Sim Pack 5:

Stern-Volmer Kinetics

Version 1.0

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 Φ^o) from an excited state, M*, as a result of unimolecular deactivation processes:

	process	rate	
$^1M^* \xrightarrow{k_R} {}^1M + h\upsilon$	fluorescence	$k_R\ [^1M^*]$	*Eq 1*
$^1M^* \xrightarrow{k_{IC}} {}^1M$	internal conversion	$k_{IC}\ [^1M^*]$	*Eq 2*
$^1M^* \xrightarrow{k_{ISC}} {}^3M^*$	intersystem crossing	$k_{ISC}\ [^1M^*]$	*Eq 3*

(* 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

usually non fluorescent

$^1M^* + Q \xrightarrow{k_q} M + Q^*$

bimolecular quenching constant

process	rate	
bimolecular quenching	$k_q\ [^1M^*]\ [Q]$	*Eq 4*

$^1M^* + Q \longrightarrow {}^1M + Q^*$

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, Φ_F

(I_F is the intensity of fluorescence and what is measured "directly" *via* fluorescence steady state spectroscopy[1])

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

$$\frac{\Phi^o_F}{\Phi_F} = \frac{I^o_F}{I_F} = \frac{\tau^o_F}{\tau_F}$$

(τ_f data can be determined by a fluorescence lifetime spectrometer, e.g., a single photon counter[2])

then:

$$\frac{\Phi^o_F}{\Phi_F} = \frac{I^o_F}{I_F} = \frac{\tau^o_F}{\tau_F} = 1 + k_q \tau_F{}^o [Q]$$

Eq 17

Footnote:

[1] Sim Pack 1: "Fluorescence", Copyright 2012, sim4t.com

[2] Sim Pack 2: "Time Correlated Single Photon Counting", Copyright 2012, sim4t.com