SUBJECT - CHEMISTRY

CLASS - B.Sc(Hons) PART-III

PAPER - V

TOPIC - Jablonski diagram

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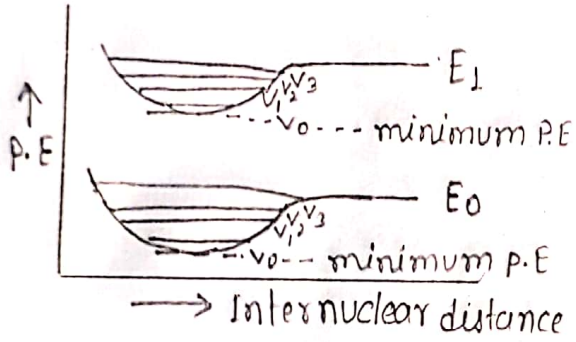
Q Give Salient features of Jablonski diagram with special reference to inter System crossing.

Ans Absorption of UV-VIS radiation induces electronic excitation or transition. This is shown by the P.E curve -



E_0 = ground electronic level

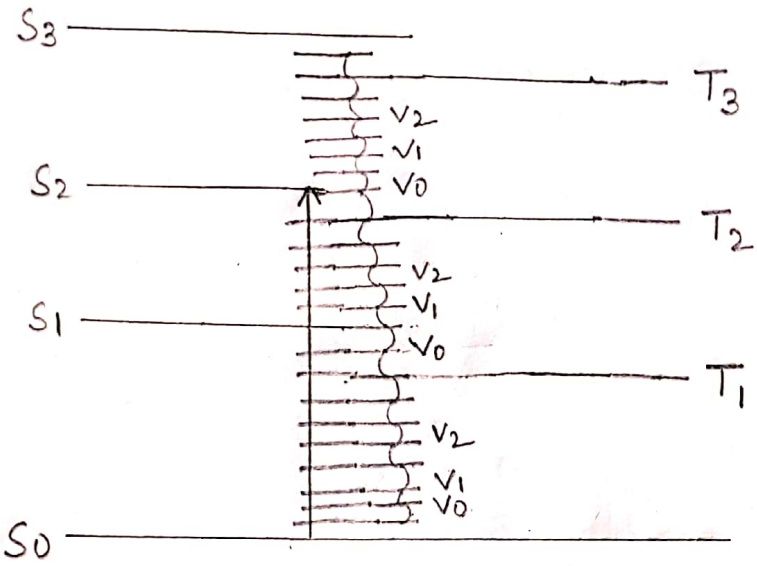
E_1 = excited electronic level

$V_0, V_1, V_2 \ldots$ = Vibrational energy levels.

The minimum in P.E of E_1 occurs at large internuclear distance than in the E_0 At the ground levels, majority of molecules reside at V_0. During $E_0 \rightarrow E_1$ excitation, the position of nuclei remains the Same and electron will still be V_0 at E_0 & E_1 Levels

Jablonski diagram Shows excited states of molecules shown by Morse P.E Vs. inter nuclear distance curves. Suppose a molecule absorbs a quantum ($h\nu$) of radiation in the Singlet ground state (S_0). in Solution, the excess Vibrational energy of S_2 will be rapidly dissipated by radiation process to the Solution.

S_2 will undergo radiation less internal conversion to an upper Vibrational level of S_1. Here, it will lose the excess Vibrational energy to the medium in 10^{-11} seconds S_1 with V_0 State has a life time of $\sim 10^{-8}$ seconds. S_1 & T_1 are major energy States in photochemical reactions. Higher S & T States are observed in non-dissociative reactions. In $S_1 \rightarrow S_2$ transition. The excess Vibrational energy is absorbed by Solvent thermally



Inter System crossing (ISC) involves spin inversion and gives to lower energy T-state. This is important because Sometimes T_1 State is more stable Than S_1 state Low energy T_1 state may have 10^{-6} Sec as the half-life intermolecular reaction is favoured by longer life time of T_1 state relative to S_1 state. $S_1 \rightarrow T_1$ ISC is spin forbidden However it occurs in few cases with 100% efficiency. The efficiency of ISC is governed by -

(1) Energy gap between lower S & T excited states. when it is large, spin forbidden is important the ISC efficiency is low or Zero. Ketones have very high ISC efficiency because S_1 & T_1 gap is low. olefins have low ISC efficiency.

(M)

(iii) The presence of heavy atoms, like S, Cl, Br, I etc increases ISC efficiency.

The Jablonski diagrams for benzophenone (Ketone) and butadiene (Olefin) are shown below –