

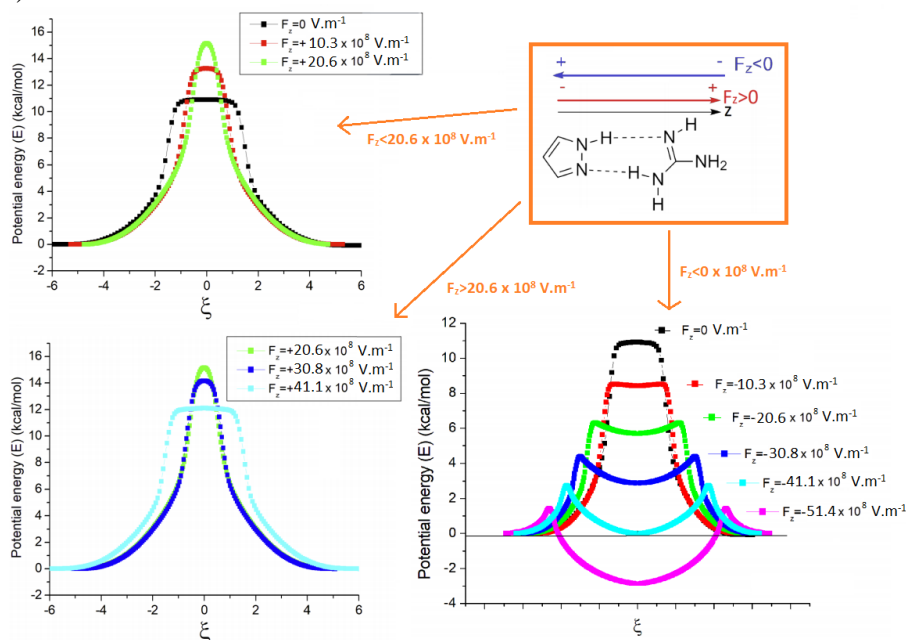
Influence of an oriented external electric field on double proton transfer reactions: from concerted to stepwise mechanism

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Double proton transfers (DPT) are important reactions in physics, chemistry and biochemistry. As an example, they are proposed to be responsible for some DNA mutations when they occur between Watson-Crick pairs [1]. Since at the heart of the double-helical DNA macromolecules or in the active site of enzymes, electric fields may reach $51.4 \times 10^8 \text{ V.m}^{-1}$, understanding the effect of an electric field on these reactions is fundamental. Matta *et al.* have already shown that it is possible to catalyze a DPT reaction using oriented external electric fields (OEEF) [2].

In this work, we studied the influence of an OEEF on the mechanism of DPT between Pyrazole and Guanidine by computational modelling, using DFT (ω B97XD/6-311++G(2d,2p)). This system was chosen as it is at the interface between a strongly asynchronous concerted mechanism and a stepwise reaction. Indeed, without OEEF, the potential energy profile along the reaction coordinate shows a wide plateau in the transition state region where the system has a strong zwitterionic character with deprotonated pyrazole in interaction with protonated guanidine [3]. We studied the reaction under the influence of an electric field oriented along the two proton transfers. In one direction, as the intensity of the field increases, we observed first an extinction of the plateau indicating that the two protons are transferred more synchronously, and then its reappearance, accompanied by an inversion in the order in which the two protons are transferred. In contrast, the concerted reaction is transformed into stepwise process under an electric field oriented in the negative direction. Finally, we explain the structural changes invoking the electronic reorganization along the reaction path within the topology of the electron localization function (ELF).



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[2] Matta C. & Arabi A., *J. Phys. Chem. B*, 122, 37, 8631-8641 (2018)

[3] Rauhut G. & Schweiger S., *J. Phys. Chem. A*, 107, 45, 9668-9678 (2003)