



CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture-27, 26-03-2018

**BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE,
PILANI**

II Semester, 2017-2018

Course No.: CHEM F111

Course Title: General Chemistry

Seating arrangement for Assignment-02 Test

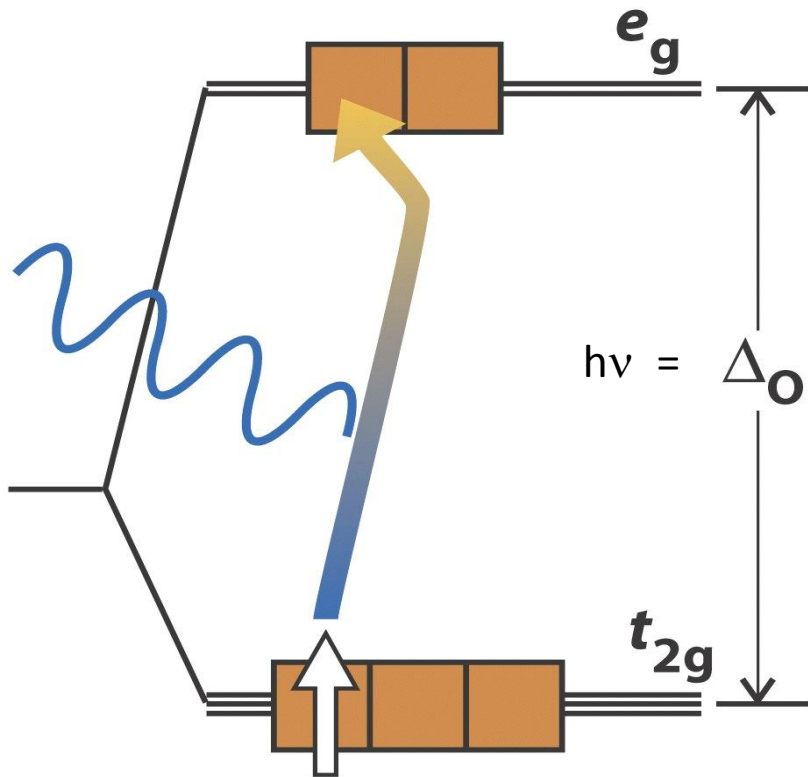
Date: 28-03-2018

Time: 17.30 hrs.

Tutorial Section	Room No	Instructor
T-1	2221	Dr. Anil Kumar
T-2	2207	Dr. Paritosh Shukla
T-3	2222	Dr. Paritosh Shukla
T-4	3248	Dr. Inamur R. Laskar
T-5	2204	Dr. Rajeev Sakhuja
T-6	2212	Dr. Madhushree Sarkar
T-7	3247	Dr. Bibhash R. Sarkar
T-8	3203	Dr. Surojeet Pande
T-9	2235	Dr. Subit K. Saha
T-10	2206	Dr. Saumi Ray
T-11	3158	Dr. Bibhash R. Sarkar
T-12	2203	Dr. Ajay K. Sah

Syllabus: L-17 to L-27 of Handout

Summary of lecture 26



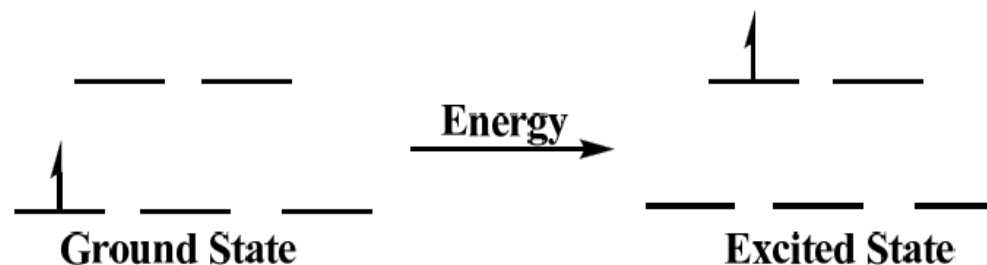
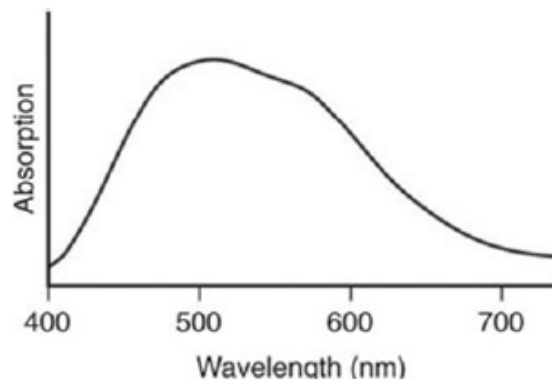
The energy gap between the e_g and t_{2g} orbitals, Δ_o , (the crystal field splitting) equals the energy of a photon:

$$\Delta_o = h\nu = \Delta E$$

As Δ_o varies, $h\nu$ will also vary and the color of the compound will change

Absorption of a photon causes a jump from a t_{2g} to an e_g orbital

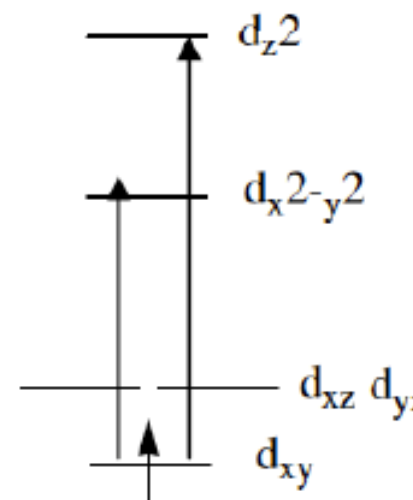
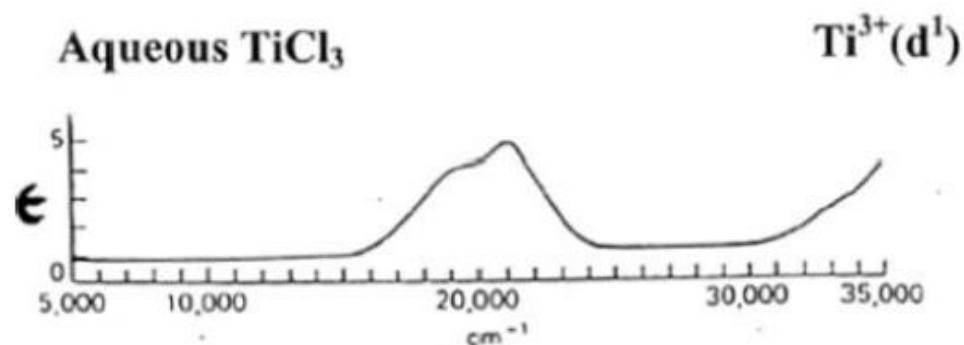
Summary of lecture 26



Absorption at 520 nm gives the complex its purple color



A more resolved absorption spectrum of the complex has a shoulder



Ground state term for d^n config.

innovate

achieve

lead

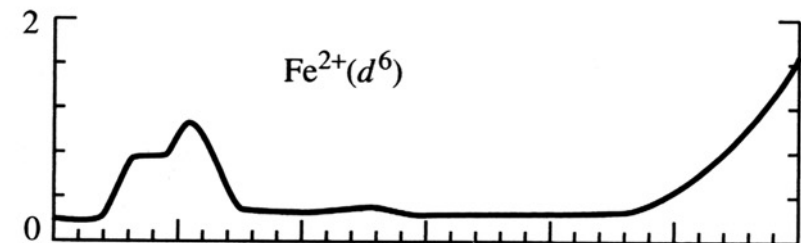
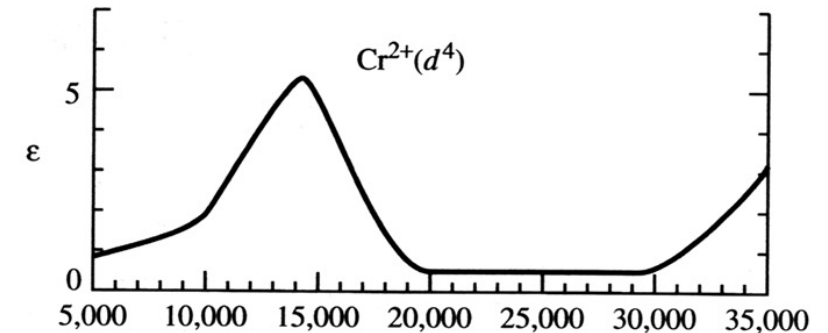
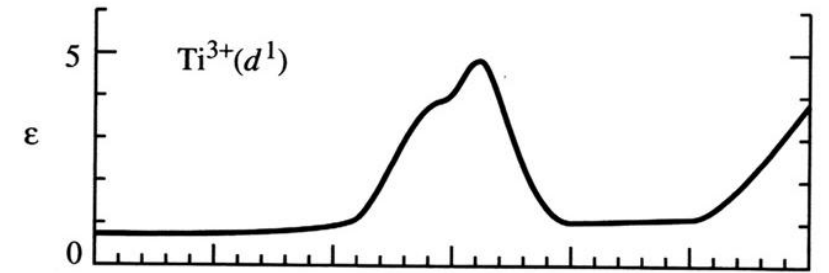
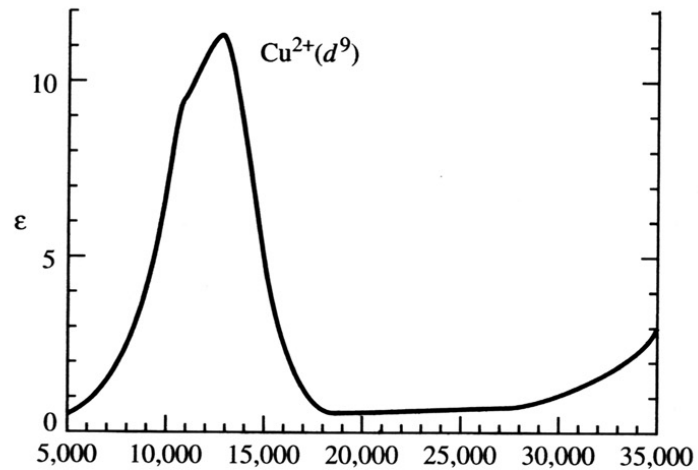
Ground terms
for d^1 - d^{10}
configurations

Configuration	Example	Ground term	m_l	M_L	S
			2 1 0 -1 -2		
d^1	Ti^{3+}	2D		2	$\frac{1}{2}$
d^2	V^{3+}	3F		3	1
d^3	Cr^{3+}	4F		3	$\frac{1}{2}$
d^4	Cr^{2+}	5D		2	2
d^5	Mn^{2+}	6S		0	$2\frac{1}{2}$
d^6	Fe^{2+}	5D		2	2
d^7	Co^{2+}	4F		3	$\frac{1}{2}$
d^8	Ni^{2+}	3F		3	1
d^9	Cu^{2+}	2D		2	$\frac{1}{2}$

Electronic spectroscopy of Oh com.



d^1 , d^4 , d^6 and d^9 usually have **one absorption**, though a side “hump”



Electronic spectroscopy of Oh com.



Absorption bands in electronic spectra are usually broad, and occur much more rapidly than molecular vibrations

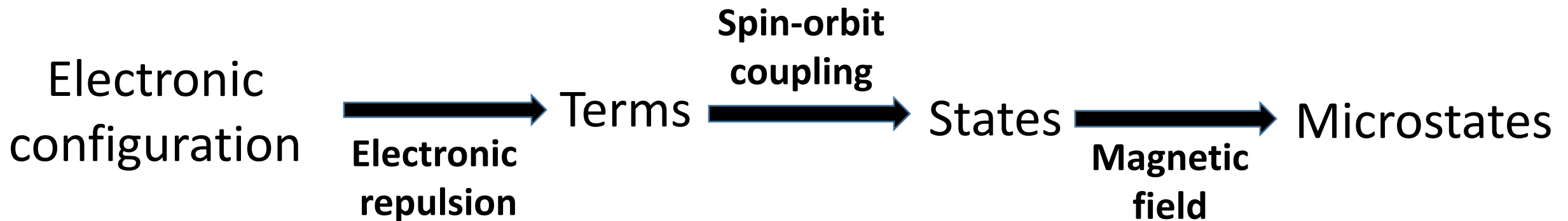
The spectra **represent a “snapshot” of molecules** in various vibrational and rotational states

Extinction coefficients will range from <1 up to $50,000 \text{ M}^{-1}\text{cm}^{-1}$ depending upon **the type of electronic transition** and whether it is permitted based on **selection rules**

Interpretation of Electronic Spec.

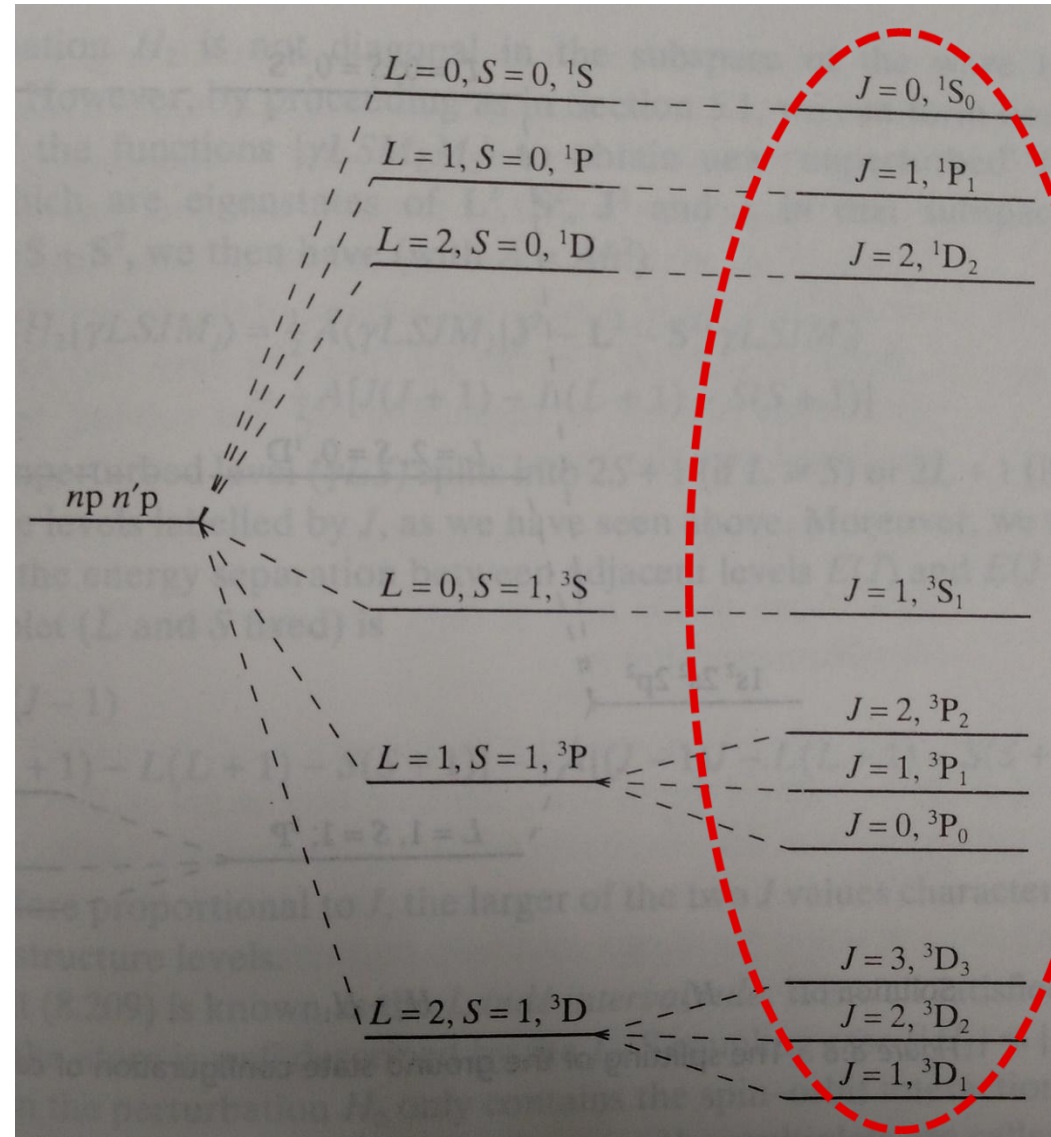


Electronic configuration is split **into terms** due to interelectronic repulsion, which is split **into states** by spin-orbit coupling, which is further split **into microstates** by magnetic field:



Fine structure for np n'p configuration

All the
transitions are
allowed?



Slide taken from
Lecture 10, slide # 26

Selection Rules for Electronic transition



- ❖ Laporte 'orbital' selection rule: Transitions which involve a change in the subsidiary quantum number $\Delta l = \pm 1$ are “Laporte allowed” and therefore have a high absorbance.
- ❖ d-d transitions are “**Laporte forbidden**” and ‘ ϵ ’ is less.

However, in complexes, d-d transitions are taking place in electronic spectra and they not only give important clues about the structure of the complex but also proof for the theories of bonding in complexes.

Transition metal ion forms a complex and surrounded by ligands, **mixing of d and p orbitals**: *breakdown of Laporte selection rule*

Selection Rules for Electronic transition



❖ Spin selection rule: During transitions between energy levels, an electron does not change its spin, i.e., $\Delta S = 0$

There should not be any change in the spin of the states and their multiplicities should be the same during the transition of electrons. That is, **singlet-singlet and triplet-triplet transitions are allowed**, while singlet-triplet and vice-versa transitions are not allowed.

Why Mn^{2+} high spin complexes are off white or pale flesh colored?

Splitting of d^n terms



Each of these free ion terms will be affected **by the ligands** in a complex and this will depend upon the geometry of the complex

D terms will also be split into T_{2g} and E_g terms in an octahedral complex

Similarly, other terms will split as follows in an octahedral field:

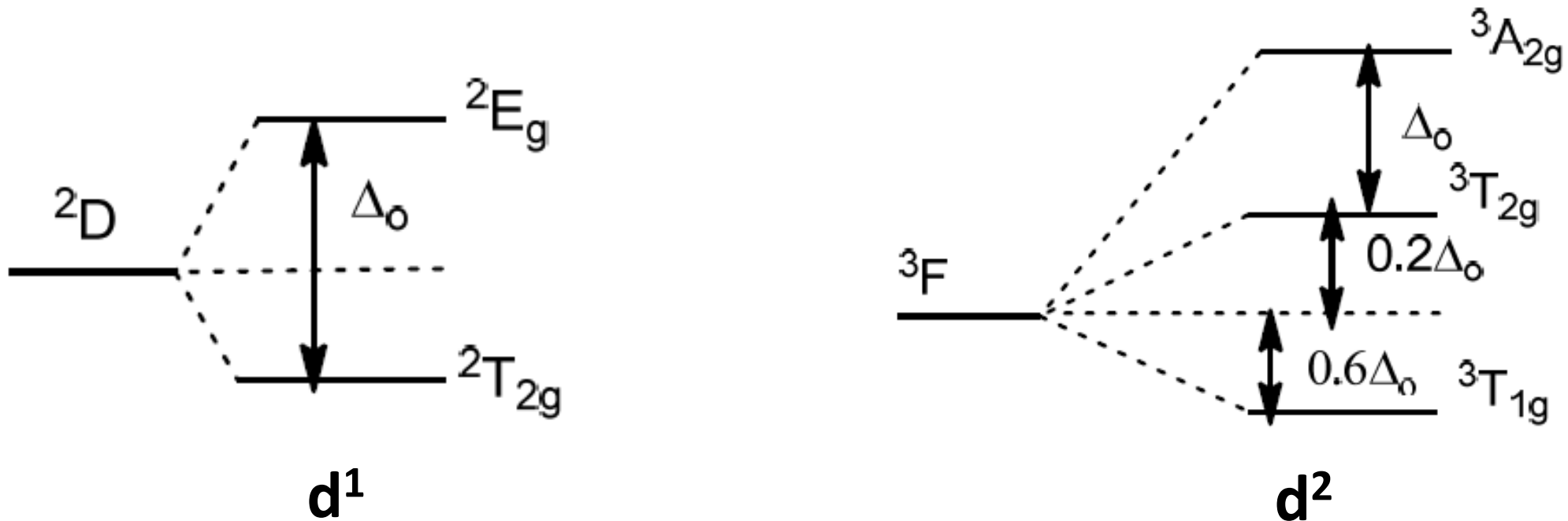
Transforming
spectroscopic terms into
Mulliken symbols

Free ion	Splitting in an octahedral	Splitting in a tetrahedral
S	A_{1g}	A_1
P	T_{1g}	T_1
D	$E_g + T_{2g}$	$E + T_2$
F	$A_{2g} + T_{1g} + T_{2g}$	$A_2 + T_1 + T_2$

d^n and d^{10-n} systems



The ground state terms obtained from d^1 and d^2 configurations are split by octahedral field and the resulting energy diagrams are shown below:



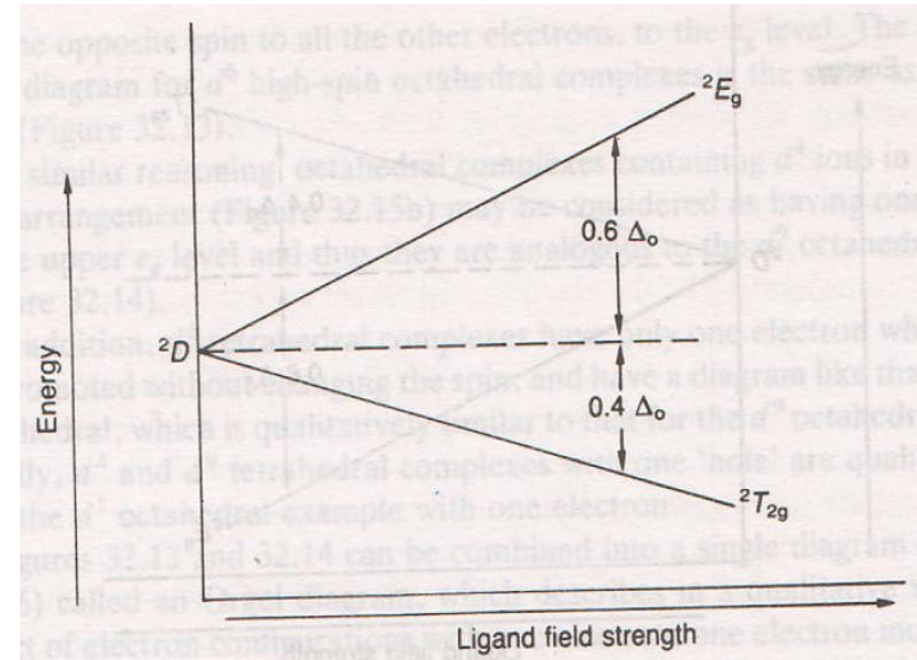
Spectra of d^1 ions

innovate

achieve

lead

$[\text{TiCl}_6]^{3-}$, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{TiF}_6]^{3-}$, and $[\text{Ti}(\text{CN})_6]^{3-}$



Splitting of energy levels for d^1 in octahedral field

HOLE Formulation



When a subshell is **more than half full**, it is simpler and more convenient to work out the terms by considering the **'HOLES'** – that is the **vacancies in the various orbitals** – rather than the larger number of electrons actually present.

In a similar way, by considering 'HOLES', the terms which arise for pairs of atoms with d^n and d^{10-n} arrangement, give rise to **identical terms**.

HOLE Formulation cont.



A d^9 system can be considered as the inverted d^1 system as far as energy levels can be considered because d^9 system has an electron vacancy, which is called a 'hole'.

An inverted energy level relationship exists between d^n and d^{10-n} systems.

$$d^9 = d^{10-1} = \text{inverted } d^1 \text{ system}$$

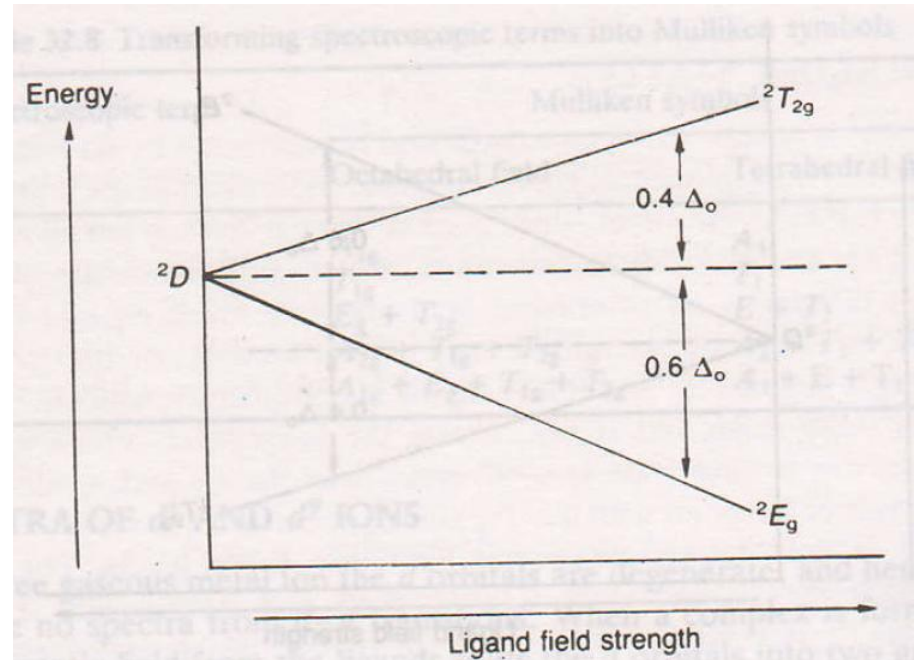
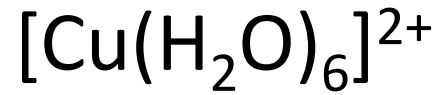
$$d^8 = d^{10-2} = \text{inverted } d^2 \text{ system}$$

Spectra of d⁹ ions

innovate

achieve

lead



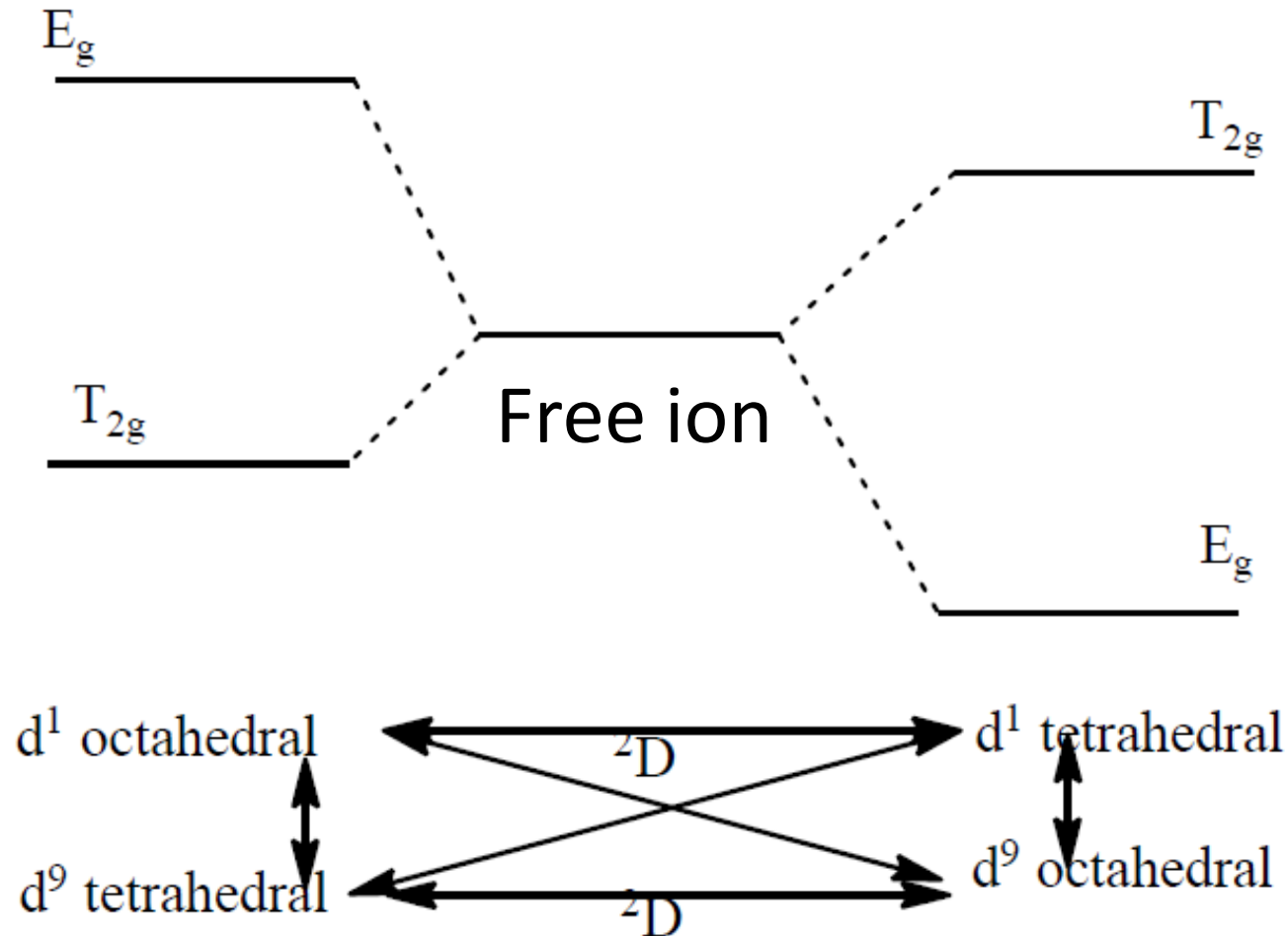
Splitting of energy levels for d⁹ configuration in octahedral field

d⁹ system: Promotion of an electron as the transfer of a hole from e_g to t_{2g}

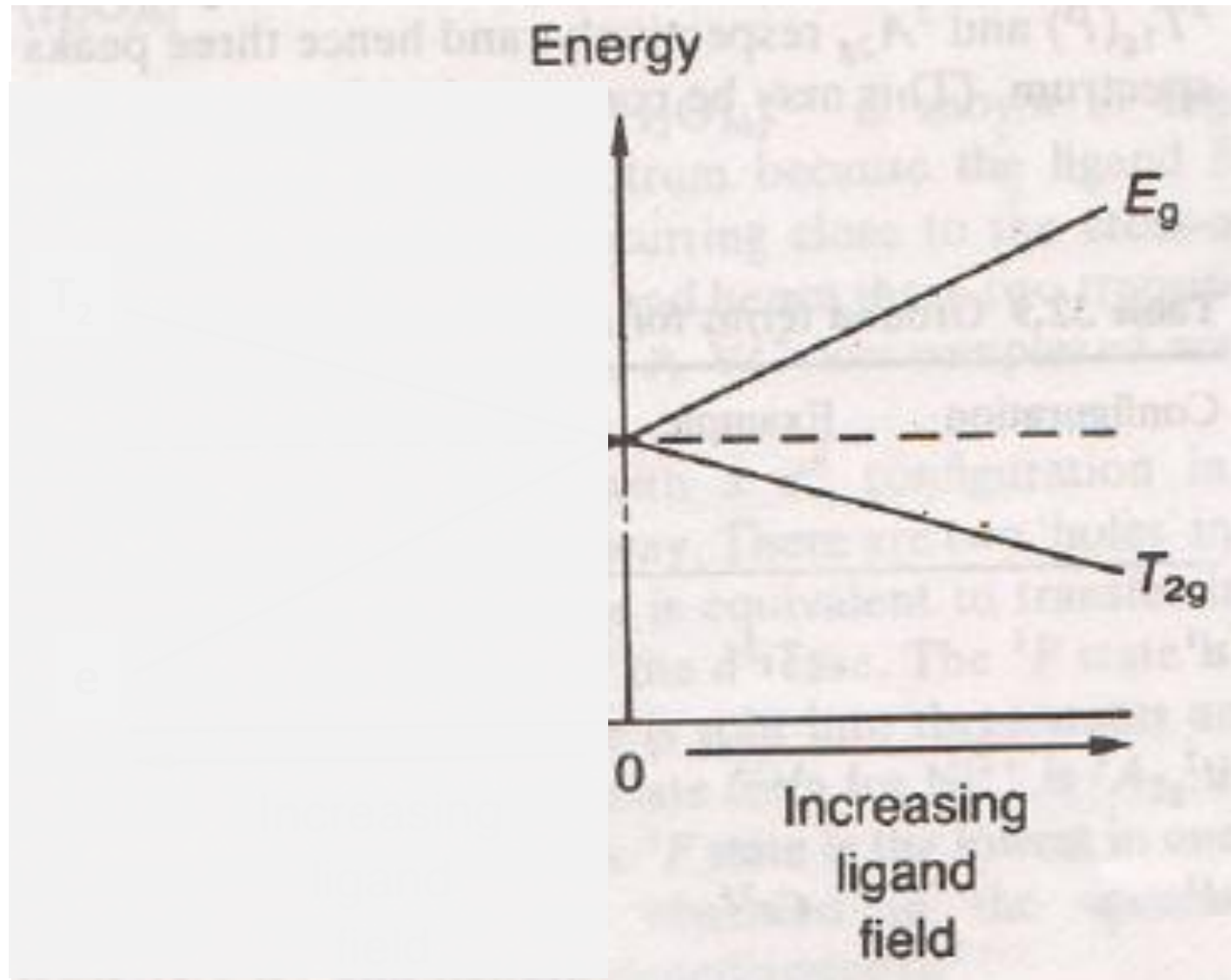
Spectra of d^1 and d^9 ions



An inverse relation exists between d^n and d^{10-n} systems (hole formalism) and also between octahedral and tetrahedral symmetries.



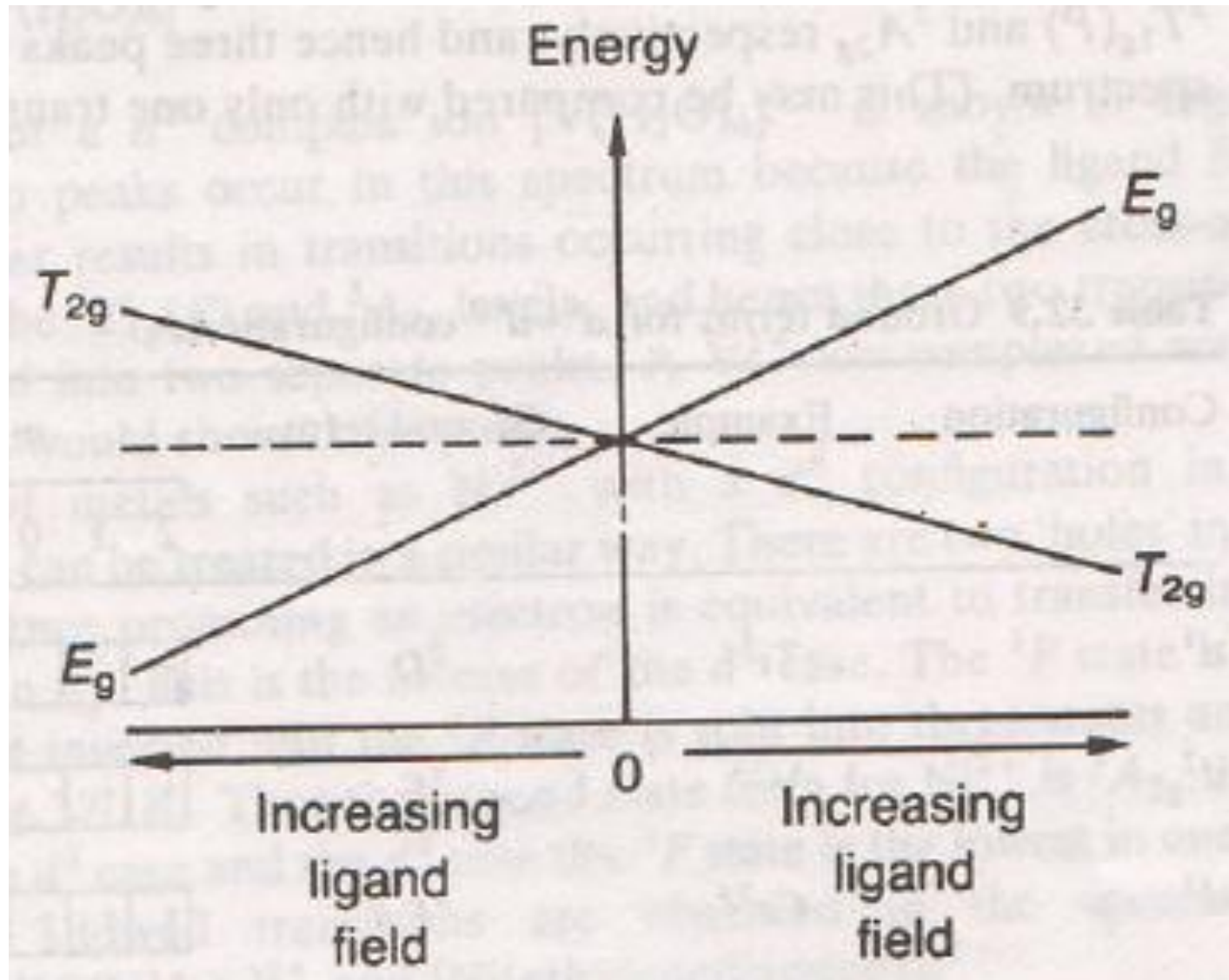
Spectra of d^1 and d^9 Oh and Td ions



d^1 octahedral

Spectra of d^1 and d^9 Oh and Td ions

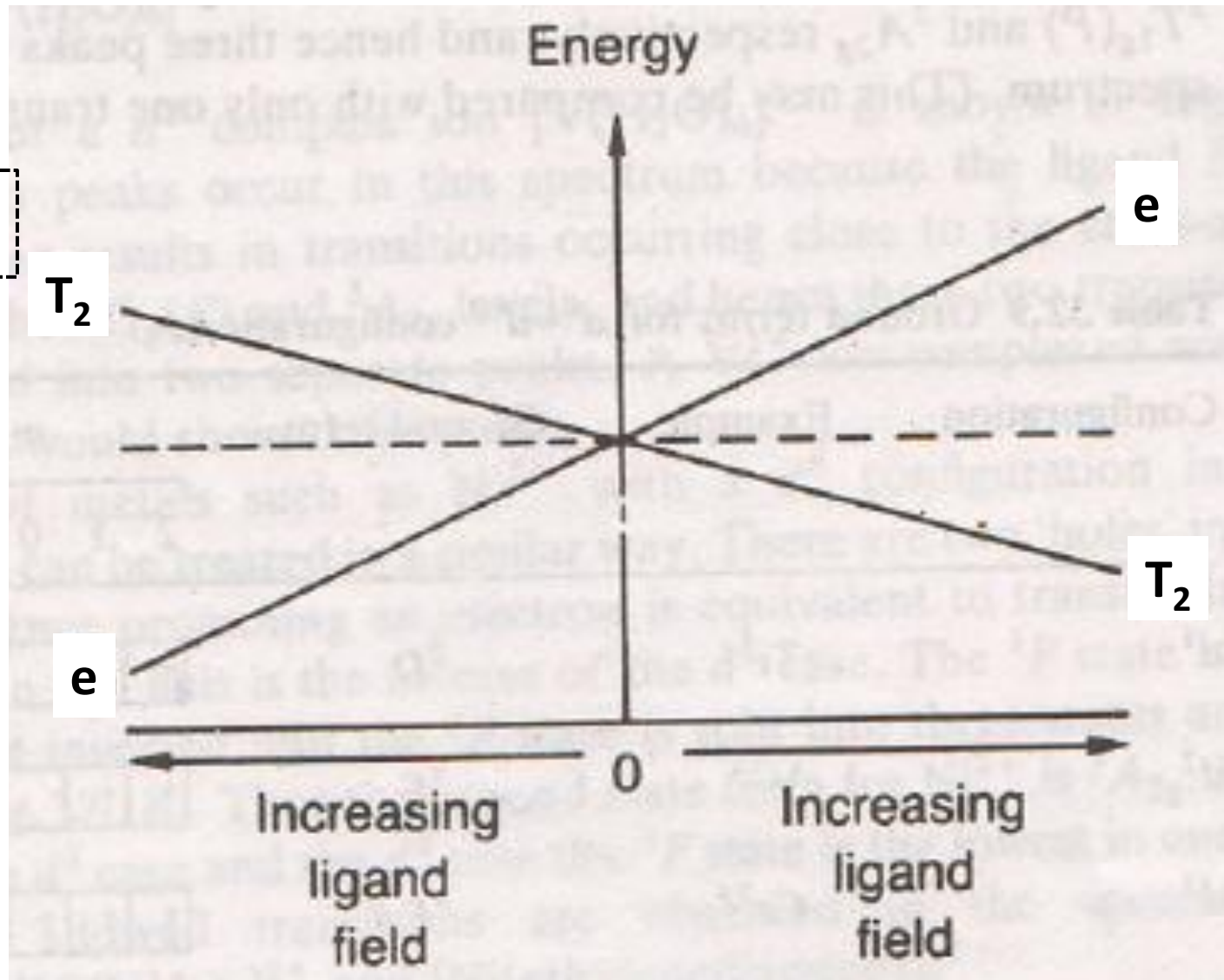
d^9 octahedral



d^1 octahedral

Spectra of d^1 and d^9 Oh and Td ions

d^1 tetrahedral

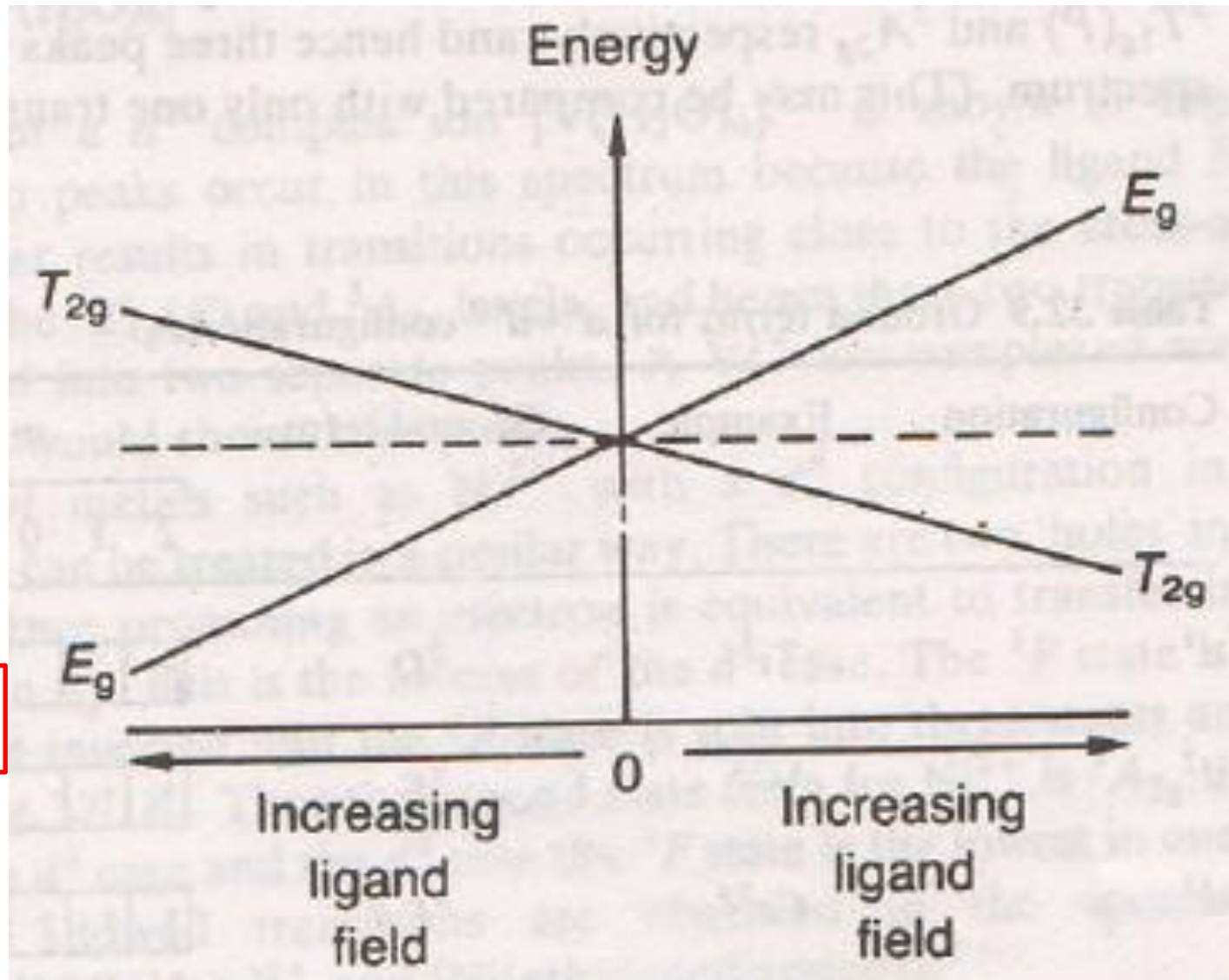


d^9 tetrahedral

Spectra of d^4 and d^6 Oh and Td ions



d^4 octahedral

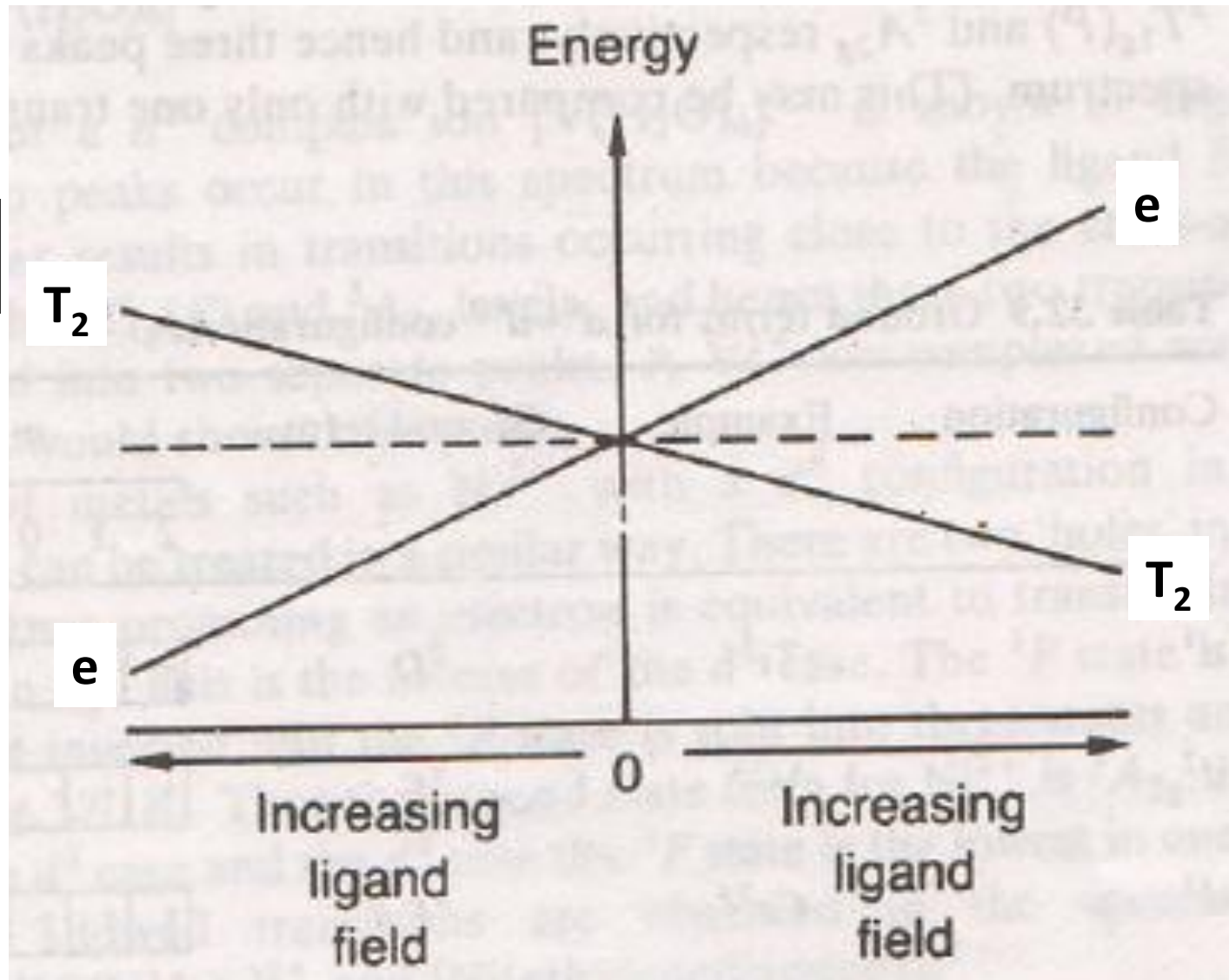


d^6 octahedral

Spectra of d^4 and d^6 Oh and Td ions



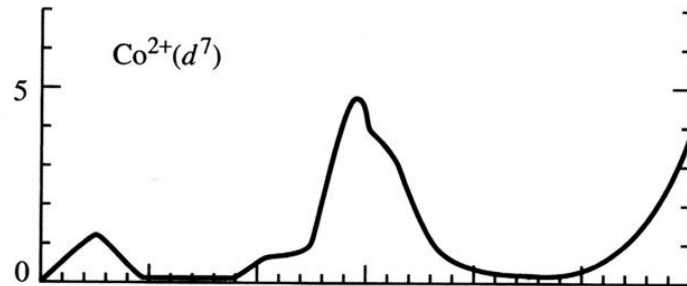
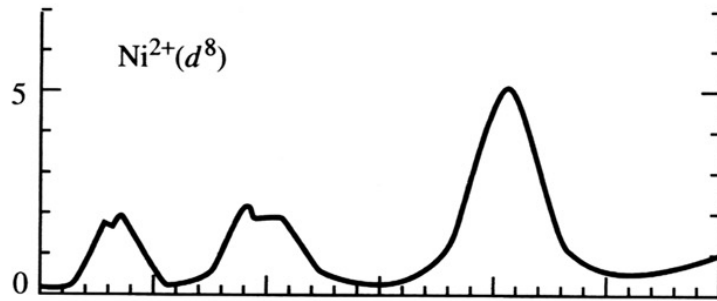
d^6 tetrahedral



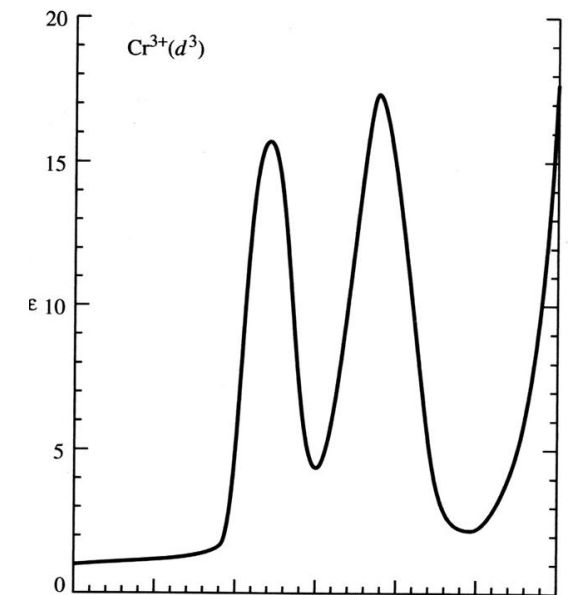
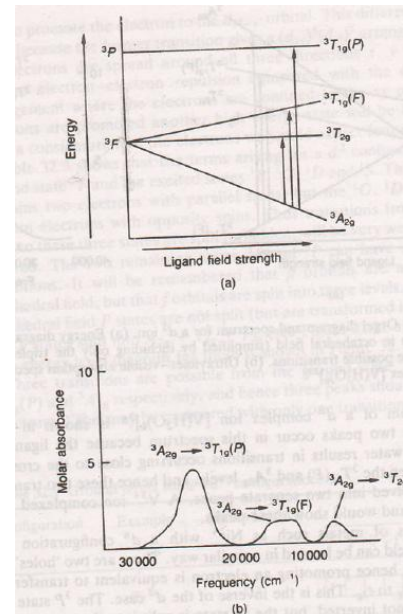
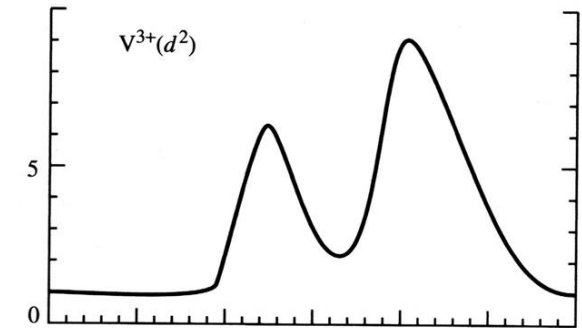
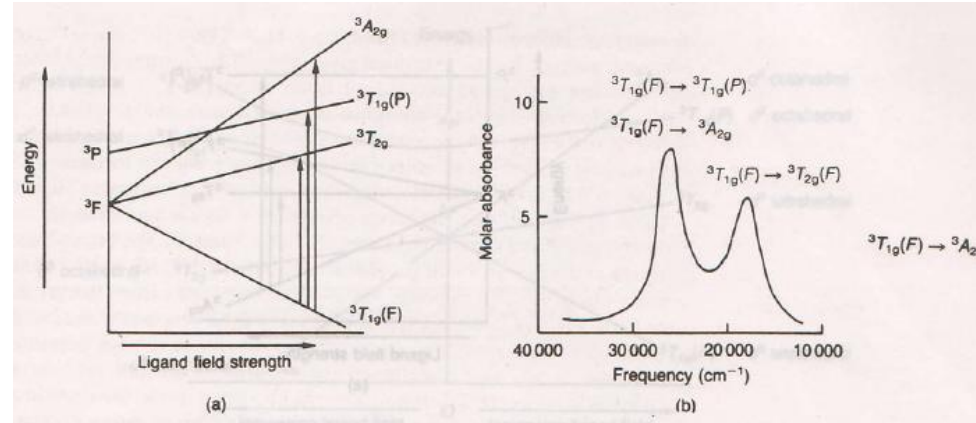
d^4 tetrahedral

Splitting of d^2 , d^3 , d^7 , and d^8 ions

d^2 , d^3 , d^7 and d^8 usually have 3 absorptions



Not in syllabus



Discussed topics.....



- ✓ Electronic spectroscopy of octahedral complexes
- ✓ Interpretation of electronic spectroscopy
- ✓ Splitting of d^n terms, hole formulation
- ✓ Selection rule for electronic transition
- ✓ Spectra of d^1 and d^9 ions

Question



Q. How many band (s) is/are expected theoretically in electronic spectrum based on the ground state term in $[\text{CrF}_6]^{4-}$ complex? Assign the electronic transition arising from ground state term.

Ans. Based on the ground state term only one band is expected.

Cr^{2+} is a d^4 system and its ground state term is 5D . Therefore, 5D will be splitted into 5E_g and $^5T_{2g}$ under ligand field. So, the electronic transition is 5E_g to $^5T_{2g}$.