

LONG-RANGE ENERGY TRANSFER IN SYSTEMS OF DIFFERENT DIMENSIONS

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The time-dependence of long-range energy transfer by dipole-dipole interaction depends on the dimension of the systems considered. This may provide a possibility to distinguish between different molecular arrangements such as spheres, discs or rods.

Introduction

The statistics of long-range energy transfer by dipole-dipole interaction from excited donor molecules to unexcited acceptor molecules was firstly treated by FÖRSTER [1] and GALANIN [2] for statistically distributed donor and acceptor molecules. Later on the influence of additional diffusion on the energy transfer was investigated by a number of authors [3, 4] and, *e.g.* applied to energy transfer ('excitons') in molecular crystals [5, 6]. In this paper we will extend the previous treatments for rigid solutions to two- and one-dimensional systems, *i.e.* for example energy transfer on surfaces or along molecular chains, respectively. It is to be expected that different dimension lead to differences in the time behaviour of the energy transfer. The following section deals with statistically distributed donors and acceptors in 'infinite' systems and the last section with single donor-acceptor pairs in finite systems of molecular dimensions. Throughout this paper we always assume that diffusion effects are negligible.

Long-range energy transfer in infinite systems of different dimensions

The time-dependence of the concentration $c_{D_m}^*$ of excited molecules (proportional to the donor fluorescence intensity) after δ -excitation may be derived from [7]

$$\frac{dc_{D_m}^*}{dt} = -n_D c_{D_m}^* - \Phi_m^s(t) c_{D_m}^*, \quad (1)$$

where n_D is the reciprocal lifetime of the donor fluorescence without energy transfer and $\Phi_m^s(t)$ is given by

$$\Phi_m^s(t) = c_A \int_0^\infty \exp[-W(r)t] a_m r^{m-1} dr. \quad (2)$$

The subscript m in Eq. (2) is the number of dimensions ($m=1, 2, 3$) of the system. The superscript s indicates that we deal with statistically distributed molecules. c_A is the volume concentration, surface concentration or linear concentration of acceptor molecules for the three-, two- or one-dimensional case, respectively. According to FÖRSTER [1, 8] the energy transfer rate $W(r)$ for dipole-dipole interaction is given by

$$W(r) = n_D \left(\frac{r_0}{r} \right)^6 = \frac{\alpha}{r^6}. \quad (3)$$

The factors a_m in (2) are

$$a_1 = 2, \quad a_2 = 2\pi \quad \text{and} \quad a_3 = 4\pi. \quad (4)$$

Evaluation of (2) and integration of (1) leads for δ -excitation of the donor molecules in the three-dimensional case to [1, 2, 6, 7]

$$c_{D_3}^*(t) = c_D^{*0} \exp \left[-n_D t - c_A \frac{4\pi}{3} (\pi \alpha t)^{1/2} \right], \quad (5)$$

in the two-dimensional case to

$$c_{D_2}^*(t) = c_D^{*0} \exp \left[-n_D t - c_A \frac{4\pi}{3} (\alpha t)^{1/3} \right], \quad (6)$$

and in the one-dimensional case to

$$c_{D_1}^*(t) = c_D^{*0} \exp \left[-n_D t - 2.26 c_A (\alpha t)^{1/6} \right]. \quad (7)$$

The acceptor fluorescences are determined by the expression

$$\frac{dc_{A_m}^*}{dt} = -n_A c_{A_m}^* + \Phi_m^s(t) c_{D_m}^*(t) \quad (8)$$

which transforms for δ -excitation of the donor molecules into

$$c_{A_m}^*(t) = \exp(-n_A t) \int_0^t \exp(n_A t') c_{D_m}^*(t') \Phi_m^s(t') dt', \quad (9)$$

where $c_{A_m}^*$ is the concentration of excited acceptor molecules. As shown in ref. [7] the differences between the acceptor fluorescences for the different dimensions are even more distinguished than those of the donor fluorescences.

Long-range energy transfer for single donor-acceptor pairs in finite systems

In this section we assume a solution which contains finite systems of molecular dimensions such as spheres, discs or rods. A number of these molecular arrangements shall be occupied by single (immobile) donor-acceptor pairs. Diffusion effects and interaction between different pairs (in different finite systems) shall be negligible. This may, e.g. be realized in micellar solutions (9, 10). If the donor-acceptor distribution in the molecular arrangements is given by a distribution function $p(r)$ with

$$\int_0^{r_{\max}} p(r) dr = 1 \quad (10)$$

(r_{\max} : maximum distance between donor and acceptor molecule in the finite system) the donor fluorescence after δ -excitation may be evaluated with

$$c_D^* = c_D^{*0} \exp(-n_D t) \int_0^{r_{\max}} \exp[-W(r)t] p(r) dr. \quad (11)$$

This has been done in Ref. [7] for various distributions $p(r)$ for both donor and acceptor fluorescences. Here we will only give approximate results for short times based on a simple analogy to the infinite systems. Since the dipole-dipole energy transfer is mainly governed by the probability of finding an acceptor molecule in the immediate surroundings of an excited donor molecule we may obtain approximate results by using the formulae for infinite system (5–7) and as an effective acceptor "concentration" 1 molecule per finite system, e.g., per sphere, disc or rod.

As a first example we treat the case of a sphere (radius R) where the donor molecule is fixed in the centre and the acceptor molecule is, on the average, equally distributed around it. With $c_A = 1/(4\pi R^3/3)$ we obtain after δ -excitation with (5) for three-dimensional energy transfer

$$c_D^* \approx c_D^{*0} \exp \left[-n_D t - \frac{1}{R^3} (\pi \alpha t)^{1/2} \right], \quad (12)$$

which should be a good approximation at least for short times. If the donor is fixed on the surface of the sphere the effective acceptor concentration must be divided by two due to obvious geometrical reasons. This leads to

$$c_D^* \approx c_D^{*0} \exp \left[-n_D t - \frac{1}{2R^3} (\pi \alpha t)^{1/2} \right]. \quad (13)$$

If both molecules, donor and acceptor, are fixed on the surface on statistical positions the energy transfer may be approximated at least in the very beginning as a two-dimensional process with an effective acceptor concentration per area $c_A = 1/(4\pi R^2)$. So we get with (6)

$$c_D^* \approx c_D^{*0} \exp \left[-n_D t - \frac{1}{3R^2} (\alpha t)^{1/3} \right]. \quad (14)$$

The same concept yields for a donor fixed in the centre of a disc (radius R) and the acceptor statistically distributed around it with $c_A = 1/(\pi R^2)$ for short times

$$c_D^* \approx c_D^{*0} \exp \left[-n_D t - \frac{4}{3R^2} (\alpha t)^{1/3} \right]. \quad (15)$$

For a rod (length L) where the donor is fixed in the middle, or at least not too near to an end of it, we obtain with the effective concentration per length $c_A = 1/L$

$$c_D^* \approx c_D^{*0} \exp \left[-n_D t - \frac{2 \cdot 26}{L} (\alpha t)^{1/6} \right]. \quad (16)$$

The formulae (12–16) are only valid for the beginning of the energy transfer. Afterwards the finite character of the systems essentially influences the kinetics of the luminescence quenching. More thorough calculations based on (11) are given in

ref. [7] especially for the acceptor fluorescences which are also in the case of finite systems more sensitive to the dimensionality of the energy transfer. As discussed extensively in this paper it is helpful for the determination of the shape of molecular arrangements, e.g., of micelles [10], to measure the time-dependence of the fluorescences of single donor-acceptor pairs affixed to the molecular systems to be investigated.

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ДАЛЬНОДЕЙСТВУЮЩИЙ ПЕРЕНОС ЭНЕРГИИ В СИСТЕМАХ РАЗЛИЧНЫХ РАЗМЕРОВ

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Зависимость дальнего действия переноса энергии от времени по механизму диполь-дипольного взаимодействия зависит от размеров исследованных систем. На основе этого возможно различить молекулярное расположение в таких системах как шары, диски и стержни.