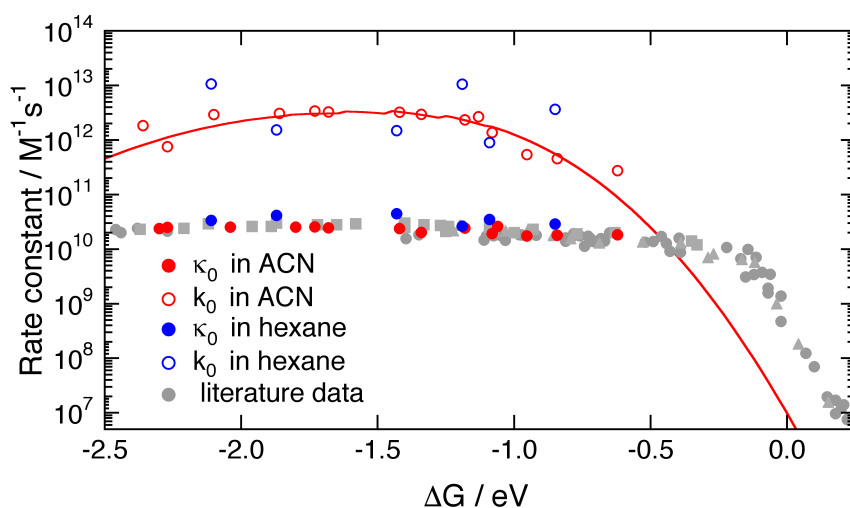


**Bimolecular Photoinduced Electron Transfer: the effect of the reorganization energy**C. Nançoz<sup>1</sup>, A. Rosspeintner<sup>1</sup>, E. Vauthey<sup>1\*</sup><sup>1</sup>University of Geneva

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.<sup>1</sup> ET processes are usually described theoretically in terms of the Marcus model, which connects the driving force of the reaction with its rate constant.<sup>2</sup> 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,  $\lambda_s$ , and from intramolecular modes,  $\lambda_i$ . The effect of  $\lambda_s$  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.<sup>3</sup> The effect of  $\lambda_i$  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  $\kappa_0$  is the diffusion-controlled rate constant. Surprisingly, the observed ET dynamics does not exhibit a significant dependence on the solvent polarity, despite very different  $\lambda_s$ . This result suggests that the intramolecular modes play a predominant role in the ET dynamics.

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