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## A TDDFT/EFP1 study on hydrogen bonding dynamics of coumarin 151 in water



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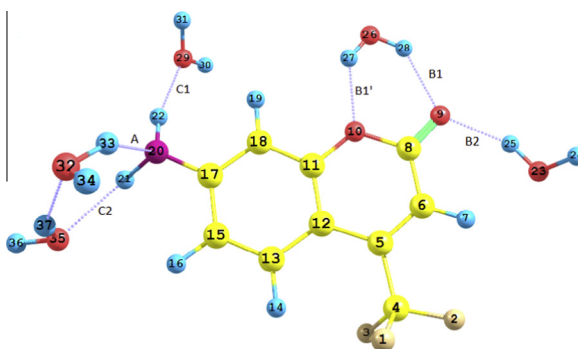
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## HIGHLIGHTS

- HB lengths and energies of C151-(H<sub>2</sub>O)<sub>5</sub> for A, B and C type HBs at S<sub>0</sub> and S<sub>1</sub> states.
- Additional HB between O of the pyrone ring and H of a water molecule.
- One HB formed between two water molecules.
- The A type HB energy decreased by 4.37 kJ/mol.
- The B and C type HB energies are increased by 5.62 and 10.21 kJ/mol, respectively.

## GRAPHICAL ABSTRACT

DFT/TDDFT combined with PCM and EFP1 method has been performed to study the ground and excited state properties of coumarin 151 with five water molecules. Hydrogen bond (HB) lengths, angles and energies of C151-(H<sub>2</sub>O)<sub>5</sub> complex for A, B1, B2, C1 and C2 types at S<sub>0</sub> and S<sub>1</sub> states were calculated. In addition to these five HBs, there are other two HBs; O10...H27-O26 similar to B1 type (B1') and O32...H37 between two water molecules. At S<sub>1</sub> state, A type (N...H-O) HB is weakened with decrease of 4.37 kJ/mol energy, whereas B and C type (C=O...H-O and N-H...O) HBs are strengthened with increase of 5.62 and 10.21 kJ/mol energy, respectively.



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## ABSTRACT

Change in energy of hydrogen bonds (HBs) upon excitation, plays an important role on the spectra of chemical and biological molecules. Effective fragment potential (EFP) method of explicit water molecules embedded in polarizable continuum medium (PCM) is used for the solvation of 7-Amino-4-(trifluoromethyl)coumarin (C151). Time dependent density functional theory (TDDFT) calculations combined with EFP/PCM had been carried out to study the electronic structure and the excited state properties of C151 with five water molecules (C151-(H<sub>2</sub>O)<sub>5</sub> complex). S<sub>0</sub> state and S<sub>1</sub> state geometries were optimized using DFT/TDDFT with PBE0 functional combined with cc-pVDZ basis set, the transition energies are computed with same basis set and functional. Change in HB energy is calculated using the procedure proposed by T. Nagata et al. to calculate solute-solvent interaction energy in Nagata et al. (2011). Upon photoexcitation of C151-(H<sub>2</sub>O)<sub>5</sub> complex, A type (N...H-O) HB is weakened with decrease of energy by 4.37 kJ/mol, whereas B and C type (C=O...H-O and N-H...O) HBs are strengthened with increase of 5.62 and 10.21 kJ/mol energy, respectively. This study again confirmed that the intermolecular hydrogen bonds between C151 chromophore and aqueous solvents are strengthened, not cleaved upon electronic excitation.

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## Introduction

Intermolecular hydrogen bonding as a site-specific interaction between hydrogen donor and acceptor molecules, play an important role in determining the physicochemical properties of liquids and solutions [1–12]. 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 works [13–20], and experimental ones [21–26]. Zhao and Han [15] using DFT and TDDFT demonstrated that, for two aromatic thiocarbonyl compounds in methanol, the excited-state HB weakening can heighten the excitation energy of a related excited state and induce an electronic spectral blueshift, whereas the excited-state HB strengthening can lower the excitation energy of a related excited state and induce an electronic spectral redshift. The similar calculations showing the hydrogen bonding effect on the electronic spectra had been made for methyl cyanide [27] and methyl isocyanide [28] 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. Apart from the influence of the solvent polarity and polarizability, HBs formed between the probes and solvents also influence their structure and photophysical properties [29–33]. The formation of hydrogen bonds can often lead to the appearance of new individuals like  $S_0$ -complexes and  $S_1$  exciplexes [34–39].

The EFP method [40–43] provides a polarizable QM-based force field to describe intermolecular interactions. The EFP method embedded with PCM, have 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 been developed for describing electronically excited states of solvated molecules. Yoo et al. [43] 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  $n \rightarrow \pi^*$  vertical transition of acetone in aqueous solution. Si and Li [44] have derived the analytic energy gradient for combined LR-TDDFT and polarizable force field methods. Minezawa et al. [45] implemented the analytic energy gradient for the combined TDDFT/EFP1 method to describe the excited state dynamics of solvated molecules. Arora et al. [46] have interfaced configuration interaction with single excitations (CIS) with the EFP method for studying the qualitative effects of solvents on the electronic spectra of molecules.

The aminocoumarin molecules represent an important class of organic compounds with extensive and diverse applications [47–50]. They possess distinct biological activity [50] and have been indicated as agents with potential antibiotic, anticancer and anticoagulant activity. They exhibit strong fluorescence in the visible region (from 350 nm to 500 nm), which makes them suitable for use as laser dyes and non-linear optical chromophores. Aminocoumarins can form one A type HB and two B type HBs due to hydrogen-bond donor properties of electronegative heteroatoms N and O, and two C type HBs via the participation of amino hydrogen atoms with oxygen atom of water molecules [11].

TDDFT calculations have been performed to study the spectral properties and HB dynamics of aminocoumarins [1,2,9,10,12–14]. The decrease in A type HB energy of C151 in ethanol for the  $S_1$  state relative to the  $S_0$  state calculated by Liu et al. in Ref. [1] was much smaller than the increase in energy of 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. [51]. Zhao et al. [11] affirmed that, in addition to solvent polarity, HBs formed between Coumarin 120 (C120) and solvent molecules also significantly affect its electronic transition energies. According to these references, formation of A type HB causes blueshift in the absorption maximum, whereas formation of B and C type HBs results in redshift. The results of the calculations by Zhou et al. [2] also indicate that, in the excited states of hydrogen-bonded coumarin–solvent complexes, B and C type HBs are stronger, whereas A type HB is weaker. These results are consistent with the earlier observed blueshift of the long wavelength band of the absorption spectra of C120 in water with respect to its positions in the spectra taken in methanol and ethanol [32]. The excited-state hydrogen bonding dynamics of 6-aminocoumarin with water molecules have been studied [12,13] and demonstrated that A type HB is the strongest hydrogen bond among three ones in the  $S_0$  state and it is extremely weakened in  $S_1$  state, which is significantly greater than the strengthening B and C type HBs. Additionally the hydrogen bond interaction and  $S_1$ -exciplex formation may be responsible for the fluorescence of the dye in nitriles. Taking into regard the complex character of HBs made by aminocoumarin molecules, it is important to study these hydrogen-bond interactions in both  $S_0$  and  $S_1$  states.

In the case of C151, there are at least five sites of hydrogen bond formation with protic solvent molecules as shown in Fig. 1; one intermolecular HB  $N \cdots H-O$  (type A) is formed by amino group of C151 with one water molecule, two intermolecular HBs

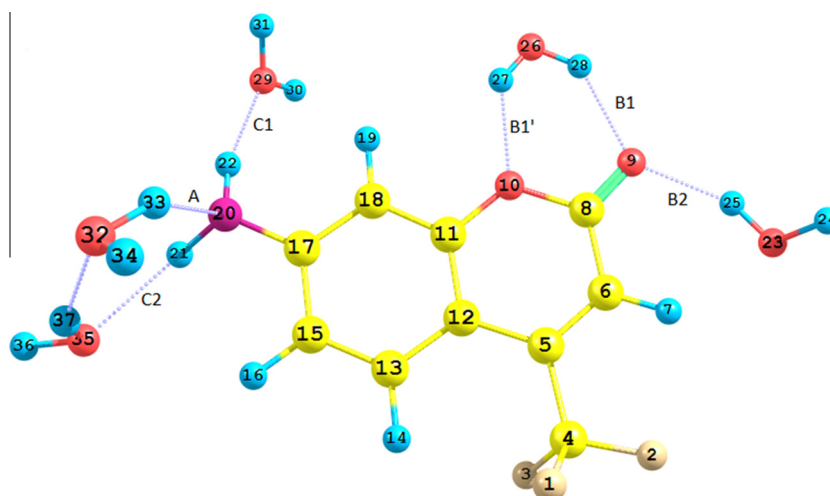


Fig. 1.  $S_0$  state optimized structure of C151–( $H_2O$ )<sub>5</sub> complex.

$\text{C}=\text{O}\cdots\text{H}-\text{O}$  (type B) are formed by carbonyl group of C151 with two water molecules and two HBs of  $\text{N}-\text{H}\cdots\text{O}$  (type C), via the participation of amino hydrogen atoms with oxygen atom of water molecules.

The aim of this study is to compute the change in A, B and C type HB energies ( $\Delta E_{\text{HB}}$ 's) of  $\text{C151}-(\text{H}_2\text{O})_5$  complex in water as a result of  $\text{S}_0 \rightarrow \text{S}_1$  transition using TDDFT/EFP1 method.

## Computational methods

Ground-state optimization of  $\text{C151}-(\text{H}_2\text{O})_5$  complex have been performed by using PBE0 [52] hybrid function with cc-pVDZ basis set [53] at a DFT level [54–59] and first singlet excited state was optimized using the TDDFT [60–68] with same functional and basis set. Based on optimized ground state geometry in water using CPCM-PBE0/cc-pVDZ [69,70] model, the transition energies were calculated by TD-CPCM-PBE0/cc-pVDZ method [71]. The explicit water molecules were added using DFT based EFP1 water model [42] in that all water molecules are treated as EFPs for DFT and TDDFT calculations. All calculations were performed using GAMESS-US software suit [72,73].

In  $\text{C151}-(\text{H}_2\text{O})_5$  complex, all water molecules formed HBs with C151, the interaction energy between solute and solvent molecules is equated to HB energy, that can be calculated by the scheme as explained by Nagata et al. in Ref. [74]. The optimized geometry of  $\text{C151}-(\text{H}_2\text{O})_5$  complex is used to compute the energy of the free solute,  $E_{\text{solute}}$  by removing solvent molecules from the system. Similarly, removing the solute allows one to compute the energy of the free solvent,  $E_{\text{solvent}}$ . Then, the solvent–solute interaction energy, ( $E_{\text{HB}}$ ) is calculated as

$$E_{\text{HB}} = E_{\text{complex}} - (E_{\text{solute}} + E_{\text{solvent}}) \quad (1)$$

By calculating  $E_{\text{HB}}$  at both  $\text{S}_0$  and  $\text{S}_1$  states, the change in HB energy can be obtained as

$$\Delta E_{\text{HB}} = (E_{\text{HB}})_{\text{S}_1} - (E_{\text{HB}})_{\text{S}_0} \quad (2)$$

From the optimized geometry of  $\text{C151}-(\text{H}_2\text{O})_5$  complex, four water molecules are removed to calculate the energy of  $\text{C151}-(\text{H}_2\text{O})$  complex and the energy of respective type of HB is calculated using Eq. (1) with the same scheme.

## Results and discussion

Fig. 1 shows the  $\text{S}_0$  state optimized structure of  $\text{C151}-(\text{H}_2\text{O})_5$  complex. As can be seen in this figure, A type intermolecular HB  $\text{N20}\cdots\text{H33}-\text{O32}$  (2.060 Å) is formed between nitrogen of C151 and one water molecule with bond angle 141.5°, two B type and two C type intermolecular HBs, namely,  $\text{O9}\cdots\text{H28}-\text{O26}$  (2.047 Å, type B1),  $\text{O9}\cdots\text{H25}-\text{O23}$  (1.889 Å, type B2),  $\text{N20}-\text{H22}\cdots\text{O29}$  (1.959 Å, type C1),  $\text{N20}-\text{H21}\cdots\text{O35}$  (1.952 Å, type C2) are formed by oxygen atom of the carbonyl group and amino hydrogen atoms of C151 with four water molecules. The calculated bond angles for  $\text{O9}\cdots\text{H28}-\text{O26}$ ,  $\text{O9}\cdots\text{H25}-\text{O23}$ ,  $\text{N20}-\text{H22}\cdots\text{O29}$  and  $\text{N20}-\text{H21}\cdots\text{O35}$  are 134.1°, 150.6°, 163.9° and 146.7°, respectively. In addition to these five HBs, there are other two HBs;  $\text{O10}\cdots\text{H27}-\text{O26}$  similar to B1 type (B1') and  $\text{O32}\cdots\text{H37}$  between two water molecules with bond lengths 1.981 Å and 1.812 Å, respectively. Table 1 lists the optimized parameters of C151 in  $\text{S}_0$  state, and  $\text{C151}-(\text{H}_2\text{O})_5$  complex in  $\text{S}_0$  and  $\text{S}_1$  state.

The C–F and C–C bond lengths (except C15–C17 and C15–C18) of  $\text{C151}-(\text{H}_2\text{O})_5$  complex are slightly shorter than the isolated C151, whereas  $\text{C8}=\text{O9}$  bond length is slightly longer due to B type HBs. The formation of A type and C type HBs causes the decrease of C17–N20 and N20–H22 bond lengths by 0.013 Å and 0.001 Å, respectively. A slight increase in N20–H21 bond

**Table 1**

Bond lengths,  $r$  (Å) and bond angles,  $A$  (°) of C151 in  $\text{S}_0$  state, and  $\text{C151}-(\text{H}_2\text{O})_5$  complex in  $\text{S}_0$  and  $\text{S}_1$  state.

$r/A$	C151	$\text{C151}-(\text{H}_2\text{O})_5$	
	$\text{S}_0$	$\text{S}_0$	$\text{S}_1$
R(1-4)	1.354	1.345	1.366
R(2-4)	1.346	1.335	1.336
R(3-4)	1.354	1.344	1.364
R(4-5)	1.515	1.510	1.469
R(5-6)	1.359	1.358	1.381
R(5-12)	1.445	1.436	1.488
R(6-8)	1.458	1.446	1.424
R(8-9)	1.205	1.214	1.228
R(8-10)	1.400	1.376	1.421
R(10-11)	1.364	1.363	1.344
R(11-12)	1.415	1.407	1.392
R(11-18)	1.393	1.384	1.404
R(12-13)	1.414	1.412	1.414
R(13-15)	1.384	1.379	1.387
R(15-17)	1.419	1.419	1.414
R(17-18)	1.403	1.403	1.419
R(17-20)	1.380	1.367	1.350
R(20-21)	1.013	1.014	1.017
R(20-22)	1.014	1.013	1.013
A(1-4-2)	107.3	107.4	107.1
A(1-4-3)	106.8	107.0	103.9
A(1-4-5)	111.3	111.0	112.4
A(2-4-3)	107.2	107.5	107.1
A(2-4-5)	112.5	112.4	112.9
A(3-4-5)	111.4	111.3	112.8
A(4-5-6)	119.2	118.8	122.6
A(4-5-12)	119.9	119.7	120.2
A(6-5-12)	120.9	121.5	117.2
A(5-6-8)	121.8	120.6	123.9
A(5-12-11)	116.7	116.6	117.0
A(6-8-10)	116.0	116.9	116.5
A(8-10-11)	122.8	123.1	120.9
A(10-11-12)	121.9	121.3	124.3
A(12-11-18)	121.9	122.6	121.2
A(11-12-13)	117.3	116.9	117.4
A(11-18-17)	119.9	119.8	120.5
A(12-13-15)	121.4	121.5	123.0
A(13-15-17)	120.7	120.7	119.1
A(15-17-18)	118.8	118.5	118.7
A(21-20-22)	113.6	116.3	121.0
A(18-17-20-22)	–	21.7	0.4
A(15-17-20-21)	–	–19.4	11

length of 0.001 Å is also observed due to the formation of A type and C type HBs. No appreciable changes in bond angles of  $\text{C151}-(\text{H}_2\text{O})_5$  complex as compared to the bond angles of C151 monomer.

In  $\text{S}_1$  state of  $\text{C151}-(\text{H}_2\text{O})_5$  complex F1–C4, F2–C4, F3–C4, C5–C6, C5–C12, C8–O9, C8–O10, C11–C18, C13–C18, C17–C18 and N20–H21 bonds are increased by 0.021, 0.001, 0.020, 0.023, 0.052, 0.014 0.045, 0.020, 0.008, 0.016 and 0.003 Å, respectively, whereas C4–C5, C6–C8, C11–O10, C11–C12, C15–C17 and C17–N20 are decreased by 0.041, 0.022, 0.019, 0.015, 0.005 and 0.017 Å, respectively. The bond angles C6–C5–C12, C8–O10–C11, C12–C11–C18, C13–C15–C17 and F1–C4–F3 bond angles are decreased by 4.3°, 2.2°, 1.4°, 1.6° and 3.1°, respectively. The bond angles C5–C6–C8, O10–C11–C12, C12–C13–C15 and H21–N20–H22 are increased by 3.3°, 3.0°, 1.5° and 4.7°, respectively. The dihedral angles C18–C17–N20–H22 and C15–C17–N20–H21 are 21.7° and –19.4°, respectively in  $\text{S}_0$  state, whereas in  $\text{S}_1$  state the dihedral angles are –0.4° and 11°, respectively. Thus the change in dihedral angles is due to umbrella-like open-close motion of the amino group.

The frontier molecular orbitals (MOs) of isolated C151 and  $\text{C151}-(\text{H}_2\text{O})_5$  complex are depicted in Fig. 2. The excited state of both isolated C151 and  $\text{C151}-(\text{H}_2\text{O})_5$  complex is mainly due to the orbital transition from HOMO to LUMO, which involves the intramolecular charge redistribution from the amino group to

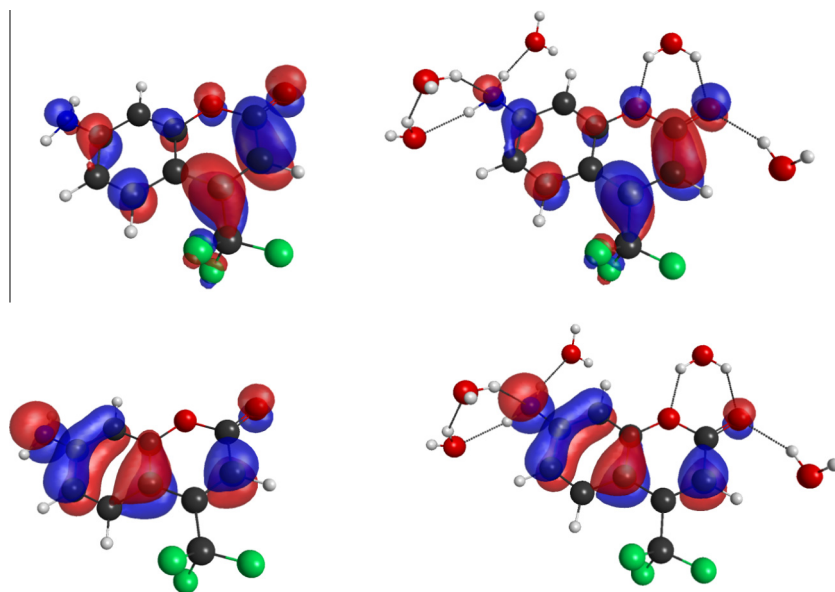


Fig. 2. HOMO (bottom) and LUMO (top) of C151 (left) and C151-(H<sub>2</sub>O)<sub>5</sub> complex (right).

pyrone (with carbonyl) group of the coumarin moiety. Furthermore, it has been confirmed by the population analysis that the Mulliken charges on amino, benzene and pyrone (with carbonyl) groups are 0.170 *e*, 0.076 *e* and −0.307 *e*, respectively at *S*<sub>0</sub> state and 0.367 *e*, 0.056 *e* and −0.425 *e* at *S*<sub>1</sub> state. Due to excitation, the Mulliken charges on N17 atom changes from −0.309 *e* to −0.179 *e*. Thus, the *S*<sub>1</sub> state of both isolated C151 and C151-(H<sub>2</sub>O)<sub>5</sub> complex may be an intramolecular charge-transfer (ICT) state.

TDDFT/PCM calculations of C151 and C151-(H<sub>2</sub>O)<sub>5</sub> complex produces the excitation energies 3.531 eV and 3.409 eV, respectively. The experimentally determined value of excitation energy for C151 in water is 3.387 eV [26], which agrees with the calculated value of C151-(H<sub>2</sub>O)<sub>5</sub> complex within the limits of calculation error (0.022 eV) due to the use of non diffuse basis set. This confirms the formation of five HBs by C151 in aqueous solvent. TDDFT calculations of C151-(H<sub>2</sub>O) complex for respective type of HB have been carried out by infinitely separating the other four water molecules and Δ*E*<sub>HBs</sub> are calculated using Eqs. (1) and (2). The electronic excitation energies corresponding to *S*<sub>0</sub> → *S*<sub>1</sub> transition and oscillation strengths of C151, C151-(H<sub>2</sub>O)<sub>5</sub> complex and C151-(H<sub>2</sub>O) complex for A, B1, B2, C1 and C2 type HBs were calculated using the TDDFT/PCM method and presented in Table 2. From

Table 2

HB lengths, *r* (Å) at *S*<sub>0</sub> and *S*<sub>1</sub> states, excitation energy (*S*<sub>0</sub> → *S*<sub>1</sub>), *E* (eV), oscillator strength, *f* of C151, C151-(H<sub>2</sub>O)<sub>5</sub> complex and respective C151-(H<sub>2</sub>O) complex for A, B1, B2, C1 and C2 type HBs.

	<i>r</i> at <i>S</i> <sub>0</sub>	<i>r</i> at <i>S</i> <sub>1</sub>	<i>E</i>	<i>f</i>
C151	–	–	3.531	0.437
			3.387 <sup>a</sup> , 3.550 <sup>b</sup> , 3.770 <sup>c</sup>	
C151-(H <sub>2</sub> O) <sub>5</sub>	–	–	3.409	0.411
C151-(H <sub>2</sub> O)-A type	2.060	3.438	3.576	0.435
C151-(H <sub>2</sub> O)-B1 type	2.047	2.048	3.503	0.433
(B1' type)	(1.981)	(1.942)		
C151-(H <sub>2</sub> O)-B2 type	1.889	1.849	3.501	0.429
C151-(H <sub>2</sub> O)-C1 type	1.959	1.924	3.470	0.430
C151-(H <sub>2</sub> O)-C2 type	1.952	1.785	3.487	0.429

<sup>a</sup> Experimental values from solvatochromic study by Krystkowiak and Maciejewski [26].

<sup>b</sup> Experimental values from gas-phase optical spectroscopy by Pryor et al. [75].

<sup>c</sup> Experimental values from calculated using gas phase B3LYP/TDDFT [76].

Table 2, it has been noticed that in the *S*<sub>1</sub> state, A type intermolecular HB is weakened due to increase of excitation energy, whereas B and C type intermolecular HBs are strengthened due to decrease of excitation energy.

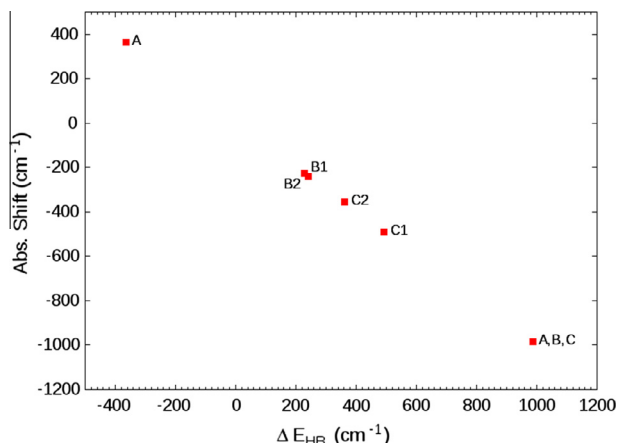
Table 3 lists the HB lengths, angles and energies of C151-(H<sub>2</sub>O)<sub>5</sub> complex for A, B1, B2, C1 and C2 type at *S*<sub>0</sub> and *S*<sub>1</sub> states. The A type HB length increased by 1.378 Å, whereas B2, C1 and C2 type HB lengths are decreased by 0.040, 0.035 and 0.167 Å, respectively. It is noted that in C151-(H<sub>2</sub>O)<sub>5</sub> complex B1 type HB increased by 0.001 Å and B1' type HB decreased by 0.039 Å. The HB between water molecules (O32...H37) decreased by 0.044 Å. A type HB energy decreased by 4.37 kJ/mol, whereas (B1 + B1'), B2, C1 and C2 type HB energies are increased by 2.74, 2.88, 5.89 and 4.32 kJ/mol, respectively. The total change in HB energy of C151-(H<sub>2</sub>O)<sub>5</sub> complex is 11.79 kJ/mol, which deviates by ~5 kJ/mol with the experimentally determined value 6.22 kJ/mol and estimated value 6.90 kJ/mol by Krystkowiak and Maciejewski [26]. The change in HB energy calculated for 6AC-(H<sub>2</sub>O)<sub>5</sub> complex using TDDFT/EFP1 methods is in good agreement with the experimentally determined value [13]. The deviation from the experimental value of change in HB energy calculated using TDDFT/EFP1 method for C151-(H<sub>2</sub>O)<sub>5</sub> complex may be due to the formation of B1' type HB in addition to B1 type HB and the formation of HB between water molecules. The total (sum of A, (B1 + B1'), B2, C1 and C2 types) change in HB energy is found to be 0.33 kJ/mol lesser the change in HB energy of C151-(H<sub>2</sub>O)<sub>5</sub> complex, that indicates the energy of HB between two water molecules increases in *S*<sub>1</sub> state.

For all the six hydrogen-bonded C151-(H<sub>2</sub>O)<sub>*n*</sub> complexes, the relationship between the hydrogen bond energy changes from states *S*<sub>0</sub> → *S*<sub>1</sub> and the absorption spectral shifts relative to C151 monomer are presented in Fig. 3. From Fig. 3, it can be found that two types of relationship exist between the *S*<sub>0</sub> → *S*<sub>1</sub> HB energy changes and the absorption spectral shifts. C151-H<sub>2</sub>O complex with A type HB shows spectral blueshift, whereas C151-H<sub>2</sub>O complex with B1, B2, C1 and C2 type HBs shows spectral redshift. C151-H<sub>2</sub>O complex with B1 and B2 type HBs shows nearly equal spectral redshift, whereas C151-H<sub>2</sub>O complex with C1 type HB shows slightly larger redshift than the C151-H<sub>2</sub>O complex with C2 type HB. C151-(H<sub>2</sub>O)<sub>5</sub> complex with all type of HBs also shows large spectral redshift. This may be the cause of blueshift and redshift on the absorption spectra of C151 imposed by the weakening of A type HB and strengthening of B and C type HBs, respectively.



**Table 3**Hydrogen bond lengths,  $r$  (Å), bond angles,  $A$  (°),  $E_{HB}$  (kJ/mol) and  $\Delta E_{HB}$  of C151–(H<sub>2</sub>O)<sub>5</sub> complex and respective C151–(H<sub>2</sub>O) complex for A, B1, B2, C1 and C2 type HBs.

Type of HB	S0			S1			$\Delta E_{HB}$
	$r$	$A$	$E_{HB}$	$r$	$A$	$E_{HB}$	
A, B, C	–	–	–230.93	–	–	–242.72	11.79
A	2.060	141.5	–31.99	3.438	101.1	–27.62	–4.37
B1	2.047	134.1	–48.66	2.048	132.2	–51.40	2.74
(B1')	(1.981)	(138.7)		(1.942)	(141.8)		
B2	1.889	150.6	–44.39	1.849	158.4	–47.27	2.88
C1	1.959	163.8	–44.23	1.924	159.4	–50.12	5.89
C2	1.952	146.7	–38.07	1.785	157.1	–42.39	4.32

**Fig. 3.** Relationship between the hydrogen bond energy changes (cm<sup>−1</sup>) and the absorption spectral shifts (cm<sup>−1</sup>) of the C151–(H<sub>2</sub>O)<sub>5</sub> complex and respective C151–(H<sub>2</sub>O) complex for A, B1, B2, C1 and C2 type HBs relative to C151 monomer.

## Conclusion

The change in HB energy of C151–(H<sub>2</sub>O)<sub>5</sub> complex and C151–(H<sub>2</sub>O) complex for A, (B1 + B1'), B2, C1 and C2 type HBs are calculated using the TDDFT/EPF1 methods along with their structure, electronic excitation energies for S<sub>0</sub> → S<sub>1</sub> transition and oscillation strengths. In C151–(H<sub>2</sub>O)<sub>5</sub> complex, formation of two additional HBs; O10...H27–O26 similar to B1 type (B1') with HB length 1.981 Å and O32...H37 between two water molecules with HB length 1.812 Å. HB lengths and HB energies of C151–(H<sub>2</sub>O)<sub>5</sub> complex for A, (B1 + B1'), B2, C1 and C2 type are calculated at S<sub>0</sub> and S<sub>1</sub> states. At S<sub>1</sub> state A type intermolecular HB is weakened due to increase in excitation energy, whereas B and C type intermolecular HBs are strengthened due to decrease in excitation energy. Therefore, upon excitation, A type HB induces blueshift whereas B and C type intermolecular HBs induce the redshift. The A type HB energy decreased by 4.37 kJ/mol, whereas (B1 + B1'), B2, C1 and C2 type HB energies are increased by 2.74, 2.88, 5.89 and 4.32 kJ/mol, respectively. In S<sub>1</sub> state, the A type and B1 type HB lengths increased by 1.378 Å and 0.001 Å, respectively, whereas B1', B2, C1 and C2 type HB lengths are decreased by 0.039, 0.040, 0.035 and 0.167 Å, respectively. The HB between water molecules (O32...H37) decreased by 0.044 Å. The total (sum of A, (B1 + B1'), B2, C1 and C2 types) change in HB energy is found to be 0.33 kJ/mol lesser the change in HB energy of C151–(H<sub>2</sub>O)<sub>5</sub> complex, thus the energy of HB between two water molecules increases at S<sub>1</sub> state.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2014.08.017>.

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