

## Describing Photoinduced Proton Coupled Electron Transfer Reactions: Exploring the Possibilities of Density-Based Index

Juan Sanz García<sup>1</sup>, Marco Campetella<sup>1</sup>, Federica Maschietto<sup>1</sup> and Ilaria Ciofini<sup>1</sup>

<sup>1</sup>École Nationale Supérieure de Chimie de Paris - Chimie ParisTech  
Équipe CTM, PSL Research University Paris, IRCP UMR8247  
11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

[juan.sanz-garcia@chimie-paristech.fr](mailto:juan.sanz-garcia@chimie-paristech.fr)

Over the last few decades, photoactive molecules capable of undergoing light driven nuclear rearrangements have gained an ever-growing interest among the scientific community. This interest arises from the wide scope of technological applications ranging from optical high capacity storage devices<sup>[1]</sup> to miniaturized photomechanical gadgets.<sup>[2]</sup> Phototriggered intramolecular proton coupled electron transfer (PCET) is a very representative example of this phenomenon. Generally, this photoinduced nuclear rearrangement results from excited state intramolecular proton transfer (ESIPT) between a proton donor and a proton acceptor group which are in close proximity. Upon photoabsorption, redistribution of electronic density across the molecule increases the acidity/basicity of the donor/acceptor groups involved resulting in a fast proton transfer in the excited state. The photoinduced enol-keto tautomerization of the 2-(2'-hydroxyphenyl)benzothiazole (HBT) (Figure 1.) is a very well-known example of this kind of intramolecular PCET.<sup>[3,4]</sup> A density-based index called  $D_{CT}$ <sup>[5]</sup> has already been used not only for the characterization of the HBT enol-keto tautomerization<sup>[4]</sup> but for other excited state processes as well.<sup>[6,7,8,9]</sup> This  $D_{CT}$  index allows in a simple and intuitive way to quantify the spatial extent of a charge transfer excitation. Although this  $D_{CT}$  density-based index has proven to be a powerful tool in the analysis of photochemical reactions, to the best of our knowledge, no work in the literature has ever reported an application of this index using wave-function theory methods. The main goal of this project is to show that the  $D_{CT}$  index is a good descriptor of the excited states not only in density functional theory (DFT) but also in wave-function theory (WFT). To this end, the  $D_{CT}$  results obtained for the photoinduced enol-keto tautomerization PCET of a HBT reduced model using both DFT and WFT approaches are analysed and compared in this study.

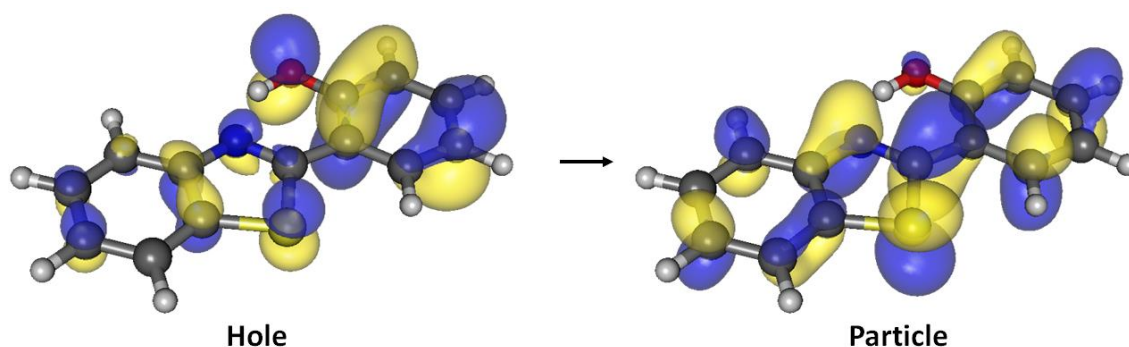


Figure 1. Natural transition orbitals ( $S_1$ ) of the enol HBT isomer.

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