SOLVATION AND BARRIERLESS ELECTRON TRANSFER: HOW DIFFERENT ARE THE DYNAMICS?

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Recent experiments on photoinduced electron transfer reactions have revealed that in many conjugated aromatic molecules the electron transfer in the excited state can proceed without the intervention of a significant activation barrier to the reactive motion [1]. Experiments also indicate that these reactions are rather strongly coupled to solvent polarization relaxation, indicated by a strong dependence of the rate on the longitudinal relaxation time, \(T_1\) of the dipolar solvent. Here we present a microscopic theory of dynamic solvent effects on a barrierless electron transfer reaction and compare the dynamics with that of solvation of the newly formed charge transfer state. We also investigate the effects of solvent translational modes on barrierless electron transfer reactions.

For an explicit microscopic calculation, we consider the following simple model of an intramolecular electron transfer reaction

\[
\hbar \gamma \quad A-B \rightarrow (A^\delta + B^\delta)^* \rightarrow A^+ - B^- ,
\]

where \(A\) and \(B\) are the two segments of the molecule and the intermediate state is the locally excited state. The reason for the absence of a sizeable activation barrier in the present problem is that there is no intermediate state of incomplete solvation of the electron in the reaction process, in contrast to a self-exchange reaction of the type \(Fe^{2+}/Fe^{3+}\) which faces a sizeable barrier.

We assume a one dimensional reaction free energy surface with the following definition of the reaction coordinate, \(X(t)\)

\[
X(t) = - \int dr \Delta D(r) \cdot P(r, t),
\]

where \(\Delta D(r)\) is the change in the displacement vector as a result of the charge redistribution arising from the electron transfer and \(P(r, t)\) is the instantaneous solvent polarization at position \(r\) at time \(t\). If the locally excited state is non-polar then \(X(t)\) is the time dependent solvation energy of the charge transfer state. We assume that the motion of the reaction coordinate can be described by a modified Smoluchowski equation for the time evolution of the probability density, \(P(X, t)\) of the reaction coordinate, with a position dependent sink term to account for the electron transfer reaction at certain specific values of the reaction coordinate. A similar equation of motion has been used earlier in the description of barrierless isomerization reactions [2]. The important parameters of this equation are the effective friction (\(\gamma\)) on the reaction coordinate, the frequency (\(\omega\)) of the (assumed) harmonic surface, a molecular rate (\(k_0\)) of electron transfer.
from the origin (where the rate is maximum) and a sink function \(S(X)\) which gives the position dependence of the rate. Sumi and Marcus [3] pointed out that \(k_o S(X)\) is determined by the nature of the coupling between the two diabatic electronic surfaces. If the coupling is strong (the adiabatic limit), then \(k_o S(X)\) may be approximated by an absorbing barrier at the position of crossing \(X_c\). For weak coupling (the non-adiabatic limit), \(k_o S(X)\) is a finite sink at \(X_c\). For the former case, the time dependent survival probability, \(P(t) = \int dX P(X,t)\), can be obtained analytically if we assume that initial vibrational relaxation on the locally excited state is so rapid that \(P(X,t=0)\) can be approximated by the equilibrium distribution. The resulting simple expression is given by

\[
P(t) = \frac{1}{2\pi} \sin^{-1}(\exp(-w^2 t / \xi)) .
\]

(3)

The electron transfer dynamics is non-exponential with a long time rate given by \(K_i = w^2 / \xi\). Eq. 3 is an important result of this work. The parameters \(\xi\) and \(w\) are determined by the reaction time correlation function, \(Q(t)\), defined by [4]

\[
Q(t) = \frac{\langle X(0) X(t) \rangle}{\langle X^2(0) \rangle} ,
\]

(4)

Note that \(Q(t)\) is identical with the solvation energy time correlation function (usually denoted by \(C_s(t)\)) of the charge transfer state. If we neglect the distortion of the solvent by the reactant, (that is assume a linear response of the solvent), then \(Q(t)\), and in turn \(\xi\) and \(w\), are determined by the dynamics of the dipolar liquid. From an analysis of the relations between these quantities, the following important expression can be derived

\[
w^2 / \xi = [ \int_0^\infty dt \, Q(t) ]^{-1} .
\]

(5)

Since \(Q(t)\) is also the solvation time correlation function, Eqs. 3 and 5 show that the long time rate of a barrierless adiabatic electron transfer reaction is exactly equal to the inverse of the average solvation time. Eqs. 3 and 5 also provide an interesting relationship between the dynamics of electron transfer and solvation which can be tested against experiments.

The correlation function \(Q(t)\) can be evaluated by following the method developed in Ref. 5. For explicit (microscopic) numerical calculation, we approximate the field \(D(r)\) by that of a point dipole at the center of a sphere that encompasses the reaction system and the solvent by a system of dipolar hard spheres for which an analytical solution of the equilibrium two-particle direct correlation function is available. The importance of the translational contribution to the solvent polarization relaxation is gauged by the parameter \(p'\), given by \(D_T / 2 D_R \sigma^2\), where \(D_T\) and \(D_R\) are the solvent translational and rotational diffusion coefficients and \(\sigma\) is the solvent molecular diameter.

The results of numerical calculations are shown in figures 1 and 2 for a liquid of dielectric constant 18 and reduced density 0.8. The reactant and the solvent molecules are of the same size. In Fig. 1, the dynamics of electron transfer is compared with the dynamics of solvation for two values of \(p'\).
Although the two processes are rather similar in the absence of translational contribution \( (p' = 0) \), they deviate from each other as \( p' \) is increased. The electron transfer dynamics is faster than the solvation dynamics at all times. In Fig. 2, the long time rate \( k_L \) is plotted against the longitudinal time \( \tau_L \) for two different values of \( p' \). The prediction of Sumi-Marcus theory \( (k_L = \tau_L^{-1}) \) is also shown for comparison. It can be seen from this figure that the dependence of \( k_L \) on \( \tau_L \) is non-trivial.

For a non-adiabatic reaction, the Smoluchowski equation has been solved numerically with a Gaussian sink function. The results have been discussed elsewhere [6].

In conclusion, we have presented a theory which treats both electron transfer and solvation dynamics within a consistent theory of polar solvent dynamics. The theory makes several predictions which can be tested against experiments.

**Fig. 1** Comparison between the dynamics of electron transfer \( (P(t): \text{dashed line}) \) and solvation \( (C_S(t): \text{solid line}) \).

**Fig. 2** Dependence of electron transfer rate \( (k_L) \) on the longitudinal relaxation time, \( \tau_L \).

**REFERENCES**


