

SOLID-STATE SPECTROSCOPY

Kinetics of Luminescence of Porous Media: The Effective Fractal Dimensionality and Penetration Depth of Chromophores

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Received August 26, 1998

Abstract—Kinetics of luminescence and the effective fractal dimensionality of porous media calculated from it are interpreted within the framework of diffusion penetration of chromophores through a surface, resulting in a decrease in their concentration inside a medium with increasing distance to its surface.

INTRODUCTION

In recent years, the dipole–dipole electronic excitation energy transfer (ET) is often used as a tool for studying various nanosystems [1–6] and porous media [7–11]. The probability of ET strongly depends on the intermolecular distance, relative orientation, and relative motion of the interacting chromophores (donors and acceptors of the electronic energy). As a result, the luminescence kinetics in the presence of ET yields information on structural and dynamic parameters of the system. This information can be obtained from comparison of experimental and theoretical kinetics of the luminescence decay and luminescence anisotropy.

The first theoretical studies of ET in porous media [12, 13] were devoted to direct (irreversible) ET from donors to acceptors. A porous medium was characterized by the fractal dimensionality d^* . The number of chromophores $N(R)$ inside a sphere of radius R (at an arbitrary point of the medium) in such a medium is proportional to R^{d^*}

$$N(R) \propto R^{d^*}. \quad (1)$$

(In a three-dimensional medium, $N(R) \propto R^3$). In this case, the luminescence kinetics $I(t)$ for the dipole–dipole ET is described by the equation

$$I(t) = I_0 \exp\{-t/\tau_0 - \gamma(t/\tau_0)^{d^*/6}\}, \quad (2)$$

where I_0 is the luminescence intensity at the initial moment, τ_0 is the lifetime of the excited state of a donor in a medium without acceptors, and a parameter γ depends on the critical radius of ET and the concentration n_A of acceptors. The careful experimental measurements showed that $\gamma \propto n_A$ [7, 9, 14]. By comparing the experimental and theoretical kinetics, one can find the fractal dimensionality of the medium.

In [15, 16], the effect of energy migration between donors on the quantum yield, anisotropy, and kinetics

of the luminescence decay was studied and the method for calculating the fractal dimensionality was suggested.

However, the simplest way of determining the fractal dimensionality of a medium is probably as follows. The concentration dependence of the quantum yield q and average luminescence lifetime τ are measured under stationary excitation. The quantities q and τ are known to be related with the luminescence kinetics by the equations

$$q = (\tau_0 I_0)^{-1} \int_0^{\infty} I(t) dt, \quad (3)$$
$$\tau/\tau_0 = \int_0^{\infty} t I(t) dt / \int_0^{\infty} I(t) dt.$$

For low concentration of acceptors (the concentration of donors should be low to avoid energy migration), we find with the help of (2) and (3)

$$q = 1 - \gamma \Gamma(1 + d^*/6), \quad (4)$$
$$\tau/\tau_0 = 1 - (d^*/6) \gamma \Gamma(1 + d^*/6),$$

where Γ is the gamma function. It follows from (4) that at low concentrations, the luminescence quantum yield and lifetime linearly decrease with increasing acceptor concentration ($\gamma \propto n_A$). However, the rates of this decrease are different. The quantum yield decreases faster by a factor of $d^*/6$ than the luminescence lifetime. Therefore, by comparing experimental concentration dependences $q(n_A)$ and $\tau(n_A)$, one can calculate the fractal dimensionality of the medium.

Note that the fractal interpretation of the kinetics (2) provokes a number of objections [18–20], and other models are also used, in which a porous medium is simulated by a set of cylindrical or spherical pores and chromophore molecules are located only on pore sur-

faces [9, 11–13, 18, 19]. The luminescence kinetics of such model media is also approximately described by equation (2) within some time interval.

The aim of this paper is to show that the kinetics (2) can be caused by the depth of penetration of chromophores inside a porous medium rather than by the fractal dimensionality of the medium or the shape and size of the pores. This penetration depth depends on the method of sample preparation. As the penetration depth increases, the effective fractal dimensionality of the medium increases from 2 to 3.

RELATION BETWEEN THE FRACTAL DIMENSIONALITY AND DEPTH OF PENETRATION OF CHROMOPHORES INTO A SAMPLE

Analysis of experimental data [7–9, 15] shows that the fractal dimensionality of porous media [calculated from equation (2)] and latex particles [14] containing chromophores incorporated through a surface lies within the range $2 < d^* < 3$. Taking into account equation (1), this can mean that the concentration of chromophores decreases with the distance from the surface inside the medium.

Indeed, let donor chromophores be located only on a surface of the medium, and the concentration ρ_A of acceptors decreases with the distance to the surface as

$$\rho_A(z) = n_A/[1 + (z/z_0)^\alpha], \quad (5)$$

where n_A is the concentration of acceptors in a near-surface layer of the medium, z_0 is the layer thickness, the coordinate axis z is perpendicular to the surface and is directed inside the medium, and α is a constant ($0 \leq \alpha < 1$). The number $N_A(R)$ of acceptors inside a sphere of radius R ($R \gg z_0$) circumscribed around an arbitrary point at the surface can be readily calculated as

$$N_A(R) = n_A \frac{2\pi}{(1-\alpha)(3-\alpha)} z_0^\alpha R^{3-\alpha}. \quad (6)$$

Comparison of this expression with (1) shows that the effective fractal dimensionality of this medium is $d^* = 3 - \alpha$. It is obvious that the luminescence kinetics of this medium will coincide with kinetics (2).

Taking into account the technology of sample preparation [7–9, 15], it is reasonable to assume that molecules penetrate inside the medium by diffusion. Then, the distribution of acceptors under the sample surface should be approximated by a Gaussian curve

$$\rho_A(z) = n_A \exp\{-(z/z_A)^2\}, \quad 0 \leq z \leq \infty, \quad (7)$$

where the parameter z_A characterizes the depth of diffusion penetration of acceptors. This depth depends on the experimental conditions.

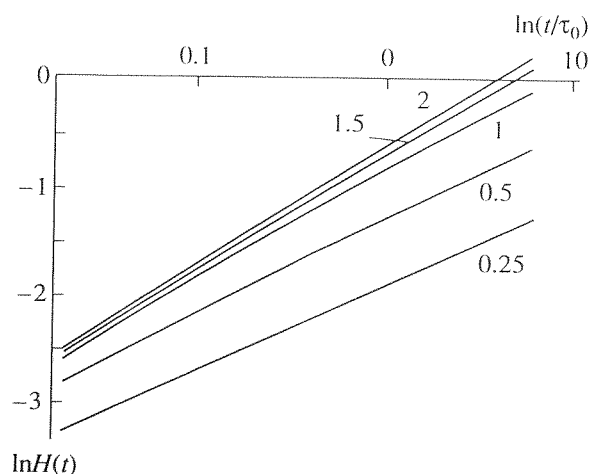


Fig. 1. Time dependence of the function $H(t)$ [see equation (11)]. Donors are localized on the surface; the distribution of acceptors is described by function (7). The numbers at the curves are values of the parameter σ_A .

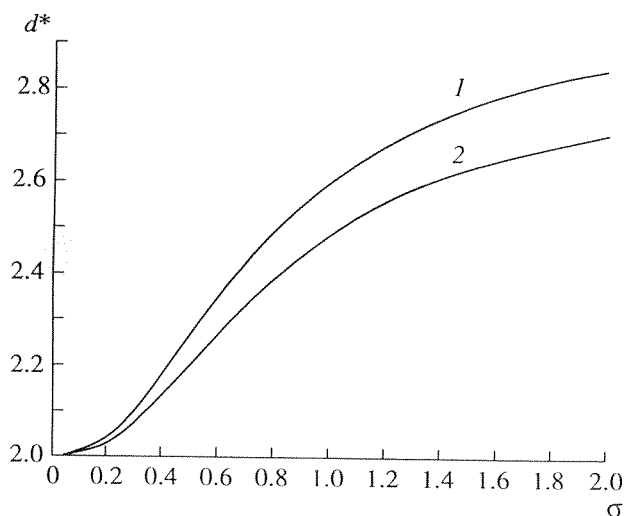


Fig. 2. Dependence of the effective fractal dimensionality d^* on the depth of penetration σ ($\sigma = \sigma_A = \sigma_D$) of chromophores inside a sample. (curve 1) donors are localized on the sample surface, and the distribution of acceptors is described by expression (7), $\sigma = \sigma_A$; (curve 2) distributions of donors and acceptors under the surface are described by expressions (13) and (7), respectively, $\sigma = \sigma_A = \sigma_D$.

By assuming the dipole–dipole mechanism of ET [17], for which the transfer rate has the form

$$w(R) = \frac{1}{\tau_0} \left(\frac{R_0}{R} \right)^6 \quad (8)$$

(where R_0 is the critical radius of ET and R is the distance between a donor and an acceptor), we obtain the

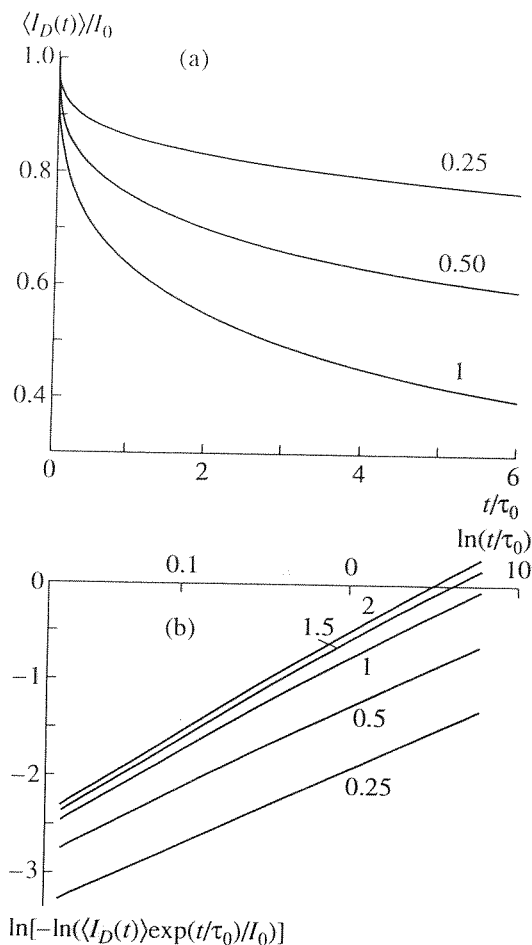


Fig. 3. Luminescence kinetics in (a) conventional and (b) logarithmic coordinates for the Gaussian distribution of donors (13) and acceptors (7). The numbers at the curves are values of the parameter σ ($\sigma = \sigma_A = \sigma_D$); $c_A = 1$.

following expressions for the luminescence kinetics

$$\begin{aligned}
 I_D(t) &= \exp\{-t/\tau_0 - c_A H(t)\}, \\
 c_A H(t) &= \int \rho_A(R) [1 - e^{-t w(R)}] d\mathbf{R}, \\
 c_A &= 2\pi n_A R_0^3.
 \end{aligned}
 \tag{9}$$

Taking into account a symmetry of the problem and introducing the dimensionless variables

$$x = z/R_0, \quad \sigma_A = z_A/R_0,
 \tag{10}$$

we obtain for the function $H(t)$

$$\begin{aligned}
 H(t) &= \int_0^\infty r dr \int_0^\infty dx \left[1 - \exp\left(-\frac{t/\tau_0}{(r^2 + x^2)^3}\right) \right] \\
 &\quad \times \exp\left[-\frac{x^2}{\sigma_A^2}\right].
 \end{aligned}
 \tag{11}$$

The results of numerical calculations of the function $H(t)$ for different values of σ_A are shown in Fig. 1. The function $\ln(H(t))$ can be well approximated in the interval $0.2 < t/\tau_0 < 6$ by a linear dependence on $\ln(t/\tau_0)$

$$H(t) \propto (t/\tau_0)^\beta,
 \tag{12}$$

where β is a parameter depending on σ_A .

Therefore, the luminescence kinetics of donors in the case of the Gaussian distribution of acceptors (7) is well described by equation (2), in which the effective fractal dimensionality is $d^* = 6\beta$. Figure 2 shows the dependence of d^* on σ_A (curve 1). One can see that the effective fractal dimensionality of the medium increases from 2 to 3 with increasing depth of penetration of acceptors into a sample.

Thus, if donors are located only on a surface of the porous medium and the distribution of acceptors over the surface is described by a decreasing functions [for example, (5) or (7)], then the luminescence kinetics of such a medium is described by equation (2) with the effective fractal dimensionality $d^* < 3$.

Let us now take into account that donor chromophores (and acceptors) should be characterized by a distribution $\rho_D(z)$ of the Gaussian shape

$$\rho_D(z) = \frac{2}{\sqrt{\pi} z_D} \exp(-z^2/z_D^2).
 \tag{13}$$

Here, a parameter z_D is the depth of diffusion penetration of donors to a sample. Unlike (7), function (13) is normalized. The luminescence kinetics $\langle I_D(t) \rangle$ observed under these conditions is found by averaging kinetics (9) with the distribution function (13):

$$\begin{aligned}
 \langle I_D(t) \rangle &= I_0 \int_0^\infty dy \frac{2}{\sigma_D \sqrt{\pi}} e^{-y^2/\sigma_D^2} \\
 &\quad \times \exp(-t/\tau_0 - c_A H(y, t)), \\
 H(y, t) &= \int_0^\infty r dr \int_0^\infty dx \left\{ 1 - \exp\left[-\frac{t/\tau_0}{(r^2 + (x-y)^2)^3}\right] \right\} \\
 &\quad \times \exp\left[-\frac{x^2}{\sigma_A^2}\right],
 \end{aligned}
 \tag{14}$$

where $y = z/R_0$ and $\sigma_D = z_D/R_0$. Taking into account the approximately equal sizes of donor and acceptor chromophores, we can assume in the calculation of kinetics (14) that during the sample preparation the donors and acceptors penetrate to the same depth inside the medium, i.e., $\sigma_A = \sigma_D$. Figure 3a presents the results of calculations for different values of the parameter σ ($\sigma = \sigma_A = \sigma_D$). Figure 3b shows these dependences recalculated in coordinates $\ln[-\ln(\langle I_D(t) \rangle \exp(t/\tau_0) / I_0)]$ and $\ln(t/\tau_0)$. As in the previous case, these curves are well

approximated by linear dependences. This means that

$$-\ln[\langle I_D(t) \rangle I_0] - t/\tau_0 \propto (t/\tau_0)^\delta, \quad (15)$$

where δ is a constant depending on σ .

Thus, if the distribution function of chromophores under the sample surface is a decreasing function of the type (7) or (13), the luminescence kinetics (14) is adequately approximated by kinetics (2), the effective fractal dimensionality of the medium being $d^* = 6\delta$. The dependence of d^* on σ is shown in Fig. 2 (curve 2). As expected, σ tends to 3 with increasing d^* .

CONCLUSION

Experimental results [7–9, 15] and kinetics (2) can be explained within the framework of the diffusion model of penetration of chromophores through a surface inside the sample. The effective fractal dimensionality of the medium calculated from kinetics (2) characterizes the depth of penetration of chromophores into the sample. As this depth increases, the effective fractal dimensionality increases from 2 to 3.

ACKNOWLEDGMENTS

E.N. Bodunov thanks INVOTAN for the financial support.

REFERENCES

- Balzani, V. and Scandola, F., *Supramolecular Photochemistry*, New York: Horwood, 1990.
- Speiser, S., *Chem. Rev.*, 1996, vol. 96, no. 6, p. 1953.
- Berberan-Santos, M.N., Canceill, J., Gratton, E., Julien, L., Lehn, J.-M., So, P., and Valeur, B., *J. Phys. Chem.*, 1996, vol. 100, no. 1, p. 15.
- Gehlen, M.N. and De Schryver, F.C., *Chem. Rev.*, 1993, vol. 93, no. 1, p. 199.
- Barzykin, A.S.V. and Tachiya, M., *Heterog. Chem. Rev.*, 1996, vol. 3, no. 1, p. 105.
- Yekta, A., Winnik, M.A., Farinha, J.P.S., and Martinho, J.M.G., *J. Phys. Chem. A*, 1997, vol. 101, no. 10, p. 1787.
- Even, V., Rademann, K., Jortner, J., Manor, N., and Reissfeld, R., *Phys. Rev. Lett.*, 1984, vol. 52, no. 24, p. 2164.
- Pines, D. and Huppert, D., *J. Phys. Chem.*, 1987, vol. 91, no. 27, p. 6569.
- Levitz, P., Drake, J.M., and Klafter, J., *J. Chem. Phys.*, 1988, vol. 89, no. 8, pp. 5224.
- Beger, V.N., Zemskii, V.I., Kolesnikov, Yu.L., and Sechkarev, A.B., *Opt. Spektrosk.*, 1988, vol. 65, no. 5, p. 1078.
- Klafter, J., Drake, J.M., Levitz, P., Blumen, A., and Zumofen, G., *J. Lumin.*, 1990, vol. 45, nos. 1–6, p. 34.
- Klafter, J. and Blumen, A., *J. Chem. Phys.*, 1984, vol. 80, no. 2, pp. 875.
- Blumen, A., Klafter, J., and Zumofen, G., *J. Chem. Phys.*, 1986, vol. 84, no. 3, p. 1397.
- Nakashima, K., Liu, Y.S., Zhang, P., Dukamel, J., Fong, J., and Winnik, M.A., *Langmuir*, 1993, vol. 9, no. 11, p. 2825.
- Pines, D. and Huppert, D., *J. Chem. Phys.*, 1989, vol. 91, no. 11, p. 7291.
- Berberan-Santos, M.N., Bodunov, E.N., and Martinho, J.M.G., *Opt. Spektrosk.*, 1996, vol. 81, no. 2, p. 243.
- Galanin, M.D., *Luminescence of Molecules and Crystals*, Cambridge: Cambridge International Science Publishing, 1996.
- Yang, C.L., Evesque, P., and El-Sayed, M.A., *J. Phys. Chem.*, 1985, vol. 89, no. 16, p. 3442.
- Yang, C.L., Evesque, P., and El-Sayed, M.A., *J. Phys. Chem.*, 1986, vol. 90, no. 7, p. 1284.
- Avnir, D., Biham, O., Lidar, D., and Malcai, O., *Science*, 1998, vol. 279, p. 39.

Translated by M. Sapozhnikov