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# Time-Dependent Density Functional Theory Study on Electronically Excited States of Coumarin 102 Chromophore in Aniline Solvent: Reconsideration of the Electronic Excited-State Hydrogen-Bonding Dynamics

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The time-dependent density functional theory method was performed to investigate the electronically excited states of the hydrogen-bonded complex formed by coumarin 102 (C102) chromophore and the hydrogen-donating aniline solvent. At the same time, the electronic excited-state hydrogen-bonding dynamics for the photoexcited C102 chromophore in solution was also reconsidered. We demonstrated that the intermolecular hydrogen bond C═O···H—N between C102 and aniline molecules is significantly strengthened in the electronically excited-state upon photoexcitation, since the calculated hydrogen bond energy increases from 25.96 kJ/mol in the ground state to 37.27 kJ/mol in the electronically excited state. Furthermore, the infrared spectra of the hydrogen-bonded C102—aniline complex in both the ground state and the electronically excited state were also calculated. The hydrogen bond strengthening in the electronically excited-state was confirmed for the first time by monitoring the spectral shift of the stretching vibrational mode of the hydrogen-bonded N—H group in different electronic states. Therefore, we believed that the dispute about the intermolecular hydrogen bond cleavage or strengthening in the electronically excited-state of coumarin 102 chromophore in hydrogen donating solvents has been clarified by our studies.

## 1. Introduction

Intermolecular hydrogen bonding, as a site-specific intermolecular interaction between hydrogen donor and acceptor molecules, is central to the understanding of microscopic structure and function in many organic and biological systems.[1–3] The nature of the intermolecular hydrogen bonding in solution is of particular interest.[4,5] Until now, many experimental and theoretical methods have been extensively performed to investigate the intermolecular hydrogen bonds.[6–18] The electronic ground-state properties of hydrogen bonds have been investigated for decades, while much less is known about the properties of hydrogen bonds in the electronically excited state.[19–29] The dynamic response of the intermolecular hydrogen bonds to photoinduced changes of charge distribution in different electronic states, which is known as the hydrogen-bonding dynamics, is of great interest in photochemistry.[30–57]

Hydrogen-bonding dynamics always occurs on ultrafast timescales, which are set by vibrational motions of the hydrogen donor and acceptor groups.[49–52] It plays an important role on the electronic excited-state dynamics of the hydrogen-bonded complexes. It has been demonstrated by Zhao et al. that the hydrogen-bonding dynamics can strongly facilitate the ultrafast radiationless deactivation processes, such as internal conversion (IC)[52] and intermolecular photoinduced electron transfer (PET).[55] Femtosecond time-resolved infrared spectroscopy has shown the potential to give a good insight into the microscopic dynamics of the intermolecular hydrogen bonding and provide information on local structures.[49–54] Chudoba et al. have studied the ultrafast response of coumarin 102 (C102) to the electronic excitation in hydrogen-donating solvents using the site-specific vibational spectroscopy in the femtosecond domain.[49] The vibrational absoption of the C═O stretching band for C102 in $CHCl_3$ or phenol solvents is drastically downshifted due to the formation of the intermolecular hydrogen bond C═O···H.[49,50] Upon photoexcitation, however, the vibrational absoption of the C═O stretching band shows an ultrafast spectral blue-shift within a 200-fs time scale.[49,52] They ascribed the blue shift to the ultrafast cleavage of the intermolecular hydrogen bond C═O···H between C102 chromophore and the hydrogen-donating solvents.[49] However, it has been demonstrated that the transient spectral blue shift should be attributed to the electronic state hopping from the ground state to the first singlet ($S_1$) state of C102 completed around 200 fs by comparison of the C═O stretching mode in different electronic states calculated by Zhao et al. using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods.[51] At the same time, they also demonstrated for the first time that the intermolecular hydrogen bond between C102 and phenol is significantly strengthened, while not cleaved, in the early time of the photoexcitation to the electronically excited-state by theoretically monitoring the stretching modes of the hydrogen-bonded C═O and O—H groups.[51] Recently, Blank and coworkers proposed a new mechanism which can simultaneously accommodate both the excited-state hydrogen bond strengthening first given by Zhao and Han and the disruption of hydrogen bonding.[47] The properties of hydrogen bonds in the electronic ground state have been quite well understood; however, much

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less has been known about the properties of hydrogen bonds in the electronically excited states and their role in photochemical processes.[48,67–69]

The mechanism of hydrogen bond cleavage upon photoexcitation of chromophores in hydrogen-donating solvents is followed by Palit et al.[53,54] They studied the hydrogen-bonded coumarin—amine complexes in solution using the time-resolved vibrational spectroscopy technique.[54] The photoinduced ET reactions between coumarin and aromatic amine solvents have been widely studied due to the C═O group of coumarin chromophore is responsible for the both the hydrogen bond formation and electron acceptance.[6–13,54] They first observed the formation of the intermolecular hydrogen bond between C102 and aniline in their steady-state infrared absorption spectra.[54] Then the sub-picosecond time-resolved infrared absorption spectroscopy was applied to study the hydrogen-bonding dynamics following photoexcitation of C102 chromophore in the hydrogen-bonded C102—aniline complex.[54] They also proposed that the intermolecular hydrogen bond between C102 and aniline is cleaved within 250 fs upon photoexcitation at 400 nm.[54] However, the hydrogen bond cleavage in the electronically excited state of hydrogen-bonded donor—acceptor complexes cannot be reasonably understood. Thus, to clarify that the intermolecular hydrogen bond between C102 and aniline is cleaved or strengthened upon photoexcitation, more theoretical studies on the hydrogen-bonding dynamics of the hydrogen-bonded C102—amine complex in electronically excited states are needed.

In the present work, the hydrogen-bonding dynamics of the photoexcited C102 in hydrogen donating aniline solvent has been investigated using the TDDFT method. The TDDFT method has become very useful for theoretically studying the hydrogen-bonding dynamics by optimizing the electronic excited-state geometric conformations of the hydrogen-bonded complexes and monitoring the spectral shifts of some characterized vibrational modes involved in the formation of hydrogen bonds in electronically excited states.[51,52,55–57] So the excited-state infrared spectra of the hydrogen-bonded C102-aniline complex are also calculated by the TDDFT method. We have demonstrated that the intermolecular hydrogen bond between C102 and aniline is transiently strengthened in the excited state upon photoexcitation at 400 nm by monitoring the spectral shift of the N—H stretching mode in different electronic states of the hydrogen-bonded C102—aniline complex. Furthermore, the intermolecular hydrogen bonding energies in different electronic states are also calculated. At the same time, the basis set superposition error (BSSE) is calculated for the intermolecular hydrogen bonding energy using the above methods is at the range of 1—2 kJ/mol, which is much smaller than the intermolecular hydrogen bonding energies. The calculated hydrogen bonding energies in different electronic states confirms the electronic excited-state hydrogen-bond strengthening. Our calculated results are in accordance with the mechanism of the hydrogen-bond strengthening in the electronically excited-state given by Zhao et al. in their previous investigations, while in contrast with the mechanism of hydrogen bond cleavage.[49–52]

## 2. Theoretical Methods

The DFT method with Becke's three-parameter hybrid exchange function with Lee—Yang—Parr gradient-corrected correlation functional (B3LYP functional) was used to perform the ground-state geometric optimization.[58] At the same time, the triple-$\zeta$ valence quality with one set of polarization functions (TZVP) was chosen as basis sets throughout.[59] On the other hand, the excited-state geometric optimization was performed using the time-dependent density functional theory (TDDFT) method with B3LYP functional and the TZVP basis set.[58–60] In both the ground-state and excited-state geometric optimizations, fine quadrature grids 4 were employed. Furthermore, the excited-state infrared spectra were also calculated at the level of the TD-B3LYP with the basis set TZVP. Harmonic vibrational frequencies in the ground state and the excited state were determined by diagonalization of the Hessian.[60] The excited-state Hessian was obtained by numerical differentiation of analytical gradients using central differences and default displacements of 0.02 Bohr.[61] The infrared intensities were determined from the gradients of the dipole moment.[61,62] All the calculations were performed by the quantum chemical Turbomole program suite.

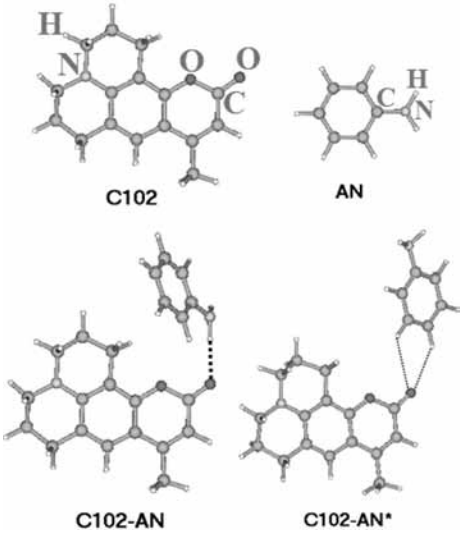

**Figure 1.** Optimized geometric structures of the hydrogen-bonded C102-AN complex as well as the isolated C102 chromophore and aniline. Dotted lines denote the intermolecular hydrogen bonds. Thinner dotted lines label weaker hydrogen bonding interactions.

## 3. Results and Discussion

The geometric structure of the hydrogen-bonded C102—aniline complex in ground state is first studied. Herein, two possible conformations of the hydrogen-bonded C102—aniline complex are discussed. The optimized ground-state conformations of the hydrogen-bonded C102—aniline complex and the involved monomers are presented in Figure 1. C102-AN stands for the case of the interaction between C═O group of C102 and the amino group of aniline, while C102-AN* is for the case of interaction between C═O group and the benzene ring moiety of aniline. From our optimization results, one can find that both the isolated C102 and aniline molecules have the planar conformations. However, the aniline molecule always resides out of the plane of C102 molecule in the C102—aniline complex. This is similar to the case of hydrogen-bonded C102—phenol complex.[51] The dihedral angle between the plane of C102 and aniline molecules is 24.2° and 57.9° for C102-AN and C102-AN*, respectively. Moreover, it is noted that the amino group of aniline becomes slightly pyramidal in both C102-AN and C102-AN* complexes.

To quantitatively study the interactions between C102 and aniline, we have calculated the interaction energies between C102 and aniline in the ground state. The calculated interaction energies are 25.96 and 6.017 kJ/mol for C102-AN and C102-AN*, respectively. In addition, the calculated distance between

**TABLE 1: Electronic Excitation Energies (in eV) and Corresponding Oscillator Strengths (in Parentheses) of the Low-Lying Electronically Excited States[a]**

| | C102 | C102-AN | C102-AN* |
|---|---|---|---|
| $S_1$ | 3.562(0.354) H→L 96.0% | 2.820 (0.001) H→L 99.8% | 3.319 (0.002) H→L 99.9% |
| $S_2$ | 4.106(0.004) | 3.454 (0.315) H-1→L 96.1% | 3.543 (0.350) H-1→L 96.1% |
| $S_3$ | 4.504(0.087) | 4.063 (0.008) | 4.102 (0.004) |
| $S_4$ | 4.632(0.000) | 4.150 (0.000) | 4.425 (0.000) |
| $S_5$ | 4.867(0.015) | 4.272 (0.002) | 4.500 (0.079) |

[a] Dominant contributions of the orbital transitions for these electronic states are also listed (H, HOMO; L, LUMO).

oxygen atom of C═O group in C102 and the nearest hydrogen atom of amino group in aniline is 2.052 Å. The distances between oxygen atom of C═O group in C102 and the two nearest hydrogen atoms of aromatic ring in aniline are calculated to be 2.782 and 3.020 Å. Therefore, it is evident that C102-AN is the more possible hydrogen-bonded C102−aniline complex in solution.

The electronic excitation energies and corresponding oscillator strengths of the low-lying electronically excited states for the isolated C102 and hydrogen-bonded C102-AN complex are presented in Table 1. For comparison, the excitation energies of C102-AN* are also listed here. One can find that the electronic excitation energies of the hydrogen-bonded C102-AN complex are correspondingly decreased compared to that of C102-AN* due to the stronger intermolecular interactions in C102-AN complex. It should be noted that the $S_2$ state of both the C102-AN and C102-AN* dimers has the largest oscillator strength and is similar to the $S_1$ state of the isolated C102. Thus, the hydrogen-bonded C102−aniline complex can be directly photoexcited to the $S_2$ state, which is similar to the hydrogen-bonded C102−phenol complex.[51] In addition, a lowest electronic state in energy with very weak oscillator strength can be found in both the complexes. So this state may be a charge transfer (CT) state below the lowest electronically excited state. Although it has been reported that this kind of CT excited state with a null oscillator strength may be fake, the calculated results can be demonstrated reliable due to that the photoinduced electron transfer process between C102 and aniline solvent has been reported in experiments.[54,63–66]

To demonstrate the nature of the low-lying electronically excited states, the frontier molecular orbitals (MOs) of the hydrogen-bonded C102-AN complex are shown in Figure 2. It can be clearly seen that the electron density of HOMO is entirely localized on the aniline molecule. However, the electron densities of LUMO+1, LUMO, and HOMO−1 orbitals are completely localized on the C102 moiety. From the contributions of the orbital transitions for the low-lying electronic states listed in Table 1, the $S_1$ state of the hydrogen-bonded C102-AN complex mainly corresponds to the orbital transition from HOMO to LUMO. Thus, it is confirmed that the lowest $S_1$ state in energy with very weak oscillator strength is a CT state and the electron transfer occurs from aniline solvent to the C102 chromophore.[55] Moreover, the $S_2$ state with the largest oscillator strength of the hydrogen-bonded C102-AN complex is dominantly corresponding to the orbital transition from HOMO−1 to LUMO. Therefore, the $S_2$ state of the hydrogen-bonded C102-AN complex should be the locally excited (LE) state on the C102 moiety.[51,63–66] In addition, it is distinct that the transition from HOMO−1 to LUMO involves the intramolecular charge redistribution from the N atom to the carbonyl group moiety. Thus, the electron density of the carbonyl group in the $S_2$ state will be increased. The intermolecular hydrogen bond between C102 and aniline may be strengthened in the $S_2$ state.

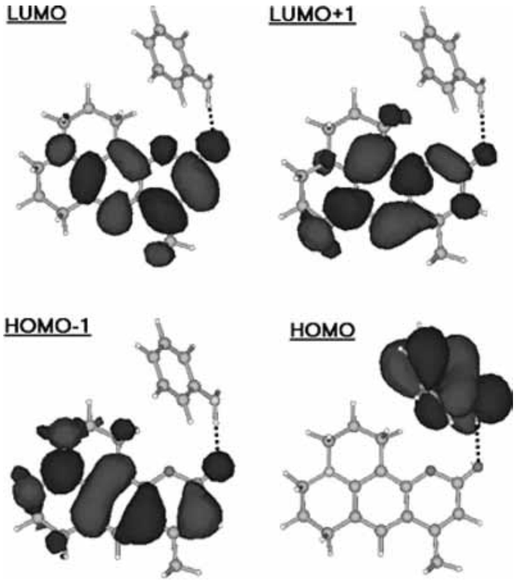

**Figure 2.** Frontier molecular orbitals (MOs) of the hydrogen-bonded C102-AN complex.

It has been demonstrated that the electronic excited-state hydrogen-bonding dynamics for organic chromophores in solution can be reliably studied using the hydrogen-bonded complex model, in which only the solvent molecules in the inner solvation shell are involved.[51–57] So we will study the hydrogen-bonding dynamics using the hydrogen-bonded C102−aniline complex as discussed above. The hydrogen-bonded C102−aniline complex is directly photoexcited to the $S_2$ state. So the geometry optimization of the hydrogen-bonded C102-AN complex in the $S_2$ state has been carried out using the TDDFT method. Moreover, to depict the hydrogen bond response upon electronic excitation, we also calculated the excited-state infrared spectra of the hydrogen-bonded C102-AN complex using the same method. It should be noted that the calculation of the infrared spectra in electronically excited states is difficult and very time-consuming.[30–38,52] Due to the LE nature of the $S_2$ state of the hydrogen-bonded C102-AN complex, only the C102 moiety is electronically excited in this state, while the aniline moiety remains in its ground state. So the stretching vibrational mode of C═O group in C102 chromophore can be influenced by both the hydrogen bonding and the electronic excitation, while the stretching mode of the hydrogen-bonded N−H group in aniline reflects directly the change of the hydrogen bonding interaction, similar to the case of the hydrogen-bonded C102−phenol complex.[51] Thus, only the infrared spectra of hydrogen-bonded C102-AN complex in different electronic states as well as the isolated aniline in the ground state at the spectral region of the N−H stretching band are shown in Figure 3.

From Figure 3, one can see that the stretching vibrational modes of the two N−H groups in the ground state of the isolated aniline molecule are the same and located at 3631 cm$^{-1}$.

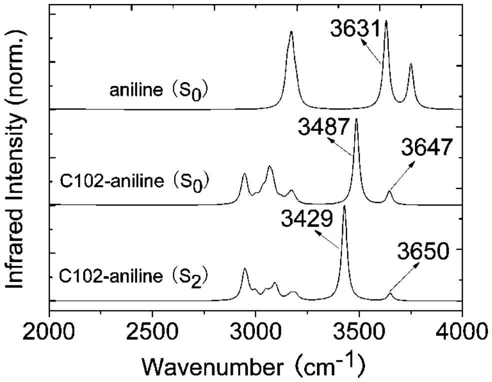

**Figure 3.** Calculated infrared spectra of the hydrogen-bonded C102-AN complex in different electronic states at the spectral region of N−H stretching vibrational band. The infrared spectra of isolated aniline in the ground state are also shown.

**TABLE 2: Calculated Hydrogen Bonding Energies $E_{HB}$ (in kJ/mol) and Corresponding Lengths (in Å) of Hydrogen Bonds and Hydrogen-Bonded Groups in Different Electronic States**

| | $E_{HB}$ | $L_{C=O}$ | $L_{O\cdots H}$ | $L_{H-N}$ |
|---|---|---|---|---|
| $S_0$ | 25.96 | 1.214 | 2.052 | 1.015 |
| $S_2$ | 37.27 | 1.228 | 1.968 | 1.019 |

However, the peak at 3631 cm$^{-1}$ is divided into two peaks with different intensity in the ground-state infrared spectra of the hydrogen-bonded C102-AN complex. The stronger peak should be assigned as the stretching vibrational mode of the H−N group in the hydrogen bond C=O···H−N, while the weak one is assigned as the stretching vibrational mode of the free N−H group in aniline molecule. It should be noted that the stretching vibrational frequency of the free H−N group in the ground-state of the hydrogen-bonded C102-AN complex is blueshifted from 3631 to 3647 cm$^{-1}$ due to the pyramidalization of the amino group in aniline molecule. In addition, the ground-state stretching mode of the hydrogen-bonded N−H group is significantly red-shifted to 3487 cm$^{-1}$. Upon electronic excitation to the $S_2$ state of the hydrogen-bonded C102-AN complex, the stretching vibrational frequency of the free N−H group is found to remain nearly unchanged. This indicates that the aniline moiety is not strongly influenced by the electronic excitation to the $S_2$ state, which is in accordance with the LE nature of the $S_2$ state of the hydrogen-bonded C102-AN complex. At the same time, the stretching vibrational mode of the hydrogen-bonded N−H group is red-shifted by 58 cm$^{-1}$ from 3487 to 3429 cm$^{-1}$ in the $S_2$ state of the hydrogen-bonded C102-AN complex. This means that the intermolecular hydrogen bonding interaction induces a larger spectral redshift of the N−H stretching mode in the excited-state than that in the ground state. Therefore, the intermolecular hydrogen bond C=O···H−N between C102 chromophore and aniline solvent is strengthened in the electronically excited-state of the hydrogen-bonded C102-AN complex.[51,66]

The calculated hydrogen bonding energies and the corresponding hydrogen bond lengths, as well as the bond lengths of hydrogen bonded groups both in the ground and excited states are listed in Table 2. It can be evidently demonstrated that the intermolecular hydrogen bond C=O···H−N is significantly strengthened, since the hydrogen bond binding energy increases from 25.96 kJ/mol in the ground state to 37.27 kJ/mol in the excited state. Therefore, the relatively weak intermolecular hydrogen bond C=O···H−N between C102 and aniline in the ground state becomes a strong hydrogen bond in the $S_2$ state. At the same time, the corresponding hydrogen bond length between oxygen and hydrogen atom decreases from 2.052 Å in the ground state to 1.968 Å in the excited state. Furthermore, the bond lengths of both the C=O and O−H groups in the hydrogen bond C=O···H−N are slightly increased in the excited state, similar to the case of the hydrogen-bonded C102-phenol complex. Moreover, the intermolecular hydrogen bond strengthening behavior upon photoexcitation to the LE state of C102 chromophore in aniline solvent may be related to the electron transfer process between C102 chromophore and aniline solvent. The strengthening of the intermolecular hydrogen bond C=O···H−N in the LE state can increase the electronic coupling between C102 and aniline molecules,[51,55–57] and thus it may facilitate the following electron transfer in the CT state of C102 chromophore.

## 4. Conclusions

In the present work, two ground-state geometric conformations of the hydrogen-bonded complexes formed by C102 chromophore and aniline have been optimized at the level of B3LYP with the TZVP basis set. A hydrogen-bonded C102−aniline complex, which is bonded by the intermolecular hydrogen bond C=O···H−N with a hydrogen bonding energy of 25.96 kJ/mol, is found to be more stable. The excited-state geometries of the hydrogen-bonded C102−aniline complex have also been optimized at the level of TD-B3LYP with the same basis set as ground state. The calculated hydrogen bonding energy for the intermolecular hydrogen bond C=O···H−N is markedly increased to 37.27 kJ/mol in the electronically excited-state of the hydrogen-bonded C102−aniline complex. Thus, it has been demonstrated that the intermolecular hydrogen bond C=O···H−N between C102 and aniline is transiently strengthened in the electronically excited state upon photoexcitation by a 400-nm laser pulse. Moreover, the intermolecular hydrogen bond strengthening has also been confirmed by monitoring the infrared spectral shift of N−H stretching mode in different electronic states of the hydrogen-bonded C102−aniline complex for the first time. Consequently, our calculated results coincide with the mechanism of the intermolecular hydrogen bond strengthening in the electronically excited-state of C102 chromophore, which are in contrast with the hydrogen bond cleavage mechanism. Our present work demonstrates the electronic excited-state hydrogen bond strengthening for C102 chromophore again. The dynamic effects of the hydrogen bonding in the electronically excited state will attract more and more attentions for photochemists. Moreover, more computational studies in our group on the intermolecular hydrogen bonding in electronically excited states for other interesting systems are ongoing.

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