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MOLECULAR SPECTROSCOPY

Monte Carlo Simulation of the Luminescence Quantum Yield in the Hopping Mechanism of Quenching

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Abstract—A theory is developed wherein an exact concentration dependence of the luminescence quantum yield is calculated by Monte Carlo technique for high concentrations of luminescent centers. The results of calculations are compared with similar dependences obtained by different approximate methods.

INTRODUCTION

The energy transfer from excited impurity centers (atoms, ions, and molecules) to unexcited centers is a widespread phenomenon [1–5]. The energy transfer between centers of the same nature is called migration of excitation, whereas the energy transfer between different centers (from donors to acceptors) is called the quenching of luminescence of donors. Depending on the value of the ratio R_q/l (where R_q is the radius of the strong quenching of a donor by an acceptor, and l is the most probable length of the excitation jump between donors), the quenching is of diffusive (when $R_q/l \gg 1$) [1, 2, 6] or hopping ($R_q/l \ll 1$) [6, 7] type. In this work, we consider the latter case.

Luminescence quenching in the case of a hopping mechanism was studied by several approximate methods [8, 9], such as the continuous time random walk (CTRW), the coherent potential approximation (CPA), and the self-consistent diagrammatic technique of Gochanour–Andersen–Fayer (GAF) [8–10] developed in [11].

These methods all give the same dependence of the luminescence quantum yield η of donors on the concentration of acceptors for high concentrations of donors. The region of high concentrations is the most interesting, because, in this case, one can compare the exactness of different methods. For the dipole–dipole interaction between impurity centers,

$$\eta/\eta_0 = 1 - \alpha c_A c_D, \tag{1}$$

$$c_A = \frac{4\pi}{3}R_{DA}^3 n_A, \quad c_D = \frac{4\pi}{3}R_{DD}^3 n_D. \tag{2}$$

Here, n_A is the concentration of acceptors; n_D is the concentration of donors; η_0 is the luminescence quantum yield of donors at $n_A = 0$; α is a numerical coefficient; and R_{DA} and R_{DD} are Förster radii for energy transfer from a donor to an acceptor and from a donor to a donor, respectively. Equation (1) is valid for $c_D > 1$, $c_A \ll 1$, and $\alpha c_A c_D < 1$.

The rates of energy transfer w_{DD} and u_{DA} for the dipole–dipole interaction are known to be determined by the expressions

$$w_{DD} = \frac{1}{\tau_0}\left(\frac{R_{DD}}{r}\right)^6, \quad u_{DA} = \frac{1}{\tau_0}\left(\frac{R_{DA}}{r}\right)^6, \tag{3}$$

where τ_0 is the excited state lifetime for donors in the absence of acceptors, and r is the distance between the centers.

The CTRW method (taking into account the Huber correction) gives the α equal to 1.11 [8, 9], and the CPA and GAF methods give 1.97 and 1.66, respectively [8, 9]. It is interesting to compare the value of α calculated by different approximate methods with the exact value, which can be obtained by Monte Carlo simulation.

Straightforward calculations are performed as follows. A fixed (sufficiently large) number of donors (N_D) and acceptors (N_A) is distributed randomly in a cube. The volume V of the cube depends on the concentration of donors:

$$V = N_D/n_D. \tag{4}$$

Periodic boundary conditions are used. The quantum yield of luminescence of donors is calculated for a specified distribution of impurity centers by Monte Carlo technique. This quantum yield is then averaged over different distributions. The dependences of quantum yield on concentrations of donors and acceptors are plotted. If these dependences are described by (1), the coefficient α is calculated.

Such an approach was used in [12] and gave unsatisfactory results, because to obtain a sufficiently correct dependence (1), it was necessary to consider distributions with a very great number of donors and acceptors.

In this work, another approach is proposed for calculating dependence (1) by Monte Carlo simulation. This approach consists in absolutely excluding the acceptors. Within this approach, it is necessary to calculate the value of $(\eta_1/\eta_0)^{-1/2}$ for each distribution of donor centers only, where η_1 is the quantum yield of the initially excited center. Then, this value must be averaged over many distributions. The desired dependence has the form

$$\eta/\eta_0 = 1 - \frac{\pi}{2} c_A \langle [\eta_1/\eta_0]^{-1/2} \rangle. \tag{5}$$

The angular brackets in (5) denote averaging over different distributions of donor centers.

Let us now turn to the derivation of equation (5).

THEORY

Consider a medium where donors and acceptors are distributed randomly. The concentration n_A of acceptors is low, and the concentration n_D of donors is high. The mean volume V_A per acceptor is equal to:

$$V_A = 1/n_A. \tag{6}$$

This volume contains the following number of donors:

$$N_D = n_D V_A = n_D/n_A \gg 1. \tag{7}$$

Let us break the medium into cells, each of them containing one acceptor. The mean volume of such a cell is equal to V_A. Let us select one of them and number all the donors within it.

Let $P_k(t)$ be the probability that the excitation is localized on the kth donor at the instant t. This probability obeys the balance equation

$$\begin{gathered} \frac{d}{dt}P_k(t) = -\frac{1}{\tau_0}P_k(t) - u_k P_k(t) + \sum_i w_{ki}[P_i(t) - P_k(t)], \\ P_k(0) = \delta_{km}. \end{gathered} \tag{8}$$

Here, u_k is the rate of energy transfer from the donor k to an acceptor (it is assumed that the acceptor is placed at the origin of coordinates), w_{ki} is the rate of hopping of excitation from the donor i to the donor k ($w_{ki} = w_{ik}$), and δ_{km} is the Kronecker symbol.

In the Laplace representation

$$\tilde{P}_k(p) = \int_0^\infty e^{-pt} P_k(t) dt, \tag{9}$$

equation (8) takes the form

$$\begin{gathered} \left(p + \frac{1}{\tau_0}\right)\tilde{P}_k(p) - \delta_{km} + u_k \tilde{P}_k(p) \\ + \sum_i w_{ki}[\tilde{P}_k(p) - \tilde{P}_i(p)] = 0. \end{gathered} \tag{10}$$

Let us introduce the Green function $\tilde{G}_{km}$, which satisfies the equation

$$\begin{gathered} \left(p + \frac{1}{\tau_0}\right)\tilde{G}_{kn}(p) - \delta_{kn} \\ + \sum_l w_{kl}[\tilde{G}_{kn}(p) - \tilde{G}_{ln}(p)] = 0. \end{gathered} \tag{11}$$

Comparison of (10) and (11) shows that $G_{kn}(t)$ is the probability that excitation is localized on the kth donor at the instant t and that the nth donor was excited at $t = 0$.

Note that equation (11) describes only migration of excitations; the quenching by acceptors is disregarded.

The function G possesses the obvious properties of

$$\begin{gathered} \sum_k \tilde{G}_{kn}(p) = 1/(p + 1/\tau_0), \\ \tilde{G}_{kn}(p) = \tilde{G}_{nk}(p) \quad (k \neq n). \end{gathered} \tag{12}$$

It is easy to show that the solution of equation (10) can be written, using the Green function, as

$$\tilde{P}_k(p) = \sum_n [\delta_{nm} - u_n \tilde{P}_n(p)]\tilde{G}_{kn}(p). \tag{13}$$

Now, we take into account that we are interested in the hopping mechanism of quenching. This implies that, in the cell under consideration, the rate u_n is nonzero only for the donor that is nearest to the acceptor. Let us designate this donor by the index 1. Then, provided that

$$u_n = u_1 \delta_{1n}, \tag{14}$$

from (13), we obtain that

$$\tilde{P}_k(p) = \tilde{G}_{km}(p) - u_1 \tilde{P}_1(p)\tilde{G}_{k1}(p). \tag{15}$$

For $k = 1$, it follows from (15) that

$$\tilde{P}_1(p) = \tilde{G}_{1m}(p)/[1 + u_1 \tilde{G}_{11}(p)]. \tag{16}$$

The probability that the excitation is still localized in the donor subsystem (the mth donor was initially excited) is determined by the sum of all $\tilde{P}_k$. Taking into account (12), (15) and (16), this sum is written as

$$\sum_k \tilde{P}_k(p) = \frac{1}{p + 1/\tau_0}\left[1 - \frac{u_1 \tilde{G}_{1m}(p)}{1 + u_1 \tilde{G}_{11}(p)}\right]. \tag{17}$$

Let us average this expression over the position of the initially excited donor (over the index m). Taking into account (12), this gives

$$\left\langle \sum_k \tilde{P}_k(p) \right\rangle_m = \frac{1}{p + 1/\tau_0} \times\left[1 - \frac{u_1}{1 + u_1\tilde{G}_{11}(p)}\frac{\tau_0}{N_D(\tau_0 p + 1)}\right]. \tag{18}$$

It is necessary now to average expression (18) over the position of the acceptor with respect to donor 1, using the nearest neighbor distribution function

$$\rho(r)dr = n_D 4\pi r^2 \exp\left(-\frac{4\pi}{3}r^3 n_D\right)dr. \tag{19}$$

Taking into account the dipole–dipole mechanism of interaction (3) between donors and acceptors, one can argue that the second term in brackets will be nonzero for $r < R_{DA}$. Also, if

$$n_D R_{DA}^3 \ll 1, \tag{20}$$

then, upon averaging in (18), using function (19), the latter can be replaced by

$$\rho dr = 4\pi r^2 n_D dr, \tag{21}$$

and the integration area over dr can be extended to infinity.

As a result, taking into account (7), we obtain

$$\left\langle\left\langle \sum_k \tilde{P}_k(p) \right\rangle_m\right\rangle_1 = \frac{1}{p + 1/\tau_0} \times\left\{1 - \frac{\pi}{2}c_A[\tilde{G}_{11}(p)/\tau_0]^{-1/2}\frac{1}{p\tau_0 + 1}\right\}. \tag{22}$$

Let us now average this expression over all possible distributions of donor centers. Finally, we obtain

$$\left\langle\left\langle\left\langle \sum_k \tilde{P}(p) \right\rangle_m\right\rangle_1\right\rangle = \frac{1}{p + 1/\tau_0} \times\left\{1 - \frac{\pi}{2}c_A\langle[\tilde{G}_{11}(p)/\tau_0]^{-1/2}\rangle\frac{1}{p\tau_0 + 1}\right\}. \tag{23}$$

Within the time representation, the function obtained is the kinetics $I(t)$ of luminescence decay of donors with $I(0) = 1$.

It is well-known [9] that the quantum yield η and $I(t)$ are related as

$$\eta/\eta_0 = \frac{1}{\tau_0}\int_0^\infty I(t)dt = \frac{1}{\tau_0}\tilde{I}(p)\Bigg|_{p=0}. \tag{24}$$

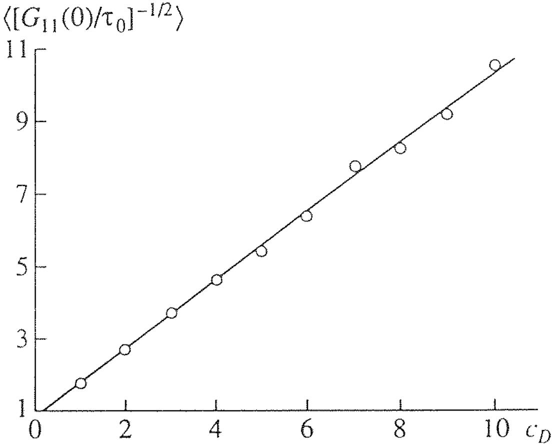

Fig. 1. The region of high concentrations. Circles: Monte Carlo calculation; straight line: the least-squares approximation.

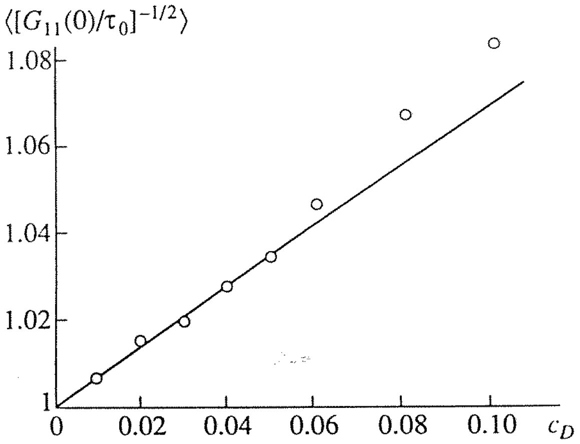

Fig. 2. The region of low concentrations. Notations are as in Fig. 1.

From (24), (23), and (2), we obtain

$$\eta/\eta_0 = 1 - \frac{\pi}{2}c_A\langle[\tilde{G}_{11}(0)/\tau_0]^{-1/2}\rangle. \tag{25}$$

It follows from equation (11) that the function $G_{11}(t)$ is the probability that excitation is localized on the initially excited donor for a given distribution of donors. Therefore, the quantity

$$\eta_1/\eta_0 = \frac{1}{\tau_0}\int_0^\infty G(t)dt = \frac{1}{\tau_0}\tilde{G}(0) \tag{26}$$

is the quantum yield of luminescence of the initially excited donor. Formula (5) follows from equations (26) and (25).

Note the two following circumstances. First, at a low concentration of donors ($n_D \longrightarrow 0$), $\tilde{G}_{11}(0) = \tau_0$ and equation (25) reproduce the well-known result of the Förster theory [1, 2, 9] for $c_A \ll 1$. Second, in view of approximations (20) and (21), used in derivation of equation (25), the latter is valid as long as the second term in the right side of (25) is smaller than unity.

RESULTS OF CALCULATIONS

The algorithm of calculation of the quantum yield of luminescence of initially excited centers by Monte Carlo technique for a fixed distribution of donors was similar to that used in [13–16]. After these simulations, the value of $\langle[\tilde{G}_{11}(0)/\tau_0]^{-1/2}\rangle$ was calculated.

Unlike [16], we did not introduce the smallest distance between donors, because, first, this would result in the exponential decay of $G_{11}(t)$ at very short times, and, second, in the CTRW, CPA, and GAF methods, the continuum approximation is used (donors and acceptors are considered to be point particles). We also did not introduce the cutoff distance, beginning from which the system of donors can be considered as a continuous medium of acceptors for the initially excited donor.

We performed final calculations for the following values of parameters. The number of donors for each distribution was taken to be 1000. Periodic boundary conditions were used. To calculate $\tilde{G}_{11}(0)$, the center with number 1 was excited 400 times for each distribution. Averaging was done over 400 distributions.

The results of calculations are presented in Fig. 1. One can see that, at $c_D > 1$, the function $\langle[\tilde{G}_{11}(0)/\tau_0]^{-1/2}\rangle$ is well-approximated by the linear dependence

$$\langle[\tilde{G}_{11}(0)/\tau_0]^{-1/2}\rangle = 0.83 + 0.95c_D. \quad (27)$$

From the slope of this dependence, we determined the coefficient α entering (1):

$$\alpha = 1.47. \quad (28)$$

This value is closest to that obtained by the GAF method.

To check the method proposed in this work, we accomplished similar calculations in the case of low concentrations of donors ($c_D < 0.1$). The results are presented in Fig. 2. The function $\langle[\tilde{G}_{11}(0)/\tau_0]^{-1/2}\rangle$ is again described by the linear dependence

$$\langle[\tilde{G}_{11}(0)/\tau_0]^{-1/2}\rangle = 1 + 0.71c_D, \quad (29)$$

but with a lower slope. After substitution of (29) into (25), we find

$$\eta/\eta_0 = 1 - \frac{\pi}{2}c_A - 1.12c_Ac_D. \quad (30)$$

Equation (30) reproduces an exact result of the GAF theory in the three-particle self-consistent approximation [9] for the hopping mechanism of quenching ($R_{DA} < R_{DD}$).

CONCLUSION

We obtained, using the method proposed in this work, the exact concentration dependence of the luminescence quantum yield [equations (1) and (28)] for high concentrations of donors and the hopping mechanism of luminescence quenching. The conclusion is made that the GAF method allows one to calculate most precisely the luminescence quantum yield at high concentrations of impurity centers in three-dimensional media compared to other analytic methods.

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REFERENCES

1. Ermolaev, V.L., Bodunov, E.N., Sveshnikova, E.B., and Shakhverdov, T.A., *Bezyzluchatel'nyi perenos energii elektronnogo vozbuzhdeniya* (Nonradiative Transfer of Electronic Excitation Energy), Leningrad: Nauka, Leningr. Otd., 1977.
2. Agranovich, V.M. and Galanin, M.D, *Electronic Excitation Energy Transfer in Condensed Matter*, Amsterdam: North-Holland 1982.
3. Van der Meer, B.W., Cooker, G. III, and Chen, S.-Y.S., *Resonance Energy Transfer: Theory and Data*, Weinheim: VCH, 1994.
4. Farinha, J.P.S., Martinho, J.M.G., Yekta, A., and Winnik, M.A., *Macromolecules*, 1995, vol. 28, no. 18, pp. 6084–6088.
5. Marcus, A.H., Fayer, M.D., and Curro, J.G., *J. Chem. Phys.*, 1994, vol. 100, no. 12, pp. 9156–9169.
6. Huber, D.L., *Phys. Rev. B.*, 1979, vol. 20, no. 6, pp. 2307–2314.
7. Burshtein, A.I., *Usp. Fiz. Nauk*, 1984, vol. 143, no. 4, pp. 553–600.
8. Bodunov, E.N., *Zh. Prikl. Spektrosk.*, 1991, vol. 55, no. 5, pp. 739–744.
9. Bodunov, E.N., *Opt. Spektrosk.*, 1993, vol. 74, no. 3, pp. 518–551.
10. Loring, R.F., Andersen, H.C., and Fayer, M.D., *J. Chem. Phys.*, 1982, vol. 72, no. 4, pp. 2015–2027.
11. Gochanour, C.R., Andersen, H.C., and Fayer, M.D., *J. Chem. Phys.*, 1979, vol. 70, no. 9, pp. 4254–4271.
12. Bodunov, E.N. and Malyshev, V.A., *Fiz. Tverd. Tela* (Leningrad), 1978, vol. 20, no. 7, pp. 2215–2217.
13. Bodunov, E.N., *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1978, vol. 42, no. 2, pp. 303–306.
14. Bodunov, E.N., *Zh. Prikl. Spektrosk.*, 1977, vol. 26, no. 6, pp. 1123–1125.
15. Bodunov, E.N., *Opt. Spektrosk.*, 1981, vol. 50, no. 5, pp. 1007–1009.
16. Engstrom, S., Lindberg, M., and Johanson, L.B.-A., *J. Chem. Phys.*, 1988, vol. 89, no. 1, pp. 204–213.