IX-F Molecular Mechanism of Photosensory Protein Function, Excitation Energy Transfer and Electron Transfer in Biological Systems

We are interested in photochemistry, photophysics, photoenergy conversion and photosignal transduction in living orgamisms. Above all, the primary interest in our laboratory is the molecular mechanism of photosensory proteins including rhodopsin and photoactive yellow protein. Using theoretical/computational techniques, we study what happens in these photosensory proteins after light illumination and how these proteins convert light energy into conformational changes.

Excitation energy transfer is a significant process in biophysics. The light-harvesting antenna system in photosynthetic purple bacteria collects and transfers photoenergy efficiently by its unique mechanism. We study this mechanism theoretically.

The electron transfer in biological systems is mostly long-range electron transfer that occurs by the electron tunneling through the protein media. Using theoretical/computational methods, we calculate the electron tunneling current in the protein matrix and analyze how intraprotein electron transfer occurs.

IX-F-1 Role of Protein in the Primary Step of the Photoreaction of Yellow Protein

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[*Proteins: Struct., Funct., Genet.* in press]

We show the unexpectedly important role of the protein environment in the primary step of the photoreaction of the yellow protein after light illumination. The driving force of the *trans*-to-*cis* isomerization reaction was analyzed by a computational method. The force was separated into two different components: the term due to the protein-chromophore interaction and the intrinsic term of the chromophore itself. As a result, we found that the contribution from the interaction term was much greater than that coming from the intrinsic term. This accounts for the efficiency of the isomerization reaction in the protein environment in contrast to that in solution environments. We then analyzed the relaxation process of the chromophore on the excited-state energy surface and compared the process in the protein environment and that in a vacuum. Based on this analysis, we found that the bond-selectivity of the isomerization reaction also comes from the interaction between the chromophore and the protein environment.

IX-F-2 Direct Measure of Functional Importance Visualized Atom-by-Atom for Photoactive Yellow Protein

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Photoreceptor proteins serve as efficient nanomachines for the photoenergy conversion and the photosignal transduction of living organisms. For instance, the photoactive yellow protein derived from a halophilic bacterium has the *p*-coumaric acid chromophore, which undergoes an ultrafast photoisomerization reaction after light illumination. To understand the structure-function relationship at the atomic level, we used a computational method to find *functionally important atoms* for the photoisomerization reaction of the photoactive yellow protein. In the present study, a "direct" measure of the functional significance was quantitatively evaluated for each atom by calculating the *partial atomic driving force* for the photoisomerization reaction. As a result, we revealed the reaction mechanism in which the specific role of each functionally important atom has been well characterized in a systematic manner. In addition, we observed that this mechanism is strongly conserved during the thermal fluctuation of the photoactive yellow protein.

IX-F-3 A Computational Study on the Stability of the Protonated Schiff Base of Retinal in Rhodopsin

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We investigated the effect of amino acids in rhodopsin on the protonation state of the Schiff base (SB) retinal. We constructed a model system consisting of SB retinal, Glu113(counterion), and eight residues. For this model, we considered two states of the SB retinal, namely, the protonated/deprotonated state. We then performed *ab initio* MO calculations at the RHF/6-31g* level. As a result, the protonated state was stabler than the deprotonated state. Interestingly, we observed an additive rule for the contribution to the stabilization energy due to each amino acid. Above all, it turned out that Ser186 and Cys187 play a significant role in the stability.

IX-F-4 Destructive Interference in the Electron Tunneling through Protein Media

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We investigated the origin of the very rapid and large fluctuation of the electron tunneling matrix element T_{DA} due to the thermal fluctuation of protein conformation which was recently observed by the simulation study (Daizadeh, I.; Medvedev, E. S.; Stuchebrukhov, A. A. *Proc. Natl. Acad. Sci. U.S.A.* **94**, 3703 (1997)). We made analysis of this phenomena by using the interatomic tunneling current map of Ru-modified azurins. We defined a new index, degree of destructive interference Q, by making an average of the intermediate level for the interatomic tunneling currents. We found an empirical relation that $|T_{DA}|$ is proportional to Q^{-1} holds true in the course of thermal fluctuation of protein conformation. Comparing maps of the interatomic tunneling currents with different values of Q, we found that the very rapid (in much less than 1 ps) and large amount (maximally 2 orders of magnitude) of fluctuations in T_{DA} are caused by the reconnection and the change in the direction of interatomic tunneling currents with considerable amplitudes. By taking the statistical average for the dynamics effect of $\log|T_{DA}|$, we found that the range of the averaged dynamic modification of electron transfer rate amounts to more than 2 orders of magnitude in the Ru-modified azurins. In the systems with a large range of dynamic modification, this nuclear dynamics effect contributes to enhance the thermally averaged electron transfer rate considerably.

IX-F-5 Unique Mechanism of Excitation Energy Transfer, Electron Transfer and Photoisomerization in Biological Systems

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We discuss unique mechanisms typical in the elementary processes of biological functions. We focus on three topics. Excitation energy transfer in the light-harvesting antenna systems of photosynthetic bacteria is unique in its structure and the energy transfer mechanism. In the case of LH2 of *Rhodopseudomonas acidophila*, the B850 intra-ring energy transfer and the inter-ring energy transfer between B800 and B850 take place by the intermediate coupling mechanism of energy transfer. The excitonic coherent domain shows a wave-like movement along the ring, and this property is expected to play a significant role in the inter-ring energy transfer between LH2's. The electron transfer in biological systems is mostly long-range electron transfer that occurs by the electron tunneling through the protein media. There is a long-standing problem that which part of protein media is used for the electron tunneling root. As a result of our detailed analysis, we found that the global electron tunneling root is a little winded with a width of a few angstrom, reflecting the property of tertiary and secondary structures of the protein and it is affected by the thermal fluctuation of protein structure. Photoisomerization of rhodopsin is very unique: The *cis-trans* photoisomerization of rhodopsin occurs only around the C11=C12 bond in the counterclockwise direction. Its molecular mechanism is resolved by our MD simulation study using the structure of rhodopsin which was recently obtained by the X-ray crystallographic analysis.

IX-F-6 Analysis of Cis-Trans Photoisomerization Mechanism of Rhodopsin Based on the Tertiary Structure of Rhodopsin

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We propose a novel mechanism (Twist Sharing Mechanism) for the *cis-trans* photoisomerization of rhodopsin, based on the molecular dynamics (MD) simulation study. New things devised in our simulations are (1) the adoption of Mt. Fuji potentials in the excited state for twisting of the three bonds C9=C10, C11=C12 and C13=C14 which are modeled using the detailed ab initio quantum chemical calculations and (2) to use the rhodopsin structure which was resolved recently by the X-ray crystallographic study. As a result, we found the followings: Due to the intramolecular steric hindrance between 20-methyl and 10-H in the retinal chromophore, the C12–C13 and C10–C11 bonds are considerably twisted counterclockwise in rhodopsin, allowing only counterclockwise rotation of the C11=C12 in the excited state. The movement of 19-methyl in rhodopsin is blocked by the surrounding three amino acids, Thr118, Met207 and Tyr268, prohibiting the rotation of C9=C10. As a result only all-*trans* form of the chromophore is obtainable as a photoproduct. At the 90 degrees twisting of C11=C12 in the course of photoisomerization, twisting energies of the other bonds amount to about 20 kcal/mol. If the transition state for the thermal isomerization is assumed to be similar to this structure, the activation energy for the thermal isomerization around C11=C12 in rhodopsin is elevated by about 20 kcal/mol and the thermal isomerization rate is decelerated by 10^{-14} times than that of the retinal chromophore in solution, protecting photosignal from the thermal noise.