- 2P320 蛋白質中電子移動反応のトンネル経路の新しいモデル
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 New model for the electron tunneling pathway of electron transfer reactions in protein media
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The electron transfer (ET) reaction in protein media performs a long-distance ET by the superexchange mechanism. We investigated electron tunneling pathways of the ET from bacteriopheophytin (Bph) anion to the primary quinone (Q_A) in photosynthetic bacterial reaction center by a combined study of molecular dynamics simulations and quantum-chemical calculations. As a result, we found that the inter-atomic tunneling currents fluctuate very rapidly and the electron tunneling pathways change drastically with time. Then, we carefully analyzed the fluctuating inter-atomic tunneling currents passing through any plane put between Bph and Q_A. We found that the sum of the thermal average of the cross terms of the two inter-atomic tunneling currents is much less than the thermal average of the square of the inter-atomic tunneling current $\langle J_{ab}^2 \rangle$. This result is related to the fact that almost all the inter-atomic tunneling currents passing through any plane fluctuate independently to one another. The sum of $\langle J_{ab}^2 \rangle$ passing through a plane is equal to the electronic factor $|T_{ba}^2|$ in the ET rate. Then, we can represent the constituents of $|T_{ba}^2|$ in the protein conformation as a map by connecting $\langle J_{ab}^2 \rangle$ with large amplitudes in each plane. We shall discuss the advantage of the new model for the electron tunneling pathway over the previous models of Beratan et al. and Dutton et al..

- 2P321 蛋白質中電子トンネリングカレントの揺らぎの起源
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 2aD01 Molecular origin of fluctuation of electron tunneling currents in protein media
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We have so far demonstrated that the electron tunneling currents in protein media fluctuate rapidly due to thermal fluctuations of the protein conformation by mean of molecular dynamics simulations and quantum chemical calculations. In the present study, we investigated what is the molecular origin of the fluctuation of tunneling currents for the electron transfer from bacteriopheophytin (Bph) anion to the primary quinone (Q_A) in photosynthetic bacterial reaction center. By the analysis, we found that there exist independent two sequences of coherent tunneling currents connecting donor and acceptor as a whole: The interatomic tunneling currents of all the bonds and spaces constituting the sequence fluctuate almost synchronously. We call this sequence as coherent sequence of currents, abbreviated as CSC. Actually, the two CSCs are the more rigidly refined forms of the Trp and Met routes which were discovered before. In the present analysis, we found that the fluctuation of the CSC in Trp originates from the fluctuation of the overlap integrals of π -orbitals in Trp residue with 2p orbitals in carbonyl oxygen which belongs to Bph. The origin of the fluctuation of the CSC in Met is under investigation.

- 2P322 FTIR 及び量子化学計算による光化学系 II におけるプラストキノン分子相互作用の解析
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 Analysis of molecular interaction of plastoquinone in photosystem II by FTIR spectroscopy and DFT calculations
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After light-induced charge separation in photosystem II (PSII), an electron is transferred to the primary quinone electron acceptor Q_A and then to the secondary quinone acceptor Q_B. Although the chemical identities of Q_A and Q_B are both plastoquinone-9 (PQ-9), their reactions and functions are rather different: the redox potential of Q_A is lower than that of Q_B, and Q_A is only singly reduced but Q_B can be doubly reduced. Such different properties between Q_A and Q_B are achieved by specific interactions of PQ-9 with surrounding proteins. However, the molecular mechanism underlying the Q_A and Q_B functions are yet to be clarified. In this study, we have analyzed the H-bond structures of Q_A and Q_B in PSII using Fourier transform infrared (FTIR) spectroscopy and density functional theory (DFT) calculations. DFT vibrational analyses were performed for PQ-1 and its radical anion (PQ-1⁻) in various model complexes having different number of H-bonds with water molecules. Comparison of the calculated spectra in the CO stretching region of PQ-1⁻ with the Q_A/Q_A and Q_B/Q_B FTIR spectra suggested that Q_A and Q_B take different H-bond structures, that is, both the CO groups are singly H-bonded in Q_A and one of them are doubly H-bonded in Q_B. In addition, Q_A/Q_A spectra obtained using different herbicides, DCMU and bromoxynil, were compared. The CO peak of Q_A was slightly higher with DCMU than with bromoxynil, indicating that the H-bond interaction of Q_A was affected by binding of different types of herbicides at the Q_B site.

- 2P323 FTIR 法による光化学系 II におけるチロシン Y_D と水分子の相互作用の検出
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 2aD05 Structural coupling of water molecules to Y_D in photosystem II as revealed by FTIR spectroscopy
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The redox-active tyrosine Y_D (D2-Tyr160) in photosystem II (PSII) serves as an accessory electron donor to P680. It undergoes proton-coupled electron transfer; when it is oxidized, a proton is released and a neutral radical Y_D[•] is formed. The recent X-ray structure of the PSII core complex revealed a H-bond network around the OH group of Y_D. This H-bond network must play an important role in the proton-transfer reaction upon Y_D oxidation. In this study, we have detected water molecules coupled to Y_D by means of light-induced Fourier transform infrared (FTIR) spectroscopy. Y_D/Y_D FTIR difference spectrum was obtained by applying five flashes to a moderately hydrated (deuterated) film of PSII core complexes from *Thermosynechococcus elongatus* at 10 °C. Along with the numerous bands arising from Tyr and protein backbones in the 1800-1100 cm⁻¹ region, differential signals were observed at 3636/3617 and 3594/3584 cm⁻¹ in the weakly H-bonded OH stretching region. These signals downshifted by 11-12 cm⁻¹ upon H₂¹⁸O substitution and disappeared in a deuterated film, and hence they were definitely assigned to the water OH vibrations. The presence of these water bands in the Y_D/Y_D spectrum indicates that at least two water molecules are structurally coupled to Y_D and their H-bond interactions are perturbed upon Y_D oxidation. These water molecules are probably involved in the H-bond network around Y_D; thus, they might play a significant role in the proton release reaction of Y_D.