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Reversible Energy Transfer

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Analysis of the transient and steady-state kinetics of reversible energy transfer shows that while the interpretation of lifetime measurements is difficult unless the donor and acceptor lifetimes are appreciably different, quantum yield measurements are relatively easy to interpret.

Die Analyse der Kinetik der Übergangszustände und der stationären Zustände der reversiblen Energieübertragung zeigt, daß im Gegensatz zu einer schwierigen Interpretation der Messungen der Lebensdauer – es sei denn die Lebensdauer von Donor und Acceptor sind wesentlich voneinander verschieden – die Messungen der Quantumausbeute verhältnismäßig einfach zu interpretieren sind.

L'analyse de la cinétique de l'état transitoire et de l'état stationnaire du transfert réversible d'énergie montre que, si l'interprétation des mesures de durée de vie est difficile, à moins queles durées de vie du donneur et de l'accepteur soient très différentes, il est par contre relativement facile d'interpréter les mesures de rendement quantique.

Energy transfer has been extensively used to investigate the details of photochemical reactions [1]. The population or depopulation of specific excited electronic states of molecules can give valuable information about the role those states assume in the mechanism. It has been suggested that transfer from one triplet excited state molecule to another, for ground singlet state molecules, is diffusion controlled in fluid solution, provided the donor excited state lies at a higher energy than that of the acceptor.

Bäckström and Sandros [2] and Sandros [3] have described the theoretical and experimental results for systems in which energy transfer is reversible. They found that reverse energy transfer may have to be taken into account when the difference in energy of the donor and acceptor excited states is less than about 2000 cm^{-1}. In an extreme case, Sandros [3] observed back energy transfer from pyrene ($E_T = 16930\ \text{cm}^{-1}$) to the nominal donor, biacetyl ($E_T = 19700\ \text{cm}^{-1}$) even though it is endothermic by almost 3000 cm^{-1} and has a rate constant five orders of magnitude smaller than that for energy transfer from biacetyl to pyrene.

Nordin and Strong [4] have emphasized the importance of the relative donor and acceptor excited state lifetimes on reversible energy transfer. They analyzed the transient kinetics for various lifetimes and energy separations of the excited states in terms of a single donor lifetime, representing the best fit to the calculated decay curves.

The general effect of back energy transfer is to reduce the value of the apparent quenching constant. Nordin and Strong [4] even found negative values under

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certain conditions. As the quenching constant is an important parameter in the interpretation of energy transfer data, it is essential to understand the conditions under which back energy transfer becomes important as well as the effect it has on rate measurements.

In the following, both the transient and steady-state kinetics of such systems are examined to establish the conditions of lifetimes and energy transfer rate constants in which reversible transfer must be considered. In addition, the effect of reversible energy transfer on the evaluation of rate constants from transient and steady-state data in terms of the normal Stern-Volmer treatment is explored. These problems assume greater importance still when paramagnetic species are used as donors and acceptors, for then spin correlation rules imply that efficient energy transfer may occur from the fluorescent state of one molecule to the phosphorescent state of another as well as the reverse.

General Mechanism

To preserve an element of simplicity, the mechanism can be limited to four steps following excitation:

$$A \xrightarrow[\Phi]{h\nu} A^* \xrightarrow{k_1} A\,, \tag{1}$$

$$A^* + B \xrightarrow{k_{\mathrm{et}}} A + B^*\,, \tag{2}$$

$$B^* + A \xrightarrow{k_{\mathrm{ret}}} B + A^*\,, \tag{3}$$

$$B^* \xrightarrow{k_2} B\,. \tag{4}$$

Steps 1 and 4 include all unimolecular transformations which depopulate A^* and B^*. Thus k_1 and k_2 represent sums of rate constants, including the radiative rate constants k_r^A and k_r^B for the donor and acceptor, respectively. Normally A^* and B^* are the lowest triplet states for ground singlet state molecules, but may be other multiplicities for paramagnetic molecules. No bimolecular steps involving two excited state molecules have been included in this simple mechanism, but they could be put in without major change [3].

Transient Kinetics

The differential equations for the two species A^* and B^*, following a delta function excitation:

$$\frac{d[A^*]}{dt} = k_{\mathrm{ret}}[A]\,[B^*] - (k_1 + k_{\mathrm{et}}[B])\,[A^*] \tag{5}$$

$$\frac{d[B^*]}{dt} = k_{\mathrm{et}}[B]\,[A^*] - (k_2 + k_{\mathrm{ret}}[A])\,[B^*] \tag{6}$$

have the solutions:

$$\begin{aligned}[A^*] = \frac{[A^*]_0}{\lambda_1 - \lambda_2}\,\{&(\lambda_1 - k_2 - k_{\mathrm{ret}}[A])\exp(-\lambda_1 t)\\ &+ (k_2 + k_{\mathrm{ret}}[A] - \lambda_2)\exp(-\lambda_2 t)\}\,,\end{aligned} \tag{7}$$

$$[B^*] = \frac{k_{\mathrm{et}}[A^*]_0\,[B]}{\lambda_1 - \lambda_2}\,\{\exp(-\lambda_2 t) - \exp(-\lambda_1 t)\} \tag{8}$$

in which λ_1 and λ_2 are the roots of:

$$(\lambda - k_2 - k_{\mathrm{ret}}[A])(\lambda - k_1 - k_{\mathrm{et}}[B]) = k_{\mathrm{et}}[B]\, k_{\mathrm{ret}}[A]\,. \tag{9}$$

They have therefore the values given by:

$$\begin{aligned} 2\lambda &= (k_1 + k_{\mathrm{et}}[B] + k_2 + k_{\mathrm{ret}}[A]) \\ &\quad \pm \{(k_1 + k_{\mathrm{et}}[B] - k_2 - k_{\mathrm{ret}}[A])^2 + 4k_{\mathrm{et}}[B]\, k_{\mathrm{ret}}[A]\}^{1/2}\,. \end{aligned} \tag{10}$$

It will be assumed in the treatment that λ_1 is the larger of the two roots. From Eq. (9), a general relationship may be found

$$\lambda_1 + \lambda_2 = k_1 + k_{\mathrm{et}}[B] + k_2 + k_{\mathrm{ret}}[A] \tag{10}$$

which connects the two lifetimes, $1/\lambda_1$ and $1/\lambda_2$, with the rate constants of the mechanism.

The concentration of the donor excited state, according to Eq. (7), decreases rapidly at first with a lifetime $1/\lambda_1$, then more slowly, eventually with lifetime $1/\lambda_2$. However, only when λ_1 and λ_2 have values of a similar order of magnitude would both parts of the decay be observable; otherwise either the first or the second term dominates the decay. On the other hand, if λ_1 and λ_2 have comparable values, the experimentally measured decay would be difficult to resolve into its two components.

At first, the concentration of the acceptor excited state increases with time, reaches a maximum value at

$$t_{\mathrm{max}} = \frac{\ln(\lambda_1/\lambda_2)}{\lambda_1 - \lambda_2}$$

then decays finally with a lifetime $1/\lambda_2$. Both λ_1 and λ_2 should be measurable from the growth and decay of the acceptor excited state, provided time resolution is adequate.

When both λ_1 and λ_2 can be measured, for example, from the acceptor, together with k_1 and k_2 (which are the reciprocals of the lifetimes of donor and acceptor excited states in the absence of acceptor and donor, respectively), the rate constants for forward and back energy transfer can be evaluated from the following equations, derived from Eqs. (9) and (10):

$$k_{\mathrm{et}}[B] = \frac{(\lambda_1 - k_1)(k_1 - \lambda_2)}{(k_1 - k_2)}\,, \tag{11}$$

$$k_{\mathrm{ret}}[A] = \frac{(\lambda_1 - k_2)(\lambda_2 - k_2)}{(k_1 - k_2)}\,. \tag{12}$$

In the case that $k_1 \gg k_2$ and also $k_1 \gg k_{\mathrm{ret}}[A]$, Eq. (9) reduces to

$$\lambda_1 = k_1 + k_{\mathrm{et}}[B]\,, \tag{13}$$

$$\lambda_2 = k_2 + k_{\mathrm{ret}}[A]\,(k_1/\lambda_1) \tag{14}$$

and the second term of Eq. (7) becomes negligible. Thus, even when there is effective back energy transfer, provided that the donor excited state has a much shorter lifetime than the acceptor excited state, the former decays with a single lifetime $1/\lambda_1$, independent of $[A]$ and thus independent of whether or not back energy transfer in fact occurs. This is so because, while the second term of Eq. (7) may have an appreciable integrated value, its contribution to $[A^*]$ will be orders of magnitude smaller than that of the first term at any one time. The longer lifetime observed for $[B^*]$ after the maximum will, however, be a function of both acceptor and donor concentrations.

For the opposite situation, that the donor excited state is longer lived than the acceptor ($k_2 \gg k_1$ and $k_2 \gg k_{\mathrm{et}}[B]$), Eq. (9) becomes:

$$\lambda_1 = k_2 + k_{\mathrm{ret}}[A]\,, \tag{15}$$

$$\lambda_2 = k_1 + k_{\mathrm{et}}[B]\,(k_2/\lambda_1)\,. \tag{16}$$

Now it is the first term of Eq. (7) that becomes negligible. Except for the initial "grow-in" of B^* with lifetime $1/\lambda_1$, both donor and acceptor excited states decay with the same lifetime, $1/\lambda_2$. This latter lifetime will depend on both donor and acceptor concentrations. Hence a simple Stern-Volmer plot of λ_2 against $[B]$ cannot give the correct energy transfer rate constant, k_{et}, unless it is corrected by the ratio k_2/λ_1.

The situation is more complicated when the lifetimes of donor and acceptor excited states are similar, especially if the forward and reverse energy transfer steps also have similar rates. The behavior of $[A^*]$ and of $[B^*]$ with time, calculated from Eqs. (7) and (8) with $k_1 = 3k_2$, $k_{\mathrm{ret}}[A] = k_{\mathrm{et}}[B] = 1.5k_2$, is shown in Fig. 1. It is evident that the evaluation of λ_1 and λ_2 from the decay of $[A^*]$ would be difficult unless the data were extremely precise and covered a wide range of $[A^*]$. With limited data, an exponential could be fitted to the decay curve, as shown by the dotted line in Fig. 1, with a lifetime between $1/\lambda_1$ and $1/\lambda_2$. This apparent lifetime is, however, virtually useless. But if $[B^*]$ can be followed, the curve should be resolvable into the two contributions, and both λ_1 and λ_2 can be determined.

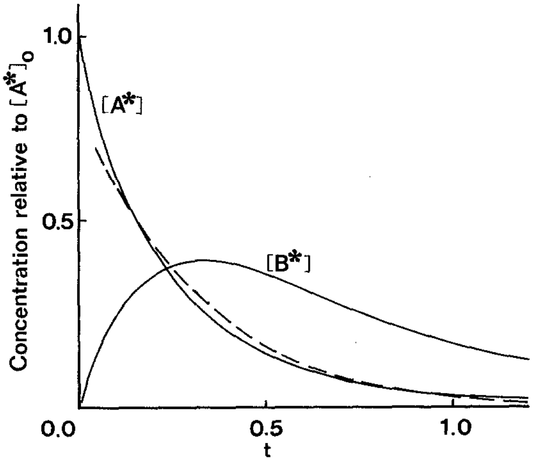

Fig. 1. Decay curves for $[A^*]$ and $[B^*]$ from Eqs. (7) and (8), with the parameters: $k_1 = 3k_2$, $k_{\mathrm{ret}}[A] = k_{\mathrm{et}}[B] = 1.5k_2$. The dotted line shows a reasonable fit of a single exponential to the curve for $[A^*]$

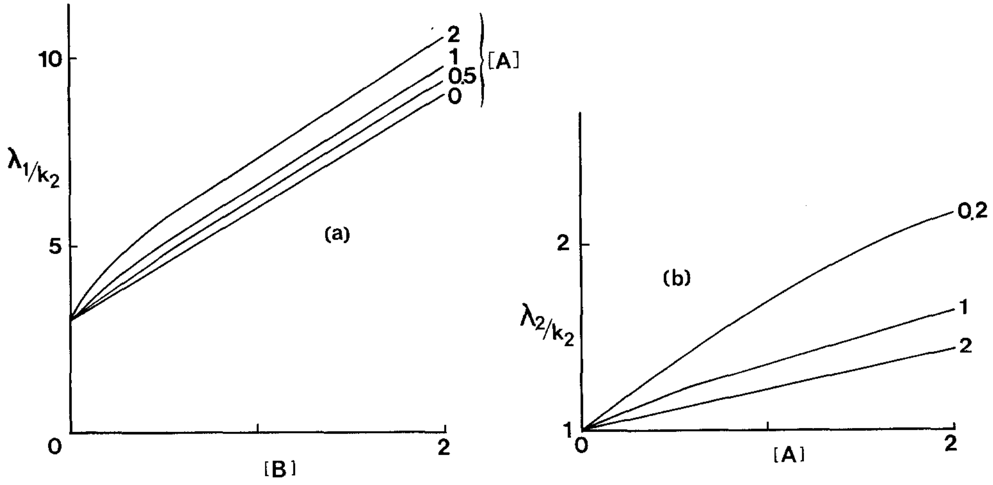

Fig. 2. (a) The dependence of λ_1/k_2 on the concentration of the acceptor species; (b) the dependence of λ_2/k_2 on the donor concentration, calculated from Eq. (10), with $k_1 = 3k_2$, $k_{et} = 3k_2$, and $k_{ret} = k_2$. Concentrations are in arbitrary units

In Fig. 2 are shown the variations of λ_1 and λ_2 with $[A]$ and $[B]$. The normal Stern-Volmer plot of λ_1 against $[B]$ in Fig. 2(a) gives approximately the correct value of k_{et} from its slope at relatively high acceptor concentration, but the curves are displaced upward as $[A]$ increases, and thus as back energy transfer assumes greater importance. The apparent intercepts of the straight portions are no longer equal to $1/k_1$. As can be seen from Fig. 2(b), λ_2 is a strong function of both $[A]$ and $[B]$.

As a rough guide, if $k_1 \geqq 10(k_2 + k_{ret}[A])$, Eq. (13) will hold approximately and the slope of λ_1 against $[B]$ will be within a few percent of the value for k_{et}, and the slope will not depend on $[A]$.

Steady-State Kinetics

The differential equations for the intermediates in Eqs. (1)–(4) on continuous illumination with absorbed intensity I_a are:

$$\frac{d[A^*]}{dt} = \Phi I_a + k_{ret}[A]\,[B^*] - (k_1 + k_{et}[B])\,[A^*]\,, \tag{17}$$

$$\frac{d[B^*]}{dt} = k_{et}[B]\,[A^*] - (k_2 + k_{ret}[A])\,[B^*]\,. \tag{18}$$

With the assumption of a steady-state for both $[A^*]$ and $[B^*]$, the solutions are:

$$[A^*]_{ss} = \frac{\Phi I_a(k_2 + k_{ret}[A])}{k_1(k_2 + k_{ret}[A]) + k_{et}[B]\,k_2}\,, \tag{19}$$

$$[B^*]_{ss} = \frac{\Phi I_a k_{et}[B]}{k_1(k_2 + k_{ret}[A]) + k_{et}[B]\,k_2}\,. \tag{20}$$

If these equations are then cast in the form appropriate to a Stern-Volmer treatment, for example, based on quenched emission of A^* and sensitized emission of B^*, the result is:

$$\frac{\Phi_0^A}{\Phi^A} = 1 + \left\{\frac{k_2}{(k_2 + k_{\text{ret}}[A])}\right\}\left\{\frac{k_{\text{et}}}{k_1}\right\}[B] \tag{21}$$

for the donor, and for the acceptor:

$$\frac{1}{\Phi^B} = \frac{1}{k_r^B \Phi}\left\{\frac{k_1(k_2 + k_{\text{ret}}[A])}{k_{\text{et}}[B]} + k_2\right\} \tag{22}$$

Eqs. (21) and (22) show that, unlike the case of lifetime measurements, steady-state quantum yields will have linear Stern-Volmer plots: Φ_0^A/Φ^A against $[B]$ for the donor emission and $1/\Phi^B$ against $1/[B]$ for the acceptor emission. The apparent Stern-Volmer quenching constant, obtained from the slope and the intercept/slope, respectively, for these two plots, will in general be given by:

$$K_{SV} = \left\{\frac{k_2}{(k_2 + k_{\text{ret}}[A])}\right\}\frac{k_{\text{et}}}{k_1}$$

when back energy transfer occurs, rather than the usual k_{et}/k_1.

However, it is then a simple matter to extract the true rate constant ratios: k_1/k_{et} and k_2/k_{ret}, from the data by a plot of the reciprocal of K_{SV} against $[A]$. The intercept of this plot is k_1/k_{et} and the slope/intercept is k_{ret}/k_2.

Conclusion

Reversible energy transfer can be recognized from the results of transient measurements by a dependence of the longer decay lifetime on acceptor concentration, as in Eqs. (14) and (16). In that case, interpretation of the results will be complicated unless the donor lifetime is appreciably shorter than that of the acceptor.

These complications do not arise with steady-state data, although the apparent Stern-Volmer constant will be a function of acceptor concentration if reverse energy transfer occurs to any appreciable extent.

References

1. For a review, see: Lamola, A. A.: In: Technique of organic chemistry, Vol. XIV, Energy transfer and organic photochemistry. Ed. by P. A. Leermakers and A. Weissberger, p. 18–132. New York: Interscience 1969.
2. Bäckström, H. L. J., Sandros, K.: Acta chem. scand. **16**, 958 (1962).
3. Sandros, K.: Acta chem. scand. **18**, 2355 (1964).
4. Nordin, S., Strong, R. L.: Chem. Physics Letters **2**, 429 (1968).

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