Electron Transfer in a Dynamically Disordered Polar Medium

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Abstract. Intramolecular electron transfer (ET) processes with the main energetic contributions coming from the solvent reorganization are investigated for a polar medium that exhibits dynamic disorder. Dynamic disorder provides a description of the anomalous relaxational behavior of correlation functions in complex glass-like systems, alternative to static disorder. In particular, the questions addressed are whether time-resolved observation of nonexponential ET in such a medium can readily distinguish experimentally between static and dynamic disorder and whether a contribution of intramolecular degrees of freedom to the ET can be identified by it.

1. INTRODUCTION

There has been a rapidly growing interest, experimentally[1–11] as well as theoretically,[12–27] in the influence of the *dynamics* of the surrounding medium on electron transfer (ET) processes. A class of reactions of particular interest are intramolecular[28] ET processes where the reaction is coupled to polarization fluctuations of the environment. For the case that the relaxation of the polarization fluctuations of the surrounding medium has a simple Debye form, and the main energetic contributions to the ET come from the solvent reorganization, the ET exhibits an approximately single-exponential time behavior, with a rate constant then given by[20,22,29]

$$k_{ET}(\tau) = \frac{k_e}{1 + Ik_e\tau}, \tag{1}$$

where τ is the longitudinal dielectric relaxation time of the solvent. I is a numerical factor depending on the free energy barrier ΔG^* of the reaction,[20,22] with

$$I = \ln 2 + 2\int_0^1 dx \frac{\exp[(1-x^2)\Delta G^*/k_BT] - 1}{1-x^2}$$

$$\approx \sqrt{\frac{\pi}{\Delta G^*/k_BT}} \exp(\Delta G^*/k_BT)$$

for $\Delta G^*/k_BT$ large. (2)

The free energy barrier is related to the standard free energy ΔG^0 of the reaction by $\Delta G^* = (\Delta G^0 + \lambda_0)^2/4\lambda_0$, λ_0 being the reorganization energy of the solvent. The rate constant k_e used in Eq. (1) is the semiclassical equilibrated ET rate constant,

$$k_e = \nu_q \exp(-\Delta G^*/k_BT), \tag{3}$$

and refers to adiabatic as well as nonadiabatic processes.[30,31] The detailed functional form of the prefactor ν_q in Eq. (3) depends on the adiabaticity of the reaction.[30] In the limit of fast dielectric relaxation of the solvent, the experimentally observed rate constant k_{ET} will be k_e.

It has been demonstrated theoretically that a nonvanishing contribution λ_i from intramolecular degrees of freedom to the total reorganization energy $\lambda = \lambda_i + \lambda_0$ can lead to considerable deviations from a single-exponential time behavior of the ET process,[20,22] and there are also recent experimental indications for this vibrational effect.[11] Such a situation voids the concept of a time-independent ET rate constant k_{ET}, and the complete time behavior of the reaction process has to be taken into account for a comparison of theory and experiment.

However, a nonexponential behavior of the observed ET process may be due not only to a competition be-

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tween fast intramolecular and slow solvational degrees of freedom, but also can be due to a non-Debye behavior of the fluctuations in the medium surrounding the ET complex. There are recent experimental indications for such an effect for the case of ET processes in higher alcohols (glycerol and propylene glycol).[9,10] These particular solvents belong to the large class of complex or "glassy" systems where fluctuations exhibit an anomalous nonexponential relaxation behavior.[32] For example, the frequency-dependent dielectric constant, involved in the polarization fluctuations, takes on a Davidson–Cole form[33,34] in those higher alcohols.

The generic physical reasons for anomalous relaxation in complex systems and the question of whether there is some universal concept that allows a unified description of anomalous relaxation in various systems are still unresolved.[35,36] *Static* models, based on inhomogeneity of the medium, as well as *dynamic* models describing complex local dynamical processes, have been both employed as possible descriptions of such relaxation behavior of fluctuations.[35,36] Particularly, a static model has been employed recently as an explanation of the findings of nonexponential ET in higher alcohols.[23] However, only its predictions for the short-time behavior of the reaction were compared with the observations.[10]

In a recent article[27] we have provided a method for a description of the complete time behavior of ET obeying the approximate Eq. (1) in a medium exhibiting static disorder. We continue this work by analyzing here instead the effect of a dynamic model for anomalous relaxation, a model which describes *dynamic disorder*, and by comparing the results with those from the corresponding model[23,27] describing static disorder. The questions we wish to address with this work are: (i) do the models considered here for static and dynamic disorder, models that describe the same anomalous relaxation behavior of the polarization fluctuations, predict a markedly different dynamic behavior of the ET process; and (ii) is it possible to distinguish nonexponential ET reaction behavior due to the contribution from intramolecular degrees of freedom from the nonexponential behavior due to anomalous relaxation behavior of the polarization fluctuations coupled to the ET?

We note that the static disorder and dynamic disorder models for ET that will be discussed in the present paper both use a certain approximation (in particular, Eq. (1)) in order to simplify the treatment. This study has, therefore, mainly a qualitative nature but can be useful in providing insight into a more rigorous mainly numerical treatment.[37]

2. STATIC AND DYNAMIC MODELS FOR ANOMALOUS RELAXATION

In many complex systems, particularly ones that show glass-like behavior, the autocorrelation function of a quantity x, with a time scale τ of the relaxation,

$$C(t/\tau) = \langle x(t)x(0)\rangle/\langle x^2\rangle, \tag{4}$$

shows an *anomalous* relaxation behavior.[32,35,36] Anomalous means here that $|d \ln C(t/\tau)/dt|$ decreases with time, i.e., the relaxation is slowing down. In case of a single-exponential relaxation, this quantity would be constant. Experimentally, the functional form of the correlation function remains relatively constant when macroscopic parameters such as the temperature are varied, whereas the time scale τ shows a strong temperature dependence.[32,34]

An example for the functional form of $C(t/\tau)$ is the Davidson–Cole (DC) form

$$C_{\mathrm{DC}}(t/\tau_0) = \Gamma(\beta, t/\tau_0)/\Gamma(\beta), \tag{5}$$

where $\Gamma(\beta, t/\tau_0)$ denotes the incomplete Gamma function,[38] and $\Gamma(\beta)$ denotes the usual Gamma function. β and the time scale τ_0 are the only parameters for this strongly nonexponential relaxation. When x in Eq. (4) represents the polarization of the medium, this particular functional form gives rise to the well-known Davidson–Cole form of the frequency-dependent dielectric constant[33,34]

$$\frac{\varepsilon_{\mathrm{DC}}(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty e^{-i\omega t}\left[-\frac{d}{dt} C_{\mathrm{DC}}(t/\tau_0)\right] dt = \frac{1}{(1 + i\omega\tau_0)^\beta}. \tag{6}$$

Other functional forms, e.g., the Kohlrausch–Williams–Watts form, are discussed in Refs. 32–34. Since Eq. (6) describes the dielectric behavior in glycerol-like solvents, we will be concerned only with the Davidson–Cole behavior in this paper.

In the static disorder approach, it is assumed that in a medium which shows anomalous relaxation the *local* relaxation behavior of the correlation function $\langle x(t)x(0)\rangle$ is single-exponential, i.e., has the Debye form. However, the medium is assumed to be inhomogeneous in this static disorder model, and the *local* relaxation time τ' varies within the medium according to a distribution function $g(\tau')$. The final form of the correlation function is then given by averaging over all local processes,

$$C(t/\tau) = \int_0^\infty d\tau' g(\tau') e^{-t/\tau'}, \tag{7}$$

where the overall time scale τ can be chosen to be the mean relaxation time with respect to the distribution $g(\tau')$, i.e., $\tau = \int d\tau' g(\tau')\tau' = \langle \tau' \rangle_g$. A particular distribution function $g(\tau')$ that reproduces a Davidson–Cole behavior of the dielectric constant, Eq. (6), is[34]

$$g_{DC}(\tau') = \frac{\sin \pi\beta}{\pi\tau'} \left(\frac{\tau'}{\tau_0 - \tau'} \right)^{\beta}, \quad \text{for } \tau' \leqq \tau_0, \tag{8}$$

with $g_{DC}(\tau')$ being zero for $\tau' > \tau_0$.

An approach based on such an inhomogeneous distribution of relaxation times within a medium makes sense physically for inhomogeneous systems such as disordered solids, or, perhaps, proteins at low temperatures,[39] although even in these cases the local dynamics may be much more complicated. However, there are many *liquid* systems, such as the higher alcohols, whose correlation functions also show an anomalous complex relaxation behavior. Particularly, here one should consider the possibility that the local relaxational behavior is the same everywhere within the medium, but obeys a more complicated dynamics. In such systems, the fluctuations of the quantity x could be coupled to one or more additional degrees of freedom which, in turn, also undergo fluctuations. Such an additional degree of freedom could be a local "free volume",[40] or, in the case of glycerol and glycerol-like solvents, the number of saturated hydrogen bonds.[41] Both quantitites could affect the local relaxation of the solvent molecules, e.g., the relaxation process being fast for a large free volume or for a small number of saturated hydrogen bonds.

Denoting by v the deviation of this new degree of freedom from its average value, we can now write down a simplified stochastic model for the local relaxation of x, the Fokker–Planck equation

$$\frac{\partial}{\partial t} P(x, v, t) = \left[\frac{1}{\tau_x(v)} \mathbf{L}(x) + \frac{1}{\tau_v} \mathbf{L}(v) \right] P(x, v, t) \tag{9}$$

for the probability distribution $P(x, v, t)$ of fluctuations. The time scale τ_v of the fluctuations of v could be the time scale of the free volume or hydrogen bond fluctuations; $\tau_x(v)$ is the v-dependent time scale of the fluctuations of x. $\mathbf{L}(x)$ and $\mathbf{L}(v)$ have both the form:

$$\mathbf{L}(x) = \frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} + x \right) \tag{10}$$

and are Fokker–Planck operators that describe Ornstein–Uhlenbeck processes which, taken by themselves, would lead to a single-exponential relaxation of the respective correlation functions. Due to the coupling of the relaxation time $\tau_x(v)$ to the v fluctuations in Eq. (9), the relaxation behavior of x is now more complicated. Such a model may be termed a model for *dynamic disorder*, in distinction from the *static disorder* models described earlier. In the former, the relaxation time τ_x is still distributed inhomogeneously in the medium at any instance of time, but it is also fluctuating locally.

It is easy to see that, employing τ_v as the overall time scale τ, the functional form of $C(t/\tau)$ depends only on the dimensionless part of the v-dependent relaxation time $\tau_x(v)$, which we will call $f(v)$:

$$f(v) = \tau_x(v)/\tau_v. \tag{11}$$

From the observation that the functional form of the correlation function $C(t/\tau)$ is relatively insensitive to the change of external parameters, e.g., to temperature change,[33,34] one may infer that a particular functional form of $f(v)$ determines the local fluctuations of x over a wide range of these parameters. Only the time scale τ_v underlies a strong dependence on them.

Particularly for the case of a Davidson–Cole behavior of the correlation function, Eqs. (5) and (6), Anderson and Ullmann[42] noticed qualitatively that a function

$$f(v) = \begin{cases} \alpha \exp[+v^2/2\beta'] & \text{for } v \geqq 0, \\ \alpha \exp[-v^2/2\beta'] & \text{for } v < 0, \end{cases} \tag{12}$$

can give a good approximate description of a Davidson–Cole function. We have made an extensive numerical study with the above choice of the "free volume"-dependent relaxation time,[37] and present in Table 1 results for the best choices of the parameter α in Eq. (12) for various values of β' to obtain Davidson–Cole behavior with a particular exponent β. Those results will be employed in this paper. The ratio of the parameter τ_0 of the Davidson–Cole form, Eq. (6), to the time scale τ_v

Table 1. Parameters β', α, and τ_v of a Dynamic Model for Davidson–Cole Behavior with Exponent β and Time Scale τ_0, Eqs. (6) and (12), and Exponent β'' for Asymptotic Behavior of Short-Time Rate Constant k_s, Eq. (20)

β'	α	τ_0/τ_v	β	β''
0.3	0.59	1.31	0.54	0.38
0.4	0.80	1.38	0.61	0.47
0.5	1.00	1.45	0.70	0.57
0.6	1.18	1.53	0.77	0.67
0.7	1.38	1.66	0.85	0.78
0.8	1.60	1.81	0.83	0.85
0.9	1.80	1.95	0.86	0.92

of the v fluctuations is constant for given parameters α and β'. This ratio is given in Table 1.

The dynamical model presented above does not attempt to provide a universal physical explanation for anomalous relaxational behavior in each individual case. Rather, it is an attempt to *model* the local fluctuations of a quantity x, e.g., the polarization. These local fluctuations, in turn, determine the dynamics of the ET process. From a phenomenological point of view, a mathematically (but not necessarily physically) correct description of the local fluctuations of a quantity is sufficient for the analysis of the effects that these fluctuations have on reaction processes that are coupled to them.

3. ET UNDER STATIC AND DYNAMIC DISORDER

The previous section provides us with the means to compare the effects of static and dynamic disorder on the ET process. Within the approximation Eq. (1) for the effects due to polarization fluctuations of Debye form, the local ET processes take place with a rate constant $k_{ET}(\tau)$. In the case of static disorder, the fraction of unreacted molecules at time t, $Q(t)$, is then given simply by an average of the local single-exponential reaction processes over all local relaxation times τ,

$$Q(t) = \int_0^\infty d\tau g(\tau) \exp[-k_{ET}(\tau)t], \tag{13}$$

In Ref. 27 a numerical method was given to approximate this function for general distributions $g(\tau)$, and we have analyzed its behavior for the case of a distribution, Eq. (8), satisfying the Davidson–Cole plot. In this case, Eq. (13) becomes

$$Q(t) = \frac{\sin(\pi\beta)}{\pi} \int_0^1 dx\, x^{\beta-1}(1-x)^{-\beta} \times \exp\left(-\frac{k_e t}{1 + Ik_e\tau_0 x}\right). \tag{14}$$

From this equation, it can be readily seen that, using k_e^{-1} as time scale, the reaction process depends on the reaction barrier parameter $\Delta G^*/k_B T$ and the time scale τ_0 of the fluctuations only via the product of parameters $Ik_e\tau_0$. Particularly, for large values of this product the behavior of $Q(t)$ can become nonexponential.[27] We shall see that this dependence of the time behavior of $Q(t)$, for a given β, on the single parameter $Ik_e\tau_0$ no longer holds for *dynamically* disordered systems.

In the dynamic disorder model, the polarization fluctuations are coupled to the v-fluctuations via Eq. (9), and a treatment[37] of the reaction problem then involves Eq. (A5). In the present paper, the simplified solution is given in which the approximation Eq. (1) is used to describe the effects due to polarization fluctuations on the local ET processes. The local rate for the ET is given again by $k_{ET}(\tau)$, but now with τ replaced by $\tau_x(v)$. The v-fluctuations then give rise to the reaction-diffusion equation:

$$\frac{\partial}{\partial t} P_r(v,t) = \left\{\frac{1}{\tau_v}\mathbf{L}(v) - k_{ET}[\tau_x(v)]\right\} P_r(v,t), \tag{15}$$

which describes the time behavior of the reactant distribution $P_r(v,t)$. The stationary distribution of the v fluctuations, $P_0(v) = \exp(-v^2/2)/\sqrt{2\pi}$, is to be used as initial reactant distribution $P_r(v, t=0)$ in Eq. (15). The unreacted fraction of molecules in the dynamic disorder model is then given by:

$$Q(t) = \int_{-\infty}^{\infty} dv\, P_r(v,t). \tag{16}$$

For the numerical solution of the above reaction-diffusion problem, we have employed the generalized moment method as described in Ref. 22.

In Fig. 1 results for the time behavior of the ET process that arises from treating the polarization fluctuations according to the static model are compared to those obtained using the above dynamic model. In order to make possible a better comparison with the qualitative form of observational curves that arise from different experiments, $\log Q(t)$ is plotted vs. t in Fig. 1a (corresponding to a fluorescence decay experiment as, for example, in Ref. 10), and $\log Q(t)$ vs. $\log t$ in Fig. 1b (corresponding to absorption experiments as, for example, in Ref. 43, which could cover a wider range of time scales).

As noted above, for a particular value of the product $Ik_e\tau_0$ the static model (with Eq. (1)) predicts a unique function for the ET time behavior. However, the dynamic model (with Eq. (1)) predicts a somewhat different behavior for different combinations of the parameters I and $k_e\tau_0$ at a fixed value of $Ik_e\tau_0$, as seen in Fig. 1. (In the dynamic model, Eq. (15), the ratio τ_v/τ_0 is given for various β's in Table 1.)

For small values of $k_e\tau_0$ the ET is single-exponential in the dynamic model, even for large values of the product $Ik_e\tau_0$. In this single-exponential regime, the rate constant is given by the averaged rate,[44] defined by

$$\langle k_{ET}\rangle = \int_{-\infty}^{\infty} dv\, P_0(v) k_{ET}[\tau(v)]. \tag{17}$$

Only for large values of $k_e\tau_v$ does the time behavior of the ET become nonexponential (as in Fig. 1a). There is a noticeable difference in the behavior of static and dynamic models and for different values of $k_e\tau_v$ for the

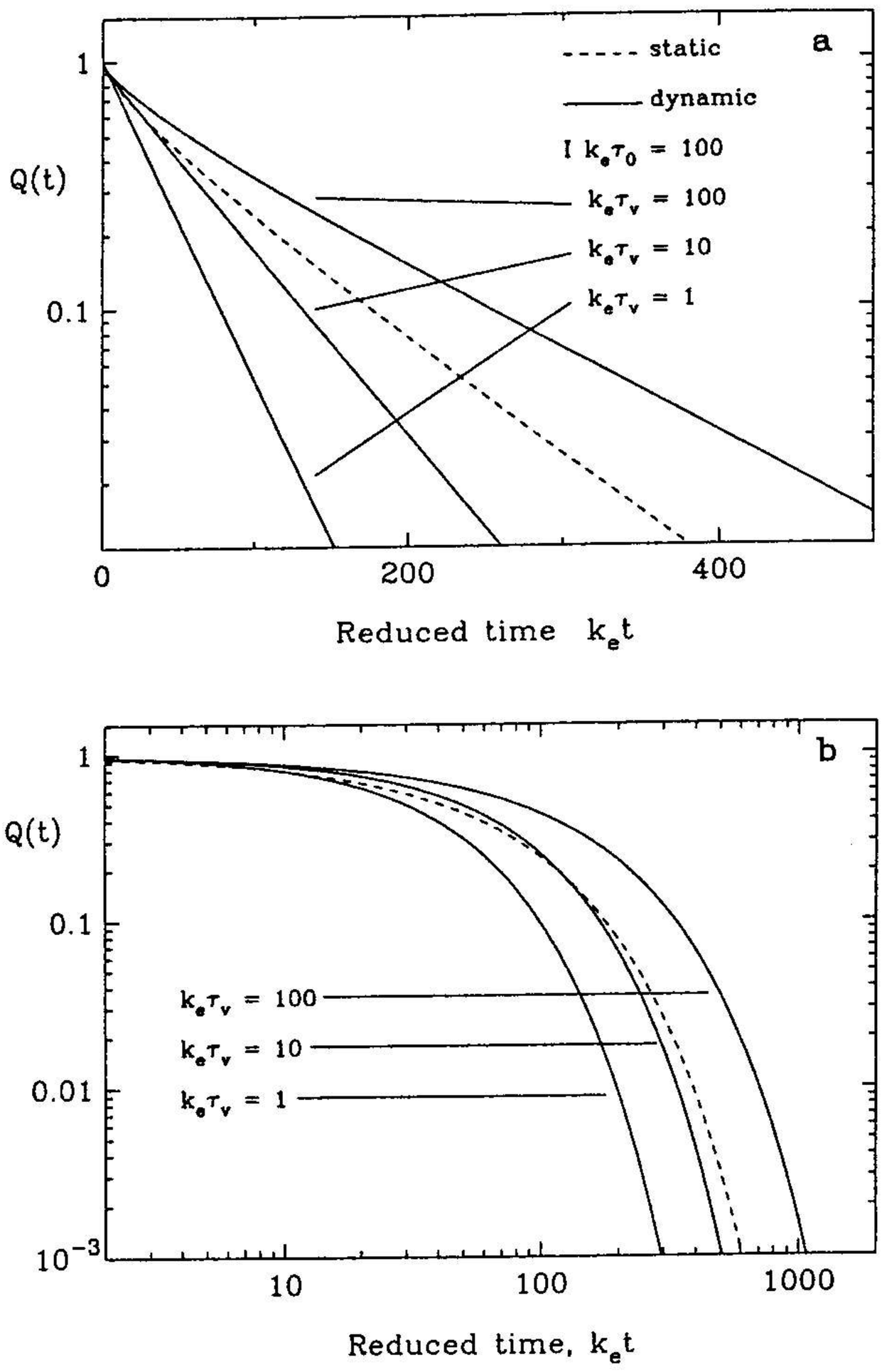

Fig. 1. Effects of static (dashed line) and dynamic disorder (solid line) on the time behavior of ET processes; $\beta' = 0.5$. a. $\log Q(t)$ vs. t; the parameters of the respective lines are (from bottom to top) $k_e\tau_v = 1, 10, 100$. b. $\log Q(t)$ vs. $\log t$; the parameters of the respective lines are (from left to right) $k_e\tau_v = 1, 10, 100$; note that τ_0 is related to τ_v according to Table 1.

dynamic model at fixed $Ik_e\tau_0$. This behavior can be seen clearly in Fig. 1. However, as seen there, for an increase of a factor 100 of $k_e\tau_v$, keeping $Ik_e\tau_0$ fixed, the time scale of the decay of $Q(t)$ at long times changes only by about a factor of 3. This somewhat logarithmic dependence of the time scale of $Q(t)$ on the time scale of the fluctuations (under the restriction of constant $Ik_e\tau_0$) may not be easily detectable in an actual experimental situation.

4. ASYMPTOTIC AND AVERAGED PROPERTIES

A simpler approach to the nonexponential behavior of the unreacted fraction $Q(t)$ is to analyze not the full time-dependence but its averaged and asymptotic properties only. Two natural quantities for such an analysis are the short-time rate constant

$$k_s = -\left.\frac{d}{dt}\right|_{t=0} Q(t), \tag{18}$$

and the mean reaction time

$$\tau_a = \int_0^\infty dt\, Q(t). \tag{19}$$

Of particular interest is how both quantities scale with the time scale τ of the fluctuations.

In the case of a static description of the anomalous relaxation of Davidson–Cole form, the short-time rate constant k_s and the mean reaction time τ_a have been determined, assuming Eq. (1), to be[23,27]

$$k_e/k_s = (1 + Ik_e\tau_0)^\beta, \tag{20}$$

and

$$k_e\tau_a = 1 + Ik_e\tau_0. \tag{21}$$

We note that for any functional form $g(\tau')$ of static disorder the mean reaction time τ_a has the general form:

$$k_e\tau_a = 1 + Ik_e\langle\tau'\rangle_g, \tag{22}$$

where $\langle\tau'\rangle_g$ is the mean relaxation time of the fluctuations, averaged over the distribution of local relaxation times $g(\tau')$. Equation (22) can be seen immediately by inserting Eq. (13) into Eq. (19). Since $\langle\tau'\rangle_g$ is the time scale of the fluctuations in the static model, the functional form of the scaling of τ_a with the time scale $\langle\tau'\rangle_g$ of the fluctuations is always linear, and it is independent of the functional form of $g(\tau')$.

For the case of ET in a dynamically disordered system, as described by the reaction-diffusion Eq. (15), the short-time rate constant k_s is given by the averaged rate defined in Eq. (17), i.e.,

$$k_s = \langle k_{ET}\rangle. \tag{23}$$

For the particular choice of $f(v)$ for the Davidson–Cole behavior, Eq. (12), we have determined k_s numerically according to Eq. (17). The results are shown in Fig. 2 and compared with results for the short-time rate constant from the static model, Eq. (20). It is seen in Fig. 2 that the numerical values for k_s from the static and from the dynamic models are fairly close. This property was observed already in the previous section. It can also be seen in Fig. 2 that the short-time rate constant from the dynamic model obeys a power law

$$k_e/k_s \propto (Ik_e\tau_0)^{\beta''} \tag{24}$$

for large values of the product $Ik_e\tau_0$. The value of the exponent β'' in Eq. (24) depends on the value of the

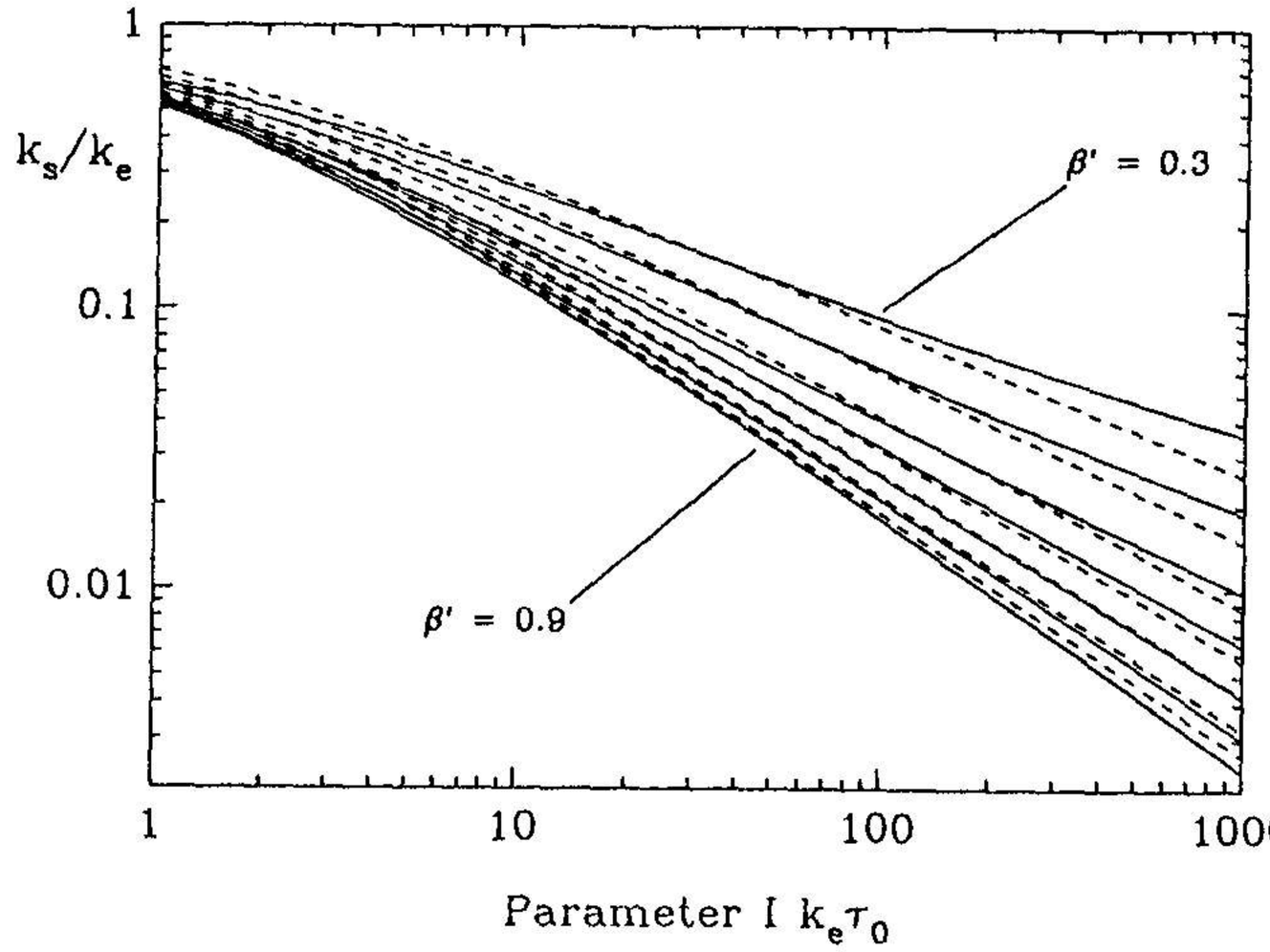

Fig. 2. Short-time rate constant k_s vs. τ_0 for static (dashed line) and dynamic (solid line) models; the parameters of the respective lines are (from bottom to top) $\beta' = 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3$.

parameter β' in the function $f(v)$, Eq. (12), and values are given in Table 1. As can be seen there, β' also determines the value of the parameter β for the corresponding Davidson–Cole function. One can see from Table 1 that for a particular value of β' the value of β for the corresponding Davidson–Cole function and the value of β'' for the asymptotic behavior of the short-time rate constant are not markedly different.

The mean reaction time τ_a, Eq. (19), of the ET process described by the reaction-diffusion, Eq. (15), can be written in the formal expression[22]

$$\tau_a = \left\langle 1 \left| \left\{ k_{ET}[\tau_x(v)] - \frac{1}{\tau_v}\mathbf{L}^+(v) \right\}^{-1} \right| 1 \right\rangle, \qquad (25)$$

where $\langle | \, | \rangle$ denotes a scalar product with $P_0(v)$ as weight function,

$$\langle h | \mathbf{A} | g \rangle = \int_{-\infty}^{\infty} P_0(v)h(v)\mathbf{A}(v)g(v)dv. \qquad (26)$$

$\mathbf{L}_0^+(v)$ is the operator adjoint to the Fokker–Planck operator, Eq. (10),

$$\mathbf{L}^+(v) = \left(\frac{\partial}{\partial v} - v\right)\frac{\partial}{\partial v}, \qquad (27)$$

and $| 1 \rangle$ is the constant function, with the value 1, and is also the eigenfunction of $\mathbf{L}^+(v)$ with the eigenvalue zero. Equation (25) can also be cast into the form

$$k_e\tau_a = \left\langle 1 \left| \left\{ 1 - \left[\frac{1}{k_e\tau_v} + If(v) \right] \mathbf{L}^+(v) \right\}^{-1} (1 + Ik_e\tau_x(v)) \right| 1 \right\rangle. \qquad (28)$$

For large values of $k_e\tau_0$, this expression can be approximated by

$$k_e\tau_a \approx c(I)k_e\tau_0, \qquad (29)$$

where

$$c(I) = (\tau_v/\tau_0)\langle 1 | [1 - If(v)\mathbf{L}^+(v)]^{-1} If(v) | 1 \rangle. \qquad (30)$$

This result demonstrates that in the dynamically disordered system the mean relaxation time of the ET depends linearly on the time scale τ_0 of the fluctuations (for slow fluctuations). Such a result was already obtained for the case of the statically disordered model. There the proportionality constant $c(I)$ was simply equal to I, see Eq. (21). Here the proportionality constant $c(I)$ is given by the matrix element, Eq. (30). We note that τ_v/τ_0 is a constant for a particular functional form of the relaxation of the correlation function, as shown in Table 1 for the Davidson–Cole case. Although the dependence of $c(I)$ on the parameter I looks more complicated here, numerical calculations show that $c(I)$ is still very close to being linear in I, so that any deviations may not be detectable experimentally.

5. DISCUSSION

In the present paper, the influence of polarization fluctuations on intramolecular ET processes was explored for the case that the fluctuations show an anomalous relaxation behavior, and that the main contribution to the reorganization energy λ comes from the solvent reorganization energy λ_0. The focus was on the effects of a particular dynamic disorder model on the time behavior of the ET process, as opposed to the effects of static disorder. Both static and dynamic disorder are

possible descriptions for anomalous relaxation of fluctuations. The treatment was centered here mainly on fluctuations of Davidson–Cole form, Eq. (6), but the analysis can be extended to other functional forms of the fluctuation relaxation time-scale function $f(v)$ and the local relaxation time-distribution function $g(\tau')$.[45]

In Section 3 we showed that the time behavior of ET processes predicted by the static disorder model differs from the time behavior predicted by the dynamic disorder model. However, for a distinction between both models on the basis of the experimentally observed ET time behavior it is necessary to know the parameters k_e and $\Delta G^*/k_BT$ for the ET system under investigation, e.g., from other experiments. The independence of the static disorder model to variations of the parameters I and $k_e\tau_0$, with the product $Ik_e\tau_0$ held constant, may not be sufficient for such an experimental distinction, considering the various uncertainties. The reason is the somewhat logarithmic dependence of the time scale of ET in the present dynamic disorder model on the variations of $k_e\tau_0$, at constant $Ik_e\tau_0$.

The results of the last section showed that the scaling behavior of both the short-time[46] rate constant k_s and the mean relaxation time τ_a with the time scale τ_0 of the fluctuations, $k_e/k_s \propto (k_e\tau_0)^{-\beta''}$ and $k_e\tau_a \propto k_e\tau_0$, respectively, are relatively independent of whether a static or the present dynamic model is employed for the model description of the Davidson–Cole fluctuations. Within the range of validity of the models employed (Appendix and Ref. 37), this fact demonstrates that an analysis of the scaling of either of these quantities does not show a marked difference between the above static and dynamic disorder models.

The scaling behavior of the mean reaction time τ_a, namely the linear dependence of τ_a on τ_0 for large τ_0, holds for both the static as well as for the present dynamic disorder model, irrespective of the form of $g(\tau)$ or $f(v)$. The scaling of the mean reaction time τ_a, therefore, does not markedly distinguish between a Debye and a non-Debye form of the polarization fluctuations nor between static and dynamic disorder.

These results for τ_a hold for the limiting case of a vanishing contribution λ_i of intramolecular degrees of freedom to the reorganization energy $\lambda = \lambda_i + \lambda_0$. It was shown earlier[22] that a nonvanishing contribution λ_i from intramolecular degrees of freedom can lead to an asymptotic behavior of the mean reaction time that has a scaling form

$$k_e\tau_a \propto (k_e\tau_0)^{\alpha} \tag{31}$$

for $0 \leqq \lambda_i/\lambda_0 < 1$, and for $\lambda_i/\lambda_0 > 1$ the mean reaction time approaches a finite value for $\tau_0 \to \infty$,

$$\tau_a \to \tau_a(\infty). \tag{32}$$

In Eq. (31) $0 < \alpha \leqq 1$ holds, and the exponent α and $\tau_a(\infty)$ in Eq. (32) both depend on λ_i/λ_0 and on the free energy barrier $\Delta G^*/k_BT$. For the limiting case $\lambda_i/\lambda_0 = 0$, the exponent α becomes unity. These results were demonstrated in Ref. 22 for polarization fluctuations of Debye form. This difference from the τ_a behavior for non-zero λ_i/λ_0 warrants further investigation and offers the possibility that it can be employed for a reliable experimental distinction between vanishing and nonvanishing contributions of intramolecular degrees of freedom to the reorganization energy.

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APPENDIX

A model for the coupling of ET processes to polarization fluctuations of Debye form with relaxation time τ that also allows for any (assumed rapid) vibrational reorganization is given by the reaction-diffusion equation

$$\frac{\partial}{\partial t} P_r(x, t; \tau) = \left[\frac{1}{\tau}\mathbf{L}(x) - k(x)\right] P_r(x, t; \tau) \tag{A1}$$

for the reactant distribution function $P_r(x, t; \tau)$.[20,22] Equation (A1) describes a polarization-dependent (i.e., x-dependent) ET reaction process, given by the x-dependent rate constant $k(x)$, which is coupled to x-fluctuations of Debye form governed by the Fokker–Planck operator $\mathbf{L}(x)$, as in Eq. (10). In the present paper, we are interested in the particular case of a vanishing energetic contribution of vibrational degrees of freedom to the reorganization energy, which results in a $k(x)$ of the form[20,22]

$$k(x) = k_e\delta(x - x_c)/P_0(x), \tag{A2}$$

where $P_0(x) = \exp(-x^2/2)/\sqrt{2\pi}$ is the stationary distribution of the x-fluctuations and where $x_c = \sqrt{2\Delta G^*/k_BT}$.

Equations (A1) and (A2) can lead to a single-exponential ET time behavior with Eq. (1) as rate constant. However, for large values of $k_e\tau$ there can be deviations from the single-exponential behavior if the free energy barrier parameter $\Delta G^*/k_BT$ is small ($\Delta G^*/k_BT \lesssim 1$). We note that all considerations in the present paper based on Eq. (1) are valid only with that restriction.

Equation (A1) also provides a starting point for a more rigorous treatment of the effects of static and dynamic disorder of polarization fluctuations:

In the case of static disorder, the time behavior of the fraction of unreacted molecules is given by an average of the time behavior of the local quantities $Q(t;\tau')$ over the distribution of local relaxation times, $g(\tau')$, i.e.,

$$Q(t) = \int d\tau' g(\tau') Q(t;\tau'). \tag{A3}$$

The τ'-dependent time behavior of the local fractions of unreacted molecules is given by

$$Q(t;\tau') = \int_{-\infty}^{\infty} dx\, P_r(x, t;\tau'), \tag{A4}$$

where $P_r(x, t;\tau')$ is the solution of Eq. (A1) with τ replaced by the local relaxation time τ'.

In the case of dynamic disorder, the x-fluctuations are coupled to the v-fluctuations via Eq. (9). This leads to a two-dimensional reaction-diffusion equation

$$\frac{\partial}{\partial t} P_r(x, v, t) = \left[\frac{1}{\tau_x(v)}\mathbf{L}(x) + \frac{1}{\tau_v}\mathbf{L}(v) - k(x)\right] P_r(x, v, t) \tag{A5}$$

for the reactant distribution function $P_r(x, v, t)$. The fraction of unreacted molecules $Q(t)$ is then obtained from the reactant distribution function by integration over all x and v,

$$Q(t) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv\, P(x, v, t). \tag{A6}$$

One can arrive at the simplified model treated in the present paper by certain approximations to the rigorous model presented above. The static disorder model, Eq. (13), is obtained by approximating the $Q(t;\tau')$ in Eq. (A4) as a single exponential with a rate constant $k_{ET}(\tau')$. A formal solution of Eq. (A1) yields the first line of (A7), while the second line of (A7) is obtained by assuming that integrating over the x-fluctuations yields approximately a single-exponential decay of $Q(t)$, the corresponding rate constant being given by Eq. (1):

$$Q(t) = \int_{-\infty}^{\infty} dx \exp\left[\left\{\frac{1}{\tau}\mathbf{L}(x) - k(x)\right\} t\right] P_0(x)$$

$$\approx \exp[-k_{ET}(\tau)t]. \tag{A7}$$

The validity of the approximation in the second half of (A7) was discussed above.

The dynamic disorder model represented by Eq. (15) is obtained from (A5) by a formal solution of the latter, and then by using the assumption employed in the second line of Eq. (A7) for the integration over the x-fluctuations, with τ replaced by $\tau_x(v)$. We then have:

$$Q(t) = \int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dx \times \exp\left[\left\{\frac{1}{\tau_x(v)}\mathbf{L}(x) + \frac{1}{\tau_v}\mathbf{L}(v) - k(x)\right\} t\right] P_0(x) P_0(v)$$

$$\approx \int_{-\infty}^{\infty} dv \exp\left[\left\{\frac{1}{\tau_v}\mathbf{L}(v) - k_{ET}[\tau_x(v)]\right\} t\right] P_0(v). \tag{A8}$$

We note that the approximation in Eq. (A8) is rigorous only in the case that the v-fluctuations are much slower than the reactive transitions along the x-coordinate, i.e., that one can perform the integration over x in the first half of (A8) at fixed v and then integrate over v. The v-fluctuations are relatively slow when $\tau_v \gg 1/k_{ET}[\tau_x(v)]$. Since $k_{ET}[\tau_x(v)]$ is largest in the half-plane $v<0$, the main contribution to the reaction comes from that half-plane. Since $\tau_x(v)$ in Eqs. (11) and (12) is very small in that half-plane, we arrive at $k_e\tau_v \gg 1$ as a condition necessary for the approximation. This consideration agrees also with the observations of a numerical analysis of the more rigorous model,[37] where we find that for $k_e\tau_v \approx 1$, i.e., in the single-exponential regime, the correct rate constant can be overestimated by the model Eq. (15). However, for $k_e\tau_v \gg 1$, i.e., in the nonexponential regime, the results for the long-time behavior of the model treated in the present paper are very close to the results from (A5). We note that there are differences in the short-time behavior.[37]

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(28) By centering our interest on intramolecular processes, we avoid additional complications that arise from a distance dependence of the ET: a static distribution or a dynamic distribution (time-dependent due to diffusion processes) of distances between donors and acceptors would have to be taken into account, too. We note that this restriction entails that such an intramolecular ET system also should show a certain stiffness of the donor–acceptor complex so that effects due to variable distances do not compete with the effects treated in this paper.
(29) Solvent relaxation time-dependent rate constants of the form Eq. (1), or its limiting form for $k_e\tau$ large, can be found readily in the literature, see Refs. 16, 20, and 25, and Refs. 14, 15, 18, and 24, respectively. They differ in what approximate expression is employed for the equilibrated rate (semiclassical, quantum-mechanical) and in how the parameter I is derived. We use here a result that was derived using a continuum model for the solvent fluctuations and neglecting the back reaction process (see Refs. 20 and 22 and the present Appendix).
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(44) Although Eq. (17) leads to the correct limiting value for $k_e\tau_0 \rightarrow 0$, i.e., to the equilibrated rate k_e, there can be corrections from a more rigorous treatment according to the Appendix and Ref. 37. However, the qualitative conclusions drawn in the text remain valid.
(45) A molecular treatment, rather than the continuum one we employed here for the solvent dynamics, may introduce additional effects; see, e.g., Wolynes, P.G. *J. Chem. Phys.*, 1987, **86**: 5133; Maroncelli, M.; Fleming, G.R. *J. Chem. Phys.*, 1987, **86**: 6221.
(46) There is both a practical and a theoretical problem with the quantity k_s: in many cases there may be a short transient period, perhaps not readily measurable in a typical experiment, so that the observable k_s is then defined by the value of dQ/dt after some transient time *after* $t = 0$. On the other hand, in the present paper and, implicitly, also in Refs. 10 and 23, it is assumed that the use of the approximation Eq. (1) takes care of this initial transient and describes the k_s that is observable experimentally. The k_s defined according to Eq. (18) in a more rigorous description of the ET process, as in the present Appendix, does differ from the k_s of those approximate models and equals k_e for both static and dynamic models, before any brief transient occurs. However, for a more reliable theoretical and experimental analysis of the short-time behavior of $Q(t)$, a different approach than a k_s defined according to Eq. (18) is needed.[37]