

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).

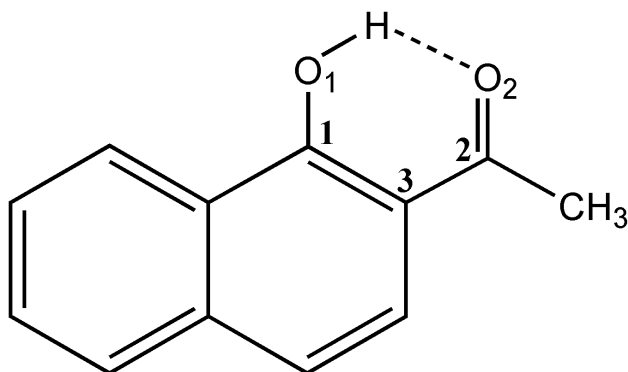
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Key words: Intramolecular hydrogen bond, ESIPT, TDDFT calculations, twisting process.

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

investigated by our TDDFT calculations at the iefpcm-b3lyp/6-31+g(d, p) theory level. The geometrical configurations for HAN in acetonitrile have been globally optimized in both the ground and lowest excited singlet states. All the electronic structure calculations were carried out using the Gaussian 09 program suite [34]. The conventional DFT and TDDFT calculations using the hybrid exchange-correlation functional B3LYP [35] was preformed, to investigate the excited-state dynamics of ESIPT in HAN. In addition, considering the solvent effects on the excited state dynamics, the integral equation formalism [36, 37] (IEF) version of the polarizable continuum [38, 39] (PCM) model was used in all calculations. The calculated energy barrier from the optimized S_1 -state conformation of HAN to its proton-transfer form is just 0.30 kcal/mol, whereas the potential energy of the proton-transfer form of HAN is 1.18 kcal/mol lower than that of the optimized S_1 -state conformation. In addition, the computed S_0 - S_1 excitation energy of HAN in acetonitrile is at 362 nm and the computed S_1 - S_0 excitation energy of HAN from its proton-transfer form is at 464 nm (see in **Table 1**), which are in excellent agreement with the experimental results of Joo and coworkers [27]. Thus, the ESIPT process of HAN in acetonitrile has been confirmed by our TDDFT computations. However, different from their conclusion, the twisting process of the COCH_3 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 [33].

Table 1. Calculated S_0 - S_1 and S_1 - S_0 transition energies (nm) of HAN in different states. The experimental absorption and fluorescence maxima are listed for comparisons.

	HAN- S_0	HAN- S_1	HAN- S_{1-PT}	Exp.
S_0 - S_1	362 (0.1426)			365
	H-L (95.6%)	----	----	
S_1 - S_0		421 (0.2283)	464 (0.2529)	467
	----	H-L (98.6%)	H-L (99.2%)	

Figure 1 shows the ground-state (S_0) and excited-state (S_1) structures of HAN in acetonitrile solvent. In state S_0 , the bond length of the intramolecular hydrogen bond $\text{H}\cdots\text{O}_2$ is 1.599 Å, which is shorten to 1.449 Å in the first excited-state S_1 due to the increase of both the acidity of H and the basicity of O_2 , as shown in **Figure 2**. When we scan the S_1 -state potential energy curve by constrained optimizations keeping the distance between H and O_2 from 1.449 to 0.999 Å in steps of -0.05 Å, a transition state S_1 -TS with a small energy barrier

0.30 kcal/mol has been obtained, as shown in **Figure 3**. The distances between atoms O1, O2 and H are 1.156 and 1.278 Å, respectively, seen in **Figure 1**. Cross the energy barrier point, we got the proton-transfer state S1-PT of HAN, whose potential energy is 1.18 kcal/mol lower than that of the S1 HAN, as shown in **Figure 3**. The bond length of intramolecular hydrogen bond O1...H in S1-PT form of HAN is 1.510 Å, which is a little weaker than that in the S1 form of HAN. The energy barrier for the reverse proton transfer from S1-PT to S1 is 1.48 kcal/mol, which is approximately quintuple to that of the forward proton transfer from S1 to S1-PT. Therefore, the ESIPT of H from atoms O1 to O2 in HAN in the first excited state is quite likely to happen. Thus, our computational results directly confirmed the occurrence of ESIPT of HAN in acetonitrile solvent. In addition, the occurrence of ESIPT of HAN in acetonitrile solvent is also supported by the calculated S1-S0 transition energies. The computed S1-S0 transition energies of HAN from its S1 and S1-PT forms are at 421 and 464 nm respectively, while the experimentally observed fluorescence maximum of HAN in acetonitrile occurs at 467 nm [27]. Therefore, the experimentally observed fluorescence maximum of HAN should come from its S1-PT form, which again confirms the occurrence of ESIPT of HAN in acetonitrile solvent.

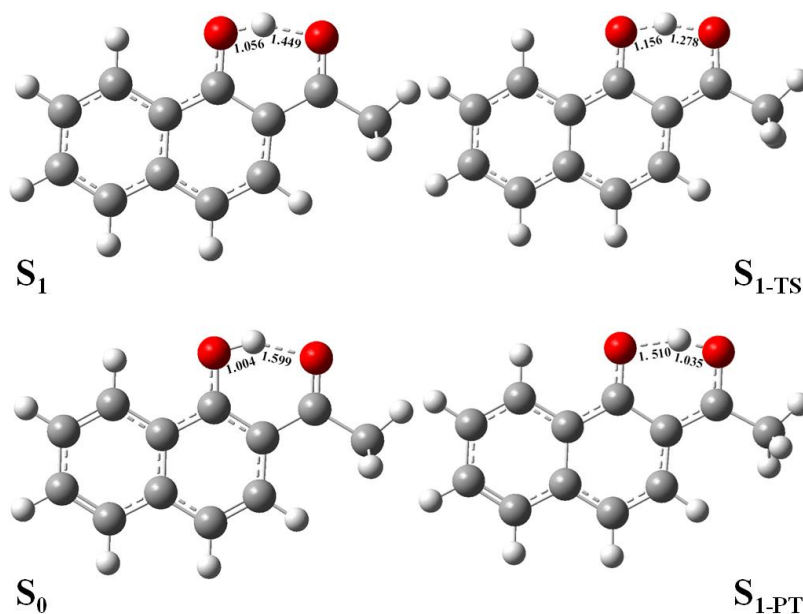


Figure 1: Ground-state (S₀) and excited-state (S₁) structures of HAN in acetonitrile solvent.

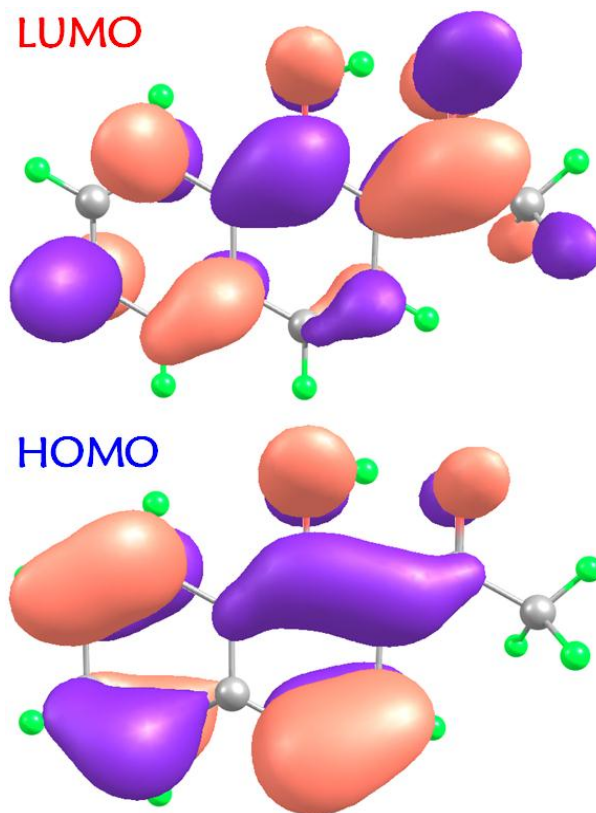


Figure 2: Frontier molecular orbitals HOMO and LUMO of HAN.

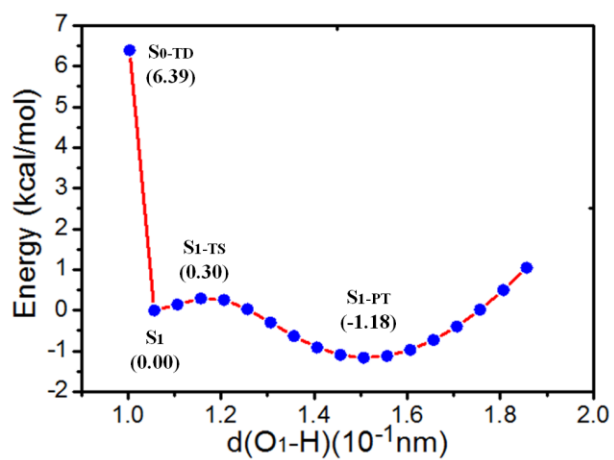


Figure 3: Scanned S1-state ESIP T potential energy curve of HAN by constrained optimizations.

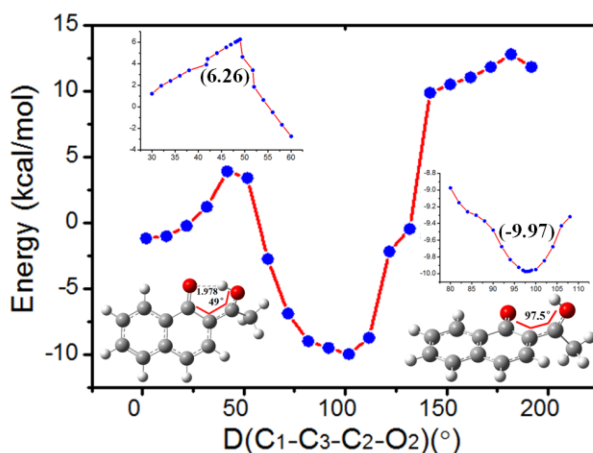


Figure 4: Scanned S1-state twisting potential energy curves of HAN by constrained optimizations.

As for the twisting process of the COCH₃ group after the ESIPT, the viewpoints of several groups are in controversy [19, 27, 33]. Joo and coworkers suggested that the minimum energy conformation of HAN in the first excited state has the intramolecular hydrogen bonding without twisting of the COCH₃ group, which was thought to be not relevant for the time scale they considered [27]. However, the calculation results of Douhal and coworkers indicated that a conformation of HAN with the COCH₃ group twisting from the molecule plane by 84° possesses a much lower energy (-6.23 kcal/mol) than the one without twisting (-0.65 kcal/mol) [19]. Contrarily, the computational results of Moreno and coworkers demonstrated that the twisting of the COCH₃ group from the molecule plane is an endothermic process, whose energies are much higher than that of the one without twisting [33].

Based on the optimized S1-PT structure of HAN, the twisting potential energy curve of HAN in S1 state has been scanned keeping the dihedral angle C1-C3-C2-O2 varying from 0° to 190° in steps of 10° and shown in **Figure 4**. An energy barrier of 6.26 kcal/mol is found at 49° of the dihedral angle and a much lower energy valley (-9.97 kcal/mol) below the proton-transfer form of HAN is found at 97.5° of the dihedral angle C1-C3-C2-O2. The twisting potential energy curves around the two dihedral angles 49° and 97.5° are again scanned keeping the dihedral angle C1-C3-C2-O2 varying in steps of 2° (in the vicinities of 49° and 97.5°, C1-C3-C2-O2 is varying in steps of 0.5°) and the fine structures are shown in **Figure 4** as the insert part. Therefore, due to the small energy barrier of 6.26 kcal/mol at 49° and the rather lower energy valley of -9.97 kcal/mol below the proton-transfer form of HAN at 97.5° as well as the excess energy of HAN upon vertical photoexcitation (6.39 kcal/mol, see **Figure 3**), the twisting process of the COCH₃ group after the ESIPT of HAN in acetonitrile

solvent may be possible, according to our calculations, which is consistent with Douhal and coworkers' work [19].

In a word, the excited state intramolecular proton transfer (ESIPT) of 1-hydroxy-2-acetonaphthone (HAN) in acetonitrile has been confirmed by our TDDFT calculations. In addition, the twisting process of the COCH₃ group of HAN after the ESIPT may be possible 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 as well as the sufficient excess energy of HAN upon vertical photoexcitation (6.39 kcal/mol).

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