



## Change in Energy of Hydrogen Bonds upon Excitation of Coumarin 1: TDDFT/EFP1 Method

M. Ramegowda

PG Department of Physics, Govt. College (Autonomous), Mandya - 571401, INDIA

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### Abstract

Density functional theory (DFT)/ Time dependent density functional theory (TDDFT) calculations combined with the effective fragment potential (EFP) method have been carried out to study the electronic structure and the excited state properties of Coumarin 1 with three water molecules (C1-(H<sub>2</sub>O)<sub>3</sub> complex). Ground-state geometries are optimized using DFT with B3LYP functional combined with cc-pVDZ basis set and transition energies are computed with same basis set and functional. Three intermolecular hydrogen bonds are formed in C1-(H<sub>2</sub>O)<sub>3</sub> complex, one N...H-O (type A) by amino group of C1 with one water molecule and two C=O...H-O (type B) by carbonyl group of C1 with two water molecules. The change in hydrogen bond energy,  $\Delta E_{HB}$  of C1-(H<sub>2</sub>O)<sub>3</sub> molecule and  $\Delta E_{HB}$  for each HB of C1-(H<sub>2</sub>O)<sub>3</sub> molecule are calculated separately. Upon excitation of C1-(H<sub>2</sub>O)<sub>3</sub> complex, A type HB is weakened with decrease of 4.783 kJ/mol energy, whereas B type HBs are strengthened with increase of 9.614 kJ/mol energy. In this theoretical work, it is confirmed again that, due to excitation, intermolecular hydrogen bonds between aminocoumarins and polar solvents are strengthened, not cleaved, as reported by Zhao's, Wiley Periodicals, Inc. J. Comput. Chem., (2011).

**Keywords:** DFT; TDDFT; cc-pVDZ; EFP; C1-(H<sub>2</sub>O)<sub>3</sub>.

### Introduction

Specific solute-solvent interactions, such as intermolecular hydrogen bonding between hydrogen donor and acceptor molecules, play an important role in determining the physicochemical properties of liquids and solutions<sup>1-11</sup>. Important results on many properties of intermolecular hydrogen bonds, including their structure, energy in the ground state and energy change upon electronic excitation of molecules, can be found in a number of theoretical<sup>12-14</sup> and experimental<sup>15-18</sup> works. Zhao and Han<sup>12</sup> using DFT and TDDFT pointed out, for two aromatic thiocarbonyl compounds in methanol, that strengthening of hydrogen bond in the excited state can lower the excitation energy and induce an electronic spectral redshift, whereas weakening of hydrogen bond can heighten the excitation energy of related excited state and induce an electronic spectral blueshift. Recently similar calculations showing the hydrogen bonding effect on the electronic spectra have been made for methyl cyanide<sup>19</sup> and methyl isocyanide<sup>20</sup> in methanol. Many molecules of donor-acceptor character, often used as probes, in their ground and excited electronic states can form hydrogen bonds with protic solvent molecules, influence the absorption and/or emission spectra as well as their structure and photophysical properties<sup>21-23</sup>. The formation of hydrogen bonds can often lead to the appearance of new individuals like S<sub>0</sub>-complexes and S<sub>1</sub>-exciplexes<sup>24-28</sup>.

The effective fragment potential (EFP) method<sup>29-31</sup> provides a polarizable QM-based force field to describe intermolecular interactions. The EFP method has been applied successfully to

QM/MM studies of molecules in clusters and in solution. The interface of the EFP model with the TDDFT method has recently been developed for describing electronically excited states of solvated molecules. Yoo et al.<sup>32</sup> have combined the linear response TDDFT (LR-TDDFT) method with the original EFP model (EFP1) and applied the hybrid method successfully to simulate the absorption spectrum of the n→π\* vertical transition of acetone in aqueous solution. Si and Li<sup>33</sup> have derived the analytic energy gradient for combined LR-TDDFT and polarizable force field methods. Minizawa et al.<sup>34</sup> implemented the analytic energy gradient for the combined TDDFT/EFP1 method to describe the excited state dynamics of solvated molecules.

The 7-aminocoumarins are important organic compounds having distinct biological activity with extensive applications<sup>35</sup> and are indicated as anticancer, antibiotic and anticoagulant agents. They show strong fluorescence in the spectral range from 350 nm to 500 nm, makes them suitable to use as laser dyes and non-linear optical chromophores. Aminocoumarins can form as many HBs with the protic solvents having hydrogen-bond donor properties as many electronegative heteroatoms N and O they include; so these molecules can form one A type (N...H-O) HB and two B type (C=O...H-O) HBs. Additionally these molecules can also form two HBs of type C (N-H...O), via participation of their amino hydrogen atoms, with oxygen atom of water molecule<sup>11</sup>.

TDDFT calculations have been performed to examine the relationship between the absorption spectra of 7-

aminocoumarins, the solvent polarity and/or formation of HBs, especially to study the effect of protic solvent hydrogen bond ability on geometries of the solute molecule and its spectra<sup>1,2,9,10</sup>. The decrease in the A type HB energy for C151 in the S<sub>1</sub> state relatively to the S<sub>0</sub> state calculated by Liu et al.<sup>1</sup> was much smaller than the increase in energy of the B and C type HBs formed by the carbonyl group and N-H bond respectively. The strengthening of C type HBs in coumarin-solvent complexes is in contradiction with the results of Gustavsson et al.<sup>36</sup>. Zhao et al.<sup>11</sup> affirmed that, the electronic transition energies are significantly affected by the HBs formed between Coumarin 120 (C120) and solvent molecules. According to these references, formation of an A type HB causes a blueshift in the absorption maximum, and formation of B and C type HBs results in redshift. The results of the calculations by Zhou et al.<sup>2</sup> also indicate that, in the excited states of hydrogen-bonded coumarin-solvent complexes, A type HB becomes weaker, whereas B and C type HBs becomes stronger. These results are consistent with the earlier observed blueshift of the long wavelength band in the absorption spectra of C120 in water with respect to its positions in the spectra taken in methanol and ethanol<sup>22</sup>. Taking into regard the complex character of HBs made by aminocoumarin molecules, it is important to study these hydrogen-bond interactions in both S<sub>0</sub> and S<sub>1</sub> states.

The compound C1 (4-methyl-7-diethylaminocoumarin) is one of the important dye among 7-aminocoumarins, which having wide applications in fluorescence probes and blue-green laser dye. In aminocoumarins, electron-donating group (amino group) at 7-position enhances the fluorescence of the dye. The photophysics study of 7-aminocoumarins reveals that the solvatochromic properties of these molecules are sensitive to the polarity and viscosity of solvent molecules<sup>37-44</sup>. C1 molecule can make one A type HB and two B type HBs (figure-1). The aim of this study is to compute the change in energy ( $\Delta E_{HB}$ ) of A and B type HBs of C1-(H<sub>2</sub>O)<sub>3</sub> complex as a result of S<sub>0</sub>→S<sub>1</sub> transition using TDDFT/EFP1 method.

## Material and Methods

**Computational methods:** Ground-state geometry of C1-(H<sub>2</sub>O)<sub>3</sub> complex at DFT level is optimized using B3LYP hybrid function with cc-pVDZ basis set. Transition energies are calculated using TDDFT with same function and basis set. The solvent molecules were added using DFT based EFP1 water model. All calculations were performed using GAMESS-US software suit<sup>45-46</sup>. The optimized geometry for C1-(H<sub>2</sub>O)<sub>3</sub> is used to compute the energy of the free solute, E<sub>solu</sub> by removing solvent molecules from the system. Similarly, removing the solute allows one to compute the energy of the free solvent, E<sub>solv</sub>. Then, the HB energy, E<sub>HB</sub> (solvent-solute interaction energy), is calculated as

$$E_{HB} = E_{\text{complex}} - (E_{\text{solu}} + E_{\text{solv}}) \quad (1)$$

By calculating E<sub>HB</sub> at both S<sub>0</sub> and S<sub>1</sub> states, the change in HB energy can be obtained as:

$$\Delta E_{HB} = (E_{HB})_{S_1} - (E_{HB})_{S_0} \quad (2)$$

## Results and Discussion

The ground state optimized structure of C1-(H<sub>2</sub>O)<sub>3</sub> complex is shown in figure-1. It can be seen from figure-1 that in ground state, A type intermolecular HB N12...H20-O18 (2.064 Å) is formed between nitrogen of C1 and one water molecule with bond angle 158.3° and three B type intermolecular HBs, namely, O17...H23-O21 (1.918 Å, type B1(a)), O9...H23-O21 (2.276 Å, type B1(b)) and O17...H26-O24 (1.858 Å, type B2) are formed by oxygen atoms of coumarin ring and carbonyl group of C1 with two water molecules. The calculated bond angles for O17...H23-O21, O9...H23-O21 and O17...H26-O24 are 168.8°, 128.2° and 160.2°, respectively. Table-1 lists the optimized parameters of C1 in S<sub>0</sub> state, and C1-(H<sub>2</sub>O)<sub>3</sub> complex in S<sub>0</sub> and S<sub>1</sub> state. Due to of B type HBs in C1-(H<sub>2</sub>O)<sub>3</sub> complex, C10=O17 bond (1.222 Å) is slightly longer than that of the isolated C1 (1.208 Å), where as the O9-C10 and C8-C10 bond lengths (1.384 Å and 1.446 Å) are shorter than that of the isolated C1 (1.403 Å and 1.454 Å). The formation of A type HB causes the increase of C3-N12, N12-C13 and N12-C15 bond lengths of the C1-(H<sub>2</sub>O)<sub>3</sub> complex by 0.004 Å, 0.007 Å and 0.006 Å respectively, than that of C1 monomer. From table-1, it is also noted that, due to excitation of C1-(H<sub>2</sub>O)<sub>3</sub> complex, the bond lengths C1-C2, C2-C3, C3-N12, C4-C5, C6-C7, C7-C8, O9-C10, C10-O17 are slightly increased and C1-O9, C3-C4, C7-C11, C8-C10, N12-C13, N12-C15 bond lengths are slightly decreased.

Figure 2 shows the frontier molecular orbitals (MOs) of isolated C1 and C1-(H<sub>2</sub>O)<sub>3</sub> complex. The S<sub>1</sub> state of both isolated C1 and C1-(H<sub>2</sub>O)<sub>3</sub> complex are mainly due to the orbital transition from HOMO to LUMO, which involves the charge transfer from the amino group to carbonyl group of the coumarin moiety. Thus, the S<sub>1</sub> state of both isolated C1 and C1-(H<sub>2</sub>O)<sub>3</sub> complex may be an intramolecular charge-transfer (ICT) state.

The electronic excitation energies, oscillation strengths and transition dipole moments for the C1, C1-(H<sub>2</sub>O)<sub>3</sub>, C1-(H<sub>2</sub>O) complexes for A type, B1 type and B2 type HBs are calculated using the TDDFT method and presented in table-2. TDDFT calculations of C1-(H<sub>2</sub>O) complex for respective type of HB have been carried out by infinitely separating the other two water molecules and  $\Delta E_{HB}$ s are calculated using equation 1 and equation 2. From table-2, interestingly, it has been noticed that, in the S<sub>1</sub> state A type intermolecular HB is weakened due to increase of transition dipole moment, oscillation strength and excitation energy, causes the blueshift. Two B type intermolecular HBs are strengthened, because of decrease in dipole moment, oscillator strength and excitation energy. Therefore, upon excitation, B type intermolecular HBs induces the redshift. Table-3 lists the HB lengths and angles, and their energies of C1-(H<sub>2</sub>O)<sub>3</sub> complex at S<sub>0</sub> and S<sub>1</sub> states. The A type and B1(a) type HBs increased by 0.904 Å and 0.004 Å respectively, where as B1(b) and B2 type HBs are decreased by

0.090 Å and 0.026 Å respectively. B1 and B2 type HB energies are increased by 7.444 and 2.170 kJ/mol respectively, where as A type HB energy decreased by 4.783 kJ/mol. With the available references, there have been no theoretical calculations or experimental measurements of HB lengths and energies for C1-(H<sub>2</sub>O)<sub>3</sub> complex. Therefore the results of this study have

been compared with the calculated values of C1-(MeOH)<sub>2</sub> complex for B type HBs by Zhou et al.<sup>2</sup> for which B1 and B2 type HB energies are increased by 16.0 kJ/mol and 6.2 kJ/mol, and the HB lengths decreased by 0.286 Å and 0.201 Å respectively.

**Table-1**  
**Bond lengths, r (Å) and bond angles, A (°) of C1 in S<sub>0</sub> state, and C1-(H<sub>2</sub>O)<sub>3</sub> complex in S<sub>0</sub> and S<sub>1</sub> state**

r/A	C1	C1-(H <sub>2</sub> O) <sub>3</sub>		r/A	C1	C1-(H <sub>2</sub> O) <sub>3</sub>	
		S <sub>0</sub>	S <sub>1</sub>			S <sub>0</sub>	S <sub>1</sub>
R(1-2)	1.393	1.392	1.402	A(1-6-5)	116.3	116.0	116.7
R(1-6)	1.412	1.410	1.410	A(1-6-7)	118.4	118.5	118.2
R(1-9)	1.364	1.367	1.349	A(1-9-10)	122.2	122.2	121.0
R(2-3)	1.414	1.413	1.420	A(2-3-4)	117.0	117.2	118.3
R(3-4)	1.427	1.428	1.411	A(2-3-12)	121.4	121.3	119.4
R(3-12)	1.383	1.387	1.399	A(4-3-12)	121.5	121.5	122.3
R(4-5)	1.385	1.384	1.402	A(3-4-5)	121.1	121.2	119.8
R(5-6)	1.410	1.412	1.413	A(3-12-13)	121.0	120.5	121.8
R(6-7)	1.449	1.447	1.477	A(3-12-15)	121.2	121.0	120.3
R(7-8)	1.363	1.367	1.393	A(4-5-6)	122.3	122.1	122.8
R(7-11)	1.505	1.505	1.492	A(5-6-7)	125.3	125.5	125.2
R(8-10)	1.454	1.446	1.421	A(6-7-8)	118.6	118.9	116.6
R(9-10)	1.403	1.384	1.434	A(6-7-11)	120.2	120.3	119.8
R(10-17)	1.208	1.222	1.237	A(8-7-11)	121.1	120.8	123.6
R(12-13)	1.463	1.470	1.461	A(7-8-10)	123.1	122.0	124.5
R(12-15)	1.462	1.468	1.457	A(8-10-9)	116.1	117.3	116.5
R(13-14)	1.534	1.534	1.539	A(8-10-17)	126.7	127.1	130.3
R(15-16)	1.535	1.534	1.538	A(9-10-17)	117.2	115.6	113.3
A(2-1-6)	122.4	123.1	121.7	A(13-12-15)	117.8	117.5	117.8
A(2-1-9)	116.0	115.8	115.1	A(12-13-14)	115.2	115.5	114.2
A(1-2-3)	120.9	120.3	120.8	A(12-15-16)	115.1	115.5	114.0
A(6-1-9)	121.6	121.1	123.2	-	-	-	-

**Table-2**

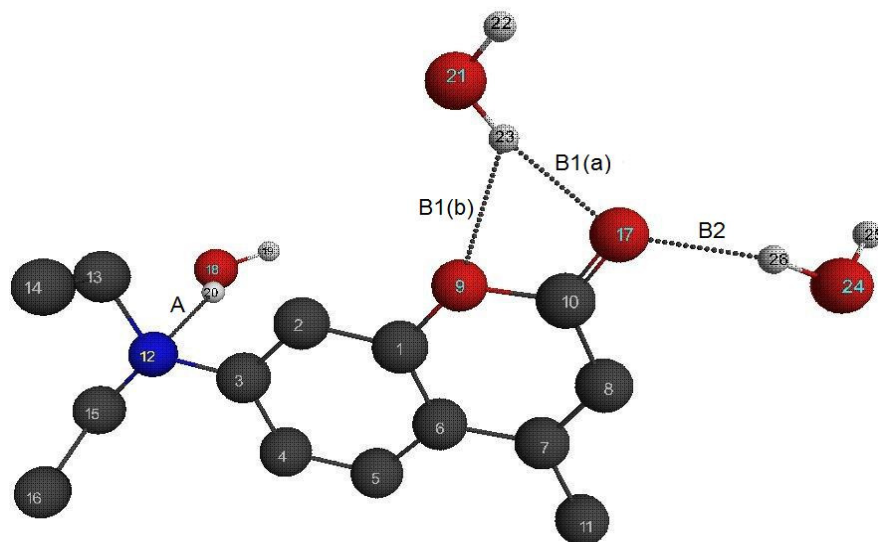
**HB lengths, r (Å) at S<sub>0</sub> and S<sub>1</sub> states, excitation energy, E (eV), oscillator strength, f, transition dipole moment, D (Debye) of C1, C1-(H<sub>2</sub>O)<sub>3</sub> complex and respective C1-(H<sub>2</sub>O) complex for A type, B1 type and B2 type HBs**

	D	r at S <sub>0</sub>	r at S <sub>1</sub>	f	E
C1	4.33043273	-	-	0.395	3.723
C1-(H <sub>2</sub> O) <sub>3</sub>	3.68507457	-	-	0.381	3.669
C1-(H <sub>2</sub> O) - A type	4.39661984	2.064	2.968	0.406	3.769
C1-(H <sub>2</sub> O) - B1 type (a, b)	4.28344793	1.918, 2.276	1.922, 2.186	0.382	3.640
C1-(H <sub>2</sub> O) - B2 type	4.28379507	1.858	1.832	0.388	3.697

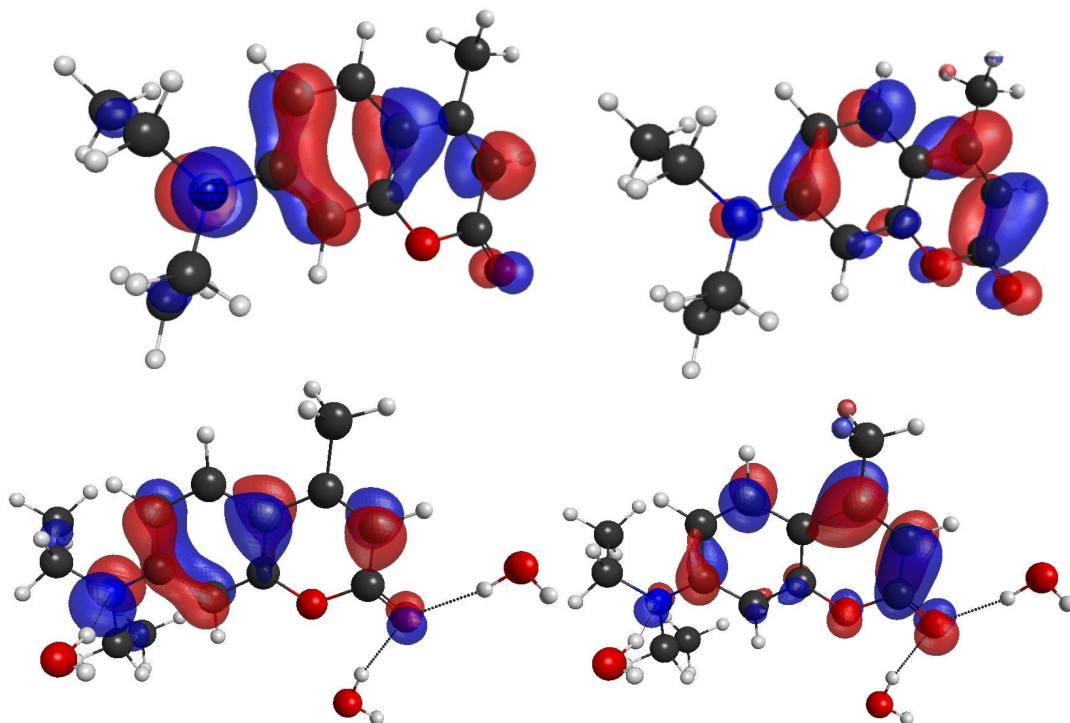
**Table-3**

**Hydrogen bond lengths, r (Å), bond angles, A (°), E<sub>HB</sub> (kJ/mol) and ΔE<sub>HB</sub> of C1-(H<sub>2</sub>O)<sub>3</sub> complex at S<sub>0</sub> and S<sub>1</sub> states**

Type of HB	S <sub>0</sub>			S <sub>1</sub>			ΔE <sub>HB</sub>
	r	A	E <sub>HB</sub>	r	A	E <sub>HB</sub>	
A and B	-	-	89.410	-	-	94.241	4.831
A	2.064	168.9	18.615	2.968	162.5	13.832	-4.783
B1 (a, b)	1.918, 2.276	158.2	35.652	1.922, 2.186	073.8	43.096	7.444
B2	1.858	160.1	34.476	1.832	164.9	36.646	2.170



**Figure-1**  
Optimized structure of C1-(H<sub>2</sub>O)<sub>3</sub> complex (Black-C, Gray-H, Red-O and Blue-N)



**Figure-2**  
HOMO (left) and LUMO (right) of C1 (top) and C1-(H<sub>2</sub>O)<sub>3</sub> complex (bottom)

## Conclusion

In this work, the structure, electronic excitation energies, oscillation strengths and transition dipole moments for the C1 molecule, C1-(H<sub>2</sub>O)<sub>3</sub>, C1-(H<sub>2</sub>O) complexes for A type, B1 type and B2 type HBs are calculated using the DFT/TDDFT methods. HB lengths and HB energies of C1-(H<sub>2</sub>O)<sub>3</sub> complex for A type, B1 type and B2 type are calculated at S<sub>0</sub> and S<sub>1</sub>

states. In S<sub>1</sub> state, A type intermolecular HB is weakened due to increase of dipole moment, oscillator strength and excitation energy, causes the blue shift whereas B type intermolecular HBs are strengthened, the dipole moment, oscillator strength and excitation energy are decreased. Therefore, upon excitation, B type intermolecular HBs induces the red shift. In the excited state, A type and B1(a) type HB lengths increased by 0.904 Å and 0.004 Å respectively, and B1(b) and B2 type HB lengths

decreased by 0.090 Å and 0.026 Å respectively. As a result of  $S_0 \rightarrow S_1$  transition, B1 and B2 type HB energies are increased by 7.444 kJ/mol and 2.170 kJ/mol respectively, and A type HB energy decreased by 4.783 kJ/mol. Thus due to excitation, intermolecular hydrogen bonds between aminocoumarins and polar solvents are strengthened, not cleaved.

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