Probing the mechanism of a unidirectional biological rotor by excited state QM/MM molecular dynamics simulations

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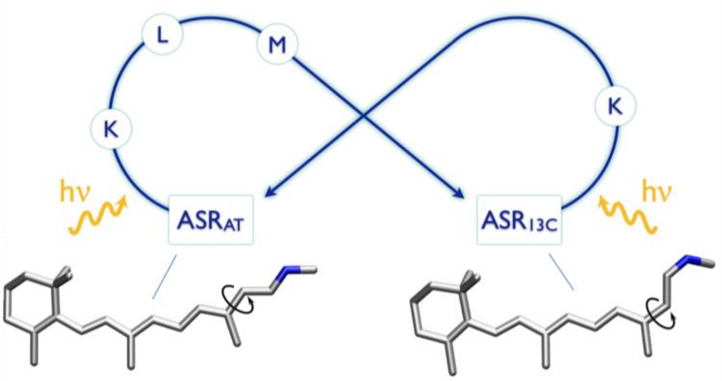
Since it's discovery, the sensory rhodopsin of the cyanobacterium Anabaena PCC 7120 (ASR)(1) has drawn attention as a potential candidate for a unidirectional molecular rotor.(2) This protein, which comprises a retinal protonated Schiff base (rPSB) covalently linked to the sidechain of a lysine, exists in two thermostable forms characterized by different stereoisomers of the rPSB. In one isomer the rPSB is in the all-*trans* (AT) conformation while in the other it is in the 13-*cis* (13C) conformation. The two forms can be reversibly transformed into each other by light absorption at different wavelengths (Scheme).



Scheme - Photocycles of ASR-AT and 13C with intermediates K, L and M.

In this contribution the primary event in ASR is investigated by means of excited state molecular dynamics simulations. In order to account for the effect of the protein environment a hybrid quantum mechanical/molecular mechanical (QM/MM) methodology is used.(3) The chromophore is described using a multiconfigurational quantum chemical method (CASPT2//CASSCF), whereas the protein is treated using a classical AMBER force field. Starting from the excited state, the trajectories evolve towards a conical intersection.(4) A trajectory surface hopping algorithm enables to switch from the S_1 to the S_0 state, thus allowing the trajectory to continue on the ground state. The isomerization process is found to be unidirectional and therefore it features a complete 360° rotation in the same direction triggered by light. These simulations provide insight into the stereoelectronic factors that control the quantum yield and the stereoselectivity of ASR photoisomerization, which were also recently found in bovine rhodopsin (Rh) and its intermediate bathorhodopsin (bathoRh)(5). Finally, the simulations are compared to the recent femtosecond spectroscopy measurements.(6)

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