

# Time Scales of Coherent Dynamics in the Light-Harvesting Complex 2 (LH2) of *Rhodobacter sphaeroides*

Andrew F. Fidler<sup>1</sup>, Ved P. Singh<sup>1</sup>, Phillip D. Long<sup>2</sup>, Peter D. Dahlberg<sup>2</sup>, and Gregory S. Engel<sup>1\*</sup>

1. Department of Chemistry, The James Franck Institute and The Institute for Biophysical Dynamics, The University of Chicago, Chicago, Illinois 60637, USA
2. Program in the Biophysical Sciences, The University of Chicago, Chicago, IL 60637

\*To whom correspondence should be addressed. E-mail: [gsengel@uchicago.edu](mailto:gsengel@uchicago.edu)

## Supplemental Information

*Electronic Structure Calculations.* We have utilized a Frenkel-exciton Hamiltonian formalism<sup>1</sup> to describe the electronic states of the complex:

$$H = \sum_{n=1}^N E_n a_n^\dagger a_n + \sum_{n \neq m} J_{nm} a_n^\dagger a_m + \sum_{n=1}^N q_{nn}(\mathbf{Q}) a_n^\dagger a_n$$

where  $E_n$  is the energy of the  $n$ th site,  $J_{nm}$  is the coupling between sites,  $a_n^\dagger$  creates an excitation on the  $n^{\text{th}}$  site, and  $q_{nn}(\mathbf{Q})$  describe fluctuations of the site energies due to the nuclear motion of the chromophore and surrounding protein environment. We assume that the site energy fluctuations are uncorrelated and treat the nuclear coordinates as composed of a continuum of harmonic oscillators. The coupling constants were taken from a previous study.<sup>2</sup> The B850 chromophores can be subdivided into an  $\alpha$  or  $\beta$  position, referring to which transmembrane  $\alpha$ -helix the chromophore is bound. The site energies for these chromophores were then set to  $E_{\alpha B850} = 12600 \text{ cm}^{-1}$  and  $E_{\beta B850} = 12095 \text{ cm}^{-1}$ , which were adjusted from a previous study to reproduce the room temperature absorption spectrum.<sup>3</sup> The B800 chromophores were assigned a site energy of  $E_{B800} = 12560 \text{ cm}^{-1}$ . The local environment can be expressed in terms of the spectral density,  $\rho(\omega)$ , which describes the spectrum of modes to which the chromophore is coupled. Parameters for the bath were taken from three pulse photon echo peak shift (3PEPS) measurements of the two individual bands, which show that the two bands have distinct local environments (i.e. the spectral density for the two bands are different).<sup>4,5</sup> The correlation function, which is related to the Fourier Transform of the spectral density, was modeled by the sum of a Gaussian, an exponential decay, and several exponentially damped sinusoids for both bands.<sup>4,5</sup>

$$M(t) = \frac{\langle \delta\omega(0)\delta\omega(t) \rangle}{\langle \delta\omega^2 \rangle} \sim \frac{1}{\langle \delta\omega^2 \rangle} \left( \langle \delta\omega_g^2 \rangle e^{-(t/\tau_g)^2} + \langle \delta\omega_e^2 \rangle e^{-t/\tau_e} + \sum_j \langle \delta\omega_j^2 \rangle e^{-t/\tau_j} \cos(\omega_j t) \right)$$

For the B800 chromophores the Gaussian time constant is 90 fs, the exponential time constant is 600 fs, and their coupling strengths ( $\sqrt{\langle \delta\omega^2 \rangle}$ ) are 100 cm<sup>-1</sup> and 90 cm<sup>-1</sup>.<sup>5</sup> For the B850 chromophores a two exponential fit was found to provide a better fit. The Gaussian time constant is 40 fs, the exponential time constants are 130 fs and 15000 fs. The coupling strengths are 80 cm<sup>-1</sup> for the Gaussian and 170 cm<sup>-1</sup> and 65 cm<sup>-1</sup> for the two exponentials. The coherent vibrational contribution parameters were taken from reference 3 and were assumed to be the same for both sets of chromophores. The total coupling strength of the B800 chromophores to the bath were reduced by 35% to reproduce the relative intensities of the two bands. The lineshape function was calculated from the spectral density as shown below:

$$g(t) = -i\lambda t + \int_0^\infty d\omega \rho(\omega) \coth\left(\frac{\hbar\omega}{k_b T}\right) (1 - \cos(\omega t)) + i \int_0^\infty d\omega \rho(\omega) \sin(\omega t)$$

Here,  $\lambda$  is the reorganization energy, and  $k_b T$  is the thermal energy. The temperature was set to 293 K for the calculations. The full Hamiltonian was then diagonalized and the excitonic lineshape functions  $g_{jj}(t)$  were calculated.

$$g_{jj}(t) = \sum_m g_m(t) |U_{mj}|^4$$

$U_{mj}$  are matrix elements of the unitary transformation matrix relating the site basis to the excitonic basis. The absorption spectrum can then be approximated by the following expression:

$$A(\omega) \propto \left\langle \int_0^\infty dt \sum_{j=1}^N \mu_j^2 \text{Exp}[-i(\omega_{jg} - \omega)t - g_{jj}(t)] \right\rangle$$

Here  $\mu_j$  is the exciton transition dipole moment, and  $\omega_{jg}$  is the energy of the j-th state, and the angular brackets indicate an ensemble average. This expression neglects relaxation processes induced by off diagonal elements of the exciton Hamiltonian. The dipole moments were taken from the crystal

structure and were assumed to be oriented between the nitrogen atoms of rings I and III. Slower degrees of freedom were accounted for by including disorder in the site energies. This inhomogeneous distribution was assumed to be Gaussian with a mean of zero and standard deviation of  $\sigma_{B850} = 275 \text{ cm}^{-1}$  and  $\sigma_{B800} = 145 \text{ cm}^{-1}$  for the B850 and B800 chromophores respectively. The absorption spectrum in Figure 1 was averaged over 1000 realizations of the Hamiltonian.

## References

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