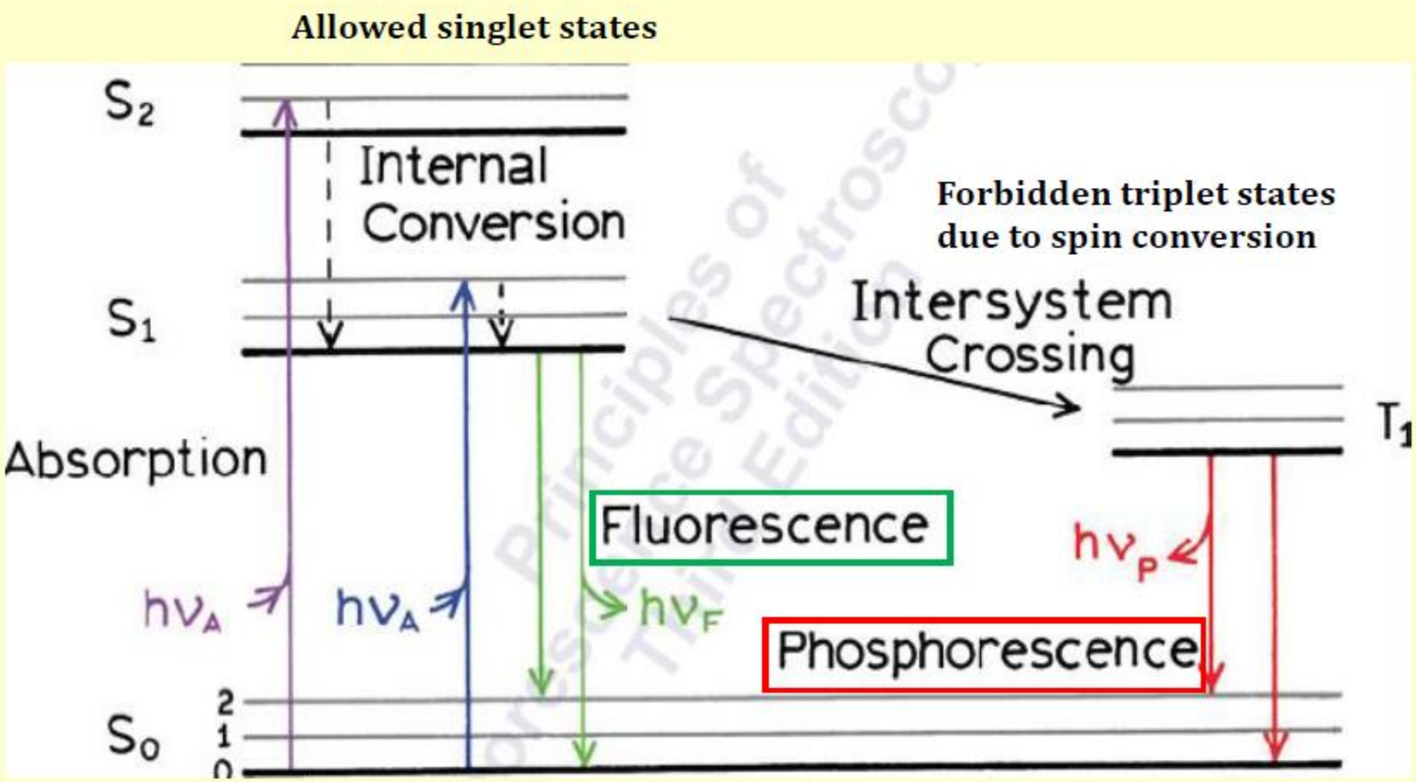
Jablonski Diagram



Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	10^{-15}
Internal Conversion	$S_n \rightarrow S_1$	10^{-14}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3}

The difference between **fluorescence and phosphorescence**

S. No.	Fluorescence	Phosphorescence
1.	These involve singlet to singlet transition. $S_1 \rightarrow S_0$	These involve triplet to singlet transition. $T_1 \rightarrow S_0$
2.	This transition is allowed transition	This transition is forbidden transition
3.	This transition is fast occurs in 10^{-8} sec	This transition is slow
4.	Efficiency is low	Efficiency is more
5.	It is less selective and sensitive	It is more selective and sensitive

The excited state lifetime

In the field of photochemistry, two important excited states are known: the singlet and the triplet excited states. The lifetime of these states are designated τ_F and τ_T respectively. However, there exists a term called the radiative lifetime, designated as τ_0. The photophysical processes that deactivated the first excited singlet state are:

$S_0 + h\nu \rightarrow S_1$	Rate = I_a	Absorption
$S_1 \rightarrow S_0 + h\nu_F$	Rate = $k_F[S_1]$	Fluorescence
$S_1 \longrightarrow S_0$ + heat	Rate = $k_{IC}[S_1]$	Internal conversion
$S_1 \longrightarrow T_1$	Rate = $k_{ISC}[S_1]$	Intersystem crossing

The radiative lifetime, τ_0, is a measure of the probability of emission, which is related to the probability of absorption. The radiative lifetime is represented by:

$$\tau_0 = \frac{1}{k_F}$$

lifetime if fluorescence was the only process deactivating the excited state, and it is the reciprocal of the first order rate constant of fluorescence.

The lifetime of the excited state (S_1) is the reciprocal of the first order rate constant for decay.

$$\tau_F = \frac{1}{k_F + k_{IC} + k_{ISC}}$$

The triplet state (T_1) formed can undergo further relaxation processes:

$T_1 \rightarrow S_0 + h\nu_P$	Rate = $k_P[T_1]$	Phosphorescence (radiative)
$T_1 \rightarrow S_0$	Rate = $k'_{ISC}[T_1]$	Intersystem crossing (non-radiative)

Where k_P is the rate constant for phosphorescence; and k′ISC is the rate constant for intersystem crossing from T_1 state to S_0.

$$\tau_T = \frac{1}{(k_P + k'_{ISC})}$$

In all cases, the excited triplet state is longer lived than the singlet counterpart because of the decay (radiative or non-radiative) of the T_1 to the S_0 state is forbidden.

Rate Constants for Excited State Deactivation

An alternative description of the quantum yield of a process emanating from an excited state is in terms of the relationship between the rate constant for the specified process and the sum of rate constants of all processes deactivating the excited state. For example, the quantum yield of fluorescence (Φ_F) is given as:

$$\Phi_F = \frac{k_F}{k_F + k_{IC} + k_{ISC}}$$

However, it is also known that $\tau_F = \frac{1}{k_F + k_{IC} + k_{ISC}}$

Therefore, $\Phi_F = k_F . \tau_F$

Therefore, it follows that $\frac{k_F}{k_F + k_{IC} + k_{ISC}} = \frac{\tau_F}{\tau_0} = \Phi_F$

If the lifetime of an excited state and the quantum yields of all processes deactivating it are known, it is possible to calculate the rate constants for the deactivating processes.

The following equations give the expressions for rate constants for the intrinsic processes (fluorescence, F; internal conversion, IC and intersystem crossing, ISC), which deactivate the excited singlet state of a molecule:

$$k_F = \frac{\Phi_F}{\tau_F}$$

$$k_{IC} = \frac{\Phi_{IC}}{\tau_F}$$

$$k_{ISC} = \frac{\Phi_{ISC}}{\tau_F}$$

Question:

For naphthalene in a glassy matrix at 77 K excited to the S_1 state, the quantum yield of fluorescence is 0.20, the quantum yield of triplet formation is 0.80, and the quantum yield of phosphorescence is 0.018.

a) Using the measured lifetime of fluorescence of 96 ns, determine the rate constant for intersystem crossing from S_1 to T_1.

b) From the measured phosphorescence lifetime of 2.6 s, determine the rate constant for intersystem crossing from T_1 to S_0.

Answer:

a) From the S_1 state,

$$k_{ISC} = \frac{\Phi_{ISC}}{\tau_F} = \frac{\Phi_T}{\tau_F} = \frac{0.8}{9.6 \times 10^{-8}} = 8.33 \times 10^{6}\ s^{-1}$$

b) From the T_1 state,

$$\Phi'_{ISC} = \Phi_T - \Phi_P = 0.80 - 0.018 = 0.792$$

$$\therefore\ k'_{ISC} = \frac{\Phi'_{ISC}}{\tau_T} = \frac{0.792}{2.6} = 0.305\ s^{-1}$$