

## From Synchronous to Sequential Double Proton Transfer: Quantum Dynamics Simulations for the Model Porphine

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Double Proton Transfer (DPT) was a widely studied topic in the last decades. Porphyrins and metalloporphyrins are one of the most common subjects of research. These “pigments of life” play a crucial role in biologically relevant processes, such as photosynthesis, oxygen transport and activations and therefore they drove to the development of theoretical models for systematic studies. Questions of interest in this field concern the nature of the DPT: concerted (called 1-step or synchronous, as well) or sequential (called 2-step or asynchronous, as well) reaction mechanism [1,2,3], influences of quantum effects on reaction rates, and possibility to control the DPT are just few examples [4].

We present a quantum-mechanical reaction dynamics approach to DPT in porphine, using the symmetric model of Smedarchina et al. [5]. Such approach has the advantage to give information about the quantum dynamics of the wave packets far away from the minimum energy path in a multidimensional space.

In order to carry out the quantum dynamics, the MCTDH method [6] was applied. The propagated nuclear wavefunctions discover a surprising phenomenon in DPT, i.e. the mechanism may switch from concerted to sequential. We conclude that, in general, it is not sufficient to consider just the potential energy surface (PES) in order to predict the mechanism of DPT. The same PES may support different reaction mechanisms depending on the initial preparation of the system. The discrimination of the mechanism calls for quantum dynamics simulations, beyond quantum chemistry calculations of the PES.

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