Supporting Information

Harel and Engel 10.1073/pnas.1110312109

SI Text

Diagonal and Lower Cross-Peak Analysis. The waiting time dependence of the diagonal and lower cross-peak are shown in the figure below along with fits to a sum of two exponential decays and a single exponential growth. The 2D spectrum is convolved with the laser spectrum, which causes a red shift in the position of the B850 bands. The first 150 fs of the signal are discarded in the fits because of large Stokes shifts arising from solvent reorganization following excitation. These decay curves are in good agreement with previous transient absorption measurements on LH2 with excitation at 800 nm and either a white light continuum probe or 850-nm probe.

The inset of the figure shows the effects of laser intensity fluctuations, which are correlated (or anticorrelated) at each waiting time. These arise because the waiting times are sampled parametrically so that at the instant the 2D spectrum is recorded, the spectrally resolved signal fluctuates with the laser intensity fluctuation at each frequency component of the pulse. We regularly observed both integrated laser intensity fluctuations as well as spectral profile changes during the course of the experiment. We estimated that these fluctuations result in roughly 10–20% change in the magnitude of the signal. The effects of such large signal variations would be magnified by orders of magnitude in a point-by-point sampling of the coherence times because the phase of the signal oscillates with the energy level difference between ground and excited states. This is in contrast to the amplitude changes observed during the waiting period, which oscillate with the energy level difference between excitons.

Upper Left Cross-Peak Beating—Electronic Versus Vibrational Coherence. The quantum-beating signal at the AD cross-peak can arise from two fundamentally different sources—electronic coherence and vibrational coherence as shown in Fig. S2. The former originates from a superposition state of two or more excitons formed by coupled BChl *a* molecules. Vibrational coherences, which can arise from vibrational states on a single chromophore, can also give rise to a quantum-beating signal. In general, these two pathways cannot be distinguished solely based on their spectral position on the 2D spectrum (1). In the case of LH2, we rule out the possibility of vibrational coherence for the following reasons: First, while vibrational coherence was observed in LH2 at 4.2 K, to the best of our knowledge amplitude oscillations above 200 cm^{-1} in any nonlinear optical measurement have never been observed at room temperature. There is no inherent reason why our measurement is more sensitive to the beating signal than other third-order measurements such as photon echo, transient absorption, and transient grating spectroscopy. In fact, because the single point detection capability of these methods, 2D spectroscopy, in comparison should be less sensitive when employed in a spectrally resolved fashion as was done here. The strong amplitude of our beating signal is at odds with these more sensitive measurements. Even for isolated BChl *a* in solution, vibrational coherence does not show beating frequencies greater than a few hundred wavenumbers even when higher frequencies are supported by the excitation bandwidth (4). While vibrational states on both the ground and excited surfaces are evident at higher energies from Raman spectra of BChl *a* solutions (2), the decay rate of nuclear coherent oscillations is expected to increase with higher vibrational modes, while the amplitude of the beating is expected to decrease (3). In LH2, where 27 BChl *a* molecules are present and their exists a nonnegligible degree of static disorder in the vibrational spectrum, vibrational coherences would be even less likely to be observed owing to rapid dephasing. In summary, large amplitude quantum-beating signals at room temperature that persist for up to 400 fs with frequencies that range from 800–1,000 cm^{-1} cannot arise from intramolecular vibrations on individual BCh a molecules or intermolecular modes resulting from solvent interactions. In LH2, vibrational coherences will decay even faster than for an individual chromophore, precluding their origin as the beating signal we observe in this work.

Fitting Procedure and Analysis. Each point in the 2D spectrum was first fit to a sum of two exponential decays and a constant offset to account for slow dynamics. After discarding the first 40 fs of signal to avoid pulse overlap effects, the residual of the biexponential decay with the data was fit to a single exponentially decaying sinusoidal function with a single frequency and phase component. Including the first 40 fs of signal resulted in large errors in the fitting procedure, likely because the coupling induced by the field is much larger than that induced by the bath. The frequency was restricted to within $+/-0.015$ rad/fs of the difference frequency between the rephasing and coherence frequencies corresponding to a particular point in the 2D spectrum. The phase was bound to lie between $-\pi$ and π. The values of this initial fit were then used as an initial guess for an unbounded fitting using a nonlinear least squares algorithm. Confidence intervals and covariance matrices were calculated for each fit. An error bar map is shown in Fig. S3 below.

1. Christensson N, et al. (2011) High frequency vibrational modulations in two-dimensional electronic spectra and their resemblance to electronic coherence signatures. *J Phys Chem B* 115:5383–5391.
2. Renge I, Mauring K, Avarmaa R (1987) Site-selection optical-spectra of bacteriochlorophyll and bacteriopheophytin in frozen-solutions. *J Lumin* 37:207–214.
3. Chachisvilis M, Pullerits T, Jones MR, Hunter CN, Sundstrom V (1994) Vibrational dynamics in the light-harvesting complexes of the photosynthetic bacterium Rhodobacter-sphaeroides. *Chem Phys Lett* 224:345–354.
4. Shelly KR, Golovich EC, Beck WF (2006) Intermolecular vibrational coherence in bacteriochlorophyll a with clustered polar solvent molecules. *J Phys Chem B* 110:20586–20595.

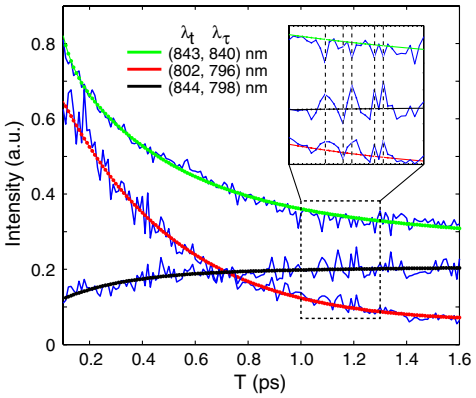

Fig. S1. Decay of B800 (red) and B850 (green) bands with waiting time. Fit of B800 to B850 energy transfer (black). Inset: Effects of laser spectral and intensity fluctuations on the 2D spectrum during the waiting time.

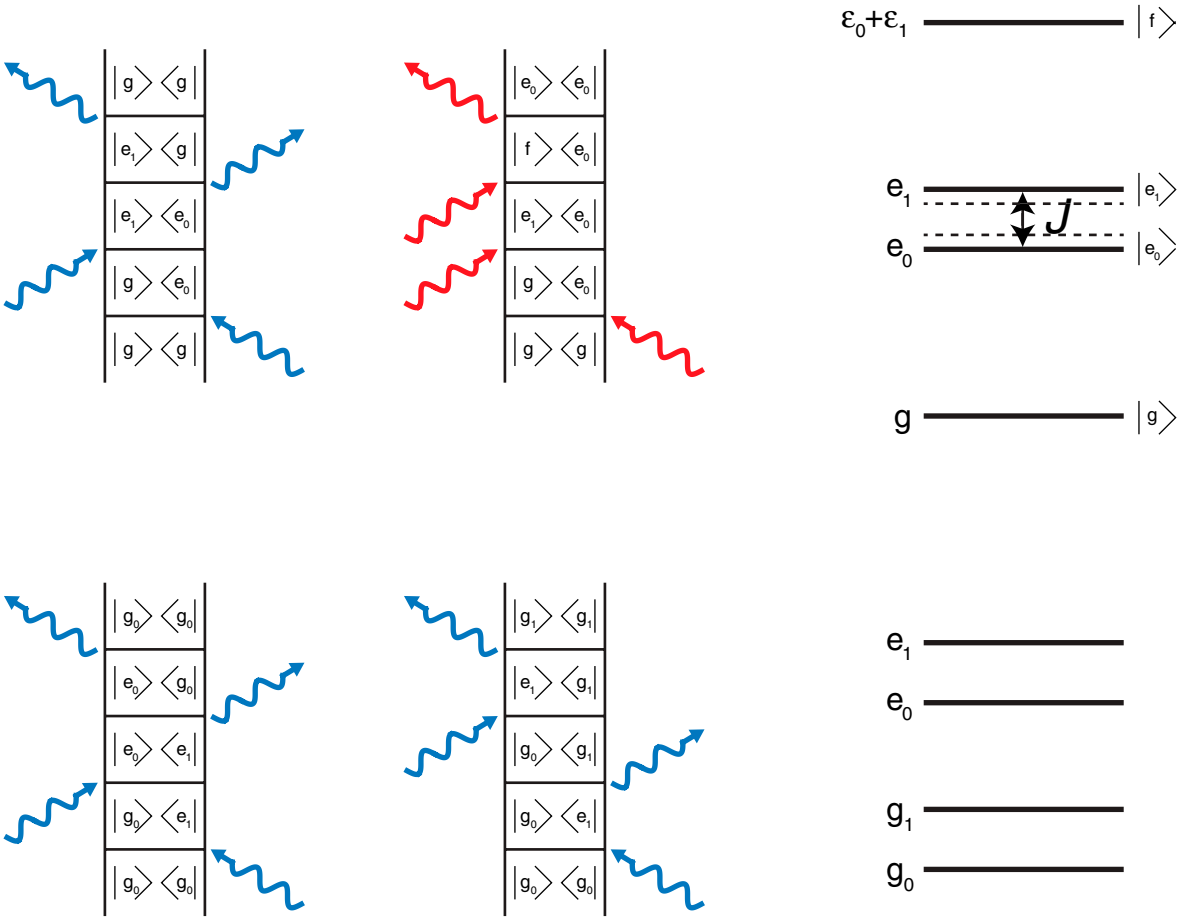

Fig. S2. Feynman diagrams contributing to quantum beats in the cross-peak of the 2D spectrum. Above pathways correspond to electronic coherence between two, coupled exciton states, $|e_1|$ and $|e_2|$. ε_1 and ε_2 (dashed lines) correspond to the energies in the site representation, prior to electronic coupling. The two-exciton state, $|f\rangle$ has energy at the sum of the two single-exciton energies $f = e_1 + e_2 = \epsilon_1 + \epsilon_2$. In the absence of coupling ($J = 0$), the ground-state bleach and excited-state absorption pathways exactly cancel. The pathways in the bottom part of the figure correspond to pathways from a single chromophore with vibrational states in the ground and first-excited electronic state. If the displacement of the excited-state potential is zero, these pathways do not contribute to observable signal.

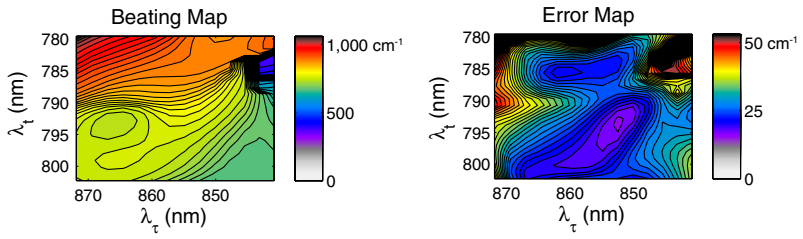

Fig. S3. Beating frequency map and associated error map corresponding to 90% confidence interval calculated for each point in the AD cross-peak of the 2D spectrum.