The photocycle of photoactive yellow protein (PYP) has drawn attention to understand the negative phototaxis behavior of *Halorhodospira halophila*. Upon photoexcitation at 446 nm ($\lambda_{\text{max}}$), p-coumaric acid embedded in PYP initiates the photocycle by trans$\rightarrow$cis isomerization\(^1\). Although various experimental and computational studies have been published, a nonradiative relaxation process that leads trans$\rightarrow$cis isomerization is still a matter of discussion\(^2\)\(^-\)\(^5\). Recently, the $S_1$ lifetime of a jet-cooled Oxyester Methyl p-Coumaric Acid (OMpCA) and its hydrogen-bonded complexes was measured to elucidate the role of the hydrogen bond by employing picosecond time-resolved pump-probe spectroscopy\(^5\). It unveiled the following characteristics: 1) the lifetime of OMpCA at the $S_1$ band origin is 9 ps while that of OMpCA-H$_2$O is 930 ps, and 2) OMpCA-H$_2$O exhibits excess energy dependence of nonradiative decay that is best fitted with a biexponential decay curve of fast and slow components. In the present work, we adapted the kinetic argument that was used to describe the excited-state dynamics of trans-stilbene\(^6\), and estimated an energy barrier height on the $S_1$ potential surface by the RRK calculation.

A gas mixture of OMpCA and solvent diluted with Ne carrier gas was expanded into vacuum through the pulsed nozzle, and skimmed by a skimmer to generate a supersonic molecular beam. A picosecond tunable UV laser, obtained by second harmonic generation of the optical parametric generation/optical parametric amplifier (OPG/OPA) system of Nd:YAG laser, crossed with a molecular beam. Electronic spectrum was acquired by mass-resolved resonance 2-photon ionization (R2PI) method via $S_1$ state. Pump-probe scheme was used to record the decay curve as a function of the time delay between pump and probe lasers. The $S_1$-lifetime was determined by the convolution fitting with a laser width of 12 ps.

The R2PI excitation spectra of OMpCA and its hydrogen-bonded complexes in the 31000 – 33100 cm\(^{-1}\) region are shown in Fig 1. Blue and red lines are the spectra recorded by nanosecond laser and picosecond laser, respectively. It is clearly seen that a spectral red-shift of hydrogen-bonded complexes increases i.e. 633 cm\(^{-1}\), 921 cm\(^{-1}\), 1396 cm\(^{-1}\) as solvent

![Fig 1. R2PI spectra of (a) OMpCA and (b)-(d) complexes](image)
basicity increases from H2O, NH3 to N(CH3)3, respectively. The electronic excited-state is more stabilized than the ground state due to a slightly extended π-conjugation.

As mentioned, the excess energy dependence of the nonradiative decay is observed for OMpCA-H2O. There exists potential energy barrier as a result of forming the hydrogen bond at the phenolic OH group. Fig 2. displays the time evolution excited at 310 cm\(^{-1}\) above the S\(_1\)-S\(_0\) origin. The curve is fitted by a double exponential curve with a fast component (80 ps) and a slow component (220 ps). We applied a kinetic model involving IVR and nonradiative decay to describe the temporal behavior of the complex.

Fig 3 shows the schematic picture of S\(_1\)-state dynamics for OMpCA complexes, where \(\lambda\) is the wavelength, \(\sigma_{\text{pump}}\) is the absorption cross section, \(\sigma_{\text{probe}}\) is the ionization cross section, \(\beta\) is the dimentioness parameter that indicates the relative strength of the absorption from the S\(_1\) state. In short, an excess energy from the S\(_1\) band origin is first redistributed into the S\(_1\) vibrational manifold by IVR. A nonradiative process, e.g. isomerization and/or internal conversion, proceeds when an excess energy overcomes the barrier. Thus, a relative value of the two components could be observed in accord with an excess energy. In fact, the plot of decay rate constant as a function of excess energy for OMpCA-H2O in Fig 4. shows the validity of this kinetic argument, indicating that the fast component is 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 for other OMpCA-complexes will be presented.