Stern–Volmer kinetic relationships

This term applies broadly to variations of *quantum yields* of *photophysical processes* (e.g. *fluorescence* or *phosphorescence*) or *photochemical reactions* (usually reaction quantum yield) with the concentration of a given reagent which may be a substrate or a *quencher*. In the simplest case, a plot of Φ^0/Φ (or M^0/M for emission) vs. concentration of quencher, [Q], is linear obeying the equation:

$$\Phi^0/\Phi \text{ or } M^0/M \; = \; 1 \; + \; K_{sv}\,[Q] \qquad (1)$$

In equation (1) K_{sv} is referred to as the Stern–Volmer constant. Equation (1) applies when a quencher inhibits either a photochemical reaction or a photophysical process by a single reaction. Φ^0 and M^0 are the quantum yield and emission intensity (*radiant exitance*), respectively, in the absence of the quencher Q, while Φ and M are the same quantities in the presence of the different concentrations of Q. In the case of dynamic quenching the constant K_{sv} is the product of the true *quenching constant* k_q and the *excited state lifetime*, τ^0, in the absence of quencher. k_q is the bimolecular reaction rate constant for the elementary reaction of the excited state with the particular quencher Q. Equation (1) can therefore be replaced by the expression (2):

$$\Phi^0/\Phi \text{ or } M^0/M \; = \; 1 \; + \; k_q \tau^0\,[Q] \qquad (2)$$

When an excited state undergoes a bimolecular reaction with rate constant k_r to form a product, a double-reciprocal relationship is observed according to the equation:

$$1/\Phi_p = (1 \; + \; 1/k_r \; \tau^0[S] \;) \; [1/(A{\cdot}B)]$$

where Φ_p is the quantum efficiency of product formation, A the efficiency of forming the reactive excited state, B the fraction of reactions of the excited state with substrate S which leads to product, and [S] is the concentration of reactive ground-state substrate. The intercept/slope ratio gives $k_r\tau^0$. If [S] = [Q], and if a photophysical process is monitored, plots of equations (2) and (3) should provide independent determinations of the product-forming rate constant k_r. When the lifetime of an excited state is observed as a function of the concentration of S or Q, a linear relationship should be observed according to the equation:

$$\tau^0/\tau \; = \; 1 \; + \; k_q \; \tau^0\,[Q]$$

where τ^0 is the lifetime of the excited state in the absence of the quencher Q.

See also *self-quenching*.
1996, *68*, 2277