2P353**Delayed fluorescence from charge separated states mediated by the excited special pair in the reaction center of bacterial photosynthesis**

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The reaction center (RC) is a membrane-bound pigment-protein complex of the photosynthetic organism, performing the initial steps of conversion of light energy to chemical energy. In the purple photosynthetic bacteria, photoexcitation of the special pair of bacteriochlorophyll (P) is followed by a series of electron transfer along the close-lying chromophores, leading to the reduction of quinones (Qa, Qb). When electron transfer to Qa or Qb is blocked, charge recombination occurs in several ways, including regeneration of P* followed by the delayed fluorescence. Here we investigate theoretically a possibility of detecting the fluorescence from the charge separated states. Though they cannot directly recombine with photoemission, they can emit a photon by virtual mediation of the excited state P* of P. This type of photoemission is fulfilled as the superexchange process from the charge separated states to photoemitted states, with the mediation of P*. In the temperature region where the P* is thermally accessible, the superexchange fluorescence from the charge separated states is buried in the band of fluorescence from P*. But when the temperature is low enough to prohibit the thermal accessibility to P*, the superexchange fluorescence band from the charge separated states reveals itself. We show the fluorescence spectrum from RC of purple bacteria as a function of temperature and that at low temperatures the superexchange fluorescence from the charge separated states should be observed with a peak reflecting their energies.

2P355**Theoretical Analysis of Proton Transfer in the Photosynthetic Reaction Center from *Rhodobacter sphaeroides***○Yu Kaneko¹, Shigehiko Hayashi², Shinji Saito³, Iwao Ohmine¹¹Dept. of Chemistry, Nagoya Univ., ²Dept. of Chemistry, Kyoto Univ., ³Institute for Molecular Science

In the photosynthetic reaction center (RC) from *Rhodobacter sphaeroides*, the long range electron and proton transfer reactions occur to reduce a bound secondary quinone molecule (Q_B). With these reactions, the RC converts light energy to chemical energy to gain the transmembrane proton gradient. We focused on the first proton transfer reaction toward Q_B which is coupled with the second electron transfer. We investigated the reaction theoretically to know how the proton transfer pathway is formed by using QM/MM calculation. In the first proton transfer, many experimental analyses show that the proton comes from the aqueous solution via HIS-H126 and HIS-H128 which are at the surface of the RC, and Ser-L223, ASP-L213, ASP-L210, ASP-M17 are important residues in the proton transfer reaction. But detailed proton transfer pathway in atomic level is still unknown. To identify the pathway, we constructed the structure at the first proton transfer state based on the X-ray structure (PDB code 1AIG), and performed geometrical optimization by using QM/MM calculation. It is found that several proton transferable pathways exist and these pathways show orientational difference of protons in hydrogen bond network. The found pathways involve water molecules, ASP, and HIS and contain nine or eight hydrogen bonds. This means multiple proton transfer occurs sequentially from the surface and is strongly affected by the interaction between water molecules and amino acid residues. We calculated minimum energy path along each pathway.

2P354**Theoretical analysis of the electronic asymmetry of the special pair in the photosynthetic reaction center: Effect of protein environment**

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Protein environment is important for the primary charge separation in the special pair (SP) in the photosynthetic reaction center. EPR study showed that the fraction of the charge localized on L-side chlorophyll of the special pair (SPL) is 68% in the wild type of *Rb. sphaeroides* by estimating spin density distribution (SDD) for SPL and SPM. SDD changed from 22 to 83% with a variety of site-directed mutagenesis. Here, we studied the electronic structure of SP and the effect of the protein environment was examined. The coordinates of SP were prepared from *Rb. sphaeroides* (PDBID: 1AIG). The positions of hydrogen atoms were optimized. The DFT calculations reproduced the experimental SDD qualitatively, and we find that the electronic correlation is important for the electronic structure of SP. Specific interactions between the protein side chain atoms and the methyl ester (Mes) groups govern the orientations of the Mes groups and cause the electronic asymmetry of SP⁺. This characteristic feature is always common in every crystal structure. Protein environment was computed using polarizable continuum model with the dielectric constant from 1 to 80. As the protein polarity increases, SPL tends to donate more electrons to the acceptor than SPM in the electron transfer procedure. SDDs of the mutant proteins were also examined, and the direct effects of the protein are discussed.

2P356**The tautomerism in the oxygen-evolving complex of photosystem II as revealed by the G=2 and G=4 EPR signals in the S2-state**

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The water oxidation in photosystem II (PSII) is catalyzed by Mn₄Ca cluster coupled with first electron acceptor, YZ+H190, by virtue of cofactor Cl- and some unknown acidic group as proton trapping site at pH > 5.7. After the recent 3.0 Å resolution crystallographic structure of cyanobacteria PSII and from our DFT/B3LYP computations for possible isomers of the monomer-trimer type Mn₄Ca cluster in each intermediate state, which binds three water molecules, one hydroxo bridge and four oxo bridges in S₀, we could determine a cyclic change of the Mn₄Ca cluster. In this model, Cl is suggested to be bound between positive R357 and Ca²⁺ ion, as a counter ion. Further, we show that H337 can trap a released proton only in S₂ and S₃, to exhibit an observed proton release pattern, 1:0:1:2, at pH > 5.7. These H337 and Cl-R357 should be counted as functional members of OEC. Interestingly, this model has three tautomers; two having nearly-equal energies in the same Mn valence states, denoted S2a(4;4,3,4) and S2b(4;4,3,4), in spite of their significantly different conformations, and the third having much higher energy than the others, in a different valence state, denoted S2c(3;4,4,4). Remarkably, the Jahn-Teller ion Mn(3) induces a normal and near-rhombic distortion both in S2a and S2b. Nevertheless, S2a and S2b have largely-split and degenerate di-μ-oxo bridged Mn-Mn bonds, respectively, indicating these are responsible for g=4 and g=2 multiline EPR signal, respectively. We will present resimulations of these signals from 1D-oriented samples.