EXCITATION ENERGY TRANSFER
IN MULTI-COMPONENT LUMINESCENT SOLUTIONS

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Based on the paper of BUDÓ and KETSKEMÉTY we derived a general equation which describes the shape of the fluorescence spectrum of multi-component solutions as a function of the emission-, absorption- and quantum yield spectrum of each component. Both radiative and non-radiative excitation energy transfers were taken into account. This equation is discussed for the cases of one-, two- and three-component solutions.

The problem of excitation energy transfer in luminescent multi-component solutions appears frequently in the literature. In many cases [1—7] considerable enhancement of the generated energy of dye lasers could be achieved by applying multicomponent systems. Recent experiments [8] threw light onto the excitation energy migration in the phycoerythrin — phycocyanin — chlorophyll *a* system of plant chloroplasts. More detailed chromatographic investigations revealed that some dyes, widely applied to luminescence investigations are, in fact, mixtures of several components. Thus, the problem of luminescence of multi-component solutions can be regarded as a theoretical and experimental topic [9—12].

Radiative energy transfer in multi-component solutions

The general equations which describe the shape of the fluorescence spectrum of a two- and three-component solution was given in our previous papers [9—11]. These expressions take into account the influence of reabsorption and secondary emission on the shape of the spectrum but neglect the contribution of higher order emissions as small one. Quite recently we demonstrated [12] that emission of at least third order should be additionally taken into account to obtain satisfactory agreement with certain experimental data.

These expressions can be generalized for arbitrary number of components under the same assumptions and formalism as given elsewhere [9, 13]. Let us assume that the luminescence of an *n*-component solution will be excited by a parallel light-

beam with a cross-section of $R^2\pi$, perpendicular to the front face of the sample. The luminescence light will be reversely directed starting from the centre of the excitation region. Its crosssection is small as compared to $R^2\pi$ and, thus, when computing the intensity of the fluorescence we can limit ourselves to the direct neighbourhood of the straight line which passes through the central point of the
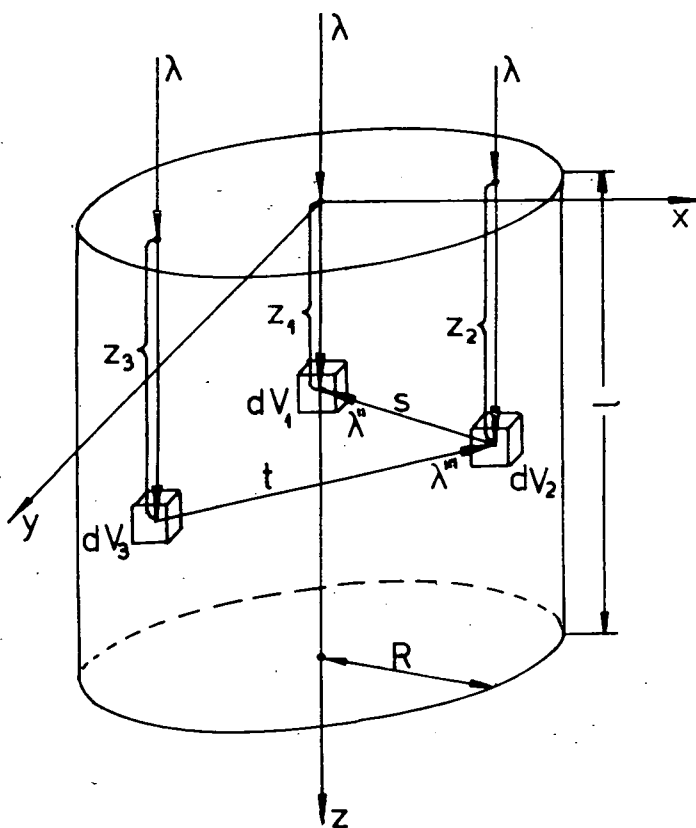

Fig. 1.

excitation region. In this case the illuminated part of the solution forms a cylinder (base radius R and height=the thickness of the sample $-l$) whose axis coincides with the z-axis of the coordinate system $Oxyz$ (Fig. 1). The exciting light which enters the solution has an intensity of E_λ at the front ($z=0$) of the sample. From this light available an arbitrary elementary volume dV at deepth z absorbs in each second the amount of quanta

$$E_\lambda k(\lambda)e^{-k(\lambda)z}dV, \qquad\qquad (1)$$

where $k(\lambda)$ is the absorption coefficient of the solution at this wavelength (λ). If no chemical reactions occur in the solution then we can assume [12] that

$$k(\lambda) = \sum_{i=1}^{n} k_i(\lambda), \tag{2}$$

where $k_i(\lambda)$ denote the absorption coefficient of each component. Let us denote the normalized true fluorescence quantum-spectrum of the successive components and their effective quantum yield* with $f_i(\lambda)$ and $\eta_i'(\lambda)$ respectively, then the magnitude and spectral distribution of the first order photoluminescence quantum flux (depending on wavelength λ') which is emitted from the volume element dV_1 can be described by the following expression:

$$d^4\varphi_P(\lambda, \lambda', z_1) = E_\lambda e^{-k(\lambda)z_1} k(\lambda) \sum_{i=1}^{n} \eta_i'(\lambda) f_i(\lambda')\, dV_1\, d\lambda' =$$

$$= E_\lambda e^{-k(\lambda)z_1} k(\lambda) \sum_{i=1}^{n} P_{ii}(\lambda, \lambda')\, dV_1\, d\lambda' \tag{3}$$

where

$$P_{ij}(\lambda, \lambda') = \eta_i'(\lambda) f_j(\lambda'). \tag{4}$$

The number of quanta emitted by first order photoluminescence, $B(\lambda, \lambda')_p d\lambda'$ in unit time and from unit area in unitary solid andle and, in the range $(\lambda', \lambda'+d\lambda')$, can be obtained by integrating expression (3) along the whole thickness of the sample. Taking into account the reabsorption of the emitted quanta inside the cuvette we obtain:

$$B(\lambda, \lambda')_P\, d\lambda' = \frac{\varrho}{4\pi n^2} E_\lambda \int_0^l e^{-[k(\lambda)+k(\lambda')]z_1} k(\lambda) \sum P_{ii}(\lambda, \lambda')\, dz_1\, d\lambda' =$$

$$= C(\lambda, \lambda') \sum_{i=1}^{n} P_{ii}(\lambda, \lambda')\, d\lambda', \tag{5}$$

where ϱ is a coefficient which takes into account the radiation losses caused by the partial reflection from the front wall of the cuvette, n is the refractive index of the solution, and $C(\lambda, \lambda')$ is defined as

$$C(\lambda, \lambda') = \frac{\varrho}{4\pi n^2} E_\lambda \frac{\alpha}{\alpha+\beta} (1 - e^{-(\alpha+\beta)}), \tag{6}$$

where $\alpha = k(\lambda) \cdot l$ and $\beta = k(\lambda') \cdot l$. Similarly, the magnitude and the spectral distribution of the second order emission from the element dV_1 (appearing as a result

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* Effective qunatum yield $\eta_i'(\lambda)$ means the ratio of the number of quanta if emitted from element dV by the i-th component to the number of quanta absorbed in this element by all components of the solution from the light at wavelength λ.

of radiative excitation energy transfer to this element from the other part of the excitation region) can be described by the following expression

$$d^4\varphi_s(\lambda, \lambda', z_1) = \int\limits_{\lambda''} \int\limits_{V_2} E_\lambda e^{-k(\lambda)z_2} k(\lambda) \sum_{i=1}^n P_{ii}(\lambda, \lambda'') \times$$

$$\times \frac{1}{4\pi s^2} k(\lambda'') e^{-k(\lambda'')s} \sum_{j=1}^n P_{jj}(\lambda'', \lambda') \, dV_2 \, d\lambda'' \, dV_1 \, d\lambda'. \tag{7}$$

Since

$$\sum_{i=1}^n P_{ii}(\lambda, \lambda'') \cdot \sum_{j=1}^n P_{jj}(\lambda'', \lambda') \equiv \sum_{i,j=1}^n P_{ij}(\lambda, \lambda') P_{ji}(\lambda'', \lambda''), \tag{8}$$

we may write

$$d^4\varphi_s(\lambda, \lambda', z_1) =$$

$$E_\lambda k(\lambda) \sum_{i,j=1}^n \left[P_{ij}(\lambda, \lambda') \int\limits_{\lambda''} P_{ji}(\lambda'', \lambda'') k(\lambda'') \frac{e^{-k(\lambda'')s - k(\lambda)z_2}}{4\pi s^2} \, dV_2 \, d\lambda'' \right] dV_1 \, d\lambda'. \tag{9}$$

The intensity and the spectral distribution of the second order emission $B(\lambda, \lambda')_s$ can be obtained by integration (as for $B(\lambda, \lambda')_p$)

$$B_s(\lambda, \lambda') = \frac{\varrho}{4\pi n^2} E_\lambda k(\lambda) \sum_{i,j=1}^n \left[P_{ij}(\lambda, \lambda') \int\limits_{\lambda''} P_{ji}(\lambda'', \lambda'') \int\limits_0^l e^{-k(\lambda')z_1} k(\lambda'') \times \right.$$

$$\left. \times \int\limits_{V_2} \frac{e^{-k(\lambda'')s - k(\lambda)z_2}}{4\pi s^2} \, dV_2 \, d\lambda'' \right] dz_1 = \frac{\varrho}{4\pi n^2} E_\lambda k(\lambda) l \sum_{i,j=1}^n P_{ij}(\lambda, \lambda') S_{ji}(\lambda'), \tag{10}$$

where S_{ji} denotes

$$S_{ji}(\lambda') = \int\limits_{\lambda''} \eta_j'(\lambda'') f_i(\lambda'') \left[\frac{1}{l} \int\limits_0^l e^{-k(\lambda')z_1} \left(\frac{k(\lambda'')}{4\pi} \int\limits_{V_2} \frac{e^{-k(\lambda'')s - k(\lambda)z_2}}{s^2} \, dV_2 \right) dz_1 \right] d\lambda''. \tag{11}$$

Eq. (11) is identical with Eq. (11) from our previous paper [13]. Introducing the following notation

$$\varkappa_{ij} = \frac{\alpha + \beta}{l(1 - e^{-(\alpha + \beta)})} S_{ji}, \tag{12}$$

we obtain

$$B_s(\lambda, \lambda') = C(\lambda, \lambda') \sum_{i,j=1}^n P_{ij}(\lambda, \lambda') \varkappa_{ij}. \tag{13}$$

Inserting Eq. (4) to Eq. (13) we may write

$$B_s(\lambda, \lambda') = C(\lambda, \lambda') \sum_{i,j=1}^n \eta_i'(\lambda) \varkappa_{ij} f_j(\lambda'). \tag{14}$$

On the basis of Eqs. (16), (17), (19) and (26) from the paper [13] we can easily prove that:

$$\varkappa_{ij} = \int\limits_0^\infty \eta_j'(\lambda'') f_i(\lambda'') M(\lambda'') \, d\lambda''. \tag{15}$$

The function $M(\lambda'')$ is given by

$$M(\lambda'') = \frac{(\alpha+\beta)(1-e^{-\alpha})(1-e^{-\beta})}{2\alpha\beta[1-e^{-(\alpha+\beta)}]} [\gamma E_i(-m\gamma) - \gamma E_i(-\gamma)] +$$

$$+ \frac{1}{2[1-e^{-(\alpha+\beta)}]} [\chi(\alpha, \gamma) + \chi(\beta, \gamma) + e^{-\beta}\psi(\alpha, \gamma) + e^{-\alpha}\psi(\beta, \gamma)], \tag{16}$$

where $\gamma = k(\lambda'')l$, $m = R/l$ and

$$E_i(x) = 0.5772 \ldots + \ln|x| + x + \frac{x^2}{2\cdot 2!} + \frac{x^3}{3\cdot 3!} + \cdots,$$

$$\psi(x, \gamma) = \frac{\gamma e^{-x}}{x} [G(-\gamma) - G(-\gamma + x)], \tag{17}$$

$$\chi(x, \gamma) = \frac{\gamma}{x} [G(-\gamma) - G(-\gamma - x)].$$

$G(x)$ is defined as $G(x) = E_i(x) - \ln|x|$.

A presice computation of the spectral distribution and the intensity of the third order emission of a multi-component solution is connected with great difficulties. According to BUDÓ and KETSKEMÉTY [13] this can be done by assuming that the ratio of emission intensity of the $(m+1)$th order of the kth component (excited by the radiative energy transfer by the mth order emission of the ith component) is independent of m and this ratio is equal to the ratio of the primary and secondary emission intensities in the same system. Comparing Eqs. (5) and (14) it can be seen that this assumption is equivalent with the premise that Eq. (15) not only describes the energy transfer to secondary emission but also the energy transfer to higher order emissions. Thus, according to Eq. (14) for third order emission we may write

$$B_t(\lambda, \lambda') = C(\lambda, \lambda') \sum_{i,j,k=1}^{n} \eta_i'(\lambda) \varkappa_{ij} \varkappa_{jk} f_k(\lambda'). \tag{18}$$

The shape of the fluorescence spectrum, $B(\lambda, \lambda')$, of an n-component solution taking into account first, second and third order emissions can be given as a sum of Eqs. (5), (15) and (18)

$$B(\lambda, \lambda') \simeq C(\lambda, \lambda') \sum_{i=1}^{n} \left[\eta_i'(\lambda) + \sum_{j=1}^{n} \eta_j'(\lambda) \varkappa_{ji} + \sum_{j,k=1}^{n} \eta_k'(\lambda) \varkappa_{kj} \varkappa_{ji} \right] f_i(\lambda'). \tag{19}$$

By applying this procedure subsequently we could easily find the approximate expressions which takes into account the contributions of the emission of arbitrary order to the fluorescence spectrum of a solution of arbitrary number of components. From Eq. (19) we can see that the successive terms with $\varkappa_{ii}$ form in the expression of $B(\lambda, \lambda')$ a decreasing geometrical progression with a quotient of $\varkappa_{ii}$. Therefore, we can write another expression for $B(\lambda, \lambda')$ which is a better approximation of the real luminescence spectrum for multicomponent solutions than Eq. (19)

$$B(\lambda, \lambda') \simeq C(\lambda, \lambda') \sum_{i=1}^{n} \left[\frac{1}{1-\varkappa_{ii}} \eta_i'(\lambda) + \sum_{\substack{j=1 \\ (j\neq i)}}^{n} \eta_j'(\lambda) \varkappa_{ji} + \sum_{\substack{j,k=1 \\ (j=k\Rightarrow j\neq i)}}^{n} \eta_\varkappa'(\lambda) \varkappa_{kj} \varkappa_{ji} \right] f_i(\lambda'). \tag{20}$$

Introducing the terms of non-radiative energy transfer into the theory
of radiative transfer

In the case of a solution in which the emission spectra of the acceptors does not overlap with the absorption spectra of the donors according to Eq. (16), all values $\varkappa_{ij}$ for $i > j$ vanish and then Eq. (20) becomes:

$$B(\lambda, \lambda') \simeq C(\lambda, \lambda') \sum_{i=1}^{n} \left[\frac{1}{1-\varkappa_{ii}} \eta_i'(\lambda) + \sum_{\substack{j=1 \\ (j<i)}}^{n} \eta_j(\lambda)\varkappa_{ji} + \sum_{\substack{j,k=1 \\ (j,k<i)}}^{n} \eta_k'(\lambda)\varkappa_{kj}\varkappa_{ji} \right] f_i(\lambda'). \quad (21)$$

Under these conditions we apply the definition of the effective quantum yield and denote the transition probability of the ith component molecule to the electronic excited state by $\eta_i^*(\lambda)$, and so we obtain the following expressions

$$\eta_1'(\lambda) = \frac{1}{k(\lambda)} k_1(\lambda)\eta_1^*(\lambda)K_1,$$

$$\eta_2'(\lambda) = \frac{1}{k(\lambda)} [k_2(\lambda)\eta_3^*(\lambda)K_2 + k_1(\lambda)\eta_1^*(\lambda)K_{12}K_2], \quad (22)$$

$$\eta_3'(\lambda) = \frac{1}{k(\lambda)} [k_3(\lambda)\eta_3^*(\lambda)K_3 + k_1(\lambda)\eta_1^*(\lambda)(K_{13}K_3 + K_{12}K_{23}K_3) + k_2(\lambda)\eta_2^*(\lambda)K_{23}K_3].$$

The constants K_i and K_{ik} denote the quantum yield of each component and the yield of non-radiative excitation energy transfer between the ith and kth component. We can easily see that for the effective quantum yield of the ith component the following equation holds

$$\eta_i'(\lambda) = \frac{K_i}{k(\lambda)} \left\{ k_i(\lambda)\eta_i^*(\lambda) + \sum_{\substack{j=1 \\ (j<i)}}^{n} k_j(\lambda)\eta_j^*(\lambda) \left[K_{ji} + \sum_{\substack{k=1 \\ (j<k<i)}}^{n} K_{jk}K_{ki} + \right. \right.$$

$$\left. \left. + \sum_{\substack{k,l=1 \\ (j<k<l<i)}}^{n} K_{jk}K_{kl}K_{li} + \dots + K_{12}K_{23} \cdot \dots \cdot K_{i-2,i-1}K_{i-1,i} \right] \right\}. \quad (23)$$

In the particular case of monocomponent solutions Eq. (21) can be written according to Eq. (25) from [13]

$$B(\lambda, \lambda') = C(\lambda, \lambda')\eta_1^*(\lambda)K_1 \frac{1}{1-\varkappa_{11}} f_1(\lambda'). \quad (24)$$

For two-component solutions we obtain:

$$B(\lambda, \lambda') = C(\lambda, \lambda') \left\{ \frac{1}{1-\varkappa_{11}} \eta_1'(\lambda)f_1(\lambda') + \left[\frac{1}{1-\varkappa_{22}} \eta_2'(\lambda) + \varkappa_{12}(1+\varkappa_{22})\eta_1'(\lambda) \right] f_2(\lambda') \right\}.$$

$$(25)$$

And for three-component solutions

$$B(\lambda, \lambda') = C(\lambda, \lambda')\left\{\frac{1}{1-\varkappa_{11}}\eta_1'(\lambda)f_1(\lambda') + \left[\frac{1}{1-\varkappa_{22}}\eta_2'(\lambda) + \varkappa_{12}(1+\varkappa_{22})\eta_1'(\lambda)\right]f_2(\lambda') + \right.$$

$$\left. + \left[\frac{1}{1-\varkappa_{33}}\eta_3'(\lambda) + \varkappa_{23}(1+\varkappa_{22}+\varkappa_{33})\eta_2'(\lambda) + (\varkappa_{13}+\varkappa_{13}\varkappa_{33}+\varkappa_{12}\varkappa_{23}+\varkappa_{11}\varkappa_{13})\eta_1'(\lambda)\right]f_3(\lambda')\right\}.$$

(26)

This equation is identical with those published previously [12].

Substituting Eq. (22) into Eq. (16) we obtain the following expressions for the $\varkappa_{ij}$'s for one-, two- and three-component solutions:

$$\varkappa_{11} = K_1 R_{11},$$

$$\varkappa_{12} = K_2 R_{12} + K_{12}K_2 R_{11},$$

$$\varkappa_{13} = K_3 R_{13} + K_{13}K_3 R_{11} + K_{12}K_{13}K_3 R_{11} + K_{23}K_3 R_{12},$$

$$\varkappa_{22} = K_2 R_{22} \tag{27}$$

$$\varkappa_{23} = K_3 R_{23} + K_{23}K_3 R_{22}$$

$$\varkappa_{33} = K_3 R_{33}$$

where

$$R_{ij} = \int\limits_0^\infty \frac{k_j(\lambda'')}{k(\lambda'')}\eta_j^*(\lambda'')f_i(\lambda'')M(\lambda'')\,d\lambda''. \tag{28}$$

As seen from Eqs. (23)—(28) to the calculation of $B(\lambda, \lambda')$ values for concrete solutions, apart from the absorption-, the emission-, and the absolute quantum yield spectrum of each component, is is necessary to know the yield values K_i and K_{ij}. These yields can be computed from the expressions obtained for the non-radiative excitation energy transfer in multi-component solutions. To this problem, however, a separate paper will be devoted [14].

We should emphasize that Eq. (26) was supported by our previous experimental data [12]. The investigations were carried out on two series of three-component solutions with a constant concentration of the first and third component varying the concentration of the second component. Yields K_i and K_{ij} were computed from the expressions obtained by generalizing the non-radiative excitation energy transfer theory of BOJARSKI and DOMSTA [15] for the multi-component case. For both solution series the agreement between Eq. (26) and the experimental data was satisfactory.

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ПЕРЕДАЧА ЭНЕРГИИ ВОЗБУЖДЕНИЯ В МНОГОКОМПОНЕНТНЫХ ЛЮМИНЕСЦЕНТНЫХ РАСТВОРАХ

И. Кечкемети и Й. Кушба

Основаясь на работах Будо и Кечкемети представлена общая формула, описывающая смещение спектров флуоресценции, как функция эмиссионного и абсорбционного спектров и квантового выхода каждого из составляющих компонентов. Приняты во внимание как излучательные, так и безызлучательные передачи энергии возбуждения. Представленное уравнение рассмотрено для одно-, двух- и трехкомпонентных растворов.