

ELEMENTARY
PHYSICOCHEMICAL PROCESSES

Perturbative Analysis of the Probability of the Nonthermal Transfer of an Electron

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Abstract—The probability of the nonthermal transfer of an electron of an excited donor-acceptor complexes was calculated from the electron coupling parameter within the framework of time-dependent perturbation theory. Using the analysis of the two first corrections of the perturbation theory series for the standard spin-boson model with the Debye spectral density of thermostat oscillators as a basis, we revealed the structure of higher corrections. This allowed us to sum up the series and obtain a new analytical expression distinct from the widely used Padé-approximation for the probability of the nonthermal transfer of an electron. The stochastic approach was shown to allow overestimation of the probability of nonthermal electron transitions by 40.0% in the solvent-controlled regime.

Keywords: electron transfer, donor–acceptor complex, nuclear subsystem nonequilibrium, nonthermal electron transition probability.

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INTRODUCTION

The charge-transfer (CT) photoexcitation of donor–acceptor complexes (DACs) by a laser pulse at an absorption band frequency leads to the formation of an ionic state with a nonequilibrium nuclear configuration. The relaxation of this state is manifested experimentally in the time dependence of the Stokes shift of the emission band of DACs [1]. In Fig. 1, a photoexcited state with a nonequilibrium nuclear configuration is represented by a wave packet on the excited therm U_1 . The motion of the wave packet along this therm from point A to the minimum corresponds to nuclear relaxation. In the case of a low exothermicity of charge recombination (CR) reactions proceeding after the photoexcitation of DACs, the wave packet necessarily passes through the therm intersection point Q_* in the process of relaxation, thus resulting in the nonthermal (hot) electron transitions from a nonequilibrium state of the nuclear subsystem. Such transitions play an important part in fast and superfast CR reactions [2–10]. The clarification of the detailed physical mechanism of nonthermal transition is undoubtedly an urgent task of a theory pretending to the quantitative description of the dynamics of superfast charge separation and recombination processes in excited DACs.

During recent decades, the experimental studies of superfast CT and CR reactions and the theoretical approaches that take nonthermal transitions into consideration are being continuously improved and modernized [5–18]. By now, a large variety of approaches

for the description of the nonequilibrium nuclear dynamics of chemical processes have been developed [2–4, 10, 19–30]. Experimentally, the nonequilibrium character of a superfast CR is manifested as the deviation of the excited DAC occupancy decay from an exponential law. Another pronounced manifestation of the nonequilibrium nature of a CR process is the

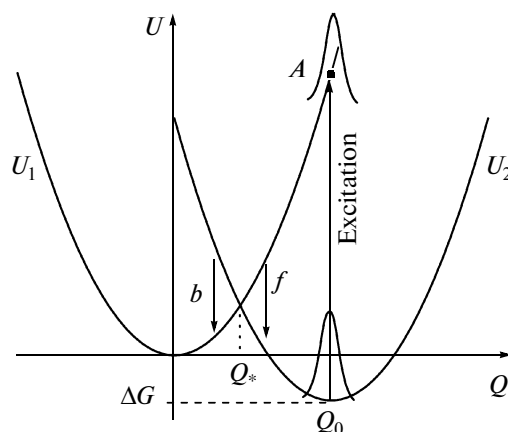


Fig. 1. Surfaces of the potential energies of the basic (U_2) and excited (U_1) states of DACs. Photoexcitation is shown as the vertical $|2\rangle \rightarrow |1\rangle$ transition. The nonthermal transition of an electron is localized within the neighborhood of the therm intersection point Q_* . The forward and backward transitions are indicated by arrows with the labels f and b , respectively.