

Influence of donor-donor transport on excitation energy transfer

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Abstract. Energy migration and transfer from acriflavine to rhodamine B and malachite green in poly (methylmethacrylate) have been investigated using the decay function analysis. It is found that the influence of energy migration in energy transfer can be described quite convincingly by making use of the theories of Loring, Andersen and Fayer (LAF) and Huber. At high acceptor concentration direct donor-acceptor transfer occurs through Förster mechanism.

Keywords. Energy transfer; energy migration; decay function.

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1. Introduction

Investigation of migration and transfer of excitation energy in molecular and ionic systems has received a great deal of attention, both theoretical and experimental. These processes are of practical importance in many fields including lasers and solar energy conversion (Peterson and Snavely 1968; Swartz *et al* 1977). One of the objectives of these theories has been the study of excited state decay of initially excited species (called donor) since a number of characteristics of these processes can be derived from such studies. A complete theory of the energy transfer from donor to acceptor through dipole-dipole interaction for static case was given by Förster (1949, 1959) and it assumes low (near zero) donor and high acceptor concentration. However, at higher donor concentration, transport of excitation energy in the donor system (known as migration) before trapping in a different species (called acceptor) greatly influences the kinetics of decay. Initial theoretical work on the effect of energy migration in decay function under energy transfer includes the phenomenological models of Burshtein (1972) and Yokota and Tanimoto (1967). Under the energy transfer process the decay may be exponential if the migration rate is higher than the rate of transfer to acceptor as treated in the Burshtein theory. If the migration rate is lower than the transfer rate to acceptors, the donor decay may be non-exponential for short times after the excitation pulse due to direct transfer to nearby acceptors; for longer times the decay becomes exponential. This latter case was dealt with in the Yokota-Tanimoto (1967) theory. Although the Yokota-Tanimoto theory was found experimentally applicable in some cases (Kellendonck and Blasse 1982), Gösele and Coworkers (Gösele and Hauser 1975; Klein *et al* 1976; Gösele 1978) have found that this theory overestimates the critical transfer distance. For the intermediate case of comparable donor-donor and donor-acceptor interaction strength Huber (1979) has given a theory based on coherent potential approximation.

Recently Loring *et al* (LAF) (1982) gave a most complete and accurate theory based on a diagrammatic expansion of the green function. This theory is applicable for all the acceptor concentrations and was experimentally verified by Miller *et al* (1983) in rhodamine 6G-malachite green system. Huber's work, which is a restricted case of LAF theory, is found to agree with the LAF (1982) theory. In a recent paper (Pandey *et al* 1988), we have found that LAF and Huber's theories explain the energy transfer in sodium fluorescein-rhodamine 6G system in boric acid glass. In the present work we have taken two donor-acceptor systems, in one of which, the donor-donor interaction is stronger than the donor-acceptor interaction while in the other the situation is reversed. It has been found that the LAF theory, and hence the Huber's theory, explains the energy transfer in these systems over a certain range of acceptor concentration. As expected, at high acceptor concentrations, Förster's (1949) well-known theory for direct transfer is applicable.

2. Experimental

Acriflavine (M/s Hopkin and William Ltd., England), rhodamine B (BDH Ltd., England), malachite green (Emerck AG Darmstadt, Germany) and poly (methyl-methacrylate) (PMMA) (BDH Ltd., England) were used without further purification. Transparent sheets of PMMA-doped dyes (thickness 0.1 cm) were made. Samples were prepared by mixing PMMA grains in chloroform, then the appropriate concentration of dyes dissolved in methanol was mixed with chloroform. This dye PMMA mixture in chloroform was slowly heated in an incubator to a temperature of 60°C with intermittent stirring. The homogeneous mass was then poured in the appropriate container to obtain transparent sheets of required shape and size and allowed to dry. The concentration of acriflavine (5×10^{-4} M) was kept constant whereas the concentration of rhodamine B and malachite green varies from 2.5×10^{-5} M to 2.5×10^{-3} M. Steady state absorption and emission spectra were recorded using a spectrophotometer (Beckman DK 2A and fluorolog Spex 1902 respectively). The decay curves were recorded using a nanosecond fluorimeter (199 Edinburgh) by single photon counting method (O'Connor and Phillips 1970). Excitation source was a thyratron-gated hydrogen lamp with a repetition rate of 20 kHz and FWHM of ~ 1.2 ns. The data were analysed in a microcomputer (PDP 11/2) with available programs using the reconvolution technique described elsewhere (Joshi *et al* 1986). Excitation and emission monochromators were monitored at 420 nm and 495 nm respectively when the decay curves were recorded. The optical density was ~ 0.1 at detection wavelength and frontal geometry was used to reduce reabsorption effects.

3. Theory

Fluorescence decay of donor in Förster kinetics of energy transfer follows convex exponential nature (Förster 1949; 1959)

$$I_D = I_0 \exp \left[\frac{-t}{\tau} - 2\gamma_{DA}(t/\tau)^{\frac{1}{2}} \right], \quad (1)$$

where τ is the lifetime of donor in the absence of energy transfer, $\gamma_{DA} = C_A/C_{0A}$, C_A is the acceptor concentration and C_{0A} is the critical acceptor concentration given by

$$C_{0A} = 3000/(2\pi^{3/2}NR_{0A}^3), \quad (2)$$

where N is the Avagadro number and R_{0A} is the critical transfer distance. By definition it is the distance at which energy transfer has the same probability as the sum of all other excited state deactivation processes of donor. R_0 can be calculated using the relation (Birks 1970)

$$R_0^6 = \frac{(9000 \ln 10)\phi_D K^2}{128\pi^5 n^4 N} \int_0^\infty \frac{F_D(\bar{\nu})\epsilon_A(\bar{\nu}) d\bar{\nu}}{\bar{\nu}^4}. \quad (3)$$

Here ϕ_D is the donor fluorescence quantum yield in the absence of energy transfer, K^2 is the molecular orientation factor, n the solvent refractive index and $\epsilon(\bar{\nu})$ the acceptor molar decadic extinction coefficient at wave number ($\bar{\nu}$). $F_D(\bar{\nu})$ is the donor fluorescence intensity at $\bar{\nu}$ (normalised to unit area on wave number scale).

According to LAF and Huber theories when the donor-donor (β) and donor-acceptor (α) interaction are of comparable strength the donor fluorescence decay follows the expression (Huber 1979)

$$I_D = I_0 \exp \left[-t/\tau - 2 \left(\frac{\gamma_{DD}}{2^{\frac{1}{2}}} + \gamma_{DA} \right) (t/\tau)^{\frac{1}{2}} \right], \quad (4)$$

where $\gamma_{DD} = C_D/C_{0D}$, C_D is the donor concentration and $C_{0D} = 3000/2\pi^{3/2}NR_{0D}^3$ (R_{0D} is critical transfer distance for donor-donor system). In case $\gamma_{DA} \ll \gamma_{DD}$, the Huber equation (4) agrees with the LAF expression (equation (69) of LAF theory) given by

$$G^*(t) = \exp [-(\pi/2\tau)^{\frac{1}{2}} X_D t^{\frac{1}{2}}] \quad (5)$$

for the probability of energy migration where X_D is the reduced concentration defined by $X_D = 4\pi n_D R_{0D}^3/3$ (n_D is the number density of donor).

The donor-donor (β) and donor-acceptor (α) interaction parameters are defined by the following equation

$$\alpha = \frac{1}{\tau}(R_{0A})^6 \quad \text{and} \quad \beta = \frac{1}{\tau}(R_{0D})^6. \quad (6)$$

The rate of energy transfer from excited donor to unexcited donor (K_{d^*d}) and from excited donor to acceptor (K_{d^*a}) are given by

$$K_{d^*d} = \frac{1}{\tau}(R_{0D}/R)^6 \quad \text{and} \quad K_{d^*a} = \frac{1}{\tau}(R_{0A}/R)^6. \quad (7)$$

4. Results and discussion

The emission spectra of acriflavine (donor) (conc. 5.0×10^{-4} M) along with absorption spectra of two acceptors, rhodamine B (conc. 5×10^{-5} M) and malachite green (conc. 3.0×10^{-4} M), in PMMA are shown in figure 1. The value of critical transfer distance

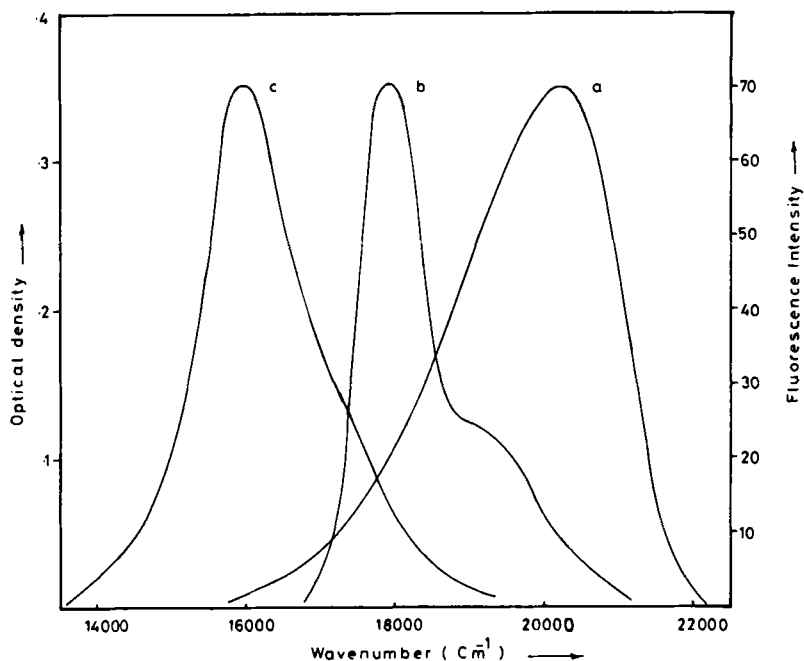


Figure 1. a. Fluorescence spectrum of acriflavine (conc. 5×10^{-4} M). b. Absorption spectrum of rhodamine B (conc. $5 \times 5 \times 10^{-5}$ M). c. Absorption spectrum of malachite green (conc. 3.0×10^{-4} M).

for donor-donor system (R_{0D}) according to equation (3) turns out to be 46 \AA (using $K^2 = 2/3$ corresponding to the random orientation of molecule, n the refractive index of PMMA = 1.49 and assuming $\phi_D = 0.8$, a value reported for cellulose acetate matrix (Birks 1970) since the lifetime of acriflavine in PMMA is found to be the same as in cellulose acetate). Similarly critical transfer distances for two donor-acceptor systems, acriflavine-rhodamine B and acriflavine-malachite green were 58.6 \AA and 34.5 \AA respectively which give $\alpha = 4.3 \beta$ for the former case and $\beta = 5.6 \alpha$ for the latter, since $\tau = 4.41 \text{ ns}$.

4.1 Acriflavine-rhodamine B system

Fluorescence decay of acriflavine (5.0×10^{-4} M) is found to have an exponential form with a lifetime of 4.41 ns (figure 2). On addition of rhodamine B (acceptor), the lifetime of donor fluorescence decreases. Addition of rhodamine B also results in deviation from exponential behaviour of donor fluorescence decay. In figures 3 and 4 we have shown the decay data of acriflavine (5.0×10^{-4} M) in the presence of rhodamine B along with the fitted function. In figure 3 the concentration of rhodamine B is 5.0×10^{-5} M while in figure 4 it is 1.0×10^{-3} M. In both the figures curve a is the fitted single exponential function whereas curve b is the fitted Förster function given by equation (1). Residuals and χ^2 values required for both the fitted curves are also shown below these figures. From residuals and χ^2 values it is clear that decay data are best fitted with the Förster function. The donor decay follows Förster function for the whole acceptor con-

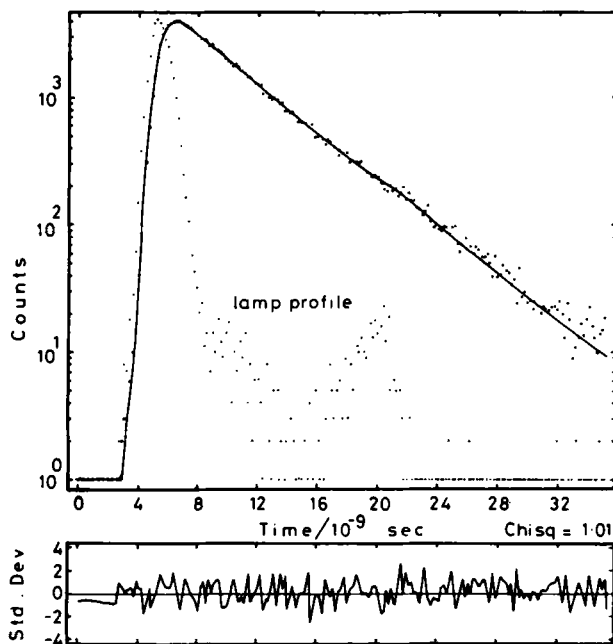


Figure 2. Fluorescence decay curve of acriflavine (conc. 5.0×10^{-4} M). Fit with single exponential function.

centration range studied. However, the fitting results in different values of observed C_{0A} and hence observed R_{0A} , for each acceptor concentration as discussed below.

In table 1, we have shown the values of reduced concentration (γ_{ob}) required for fitting the Förster function and hence the values of critical acceptor concentration (C_{0A})_{ob} and critical transfer distance (R_{0A})_{ob}. From table 1 it is evident that as acceptor concentration increases, the observed value of critical transfer distance decreases and finally attains a constant value of $\sim 58 \text{ \AA}$ after a concentration of 5.0×10^{-4} M which is in agreement with the spectroscopically calculated value of 59 \AA . Agreement in the values of R_{0A} obtained from the analysis of decay curves and its value calculated from spectroscopic measurements suggests that direct transfer to acceptor through Förster mechanism dominates over migration at higher acceptor concentration (after 5.0×10^{-4} M) such as that which corresponds to the transfer between static species. However, the fitting of data with Förster function at lower acceptor concentration with large and variable value of the observed critical transfer distance appears inconsistent with the Förster theory. This inconsistency is expected since Förster's theory assumes very low donor concentration which is not true in the present case. In fact since the donor-donor and donor-acceptor interaction strengths are comparable, the donor-donor and donor-acceptor transfer rates given by equation (6) also become comparable at these concentrations and thereby the energy migration becomes significant. In such cases the LAF and Huber theories lead to the modified decay function given by equation (4). This modified function has the same form as Förster function with γ_{DA} replaced by $\gamma_{DD}/2^{\frac{1}{2}} + \gamma_{DA}$. Now if we calculate the value of $\gamma_{DD}/2^{\frac{1}{2}} + \gamma_{DA}$ from spectroscopic measurements (designated as γ_{cal}), we find from table 1 that such values

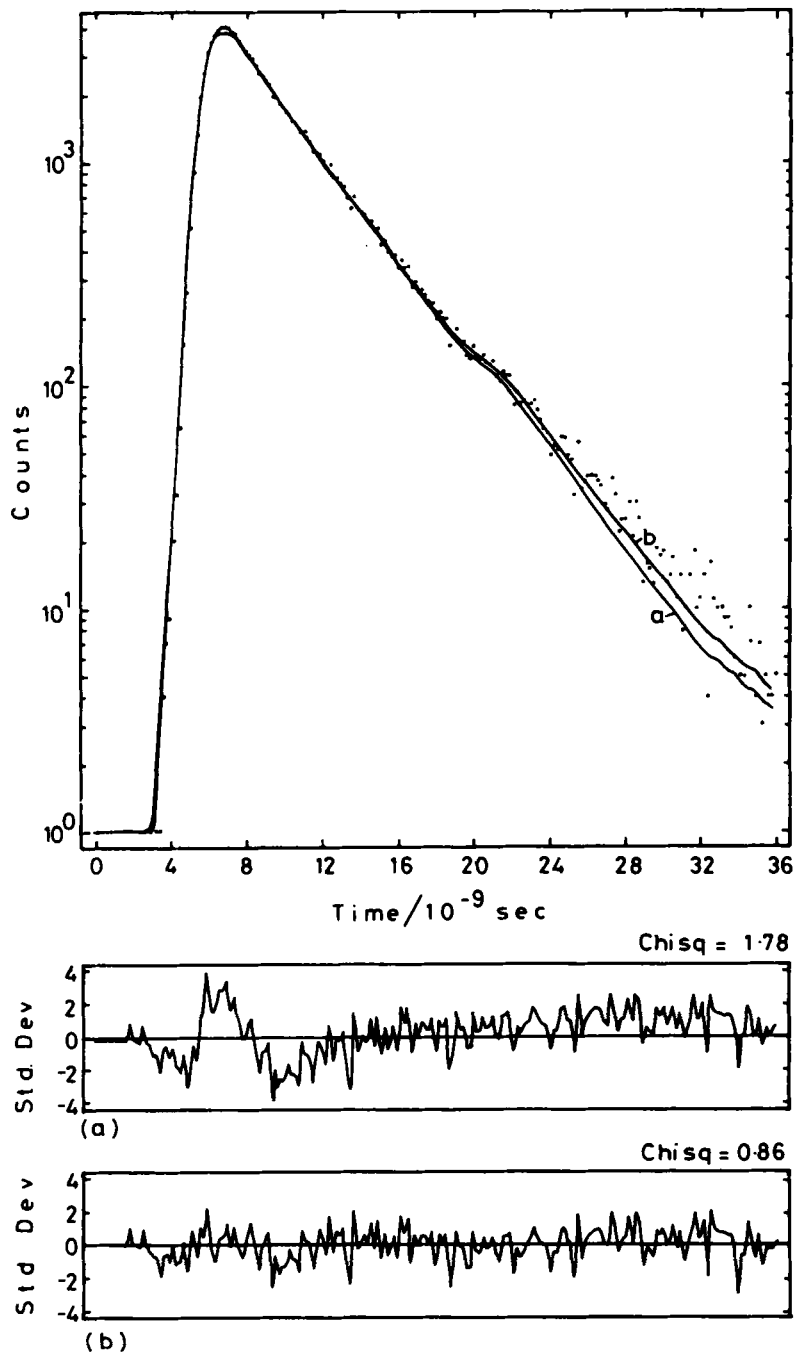


Figure 3. Fluorescence decay of acriflavine (conc. 5.0×10^{-4} M) in the presence of rhodamine B (conc. 5.0×10^{-5} M) (a) Fit with single exponential expression. (b) Fit with Förster's expression. The residuals and χ^2 values for curves (a) and (b) are also shown.

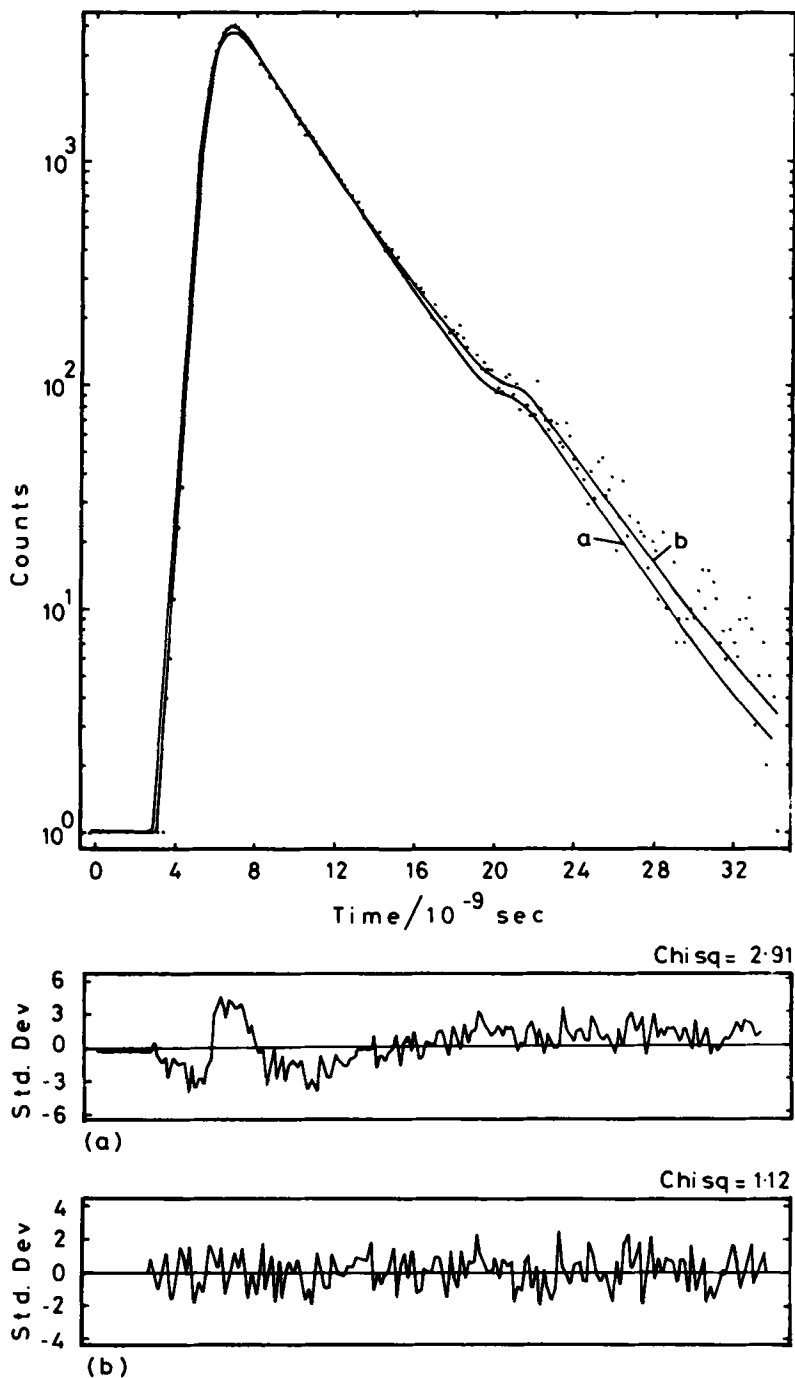


Figure 4. Fluorescence decay of acriflavine (conc. 5.0×10^{-4} M) in the presence of rhodamine B (conc. 1.0×10^{-3} M). (a) Fit with single exponential expression. (b) Fit with Förster's expression. The residuals and χ^2 values for curves (a) and (b) are also shown.

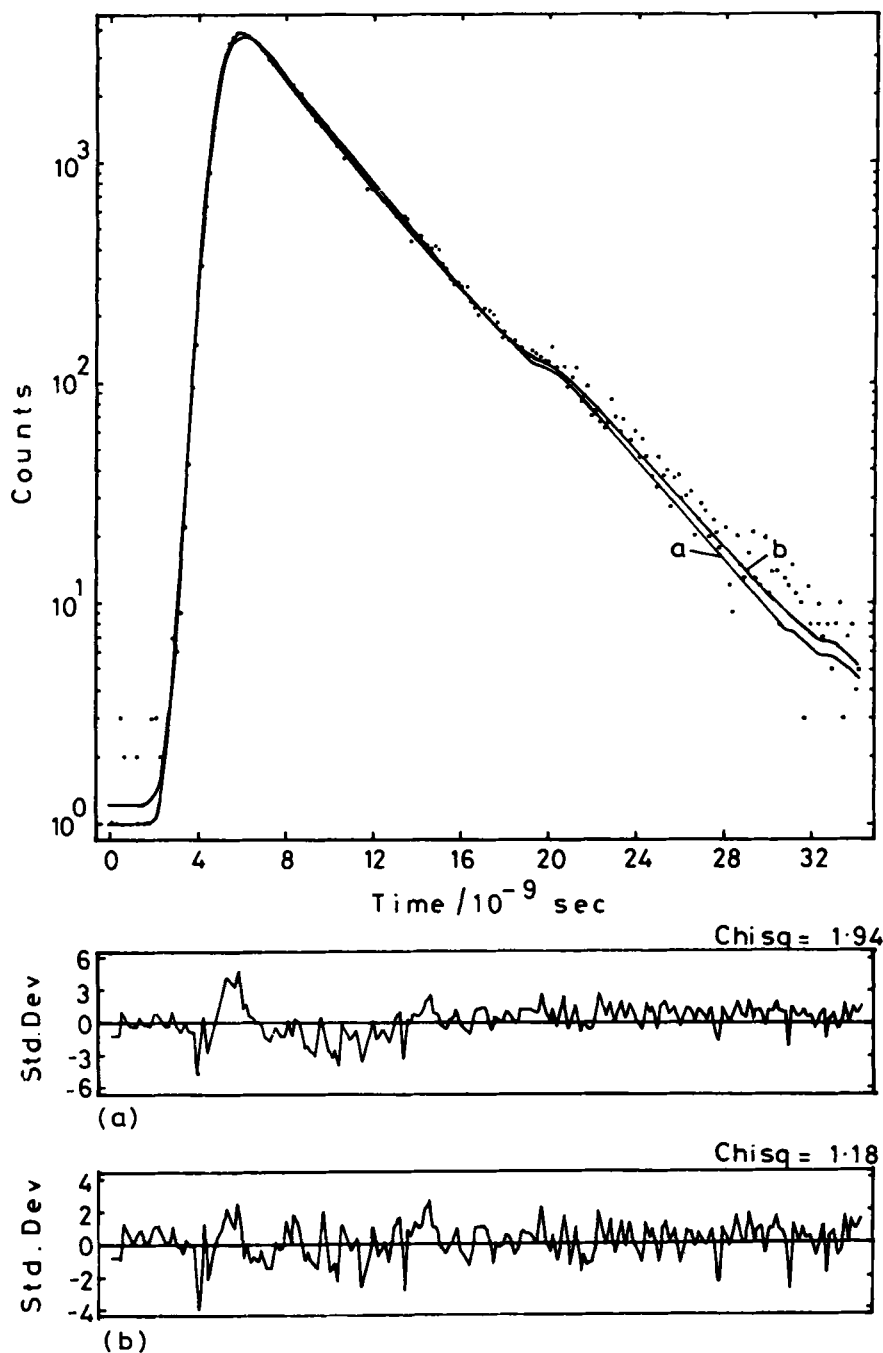


Figure 5. Fluorescence decay of acriflavine (conc. 5.0×10^{-4} M) in the presence of malachite green (conc. 1.0×10^{-3} M). (a) Fit with single exponential expression. (b) Fit with Förster's expression. The residuals and χ^2 values for curves (a) and (b) are also shown.

are in perfect agreement with γ_{ob} . This agreement can be better realised from the corresponding $(R_{0A})_{cal}$ and $(R_{0A})_{ob}$ values also given in table 1. Therefore, at low and comparable acceptor concentrations (up to $\sim 5.0 \times 10^{-4}$ M), LAF and Huber theories satisfactorily explain the energy transfer in this system. As mentioned before, at high acceptor concentrations direct transfer is dominant through Förster's mechanism.

4.2 Acriflavine-malachite green system

The decay data of acriflavine in the presence of malachite green are found to fit in Förster expression for the whole of the concentration range used. Decay points of acriflavine (5.0×10^{-4} M) in the presence of malachite green (1.0×10^{-3} M) are shown in figure 5. The solid line curve a is the single exponential function while curve b is the Förster function fitted to the data. It can be seen that the decay points are best fitted with the Förster function. The observed values of reduced concentration (γ_{ob}), the

Table 1. Experimentally observed and spectroscopically calculated values of various parameters in acriflavine-rhodamine B system.

$C_A (\times 10^{-4} \text{ M})$	Observed values			Spectroscopic values		
	γ_{ob}	$(C_{0A})_{ob}$ ($\times 10^{-3} \text{ M}$)	$(R_{0A})_{ob}$ (\AA)	$(\gamma_{DD} = 0.108)$		
				γ_{DA}	γ_{cal} ($= \gamma_{DD}/2^{\frac{1}{2}} + \gamma_{DA}$)	$(R_{0A})_{cal}$ (\AA)
0.25	0.086	0.29	115.6	0.011	0.087	116.01
0.50	0.104	0.48	97.7	0.022	0.098	95.70
0.75	0.113	0.66	87.8	0.033	0.109	87.10
1.00	0.126	0.79	82.7	0.045	0.121	81.50
2.50	0.193	1.29	70.2	0.112	0.188	69.72
5.00	0.310	1.61	65.2	0.225	0.301	64.60
7.50	0.339	2.21	58.7	0.337	0.413	62.70
10.00	0.476	2.10	59.7	0.450	0.526	61.72
25.00	1.100	2.27	58.2	1.126	1.202	60.10

Table 2. Experimentally observed and spectroscopically calculated values of various parameters in acriflavine-malachite green system.

$C_A (\times 10^{-4} \text{ M})$	Observed values			Spectroscopic values		
	γ_{ob}	$(C_{0A})_{ob}$ ($\times 10^{-3} \text{ M}$)	$(R_{0A})_{ob}$ (\AA)	$\gamma_{DD} = 0.108$		
				γ_{DA}	γ_{cal} ($= \gamma_{DD}/2^{\frac{1}{2}} + \gamma_{DA}$)	$(R_{0A})_{cal}$ (\AA)
2.5	0.095	2.63	55.4	0.022	0.098	56.0
5.0	0.117	4.27	47.1	0.045	0.121	47.6
7.5	0.140	5.35	43.7	0.068	0.144	44.1
10.0	0.151	6.62	40.7	0.091	0.167	42.1
25.0	0.240	10.41	35.04	0.229	0.305	37.9
50.0	0.430	11.62	33.78	0.458	0.534	36.3

critical acceptor concentration and the critical transfer distance $(R_{0A})_{ob}$, are shown in table 2. It can be seen that the observed critical transfer distance $(R_{0A})_{ob}$ agrees with its spectroscopically calculated value only after a concentration of 2.5×10^{-3} M. Thus at malachite green concentration higher than 2.0×10^{-3} M, the direct transfer to acceptor through Förster mechanism dominates. As before, the higher values of critical transfer distance at concentration lower than 2.5×10^{-3} M are again explained on the basis of Huber and LAF theories. Spectroscopically calculated values of γ_{DD} , γ_{DA} and hence $\gamma_{cal} (= \gamma_{DD}/2^{\frac{1}{2}} + \gamma_{DA})$ are given in table 2. The agreement is perfect in γ_{cal} , $(R_{0A})_{cal}$ and γ_{ob} , $(R_{0A})_{ob}$ respectively up to a concentration of 1.0×10^{-3} M. In this system the transfer at acceptor concentration lower than 2.5×10^{-4} M was found to be insignificant. This is due to the low value of parameter α in this system compared to the acriflavine-rhodamine B system discussed above. Secondly, the migration is important up to a much higher acceptor concentration than that in the previous system, expectedly so due to the large β value compared to α in this system.

5. Conclusion

In both the systems studied here we find that the influence of energy migration on energy transfer can be explained by the most general theory of LAF and its restricted case considered in Huber's theory. Up to a certain acceptor concentration the energy migration between donors modulates the direct transfer to the acceptor. For a given donor concentration this acceptor concentration depends on the relative values of α and β . Above these acceptor concentrations migration becomes insignificant in both the systems and only direct transfer through Förster's mechanism takes place.

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References

- Birks J B 1970 *Photophysics of aromatic molecules* (New York: Wiley Interscience) pp. 207 and 569
- Burshtein A I 1972 *Sov. Phys. JETP* **35** 882
- Förster Th 1949 *Z. Naturforsch.* **49** 321
- Förster Th 1959 *Disc. Faraday Soc.* **27** 7
- Gösele U and Hauser M 1975 *Chem. Phys. Lett.* **11** 445
- Gösele U 1978 *Spectrosc. Lett.* **11** 445
- Huber D L 1979 *Phys. Rev.* **B20** 2307 5333
- Joshi G C, Tripathi H B and Pant D D 1986 *Indian J. Phys.* **B60** 7
- Kellendonck F and Blasse G 1982 *J. Phys. Chem. Solids.* **43** 481
- Klein U K A, Fray R, Hauser M and Gösele U 1976 *Chem. Phys. Lett.* **41** 139
- Loring R F, Anderson H C and Fayer M D 1982 *J. Chem. Phys.* **76** 2015
- Miller R J D, Pierre M and Fayer M D 1983 *J. Chem. Phys.* **78** 5138
- O'Connor D V and Phillips D 1970 *Time-correlated single photon counting* (New York, Academic Press)
- Peterson O G and Snavely P B 1968 *Bull. Am. Phys. Soc.* **13** 397
- Pandey K K, Joshi H C and Pant T C 1988 *Chem. Phys. Lett.* **148** 472
- Swartz B A, Cole T and Zewail A H 1977 *Opt. Lett.* **1** 73
- Yokota M and Tanimoto O 1967 *J. Phys. Soc. Jpn.* **22** 779