Bimolecular Photoinduced Electron Transfer: the effect of the reorganization energy

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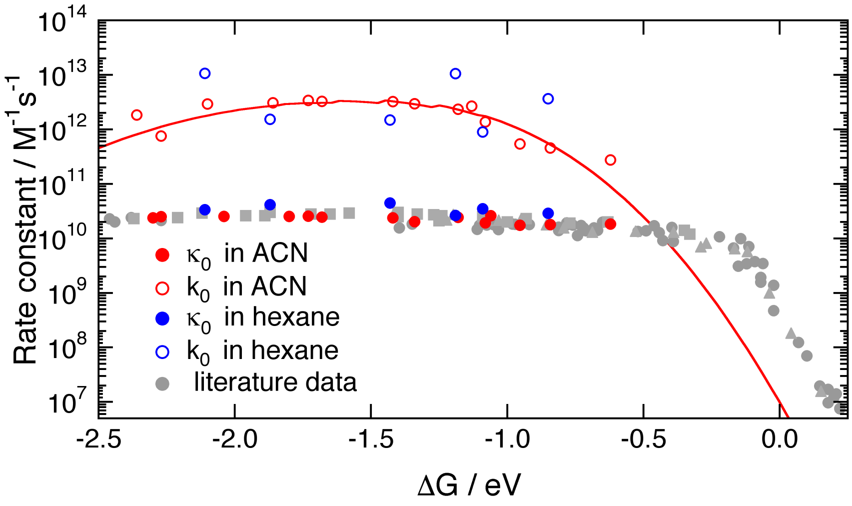
Electron transfer (ET) is one of the simplest chemical reactions, as it does not require the formation or the breaking of a chemical bond. Moreover, photoinduced ET it is one of the most investigated photochemical reactions.[1] ET processes are usually described theoretically in terms of the Marcus model, which connects the driving force of the reaction with its rate constant.[2] The latter depends on several additional parameters such as the temperature, the reorganization energy and the electronic coupling between the initial and final states.

We will present a study focussing on the reorganization energy, which is composed of the contribution from the solvent, λ_s, and from intramolecular modes, λ_i. The effect of λ_s was investigated by measuring the dynamics of bimolecular photoinduced ET reactions in an apolar solvent and by comparison with previous results in a polar solvent.[3] The effect of λ_i was studied by performing measurements with perdeuterated compounds.



The above figure illustrates the driving force dependence of the ET rate constant in hexane and in acetonitrile (ACN). Here, k_0 is the intrinsic, diffusion-free, bimolecular ET rate constant, whereas k_0 is the diffusion-controlled rate constant. Surprisingly, the observed ET dynamics does not exhibit a significant dependence on the solvent polarity, despite very different λ_s. This result suggests that the intramolecular modes play a predominant role in the ET dynamics.

[1] Tatu Kumpulainen, Bernhard Lang, Arnulf Rosspeintner, Eric Vauthey, *Chemical Reviews,* **2017**, DOI: 10.1021/acs.chemrev.6b00491
[2] R. A. Marcus, *The Journal of Chemical Physics.* **1956,** 24, 966-78.
[3] Arnulf Rosspeintner, Gonzalo Angulo, Eric Vauthey, *Journal of the American Chemical Society,* **2014,** 136, 2026-2032.