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# COMMUNICATION

# Solvent effects on the energy barrier of excited state proton transfer in 3-hydroxyflavone

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**Abstract:** The energy barrier of excited state proton transfer (ESPT) process in 3-hydroxyflavone (3HF) was studied considering the solvent effects. It was found that the ESPT energy barrier increased with the increase of solvent polarity. But the ESPT energy barrier of 3HF in methanol is lower than in vacuum, n-hexane and acetonitrile. It was found that methanol molecule lowers the ESPT energy barrier by forming a seven-membered-ring 3HF-methanol complex.

**AMS subject classifications**: 74E40, 78M50

**Keywords**: excited state proton transfer; hydrogen bond; solvent effect; duel emission

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3-hydroxyflavone (3HF) is a classic molecule which shows excited state proton transfer (ESPT).[1-12] It reported the ESPT process in 3HF is solvent dependence.[1-4] In non-polar solvents, such as hydrocarbon solvents, only tautomer (T*) emission was observed. But in alcohols, there are duel emissions. One emission is located at around 405 nm, named as normal form emission (N*), the other emission is located at around 530 nm which comes from tautomer form (T*). Woolfe et al. measured the activation energy for the excited state proton transfer (ESPT) in hydrocarbon and methanol solvents.[2] They found ESPT activation energy in methanol-d is lower than in methyl-cyclohexane. However, there are no theoretical studies to elucidate the alcohol solvent effect. There are many people found that solvent molecules often takes part in the ESPT process.[13-15] It was reported that water wire lowers the ESPT energy barrier.[14]

In this communications, the ESPT processes were studied using time-dependence (TD)

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density functional theory (DFT) methods. B3LYP functional and 6-31G (d, p) basis set were used. IEFPCM model was used to consider the solvent effect. N-hexane, acetonitrile and methanol solvents were considered in calculations. All the potential energy minima have been confirmed by no imaginary frequency mode in vibrational analysis. The first excited state potential energy curves have been scanned by constrained optimizations fixing the hydrogen bond O---H distance at a series of values. It was found that the ESPT energy barrier increased with increase of solvent polarity. But the seven-membered-ring hydrogen bonding complex of 3HF-methanol obtains lower energy barrier than 3HF monomer.

The ground states of 3HF monomer and 3HF-methanol seven-membered-ring complex were optimized and the optimized structures are shown in **Figure 1**. In the optimized 3HF, the length of hydrogen bond ($HB_1$) between carbonyl oxygen atom and hydroxyl hydrogen atom is 1.937 Angstrom. In seven-membered-ring 3HF-methanol complex, the length of hydrogen bond ($HB_2$) between carbonyl oxygen atom and methanol hydroxyl hydrogen atom is 1.855 Angstrom. The length of hydrogen bond ($HB_3$) between 3HF hydroxyl hydrogen atom and methanol hydroxyl oxygen atom is 1.736 Angstrom. So that, the hydrogen bonds in 3-HF methanol are shorter than in 3HF monomer.

The first singlet excited states of 3HF and 3HF-methanol were also optimized. The $HB_1$ length is 1.692 Angstrom, $HB_2$ is 1.617 Angstrom and $HB_3$ is 1.463 Angstrom. All of the hydrogen bonds are strengthened after 3HF and 3HF-methanol complex has been excited.

The first excited state potential energies were calculated as along ESPT path of 3HF in vacuum, n-hexane and acetonitrile. The results were plotted in **Figure 2**. There are small energy barriers on the ESPT paths. The barriers are 1.167 kcal/mol in vacuum, 1.243 kcal/mol

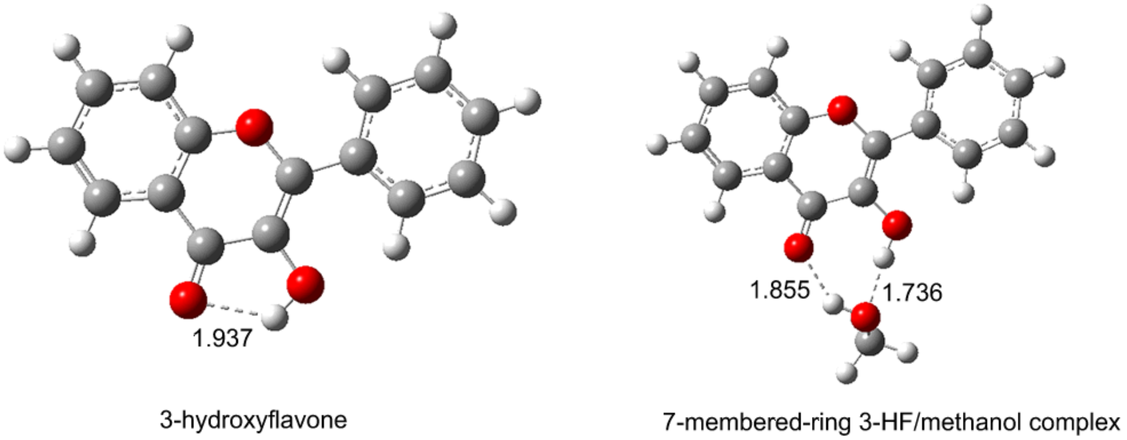

**Figure 1**: The ground state structures of 3HF and 3HF-methanol seven-membered-ring complex were optimized at B3LYP/6-31G(d,p) level.

in n-hexane and 1.60 kcal/mol in acetonitrile. It shows an increase of energy barrier with the increasing of solvent polarity. This increase may be contributed to the stability of E* species. It reported that polar solvents stabilize the more polar E*, thus lowering the E* potential energy basin with respect to the T* basin and the transition state.[16] Using the same calculation methods, Jiang et al. and Dai et al. reported ESPT energy barrier of 3HF in methylhexane is 2.058 kcal/mol[11] and 1.99 kcal/mol in vacuum[10], respectively. The results of them are a little larger than ours. It may contribute to the different functional and bases set they used with us. Therefore, the larger polar solvent will show the lower ESPT energy barrier.

The potential energy curves along the ESPT path of 3HF-methanol seven-membered-ring complex are plotted in **Figure 3**. It shows that ESPT energy barrier of 3HF-methanol complex is 0.70 kcal/mol. The ESPT energy barrier of complex is smaller than in vacuum and acetonitrile. Woolfe et al. obtained ESPT activation energy 1.81 kcal/mol in methanol-d and 5.23 kcal/mol in methylhexane.[2] Thought the values are larger than our results, it was found lower energy barrier in methanol than in methylhexane.

In summary, we calculated the potential energies of the first excited state of 3HF and 3HF-methanol seven-membered-ring complex along the ESPT path. The results show that the energy barriers of ESPT are increased with the increase of polarity of solvents. The 3HF-methanol seven-membered-ring complex has a lower ESPT energy barrier than 3HF in vacuum. These results are consistent with some experimental results. But the results about the lower ESPT energy barrier of 3HF-methanol complex than of 3HF monomer are difficult to understand the duel emission in alcohols. Furthermore, more detail or higher level calculations, ultrafast time-resolved experiments are needed to elucidate the fluorescent properties of 3HF.

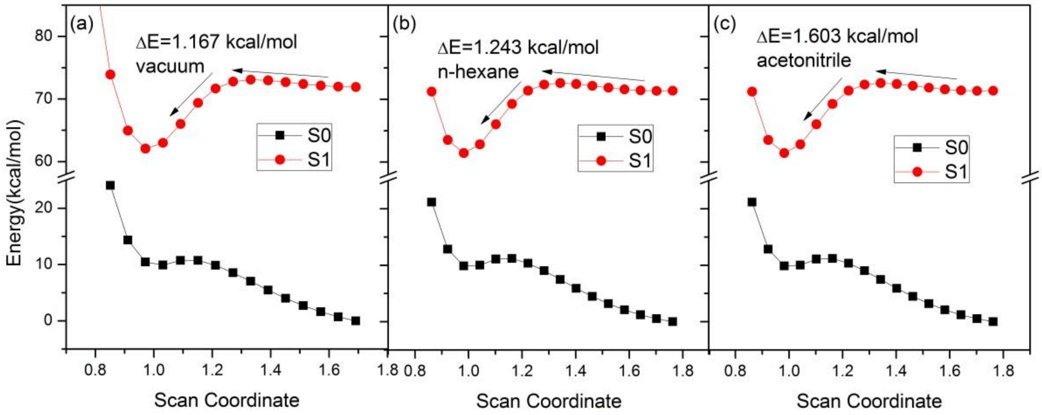

**Figure 2**: The first excited state potential energies along the ESPT path of 3HF in vacuum, n-hexance and acetonitrile were calculated. IEFPCM model and TD-B3LYP/6-31G(d,P) were used.

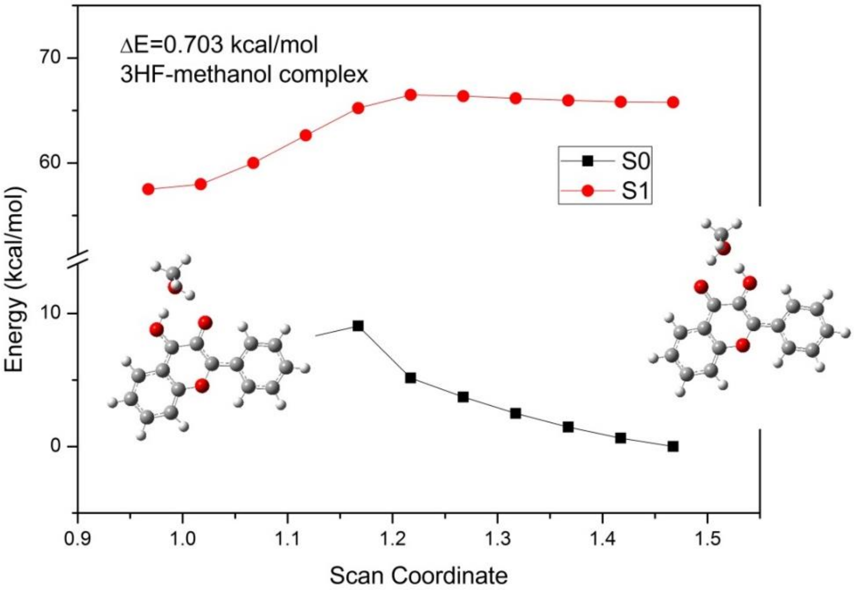

**Figure 3**: The first excited state potential energies of seven-membered-ring 3HF-methanol complex along the ESPT path in methanol.

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