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Chemical Physics 325 (2006) 359–364

Chemical Physics

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Near-contact adiabatic suppression of electron transfer in the inverted region

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Received 27 October 2005; accepted 3 January 2006
Available online 3 February 2006

Abstract

A few theories of activated electron transfer in inverted Marcus region are used for bridging the non-adiabatic, solvent controlled and deeply adiabatic transfer. The simple analytical interpolation between dynamic and stochastic theories provides a continuous description of the electron transfer rate at any non-adiabatic coupling between the diabatic states. When coupling increases with shortening of inter-particle distance the pre-exponent of the Arrhenius transfer rate first increases being quadratic in coupling, then levels off approaching the "dynamic solvent effect" (DSE) region and finally is cut off exponentially due to adiabaticity of the transfer.

These changes affect significantly the spatial dependence of the transfer rate near the contact provided the coupling there is strong. The rate tends to zero at contact distance being strongly suppressed nearby adiabatically. It is much smaller then the perturbation (golden rule) and even DSE results. The latter is actually unattainable anywhere if contact tunneling is really strong. The transfer rate is a bell-shaped curve adiabatic and non-adiabatic on the opposite sides and sensitive to the friction (DSE damping) only in between, near the maximum.

Keywords: Electron transfer; Inverted region; Transfer rate

1. Introduction

The electron transfer rate is a fundamental property used in the theories of intra-molecular and inter-molecular reactions in dense media [1–4]. For electron transfer reactions the potential surface consists of the two diabatic energy levels 1 and 2 which are commonly assumed to be parabolic and even identical but shifted relative to one another. Recently, we studied the resonant electron transfer when the free energy of the reaction $\Delta G = 0$ [5]. Here, we turn to the opposite case when the transfer $1 \rightarrow 2$ is irreversible and proceeds in Marcus inverted region (Fig. 1), where the free energy is negative and large:

$$-\Delta G > \lambda \gg k_B T, \tag{1.1}$$

where λ is the reorganization energy of electron transfer and k_B is the Boltzmann constant. This is for instance the highly exergonic ionization turning the neutral reactants to the pair of the counter-ions:

$$D + A \rightarrow D^+ + A^-.$$

In general the distant dependent rate of electron transfer

$$W = W_0 e^{-U/T} \tag{1.2}$$

is a product of exponential Arrhenius factor (from now on $k_B = 1$) and the pre-exponent W_0 whose r-dependence is very specific for different inter-reactant distances r. The activation energy

$$U = \frac{(\Delta G + \lambda)^2}{4\lambda} \tag{1.3}$$

is also r-dependent through both $\Delta G(r)$ and $\lambda(r)$ [3,4].

The free energy contains the Coulomb contribution which in case of electrostatic attraction between counter-ions reduces its value:

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doi:10.1016/j.chemphys.2006.01.001

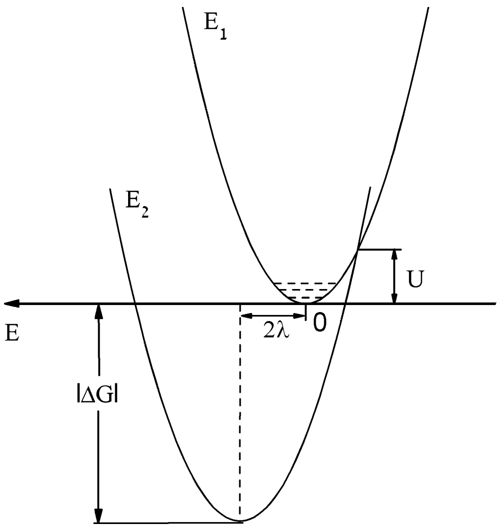

Fig. 1. The intersection of the parabolic diabatic energy levels in the inverted Marcus region.

$$\Delta G(r) = \Delta G_0 - \frac{e^2}{\epsilon r}, \tag{1.4}$$

where $\Delta\ G_0 = \Delta G(\infty)$ and ϵ is the static dielectric constant of the solvent. The polar surrounding of the ions affects also the reorganization energy making it distance dependent:

$$\lambda(r) = \lambda_i + \lambda_0(2 - \sigma/r), \tag{1.5}$$

where λ_i is the so-called inner-sphere reorganization energy and

$$\lambda_0 = \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon}\right)\frac{e^2}{\sigma}$$

is the outer-sphere reorganization energy (of polar surrounding with optical dielectric constant ϵ_0) at contact distance σ. In highly polar solvents considered here the Coulomb interaction is negligible, that is the free energy is actually constant ($\Delta G(r) = \Delta G_0 = \text{const.}$) and the reorganization energy is large compared to the small inner-sphere contribution neglected further on ($\lambda_i = 0$).

The r-dependence of $W_0(r)$ results mainly from the distance dependence on the non-adiabatic coupling which increases exponentially with reduction of distance:

$$V(r) = V_0 \mathrm{e}^{-\frac{r-\sigma}{L}}, \tag{1.6}$$

where L is the tunnelling length. The tunneling determines the level splitting $2V$ at the crossing point of the diabatic energy levels. The transfer is non-adiabatic at large distances where the splitting is small but becomes adiabatic at contact if the coupling there is strong enough. In between it passes through the so-called dynamic solvent effect (DSE), when the transfer is limited by diffusion along the reaction coordinate to the crossing point [6,7]. Moreover, Zusman proposed the formula that sewed together the perturbation theory and DSE [6]. The latter becomes the upper limit of the transfer rate achieved at the largest $V \sim V_0$.

The DSE was obtained and studied a lot of times in the intramolecular transfer and in the solid state [8–15]. However, it was common until recently to use mainly the perturbation theory in the theories of electron transfer in liquids presuming that V_0 is small enough [3,4]. However, the precise fitting of transfer kinetics showed us that the true V_0 is as large that the DSE should be taken into account [16]. Now we think that this is not enough. We are going to show here that even at more reliable, much smaller $V_0 \sim 20$ meV the transfer becomes adiabatically suppressed at contact making DSE limit unattainable.

2. Pre-exponent dependence on distance

To cover the whole range of inter-particle distances one has to use a number of theories valid at different coupling, V, and the damping parameter γ, which is actually a friction along the reaction coordinate. The relationship between all these theories and their results was studied earlier [17] and presented in two-dimensional domain (V, γ). The latter is reproduced in Fig. 2 in slightly different notations and used further on to reconstruct the space dependence of $W_0(r)$ and $W(r)$ at high collision frequency γ. However, the value of the latter should not exceed the borders shown by the double line in Fig. 2. Within these limits the crossing region is passed by a single free pass. It is also presumed that $V \ll T$. Under these conditions the velocity of passing conserves during the crossing allowing the classical Landau–Zener formula to be employed [17].

It should be also noted that in Ref. [17] a bit different presentation of the transfer rate (1.2) was used:

$$W(r) = A\Gamma_{\mathrm{TST}} = A\frac{\omega}{2\pi}\mathrm{e}^{-U/T}, \tag{2.1}$$

where Γ_{TST} is the canonical expression of the transition state theory (TST) rate through the linear frequency of the free vibrations in parabolic potential well, $\omega/2\pi$. We see from the comparison that

$$W_0(r) = \frac{\omega}{2\pi}A(r) \tag{2.2}$$

has the same r-dependence as $A(r)$.

In particular, within the second order perturbation theory $W_0(r)$ has the commonly used form [3,4,17–21]:

$$W_0^{\mathrm{PT}} = \frac{V^2}{\hbar}\sqrt{\frac{\pi}{\lambda T}} = \frac{\omega}{2\pi}A_{\mathrm{PT}}, \tag{2.3}$$

where

$$A_{\mathrm{PT}} = 2\sqrt{\pi\Delta} \quad \text{and} \quad \Delta = \frac{\pi^2 V^4}{\hbar^2\omega^2\lambda T} = \alpha^2. \tag{2.4}$$

Parameter

$$\alpha = \sqrt{\Delta} = \frac{\pi V^2}{\hbar\omega\sqrt{\lambda T}} \tag{2.5}$$

is space dependent due to exponential decrease of coupling (tunnelling) strength with inter-particle distance according to Eq. (1.6). Parameter α chosen as an ordinate in Fig. 2