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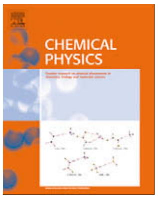

Reversible energy quenching and conservation

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ABSTRACT

The kinetics of reversible energy transfer from photo-excited donors to energy acceptors is studied at arbitrary concentrations of both and any relationship between the decay-times of the reactants. The backward reaction of transfer products in a bulk is included in the consideration. Its contribution to delayed fluorescence, resulting from the energy conservation on the long-lived acceptors, is specified.

1. Introduction

The reversible energy transfer from the excited donor D^* to the energy acceptors is given by the simplest reaction scheme

$$\begin{array}{ccccc} D^* & + A & \underset{W_B}{\overset{W_F}{\rightleftarrows}} & D & + A^*, \\ \downarrow \tau_D & & & & \downarrow \tau_A \end{array} \tag{1.1}$$

where τ_A and τ_B are the life-times of excited reactants. The transfer reactions in diluted solutions is the usual subject of the Encounter Theory that enables specifying the reaction kinetics and the quantum yields of the luminescence and transfer products.

The input data are the forward and backward transfer rates, W_F and W_B, as well as encounter diffusion coefficient D. For a forward dipole–dipole energy transfer the position dependent rate is given by the Förster formula [1]:

$$W_F(r) = \frac{\alpha}{r^6}. \tag{1.2}$$

It decreases as a power of distance r between the donor and acceptor of energy. If the transfer is performed by the exchange interaction of Dexter type then [2]

$$W_F(r) = W_0 \exp\left(-\frac{r-\sigma}{L}\right) \tag{1.3}$$

where σ is a contact distance and L is the characteristic transfer length. In line with the true space dependent rates, there is also the popular contact approximation for them:

$$W_F(r) = k_f \delta(r-\sigma) \quad \text{where} \quad k_f = \int_0^\infty W_F(r) 4\pi r^2 dr \tag{1.4}$$

For the short range interaction it is obtained from the last expression by the limiting transition

$$L \to 0, \quad W_0 \to \infty, \quad \text{while} \quad k_f = const.$$

This approximation is not applicable to static quenching, but is very often used (from Smoluchowski times) for a description of contact diffusional quenching.

The kinetic scheme for reversible inter-molecular transfer (1.1), includes the backward rate W_B that relates to a forward one, via equilibrium constant γ:

$$\frac{W_F}{W_B} = \frac{k_f}{k_b} = \frac{1}{\gamma} = \exp(-\Delta G/T), \tag{1.5}$$

where ΔG is the difference between the free energy of the products and initial reactant states (the Boltzmann constant k_B is set to 1).

The irreversible analog of this process, performing the quenching of initial excitation at $W_B = 0$ is perfectly described by means of differential encounter theory (DET) [3]. In solid solutions (in absence of encounter diffusion) the "static quenching" kinetics obtained with DET reproduces the exact multi-particle solution of the problem which is valid at any acceptor concentration $c = [A]$. However, DET can do nothing with a reversible transfer when $W_B \neq 0$ and the backward process plays an important role in energy quenching or conservation.

On the contrary, the relatively new integral encounter theory (IET) describes the reversible transfer reactions as well as irreversible ones but only in the lowest order concentration approximation (with respect to c) [4,5]. As a result, IET is inapplicable to the long time quenching which is a multi-particle one, although it allows to describe reasonably (in the lowest concentration approximation) the preceding diffusion–accelerated reaction. More accurate

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description of the latter is given by the modified encounter theory (MET) [6,7]. Taking more consistently all the binary terms, MET corrects the kernel of IET, improving the kinetics of diffusion accelerated process and avoiding the false long time behavior of IET. Using both theories which are identical in static stage, we will indicate the diffusion–accelerated one, where they become different, giving preference to MET.

In the next section, we will present the formalism of both theories, MET and IET, using the position dependent rates of dipole–dipole and "exchange" energy transfer, which are the alternatives to the contact one studied earlier [8–10]. They will be used to study the decay of donor excited state population, $N^*(t)$, as well as the quantum yield of fluorescence quenching:

$$\eta = \int_0^\infty N^*(t)dt/\tau_D = \widetilde{N}^*(0)/\tau_D. \tag{1.6}$$

In Section 3 we will consider the static quenching and then turn to the diffusion–accelerated one (Section 4). The kinetics of the reversible energy transfer, immediately following the δ-pulse excitation, will be analyzed at different ratio of forward and backward rates and the arbitrary relationship of excitation life-times. Then the same will be done in a long run taking into account the subsequent backward reaction in the bulk, proportional to the donor concentration $\rho = [D]$. The latter results in equilibration of the excited states whose final decay is the same in both theories. Their analysis and comparison is performed with a numerical program developed in Ref. [11] and the results are summarized in Section 5.

2. Integral encounter theories of energy transfer

Owing to a request for a detailed balance (1.5), the kernels of IET equations for inter-molecular energy transfer (see Eq. (3.14) in review [4]) relate to each other as $S(t) = \gamma R(t)$ [12]. This relationship allows representing these equations in the following form:

$$\dot N^*(t) = -c\int_0^t d\tau R(\tau)N^*(t-\tau) + \gamma\rho \times \int_0^t d\tau R(\tau)N_A^*(t-\tau) - \frac{N^*(t)}{\tau_D} \tag{2.1}$$

$$\dot N_A^*(t) = c\int_0^t d\tau R(\tau)N^*(t-\tau) - \gamma\rho \times \int_0^t d\tau R(\tau)N_A^*(t-\tau) - \frac{N_A^*(t)}{\tau_A}, \tag{2.2}$$

where $N^*(t) = [D^*]_t/[D^*]_0$ and $N_A^*(t) = [A^*]_t/[D^*]_0$ – the survival probabilities for the time t of excited donors and acceptors in the bulk. Such equations have been already used, employing the contact approximation: Eq. (3.127) in the same review [4]. Extending them to a distant transfer, we preserve the original IET definition of the kernel

$$\widetilde R(s) = \left(s+\frac{1}{\tau_D}\right)\int [W_F(r)\tilde\nu(r,s) - W_B(r)\tilde\mu(r,s)]d^3r, \tag{2.3}$$

via position dependent rates and the pair correlation functions. The latter obey the set of auxiliary equations:

$$\dot\nu(r,t) = -W_F(r)\nu + W_B(r)\mu + D\Delta\nu - \frac{\nu}{\tau_D},$$

$$\nu(r,0) = 1, \quad \left.\frac{\partial\nu}{\partial r}\right|_{r=\sigma} = 0 \tag{2.4}$$

$$\dot\mu(r,t) = W_F(r)\nu - W_B(r)\mu + D\Delta\mu - \frac{\mu}{\tau_A},$$

$$\mu(r,0) = 0, \quad \left.\frac{\partial\mu}{\partial r}\right|_{r=\sigma} = 0 \tag{2.5}$$

Here we imply for simplicity that the diffusion coefficients for the forward and backward reactions are the same and there is no inter–particle interaction.

The equations for modified encounter theory (MET) are almost the same, except the kernel:

$$\dot N^*(t) = -c\int_0^t d\tau R_m(\tau)N^*(t-\tau) + \gamma\rho\int_0^t d\tau R_m(\tau)N_A^*(t-\tau) - \frac{N^*(t)}{\tau_D} \tag{2.6}$$

$$\dot N_A^*(t) = c\int_0^t d\tau R_m(\tau)N^*(t-\tau) - \gamma\rho\int_0^t d\tau R_m(\tau)N_A^*(t-\tau) - \frac{N_A^*(t)}{\tau_A}, \tag{2.7}$$

The modified kernel of the integral MET equations has the following definition

$$\widetilde R_m(s) = \left[s+\frac{1}{\tau_D}+c\widetilde R(0)\right]\int [W_F(r)\tilde\nu_m(r,s) - W_B(r)\tilde\mu_m(r,s)]d^3r, \tag{2.8}$$

via the position dependent rates and the pair correlation functions. The latter obey the set of auxiliary equations:

$$\dot\nu_m(r,t) = -W_F(r)\nu_m + W_B(r)\mu_m + D\Delta\nu_m - \left[\tau_D^{-1} + c\widetilde R(0)\right]\nu_m, \tag{2.9}$$

$$\dot\mu_m(r,t) = W_F(r)\nu_m - W_B(r)\mu_m + D\Delta\mu_m - \left[\tau_A^{-1} + \gamma\rho\widetilde R(0)\right]\mu_m, \tag{2.10}$$

where the initial and boundary conditions remain the same as in IET (see Eqs. (2.4) and (2.5)). These results follow from the general matrix formulation of MET [13,14]. They make the applicability of the so modified integral theory to a higher acceptor concentration than IET. The difference between them indicates the scale of corrections at any time, giving preference to MET where they are large.

Making the Laplace transformation of Eqs. (2.1) and (2.2) or (2.6) and (2.7), one can resolve them relative to $\widetilde N^*(s)$ and $\widetilde N_A^*(s)$, getting the following results:

$$\widetilde N^*(s) = \frac{1}{s+\tau_D^{-1}+\widetilde\Sigma(s)}, \quad \widetilde N_A^*(s) = \frac{\widetilde\Sigma(s)}{\left(s+\tau_A^{-1}\right)\left(s+\tau_D^{-1}+\widetilde\Sigma(s)\right)}, \tag{2.11}$$

where the "mass operator" can be defined through the kernels $\widetilde R(s)$ (or $\widetilde R_m(s)$) of the corresponding integral equations in the following way:

$$\widetilde\Sigma(s) = \frac{c\widetilde R(s)}{1+\gamma\rho\widetilde R(s)/\left(s+\tau_A^{-1}\right)} \tag{2.12}$$

Note that the numerator of this expression represents the initial stage of the reaction (geminate stage) following the light excitation. It corresponds to the first terms in the rhs of Eqs. (2.1) and (2.2) and (2.6) and (2.7) while the term in the denominator takes into account the subsequent reaction in the bulk represented by the second terms of the same equations.

3. Static quenching

Let us turn to the solid or highly viscous solutions, where diffusion is frozen ($D = 0$). Generally speaking, IET is not applicable to such systems because the transfer there is essentially multi-particle (to all partners simultaneously), while IET is only the lowest order (binary) approximation with respect to the partner concentration c, reproducing only the short time kinetics of irreversible