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Hydrogen-bonding study of photoexcited 4-nitro-1,8-naphthalimide in hydrogen-donating solvents

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Abstract: The solute–solvent interactions of 4-nitro-1,8-naphthalimide (4NNI) as a hydrogen bond acceptor in hydrogen donating methanol (MeOH) solvent in electronic excited states were investigated by means of the time-dependent density functional theory(TDDFT). We calculated the S_0 state geometry optimizations, electronic transition energies and corresponding oscillation strengths of the low-lying electronically excited states for the isolated 4NNi and hydrogen-bonded 4NNi-$(MeOH)_{1,4}$ complexes using the density functional theory (DFT) and TDDFT methods. The electronic excitation energies of the hydrogen-bonded complexes are correspondingly decreased compared to that of the isolated 4NNi, which revealed that the intermolecular hydrogen bond C=O$\cdots$H–O and N=O$\cdots$H–O in the hydrogen-bonded 4NNi-$(MeOH)_{1,4}$ are strengthened in the electronically excited state. The calculated results are consistent with the mechanism that hydrogen bond strengthening will induce a redshift of the corresponding electronic spectra, while hydrogen bond weakening will cause a blueshift. Furthermore, we believe that the deduction we used to depict the trend of the hydrogen bond changes in excited states exists in many other fluorescent dyes in solution.

Keywords: 4-nitro-1,8-naphthalimide; Excited state; Hydrogen bonding dynamics; Electronic spectra

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1 Introduction

Solute-solvent interactions play a fundamental role in the photophysics and photochemistry of organic and biological chromophores in solution [1–7]. Intermolecular hydrogen bonding, which is an important type of solute–solvent interaction, has been investigated extensively by many experimental and theoretical methods [8–17]. Some studies show that the solvent polarity can affect the photophysics of excited states [18–26]. Moreover, site-specific interactions via hydrogen bond linking a solute with a polarizable functional group and a protic solvent can strongly affect the photophysics of excited states [27–36].

Based on the achievement in the past, the hydrogen bonding effects are central to understanding the structures and dynamics of many important molecular systems [37–40]. Experiments performed using the femtosecond time-resolved vibrational spectroscopy have shown the potential to monitor hydrogen-bonding dynamics. Hydrogen-bonding dynamics always occurs on ultrafast timescales, which plays an increasingly important role in many photophysical processes and photochemical reactions [41–53]. It has been confirmed by Zhao et al. that the intermolecular hydrogen bond in many molecular systems is greatly strengthened in the electronically excited state. Electronic excite-state hydrogen bond strengthening is closely linked with many ultrafast radiationless deactivation processes, such as ultrafast internal conversion(IC) [43] and intersystem crossing (ISC) [41], vibrational energy relaxation (VER) [54], twisted intramolecular charge transfer(TICT) [47] and intermolecular photoinduced electron transfer (PET) [45].

Previously, we studied the excited-state hydrogen-bonding dynamics of the hydrogen bonded complexes between 4-amino-1,8-naphthalimide (4ANI) and MeOH molecules in electronically excited states using the DFT and the TDDFT method [55]. The results indicated that the intermolecular hydrogen bonds C=O$\cdots$H–O and N–H$\cdots$O–H in the hydrogen-bonded 4ANi-$(MeOH)_{1,4}$ complexes are strengthened in the electronically excited state.

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However, the effects of structural alterations on the intermolecular hydrogen bond have not been studied in detail. The photophysics and photochemistry of 4-nitro -1,8-naphthalimide (4NNI) and its derivatives have been investigated widely [56–60]. Cuccovia investigated the kinetics of the aromatic nucleophilic substitution of the nitrogroup of 4-nitro-Nn-butyl-1,8-naphthalimide (4-NBN) by n-heptanethiol (RSH) [61]. Nitronaphthalimides, a particularly interesting group of nitroaromatics, are used for staining cells in hypoxia and are also important in photodynamic therapy [62–65]. Besides, 4NNI is very sensitive to both the intramolecular and intermolecular interactions, such as hydrogen bonding, polarity, stericinteraction, and so forth. However, so far little scientific information of intermolecular hydrogen bonds exists between the 4NNI and methyl alcohol molecules. In the present paper, we study the excited-state hydrogen-bonding of the hydrogen bonded complexes between 4NNI and methyl alcohol molecules in electronically excited states by theoretical calculation. In this study, the ground state structures for the isolated 4NNI monomer and the hydrogen-bonded 4NNI-$(MeOH)_{1,4}$ complexes were performed using the density functional theory (DFT). Electronic transition energies as well as corresponding oscillation strengths of the low-lying electronically excited states were investigated using the TDDFT method. We demonstrate that the electronic spectra of the hydrogen-bonded 4NNi-$(MeOH)_{1,4}$ is red-shifted, which indicates that the intermolecular hydrogen bonds in the hydrogen-bonded 4NNI-$(MeOH)_{1,4}$ complexes are strengthened in the electronically excited state. The calculated the spectral shifts confirmed the mechanism of the hydrogen bond strengthening in the electronically excited state. Different substitutions of amino and nitro groups exerted influence on the lengths of the hydrogen bond, the electronic excitation energy and the orbital transition.

2 Theoretical Methods

In this work, the isolated 4NNI monomer as well as the hydrogen-bonded 4NNI-$(MeOH)_{1,4}$ complex were studied using density functional theory (DFT) with Becke's three-parameter hybrid exchange function with Lee-Yang-Parr gradient-correlated correlation functional (B3LYP hybrid functional) [66] in the ground state. The 6-31G(d,p) [67–70] was chosen as basis sets throughout. For the excited state, however, electronic transition energies as well as corresponding oscillation strengths were performed using the time-dependent density functional theory(TDDFT) method with B3-LYP hybrid functional [71, 72]. Frequency calculations have been also performed using the same methods as those for the geometry optimizations to confirm the presence of a local minimum. All calculations were performed using the Gaussian 09 program package [73].

3 Results and Discussion

3.1 Ground-State Geometric Conformations

To understand the ultrafast hydrogen-bonding dynamics between the 4NNI and MeOH molecules, ground-state geometric optimizations of the isolated 4NNI and hydrogen-bonded 4NNI-$(MeOH)_{1,4}$ complexes were performed using DFT method, which are denoted as 4NNI-$(MeOH)_a$, 4NNI-$(MeOH)_b$, 4NNI-$(MeOH)_c$, 4NNI-$(MeOH)_d$ and 4NNI-$(MeOH)_4$. The optimized ground-state structures of the 4NNI monomer, 4NNI-$(MeOH)_a$, 4NNI-$(MeOH)_b$, 4NNI-$(MeOH)_c$, 4NNI-$(MeOH)_d$ and 4NNI-$(MeOH)_4$ are shown in Figure 1. In fact, there are two conformations of the 4NNI, the difference is whether the CH_3 group and fluorenone moieties is coplanar or out of the plane. It should be noted that there exists a lower energy for out-of-plane conformation than that of the in-plane conformation. There is the larger dihedral angle (61°) between the plane of 4NNI molecule and the CH_3-group. There are two dihedral angles (28° and 27°) between the benzene ring and the two N=O groups, which indicates two N=O groups are not co-planar with the plane of 4NNI molecule. The methanol molecule as hydrogen-bond donor resides out of the plane of 4NNI molecule and forms hydrogen-bonded 4NNI-$(MeOH)_{1,4}$ complexes. Some of the most important structural parameters have been listed in table 1.The bond lengths of free C=O and two N=O groups of nitro in 4NNI monomer are calculated to be 1.223 Å, 1.230 Å and 1.232 Å, respectively. The two C=O bond lengths in the hydrogen bond C=O···H–O are lengthened to the same numerical value for 1.229 Å in the hydrogen-bonded 4NNI-$(MeOH)_4$ complex. Additionally, one of the two N=O lengths in the hydrogen bond N=O···H–O is lengthened to 1.233 Å and the other is lengthened to 1.232 Å. We find that intermolecular hydrogen bond plays a key role in the slight lengthening of the bond lengths of C=O and the two N=O. The lengths of the hydrogen bond C=O···H–O between O and H atoms are calculated to be 1.917 Å and 1.923 Å in the hydrogen-bonded 4NNi-$(MeOH)_{a,b}$ complexes. The lengths of the hydrogen bond C=O···H–O between O and H atoms in the hydrogen-bonded 4NNi-$(MeOH)_4$ complex are calculated to be 1.923 Å and 1.925 Å which are longer than C=O$\cdots$H–O in 4NNi-(MeOH)$_{a,b}$ dimer. It is noted that the hydrogen bond C=O$\cdots$H–O is weakened as a result of the formation of the hydrogen bond N=O$\cdots$H–O. In addition, the calculated the hydrogen bond N=O$\cdots$H–O between O and H atoms distance are 2.017 Å and 2.085 Å in the 4NNi-(MeOH)$_{c,d}$ dimers, respectively. We observe that the distances between O and H atoms for hydrogen bond N=O$\cdots$H–O are 2.038 Å and 2.121 Å in 4NNi-(MeOH)$_4$ complex, which are slightly longer than N=O$\cdots$H–O in 4NNi-(MeOH)$_{c,d}$ dimers. The formation of the intermolecular hydrogen bonds C=O$\cdots$H–O can weaken the hydrogen bond N=O$\cdots$H–O in the hydrogen-bonded 4NNi-(MeOH)$_4$ complex.

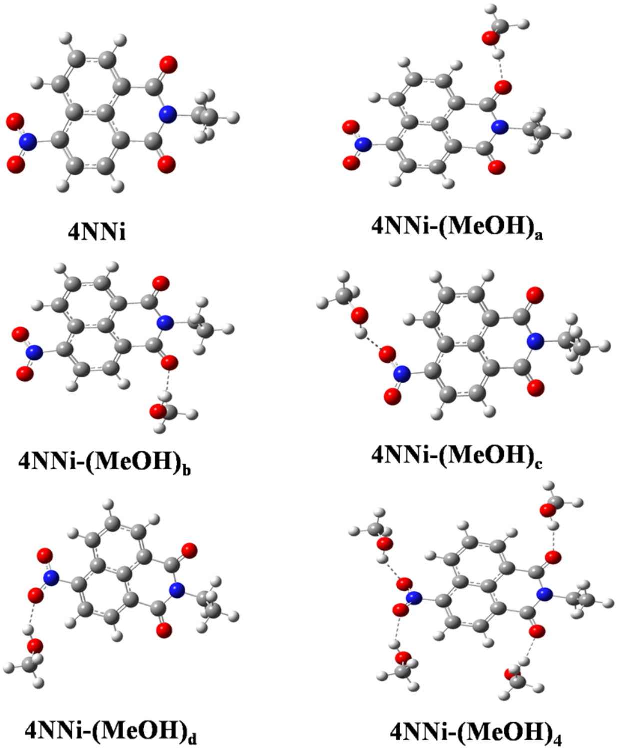

Figure 1: Geometric structures of 4NNi monomer and hydrogen-bonded 4NNi-(MeOH)$_{1,4}$ complexes.

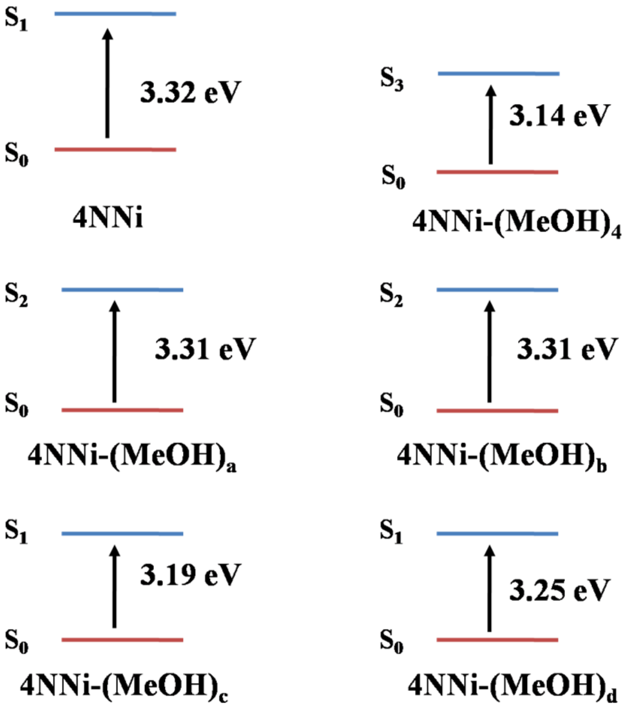

Figure 2: Electronic excitation energies of 4NNi monomer and hydrogen-bonded 4NNi-(MeOH)$_{1,4}$ complexes.

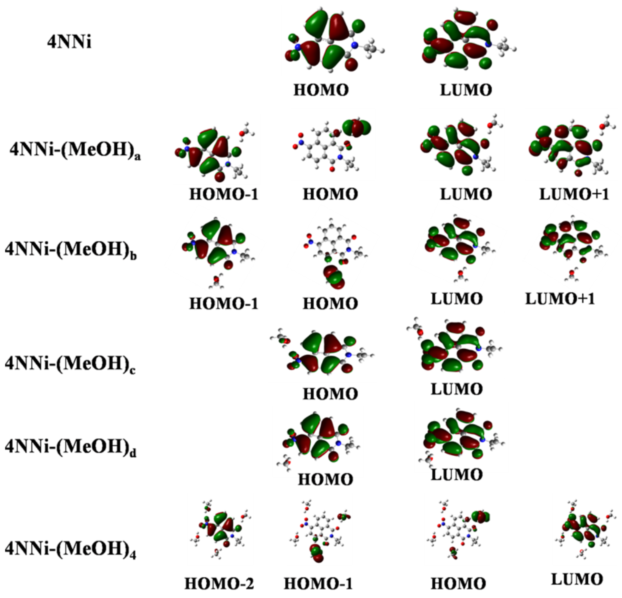

Figure 3: Frontier molecular orbitals (MOs) of the hydrogen-bonded 4NNi-(MeOH)$_{1,4}$ complexes.

3.2 Calculated Electronic Spectra

The electronic excitation energies and corresponding oscillator strengths of the low-lying excited states of 4NNi-(MeOH)$_{1,4}$ complexes and the isolated molecules are calculated using TDDFT method and represented in Table 2. We analyzed the electronic excitation energies of the hydrogen-bonded complexes in Figure 2. It is noted

Table 1: Calculated lengths of hydrogen bonds (in Å) and hydrogen bonding groups for isolated 4NNi and hydrogen-bonded4NNi-(MeOH)$_{1,4}$ complexes in ground state.

	$L^{A}_{O...H}$	$L^{B}_{O...H}$	$L^{C}_{O...H}$	$L^{D}_{O...H}$	$L^{A}_{C=O}$	$L^{B}_{C=O}$	$L^{C}_{N=O}$	$L^{D}_{N=O}$
4NNi	-	-	-	-	1.223	1.223	1.230	1.232
4NNi-(MeOH)$_a$	1.917	-	-	-	1.230	1.222	1.231	1.229
4NNi-(MeOH)$_b$	-	1.923	-	-	1.222	1.230	1.232	1.229
4NNi-(MeOH)$_c$	-	-	2.017	-	1.223	1.223	1.237	1.227
4NNi-(MeOH)$_d$	-	-	-	2.085	1.223	1.223	1.229	1.235
4NNi-(MeOH)$_4$	1.923	1.925	2.038	2.121	1.229	1.229	1.233	1.232

Table 2: Calculated electronic excitation energies (nm) and corresponding oscillator strengths of isolated 4NNi as well as hydrogen-bonded 4NNi-(MeOH)$_{1,4}$ complexes.

	4NNi	4NNi-(MeOH)$_a$	4NNi-(MeOH)$_b$	4NNi-(MeOH)$_c$	4NNi-(MeOH)$_d$	4NNi-(MeOH)$_4$
S_1	373.17 (0.1566) H→L 59.6%	398.59 (0.0002)	400.65 (0.0002)	388.03 (0.1920) H→L 61.3%	381.28 (0.1672) H→L 63.5%	412.86 (0.0002)
S_2	369.57 (0.0211)	374.79 (0.1804) H-1→L 63.1%	374.24 (0.1795) H-1→L 63.1%	380.42 (0.0121)	373.87 (0.0007)	404.59 (0.0006)
S_3	344.43 (0.0002)	357.67 (0.0001)	354.93 (0.0028)	372.17 (0.0003)	367.96 (0.0058)	395.08 (0.1526) 104 ->107 H-2→L 62.5%
S_4	334.81 (0.0053)	344.13 (0.0002)	344.26 (0.0003)	340.54 (0.0052)	342.24 (0.0023)	384.48 (0.0067)
S_5	324.43 (0.0159)	331.89 (0.0177)	331.87 (0.0163)	334.85 (0.0042)	338.38 (0.0057)	376.08 (0.0038)
Exp	363					405

that a larger blue shift appears in the electronic excitation energies of the 4NNi-(MeOH)$_{1,4}$ complexes compared to isolated 4NNi molecule, which indicates that the intermolecular hydrogen bonding is strengthened in excited states of hydrogen-bonded 4NNi-(MeOH)$_{1,4}$ complexes. The hydrogen-bonded 4NNi-(MeOH)$_{a,b}$ can be initially photoexcited to the S_2 state with the largest oscillator strength. Moreover, the S_2 state of the 4NNi-(MeOH)$_{a,b}$ is very close in energy to the S_1 state of isolated 4NNi. Compared the electronic excitation energies of 4NNi monomer, hydrogen-bonded 4NNi-(MeOH)$_{a,b}$ has an additional electronic state (S_1 dark state)with very small oscillator strength. This dark state is located 0.3 eV below the S_1 state of isolated 4NNi. The S_1 state of the 4NNi-(MeOH)$_{a,b}$ with weak oscillator strength is lower in energy than any intermolecular excited states of 4NNi, which might be from the interactions between 4NNi and MeOH.

For the case of the hydrogen-bonded 4NNi-(MeOH)$_{c,d}$, the S_1 state has the maximum oscillator strength. For the case of the hydrogen-bonded 4NNi-(MeOH)$_4$, two additional dark states are lying lower in energy than the S_1 state of isolated 4NNi. For the 4NNi-(MeOH)$_4$, the S_1 state and the S_2 state are all dark states. The interactions between 4NNi and MeOH may be the reason for the formation of lower-lying dark states for 4NNi-(MeOH)$_4$. Obviously, there is the largest oscillator strength from $S_0 \rightarrow S_3$ for the 4NNi-(MeOH)$_4$. The transition energy for $S_0 \rightarrow S_3$ for the 4NNi-(MeOH)$_4$ is close to the electronic excitation energy for $S_0 \rightarrow S_1$ for the 4NNi. Our results show that the influence of the intermolecular hydrogen-bonding interactions lowered the electronic excitation energy.

Obviously, the absorption peak of the 4NNi-(MeOH)$_{c,d}$ is more red-shifted than the S_2 absorption peak of 4NNi-(MeOH)$_{a,b}$. Our results have clearly demonstrated that the hydrogen bond N=O$\cdots$H–O has more effect in the S_1 absorption peak than the hydrogen bond C=O$\cdots$H–O. The calculated absorption peak of the hydrogen-bonded 4NNi-(MeOH)$_4$ is 395 nm, which is a larger redshift than isolated 4NNi. The reason is the solute-solvent intermolecular hydrogen-bonding interactions. These results also coincide with the experimental absorption spectra of 4NNi in nonpolar and polar solvents. The experimental results are also correspondingly listed in Table 2. The electronic spectra of the hydrogen-bonded 4NNi-(MeOH)$_{1,4}$ are redshifted so the intermolecular hydrogen bonds are strengthened. In all, there are different degrees of redshift for the hydrogen-bonded 4NNi-(MeOH)$_{1,4}$ compared with isolated 4NNi moleculer. This may be important information for us when investigating the electronically excited-state dynamics of the hydrogen-bonded complex in solution.

3.3 Frontier Molecular Orbitals

The results in Figure 3 show that the frontier molecular orbitals (MOs) of the hydrogen-bonded 4NNi-$(MeOH)_{1,4}$ complexs can directly provide insight into the nature of the excited states. The frontier molecular orbitals (MOs) of the hydrogen-bonded 4NNi-$(MeOH)_{1,4}$ complexs are shown in Figure 3. It is clear that the orbital transition from HOMO to LUMO of 4NNi corresponds to the electronic excitation transition for $S_0 \rightarrow S_1$ with the largest oscillator. The HOMO and LUMO orbitals are the π and π^* character, respectively, which indicates the electronic excitation transition for $S_0 \rightarrow S_1$ is the $\pi\pi^*$ character.

For the 4NNi-$(MeOH)_{a,b}$, the S_0-S_2 transition with the largest oscillator strength corresponds to the orbital transition from HOMO-1 to LUMO. It is clear that from HOMO-1 to LUMO the electron densities are transited from 4NNi moiety to 4NNi moiety with orbital overlap. The orbital transition from HOMO to LUMO of a hydrogen-bonded 4NNi-$(MeOH)_{a,b}$ complex corresponds to the electronic excitation transition for $S_0 \rightarrow S_1$ with very weak oscillator strength. Because the electron densities change from HOMO to LUMO are transited from MeOH molecule to 4NNi moiety without orbital overlap. However, the S_1 state with the largest oscillator strength of the 4NNi-$(MeOH)_{c,d}$ corresponds to the orbital transition from HOMO to LUMO which implies that the $\pi\pi^*$ type transition is dominated from HOMO to LUMO.

For the 4NNi-$(MeOH)_4$, the orbital transition from HOMO-2 to LUMO corresponds to electronic excitation states transition $S_0 \rightarrow S_3$ with the largest oscillator strength. The electron density of HOMO and HOMO-1 for the 4NNi-$(MeOH)_4$ is partially populated on the MeOH molecule(hydrogen-bonded donor). However, the electron densities of LUMO+1, LUMO and HOMO-2 orbitals are separately populated on the 4NNi moiety (hydrogen-bonded accepter). In conclusion, the orbital transition is in agreement with the discussion about the electronic excitation states transition. The electron densities in the carbonyl group and nitro group can affect orbital transition for both the intermolecular hydrogen bond $C=O\cdots H-O$ and $N=O\cdots H-O$, respectively.

4 Conclusions

In summary, the ground-state conformations of the isolated 4NNi and 4NNi-$(MeOH)_{1,4}$ complexes in hydrogen donating methanol solvents are optimized using the DFT method, and electronic transition energies and corresponding oscillation strengths of the low-lying electronically excited states are calculated using the TDDFT method. For the hydrogen-bonded 4NNi-$(MeOH)_{1,4}$ complexes, 4NNi and MeOH molecules form intermolecular hydrogen bond $C=O\cdots H-O$ and $N=O\cdots H-O$. The electronic spectra of the hydrogen-bonded 4NNi-$(MeOH)_{1,4}$ shows different degree of redshift compared with the isolated 4NNi, which indicates the intermolecular hydrogen bondings are strengthened. We believe that the hydrogen bond strengthening behavior in electronically excited states can be widely used in many fluorescent dyes.

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