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ロドプシンとイソロドプシンの光応答性に関する非断熱 ab initio トラジェクトリ法による理論的研究

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A theoretical study on photo-responses of rhodopsin and isorhodopsin

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Rhodopsin (Rh) has 11-cis retinal as chromophore and is the photosensitive chemical found on the outer segment of rod-like cells in the retina, the light-sensing structure of eyes. Isorhodopsin (isoRh) is an Rh analogue that contains 9-cis retinal embedded in the same opsin environment. Despite their similarity, the photoisomerization period and quantum yield are largely different. Rhodopsin photoisomerization is experimentally known to be faster and more efficient

Here, we carried out Quantum Mechanics/Molecular Mechanics (QM/MM) trajectory surface hopping (TSH) direct dynamics calculations for Rh and isoRh with 162 runs for each in order to understand the origin of discrepancies in the rate and efficiency[1]. The transition probability is estimated on the basis of Zhu-Nakamura (ZN) theory[2]. Comparison is made with our previous *in vacuo* calculations[3,4]. The QM treatment was at the CASSCF(6,6) level with the mechanical embedding using the 6-31G basis set. The MM part is described by AMBER.

The simulation reproduced faster and more efficient isomerization in rhodopsin than in isorhodopsin. The reaction times in Rh and isoRh were 187 and 344 fs, and the quantum yields were 0.52 and 0.31. The corresponding experimental values are 200 and 600 fs for the reaction times and 0.65 and 022 for the yields. The opposite rotation of ϕ_9 and ϕ_{11} ('wring-a-wet-towel' motion) takes place upon photoexcitation, which also does without opsin. The wring-a-wet-towel motion is dynamically enhanced in comparison with the one expected from locations of the MECI.

Figure 1 shows the diagram of the active twist angle and the length of the active bond for five typical trajectories for Rh and isoRh. Fast and straightforward dynamics in Rh is shown in Figure 1(a) whereas complicated excited-state dynamics is illustrated in the isoRh case in Figure 1(b). The faster and more efficient photoisomerization of Rh than of isoRh is due to a straightforward and fast excited-state dynamics for Rh in

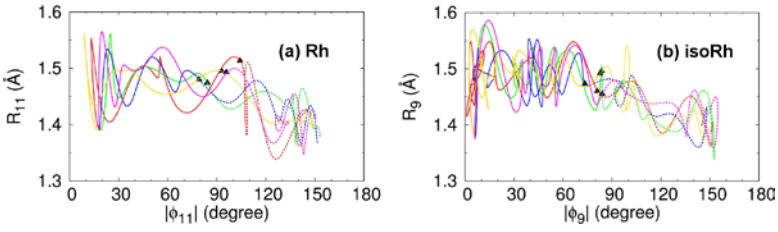

Figure 1. Change in length of the active bond -C_n-C_{n+1}- against the absolute value of the dihedral angle C_{n-1}-C_n-C_{n+1}-C_{n+2} for typical (a) Rh (n=11) and (b) isoRh (n=9) trajectories leading to the all-trans form. The solid and dashed lines show that trajectories are in the excited and ground states and the black triangles correspond to transition from the excited state to the ground state.

contrast with a complicated dynamics in a back and forth fashion especially in the excited state for isoRh. This difference would be mainly due to the dihedral that needs to be twisted in the isoRh case (-C9=C10-) is situated within the narrow gap between Thr118 and Tyr268 as shown in Figure 2(b). In Rh, the twisting area (-C11=C12-) is off from the two sandwiching residues as shown in Figure 2(a).

Photoexcitation of Rh gives only bathoRh (and the reactant) whereas the isoRh excitation yields a 9,11-dicis analog in addition to bathoRh (and the reactant). The rigorous selectivity in rhodopsin would be another reason why rhodopsin is selected biologically.

Comparison with our previous opsin-free investigations reveals that opsin tends to confine the twist of the active dihedral to only one direction When the opsin environment was totally ignored, the calculated quantum yield was only 0.27 and 0.13, respectively in sharp contrast with the values of 0.51 and 0.31 in opsin, respectively. This would be mainly due to the unidirectional rotation in opsin environment. The twist-confinement totally blocks simultaneous twisting of ϕ_9 and ϕ_{11} (=C10–C11=C12–C13=) and enhance the quantum yields. Also found is the fact that the opsin funnels transitions into the vicinity of minimum energy conical intersections (MECI). The opsin would prevent inefficient, premature hops especially in the isoRh case.

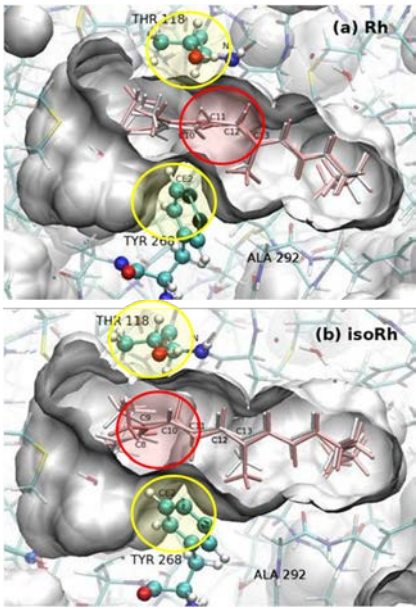

Figure 2. Superimposed structures of Frank-Condon geometry (gray) and geometry at the MECI (pink) for isorhodopsin. The twisting parts of retinal (red circle) and sandwiching Thr118 and Tyr268 (yellow circles) are highlighted. The twisting part is sandwiched between the two residues.

The present simulation reveals that the Weiss-Warshel model for cis-trans photoisomerization is not applicable for rhodopsin because the branching ratio after transition is crucial. In the model, it is assumed that a trajectory goes back and forth around the crossing point in the excited state. In their scheme, if the transition takes place when the trajectory go forth, the product is generated and if it does when the trajectory go back, the ground state reactant is regenerated. The analysis of trajectories, however, reveals that the picture totally breaks down, and that branching ratio at the first transition is crucial.

The present ZN-QM/MM-TSH is found to be a promising approach to investigate reactions in biomolecules.

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