Quantum Dynamics study of the Excited State Intramolecular Proton Transfer process in 3-Hydroxychromone

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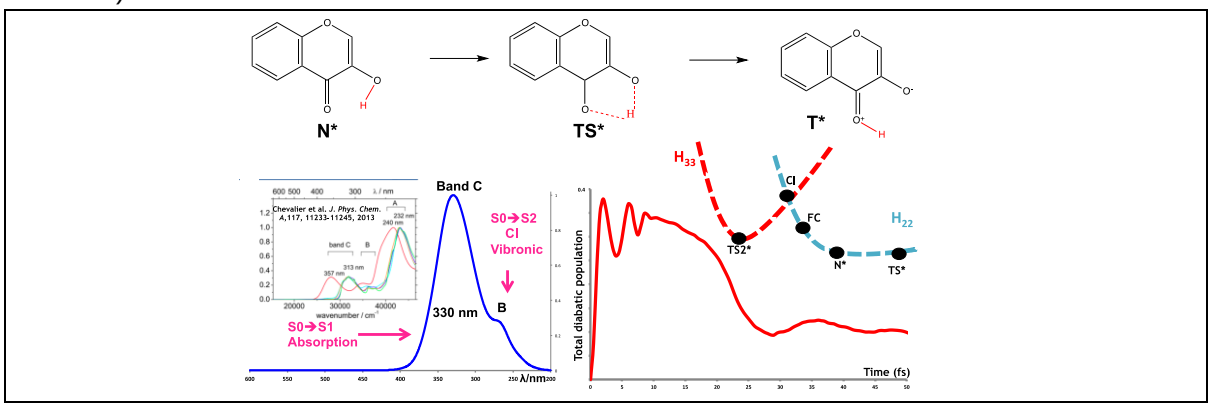
The ESIPT process of 3-Hydroxychromone (3-HC)[1] was studied with DFT and TD-DFT calculations to analyze the potential energy surfaces. We also developped a model for the potential energy surfaces to perform quantum dynamics calculations in full dimensionality.

3-HC dyes show two fluorescence bands (i.e. from the Normal (N*) and Tautomer (T*) forms) induced by an ESIPT process. This property is interesting for applications as biological sensors[2]. 3-HC, which is a prototype system to understand its derivatives, presents a unique behavior: its ESIPT process presents two rate constants, one ultrafast (fs) and a slow one (ps), irrespectively of the solvent polarity[1,2].

We highlighted the presence of a conical intersection (CI) between the first and the second excited states close to Franck Condon (FC) and the existence of several stationary points on the first excited state that were never discussed before. These new critical points play a significant role in the wave packet trapping within the FC region inducing the slow ESIPT process.

One of the major challenges in theoretical chemistry concerns the study of photochemical processes in large molecules (several tens of modes), where a CI plays a crucial role by transferring population between electronic states[3,4]. This requires the calculation of more than one electronic state and the non-adiabatic couplings between them, the development of models of potential energy surfaces and couplings, and the use of modern quantum dynamics simulation methods (i.e. ML-MCTDH)[4].



KEYWORDS: ESIPT, 3HC, 3HF, ML-MCTDH, NON-ADIABATIC,TD-DFT,DFT

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