Comment

Comment on "Energy and charge transfer in solutions. The role of donor excitation natural decay"

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A recent reanalysis by Mikhelashvili and Mikhaeli of the effect of the spontaneous decay of the donor on the kinetics of Förster's electronic energy transfer is discussed critically. It is shown that their treatment is incorrect.

1. Introduction

The standard theory for electronic energy transfer in condensed media is that of Förster and Dexter [1–3]. From it, kinetic laws for a variety of situations have been derived throughout the years (for reviews, see e.g. refs. [4–7]). In particular, the case of direct energy transfer by the dipolar mechanism in rigid media, first considered by Förster [8], has been extended by several authors [9–14].

In a recent Letter in this Journal, Mikhelashvili and Mikhaeli [15] (denoted MM) criticize a premise common to all previous treatments, namely the multiplicative nature of the intrinsic decay of the donor. In this note, it will be shown that their argument is unsound.

2. Kinetics of direct energy transfer

The donor decay law $p(t)$ for direct energy transfer in rigid solution is usually written as [14]

$$p(t)=exp\left(-\frac{t}{\tau}-N\int_0^\infty f(r)\{1-\exp[-w(r)t]\}\,dr\right), \tag{1}$$

where τ is the donor's lifetime in the absence of transfer, $f(t)$ the distance distribution function for the donor–acceptor pair, $w(r)$ the rate constant for transfer [#1] and N the number of acceptors around each donor. This expression, valid for not too high a concentration of acceptors, is to be compared with eq. (9) of MM, where $f(r)$ is missing. The same problem also occurs with all subsequent averaged decay laws, namely eqs. (13), (19) and (20) in MM's Letter. Even if one considers that

$$Nf(r)=ng(r)u(r)\,, \tag{2}$$

where n is the number density of acceptors, $g(r)$ is the radial distribution function and $U(r)$ equals 1, $2\pi r$ or $4\pi r^2$ in one, two and three dimensions, respectively, and writes

$$d\mathbf{r}=u(r)\,dr\,, \tag{3}$$

as in eqs. (13), (19) and (20) of MM's Letter, there remains a discrepancy, even assuming $g(r)=1$, as N has been substituted incorrectly for n. This is, however, a minor mistake compared to the main point raised by MM.

Eq. (1) in this Comment may be obtained from

$$\frac{dN_d(t)}{dt}=-\frac{1}{\tau}N_d(t)-w(t)N_d(t)\,, \tag{4}$$

where $N_d(t)$ is the number of excited donors and the time-dependent rate coefficient $w(t)$ is

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[#1] For simplicity the dependence on relative orientation is neglected, i.e. an isotropic mechanism is assumed.

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$$w(t)=N\int_0^\infty f(r,t)w(r)\,dr\,, \qquad (5)$$

the (time-dependent) distance distribution function $f(r, t)$ being given by

$$f(r,t)=\frac{N_a(r,t)}{\int_0^\infty N_a(r,t)\,dr}\,, \qquad (6)$$

where $N_a(r, t)$ is the total number of acceptors at a distance r from excited donors. As the disappearance of an excited donor entrains that of the acceptor partner, one has, in agreement with MM,

$$\frac{\partial N_a(r,t)}{\partial t}=-\frac{1}{\tau}N_a(r,t)-w(r)N_a(r,t)\,. \qquad (7)$$

Integration of eq. (7) yields

$$N_a(r,t)=N_a(r,0)\exp(-t/\tau)\exp[-w(r)t]\,, \qquad (8)$$

but as $N_a(r, 0)=N_0Nf(r)$, where N_0 is the initial number of excited donors, eq. (8) becomes

$$N_a(r,t)=N_0Nf(r)\exp(-t/\tau)\exp[-w(r)t]\,. \qquad (9)$$

Substitution into eq. (6) gives

$$f(r,t)=\frac{f(r)\exp[-w(r)t]}{\int_0^\infty f(r)\exp[-w(r)t]\,dr}\,. \qquad (10)$$

The denominator is close to unity for all times of interest, hence

$$f(r,t)\approx f(r)\exp[-w(r)t]\,. \qquad (11)$$

MM erroneously identify $f(r, t)$ with $N_a(r, t)$, whilst the correct result is eq. (6). As has been shown here, although $N_a(r, t)$ depends on the spontaneous decay rate, this dependence does not propagate to the time-dependent rate coefficient. While MM lead one to conclude that the number of acceptors around excited donors decreases with time, these are in fact always surrounded by N acceptors: It is only their distance distribution function that evolves with time. Eq. (1) therefore remains valid. It should also be remarked that eq. (1), a limiting case of the Golubov–Konobeev decay law [9], is not usually obtained from eqs. (4)–(6), as MM state, see refs. [9–14]. Indeed, the opposite is more correct: eqs. (4), (5) and (11) may be obtained by the differentiation of eq. (1). But it should be noted that eqs. (4) and (5) also apply to fluid media, in which case $f(r, t)$ no longer satisfies eq. (11) owing to molecular diffusion [16].

MM also claim that experimental energy transfer results yield effective critical radii R_0 higher than the spectroscopically evaluated ones by a factor of 1.16 to 1.20. This statement is questionable, as it is based only on two (1963 and 1968) references.

Since 1968, many studies showed quantitative agreement with theory (see e.g. ref. [17] for a review of some time-resolved experiments), not to mention previous work cited in refs. [3,18,19]. Although with known limitations [2–4,20], the Förster–Dexter theory has passed all experimental tests, including recent picosecond and sub-picosecond studies [21–26].

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