

KINETIC ANALYSES OF PHOTSENSITIZED REACTIONS INVOLVING ENERGY TRANSFER FROM TWO DISTINCT EXCITED STATES

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Summary

This paper presents general equations for treating sensitized reactions when two different excited states of the sensitizer both contribute to sensitization. Specific equations are presented for common limiting conditions, including cases where the two excited states are and are not interconvertible.

1. Introduction

Electronic energy transfer can be exploited in several ways to obtain mechanistic information about photoreactions [1, 2]. Stern-Volmer quenching studies have been widely used to estimate excited state lifetimes. Sensitization studies allow measurements of intersystem crossing yields. A combination of selective quenching and sensitization experiments can often identify the multiplicity of the excited state responsible for a given photo-reaction. Quantitative sensitization studies [2] can also disclose excited state lifetimes, although they have not been used very often for this purpose. There are some situations where only sensitization experiments can provide the necessary information.

(1) Only a comparison of $k_t\tau$ values derived from sensitization studies with $k_q\tau$ values derived from quenching studies can tell whether the same excited states are involved [3, 4] and whether quenching is wholly due to energy transfer [4].

(2) Only sensitization studies can disclose excited state lifetimes of sensitizers which undergo no detectable emission or reaction [5, 6].

(3) Sensitization studies can detect excited states with lifetimes in the $1 \text{ ns} > \tau > 10 \text{ ps}$ range, *i.e.* too short for conventional flash spectroscopic identification and even, at the shorter end, too short for significant quenching [3, 7].

(4) Sensitization studies can expose the presence of two independent excited states when either or both are subject to constraints (2) or (3) [7, 8].

This paper is devoted to situation (4). Interest in bichromophoric compounds has mushroomed recently. It is obvious that in such compounds excitation may be spread over both chromophores. At the same time, recognition has grown that single compounds may exist in different conformations which upon excitation become kinetically distinct excited states [7 - 9].

2. Basic equations

The following equation describes the well-known linear double reciprocal relation between sensitized quantum yields and acceptor concentration [A] when only one excited state of the sensitizer D is involved:

$$\Phi_{\text{sens}}^{-1} = \phi_{(D^*)}^{-1} \alpha^{-1} \left(1 + \frac{1}{k_t [A] \tau_{D^*}} \right) \quad (1)$$

where $\phi_{(D^*)}$ is the probability that light absorption yields the requisite donor excited state (ϕ_{ISC} in triplet-sensitized reactions), α is the efficiency with which the acceptor excited state undergoes the sensitized reaction being monitored, k_t is the bimolecular rate constant for energy transfer from D^* to the ground state of A and τ_{D^*} is the kinetic lifetime of the donor excited state [2]. It must be remembered that if the sensitized reaction is reversible, or if the product is also a quencher, eqn. (1) must be corrected for conversion as described in ref. 2. The intercept of a plot of Φ_{sens}^{-1} vs. $[A]^{-1}$ is $\phi_{D^*}^{-1} \alpha^{-1}$; if either is known, the other is thereby measured [10]. The ratio of intercept to slope equals $k_t \tau_{D^*}$; as usual, if k_t is known or diffusion controlled, τ_{D^*} is thereby measured.

Let us now consider a compound (or mixture of two compounds) that absorbs light to yield two distinct but interconverting excited states L^* and S^* (the L and S arbitrarily but conveniently distinguish the longer and shorter lived excited states, as determined by the values of $k_{d(L)}$ and $k_{d(S)}$, the pseudo first order rate constants for irreversible decay of each state by all chemical and physical processes available to it). Scheme 1 indicates all the relevant processes, rate constants and probabilities.

Steady state analysis of $[A^*]$, $[L^*]$ and $[S^*]$ produces

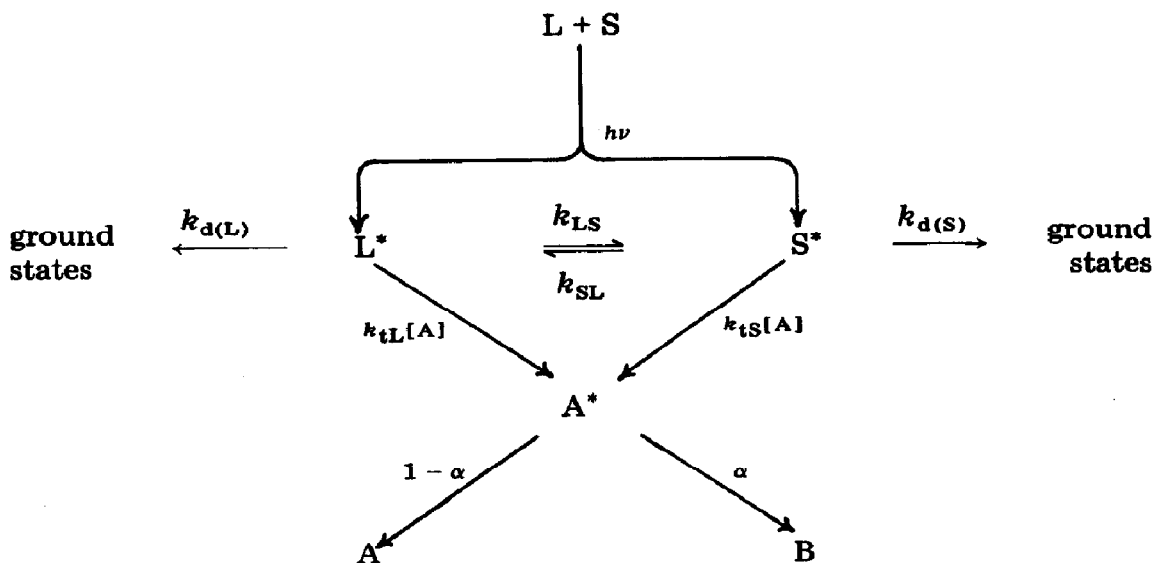
$$\alpha \Phi_B^{-1} = \frac{(1 + K_S A)(1 + K_L A) - \phi_{SL} \phi_{LS}}{K_S A \{F_S(1 + K_L A) + F_L \phi_{LS}\} + K_L A \{F_L(1 + K_S A) + F_S \phi_{SL}\}} \quad (2)$$

where

$$\phi_{LS} = k_{LS}(k_{LS} + k_{d(L)})^{-1} = k_{LS} \tau_L \quad (3a)$$

$$\phi_{SL} = k_{SL}(k_{SL} + k_{d(S)})^{-1} = k_{SL} \tau_S \quad (3b)$$

$$K_S = k_{tS} \tau_S \quad K_L = k_{tL} \tau_L \quad (3c)$$



Scheme 1.

$$\alpha\Phi_B^{-1} = \frac{(1 + \phi'_{SL} + K'_S A)(1 + \phi'_{LS} + K'_L A) - \phi'_{SL}\phi'_{LS}}{K'_S A \{F_S(1 + \phi'_{LS} + K'_L A) + F_L \phi'_{LS}\} + K'_L A \{F_L(1 + \phi'_{SL} + K'_S A) + F'_S \phi_{SL}\}} \quad (2')$$

where

$$\phi'_{LS} = k_{LS}/k_{d(L)} = k_{LS}\tau'_L \quad (3a')$$

$$\phi'_{SL} = k_{SL}/k_{d(S)} = k_{SL}\tau'_S \quad (3b')$$

$$K'_S = k_{tS}/k_{d(S)} \quad K'_L = k_{tL}/k_{d(L)} \quad (3c')$$

In these equations α has the same meaning as in eqn. (1) and A stands for the concentration of acceptor. The meanings of F_L and F_S vary as indicated in Table 1. The differences between eqns. (2) and (2') involve the definitions of τ_S and τ_L , as indicated in eqns. (3) and (3'); one or the other form is more easily manipulated under different boundary conditions. Unless specifically indicated, τ values will be defined as in eqns. (3).

The numerators and denominators of eqns. (2) and (2') can both be divided by A^2 [11] since $[A]$ is never zero in a sensitization experiment. After regrouping, eqns. (2) and (2') reduce to

$$\alpha\Phi_B^{-1} = \frac{K_S K_L + (K_S + K_L)x + (1 - \phi_{LS}\phi_{SL})x^2}{fK_S K_L + \{(F_S + F_L \phi_{LS})K_S + (F_L + F_S \phi_{SL})K_L\}x} \quad (4)$$

$$\alpha\Phi_B^{-1} = \frac{K'_S K'_L + \{K'_S(1 + \phi'_{LS}) + K'_L(1 + \phi'_{SL})\}x + (1 + \phi'_{LS} + \phi'_{SL})x^2}{fK_S K_L + \{(F_S + f\phi'_{LS})K'_S + (F_L + f\phi'_{SL})K'_L\}x} \quad (4')$$

where $x = [A]^{-1}$ and $f = F_L + F_S$. Both equations are of the basic form

TABLE 1

 F_L and F_S in different situations of L and S^a

Multiplicity	Different compounds	Bichromophoric	Different conformations ^b
Singlet, F_L	$\frac{\epsilon_L[L]}{\epsilon_L[L] + \epsilon_S[S]}$	$\frac{\epsilon_L}{\epsilon_L + \epsilon_S}$	$\frac{\epsilon_L\chi_L}{\epsilon_L\chi_L + \epsilon_S\chi_S} \approx \chi_L$
Singlet, F_S	$\frac{\epsilon_S[S]}{\epsilon_L[L] + \epsilon_S[S]}$	$\frac{\epsilon_S}{\epsilon_L + \epsilon_S}$	$\frac{\epsilon_S\chi_S}{\epsilon_L\chi_L + \epsilon_S\chi_S} \approx \chi_S$
Triplet, F_L	$\frac{\epsilon_L[L]\phi_{ISC}^L}{\epsilon_L[L] + \epsilon_S[S]}$	$\frac{\epsilon_L\phi_{ISC}^L}{\epsilon_L + \epsilon_S}$	$\frac{\epsilon_L\chi_L\phi_{ISC}^L}{\epsilon_L\chi_L + \epsilon_S\chi_S} \approx \chi_L\phi_{ISC}^L$
Triplet, F_S	$\frac{\epsilon_S[S]\phi_{ISC}^S}{\epsilon_L[L] + \epsilon_S[S]}$	$\frac{\epsilon_S\phi_{ISC}^S}{\epsilon_L + \epsilon_S}$	$\frac{\epsilon_S\chi_S\phi_{ISC}^S}{\epsilon_L\chi_L + \epsilon_S\chi_S} \approx \chi_S\phi_{ISC}^S$

^aThe ϵ s are ground state extinction coefficients; the χ s are ground state equilibrium fractions: $\chi_L + \chi_S = 1$.

^bThe approximate values are exact when $\epsilon_L = \epsilon_S$.

exemplified by

$$\alpha\Phi_B^{-1} = \frac{a + bx + cx^2}{fa + dx} \quad (5)$$

where the values of a , b , c and d are obvious from eqns. (4) and (4'). Equation (5) indicates a hyperbolic dependence of Φ_B^{-1} on $[A]^{-1}$, so that the usual double-reciprocal plot curves but attains an asymptotic linearity at low acceptor concentrations (high values of x). In this respect the sensitization equations resemble those for quenching when two excited states are involved [12 - 14]. As with curved quenching plots [15], it is best to analyze data by computer fit. Good precision requires far more data than for a linear plot, especially in the region of maximum curvature and at low enough $[A]$ values to establish the oblique asymptote.

The first derivative of eqn. (5) evaluated at $x = 0$ establishes values for the intercept and the initial slope:

$$\text{intercept}_0 = \frac{1}{f} \quad (6)$$

$$\frac{\text{intercept}_0}{\text{slope}_0} = \frac{fa}{fb - d} \quad (7)$$

Solving for the oblique asymptote yields the following equations for the final slope and the intercept of the asymptote extrapolated to $x = 0$:

$$\text{intercept}_r = \frac{bd - fac}{d^2} \quad (8)$$

$$\frac{\text{intercept}_f}{\text{slope}_f} = \frac{bd - fac}{cd} \quad (9)$$

Equations (4) and (4') contain seven independent parameters of mechanistic interest: α , F_L , F_S , $k_{tS}\tau_S$, $k_{tL}\tau_L$, $k_{LS}\tau_L$ and $k_{SL}\tau_S$. The factor α relates only to the behavior of the excited acceptor and therefore appears on the left-hand side of the equations. It would be silly to do studies with two sensitizer excited states unless the value of α were already known.

The other six parameters all relate to the sensitizer. The actual intercept at $x = 0$ *always* equals $(F_L + F_S)^{-1}$ no matter what boundary conditions simplify a , b , c and d . The F values are composed of two ground state parameters (extinction coefficients and concentrations) which usually can be measured independently and, for triplet sensitization, intersystem crossing yields. The $k_t\tau$ terms are what usually emerge from intercept/slope ratios.

The ϕ_{LS} and ϕ_{SL} terms indicate how efficiently interconversion of the two excited states competes with irreversible decay; their values can vary from 0 to 1 (in eqn. (4)) or from 0 to ∞ (in eqn. (4')). Each extreme defines a boundary condition which represents a common mechanism. In general, only four independent parameters can be evaluated from plots which follow eqn. (5). Therefore, some of the six independent parameters on the right-hand side of eqns. (4) and (4') must be evaluated by experiments other than sensitization.

If often happens that $k_{tS} = k_{tL}$, *i.e.* when both energy transfer processes are diffusion controlled. Replacement of k_{tS} and k_{tL} with a single k_t value does not simplify eqns. (4) and (4') significantly but does simplify some equations coming later.

3. General case

The most complicated scheme assumes that all interconversions and decay processes are competitive. The parameters in eqns. (4) and (4') are then fitted to eqns. (7) - (9) as follows:

$$\frac{\text{intercept}_0}{\text{slope}_0} = \frac{fK_S K_L}{F_S K_L (1 - \phi_{SL}) + F_L K_S (1 - \phi_{LS})} \quad (10)$$

$$\frac{\text{intercept}_0}{\text{slope}_0} = \frac{fK'_S K'_L}{F_S K'_L + F_L K'_S} \quad (10')$$

$$\text{intercept}_f = \frac{(F_L + F_S \phi_{SL}) K_L^2 + (F_S + F_L \phi_{LS}) K_S^2 + (F_L \phi_{LS} + f \phi_{LS} \phi_{SL}) K_L K_S}{\{(F_L + F_S \phi_{SL}) K_L + (F_S + F_L \phi_{LS}) K_S\}^2} \quad (11)$$

$$\text{intercept}_f =$$

$$\frac{(F_L + f \phi'_{SL})(1 + \phi'_{SL}) K_L'^2 + (F_S + f \phi'_{LS})(1 + \phi'_{LS}) K_S'^2 + \{(F_L + f \phi'_{SL}) \phi'_{SL} + (F_S + f \phi'_{LS}) \phi'_{LS}\} K'_L K'_S}{\{(F_S + f \phi'_{LS}) K'_S + (F_L + f \phi'_{SL}) K'_L\}^2} \quad (11')$$

$$\frac{\text{intercept}_t}{\text{slope}_t} = \frac{(F_L + F_S \phi_{SL})K_L^2 + (F_S + F_L \phi_{LS})K_S^2 + (F_L \phi_{LS} + f \phi_{LS} \phi_{SL})K_L K_S}{(1 - \phi_{SL} \phi_{LS})\{(F_L + F_S \phi_{SL})K_L + (F_S + F_L \phi_{LS})K_S\}} \quad (12)$$

$$\frac{\text{intercept}_t}{\text{slope}_t} = \frac{(F_L + f \phi'_{SL})(1 + \phi'_{SL})K_L'^2 + (F_S + f \phi'_{LS})(1 + \phi'_{LS})K_S'^2 + \{(F_L + f \phi'_{SL})\phi'_{SL} + (F_S + f \phi'_{LS})\phi'_{LS}\}K_L' K_S'}{(1 + \phi'_{LS} + \phi'_{SL})\{(F_S + f \phi'_{LS})K_S' + (F_L + f \phi'_{SL})K_L'\}} \quad (12')$$

These equations are not as complicated as they appear. For example, the coefficient of K_L^2 in the numerators of eqns. (11) and (12) is simply the total probability of forming L^* -- both from ground state L and from S^* . Depending on the F values and the extent of excited state interconversion, the initial and final slopes can be determined primarily by K_S and K_L respectively or by mixtures of the two.

Although the $1 - \phi_{SL} \phi_{LS}$ term in the denominator of eqn. (12) approaches zero as the extent of interconversion increases, the K_L and K_S terms also decrease so that the slope does not approach infinity. In fact, as the equivalent eqn. (12') shows, with the K s independent of the ϕ s the slope decreases as the extent of interconversion increases. This fact will be made more obvious by the examples given later.

As has been pointed out previously, plots according to any equation like eqn. (5) can curve up or down or be linear [12 - 14]. The second derivative of eqn. (5) yields the following expression for the curvature:

$$\text{curvature} = \frac{2a(d^2 + f^2ac - fbd)}{(fa + dx)^3} \quad (13)$$

A linear plot results whenever $d^2 + f^2ac = fbd$, as well as in the trivial case when there is no energy transfer from one or the other excited state ($a = 0$). Incorporation of the coefficients in eqn. (4) results in

$$\frac{(F'_S - f)K_S^2}{F'_L} + \frac{(F'_L - f)K_L^2}{F'_S} + \frac{(2F'_L F'_S - fF'_L - fF'_S)K_L K_S}{F'_L F'_S} + \frac{f^2(1 - \phi_{LS} \phi_{SL})K_L K_S}{F'_S F'_S} \begin{matrix} \geq \\ < \end{matrix} 0 \quad (14)$$

$$F'_S = F_S + F_L \phi_{LS} \quad (15a)$$

$$F'_L = F_L + F_S \phi_{SL} \quad (15b)$$

The first three terms in expression (14) must be negative (or zero) since $F'_L \leq f \geq F'_S$; the fourth term is positive (or zero), since $\phi_{LS} \leq 1 \geq \phi_{SL}$. Therefore the following expression describes the conditions for curvature:

$$\left| \frac{(F'_S - f)K_S^2}{F'_L} + \frac{(F'_L - f)K_L^2}{F'_S} + \frac{(2F'_S F'_L - fF'_L - fF'_S)K_L K_S}{F'_L F'_S} \right| \begin{matrix} \geq \\ < \end{matrix} \frac{f^2(1 - \phi_{LS} \phi_{SL})K_L K_S}{F'_L F'_S} \quad (16)$$

A linear plot results if the two sides of expression (16) are equal. The plot is concave downward if the left-hand side is larger than the right-hand side; the plot is concave upward if the opposite inequality obtains.

4. Special cases

4.1. Case 1: no interconversion of states ($k_{SL}\tau_S = k_{LS}\tau_L = 0$)

Under these conditions $1/\tau = k_d$ and eqn. (2) collapses to

$$\alpha\Phi^{-1} = \frac{(1 + k_{tS}\tau_S A)(1 + k_{tL}\tau_L A)}{F_S k_{tS}\tau_S A(1 + k_{tL}\tau_L A) + F_L k_{tL}\tau_L A(1 + k_{tS}\tau_S A)} \quad (17)$$

Equations (4) and (4') collapse to

$$\alpha\Phi^{-1} = \frac{K_S K_L + (K_S + K_L)x + x^2}{fK_S K_L + (F_S K_S + F_L K_L)x} \quad (18)$$

where

$$\frac{\text{intercept}_0}{\text{slope}_0} = \frac{fK_S K_L}{F_L K_S + F_S K_L} = \frac{fk_{tS}\tau_S}{F_S + F_L \kappa} \quad (19)$$

$$\text{intercept}_f = \frac{F_S K_S^2 + F_L K_L^2}{(F_S K_S + F_L K_L)^2} = \frac{F_L^{-1}(1 + \kappa^2 F_S)}{1 + 2\kappa F_S/F_L + \kappa^2 F_S^2/F_L^2} \quad (20)$$

$$\frac{\text{intercept}_f}{\text{slope}_f} = \frac{F_S K_S^2 + F_L K_L^2}{F_S K_S + F_L K_L} = k_{tL}\tau_L \left(\frac{F_L + \kappa^2 F_S}{F_L + \kappa F_S} \right) \quad (21)$$

$$\kappa = k_{tS}\tau_S/k_{tL}\tau_L \quad (22)$$

This set of boundary conditions has already been reported twice in the literature, for benzoylcyclohexanes [9] and benzoylpiperidines [8], although a curved sensitization plot was reported for the latter only.

Equations (19) - (21) are factored to emphasize what happens when $k_{tS}\tau_S \ll k_{tL}\tau_L$ (i.e. $\kappa \approx 0$) and $F_S \approx F_L$:

$$\text{intercept}_0/\text{slope}_0 \approx k_{tS}\tau_S(1 + F_L/F_S) \quad (23)$$

$$\text{intercept}_f \approx F_L^{-1} \quad (24)$$

$$\text{intercept}_f/\text{slope}_f \approx k_{tL}\tau_L \quad (25)$$

Although the final intercept and slope approach is determined only by F_L and $k_{tL}\tau_L$, the initial slope is not determined simply by $k_{tS}\tau_S$ and F_S but is affected by the value of F_L .

If it is known from independent experiments that L* and S* do not or cannot interconvert, analysis of data plotted according to eqn. (18) affords all the parameters of mechanistic interest.

4.2. Case 2: complete equilibration of states

Equation (4) collapses to $1/f$ when $k_{LS}\tau_L$ and $k_{SL}\tau_S$ are set exactly equal to unity, so eqn. (4') must be used. However, inspection of eqn. (4) shows that the x^2 term disappears as equilibrium is approached, reflecting the linear plot actually obtained. The new boundary conditions are $k_{LS}\tau_L'k_{SL}\tau_S' \gg 1$; there is only one actual lifetime τ_e .

Under these conditions, eqn. (4') simplifies to

$$\alpha\Phi_B^{-1} = \frac{K'_S K'_L + (K'_S + K'_L)x + (\phi'_{SL} + \phi'_{LS})x^2}{fK'_S K'_L + f(K'_S + K'_L)x} \quad (26)$$

Because of the boundary conditions chosen $d = fb$, so that

$$\alpha\Phi_B^{-1} = \frac{a + bx + cx^2}{fa + fbx} = \frac{1}{f} \left(1 + \frac{cx^2}{a + bx} \right) \quad (27)$$

The intercept remains $1/f$ but the initial slope is zero! This anomaly arises because the boundary condition implies $k_d = 0$ for both states. The actual plot is described by

$$\text{intercept} = \frac{1}{f} \left\{ 1 - \frac{\gamma^2}{k_{tS}k_{tL}(k_{SL} + k_{LS})\tau_e} \right\} \approx \frac{1}{f} \quad (28)$$

$$\gamma = \chi_S k_{tS} + \chi_L k_{tL} \quad (29)$$

$$\chi_S + \chi_L = 1 = \frac{k_{LS}}{k_{SL} + k_{LS}} + \frac{k_{SL}}{k_{SL} + k_{LS}} \quad (30)$$

$$1/\tau_e = \chi_S k_{d(S)} + \chi_L k_{d(L)} \quad (31)$$

$$\frac{\text{intercept}_t}{\text{slope}_t} = \gamma\tau_e - \frac{k_{tS}k_{tL}}{(k_{SL} + k_{LS})\gamma} \approx \gamma\tau_e \quad (32)$$

The plot deviates only slightly from being linear throughout since the second term in eqn. (28) is extremely small.

Note that when $k_{tS} = k_{tL} = k_t$, $\gamma = k_t$. Equations (28) and (32) indicate curvature in the plot when $k_t \geq (k_{SL} + k_{LS})$. This corresponds to interference by acceptor in the equilibrium, a phenomenon which has already been shown to cause curvature in Stern-Volmer quenching plots [16]. However, because of the boundary conditions chosen, a sensitization plot has already reached within experimental error of $\Phi_B = f\alpha$ by the time enough acceptor is present to upset equilibration.

It is important to note that a linear sensitization plot is no more indicative of a single excited state donor than is a linear quenching plot [12 - 14]. With luck, a combination of quenching and sensitization studies can distinguish three situations: one donor, two equilibrated donors and two partially equilibrated donors in which the curvature coincidentally equals zero. This differentiation is possible only if the two donor states undergo different quenchable reactions.

4.3. Case 3: interconversion of states is irreversible in one direction

$$1/\tau_S = k_{d(S)} \quad 1/\tau_L = k_{d(L)} + k_{LS} \quad k_{SL} = 0$$

One clear-cut example has appeared involving rotation of an unreactive excited conformation into one which reacts far faster than it can rotate back to an unreactive form [7]:

$$\alpha\Phi_B^{-1} = \frac{K_S K_L + (K_S + K_L)x + x^2}{fK_S K_L + (F'_S K_S + F_L K_L)x} \quad (33)$$

$$\frac{\text{intercept}_0}{\text{slope}_0} = \frac{fK_S K_L}{F_S K_L + F_L F_S (1 - \phi_{LS})} = \frac{fK_S}{F_S + F_L \kappa (1 - \phi_{LS})} \quad (34)$$

$$\text{intercept}_t = \frac{F_L K_L^2 + F'_S K_S^2 + F_L \phi_{LS} K_S K_L}{F_L^2 K_L^2 + F_S'^2 K_S^2 + 2F_L F'_S K_S K_L} = F_L^{-1} \left\{ \frac{1 + F'_S \kappa^2 / F_L + \phi_{LS} \kappa}{1 + (F'_S \kappa)^2 / F_L^2 + 2F'_S \kappa / F_L} \right\} \quad (35)$$

$$\frac{\text{intercept}_t}{\text{slope}_t} = \frac{F_L K_L^2 + F'_S K_S^2 + F_L \phi_{LS} K_S K_L}{F_L K_L + F'_S K_S} = \frac{K_L + K_S (\phi_{LS} + F'_S K / F_L)}{1 + F'_S \kappa / F_L} \quad (36)$$

$$\frac{\text{intercept}_t}{\text{slope}_t} \approx k_{tL} \tau_L + \phi_{LS} k_{tS} \tau_S \quad (37)$$

Again, the equations are factored to show that eqns. (34) and (35) approach eqns. (23) and (24) respectively as κ approaches zero, while eqn. (36) approaches eqn. (37).

It is equally possible to derive analogous equations for the case where $k_{LS} = 0$. Since the two states have been defined arbitrarily, this exercise is unnecessary.

4.4. Case 4: one state only converts into the other, which only decays

$$1/\tau_S = k_{d(S)} \quad 1/\tau_L = k_{LS} \quad k_{SL} = 0$$

This case is a special example of case 3, so eqns. (34) - (36) collapse to

$$\frac{\text{intercept}_0}{\text{slope}_0} = \frac{fk_{tS} \tau_S}{F_S} \quad (38)$$

$$\text{intercept}_t = \frac{F_L K_L^2 + F_L K_L K_S + fK_S^2}{F_L^2 K_L^2 + 2fF_L K_L K_S + f^2 K_S^2} = F_L^{-1} \left(\frac{1 + \kappa + f\kappa^2 / F_L}{1 + 2f\kappa / F_L + f^2 \kappa^2 / F_L^2} \right) \quad (39)$$

$$\frac{\text{intercept}_t}{\text{slope}_t} = \frac{F_L K_L^2 + fK_S^2 + F_L K_L K_S}{F_L K_L + fK_S} = \frac{k_{tL} \tau_L + k_{tS} \tau_S (1 + f\kappa / F_L)}{1 + f\kappa / F_L} \quad (40)$$

5. Examples

Figure 1 displays four examples of case 1 (no interconversion of states) with $F_S = F_L = 0.5$ ($f = 1$).

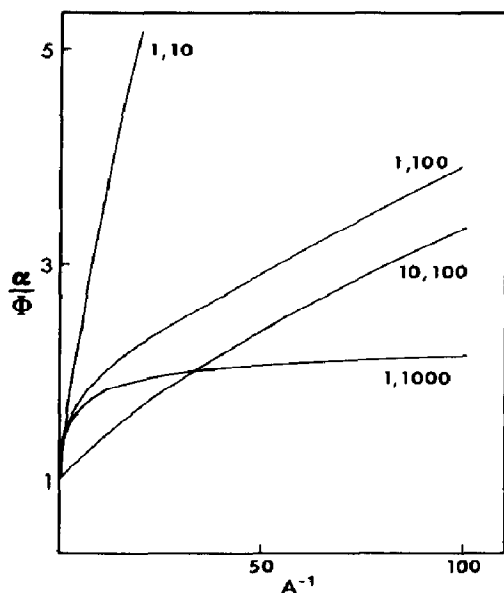


Fig. 1. Representative sensitization plots for two non-interconverting excited states with $F_S = F_L = 0.5$. The numbers on each curve indicate the values of K_S and K_L respectively.

It is noteworthy that, of the examples shown, that with the biggest spread of K values ($K_S = 1 \text{ M}^{-1}$, $K_L = 1000 \text{ M}^{-1}$) is the farthest from having reached its oblique asymptote. The $x = 50$ and $x = 100$ points determine a line with intercept 1.94 and intercept/slope ratio of only 822 M^{-1} , whereas the true asymptote intercepts at 2.0 and has an intercept/slope value of 999. In the (1, 100) case, the same two concentration points determine a line with intercept 1.90 and intercept/slope ratio of 94 M^{-1} , in comparison with the asymptotic values of 1.96 and 99 M^{-1} ; in the (1, 10) case, the same two points (not shown in the Fig. 1) yield apparent values of 1.64 and 9.0 M^{-1} compared with the true values of 1.67 and 9.2 M^{-1} . The (10, 100) plot has the same shape as the (1, 10) plot except for a ten-fold stretching of the ordinate; its true asymptote has intercept 1.67 and intercept/slope ratio 91.8 M^{-1} ; the $x = 50$ and $x = 100$ points lie on a line with intercept 1.42 and intercept/slope ratio 72. The higher the K value, the lower are the values of $[A]$ required to determine the final slope accurately.

Figures 2 and 3 illustrate how varying amounts of state interconversion alter the plots. In both cases, $F_S = \frac{2}{3}$, $F_L = \frac{1}{3}$, $K'_S = 1 \text{ M}^{-1}$ and $K'_L = 300 \text{ M}^{-1}$. In Fig. 2 either ϕ'_{LS} or ϕ'_{SL} is zero. The middle curve exemplifies both ϕ'_{LS} and ϕ'_{SL} being zero; its asymptotic intercept and intercept/slope ratio are 2.96 and 2.98 M^{-1} respectively, and its initial intercept/slope ratio is 1.5 M^{-1} .

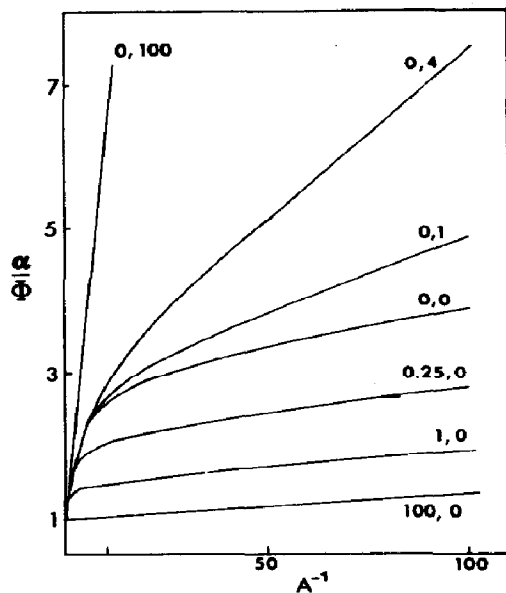


Fig. 2. Representative sensitization plots when interconversion between two excited states is one way with $F_S = 2/3$, $F_L = 1/3$, $K'_S = 1$ and $K'_L = 300$. The numbers on each curve indicate the values of ϕ'_{SL} and ϕ'_{LS} respectively.

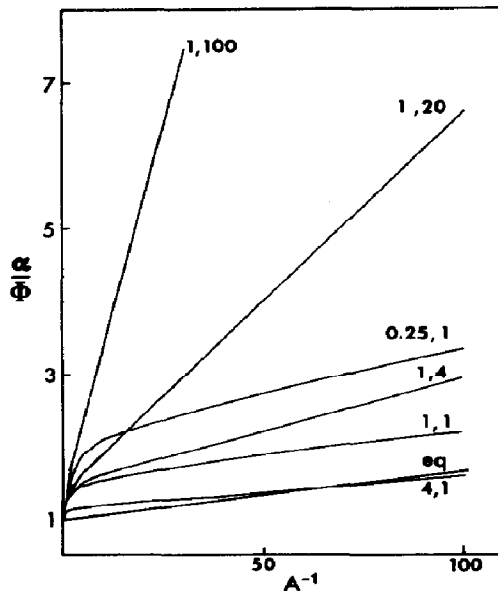


Fig. 3. Representative sensitization plots for two interconverting excited states as the extent of interconversion varies: $F_S = 2/3$, $F_L = 1/3$, $K'_S = 1$ and $K'_L = 300$. The numbers on each curve indicate the values of ϕ'_{SL} and ϕ'_{LS} respectively. The curve marked "eq" represents equilibrium ($\phi_{SL} = \phi_{LS} = 100$).

Increasing ϕ'_{LS} increases the final slope and decreases the asymptotic intercept. The latter effect is gradual, the value still being 2.78 when $\phi'_{LS} = 4$ but only 1.25 when $\phi'_{LS} = 100$. The increase in the slope is closely but not exactly proportional to the decreasing τ_L ($= \tau'_L = k_d + k_{LS}$); the value of the intercept/slope ratio decreases from 298 to 148 to 58 to 2.5 M^{-1} as ϕ_{LS} rises from 0 to 100.

As ϕ'_{SL} rises, final slopes and intercepts both decrease gradually so that the value of the intercept/slope ratio remains constant at 300 M^{-1} . Rather remarkably, the initial intercept/slope ratio remains invariant at 2.5 M^{-1} as both ϕ'_{SL} and ϕ'_{LS} increase. Of course, if the main fate of S^* or L^* is irreversible conversion to the other, as in the two extreme curves, one observes a plot that does not deviate experimentally from linearity.

Figure 3 has the same F and K values as Fig. 2. The situation where ϕ'_{LS} and ϕ'_{SL} are both unity results in a curve with final intercept 1.49, intercept₀/slope₀ ratio 1.5 M^{-1} and intercept_f/slope_f ratio 200 M^{-1} . Further increasing both ϕ'_{LS} and ϕ'_{SL} lowers the intercept until the linear equilibrium plot results. Note that its slope is about double that of the ($\phi'_{LS} = 0$, $\phi'_{SL} = 100$) situation in Fig. 2.

Lowering ϕ'_{LS} changes the plot only slightly; the (1, 1) case in Fig. 3 lies only slightly above the (1, 0) curve in Fig. 2.

Increasing ϕ'_{LS} again raises the final slope substantially but not as drastically as when $\phi'_{SL} = 0$. Thus, at ($\phi'_{SL} = 1, \phi'_{LS} = 100$), intercept_f is 1.28 and $\text{intercept}_f/\text{slope}_f$ is 6.3 M^{-1} .

Figures 4 and 5 demonstrate how variations in F_S and F_L change sensitization plots. In both cases, $K'_S = 1 \text{ M}^{-1}$ and $K'_L = 300 \text{ M}^{-1}$; in Fig. 4, $\phi'_{SL} = \phi'_{LS} = 0$; in Fig. 5, $\phi'_{SL} = \phi'_{LS} = 1$. When $F_S = F_L = 0.50$, the $\text{intercept}_0/\text{slope}_0$ ratio is 2.0 M^{-1} , the intercept_f is 1.99 and the $\text{intercept}_f/\text{slope}_f$ ratio is 299 M^{-1} . Note that the oblique asymptote adequately defines the behavior of L^* but the initial slope provides a $k_t\tau$ value double the true value of K'_S . Unfortunately, the true value of K'_S is difficult to extract from the data. Equation (4') predicts an $\alpha\Phi^{-1}$ value of 1.20 at $[A]^{-1} = 0.5$ (2 M acceptor). If this one point is used to estimate the initial slope, a value of 2.5 M^{-1} results.

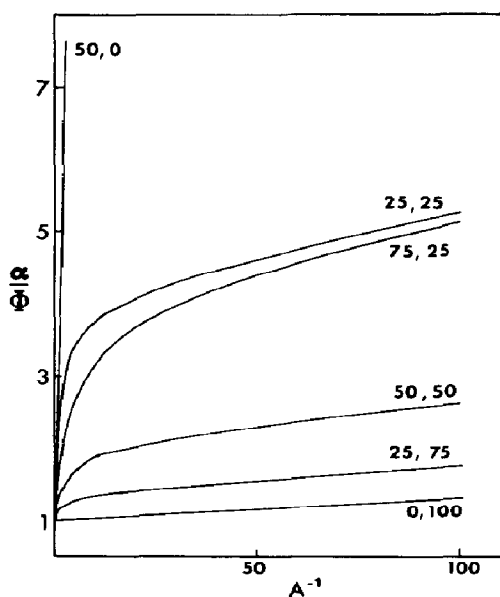


Fig. 4. Representative sensitization plots for two non-interconverting excited states as initial populations vary: $K'_S = 1, K'_L = 300$ and $\phi'_{SL} = \phi'_{LS} = 0$. The numbers on each curve indicate the percentage values of F_S and F_L respectively.

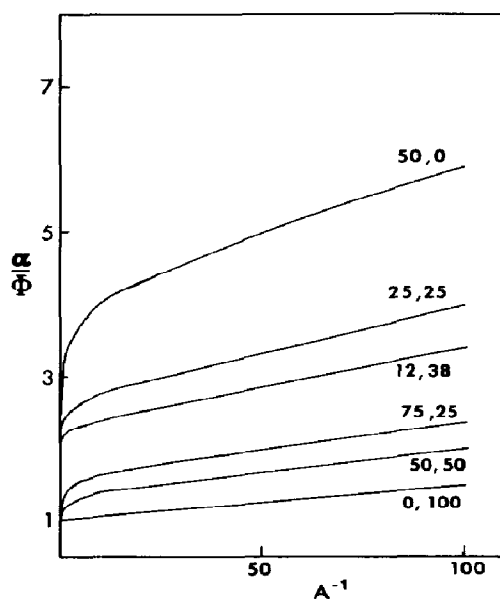


Fig. 5. Representative sensitization plots for two interconverting excited states as initial populations vary: $K'_S = 1, K'_L = 300$ and $\phi'_{SL} = \phi'_{LS} = 1$. The numbers on each curve indicate the percentage values of F_S and F_L respectively.

Keeping $f = 1$ but increasing the contribution of F_L lowers both the final slope and the intercept until a linear plot is obtained with the $\text{intercept}/\text{slope}$ ratio still equal to 300 M^{-1} when $F_S = 0$. As the contribution of F_S is increased, the final slope and intercept both rise so that their ratio remains constant. Again, when F_L becomes negligibly small a linear plot results. Cutting f by half while keeping the F_S/F_L ratio unchanged doubles all slopes and intercepts, such that values of $\text{intercept}/\text{slope}$ ratios are independent of f .

Figure 5 demonstrates the very different dependence on F values when there is state interconversion. The general trends are the same as in Fig. 4 except that distinct curvature is now apparent even when $F_L = 0$.

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