3ES03　S$_1$ excited-state dynamics of OMpCA and its hydrogen-bonded complexes

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The photocycle of photoactive yellow protein (PYP) has drawn attention to understand the negative phototaxis behavior of *Halorhodospira halophila*. Upon photoexcitation at 446 nm (λ_{max}), p-coumaric acid embedded in PYP initiates the photocycle by trans→cis isomerization[1]. Although various experimental and computational studies have been published, a nonradiative relaxation process that leads trans→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
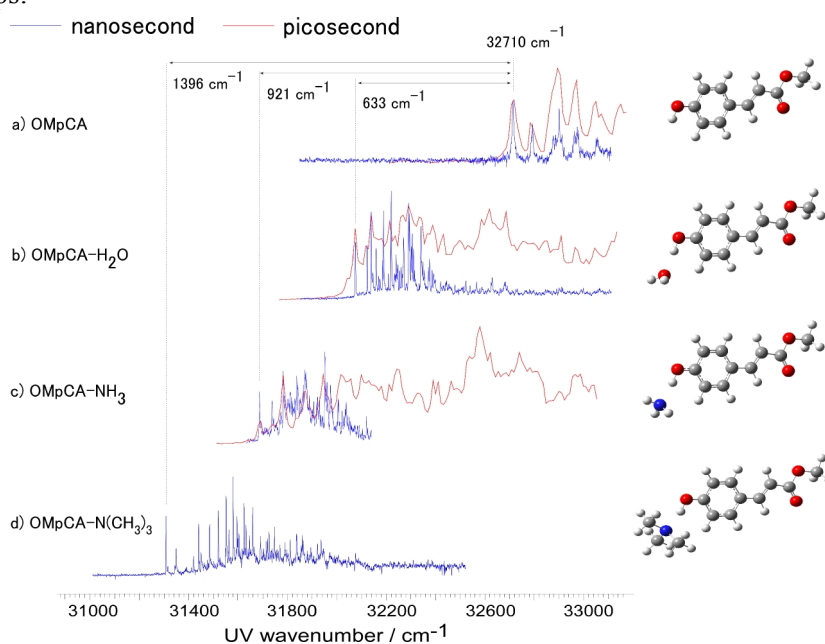

Fig 1. R2PI spectra of (a) OMpCA and (b)-(d) complexes

basicity increases from H_2O, NH_3 to $N(CH_3)_3$, 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-H_2O. 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.
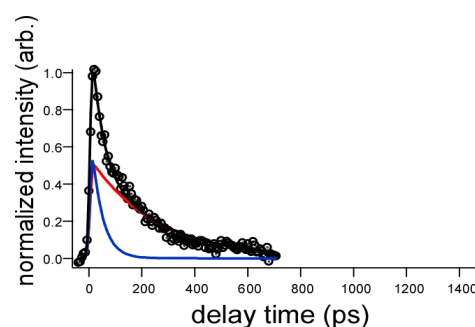

Fig 2. The observed decay curve of OMpCA-H_2O above 310 cm^{-1} from the S_1-S_0 band origin.

Fig 3 shows the schematic picture of S_1-state dynamics for OMpCA complexes, where λ is the wavelength, $σ_{pump}$ is the absorption cross section, $σ_{probe}$ is the ionization cross section, β is the dimentionless 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-H_2O 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.
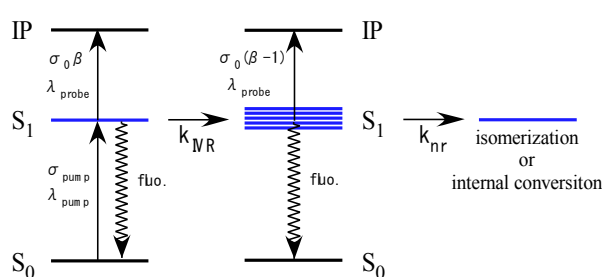

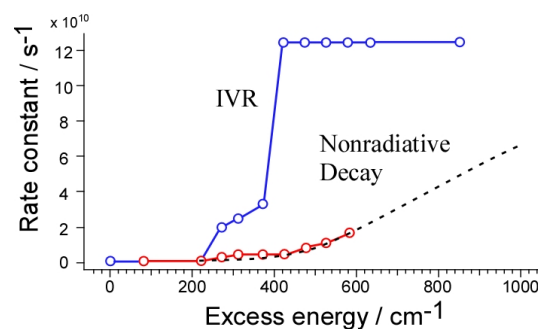Fig 3. Schematic picture of the two-step kinetic model of the excited OMpCA complex

Fig 4. Plot of the observed decay rate constant of S_1 state vs excess energy for OMpCA-H_2O

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