

EFFECTS PRODUCED BY EXCITATION TRANSFER BETWEEN LUMINESCENT MOLECULES IN FLUORESCENT SOLUTIONS

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(Received June 1, 1974)

The method of treating the problem of effects produced by excitation transfer between luminescent molecules in fluorescent solutions, put forward by the author, is further developed and extended to the case of solutions containing different kinds of dissolved luminescent molecules.

The considerations described below are devoted to the problem of effects produced by excitation transfer between luminescent molecules (*LMs*) in (rigid) solutions. Several methods of treating this problem were already proposed (for references see e.g. [4]; a critical review of theories published before 1968 is given in a paper by KNOX [5]). One of these was put forward by the present writer [4]. It was applied so far to solutions of identical *LM* only. Our aim is to develop further the theory and to extend its application to solutions containing two (or more) kinds of dissolved *LM*. In our treatment the notion of a luminescent centre (*LC*) plays an essential role.

A *LC* is assumed to consist of a donor molecule (*D*) situated in the centre of its "active sphere" in which also a few acceptor molecules (*As*) may be present. By we denote a *LM* excited directly by the exciting light, and by *A* a *LM* unexcited at the moment of the excitation of *D*. The radius of the active sphere may be chosen somewhat arbitrarily, but must be in any case large enough to allow direct excitation transfer from *D* to *As* situated outside the active sphere to be neglected, but otherwise rather small for convenience of calculation. In the following the intensity of the exciting light is assumed to be low enough practically not to affect the numerical density of unexcited *LMs* in the solution and to make possible for more than one *D* to appear in a practically negligible *LC* (this would be not the case if e.g. intensive laser light were used for excitation).

In an excited solution, various *LCs* containing various numbers of *As* will appear with different probabilities. The derivation of expressions for the probability distribution of *LC* given below is based on SMOLUCHOWSKI'S theory of fluctuations [6]. Smoluchowski derived among others an expression for the probability $W(n)$ of *n* molecules appearing in a volume element of a perfect gas [6]. Later on he has shown that the same expression is valid in the case of colloidal solutions. The fact that the colloidal particles can be observed directly by means of a microscope per-

mitted to TH. SVEDBERG the experimental verification of Smoluchowski's theory. The results obtained agree very well with the theoretical predictions [7]. In the simplest case of solutions containing only one kind of dissolved *LM*, Smoluchowski's expression for $W(n)$ can be even directly applied without any modification to the probability distribution of various *LCs* (as was already done in [4]), in cases when the influence of intermolecular forces on this distribution can be neglected.

A *LC* is created at the moment in which a *LM* becomes excited, *i.e.*, it becomes a *D*. The probability $P(k)$ that the created *LC* contains, apart from *D*, $(k-1)$ *As* (k denoting the total number of *LMs* in the centre) is given, as mentioned above, by Smoluchowski's distribution (=Poisson distribution) which reads in our notations

$$P(k) = e^{-\chi} \frac{\chi^{k-1}}{(k-1)!}, \quad k = 1, 2, 3, \dots \quad (1)$$

fulfilling the condition

$$\sum_{k=1}^{\infty} P(k) = 1. \quad (2)$$

Here $\chi = \frac{4}{3} \pi R_a^3 N = vN$, where $v \text{ cm}^3$ is the volume of the active sphere (of radius R_a) and $N \text{ cm}^{-3}$ the numerical density of unexcited *LMs* in the solution.

In each particular centre, the following processes will occur after the moment of excitation: excitation transfers and back transfers between pairs of *LM* with a rate μ depending on the mutual distances and orientations of *LMs*, and decay of the excited *LMs* due to emission of fluorescence and to radiationless transitions. Due to transfers of excitation from *D* to *As*, the *As* become excited and can emit fluorescence, thus causing a partial depolarization of fluorescence of the solution.

This results from the fact that the emission anisotropy (*EA*) of fluorescence of *As* is always very low [3]. In rigid or very viscous solutions considered here, the *EA* of *D* fluorescence is usually rather high. Thus the *EA* of fluorescence may be neglected in a fair approximation.

Our principal aim is to give an expression for the mean value of $EA\langle r \rangle$ of steadily excited fluorescence as a function of concentration of the solution. The probabilities of emission by *D* and by *As* in each particular centre appear in this expression. First of all these probabilities must be determined for a particular configuration of *LMs* in the *LC* and then averaged (by means of a computer) over all possible configurations in this centre.

Let us illustrate the procedure on a simple example of a *LC* containing one *A*. Let γ denote the probability for unit time of transition with emission of fluorescence, q that of radiationless transition, μ the rate of excitation transfer between *D* and *A* for a particular configuration (mutual distances and orientations of *D* and *A*), p_D and p_A the probabilities of *D* and *A*, respectively, being excited. We have to solve the following set of two coupled differential equations:

$$\frac{dp_D}{dt} = -(\gamma + q + \mu)p_D + \mu p_A \quad (3)$$

and

$$\frac{dp_A}{dt} = -(\gamma + q + \mu)p_A + \mu p_D. \quad (4)$$

The solution with the initial conditions $p_D=1$ and $p_A=0$ for the moment of excitation $t=0$ reads:

$$p_D(t) = \frac{1}{2} (e^{-(\gamma+q)t} + e^{-(\gamma+q+2\mu)t}), \quad (5)$$

$$p_A(t) = \frac{1}{2} (e^{-(\gamma+q)t} - e^{-(\gamma+q+2\mu)t}). \quad (6)$$

The probability of emission by D is

$$F_D = \gamma \int_0^{\infty} p_D dt = \eta \frac{1 + \mu\eta\tau_0}{1 + 2\mu\eta\tau_0} \quad (7)$$

and that by A

$$F_A = \gamma \int_0^{\infty} p_A dt = \eta \frac{\mu\eta\tau_0}{1 + 2\mu\eta\tau_0}. \quad (8)$$

The probability of the conversion of excitation energy into heat by D is

$$Q_D = q \int_0^{\infty} p_D dt = (1 - \eta) \frac{1 + \mu\eta\tau_0}{1 + 2\mu\eta\tau_0} \quad (9)$$

and that by A

$$Q_A = (1 - \eta) \frac{\mu\eta\tau_0}{1 + 2\mu\eta\tau_0}. \quad (10)$$

The following substitutions were made in Eqs. (7)–(10):

$$\tau_0 = \frac{1}{\gamma} \quad \text{and} \quad \eta = \frac{\gamma}{\gamma + q} \quad (\eta \text{ is the yield of fluorescence}).$$

Clearly $F_D + F_A = \eta$ and $Q_D + Q_A = 1 - \eta$. Eqs. (7) and (8) were already obtained by FÖRSTER [1] and later (without knowledge of Förster's paper) in a different way and differently normalized by myself [2, 3], where an error is corrected.

Since μ depends on mutual distances and orientations of LM the values of F_D , F_A , Q_D and Q_A given by Eqs. (7)–(10) depend on values of μ . By averaging these expressions over all distances and orientations of LM (over all μ occurring in the centre) one obtains the mean values $\langle F_{D2} \rangle$, $\langle F_{A2} \rangle$, $\langle Q_{D2} \rangle$ and $\langle Q_{A2} \rangle$, being the respective probabilities of emission by D and by A and those of the conversion of the excitation energy into heat by D and by A .

Such calculation was already performed for $\mu = \frac{F^2}{\tau_0} \left(\frac{R_0}{R} \right)^6$, where F^2 is the orientational factor and R the mutual distance of LMs [3].

In the general case of a LC containing k LMs , a set of k coupled differential equations must be solved and the obtained expressions for F_{Dk} , F_{Ak} , Q_{Dk} and Q_{Ak} averaged over all configurations. The mean values of these quantities $\langle F_{Dk} \rangle$, $\langle F_{Ak} \rangle$, $\langle Q_{Dk} \rangle$ and $\langle Q_{Ak} \rangle$ thus obtained are the probabilities of emission and conversion into heat by D and As , respectively.

If the probability distribution $P(k)$ of LC (Eq. (1)) is taken into account, the corresponding probabilities \overline{F}_D , \overline{F}_A , \overline{Q}_D and \overline{Q}_A for the whole solution can be obtained:

$$\overline{F}_D = \sum_{k=1}^{\infty} P(k) \langle F_{Dk} \rangle = e^{-\chi} \sum_{k=1}^{\infty} \frac{\chi^{k-1}}{(k-1)!} \langle F_{Dk} \rangle, \quad (11)$$

$$\overline{F}_A = e^{-\chi} \sum_{k=1}^{\infty} (k-1) \frac{\chi^{k-1}}{(k-1)!} \langle F_{Ak} \rangle = e^{-\chi} \chi \sum_{k=2}^{\infty} \frac{\chi^{k-2}}{(k-2)!} \langle F_{Ak} \rangle, \quad (12)$$

$$\overline{Q}_D = e^{-\chi} \sum_{k=1}^{\infty} \frac{\chi^{k-1}}{(k-1)!} \langle Q_{Dk} \rangle, \quad (13)$$

and

$$\overline{Q}_A = e^{-\chi} \chi \sum_{k=2}^{\infty} \frac{\chi^{k-2}}{(k-2)!} \langle Q_{Ak} \rangle. \quad (14)$$

The quantum yield $\overline{\eta}$ of the solution (the meaning $\overline{\eta}$ being not the same as that of η in Eqs. (7)–(10)) is

$$\overline{\eta} = \frac{\overline{F}_D + \overline{F}_A}{\overline{F}_D + \overline{F}_A + \overline{Q}_D + \overline{Q}_A}. \quad (15)$$

The emission anisotropy (EA) of fluorescence of the solution, if the EA of fluorescence of As is neglected, reads

$$r = r_0 \frac{\overline{F}_D}{\overline{F}_D + \overline{F}_A}, \quad (16)$$

where r_0 denotes the EA of fluorescence emitted by D .

Let us now consider the case of mixed solutions containing two kinds of dissolved LM , m and m' . If the solution is excited by monochromatic light absorbed by both m and m' , two groups of LX with different donors D and D' are created: D -centres and D' -centres.

The relative numbers of these centres depend on the ratio of the numerical densities $\frac{N}{N'}$ of m and m' and their molar absorption coefficients $\frac{\alpha}{\alpha'}$ for the absorbed light.

These relative numbers may be written as

$$W_D = \frac{N\alpha}{N\alpha + N'\alpha'} = \frac{\chi\alpha}{\chi\alpha + \chi'\alpha'} \quad \text{for } D\text{-centres} \quad (17)$$

and

$$W_{D'} = \frac{N'\alpha'}{N\alpha + N'\alpha'} = \frac{\chi'\alpha'}{\chi\alpha + \chi'\alpha'} \quad \text{for } D'\text{-centres} \quad (18)$$

where $\chi = \nu N$ and $\chi' = \nu N'$, ν being the volume of the active sphere.

The probability that a LC is a D -centre containing k m -molecules ($1D + (k-1)As$) and l m' -molecules (lA' s) is the product of the corresponding probabilities multiplied with W_D :

$$P_{kl} = \frac{\alpha\chi}{\alpha\chi + \alpha'\chi'} e^{-(\chi+\chi')} \frac{\chi^{k-l}}{(k-l)!} \frac{\chi'^l}{(l)!}, \quad (19)$$

$$k = 1, 2, 3, \dots \quad \text{and} \quad l = 0, 1, 2, 3, \dots$$

The corresponding expression for D' -centres is

$$P'_{lk} = \frac{\alpha'\chi'}{\alpha\chi + \alpha'\chi'} e^{-(\chi+\chi')} \frac{\chi'^{l-1}}{(l-1)!} \frac{\chi^k}{k!}, \quad (20)$$

$$l = 1, 2, 3, \dots \quad \text{and} \quad k = 0, 1, 2, 3, \dots$$

Eqs. (19) and (20) are so normalized that

$$\sum_{k=1}^{\infty} \sum_{l=0}^{\infty} P_{kl} + \sum_{l=1}^{\infty} \sum_{k=0}^{\infty} P'_{lk} = 1.$$

In a way similar to that used in Eqs. (4)–(10), various quantities for each particular LC have to be calculated. Let the probabilities of emission by D , by an A and by an A' , respectively, averaged over all configurations in a Dkl centre be denoted by $\langle F_{Dkl} \rangle$, $\langle F_{Akl} \rangle$ and $\langle F_{A'kl} \rangle$ for and those of the conversion into heat due to radiationless transitions in D , A and A' , by $\langle Q_{Dkl} \rangle$, $\langle Q_{Akl} \rangle$ and $\langle Q_{A'kl} \rangle$, respectively. The corresponding values for the total solution (for all D -centres) are

$$\overline{F}_D = \sum_{k=1}^{\infty} \sum_{l=0}^{\infty} P_{kl} \langle F_{Dkl} \rangle, \quad (21)$$

$$\overline{F}_A = \sum_{k=1}^{\infty} \sum_{l=0}^{\infty} P_{kl} (k-1) \langle F_{Akl} \rangle, \quad (22)$$

$$\overline{F}_{A'} = \sum_{k=1}^{\infty} \sum_{l=0}^{\infty} P_{kl} l \langle F_{A'kl} \rangle \quad (23)$$

$$\overline{Q}_D = \sum_{k=1}^{\infty} \sum_{l=0}^{\infty} P_{kl} \langle Q_{Dkl} \rangle, \quad (24)$$

$$\overline{Q}_A = \sum_{k=1}^{\infty} \sum_{l=0}^{\infty} P_{kl} (k-1) \langle Q_{Akl} \rangle, \quad (25)$$

$$\overline{Q}_{A'} = \sum_{k=1}^{\infty} \sum_{l=0}^{\infty} P_{kl} l \langle Q_{A'kl} \rangle. \quad (26)$$

Similar expressions for the D' -centres (\overline{F}'_D , \overline{F}'_A , $\overline{F}'_{A'}$, \overline{Q}'_D , $\overline{Q}'_{A'}$, \overline{Q}'_A) result if P'_{lk} and D' are used instead of P_{kl} , and k and l are interchanged. The obtained values of \overline{F}_D etc. and those of \overline{F}'_D etc. depend on the assumptions made, and in particular on those concerning the transfer and the back transfer of excitation between LM s

of the same and different type. The pertinent calculations were started by H. CHEREK of this Institute (private communication). Let us give some expressions which may be useful in certain applications. The ratio of the intensities of fluorescence bands emitted by m and m' is

$$\frac{J}{J'} = \frac{\overline{F_D} + \overline{F_A} + \overline{F'_A}}{\overline{F_{D'}} + \overline{F_{A'}} + \overline{F_{A'}}}. \quad (27)$$

The emission anisotropy of fluorescence emitted by m -molecules is given by

$$r = r_0 \frac{\overline{F_D}}{\overline{F_D} + \overline{F_A} + \overline{F'_A}}, \quad (28)$$

where r_0 is the emission anisotropy of fluorescence of D .

The corresponding expression for fluorescence of m' reads

$$r' = r'_0 \frac{\overline{F_{D'}}}{\overline{F_{D'}} + \overline{F_{A'}} + \overline{F_{A'}}}. \quad (29)$$

By means of Eqs. (21)–(26) one obtains for the fraction ΔE of the total energy E absorbed by D -centres transferred in these centres to A' s

$$\Delta E = E \frac{\overline{F_{A'}} + \overline{Q_{A'}}}{\overline{F_D} + \overline{F_A} + \overline{F_{A'}} + \overline{Q_D} + \overline{Q_A} + \overline{Q_{A'}}}. \quad (30)$$

The quantum yield of the total fluorescence emitted by D -centres (emitted both by m and m') reads

$$\bar{\eta} = \frac{\overline{F_D} + \overline{F_A} + \overline{F_{A'}}}{\overline{F_D} + \overline{F_A} + \overline{F_{A'}} + \overline{Q_D} + \overline{Q_A} + \overline{Q_{A'}}}. \quad (31)$$

Expressions similar to those given by Eqs. (30) and (31) may be easily written for D' -centres.

In the case when $\alpha' = 0$, all $P'(lk) = 0$, and only one group of centres is created (see Eq. (22)). Eq. (20) becomes simply

$$P_{kt} = e^{-(x+x')} \frac{\chi^{k-1}}{(k-1)!} \frac{\chi'^t}{t!}. \quad (20a)$$

Let us remark that Eq. (19) for $\chi' = 0$ becomes identical with Eq. (1). The expressions given in this paper for the case of fluorescent solutions containing two kinds of dissolved LM may be very easily extended to solutions containing more than two kinds of LM .

The number of terms which must be taken into account in expressions given here in the form of infinite series depends on the concentration of the solution and must be determined for each particular case separately.

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ЭФФЕКТЫ, ВЫЗВАННЫЕ ПЕРЕНОСОМ ВОЗБУЖДЕНИЯ МЕЖДУ ЛЮМИНЕСЦИРУЮЩИМИ МОЛЕКУЛАМИ, В ФЛУОРЕСЦИРУЮЩИХ РАСТВОРАХ

А. Яблоński

Метод трактовки проблемы эффектов, вызванных переносом возбуждения между молекулами в флуоресцирующих растворах, выдвинутый автором, распространяется на случай растворов, содержащих различные сорта растворенных люминесцентных молекул.