J. Phys. Chem. A **2007,** *111,* 2469−2474

Early Time Hydrogen-Bonding Dynamics of Photoexcited Coumarin 102 in Hydrogen-Donating Solvents: Theoretical Study

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Received: December 7, 2006; In Final Form: January 8, 2007

To study the early time hydrogen-bonding dynamics of chromophore in hydrogen-donating solvents upon photoexcitation, the infrared spectra of the hydrogen-bonded solute−solvent complexes in electronically excited states have been calculated using the time-dependent density functional theory (TDDFT) method. The hydrogen-bonding dynamics in electronically excited states can be widely monitored by the spectral shifts of some characteristic vibrational modes involved in the formation of hydrogen bonds. In this study, we have demonstrated that the intermolecular hydrogen bonds between coumarin 102 (C102) and hydrogen-donating solvents are strengthened in the early time of photoexcitation to the electronically excited state by theoretically monitoring the stretching modes of C═O and H−O groups. This is significantly contrasted with the ultrafast hydrogen bond cleavage taking place within a 200-fs time scale upon electronic excitation, proposed in many femtosecond time-resolved vibrational spectroscopy experiments. The transient hydrogen bond strengthening behaviors in excited states of chromophores in hydrogen-donating solvents, which we have demonstrated here for the first time, may take place widely in many other systems in solution and are very important to explain the fluorescence-quenching phenomena associated with some radiationless deactivation processes, for example, the ultrafast solute−solvent intermolecular electron transfer and the internal conversion process from the fluorescent state to the ground state.

Introduction

The phenomenon of hydrogen bonding has been recognized for its importance in physics, chemistry, and biology. The nature of the hydrogen bond in solution is of particular interest and has been investigated extensively by diverse experimental and theoretical methods since solute−solvent interactions play a fundamental role in molecular nonequilibrium processes in liquids.[1−26] In some cases, the solute molecules in the ground state can form hydrogen-bonded complexes with the solvent molecules. Upon photoexcitation, as a consequence of significant difference in charge distribution for the different electronic states, the solute and solvent molecules that are engaged in the formation of hydrogen bonds need to reorganize themselves.[1−8,19] This process is defined as hydrogen-bonding dynamics, and it controls the excited-state dynamics of hydrogen-bonded complexes in a significant way.[9−19] Until now, however, there has been very little information on the structural and relaxation dynamics of hydrogen bonds upon photoexcitation.[9,16]

As we know, hydrogen-bonding dynamics occurs on ultrafast time scales mainly set by vibrational motions of the hydrogen donor and acceptor groups.[10−15] Therefore, experiments performed using the femtosecond time-resolved vibrational spectroscopy have shown the potential to monitor hydrogen-bonding dynamics.[1,19] The changes in site-specific hydrogen-bonding interactions can induce spectral shifts of some characteristic vibrational modes involved in the formation of hydrogen bonds.[1−13] So, in studies of the ultrafast response of coumarin 102 (C102) to electronic excitation in hydrogen-donating solvents using site-specific vibrational spectroscopy in the femtosecond domain, insights into local changes in site-specific hydrogen-bonding interactions between C102 and the hydrogen-donating solvents have been provided.[1,11−14] Upon electronic excitation, the vibrational absorption of the C═O stretching band for the C102 chromophore in $CHCl_3$ or phenol solvents, which is drastically downshifted because of the formation of hydrogen bond C═O···H in the ground state, shows an ultrafast spectral blueshift within a 200-fs time scale.[1,11−13] Nibbering and co-workers ascribed it to the ultrafast cleavage of hydrogen bond C═O···H in the excited state upon electronic excitation for the first time.[1,13] Palit and co-workers then followed this mechanism of hydrogen bond cleavage upon photoexcitation of chromophore in hydrogen-donating solvents.[17,19] Furthermore, the photon echo experiments demonstrated that the electronic state hopping from ground to the initially excited state of C102 completes around 200 fs, that is, the C102 molecule gets to its equilibrium positions of initially excited state within 200-fs time scale after electronic excitation.[13] Since the hydrogen-bonding dynamics and the electronic state hopping take place in the same time scale, they should be coupled to each other.[13] Because of the limited spectral resolution for the femtosecond laser pulses, hydrogen-bonding dynamics occurring in the early time of photoexcitation is difficult to monitor directly in the femtosecond experiments.

Theoretical calculations for excited states can give a clear picture of the early time hydrogen bond response to electronic excitations.[23−32] Recently, Sobolewski and Domcke investigated the equilibrium geometries and vibrational spectra of anthranilic acid (AA) and salicylic acid (SA) in $S_1(\pi\pi^*)$ excited state using the time-dependent density functional theory (TDDFT) method.[25] By theoretically monitoring the spectral shift of some characteristic hydrogen-bonding vibrational modes in excited states,

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10.1021/jp068420j CCC: $37.00

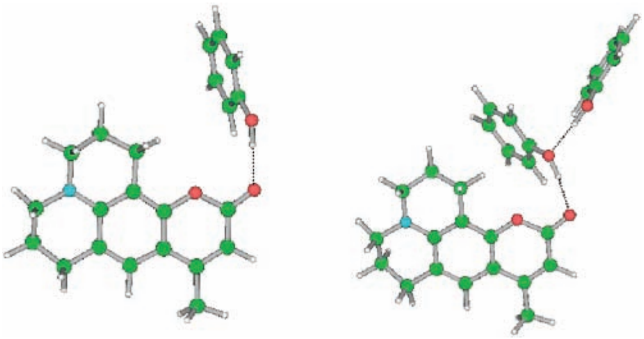

Figure 1. Geometric structures of hydrogen-bonded C102−(phenol)$_{1,2}$ complexes. Dotted lines denote the intermolecular hydrogen bonds. Taken as ref 13.

a significant strengthening of the intramolecular hydrogen bond upon electronic excitation was predicted for both systems. Their theoretical results were in excellent agreement with the recent UV−IR double-resonance experiment performed by Southern et al.[26] This suggested that the TDDFT method is a reliable tool for the calculation of the infrared spectra in the electronically excited state.[24−32] However, to our knowledge, there have been no such theoretical studies about hydrogen-bonding dynamics in electronically excited states of chromophores in hydrogen-donating solvents. In the present work, we have employed the TDDFT method for the calculations of excited-state minimum geometries, energetics, vibrational frequencies, and IR intensities of the isolated C102 and hydrogen-bonded C102−(phenol)$_{1,2}$ complexes (see Figure 1). Since only the inner solvent molecules can be attributed to the early time hydrogen-bonding dynamics occurring in ultrafast time scale, the hydrogen-bonded complexes proposed here are good models for studying the ultrafast hydrogen-bonding dynamics in solutions. The C102−phenol and C102−(phenol)$_2$ correspond to high and low concentrations of C102 in phenol solvent, respectively.[11] We focused our attention on the transient changes of intermolecular hydrogen bonds in the early time of electronic excitation to see whether the hydrogen bond could be cleaved.

Theoretical Methods

In the present work, generalized gradient approximation (GGA) for exchange correlation potential [B-P86] was employed both in the density functional theory (DFT) calculation for ground state and time-dependent density functional theory (TDDFT) calculation for excited state.[33−38] The resolution-of-the-identity (RI) approximation was also used to improve the efficiency without sacrificing the accuracy of the results.[34−36] 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.[37] Fine quadrature grids of size 4 were also employed. Harmonic vibrational frequencies in the ground state and the excited state were determined by diagonalization of the Hessian. The excited-state Hessian was obtained by numerical differentiation of analytical gradients using central differences and default displacements of 0.02 Bohr. The IR intensities were determined from the gradients of the dipole moment.[33] All the electronic structure calculations were carried out using the TURBOMOLE program suite.[38]

Results and Discussion

Geometric Structures of Hydrogen-Bonded Complexes. To delineate the detailed aspects of hydrogen-bonding dynamics, we have been motivated to theoretically study the isolated C102 and hydrogen-bonded C102−(phenol)$_{1,2}$ complexes. In Figure 1, the geometric structures of the hydrogen-bonded C102−(phenol)$_{1,2}$ complexes in ground state are shown. C102 is used as an ideal probe molecule to study the hydrogen-bonding dynamics, since the C═O group is the only site that is responsible for hydrogen bond formation in hydrogen-donating environments.[17,19] Thus, one can find that only the hydrogen bond C═O···H−O can be formed between C102 and phenols. In both the conformations, the hydrogen bond C═O···H−O remains in the plane of the C102 molecule. However, the phenyl moiety resides out of the plane. The length of the hydrogen bond C═O···H−O between H and O atom is 1.786 and 1.680 Å for the hydrogen-bonded C102−phenol and C102−(phenol)$_2$ complexes, respectively. This indicates that the hydrogen bond C═O···H−O is strengthened because of the influence of the other hydrogen bond O−H···O−H with a hydrogen bond length of 1.778 Å. In addition, the hydrogen bond binding energies of C═O···H−O are calculated to be 36.8 kJ/mol for the C102−phenol dimer. As predicted by the lengths of hydrogen bonds, a stronger hydrogen bond C═O···H−O with a binding energy of 54.3 kJ/mol and a weaker hydrogen bond O−H···O−H with a binding energy of 36.9 kJ/mol coexist in the C102−(phenol)$_2$ trimer. Interestingly, we can find that the lengths of both the C═O and H−O bonds are increased because of the formation of the hydrogen bond C═O···H−O. The C═O bond length is increased to 1.231 Å from 1.215 Å for the hydrogen-bonded dimer. For the more strongly hydrogen-bonded trimer, the C═O bond is lengthened to 1.237 Å. So, this suggests that the C═O bond length will be increased with the strengthening of the intermolecular hydrogen-bonding interactions. At the same time, the H−O bond length is also influenced by the formation of the intermolecular hydrogen bonds C═O···H−O and O−H···O−H. For the hydrogen-bonded C102−phenol dimer, the H−O bond length is increased to 0.995 Å from the free bond length of 0.974 Å. In the hydrogen-bonded C102−(phenol)$_2$ trimer, the H−O bond lengths are 1.007 and 0.993 Å for the hydrogen bonds C═O···H−O and O−H···O−H, respectively. Therefore, we can also conclude that the H−O bond will be lengthened in stronger hydrogen bonds.

TABLE 1: Calculated Electronic Excitation Energies (eV) and Corresponding Oscillator Strengths (in the Parenthesis) of the Low-Lying Electronically Excited States for Isolated C102 and Hydrogen-Bonded C102−(phenol)$_{1,2}$ Complexes

	C102	C102−phenol	C102−(phenol)$_2$
S_1	3.066(0.232)	2.126(0.001)	2.191(0.000)
S_2	3.614(0.042)	2.931(0.213)	2.400(0.002)
S_3	3.868(0.000)	3.123(0.001)	2.875(0.211)
S_4	4.010(0.074)	3.385(0.000)	3.115(0.000)
S_5	4.379(0.061)	3.596(0.044)	3.214(0.000)

Nature of Low-Lying Excited States. Before we discuss the properties of excited states for C102 and its hydrogen-bonded complexes, it is useful to understand the nature of the low-lying electronically excited states. The electronic excitation energies and corresponding oscillator strengths of the hydrogen-bonded C102−(phenol)$_{1,2}$ complexes as well as the C102 monomer are presented in Table 1. The S_2 state of the C102−phenol dimer has the largest oscillator strength. Thus, the hydrogen-bonded C102−phenol dimer can be initially photoexcited to the S_2 state. Moreover, the S_2 state of the dimer is very close in energy to the S_1 state of isolated C102. By comparing the electronic excitation energies of hydrogen-bonded C102−phenol dimer with that of C102 monomer, an additional electronic state with very small oscillator strength can be found. This dark state is located 0.9 eV below the S_1 state of isolated

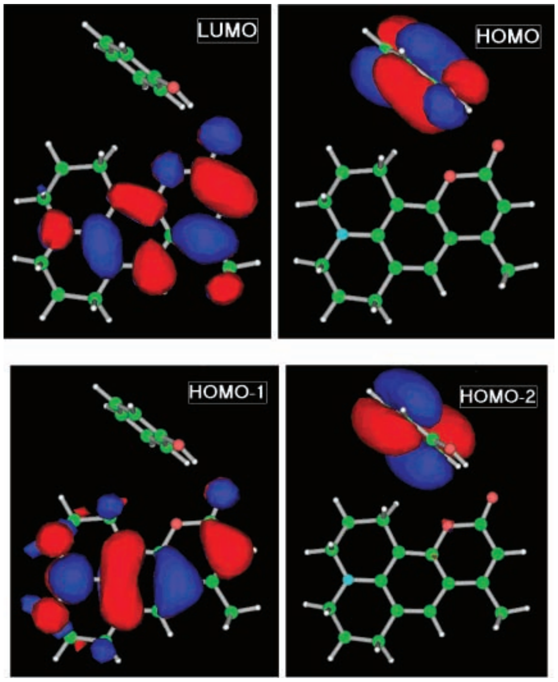

Figure 2. Frontier molecular orbitals (MOs) of hydrogen-bonded C102−phenol complex.

C102. Since the S_1 state of the C102−phenol dimer with weak oscillator strengths is lower in energy than any intramolecular excited states of isolated C102, it might be from the interactions between C102 and phenol.[39] It can be expected that in the S_2 state of the hydrogen-bonded C102−phenol dimer only the C102 molecule is electronically excited while the phenol moiety remains in its electronic ground state. We can also find that the excitation energies for all the electronic excited states of isolated C102 are correspondingly lowered because of the influence of the intermolecular hydrogen-bonding interactions. Furthermore, the corresponding oscillator strengths are slightly reduced. For the case of the hydrogen-bonded C102−$(\text{phenol})_2$ trimer, two additional dark states are lying lower in energy than the S_1 state of isolated C102. The S_3 state of the trimer with the largest oscillator strength is close in energy to the S_1 state of C102 monomer. So, the lower-lying dark states may also be from the interactions between C102 and phenols.[39] All of the calculated maximum absorption energies of the hydrogen-bonded complexes are around 400 nm, which is in good agreement with the maximum absorption peak in experiments.[1,11]

As we know, molecular orbitals (MOs) analysis can directly provide insight into the nature of the excited states.[40] In Figure 2, we show the frontier molecular orbitals of the hydrogen-bonded C102−phenol dimer. It can be clearly seen that both the electron densities of LUMO and HOMO-1 orbitals are entirely localized over the C102 molecule. However, both the densities of HOMO and HOMO-2 orbitals are completely localized in the phenol moiety. From the TDDFT calculations of all the geometric conformations, the S_2 state with the largest oscillator strength of the hydrogen-bonded dimer corresponds to the orbital transition from HOMO-1 to LUMO. Thus, the S_2 state of the C102−phenol dimer should be the locally excited (LE) state on C102 moiety.[39,40] It is evident that the S_2 state is of the $\pi\pi^*$ character from Figure 2. In addition, the lone pair electron of nitrogen atom can be excited into the conjugative moiety of C102 molecule. The charge redistribution occurs in C102 molecule upon photoexcitation to the S_2 state of the C102−phenol dimer. However, the S_1 state of the C102−phenol dimer may be charge-transfer (CT) state, since it corresponds to the orbital transition from HOMO to LUMO. So, charge-transfer reaction between C102 and hydrogen-donating solvents may take place in this CT state. C102 chromophore is usually used as good probe for studying the solvation dynamics. The intermolecular charge-transfer reaction between C102 and solvents occurs much slower than the solvation dynamics.[22] Thus, the CT state should not contribute to the early time hydrogen-bonding dynamics within 200-fs time scale. Herein, we will focus our attention on the early time hydrogen bond response on the photoexcitation only in the LE state. As discussed above, the photoexcited C102 molecule can get to the equilibrium geometry of initially excited state within 200-fs time scale. Thus, only the LE state can be involved in the early time hydrogen-bonding dynamics. For the case of the hydrogen-bonded C102−$(\text{phenol})_2$ complex, the S_3 state has the LE nature which is localized on C102, while the two lower-lying states are of the CT character between C102 and phenols. Therefore, only the S_3 state of the hydrogen-bonded C102−$(\text{phenol})_2$ complex is associated with the early time hydrogen-bonding dynamics occurring within 200-fs time scale.

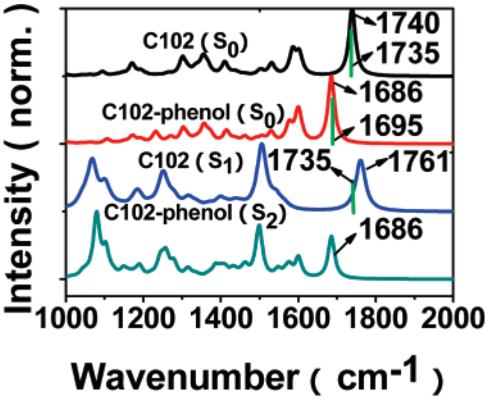

Figure 3. Calculated C═O stretching bands of isolated C102 and hydrogen-bonded C102−phenol dimer in different electronic states. The green lines show the experimental C═O stretching vibrational frequency in different states.

Infrared Spectra of Ground and Excited States. As is well-known, the vibrational frequencies of the stretching vibrations of C═O and O−H groups involved in hydrogen bonds can provide a clear-cut signature of the hydrogen-bonding dynamics.[19,25] Herein, all of the IR spectra of isolated molecules and the hydrogen-bonded complexes in both the ground state and the excited state initially prepared by photoexcitation at 400 nm are calculated. The calculation of the IR spectra in electronically excited states is difficult and very time-consuming. The calculated IR spectra in different electronic states at the spectral range from 1000 to 2000 cm^{-1} are shown in Figure 3. The C═O stretching band of C102 chromophore in nonpolar C_2Cl_4 solvent measured by the femtosecond vibrational spectroscopy is also shown as green lines. One can find that the calculated C═O stretching vibrational frequency in the ground state (1740 cm^{-1}) is in good agreement with the experimental value (1735 cm^{-1}). Upon electronic excitation, the C═O stretching band is blueshifted from 1740 cm^{-1} in the ground state to 1761 cm^{-1} in the relaxed S_1 state. The spectral shift of the C═O stretching band in excited states can be driven by changes of local charge distribution, since the electronic state hopping from ground state to the S_1 state is followed by the intramolecular charge redistribution in the S_1 state of C102.[1,13] Thus, the ultrafast blueshift of the C═O stretching band should be attributed to the electronic state hopping from ground state to the S_1 state of C102 which occurs around 200 fs.

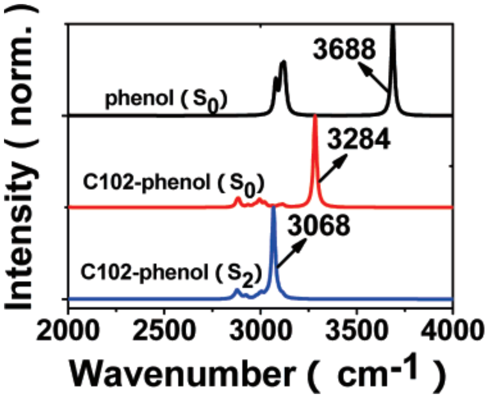

Figure 4. Calculated IR spectra of hydrogen-bonded C102−phenol dimer at the spectral region of O−H stretching band.

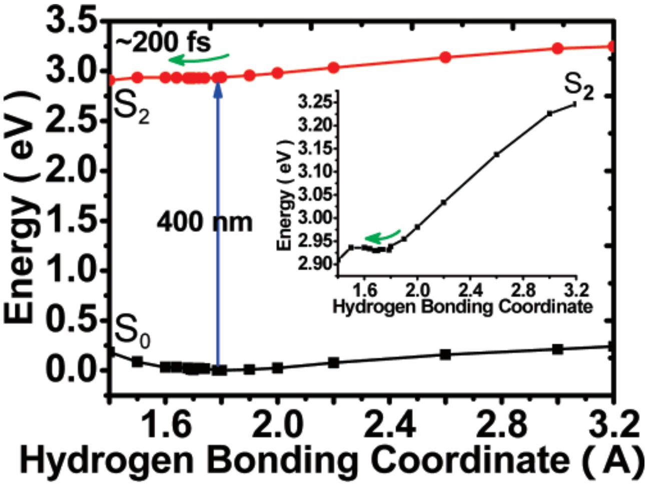

Figure 5. Potential energy curves for ground state (S_0) and the excited state (S_2) of the hydrogen-bonded C102−phenol complex along with the hydrogen-bonding coordinate (distance between O and H in hydrogen bond C═O···H−O, Å). The inset shows the detailed potential energy curve of the S_2 state.

In Figure 3, the calculated vibrational absorption spectra of hydrogen-bonded C102−phenol dimer in the spectral region of the C═O stretching band are shown. The C═O stretching bands of C102 monomer in different electronic states are used here for comparison. The C═O stretching vibrational frequency in the ground state is strongly downshifted by 55 cm^{-1} from 1741 to 1686 cm^{-1} because of the formation of hydrogen bond C═O···H−O, which is in accordance with the experimental results for C102 in polar phenol solvent (downshifted from 1735 to 1695 cm^{-1}).[11,13] However, compared with the C═O stretching vibrational frequency of isolated C102 in the excited state, the C═O stretching vibrational frequency of hydrogen-bonded C102−phenol complex in the excited state is downshifted by 75 cm^{-1} from 1761 to 1686 cm^{-1}. That is to say, the C═O stretching mode has a larger redshift which is induced by the intermolecular hydrogen bond C═O···H−O between C102 and phenol in the excited state (75 cm^{-1}) than in the ground state (55 cm^{-1}).

The IR spectra of hydrogen-bonded C102−phenol dimer in different electronic states and the free phenol in the ground state in the spectral region of the O−H stretching band are shown in Figure 4. The formation of hydrogen bond C═O···H−O between C102 and phenol induces a strong redshift of 404 cm^{-1} for the O−H stretching band from the free O−H stretching vibrational frequency of 3688 cm^{-1} for isolated phenol. Upon electronic excitation to the excited state of hydrogen-bonded C102−phenol dimer, the O−H stretching band continues to downshift from 3284 to 3068 cm^{-1}. This means that the intermolecular hydrogen-bonding interactions can induce a larger spectral redshift of the O−H stretching band in the excited state than that in the ground state.

As discussed above, both the C═O and O−H stretching bands in the ground state are strongly downshifted because of the formation of intermolecular hydrogen bond C═O···H−O between C102 and phenol. Interestingly, in the excited state, the intermolecular hydrogen-bonding interactions can induce larger spectral redshifts for both the C═O and O−H stretching modes in the hydrogen-bonded C102−phenol complex. Since the stretching mode can undergo a shift to lower frequency for stronger hydrogen-bonding interaction,[41,42] the larger redshift of the C═O and O−H stretching bands in excited states evidently suggests that the intermolecular hydrogen bond C═O···H−O should be strengthened in the excited states.

Potential Energy Curves. In Figure 5, the calculated potential energy curves are shown for the ground state and the S_2 state of the hydrogen-bonded C102−phenol dimer with the hydrogen-bonding coordinate. This will be helpful for understanding the mechanism of hydrogen-bonding dynamics in the excited states of hydrogen-bonded complexes.[23−25] The hydrogen-bonded C102−phenol complex is optimized using the same method as above through partial relaxation except the hydrogen-bonding degrees of freedom before the calculations of electronic excitation. As shown in Figure 5, the hydrogen-bonded C102−phenol dimer is transiently excited from the equilibrium ground state to the S_2 state by a laser pulse at around 400 nm, which is in very good agreement with the experimental excitation wavelength. Then, the hydrogen-bonded C102−phenol complex in the Franck−Condon (FC) region of S_2 state relaxes to the equilibrium region of the same electronic state within 200 fs, since the electronic state hopping from ground state to electronically excited state has been experimentally observed to be completed in this time scale.[13] From the potential energy curve of the S_2 state along the hydrogen-bonding coordinate, the length of the hydrogen bond C═O···H−O between H and O atoms is shortened from 1.786 to 1.691 Å during the relaxation process. Therefore, the substantial strengthening of intermolecular hydrogen-bonding interactions between C102 and hydrogen-donating solvents takes place in the early time of electronic excitation.

TABLE 2: Hydrogen Bond Binding Energies E_{HB} (kJ/mol) and the Corresponding Hydrogen Bond Lengths $L_{O\cdots H}$ (Å) between Oxygen and Hydrogen Atoms. The Bond Lengths of $L_{C=O}$ (Å) and L_{H-O} (Å) and Dipole Moment μ (D) in Different Electronic States Are Also Shown

	phenol		C102		C102−phenol					C102−(phenol)$_2$[a]					C102−(phenol)$_2$[b]		
	L_{H-O}	μ	$L_{C=O}$	μ	E_{HB}	$L_{C=O}$	$L_{O\cdots H}$	L_{H-O}	μ	E_{HB}	$L_{C=O}$	$L_{O\cdots H}$	L_{H-O}	μ	E_{HB}	$L_{O\cdots H}$	L_{H-O}
S_0	0.974	1.35	1.215	7.32	36.8	1.231	1.786	0.995	10.0	54.3	1.237	1.680	1.007	9.59	36.9	1.778	0.993
S_1			1.220	11.9													
S_2					51.5	1.246	1.691	1.007	12.9								
S_3										62.7	1.253	1.580	1.025	11.8	36.1	1.723	1.001

[a] Hydrogen bond C═O···H−O. [b] Hydrogen bond O−H···O−H.

Hydrogen Bond Binding Energy. Because of the LE nature of the electronically excited states of the hydrogen-bonded complexes considered here, the hydrogen bond binding energy in excited states can be easily computed by the energy of the hydrogen-bonded complex in the excited state minus the energy of C102 in its S_1 state and the energy of phenol in its ground state. The calculated hydrogen bond binding energies for the hydrogen-bonded C102−(phenol)$_{1,2}$ complexes and the corresponding hydrogen bond lengths in the excited states are listed in Table 2. It can be seen that the hydrogen bond O−H···O−H between two phenols remains nearly unchanged upon electronic excitation. However, the binding energy of hydrogen bond C═O···H−O between C102 and phenol in the excited states is substantially larger than that in the ground state for both the C102−phenol and C102−(phenol)$_2$ complexes. So, the intermolecular hydrogen-bonding interactions between C102 and phenols are evidently strengthened in the electronically excited states. Furthermore, the calculated dipole moments and lengths of the bonds associated with the formation of hydrogen bonds are also shown in Table 2. One can find that there are no significant changes of dipole moments between ground and the LE states for the hydrogen-bonded complexes. This means that no marked charge redistribution occurs between C102 and phenols, and this is consistent with the LE nature of the excited states. Both the C═O and H−O bonds are lengthened, while the length of hydrogen bond C═O···H−O is correspondingly shortened in the excited states of the hydrogen-bonded complexes. Thus, the strengthening of the intermolecular hydrogen bond C═O···H−O in the initially photoexcited states can be strongly supported.

In this work, the intermolecular hydrogen bonds strengthening behavior for chromophores in hydrogen-donating solvents upon electronic excitation, which is similar to the intramolecular hydrogen bond strengthening for the gas-phase anthranilic acid (AA) and salicylic acid (SA) in the $S_1(\pi\pi^*)$ excited state,[25] is demonstrated for the first time. The novel transient hydrogen bond strengthening behavior upon photoexcitation may take place widely in many other systems in solution. Since fluorescence of chromophore in hydrogen-donating environments can be strongly quenched via hydrogen-bonding interactions,[43−50] the ultrafast hydrogen bond strengthening may play an important role for directly influencing the early time radiationless deactivation processes associated with the fluorescence quenching. Further investigations on the role of hydrogen bond strengthening for the fluorescence quenching are ongoing.

Conclusions

In summary, we theoretically studied the hydrogen-bonded C102−(phenol)$_{1,2}$ complexes, especially focusing on the transient change of the intermolecular hydrogen bonds between chromophores and hydrogen-donating solvents upon photoexcitation. It is distinctly demonstrated for the first time that the intermolecular hydrogen bonds between chromophores and hydrogen-donating solvents are transiently strengthened, not cleaved, in the early time of photoexcitation to the electronically excited states of chromophores in the hydrogen-donating solvents. Following the electronic state hopping from ground state to S_1 state of C102 completed around 200 fs, a transient blueshift for the calculated C═O stretching band of C102 can be found in the electronically excited state. Thus, the ultrafast blueshift taking place within the 200-fs time scale observed in experiments should be attributed to the electronic state hopping from ground state to excited state of C102. Moreover, the hydrogen-bonded C102−phenol complex can be initially excited to the S_2 state of the LE nature localized on the C102 moiety in the early time of photoexcitation at 400 nm. The infrared spectra of the hydrogen-bonded solute−solvent complexes in the electronically excited states were calculated for the first time. The strengthening of intermolecular hydrogen bonds between C102 and hydrogen-donating solvents was confirmed by the calculated infrared spectra for the hydrogen-bonding groups. The strongly downshifted C═O and O−H stretching bands in the ground state, because of the formation of intermolecular hydrogen bond C═O···H−O between C102 and phenol, can be induced by larger spectral redshifts of the intermolecular hydrogen-bonding interactions in the electronically excited state. Therefore, it is clearly demonstrated that the intermolecular hydrogen bonds between C102 and hydrogen-donating solvents are strengthened upon photoexcitation.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 20373071 and No. 20333050).

Supporting Information Available: Optimized geometric coordinates of the molecules involved here are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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