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Simulation of Femtosecond Phase-Locked Double-Pump Signals of Individual Light Harvesting Complexes LH2

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Abstract

Recent phase-locked femtosecond double-pump experiments on individual light harvesting complexes LH2 of purple bacteria at ambient temperature revealed undamped oscillatory responses on a time scale of at least 400 fs [R. Hildner et al, *Science*, **340**, 1448 (2013)]. Using an excitonic Hamiltonian for LH2 available in the literature, we simulate these signals numerically by a method which treats excitonic couplings and exciton-phonon couplings in a non-perturbative manner. The simulations provide novel insights into the origin of coherent dynamics in individual LH2 complexes.

Deciphering the numerous intriguing facets of photosynthesis, one of the most important biochemical processes occurring on Earth, has been an active area of research over many decades¹⁻⁴. This research has provided illuminating insights in the cellular level architecture and the mechanisms of the machinery used by green plants, algae and photosynthetic bacteria to carry out the extremely complex process of absorption of solar energy and its conversion to chemical energy⁵⁻⁷.

Our understanding of the photophysics of light harvesting has been largely shaped by data delivered by femtosecond nonlinear ensemble spectroscopy^{1–11} and single-molecule (SM) spectroscopy^{12,13}. Yet, both of these spectroscopies have significant intrinsic limitations. Ensemble spectroscopy provides the responses averaged over an ensemble of species, while the excited-state dynamics of photosynthetic systems vary dramatically among individual complexes and even within a single complex over time due to the high degree of (conformational and electronic) disorder. SM spectroscopy, on the other hand, monitors signals of individual species and is free of inhomogeneous broadening. However, it usually relies on the detection of fluorescence, which is emitted on nanosecond timescale. Therefore, significant dynamic processes occurring on femtosecond to picosecond timescales cannot be resolved.

Recently, van Hulst and coworkers combined the best of both worlds, extending SM spectroscopy into the femtosecond time domain^{14–18}. In this technique, individual chromophores are interrogated by two^{14–17} or three¹⁸ femtosecond phase-locked pulses and the time resolution is achieved through the detection of the SM fluorescence as a function of the interpulse delay(s). After the demonstration for single chromophores^{14–17}, double-pump femtosecond SM spectroscopy has been applied to individual LH2 complexes of purple bacteria under physiological conditions¹⁹. It was found that signals of individual LH2 complexes are oscillatory and, unexpectedly, do not exhibit decay on a timescale of ~ 400 fs¹⁹.

Previously, we have developed a computational method to simulate femtosecond double-pump SM signals of molecular aggregates and applied it to light harvesting complexes II (LHCII) of higher plants²⁰. In the present work, we extend the analysis to account for environment-induced fluctuations and employ it to the simulation and interpretation of femtosecond responses of individual LH2 complexes.

The LH2 complex of the purple bacterium *R. acidophila* (PDB ID: 1kzu²¹) consists of 27 bacteriachlorophyll a (Bchl_a) molecules arranged in two concentric B800 and B850 rings labeled according to their central absorption wavelength. In the present work, we adopt a description in which all relevant excitonic and vibrational degrees of freedom of

LH2 are included into the system Hamiltonian H^{22-24} . This Hamiltonian, which comprises 27 excitonic states and 17 high-frequency vibrational modes, has been well characterized in previous studies^{21,25-28} and can be written as

$$H = H_{\text{ex}} + H_{\text{vib}} + H_{\text{ex-vib}}. \quad (1)$$

Here H_{ex} is the Frenkel-exciton Hamiltonian, H_{vib} describes molecular vibrations, and $H_{\text{ex-vib}}$ is responsible for the exciton-vibrational coupling, which is taken as diagonal in the site representation and linear in the vibrational modes:

$$\begin{aligned} H_{\text{ex}} &= \epsilon_g |g\rangle\langle g| + \sum_{m=1}^{27} \epsilon_m |m\rangle\langle m| + \sum_{n \neq m}^{27} J_{nm} |n\rangle\langle m|, \\ H_{\text{vib}} &= \sum_{q=1}^{17} \hbar \omega_q b_q^\dagger b_q, \\ H_{\text{ex-vib}} &= \sum_{q=1}^{17} \sum_{m=1}^{27} \chi_{qm} \hbar \omega_q (b_q^\dagger + b_q) |m\rangle\langle m|. \end{aligned} \quad (2)$$

Here, $|g\rangle$ denotes the state in which all Bchls are in the electronic ground state, $|m\rangle$ denotes the state in which the m th Bchl is excited, ϵ_m is the electronic energy, J_{nm} is the electronic coupling (transfer integral) between the Bchl n and m , $b_q^\dagger$ (b_q) is the creation (annihilation) operator of the q th vibrational mode with frequency ω_q , and χ_{qm} is the exciton-vibrational coupling which is quantified by the Huang-Rhys factor $S_{qm} = \chi_{qm}^2$.

The interaction of LH2 with two phase-locked laser pulses is described in the dipole approximation and in the rotating wave approximation as

$$H_F(t) = -(E(t)X^\dagger + E^*(t)X), \quad (3)$$

where

$$\begin{aligned}
E(t) &= E_0 \left(f_1(t) e^{-i\omega_1 t} + f_2(t - \tau) e^{i(\phi - \omega_2 t)} \right), \\
X &= \sum_{m=1}^{27} (\mathbf{e} \boldsymbol{\mu}_m) |g\rangle \langle m|,
\end{aligned} \tag{4}$$

E_0 is the amplitude of the pulses, $f_1(t)$ and $f_2(t)$ are their dimensionless temporal envelopes, ω_1 and ω_2 are the pulse carrier frequencies, τ and ϕ are the time delay and phase difference of the pulses, $\mathbf{e}$ is the unit vector of the pulse polarization, and $\boldsymbol{\mu}_m$ is the transition dipole moment of m th Bchla.

In the femtosecond double-pump SM experiments of Ref.¹⁹, individual LH2 complexes are embedded in a polymer matrix at ambient temperature. This environment is highly heterogeneous and exhibits thermal fluctuations, which modulate the parameters specifying H and $H_F(t)$ (see Refs.^{29,30} for a detailed discussion). In a typical SM experiment, the signal as a function of the time delay τ is detected with a certain time step Δ_τ ,

$$\tau = j\Delta_\tau, \quad j = 0, 1, 2, \dots \tag{5}$$

In Ref.¹⁹, for example, $\Delta_\tau \approx 25$ fs. The time interval between the measurements j and $j+1$ is much longer than any relevant microscopic time interval specifying dynamics and fluorescence detection of the individual LH2. It is therefore safe to assume that there is no correlation between the values of the parameters of the Hamiltonians (1) and (3) in any two consecutive measurements. Such a measurement protocol can be simulated by introducing a stochastic modulation of the parameters^{29,30}. For LH2, as for other pigment-protein complexes, the dominant contribution to the static disorder comes from electronic energies^{31–34}. Hence, we adopt the following modulation law

$$\epsilon_m(\tau) = \bar{\epsilon}_m + \delta_m r_m(\tau). \tag{6}$$

Here $\epsilon_m(\tau)$ is a stochastic realization of the site energy at a specific time delay τ , $\bar{\epsilon}_m$ represents its mean value, δ_m controls the amplitude of modulations, and $r_m(\tau)$ is a random Gaussian variable with unit dispersion. Due to these modulations, H depends on τ parametrically and can be regarded as snapshot Hamiltonian.

The double-pump SM signal is defined as the total (relaxed) fluorescence of a single LH2 complex measured as a function of the interpulse delay τ ^{20,29}:

$$I(\tau) = \text{Tr} \left\{ \sum_{m=1}^{27} |m\rangle \langle m| \rho(t_f) \right\}. \quad (7)$$

Here t_f is any time moment after the passing of the second pump pulse, and the density matrix $\rho(t)$ satisfies the Liouville equation

$$\partial_t \rho(t) = -\frac{i}{\hbar} [H + H_F(t), \rho(t)]. \quad (8)$$

Since all vibrational modes with significant exciton-vibrational coupling are included in the system Hamiltonian H , Eq. (8) adequately describes evolution of $\rho(t)$ on the time scale of $\tau \sim 400$ fs typical for the experiments of Ref.¹⁹. There exist several inter- and intramolecular relaxation processes, which are not described by Eq. (8). However, as argued in Ref.²⁹, these processes do not affect the total population $\rho(t_f)$ and need not be accounted for. The impact of a liquid solvent, which is usually described by the coupling of the system to an overdamped harmonic bath³⁵, should not be considered in the present case, because the individual LH2s are embedded in a polymer matrix and are not in direct contact with a solvent.

The signal of Eq. (7) can be expressed as an expansion in the system-field coupling^{20,29},

$$I(\tau) = \sum_{k=2,4,6,\dots} I_k(\tau) \quad (9)$$

where $I_k(\tau) \sim E_0^{2k}$. In the SM experiment of Ref.¹⁹, the signal was controlled to scale linearly

with the pump-pulse intensity, $I(\tau) \sim E_0^2$. In this case, the SM signal can be associated with the lowest-order contribution $I_2(\tau)$, which can be evaluated as²⁰

$$I_2(\tau) = \sum_{a,b=1}^2 \sigma_{ab}(\tau)$$

where

$$\sigma_{ab}(\tau) = 2\text{Re} \int_{-\infty}^{\infty} dt \int_0^{\infty} dt_1 E_a^*(t) E_b(t - t_1) R(t_1) \quad (10)$$

and $R(t)$ is the linear response function. Since the characteristic energies of the high frequency molecular modes are much higher than $k_B T$ (k_B is the Boltzmann constant, and T is the bath temperature), $R(t)$ can be evaluated as

$$R(t) = \sum_{n,n'=1}^N C_{nn'} \langle \mathbf{0}_{\text{vib}} | \langle n | e^{-iH_S t} | n' \rangle | \mathbf{0}_{\text{vib}} \rangle, \quad (11)$$

where $C_{nn'} = (\mathbf{e}\boldsymbol{\mu}_n)(\mathbf{e}\boldsymbol{\mu}_{n'})$ are geometrical factors and $|\mathbf{0}_{\text{vib}}\rangle$ is the vacuum state for the high-frequency vibrational modes.

In the simulations, we assume that the pulses have Gaussian envelopes

$$f_a(t) = \exp\{-\Gamma_a^2 t^2\} \quad (12)$$

where $\Gamma_a = 2\sqrt{\ln 2}/\tau_a$ and τ_a are the pulse durations (full width at half maximum). In this case, the integration over t in Eq. (10) can be performed analytically, yielding

$$I(\tau) \sim \text{Re} \int_0^{\infty} dt_1 A(\tau, t_1) R(t_1). \quad (13)$$

Here

$$A(\tau, t_1) = c_1 e^{-\Gamma_1^2 t_1^2/2} e^{i\omega_1 t_1} + c_2 e^{-\Gamma_2^2 t_2^2/2} e^{i\omega_2 t_1} + c_{12} e^{-\omega^2/\gamma^2} e^{i\Omega t_1} \left(e^{-\Gamma^2(\tau-t_1)^2/2} e^{-i(\phi-\xi\omega\tau)} + e^{-\Gamma^2(\tau+t_1)^2/2} e^{i(\phi-\xi\omega\tau)} \right), \quad (14)$$

where

$$\gamma^2 = \Gamma_1^2 + \Gamma_2^2, \quad \Gamma^2 = \frac{(\Gamma_1 \Gamma_2)^2}{\gamma^2}, \quad \xi = 2 \frac{\Gamma_2^2}{\gamma^2}, \quad (15)$$

$$\omega = (\omega_2 - \omega_1)/2, \quad \Omega = \frac{\Gamma_2^2 \omega_1 + \Gamma_1^2 \omega_2}{\gamma^2} \quad (16)$$

and

$$c_1 = \sqrt{\frac{\pi}{2\Gamma_1^2}}, \quad c_2 = \sqrt{\frac{\pi}{2\Gamma_2^2}}, \quad c_{12} = \sqrt{\frac{\pi}{\gamma^2}}. \quad (17)$$

The parameters of the LH2 Hamiltonian are taken from the previous studies^{21,25–28} and are collected in Sec. I of Supplementary Information. The amplitudes δ_m of the modulation of the site energies $\epsilon_m(\tau)$ are retrieved from Ref.³³. The carrier frequencies of the two pump pulses are set in resonance with the B800 and B850 bands of the linear absorption spectrum of LH2, respectively, that is $\omega_1 = 12468 \text{ cm}^{-1}$ (802 nm) and $\omega_2 = 11655 \text{ cm}^{-1}$ (858 nm)¹⁹. The pump pulses are assumed to be polarized along the X axis of the molecular frame, $\mathbf{e} \parallel X$. The effect of other choices of $\mathbf{e}$ on the signals is discussed in Sec. V of Supplementary Information.

For specific values of the model parameters, the propagator in the linear response function $R(t)$ of Eq. (11) has been evaluated by using the Davydov D_1 *Ansatz*^{36–38}

$$\begin{aligned} |\Psi_{D_1}(t)\rangle &= e^{-\frac{i}{\hbar} H_S t} |n\rangle |\mathbf{0}_{\text{vib}}\rangle \\ &= \sum_{n=1}^{27} \alpha_n(t) |n\rangle \exp \left\{ \sum_{q=1}^{17} [\lambda_{nq}(t) b_q^\dagger - \text{H.c.}] \right\} |\mathbf{0}_{\text{vib}}\rangle. \end{aligned} \quad (18)$$

The application of the Dirac-Frenkel variational principle yields the equations of motion for the time-dependent parameters $\alpha_n(t)$ and $\lambda_{nq}(t)$ (see Sec. II of Supplementary Information). The derivation of the equations of motion as well as the means to control the accuracy of the *Ansatz* are described in detail in Refs.^{36–38}. For the diagonal form of the exciton-vibrational coupling (Eq. 2), the Davydov D_1 *Ansatz* provides a numerically accurate evaluation of the linear response function (11). It should be noted that the response function $R(t)$ represents nonadiabatic nuclear dynamics on 27 coupled electronic potential-energy surfaces with 17

inseparable vibrational degrees of freedom.

Eq. (14) reveals that the SM signal $I(\tau)$ is composed of a τ -independent background (the aggregate interacts twice with the same pulse) and a τ -dependent contribution (the aggregate interacts once with pulse 1 and once with pulse 2). Furthermore, $I(\tau)$ does not monitor vibronic wavepackets which are associated with populations of the aggregate density matrix $\rho_{nn}(\tau)$ in the manifold of singly-excited excitonic states $|n\rangle$. The signal rather monitors the evolution of excitonic coherences $\rho_{gn}(\tau)$, which are described by the linear response function (11). Furthermore, Eq. (14) predicts that the signal can be represented as

$$I(\tau) = \theta(\tau) \cos[\phi - \varphi(\tau) - \omega\tau] \quad (19)$$

where the explicit form of $\theta(\tau)$ and $\varphi(\tau)$ depends on $R(t)$ and the pulse shapes. Hence the SM signal exhibits a universal "cosine" dependence on ϕ for fixed τ . This is a direct consequence of the weak system-field coupling approximation and is consistent with the experimental data of Ref.¹⁹ and with the simulations of Ref.³⁴. On the other hand, ϕ determines the initial (at $\tau = 0$) value of the signal^{29,30}. When the two pump pulses overlap ($\tau = 0$) and have relative phase $\phi = \pi$, they cancel each other (destructive interference) and do not excite the LH2 complex at all, yielding $I(0) = 0$. Overlapping pulses with $\phi = 0$ or 2π , on the other hand, reinforce each other (constructive interference) and $I(0)$ attains its maximum value. In general, ϕ determines the relative phases of oscillations in SM signals. That is why different experimental realizations of SM signals exhibit a variety of oscillatory transients which are shifted with respect to each other (see Fig. 1 of Supplementary Information), as predicted by Eq. (19). Keeping these considerations in mind, we set $\phi = 0$ in the subsequent simulations. This implies $I(\tau) = I(-\tau)$.

To establish a reference picture as well as to uncover how the dynamics generated by the Hamiltonian (1) manifests itself in SM signals, we first assume that modulations of the site energies can be neglected. Fig. 1 shows the SM signals evaluated for pump pulses of duration

Figure 1: SM signals $I(\tau)$ simulated for pulse durations (a) $\tau_1 = \tau_2 = 15$ fs and (b) $\tau_1 = 15$ fs, $\tau_2 = 60$ fs.

$\tau_1 = \tau_2 = 15$ fs (a) and $\tau_1 = 15$ fs, $\tau_2 = 60$ fs (b). The signal in Fig. 1(a) corresponds to short pulses which provide good temporal resolution. The signal exhibits fast high-frequency oscillations with a period of $\tau_{\text{fast}} \approx 39$ fs superimposed on slow low-frequency beatings with a period of $\tau_{\text{slow}} \approx 287$ fs. Fast oscillations and slow beatings have also been found in the signals simulated in Ref.³⁴. The oscillations and beatings in Fig. 1(a) are of vibronic character: Their periods depend on the excitonic couplings J_{nm} as well as on the exciton-vibrational couplings S_{qm} (polaron effect) decreasing with the decrease of S_{qm} (see Sec. IV of Supplementary Information). The modulation of S_{qm} may thus be responsible for the broad distribution of τ_{slow} in the signals of Ref.¹⁹. The amplitude of the low-frequency beatings slightly decreases with τ , owing to incomplete rephasing of the vibronic dynamics in the excited-state manifold. The signal in Fig. 1(b) has been calculated for the pulse durations of Ref.¹⁹. Since $\tau_2 > \tau_{\text{fast}}$, the high-frequency oscillations cannot be detected in the signal of Fig. 1(b) and in the signals of Ref.¹⁹. On the other hand, the low-frequency beatings in Fig. 1(a) and (b) look the same, since $\tau_2 = 60$ fs is much shorter than τ_{slow} . These are the beatings which were detected in the SM double-pump signals reported in Ref.¹⁹ (cf. Fig. 1 of Supplementary Information).

To clarify the origin of the low-frequency beatings, Fig. 2 shows SM signals simulated without coupling between the B800 and B850 rings of LH2 (J_{nm} are artificially set to zero if Bchl m and n belong to different rings). The signal in panel (a) is simulated for short pulses ($\tau_1 = \tau_2 = 15$ fs), while the signal in panel (b) is simulated for the experimental values of the pulse durations¹⁹ ($\tau_1 = 15$ fs, $\tau_2 = 60$ fs). Let us first analyze the low-frequency beatings

Figure 2: SM signals $I(\tau)$ simulated for pulse durations (a) $\tau_1 = \tau_2 = 15$ fs and (b) $\tau_1 = 15$ fs, $\tau_2 = 60$ fs. The electronic coupling between the B800 and B850 rings is set to zero.

which are seen in both panels of Fig. 2. The period of these beatings is ~ 106 fs, which is almost three times shorter than $\tau_{\text{slow}} \approx 287$ fs obtained with the coupling between the rings. The ~ 106 fs beatings manifest coherent vibronic dynamics inside the B800 and B850 rings. Since a small fraction of SM signals exhibiting ~ 100 fs oscillations has been detected in Ref.¹⁹, these signals may reveal responses of individual B800 and B850 rings. On the other hand, Fig. 2 demonstrates that intra-ring excitonic couplings alone cannot produce ~ 200 fs oscillations in the SM signals, contrary to what has been found in Ref.³⁴. The value of ~ 200 fs dominates the distribution over the oscillation periods extracted from the SM signals of Ref.¹⁹. One thus concludes that the majority of these signals depend on the B800-B850 inter-ring coupling, but are not exclusively determined by this coupling as was assumed in Ref.¹⁹. As for the high-frequency oscillations, they are clearly seen in Fig. 2(a) (short pulses) but cannot be resolved in panel Fig. 2(b) (experimental pulses), as expected. The period of these oscillations, ~ 33 fs, is shorter than that obtained with the B800-B850 inter-ring coupling.

Let us now discuss how the modulation of the site energies affects SM signals. We assume that modulations of $\epsilon_m(\tau)$ are uncorrelated for different m and τ , but the modulation amplitudes $\delta_{B800} = 60 \text{ cm}^{-1}$ and $\delta_{B850} = 130 \text{ cm}^{-1}$ are different for the Bchl a molecules belonging to the B800 and B850 rings (see Ref.³³ and references therein). Fig. 3 shows the SM signals simulated with a fine discretization step $\Delta_\tau = 5$ fs (upper panels) and with the experimental discretization step $\Delta_\tau = 25$ fs¹⁹ (lower panels). The signals in panels (a, c) correspond to short pulses ($\tau_1 = \tau_2 = 15$ fs), while the signals in panel (b,d) correspond to

the experimental pulse durations ($\tau_1 = 15$ fs, $\tau_2 = 60$ fs)¹⁹.

Let us first consider the signal in panel (a), which corresponds to optimal conditions for information acquisition (short pulses and fine discretization step). For $\tau \leq 100$ fs, the level of noise is rather low and the high-frequency oscillations are clearly seen in the signal. For $\tau > 100$ fs, not only the high-frequency oscillations are buried in noise, but also the second maximum due to the low-frequency beating is not clearly visible. Apparently, the level of noise in SM signals increases with τ . This phenomenon can be understood by the following considerations. For overlapping short pump pulses, the signal is independent of modulations of any parameters of H since no dynamic evolution occurs. For non-overlapping short pulses, the effect of the modulation is small if τ is shorter than the timescale at which the SM signal changes significantly, $\tau \lesssim \tau_{\text{slow}}/2$, but the effect becomes substantial if $\tau \gtrsim \tau_{\text{slow}}/2$. Furthermore, the second pump pulse is in resonance with the B850 ring and $\delta_{B850} > \delta_{B800}$, which renders the contribution from the B850 ring noisier than that from the B800 ring.

The signal in panel (b) (experimental pulses and fine discretization step) does not resolve the high-frequency oscillations (due to the reasons explained above), while the first maximum in $I(\tau)$ induced by the low-frequency beating is visible reasonably well. The lower panels (c, d) of Fig. 3 depict the same signals as in the upper panels, but are simulated with the experimental discretization step, $\Delta_\tau = 25$ fs. Since this discretization step almost coincides with the period of the high-frequency oscillations, it comes as no surprise that these oscillations are not seen in the lower panels of Fig. 3 and could not be detected in the SM signals of Ref.¹⁹. This argument has also been pointed out in Ref.³⁴. On the other hand, both the first and second maximums due to the low-frequency beating can be imagined in the signals in the lower panels. The signals in the lower panels look qualitatively the same, despite they were calculated for different pulse durations. These signals are also very similar to the experimental ones (cf. Fig. 1 of Supplementary Information).

An interesting question is whether one can uncover the modulation law (6) by analyzing experimental SM signals. We suggest that this can be done if the number $\mathcal{N}$ of detected

Figure 3: SM signals $I(\tau)$ simulated for excitonic energy modulation amplitudes $\delta_{B800} = 60 \text{ cm}^{-1}$ and $\delta_{B850} = 130 \text{ cm}^{-1}$. The discretization step Δ_τ is 5 fs (upper panels) and 25 fs (lower panels). Panels (a) and (c) correspond to $\tau_1 = \tau_2 = 15 \text{ fs}$, while panels (b) and (d) correspond to $\tau_1 = 15 \text{ fs}$ and $\tau_2 = 60 \text{ fs}$.

signals $I(\tau, n)$ ($n = 1, 2, \dots, \mathcal{N}$) is sufficiently large. In this case, the ensemble double-pump signal is given by $\bar{I}(\tau) = \mathcal{N}^{-1} \sum_n I(\tau, n)$. Furthermore, one can also determine the variance $\mathcal{N}^{-1} \sum_n I(\tau, n)^2 - \bar{I}(\tau)^2$ as well as higher-order moments, which are not accessible in ensemble spectroscopy. This may provide insight into stochastic properties of the environment-induced modulations.

To summarize, we have simulated phase-locked double-pump SM signals of LH2 complexes in the limit of weak system-field coupling. The simulated signals exhibit undamped small-amplitude high-frequency oscillations with a period of $\sim 30 \text{ fs}$, superimposed on high-amplitude low-frequency beatings with a period of $\sim 200 - 300 \text{ fs}$. The oscillations and beatings are of vibronic origin since their periods depend on excitonic inter-state couplings as well as on exciton-vibrational coupling (polaron effect), which supports the current consensus on the vibronic character of long-lived coherences in light harvesting complexes^{11,34,39}. The double-pump SM signals monitor the evolution of the coherences between the excitonic ground state and the manifold of single-exciton states. Hence the signals cannot be directly associated with the dynamics of energy transfer between Bchls within individual LH2 com-

plexes.

The comparison of the simulated signals with the experimental signals of Ref.¹⁹ reveals that (i) The low-frequency beatings in the LH2 signals depend on the coupling between the B800 and B850 rings, but are not solely determined by this coupling. (ii) The absence of the high-frequency oscillations in the SM signals of Ref.¹⁹ can be explained by the (relatively) long duration of the second pump pulse and by a too coarse discretization in the interpulse time delay. An optimization of the experiment along these two directions (shorter pulses and a smaller discretization step) would increase the information content of the double-pump SM signals. It should also be noted that the heterogeneity of excited-state energies of LH2 is larger than for most pigment-protein complexes³². One can thus expect that femtosecond double-pump SM experiments on other pigment-protein complexes may reveal more informative signals.

The experiment of Ref.¹⁹ was performed with weak laser pulses, since the SM signals were controlled to scale linearly with the pulse intensity. However, an earlier variant of SM pump-probe experiments by van Hulst and coworkers employed strong laser pulses and saturation effects⁴⁰, and the same experimental method has been applied recently to individual LH2s⁴¹. Very recently, the influence of the pump-pulse amplitude on the responses of individual LH2 complexes has been theoretically studied in Ref.³⁴. A recent analysis of strong-field responses of individual chromophores³⁰ suggests that the adjustment of the strength of the system-field coupling (by changing the laser pulse intensity) can be an efficient tool for the enhancement of information content of femtosecond double-pump SM signals of light harvesting complexes. The use of stronger laser pulses can also improve the temporal resolution⁴².

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Supporting Information

Parameters of the system Hamiltonian, time-dependent variational approach on the basis of Davydov D₁ Ansatz, different SM signals extracted from experimental measurement, a brief analysis of polaron effects, and effect of polarization of the pump pulses on the SM signals.

References

- (1) Van Amerongen, H.; Valkunas, L.; van Grondelle, R. *Photosynthetic Excitons*; World Science: Singapore, 2000.
- (2) Ishizaki, A.; Fleming, G. R. Quantum Coherence in Photosynthetic Light Harvesting. *Annu. Rev. Condens. Matter. Phys.* **2012**, 3, 333-361.
- (3) Chen, L. P.; Shenai, P.; Zheng, F. L.; Somoza, A.; Zhao, Y. Optimal Energy Transfer in Light-Harvesting Systems. *Molecules.* **2015**, 20, 15224-15272.
- (4) Blankenship, R. E. *Molecular Mechanisms of Photosynthesis*; World Scientific: London, UK, 2002.
- (5) Croce, R.; van Amerongen, H. Natural strategies for photosynthetic light harvesting. *Nat. Chem. Biol.* **2014**, 10, 492-501.

- (6) Romero, E.; Novoderezhkin, V. I.; van Grondelle, R. Quantum design of photosynthesis for bio-inspired solar-energy conversion. *Nature*, **2017**, 543, 355-365.
- (7) Scholes, G. D.; Fleming, G. R.; Chen, L. X.; Aspuru-Guzik, A.; Buchleitner, A.; Coker, D. F.; Engel, G. S.; van Grondelle, R.; Ishizaki, A.; Jonas, D. M.; Lundeen, J. S.; McCusker, J. K.; Mukamel, S.; Ogilvie, J. P.; Olaya-Castro, A.; Ratner, M. A.; Spano, F. C.; Whaley, K. B.; Zhu, X. Using coherence to enhance function in chemical and biophysical systems. *Nature*, **2017**, 543, 647-656.
- (8) Abramavicius, D.; Palmieri, B.; Voronine, D. V.; Šanda, F.; Mukamel, S. Coherent Multidimensional Optical Spectroscopy of Excitons in Molecular Aggregates: Quasiparticle versus Supermolecule Perspectives. *Chem. Rev.* **2009**, 109, 2350-2408.
- (9) Segale, D.; Karavitis, M.; Fredj, E.; Apkarian, V. A. Quantum coherent dissipation: a glimpse of the “cat”. *J. Chem. Phys.* **2005**, 122, 111104.
- (10) Jang, S. J.; Mennucci, B. S. Delocalized excitons in natural light harvesting complexes, arXiv:1804.09711.
- (11) Mirkovic, T.; Ostroumov, E. E.; Anna, J. M.; van Grondelle, R.; Govindjee.; Scholes, G. D. Light Absorption and Energy Transfer in the Antenna Complexes of Photosynthetic Organisms. *Chem. Rev.* **2017**, 117, 249-293.
- (12) Kondo, T.; Chen, W. J.; Schlau-Cohen, G. S. Single-Molecule Fluorescence Spectroscopy of Photosynthetic Systems. *Chem. Rev.* **2017**, 117, 860-898.
- (13) Gruber, J. M.; Malý, P.; Krüger, T. P. J.; van Grondelle, R. From isolated light-harvesting complexes to the thylakoid membrane: a single-molecule perspective. *Nanophotonics*. **2018**, 7, 81-92.
- (14) Brinks, D.; Stefani, F. D.; Kulzer, F.; Hildner, R.; Taminiau, T. H.; Avlasevich, Y.;

- van Hulst, N. F. Visualizing and controlling vibrational wave packets of single molecules. *Nature*. **2010**, 465, 905-908.
- (15) Hildner, R.; Brinks, D.; Stefani, F. D.; van Hulst, N. F. Electronic coherences and vibrational wave-packets in single molecules studied with femtosecond phase-controlled spectroscopy. *Phys. Chem. Chem. Phys.* **2011**, 13, 1888-1894.
- (16) Brinks, D.; Hildner, R.; van Dijk, E. M. H. P.; Stefani, F. D.; Nieder, J. B.; Hernando, J.; van Hulst, N. F. Ultrafast dynamics of single molecules. *Chem. Soc. Rev.* **2014**, 43, 2476-2491.
- (17) Piatkowski, L.; Accanto, N.; van Hulst, N. F. Ultrafast meets ultrasmall: controlling nanoantennas and molecules. *ACS Photonics*. **2016**, 3, 1401-1414.
- (18) Leibel, M.; Toninelli, C.; van Hulst, N. F. Room-temperature ultrafast nonlinear spectroscopy of a single molecule. *Nat. Photon.* **2018**, 12, 45-49.
- (19) Hildner, R.; Brinks, D.; Nieder, J. B.; Cogdell, R. J.; van Hulst, N. F. Quantum coherent energy transfer over varying pathways in single light-harvesting complexes. *Science*. **2013**, 340, 1448-1451.
- (20) Chen, L. P.; Gelin, M. F.; Domcke, W.; Zhao, Y. Theory of femtosecond coherent double-pump single-molecule spectroscopy: Application to light harvesting complexes. *J. Chem. Phys.* **2015**, 142, 164106-164118.
- (21) Prince, S. M.; Papiz, M. Z.; Freer, A. A.; McDermott, G.; Hawthornthwaite-Lawless, A. M.; Cogdell, R. J.; Isaacs, N. W. Apoprotein structure in the LH2 complex from *Rhodospseudomonas acidophila* strain 10050: modular assembly and protein pigment interactions. *J. Mol. Biol.* **1997**, 268, 412-423.
- (22) Huynh, T. D.; Sun, K. W.; Gelin, M. F.; Zhao, Y. Polaron dynamics in two-dimensional photon-echo spectroscopy of molecular rings. *J. Chem. Phys.* **2013**, 139, 104103-104113.

- (23) Chernyak, V.; Mukamel, S. Collective coordinates for nuclear spectral densities in energy transfer and femtosecond spectroscopy of molecular aggregates. *J. Chem. Phys.* **1996**, 105, 4565-4583.
- (24) Mukamel, S.; Abramavicius, D. Many-Body Approaches for Simulating Coherent Non-linear Spectroscopies of Electronic and Vibrational Excitons. *Chem. Rev.* **2004**, 104, 2073-2098.
- (25) Anda, A.; Hansen, T.; Vico, L. D. Multireference Excitation Energies for Bacteriochlorophylls A within Light Harvesting System 2. *J. Chem. Theory. Comput.* **2016**, 12, 1305-1313.
- (26) Madiet, M. E.; Abdurahman, A. Renger, T. Intermolecular Coulomb Couplings from Ab Initio Electrostatic Potentials: Application to Optical Transitions of Strongly Coupled Pigments in Photosynthetic Antennae and Reaction Centers. *J. Phys. Chem. B.* **2006**, 110, 17268-17281.
- (27) Renger, T.; Müh, F. Understanding photosynthetic light-harvesting: a bottom up theoretical approach. *Phys. Chem. Chem. Phys.* **2013**, 15, 3348-3371.
- (28) Cherepy, N. J.; Shreve, A. P. Moore, L. J.; Boxer, S. G.; Mathies, R. A. Electronic and Nuclear Dynamics of the Accessory Bacteriochlorophylls in Bacterial Photosynthetic Reaction Centers from Resonance Raman Intensities. *J. Phys. Chem. B.* **1997**, 101, 3250-3260.
- (29) Palacino-González, E.; Gelin, M. F.; Domcke, W. Theoretical aspects of femtosecond double-pump single-molecule spectroscopy. I. Weak-field regime. *Phys. Chem. Chem. Phys.* **2017**, 19, 32296-32306.
- (30) Palacino-González, E.; Gelin, M. F.; Domcke, W. Theoretical aspects of femtosecond double-pump single-molecule spectroscopy. II. Strong-field regime. *Phys. Chem. Chem. Phys.* **2017**, 19, 32307-32319.

- (31) Novoderezhkin, V. I.; Rutkauskas, D.; van Grondelle, Rienk. Dynamics of the Emission Spectrum of a Single LH2 Complex: Interplay of Slow and Fast Nuclear Motions. *Biophys. J.* **2006**, 90, 2890-2902.
- (32) Schlau-Cohen, G. S.; Wang, Q.; Southall, J.; Cogdell, R. J.; Moerner, W. E. Single-molecule spectroscopy reveals photosynthetic LH2 complexes switch between emissive states. *Proc. Nat. Acad. Sci. USA.* **2013**, 110, 10899-10903.
- (33) Rancova, O.; Abramavicius, D. Static and Dynamic Disorder in Bacterial Light-Harvesting Complex LH2: A 2DES Simulation Study. *J. Phys. Chem. B.* **2014**, 118, 7533-7540.
- (34) Caycedo-Soler, F.; Lim, J.; Oviedo-Casado, S.; van Hulst, N. F.; Huelga, S. F.; Plenio, M. B. Theory of Excitonic Delocalization for Robust Vibronic Dynamics in LH2. *J. Phys. Chem. Lett.* **2018**, 9, 3446.
- (35) Novoderezhkin, V. I.; Cohen Stuart, T. A.; van Grondelle, R. Dynamics of exciton relaxation in LH2 antenna probed by multipulse nonlinear spectroscopy. *J. Phys. Chem. A.* **2011**, 115, 3834-3844.
- (36) Sun, J.; Luo, B.; Zhao, Y. Dynamics of a one-dimensional Holstein polaron with the Davydov ansätze. *Phys. Rev. B.* **2010**, 82, 014305-014318.
- (37) Luo, B.; Ye, J.; Guan, C. B.; Zhao, Y. Validity of time-dependent trial states for the Holstein polaron. *Phys. Chem. Chem. Phys.* **2010**, 12, 15073-15084.
- (38) Ye, J.; Sun, K. W.; Zhao, Y.; Yu, Y. J.; Lee, C. K.; Cao, J. S. Excitonic energy transfer in light-harvesting complexes in purple bacteria. *J. Chem. Phys.* **2012**, 136, 245104-245120.
- (39) Malý, P.; Somsen, O. J. G.; Novoderezhkin, V. I.; Mančal, T.; van Grondelle, R. The

- Role of Resonant Vibrations in Electronic Energy Transfer. *Chem. Phys. Chem.* **2016**, 17, 1356-1368.
- (40) van Dijk, E. M. H. P.; Hernando, J.; Garcia-Parajo, M. F.; van Hulst, N. F. Single-molecule pump-probe experiments reveal variations in ultrafast *J. Chem. Phys.* **2005**, 123, 064703-064710.
- (41) Malý, P.; Gruber, J. M.; Cogdell, R. J.; Mančal, T.; van Grondelle, R. Ultrafast energy relaxation in single light-harvesting complexes. *Proc. Nat. Acad. Sci. USA.* **2016**, 113, 2934-2942.
- (42) Gelin, M. F.; Egorova, D.; Domcke, W. Strong and Long Makes Short: Strong-Pump Strong-Probe Spectroscopy. *J. Phys. Chem. Lett.* **2011**, 2, 114-119.

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