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ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES :–

Electronic spectra of transition metal complexes and ions are observed in the visible and U.V region. Absorption spectra show the particular wavelength of light absorbed, that is the particular amount of energy required to promote an electron from one energy level to a higher energy level, whilst emission spectra show that the energy emitted when the electron falls back from the ~~excitted~~ excited level to a lower level. Transitions involving the outer shell of electrons are generally observed in the wavelength ~~level~~ region 100000 cm-1 to 10000 cm-1, but most spectra are measured in the 50,000 – 10 000 cm-1 region (200 – 1000 nm). The ~~interpretation~~ interpretation of spectra provides a most useful tool for the description and understanding of the energy level present.

Energy levels in an atom are described in terms of four quantum numbers:

1.) n the principle quantum numbers which may have values 1, 2, 3 - - - corresponding to the shell of electrons around the nucleus.

2.) l is the subsidiary quantum number and values are $0, 1, 2 \cdots (n-1)$. They describe the orbital angular momentum or shape of the orbital.

3) m the magnetic quantum number may have values from $+l, (l-1) \cdots 0 \cdots -l$.

4.) m_s the electronic spin quantum number which has a value of either $+1/2$ or $-1/2$.

The build up electrons in the elements follow three simple rules:

i) Electrons normally occupy the orbitals of lowest energy.

ii) Hunds rule: when several orbitals have similar energy, electrons are not paired or in the ground state an atom will contain the maximum number of unpaired electron spins.

iii) The Pauli exclusion Principle: no two electrons in one atom can have all four quantum numbers of the same value.

The spectra of transition metal complex is not as it appears from just the splitting of d-orbital with electrons get promotted from the lower energy orbital set to a higher energy orbital set.

Actually energy level of transition metal ~~can~~ atom or ion with a particular electronic configuration are described not only by the electronic configuration itself but also by different types of electronic interaction such as spin-spin, orbital-orbital or spin-orbital ~~wh~~ which is some special symbol called as term symbols.

Determination of ground state term of free atoms or ions :

i) All the l-~~level~~ vectors (l = orbital angular momentum quantum number) of the electron couple together electrostatically to give the resultant vector L, which is resultant orbital angular momentum quantum number. Different ~~Number~~ of values of L define the state of The free atom or ions as a whole those of l- define the state of electrons only.

L is always always an integer, including 0.

Values of L = 0, 1, 2, 3, 4, 5 ......
S, P, D, F, G, H ....

L values for the electrons in any filled orbital is zero.

$$L = l_1 + l_2 + l_3 + \dots\dots = \Sigma l.$$

ii) Similarly all s vectors (s = spin angular momentum quantum number) also combine to give the resultant spin angular momentum quantum number S. S is an integer, or 1/2 integer depending on the number of unpaired electrons. S value for the electrons in any of the completely filled orbital is zero. $S = \Sigma s$

The quantity (2S+1) is known as multiplicity of L state. This quantity gives the permitted values of J for the given values of L.

iii) Finally L and S vectors couple together to give a resultant vector J which is called resultant inner quantum number or total angular momentum quantum number of the atom. The process L-S coupling symbolically represented as $(l_1+l_2+l_3+\cdots)+(s_1+s_2+s_3+\cdots)=L+S=J$

Possible number of J is (2S+1) when $L \geq S$ and (2L+1) when $L < S$.

When $L=0$, J can have one value, $J=S$. J is always positive never negative. Different values of J vary in integral step between (L+S) and (L-S).

The ground state of an atom or ion is represented by

$$\text{multiplicity}\,L_J = {}^{2S+1}L_J = {}^{n+1}L_J$$

Rule for writting ground state terms;

i) The ground state term will be that which has the highest value of spin multiplicity or which has maximum number of unpaired electrons.

ii) If there are several terms with the same spin multiplicity possible for an atom or ion, the term having the largest value of L will be the ground state term.

iii) For a half filled or less than half filled shell, the ground state term is that which has the lowest value of J and for a more than half filled shell, the ground state is which has the highest values of J.