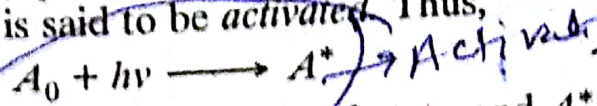


has higher energy than the corresponding ground state. The energy sequence is as follows:

$$E_{S_1} > E_{T_1}; E_{S_2} > E_{T_2}; E_{S_3} > E_{T_3} \text{ and so on.}$$

On absorption of light photon, the electron of the absorbing molecule may jump from  $S_0$  to  $S_1$ ,  $S_2$  or  $S_3$  singlet excited state depending upon the energy of the light photon absorbed, as shown in Jablonski diagram (Fig. 2). For each singlet excited state ( $S_1$ ,  $S_2$ ,  $S_3$ , etc.), there is a corresponding triplet excited state ( $T_1$ ,  $T_2$ ,  $T_3$ , etc.). The molecule, whether in singlet or triplet excited state, is said to be activated. Thus,



where  $A_0$  is the molecule in the ground state and  $A^*$  is the molecule in the excited state.

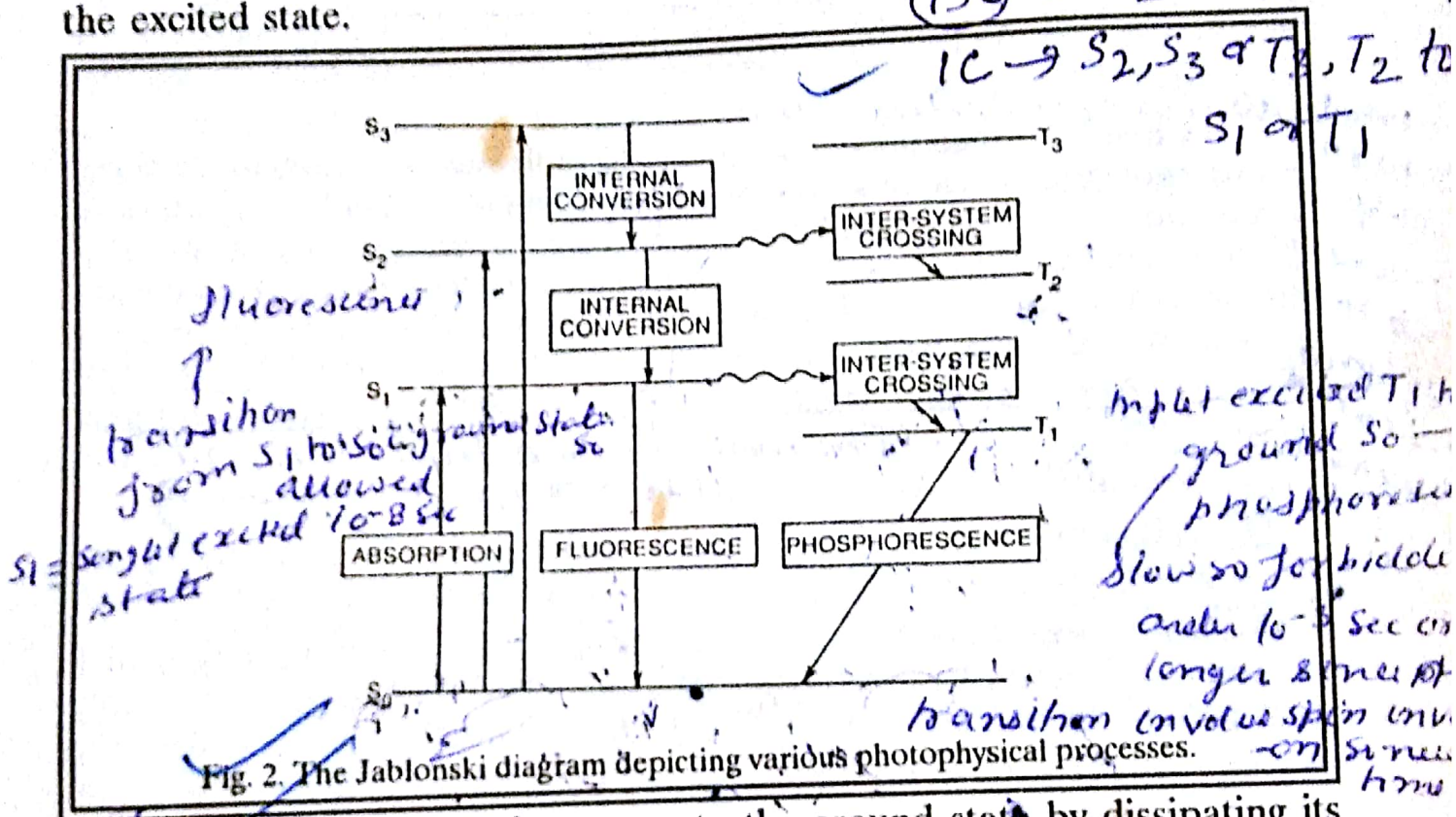


Fig. 2. The Jablonski diagram depicting various photophysical processes.

The activated molecule returns to the ground state by dissipating its energy through the following general types of processes:

**1. Non-radiative Transitions.** These transitions involve the return of the activated molecule from the higher excited states ( $S_3$ ,  $S_2$ , or  $T_3$ ,  $T_2$ ) to the first excited state ( $S_1$  or  $T_1$ ). These transitions do not involve the emission of any radiations and are thus referred to as non-radiative or radiationless transitions. The energy of the activated molecule is dissipated in the form of heat through molecular collisions. The process is called internal conversion (IC) and occurs in less than about  $10^{-11}$  second.

The molecule may also lose energy by another process called intersystem crossing (ISC). This process involves transitions between states



Transition from  $T_1$  to  $S_0$  → phosphorescence  
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rather slow

of different spins, i.e., different multiplicity, as, for example, from  $S_2$  to  $T_2$  or  $S_1$  to  $T_1$ . These transitions are also non-radiative or radiationless. Spectroscopically, such transitions are forbidden. However, they do occur though at relatively slow rates.

*allowed* 2. **Radiative Transitions.** These transitions involve the return of activated molecule from the singlet excited state  $S_1$  and triplet excited state  $T_1$  to the ground state  $S_0$ . Such transitions are accompanied by the emission of radiation. Spectroscopically, the transition from  $S_1$  to  $S_0$  state is an 'allowed' transition and occurs in about  $10^{-8}$  second. The emission of radiation in this transition is called **fluorescence**.

The transition from the triplet excited state  $T_1$  to the ground state  $S_0$  is rather *slow* since it is a 'forbidden' transition, as already mentioned. The emission of radiation in this transition is called **phosphorescence**. The life times of phosphorescence are much longer being of the order of  $10^{-3}$  sec or greater, since the transition involves spin inversion which needs time for its occurrence.

Both fluorescent and phosphorescent radiations are of shorter frequencies than the exciting light. This is obviously because some part of the light energy absorbed by the molecules is dissipated in the form of heat during the non-radiative transitions.

*molecule in singlet excited state* 3. **Chemical Reactions.** The activated molecule may also lose energy by undergoing chemical reaction. Since the molecule in singlet excited state