

Short- and Long-Range Order Effects on Resonance Energy Transfer in Crystals and Glasses*

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Abstract—Resonance energy transfer by the Förster–Dexter mechanism in a cubic crystal and in a rigid homogeneous medium is studied. The homogeneous medium is modeled using a hard-sphere fluid (HSF) radial distribution function. This distribution is more realistic than the commonly used uniform distribution with excluded volume (UDEV) function. For the dipole–dipole mechanism, both models yield essentially the same donor luminescence decay, except for small critical radii. For the exchange mechanism, however, the two models differ significantly. In particular, to fit a given experimental decay, the UDEV model requires both a larger effective Bohr radius and a larger rate constant at collisional distance than the HSF model. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Current models of intermolecular quenching of luminescence (both fluorescence and phosphorescence) by nonradiative resonance energy transfer (RET) in a homogeneous medium are largely based on the pioneering results of Förster [1] and Dexter [2], which are remarkable for their simplicity and accuracy [3–7]. Recent developments [6, 8] have refined and established the limits of validity of these early approaches, but moderate quantitative improvements are achieved only at the cost of considerable computational work imposed by molecular details [8]. For most studies not involving molecular aggregates, the modeling of molecules as point particles seems to be a fairly good approximation, even for distances as short as a few angstrom [9, 10]. In this work, calculations will be exclusively based on the basic Förster–Dexter theory, the purpose being to investigate the effect of short-range order on the luminescence decay of the donor.

In the modeling of RET between neutral molecules in a homogeneous medium, the acceptors surrounding the excited donor are usually assumed to be pointlike and randomly distributed in space. In this case, the donor–acceptor radial distribution function, $g(r)$, does not depend on the distance r between the particles and is equal to unity for $0 \leq r < \infty$; i.e., the quenchers are randomly and independently distributed around the excited

molecule. The donor luminescence decay with quenching (normalized to unity at initial time) is given by

$$I(t) = \exp(-t/\tau_0) \exp\left(-4\pi n_q \int_0^\infty (1 - e^{-k(r)t}) g(r) r^2 dr\right), \quad (1)$$

where τ_0 is the intrinsic lifetime of energy donor, n_q is the quencher concentration (the number density), and $k(r)$ is the rate of RET. For the derivation of this equation, it is assumed that the concentration of donor molecules is very small and that donor and acceptor molecules do not diffuse significantly during the donor lifetime. In the case of RET by the dipole–dipole mechanism [1],

$$k(r) = \frac{1}{\tau_0} \left(\frac{R_0}{r}\right)^6, \quad (2)$$

where R_0 is the critical or Förster radius, determined by the overlap of donor luminescence and acceptor absorption spectra, donor quantum yield, and refractive index of the medium. The parameter R_0 takes values between 10 and 70 Å [4–7].

For RET by the exchange mechanism [2],

$$k(r) = k(0) \exp(-2r/L), \quad (3)$$

where $k(0)$ is the quenching rate for zero distance between donor and acceptor and L is the so-called effective average Bohr radius. The exponential distance dependence of Eq. (3) results from the extent of spatial overlap of the electron clouds of excited molecule and

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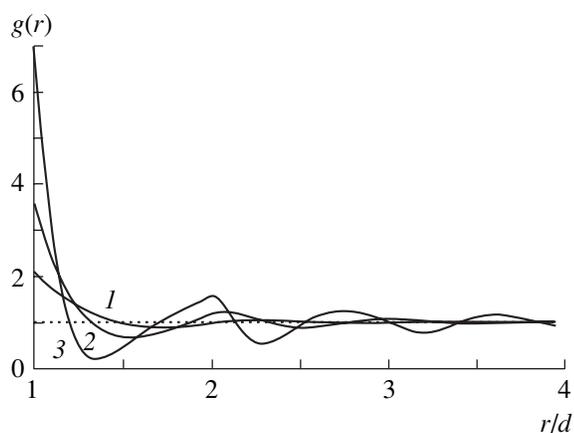


Fig. 1. Hard-sphere fluid (HSF) radial distribution function, $g(r)$, for fluid densities $\rho = 0.5$ (1), 0.8 (2), and 1.1 (3).

quencher. The parameter L , initially introduced by Dexter [2] for RET between atoms by the exchange mechanism, originates 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 [11]. For RET by the exchange mechanism, L was reported to take values between 0.7 and 6 Å [4, 11, 12], a typical value being around 1.5 Å.

Equations (2) and (3) are only approximate. Apart from the above-mentioned deviations to the basic tenets of the Förster–Dexter formalism, the true rate constants are not only functions of relative distance but also functions of relative orientation. In the following, an isotropic interaction will be assumed for simplicity.

Molecules are also not point particles. The problem of RET between particles of finite size was first considered by Rikenglaz and Rozman [13, 14] (a short review on this subject for the exchange mechanism is given in [11]). The molecules were modeled as spheres, and a distance of closest approach (collisional radius) d was introduced. The radial distribution function used in Eq. (1) was the unit step function, meaning that a uniform distribution is assumed for distances larger than d ,

$$g(r) = \begin{cases} 0 & \text{if } r < d, \\ 1 & \text{if } r > d. \end{cases} \quad (4)$$

This model will be called a uniform distribution with excluded volume (UDEV). Taking into account Eq. (4), Eq. (1) becomes

$$I(t) = \exp(-t/\tau_0) \exp(-cH(t)),$$

$$H(t) = 4\pi \int_1^{\infty} (1 - e^{-k(x)t}) g(x) x^2 dx, \quad (5)$$

where $c = n_q d^3$ and $x = r/d$.

Note that, in this case, the excluded volume is properly taken into account only for the donor–acceptor

pair. Acceptors are still assumed to be independently distributed. This means that the model is not appropriate for very high acceptor concentrations.

Both the dipole–dipole [13] and exchange [14] mechanisms of RET were investigated in connection with this distribution. For the last case, it is preferable to rewrite the rate constant of RET (Eq. (3)) as [11]

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

$$= \frac{1}{\tau_0} \exp\left[\gamma - \frac{2(r/d-1)}{L/d}\right]. \quad (6)$$

Now, k_0 is the quenching rate constant for the distance of closest approach, and γ is a dimensionless parameter defined as

$$\gamma = \ln(k_0 \tau_0). \quad (7)$$

This parameter takes values from -3 to 20 [11, 13–15], depending on the system. 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 .

It is well known that the introduction of a distance of closest approach according to Eq. (4) leads to an exponential decay for short times ($k(d)t \ll 1$ in Eq. (5)). For long times, no noticeable difference exists between the decays with $d = 0$ and with $d > 0$.

In fact, the radial distribution function is a more complicated function of distance than a step function (Eq. (4)). In crystals, there is a long-range order. On the other hand, in liquids and molecular glasses, and even in the absence of a Coulombic or van der Waals potential, a short-range order exists owing simply to the finite size of the molecules, and the radial distribution function has the shape of damped oscillations (see Fig. 1). If the density of the fluid decreases, the amplitude of the oscillations decreases. The radial distribution function approaches a step function shape (UDEV model) only for a dilute gas. Several fluid models exist for the evaluation of $g(r)$. The simplest one is that of hard spheres [16]. The hard-sphere fluid (HSF) was, namely, used in [17, 18] in the study of the rate constant of diffusion-controlled reactions, $k(t)$. It was shown that the time dependence of the reaction rate is the same as for the step function Eq. (4), with $k(t) = \alpha + \beta \sqrt{t}$, but the two parameters, α and β , have more realistic values.

In this paper, the luminescence decay law resulting from quenching by dipole–dipole and exchange mechanisms in crystals and homogeneous fluids is investigated taking into account the long- and short-range order of these media.

2. DIPOLE–DIPOLE INTERACTION

Crystals. Let the host molecules form a cubic lattice with lattice constant d , and let the donor and acceptor molecules be substitutional impurities, i.e., occupying lattice sites. The distance between donor and acceptor molecules takes only discrete values d , $\sqrt{2}d$, $\sqrt{3}d$, and so on. In this case, the luminescence decay law can be written as [19–22]

$$I(t) = \exp(-t/\tau_0) \exp\left\{ \sum_i \ln(1 - c + ce^{-k(r_i)t}) \right\}, \quad (8)$$

where the sum runs over all lattice sites and $c = n_q d^3$. We will call this model the long-range order (LRO) model. For a continuous distribution of pointlike molecules ($g(r) = 1$ for all r) and for dipole–dipole interaction, the decay is well known:

$$I(t) = \exp(-t/\tau_0) \exp(-cH_{dd}(t)),$$

$$H_{dd}(t) = \frac{4\pi^{3/2}}{3} \left(\frac{R_0}{d}\right)^3 \left(\frac{t}{\tau_0}\right)^{1/2}. \quad (9)$$

Our numerical calculations show that noticeable differences between Eqs. (8) and (9) exist only if $R_0/d < 1.4$ (e.g., $R_0 < 7 \text{ \AA}$ if $d = 5 \text{ \AA}$). This is an expected result given the usual long-ranged nature of the dipole–dipole interaction.

Fluids. To compute the luminescence decay (Eq. (1)) in a glass, the appropriate radial distribution function $g(r)$ for the acceptors surrounding the donor must be used. This function was investigated for several models of liquid structure. We will use the hard-sphere fluid (HSF) model [16] owing to the following reasons. Firstly, this model is the natural next step in the modeling of RET by the UDEV model. Secondly, HSF was previously investigated in detail: analytical solutions for $g(r)$ [23–28] and its Laplace transform [23] are known, and tables of $g(r)$ for different values of fluid density are available [26, 29, 30]. Thirdly, the computed $g(r)$ for hard spheres has an overall good agreement with simulation data, although some discrepancies are observed, especially at the highest densities [29, 31].

In this paper, we will use the detailed tables given in [26]. The radial distribution function for several values of fluid dimensionless (or reduced) density ρ , where

$$\rho = n_f d^3, \quad (10)$$

n_f and d being the number density and the hard-sphere diameter of fluid molecules, respectively, is shown in Fig. 1.

The dimensionless density ρ is connected to the packing density, η , which is the fraction of the volume occupied by the spheres, by

$$\rho = \frac{6}{\pi} \eta. \quad (11)$$

Note that there is a simple analytical solution for $g(r)$ at $r = d$ [25],

$$g(d) = \frac{1 + \eta/2}{(1 - \eta)^2}. \quad (12)$$

To simplify the calculations, we will suppose that donor, acceptor, and solvent molecules are all spherical molecules with a common diameter, d . In this case, the radial distribution functions for the donor–acceptor pair in Eq. (5) and for an HSF coincide. For the calculations, $g(r)$ for $\rho = 0.8$ and 1.1 is used. At these fluid densities, the difference between the step function Eq. (4) and $g(r)$ for an HSF is pronounced: From Eq. (12) and [26], $g(d) \approx 3.58$ for $\rho = 0.8$ and $g(d) \approx 7.16$ for $\rho = 1.1$. Also, the hard-sphere solid and fluid phases are in thermodynamic equilibrium over a density interval from 0.943 to 1.04 [30, 32].

Our calculations of the donor luminescence decay kinetics taking into account the HSF radial distribution function show that a noticeable difference between Eqs. (5) and (9) is observed if $R_0/d < 2$ (see Fig. 2a where the values $R_0 = 8 \text{ \AA}$, $d = 5 \text{ \AA}$, and $\rho = 1.1$ are used). This difference practically disappears if the R_0 used in Eq. (9) is slightly decreased (e.g., from 8 to 7.9 \AA in the case of parameters used in Fig. 2a).

Note that the difference between Eqs. (5) and (9) is more pronounced if the step function Eq. (4) is used in Eq. (5) (Fig. 2b). In this case, the Förster radius R_0 in Eq. (9) must be decreased from 8 to 7.7 \AA (the other parameters being the same as in Fig. 2a) to suppress the difference between the two decays in the time interval $0 < t/\tau_0 < 3$.

The reason for the HSF model to be closer to the Förster kinetics Eq. (9) (pointlike particles) than to the UDEV model is as follows: The HSF radial distribution function deviates from unity in an oscillatory way (see Fig. 1) with values below unity ($g(r) = 0$ for $0 < r < d$) and above unity ($g(r) > 1$ for $d \leq r < 1.3d$), and there is a nearly complete cancellation of effects.

3. EXCHANGE MECHANISM

Recently [11], the UDEV model for fluorescence quenching with exponential distance dependence was studied in detail. Three different situations were identified: weak ($\gamma < 2$), intermediate ($2 < \gamma < 5$), and strong ($\gamma > 5$) quenching. It was shown that the parameters L , d , and γ were correlated and cannot be independently determined from a fluorescence decay. At most, it is possible to determine L and γ , while fixing d . Following [11], we will also consider three such situations. Namely, in our numerical calculation, we will use the values $\gamma = -2, 4$, and 10 and $L/d = 0.2, 0.5$, and 0.8 as typical experimental values [4, 11, 15].

Crystals. Here, the decay law Eq. (5) calculated with the step function Eq. (4) (UDEV model) and Eq. (8) (LRO) are compared. We will label the lumines-

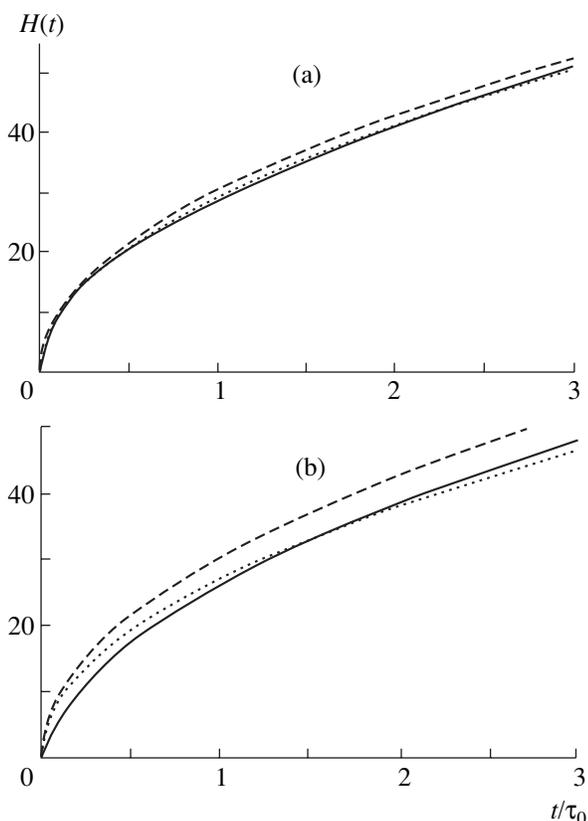


Fig. 2. Function $H(t)$ calculated for the dipole–dipole mechanism and for three different radial distribution functions. (a) HSF with density $\rho = 1.1$, $d = 5$ Å, $R_0 = 8$ Å (solid line); molecules are point particles (radial distribution function is equal to unity everywhere), $R_0 = 8$ Å (dashed line) and $R_0 = 7.9$ Å (dotted line). (b) HSF with density $\rho = 1.1$, $d = 5$ Å, $R_0 = 8$ Å (solid line); the radial distribution function is a step function (UDEV model), the distance of closest approach $d = 5$ Å, $R_0 = 8$ Å (dashed line) and $R_0 = 7.7$ Å (dotted line).

cence decays obtained with Eqs. (8) and Eq. (5) as “experimental” (LRO) and “theoretical” (UDEV), respectively. The parameters for the exchange interaction (Eq. (6)) will be denoted as γ_0 and L_0 for the experimental kinetics and γ and L for the theoretical kinetics.

Calculations show that, in the case of weak quenching, the second exponential factor of Eq. (8) is almost a linear function of time for $t/\tau_0 < 3$. Thus, we can rewrite Eq. (8) as

$$I(t) \approx \exp(-t/\tau_0) \left[1 - c \frac{t}{\tau_0} e^{\gamma_0} \sum_i e^{-2(x_i-1)/b_0} \right], \quad (13)$$

where $b_0 = L_0/d$. Similarly, Eq. (5), where $g(x)$ is a step function, gives

$$I(t) \approx \exp(-t/\tau_0) \left[1 - 4\pi c \frac{t}{\tau_0} e^{\gamma} \frac{1}{4} b(2 + 2b + b^2) \right], \quad (14)$$

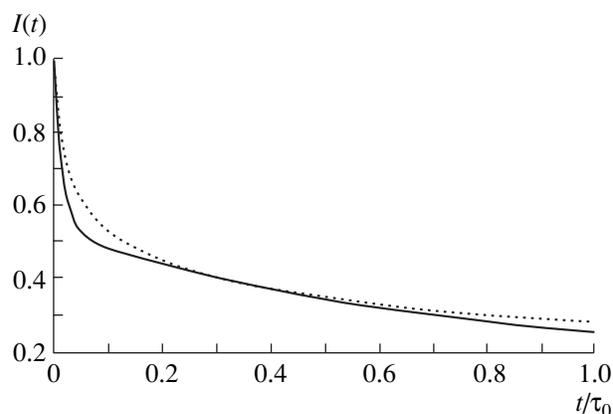


Fig. 3. Luminescence decay calculated for the exchange mechanism in a cubic lattice ($\gamma = 4$, solid line) and according to the UDEV model ($\gamma = 5.2$, dotted line). The lattice constant is equal to the distance of closest approach, $d = 5$ Å, quencher concentration $c = 0.1$, and $L/d = 0.2$. Parameter $\gamma = 5.2$ of the dotted curve is chosen to bring together the two decays as much as possible.

where $b = L/d$. Therefore, the experimental luminescence decay Eq. (13) can be fitted by the theoretical decay Eq. (14) for a continuous set of parameters γ and L/d . For example, if the experimental decay Eq. (13) is computed with parameters $\gamma_0 = -2$ and $L_0/d = 0.2$, the theoretical decay fits equally well the experimental one with a set of parameters from $\{\gamma = -0.45, L/d = 0.2\}$ to $\{\gamma = -3.8, L/d = 1.5\}$. If, on the other hand, $\gamma_0 = -2$ and $L_0/d = 0.8$ in the experimental decay, then the set of parameters in Eq. (14) is even larger: from $\{\gamma = -0.65, L/d = 0.4\}$ to $\{\gamma = -5.5, L/d = 20\}$. Thus, parameters γ and L/d are correlated and cannot be independently determined from the luminescence decay.

For the intermediate case, the luminescence decay is a more complex function of time. For some values of the parameters, experimental (LRO) and theoretical (UDEV) decays cannot be made to agree (see Fig. 3). The experimental decay has a pronounced two-exponential behavior.

In the strong quenching limit, experimental and theoretical decays can be well reconciled ($t/\tau_0 < 3$), but the recovered UDEV parameters (γ and L/d) differ from the LRO parameters (γ_0 and L_0/d). For example, the experimental values $\gamma_0 = 10$ and $L_0/d = 0.5$ correspond to the theoretical values $\gamma = 11.2$ and $L/d = 0.35$. Analogously, LRO values $\gamma_0 = 10$ and $L_0/d = 0.8$ correspond to UDEV values $\gamma = 11.8$ and $L/d = 0.49$. Hence, the parameter L/d obtained by fitting the experimental decay (LRO) with the UDEV model can be two times smaller than the experimental one.

Fluids. In this case, luminescence decays according to the UDEV and HSF models are compared. The radial distribution function for $\rho = 0.8$ and 1.1 is used. To simplify the comparison procedure (thus avoiding the effect of quencher concentration, c), only the func-

tion $H(t)$ in Eq. (5) is investigated. Again, the function $H(t)$ obtained with the step function Eq. (4) is called “theoretical” (UDEV), and the function $H(t)$ obtained with the HSF $g(r)$ is called “experimental.”

In the weak quenching limit, $H(t)$ is almost a linear function of time. For the experimental decay (HSF),

$$H(t) = H_{\text{HSF}}(t) \approx 4\pi \frac{t}{\tau_0} e^{\gamma_0} \int_1^{\infty} e^{-2(x-1)/b_0} g(x) x^2 dx, \quad (15)$$

and for the theoretical decay (UDEV),

$$H(t) = H_{\text{UDEV}}(t) \approx 4\pi \frac{t}{\tau_0} e^{\gamma} \frac{1}{4} b(2 + 2b + b^2). \quad (16)$$

As can be seen, the experimental function, $H_{\text{HSF}}(t)$, can be fitted equally well by the theoretical one, $H_{\text{UDEV}}(t)$, for a continuous set of parameters γ and L/d . For example, if $\rho = 1.1$, $\gamma_0 = -2$, and $L_0/d = 0.2$, the theoretical curve fitting the experimental one can be obtained using sets of parameters from $\{\gamma = -0.49, L/d = 0.18\}$ to $\{\gamma = -6.4, L/d = 20\}$. Only when a quadratic term in time is introduced (weak but not very weak quenching) does this correlation disappear [11].

In the intermediate case, both the theoretical and experimental functions are no longer linear, and no satisfactory fit of the HSF decay with the UDEV model is possible in general. There is indeed a strong difference at short times in most cases (see Fig. 4). This difference depends on fluid concentration and decreases with decreasing fluid density. As for crystals, the experimental decay (HSF) has a pronounced two-exponential behavior.

In the strong quenching limit ($\gamma_0 \geq 10$ and $L_0/d \geq 0.2$ or $\gamma_0 \geq 4$ and $L_0/d \geq 0.5$), the experimental and theoretical decays are not linear functions of time, and the experimental decays can be well fitted, but parameters γ_0 , L_0/d and γ , L/d are different. This difference is nevertheless not large and decreases with increasing values of the parameters. For example, if $\gamma_0 = 4$ and $L_0/d = 0.5$ in the experimental decay, then $\gamma = 4.3$ and $L/d = 0.49$ for the theoretical one. If $\gamma_0 = 10$ and $L_0/d = 0.8$, then $\gamma = 10.09$ and $L/d = 0.8$. The precisions of the obtained values are ± 0.05 for γ and ± 0.01 for L/d . Note that, in the strong quenching limit, the obtained values are not dependent on fluid concentration: they are quantitatively the same for $\rho = 0.8$ and 1.1 , although $g(d)$ for these fluid densities differ by nearly a factor of two (see Eq. (12)). The situation approaches in this limit what was already observed for the dipole–dipole case in Section 2.

In [11], two molecular pairs were experimentally studied in rigid glasses at 77 K by picosecond single-photon timing: C_{70} –bromobenzene and phenanthrene–iodide. In these systems, the quenching of fluorescence occurs by the external heavy-atom effect, but the distance dependence is similar to that of the exchange mechanism. In the first system, the very different size

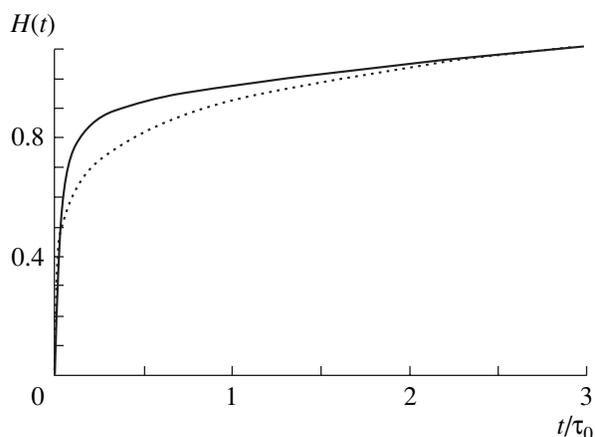


Fig. 4. Function $H(t)$ calculated for the exchange mechanism according to the HSF model ($\rho = 1.1$, $d = 5 \text{ \AA}$, $\gamma_0 = 4$, $L_0/d = 0.2$, solid line) and to the UDEV model ($d = 5 \text{ \AA}$, $\gamma = 7.9$, $L/d = 0.13$, dotted line). Parameters $\gamma = 7.9$ and $L/d = 0.13$ of the dotted curve are chosen to bring together the two decays as much as possible.

of solvent (7 : 2 (v/v) methylcyclohexane–toluene) and one of the solute (C_{70}) molecules makes questionable the application of the HSF model as developed here, where solvent and solute are assumed to have identical size. The second system, where all sizes are comparable, is in the intermediate quenching case. Using $d = 7.4 \text{ \AA}$ and $\tau_0 = 64.4 \text{ ns}$, the values $L = 1.7 \text{ \AA}$ and $k_0 = 0.12 \text{ ns}^{-1}$ (which give $L/d = 0.23$ and $\gamma = 2.05$) were obtained [11] by fitting experimental fluorescence decays with the UDEV model. In this particular system, fits with the HSF model were also satisfactory. Different values for γ and L/d are obtained, but depend on the fluid density used. For $\rho = 0.8$, we obtain $L/d = 0.17$ and $\gamma = 1.23$ (or $L = 1.3 \text{ \AA}$ and $k_0 = 0.053 \text{ ns}^{-1}$) for $t/\tau_0 < 3$. For a higher fluid density, $\rho = 1.1$, $L/d = 0.14$, and $\gamma = 0.85$ (or $L = 1.0 \text{ \AA}$ and $k_0 = 0.036 \text{ ns}^{-1}$) are obtained instead. Thus, for the phenanthrene–iodide system, introduction of a more realistic radial distribution function (HSF model) allows one to estimate parameters L and k_0 at 1.0 – 1.3 \AA and 0.036 – 0.053 ns^{-1} , respectively. These values are significantly smaller than those estimated with the UDEV model.

4. CONCLUSIONS

In this paper, the radial distribution function for the hard-sphere fluid model (HSF) was used to calculate the quenching of luminescence by dipole–dipole and exchange RET mechanisms. The HSF model takes into account the short-range order existent in fluids owing to the finite size of the molecules, which are modeled as rigid spheres.

For the dipole–dipole mechanism, the luminescence decay law obtained within the framework of this model hardly differs from the usual Förster decay law for

pointlike particles. The Förster radius is at most slightly different.

For the short-ranged exchange mechanism, the decay laws obtained with the use of the hard-sphere fluid radial distribution function and with the step function are practically identical if quenching is strong, but the two sets of parameters γ and L/d are different. Parameter L/d is smaller for the HSF model, because the radial distribution function at the distance of closest approach is noticeably larger than unity. In the very weak quenching limit, parameters γ and L/d are correlated and cannot in principle be independently determined from luminescence decays. In the intermediate case, the luminescence decay laws usually have quite different time dependences for the uniform distribution with excluded volume and HSF radial distribution functions, but in some cases they can be made to agree.

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