Simulation of the Two-Dimensional Electronic Spectroscopy and Energy Transfer Dynamics of Light-Harvesting Complex II at Ambient Temperature

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ABSTRACT: We simulate the two-dimensional electronic spectra (2DES) of the light-harvesting complex II (LHCII) at room temperature by combining the hierarchical equations of motion method and the equation-of-motion phase-matching approach. The laser-excited population dynamics of LHCII is also calculated to help understanding the 2DES. Three different excitation schemes are studied, including (1) only the chlorophyll (Chl) b Q states of LHCII are excited, (2) only the Chl a Q states are excited, and (3) both the Chl b and Chl a states are excited. The energy transfer pathways and time scales revealed from the 2DES in schemes (1) and (2) agree with the recent experimental studies for the Chl b to Chl a energy transfer and the excitation energy relaxation process within the Chl a manifold. We also propose a different way to better present the signals of bottleneck states by investigating the diagonal peaks of the 2DES in scheme (3).

1. INTRODUCTION

The initial step of photosynthesis is the absorption of sunlight by the light-harvesting antennas, followed by the excitation energy transfer (EET) to the reaction center, where the consecutive chemical reactions start.1 Under the evolutionary pressure, the EET efficiency in photosynthetic light-harvesting complexes has been developed to achieve near unity quantum efficiency.2,3 Understanding the EET processes in light-harvesting complexes is crucial to reveal their structure–function relationship and to provide promising ideas in developing new renewable energy technologies.4,5 Because the EET processes are usually ultrafast, femtosecond optical spectroscopy is a powerful method for such studies. However, the large number of pigments in the light-harvesting complexes makes it difficult for the traditional transient absorption method to unambiguously isolate the peaks originating from different initially excited states.5

Timely, the two-dimensional electronic spectroscopy (2DES) developed over the past decade6–8 provides a new tool to study the EET dynamics. By adding an extra frequency dimension to resolve both pump and probe frequencies at a given delay time, the 2DES can identify the locations of excitonic states and map the energy flow.4,9–11 Recently, the 2DES has been used to study EET dynamics and quantum coherence phenomena in various light-harvesting complexes, such as the Fenna–Matthews–Olson (FMO) complex from green sulfur bacteria,12–14 the PES45 and PC645 complexes from the marine cryptophyte algae,15–17 the light-harvesting complex 2 (LH2) from purple bacteria,18–20 and the reaction center of photosynthetic system II (PS II)21–23 from higher plants.

In higher plants, the light-harvesting complex II (LHCII) consists over 50% of the world’s chlorophylls.7 High-resolution crystal structures show that24,25 the LHCII complex is a heterotrimERIC system composed of three similar monomeric subunits. Each monomer binds eight chlorophylls a (Chl a), six chlorophylls b (Chl b), and four carotenoids as photoactive cofactors. The 2DES has also been applied to study the EET process in the LHCII complex. Schlau-Cohen et al. first reported the 2DES of LHCII at 77 K.26 By identifying the cross peaks and tracing the peak amplitudes at different waiting times, they observed previously unrecorded sub-100 fs component of the EET dynamics and examined the pathways of energy flow, which are found to agree well with previous theoretical prediction.27 Later, polarized 2DES was employed...
to elucidate the uncoupled transition energies and quantum electronic coherence in LHCII.\textsuperscript{28,29}

The first room-temperature 2DES of LHCII were obtained by Tan and co-workers.\textsuperscript{30} They focused on studying the EET dynamics in LHCII from the Q\(_b\) band of Chl \(b\) to that of the Chl \(a\) by tuning the excitation spectrum to cover only the Q\(_b\) transition of the Chl \(b\) manifold. Three different time scales (0.3, 2.3, and >10 ps) were determined and a bottleneck state was identified, which is in agreement with previous low-temperature 2DES experimental\textsuperscript{36} and theoretical studies.\textsuperscript{27}

Similar methods were also applied to examine the EET dynamics of LHCII aggregates.\textsuperscript{31} Recently, broad band 2DES experiments at ambient temperature were presented by Duan et al.,\textsuperscript{32} in which time scales and pathways of the energy transport were identified with the aid of theoretical simulations using the second-order time nonlocal quantum master equation method. In a recent work, Tan’s group also observed the bidirectional energy flow in the Chl \(a\) manifold in LHCII at physiological temperature using 2DES.\textsuperscript{33}

Theoretical simulations of the EET dynamics and the 2DES are essential to explain the experimental results.\textsuperscript{34–39} In many light-harvesting complexes, the intermolecular electronic coupling and the intramolecular electron-vibrational coupling are similar in strength (i.e., the system is in the intermediate coupling regime), which makes many perturbative theories invalid.\textsuperscript{28,29} In such cases, the nonperturbative hierarchical equations of motion (HEOM) method\textsuperscript{41–44} provides a powerful tool to simulate the EET dynamics\textsuperscript{46,47} and different types of spectroscopic signals.\textsuperscript{48–50} In simulating the 2DES, two different theoretical frameworks are often used: the optical response function approach\textsuperscript{50} and the equation-of-motion phase-matching approach (EOM-PMA).\textsuperscript{51–53} Combined with different methods to simulate the dissipative quantum dynamics, both frameworks have been widely used to simulate the 2DES of light-harvesting complexes.\textsuperscript{32,37–39,54–56}

In this work, we simulate the 2DES and the EET dynamics of the LHCII complex at room temperature. Effects of finite pulse width on the 2DES are considered by combining the HEOM method and the EOM-PMA approach, which is referred as the HEOM-PMA approach in ref 39. Three different laser excitation schemes are considered: (1) only the Q\(_b\) bands of the Chl \(b\) molecules are excited; (2) only the Q\(_b\) bands of the Chl \(a\) molecules are excited; (3) both the Chl \(a\) and Chl \(b\) molecules are excited. The first two schemes correspond to the recent two-color 2DES study of the energy transfer from the Chl \(b\) molecules to Chl \(a\) manifold of LHCII\textsuperscript{30} and the study of excitation energy equilibration process within the Chl \(a\) manifold,\textsuperscript{33} respectively. In the third scheme, the EET process including both the Chl \(b\) and Chl \(a\) manifolds can be investigated.

The remaining sections of this paper are arranged as follows. In Section 2, we briefly present the excitonic Hamiltonian model of LHCII, the HEOM method, and the EOM-PMA approach to simulate the 2D spectra. In Section 3, simulated 2D spectra of LHCII in the above three laser excitation schemes are presented and compared with experimental results. To better understand the 2DES, laser-induced EET population dynamics by the same excitation pulses is also simulated using HEOM. Finally, conclusions and discussions are made in Section 4.

2. THEORETICAL MODEL AND METHODS

The molecular Hamiltonian of the LHCII complex monomer is described by \(N\) two-level chromophores coupled to a phonon bath

\[
H_{\text{mol}} = H_e + H_{\text{ph}} + H_{e-\text{ph}}
\]

Here, the excitonic Hamiltonian \(H_e\) describes the electronic degrees of freedom

\[
H_e = \sum_{m=1}^{N} \epsilon_m a_m^\dagger a_m + \sum_{m=1}^{N} \sum_{n<m} J_{mn} (a_m^\dagger a_n + a_n^\dagger a_m)
\]

where \(\epsilon_m\) is the site energy of the \(m\)th chromophore, \(J_{mn}\) is the interchromophore electronic coupling, and \(a_m^\dagger\) and \(a_m\) are the creation and annihilation operators of the electronic transition on the \(m\)th chromophore.

The vibrational (phonon) degrees of freedom are described by a group of harmonic oscillators, whose Hamiltonian \(H_{\text{ph}}\) is given by

\[
H_{\text{ph}} = \sum_{m=1}^{N} \sum_{j=1}^{N_m} \left( \frac{p_{mj}^2}{2} + \frac{1}{2} \omega_{mj}^2 x_{mj}^2 \right)
\]

where \(N_m\) is the number of vibrational modes belonging to chromophore \(m\), and \(x_{mj}\) and \(p_{mj}\) are the position and momentum of the \(j\)th harmonic oscillator bath mode with frequency \(\omega_{mj}\). The electron–phonon (or electronic-vibrational) coupling term \(H_{e-\text{ph}}\) causes site energy fluctuations that are independent for each chromophore

\[
H_{e-\text{ph}} = \sum_{m=1}^{N} \sum_{j=1}^{N_m} \epsilon_m x_{mj} a_m^\dagger a_m = \sum_{m=1}^{N} F_m a_m^\dagger a_m
\]

where the collective bath coordinate \(F_m\) is defined as \(F_m = \sum_{j=1}^{N_m} \epsilon_m x_{mj}\).

The spectral density \(J_m(\omega)\) is used to characterize electron–phonon interaction on the \(m\)th chromophore, which is defined as

\[
J_m(\omega) = \frac{\pi}{2} \sum_{j=1}^{N_m} \frac{\epsilon_m^2}{\omega_{mj}} \delta(\omega - \omega_{mj})
\]

In this study, the coupling phonon bath spectral density \(J_m(\omega)\) is assumed to be the same for all chromophores and the Debye-type spectral density is used

\[
J(\omega) = \frac{\eta \gamma^2}{\omega^2 + \gamma^2}
\]

which assumes overdamped Brownian motion for the energy gap fluctuations in the classical (high temperature) limit.

To simulate the 2DES, as well as the laser-induced population dynamics, the total Hamiltonian for the molecular system coupled to an electromagnetic field is given by

\[
H = H_{\text{mol}} + H_{\text{int}}
\]

where \(H_{\text{int}}\) describes the interaction between the molecular system and the laser field

\[
H_{\text{int}} = -\mu \cdot E(t)
\]

where \(\mu\) is the total dipole operator that is expressed via the transition dipole moments of individual molecules \(\mu_m\) according to
\[ \mathbf{\mu} = \sum_{m=1}^{N} \mathbf{\mu}_m (a_m + a_m^\dagger) = \mathbf{X} + \mathbf{X}^\dagger \]  

(9)

where

\[ \mathbf{X} = \sum_{m=1}^{N} \mathbf{\mu}_m a_m \]  

(10)

The excitation and probe laser pulses are treated as classical electromagnetic field, and the time-dependent electric field is described as

\[ \mathbf{E}(t) = \sum_{n=1}^{3} [E_n(t - \tau_n) \exp\{-i(\omega_n t - \mathbf{k}_n \cdot \mathbf{r})\} + c.c.\hat{\mathbf{e}}_n] \]  

(11)

where \( E_n(t - \tau_n) \) is the laser pulse profile, \( \omega_n \) is the frequency of the pulse, \( \mathbf{k}_n \) is the wave vector, and \( \hat{\mathbf{e}}_n \) is the unit vector representing the polarization of electric field. In this work, we adopt Gaussian pulse profiles \( E_n(t) = \exp[-4\ln 2 (t - \tau_n)^2/\tau_p^2] \), where \( \tau_p \) is the envelop central time and \( \tau_p \) is the pulse duration defined by full width at half-maximum (FWHM) of the pulse amplitude, corresponding to a FWHM of 4 ln 2/(\pi\tau_p) in the frequency domain.

Accurate simulation of the EET dynamics and related spectroscopic signals is still a challenge in the intermediate interaction regime where the intermolecular coupling and the rephasing signal in the 2DES interaction regime where the intermolecular coupling and the direct interaction between the LHCII complex and the laser field is described as

\[ S_{\omega_s}(\omega_x, T, \omega_x) = \int_{0}^{\infty} \int_{0}^{\infty} \mathbf{X} \cdot \hat{\mathbf{e}}_s [\rho_1(t) - \rho_2(t) - \rho_3(t)] \]  

(12)

Here, \( \langle \cdots \rangle \) denotes the average over the electronic degrees of freedom, \( \mathbf{X} \) is the transition dipole operator defined in eq 10, and \( \hat{\mathbf{e}}_s \) represents the signal orientation, which is assumed to be the polarization vector of the fourth local oscillator pulse. More details of the HEOM-PMA method can be found in ref 39.

The coherence time and population time of 2DES are obtained by \( \tau = \tau_2 - \tau_1 \) and \( T = \tau_1 - \tau_2 \). To calculate the third-order nonrephasing signal \( P^{(3)}_{\omega_s}(t) \), we just exchange the order of the first two laser pulses, i.e., \( \tau = \tau_1 - \tau_2 \). With the prescription for the calculation of \( P^{(3)}_{\omega_s}(t) \) and \( P^{(3)}_{\omega_s}(t) \), the 2D spectrum is then given by double Fourier transform of the photon echo polarization field with respect to \( \tau = t - t_3 \).

\[ S_{\omega_s}(\omega_x, T, \omega_x) = \int_{0}^{\infty} \int_{0}^{\infty} \mathbf{X} \cdot \hat{\mathbf{e}}_s [\rho_1(t) - \rho_2(t) - \rho_3(t)] \]  

(13)

The 2DES and the EET dynamics of the LHCII monomer are simulated using the theoretical methods presented above. In the excitonic Hamiltonian of the LHCII complex, the coupling constants between different pigments are obtained previously by Novoderezhkin et al.27 and the site energies are taken from refs 27 and 32. The parameters for the Debye spectral density in eq 6 are \( \gamma^{-1} = 50 \text{ fs} \) and \( \eta = 100 \text{ cm}^{-1} \). The 50 fs bath relaxation time scale is consistent with the fast dephasing time of 47 fs by recent measurement of the electronic coherence in LHCII.30 The static disorder is assumed to be independent for different chromophores and is described by a Gaussian distribution with a FWHM of 120 cm\(^{-1}\). All of the simulations are performed at 298 K. In the calculation, 1000 averages over the static disorder in site energies and molecular orientations are included.

Figure 1 shows the calculated linear absorption spectra (solid black) and the experimental result (open circles). When the energy is below 15 500 cm\(^{-1}\), the calculated result agrees well with the experimental one. When the energy is greater than 15 500 cm\(^{-1}\), the intensity of the simulated absorption spectra becomes too small compared with the experimental result, which has a vibronic tail and small contributions from the Chl a \( S_0 \) to \( S_1 \) \( (Q_a) \) transition.26,64,65

3.1. EET from Chl b to Chl a Molecules. We first investigate the case where only the Chl b manifold is excited, similar to the recent experiment in ref 30. The excitation pulse,
as shown by the blue dotted curve in Figure 1, is a Gaussian pulse whose center frequency is $15,385 \text{ cm}^{-1}$, with a FWHM of $350 \text{ cm}^{-1}$, corresponding to $42 \text{ fs}$ duration in the time domain. To mimic the experimental setup of the two-color 2DES, the probe pulse is set as a $20 \text{ fs}$ broad band Gaussian with the center frequency at $14,500 \text{ cm}^{-1}$.

Figure 2 shows the calculated 2D spectra at different waiting times $T$. Because the Chl $b$ manifold is not efficiently excited by the excitation pulse, the 2D spectra show only two peaks: the diagonal peak corresponding to the Chl $b$ manifold and the off-diagonal peak corresponding to the energy transfer from the initially excited Chl $b$ to Chl $a$ states. Overall, the simulated two-color 2DES agree well with the experimental results in ref 30, except that the width in the $\omega_p$ direction is significantly smaller than that in the experimental spectra. This is likely due to the shape of Gaussian probe pulse, which is different from the experiment. As shown previously, this difference will cause an asymmetric distortion of the 2D peak shape.

As shown in Figure 2, the Chl $b$ peak gradually becomes weaker and the off-diagonal peak becomes stronger, which indicates the energy transfer from the Chl $b$ to Chl $a$ states. Within the first $2.5 \text{ ps}$, the intensity of the Chl $b$ peak decreases significantly due to the fast energy transfer. The change of the Chl $b$ peak intensity becomes much slower between $T = 2.5$ and $5 \text{ ps}$, indicating that there is a slow component of the excitation energy transfer. Both time scales are consistent with the experimentally measured time scales of $2.3$ and $>10 \text{ ps}$, obtained from global analysis of the 2DES data.

The vertical cuts of the 2DES can be used to analyze the EET dynamics. The vertical slices of the two-color 2DES at the excitation frequency $\omega_\tau = 15,400 \text{ cm}^{-1}$ (which corresponds to the absorption peak of the Chl $b$ manifold) are thus calculated.

Figure 2. Two-color 2DES of the LHCII calculated by HEOM-PMA with different waiting times $T$ at $298 \text{ K}$. The horizontal and vertical axes correspond to the pump frequency $\omega_\tau$ and the probe frequency $\omega_p$, respectively.
and plotted in Figure 3. As the waiting time becomes longer, the Chl $b$ peak decreases and the Chl $a$ peak increases due to energy transfer. The center of the Chl $a$ peak also shifts toward lower frequencies at longer waiting time, indicating that the excitation energy starts to concentrate on the lowest-energy Chl $a$ states. In the curves shown in Figure 3, a small shoulder also develops in the 15 100−15 200 cm$^{-1}$ region, which is an indication of the evolution of intermediate states during the EET process from Chl $b$ to Chl $a$ states.

To better understand the 2DES and the EET process, the laser-excited population dynamics is simulated using the HEOM method and the results are shown in Figure 4. In the simulation, the LHCII monomer is excited by the same laser pulse that is used as the excitation pulse in calculating the 2DES, i.e., a narrow band pulse (42 fs) with center frequency at 15 385 cm$^{-1}$ corresponding to the blue dotted curve in Figure 2. As shown in Figure 4a, the population dynamics of the Chl $b$ manifold can be classified into two categories. The dynamics of b601, b608, and b609 show fast relaxations and equilibrate within about 5 ps. The populations of b605, b606, and b607 relax slowly and equilibrate in about 30 ps. The two time scales origin from the different spatial arrangements of the pigments. The b601, b608, and b609 pigments are on the stromal side and are close to the sink a610, which is also on the stromal side, whereas the b605, b606, and b607 pigments are on the lumenal side.24 The different spatial arrangements of the Chl $b$ pigments thus result in the two major energy transfer pathways in LHCII as revealed by the 2DES experiment at 77 K.26

By comparing the results shown in Figure 4a,b, the energy transfer pathways from the Chl $b$ to Chl $a$ manifolds can be identified. We first focus on the b605, b606, b607, and a604 pigments, which belong to the slow branch. The long-time population dynamics of the three pigments are nearly identical, indicating that they relax via the same pathway. Among all of the pigments in the Chl $a$ manifold, the population dynamics of a604 is very similar to that of the above three pigments at the long times, especially the b605 pigment, indicating that a604 and b605 are the long-lived bottleneck states. At short times within 500 fs, the population dynamics of b606 and a604 are almost opposite, indicating that there is fast energy transfer from b606 to a604. The population dynamics of b607 is similar to that of b606 but with a smaller energy transfer rate to a604.

After 3 ps, a local equilibrium between the b605, b606, b607, and a604 pigments is established and their population dynamics start to show the same behavior. The time scales of Chl $b$ population dynamics coincide with the peak intensity evolution of the two-color 2D spectra, as discussed previously.

For the population dynamics of the Chl $a$ manifold shown in Figure 4b, an obvious feature is that the population of a610 keeps increasing and possesses the largest population at long time, indicating that it is the sink state. The populations of a611 and a612 are similar to those of a610 because they are strongly coupled. The populations of a602 and a603 reach equilibrium faster than a613 and a614, indicating that a602 and a603 belong to the faster energy transfer branch. More details of the energy relaxation within the Chl $a$ manifold are discussed in the next subsection.

Figure 4c shows the sum populations of all of the Chl $b$ and Chl $a$ excited states, which reflect the overall energy transfer from the Chl $b$ manifold to the Chl $a$ manifold. Three time scales of Chl $b$ manifold are identified by fitting the population dynamics.
relaxation to sum of exponentials, which are 0.58, 2, and 11 ps respectively. The last two time scales agree well with the experiment in ref 30, whereas the fastest component is found to be slower than the experimental observation at 0.3 ps. This could be due to the neglect of high-frequency vibrational modes in our model Hamiltonian, which are found to increase the subpicosecond EET rate.67

3.2. EET within the Chl a Manifold. Using a different set of parameters for the excitation and probe pulses, we simulate the case corresponding to the recent 2DES experiment33 in which only the Chl a manifold was excited. In the calculation, the probe pulse is set to be the same as the excitation pulse, which are Gaussian pulses centered at 14 835 cm$^{-1}$ with a time duration of 38 fs, as shown by the red dashed curve in Figure 1. The simulated 2DES at different waiting times are shown in Figure 5. As both the excitation and probe pulses cover only the Chl a manifold, there is only one diagonal peak in the 2DES.33

At early population times ($T \leq 100$ fs) shown in Figure 5a–c, the 2DES are diagonally stretched, which indicates that all of the Chl a states are excited, especially there are clearly signals at high frequencies corresponding to Chl a with higher energy. For the population time at $T = 50$ fs, we observed that the shape of peaks starts to become rounder due to the motion of the vibrational degrees of freedom. With the increase of the waiting time $T$, the peak shapes in the 2DES shown in Figure 5d–f evolve as the result of excitation energy relaxation within the Chl a manifold. The vertical cuts of the 2DES at different excitation frequencies 14 650, 14 800, and 14 950 cm$^{-1}$ at waiting times of 100 fs (Figure 5c) and 12.5 ps (Figure 5f) are plotted in Figure 6a,b. At the early waiting time $T = 100$ fs shown in Figure 6a, the peak centers at different times are clearly different. At longer waiting time $T = 12.5$ ps, the peaks of different slices are the same as shown in Figure 6b, indicating that the signal becomes independent of the excitation frequency.
at the long waiting times. Despite the peak of the black curve (slice at 14 950 cm$^{-1}$) in Figure 6b coincides with other two curves, its shape is still slightly different from that of the other two. Thus, the equilibration among the Chl $a$ manifold completes on a time scale slightly longer than 12.5 ps. The above results also agree well with the experiment.33

The laser-excited population dynamics is then calculated using the HEOM method. The excitation pulse is the same as that used in the calculation of 2DES in Figure 5, and the results are shown in Figure 7. As the laser pulse excites primarily the Chl $a$ manifold, the population of the Chl $b$ states is about 5 times smaller than that of the Chl $a$ states. It can be seen that the a613 and a614 states equilibrate on a fast time scale within about 1 ps. The a602 and a603 states relax with a time scale around 5 ps, and the a604 state equilibrates on a time scale around 15 ps. These results of the subpicosecond and 5 ps time scales agree well with the experimental studies.33 The a611 and a612 states couple strongly with the sink state a610 as their relaxations show rather similar behavior at longer times. In the short-time regime, we also find population oscillations between a611 and a612 up to 400 fs at room temperature. This indicates that they are coupled tightly, such that they can act as efficient bridges to funnel the excitation energy to the sink state at a610 by excitation energy delocalization. However, no oscillations in the peaks of the 2DES are shown in Figure 5. This should be due to the broadening of neighboring peaks.

3.3. Simultaneous Excitation of the Chl b and Chl a Manifolds. As discussed previously, the intermediate states b605 and a604 play an important role in the EET of the slow branch also including b606 and b607. To better present the signals related to the intermediate states, we study a 2DES scheme in which the Chl $b$ and Chl $a$ manifolds are excited simultaneously. In this scheme, both the excitation and probe pulses are the same Gaussian pulse, with the center frequency at 15 100 cm$^{-1}$ and a 20 fs duration time, as shown in the purple dash-dotted line in Figure 1.

The calculated 2DES are shown in Figure 8. At $T = 0$ fs, the 2D spectra are stretched in the diagonal direction due to the inhomogeneous broadening. As the waiting time becomes longer, the cross peak between the Chl $b$ and Chl $a$ manifolds develops, indicating the energy transfer from Chl $b$ to Chl $a$ states. Although the off-diagonal peaks are often used to study EET dynamics, it has been shown in the literature that the diagonal peaks can also be used to study the energy transfer dynamics.10,37,56,57,68 An interesting observation shown in Figure 8 is that the low-frequency tail of the Chl $b$ diagonal peak starts to bend toward the lower right cross peak at $T = 300$ fs, especially in the region from 15 050 to 15 200 cm$^{-1}$.

To better investigate the evolution of the diagonal peaks, the diagonal cuts of the 2DES at different waiting times are plotted in Figure 9. Because intensities of the 2DES peaks decrease with the increase of the waiting time $T$, the diagonal slices are normalized at the peak of the Chl $b$ manifold. Evolution of the peak intensities in Figure 8 shows clearly the energy transferring process from Chl $b$ to Chl $a$ states. The gradual shift of the Chl $a$ peak to the lower frequency side at longer waiting time indicates the energy relaxation process within the Chl $a$ manifold, which is discussed in the previous Section 3.2. A new peak on the left side of the main Chl $b$ peak is clearly seen in Figure 9, which gradually increases with time till $T = 1250$ fs and then decreases. The peak position is consistent
with the excitation energies of b605 and a604. By comparing with the previous results on the energy transfer dynamics in Figure 4a,b, the new peak should be associated with the intermediate states, i.e., the bottleneck states b605 and a604, as shown in Figure 4. The dynamics of the new peak agrees well with the evolution of the off-diagonal peak at \( \omega_t = 15,300 \text{ cm}^{-1} \) and \( \omega_z = 15,000 \text{ cm}^{-1} \) observed in the two-color 2DES experiment,\(^{30}\) which was assigned as signature of the bottleneck state.

### 4. CONCLUSIONS

In conclusion, we have simulated the 2DES of the LHCII complex at room temperature. To help understand the spectroscopic features and time scales in the 2DES, laser-excited population dynamics is also simulated. The energy transfer pathways and time scales revealed in three different excitation and probe schemes are analyzed in detail. The current theoretical study based on a previously developed Hamiltonian model\(^{26,27}\) reproduces most of the EET dynamics observed in the 2DES experiment results presented in refs 30 and 33.

In the first scheme where energy transfer from the Chl b to Chl a manifolds is investigated, two major energy transfer pathways in LHCII are clearly identified. The 2DES signal clearly indicates that b605 and a604 are the bottleneck states for the slow energy transfer branch. The three different time scales obtained from the simulation also agree to those in the two-color 2DES experiment,\(^{30}\) except that the fastest time scale of 580 fs is slower than that of 300 fs determined experimentally, which should be due to the neglect of high-frequency vibrational modes in the current model. Because of the high computational costs, the Hamiltonian model is not
optimized to better match the experimental results. Further refinement of the model parameters, along with the inclusion of high-frequency modes, could be the subject of future works. In the study of excitation energy relaxation within the Chl a manifold, the simulated 2DES, as well as the subpicosecond and 5 ps energy relaxation time scales, are in excellent agreement with the experiment. In our simulation of the laser-excited population dynamics, population oscillations between a611 and a612 up to 400 fs are also observed, which indicate a high efficiency energy transfer sink in the LHCIIs.

Finally, in the third scheme where both the Chl b and Chl a manifolds are excited, we show that signals of the bottleneck transfer pathways involving intermediate processes.

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