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Component spectroscopic properties of light-harvesting complexes with DFT calculations

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Abstract: Photosynthesis is a fundamental process in biosciences and biotechnology that influences profoundly the research in other disciplines. In this paper, we focus on the characterization of fundamental components, present in pigment-protein complexes, in terms of their spectroscopic properties such as infrared spectra, nuclear magnetic resonance, as well as nuclear quadrupole resonance, which are of critical importance for many applications. Such components include chlorophylls and bacteriochlorophylls. Based on the density functional theory method, we calculate the main spectroscopic characteristics of these components for the Fenna-Matthews-Olson light-harvesting complex, analyze them and compare them with available experimental results. Future outlook is discussed in the context of current and potential applications of the presented results.

Introduction

The process of photosynthesis is important for a multitude of reasons, including its usage by living cells and organisms to help them convert light energy into the chemical energy to fuel life. Common example of the photosynthesis process is the conversion of carbon dioxide and water into the carbohydrate and oxygen in presence of light. In this case, the light harvesting (chlorophyll) absorbs light from sun, converting it into the chemical energy. Light-harvesting complexes (LHCs) are that part of photosynthetic systems that channel energy from the antenna to the reaction centre (RC). LHC proteins are fundamental to this type of photosynthesis, which is prevalent for terrestrial plants and known as oxygenic (e.g., Bína *et al.*, 2019). For example, eukaryotes and cyanobacteria carry out oxygenic photosynthesis (OP), producing oxygen. There is another type of photosynthesis, known as anoxygenic (AP), which is carried out by other types of bacterial phototrophs. Normally, it is a bacterial photosynthesis that occurs under anaerobic conditions. In either of these cases, for photosynthesis to continue, the electron lost from the Reaction Center (RC) pigment must be replaced, but the source of this electron is different for these two types of photosynthesis. In OP, the water molecule is split and supplies the electron to the RC (oxygen is generated as a byproduct and is released, and hence the name of this type of photosynthesis). In AP, other reduced compounds serve as the electron donor (e.g., hydrogen sulfide or thiosulfate) and oxygen is not generated (instead, elemental sulfur or sulfate ions are generated, respectively). As a result, the structure of photosynthetic apparatus in these two cases is different, but in both cases this apparatus is a sophisticated machinery that consists of several complexes whose components are encoded by both nuclear and chloroplast genes (Rochaix, 2016). In nature, these genetic systems in all photosynthetic organisms act in a coordinate manner, so that with continuous environmental changes they are able to adapt, to protect themselves, and to maintain optimal photosynthetic activity.

In this paper, we are interested in some particular spectroscopic properties of major components of LHCs that play a vital role in photosynthesis, namely bacteriochlorophylls and chlorophylls, focusing mainly on the AP case. Firstly, we note that the AP pigments are similar to chlorophylls with main differences attributed to molecular detail and peak wavelength of light absorbed. For example, while the maximum absorption of electromagnetic photons in the near-infrared region for Bacteriochlorophylls (BChls) is typically within their natural membrane milieu, the Chlorophyll-a (Chl-a) has a shorter peak absorption

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wavelength. Secondly, while chlorophylls are the most abundant natural organic pigments on this planet, visible from outer-space (Grimm *et al.*, 2006), they are unstable and very sensitive to the environmental conditions, which can bring various modifications, changing not only their photosynthetic function but even their usefulness in supporting life (including heterotrophic organisms). At the same time, the adaptation of the entire photosynthetic apparatus, mentioned above, are largely due to the evolution of chlorophylls to fulfil their functions in the photosynthesis. For example, in OP LHCs they strongly absorb light and transfer the excitation energy, while in the photosynthetic RC complexes specialized chlorophylls play an important role in primary charge separation, as well as energy transduction processes. In doing so, they contribute significantly to the stabilization, regulation, and protection of the photosynthetic apparatus.

In our quest to better understand photosynthesis, both plants and photosynthetic bacteria are important to analyze with advanced methodologies not only in their entirety, but also component-wise. Such an analysis would contribute to our ability of using more efficiently their obvious advantages related to their rapid growth in chemically defined media and controlled environments. As a result, it will add to the progress in the areas of design and synthesis of pigments for applications ranging from photocatalytic to novel optoelectronic devices in biosensing and bioplasmonics. Therefore, the characterization of fundamental components, present in Pigment-Protein Complexes (PPCs), in terms of their spectroscopic properties such as infrared (IR) spectra, nuclear magnetic resonance (NMR), as well as nuclear quadrupole resonance, is of crucial importance. In what follows, we address this issue in detail, specifically focusing on the example of BChls and Chls in the context of one of the most studied LHCs. The rest of the paper is organized as follows. In Section "Chrolophylls and Bacteriochlorophylls as Main Components of LHCS" we provide details on the main components of PPCs which are studied here, while Section "Photosynthetic Apparatus in Anoxygenic Bacteria" is devoted to the description of the photosynthetic apparatus in anoxygenic bacteria, focusing on the FMO complex. Sections "Theoretical Details" and "Computational Details" give details of our theoretical model and its computational implementation. Section "Results and Discussions" presents the results obtained with DFT and Section "Applications and Future Outlook" provides insight into their current and potential applications. Our main results are summarized in Section "Conclusions".

Chrolophylls and Bacteriochlorophylls as Main Components of LHCS

The studies of spectroscopic properties of Chrolophylls and Bacteriochlorophylls provide an important basis, on the component level, for advancing our understanding of the function of PPCs. Ultimately, such studies are also necessary for our progress in implementing efficient control when moving from single LHCs to a network. For example, it could be control against the damage due to changing environmental conditions, where LHCs have to work as a switch between harvesting and protective states enabling tracking the light intensity fluctuations in nature and smoothing electron transport flow oscillations (Ruban, 2018). Not only the regulated conformational flexibility, but also component properties are responsible for the efficiency of these operations. In all such cases it is critical to build physics-based mathematical models in a bottom-up approach (validated by experimental results whenever possible), starting from the fundamental components, which can then be tested on larger *in vivo* systems (Grubera *et al.*, 2018; Badu *et al.*, 2020). Using this approach, we can build man-made structures mimicking the general property of biological systems to utilize the same system properties for different purposes.

Chlorophylls, whose name originated from two Greek words (chloros-green and phyllon-leaf), are abundant on Earth and are produced naturally in estimated quantity between 109 and 1012 tons annually (Grimm *et al.*, 2006). They play a key role in processes which support life, including non-photosynthesizing forms of life. Over the past years, many new chlorophylls have been isolated with the development of new chromatographic techniques. Substantial progress has also been achieved in our better understanding the crystal structures of many classes of chlorophyll-protein complexes by using increasingly sophisticated spectroscopic techniques, as well as in our ability to selectively modify the pigments and the proteins by using novel methodologies. All this contributed to the current body of knowledge about PPCs. Nevertheless, due to this diversity and inherent sensitivity, further insight and elucidation of Chl structure and properties within PPCs still represent a formidable challenge. One of the reasons for that is that Chls are chemically unstable to both acids and bases, to oxidation and light. Our particular interest here is in Chl-a. It is well known since earlier works on the subject (e.g., Fenna and Matthews, 1975) that the chemical structure of Bchl differs from Chl-a (it has two extra hydrogen atoms in ring II and an acetyl group in place of the vinyl group on ring I). In bacteriochlorophyll, a magnesium ion is located at the center of the porphyrin ring coordinated by four pyrrole nitrogen. The pigments used in the process of photosynthesis are usually water insoluble, but there exists a particular type of bacteriochlorophyll protein that is soluble in water, and we discuss this in the subsequent section. We have included in our study here both, BChls, originally reported in (Fenna and Matthews, 1975), and Chl-a. Clearly that on a larger scale, when considering the Bchl-protein e.g., interactions between chlorophyll and protein including liganding to the magnesium atom, hydrogen bonding and hydrophobic interactions would play an important role in the final arrangement of the chlorophyll molecules (*in vivo*). However, for the reasons highlighted above, our focus here on the component analysis.

The studies of Chl and BChl properties have been receiving continuous attention, particularly in the context of their representatives in various simplified systems, and such studies included DFT and *ab initio* quantum chemical calculations (Wan *et al.*, 2011; Najdanova *et al.*, 2018). Moreover, an increasing amount of experimental research is devoted to engineering Chl and Bchl pigments that are bound to photosynthetic light-harvesting proteins as one of the promising strategies to regulate spectral coverage for photon capture and to improve the photosynthetic efficiency of these proteins (Saga *et al.*, 2019). This provides us with an additional motivation for the analysis of component spectroscopic properties by using such powerful tools as DFT.

Our focus from now on turns to a special type of LHCs, found in the photosynthetic green sulfur bacteria, which synthesize a complex mixture of bacteriochlorophylls and chlorophylls.

Photosynthetic Apparatus in Anoxygenic Bacteria

One of the most studied LHCs is the Fenna-Matthews-Olson (FMO) complex (Fenna and Matthews, 1975; Olson, 2004; Schmidt *et al.*, 2011; Yeh and Kais, 2014; Barroso-Flores, 2017; Maiuri *et al.*, 2018; Kim *et al.*, 2020; Claridge *et al.*, 2020), which is part of the photosynthetic apparatus of a family of obligately anaerobic photoautotrophic bacteria such as the green sulfur bacteria (Chlorobiaceae). These bacteria are predominately aquatic and similar to, e.g., purple sulfur bacteria (Chromatiaceae), but their photosynthetic metabolism is somewhat different from that of algae or green plants. In particular, for them, water does not serve as an electron-donating substrate and molecular oxygen is not generated (sulfide ions are mainly used as electron donors), hence we are dealing with AP (see Section "Introduction"). The FMO complex, the first PPC that structure analyzed by x-ray spectroscopy, is water-soluble.

The structure of the FMO complex is homotrimeric with C3-symmetry, where each monomer contains eight bacteriochlorophyll-a (BChl-a) molecules. The original paper by Fenna and Matthews, (1975) reported seven such molecules (see also a review by Olson, (2004) with the subsequent more recent discovery and analysis of the eighth BChl-a molecule, see e.g., (Schmidt *et al.*, 2011; Yeh and Kais, 2014). It was demonstrated by both theory and (crystallography) experiment that this loosely-bound eighth pigment in each subunit is the linker to the baseplate. These molecules are bound to the protein scaffold via ligation of their central magnesium atom (more precisely, to amino acids of the protein or water-bridged oxygen atoms). The FMO complex mediates the excitation energy transfer from light-harvesting chlorosomes to the membrane-embedded bacterial RC, and there is also an exciton interaction between the bacteriochlorophyll molecules (Olson, 2004). Given all currently known information, it is possible to calculate structure-based optical spectra with various degrees of approximations, e.g., with an only excitonic coupling of BChls or better by approximating pigment-protein coupling. Moreover, such approximations are currently extendable to include also the Reaction Center (RC), so the entire FMO-RC super-complex can be analyzed. Before moving in the next section to our analysis of component spectroscopic properties in such complexes, we will briefly summarize the energy processes involved in the context of the components of interest. Chrolophylls have evolved to fulfill several functions in photosynthesis. They are incorporated into LHCs. As we know from the OP discussion in Section "Introduction", they strongly absorb light and it has been often stated that they transfer the excitation energy with quantum efficiency near 100% (e.g., Grimm *et al.*, 2006). Given the nanometer distances between chlorophylls, which vary widely between 0.9–2.4 nm (Keren and Paltiel, 2018), it is plausible that light harvesting in photosynthesis employs both classical and quantum mechanical processes. An exciton, when a chlorophyll absorbs a photon and an electron is excited to a higher energy level, can transfer from chlorophyll to chlorophyll (under the assumptions of their closedness and minimal exciton energy dissipation through heat). The FMO complex example, studied in Keren and Paltiel, (2018), shows that the electron excitation could transfer energy to the vibrations, and these could, in turn, modulate electron transfer, thereby giving rise to beats without the need to invoke quantum coherence. This conclusion preceded an extensive debate in the literature about possible processes of quantum coherence in these LHCs with some conclusive arguments that such coherence has no significance to the functioning of the complex (Wilkins and Dattani Nikesh, 2015). Some of the works specifically highlighted the importance of originally-discovered seven BChls in these possible processes (Barroso-Flores, 2017; Zhu *et al.*, 2012). Along its way, this direction brought about new ideas connected with the evolution analysis of the FMO complex with more sophisticated algorithms currently available such as artificial intelligence and machine learning techniques (Barroso-Flores, 2017; Rodriguez and Kramer, 2019). The current status of the issue of the apparent preservation of a fragile quantum "superposition" state in FMO complexes, in our opinion, has been summarized in (Maiuri *et al.*, 2018) which supported the role of coherent coupling in photosynthesis but changed the previous view of how long-lived quantum coherence could be detected. This conclusion was derived based on the possibility to set up vibrations on one bacteriochlorophyll molecule in the protein with a pump pulse (and probing a separate bacteriochlorophyll in that same protein, so that an overall signal from the combined effect of the pump and probe pulses could be generated). The demonstrated coherence experiment, that can be probed at the absorption resonances of other bacteriochlorophyll molecules, is pertinent to the ground state. It also highlighted that the energy transfer in the FMO complex is influenced by vibrionic coupling in LHCs, and its efficiency is dependent on the exploration and utilization of the coupled vibrational environment of this complex. It should also be noted that it has been argued for quite some time that light-harvesting regulation in LHCII is coupled with structural changes as many experiments demonstrated large variations of the excitonic coupling strength when analyzing various chlorophyll pairs (Liguori *et al.*, 2015). This has also accelerated the interest to LHCs from the molecular dynamics community with the attempts to develop a more microscopic picture of the dynamics, with the ambitions for atomistic and fully quantum-mechanical models of the whole process reproducing the experimentally obtained spectra (e.g., Hein *et al.*, 2012; Kramer and Rodriguez, 2020; Segatta *et al.*, 2019). Largely, these ambitions have been limited to simplified theoretical models for LHCs considered as an exciton system coupled to a bath under additional assumptions and approximations of vibrational modes of the pigments. While such coupled models are becoming increasingly important, in moving to the design of artificial systems, one would also need to know more about the component spectral characteristics of underlying biochemical complexes.

Theoretical Details

To understand the FMO complex role in the photosynthesis, many computational and experimental studies have been carried out by using various techniques ranging from the density functional theory to NMR (e.g., Maiuri *et al.*, 2018; Chen *et al.*, 2017; Saer *et al.*, 2017; Thyrhaug *et al.*, 2018; Nalbach *et al.*, 2015; Makarska-Bialokoz and Kaczor, 2014; van Gammeren *et al.*, 2004; Sinnecker *et al.*, 2002; Sundholm, 1999; Taguchi *et al.*, 2014; Xu *et al.*, 2012; Badu and Melnik, 2017; Jurinovich *et al.*, 2014). The interest in such studies has been further fueled by the importance of this complex in the design of artificial energy transport networks such as those which might find application in solar cells (Baker *et al.*, 2017). In the context of this complex, the environmental effect of the light-harvesting phenomenon has also attracted considerable attention from the researchers (Sarovar *et al.*, 2011; Huo and Coker, 2017). More refined atomistic and quantum mechanical calculations have been directed to the analysis of time-dependent phenomena associated with the process of photosynthesis (Hoyer *et al.*, 2010; Ishizaki and Fleming, 2011; Scholes, 2010; Shim *et al.*, 2012) which has stimulated further debates on the role of classical and quantum processes in the energy transfer in such LHCs, as discussed in the previous section. In this context, high-performance computing algorithms for models based on Hierarchical Equations of Motion have also been developed (e.g., Kreisbeck *et al.*, 2011) and the spectral density of the FMO complex was analyzed with DFT (Renger *et al.*, 2012). We also mention here computational works with molecular dynamics and DFT methodologies (Jurinovich *et al.*, 2014; Higashi and Saito, 2016; König and Neugebauer, 2013; Thyrhaug *et al.*, 2016) and experimental works on mass spectrometry of the FMO complex (Tronrud *et al.*, 2009; Wen *et al.*, 2011). In the earlier works, the optical properties such as the absorption spectra of the FMO complex were analyzed by using both analytical and experimental methods (Brixner *et al.*, 2005). The work (O'Malley and Collins, 2001) has also deserved to be mentioned where DFT studies on models of BChls and Chls have related to the influence of magnesium legation and the formation of radical orbitals without significant change in the hyperfine coupling properties of the systems.

When it comes to the detailed analysis of some key component spectral properties, we note that the nuclear quadrupole parameters of Chl-a, e.g., have been known for a long time (Lumpkin, 1975), whereas analogous spectroscopic properties of BChls have not been reported. As already mentioned, we focus in the paper on the primary seven BChls of the FMO complex, with additional remarks on other pigments when necessary. Hence, the particular structure of the FMO complex that is of interest here is shown in Fig. 1.

In summarizing our model for computation, we start by writing the equation for chemical shift of a molecule as (Facelli, 2011)

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

where σ is shielding tensor and σ_{iso} is the isotropic value of the shielding tensor in the standard reference taken in the NMR experiment. Mathematically, the shielding tensor is expressed as follows:

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

In the above equation, we write the indices of the shielding tensor as $\alpha, \beta = 1; 2; 3$ and E, B and μ are the total energy, magnetic field and magnetic moment, respectively. In this manuscript, we consider tetra methyl saline (TMS)

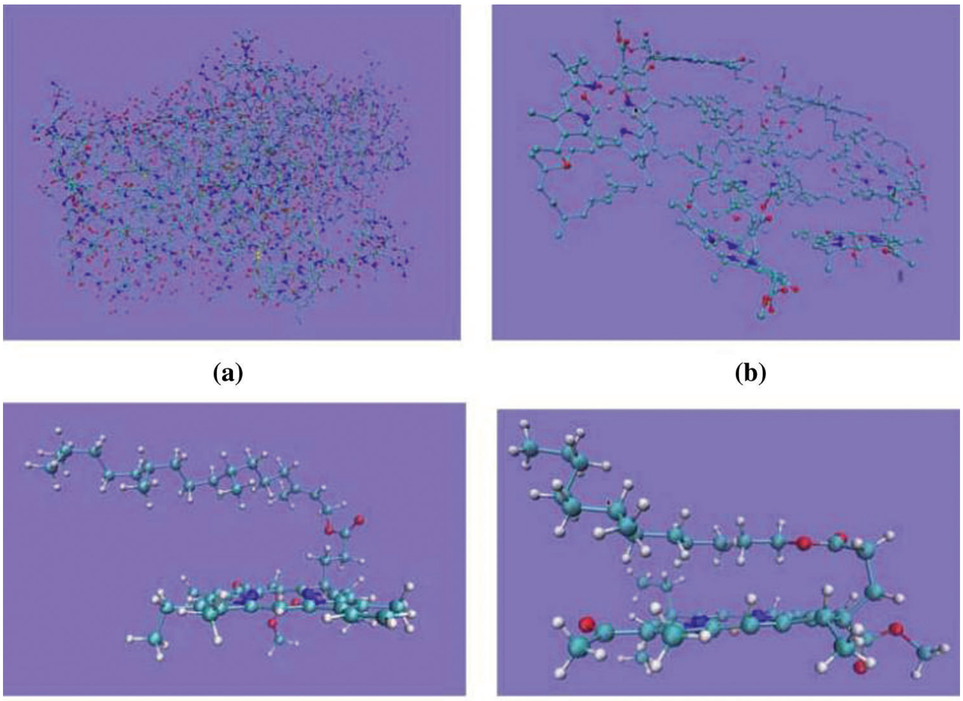

(a) (b) (c) (d)

FIGURE 1. (Color online) (a) Schematic of the atomic structure of FMO complex of interest (BChls-a wrapped in a string bag of protein), (b) the model structure for BChls without protein (c) the model structure for Chl-a, and (d) the optimized structure of BChl. These structures are generated by using VMD tool.

as a reference to calculate the change in shielding tensor of the green sulfur bacteria. The isotropic value of the shielding tensor in the right-hand side of above equation is given as $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$, where σ_{ij} is the component of $\sigma_{iso.}$

Another important characteristic analyzed here is pertinent to the nuclear quadrupole interaction properties of bacteriochlorophylls of the FMO complex which are calculated by using the equation (Dybowski, 2003)

$$\eta_Q = \frac{V_{YY} - V_{XX}}{V_{ZZ}}, \tag{3}$$

where Q is the nuclear quadrupole moment and V_{XX}, V_{YY}, V_{ZZ} are the principal components of the electric field gradient. Note also that traceless V_{ij} follows the inequality relation in the form:

$$|V_{zz}| \geq |V_{YY}| \geq |V_{XX}|, \tag{4}$$

where

$$\sum_i V_{ii} = 0, \; i = X, \; Y, \; Z. \tag{5}$$

From above relations one can express

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

and

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

Finally, one can calculate the quadrupole interaction constant as

$$C_Q = \frac{1}{h}eQV_{ZZ}, \tag{8}$$

where, as before, the nuclear quadrupole moment of the nuclei is Q, the Planck constant is h, and the electronic charge is e. Next we provide details of the computational implementation before going to the main results and discussion.

Computational Details

The component spectroscopic properties of the FMO complex have been calculated by using the DFT implemented in the Gaussian 09 set of programs (Frisch *et al.*, 2009). In particular, the calculation of the NMR spectra has been carried out by using PBE1PBE functions developed by Perdew, Burke and Ernzerhof (Adamo and Barone, 1999; Perdew *et al.*, 1996). Furthermore, the DFT methodology is well established and have been used for many other important and elaborate systems and complexes (e.g., (Du *et al.*, 2015; Prabhakar and Melnik, 2017; Prabhakar and Melnik, 2018) and references therein). In our specific case here, the calculation of nuclear magnetic resonance properties has been performed by using the gauge-including atomic orbital (GIAO) method. The chemical shift has been calculated by taking the difference in shielding tensors from the chemical shift of the carbon atom in Tetra Methyl Saline (TMS). The Gaussian broadening has been added to the NMR spectra for the chemical shifts of the carbon atoms. The atomic structures of the FMO BChls have been directly taken from the protein data bank (Tronrud *et al.*, 2009; Wen *et al.*, 2011) and for chlorophyll-a, the structure has been taken from the reference (Sundholm, 1999). We have added the hydrogen atoms at the dangling bonds in the structure of BChls. Then, we have optimized the atomic configuration to get the ground state eigenenergy of the components. During the optimization, with the H atoms in the molecules, we kept the other atoms fixed (with respect to the original structure). The optimization has been carried out for all atomic configurations of BChls in order to analyze the influence of the protein environment. Finally, we have used the VMD tools for the separation of different BChls from the entire structure of the FMO complex (e.g., (Humphrey *et al.*, 1996)).

In order to calculate the NMR spectra of the resulting component systems, we have calculated the NMR chemical shielding tensor for all ^{13}C atoms. Then, these calculated shielding tensors of each ^{13}C nuclei have been subtracted from the shielding tensor of ^{13}C in TMS. Finally, we have calculated the chemical shift of each particular ^{13}C atom, according to the formula given in Section “Theoretical Details”. During the calculation of the NMR spectra, we have implemented a combination of Gaussian and Lorentzian broadenings to the chemical shifts of the system. Specifically, we have used the Gaussian broadening of 2 ppm for the carbon atoms with chemical shifts below 60 ppm and the Lorentzian broadening of width 7 ppm for the carbon atoms with values of the chemical shift above 60 ppm.

Results and Discussions

The VMD generated atomic structure of Fenna-Matthews-Olsen light-harvesting complex taken from protein data bank is shown in Fig. 1(a) and the component-based structures of BChls that are of interest here without protein are shown in Fig. 1(b). These component BChls have been isolated from the entire FMO complex in such a way that the electronic structures of all the atoms remain the same, which allows performing the atomistic quantum mechanical calculations on the individual fundamental components of the FMO complex. The results for the NMR spectra of such BChls are presented in Figs. 2(a)–2(h). Analogous results for Chl-a are presented in Fig. 3(a). From Fig. 2 it is clear that BChls taken from the same structures exhibit quite different NMR spectra which apparently demonstrates that the NMR spectra are very sensitive to the own structures of BChls. Evidently, the characteristics of local environments would influence this sensitivity further (as well as dihedral angles for the links between the tail and the porphyrin ring, etc.). The position of the magnesium atom at the center of the porphyrin ring also plays an important role in the NMR spectrum. From the NMR spectrum of Chl-a, we observe that the first pronounced peak of the ^{13}C NMR chemical shift in Fig. 3(a) is approximately around 50 ppm and the second peak is around 150 ppm. There are experimental measurements done on the Chl-a using the magic angle-spinning technique and Fourier transform infrared spectroscopy (Andrew, 1981; Brown *et al.*, 1984; Li *et al.*, 2018). It is also known that when Chl-a is hydrated, it becomes solid in the form of powder, otherwise, it exists as a viscous fluidic form. In a number of the experiments mentioned, the solid-state of the Chl-a system was used and

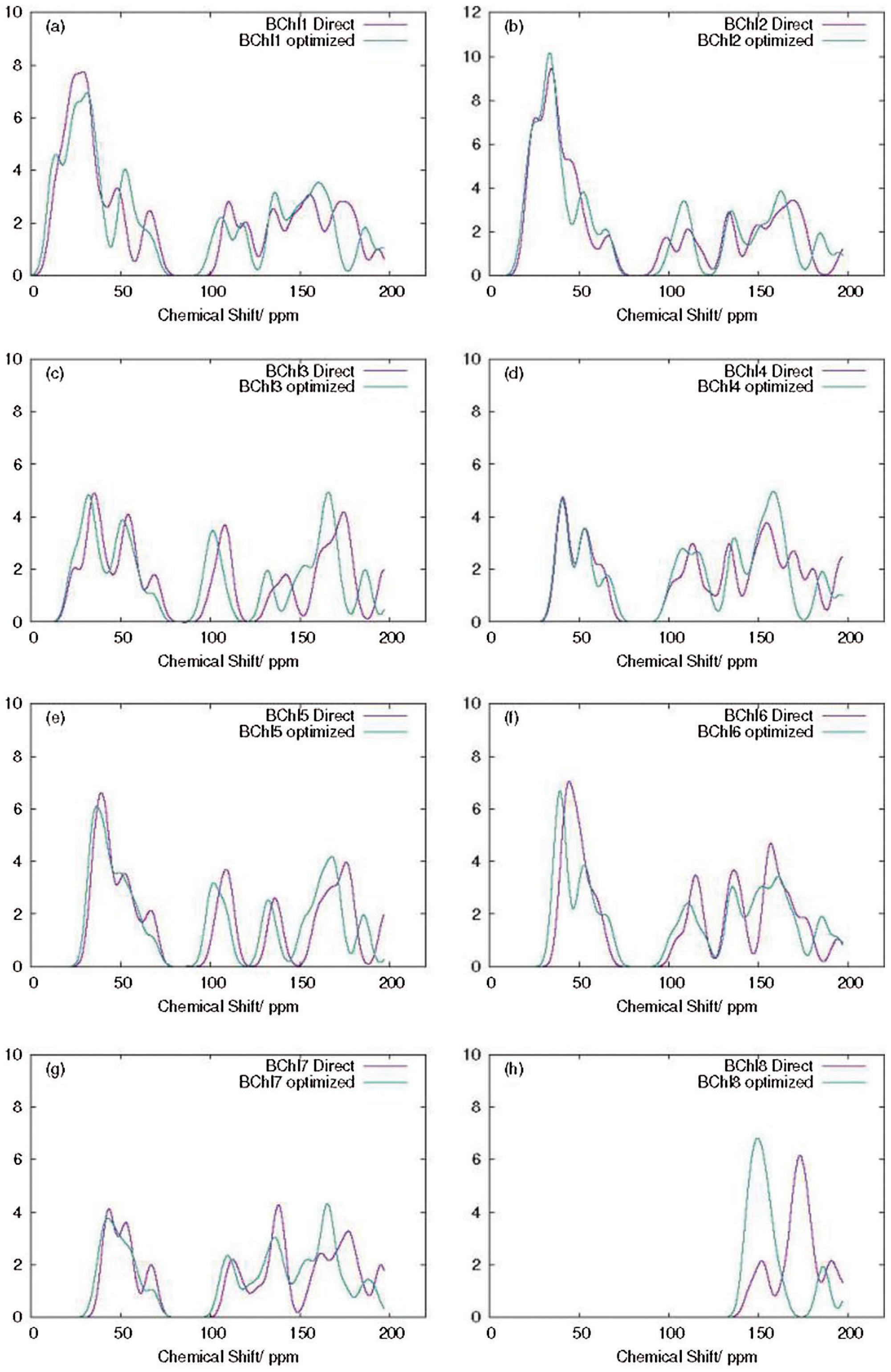
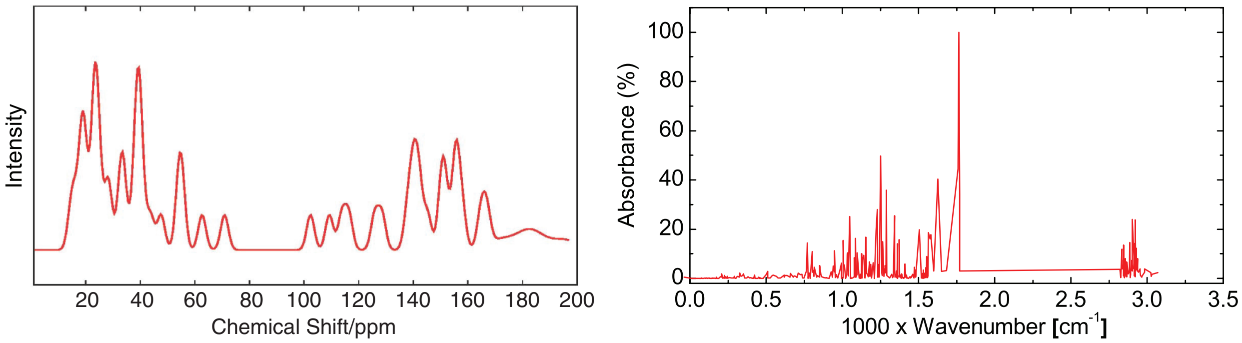


FIGURE 2. (Color online) NMR ^{13}C chemical shift of BChls-a from the FMO LHC ("purple"-directly taken from the database, "green"-optimized).

the reported peaks in ^{13}C chemical shift were at around 50 ppm and 150 ppm, which is in close agreement to the results presented here. In the structure of BChls, there are several kinds of functional groups and the different kinds of bonds based on the position of the atoms: carbon, oxygen, nitrogen, and hydrogen. Usually, the chemical shift for the carbon atoms in a particular molecule varies depending on the type of bonding and the atom around it. In general, the single bonded carbons have a smaller chemical shift in comparison to the double-bonded carbons. Also, some of the ^{13}C NMR chemical shifts between 120 to 150 ppm correspond to the carbons with double bonds present both in the aliphatic chain and the aromatic ring of the molecule. Thus, by observation of the peaks in the NMR chemical shift spectra one can find the corresponding carbon atom with its bonding characteristics. More broadly, the structure of a molecule can be predicted from the NMR chemical shift spectra. Additionally, if the NMR chemical shift of a carbon atom is different among all the BChls, which is indeed the case in Fig. 2, then one can conclude that there



(a) (b)

FIGURE 3. Spectral characteristics of Chl-a: (a) NMR ^{13}C chemical shift and (b) absorption spectrum.

are some changes either in the bonding or in the environment or both. Under the photosynthetic processes involving these BChls, there will be significant changes in their electronic structure which will ultimately change the bond parameters in the molecule. This can be elucidated via the determination of the ^{13}C NMR spectra of the system.

Similar to the component spectral characteristics of other characteristics reported here, infrared spectra of FMO fundamental components have been calculated on optimized structures, as detailed in Section "Computational Details" and demonstrated by Fig. 4, where IR absorption spectra of BChl7 are given as an example for the original and optimized geometries. The infrared spectra of the optimized structures of BChls are presented in Fig. 5, while the corresponding plot for Chl is given in Fig. 3(b). We observe that the peaks for each of the BChl molecules are between 1000 and 2000 cm^{-1}. These peaks in the IR spectra correspond to the minimum absorption of the IR frequency, which is also very sensitive to the magnesium atom with respect to the porphyrin ring, as well as to the tail connected to the BChl system. The IR spectra provide another physical quantity that is useful in determining the structure of the molecular systems of interest here. Indeed, the peaks in IR spectra represent the frequencies resonant with the absorption frequencies of the different species in the FMO complex. Similar to NMR chemical shift characteristics, the IR frequency depends on the mass and the bonding characteristics of the atom in the molecule. It can be seen that the absorption resonant frequencies in the IR spectra are in the region below 1800 cm^{-1} (0.22 eV), as well as in the region around 3000 cm^{-1} (0.37 eV). These peaks are appearing by the virtue of structural variations in the different regions of the molecule. Furthermore, there is a very large gap of the IR frequency between 1800 cm^{-1} to 3000 cm^{-1} which in some situations may indicate a higher order transition of the photons during photosynthesis processes.

Finally, we have also analyzed quadrupole interaction and hyperfine parameters for the fundamental FMO complex components. Tab. 1 summarizes the quadrupole interaction parameters for the ^{14}N nucleus of BChl1 for different types of the basis sets, while Tab. 2 presents the results of calculation of the quadrupole interaction parameters for different atoms present in BChls.

Analyzing the quadrupole interaction parameters, we see that the asymmetry parameters for pyrrole nitrogen are found in the range between 0.3 and 0.8, whereas for the magnesium nuclei, they are around 0.45. Furthermore, the quadrupole resonance frequencies are found in the range between 2 and

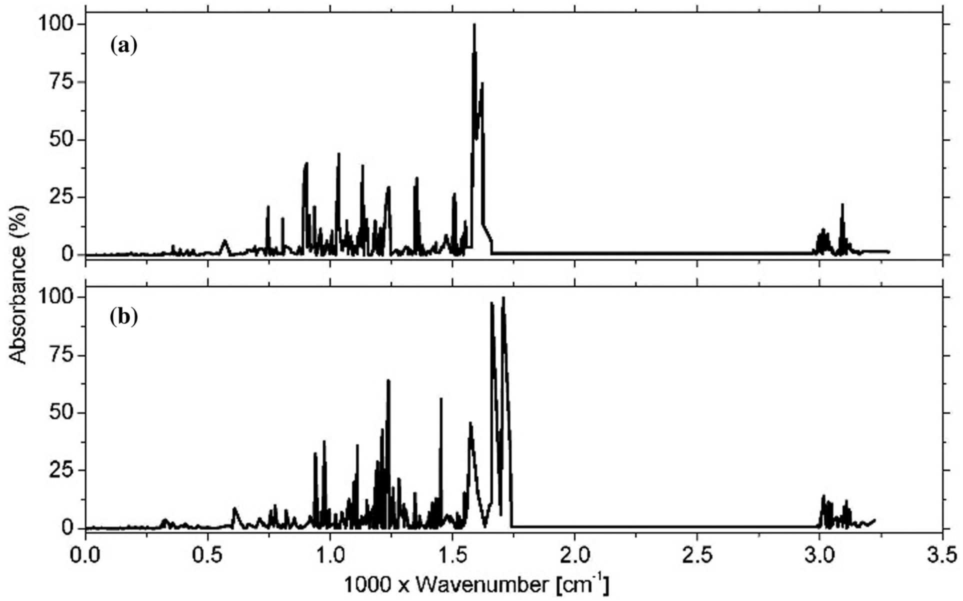


FIGURE 4. Infrared absorption spectra for a BChl (a) Geometry taken directly from the FMO complex (b) Component BChl after full optimization.

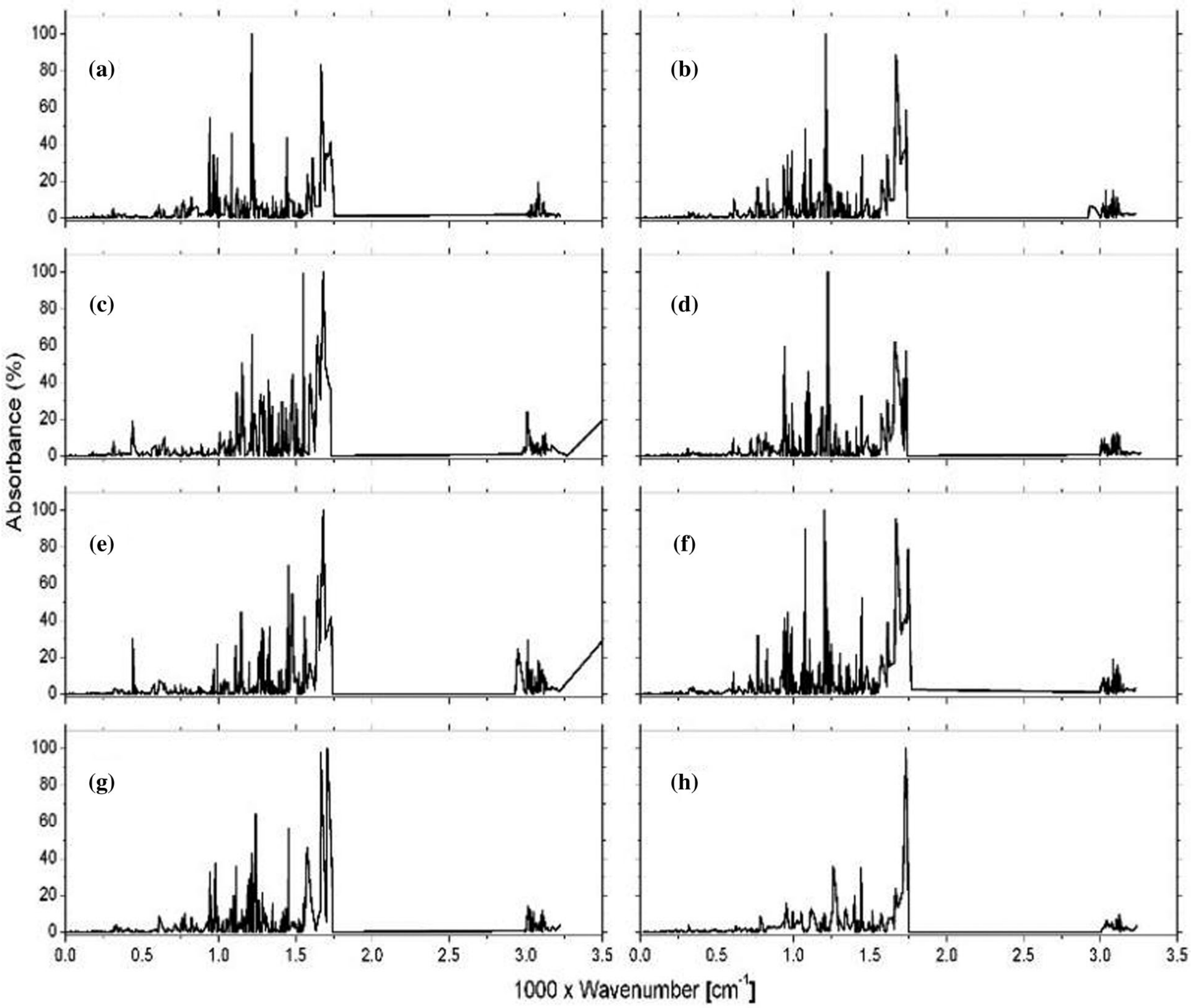


FIGURE 5. Infrared absorption spectra (intensity in arbitrary units and frequencies in cm^{-1}) for BChls taken from the FMO complex.

TABLE 1

Calculated values of quadrupole interaction parameters for a BChl from the FMO complex (Frequencies in MHz and EFG tensors are in atomic units)

Basis Set	V_{XX}	V_{YY}	V_{ZZ}	η	e^2qQ/h
3-21G	−0.326	−0.151	0.477	0.367	2.316
6-31G	−0.368	−0.164	0.533	0.382	2.588
6-311G	−0.431	−0.180	0.611	0.410	2.969
6-311G(dp)	−0.360	−0.231	0.591	0.218	2.873

4 MHz for the case of the nitrogen nuclei, but their values exhibit significant variations for the case of magnesium nuclei. We have also calculated the isotropic hyperfine coupling constant, i.e., Fermi's coupling constant and the anisotropic hyperfine coupling constant for the nitrogen nuclei in the porphyrin ring for one of BChls and presented them in Tab. 3. The variations in the hyperfine coupling constants are observed due to different positions and the orientation of the nitrogen nuclei in the plane of the porphyrin ring in the FMO complex.

Applications and Future Outlook

The presented results are relevant in the context of the design and synthesis of pigments for various applications, including photocatalysis, as well as for biological optoelectronic devices for the use in biosensing and bioplasmonics. We note, for example, that plasmonic bio-sensing properties of LHCs, including the FMO complex, have already been studied in the literature (e.g., (Chen *et al.*, 2017)). One of the ideas is to couple a nanowire to specific sites (BChls) of

TABLE 2

Calculated values of quadrupole interaction parameters for the primary BChls from the FMO complex (Frequency in MHz and EFG tensors are in atomic units). Here we have used quadrupole moments for the atoms as Q(^{25}Mg) = 0.1994 barn and N(^{14}N) = 0.02068 barn

	Atom	V_{XX}	V_{YY}	V_{ZZ}	η	e^2qQ/h
BChl11	Mg	−0.631	0.165	0.466	0.476	3.067
	N_a	−0.486	−0.071	0.557	0.747	2.706
	N_b	−0.490	0.052	0.438	0.788	2.379
	N_c	−0.431	−0.180	0.611	0.410	2.969
	N_d	−0.564	0.119	0.445	0.577	2.740
BChl12	Mg	−0.222	−0.094	0.315	0.405	14.689
	N_a	−0.450	0.085	0.365	0.624	2.187
	N_b	−0.488	0.208	0.280	0.146	2.371
	N_c	−0.383	−0.291	0.674	0.136	3.274
	N_d	−0.468	0.150	0.318	0.358	2.274
BChl13	Mg	−0.729	0.246	0.482	0.323	33.927
	N_a	−0.561	0.052	0.509	0.815	2.724
	N_b	−0.607	0.180	0.427	0.406	2.949
	N_c	−0.573	0.034	0.539	0.882	2.785
	N_d	−0.601	0.136	0.465	0.548	2.918
BChl14	Mg	−0.649	0.179	0.470	0.448	30.226
	N_a	−0.500	−0.099	0.599	0.668	2.912
	N_b	−0.575	0.136	0.439	0.528	2.794
	N_c	−0.480	−0.139	0.619	0.552	3.007
	N_d	−0.583	0.146	0.436	0.498	2.831
BChl15	Mg	−0.720	0.235	0.486	0.349	33.548
	N_a	−0.562	0.054	0.508	0.809	2.729
	N_b	−0.586	0.157	0.429	0.464	2.848
	N_c	−0.545	−0.012	0.557	0.959	2.706
	N_d	−0.604	0.146	0.458	0.516	2.936
BChl16	Mg	−0.667	0.142	0.526	0.576	31.066
	N_a	−0.481	−0.141	0.622	0.548	3.023
	N_b	−0.567	0.148	0.418	0.476	2.753
	N_c	−0.521	−0.147	0.668	0.560	3.246
	N_d	−0.571	0.097	0.474	0.662	2.775
BChl17	Mg	−0.730	0.179	0.551	0.509	33.988
	N_a	−0.456	−0.160	0.616	0.479	2.993
	N_b	−0.573	0.148	0.425	0.484	2.786
	N_c	−0.471	−0.160	0.632	0.492	3.069
	N_d	−0.590	0.132	0.458	0.552	2.866

the FMO complex with the goal to use single photons to detect local defects or modifications of the complex, e.g., caused by environmental effects. This or similar ideas can be used for other hybrid bio-sensing and bio-plasmonic devices, where the component spectroscopic properties of specific sites (BChls) are of direct relevance.

In what follows, we also briefly discuss some additional and potential application areas where some of the results and/or ideas presented here could be useful. Photosynthetic chloroplasts are used for the production of bioactive compounds as well as in biomedicine (Nielsen *et al.*, 2013; Sasaki *et al.*, 2005; Suchkov and Herrera, 2014). Chls as such are powerful photosensitizers and they can be applied as natural biocides to non-photosynthetic organisms. Their subsequent irradiation with light allows for spatial and temporal control of phototoxicity, the property which is important in photodynamic therapies (Grimm *et al.*, 2006). Some photosynthetic bacteria can be used for purifying the wastewater and biomass recovery in the field of health and environmental science (Wang *et al.*, 2016). The ability of

TABLE 3

Calculated values of EPR parameters i.e., isotropic and anisotropic hyperfine coupling constants for ^{14}N nuclei in a BChl from the FMO complex (MHz))

Atom	A	B_{aa}	B_{bb}	B_{cc}
N_a	7.179	−3.508	5.869	5.869
N_b	−1.162	−1.214	0.567	0.647
N_c	−3.772	−4.069	1.958	2.112
N_d	8.450	−1.148	0.971	2.119

LHCs to switch between different states, e.g., efficient light-harvesting and a photoprotective function, is another application area of interest in this context (Grubera *et al.*, 2018; Liguori *et al.*, 2015) which require further analysis of the mechanisms behind switching (activation/deactivation) of specific Chls (Cupellini *et al.*, 2020).

The transfer of the mechanisms of photosynthesis to emerging solar energy technologies would also require our better and detailed knowledge of system components properties. The idea of geometric constraints in applications to complex systems has been known for quite some time (e.g., (Melnik *et al.*, 2003)). More recently, this idea has received an interesting development in the analysis of constrained geometric dynamics in the context of FMO complexes (Fokas *et al.*, 2014). It has allowed studying the flexibility in the protein network in these complexes by efficiently generating the accessible conformational states, starting from the crystal structures reported in the literature and in the end reducing uncertainty in excitation energy transfer. The next step would be to design efficient energy transfer networks (Saer *et al.*, 2017).

The fast progress in the biosynthesis of chlorophylls and its regulation, as well as our better understanding of their evolution over geological timescales, opens new opportunities. The ultimate knowledge of chlorophyll properties and functions would lead not only to therapeutic medical applications mentioned already, but also to more efficient diagnostics, the development of remote, non-invasive monitoring of individual biosystems, ecosystems, and someday systems at the planetary scale. The applications brought about by the research on photosynthesis are becoming intrinsically interdisciplinary. As it was pointed out in Barroso-Flores, (2017), it is not only the study of the origin of life but also of its evolution are in the heart of this topic.

Conclusions

Using the density functional theory, we have carried out a detailed analysis of the nuclear magnetic resonance properties of fundamental components of the Fenna-Matthews-Olson light-harvesting complex. We have demonstrated that the resonant peaks of NMR chemical shift spectra are in different locations, revealing their sensitivity to the structure of BChls, local environments, and other identified characteristics. The positions of the peaks observed in the NMR spectrum of Chl-a obtained from DFT calculations are in close agreement with the experimental results reported in the literature. We have quantified the infrared absorption spectra of fundamental components of the analyzed LHC, establishing sources of their sensitivity. We have concluded that the IR spectra of BChls suggest that there are two distinct infrared energy bands, that can be found in the vicinity of 0.22 eV and above 0.37 eV. The analysis of the nuclear quadrupole and hyperfine coupling properties has included the quantification of the asymmetry parameters and the quadrupole frequencies which may change according to BChl chemical structures. Finally, current and potential applications of the presented results, along with future outlook, have been highlighted.

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References

Adamo C, Barone V (1999). Toward reliable density functional methods without adjustable parameters: the PBE0 model. *Journal of Chemical Physics* **110**: 6158–6170. DOI 10.1063/1.478522.

Andrew ER (1981). Magic angle spinning. *International Reviews in Physical Chemistry* **1**: 195–224. DOI 10.1080/01442358109353320.

Badu S, Melnik R (2017). NMR properties of Fenna-Matthews-Olson light harvesting complex: photosynthesis and its biomedical applications. *IEEE First Ukraine Conference on Electrical and Computer Engineering (UKRCON), Proceedings, IEEE, Kyiv*, 318–321.

Badu S, Melnik R, Singh S (2020). Analysis of photosynthetic systems and their applications with mathematical and computational models (submitted).

Baker LA, Lewis A, Habershon S (2017). Photosynthesis, pigment-protein complexes and electronic energy transport: simple models for complicated processes. *Science Progress* **100, SI**: 313–330. DOI 10.3184/003685017X14967574639964.

Barroso-Flores J (2017). Evolution of the Fenna-Matthews-Olson Complex and its quantum coherence features. Which Led the Way? *ACS Central Science* **3**: 1061–1062. DOI 10.1021/acscentsci.7b00386.

Bína D, Durchan M, Kuznetsova V, Vacha F, Litvinac R, Polivka T (2019). Energy transfer dynamics in a red-shifted violaxanthin-chlorophyll a light-harvesting complex.

Biochimica et Biophysica Acta (BBA)–Bioenergetics **1860**: 111–120. DOI 10.1016/j.bbabio.2018.11.006.

Brixner T, Stenger J, Vaswani HM, Cho M, Blankenship RE, Fleming GR (2005). Two-dimensional spectroscopy of electronic couplings in photosynthesis. *Nature* **434**: 625–628. DOI 10.1038/nature03429.

Brown CE, Spencer RB, Burger VT, Katz JJ (1984). Crosspolarization/magic-angle sample-spinning ^{13}C NMR spectroscopic study of chlorophyll a in the solid state. *Proceedings of the National Academy of Sciences* **81**: 641–644. DOI 10.1073/pnas.81.2.641.

Chen GY, Lambert N, Shih YA, Liu MH, Chen YN, Nori F (2017). Plasmonic bio-sensing for the Fenna-Matthews-Olson complex. *Scientific Reports* **7**: 39720. DOI 10.1038/srep39720.

Claridge K, Padula D, Troisi A (2020). On the arrangement of chromophores in light harvesting complexes: chance versus design. *Faraday Discussions* **221**: 133–149. DOI 10.1039/C9FD00045C.

Cupellini L, Calvani D, Jacquemin D, Mennucci B (2020). Charge transfer from the carotenoid can quench chlorophyll excitation in antenna complexes of plants. *Nature Communications* **11**: 662. DOI 10.1038/s41467-020-14488-6.

Du JL, Wen B, Melnik R, Kawazoe Y (2015). Cluster characteristics and physical properties of binary Al-Zr intermetallic compounds from first principles studies. *Computational Materials Science* **103**: 170–178. DOI 10.1016/j.commatsci.2015.03.039.

Dybowski C (2003). Encyclopedia of Nuclear Magnetic Resonance. *Advances in NMR 9*. In: David M., Grant (University of Utah) and Robin K. Harris (University of Durham) (ed.). John Wiley and Sons: ISBN 0-471-49082-2.

Facelli JC (2011). Chemical shift tensors: theory and application to molecular structural problems. *Progress in Nuclear Magnetic Resonance Spectroscopy* **58**: 176–201. DOI 10.1016/j.pnmrs.2010.10.003.

Fenna RE, Matthews BW (1975). Chlorophyll arrangement in a bacteriochlorophyll protein from chlorobium limicola. *Nature* **258**: 573–577. DOI 10.1038/258573a0.

Fokas AS, Cole DJ, Chin AW (2014). Constrained geometric dynamics of the Fenna-Matthews-Olson complex: the role of correlated motion in reducing uncertainty in excitation energy transfer. *Photosynthesis Research* **122**: 275–292. DOI 10.1007/s11120-014-0027-3.

Frisch MJEA, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson G, Nakatsuji H (2009). Gaussian 09, revision D. 01.

Grimm B, Porra RJ, Rüdiger W, Scheer H (eds.) (2006). *Chlorophylls and bacteriochlorophylls: biochemistry, biophysics, functions and applications*. vol. 25. Springer Science & Business Media.

Grubera JM, Malya P, Kruger TPJ, Grondelle R (2018). From isolated light-harvesting complexes to the thylakoid membrane: a single-molecule perspective. *Nanophotonics* **7**: 81–92. DOI 10.1515/nanoph-2017-0014.

Hein B, Kreisbeck C, Kramer T, Rodriguez M (2012). Modelling of oscillations in two-dimensional echo-spectra of the Fenna-Matthews-Olson complex. *New Journal of Physics* **14**: 023018. DOI 10.1088/1367-2630/14/2/023018.

Higashi M, Saito S (2016). Quantitative evaluation of site energies and their uctuations of pigments in the Fenna-Matthews-Olson complex with an efficient method for generating a potential energy surface. *Journal of Chemical Theory and Computation* **12**: 4128–4137. DOI 10.1021/acs.jctc.6b00516.

Hoyer S, Sarovar M, Whaley KB (2010). Limits of quantum speedup in photosynthetic light harvesting. *New Journal of Physics* **12**: 065041. DOI 10.1088/1367-2630/12/6/065041.

Humphrey W, Dalke A, Schulten K (1996). VMD: visual molecular dynamics. *Journal of Molecular Graphics* **14**: 33–38. DOI 10.1016/0263-7855(96)00018-5.

Huo P, Coker DF (2017). Excitation energy transfer in light-harvesting systems: theory, models, and application. In *Ultrafast Dynamics at the Nanoscale*, pp. 311–354. Jenny Stanford Publishing.

Ishizaki A, Fleming GR (2011). On the interpretation of quantum coherent beats observed in two-dimensional electronic spectra of photosynthetic light harvesting complexes. *Journal of Physical Chemistry B* **115**: 6227–6233. DOI 10.1021/jp112406h.

Jurinovich S, Curutchet C, Mennucci B (2014). The Fenna-Matthews-Olson protein revisited: a fully polarizable (TD) DFT/MM description. *ChemPhysChem* **15**: 3194–3204. DOI 10.1002/cphc.201402244.

Keren N, Paltiel Y (2018). Photosynthetic energy transfer at the quantum/classical border trends in plant. *Science* **23**: 497–506.

Kim YB, Morozov D, Stadnytskyi V, Savikhin S, Slipchenko LV (2020). Predictive first-principles modeling of a photosynthetic antenna protein: the fenna-matthews-olson complex. *Journal of Physical Chemistry Letters* **11**: 1636–1643. DOI 10.1021/acs.jpclett.9b03486.

König C, Neugebauer J (2013). Protein effects on the optical spectrum of the Fenna-Matthews-Olson complex from fully quantum chemical calculations. *Journal of Chemical Theory and Computation* **9**: 1808–1820. DOI 10.1021/ct301111q.

Kramer T, Rodriguez M (2020). Effect of disorder and polarization sequences on two-dimensional spectra of light-harvesting complexes. *Photosynthesis Research* **144**: 147–154. DOI 10.1007/s11120-019-00699-6.

Kreisbeck C, Kramer T, Rodriguez M, Hein B (2011). High-performance solution of hierarchical equations of motion for studying energy transfer in light-harvesting complexes. *Journal of Chemical Theory and Computation* **7**: 2166–2174. DOI 10.1021/ct200126d.

Li X, Zhou R, Xu K, Xu J, Jin J, Fang H, He Y (2018). Rapid determination of chlorophyll and pheophytin in green tea using fourier transform infrared spectroscopy. *Molecules* **23**: 1010. DOI 10.3390/molecules23051010.

Liguori N, Periole X, Marrink SJ, Croce R (2015). From light-harvesting to photoprotection: structural basis of the dynamic switch of the major antenna complex of plants (LHCII). *Scientific Reports* **5**: 15661. DOI 10.1038/srep15661.

Lumpkin O (1975). ^{25}Mg and ^{14}N nuclear quadrupole resonances in chlorophyll-a and magnesium phthalocyanine. *Journal of Chemical Physics* **62**: 3281–3283. DOI 10.1063/1.430881.

Maiuri M, Ostroumov EE, Saer RG, Blankenship RE, Scholes GD (2018). Coherent wavepackets in the Fenna-Matthews-Olson complex are robust to excitonic structure perturbations caused by mutagenesis. *Nature Chemistry* **10**: 177–183. DOI 10.1038/nchem.2910.

Makarska-Bialokoz M, Kaczor AA (2014). Computational analysis of chlorophyll structure and uv-vis spectra: a student research project on the spectroscopy of natural complexes. *Spectroscopy Letters* **47**: 147–152. DOI 10.1080/00387010.2013.781038.

Melnik RVN, Uhlherr A, Hodgkin J, Hoog F (2003). Distance geometry algorithms in molecular modelling of polymer and composite systems. *Computers and Mathematics with Applications* **45**: 515–534. DOI 10.1016/S0898-1221(03)80034-2.

Najdanova M, Siehl HU, Berger S (2018). A comparison of the H-1, C-13-, and N-15-NMR data of chlorophyll a and chlorophyll b guided by quantum chemical calculation. *Journal of Physical Organic Chemistry* **31**: SI e3802. DOI 10.1002/poc.3802.

Nalbach P, Mujica-Martinez CA, Thorwart M (2015). Vibronically coherent speed-up of the excitation energy transfer in the Fenna-Matthews-Olson complex. *Physical Review E* **91**: 022706. DOI 10.1103/PhysRevE.91.022706.

Nielsen AZ, Ziersen B, Jensen K, Lassen LM, Olsen CE, MØller BL, Jensen PE (2013). Redirecting photosynthetic reducing power toward bioactive natural product synthesis. *ACS Synthetic Biology* **2**: 308–315. DOI 10.1021/sb300128r.

Olson JM (2004). The FMO protein. *Photosynthesis Research* **80**: 181–187. DOI 10.1023/B:PRES.0000030428.36950.43.

O'Malley PJ, Collins SJ (2001). The effect of axial Mg ligation on the geometry and spin density distribution of chlorophyll and bacteriochlorophyll cation free radical models: a density functional study. *Journal of the American Chemical Society* **123**: 11042–11046. DOI 10.1021/ja010522u.

Perdew JP, Burke K, Ernzerhof M (1996). Generalized gradient approximation made simple. *Physical Review Letters* **77**: 3865–3868. DOI 10.1103/PhysRevLett.77.3865.

Prabhakar S, Melnik R (2017). Wettability alteration of calcite oil wells: Influence of smart water ions. *Scientific Reports* **7**: 17365. DOI 10.1038/s41598-017-17547-z.

Prabhakar S, Melnik R (2018). Influence of Mg^{2+}, SO_4^{2-} and Na^+ ions of sea water in crude oil recovery: DFT and ab-initio molecular dynamics simulations. *Colloids and Surfaces* **539**: 53–58. DOI 10.1016/j.colsurfa.2017.12.009.

Renger T, Klinger A, Steinecker F, Busch MS, Numata J, Müh F (2012). Normal mode analysis of the spectral density of the Fenna-Matthews-Olson light-harvesting protein: how the protein dissipates the excess energy of excitons. *Journal of Physical Chemistry B* **116**: 14565–14580. DOI 10.1021/jp3094935.

Rochaix JD (2020). The dynamics of the photosynthetic apparatus in algae. In *Photosynthesis in Algae: Biochemical and Physiological Mechanisms* pp. 57–82. Springer, Cham.

Rodriguez M, Kramer T (2019). Machine learning of two dimensional spectroscopic data. *Chemical Physics* **520**: 52–60. DOI 10.1016/j.chemphys.2019.01.002.

Ruban AV (2018). Light harvesting control in plants. *FEBS Letters* **592**: 3030–3039. DOI 10.1002/1873-3468.13111.

Saer RG, Stadnytskyi V, Magdaong NC, Goodson C, Savikhin S, Blankenship RE (2017). Probing the excitonic landscape of the chlorobaculum tepidum Fenna-Matthews-Olson (FMO) complex: a mutagenesis approach. *Biochimica et Biophysica Acta (BBA)-Bioenergetics* **1858**: 288–296. DOI 10.1016/j.bbabio.2017.01.011.

Saga Y, Kawano K, Otsuka Y, Imanishi M, Kimura Y, Matsui S, Asakawa H (2019). Selective oxidation of B800 bacteriochlorophyll a in photosynthetic lightharvesting protein LH2. *Scientific Reports* **9**: 3636. DOI 10.1038/s41598-019-40082-y.

Sarovar M, Cheng YC, Whaley KB (2011). Environmental correlation effects on excitation energy transfer in photosynthetic light harvesting. *Physical Review E* **83**: 011906. DOI 10.1103/PhysRevE.83.011906.

Sasaki K, Watanabe M, Suda Y, Ishizuka A, Noparatnaraporn N (2005). Applications of photosynthetic bacteria for medical fields. *Journal of Bioscience and Bioengineering* **100**: 481–488. DOI 10.1263/jbb.100.481.

Schmidt ABM, Muh F, El-Amine Madjet M, Renger T (2011). The eighth bacteriochlorophyll completes the excitation energy funnel in the FMO protein. *Journal of Physical Chemistry Letters* **2**: 93–98. DOI 10.1021/jz101541b.

Scholes GD (2010). Quantum-coherent electronic energy transfer: Did nature think of it first? *Journal of Physical Chemistry Letters* **1**: 2–8. DOI 10.1021/jz900062f.

Segatta F, Cupellin L, Garavelli M, Mennucci B (2019). Quantum chemical modeling of the photoinduced activity of multichromophoric biosystems. *Chemical Reviews* **119**: 9361–9380. DOI 10.1021/acs.chemrev.9b00135.

Shim S, Rebentrost P, Valleau S, Aspuru-Guzik A (2012). Atomistic study of the long-lived quantum coherences in the Fenna-Matthews-Olson complex. *Biophysical Journal* **102**: 649–660. DOI 10.1016/j.bpj.2011.12.021.

Sinnecker S, Koch W, Lubitz W (2002). Chlorophyll a radical ions: a density functional study. *Journal of Physical Chemistry B* **106**: 5281–5288. DOI 10.1021/jp013758t.

Suchkov S, Herrera AS (2014). The role of human photosynthesis in predictive, preventive and personalized medicine. *EPMA Journal* **5**: A146. DOI 10.1186/1878-5085-5-S1-A146.

Sundholm D (1999). Density functional theory calculations of the visible spectrum of chlorophyll a. *Chemical Physics Letters* **302**: 480–484. DOI 10.1016/S0009-2614(99)00194-3.

Taguchi AT, O'Malley PJ, Wraight CA, Dikanov SA (2014). Nuclear hyperfine and quadrupole tensor characterization of the nitrogen hydrogen bond donors to the semiquinone of the QB site in bacterial reaction centers: a combined x- and s-band (14, 15) N ESEEM and DFT study. *Journal of Physical Chemistry B* **118**: 1501–1509. DOI 10.1021/jp411023k.

Thyrhaug E, Tempelaar R, Alcocer MJP, Zidek K, Bina D, Knoester J, Jansen TLC, Zigmantas D (2018). Identification and characterization of diverse coherences in the Fenna-Matthews-Olson complex. *Nature Chemistry* **10**: 780–786. DOI 10.1038/s41557-018-0060-5.

Thyrhaug E, Zidek K, Dostál J, Bína D, Zigmantas D (2016). Exciton structure and energy transfer in the Fenna-Matthews-Olson complex. *Journal of Physical Chemistry Letters* **7**: 1653–1660. DOI 10.1021/acs.jpclett.6b00534.

Tronrud DE, Wen J, Gay L, Blankenship RE (2009). The structural basis for the difference in absorbance spectra for the FMO antenna protein from various green sulfur bacteria. *Photosynthesis Research* **100**: 79–87. DOI 10.1007/s11120-009-9430-6.

van Gammeren AJ, Hulsbergen FB, Erkelens C, De Groot HJM (2004). Synthetic analogues of the histidine-chlorophyll complex: a NMR study to mimic structural features of the photosynthetic reaction center and the light harvesting complex. *JBIC Journal of Biological Inorganic Chemistry* **9**: 109–117. DOI 10.1007/s00775-003-0507-y.

Wan L, Qi DD, Zhang YX (2011). The effect of beta-saturated pyrrolic rings on the electronic structures and aromaticity of magnesium porphyrin derivatives: a density functional study. *Journal of Molecular Graphics and Modelling* **30**: 15–23. DOI 10.1016/j.jmgm.2011.05.003.

Wang H, Zhang G, Peng M, Zhou Q, Li J, Xu H, Meng F (2016). Synthetic white spirit wastewater treatment and biomass recovery by photosynthetic bacteria: feasibility and process influence factors. *International Biodeterioration & Biodegradation* **113**: 134–138. DOI 10.1016/j.ibiod.2016.01.001.

Wen J, Zhang H, Gross ML, Blankenship RE (2011). Native electrospray mass spectrometry reveals the nature and stoichiometry of pigments in the FMO photosynthetic antenna protein. *Biochemistry* **50**: 3502–3511. DOI 10.1021/bi200239k.

Wilkins DM, Dattani Nikesh S (2015). Why quantum coherence is not important in the Fenna-Matthews-Olsen Complex. *Journal of Chemical Theory and Computation* **11**: 3411–3419. DOI 10.1021/ct501066k.

Xu J, Terskikh VV, Huang Y (2012). ^{25}Mg solid-state NMR: a sensitive probe of adsorbing guest molecules on a metal center in metal organic framework CPO-27-Mg. *Journal of Physical Chemistry Letters* **4**: 7–11. DOI 10.1021/jz301954t.

Yeh SH, Kais S (2014). Simulated two-dimensional electronic spectroscopy of the eight-bacteriochlorophyll FMO complex. *Journal of Chemical Physics* **141**: 234105. DOI 10.1063/1.4903546.

Zhu J, Kais S, Aspuru-Guzik A, Rodriques S, Brock B, Love PJ (2012). Multipartite quantum entanglement evolution in photosynthetic complexes. *Journal of Chemical Physics* **137**: 074112. DOI 10.1063/1.4742333.