Quadrant II – Transcript and Related Materials
Programme:T.Y.B.Sc.

Subject: Chemistry

Semester :VI

Course Code: CHC 108

Course Title: Physical Chemistry

Unit : 2

SECTION B

Title of the unit : Molecular Spectroscopy - 2

Module Name: Singlet and Triplet State .

Name of the Presenter: Brenda Dias Barreto

SINGLET STATE AND TRIPLET STATE:

• Singlet and Triplet state arise from multiplicity considerations of spectroscopy.

• It defines the number of unpaired electrons in the absence of a magnetic field .

• Systems having 0,1,2,3….unpaired electrons refer to singlet state, doublet state, triplet state respectively.

• It means that (n+1) field degeneracy (equal energy states) will be associated with electron spin irrespective of the molecular orbitals occupied.

Singlet State

Most molecules have an even number of electrons in the ground state.

• All these electrons are spin paired i.e.no unpaired electrons.

• The quantity 2S + 1 where S – total electron spin

• This is known as spin multiplicity of the state.

• It is the degeneracy of the spin angular momentum

In most of organic molecules , the spins are paired (i.e.no unpaired electrons) ↑↓,

the upward orientation of the electron spin is cancelled by the downward orientation ,in the ground state ,hence S = 0

• $s_1 = ½$ and $s_2 = - ½$,$S = s_1 + s_2 = ½ - ½ = 0$

•Hence 2S + 1 = 1 .

• Thus the spin multiplicity is one and it is known as singlet state.

• This is called ground singlet state.

• The orbitals corresponding to higher energy level are vacant.

<u>Triplet State</u>

• When a molecule in the ground singlet state absorbs uv or visible radiation of proper frequency , one electron passes into the vacant orbital present in the higher energy level.

• During such transition two spin possibilities arise

• The spin orientation of the two single electrons may be either parallel (↑↑) Or anti parallel (↑↓)

• If the spin is parallel then S = s1 + s2 = ½ + ½ = 1

• Hence 2S + 1 = 3

• The spin multiplicity of the molecule is 3.

• Hence the molecule is in the triplet excited state. T

<u>SINGLET STATE AND EXCITED STATE</u>

• The ground singlet state of the system has no unpaired electrons .

• The excited singlet state of the system has two electrons one in the ground state and the other in the higher energy state , but spins of both are antiparallel and so no unpaired electrons.

• In the excited triplet state of the system ,the two electrons (one in the ground state) and the other in the higher energy state (excited state) have their spin parallel.

<u>EXAMPLES</u>:

• Almost all molecules exist in a singlet state, but molecular oxygen is an exception.

• At room temperature, O_2 exists in a triplet state, which can only undergo a chemical reaction by making the forbidden transition into a singlet state.

• This makes it kinetically non reactive despite being thermodynamically one of the strongest oxidants.

• Photochemical or thermal activation can bring it into the singlet state which makes it kinetically as well as thermodynamically a very strong oxidant.

Characteristics:

The lifetime of the excited singlet state is 10 -9 to 10-6 s and that of triplet excited state is 10-5 to 10-3 s.

• The excited triplet state is lower in energy than the excited singlet state hence singlet state are more reactive than the triplet states.

• The excited triplet state is more stable as compared to the excited singlet state.

• The excited triplet state has two unpaired electrons hence it shows paramagnetic behaviour.

The excited singlet state has no unpaired electrons hence it shows diamagnetic behaviour.

INTER SYSTEM CROSSING:

• When a singlet state non radiatively passes to a triplet state, or conversely a triplet transitions to a singlet, that process is known as intersystem crossing.

• The spin of the excited electron is reversed.

• This process occurs when the vibrational levels of the two excited states overlaps as there is no energy gained or lost in the transition.

• Intersystem crossing is most common in heavy-atom molecules (e.g. those containing iodine or bromine).

• This process is called “spin orbit coupling“ as it involves coupling of the electron spin with the orbital angular momentum of non-circular orbits.

• The presence of paramagnetic species in solution enhances intersystem crossing

APPLICATIONS:

- The rate of intersystem crossing can be adjusted to either favour or disfavour formation of the triplet state.

- Methods of adjusting the rate of intersystem crossing include the addition of Mn^{2+} to the system, which increases the rate of intersystem crossing for rhodamine and cyanine dyes.

- Fluorescent biomarkers, which include quantum dots and fluorescent proteins, are optimized to maximize quantum yield and intensity of fluorescent signal, which is obtained by decreasing the rate of intersystem crossing.

- The changing of the metal that is a part of the photosensitizer groups bound to CdTe quantum dots (nanometer sized semiconductor with a core shell structure which emit light when energy is applied))can also affect rate of intersystem crossing, as the use of a heavier metal can cause intersystem crossing to be favoured due to the heavy atom effect.