Electronic Supplementary Information

Effect of solvent environment on excited state intramolecular proton transfer in 2-(4-(dimethylamino) phenyl)-3-hydroxy-6, 7-dimethoxy-4h-chromen-4-one

Yunpeng Chen,[1, ab] Yunfan Yang,[1, a] Yu Zhao,[a] Shixing Liu*[a] and Yongqing Li*[a]

[a]*Department of Physics, Liaoning University, Shenyang 110036, P. R. China*

[b] *State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China*

*Corresponding author.

E-mail addresses: liushixing@lnu.edu.cn (Shixing Liu).

E-mail addresses: yqli@lnu.edu.cn (Yongqing Li).

[1]These authors contributed equally to this work.

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The geometric structure of HOF based on B3LYP-D3/6-31 G (d, p)

The bond lengths and bond angles of the hydrogen bond O1-H2···O3 calculated by B3LYP-D3/6-31G (d, p) levels of theory in the S_0 and S_1 states (**Table S1**).

In Toluene, THF, DCM, ACN and DMSO, for the normal HOF molecule the bond lengths of O1-H2 are 0.982670 Å, 0.982280 Å, 0.982250 Å, 0.982100 Å and 0.982100 Å in the S_0 state, and the bond lengths of O1-H2 are 1.00627 Å, 1.00283 Å, 1.00251 Å, 1.00122 Å and 1.00111 Å in the S_1 state, respectively. The bond lengths of H2-O3 are 1.96515 Å, 1.97090 Å, 1.97147 Å, 1.97393 Å and 1.97393 Å in the S_0 state, and decrease to 1.76977 Å, 1.79283 Å, 1.79518 Å, 1.80482 Å and 1.80565 Å in the S_1 state, respectively. The bond angles O1-H2-O3 are also analyzed presented in **Table S1**. The bond angle O1-H2-O3 is closer to 180 degrees in the S_1 state than in the S_0 state. The analyses of hydrogen-bond parameters prove that the hydrogen bond strength is enhanced from the S_0 to S_1 state.

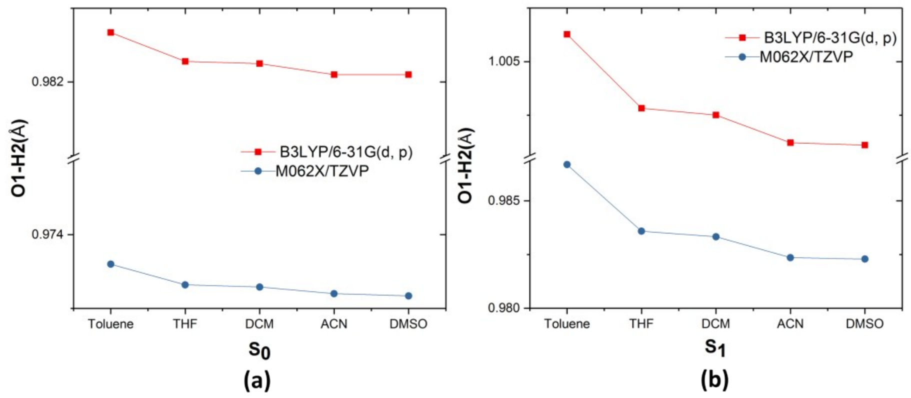
Table S1 Bond lengths and angles of S_0 and S_1 states for the title molecule HOF in different solvents, the level of theory is B3LYP-D3/6-31G (d, p).

Species	States	O1-H2(Å)	H2-O3(Å)	δ(O1-H2-O3)
Toluene	S_0	0.982670	1.96515	121.265
	S_1	1.00627	1.76977	128.182
THF	S_0	0.982280	1.97090	121.055
	S_1	1.00283	1.79283	127.513
DCM	S_0	0.982250	1.97147	121.025
	S_1	1.00251	1.79518	127.441
ACN	S_0	0.982100	1.97393	120.942
	S_1	1.00122	1.80482	127.117
DMSO	S_0	0.982100	1.97393	120.942
	S_1	1.00111	1.80565	127.091

Comparison of hydrogen-bond parameters with different functionals and basis sets

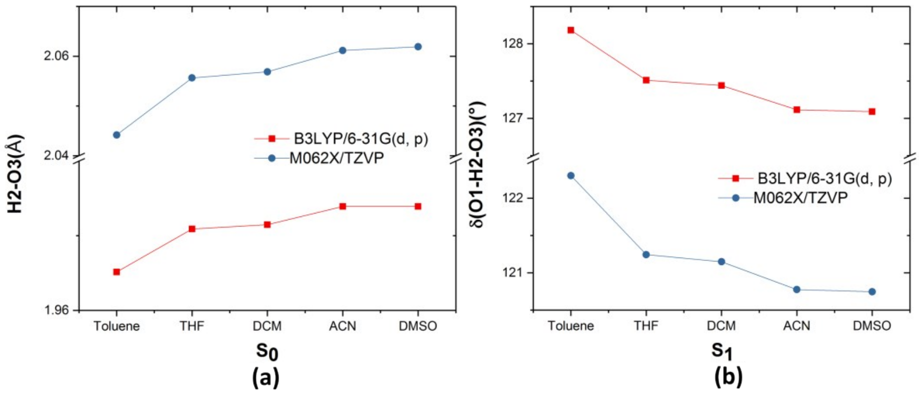
To testify correctness of the law between the solvent polarity and hydrogen bonding intensity, the variation of hydrogen-bond parameters calculated by the two computational levels is presented in **Figure S1-S3**.

With the solvent polarity increasing the calculated parameters show a consistent changing trend in different electronic states.



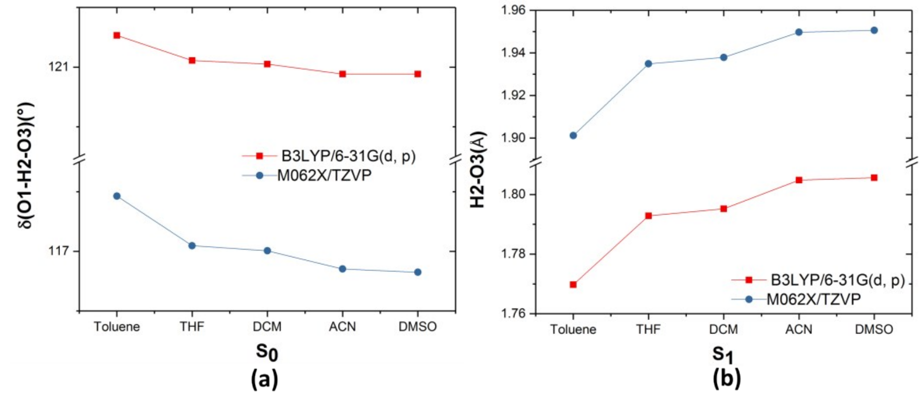
(a) (b)

Figure S1 The calculated O1-H2 bond length of normal HOF molecule in S_0 (a) and S_1 (b) state. The computational levels are B3LYP-D3/6-31G(d, p) (red) and M062X-D3/TZVP (blue), respectively.



(a) (b)

Figure S2 The calculated distance of H2···N3 of normal HOF molecule in S_0 (a) and S_1 (b) state. The computational levels are B3LYP-D3/6-31G(d, p) (red) and M062X-D3/TZVP (blue), respectively.



(a) (b)

Figure S3 The calculated hydrogen-bond angle δ(O1-H2-O3) of normal HOF molecule in S_0 (a) and S_1 (b) state. The computational levels are B3LYP-D3/6-31G(d, p) (red) and M062X-D3/TZVP (blue), respectively.

The comparison of hydrogen-bond parameters with different computational method is presented in **Figure S1-S3**. It is found that the same conclusion can be obtained when the different functionals and basis sets are used for the geometry optimization.

Excited state infrared (IR) vibrational spectra under different solvents

In the **Figure S4**, the ascending order of IR vibration frequencies of O1-H2 bond calculated by B3LYP-D3/6-31G (d, p) level of theory is 3149.81 cm^{-1} (Toluene) < 3200.58 cm^{-1} (THF) < 3205.50 cm^{-1} (DCM) < 3225.43 cm^{-1} (ACN) < 3227.12 cm^{-1} (DMSO) in the S$_1$ state.

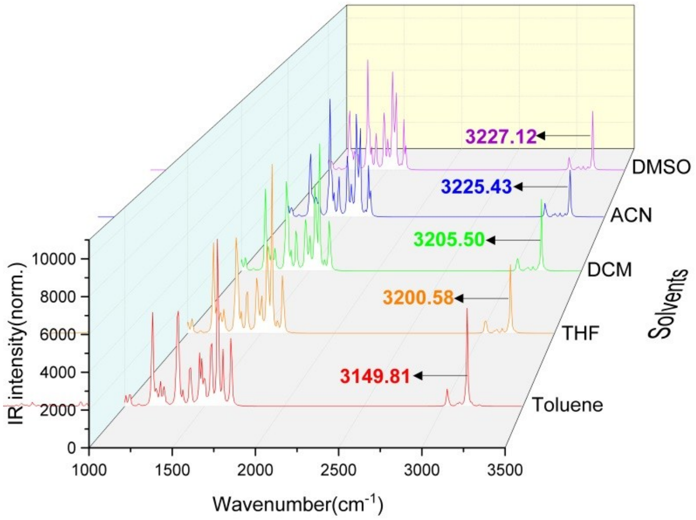


Figure S4 IR vibrational spectra for the normal HOF molecule of S$_1$ state under different solvents, based on B3LYP-D3/6-31G (d, p) level of theory. The IR frequencies of O1-H2 are calculated and analysed.