

Real-time tracking of phytochrome's orientational changes during Pr photoisomerization

Yang, Yang

Linke, Martin

Von Haimberger, Theodore

Hahn, Janina

Matute, Ricardo

González, Leticia

Schmieder, Peter

Heyne, Karsten

Photoisomerization of a protein bound chromophore is the basis of the light sensing and signaling responses of many photoreceptors. Z-to-E photoisomerization of the Pr Cph1?2 phytochrome has been investigated by polarization resolved femtosecond visible pump-infrared probe spectroscopy, which yields structural information on the Pr excited (Pr^*), Pr ground, and lumi-R product states. By exhaustive search analysis, two photoreaction time constants of (4.7 ± 1.4) and (30 ± 5) ps were found. Ring D orientational change in the electronic excited state to the transition state (90° twist) has been followed in real-time. Rotation of ring D takes place in the electronically excited state with a time constant of 30 ± 5 ps. The photoisomerization is best explained by a single rotation around C15=C16 methine bridge in the Pr^* state and a diffusive interaction with its protein surrounding. © 2012 American Chemical Society.