

## A KINETIC ANALYSIS OF THE ENERGY TRANSFER METHOD FOR MEASUREMENT OF INTERSYSTEM CROSSING YIELDS

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### Summary

A steady state kinetic analysis of the energy transfer between two molecules shows that measurement of the intersystem crossing yields via the relative emission yields of absorbance-matched solutions of a donor, an acceptor and a donor-acceptor mixture will yield the same results whether or not the energy transfer is reversible. The essential criterion for this to be true is that direct quenching to the ground state, as opposed to quenching by the energy transfer, must be unimportant in both directions. If this condition is not met, the behaviour of the system becomes very complex.

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### 1. Introduction

Intersystem crossing yields are fundamental quantities essential to the understanding of photochemical and photophysical pathways in molecules. In fluid solutions values have been measured for a number of organic molecules [1 - 4] and some transition metal complexes [5 - 8]. Sabbatini *et al.* [8] summarized and commented on the available methods, and opted for the energy transfer method for reasons of convenience.

This method has obvious appeal for several reasons. It is simple, requiring only a good fluorescence spectrometer. Most importantly, it gives the intersystem crossing yield under the same conditions as those of photochemistry and solution emission spectroscopy. The values obtained are therefore directly applicable to discussions of the pathways for photochemical and photophysical processes in solution. In contrast, the values obtained by some of the other methods are obtained from studies of low temperature glasses, or solids, and may not be very relevant in a photochemical context.

However, for the energy transfer method to succeed, a number of conditions must be met. Some are obvious, such as the need for thermal stability

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of the two species, the absence of thermal reaction between them, the absence of complex formation, the adherence to Beer's law, some overlap of the absorption spectra, so that absorbance-matched solutions can be prepared in a suitable solvent without solubility problems, and a well-characterized emission from each component in solution, sufficiently separated in wavelength that each can be measured in the presence of the other, even when a significant intensity difference exists between them.

For systems involving metal complexes, several pairs of species were studied [9], and the work demonstrated the usefulness of the method, which was elegant in its simplicity. The emission was measured from three absorbance-matched solutions: first the emission  $E_D^0$  of the donor (D) from a solution of D alone, second the emission  $E_A^0$  of the acceptor (A) from a solution of A alone and third of D and A emissions,  $E_D$  and  $E_A$  respectively, from a mixture of the first two solutions in a known fractional ratio  $\alpha_D:\alpha_A$ . Defining an experimental parameter  $R = (\alpha_D - E_D/E_D^0)/(E_A/E_A^0 - \alpha_A)$  which contains only observables, it was then shown that  $R = \eta_i^A/\eta_i^D\eta_{et}$ . Here  $\eta_i^A$  and  $\eta_i^D$  are the intersystem crossing yields in A and D respectively and  $\eta_{et}$  is the fractional efficiency of energy transfer in  $D^* + A$  collisions (see below). In the earlier work [9], arguments were presented to support  $\eta_{et} = 1$  for the systems studied. Hence a knowledge of either  $\eta_i^A$  or  $\eta_i^D$  enabled the other to be determined.

The values obtained [9] were in general in good agreement with those from other methods. However, for some systems the method was not so successful. Thus for the  $\text{Cr}(\text{phen})_3^{3+}-\text{Cr}(\text{CN})_6^{3-}$  system (phen  $\equiv$  1,10-phenanthroline), the quoted yield of 0.21 differs markedly from the near-unity value for the analogous  $\text{Cr}(\text{bpy})_3^{3+}$  complex (bpy  $\equiv$  2,2'-bipyridine) and is only about one-fifth the value recently measured [10]. Also, the  $\text{Cr}(\text{en})_3^{3+}-\text{Cr}(\text{CN})_6^{3-}$  system (en  $\equiv$  ethylenediamine) has been found to give  $R$  values extremely sensitive to the solution conditions [11, 12], despite the implication from the above expression for  $R$  that it should be constant for a given pair of complexes.

The purpose of this paper is therefore to expand in scope the kinetic theory of this method. In particular, we set out to explore the effects of reverse energy transfer and of forward and reverse energy transfer efficiencies of less than unity. For completeness and to establish the procedure for the more complex case, we begin with a steady state analysis of the basic scheme involving only forward energy transfer and quenching.

## 2. Theory

Let us consider the steady irradiation of a general solution consisting of a mixture of two absorbance-matched solutions of D and A, mixed in the ratio  $\alpha_D:\alpha_A$ . The kinetic scheme for the general case is shown in Fig. 1. This shows explicitly that quenching of  $D^*$  by A may lead either to  $D + A^*$  (with a rate constant  $k_{et}$ ) or to  $D + A$  (with a rate constant  $k_g^D$ ) and likewise for the reverse quenching processes.

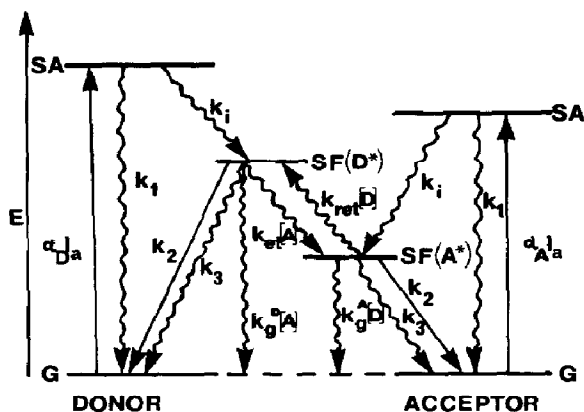


Fig. 1. Kinetic processes for the forward and reverse energy transfer between D and A molecules: G, ground state; SA, lowest spin-allowed excited state; SF, lowest spin-forbidden excited state. The spin-forbidden states are designated D\* and A\* in the text.

### 2.1. Case I: no quenching or energy transfer effects of the donor on the acceptor

In this case the processes corresponding to rate constants  $k_q^A$  and  $k_{ret}$  shown in Fig. 1 are considered to be negligible. Applying the steady state assumption to A\* and D\* gives

$$[D^*]_{ss} = \eta_i^D I_a \alpha_D (\Sigma k_D + k_q^D [A])^{-1} \quad (1)$$

$$[A^*]_{ss} = \frac{\eta_i^A I_a \alpha_A (\Sigma k_D + k_q^D [A]) + \eta_i^D I_a \alpha_D k_{et} [A]}{\Sigma k_A (\Sigma k_D + k_q^D [A])} \quad (2)$$

where  $k_q^D = k_{et} + k_g^D$ ,  $\Sigma k_D$  and  $\Sigma k_A$  are the reciprocal lifetimes of the emitting states D\* and A\* in the absence of quencher and  $I_a$  is the total rate of light absorption by the solution.  $I_a$  has been divided between D and A in the proportion  $\alpha_D : \alpha_A$  on the basis that Beer's law is obeyed. In eqn. (2), the first term in the numerator corresponds to direct excitation of A, the second to energy transfer from D\*.

Now, for three absorbance-matched solutions, (1) D only, (2) A only and (3) D:A in a ratio  $\alpha_D : \alpha_A$  (with  $\alpha_D + \alpha_A = 1$ ), the emission intensities will be given by

$$E_D^0 = J_D k_2^D [D^*]_{ss}^0 = J_D \frac{k_2^D I_a \eta_i^D}{\Sigma k_D} \quad (3)$$

for solution 1

$$E_A^0 = J_A k_2^A [A^*]_{ss}^0 = J_A \frac{k_2^A I_a \eta_i^A}{\Sigma k_A} \quad (4)$$

for solution 2 and

$$E_D = J_D \frac{k_2^D I_a \eta_i^D \alpha_D}{\Sigma k_D + k_q^D [A]} \quad (5)$$

$$E_A = J_A \frac{k_2^A I_a \{ \eta_i^A \alpha_A (\Sigma k_D + k_q^D [A]) + \eta_i^D \alpha_D k_{et} [A] \}}{\Sigma k_A (\Sigma k_D + k_q^D [A])} \quad (6)$$

for solution 3.

In these equations  $J_D$  and  $J_A$  are proportionality constants reflecting the experimental relationships between the signal and the quantum yield for the two emissions. Equations (3) and (4) follow from eqns. (1) and (2) with  $\alpha_D = 1$  and  $[A] = 0$  and with  $\alpha_A = 1$  and  $[D] = 0$  respectively.

In consequence

$$\frac{E_D}{E_D^0} = \frac{\alpha_D \Sigma k_D}{\Sigma k_D + k_q^D [A]} = \alpha_D (1 - \eta_q^D) \quad (7)$$

where  $\eta_q^D = k_q^D [A] / (\Sigma k_D + k_q^D [A])$ , the total efficiency of quenching of  $D^*$  by A.

Likewise

$$\begin{aligned} \frac{E_A}{E_A^0} &= \frac{\eta_i^A \alpha_A (\Sigma k_D + k_q^D [A]) + \eta_i^D \alpha_D k_{et} [A]}{\eta_i^A (\Sigma k_D + k_q^D [A])} \\ &= \alpha_A + \alpha_D \eta_{et}' \frac{\eta_i^D}{\eta_i^A} \end{aligned} \quad (8)$$

where  $\eta_{et}' = k_{et} [A] / (\Sigma k_D + k_q^D [A])$ , i.e. the efficiency of quenching by energy transfer from  $D^*$  to A. Therefore

$$\begin{aligned} R &= \frac{\alpha_D - E_D/E_D^0}{E_A/E_A^0 - \alpha_A} = \frac{\eta_q^D}{\eta_{et}'} \frac{\eta_i^A}{\eta_i^D} \\ &= \frac{\eta_i^A}{\eta_i^D} \frac{1}{\eta_{et}} \end{aligned} \quad (9)$$

where  $\eta_{et} = \eta_{et}' / \eta_q^D = k_{et} / (k_{et} + k_g^D)$ , the fractional efficiency of energy transfer in  $D^*$  quenching by A.

The result obtained in this way is the same as that previously given by Bolletta *et al.* [9], obtained somewhat differently.

## 2.2. Case II: reversible energy transfer and quenching

Now let us consider the full scheme of Fig. 1, which now includes  $k_{ret}$  and  $k_g^A$  for reverse energy transfer and quenching. With the same procedure

$$[D^*]_{ss} = \frac{(\Sigma k_A + k_g^A [D]) \eta_i^D \alpha_D I_a + k_{ret} [D] \eta_i^A \alpha_A I_a}{DEN} \quad (10)$$

$$[A^*]_{ss} = \frac{(\Sigma k_D + k_g^D [A]) \eta_i^A \alpha_A I_a + k_{et} [A] \eta_i^D \alpha_D I_a}{DEN} \quad (11)$$

where  $\text{DEN} = (\Sigma k_A + k_q^A[D])(\Sigma k_D + k_q^D[A]) - k_{et}k_{ret}[A][D]$ .

Hence, after some substitutions and rearrangements,

$$\frac{E_D}{E_D^0} = \frac{(1 - \eta_q^D)(\eta_i^D\alpha_D + \eta_{et}'\eta_i^D\alpha_D)}{(1 - \eta_{et}'\eta_{ret}')\eta_i^A} \quad (12)$$

and

$$\frac{E_A}{E_A^0} = \frac{(1 - \eta_q^A)(\eta_i^A\alpha_A + \eta_{ret}'\eta_i^A\alpha_A)}{(1 - \eta_{et}'\eta_{ret}')\eta_i^D} \quad (13)$$

This finally leads to

$$R = \frac{\eta_i^A}{\eta_i^D} \frac{\eta_i^A\eta_{ret}'\alpha_A(1 - \eta_q^D) + \eta_i^D\alpha_D(\eta_{et}'\eta_{ret}' - \eta_q^D)}{\eta_i^D\eta_{et}'\alpha_D(\eta_q^A - 1) + \eta_i^A\alpha_A(\eta_q^A - \eta_{et}'\eta_{ret}')} \quad (14)$$

### 3. Discussion

It is evident that in those systems where reverse energy transfer and quenching do not occur, case I, it is predicted that the experimental parameter  $R$  is a constant for a given system, independent of the concentrations of D and A in the solution or the proportion of solution mixing. For many systems studied this has been found to be true within experimental error. The range of  $\alpha_D$  over which this can be studied is quite limited, however, since as  $\alpha_D$  diverges from 0.5 the differences in the numerator and denominator of the expression for  $R$  become progressively smaller and more sensitive to experimental uncertainties.

In contrast with this simple situation, eqn. (14) implies for the general case a complex dependence of  $R$  on  $\alpha_D$  and the concentrations of D and A in the solution, via  $\eta_{et}'$ ,  $\eta_{ret}'$ ,  $\eta_q^A$  and  $\eta_q^D$ . Further analysis of this is complicated by the large number of variables. Nevertheless, at least one important result can be obtained.

Let us consider the special case where energy transfer is reversible, but efficient in the sense that  $k_g^A \ll k_{ret}$  and  $k_g^D \ll k_{et}$  so that  $\eta_{et} = 1$  and  $\eta_{ret} = 1$ . Then  $\eta_q^D = \eta_{et}'$ ,  $\eta_q^A = \eta_{ret}'$  and eqn. (14) reduces to  $R = \eta_i^A/\eta_i^D$ , as before for case I. In conclusion, therefore,  $R$  has the value  $\eta_i^A/\eta_i^D$  whether or not energy transfer is reversible; it is only necessary that quenching directly to the ground state is not an important process for transfer in either direction. Indeed the corollary of this result seems to be even more important; if it is observed for any system that  $R$  is *not* a constant, but varies with concentration of D or A or with  $\alpha_D$ , then, in the absence of static quenching or other effects not considered here, this is a clear indication of a non-unity value for either  $\eta_{et}$  or  $\eta_{ret}$ . In the earlier work [9] it was assumed that  $\eta_{et} = 1$  for the systems investigated. What is now revealed is that this was required by the observation that  $R$  is independent of  $\alpha_D$  and the concentrations of D and A in the solution.

Beyond this important result, the analysis of a completely general case is dependent on so many variables that here it is worth pursuing only so far as to obtain some sense of the extent and manner in which the  $R$  value may vary with changes in the concentrations of D and A and  $\alpha_D$ . Considering eqn. (14) to be of the form

$$R = \frac{\eta_i^A F_1 + F_2}{\eta_i^D F_3 + F_4}$$

it should be noted that  $F_1$  and  $F_4$  always lie in the range  $0 \rightarrow 1$ , while  $F_2$  and  $F_3$  always lie in the range  $0 \rightarrow -1$ . All are functions of  $\alpha_D$  and concentration (through the dependence of  $\eta_q^D$ ,  $\eta_q^A$ ,  $\eta_{ret}'$  and  $\eta_{et}'$  on  $[A]$  and  $[D]$ ) for a given set of state lifetimes, rate constants and intersystem crossing yields. As a result,  $R$  may be positive or negative, and since the denominator,  $F_3 + F_4$ , can change sign through 0,  $R$  can exhibit some dramatic changes in value for minor changes in  $\alpha_D$ . All these features have been observed in our calculations, and behaviour reminiscent of this is exhibited experimentally in the system  $\text{Cr(en)}_3^{3+}$ - $\text{Cr(CN)}_6^{3-}$  in a 1:1 molar ratio of dimethylformamide: water [11, 12]. The obvious complexities of the system, however, suggest that it would be difficult to pursue detailed experimental studies in this regime.

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