Ultrafast Pump-Probe Study of Halide Dependence in Primary Reaction Dynamics of Halorhodopsin

TAKUMI NAKAMURA, SATOSHI TAKEUCHI, RIKEN, MIKIHIRO SHIBATA, HIDEKI KANDORI, Nagoya Institute of Technology, TAHEI TAHARA, RIKEN — Halorhodopsin is a retinal protein in Haloarchaeal cell membrane. The light-induced all-trans to 13-cis isomerization of the retinal chromophore triggers unidirectional chloride-ion pump in millisecond timescale. Here, we present pump-probe study of the primary ultrafast dynamics of Natronobacterium pharaonis halorhodopsin that contains Cl\(^-\), Br\(^-\) or I\(^-\). All the temporal behaviors of the S\(_1\) absorption, ground-state bleaching, and stimulated emission consisted of three components, and their time constants showed halide-ion dependency. The \(\sim\)50-fs component corresponds to the spectral shift of the S\(_1\) absorption and stimulated emission bands, which is due to the wavepacket motion from the Franck-Condon region, forming the reactive and nonreactive S\(_1\) states. Referring to previous reports, the \(\sim\)2-ps component is assignable to the isomerization process from the reactive S\(_1\) state to the ground-state 13-cis form via the conical intersection, while the \(\sim\)5-ps component to the internal conversion of the nonreactive S\(_1\) state. Quantitative analysis indicated that the isomerization quantum yield increased in order of Cl\(^-\), Br\(^-\) and I\(^-\). On the basis of the halide-ion dependence observed, we discuss the relation between the initial halide-ion pump process and the isomerization mechanism.