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COMMUNICATION

Surrounding Amino Acid Residues Effect on the Absorption Spectrum of Chlorophyll A: A Computational Study

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Abstract: Herein, several amino acid residues were considered to study the non-covalent bond effect on the absorption spectrum of chlorophyll a by using DFT/TD-DFT method. B3LYP functional were found better than other functional to study the vertical excited energy of chlorophyll a. The theoretical results showed that the surrounding amino acid residues induce red shift of the absorption spectra of chlorophyll a. And the histidine induces the largest red-shifts. It concluded that the N---Mg coordination bond effect on the absorption spectrum is more important than hydrogen bond. On the other hand, it showed that the absorption of P700 is more sensitive to response the surrounding amino acid residues than that of P680.

AMS subject classifications: 74E40; 78A10; 78M50; 92C40
Keywords: hydrogen bond; coordination bond; photosynthesis system; center pigments

Chlorophylls are well known as antenna in photosynthetic system. The spectroscopic properties of chlorophylls have attracted significant attention from both experimental and theoretical chemists in the past years [1-9]. Gouterman showed that there are Soret band (or B band, about 400 nm) and Q band (about 660 nm, include Q_y and Q_x bands) in absorption spectrum of porphyrins[1]. Sundholm et al. studied the electronic absorption spectrum of bacteriochlorophyll b by using density functional theory (DFT) method, B3LYP density functionals were used, the calculated spectra were blue shift than experimental results [2]. In their calculations, the histidine residues binding to the magnesium atoms were modeled by a ligating imidazole [2]. Recently, Graczyk et al. performed a computational study on linear

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and non-linear electronic spectroscopy of chlorophylls, and CAM-B3LYP functional was used [3]. Though many works have been done, there are few studies which focus on the effect of surrounding environment on the electronic absorption spectra of chlorophylls. Actually, the centre pigments, P680 and P700, in photosystem II and I both are chlorophyll a dimers, but their absorption spectra are different. It may be contributed by the effect of surrounding proteins because the non-covalent bond always induces the blue or red shift of absorption spectrum of organic molecule [10-12].

In this communication, the effect of surrounding amino acid residues on the absorption spectrum of chlorophyll a was investigated by DFT and time-dependent DFT (TD-DFT) methods. Both P680 and P700 were investigated. The surrounding environment of P680 and P700 were obtained from Ref. [13] and [14], respectively. The chlorophyll a dimer in P680 is named P_{D1} and P_{D2}, but in P700 is named eC-A1 and eC-B1. There are several amino acid residues ligant to chlorophyll a dimer by non-covalent both in P680 and in P700, including histidine, tyrosine, threonine, serine, phenylalanine etc. Barber and Iwata showed P_{D1} in P680 ligand with one histidine (His) and one threonine (Thr), and P_{D2} ligand with one His and one serine (Ser) [13]. Jordan et al. showed that eC-A1 in P700 ligand with His, tyrosine (Tyr), Thr and one water molecule, and eC-B1 in P700 ligand with only one His [14].

All the calculations were performed by using Gaussian 09D program [15]. The ground state optimization structures were calculated at DFT level, frequency analysis was performed subsequently, and it was systematically checked that all vibrational frequencies are real. All the vertical excited energies (VEEs) were calculated at TD-DFT level. In this

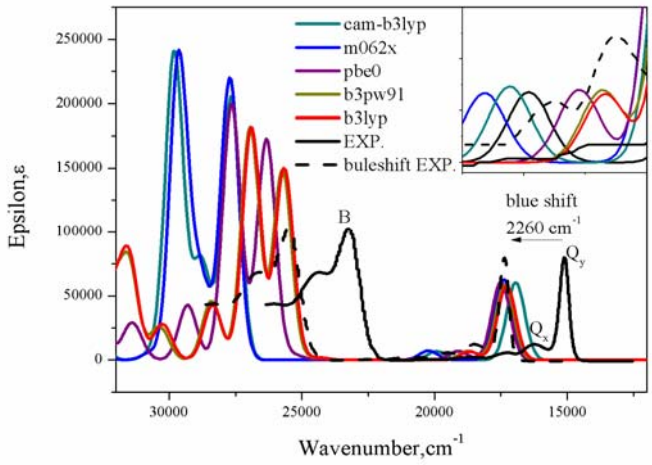

Figure 1: Functional variation on the absorption spectra of chlorophyll a. Method: B3LYP/TD-B3LYP with 6-31G (d, p) basis set and 400 cm^{-1} broadening factor. EXP.: experimental spectrum of chlorophyll a in ethanol [16], Q_y, Q_x and B band were labeled. Buleshift EXP.: the blue shift of experimental spectrum by 2260 cm^{-1}

study, the phytyl tail in chlorophyll a was replaced by methyl group to simplify the computational calculation. It was reported that phytyl chain replaced by methyl group has little effect on the calculated electronic absorption spectrum [3].

At first, several DFT functional were tested for chlorophyll a. The ground state geometry of chlorophyll a (eC-A1) was optimized using B3LYP functional and the 6-31G (d, p) basis set. The initio geometry was obtained from RCSB Protein Data Bank (1JB0) [14]. Subsequently, VEEs were calculated by employing a few frequently used functional and 6-31G (d, p) basis set. 24 electronic excited states were calculated. The computed results were shown in **Figure 1**. All the computed spectra were broadened by Gaussian function with a half width at half height 400 cm^{-1}. The experimental spectrum of chlorophyll a in ethanol was used [16]. The calculated spectra were blue shift than the experimental result consistent with the Sundholm et al. reported [2]. Wavenumber representation is used here to replace wavelength representation, which is better to reflect the effect of functional on absorption energy level. In order to compare the calculated VEEs with the experimental results, the absorption spectrum of chlorophyll a in ethanol solution was blue-shifted by 2260 cm^{-1} in **Figure 1** (dash line). Considering the Q_y, Q_x (see detail in the insert of **Figure 1**) and B band at the same time, the best result was obtained from B3LYP/TD-B3LYP functional. So, the following calculations were performed at B3LYP/6-31G (d, p) level. The calculated positions of those three bands (Q_y, Q_x and B) are almost the same as the blue-shifted experimental absorption spectrum. It means that the TD-B3LYP/6-31G (d, p) method overestimate the VEEs of the chlorophyll a by about 2260 cm^{-1} (0.28 eV).

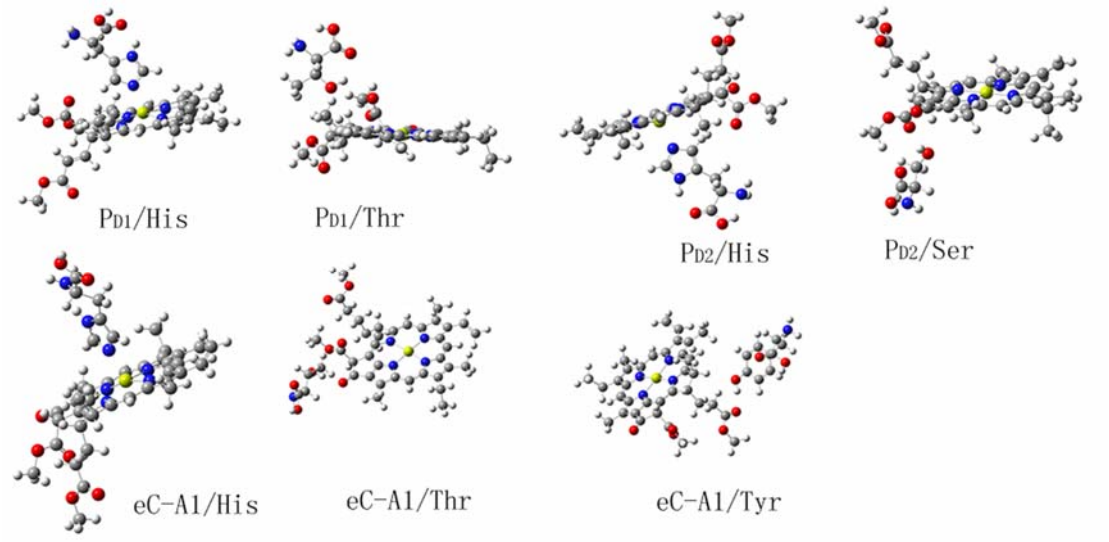

Figure 2: The structures of Chlorophyll a with amino acid residues. The phytyl train was replaced by methyl group here.

In order to investigate the non-covalent bond effect on the absorption spectrum of chlorophyll a, several amino acids surrounding chlorophyll a were considered here. The initio geometries were taken from the crystal structures of P700 and/or P680 pigments [13, 14]. To simplify the calculation, only one surrounding molecule was considered at the same time. For the flexible of the chlorophyll-amino acid complex structure, the amino acid molecule position may be changed greatly from their initio geometries during the geometry optimization. Generally, the crystal structures of P700 and P680 are almost the optimized structures, there should be no great changes between crystal structure and computational optimized structure. So, the N atom in amino acid $-NH_2$ group and Mg atom in chlorophyll a were fixed during the geometry optimization. Therefore, the optimized geometry will not be changed too much from the initio crystal structure during the optimized calculation. From P680 and P700 structure, seven complexes were calculated here (see **Figure 2**), including P_{D1}/His, P_{D1}/Tyr, P_{D2}/His, P_{D2}/Ser, eC-A1/His, eC-A1/Tyr, eC-A1/Thr. VEEs of these seven complexes at their optimized ground state were obtained. The VEEs of P_{D1} and eC-A1 were also calculated then. Though P_{D1} and eC-A1 have some difference in conformations, their absorption spectra show little difference (**Table 1**). The optimized structures of those seven complexes are shown in **Figure 2**. It shows that all the amino acid molecules are ligand to chlorophyll a by hydrogen bonding except the His (N---Mg coordination bond).

After ground state geometry optimization and frequency analysis, VEEs of those seven complexes were calculated at TD-B3LYP/6-31G (d, p) level. The results of Q_y, Q_x and B bands were shown in **Table 1**. The Q_y band is major contributed by the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), Q_x is major by HOMO-1 to LUMO, and B band is mixed but major contributed by HOMO to LUMO+1. The frontier molecular orbitals of chlorophyll a are shown in **Figure 3**. It shows that all the molecular orbitals are located at porphorins ring. The molecular orbitals of the seven complexes (not shown) which are discussed here are similar to chlorophyll a. **Table 1** shows

Table 1 The vertical excited energies (nm) of chlorophyll a complexes. The data in bracket are oscillator strength. TD-B3LYP/6-31G (d, p)

	P_{D1}/His	**P_{D1}/Thr**	**P_{D2}/Ser**	**P_{D1}**	**eC-A1/ His**	**eC-A1/ Thr**	**eC-A1/ Tyr**	**eC-A1**
Q_y	581.0 (0.2020)	580.24 (0.2159)	580.97 (0.2186)	578.25 (0.2191)	582.71 (0.1980)	582.62 (0.2455)	579.19 (0.2107)	578.78 (0.2149)
Q_x	555.48 (0.0327)	536.75 (0.0267)	537.50 (0.0292)	535.21 (0.0254)	555.38 (0.0335)	542.79 (0.0352)	536.52 (0.0276)	535.75 (0.0254)
B	401.26 (0.3000)	394.1 (0.4160)	394.32 (0.4937)	391.67 (0.4613)	399.90 (0.2545)	395.81 (0.3594)	391.02 (0.5652)	390.11 (0.5279)

that all of those amino acid molecules induce red-shift of the absorption spectrum to chlorophyll a. The red-shift of B band is larger than Q_y band. And the Q_x band is more sensitive to amino acid molecules than Q_y band. The biggest red shift absorption is obtained from His which ligand to chlorophyll a by N---Mg coordination bond (**Figure 2**). Especially, the Q_x and B band have about 20 nm (682 cm^{-1}) and 10 nm (610 cm^{-1}) red shifts, respectively. For the same amino acid, the histidine and threonine induce red shift for eC-A1 more than for P_{D1}. This means that the absorption of P700 is more sensitive to surround amino acid residues than that of P680.

In summary, the surrounding amino acid induces red shift of the absorption spectrum of chlorophyll a. And the N---Mg coordination bond induces more red shift of absorption than hydrogen bond. His and Thr amino acids induce eC-A1 red shift more than P_{D1}. The absorption of P700 is more sensitive to surround environment than that of P680. In P680, there are two amino acids ligand to each chlorophyll a (P_{D1} or P_{D2}). In P700, there are three amino acids ligand to eC-A1. There are more amino acid molecules surrounding P700 than P680. In addition, there is a water molecular lies behind the eC-A1, which may contribute to the red shift absorption of P700 too. These may be the reason of the absorption spectrum of P700 red shift more than P680. So, it is important to investigate the surrounding protein in photosynthetic system when the absorption spectrum was discussed.

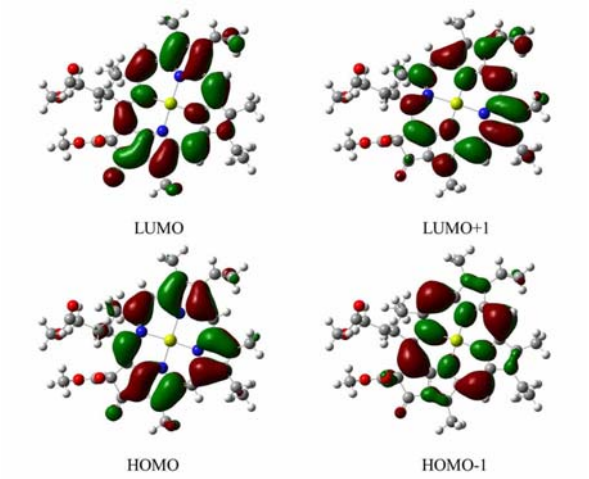

Figure 3: The frontier molecular orbitals of chlorophyll a (eC-A1).

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