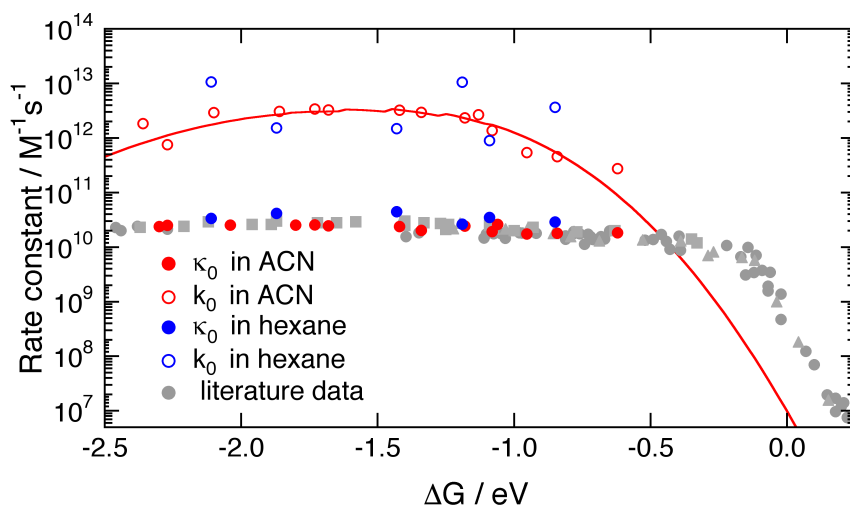


Bimolecular Photoinduced Electron Transfer: the effect of the reorganization energyC. Nançoz¹, A. Rosspeintner¹, E. Vauthey^{1*}¹University of Geneva

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 κ_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.

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