

MIGRATION OF THE EXCITATION ENERGY IN LUMINESCENT MEDIA

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Assuming the dipol-dipol mechanism of the non-radiative excitation energy transfer and the occurrence of dimers in the luminescence center, there was analysed the influence of selfquenching as well as excitation energy remigration on the quantum yields of photoluminescence (PL), emitted by molecules D_0 , D_1 and D_2 vs. reduced concentration g and the value of the dimerization constant K in the case of two — and three dimensional systems.

There was also considered the influence of g and K on the PL quantum yield of the molecules of order n , i.e. those which acquired excitation energy after n nonradiative transfers. A discussion of the result obtained is presented.

Introduction

The theory of non-radiative excitation energy transfer has been successfully applied to explain among others the concentration effects such as sensitized luminescence, concentration depolarization and also in many cases the luminescence concentration quenching [1]. Recently it has found a wide application to investigate more specialized systems [2—6] in particular to investigate two-dimensional systems, systems with a partial orientation of active molecules and also to investigate biopolymers and their dynamic structure.

The information as to the non-radiative excitation energy transfer between the molecules of the same kind can be obtained basing on the investigations of PL concentrational depolarization phenomenon observed in viscous and rigid solutions.

In the latter case it is essential to regard the excitation energy remigration to molecules D_0 — being primary absorbers of the exciting light. Hence the necessity of analyzing the destiny of the excitation energy in the nearest environment of molecule D_0 , and in particular of the contribution of molecules D_1 from the nearest environment of molecule D_0 to the observed luminescence. In the present paper we shall take into account the influence of dimers as quenching centres on energy remigration to molecules D_0 .

We shall also determine the participation of molecules D_0 , D_1 and D_2 in the observed luminescence in the case of two dimensional systems and also we shall discuss how the number of non-radiative transfers occurring in solution before the emission act depends on the concentration of active molecules and on the equilibrium constant in the process of forming dimers.

General remarks

In the discussion below we shall limit ourselves to the solutions containing two kinds of active molecule-monomers D and dimers D_n distributed statistically in a non-active medium.

We accept that the non-radiative energy transfer from excited molecule D^* to D or to D_n occurs by the long range transfer mechanism, where the interaction between active molecules varies as the sixth power of the reciprocal separation [7]. The calculating of the PL-quantum yield of molecules D_0 , which is necessary for finding the emission anisotropy [8—10], we shall carry out with the help of the model of luminescence centre called later on the model of most probable path* (MPP model). According to this model the luminescence centre consists of a molecule of type D_0 and molecules D_1, D_2, \dots, D_n between which the excitation energy can be transferred in a non-radiative way with most probability.

We assume that each of molecules D_1 being a monomer can lose the excitation energy as a result of fluorescence emission (relative probability \mathcal{P}_F) internal conversion (\mathcal{P}_q), non-radiative transfer to monomer molecule D (\mathcal{P}_{DD}) or to dimer molecule D_n (\mathcal{P}_{DD_n}).

For these probabilities for two-dimensional systems we have obtained the expressions [13]:

$$\mathcal{P}_F = \eta_0[1 - F(g)]; \quad \mathcal{P}_q = (1 - \eta_0)[1 - F(g)], \quad (1)$$

$$\mathcal{P}_{DD} = \beta F(g), \quad \mathcal{P}_{DD_n} = (1 - \beta) F(g), \quad (2)$$

where

$$F(g) = g \int_0^{\infty} \exp[-(t^3 + gt)] dt, \quad (3)$$

$$\beta = \frac{g_0}{g}, \quad g = g_D + g_{D_n} = \Gamma\left(\frac{2}{3}\right) \left[\left(\frac{R_{0D}}{\langle R_D \rangle} \right)^2 + \left(\frac{R_{0D_n}}{\langle R_{D_n} \rangle} \right)^2 \right]. \quad (4)$$

$\langle R_D \rangle$ is the radius of the circle satisfying relation $n_D \pi \langle R_D \rangle^2 = 1$, where n_D is a number of monomer molecules per unit area similarly $\langle R_{D_n} \rangle$ for dimers, $\Gamma\left(\frac{2}{3}\right)$ is gamma function.

Within the MPP model with three molecules D_0, D_1 and D_2 and when the fourth molecule D_3 of the monomer molecules not belonging to the luminescence centre is taken into account there are possible four situational distributions of these molecules differing by the distance of their neighbourhood. As it was proved in ref. [11] it is sufficient to regard two of these distributions; they are presented in Fig. 1 in ref. [14]. Because molecules D_i belonging to the luminescence centre can be monomers D as well as dimers D_n for each of the situational distributions A and B there are possible the distributions of molecules D and D_n listed in Table I; in this table there are also given the probabilities of these distributions.

* More information as to the MPP model can be found in [11, 12].

Table I

No	Distribution D_0 D_1 D_2			Probability
1	D	D	D	$p_1 = \varphi^3$
2	D''	D	D	$p_2 = p_3 = p_4 = \varphi^2(1-\varphi)$
3	D	D	D''	
4	D	D''	D	
5	D''	D''	D	$p_5 = p_6 = p_7 = \varphi(1-\varphi)^2$
6	D''	D	D''	
7	D	D''	D''	
8	D''	D''	D''	$p_8 = (1-\varphi)^3$

The probability that a molecule chosen at random may be a monomer or a dimer amounts, respectively:

$\varphi = \frac{n_D}{n}$ and $1-\varphi = \frac{n_{D''}}{n}$, where $\eta_D, \eta_{D''}, n$ denote the concentrations of monomers, dimers and analytical concentration expressed in molecule number per area unit.

PL quantum yields of molecules D_0, D_1 and D_2

Mean PL quantum yield $\langle \frac{\eta_{(0)}}{\eta_0} \rangle$ of molecules of type D_0 can be expressed in the following way [15]:

$$\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle^{(2)} = \varphi^3 \left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_3^{(2)} + \varphi^2(1-\varphi) \left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2^{(2)} + \varphi(1-\varphi) \left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_1^{(2)}, \quad (5)$$

where η_0 is PL quantum yield of solution at $n \rightarrow 0$, $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_3^{(2)}$, $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_2^{(2)}$ and $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle_1^{(2)}$ denote mean quantum yields (from situational distributions A and B) of molecules of type D_0 corresponding to distributions 1,3, and 4 and 7 (comp. Table 1). The index at the right side below the symbol of the mean value denotes the number of monomer molecules being in the direct neighbourhood in the luminescence centre; index (2) or (3) at the right side above means that the yield refers to a two — or three — dimensional system similarly as yield $\left\langle \frac{\eta_{(0)}}{\eta_0} \right\rangle^{(2)}$ so yields $\left\langle \frac{\eta_1}{\eta_0} \right\rangle^{(2)}$ and $\left\langle \frac{\eta_2}{\eta_0} \right\rangle^{(2)}$ can be put down in the form:

$$\left\langle \frac{\eta_1}{\eta_0} \right\rangle^{(2)} = \varphi^3 \left\langle \frac{\eta_1}{\eta_0} \right\rangle_3^{(2)} + \varphi^2(1-\varphi) \left\langle \frac{\eta_1}{\eta_0} \right\rangle_2^{(2)}, \quad (6)$$

$$\left\langle \frac{\eta_2}{\eta_0} \right\rangle^{(2)} = \varphi^3 \left\langle \frac{\eta_2}{\eta_0} \right\rangle_3^{(2)}, \quad (7)$$

where $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_3^{(2)}$ and $\left\langle \frac{\eta_2}{\eta_0} \right\rangle_3^{(2)}$ denote the PL yields of molecules D_1 and D_2 corresponding to distribution 1 and $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_2^{(2)}$ the PL yield of molecules D_1 corresponding to distribution 3 in Table I. Yields $\left\langle \frac{\eta_{(i)}}{\eta_0} \right\rangle_k^{(2)}$ ($k=1, 2, 3$), $\left\langle \frac{\eta_1}{\eta_0} \right\rangle_l^{(2)}$ ($l=2, 3$) and $\left\langle \frac{\eta_2}{\eta_0} \right\rangle_3^{(2)}$ have an identical form as for three dimensional systems [15], with the proviso that the occurring there functions $f(\gamma)$, $\langle Q \rangle$, α and P_{DD} should be replaced by $F(g)$, $\langle Q' \rangle$, β and \mathcal{P}_{DD} , where $\langle Q \rangle$ is Ore factor [16] meaning the probability that if molecule D_1 is the nearest neighbour of molecule D_0 , then molecule D_0 is the nearest neighbour of molecule D_1 at the assumption of statistical distribution of molecules D and D_n in solution.

For two-dimensional systems function $\langle Q' \rangle = \langle Q'(g_D) \rangle$ was given in ref. [17]. Finally we get for PL quantum yields of molecules D_0 , D_1 and D_2 :

$$\left\langle \frac{\eta_{(i)}}{\eta_0} \right\rangle^{(2)} = \varphi(1-F) \left\{ \frac{\varphi^2}{2} \left[2 + \frac{\langle Q' \rangle (\beta F)^2}{M_1} + \frac{(1 - \langle Q' \rangle) (\beta F)^2}{M_2} \right] + \frac{\varphi(1-\varphi)}{1 - (\beta F)^2} + \frac{1-\varphi}{1 - \beta F} \right\}, \quad (8)$$

$$\left\langle \frac{\eta_1}{\eta_0} \right\rangle^{(2)} = \frac{\varphi^2(1-F)(\beta F)^2}{2} \left[\frac{\varphi}{M_1} + \frac{\varphi}{M_2} + \frac{2(1-\varphi)}{1 - (\beta F)^2} \right], \quad (9)$$

$$\left\langle \frac{\eta_2}{\eta_0} \right\rangle^{(2)} = \frac{\varphi^3(1-F)(\beta F)^2}{2} \left[\frac{1 - \langle Q' \rangle}{M_1} + \frac{\langle Q' \rangle}{M_2} \right], \quad (10)$$

where

$$M_1 = 1 - \langle Q' \rangle (2 - \langle Q' \rangle) (\beta F)^2, \quad (11)$$

$$M_2 = 1 - (1 - \langle Q' \rangle)^2 (\beta F)^2. \quad (12)$$

Expressions (8)–(12) describe the concentration changes of PL quantum yields of molecules D_0 , D_1 and D_2 taking into account the presence of dimers D_n in the luminescence centre. These changes are shown in Fig. 1 for several values of the dimensionless dimerization constant* Kg . In Fig. 1A there are presented the changes of PL quantum yield of the primary absorbers of exciting light — molecules D_0 — vs. the reduced concentration g in the case of two-dimensional systems (solid lines) and three-dimensional systems** (dotted lines). A comparison of curves a , b and c proves that remarkable differences of the yields courses $\left\langle \frac{\eta_{(i)}}{\eta_0} \right\rangle$ occur only

* Constant $Kg = g_{D_n}/g_D^2$ is connected with equilibrium constant $K = n_{D_n}/n_D^2$ by the dependence $Kg = Kn_{D_n}^2/\Gamma \left(\frac{2}{3} \right) n_{0D_n}$.

** Curve $\left\langle \frac{\eta_{(i)}}{\eta_0} \right\rangle^{(2)}$ for a three-dimensional system and $K\gamma = 0.1$ which in our notation would be denoted by b' , has not been presented in the figure, because this curve completely overlaps with the solid curve c .

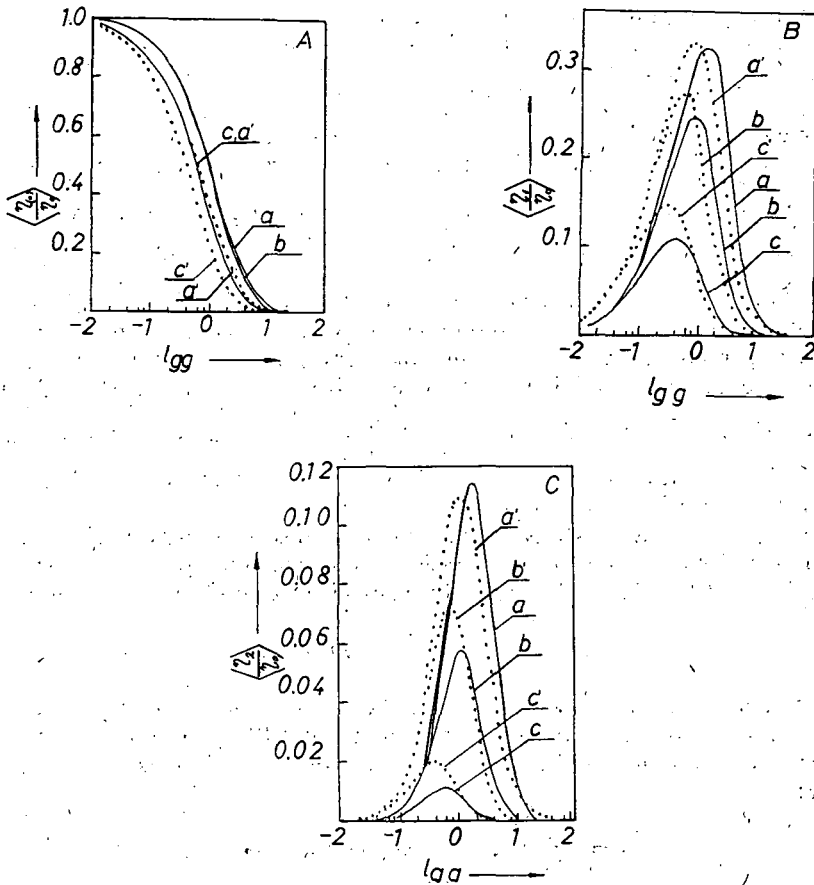


Fig. 1. Concentration dependences of PL-quantum yields of molecules D_0 and their nearest neighbours D_1 and D_2 . Solid and dotted lines concern the two- and three-dimensional systems

$$a - Kg = 0; \quad b - Kg = 0,1; \quad C - Kg = 1,0;$$

$$a' - K\gamma = 0; \quad b' - K\gamma = 0,1; \quad C' - K\gamma = 1,0.$$

Solid curves $\langle \frac{\eta_{(0)}}{\eta_0} \rangle^{(2)}$, $\langle \frac{\eta_1}{\eta_0} \rangle^{(2)}$ and $\langle \frac{\eta_2}{\eta_0} \rangle^{(2)}$ are plotted on the basis of exprs. (8), (9) and (10); similar dotted curves—on the basis of the same expressions with functions $F(g)$, $\langle Q \rangle$, β and \mathcal{P}_{DD} replaced by $f(g)$, $\langle Q \rangle$, α and P_{DD} (comp. ref. [15])

for strongly dimerizing systems. A similar situation is observed in the case of three-dimensional systems. It is seen that the yield drop $\langle \frac{\eta_{(0)}}{\eta_0} \rangle$ in the case of three-dimensional systems is bigger than for two-dimensional systems which is understandable because of a bigger probability of non-radiative energy transfer from molecules D_0

to their nearest neighbours in three-dimensional systems than in two-dimensional ones ($\mathcal{P}_{DD} > \mathcal{P}_{DD}$ at the same value of reduced concentration).

The courses of the concentration changes of yield $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$ are shown in Fig. 1B. For each value of Kg there exist an "optimal" concentration at which the PL quantum yield of molecules D_1 is maximum. The same refers to three-dimensional systems (dotted lines) as well as to yield $\left\langle \frac{\eta_2}{\eta_0} \right\rangle$ (comp. Fig. 1C). From Figs. 1B and 1C we can see that the courses of concentration changes of $\left\langle \frac{\eta_1}{\eta_0} \right\rangle$ and $\left\langle \frac{\eta_2}{\eta_0} \right\rangle$ for two-dimensional systems (solid lines) and three-dimensional systems (dotted lines) are similar, but the curves corresponding to two-dimensional systems are shifted towards larger concentrations. In our considerations we limited ourselves to the luminescence centre containing only three active molecules D_0 , D_1 and D_2 . The question arises whether the found values $\left\langle \frac{\eta^{(0)}}{\eta_0} \right\rangle$ are a sufficiently good approximation of the values which could be expected when a larger number of active molecules in the centre is taken into account.

An appropriate analysis as to the emission anisotropy was carried out earlier [11, 17] both for two- and three-dimensional systems. By that we have proved that the applied MPP model with three molecules gives a good approximation.

PL quantum yields of molecules $D^{(m)}$

It seems to be interesting to regard the participation of quantum yields $\eta^{(m)}$ of molecules $D^{(m)}$ of each particular order in the total PL quantum yield of solution, η , determined as a sum of PL quantum yields of the molecules of all the orders, namely:

$$\eta = \sum_{m=0}^{\infty} \eta^{(m)}, \quad \text{where} \quad \eta^{(m)} = \mathcal{P}_F \cdot \mathcal{P}_{DD}^m, \quad (13)$$

\mathcal{P}_F and \mathcal{P}_{DD} are determined by exprs. (1) and (2).

In Fig. 2A there are presented the concentration dependences of yields $\eta^{(m)}$ for two-dimensional systems calculated on the basis of expression

$$\frac{\eta^{(m)}}{\eta_0} = (1-F)(\beta F)^m, \quad (14)$$

obtained after putting eq. (1) and (2) into (13). The solid curves correspond to the case when concentration quenching does not occur ($Kg=0$). It is seen that in the range of concentration $g < 0.1$ the photoluminescence emitted by molecules $D^{(0)}$ predominates clearly the PL yields of the molecules of higher orders. In the range of critical concentrations ($g \approx 1$) the contribution of yields $\eta^{(1)}$ and $\eta^{(2)}$ is pronounced (curves *b* and *c*). Finally in the range of very large concentrations the participation of PL of molecules $D^{(0)}$ as well as $D^{(n)}$ becomes comparable. The dotted curves (*b* and *c*) present the concentration changes of yields $\eta^{(1)}$ and $\eta^{(2)}$ for strongly dimerizing systems ($Kg=1.0$).

The influence of concentration quenching is clearly seen for concentration $g > 0.1$; for quantum yields of higher order it is even bigger. The corresponding curves have not been given in the figure.

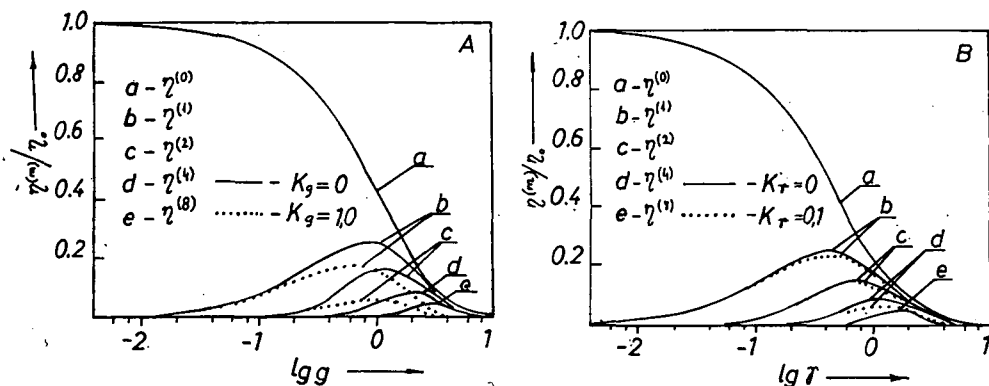


Fig. 2. Photoluminescence quantum yields of molecules $D^{(m)}$ Figs. A and B refer to the two- and three-dimensional system, respectively

In Fig. 2B there are presented similar dependences for three-dimensional systems. The dotted lines present the concentration changes of quantum yields $\eta^{(1)}$, $\eta^{(2)}$ and $\eta^{(4)}$ for value $K_q = 0.1$ corresponding to strongly dimerizing dyes in solutions [19]. The influence of concentration quenching is in this case relatively slight. As seen from Figs. 2A and 2B the courses of yields $\eta^{(m)}$ for two- and three-dimensional systems are similar, but values $\eta^{(0)}$ corresponding to the same concentration g are in the case of two-dimensional systems remarkably bigger. This is connected with the decreasing probability of non-radiative excitation energy transfer in two-dimensional systems caused by the absence of acceptor molecules outside the plane of the system regarded. A still bigger stopping of excitation energy transfer should occur in one-dimensional systems which has been noticed by VAVILOV [20] and experimentally confirmed later on [21].

Number of non-radiative transfer of excitation energy

Knowing yields $\eta^{(m)}$ we can compute the mean number $\langle m \rangle$ of non-radiative transfer occurring before the emission of radiation. According to the definition of the order of molecule $D^{(m)}$ yields $\eta^{(m)}$ represent this part of the total number of luminescence quanta which have been emitted by excited molecules after m non-radiative transfers of the energy originating from the primary absorbers of exciting light. And so

$$\langle m \rangle = \frac{\sum_{m=0}^{\infty} m \eta^{(m)}}{\sum_{m=0}^{\infty} \eta^{(m)}} \quad (15)$$

Taking into account expr. (14) in expr. (15) we get* after simple transformations:

$$\langle m \rangle = (1 - \beta F)(\beta F)[1 + 2(\beta F) + 3(\beta F)^2 + \dots + k(\beta F)^{k-1} + \dots] = \frac{\beta F}{1 - \beta F}. \quad (16)$$

In Table II there are listed the values of the mean number of transfers $\langle m \rangle$ computed on the basis of Eq. (16) for several values of dimerization constant.

Table II.

$K_g \backslash g$	0.01	0.1	0.2	0.4	0.6	1.0	2.0	4.0	10.0
0	0.009	0.093	0.193	0.417	0.677	1.32	3.88	15.7	174.9
0.001	0.009	0.093	0.193	0.417	0.676	1.31	3.83	14.6	63.8
0.1	0.009	0.092	0.189	0.396	0.618	1.09	2.12	2.6	1.6
$K_\gamma \backslash \gamma$	0.01	0.1	0.2	0.4	0.6	1.0	2.0	4.0	10.0
0	0.018	0.189	0.402	0.908	1.52	3.13	9.55	30.9	199.0
0.01	0.018	0.189	0.400	0.901	1.50	3.00	7.93	13.9	10.4
0.1	0.018	0.186	0.390	0.846	1.33	2.27	3.41	2.9	1.6

In the case of the absence of concentration quenching in system ($K_g=0$) the number of transfers $\langle m \rangle$ increases quickly together with concentration g in range $g>1$. When in a solution besides monomers appear also non-luminescent dimers, the number of transfer $\langle m \rangle$ increases more slowly, first of all in the range of moderate concentrations.

Besides in the range of largest concentrations there occurs a drop of transfers number $\langle m \rangle$ after reaching the maximum (comp. the line for $K_g=0.1$). This fact is more visible in the case of three-dimensional systems (comp. the lines for $K_\gamma=0.01$ and $K_\gamma=0.1$), for which a similar regularity is observed. The decreasing number of transfers $\langle m \rangle$ in the range of largest concentrations is undoubtedly connected with the strong concentration quenching leading to a pronounced shortening of the mean lifetime τ of active molecules in excited state.

Final remarks

We hope that determining the PL-quantum yields of the molecules D_0 and their nearest neighbours D_1 and D_2 vs. concentration of the active molecules may be useful to describe the concentration changes of PL emission anisotropy of systems with a partial ordering of molecular dipole orientation. It seems also that the analysis

* $\beta F \equiv \beta(g)F(g) < 1$ for all g .

concerning the PL quantum yields of the molecules $D^{(m)}$ of order m as well as the number of non-radiative transfers occurring before PL-emission act may be profitable in relation to the problem of photosynthesis.

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МИГРАЦИЯ ЭНЕРГИИ ВОЗБУЖДЕНИЯ В ЛЮМИНЕСЦИРУЮЩИХ СРЕДАХ

Ч. Боярки

Принимая диполь — дипольный механизм безизлучательного переноса энергии возбуждения как и присутствие димеров в центре люминесценции, проанализировано влияние само-тушения а также миграции энергии возбуждения на квантовые выходы фотолюминесценции (ФЛ) испускаемой молекулами D_0 , D_1 и D_2 в зависимости от приведенной концентрации g и от значения константы димеризации K в случае систем двух- и трех измерений.

Рассмотрено также влияние g и K на относительный квантовый выход ФЛ молекул n -го класса, значит таких молекул, которые получили энергию возбуждения после n безизлучательных переносов. Проведена дискуссия полученных результатов.