Femtosecond time-resolved spectroscopy of bacteriorhodopsin and octopus rhodopsin

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Developing ultrashort visible pulse, we have been working on femtosecond time-resolved spectroscopy. The time-resolution of sub-10-fs enables us to observe electronic dynamics and dynamics of molecular vibration modes simultaneously.

Primary reaction of vision is ultrafast photo-isomerization of retinal which is a chromophore of rhodopsin. The ultrafast photo-isomerization finishes in a few hundred femtoseconds. In this talk, we will show the ultrafast dynamics in the photo-isomerization observed in bacteriorhodopsin and octopus rhodopsin.

In the study of bacteriorhodopsin, we found the real-time frequency change of molecular vibration modes. The frequency modulation of the C=C stretching mode in 200 fs period reflects a coupled torsion mode around the C_{13}=C_{14} bond leading to the photoisomerization around the C=C bond. Mode merge between in-plane and out of plane C=C-H bending modes was also observed in the same period synchronized with the frequency modulation on the C=C stretching mode. It confirmed that the molecular vibration modes are affected by structural deformation during the ultrafast photo-isomerization.

In the work of octopus rhodopsin, we found that the octopus rhodopsin follows similar dynamics with different time constants compared with bacteriorhodopsin. The photo-isomerization was found to be much faster completing at 81 fs. The frequency modulations of molecular vibration modes were observed in a period of ~500fs, reflecting torsional motion around the C=C double bond before thermalization.