X-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.

X-F-1 Torsion Potential Works in Rhodopsin

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We investigate the role of protein environment of rhodopsin and the intramolecular interaction of the chromophore in the cis-trans photoisomerization of rhodopsin by means of a newly developed theoretical method. We theoretically produce modified rhodopsins in which a force field of arbitrarily chosen part of the chromophore or the binding pocket of rhodopsin is altered. We compare the equilibrium conformation of the chromophore and the energy stored in the chromophore of modified rhodopsins with those of native rhodopsins. This method is called site-specific force field switch (SFS). We show that this method is most successfully applied to the torsion potential of rhodopsin. Namely, by reducing the twisting force constant of the C11=C12 of 11-cis retinal chromophore of rhodopsin to zero, we found that the equilibrium value of the twisting angle of the C11=C12 bond is twisted in the negative direction down to about –80 degrees. The relaxation energy obtained by this change amounts to an order of 10 kcal/mol. In the case that the twisting force constant of the other double bond is reduced to zero, no such large twisting of the bond happens. From these results we conclude that a certain torsion potential is applied specifically to the C11=C12 bond of the chromophore in the ground state of rhodopsin. This torsion potential facilitates the bond-specific cis-trans photoisomerization of rhodopsin. This kind of the mechanism is consistent with our torsion model proposed by us more than a quarter of century ago. The origin of the torsion potential is analyzed in detail on the basis of the chromophore structure and protein conformation, by applying the SFS method extensively.

X-F-2 Role of Protein in the Primary Step of the Photoreaction of Yellow Protein

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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.

X-F-3 Direct Measure of Functional Importance Visualized Atom-by-Atom for Photoactive Yellow Protein: Application to Photoisomerization Reaction

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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.