Supporting Information: Energy Transfer Observed in Live Cells Using Two-Dimensional Electronic Spectroscopy

Peter D. Dahlberg,[1] Andrew F. Fidler,[2] Justin R. Caram,[2] Phillip D. Long,[1] and Gregory S. Engel[2*]

1. Graduate Program in the Biophysical Sciences, Institute for Biophysical Dynamics, and the James Franck Institute, The University of Chicago, Chicago, IL 60637

2. Department of Chemistry, Institute for Biophysical Dynamics, and the James Franck Institute, The University of Chicago, Chicago, IL, 60637

* Corresponding Author E-mail: gsengel@uchicago.edu

Regression parameters for decay of B800:

The waiting time decay *in vivo* followed a bi-exponential function of the form

$$y = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$$

while the isolated LH2 followed a mono-exponential function of the form

$$y = A_1 e^{-\frac{t}{\tau_1}}$$

Table S1: Regression parameters for decay of B800

Sample	A_1	τ_1	A_2	τ_2
In vivo	0.75 ± 0.05	692 ± 72 fs	0.20 ± 0.06	87 ± 58 fs
Isolated LH2	0.78 ± 0.01	661 ± 21 fs	N/A	N/A

Regression parameters for decay of B850:

The waiting time decays followed a mono-exponential function with a non-decaying component of the form

$$y = A_1 e^{-\frac{t}{\tau_1}} + C$$

Table S2: Regression parameters for decay of B850:

Sample	A_1	τ_1	C
In vivo	0.12 ± 0.01	323 ± 106 fs	0.04 ± 0.02
Isolated LH2	0.44 ± 0.02	225 ± 35 fs	0.22 ± 0.02

Supporting Figures:

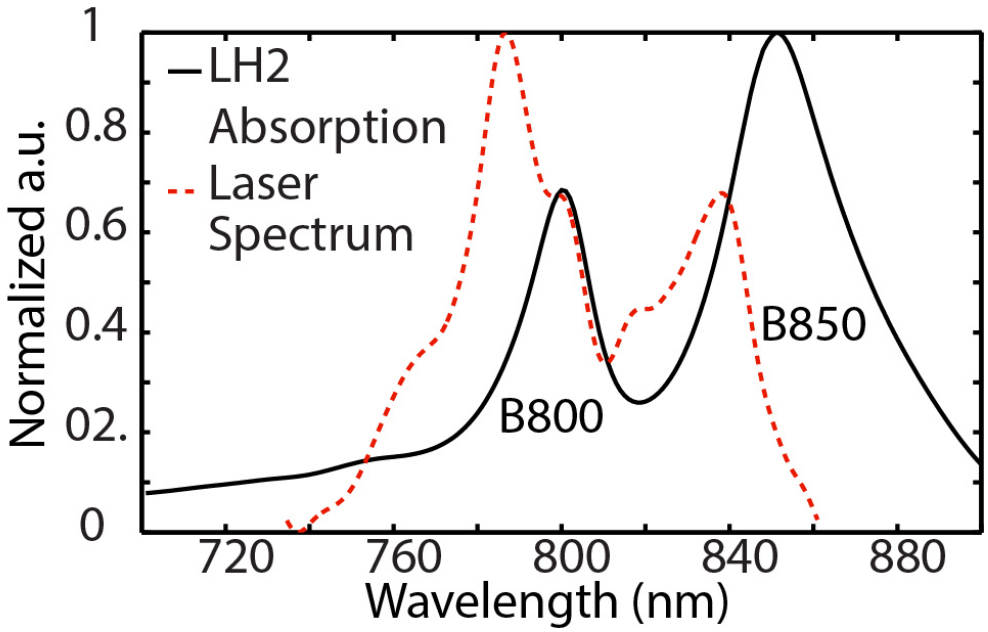

Figure S1: The characteristic linear absorption spectra of LH2 (solid black) showing the two peaks at 800 nm and 850 nm arising from the two rings of bacteriochlorophyll a known as B800 and B850 respectively. The excitation spectra (dashed red) of the laser, which was broadened using filament generation in argon gas, excites the entire B800 absorption band and the blue edge of the B850 band.

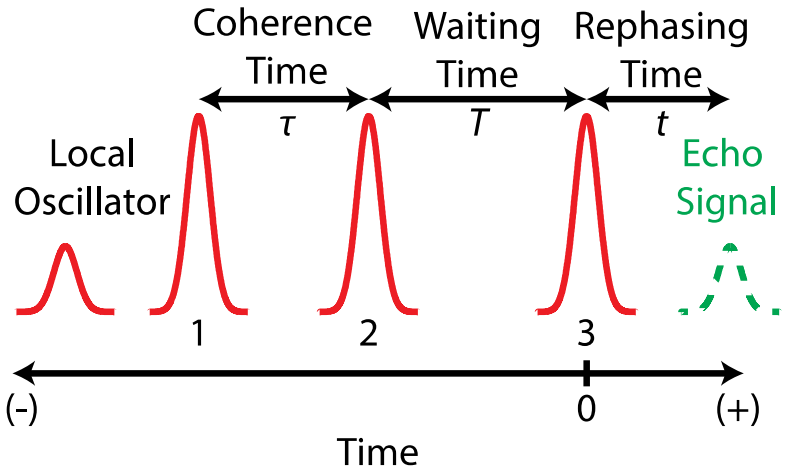

Figure S2: A two-dimensional electronic spectroscopy pulse sequence. Pulse 1, the first pulse to interact with the sample, creates a superposition between ground and excited states that evolves phase for the coherence time, τ, at which point pulse 2 interacts with the sample. Pulse 2 creates a population or superposition of excited states that evolves for the waiting time T. Pulse 3 then interacts, returning the system to a quantum coherence, which evolves phase in the opposite manner for a rephasing time, t. At $t \approx \tau$, if the system retained memory of the phase evolved during the coherence time, the electronic dipoles realign and a photon echo signal is emitted. This echo is co-propagated with the LO into a spectrometer where they interfere and are detected on a camera encoding relative phase and amplitude.

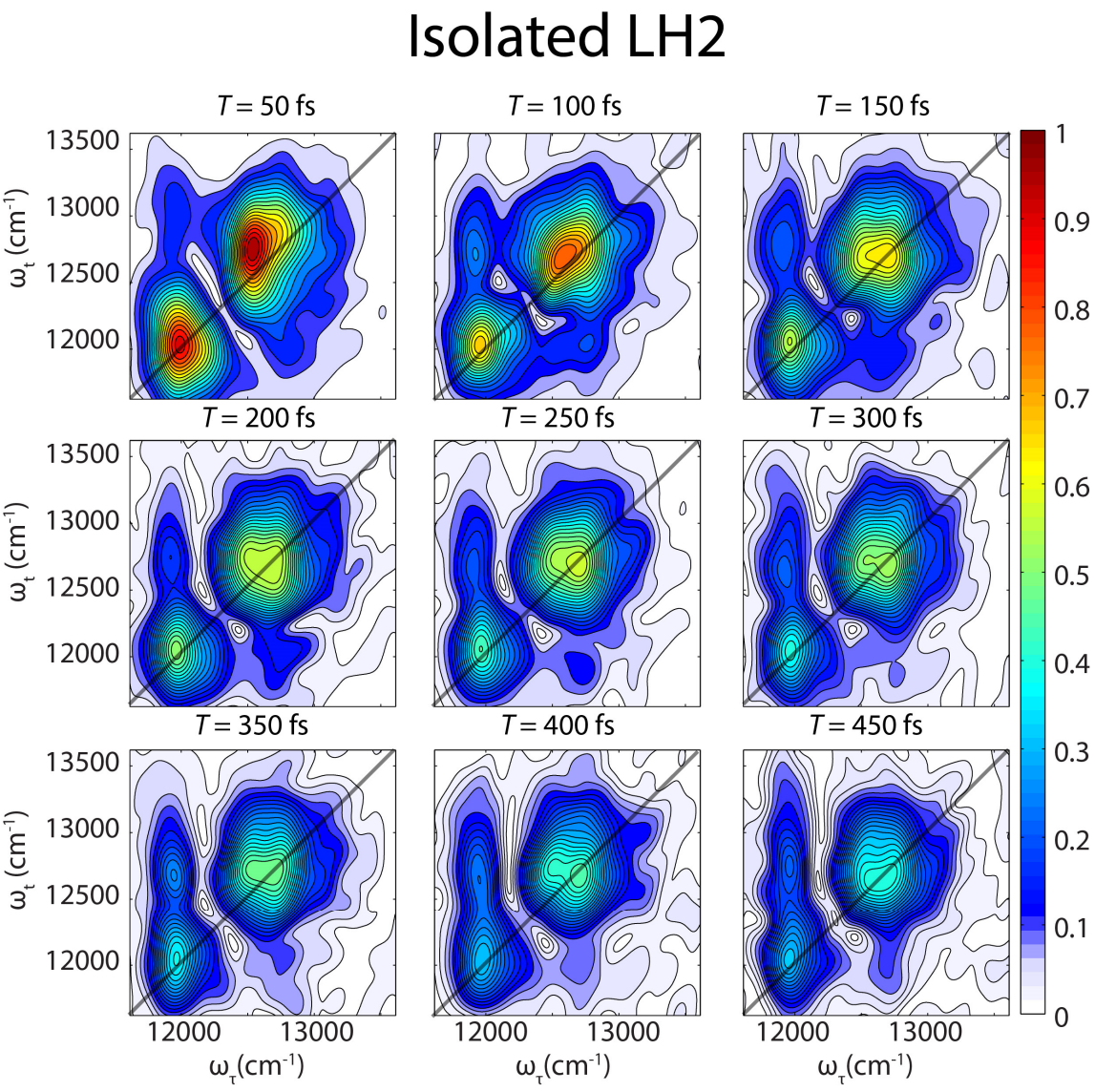

Figure S3: A waiting time series of 2D spectra acquired with UVA-GRAPES on isolated LH2 of *R. sphaeroides* in detergent micelles.

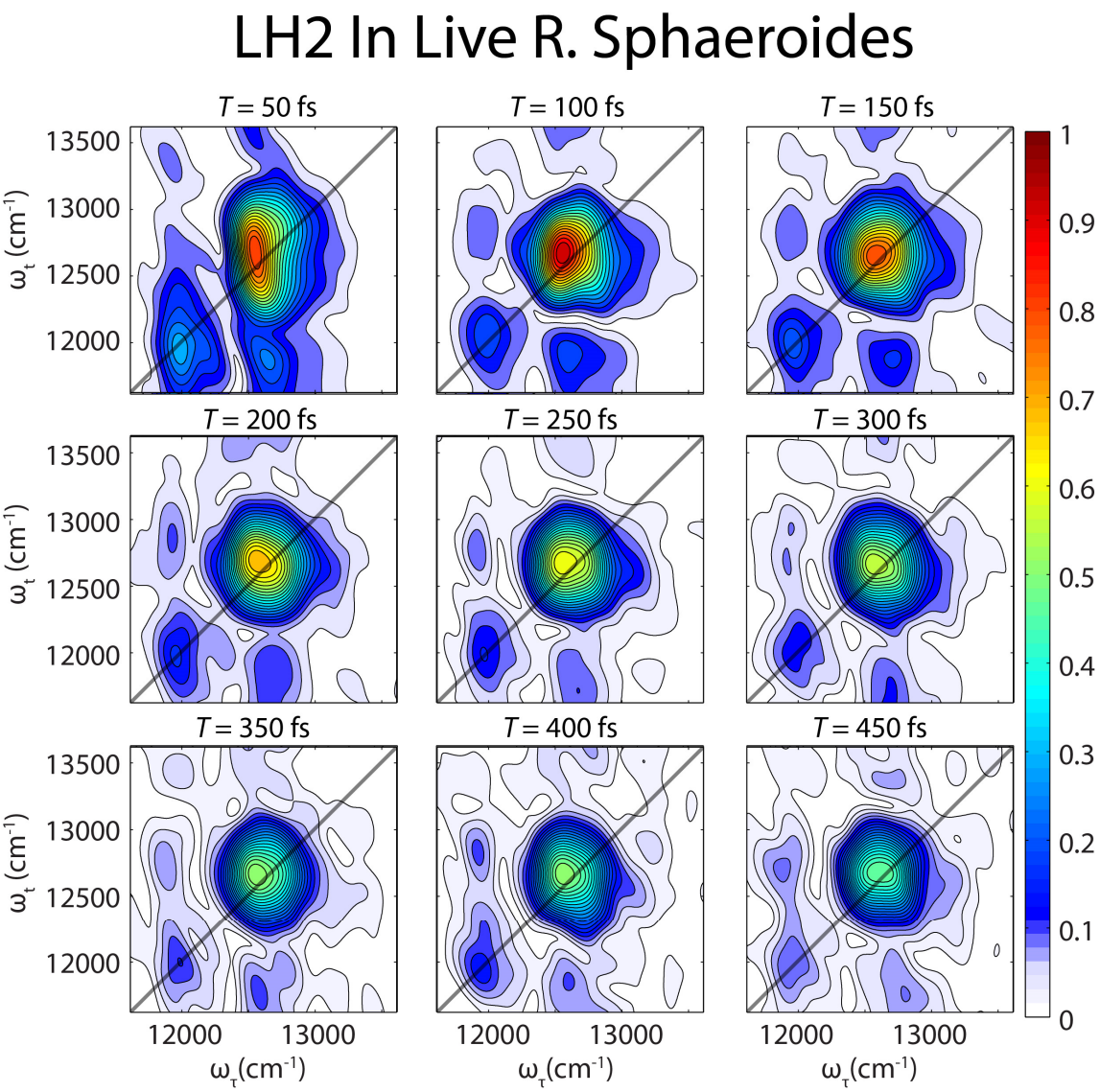

Figure S4: A waiting time series of 2D spectra acquired with UVA-GRAPES on live cells of *R. sphaeroides.*

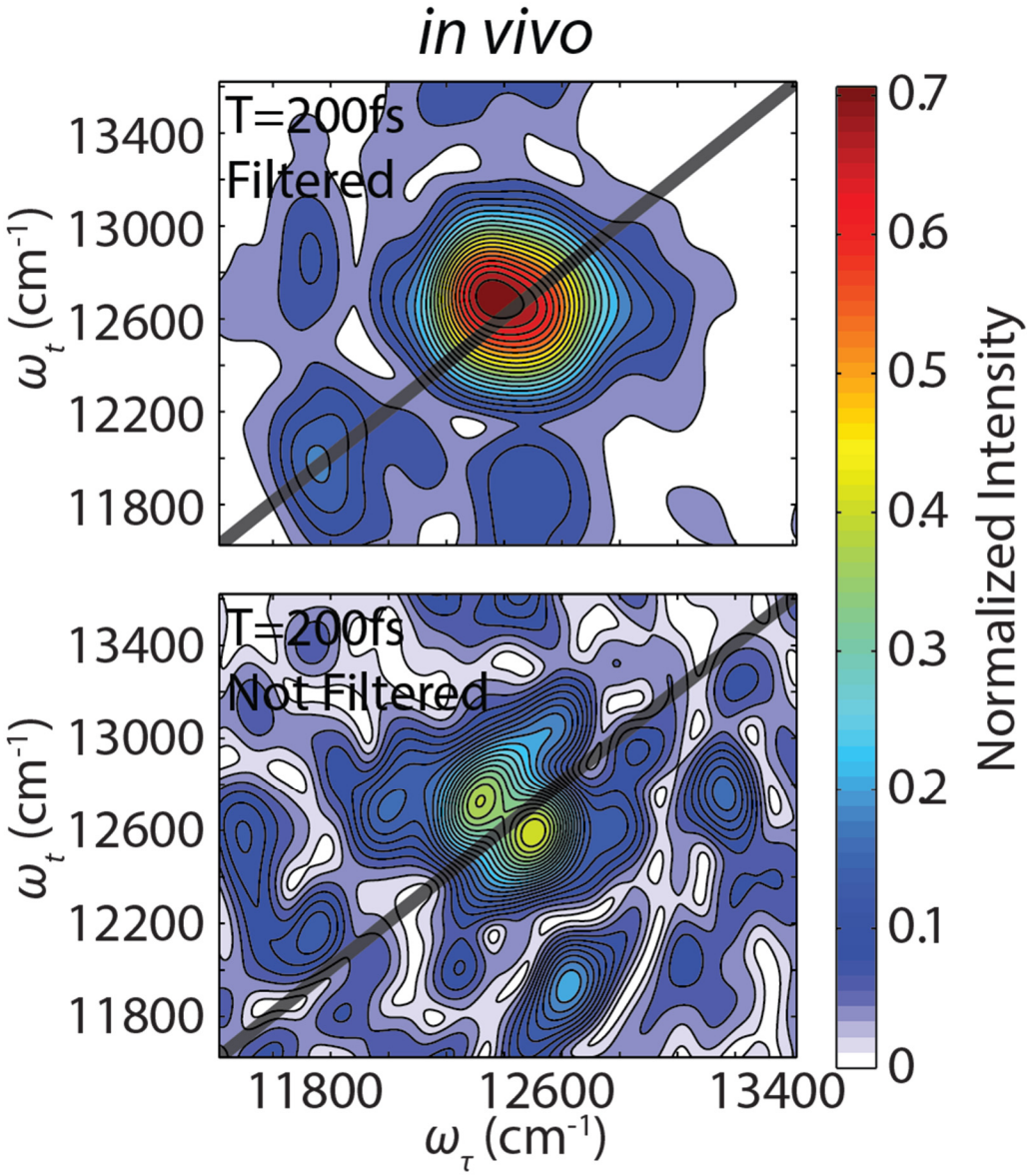

Figure S5: 2DES spectra of whole cells taken at T=200 fs with filtering in the ω_T domain (*top)* and without filtering in the ω_T domain *(bottom)*. Without filtering the signal is dominated by scatter artifacts that obscure the nature of the energetic coupling within LH2.

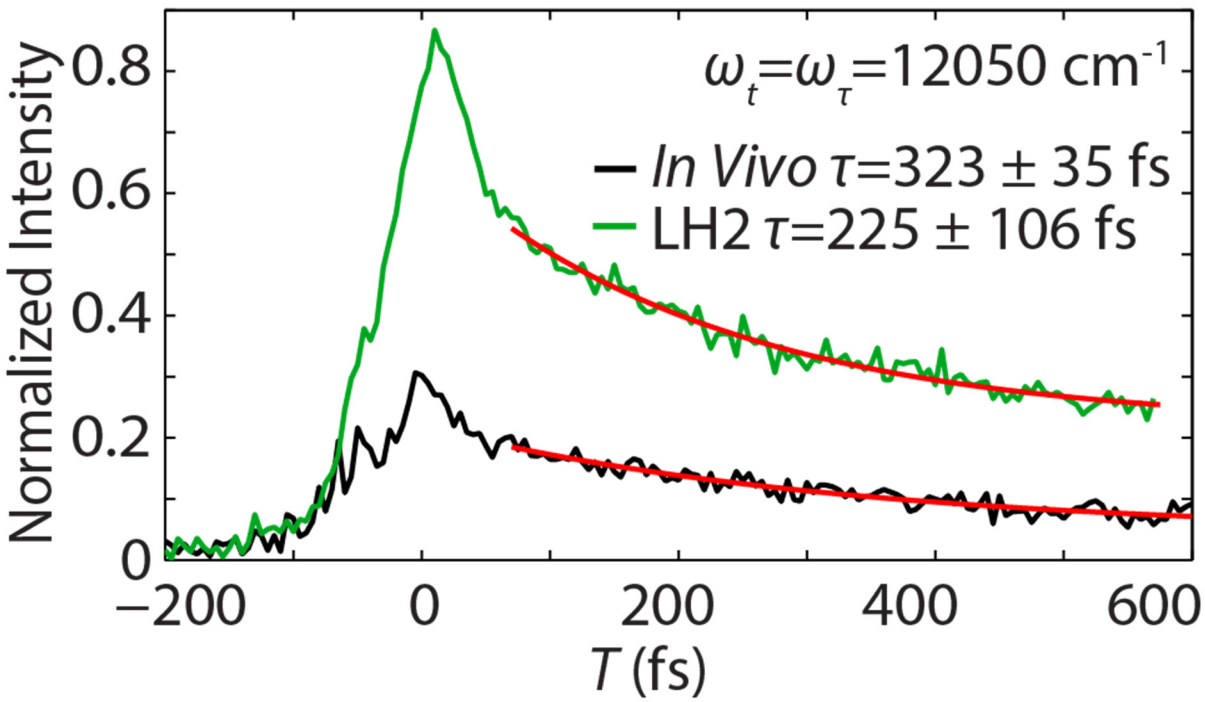

Figure S6: Waiting time traces extracted from the diagonal peak at $\omega_\tau=\omega_t=12050\ cm^{-1}$. The traces were analyzed beginning at T=70 fs to avoid artifacts from the instrument response function measured to be 35 fs. Both traces followed a mono-exponential decay with a constant offset. The decay rate of ~300 fs is too fast to be inter-complex and is likely a vibrational relaxation out of the bandwidth of the experiment. The cause of the difference in intensities between *in vivo* and isolated LH2 is unknown and is subject of further investigation. The negative time signal arises from resonant response due to pulse ordering (3,2,1,LO) specific to the gradients within the GRAPE spectrometer.