

Supporting Information

Dynamics of the Excited State in Photosynthetic Bacterial Reaction Centers

William W. Parson[†]

[†]Department of Biochemistry

University of Washington

Seattle, WA 98195

Email: parson@u.washington.edu

Figures S1 and S2 show spectra of the calculated Boltzmann-weighted Franck-Condon factors (FC_B) for a model identical to that used to generate Figures 1 and 2 of the main text except that the three vibrational modes had energies of 20, 50 and 90 cm^{-1} and dimensionless displacements (Δ) of 1.1, 0.7 and 0.2, respectively, in the diabatic CT state relative to the ground states (Huang-Rhys parameters $S = \Delta^2/2$ of 0.605, 0.245 and 0.020). The displacements in the exciton state with respect to the ground state were 0.1 for all three modes ($S = 0.005$), the same as in Figures 1 and 2. Excitation energies ($h\nu$) are expressed relative to the 0-0 excitation of the diabatic exciton state ($h\nu_{00}$, *vertical dashed line*). The 0-0 excitation energy of the diabatic CT state (*vertical dotted line*) was either 400 cm^{-1} above $h\nu_{00}$ (Figure S1), or 400 cm^{-1} below $h\nu_{00}$ (Figure S2). The electronic-interaction matrix element ($|V|$) was either 0, 200, 300 or 400 cm^{-1} and the temperature either 80 K or 300 K, as indicated. FC_B was calculated by equation (1) of the main text.

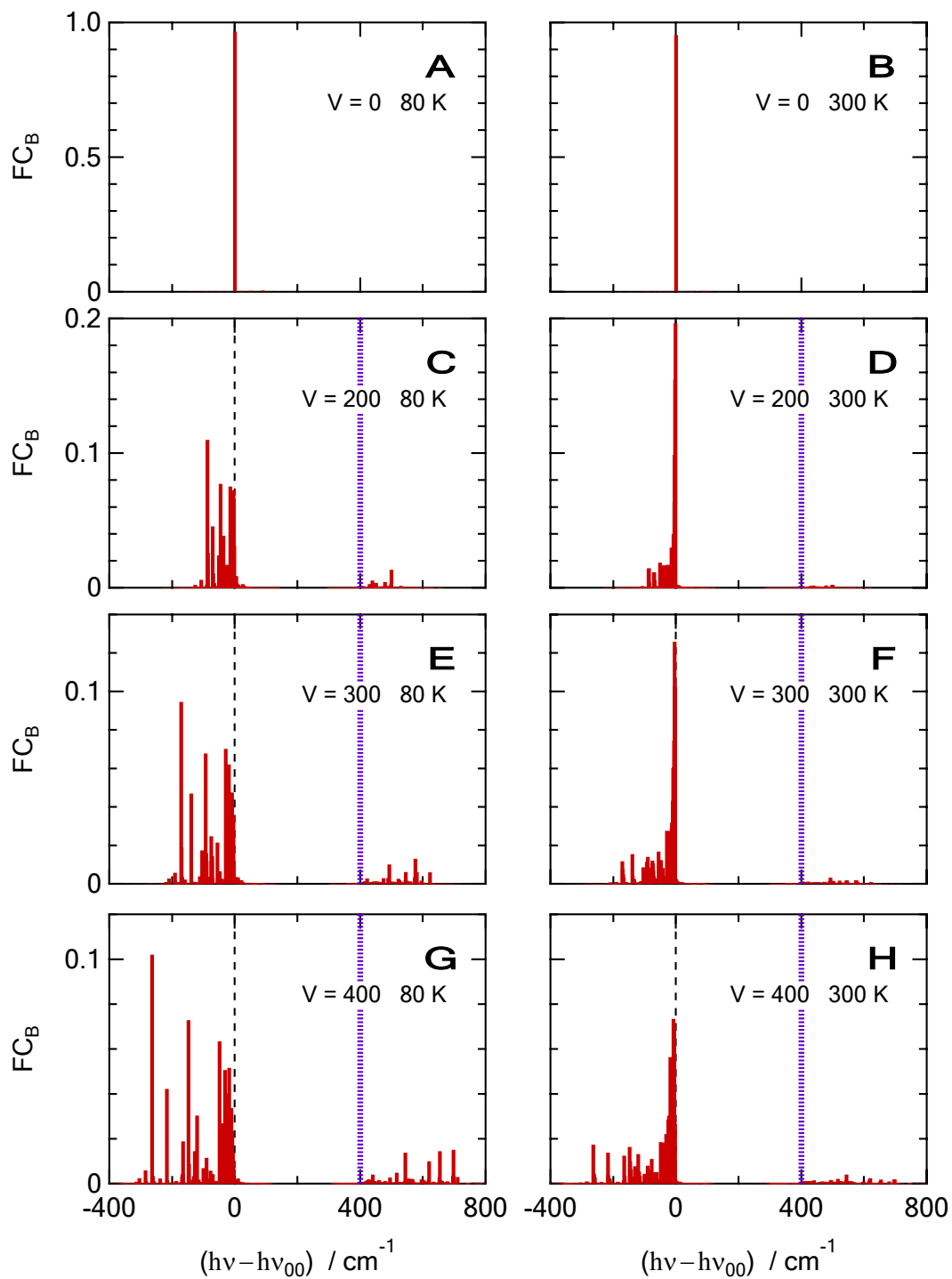


Figure S1. Boltzmann-weighted Franck-Condon factors (FC_B) for absorption at either 80 K (*left*) or 300 K (*right*) by a system in which exciton and CT excitations are coupled to three vibrational modes with the parameters given above. The 0-0 excitation energy of the diabatic CT state (*vertical dotted line*) was 400 cm^{-1} above $h\nu_{00}$.

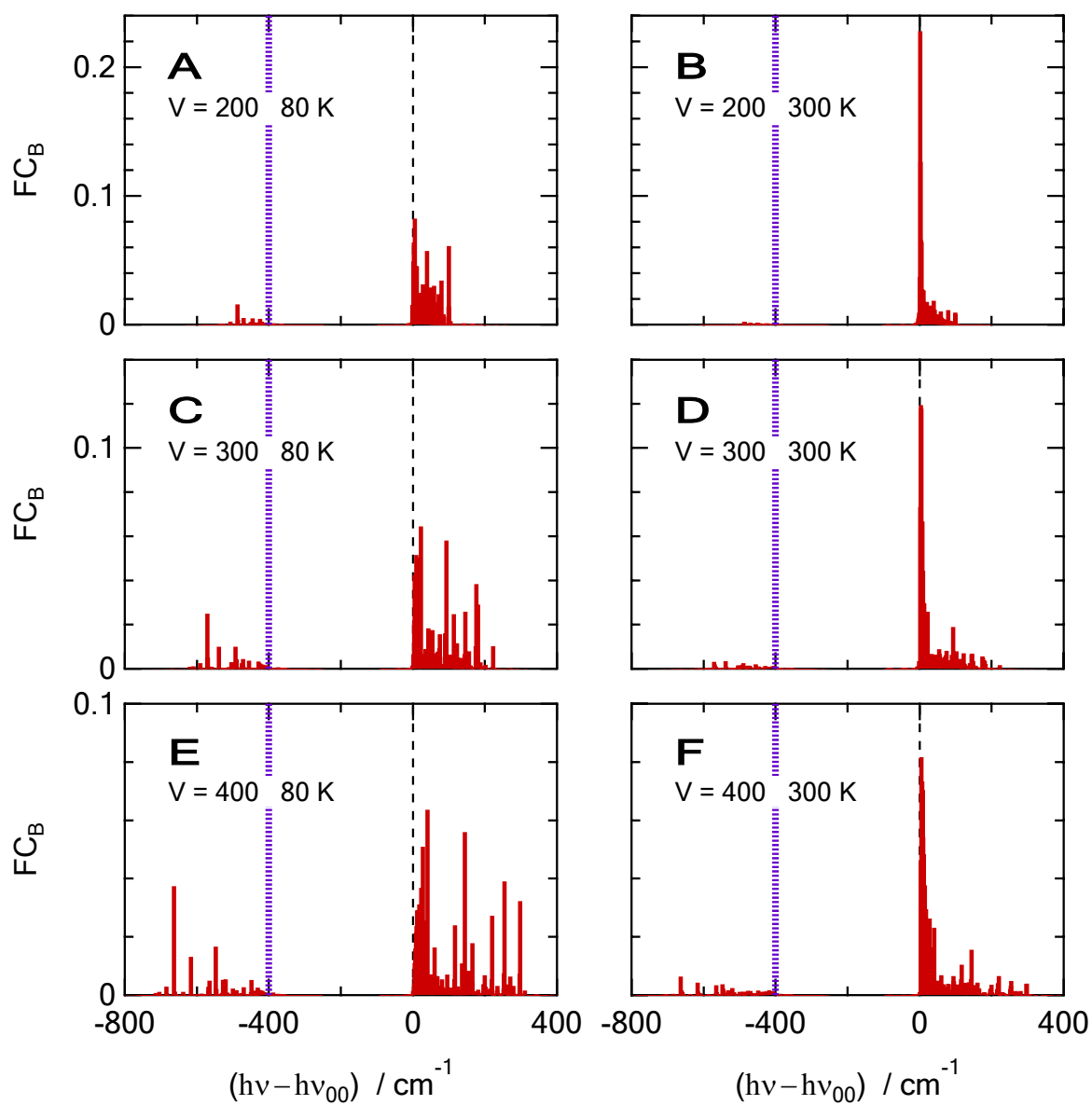


Figure S2. The same as Figure S1 except that the 0-0 excitation energy of the diabatic CT state (*vertical dotted line*) was 400 cm^{-1} below $h\nu_{00}$.

Figure S3 shows calculated Boltzmann-weighted dipole strengths of the vibronic absorption lines of a homodimer with strong exciton interactions but no CT states. Each of the monomers is assumed to have a single excited state and three harmonic vibrational modes with energies of 20, 50 and 90 cm^{-1} and Huang-Rhys factors of 0.605, 0.245 and 0.020, respectively (the same as those of the CT state in Figures S1 and S2). The exciton-interaction matrix element is +300 cm^{-1} (the same as in Figure S1E). The angle between the transition dipoles of the monomers is 165° , resembling the angle between the Q_y transitions of bacteriochlorophylls P_L and P_M in the reaction center. With this geometry, most of the dimer's dipole strength appears in an absorption band 300 cm^{-1} to the red of the monomers' ΔE_{00} . Lowering the temperature from 300 to 80 K strengthens vibronic lines on the blue side of the band relative to those on the red side, shifting the spectrum slightly to the *blue*.

The Boltzmann-weighted dipole strengths in Figure S3 were calculated as

$$DS_B(\nu, T) = \sum_{i=1}^I B(i, T) \sum_{j=1}^J \delta_{h\nu, E_j - E_i} \left| \sum_{l=1}^L c_l^j \vec{\mu}_l \Pi_m \Omega(m, i, l) \right|^2. \quad (\text{S1})$$

Here I and L are, respectively, the total numbers of vibronic ground and excited basis states, and J is the number of the dimer's excited eigenstates; E_i and E_j are the energies of ground state i and excited eigenstate j ; $B(i, T) = Z^{-1} \exp(-E_i/k_B T)$ is the Boltzmann population of ground state i at temperature T ; $Z = \sum_i^I \exp(-E_i/k_B T)$; the delta function $\delta_{h\nu, E_j - E_i}$ is 1 if $h\nu = E_j - E_i$, and zero otherwise; c_l^j is the coefficient for excited basis state l in eigenvector j ; $\Omega(m, i, l)$ is the overlap integral for excitation of harmonic oscillator m from ground level i to exciton level l ; and $\vec{\mu}_l$ is the electronic transition dipole for basis excitation l . Equation (1) of the main text is a generalization of equation (S1) for a system that includes CT states, but with the dependence on the vectorial factors $\vec{\mu}_l$ omitted because these are assumed to have the same magnitude and orientation for all the exciton basis transitions and a magnitude of zero for CT transitions.

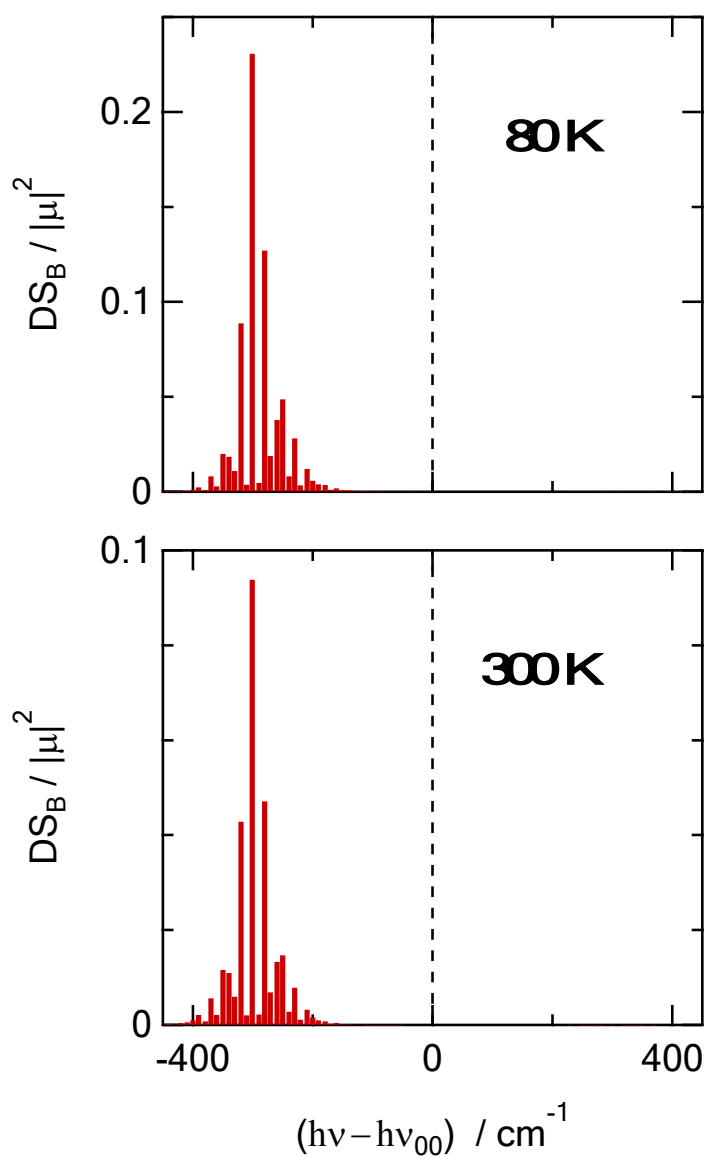


Figure S3. Stick spectra of the Boltzmann-weighted vibronic dipole strength (DS_B) at (*top*) 80 and (*bottom*) 300 K for the homodimer described above, in which the two molecules have strong exciton interactions but no CT interactions. The divisor for the ordinate scale ($|\mu|^2$) is the squared amplitude of the monomers' electronic transition dipole (μ_l in equation S1), which is assumed to be the same for all vibrational levels (l). Energies are expressed relative to the monomers' 0-0 excitation energy ($h\nu_{00}$, *dashed line*).

Figure S4 and Table S1 illustrate the effects of temperature on the Boltzmann-weighted Franck-Condon factors (FC_B) for a system with ground, exciton and CT electronic states and a single, harmonic vibrational mode. The zero-point energy of the CT basis state is taken to be 400 cm^{-1} above the corresponding energy of the exciton state, and the electronic-interaction matrix element ($|V|$) that mixes exciton and CT states is 400 cm^{-1} . The vibrational mode has an energy of 20 cm^{-1} and Huang-Rhys factors of 0.005 and 0.605 for conversion of the ground state to the exciton and CT states, respectively (the same as the lowest-frequency mode in Figures S1 and S2). The figure shows the calculated spectrum of $FC_B(\nu, T)$ in the region of the main absorption band, which lies to the red of the of the exciton basis state's 0-0 energy ($h\nu_{00}$). When the temperature is decreased from 300 to 80 K, vibronic lines farther to the red gain strength relative to those at higher energies as they do in the three-mode models used for Figures 1 and S1. Table S1 gives the factors that enter into selected values of $FC_B(\nu, T)$ at 80 and 300 K, according to equation (1) of the main text. The lines close to $h\nu_{00}$ in the spectrum for 300 K are dominated by excitations to relatively high eigenstates from correspondingly high vibrational levels of the ground state, which have much smaller Boltzmann factors ($B(i, T)$) at 80 K.

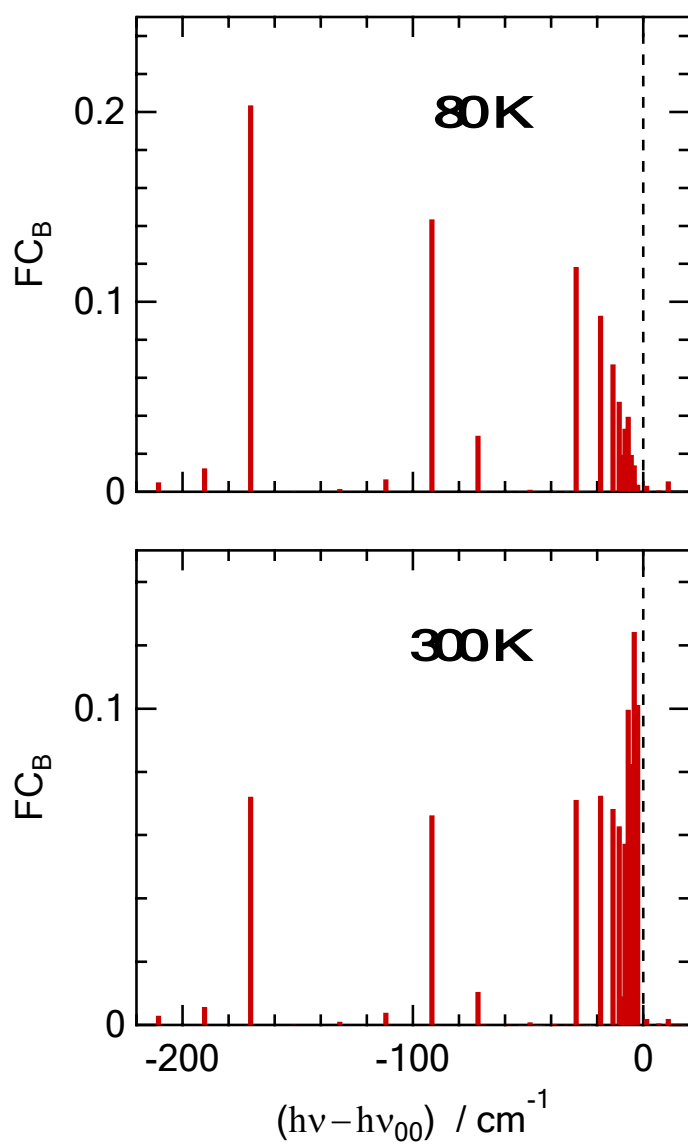


Figure S4. Calculated Boltzmann-weighted Franck-Condon factors for a system with three electronic states (ground, exciton and CT) and a single vibrational mode, at 80 K (*top*) and 300 K (*bottom*). The model and the values of its parameters are given above. The figure shows only the spectral region of the system's main absorption band.

Table S1: Components of $FC_B(v,T)$ in a System with 3 Electronic States (Ground, Exciton and CT) and 1 Vibrational Mode¹

i	j	l	$h\nu - h\nu_{00}$ cm ⁻¹	$ \mathcal{Q}(i,l) ^2$	$ c_l^j ^2$	$B(i,T)$ 300 K	$FC(i,j,l,T)$ 300 K	$B(i,T)$ 80K	$FC(i,j,l,T)$ 80 K
1	1	1	-170.4	0.99501	0.67593	0.10721	0.07210	0.30236	0.20335
1	1	2	-170.4	0.00498	0.05574	0.10721	0.00003	0.30236	0.00008
							0.07213		0.20343
2	2	1	-91.8	0.00498	0.09448	0.09740	0.00005	0.21101	0.00010
2	2	2	-91.8	0.98509	0.68982	0.09740	0.06619	0.21101	0.14339
2	2	3	-91.8	0.00246	0.04372	0.09740	0.00001	0.21101	0.00002
							0.06625		0.14351
3	3	2	-29.2	0.00246	0.09112	0.08849	0.00002	0.14725	0.00003
3	3	3	-29.2	0.98017	0.81996	0.08849	0.07112	0.14725	0.11835
3	3	4	-29.2	0.00163	0.00876	0.08849	$< 5 \times 10^{-6}$	0.14725	$< 5 \times 10^{-6}$
							0.07114		0.11838
4	4	3	-18.5	0.00163	0.02080	0.08040	$< 5 \times 10^{-6}$	0.10276	$< 5 \times 10^{-6}$
4	4	4	-18.5	0.97690	0.92285	0.08040	0.07248	0.10276	0.09265
							0.07248		0.09265
10	10	10	-6.5	0.96722	0.98712	0.04522	0.04317	0.01187	0.01133
11	11	11	-6.5	0.96625	0.98852	0.04108	0.03924	0.00828	0.00791
							0.08241		0.01924
12	12	12	-3.9	0.96538	0.98964	0.03732	0.03566	0.00578	0.00552
13	13	13	-3.9	0.96457	0.99056	0.03391	0.03240	0.00403	0.00385
14	14	14	-3.9	0.96383	0.99132	0.03081	0.02944	0.00282	0.00269
15	15	15	-3.9	0.96314	0.99167	0.02799	0.02674	0.00196	0.00188
							0.12424		0.01394

¹See the text above for the electronic energies and other parameters of the model.

i = vibrational level of ground state; j = excited eigenstate; l = vibrational level of exciton basis state.

$h\nu - h\nu_{00}$ = excitation energy relative to ΔE_{00} for the exciton state.

$\mathcal{Q}(i,l)$ = nuclear overlap integral for excitation from ground vibrational level i to exciton level l .

c_l^j = coefficient for exciton basis state l in eigenvector j .

$B(i,T)$ = Boltzmann factor for the relative population of ground level i at temperature T .

$FC(i,j,l,T) = B(i,T) \times |c_l^j|^2 \times |\mathcal{Q}(i,l)|^2$ (contribution of basis states i and l to the Boltzmann-weighted Franck-Condon factor for frequency ν at temperature T).

Entries in **Bolt font** are the sums of $FC(i,j,l,T)$ for each energy and temperature.