Photosynthetic water oxidation is catalyzed at the Mn$_4$Ca cluster in photosystem II. Six carboxyl groups and one imidazole group function as ligands to the Mn$_4$Ca cluster. To clarify electronic and vibrational structure of the Mn$_4$Ca cluster, we have performed the normal mode analysis of the Mn$_4$Ca cluster including the amino acid ligands using QM/MM calculations. The calculated S$_1$/S$_2$ difference spectra satisfactorily reproduced the symmetric COO$^-$ spectrum. In addition, the $^{13}$C/$^{12}$C double difference spectrum of D1–A344 (C–terminus) was well reproduced. These data provide the information of the oxidation states of the individual Mn ions in the S$_1$ and S$_2$ states as well as the assignments of the FTIR bands of amino acid ligands.

The high-resolution X-ray structure of photosystem II shows the ligand structure of the Mn$_4$Ca cluster and postulated proton pathways. However, the roles of amino acid residues involved in the O2 evolution mechanism remain to be clarified. In this study, we constructed the site-directed mutants of amino acid residues on the D1 and D2 subunits responsible for the ligands to the Mn$_4$Ca cluster and putative proton pathways using the cyanobacterium Synechocystis sp. PCC 6803 and investigated the effects of mutation on the growth and O2-evolving reaction. The mutants of residues outside the first shell grew photoautotrophically, whereas those of the direct ligands to the Mn$_4$Ca cluster did not. Spectroscopic characterization of the photoautotrophic mutants is underway.

The excitation energy transfer (EET) mechanism depends on the degrees of EET interaction V and reorganization energy in the reaction system. In the photosynthetic antenna system, because some values of V are in the intermediate coupling cases, it is difficult to analyze the EET dynamics under simple perturbation theory. Recently, we qualitatively improved the variational master equation by McCutcheon and Nazir[1]. There however exist the quantitative differences between the results by our theory and those by the hierarchy equation of motion. We studied the refinement of the disagreements by analyzing the local minima states in the free energy and the damping effect by the higher order perturbation terms.