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SOLID-STATE SPECTROSCOPY

Luminescence Quenching in Fractal Media Accelerated by Migration

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Abstract—Concentration dependences of the luminescence quantum yield and anisotropy are studied in fractals. It is shown that these dependences at high concentrations of luminescent molecules can be used for determining fractal dimensionality of the media under study.

INTRODUCTION

Currently, radiationless energy transfer (RET) from an excited molecule to an unexcited molecule is widely used in biophysics [1] and physics of polymers [2–8] and porous glasses [9–15] to study various statistical properties of media. This is explained by the high sensitivity of RET to the distance between interacting molecules.

The quantity being measured in these experiments is the decay kinetics of initially excited molecules, which is described by the diagonal part $G_d(t)$ of the Green function for the excitation transport.

If RET occurs between molecules of the same type (migration of excitations), the function $G_d(t)$ is uniquely related to the decay kinetics of luminescence anisotropy $r(t)$ by the equation

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(0) + 2I_{\perp}(0)} \propto G_d(t). \qquad (1)$$

Here, $I_{\parallel}(t)$ and $I_{\perp}(t)$ are intensities of polarized luminescence at time t in the directions parallel and perpendicular to polarization of the exciting pulse, respectively.

If RET occurs between molecules of different types (from donors to acceptors, the concentration of donors being low enough that migration of excitations is absent), the total intensity $I(t)$ of luminescence of donors is also proportional to $G_d(t)$:

$$I(t) \propto G_d(t). \qquad (2)$$

Specific properties of a medium (for example, its fractal dimensionality) are manifested in a different decrease of $G_d(t)$ in time [2–14].

Undoubtedly, not only the kinetics of luminescence decay is of interest, but also the dependence of the luminescence quantum yield η and anisotropy on concentrations of donors and acceptors in fractal structures (for example, in viscous solutions of polymer molecules or in porous glasses). Such information, which is obtained from simple experiments, can improve our understanding of statistical properties of fractal media.

As far as we know, this problem has not been theoretically solved. In this connection, papers [6, 15] should be mentioned. In [6], an attempt was made to calculate the kinetics of luminescence decay for donor molecules in polymer media taking into account energy migration. The authors of [6] used the self-consistent GAF (Gochanour–Anderson–Fayer) method developed in [16]. However, the equations obtained in [6] can be solved only numerically, and the net calculations and conclusions were only made for the time dependence of the diagonal part $G_d(t)$ of the Green function.

In [15], the kinetics of luminescence quenching of donors by acceptors was calculated in media with fractal dimensionality by the method of continuous time random walks (CTRW) taking into account the migration of excitations and assuming a dipole–dipole interaction between molecules. Theoretical results were compared with experimental data on luminescence of molecules adsorbed on a surface of porous glasses. The only fitting parameter was the fractal dimensionality of a medium, which was found from this comparison.

Concentration dependences of the luminescence quantum yield η and anisotropy r were studied in [9, 10]. In these papers, spectral luminescent properties of dyes adsorbed on porous glasses were investigated. The authors of [9, 10] found a nonlinear dependence of the quantum yield and anisotropy on the volume concentration n_D of donor molecules in the region of low concentrations:

$$\eta_0/\eta = 1 + An_D^{\alpha}, \quad r_0/r = 1 + Bn_D^{\alpha}. \qquad (3)$$

In equations (3), η_0 and r_0 are the luminescence quantum yield and anisotropy for ultimately low concentrations of donors (n_D) and acceptors (n_A) ($n_D \longrightarrow 0$, $n_A \longrightarrow 0$), respectively; and A and B are numerical coefficients. The exponent α lies within the range of $1/3 < \alpha < 2/3$. In three-dimensional media, these dependences should be linear [17]. Based on this fact, the

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authors of [9, 10] draw the conclusion that the media under study possess fractal structure.

In this paper, we use the CTRW method [17] to solve the stated problem. This method allows us to obtain a number of analytic results for concentration dependences of the luminescence quantum yield and anisotropy in fractal structures in the case of an arbitrary multipolarity of the interaction between molecules. These dependences differ from those for three-dimensional media, and can thus be used for determining the fractal dimensionality of media under study.

DERIVATION OF THE EQUATIONS

Incoherent migration of excitations is described by a system of balance equations

$$\frac{d}{dt}P(\mathbf{x}_i, \mathbf{x}_j, t) = -\frac{1}{\tau_0}P(\mathbf{x}_i, \mathbf{x}_j, t)$$

$$+\sum_{k}^{N}[w(\mathbf{x}_i, \mathbf{x}_k)P(\mathbf{x}_k, \mathbf{x}_j, t) - w(\mathbf{x}_k, \mathbf{x}_i)P(\mathbf{x}_i, \mathbf{x}_j, t)] \quad (4)$$

$$-\sum_{m}^{M}u(\mathbf{x}_m, \mathbf{x}_i)P(\mathbf{x}_i, \mathbf{x}_j, t), \quad P(\mathbf{x}_i, \mathbf{x}_j, 0) = \delta_{ij}.$$

Here, subscripts i, j, k, and m number molecules; N is the number of donors; M is the number of acceptors; $\mathbf{x}_i$ are spatial coordinates of the ith molecule; $P(\mathbf{x}_i, \mathbf{x}_j, t)$ is the probability of finding an excitation at the ith donor at time t if the jth donor was excited at time $t = 0$; τ_0 is the excited state lifetime for the donor; $w(\mathbf{x}_i, \mathbf{x}_j)$ is the rate of energy transfer from the jth donor to the ith donor; $u(\mathbf{x}_m, \mathbf{x}_i)$ is the rate of energy transfer from the ith donor to the mth acceptor; and δ_{ij} is the Kronecker delta.

For multipole interaction of impurity centers,

$$w(R) = \frac{1}{\tau_0}\left(\frac{R_{DD}}{R}\right)^6, \quad u(R) = \frac{1}{\tau_0}\left(\frac{R_{DA}}{R}\right)^6, \quad (5)$$

where $R = |\mathbf{x}_i - \mathbf{x}_j|$, R_{DD} and R_{DA} are Förster radii for energy transfer between donors and donors and acceptors, respectively; and $s = 6$, 8, and 10 for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively.

In the CTRW method, equations (4) are first written in the integral form [17, 18]

$$P(\mathbf{x}_i, \mathbf{x}_j, t) = \delta_{ij}\exp\left[-t\left(1/\tau_0 + \sum_k w(\mathbf{x}_k, \mathbf{x}_i)\right.\right.$$

$$\left.\left.+\sum_m u(\mathbf{x}_m, \mathbf{x}_i)\right) + \int_0^t dt'\sum_k \exp\left[-(t-t')\right.\right.$$

$$\left.\left.\times\left(1/\tau_0 + \sum_{l\neq k} w(\mathbf{x}_l, \mathbf{x}_i) + \sum_m u(\mathbf{x}_m, \mathbf{x}_i)\right)\right]\right. \quad (6)$$

$$\times\, w(\mathbf{x}_i, \mathbf{x}_k)\exp[-(t-t')w(\mathbf{x}_k, \mathbf{x}_i)]P(\mathbf{x}_k, \mathbf{x}_j, t').$$

Then, an iteration series corresponding to (6) is written. The terms of this series are averaged under the condition that correlations between molecules surrounding various molecules are small and excitation does not return to the initial molecule during migration. The series thus obtained is convoluted in the integral equation for the total Green function $G(\mathbf{x} - \mathbf{x}', t)$ (this function represents the probability density of finding an excitation at point $\mathbf{x}$ at time t, if, at $t = 0$, the excitation was at point $\mathbf{x}'$)

$$G(\mathbf{x} - \mathbf{x}', t) = G_d(t)\delta(\mathbf{x} - \mathbf{x}') + \int_0^t dt' G_d(t-t')\bar{d}V_d$$

$$\times\int dR\rho_D(R)R^2 w(\mathbf{x} - \mathbf{x}_1)\exp[-t'w(\mathbf{x}_1 - \mathbf{x}')] \quad (7)$$

$$\times\, G(\mathbf{x}_1 - \mathbf{x}', t'), \quad G(\mathbf{x} - \mathbf{x}', t) = \delta(\mathbf{x} - \mathbf{x}').$$

Here, $R = |\mathbf{x} - \mathbf{x}_1|$, and $\bar{d}$ is the dimensionality of the space:

$$V_d = \pi^{\bar{d}/2}/\Gamma(1 + \bar{d}/2), \quad (8)$$

where $\Gamma(x)$ is a gamma function, $\rho_D(R)$ [and a similar function $\rho_A(R)$] is the probability density of finding a donor (an acceptor) at the distance R from the origin of coordinates in the fractal structure under study. In three-dimensional media ($\bar{d} = 3$),

$$\rho_D = n_D, \quad \rho_A = n_A. \quad (9)$$

In the self-similar structures (fractals) [3, 19–22],

$$\rho_D(R) = \sigma_D R^{\bar{d}-3}, \quad \rho_A(R) = \sigma_A R^{\bar{d}-3}. \quad (10)$$

The constants σ_D and σ_A represent concentrations of molecules inside a fractal.

The diagonal part $G_d(t)$ of the Green function in (7) is represented as a product of three factors [see equations (6) and (7)]

$$G_d(t) = \exp(-t/\tau_0)Q_A(t)Q_D(t), \quad (11)$$

where

$$Q_D(t) = \exp\left\{-\bar{d}V_d\sigma_D\int_0^\infty R^{\bar{d}-1}[1 - e^{-tw(R)}]dR\right\}, \quad (12)$$

$$Q_A(t) = \exp\left\{-\bar{d}V_d\sigma_A\int_0^\infty R^{\bar{d}-1}[1-e^{-tu(R)}]dR\right\}. \quad (13)$$

The kinetics of luminescence decay $I(t)$ is related to the Green function by the known equation [17], which follows from the physical meaning of $G(\mathbf{x}, t)$

$$I(t) = \Lambda_0\int G(\mathbf{x}, t)d\mathbf{x}, \quad (14)$$

where Λ_0 is the initial density of excitations (which is assumed to be spatially uniform).

Taking into account (7) and (11)–(14), we obtain the well-known equation for $I(t)$ [17, 18, 23]

$$I(t) = \Lambda_0 e^{-t/\tau_0}Q_A(t)Q_D(t) - \int_0^t e^{-(t-t')/\tau_0}Q_A(t-t')\frac{dQ_D(t-t')}{dt}I(t')dt'. \quad (15)$$

The only difference between this equation and the conventional equation for three-dimensional media consists in the form of functions $Q_D(t)$ and $Q_A(t)$.

In order to partially take into account the possibility of excitation returning to the initial molecule, in the CTRW method, instead of function (12), another function is commonly used [17, 18], which was suggested in [24]. Generalization of this approach to fractal structures yields

$$Q_D(t) = \exp\left\{-\bar{d}V_d(\sigma_D/2)\times\int_0^\infty R^{\bar{d}-1}[1-e^{-2tw(R)}]dR\right\}. \quad (16)$$

Therefore, the kinetics of luminescence decay $I(t)$ is calculated in CTRW method from equation (15), in which functions $Q_D(t)$ and $Q_A(t)$ are described by (16) and (13), respectively.

The luminescence quantum yield and anisotropy are related to $I(t)$ and $G_D(t)$ by equations [17]

$$\eta/\eta_0 = \int_0^\infty I(t)dt/(\tau_0\Lambda_0), \quad (17)$$

$$r/r_0 = \eta_1/\eta = (\eta_0/\eta)\int_0^\infty G_d(t)dt/\tau_0, \quad (18)$$

where η_1 is the luminescence quantum yield of initially excited molecules. The diagonal part $G_D(t)$ of the Green function in (18) is defined by expressions (11), (13), and (16).

Note that, due to approximations made in the derivation of equation (7), all the formulas are valid for the hopping mechanism of luminescence quenching [17, 18]: the most probable length of the excitation jump from one donor to another should exceed the radius of strong quenching of a donor by an acceptor. In the case of the same multipolarity of the interaction, this means that the inequality $R_{DD} < R_{DA}$ should be satisfied.

CONCENTRATION DEPENDENCES AND DISCUSSION

To obtain the concentration dependence of the quantum yield (17), we integrate equation (15) over time. The resulting equation has the solution

$$\eta/\eta_0 = \frac{\int_0^\infty \exp(-t/\tau_0)Q_A(t)Q_D(t)dt/\tau_0}{1+\int_0^\infty \exp(-t/\tau_0)Q_A(t)\frac{dQ_D(t)}{dt}dt}. \quad (19)$$

Taking into account (11), (18), and (19), for the luminescence anisotropy we obtain

$$r/r_0 = 1+\int_0^\infty \exp(-t/\tau_0)Q_A(t)\frac{dQ_D(t)}{dt}dt. \quad (20)$$

For the multipole interaction of molecules, from (16) and (13), we obtain

$$Q_D(t) = \exp[-\gamma_D(t/\tau_0)^{\bar{d}/s}], \quad \gamma_D = 2^{\bar{d}/s-1}V_d\sigma_D R_{DD}^{\bar{d}}\Gamma(1-\bar{d}/s), \quad (21)$$

$$Q_A(t) = \exp[-\gamma_A(t/\tau_0)^{\bar{d}/s}], \quad \gamma_A = V_d\sigma_A R_{DA}^{\bar{d}}\Gamma(1-\bar{d}/s). \quad (22)$$

In the case of low concentrations of molecules ($\gamma_A \ll 1$, $\gamma_D \ll 1$), it follows from (19)–(22) that

$$\eta/\eta_0 = 1-\gamma_A\Gamma(1+\bar{d}/s)+0.5\gamma_A^2\Gamma(1+2\bar{d}/s) - \gamma_A\gamma_D[\Gamma^2(1+\bar{d}/s)-0.5\Gamma(1+2\bar{d}/s)], \quad (23)$$

$$r/r_0 = 1-\frac{\bar{d}}{s}\gamma_D[\Gamma(\bar{d}/s)-(\gamma_A+\gamma_D)\Gamma(2\bar{d}/s)]. \quad (24)$$

For three-dimensional media ($\bar{d} = 3$) and the dipole–dipole interaction of molecules ($s = 6$), dependences (23) and (24) coincide with those presented in [17].

For high concentrations ($\gamma_A + \gamma_D \gg 1$), from (19)–(22), we obtain

$$\eta_0/\eta = \frac{\gamma_D}{\gamma_A+\gamma_D}+\frac{\gamma_A(\gamma_A+\gamma_D)^{s/\bar{d}-1}}{\Gamma(1+s/\bar{d})}, \quad (25)$$

$$r/r_0 = \frac{\gamma_A}{\gamma_A+\gamma_D}+\frac{\gamma_D\Gamma(1+s/\bar{d})}{(\gamma_A+\gamma_D)^{s/\bar{d}+1}}. \quad (26)$$

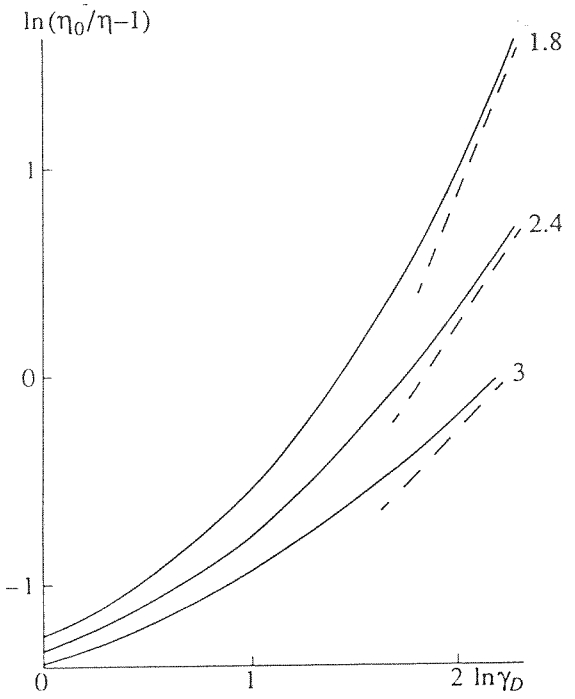

Fig. 1. Concentration dependences of the luminescence quantum yield. The values of $\bar{d}$ are shown near the curves, $\gamma_A = 0.2$.

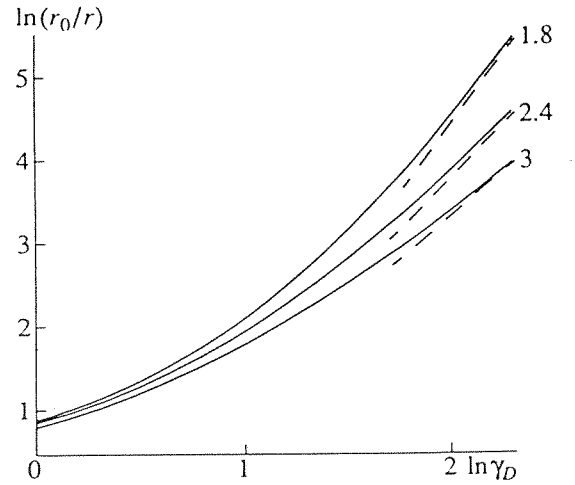

Fig. 2. Concentration dependences of the luminescence anisotropy. The values of $\bar{d}$ are shown near the curves, $\gamma_A = 0$.

In the case of $\bar{d} = 3$ and $s = 6$, equations (25) and (26) also coincide with those presented in [17].

Expressions (23) and (24) suggest a linear dependence of the luminescence quantum yield and anisotropy on concentrations σ_A and σ_D of molecules in a fractal medium (for low concentrations). In [8, 11, 13, 14], the linear dependence

$$\sigma_A \propto n_A \tag{27}$$

was found between σ_A and concentration n_A of molecules adsorbed on a surface of latex particles and porous glasses.

This results in the coincidence of functions (23) and (24) for fractals and three-dimensional media. The only difference is in the values of numerical coefficients in front of σ_A, σ_D, and n_A, n_D, respectively. For this reason, it is difficult to use equations (23) and (24) to determine the fractal dimensionality of the medium under study.

In the general case, the relation between the volume (n) and fractal (σ) concentrations of molecules can be nonlinear, because this relation depends on three factors: a change in the mean volume concentration n of molecules can be accompanied by simultaneous changes in the number of fractal clusters formed by molecules, in the size of these clusters, and in fractal concentrations (σ_A and σ_D) in each cluster. If the first two factors are constant under experimental conditions, then the relation between n and σ will be linear.

Nonlinear dependences (3) found in [9, 10] are probably caused by the conditions of preparation of the samples studied. The above three factors simultaneously changed in these samples with increasing volume concentration of molecules.

In the region of high concentrations of donors ($\gamma_D \gg 1$) and low concentrations of acceptors ($\gamma_A \ll 1$), equations (25) and (26) give nonlinear dependences of the luminescence quantum yield and anisotropy on the fractal concentration σ_D ($\gamma_D \propto \sigma_D$)

$$\eta_0/\eta \approx 1 + \gamma_A \gamma_D^{s/\bar{d}-1}/\Gamma(1 + s/\bar{d}), \tag{28}$$

$$r_0/r \approx \gamma_D^{s/\bar{d}}/\Gamma(1 + s/\bar{d}). \tag{29}$$

These dependences substantially differ (by the exponent) from those for three-dimensional media and can be used to determine the fractal dimensionality of media.

Note that the exponent depends both on the fractal dimensionality $\bar{d}$ of the medium and on the type s of interaction between molecules.

It is easy to show that the kinetics of luminescence decay at long times is exponential [13]:

$$I(t) \propto \exp(-t/\tau_0 - kt). \tag{30}$$

If the condition $\gamma_A \ll \gamma_D$ is satisfied, then the rate constant k in (30) is equal to unity:

$$k = \frac{1}{\tau_0}\gamma_A \gamma_D^{s/\bar{d}-1}/\Gamma(1 + s/\bar{d}). \tag{31}$$

Figures 1 and 2 show the results of numerical calculations of η_0/η and r_0/r for $\gamma_A \ll 1$ from equations (19) and (20) ($s = 6$; and $d = 3$, 2.4, and 1.8). The dashed curves correspond to calculations according to (28) and (29). These calculations support the above conclusions.

CONCLUSION

Thus, we obtained equations describing the concentration quenching of luminescence in fractal structures for an arbitrary multipolarity of the interaction between molecules. The analytic results for concentration dependences of the luminescence quantum yield and anisotropy can be used for experimental determination of the fractal dimensionality of media.

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