

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 ligand 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

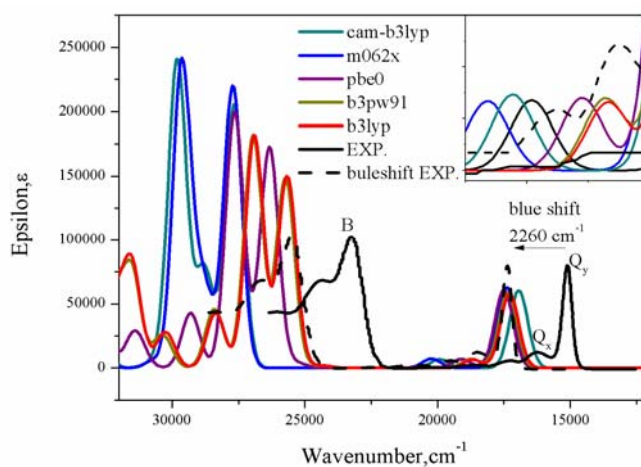


Figure 1: Functional variation on the absorption spectra of chlorophyll a. Method: B3LYP/TD-B3LYP with 6-31G (d, p) basis set and 400 cm^{-1} broadening factor. EXP.: experimental spectrum of chlorophyll a in ethanol [16], Q_y , Q_x and B band were labeled. Buleshift EXP.: the blue shift of experimental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