

## TDDFT assessment of excited state intramolecular proton transfer in a panel of chromophore 2-hydroxypyrene-1-carbaldehyde

Hui Li, Hang Yin, Xiaochun Liu and Ying Shi\*

*Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China*

Received 20 February 2016; Accepted (in revised version) 10 April 2016  
Published Online 12 August 2016

---

**Abstract.** Time dependent density functional theory method at the def-TZVP/B3LYP level was employed to investigate excited state intramolecular proton transfer (ESIPT) properties of 2-hydroxypyrene-1-carbaldehyde (HC). Our calculated results of the primary bond lengths and infrared vibrational spectroscopic information show that, upon photoexcitation, the intramolecular hydrogen bond is significantly strengthened in  $S_1$  state, which facilitates the proton transfer process effectively. Furthermore, the electron density distributions of frontier molecular orbitals were demonstrated to be a positive factor for the ESIPT. By the monitor of the characteristic peaks stretching vibration of O-H group in the IR spectra, we have further confirmed the occurrence of ESIPT. The constructed potential energy surface of the  $S_1$  state has also been used to explain the proton transfer process and evaluate the radiationless pathway, indicating that the ESIPT process occurs most easily in HC molecule.

**PACS:** 33.15.Fm

**Key words:** Time dependent density functional theory; excited state intramolecular proton transfer; hydrogen bonding

---

## 1 Introduction

Ever since the seminal experimental observation of the excited-state intramolecular proton transfer (ESIPT) reaction of methyl salicylate (MS) by Weller et al. in the middle of the last century [1], the phenomenon of photoinduced proton transfer process has attracted countless works in many fields of chemistry and molecular biology [2-15]. A very fascinating feature of molecules undergoing ESIPT is the presence of a strong intramolecular

---

\*Corresponding author. *Email address:* shi\_ying@jlu.edu.cn (Y. Shi)

hydrogen bond, in which the acidity and basicity relations can be controllable by photoexcitation. As a consequence, the electronic excitation of such molecules represent large Stokes shift due to the characteristic conversion from an excited enol ( $E^*$  form) to an excited keto ( $K^*$  form) tautomer along a preformed hydrogen bond. It is worth mentioning that the ESIPT process was found to proceed exceptionally fast at a subpicosecond time scale because it involves a negligible activation barrier [16-22]. This ultrafast nature of ESIPT molecules attracts highest scientific interest whereby paving potential avenues for prospective applications, such as luminescent materials [23, 24], fluorescent chemosensors [25], photostabilizers [26, 27], molecular probes [28], metal ion sensors [29-31], and organic light emitting devices (OLEDs) [32, 33].

2-hydroxypyrene-1-carbaldehyde, hereafter also HC, possessing exclusively an intramolecular  $O_2-H_{10}\cdots O_1$  hydrogen bond to form a strong quasi-aromatic chelating ring, is a typical panel of chromophore exhibiting the phenomenon of ESIPT (Fig. 1). In the year of 1988, Einhorn and coworkers first provided a new methodology, for ortho-hydroxylation of aromatic aldehydes via ortho-lithiated aromatic amino alkoxides, to synthesize HC. They reported that HC molecule is a starting material for the synthesis of pyrenofurans, which showing exceptional mutagenic activities [34]. Until now, however, the complete picture of photophysical and photochemical characteristics for HC has remained poorly understand. Moreover, we are yet to elucidate the finer details of ESIPT process of the intramolecular hydrogen bonding ring system. Thus, theoretical investigations to get thoroughly insights into the inner intricacies involved in the ESIPT process of HC are needed.

In present work, we concentrated our efforts on unraveling the dynamics and mechanisms of the ESIPT process of HC. We investigated the structural and electronic properties in the ground ( $S_0$ ) and first excited ( $S_1$ ) states, using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) method, respectively. Furthermore, its proton-transfer tautomer have been globally optimized and found stable. Simultaneously, the vertical single state excitation energy, corresponding to the oscillator strengths in different electronic states, and the frontier molecular orbitals (MOs) were presented. Further verification of the occurrence of proton transfer reaction was also implemented via IR spectra analysis. In addition, the potential energy curve as a function of the proton-transfer coordinate was calculated, which provide us a very effective way to ensure the occurrence of ESIPT.

## 2 Theoretical methods

In our work, all the electronic structure calculations were carried out using the TURBO-MOLE program suite [35-40]. The ground-state geometry optimization was performed using density functional theory (DFT). Vertical singlet state excitation energy calculations and excited state geometry were optimized by means of the time dependent density functional (TDDFT) method. We employed the B3-LYP (Becke's three-parameter hybrid