Modeling multistage ultrafast photoinduced electron transfer in complex environments with multiple relaxation timescales

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Photoinduced separation of charges in certain kinds of molecular devices proceeds as a sequence of electron transfer (ET) steps involving several redox centers in the molecule. Since many of these elementary ET reactions are ultrafast, their kinetics and yields are strongly influenced by nonequilibrium dielectric polarization produced in vicinity of the redox sites by optical and radiationless electronic transitions [1]. This feature allows one to control the overall charge separation (CS) yield by adjusting the structure and spatial geometry of the molecule, as well as energetic characteristics of the individual ET steps [2].

The problem of theoretical description of multistage sequential ET was considered recently in the paper [1]. The commonly applied approach here suggests the use of the so-called "energy-gap reaction coordinates", introduced by mapping the environmental degrees of freedom to the vertical energy gaps between the reactant and product states for all elementary ETs. These coordinates however are inappropriate for ultrafast sequential processes, because they are not orthogonal and, therefore, different stages can affect each other's kinetics in the nonequilibrium reactions. A new model of multistage photoinduced ET, proposed in [1], involves the configuration space of *independent* polarization coordinates, and is shown to describe properly the nonequilibrium polarization around the redox sites in the compound. The dimensionality of the space is related to the number of active sites.

We report here an extension of our previous theory [1] allowing one to take into account complex dynamics of dielectric relaxation in vicinity of the redox sites. This extension is important for studying ultrafast multistage ET in non-Debye solvents or biological environments such as polymer blend. Our approach suggests the use of the two coordinate subspaces: the subspace of independent "polarization" coordinates (as mentioned above), and the subspace of "relaxation" modes (as internal coordinates). The new configuration space is formed as the direct product of these two subspaces. The metric properties of this combined space are studied and allow establishing relations between reorganization energies for each elementary ETs, relaxation characteristics of the environment and arrangement of the free energy surfaces (FESs) in the combined space. A general procedure is developed for constructing the diabatic FESs, based on the step-by-step inclusion of electronic states to the model.

Feasibility of the suggested approach is illustrated by its application to a simple model ET reaction involving the molecular compound with 3 redox sites (D, A_1 and A_2) and polar solvent with 2 relaxation times (τ_1 and τ_2). The resulting mathematical model is shown to be fully consistent with the specific models of Najbar/Tachiya (2-stage ET) and Sumi/Marcus (ET in 2-mode environment) developed earlier [3,4].

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References

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