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Photoinduced Proton Coupled Electron Transfer (PCET1,2) reactions constitute an important class of reactions of biological3 and technologic4 relevance. They are increasingly recognized in areas such as synthetic chemistry and photocatalysis as well as in energy transformation reactions in natural and artificial systems.5 From a mechanistic point of view, these reactions can be distinguished by the degree of synchronicity and directionality by which both the proton and the electron are transferred following photoexcitation. Theoretical and computational methods can contribute to the molecular interpretation of the PCET mechanism and of spectroscopic data. We report a theoretical and computational study of photoinduced PCET reactions via organic catalyst excitation among the intracellular domain. We have studied the mechanism ruling the PCET reactions in a model system in aqueous solution, taking into account the numerous effects arising from the multi-layer biological system: the kinetics and the thermodynamics of PCET reactions in solution depend on a fine interplay of the electronic and the nuclear motion, as well as of solute-solvent interactions, which represent crucial features in standard electronic methods to properly describe the electronic density along the proton transfer coordinate and the resulting potential energy surface.6-8 To investigate the adiabaticity and the non-adiabaticity of the catalyst's excited electron states involved, Time-Dependent DFT (TD-DFT) calculations were performed alongside a clear investigation of the ground state properties. This allowed for the analysis of the proper reactive excited state species of the catalyst for the PCET reaction of interest. The next step consisted into simulating the PCET reaction with the molecular counterpart. The reaction pathway was analyzed by simulating various potential scenarios through a computational study of the excited states of the complex, in gas-phase first and then through a simulated solvation by water molecules. The TD-DFT was also adopted to simulate the steady-state and transient UV–Visible spectra of neutral and excited complex. By combining theoretical predictions with experimental data, we aimed to enhance the understanding of the reaction at an atomistic and molecular level, providing new insights beyond experimental observation. This study can contribute to a better understanding of the PCET reaction as well as to the interpretation of spectroscopic time resolved data9, that suggest an ultrafast kinetics of the PCET process.

**Primary author(s) :** Mr. CASCONE, Luca (Scuola Superiore Meridionale)

**Presenter(s) :** Mr. CASCONE, Luca (Scuola Superiore Meridionale)