

Multistep reversible excitation transfer in a multicomponent rigid solution: II. Modeling the dynamics of radiationless transfer as a time-resolved Markov chain

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Abstract

To determine the effect of nonradiative excitation energy transfer on the fluorescence of a rigid multicomponent solution, a new analytical method was developed by treating this transfer as a time-resolved Markov chain (TRMC). In the TRMC approach, we assume that the Markov chain under consideration is governed by bivariate joint probability mass-density functions. One of the random variables is discrete and represents the state number to which the process passes at a given step, while the other random variable is continuous and determines the moment in time at which this transition occurs. In general, the time distributions of this second variable can be arbitrary, continuous or discrete, and not just exponential, as required by the method known as continuous time Markov chains (CTMC). The correctness of the TRMC method is confirmed by the fact that the time courses of fluorescence intensities calculated by this method agree with those calculated using ordinary analytical methods. In the section on calculating the quantum yields of individual components, the suitability of a method known as discrete time Markov chains (DTMC) was found. However, we argue that the DTMC method does not refer to time and propose to rename it as time-unspecified Markov chain (TUMC). The results generated by TRMC, when integrated over time, become equivalent to those generated by TUMC. The fluorescence cases of binary and ternary solutions are discussed in detail.

Abbreviations

CTMC	continuous time Markov chain	NET	nonradiative excitation transfer
DTMC	discrete time Markov chain	RNET	reversible nonradiative energy transfer
FRET	Förster resonance energy transfer	SPDF	subnormalized probability density function
MCS	multicomponent solution	TRMC	time-resolved Markov chain
MEE	molecular electronic excitation	TUMC	time-unspecified Markov chain

Symbols and notation

Latin letters

a_{ij}	distance of the closest approach of the i th and j th component molecules. Eqs. (13), (36)
c_i	concentration of the i th component molecules. Eq. (13)
$E(t)$	SPDF vector of effective fluorescence. Eq. (131)
$\mathcal{F}_i^{(1)}(t)$	cumulative distribution function of one-step events on i th component molecules. Eq. (18)
$f(x)$	special function. Eq. (46)
$g(\gamma, \tau, t)$	auxiliary function. Eq. (41)
$g_i(t)$	auxiliary function. Eq. (165)
h	time segment, Eq. (49)
$h_i(t)$	auxiliary function. Eq. (165)
I_n	identity matrix of dimension $n \times n$. Eq. (110)
J	state number random variable. Sect. 3.3
$k_{ij}(r)$	bimolecular transfer rate. Eqs. (13), (35)
$\mathbb{K}_{ij}(t)$	distance-averaged transfer rate. Eqs. (13), (36), (38)
k_r	matrix of radiative rate constants. Eq. (11)
k_{nr}	matrix of nonradiative rate constants. Eq. (12)
m	the number of terminating states taken into account. Sect. 3.2

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n	the number of components in the MCS under consideration. Sect. 1.2
N	fundamental matrix of the matrix $P^{(1)}$. Eq. (113)
$\hat{N}(s)$	fundamental matrix of the matrix $\hat{P}^{(1)}(s)$. Eq. (91)
$O_{m \times n}$	zero matrix of dimension $m \times n$. Eq. (63)
P	transition probability matrix. Eq. (101)
$P^{(1)}$	one-step transition probability matrix. Eq. (63)
$P^{(\mu)}$	μ -step transition probability matrix. Eq. (66)
$\mathbb{P}(t)$	transition SPDF matrix. Eq. (70)
$\mathbb{P}^{(1)}(t)$	one-step transition SPDF matrix. Eqs. (50), (59)
$\mathbb{P}^{(\mu)}(t)$	μ -step transition SPDF matrix. Eqs. (67), (69)
$\mathcal{P}(t)$	residence probability matrix. Eq. (122)
$\mathcal{P}^{(1)}(t)$	one-step residence probability matrix. Eq. (15)
$R_i^{(1)}(t)$	marginal distribution of the random variable T in the state i . Eq. (53)
R_{0ij}	Förster radius for NET from i th component molecules to j th component molecules. Eq. (35)
s	Laplace variable. Eq. (72)
\mathcal{S}	state space. Sect. 3.3
t	time. Eq. (1)
t_μ	moment of the beginning of step numbered μ . Eq. (51)
T	time random variable. Subsection 3.3
\mathcal{T}	time space. Subsection 3.3
$W(t)$	auxiliary vector. Eq. (136)
$x_i(s)$	NET parameter. Eq. (78)

Greek letters

γ_{ij}	reduced concentration for NET from i th to j th component. Eq. (37)
Γ_i	sum of reduced concentrations for NET from the i th component. Eq. (40)
ζ	probability matrix of internal conversion, Eq. (105)
$\zeta^{(1)}$	probability matrix of one-step internal conversion. Eq. (33)
$Z^{(1)}(t)$	SPDF matrix of one-step internal conversion. Eq.(27), (44)
θ	matrix of numbers of MEE transfers. Eq. (104)
$\theta^{(1)}$	probability matrix of one-step NET. Eqs. (31), (63)
$\Theta(t)$	matrix of intensities of MEE transfer. Eq. (95)
$\Theta^{(1)}(t)$	SPDF matrix of one-step NET. Eqs. (23), (59)
μ	index of a stochastic process, step number, step number. Eq. (4)
\mathcal{M}	index set of a stochastic process. Eq. (4)
$\rho_i^{(1)}(t)$	PDF of one-step deexcitation of the i th component molecules. Eq. (19)
τ_0	matrix of fluorescence lifetimes at very low concentrations. Eq. (7)
τ_r	matrix of radiative lifetimes. Eq. (120)
ϕ	probability matrix of photon emission. Eq. (2)
ϕ_0	matrix of absolute quantum yields. Eq. (8)
$\phi^{(1)}$	probability matrix of one-step photon emission. Eq. (32)
$\Phi(t)$	SPDF matrix of photon emission. Eq. (1)
$\Phi^{(1)}(t)$	SPDF matrix of one-step photon emission. Eq. (25)
ψ	probability matrix of deexcitation. Eqs. (104), (112)
$\psi^{(1)}$	probability matrix of one-step deexcitation. Eq. (63), (64)
$\Psi(t)$	SPDF matrix of deexcitation. Eq. (95), (97)
$\Psi^{(1)}(t)$	SPDF matrix of one-step deexcitation. Eq. (59), (60)

1. Introduction

The phenomenon of non-radiative excitation transfer (NET) between fluorescent particles being at sufficiently small distances from each other has been studied for more than 100 years. The earliest works related to this issue concerned collisional transfer in gases [1-4]. This type of transfer occurs in systems where momentary direct contact of molecules with each other is possible. Later, as a result of the work of Förster [5,6] and Dexter [7], fluorescence studies of molecular systems in which the NET processes take place at a distance were strongly developed. Direct contact between the molecules involved in the energy transfer is not necessary in such systems. This type of NET allows to describe the properties of fluorescence emitted by rigid systems, but to some extent also by liquid systems. The condition for the appearance of the mechanism of energy transfer at a distance is a greater or lesser overlap of the emission spectra of the donor and absorption of the acceptor of the excitation energy. This transfer can occur not only between different fluorescent molecules, but also between different fluorescent chromophore groups located on the same macromolecule [8,9].

In this work, in order to shorten our considerations, we will limit ourselves to describing the fluorescence properties of rigid solutions of various types of single-chromophore molecules. For the same reasons, in our considerations we will omit single-component solutions as relatively simple, the properties of which are easily described from the expressions obtained for binary solutions. We will assume that the solvent used is non-fluorescent, and that each of the solute types of fluorescent molecules is a separate component of the solution.

1.1 *The state of NET description in multicomponent solutions to date*

Most work on the theoretical description of the fluorescence of systems containing more than one component was devoted to two-component systems. The initial work dealt with the situation when only one component called the excitation energy donor was directly excited, and then the excitation energy could be radiationlessly transferred to the second component called the excitation energy acceptor. For such conditions, the quantum yield and fluorescence decay function of the donor were calculated, assuming a one-step transfer of molecular excitation energy (MEE) to the acceptor. For dipole-dipole interaction, the work of Förster [6] is of primary importance here, and for exchange interaction the work of Inokuti and Hirayama [10]. The effect of MEE migration in the donor system on these quantities was considered in [11] and [12]. The effect of back transfer, that is, the additional transfer of MEE from the acceptor to the donor, on fluorescence yield was considered in [13]. In non-viscous solutions, the presence of material diffusion further increases the intensity of radiationless MEE transfer between molecules. The effect of diffusion on the decay of donor fluorescence was considered in the works [14] and [15]. The effect of diffusion and migration in the donor system on the fluorescence yield of the donor was considered in the work [16], and the effect of diffusion and back transfer on the decay of the fluorescence intensity of the donor and acceptor was discussed in the work [17]. Consideration of the effect of correlation between the successive

NETs was undertaken in the works [18-21]. It should be noted that if back transfer is included in the description of the fluorescence of a binary system, such terms as excitation energy donor and/or excitation energy acceptor become unclear and thus of little use. In such a case, it is better to number the individual components of the system and relate the theoretical results obtained to the components with specific numbers. This problem becomes especially important for systems where the number of components is greater than two.

In the first works on the description of the fluorescence intensity of ternary solutions, it was assumed that the fluorescence efficiencies of individual components as well as the MEE transfer efficiencies between components were parameters to be determined by matching the postulated theoretical expressions with experimental data [22,23]. To reduce the number of parameters determined in this way, consideration was limited to cases where NET between components is unidirectional and no back transfer is possible. In the case of multicomponent systems, however, such a way of determining the values of emission and transfer parameters leads to an ill-conditioned system of equations. The papers [24-26] show how the values of these parameters can be determined from independent measurements and using expressions obtained from extending to ternary systems the method developed in [11]. Considerations of MEE transfer in binary and ternary systems were also given in [27-29] when discussing the use of these systems as active substances in dye lasers. An algorithm for decomposing the fluorescence spectrum of a ternary mixture assuming linear Stern-Volmer extinction kinetics is given in [30].

So far, attempts to describe the effect of NET on the fluorescence properties of multi-component solutions (MCS), that is, solutions containing any number of different fluorescent components, have been made in two papers. In [31], expressions describing the quantum yields of the individual components of a multicomponent solution adequate for the situation when in each pair of solution components, NET takes place in only one direction and has a hopping character. Expressions describing, under analogous conditions, both the quantum yields and fluorescence decay of the individual components taking into account MEE back-transfer were obtained in [32].

1.2 *Aim of the study. Basic parameters describing the effect of NET on MCS fluorescence*

In this work, as in [33], the object of our consideration is the fluorescence properties of MCS containing n different fluorophores dissolved in an optically inactive solvent. We assume that the individual fluorophores do not react with each other, and that they all exhibit single-exponential fluorescence decays at low concentrations. Furthermore, we assume that in the described system the effect of material diffusion on NET efficiency can be neglected, and that individual fluorophores of MCS do not emit delayed fluorescence and/or phosphorescence. From the point of view of the properties of the fluorescence emitted by MCS, the processes of excitation energy transfer between the individual components are of fundamental importance. Radiative transfer processes were discussed in detail in [33], while the purpose of this work is to discuss the effect of radiationless transfer on the temporal distribution of fluorescence emitted by individual solution components. In [33], it was

shown that in the latter aspect the quadratic, $n \times n$ matrix $\Phi(t)$ is important

$$\Phi(t) = \left[\Phi_{ij}(t) \right]_{n \times n} \quad (1)$$

The individual elements $\Phi_{ij}(t)$ of this matrix describe the probability density distributions of the emission of a light quantum by the j th component molecule at time t , assuming that at $t = 0$ the excitation light generated the excited state of the i th component molecule. The $\Phi(t)$ matrix is therefore fundamental for describing the time dependence of the intensity of the observed fluorescence after pulsed excitation. Note that the row number of the $\Phi(t)$ matrix here specifies the number of the component to which MEE is delivered, and the column number specifies the number of the component whose fluorescence is observed.

To describe the intensity of fluorescence observed after excitation with light of constant intensity, it is sufficient to use the $n \times n$ element ϕ matrix

$$\phi = \left[\phi_{ij} \right]_{n \times n} \quad (2)$$

whose elements ϕ_{ij} are the probabilities of emitting a quantum of light by the j th component molecule if the excitation light generated the excited state of the i th component molecule. From the definitions of ϕ_{ij} and $\Phi_{ij}(t)$, it follows that the ϕ matrix can be obtained by integrating the $\Phi(t)$ matrix over time from zero to infinity

$$\phi = \int_0^{\infty} \Phi(t) dt \quad (3)$$

It is worth noting that the ϕ and $\Phi(t)$ matrices refer to the probabilities of only those MEE deactivation processes that lead to light quantum emission, and do not refer, for example, to the probabilities of radiationless deactivation processes. Therefore, in general, the elements of the ϕ matrix do not satisfy the normalization condition, and usually there is $\sum_{j=1}^n \phi_{ij} < 1$. The main part of the paper is devoted to a discussing of how to find the elements of the $\Phi(t)$ and/or ϕ matrix that characterize the fluorescence of rigid MCS.

1.3 NET in MCS as a multi-step process

In determining the values of the elements of the ϕ and $\Phi(t)$ matrices, we will assume that the time evolution of a MEE in MCS is multistep. Each of these steps begins when an MEE localizes to a given fluorescent molecule and continues until that MEE is transferred to another fluorescent molecule, or is converted to other types of energy. In our discussion, we will numerate the successive steps of a given MEE using the index μ , which we will call step number. We will assume that the set \mathcal{M} of values of μ is countable and discrete

$$\mathcal{M} = \{\mu \in \mathbb{N}\} = \{1, 2, \dots\} \quad (4)$$

We assign $\mu = 1$ to the step that begins with the excitation of the molecule directly with an external light beam, we assign $\mu = 2$ to the step in which MEE was delivered to the molecule as a

result of one transfer from the directly excited molecule, we assign $\mu = 3$ to the step in which MEE was delivered to the molecule as a result of two transfers from the directly excited molecule, and so on. We will also assume that the processes for MEE transfer and conversion are homogeneous, that is, their probabilities are independent of the current value of the μ step number. Under such conditions, the multistep MEE transfer kinetics are a simple composite of repeating the same single-step kinetics.

2. One-step NET kinetics in MCS

2.1 Rates of basic processes occurring in MCS after optical excitation

Absorption of photons from the excitation beam in the MCS under study causes the appearance of excited molecules in the excitation region. Our considerations will apply to situations in which the number of excited molecules is small compared to the total number of molecules in the illuminated part of the solution. This condition is usually met when using conventional excitation light sources. If a laser is used, its intensity should be weakened accordingly. The excitation energy remains on a given molecule for a shorter or longer period of time, but never permanently. This is because for each excited molecule there are a certain number of de-excitation pathways [34]. For simplicity, we will consider only three of them: fluorescence emission, internal conversion, and energy transfer to other molecules in the system.

2.1.1 Case of isolated fluorescent molecules

The simplest description of MCS fluorescence is for the case when the concentrations of components are small enough that MEE transfer between components can be neglected. Then the off-diagonal elements of the $\Phi(t)$ matrix become zeros, so that the matrix reduces to the diagonal matrix $\Phi_0(t)$

$$\Phi_0(t) = \text{diag}(\Phi_{01}(t), \dots, \Phi_{0n}(t)) \quad (5)$$

In our considerations, we will assume that the functions $\Phi_{0i}(t)$ decrease exponentially with time and have the form

$$\Phi_{0i}(t) = k_{ri} \exp(-t/\tau_{0i}) \quad (6)$$

where k_{ri} is the rate constant for fluorescence emission, and τ_{0i} is the average fluorescence lifetime of the i th component molecules. Analogous to (5), the τ_{0i} times can be treated as elements of the τ_0 matrix

$$\tau_0 = \text{diag}(\tau_{01}, \dots, \tau_{0n}) \quad (7)$$

Similarly, at low component concentrations, the quantum yield matrix ϕ given by equation (2) can be replaced by a diagonal matrix ϕ_0 of the form

$$\phi_0 = \text{diag}(\phi_{01}, \dots, \phi_{0n}) \quad (8)$$

where ϕ_{0i} is the absolute fluorescence quantum yield of the i th component. If we assume that for the molecules of the i th component, the rate constant for internal conversion is k_{ni} , then the

magnitudes τ_{0i} and ϕ_{0i} depend on the rate constants k_{ri} and k_{nri} according to the equations

$$\tau_{0i} = \frac{1}{k_{ri} + k_{nri}} \quad (9)$$

$$\phi_{0i} = \frac{k_{ri}}{k_{ri} + k_{nri}} \quad (10)$$

The quantities τ_{0i} and ϕ_{0i} can be determined experimentally by measuring the fluorescence of each MCS component separately. Then, the diagonal matrices $k_r = \text{diag}(k_{r1}, \dots, k_{rn})$ and $k_{nr} = \text{diag}(k_{nr1}, \dots, k_{nrn})$ containing the rate constants k_{ri} and k_{nri} , respectively, can be calculated using the expressions

$$k_r = \phi_0 \tau_0^{-1} \quad (11)$$

$$k_{nr} = (I_n - \phi_0) \tau_0^{-1} = (I_n - \phi_0) \phi_0^{-1} k_r \quad (12)$$

where I_n is the identity matrix of dimension $n \times n$.

2.1.2 Case of mutually interacting fluorescent molecules

If the distance between the fluorescent molecules of the system under consideration is not very large, then their mutual interaction becomes important. Of primary importance here is the dipole-dipole interaction and the exchange interaction. As a result of this interaction, NET from one molecule to another becomes possible [34]. For now, we will not go into detail about the nature of the interaction of fluorescent molecules in the MCS under consideration, and we will only assume that in our system, the interaction of molecules can lead to NET defined by rate constants $k_{ij}(r)$, which depend on the type of interacting molecules and on the distance r between them. Rate $k_{ij}(r)$ describes homotransfer when $j = i$, and heterotransfer when $j \neq i$.

Finding expressions to describe macroscopically observed fluorescence intensity decays and/or observed fluorescence yields, by directly using rates $k_{ij}(r)$ is difficult. Therefore, many authors use rates that result from averaging bimolecular rates $k_{ij}(r)$ over all possible distances between interacting molecules. Such averaged rates (sometimes called second order rates) can be calculated from the expression [6,35,36]

$$\bar{k}_{ij}(t) = 4\pi c_j \int_{a_{ij}}^{\infty} r^2 k_{ij}(r) \exp[-k_{ij}(r)t] dr \quad (13)$$

where c_j is the concentration of the component j , and a_{ij} is the distance of the closest approach of the i th and j th component molecules. In considering the effect of NET on MCS fluorescence, it is also convenient to use the $\bar{k}(t)$ matrix formed from rates $\bar{k}_{ij}(t)$

$$\bar{k}(t) = [\bar{k}_{ij}(t)]_{n \times n} \quad (14)$$

The technique of using such time-dependent rate coefficients is widely discussed in the paper [37]. The second order rates defined by equation (13) describe well the energy transfer in systems where no migration of excitation energy occurs between molecules of the same component. However, if in the considered

system the excitation energy migration occurs, then the rates (13) become insufficient, because then the process of energy transfer from component i to component j becomes multistep, and then in the process of transfer more or less important become correlations of positions of interacting molecules. Rates $\bar{k}_{ij}(t)$ do not take into account these correlations, hence expressions obtained using them for systems with migration must be considered approximate. A model that uses rates described by equation (13) is called a hopping model.

The model taking into account correlations of the positions of active molecules in the description of the transfer of excitation energy was introduced in [18] and developed in [19-21]. This model, referred to by the acronym SCDM (selfconsistent diagrammatic model), is thus considered by the authors to be inherently superior to the hopping model. This seems to be confirmed also by comparisons of the results predicted by this model with experimental data [38-41]. SCDM results generally describe the experimental data better than hopping model results. However, these works also show that also the results generated by the hopping model satisfactorily describe the experimental data, but mostly under the assumption of an additional excitation energy quenching mechanism caused by assuming a non-zero probability of its degradation during the transfer process. In addition, the results of the SCDM model are not exact but are the results of the so-called three-body approximation, the accuracy of which does not seem to be sufficiently studied. The disadvantage of the SCDM model is that it is extremely complicated and the necessary calculations are tedious. Currently, there is no extension of the SCDM to a multicomponent system. For these reasons, in this paper, the radiationless transfer of excitation energy between the individual components will be described only in the framework of the hopping model. To shorten and simplify the work, in our considerations we will not take into account the possibility of the aforementioned energy quenching accompanying the energy transfer process.

2.2 Probability density functions and probabilities characterizing one-step deexcitation

Suppose that a number of molecules of component i were excited at time $t = 0$. In general, the process of deexcitation of these molecules should be considered as a multi-step process during which the energy of excitation, before the final conversion to photon or heat, is repeatedly transferred both among molecules of component i and molecules belonging to other components of the system. Let us now consider only the one-step deexcitation processes that immediately follow the moment of excitation. Of importance here are the distance-averaged $\mathcal{P}_i^{(1)}(t)$ probabilities of the excitation surviving on the i th component molecule from the moment of excitation at $t = 0$ to any time $t \geq 0$. These probabilities can be understood as elements of the diagonal matrix $\mathcal{P}^{(1)}(t)$

$$\mathcal{P}^{(1)}(t) = \text{diag}(\mathcal{P}_1^{(1)}(t), \dots, \mathcal{P}_n^{(1)}(t)) \quad (15)$$

Each probability $\mathcal{P}_i^{(1)}(t)$ is described here by a differential equation

$$\frac{d\mathcal{P}_i^{(1)}(t)}{dt} = -\mathcal{P}_i^{(1)}(t) \left(\sum_{j=1}^n \mathbb{k}_{ij}(t) + k_{ri} + k_{nr i} \right) \quad (16)$$

The solution of Eq. (16) with initial condition $\mathcal{P}_i^{(1)}(0) = 1$ is

$$\mathcal{P}_i^{(1)}(t) = \exp \left(- \int_0^t \sum_{j=1}^n \mathbb{k}_{ij}(t') dt' - (k_{ri} + k_{nr i}) t \right) \quad (17)$$

In addition to probability $\mathcal{P}_i^{(1)}(t)$, the probability density $\rho_i^{(1)}(t)$ of occurrence of any of the events that deexcite the i th component molecule in one step is important for the description of NET in MCS. To determine $\rho_i^{(1)}(t)$ let us first note that using expression (17) we can determine the cumulative distribution function $\mathcal{F}_i^{(1)}(t)$ of such events

$$\mathcal{F}_i^{(1)}(t) \equiv 1 - \mathcal{P}_i^{(1)}(t) \quad (18)$$

The requested function $\rho_i^{(1)}(t)$ is the first derivative of this distribution function, by which, after considering (17) and (18), we obtain

$$\rho_i^{(1)}(t) = \mathcal{P}_i^{(1)}(t) \left(\sum_{j=1}^n \mathbb{k}_{ij}(t) + k_{ri} + k_{nr i} \right) \quad (19)$$

It is easy to see that each of the $\rho_i^{(1)}(t)$ functions have the properties of the probability density function, and as such satisfies the normalization condition

$$\int_0^{\infty} \rho_i^{(1)}(t) dt = 1 \quad (20)$$

To better understand the properties of $\rho_i^{(1)}(t)$, let us rewrite Eq. (19) in the form

$$\rho_i^{(1)}(t) = \sum_{j=1}^n \Theta_{ij}^{(1)}(t) + \Phi_i^{(1)}(t) + Z_i^{(1)}(t) \quad (21)$$

In this equation, we can understand the expressions of $\Theta_{ij}^{(1)}(t)$ as elements of the square matrix $\Theta^{(1)}(t)$

$$\Theta^{(1)}(t) = \left[\Theta_{ij}^{(1)}(t) \right]_{n \times n} \quad (22)$$

The physical meaning function $\Theta_{ij}^{(1)}(t)$ is that the product $\Theta_{ij}^{(1)}(t) dt$ is equal to the probability of one-step NET from the i th component molecule to the j th component molecule in the interval $(t, t + dt)$. $\Theta_{ij}^{(1)}(t)$ elements are subnormalized probability density functions (SPDFs) describing the time evolution of the distance-averaged probability for NET between molecules of the same type ($i = j$) and different types ($i \neq j$). Justification for the term "subnormalized" used here can be found in the form of equation (31), where we always have $\theta_{ij}^{(1)} \leq 1$. Based on (19) and (21)), we can write

$$\Theta_{ij}^{(1)}(t) = \mathcal{P}_i^{(1)}(t) \mathbb{k}_{ij}(t) \quad (23)$$

In matrix notation, equation (23) takes the form of

$$\Theta^{(1)}(t) = \mathcal{P}^{(1)}(t) \mathbb{k}(t) \quad (24)$$

where the $\mathcal{P}^{(1)}(t)$ matrix is defined by equation (15), and the $\mathbb{k}(t)$ matrix is given by equations (13) and (14). In Eq. (21),

functions $\Phi_i^{(1)}(t)$ are SPDFs describing the time evolution of the average probability for spontaneous conversion of the excitation energy, actually residing on the i th kind molecule, to photon. The physical meaning of function $\Phi_i^{(1)}(t)$ is that the product $\Phi_i^{(1)}(t) dt$ is equal to the average probability of quantum of light emission from the i th component molecule in the interval $(t, t + dt)$, assuming that it was excited at time $t = 0$. We will consider these functions as elements of the diagonal matrix $\Phi^{(1)}(t)$

$$\Phi^{(1)}(t) = \text{diag} \left(\Phi_1^{(1)}(t), \dots, \Phi_n^{(1)}(t) \right) \quad (25)$$

whereby, based on (19) and (21), we assume that

$$\Phi^{(1)}(t) = \mathcal{P}^{(1)}(t) k_r \quad (26)$$

where the k_r matrix is defined by Eq. (11). And finally, the functions $Z_i^{(1)}(t)$ in equation (21) are SPDFs describing the time evolution of the average probability for the excitation energy internal conversion into heat. The physical meaning of the function $Z_i^{(1)}(t)$ is that the product $Z_i^{(1)}(t) dt$ is equal to the average probability of degradation of MEE to heat on the i th component in the time interval $(t, t + dt)$, assuming that it was excited at time $t = 0$. By analogy with (25) and (26), we will assume that

$$Z^{(1)}(t) = \text{diag} \left(Z_1^{(1)}(t), \dots, Z_n^{(1)}(t) \right) \quad (27)$$

$$Z^{(1)}(t) = \mathcal{P}^{(1)}(t) k_{nr} \quad (28)$$

where the k_{nr} matrix is defined by Eq. (12). After taking into account (12) and (26), one can also write

$$Z^{(1)}(t) = \Phi^{(1)}(t) (I_n - \phi_0)^{-1} \quad (29)$$

Note that it follows from Eqs. (20) and (21) that the functions $\Theta_{ij}^{(1)}(t)$, $\Phi_i^{(1)}(t)$, and $Z_i^{(1)}(t)$ are normalized in the sense given below

$$\int_0^{\infty} \left(\sum_{j=1}^n \Theta_{ij}^{(1)}(t) + \Phi_i^{(1)}(t) + Z_i^{(1)}(t) \right) dt = 1 \quad (30)$$

2.2.1 One-step NET kinetics under steady-state conditions

Under steady-state conditions, both the intensity of the excitation light and the intensity of the fluorescence emitted by the MCS is constant over time. Then the processes of excitation energy transfer and conversion cease to depend directly on shape of the time courses of $\Theta_{ij}^{(1)}(t)$, $\Phi_i^{(1)}(t)$, and $Z_i^{(1)}(t)$ functions contained in the $\Theta^{(1)}(t)$, $\Phi^{(1)}(t)$, and $Z^{(1)}(t)$ matrices, respectively, but depend on $\theta_{ij}^{(1)}$, $\phi_i^{(1)}$, and $\zeta_i^{(1)}$ probabilities which are the integrals of these functions taken over time from zero to infinity. These probabilities refer to events that may occur after the arrival of MEE on the component i molecule. They can be represented as matrices $\theta^{(1)}$, $\phi^{(1)}$, and $\zeta^{(1)}$ satisfying the conditions

$$\theta^{(1)} = \left[\theta_{ij}^{(1)} \right]_{n \times n} = \int_0^{\infty} \Theta^{(1)}(t) dt \quad (31)$$

$$\phi^{(1)} = \text{diag}(\phi_1^{(1)}, \dots, \phi_n^{(1)}) = \int_0^\infty \Phi^{(1)}(t) dt \quad (32)$$

$$\begin{aligned} \zeta^{(1)} &= \text{diag}(\zeta_1^{(1)}, \dots, \zeta_n^{(1)}) = \int_0^\infty Z^{(1)}(t) dt \\ &= \phi^{(1)} (I_n - \phi_0) \phi_0^{-1} \end{aligned} \quad (33)$$

where $\theta_{ij}^{(1)}$ denotes the probability of transferring MEE to the j th component molecule, $\phi_i^{(1)}$ denotes the probability of emitting MEE in the form of photon, and $\zeta_i^{(1)}$ denotes the probability of converting MEE into heat. It follows from Eqs. (30)-(33) that

$$\sum_{j=1}^n \theta_{ij}^{(1)} + \phi_i^{(1)} + \zeta_i^{(1)} = 1 \quad (34)$$

In the next subsection we find expressions to calculate the values of $\theta_{ij}^{(1)}(t)$, $\Phi_i^{(1)}(t)$, $Z_i^{(1)}(t)$, $\theta_{ij}^{(1)}$, $\phi_i^{(1)}$, and $\zeta_i^{(1)}$ parameters in the presence of Förster resonance energy transfer (FRET).

2.2.2 Averaged transfer rates in the case of FRET

If the NET process in the considered MCS has a dipole-dipole character, then the rate $k_{ij}(r)$ in Eq. (13) can be described by the equation [42]

$$k_{ij}(r) = \frac{1}{\tau_{0i}} \left(\frac{R_{0ij}}{r} \right)^6 \quad (35)$$

where r is the distance of interacting molecules, and R_{0ij} is the Förster radius [34]. Insertion of (35) into (13) yields

$$\mathbb{k}_{ij}^{(1)}(t) = \frac{\gamma_{ij}}{\sqrt{\tau_{0i} t}} \text{erf} \left[\frac{R_{0ij}^3}{a_{ij}^3} \sqrt{\frac{t}{\tau_{0i}}} \right] \quad (36)$$

where

$$\gamma_{ij} = \frac{2}{3} \pi^{3/2} R_{0ij}^3 c_j \quad (37)$$

Expression (36) simplifies significantly if one assumes that the dimensions of the interacting molecules are negligibly small, or alternatively, that their minimum mutual distance a_{ij} is equal to zero. Then we obtain

$$\mathbb{k}_{ij}^{(1)}(t) = \frac{\gamma_{ij}}{\sqrt{\tau_{0i} t}} \quad (38)$$

Equation (38) corresponds to Eq. (8.3) in [43]. Because of its uncomplicated structure and good agreement with experimental data the expression (38) was in its more or less explicit form used by many authors [6,11,17,32,35,36]. In the present work, we will also use this expression. Inserting (38) into (17) leads to

$$\mathcal{P}_i^{(1)}(t) = g(\Gamma_i, \tau_{0i}, t) \quad (39)$$

where

$$\Gamma_i = \sum_{j=1}^n \gamma_{ij} \quad (40)$$

and

$$g(\Gamma, \tau, t) = \exp \left(-2\Gamma \sqrt{\frac{t}{\tau} - \frac{t}{\tau}} \right) \quad (41)$$

After inserting (38) and (39) into (23), we find $\theta_{ij}^{(1)}(t)$.

$$\theta_{ij}^{(1)}(t) = \frac{\gamma_{ij}}{\sqrt{\tau_{0i} t}} g(\Gamma_i, \tau_{0i}, t) \quad (42)$$

After inserting (39) sequentially into (26) and (28), we find $\Phi_i^{(1)}(t)$ and $Z_i^{(1)}(t)$.

$$\Phi_i^{(1)}(t) = \frac{\phi_{0i}}{\tau_{0i}} g(\Gamma_i, \tau_{0i}, t) \quad (43)$$

$$Z_i^{(1)}(t) = \frac{1 - \phi_{0i}}{\tau_{0i}} g(\Gamma_i, \tau_{0i}, t) \quad (44)$$

Averaged over distances, the probability $\theta_{ij}^{(1)}$ of a one-step transfer can be calculated from (31), (23), (38), (39), and (41)

$$\theta_{ij}^{(1)} = \frac{\gamma_{ij}}{\Gamma_i} f(\Gamma_i) \quad (45)$$

where

$$f(x) = \sqrt{\pi} x \exp(x^2) [1 - \text{erf}(x)] \quad (46)$$

Distance averaged probability of one-step photon emission can be calculated from (32), (26), (39), and (41). This yields

$$\phi_i^{(1)} = \phi_{0i} [1 - f(\Gamma_i)] \quad (47)$$

Eq. (47) have been first obtained by Förster [6]. Given $\phi_i^{(1)}$, the distance-averaged probability of one-step excitation conversion into heat, $\zeta_i^{(1)}$, can be calculated from Eq. (33)

$$\zeta_i^{(1)} = \frac{1 - \phi_{0i}}{\phi_{0i}} [1 - f(\Gamma_i)] \quad (48)$$

3. Multistep NET kinetics in MCS. Finding the values of individual elements of matrices $\Phi(t)$ and ϕ

In this section, assuming the hopping mechanism of NET, we will discuss how to find expressions to calculate the values of the elements of the matrices $\Phi(t)$ and ϕ under conditions of multi-stage, forward and reverse energy transfer between all components of the considered MCS.

3.1 Introductory remarks

At the outset, it should be acknowledged that the expressions to calculate the values of the elements of the $\Phi(t)$ and ϕ matrices can be found by slightly modifying (see also Section 4) the method described in the paper [32]. This method amounts to solving an appropriate system of algebraic equations. In this work, however, we will use a simpler, and in our opinion more intuitive, method using the Markov chain technique for the same purpose.

The Markov chain technique is based on the fact that the internal changes of the described system are modeled in such a way that the current state of the chain object wanders among a finite number of possible states, according to the probability distribution functions assigned to each of these states. In the case of MCS, we determine that the Markov chain object is MEE.

The time evolution of MEE takes the form of a chain of individual stages or steps. From equations (42)-(48), it can be seen that, under our conditions, the probabilities of MEE transition between states do not depend on the value of the μ index, which means that the Markov chains describing MEE transfer in MCS are homogeneous. A closer examination of the issues related to Markov chains allows us to suppose that for the description of MCS fluorescence, well-known methods operating in the discrete state space are potentially useful, in particular: 1) a method known as discrete time Markov chains (DTMC), and 2) a method known as continuous time Markov chains (CTMC).

The DTMC method operates with time-independent probabilities of transitions between states, which suggests that it may be appropriate for describing the fluorescence properties of a given MCS only under steady-state conditions, when the probabilities of one-step processes are constant in time. Taking into account the fact that the averaged transition probabilities (45)-(48) remain constant over time, we can claim that the Markov chain formed with these probabilities will be a stationary stochastic process. Unfortunately, the name DTMC is misleading, since time as such does not appear in the DTMC model. Within DTMC, it is customary, without ensuring the necessary accuracy, to assign the term "time" to the values of μ index specified in Eq. (4). However, this index is not time, if only because it does not have the dimension of time. The real time t can possibly be introduced into the DTMC, by assuming the relationship holds

$$t_\mu = \mu h \quad (49)$$

where $h > 0$ is the chosen time segment. Under this assumption, the values of t_μ indicate the moments of time at which the MEE transition from one state to another occurs. However, when a given Markov chain involves a steady state, the t_μ moments have no experimentally determinable counterparts.

Under pulsed MCS fluorescence excitation, the averaged probabilities of one-step processes depend on time, for example, as shown by expressions (42)-(44). In the CTMC method, the probabilities of one-step processes are treated as time-dependent, however, these dependencies must be exponential [44,45], which is not fulfilled in equations (42)-(44). To solve this problem, in this work we introduce a new type of Markov chains, which we call time-resolved Markov chains (TRMC). In a sense, the TRMC method is an extension of the DTMC method to the case where the probabilities of transitions between process states depend on time in any way. In addition, the TRMC method, unlike the CTMC method, allows consideration of excitation energy migration processes among molecules of the same component, whereas under CTMC, transitions within the same state are not allowed [46].

3.2 Kinds of MEE states and transitions in MCS

The time evolution of a single MEE in MCS involves its random wandering among fluorescing molecules, which in each case ends with either the emission of a photon of fluorescence or the conversion of a given MEE to heat. We will call the different stages of this wandering the MEE states. MEE transitions from one state to another occur with a certain probability and occur at random but statistically distributed moments of time.

Thus, we can understand MEE wandering in MCS as a kind of stochastic process governed by two random variables, one of which determines the type of state to which the MEE transitions, and the other determines the moment of time at which this transition occurs. In the case of MCS, we distinguish three types of states that can characterize an MEE:

- a. **States in which the MEE is localized to one of the fluorescent molecules.** We will assume that the number of such states is equal to the number of n fluorescent components present in the system under consideration.
- b. **States in which MEE is immediately converted to a photon.** It seems obvious that the total number of states of this type assigned to a given system cannot be greater than the number n of components. The specific number of such states assumed depends on how much information concerning the dynamics of fluorescence decay we want to acquire. Typically, from our considerations we want to extract information about the time distribution of photons emitted by each individual component, hence we will generally assume that the number of such states is equal to the number n of components in the system.
- c. **States in which MEE is immediately converted to heat.** The total number of states in this group, as in (b), depends not only on the number of components but also on how much information regarding the radiationless deactivation of the excitation we want to obtain. Among the various variants of the organization of this group, it is possible, for example, to represent all radiationless relaxation acts as transitions to one common state.

Note that type (a) MEE states can be produced either by direct excitation with external light or by MEE transitions between type (a) states, while type (b) and (c) states can only be produced by MEE transitions from type (a) states.

Within DTMC terminology, the states described in (a) should be classified as transient states because there is always a non-zero probability of transition from these states to states (b) or (c). The states (b) and (c) act analogously to absorbing states; however, these states cannot be classified strictly as absorbing states due to the fact that once they are reached, the MEE immediately disappears. Therefore, we will classify such states as a new type of states, which we call terminating states. Terminating states cannot be called transient states because MEE is transferred from them to unspecified states that are not elements of the process under consideration. The properties of the terminating state are different from these of the absorbing state in the sense that once the terminating state is reached, the question of the further evolution of the process object becomes meaningless, whereas once the absorbing state is reached, every subsequent event means that the object remains in the same state. In our model of MCS fluorescence, absorbing states do not occur at all, since no objects are experimentally observed whose optical excitation could last indefinitely. The introduction of terminating states makes the mathematical description of MEE transfer processes more relevant to what happens in a given MCS in reality. The achievement of a terminating state means the immediate termination of the course of possible events associated with a given individual act of excitation.

Each change in the state of a given MEE is classified as an event. We will assume that we know the time distributions of these events, described by known time-dependent SPDFs. In

finding expressions describing the elements of the $\Phi(t)$ and ϕ matrices, we will consider only those MEE events that are caused by NET and by spontaneous, emission, and internal conversion processes. These events are

- i. **Nonradiative transfer of the MEE from the i th component molecule to the j th component molecule.** The probability of transferring the excitation energy between these molecules is equal to $\theta_{ij}^{(1)}$ calculated from Eqs. (31) and (45). The SPDFs describing the time distribution of these events after the act of excitation are given by $\Theta_{ij}^{(1)}(t)$ functions defined by Eqs. (23) and (42). As a result of such transfers a given MEE goes from state i to state j . If $j = i$, that is, when the energy transfer occurs between molecules of the same component, then we consider that after the act of transfer the given MEE remains in state i .
- ii. **Spontaneous conversion of the MEE to photon (emission of fluorescence).** The probability for photon emission is given by $\phi_i^{(1)}$ expressed by Eqs. (32) and (47). The SPDFs describing the time distribution of such events after excitation are given by functions $\Phi_i^{(1)}(t)$ expressed by Eqs. (26) and (43).
- iii. **Internal conversion of the MEE to heat (internal de-excitation).** The probability for internal de-excitation is given by $\zeta_i^{(1)}$ expressed by Eqs. (33) and (48). The SPDFs describing the time distribution of such events after excitation are given by functions $Z_i^{(1)}(t)$ expressed by Eqs. (28) and (44).
- iv. **Events that could potentially occur after MEE reaches the terminating state.** Since in the terminating state MEE immediately vanishes, we assume that all SPDFs describing MEE transitions from terminating states are equal to zero. The total number of states characterizing MEE in a given MCS is equal to $n + m$, where n is the number of components and m is the assumed number of terminating states.

3.3 Probability distributions of interstate transitions, Markov property

Given equations (22)-(29), one can conclude that each interstate MEE transition in MCS is governed by the probability distribution of the bivariate random variable (J, T) [47-49]. The random variable J is the number of the state in which the MEE will reside in the next step. It is a discrete variable expressed by j values from the set $\mathcal{S} = \{1, 2, \dots, n + m\}$. The random variable T determines the moments of MEE transition between states. It is a continuous variable expressed by values of t from the set $\mathcal{T} = \mathbb{R}_+^0$. The values of both variables are determined by assuming that at time $t = 0$ MEE is located on one of the component i molecules. Under such conditions, for each state $i \in \mathcal{S}$ we have a separate joint probability mass-density function $\mathbb{P}_{iJT}^{(1)}(j, t)$ having the property that the product of $\mathbb{P}_{iJT}^{(1)}(j, t) dt$ is equal to the transition probability of MEE from state i to state j in the time interval $(t, t + dt)$. The exact form of each of these functions depends on the mechanism adopted for the transfer of

MEE between states, the number of terminating states assumed, and the individual properties of these states. For simplicity of notation, we will write the function $\mathbb{P}_{iJT}^{(1)}(j, t)$ as $\mathbb{P}_{ij}^{(1)}(t)$. For example, if we assign to each component of the solution one terminating state corresponding to photon emission and one terminating state corresponding to the conversion of MEE to heat, then $\mathbb{P}_{ij}^{(1)}(t)$ can be given by the expression

$$\mathbb{P}_{ij}^{(1)}(t) = \begin{cases} \Theta_{ij}^{(1)}(t), & \text{if } (1 \leq j \leq n) \\ \Phi_i^{(1)}(t) \delta_{i, (j-n)}, & \text{if } (n < j \leq 2n) \\ Z_i^{(1)}(t) \delta_{i, (j-2n)}, & \text{if } (2n < j \leq 3n) \\ 0, & \text{if } (n < i \leq n + m \text{ or } t < 0) \end{cases} \text{ and } 1 \leq i \leq n \quad (50)$$

where $\delta_{i,j}$ is the Kronecker delta. We constructed the functions $\mathbb{P}_{ij}^{(1)}(t)$ in such a way that with respect to the random variable J they are probability mass functions, and with respect to the random variable T they are probability density functions. The stochastic process defined in this work as TRMC is a sequence of values of a bivariate random variable (J, T) , which can be written as

$$\{(j_\mu, t_\mu); \mu = 2, 3, \dots\} \quad (51)$$

Here j_μ are the numbers of the states in which the MEE is located at each step of the process, and the values of t_μ determine the moments of transition of the MEE to these states. For step $\mu = 1$, we take $t_1 = 0$, and the value of j_1 specifies the number of the component excited by the external light beam. We can assume that the process (51) is Markovian if, for $j_{\mu+1} \in \mathcal{S}$, $t_{\mu+1} \in \mathcal{T}$, and $\mu \in \mathcal{M}$, there occurs

$$\begin{aligned} & \Pr \left\{ (J_{\mu+1} = j_{\mu+1}, T_{\mu+1} = t_{\mu+1}) \middle| (J_2 = j_2, T_2 = t_2), \right. \\ & \quad \left. (J_3 = j_3, T_3 = t_3), \dots, (J_\mu = j_\mu, T_\mu = t_\mu) \right\} \\ & = \Pr \left\{ (J_{\mu+1} = j_{\mu+1}, T_{\mu+1} = t_{\mu+1}) \middle| (J_\mu = j_\mu, T_\mu = t_\mu) \right\} \end{aligned} \quad (52)$$

for any set of states j_2, \dots, j_μ in \mathcal{S} and any set of times t_2, \dots, t_μ in \mathcal{T} . The denotation \Pr in (52) stands for probability measure. Non-Markovian process, on the other hand, exhibits memory effects, meaning that the future state depends not only on the present state but also on past states and the specific path the process has taken to reach its current state. For TRMC, we assume that the distributions of the random variable (J, T) taken for different values of μ are mutually independent. Therefore, a given TRMC satisfying condition (52) should be qualified as Markovian even if the associated time distributions of the (J, T) variable are not memoryless.

There are two marginal distributions associated with each of the distributions defined by Eq. (50). The marginal distributions of the random variable T are obtained by summing (50) over all values of j . This gives

$$R_i^{(1)}(t) = \sum_{j=1}^{n+m} \mathbb{P}_{ij}^{(1)}(t) = \begin{cases} \rho_i^{(1)}(t), & \text{if } 1 \leq i \leq n \\ 0, & \text{if } n < i \leq n + m \text{ or } t < 0 \end{cases} \quad (53)$$

where $\rho_i^{(1)}(t)$ are defined by Eq. (19). The function $R_i^{(1)}(t)$ represents the temporal probability density distribution of any event in state i . The marginal distributions $P_{ij}^{(1)}$ of the random variable J are obtained by integrating (50) over all values of t

$$P_{ij}^{(1)} = \int_0^{\infty} \mathbb{P}_{ij}^{(1)}(t) dt \quad (54)$$

This gives

$$P_{ij}^{(1)} = \begin{cases} \theta_{ij}^{(1)}, & \text{if } 1 \leq j \leq n \\ \phi_i^{(1)} \delta_{i,(j-n)}, & \text{if } n < j \leq 2n \\ \zeta_i^{(1)} \delta_{i,(j-2n)}, & \text{if } 2n < j \leq 3n \\ 0, & \text{if } n < i \leq n+m \end{cases} \text{ and } 1 \leq i \leq n \quad (55)$$

$P_{ij}^{(1)}$ distributions are univariate discrete probability distributions of the random variable J . As can be seen from equation (54), the $P_{ij}^{(1)}$ distributions describe the summary probabilities of transitions between states without indicating the moments at which these transitions occur. Therefore, we called the stochastic process associated with these distributions a time-unspecified Markov chain (TUMC). Time here ceases to be a random variable, hence TUMC involves only one random variable J . This process can be written as

$$\{j_{\mu}; \mu = 2, 3, \dots\} \quad (56)$$

TUMC is Markovian if it occurs

$$\begin{aligned} & \Pr\left\{(J_{\mu+1} = j_{\mu+1}) | (J_2 = j_2), (J_3 = j_3), \dots, (J_{\mu} = j_{\mu})\right\} \\ &= \Pr\left\{(J_{\mu+1} = j_{\mu+1}) | (J_{\mu} = j_{\mu})\right\} \end{aligned} \quad (57)$$

Because the probability distributions underlying TUMC satisfy relation (54), this process can be applied to steady-state NET analysis. Note that the process referred to here as TUMC is equivalent to the process known as DTMC. However, since we believe DTMC does not refer to time, we propose to rename it TUMC.

3.4 The one-step transition matrices

The basis of the TRMC method is to collect all SPDFs characterizing one-step EEM transitions in a given MCS as elements of a quadratic $(n+m) \times (n+m)$ $\mathbb{P}^{(1)}(t)$ matrix called one-step transition SPDF matrix. We prefer to write these matrices in the so-called canonical form. In this form, the first n rows of the $\mathbb{P}^{(1)}(t)$ matrix refer to transient states. In these states, MEE is localized on the molecule of any of the n components of our system, and the row number assigned to a given state is also the number of that component. For $1 \leq i \leq n$, the elements of row i in the $\mathbb{P}^{(1)}(t)$ matrix are the SPDFs $\theta_{ij}^{(1)}(t)$, $\phi_i^{(1)}(t)$, and $Z_i^{(1)}(t)$. The remaining m rows of the $\mathbb{P}^{(1)}(t)$ matrix refer to states in which MEE immediately ceases to exist. If in a given state, MEE immediately disappears, then upon reaching that state, MEE is no longer able to move to other states. Therefore, we assume that all elements of the $\mathbb{P}^{(1)}(t)$ matrix located in the rows corresponding to such states are zeros. In the fluorescent

systems, states of this type characterize the MEE after its conversion to photon or heat and we classify them as terminating states.

The simplest one-step transition SPDF matrix characterizing MCS can be constructed when the number of solution components is limited to $n = 2$. The steady-state fluorescence of such a system can be analyzed using the six-state Markov chain shown in Fig. 1. In this figure, the red circles correspond to transient states, and the blue circles and gray circles correspond to terminating states.

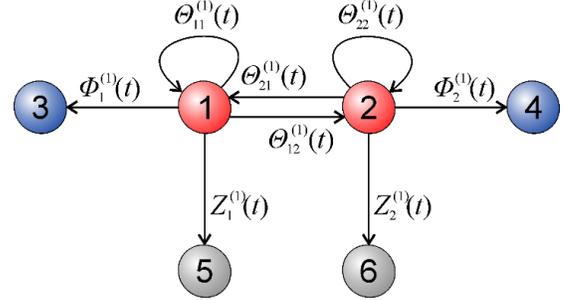


Figure 1. Six-state Markov process diagram showing states, events and their SPDFs in a two-component system. The red circles illustrate the states of transient localization of MEE on the molecules of component 1 and 2, respectively. The blue circles and gray circles illustrate the terminating states in which MEE is immediately converted into either photons or heat, respectively.

In states 1 and 2, MEE resides on molecules belonging to component 1 or 2, respectively. In states 3 and 4, MEE is immediately converted to photon which is observed as fluorescence emitted by component 1 and 2, respectively. When state 5 or 6 is reached, MEE is internally converted to heat. In this approach, the number of transient states is given by $n = 2$, the number of terminating states is given by $m = 4$, making $\mathbb{P}^{(1)}(t)$ a 6×6 matrix of the form

$$\mathbb{P}^{(1)}(t) = \begin{bmatrix} \theta_{11}^{(1)}(t) & \theta_{12}^{(1)}(t) & \phi_1^{(1)}(t) & 0 & Z_1^{(1)}(t) & 0 \\ \theta_{21}^{(1)}(t) & \theta_{22}^{(1)}(t) & 0 & \phi_2^{(1)}(t) & 0 & Z_2^{(1)}(t) \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (58)$$

The row numbers of this matrix correspond to the state numbers illustrated in Fig. 1. As elements of the first row of matrix (58), we have probabilities of one-step events possible when MEE resides on molecules of component 1. The fourth element of this row is zero because we assume that state 4 is directly reachable only from state 2. Similarly, the sixth element of this row is zero because we assume that state 6 is also directly reachable only from state 2. The second row of matrix $\mathbb{P}^{(1)}(t)$, which deals with possible events when MEE resides on molecules of component 2, is constructed analogously. Rows 3-6 of matrix (58) contain probabilities of MEE transitions that, according to our model, could occur from terminating states to all possible states. Since there is no MEE in the terminating state, these probabilities are

all zeros. For further considerations, it is advantageous to divide the $\mathbb{P}^{(1)}(t)$ matrix into blocks according to the scheme

$$\mathbb{P}^{(1)}(t) = \begin{bmatrix} \Theta^{(1)}(t) & \Psi^{(1)}(t) \\ O_{m \times n} & O_{m \times m} \end{bmatrix} \quad (59)$$

Here $\Theta^{(1)}(t)$ is an $n \times n$ submatrix describing transitions between transient states, $\Psi^{(1)}(t)$ is an $n \times m$ submatrix describing the excitation transitions from the transient to terminating states, and $O_{m \times n}$ and $O_{m \times m}$ are the $m \times n$ and an $m \times m$ zero submatrices, respectively. Since the matrices $\Theta^{(1)}(t)$, $\Psi^{(1)}(t)$, and O are blocks separated from a larger matrix, we will call them submatrices in the following discussion. SPDFs that are elements of the $\Theta^{(1)}(t)$ submatrix are expressed by $\Theta_{ij}^{(1)}(t)$ functions defined by Eqs. (23), and in the case where the transfer mechanism is FRET, they can be expressed by functions given by Eq. (42). The submatrix $\Psi^{(1)}(t)$ consists of two subsubmatrices, $\Phi_i^{(1)}(t)$ and $Z_i^{(1)}(t)$, according to the scheme

$$\Psi^{(1)}(t) = \begin{bmatrix} \Phi^{(1)}(t) & Z^{(1)}(t) \end{bmatrix} \quad (60)$$

All SPDFs in $\Psi^{(1)}(t)$ describe the transitions of MEE from a particular component distinguished by the row number i to the terminating states distinguished by the column number $j = n + l$, where l is a column number in submatrix $\Psi^{(1)}(t)$. The diagonal subsubmatrix $\Phi^{(1)}(t)$ has the form given by equation (25). Its $\Phi_i^{(1)}(t)$ elements are defined by equation (26), and in the case of FRET can be functions given by equation (43). The diagonal subsubmatrix $Z^{(1)}(t)$ has the form given by equation (27), and its elements $Z_i^{(1)}(t)$ are defined by equation (28), and in the case of FRET can be functions given by equation (44). The elements of the transient rows of the matrix $\mathbb{P}^{(1)}(t)$ are not normalized in such a way that their sum in each row is equal to unity, but are normalized in such a way that the integral of the sum of the elements in a given row, taken from zero to infinity, is equal to unity

$$\int_0^{\infty} \sum_{j=1}^{n+m} \mathbb{P}_{ij}^{(1)}(t) dt = 1, \quad 1 \leq i \leq n \quad (61)$$

The latter property follows from equation (30).

In the case when MCS fluorescence is excited with continuous light, then the TUMC formalism can be used instead of the TRMC formalism to describe MEE transfer. Then, according to (55), the probabilities of MEE transitions between possible states of the system shown in Fig. 1 are sufficiently described by a time-independent $P^{(1)}$ matrix of the form

$$P^{(1)} = \begin{bmatrix} \theta_{11}^{(1)} & \theta_{12}^{(1)} & \phi_1^{(1)} & 0 & \zeta_1^{(1)} & 0 \\ \theta_{21}^{(1)} & \theta_{22}^{(1)} & 0 & \phi_2^{(1)} & 0 & \zeta_2^{(1)} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (62)$$

The $P^{(1)}$ matrix is called the one-step transition probability matrix. As with the $\mathbb{P}^{(1)}(t)$ matrix, it is convenient to divide the $P^{(1)}$ matrix into blocks according to the scheme

$$P^{(1)} = \begin{bmatrix} \theta^{(1)} & \psi^{(1)} \\ O_{m \times n} & O_{m \times m} \end{bmatrix} \quad (63)$$

Here $\theta^{(1)}$ is an $n \times n$ submatrix describing transitions between transient states, $\psi^{(1)}$ is an $n \times m$ submatrix describing the excitation transitions from the transient to terminating states, while $O_{m \times n}$ and $O_{m \times m}$ denote the $m \times n$ and an $m \times m$ zero matrices, respectively. In our case, the elements of the $\theta^{(1)}$ submatrix are $\theta_{ij}^{(1)}$ probabilities given by Eq. (45). As with $\Psi^{(1)}(t)$ submatrix, the $\psi^{(1)}$ submatrix can be represented as a composite of two subsubmatrices, in this case $\phi^{(1)}$ and $\zeta^{(1)}$

$$\psi^{(1)} = \begin{bmatrix} \phi^{(1)} & \zeta^{(1)} \end{bmatrix} \quad (64)$$

The $\phi^{(1)}$ subsubmatrix is the same as matrix (32) and contains the $\phi_i^{(1)}$ probabilities for one-step light quantum emission by the molecules of the individual components of the system calculated, for example, from equation (47). The $\zeta^{(1)}$ subsubmatrix is the same as matrix (33) and contains the $\zeta_i^{(1)}$ probabilities of one-step internal conversion of the excitation energy to heat, calculated, for example, from Eq. (48). Each of the first n rows of the $P^{(1)}$ matrix contains the probabilities of all events that occur in the MEE state corresponding to that row. Therefore, the elements of these rows are normalized so that the sum of the elements in a given row equals unity

$$\sum_{j=1}^n P_{ij}^{(1)} = 1, \quad 1 \leq i \leq n \quad (65)$$

Expression (65) is equivalent to expression (34).

3.4.1 The problem of stochasticity of the transition matrices

One of the basic assumptions in the consideration of Markov chains is the stochasticity of the transition matrices. With our notation, this means that one-step transition matrices should be nonnegative, and that the sum of the elements in each of their rows should be equal to unity [50-54]. The above assumption can also be formulated in such a way that the individual rows of the transition matrix are probability vectors [55-58]. Such properties are overtly observed in TUMC/DTMC and less overtly in CTMC, where so-called rate matrices become more important than transition matrices.

In this work, the rows of the transition matrices corresponding to the terminating states are completely filled with zeros, and in the case of TRMC, the elements of these matrices are not probabilities, but probability densities. Therefore, the transition matrices discussed in this work cannot be qualified as stochastic matrices in existing sense of the word. However, it seems that they can be qualified as a new type of matrices, which we call extended stochastic matrices. In TUMC considerations, the individual rows of extended stochastic matrices are extended probability vectors, and in TRMC considerations, they are extended SPDF vectors. The components of the extended

probability vectors are probabilities, and the sum of these components is equal to either unity or zero. The components of the extended SPDF vectors are SPDFs, and the sum of these components is also equal to either unity or zero, but after they have been integrated over time. The basic property of stochastic matrices is that the product of stochastic matrices is stochastic [58]. Extended stochastic matrices also have this property.

3.4.2 Probability of reaching a given state in multiple steps

The probability distributions $P_{ij}^{(1)}$ and $\mathbb{P}_{ij}^{(1)}(t)$ describe MEE transitions from state i to state j in one step. From the point of view of describing the fluorescence intensities of the individual components of MCS, it is important to know the probabilities of reaching the selected states in multiple steps. For TUMC, we will assume that the probability $P_{ij}^{(\mu)}$ of MEE reaching state j in $\mu > 1$ steps and as a result of the initial placement of MEE in state i , can be calculated in the same way as for DTMC [45,46,51,54,57]. In our notation, this means

$$P_{ij}^{(\mu)} = \sum_{q=1}^{\mu-1} P_{iq}^{(\mu-1)} P_{qj}^{(1)} \quad (66)$$

In the case of TRMC, when we use the bivariate probability distribution $\mathbb{P}_{ij}^{(\mu)}(t)$ of reaching state j from state i at time t as a result of the μ -step transfer of excitation energy, relation (66) requires modification. This modification consists in replacing simple products of probabilities by convolutions of the corresponding SPDFs. This is because in this case the random variable $T^{(\mu)}$ is the sum of the independent random variables $T^{(\mu-1)}$ and $T^{(1)}$. Thus, we will assume that the bivariate probability distributions $\mathbb{P}_{ij}^{(\mu)}(t)$ of reaching state j from state i at time t , as a result of μ -step transfer of excitation energy, are given by the expression

$$\mathbb{P}_{ij}^{(\mu)}(t) = \sum_{q=1}^{\mu-1} \left(\mathbb{P}_{iq}^{(\mu-1)} * \mathbb{P}_{qj}^{(1)} \right)(t) \quad (67)$$

where the sign $*$ denotes convolution operation over time. Our bivariate probability distributions are zero for $t < 0$, so the convolution in (67) is understood as follows

$$\left(\mathbb{P}_{iq}^{(\mu-1)} * \mathbb{P}_{qj}^{(1)} \right)(t) = \int_0^t \mathbb{P}_{iq}^{(\mu-1)}(t') \mathbb{P}_{qj}^{(1)}(t-t') dt' \quad (68)$$

In these equations, the instant $t = 0$ denotes the moment at which external factors give rise to state i of the system. Equation (67) does not imply any additional restrictions on the type of time dependence of the probability distributions $\mathbb{P}_{ij}^{(\mu)}(t)$. In particular, they can be memoryless distributions, as is required in CTMC, but this is not necessary here.

3.5 Calculation of MCS fluorescence parameters after pulse excitation

The fluorescence emission observed after δ -pulse excitation can be understood as a composite of emissions of excited molecules described by different step number values. The emission of molecules directly excited by an external light source is assigned a step number value of 1, the emission of molecules

that have obtained their excitation as a result of a single transfer from directly excited molecules is assigned a step number value of 2, the emission of molecules that obtained their excitation by a two-step transfer from directly excited molecules is assigned a step number value of 3, and so on. It follows from relation (67) that the SPDFs describing the time dependence of the fluorescence emitted by molecules characterized by a step number value of μ are given by the elements of the $\mathbb{P}^{(\mu)}(t)$ matrix, which is the μ th convolution power over time of the $\mathbb{P}^{(1)}(t)$ matrix

$$\mathbb{P}^{(\mu)}(t) = \left(\mathbb{P}^{(1)} \right)^{* \mu}(t) \equiv \underbrace{\left(\mathbb{P}^{(1)} * \mathbb{P}^{(1)} * \dots * \mathbb{P}^{(1)} \right)}_{\mu}(t) \quad (69)$$

The entire fluorescence of the multicomponent system is described by the matrix $\mathbb{P}(t)$, which is the sum of all convolution powers of the $\mathbb{P}^{(1)}(t)$ matrix

$$\mathbb{P}(t) = \mathbb{P}^{(1)}(t) + \left(\mathbb{P}^{(1)} \right)^{*2}(t) + \left(\mathbb{P}^{(1)} \right)^{*3}(t) + \dots \quad (70)$$

We will call the $\mathbb{P}(t)$ matrix the transition SPDF matrix. As can be seen from equation (70), in our approach there is no strict correspondence between the step number and the real time. According to this equation, at any instant t in the considered system there can exist simultaneously an essentially unlimited number of excited molecules characterized by different values of the step number. The essence of the significance of the matrix $\mathbb{P}(t)$ lies in the fact that its elements describe the observed fluorescence properties of the considered multicomponent system taking into account the NET process. Since the direct calculation of the matrix $\mathbb{P}(t)$ as an infinite series of multiple convolution integrals is not possible, it is reasonable to proceed further by considering the matrix $\hat{\mathbb{P}}(s)$ which is the elementwise Laplace transform of the matrix $\mathbb{P}(t)$

$$\hat{\mathbb{P}}(s) = \mathcal{L}(\mathbb{P}(t)) = \left[\hat{\mathbb{P}}_{ij}(s) \right]_{(n+m) \times (n+m)} \quad (71)$$

where

$$\mathcal{L}(f(t)) = \hat{f}(s) = \int_0^{\infty} \exp(-st) f(t) dt \quad (72)$$

Because

$$\left(\mathbb{P}^{(1)} \right)^{* \mu}(t) = \mathcal{L}^{-1} \left[\left(\hat{\mathbb{P}}^{(1)} \right)^{\mu}(s) \right] \quad (73)$$

it follows from Eq. (70) that

$$\hat{\mathbb{P}}(s) = \sum_{\mu=1}^{\infty} \left(\hat{\mathbb{P}}^{(1)}(s) \right)^{\mu} \quad (74)$$

Thanks to the Laplace transformation, it becomes possible to replace the convolution powers of $\mathbb{P}^{(1)}(t)$ by the ordinary powers of $\hat{\mathbb{P}}^{(1)}(s)$. In this work we deal with systems for which the functions $\Theta_{ij}^{(1)}(t)$, $\Phi_i^{(1)}(t)$, and $Z_i^{(1)}(t)$, which are elements of the matrix $\mathbb{P}^{(1)}(t)$, are given by equations (23)-(29). This means that these functions are integrable in the interval $[0, \infty)$, and this allows us to conclude that Laplace transforms of these functions, $\hat{\Theta}_{ij}^{(1)}(s)$, $\hat{\Phi}_i^{(1)}(s)$, and $\hat{Z}_i^{(1)}(s)$ exist, and thus the $\hat{\mathbb{P}}(s)$ transform exists. The matrix $\mathbb{P}(t)$ can then be calculated by the

inverse Laplace transform, element by element, of the matrix $\hat{\mathbb{P}}(s)$ given by equation (74)

$$\mathbb{P}(t) = \mathcal{L}^{-1}\left(\hat{\mathbb{P}}(s)\right) \quad (75)$$

To do this, we first take a closer look at the elements of the $\hat{\mathbb{P}}^{(1)}(s)$. One can see from Eqs. (59) and (71) that structure of the $\hat{\mathbb{P}}^{(1)}(s)$ matrix is analogous to that of the $\mathbb{P}^{(1)}(t)$ matrix

$$\hat{\mathbb{P}}^{(1)}(s) = \begin{bmatrix} \hat{\Theta}^{(1)}(s) & \hat{\Psi}^{(1)}(s) \\ \mathbf{O}_{m \times n} & \mathbf{O}_{m \times m} \end{bmatrix} \quad (76)$$

Here, the submatrix $\hat{\Theta}^{(1)}(s)$ is the Laplace transform of the submatrix $\Theta^{(1)}(t)$ given by Eq. (24). It follows from Eqs. (42) and (72) that if the energy transfer is FRET, then the elements of the $\hat{\Theta}^{(1)}(s)$ submatrix can be given by

$$\hat{\Theta}_{ij}^{(1)}(s) = \frac{\gamma_{ij}}{\Gamma_i} f[x_i(s)] \quad (77)$$

where

$$x_i(s) = \frac{\Gamma_i}{\sqrt{s \tau_{0i} + 1}} \quad (78)$$

In Eq. (76) the submatrix $\hat{\Psi}^{(1)}(s)$ is the Laplace transform of the submatrix $\Psi^{(1)}(t)$ present in Eq. (59). If $\Psi^{(1)}(t)$ is structured according to expression (60), then $\hat{\Psi}^{(1)}(s)$ has the form

$$\hat{\Psi}^{(1)}(s) = \begin{bmatrix} \hat{\Phi}^{(1)}(s) & \hat{Z}^{(1)}(s) \end{bmatrix} \quad (79)$$

Using (25) (43) and (72) we get

$$\hat{\Phi}^{(1)}(s) = \text{diag}\left(\hat{\Phi}_1^{(1)}(s), \dots, \hat{\Phi}_n^{(1)}(s)\right) \quad (80)$$

where

$$\hat{\Phi}_i^{(1)}(s) = \phi_{0i} \frac{1 - f[x_i(s)]}{s \tau_{0i} + 1} \quad (81)$$

It follows from Eqs. (27) and (29) that

$$\hat{Z}^{(1)}(s) = \text{diag}\left(\hat{Z}_1^{(1)}(s), \dots, \hat{Z}_n^{(1)}(s)\right) \quad (82)$$

where

$$\hat{Z}_i^{(1)}(s) = \frac{1 - \phi_{0i}}{\phi_{0i}} \hat{\Phi}_i^{(1)}(s) \quad (83)$$

It should be noted that expressions (77), (78), and (81) are valid under the assumption that the intermolecular distances of closest approach, a_{ij} , are negligibly small, and that the transfer rate $k_{ij}^{(1)}(t)$ is given by Eq. (38). If we wish to assume $a_{ij} > 0$, then for FRET the rate $k_{ij}^{(1)}(t)$ is given by expression (36). In this case, analytical expressions for the transforms $\hat{\Theta}_{ij}^{(1)}(s)$, $\hat{\Phi}_i^{(1)}(s)$, and $\hat{Z}_i^{(1)}(s)$ are not available, which does not preclude the possibility of solving this problem numerically. An important property of the transforms $\hat{\Theta}_{ij}^{(1)}(s)$, $\hat{\Phi}_i^{(1)}(s)$, and $\hat{Z}_i^{(1)}(s)$ is their values for $s = 0$. Based on equations (31)-(33), the following relationships occur

$$\hat{\Theta}_{ij}^{(1)}(s = 0) = \theta_{ij}^{(1)} \quad (84)$$

$$\hat{\Phi}_i^{(1)}(s = 0) = \phi_i^{(1)} \quad (85)$$

$$\hat{Z}_i^{(1)}(s = 0) = \zeta_i^{(1)} \quad (86)$$

The elements of the matrix $\hat{\mathbb{P}}^{(1)}(s)$ are by definition nonnegative. Furthermore, based on equations (31)-(34) and using the definition of the Laplace transform, one can conclude that these elements are also less than unity. Hence we can expect

$\lim_{k \rightarrow \infty} \left(\hat{\mathbb{P}}^{(1)}\right)^k(s) = 0$, i.e., that the series (74) converges. If it is indeed the case, then Eq. (74) can be rewritten as [50,59,60]

$$\hat{\mathbb{P}}(s) = \left(I_{n+m} - \hat{\mathbb{P}}^{(1)}(s)\right)^{-1} - I_{n+m} \quad (87)$$

Note here that formula (87) does not hold when terminating states are replaced by absorbing states in our model. In that case, the series (74) ceases to converge and the $I_{n+m} - \hat{\mathbb{P}}^{(1)}(s)$ matrix becomes singular. In the model developed in this paper, the $I_{n+m} - \hat{\mathbb{P}}^{(1)}(s)$ matrix is nonsingular. It can be shown [60] that if $\hat{\mathbb{P}}^{(1)}(s)$ is given by expression (76), then the matrix $\hat{\mathbb{P}}(s)$ has a block structure analogous to that of the matrix $\hat{\mathbb{P}}^{(1)}(s)$

$$\hat{\mathbb{P}}(s) = \begin{bmatrix} \hat{\Theta}(s) & \hat{\Psi}(s) \\ \mathbf{O}_{m \times n} & \mathbf{O}_{m \times m} \end{bmatrix} \quad (88)$$

where

$$\hat{\Theta}(s) = \hat{N}(s) - I_n \quad (89)$$

$$\hat{\Psi}(s) = \hat{N}(s) \hat{\Psi}^{(1)}(s) \quad (90)$$

and the $n \times n$ matrix $\hat{N}(s)$ is calculated from the relation

$$\hat{N}(s) = \left(I_n - \hat{\Theta}^{(1)}(s)\right)^{-1} \quad (91)$$

To be in line with the literature on Markov chains [61-64], the matrix $\hat{N}(s)$ may be called the fundamental matrix of the matrix $\hat{\mathbb{P}}^{(1)}(s)$. If the $\hat{\Psi}^{(1)}(s)$ submatrix is structured as in expression (79), then

$$\hat{\Psi}(s) = \begin{bmatrix} \hat{\Phi}(s) & \hat{Z}(s) \end{bmatrix} \quad (92)$$

where

$$\hat{\Phi}(s) = \hat{N}(s) \hat{\Phi}^{(1)}(s) \quad (93)$$

$$\hat{Z}(s) = \hat{N}(s) \hat{Z}^{(1)}(s) \quad (94)$$

Having calculated the matrix $\hat{\mathbb{P}}(s)$, we can proceed to calculate the matrix $\mathbb{P}(t)$. Equations (75) and (88) imply that the matrix $\mathbb{P}(t)$ has the form

$$\mathbb{P}(t) = \begin{bmatrix} \Theta(t) & \Psi(t) \\ \mathbf{O}_{m \times n} & \mathbf{O}_{m \times m} \end{bmatrix} \quad (95)$$

where $\Theta(t)$ and $\Psi(t)$ can be calculated by the inverse Laplace transforms of the $\hat{\Theta}(s)$ and $\hat{Z}(s)$ submatrices given by (93) and (94), respectively. As can be seen from (89), the matrix $N(t)$ can be calculated using equation

$$N(t) = I_n \delta(t) + \Theta(t) \quad (96)$$

However, due to the presence of the $\delta(t)$ function in this equation, it can be difficult to represent $\hat{N}(t)$ in numerical form. By analogy with the $\hat{\Psi}(s)$ submatrix, the structure of the $\Psi(t)$ submatrix is closely dependent on the structure of the $\hat{\Psi}^{(1)}(s)$ submatrix. If $\hat{\Psi}^{(1)}(s)$ is structured as in Eq. (79), then $\Psi(t)$ contains two subsubmatrices, $\Phi(t)$ and $Z(t)$, according to the scheme

$$\Psi(t) = [\Phi(t) \quad Z(t)] \quad (97)$$

The time courses of the elements of the $\Phi(t)$ and $Z(t)$ submatrices can be calculated by the inverse Laplace transform of the $\hat{\Phi}(s)$ and $\hat{Z}(s)$ submatrices given by Eqs. (93) and (94), respectively. It follows from equations (93) and (96) that the subsubmatrix $\Phi(t)$ can be represented as convolutions

$$\Phi(t) = (\hat{N} * \Phi^{(1)})(t) = \Phi^{(1)}(t) + (\Theta * \Phi^{(1)})(t) \quad (98)$$

Here, the first component on the right describes the course of fluorescence intensity produced by direct excitation with external light, and the second component describes fluorescence produced by MEE transfer between solution components. Using (83) we can also write

$$Z(t) = \frac{1 - \phi_{0i}}{\phi_{0i}} \Phi(t) \quad (99)$$

From the above equations, we conclude that the fluorescence of a multicomponent system can be understood as the result of the emission of light quanta by a theoretical set of molecules among which no excitation energy transfer occurs and which are subject only to one-step processes described by the SPDFs contained in the diagonal $\Phi^{(1)}(t)$ and $\hat{Z}^{(1)}(t)$ matrices. In this theoretical set of molecules, the reversible nonradiative energy transfer (RNET) effect is replaced by a modified excitation pulse shape that varies depending on which component of the system is excited and which is observed. All the necessary excitation pulse shapes are described by the elements of matrix $\hat{N}(t)$. In the case where NET is determined by dipole-dipole interaction, the necessary elements of the matrices $\hat{\Theta}^{(1)}(s)$, $\hat{\Phi}^{(1)}(s)$, and $\hat{Z}^{(1)}(s)$ can be found from equations (77), (81), and (83). If the elements of the $\hat{P}^{(1)}(s)$ matrix are numbers, then the results of expressions (91)-(99) are numbers that are the values of the elements of the $\hat{N}(t)$, $\Theta(t)$, $\Phi(t)$, and $Z(t)$ matrices, while if the elements of the $\hat{P}^{(1)}(s)$ matrix are expressions, then the results of the calculations are expressions that can, for example, be used to calculate the values of the elements of the aforementioned four matrices.

The $\hat{N}(t)$, $\Theta(t)$, $\Phi(t)$, and $Z(t)$ matrices contain important information about the dynamics of excitation energy wandering in the multicomponent system. A brief description of the physical significance of the elements of these matrices is given in the summary below.

$\Theta(t)$ - The value of the element $\Theta_{ij}(t)$ is equal to the average intensity of MEE transfers (average number of transfers

per unit time) to molecules of the j th component at time t , induced by the excitation of a single molecule of the i th component at time $t = 0$. The mere act of excitation with light of a molecule of the i th component is not treated as a transfer here.

$\hat{N}(t)$ - As can be seen from equation (96), the physical meaning of the $\hat{N}(t)$ matrix elements is very similar to the physical meaning of the $\Theta(t)$ matrix elements, except that the $\hat{N}(t)$ matrix relates to the intensity of visits, not the intensity of transfers. For $j = i$, the additional intensity of visits occurs at time $t = 0$, as represented by the $I_n \delta(t)$ term on the right side of equation (96).

$\Phi(t)$ - The element ij of the matrix $\Phi(t)$ has the meaning that the product $\Phi_{ij}(t)dt$ is equal to the probability that a light quantum will be emitted by the j th component molecule in the time interval $(t, t + dt)$ assuming that the i th component molecule was excited by the excitation light at time $t = 0$.

$Z(t)$ - The element ij of the matrix $Z(t)$ has the meaning that the product $Z_{ij}(t)dt$ is equal to the probability that the MEE generated by a single quantum of excitation light on the i th component molecule will be converted to heat on the j th component molecule in the time interval $(t, t + dt)$.

Since in our system each individual excitation ends with the transfer of that excitation to the terminating state, it seems reasonable to say that the time integral taken from zero to infinity from the total sum of elements in each row of the $\Phi(t) + Z(t)$ matrix is equal to unity

$$\int_0^\infty \sum_{j=1}^n (\Phi_{ij}(t) + Z_{ij}(t)) dt = 1 \quad (100)$$

This is easily proved for a two-component system by using Eqs. (145), and (30); however, for a larger number of components, the proof becomes tedious.

3.6 Calculation of steady-state MCS fluorescence parameters

By analogy with δ -pulse fluorescence excitation, the matrix describing the MEE properties of MCS resulting from continuous excitation can be understood as the sum of matrices describing the MEE properties of molecules characterized by all step numbers. It follows from relation (66) that the MEE properties of molecules characterized by a step number with a value of μ are described by the elements of the matrix that is the μ th power of the $P^{(1)}$ matrix defined by equation (63). Hence, the averaged MEE properties for MCS excited by continuous light, including all step number values, are described by the matrix P , which is the sum of powers of the $P^{(1)}$ matrix according to the expression

$$P = \sum_{\mu=1}^{\infty} (P^{(1)})^\mu \quad (101)$$

After taking into account that from relation (54) follows

$$P^{(1)} = \hat{P}^{(1)}(s=0) \quad (102)$$

and after using Eqs. (101) and (74), we find that

$$P = \int_0^{\infty} \mathbb{P}(t) dt = \hat{\mathbb{P}}(s=0) \quad (103)$$

The above equation allows us to determine the values of the elements of the P matrix when the $\mathbb{P}(t)$ or $\hat{\mathbb{P}}(s)$ matrix is known. If the structure of the matrix $\mathbb{P}(t)$ is blocky and given by equations (95) and (97), it follows from equation (103) that the matrix P also has a blocky structure

$$P = \begin{bmatrix} \theta & \psi \\ O_{m \times n} & O_{m \times m} \end{bmatrix} \quad (104)$$

where

$$\psi = [\phi \quad \zeta] \quad (105)$$

Thus, the following relationships take place

$$\theta = \int_0^{\infty} \Theta(t) dt = \hat{\Theta}(s=0) \quad (106)$$

$$\psi = \int_0^{\infty} \Psi(t) dt = \hat{\Psi}(s=0) \quad (107)$$

$$\phi = \int_0^{\infty} \Phi(t) dt = \hat{\Phi}(s=0) \quad (108)$$

$$\zeta = \int_0^{\infty} Z(t) dt = \hat{Z}(s=0) \quad (109)$$

Expressions (106), (108), and (109) can be useful for finding the elements of the θ , ϕ , and ζ submatrices, especially when we know the expressions describing the elements of the $\hat{\Theta}(s)$, $\hat{\Phi}(s)$, and/or $\hat{Z}(s)$ submatrices. The θ , ϕ , and ζ submatrices contain important information about the excitation energy wandering in the system under consideration. Their physical meanings are related to the physical meanings of the elements of the $\Theta(t)$, $\Phi(t)$, and $Z(t)$ submatrices. A brief discussion of these meanings is given in the summary below.

θ - The θ_{ij} element of the θ submatrix represents the average number of MEE transfers to the j th component molecules before its final transfer to the terminating state, assuming that the originally excited molecule belonged to the i th component. The act of primary excitation by light of the i th component molecule is not included in the number of transfers.

ϕ - The ϕ_{ij} element of the ϕ submatrix is the probability that the MEE delivered to the i th component molecule will be converted to a photon on the j th component molecule, taking into account the processes of spontaneous emission, internal conversion, and RNET. The ϕ submatrix has the same meaning as that defined by equation (2).

ζ - The ζ_{ij} element of the ζ submatrix is the probability that the MEE delivered to the i th component molecule will be converted to heat on the j th component molecule, taking into account the processes of spontaneous emission, internal conversion, and RNET.

On the other hand, the elements of the P matrix can be found by applying the TUMC method. It can be seen from equation (101) that the sum of $P + I_{n+m}$ constitutes a Neumann series. Since all elements of the $P^{(1)}$ matrix are positive and smaller than unity, we can suppose that in most cases $\lim_{k \rightarrow \infty} (P^{(1)})^k = 0$ occurs, and that the series (101) converges. Then expression (101) can be written in the form [59]

$$P = (I_{n+m} - P^{(1)})^{-1} - I_{n+m} \quad (110)$$

If the matrix $I_n - \theta^{(1)}$ calculated from the matrix $P^{(1)}$ given by expression (63) is not singular, then it can be shown [60] that the matrix P has a block structure analogous to the $P^{(1)}$ matrix given by Eqs. (104) and (105), and the θ and ψ submatrices satisfy the relations

$$\theta = N - I_n \quad (111)$$

$$\psi = N \psi^{(1)} \quad (112)$$

where the matrix N is given by

$$N = (I_n - \theta^{(1)})^{-1} \quad (113)$$

As with $\hat{N}(s)$ given by Eq. (91), the N matrix can be called the fundamental matrix of the $P^{(1)}$ matrix. By comparing (91) with (113) and taking into account (84), it can be shown that

$$N = \int_0^{\infty} \mathbb{N}(t) dt = \hat{\mathbb{N}}(s=0) \quad (114)$$

Based on [61,63,65], it can be concluded that if the initial light excitation occurred to the i th state, then the ij th entry of the N matrix describes the average number of visits of excitation energy to the j th state before it reaches one of the terminating states. And the sum of the elements contained in the i th row of the matrix N determines the average number of visits of the MEE to the molecules of all the components of the system before it reaches one of the terminating states, assuming that light excitation triggered the formation of the MEE in state i . From Eqs. (112) and (64) it follows that

$$\phi = N \phi^{(1)} \quad (115)$$

$$\zeta = N \zeta^{(1)} \quad (116)$$

In order to use equations (111), (115), and (116) to calculate the θ , ϕ , and ζ submatrices, the elements of the $P^{(1)}$ matrix must be known. In the case where NET is determined by dipole-dipole interaction, the necessary elements of the $\theta^{(1)}$, $\phi^{(1)}$, and $\zeta^{(1)}$ submatrices can be found from equations (45), (47), and (48). If the elements of matrix $P^{(1)}$ are numbers, then the result of expressions (113), (111), (115), and (116) are numbers that are the values of the elements of matrices N , θ , ϕ , and ζ . On the other hand, if the elements of the $P^{(1)}$ matrix are expressions, then the results of the calculations are expressions that can, for example, be used to calculate the values of the elements of θ , ϕ , and ζ submatrices. It is worth noting that with respect to the elements of the ϕ and ζ submatrices, equation (100) takes the form

$$\sum_{j=1}^n (\phi_{ij} + \zeta_{ij}) = 1 \quad (117)$$

Intuitively, this equation follows from the assumption that every MCS excitation, sooner or later, ends with the transfer of excitation energy to the terminating state. Strict justification of equation (117), however, seems difficult.

3.7 Finding the residence probability matrix $\mathcal{P}(t)$

In the considerations carried out within the framework of CTMC, of fundamental importance is the so-called transition function [44], Markov state density function [66], or transition probability function [57,62]. This function is presented in the form of a matrix $\mathcal{P}(t)$, in which a given element $\mathcal{P}_{ij}(t)$ has the meaning of the probability of the system being in state j at time t , assuming that at time $t = 0$ the system was in state i . In the case of fluorescence of a multicomponent system, the element $\mathcal{P}_{ij}(t)$ defines the probability of locating the excitation energy at time t on the molecule of component j if the initial excitation was located at time $t = 0$ on molecule of component i . The matrix $\mathcal{P}(t)$ is thus a square matrix of size $n \times n$. It can be seen that in our calculations, the values of the elements $\mathcal{P}_{ij}(t)$ are contained, for example, in the values of the elements $\Phi_{ij}(t)$ of the $\Phi(t)$ matrix, which can be calculated using the values of the $\hat{\Phi}(s)$ transform given by Eq. (93). The probability of emission of a photon by a given molecule is proportional to the probability of presence of this molecule in the excited state. Taking into account relation (161) from Appendix A we conclude that

$$\mathcal{P}_{ij}(t) = \Phi_{ij}(t) \tau_{ij} \quad (118)$$

where $\tau_{ij} = 1/k_{rj}$ is the radiative lifetime [34] of the j component molecules. Using matrix notation, equation (118) can be written as

$$\mathcal{P}(t) = \Phi(t) \tau_r \quad (119)$$

where

$$\tau_r = \text{diag}(\tau_{r1}, \dots, \tau_{rn}) \quad (120)$$

As equations (95) and (97) show, the matrix $\Phi(t)$ is a submatrix of the matrix $\mathbb{P}(t)$. Hence, equation (119) also shows what the relationship is between the $\mathcal{P}(t)$ and $\mathbb{P}(t)$ matrices. Using (119), (93) and (26), we also obtain that

$$\hat{\mathcal{P}}(s) = \hat{N}(s) \hat{\mathcal{P}}^{(1)}(s) \quad (121)$$

where $\hat{\mathcal{P}}^{(1)}(s)$ is the Laplace transform of the matrix $\mathcal{P}^{(1)}(t)$, given by Eq. (15). The probability $\mathcal{P}_i^{(1)}(t)$ is the one-step survival probability of MEE on the i th component molecule, which can be calculated using Eq. (17). In time space, equation (121) takes the form

$$\mathcal{P}(t) = (\hat{N} * \mathcal{P}^{(1)})(t) \quad (122)$$

In the extreme case, when in the considered MCS the transfer of MEE to terminating states disappears, one can expect that the probabilities $\mathcal{P}_{ij}(t)$ satisfy the relation

$$\sum_{j=1}^n \mathcal{P}_{ij}(t) = 1 \quad (123)$$

It can also be shown that if all elements of the matrix $\mathcal{P}^{(1)}(t)$ are memoryless functions, that is, such that

$$\mathcal{P}_i^{(1)}(t+u) = \mathcal{P}_i^{(1)}(t) \mathcal{P}_i^{(1)}(u) \quad (124)$$

then the matrix $\mathcal{P}(t)$ satisfies the equation

$$\mathcal{P}(t+u) = \mathcal{P}(t) \mathcal{P}(u) \quad (125)$$

called the Chapman-Kolmogorov equation [44,57,64,67-70]. This equation is the basic equation of the CTMC method, which we mentioned at the beginning of Section 3. In our consideration of multicomponent fluorescent systems involving NET, condition (124) is not satisfied, and so neither is relation (125). However, when we use the TRMC method and calculate the $\Phi(t)$ function from equation (89) and the $\mathcal{P}(t)$ function from equation (121), the significance of the Chapman-Kolmogorov equation becomes irrelevant.

3.8 Discrete time vs. continuous time in the Markov chain formalism

The results of this work indicate that using the term "time" to describe the step number in DTMC is not justified. The step number cannot be time because it is a dimensionless quantity, it does not have the dimension of time. The practice of calling a step number a discrete time leads to the misconception that DTMC contains time, while this is not the case. As we emphasized at the end of Subsection 3.3, time is unspecified here. The difference between step number and time is clearly visible in the TRMC model introduced in this work, where the two quantities appear independently of each other. It can be surmised that the argument for the identification of step number and time became the Chapman-Kolmogorov equations. In the case of DTMC, these equations follow from relation (66) and take the form [46,62,64,67,69,71]

$$P_{ij}^{(\mu+\nu)} = \sum_{q=1}^n P_{iq}^{(\mu)} P_{qj}^{(\nu)} \quad (126)$$

or

$$P^{(\mu+\nu)} = P^{(\mu)} P^{(\nu)} \quad (127)$$

while in the case of CTMC, expressions (124) and (125) were taken as one of the forms of the Chapman-Kolmogorov equations. Despite the great similarity of the Chapman-Kolmogorov equations in DTMC and CTMC, the probability matrices $P^{(\mu)}$ and $\mathcal{P}(t)$ considered by these equations have different physical meanings. Therefore, this similarity cannot provide a basis for conclusions about the existence of a relationship between step number and real time. The postulation of the fulfillment of equations (124) and (125) in the CTMC framework allowed only a partial solution to the problem of time in Markov processes, as it simultaneously made it possible to describe in the CTMC framework only processes in which the temporal probability density distributions of transitions between states, defined by the elements of the matrix $\mathbb{P}^{(1)}(t)$, can be exclusively continuous and exclusively exponential. From equation (67), it follows that in the TRMC framework, the Chapman-Kolmogorov equation can be written as

$$\mathbb{P}^{(\mu+\nu)}(t) = (\mathbb{P}^{(\mu)} * \mathbb{P}^{(\nu)})(t) \quad (128)$$

The Chapman-Kolmogorov equation in the form given by equation (125) need not apply here, and hence there is no need for the elements of the $\mathbb{P}^{(1)}(t)$ matrix to be purely memoryless functions. It is also worth noting that, given equation (52), the TRMC process can be qualified as Markovian, regardless of whether the elements of the $\mathbb{P}^{(1)}(t)$ matrix have the form of memoryless functions or not.

Within the TRMC model introduced in this work, real time appears next to "discrete time" (actually: step number), rather than as an extension of "discrete time" to the \mathbb{R}_+^0 region. In this new approach, the Chapman-Kolmogorov equations in the version of expressions (124) and (125) lose their fundamental meaning. This makes it unnecessary to use transition rate matrix Q under TRMC framework, unlike CTMC, and the temporal event distribution functions do not have to be exponential and can be arbitrary.

The TRMC model we introduced, in addition to using continuous time as, for example, in expressions (42)-(44), can also use discrete time, for example, by assuming that the elements of the $\mathbb{P}^{(1)}(t)$ matrix are of the form

$$\mathbb{P}_{ij}^{(1)}(t) = \sum_k A_{ijk}^{(1)} \delta(t - t_{ijk}^{(1)}) \quad (129)$$

where $A_{ijk}^{(1)}$ are the transition probabilities of a one-step transition of the described system from state i to state j at time $t_{ijk}^{(1)}$, and $\delta(t)$ is the Dirac delta. Note, however, that in Eq. (129) it is actually not the time that is discrete, but the probability density distributions of transitions between states.

4. Comparison of TRMC results with analogous results obtained by usual analytical methods

In paper [32], it is shown that the fluorescence decay of individual components in an n -component system with a random distribution of molecules can be described by a system of equations of the form

$$\hat{N}_i = \hat{\phi}_i^{(0)} \left[1 - \hat{A}_{ii} \right]^{-1} \left[N_{0i} + \sum_{\substack{k=1 \\ k \neq i}}^n \left(\hat{\phi}_k^{(0)} \right)^{-1} \hat{A}_{ki} \hat{N}_k \right], \quad (130)$$

$i = 1, 2, \dots, n$

where N_{0i} is the number of excited molecules of component i at time $t = 0$, and N_i is the number of these molecules at any time $t > 0$.

In order to be able to compare this result with the results of the present work, it is convenient to introduce the SPDF vector of effective fluorescence, $E(t)$ of the form

$$E(t) = \left[\sum_{j=1}^n X_j \Phi_{ji}(t) \right]_{1 \times n} = X \Phi(t) \quad (131)$$

where $X_i = N_{0i}/N_0$, $N_0 = \sum_{i=1}^n N_{0i}$, and $X = [X_i]_{1 \times n}$. The $E_i(t)$ elements of this vector are such that the product $E_i(t) dt$ is equal to the probability that a photon absorbed by the

multicomponent system from an excitation light beam at time $t = 0$, will result in the emission of a quantum of light by a component i molecule in the time interval $(t, t + dt)$. Using the terminology of the present work, such symbols in (130) as \hat{N}_i , $\hat{\phi}_i^{(0)}$, \hat{A}_{ki} , should be interpreted as follows

$$\hat{N}_i = N_0 \frac{\tau_{0i}}{\phi_{0i}} \hat{E}_i(s) \quad (132)$$

$$\hat{\phi}_i^{(0)} = \frac{\tau_{0i}}{\phi_{0i}} \hat{\Phi}_i^{(1)}(s) \quad (133)$$

$$\hat{A}_{ki} = \hat{\Theta}_{ki}^{(1)}(s) \quad (134)$$

Thus equation (130) can be written as

$$\hat{E}_i(s) = \hat{\Phi}_i^{(1)}(s) \left(1 - \hat{\Theta}_{ii}^{(1)}(s) \right)^{-1} \times \left(X_i + \sum_{\substack{k=1 \\ k \neq i}}^n \left(\hat{\Phi}_k^{(1)}(s) \right)^{-1} \hat{\Theta}_{ki}^{(1)}(s) \hat{E}_k(s) \right) \quad (135)$$

After introducing the auxiliary vector $\hat{W}(s)$, such that

$$\hat{E}(s) = \hat{W}(s) \hat{\Phi}^{(1)}(s) \quad (136)$$

where the diagonal matrix $\hat{\Phi}^{(1)}(s)$ is given by Eq. (80), we obtain

$$\hat{W}_i(s) \left(1 - \hat{\Theta}_{ii}^{(1)}(s) \right) - \sum_{\substack{k=1 \\ k \neq i}}^n \hat{W}_k(s) \hat{\Theta}_{ki}^{(1)}(s) = X_i, \quad (137)$$

$i = 1, 2, \dots, n$

or

$$\hat{W}(s) \left(I_n - \hat{\Theta}^{(1)}(s) \right) = X \quad (138)$$

where $\Theta^{(1)}(s)$ is a Laplace transform of the matrix $\Theta^{(1)}(t)$ is defined by Eq. (23). Using Eqs. (131) and (136), it is easy to convert (138) to the form

$$\hat{\Phi}(s) = \left(I_n - \hat{\Theta}^{(1)}(s) \right)^{-1} \hat{\Phi}^{(1)}(s) \quad (139)$$

which is our Eq. (93). This shows that the results obtained using our TRMC method are consistent with the results obtained for the same problem obtained by usual analytical methods.

5. Examples of applications of TUMC and TRMC methods to describe RNET in simple multicomponent systems

In this section, we will provide examples of using the TRMC and TUMC methods to find expressions describing the elements of the matrices $\hat{\Phi}(s)$ and ϕ .

5.1 Two-component fluorescent mixture

Excitation energy transfer in a binary system has already been partially discussed in Subsection 3.4. A prerequisite for detailed calculations is knowledge of the concentrations of the components c_1 and c_2 , their lifetimes τ_{01} and τ_{02} , the quantum

yields ϕ_{01} and ϕ_{02} , and the four Förster radii R_{0ij} , $i, j \in \{1, 2\}$. With these data we are able to calculate the values of the Laplace transforms $\hat{\Theta}_{ij}^{(1)}(s)$, $\hat{\Phi}_i^{(1)}(s)$, and $\hat{Z}_i^{(1)}(s)$, ($i, j \in \{1, 2\}$) of the SPDFs defined by Eqs. (23)-(28). In the special case where RNET is due to dipole-dipole interaction, these functions are given by Eqs (77), (81), and (83). If our goal is to find functions describing the elements of the matrix $\hat{\Phi}(s)$ then we first create the matrix $\hat{P}^{(1)}(s)$ defined by equations (76) and (79). The elements of this matrix describe the kinetics of the transitions between the six states of the system shown in Fig. 2.

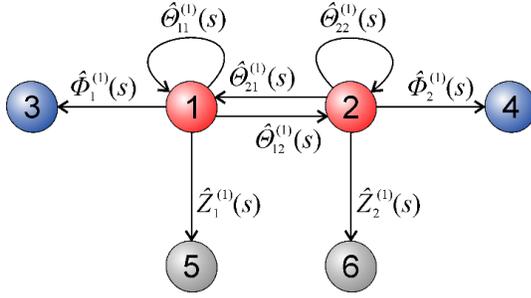


Figure 2. Six-state diagram of the Markov process for a binary system. The basic features of this diagram are the same as in Fig. 1. Instead of the $\Theta_{ij}^{(1)}(t)$, $\Phi_i^{(1)}(t)$, and $Z_i^{(1)}(t)$ functions, the Laplace transforms of these functions $\hat{\Theta}_{ij}^{(1)}(s)$, $\hat{\Phi}_i^{(1)}(s)$, and $\hat{Z}_i^{(1)}(s)$ are placed.

In the considered case we have $n=2$, and the submatrices $\hat{\Theta}^{(1)}(s)$, $\hat{\Phi}^{(1)}(s)$ and $\hat{Z}^{(1)}(s)$ defined by Eqs. (76) and (79) take the forms

$$\hat{\Theta}^{(1)}(s) = \left[\hat{\Theta}_{ij}^{(1)}(s) \right]_{2 \times 2} \quad (140)$$

$$\hat{\Phi}^{(1)}(s) = \text{diag}(\hat{\Phi}_1^{(1)}, \hat{\Phi}_2^{(1)}) \quad (141)$$

$$\hat{Z}^{(1)}(s) = \text{diag}(\hat{Z}_1^{(1)}, \hat{Z}_2^{(1)}) \quad (142)$$

while the fundamental matrix $\hat{N}(s)$ of the matrix $\hat{P}^{(1)}(s)$ defined by (91) is given by the expression

$$\hat{N}(s) = \left(I_2 - \hat{\Theta}^{(1)}(s) \right)^{-1} = \frac{1}{D} \begin{bmatrix} 1 - \hat{\Theta}_{22}^{(1)} & \hat{\Theta}_{12}^{(1)} \\ \hat{\Theta}_{21}^{(1)} & 1 - \hat{\Theta}_{11}^{(1)} \end{bmatrix} \quad (143)$$

where

$$D = \left(1 - \hat{\Theta}_{11}^{(1)} \right) \left(1 - \hat{\Theta}_{22}^{(1)} \right) - \hat{\Theta}_{12}^{(1)} \hat{\Theta}_{21}^{(1)} \quad (144)$$

Knowing the matrix $\hat{N}(s)$, we can use equation (93) to calculate the desired matrix $\hat{\Phi}(s)$

$$\hat{\Phi}(s) = \frac{1}{D} \begin{bmatrix} (1 - \hat{\Theta}_{22}^{(1)}) \hat{\Phi}_1^{(1)} & \hat{\Theta}_{12}^{(1)} \hat{\Phi}_2^{(1)} \\ \hat{\Theta}_{21}^{(1)} \hat{\Phi}_1^{(1)} & (1 - \hat{\Theta}_{11}^{(1)}) \hat{\Phi}_2^{(1)} \end{bmatrix} \quad (145)$$

From the above expression, it can be seen that the course of fluorescence intensity of a binary solution is in general non-exponential, regardless of which component is excited by an external pulse of light. If there is no NET from component 2 to component 1, that is, if $\hat{\Theta}_{21}^{(1)}(s) = 0$, then expression (145) reduces to

$$\hat{\Phi}(s) = \begin{bmatrix} \frac{\hat{\Phi}_1^{(1)}}{1 - \hat{\Theta}_{11}^{(1)}} & \frac{\hat{\Theta}_{12}^{(1)} \hat{\Phi}_2^{(1)}}{1 - \hat{\Theta}_{11}^{(1)} - \hat{\Theta}_{22}^{(1)}} \\ 0 & \frac{\hat{\Phi}_2^{(1)}}{1 - \hat{\Theta}_{22}^{(1)}} \end{bmatrix} \quad (146)$$

Considering the results given in Appendix B, from Eq. (146) we see that then if only component 2 is excited, then its fluorescence decays exponentially, regardless of the form of the $\hat{\Theta}_{22}^{(1)}(s)$ and $\hat{\Phi}_2^{(1)}(s)$ functions. If only component 1 is excited under the same conditions, then one observes fluorescence of both components, whose time courses are generally nonexponential.

For finding the ϕ matrix, we can use two methods. The first method concerns the situation when we know the matrix (145). Then it is enough to use expressions (108), (84) and (85). This gives

$$\phi = \frac{1}{d} \begin{bmatrix} (1 - \theta_{22}^{(1)}) \phi_1^{(1)} & \theta_{12}^{(1)} \phi_2^{(1)} \\ \theta_{21}^{(1)} \phi_1^{(1)} & (1 - \theta_{11}^{(1)}) \phi_2^{(1)} \end{bmatrix} \quad (147)$$

where

$$d = \left(1 - \theta_{11}^{(1)} \right) \left(1 - \theta_{22}^{(1)} \right) - \theta_{12}^{(1)} \theta_{21}^{(1)} \quad (148)$$

The quantities $\theta_{ij}^{(1)}$ and $\phi_i^{(1)}$ occurring here can be calculated, for example, from expressions (45)-(47). The second way to find the eta matrix is to use the TUMC method. We begin by constructing a $P^{(1)}$ matrix such as shown in expression (62) by determining the values of the elements of the $\theta^{(1)}$, $\phi^{(1)}$, and $\zeta^{(1)}$ submatrices based on equations (63), (64), and (45)-(48). Based on Eq. (113), the fundamental matrix N of the $P^{(1)}$ matrix is given by

$$N = \frac{1}{d} \begin{bmatrix} 1 - \theta_{22}^{(1)} & \theta_{12}^{(1)} \\ \theta_{21}^{(1)} & 1 - \theta_{11}^{(1)} \end{bmatrix} \quad (149)$$

where d is given by Eq. (148). Knowing the N matrix, we can use Eq. (115) to calculate the desired ϕ matrix. The result thus obtained is, for obvious reasons, the same as that presented by expression (147).

5.2 Three-component fluorescent mixture

In this subsection, we sketch the course of calculating the elements of the $\hat{\Phi}(s)$ and ϕ matrices for the ternary solution when NET is described by expression (38). For the sake of shortening our considerations, we will limit ourselves to using the TRMC method only. A schematic of the NET, spontaneous emission, and internal conversion processes occurring in this system is shown in Fig. 3. The way the states are numbered and the associated colors are the same here as in the previous figures. The quantities $\Theta_{ij}^{(1)}$ are SPDFs describing the kinetics of one-step excitation energy transfer between states 1, 2, and 3. These states correspond to the presence of excitation energy on the molecules of the individual system components. The $\Phi_i^{(1)}$ and $Z_i^{(1)}$ quantities are SPDFs describing the kinetics of one-step spontaneous emission and internal conversion, respectively.

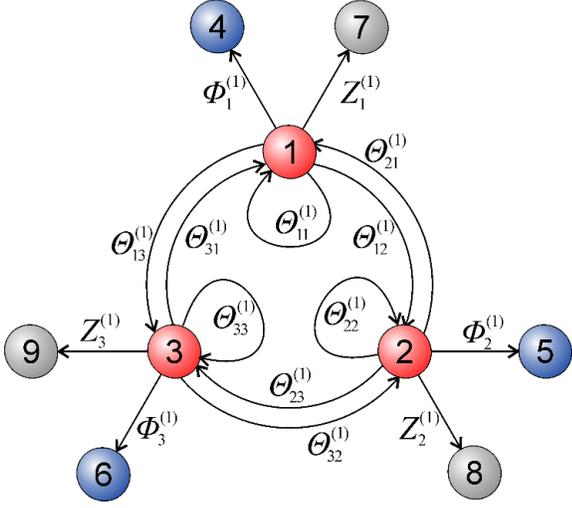


Figure 3. Nine-state Markov process diagram showing states, events, and their SPDFs in a three-component system. The red circles illustrate the states of transient localization of MEE on molecules of component 1, 2, and 3, respectively. The blue circles and gray circles illustrate the terminating states in which MEE is instantaneously converted to either photons or heat, respectively. The symbols $\theta_{ij}^{(1)}$, $\phi_i^{(1)}$, and $Z_i^{(1)}$ denote the SPDFs describing the MEE transitions indicated by the arrows.

We assume that for this system we know the three component concentrations c_i , the three lifetimes τ_{0i} , the three quantum yields ϕ_{0i} , and the nine Förster radii R_{0ij} , where $i, j \in \{1, 2, 3\}$. These data and the expressions (77)-(83) allow us to calculate all the elements of the matrix $\hat{P}^{(1)}(s)$. Using equation (91) we find the elements of the matrix $\hat{N}(s)$. This gives

$$\left. \begin{aligned} \hat{N}_{ii}(s) &= \frac{1}{D} \left[(1 - \hat{\theta}_{jj}^{(1)}) (1 - \hat{\theta}_{kk}^{(1)}) - \hat{\theta}_{jk}^{(1)} \hat{\theta}_{kj}^{(1)} \right] \\ \hat{N}_{ij}(s) &= \frac{1}{D} \left[\hat{\theta}_{ij}^{(1)} (1 - \hat{\theta}_{kk}^{(1)}) + \hat{\theta}_{ik}^{(1)} \hat{\theta}_{kj}^{(1)} \right] \end{aligned} \right\} \quad (150)$$

$i, j, k = \{1, 2, 3\}, \quad k \neq j \neq i$

where

$$\begin{aligned} D &= (1 - \hat{\theta}_{11}^{(1)}) (1 - \hat{\theta}_{22}^{(1)}) (1 - \hat{\theta}_{33}^{(1)}) \\ &\quad - (1 - \hat{\theta}_{11}^{(1)}) \hat{\theta}_{12}^{(1)} \hat{\theta}_{23}^{(1)} - (1 - \hat{\theta}_{22}^{(1)}) \hat{\theta}_{13}^{(1)} \hat{\theta}_{31}^{(1)} \\ &\quad - (1 - \hat{\theta}_{33}^{(1)}) \hat{\theta}_{12}^{(1)} \hat{\theta}_{21}^{(1)} - \hat{\theta}_{12}^{(1)} \hat{\theta}_{23}^{(1)} \hat{\theta}_{31}^{(1)} - \hat{\theta}_{13}^{(1)} \hat{\theta}_{32}^{(1)} \hat{\theta}_{21}^{(1)} \end{aligned} \quad (151)$$

We compute the desired elements of the matrix $\hat{\phi}(s)$ using expression (93). In this way, we obtain

$$\left. \begin{aligned} \hat{\phi}_{ii}(s) &= \frac{1}{D} \left[(1 - \hat{\theta}_{jj}^{(1)}) (1 - \hat{\theta}_{kk}^{(1)}) - \hat{\theta}_{jk}^{(1)} \hat{\theta}_{kj}^{(1)} \right] \hat{\phi}_i^{(1)} \\ \hat{\phi}_{ij}(s) &= \frac{1}{D} \left[\hat{\theta}_{ij}^{(1)} (1 - \hat{\theta}_{kk}^{(1)}) + \hat{\theta}_{ik}^{(1)} \hat{\theta}_{kj}^{(1)} \right] \hat{\phi}_j^{(1)} \end{aligned} \right\} \quad (152)$$

$i, j, k = \{1, 2, 3\}, \quad k \neq j \neq i$

Expressions describing elements of the matrix ϕ are found using relation (108), which gives

$$\left. \begin{aligned} \phi_{ii} &= \frac{1}{d} \left[(1 - \theta_{jj}^{(1)}) (1 - \theta_{kk}^{(1)}) - \theta_{jk}^{(1)} \theta_{kj}^{(1)} \right] \phi_i^{(1)} \\ \phi_{ij} &= \frac{1}{d} \left(\theta_{ij}^{(1)} - \theta_{ij}^{(1)} \theta_{kk}^{(1)} + \theta_{ik}^{(1)} \theta_{kj}^{(1)} \right) \phi_j^{(1)} \end{aligned} \right\} \quad (153)$$

$i, j, k = \{1, 2, 3\}, \quad k \neq j \neq i$

where

$$\begin{aligned} d &= (1 - \theta_{11}^{(1)}) (1 - \theta_{22}^{(1)}) (1 - \theta_{33}^{(1)}) \\ &\quad - (1 - \theta_{11}^{(1)}) \theta_{23}^{(1)} \theta_{32}^{(1)} - (1 - \theta_{22}^{(1)}) \theta_{13}^{(1)} \theta_{31}^{(1)} \\ &\quad - (1 - \theta_{33}^{(1)}) \theta_{12}^{(1)} \theta_{21}^{(1)} - \theta_{12}^{(1)} \theta_{23}^{(1)} \theta_{31}^{(1)} - \theta_{13}^{(1)} \theta_{32}^{(1)} \theta_{21}^{(1)} \end{aligned} \quad (154)$$

When NET processes are not reversible in the system under study, the expressions for $\hat{\phi}(s)$ and ϕ simplify significantly.

For example, considering the condition $\hat{\theta}_{ij}^{(1)}(s) = 0$ when $j < i$ causes the matrix (153) to reduce to the form

$$\phi = \begin{bmatrix} K_1 & K_{12} K_2 & (K_{13} + K_{12} K_{23}) K_3 \\ 0 & K_2 & K_{23} K_3 \\ 0 & 0 & K_3 \end{bmatrix} \quad (155)$$

where

$$K_i = \frac{\phi_i^{(1)}}{1 - \theta_{ii}^{(1)}} \quad (156)$$

$$K_{ij} = \frac{\theta_{ij}^{(1)}}{1 - \theta_{ii}^{(1)}} \quad (157)$$

The last three expressions are in agreement with the analogous expressions given in the paper [24]

6. Conclusions

The main achievements of this work can be listed as follows

1. To determine the effect of RNET on the values of parameters characterizing the fluorescence of MCS containing n components, we used a suitably adapted Markov chain technique. To the best of our knowledge, the Markov chain technique has not yet been used for this purpose.
2. In our considerations, the DTMC model was subject to adaptation. We found it expedient to introduce a new kind of state of the Markov process object, which we called the terminating state. The characteristic property of the terminating state is that upon transition to this state the Markov process object immediately ceases to exist. The object of our Markov process is MEE. The introduction of terminating states makes it possible to include events such as fluorescence photon emission or internal conversion in a given process. It is also important in the computational process that the replacement of absorbing states by terminating states makes $I_n - P^{(1)}$ and/or $I_n - \hat{P}^{(1)}(s)$ matrices invertible.
3. To find the time characteristics of the fluorescence emission probabilities of the individual MCS, we introduced a new type of Markov chain, which we called the time-resolved Markov chain (TRMC). What is significant for

TRMC is that the individual rows of its transition matrix are filled not by univariate discrete probability distributions, but by bivariate probability mass-density functions. Unlike CTMC, in our TRMC model the time distributions of events possible in each state need not be exponential, and can be arbitrary.

4. Within TRMC, the step number μ is independent of real time. The time distributions of the time fluorescent random variable T considered at different values of μ are mutually independent. This fact is important in qualifying whether a given process is Markovian or not. We consider any TRMC that satisfies the modified Markov property (52) to be Markovian, regardless of whether the time distributions of events at each step of the process are exponential or not.
5. In our opinion, contrary to its name, the commonly used DTMC method does not include time. We argue that in DTMC, time is unspecified, hence we propose renaming DTMC as TUMC.
6. Under TRMC, time is always continuous. On the other hand, discrete or continuous can be the temporal probability density distributions of the chain object's transition between states. A variant of TRMC using continuous time is obtained if the time distributions of the probability densities of one-step transitions between states of the chain object are continuous. A variant using discrete time can be obtained by assuming that the time distributions of these probability densities are discrete, e.g., such as that defined by equation (129).
7. Unlike CTMC, using TRMC, transitions within the same state can be taken into account. In the case of MCS, this makes it possible, for example, to determine the effect of MEE migration on the fluorescence intensity of individual components.
8. We have shown that the results obtained using the TRMC method are equivalent to those obtained using conventional analytical methods. However, the TRMC method is simpler and more perceptual. We have also shown that the previously known CTMC method is a special case of our TRMC method. The two methods become equivalent when the temporal probability density distributions of transitions between process states are described by exponential (memoryless) functions.
9. In this work, the TRMC method has been successfully applied to describe the course of a relatively narrow range of phenomena involving MCS fluorescence. In our opinion, the range of applications of this method can be much broader. Undoubtedly, there is a need for further work on both its applications and its theoretical basis.

7. Appendices

7.1 Appendix A: Relationship between $\Phi_{ij}(t)$ and $\mathcal{P}_{ij}(t)$

Suppose that at time $t = 0$ in our MCS we have produced N_{0i}^* excited molecules of component i . According to the definition of probability $\mathcal{P}_{ij}(t)$ given in Subsection 3.7, the number $N_{ij}^*(t)$ of excited molecules of component j at time t is equal to

$$N_{ij}^*(t) = \mathcal{P}_{ij}(t) N_{0i}^* \quad (158)$$

The time-dependent intensity of the induced fluorescence of component j can be described in two ways, either

$$I_{ij}(t) = c N_{0i}^* \Phi_{ij}(t) \quad (159)$$

or

$$I_{ij}(t) = c N_{ij}^* k_{vj} \quad (160)$$

where c is a constant. From equations (158)-(160), it follows that

$$\Phi_{ij}(t) = \mathcal{P}_{ij}(t) k_{vj} \quad (161)$$

7.2 Appendix B: Exponentialization of fluorescence decays of individual components in the absence of heterotransfer

In the case where there is only homotransfer in a given MCS and no heterotransfer, the $\Theta^{(1)}(t)$ matrix becomes a diagonal matrix. It follows from equation (91) that the fundamental matrix $\hat{N}(s)$ is then also diagonal, and its non-zero elements $\hat{N}_{ii}(s)$ are of the form

$$\hat{N}_{ii}(s) = \left(1 - \hat{\Theta}_{ii}^{(1)}(s)\right)^{-1} \quad (162)$$

From equation (93), we can see that, under these conditions, the matrix $\hat{\Phi}(s)$ containing the Laplace transforms of the fluorescence decay functions of the individual MCS components is also diagonal. It is easy to see that the non-zero elements of this matrix are given by the expression

$$\hat{\Phi}_{ii}(s) = \frac{\hat{\Theta}_{ii}^{(1)}(s)}{1 - \hat{\Theta}_{ii}^{(1)}(s)} \quad (163)$$

Assuming that $\Theta_{ii}^{(1)}(t)$ and $\Phi_{ii}^{(1)}(t)$ are described by Eqs. (23) and (26), respectively, and that in Eq. (17) $k_{ij}(t) = 0$ for $j \neq i$, we can write

$$\hat{\Phi}_{ii}(s) = \frac{(\phi_{0i}/\tau_{0i}) \int_0^\infty g_i(t) h_i(t) dt}{1 + \int_0^\infty g_i(t) dh_i(t)} \quad (164)$$

where

$$g_i(t) = \exp\left[-(s + \tau_{0i}^{-1})t\right], \quad h_i(t) = \exp\left[-\int_0^t k_{ii}(t') dt'\right] \quad (165)$$

Calculating the integral in the denominator of expression (164) by parts, we find that

$$\hat{\Phi}_{ii}(s) = \frac{\phi_{0i}}{\tau_{0i}} \frac{1}{s + \tau_{0i}^{-1}} \quad (166)$$

It follows that in the absence of heterotransfer, the time course of the original function from transform (163) is exponential and described by the expression

$$\Phi_{ii}(t) = \frac{\phi_{0i}}{\tau_{0i}} \exp\left(-\frac{t}{\tau_{0i}}\right) \quad (167)$$

This is despite the fact that the time courses of the functions $\Theta_{ii}^{(1)}(t)$ and $\Phi_{ii}^{(1)}(t)$ are not exponential. For example, this occurs under conditions where equations (42) and (43) reduce to the form of

$$\Theta_{ii}^{\text{os}}(t) = \frac{\gamma_{ii}}{\sqrt{\tau_{oi} t}} g(\gamma_{ii}, \tau_{oi}, t) \quad (168)$$

$$\Phi_i^{\text{os}}(t) = \frac{\phi_{oi}}{\tau_{oi}} g(\gamma_{ii}, \tau_{oi}, t) \quad (169)$$

where the function $g(\gamma_{ii}, \tau_{oi}, t)$ is defined by equation (41).

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