

Non-exponentiality in electron transfer kinetics: Static versus dynamic disorder models

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Abstract. Non-exponential electron transfer kinetics in complex systems are often analyzed in terms of a quenched, static disorder model. In this work we present an alternative analysis in terms of a simple dynamic disorder model where the solvent is characterized by highly non-exponential dynamics. We consider both low and high barrier reactions. For the former, the main result is a simple analytical expression for the survival probability of the reactant. In this case, electron transfer, in the long time, is controlled by the solvent polarization relaxation—in agreement with the analyses of Rips and Jortner and of Nadler and Marcus. The short time dynamics is also non-exponential, but for different reasons. The high barrier reactions, on the other hand, show an interesting dynamic dependence on the electronic coupling element, V_{el} .

Keywords. Non-exponential dynamics; adiabatic surface; solvent reorganization energy.

1. Introduction

Electron transfer reactions often show non-exponential kinetics. The probable cause for this non-exponentiality has been a subject of considerable discussion in the literature in the recent past. For biological electron transfer reactions, this non-exponentiality is usually attributed to the existence of multiple configurations often observed in the biosystems, each with different activation energy and solvent environment. Understanding of this non-exponentiality, therefore, is highly non-trivial and requires the elucidation of reaction parameters for the different configurations. We shall not discuss this any further. Electron transfer reactions can be strongly non-exponential even in homogeneous phase, such as in liquids and glasses. Actually, the Sumi-Marcus theory¹ was first formulated to explain such non-exponentiality observed in low or zero barrier photo-electron transfer reactions. Now, the non-exponentiality in Sumi-Marcus theory comes from the widening of the reaction zone due to the participation of a low frequency intra-molecular vibration in the electron transfer. The extent of this intrinsic non-exponentiality depends on the width of the reaction window determined by the ratio of the re-organization energies of the solvent and the vibrational modes and the degree of non-exponentiality is rather limited. There can, however, be another source of non-exponentiality in homogeneous systems. This is the non-Debye dielectric relaxation of the medium. In this article, we briefly discuss this issue.