

Supplementary Information

Exciton-vibrational resonance and dynamics of charge separation in photosystem II reaction center

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Table S1. The site energies and exciton couplings for the 4-state model of PSII-RC. Unperturbed energies of the zero-phonon transitions for the three excited states and CT are shown together with couplings (all quantities are in cm^{-1}).

	P_{D1}	P_{D2}	Chl_{D1}	$P_{D2}^+P_{D1}^-$
P_{D1}	15020	150	-42	75
P_{D2}	150	15020	-56	-75
Chl_{D1}	-42	-56	14780	0
$P_{D2}^+P_{D1}^-$	75	-75	0	14520

Table S2. Energies and intensities of exciton-vibrational components of the absorption corresponding to the three different positions of the CT level (with unperturbed energies of other diabatic states). The values of the CT shift E_{CT} and other parameters of the model are the same as in Figure 2. Only 7 lowest vibronic eigenstates ($b=1-7$) are shown. Their energies ω are counted from ZPL of Chl_{D1} , intensities I are calculated as dipole strengths of the transitions to b -th level from the lowest vibrational sublevel of the ground (the only populated in the low-temperature limit). Participation of the four diabatic states (i.e. P_{D1} , P_{D2} , Chl_{D1} , and $P_{D2}^+P_{D1}^-$, respectively) in the vibronic eigenstates are shown with highlighting (by bold) of the biggest contributions to the localized and mixed states.

$E_{CT}(\text{cm}^{-1})$	b	$\omega(\text{cm}^{-1})$	$I(\text{Debye}^2)$	P_{D1}	P_{D2}	Chl_{D1}	$P_{D2}^+P_{D1}^-$
-30	1	-307.07	0.565	0.0151	0.0152	0.0000	0.9697
	2	-11.38	17.632	0.0009	0.0445	0.9222	0.0324
	3	7.35	2.576	0.1386	0.1053	0.0489	0.7072
	4	34.60	0.041	0.0190	0.0195	0.0042	0.9572
	5	35.63	0.023	0.0155	0.0155	0.0001	0.9689
	6	36.09	0.003	0.0152	0.0151	0.0003	0.9695
	7	144.19	13.566	0.3533	0.3434	0.0048	0.2984
+40	1	-239.52	0.804	0.0203	0.0206	0.0001	0.9591
	2	-10.73	15.974	0.0027	0.0277	0.9667	0.0029
	3	50.61	8.582	0.2503	0.2305	0.0088	0.5104
	4	98.38	0.026	0.0287	0.0292	0.0017	0.9403
	5	100.59	0.075	0.0203	0.0206	0.0001	0.9591
	6	100.61	0.001	0.0204	0.0204	0.0001	0.9591
	7	172.34	9.173	0.2357	0.2314	0.0040	0.5289
+140	1	-144.89	1.530	0.0347	0.0356	0.0003	0.9294
	2	-10.55	15.394	0.0040	0.0235	0.9709	0.0015
	3	86.47	14.293	0.3838	0.3643	0.0067	0.2453
	4	189.24	0.114	0.0682	0.0697	0.0038	0.8583
	5	195.21	0.145	0.0348	0.0356	0.0002	0.9293
	6	195.25	0.002	0.0349	0.0353	0.0002	0.9295
	7	240.89	3.478	0.0927	0.0955	0.0050	0.8069

Explicit expressions for the Redfield tensor

To describe the dynamics of one-exciton populations $\rho_{b_1b_2}(T)$ we need the Redfield tensor $R_{b_1b_2,b_3b_4}$. In the Liouville space the populations are given by vector $\rho_\alpha(T)$, whereas the one-exciton relaxation tensor is $R_{\alpha\beta}$, with $\alpha=b_1+(b_2-1)N_b$ and $\beta=b_3+(b_4-1)N_b$, where N_b is the vibronic cutoff, i.e. the number of one-exciton vibronic states included into the modelling of the dynamics. The $R_{\alpha\beta}$ tensor can be expressed as a product $B \otimes A$ of the tensors $B_{b_2b_4}$ and $A_{b_1b_3}$. In matrix notations:

$$\begin{aligned} R &= - \sum_{n,j,s} \overline{(\varphi_n^{js})^2} (B_n^{js} \otimes A_n^{js} + A_n^{js} \otimes B_n^{js}) - \sum_n \overline{(\Phi_n)^2} (B_n^e \otimes A_n^e + A_n^e \otimes B_n^e) + \sum_n (B_n \otimes I + I \otimes B_n) \\ B_n^e &= C_n^+ C_n; \quad A_n^e = B_n^e * J; \quad C_n = \sum_{a,b} |a\rangle C_{na,b}^e \langle b| \\ B_n^{js} &= C_n^+ Q_n^{js} C_n; \quad A_n^{js} = B_n^{js} * J; \quad Q_n^{js} = Q_{js} - \Delta_n^{js} \\ B_n &= \overline{(\Phi_n)^2} C_n^+ C_n (C_n^+ C_n * J) + \sum_{js} \overline{(\varphi_n^{js})^2} C_n^+ Q_n^{js} C_n (C_n^+ Q_n^{js} C_n * J) \end{aligned} \quad (S1)$$

where I is a delta-operator, C_n is a fragment of the C^e corresponding to a fixed electronic site n (the sum of independent contributions from different sites appears since we use an uncorrelated fluctuation model). In terms like $C_n Q_n C_n$ we assume a matrix multiply, $B * J$ denotes an array multiply (product of the elements of the matrices), \otimes stand for a Kronecker tensor product. Such a form is useful for numerical evaluation of the Redfield tensor. The dynamics of vibronic populations is then given by:

$$\rho_\alpha = -i\omega_\alpha \rho_\alpha - \sum_\beta R_{\alpha\beta} \rho_\beta \quad (S2)$$

where $\omega_\alpha = \omega_{b_1b_2} = \omega_{b_1} - \omega_{b_2}$. The ground-state dynamics is purely vibrational and is given by populations $\rho_{c_1c_2}(T)$ and the Redfield tensor $R_{c_1c_2,c_3c_4}$. In the Liouville space we have populations $\rho_\gamma(T)$ and relaxation tensor $R_{\gamma\delta}$, with $\gamma=c_1+(c_2-1)N_c$ and $\delta=c_3+(c_4-1)N_c$, where N_c is vibrational cutoff for the ground state. In matrix notations:

$$\begin{aligned} R &= - \sum_{j,s} \overline{(\varphi_g^{js})^2} (B_g^{js} \otimes A_g^{js} + A_g^{js} \otimes B_g^{js}) + (B_g \otimes I + I \otimes B_g) \\ B_g^{js} &= C^+ Q_g^{js} C; \quad A_g^{js} = B_g^{js} * J; \quad Q_g^{js} = Q_{js} - \Delta_g^{js}; \quad B_g = \sum_{js} \overline{(\varphi_g^{js})^2} C^+ Q_g^{js} C (C^+ Q_g^{js} C * J) \end{aligned} \quad (S3)$$

where C is the same as C^g . The dynamics of vibrational populations is:

$$\rho_\gamma = -i\omega_\gamma \rho_\gamma - \sum_\delta R_{\gamma\delta} \rho_\delta \quad (S4)$$