



Hydrogen-bonding dynamics of photoexcited coumarin 138 and 339 in protic methanol solution: Time-dependent density functional theory study



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ABSTRACT

The ground and electronically excited-state intermolecular hydrogen bonds between coumarin 138 (C138)/coumarin 339 (C339) and the protic methanol solvent are investigated by using time-dependent density functional theory method. The methanol solvent can act as a hydrogen-donating or hydrogen-accepting moiety at the proper site of organic chromophore. Our theoretical investigation explores the formation of one and multiple hydrogen bonds and demonstrates the strengthening of the intermolecular hydrogen bonds in the excited state. According to our calculation, upon photoexcitation the isolated coumarins and hydrogen-bonded clusters are initially excited to the first excited state and the intermolecular hydrogen bonds are strengthened in the excited state. The obvious red shifts, as large as 21 nm, of the steady-state absorption spectra are observed. In addition, the infrared spectra in the ground and excited states are calculated to explore the hydrogen bonding dynamics. The calculated C=O, N–H, O–H stretching modes are red shifted induced by the electronic excitation and intermolecular hydrogen bond interaction. The strengthening of the intermolecular hydrogen bonds is also confirmed by the geometric parameters in the ground and excited states with TDDFT method.

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1. Introduction

Intermolecular hydrogen bond is one of the site-specific interactions, which plays a fundamental role in molecular photochemistry of organic and biological chromophores in solution [1–7]. This intermolecular interaction can assemble multiple molecules into a cluster, which is formed in the ground state and influence a series of photophysical processes, such as internal conversion (IC), photoinduced proton transfer (PPT), and photoinduced electron transfer (PET) [8–14]. The numerous researchers and engineers are making efforts to understand the hydrogen bonding dynamics with theoretical and experimental methods, exploring the applications in photoelectronics, such as fluorescence probe, optical sensor and light emitting devices [6,15–22]. The hydrogen bonds in the electronically excited states can modulate the molecular non-equilibrium processes [23–27]. Because of the ultrafast time scale, the knowledge of excited-state hydrogen-bonding dynamics is rather limited. In experiments the ultrafast spectroscopy technology is widely explored to study the excited-state dynamics, however, it is also limited by the spectral resolution for the femtosecond laser

pulses. The theoretical calculations are useful to describe the early time hydrogen bond response to the electronic excitation and explain the mechanism of photophysical processes. In the past years, the time-dependent density functional theory (TDDFT) method is extensively employed to investigate the excited-state dynamics, which have been demonstrated a reliable tool to study the ultrafast photophysical phenomenon [20,28–33].

The coumarins are famous dyes, popularly used in solutions as amplifying media in tunable dye lasers. The coumarin dyes have a heterocyclic structure, which are numbered according to the specific structural features [34–38]. Different coumarins find various applications in photochemistry and photobiology. They are widely utilized as solvation probe to monitor the nature of a solvent, owing to its rigid structure and the large change in dipole moment that is caused by photoexcitation. In this paper we pay attention to two coumarin dyes namely coumarin 138 (C138) and coumarin 339 (C339) with different molecular conformations. The C138 molecule has a carbonyl group, which is active in solution and can act as a hydrogen acceptor in the protic solution [38]. In C339 molecule, there are both carbonyl group as hydrogen acceptor and imino group as hydrogen donor. Therefore, the intermolecular interactions between C339 and protic solvent are much complicated.

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In the present work, we are motivated to investigate the excited-state dynamics and corresponding photophysical properties of isolated C138, C339 and the corresponding hydrogen-bonded complexes in protic methanol solution. Because of the structural variations, these two coumarin molecules would be involved with different interactions in solution. The geometries of isolated coumarins and hydrogen-bonded complexes both in the ground and excited states are optimized with B3LYP functional. Since only the solvent molecules in the first solvation shell can contribute mostly to the hydrogen-bonding dynamics, we focused our attention on the solvent molecule directly correlated with C138 molecule. The steady-state absorption and fluorescence spectra and frontier molecular orbitals are compared between the isolated coumarins and hydrogen-bonded complexes. The vibrational motions of the hydrogen donor and acceptor groups in different electronic states are monitored to study the hydrogen bonding dynamics. With the TDDFT calculations, it is demonstrated the strengthening of the intermolecular hydrogen bonds in the excited state.

2. Theoretical method

The density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods were employed to study the structural, electronic and photophysical properties of isolated coumarins and hydrogen-bonded complexes. Becke's three parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation (B3LYP functional) and 6-311++G(d, p) basis set were employed in all the DFT and TDDFT calculations [39–43]. The optimized geometries of the ground state were obtained by using DFT method. All the vertical excited energies calculation, steady-state spectra simulation and geometric optimization in the excited state were performed by using TDDFT method. The solvent effect is considered with CPCM solvent model and cyclohexane and methanol are selected as solvents. The local minima were confirmed by the absence of an imaginary mode in vibrational analysis calculations. In the present work, all the calculations were performed using Gaussian 09 program suite [44].

3. Discussion and results

In the molecule of C138, there is carbonyl group which is responsible for the intermolecular hydrogen bond formation of $\text{C}=\text{O} \cdots \text{H}-\text{O}$ in protic solution. For C339, it is found that the intermolecular hydrogen bond $\text{N}-\text{H} \cdots \text{O}$ is formed between the imino group and methanol, and $\text{C}=\text{O} \cdots \text{H}-\text{O}$ is formed between the carbonyl group and methanol, respectively. Other possible intermolecular hydrogen bonds are also considered, however the strengths of these other hydrogen bonds are very weak and have little influence on the photophysical properties. Therefore, when considering the first solvent shell intermolecular hydrogen bonding interactions in protic solution, one intermolecular hydrogen bond in 138-MeOH and two intermolecular hydrogen bonds in 339-MeOH are studied. Fig. 1 shows the optimized geometries of isolated C138/C339 and hydrogen-bonded C138-Methanol (C138-MeOH)/C339-Methanol (C339-MeOH) complexes in the ground state with DFT method. For these coumarin molecules, they have a large conjugated heterocyclic structure and the conjugated group can keep a good planarity. The introduction of the intermolecular hydrogen bonding interactions has negligible influence on the molecular conformation of coumarin. Because of the existence of the intermolecular interaction, in C138-MeOH complex the $\text{C}=\text{O}$ bond is lengthened from 1.206 to 1.215 Å. The calculated intermolecular hydrogen bond length $\text{C}=\text{O} \cdots \text{H}-\text{O}$ in C138-MeOH is 1.944 Å in the ground state. In C339-MeOH complex, there are

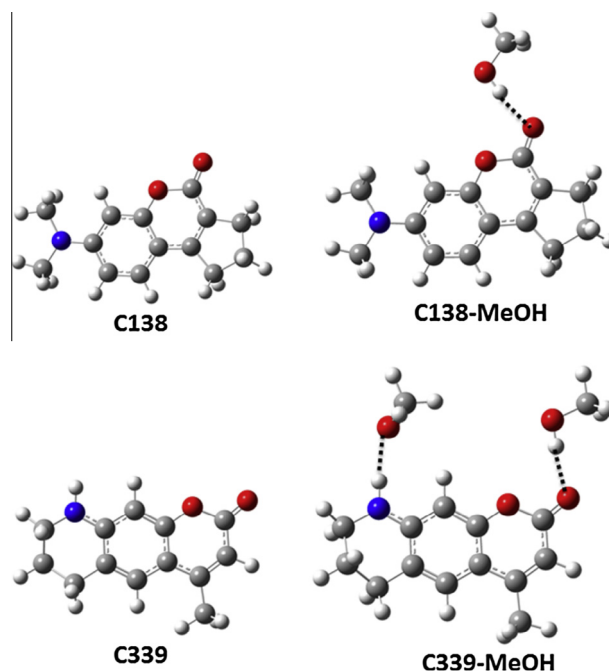


Fig. 1. The optimized structures of isolated C138/C339 and hydrogen-bonded complexes in the ground state. Red: O; Blue: N; Grey: C; White: H. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

two methanol molecules connected with C339 by the intermolecular hydrogen bonds. The methanol act as a hydrogen donor in the $\text{C}=\text{O} \cdots \text{H}-\text{O}$ interaction, oppositely, a hydrogen acceptor in the $\text{N}-\text{H} \cdots \text{O}$ interaction in C339-MeOH complex. In this three-molecule complex, the $\text{C}=\text{O}$ bond is lengthened from 1.206 to 1.217 Å and $\text{N}-\text{H}$ bond is lengthened from 1.008 to 1.015 Å due to the formation of intermolecular hydrogen bonds. The calculated intermolecular hydrogen bond length of $\text{C}=\text{O} \cdots \text{H}-\text{O}$ is 1.946 Å and $\text{N}-\text{H} \cdots \text{O}$ is 2.021 Å in C339-MeOH complex in the ground state.

Fig. 2 shows the calculated steady-state absorption and fluorescence spectra of C138, C138-MeOH, C339 and C339-MeOH. The solvent effect is considered in our calculations by using the CPCM solvent model. The coumarins are dissolved in nonpolar cyclohexane and protic methanol solutions. When the solvent is protic, the intermolecular hydrogen bonds connect coumarin and solvent molecules as a complex. For both the coumarin monomers and hydrogen-bonded complexes, the absorption are mostly distributed in the range of 200–450 nm. It's noted that there are two absorption peaks near 250 and 360 nm, which attribute to the photoexcitation from the ground state to S_2 and S_1 excited states, respectively. The strongest absorption is around 360 nm for all the investigated systems, from the S_1 photoexcitation. Though C138 and C339 have obvious difference in the molecular conformation, the absorption peaks appear in the same area. The strongest absorption peaks of C138 and C339 are 352 and 350 nm in cyclohexane solution, respectively. There are much stronger distributions in absorption spectra of C138 systems in the high energy area near 250 nm, comparing with those of C339 systems. It is remarkably found that the absorption spectra of hydrogen-bonded complexes are red shifted in comparison with respective monomers in the low energy range. The strong absorption peak of hydrogen-bonded C138-MeOH complex is 364 nm, which is red shifted by 12 nm, comparing to that of isolated C138. The absorption spectra of C339-MeOH are also red shifted to the low energy range and the 21 nm red shift of absorption peak is observed from 350 to 371 nm. The red shift of the absorption

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