Acta Physica Academiae Scientiarum Hungaricae, Tomus 50 (3), pp. 201—206 (1981)

ORIENTATION FACTOR IN THE THEORY OF CONCENTRATIONAL QUENCHING OF LUMINESCENT SOLUTIONS*

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(Received 17. VII. 1980)

The paper deals with the influence of the orientation factor on the photoluminescence quantum yield for solutions in which restricted rotations of active molecules occur. It has been shown that critical concentrations depend on the mean value of the orientation factor of the form $\langle\sqrt[6]{\langle\varkappa^2\rangle}\rangle$ for one-dimensional systems, $\langle\sqrt[3]{\langle\varkappa^2\rangle}\rangle$ for two-dimensional systems, and $\langle\sqrt{\langle\varkappa^2\rangle}\rangle$ for three-dimensional ones.

1. Introduction

Luminescent molecules excited to the first electronic state can lose the excitation energy through a nonradiative transfer to molecules in the ground state. The theory of long-range electronic excitation energy transfer via dipole-dipole interactions developed by FÖRSTER [1, 2] gave the explanation of the phenomenon. Various problems concerning luminescent systems as well as molecular biology systems have been solved using this theory [2—8]. The nonradiative excitation energy transfer rate constant can be expressed as [1]

$$k_{AB} = (k_F + k_q)\, k^2(\bar{R}_0/R)^6\,, \tag{1}$$

where k_F and k_q are rate constants of the photoluminescence and internal conversion, respectively; k^2 is an orientation factor[1] dependent on the relative orientation of the transition moments of the excited A^* and unexcited B; $\bar{R}_0$ is the so-called "isotropic" critical distance, i.e. it is the value of R for which $k_{AB} = k_F + k_q$ when, simultaneously, $k^2 = 1$. The rate constant k_{AB} depends markedly on k^2, which can vary from 0 to 6 [9]. It is therefore important to determine the mean value of the orientation factor in case of the energy transfer within a system of molecules oriented at random or a system in which certain molecule orientation prevails. The problem was partly solved for

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* This work was carried out under the Research Project MR. I. 9.—4.5.3.

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[1] k^2 differs from the orientation factor $\varkappa^2$ as defined in [1] by a constant factor 3/2 (see also Eq. (2)); i.e. relation $k^2 = 3/2\ \varkappa^2$ is satisfied.

solutions by MAKSIMOV and ROZMAN [10]. DALE and EISINGER [8] presented an extensive study of this problem for interacting molecule pairs.

In this work we would like to present theoretical considerations of the orientation factor influence on the photoluminescence of viscous solutions in which restricted rotations of the transition moments of active molecules may also occur. The problem will be treated uniformly for solutions of different dimensions ($l = 1, 2$ and 3).

2. Theoretical considerations

Recently [11—13], the problem of the excitation energy transfer efficiency for solutions of different dimensions was studied for the energy transfer process regarded as a multistep one. It was assumed, among others, that the solutions are rigid to the extent to which the material diffusion can be neglected, and simultaneously liquid enough to allow for the complete rotation of molecules during the excitation energy transfer lifetime. Under this assumption a so-called isotropic value $\langle \varkappa^2 \rangle = 2/3$ [9, 10] i.e. $\langle k^2 \rangle = 1$ could be taken in these works as the mean value of the orientation factor. The assumption of complete molecule rotation is, however, not valid for solutions of sufficiently high viscosity, where during a time interval, τ_l (time of excitation energy localization on a single molecule) between the instant of excitation of the molecule A and the instant of transferring this energy from A^* to one of the neighbouring molecules B, more or less restricted rotations of the molecules involved are possible.

The temporary value of the orientation factor for a pair of molecules A^* and B is given by [1, 9]

$$k_{AB}^2 = \frac{3}{2}\left[\hat{\varepsilon}_A \hat{\varepsilon}_B - 3(\hat{\varepsilon}_A \hat{R}_{AB})(\hat{\varepsilon}_B \hat{R}_{AB})\right]^2, \tag{2}$$

where $\hat{\varepsilon}_A$, $\hat{\varepsilon}_B$ and $\hat{R}_{AB}$ are unit vectors for the transition moments of the molecules A^* and B and the distance between them, respectively.

The rotational motions of molecules due to their statistical nature cause, that the excitation energy transfer rates depend on values $\langle k_{AB}^2 \rangle$ averaged over the time τ_l. These in turn depend on the initial orientation of the transition moments of the interacting molecules A^* and B.

In our considerations of the influence of orientation factor on the efficiency of the excitation energy transfer in solutions of different dimensions we have adopted the same assumptions, in principle, as in [11—13]. However, unlike those earlier works, individual values of $\langle k_{AB}^2 \rangle$ for each pair of molecules are taken into consideration. Thus we assume that the solution contains donor D and acceptor A molecules, the probability of energy transfer from an excited molecule D^* to molecules D and A around it, forming together a so-called luminescence centre, depending on their configuration. This configuration is defined by orientations of the transition moments of molecules D and A, and their vector positions relative to the orientation of the molecule D^*.

Assuming that the molecule orientations and distances between them are statistically independent, the probability $P(D^* = D_{(\sigma)})$ of D^* belonging to the centre of type σ (i.e. characterized by a specific configuration of molecules D and A with respect to D^* can be written as

$$P(D^* = D_{(\sigma)}) = \prod_{i=1}^{N_D-1} \left(\frac{l}{R^l} x_i^{l-1} dx_i\right) \cdot \prod_{i=1}^{N_D-1} n(\hat{\omega}_i)\, d\hat{\omega}_i \cdot \prod_{j=1}^{N_A} \left(\frac{l}{R^l} y_j^{l-1} dy_j\right) \cdot \prod_{j=1}^{N_A} n(\hat{\varrho}_j)\, d\hat{\varrho}_j , \tag{3}$$

where the first and third terms are probabilities of D lying within $x_i \div x_i + dx_i$, and A lying within $y_j \div y_j + dy_j$, respectively, from the molecule D^*; the second and fourth terms can be regarded as probabilities of specific orientations of the transition moments and position vectors of type D and A molecules, respectively, relative to the transition moment of the molecule D^*; $\hat{\omega}_i$ and $\hat{\varrho}_j$ represent sets of angles defining the unit vectors of moments and distances, while $n(\hat{\omega}_i)$ and $n(\hat{\varrho}_j)$ are their distribution functions for D and A, respectively. N_D and N_A denote numbers of donor (including D^*) and acceptor molecules, respectively, in an l-dimensional volume of radius R.

It has been shown that for a multistep process of excitation energy transfer from molecules D to A the photoluminescence quantum yield η of a solution is given by [11]

$$\eta = P_F/(1 - P_{DD}) , \tag{4}$$

where P_F and P_{DD} are mean probabilities of fluorescence of an excited molecule D^*, and nonradiative excitation energy transfer from D^* to D, respectively.

For the modified definition of the luminescence centre as presented above (see also remarks in [11]) the probabilities P_F and P_{DD} can be described by the following formulae

$$P_F = \lim_{R\to\infty} P_F(R) = \lim_{R\to\infty} \sum_{(\sigma)} \frac{k_F}{k_{(\sigma)}} P(D^* = D_{(\sigma)}), \tag{5}$$

$$P_{DD} = \lim_{R\to\infty} P_{DD}(R) = \lim_{R\to\infty} \sum_{(\sigma)} \frac{k_{DD(\sigma)}}{k_{(\sigma)}} P(D^* = D_{(\sigma)}) , \tag{6}$$

where

$$k_{(\sigma)} = k_F + k_q + k_{DD(\sigma)} + k_{DA(\sigma)}, \tag{7}$$

$$k_{DD(\sigma)} = (k_F + k_q)\, \bar{\bar{R}}_{0D}^6 \sum_i \langle k_i^2 \rangle / x_i^6 , \tag{8}$$

$$k_{DA(\sigma)} = (k_F + k_q)\, \bar{\bar{R}}_{0A}^6 \sum_j \langle k_j^2 \rangle / y_j^6 . \tag{9}$$

Here $\bar{R}_{0D}$ and $\bar{R}_{0A}$ denote "isotropic" critical distances for the nonradiative energy transfer from D^* to D, and from D^* to A, respectively.

Since the molecule distance and moment distribution functions are continuous it follows from (5) that

$$P_F = \frac{k}{k_F + k_q} \lim_{R \to \infty} \underbrace{\int_0^R \int_{\hat{\omega}} \cdots \cdots \int_0^R \int_{\hat{\varrho}}}_{(N_D - 1) + N_A} \times$$

$$\times \frac{\prod_{i=1}^{N_D - 1} \left(\frac{l}{R^l} x_i^{l-1} \, dx_i \cdot n(\hat{\omega}_i) \, d\hat{\omega}_i \right) \cdot \sum_{j=1}^{N_A} \left(\frac{l}{R^l} y_j^{l-1} \, dy_i \cdot n(\hat{\varrho}_j) \, d\hat{\varrho}_j \right)}{1 + \left[\bar{R}_{0D}^6 \sum_{i=1}^{N_D - 1} \langle k_i^2 \rangle / x_i^6 + \bar{R}_{0A}^6 \sum_{j=1}^{N_D} \langle k_j^2 \rangle / y_j^6 \right]} . \tag{10}$$

Following the calculation procedure of [11—13], which permits separation of integrals over x, y, and $\hat{\omega}$ and $\hat{\varrho}$, we arrive at the formula

$$P_F = \eta_0 \, [1 - F(z)] \, , \tag{11}$$

where $\eta_0 = k_F/(k_F + k_q)$ is the absolute yield of donor molecules for their concentration in the solution $c_D \to 0$ with simultaneous $c_A = 0$, c_A being the acceptor concentration; $F(z)$ is desribed by

$$F(z) = z \int_0^\infty \exp \left[-(x^{6/l} + zx) \right] dx \, , \tag{12}$$

where

$$z = z_D + z_A = \Gamma \left(\frac{6 - l}{6} \right) \left\{ \left\langle \sqrt[6/l]{\langle k_D^2 \rangle} \right\rangle \left(\frac{\bar{R}_{0D}}{\tilde{R}_D} \right)^l + \left\langle \sqrt[6/l]{\langle k_A^2 \rangle} \right\rangle \left(\frac{\bar{R}_{0A}}{\tilde{R}_A} \right)^l \right\} . \tag{13}$$

Here

$$\left\langle \sqrt[6/l]{\langle k_D^2 \rangle} \right\rangle = \int_{\hat{\omega}} \sqrt[6/l]{\langle k_D^2 \rangle} \, n(\hat{\omega}_D) \, d\hat{\omega}_D \tag{14}$$

and

$$\left\langle \sqrt[6/l]{\langle k_A^2 \rangle} \right\rangle = \int_{\varrho} \sqrt[6/l]{\langle k_A^2 \rangle} \, n(\hat{\varrho}_A) \, d\hat{\varrho}_A \, . \tag{15}$$

$\tilde{R}_D$ and $\tilde{R}_A$ are radii, in the l-dimensional space, of the volume occupied, in the average, by a single molecule of the donor and acceptor, respectively.

The probability P_{DD} can be calculated in a similar manner, starting from relation (6). As a result the following formula is obtained

$$P_{DD} = (z_D/z) \cdot F(z) . \tag{16}$$

Substitution of (16) and (11) into formula (4) yields

$$\eta/\eta_0 = \frac{1 - F(z)}{1 - (z_D/z)\, F(z)} , \tag{17}$$

which gives the relative quantum yield of the system as a function of z. As relations (11), (12), (16) and (17) are identical with corresponding relations in [11—13] it follows that z should be regarded as a reduced concentration in the l-dimensional space.

This quantity, defined by (13), can also be described with a simpler formula

$$z = \Gamma\left(\frac{6-l}{6}\right)\left[\left(\frac{R_{0D}}{\tilde{R}_D}\right)^l + \left(\frac{R_{0A}}{\tilde{R}_A}\right)^l\right] \tag{18}$$

identical with that in [12, 13] provided that R_{0D} and R_{0A} satisfy the relations

$$R_{0D}^6 = \bar{R}_{0D}^6 \left\langle \sqrt[6/l]{\langle k_D^2 \rangle} \right\rangle^{6/l} , \tag{19}$$

$$R_{0A}^6 = \bar{R}_{0A}^6 \left\langle \sqrt[6/l]{\langle k_A^2 \rangle} \right\rangle^{6/l} . \tag{20}$$

R_{0D} and R_{0A} may be regarded as averaged critical distances reflecting the dependence of the orientation factor value on the energy transfer rate. It follows therefore that changes of this factor can be reduced to changes of the critical distance R_0 or critical l-dimensional concentration c_0 corresponding to that distance.

3. Conclusions and final remarks

The following relation between the l-dimensional critical concentration c_0 and averaged critical distance R_0 is satisfied

$$c_0 = \alpha / R_0^l . \tag{21}$$

Here α is a constant, depending on the dimension of the system, equal to 1/2, $1/4\pi$, and $3/4\pi$ for $l = 1, 2$ and 3, respectively. Hence from relations (19) and (20) it follows that critical concentrations c_0 for solutions of different dimensions depend on different mean values of the orientation factor, namely

a) $l = 1 \qquad c_0 = \bar{c}_0 / \left\langle \sqrt[6]{\langle k^2 \rangle} \right\rangle,$ (22)

b) $l = 2 \qquad c_0 = \bar{c}_0 / \left\langle \sqrt[3]{\langle k^2 \rangle} \right\rangle,$ (23)

c) $l = 3 \qquad c_0 = \bar{c}_0 / \left\langle \sqrt{\langle k^2 \rangle} \right\rangle,$ (24)

where $\bar{c}_0$ denote the appropriate "isotropic" critical concentrations.

The equations under consideration describe the behaviour of luminescent systems with respect to the rate of nonradiative excitation energy transfer between active molecules. They render possible the determination of the energy transfer efficiency with respect not only to the dimension of the solution, but also to the extent to ordering of molecule transition moments due to their rotation and distribution of directions of the rotational axes.

It can be expected that the analysis presented in this paper, as the considerations of the excitation energy transfer dependence on time [14] will help to distinguish between different arrangements of luminescent systems.

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