Optics and Spectroscopy, Vol. 85, No. 6, 1998, pp. 869–872. Translated from Optika i Spektroskopiya, Vol. 85, No. 6, 1998, pp. 948–951.

MOLECULAR SPECTROSCOPY

Hopping Mechanism of Luminescence Quenching and the Diffusion Approximation

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Received November 11, 1997

Abstract—The kinetics of luminescence decay is studied in the case of the hopping mechanism of quenching, assuming that migration of electronic excitations is described by the diffusion equation. It is shown that an adequate consideration of quenching in the boundary condition yields within this approach the correct dependence of the luminescence decay rate on the concentration of molecules and Förster radii of energy transfer.

INTRODUCTION

Radiationless energy transfer of electronic excitations has attracted the attention of researchers for a long time [1–4]. In recent years this is associated with the use of energy transfer as a tool for studying the structure of media and kinetics of processes occurring in them [1–16].

Energy transfer between similar molecules is referred to as migration of excitations, and that between different molecules (from donors D to acceptors A) is referred to as quenching of the excited states of donors.

Note that the most widespread mechanism of energy transfer is the dipole–dipole one, when the rates of migration w and quenching u are written in the form [1–3]:

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

Here τ_0 is the inherent lifetime of the excited state of a donor, R_{DD} and R_{DA} are Förster (critical) radii for the donor $\longrightarrow$ donor and donor $\longrightarrow$ acceptor energy transfer, respectively, and R and r are distances between the interacting molecules.

There are two fundamentally different approaches to the theoretical description of energy transfer, depending on the r_q/l ratio, where r_q is the radius of strong quenching of a donor by an acceptor and l is the most probable length of the hop of excitation between donors [17].

For $r_q/l \gg 1$, migration occurs by small steps. Each step results only in a small change in the rate $u(r)$, and migration in a medium with acceptors can be described by the diffusion equation [2, 17–21]. The solution of this equation shows that in the case of efficient migration the donor luminescence decays exponentially, beginning from a certain moment

$$I(t) = I_0 \exp[-t/\tau_0 - kt/\tau_0]. \qquad (2)$$

The decay rate k is expressed in terms of the critical radius R_{DA}, the diffusion coefficient D of excitations and the concentration n_A of acceptors as:

$$k = 0.68 \cdot 4\pi(D\tau_0)^{3/4} R_{DA}^{3/2} n_A. \qquad (3)$$

The diffusion coefficient D can be calculated by different methods [22]. For example, in the three-particle version of the GAF method [23], it has the form

$$D = 0.43 R_{DD}^2 (4\pi R_{DD}^3 n_D/3)^{4/3}/\tau_0, \qquad (4)$$

where n_D is the concentration of donors. By substituting (4) in (3), we find

$$k = 0.26(4\pi R_{DA}^3 n_A/3) \times (4\pi R_{DD}^3 n_D/3)(R_{DD}/R_{DA})^{3/2}. \qquad (5)$$

In another limiting case ($r_q/l \ll 1$), the size of the quenching region around an acceptor is so small compared to l that the excitation can enter this region and escape it by one step (jump). In this case, as is stated in a review [17], the diffusion description is invalid and the luminescence quenching occurs by hopping.

The hopping mechanism of luminescence quenching is described by several approximate methods [22], such as the continuous time random walk (CTRW), the effective medium approximation (EMA), and the self-consistent GAF method. At sufficiently strong migration, these methods also yield the exponential kinetics of the luminescence decay (2). However, in this case the dependence of the luminescence decay rate on Förster radii R_{DD} and R_{DA} is different. For example, in the CTRW method gives the expression [17, 22]

$$k = 1.11(4\pi R_{DD}^3 n_D/3)(4\pi R_{DA}^3 n_A/3). \qquad (6)$$

Other methods give similar dependences on R_{DD} and R_{DA}. The only difference is the numerical factor in front of the parentheses in (6) which is equal to 1.66 and 1.97

0030-400X/98/8506-0869$15.00

in GAF and EMA methods, respectively. Dependence (6) was confirmed by Monte Carlo calculations [24].

Note that in a medium without acceptors CTRW, EMA, and GAF methods predict nevertheless the diffusion mechanism energy migration between donors. The diffusion coefficient is described by formula (4) with different numerical factors for method [22] (0.40 and 0.12 for CTRW and EMA methods, respectively).

The aim of this paper is to show that the hopping mechanism of luminescence quenching is also adequately described by the diffusion approximation. However, because of the short-range nature of the energy transfer rate $u(r)$ as compared to migration rate $w(R)$, the luminescence quenching should be taken into account in the boundary condition. In this case the decay rate k can be presented in the form (6) accurate to a numerical factor.

BASIC EQUATIONS

We calculate the kinetics $I(t)$ by the method [21] which is similar to the method of Wigner–Seitz cells in the theory of the electronic states in crystals. According to this method, we consider that acceptors are located in the centers of spheres of radius L. This radius is determined from the condition

$$(4\pi/3)L^3 = V/N_A = v_A, \quad v_A = 1/n_A. \tag{7}$$

Here, N_A is the total number of acceptors in the entire volume V of a medium, v_A is the average volume per one acceptor. These spheres (cells) are close-packed in the volume V. Therefore, we neglect fluctuations of the average distance between acceptors. This approximation is good if the concentration of acceptors is sufficiently low. Note that the cells differ from each other by positions of donors within them and, hence, by the distance r_i between the acceptor and the nearest neighboring donor. The subscript i denotes the number of the cell.

Let $C_i(R, t)$ be the concentration of excited donors at time t at the distance R from the center of the ith cell. The average concentration of excitations in the ith cell is

$$n_i(t) = v_A^{-1}\int C_i(R, t)d\mathbf{R}. \tag{8}$$

Integration in (8) is accomplished over the volume of the ith cell.

We can now represent the normalized ($I(0) = 1$) kinetics of luminescence in the form

$$I(t) = \sum_i^{N_A} n_i(t)/\sum_i^{N_A} n_i(0). \tag{9}$$

By assuming that at the initial instant of time the concentration of excited donors in all cells is the same, i.e.,

$$n_1(0) = n_2(0) = \ldots = n_0, \tag{10}$$

we obtain

$$I(t) = N_A^{-1}\sum_i^{N_A} n_i(t)/n_0. \tag{11}$$

Within the framework of diffusion approximation, the function $C_i(r, t)$ satisfies the equation [21]: (for distances greater than the average distance between donors)

$$\frac{\partial}{\partial t}C_i(R, t) = -\frac{1}{\tau_0}C_i(R, t) + D\Delta C_i(R, t),$$
$$\frac{\partial}{\partial R}C_i(R, t)|_{R=L} = 0. \tag{12}$$

The boundary condition means that we neglect the transfer of excitation from one cell to another.

As will be shown below, the decay rate k in equation (2) is determined only by the behavior of $C_i(R, t)$ near the center of the cell. Therefore, to find $C_i(R, t)$ (at low acceptor concentrations) one can use the limit $L \longrightarrow \infty$ and demand that $C_i(R, t) \longrightarrow n(t)$ for $R \longrightarrow \infty$, where $n(t)$ is the average concentration of excitations in the medium. Note that for $R \longrightarrow \infty$, it follows from (8) that

$$n_i(t) \approx n_0\exp(-t/\tau_0), \tag{13}$$

i.e., the average concentration of excitations is independent of the cell number.

Let us now write the boundary condition at the center of the cell. On the one hand, in the case of quenching by hopping, excitation vanishes when it reaches the donor nearest to the acceptor, i.e., to the center of the cell. The rate of this process in the ith cell is $u(r_i)$.

If the concentration of donors is n_D, then the volume v_D of radius R_0

$$v_D = (4\pi/3)R_0^3 = 1/n_D \tag{14}$$

corresponds to each donor. Contains a donor with the unit probability. Therefore, a sphere with of radius R_0 with a center in the center of the cell. The probability that this donor is excited is equal to $C_i(R_0, t)v_D$. (We take into account that an approximate equation $C_i(R_0, t) \approx C_i(0, t)$ holds due to the diffusion approximation.) Therefore, we can conclude that the number of excitations in the ith cell will decrease with the rate $u(r_i)C_i(R_0, t)v_D$.

On the other hand, within the diffusion approximation, a sphere of radius R_0 around the center of the ith cell serves as a trap for excitation. For this reason, the number of excitations vanished per unit time will be equal to the flux of excitations $4\pi DR_0^2\partial C_i(R, t)/\partial R|_{R=R_0}$ falling on this sphere.

By equating these two rates, we obtain the boundary condition

$$4\pi DR_0^2\partial C_i(R, t)/\partial R|_{R=R_0} = (4\pi/3)R_0^3u(r_i)C_i(R_0, t). \tag{15}$$

CALCULATION OF THE LUMINESCENCE DECAY RATE IN THE DIFFUSION APPROXIMATION

Let us solve now equation (12) with boundary condition (15) and asymptotic condition (13).

It is convenient to turn to the function [21]

$$\varphi_i(R, t) = \frac{C_i(R, t)}{n_0 \exp(-t/\tau_0)}, \quad (16)$$

which satisfies the evident equation

$$\partial\varphi_i/\partial t = D\Delta\varphi_i \quad (17)$$

and the boundary condition resulting from (15)

$$D\partial\varphi_i/\partial R|_{R=R_0} = R_0 u(r_i)\varphi_i(R_0, t)/3, \quad (18)$$

with $\varphi_i(R, t) = 1$ at $t = 0$.

Let us present the solution of equations (17) and (18) in the form [21, 25]:

$$\varphi_i(R, t) = \varphi_i^{st}(R) + \varphi_i'(R, t), \quad (19)$$

where the function $\varphi_i^{st}(R)$ satisfies the stationary diffusion equation

$$D\Delta\varphi_i^{st}(R) = 0 \quad (20)$$

and the asymptotic condition $\varphi_i^{st}(R) \longrightarrow 1$ at $R \longrightarrow \infty$, while the function $\varphi_i'(R, t)$ satisfies the non-stationary diffusion equation and the following initial condition

$$\varphi_i'(R, 0) = 1 - \varphi_i^{st}(R). \quad (21)$$

Note that at long times, $\varphi_i'(R, t) \longrightarrow 0$.

Therefore, the stationary distribution of excitations $\varphi_i^{st}(R)$ is established in each cell after some time. The greater the diffusion coefficient, the shorter the time of the establishment of this distribution.

By solving equations (20) and (18), we find

$$\varphi_i^{st}(R) = (1 - A_i/R),$$
$$A_i = u(r_i)/[4\pi D n_D + u(r_i)/R_0]. \quad (22)$$

According to the definition of the function $\varphi_i^{st}(R)$, we have [taking into account (16), (13) and with an accuracy to small terms of the order of n_A]

$$C_i(R, t) = (1 - A_i/R)n(t), \quad (23)$$

$$\partial C_i/\partial R|_{R=R_0} = (A_i/R_0^2)n(t). \quad (24)$$

Taking into account (8), we obtain after integration of (12) over the volume of the ith cell the equation

$$dn_i(t)/dt = -\tau_0^{-1} n_i(t) - 4\pi D n_A A_i n(t). \quad (25)$$

By averaging this equation according to (11), we obtain

$$dI(t)/dt = -\tau_0^{-1} I(t) - kI(t), \quad (26)$$

where

$$k = 16\pi^2 D n_A n_D \int A_i r_i^2 dr_i. \quad (27)$$

The substitution of expressions (22) and (4) into (27) yields

$$k = 1.79(4\pi n_A R_{DA}^3/3)(4\pi n_D R_{DD}^3/3). \quad (28)$$

Within a numerical factor, this result coincides with expression (6). Therefore, the analytic dependence of the luminescence decay rate k on the concentration of donors and acceptors and Förster radii of energy transfer is reproduced in the diffusion approximation.

CONCLUSIONS

The hopping mechanism of luminescence quenching is usually studied by the CTRW, GAF and EMA methods because it is stated [17] that migration and quenching of luminescence can be described by the diffusion equation. We showed that this statement is erroneous. The luminescence kinetics in this case can also be described by the diffusion approximation. In this case, migration of excitations obeys the classical diffusion equation and the quenching (taking into account the short-range donor–acceptor interaction) is taken into account by the boundary condition. This approach gives correct analytic dependence (28) for the luminescence decay rate k with the numerical factor 1.79 close to those obtained by the CTRW, GAF, and EMA methods (1.11, 1.66, and 1.97, respectively).

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Translated by M. Drobizhev