FLUORESCENCE AND THE KINETICS OF EXCITED SINGLET STATES

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This lecture is dedicated to Professor A. Weller on the occasion of his 60th birthday

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Four basic rules for treating the kinetics of processes in the first excited singlet state are given. General formulae for investigating the responses of stationary, phase fluorometric, δ-flash and general time dependent excitation are derived for systems with one and two excited species.

The breakdown of usual kinetic concepts in cases of time dependent rate factors, especially Förster—Galanin type energy transfer and nonstationary diffusion, is briefly demonstrated and a novel kinetic procedure, called convolution kinetics is given in three rules. — Dynamic tests and examples for calculations of the new kinetics (excimer as donor, multistep and two step energy transfer) are reported.

0. Introductory considerations

The spectroscopic significance of molecular fluorescence may be poor enough to justify its usual treatment as an appendix to general optical spectroscopy, as it has to do essentially with the longest wavelength singlet-singlett transition only. Most of the interesting phenomena in connexion with fluorescence refer to the time behaviour of molecular ensembles. It is the aim of this lecture to show that fluorescence phenomena can be treated in terms of chemical kinetics.

0.1 Generation and deactivation of exited molecules

In accordance with Vavilov's law each absorbed light quantum transfers one molecule in its *f*irst *e*xcited *s*inglet state, which happens within a negligibly short time, of, say, 10^{-23} s; the very few exceptions need not be mentioned. Chemically speaking, a 'jump' from a minimum of the ground state hypersurface to a minimum of the FES (abbreviation for 'first excited singlet state') and from one thermally equilibrated state to the other, takes place. The detailed mechanism of the various ultrafast processes incorporated in that 'Vavilov-jump' $S_v \rightarrow S_1^*$ cannot yet quantitatively be elucidated in cases of practical importance, as subpicosecond kinetic spectroscopy is at its very beginning. In the following we deal with the FES of various species A, B, ...which we denote A^*, B^*, ... omitting the suffix.

After the Vavilov-jump of a species $A \rightarrow A^*$, say, the various processes appearing in Jablonski's term scheme can take place, namely spontaneous emission (SE),

intersystem crossing (ISC), and internal conversion (IC). From the 'Jablonski-processes' only the SE: $A^* \xrightarrow{n_e} A + h\nu$ is of fundamental necessity marking the upper limit to the lifetime τ of species in the FES: $\tau = 1/n_e \leqq 10^{-6}$ s*). The significance of IC with rate constant n_1 and ISC with rate constant n_{ST} may vary from case to case depending on conditions. Besides the conditional IC and ISC there is a wealth of other conditional processes or types of physicochemical behaviour which may be classified by the keywords 'photochemistry' and 'energy transfer'. The range of rates of 'conditional' processes starting from the FES is between 'negligible' and 'widely outdoing' compared to the rate n_e of 'necessary' SE.

0.2 Photochemical processes

[1] Chemical reactions in the ground state correspond to movements along reaction pathways on the ground state hypersurface. The energy of cols between the minima corresponding to different chemical species has to do with the activation energy. Usually, species are in thermal equilibrium and need activation energy to undergo chemical change. It is perhaps one of the important features of the FES that quite analogously to the ground state there is a FES-hypersurface with almost the same conditions for chemical processes as in the ground state. But in many cases the FES-reactivities are higher because of higher electronic energy content from which lower activation energies E_a^* may result. But the complexity of chemical behaviour is drastically reduced in the FES compared to the chemistry in the ground state or even in the (longer lived) excited triplet state. We only need consider

0.21 Monomolecular processes, for instance

dissociation $A^* \xrightarrow{n_d} P^* + Q$
isomerization $A^* \rightarrow B^*$

0.22 Bimolecular processes such as

association $A^* + B \xrightarrow{k_a} (AB)^*$
quenching $A^* + Q \rightarrow A + Q$
collisional energy transfer

$$A^* + B \rightarrow A + B^*$$

(Förster type transfer needs particular kinetic treatment.) All these processes except quenching can be thought of as movements on the same FES-hypersurface being called adiabatic as energy changes smoothly and moderately, excitation being essentially conserved. The Jablonski-processes, however, though being monomolecular, too, are connected with discontinuous transitions between different hypersurfaces as is quenching (probably); this behaviour is called diabatic.

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* If no measuring value n_e is available, a crude estimate is given by Ladenburg's formula $n_e \approx 1{,}5 n \bar{\nu}^2 \cdot f$
(n refractive index, $\bar{\nu}$ center of gravity wave number of fluorescence spectrum, f oscillator strength of longest wavelength absorption transition).

1. The four rules of FES-kinetics

There are 4 rules necessary to deal quantitatively with FES-kinetics and to investigate it with the aid of fluorescence. The first rule was introduced already in the context of the Vavilov-jump and will only be repeated here. A second rule follows from that all bimolecular processes in FES are practically exactly pseudo first order. This is because all concentrations of excited species A^*, B^*, ... are so small that the concentrations of unexcited partners must be very much larger and thus can be taken together with the bimolecular rate constant k_a to get a brutto first order rate constant $k_a \cdot [P]$ comparable to n_e (of SE). All monomolecular processes are of the first order per se, ergo ... (see below).

A third rule follows from the fact that light intensities from conventional sources are small (it is not valid with high power laser excitation).

1st rule: Each absorbed light quantum transfers a molecule to its first excited singlet state;

2nd rule: All processes starting from the first excited singlet state are of the first order;

3rd rule: All concentrations of unexcited species are taken to be constant in kinetics of first excited singlet state.

These three rules usually suffice to write down the kinetic (simultaneous first order) differential equations of a FES-reaction scheme, which either must be given or is constructed for trial. The fourth rule is necessary for the understanding of fluorescence. It may be derived as follows:

Suppose a complex reaction mechanism be given (not necessarily in the FES). Looking at some part of it we may see educts, intermediates, products and forward and backward reaction steps

$$\begin{array}{c} \ldots U \rightleftharpoons V+W \rightleftharpoons X+\ldots \\ \Big\downarrow k_y \\ Y+Z \end{array}$$

From a certain species V, say, may start a first order process with rate constant k_y one of the products of which, Y, is not produced otherwise. Then if it is possible to measure the rate of production of Y

$$\frac{d[Y]}{dt} = k_y[V]\left(= -\frac{\delta_y[V]}{dt}\right),$$

we see that we thus can know $[V]$ at any instant of time! This is valid irrespective of all other processes which may influence $[V]$ (the process with k_y is only one of which and thus is denoted by δ_y). In FES kinetics all processes are of the first order. Thus, instead of considering the concentrations $[U]$, $[V]$, $[Y]$, ... we may write in the same equations the amounts (=numbers of species or moles in the reaction vessel) denoted by $\langle U\rangle$, $\langle V\rangle$, $\langle Y\rangle$, ... In case of the 'reaction SE': $A^* \xrightarrow{n_e} A + h\nu$, we may identify A^* with V and $h\nu$ with Y (the fluorescence quanta of A^* will not be produced otherwise). While it would be difficult to measure the rate of photochemically produced A, it is easy to measure the number of light quanta escaping from the vessel ... It is the total

quantum flux which in principle we get by measuring the fluorescence intensity on all elements of a closed surface surrounding the cuvette.

4th rule: The fluorescence flux (=integral intensity over a closed surface surrounding the fluorescence cuvette) of a species is at any time *equal* to the number of corresponding excited species (in FES) times its spontaneous emission rate constant.

If only a spectral or spatial fraction of fluorescence is measured, rule 4 is valid with 'proportional' instead of 'equal'. In general it is a serious mistake (made even by well-known scientists) to say that fluorescence intensity be proportional to the "concentration" of excited species: This statement is as wrong as the claim that radioactivity be given by the "concentration" of active matter. Really in both cases it is the amount or number of species considered**). Really we ought to be sure that our fluorescence spectrometer measures the integral of excited species' concentration distribution over the sample space and not its concentration, which is a complicated function of exitation geometry etc. in most cases (!) This function must be known if reabsorption cannot be neglected.

1.1 Simple applications of rules 1—4.

If only one excited species is present (namely in the absence of adiabatic photoreactions) we get according to rules 1—3

$$\frac{d\langle A^*\rangle}{dt} = -n\langle A^*\rangle + I_a(t) \tag{1}$$

where $$n = \sum n_i = n_e + n_{ST} + \ldots + n_a[P] + \ldots \tag{2}$$

The solution function $\langle A^*\rangle(t)$ depends strongly on $I_a(t)$, the time dependence of excitation. The most simple case to realize is:

1.1.1. The photostationary state

If $I_a = I_{as}$ = constant and $t \to \infty$ we get from Eq. (1)

$$\langle A^*\rangle_s = \frac{I_{as}}{n} \tag{3}$$

from which follows the stationary fluorescence flux F_s when applying the 4th rule

$$F_s = n_e\langle A^*\rangle_s = \frac{n_e}{n} I_{as}. \tag{3a}$$

** Perhaps we can understand the 4th rule better from $\operatorname{div} \vec{f}_A = -\frac{\delta_e[A^*]}{dt}$ where $\vec{f}_A$ is the fluorescence intensity (=flux density) vector, and the right hand side represents the time change of concentration $[A^*]$ by emission. Applying Gauss' theorem we see that the flux F_A (=surface integral of $\vec{f}_A$) is found by integration of concentration over the space giving $\frac{\delta_e}{dt}\int [A^*]\,dv = -\frac{\delta_e\langle A^*\rangle}{dt}$ which is $= n_e\langle A\rangle^*$ according to our above reasoning. Our 'divergence principle of fluorescence' may also not be very familiar to spectroscopists, but is in accordance with general principles.

In the stationary state, the fluorescence quantum yield $\Phi = \frac{n_e}{n} = \frac{F_s}{I_{as}}$ can be determined from the fluxes (intensities) F_s and I_{as}. Inserting Eq. (2) in Eq. (3) and marking entities referring to concentration of partner or quencher $[P]=0$ by index 0, we get the Stern—Volmer—Eq.

$$\frac{\langle A^* \rangle_{so}}{\langle A^* \rangle_s} = \frac{F_{so}}{F_s} = 1 + \frac{n_a}{n_o}[P]. \tag{4}$$

While the absolute measurement of quantum yield Φ needs 'integrating photometry' with respect to direction and wavelength, a Stern—Volmer plot needs only a spatial and/or spectral fraction of F_s, or an instrumental signal, provided the over all proportionality factors do not vary with concentration $[P]$. In the case of several quenchers all the concentrations except one must be constant.

1.1.2. The δ-excitation

The solution of Eq. (1) in the case that $I_\delta = \delta(t-O)$ is called the δ-response $\langle A^* \rangle_\delta$.

$$\delta(t-o) = o \text{ if } t \neq o \text{ but } \int_{o+\varepsilon}^{o+\varepsilon} \delta(t-o)\,dt = 1$$

ε is an arbitrarily small number. For many reasons we make use of Laplace transform. If we denote $\mathbf{L}\langle A^* \rangle_\delta = y_0$, $\mathbf{L}t = x$, with $\mathbf{L}\delta(t-O) = 1$, the transformed Eq. (1) reads

$$y_o x = -n y_o + 1; \; y_o = (x+n)^{-1}.$$

The backward transform yields $\mathbf{L}^{-1} y_\delta = \langle A^* \rangle_\delta = e^{-nt}$ for $t > O$ and $\langle A^* \rangle_\delta = O$ for $t < O$.
The δ-response according to Eq. (6) is typical for a directly excited species without population by other processes, while a linear Stern—Volmer plot is not, as it may result from more complicated mechanisms, too.

1.1.3. Arbitrary time dependence of excitation

Analogously to δ-excitation we get by Laplace transform if $\mathbf{L}\langle A^* \rangle = y$ and $\mathbf{L}I_a = J$: $y = (1+n)^{-1} \cdot J$. The transform of the δ-response is multiplied with the transform of I_a. Applying the rule for backward transform of a product we get

$$\langle A^* \rangle = \langle A^* \rangle_\delta * I_a = I_a * \langle A^* \rangle_\delta = \int_{\vartheta=o}^{t} I_a(t-\vartheta)\langle A^* \rangle_\delta(\vartheta)\,d\vartheta. \tag{7}$$

The response on arbitrary excitation is given by the convolution 'product' of δ-response and excitation function. As this can be performed for any $I(t)$, obviously all kinetic information is contained in $\langle A^* \rangle_\delta$. No other choice of I_a can give additional knowledge.

1.1.4. The phase fluorimeter response (= Fourier transform of δ-response)

In this case

$$I_a = I_{as}(1+q\cos\omega t), \text{ resp. } I_{as}(1+qe^{i\omega t}), \tag{8}$$

where $o \leqq q \leqq 1$. Again one looks at the behaviour for $t \to \infty$.

By inserting Eq. (8) in Eq. (7) we can convince ourselves that the corresponding $\langle A^* \rangle_P$ is the Fourier transform of $\langle A^* \rangle_\delta$. This is important because excitation of the form Eq. (8) can be realized with much better approach to ideality than δ-excitation and the strain of the system by light intensity may be kept much smaller.

The mathematical procedure of $\langle A^* \rangle_P$ calculation is extremely simple, namely almost the same as in the photostationary state. Allowing for the time-dependent term in Eq. (8), n merely has to be replaced with $(n+i\omega)$ where the factor $e^{i\omega t}$ appears. The result may be written in the form

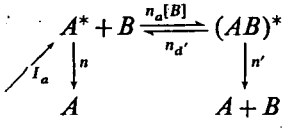
$$\langle A^* \rangle_P = \frac{I_{as}}{n}(1+m\cos(\omega t-\varphi)), \text{ resp. } \frac{I_{as}}{n}(1+me^{i(\omega t-\varphi)}), \tag{9}$$

where $m = q \cdot \cos\varphi$ and $n = \omega \cot\varphi$.

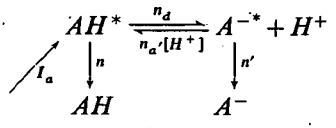
1.2. Systems with 2 excited species

There are two types of such systems. Either the photochemical primary process (starting from the directly excited species) is bimolecular and its inverse process is monomolecular or vice versa. Examples of the former are excimer and exciplex systems, while FES protolytic reactions belong to the latter.

Exciplex/excimer system



FES Protolytic reaction



In both systems we suppose that only one of the two excited species is primarily optically populated (only with the protolytic reaction it is possible — in a narrow pH region — to generate AH^* and A^{-*} simultaneously by light absorption but without being faced with new aspects). In the left hand side system if $B = A$ we have an excimer system.

Applying rules 1—3 to both systems we find, after proper arrangement, simultaneous first order differential equations with constant coefficients; the meanings of X, Y, and the n_{ik} are given in List 1.

$$\frac{dX}{dt} = n_{11}X + n_{12}Y + I_a \quad \frac{dY}{dt} = n_{21}X + {}_{22}Y. \tag{10}$$

List 1

$X = \langle A^* \rangle \quad Y = \langle (AB)^* \rangle$		$X = \langle AH^* \rangle \quad Y = \langle A^{-*} \rangle$
$-(n + n_a[B])$	n_{11}	$-(n + n_d)$
n'_d	n_{12}	$n'_a[H^+]$
$n_a[B]$	n_{21}	n_d
$-(n' + n'_d)$	n_{22}	$-(n' + n'_a[H^+])$

The characteristic equation following from Eq. (10) we need not solve.

$$(\lambda + n_{11})(\lambda + n_{22}) - n_{12}n_{21} = 0 \tag{10a}$$

Instead of its roots λ_1 and λ_2 we consider Vieta's identities

$$\lambda_1 + \lambda_2 = -(n_{11} + n_{22}) \quad \lambda_1\lambda_2 = n_{11}n_{22} - n_{12}n_{21} \tag{11}$$

With the meaning of the n_{ik} from *List 1* we see that all four kinetic constants of the above reaction schemes can be determined by plotting the experimentally determined left hand sides of Eqs. (12) versus concentration of the unexcited reaction partner. The equations of the stratight lines are given below ,continuing *List 1*

$n + n' + n'_d + n_a[B]$	$\lambda_1 + \lambda_2$	$n + n' + n_d + n'_a[H^+]$
$n(n' + n'_d) + n'n_a[B]$	$\lambda_1\lambda_2$	$n(n' + n'_a[H^+]) + n'n_d$

(12)

1.2.1. The δ-responses

By the Laplace procedure (or another one) we find from Eqs. (10)

$$X_\delta = -\frac{\lambda_1 + n_{22}}{\lambda_2 - \lambda_1} e^{-\lambda 1^t} + \frac{\lambda_2 - n_{22}}{\lambda_2 - \lambda_1} e^{-\lambda 2^t}$$

$$Y_\delta = \frac{n_{21}}{\lambda_2 - \lambda_1} (e^{-\lambda 1^t} - e^{-\lambda 2^t}) \tag{13}$$

(With respect to Eqs. (11) various equivalent preexponential factors can be written). If at least one of the biexponential functions can be measured there are various procedures to determine λ_1 and λ_2, from which, as we have seen, the kinetic constants can be ascertained. Practically, this 'λ-procedure' will function only if λ_1 and λ_2 are sufficiently different, factor ...23 at least, and if the participating processes are not too fast. In many cases of partical importance $\lambda_2 \simeq 300$ ps needing 20...30 ps time resolving power, which no commercially available decay time measuring apparatus really affords with biexponential problems. Usually only the slower time constant λ_1 can be measured which is of less significance.

Fig. 1 shows the result of a discussion of Eqs. (10a) for an excimer system. We see that $n < \lambda_1 < n'$. As n'_d may be $10^8 \ldots 10^9\,s^{-1}$, $n_a[B]$ must then be of the same order of magnitude to give reasonable excimer formation and thus one needs a time resolution

in the ps region. Fortunately, the time dependent measurements can be combined with stationary results; otherwise FES kinetic analysis would be restricted to 'show' systems such as pyrene excimers [3].

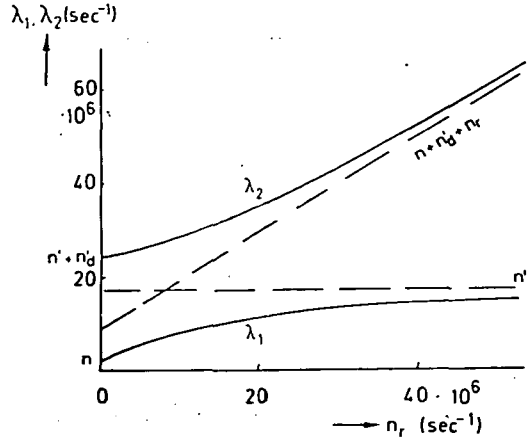


Fig. 1.

1.2.2. The photostationary state

The procedure of solving Eqs. (10) with $I_a = I_{as} = \text{const.}$ is not simpler than applying Eq. (7) to Eqs. (13), which can be done without specifying for the *l.h.s.* or *r.h.s.* scheme. We get

$$X_s = -I_{as}\frac{n_{22}}{\lambda_1\lambda_2} \quad Y_s = I_{as}\frac{n_{21}}{\lambda_1\lambda_2} \tag{14}$$

Inserting the *l.h.s.* constants of *List 1* we get the Stern—Volmer-relation and a complementary one

$$\frac{F_{Aso}}{F_{As}} = 1 + [B]/[B]_{1/2} \quad \frac{F_{ABs\infty}}{F_{AB}} = 1 + [B]_{1/2}/[B]. \tag{15}$$

With the common 'half value concentration'

$$[B]_{1/2} = \frac{n(n' + n'_d)}{n' n_a} \tag{16}$$

In Eqs. (15) the index *'Aso'* means 'of species A in the stationary state at concentration O'. Index '$ABS\infty$' means 'species AB, stationary at concentration versus ∞'. In both formulae, 'o' and '∞' are sometimes replaced with 'max'. Moreover, in accordance with reasons given in the context of Eq. (4), the quotients of total fluxes Eqs. (15) may be replaced with the quotients of

i) relative fluxes ('intensities')
ii) quantum yields $\varphi_{I_{max}}/\varphi_I$
iii) amounts of excited species $\langle I^*\rangle_{max}/\langle I^*\rangle$, where I^* means A^* or $(AB)^*$.

Finally, introducing the quantum yield quotients in Eqs. (15) we find what sometimes

is called the 'adiabaticity relation'

$$\frac{\Phi_A}{\Phi_{A\max}} + \frac{\Phi_{AB}}{\Phi_{AB\max}} = 1 \tag{17}$$

Eqs. like (17) will hold for all systems, where processes deactivating excited species (to the ground state) are in competition with the adiabatic processes (producing excited species) exclusively and no additional deactivation taking place 'in between' excited educt and product. Eqs. (15)—(17) were derived for the exciplex/excimer systems *l.h.s.* For the FES protolytic reactions and possibly for other systems obeying the *r.h.s.* scheme, no such symmetrical Stern—Volmer type equations as (15) are valid. If $[H^+]=0$ we get $\varphi_{A^-max}=\frac{n_d}{n+n_d}\cdot\frac{n'_e}{n'}$ and simultaneously $\varphi_{AH\,min}=\frac{n_e}{n+n_d}$ whereas $\varphi_{AH\,max}=\frac{n_e}{n}$ with. $[H^+]\to\infty$ as can be derived from Eqs. (14) inserting the constants of *List 1*, *r.h.s.*, and rule 4. Instead of Eqs. (15) we have

$$\left(\frac{F_{AHs\infty}}{F_{AHs}}-1\right)^{-1} = \frac{n}{n_d}\left(1+\frac{n'_a[H^+]}{n'}\right) \quad \frac{F_{A^-so}}{F_{A^-s}} = 1+\frac{n'_a[H^+]}{(n+n_d)n'} \tag{18}$$

Remarks i)—iii) (behind Eq. (16)) and a relation corresponding to Eq. (17) are valid, too. The more complicated behaviour Eqs. (18) allows the kinetic analysis to be performed almost completely in the stationary state, as was done by Weller as long ago as the 50ies! Another relation, which is valid for both reaction schemes again, follows immediately from the second Eq. (10)

$$\frac{Y_s}{X_s} = -\frac{n_{21}}{n_{22}} \tag{19}$$

Refering to List 1 and making use of remarks i)—iii) various useful formulae may be derived from Eq. (19). It is true, a Stern—Volmer procedure does not need the spectral characteristics of the instrument to be known as is the case with Eq. (19) and relations derived from it. The most commercially available fluorescence spectrometers measure wrong if the penetration depth of excitation changes or if cuvettes with optical disadvantages (such as tubes) are used. The quotient of two fluorescence components, however, is measured correctly in such cases even with turbid samples. Instrument manufacturers have solved the problem of allowing for different spectral characteristics much better than that of changing sample geometry. Fluorescence probing in biological systems for investigation of surface phenomena *etc.* is preferably based on Eq. (19).

1.2.3. Phase fluorimeter responses (two excited species)[4]

With the Eq. (7) procedure we find from Eqs. (8) and (13)

$$X_p = I_{as}\left(-\frac{n_{22}}{\lambda_1\lambda_2}+pe^{i\omega t}\,\frac{(i\omega-n_{22})[\lambda_1\lambda_2-\omega^2-i\omega(\lambda_1+\lambda_2)]}{(\lambda_1\lambda_2-\omega^2)^2+\omega^2(\lambda_1+\lambda_2)^2}\right. \tag{20a}$$

$$Y_P = I_{ah}\left(\frac{n_{21}}{\lambda_1\lambda_2}+pe^{i\omega t}n_{21}\,\frac{\lambda_1\lambda_2-\omega^2-i\omega(\lambda_1+\lambda_2)}{(\lambda_1\lambda_2-\omega^2)^2+\omega^2(\lambda_1+\lambda_2)^2}\right. . \tag{20b}$$

Both Eqs. (20) and (20b) may be brought to the form of Eq. (9)

$$X_P = -I_{as}\frac{n_{22}}{\lambda_1\lambda_2}(1+pe^{i(\omega t-\Psi)}) \tag{21a}$$

$$Y_P = I_{as}\frac{n_{21}}{\lambda_1\lambda_2}(1+re^{i(\omega t-x)}) \tag{21b}$$

The expression for the phase angle Ψ of the primarily excited species

$$\omega\cot\Psi = \frac{(\omega^2-\lambda_1\lambda_2)n_{22}+\omega^2(\lambda_1+\lambda_2)}{\lambda_1\lambda_2-\omega^2+(\lambda_2+\lambda_2)^2} = \frac{n_{12}n_{21}n_{22}-n_{11}(\omega^2+n_{22}{}^2)}{n_{12}n_{21}+n_{22}{}^2+\omega^2} \tag{22a}$$

is not simple and needs curve fitting for evaluation. The expressions for the 'modulation degrees' p and r following from Eq. (20) may be omitted as these parameters are difficult to measure with reasonable accuracy. The phase angle χ of the secondarily excited species, however, is very convenient for evaluation

$$\omega\cot X = \frac{\lambda_1\lambda_2-\omega^2}{\lambda_1+\lambda_2} \tag{22b}$$

By plotting the *l.h.s.* of Eq. (22b) versus ω^2 one gets $\lambda_1\cdot\lambda_2$ and $\lambda_1+\lambda_2$ from straight line parameters. Having performed these measurements for various concentrations of the unexcited reaction partner, Eqs. (12) are applied to find the kinetic constants. One can see that phase fluorometry at a set of different frequencies is essentially equivalent to measuring δ-responses.

Finally we get a simple relation between measurable parameters and kinetic constants by first forming the ratio of periodic and constant term in Eqs. (20a) and (20b), respectively, and then the quotient of these ratios. With the notations of Eqs. (21) we get formally similar to Eqs. (9)

$$\frac{r}{p} = n_{22}(\omega^2+{}^2_{22})^{-1/2} = \cos(\chi+\psi); \quad -n_{22} = \omega\cot(\chi-\psi) \tag{23}$$

As only one parameter, n_{22}, is determined experimentally, the modulations degrees' quotient ma be a reasonable magnitude, too. The *r.h.s.* Eq. (23) which also may be derived from Eqs. (22a, b) is very useful in the *r.h.s.* cases of List 1.

2. FES kinetics with time dependent rate factors

It is a common feature of Förster—Galanin type energy transfer [5] ET and of diffusion controlled molecular encounter according to Smoluchowski's theory that the rate factors $k_{A\to B}$ and k_{diff} of both these bimolecular processes explicitly depend on time. In Smoluchowski's expression

$$k_{\text{diff}} = k_{SE}\left(1+\frac{b}{t^{1/2}}\right) \tag{25}$$

the constant $b=10^{-4}...10^{-5}\ s^{1/2}$ allowing for non-stationary diffusion is small enough to be neglected in many cases, but the similar time dependence of ET is essential

$$\bar{k}_{A\to B} = [B]_o^{-1} \cdot \left(\frac{n}{t}\right)^{1|2} \tag{26}$$

$[B]_0$ denotes the critical concentration of unexcited acceptor B and n the reciprocal lifetime of the excited donor A^* in the absence of B. While Eq. (65) is given in usual form, Eq. (26) is perhaps not so well known. ET kinetics is usually described by the decay function $F(t)/F(o)$ which means the relative fluorescence flux ('intensity') after δ-excitation and is identical with

$$\langle A^*\rangle_\delta = \exp - \left(nt + 2\frac{[B]}{[B]_o}(nt)^{1/2}\right) \tag{27}$$

In the total rate of decay

$$\frac{d\langle A^*\rangle_\delta}{dt} = -\left(n + \frac{[B]}{[B]_0}\left(\frac{n}{t}\right)^{1/2}\right)\langle A^*\rangle_\delta \tag{27a}$$

we notice the rate factor $\bar{k}_{A\to B}$ given by Eq. (26) while n describes the deactivation. The special type of ET kinetics [5] is a consequence of

a) the strong dependence of the fundamental transfer rate n_{ET} on the distance r of a donor-acceptor pair; r_0 denotes the critical distance $n_{ET}=n\left(\frac{r_0}{r}\right)^6$

b) the distribution of the (great number of) unexcited acceptors in the surrounding of any excited donor. The form of Eqs. (26) and (27) is characteristic of homogeneous random three dimensional distribution. Other dimensionalities and/or spatial limitations of distribution will give rise to functions different from Eqs. (26) and (27) and thus may be recognized [6]. It was shown some time ago [7] that processes with time dependent rate factors such as Eqs. (25) and (26) must not be contained in kinetic differential equations as results turn out to be more or less nonsensical. This can shortly be seen for instance from Eq. (16) by replacing n_a with $\bar{k}_{A\to B}$ from Eq. (26). In the stationary state $t\to\infty$ we get $[B]_{1/2}\to\infty$ which means no ET taking place at finite acceptor concentrations $[B]$ and no B^* being formed. Really the whole concept of kinetic differential equations is valid only if all participating processes obey coefficients or rate factors which are independent of time!

Only the response on direct δ-excitation is equally fundamental with and without time dependent rate factors. This so-called ideal decay function must be known from statistical calculations [5, 6] or ultimately by experiment then allowing all cases of kinetic schemes and types of excitation to be treated by the general mathematical procedure called 'convolution kinetics'. On direct excitation the ideal decay function f_δ is identical with the δ-response, *e.g.* $\langle A^*\rangle_\delta = f_{A\delta}$ in the case of Eq. (27) but for the kinetically formed species Y in section 1.2, $f_{Y\delta}=\exp(-n_{22}t)$ and is not given by Y_δ from Eq. (13).

In one of the simplest but non trivial cases of convolution kinetics direct excitation of A by light with $I_a(t)$

$$\begin{array}{ccc} & A^* \xrightarrow{k(t)} & B^* \\ I_a \nearrow & \downarrow n & \downarrow n' \\ & A & B \end{array}$$

strangely enough Eq. (7) from section 1.13 should be applied to get

$$\langle A^* \rangle = I_a * f_{A\delta} \tag{7}$$

In the case of ET, $k(t)$ in the above scheme is given by Eq. (26) and $f_{A\delta} = \langle A^* \rangle_\delta$ is given by Eq. (27). In the important stationary case $I_a = I_{ao}$ const. we get from Eq. (7) by calculating the convolution integral

$$\langle A^* \rangle_s = \frac{I_{ao}}{n} (1 - \sqrt{\pi}\gamma \exp \gamma^2 \operatorname{erfc} \gamma) \tag{28}$$

$$\gamma = [B]/[B]_o$$

Eq. (28) is is accordance with Förster's result [5] which was derived in another way (but is misprinted in the original paper).

It should be noticed that with time dependent $k(t)$ Eq. (7) cannot be derived by the differential equations procedure nor by Laplace transform. Consequently Eq. (28) needs a reasonable foundation, too. In order to justify the use of Eq. (7) with $k(t)$ we could refer to Kubo's linear response theory[8]. The next question for the time dependence of $\langle B^* \rangle$ is not answered by this theory, much less how to treat more complicated reaction schemes. A new complete general procedure will be given below. Before this Eq. (28) deserves some more attention.

Without much reasoning, $\langle B^* \rangle_s$ for the stationary state is derived with the aid of the adiabaticity relation Eq. (17) knowing that $\langle A^* \rangle_{smax} = I_{ao/n}$ and $\langle B^* \rangle_{smax} = I_{ao/n'}$ (as for $\gamma \to \infty B^*$ behaves like it were directly excited). We get

$$\langle B^* \rangle_s = \frac{I_{ao}}{n'} \sqrt{\pi}\gamma \exp \gamma^2 \operatorname{erfc} \gamma \tag{28a}$$

Moreover, as there is no backward step in the reaction scheme, we can find the phase fluorimeter response $\langle A^* \rangle_p$ by the replacement procedure $n \to n + i\omega$, *cf.* section 1.14. But as n is contained in γ, too, we additionally must replace $\gamma \to \gamma \cdot \left(\frac{n}{n+i\omega}\right)^{1/2}$ in Eq. (28). Using the tabulated values [9] of the complex erfc, $\langle A^* \rangle_p$ follows in closed form (needing no numerical approximation, but collecting the real and imaginary parts is laborious). Finally, as can be later clearly understood, $\langle B^* \rangle_p$ would follow consequently from Eq. (28a) with the γ transform mentioned and $n' \to n' + i\omega$.

2.1. Introduction to the new concept of 'convolution kinetics'

As we mentioned already, the ideal decay function $f_{X\delta}$ of excited species X^* (on direct excitation being identical with $\langle X^* \rangle_\delta$) is considered as fundamental for the behaviour of X^* in FES kinetics. In order to find $f_{X\delta}$ we may need to solve a master equation as with ET [5]. But for systems with time-independent rate factors only, $f_{X\delta}$ follows from ordinary FES kinetics presented in main section 1. In the final analysis questions concerning the ideal decay function must be decided by experiment.

Excitation with the intensity $I_a(t)$, (more correctly speaking $I_a(t)$ is a flux distribution), has the same effect as excitation with a continuous sequence of short pulses

similar to δ-functions with area $I_a(\vartheta)d\vartheta$. Thus $I_a(t-\vartheta)d\vartheta$ produces at time $t-\vartheta$ an incremental amount of excited molecules $d\langle A^*\rangle$, decaying during the time interval ϑ according to $f_{A\delta}$ up to the remainder $I_a(t-\vartheta)\cdot f_{A\delta}(\vartheta)\cdot d\vartheta$. The total amount of $\langle A^*\rangle$ at time t result from the sum (integral) of all such remainders generated by all foregoing incremental δ-excitations. The procedure of summing up these remainders is nothing else but the convolution Eq. (7) in the form given in section 1.1.3. Thus the general significance of Eq. (7) is established.

We now understand why the rate of change of a population $\langle A^*\rangle$ or $\langle X^*\rangle$ is in general not given by its time derivative. This may be illustrated by many examples. In order to predict the development of the number of students at a university, one must know the time dependent probability of a student's stay there $\sim f_{St\delta}$, but the total number of students at any time $\sim\langle St\rangle$ is of little use. One must know how many students are in the first year, second year, and so on. This detailed information would not be needed if the probability of stay were described by a time independent rate factor *viz.* were given by a simple exponential $f_{St\delta}\infty e^{-nt}$. The latter is usually the case in chemical kinetics then justifying the well known concept of rate constants.

Allowing for the age structure of a population, or in other words its temporal inhomogeneity, by the convolution concept depends on the following prerequisits: The individuals neither interact nor interfere, (the latter means no square or higher terms in number or concentration), and there is a unique ideal decay function (= time dependenee of the probability of belonging to the population).

For completeness and for practical reasons we need a procedure for treating excitation of species B^* on the expense of the precursor A^* by a photochemical process. In case that $\langle A^*\rangle$ was δ-excited, the total rate of its depopulation will be a sum of as much terms as there are contributing processes

$$\frac{df_{A\delta}}{dt} = -\sum k_i f_{A\delta} \tag{29}$$

The k_i may or may not depend on time and/or concentration of unexcited reaction partner. In the general Eq. (27) the total rate is given by Eq. (27.a). In the general Eq. (29) the term $k_j f_{A\delta}$, say, is increasing $\langle B^*\rangle$ at the expense of the precursor. At time $t-\vartheta$ the incremental amount $k_j f_{A\delta}(t-\vartheta)d\vartheta$, is produced from which the remainder which is still excited at time t is got by the factor $f_{B\delta}$, thus

$$\langle B^*\rangle/_{A(\delta)\to B} = \int_0^t k_j f_{A\delta}(t-\vartheta) f_{B\delta}(\vartheta)\, d\vartheta = k_j f_{A\delta} * f_{B\delta} \tag{30}$$

Index$/_{A(\delta)\to B}$ means B^* is produced from A^* which was δ-excited; for this case we solved the problem. In the case of Eq. (27), $k_j = \gamma\left(\frac{n}{t}\right)^{1/2}$ ($\gamma = [B]/[B]_o$). The whole 'production term' is here

$$p_{A(\delta)\to B} = k_j f_{A\delta} = -\left(\frac{df_{A\delta}}{dt} + n f_{A\delta}\right) \tag{31}$$

which means that we take only the term producing B^* from A^*. If A^* is excited by general light absorption $I_a(t)$, (direct excitation is the mark of species we denote A),

we get as I_a means a sequence of quasi δ-impulses

$$\langle B^* \rangle|_{A(I_a)\to B} = I_a * \langle B^* \rangle|_{A(\delta)\to B} \tag{32}$$

and making use of Eq. (30). Obviously, the production term of A^* is identical with $I_a(t)$

$$p_{(I_a)\to A} = I_a \tag{33}$$

Finally, B^* could be the precursor of C^*. Then we find

$$\langle C^* \rangle|A(I_a) \to B \to C = I_a * p_{A(\delta)\to B} * p_{B\to C} * f_{C\delta} = p_C * f_{C\delta} \tag{34}$$

A general straight forward procedure is given in the next section, where the construction of production terms is explained. If backward steps and/or direct excitation of more than 1 species take place, sums of production terms are incorporated.

2.2. The basic rules of convolution kinetics

I) The amount of excited species X^* is found by convolution of its production term p_X with its ideal decay function (= δ-response on direct excitation).

$$\langle X^* \rangle = p_X * f_{X\delta}$$

II) The production term p_X is given by convolution of the p_{X-1} of the precursor $X-1$ with the derivative of its ideal decay function $df_{X-1,\delta}/dt$ omitting the terms not producing X^* from X^*-1.

III) The production term p_A of the primary excited species is given by the absorbed excitation flux (density) I_a.

If more than 1 species is directly optically excited, I_a must be split. With chemical excitation, branching and backward steps (giving somewhat like loops of production terms) may be incorporated.

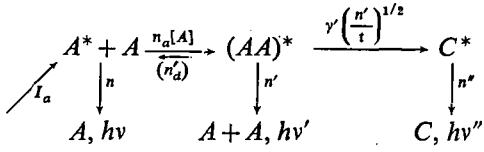
Rules I—III are valid in cases of constant coefficients, too, as convolution kinetics are the more general, superimposed procedure. Rule 4 of section 1 which connects fluorescence to the amounts of excited molecules is valid in convolution kinetics without change.

2.3. Experimental proofs and applications of convolution kinetics

The breakdown of ordinary kinetics with time dependent rate factors is most obvious in all types of photostationary experiments to which phase fluorimetry formally belongs, too. On the other hand, discrepancies between convolution kinetics and the old kinetics become smaller the more the excitation is similar to direct δ-excitation which is not possible for excimers and other excited photoproducts. Anyway, time dependent measurements are more conclusive in FES kinetics as a consequence of ambiguity of stationary fluorescence measurements because of *e.g.* static quenching and spurious effects.

2.3.1. The first dynamic test of convolution kinetics [10] was performed with pyrene excimer $(AA)^*$ as the donor and diethylthiacarbocyanine iodide C as the acceptor in ET, whereby the excimer was generated chemically after practically δ-shaped

excitation of the monomer A: $I_a = I_{ao} \cdot \delta(0)$ with $I_{ao} = \text{const}$. The concentration $[A] \ll [A]_{1/2}$ was chosen small enough to get a significantly biexponential time dependence of $\langle (AA)^* \rangle$, *cf.* Eq. (13) and list 1.



With pyrene excimers, $n'_d \approx 0$ below room temperature. So it is easier to control that direct ET $A^* \rightarrow C$ does not take place. Anyway the acceptor concentration must be small $\gamma = [C]/[C]_o \leqq 0.2$.

Considering the reaction scheme and applying rules I—III we get

$$\begin{aligned}
&a)\ p_A = I_a = I_{ao}\delta(0) && d)\ f_{A\delta} = \exp -(n + n_a[A])t \\
&b)\ p_{AA} = p_A * n_a[A] f_{A\delta} && e)\ p_{AA\delta} = \exp -(n't + 2\gamma'\sqrt{n't}) \qquad (35) \\
&c)\ p_C = p_{AA} * \gamma' \left(\frac{n'}{t}\right)^{1/2} f_{AA\delta} && f)\ f_{C\delta} = \exp -n''t
\end{aligned}$$

If I_a were not δ-shaped, one convolution more with $I_a(t)$ would be necessary for constructing the production terms. Finally

$$\begin{aligned}
&a)\ \langle A^* \rangle = I_{ao} f_{A\delta} \\
&b)\ \langle (AA)^* \rangle = I_{ao} n_a[A] f_{A\delta} * f_{AA\delta} \qquad (36) \\
&c)\ \langle C^* \rangle = I_{ao} n_a[A] f_{A\delta} * \gamma' \sqrt{n't}\, f_{AA\delta} * f_{C\delta}
\end{aligned}$$

While Eq. (36a) is the same as one gets from the differential equation (since coefficients are constant), one would find for the excimer AA^* by applying usual solving methods of linear differential equations

$$\langle (AA)^* \rangle = I_{ao} n_a[A] \exp -(n't + 2\gamma'\sqrt{n't} \int_{\vartheta=o}^{t} \exp(n'\vartheta + 2\gamma'\sqrt{n'\vartheta} - (n' + n_a[A])\vartheta)\, d\vartheta$$

according to this (wrong) equation the terms γ' describing the influence of ET are insignificant except at the very beginning, which could be shown by calculating the integral in closed form. The (correct) Eq. (36b) reads explicitly

$$\langle (AA)^* \rangle = I_{ao} n_a[A] \exp\{-(n - n_a[A])t\} \int_{\vartheta=o}^{t} \exp\left((n + n_a[A])\vartheta - n'\vartheta - 2\gamma'\sqrt{n'\vartheta}\right) d\vartheta \qquad (37)$$

In this equation, where also the integral can be calculated in closed form, ET keeps its influence during the whole time of interest. From the above wrong equation, $\langle (AA^*) \rangle$ is proportional to Dawson's function $D(\sqrt{n't} + \gamma')$ which vanishes for large values of the argument, while from Eq. (37) $\langle (AA^*) \rangle$ is really proportional to erf $(\sqrt{n't} + \gamma')$ approaching unity for larger values of the argument.

Altogether, the discrepancies between correct and wrong treatment are not very pronounced with the excimer, mainly because $\gamma' \leqq 0.2$ is rather small. Yet if the excimer quantum efficiency is calculated from

$$\Phi' = \frac{n'_e \int_0^\infty \langle (AA^*) \rangle \, dt}{\int_0^\infty I_a \, dt} \tag{38}$$

using the separately measured kinetic constants and $[A] = 0.02$ M

$$n = 2.9 \times 10^6 s^{-1} \quad n' = 33.8 \times 10^6 s^{-1} \quad n_a = 8.6 \times 10^7 M^{-1} s^{-1}$$

the dependence of Φ' on γ' agrees very well with the theory. (solvent was a cyclohexanol/paraffin oil mixture).

Inserting the constants in the above wrong equation Φ' is calculated about 30% too large at $\gamma' = 0.18$ (by underestimate of ET).

The disproof of the old kinetics and verification of convolution kinetics become convincingly significant when looking at C^*. The production term Eq. (35c)

$$p_C = I_{a0} n_a [A] \exp -(n + n_a[A]) t \cdot 2 \int_{\vartheta=0}^{t} \exp -(n' - n - n_a[A]) \vartheta - 2\gamma' \sqrt{n' \vartheta} \, d\sqrt{n' \vartheta}$$

can also be calculated exactly. As in our case $n' \gg n + n_a[A]$ we get to a good approximation

$$p_C \approx I_{a0} n_a [A] \exp -(n + r_a[A]) t \gamma' \exp \gamma'^2 \sqrt{\pi} [\operatorname{erf}(\sqrt{n' t} - \gamma') - \operatorname{erf} \gamma']$$

With $\gamma' = 0.18$ the term in square brackets becomes ≈ 0.8 for $t < 2/n' \approx 60$ ns, while the duration of all three responses Eq. (36) are about 300 ns. Making use of the approximation

$$p_C \approx I_{a0} n_a [A] \exp -(n + n_a[A]) t \gamma' \exp \gamma'^2 \sqrt{\pi} \tag{39}$$

we get instead of the exact Eq. (36c)

$$\langle C^* \rangle \approx I_{a0} n_a [A] \sqrt{\pi} \gamma' \exp \gamma'^2 \frac{\exp -(n + n_a[A]) t}{n'' - n - n_a[A]}$$

Analogously to Eq. (38) and making use of $n'' \gg n + n_a[A]$, which was measured $n'' = 6.6 \times 10^8 s^{-1}$, we get for the quantum efficiency of the acceptor C (the cyanine dye)

$$\Phi'' \frac{n''}{n''_e} = \frac{\Phi''}{\Phi''_0} \approx \frac{\sqrt{\pi} \, n_a [A] \gamma' \exp \gamma'^2}{n + n_a[A]} \tag{40}$$

$\Phi''_o = \frac{n''_e}{n''} = \frac{\Phi''}{\Phi''}$ means the quantum yield on direct excitation of C, which was determined separately $\Phi''_o = 0.72$.

Eq. (39) as well as Eq. (40) were found in excellent agreement with the experimental results: The slowest preceding process is the decay of excited pyrene monomer

A^* with time law exp $-(n+n_aA)t$, which must be rate controlling for the fast decaying species C^*, too. This was clearly observed from the time dependence of C^* fluorescence*** in accordance with Eq. (39) and with the exact Eq. (36c). From the old kinetics applied to the reaction scheme we get

$$\frac{d\langle C^*\rangle}{dt} = -n''\langle C^*\rangle + \gamma'\left(\frac{n'}{t}\right)^{1/2}\langle (AA)^*\rangle$$

Consequently inserting $\langle (AA)^*_\cdot\rangle = \ldots$ from the "wrong companion" of Eq. (37) and tediously solving that differential equation, we get a 30% faster decay. The relative quantum efficiency following with $\gamma'=0.18$ from Eq. (40) is $\Phi''/\Phi''_0=0.11$ while the experimental value was 0.12. In convolution kinetics, quantum efficiency is the same irrespective whether Eq. (40) or the stationary treatment is applied. The experimental evaluation of Eq. (40) needs the areas under the fluorescence time dependences (decay functions) to be compared with integral intensity of the excitation flash, what was practised by direct excitation of C^*. With the old kinetics inserting the (wrong) function $\langle C^*\rangle$ which we get from the above differential equation into Eq. (40), we get $\Phi''/\Phi''_0=0.025$ at $\gamma'=0.18$ what is some 100% wrong; calculating the photostationary efficiency gives the totally nonsensical result $\Phi''=0$(!). The reason why the breakdown of the differential equations procedure is more striking with C^* than with the excimer $(AA)^*$ comes from that ET is only moderately diminishing Φ' of $(AA)^*$, but Φ'' is compared to zero efficiency.

2.3.2. Multistep ET.

In the case of self overlap of the fluorescence spectrum with the absorption spectrum of the same molecule, which is realized *e.g.* with perylene and may fluorescent dyes, $\gamma \approx 1$ and even more is possible.

The reaction scheme is

$$\begin{array}{ccccccc} & & A_1^* & \xrightarrow{\gamma\left(\frac{n}{t}\right)^{1/2}} & A_2^* & \xrightarrow{\gamma\left(\frac{n}{t}\right)^{1/2}} & A_3^* \longrightarrow \ldots \\ I_a & & \downarrow n & & \downarrow n & & \downarrow n \\ & & A & & A & & A \end{array}$$

The index $i=1, 2, \ldots$ of A_i^* means ... excited in the first, second, ... step. All ideal decay functions $f_{i\delta}$; $i=1, 2, \ldots$ are the same:

$$f_\delta = \exp -\left(nt + 2\gamma\sqrt{nt}\right) \tag{41}$$

and the term r by which the recursion from p_i to p_{i-1} is given, is also the same for all p_i

$$r = \gamma\left(\frac{n}{t}\right)^{1/2} f_\delta = -\left(\frac{df_\delta}{dt} + nf_\delta\right) \tag{42}$$

*** All time dependences of fluorescence were measured with ORTEC single photon counting system

as it follows from Eq. (41). Thus we get from the reaction scheme if $I_a=\delta(0)$

$$\begin{aligned}\langle A_1^*\rangle &= f_\delta \\ \langle A_2^*\rangle &= f_\delta * r \\ \langle A_3^*\rangle &= f_\delta * r * r \\ &\cdots \\ \langle A_i^*\rangle &= f_\delta * r * r * \ldots \\ &\qquad (\mathrm{i}-1 \text{ terms})\end{aligned} \tag{43}$$

Unfortunately, there is no power type notation for repeated convolution of equal terms. The Laplace transform of Eq. (42) reads if we denote $Lf_\delta=g$ and $Lt=x$

$$Lr = -(xg-1+ng) = -g(x+n) \tag{44}$$

The individual $\langle A_i^*\rangle$ cannot directly be measured, however, the sum

$$\langle A^*\rangle = \sum_{i=1}^{\infty} A_i^*$$

With the transform of the sum we obtain with Eqs. (43) and (44)

$$L\langle A^*\rangle = g\sum_{i=1}^{\infty}[1-g(x+1)]^{i-1} = \frac{g}{1-[1-g(x+n)]} = \frac{1}{x+n} \tag{45}$$

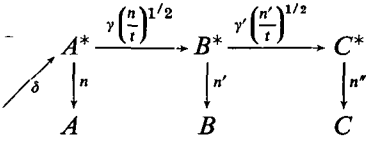
The result of the backward transform of the surprisingly simple Eq. (45) is

$$\langle A^*\rangle = L^{-1}\frac{1}{x+n} = \exp -nt \tag{46a}$$

In the corresponding case of multistep collisional transfer with $n_a[A]$ instead of $\gamma\left(\frac{n}{t}\right)^{1/2}$ one gets the same final formula Eq. (45). But ET is very fast over distances shorter than the critical distance which may give raise to random walk of excitation; $\gamma \geqq 1$ means that about 1/3 of excited donors A^* do have 2 or more acceptors A within the critical distance. Quenchers (*e-g.* impurities) without a normal chance of interaction with A^* may act as traps if excitation reaches an A in their neighbourhood; one may speak of a Förster—Galanin exciton (even in homogeneous solutions). Decisive experiments on that field are extremely difficult to realize because many trivial effects may strongly influence the results. Our latest approach was:

2.3.4. Energy transfer in two steps [11]

The reaction scheme differs from that of section 2.3.2 so far as the first donor A as well as the first acceptor (=second donor) B and the second acceptor C are different molecules; thus $\gamma\left(=\frac{[B]}{[B]_o}\right)$ and $\gamma'\left(=\frac{[C]}{[C]_o}\right)$ may be chosen arbitratily (within the limits of preventing undesired other effects).



A system which was expected to fulfill the most important prerequisits fairly well is with

A=1, 2-Benzofluorene; $1/n$=55 ns

B=9, 10-Diphenylanthracene; $1/n'$=8.1 ns

C=Dimethyloxacarbocyanine iodide; $1/n''$=0.6 ns

in the solvent cyclohecanol/triethyleneglycol 4:1 with the viscosity 49 cp. The absorption and fluorescence spectra together with properly chosen concentrations, γ=0,75 and $\gamma' \leqq 0.46$, guarantee direct optical excitation of A only and negligible immediate ET $A^* \rightarrow C$. Trivial reabsorption of A^* fluorescence by B and/or C does not exceed 5%. B^* fluorescence is more strongly reabsorbed by C, but this does not influence the time dependence of $\langle B^* \rangle$. As A shows very small self overlap, ET $A^* \rightarrow A \rightarrow B$ and $A^* \rightarrow A \rightarrow C$ are negligible, only $B^* \rightarrow B \rightarrow C$ may have a small influence.

Having some experience with convolution kinetics already and supposing $I_a = I_{ao} \cdot \delta(0)$ we may write down immediately

$$a) \qquad \langle A^* \rangle = I_{ao} \exp -(nt + 2\gamma\sqrt{n}\,t)$$

$$b) \qquad \langle B^* \rangle = \langle A^* \rangle \gamma \left(\frac{n}{t}\right)^{1/2} * \exp -(n't + 2\gamma'\sqrt{n'}\,t) \qquad (46b)$$

$$c) \qquad \langle C^* \rangle = \langle B^* \rangle \gamma' \left(\frac{n'}{t}\right)^{1/2} * \exp -n''t$$

The convolution integral in the kinetically most significant Eq. (46b) must be computed numerically. $\langle C^* \rangle(t)$ was not expected to be very different in shape comparing the differential equations result and that of convolution kinetics, however, its quantum efficiency.

As expected, the over alltime dependences are all similar to $\langle A^* \rangle$ which is rate controlling. A significant feature of $\langle B^* \rangle$, when normalized to equal maximum height with $\langle A^* \rangle$, is an overshoot with Eq. (46b) and in disagreement with the old kinetics. But as regards the most exciting expectation, the quantum efficiency of C^* fluorescence, the experiment was disappointing: As was especially significant with stationary

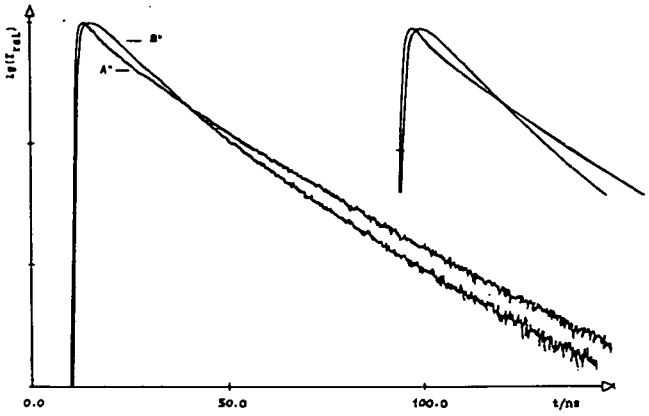


Fig. 2. Measured and calculated fluorescence time dependences of A^* and B^*; (the old kinetics give practically no overshoot). The time dependence of C^*, whichis not shown, is very similar to that of B^*. Concentrations $[A]=2.0\cdot10^{-2}$; $[B]=8.8\cdot10^{-3}$; $[C]=1.55$ mol/l, each.

measurements, ET $B^*\rightarrow C$ is strongly violating the adiabaticity principle. This seems to be a very general effect, which we observed with C=Trypaflavine, Safranine T, Acridine Yellow, Acridine Red, *etc.* (but not with Uranine in alkaline media). As B^* lifetime is <10 ns and the concentrations $[C]<5\times10^{-3}$ M, a static quenching effect must be operative; no significant deviations in the time dependences $\langle B^*\rangle$ and $\langle C^*\rangle$ were observed and, of course, no influences in the absorption spectra. We postulate complexes in the ground state (BC), weak enough not to influence the ET acceptor features of B- or C-part but preventing emission mainly of C as $[C]\ll[B]$.

This new static quenching effect is also observed if C is excited directly and B is added, even though B absorbes only at much shorter wavelengths.

2.2.4. Concluding remarks

The understanding of FES kinetics with time dependent rate factors should be critically revised on the basis of the new concept presented here. Many conclusions from using Förster—Galanin ET as a spectroscopic ruler have been more or less wrong, as perhaps has been the case with nonstationary diffusion phenomena often obscured as cage effects.

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ФЛУОРЕСЦЕНЦИЯ И КИНЕТИКА ВОЗБУЖДЕННЫХ СОСТОЯНИЙ

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В работе описивается четыре основных правила для описания кинетики процессов в первом возбужденном состоянии. Получены обобщенные формулы для исследования систем с одним и двумя родами возбужденных состояний для случая стационарной, фазово-флуорометрической, δ — образной и для произвольной формы возбуждения.

Доказано неприменимость обычных кинетических представлений в случае коэффициентов скорости зависящих от времени, особенно для случая передачи энергии типа Ферстера-Галанина и для нестационарной диффузии. Приводится новый кинетической приём в трёх правилах, названный кинетической свёрткой. — Сообщается динамическая проверка и примеры для вычисления (эксимер как донор и двухступенчатый перенос энергии).