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Fluorescence quenching with exponential distance dependence: Application to the external heavy-atom effect

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A model for fluorescence quenching with exponential distance dependence is developed and applied to external heavy-atom quenching. The systems studied are C_{70}-bromobenzene and phenanthrene-iodide, in liquid solutions at room temperature and in rigid glasses at 77 K. The predicted parameter correlation is observed in the two systems, which correspond to two extreme and opposite situations, strong and weak quenching. A detailed analysis of the fitted parameters allows the determination of the effective Bohr radii L and of the intrinsic unimolecular rate constants for quenching at contact, k_0. The unusually high value of L for the C_{70}-bromobenzene pair is tentatively attributed to the extended size of the external part of the π orbitals of the fullerene. The room temperature quenching rate constant computed with the determined low-temperature parameters is shown to be in good agreement with the experimental one for both systems studied.
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I. INTRODUCTION

The intermolecular quenching of phosphorescence by resonance electronic energy transfer and the intermolecular quenching of luminescence (both fluorescence and phosphorescence) by electron transfer are known to closely follow an exponential dependence with distance,[1]

$$k(r)=A\exp\left(-\frac{2r}{L}\right)=k_0\exp\left[-\frac{2(r-d)}{L}\right], \tag{1}$$

where k_0 is the quenching rate constant for the distance of closest approach (collisional radius) d, and L is called the effective tunneling length in the context of electron transfer, and effective average Bohr radius in the context of electronic energy transfer. Equation (1) is only approximate, one reason being that the molecular shape is usually far from spherical. The true rate constant is not only a function of relative distance but also of relative orientation. The exponential distance dependence of Eq. (1) results from the extent of spatial overlap of the electron clouds of excited molecule and quencher. The parameter L, initially introduced by Dexter for resonance electronic energy transfer between atoms by the exchange mechanism,[2] originated from the simplified form of the electronic wave functions at large distances from the nuclei. In the molecular case, L is best regarded as an empirical parameter. For energy transfer by the exchange mechanism, L was reported to take values between 0.7 and 6 Å, depending on the donor–acceptor pair.[3] A typical value of L for intermolecular electron transfer[4,5] is 1.5 Å.

Luminescence can also be quenched by off-resonance enhanced intersystem crossing. This may occur either by interaction with paramagnetic quenchers, or by quenchers with strong intramolecular spin–orbit coupling, the so-called heavy-atom quenchers. According to Minaev *et al.*,[6] in the last case, the off-resonance quencher promotes intersystem crossing by back-charge transfer. In a study of the fluorescence quenching of several aromatic compounds by the paramagnetic O_2 molecule, and where off-resonance enhanced intersystem crossing is probably operative, Camyshan *et al.*[7] found values of L between 1 and 2 Å. Finally, for the external heavy-atom effect, values of L similar to those of the other mechanisms are expected. An estimate of L for this effect can be made on the basis of the already mentioned theoretical work by Minaev *et al.*,[6] where from the computed distance dependence of the radiative constant for $T_1 \rightarrow S_0$ in ethylene in the presence of Br^- one obtains an exponential dependence with $L=0.94$ Å. In studies of the quenching of carbazole[8] and phenanthrene[9] fluorescence by iodide, Najbar *et al.* report estimated values of L of 1.3 and 1.8 Å, respectively.

The decay law for luminescence quenching with exponential distance dependence was considered by several authors. In a pioneering work, Inokuti and Hirayama[10] obtained a much used decay law (hereafter called IH law) for the decay of luminescence in rigid medium, under the assumption of point particles. Later, Hara and Gondo[11] considered the case of particles of finite size, but their results contained some errors that were corrected by Taen.[12] Before Hara and Gondo, Rikenglaz and Rozman[13] also considered the problem with $d>0$, obtaining the correct solution and also a simplified but not very accurate equation for the decay (later used by Brown and Wilkinson,[3] but given with two errors in the respective paper). Several extensions of the decay law, taking into account the effect of molecular diffusion, are available.[1]

In this paper, the fluorescence decay law resulting from quenching by a mechanism with an exponential dependence and nonzero distance of closest approach, Eq. (1), is applied to the external-heavy atom effect. The formalism is reanalyzed in Sec. II, with some new parameters introduced, and

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recast in a convenient form for infinite three-dimensional rigid and fluid media (rapid diffusion limit). The problem of parameter recovery is considered in some detail. In Sec. IV, the results are applied to the experimental study of the fluorescence quenching of two molecules, C_{70} and phenanthrene, by two heavy-atom quenchers, bromobenzene and iodide, respectively. The main conclusions are summarized in Sec. V.

II. THEORY

A. Formalism

Fluorescence decay by quenching is in competition with the intrinsic decay (rate constant $1/\tau_0$). It is efficient only if the rate constant for quenching is greater than or equal to the intrinsic decay rate. In their pioneering treatment of exchange energy transfer, Hinokuti and Hirayama[10] defined a dimensionless parameter γ,

$$\gamma=\ln(A\tau_0)=\ln[k(0)\tau_0]. \tag{2}$$

This parameter is a measure of the efficiency of quenching for $r=0$. By analogy with the dipole–dipole mechanism, where a critical distance R_0 is defined as the distance for which the intrinsic decay and the transfer process (in a pair) have identical rate constants, Inokuti and Hirayama[10] also defined the same critical distance for the exchange mechanism. From the condition

$$k(R_0)=\frac{1}{\tau_0} \tag{3}$$

one easily obtains that

$$R_0=\frac{L}{2}\ln(A\tau_0)=\frac{L}{2}\gamma. \tag{4}$$

The introduction of a nonzero distance of closest approach d leads us to the following generalization of parameter γ:

$$\gamma=\ln(k_0\tau_0)=\ln(A\tau_0)-\frac{2d}{L}, \tag{5}$$

where k_0 is the quenching rate constant at contact, $k_0=k(d)$.

Note that a low value of γ can result either from a low absolute quenching effect (low k_0), or from a short intrinsic lifetime τ_0. Likewise, a high value of γ can result either from a high absolute quenching effect (high k_0), or from a long intrinsic lifetime τ_0.

The critical radius can now be written

$$R_0=d+\frac{L}{2}\gamma, \tag{6}$$

and the rate constant

$$k(r)=\frac{1}{\tau_0}\exp\left[\frac{2}{L}(R_0-r)\right]=\frac{1}{\tau_0}\exp\left[\gamma\left(1-\frac{r-d}{R_0-d}\right)\right]. \tag{7}$$

For the dipole–dipole mechanism of electronic energy transfer, the distance $r_{\max}=2R_0$, for which the rate constant is 1/64th of the intrinsic decay rate, is usually taken as the maximum distance for which the quenching is significant.[14] Application of the same criterion to the exchange mechanism yields

$$r_{\max}=R_0+3\ln 2L\approx R_0+2L=d+2L\left(1+\frac{\gamma}{4}\right). \tag{8}$$

This definition of $r_{\max}$ (distance for which the rate constant is 1/64th of the intrinsic decay rate) does not imply that quenching for distances larger than $r_{\max}$ cannot occur. However, the respective probability is very low, and $r_{\max}$ is a useful measure of the interaction range.[14]

It follows from Eq. (8) that the lowest meaningful value for the parameter γ is -4, corresponding to $r_{\max}=d$, and thus to very weak quenching. Below this value, the quenching is entirely negligible. In general, the quenching process can be said to take place almost exclusively in a spherical shell around the excited molecule delimited by spheres of radii d and $r_{\max}$, and whose thickness is $2L(1+\gamma/4)$.

It is interesting to note that for very low quenching efficiencies the exponential mechanism implies negative R_0 values, whereas in the dipole–dipole mechanism, values close to zero are obtained. In both cases this is a consequence of the respective distance dependence, and no direct physical meaning is attributable to these hypothetical distances.

B. Decay law

The decay law is conveniently obtained from the following approach:[15]

The general decay law $I(t)$ with quenching is given by

$$I(t)=\exp(-t/\tau_0)\exp\left(-\int_0^t k(u)\,du\right), \tag{9}$$

where the time-dependent rate constant is

$$k(t)=\int_0^\infty N(r,t)k(r)\,dr, \tag{10}$$

and $N(r,t)$ is the number of quenchers at a distance r at time t. Note that Eq. (10) implies an assumption of additivity of contributions from different quenchers. It is also implicitly assumed in Eq. (9) that the intrinsic lifetime is the same, irrespective of the distance between fluorophore and quencher. This assumption is a reasonable one for fluorescence.

In a fluid medium, $N(r,t)$ is obtained from a diffusion equation.[1] Two limiting cases suffice for our purposes.

1. Rapid diffusion limit

This limit is, for instance, verified in liquid solutions at room temperature with relatively low quenching efficiencies. In such a case, $N(r,t)$ is time independent, and constantly equal to the equilibrium value $N(r)=N(r,0)$,

$$N(r)=Nf(r)=N_A[Q]4\pi r^2 g(r), \tag{11}$$

where $f(r)$ is the distance distribution function and $g(r)$ is the radial distribution function. It is clear that the short-time rate constant for any system, whether with or without diffusion, coincides with the rapid diffusion limit result, since the initial distribution of acceptors is always the equilibrium one.

Assuming that the radial distribution function is a step function, i.e., that the quenchers are randomly and independently distributed around the excited molecule, and that no stable charge-transfer complex exists,

$$g(r)=\begin{cases}0 & \text{if } r<d\\ 1 & \text{if } r>d,\end{cases} \tag{12}$$

where d is the distance of closest approach, one obtains, with

$$k=k_q[Q], \tag{13}$$

that the decay is exponential, with

$$k_q=\frac{4}{3}\pi N_A\int_d^\infty 3r^2k(r)dr, \tag{14}$$

and if the rate constant is assumed to vary exponentially with distance according to Eq. (1), one gets from Eq. (14) that the quenching rate constant is in the rapid diffusion limit,

$$k_q=k_{rd}=\pi N_A\left[1+2\frac{d}{L}+2\left(\frac{d}{L}\right)^2\right]L^3k_0. \tag{15}$$

This equation was obtained before in a different but equivalent form.[13]

2. Static limit

This limit corresponds to diffusionless molecules, e.g., in a low-temperature glass. One has

$$\begin{aligned}N(r)&=Nf(r)\exp[-k(r)t]\\&=N_A[Q]4\pi r^2g(r)\exp[-k(r)t],\end{aligned} \tag{16}$$

and therefore, with the previously assumed step radial distribution function, Eq. (12),

$$k_q(t)=\frac{4}{3}\pi N_A\int_d^\infty 3r^2k(r)\exp[-k(r)t]dr, \tag{17}$$

hence

$$\int_0^t k_q(u)du=\frac{4}{3}\pi N_A\int_d^\infty 3r^2(1-\exp[-k(r)t])dr. \tag{18}$$

Inserting Eqs. (1) and (18) into Eq. (9), the decay law becomes[12,13]

$$\begin{aligned}I(t)=\exp\left(-\frac{t}{\tau_0}\right)\exp\Bigg\{&-4\pi N_A[Q]\\&\times\int_d^\infty r^2[1-\exp(-Ate^{-2r/L})]dr\Bigg\}.\end{aligned} \tag{19}$$

This decay law admits several alternative forms. A convenient one is obtained by performing the change of variable $x=2(r-d)/L$, giving

$$\begin{aligned}I(t)=\exp\left(-\frac{t}{\tau_0}\right)\exp\Bigg\{&-\alpha\int_0^\infty 3(x+\beta)^2\\&\times\left[1-\exp\left(-\frac{t}{\tau_0}e^{\gamma-x}\right)\right]dx\Bigg\},\end{aligned} \tag{20}$$

with

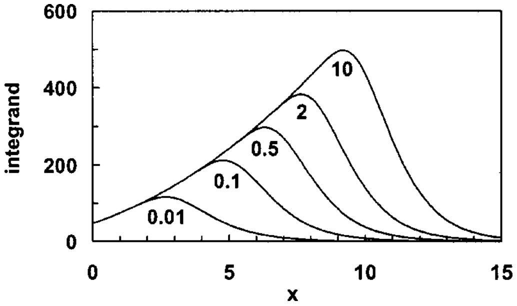

FIG. 1. Integrand function in Eq. (20) for several values of the dimensionless time t/τ_0, and for $\gamma=8$ and $\beta=4$.

$$\alpha=V_m[Q], \tag{21}$$

where

$$V_m=\frac{4}{3}\pi N_A\left(\frac{L}{2}\right)^3, \tag{22}$$

and with

$$\beta=\frac{2d}{L}, \tag{23}$$

and γ is given by Eq. (5). The decay law is therefore a function of the dimensionless parameters α, β, and γ. This decay law reduces to the Inokuti–Hirayama one for $\beta=0$. The general decay law also converges to the IH law for very long times. Indeed, the integrand's maximum increases and shifts to higher x values with time, as shown in Fig. 1 for $\beta=4$ and $\gamma=8$.

C. Numerical aspects

The integrand in Eq. (20) decays very quickly to zero after a certain value of x (this value of x increases with time). This means that for the computation of the decay law with recourse to numerical integration, it is appropriate to use a finite upper integration limit. This value can be found as follows: The longest time for which the decay is recorded seldom exceeds $5\tau_0$. Also, taking $L=1$ Å, $d=5$ Å, and $R_0=10$ Å, an upper bound for γ is obtained from Eq. (6), $\gamma=10$. A plot of the integrand of the decay law, Eq. (20), is shown in Fig. 2 for $t=5\tau_0$, $\gamma=10$, and for $\beta=0$, 5, and 10. Inspection of the plot suggests that the upper integration limit can be set equal to 20, or to even less, depending on the

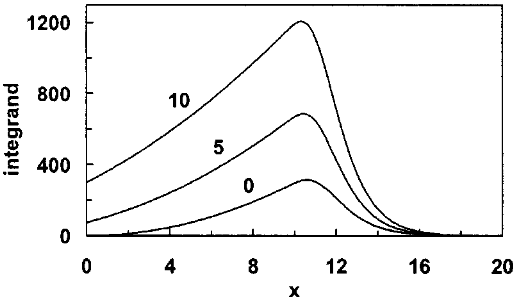

FIG. 2. Integrand function in Eq. (20) for $t=5\tau_0$, $\gamma=10$, and for $\beta=0$, 5, and 10.

system (cf. also Fig. 1). This was confirmed by a rigorous evaluation of the truncation error, that was always negligible.

One also observes that the integrand goes as $3(x+\beta)^2$ almost up to the maximum, and then decreases sharply at approximately $x=\gamma+\ln(t/\tau_0)$. This means that for very long times, or very large γ, the integrand can be approximately replaced by $3(x+\beta)^2$, and the upper integration limit by $\gamma+\ln(t/\tau_0)$, yielding

$$\begin{aligned} I(t) &= \exp\left(-\frac{t}{\tau_0}\right)\exp\left(-\alpha\int_0^{\gamma+\ln(t/\tau_0)} 3(x+\beta)^2\,dx\right)\\ &= \exp\left(-\frac{t}{\tau_0}\right)\exp\{-\alpha([\ln(e^{\gamma+\beta}t/\tau_0)]^3-\beta^3)\}, \end{aligned} \qquad (24)$$

the limiting form being

$$\begin{aligned} I(t) &= \exp\left(-\frac{t}{\tau_0}\right)\exp\{-\alpha[\ln(e^{\gamma+\beta}t/\tau_0)]^3\}\\ &= \exp\left(-\frac{t}{\tau_0}\right)\exp\{-\alpha[\ln(At)]^3\}. \end{aligned} \qquad (25)$$

This interesting decay law can be rigorously derived from a suitable series expansion.[13] However, it is usually attained only for very long times, and is of little practical interest in the fields of molecular energy transfer and enhanced intersystem crossing. It is nevertheless appropriate for the reaction of solvated electrons.[1]

D. Parameter correlation

1. General aspects

The general decay law, Eq. (20), is a function of the three dimensionless parameters α, β, and γ (the intrinsic lifetime τ_0 is usually known). From a fit of this law to the experimental decay it is, in principle, possible to recover these parameters, when they have a significant effect on the decay. However, parameter correlation cannot be excluded *a priori*. Specifically, we investigate here the recovery of parameter β, from which the distance of closest approach d can be calculated.

It was shown by Rikenglaz and Rozman[13] and by Taen[12] that the introduction of a nonzero distance of closest approach significantly affects the shape of the decay law, that is, the decay law corresponding to the parameter set (α, β, γ) is in general quite different from that for the IH set $(\alpha, 0, \gamma)$. However, it is important to ask if the true parameter set $(\alpha_1, \beta_1, \gamma_1)$ is the only one that adequately describes the experimental decay, recorded in a finite time range and contaminated with noise. In particular, is there an IH set $(\alpha_0, 0, \gamma_0)$ equivalent to the set $(\alpha_1, \beta_1, \gamma_1)$ in terms of goodness of fit?

This question can be pragmatically answered by performing two fits to the experimental decay: The first fit, with the general decay law containing the three fitting parameters (α, β, γ), and a second one, with the IH law, which has only two fitting parameters (α, γ). If the two fits are equally good, as judged by the respective chi-squared values and associated residues plot, then parameter correlation is present. An alternative approach is to perform a correlation analysis of the parameters of the general fit, but the task is much more delicate and time consuming.

2. Small γ

The mathematical form of the parameter correlation is now discussed. Performing a series expansion of the integrand of the decay law, and integrating term by term

$$\begin{aligned} &\alpha\int_0^\infty 3(x+\beta)^2\left[1-\exp\left(-\frac{t}{\tau_0}e^{\gamma-x}\right)\right]dx\\ &\quad= -3\sum_{n=1}^{\infty}\frac{1}{n!n^3}\left(-\frac{t}{\tau_0}\right)^n \alpha e^{n\gamma}(2+2n\beta+n^2\beta^2). \end{aligned} \qquad (26)$$

If the IH decay law ($\beta=0$) and the general decay law are both to fit equally well with the experimental decay, all coefficients should exactly match. This is not possible in general, but two coefficients of the expansion can always be made to coincide. Taking the first and second coefficients, the following system of equations is obtained:

$$\begin{aligned} \alpha_0 e^{\gamma_0} &= \alpha e^{\gamma}(1+\beta+\tfrac{1}{2}\beta^2)\\ \alpha_0 e^{2\gamma_0} &= \alpha e^{2\gamma}(1+2\beta+2\beta^2), \end{aligned} \qquad (27)$$

which gives

$$\begin{aligned} \alpha &= \frac{1+2\beta+2\beta^2}{(1+\beta+\frac{1}{2}\beta^2)^2}\alpha_0\\ \gamma &= \gamma_0+\ln\left(\frac{1+\beta+\frac{1}{2}\beta^2}{1+2\beta+2\beta^2}\right), \end{aligned} \qquad (28)$$

and thus, if for a given set (α, β, γ) a fit with the IH law is good, the parameters (a_0, γ_0) of this law will obey Eqs. (28). From these equations it is seen that the parameter γ_0 changes slightly with β, varying between γ and $\gamma+\ln 4 \approx \gamma+1.39$, while the parameter α_0 increases continuously with β.

The series expansion coefficients can be written as

$$c_n = f_n c_n^0, \qquad (29)$$

where

$$f_n = \frac{1+n\beta+\dfrac{n^2}{2}\beta^2}{1+\beta+\frac{1}{2}\beta^2}\left(\frac{1+\beta+\frac{1}{2}\beta^2}{1+2\beta+2\beta^2}\right)^{n-1}. \qquad (30)$$

It is clear that $f_1=f_2=1$ for all β. The following f_n coefficients ($n=3,4,\ldots$) are still reasonably close to unity for small β. Even for large β, $f_3=0.5625$ and $f_4=0.25$. Furthermore, a partial compensation also occurs because the series coefficients are alternately positive and negative. In this way, when the decay law is well represented by the first few coefficients, which implies a low value of γ ($\gamma<2$), a correlation of parameters in the form of Eq. (28) is expected. Note that for very low γ, not even the second term of the expansion in Eq. (26) is significant, and only one equation ties the three parameters. The situation is, however, of little practical relevance.

3. Large γ

For reasonably large values of γ ($\gamma>5$), many coefficients in the expansion contribute to the decay, and Eqs. (28) are no longer valid. This does not mean, however, that in these conditions the three parameters can be unambiguously obtained. In fact, by performing the variable change $y=x+\Delta\beta$, the integral in Eq. (20) can be written as

$$\int_0^\infty 3(x+\beta_1)^2\left[1-\exp\left(-\frac{t}{\tau_0}e^{\gamma_1-x}\right)\right]dx$$
$$=\int_0^\infty 3(x+\beta)^2\left[1-\exp\left(-\frac{t}{\tau_0}e^{\gamma-x}\right)\right]dx$$
$$-\int_0^{\Delta\beta} 3(x+\beta)^2\left[1-\exp\left(-\frac{t}{\tau_0}e^{\gamma-x}\right)\right]dx, \qquad (31)$$

where

$$\beta=\beta_1-\Delta\beta, \quad \gamma=\gamma_1+\Delta\beta. \qquad (32)$$

Now, the first term in the right-hand side of Eq. (31) is identical in form to the left-hand side. When the second term in the r.h.s. is negligible with respect to the first, or when it is constant for all times of interest, a correlation is observed, as follows from Eqs. (32), that imply a linear relation between the parameters γ and β,

$$\gamma=(\gamma_1+\beta_1)-\beta, \qquad (33)$$

the parameter α remaining constant at α_1. The correlation is possible when the second term in the r.h.s. is a constant because the decay law is an exponential function of Eq. (31), and the constant is absorbed in the pre-exponential factor, that is automatically adjusted in the process of curve fitting. Fulfillment of the linear correlation for $\Delta\beta$ values significantly different from 0 is only possible for large γ. Consider Fig. 1, for instance ($\gamma=8$, $\beta=4$). All the curves shown, including the extreme ones, that define the time interval of experimental relevance, practically coincide for $x<2$. In general, it follows from the form of the integrand that the maximum value $x_{\max}$ can be found from

$$\frac{t}{\tau_0}\exp(\gamma-x_{\max})=2.5, \qquad (34)$$

where 2.5 is chosen so that the term within square brackets in Eq. (20) is close to unity. Considering a minimum reduced time $t/\tau_0=0.01$, $x_{\max}=\gamma-5.5$. Using Eq. (32),

$$x_{\max}=\gamma_1+\Delta\beta-5.5. \qquad (35)$$

If $\Delta\beta>0$, then $x_{\max}=\Delta\beta$ and it follows from Eq. (35) that the linear correlation is valid for $\gamma_1>5.5$, and for all values of $\Delta\beta$, that is, $\beta=0$ (IH law) until $\beta=\beta_1$. If, on the other hand, $\Delta\beta<0$, then $x_{\max}=0$ and it follows from Eq. (35) that $\Delta\beta>5.5-\gamma_1$. For $\Delta\beta=5.5-\gamma_1$, $\gamma=5.5$. For the linear correlation to be valid, the minimum possible value for γ is therefore 5.5. The numerical value, found for a minimum reduced time of 0.01, can in practice be somewhat lower, depending on the relative contribution of the short times of the decay to the overall goodness-of-fit chi-squared parameter.

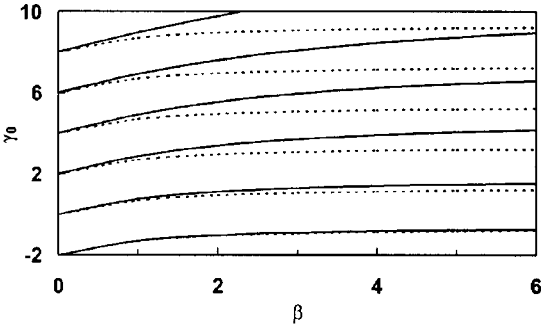

FIG. 3. Fitted parameter γ_0 as a function of β. For each curve, $\gamma=\gamma_0(0)$. the dotted lines correspond to Eq. (28).

4. Intermediate γ

Even when Eqs. (28) and (33) are not valid, i.e., when γ is neither small ($\gamma<2$) nor large ($\gamma>5$), a correlation is in principle still possible, with the parameter α departing from α_1. This is indeed observed. To demonstrate this correlation in a simple way (the general analytical study being not feasible), the integral in Eq. (20) was numerically fitted with the integral of the IH decay law. The resulting parameter correlation is shown in Figs. 3 and 4. In all cases a satisfactory fit was obtained.

It should be noted that the parameter correlation to be observed when fitting the fluorescence decays will not be quantitatively identical to the present one, as a further parameter (normalization constant) exists. The fact that a satisfactory fit can be made even with one parameter less, conclusively proves that it is not possible in general to recover all three parameters (α, β, γ) from the experimental fluorescence decays.

III. EXPERIMENT

A. Systems studied

The systems studied were C_{70}-bromobenzene and phenanthrene-sodium iodide. Samples were prepared in solvent mixtures that gave good glasses at low temperatures and having constant concentrations of C_{70} and phenanthrene but with several quencher concentrations. C_{70} (Aldrich, 99%) was dissolved in a 7:2 (v/v) methylcyclohexane-toluene mixture (to be referred to as MT) and phenanthrene (Fluka ≥97.0 % HPLC grade) was dissolved in a 4:1

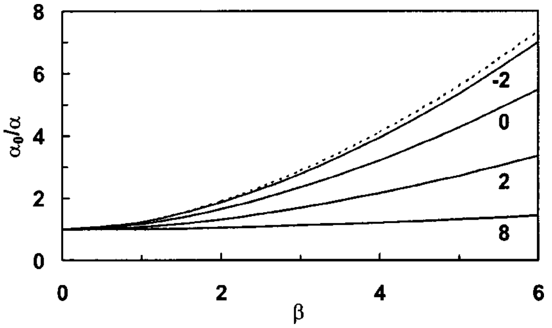

FIG. 4. Fitted parameter ratio α_0/α as a function of β. The value of γ is displayed for each curve. The dotted line corresponds to Eq. (28).

ethanol-methanol mixture (to be referred to as EM). Pure bromobenzene also gives a clear glass at 77 K. Methylcyclohexane (Aldrich, 99% spectrophotometric grade), toluene (Merck, spectroscopic grade), ethanol (Merck, spectroscopic grade), methanol (Riedel de Haën, spectroscopic grade), bromobenzene (Riedel de Haën, 98%), and sodium iodide (Aldrich, 99.999%) were used as supplied. Fullerene and phenanthrene concentrations were typically 5×10^{-5} mol L^{-1} and 1×10^{-5} mol L^{-1}, respectively. The solutions were not degassed. The concentrations of the quenchers in the low-temperature glasses were calculated from the room-temperature ones, by using the appropriate volume contraction factors.[16]

B. Fluorescence decays

Time resolved picosecond fluorescence measurements were performed using the single-photon timing method with laser excitation. The setup consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye (Rhodamine 6G) laser, delivering 3–4-ps pulses (with approximately 40 nJ pulse) at a frequency of 3.4 MHz. Intensity decay measurements were made by alternate collection of impulse and decay, with the emission polarizer set at the magic angle position. Impulse was recorded slightly away from excitation wavelength with a scattering suspension. For the decays, a cutoff filter was used, effectively removing all excitation light. C_{70} solutions were excited at 593 nm and phenanthrene solutions at 292 nm. The emission signal passed through a depolarizer, a Jobin-Yvon HR320 monochromator with a grating of 100 lines/mm, and was recorded on a Hammamatsu 2809U-01 microchannel plate photomultiplier as a detector. A time scale range of 1.37–2.75 ps/channel was used for the C_{70} samples and 96.7–286 ps/channel for phenanthrene samples. The instrument response function had an effective full width at half maximum of 35 ps. Usually no less than 10 000 counts for C_{70} and 20 000 counts for phenanthrene were accumulated at the maximum channel.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. C_{70}-bromobenzene

The room-temperature fluorescence decays in MT were single exponential for all quencher concentrations. In the absence of quencher, the measured lifetime was 630 ps. In pure bromobenzene, the measured lifetime was 270 ps. Both values are in good agreement with previous reports.[17,18]

The room-temperature quenching of C_{70} fluorescence by bromobenzene in MT follows a linear Stern–Volmer plot, both in terms of lifetimes and in terms of steady-state intensities[18] with a redetermined quenching constant $k_q = k_{rd} = (2.3\pm0.3)\times10^8$ L mol^{-1} s^{-1}. The low-temperature fluorescence decays in the MT glass were single exponential in the absence of quencher, with a lifetime of 720 ps, but were nonexponential in the presence of bromobenzene, as expected from Eq. (20). The low-temperature decays were always well fitted with Eq. (20), with the intrinsic lifetime fixed at 720 ps.

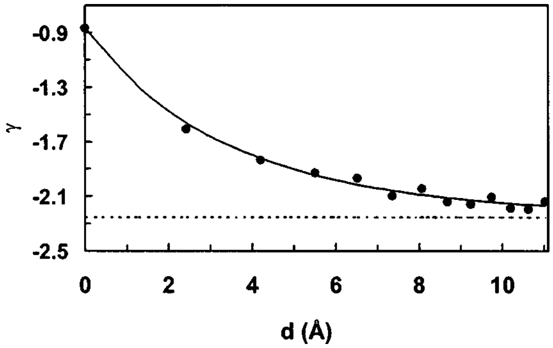

FIG. 5. Fitted parameter γ as a function of d for the C_{70}-bromobenzene system. The solid line corresponds to Eq. (28). The horizontal dotted line is the asymptotic value for $\beta\to\infty$.

For a bromobenzene concentration of 8.23 mol L^{-1}, several fits were performed, using different values of parameter β between 0 and 12. The fits were equally good for all values of β (chi-squared values always less than 1.1), demonstrating the predicted parameter correlation. The fitted γ parameter is shown in Fig. 5 as a function of parameter d, the distance of closest approach. This distance is computed for each β using Eq. (23). It is seen that the quenching is weak, the highest value of γ still being negative. The solid line is the predicted parameter correlation from Eq. (28), and is in very good agreement with the results from the individual fits.

The calculated effective average Bohr radius L, computed from parameter α according to Eqs. (21) and (22), is shown in Fig. 6 as a function of parameter d. The solid line is again the predicted parameter correlation from Eq. (28), and is seen to be in very good agreement with the results from the individual fits. The rate constant k_0, calculated from Eq. (5), is shown in Fig. 7 as a function of parameter d. The solid line is again the value predicted from Eq. (28).

For this system, the computed rapid diffusion rate constant takes the same value irrespective of d, as expected for a weak quenching case. For the 8.23 mol L^{-1} bromobenzene solution, the computed value is $k_{rd} = 1.6\times10^8$ L mol^{-1} s^{-1}, very close to the experimental room temperature value, $(2.3\pm0.3)\times10^8$ L mol^{-1} s^{-1}.

Given the existence of parameter correlation, it is only possible to obtain values for parameters L and k_0 if a value of d is assumed. The distance of closest approach can be calculated from known or estimated van der Waals radii. The

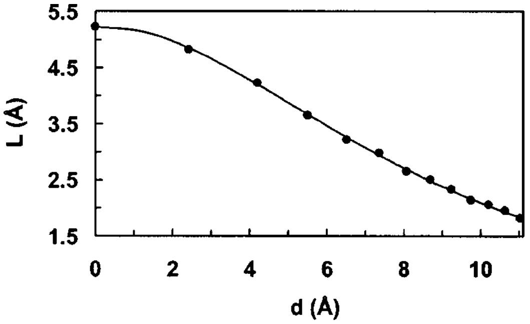

FIG. 6. Computed effective average Bohr radius L as a function of d for the C_{70}-bromobenzene system. The solid line corresponds to Eq. (28).

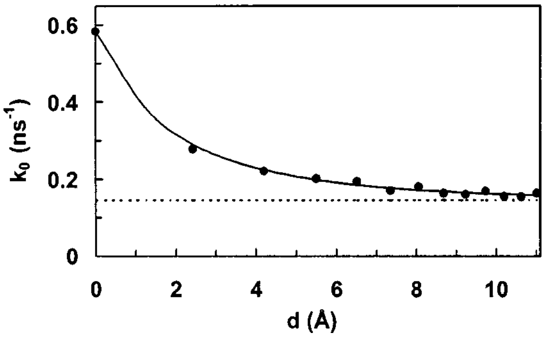

FIG. 7. Calculated rate constant k_0 as a function of d for the C_{70}-bromobenzene system. The solid line corresponds to Eq. (28). The horizontal dotted line is the asymptotic value for $\beta \to \infty$.

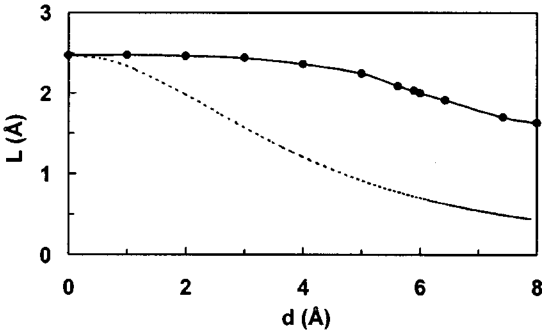

FIG. 9. Computed effective average Bohr radius L as a function of d for the phenanthrene-iodide system. The dashed line corresponds to Eq. (28).

average van der Waals radius of C_{70} is known from crystallographic determinations to be 5.3 Å.[19] For bromobenzene, an average radius of 2.9 Å was estimated by the method of atomic contributions.[20] A value of $d=8.2$ Å is thus obtained ($\beta=6.2$). Using the distance d, values of $L=2.6$ Å and $k_0=0.17\ \text{ns}^{-1}$ follow. The relatively high value of L is attributed to the fact that, owing to the carbon skeleton curvature in fullerenes, π orbitals are symmetric, with an outer lobe considerably larger than that of planar aromatic compounds.[21] The value of $k_0=1.7\times10^8\ \text{s}^{-1}$ should be compared with the intrinsic intersystem crossing ratio of C_{70}, $k_{\text{ISC}}\approx 1/\tau_0=1.5\times10^9\ \text{s}^{-1}$, and explains why the quenching is weak (low γ). The quenching is thus only noticeable for high quencher concentrations, where more than one quencher molecule is effective.

From Eqs. (6) and (8), a critical radius $R_0=5.4$ Å and a maximum distance for quenching $r_{\max}=10.7$ Å are obtained. The thickness of the spherical shell where quenching occurs is therefore only 2.5 Å.

A global analysis of three different decays with three different quencher concentrations gives essentially the same results.

B. Phenanthrene-iodide

The room-temperature fluorescence decays in EM were single exponential for all quencher concentrations. In the absence of quencher, the measured lifetime was 15.0 ns.

The room-temperature quenching of phenanthrene fluorescence by iodide in EM follows a linear Stern–Volmer plot up to a 2 mol L^{-1} concentration (value close to the solubility limit), both in terms of lifetimes and in terms of steady-state intensities, with a quenching constant $k_q=k_{rd}=(2.1\pm0.2)\times10^8\ \text{L mol}^{-1}\,\text{s}^{-1}$. The low-temperature fluorescence decays in the EM glass were single exponential in the absence of quencher, with a lifetime of 64.4 ns, but were nonexponential in the presence of iodide, as expected from Eq. (20).

The low-temperature decays were reasonably well fitted with Eq. (20), with the intrinsic lifetime fixed at 64.4 ns.

For an iodide concentration of 0.37 mol L^{-1}, several fits were performed, using different values of parameter β between 0 and 8. The fits were equally good for all values of β (chi-squared values always less than 2.6), demonstrating the predicted parameter correlation. The fitted γ parameter is shown in Fig. 8 as a function of parameter β. The linear dependence predicted from Eq. (32) is observed down to $\gamma\approx4.5$. It is also seen that the quenching effect is now much more pronounced than for the C_{70}-brombenzene system, the highest value of γ, γ_0, being close to 6.

The calculated effective average Bohr radius L, computed from parameter α according to Eqs. (21) and (22), is shown in Fig. 9 as a function of parameter d. The dashed line is the predicted parameter correlation from Eq. (28), and is seen not to be in agreement with the results from the individual fits, as expected for high values of γ. The rate constant k_0, calculated from Eq. (5), is shown in Fig. 10 as a function of parameter d.

For this system, the computed rapid diffusion rate constant is a function of parameter d, as shown in Fig. 11, and is

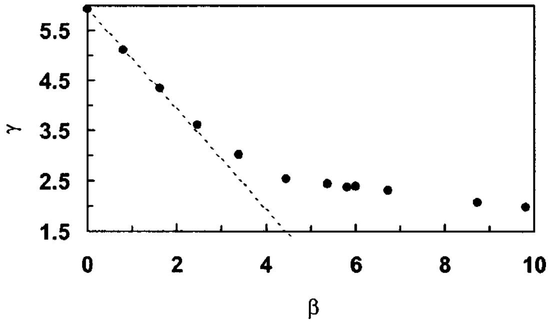

FIG. 8. Fitted parameter γ as a function of β for the phenanthrene-iodide system. The dashed line corresponds to Eq. (33).

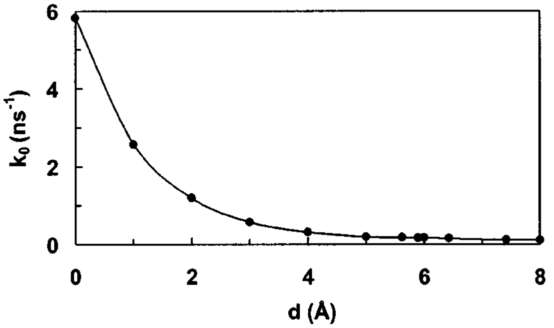

FIG. 10. Calculated rate constant k_0 as a function of d for the phenanthrene-iodide system.

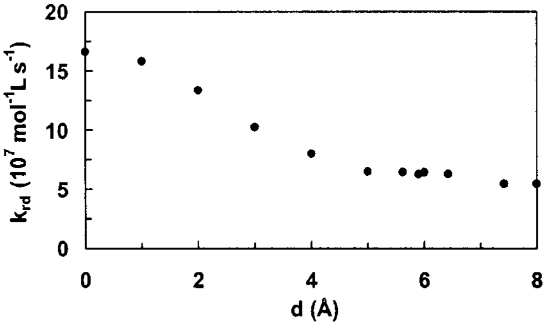

FIG. 11. Calculated rapid diffusion rate constant k_{rd} as a function of d for the phenanthrene-iodide system.

always significantly lower than the room-temperature experimental value.

Given the existence of parameter correlation, it is only possible to obtain values for parameters L and k_0 if a value of d is assumed.

The distance of closest approach is again calculated from known or estimated van der Waals radii. The average van der Waals radius of phenanthrene, as obtained by the method of atomic contributions,[20] is 3.4 Å. The radius of the quencher is either 2.2 Å for the bare iodide ion, or 4.0 Å for the solvated ion.[22] Values of d=5.6 Å and d=7.4 Å are thus obtained (corresponding to β=5.4 and β=8.7, respectively). From these distances of closest approach, values of L=2.1 Å and $k_0=0.18$ ns^{-1}, and of L=1.7 Å and $k_0=0.12$ ns^{-1}, respectively, are obtained. The two values of k_0 are similar, and much higher than the intrinsic decay rate of phenanthrene, $1/\tau_0=10.016$ ns^{-1}, explaining why the quenching is quite effective (high γ). Unlike the situation with C_{70}, the quenching is in this case noticeable even for relatively low quencher concentrations.

From Eqs. (6) and (8), critical radii $R_0=8.2$–9.2 Å and maximum distances for quenching $r_{\max}$=12.4–12.6 Å are obtained. The thickness of the spherical shell where quenching occurs is therefore considerable, 6.7 and 5.2 Å, respectively.

Analysis of the decays corresponding to different concentrations of iodide gives essentially the same results.

Although the above results do not allow a clear option between bare and solvated iodide ions, the more reasonable L value for the second case favors the possibility that the iodide ions present in the glass are always solvated, and never in direct contact with phenanthrene. A stronger reason favoring this hypothesis is now given. The observed discrepancy between the experimental and computed rapid diffusion rate constants can be tentatively explained as follows: In the low-temperature glass, the iodide ions are solvated at the moment of excitation of phenanthrene by light absorption, and remain as such throughout the decay time. On the other hand, in the fluid solvent at room temperature, the solvation shell is constantly breaking and reforming, and the possibility exists that the excited phenanthrene molecule will directly interact with the bare iodide ion, forming a very weak complex. Assuming that the low-temperature distance dependence for the rate constant still holds, but that shorter distances are allowed in the liquid, with a new minimum distance of 5.6 Å corresponding to the distance of closest approach between phenanthrene and a bare iodide ion, a new and higher k_0 is obtained, $k_0=1.0$ ns^{-1}. The corresponding k_{rd} is now 2.8×10^8 L mol^{-1} s^{-1}, in good agreement with the room-temperature experimental value, considering all the approximations involved.

C. Comparison of the two systems

The two systems studied correspond to two extreme and opposite cases of quenching efficiency. While the intrinsic quenching constants k_0 are very similar, in the case of C_{70} the competing decay processes are faster (very short lifetime), and the quenching inefficient (low γ) while in the case of phenanthrene the competing decay processes are slower (long lifetime), and the quenching efficient (high γ). The calculated effective average Bohr radius for the phenanthrene-iodide pair falls in the usual range for this parameter, while the unusually high L for the C_{70}-bromobenzene pair is attributed to the peculiar nature of the fullerene π orbitals. The fact that the low-temperature intrinsic quenching constants k_0 are very similar for the two pairs ($k_0=0.17$ ns^{-1} for C_{70}-bromobenzene and $k_0=0.12$ ns^{-1} for phenanthrene-iodide) deserves detailed attention, as the two quenchers used are known to have very different quenching efficiencies for a given molecule: Bromobenzene is a weaker heavy-atom quencher than iodide. This effective quencher order was namely observed in fullerenes, the iodinated quenchers having room-temperature bimolecular quenching rate constants one order of magnitude higher than those of brominated ones.[18,23] The same order is in fact observed with the present systems, if allowance is made for the fact that the iodide ion is solvated at low temperature, and is for this reason a weaker quencher than at room temperature, for which the estimated rate constant for the quenching of phenanthrene is $k_0=1.0$ ns^{-1}.

V. CONCLUSIONS

In this work, a model for fluorescence quenching with exponential distance dependence was studied in detail and applied to external heavy-atom quenching. In this model, the decay law is a function of three dimensionless parameters, α, β, and γ. The parameters β and γ are shown to be correlated, and cannot be independently determined from fluorescence decays. The systems studied were C_{70}-bromobenzene and phenanthrene-iodide, in liquid solutions at room temperature and in rigid glasses at 77 K. The predicted parameter correlation was observed for the two systems, which correspond to two extreme and opposite situations, strong and weak quenching. A detailed analysis of the determined parameter allowed the calculation of the effective average Bohr radii L and of the intrinsic unimolecular rate constants for quenching at contact, k_0. The unusually high value of L for the C_{70}-bromobenzene is attributed to the extended size of the external part of the π orbital of the fullerene. The room-temperature quenching rate constant computed with the determined low-temperature parameters was shown to be in good agreement with the experimental one for both systems.

A systematic study of several systems is underway, in order to assess the general applicability of the model, and in order to correlate the parameters of the model, namely L and k_0, with the structure of fluorophores and quenchers.

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[1] S. A. Rice, *Diffusion-Limited Reactions*, Comprehensive Chemical Kinetics, Vol. 25, edited by C. H. Bamford, C. F. H. Tipper, and R. G. Compton (Elsevier, Amsterdam, 1985).
[2] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).
[3] A. Brown and F. Wilkinson, J. Chem. Soc., Faraday Trans. 2 **75**, 880 (1979).
[4] S. Strauch, G. McLendon, M. McGuire, and T. Guarr, J. Phys. Chem. **87**, 3579 (1983).
[5] R. C. Dorfman, Y. Lin, and M. D. Fayer, J. Phys. Chem. **93**, 6388 (1989).
[6] B. F. Minaev, S. Knuts, and H. Agren, Chem. Phys. **181**, 15 (1994).
[7] S. V. Camyshan, N. P. Gritsan, V. V. Krolev, and N. M. Bazhin, Chem. Phys. **142**, 59 (1990).
[8] J. Najbar and I. H. Munro, J. Lumin. **17**, 135 (1978).
[9] M. Mac, W. Jarzeba, and J. Najbar, J. Lumin. **37**, 139 (1987).
[10] M. Inokuti and F. Hirayama, J. Chem. Phys. **43**, 1978 (1965).
[11] A. Hara and Y. Gondo, J. Chem. Phys. **85**, 1894 (1986).
[12] S. Taen, J. Chem. Phys. **108**, 6857 (1998).
[13] M. M. Rikenglaz and I. M. Rozman, Opt. Spectrosc. **36**, 106 (1974).
[14] B. Valeur, *Molecular Fluorescence* (Wiley-VCH, Weinheim, 2002).
[15] M. N. Berberan-Santos, Chem. Phys. Lett. **196**, 220 (1992).
[16] W. G. Herkstroeter, in *Creation and Detection of the Excited State*, edited by A. A. Lamola (Dekker, New York, 1971), Vol. 1, Part A.
[17] A. Fedorov, M. N. Bergeran-Santos, J.-P. Lefèvre, and B. Valeur, Chem. Phys. Lett. **267**, 467 (1997).
[18] S. Foley, M. N. Berberan-Santos, A. Fedorov, R. V. Bensasson, S. Leach, and B. Gigante, Chem. Phys. **263**, 437 (2001).
[19] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York, 1996).
[20] J. T. Edward, J. Chem. Educ. **47**, 261 (1970).
[21] R. C. Haddon, Acc. Chem. Res. **25**, 127 (1992).
[22] E. Hawlicka and R. Grabowski, Ber. Bunsenges. Phys. Chem. **94**, 486 (1990).
[23] I. Texier, M. N. Berberan-Santos, A. Fedorov, M. Brettreich, H. Schönberger, A. Hirsch, S. Leach, and R. V. Bensasson, J. Phys. Chem. A **105**, 10278 (2001).