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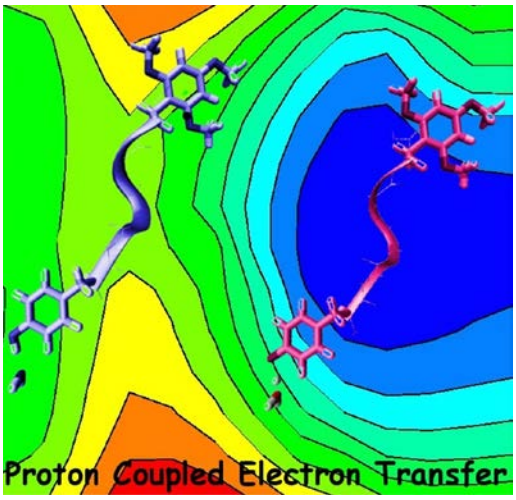
CHARGE AND PROTON TRANSFER REACTION: INSIGHT FROM THEORY[*]



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We briefly describe the calibration of standard electronic methods in dealing proton coupled electron transfer reactions, and the use of new parameters ad hoc designed to capture both electronic and nuclear changes driven by such complex processes, often involving excited electronic states.

Reactions based on Proton Coupled Electron Transfer (PCET), including the so called Excited State Proton Transfer (ESPT) events[1,2], play a key role in the mechanism of many biological and electrochemical processes, providing lower energy paths to activate molecular transformations in Nature[3,4].

Examples of miraculous PCET molecular machines are well given by Photosystem II (PSII) and Ribonucleotide reductase (RNR), where PCET processes involving aromatic residues are believed to be critical for function. As matter of fact, it is amazing the way by which PSII uses solar photons to drive the oxidation of water to dioxygen, thereby producing electrons and protons to reduce carbon dioxide[5]. Therefore, this system is a good starting point for the construction of artificial photosynthetic machines to produce clean fuel from sunlight and water.

The modeling of PCETs is a really exciting and challenging task. Theoretical studies can be crucial for investigating complex biological processes like those involved in cellular respiration and photosynthesis, as well as for the design of catalysis in various energy conversion processes.

A theoretical study needs to afford many issues when dealing with PCET processes. A first challenge for theoretical approaches regards the accurate description of both the ground and excited state Potential Energy Surface (PES) associated to a given reaction, in order to have a clear definition of the reaction space, including micro and bulk solvation effects[6]. This initial step of methodological calibration is really important for the accuracy of the following analysis of the several effects on the PCET kinetics and thermodynamics properties.

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Another theoretical challenge is represented by the description and the analysis of the excited state reactivity. In this direction it is very promising the development of new tools, such electronic density based indices[7,8], i.e. parameters *ad hoc* designed to search and to analyze, for example, possible excited state minimum energy reaction pathways.

Moving from the considerations above, here we discuss two themes: (i) testing the performance and the robustness of different theoretical models in the description of PCET processes in both gas and solvent phase; (ii) developing new electronic density based indices able to analyze charge transfer events and reaction paths.

To deal with the first problem, far from straightforward, we modeled the PCET reaction in a radical cation model well characterized from an experimental point of view by Giese and coworkers[9].

In this system a trimethoxy-phenyl-alanine residue acts as electron acceptor, a tyrosine residue as electron and proton donor, and a water molecule as proton acceptor (Fig. 1a).

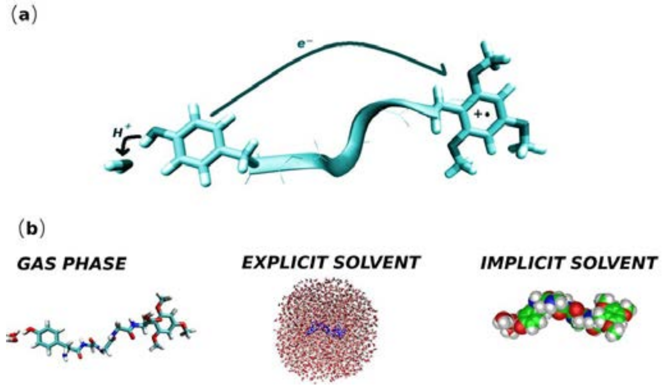

Fig. 1 - a) Graphical sketch of the analyzed PCET reaction; b) peptide-water model in several environments (gas phase, explicit, and implicit solvent)

The PCET event has been simulated scanning the PES along the oxygen-hydrogen distance of the tyrosine, and by monitoring the spin density shift along the peptide chain.

We constructed PCET energy profiles by testing the robustness of a large number of density functionals, and comparing their performances to Hartree-Fock and post Hartree-Fock results, in both gas and solvent phase, considering for the latter case both an implicit and an explicit representation of the solvent (Fig. 1b).

Our results showed that the percentage of Hartree-Fock exchange present in the functional is a key parameter in determining the ability of density functionals to describe these charge transfer phenomena. This is true in the gas phase but even more important in the solution, especially when this latter is represented by a continuum model.

Once tuned the methodological approach for the electronic problem we introduced new tools enabling us to analyze also excited states reactivity.

For this reason the ESPT reaction between 7-hydroxy-4-(trifluoromethyl)coumarin and 1-methylimidazole (Fig. 2) has been considered.

For a better understanding of how the proton transfer relates to the relaxation of the electronic density, a potential energy surface for the excited state (ES-PES) was constructed scanning along the oxygen-hydrogen (O-H) and the oxygen-nitrogen (O-N) distances (Fig. 2a).

The calculated PES was then explored by using two density based indices, hereafter indicated as D_{CT} [7] and $D_{CT,react}$ [8] respectively, to check their ability to reproduce the minimum energy path of the reaction. More specifically, D_{CT} represents the distance between the barycenters of two functions $\rho_+(r)$ and $\rho_-(r)$, describing the spatial increase and decrease of electronic density following the electronic excitation, respectively. $D_{CT,react}$ is an analog parameter including also the effect of a nuclear rearrangement between the considered electronic states.

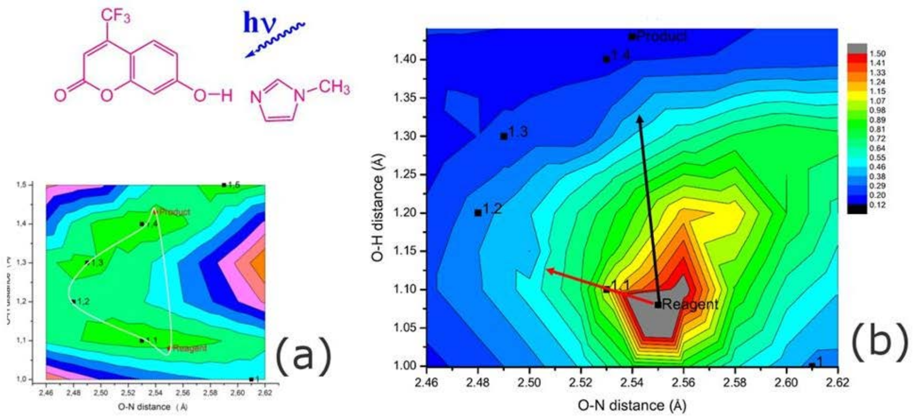

Fig. 2 - a) Potential energy surface and b) $D_{CTreact}$ index map computed for ESPT involving 7-hydroxy-4-(trifluoromethyl)coumarin and 1-methylimidazole

By inspection of Fig. 2b it can be observed how the computed $D_{CT,react}$ values decrease going from the reactants to the products. By comparing the ES-PES and $D_{CT,react}$ values in the region closest to the reagent, it is possible to notice that the minimum energy path, involving a combined shortening of the O-N distance and an elongation of the O-H distance, corresponds to the steepest variation of the $D_{CT,react}$. Therefore, the $D_{CT,react}$ index describes the qualitative concept that the coumarin molecule tends to strongly reduce the charge separation induced by the electronic excitation with a structural reorganization, leading to a ESPT reaction.

In conclusion, we have shown the importance of the theoretical insight in such complex systems involving charge transfer phenomena. Moreover, we briefly illustrated the development of new theoretical tools, *ad hoc* designed to effectively account for both the electronic and nuclear rearrangement in excited states. The use of such parameters can strengthen the capability of a theoretical analysis for intriguing *phenomena* like PCET reactions.

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