

COMMUNICATION

Theoretical Confirmation of the Excited State Intramolecular Proton Transfer and Twisting Process of 1-hydroxy-2-acetonaphthone in Solution: A TDDFT Study

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Abstract: The excited state intramolecular proton transfer (ESIPT) of 1-hydroxy-2-acetonaphthone (HAN) in acetonitrile, which was recently studied by Joo and coworkers with time-resolved fluorescence (J. Phys. Chem. B 2015, 119, 2620-2627.), has been confirmed by our TDDFT calculations. The computed S0-S1 excitation energy of HAN in acetonitrile is at 362 nm and the computed S1-S0 excitation energies of HAN from its normal and proton-transfer forms are at 421 and 464 nm respectively, which are in excellent agreement with the experimental results of Joo and coworkers. However, different from their conclusions, the twisting process of the COCH₃ group of HAN maybe possible after the ESIPT in the excited state, due to the small energy barrier (6.26 kcal/mol) above and much lower energy valley (-9.97 kcal/mol) below the proton-transfer form of HAN, which is consistent with the results of Douhal and coworkers (J. Phys. Chem. A 2000, 104, 8424-8431).

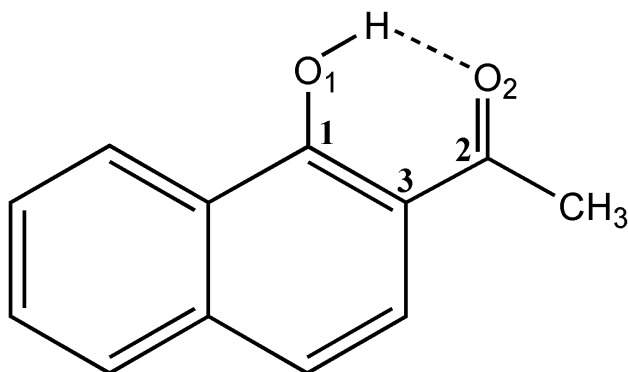
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It is well-known that intramolecular proton transfer is often induced by an electronic transition due to the variation of the acidity of a proton in different electronic states. Excited state intramolecular proton transfer (generally abbreviated as ESIPT) has been used as a

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model system to investigate the proton transfer dynamics, as it can be initiated by a short pulse of light [1-4]. In general, an ESIPT reaction takes place on a time scale ranging from ten femtoseconds to several tens of picoseconds and the ultrafast reaction rate suppresses fluorescence of the reactant to result in a large Stokes shift as well as dual emission, which makes ESIPT compounds usually used as OLED materials [5, 6], spectroscopy tools [7,8], and fluorescence probes in biology [9,10]. Since the work by Weller [11], the ESIPT reactions of methyl salicylate and related compounds have been studied extensively [12-15], which show large Stokes shifts of $\sim 10000\text{ cm}^{-1}$ because of the absence of the emission of the normal form, and the ESIPT has been confirmed by various spectroscopies. HAN, a two-ring analog of methyl salicylate, is used to probe the effect of microenvironments and chemical biological caging [16, 17]. However, the occurrence of ESIPT in HAN, whose molecular structure is shown in **Scheme 1**, has been in controversy [18-22], primarily due to its much smaller Stokes shift of $\sim 6000\text{ cm}^{-1}$ compared to those of typical ESIPT compounds. Recently, the occurrence of ESIPT of HAN in liquid seems to reach an agreement between several groups [23-26].



Scheme 1. Molecular structure of HAN with some atoms showing numbers. Dashed line indicates the intramolecular hydrogen bond.

Very recently, Joo and coworkers have studied the dynamics of ESIPT of HAN in acetonitrile by the time-resolved high-resolution fluorescence spectral technique to record the nuclear wave packet motions in the excited state [27]. They recorded the population dynamics of both the normal and tautomer forms together with the wave packet motions of the tautomer in the excited state, which were considered as the evidence of the occurrence of ESIPT in HAN. On the other hand, time-dependent density functional theory (TDDFT) method has been successfully used by several groups in investigating the ESIPT process of various compounds [28-32]. However, computational confirmation (especially that based on TDDFT calculations) of the ESIPT in HAN has been scarce [19, 33].

Therefore, in the present work, the ESIPT process of HAN in acetonitrile has been