External heavy-atom effect on fluorescence kinetics

Mário N. Berberan-Santos

Centro de Química-Física Molecular, Instituto Superior Técnico, 1049-001 Lisboa, Portugal. E–mail: berberan@ist.utl.pt

Fluorescence quenching in fluid solution by the external heavy-atom effect usually follows simple Stern–Volmer kinetics, and the quenching effect is gauged by the magnitude of the bimolecular quenching rate constant. However, it is the increased unimolecular $S_1 \rightarrow T_n$ intersystem crossing rate constant of the perturbed fluorophore in the perturber–fluorophore complex that can be directly compared with that of the unperturbed fluorophore. From a simple model for external heavy atom quenching in fluid solution, the decay law is predicted to be singly exponential for all quencher concentrations, and a new expression for the unimolecular $S_1 \rightarrow T_n$ intersystem crossing rate constant of the perturbed fluorophore is obtained. The same problem, but in rigid solution, is also discussed for the first time. The model now predicts a nonexponential fluorescence decay law, from which the unimolecular $S_1 \rightarrow T_n$ intersystem crossing rate constant of the perturbed fluorophore can be directly determined.

1. Introduction

The quenching of fluorescence by heavy atoms (*i.e.*, atoms of large atomic number), a phenomenon first identified as physical quenching by F. Perrin,[1] has been the subject of many studies.[2–18] Heavy atom quenching of fluorescence may occur in two different ways. Firstly, the heavy atom can be part of the chromophore under study; this is referred to as the internal heavy-atom effect.[2,4] If however the heavy atom is external to the chromophore, either intramolecularly (quenching moiety[11,14]) or intermolecularly, as the quencher (*e.g.* I⁻, Xe) or part of the quencher [*e.g.* CH₃I, Hg(CH₃)₂] then it is said to be the external heavy-atom effect.[3,4] The external process requires close contact between perturber and fluorophore, usually in the form of a statistical (contact) charge-transfer complex (exciplex with binding energy smaller than *kT*). In fluid media, this complex is short-lived, as it is both brought about and broken apart by the incessant diffusive motion of quencher and fluorophore. In rigid media, *e.g.* low temperature organic glasses, diffusion is prevented and the quenching is static: the perturber is effective only in the statistical pairs, trios, *etc.* that were trapped upon cooling (assuming that aggregation due to decreased solubility is unimportant).

Heavy atoms in the fluorophore or in close contact to it increase the rate of intersystem crossing (ISC) by strengthening spin–orbit coupling,[2,3] like in the electronic transitions in heavy atoms (*e.g.* Hg). Thus, the decrease of fluorescence yield (radiative transition $S_1 \rightarrow S_0$) is in most cases explained by an increase in the probability of the competing $S_1 \rightarrow T_n$ radiationless transition of the fluorophore. In some exceptional cases however, the incorporation of one or more heavy atoms in the structure (internal effect) significantly shifts the singlet and triplet energy levels with respect to those of the unperturbed chromophore,[19] modifying its photophysics in a manner unrelated to spin–orbit coupling strength variation. In the absence of such effects, the internal heavy-atom effect, resulting from the substitution of one or more light atoms
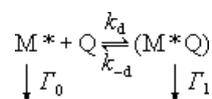
(usually hydrogens) by heavy atoms (usually bromines or iodines) on a given chromophore, is gauged by the concomitant increase of the $S_1 \rightarrow T_n$ intersystem crossing rate constant.

In the case of the external heavy-atom effect in fluid solution, simple Stern–Volmer kinetics is observed, and the effect is usually gauged by the magnitude of the bimolecular quenching rate constant.[5,7–10,13,18–20] It seems however desirable to also obtain from the experimental results the (unimolecular) $S_1 \rightarrow T_n$ intersystem crossing rate constant of the perturbed fluorophore. In fact, it is this constant that can be directly compared with that of the unperturbed fluorophore. Surprisingly, this was attempted in only one study,[21] but the derived equations were not general enough. In the present note, a simple kinetic scheme for external heavy atom quenching in fluid solution is proposed, and from it an expression for the (unimolecular) $S_1 \rightarrow T_n$ intersystem crossing rate constant of the perturbed fluorophore in the fluorophore–perturber(s) complex(es) is obtained, valid for all quencher concentrations. The corresponding fluorescence kinetics for solid solutions (rigid media) is also discussed. It is shown that analysis of experimental results should in this case allow a direct determination of the unimolecular $S_1 \rightarrow T_n$ intersystem crossing rate constant of the perturbed fluorophore, along with other parameters.

2. Kinetics in a fluid medium

A. Dilute solutions

For the external heavy atom quenching of the fluorescence of an excited molecule M* by a relatively dilute solution of quencher Q in a fluid medium, the following mechanism is considered:

$$M^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (M^*Q)$$
$$\downarrow \Gamma_0 \qquad \qquad \downarrow \Gamma_1$$

It is assumed that no stable (bound) complex between the ground or excited state fluorophore and Q exists. (M*Q) is therefore a statistical (contact) complex. It is also assumed that: (i) the concentration of M is much smaller than that of Q, as usual; (ii) Q is relatively dilute (below 0.1 M, say), so that the probability of statistical complexes of the type (M*Q$_n$), with $n > 1$, is negligible; (iii) no excited processes exist involving M* and Q, other than enhanced ISC. Electron transfer, in particular, is not considered.

The rate constants k_d and k_{-d} correspond to the formation and dissociation of the complex by mutual diffusion, and the rate constants Γ_0 and Γ_1 account for all unimolecular decay processes; the rate constant of the unperturbed fluorophore is therefore

$$\Gamma_0 = k_F + k_{IC} + k_{ISC}^0 = \frac{1}{\tau_0} \qquad (1)$$

where k_F is the radiative rate constant, k_{IC} is the internal conversion rate constant, k_{ISC} is the intersystem crossing rate constant, and τ_0 is the intrinsic lifetime. The effect of the perturber on the radiative and internal conversion processes is neglected, since the complex is assumed to be unstable, and the radiative transition (fluorescence) spin-allowed. It is therefore assumed that the perturbed fluorophore relaxation processes only differ by an increased intersystem crossing rate

$$\Gamma_1 = k_F + k_{IC} + k_{ISC}^1 = \frac{1}{\tau_1} \qquad (2)$$

or,

$$\Gamma_1 = \Gamma_0 + \Delta k_{ISC} \qquad (3)$$

where $\Delta k_{ISC} = k_{ISC}^1 - k_{ISC}^0$. In this way, the total fluorescence intensity will be directly proportional to the sum [M*] + [(M*Q)], since the radiative rate constant is the same for both species.

Considering the usual steady-state experiment (low intensity continuous irradiation, with intensity I), and supposing that only isolated molecules M are directly excited (i.e., that the fraction of M involved in ground state statistical pairs (MQ) is negligible), the following rate equations apply,

$$\frac{d[M*]}{dt} = I - \Gamma_0[M*] - k_d[M*][Q] + k_{-d}[(M*Q)] \qquad (4)$$

$$\frac{d[(M*Q)]}{dt} = -\Gamma_1[(M*Q)] + k_d[M*][Q] - k_{-d}[(M*Q)] \qquad (5)$$

One obtains for the photostationary state that

$$[M*] = \frac{I}{\Gamma_0 + \dfrac{k_d \Gamma_1 [Q]}{k_{-d} + \Gamma_1}} \qquad (6)$$

$$[(M*Q)] = \frac{k_d}{k_{-d} + \Gamma_1}[M*][Q] \qquad (7)$$

hence

$$[M*] + [(M*Q)] = I \frac{1 + \dfrac{k_d[Q]}{k_{-d} + \Gamma_1}}{\Gamma_0 + \dfrac{k_d \Gamma_1 [Q]}{k_{-d} + \Gamma_1}} \qquad (8)$$

For [Q] = 0, eqn. (8) reduces to

$$[M*]_0 = \frac{I}{\Gamma_0} \qquad (9)$$

The ratio of the fluorescence intensities in the absence, and in the presence of quencher, F_0 and F, respectively, is now obtained as

$$\frac{F_0}{F} = \frac{[M*]_0}{[M*] + [(M*Q)]} = \frac{1 + \dfrac{k_d}{k_{-d} + \Gamma_1}\left(\dfrac{\Gamma_1}{\Gamma_0}\right)[Q]}{1 + \dfrac{k_d}{k_{-d} + \Gamma_1}[Q]} \qquad (10)$$

Using eqn. (3), eqn. (10) becomes

$$\frac{F_0}{F} = 1 + \frac{\dfrac{k_d}{k_{-d} + \Gamma_1}\Delta k_{ISC}\tau_0[Q]}{1 + \dfrac{k_d}{k_{-d} + \Gamma_1}[Q]} \qquad (11)$$

Two limiting cases are now considered:

(a) $\Gamma_1 \gg k_{-d}$

For a solvent with a viscosity similar to that of a light alkane or water (ca. 0.5–1 cP; 1 cP = 10^{-3} Pa s), and at room temperature, the statistical complex lasts for only 5–50 ps (see the Appendix). In order to have $\Gamma_1 \gg k_{-d}$, the perturbed fluorophore lifetime cannot exceed a few picoseconds, i.e., it must be much shorter than the life span of the momentary complex. This implies a very high ISC rate induced by the perturber. In more viscous media, and/or at lower temperatures, the same inequality is fulfilled with correspondingly increased lifetimes. Whenever $\Gamma_1 \gg k_{-d}$ is valid, one receives from eqn. (11) the expected full diffusion-control result,

$$\frac{F_0}{F} = 1 + k_d \tau_0 [Q] \qquad (12)$$

All information concerning the rate of intersystem crossing is of course lost. Eqn. (12) is only approximately valid since transient effects are not considered.

(b) $k_{-d} \gg \Gamma_1$

In most cases, the dissociation rate constant of the complex is much higher than the decay rate of the perturbed fluorophore, $k_{-d} \gg \Gamma_1$, i.e., the perturbed fluorophore lifetime should greatly exceed that of the momentary complex. Again for a solvent with a viscosity similar to that of a light alkane or water, and at room temperature, $k_{-d} \gg \Gamma_1$ imposes on the perturbed fluorophore lifetime a lower limit of a few hundred picoseconds.

In the absence of strong electrostatic interaction (as would happen if M and Q were both charged species), the ratio k_d/k_{-d} is simply Avogadro's constant times $(4/3)\pi R_c^3$, where

R_c is the collision distance for the complex[22–24] (see also the Appendix). In this way, k_d/k_{-d} is a molar volume, V_m, close to that of the transient complex (M*Q). Eqn. (11) can thus be rewritten as

$$\frac{F_0}{F} = 1 + \frac{V_m \Delta k_{ISC} \tau_0 [Q]}{1 + V_m [Q]} \qquad (13)$$

For dilute solutions of Q, $V_m[Q] \ll 1$, and eqn. (13) reduces to

$$\frac{F_0}{F} = 1 + V_m \Delta k_{ISC} \tau_0 [Q] \qquad (14)$$

which has the Stern–Volmer form, $F_0/F = 1 + k_q \tau_0 [Q]$. The Stern–Volmer bimolecular quenching rate constant k_q is therefore related to the unimolecular intersystem crossing rate constants by

$$k_q = V_m \Delta k_{ISC} \qquad (15)$$

and the intersystem crossing rate constant of the perturbed fluorophore is

$$k_{ISC}^1 = k_{ISC}^0 + \frac{k_q}{V_m} \qquad (16)$$

which is the desired relation. An equation identical to eqn. (14) is obtained for the corresponding time-resolved experiment (flash excitation) where τ_0/τ is substituted for F_0/F, again under the assumption that $V_m[Q] \ll 1$.

It is of interest to note that the assumptions made above effectively correspond to a fast excited-state equilibrium between M* and (M*Q). This leads directly to the well-known result for excimer kinetics (high-temperature limit[20]) of a singly exponential decay whose decay constant is the average of the intrinsic decay constants of the two species. This result can be generalized and understood as follows: if a certain species participates in several fast equilibria,[25] then the decay of any of those species will be singly exponential, and the common decay rate will be the weighted average of all intrinsic decay rates (one for each species), the weighting factor being the fraction of time spent in each form, or equivalently, the fractional amount of each species. For the present problem one obtains

$$\Gamma = \frac{1}{\tau} = (1 - \alpha) \Gamma_0 + \alpha \Gamma_1 \qquad (17)$$

where α is the fraction of M* present as the statistical complex,

$$\alpha = \frac{V_m [Q]}{1 + V_m [Q]} \qquad (18)$$

and using eqn. (1) and (2), eqn. (13) is obtained from eqn. (17).

Owing to the fast equilibrium assumption, the inclusion of direct excitation of statistical ground state complexes (MQ) in the kinetic scheme, important for not too small α, does not change the final result, eqn. (13).

Within the two species model, eqn. (13) is more general than eqn. (14), because this last equation is only valid if $V_m[Q] \ll 1$. However, eqn. (13) will certainly fail if $V_m[Q] \geq 0.1$, since then complexes of the type (M*Q_n), with $n > 1$, become significant. This can be shown as follows: using again a molar volume for the complex, V_m, the probability that a given M* molecule will have n perturbers within that volume, (i.e., that a complex (M*Q_n) will be formed), is approximately given by the Poisson distribution,

$$P(n) = \frac{\bar{n}^n}{n!} \exp(-\bar{n}) \qquad (19)$$

where $\bar{n} = V_m[Q]$ is the average number of perturbers in "contact" with a generic M* fluorophore. Then, for $V_m[Q] = 0.1$ the calculated fraction of M* involved in complexes is 9.5%, and of these complexes, 94% have $n = 1$. But for $V_m[Q] = 0.5$, complexes with $n > 1$ already amount to 25% of all complexes. Consideration of complexes of the type (M*Q_n), with $n > 1$, is therefore required for $V_m[Q] > 0.1$, at least.

B. Concentrated solutions

Only fast excited state equilibrium (implying moderate perturber efficiency) is considered here. It is assumed that M* and (M*Q_n) ($n = 1, 2, ...$) have a common radiative rate constant, but that the ISC rate constant of (M*Q_n) is a linear function of n.[26]

$$\Gamma_n = \Gamma_0 + n \Delta k_{ISC} \qquad (20)$$

Eqn. (20) is a key assumption that appears to be experimentally validated by the linearity of Stern–Volmer plots with concentrated quenchers [see eqn. (24) below].

The fraction of each type of complex is approximately given by the Poisson distribution used above. For very concentrated solutions however, the existence of a maximum coordination number (maximum number of quenchers around the fluorophore) must be accounted for. This is particularly important for small fluorophores and bulky quenchers.

The correct distribution, valid for the entire concentration range, is the binomial one,

$$P(n) = \binom{N}{n} \left(\frac{\bar{n}}{N} \right)^n \left(1 - \frac{\bar{n}}{N} \right)^{N-n} \qquad (21)$$

where $\bar{n} = V_m[Q]$ is the average number of perturbers in "contact" with a generic M* fluorophore, $N = V_m [Q]_0$ is the maximum coordination number, and $[Q]_0$ is the concentration of the quencher in a pure quencher medium.

As discussed in Section 2A, the decays of M* and of all the (M*Q_n) ($n = 1, 2, ..., N$) will be single exponential, with a common decay rate constant given by

$$\Gamma = \sum_{n=0}^{N} \binom{N}{n} \left(\frac{\bar{n}}{N} \right)^n \left(1 - \frac{\bar{n}}{N} \right)^{N-n} (\Gamma_0 + n \Delta k_{ISC}) \qquad (22)$$

or

$$\Gamma = \Gamma_0 + \bar{n} \Delta k_{ISC} = \Gamma_0 + V_m \Delta k_{ISC} [Q] \qquad (23)$$

and a Stern–Volmer relation identical to eqn. (14) follows,

$$\frac{\tau_0}{\tau} = 1 + V_m \Delta k_{ISC} \tau_0 [Q] \qquad (24)$$

It is thus concluded that eqn. (14) is obeyed for all concentrations of Q, and is in fact more general than eqn. (13)!

C. Application

As an example of the application of eqn. (24), consider the quenching of the fluorescence of a derivative of the fullerene C_{70} by bromobenzene, in methylcyclohexane–bromobenzene mixtures at room temperature.[27] A linear Stern–Volmer plot is obtained for the entire concentration range, with a quenching rate constant of 1.4×10^8 dm^3 mol^{-1} s^{-1}, *i.e.*, well below diffusion control. Using van der Waals radii of 0.53 and 0.30 nm for the C_{70} derivative and for the quencher molecule, respectively, a molar volume of 1.4 dm^3 mol^{-1} is obtained for the encounter complex. From eqn. (24), one thus obtains that $\Delta k_{ISC} = k_{ISC}^1 - k_{ISC}^0 = 9.7 \times 10^7$ s^{-1}. Since the ISC rate of the unperturbed fullerene derivative in pure methylcyclohexane is 9.1×10^8 s^{-1},[27,28] it follows that $k_{ISC}^1 = 1.0 \times 10^9$ s^{-1}.

3. Kinetics in a rigid medium

For the external heavy atom quenching of the fluorescence of an excited molecule M* by a quencher Q in a rigid medium, the statistical complexes are static, since molecular translational motion is negligible in the time scale of interest. In this way, in order to have a significant effect, relatively concentrated solutions are required. This implies that not only the (M*Q) complex will be present, but that complexes of the type (M*Q$_n$) ($n = 2, 3,..., N$) will also exist in significant amounts. Assuming again that M* and (M*Q$_n$) have a common radiative rate constant, but that the ISC rate constant of (M*Q$_n$) is given by eqn. (20), the global fluorescence intensity will be given by

$$F = P(0)F_0 + P(1)\frac{\Phi_1}{\Phi_0}F_0 + P(2)\frac{\Phi_2}{\Phi_0}F_0 + ... + P(N)\frac{\Phi_N}{\Phi_0}F_0 \quad (25)$$

where

$$\frac{\Phi_n}{\Phi_0} = \frac{1}{1 + n\Delta k_{ISC}\tau_0} \qquad (26)$$

Here, and in opposition to the dynamic case, inclusion of direct absorption of exciting light by the static complexes in the kinetic model is mandatory, since F deviates from F_0 only for significant fractions of (M*Q$_n$).

Using eqn. (21) and (26), eqn. (25) can finally be rewritten as

$$\frac{F}{F_0} = \sum_{n=0}^{N} \binom{N}{n}\left(\frac{\bar{n}}{N}\right)^n\left(1 - \frac{\bar{n}}{N}\right)^{N-n}\frac{1}{1 + n\Delta k_{ISC}\tau_0} \qquad (27)$$

From this equation, a curved Stern–Volmer plot is predicted.

A limiting situation can be obtained from eqn. (27): if the complexes are essentially nonfluorescent, then eqn. (27) reduces to

$$\frac{F}{F_0} = \left(1 - \frac{\bar{n}}{N}\right)^N \qquad (28)$$

Eqn. (28) can in principle be used to obtain V_m and N from experiment. If $\bar{n} \ll N$ and N is large, eqn. (28) becomes

$$\frac{F}{F_0} = \exp(-V_m[Q]) \qquad (29)$$

i.e., a Perrin type[29] static quenching is obtained.

For the time-resolved experiment (flash excitation), a nonexponential decay law is predicted by the model:

$$I(t) = \sum_{n=0}^{N} \binom{N}{n}\left(\frac{\bar{n}}{N}\right)^n\left(1 - \frac{\bar{n}}{N}\right)^{N-n}\exp[(-\Gamma_0 + n\Delta k_{ISC})t] \qquad (30)$$

or, finally

$$I(t) = \exp(-\Gamma_0 t)\left[1 - \frac{\bar{n}}{N}(1 - e^{-\Delta k_{ISC}t})\right]^N \qquad (31)$$

If $\bar{n} = N$, the decay is singly exponential for all times. If $\bar{n} \ll N$, and N is large, the general eqn. (31) reduces to

$$I(t) = \exp(-\Gamma_0 t)\exp[-\bar{n}(1 - e^{-\Delta k_{ISC}t})] \qquad (32)$$

For long times, an exponential decay is recovered, with a fractional amplitude equal to the fraction of unperturbed molecules. For very short times, the decay is again exponential, with a decay constant $\bar{\Gamma} = \Gamma_0 + \bar{n}\Delta k_{ISC}$, as in a fluid medium. It is interesting to note that a decay law mathematically identical to eqn. (32) occurs in several dynamic quenching processes in micelles.[30(ref.therein)]

Analysis of the experimental steady state intensity *vs.* [Q], eqn. (27), or of the experimental decay for a single quencher concentration, eqn. (31), should allow the determination of V_m, N, and Δk_{ISC}.

4. Discussion and conclusions

For external heavy atom quenching in fluid solution, a simple Stern–Volmer kinetics is usually observed, and the magnitude of the effect is measured by the bimolecular quenching rate constant. However, it is the unimolecular $S_1 \rightarrow T_n$ intersystem crossing rate constant of the perturbed fluorophore in the perturber–fluorophore complex that can be directly compared with that of the unperturbed fluorophore. In this communication, a simple kinetic model for external heavy atom quenching in fluid solution was presented, yielding the observed Stern–Volmer behaviour for the whole composition range, and from it an explicit expression for decay rate constant, eqn. (23), and unimolecular $S_1 \rightarrow T_n$ intersystem crossing rate constant of the perturbed fluorophore, eqn. (16), are obtained. The calculation of the intersystem crossing rate constant by means of this relation requires the calculation of the molar volume associated to the complex, V_m. This volume may be estimated (from M and Q molecular dimensions) with reasonable accuracy. For the external heavy atom quenching of the fluorescence in a rigid medium, simple expressions for the fluorescence intensity, eqn. (27), and for the fluorescence decay, eqn. (31), were obtained. Analysis of experimental results should in this case allow the independent determination of V_m, of N, and of the unimolecular $S_1 \rightarrow T_n$ intersystem crossing rate constant of the perturbed fluorophore.

Acknowledgements

Appendix—equilibrium constant for a statistical complex (MQ)

Suppose that M and Q are solutes, whose molecules are spheres of radii R_M and R_Q, respectively, immersed in a continuum.[31] Suppose further that the concentration of Q is much higher than that of M. If the encounter complex (MQ) is defined as the entity made up by the joined spheres, with a center-to-center distance $R_c = R_M + R_Q$ (collision diameter), and if the complex is formed only by chance (statistical complex), then the fraction of M molecules present as the collision complex is always negligible, except for very concentrated solutions of Q, where most of the spheres are forced into permanent contact. This happens because for relatively dilute solutions, the probability of finding a Q molecule in contact with a M molecule is essentially zero (it is the probability of a single value out of a continuous distribution).

If however the collision complex is defined as a somewhat more loose entity, for which the center-to-center distance is contained between R_c and $R_c + \Delta R$, then a finite fraction of pairs will exist in the form of collision complexes. This second definition of statistical complexes is more realistic, given the molecular (granular) nature of the solvent, which leads to encounter processes, as opposed to gas phase collisions. If ΔR is arbitrarily chosen as $\Delta R = (2^{1/3} - 1) R_c = 0.26\ R_c$,[32] then the volume of the spherical shell around M that can be occupied by the center of a Q molecule is exactly $v = (4/3)\pi R_c^3$. The probability of finding an M molecule with a nearby Q molecule, with a center between R_c and $R_c + \Delta R$, will thus be $N_Q v/V$, where N_Q is the total number of Q molecules, and V is the volume of solution. This probability can be rewritten as $[Q] N_A v$, or $[Q] V_m$, where N_A is Avogadro's constant and V_m is a molar volume, $V_m = v N_A$. In this way, the number of M molecules present as complexes is $[Q] V_m N_M$, while that present as free M molecules is $(1 - [Q] V_m) N_M$. The corresponding concentrations are then $[Q] V_m N_M/V$ and $(1 - [Q] V_m) N_M/V$, respectively. If the possibility of complexes with two or more Q molecules is to be discarded, then one must have $V_m[Q] \ll 1$, and the concentrations of complexed and free M molecules become $[Q] V_m N_M/V$ and N_M/V. The equilibrium constant for the formation of the complex is therefore

$$K = \frac{V_m[Q](N_M/V)}{[Q](N_M/V)} = V_m$$

Since this constant can also be written in terms of the kinetic rate constants for the formation and dissociation of the complex, k_d and k_{-d}, the relation $V_m = k_d/k_{-d}$ is finally obtained.

This relation allows the calculation of k_{-d} from the values of k_d and V_m. Using the well-known approximate relation $k_d = (8RT)/(3\eta)$, where R is the perfect gas constant, T is the temperature, and η is the viscosity of the medium, one obtains $k_{-d} = (2k_BT)/(\pi R_c^3\eta)$, where k_B is the Boltzmann constant. If $T = 300$ K, $R_c = 3$ Å, and $\eta = 1$ cP $= 10^{-3}$ Pa s, then $k_{-d} = 10^{11}$ s^{-1}, and the lifetime of the statistical complex, $1/k_{-d}$, is 10 ps.

References

1   (a) F. Perrin, *J. Phys. Radium*, 1926, **7**, 390; (b) F. Perrin, *J. Chim. Phys.*, 1928, **25**, 531; (c) F. Perrin, *Fluorescence*, Hermann, Paris, 1931.

2   D. S. McClure, *J. Chem. Phys.*, 1949, **17**, 905.

3   M. Kasha, *J. Chem. Phys.*, 1952, **20**, 71.

4   S. P. McGlynn, R. Sunseri and N. Christodouleas, *J. Chem. Phys.*, 1962, **37**, 1818.

5   T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, 1965, **61**, 620.

6   S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 1966, **66,** 199.

7   A. R. Horrocks and F. Wilkinson, *Proc. R. Soc. London, Ser. A*, 1968, **A306**, 257.

8   R. P. DeToma and D. O. Cowan, *J. Am. Chem. Soc.*, 1975, **97**, 3283.

9   J. Bendig, S. Helm and D. Kreysig, *Chem. Phys. Lett.*, 1978, **54**, 466.

10 H. Dreeskamp and J. Pabst, *Chem. Phys. Lett.*, 1979, **61**, 262.

11 (a) S. A. Nairn, C. L. Braun, P. Caluwe and M. Szwarc, *Chem. Phys. Lett.*, 1978, **54**, 469; (b) R. S. Davidson, R. Bonneau, J. Joussot-Dubien and K. R. Trethewey, *Chem. Phys. Lett.*, 1980, **74**, 318.

12 M. A. Morgan and G. C. Pimentel, *J. Phys. Chem.*, 1989, **93**, 3056.

13 J. M. G. Martinho, *J. Phys. Chem.,* 1989, **93**, 6687.

14 G. Basu, K. M. Kubasic and D. Anglos, *J. Phys. Chem.*, 1993, **97**, 3956.

15 B. F. Minaev, S. Knuts and H. Agren, *Chem. Phys.*, 1994, **181**, 15.

16 T.-S. Kim, Y. S. Choi and K. Yoshihara, *Chem. Phys. Lett.*, 1995, **247**, 541.

17 M. Maeda, U. Graf and S. Hirayama, *Chem. Phys. Lett.*, 1996, **257**, 175.

18 S. S. Jayanthi and P. Ramamurthy, *J. Chem. Soc. Faraday Trans.*, 1998, **94**, 1675.

19 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin, Menlo Park, CA, 1978.

20 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, New York, 1970.

21 Y. Shimizu and T. Azumi, *J. Phys. Chem.*, 1982, **86**, 22.

22 M. Eigen, *Z. Phys. Chem. (Munich)*, 1954, **1**, 176.

23 R. M. Fuoss, *J. Am. Chem. Soc.*, 1958, **80**, 5059.

24 J. I. Steinfeld, J. S. Francisco and W. L. Hase, *Chemical Kinetics and Dynamics*, Prentice-Hall, Upper Saddle River, NJ, 2nd edn., 1999.

25 For the purposes of the discussion, 'fast' means 'occurring on a time scale much shorter than that of the fastest intrinsic decay'.

26 J. Najbar, *Chem. Phys. Lett.*, 1982, **90**, 154.

27 S. Foley, M. N. Berberan-Santos, A. Fedorov, D. J. McGarvey, C. Santos and B. Gigante, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, ed. P. V. Kamat, D. M. Guldi and K. M. Kadish, Electrochem. Soc., Pennington, NJ, 1999, vol. 7, pp. 368–380.

28 S. Foley, M. N. Berberan-Santos, A. Fedorov, D. J. McGarvey, C. Santos and B. Gigante, *J. Phys. Chem. A*, 1999, **103**, 8173.

29 F. Perrin, *C. R. Acad. Sci. (Paris)*, 1924, **178**, 1978.

30 E. N. Bodunov, M. N. Berberan-Santos and J. M. G. Martinho, *Chem. Phys. Lett.*, 1998, **297,** 419.

31 In Fuoss's derivation, ref. 23, both particles are point-like and the collision complex is defined as a pair for which the distance between particles is smaller or equal than a certain value *a*.

32 Other slightly different values for hard sphere models are found in the literature, namely $\Delta R = (2^{1/2} - 1)$ $R_c = 0.41$ R_c,[33] $\Delta R = 0.43$ R_c,[34] and $\Delta R = 0.7$ R_c,[34] the last value being less appropriate in our case, as it is obtained from a model where solute and solvent molecules have the same size.

33 J. W. Moore and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 3rd edn., 1981.

34 S. W. Benson, *The Foundations of Chemical Kinetics*, McGraw-Hill, New York, 1960.