Sim Pack 5:

Stern-Volmer Kinetics

Version 1.0

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Learning Outcomes:

After reading these notes you will learn about the following terms:

- Bimolecular quenching
- Stern-Volmer Kinetics
- Bimolecular quenching constant
**Bimolecular Processes (Quenching)**

Previously\(^1\) we developed a kinetic scheme to derive an expression for the amount of fluorescence observed (i.e., the quantum yield \(\Phi^0\)) from an excited state, \(M^*\), as a result of unimolecular deactivation processes:

\[
\begin{align*}
\text{process} & \quad \text{rate} \\
1^1M^* & \xrightarrow{k_R} 1^1M + h\nu & k_R \ [1^1M^*] & \text{Eq 1} \\
1^1M^* & \xrightarrow{k_{IC}} 1^1M & k_{IC} \ [1^1M^*] & \text{Eq 2} \\
1^1M^* & \xrightarrow{k_{ISC}} 3^3M^* & k_{ISC} \ [1^1M^*] & \text{Eq 3}
\end{align*}
\]

(* denotes electronically excited)

We can expand the kinetic scheme above to include *bimolecular* interactions where a quencher, \(Q\), deactivates \(M^*\):

**Footnote**

\(^1\) Sim Pack 1: “Fluorescence”, Copyright 2012, sim4t.com
Fluorescence quenching is an example of energy transfer.

Energy exchange occurs through short distances ~ 2nm (i.e., via collisions between the excited state and Q):
Since, the intensity of fluorescence\(^1\), \(I_F \propto \) to the quantum yield\(^1\) of fluorescence, \(\Phi_F\).

\(I_F\) is the intensity of fluorescence and what is measured “directly” \textit{via} fluorescence steady state spectroscopy\(^1\).

In addition, for dynamic quenching (when one excited state is deactivated by one quencher):

\[\frac{\Phi^0_F}{\Phi_F} = \frac{I^0_F}{I_F} = \frac{\tau^0_F}{\tau_F}\]

\(\tau_f\) data can be determined by a fluorescence lifetime spectrometer, e.g., a single photon counter\(^2\).

\[\frac{\Phi^0_F}{\Phi_F} = \frac{I^0_F}{I_F} = \frac{\tau^0_F}{\tau_F} = 1 + k_q \tau^0_F [Q] \quad \text{Eq 17}\]

\textbf{Footnote:}

\(^1\) Sim Pack 1: “Fluorescence”, Copyright 2012, sim4t.com
