MOLECULAR DYNAMICS OF THE QUASI-CARNO CYCLE FOR RETINAL ISOMERIZATION MOLECULAR MACHINE

K.B. Egorova*, K.V. Shaitan
M.V. Lomonosov Moscow state university, Biological faculty, Biophysics department, 119899 Moscow

The effect of specially simulated protein environment on excited and unexcited retinal was observed using the molecular dynamic method.

Rhodopsin isomerization is the initial reaction of visual perception. Retinal is a chromophore that absorbs light and triggers proton transfer reactions. Absorption of a photon induces the initial reaction accompanied by conformational changes of protein. Then, subsequent reactions take place.

In the process of the 11–cis retinal molecule isomerization in solution, 9–cis, 13–cis and all–trans forms are generated. Upon photoexcitation, the all-trans retinal in a solution is transformed to 9-cis, 11-cis and 13-cis forms. The quantum yield of the above-mentioned isomers is low. In contrast, the protonated Shiff base of retinal in visual rhodopsin photoisomerizes to the all–trans form with an efficiency of 67%. The protonated retinal in bacteriorhodopsin photoisomerizes to the 13–cis form with an efficiency of 64%.

The internal rotation barriers in various electronic states of retinal molecule were studied using the self-consistent field with the 6-31 G basis set. In the ground state of the initial retinal molecule barriers of two types are observed: from 2.2 to 8 kcal/mole at single bonds and from 43 to 47 kcal/mole at double bonds. In protonated retinal an alternate increase in the barrier height with increasing distance from the center of the molecule is observed.

In T_1 state of initial retinal, barriers at formally single bonds are about 4 kcal/mole, and barriers at formally double bonds are from 7 kcal/mole to 14 kcal/mole. Protonation causes an increase in barriers at all bonds up to 10,8-19 kcal/mole. Barrier distributions in T_1 and S_1 states in retinal was supposed to resemble each other, as we investigated in butadiene.

The following parameters were used in calculations of molecular dynamics: trajectory length, 10 ns with a step of 1 fs; T = 2000K. A collision thermostat simulating viscous water environment was applied. The standard potential field (Amber 96) was corrected taking into account the results of the quantum–chemical calculations mentioned above. The values of efficient atomic charge were calculated in the STO-3G basis in the geometry of the trans-form. To simulate the protein environment, the distance between the ends of the retinal was taken to be constant.

It was found that the protein environment exerts a considerable effect on the isomerization process. Collective degrees of freedom were discovered in excited retinal with fixed ends. It was shown that the process of visual perception can be considered as a cycle similar to the Carno cycle for the heat engine. Thus, a preliminary strain of retinal caused by its interaction with protein corresponds to the compression stage of the Carno cycle. Upon excitation (heating) of strained retinal, isomerization along a collective degree of freedom begins. This stage is not accompanied by scaled nuclear displacement and involves some torsion angles. Further relaxation of system with redistribution of proton density corresponds to the cooling stage of the Carno cycle. Then, the system returns to its initial condition.

Tel: +7(095)939–57–38, E-mail: *ksenia@biophys.msu.ru*