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NMR Properties of Fenna-Matthews-Olson Light Harvesting Complex: Photosynthesis and its Biomedical Applications

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***Abstract*—In this article we study the structural properties of the bacteriochlorophyll taken from the Fenna-Matthews-Olson (FMO) light harvesting complex found in the green sulphur bacteria. This study is motivated by a range of applications of photosynthetic complexes, including their increasing role in biomedicine, where our better understanding of their properties become critical. Specifically, in our current study we present the nulcear magnetic resonance (NMR) spectrum of the bacteriochlorophyll that is directly taken from the FMO complex, as well as the spectrum for this system for its optimized geometry. We use density functional theory to calculate the optimized geometry and the NMR spectra of the bacteriochlorophyll. From our calculations we found that the chemical shift values are slightly lower for the optimized geometry of the bacteriochlorophyll than the values obtained for the unoptimized bacteriochlorophyll. The differences observed between these two spectra are due to the fact that the unoptimized structure of the bacteriochlorophyll possess the influence of the protein environment of FMO complex.**

Keywords: Photosynthesis, FMO complex, Bacteriochlorophyll, DFT, NMR spectra

I. Introduction

The bacteriochlorophyll is one of the most important molecular systems found in the light harvesting complex in which the photosynthesis event occurs. Most recently bacteriochlorophylls found in the light harvesting complexes are being used for the photodynamic therapy for treatment of some forms of cancer. In order to understand the application of these photosynthetic materials in biomedicine, as well as in the plant cycle and other life science applications, it is very important to understand the structure of these molecules.

It should also be noted that photosynthetic bacteria are good source of producing vitamin B12 which has very important medical applications such as in the treatment of anemia, neuritis and eye problems. There are a number of other applications of photosynthetic bacteria such as the production of coenzyme Q10 which is used in the treatment of certain kinds of heart disease, brain vascular injury as well as the anemia. Furthermore, these bacteria can also be used to produce the porphyrin and ribonucleic acids (RNA) which also have a range of potential applications in the treatment of some diseases as well as the deficiencies in the human body [1]. In the current advances it has been reported that the photosynthetic chloroplasts are being used for the production of bioactive compounds and for other biomedical applications [1], [2], [3]. In the recent studies it has been demonstrated that the photosynthetic bacteria can be used in the field of health and environmental science in the purification of wastewater and biomass recovery [4]. Bacteriochlorophyll and other molecules obtained from its chemical modification can be used as the photodynamic radiotherapic agent because of their photo sensitivity [6]. One of the most common photosynthetic light harvesting complexes that has many current and potential applications and is soluble in water is known as the Fenna-Matthews-Olson complex which is found in the green sulfur bacteria. The molecular structure of the Fenna-Matthews-Olson complex is shown in Figure 1(a). The FMO protein complex contains seven bacteriochlorophyll (Bchl)a molecules wrapped in a string bag of protein that plays an important role in green sulfur bacteria to connect the chlorosome to the reaction center where the photosynthesis event occur. Recently the eighth bacteriochlorophyll has been found by the experiment.

The bacteriochlorophylls contained in the FMO light harvesting complex are the most important components that play a vital role in the photosynthesis process as well as in biomedical applications. Therefore, it is very important to have thorough understanding of the structure of these bacteriochlorophylls at molecular level. The bacteriochlorophylls available in the photosynthetic FMO light harvesting complex consists of a porphyrin ring with the magnesium ion at its center, and the magnesium ion is coordinated to four nitrogen atoms which are known as the pyrrole nitrogens. There is a long hydrocarbon chain connected to the porphyrin ring of the bacteriochlorophyll that is known as the phythyl chain. In the literature, several advancements have been reported on the computational study of the FMO complex using molecular dynamics simulation as well as the density functional theory to

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determine its spectral density, excitation energy and the optical spectrum [5], [7], [8], [9]. We also note that the quantum coherence studies of the FMO complex have been reported in several recent works to elucidate the quantum mechanical time dependent phenomenon associated with the process of photosynthesis [10], [11], [12], [13]. Here in this paper we will describe the NMR spectra for a bacteriochlorophyll monomer taken from the FMO complex with and without optimization of the geometry using density functional theory. The results obtained from our calculations will be discussed in the context of applications.

II. Theory and Methodology

The chemical shift of a nucleus is defined by the relation [18]

$$\delta = \sigma_{iso} - \sigma, \tag{1}$$

where σ is the shielding tensor which describes the magnetic polarizability of an atomic nucleus under study and the σ_{iso} is the isotropic value of the shielding tensor of the standard reference taken in the NMR experiment. Mathematically, the shielding tensor is defined by the relation,

$$\sigma_{\alpha\beta} = \left(\frac{\partial^2 E}{\partial \mu_\alpha \partial B_\beta}\right). \tag{2}$$

where $\alpha, \beta = 1,2,3$ are the tensor indices, E is the total electronic energy, B is magnetic field and μ is the magnetic moment. In calculating the chemical shift we take the difference between the measured shielding tensor and the shielding tensor of the reference system. In our calculation we have taken the tetra methyl saline (TMS) as a reference system. Also the value of the isotropic shielding coefficient can be calculated by averaging three principle components of the shielding tensor from the shielding tensor matrix i.e $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$. Furthermore, another quantity that describes the electronic structure properties of the system is known as the nuclear quadrupole interaction. In this paper we also calculate the quadrupole interaction properties such as the asymmetry parameter and the quadrupole frequency for the nuclei ^{14}N and ^{25}Mg available in each bacteriochlorophyll of FMO complex.

If V_{XX}, V_{YY} and V_{ZZ} are the principal components of the electric field gradient (EFG) tensors, then the asymmetry parameter of the system can be expressed as

$$\eta_Q = [V_{YY} - V_{XX}]/V_{ZZ}, \tag{3}$$

where symbol Q stands for the nuclear quadrupole moment and the EFG tensor follow the order

$$|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}| \tag{4}$$

and the EFG tensor is traceless

$$\sum_i V_{ii} = 0. \tag{5}$$

From above relations one can express

$$V_{XX} = -(1 + \eta_Q)V_{ZZ}/2, \tag{6}$$

$$V_{YY} = -(1 - \eta_Q)V_{ZZ}/2. \tag{7}$$

From the values of the electric field gradient tensor and the quadrupole moment of the nuclei, the quadrupole coupling constant can be obtained as

$$C_Q = eQeq/h; \quad eq = V_{ZZ}, \tag{8}$$

where Q is the nuclear quadrupole moment of the nuclei under study which is expressed in the unit barn, h is Plank's constant and e is the electronic charge.

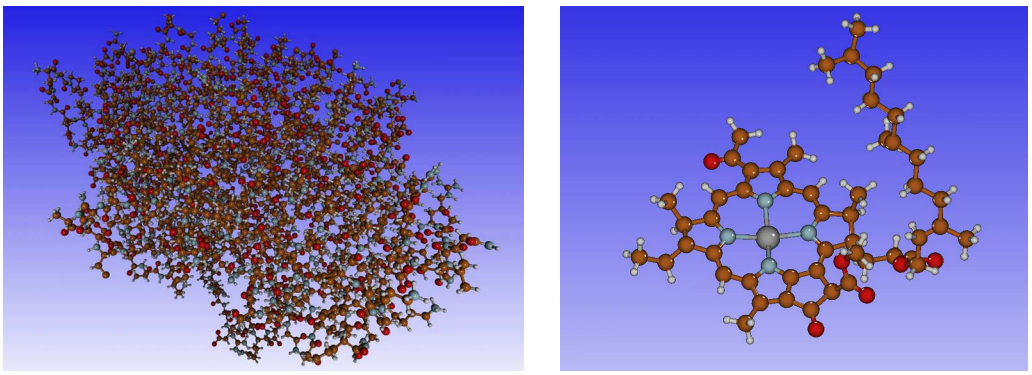
III. Computational Details

In order to calculate the NMR magnetic shielding tensors we have used the density functional theory implemented by the Gaussian 09 set of programs. In particular, the calculation of these NMR spectra has been carried out by using the density functional PBE1PBE developed by Purdew, Burke and Ernzerhof [14], [15]. The chemical shift of a particular carbon atom in bacteriochlorophyll has been determined by taking the difference of its shielding tensor from the shielding tensor of the carbon atom in tetra methyl saline (TMS). In calculation of the NMR spectra we have implemented the Gaussian broadening for the chemical shifts of the carbon atoms obtained from the density functional method. More specifically, the combination of Gaussian and Laurentzian broadenings is applied to the chemical shift of each atom to calculate the NMR spectra.

The structures of the FMO complex used here in our study have been taken from the protein data bank which was determined by the X-ray crystallographic method [16], [17] and for chlorophyll *a*, the structure has been taken from the available literature. Since the crystal structure of the FMO complex used in our study was determined by using the X-ray crystallographic technique, the coordinates of the hydrogen atoms are not included in the PDB structure of the FMO protein. Hence, the hydrogen atoms have been added to the geometries obtained from this PDB structure to cap the dangling bonds. Then the system was partially optimized for hydrogen atoms using density functional theory implemented by the Gaussian 09 set of programs. The partial optimization of the hydrogen atoms has been done to get the ground state geometry of molecules. During partial optimization the geometry of the other atoms was kept as it was in the original structure. This means that the electronic structure of these isolated systems includes all those effects that were coming from their interactions with the environment of the protein. Finally, the separation of seven different chlorophylls has been acheived by using the molecular visualization software VMD.

IV. Results and Discussion

Here in the model structure of the bacteriochlorophyll, only seven bacteriochlorophylls are shown. As we already mentioned, there is also experimental evidence for the existence of eighth bacteriochlorophyll in the FMO complex [17]. It is known that the FMO complex has a particular feature, i.e. it can be crystallized very easily which is the subject of



(a) (b)

Fig. 1. Molecular structure of the Fenna-Mathews-Olson light harvesting complex (a) The whole structure with addition of hydrogen and (b) The model structure for singe bacteriochlorophyll

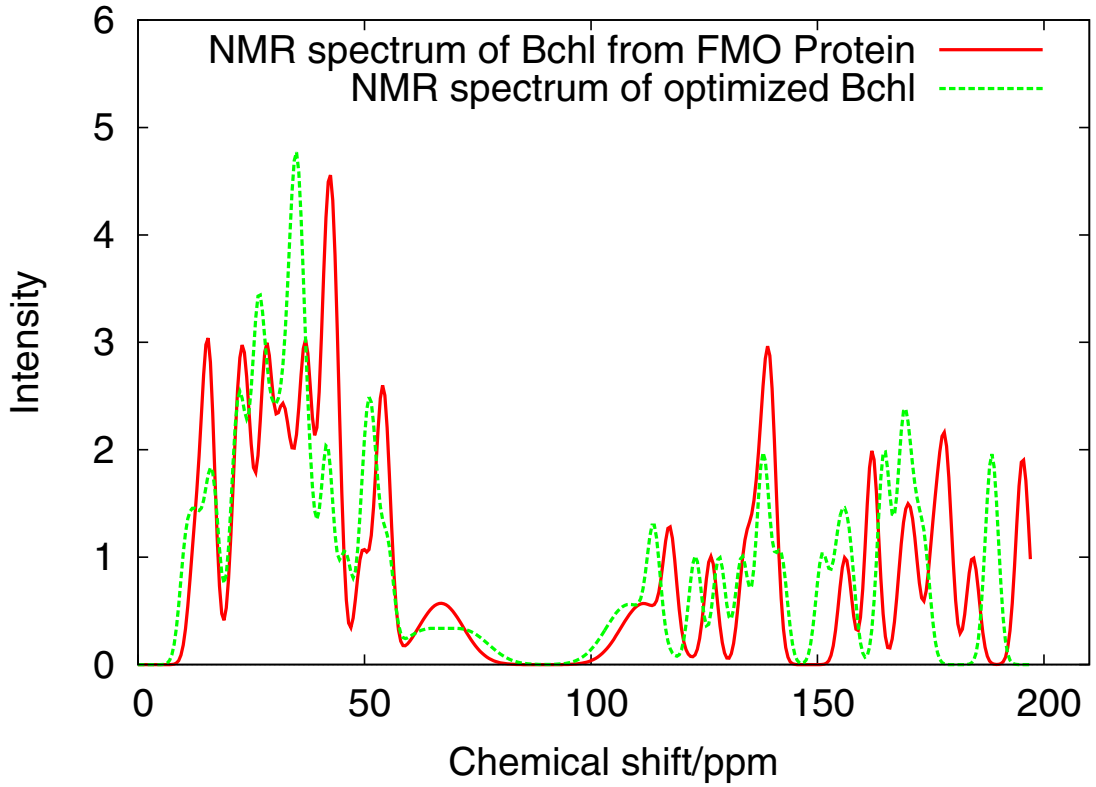


Fig. 2. NMR spectra of the bacteriochlorophyll taken from the FMO complex and its optimized geometry

interest for the atomistic study. The structure of this FMO complex has been taken from the protein data bank [16]. From this complex seven bacteriochlorophylls have been isolated in such a way that the electronic structure of all the atoms is unchanged. To each of these isolated bacteriochlorophylls we have added the hydrogen atoms to saturate the dangling bond and then performed partial optimization of hydrogen atoms using density functional theory.

The structure of the full FMO complex taken from the protein data bank is shown in Figure 1a and the single bacteriochlorophyll separated from protein is shown in Figure 1b. Using density functional theory we have studied the NMR spectrum for the bacteriochlorophyll taken from the FMO light harvesting complex. For this single bacteriochlorophyll molecule we have also performed the full geometry optimization using density functional theory. As a result of optimization, the electronic structure of this system will be completely changed from the original structure directly taken form the FMO protein. For this completely optimized structure of bacteriochlorophyll, we calculated the NMR spectra using

the same density functional and basis set as it was used for the unoptimized structure. The results for NMR spectra for these two molecular configurations of the same bacteriochlorophyll have been presented in Figure 2.

From these results we see that the patterns of the NMR chemical shift are the same in both these cases, but there is a small shift in the peaks of the NMR spectra for the optimized system compared to the values of the unoptimized structure.

For the optimized structures of the bacteriochlorophyll we have also determined the infrared spectra using density functional theory. The peaks in IR spectra correspond to the minimum absorption of the IR frequency. The variations in the absorption frequency that we have observed indicate the structural variation in the bacteriochlorophylls under study. The position of magnesium atom with respect to the porphyrin ring, as well as the tail connected to the bacteriochlorophyll system, also play the role in the variation of the infrared absorption spectra.

We have also investigated the quadrupole interaction parameters for the different bacteriochlorophylls present in the FMO complex. In particular, we obtained the results for the electric field gradients of the magnesium and the pyrrole nitrogens for seven types of the chlorophyll taken from a unit of FMO complex. In calculating the quadrupole interaction parameters we have used quadrupole moments for the atoms as Q(^{25}Mg) =0.1994 barn and N(^{14}N)=0.02068 barn. In order to carry out a comprehensive study of the quadrupole properties of several bacteriochlorophyll systems it is very important to see the change in these parameters with respect to the basis set. For this purpose we have studied the variations in these parameters for ^{14}N nucleus of BChl1 with the change in the size of the basis set. From the obtained results of the quadrupole parameters of the ^{14}N nuclei of the BCHl1, we have concluded that the quadrupole parameters are very small for the 3-21G basis set, but on increasing the size of the basis set the values start to become more consistent. The convergence of the basis set starts at the basis set level 6-311G. Therefore, we have studied the quadrupole parameters for the system with this basis set. Details of these results will be presented in our forthcoming publication. Finally, we have also analysed the quadruple interaction parameters for BChl1 using Hartree-Fock theory and found that the results show a similar trend as it is found in the case of the density functional calculations.

V. Conclusions

In conclusion, we establish that the effect of the protein environment on the bacteriochlorophyll taken from the FMO light harvesting complex has a significant effect as seen from the changes in the NMR spectra. As a result, this study provides deeper insight into the sensitivity of the physical properties with respect to the structural changes which ultimately help us to better understand biological phenomena in the plants, to start with. Furthermore the study of the NMR spectra of the modified bacteriochlorophylls and time dependent phenomena pertinent to their behaviour will also provide us with better understanding of the process of photodynamic therapy for cancer treatment in human body, as well as other applications discussed in our introductory part.

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