



Contribution ID: 176

Type: **Contributed talk**

Multi-step 11-*cis* to all-*trans* retinal photoisomerization in bestrhodopsin, an unusual microbial rhodopsin

Tuesday, June 24, 2025 4:55 PM (20 minutes)

Rhodopsins constitute a broad class of sensory photoreceptors with retinal chromophores bound to the protein via a retinal Schiff base (RSB). Microbial rhodopsins are mostly activated through an all-*trans* to 13-*cis* photoisomerization reaction, whereas animal rhodopsins are invariably activated through an 11-*cis* to all-*trans* isomerization reaction. The recently discovered bestrhodopsins constitute a subfamily of very special bistable microbial rhodopsins. The *P. antarctica* bestrhodopsin photochemistry involves a very peculiar all-*trans* to 11-*cis* isomerization and vice versa, rather than the all-*trans* to 13-*cis* photoreaction of canonical microbial rhodopsins, and hence resemble animal rhodopsins in that regard. Here, we present the 11-*cis* to all-*trans* photoreaction as determined by femtosecond to sub-millisecond transient absorption (TA) and femtosecond stimulated Raman spectroscopy (FSRS). The primary photoreaction involves ultrafast isomerizations in 240 fs from the 11-*cis* RSB reactant to a mixture of highly distorted all-*trans* and 13-*cis* RSB isomeric photoproducts. The 13-*cis* RSB isomer fraction of the primary photoproduct then *thermally* isomerizes to a distorted all-*trans* RSB in 120 ps. To rationalize this highly unusual phenomenology, we propose bicycle pedal models for the branched photoisomerizations from the 11-*cis* reactant to all-*trans* and 13-*cis* RSB isomer products, with corotation of the C11=C12 and C13=C14 double bonds. The former fraction undergoes bicycle pedal motion aborted at the C13=C14 double bond, resulting in an all-*trans* RSB isomer. The latter fraction undergoes a full bicycle pedal motion of both C11=C12 and C13=C14 double bonds, resulting in a 13-*cis* RSB isomer. The primary products are trapped high up the ground state potential energy surface (PES) owing to steric interactions with the protein binding pocket. Due to the resulting low energetic barrier on the ground state PES, thermal isomerization from 13-*cis* to all-*trans* RSB occurs in 120 ps. We suggest that the mechanism for simultaneous production of two different isomers may generally apply for rhodopsins, where the production of only one isomer as in most animal and microbial rhodopsins may be regarded as limiting cases.

Authors: Prof. BROSER, Matthias (Humboldt University Berlin); Dr KAZIANNIS, Spyridon (The Extreme Light Infrastructure ERIC); Dr VAN STOKKUM, Ivo H.M. (Vrije Universiteit Amsterdam); Dr MUKHERJEE, Atripan (The Extreme Light Infrastructure ERIC); Dr DOSTAL, Jakub (The Extreme Light Infrastructure ERIC); Mr BUSSE, Wayne (Humboldt University Berlin); Mr MUNHOVEN, Arno (Humboldt University Berlin); Dr BERNARDO, Cesar (The Extreme Light Infrastructure ERIC); Prof. HEGEMANN, Peter (Humboldt University Berlin); Dr KLOZ, Miroslav (The Extreme Light Infrastructure ERIC); KENNIS, John T.M. (Vrije Universiteit Amsterdam)

Presenter: KENNIS, John T.M. (Vrije Universiteit Amsterdam)

Session Classification: Session 8 - Biosystems II