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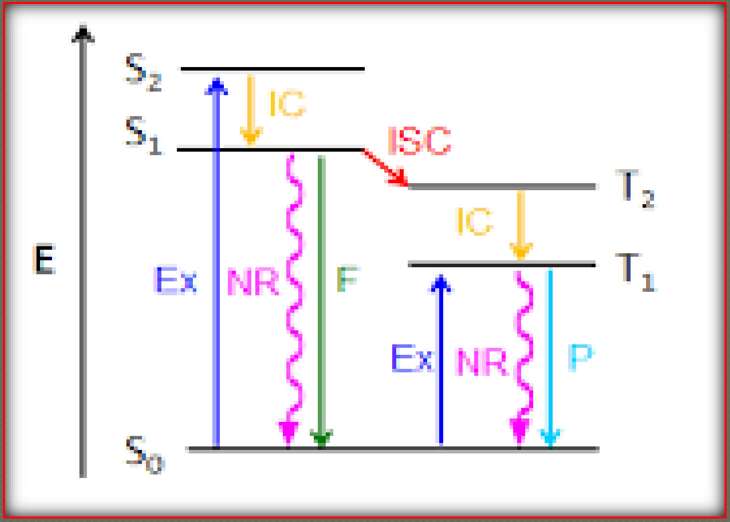
JABLONSKI DIAGRAM



JABLONSKI DIAGRAM

- When a molecule absorbs electromagnetic radiation it goes to higher energy state and is known as electronically excited state
- Returning of electronically excited state to ground state takes place by releasing its excess energy in number of ways, is termed as de-excitxtion/ deactivation/relaxation
- Relaxation/ De-excitation/ Deactivation of electronically excited state is graphically represented by Jablonski diagram

FEATURES OF JABLONSKI DIAGRAM

- Vertical axis represents Energy
- Singlet state (S)
- Triplet excited state(T)
- Bold horizontal lines – Electronic energy states
- Thin lines – Vibrational energy states
- Non radiative transitions – Wavy arrows
- Radiative transitions – straight arrows

NOMENCLATURE OF SPIN STATES

The naming of electronic states is based on the total spin of the electron, S

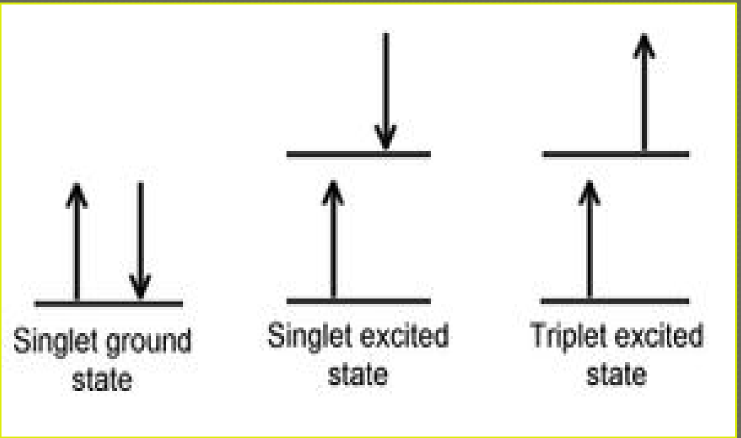
Multiplicity = 2S+1, S= Total spin angular momentum (Sum of all the electron spins)

For singlet state, S = 1/2 - 1/2 = 0

2S+1 = 2(0) + 1 = 1

For triplet state, S = 1/2 +1/2 = 1

2S+1 = 2(1)+1 = 3



S_0 = Singlet ground state

S_1= First excited singlet state

S_n = n th excited singlet state

T_1 = First excited triplet state

T_n = n th excited triplet state

INTRPRETATION OF JABLONSKIDIAGRAM

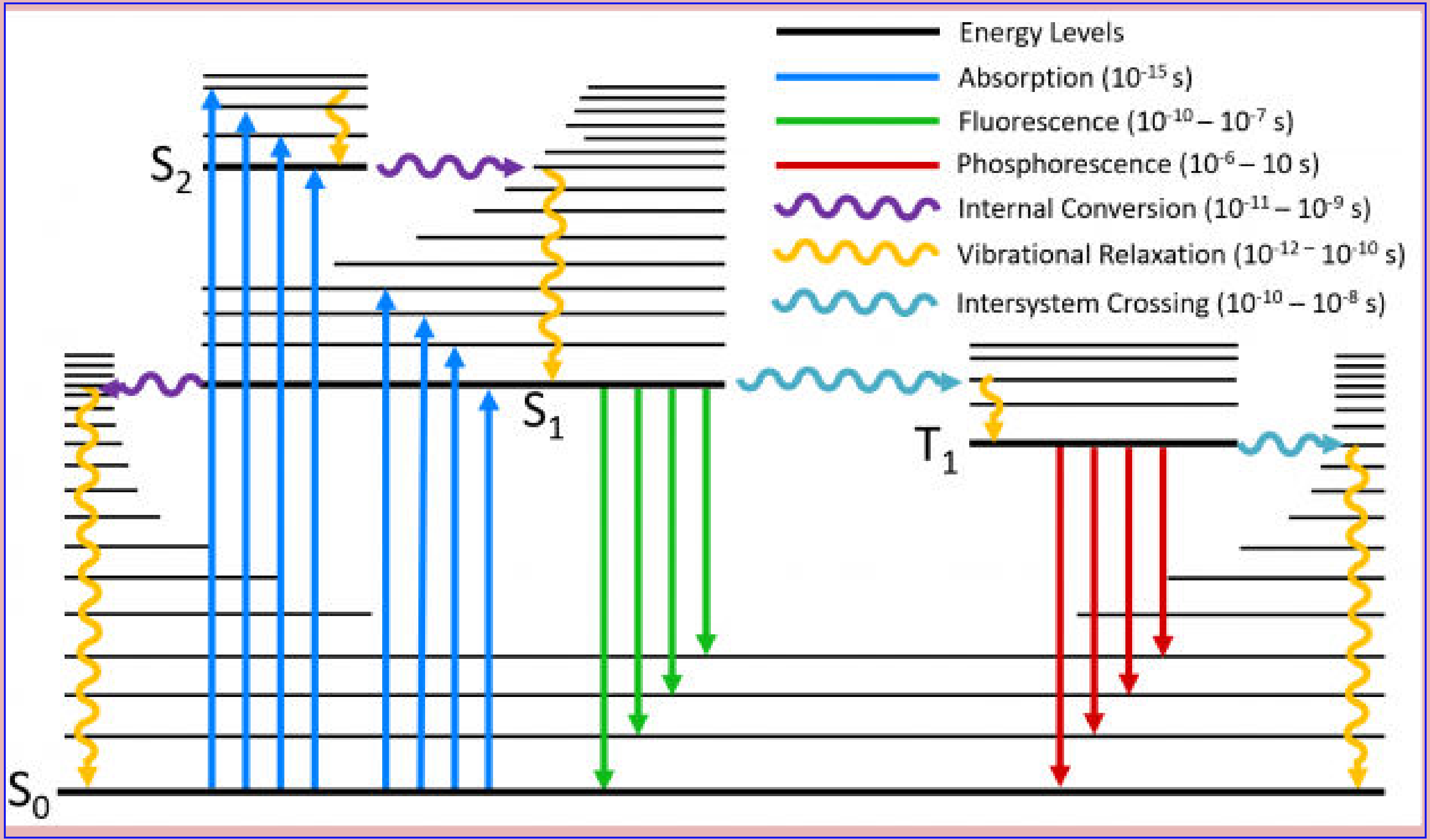
Definition

It is a graphical presentation of electronic levels with multiplets used to illustrate all types of transitions

Energy levels

These are shown by horizontal lines with energy increasing along the vertical axis. As energy increases the vibrational levels become more closely spaced and eventually form a continuum.

Various Radiative and Non-radiative transitions that can transfer the energy between the molecular states are represented by different colored arrows



Graphical representation of Jablonski diagram

Absorption and emission are two important aspects to discuss in Jablonski diagram.

Absorption

- The absorbance of a photon of a particular energy by the molecule results in excitation of electron from lower to higher energy level and is a radiative transition
- It is shown by straight blue color arrow pointing upwards in the diagram.
- At room temperature, the majority of molecules will be in the lowest vibrational level of the ground state (Boltzmann distribution). Absorption of a photon promotes the molecule from the ground state S_0 to one of the vibrational levels of the singlet excited states (S_1, S_2, …). Direct excitation to the triplet excited states (T_1,T_2,…) is not possible due to conservation of angular momentum
- Fastest transitions occurs in the time scale of 10^{-15} sec

Emission

- In the excited state the molecules exist for a few Nano seconds
- The process of relaxation of excited state is known as emission

Relaxations of electronically excited state can takes place by number of methods

RELAXATION

- **Non-Radiative transition**
  - Vibrational Relaxation (VR)
  - Internal Conversion (IC)
  - Intersystem Crossing (ISC)
- **Radiative transition**
  - Fluorescence
  - phosphorescence

VIBRATIONAL RELAXATION

This is a phenomenon in which relaxation occurs between the vibrational levels of same electronic state

$$S_2, V_x \xrightarrow{\text{Heat}} S_2, V_0$$

In the diagram it is shown by yellow color wavy arrows

This process is also very fast and occurs in the time-scale of $10^{-12} - 10^{-10}$ sec

Here excess vibrational energy is lost to vibrational modes within either the same molecule (intramolecular) or to surrounding molecules (intermolecular) until the lowest vibrational level of the electronic state is reached.

INTERNAL CONVERSION

This is a phenomenon in which relaxation occurs between the vibrational levels of two different electronic states of same spin multiplicity

$$S_2, V_x \xrightarrow{\text{Heat}} S_1, V_0$$

It is shown by purple color wavy arrows in the diagram

This process is also very fast and occurs in the time-scale of $10^{-11} – 10^{-9}$ sec

Internal conversion is immediately followed by vibrational relaxation. The rate of internal conversion is inversely proportional to the energy gap between the two electronic states. Internal conversion of the closely spaced higher singlet excited states ($S_3 \rightarrow S_2$, $S_2 \rightarrow S_1$ etc.) will proceed rapidly. Because of wider energy gap between the S_1 and the S_0 it occurs on a slower timescale.

INTERSYSTEM CROSSING

This is a phenomenon in which relaxation occurs between the vibrational levels of two different electronic states of different spin multiplicity

$$S_1, V_x \xrightarrow{\text{Heat}} T_1, V_0$$

This is indicated by horizontal aqua color wavy arrows from one column to another in the diagram

This is forbidden and delayed process however, for some molecules spin-orbit coupling between the spin angular momentum and the orbital angular momentum makes it possible.

The presence of heavy atoms also increases the spin - orbit coupling hence, favors the ISC

After ISC the molecule will immediately undergo vibrational relaxation to the ground vibrational level of T_1.

FLUORESCENCE

Fluorescence is the radiative transition between two electronic states of the same spin multiplicity.

$S_2, V_x \xrightarrow{h\nu} S_0, V_0$ $S_1, V_0 \xrightarrow{h\nu} S_0, V_0$

It is shown by green color straight arrows going down in the diagram

This process occurs in the time-scale of $10^{-9} - 10^{-7}$ sec

Fluorescence takes place as a consequence of the rapid vibrational relaxation and internal conversion , with some exceptions, from the first electronic excited singlet state to the singlet ground state.

PHOSPHORESCENCE

Phosphorescence is the radiative transition between two electronic states of different spin multiplicity.

$$T_1, V_x \xrightarrow{h\nu} S_0, V_0$$

It is shown by red color straight arrows going down in the diagram

Similarly to intersystem crossing; phosphorescence is a forbidden transition but is weakly allowed due to spin-orbit coupling.

The lifetime of the triplet state may be long enough and therefore phosphorescence occurs on a much longer timescale compared to fluorescence.

This process occurs in the time-scale of 10^{-6} – 10 sec, even minutes or more.

Thank you