Electric field effects on kinetics of electron transfer reactions: connection between experiment and theory

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The dependence of the rate constant for electron transfer on energy can be systematically studied by measuring kinetics in an applied electric field. General relationships are developed between observed electric-field-modulated kinetics and theoretical expressions for the electron transfer rate constant, including both the energy dependence of the nuclear (Franck–Condon) and superexchange electronic factors. The technique described here augments the well-known approach of using chemical substitution of donors and acceptors as a probe of the dependence of rate on energy.

1. Introduction

The kinetics of electron transfer reactions can be systematically varied by application of an external electric field [1–3] [#1]. The sensitivity of the kinetics to electric fields depends on the magnitude of the change in charge distribution when the process occurs and on the curvature of rate versus energy profile characteristic of the particular reaction under consideration. A schematic illustration of a photoinduced electron transfer reaction which serves to define the notation is presented in fig. 1A. Fig. 1A exhibits an example of both charge separation $^*DA \rightarrow D^+A^-$ (CS with rate constant k_S) and charge recombination $D^+A^- \rightarrow DA$ (CR with rate constant k_R) recombinations, where D and A are a donor and acceptor, respectively. The difference electric dipole moment between the reactant and product states is $\Delta\mu_{et} = \mu(D^+A^-) - \mu(^*DA)$ for CS and $\Delta\mu_{et} = \mu(DA) - \mu(D^+A^-)$ for CR. By varying the applied field strength it is possible to tune the free energy change between reactants and products thereby affecting the rate. This is entirely analogous to the well-developed approach of varying the redox potential of donors or acceptors which are dispersed in liquid or solid solution or are covalently connected [5–8]. Because it is difficult to change the redox potential of a molecule without a substantial change in its structure, studies over a wide range of driving force suffer from the possible limitation that other factors, such as the reorganization energy or electronic coupling, may also vary. To some extent this problem is avoided in electric field modulation experiments because a single molecular system is used, and the driving force is varied with an external source. However, there may be significant and interesting effects on the electronic coupling when low-lying states mediate the coupling between the initial and final states as discussed elsewhere [1,9] and in section 2.2 below. Because the charge displacement associated with internal conversion k_{nr}, fluorescence k_f, or energy transfer is typically smaller than that associated with CS or CR reactions, the electric field effect on the former is likely to be much smaller and will be neglected in the following.

The change in electron transfer (ET) rate can be observed in real time by measuring a transient population, or the change can be observed using steady-state emission when the emission competes with ET. Recombination or delayed fluorescence can also be affected by an electric field, and studies of electrophotoluminescence in semiconductors [10], photoconductors [11], organic donor/acceptor systems

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[#1] When monitored optically, electrochromism is always present [4] and must be accounted for in the analysis.

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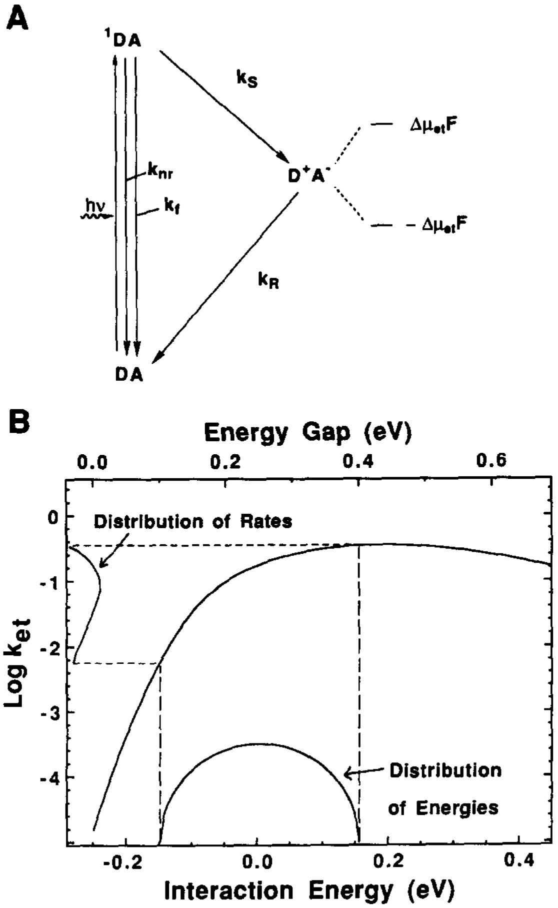

Fig. 1. Schematic illustration of the origin of the effect of an applied electric field on a photoinduced electron transfer process. (A) Energy level diagram defining the change in dipole moment $\Delta\mu_{et}$ accompanying formation of a charge separated state D^+A^- from a singlet excited state ^{1}DA (rate constant k_S) or charge recombination (rate constant k_R) to form the ground state DA. Only product electric dipoles which are parallel and antiparallel to the applied field direction are illustrated. (B) Typical dependence of the rate of electron transfer on the free energy for electron transfer. The distribution of rates associated with the application of an electric field on an isotropic sample is illustrated for the particular case of $|\Delta U| = 0.15$ eV.

[12] and photosynthetic proteins [13] are examples. In semi- and photo-conductors, emission can be from the conduction band (delocalized) or trap sites in the band gap region (localized). In organic donor/acceptor and photosynthetic systems delayed fluorescence results from localized states. There have been relatively few studies of electric field effects using transient absorption.

A great deal of experimental and theoretical effort has been devoted to understanding ET in photosynthetic reaction centers (RCs), and electric field effects provide a useful perturbation. In vivo the generation of a transmembrane potential (electrogenicity) is associated with intermediate energy storage, so understanding the sensitivity of various ET steps to a field is directly relevant to understanding the regulation of energy storage in the natural system. The electrogenic steps in membrane-bound systems are expected to be affected by an externally applied electric field because they involve the generation of a large difference dipole $\Delta\mu_{et}$. One artificial method for generating an electric field across a membrane is to impose a salt, pH or ATP gradient across the membrane [14–16]. A second related technique uses electrodes [13] and a solution of osmotically swollen chloroplasts [17]. Using this technique, the increase in fluorescence in an applied electric field has been suggested to be related to a decrease of forward ET to the quinone [18]. In both of the above techniques the samples are isotropic and the voltage was calibrated using the carotenoid band shift [19,20]. A third technique involves the use of reaction centers (RCs) in Langmuir–Blodgett film multilayers deposited on a transparent electrode with a reflecting electrode deposited on top of the multilayer [21]. The sample is oriented, but bipolar with respect to the applied electric field. A fourth technique uses a polar oriented monolayer of RCs in an electrochemical cell [2,22]. The effect was monitored using the transient current produced when the sample was flashed, thus eliminating the complication of electrochromism [4,8]. This technique has been used to measure both the electric field effect on the kinetics of CR [22] and of the accompanying electrogenicity [23].

We have measured the electric field effect on several different rate constants in photosynthetic RCs dissolved in polymer films or frozen glasses and sandwiched between two electrodes [1,3,24–27]. The orientational distribution of RCs is isotropic with respect to the applied field direction. This technique has the advantage that high electric fields can be achieved over a wide range of temperatures. The electric field effect on kinetics in isotropic samples has been measured both by observing the change in absorbance (ground state recovery) or fluorescence competing with CS [3,24]. In a series of experiments, we have shown how electric field effect data obtained using isotropic samples can be fit to a distribution function which describes the distribution of rates as a function of the energy shift ΔU in the applied field $\boldsymbol{F}$ (see fig. 1B). The distribution function used was a cumulant expansion:

$$k_{\mathrm{et}}(\boldsymbol{F})=\exp\left(\sum_{n=0}^{\infty} P_n\,\Delta U^n\right) \tag{1}$$

in powers of the interaction energy $\Delta U=-\Delta\boldsymbol{\mu}_{\mathrm{et}}\cdot\boldsymbol{F}$, where $\Delta\boldsymbol{\mu}_{\mathrm{et}}$ is the change in dipole moment between the final and initial states (see fig. 1A), and $\boldsymbol{F}$ is the external electric field [#2]. This function can be easily adapted to analyze data obtained using oriented or isotropic samples. Consequently, the results of all of the experimental approaches described above can be analyzed in terms of eq. (1). Because it is difficult to obtain fields greater than about 2 MV/cm and because $\Delta\boldsymbol{\mu}_{\mathrm{et}}$ is typically less than 100 D, the number of cumulants which can be obtained under realistic experimental conditions is between 1 and 4 [1,24, 26]. We have shown elsewhere how to relate data with a single cumulant to Marcus theory [26,29]. In this paper, we show how data analyzed using a cumulant expansion in powers of the interaction energy can be related to quantum-mechanical ET theories.

2. Relationship of electric field effect to electron transfer theory

It is preferable to use the general technique of obtaining cumulants from the data and then comparing these with known theories, rather than the more precarious tack of assuming that the form of a particular theory will fit the data. The cumulant expansion has a direct relationship with any theory of ET because the theoretical expression for the rate constant can be expanded in cumulants of the interaction energy. In the following, we outline how to calculate the cumulants of ΔU using the saddle point approximation to calculate the Franck–Condon (FC) factor, followed by the cumulants of ΔU for the electronic factor when superexchange is important.

The theory of the electric field dependence of the quantum-mechanical rate constant for isotropic systems has been discussed by us [1], Bixon and Jortner [30], and Lin and co-workers [31]. The treatment of Lin and co-workers used a moment expansion of the rate constant [31]. The rate constant was orientation averaged for an isotropic sample. However, since the rate constant is not observed directly in an experiment, no connection with experimental observables was made [31]. The cumulant expansion was introduced by Bixon and Jortner for data analysis [30]; however, the terms in the cumulant expansion were not related to any theoretical parameters. The expansion of the rate constant in powers (i.e. cumulants) of time in ref. [30] is not applicable, rather, as shown below, it is the expansion of the rate constant in cumulants of interaction energy which is relevant to the electric field effect experiment. Furthermore, due to a failure to include the dependence of the crossing point Q_{13}^{*} on the relative disposition of the potential energy surfaces (see ref. [24], section 2.2, and Appendix), these authors incorrectly calculated the electric field dependence of the superexchange matrix element.

We choose as our starting point the result from first-order, time-dependent perturbation theory giving the transition probability as:

$$k_{\mathrm{et}}=(2\pi/\hbar)\langle\Psi_+|H'|\Psi_-\rangle^2\rho\,, \tag{2}$$

where $\Psi_{+,-}$ is the total wavefunction of the reactants (+) and products (−), H' contains the terms in the Hamiltonian which couple reactants and products, and ρ is the density of states. In order to convert this equation to a more usable form, we employ the correlation function method of evaluation. The total wavefunction Ψ is the product of the electronic wavefunction ψ and the vibrational wavefunction χ. The perturbation H' which couples the reactant state Ψ_+ and product state Ψ_- can be electron exchange, Born–Oppenheimer breakdown or overlap of non-orthognonal wavefunctions, depending on the basis in which one is working [32]. It is common to calculate the transition probability in eq.

[#2] The definition of the cumulants P_n in eq. (1) differs from the formal definition of cumulants C_n in Van Kampen [28] such that $P_n=C_n(i^n/n!)$. This has been done for convenience to adapt the cumulant expansion for use as a fitting function for electric field effect data. The factor of i^n has been omitted in the moment expansion as well (eq. (5)).

(2) using the Condon approximation which allows the separation of the electronic and nuclear factors [33]:

$$k_{\mathrm{et}}=(2\pi/\hbar)|\langle\psi_+|H'|\psi_-\rangle|^2|\langle\chi_+|\chi_-\rangle|^2\rho\,, \quad (3)$$

where the electronic coupling $V=|\langle\psi_+|H'|\psi_-\rangle|$, and the Franck–Condon factor is $\mathrm{FC}=|\langle\chi_+|\chi_-\rangle|^2\rho$.

The moment expansion of the rate constant is given by (see footnote 1)

$$k_{\mathrm{et}}(\Delta U)=\left[\sum_{n=0}^{\infty}\left(\frac{M_n\Delta U^n}{n!}\right)\right], \quad (4)$$

where the moments M_n read

$$M_n=k_{\mathrm{et}}(0)\left(\frac{1}{\mathrm{FC}(0)}\frac{\partial^n\mathrm{FC}(0)}{\partial\Delta U^n}+\frac{1}{V^2(0)}\frac{\partial^n V(0)^2}{\partial\Delta U^n}\right) \quad (5)$$

are calculated using the electronic and nuclear factors (each treated as functions of the interaction energy) which are expanded about the zero-field value $\Delta U=0$. In principle, consideration of the electric field dependence of both the electronic and nuclear factors will introduce a contribution due to cross terms in eq. (5). For many systems this contribution is small. For example, the neglect of cross terms is rigorously valid up to second order for activationless reactions (i.e. when the slope of the FC versus ΔU curve is zero). In cases where cross terms are important, the cumulants P_n in eq. (1) can be obtained from the moments M_n (see footnote 1). For the present definition of P_n (see footnote 1) this relationship is given by

$$P_1=M_1\,,$$
$$P_2=\tfrac{1}{2}(M_2-M_1^2)\,,$$
$$P_3=\tfrac{1}{6}(M_3-3M_2M_1+2M_1^3)\,,$$
$$P_4=\tfrac{1}{24}(M_4-4M_3M_1+12M_2M_1^2-6M_1^4-3M_2^2)\,. \quad (6)$$

In sections 2.1 and 2.2, expressions are developed for the cumulants P_n of the FC and electronic factors separately. The contribution of the cumulant for each factor in each power of ΔU is additive in eq. (1).

2.1. Cumulant expansion of the Franck–Condon factor

In order to evaluate eq. (3) the correlation function technique can be applied by expressing the density of states term as $\rho=\delta(\epsilon_- -\epsilon_+)$ and converting eq. (3) into a time integral using the integral representation for the δ function [34]:

$$k_{\mathrm{et}}=\left(\frac{V}{\hbar}\right)^2\int_{-\infty}^{\infty}C(\tau)\exp(-\mathrm{i}\epsilon\tau)\,\mathrm{d}\tau\,, \quad (7)$$

where $\epsilon=\epsilon_- -\epsilon_+$ is in units of $\hbar$. The correlation function in eq. (7) can be written as $C(\tau)=\exp[f(\tau)]$ where

$$f(\tau)=\sum_{n=1}^{N}S_n[-(2\nu_n+1)+\nu_n\exp(-\mathrm{i}\omega_n\tau)+(\nu_n+1)\exp(\mathrm{i}\omega_n\tau)]\,. \quad (8)$$

S_n is the reduced linear electron–phonon coupling, and ω_n is the frequency of the nth mode. This expression is the correlation function required for calculation of the Franck–Condon factor for a single mode. The saddle point or stationary phase approximation for evaluating the correlation function consists of the following steps [35]: (1) Expand the exponent $f(\tau)$ in a Taylor series. (2) Set the first derivative of the exponent in eq. (7) equal to zero, $f'(\tau)-\mathrm{i}\epsilon=0$. This is the saddle point value or τ_{sp}. (3) Truncate the series after the quadratic term and solve the resulting Gaussian integral. (4) Substitute the saddle point value τ_{sp} from step (2) into the equation obtained in step (3).

The function $f(\tau)$ is expanded in a Taylor series about τ_{sp}

$$f(\tau)=f(\tau_{\mathrm{sp}})+f'(\tau_{\mathrm{sp}})(\tau-\tau_{\mathrm{sp}})+\tfrac{1}{2}f''(\tau_{\mathrm{sp}})(\tau-\tau_{\mathrm{sp}})^2+\ldots\,, \quad (9)$$

in which the derivatives with respect to τ are represented by primes. The saddle point τ_{sp} is obtained from the equation $f'(\tau_{\mathrm{sp}})-\mathrm{i}\epsilon=0$. For a single mode the solution is

$$\tau_{\mathrm{sp}}=-\frac{\mathrm{i}}{\omega}\ln\left(\frac{\epsilon\pm[\epsilon^2+4S^2\omega^2\nu(\nu+1)]^{1/2}}{2S\omega(\nu+1)}\right). \quad (10)$$

Since the term $f'(\tau_{\mathrm{sp}})-\mathrm{i}\epsilon=0$, $C(\tau)$ has a Gaussian form if the series is truncated after the quadratic term,

$$\mathrm{FC}(\epsilon)=\left(\frac{2\pi}{f''(\tau_{\mathrm{sp}})}\right)^{1/2}\exp[f(\tau_{\mathrm{sp}})-\mathrm{i}\epsilon\tau_{\mathrm{sp}}]\,. \tag{11}$$

The expansion of eq. (11) in cumulants of energy which can be related to the electric field effect experiment, involves several steps. Beginning with the logarithm of the FC factor

$$\ln[\mathrm{FC}(\epsilon)]=-\tfrac{1}{2}\ln[f''(\tau_{\mathrm{sp}})/2\pi] +f(\tau_{\mathrm{sp}})-\mathrm{i}\epsilon\tau_{\mathrm{sp}}\,, \tag{12}$$

we expand around τ_0, the saddle point of the zero-field value. The interaction energy in an electric field is given by $\Delta U=\epsilon-\epsilon_0$, where ϵ_0 is the zero-field value of the energy. In order to expand in powers of ΔU the difference is taken between the saddle point condition at ϵ in an applied electric field and at the zero-field value of ϵ_0,

$$\mathrm{i}(\epsilon-\epsilon_0)=f'(\tau_{\mathrm{sp}})-f'(\tau_0)\,. \tag{13}$$

The expansion up to the fourth-order term in powers of τ_{sp} around the zero-field energy ϵ_0 can be expressed as:

$$\Delta U=f''(\tau_0)(\tau_{\mathrm{sp}}-\tau_0)+\tfrac{1}{2}f'''(\tau_0)(\tau_{\mathrm{sp}}-\tau_0)^2 +\tfrac{1}{6}f^{\mathrm{iv}}(\tau_0)(\tau_{\mathrm{sp}}-\tau_0)^3\,. \tag{14}$$

The expansion of $\ln[f''(\tau_{\mathrm{sp}})]$ in the prefactor gives

$$\begin{aligned}\ln[f''(\tau_{\mathrm{sp}})]&=\ln[f''(\tau_0)]+\frac{f'''(\tau_0)}{f''(\tau_0)}(\tau_{\mathrm{sp}}-\tau_0)\\&+\frac{f''(\tau_0)f^{\mathrm{iv}}(\tau_0)-f'''(\tau_0)^2}{2f''(\tau_0)^2}(\tau_{\mathrm{sp}}-\tau_0)^2\\&+[f^{\mathrm{v}}(\tau_0)f''(\tau_0)^2-3f^{\mathrm{iv}}(\tau_0)f'''(\tau_0)f''(\tau_0)\\&+2f'''(\tau_0)^3](\tau_{\mathrm{sp}}-\tau_0)^3[6f''(\tau_0)^3]^{-1}\\&+[f^{\mathrm{vi}}f''^3-4f^{\mathrm{v}}f'''f''+6f'''^2f''^3+6f^{\mathrm{iv}}f'''^2f''\\&-3f^{\mathrm{iv}2}f''^2-6f'''^4](\tau_{\mathrm{sp}}-\tau_0)^4[24f''^4]^{-1}\,,\end{aligned} \tag{15}$$

where f^{iv}, f^{v} and f^{vi} are the fourth, fifth and sixth derivatives of $f(\tau)$ with respect to τ (the τ_0 argument is dropped for compactness in the last two lines of eq. (15)).

In order to get the expansion in terms of ΔU only, it is necessary to replace all of the τ_{sp} by inverting the power series in eqs. (8) and (15). To do this we use the relationship:

$$\frac{\partial[f'(\tau_{\mathrm{sp}})-f'(\tau_0)]}{\partial(\tau_{\mathrm{sp}})}\frac{\partial(\tau_{\mathrm{sp}})}{\partial\Delta U}=\mathrm{i}\,. \tag{16}$$

Therefore

$$\frac{\partial(\tau_{\mathrm{sp}})}{\partial\Delta U}=\frac{\mathrm{i}}{f''(\tau_{\mathrm{sp}})}\,. \tag{17}$$

This relation can be used to expand τ_{sp} in powers of ΔU

$$\begin{aligned}\tau_{\mathrm{sp}}&=\tau_0+\frac{\mathrm{i}\Delta U}{f''(\tau_0)}+\frac{f'''(\tau_0)}{2f''(\tau_0)^3}\Delta U^2\\&+\mathrm{i}\frac{f^{\mathrm{iv}}(\tau_0)f''(\tau_0)-3f'''(\tau_0)^2}{6f''(\tau_0)^5}\Delta U^3\\&+[15f'''(\tau_0)^3+f^{\mathrm{v}}(\tau_0)f''(\tau_0)^2\\&-10f^{\mathrm{iv}}(\tau_0)f'''(\tau_0)f''(\tau_0)][24f''(\tau_0)^7]^{-1}\Delta U^4\,.\end{aligned} \tag{18}$$

This value for τ_{sp} is substituted into eqs. (8) and (15) which are inserted into eq. (12) to obtain the cumulant expansion of the logarithm of the Franck–Condon factor. Note that due to the form of the Franck–Condon factor, the moments $M_n=(1/n!)\times(\partial^n\mathrm{FC}/\partial\Delta U^n)$ have not appeared explicitly in the calculation, and the cumulants can be obtained directly using the moments f^n of the expansion about τ_0. The functional dependence of the moments f^n on τ_0 are omitted in the following equations for brevity. Note that $P_0=\ln[\mathrm{FC}(\epsilon_0)]$.

$$\begin{aligned}P_1&=-\mathrm{i}\left(\tau_0-\frac{f'''}{2f''^2}\right),\\P_2&=\frac{2f''^3+f^{\mathrm{iv}}f''-2f'''^2}{4f''^4},\\P_3&=-\mathrm{i}\frac{4f^{\mathrm{iv}}f'''f''-f^{\mathrm{v}}f''^2+8f'''f''^3-5f'''^3}{12f''^6}\\P_4&=\\&\frac{5f^{\mathrm{v}}f'''f''-24f'''^2f''^3-195f^{\mathrm{iv}}f'''^2f''+3f^{\mathrm{iv}2}f''^2}{48f''^8}\\&+\frac{10f^{\mathrm{iv}}f''^4+24f'''^4-f^{\mathrm{vi}}f''^3}{48f''^8}\,.\end{aligned} \tag{19}$$

The derivatives of $f(\tau)$, in turn, can be related to the theoretical parameters (e.g. S, the electron–phonon coupling and ω, the frequency in a linear coupling model), from the moments of eq. (8) with respect to $\tau=\tau_0$. For example, if $\tau_0=0$,

$$f'(0)=\mathrm{i}\sum_{n=1}^{N} S_n\omega_n\,,$$

$$f''(0)=-\sum_{n=1}^{N} S_n\omega_n^2(2\nu_n+1)\,,$$

$$f'''(0)=-\mathrm{i}\sum_{n=1}^{N} S_n\omega_n^3\,,$$

$$f^{\mathrm{iv}}(0)=\sum_{n=1}^{N} S_n\omega_n^4(2\nu_n+1)\,,$$

$$f^{\mathrm{v}}(0)=\mathrm{i}\sum_{n=1}^{N} S_n\omega_n^5\,,$$

$$f^{\mathrm{vi}}(0)=-\sum_{n=1}^{N} S_n\omega_n^6(2\nu_n+1)\,. \tag{20}$$

Note that $f'(0)=\mathrm{i}\lambda$, where λ is the reorganization energy. Although six moments in the expansion are required to obtain four cumulants, only four parameters (two S_n and two ω_n) are obtained.

2.2. Cumulant expansion of the superexchange matrix element

The role of the electronic states of the medium between a donor and acceptor is often described in terms of the superexchange formalism. Superexchange was first developed to explain anti-ferromagnetic coupling in transition metal oxides [36,37]. In ET theory, the second-order term was introduced by Halpern and Orgel to explain ET rate constants in binuclear transition metal compounds which appear to depend on the nature of the bridging ligand [38]. They considered direct overlap, double exchange and superexchange mechanisms which may add constructively or may interfere with one another. McConnell used the superexchange matrix element to account for the influence of the number of carbon atoms on the electron hopping frequency between covalently bound phenyl systems [39]. Many subsequent treatments of the superexchange have appeared in the literature [40–46].

In order to discuss the second-order matrix element, we introduce the zeroth-order states: 1 - reactants; 2 - bridge or mediating state; 3 - products, illustrated in fig. 2. The probability amplitude of either state 1 or state 3 on state 2 can be written as

$$|\psi_+\rangle=|1\rangle+\frac{V_{12}}{\Delta U_{21}(Q^*_{13})}\,|2\rangle$$

and

$$|\psi_-\rangle=|3\rangle+\frac{V_{23}}{\Delta U_{23}(Q^*_{13})}\,|2\rangle\,. \tag{21}$$

In writing these expressions, the Condon approximation has been invoked, and therefore the magnitude of the probability amplitude is calculated at the nuclear configuration of the crossing point Q^*_{13} between the reactant and product states (fig. 2). The couplings V_{12} and V_{23} are the electronic couplings of state 1 to 2 and 2 to 3, respectively. The electric field

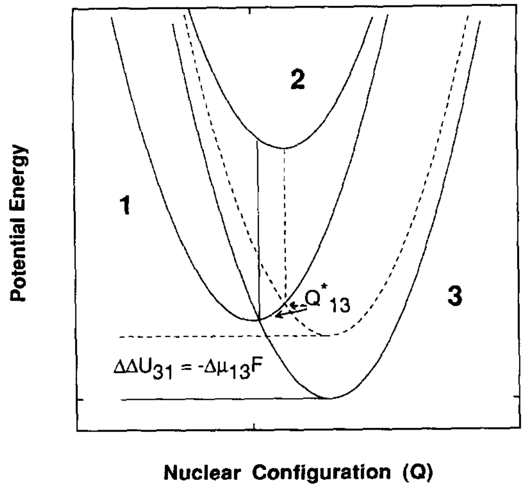

Fig. 2. Schematic illustration of the potential energy surfaces relevant to the calculation of electric field effects on electron transfer kinetics when superexchange via a mediating state is significant. The reactants 1, mediating 2, and products 3 potential energy surfaces are shown as solid lines at zero electric field along a single vibrational coordinate Q. Dashed lines are used to indicate the effect of an applied field on the dipolar product state (i.e. D^+A^- oriented opposing the field for a charge separation reaction). The field-dependent shift in the driving force of the reaction $\Delta\Delta U_{31}$ gives rise to a change in the position of the crossing point Q^*_{13} and therefore also the energy gap to the mediating state $\Delta U_{21}(Q^*_{13})$ indicated with vertical lines. Shifted energy levels and energy gaps are given by dashed lines compared to the solid lines at zero applied field. In many cases, the mediating state 2 may also be dipolar, and its energy may also shift in the field [24].

dependence of the overlap of the electronic wavefunctions is difficult to compute and has been assumed to be small. The matrix elements V_{12}, V_{23} and V_{13} have been assumed to be independent of electric field. Note that $\Delta U_{21}(Q_{13}^*) = \Delta U_{23}(Q_{13}^*)$ at the crossing point Q_{13}^*. Ignoring higher terms:

$$V = |\langle \psi_+ | H' | \psi_- \rangle| = V_{13} + \frac{2V_{12}V_{23}}{\Delta U_{21}(Q_{13}^*)}, \tag{22}$$

where the first and second terms are the direct and superexchange contributions, respectively. The superexchange component will be important if V_{13} is small or vanishes by symmetry. In order to calculate the superexchange coupling, estimates of the electronic couplings V_{12} and V_{23} are needed as well as an estimate for the vertical energy difference between the crossing point and state 2. If the frequencies and displacements of the normal modes are known the potential energy surfaces can be calculated.

Using the notation introduced above, the harmonic potential energy surfaces for the three states involved in superexchange coupling are

$$U_1(Q) = \sum_{n=1}^{N} \tfrac{1}{2}\omega_n^2 Q_n^2 + \Delta U_{13},$$

$$U_2(Q) = \sum_{n=1}^{N} \tfrac{1}{2}\omega_n^2 (Q_n - \gamma_n)^2 + \Delta U_{23},$$

$$U_3(Q) = \sum_{n=1}^{N} \tfrac{1}{2}\omega_n^2 (Q_n - \eta_n)^2 . \tag{23}$$

The equilibrium position of states 1, 2, and 3 are $Q_n = 0$, γ_n, and η_n, respectively (i.e. $\eta_n = 2S_n^{1/2}$). The nuclear displacements are in units of the root-mean-square zero-point displacement $(1/(2\omega_n))^{1/2}$ for the nth mode). The potential energy surface is N-dimensional. ΔU_{13} and ΔU_{23} are the internal energy changes between states 1 and 3 and 2 and 3, respectively.

In order to apply the superexchange mechanism to a given reaction, information is needed on what the intermediate state(s) are, including their energies and electronic couplings. These should be compared with an estimate for the electronic coupling of the ET reaction under study. By fitting the $\log(k_{\mathrm{et}})$ versus ΔU curve and applying the techniques of section 2.1 to the electric field effect to obtain the theoretical parameters S_n and ω_n, the FC factor is obtained. If the FC factor is known, the electronic coupling V can be calculated from eq. (3). A comparison of the estimate for the superexchange electronic coupling and the calculated coupling can be made to determine the validity of a given superexchange model.

The application of an electric field affects the potential energies of electronic states as illustrated schematically in fig. 2. Since a change in the potential energy affects the magnitude of the superexchange matrix element, the electronic factor may affect the observed electric field dependence of the ET rate constant. The potential energy surfaces which give rise to the field dependence are eq. (23). Substituting these into eq. (22), the moments of the superexchange electronic matrix element can be calculated. The effect of an applied electric field cannot be modeled by simply adding an energy term equal to $-\Delta\boldsymbol{\mu}_{\mathrm{et}}\cdot\boldsymbol{F}$ to the denominator of eq. (22) as was done by Bixon and Jortner [30]. Their approach ignores the fact that the position of the crossing point changes with a shift in energy of the potential energy surfaces.

Starting with the definition of the electronic factor within the superexchange calculation (eq. (22)) we calculate the moment expansion using the definitions $Q_n^* = \eta_n/2(1 - \Delta\Delta U_{13}/\lambda)$, $\Delta U_{21}(Q_{13}^*) = U_2(Q_{13}^*) - U_1(Q_{13}^*)$ and $\Delta\Delta U_{13} = \Delta U_{13} - \Delta\boldsymbol{\mu}_{13}\cdot\boldsymbol{F}$, and $\Delta\Delta U_{23} = \Delta U_{23} - \Delta\boldsymbol{\mu}_{23}\cdot\boldsymbol{F}$ ($\Delta\boldsymbol{\mu}_{13}$ and $\Delta\boldsymbol{\mu}_{23}$ are the electric difference dipole moments of the initial 1 and intermediate state 2 with respect to state 3). These quantities are substituted into eq. (23) to yield

$$V^2 = \Bigg[2V_{12}V_{23} \Bigg/ \Bigg(\sum_{n=1}^{N} \tfrac{1}{2}\omega_n^2 \times [\gamma_n^2 - \eta_n\gamma_n(1 - \Delta\Delta U_{13}/\lambda)] + \Delta\Delta U_{23} - \Delta\Delta U_{13} \Bigg) \Bigg]^2 . \tag{24}$$

Eq. (24) can be expanded in moments of $\Delta U = \Delta\Delta U_{13}$, $\partial^n V^2 \partial \Delta U^n$ using the form $V = 2V_{12}V_{23}/(B - C\Delta\boldsymbol{\mu}_{13}\cdot\boldsymbol{F})$ where $B = \Delta U_{21}(Q_{13}^*)$ and

$$C = \sum_{n=1}^{N} \frac{\omega_n^2}{2} \left(\frac{\eta_n\gamma_n}{\lambda} \right) + \frac{\Delta\mu_{23}}{\Delta\mu_{13}} - 1 . \tag{25}$$

The moments of V^2 are given by

$$M_1=V^2\left(-\frac{2C}{B-C\Delta U}\right),$$

$$M_2=V^2\left(\frac{6C^2}{(B-C\Delta U)^2}\right),$$

$$M_3=V^2\left(-\frac{24C^3}{(B-C\Delta U)^3}\right),$$

$$M_4=V^2\left(\frac{120C^4}{(B-C\Delta U)^4}\right). \qquad (26)$$

The cumulants P_n are calculated from the moments using eq. (6).

The order of magnitude of the effect can be estimated from the magnitude of $2C/(B+C\Delta U)$. Since it is assumed that only four cumulants have been obtained experimentally, only four parameters (two S_n and two ω_n) can be obtained. In general, the effect of an electric field on the superexchange matrix element is a small effect and can be mitigated further if the intermediate state is dipolar [24] and its dipole has approximately the same direction as $\Delta\boldsymbol{\mu}_{13}$ (i.e. $\Delta\boldsymbol{\mu}_{23}\approx 0$). Furthermore, since the sign of C is determined by whether $\gamma_n>\eta_n$ ($C>0$) or $\gamma_n<\eta_n$ ($C<0$), it is possible that $\gamma_n>\eta_n$ for one mode and $\gamma_n<\eta_n$ for the other, thus the contribution due to each mode can cancel giving rise to a very small electric field dependence.

3. Conclusion

The use of a cumulant expansion as a fitting function for electric field effect data is a natural choice given its mathematical similarity with the form of rate theories of the FC factor shown in section 2.1. The same technique can be applied to any method for calculation of the FC factor [42,43]. The connection between the cumulants in eq. (1) and the electron–phonon couplings S_n and frequencies ω_n allows quantitative information to be extracted from the experiment. The range of energies accessible in practical electric field effect experiments limit the information which is obtained. The reorganization energy can be measured if at least one cumulant is determined and the relative contribution of low- and high-frequency modes can be measured if four or more cumulants are obtained.

The electric field effect on rate constant due to a superexchange mechanism can be included in the analysis. The analysis presented here shows that for a system in which more than one vibrational mode is coupled to the reaction, the electronic factor is not expected to have as large a field dependence as the electric field effect due to the FC factor.

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Appendix

The position of the crossing point Q^*_{13} in multi-dimensional nuclear coordinate space can be determined using the potential energy surfaces given in eq. (23) using the method of Lagrange multipliers. The condition for intersection on the multi-dimensional surface was used to solve for the crossing point in a single dimension ($U_1(Q^*_{13})=U_3(Q^*_{13})$) is used as a constraint. Substituting in eq. (23) the constraint becomes

$$\sum_{n=1}^{N}\tfrac{1}{2}\omega_n^2(-2Q_n\eta_n+\eta_n^2)-\Delta U_{13}=0\,. \qquad (\mathrm{A.1})$$

The function which must be minimized is

$$\sum_{n=1}^{N}\frac{\delta}{\delta Q_n}\{\tfrac{1}{2}\omega_n^2Q_n^2+\Delta U_{13}+\theta[\tfrac{1}{2}\omega_n^2(-2Q_n\eta_n+\eta_n^2)-\Delta U_{13}]\}=0\,, \qquad (\mathrm{A.2})$$

where θ is the variational parameter. The derivative is

$$\sum_{n=1}^{N}\omega_n^2Q_n-\theta(\omega_n^2\eta_n)=0\,, \qquad (\mathrm{A.3})$$

which gives an equation for the crossing point in the ith dimension in terms of the Lagrange multiplier:

$$Q_n^*=\eta_n\theta\,, \qquad (\mathrm{A.4})$$

where Q_n^* here represents the vector component of Q^*_{13} along the ith normal mode. In order to obtain the value of θ, eliminate Q_n from the equation using eq. (A.2) to give the Lagrange multiplier

$$\theta=\tfrac{1}{2}(1-\Delta U_{13}/\lambda)\,, \qquad \text{(A.5)}$$

where λ is the reorganization energy given by $\lambda=\sum\tfrac{1}{2}\omega_n^2\eta_n^2$.

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