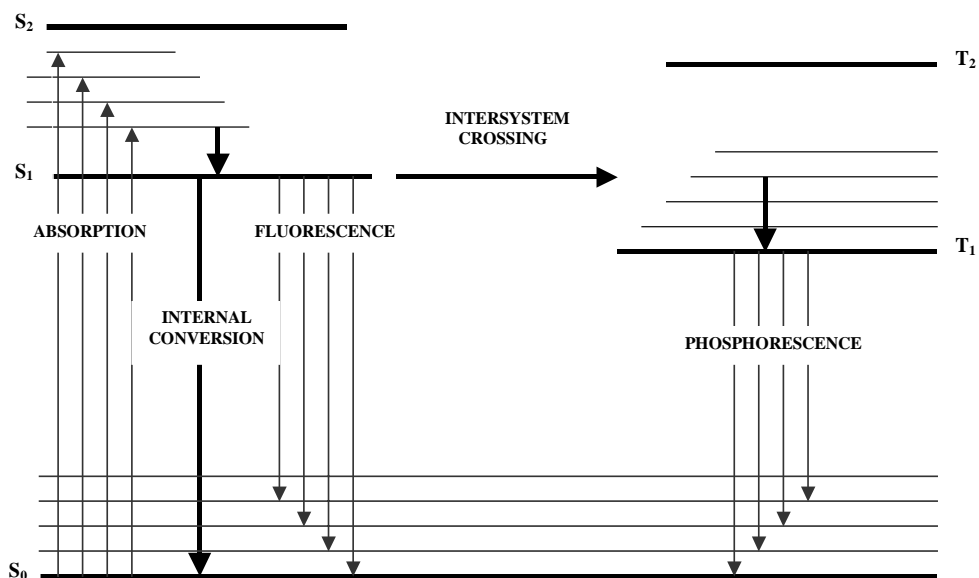




Theory of Fluorescence Decay

Fluorescence is the emission of light from a molecule resulting from a transition from one electronic state to a lower electronic state of the same multiplicity. The most commonly observed fluorescence from organic molecules is caused by a transition from an excited singlet state to the ground singlet state. A highly simplified *Jablonski diagram* illustrates the processes involved.

The various processes that occur in the excited state of a molecule include:



- Emission of a photon - this results in fluorescence if the transition is between states of the same multiplicity and in phosphorescence if the transition is between states of different multiplicities.
- Internal conversion (IC) - the non-radiative loss of excitation energy through conversion of an excited state to a highly excited vibrational level of a lower state of the same multiplicity. The excitation energy in this case dissipates as heat.
- Inter-system crossing (ISC) - the non-radiative transition from a singlet state to a triplet state (or vice versa).
- Quenching - the non-radiative loss of excitation energy via encounter with another molecule (quencher).

Each of these processes has a characteristic time in which it occurs. Emission and internal conversion typically occur on the picosecond through hundreds of nanoseconds time scale. Inter-system crossing also occurs in this time range when it is an effective mechanism for de-excitation of the excited state. Quenching is concentration-dependent, but commonly will compete with emission at millimolar and higher concentrations for good quenchers, as the quenching process is a diffusion-controlled process. Lastly, the molecule may undergo a photochemical conversion such as dissociation.

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