論文 / 著書情報
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題目(和文)	フェムト秒電子・振動分光による光受容タンパク質および基本分子における超高速光異性化反応の研究
Title(English)	Ultrafast Photoisomerization in Photoreceptor Proteins and Fundamental Molecules Studied by Femtosecond Electronic and Vibrational Spectroscopy
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種別(和文)	論文要旨
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論文要旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Photoisomerization achieves the isomerization process that is energetically unfavorable in thermal reactions in the ground state. Therefore, photoisomerization plays a key role to convert light into the chemical energy in various systems including photoreceptor proteins. Photoisomerization is one of the most important reactions in fundamental science, and has been studied by various spectroscopic approaches. However, the microscopic mechanisms of photoisomerization still remain unclear. To address this issue, in this dissertation, photoisomerization reactions in rhodopsins and a cyanine dye are studied by femtosecond time-resolved absorption, fluorescence, and Raman spectroscopies that enable direct observation of the photoisomerization process taking place on an ultrashort timescale.

Generally, *cis-trans* photoisomerization proceeds faster than trans-cis photoisomerization in solution. However, it is still unexplored that the same is true in the protein matrix. To address this issue, femtosecond Kerr-gate fluorescence measurements of *Anabaena* sensory rhodopsin (ASR) were carried out. ASR is a unique rhodopsin that can possess not only the all-*trans* protonated retinal Schiff base (PRSB) but also the 13-*cis* PRSB. Therefore, the phtoisomerization dynamics of all-*trans* and 13-*cis* PRSBs can be directly compared in the same protein matrix. It was shown that, in ASR, the photoisomerization of the 13-*cis* PRSB proceeds with a time constant of 250 fs whereas that of the all-*trans* PRSB takes place with a time constant of 700 fs. This indicates that the cis-trans photoisomerization of PRSB is faster than trans-cis photoisomerization in the ASR protein as in the case of the photoisomerization in solution.

KR2 is a newly discovered light-driven sodium ion pump rhodopsin. However, the photoreaction dynamics of KR2 and mechanisms for their functions have not been fully elucidated. Especially, photoisomerization dynamics of the all-*trans* retinal of KR2 is still unexplored. To address this issue, femtosecond time-resolved absorption measurement of KR2 at pH 8 (pH of seawater) was carried out. It was found that the photoisomerization of the PRSB in KR2 takes place with a time constant of 180 fs. This reaction occurs several times faster than that in bacteriorhodopsin (~500 fs). It has been reported that the Schiff base in KR2 in crystal is distorted differently with respect to that in bacteriorhodopsin. This suggests that the structural difference of the Schiff base in the initial ground state gives rise to the difference in the photoisomerization rate.

Femtosecond time-resolved absorption measurements of KR2 at pH 8 also revealed that photoexcitation of KR2 generates the reactive S_1 state (lifetime 180 fs) that undergoes photoisomerization as well as the non-reactive S_1 states (lifetimes 3 ps and 30 ps) that do not isomerize and relax back to the original S_0 state. To clarify the origin of these S_1 states, femtosecond absorption measurements were carried out at pH values ranging from 4 to 11. The obtained data revealed that the pH dependence of the yield of the reactive S_1 state correlates well with the degree of the deprotonation of Asp116, the counterion of the PRSB in KR2. This indicates that KR2’s having the deprotonated and protonated Asp116 coexist in the S_0 state, yielding the reactive and non-reactive S_1 states by photoexcitation, respectively. This implies that the interaction between the PRSB and the Asp116 is requisite for the photoisomerization in KR2.

The structural dynamics during photoisomerization (including the structure in the transition state) has been rarely observed. To track the structural changes during photoisomerization directly, barrierless photoisomerization of a cyanine dye was studied by femtosecond stimulated Raman spectroscopy (FSRS) using Raman pump wavelengths (λ_R) ranging from 740 to 1100 nm. The temporal behavior of the vibrational bands in the obtained FSRS spectrum changes depending on the λ_R, suggesting that the different λ_R probes the different regions on the potential energy surface of the S_1 state. The λ_R dependence of the FSRS spectra at various delays indicates the continuous twisting motion of the cyanine dye in the S_1 state.

Through this dissertation, it was shown that the photoisomerization dynamics drastically changes with various factors such as the difference in the initial structure and the interaction with surroundings. It was also demonstrated that structural change in the course of photoisomerization can be captured by using femtosecond vibrational spectroscopy.