Supporting Information

Photochemical Reaction Dynamics of the Primary Event of Vision Studied by a Hybrid Molecular Simulation

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Supporting Information includes figures of the time evolution of the C_{11}=C_{12} dihedral angle along the thirteen 11-cis → all-trans photoisomerization trajectories at 300 K (Fig. SI-1). Depicted are also the potential energies of the chromophore along a trajectory without the protein surroundings (Fig. SI-2), and along a trajectory at 0 K (Fig. SI-3). Finally, the time evolutions of (a) mean angles, $\bar{\theta}(t_g)$, and (b) amplitudes, $A(t_g)$, of the HOOP motions evaluated by Eqs. (2) and (4) in the main text along the trajectory at 0 K are presented in Fig. SI-4.

Supporting Information also includes captions of movies (Rh_trajectory.mpg and Rh_protein.mpg).

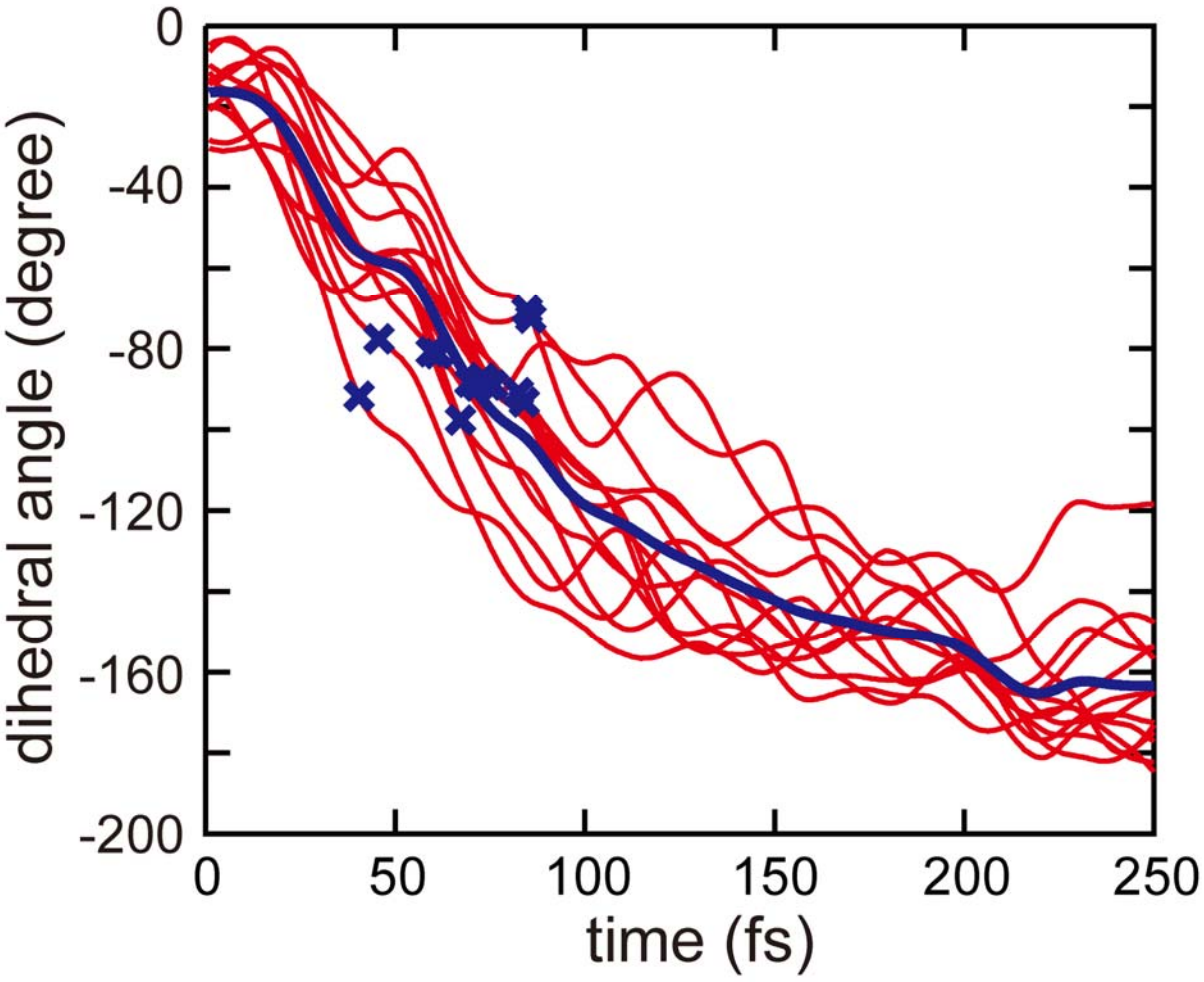

Figure SI-1: Time evolution of the C_{11}=C_{12} dihedral angle along thirteen 11-cis → all-trans trajectories of the photoisomerization at 300 K. Red and blue curves show the dihedral angles of the individual trajectories and the averaged over the trajectories. Blue crosses indicate the electronic transitions from the excited state to the ground state along the trajectories.

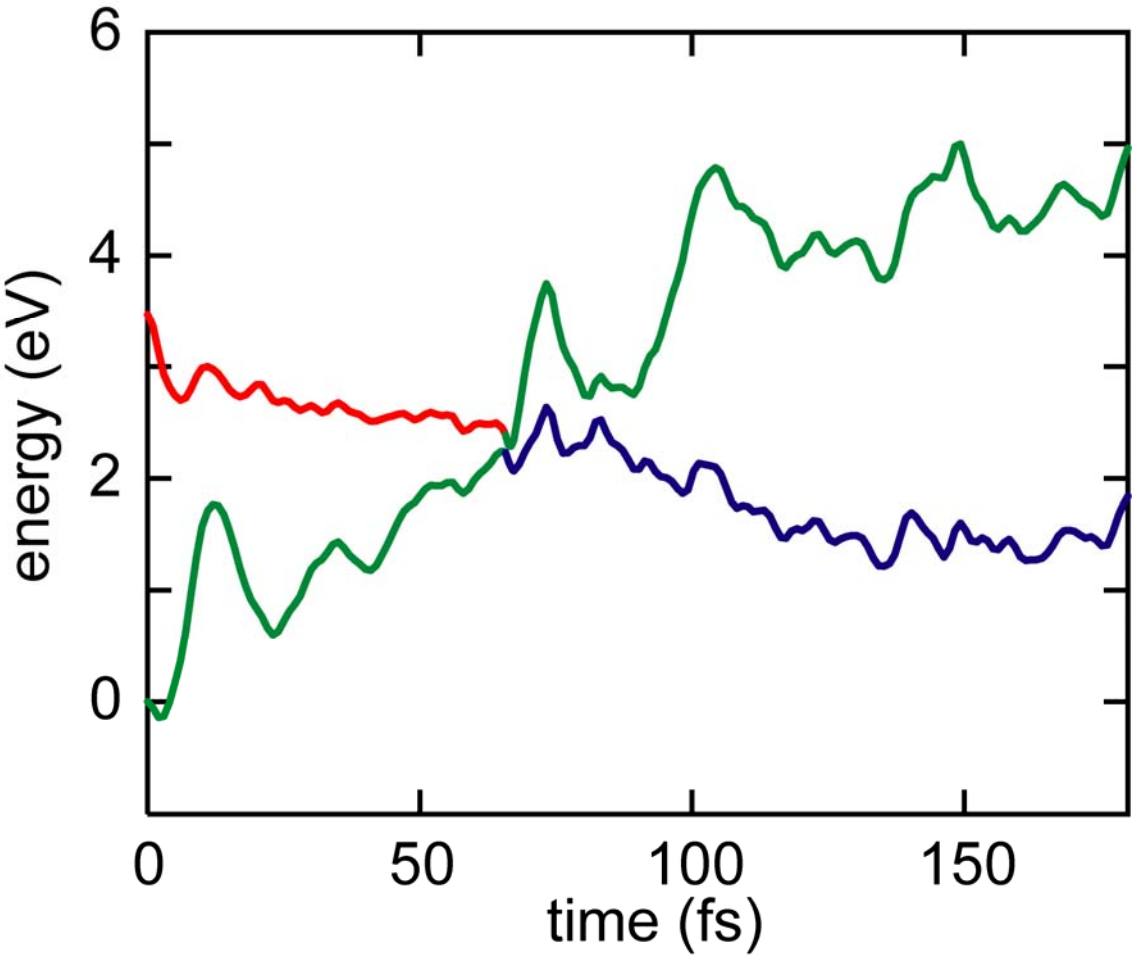

Figure SI-2: Time evolution of the potential energies of the chromophore along the trajectory in the absence of protein. The red curve indicates the potential energy in the excited state along the excited state trajectory after vertical excitation at $t = 0$; the blue curve indicates the potential energy in the ground state after energy crossing at $t = 65.5$ fs; the electronic states were computed by the state-averaged CASSCF method. Green curves show the potential energies of ground and excited state along that part of the trajectory which is in the excited and ground states, respectively.

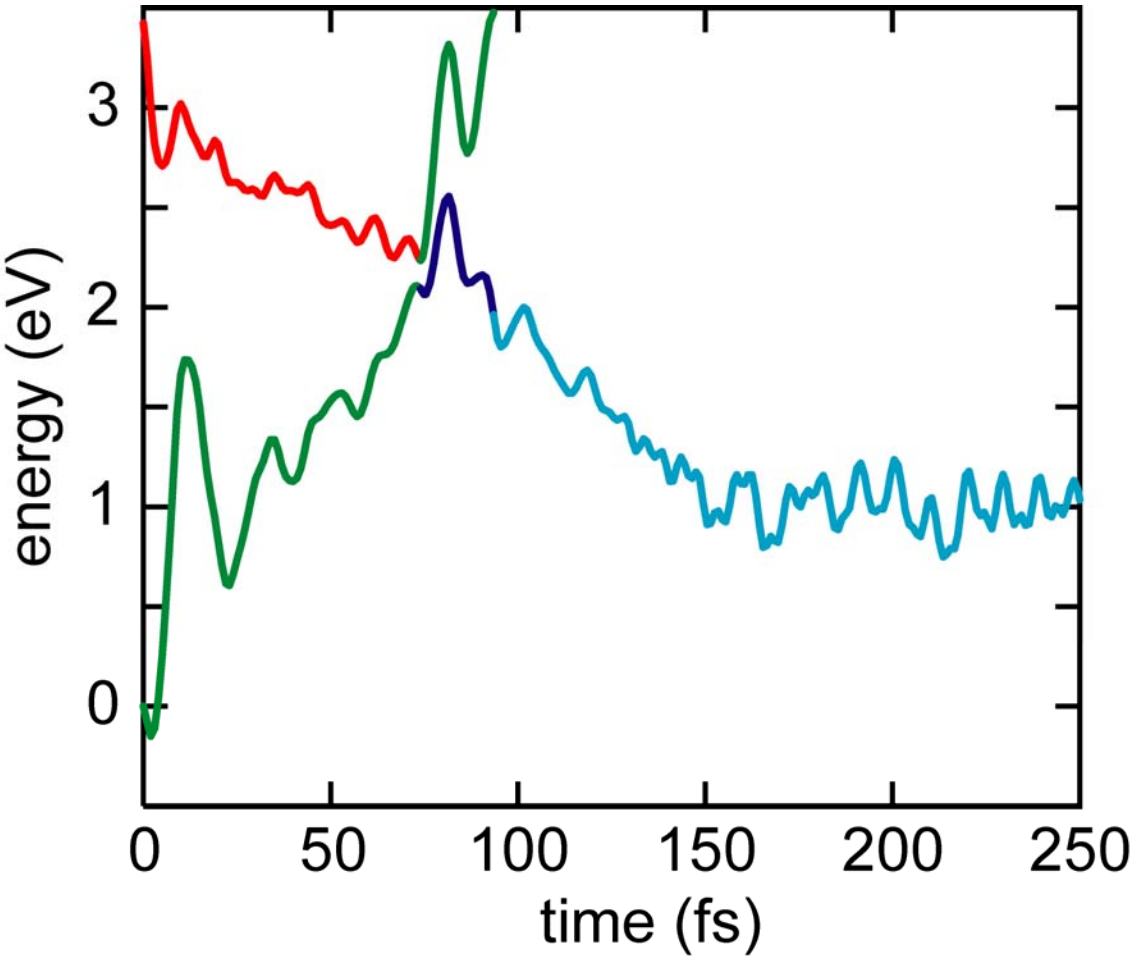

Figure SI-3: Time evolution of the potential energies of the chromophore along a trajectory at 0 K. The red curve indicates the potential energy in the excited state along the excited state trajectory after vertical excitation at t = 0. Dark and light blue curves indicate the potential energy in the ground state after the crossing at t = 74.0 fs computed by the state-averaged and state specific CASSCF methods, respectively. The potential energy of the state specific CASSCF calculation is shifted by a constant to connect the energy with that of the state averaged CASSCF calculation at the switching time. Green curves show the potential energies of ground and excited state along that part of the trajectory which is in the excited and ground states, respectively.

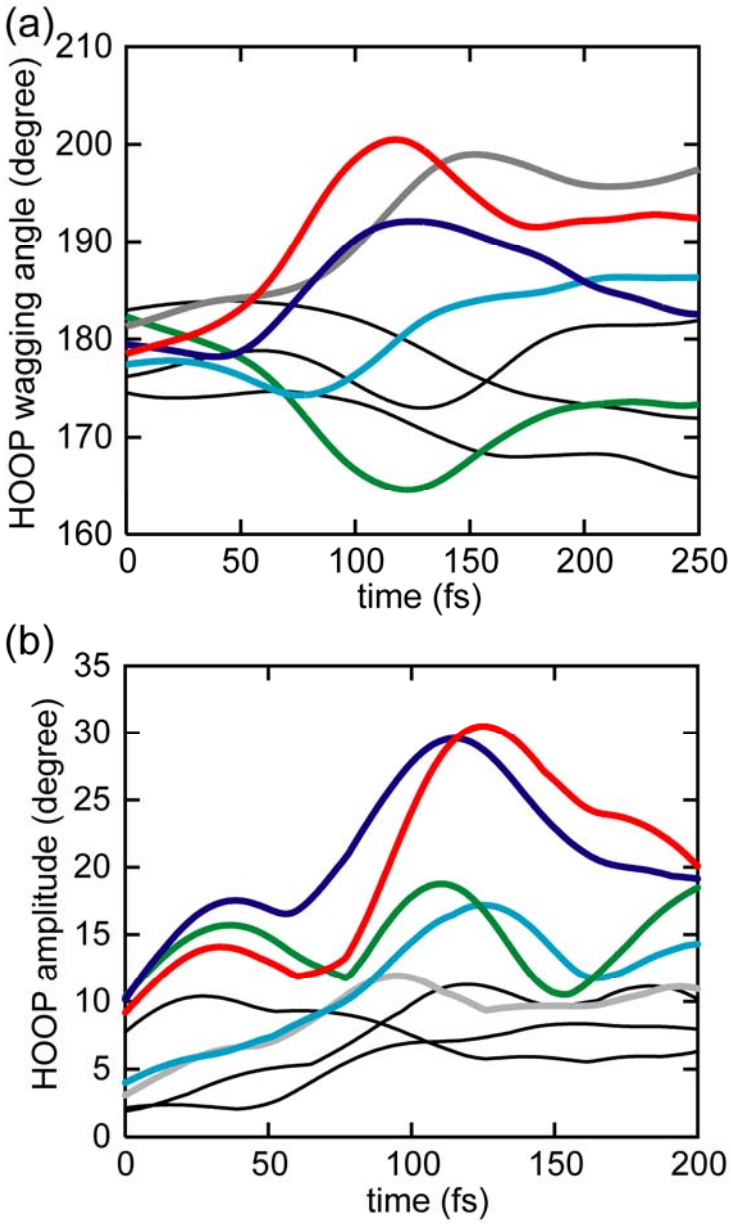

Figure SI-4: Time evolution of (a) mean angles, $\bar{\theta}(t_g)$, and (b) mean amplitudes, $A(t_g)$, of the HOOP motions evaluated by Eqs. (2) and (4), respectively, along a trajectory at 0 K. Colored curves indicate the wagging angles at C_{10} (red), C_{12} (dark blue), C_{11} (green), C_8 (gray), and C_{14} (light blue), and thin black curves show those at C_7, C_{13}, and N_ζ, respectively.

Movie Captions

Rh_trajectory.mpg: The movie shows the molecular motion involved in retinal photoisomerization in Rh. The trajectory corresponds to the one whose potential energy time evolution is depicted in Fig. 2. The retinal chromophore and the surrounding protein environment are drawn in red licorice and line representations, respectively.

Rh_protein.mpg: The movie shows conformational changes of the protein induced by retinal photoisomerization illustrated in Fig. 9. Tubes correspond to α-helix III (left) and α-helix VII (right), which include Ala-117 and Lys-296-chromophore, respectively. The geometries of α-helices and Ala-117 at t = 0 fs are depicted in orange.