Asymmetry in Charge Transfer Pathways Caused by Pigment-protein Interactions in the Photosystem II Reaction Center Complex

– Supplementary Material –

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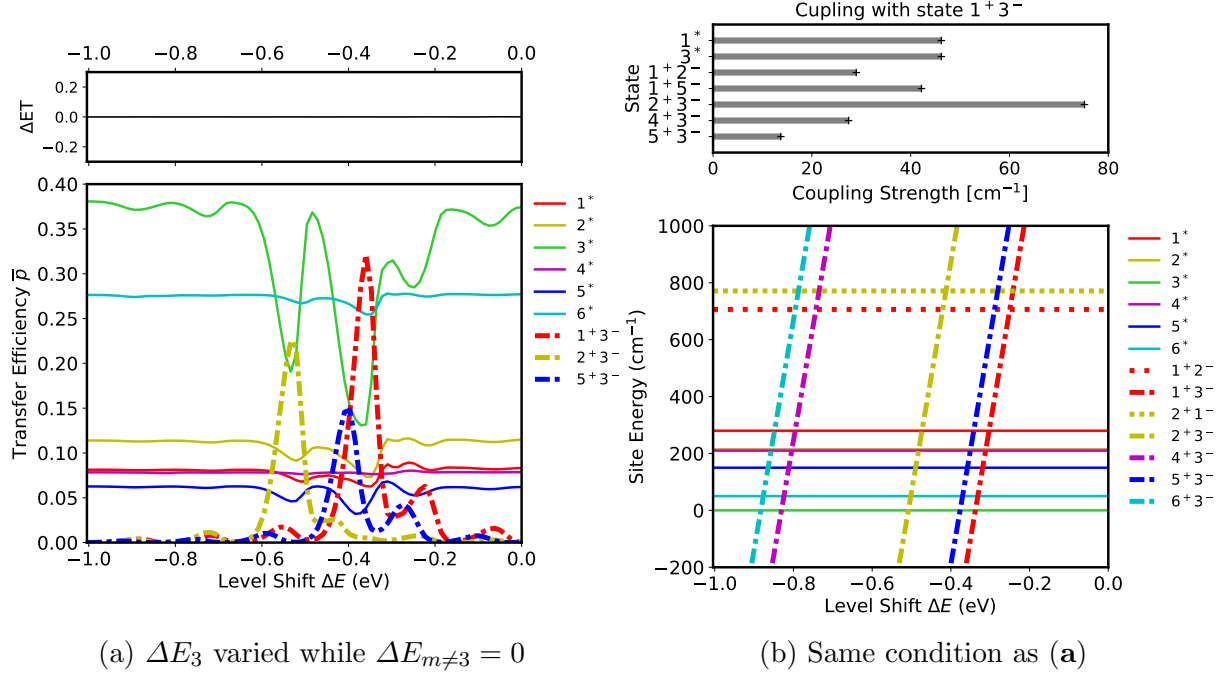# S.1. Primary Charge Transfer States

(a) ΔE_3 varied while $\Delta E_{m\neq 3} = 0$ (b) Same condition as (a)

Figure S1: Transfer efficiencies, site energy change, and coupling strength. (**a**) Transfer efficiencies and ΔET have been computed with $\tau = 1\,\mathrm{ps}$ and $T = 77\,\mathrm{K}$ for a range of level shifts at $\mathrm{Chl_{D1}}$, that is ΔE_3. The level shift at all other pigments is zero as $\Delta E_{m\neq 3} = 0$. CT states of less than 0.02 transfer efficiencies are not displayed. In contrast with Fig.7, ΔET does not change from zero because none of the active CT states involves $\mathrm{Pheo_{D1}^-}$ or $\mathrm{Pheo_{D2}^-}$. (**b**) The site energies ε_{mn} are shown for the values of ΔE_3. The top panel shows the major states coupled with $|1^+3^-\rangle$, extracted from Fig. 5b for those above $10\,\mathrm{cm^{-1}}$.

S.2. The second CT pathway, $\text{FEs} \to |3^+5^-\rangle \to |1^+5^-\rangle$
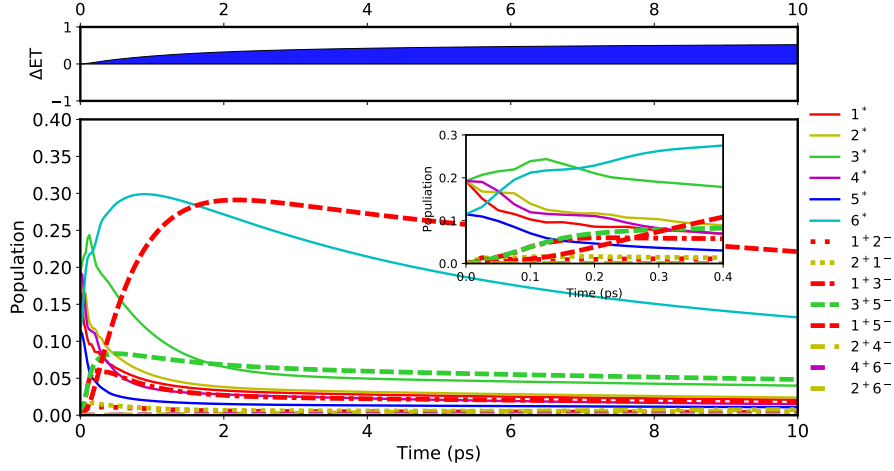
(a) $T = 77\,\text{K}$
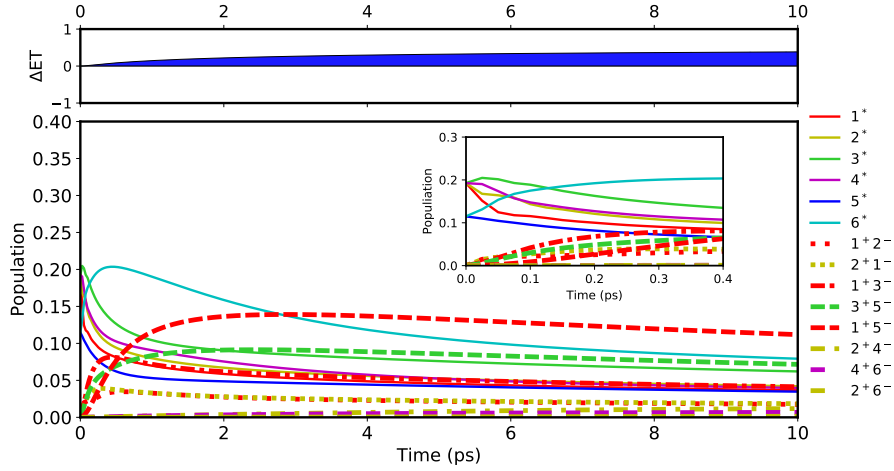
(b) $T = 300\,\text{K}$

Figure S2: Population and ΔET dynamics of FE and CT states for the CT pathway of $\text{FEs} \to |3^+5^-\rangle \to |1^+5^-\rangle$. Out of the 36 states used for computations, only the 14 selected states are displayed for clarity. The levels shifts are set to $\Delta E_3 = -2600\,\text{cm}^{-1}$, $\Delta E_5 = -6000\,\text{cm}^{-1}$, and $\Delta E_2 = \Delta E_4 = \Delta E_6 = 0$. ΔET at each moment of time t has been computed by setting $\tau = t$ in Eq. 7. The insets show the populations for the first 400 fs. (**a**) Results for 77 K. (**b**) Results for 300 K.
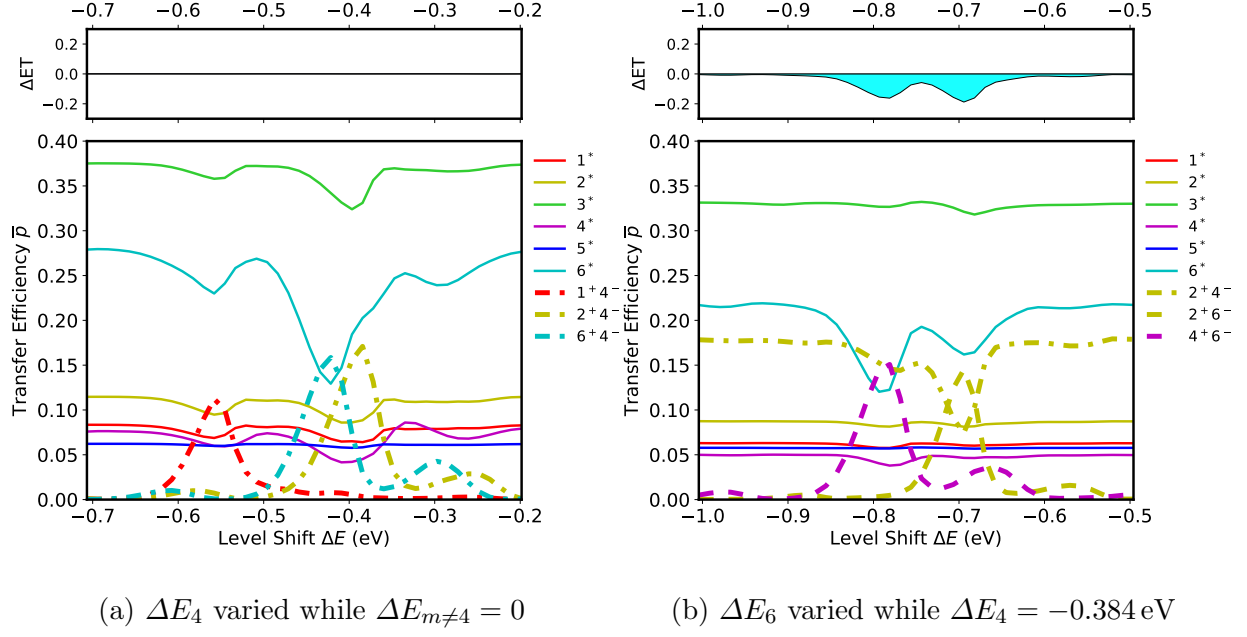
S.3. Primary and secondary CT states in D2

(a) ΔE_4 varied while $\Delta E_{m \neq 4} = 0$ (b) ΔE_6 varied while $\Delta E_4 = -0.384\,\mathrm{eV}$

Figure S3: Transfer efficiencies and ΔET with $\tau = 1\,\mathrm{ps}$ at $T = 77\,\mathrm{K}$. CT states with transfer efficiencies less than 0.02 are not shown. $\Delta E_m = 0$ for $m = 2, 3, 5$. (a) The level shift ΔE_4 varied while $\Delta E_{m \neq 4} = 0$. (b) The level shift ΔE_6 varied while $\Delta E_4 = -3100\,\mathrm{cm}^{-1}$.