A linear response approach to kinetics with time-dependent rate coefficients

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Kinetics with time-dependent rate coefficients are treated by a linear response formalism. Results obtained are applied to several cases: excimer formation, relaxation after sudden perturbation and energy migration and transfer. Literature results are critically commented.

1. Introduction

Complex kinetics with time-dependent rate coefficients become of importance, because progress in experimental techniques for the study of fast chemical and photochemical processes demands increasingly sophisticated kinetic models [1–3]. Time-dependent rate coefficients arise whenever the "well-stirred reactor" assumption of classical kinetics fails. In particular, this occurs for fast contact processes such as fluorescence collisional quenching if diffusion influenced [4] and for long-range processes such as dipolar energy transfer, wich can take place even in the complete absence of molecular translational motion [4]. The notion that a time-dependent rate coefficient is a mere (hopefully useful) device that allows one to extend the use of the language of classical kinetics beyond its realm is not always appreciated, and has been the cause of errors in the treatment of complex kinetics.

Some controversy exists in the literature [5–12] concerning the use of differential equations to describe the concentration time evolution of species participating in reactions with time-dependent rate coefficients. Hauser et al. [8–10] based on the concept of convolution integral proposed several rules to calculate the time evolution profiles of the concentrations and concluded for the inapplicability of kinetic differential equations. This conclusion was criticized by Sienicki and Durocher [11], who showed that

there exists a direct relation between the convolution procedure and the differential kinetic equations, by using an ensemble average procedure. The equivalence between the differential kinetic equations and the "convolution" kinetics has already been proved, provided the appropriate rate coefficient is used [3,12].

In this work, an attempt is made to clarify what is meant by a time-dependent rate coefficient, and how it may be used within a linear response approach. The scope and limitations of the theory are examined, as well as some published treatments of complex kinetics with time-dependent rate coefficients. The structure of the article is as follows: in section 2, several schemes of increasing complexity are treated by a linear response approach. In section 3, selected applications of the developed formalism are discussed: excimer formation, relaxation kinetics and energy migration and transfer. Finally, the main conclusions are summarized.

2. Formalism

2.1. A single species

We begin by considering the time evolution of the concentration of a single species i, which may in fact exist as part of a network of kinetic processes. This

species i is produced at a rate $P_i(t)$ and disappears at a rate $k_i(t)C_i(t)$ (see scheme 1).

The main problem is to find the time evolution of C_i, i.e. $C_i(t)$. To do so, we make two assumptions: (i) when $P_i(t) = \delta(t)$, the system's response (Green's function), $f_i(t)$, is known and (ii) for a general production rate $P_i(t)$, the system behaves linearly and is stationary, therefore

$$C_i = P_i \otimes f_i, \tag{1}$$

where $\otimes$ stands for the convolution integral [#1]. The linear response assumption, that is additivity of responses to different stimuli, implies the absence of saturation effects, i.e. that one is sampling from an essentially infinite population. A material balance may be written for scheme 1,

$$\frac{dC_i}{dt} = P_i - k_i C_i. \tag{2}$$

Indeed, this is the usual approach for kinetics with time-independent rate coefficients. Here, however, one need not of course solve this equation to obtain C_i, as it is already given by eq. (1). Eq. (2) must instead be considered as the *defining equation* for $k_i(t)$.

Solving eq. (2) for k_i one obtains, with the help of eq. (1) and using eq. (A.6) (Appendix A),

$$k_i = -\frac{P_i \otimes df_i/dt}{P_i \otimes f_i}. \tag{3}$$

For δ-function production, this equation reduces to

$$k_{i\delta} = -\frac{df_i/dt}{f_i} = -\frac{d \ln f_i}{dt}, \tag{4}$$

or

$$f_i = \exp\left(-\int_0^t k_{i\delta}(u)\, du\right). \tag{5}$$

[#1] Some properties of the convolution that will be used in this work are listed in Appendix A.

Eq. (4) is the usual way of *defining* $k_{i\delta}$ [13] [#2]. Substitution of eq. (5) in eq. (3) finally yields [12,14]

$$k_i = \frac{P_i \otimes (k_{i\delta} f_i)}{P_i \otimes f_i}. \tag{6}$$

One therefore gets the somewhat unexpected result that the generalized time-dependent rate coefficient is a function of the production rate. The importance of eq. (6) becomes apparent when more than one species is considered, as will be seen below. At this point it may be remarked that use of this generalized rate coefficient allows one to extend the procedures of formal kinetics to cases where time-dependent rate coefficients are necessary. Note that k_i verifies the following two properties: (a) for $P_i(t) = \delta(t)$, $k_i(t)$ reduces to $k_{i\delta}(t)$; (b) if $k_{i\delta}(t)$ is time independent, $k_i = k_{i\delta}$ for any $P_i(t)$.

2.2. A single species with two decay channels

The situation depicted in scheme 2 is a simple extension of scheme 1, where there is now an additional decay channel, with a time-independent rate coefficient Γ_i. As it can be added to $k_i(t)$ to yield the total rate coefficient for decay, this case is expected to reduce to that of scheme 1, with a time-dependent rate coefficient $k_i'(t) = \Gamma_i + k_i(t)$. From eq. (6) one obtains

$$k_i'(t) = \frac{P_i \otimes (k_{i\delta}' f_i)}{P_i \otimes f_i}, \tag{7}$$
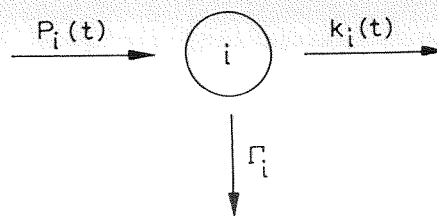
but, as $k_{i\delta}'(t) = \Gamma_i + k_{i\delta}(t)$, it indeed follows that eq. (6) continues to hold.

It is of interest to consider the steady state for this

[#2] Note that $k_{i\delta}$ can be obtained for any positive function f_i. For example if $f_i = \exp(-at - bt^{1/2})$, one obtains $k_{i\delta} = a + \frac{1}{2}bt^{-1/2}$; and if $f_i = \sum_j a_j \exp(-k_j t)$, then $k_{i\delta} = \sum_j a_j k_j \exp(-k_j t)/\sum_j a_j \exp(-k_j t)$.

Scheme 1.

Scheme 2.

scheme, i.e. the limit $t \to \infty$ for continuous production P_i. If for long time P_i stabilizes at a constant value P_i^∞, then, using eq. (A.7), eq. (1) becomes

$$C_i^{ss} = P_i^\infty \int_0^\infty f_i(u) \, du \, , \qquad (8)$$

and eq. (6) becomes

$$k_i^{ss} = \frac{\int_0^\infty k_{i\delta}(u) f_i(u) \, du}{\int_0^\infty f_i(u) \, du} \, . \qquad (9)$$

But, integrating by parts,

$$\int_0^\infty k_{i\delta}(u) f_i(u) \, du = 1 - \Gamma_i \int_0^\infty f_i(u) \, du \, , \qquad (10)$$

and hence

$$k_i^{ss} = \frac{1}{\int_0^\infty f_i(u) \, du} - \Gamma_i \, . \qquad (11)$$

### 2.3. A single species with two production modes

This case is shown in scheme 3. We consider that the time evolution of C_i is not the same for both production modes, hence two rate coefficients exist for δ-production, $k_{i\delta}^a(t)$ and $k_{i\delta}^b(t)$, and consequently,

$$f_i^a(t) = \exp\left(-\int_0^t k_{i\delta}^a(u) \, du\right) , \qquad (12a)$$

$$f_i^b(t) = \exp\left(-\int_0^t k_{i\delta}^b(u) \, du\right) . \qquad (12b)$$

The total concentration of species i can be viewed as the sum of those coming from a and b sources, viz.

$$C_i(t) = C_i^a(t) + C_i^b(t) \, , \qquad (13)$$
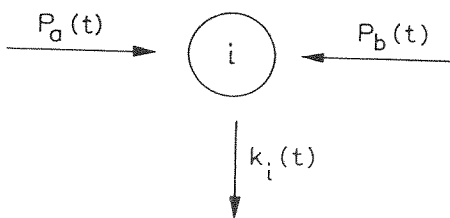
Scheme 3.

where

$$C_i^a(t) = P_a(t) \otimes f_i^a(t) \, , \qquad (14a)$$

$$C_i^b(t) = P_b(t) \otimes f_i^b(t) \, . \qquad (14b)$$

Note that eq. (13) results from a linearity *assumption*.

Again, rate coefficients k_i^a and k_i^b can be defined, and directly from eq. (6),

$$k_i^a = \frac{P_a \otimes (k_{i\delta}^a f_i^a)}{C_i^a} \, , \qquad (15a)$$

$$k_i^b = \frac{P_b \otimes (k_{i\delta}^a f_i^b)}{C_i^b} \, . \qquad (15b)$$

The overall rate coefficient k_i of scheme 3 is now *defined* by the equation

$$\frac{dC_i}{dt} = P_a + P_b - k_i C_i \, . \qquad (16)$$

But from eqs. (13) and (14), upon substitution in eq. (16),

$$\frac{d}{dt} (P_a \otimes f_i^a + P_b \otimes f_i^b) = P_a + P_b - k_i C_i \, . \qquad (17)$$

Using eq. (A.5), one obtains

$$k_i C_i = P_a \otimes (k_{i\delta}^a f_i^a) + P_b \otimes (k_{i\delta}^b f_i^b) \qquad (18)$$

and, substituting eqs. (15) into eq. (18), one finally gets

$$k_i = \frac{C_i^a}{C_i} k_i^a + \frac{C_i^b}{C_i} k_i^b \, , \qquad (19)$$

and thus k_i is the weighted average of k_i^a and k_i^b. Eq. (18) is an important relation, as it is the production term for hypothetical species j produced from species i with a rate coefficient k_i.

2.4. Sequential processes

Consider now the more complicate case of sequential kinetics as defined by scheme 4 where k_i are time dependent and $C_i(0) = 0$ ($i > 1$). The time evolution of **1** is obviously
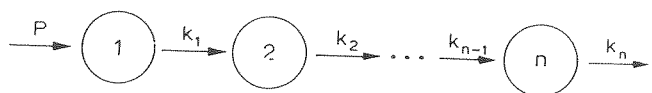
Scheme 4.

$$C_1 = P \otimes f_1 , \tag{20}$$

where

$$f_1 = \exp\left(- \int_0^t k_{1\delta}(u)\, du \right) . \tag{21}$$

The time evolution of the other species is not so easy to obtain if one reasons on the basis of formal kinetics [12]. The production rate for **2** is here clearly $k_1 C_1$, hence

$$C_2 = (k_1 C_1) \otimes f_2 , \tag{22}$$

where

$$k_1 = \frac{P \otimes (k_{1\delta} f_1)}{P \otimes f_1} \tag{23}$$

and

$$f_2 = \exp\left(- \int_0^t k_{2\delta}(u)\, du \right) . \tag{24}$$

From eqs. (20) and (23), eq. (22) finally becomes

$$C_2 = P \otimes (k_{1\delta} f_1) \otimes f_2 . \tag{25}$$

This relation is easily generalized to any n,

$$C_n = P \otimes (k_{1\delta} f_1) \otimes (k_{2\delta} f_2) \otimes \ldots \otimes f_n . \tag{26}$$

One again sees the usefulness of the concept of a generalized rate coefficient, as given by eq. (6).

2.5. Two coupled species

Consider now scheme 5 where, for simplicity, it is assumed that only k_1 is time dependent and that $C_2(0) = 0$. The relations needed for the solution of this scheme have already been obtained. For species 2, the situation is analogous to scheme 2, hence
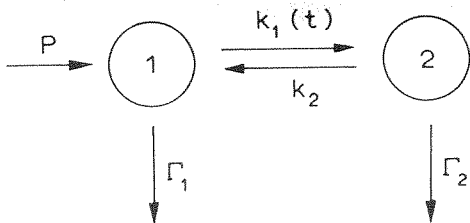
Scheme 5.

$$C_2 = (k_1 C_1) \otimes f_2 , \tag{27}$$

where

$$f_2 = \exp[- (k_2 + \Gamma_2)t] . \tag{28}$$

For species **1**, scheme 3 applies, therefore

$$C_1 = P \otimes f_1^e + (k_2 C_2) \otimes f_1^i , \tag{29}$$

where we now distinguish between the external production $(P(t))$ and internal production $(k_2 C_2(t))$ responses. The production term $k_1 C_1$ appearing in eq. (27) is given by (compare eq. (18))

$$k_1 C_1 = P \otimes k_{1\delta}^e f_1^e + k_2 C_2 \otimes k_{1\delta}^i f_1^i . \tag{30}$$

Substitution of this equation in eq. (27) yields

$$C_2 = P \otimes (k_{1\delta}^e f_1^e) \otimes f_2 + k_2 C_2 \otimes (k_{1\delta}^i f_1^i) \otimes f_2 . \tag{31}$$

The two coupled equations (29) and (31) may be solved either by Laplace transformation, yielding

$$C_1 = P \otimes f_1^e + P \otimes P' \otimes (k_{1\delta}^e f_1^e) \otimes (k_2 f_2) \otimes f_1^i , \tag{32}$$

$$C_2 = P \otimes P' \otimes (k_{1\delta}^e f_1^e) \otimes f_2 , \tag{33}$$

where P', which we shall call secondary production rate, is

$$P' = \mathcal{L}^{-1}\left[\frac{1}{1 - \mathcal{L}[k_{1\delta}^i f_1^i]\mathcal{L}[k_2 f_2]} \right] , \tag{34}$$

or, by repeatedly substituting the left side of eq. (31) in itself, giving directly the expansion of eqs. (32) and (33),

$$C_1 = P \otimes f_1^e + P \otimes (k_{1\delta}^e f_1^e) \otimes (k_2 f_2) \otimes f_1^i + P$$

$$\otimes (k_{1\delta}^e f_1^e) \otimes (k_2 f_2) \otimes (k_{1\delta}^i f_1^i) \otimes (k_2 f_2) \otimes f_1^i + \ldots , \tag{35}$$

$$C_2 = P \otimes (k_{1\delta}^e f_1^e) \otimes f_2$$
$$+ P \otimes (k_{1\delta}^e f_1^e) \otimes (k_2 f_2) \otimes (k_{1\delta}^i f_1^i) \otimes f_2$$
$$+ P \otimes (k_{1\delta}^e f_1^e) \otimes (k_2 f_2) \otimes (k_{1\delta}^i f_1^i)$$
$$\otimes (k_2 f_2) \otimes (k_{1\delta}^i f_1^i) \otimes f_2$$
$$+ \ldots . \tag{36}$$

In these expansions, each term is associated with a number n of association steps in the association-dissociation cycle, $n = 1$ for the first term, $n = 2$ for the

second term, and so on. Note that the first association step in each term always occurs through the external mode ($k_{1\delta}^e f_1^e$), while subsequent steps are described by the internal mode ($k_{1\delta}^i f_1^i$), as one should expect.

A similar kinetic scheme was already studied by Hauser et al. [5,8] and Sienicki and Winnik [15] also using convolution procedures. However, neither of the authors differentiate between the two production modes considered here and were thus unable to recover the correct time evolutions.

It is of interest to study the long-time behaviour when the production P stabilizes for $t \to \infty$, i.e., the steady-state of the system. The limits $C_1^{ss} = \lim_{t \to \infty} C_1$ and $C_2^{ss} = \lim_{t \to \infty} C_2$ can be calculated from eqs. (32) and (33) by using eq. (A.7),

$$C_1^{ss} = P_\infty \int_0^\infty f_1^e(u)\, du$$

$$+ P_\infty \int_0^\infty P'(u)\, du \int_0^\infty k_{1\delta}^e(u) f_1^e(u)\, du$$

$$\times \int_0^\infty k_2 f_2(u)\, du \int_0^\infty f_1^i(u)\, du, \qquad (37)$$

$$C_2^{ss} = P_\infty \int_0^\infty P'(u)\, du \int_0^\infty k_{1\delta}^e(u) f_1^e(u)\, du \int_0^\infty f_2(u)\, du. \qquad (38)$$

These expressions can be further simplified to (Appendix B)

$$C_1^{ss} = P_\infty \frac{k_1^{e,ss}}{k_1^{e,ss} + \Gamma_1} \frac{k_2}{k_2 + \Gamma_2} \frac{1}{k_1^{i,ss} + \Gamma_1}$$

$$\times \left(1 - \frac{k_1^{i,ss}}{k_1^{i,ss} + \Gamma_1} \frac{k_2}{k_2 + \Gamma_2} \right)^{-1}$$

$$+ P_\infty \frac{1}{k_1^{e,ss} + \Gamma_1}. \qquad (39)$$

$$C_2^{ss} = P_\infty \frac{k_1^{e,ss}}{k_1^{e,ss} + \Gamma_1} \frac{1}{k_2 + \Gamma_2}$$

$$\times \left(1 - \frac{k_1^{i,ss}}{k_1^{i,ss} + \Gamma_1} \frac{k_2}{k_2 + \Gamma_2} \right)^{-1}. \qquad (40)$$

From eq. (30) one also obtains

$$k_1^{ss} = \left(1 + \frac{1}{(1 + \Gamma_2/k_2)(1 + \Gamma_1/k_1^{i,ss}) - 1} \right)$$

$$\times \left(\frac{1}{k_1^{e,ss}} + \frac{1}{k_1^{i,ss}} \frac{1}{(1 + \Gamma_2/k_2)(1 + \Gamma_1/k_1^{i,ss}) - 1} \right)^{-1}. \qquad (41)$$

If $k_1^{i,ss} = k_1^{e,ss} = \overline{k}_1^{ss}$, eq. (41) gives simply $k_1^{ss} = \overline{k}_1^{ss}$. If $k_2 = 0$, $k_1^{ss} = k_1^{e,ss}$, as could be expected.

Consider again scheme 5, but with $\Gamma_1 = \Gamma_2 = 0$, i.e., 1 and 2 are interconverting but otherwise stable species. Suppose further that P, the external production, vanishes for long times. With these assumptions, 1 and 2 are expected to evolve towards an equilibrium. Indeed, taking the limit $t \to \infty$ on both sides of eqs. (32) and (33) gives [3]

$$C_1^\infty = P_\infty' \int_0^\infty P(u)\, du \int_0^\infty k_{1\delta}^e(u) f_1^e(u)\, du$$

$$\times \int_0^\infty k_2 f_2(u)\, du \int_0^\infty f_1^i(u)\, du, \qquad (42)$$

$$C_2^\infty = P_\infty' \int_0^\infty P(u)\, du \int_0^\infty k_{1\delta}^e(u) f_1^e\, du \int_0^\infty f_2(u)\, du, \qquad (43)$$

where (Appendix C)

$$P_\infty' = \frac{1}{1/k_2 + 1/k_1^{i,ss}}. \qquad (44)$$

Hence, using the results of Appendix B,

$$C_1^\infty = \frac{1/k_1^{i,ss}}{1/k_2 + 1/k_1^{i,ss}} \int_0^\infty P(u)\, du, \qquad (45)$$

$$C_2^\infty = \frac{1/k_2}{1/k_2 + 1/k_1^{i,ss}} \int_0^\infty P(u)\, du. \qquad (46)$$

In this way, one has, in the equilibrium, the familiar form

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[3] In this case $P'(t)$ goes to a constant, nonzero value as $t \to \infty$ (Appendix C), hence $\int_0^\infty P'(u)\, du$ will diverge. The order of P and P' is therefore reversed before applying property (A.7) of convolution.

$$k_1^{i,ss} C_1^\infty = k_2 C_2^\infty , \qquad (47)$$

and $k_1^{i,ss}$ is the equilibrium value of the global rate coefficient $k_1(t)$, that is $k_1^\infty = k_1^{i,ss}$, as can be checked directly from eq. (30) or (41).

Suppose now that the system, initially in the equilibrium state obtained before is suddenly perturbed, and thus forced to evolve to a new equilibrium.

We now describe its evolution for that case, and start by noting that **1** and **2** exist in initial concentrations C_1^0 and C_2^0. The appropriate evolution equations are

$$C_1 = C_1^0 \delta \otimes f_1^e + k_2 C_2 \otimes f_1^i , \qquad (48)$$

$$C_2 = C_2^0 \delta \otimes f_2 + k_1 C_1 \otimes f_2 , \qquad (49)$$

where (compare eq. (18))

$$k_1 C_1 = k_2 C_2 \otimes k_{1\delta}^i f_1^i + C_1^0 \delta \otimes k_{1\delta}^e f_1^e . \qquad (50)$$

The use of f_1^e as the response function for the pre-existent **1** molecules, in concentration C_1^0, will be justified in section 3. Solution of the system (48)–(50) is

$$C_1 = C_1^0 \delta \otimes f_1^e + C_1^0 \delta \otimes P' \otimes (k_{1\delta}^e f_1^e) \otimes (k_2 f_2) \otimes f_1^i$$
$$+ C_2^0 \delta \otimes P' \otimes (k_2 f_2) \otimes f_1^i , \qquad (51)$$

$$C_2 = C_1^0 \delta \otimes P' \otimes (k_{1\delta}^e f_1^e) \otimes f_2 + C_2^0 \delta \otimes P' \otimes f_2 , \qquad (52)$$

where $P'(t)$ is given by eq. (34).

The equilibrium concentrations are obtained as before, the final results being

$$C_1^\infty = \frac{1/k_1^{i,ss}}{1/k_2 + 1/k_1^{i,ss}} (C_1^0 + C_2^0) , \qquad (53)$$
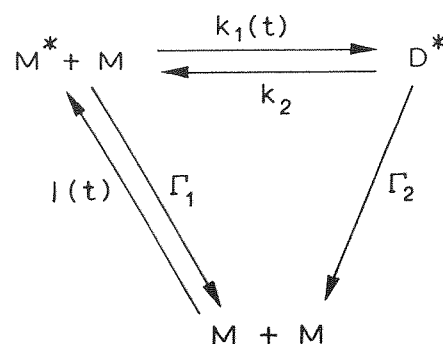
$$C_2^\infty = \frac{1/k_2}{1/k_2 + 1/k_1^{i,ss}} (C_1^0 + C_2^0) , \qquad (54)$$

where again $k_1^{i,ss} = k_1^\infty$.

3. Selected applications

3.1. Monomer–excimer kinetics

Intermolecular excimer formation kinetics in solution can be represented by the mechanism of scheme 6, where the electronically excited monomer (M*), produced at a rate $I(t)$, may decay towards

Scheme 6.

the ground state at an intrinsic rate $\Gamma_1 = 1/\tau_1$, τ_1 being the monomer lifetime, or may react with an unexcited monomer (M) by a diffusion-influenced process to yield the excimer (D*). This may reverse back to the excited-plus-unexcited pair of monomers with rate constant k_2 or decay at an intrinsic rate $\Gamma_2 = 1/\tau_2$, τ_2 being the excimer lifetime, to yield two ground state monomers. In general, photon density is such that $[M^*] \ll [M]$, and the excimer formation process is pseudo-unimolecular. The forward rate coefficient k_1 is in general time dependent owing to the time evolution of the distribution function of M around M*. Two distinct production modes exist for the excited monomer: light absorption and excimer dissociation. Excitation by photon absorption is a spatially random sampling process, and therefore ground state monomers are uniformly distributed around the excited one in the absence of short range potentials. On the other hand, excimer dissociation produces a highly non-uniform distribution, mainly as a consequence of the existence of a ground state monomer close to the excited one, former partner in the excimer. Nevertheless, there exists a background distribution superposed on this monomer. This distribution is not the same for all excited monomers produced by excimer dissociation. Indeed, it will be close to uniform for the first excimers formed but less so as time progresses. On the other hand, the average waiting time between excimer formation and dissociation (excimer effective lifetime $(k_2 + \Gamma_2)^{-1}$) allows some evolution of the background distribution towards the uniform one. An exact treatment of this aspect appears to be very difficult. Application of the linear response approach requires the system response to be the same for a given production act: in this case, one should have the same distribution every

time the excimer dissociates. The application of the linear response formalism to monomer–excimer kinetics will thus rest on an approximation: the background distribution is assumed to be always uniform. One should note that this approximation is reasonable: for concentrated solutions, monomer depletion is not very important, and the uniformity assumption holds; for dilute solutions, the background is negligible compared with the nearest-neighbour contribution [3,16]. There is now (limited) experimental evidence that this approximation does not substantially prevent the applicability of the linear response approach to monomer–excimer kinetics [17]. In this way, monomer–excimer kinetics is well described by the results obtained for scheme 5 in the previous section, where we identify the external production mode with light absorption and the internal production mode with excimer dissociation, species 1 with excited monomer and species 2 with the excimer. Time-resolved observables, including the derivation of expressions for $f_1^e(t)$ and $f_1^i(t)$, have been fully treated elsewhere [3,16]. Eqs. (39)–(41) of this work complement these, as they pertain to the steady-state experiment.

3.2. Relaxation kinetics

We now turn to ground-state reactions, specifically the disturbance of a state of dynamic equilibrium by a sudden perturbation (T-jump, P-jump, etc). The system will thus evolve (relax) towards a new state of equilibrium. For the simple equilibrium $A \rightleftharpoons C$ this is the case that was treated in section 2.5, where $A \rightarrow C$ is pseudo-unimolecular and diffusion influenced and $C \rightarrow A$ is truly unimolecular, that is, the complete equilibrium is $A + B \rightleftharpoons C$, where $[B] \gg [A]$ and thus incorporated in the forward rate coefficient. The survival probability $f_1^e(t)$ will in this case correspond to the unperturbed initial equilibrium distribution of B-type molecules around A-type molecules, not necessarily a uniform one. On the other hand, $f_1^i(t)$ corresponds to the geminate pair A, B at the encounter distance plus a background that again is the unperturbed equilibrium distribution only at time zero. The formal time evolution equations for this problem are eqs. (51) and (52), and for the new equilibrium state eqs. (53) and (54). One thus obtains for the equilibrium constant

$$K = \frac{k_1^{i,ss}}{k_2}, \tag{55}$$

where

$$k_1^{i,ss} = \frac{\int_0^\infty k_1^i(t) f_1^i(t)\, dt}{\int_0^\infty f_1^i(t)\, dt} = \frac{1}{\int_0^\infty f_1^i(t)\, dt}. \tag{56}$$

For a given initial background distribution one has [3,16]

$$f_1^i(t) = \frac{k_{1\delta}(t)}{k_{1\delta}(0)} f_1^e(t), \tag{57}$$

where $k_{1\delta}(t)$ is the Collins–Kimball rate coefficient and $k_{1\delta}(0) = k_a[B]$, k_a being the intrinsic (chemical) bimolecular rate constant and $[B]$ the concentration of B, hence

$$k_1^{i,ss} = \frac{k_a[B]}{\int_0^\infty k_{1\delta}(t) f_1^e(t)\, dt}. \tag{58}$$

If the initial background concentration is uniform, then

$$f_1^e(t) = \exp\left(-\int_0^t k_{1\delta}(u)\, du \right) \tag{59}$$

and the forward rate constant at the new state of equilibrium becomes

$$k_1^{i,ss} = k_a[B], \tag{60}$$

whereas the equilibrium constant is

$$K = \frac{k_a[B]}{k_2}, \tag{61}$$

as found by Keizer [18]. Nevertheless, it should be stressed that the present treatment contains an important simplification, i.e., the assumption that, after each dissociation step $C \rightarrow A + B$, the background concentration is that of the initial equilibrium state. This approximation should be a reasonable one for small perturbation that will not strongly affect concentration radial profiles.

3.3. Energy migration and transfer

The kinetics of electronic energy transfer in condensed matter has been recently treated by the linear response approach [12] or an equivalent theory [19–

22]. The simplest case is that of sequential, irreversible transfer, to which the results given in section 2.4 directly apply. If the entities participating in scheme 5 are regarded as sucessive generations of the same species, the process described is pure energy migration, and summing the concentration of all generations one finds that the global decay is not affected by the existence of migration amongst the molecules [19], as originally obtained by Förster from the master equation [23]. A more demanding case is that represented by scheme 7, where energy migration and energy transfer coexist. Excited donors D, produced at a rate $P(t)$ may transfer energy to acceptors with a time dependent rate coefficient k_{DA} or may transfer energy amongst themselves with a time-dependent rate coefficient k_{DD}. A third decay channel is the intrinsic unimolecular decay, with a time-independent rate constant Γ_D. Using the results obtained in section 2, the concentration of the successive generations of D molecules is given by

$$D_1 = P \otimes f, \tag{62}$$

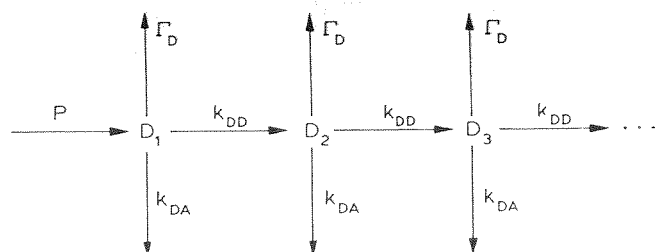$$D_2 = P \otimes (k_{DD} f) \otimes f, \tag{63}$$

$$D_3 = P \otimes (k_{DD} f) \otimes (k_{DD} f) \otimes f, \tag{64}$$

etc., where the survival probability is

$$f(t) = \exp(-\Gamma t) \exp\left(-\int_0^t k_{DA}(u)\,du\right)$$

$$\times \exp\left(-\int_0^t k_{DD}(u)\,du\right). \tag{65}$$

Summing all generations, one obtains for the global concentration of D molecules

$$D = P \otimes P' \otimes f, \tag{66}$$

Scheme 7.

where

$$P' = \mathscr{L}^{-1}\left[\frac{1}{1 - \mathscr{L}[k_{DD} f]}\right]. \tag{67}$$

Eq. (66) was obtained by Sienicki and Winnik [19], and describes the fluorescence decay of the donor species in the presence of migration and transfer to an acceptor species. Its formal simplicity and compactness are remarkable, as compared with the results of other models [24,25]. In a subsequent paper, Sienicki and Mattice [20] attempted a refined version of the original treatment that "accounts for the correlations between molecules". We believe their result to be incorrect, owing to a misinterpretation of the linear response treatment. Indeed, the survival probability $f(t)$ that should be used always refers to the system *without feedback* (see section 2), while the improved survival probabilities considered in ref. [20] result from it. Indeed, it is eq. (66) that has to be compared with the probability of residence of excitation in the donor's ensemble computed from LAF theory [24]. Therefore it is incorrect to state that the return of excitation should be incorporated in $f(t)$, as stated in refs. [19,20]. It should also be noted that no approximations are involved in scheme 7 beyond the assumption that the rate coefficients $k_{DD}(t)$ and $k_{DA}(t)$ are the same for all generations. Indeed, only if every jump resets the system (on the average), do the rate coefficients remain unchanged. This is not totally correct, but should hold at least for k_{DD} comparable to, or larger than, k_{DA}.

The process of energy migration can be monitored through the fluorescence anisotropy decay. The anisotropy of indirectly excited donor molecules is usually negligible [26], and owing to the additive nature of this observable, the overall anisotropy is simply the initial one times the probability that the excitation is on first-generation molecules. It is not easy to compute this probability within linear response theory. In fact, the successive generations considered in schemes 4 and 7 may contain the same molecules, as excitation returns many times to a given site. Therefore, a generation is a mixture of sites previously visited a variable number of times, and the original sites cannot be separately counted.

Sienicki, Itagaki and Mattice have recently proposed a model for depolarization of the fluorescence

based on a generalization of the arguments used for the derivation of eq. (66) [21]. A serious objection to their treatment is on the validity of the linear response assumption. That assumption breaks down in this case when applied to macroscopic populations, as we shall prove. The above mentioned authors consider, for instance, that for a pair ensemble, the sequence of scheme 8, where D_1 are the directly excited molecules and D_2 the indirectly excited ones, leads to the following time evolution for $D_1^{(2)}$,

$$D_1^{(2)} = P \otimes (k_{DD}f) \otimes (k_{DD}f) \otimes f, \qquad (68)$$

where $f(t)$ is the survival probability (eq. (65) with $k_{DA} = 0$ and $\Gamma = 0$). This result is no longer valid since a distribution of distances $g(r)$ is considered. Indeed, the correct result is

$$D_1^{(2)}(t) = \int\limits_0^\infty g(r) D_1^{(2)}(r, t)\, dr, \qquad (69)$$

where

$$D_1^{(2)}(r, t) = P \otimes [k_{DD}(r)f(r, t)]$$
$$\otimes [k_{DD}(r)f(r, t)] \otimes f(r, t), \qquad (70)$$

which is different from eq. (68), where $k_{DD}(t)$ and $f(t)$ are pre-averaged quantities,

$$k_{DD}(t) = \int\limits_0^\infty g(r)f(r, t)k_{DD}(r)\, dr, \qquad (71)$$

$$f(t) = \int\limits_0^\infty g(r)f(r, t)\, dr, \qquad (72)$$

that is, the distance average integral and the convolution integrals cannot, in general, be interchanged. For the general case, the decay should be written

$$D_1^{(2)}(t) = \int\limits_0^\infty \int\limits_0^\infty \int\limits_0^\infty g(r_1, r_2, r_3)$$
$$\times D_1^{(2)}(r_1, r_2, r_3, t)\, dr_1\, dr_2\, dr_3, \qquad (73)$$

where

Scheme 8.

$$D_1^{(2)}(r_1, r_2, r_3, t) = P \otimes [k_{DD}(r_1)f(r_1, t)]$$
$$\otimes [k_{DD}(r_2)f(r_2, t)] \otimes f(r_3, t). \qquad (74)$$

If the hops are uncorrelated, as in scheme 4,

$$g(r_1, r_2, r_3) = g(r_1)g(r_2)g(r_3), \qquad (75)$$

$g(r)$ being the common density function for a uniform distance distribution, and eq. (68) is obtained from eq. (73). If on the other hand, hops are correlated, the distances are no longer independent. In the case of molecular pairs, the distance is the same for all jumps, therefore

$$g(r_1, r_2, r_3) = g(r_1)\delta(r_2 - r_1)\delta(r_3 - r_1), \qquad (76)$$

and eqs. (69) and (70) are obtained, instead of eq. (68). One may note that Huber's pair model invoked in ref. [21] precisely results from approximate averaging over the distance in a manner similar to that of eq. (69) [27]. The objection raised also applies to the results of ref. [22].

4. Summary and conclusions

A linear response approach is applied to kinetics with time-dependent rate coefficients, and its scope and limitations are discussed. Several important applications are examined, including excimer formation, relaxation kinetics, and energy migration and transfer. The formalism developed, although with some limitations for cases with feedback, allows to extend the simple macroscopic formalism of classical kinetics to complex, important situations.

Acknowledgement

Appendix A. Some properties of the convolution integral

In this Appendix, several useful properties of the

convolution integral are given. Properties 1–4 are found in most mathematical handbooks and are included here for completeness only.

The convolution between two functions $f(t)$ and $g(t)$, $f \otimes g$ is defined by

$$f \otimes g = \int_0^t f(t-u)g(u)\, \mathrm{d}u \,. \tag{A.1}$$

The following properties are obeyed by the convolution:

1. Commutativity:

$$f \otimes g = g \otimes f \,. \tag{A.2}$$

2. Associativity:

$$(f \otimes g) \otimes h = f \otimes (g \otimes h) \,. \tag{A.3}$$

3. Neutral element:

$$f \otimes \delta = f \,. \tag{A.4}$$

4. Laplace transform:

$$\mathscr{L}[f \otimes g] = \mathscr{L}[f]\mathscr{L}[g] \,. \tag{A.5}$$

5. Derivative:

$$\frac{\mathrm{d}}{\mathrm{d}t}(f \otimes g) = f \otimes \frac{\mathrm{d}g}{\mathrm{d}t} + g(0^+)f \,. \tag{A.6}$$

6. Long-time limit:

$$\lim_{t \to \infty} f \otimes g \otimes \dots \otimes z = f(\infty) \int_0^\infty g(u)\, \mathrm{d}u \dots \int_0^\infty z(u)\, \mathrm{d}u \,. \tag{A.7}$$

Appendix B. Steady-state values for scheme 5

Eqs. (33) and (34) may be simplified by using expressions analogous to eqs. (10) and (11),

$$\int_0^\infty k_{1\delta}^{\mathrm{e}}(u)f_1^{\mathrm{e}}(u)\, \mathrm{d}u = 1 - \Gamma_1 \int_0^\infty f_1^{\mathrm{e}}(u)\, \mathrm{d}u \,, \tag{B.1}$$

$$\int_0^\infty f_1^{\mathrm{e}}(u)\, \mathrm{d}u = \frac{1}{k_1^{\mathrm{e,ss}} + \Gamma_1} \,, \tag{B.2}$$

$$\int_0^\infty f_2(u)\, \mathrm{d}u = \frac{1}{k_2 + \Gamma_2} \,, \tag{B.3}$$

$$\int_0^\infty f_1^{\mathrm{i}}(u)\, \mathrm{d}u = \frac{1}{k_1^{\mathrm{i,ss}} + \Gamma_1} \,, \tag{B.4}$$

and by noting that

$$\int_0^\infty P'(u)\, \mathrm{d}u = \mathscr{L}[P'(u)]_{s=0}$$

$$= \left(1 - \int_0^\infty k_{1\delta}^{\mathrm{i}}(u)f_1^{\mathrm{i}}(u)\, \mathrm{d}u \int_0^\infty k_2 f_2(u)\, \mathrm{d}u \right)^{-1}, \tag{B.5}$$

or, using eqs. (B.1)–(B.3),

$$\int_0^\infty P'(u)\, \mathrm{d}u = \left(1 - \frac{k_1^{\mathrm{i,ss}}}{k_1^{\mathrm{i,ss}} + \Gamma_1} \frac{k_2}{k_2 + \Gamma_2}\right)^{-1} \tag{B.6}$$

Substitution of these relations in eqs. (37) and (38) yields (39) and (40).

Appendix C. Evaluation of $\lim_{t \to \infty} P'(t)$

The secondary production rate $P'(t)$ is given by eq. (34),

$$P'(t) = \mathscr{L}^{-1}\left[\frac{1}{1 - \mathscr{L}[k_{1\delta}^{\mathrm{i}}f_1^{\mathrm{i}}]\mathscr{L}[k_2 f_2]}\right]. \tag{C.1}$$

In order to evaluate $\lim_{t \to \infty} P'(t)$ one uses the final value theorem of Laplace transform theory,

$$\lim_{t \to \infty} P'(t) = \lim_{s \to 0} s\mathscr{L}[P'(t)] \,, \tag{C.2}$$

or from eq. (C.1)

$$P'_\infty = \lim_{t \to \infty} P'(t) = \lim_{s \to 0} \frac{s}{1 - \mathscr{L}[k_{1\delta}^{\mathrm{i}}f_1^{\mathrm{i}}]\mathscr{L}[k_2 f_2]} \,, \tag{C.3}$$

but

$$\lim_{s \to 0} \mathscr{L}[k_{1\delta}^{\mathrm{i}}f_1^{\mathrm{i}}] = \lim_{s \to 0} \int_0^\infty \mathrm{e}^{-su} k_{1\delta}^{\mathrm{i}}(u)f_1^{\mathrm{i}}(u)\, \mathrm{d}u \,, \tag{C.4}$$

$$\lim_{s \to 0} \mathscr{L}[k_2 f_2] = \lim_{s \to o} \int_0^\infty e^{-su} k_2 f_2(u) \, du . \qquad (C.5)$$

Using the linear approximation, valid for small s,

$$e^{-su} \approx 1 - su , \qquad (C.6)$$

one obtains, retaining only the terms linear in s,

$$P'_\infty = \lim_{s \to 0} s$$

$$\times \left\{ 1 - \left(\int_0^\infty k_{1\delta}^i(u) f_1^i(u) \, du \right) \left(\int_0^\infty k_2 f_2(u) \, du \right) \right.$$

$$+ s \left[\left(\int_0^\infty k_{1\delta}^i(u) f_1^i(u) \, du \right) \left(\int_0^\infty u k_2 f_2(u) \, du \right) \right.$$

$$\left. \left. + \left(\int_0^\infty u k_{1\delta}^i(u) f_1^i(u) \, du \right) \left(\int_0^\infty k_2 f_2(u) \, du \right) \right] \right\}^{-1} .$$

$$(C.7)$$

If $\Gamma_1, \Gamma_2 > 0$, $P'_\infty = 0$; if $\Gamma_1 = \Gamma_2 = 0$ one has (see Appendix B)

$$\int_0^\infty k_{1\delta}^i(u) f_1^i(u) \, du = \int_0^\infty k_2 f_2(u) \, du = 1 , \qquad (C.8)$$

hence

$$P'_\infty = \left(\int_0^\infty u k_2 f_2(u) \, du + \int_0^\infty u k_{1\delta}^i(u) f_1^i(u) \, du \right)^{-1} .$$

$$(C.9)$$

Integrating by parts one finally obtains

$$P'_\infty = \frac{1}{1/k_2 + 1/k_1^{i,ss}} . \qquad (C.10)$$

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