1A1a   Excited-state dynamics of jet-cooled OMpCA and its hydrogen-bonded complexes studied by picosecond time-resolved spectroscopy

○Yasunori Miyazaki[1], Daiki Shimada[1], Yoshiya Inokuchi[1], Takayuki Ebata[1]

1. Graduate School of Science, Hiroshima University

The photocycle of photoactive yellow protein (PYP) has drawn attention to understand the negative phototaxis behavior of *Halorhodospira halophila*. Upon photoexcitation, p-coumaric acid embedded within PYP absorbs blue light and initiates the photocycle, presumably by trans-cis isomerization. Although extensive studies have been carried out, the photoinduced reaction mechanism is still a matter of discussion. Therefore, we use jet-cooled oxyester methyl p-coumaric acid (OMpCA) to explore the excited-state dynamics of solvent-free OMpCA as well as the effect of the hydrogen-bonding to the phenolic OH on potential energy surface by using picosecond time-resolved pump-probe spectroscopy.

A vaporized OMpCA (and solvent) is diluted with Ne carrier gas, expanded into vacuum and skimmed by a skimmer to generate a supersonic molecular beam. From time-resolved pump-probe spectroscopy, the lifetime of the S_1 state is determined by the convolution fitting of the observed decay curve.

The time-resolved measurement of the S_0-S_1 transition of each species reveals the following characteristics: 1) the lifetime of OMpCA at the S_1 band origin is 9 ps while those of OMpCA-H_2O and OMpCA-NH_3 are 930 ps and 6 ns, respectively. 2) the complexes exhibit a biexponential decay curve with fast and slow components. Thus, solvent-free OMpCA undergoes barrierless nonradiative decay but the complex does not. To describe the temporal behavior of the complex, we adopted a two-step kinetic model (see Fig 1). An excess energy is first redistributed into the S_1 vibrational manifold by IVR, and leads a nonradiative process, e.g. isomerization and internal conversion, as the excess energy overcomes energy barrier. Fig 2. shows the plot of decay rate constant vs excess energy of OMpCA-H_2O, indicating that the fast component is due to IVR and the slow component is a nonradiative process. The extrapolated line is based on the RRK fitting with the barrier height of 205 cm^{-1}. A detail of the analysis and dynamics associated with potential energy barrier will be presented.
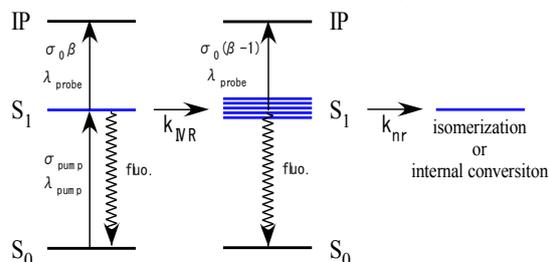
Fig 1. Schematic drawing of the two-step kinetic model of the excited OMpCA complex
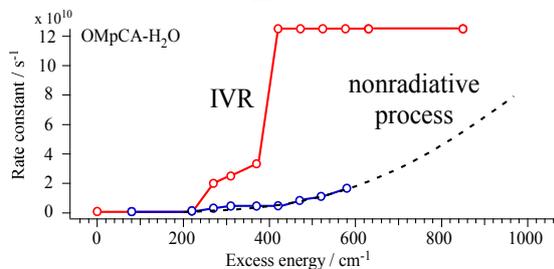
Fig 2. Plot of the observed decay rate constant of S_1 state vs excess energy for OMpCA-H_2O