A¹. Based on the present result, we examined the analysis of the dynamic disorder by means of the single-molecule spectroscopy with use of the Dutton law by Xie and co-workers.

3P-262 光化学系 II 反応中心における Q_A⁻ラジカルアニオンによる励起三重項消去機構

Mechanism of Triplet Quenching in the Photosystem II Reaction Center by the Q_A⁻ radical anion

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In photosystem II (PSII) of plant and cyanobacteria, primary charge separation takes place between the chlorophyll (Chl) dimer P₆₈₀ and pheophytin (Pheo) to form the P₆₈₀⁺Pheo⁻ radical pair. The electron is transferred to the primary quinone acceptor Q_A and then the secondary acceptor Q_B, while the hole is transferred to the Mn cluster to oxidize water. When the electron transfer is blocked at Q_A, P₆₈₀⁺Pheo⁻ recombines to form an excited triplet state on the monomer Chl, Chl_{D1}^{*}. It has been known that under strong light illumination, a Q_A⁻ radical is accumulated and subsequently doubly reduced Q_A is formed, which is finally released from the PSII protein. In the absence of Q_A, ³Chl_{D1}^{*} decays with a lifetime of ~1 ms, whereas in the presence of Q_A⁻, ³Chl_{D1}^{*} is quenched much faster in 2-10 μs. In this study, we have theoretically investigated the mechanism of triplet quenching in PSII. The ³Chl_{D1}^{*} quenching by Q_A⁻ was explained by a reaction sequence involving an intermediate state. The first step is triplet energy transfer from ³Chl_{D1}^{*} to Pheo, and the second step is reduction of ³Pheo^{*} by Q_A⁻. Molecular vibrations of Pheo and Q_A are crucial in calculation of the rate constants of these reaction steps. We determined the frequencies and Huang-Rhys factors of the molecular vibrations by quantum chemical calculations. The rate constant calculated using these values reproduced the fast μs lifetime of ³Chl_{D1}^{*} in the presence of Q_A⁻. The temperature dependence of the rate constant was also in agreement with previous experiments.

3P-263 光合成における励起エネルギー移動理論: コヒーレントとインコヒーレント極限をつなぐ

Theory of excitation energy transfer connecting coherent and incoherent limit in photosynthesis

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In photosynthetic antenna protein, excitation energy transfer (EET) between pigments occurs, where it is considered that the quantum-mechanical coherence among pigments plays an important role.

In considering EET with the coherence, there are two important interactions: pigment-pigment coupling J and pigment-protein coupling W. The former induces EET and the latter disturbs the coherence between excited states of pigments. When J << W, a localized excitation on a pigment is transferred incoherently. In this situation, the Forster theory, the most traditional theory, is justified. Whereas, when J >> W, EET occurs coherently. In this situation, the excited state described as "exciton", where the state is delocalized on pigments. Theories considering the exciton are categorized as the generalized Forster and the Redfield theory.

Thus, these previous theories limit their applicable scope as J << W or J >> W. However, a situation for J and W strongly depends on the structure of the proteins. Since the structure is varied in reality, the situation may be not only these limit cases. To describe EET in real proteins correctly, we need a theory with wide scope including J ~ W as well as J >> W and J << W.

We succeeded in developing such a global theory, where key points are 1) partition of the Hamiltonian into the perturbative part and 2) using "semi-diagonalizing" basis set. We show the coherent dynamics of excitation on pigments in real proteins calculated by our theory, and also discuss here a role played by the coherence.

3P-264 タンパク質媒体中電子移動反応の平均化したトンネル経路

Average electron tunneling route of the electron transfer in protein media

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For the electron-transfer (ET) reaction in protein media, the interatomic tunneling currents J_{ab}'s change drastically according to the thermal fluctuation of protein conformation. This fluctuation of J_{ab}'s yields the rapid and large fluctuation of the value of the tunneling matrix element T_{DA}. Under such situations, we develop a theory for obtaining the average electron tunneling route in which the fluctuation of J_{ab}'s and the quantum-interference effect among the J_{ab}'s are taken into account. The average route was correlated with the electronic factor <T_{DA}²> in the case of ET by the elastic tunneling mechanism. The average route was expressed with use of the mean-square J_{ab}'s corrected by the quantum-interference effect. We applied this method to the ET from the bacteriopheophytin anion to the primary quinone in the bacterial photosynthetic reaction center. We obtained J_{ab}'s by a combined method of MD simulations and quantum chemical calculations. We found that much destructive interference works among the J_{ab}'s even after taking the average. Examining the map of the mean-square J_{ab}'s corrected by the quantum-interference effect, we found that the two groups of small numbers of J_{ab}'s which mutually coupled with high correlation in each group form the two routes, Trp route and Met route. Each of the two average tunneling routes is composed of a few major pathways in the Pathways model which are fused at considerable part to each other. We also analyzed the average tunneling route for the ET by the inelastic tunneling mechanism.

3P-265 タンパク質中電子移動における非弾性トンネル機構の観測

Observation of the inelastic tunneling mechanism in the electron transfer in protein media

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Theoretically it was verified that the inelastic tunneling mechanism (ITM) works in the electron transfer (ET) in protein environment¹. In order to make the ITM experimentally observable, we computationally investigated the ET in the reaction center and clarified its feature as follows: (1) The ITM predominantly works to reduce the rapid decrease of the ET rate in the inverted region of the energy gap law. (2) Such effect is similar to the role of quantum mode in the Franck-Condon factor. (3) At the very low temperature, however, the role of the ITM is considerably reduced while the role of the quantum mode is not affected by the temperature. (4) The C-H stretching mode contributes significantly to the ITM. (5) The external electric field effect is much larger for the ITM than the elastic tunneling mechanism (ETM). We are examining whether these properties of the ITM can be applied to design a useful molecular electric device.

Reference 1: H. Nishioka, A. Kimura, T. Yamato, T. Kawatsu and T. Kakitani, J. Phys. Chem. B, 109, 15621-15635 (2005).

3P-266 ホタル化学発光反応におけるルシフェリン中間体M420 対する K⁺ イオンの効果

Effect of K⁺ on a luciferin intermediate M₄₂₀ in a reaction process of firefly chemiluminescence

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The reaction pathway of chemiluminescence (CL) of firefly luciferin (Ln) in deoxygenated dimethyl-sulfoxide (DMSO) added potassium *t*-butoxide (*t*-BuOK) was investigated. The light emitter is supposed to be an excited oxyluciferin (OxylLn^{*}) formed by the decomposition of dioxetanone (DOX).

Intermediates of Ln were produced prior to the formation of DOX by evacuating oxygen in DMSO. The intermediate with the absorption maximum at ~420nm (called M₄₂₀) was observed over the concentrations 3.6 ~ 30mM of *t*-BuOK. By adding oxygen gas into M₄₂₀, light emission could be detected. Under content rate of water to DMSO, [H₂O]=0.2% and *t*-BuOK concentration, [*t*-BuOK]=5mM, the time-resolved CL spectra of M₄₂₀ showed both of 510- and 620nm-colored light emissions. Two products formed from M₄₂₀ after 510- and 620nm-emissions were founded by stopping oxygen-flow half way. The two products called N₄₂₀ and P₅₃₅ showed the absorbance and fluorescence peaks at ~420nm and ~560nm, and at ~535nm and 620nm, respectively.

The role of potassium cation (K⁺) was investigated. Under [H₂O]= 0.2% and [*t*-BuOK]=10mM, 18-crown-6 ether added in M₄₂₀ solution trapped efficiently K⁺ to decrease the CL intensity of M₄₂₀, while 15-crown-5 ether had no effect on it.

We concluded that a) 510nm-light emitter in the CL of M₄₂₀ is an unknown excited species X^{*} which could be changed into N₄₂₀, and 620nm-light was emitted from the excited P₅₃₅^{*} and b) the interaction of K⁺ with COO⁻ at C₄ site may play a key role in the formation of DOX.

3P-267 蛍光褪色回復法によるシアノバクテリア細胞内でのフィコビリソームの拡散運動の測定

Measurement of diffusion of phycobilisomes inside cyanobacterial cells by fluorescence recovery after photobleaching (FRAP) technique

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Phycobilisomes (PBS) are the light-harvesting antennae-pigment protein complexes in cyanobacteria and red algae. PBS with diameters of 32-70 nm are attached on the cytoplasmic surface of the thylakoid membranes and transfer the excitation energy mainly to photosystem (PS) II. It has been considered that PBS diffusion is a prerequisite for the regulation of the distribution of excitation energy (state transition) between PS I and PS II. Measurement of fluorescence recovery after photobleaching (FRAP) has been used to observe the diffusion of fluorescent molecules inside a cell. PBS diffusion in a cyanobacterium *Synechococcus* 7942 observed by FRAP suggested the PBS diffusion to be responsible for the state transition. We tested PBS-FRAP technique for a filamentous bacterium *Nostoc* sp., and compared the results with those in *Synechococcus* 7942. We carefully studied the fluorescence emission spectra at the bleached point and multiple non-bleached points inside multiple cells after laser-irradiation to distinguish the PBS diffusion process from the fluorescence increase due to PBS damages. In *Synechococcus* 7942, diffusion of PBS into the bleaching point gave a diffusion coefficient of 3.1×10⁻¹¹ cm²s⁻¹ at 25°C. In *Nostoc* sp., we detected increase in PBS fluorescence even outside the bleached spot. We will discuss different responses to the intense light irradiation and cell structures between these two organisms.

3P-268 極低温時間分解蛍光測定による中心目珪藻 *Chaetoceros*

gracillii の光化学系 I 超分子複合体内のエネルギー移動の解析
Light-harvesting process of photosystem I of a diatom *Chaetoceros gracillii* studied by time-resolved fluorescence at cryogenic temperature

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