Ultrafast Hydrogen Bond Strengthening of the Photoexcited Fluorenone in Alcohols for Facilitating the Fluorescence Quenching†

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The time-dependent density functional theory (TDDFT) method was performed to investigate the excited-state hydrogen-bonding dynamics of fluorenone (FN) in hydrogen donating methanol (MeOH) solvent. The infrared spectra of the hydrogen-bonded FN−MeOH complex in both the ground state and the electronically excited states are calculated using the TDDFT method, since the ultrafast hydrogen-bonding dynamics can be investigated by monitoring the vibrational absorption spectra of some hydrogen-bonded groups in different electronic states. We demonstrated that the intermolecular hydrogen bond C═O···H−O between fluorenone and methanol molecules is significantly strengthened in the electronically excited-state upon photoexcitation of the hydrogen-bonded FM−MeOH complex. The hydrogen bond strengthening in electronically excited states can be used to explain well all the spectral features of fluorenone chromophore in alcoholic solvents. Furthermore, the radiationless deactivation via internal conversion (IC) can be facilitated by the hydrogen bond strengthening in the excited state. At the same time, quantum yields of the excited-state deactivation via fluorescence are correspondingly decreased. Therefore, the total fluorescence of fluorenone in polar protic solvents can be drastically quenched by hydrogen bonding.

1. Introduction

The solute−solvent interactions, which play a fundamental role for molecular nonequilibrium processes in liquids, have been one of the focal points of solution chemistry.[1−50] Solute−solvent interactions are mainly due to the dielectric properties of the solvents. Since the range of the Coulomb interaction is large compared to the structure in the radial distribution function of the solvent, such interactions are often termed "nonspecific", implying that no specific chemical bonds are formed or broken between the solute and the solvent.[1−5] Intermolecular hydrogen bonding, as a site-specific interaction between hydrogen donor and acceptor molecules, is another important type of solute−solvent interactions.[4,6] It is central to the understanding of microscopic structure and function in many molecular systems, such as hydrogen-bonded water or alcohols networks, proteins, and DNA building blocks of the life.[6−32] The dynamic aspects of polar solvation have been studied extensively and have resulted in a detailed description of polar solvation.[4] In contrast, relatively few studies on the dynamic aspects of solvation by site-specific hydrogen bonding interactions have been carried out.[6−17,31] So we have not much information on structural and relaxation dynamics of hydrogen bonds after electronic excitation of chromophores in hydrogen donating environments.

Hydrogen-bonding dynamics occurs on ultrafast time scales 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.[6−32] Thus, femtosecond time-resolved vibrational spectroscopy has shown the potential to give a good insight into the microscopic dynamics and provide information on local structures.[7,31] On the other hand, time-dependent density functional theory (TDDFT) method has been demonstrated as a reliable tool to calculate the vibrational absorption spectra in electronically excited states.[27−38] So TDDFT method has become very useful for theoretically studying the hydrogen-bonding dynamics by monitoring the spectral shifts of some characterized vibrational modes involved in the formation of hydrogen bonds in different electronic states. In the previous paper, we have studied the early time hydrogen-bonding dynamics of the photoexcited coumarin chromophore in hydrogen donating solvents using the TDDFT method.[31] In this work, the TDDFT method has also been used to investigate extensively the excited-state hydrogen-bonding dynamics of the fluorenone chromophore.

As we know, fluorescent chromophores are optically active probe molecules with widespread applications in chemistry and biology.[5,39−50] The primary photophysics of fluorenone has been well studied because fluorenone exhibits some rather unique spectroscopic and photophysical properties that have made it the subject of many investigations.[16,39] In general, fluorenone is very weakly fluorescent in solution. In aprotic solvents, processes following excitation to the S_1 state are governed essentially by the dependence of intersystem crossing (ISC) to the triplet state on the solvent polarity. However, in protic solvents, the triplet state yield falls and the internal conversion (IC) from the fluorescent state to ground state becomes the most important dissipative process.[16,39] In this quenching process, the hydrogen bond acts as an efficient accepting mode for radiationless deactivation processes.[39] It has been demonstrated that deactivation of excited-state via IC can be strongly enhanced by the intermolecular hydrogen bonding interactions.[16,39] So the hydrogen-bonding dynamics in fluorescent states may play an important role for this quenching process. However, we do not have much knowledge about the hydrogen-bonding dynamics in electronically excited states of fluorenone chromophore in hydrogen donating solvents.

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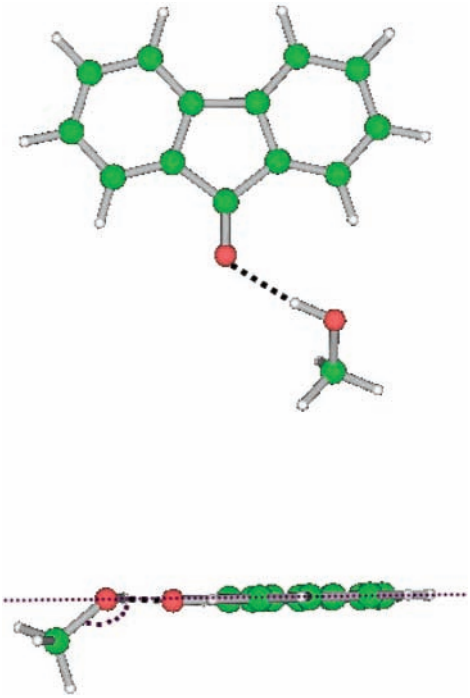

Figure 1. Optimized geometric structures of the hydrogen-bonded FN−MeOH complex.

In the present work, to delineate the detailed aspects of hydrogen-bonding dynamics, we have been motivated to study theoretically the hydrogen-bonded FN−MeOH complex as well as the isolated fluorenone (FN) chromophore (see Figure 1). We focused our attention on the transient changes of intermolecular hydrogen bonds following the electronic excitation of the hydrogen-bonded FN−MeOH complex. Since only the solvent molecules in the inner solvation shell can be attributed to the early time hydrogen-bonding dynamics occurring in ultrafast time scale, the hydrogen-bonded complex proposed here is a good model for studying the ultrafast hydrogen-bonding dynamics in solutions.[31] The geometric structures and energetics of the hydrogen-bonded complexes in ground state and the S_1 electronic state, which corresponds to the state photoexcited by 400 nm laser pulse in experiment, were investigated here. In particular, the vibrational absorption of hydrogen-bonded groups and the hydrogen bond binding energies in different electronic states were analyzed in detail, since they could directly provide indication of the hydrogen-bonding dynamics. In this work, we theoretically demonstrated that the intermolecular hydrogen bond C═O···H−O between fluorenone and methanol is strengthened in the electronically excited-state of the hydrogen-bonded complex upon photoexcitation. The hydrogen bond strengthening facilitates the radiationless deactivation from the fluorescent state to ground state via IC process, and thus the hydrogen bond can act as an efficient accepting mode for radiationless deactivation processes. Moreover, the experimental spectra of fluorenone chromophore in the hydrogen donating solvents can be reasonablely explained by the hydrogen bond strengthening mechanism.

2. Theoretical Methods

All the electronic structure calculations were carried out using the *TURBOMOLE* program suite.[51−55] The geometry optimizations of the isolated monomers and the hydrogen-bonded solute−solvent complexes considered here for the ground state were performed, using density functional theory (DFT) with Becke's three-parameter hybrid exchange function with Lee−Yang−Parr gradient-corrected correlation functional (B3-LYP functional).[52] The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen for basis sets throughout.[53] The excited-state electronic structures were calculated using time-dependent density functional theory (TD−DFT) with B3-LYP hybrid functional and the TZVP basis set. Fine quadrature grids 4 were also employed.[54] Both the convergence thresholds for the ground-state and excited-state optimization were reset to be 10^{-8} (default settings are 10^{-6}). The excited-state Hessian was obtained by the numerical differentiation of analytical gradients using central differences and default displacements of 0.02 Bohr.[55] The infrared intensities were determined from the gradients of the dipole moment.

3. Results and Discussion

Geometric Structures in the Ground State. To investigate the ultrafast hydrogen-bonding dynamics of the fluorenone chromophore in alcoholic solvents, a hydrogen-bonded fluorenone−alcohol complex has been used here. As we know, alcoholic molecules tend to cluster together either in pure alcohols or in concentrated alcohol−water solution.[56,57] Moreover, it has been indicated that the hydrogen bond cooperative and geometric effects may play important roles in some hydrogen-bonding systems.[58−63] Therefore, many solvation shells around the fluorenone chromophore can be formed by the alcoholic solvents. Since the hydrogen-bonding dynamics takes place on ultrafast time scales mainly set by vibrational motions of the hydrogen donor and acceptor groups, only the alcoholic molecules in the inner solvation shell of the photoexcited fluorenone chromophore can be attributed to the early time hydrogen-bonding dynamics occurring in ultrafast time scale.[31,32] In addition, the C═O group of fluorenone is the only site which is responsible for both hydrogen bond formation and electron acceptance, only one hydrogen bond C═O···H−O can be formed between fluorenone and methanol.[16,17] Consequently, the only one methanol in the first solvation shell, which is directly hydrogen-bonded with fluorenone chromophore, is involved in this work without consideration of the bulk effect of the outer solvation shells. The hydrogen-bonded FN−MeOH complex as well as the involved fluorenone and methanol monomers have been fully optimized. In Figure 1, the optimized geometric structure of the hydrogen-bonded FN−MeOH dimer is shown. The hydrogen bond C═O···H−O formed between fluorenone and methanol molecules remains on the plane of the fluorenone molecule, while the methyl group of methanol molecule resides out of the plane. The angles formed by C═O···H and O−H···O are calculated to be 125 and 168°, respectively. In addition, the calculated dihedral angle between the plane of fluorenone molecule and the C−O group of methanol molecule is −137°. The bond lengths of free C═O and H−O groups in isolated fluorenone and methanol molecules are calculated to be 1.212 and 0.963 Å, respectively, while the calculated bond lengths in the hydrogen bond C═O···H−O are lengthened to 1.219 and 0.972 Å for the C═O and H−O groups, respectively. Thus, the bond lengths of the hydrogen-bonded groups are slightly lengthened due to the formation of intermolecular hydrogen bond C═O···H−O, similar to the case of the hydrogen-bonded coumarin 102-phenol complex.[31] In addition, the length of the hydrogen bond C═O···H−O between oxygen and hydrogen atoms is calculated to be 1.906 Å, and the calculated hydrogen bond binding energy is 27.85 kJ/mol. Herein, both the bond length and binding energy for hydrogen bond C═O···H−O suggest that the intermolecular hydrogen

TABLE 1: Electronic Excitation Energies (nm) and Corresponding Oscillator Strengths of the Hydrogen-Bonded FN−MeOH Complex as Well as the Isolated Fluorenone (FN)

	FN	FN−MeOH
S_1	392(0.004)	411(0.003)
S_2	390(0.000)	375(0.000)
S_3	305(0.016)	345(0.003)
S_4	276(0.032)	314(0.036)
S_5	255(0.000)	281(0.034)
S_6	249(0.869)	250(0.137)
S_7	242(0.043)	250(0.719)
S_8	233(0.005)	247(0.058)
S_9	226(0.003)	239(0.000)

bond C═O···H−O between fluorenone and methanol is not very strong. By the way, Samant et al. have also mentioned a plane conformation with a methanol molecule in the plane of fluorenone.[16] Since this geometric conformation of the hydrogen-bonded FN−MeOH complex is much less stable than our conformation discussed above,[64] we will mainly investigate the geometric conformation shown in Figure 1 in this work.

Electronic Spectra. The electronic excitation energies and corresponding oscillator strengths of the hydrogen-bonded FN−MeOH complex as well as the fluorenone and methanol monomers are presented in Table 1. One can find that the absorption maxima for both fluorenone monomer and hydrogen-bonded FN−MeOH complex are located in higher energy levels than the S_1 state, which is in accordance with the experimental absorption spectra of fluorenone in nonpolar and polar solvents.[16,39] In addition, the electronic excitation energies of the hydrogen-bonded complex are correspondingly decreased compared to that of the isolated fluorenone due to the solute−solvent intermolecular hydrogen bonding interactions. The oscillator strengths of the lowest excited S_1 state of both the fluorenone molecule and the fluorenone-methanol complex are very small, which may be due to the $\pi-\pi^*$ excitation for the S_1 state. The relatively weak S_1absorption peak is calculated to be at 392 and 411 nm for the isolated fluorenone and the hydrogen-bonded FN−MeOH complex, respectively. It is in good agreement with the S_1 absorption peaks of the non-hydrogen-bonded and hydrogen-bonded forms for fluorenone in methanol located at around 379 and 403 nm in the experimental absorption spectra.[16] Moreover, we know that the two forms in the ground state are in equilibrium. Since it is observed that the absorption peak at 379 nm is stronger than the peak at 403 nm in experiments, the equilibrium is strongly in favor of the free form.[16] This is in accordance with the relatively small hydrogen bond binding energy in ground state calculated above. To distinctly see the shape of the absorption spectra, we show the calculated absorption spectra from 170 to 700 nm in Figure 2. It can be clearly found that the very strong absorption peaks for isolated fluorenone and its hydrogen-bonded complex are at around 250 nm. However, a stronger absorption band is located below 200 nm. Moreover, there has a relatively weak S_1 absorption band at around 400 nm. One can see that all the calculated absorption spectral features are in good agreement with the spectral results recorded in experiments.[16] It is confirmed that the hydrogen-bonded FN−MeOH complex presented here can be viewed as a good model to simulate the solute−solvent interaction between the fluorenone chromophore and the methanol solvent without consideration of the bulk effect of the methanol solvent in the outer solvation shells. On the other hand, it can also demonstrated that the intermolecular hydrogen bonding interaction between fluorenone and the methanol in the first solvation shell

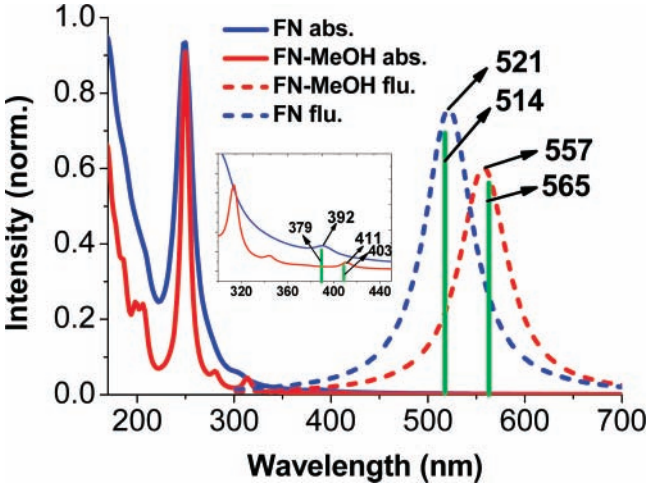

Figure 2. Calculated absorption and fluorescence spectra of isolated fluorenone and the hydrogen-bonded FN−MeOH complex. Inset shows the details of the absorption bands for the S_1 state; Green lines denote the corresponding peaks in experiments.

plays a dominant role on the steady-state and dynamic spectral properties of the fluorenone chromophore in methanol solvent.

From the calculated electronic excitation energies, we can find that the methanol moiety in hydrogen-bonded FN−MeOH dimer will remain in its electronic ground state upon photoexcitation by 400 nm laser pulse used in the experiment, while the fluorenone moiety of the hydrogen-bonded FN−MeOH complex can be electronically excited to the S_1 state. Thus, we consider only the S_1 state in the present work. The electronically excited S_1 state of isolated fluorenone and its hydrogen-bonded FN−MeOH complex are fully optimized using the ground-state optimized geometric conformations as the initial conformations with the TDDFT method. Consequently, the fluorescence emission energies for the isolated fluorenone and the hydrogen-bonded complex are calculated. We also show the calculated fluorescence spectra in Figure 2. The fluorescence maxima are located at 521 nm for the isolated fluorenone while they are at 557 nm for the hydrogen-bonded FN−MeOH complex; i.e., the formation of hydrogen bond C═O···H−O can induce fluorescence peak shifts by 36 nm to the red. The dual fluorescence behavior of fluorenone in alcoholic solutions at the room temperature has been observed in experiments.[16] The two emission bands with maxima at 514 and 565 nm, respectively, are believed to arise from the S_1 state of the non-hydrogen-bonded (or free) fluorenone and the hydrogen-bonded complex, respectively. Therefore, the assignments for the two fluorescence bands in experiments can be confirmed, and the calculated fluorescence emission energies here are in good agreement with the experimental fluorescence spectra. At the same time, it is demonstrated that the calculated excited states of isolated fluorenone and the hydrogen-bonded FN−MeOH complex using the TDDFT method can well delineate the excited states of the non-hydrogen-bonded and hydrogen-bonded forms in solution.

Frontier Molecular Orbitals (MOs). Before discussing the hydrogen-bonding dynamics in S_1 state of the hydrogen-bonded FN−MeOH complex, it is useful to understand the nature of the excited state. The frontier molecular orbitals (MOs) of the hydrogen-bonded FN−MeOH complex are shown in Figure 3. Since the S_1 state of the hydrogen-bonded complex corresponds to the orbital transition from HOMO to LUMO according to our TDDFT results, only the HOMO and LUMO orbitals are exhibited here. The π character for the HOMO as well as the π^* character for LUMO can be clearly seen from Figure 3. Therefore, it is confirmed that the S_1 state is due to a distinct

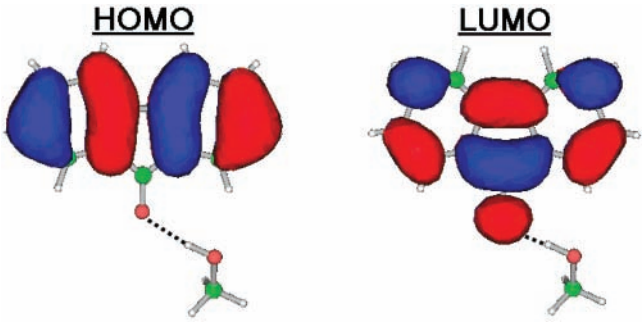

Figure 3. Frontier molecular orbitals (MOs) of the hydrogen-bonded FN−MeOH complex.

$\pi\pi^*$ feature. Moreover, the unoccupied orbital of oxygen atom in C═O group is also involved in the transition. So the charge transfer can occur between the aromatic moiety and the C═O group. Thus, the electron density of the C═O group increases after the transition from HOMO to LUMO. Meanwhile, the change of electron density in the C═O group can directly influence the intermolecular hydrogen bonding between C═O and H−O groups.

Moreover, it should be noted that the electron densities of both the HOMO and LUMO are strictly localized on the fluorenone moiety. So upon photoexcitation to S_1 state of the hydrogen-bonded FN−MeOH dimer, only the fluorenone moiety can be electronically excited while the methanol molecule always remains in its electronic ground state. This is in accordance with the discussion about the electronic excitation energies. As a result, the S_1 state of the hydrogen-bonded FN−MeOH complex can be assigned as a locally excited (LE) state on fluorenone molecule.[65] According to our calculated results, the dipole moment of isolated fluorenone is increased to 5.982 D upon excitation to the S_1 state from 3.520 D in ground state. This can be attributed to the intramolecular charge transfer between the aromatic moiety and carbonyl group in fluorenone. However, the dipole moment of the hydrogen-bonded FN−MeOH complex is calculated to be 4.061 and 6.759 D for ground state and the S_1 state, respectively. It is evidently shown that no significant change of dipole moment of fluorenone in both ground and excited states can be induced by the intermolecular hydrogen bonding interactions. So there has been no drastic intermolecular charge redistribution between fluorenone and methanol molecules. This is in accordance with the LE nature of the S_1 state for the hydrogen-bonded FN−MeOH dimer. The LE nature of the excited-state for fluorenone chromophore in hydrogen donating methanol solvent may make it easy to monitor the early time hydrogen-bonding dynamics in the electronically excited states.[31]

Vibrational Absorption Spectra. It has been demonstrated that the early time hydrogen-bonding dynamics can be investigated by monitoring the vibrational absorption spectra of some hydrogen-bonded groups in electronically excited states.[9,31] To depict the hydrogen bond response upon electronic excitation, we calculated the excited-state infrared spectra of the hydrogen-bonded FN−MeOH complex as well as the isolated fluorenone using the TDDFT method. The vibrational absorption spectra of isolated fluorenone in different electronic states are shown in Figure 4. Since the changes of site-specific hydrogen bonding interactions can induce the spectral shifts of some characterized vibrational modes involved in the potential formation of hydrogen bonds, we have only given the stretching vibrational frequency of C═O group in different electronic states here.[11,16] It is noted that the stretching mode of C═O group drastically

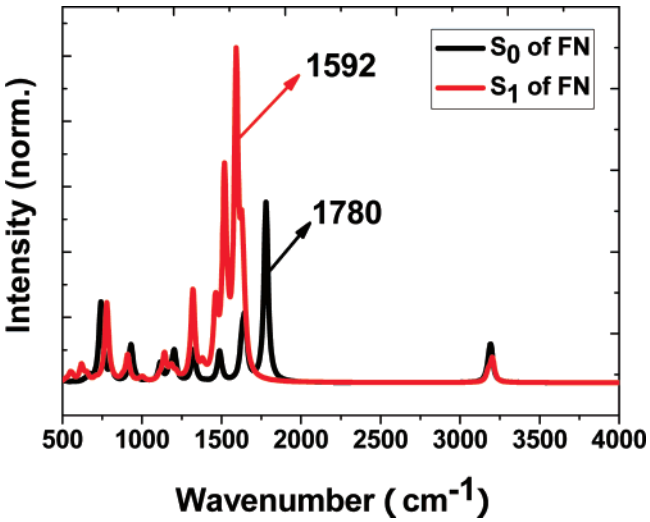

Figure 4. Calculated vibrational absorption spectra of isolated fluorenone in different electronic states.

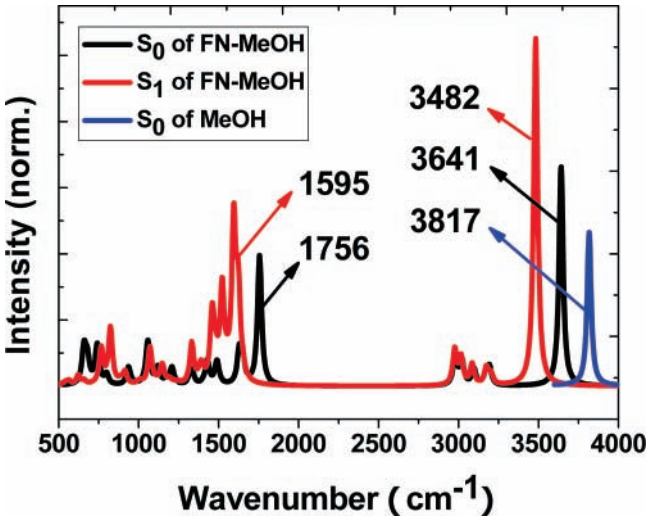

Figure 5. Calculated vibrational absorption spectra of the hydrogen-bonded FN−MeOH complex in different electronic states. The H−O stretching vibrational band of free methanol in ground state is also shown.

shifts to the red by 188 cm^{-1} upon electronic excitation (from 1780 cm^{-1} in ground state to 1592 cm^{-1} in S_1 electronic state).

The calculated vibrational absorption spectra of the hydrogen-bonded FN−MeOH complex are shown in Figure 5. Herein, the stretching vibrational frequencies of both C═O group and H−O group in different electronic states are given. One can find that the formation of intermolecular hydrogen bond C═O···H−O induces the stretching mode of C═O group a slight redshift of 24 cm^{-1} (from 1780 cm^{-1} in isolated fluorenone to 1756 cm^{-1} in the hydrogen-bonded FN−MeOH complex). As discussed above, the stretching mode of C═O group can be drastically red-shifted by 188 cm^{-1} upon electronic excitation. Therefore, both the electronic excitation and intermolecular hydrogen bonding interactions can shift the stretching vibrational mode of C═O group to the red. However, the hydrogen bonding interactions cannot significantly influence the stretching mode of C═O group in ground state, by comparison to the electronic excitation. As a result, the stretching mode of C═O group is not a sensitive vibrational mode to monitor the hydrogen-bonding dynamics. However, the stretching mode of H−O group in ground state is markedly red-shifted from 3817 to 3641 cm^{-1} due to the formation of intermolecular hydrogen bond

TABLE 2: Calculated Hydrogen Bond Binding Energies E_b (kJ/mol) and Corresponding Lengths of Hydrogen Bonds and Hydrogen-bonding Groups in Different Electronic States

	MeOH	FN	FN−MeOH			
	L_{O-H}	$L_{C=O}$	E_b	$L_{C=O}$	$L_{O\cdots H}$	L_{O-H}
S_0	0.963	1.212	27.85	1.219	1.906	0.972
S_1		1.250	42.62	1.259	1.802	0.981

C═O···H−O. So the stretching mode of H−O group in the hydrogen-bonded FN−MeOH complex can be significantly influenced by the hydrogen bonding. On the other hand, as discussed above, the methanol moiety remains in its electronic ground state upon photoexcitation to the S_1 state of the hydrogen-bonded complex. Thus, the stretching vibrational mode of H−O cannot be strongly influenced by the electronic excitation. So the hydrogen-bonding dynamics can be distinctly reflected by monitoring the changes of the stretching vibrational mode for the H−O group in different electronic states. From Figure 5, the stretching mode of H−O group in ground state is red-shifted by 176 cm^{-1} due to the formation of intermolecular hydrogen bond C═O···H−O. Upon electronic excitation to the S_1 state of the hydrogen-bonded FN−MeOH complex, a larger redshift of 335 cm^{-1} will be found. The additional redshift of 159 cm^{-1} should be attributed to the hydrogen bond strengthening in the excited-state of the hydrogen-bonded complex.[31,66−68] Therefore, it can be strongly demonstrated that the hydrogen-bonding dynamics in the electronically excited-state can be distinctly monitored by the H−O stretching mode.

Hydrogen Bond Strengthening. Due to the LE nature of the electronically excited S_1 state of the hydrogen-bonded FN−MeOH complex, the hydrogen bond binding energy in excited states can be easily calculated by the energy of the hydrogen-bonded complex in the S_1 state minus the energy of isolated fluorenone in its S_1 state and the energy of methanol in its ground state. The calculated hydrogen bond binding energies and the corresponding hydrogen bond lengths, as well as bond lengths of the hydrogen-bonded groups both in the ground and excited states are listed in Table 2. It can be evidently concluded that the intermolecular hydrogen bond C═O···H−O is significantly strengthened since the binding energy increases from 27.85 kJ/mol in ground state to 42.62 kJ/mol in the excited state. Therefore, the relatively weak intermolecular hydrogen bond C═O···H−O between fluorenone and methanol in ground state becomes a strong hydrogen bond upon electronic excitation to the S_1 state. Furthermore, the corresponding hydrogen bond length between oxygen and hydrogen atom decreases from 1.906 Å in the ground state to 1.802 Å in the excited state. Meanwhile, the bond lengths of both the C═O and H−O groups are slightly increased in the excited state. All the calculated results are similar to the case of the hydrogen-bonded coumarin 102−phenol complex, in which the hydrogen-bonding strengthening has also been demonstrated upon photoexcitation to the electronically excited state.[31] From our calculated results, the strengthening of the intermolecular hydrogen bond C═O···H−O in the photoexcited electronic state of the hydrogen-bonded FN−MeOH complex can be strongly supported. This is significantly contrasted with the ultrafast hydrogen bond cleavage taking place within a subpicosecond time scale upon electronic excitation, proposed in the femtosecond time-resolved absorption spectroscopy studies.[16]

Fluorescence Quenching. A schematic view of the equilibrium between the free and hydrogen-bonded forms in both ground state and the excited-state is shown in Figure 6. As discussed above, the fluorenone chromophore in alcoholic solution is located in the equilibrium between the non-hydrogen-bonded (or free) and the hydrogen-bonded forms in the ground electronic state. Since the intermolecular hydrogen bonding interactions are not very strong in ground state according to our calculations, the equilibrium remains strongly in favor of the free molecules in ground state. Upon photoexcitation, the relatively weak hydrogen bonds between fluorenone and methanol solvents in ground state can be significantly strengthened in the electronically excited states. Therefore, the equilibrium in excited states will become markedly in favor of the hydrogen-bonded forms. At the same time, some free fluorenone molecules will also have the tendency to form intermolecular hydrogen bonds upon electronic excitation. Therefore, the hydrogen bond strengthening can be used to explain well the spectral features in experiments: the absorption band of the non-hydrogen-bonded fluorenone is stronger than that of the hydrogen-bonded form in ground state; on the contrary, the fluorescence band of the hydrogen-bonded form is stronger than that of the non-hydrogen-bonded form upon electronic excitation to excited states.[16] Furthermore, it should be noted that the total fluorescence of fluorenone in polar protic solvents are drastically quenched compared to that in polar aprotic solvents.[16,39] That is to say that with the increasing of the hydrogen-bonded forms in electronically excited states the quantum yields of excited-state deactivation via fluorescence are decreased. The radiationless deactivation via internal conversion (IC) becomes the main dissipative channel.[39] So the radiationless deactivation via IC can be significantly facilitated by the hydrogen bond strengthening in the excited state, since the IC process can be strongly influenced by the solute−solvent intermolecular interactions.[39,69,70] As a result, the hydrogen bond strengthening in the electronically excited-state plays an important role for increasing the IC process from the fluorescent state to the ground state.

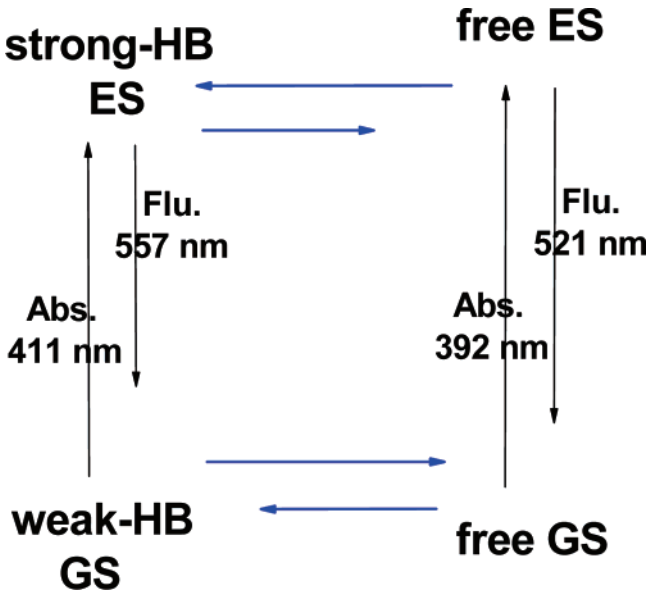

Figure 6. Schematic view of the equilibrium between the free and hydrogen-bonded forms both in ground state and the excited state. The blue arrows denote that the equilibrium remains in favor of the free molecules in ground state and becomes in favor of the hydrogen-bonded forms in the excited state.

4. Conclusion

The excited-state hydrogen-bonding dynamics of fluorenone chromophore in hydrogen donating methanol solvents was investigated using the time-dependent density functional theory

(TDDFT) method. The geometric structures and energetics of the hydrogen-bonded FN−MeOH complex as well as the isolated fluorenone in ground state and the S_1 state were discussed. All the calculated spectral features are in good agreement with the spectral results recorded in experiments. This demonstrates that the ground state and the S_1 state of the hydrogen-bonded FN−MeOH complex presented here can well delineate the ground and electronically excited states of fluorenone in methanolic solution. To investigate the detailed aspects of hydrogen-bonding dynamics, the vibrational absorption spectra of hydrogen-bonded groups both in ground state and the electronically excited-state are also calculated using the TDDFT method. By monitoring the spectral shift of the stretching vibrational mode for the hydrogen-bonded O−H group in different electronic states, it is demonstrated that the intermolecular hydrogen bond C═O···H−O between fluorenone and methanol is significantly strengthened in the electronically excited-state upon photoexcitation. Moreover, it was proposed that the radiationless deactivation of the fluorescent state via IC can be facilitated by the hydrogen bond strengthening in the excited state. At the same time, the quantum yields of excited-state deactivation via fluorescence are correspondingly decreased. As a result, the hydrogen bond strengthening plays an important role for increasing the IC process from the fluorescent state to ground state. All the other spectral features in experiments can also be explained well by the hydrogen bond strengthening in the excited state.

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