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Time-dependent density functional theory (TDDFT) study on the electronic spectroscopic blue-shift phenomenon and photoinduced charge transfer of firefly luciferin anion in aqueous solution: Insight into the excited-state hydrogen bond weakening mechanism

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ABSTRACT

In this work, the time-dependent density functional theory (TDDFT) method was performed to investigate the electronic spectra and charge transfer in excited states of firefly luciferin anion (NRO$^-$) in aqueous solution. A novel electronic spectral blue-shift (usually red-shift) phenomenon of NRO$^-$ was observed due to the significant influence of intermolecular hydrogen bonds between firefly luciferin anion and water molecules. We theoretically demonstrated that the excited-state intermolecular hydrogen bond weakening is confirmed by the increase of hydrogen bond length and decrease of hydrogen bond binding energy from our optimized ground-state and excited-state geometric conformations of the hydrogen-bonded NRO$^-$–H$_2$O complex. The hydrogen bond weakening behavior could also be indicated by photoinduced charge transfer from the carboxyl group to the planar part of NRO$^-$ in the excited state. Furthermore, we pointed out that the electronic spectral blue-shift should be ascribed to the intermolecular hydrogen bond weakening in this electronic excited state. The weakened hydrogen bonding interaction in the excited state would induce smaller downshift for the excited-state energy level than that for ground-state energy level. As a result, the energy gap between the excited state and ground state becomes larger, which means that the spectral peak corresponding to the electronic excited state will shift to the blue induced by the excited-state hydrogen bond weakening dynamics.

1. Introduction

Hydrogen bond plays significant roles on determining structures and properties of many chemical complexes and biomolecules [1–9]. It has been widely investigated by both theoretical and experimental methods in the last decades [1,2,4–19]. Intermolecular hydrogen bond has profound influence on the photochemical and photophysical properties of chromophores [11,20,21]. It has been demonstrated that the excited-state intermolecular hydrogen bond can strongly facilitate some important radiationless deactivation processes: internal conversion (IC), solute–solvent intermolecular electron transfer, photoinduced electron transfer (PET), excited-state proton transfer, and so on, in their previous studies on a series of chromophores in hydrogen bonding surroundings [19,21,22].

Bioluminescence, the beautiful natural light emission from living organisms, has attracted the attention of scientists for many years [23–26]. In recent years, bioluminescence from luciferase has become an extremely important tool in the study of gene expression and gene regulation [27]. D-Luciferin is the chromosphere found in Lampyridae, a family of winged insects. It is the natural substrate of the firefly luciferase, first isolated and purified by McElroy et al. [28,29], and has been investigated for decades [30]. Although all species of fireflies use D-luciferin, the color of light emitted by different species varies greatly in the range of 552 nm (green-yellow) to 582 nm (orange). This is attributed to that the absorption and emission spectrum of firely luciferin are largely influenced by environments conditions like the associated amino acid, temperature, pH and the presence of divalent metal ions such as Mg^{2+} and Cu^{2+} [31–34]. In aqueous solution the carboxylic acid moiety of the molecule is deprotonated at physiological pH. In gas phase, there are two kinds of ways for deprotonation: one is forming the phenolate isome by deprotonation of the phenolic hydroxyl; the other is forming the carboxylate isomer by deprotonation of the carboxylic acid

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group. Most recently, Støchkel et al. reported that the phenolate isomer lies higher in energy by 0.22 eV and indicated that the anion of firely luciferin is in the carboxylate form in gas phase [35]. On the other hand, Chen et al. reported the first systematic theoretical investigation on all the possible light emitters of firefly using a multireference method [36]. Although, the properties of firely luciferin anion are widely investigated, few researches provide the detailed knowledge on the interaction such as the hydrogen bonds between firely luciferin anion and the solvents. Herein, we focus our attention on the systematic study of the hydrogen-bonded firely luciferin anion in both ground and excited states.

It has been demonstrated the time-dependent density functional theory (TD-DFT) method can perfectly describe the intramolecular and intermolecular hydrogen bonding in both the ground state and electronically excited states, widely [37–44]. TD-DFT method has been used to investigate the reaction mechanisms for the formation of the keto-form of oxyluciferin (OxyLH2) from the luciferin of fireflies [43]. Zhao and Han have demonstrated that excited-state intermolecular hydrogen bond strengthening or weakening is corresponding to the red-shift or blue-shift of the electronic spectrum, respectively [38–42]. Moreover, we have first reported an electronic spectral rule on the electronic excited-state hydrogen bonding dynamics [9,22]. If the electronic spectral peak shifts to the red induced by the intermolecular hydrogen bonding interactions, the hydrogen bonds in the excited state corresponding to the electronic spectral peak will be strengthened. If the hydrogen bonds induce the electronic spectral peak shift to the blue, the hydrogen bonds in the corresponding electronic excited state will be weakened [9,22]. In the previous works, intermolecular hydrogen bond formed by thiocarbonyl, S = O···H–O is reported to be weakened in excited states [44]. In the present work, we investigate the photophysical and photochemical properties of firely luciferin anion and water dimer in both the ground and excited states. Firely luciferin anion is in the carboxylate form (NRO^-). Two intermolecular hydrogen bonds formed between the carboxylate ion and water molecule are demonstrated to be weakened in excited states by the calculated results. The calculated absorption spectrum of NRO^- is consistent with the experiments very well [35].

2. Computational methods

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) were employed for our ground state and excited state computations, respectively [45]. All geometry optimizations were carried out using B3-LYP functional with triple zeta valence plus polarization (def-TZVP) basis set [46]. All the quantum chemical calculations were performed using the TURBOMOLE program suite [47].

3. Result and discussion

3.1. Optimized geometrical structures in the ground state

The optimized geometry of NRO^- and $NRO^-–H_2O$ in the ground state are shown in Fig. 1. The bond length of the $C_5 = O_1$ double bond and the $C_5–O_2$ bond in the carboxyl of NROH is 1.203 and 1.347 Å in the optimized structure. As shown in Table 1, they change to 1.244 and 1.238 Å in NRO^- anion. It is ascribed to resonance effect, the $C_5 = O_1$ double bond and the $C_5–O_2$ bond vary to two double bond-like carbon-oxygen bonds with the nearly same bond length. When interact with one water molecule, they become longer to 1.250 and 1.246 Å accompanied by forming two hydrogen bonds $C_5 = O_1 \cdots H_{w1}–O_w$ and $C_5 = O_2 \cdots H_{w2}–O_w$ with the bond length of 2.103 and 2.043 Å, respectively. Furthermore, these two hydrogen bonds are in the same plane. Several important dihedral angles are shown in Table 1. One can find that two parts of the molecule at each side of $C_1–C_2$ bond are almost in the same plane in both NRO^- and $NRO^-–H_2O$. However, only C_4 is upper the plane with a little angle (the dihedral angle of $N_2–C_3–C_4–S_2$ is − 7.4° in NRO^- anion). And the angle becomes larger as − 16.7° in $NRO^-–H_2O$.

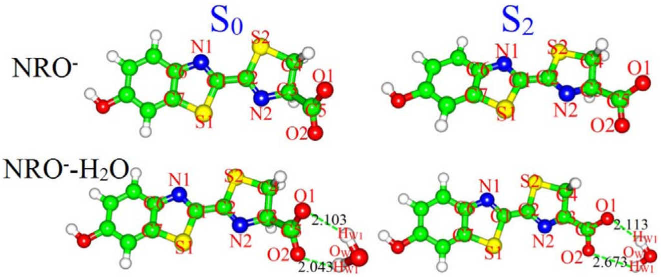

Fig. 1. Optimized geometry of NRO^- and $NRO^-–H_2O$ complexes in the ground state and S_2 state. Dotted lines denote the intermolecular hydrogen bonds. The hydrogen bond lengths are indicated in the figure.

Table 1
Important angles and bond length of optimized structures, the binding energy (kJ/mol) of $NRO^-–H_2O$ in the ground and excited states are also shown.

	Anion		Anion-H_2O	
	S_0	S_2	S_0	S_2
$N_1–C_6–C_7–S_1$	0.2	− 0.1	0	− 0.1
$N_2–C_3–C_4–S_2$	− 7.4	− 38.2	− 16.7	− 38.6
$S_1–C_1–C_2–S_2$	177.6	177.8	179.0	176.8
$N_1–C_1–C_2–N_2$	− 178.5	174.2	177.4	174.8
$C_2–N_2–C_3–C_5$	127.2	160.5	135.6	159.9
$O_1–C_5–O_2$	132.2	118.2	130.0	120.0
$C_6–N_1$	1.380	1.353	1.380	1.353
$N_1–C_1$	1.292	1.334	1.291	1.330
$C_1–C_2$	1.454	1.415	1.459	1.424
$C_2–N_2$	1.271	1.294	1.269	1.292
$N_2–C_3$	1.439	1.470	1.453	1.459
$C_3–C_5$	1.636	1.522	1.596	1.561
$C_3–C_4$	1.551	1.533	1.546	1.525
$C_4–S_2$	1.853	1.833	1.852	1.833
$C_5–O_1$	1.244	1.257	1.250	1.228
$C_5–O_2$	1.238	1.285	1.246	1.270
$C_5 = O_1 \cdots H_{w1}–O_w$			2.103	2.113
$C_5 = O_2 \cdots H_{w2}–O_w$			2.043	2.673
$O_w–H_{w1}$			0.972	0.967
$O_w–H_{w2}$			0.975	0.963
E_b			74.57	72.04

3.2. Electronic transition energy

In order to investigate the excited-state hydrogen bonding dynamics of the hydrogen-bonded $NRO^-–H_2O$ complex, the electronic transition energy and corresponding oscillator strength for the low-lying electronically excited states of the dimer and isolated NRO^- anion are calculated using the TDDFT method. The results are listed in Table 2. To clarify the influence of intermolecular hydrogen bond on the absorption spectrum, the abruption spectrum of NRO^- and $NRO^-–H_2O$ are calculated. As the spectrum of NRO^- shown in Fig. 2, the absorption in the visible region at 543 nm in agreement with the experimental results 535 nm very well, while 282 nm in the ultraviolet region don't agree with the experience 265 nm precisely enough [35]. Furthermore, one can find that the absorption at 543 nm blue-shifts to 482 nm in the spectrum of $NRO^-–H_2O$. As indicated in Table 1, all exited energies of $NRO^-–H_2O$ dimer are increased, which is corresponding to the blue-shift of the absorption spectrum. Excited-state hydrogen bond strengthening can lower the excitation energy of a related excited state and therefore induce the electronic spectra red-shift. Moreover, excited-state hydrogen bond weakening can enlarge the excited energy and induce the electronic spectral blue-shift [9,22]. Therefore, hydrogen bonds of $NRO^-–H_2O$ are expected be weakened in the excited states according to above relationship on the electronic excited-state hydrogen bonding dynamics.

On the other hand, the oscillator strength of the S_2 state of NRO^- is the largest, corresponding to the maximum absorption at 483 nm,