.2)}{0.01 M \times 1.5 cm}$

$= 46.598 \, M^{-1} cm^{-1}$