MODELING OF INTER-CHLOROPHYLL COUPLINGS IN THE PHOTOSYNTHETIC FCP COMPLEX

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INTRODUCTION

Photosynthesis has always been one of the most essential processes throughout the development of life on Earth and still has this crucial role today. However, one of the most important, but oftentimes forgotten type of photosynthesis–carrying organisms are diatoms – microalgae accounting for nearly 20 % of global carbon dioxide fixation [1]. Moreover, diatoms have an exceptional light-harvesting complex, fucoxanthin-chlorophyll protein (FCP), which differs from the light-harvesting complex found in higher plants, as it has such chromophores as chlorophyll *c* and fucoxanthin, which guarantee light absorption in the blue-green visible region available in water.

METHODS

The geometry data of FCP from the diatom *Phaeodactylum tricornutum* was taken from 6A2W Protein Data Bank structure. Then chlorophylls (Chl) coordinates were extracted from a protein structure and their phytyl tails were removed, as the removal of phytyl tail has little result on the Q_y transition dipole moment value. Afterward, DFT geometry optimization and frequency calculations for all tailless Chl were done, as well as S_1 state calculations of optimized S_0 geometry with CAM-B3LYP functional and 6-31G(d) basis set. The mean of Chl *a* dipole moments' absolute values were normalized to the expected vacuum value of 5.47 D [2]. The ratio of Chl *a* to Chl *c* transition dipole moments was estimated to be around 1.6 [3] and thus the Chl *c* transition dipole moments were scaled accordingly. Thereafter chlorophylls' interaction energy was calculated using the point dipole approximation (PDA). From the results of interaction energy calculations, energy transfer rates were calculated in the Förster regime. All energies of Chl *a* were made equal and pigments' energies were shifted to the values know from the available experimental data. Such parameters as disorder, low- or high-frequency spectral densities were taken from previously available models [4,5].

RESULTS

Table 1. Absolute dipole moments of Chl *a* and *c* in FCP from *Phaeodactylum tricornutum* with axis corresponding to the PDB file orientation.

Chl residue No.	μ_x,D	μ_y,D	μ_z,D	$\lvert\vec{\mu}\rvert$, D	$\lvert\vec{\mu}\rvert_{init}$, D	Q_y, cm^{-1}
*a*401	-1.29	4.07	-3.50	5.52	5.26	17517.55
*a*402	2.29	-1.55	4.69	5.45	5.19	17472.38
$c_2$403	-0.60	2.41	-2.21	3.33	1.93	17730.48
*a*404	-3.10	4.15	1.37	5.36	5.11	17527.23
*a*405	-3.82	-3.18	2.22	5.44	5.18	17537.71
*a*406	1.30	-3.66	3.92	5.52	5.26	17494.96
*a*407	1.86	1.51	-4.93	5.48	5.22	17509.48
$c_1$408	1.22	-2.63	1.98	3.51	2.03	17812.75
*a*409	-2.88	3.53	-3.13	5.52	5.26	17516.74

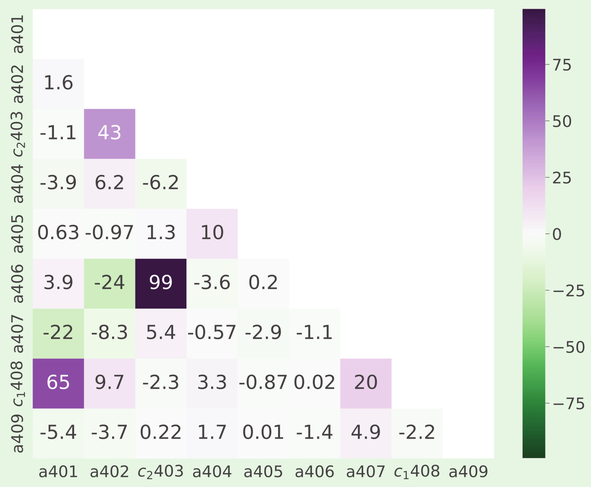

Figure 1. Interaction energies (cm^{-1}) of chlorophylls obtained using the point dipole approximation

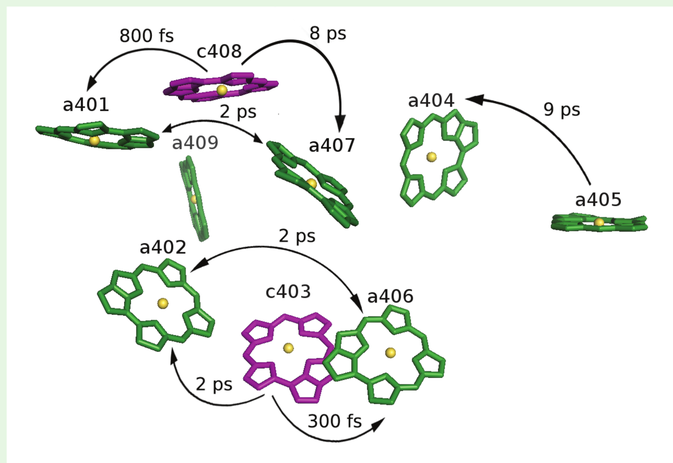

Figure 2. Visualization of Chl arrangement in FCP from *Phaeodacylum tricornutum*. Arrows denote fastest energy transfer pathways at 300 K.

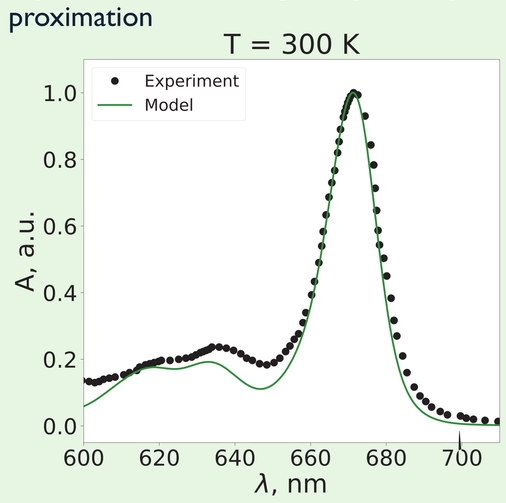

Figure 3. FCP absorption spectra at T=300 K. Experimental data taken from [6]

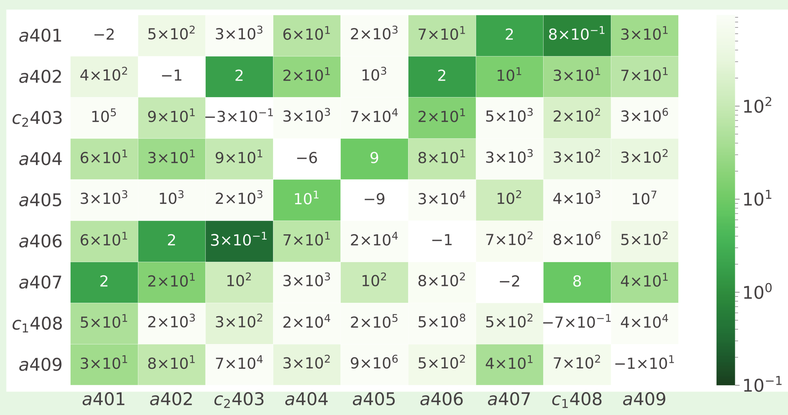

Figure 4. Inverse Förster transfer rates $k^{-1}_{m\leftarrow n}$ (in ps) between chlorophylls in FCP from *Phaeodactylum tricornutum*.

CONCLUSIONS

- TD-DFT methodology was successfully applied to model the first excited state S_1 of chlorophylls from FCP and such excited state properties as transition dipole moment, transition energy were calculated.
- Point dipole approximation was used to calculate the interaction energies of chlorophyll molecules in FCP complex.
- Förster energy transfer results indicate that the fastest transfer happens between the chlorophyll molecules that are in near proximity. Moreover, there are energy transfers that last only a few picoseconds from chlorophyll *c* to *a*, which agrees with experimental data.

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