

where the solvation time τ_s and α are determined by many factors, including the Davidson–Cole exponent, β . These two exponents (α and β) need not be equal, although they may sometimes be close to each other in value.

Equations (5–7) describe the dynamic disorder model. In contrast to the static disorder model, here the solvent relaxation is not quenched.

The experimental observable is the reactant survival probability, $P(t)$, defined by

$$P(t) = \int_{-\infty}^{\infty} dX P(X, t). \quad (9)$$

2.2b. High barrier reactions

The situation is quite different for the high barrier adiabatic reactions. Here a formulation following Hynes can be used to obtain the long time rate of electron transfer. This scheme, interestingly however, provides a rate not too different from that of Rips and Jortner. For non-exponential $\Delta(t)$ the rate shows fractional dependence on τ_{DC} . In the present model, the solvent dependent rate of electron transfer of an adiabatic reaction is obtained by solving the well-known Grote–Hynes formulae

$$k_{et} = (\lambda_r/\omega_b) k^{TST}, \quad (10)$$

$$\lambda_r = \frac{\omega_b^2}{\lambda_r + \zeta(\lambda_r)}, \quad (11)$$

$$\Delta(z) = \frac{1}{z^2 + \omega_R^2 + z\zeta(z)}, \quad (12)$$

where k^{TST} is the transition state rate of the bi-stable (double well) system with a barrier frequency ω_b , reactant well frequency ω_R and an activation energy which is determined by the Marcus theory. In the above equation, λ_r is the reactive frequency, $\zeta(z)$ is the frequency dependent reactive friction and $\Delta(z)$ is the Laplace transform of the solvation time correlation function $\Delta(z) = \int_0^\infty dt \exp(-zt) \Delta(t)$. The solvent dependence is determined by the curvature of the adiabatic surface near the barrier top. This curvature is determined by ω_b which in turn is determined by the electronic coupling V_{el} between the two surfaces. For harmonic diabatic surfaces, this relation between the barrier curvature (ω_b) and the electronic coupling is given by the following simple relation

$$\omega_b^2 = \omega_R^2 [1 + \lambda/V_{el}]. \quad (13)$$

The above equation shows that we have a cusp-like barrier for a weakly adiabatic reaction and a broad barrier for an adiabatic reaction. It is curious to note that in this model, the dynamic solvent effects also depend on the solvent reorganization energy (λ) through the ratio λ/V_{el} . We shall show below that this has an important role to play in determining the dynamic solvent effect and is in fact connected to a previous observation of Rips and Jortner.

We next present the results.

3. Results and discussion

In order to obtain the time dependent reactant survival probability, we first need to calculate the solvation time correlation function, $\Delta(t)$. We have calculated this $\Delta(t)$ for