# Distance Dependence of Electron-Transfer Quenching in Rigid Media: A Discrete Site Model of Electron Transfer and Electron Exchange

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Abstract. The quenching of the luminescence of five emitters which span lifetimes of 1 ns to 10 s has been investigated in rigid media. The mechanism is in every case either electron transfer or electron exchange. The data are analyzed according to a model of statistical distribution similar to the *Perrin* action sphere model, except that the distances between emitters and quenchers are allowed to vary only in increments of the solvents' molecular diameter. It is concluded that in all studied cases quenching takes place only if the two molecules are in *van der Waals* contact. The distribution of charged species in highly polar liquids or glasses is considered specifically. It is suggested that even in such cases the simple statistical distribution is obtained.

Introduction

There have been several efforts [1] to determine the distance at which an electron-transfer (ET) process takes place between two individual molecules M and Q, as in the photoinduced ET process

$$h\nu$$
$$M \rightarrow M^* ; M^* + Q \rightarrow M^{\cdot +(-)} + Q^{\cdot -(+)} \quad (1)$$
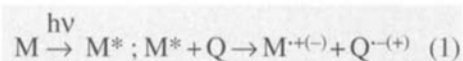
In fluid solvents this process is mostly diffusion-controlled [2] and the question must, therefore, be assessed under diffusionless conditions where the molecules keep a fixed distance during observation. It would, therefore, be desirable to prepare assemblies of M and Q at well defined separations, such as in covalently linked systems or in monomolecular layers.

In the first case, bichromophoric molecules have been prepared in which M and Q are separated by a rigid chain of saturated spacers [3]. The length of the chain can be varied by increments, and the rate constant of ET can be determined from the quenching of the luminescence of the emitter M* by the quencher Q. In some cases this quenching takes place over quite

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large distances, but it has been concluded that this type of intramolecular ET results from a through-bond interaction between M* and Q. Thus, no conclusion could be drawn concerning the distance at which it would occur between two separate molecules M* and Q interacting only through space (or perhaps through the solvent).

The situation with respect to monolayer experiments is also not conclusive. Some results have given quenching distances as large as 80 Å in times of ns [4], and it has been questioned to what extent the long saturated chains which must be attached to the molecules to form stable monolayers may contribute to some sort of through-bond interaction even though there is no covalent bonding between them. The question of the role of defects in such films also remains unresolved [4].

Other investigations of the distance dependence of ET have relied on rigid solutions in which the molecules M and Q are distributed at random [5]. The distance distribution can be obtained from a statistical analysis and interpreted according to the 'sphere of action' model of *Perrin* [6]. In this simple model it is assumed that there is a well-defined distance L such that M*/Q pairs separated by $l < L$ show total quenching, while those for which $l > L$ show no quenching (l is the centre-to-centre separation of M and Q). From such models it has been suggested that ET can take place between molecules which are

not in *van der Waals* contact, though the calculated distances remain much shorter than the largest ones derived from the monolayer experiments. One of the largest separations l reported is 16 Å for the quenching of a phosphorescence in the time scale of several seconds [1c].

Critical Remarks about the 'Sphere of Action' Model

Average Nearest Distances $\bar{l}$

The spatial distribution of Q molecules with respect to one M* has been usually derived from a simple mathematical model which gives the average nearest centre-to-centre distance $\bar{l}$ of randomly distributed points of concentration [Q] as [5]

$$\bar{l} = [(4/3) \pi N_A [Q]]^{-1/3} \quad (2)$$

These points are then taken as being the centres of the quenchers Q which are assumed to be spheres of a volume equal to their molecular volume. From such models it was concluded for instance that quenching by ET takes place at $\bar{l} = 12$ Å when the molecular radius of M* is 6 Å and that of Q is 4 Å. Since then the edge-to-edge distance is 2 Å it results that ET has taken place between molecules which are not in *van der Waals* (*vdW*) contact [5]. On the other hand, this latter distance is too small to allow the conclusion, that ET has, therefore, taken place across one solvent molecule.

A way out of this ambiguity is to replace the continuum model by a model of discrete sites. Here, we take the example of M* = [Ru(bipy)₃]²⁺ (RU) and Q = methylviologen (MV):

i) In a rigid system, M* and Q can be in *vdW* contact, or they can be separated by one solvent molecule, or by two, *etc.* It is unrealistic to consider edge-to-edge distances smaller than the solvent's molecular diameter which, for glycerol (G) for instance, is *ca.* 5 Å, assuming its shape to be sphere like (*Fig. 1a* and *c*). Situations may exist in which M* and Q are separated by a distance smaller than the solvent diameter, as exemplified in *Fig. 1b*. Here, the volume between M* and Q is indeed part of the 'free' volume of the liquid (or glass), *i.e.*, the volume accessible under pressure. This volume is, however, very small compared to the total volume, and it can be concluded that cases (*b*) are statistically not significant compared to cases (*a*) and (*c*).

ii) The centre-to-centre distances of *Eqn. 2* are reasonable approximations for the distribution of molecules of nearly

spherical symmetry. Some molecules such as RU can approximate to such a model. Others like MV do not: a space-filling molecular model shows its dimension to be roughly $15 \times 7 \times 4$ Å^3. If the distance between such a molecule and some spherical molecule is calculated from *Eqn. 2*, no conclusion can be drawn about their edge-to-edge separation since an uncertainty of 6 Å is implied in the different orientations of the molecular axes for a fixed centre-to-centre separation (*Fig. 1d*).

iii) It has already been noted that further problems arise in the statistical definition of the centre-to-centre distances when molecules carry electrical charges. Ions of the same charge repell each other and have, therefore, greater average separations than neutral species, whereas ions of opposite charges will be found in closer association. The statistical model neglects forces acting between M and Q.

Microscopic Motions

In quenching experiments which rely on a statistical distribution of molecules in rigid co-dissolved systems, it is essential that any translational motion of the molecules be negligible during the lifetime of M*. According to the macroscopic viscosity (which is known for glycerol and other organic glasses at various temperatures), the translational motion is certainly negligible in the timescale of ns to µs [7]. Questions arise, however, when excited state life-times of the order of seconds are considered, as in phosphorescence quenching measurements. The mean translational distance $\bar{x}$, given by

$$\bar{x} = \sqrt{(kT/3 \, \pi \, r \, \eta) \cdot t} \tag{3}$$

for a molecule of radius r in a medium of viscosity η during a time t, is of the order of 6 Å when $\eta = 4 \cdot 10^7$ poise (*e.g.* MTHF glass near 80 K) and $t = 4$ s. This suggests that microscopic motions of the order of molecular dimensions may not be negligible in some 'soft' glasses when quenching takes place over a time scale of seconds.

Reproducibility of Quenching Slopes

The use of solid samples in fluorimetry makes problems of reproducibility which must be considered when different quenching slopes are compared. Variations of the order of 10% of light-intensity measurements are commonplace, and somewhat larger differences in quenching slopes can be found between experiments reported by different laboratories. For the RU/MV system in glycerol, for example, we find a quenching slope of -5.4 ± 0.5M^{-1} from five runs (*vide infra*), while a value of -3.0M^{-1} has been reported previously [5]. Similar variations have been observed in luminescence-quenching experiments in polymer films [9], and some caution is, therefore, required about the significance of small differences in quenching slopes.

Results and Discussion

The Model of Discrete Sites

In our model a volume V is divided into n sites of volume v equal to the solvent's molecular volume. The solute molecules can occupy one or more sites according to their volume and shape. A molecule M is placed at the centre of the volume V, then q quencher molecules Q are placed at random in the remaining sites. The distance of M to the nearest Q is given according to the rank of the site such that M can be in contact with Q, separated from it by one site (*i.e.*, one solvent molecule), by two sites (*i.e.*, two solvent molecules) *etc.*

This model is easily subjected to an exact mathematical treatment if the only quantity required is the probability of finding at least one Q in the first solvation shell (*i.e.*, in *VdW* contact with M), or in the second or in the third solvation shell, *etc.* If there are s solvent molecules of volume v in the shell of interest, the probability of *not* finding the first Q in that shell is $(V-sv)/V$, and the probability of finding all Q outside the shell is $[(V-sv)/V]^q$.

This treatment leads to the well known logarithmic form of the static quenching sphere model of *Perrin*, on the assumption that only those M contribute to the luminescence intensity I_Q which have *no* quencher in the shell of interest:

$$\ln (I_Q/I_0) = q \cdot \ln [1-(sv/V)] \tag{4}$$

The number q of Q present in the volume V is related to the quencher concentration by $[Q] = q/VN_A$. *Table 1* lists the molecules used as solvents, emitters M and quenchers Q in this work, with their volumes and the shapes assumed in the discrete site models.

Quenching Slope, Half-quenching Concentration

According to *Eqn. 4*, the extent of quenching is expressed by the quenching slope X

$$X = \ln (I_Q/I_0)/[Q] \tag{5}$$

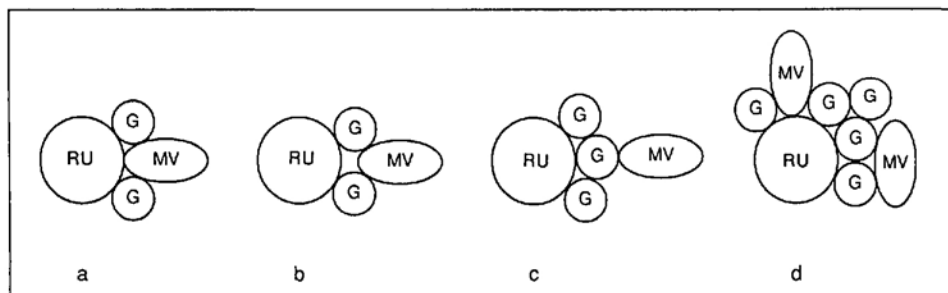or by the related quantity defined as the half-quenching concentration $[Q]_{1/2}$

Fig. 1. *Geometrical arrangement of M* * = [Ru(bipy)₃]²⁺ (RU) and Q = methylviologen (MV) in glycerol (G). a) vdW-contact; b) separation by less than one solvent molecule; c) separation by one solvent shell; d) consideration of non sperical shape of MV.*

Table 1. *Molecular Volumes (v) and Number of Sites (s) for the Compounds Used in this Work for the Computer Simulations of the Discrete Site Model*

Molecule	Volume (v) [Å³]	Sites (s)	Shape
Glycerol	125	1	
EtOH	70	1	
Et₂O	130	2	
Methylviologen (MV)	300	2	
[Ru(bipy)₃]²⁺ (RU)	950	8	cube
Rhodamine B (RHO)	730	6	linear
Cyanine (CY)	520	4	linear
Benzophenone (BP)	300	4	T-shape
Carbazole (CZ)	280	4	linear
Naphthalene (NP)	200	3	linear
1-Methylnaphthalene (MeNP)	200	3	linear

$$[Q]_{1/2} = \ln 0.5/X = -0.7/X \qquad (6)$$

Volume of Action

In the *Perrin* model, the interaction between pairs of 'mathematical points' is implicitly assumed to be isotropic: any one M or Q is surrounded by a 'sphere of action'. However, as noted above, real molecules seldom resemble spheres. A 'volume of action' could still be defined as the volume which can contain active Q. This is a meaningful mathematical concept, because it can be used directly in a probability equation in the same way as a 'sphere of action', but it does not imply an isotropic quenching action.

If it is assumed that direct contact of M and Q is the necessary and sufficient condition for quenching, then the volume of action can be calculated from the volumes of M and Q, but these must be average volumes over many possible relative angular distributions. Note that the actual shapes of M and of Q are now important, the volume of action depending on both. This is quite different from the simple *Perrin* action sphere model, since the action volumes can be substantially larger when M and/or Q have shapes which differ greatly from a sphere. A quenching situation beyond *vdW* contact is readily included by adding one, or two, or more solvent shell volumes.

Distribution of Electrically Charged Molecules

So far the distribution of Q around M has been treated according to a random pattern as if there were no forces acting between them. It is now necessary to consider the case of ionic species M and Q which exhibit electrostatic interaction.

When the overall energy balance of the association process of two ions is considered, it is important to take into account the electrostatic energy as well as the solvation energies. In the case of two ions of opposite charges, the energy balance from the initial state of associated ions (in *vdW* contact) to the final state of separate ions at infinity is

$$\Delta E = 2 \cdot E_{solv}^{ion} - E_{solv}^{dip} + E_{coul} \qquad (7)$$

The *Onsager* equation for the solvation of a contact ion pair in a very polar solvent where $f(D) \approx 1$ ($f(D) = 2(D-1)/(2D+1)$ is the *Onsager* solvent polarity function of the static dielectric constant D) is:

$$E_{solv}^{dip} = -\frac{\mu^2}{2a^3} f(D) = -\frac{\mu^2}{2a^3} \qquad (8)$$

Table 2. *Luminescence Spectra Maxima and Lifetimes of Molecules Used in this Work*

Molecule	λ_{max} [nm]	τ_{lum}
$[Ru(bipy)_3]^{2+}$ (RU)	610	900 ns
Rhodamine B (RHO)	540	4 ns
Cyanine (CY)	535	< 1 ns
Benzophenone (BP)	420	5 ms
Carbazole (CZ)	430	0.6 s

For a simple model of two spherical ions of charge Ze and of similar radii r the dipole moment is $\mu = Ze \cdot 2r$ and the *Onsager* cavity radius a is defined as $a^3 = 2r^3$ [10]. Hence

$$E_{solv}^{dip} = -\frac{(Ze)^2}{r} \qquad (9)$$

In the case of a very polar solvent where $F(D) \approx 1$ ($F(D) = 1-1/D$ is the *Born* solvent polarity function) the solvation energy of one of these ions is given by the *Born Eqn.* [11]

$$E_{solv}^{ion} = -\frac{(Ze)^2}{2r} F(D) = -\frac{(Ze)^2}{2r} \qquad (10)$$

It follows from *Eqns. 9* and *10* that ΔE of *Eqn. 7* is determined by the electrostatic term alone

$$E_{coul} = -\frac{(Ze)^2}{4r} \qquad (11)$$

In the case of two ions with charges of the same sign the solvation terms in *Eqn. 7* do not cancel out. The ion pair is now approximated as a (spherical) superion of charge $2 \cdot Ze$ and radius a. From the *Born* equation, this superion is better solvated than the two individual solvated ions due to the quadratic dependence of the solvation energy on the charge. The surprising prediction is that such ions tend to *associate* in very polar solvents, since the difference in the solvation energies is indeed larger than the electrostatic repulsion term. When M and Q carry charges of the same sign, the distribution of the counterions must, therefore, be considered as well: if there is a substantial degree of association with the latter, these ion pairs can then be treated like neutral dipoles for which the simple statistical distribution is expected to apply. Experimental quencher concentrations are in many cases quite high, of the order of 0.1M and even higher, so that on grounds of statistics alone the association to ions pairs can become important.

The equilibrium constant K for the association of the ions M and Q with their counterions can be estimated from the free energy ΔG, taking the enthalpy change

ΔH as being simply the electrostatic term of *Eqn. 11*. The entropy change is obtained from the relative volumes which can be occupied by the counterions when they are free in the volume V or in contact with M or Q, respectively, in a volume v corresponding to the solvation shell. If we consider only the ion-counterion association of the quencher Q whose concentration is usually higher than [M], one can estimate that it is virtually complete at concentrations [Q] > 0.05M. This implies that there is no electrostatic contribution to the free energy of association of the (uncharged) Q-counterion pair with any charged or neutral M.

There is experimental evidence for the ion-counterion association in polar solvents. For example the absorption spectrum of benzophenone radical anion depends on the counterion in solvents like alcohols, which is difficult to understand unless these ions are statistically in close proximity [12].

Luminescence Quenching by Electron Transfer (ET) in the ns to µs Time Scale

Methyl viologen (MV) has been used as Q for the luminescence quenching of three different M: Rhodamine B (RHO) and a cyanine dye (CY) which have fluorescence lifetimes of 4 ns and 1 ns, respectively, and the formally doubly charged complex $[Ru(bipy)_3]^{2+}$ (RU) which has a luminescence lifetime of 5 µs. The properties of these molecules are listed in *Table 2*.

In all three cases, it is found that the luminescence intensity decreases with increasing [Q] according to the exponential law of static quenching. The quenching functions are shown in *Fig. 2*; they have been averaged from several runs of measurements so that the reproducibility of these experiments could be assessed, and a limit of uncertainty could be given for the quenching slopes. These can now be compared to those obtained from computer simulations and from the analytical treatment of *Eqn. 4*. In *Table 3*, this comparison is made according to a model of contact quenching and of quenching at

separations of one solvent shell and of two solvent shells.

It is immediately clear that the experimental data can be fitted to *contact* quenching only, and this in all three cases. The conclusion is that ET up to the µs time scale requires *vdW* contact of the molecules, no matter how exergonic the reaction is. The close agreement between experiment and calculation based on the model of contact quenching in the case of RU shows that the close approach of M and Q carrying charges of equal sign takes place as expected from the arguments developed above.

Finally, the static nature of the quenching is shown by the invariance of the luminescence decay kinetics with quencher concentration. In the case of RU, we find that the luminescence decays according to first-order kinetics within experimental error, and that the lifetime is independent of quencher concentration (*Fig. 3*). This is in agreement with the conclusion derived from the quenching slope, that is ET between contact pairs takes place in sub-ns times but does not occur within the available time window as soon as M is separated from Q by just one single solvent molecule.

Luminescence Quenching by Electron Exchange (EE) in the ms to s Time Scale

The phosphorescences of benzophenone (BP, lifetime 5 ms) and of carbazole (CZ, lifetime 7 s) in rigid $Et_2O/EtOH$ glass at 77 K are quenched by naphthalene (NP) and 1-methylnaphthalene (MeNP) through a *Dexter*-type electron exchange (EE) mechanism, a process which involves a double ET between M and Q [13]. Although the quenching function apparently does follow the *Perrin* relationship, the phosphorescence decay kinetics are non-exponential in the presence of Q (see *Ta-*
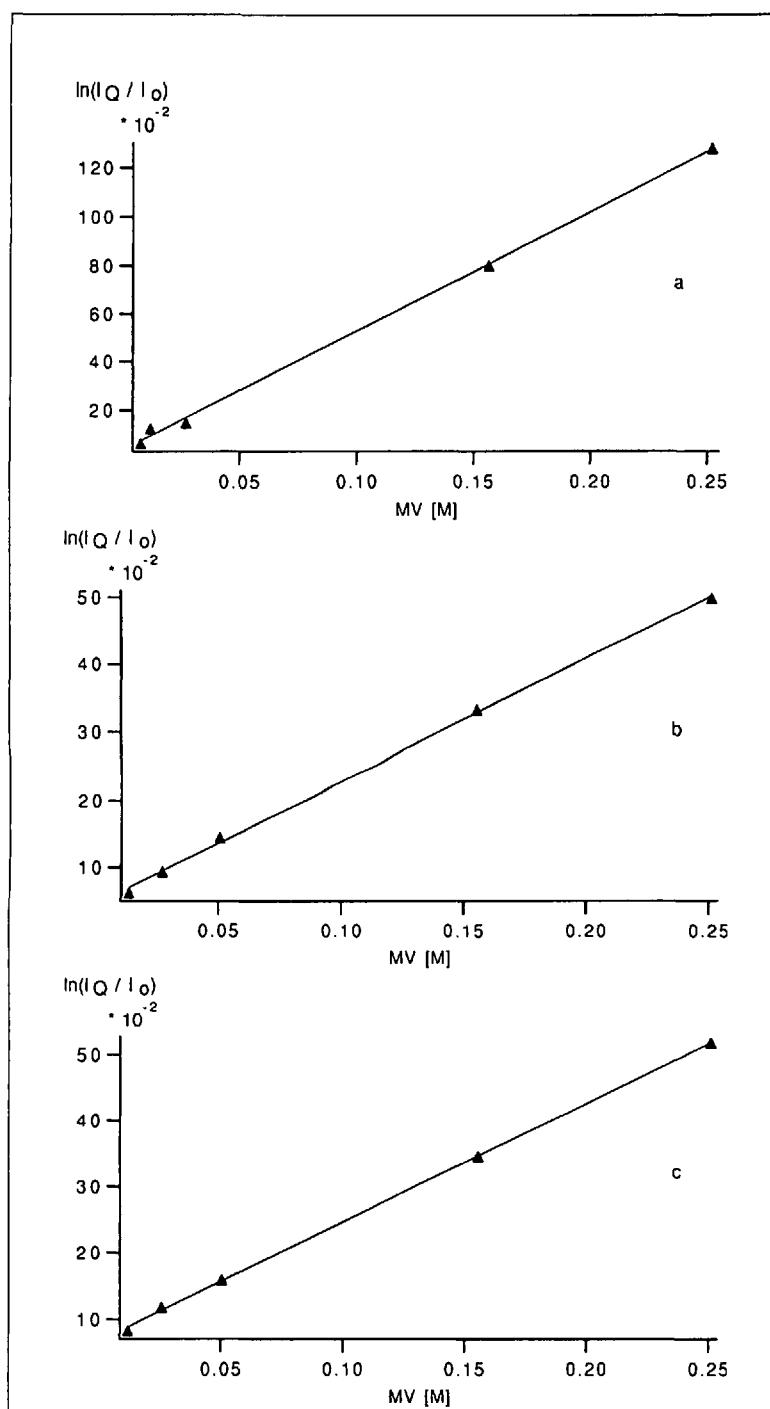

Fig. 2. *Quenching plots of $[Ru(bipy)_3]^{2+}$ (a), Rhodamine B (b), and cyanine (c) by methylviologen (MV) in rigid glycerol*

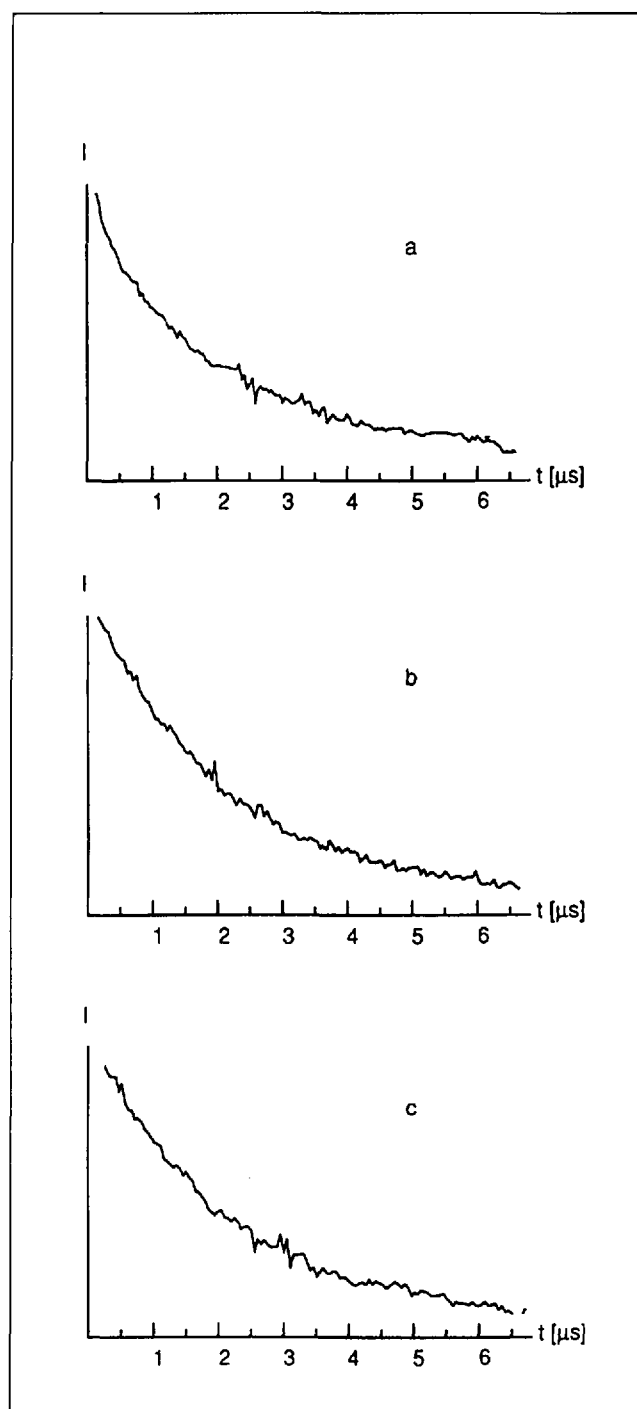Fig. 3. *Luminescence decay curves of $[Ru(bipy)_3]^{2+}$ in rigid glycerol at −25°. a)* Without quencher; *b)* with methylviologen 0.05M; *c)* with methylviologen 0.25M. Intensity I: arbitrary units.

ble 4 and *Fig. 4*). The *Perrin* action sphere model is then no longer applicable, and any 'radius of action' derived from the quenching slopes given in *Table 4* must be viewed with extreme caution. However, the decay curves can yield the ratio between 'quenched' and 'free' M, the latter being those molecules which phophoresce with the lifetime of the samples containing no Q. At long times the decay becomes exponential and follows the normal phosphorescence lifetime. This part of the luminescence must, therefore, correspond to the 'free' M, *i.e.*, those which have no Q within any active distance. The extrapolation of the final exponential decay to zero time thus provides a measure of the initial phosphorescence intensity.

We first discuss in detail the quenching of the BP-phosphorescence by MeNP. In a model of discrete sites M=BP can be represented by four sites of 70 Å^3 each to give its molecular volume of 300 Å^3, one of these sites representing the carbonyl group. In this model, a molecule of EtOH corresponds to one site, a molecule of Et$_2$O to two sites, and Q=MeNP occupies three sites in a row. The phosphorescence of BP originates from the n-π^* triplet state which is a local excitation of the carbonyl group [14]. There are then 23 quenching sites which are in contact with this excitation site in a model of cubic arrays, whereas there would be 50 sites in contact with the entire BP molecule. The restriction of quenching action to the 23 sites in contact with the carbonyl group leads to a reasonable agreement with the experimental ratio of quenched to free emitters for various MeNP concentrations (*Table 4*).

Turning now to the quenching of the CZ-phosphorescence by NP the observed ratio of unquenched ('free') M as a function of [NP] is shown in *Column 6* of *Table 4*. The quenching slope of the *Perrin* plot of -7.7M^{-1} is much steeper than that for BP/MeNP. These data agree also with a model of *vdW* contact between M and Q. Computer simulations of the discrete site model show that the quenching slope would be much larger if quenching could take place across one molecule of EtOH. In this model CZ is represented by four sites in a row, and it is assumed that contact at any site leads to quenching. This differs from the case of BP due to the fact that the CZ-phosphorescence originates from a π-π^* triplet state whose excitation is delocalized over the entire molecule. There is another important difference: If it is assumed that any relative orientation of the NP- and CZ-π-systems leads to quenching, then the active volume comes out too large (*Column 4*). Thus co-planarity of the

π-systems seems to be a requirement for electron exchange. This shows that the orientation of electron donor and acceptor orbitals may well be important in some cases, but a detailed investigation of such effects presents considerable experimental problems which are beyond this work. It may be noted that similar quenching experiments with these same chromophores linked by methylene spacers are also in agreement with the *Dexter* mechanism of through-space electron exchange [1j] implying an exponential distance dependence.

Table. 3. *Experimental, Calculated and Computer-Simulated Quenching Slopes of the Fast Emitters with Methylviologen in Glycerol*

Molecule	exp.	cal.(1)	cal.(2)	sim.(1)	sim.(2)
[Ru(bipy)$_3$]$^{2+}$ (RU)	−5.3	−4.1	−18	−5.1	−22
Rhodamine B (RHO)	−1.8	−3.9	−17	−4.9	−21
Cyanine (CY)	−2.5	−3.6	−16	−4.5	−20

Table. 4. *Fractions f of 'Free' (Unquenched) Emitter Populations in Benzophenone/Methylnaphthalene (BP/MeNP) and Carbazole/Naphthalene (CZ/NP). N:* number of quenchers for 1000 sites. f in *Column 1:* assuming that all contact sites lead to quenching; *2:* assuming that only contact with the carbonyl group leads to quenching; *3:* experimental values; *4:* assuming that all orientations lead to quenching; *5:* assuming that only parallel aromatic plane orientations lead to quenching; *6:* experimental values.

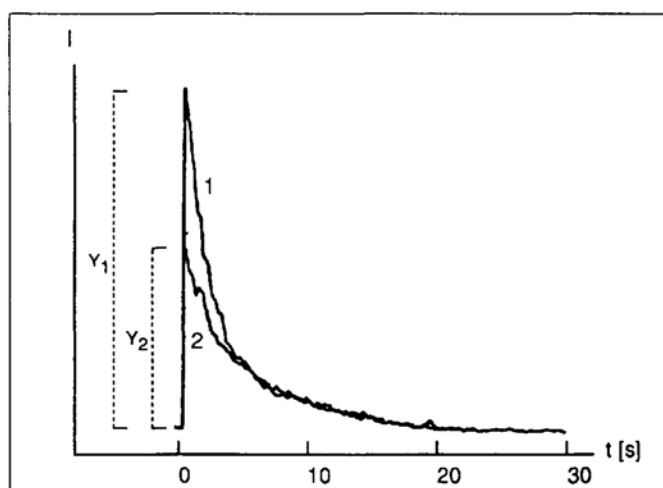|	BP/MeNP			CZ/NP		
N	1	2	3	4	5	6
6				0.45	0.77	0.77
10				0.28	0.64	0.60
16				0.12	0.49	0.51
28	0.48	0.86	0.87			
31				0.02	0.25	0.30
56	0.23	0.74	0.73			
70	0.16	0.68	0.70			

Fig. 4. *Phosphorescence of carbazole* (2·10^{-2} M in EtOH/EtOEt 2:1 at 77 K) *without Q* (Curve 1) *and with Q = naphthalene (NP)* ([NP]=0.1M, *Curve 2,* non-exponential decay). Y_1 corresponds to the total number of emitters, Y_2 to the number of free emitters. Intensity I: arbitrary units.

Why Are the Quenched Phosphorescence Decays Non-exponential?

The non-exponential decay of the phosphorescence of BP [15] and CZ [16] in the presence of quenchers has been attributed to a distance distribution of M/Q pairs within the *Dexter* EE model which assumes an exponential decrease of the quenching rate constant with distance. This treatment considers the centre-to-centre M/Q distance as a continuous variable, while we have pointed out above that this is unrealistic when this distance is of the order of molecular dimensions. It remains

that, in a simple model of discrete sites, the *Perrin* action volume theory should remain valid, so that quenching should be 'instantaneous' when M is in contact with Q, but should be 'infinitely slow' otherwise. Why then are the quenched phosphorescence decays non-exponential in these cases? Two factors could be responsible:

i) *Microscopic motions.* The action volume model assumes that the molecules do not move during the observation. This is clearly true for molecules in rigid matrices and excited state lifetimes shorter than a few µs, but there is evidence that translational motions of a few Å can take place over times of seconds in some soft glasses such as MTHF at 77 K, and in some mixed glasses [17]. This would of course lead to non-exponential decays.

ii) *Long-range triplet-triplet energy transfer of the* Förster *type.* In fluid media this mechanism does generally not play a role. In the present rigid systems the very long lifetime of the triplet donor state may, however, partly offset its low transition probability. (The quantum yield of phosphorescence for BP is ~ 1 in our matrix without Q.) An estimate of the critical transfer distance R is obtained as follows (*cf.* [18]).

Consider a singlet-singlet (SS) and a triplet-triplet energy-transfer system with same spectral overlap, energy range and quantum yield of donor (M) emission = 1. For the critical transfer distances, we obtain

$$\frac{R(TT)}{R(SS)} = \sqrt[6]{\frac{\mu_Q^2(T_0 \to T_1)}{\mu_Q^2(S_0 \to S_1)}} \qquad (12)$$

μ_Q is the transition moment for the respective acceptor (Q) transition which in turn is proportional to the square root of the corresponding radiative rate constant $(k_Q)^{1/2}$. Hence

$$\frac{R(TT)}{R(SS)} = \sqrt[6]{\frac{k_Q(T_0 \to T_1)}{k_Q(S_0 \to S_1)}} \qquad (13)$$

Taking Q = NP the ratio of the radiative rate constants in *Eqn. 13* is of the order of 10^{-6}. The critical $R(SS)$ can reach up to 100 Å, hence R may well come to some 10 Å. Triplet-triplet energy transfer may even take place beyond this distance although its effect on the observed emission kinetics *de facto* disappears. The role of the *Förster* mechanism of long-range triplet-triplet energy transfer, therefore, requires further detailed investigations in such systems, since the non-exponential regions of long-lived phosphorescence decays could

perhaps be traced to such long-range interactions.

Conclusions

The application of the *Perrin* action sphere model to real molecular systems presents two difficulties which have been ignored in many cases:

1) The distance between two molecules at the microscopic level cannot be treated as a continuous variable. Any realistic model must be based on the discrete distribution of molecules.

2) The average centre-to-centre distances of non-spherical molecules are useless quantities. Only the definition of 'contact' or 'separation' (by *n* solvent shells) can be useful, and even so the detailed microscopic nature of the contact must be taken into account. This requirement may appear obvious for molecules which contain only one specific active site (*e.g.* a 'chromophore' involved specifically in the action of emission or quenching).

3) A model of discrete sites takes into account both the discontinuous separations of molecules by solvent shells, and the approximative shapes of emitter (M) and quencher (Q) molecules. Computer simulations support the use of suitably modified *Perrin* equations as reasonably exact analytical solutions based on the concept of the 'quenching volume' in some (but by no means all) instances.

4) According to this model of discrete sites, the *vdW* contact between M and Q is a necessary (though not always sufficient) condition for ET in the ns to s timescale. This conclusion differs from previous appraisals of the same experimental results, based on models of continuously variable intermolecular distances.

Experimental

The steady-state luminescence spectra were measured on a conventional fluorimeter fitted with a *Dewar* vessel in which six sample tubes could be lowered in turn into the excitation beam. This arrangement improves the reproducibility of the measurements, since it is not necessary to open the cover of the *Dewar* vessel to change samples. The luminescence decay kinetics were measured by excitation with a nitrogen laser (*Oxford Lasers* type *KX-1*) of *ca.* 15 ns pulse duration. A grating monochromator was used to select the luminescence wavelength, the intensity being measured by a photomultiplier tube (*EMI 9785 C*) and displayed on a storage oscilloscope/ vidicon digitizer system which has been described previously [8].

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