

# Electron Localization Function in Excited States: The Case of the Ultrafast Proton Transfer of the Salicylidene Methylamine

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The physical characterization of the chemical bond in the ground state has been a central theme to theoretical chemistry. Among many techniques, quantum chemical topology (QCT) has emerged as a robust technique to understand the features of the chemical bond and electron organization within molecules. One consolidate tool within QCT is the topological analysis of the electron localization function (ELF). Most research on ELF and chemical bond has focused either on singlet ground states or the first excited triplet. However, most photochemical reactions and photophysical processes occur in excited states with the same spin-symmetry as the ground state. In this work, we develop a proposal on how to compute the ELF in excited states of any symmetry within linear-response time-dependent density functional theory. Then, we study the evolution of the chemical bonds in the ground- and excited-state intramolecular proton transfer (ESIPT) of a prototypal Schiff base (the salicylidene methylamine). We found that the topological analysis of the ELF along reaction paths explains the presence of a barrier for the proton transfer in the ground state and the absence of it in the excited state. Briefly, in the ground state, the cleavage of the O-H bond results in a structure with high electrostatic potential energy due to an excess of electron lone-pairs (3) in the oxygen atom, which explains the barrier. In the excited state, the electronic transition promotes an enhancement of the basicity of nitrogen by allocating three nonbonding electrons in the basin of its lone-pair. This excess of electrons in the N exerts an electrostatic attraction of the proton, which we suggest as the primary driven-force of the barrierless reaction. Because in excited states the molecule can develop more vibrational kinetic energy than in the

ground state, we performed an ab initio molecular dynamics of the proton transfer in the excited state and corroborate that our conclusions on the topology of the ELF do not change due to dynamic effects. © 2019 American Chemical Society.