1SAA-01 天然光合成における水分解・酸素発生光化学系 II
Water-splitting and oxygen-evolving photosystem II in natural photosynthesis
Nobuo Kamiya (Osaka City University)

Photosystem II (PSII) performs light-induced water-splitting reactions, which lead to the formation of molecular oxygen in natural photosynthesis. PSII consists of twenty protein subunits, and many cofactors with a total molecular weight of 350 kDa for a monomer. The crystal structure of PSII has been reported at a resolution of 1.9 Å, in which the oxygen-evolving center (OEC) is clearly identified as a chemical composition of Mn4CaO5(H2O)4. Five oxygen atoms form oxo-bridges between the metal ions, and four water molecules directly ligated to the OEC. The significant feature of the OEC is its distorted chair form. The large distortion from a symmetric cubane is caused by the existence of Ca and O5, the fifth oxo-bridge connecting three Mn ions and one Ca ion.

1SAA-02 ESRでわかる Mn クラスターの電子構造と機能
Electronic structure and function of Mn cluster correlated with crystal structure observed by Electron Spin Resonance
Hiroyuki Mino (Grad. Sch. Sci., Nagoya Univ.)

Recently, Umema et al. have obtained an X-ray crystal structure of photosystem II (PS II) with 1.9 Å resolution and have revealed the atoms that compose the oxygen evolving complex (Mn cluster) and the coordinated amino acids. The work gives a great impact and provides a key to elucidate the secret of the oxygen evolving mechanism. Up to now, many EPR works have been performed to investigate Mn cluster, which gives good information to interpret electronic structure in intermediate states. These works are essential for elucidation oxygen evolving mechanism. In this symposium, we will discuss recent EPR works based on crystal structure.

1SAA-03 QM/MM 法による光合成酵素発生中心 S1 状態の電子状態解析
QM/MM study on the photosystem II oxygen evolving complex at the S1 state

Oxygen-evolving complex (OEC) is a key reaction center in photosystem II (PSII) which catalyzes the "2H2O → O2 + 4H+ + 4e−" reaction through five redox states (S1, i = 0–4). Umema and co-workers have determined a high-resolution X-ray structure, and it was found that OEC is involved in many hydrogen-bonds (H-bonds) with waters and neighboring residues. However, it is not yet clarified for the relationship between H-bonds and OEC electronic structures. In this study, OEC electronic structures were examined at the S1 state in some different H-bond networks by using a high level QM/MM method. We used a large QM region including second coordination amino acids and waters (Total 380 atoms). Calculated ground state is singlet in consistent with experimental results.

1SAA-04 多参照波動関数理論で解く光合成系 IIマンガンクラスターの電子構造
Entangled quantum electronic wavefunctions of the Mn4CaO5 cluster in photosystem II
Yuki Kurashige, Takeshi Yanai (Institute for Molecular Science)

It is a long-standing goal to understand the reaction mechanisms of catalytic metalloenzymes at an entangled many-electron level, but this is hampered by the exponential complexity of quantum mechanics. Here, by exploiting the special structure of quantum states and using the density matrix renormalization group, we compute near-exact many-electron wavefunctions of the Mn4CaO5 cluster of photosystem II, with more than 1018 quantum degrees of freedom. Our calculations support recent modifications to the X-ray crystal structure. We further identify multiple low-lying energy surfaces, highlighting multistate reactivity in the chemistry of the cluster. Mn spin-projections for current candidates were determined directly from our wavefunctions.

1SAA-05 OECに関する理論的研究
Theoretical Study on OEC
Shin Nakamura (RIKEN)

The water oxidation mechanism in OEC is studied theoretically by BS-UHF method. We have obtained the most plausible form of S1 state which is consistent with various experimental data such as EXAFS, ESR and X-ray results. The possible S2 forms are also presented. Considering the experimental data of Sr replaced for Ca, we confirm our arguments on S1, S2 and partially on S3. Natural orbital analysis is used for the consistency. The role of protein environment for OEC function is discussed based on the results of all atom (1,200,000) classical MD of PSII. Finally, OEC-inspired man-made electrode design-principle is to be presented.

1SAA-06 人工的な遷移金属錯体を触媒とする酸素発生反応
Water Oxidation Catalyzed by Artificial Transition Metal Complexes
Shigeyuki Masaoka (IMS)

Water oxidation (2H2O → O2 + 4H+ + 4e−) is one of two half-reactions for water splitting, and is considered the main bottleneck for the development of energy-conversion schemes based on sunlight or electricity. In nature, the water oxidation is efficiently catalyzed by the oxygen evolving complex (OEC) in photosystem II (PSII). Because the replication of the OEC is extremely difficult, some easy-to-synthesize complexes have been investigated for the last decades. Recently we reported that some transition metal complexes serve as active water oxidation catalysts, the details of which will be presented in this talk.