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Analysis of transformations of the ultrafast electron transfer photoreactions mechanism in liquid solutions by the rate distribution approach.

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Representation of the experimental reaction kinetics in the form of the rate distribution is shown to be an effective method for analysis of the mechanisms of these reactions and for comparisons of this kinetics with QC calculations as well as with the experimental data on the medium mobility. Rate constants distribution function $P(k)$ can be obtained directly from the experimental kinetics $N(t)$ by the inverse Laplace transform. Application of this approach to the kinetic data for several excited-state electron transfer reactions reveals the transformations of their rate control factors in the time domain of 1–1000 ps. In neat electron donating solvents two components are observed. The fastest component ($k > 1 \text{ ps}^{-1}$) was found to be controlled by the fluctuations of the overall electronic coupling matrix element, involving all the reactant molecules, located inside the interior of the solvent shell, rather than for specific pairs of reactant molecules. The slower component ($1 > k > 0.1 \text{ ps}^{-1}$) is controlled by the medium reorganization (longitudinal relaxation times, τ_L). Substantial contribution of the non-stationary diffusion controlled reaction is observed in diluted solutions ($[Q] < 1 \text{ M}$). No contributions of the long-distance electron transfer (electron tunnelling) proposed earlier for the excited-state electron transfer between perylene and tetracyanoethylene in acetonitrile is observed. The rate distribution approach provides simple and efficient method for quantitative analysis of the reaction mechanism and transformations of the rate control factors in the course of the reactions.

Introduction

The goal of this paper is to attract the attention to the advantages of the rate distribution approach for the analysis of photoreaction kinetics. Picosecond kinetics of ultrafast chemical reactions, especially of electron transfer (ET) reactions, is studied experimentally in details¹. Various theoretical studies of these reactions involved MD and QC calculations^{2–4} as well as the uniform models^{5,6}. However, a problem of correct quantitative comparison of these data is very important. In particular, a well-known ambiguity of the recovery of the reaction mechanism from the reaction kinetics $N(t)$ can be misleading, when simple coincidence of the experimental and simulated data is considered as a confirmation of the postulated mechanism. In this paper we discuss the advantages of a different approach to the analysis of ultrafast reaction mechanism – the consideration of the distribution of rate constants $P(k)$ (a Laplace original) which uses the inverse Laplace transform of the experimental kinetics (a Laplace image) by rather formal and simple mathematical procedure and requires no preliminary hypothesis on the reaction mechanism.

Electron transfer (ET) reactions are the fastest chemical reactions since they involve only small changes of nuclear coordinates. In photochemical reactions the photon absorption generates the excited molecules initially in nuclear coordinates, corresponding to the ground electronic state (Franck-Condon state). Ultrafast ET usually competes with various relaxation processes¹ that can influence or even control the rate of the reaction. Very often this competition causes serious complications in the analysis of experimental kinetics of the ultrafast ET. The rate of ET is controlled⁷ predominantly by electronic coupling matrix element, V_{AD} , related to the overlap of electron donating and accepting molecular orbitals, and Franck-Condon factor, related to intramolecular and medium reorganization parameters (which neglects low frequency vibrations) or Franck-Condon weighted density of states (FCWD) (which takes them into account)

$$k_{\text{ET}} = (4\pi^2/h) V_{\text{AD}}^2 \text{FCWD}, \quad (1)$$

where h is a Planck constant. Molecular dynamics (MD) and quantum chemistry (QC) calculations demonstrate that very fast (~ 0.01 – 0.05 ps) and wide range (ca. 0.0001 – 0.2 eV) fluctuations of V_{AD} occur in liquid solutions^{2–4}. Castner et al.²

even considered V_{AD} as a dynamical variable. But the probability of the reaction to occur during each high-amplitude fluctuation is rather small (< 0.1) and one can use another approach – the consideration of the distribution of rate constants $P(k)$, reflecting statistical probability of given values of V_{AD} and $k^{8,9}$. This approach is convenient for comparison of the experimental rates with both molecular mobility of the reactant molecules and medium and with the results of MD and QC calculations, which provide the distribution of the electronic coupling matrix element $P(V_{AD}^2)^{2-4}$.

The goal of this paper is to analyze the experimental kinetics of several ultrafast ET reactions and to reveal the possible transformations of the rate control factors in the course of the reaction. Rate distribution approach* was found to be quite appropriate for this analysis since it represents experimental kinetics of the reaction in more convenient and clear form than conventional forms of a sum of several exponential functions or time dependent rate constant that have rather smooth shape. Rate distribution $P(k)$ for a given system usually consists of several bands and represents some kind of the “rate spectrum”. These bands correspond to different rate control factors and show what kinds of the molecular mobility and solvent dynamics are responsible for ET rates during the course of the reaction (electronic coupling, reorientation of the reactant molecules, translational diffusion, electron tunnelling).

There are several fitting procedures for recovery of the distribution of rate constants $P(k)$ (a Laplace original) from experimental kinetics $N(t)/N(0)$ (a Laplace image)⁷

$$N(t)/N(0) = \int_0^\infty P(k) \exp(-kt) dk \quad (2)$$

In general case the direct inversion of the Laplace transform for recovery of the arbitrary probability densities of the rate constants $P(k)$ has serious drawbacks, related to numerical instability, when the experimental data are intrinsically noisy⁸. But in many chemical systems this problem is simplified considerably and the total rather wide rate spectrum can be presented as a sum of several bands $P_\Sigma(k) = \sum_n A_n P_n(k)$, using the property of the additivity of the Laplace transform (total $P_\Sigma(k) = a_1 P_1(k) + a_2 P_2(k)$ when $N_\Sigma(t)/N(0) = a_1 N_1(t) + a_2 N_2(t)$). Each component can have different $P_n(k)$ and $N_n(t)$, depending on the physical behaviour of the rate control factor.

To obtain $P(k)$ in the form of the continuous function one has to express $N(t)/N(0) = \sum_n A_n N_n(t)$ as the sum of some functions that have the Laplace originals in the form of

* In chemical literature the rate distributions are designated usually as $P(k)$ and the reactant decay or consumption kinetics as $N(t)$, but in mathematical literature Laplace originals are designated traditionally as $f(t)$ and Laplace images as $F(s)$. Since this paper is intended for specialists in photochemistry and biokinetics we prefer to use chemical terminology to prevent any misunderstanding.

continuous functions $P_n(k)$. For instance, the Laplace original $P(\ln k) = (k/\gamma_0)^m \exp(-k/\gamma_0)/(m-1)!$ (corresponding to the Laplace image $N_n(t) = 1/(1+\gamma_0 t)^m$) is close to a Gaussian distribution $P(\ln k) = (1/\sigma\sqrt{2\pi})^{1/2} \exp(-(\ln k - \ln k_0)^2/2\sigma^2)$ with σ

= 0.3–0.5 (Fig. 1, Table 1). When $P_n(k)$ for each rate control factor is close to a Gaussian distribution, the total experimental kinetics can be approximated by a sum of Laplace images specific for these mechanisms in the form of hyperbolic functions

$$N_\Sigma(t)/N(0) = \sum_n A_n/(1 + \gamma_n t)^m \quad (3)$$

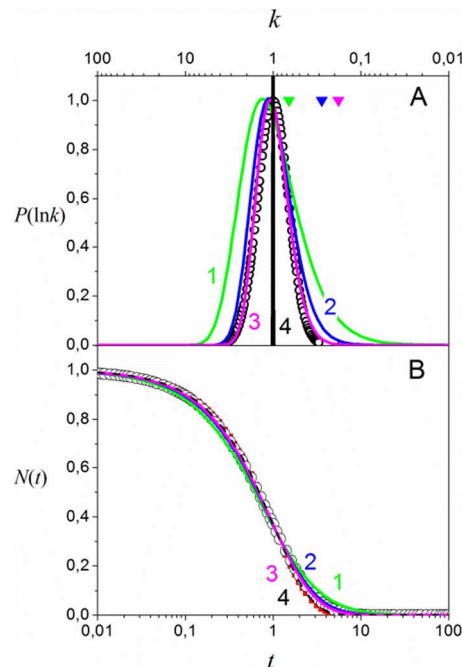


Fig. 1. Gauss distribution of the rate constants with $\ln k_1 = 0$ and $\sigma = 0.4$ (circles), δ -function, corresponding to the exponential decay with $\ln k_1 = 0$ (4), and distributions of the rate constants, corresponding to the Laplace originals $P(\ln k) = A_n (k/\gamma_n)^m \exp(-k/\gamma_n)/(m-1)!$, with $m = 2$ (1), 4 (2), 6 (3); triangles show the values of k_1 , corresponding to these distribution functions (A). Simulated decay kinetics for the Gauss distribution of rate constants with $k_1 = 1$ and $\sigma = 0.4$ (circles), it's fitting by the Laplace images $N(t) = A_n/(1 + k_1 t)^m$ with $m = 2$ (1), 4 (2), 6 (3) (solid lines) and exponential function (4) (B).

In such a case all the parameters A_n and γ_n can be obtained directly from the experimental kinetics, using any kind of the standard mathematical software package. It should be mentioned that usual presentation of the experimental data on non-exponential kinetics in the form of poly-exponential functions $N(t)/N(0) = \sum_n A_n \exp(-k_n t)$ is not convenient to describe the distribution $P(k)$ since the inverse Laplace transform of the exponential function is δ -function, and one obtains only several amplitudes for discrete (sometimes rather arbitrary) values of k_n . In the case of hyperbolic approximation (2) one obtains $P(k)$ in the form of continuous functions

$$P(k) = \sum_n A_n (k^{m-1}/\gamma_n^m) \exp(-k/\gamma_n) / (m-1)!, \quad (4)$$

or

$$P(\ln k) = \sum_n A_n (k/\gamma_n)^m \exp(-k/\gamma_n) / (m-1)!. \quad (5)$$

Table 1. Parameters, obtained by approximating by Laplace transform image $N(t) = 1/(1 + \gamma_1 t)^m$ of the exponential decay $N(t) = \exp(-k_0 t)$ and the decay with Gaussian distribution of the rate constants $P(\ln k) = (1/\sigma\pi^{1/2}) \exp(-(\ln k - \ln k_0)^2/2\sigma^2)$ ($\sigma = 0.4$).

m	(m - 1)!	Gaussian distribution ($\sigma = 0.4$)		Exponential decay	
		γ_1/k_0	γ_1/k_0	γ_1/k_0	σ^*
2	1	0.666	0.673		
4	6	0.285	0.290	0.5	
6	120	0.180	0.184	0.4	
8	5040	0.132	0.135	0.35	
10	362880	0.104	0.106	0.31	
50			0.0204	0.14	
100			0.0101	0.10	

The value of σ for various m was estimated by plotting of $k^m \exp(-k) / (m - 1)!$ and measurement of half-width at half-maximum.

Both distribution functions (4) and (5) are normalized in coordinates $P(k)$ vs k and $P(\ln k)$ vs $\ln k$, respectively. The width of the distribution functions $P(\ln k) = (k/\gamma_n)^m \exp(-k/\gamma_n) / (n - 1)!$ with $m = 4 - 10$ corresponds to a Gaussian distribution with $\sigma \approx 0.5 - 0.3$, that is close to the width of the distribution of an electronic coupling matrix elements ($\sigma \approx 0.5$), obtained by QC and MD simulation for electron acceptor organic molecules in electron donating solvents³. Similarly one can use the Becquerel function $N(t)/N(0) = 1/(1 + \beta_n t/m)^m$, which has the advantage of β_n being nearly independent of m . However in this case one cannot vary σ by variations of m . The examples of some other kinds of $P_n(k)$ and $N_n(t)$ are considered below in the discussions of non-stationary diffusion and electron tunnelling.

Kinetics of ET in neat solvents. Competition of electronic coupling control and reorientation control.

The rate distribution approach was used for analysis of experimental kinetics of the excited-state ET in the picosecond range for perylene derivatives^{10, 11} and coumarins in various neat electron donating solvents² (Table 2). MD and QC calculations of Scherer³ demonstrated that fluctuations of the overall electronic coupling matrix element to all the reactant molecules, located inside the interior of the solvent shell, $P(\ln(V_{\text{Max}}^2))$ for oxazine in neat N,N-dimethylaniline is close to Gaussian distribution with $\sigma = 0.4$ and $\ln V_{\text{Max}} = -6.5$ or to $P(\ln(V_{\text{Max}}^2)) = ((V^2/V_{\text{Max}}^2)^6) \exp(-V^2/V_{\text{Max}}^2)/120$ with $V_{\text{Max}}^2 = 0.00025 \text{ eV}^2$. As a result one can describe the experimental decay kinetics (Figs. 1A and 2A) by a sum of several hyperbolic functions with $m = 6$

$$N(t)/N(0) = A_1/(1 + \gamma_1 t)^6 + A_2/(1 + \gamma_2 t)^6 \quad (6)$$

corresponding to $P(\ln(\sum_n V_n^2))$ and to $P(\ln(1/\tau_L))$, where τ_L is longitudinal relaxation time of the solvent. In this case

$$P(\ln k) = A_1(k/\gamma_1)^6 \exp(-k/\gamma_1)/120 + A_2(k/\gamma_2)^6 \exp(-k/\gamma_2)/120 \quad (7)$$

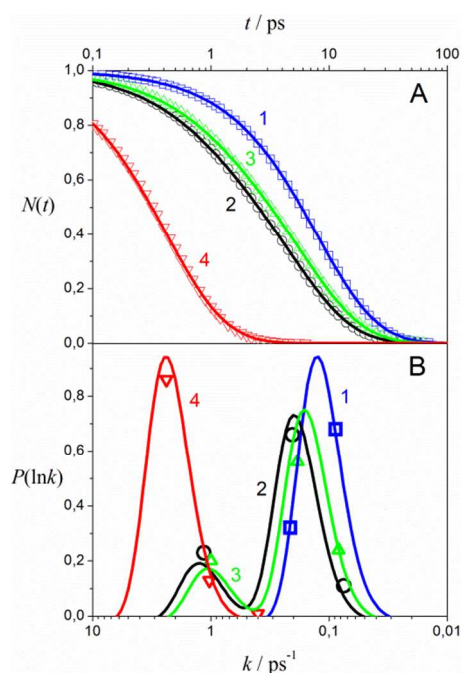


Fig. 2. Experimental kinetics $N(t)$ of the excited-state ET reactions of 3-methylperylene (1), perylene (2), 3-perylenylmethanol (3), and 3-cyanoperylene (4) in neat N,N-dimethylaniline according to¹⁰, their fitting by eqn (6) (A) and the corresponding rate distribution functions $P(\ln k)$, obtained by eqn (7) (B). Points show the rate constants of the polyexponential approximations and their amplitudes.

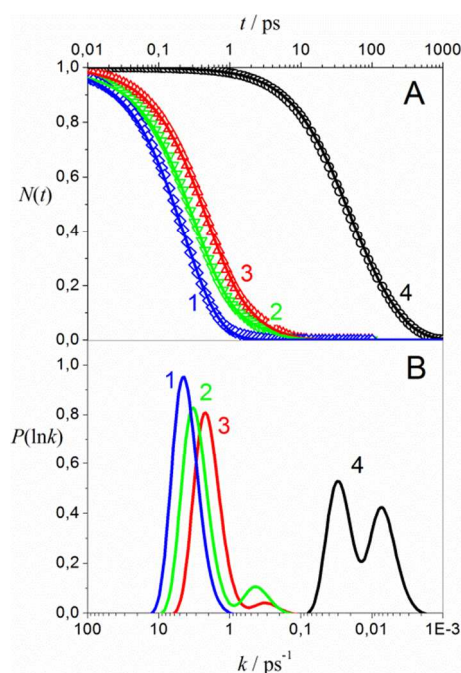


Fig. 3. Experimental kinetics of the excited-state ET reactions of coumarin 152 in neat electron donating solvents (points): N,N-dimethyl-*p*-toluidine (1), N,N-dimethyl-*m*-toluidine (2), N,N-dimethylaniline (3), and triethylamine (4) according to², their fitting by eqn (6) (A) and the distribution functions, obtained by eqn (7) (B).

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Table 2. Kinetic parameters of quenching of the excited molecules of perylene derivatives in neat *N,N*,dimethylaniline and in some other amines, coumarin 152 in various neat electron donating solvents and in the mixtures of *N,N*,dimethylaniline with toluene, and coumarin 151 in the mixtures of *N,N*,dimethylaniline with chlorobenzene (eqn (6)) (obtained from the experimental data^{2,10,11}).

	M*	Q (f_0) *	ΔG_{CS}^* / eV (in MeCN)	A_1	k_1 (γ_1)** / ps ⁻¹	A_2	k_2 (γ_2)** / ps ⁻¹
1	PeH	PhNMe ₂ ¹⁰	-0.13	0.22	1.26 (0.21)	0.78	0.20 (0.033)
2	PeMe	PhNMe ₂ ¹⁰	-0.13			1.00	0.13 (0.021)
3	PeCH ₂ OH	PhNMe ₂ ¹⁰	-0.13	0.20	1.06 (0.176)	0.80	0.16 (0.027)
4	PeCN	PhNMe ₂ ¹⁰	-0.22	1.02	2.41 (0.40)		
5	PeCN	PhNMeEt ¹¹		0.95	3.9 (0.65)	0.06	0.50 (0.083)
6	PeCN	PhNEt ₂ ¹¹	-0.24	0.74	3.0 (0.50)	0.25	0.55 (0.091)
7	PeCN	PhNHEt ¹¹	-0.19	0.55	2.6 (0.43)	0.45	0.4 (0.07)
8	Coumarin 152	NEt ₃ ²	0.96 V ***	0.56	0.03 (0.005)	0.44	0.007 (0.001)
9	Coumarin 152	PhNMe ₂ ²	0.76 V ***	0.85	2.2 (0.37)	0.15	0.37 (0.062)
10	Coumarin 152	mMeC ₆ H ₄ NMe ₂ ²		0.87	3.3 (0.55)	0.12	0.43 (0.072)
11	Coumarin 152	pMeC ₆ H ₄ NMe ₂ ²		1.00	4.5 (0.75)	-	-
12	Coumarin 152	PhNMe ₂ (0.99) + PhCl ²		0.62	2.0 (0.34)	0.38	0.6 (0.10)
13	Coumarin 152	PhNMe ₂ (0.78) + PhCl ²		0.62	1.4 (0.23)	0.38	0.3 (0.05)
14	Coumarin 152	PhNMe ₂ (0.59) + PhCl ²		0.49	1.14 (0.19)	0.51	0.2 (0.04)
15	Coumarin 152	PhNMe ₂ (0.31) + PhCl ²		0.42	0.4 (0.07)	0.58	0.07 (0.012)
16	Coumarin 151	PhNMe ₂ (1.00) ²		1.02	3.7 (0.62)	-	-
17	Coumarin 151	PhNMe ₂ (0.86) + Toluene ²		0.84	2.8 (0.47)	0.16	0.37 (0.061)
18	Coumarin 151	PhNMe ₂ (0.64) + Toluene ²		0.67	2.0 (0.34)	0.33	0.18 (0.03)
19	Coumarin 151	PhNMe ₂ (0.55) + Toluene ²		0.59	2.5 (0.42)	0.41	0.26 (0.044)

* f_0 is a mole fraction of PhNMe₂.

** Values of the parameters γ_1 and γ_2 , obtained by the Laplace transform eqn (7), are shown in parenthesis.

*** Values of the electron donor oxidation potentials E_0 (V).

PeMe – 3-methylperylene; PeH – perylene; PeCH₂OH – 3-pyrenylmethanol; PeCN – 3-cyanoperylene; PhNMe₂ – *N,N*-dimethylaniline; PhNEt₂ – *N,N*-diethylaniline; PhNMeEt – *N*-methyl-*N*-ethylaniline; PhNHEt – *N*-ethylaniline; NEt₃ – triethylamine; mMeC₆H₄NMe₂ – *N,N*-dimethyl-*m*-toluidine; pMeC₆H₄NMe₂ – *N,N*-dimethyl-*p*-toluidine, PhCl – chlorobenzene; MeCN – acetonitrile.

Only one or two components were obtained for all the systems listed in the Table 2. Fitting with 3 or 4 pairs of the parameters A_n and γ_n , still yields several components with identical γ_n . Two areas of the rate constants can be detected: $\gamma_1 = 0.2\text{--}0.7$ ps⁻¹ ($k_1 = 1\text{--}4$ ps⁻¹) and $\gamma_2 = 0.002\text{--}0.1$ ps⁻¹ ($k_2 = 0.01\text{--}0.5$ ps⁻¹).

We compared the obtained $P(\ln k)$ with the experimental parameters of molecular mobility of the solvents: longitudinal relaxation times^{11,12}, τ_L , the rates of rotation of *PeCN in PhNMe₂, τ_{Rot} , measured by optically heterodyned polarization spectroscopy¹⁰, dielectric relaxation times^{13,14}, τ_{Diel} , and medium viscosity (η). Fig. 4 shows that the values of k_1 are weakly sensitive to the medium viscosity ($k_1 \approx 4/\eta^{1/2}$) and exceed the rate of the medium and reactants reorganization ($1/\tau_L$). In contrast, the values of k_2 depend linearly on the reciprocal viscosity of the medium as $k_2 \approx 0.8/\eta$, and are close to $1/\tau_L$. The values of $1/\tau_{Rot}$ and $1/\tau_{Diel} \approx 0.02/\eta$ were found to be considerably smaller than k_2 .

Comparison of the solvent viscosity effects on k_1 and k_2 shows that the observed two peaks of experimental $P(\ln k)$ correspond actually to the different fractions of reactant molecules with different physical behaviour of ET, rather than

to the two wings of the same distribution. In all analyzed systems the two kinds of reactant pairs were found: (i) pairs, having optimal preliminary orientation, with reactivity controlled by fluctuations of electronic coupling ($k_1 = 1\text{--}4$ ps⁻¹); and (ii) pairs, which require some reorientation (reorganization of the medium and reactants) after excitation to react ($k_2 = 0.01\text{--}0.5$ ps⁻¹).

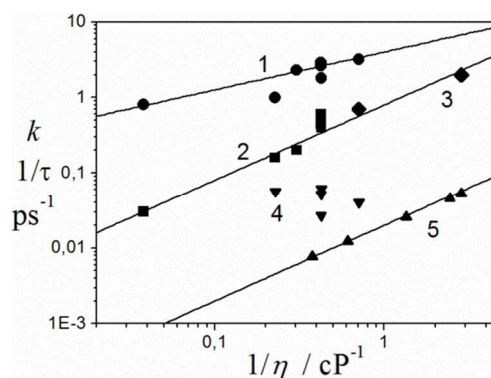


Fig. 4. Dependences of the experimental ET rate constants k_1 (1) and k_2 (2) for quenching of *PeCN in various neat amines^{10,11}, the rates of longitudinal relaxation of the solvent^{11,12}, $(1/\tau_L)$ (3), the rates of rotation of *PeCN¹⁰, $(1/\tau_{rot})$ (4), and the rates of the dielectric relaxation^{13,14} $(1/\tau_{die})$ (5) on the medium viscosity.

In the original experimental work of Vauthey et al.¹⁰ three types of ET-reactive PeX molecules in PhNMe₂ were considered: (1) molecules with optimal mutual orientation for ET (reacting with the rate constant k_{ET}), (2) molecules that have first to rotate (k_R), and (3) molecules that have first to diffuse (k_T). The authors simulated the experimental kinetics with polyexponential function $N(t)/N(0) = \sum_m n_m \exp(-k_m t)$, using variable parameters n_m and k_m . Close optimal values of $k_{ET} \approx 0.7\text{--}0.9 \text{ ps}^{-1}$ were obtained for various PeX, when k_R was supposed to be equal to $1/\tau_L$. The authors¹⁰ evaluated relative populations of the first two kinds of PeX molecules ($n_{ET}/n_R \sim 1:20$ for PeH and PeCH₂OH, ca. 1:2 for PeCN and $\ll 1$ for PeMe), that are similar but smaller than the ratios A_1/A_2 obtained here. Direct application of the Laplace transform shows also some variations of k_1 in the range $1\text{--}4 \text{ ps}^{-1}$ for various PeX.

In their very recent work Vauthey et al.¹⁵ used Monte-Carlo simulation to obtain the dependence of orientational probability on the angle between the dipole vectors of PhNMe₂ and PeCN (PeH) molecules. It was shown that for the majority of PeCN molecules this angle is in the range $(0.5\text{--}1.5)\pi$ due to dipole-dipole interaction, while for PeH (which dipole moment is zero) no preferential orientations exist. This is consistent to the distribution functions shown in Fig. 2: for PeCN only one band is observed which corresponds to the reaction controlled by electronic coupling matrix element at optimal mutual orientations of reactant molecules. Two bands observed for PeH correspond to minor fraction (~ 0.2) which reaction is controlled by electronic coupling and major fraction which has too small V_{AD} and requires some reorientation to react. Thus, in spite of the essential anisotropy of V_{AD} and reactivity of both PeH and PeCN molecules due to dipole-dipole interaction, the majority of PeCN molecules have already the optimal orientation for ET in the ground state. On the contrary, in PeH molecules only a quarter of population has such favourable ground-state orientation and major fraction requires some reorientation or medium reorganization to react. To compare the fluorescence quantum yields of PeCN and PeH measured experimentally in neat PhNMe₂¹⁵ with $P(k)$ obtained here one can express these yields as a function of A_n , k_n and lifetimes τ_0 of PeH and PeCN in inert solvents. Reasonable agreement (taking into account real accuracies of completely different experimental methods of steady-state measurements of small fluorescence quantum yields and decay kinetics) can be seen between the experimental $\varphi_0/\varphi \approx 1200$ and 12000 for PeH and PeCN in neat PhNMe₂ and similar values calculated from the kinetics of *PeX decay and expressed as $\varphi_0/\varphi = (A_1 k_1 + A_2 k_2) \tau_0 \approx 1900$ and 11000 , respectively for PeH and PeCN.

It is worthwhile to compare the obtained distributions $P(k)$ with the distributions of electronic coupling matrix element $P(V^2)$, obtained earlier by QC and MD calculations for various

similar systems²⁻⁴. Castner et al.² and Scherer^{3,4} obtained rather wide distributions $P(\ln V^2)$ for fluctuations of $\ln V^2$ for the single pairs of reactant molecules in the interior of the solvent shell ($r_{AD} < 0.9 \text{ nm}$) for coumarin 152 and oxazine in neat PhNMe₂. These $P(\ln V^2)$ can be described by Gaussian distribution with $V_{Max}^2 \approx 2 \times 10^{-5} \text{ eV}^2$ and $\sigma \approx 3$. However much narrower distribution $P(\ln(\sum_n V_n^2))$ with the value of V_{Max}^2 two orders of magnitude higher ($V_{Max}^2 = 0.0015 \text{ eV}^2$, $\sigma \approx 0.5$) was obtained in the same work of Scherer³ for a sum of V^2 for all electron donor molecules, located in the first solvation layer (the overall V^2) (Fig. 5). The width of this distribution $P(\ln(\sum_n V_n^2))$ is very close to the width of the experimental distributions $P(\ln k)$ listed in the Table 2. One can estimate the Franck Condon weighted density of states, *FCWD*, for the radiationless mechanism of ET for perylene, its derivatives and coumarins in PhNMe₂ by comparing of the obtained values of $k_1 \approx 1\text{--}5 \text{ ps}^{-1}$ with the overall ET coupling, using the standard expression (eqn (1)). Fig. 5 shows that the fast bands of the experimental rate distributions $P(\ln k)$ in neat solvents are close to the $P(\ln(\sum_n V_n^2))$ when Franck-Condon factor *FCWD* $\approx 0.15 \text{ eV}^{-1}$. Close values of *FCWD* $\approx 0.1\text{--}0.3 \text{ eV}^{-1}$ were obtained from the experimental parameters of ET for various charge separation and charge recombination reactions with $\Delta G_{ET} \approx -(0.5\text{--}1.2) \text{ eV}$ ^{16,17}. Thus, fast fraction of the experimental distribution $P(\ln k)$ with $k_1 \approx 1\text{--}5 \text{ ps}^{-1}$ can be attributed to the activationless radiationless transition (non-adiabatic) mechanism of ET (involving internal vibrational modes of the reactant molecules). The former is controlled by the sum $\sum_n V_n^2$ for all electron donor molecules located in the first solvation layer, rather than by preliminary medium reorganization. The reactant molecules which have no optimal mutual orientation in the ground state prior to the photoexcitation to provide sufficient values of $\sum_n V_n^2$ ($\sim 0.001\text{--}0.01 \text{ eV}^2$) require some preliminary reorganization of the medium to react and have $k_2 < 1 \text{ ps}^{-1}$.

Kinetics of ET in mixed solvents. Concentration effects on ET inside the interior of the solvent shell.

Dilution of an electron-donating solvent by inert solvent was found² to cause a decrease of the amplitude of fast component, related to the electronic coupling rate control, and an increase of slower component, related to the reorientation control (Table 2, Fig. 6). For coumarin 151 in mixtures PhNMe₂-toluene the slope of the linear dependence of A_1 on the mole fraction of PhNMe₂, f_Q , (Fig. 7) is close to 1 ($A_1/(A_1 + A_2) \approx 1.0 f_Q$), indicating the absence of the specific solvation of coumarin 151 by the components of the solvent and equal concentrations of the electron donor molecules inside the interior of the solvent shell and in the total volume. For coumarin 152 two components are observed (Fig. 6) even in neat PhNMe₂, indicating that a certain part of the excited molecules requires some preliminary reorientation or medium reorganization to react. This effect can be attributed to dimethylamino group (instead of amino group in coumarin 151), which hinders optimal mutual orientation of coumarin 152 and electron donor molecules even in neat PhNMe₂. In the

mixtures of PhNMe₂ with chlorobenzene $A_1/(A_1 + A_2) \approx 0.2 + 0.5f_Q$, and the fast component does not disappear even at small concentrations of PhNMe₂, which may indicate the formation of some ground-state complex between coumarin 152 and PhNMe₂.

function. Time dependent rate constant for non-stationary diffusion is known to be expressed by Smoluchowski equation^{5,6}

$$k_{\text{diff}}(t) = 4\pi r_Q D(1 + r_Q/(\pi D t)^{1/2}), \quad (8)$$

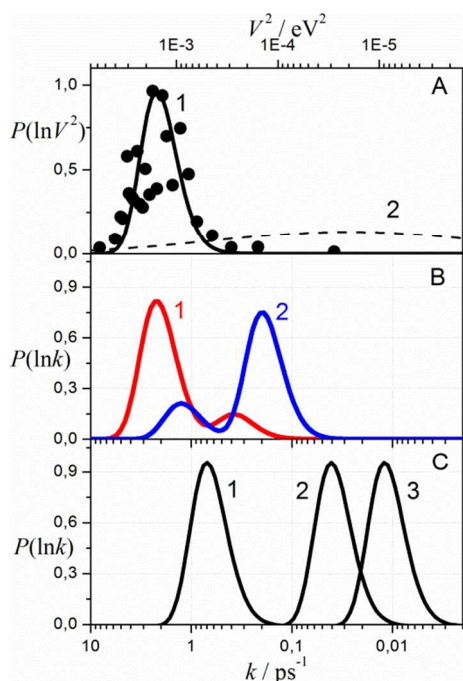


Fig. 5. Distribution of overall electronic coupling matrix element (a sum of V^2 to all electron donor molecules, located in the interior of the solvent shell) $P(\ln(\sum_n V_n^2))$ for oxazine in neat *N,N*-dimethylaniline³ (points and solid line 1) and distribution function for the fluctuations of V^2 for a single pairs of reactant molecules in the interior of the solvent shell³ (dash line 2) (A). Experimental distributions of ET rate constants $P(\ln k)$ for coumarin 152 (1) and perylene (2) in neat PhNMe₂ (B). Relaxation times presented in the form of the distribution functions $P(\ln k) = (k/5.5 \tau)^5 \exp(-k/5.5 \tau)/120 : \tau_{\text{rot}}$ of *PeCN in PhNMe₂¹⁰ (2), and τ_{Diel} ^{13,14} (C). The scale of the panel (A) for V^2 corresponds to the scale of the other two panels for k at $F_{\text{FC}} = 0.15 \text{ eV}^{-1}$ (see eqn (1)).

A decrease of k_1 with the decrease of PhNMe₂ concentration ($k_1 \approx 0.17(1 + 20f_Q)$ for coumarin 151 in toluene, $k_1 \approx 0.09(1 + 20f_Q)$ for coumarin 152 in chlorobenzene) (Fig. 7) indicates that this rate is controlled by the total ET coupling to all reactant molecules located inside the interior of the solvent shell similarly to ET in neat solvents. One can estimate the maximum number of PhNMe₂ molecules inside the interior of the solvent shell from the relative slope $s \approx 20$ of the plot k_1 vs. mole fraction of PhNMe₂, f_Q . That is close to the estimations of $s \approx 13-16$ given in¹⁰.

Kinetics of ET in diluted solutions. Diffusion control of ET.

Kinetics of the ET in diluted solutions ($[Q] < 1 \text{ M}$), studied for perylene in MeCN in the presence of various concentrations of tetracyanoethylene by Vauthey et al.¹⁸, is strongly non-exponential (Fig. 8). This kinetics was discussed earlier in terms of interplay of non-stationary diffusion and distant ET (electron tunnelling)¹⁹⁻²³.

In several cases, including non-stationary diffusion, $P(\ln k)$ cannot be described by hyperbolic function (3) or by Gaussian

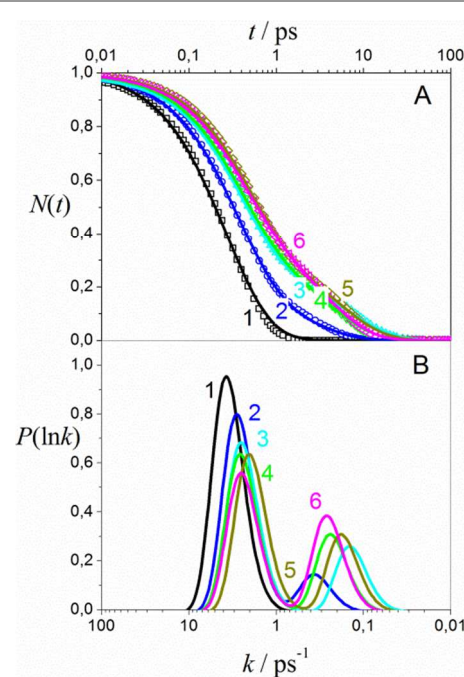


Fig. 6. Experimental kinetics of the excited-state ET reactions of coumarin 151 in neat *N,N*-dimethylaniline and its mixtures with toluene (points) according to² and their fitting by eqn (6) (A); the rate distribution functions, obtained by eqn (7) (B). Mole fractions of PhNMe₂: 1.00 (1); 0.86 (2); 0.81 (3); 0.71 (4); 0.64 (5); and 0.55 (6).

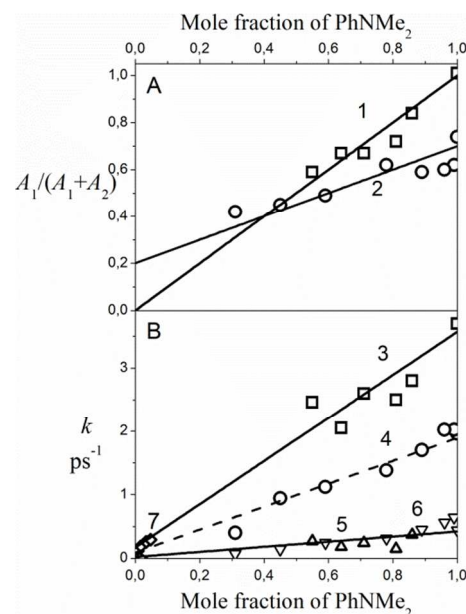


Fig. 7. Dependence of an amplitude of the fast component A_1 on the mole fraction of PhNMe₂ for coumarin 151 in mixtures PhNMe₂-toluene (1) and coumarin 152 in mixtures PhNMe₂-PhCl (2) (A). Dependence of the rate constants k_1 (3, 4) and k_2 (5, 6) on the mole fraction of PhNMe₂ for coumarin 151

in mixtures PhNMe₂-toluene (3, 5) and coumarin 152 in mixtures PhNMe₂-PhCl (4, 6) (B).

where r_Q is a radius of quenching, D is a diffusion coefficient. In this case the diffusion controlled kinetics can be described as

$$N(t)/N(0) = \exp(-C_Q 4\pi r_Q D (1 + r_Q/(\pi D t)^{1/2}) t) = \exp(-C_Q 4\pi r_Q D t) \exp(-C_Q 4\pi^{1/2} r_Q^2 D^{1/2} t^{1/2}), \quad (9)$$

where $C_Q = 0.6[Q]$ is the quencher concentration in molecules/nm³. That corresponds to the Laplace original (at $k_{\text{Diff}} \geq 4\pi r_Q D$)

$$P(\ln(C_Q k_{\text{Diff}})) = (k_{2D}/2(\pi(k_{\text{Diff}} - k_{1D})^3)^{1/2}) \exp(-k_{2D}^2/4(k_{\text{Diff}} - k_{1D}))/k_{\text{Diff}}, \quad (10)$$

where $k_{1D} = C_Q 4\pi r_Q D$ and $k_{2D} = C_Q 4\pi^{1/2} r_Q^2 D^{1/2}$. This distribution function is normalized in coordinates $P(\ln(C k_{\text{Diff}}))$ vs. $\ln k$ and has a narrow maximum at stationary value of pseudounimolecular diffusion rate constant $k = k_{\text{Diff}} C_Q = C_Q 4\pi r_Q D$ and long tail for higher values of k , corresponding to non-stationary diffusion at short times (short distances).

It was found that the total decay kinetics of *PeH in the presence of tetracyanoethylene can be fitted well by a combination of two functions, corresponding to the distribution $P(\ln k)$ inside the interior of the solvent shell and to nonstationary diffusion of the quencher molecules (Fig. 8)

$$N(t)/N(0) = A_1/(1 + \gamma_1 t)^6 + A_2 \exp(-C_Q 4\pi r_Q D (1 + r_Q/(\pi D t)^{1/2}) t). \quad (11)$$

Using two hyperbolic functions with different k_1 and k_2 instead of one, provides no improvement of the fitting. Obtained results are shown in Table 3.

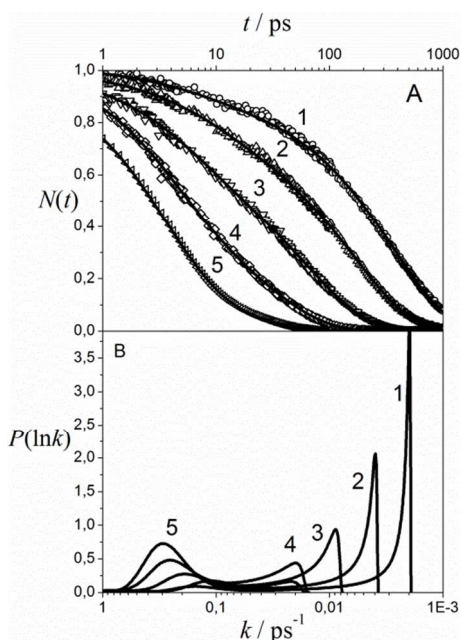


Fig. 8. Experimental kinetics of the excited-state ET reaction of perylene at various concentrations of tetracyanoethylene in MeCN (points, 1 - 0.08, 2 - 0.16, 3 - 0.32, 4 - 0.64, 5 - 0.9 M)¹⁷ and their fitting by eqn (11) (lines) (A). The rate distribution functions obtained from the experimental data by eqns (7 and 10) (B).

Table 3. Approximations of the decay kinetics of excited perylene at various concentrations of tetracyanoethylene in MeCN (according to the experimental data¹⁸, $\Delta G_{\text{CS}}^* = -2.14$ eV) by a combination of the reaction inside the interior of the solvent shell and non-stationary diffusion (eqn (11)).

Concentration of C ₂ (CN) ₄ , [M]	A ₁	k ₁ (γ ₁) * / ps ⁻¹	A ₂	r _Q / nm
0.08	0.06	0.10 (0.017)	0.94	1.05
0.16	0.15	0.11 (0.019)	0.86	1.02
0.32	0.24	0.19 (0.032)	0.78	1.06
0.64	0.44	0.26 (0.043)	0.61	1.03
0.9	0.73	0.30 (0.049)	0.25	1.08

* Values of parameters γ_1 obtained by the Laplace transform (eqn (11)) are shown in parenthesis.

The first fraction with $N(t) = A_1/(1 + \gamma_1 t)^6$ has $k_1 = 0.1-0.3$ ps⁻¹ similar to the rates of ET in neat solvents and in mixed solvents. Obtained values of the diffusion parameters $r_Q = 1.0-1.05$ nm and $D = 0.003$ nm² ps⁻¹ = 3×10^{-5} cm² s⁻¹ for the second fraction are close to published data for diffusion in MeCN¹⁹. Rate constants k_1 linearly depend on the mole fraction of the quencher as $k_1 \approx 0.1(1 + 45 f_Q)$. This slope is similar to that observed for coumarins in mixed solvents and also indicates the increase of the overall electronic coupling $\sum_n V_n^2$ with the increase of the quencher concentration. The dependence of an amplitude A_1 on the mole fraction of the quencher can be approximated by $(A_1/(A_1 + A_2)) \approx 1 - \exp(-20 f_Q)$ (Fig. 9), which gives a number of molecules inside the interior of the solvent shell $s \approx 20$ and indicates the absence of any specific association of perylene and quencher molecules.

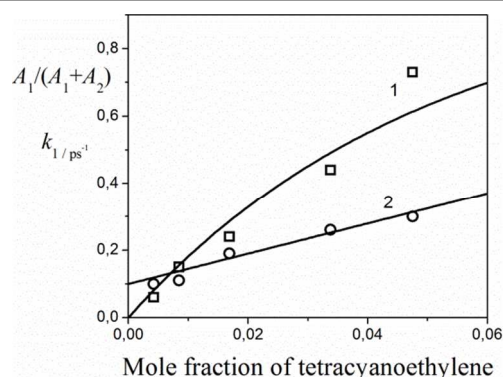


Fig. 9. Dependence of amplitude of the fast component A_1 (1) of the decay kinetics of excited perylene and of the rate constants k_1 (2) on the mole fraction of tetracyanoethylene in MeCN.

Competition of various mechanisms of ET

The results, obtained for various systems discussed here, show that actually the kinetics of these reactions can be considered as a competition of different mechanisms rather than their interplay since in different time domains the different mechanisms dominate. Fig. 10 demonstrates the time evolution of the number of *PeH molecules with different ET rates in

neat PhNMe₂. One can see that the radiationless ET mechanism prevails in the time domain 0.1–1 ps, and the medium reorganization control prevails in the time domain 2–20 ps. Similar competition in different time domains is observed in the diluted solutions, where ET inside the interior of the solvent shell prevails in the time domain 1–10 ps and non-stationary diffusion control prevails in the time domain 10–1000 ps. In the first approximation their interplay can be neglected.

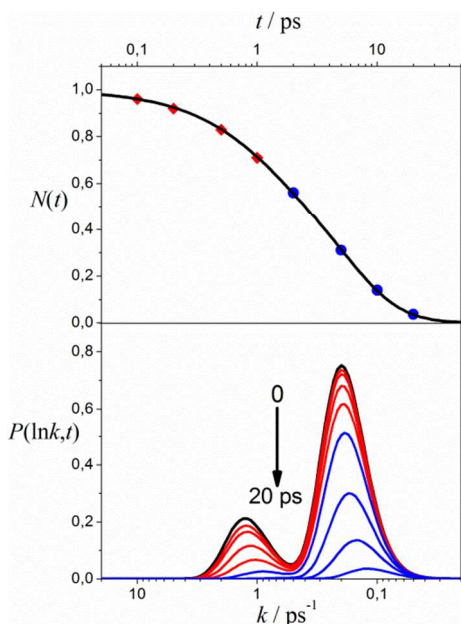


Fig. 10. Kinetics of the decay of *PeH in neat N,N-dimethylaniline (top panel) and rate distributions (bottom panel) at various times $t = 0, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20$ ps (marked by points in the top panel). Initial distribution is shown by black line, distributions in time domain 0.1-1 ps by red lines, and distributions in time domain 2-20 ps by blue lines.

The rate distribution approach provides very simple method for the analysis of the competition of various mechanisms of fast reactions. One can compare the experimentally obtained “spectrum” of rates for the system under investigation with $P(\ln k)$ for known or simulated mechanisms (similarly to ordinary spectral analysis, when absorption or emission spectrum of some mixture is compared with the spectra of possible components). Here we shall consider kinetics of ET reaction of excited perylene with tetracyanoethylene in MeCN as an example. Various mechanisms were discussed for this reaction, trying to explain the deviations of the experimental kinetics from the Smoluchowski equation for ordinary non-stationary diffusion: the electron tunneling (distant or remote ET)^{5, 6, 20–23} and the so called two-channel reaction,^{5, 6, 19–21, 23} which assumes the formation of both ground-state and electronically excited radical ions of perylene. A consideration of the rate distribution provides a possibility to check these hypotheses simply by comparison of the experimental $P(\ln k)$ with that expected for electron tunneling and two-channel mechanisms.

Kinetics of electron tunneling can be described by stepwise approximation²⁴, as

$$N(t)/N(0) \approx \exp[-C_Q (4\pi/3) (a/2)^3 (\ln k_0 t)^3] \quad (12)$$

where C_Q is a quencher concentration (molecules/ nm^3). This approximation uses very strong distance dependence of ET rate. In this case the distribution function can be expressed as

$$P(\ln k) \approx 4\pi C_Q (a/2)^3 (\ln(k_0/k))^2 \exp[-C_Q (4/3)\pi (a/2)^3 (\ln(k_0/k))^3] \quad (13)$$

Fig. 11 shows an example of this distribution for the reaction of excited perylene with tetracyanoethylene in MeCN simulated for $[\text{TCNE}] = 0.32$ M and $a = 0.2$ nm (green line) together with the experimentally obtained $P(\ln k)$ at the same concentration (black line). One can see that in the range $k < 0.05$ ps^{-1} (corresponding to $r_{\text{AD}} > 1$ nm) the diffusion controlled reaction dominates and the possible contribution of an electron tunneling is negligible. On this reason the experimental kinetics cannot be used for the determination of the parameters of electron tunneling and of the electronic coupling decay parameter a as it was done earlier^{5, 6, 20–23}. In these works the contribution of the reaction inside the interior of the solvent shell in low viscous solvent (MeCN) was erroneously attributed to the distant ET. Nevertheless, in more viscous solvents where $P(\ln k_{\text{Diff}})$ is shifted into the range of smaller k (e.g. dash line 5 in Fig. 10 for $\eta = 3$ cP) electron tunneling can provide considerable contribution into the total kinetics in the range of $k = 0.008 - 0.03$ ps^{-1} .

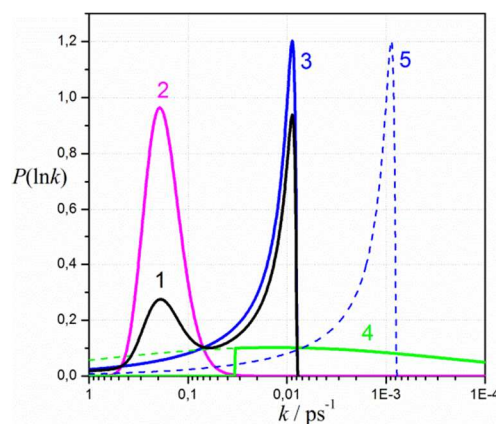


Fig. 11. Simulated normalized rate distribution functions $P(\ln k)$ for ET reaction inside the interior of the solvent shell (2 - eqn (7), $k_1 = 0.1*(1 + 4f_0)$), non-stationary diffusion controlled reaction in MeCN (3 - eqn (10), $D = 0.003$ nm^2 ps, $r_Q = 1.05$ nm), electron tunneling (4 - eqn (13), $k_0 = (4\pi^2/h) V_0^2 \text{FCWD} = 300$ ps^{-1} , $a = 0.2$ nm, line 4 corresponds to $r_{\text{MQ}} > 1$ nm), diffusion controlled reaction in viscous solvent (5 - eqn (10), $D = 0.0003$ nm^2 ps, $r_Q = 1.05$ nm), and the experimental rate distribution function for the decay of *PeH in MeCN at 0.32 M¹⁸ (1 - eqns (7 and 10)).

The reaction of excited perylene with tetracyanoethylene is exergonic^{6, 19} and formation of both the ground ($\Delta G_{\text{ET}}^* = -2.14$ eV) and the excited ($\Delta G_{\text{ET}}^* = -0.6$ eV) electronic states of perylene radical cations is thermodynamically possible.^{5, 6, 19–21, 23} On this reason it was supposed that the faster initial rate than that expected for the reaction controlled by non-stationary diffusion can be attributed to some contribution of faster rate of

the formation of the excited radical cations of perylene. According to the Marcus theory one can expect at short r_{AD} the faster rate of this reaction than that for very strongly exergonic reaction yielding the ground-state radical cations. To estimate the rates of these reactions inside the interior of the solvent shell one cannot use the conventional expressions for the medium reorganization energy, λ_s , and energy gap, $\Delta E_{ET} = -(\Delta G_{ET} + \lambda_s)$ since they should fail at such short distances. Formal estimations contradict this hypothesis since they yield the reorganization energies $\lambda_s = 1.3\text{--}1.6$ eV and the rate constants $k \approx 10^3\text{--}10^4$ ps⁻¹ for the ground state radical cation formation (such fast k_{ET} causes static quenching of the excited molecules and is close to the frequency factor $(4\pi^2/h)V_{AD}^2$ for the radiationless transition mechanism, since $FCWD \approx 1$ eV⁻¹ for isoergonic transition) and $k \approx 2 - 0.003$ ps⁻¹ for the excited radical ions (for $r_{AD} = 0.6\text{--}0.8$ nm, $\rho_A = \rho_D = 0.3$ nm, $n = 1.34$, $\varepsilon = 37$ for MeCN using $\lambda_s = 1.44(1/\rho_A + 1/\rho_D - 1/r_{AD})(1/n^2 - 1/\varepsilon)$, Eq (1) and $FCWD(r_{MQ}) = [1/(2\pi)]^{1/2} \times \sum_m \{[\exp(-S) \times S^m/m!] \times \exp[-(\Delta E_{ET} - m h \nu_V)^2/2^2]\}$, where $S = \lambda_s/h \nu_V = 2$, $h \nu_V = 0.2$ eV, $\sigma = (2\lambda_s k_B T)^{1/2}$). At the same time estimation of λ_s from experimental emission frequency of the exciplex of durene with 9,10-dicyanoanthracene in MeCN²⁵ yields $\lambda_s = 0.6$ eV and $k \approx 10$ ps⁻¹ for the ground state and $k \approx 2 \times 10^3$ ps⁻¹ for the excited radical ions formation and can support this hypothesis (for smaller $r_{AD} \approx 0.4$ nm). The distributions $P(\ln k)$, obtained from the experimental kinetics of *PeH decay in the presence of TCNE in MeCN in the range 0.1–1000 ps, providing $k = 0.1\text{--}0.3$ ps⁻¹, depending on the concentration of TCNE (Table 3). Experimental distributions $P(\ln k)$ in this range of $k = 0.1\text{--}0.3$ ps⁻¹ for *PeH + TCNE show no difference with the distributions, observed for other systems with small $-\Delta G_{CS}^*$, where the formation of excited radical ions is thermodynamically impossible. On this reason these values $k = 0.1\text{--}0.3$ ps⁻¹ can be attributed to ET inside the interior of the solvent shell. Thus, experimental decay kinetics of *PeH cannot confirm or deny the hypothesis of the two-channel reaction.

Recently Vauthey with coworkers²⁶ used a combination of femtosecond time resolved fluorescence up-conversion, infrared and visible transient absorption spectroscopy to follow the vibrational energy redistribution in the product after charge separation and subsequent charge recombination. For highly exergonic reaction of *PeH with TCNE the donor was found to be formed in a very hot vibrational state, whereas the acceptor is mostly cold, in contrast to less exergonic reactions where both donor and acceptor are found to be vibrationally hot. This asymmetric energy redistribution was attributed to the formation of the donor cation radical in an electronic excited state upon charge separation that confirms the possibility of the two-channel reaction mechanism.

It should be mentioned that Laplace images in the form of hyperbolic functions $N(t)/N(0) = 1/(1 + \gamma_0 t)^m$ with variable fractional $m < 3$ were used earlier for formal description of non-exponential kinetics of some ultrafast photoreactions (predominantly in biophysics for photoisomerization, electron transfer, etc.)^{7, 25}. In these cases the experimental kinetics $N(t)$ was described by the smooth asymmetric distribution function

$P(k)$ with one maximum, containing two variable parameters (γ_0 and m) $P(\ln k) = ((mk/\gamma_0)^m/\Gamma(m)) \exp(-mk/\gamma_0)$. For instance, kinetics of photoisomerization of a bacterial phytochrome system in two thermally stable states of the photocycle²⁵ was described using $\gamma_0 = 0.064$ ps⁻¹, $m = 1.9$ and non-exponential kinetics was attributed to some distribution of rates related to the variations of conformations of protein substrates, the shape of potential energy surface and activation barrier²⁵. But the same experimental kinetics $N(t)/N(0)$ can be described with the same accuracy by a sum of two functions according to eqn (6) with parameters $A_1 = 0.28$, $\gamma_1 = 0.003$ ps⁻¹, $A_2 = 0.72$, $\gamma_2 = 0.013$ ps⁻¹, $m = 6$ (Fig. 11). These two components can be attributed to different mechanisms of the reaction, or different fractions of the bacterial phytochrome system. Thus, approximation of some kinetics by functions $N(t)/N(0) = 1/(1 + \gamma_0 t)^m$ with variable fractional $m < 3$ is suitable only for formal description of the reaction kinetics rather than for analysis of their actual mechanism.

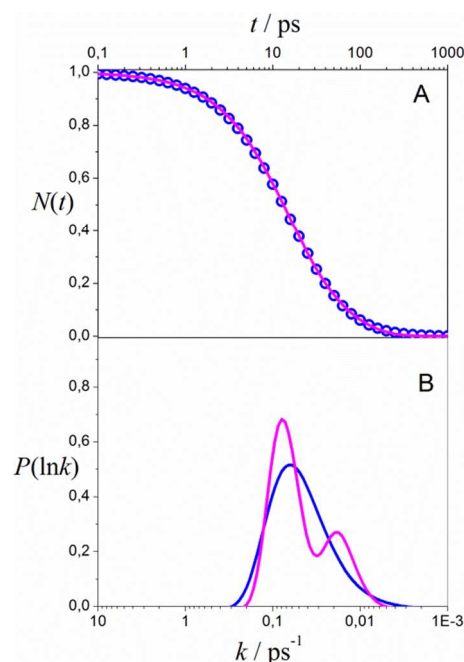


Fig. 12. The difference between the descriptions of non-exponential kinetics by expansion in series of hyperbolic functions (eqn (2)) and by one term approximation with fractional $m < 3$ (eqns (3-5)). Experimental data on photoisomerization dynamics of a bacterial phytochrome system in the two thermally stable states of the photocycle (from ref. 9) are shown by circles (eqn (3)), $k_0 = 0.064$ ps⁻¹, $m = 1.9$ and their expansion in a series of hyperbolic functions (eqn (2)), $A_1 = 0.28$, $k_1 = 0.003$ ps⁻¹, $A_2 = 0.72$, $k_2 = 0.013$ ps⁻¹, $m = 6$ are shown by lines (A). The corresponding rate distributions $P(\ln k)$ (eqns (4) and (6)) (B).

This discussion demonstrates how the consideration of the rate distributions can reveal important features of the reaction kinetics and mechanism. The rate distributions, obtained directly from the experimental kinetic data by rather simple formal mathematical transform without using any hypothesis, allows to avoid difficulties, arising, when one compares the experimental data with simulated data, corresponding to some hypothetical mechanism. In the latter case important

complications can arise, due to a loss of information, which occurs during the integration (necessary for simulation^{5,6} of $k(t) = \int_0^\infty W(r_{\text{MQ}}) n(r_{\text{MQ}}, t) d^3r_{\text{MQ}}$). The integral can be described by smaller number of parameters than the integrand and many various integrands can correspond to the given integral function. On this reason one cannot consider a good description of the experimental kinetics $N(t)$ by any position dependent rate $W(r_{\text{MQ}})$ ^{5,6} as an evidence for a given mechanism, ignoring various other possible $W(r_{\text{MQ}})$, which also can describe $N(t)$ and $k(t)$ with similar accuracy. This corresponds to the well-known principle of chemical kinetics, asserting that a given experimental kinetics $N(t)$ always can be described by many different mechanisms and some independent data are necessary to choose one of these mechanisms (or the *simplest* one can be chosen according to the Occam's Razor principle). This unreliability of the continual approaches and of the assumption on the uniform spatial distribution^{5,6} of the reactant molecules should be taken into account in all discussions of the reaction mechanisms.

Conclusions

The presentation of the experimental kinetics of ultrafast reactions in the form of rate distribution provides quantitative description of this kinetics in very simple and clear graphical form. This approach reveals the evolution of ET mechanism in the course of the reaction and transformations of physical behaviour of rate control factors in the time domain 0.1–1000 ps. It is important that this representation requires no preliminary assumptions on the reaction mechanism and uses rather formal mathematical procedure of an expansion of the experimental kinetics $N(t)$ into series of functions $\sum_n A_n N_n(t)$ which have Laplace originals in the form of continuous functions $P_n(k)$. The rate distribution approach can reveal new physical insights into the reaction mechanism and has some advantages for the analysis of experimental kinetics of ultrafast reactions and for comparison with various theoretical models of these reactions.

Several examples considered in this paper using the rate distribution approach show that in the time domain 0.1–1 ps the radiationless transition mechanism of ET dominates and the reaction rate is not sensitive to molecular mobility. In the time domain 1–30 ps the reaction is controlled by preliminary reorganization of the medium and mutual reorientation reactant molecules (librations), necessary to reach the sufficient value of the electronic coupling for activationless radiationless ET. The ratio of these two fractions depends on the dominant mutual orientation of the reactant molecules in the ground state, prior to their photoexcitation. Non-stationary diffusion control dominates at $t > 10$ ps. Substantial contribution of the reaction inside the interior of the solvent shell into total ET kinetics is observed even in diluted solutions. No contribution of the discussed earlier^{5,6,19–21,23} remote ET (electron tunnelling) was detected in the excited-state ET reactions of perylene with tetracyanoethylene in MeCN. Only in viscous solvents ($\eta > 3$

cP) one can expect some contribution of electron tunnelling in time domain 30–100 ps.

The description of ultrafast ET kinetics in terms of distribution of rate constants is consistent with their description in terms of a dynamical variable coupled to the solvation dynamics² since fluctuations of electronic coupling are much faster (~ 50 ps⁻¹) than average ET rate (< 5 ps⁻¹) and only a small fraction (< 0.1) of excited molecules has a chance to react during each high amplitude fluctuation. The fastest observed rates of ET $\sim 1\text{--}5$ ps⁻¹ were found to be controlled by the total electronic coupling to all electron donor molecules located in the interior of the solvent shell (by a sum of V^2), rather than by the average value of V^2 for a single pair of reactant molecules in the interior of the solvent shell. The rate distribution approach confirms the main features of ultrafast ET reactions^{1,2,10,11} and provides possibilities for more detailed quantitative analysis of their kinetics. Examples considered here show that the rate distribution approach and the inverse Laplace transform can have wider capabilities than used until now in chemical kinetics for analysis of the mechanisms of various complex chemical reactions and for determining of their rate constants from the experimental data.

Biography

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Competing financial interests

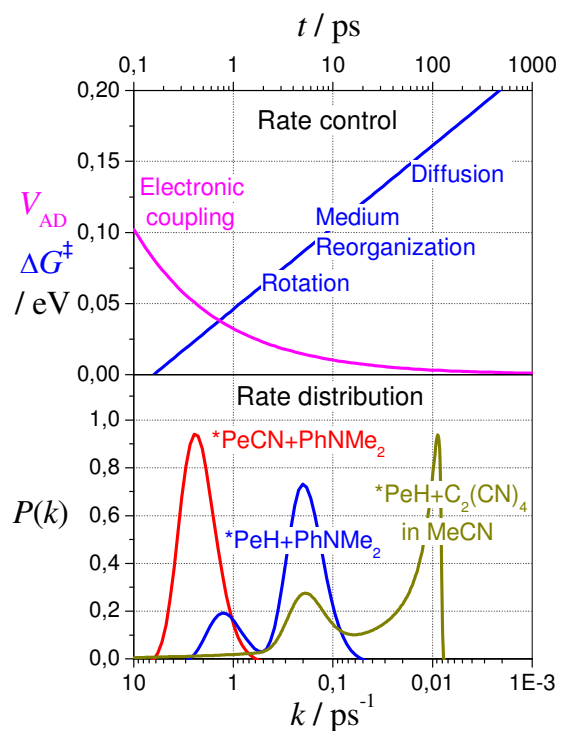
The authors declare no competing financial interests.

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Rate distribution functions $P(k)$, obtained directly from the experimental kinetics $N(t)$ by the inverse Laplace transform, demonstrate transformations of the rate control factors in the course of ultrafast ET reactions