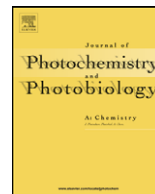




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Revisiting the electronic excited-state hydrogen bonding dynamics of coumarin chromophore in alcohols: Undoubtedly strengthened not cleaved

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ABSTRACT

In the present work, the electronic excited-state hydrogen bonding dynamics of coumarin chromophore in alcohols is revisited. The time-dependent density functional theory (TDDFT) method has been performed to investigate the intermolecular hydrogen bonding between Coumarin 151 (C151) and methanol (MeOH) solvent in the electronic excited state. Three types of intermolecular hydrogen bonds can be formed in the hydrogen-bonded C151–(MeOH)₃ complex. We have demonstrated again that intermolecular hydrogen bonds between C151 and methanol molecules can be significantly strengthened upon photoexcitation to the electronically excited state of C151 chromophore. Our results are consistent with the intermolecular hydrogen bond strengthening in the electronically excited state of Coumarin 102 in alcoholic solvents, which has been demonstrated for the first time by Zhao et al. At the same time, the electronic excited-state hydrogen bond cleavage mechanism of photoexcited coumarin chromophores in alcohols proposed in some other studies about the hydrogen bonding dynamics is undoubtedly excluded. Hence, we believe that the two contrary dynamic mechanisms for intermolecular hydrogen bonding in electronically excited states of coumarin chromophores in alcohols are clarified here.

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1. Introduction

The solute–solvent interaction, especially involving the intermolecular hydrogen bonding, has been found to be very important in determining the molecular nonequilibrium processes in solution [1]. Intermolecular hydrogen bonding, as a site-specific interaction, represents an important type of local interaction in which a hydrogen atom is linked to donor and acceptor between hydrogen donor and acceptor groups [2]. The photoexcitation can induce the changes of the hydrogen bonding due to the charge redistribution in the different electronic states. This is the so-called electronic excited-state hydrogen bonding dynamics [3–8]. The excited-state hydrogen bonding dynamics occurs on ultrafast timescales mainly set by vibrational motions of the hydrogen donor and acceptor groups, and it controls the excited-state dynamics of hydrogen-bonded complexes in a significant way. Very recently, Zhao et al. have demonstrated for the first time that the hydrogen bonding dynamics in electronically excited states is significantly associated with many important electronic excited-state phenomena in the hydrogen bonding environment, such as photoinduced electron transfer, internal conversion, and fluorescence quenching [9–12].

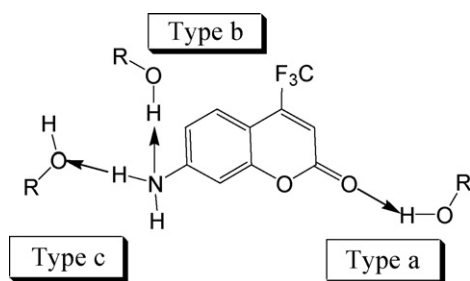
To get better understanding of the hydrogen bonding dynamics in electronically excited states of different molecules in solution, diverse experimental and theoretical methods has been performed [3–39]. Chudoba et al. have studied the excited-state infrared (IR) spectra of Coumarin 102 (C102) dye in hydrogen-donating solvents using the site-specific vibrational spectroscopy in the femtosecond domain [4]. They proposed that the intermolecular hydrogen bond C=O...H–O formed between C102 and alcoholic solvents can be cleaved within a 200 fs timescale upon electronic excitation [4]. However, Zhao and Han have theoretically demonstrated for the first time that the intermolecular hydrogen bonds between the C102 chromophore and hydrogen-donating solvents can be significantly strengthened, while not cleaved, in the early time of photoexcitation to the electronically excited state of the chromophore [5]. It is very interesting that the two research groups have given two completely contrary conclusions on the hydrogen bonding dynamics in electronically excited states of coumarin chromophores in alcoholic solvents [5,9–12]. To confirm that the intermolecular hydrogen bonds between the coumarin dyes and alcoholic solvents are cleaved or strengthened, we theoretically investigated the intermolecular hydrogen bonding interactions between a coumarin dye and alcohols in the electronically excited states using the time-dependent density functional theory (TDDFT) method. Sobolewski and Domcke have theoretically studied photophysics of many hydrogen-bonded systems using the TDDFT method [13,14]. Douhal et al. have investigated perfectly the

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excited-state dynamics in hydrogen bonding surroundings [7,8]. Mataga et al. have contributed very profoundly to the recognition of the role of hydrogen bonds in photochemistry [35–38].

Coumarin is an important type of dyes for studying the nature of solute–solvent interaction, because they can readily be incorporated as solvation probes into many types of chemical environments [39,40]. Coumarin 151 (here denoted as C151, 7-amino-4-trifluoromethylcoumarin) is a popularly used solvation probe and has been extensively studied by many steady-state and time-resolved spectroscopic methods [41–46]. Pal and coworkers have investigated the photophysical properties of C151 in a sequence of solvents, from nonpolar solvents to the solvents of moderate to higher polarities [41,42]. They found that the fluorescence quantum yield as well as the absorption and fluorescence maxima of C151 in the protic alcohols is lower than those in the aprotic solvents of similar polarities [41]. They attributed this to the intermolecular hydrogen bonding interaction between C151 and the solvent molecules, which caused an extra stabilization for both S_0 and S_1 states of the coumarin dye [42]. Topp and coworkers have studied the fluorescence depolarization rates of C151 in linear alcohols and found the evidence for the intermolecular hydrogen bond between C151 and the alcoholic solvents in the electronic excited state [43–45]. Therefore, the formation of the intermolecular hydrogen bond between C151 dye and the alcoholic solvents in both ground state and the electronic excited state has been experimentally demonstrated. However, quite a few theoretical works have been done in order to give a better description on the site-specific intermolecular hydrogen bonding in the electronically excited state of C151 dye in the polar protic solvents. In the present work, the intermolecular hydrogen bonding properties between C151 and the protic methanol solvent in both the ground state and electronically excited state have been theoretically investigated.

As illustrated in Scheme 1, C151 can form three types of hydrogen bonds which include participation of the carbonyl oxygen: C=O...H–O (type a), amino nitrogen: N...H–O (type b), and amino hydrogen: N–H...O–H (type c) [40]. Since the excited-state hydrogen bonding dynamics takes place on ultrafast timescales mainly set by vibrational motions of the hydrogen donor and acceptor groups, only the solvent molecules in the first solvation shell of the photoexcited chromophore can be attributed to the early time hydrogen bonding dynamics in the electronic excited state [9–11]. Hence, only the solvent molecule in the first solvation shell, which is directly hydrogen-bonded with the chromophore, is involved in the work without consideration of the bulk effect of the outer solvation shells. In order to give a clear picture of the hydrogen bonding in the electronically excited state of the C151 in alcoholic solvents, geometric conformations of the hydrogen-bonded C151–(MeOH)₃ complex as well as the isolated C151 in both the ground state and electronically excited state are optimized using the DFT and TDDFT methods in this work. In addition, the hydrogen bond binding ener-



Scheme 1. Illustration of different types of intermolecular hydrogen bonds between Coumarin 151 (C151) and the alcoholic solvent (taken from Ref [40]). Here R refers to the methyl group.

gies and the bond lengths of the three types of hydrogen bonds are calculated. The basis set superposition error (BSSE) value for the intermolecular hydrogen bond binding energy using the above methods is at the range of 1–3 kJ/mol, which is much smaller than the calculated intermolecular hydrogen bond binding energies.

2. Computational methods

Geometric structures and energetics of the isolated monomers and the hydrogen-bonded solute–solvent complexes were investigated using the density functional theory (DFT) and generalized gradient approximation (GGA) for exchange correlation potential BP-86 for ground state, but for excited state, the calculation was performed using the time-dependent density functional theory (TDDFT) method with the same exchange correlation potential [47–52]. The resolution-of-the-identity (RI) approximation was also used to improve the efficiency without sacrificing the accuracy of the results [48–50]. The triple- ζ valence quality with one set of polarization functions (TZVP) was chosen as basis sets and the corresponding auxiliary basis sets for the RI approximation throughout [51]. All the electronic structure calculations were carried out using the Turbomole program suite [47–52].

3. Results and discussions

The optimized geometric structure of the isolated C151 and the hydrogen-bonded C151–(MeOH)₃ complex in the ground state are shown in Fig. 1. The intermolecular hydrogen bonds between carbonyl group of C151 and the hydroxyl group of methanol are of the type a and first discussed here. From the side sight of the optimized geometric of the C151–(MeOH)₃ complex we can see that the hydrogen bond C=O...H–O remains in the plane of the C151 molecule. However, the methyl group resides out of the plane. In addition, another weak hydrogen bond C–H...O–H can also be formed between C151 dye and methanol. The length of the hydrogen bond between H and O is calculated to be 1.908 and 2.482 Å for the hydrogen bonds C=O...H–O and C–H...O–H, respectively. It is evident that the former hydrogen bond is stronger than the later one. The binding energy of these intermolecular hydrogen bonds between C151 and methanol molecules is calculated to be 23.95 kJ/mol. It mainly attributes to the strong hydrogen bond C=O...H–O. It is noted that the calculated bond lengths of the hydrogen-bonded C=O and H–O groups are 1.222 and 0.983 Å, respectively. While the bond length of free C=O and H–O groups in isolated C151 and methanol molecules are calculated to be 1.212 and 0.963 Å, respectively. It is clear that the hydrogen-bonded C=O and H–O groups are slightly lengthened in hydrogen-bonded complexes, which is similar to the previous studies [5,9].

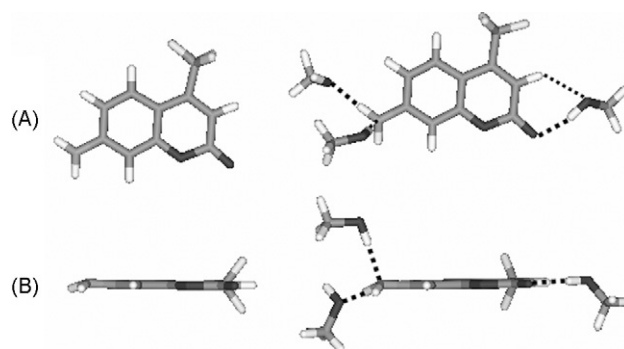


Fig. 1. Optimized geometric structures of the isolated C151 and hydrogen-bonded C151–(MeOH)₃ complex in the ground state. (A) Top view; (B) side view.

The intermolecular hydrogen bond N...H-O, which is the type b, is formed between amino nitrogen atom and hydroxyl hydrogen atom. One can find that the two amino hydrogen atoms reside out of the plane of the C151 molecule for both the isolated C151 and the hydrogen-bonded C151-(MeOH)₃ complex. The angle formed by C-N...H is calculated to be 109.48°, which suggests that the intermolecular hydrogen bond N...H-O is nearly perpendicular to the plane of C151. The calculated bond length of the hydrogen bond N...H-O is 2.017 Å and its binding energy is 11.17 kJ/mol. Moreover, the bond length of the H-O group is increased to 0.984 Å from the free bond length of 0.963 Å due to the formation of the hydrogen bond N...H-O.

The intermolecular hydrogen bond N-H...O-H is of the type c and also resides outside of the C151 plane. The hydrogen bond length and the binding energy are calculated to be 1.925 Å and 27.34 kJ/mol. The bond lengths of N-C and H-O groups in the hydrogen-bonded C151-(MeOH)₃ complex are increased to 1.029 and 0.973 Å from free bond length of 1.014 and 0.963 Å in the isolated C151 and methanol, respectively. Herein it should be noticed that there actually exist two hydrogen bonds of the type c. only one hydrogen bond of the type c is considered owing to the two hydrogen bonds are equivalent. From our calculated results it can be concluded that the hydrogen-bonded groups are slightly lengthened in the hydrogen-bonded complexes due to the formation of intermolecular hydrogen bonding, which is consistent with the previous works of Zhao et al. [5,9–11].

The electronic excitation energies and the corresponding oscillation strengths of the low-lying electronically excited states for the hydrogen-bonded C151-(MeOH)₃ complex and the isolated C151 are calculated using the TDDFT method and presented in Table 1. One can find that the S₁ state of the C151 monomer has the largest oscillator strength, which means the absorption maxima of the isolated C151 located in the S₁ state [5–10]. The S₁ absorption peak is calculated to be at 385 nm. For the hydrogen-bonded C151-(MeOH)₃ complex, the S₃ state has the largest oscillator strength. So it can be initially photoexcited to the S₃ state of the hydrogen-bonded complex [10]. The calculated absorption peak of hydrogen-bonded C151-(MeOH)₃ is at 388 nm, which is good agreement with the maximum absorption at 378 nm observed in the steady-state absorption spectra [41]. Therefore, it is demonstrated that the absorption peak can be slightly red-shifted due to the formation of the intermolecular hydrogen bond. By comparing the electronic excitation energies of hydrogen-bonded C151-(MeOH)₃ complex with that of the C151 monomer, we find the S₃ state of the hydrogen-bonded C151-(MeOH)₃ complex is very close in energy to the S₁ state of C151 monomer, so it can be supposed that in the S₃ state of the hydrogen-bonded

Table 1

Calculated electronic excitation energies (nm) and corresponding oscillator strengths of the low-lying electronically excited states for isolated C151 and hydrogen-bonded C151-(MeOH)₃ complex.

	C151	C151-(MeOH) ₃
S ₁	385 (0.221) H → L 84.3%	524 (0.000) –
S ₂	349 (0.005)	456 (0.001)
S ₃	348 (0.033) –	388 (0.258) H → L 83.6%
S ₄	285 (0.021)	343 (0.048)
S ₅	268 (0.045)	338 (0.000)
S ₆	251 (0.000)	320 (0.001)
S ₇	238 (0.046)	298 (0.000)
S ₈	228 (0.000)	294 (0.001)
S ₉	226 (0.001)	290 (0.000)

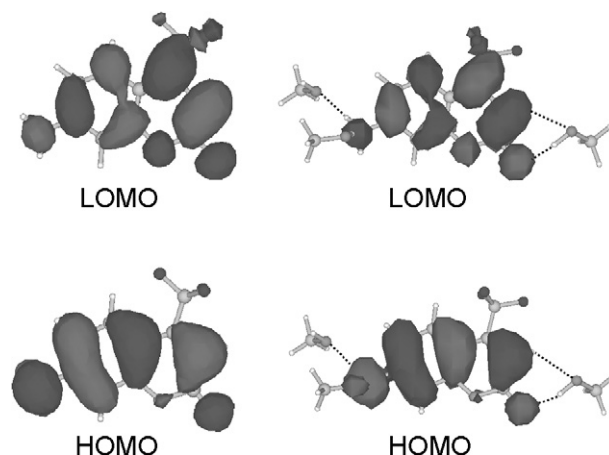


Fig. 2. Frontier molecular orbitals of the C151 monomer and the hydrogen-bonded C151-(MeOH)₃ complex.

C151-(MeOH)₃ complex only the C151 molecule is electronically excited while the methanol moiety remains in its electronic ground state. This is similar to the case of hydrogen-bonded C102-alcohol complex [5].

The frontier molecular orbitals (MOs) of the hydrogen-bonded C151-(MeOH)₃ complex and the C151 monomer are shown in Fig. 2. From the TDDFT calculations of all the geometric conformation, the S₁ state of the isolated C151 corresponds to the orbital transition from HOMO to LUMO, it is obvious that the π character for the HOMO as well as the π* character for LUMO can be seen from Fig. 2, so the S₁ state of C151 monomer have the π-π* feature [5]. In addition, the S₃ state of the C151-(MeOH)₃ complex with the largest oscillator strength corresponds to the orbital transition from HOMO to LOMO, but the electron densities of HOMO and LOMO are entirely localized on the C151 molecule for the hydrogen-bonded C151-(MeOH)₃ complex. Thus, the S₃ state of the hydrogen-bonded C151-(MeOH)₃ complex should be the locally excited (LE) state on the C151 moiety. So it can be confirmed that only the C151 moiety is electronically excited in the S₃ state of the hydrogen-bonded C151-(MeOH)₃ complex [9,10].

The excited-state geometric optimizations for hydrogen-bonded C151-(MeOH)₃ complex and the isolated C151 have been performed using the TDDFT method. For the C151 monomer the dihedral angle between the plane of C151 molecule and the plane of amino group (-NH₂) is calculated to be 17.7° and 5.7° for the ground and excited state, respectively. For the case of the hydrogen-bonded C151-(MeOH)₃ complex, the dihedral angle between the plane of C151 molecule and the plane of amino group (-NH₂) is decreased to 17.7° in the excited state from 24.5° in ground state. It is clear that the C151 molecule becomes more planar in the electronically excited state. Thus, the lone pair electron of the amino nitrogen can be easily delocalized over the C151 molecule [5]. So the dipole moment of the isolated C151 and the hydrogen-bonded C151-(MeOH)₃ complex are increased in the excited states compared with that in the ground state. According to our result, the dipole moment of the isolated C151 is 7.086 and 11.5 D in ground state and the S₁ state, respectively. The dipole moment of the hydrogen-bonded C151-(MeOH)₃ complex is increased to 16.97 D in the electronically excited state from 11.37 D in ground state.

The calculated hydrogen bond binding energies for the three types of intermolecular hydrogen bonds as well as the corresponding bond lengths of the hydrogen bonds and the hydrogen-bonded groups in the ground and excited states for the hydrogen-bonded C151-(MeOH)₃ complex are listed in Table 2. For the intermolecular hydrogen bond C=O...H-O of type a, the hydrogen bond length of

Table 2
Calculated hydrogen bond binding energies E_b (in kJ/mol) and the corresponding hydrogen bond lengths (in Å) of the three types of hydrogen bonds in ground state (GS) and the electronically excited states (ES) of the hydrogen-bonded C151–(MeOH)₃ complex.

	C=O...H-O (Type a)				N...H-O (Type b)			N-H...O-H (Type c)			
	E_b	C=O	O...H	H-O	E_b	O-H	N...H	E_b	N-H	H...O	O-H
GS	23.95	1.222	1.908	0.983	11.17	0.984	2.017	27.34	1.029	1.925	0.972
ES	32.68	1.229	1.888	0.985	9.889	0.981	2.060	36.67	1.036	1.834	0.973

O...H is calculated to be 1.888 Å in the excited state, which is shortened compared with that in the ground state. At the same time, the calculated bond length of the hydrogen-bonded C=O and H-O groups are slightly increased to 1.229 and 0.985 Å in the excited state. The changes of the bond lengths for the hydrogen bond C=O...H-O suggest that intermolecular hydrogen bond C=O...H-O is strengthened in the excited state compared to that in the ground state. Furthermore, one can find that the calculated hydrogen bond binding energy for this hydrogen bond is significantly increased to 32.68 kJ/mol in the excited state from 23.95 kJ/mol in ground state. Thus, it is confirmed that the intermolecular hydrogen bond C=O...H-O is strengthened in the electronically excited state. For the intermolecular hydrogen bond N...H-O of the type b, the hydrogen bond binding energy is calculated to be 11.17 kJ/mol in ground state and 9.889 kJ/mol in excited state. It is distinct that this intermolecular hydrogen bond N...H-O is weak in both the ground state and electronically excited state. Moreover, this weak intermolecular hydrogen bond cannot be strongly changed in the different electronic states. The hydrogen bond binding energy of the intermolecular hydrogen bond N-H...O-H, which is of the type c, is calculated to be 36.37 kJ/mol in the electronically excited state of the hydrogen-bonded C151–(MeOH)₃ complex. By comparison with the ground-state binding energy of 27.34 kJ/mol, it is distinct that the intermolecular hydrogen bond N-H...O-H is much stronger in the electronically excited state than that in the ground state. At the same time, the hydrogen bond length between oxygen and hydrogen atom is decreased from 1.925 Å in the ground state to 1.834 Å in the excited state. The bond lengths of the hydrogen-bonded N-H and O-H groups are correspondingly increased in the excited state, which is similar to the intermolecular hydrogen bond C=O...H-O. From the discussion above, it has been demonstrated that the strong intermolecular hydrogen bonds between C151 and methanol molecules can be strengthened in the electronically excited state. Therefore, our investigations in this work strongly support the strengthening mechanism of the intermolecular hydrogen bond upon photoexcitation to the electronically excited state of the coumarin chromophores [5]. Our theoretical studies on the electronic excited-state hydrogen bonding dynamics will be helpful and useful for photochemists to understand the complex molecular photophysics and photochemistry in hydrogen bonding surroundings, such as the intramolecular charge transfer (ICT); excited-state proton transfer (ESPT); photoisomerization dynamics; multi-photon absorption and fluorescence; and drastic fluorescence quenching phenomena; etc. [53–67].

4. Conclusion

In the present work, the electronic excited-state hydrogen bonding dynamics of coumarin chromophores in alcohols is revisited. Three types of intermolecular hydrogen bonding interactions between Coumarin 151 (C151) and the hydrogen donating methanol (MeOH) solvent in the electronically excited state are investigated using the time-dependent density functional theory (TDDFT) method. In our optimized geometric conformations of the hydrogen-bonded C151–(MeOH)₃ complex, three types of intermolecular hydrogen bonds: C=O...H-O (type a), N...H-O (type b)

and N-H...O-H (type c) can be formed in the ground state of the C151 chromophore in the methanol solvent. Both the hydrogen bonds C=O...H-O and N-H...O-H are much stronger than the hydrogen bond N...H-O. In the electronically excited state, this weak intermolecular hydrogen bond N...H-O cannot be strongly changed. However, both the strong intermolecular hydrogen bonds C=O...H-O and N-H...O-H are significantly strengthened upon photoexcitation to the electronically excited state. Our theoretical results are in accordance with the spectroscopic results obtained in the fluorescence depolarization experiments. Moreover, our results have strongly confirmed that the intermolecular hydrogen bonds formed between the ground-state coumarin chromophore and alcoholic solvents can be significantly strengthened in the electronically excited state of coumarin chromophore, which has been demonstrated for the first time in the previous studies by Zhao et al. At the same time, the hydrogen bond cleavage mechanism upon photoexcitation of the coumarin chromophore has been excluded by our studies.

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