

Dynamics of photo-induced electron transfer in fluid solution in the context of a Generalized Langevin treatment with almost fully experimentally determined quantities

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The dynamics of unimolecular photo-triggered reactions like electron transfer can be strongly affected by the surrounding medium, the solvent in liquid solutions, 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 very few examples of direct comparison with experiments.^[1] To this end, we have performed fluorescence broadband measurements with sub-picosecond time resolution of a model chemical compound composed of an electron donor (D) and a covalently linked acceptor (A) in a set of solvents changing both viscosity and dielectric permittivity. In order to estimate the free energy surface (FES) of the reaction, stationary absorption and fluorescence provide its key quantities. On the other hand, similar dynamics of a non-reacting substance, Coumarin 153, provide the calibrating tool to obtain the non-markovian friction over the FES which is assumed to be solute independent.

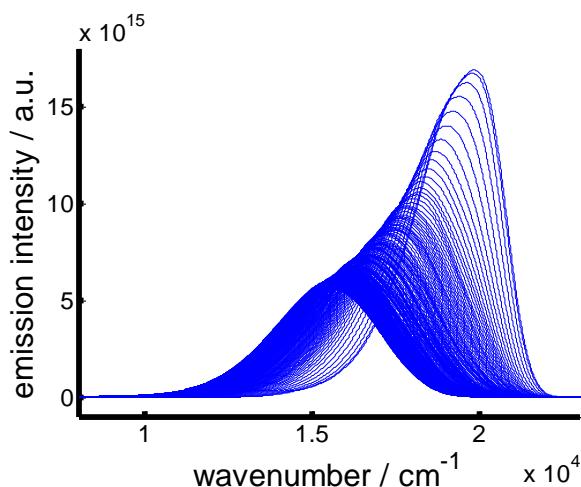


Figure 1. GLE-simulated evolution of the time resolved emission spectra of 3-(p-N,N-dimethylaminophenyl)-perylene in acetonitrile.

With this data in hand, we have performed simulations using the Generalized Langevin equation (GLE) with a friction kernel with memory,^[2] extracted from the measurements with C153, and a FES from the stationary experiments of the D-A molecule (3-(p-

-N,N-dimethylaminophenyl)-perylene). In most of the cases the simulations reproduce properly the experimental dynamics of the first and second moments of the spectra. However there are deviations ascribed to failures in the solvatochromism model employed to construct the FES at very long times and to vibrational cooling at very short times. A clear deviation of the dynamics is only observed at very high viscosities most likely due to a difference in the specific solvation of the D-A molecule and C153. We have compared the data with the Generalized Smoluchowski differential equation (GSE), in which the friction is substituted by a time dependent diffusion coefficient, as the friction is overdamped. In many cases the dynamics are also well reproduced by the GSE model, but discrepancies are much more important for the GSE at low polarities and high viscosities.

The proposed method can be used to predict the dynamics of any other reacting system for which the FES parameters are provided as no fitting parameters enter the GLE simulations, within the applicability limits found for the model in this work.

Funding: Narodowe Centrum Nauki “Sonata-bis”, grant number 2013/10/E/ST4/00534 and SNF (IZK0Z2_170389).

Acknowledgement: AR thanks Niko Ernsting for help with the FLUPS

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