

How good is the generalized Langevin equation to describe the dynamics of photo-induced electron transfer in fluid solution?

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The dynamics of unimolecular photo-triggered reactions can be strongly affected by the surrounding medium for which a large number of theoretical descriptions have been used in the past. An accurate description of these reactions requires knowing the potential energy surface and the friction felt by the reactants. Most of these theories start from the Langevin equation to derive the dynamics, but there are few examples comparing it with experiments.[1]

Here we explore the applicability of a Generalized Langevin Equation (GLE) with an arbitrary potential and a non-markovian friction.[2] To this end we have performed broadband fluorescence measurements[3] with sub-picosecond time resolution of a covalently linked organic electron donor-acceptor system in solvents of changing viscosity and dielectric permittivity. The free energy surface (FES) of the reaction is established using stationary electronic spectroscopy, while the dynamics of a non-reacting reference provide the calibrating tool for the non-markovian friction over the FES. In addition, the simpler and computationally faster Generalized Smoluchowski Equation (GSE) is also applied for comparison.[4]

While both approaches reproduce the measurements in most of the solvents reasonably well, the GSE shows larger discrepancies whenever the dynamics become slow. At long times some differences arise from the intrinsic shortcomings of the solvatochromic model and at short times from the excess excitation energy.

The here applied method can be used to predict the dynamics of any other reacting system, given the FES parameters and solvent dynamics are provided. Thus **no fitting parameters** enter the simulations, within the applicability limits found for the model in this work.

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