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A theoretical study on the red- and blue-shift hydrogen bonds of *cis-trans* formic acid dimer in excited states

Research Article

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Abstract: The excited states of *cis-trans* formic acid dimer and its monomers have been investigated by time-dependent density functional theory (TDDFT) method. The formation of intermolecular hydrogen bonds O_1-H_1•••O_2=C_2 and C_2-H_2•••O_4=C_1 induces bond length lengthening of the groups related to the hydrogen bond, while that of the C_2-H_2 group is shortened. It is demonstrated that the red-shift hydrogen bond O_1-H_1•••O_2=C_2 and blue-shift hydrogen bond C_2-H_2•••O_4=C_1 are both weakened when excited to the S_1 state. Moreover, it is found that the groups related to the formation of red-shift hydrogen bond O_1-H_1•••O_2=C_2 are both strengthened in the S_1 state, while the groups related to the blue-shift hydrogen bond C_2-H_2•••O_4=C_1 are both weakened. This will provide information for the photochemistry and photophysical study of red- and blue-shift hydrogen bond.

Keywords: *Cis-trans formic acid dimer • Red-shift hydrogen bond • Blue-shift hydrogen bond • Excited state • TDDFT*

1. Introduction

Like a typical intermolecular interaction force, noncovalent interaction plays an important role in the field of chemistry, biology and physics. Moreover chemical and biological process, such as molecule recognition and self-assembly, is based on noncovalent interactions [1]. Hydrogen bonding is considered a ubiquitous phenomenon in many branches of science and demostrates its importance in solute-solvent interaction, supermolecule chemistry and proteins folding [2-8]. The hydrogen bond is usually viewed as D-H•••A, in which D is an element with higher electronegativity compared to the hydrogen atom, such as O, N or F, and A would be an electronegative element with electronic pairs, or a region with excess electron density such as a benzene molecule [9-18]. In some cases, the hydrogen bond can also be found as D-H•••H-A, which is a dihydrogen bond with two hydrogen atoms of opposite charge [19]. Hydrogen bonding in its ground and excited states has been widely studied by theoretical and experimental methods. In addition, the concept of the hydrogen bonding is still evolving with the improvement of laboratory instruments, high-level computational and simulation [8].

The simplest carboxylic acid, formic acid (FA) plays an important role in human metabolism and environmental issues [20]. FA is one of the most often investigated compounds and has been widely studied by experimental and theoretical methods [20-28]. In addition, FA is a suitable model to study conformations changes, which have two planar conformers (*cis* and *trans* [21]) that differ by orientation of the O-H group. It has been demonstrated that the *trans* FA isomer is lower in energy than *cis* FA isomer [21]. The FA molecule has C=O and O-H groups, which can act as a hydrogen bond acceptor and a hydrogen bond donor respectively [22].

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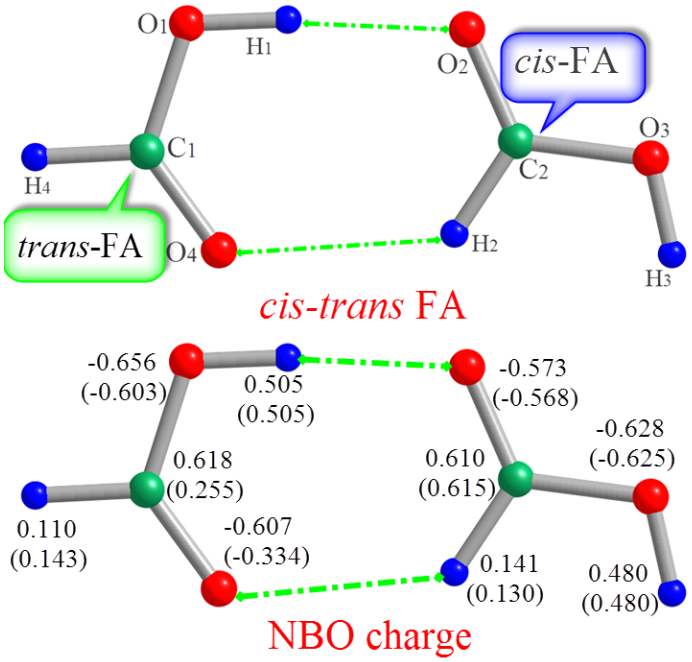

Figure 1. The optimized geometric structure of *cis-trans* FA dimer and its calculated NBO charges in the ground and S_1 states (in the parentheses).

There are two intermolecular hydrogen bonds can be formed between FA monomers, O-H•••O and C-H•••O [1,29-37]. Formic acid dimers can form a variety of hydrogen-bonded structures, such as *trans-trans* dimer and *cis-trans* dimer [29-34]. These can be offered as a general model for the study of molecular systems involving C-H•••O and O-H•••O hydrogen bonds, whose properties and reactions are important in the science of life [23,35-37]. The hydrogen bond of *trans-trans* and *cis-trans* dimer has been widely studied by experiment and theoretical methods [35-38]. It has been demonstrated that the hydrogen bond O-H•••O of the *trans-trans* non-cyclic FA dimer red-shifts compared to the monomer FA, while the C-H•••O hydrogen bond blue-shifts [38].

The lengthening accompanied by the lowering of the stretching vibrational frequency of the groups related to the formation of hydrogen bond is known as a characteristic feature of the hydrogen bond [39]. However, the bond length of the C-H bond in the *cis-trans* FA dimer is shortened and its stretching vibrational frequency is blue-shifted compared to the FA monomer [38]. It can be seen that most of these studies focused on the red- and blue-shifted hydrogen bonds of FA dimer in ground states [35-39]. In this paper, we will primarily focus on the behaviors of red- and blue-shifted hydrogen bonds of *cis-trans* FA dimer in their excited states, which will provide insight into their photochemistry and photophysical properties.

2. Theoretical details

The density functional theory (DFT) method with Becke's three-parameter hybrid exchange function with Lee-Yang-Parr gradient-corrected correlation functional (B3LYP functional) was used to calculate the ground states of the *cis-trans* FA dimer and its monomers [40,41]. The excited states were calculated using time-dependent functional theory (TDDFT) method with the B3LYP functional. The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as the basis set throughout [42] and fine quadrature grids of size 4 were chosen [43]. All the calculated vibrational frequencies are scaled by the factor of 0.961 to account for anharmonicity effects [44]. In this paper, the electronic structure and spectra calculations were carried out using the TURBOMOLE program suit [40-44]. The MP2 method has also been performed in order to optimize the geometry structures, calculate interaction energies and natural bond orbital (NBO) with a aug-cc-pvtz basis set [45].

3. Results and discussion

In this paper, the *cis-trans* FA dimer and its monomers are provided for the study of red- and blue-shift hydrogen bonds in the ground and excited states. Fig. 1 shows the optimized geometric structures of *cis-trans* FA dimer

Table 1. The calculated bond lengths (Å) and hydrogen bond binding energies E_{HB} (kJ mol^{-1}) of *cis-trans* FA dimer in ground states (GS) and excited states (ES) by DFT and MP2 methods.

	trans-FA		*cis*-FA		*cis-trans* FA dimer			
	GS	ES	GS	ES	GS(DFT)	GS(MP2)	ES	L_{ES-GS}
C_1-O_1	1.346	1.385	-	-	1.326	1.327	1.377	0.051
O_1-H_1	0.972	0.969	-	-	0.992	0.991	0.988	-0.004
O_1-H_1•••O_2	-	-	-	-	1.775	1.742	1.779	0.004
C_2=O_2	-	-	1.191	1.333	1.204	1.210	1.203	-0.001
C_2-O_3	-	-	1.353	1.369	1.340	1.340	1.339	-0.001
O_3-H_3	-	-	0.967	0.965	0.967	0.966	0.967	0.000
C_2-H_2	-	-	1.105	1.101	1.099	1.095	1.100	0.001
H_2•••O_4-C_1	-	-	-	-	2.331	2.279	2.439	0.108
C_1=O_4	1.198	1.327	-	-	1.209	1.215	1.331	0.122
C_1-H_4	1.097	1.091	-	-	1.098	1.093	1.091	-0.007
E_{HB}	-	-	-	-	-45.30	-46.55	-41.34	-

and its NBO charges in the ground and S_1 states. All the atoms of the *cis-trans* FA dimer are labeled The *trans* FA and *cis* FA differ by orientation of the O-H group. There are two intermolecular hydrogen bonds are formed in the *cis-trans* FA dimer, one is O_1-H_1•••O_2=C_2 bond and the other is C_2-H_2•••O_4=C_1 bond. The hydrogen bond O_1-H_1•••O_2 is the more common form which has been studied extensively, while the hydrogen bond C_2-H_2•••O_4=C_1 involving C-H bond has rarely been investigated. Research has shown that the C-H bond of *cis-trans* FA dimer is shortened after the formation of intermolecular hydrogen bond, which is different from the changes of normal hydrogen bond [35,38,39].

The bond lengths and hydrogen bond interaction energies of the *cis-trans* FA dimer in the ground state and the S_1 state have been calculated by DFT and MP2 method and are provided in Table 1. The formation of an intermolecular hydrogen bond usually induces the lengthening of the groups related to the hydrogen bond. The bond length of O_1-H_1 group of *trans*-FA in the ground state is calculated to be 0.972 Å, which is consistent with the experimental results and lengthened to 0.992 Å with the hydrogen bonded to *cis* FA [20]. The bond length of C_2=O_2 of monomer *cis* FA is lengthened from 1.191 Å to 1.204 Å for *cis-trans* FA dimer. The bond lengths of O_1-H_1 and C_2=O_2 in *cis-trans* FA dimer are both lengthened, which indicates the formation of an intermolecular hydrogen bond O_1-H_1•••O_2=C_2. For the *cis-trans* FA dimer, the bond lengths of O_1-H_1 and C_2=O_2 are shortened about 0.004 Å and 0.001 Å after being excited to the S_1 state, while the bond length of intermolecular hydrogen bond O_1-H_1•••O_2=C_2 is lengthened about 0.004 Å after photo-excitation. The hydrogen bond interaction of O_1-H_1•••O_2=C_2 is weakened in the S_1 state when compared to the ground state. This is different from the hydrogen bond strengthening theory provided by Zhao *et al.* [3,5,7]. The bond length of the C_1=O_4 group in the ground state is calculated to be 1.198 Å, which increases to 1.209 Å when hydrogen bonds to the *cis* FA. The bond length of C_2-H_2 group of the *cis* FA is calculated to be 1.105 Å, which decreases to 1.099 Å when the hydrogen bonds to *trans* FA. A possible explanation could be the bond length of C_2-H_2 is shortened due to the formation of C_2-H_2•••O_4=C_1 intermolecular hydrogen bond. This is very different from previous studies that suggest the formation of an intermolecular hydrogen bond induces the lengthening of the groups related to the hydrogen bond. When exited to the S_1 state, the bond length of C_2-H_2 and O_4=C_1 are lengthened by about 0.001 Å and 0.122 Å compared to the ground state respectively. It is interesting that the bond length of intermolecular hydrogen bond C_2-H_2•••O_4=C_1 is lengthened by 0.108 Å. This is different from the previous study that found that if the intermolecular hydrogen bond is lengthened, the groups related to the formation of hydrogen bond should be shortened. It can be seen that both the intermolecular hydrogen bonds O_1-H_1•••O_2=C_2 and C_2-H_2•••O_4=C_1 are shortened after being excited to the S_1 state. The intermolecular hydrogen bond interaction energy of the *cis-trans* FA dimer is calculated as -45.30 kJ mol^{-1} by the DFT method, which is consistent with the MP2 method of -46.55 kJ mol^{-1}. When excited to the S_1 state, the *cis-trans* FA dimer intermolecular interaction energy decreases to -41.34 kJ mol^{-1}. Theis evidence indicates that the intermolecular hydrogen bonds O_1-H_1•••O_2=C_2 and C_2-H_2•••O_4=C_1 are both weakened, which is consistent with the bond length change of the two intermolecular hydrogen bonds.

Table 2. Calculated Electronic excited energies *E* (eV) and the corresponding oscillator strengths (in the parenthesis) of *cis-trans* FA dimer and its monomers.

	***trans*-FA**	***cis*-FA**	***cis-trans* FA dimer**
S_1	5.831(0.001) HOMO→LUMO 99.6%	5.728(0.002) HOMO→LUMO 99.6%	5.868(0.002) HOMO→LUMO +1 95.1%
S_2	7.821(0.035)	7.336(0.021)	5.907(0.000)
S_3	8.713(0.003)	8.149(0.005)	6.169(0.000)
S_4	8.823(0.186)	8.740(0.190)	7.148(0.004)
S_5	9.209(0.000)	9.069(0.000)	7.309(0.002)
S_6	9.413(0.107)	9.095(0.158)	7.702(0.000)

Electronic excitation energies and the corresponding oscillator strengths of the *cis-trans* FA dimer and its monomers have been calculated and provided in Table 2. The S_1 state is the first excitation state, which is also the lowest energy state by definition. For the *trans* FA monomer, the electronic excitation energies of the S_1 state and the S_2 state were calculated to be 5.831 eV and 7.821 eV respectively, with corresponding oscillator strengths of 0.001 and 0.035. It can be seen that the oscillator strength of the S_2 state is larger than that of the S_1 state. The S_1 state has the lowest electronic excitation energy and is also the fluorescent state. For the *cis* FA monomer, the electronic excitation energy and the corresponding oscillator strengths are similar to those of the *trans* FA monomer. For the *cis-trans* FA dimer, the electronic excitation energy of the S_1 state is 5.868 eV, which is little larger than that of the *trans* FA and *cis* FA monomers. The corresponding oscillator strength of the S_1 state is similar to that of the *trans* FA and *cis* FA conformations. In addition, the S_1 states of *trans* FA and *cis* FA conformations both correspond to the HOMO→LUMO transition, while that of *cis-trans* FA dimer corresponds to the transition from HOMO to LUMO+1.

The NBO analysis as well as the molecular orbital calculation was performed to obtain information regarding the distribution of the partial atomic charges and electron density of the *cis-trans* FA dimer and its monomers. In the Table 3, the NBO occupancies of the bonds related to the formation of intermolecular hydrogen bonds of the *cis-trans* FA monomer and NBO donor → NBO acceptor transfer are provided. For the O_1-H_1 bond, the atomic orbital of the O_1 atom is at 78.26% and that of H_1 atom is 21.74%. In contrast to O_1-H_1, the attribution of atomic orbital of the O_1 atom for C_1-O_1 bond is 67.53%. Therefore, the charge variation on O_1 is more attributable to the C_1-O_1 bond change than to O_1-H_1. In the C_2-H_2 bond, the C_2 atomic orbital is 57.93% and H_2 atomic orbital is 42.07 %, while that of C_2 atom in C_2-O_2 bond is 24.88% and 31.82% in C_2-O_3 bond. This indicates that the charge distribution change of the C_2 atom is more attributed to C_2-O_2 and C_2-O_3 bonds rather than C_2-H_2. In the *cis-trans* FA dimer, the electrons of $\sigma(O_1\text{-}H_1)$ increase 0.00007 compared to that of its monomer. This number is so small that it can be ignored. The electrons of $\sigma^*(O_1\text{-}H_1)$ and $\sigma^*(C_2\text{-}O_2)$ in *cis-trans* FA is calculated to be 0.03430 and 0.01125, which increase 0.02488 and 0.00049 compared to *trans* FA and *cis* FA monomers. The electrons of $\sigma^*(C_1\text{-}O_4)$ of the *cis-trans* FA dimer increases 0.00144 in contrast to the *trans* FA monomer, while that of $\sigma^*(C_2\text{-}H_2)$ decreases 0.00598 compared to *cis* FA monomer. It is known that the increase of electron density in the σ*(D-H) antibonding orbital is caused by the electron-density transfer from the lone electron pairs of A atom to the D-H σ* antibonding orbital in the D-H•••A hydrogen bond. This in turn weakens the N-H bond and leads to its elongation accompanied by a red shift of its stretching vibrational frequency. This is consistent with the elongation of C_1-O_4, O_1-H_1 and C_2-O_2 bonds. The shortening of the C_2-H_2 bond is caused by an intramolecular electron density transfer from LP(1) O_7 atom (stabilization energy of 21.92 kcal mol^{-1}), LP(2) O_7 atom (stabilization energy of 21.92 kcal mol^{-1}) and LP(1) O_8 (stabilization energy of 4.61 kcal mol^{-1}) to BD*(1) C_2-H_2. The stabilization energy of the LP(1) O_4→BD*(1) C_2-H_2 (0.90 kcal mol^{-1}<1) is so small that it can be ignored.

The analyses of the NBO charge population of atoms related to the formation of hydrogen bond could provide insight into the change of hydrogen bond interaction in the ground and excited states. The calculated NBO charge of the labeled atoms in the ground and S_1 states is provided in Fig. 1. The charge of atom C_1 is calculated to be 0.618 in the ground state, which decreases to 0.255 when excited to the S_1 state. The charge of atom O_1 changes by 0.053 from -0.656 in the ground state to -0.603 in the S_1 state. This indicates that the NBO charge of atom O_1 gets less negative after excitation, which implies that interaction between atoms C_1 and O_1 is weakened. This

Table 3. NBO occupancies in the bonds related to the formation of hydrogen bonds of *cis-trans* FA and NBO donor →NBO acceptor transfer with corresponding stabilization energies ($E^{(2)}$).

	bond	$n^{\sigma(a)}$ (electrons)	%	$n^{\sigma*}$ (electrons)	donor → acceptor[(b)]	$E^{(2)}$ (kcal mol^{-1})
***cis-trans* FA**	O_1-H_1	1.98892 (0.00007)	O_1 78.26% H_1 21.74%	0.03430 (0.02488)	$E^{(2)}_{LP(1)\ O2\rightarrow BD^*(1)O1\text{-}H1}$	6.31
	C_1-O_4	1.99875 (-0.00015)	C_1 35.02% O_4 64.98%	0.01435 (0.00144)	$E^{(2)}_{LP(1)\ O4\rightarrow BD^*(1)C2\text{-}H2}$	0.90
	C_2-O_2	1.99784 (-0.00034)	C_2 34.90% O_2 65.10%	0.01125 (0.00049)	$E^{(2)}_{LP(2)O2\rightarrow BD^*(1)\ O1\text{-}H1}$	14.63
	C_2-H_2	1.99004 (-0.00028)	C_2 57.93% H_2 42.07%	0.05184 (-0.00598)	$E^{(2)}_{LP(1)O7\rightarrow BD^*(1)\ C2\text{-}H2}$ $E^{(2)}_{LP(2)\ O7\rightarrow BD^*(1)C2\text{-}H2}$ $E^{(2)}_{LP(1)\ O8\rightarrow BD^*(1)C2\text{-}H2}$	2.42 21.92 4.61
***trans*-FA**	O_1-H_1	1.98885	-	0.00942	-	-
	C_1-O_4	1.99890	-	0.01291	-	-
***cis*-FA**	C_2-O_2	1.99818	-	0.01076	-	-
	C_1-H_2	1.99032	-	0.05782	-	-

(a) Values in parentheses are NBO occupancies variations relative to the monomers. (b) BD denotes σ bonding orbital; BD denotes σ* antibonding orbital, BD and BD* (1) denotes σ orbital; LP denotes valence lone pair, LP(1) and (2) denote the first and the second lone pair electron, respectively.*

is consistent with the bond length lengthening of C_1-O_1 group. The NBO charge of the O_2 atom is calculated as -0.573 in the ground state, which changes to 0.005 in the S_1 state. This indicates that the hydrogen bond interaction O_1-H_1•••O_2-C_2 is weakened when excited to the S_1 state. This result is in good agreement with the bond length lengthening of intermolecular hydrogen bond O_1-H_1•••O_2-C_2 between the ground and S_1 states. The NBO charges of atoms O_4 and atom H_2 in ground state are calculated to be -0.607 and 0.141, which change to -0.334 and 0.130 when excited to the S_1 state. The charge on O_4 gets less negative and that of H_2 gets less positive. Therefore, hydrogen bond interaction between C_1=O_4 and C_2-H_2 gets weakened in the S_1 state compared to the ground state. This is consistent with the bond length change of C_2-H_2•••O_4=C_1 between ground and the S_1 state. It can be seen that the results of NBO analysis are consistent with the bond length change.

It is well-known that analysis of molecular orbitals (MOs) can provide insight into the nature of the excited states [46]. The frontier molecular orbitals (MOs) of the *cis-trans* FA dimer and its monomers are shown in Fig. 2. The S_1 states of *trans* FA and *cis* FA both correspond to the HOMO → LUMO transition. For the monomers *cis* FA and *trans* FA, the HOMO and LUMO orbital has π and π* characteristics respectively. For the *cis-trans* dimer, the electron densities of *trans* FA is similar to that of *trans* FA monomer, while electron densities distribution of *cis* FA is very different from its monomer. The electron density of C_1=O_4 in HOMO shifts to the C_1 atom when photo-transition to the LUMO orbital and that of C_2-H_2 decreases after excitation. This induces the intermolecular hydrogen bond interaction of C_2-H_2•••O_4=C_1 in the S_1 state. The electron density change is consistent with the change of bond length as discussed before.

It is well-known that electrostatic potential (ESP) maps can illustrate charge distributions. Knowledge of charge distributions can be used to determine the charge properties of the molecules and how they interact with one another. Therefore, to determine the charge distribution, the ESP of the *cis-trans* FA dimer in the ground and the S_1 excited states has been mapped onto a density isosurface (0.0004) and shown in Fig. 4. According to the conventional color spectrum in ESP maps, the blue region of a ESP map corresponds to the area of highest electrostatic potential which is the region of lowest electronegativity and characterized by a relative absence of electrons, while the red region of the ESP map corresponds to the area of lowest electrostatic potential which is the region of greatest electronegativity and characterized by an abundance of electrons. For the *trans* FA conformation, the electrostatic potential of the H_1 atom is only slightly changed between the ground and S_1 states. The red region of O_1 and O_4 atoms shift to C_1 atom when excited to the S_1 state, which induce a decrease in electron density associated with the O_1 and O_4 atoms and an increase in electron density for the C_1 atom. For the *cis* FA, the blue region of C_2 atom and the red region O_2 atom shift to H_2 atom when excited to the S_1 state, which lead to an increase of electron density associated with theH_2 atom and the decrease of electron density of the O_2 atom. The decrease of electron density of the O_2 atom results in the weakening hydrogen bond interaction of O_1-H_1•••O_2. The decrease of electron density of

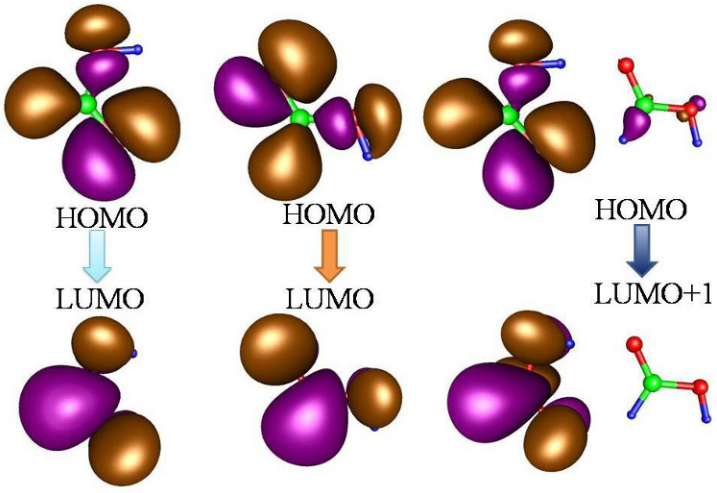

Figure 2. The frontier molecular orbitals of *cis-trans* FA dimer and its monomers corresponding to the S_1 state.

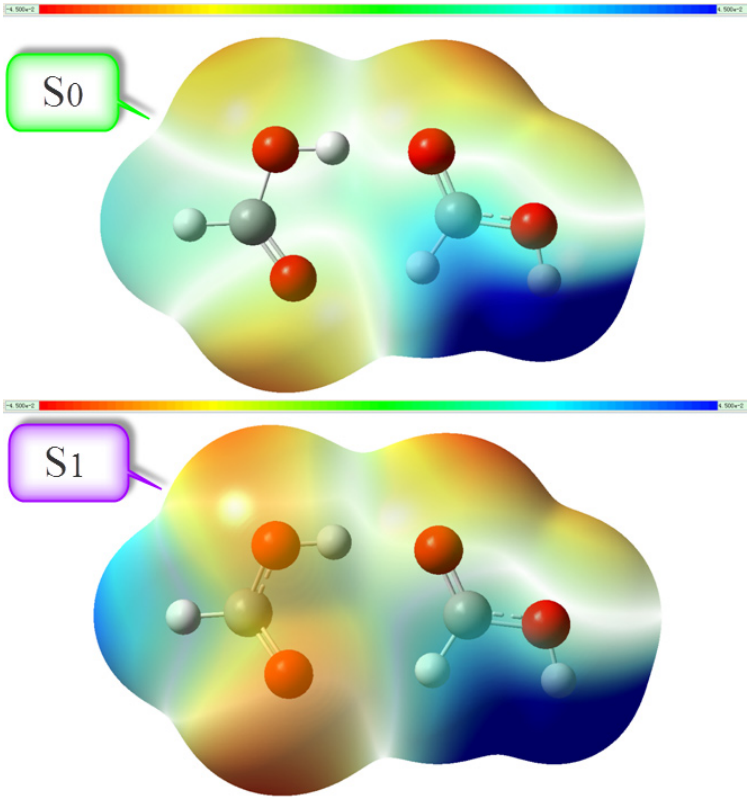

Figure 3. The electrostatic potentials of *cis-trans* FA dimmer in the ground and S_1 states. The scale spans from -0.045 (red) to +0.045 (blue) with density isosurface (0.0004).

O_4 atom and the increase of electron density of H_2 atom leads to the weakening of hydrogen bond interaction C_2-H_2•••O_4. This conclusion from ESP analysis is consistent with the bond length changes and NBO analysis.

The infrared spectra of *trans* FA, *cis* FA and *cis-trans* FA dimer in the ground and the S_1 excited states are provided in Fig. 4. The green lines denote the corresponding experimental data. The infrared spectra of *trans* FA in the ground and S_1 states are shown in panel 1. The stretching absorption peak appearing at 3569 cm^{-1} corresponds to the O_1-H_1 group, which is a little larger than the experimental result of (3550 cm^{-1}) [20,23,39]. The peak appearing at 1748 cm^{-1} corresponds to the stretching vibration of C_1=O_4 group, which is consistent with the experimental result (1767 cm^{-1})

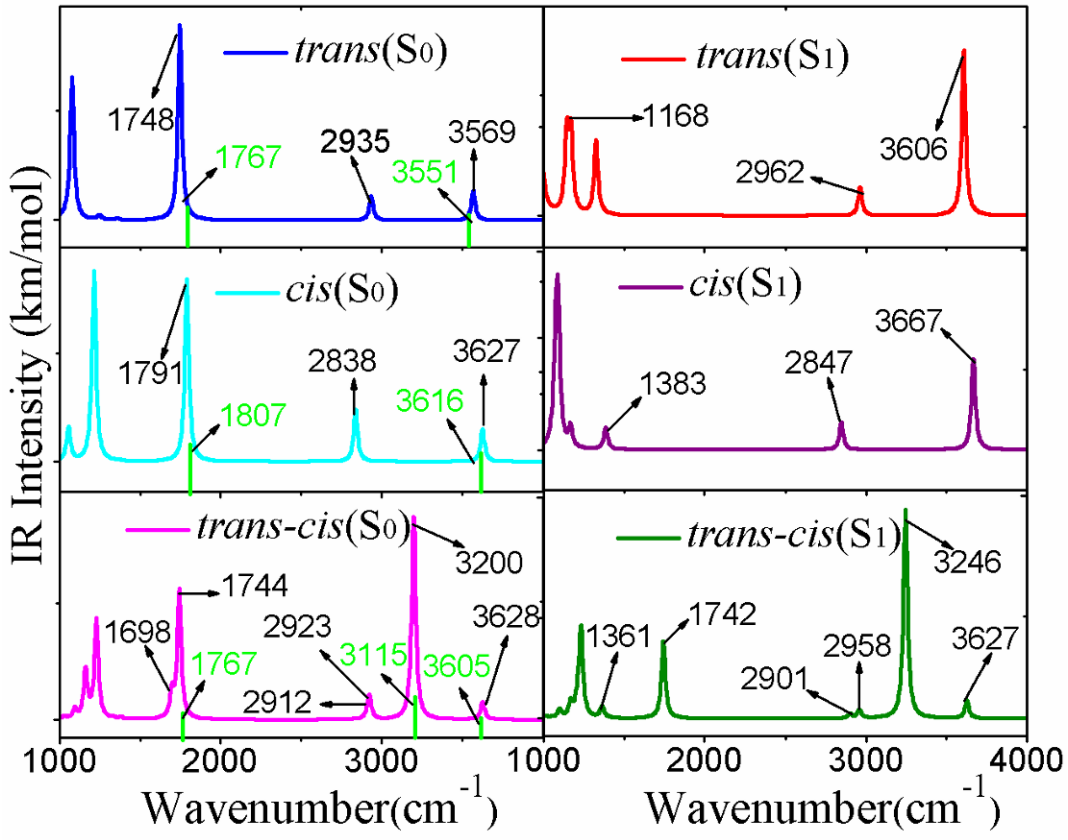

Figure 4. The infrared spectra of *cis-trans* FA dimer and its monomers in the ground and excited states. The green lines denote the corresponding experimental results.

[20,23]. Panel 2 shows the infrared spectra of *cis* FA in the ground and S_1 states. Peaks located at 1791 cm^{-1} and 2838 cm^{-1} correspond to the stretching absorption frequency of C_2=O_2 and C_2-H_2 groups. The stretching absorption peak of C_2=O_2 is consistent with the experimental result (1806 cm^{-1}) [20,23]. The peak appearing at 3627 cm^{-1} corresponds to the stretch vibration of O_3-H_3 group, which is a little larger than the experimental result (3616 cm^{-1}) [20,23]. Panel 3 shows the infrared spectra of *cis-trans* FA dimer in ground and the S_1 states. The peak located at 3200 cm^{-1} in the ground state corresponds to the stretching absorption peak of O_1-H_1 group, which is very close to the experimental result (3115 cm^{-1}). The stretching absorption peak of the O_1-H_1 group of the *trans* FA monomer red-shifts from 3569 cm^{-1} to 3200 cm^{-1} of *cis-trans* FA dimer. The stretching absorption peak of C_2=O_2 red-shifts about 47 cm^{-1} from 1791 cm^{-1} of monomer *cis* FA to 1744 cm^{-1} of *cis-trans* FA dimer. This is consistent with the bond length lengthening by 0.02 Å and 0.013 Å of O_1-H_1 and C_2=O_2 bonds of *cis-trans* FA dimer compared to its monomers in the ground state. The formation of hydrogen bond H_1•••O_2=C_2 induces the stretching absorption peaks of O_1-H_1 and C_2=O_2 groups to a lower number. Moreover, the stretching absorption peak of C_1=O_4 group red-shifts about 50 cm^{-1} from 1748 cm^{-1} for *trans* FA to 1698 cm^{-1} for *cis-trans* FA dimer, while that of C_2-H_2 group blue-shifts from 2838 cm^{-1} in *cis* FA to 2912 cm^{-1} in *cis-trans* FA dimer. This is consistent with the results provided by Zhou *et al.* [39].The red-shift of the stretching absorption peaks of C_1=O_4 is consistent with its bond lengthening by 0.011 Å, and blue-shift of C_2-H_2 is consistent with its bond length shortening by 0.006 Å.

For the *cis-trans* FA dimer, the stretching absorption peaks of O_1-H_1 and C_2=O_2 blue-shift to 3246 cm^{-1} and 1742 cm^{-1} respectively when excited to the S_1 state. This is consistent with their bond length shortening of 0.004 Å and 0.001 Å. The blue-shifts of O_1-H_1 and C_2=O_2 are consistent with the interaction of NBO charges which has been discussed before. The blue-shift of O_1-H_1 and C_2=O_2 indicates the weakening of intermolecular hydrogen bond O_1-H_1•••O_2=C_2 in the S_1 excited state. The angle of O_1-C_1-O_4 in the ground state is calculated to be 126°, which changes to 107° when in the S_1 state. The blue-shift of O_1-H_1 is related to the change of angle O_1-C_1-O_4 after photo-excitation and the stretching absorption peak of C_2-H_2 red-shifts from 2912 cm^{-1} in the ground state to 2901 cm^{-1} in the S_1 state.

The stretching absorption peak of C_1=O_4 red-shifts from 1698 cm^{-1} in the ground state to 1361 cm^{-1} in the S_1 state. This is consistent with their bond length lengthening by 0.001 Å and 0.122 Å in the S_1 state compared to the ground state. The charge of atom C_1 is calculated to be 0.618 in ground state, which changes to 0.255 when excited to the S_1 state. The NBO charge of atom O_4 changes about 0.273 from -0.607 in the ground state to -0.334 in the S_1 state. This indicates that the NBO charge of C_1 atom get less positive and the charge of the O_4 atoms gets less negative after excitation, which implies that interaction between atoms C_1 and O_4 is weakened. This is consistent with its change of bond length and shift of vibrational frequencies. It is demonstrated that the two intermolecular hydrogen bonds O_1-H_1•••O_2=C_2 and C_1=O_4•••H_2-C_2 are both weakened when excited to the S_1 state. It is interesting that the bonds related to the formation of hydrogen bond O_1-H_1•••O_2=C_2 are both strengthened while that of hydrogen bond C_1=O_4•••H_2-C_2 is weakened when excited to the S_1 state. All of them are consistent with the bond length and NBO analysis.

4. Conclusion

The *cis-trans* FA dimer and its monomers in the ground and the S_1 excited state have been investigated by DFT and TDDFT method. Two intermolecular hydrogen bonds O_1-H_1•••O_2=C_2 and C_1=O_4•••H_2-C_2 are formed between *cis* FA and *trans* FA. The bond lengths of O_1-H_1, O_2=C_2 and C_1=O_4 groups in ground state are all lengthened by the formation of an intermolecular hydrogen bond, while that of H_2-C_2 is shortened compared to monomer *cis* FA. It is demonstrated that the two intermolecular hydrogen bonds O_1-H_1•••O_2=C_2 and C_1=O_4•••H_2-C_2 are both lengthened in the S_1 state compared to the ground state. It is interesting that the bond lengths of O_1-H_1 and O_2=C_2 bonds are both shortened when excited to the S_1 state, while that of C_1=O_4 and H_2-C_2 bonds are both lengthened. The stretching absorption peak of C_2-H_2 for *cis-trans* FA dimer blue-shifts to a larger frequency in the ground state, while the red-shifts to lower frequency when excited to the S_1 state. This work will provide information for the studies of the photochemistry and photophysical properties of the red-shift and blue-shift hydrogen bond.

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