ELECTRONIC SPECTRA

- Very complex spectra.
- Observed in UV & visible regions of electromagnetic spectrum.
- Complex spectra because electronic transition between two electronic states is always accompanied by simultaneous transitions between the vibrational & rotational energy levels. We can say that electronic spectra have vibrational & rotational fine structure.

$\Delta E = E' - E''$ → Energy of ground state.
↙
Energy of excited state

Assuming that Born-Oppenheimer approximation is valid for both ground & excited state.

$\Delta E = E_{el}' + E_{rot}' + E_{vib}' - (E_{el}'' + E_{rot}'' + E_{vib}'')$

(E_{trans}' & E_{trans}'' being not quantized)

$\Delta E = (E_{el}' - E_{el}'') + (E_{vib}' - E_{vib}'') + (E_{rot}' - E_{rot}'')$

$= \Delta E_{el} + \Delta E_{vib} + \Delta E_{rot}$.

$\Delta E_{el} \gg \Delta E_{vib} >> \Delta E_{rot}$

$\bar{\nu} = \frac{\Delta E}{hc} = \frac{\Delta E_{el} + \Delta E_{vib} + \Delta E_{rot}}{hc}$ cm^{-1} (Bohr frequency condition)

Franck-Condon Principle:

- Guiding principle for investigating the vibrational structure of electronic spectra.
- It states that an electronic transition takes place so rapidly that a vibrating molecule does not change

its internuclear distance appreciably during the transition.

- This principle as an approximation is true since the electrons move so much faster than the nuclei that during the electronic transition the nuclei do not change their position. Hence, an electronic transition may be represented by a vertical line on a plot of potential energy versus the internuclear distance.

Demonstration of Franck-Condon Principle:

In the fig. 30, two potential energy curves are shown for a diatomic molecule in the ground electronic state (E_0) & in the first excited electronic state (E_1). Since the bonding in the excited state is weaker than in the ground state, the minimum in the potential energy curve for the excited state occurs at a slightly greater internuclear distance than the corresponding minimum in the ground electronic state. Quantum mechanically, molecule is in the centre of the ground vibrational level of the ground electronic state. Thus, when a photon falls on the molecule, the most probable electronic transition, according to Franck-Condon principle, takes place from $v''=0$ to $v'=2$ ($0 \to 2$ transition) & hence have the highest intensity. (fig. 31)

We have other less intense lines in the spectra (fig. 31) which are due to transitions from $v''=0$ to other vibrational levels of the excited electronic state.

Electronic Spectra of Polyatomic Molecules

- More complex.
- The vibrational structure & rotational fine structure of electronic spectra can only be observed in the gaseous state & that too of small molecules. This is because large molecules have very high moments of inertia & in solution, rotational energy levels are not well defined. Hence, rotational fine structure is absent for large molecules & in solution. Also, vibrational transitions are broad. Thus, electronic spectra of molecules in solution has large unresolved bands rather than sharp peaks.

Here we can study organic compounds, particularly those containing groups like C=C, C=O, -N=N- & extensively conjugated systems.

According to Molecular Orbital Theory (MOT), the electrons can be classified as σ, π or n (non-bonding) depending on the molecular orbital they occupy (σ, π or n molecular orbital).

Generally, for organic compounds, electronic transitions involve promotion of the electrons in σ, π & n orbitals in the ground state to σ^* & π^* anti-bonding orbitals in the excited state. (Fig. 33).

We can say that only the transitions of the type $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$ are allowed.

There is no n^* anti-bonding orbitals because electrons in the n orbitals are not involved in bond formation.