2P253 光電子収量分光による非真空環境下の生体関連分子の電子構造観察：クロロフィル a 測定の試み
Observation of the electronic structure of bio-related molecule in non-vacuum environment by using photoemission: Trial to Chlorophyll a

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To elucidate various bio-related processes, the electronic structures of key molecules are indispensable. For non-living materials, Photoelectron Spectroscopy (PES) is a powerful technique and widely used to examine their electronic structures. However, PES needs vacuum environment and its application to bio system has been much limited. In this study, we tried to observe the electronic structure of bio-related molecule in non-vacuum environment by using Photoelectron Yield Spectroscopy (PYS) because PYS can be carried out not only in vacuum but also in atmospheric condition. The observed electronic structure of chlorophyll a solution, which is a key molecule in photosynthesis, will be reported.

2P254 光捕集アンテナにおける色素の励起エネルギーの揺らぎに関する理論的研究
Theoretical Studies on Excitation Energy Fluctuations of Pigments in a Light-Harvesting Complex

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Excitation energy fluctuations of pigments in light-harvesting complexes play an important role in the excitation energy transfer dynamics. However, the detailed mechanism is still unknown. The high computational cost of reliable electronic structure calculations for excited states prevents us from carrying out a large number of sampling needed to evaluate the excitation energy fluctuations. To overcome this difficulty, we develop a new method called molecular mechanics with Shepard interpolation corrections (MMSIC), which enable us to generate potential energy surfaces for pigments in light-harvesting complexes efficiently. We illustrate the new method by application to bacteriochlorophyll a pigments in the Fenna-Matthews-Olson complex.

2P255 OEC の Kok-S2 状態の反応活性部位の分子構造に関する B3LYP 計算：Mn4 の配位水分子のプロトン化状態
A B3LYP study on molecular structures of active site at the Kok-S2 state of OEC: protonation states of Mn4-ligated water molecules

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The Kok cycle shows that during the catalysis of photosynthetic water oxidation, the oxygen evolving complex passes through five oxidation states (S0 to S4). Using B3LYP method, we determined the molecular structure at the S2 state in doublet, where the two water ligands on Mn4 are H2O molecule (W1) and OH anion (W2). In this work, we found that a Grotthuss-proton transfer (PT) mechanism along a hydrogen bonding network from W1 to Asp61 would thermodynamically proceed from the previous S2 structure. The product, where both of W1 and W2 are OH anions, is energetically lower than the reactant. The oxidation states of (Mn1, Mn2, Mn3, Mn4) = (III, IV, IV, IV) do not change before and after the PT reaction. We will suggest that the product is the Kok-S2 state.

2P256 水分解 Mn₄Ca クラスター S₃ 状態に関する理論的研究
Theoretical Study of the S₃ state of the Mn₄Ca-cluster in Photosystem II: A compact chair form consisting of the short Mn-Mn pairs

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Mn₄Ca-cluster in photosystem II protein accumulates the oxidizing equivalents and catalyzes the water-splitting reaction of photosynthesis. The cluster shows the structural change when it transits from the S₂ state to the S₃ state in the Kok-cycle. For example, the number of the long (R>3 Å) Mn-Mn or Mn-Ca pairs decreases in the Mn-EXAFS spectra. While, the short (2.7-2.8 Å) Mn-Mn pairs have been found in the spectra. Thus, the cluster consisting of 2.7-2.8 Å Mn-Mn pairs has been expected for S₃ state. We investigated the possible S₃ state cluster by using DFT calculation based on the chair form shown in the crystal structure. We will report the ligand environment of the cluster and the dependence on the deprotonated water (OH⁻) site.

2P257 光合成酸素発生中心(PSII-OEC)の立体構造と電荷状態変化についての理論的研究
Theoretical investigation on the conformation-charge relationship of the photosystem II oxygen evolving complex (PSII-OEC)

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Photosystem II oxygen evolving complex (OEC) catalyzes a four-electron-oxidation of two water molecules. This reaction is important in photosystem and is one of the most important systems in life. Reaction mechanisms of OEC have attracted considerable attentions, however, the knowledge is still limited for many difficulties. Especially for (1) relationships between the OEC core structures and the Mn charge states and (2) interactions from surrounding amino acid residues, water molecules and protons. In this study, accurate QM/MM calculations were performed by taking a large QM region at the S0, S1 and S2 states.

2P258 Ca 除去と Sr 置換をした Mn クラスターの ENDOR 法による研究
ENDOR studies on Ca depleted and Sr substituted Mn cluster in photosystem II

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Electron nuclear magnetic resonance (ENDOR) was applied to the S₂ state Mn cluster to reveal locations of protons which are not detected in the X-ray crystal structure analysis. Similar ENDOR spectra of the S₂ state spinach membranes and *thermosynechococcus elongatus* were observed and indicating there are no structural difference in two species. ENDOR studies also revealed that the positions of protons were modified by the Ca-depletions and recovered by Sr-substitutions. These results indicates Ca is essential for the hydrogen bonding network.