EFFECT OF ELECTRONIC-STATE MODULATION BY PHONON FIELDS ON THE KINETIC PARAMETERS OF NONADIABATIC ELECTRON-TRANSFER REACTIONS

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The kinetic parameters of nonadiabatic electron transfer in a polar medium are calculated in terms of the Pekar model without using the Condon approximation. It is shown that the distortion of electronic states arising from electron interaction with medium polarization can substantially influence the values of both the transmission coefficient and the activation energy. The effect was examined as a function of the electron's donor and acceptor properties, the reaction's free energy, and the electron transfer distance.

According to the Franck–Condon principle, nonadiabatic electron transitions from ion A^{Z_1} to ion B^{Z_2} will occur with appreciable probability under the condition that the electron's energy levels in ions A and B are approximately the same. In reactions occurring in polar media, equalization of the electronic energy levels is accomplished via medium-polarization fluctuations. It has been shown in [1, 2] that these polarization fluctuations produce a modulation of the electronic states. In particular, the electronic resonance integral was estimated in [2] in the Condon approximation, and it was shown that calculations including this modulation can lead to results strongly differing from those obtained when this effect is disregarded. Yet the distortion of the potential-energy surfaces that is caused by modulation of the electronic states had not been taken into account in [2]. It is the aim of the present work to study these effects in more detail. Here we shall limit ourselves to the case where the phonon spectrum (i.e., the vibration spectrum of medium polarization) is entirely classical.

Then, according to Kubo and Toyozawa [3], the expression for the probability of nonadiabatic electron transfer occurring in unit time can be written symbolically in the classical limit as

$$W_{if} \sim \frac{1}{\hbar Z_i} \int dP |V_i(P)|^2 \exp[-U_i(P)/kT] \delta(U_i(P) - U_f(P)), \quad (1)$$

where $U_i(P)$ and $U_f(P)$ are the potential-energy surfaces of the initial and final state as functions of inertial medium polarization $\mathbf{P}(\mathbf{r})$ (in essence they are free-energy surfaces of the system), $V_i(P)$ is the electron resonance integral, which is a functional of $\mathbf{P}(\mathbf{r})$, integration is performed over all possible realizations of $\mathbf{P}(\mathbf{r})$ and $\beta = 1/kT$.

To calculate the transition probability via reaction (1) one must know the electronic wave functions, φ_i and φ_f, of the initial and final reaction channel for arbitrary fluctuations of inertial medium polarization $\mathbf{P}(\mathbf{r})$. Hence we shall attempt to calculate the transition probability by the variational method. In the case of strong binding with the medium, the chief contribution to the multidimensional integral in (1) is made by a narrow neighborhood of some configuration $\mathbf{P}^*(\mathbf{r})$ (the transition configuration) where the expression under the integral sign has a maximum [3]. It had been shown in [2] in terms of the Condon approximation, but neglecting distortion of the potential-energy surfaces owing to this modulation of the electronic states, that the polarization $\mathbf{P}^*(\mathbf{r})$ [4, 5] corresponds to the transition configuration:

$$\mathbf{P}^*(\mathbf{r}) = (1-\theta^*)\mathbf{P}_{0i}(\mathbf{r}) + \theta^* \mathbf{P}_{0f}(\mathbf{r}), \quad (2)$$

where θ^* is the Brønsted symmetry factor, and $\mathbf{P}_{0i}(\mathbf{r})$ and $\mathbf{P}_{0f}(\mathbf{r})$ are the equilibrium values of polarization in the initial and final state which are linked to the electrostatic inductions

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TABLE 1. Kinetic Parameters for a Symmetric System in the Condon Approximation

P/S	γ	ξ^*	E_a/E_a^0
0	0,613	0,376	0,811
0,5	0,725	0,418	0,864
1	0,786	0,439	0,893
2	0,850	0,459	0,925
−0,1	0,547	0,359	0,795

TABLE 2. Kinetic Parameters for a Symmetric System Obtained while Including Modulation of the Overlap Integral (going beyond the Condon approximation)

P/S	$2\alpha_p R$	γ	ξ^*	E_a/E_a^0	$\exp\left(-\frac{\Delta E_a}{kT}\right)$	S/S_0	W/W_0
0	1	0,599	0,360	0,812	9,560	1,493	14,276
	4	0,541	0,301	0,825	8,200	6,270	51,46
	8	−0,515					
1	1	0,783	0,433	0,893	12,900	1,543	19,91
	4	0,774	0,414	0,895	12,31	6,10	75,10
	8	0,761	0,388	0,902	10,500	45,78	480,8
2	1	0,849	0,455	0,925	14,670	1,573	23,08
	4	0,846	0,445	0,926	14,36	6,35	91,10
	8	0,840	0,427	0,929	12,90	46,52	600,5

TABLE 3. Kinetic Parameters for an Asymmetric System in the Condon Approximation

P_i/S	$P_f S$	$\frac{\Delta F_0}{(5/32)ce^2\alpha_p}$	γ_i	γ_f	ξ^*	η^*	E_a/E_a^0
		−1,5	0,809	0,306	0,639	0,125	0,566
		−1	0,748	0,435	0,547	0,211	0,679
0	0	−0,5	0,684	0,532	0,460	0,293	0,756
		+0,5	0,532	0,684	0,293	0,460	0,852
		+1	0,435	0,748	0,211	0.547	0,884
		−1,5	0,835	0,733	0,548	0,334	0,843
		−1	0,819	0,751	0,511	0,369	0,863
1	1	−0,5	0,803	0,769	0,475	0,403	0,879
		+0,5	0,769	0,803	0,403	0,475	0,905
		+1	0,751	0,819	0,369	0,511	0,916
		−0,2	0,497	0,309	0,340	0,212	0,706
		−0,1	0,477	0,393	0,324	0,263	0,729
−0,3	−0,3						
		+0,1	0,394	0,477	0,263	0,324	0,765
		+0,2	0,309	0,497	0,212	0,340	0,780
		−2	0,780	0,515	0,510	0,277	0,786
		−1	0,707	0,642	0,389	0,409	0,858
0,5	0	0	0,625	0,748	0,273	0,547	0,905
		+0,5	0,580	0,796	0,217	0,619	0,923
		+1	0,531	0,843	0,163	0,695	0,939
		−0,554	0,9	0,597	0,798	0,117	0,468
		0	0,860	0,631	0,725	0,165	0,588
0	1	+0,815	0,8	0,677	0,625	0,237	0,707
		+2,05	0,7	0.741	0,481	0,349	0,815

$\mathbf{D}_A(\mathbf{r})$, $\mathbf{D}_B(\mathbf{r}-\mathbf{R})$, $\mathbf{D}_e^{(A)}(\mathbf{r}, \mathbf{P}_{0i})$ and $\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R}, \mathbf{P}_{0f})$, set up by ions A and B and by the electron localized at ion A and at ion B via the relations

$$\mathbf{P}_{0i}(\mathbf{r}) = \frac{c}{4\pi}[\mathbf{D}_A(\mathbf{r}) + \mathbf{D}_e^{(A)}(\mathbf{r}, \mathbf{P}_{0i}) + \mathbf{D}_B(\mathbf{r}-\mathbf{R})] \equiv$$

$$\equiv \mathbf{P}_{0i}^A(\mathbf{r}) + \mathbf{P}_{0i}^B(\mathbf{r}), \tag{3}$$

$$\mathbf{P}_{0f}(\mathbf{r}) = \frac{c}{4\pi}[\mathbf{D}_A(\mathbf{r}) + \mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R}, \mathbf{P}_{0f}) + \mathbf{D}_B(\mathbf{r}-\mathbf{R})] \equiv \mathbf{P}_{0f}^A(\mathbf{r}) + \mathbf{P}_{0f}^B(\mathbf{r}), \tag{4}$$

where $c = 1/\varepsilon_0 - 1/\varepsilon$, is the parameter of polaron theory.

Using (3) and (4) we also can write $\mathbf{P}^*(\mathbf{r})$ as

$$\mathbf{P}^*(\mathbf{r})=\mathbf{P}_A^*(\mathbf{r})+\mathbf{P}_B^*(\mathbf{r}), \tag{5}$$

where

$$\mathbf{P}_A^*(\mathbf{r})=(c/4\pi)\,[\mathbf{D}_A(\mathbf{r})+(1-\theta^*)\mathbf{D}_e^{(A)}(\mathbf{r},\mathbf{P}_{0i})\,], \tag{6}$$

$$\mathbf{P}_B^*(\mathbf{r})=(c/4\pi)\,[\mathbf{D}_B(\mathbf{r}-\mathbf{R})+\theta^*\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R},\mathbf{P}_{0f})\,]. \tag{7}$$

Thus, in this approximation the fully defined polarization fluctuation described by relations (2) to (7) corresponds to the transition configuration. One can see from (6) and (7) that, if we disregard the constant terms that are proportional to $\mathbf{D}_A$ and $\mathbf{D}_B$, the polarization near each of the ions differs from the equilibrium polarization only in intensity; the fluctuation intensities near ions A and B are interrelated and governed by symmetry factor θ^*.

Natural generalizations of relations (6) and (7) are

$$\mathbf{P}_A(\mathbf{r})=(c/4\pi)\,[\mathbf{D}_A(\mathbf{r})+\xi\mathbf{D}_e^{(A)}(\mathbf{r},\mathbf{P}_{0i})\,], \tag{8}$$

$$\mathbf{P}_B(\mathbf{r})=(c/4\pi)\,[\mathbf{D}_B(\mathbf{r}-\mathbf{R})+\eta\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R},\mathbf{P}_{0f})\,], \tag{9}$$

where ξ and η are independent variables.

Relations (8) and (9) imply that among all the many diverse polarization fluctuations, in a first approximation we admit variation of the independent, spherically symmetric intensity fluctuations of the polarization near each of the ions. The values of parameters ξ^* and η^*, corresponding to the transition configuration will be found from the condition that the expression under the integral sign in (1) have a maximum.

Thus, all the many diverse variables describing the polarization variation here are replaced by two (ξ and η). The calculation can of course be further complicated by introducing a larger number of variables, but in the present paper we limit ourselves to the above approximation.

In looking for the electronic wave functions of the initial and final reaction channel we shall limit ourselves in the present work to the two-level approximation for basic states $\varphi_{\gamma A}$ and $\varphi_{\mu B}$ [1]. In the following we shall drop suffixes γ and μ. We shall use the direct variational method of [6] to calculate φ_A and φ_B. We select the spherically symmetric functions

$$\begin{aligned}\varphi_i(\mathbf{r})\equiv\varphi_A(\mathbf{r})&=(\alpha_i^3/\pi)^{1/2}\exp\,[-\alpha_i(\xi,\eta)\mathbf{r}],\\ \varphi_f(\mathbf{r})\equiv\varphi_B(\mathbf{r})&=(\alpha_f^3/\pi)^{1/2}\exp\,[-\alpha_f(\xi,\eta)\,|\mathbf{r}-\mathbf{R}|]\end{aligned} \tag{10}$$

as functions to be varied.

We have $\mathbf{P}(\mathbf{r})=\mathbf{P}_A(\mathbf{r})+P_B(\mathbf{r})$; therefore, with (8) and (9) the expressions for the potential-energy surfaces of the initial and final state can be written down as [6]

$$U_i(\xi,\eta)=F_i(\xi,\eta)+U(\xi,\eta)+J_i, \tag{11}$$

$$U_f(\xi,\eta)=F_f(\xi,\eta)+U(\xi,\eta)+J_f, \tag{12}$$

where

$$\begin{aligned}U(\xi,\eta)=(c/8\pi)\xi^2\int d^3r[\mathbf{D}_e^{(A)}(\mathbf{r},\mathbf{P}_{0i})\,]^2+(c/8\pi)\eta^2\int d^3r[\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R},\mathbf{P}_{0f})\,]^2+\\ +(c/4\pi)\xi\eta\int d^3r\mathbf{D}_e^{(A)}(\mathbf{r},\mathbf{P}_{0i})\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R},\mathbf{P}_{0f})-(c/4\pi)\int d^3r[\mathbf{D}_A(\mathbf{r})+\mathbf{D}_B(\mathbf{r}-\mathbf{R})\,]^2,\end{aligned} \tag{13}$$

$$\begin{aligned}F_i(\xi,\eta)=K_i-(c/4\pi)\xi\int d^3r\mathbf{D}_e^{(A)}(\mathbf{r},\mathbf{P}_{0i})\mathbf{D}_e^{(A)}(\mathbf{r})-(z_1e^2/\varepsilon_*)\int d^3r|\varphi_i|^2/r-\\ -(c/4\pi)\eta\int d^3r\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R},\mathbf{P}_{0f})\mathbf{D}_e^{(A)}(\mathbf{r})-(z_2e^2/\varepsilon_*)\int d^3r|\varphi_i|^2/|\mathbf{r}-\mathbf{R}|,\end{aligned} \tag{14}$$

$$\begin{aligned}F_f(\xi,\eta)=K_f-(c/4\pi)\eta\int d^3r\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R},\mathbf{P}_{0f})\mathbf{D}_e^{(B)}(\mathbf{r})-\\ -(z_2e^2/\varepsilon_*)\int d^3r|\varphi_f|^2/|\mathbf{r}-\mathbf{R}|-(c/4\pi)\xi\int d^3r\mathbf{D}_e^{(A)}(\mathbf{r},\mathbf{P}_{0i})\mathbf{D}_e^{(B)}(\mathbf{r})-(z_1e^2/\varepsilon_*)\int d^3r|\varphi_f|^2/r,\end{aligned} \tag{15}$$

TABLE 4. Kinetic Parameters for a Symmetric System in the Condon Approximation Obtained while Including the Mutual Effect of the Ion Fields on Energies and Wave Functions of the Electronic States

P/S	$2\alpha_p R$	ν	ξ*	E_a/E_a^0
0	4		No solution	
	6	0,352	0,291	1,252
	8	0,402	0,323	0,953
	10	0,414	0,328	0,886
1	2	0,492	0,349	2,834
	4	0,530	0,377	1,206
	6	0,551	0,380	1,057
	8	0,575	0,383	1,009
	10	0,594	0,386	0,983
−0,1	6		No solution	
	8	0,355	0,297	1,006
	10	0,382	0,314	0,884

TABLE 5. Kinetic Parameters for a Symmetric System in the Condon Approximation Obtained while Including the Mutual Effect of the Ion Fields, Only on the Energies of the Electronic States

P/S	$2\alpha_p R$	ν	ξ*	E_a/E_a^0
0	2		No solution	
	4	0,239	0,3215	1,567
	6	0,313	0,3207	1,001
	8	0,354	0,3212	0,913
	10	0,382	0,3225	0,878

where K_i and K_f are the kinetic energies of the electron when it is in states φ_i and φ_f, i.e.,

$$K_i=(\hbar^2/2m)\int d^3r|\nabla\varphi_i|^2;\quad K_f=(\hbar^2/2m)\int d^3r|\nabla\varphi_f|^2. \tag{16}$$

Inductions $\mathbf{D}_e^{(A)}(\mathbf{r})$ and $\mathbf{D}_e^{(B)}(\mathbf{r})$ and the corresponding equilibrium quantities $\mathbf{D}_e^{(A)}(\mathbf{r},\mathbf{P}_{0i})$ and $\mathbf{D}_e^{(B)}(\mathbf{r}-\mathbf{R},\mathbf{P}_{0f})$ are functionals of wave functions φ_i and φ_f [6]:

$$\mathbf{D}_e^{(A)}(\mathbf{r})=-e\int d^3x|\varphi_i(\mathbf{x})|^2(\mathbf{r}-\mathbf{x})/|\mathbf{r}-\mathbf{x}|^3, \tag{17}$$

$$\mathbf{D}_e^{(B)}(\mathbf{r})=-e\int d^3x|\varphi_f(\mathbf{x})|^2(\mathbf{r}-\mathbf{x})/|\mathbf{r}-\mathbf{x}|^3. \tag{18}$$

The corresponding expressions for the equilibrium quantities are obtained by merely writing φ_i and φ_f for φ_{i0} and φ_{f0}.

Quantities $\alpha_i(\xi, \eta)$ and $\alpha_f(\xi, \eta)$ (see (10)) characterizing the reciprocal radius of electron localization in the initial and final state are regarded as parameters to be varied, and for arbitrary ξ and η they are determined from the equations:

$$\partial F_i/\partial\gamma_i=0;\quad \partial F_f/\partial\gamma_f=0, \tag{19}$$

where symbols $\gamma_i = \alpha_i/\alpha_{io}$ and $\gamma_f = \alpha_f/\alpha_{fo}$ have been introduced, while α_{io} and α_{fo} are the values of α_i and α_f in the initial and final equilibrium configuration, respectively.

The equilibrium configurations are determined by the equations:

$$\partial U_i/\partial\xi=0;\quad \partial U_i/\partial\eta=0;\quad \partial U_f/\partial\xi=0;\quad \partial U_f/\partial\eta=0, \tag{20}$$

whence, with (11) to (19), we obtain:

$$\begin{aligned}&\xi_{0i}=1;\ \eta_{0i}=0,\\ &\xi_{0f}=0;\ \eta_{0f}=1.\end{aligned} \tag{21}$$

In order to estimate the importance of the different effects we shall limit ourselves in the further calculation to seeking the maximum of the function under the integral sign in (1) and the values of the function in this point while neglecting any change in width of the region of integration that provides the chief contribution to the integral when we allow for particular effects. Moreover, we write the electronic resonance integral approximately as

$$V_i(P) \approx V(P) S_{if}(P), \tag{22}$$

where

$$S_{if}(P) = \int d^3 r \varphi_i(r) \varphi_f(r), \tag{23}$$

and we shall neglect any dependence of V on P.

Then the equations for determining the location of the maximum (ξ^*, η^*) in the function under the integral sign in (1) are

$$kTd \ln S_{if}^2(\xi, \eta)/d\xi - dU_i(\xi, \eta)/d\xi = 0, \tag{24}$$

$$U_i(\xi, \eta) = U_f(\xi, \eta). \tag{25}$$

It must be pointed out that in (24) we have to calculate the total derivatives with respect to ξ while taking into account that η according to Eq. (25) depends on ξ, while γ_i and γ_f according to Eqs. (19) depend on ξ and η.

The results of the calculation for different particular cases are reported in Tables 1 to 5. Table 1 shows the results obtained in the calculation for a symmetric system (identical ions: $z_i = z_f$, $J_i = J_f$) with different values of the parameter $P/S = 16z/5c\varepsilon$, where any dependence of overlap integral S_{if} on ξ and η was disregarded (the Condon approximation), i.e., neglecting the first term in Eq. (24), and where the mutual effect of the fields set up by ions A and B and by the polarization fluctuations near ions A and B also were disregarded, i.e., neglecting the term containing the product $\xi \cdot \eta$ in (13) and neglecting the last two terms in (14) and (15). For a symmetric system one evidently has $\xi^* = \eta^*$ and $\gamma_i(\xi^*) = \gamma_f(\eta^*) \equiv \gamma$. In the case being discussed, γ_i depends only on ξ, and γ_f depends only on η.

One can see from Table 1 that inclusion of electronic-state modulation by the phonon field has the effect that activation energy E_a is lower than activation energy E_a° calculated without including this effect (i.e., for $\gamma_i = \gamma_f = 1$). This depression of the activation energy is larger for smaller parameters P/S. The effect of electronic-state modulation by the phonon field is particularly noticeable in the values of γ and ξ^*, which strongly differ from the corresponding ones ($\gamma = 1$ and $\xi^* = {}^1/_2 = \theta^*$) obtained without including this modulation; moreover, γ and ξ^* decrease with decreasing P/S, and for $P/S \lesssim -0.5$ there is no solution in the region of positive values of γ, which practically implies delocalization of the electron in the transition configuration.

Table 2 reports results which illustrate the effect produced by the dependence of S_{if} on ξ and η, on the position of the maximum (ξ^*, η^*) (non-Condon behavior) and on the kinetic parameters in a symmetric system; these results were calculated with the same assumptions as the ones of Table 1, except that now the first term in Eq. (24) was taken into account. One can see when comparing the results of Tables 1 and 2 that in the approximation discussed here, a dependence of S_{if} on ξ and η has little effect on the position of the maximum at small electron transfer distances ($2\alpha_p R \equiv 5mce^2R/8\hbar^2 \lesssim 4$), i.e., the Condon approximation works well at these distances. The effect produced by the dependence of S_{if} on ξ and η increases, of course, with increasing transfer distance, and it must be taken into account at $2\alpha_p R \gtrsim 8$.

One can see from (8) and (9) that quantities ξ and η in the classical limit considered here are true analogs of the complex quantity θ [1]. One can readily see when neglecting the effect of modulation of the electronic wave functions on the shape of the potential-energy surfaces that the conditions governing applicability of the Condon approximation are described by inequalities of the type of (25) in [2].

We notice that γ is smaller, i.e., the degree of delocalization of the electron in the transition configuration is larger, the larger the distance of electron transfer.

Table 3 reports results for a calculation that was performed with the same assumptions as made in obtaining the results of Table 1, but now for an asymmetric system (different ions). In the model adopted, strictly speaking, the quantities ΔF_0 (the free energy of the reaction)

and P_i/S, P_f/S are no absolutely independent parameters; but one still can see from Table 3 that for asymmetric systems, modulation of the electronic states by the phonon field can have a highly significant effect on activation energy.

Table 4 reports results of a calculation for symmetric systems which was performed while including the mutual effect of the fields set up by the ions and by the polarization fluctuations around them (i.e., allowing for terms proportional to $\sim\xi\eta$) but disregarding the first term in (24) (i.e., disregarding modulation of the overlap integral S_{if}). It is important to note that as before we have used the two-level approximation and spherically symmetric wave functions, but unlike the earlier case, parameters γ_i and γ_f in these functions now are functions of the two variables ξ and η, i.e., we included a spherically symmetric "distortion" of the state on one ion by the field produced by the second ion and by the polarization around it.

One can see from Table 4 that depending on the transfer distance between the ions, the activation energy calculated while allowing for modulation of the electronic states can be smaller as well as larger than that calculated without including this effect. The mutual effect of the two ion fields is felt at rather large distances between them (compare Tables 1 and 4). The mutual effect of the fields also results in disappearance of the solution in the physical region ($\gamma > 0$) when the ions come sufficiently close. But one must remember the fact that at small distances polarization of the states may occur, so that it becomes necessary to use more complicated functions for φ_i and φ_f.

Finally, Table 5 reports the results of a simplified calculation for a symmetric system differing from the calculation of Table 4 only in that the mutual effect of the ion fields on the state energies has been included while the effect on their wave functions was disregarded, i.e., the interaction with the "foreign" ion has been regarded as coulombic interaction of a point charge with an external field. One can see then comparing Tables 4 and 5 that this approximation is better the larger the distance between the ions.

It follows from the above discussion that modulation of the electronic states by the phonon field can have a substantial effect on the kinetic parameters of an electron transfer reaction, and this effect must be taken into account in theoretical discussions of processes involving weakly bound, solvated, and trapped electrons. The method outlined above can be modified to include more complicated effects such as polarization of the electronic states, multiparameter polarization fluctuations, changes in the internal structure of the reactants, etc.

LITERATURE CITED

1. A. M. Kuznetsov, Élektrokhimiya, 18, 594 (1982).
2. A. M. Kuznetsov, Élektrokhimya, 18, 598 (1982).
3. R. R. Dogonadze and A. M. Kuznetsov, in: Progress in Science and Technology, Kinetics and Catalysis Series, Vol. 5 [in Russian], VINITI, Moscow (1978).
4. A. M. Kuznetsov, Nouv. J. Chim., 5, 427 (1981).
5. R. R. Dogonadze and A. M. Kuznetsov, Zh. Vses. Khim. Ova., 19, 242 (1974).
6. S. I. Pekar, Research in Electron Theory of Crystals [in Russian], GITTL, Moscow–Leningrad (1951).