Prediction of the Influence of Concentration on the Photoluminescence Decay Time of Solutions*

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A formula for the donor photoluminescence decay time in its dependence on the concentrations of donor D and acceptor A has been derived from equations for the non-radiative excitation energy transfer between randomly distributed donor and acceptor molecules within a nonactive medium. In the limit $[D]/[A] \to 0$ the formula becomes identical with that of Galanin [7], while in the absence of concentration quenching the fluorescence decay time does not depend on the concentrations.

1. Introduction

A number of effects such as the donor photoluminescence (PL) quenching, acceptor PL sensibilization, PL concentration depolarization, and also the concentration dependence of the PL decay time can be explained by non-radiative electronic excitation energy transfer (NEEET) between donor (D) molecules as well as donor and acceptor (A) molecules [1–4].

Among the studies of concentration dependent effects there are relatively few concerned with changes of the PL decay time τ. This regards especially theoretical works [5–12]. In the first phenomenological theory of the effect, developed by Vavilov [5], several empirical constants of rather ambiguous physical meaning were used. The theory developed by Galanin [7] is applicable, as will be shown further on, only if the reduced concentrations of acceptor and donator molecules γ_A, γ_D fulfill the condition

$$\gamma_A \gg \gamma_D . \tag{1}$$

The NEEET from D^* to A is in this case a one-step process.

In the general case of arbitrary concentrations the transfer of energy from D^* to A can proceed in many steps according to the scheme

$$\begin{aligned} D^* + D + \cdots + D + A &\xrightarrow{k_{DD}} D + D^* + \cdots + D + A \\ &\xrightarrow{k_{DD}} D + D + \cdots + D^* + A \xrightarrow{k_{DA}} \\ &\to D + D + \cdots + D + A^* , \end{aligned} \tag{2}$$

where k_{DD} and k_{DA} are the rate constants for NEEET processes between D^* and D, and D^* and A, respectively.

It has been shown in a number of experimental works that it is necessary to take into account the multistep process (2) if inequality (1) is not satisfied [13–15]. This was confirmed by investigations of the dependence of the donor PL quantum yield on the acceptor concentration and on the quenching by dimers. The exact solution of the problem of concentration dependence of the PL decay time with the multistep NEEET process (2) taken into account is presented in this paper [16].

2. Photoluminescence Decay Time

As in our previous papers [18, 19] the following assumptions and notations have been adopted:

1. Donor D and acceptor A molecules, are randomly distributed.
2. The absorption and emission spectra of D as well as the emission spectrum of D and the absorption spectrum of A overlap partially.
3. The NEEET process occurs between molecules D^* excited to the first singlet state and the molecules D and A in the ground state by dipole-dipole interaction, i. e. its rate constants k_{DD} and k_{DA} are proportional to the reciprocal of the sixth power of the donor-acceptor distance.
4. The desactivation of a D^* molecule depends essentially on the configuration σ of unexcited molecules D and A in the vicinity of D^*. This configuration is assumed to be invariant in time and determined by the distances of the molecules D and A from D^*. The probability of a configura-

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tion σ is denoted by P_σ. PL emission (rate constant k_F), internal conversion (k_q), NEEET from D* to D($k_{\mathrm{DD}\sigma}$) or from D* to A($k_{\mathrm{DA}\sigma}$) are competing processes.

5. The relative probabilities of the said processes amount to
$$P_\alpha = \sum_\sigma k_{\alpha\sigma} k_\sigma^{-1} P_\sigma, \quad \alpha = F, q, \mathrm{DD} \text{ or } \mathrm{DA}, \tag{3}$$
where
$$k_\sigma = k_\mathrm{F} + k_\mathrm{q} + k_{\mathrm{DD}\sigma} + k_{\mathrm{DA}\sigma}. \tag{4}$$
6. The excited molecules D* can be classified into types $\mathrm{D}^{(m)}$ of order m, where m is the number of preceding energy transfer steps. $\mathrm{D}^{(0)}$ denotes a molecule excited directly by the external light. Molecules $\mathrm{D}^{(m)}$ in a configuration σ are designated by $\mathrm{D}_\sigma{}^{(m)}$, and their number by $N_\sigma{}^{(m)}$.

Note that molecules $\mathrm{D}_\sigma{}^{(m)}$ can produce molecules $\mathrm{D}^{(m+1)}$ or lose their energy by one of the other processes specified in assumption 4.

The PL decay time can be calculated from the defining relation

$$\tau = \frac{\sum\limits_{m=0}^{\infty} \sum\limits_{\sigma} \int\limits_0^{\infty} t\, N_\sigma{}^{(m)}(t)\,\mathrm{d}t}{\sum\limits_{m=0}^{\infty} \sum\limits_{\sigma} \int\limits_0^{\infty} N_\sigma{}^{(m)}(t)\,\mathrm{d}t}, \tag{5}$$

where t is the time elapsed since a flash illumination.

The integrals

$$I_\sigma{}^{(m)} = \int\limits_0^\infty N_\sigma{}^{(m)}(t)\,\mathrm{d}t \quad \text{and} \quad I_{\sigma t}^{(m)} = \int\limits_0^\infty t'\, N_\sigma{}^{(m)}(t')\,\mathrm{d}t' \tag{6}$$

can be determined from the set of the Eqs. [18]

$$\dot{N}_\sigma{}^{(0)}(t) = -k_\sigma N_\sigma{}^{(0)}(t), \tag{7'}$$

$$\dot{N}_\sigma{}^{(m)}(t) = -k_\sigma N_\sigma{}^{(m)}(t) + [\sum k_{\mathrm{DD}\sigma'} N_{\sigma'}^{(m-1)}(t)]P_\sigma, \quad m = 1, 2, 3, \ldots, \infty, \tag{7''}$$

with the initial and final conditions

$$N_\sigma{}^{(0)}(0) = N_{0\sigma}, \quad N_\sigma{}^{(0)}(\infty) = 0, \tag{8}$$
$$N_\sigma{}^{(m)}(0) = N_\sigma{}^m(\infty) = 0, \quad (m = 1, 2, \ldots, \infty).$$

The method of calculating $I_\sigma{}^{(m)}$ has been presented elsewhere [18]. The result was

$$I_\sigma{}^{(m)} = (N_{0\sigma}/k_\sigma)(P_\mathrm{DD})^m. \tag{9}$$

To calculate $I_{\sigma t}^{(m)}$, Eqs. (7′) and (7″) are multiplied by t and integrated over t within the range $0, \infty$. Using the identity

$$t\,\mathrm{d}N_\sigma{}^{(m)} \equiv \mathrm{d}(t N_\sigma{}^{(m)}) - N_\sigma{}^{(m)}\mathrm{d}t,$$

(8) and (6) one gets

$$k_\sigma I_{\sigma t}^{(0)} = I_\sigma{}^{(0)}, \tag{10}$$
$$k_\sigma I_{\sigma t}^{(m)} = I_\sigma{}^{(m)} + (\sum_{\sigma'} k_{\mathrm{DD}\sigma'} I_{\sigma' t}^{(m-1)}) P_\sigma. \tag{10''}$$

By multiplying (10) by $k_{\mathrm{DD}\sigma}/k_\sigma$ and sumning up both sides with respect to σ we obtain, using (9),

$$\sum k_{\mathrm{DD}\sigma} I_{\sigma t}^{(0)} = N_0 \cdot K \tag{10'}$$

with

$$K = \sum_\sigma (k_{\mathrm{DD}\sigma}/k_\sigma{}^2) P_\sigma, \quad N_{0\sigma} = N_0 P_\sigma \tag{11}$$

and N_0 the number of directly excited donors at time $t = 0$. The system of Eqs. (10′) and (10″) leads to (see Appendix 1):

$$I_{\sigma t}^{(m)} = (N_{0\sigma}/k_\sigma{}^2) P_\mathrm{DD}^m + m(N_{0\sigma}/k_\sigma) K P_\mathrm{DD}^{m-1}. \tag{12}$$

After substitution of (9) and (12) into (5) and using the denotations

$$L = \sum_\sigma P_\sigma/k_\sigma{}^2 \tag{13}$$

and

$$P_\mathrm{F} = \sum_\sigma (k_\mathrm{F} P_\sigma)/k_\sigma \tag{14}$$

we obtain

$$\tau = \frac{k_\mathrm{F} L \sum\limits_{m=0}^{\infty} P_\mathrm{DD}^m + K P_\mathrm{F} \sum\limits_{m=0}^{\infty} m P_\mathrm{DD}^{m-1}}{P_\mathrm{F} \sum\limits_{m=0}^{\infty} P_\mathrm{DD}^m}. \tag{15}$$

As $P_\mathrm{DD} < 1$ [see definition (3)] we have

$$\sum_{m=0}^{\infty} m P_\mathrm{DD}^{m-1} = (1 - P_\mathrm{DD})^{-2} \quad \text{and}$$
$$\sum_{m=0}^{\infty} P_\mathrm{DD}^m = (1 - P_\mathrm{DD})^{-1}. \tag{16}$$

Thus

$$\tau = L k_\mathrm{F}/P_\mathrm{F} + K(1 - P_\mathrm{DD})^{-1}. \tag{17}$$

To determine τ it is necessary to calculate L and K. $P_\mathrm{F}$and P_DD have been calculated elsewhere [18] with the result

$$P_\mathrm{F} = \eta_0[1 - f(\gamma)] \quad \text{and} \quad P_\mathrm{DD} = \alpha f(\gamma), \tag{18}$$

with $\eta_0 = k_\mathrm{F}/(k_\mathrm{F} + k_\mathrm{q})$,

$$f(\gamma) = (\pi)^{1/2} \gamma \exp(\gamma^2)[1 - \mathrm{erf}(\gamma)], \tag{19}$$

and

$$\gamma = \gamma_\mathrm{D} + \gamma_\mathrm{A} = \frac{(\pi)^{1/2}}{2}\left(\frac{C_\mathrm{D}}{C_\mathrm{0D}} + \frac{C_\mathrm{A}}{C_\mathrm{0A}}\right); \quad \alpha = \gamma_\mathrm{D}/\gamma. \tag{20}$$

C_D and C_A, and C_0D and C_0A denote concentrations and critical concentrations, respectively, of the donor and the acceptor.

The calculation of L yields (see Appendix 2)

$$L = \tau_G P_F / k_F , \tag{21}$$

where

$$\tau_G = \tau_0 [1 + \gamma^2 - (1.5 + \gamma^2) f(\gamma)] / (1 - f(\gamma)) \tag{22}$$

is the PL decay time as obtained [20] by Galanin [7]. For K the following formula was obtained (see Appendix 3):

$$K = \tau_0 \{ \tfrac{1}{2}\, \alpha\, f(\gamma) - \alpha\, \gamma^2 [1 - f(\gamma)] \} . \tag{23}$$

Substitution of (18), (21), (22), and (23) into (17), together with adoption of the possibility of monomer quenching [21] results in the final formula for the concentration dependence of the PL decay time:

$$\frac{\tau}{\tau_0} = \frac{1 + \gamma^2 - (1.5 + \gamma^2) f + \alpha\, \alpha_0\, f (f + \gamma^2 - \tfrac{1}{2}) - \alpha\, \alpha_0\, \gamma^2}{(1 - f)\,(1 - \alpha\, \alpha_0\, f)} , \tag{24}$$

where $f \equiv f(\gamma)$, and α_0 denotes the probility that no degradation of the excitation energy during the transfer between monomers takes place.

For the limiting case $\gamma_A \to 0$, $\alpha \to 1$, $\alpha_0 = 1$ (no monomer quenching), formula (24) gives a constant decay time in the entire range of concentrations ($\tau = \tau_0$). On the other hand, for $\gamma_A \gg \gamma_D$, $\alpha \to 0$ formula (24) becomes (22) as obtained by Galanin. Figure 1 shows $\tau(c)/\tau_0$ as described by formula (24) for several values of the parameter $\alpha = \gamma_D/\gamma$ ($\alpha_0 = 1$, solid lines) and for $\alpha_0 < 1$ (monomer quenching). The effect of this quenching is especially pronounced for $\gamma_D \gg \gamma_A$ (compare curves *a*, *a'* and *c*, *c'*).

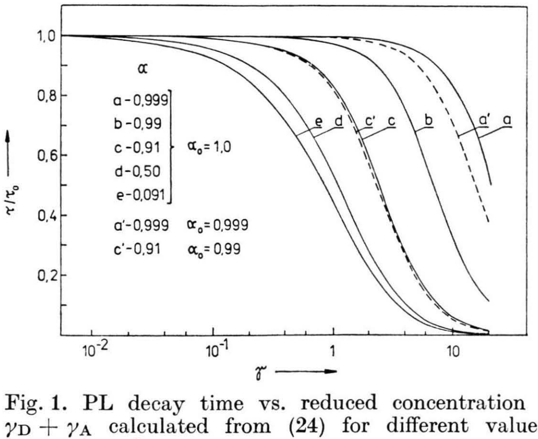

Fig. 1. PL decay time vs. reduced concentration $\gamma = \gamma_D + \gamma_A$ calculated from (24) for different values of $\alpha = \gamma_D/\gamma$ and α_0.

3. Discussion and Final Remarks

Formula (24) may be adopted for systems with dimers as acceptor. In this case

$$\gamma_A = \gamma_{D_{\|}} = (\pi^{1/2}/2) \cdot (C''/C_0''),$$

where C'' and C_0'' are the concentration and critical concentration, respectively, of dimers $D_{\|}$, and

$$\alpha = [(1 + 4 K_\gamma \gamma)^{1/2} - 1] / (2 \gamma K_\gamma) . \tag{25}$$

The dimensionless constant $K_\gamma = \gamma_{D_{\|}} / \gamma_D{}^2$ is related to the dimerization constant $K = C''/C'^2$ through the relation

$$K_\gamma = 2 K C_0'^2 / (\pi^{1/2} C_0'') ; \tag{26}$$

there C' and C_0' are the monomer concentration and critical concentration, respectively.

The curves representing τ/τ_0 calculated with (24) for several values of K_γ are shown in Figure 2. Characteristic for low values of K_γ is a particularly steep drop of τ/τ_0. The lower the value of K_γ the higher is the concentration for which this drop occurs. The quantity $\alpha = \gamma_D/\gamma$ depends now on the concentration [cf. (25)]. For low values of K_γ, $\alpha \approx 1$ within a wide range of concentrations, while for $K_\gamma \gg 1$ and in the high concentration region $\alpha \cong 0$ and the curves calculated according to (24) and (22) differ but slightly (compare dashed curve and curve *f*).

Presented in Fig. 2 are also experimental results for Rhodamine 6 G in glycerin solutions, taken from Ref. [22]. The experimental values of τ/τ_0, corrected for secondary effects, remain constant within

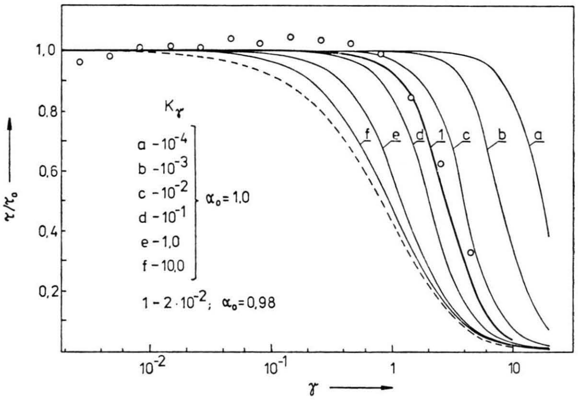

Fig. 2. PL decay time for rhodamine 6 *G* (○) in pure glycerin solutions versus $\gamma = \gamma_D + \gamma_{D''}$. Continuous lines: theoretical curves calculated from (24) for different values K_γ; dashed line: theoretical curve calculated from (22).

a wide range of concentrations, dropping steeply afterwards. This is the typical course of concentration dependent changes of τ/τ_0 as observed experimentally for other luminescent systems [5 – 10]. Curve 1 has been calculated from (24) for $K_\gamma = 0.02$ and $\alpha_0 = 0.98$. A good agreement of the experimental results with the theoretical curve in the entire range of concentrations is evident. It should be pointed out that the dimerization constant K and concentrations C', C'', C_0, and C_0'' therefore also K_γ and γ, have been determined experimentally. Relation (24) corresponds to a multistep NEEET process as described by (2) and relation (22) to a single-step NEEET process. Thus relation (22) does allow for the migration of energy from donors of the zeroth order only (excited directly).

An other description of the multistep process is given in [17]. The formula obtained in that paper starts from the assumption that NEEET occurs upon completion of the vibrational relaxation in the excited state, and the mean time of localization of the excitation energy on molecules of any order is the same. This assumption has led to an expression predicting a rise of τ/τ_0 followed by its drop with increasing concentration.

The expression gave a correct description of experimental results however for a lowered value of probability α_0 only [22]. It has been shown in [23] that for a regular lattice of donor molecules the assumption under consideration is valid. Nonetheless it is the author's opinion that for the general case of random distribution of molecules D and A in the solution it may prove incorrect.

The analysis of relation (24) carried out in the preceding section has led to the conclusion that the NEEET process in an assembly of molecules of the same kind does not change the value of τ/τ_0 as long as no PL quenching occurs in this assembly. Note that formula (24) obtained in this work has been derived without any simplifications of mathematics from a set of kinetic equations (7) which proved to play the essential part in the solving of the problem under consideration.

Appendix 1

For $m = 1$ formula (10″) leads to

$$I_{\sigma t}^{(1)} = I_\sigma{}^{(1)}/k_\sigma + \big(\sum_{\sigma'} k_{\mathrm{DD}\sigma'}\, I_{\sigma' t}^{(0)}\big)\,(P_\sigma/k_\sigma)\,. \tag{A.1}$$

Substitution of (9) and (10′) in (A.1) results into

$$I_{\sigma t}^{(1)} = (N_{0\sigma}/k_\sigma{}^2)\,P_{\mathrm{DD}} + N_{0\sigma}\,K/k_\sigma\,. \tag{A.2}$$

In a similar fashion (10″) gives

$$I_{\sigma t}^{(2)} = I_\sigma{}^{(2)}/k_\sigma + \big(\sum_{\sigma'} k_{\mathrm{DD}\sigma'}\, I_{\sigma' t}^{(1)}\big)\,P_\sigma/k_\sigma\,. \tag{A.3}$$

Substituting relations (9) and (A.2) for $I_\sigma{}^{(2)}$ and $I_{\sigma' t}^{(1)}$ respectively, we obtain

$$I_{\sigma t}^{(2)} = (N_{0\sigma}/k_\sigma{}^2)\,P_{\mathrm{DD}}^2 \tag{A.4}$$

$$+\Big[N_0\,P_{\mathrm{DD}}\sum_{\sigma'}(k_{\mathrm{DD}\sigma'}/k_{\sigma'}^2)\,P_{\sigma'} + N_0\,K\sum_{\sigma'}\frac{k_{\mathrm{DD}\sigma'}}{k_{\sigma'}}\,P_{\sigma'}\Big]\frac{P_\sigma}{k_\sigma}\,.$$

The first sum in the bracket is K, the other sum is equal to P_{DD} (compare formulae (11) and (3)). Thus, finally, we have

$$I_{\sigma t}^{(2)} = (N_{0\sigma}/k_\sigma{}^2)\,P_{\mathrm{DD}}^2 + (2\,N_{0\sigma}\,K/k_\sigma)\,P_{\mathrm{DD}}\,. \tag{A.5}$$

Hence the general formula (12).

Appendix 2. Calculation of L

The identity $1/k_\sigma{}^2 = \int_0^\infty t\exp(-k_\sigma t)\,\mathrm{d}t$ applied to formula (13) yields

$$L = \sum_\sigma P_\sigma/k_\sigma{}^2 = \int_0^\infty t\big[\sum_\sigma P_\sigma \exp(-k_\sigma t)\big]\,\mathrm{d}t\,. \tag{A.6}$$

For an equal-probability distribution of molecules D and A in the volume V of a sample there is (see assumption 4)

$$P_\sigma = V^{-(N_{\mathrm{D}}-1+N_{\mathrm{A}})}\,\mathrm{d}\boldsymbol{R}_1\ldots\mathrm{d}\boldsymbol{R}_{N_{\mathrm{D}}-1}\cdot\mathrm{d}\boldsymbol{r}_1\ldots\mathrm{d}\boldsymbol{r}_{N_{\mathrm{A}}}\,, \tag{A.7}$$

where $\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots$ and $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots$ are the distances D-D$^{(0)}$ and A-D$^{(0)}$, respectively. According to (A.7) and (4) the sum in the integral in relation (A.6) can be written as

$$\sum_\sigma P_\sigma \exp(-k_\sigma t)$$

$$= \exp\Big(-\frac{t}{\tau_0}\Big)\int \exp(-k_{\mathrm{DD}\sigma}\,t)\,\frac{\mathrm{d}\boldsymbol{R}_1\ldots\mathrm{d}\boldsymbol{R}_{N_{\mathrm{D}}-1}}{V^{N_{\mathrm{D}}-1}}$$

$$\cdot\int \exp(-k_{\mathrm{DA}\sigma}\,t)\,\frac{\mathrm{d}\boldsymbol{r}_1\ldots\mathrm{d}\boldsymbol{r}_{N_{\mathrm{A}}}}{V^{N_{\mathrm{A}}}}\,, \tag{A.8}$$

where

$$k_{\mathrm{DD}\sigma} = (k_{\mathrm{F}} + k_{\mathrm{q}})\sum_{j=1}^{N_{\mathrm{D}}-1}\Big(\frac{R_{0\mathrm{D}}}{R_j}\Big)^6\,;$$

$$k_{\mathrm{DA}\sigma} = (k_{\mathrm{F}} + k_{\mathrm{q}})\sum_{i=1}^{N_{\mathrm{A}}}\Big(\frac{R_{0\mathrm{A}}}{r_i}\Big)^6\,;\quad \tau_0 = (k_{\mathrm{F}} + k_{\mathrm{q}})^{-1}\,.$$

Formula (A.8) represents a normalized decay function $\varrho(t) = N^{(0)}(t)/N^{(0)}(0)$ for the excited state of molecules $\mathrm{D}^{(0)}$ averaged over all configuration σ of molecules D and A. The limiting value of the last integral (A.8) is

$$\lim_{V\to\infty} \int \exp(-k_{\mathrm{DA}\sigma}\, t)\, \frac{\mathrm{d}\mathbf{r}_1 \dots \mathrm{d}\mathbf{r}_{N_\mathrm{A}}}{V^{N_\mathrm{A}}} = \exp\left[-2\,\gamma_\mathrm{A}\left(\frac{t}{\tau_0}\right)^{1/2}\right]; \quad \lim_{V\to\infty} \frac{N_\mathrm{A}}{V} = C_\mathrm{A}. \tag{A.9}$$

This result has been obtained by Förster [21]. and also by other investigators [7, 18].

An analogous result holds true for the first integral in (A.8). Thus

$$\varrho(t) = \sum_\sigma P_\sigma \exp(-k_\sigma\, t) = \exp\left\{-\left[\frac{t}{\tau_0} + 2\,\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right]\right\}. \tag{A.10}$$

Substitution of (A.10) in (A.6) leads, together with [7]

$$\tau_\mathrm{G} = \int_0^\infty t \exp\left\{-\left[\frac{t}{\tau_0} + 2\,\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right]\right\} \mathrm{d}t \Big/ \int_0^\infty \exp\left\{-\left[\frac{t}{\tau_0} + 2\,\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right]\right\} \mathrm{d}t$$

to

$$L = \int_0^\infty t \exp\left\{-\left[\frac{t}{\tau_0} + 2\,\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right]\right\} \mathrm{d}t = \tau_\mathrm{G} \int_0^\infty \exp\left\{-\left[\frac{t}{\tau_0} + 2\,\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right]\right\} \mathrm{d}t$$
$$= \tau_\mathrm{G}\, \tau_0 \{1 - \gamma (\pi)^{1/2} \exp(\gamma^2)\, [1 - \operatorname{erf}(\gamma)]\} = \tau_\mathrm{G} \frac{P_\mathrm{F}}{k_\mathrm{F}}.$$

Appendix 3. Calculation of K

From the relation

$$\frac{k_{\mathrm{DD}\sigma}}{k_\sigma^2} = -\int_0^\infty t \exp\left[-\left(\frac{t}{\tau_0} + k_{\mathrm{DA}\sigma}\, t\right)\right] \frac{\mathrm{d}}{\mathrm{d}t} \exp(-k_{\mathrm{DD}\sigma}\, t)\, \mathrm{d}t$$

it follows

$$K = \sum_\sigma \frac{k_{\mathrm{DD}\sigma}}{k_\sigma^2} P_\sigma = -\int_0^\infty t \exp\left(-\frac{t}{\tau_0}\right) \cdot \left[\sum_\sigma P_\sigma \exp(-k_{\mathrm{DA}\sigma}\, t) \frac{\mathrm{d}}{\mathrm{d}t} \exp(-k_{\mathrm{DD}\sigma}\, t)\right] \mathrm{d}t. \tag{A.11}$$

The term in the brackets can be calculated in a similar way as (A.9). As a result the following relation is obtained:

$$\sum_\sigma P_\sigma \exp(-k_{\mathrm{DA}\sigma}\, t) \frac{\mathrm{d}}{\mathrm{d}t} \exp(-k_{\mathrm{DD}\sigma}\, t)$$
$$= \exp\left[-2\,\gamma_\mathrm{A}\left(\frac{t}{\tau_0}\right)^{1/2}\right] \frac{\mathrm{d}}{\mathrm{d}t} \exp\left[-2\,\gamma_\mathrm{D}\left(\frac{t}{\tau_0}\right)^{1/2}\right]$$
$$= -\frac{\gamma_\mathrm{D}}{(\tau_0\, t)^{1/2}} \exp\left[-2\,\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right]. \tag{A.12}$$

After substitution of (A.12) in (A.11) we have, finally,

$$K = \frac{\gamma_\mathrm{D}}{(\tau_0)^{1/2}} \int_0^\infty (t)^{1/2} \exp\left\{-\left[\frac{t}{\tau_0} + 2\,\gamma\left(\frac{t}{\tau_0}\right)^{1/2}\right]\right\} \mathrm{d}t$$
$$= \tau_0 \left\{\frac{1}{2} \frac{\gamma_\mathrm{D}}{\gamma} f(\gamma) - \gamma\, \gamma_\mathrm{D} [1 - f(\gamma)]\right\}.$$

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