Subject	Chemistry
Paper No and Title	8/ Physical Spectroscopy
Module No and Title	34/ Excited states: internal and external conversion, fluorescence, intersystem crossing, phosphorescence. Kinetics and rate constants. Stern-Volmer equation.
Module Tag	CHE_P8_M34

Principal Investigator		Co- Principal Investigator and Technical Coordinator
Prof A.K.Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi		Dr Vimal Rarh Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi *Specialised in : e-Learning and Educational Technologies*
Paper Coordinator	**Content Writer**	**Reviewer**
Prof. Rita Kakkar Professor Department of Chemistry University of Delhi	Prof. Rita Kakkar Professor Department of Chemistry University of Delhi Ms Bharti Badhani Deparment of Chemistry University of Delhi	Prof. S.P. Gupta Department of Applied Sciences National Institute of Technical Teachers' Training and Research (NITTTR) Bhopal

Anchor Institute : SGTB Khalsa College, University of Delhi

CHEMISTRY	PAPER No. : 8 (PHYSICAL SPECTROSCOPY)
	MODULE NO. : 34 (EXCITED STATES: INTERNAL AND EXTERNAL CONVERSION, FLUORESCENCE, INTERSYSTEM CROSSING, PHOSPHORESCENCE. KINETICS AND RATE CONSTANTS. STERN-VOLMER EQUATION.)

CHEMISTRY	PAPER No. : 8 (PHYSICAL SPECTROSCOPY)
	MODULE NO. : 34 (EXCITED STATES: INTERNAL AND EXTERNAL CONVERSION, FLUORESCENCE, INTERSYSTEM CROSSING, PHOSPHORESCENCE. KINETICS AND RATE CONSTANTS. STERN-VOLMER EQUATION.)

1. Learning Outcomes

In this module, we shall learn about

  (a) Excited states and how they are dissipated by internal and external conversion
  (b) Emission of photon as fluorescence
  (c) Intersystem crossing and observation of phosphorescence
  (d) The various processes involved and their rate constants
  (e) The quenching of fluorescence and the Stern-Volmer equation

2. Introduction

It is observed that a coloured solution continuously absorbs light to go to an excited state. If the excited molecules were not returning to the ground state, a stage would come when the molecule would stop absorbing radiation, as all the molecules would have gone to the excited state. The re-emission of energy by an excited molecule is discussed in this module. The various processes are discussed in terms of a diagram, called the Jablonski diagram.

3. Jablonski Diagram

The various processes whereby an excited state returns to the ground state are conveniently represented in a Jablonski diagram (Fig. 1).

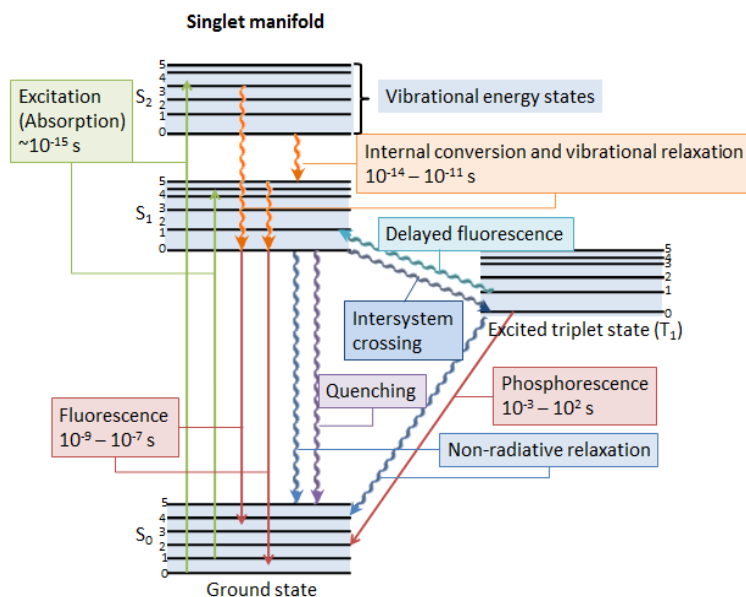| CHEMISTRY	PAPER No. : 8 (PHYSICAL SPECTROSCOPY)
	MODULE NO. : 34 (EXCITED STATES: INTERNAL AND EXTERNAL CONVERSION, FLUORESCENCE, INTERSYSTEM CROSSING, PHOSPHORESCENCE. KINETICS AND RATE CONSTANTS. STERN-VOLMER EQUATION.)

Figure 1: Jablonski diagram, showing electronic and vibrational energy levels

The ground state is labelled as S_0 and succeeding states as S_1, S_2, …etc. The first excited singlet is thus labelled S_1 and is the most important state, since all other singlet states have extremely short lifetimes and immediately drop to this state. Excitation usually takes a molecule to a high vibrational level according to the Franck-Condon principle. In less than 10^{-12} s, the molecule relaxes to the ground vibrational level of the excited singlet state. The process is called *vibrational relaxation (VR)*. The excited state may get deactivated by any of two processes: *internal* and *external conversion*. These processes are radiationless and are thus represented as wavy arrows in Figure 1. When the deactivation is by collision with another molecule, solvent molecule or the walls of the container, it is called external conversion. In some cases, there may be a crossing of the potential energy curve of the upper state with the ground state and the molecule may cross over to a high vibrational level of the ground state and then come to the ground vibrational level of the ground state by vibrational relaxation. This process is called internal conversion.

If none of these competing radiationless processes occurs, the molecule returns to the ground state by emitting radiation in the form of *fluorescence*. It is the reverse of excitation, but occurs at longer wavelengths due to the Franck-Condon principle (Fig. 2). On excitation, the molecule is taken to a high excited vibrational level of the excited state, governed by the Franck-Condon principle. Vibrational relaxation brings it down to the ground vibrational state from which fluorescence occurs. Since the energy difference is smaller for fluorescence than for excitation, the latter occurs at longer wavelength. This is called *Stokes shift*.

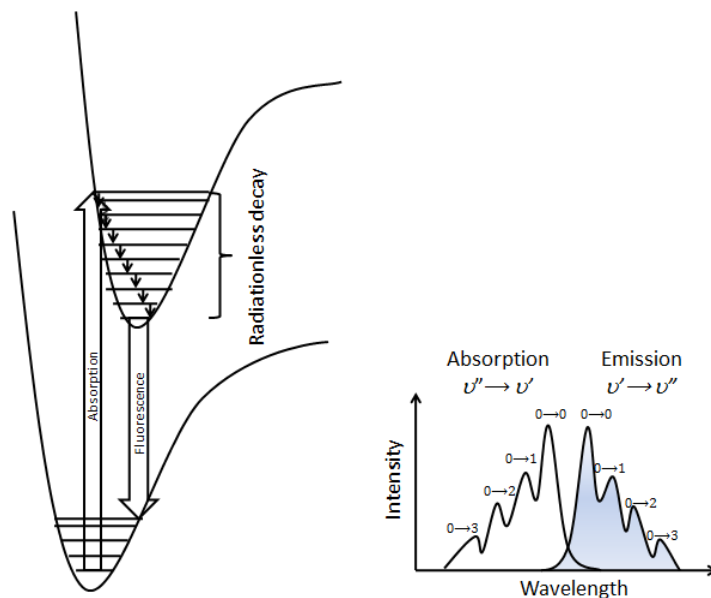| CHEMISTRY	PAPER No. : 8 (PHYSICAL SPECTROSCOPY)
	MODULE NO. : 34 (EXCITED STATES: INTERNAL AND EXTERNAL CONVERSION, FLUORESCENCE, INTERSYSTEM CROSSING, PHOSPHORESCENCE. KINETICS AND RATE CONSTANTS. STERN-VOLMER EQUATION.)

Figure 2: Fluorescence

As shown in Figure 2, only the (0,0) transitions for absorption and fluorescence coincide. Absorption shows the vibrational structure for the excited state, while in fluorescence, the vibrational structure corresponds to the ground electronic state. There is still an approximate mirror image relationship between the absorption and fluorescence spectra. This mirror image relationship is observed for molecules that are rigid, such as polyaromatics like anthracene, for which other dissipative processes, such as internal conversion, do not occur. Fluorescence lifetimes are of the order of ~10^{-8} s.

Sometimes, there is a crossing of the potential energy curves of the excited singlet (S_1) and triplet (T_1) states. The latter is slightly lower in energy (Fig. 3), but the two potential energy curves may cross. The molecule may cross over to the triplet state by a process called *intersystem crossing*. Once there, it cannot easily come to the ground state singlet because this process involves change in spin and is electric-dipole forbidden. However, it returns to the ground state by a process called *phosphorescence.* Since it is forbidden, phosphorescence is slow and typical lifetimes are larger than 10^{-3} s. Unlike fluorescence, it persists even after the radiation is switched off. It is enhanced by triplet sensitizers like molecular oxygen, which transfers its triplet energy to the molecule. Since triplet states are lower in energy than excited singlets, phosphorescence occurs at a longer wavelength than fluorescence.

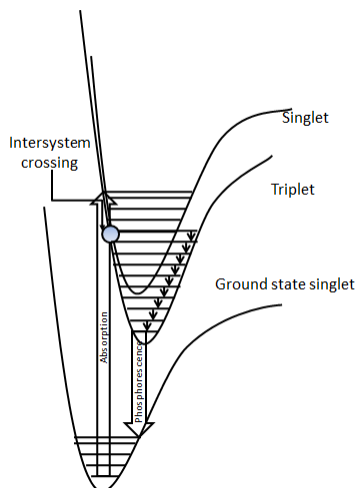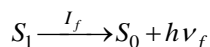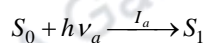| CHEMISTRY	PAPER No. : 8 (PHYSICAL SPECTROSCOPY)
	MODULE NO. : 34 (EXCITED STATES: INTERNAL AND EXTERNAL CONVERSION, FLUORESCENCE, INTERSYSTEM CROSSING, PHOSPHORESCENCE. KINETICS AND RATE CONSTANTS. STERN-VOLMER EQUATION.)

Figure 3: Intersystem crossing from S_1 state to T_1 state

Let us now understand the kinetics of the various processes involved, since they involve varying time scales.

4. Kinetics of Photochemistry

Photochemistry is the study of processes initiated by light. The primary step in photochemistry is absorption of radiation (intensity = I_a) by the ground state S_0. If the only process that deactivates the excited state is fluorescence, the following two processes occur

$$S_0 + h\nu_a \xrightarrow{I_a} S_1$$

$$S_1 \xrightarrow{I_f} S_0 + h\nu_f$$

The rate of disappearance of the excited state S_1 molecules is given by

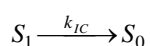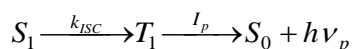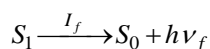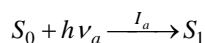$$\frac{d[S_1]}{dt} = I_a - k_f[S_1] \qquad (1)$$

where k_f is the fluorescence rate constant and is first order ($I_f = k_f[S_1]$). The lifetime of the excited state is $\tau_0 = 1/k_f$. This is also called the *intrinsic* or *natural* lifetime of the excited state.

CHEMISTRY	PAPER No. : 8 (PHYSICAL SPECTROSCOPY)
	MODULE NO. : 34 (EXCITED STATES: INTERNAL AND EXTERNAL CONVERSION, FLUORESCENCE, INTERSYSTEM CROSSING, PHOSPHORESCENCE. KINETICS AND RATE CONSTANTS. STERN-VOLMER EQUATION.)

Other processes may also deactivate the excited state. These include intersystem crossing (rate constant k_{ISC}) or internal conversion (rate constant k_{IC}). In the presence of these competing processes, the set of equations gets modified to

$$S_0 + h\nu_a \xrightarrow{\;I_a\;} S_1$$

$$S_1 \xrightarrow{\;I_f\;} S_0 + h\nu_f$$

$$S_1 \xrightarrow{\;k_{ISC}\;} T_1 \xrightarrow{\;I_p\;} S_0 + h\nu_p$$

$$S_1 \xrightarrow{\;k_{IC}\;} S_0$$

The steady state approximation for the excited state S_1 gives

$$\frac{d[S_1]}{dt} = I_a - k_f[S_1] - k_{ISC}[S_1] - k_{IC}[S_1] = 0$$
$$\Rightarrow I_a = (k_f + k_{ISC} + k_{IC})[S_1] \tag{2}$$

Efficiencies of photochemical processes are described by quantum yields, defined as

$$\phi = \frac{\text{Rate of a specified process}}{\text{Rate of photon absorption}}$$

The quantum yield for fluorescence is defined as the fraction of molecules undergoing fluorescence and is given by

$$\phi_f = \frac{\text{Rate of fluorescence}}{\text{Rate of all processes}} = \frac{k_f[S_1]}{(k_f + k_{ISC} + k_{IC})[S_1]} = \frac{k_f}{k_f + k_{ISC} + k_{IC}} \tag{3}$$

Due to these competing processes, the observed lifetime is reduced to

$$\tau = \frac{1}{k_f + k_{ISC} + k_{IC} + \ldots} \tag{4}$$

The denominator is a sum of first-order rate constants and hence the quenching process remains first order.

| CHEMISTRY	PAPER No. : 8 (PHYSICAL SPECTROSCOPY)
	MODULE NO. : 34 (EXCITED STATES: INTERNAL AND EXTERNAL CONVERSION, FLUORESCENCE, INTERSYSTEM CROSSING, PHOSPHORESCENCE. KINETICS AND RATE CONSTANTS. STERN-VOLMER EQUATION.)

Thus, we may write equation (3) as

$$\phi_f = \frac{k_f}{\sum_i k_i} = \frac{\tau}{\tau_0} \qquad (5)$$

Hence, since other energy wastage processes reduce the lifetime of the excited species, $\phi_f < 1$ and $\tau < \tau_0$. The lifetime τ is related to the intrinsic or natural lifetime by $\tau = \tau_0 \phi_f$.

Besides these processes, quenching of fluorescence may also occur due to external molecules. For example, dissolved oxygen promotes intersystem crossing and increases phosphorescence. In the presence of a quencher, an additional second order process has to be taken into account:

$$S_1 + Q \xrightarrow{k_q} S_0 + Q$$
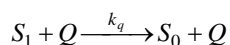
This modifies equation (3) to

$$\phi_f = \frac{k_f[S_1]}{(k_f + k_{ISC} + k_{IC} + k_q[Q])[S_1]} = \frac{k_f}{k_f + k_{ISC} + k_{IC} + k_q[Q]} \qquad (6)$$

If we designate the quantum yield in the absence of quencher as ϕ_f^0, we may write

$$\frac{\phi_f^0}{\phi_f} = \frac{k_f}{k_f + k_{ISC} + k_{IC}} \frac{k_f + k_{ISC} + k_{IC} + k_q[Q]}{k_f} = 1 + \frac{k_q[Q]}{k_f + k_{ISC} + k_{IC}} \qquad (7)$$
$$= 1 + K_{SV}[Q]$$

This is called the *Stern-Volmer equation* and K_{SV} the Stern-Volmer constant, which is equal to $\frac{k_q}{k_f + k_{ISC} + k_{IC}} = k_q \tau$.

If ϕ_f^0 / ϕ_f, the relative quantum yield, is plotted against the concentration of the quencher $[Q]$, a straight line is obtained with intercept equal to '1' and slope equal to K_{SV}. The relative quantum yield can be replaced by the relative fluorescence intensity (I_f^0 / I_f), which is easily measured. Also, since the lifetime is proportional to the quantum yield, the ratio τ_0/τ may be used instead. If τ, the fluorescence lifetime in the absence of quencher is known, k_q can be determined from the slope of the Stern-Volmer plot. The lifetime can be easily measured by observing the first-order rate of decay of the excited state (Fig. 4). Since the fluorescence intensity is proportional to the excited state concentration, a plot of $\ln(I_f)$ versus time gives a straight line with slope $-k$, where k is the combined rate constant of all the processes and is the reciprocal of the lifetime, τ. Larger

the value of k_q, more efficient is the quencher. Thus, among the halide ions, the quenching efficiency increases as Cl⁻ < Br⁻ < I⁻.

Figure 4 shows the Stern-Volmer plot for the measured data on the quenching of fluorescence of riboflavin (in 0.02 M acetic acid) by halide ions. For this, the value of K_{SV} obtained is 6.3 dm³ mol⁻¹ for quenching by chloride ions. The literature value of τ is ~ 5 ns. This gives a value of (6.3 dm³ mol⁻¹)/(5×10⁻⁹ s) ≈ 1.3×10⁹ dm³ mol⁻¹ s⁻¹ for k_q.
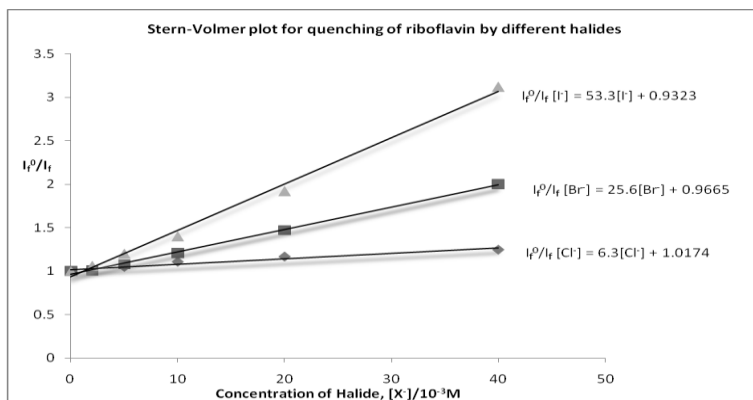

Figure 4: Stern-Volmer plot of quenching of fluorescence of riboflavin in 0.02 M acetic acid by halide ions

5. Summary

- Excited states lose their excess energy by various ways.
- Radiationless processes are internal and external conversion.
- If the molecule survives these processes, it may undergo fluorescence.
- If the excited state has a long lifetime, it may undergo intersystem crossing to a triplet state.
- From here, it may undergo phosphorescence.
- All these processes are first-order processes.
- An external molecule may also quench fluorescence. Since this involves collision, it is a second order process.
- The quenching of fluorescence is given by the Stern-Volmer equation.

CHEMISTRY	PAPER No. : 8 (PHYSICAL SPECTROSCOPY)
	MODULE NO. : 34 (EXCITED STATES: INTERNAL AND EXTERNAL CONVERSION, FLUORESCENCE, INTERSYSTEM CROSSING, PHOSPHORESCENCE. KINETICS AND RATE CONSTANTS. STERN-VOLMER EQUATION.)