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Intermolecular Hydrogen Bonding effect on Excited state properties of 3and 4-Aminocoumarins: A theoretical study

Mariyappa Ramegowda^{*}, Boodanuru P Archana, Farzeen Athar, Dudda J Ranjitha and Shabreen Sultana Department of Physics, Govt. College (Autonomous), Mandya, 571401, INDIA

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Abstract

Intermolecular hydrogen bonds, including their structure, energy in the ground state (S_0) and energy change upon electronic first excitation state (S_1) of 3- and 4-aminocoumarin molecules (nAC, n=3,4) in water are investigated theoretically using density functional theory (DFT) and time dependent DFT (TDDFT) interfaced with the effective fragment potential (EFP)/ polarizable continuum model (PCM) method of salvation. The ground and excited state properties of nAC with five water molecules (nAC-(H₂O)₅ complex) have been carried out using TDDFT/B3LYP/EFP/PCM/6-31G(d,p) method. Upon photoexcitation of 3AC-(H₂O)₅ complex, A type (N···H-O) hydrogen bond (HB) is weakened, B and C type (C=O···H-O and N-H···O) HBs are strengthened. In the S₁ state of 4AC-(H₂O)₅ complex, A and B type HBs are weakned, and C type HB is strengthned. The weakening of B type HBs in 4AC water complex shows the uncommon behavior of aminocoumarin molecules, resolved by NBO analysis.

Keywords: TDDFT, EFP, B3LYP, 6-31G(d,p), nAC-(H₂O)₅.

Introduction

A nonspecific interaction between solute and solvent molecules is mainly due to the dielectric properties of the solvent, arising from electrostatic forces.¹ However, an atom or a group with a lone pair of electrons in a molecule can form hydrogen bonded complex with proton-donating group of the solvent molecules²⁻⁶. The hydrogen bond formed by organic and biological molecules in solution plays an important role in the photochemistry at both ground and excited-states⁷⁻¹⁷. The structure, energy and intermolecular HB interactions of organic and biological molecules in both ground and excited states have theoretically¹⁸⁻²² studied been extensively and experimentally²³⁻²⁸. The theoretical studies¹⁸⁻¹⁹ demonstrated that the strengthening (weakening) of HB can decrease (increase) the excitation energy of a related excited state. The chromophores of donor-acceptor character can form hydrogen bonds with protic solvent molecules which influence their structure and photophysical properties in their ground and excited electronic states²⁹⁻³⁹.

The effective fragment potential $(EFP)^{40}$ is a discrete method that accounts for solvent molecules explicitly and provides a polarizable QM-based force field to describe intermolecular interactions. The EFP method was developed specifically for water $(EFP1)^{40.43}$, can be embedded with PCM have been applied to study QM molecular behavior in water. The TDDFT/EFP1 and TDDFT/EFP1/PCM methods were applied effectively to investigate the interaction of chromophores with water molecules at the excited state^{44.46}.

Coumarin derivatives represent an important class of organic compounds, exhibit excellent biological and medical activities⁴⁷⁻⁴⁸. Aminocoumarins shows fluorescence in the region 350 - 500 nm, makes them to use as laser dyes and non-linear optical chromophores⁴⁹⁻⁵⁹. Coumarins with amino group at position 3 have been synthesized and their biological activities such as central nervous system depressant, antibacterial, antiallergic and insect-growth regulatory effects have been studied⁶⁰⁻⁶³. In the literature, it is also found that the derivatives of 4-aminocoumarin shows some biological activity⁶⁴⁻⁶⁵.

Aminocoumarins can form five HBs; one A type, two B type and two C type due to the participation of hetero atoms N and O, and hydrogen atoms of amino group. The spectral properties and HB dynamics of aminocoumarin derivatives have been studied extensively by number of researchers,^{7,8,14,15,17,18} and demonstrated that the decrease in A type HB energy in the S₁ state relative to the S₀ state was much smaller than the increase in energy of B and C type HBs formed by the carbonyl group and N-H bond, respectively. In the case of nAC molecules, there are at least five sites of hydrogen bond formation with water molecules as shown in figure-1; one A type, two B type and two C type.

The aim of this study is to compute the change in A, B and C type HB energies (ΔE_{HB} 's) of nAC-(H₂O)₅ complexes as a result of S₀ \rightarrow S₁ transition using TDDFT/PCM/EFP1 method and to study the excited state properties of nAC due to HB interaction.



S₀ state optimized structure of (a) 3AC (b) 4AC (c) 3AC-(H₂O)₅ and (d) 4AC-(H₂O)₅

Methodology

Computational methods: The optimization of nAC molecules, and nAC-(H₂O)₅ complexes have been performed at the DFT level⁶⁶⁻⁷¹ using B3LYP⁷²⁻⁷³ hybrid function with 6-31G(d,p) basis set.⁷⁴ The geometries at the excited state were optimized using the TDDFT⁷⁵⁻⁸² with same functional and basis set. Based on optimized ground state geometry the excitation energies were TDDFT/B3LYP/PCM/EFP1/6-31G(d,p) calculated bv method.⁸²⁻⁸⁵ The relaxed geometry of the first excited state is used to calculate the fluorescence spectra. The explicit water molecules were added using DFT based EFP1 water model⁸⁶ in that all water molecules are treated as EFPs for DFT and TDDFT calculations. Natural atomic orbital and Natural bond orbital analysis have been carried out to calculate charge on each atom at S_0 and S_1 states using NBO6.0⁸⁷ package. All calculations were performed using GAMESS-US software suit^{88,89}

Five water molecules formed HB with nAC in nAC-(H_2O)₅ complexes. The HB energy is computed by equating interaction energy between solute and solvent molecules using the scheme explained by Nagata et al. in ref. 90. The optimized geometry of complexes is used to compute the energy of free solute, E_{solu} by removing solvent molecules from the system. Then, the solvent-solute interaction energy, (E_{HB}) is calculated as

 $E_{\rm HB} = E_{\rm complex} - (E_{\rm solu} + E_{\rm solv}) \tag{1}$

Where $E_{complex}$ is total energy of the complex and E_{solv} is total

EFP energy. By calculating E_{HB} at both S_0 and S_1 states, the change in HB energy can be obtained as $\Delta E_{HB} = (E_{HB})_{S1} - (E_{HB})_{S0}$ (2)

By removing four water molecules from the optimized geometry of $nAC-(H_2O)_5$ complex, $nAC-(H_2O)$ complex is formed for each type of HB and their energies are calculated using equation-1 with the same scheme.

Results and Discussion

Electronic structure in ground state: The S₀ state optimized structures of nAC and nAC-(H₂O)₅ complexes are shown in figure-1. The A type (N---H-O) HB is formed between the nitrogen atom of the amino group of nAC and the hydrogen atom of the one water molecule, B type (C=O---H-O) HBs are formed between the oxygen atom of the carbonyl group of nAC and the hydrogen atom of the two water molecules. Similarly, C type (N-H---O-H) HBs are formed between the hydrogen atoms of the amino group of nAC and the oxygen atom of the two water molecules. One intramolecular HB (C=O---H-N) between the oxygen of the carbonyl and hydrogen of the amino group is formed in 3AC. In 4AC- $(H_2O)_5$ complex oxygen of the pyrone ring forms a HB (B1') with the water molecule which forms B1 type HB. In addition to these HBs, there is a formation of two intermolecular HBs between water molecules (WHB) in both complexes. The calculated bond lengths and bond angles for nAC and nAC-(H₂O)₅ complexes at S_0 and S_1 states are

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presented in table-1. In complexes, the formation of hydrogen bonds can slightly change the structure of nAC. In pyrone ring, due to the formation of B type HB, O1-C2, C2-C3 bond lengths decreases and O1-C6, C3-C4, C2-O11 bond lengths increases. No change in the C4-C5 bond length in 4AC and it decreases in 3AC, whereas the converse effect is observed for C5-C6 bond. Similarly, due to the formation of A type HB C-N bond length decreases, one N-H bond length slightly expands and another slightly contracts. There is no distortion of the benzene ring due to the formation of HBs in both 3AC and 4AC complexes. The change of bond lengths for O1-C2, O1-C6 C2-C3, C2-O11 C4(3)-N12 in 4AC-(H₂O)₅ complex is greater as compared to 3AC-(H₂O)₅ complex. No appreciable changes in bond angles of nAC in complexes as compared to the bond angles of monomers.

Table-1
Bond lengths, r (Å) and bond angles, A (°) of nAC in S ₀ state, and nAC-(H ₂ O) ₅ complexes at S ₀ and S ₁ states

	3AC	3AC-	(H ₂ O) ₅	4AC	4AC-(H ₂ O) ₅		
r/A	S ₀	S ₀	S ₁	S ₀	S ₀	S ₁	
R(1-2)	1.367	1.366	1.425	1.408	1.397	1.373	
R(1-6)	1.376	1.378	1.372	1.358	1.369	1.399	
R(2-3)	1.479	1.473	1.437	1.441	1.418	1.405	
R(3-4)	1.364	1.370	1.404	1.369	1.375	1.448	
R(4-5)	1.439	1.432	1.416	1.461	1.461	1.408	
R(5-6)	1.407	1.407	1.430	1.409	1.412	1.444	
R(2-11)	1.215	1.223	1.248	1.210	1.228	1.248	
R(5-7)	1.410	1.411	1.421	1.408	1.409	1.451	
R(6-10)	1.393	1.394	1.388	1.400	1.398	1.380	
R(7-8)	1.389	1.388	1.390	1.389	1.390	1.377	
R(8-9)	1.403	1.404	1.400	1.402	1.402	1.415	
R(9-10)	1.392	1.393	1.406	1.389	1.390	1.416	
R(3,4-12)	1.374	1.369	1.366	1.375	1.362	1.343	
R(12-18)	1.011	1.010	1.012	1.010	1.009	1.014	
R(12-19)	1.008	1.010	1.017	1.009	1.014	1.016	
A(2-1-6)	122.9	123.2	121.0	122.1	121.1	121.0	
A(1-2-3)	117.4	118.0	116.1	116.0	116.9	118.7	
A(1-6-5)	120.7	120.0	122.3	122.6	122.7	122.1	
A(2-3-4)	120.1	119.1	123.5	123.2	123.8	121.3	
A(3-4-5)	120.6	121.3	118.4	118.9	117.9	119.5	
A(6-5-7)	117.4	117.5	117.7	118.2	118.2	116.9	
A(5-6-10)	122.3	122.4	120.8	121.0	121.2	122.1	
A(5-7-8)	120.8	120.8	121.4	121.0	120.6	120.0	
A(6-10-9)	119.0	118.8	120.1	119.7	119.5	119.7	
A(7-8-9)	120.3	120.3	119.8	119.8	120.2	121.8	
A(8-9-10)	120.1	120.2	120.4	120.3	120.3	119.5	

Electronic structure in excited state: In the S₁ state of nAC-(H₂O)₅ complexes C3-C4, C5-C6, C2=O11, C5-C7, C9-C10 bond lengths increases, whereas C2-C3, C4-C5, C6-C10 bond lengths decreases. The ground and excited state HB lengths of nAC-(H₂O)₅ complexes are displayed in table-2. In both complexes, upon molecular excitation, A type HB expands and C type HBs contracts due to which C-N bond length decreases and N-H bond lengths increases. B type HBs contracts in 3AC- $(H_2O)_5$ complex and slightly expands in 4AC- $(H_2O)_5$ complex. In 3AC-(H₂O)₅ complex O1-C2 bond length increases, O1-C6 bond length decreases, whereas in 4AC-(H₂O)₅ complex O1-C2 bond length decreases and O1-C6 bond length increases. In the S_1 state, variation of bond lengths in pyrone and benzene ring causes the change in bond angles less than 3. In 3AC-(H₂O)₅ complex, one WHB is elongated and another gets contracted, whereas in 4AC-(H₂O)₅ complex, both WHBs are contracted.

C-C-N-H dihedral angles of both complexes are given in table-3. In $3AC-(H_2O)_5$ complex C2-C3-N12-H19 and C4-C3-N12H18 dihedral angles changes from -20.1° to -4.9° and 14.2° to -2.0°, respectively due to molecular excitation. In the S₁ state of 4AC-(H₂O)₅ complex the dihedral angles C3-C4-N12-H19 and C5-C4-N12-H18 changes by 8.2° and -11.6°, respectively. Thus, the umbrella-like open-close motion of the amino group causes the change of dihedral angles in both complexes.

Molecular electrostatic potential (MEP) and NBO analysis: Molecular electrostatic potential (MEP), computed at the B3LYP level are depicted graphically in figure-2 along with the natural charges on various atoms and groups. The color code of these maps was in the range from -0.001 to 0.001 a. u. for negative (red color) and the positive (blue color) charge density regions. In both molecules most negative potential regions were mainly localized over O1, O11 and N12 atoms showing the most favourable sites for electrophilic attack. Meanwhile, a maximum positive regions are localized over benzene and pyrone rings (except O1), which are indicated possible sites for nucleophilic attack.

 $Table - 2 \\ Intramolecular HB length, r (Å) of 3AC at S_0 state and intermolecular HB lengths of nAC-(H_2O)_5 complexes at S_0 and S_1 \\ extended$

Statts								
r/A	3AC	3AC-	(H ₂ O) ₅	4AC-(H ₂ O) ₅				
	S ₀	S ₀	S ₁	S ₀	S ₁			
C=OH-N	2.278	-	-	-	-			
NH-O (A)	-	2.035	2.378	2.117	2.566			
С=ОН (В1)	-	1.930	1.851	1.941	1.957			
OH (B1')	-	-	-	2.074	2.076			
С=ОН (В2)	-	2.024	1.931	1.928	1.948			
N-HO (C1)	-	1.954	1.780	1.872	1.752			
N-HO (C2)	-	1.851	1.718	2.029	1.850			
HO (WHB1)	-	1.724	1.706	1.866	1.841			
HO (WHB2)	-	2.022	2.053	1.810	1.784			

The dihedral angles, A (°) of nAC in S_0 state, and nAC-(H ₂ O) ₅ complexes in S_0 and S_1 states									
А	3AC	3AC-(H ₂ O) ₅			4AC	4AC-(H ₂ O) ₅			
	S ₀	S ₀	S ₁	А	S ₀	S ₀	S_1		
A(2-3-12-19)	-21.7	-20.1	-4.9	A(3-4-12-19)	-13.0	-18.5	-10.3		
A(4-3-12-18)	16.1	14.2	-2.0	A(5-4-12-18)	29.3	12.5	0.9		



Molecular electrostatic potential of 3AC and 4AC molecules at (a) S₀ and (b) S₁ states in complexes with natural charges on various atoms and groups

NBO analysis of nAC-(H_2O_{15} complexes at S_0 and S_1 state have been carried out along with the calculation of HOMO and LUMO. The frontier molecular orbitals (MOs) of isolated nAC are depicted in figure-3. The natural charges on O1, O11 and N12 atoms are -0.497, -0.661 and -0.911e, respectively in 3AC-(H₂O)₅ and -0.525, -0.681 and -0.887e respectively in 4AC-(H₂O)₅ complex. The MEP and natural charges on O1 atom indicating the possibility of B1' type HB formation in 4AC- $(H_2O)_5$ complex. At the S₀ state, natural charges on pyrone (with carbonyl), benzene and amino groups are 0.572, 0.227 and 0.070e, respectively for 3AC-(H₂O)₅ complex and 0.518, 0.280 and 0.082*e*, respectively for $4AC-(H_2O)_5$ complex. In the S₁ state, natural charges on O1, O11 and N12 atoms are -0.516, -0.708 and -0.752e, respectively in 3AC-(H₂O)₅ and -0.517, -0.593 and -0.816e respectively in 4AC-(H₂O)₅ complex. In the excited state of 3AC-(H₂O)₅ complex, the natural charges on benzene ring and amino group are increased by 0.031 and 0.070e, respectively and decreased by 0.110e on pyrone ring (with carbonyl group), whereas in $4AC-(H_2O)_5$ complex, natural charges on pyrone (with carbonyl) and amino groups are increased by 0.007 and 0.080e, respectively and decreased by 0.226e on benzene ring. Upon excitation, natural electronic charge on N12 atom decreases in both complexes, while natural electronic charges on O1 and O11 atoms increases in 3AC-(H₂O)₅, and decreases in 4AC-(H₂O)₅, which accounts for the weakening of B type HB in 4AC-(H₂O)₅ complex. From figire-3 it can also be observed that the intramolecular redistribution of electronic charges from the amino group and the benzene ring to

pyrone ring and carbonyl group of coumarin moiety in 3AC- $(H_2O)_5$ complex, while in 4AC- $(H_2O)_5$ complex the charge transfer is from pyrone ring, amino and carbonyl groups to benzene ring. Thus, the excited state in both complexes may be an intramolecular charge-transfer (ICT) state.

The natural bonding (Lewis) and antibonding (non-Lewis) orbitals for C=O, C-N and N-H bonds of nAC-(H₂O)₅ complexes are displayed in figure-4 along with occupancy and orbital energy. The non-Lewis occupancy of C=O is 0.341 and 0.340 in 3AC-(H₂O)₅ and 4AC-(H₂O)₅ with orbital energy -8.77 and 29.93 kJ/mol, respectively. So, in the S₁ state, the natural electronic charge on O12 atom increases in 3AC-(H₂O)₅ and decreases in 4AC-(H₂O)₅ complex, due to which B type HBs strengthen in 3AC-(H₂O)₅ and weaken in 4AC-(H₂O)₅ complex. The non-Lewis occupancy of C-N is 0.015 and 0.016 in 3AC-(H₂O)₅ and 4AC-(H₂O)₅ with orbital energy 1271 and 1248 kJ/mol, respectively. In the S_1 state, due to lower energy antibonds, the charge transfer from N atom is lesser in 4AC-(H₂O)₅ complex as compared to 3AC-(H₂O)₅ complex. This may be the reason for lesser change in A type HB energy at the excited state of 4AC-(H₂O)₅ complex. The electron density in Lewis and non-Lewis NBOs are 97.23 and 2.77%, respectively in 3AC-(H₂O)₅, and 96.54 and 3.46%, respectively in 4AC- $(H_2O)_5$ complex. Thus, the absorption energy of $4AC-(H_2O)_5$ complex is mainly due to ICT than the change in HB energy.



Figure-3 Molecular orbitals of 3AC and 4AC molecules



Natural bonding and antibonding orbitals of C=O, C-N and N-H bonds in 3AC-(H₂O)₅ and 4AC-(H₂O)₅ complexes. Occupancy and orbital energy (kJ/mol) are given in parenthesis

Electronic spectra and excited state properties: To elucidate the influences of different types of hydrogen bonds on the spectral properties of nAC-(H₂O)₅ complexes in water, the absorption wavelengths with corresponding oscillation strengths of nAC and nAC-(H₂O)₅ complexes in the gas phase and in solvents at S_1 state are calculated and listed in table-4. The assignments of the electronic excitations in table-4 reveals that the major contributions (~ 90%) of the orbital transitions at S_1 state come from HOMO (H) to LUMO (L) for both molecules. Figure-5 displays the absorption spectra of nAC monomers and their water complexes. 3AC molecule produce the intense absorption wavelengths 306.1 nm in the gas phase, 320.5 nm in water, 317.8 nm in ether and 320.2 nm in methanol. The absorption wavelengths for 3AC-(H₂O)₅ complex are found to be 324.8 nm in gas phase and 331.8 nm in water, which are red shifted as compared to absorption wavelengths of 3AC, due to formation of HBs. 4AC and 4AC-(H₂O)₅ molecules are 289.6 and 288.9 nm in the gas phase, and 285.0 and 287.2 nm in water, respectively. The absorption wavelengths for 4AC and 4AC-(H₂O)₅ complex in both gas phase and water are found to be nearly equal, but the oscillator strength increases in water. It is also observed that the formation of HBs with 4AC molecule does not affect its absorption spectra in the appreciable range. The emission wavelength from fluorescence spectra of 3AC in ether and methanol, and 4AC in water is calculated as 380.3 405.3 and 346.7 nm, respectively (figure-6). To compare our calculated values with the available experimental values from the literature, we have simulated the absorption and emission spectra of 3AC in ether and methanol are 321.0 and 324 nm⁹⁰, respectively, 4AC in water is 291 nm⁹¹ and the emission wavelength of 3AC in ether values.

Hydrogen bond dynamics: In order to compute HB energy of particular type, TDDFT calculations for nAC-(H₂O) complex have been carried out by infinitely extrication of other four EFP water molecules and ΔE_{HB} s are calculated using equation-1 and equation-2. The electronic excitation energies corresponding to $S_0 \rightarrow S_1$ transition of nAC-(H₂O)₅ complex for A, B and C type HBs were calculated using the TDDFT/PCM/EFP1 method and

presented in table-5. From this table, it has been noticed that, in the case of 4AC, due to molecular excitation E_{HB} decreases for the S_1 state of 3AC, A type intermolecular HB is weakened, whereas B and C type intermolecular HBs are strengthened. In

A and B type HBs and increases slightly for C type HBs.]



Simulated real-time TD-DFT absorption spectra of 3AC (blue curves), 4AC (violet curves) molecules and their water complexes. 1, 2-monomers in gas phase and water, 3, 4-complexes in gas phase and water, 5, 6-monomer in methanol and ether

Table-4

Absorption wavelengh ($S_0 \rightarrow S_1$), λ (nm), oscillator strength, f and assignment of electronic excitations of nAC and nAC-(H₂O)₅ complexes in gas phase and in solvent. Only selected transitions with enough oscillator strength around the main neak are included

Molecule	Solvent/gas phase	λ	f	Wave function (excitation amplitude)			
3AC	Gas phase	306.1	0.339	H - 1 → L (0.566), H → L + 1 (0.697) H - 1 → L + 2 (0.202), H → L + 2 (0.351)			
	Water	320.5	0.609	$\mathrm{H} \rightarrow \mathrm{L} \ (0.995)$			
	Ether	317.8 321.0 ^a	0.431	$H \to L (0.986), H - 1 \to L + 1 (0.110)$			
	Methanol	320.2 324.0 ^a	0.409	$H \rightarrow L (0.987), H - 1 \rightarrow L + 1 (0.104)$			
3AC-(H ₂ O) ₅	Gas phase	324.8	0.316	$H \rightarrow L \ (0.982), H - 1 \rightarrow L + 1 \ (0.120)$			
	Water	331.8	0.530	$\mathrm{H} \rightarrow \mathrm{L} \ (0.995)$			
4AC	Gas phase	289.6	0.141	$H \rightarrow L (0.926), H \rightarrow L + 2 (0.116)$ $H - 1 \rightarrow L (0.303)$			
	Water	285.0 291.0 ^b	0.386	$H \rightarrow L (0.958), H - 1 \rightarrow L (0.303)$ $H - 1 \rightarrow L + 1 (0.158)$			
4AC-(H ₂ O) ₅	Gas phase	288.9	0.141	$H \rightarrow L (0.926), H - 1 \rightarrow L (0.24)$			
	Water	287.5 291.0 ^b	0.370	$H \to L \ (0.977), H - 1 \to L + 1 \ (0.172)$			

Experimental values from absorption spectral study by ^a Subba rao et al. 91 and ^b Stamboliyska et al. 92.



Simulated real-time TD-DFT emission spectra of 3AC and 4AC. 1, 2 - 3AC in methanol and ether, 3 - 4AC in water

Table-5
Absorption spectral shifts, ΔE (kJ/mol), hydrogen bond energy, E _{HB} and ΔE _{HB} of nAC-(H ₂ O) ₅ and respective nAC-(H ₂ O)
complexes for A, B and C type HBs

Type of HB	3AC-(H ₂ O) ₅				4AC-(H ₂ O) ₅			
	ΔE	(E _{HB}) _{S0}	(E _{HB}) _{S1}	ΔE_{HB}	ΔE	(E _{HB}) _{S0}	(E _{HB}) _{S1}	ΔE_{HB}
A, B, C	-12.71	-237.57	-245.42	7.85	3.19	-248.38	-243.27	-5.11
А	1.47	-35.73	-29.41	-6.33	7.13	-32.92	-31.76	-1.17
B1 + (B1')	-7.58	-39.95	-42.68	2.73	5.49	-52.25	-49.45	-2.80
B2	-6.28	-35.90	-37.32	1.43	5.97	-40.24	-37.91	-2.32
C1	-7.77	-35.12	-38.04	2.92	9.09	-40.83	-41.63	0.80
C2	-10.16	-37.15	-42.46	5.31	9.43	-32.58	-33.72	1.13

In 3AC-(H₂O)₅ complex, A type HB energy decreased by 6.33 kJ/mol, whereas B1, B2, C1 and C2 type HB energies are increased by 2.73, 1.43, 2.92 and 5.31 kJ/mol, respectively. The total (sum of A, B1, B2, C1 and C2 types) change in HB energy is found to be 1.79 kJ/mol lesser the change in HB energy of 3AC-(H₂O)₅ complex. This indicates that the total change in energy of WHBs increases at S₁ state. The scheme applied in

this work having the limitation for the calculation of E_{HB} of individual WHB. In 4AC-(H₂O)₅ complex, A, B1 and B2 type HB energies are decreased by 1.17, 2.80 and 2.32 kJ/mol, whereas C1 and C2 type HB energies are increased by 0.80 and 1.13 kJ/mol, respectively. The change in HB energy of 4AC-(H₂O)₅ complex is found to be 0.76 kJ/mol lesser than the sum of HB energy of A, B1, B2, C1 and C2 type, which indicates that the total change in energy of WHBs decreases at S₁ state. Upon excitation, ΔE_{HB} increased by 7.85 kJ/mol in 3AC-(H₂O)₅ complex and decreased by 5.11 kJ/mol in 4AC-(H₂O)₅ complex. Thus, due to the formation of HBs by 3AC with water molecules redshift is observed in the absorption spectra, whereas in the case of 4AC, no spectral shift is observed. This may be due to the favourable ICT in 4AC as compared to 3AC in their complexes at S₁ state.

The plot of absorption spectral shift, ΔE dependence on ΔE_{HB} for various types of HBs of nAC-(H₂O)₅ complex relative to nAC monomer is given in figure-7. In 3AC-(H₂O)₅ complex blueshift of spectral line due to A type HB and redshift of spectral line due to B and C type HBs (figure-7a), whereas in 4AC-(H₂O)₅ complex A and B type HBs shows blueshift, and C type HBs shows slightly redshift (figure-7b). The effect of A, B and C type HBs in 3AC-(H₂O)₅ complex shows spectral redshift, whereas in 4AC-(H₂O)₅ complex shows spectral blueshift. This may be the cause of spectral redshift on the absorption spectra of 3AC in water imposed by strengthening of B and C type HBs, and weakening of A type HB. In case of 4AC-(H₂O)₅ complex, the weakening of A, B type HBs and slight strengthening of C type HBs may not cause a spectral shift in the absorption spectra of 4AC in water due to the high percentage of electron density in non-Lewis NBOs as compared to 3AC.

Conclusion

In this work, hydrogen bonding sites and electronic excitation energy of 3AC and 4AC have been investigated by means of TDDFT/PCM/B3LYP/EFP1/6-31G(d,p) method augmented with explicit inclusion of five water molecules. Both 3AC and 4AC molecules formed five HBs with water molecules; one A type, two B type and two C type. An intra-molecular HB (2.278 Å) is observed in 3AC between the oxygen of the carbonyl group and hydrogen of the amine group. As a result of the $S_0 \rightarrow S_1$ transition of 3AC, A type HB weekend by 6.33 kJ/mol, whereas B1, B2, C1 and C2 type HBs are strengthened by 2.73, 1.43, 2.92 and 5.31 kJ/mol, respectively. In the S1 state of 4AC in water A, B1 and B2 type HBs weekend by 1.17, 2.80 and 2.32 kJ/mol, whereas C1 and C2 type HBs strengthened by 0.80 and 1.13 kJ/mol, respectively. The molecular excitation of 3AC- $(H_2O)_5$ complex in water results in the elongation of A type HB by 0.343 Å, and contraction of B1, B2, C1 and C2 type HBs by 0.079, 0.093, 0.174 and 0.133 Å, respectively, whereas in the S_1 state of 4AC-(H₂O)₅ complex, A, B1, B1' and B2 type HBs are elongated by 0.449, 0.016, 0.002 and 0.020 Å, and C1, C2 type HBs are contracted by 0.120 and 0.179 Å, respectively. In 3AC-(H₂O)₅ complex, two WHBs are formed; upon excitation, one WHB is elongated and other gets contracted. In 4AC-(H₂O)₅ complex, there is also formation of two WHBs and are contracted at S_1 state. In 3AC-(H₂O)₅ complex, the quantitative decrease in bond length of WHB is lower than the increase in bond length of WHB, which causes the blueshift effect on absorption spectra of 3AC-(H₂O)₅ complex by ~1.79 kJ/mol. In the S_1 state of 4AC-(H₂O)₅ complex both WHBs gets contract and causes redshift effect on absorption spectra by ~0.76 kJ/mol.

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Figure-7

The plot of absorption spectral shift, ΔE dependence on ΔE_{HB} for various types of HBs of (a) 3AC-(H₂O)₅ and (b) 4AC-(H₂O)₅ complexes relative to their monomer

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