Intraband Exciton Transitions in Photosynthetic Complexes Revealed by Novel Five-Wave-Mixing Spectroscopy

Matthias Kizmann, Hari Kumar Yadalam, Vladimir Y. Chernyak, and Shaul Mukamel*





III Metrics & More

ABSTRACT: We calculate the $\chi^{(4)}$ optical response of an oriented photosystem II reaction center of purple bacteria described by the Frenkel exciton model using nonlinear exciton equations (NEE). This approach treats each chromophore as an anharmonic oscillator and provides an intuitive quasiparticle picture of nonlinear spectroscopic signals of interacting excitons. It provides a computationally powerful description of nonlinear spectroscopic signals that avoids complete diagonalization of the total Hamiltonian. Expressions for the second- and the fourth-order nonlinear signals are derived. The NEE have been successfully employed in the past to describe even-order-wave-mixing. Here, we extend them to aggregates with broken inversion symmetries. Even-order susceptibilities require the introduction of permanent



Article Recommendations

dipoles, which allow to directly probe low-frequency intraband transitions of excitons.

1. INTRODUCTION

Nonlinear spectroscopy provides the most valuable information about ultrafast electronic and vibronic dynamics in molecules. Odd-order techniques such as three-wave-mixing $\chi^{(2)}$ (sum- or difference frequency generation) and five-wave-mixing $\chi^{(4)}$ reveal dynamics at interfaces since the signals usually vanish in the bulk.^{1–5} Various four-wave-mixing $\chi^{(3)}$ -techniques have been widely used to study light harvesting in photosynthetic complexes.^{6–8} Recent studies involved the combination of visible and infrared pulses to study electronic and vibrational transitions.^{9–13}

Photosystem II is one of the most prominent photosynthetic light-harvesting complexes and consists of a large protein dimer. It absorbs and transfers sunlight energy to the reaction center, where the excitation energy is converted to chemical potential energy through fast charge separation.¹⁴ The energy transport from the light-harvesting complexes to the reaction center and the charge separation inside the reaction center have been studied by nonlinear spectroscopy. $\chi^{(3)}$ -spectroscopies like photon echoes^{6,8} have been used extensively to study the exciton transport inside the light-harvesting complexes, whereas Stark spectroscopy¹⁵ reveals information about the static dipole moments of individual chlorophyll chromophores.

The theoretical description of nonlinear optical signals of photosynthetic aggregates usually employs the sum-over-state (SOS) approach, where the system is described by its global eigenstate basis. It should be noted that a system of coupled harmonic oscillators is linear; all nonlinear signals vanish. This implies a massive cancellation of a large number of SOS contributions. For the Frenkel exciton model of molecular aggregates, the nonlinear exciton equations (NEE) provide an alternative, more compact description of nonlinear signals, compared to the SOS approach.^{16–18} Here, the system is treated as a collection of anharmonic oscillators such that the cancellation of harmonic contributions is built in from the outset, considerably reducing the number of terms. Alternatively, the same expressions can also be obtained using Green function techniques.¹⁹ For an aggregate consisting of N chromophores, the various contributions in the SOS picture scale as N^2 or N(N-1), while the final response scales as their difference N. The NEE approach has been successfully applied to describe four-wave-mixing in photosynthetic complexes.^{16,20–22}

Five-wave-mixing $\chi^{(4)}$ -processes have received considerably less attention than $\chi^{(3)}$. Like three-wave mixing, these processes only appear in systems with broken inversion symmetry and have been therefore widely used to study electronic and vibrational dynamics at interfaces^{23–25} as well as chiral systems.^{26–28} Stark measurements¹⁵ as well as chiral signatures

Received:August 21, 2023Revised:November 15, 2023Accepted:November 16, 2023Published:December 21, 2023





of photosynthetic complexes^{29–31} suggest that $\chi^{(4)}$ -processes should also be observable. $\chi^{(4)}$ -techniques introduce additional control parameters that may be used to obtain valuable information about the light-harvesting mechanism and refine theoretical models of photosynthetic aggregates.

In this paper, we study the reaction center of photosynthetic bacteria by extending the quasiparticle NEE picture to Frenkel exciton aggregates with broken central inversion symmetry. Breaking the inversion symmetry of the electronic wave functions of the individual chromophores results in permanent dipole moments. By including them in the NEE, we show that they generate even-order susceptibilities, which are responsible for three- and five-wave mixing signals. Three-wave-mixing signals are described by single-exciton Green functions, while five-wave-mixing signals are given by both single-exciton Green functions and an exciton—exciton scattering matrix that describes their interactions. We find that the permanent dipoles lead to an additional, nonlocal, anharmonicity in the NEE, which affects the scattering matrix and the two-exciton resonances.

The permanent dipole transitions of individual chromophores have a vanishing transition frequency and are thus driven by DC fields, and they further couple different excitonic states within the same exciton manifold. $\chi^{(3)}$ -spectroscopic techniques can observe only the effect of the permanent dipoles on the single exciton manifold. We show how intraband transitions in the doubly excited manifold can be studied with sequences of ultrashort pulses by five-wave-mixing signals. Simulations are carried out for the photosystem II reaction center of purple bacteria.

2. NONLINEAR EXCITON EQUATIONS

An aggregate of N two-level chromophores is described by the Frenkel exciton Hamiltonian

$$H = H_0 + H_{d-d} \tag{1}$$

where

$$H_0 = \sum_{n=1}^{N} \hbar \tilde{\Omega}_n B_n^{\dagger} B_n \tag{2}$$

describes the free chromophores and $B_n^{\dagger} = |1\rangle_{nn} \langle 0|(B_n = |0\rangle_{nn} \langle 1|)$ are exciton creation (annihilation) operators at site *n*, which satisfy the Pauli commutations $[B_n, B_m^{\dagger}] = \delta_{nm}(1 - 2B_n^{\dagger}B_n)$. Here, $|0\rangle_n (|1\rangle_n)$ denotes the ground (excited) state of the *n*th chromophore. The chromophores interact via the dipole–dipole coupling

$$H_{\rm d-d} = \sum_{i,j} \mathbf{d}_i^T \beta_{ij} \mathbf{d}_j \tag{3}$$

with the 3 × 3 matrix $\beta_{i,j} = (\mathbb{I} - \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}^T)/r_{ij}^3$. Here, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the *i*th and the *j*th chromophore and $\hat{\mathbf{r}}_{ij}$ is the corresponding unit vector. The dipole vector operator is given by

$$\mathbf{d}_{i} = \boldsymbol{\mu}_{i}^{(01)} (|0\rangle_{ii} \langle 1| + |1\rangle_{ii} \langle 0|) + \boldsymbol{\mu}_{i}^{(00)} |0\rangle_{ii} \langle 0| + \boldsymbol{\mu}_{i}^{(11)} |1\rangle_{ii} \langle 1|$$
(4)

Here, $\boldsymbol{\mu}_{i}^{(01)}$ denotes the transition dipole moment, and $\boldsymbol{\mu}_{i}^{(00)}$ and $\boldsymbol{\mu}_{i}^{(11)}$ are the permanent dipoles in the ground and excited state, respectively. Note that these dipoles vanish for chromophores with inversion symmetry, where the electronic wave functions are eigenfunctions of the parity operator. The



Figure 1. Diagrams depicting the different contributions in the NEE. Time evolves from the past on the left to the future on the right. The left (right) column shows the diagrams where the signal is generated by the transition (permanent) dipole moment, respectively. The dipole moment generating the signal is marked in red. The corresponding equations are given in eq 39 (eq 40), where the diagrams from the top to the bottom correspond to the first until the last term, respectively. Here, the single lines represent the singleexciton Green's function with a forward-pointing arrow denoting $G_{ij}(t-t') = \Theta(t-t') \operatorname{Tr}\{B_j^{\dagger}(t')|g\rangle\langle g|B_i(t)\}\$ and a backward-pointing arrow denoting $G_{ii}^{\dagger}(t-t') = \Theta(t-t') \operatorname{Tr}\{B_i^{\dagger}(t)|g\rangle\langle g|B_i(t')\}$, where $|g\rangle\langle g|$ denotes the ground state of the aggregate. The dashed line denotes either a forward- or backward-pointing arrow, depending on the time-ordering. The black dots denote interactions with the optical fields and transition dipole moments, and the white dots denote interactions with the infrared fields and permanent dipole moments. The gray rectangles with a forward-pointing arrow denote excitonexciton scattering (cf. eq 20) and a backward-pointing arrow denotes complex conjugated scattering.

dipole operator may be alternatively expressed in terms of the excitation operators

$$\mathbf{d}_i = \boldsymbol{\mu}_i (B_i + B_i^{\dagger}) + \boldsymbol{\mu}_i^{(00)} + \boldsymbol{\nu}_i B_i^{\dagger} B_i$$
(5)

with $\mu_i = \mu_i^{(01)}$ and $\nu_i = \mu_i^{(11)} - \mu_i^{(00)}$ represents the difference between the permanent dipoles in the excited and the ground state.

Using eqs 3 and 5, the total Hamiltonian (cf. eq 1) finally assumes the form

$$H = \sum_{mn} \left(h_{mn} B_m^{\dagger} B_n + p_{mn} B_m^{\dagger} B_n^{\dagger} B_m B_n \right)$$
(6)

with

$$h_{mn} = \delta_{mn} (\hbar \tilde{\Omega}_m + 2\sum_k \boldsymbol{\mu}_k^{(00)T} \beta_{km} \boldsymbol{\nu}_m) + 2 \boldsymbol{\mu}_m^T \beta_{mn} \boldsymbol{\mu}_n$$
(7)

$$p_{mn} = \boldsymbol{\nu}_m^T \boldsymbol{\beta}_{mn} \boldsymbol{\nu}_n \tag{8}$$

where we have invoked the rotating wave approximation (RWA), i.e., neglected terms proportional to B_i , B_iB_j , $B_i^{\dagger}B_iB_j$, and their complex conjugates in the dipole–dipole interaction Hamiltonian in eq 3, and further ignored the constant energy shift $2\sum_{mn}\mu_m^{(00)T}\beta_{mn}\mu_n^{(00)}$.

The exciton interaction with classical external fields is given by the Hamiltonian

$$H_{\rm F-Cr} = -\sum_{n=1}^{N} \left(E_n(t) B_n^{\dagger} + \frac{1}{2} \tilde{\mathcal{E}}_n(t) B_n^{\dagger} B_n + \text{h. c.} \right)$$
(9)

where we have also invoked the RWA for the interaction with the transition dipole moments and neglected the coupling of the electric field with the ground state permanent dipole moment since it does not lead to radiation. We denote the interactions with the transition and the difference of permanent dipole moments by $E_n(t) = \mu_n \cdot \mathbf{E}(\vec{r}_n, t)$ and $\tilde{E}_n(t) = \nu_n \cdot \mathbf{E}(\mathbf{r}_n, t)$ +h. c., respectively. This distinction is necessary because of the generally different orientations of the permanent and transition dipole moments. Note that resonant interactions with the permanent dipoles require lower frequency (DC or infrared) fields, while resonant interactions with transition dipole moments involve visible or UV fields.

Even though the permanent dipole of each chromophore is resonant only for DC fields with vanishing frequencies, they lead to resonant transitions with finite frequency fields in the entire aggregate. This can be seen by expressing the deexcitation operators of individual chromophores $B_n =$ $|0\rangle_{nn}\langle 1|$ in terms of the eigenstate deexcitation operators of the aggregate $\mathcal{B}_e = \sum_n U_{en}B_n$, with $U_{en} = \langle e|1\rangle_n$ describing the overlap of the eigenstate *e* of the aggregate with the state where the *n*th chromophore is excited. The sum over the permanent dipoles in the excited states is then given by the operator

$$\sum_{n} \nu_{n} B_{n}^{\dagger} B_{n} = \sum_{e,e'} \nu_{e,e'} \mathcal{B}_{e'}^{\dagger} \mathcal{B}_{e}$$
(10)

with $\nu_{e,e'} = \sum_n U_{ne}^{\dagger} \nu_n U_{en}$. Note that while eq 10 represents transitions within the single-excitation manifold, similar relations can be obtained for higher manifolds. The permanent dipole thus leads to intraband transitions, which can be driven resonantly with the infrared fields. Equation 10 furthermore shows that these transitions only appear as long as the difference between the permanent dipoles in the excited and ground state is finite, which is well known in the DC Stark shift.

The induced transitions within the *n*th excitation band can be investigated by 2n + 1 wave mixing since 2n fields are needed to reach the *n*th excitation manifold and go back to the ground state (or populate the *n*th excitation manifold), and 1 interaction with the permanent dipole can probe an intramanifold transition. $\chi^{(3)}$ -spectroscopies involving permanent dipole transitions can thus reach only the single exciton manifold. Here, we explore intraband transitions in the twoexciton states, as revealed by five-wave-mixing signals. We need to calculate the fourth-order contribution in the electric fields to dipole operator $\mathbf{P}(t) = \sum_n \mathbf{d}_n(t)$

$$\langle \mathbf{P} \rangle^{(4)}(t) = \sum_{i} \boldsymbol{\mu}_{i} \langle B_{i} \rangle^{(4)}(t) + \boldsymbol{\nu}_{i} \langle B_{i}^{\dagger} B_{i} \rangle^{(4)}(t) + \text{h. c.}$$
(11)

Equation 11 can be calculated in the Heisenberg picture using the NEE. For our Frenkel exciton model, the hierarchy of equations can be exactly truncated for three-exciton states and higher because the Hamiltonian in eq 1 is number-conserving (provided non-RWA terms in the dipole–dipole interaction Hamiltonian are neglected). The equations of motion, following from the Heisenberg picture $-i\hbar \frac{d}{dt}B_m = [H, B_m]$, are given by

pubs.acs.org/JCTC

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \left\langle B_{m} \right\rangle = h_{mn} \left\langle B_{n} \right\rangle + \mathcal{U}_{mn,kl} \left\langle B_{n}^{\dagger} \right\rangle Y_{kl} + \mathcal{P}_{mn,kl} \left\langle B_{n}^{\dagger} \right\rangle$$
$$(E_{k}(t) \left\langle B_{l} \right\rangle + E_{l}(t) \left\langle B_{k} \right\rangle) - E_{m}(t) - \tilde{\mathcal{E}}_{m}(t) \left\langle B_{m} \right\rangle$$
$$+ 2\tilde{\mathcal{E}}_{m}(t) \mathcal{P}_{mn,kl} \left\langle B_{n}^{\dagger} \right\rangle Y_{kl}$$
(12)

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \left\langle B_{m}^{\dagger}B_{n} \right\rangle = \tilde{\mathcal{F}}_{mn,kl} \left\langle B_{k}^{\dagger}B_{l} \right\rangle + Y_{mj}^{*} \mathcal{U}_{nj,kl} Y_{kl} - Y_{nj} \mathcal{U}_{mj,kl} Y_{kl}^{*} - E_{n}(t) \left\langle B_{m}^{\dagger} \right\rangle + E_{m}^{*}(t) \left\langle B_{n} \right\rangle + (\tilde{\mathcal{E}}_{m}(t) - \tilde{\mathcal{E}}_{n}(t)) \left\langle B_{m}^{\dagger} \right\rangle \langle B_{n} \rangle + Y_{mj}^{*} \mathcal{P}_{nj,kl} (E_{k}(t) \langle B_{l}^{\dagger} \rangle + E_{l}^{*}(t) \langle B_{k} \rangle) - Y_{nj} \mathcal{P}_{mj,kl} (E_{k}(t) \langle B_{l}^{\dagger} \rangle + E_{l}^{*}(t) \langle B_{k} \rangle)$$
(13)

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} Y_{mn} = (\mathcal{F}_{mn,kl} + \mathcal{U}_{mn,kl}) Y_{kl} - (\delta_{mk}\delta_{nl} - \mathcal{P}_{mn,kl}) (\langle B_k \rangle$$
$$E_l(t) + \langle B_l \rangle E_k(t)) - (\delta_{mk}\delta_{nl} - \mathcal{P}_{mn,kl})$$
$$(\tilde{\mathcal{E}}_k(t) + \tilde{\mathcal{E}}_l(t)) Y_{kl}$$
(14)

with the tetradic matrices

$$\mathcal{F}_{mn,kl} = \delta_{mk} h_{nl} + h_{mk} \delta_{nl} \tag{15}$$

$$\mathcal{U}_{mn,kl} = 2p_{mn}\delta_{mk}\delta_{nl} - \delta_{mn}\mathcal{F}_{mn,kl}$$
(16)

$$\tilde{\mathcal{F}}_{mn,kl} = \delta_{mk} h_{nl} - h_{mk} \delta_{nl} \tag{17}$$

and

$$\mathcal{P}_{mn,kl} = \delta_{nm} \delta_{nk} \delta_{ml} \tag{18}$$

 $Y_{mn} = \langle B_m B_n \rangle$ denotes the double exciton variables. Here, we neglect pure dephasing terms, which allows us to factorize products of excitation operators like $\langle B_m^{\dagger} B_n \rangle = \langle B_m^{\dagger} \rangle \langle B_n \rangle$ and $\langle B_m^{\dagger} B_n B_k \rangle = \langle B_m^{\dagger} \rangle Y_{nk}$ in the source terms on the right-handside. Note that this factorization is not performed for the lefthand side and the first term on the right-hand side of eq 13 since these terms describe the free evolution of the permanent dipole. In eqs 12–14 and hereafter, we adopt the Einstein sum convention, i.e., repeated indices are to be summed over.

These equations of motion can now be solved iteratively for increasing numbers of field interactions. A detailed derivation is provided in Appendix B. Equation 11 shows that the signal can either be generated by the dipole transition operator or the permanent dipole. The respective processes are depicted in the left and right columns in Figure 1 and the solutions are given in eqs 39 and 40. The nonlinear response is formulated in terms of the two-exciton scattering matrix, which satisfies the Bethe–Salpeter equation³²

$$\mathcal{G}(\omega) = \mathcal{G}_0(\omega) + \mathcal{G}_0(\omega)\Gamma(\omega)\mathcal{G}_0(\omega) \tag{19}$$

where $\mathcal{G}(\omega)$ is the two-exciton Green's function and $\mathcal{G}_0(\omega)$ denotes the free two-exciton Green's function of the harmonic system (ignoring the anharmonicities). The scattering matrix thus describes the correction to the free two-exciton Green's function added by the anharmonicities of the chromophores. It can be calculated using eq 38 and is given by



Figure 2. (a) Four temporally well-separated optical pulses followed by an infrared pulse that stimulates the signal are sent into the sample. (b), energy levels of the photosystem II reaction center shown in Figure 3. There are 6 single-exciton eigenstates (*e*) and 15 two-exciton eigenstates (*f*) (c) The pulse sequence and time delays. (d) Three ladder diagrams describing the signal. Blue arrows denote interactions of optical pulses and transitions with the transition dipole moment μ_{i} and the red arrow denotes interaction with infrared pulses via permanent dipole ν_{i} .

$$\Gamma_{mn,kl}(\omega) = [(1 - \delta_{mn})\delta_{mk}\delta_{nl} - (2p_{mn} - \delta_{mn}\omega)\mathcal{G}_{0mn,kl}(\omega)]^{-1} (2p_{kl} - \delta_{kl}\omega)$$
(20)

The interaction between the static dipole moments leads to a nonlocal nonlinearity. Therefore, the scattering matrix is tetradic with size N^2 where N is the number of chromophores in the aggregate. By neglecting the interaction between the static dipole moments p_{mn} , the scattering matrix reduces to the known result¹⁶ for coupled two-level systems, and the matrix scales as $N \times N$

$$\Gamma_{mn,kl}(\omega) = -\delta_{mn}\delta_{kl}\mathcal{G}_{0mm,kk}^{-1}(\omega) \tag{21}$$

3. DETECTING TWO-EXCITON COHERENCES

To observe the role of the permanent dipole transitions in the coherence between the two-exciton states, we focus on the



Figure 3. Photosystem II reaction center complex consists of six chlorophylls and is described by the Frenkel exciton model. The *y*-axis is pointing slightly toward the reader while the *x*-axis is pointing slightly away. Data taken from the 5MDX PDB structure.³⁵

signal generated by the permanent dipole moments (right column in Figure 1 and eq 44). Four temporally well-separated short visible pulses are sent into the sample, and the infrared signal emitted by the permanent dipoles is heterodyned. We focus on the signal stimulated by a fifth infrared pulse in the phase-matching direction $\mathbf{k}_s = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4$, as shown in Figure 2a. The emitted radiation can be alternatively detected in the near-infrared using electro-optic sampling.^{33,34} Figure 2b depicts the energy level scheme for the photosystem II reaction center shown in Figure 3. The delay time variables are listed in Figure 2c. The three ladder diagrams for the signal, using the

RWA, are shown in Figure 2d. Blue arrows involve the transition dipoles, and red arrows involve permanent dipoles. The signal is finally given by

$$S(t_4, t_3, t_2, t_1) = \chi_{mijkl}^{(4)}(t_4, t_3, t_2, t_1) \mathcal{E}_m E_{4,i}^* E_{3,j}^* E_{2,k} E_{1,l}$$
(22)

where $\chi_{mijkl}^{(4)}(t_4, t_3, t_2, t_1)$ denotes the nonlinear response of the reaction center, given in eq 44, and $E_{\alpha,i}$ is the scalar product of the polarization of the α th pulse with the transition dipole moment μ_{ij} and \mathcal{E}_m is the scalar product of the polarization of the measured infrared field with the permanent dipole ν_m .

A Fourier transform over the delay time t_2 reveals twoexciton ω_{fg} resonances and a Fourier transform over the delay time t_4 shows the coherence between different two-exciton $\omega_{ff'}$ and single-exciton $\omega_{ee'}$ states induced by the permanent dipoles. Figure 4 shows the corresponding 2D spectra of an oriented aggregate for different polarization directions of the infrared field

$$W(\Omega_4, \Omega_2) = \int_0^\infty dt_4 dt_2 S(t_4, 0, t_2, 0) e^{i(\Omega_4 t_4 + \Omega_2 t_2)}$$
(23)

Here, we have neglected the effects of permanent dipole interactions on the scattering matrix. Therefore, the remaining anharmonicity is local, and the scattering matrix can be expressed according to eq 21. This approximation is justified due to the weak permanent dipole moments, which lead to low interaction energies that are negligible in comparison to the two-exciton energies. The 2D spectra depict the two-exciton resonances along the y-axis and the intraband coherences along the x-axis. Hamiltonian parameters are given in Table 1 in Appendix A. The number of intraband coherences increases at higher two-exciton frequency Ω_2 , since only downward (in energy) transitions with the permanent dipole moment generate a signal. The dependence of the resonances on the measured polarization direction reveals information about the direction of the permanent dipoles as well as the composition of single and double excitons in terms of the excitations of the individual chromophores. Transitions between two states within the same band are allowed only if both states share at least one common excitation of the same chromophore.

Figure 4 shows that the double- and single-exciton coherences exhibit considerable spectral overlap but always possess the opposite sign of their resonances, depending on their origin from either the first or the last two ladder diagrams in Figure 2d, respectively. This can be seen in peak A in the middle column of Figure 4. The second and third rows in that

pubs.acs.org/JCTC



Figure 4. 2D $\chi^{(4)}$ spectra of the photosystem II reaction center, given by the imaginary part of the signal $\Im\{W(\Omega_4, \Omega_2)\}$ (cf. eq 23). All optical fields are polarized along the *y*-axis, while different polarizations of the infrared field are shown in the columns. Left column: *x*-polarized signal. Ω_2 reveals double-exciton ω_{fg} frequencies (marked as blue lines on the right side) while Ω_4 shows the intraband single-exciton $\omega_{ee'}$ and two-exciton $\omega_{ff'}$ resonances. The aggregate orientation is shown in Figure 3. The first row shows the imaginary part of eq 23, the second row shows the contribution due to the two-exciton $\omega_{ff'}$ intraband transitions (cf. first ladder diagram in Figure 2d), and the third row shows the contributions from the single-exciton $\omega_{ee'}$ intraband transitions (cf. second and third ladder diagram in Figure 2d). Middle column: same but for the *y*-polarized signal. Right column: same but for *z*-polarized signal.



Figure 5. (a) Imaginary part of the diagonal elements of the single-exciton Green function. The *y*-axis shows the single-exciton resonances (black horizontal lines) while the *x*-axis shows the decomposition of the single-excitons into chromophore excitations. Higher single-exciton energies are mostly concentrated on $P_{\rm D1}/P_{\rm D2}$ since those are the most strongly coupled chromophores. (b) Imaginary part of the diagonal elements of the scattering matrix. The black horizontal lines depict the two-exciton resonances. The scattering matrix depicts the interaction between chromophore excitations due to the disallowed double excitation of a single chromophore.

column reveal that this peak is given by the sum of a doubleand single-exciton coherence with opposite sign. The peak possesses the same sign as the single-exciton coherence but changes the sign on its tail due to the contribution of the double-exciton coherence. This behavior can be explained by the shorter lifetimes of the double-exciton states, which lead to smaller but broader double-exciton coherences.

The largest difference between double- and single-exciton coherences is for $\Omega_2 = 30114$ cm⁻¹. The corresponding resonances along Ω_4 are marked as peaks B, C, and D in the middle column of Figure 4. Looking at the spectra for the isolated double- and single-exciton coherences in the second and third rows, respectively, we can identify peaks B and D with double-exciton coherences and peak C with a singleexciton coherence. Note that the single-exciton coherence C shows up along multiple two-exciton resonances since the two contributing single-exciton states can be reached through all of the respective double-exciton states. This difference can be understood by looking at the diagonal elements of the scattering matrix $\mathfrak{F}_{ii}(\omega)$, which describes the anharmonicity of the aggregate, which in our case is given by the fact that double excitations of a single chromophore are disallowed. The scattering matrix is depicted in Figure 5b. Its strongest peaks are located at the central two chromophores and belong to the same two-exciton resonance as peaks B-D in Figure 4. This two-exciton resonance $\omega_{f_{13}} = 30,114 \text{ cm}^{-1}$ lies very close to the sum of the two single-exciton frequencies $\omega_{e_3} = 14,892 \text{ cm}^{-1}$ and $\omega_{e_6} = 15,225 \text{ cm}^{-1}$, $(\omega_{e_3} + \omega_{e_6}) - \omega_{f_{13}} \approx 3 \text{ cm}^{-1}$. One might expect that this double exciton state is mainly given by the direct product of these single exciton states. However, looking at the single-exciton Green's function in Figure 5a shows that



Figure 6. (a) Two-exciton states decomposed in terms of chromophore excitations. The two-exciton states are numbered according to increasing energy. Here, we assumed large energy gaps for doubly excited chromophores, which means that we can disregard these double excitations, leading to a total number of 15 two-exciton states. (b) Two-exciton states decomposed in terms of products of single-exciton states $|e, e'\rangle$. The single-exciton energies are numbered according to increasing energies. The matrix entries are more localized in this representation since chromophore excitation entanglement due to the single-exciton states is hidden in this basis.

these two single-exciton states possess a strong overlap in the central two chromophores, which would lead to disallowed double-excitations. This explains why the scattering matrix also strongly peaks at these chromophores. Consequently, this twoexciton state cannot be described as a direct product of two single excitations and is therefore entangled in the singleexciton decomposition

$$|f_{13}\rangle = \sum_{e,e'} c_{f_{13},e,e'}|e, e'\rangle$$
(24)

where $c_{f_{13},e,e'} < 1$ for all e, e' and $|e, e'\rangle$ denotes the direct product of two single-exciton states. This can also be seen in Figure 6b, which shows the decomposition of the two-exciton resonances in terms of direct products of single-exciton states. The permanent dipole transitions in the two-exciton band can be expressed in terms of the permanent dipole transitions in the single-exciton band through

$$\nu_{ff'} = \sum_{e,e',\tilde{e}} c_{f,e,\tilde{e}} c_{f',e',\tilde{e}}^* \nu_{ee'}$$
(25)

Therefore, the intraband coherences coincide if both f and f' are given by direct products of two single-exciton states. A difference in the behavior of intraband coherences in the double- and single-exciton band thus indicates entanglement of the respective double-exciton states reflected by their decomposition into direct products of single-exciton states.

The polarization dependence of the peaks can reveal information about the relationship of the different permanent dipoles. The single-exciton coherence peak C in Figure 4, for example, results from a transition between the third and sixth single-exciton state (from the bottom). Figure 5a shows that both states are mainly located at the P_{D1} and P_{D2} chromophores. Therefore, the peak intensities for different polarization directions are mainly given by the difference between the permanent dipole moments of chromophores P_{D1} and P_{D2} . The dipole moment directions are given in Table 2 in Appendix A. The same single-exciton coherence also contributes to peak A. Peak A has a contribution from an intraband coherence between the two two-exciton states $\omega_{f_{15}}$ = 30249 cm⁻¹ and ω_{f_0} = 29909 cm⁻¹ and is also mainly given by the difference of the permanent dipoles of the chromophores P_{D1} and P_{D2} . This can be seen by examining the overlap of these two states in Figure 6a. There is a strong overlap at the

two double-excitations P_{D1}/Chl_{D2} and P_{D2}/Chl_{D2} with approximately the same value but opposite sign. Therefore, the permanent dipole contribution from Chl_{D2} cancels out and the difference between the permanent dipoles at P_{D1} and P_{D2} remains. The same polarization dependence can be observed in peak D, which corresponds to the two two-exciton states $\omega_{f_{13}} =$ $30,114 \text{ cm}^{-1}$ and $\omega_{f_2} = 29,672 \text{ cm}^{-1}$. Peak B corresponds to a coherence between the two-exciton states $\omega_{f_{13}} = 30,114 \text{ cm}^{-1}$ and $\omega_{f_9} = 29,909 \text{ cm}^{-1}$ and its polarization dependence is mainly given by the permanent dipoles of the chromophores P_{D1} , P_{D2} , Chl_{D2} , and Pheo_{D2} .

4. CONCLUSIONS

Using the quasiparticle picture represented by the NEE, we calculated the second- and fourth-order susceptibilities of the oriented photosystem II reaction center. Permanent dipole moments in the interaction between chromophores and fields induce intraband transitions that generate infrared signals. The NEE expresses the nonlinear response of molecular aggregates in terms of single-exciton Green functions and exciton—exciton scattering matrices. This treatment avoids diagonalization of the entire system Hamiltonian and is thus computationally advantageous for large aggregates. Additionally, it provides a physical picture of the nonlinear response in terms of scattering quasiparticles.

We have shown how five-wave mixing can be used to reveal the effects of permanent dipole moments on the two-exciton states. Our signals provide information about both the permanent dipole moment directions and the composition of two-exciton states. A difference in the observed behavior between single- and double-exciton coherences emerges due to entanglement in the two-exciton states when decomposed into products of single-exciton states. We considered a sample of oriented molecules. Furthermore, the permanent dipole moments lead to a chiral response of the rotationally averaged samples. The chiral response of molecular aggregates will be a natural extension of this study.

We have focused on the intraband coherences introduced by the permanent dipole moments. The diagrams in Figure 2 could also be used to study two-exciton transport or other twoexciton dynamics like diffusion. Double excitations of single chromophores can be implemented easily in the current formalism.¹⁶ Studying two-exciton coherences where the lower

pubs.acs.org/JCTC

	P_{D1}	$P_{\rm D2}$	Chl _{D1}	Chl _{D2}	Pheo _{D1}	Pheo _{D2}
P_{D1}	15,080	158	-27.3	-41.8	-4	12.6
$P_{\rm D2}$	158	15,015	-46.8	-22	15.1	-3
Chl _{D1}	-27.3	-46.8	14,800	3.5	43.5	-2.2
Chl_{D2}	-41.8	-22	3.5	15,010	2.4	41.7
Pheo _{D1}	-4	15.1	43.5	2.4	14,950	1.5
Pheo _{D2}	12.6	-3	-2.2	41.7	1.5	14,850
^{<i>a</i>} Data taken from (Gelzinis et al. ¹⁵					

Table 1. Hamiltonian Parameters h_{mn} in eq 7 in Wave Numbers cm^{-1a}

two-exciton state is localized at a single chromophore could reveal information about exciton-exciton fusion time-scales which is the first step toward exciton-exciton annihilation. The presented theory could furthermore be extended to the case of weak exciton-phonon coupling and disorder, which will include the effects of transport on the two-exciton manifold. So far, it is not clear whether the NEE¹⁶⁻¹⁸ or the Green function technique¹⁹ is more suitable for this generalization. Including exciton-phonon coupling and disorder will lead to broader intraband coherence peaks due to the increased dephasing times. Comparing the widths to those of the twoexciton coherences can provide additional information about the pure dephasing rates in the two-exciton manifold.

APPENDIX A

Hamiltonian Parameters

Hamiltonian parameters are given in Table 1. Dipole moment directions are given in Table 2.

Table 2. Dipole Moment Directions in D Taken from Gelzinis et al.¹⁵

	μ_x	μ_y	μ_z	$ u_x$	$ u_y$	ν_z
$P_{\rm D1}$	1.08	-3.74	2.05	0.32	-1.07	1.07
$P_{\rm D2}$	-0.66	3.73	2.24	-0.13	1.15	1.15
Chl_{D1}	-0.33	4.06	1.67	0.29	1.34	0.73
Chl_{D2}	0.11	-4.04	1.74	-0.36	-1.31	0.75
Pheo _{D1}	1.65	-0.55	-2.92	0.84	0.10	-0.99
$Pheo_{D2}$	-1.77	0.19	-2.90	-0.89	-0.19	-0.93

APPENDIX B

Solution to the Nonlinear Exciton Equations

Since the molecules are assumed to be initially in the ground state, the zeroth order contribution in the fields to both singleand two-exciton variables vanishes. The first-order contribution to $\langle B_m \rangle$ is given by

$$\langle B_m \rangle^{(1)}(t) = -\int \mathrm{d}\tau G_{mn}(t-\tau) E_n(\tau)$$
⁽²⁶⁾

with the single-exciton Green's function $G_{nm}(t) = -i\Theta(t) \left[\exp\left(-\frac{i}{\hbar}ht\right) \right]_{nm}$. Note that here and in the following Einstein's sum convention is used. Higher-order corrections to the single- and two-exciton variables can now be found iteratively by coupling them to lower-order corrections. All relevant orders are given by

$$\langle B_m \rangle^{(2)}(t) = -\int dt' G_{mn}(t-t') \tilde{\mathcal{E}}_n(t') \langle B_n \rangle^{(1)}(t')$$

$$V^{(2)}(t) = -\int dt' G(t-t') \langle B_n \rangle^{(1)}(t')$$

$$(27)$$

$$V^{(2)}(t) = -\int dt' G(t-t') \langle B_n \rangle^{(1)}(t')$$

$$(27)$$

 \mathcal{O}

(1) (1)

$$\begin{split} Y_{mn}^{(1)}(t) &= -\int dt \left[\mathcal{G}(t-t')(\mathbb{I} - \mathcal{P}) \right]_{mn,kl}(E_{k}(t')\langle B_{l}\rangle^{(1)}(t') (28) \\ &+ (k \leftrightarrow l)) \\ \langle B_{m}\rangle^{(3)}(t) &= \int dt' G_{mn}(t-t')(\mathcal{U}_{nr,kl}\langle B_{r}^{\dagger}\rangle^{(1)}(t')Y_{kl}^{(2)}(t') \qquad (29) \\ &+ \mathcal{P}_{nr,kl}\langle B_{r}^{\dagger}\rangle^{(1)}(t')(E_{k}(t')\langle B_{l}\rangle^{(1)}(t') \\ &+ (k \leftrightarrow l)) \\ &- \int dt' G_{mn}(t-t')(\mathcal{E}_{nr,kl}\langle B_{r}^{\dagger}\rangle^{(1)}(t')Y_{kl}^{(2)}(t') \\ Y_{mn}^{(3)}(t) &= \int dt' [\mathcal{G}(t-t')(\mathbb{I} - \mathcal{P})]_{mn,kl} \qquad (30) \\ &\times (E_{k}(t')(\langle B_{l}\rangle^{(2)}(t') + \tilde{\mathcal{E}}_{k}(t')Y_{kl}^{(2)}(t')) \\ &+ (k \leftrightarrow l)) \\ \langle B_{m}\rangle^{(4)}(t) &= \int dt' G_{mn}(t-t')(\mathcal{U}_{nr,kl}(\langle B_{r}^{\dagger}\rangle^{(2)}(t')Y_{kl}^{(2)}(t') \qquad (31) \\ &+ \langle B_{r}^{\dagger}\rangle^{(1)}(t')Y_{kl}^{(3)}(t')) + \mathcal{P}_{nr,kl} \\ &\times (\langle B_{r}^{\dagger}\rangle^{(2)}(t')(E_{k}(t')\langle B_{l}\rangle^{(1)}(t') + (k \leftrightarrow l))) \\ &+ \langle B_{r}^{\dagger}\rangle^{(1)}(t')\mathcal{P}_{nr,kl} \times \langle B_{r}^{\dagger}\rangle^{(2)}(t')Y_{kl}^{(2)}(t') \\ &- \tilde{\mathcal{E}}_{n}(t')\mathcal{P}_{nr,kl} \times \langle B_{r}^{\dagger}\rangle^{(2)}(t')Y_{kl}^{(2)}(t') \end{split}$$

Here, we have introduced the two-exciton Green's function $\mathcal{G}_{mn,kl}(t) = -i\Theta(t) \left[\exp\left(-\frac{i}{\hbar} (\mathcal{F} + \mathcal{U})t\right) \right]_{nm,kl}$

Equation 27 can be used to express the second-order response as

$$\mathbf{P}^{(2)}(t) = \boldsymbol{\mu}_{m} \iint dt' dt'' G_{mn}(t-t') G_{nk}(t'-t'') \tilde{\mathcal{E}}_{n}(t') E_{k}(t'')$$
(32)

The third-order correction to the single exciton variable can be calculated analogously to the case of four-wave mixing. Combining eqs 29 and 28 and ignoring the last term, we have

$$\langle B_n \rangle^{(3)}(t) = -\int_{-\infty}^{\infty} \mathrm{d}\tau_1 \int_{-\infty}^{\infty} \mathrm{d}\tau_2 G_{nm}(t-\tau_1) \langle B_r \rangle^{(1)}(\tau_1)^* \\ \times \left[\mathcal{U}\mathcal{G}(\tau_1-\tau_2)(\mathbb{I}-\mathcal{P}) - \mathcal{P}\delta(\tau_1-\tau_2) \right]_{mr,kl} \\ (\langle B_k \rangle^{(1)}(\tau_2) E_l(\tau_2) + \langle B_l \rangle^{(1)}(\tau_2) E_k(\tau_2))$$
(33)

To simplify this expression, we introduce the (tetradic) scattering matrix $\Gamma(t)$

$$\int_{-\infty}^{\infty} d\tau \Gamma(t-\tau) \mathcal{G}_0(\tau-t')$$

= $-\mathcal{P}\delta(t-t') + \mathcal{U}\mathcal{G}(t-t')(\mathbb{I}-\mathcal{P})$ (34)

$$\Gamma(\omega)\mathcal{G}_0(\omega) = -\mathcal{P} + \mathcal{U}\mathcal{G}(\omega)(\mathbb{I} - \mathcal{P})$$
(35)

with the zero-order Green's function $\mathcal{G}_{0nm,kl}(t) = iG_{nk}(t)G_{ml}(t)$ describing the two-exciton Green's function of a harmonic system ($\mathcal{U}=0$).

The double-exciton Green's function $\mathcal{G}(\omega)$ can be expressed through the zero-order Green's function $\mathcal{G}_0(\omega)$ using the Dyson series

$$\mathcal{G}(\omega) = \mathcal{G}_0(\omega) + \mathcal{G}_0(\omega)\mathcal{U}\mathcal{G}(\omega) \tag{36}$$

which leads to

$$\mathcal{U}\mathcal{G}(\omega) = (\mathbb{I} - \mathcal{U}\mathcal{G}_0(\omega))^{-1}\mathcal{U}\mathcal{G}_0(\omega)$$
(37)

This result can then be used in eq 35 to calculate the scattering matrix, which is given by

$$\Gamma(\omega) = (\mathbb{I} - \mathcal{U}\mathcal{G}_0(\omega))^{-1}(\mathcal{U} - \mathcal{P}\mathcal{G}_0^{-1}(\omega))$$
(38)

Using the scattering matrix, the five-wave mixing $\chi^{(4)}$ -signal originating from the *m*th transition dipole moment can be obtained from

$$\langle B_{m} \rangle^{(4)}(t) = -\int dt' dt'' d\tau G_{mn}(t-t') \tilde{\mathcal{E}}_{n}(t') G_{nr}(t'-t'') \times \Gamma_{rs,kl}(t''-\tau) \langle B_{s}^{\dagger} \rangle^{(1)}(t'') \times (\langle B_{k} \rangle^{(1)}(\tau) \langle B_{l} \rangle^{(1)}(\tau) + (k \leftrightarrow l)) - \int dt' dt'' d\tau G_{mn}(t-t') \Gamma_{nr,kl}(t'-\tau) \times G_{rs}^{*}(t'-t'') \tilde{\mathcal{E}}_{s}(t'') \langle B_{s}^{\dagger} \rangle^{(1)}(t'') \times (\langle B_{k} \rangle^{(1)}(\tau) \langle B_{l} \rangle^{(1)}(\tau) + (k \leftrightarrow l)) - \int dt' dt'' d\tau G_{mn}(t-t') \Gamma_{nr,kl}(t'-\tau) \times 3 \langle B_{r}^{\dagger} \rangle^{(1)}(t') (\langle B_{k} \rangle^{(1)}(\tau) G_{lq}(\tau-t'') \times \tilde{\mathcal{E}}_{q}(t'') \langle B_{q} \rangle^{(1)}(t'') + (k \leftrightarrow l))] - \int dt' dt'' d\tau d\tau d\tau' d\tau'' G_{mn}(t-t') \Gamma_{nr,kl}(t'-\tau) \times \langle B_{r}^{\dagger} \rangle^{(1)}(t') (\mathcal{G}_{0kl,sr}(\tau-t'') \tilde{\mathcal{E}}_{s}(t'') \times \mathcal{G}_{0sr,pq}(t''-\tau') + (k \leftrightarrow l)(p \leftrightarrow q)) \times \Gamma_{pq,uv}(\tau'-\tau'') (\langle B_{u} \rangle^{(1)}(\tau'') \langle B_{v} \rangle^{(1)}(\tau'') + (u \leftrightarrow v)) - \int dt' dt'' dt''' G_{mn}(t-t') \tilde{\mathcal{E}}_{n}(t') G_{nr}(t'-t'') \times \tilde{\mathcal{E}}_{r}(t'') G_{rs}(t''-t''') \tilde{\mathcal{E}}_{s}(t'') \langle B_{s} \rangle^{(1)}(t''')$$
(39)

The radiation emitted by the *m*th permanent dipole is given by

<

$$B_{m}^{\dagger}B_{m}\rangle^{(4)}(t) = \int dt' d\tau \langle B_{m}\rangle^{(1)}(t) G_{mj}(t-t')\Gamma_{jr,kl}(t'-\tau) \times \langle B_{r}^{\dagger}\rangle^{(1)}(t')(\langle B_{k}\rangle^{(1)}(\tau) \langle B_{l}\rangle^{(1)}(\tau) + (k \leftrightarrow l)) - i\int dt' d\tau dt'' d\tau' G_{mi}^{*}(t-t'')G_{mj}(t-t') \times G_{rs}^{*}(t'-t'')\Gamma_{is,uv}^{*}(t''-\tau') \times (\langle B_{u}^{\dagger}\rangle^{(1)}(\tau') \langle B_{v}^{\dagger}\rangle^{(1)}(\tau') + (u \leftrightarrow v)) \times (\langle B_{p}\rangle^{(1)}(\tau) \langle B_{q}\rangle^{(1)}(\tau) + (p \leftrightarrow q)) + \int dt' dt'' G_{mk}^{*}(t-t'')\tilde{\mathcal{E}}_{k}(t') \langle B_{k}^{\dagger}\rangle^{(1)}(t'') + \int dt' dt'' \langle B_{m}^{\dagger}\rangle^{(1)}(t) G_{mj}(t-t')\tilde{\mathcal{E}}_{j}(t') \times G_{jk}(t'-t'')\tilde{\mathcal{E}}_{k}(t') \langle B_{k}\rangle^{(1)}(t'') + h. c.$$
(40)

The first two terms only contain one interaction with the permanent dipole which generates the signal, the first in the single- and the second in the double-exciton manifold. The last two terms contain three interactions with the permanent dipole moment. The first (second) column in Figure 1 connects the terms of eq 39 (eq 40) to diagrams.

Since the radiation frequency emitted by the transition dipole moments is much higher than that emitted from the permanent dipole moment, both signals can be readily separated by the observed frequency regime. If the generated signal is heterodyned with an infrared field, the contribution from the transition dipole moments in eq 39 can be neglected and the signal is given by

$$\Re\{\mathcal{S}(t_4, t_3, t_2, t_1)\} = \int_{-\infty}^{\infty} \mathrm{d}t \mathbf{E}_{\mathrm{inf}}(t) \cdot \langle \mathbf{P} \rangle^{(4)}(t)$$
(41)

$$= \int_{-\infty}^{\infty} \mathrm{d}t \Re\{\mathcal{E}_m(t) \langle B_m^{\dagger} B_m \rangle^{(4)}(t)\}$$
(42)

where \Re denotes the real part. The phase-matching direction $\mathbf{k}_s = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4$ for the time-ordered pulses is chosen by selecting the terms in eq 40 where the complex conjugated optical fields are the third and fourth pulses in the sequence of optical fields. We obtain

$$S(t_4, t_3, t_2, t_1) = \chi_{mijkl}^{(4)}(t_4, t_3, t_2, t_1) \mathcal{E}_m E_{4,i}^* E_{3,j}^* E_{2,k} E_{1,l}$$
(43)

with

$$\begin{split} \chi_{mijkl}^{(4)}(t_4, t_3, t_2, t_1) &= \int dt_- dt_+ G_{mr}(t_-) \Gamma_{rs,pq}(t_+ - t_-) \\ &\times (G_{mi}^{\dagger}(t_4) G_{sj}^{\dagger}(t_{43} - t_-) \\ &+ (t_4, i) \leftrightarrow (t_{43}, j)) \\ &\times (G_{pk}(t_{42} - t_+) G_{ql}(t_{41} - t_+) \\ &+ (t_{42}, k) \leftrightarrow (t_{41}, l)) \\ &+ \int dt_- dt_+ G_{mr}^{\dagger}(t_-) \Gamma_{rs,pq}^{*}(t_+ - t_-) \\ &\times (G_{pi}^{\dagger}(t_4 - t_+) G_{qj}^{\dagger}(t_{43} - t_+) \\ &+ (t_4, i) \leftrightarrow (t_{43}, j)) \\ &\times (G_{mk}(t_{42} - t_+) G_{sl}(t_{41} - t_+) \\ &+ (t_{42}, k) \leftrightarrow (t_{41}, l)) \\ &+ i \int dt_- dt_+ d\overline{t}_- d\overline{t}_+ G_{mr}^{\dagger}(\overline{t}_-) \\ &\times G_{ms}(t_-) (G_{yx}^{\dagger}(\overline{t}_- - t_-) \\ &- G_{yx}(t_- - \overline{t}_-)) \Gamma_{rx,uv}^{*}(\overline{t}_+ - \overline{t}_-) \\ &\times G_{vj}^{\dagger}(t_{43} - t_+) + (t_{44}, i) \leftrightarrow (t_{43}, j)) \\ &\times (G_{pk}(t_{42} - t_+) G_{ql}(t_{41} - t_+) \\ &+ (t_{42}, k) \leftrightarrow (t_{41}, l)) \end{split}$$

Here, $t_{ij} = t_i + t_{i-1} + ... + t_j$ denotes the sum over time intervals from the *i*th to the *j*th interval, $E_{\alpha,i}$ is the scalar product of the polarization of the α th pulse with the transition dipole moment μ_i and \mathcal{E}_m is the scalar product of the polarization of the measured infrared field with the permanent dipole ν_m .

AUTHOR INFORMATION

Corresponding Author

Shaul Mukamel – Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, California 92614, United States; orcid.org/0000-0002-6015-3135; Email: smukamel@uci.edu

Authors

- Matthias Kizmann Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, California 92614, United States; orcid.org/0000-0001-6014-9622
- Hari Kumar Yadalam Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, California 92614, United States; orcid.org/0000-0001-9340-7683
- Vladimir Y. Chernyak Department of Chemistry, Wayne State University, Detroit, Michigan 48202, United States; Department of Mathematics, Wayne State University, Detroit, Michigan 48202, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jctc.3c00919

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr Jérémy R. Rouxel for useful discussions. V.Y.C. and S.M. gratefully acknowledge the support of the US Department of Energy, Office of Science, Basic Energy Sciences Award DESC0022134. M.K and H.K.Y acknowledge the support of the National Science Foundation (grant CHE-2246379). M.K. acknowledges the support from the Alexander von Humboldt Foundation through the Feodor Lynen program. S.M. is a senior fellow at the Hagler Institute for Advanced Study at Texas AM University.

REFERENCES

(1) Heinz, T. F.; Himpsel, F. J.; Palange, E.; Burstein, E. Electronic transitions at theCaF2/Si(111) interface probed by resonant three-wave mixing spectroscopy. *Phys. Rev. Lett.* **1989**, *63*, 644–647.

(2) Wang, J.; Chen, X.; Clarke, M. L.; Chen, Z. Detection of chiral sum frequency generation vibrational spectra of proteins and peptides at interfaces in situ. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 4978–4983.

(3) Wang, H.-F.; Velarde, L.; Gan, W.; Fu, L. Quantitative Sum-Frequency Generation Vibrational Spectroscopy of Molecular Surfaces and Interfaces: Lineshape, Polarization, and Orientation. *Annu. Rev. Phys. Chem.* **2015**, *66*, 189–216.

(4) Fu, L.; Liu, J.; Yan, E. C. Y. Chiral Sum Frequency Generation Spectroscopy for Characterizing Protein Secondary Structures at Interfaces. J. Am. Chem. Soc. 2011, 133, 8094–8097.

(5) Ge, A.; Inoue, K.-i.; Ye, S. Probing the electrode-solution interfaces in rechargeable batteries by sum-frequency generation spectroscopy. *J. Chem. Phys.* **2020**, *153*, 170902.

(6) Romero, E.; Augulis, R.; Novoderezhkin, V. I.; Ferretti, M.; Thieme, J.; Zigmantas, D.; van Grondelle, R. Quantum coherence in photosynthesis for efficient solar-energy conversion. *Nat. Phys.* **2014**, *10*, 676–682.

(7) Malý, P.; Gruber, J. M.; Cogdell, R. J.; Mančal, T.; van Grondelle, R. Ultrafast energy relaxation in single light-harvesting complexes. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*, 2934–2939.

(8) Duan, H.-G.; Prokhorenko, V. I.; Cogdell, R. J.; Ashraf, K.; Stevens, A. L.; Thorwart, M.; Miller, R. J. D. Nature does not rely on long-lived electronic quantum coherence for photosynthetic energy transfer. *Proc. Natl. Acad. Sci. U.S.A.* **2017**, *114*, 8493–8498.

(9) Oliver, T. A. A.; Lewis, N. H. C.; Fleming, G. R. Correlating the motion of electrons and nuclei with two-dimensional electronic–vibrational spectroscopy. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 10061–10066.

(10) Gaynor, J. D.; Sandwisch, J.; Khalil, M. Vibronic coherence evolution in multidimensional ultrafast photochemical processes. *Nat. Commun.* **2019**, *10*, 5621.

(11) Song, Y.; Konar, A.; Sechrist, R.; Roy, V. P.; Duan, R.; Dziurgot, J.; Policht, V.; Matutes, Y. A.; Kubarych, K. J.; Ogilvie, J. P. Multispectral multidimensional spectrometer spanning the ultraviolet to the mid-infrared. *Rev. Sci. Instrum.* **2019**, *90*, 013108.

(12) Arsenault, E. A.; Bhattacharyya, P.; Yoneda, Y.; Fleming, G. R. Two-dimensional electronic-vibrational spectroscopy: Exploring the interplay of electrons and nuclei in excited state molecular dynamics. *J. Chem. Phys.* **2021**, *155*, 020901.

(13) Nguyen, H. H.; Song, Y.; Maret, E. L.; Silori, Y.; Willow, R.; Yocum, C. F.; Ogilvie, J. P. Charge separation in the photosystem II reaction center resolved by multispectral two-dimensional electronic spectroscopy. *Sci. Adv.* **2023**, *9*, No. eade7190.

(14) Vinyard, D. J.; Ananyev, G. M.; Charles Dismukes, G. Photosystem II: The Reaction Center of Oxygenic Photosynthesis. *Annu. Rev. Biochem.* **2013**, *82*, 577–606.

(15) Gelzinis, A.; Abramavicius, D.; Ogilvie, J. P.; Valkunas, L. Spectroscopic properties of photosystem II reaction center revisited. *J. Chem. Phys.* **2017**, *147*, 115102.

(16) Kühn, O.; Chernyak, V.; Mukamel, S. J. Chem. Phys. 1996, 105, 8586–8601.

(17) Chernyak, V.; Zhang, W. M.; Mukamel, S. Multidimensional femtosecond spectroscopies of molecular aggregates and semiconductor nanostructures: The nonlinear exciton equations. *J. Chem. Phys.* **1998**, *109*, 9587–9601.

(18) Mukamel, S.; Oszwaldowski, R.; Abramavicius, D. Sum-overstates versus quasiparticle pictures of coherent correlation spectroscopy of excitons in semiconductors: Femtosecond analogs of multidimensional NMR. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, 75, 245305.

(19) Chernyak, V.; Wang, N.; Mukamel, S. Four-wave mixing and luminescence of confined excitons in molecular aggregates and nanostructures. many-body green function approach. *Phys. Rep.* **1995**, 263, 213–309.

(20) Meier, T.; Chernyak, V.; Mukamel, S. Multiple Exciton Coherence Sizes in Photosynthetic Antenna Complexes viewed by Pump–Probe Spectroscopy. J. Phys. Chem. B **1997**, 101, 7332–7342. (21) Abramavicius, D.; Voronine, D. V.; Mukamel, S. Doublequantum resonances and exciton-scattering in coherent 2D spectroscopy of photosynthetic complexes. Proc. Natl. Acad. Sci. U.S.A. **2008**, 105, 8525–8530.

(22) Abramavicius, D.; Palmieri, B.; Voronine, D. V.; Sanda, F.; Mukamel, S. Coherent Multidimensional Optical Spectroscopy of Excitons in Molecular Aggregates; Quasiparticle versus Supermolecule Perspectives. *Chem. Rev.* **2009**, *109*, 2350–2408.

(23) Harris, A. L.; Rothberg, L. Surface vibrational energy relaxation by sum frequency generation: Five-wave mixing and coherent transients. J. Chem. Phys. **1991**, *94*, 2449–2457.

(24) Voelkmann, C.; Reichelt, M.; Meier, T.; Koch, S. W.; Höfer, U. Five-Wave-Mixing Spectroscopy of Ultrafast Electron Dynamics at a Si(001) Surface. *Phys. Rev. Lett.* **2004**, *92*, 127405.

(25) Meier, T.; Reichelt, M.; Koch, S. W.; Höfer, U. Femtosecond time-resolved five-wave mixing at silicon surfaces. *J. Phys.: Condens. Matter* **2005**, *17*, S221–S244.

(26) Balakin, A.; Boucher, D.; Fertein, E.; Masselin, P.; Pakulev, A.; Resniansky, A.; Shkurinov, A.; Koroteev, N. Experimental observation of the interference of three- and five-wave mixing processes into the signal of second harmonic generation in bacteriorhodopsin solution. *Opt. Commun.* **1997**, *141*, 343–352.

(27) Romero, L. C. D.; Meech, S. R.; Andrews, D. L. Five-wave mixing in molecular fluids. J. Phys. B: At., Mol. Opt. Phys. 1997, 30, 5609–5619.

(28) Ayuso, D.; Neufeld, O.; Ordonez, A. F.; Decleva, P.; Lerner, G.; Cohen, O.; Ivanov, M.; Smirnova, O. Synthetic chiral light for efficient control of chiral light-matter interaction. *Nat. Photonics* **2019**, *13*, 866–871.

(29) Germano, M.; Shkuropatov, A. Y.; Permentier, H.; de Wijn, R.; Hoff, A. J.; Shuvalov, V. A.; van Gorkom, H. J. Pigment Organization and Their Interactions in Reaction Centers of Photosystem II: Optical Spectroscopy at 6 K of Reaction Centers with Modified Pheophytin Composition. *Biochemistry* **2001**, *40*, 11472–11482.

(30) Georgakopoulou, S.; van der Zwan, G.; Bassi, R.; van Grondelle, R.; van Amerongen, H.; Croce, R. Understanding the Changes in the Circular Dichroism of Light Harvesting Complex II upon Varying Its Pigment Composition and Organization. *Biochemistry* **2007**, *46*, 4745–4754.

(31) Lee, H.; Cheon, S.; Cho, M. Chiroptical nature of two-exciton states of light-harvesting complex: Doubly resonant three-wave-mixing spectroscopy. *J. Chem. Phys.* **2010**, *132*, 225102.

(32) Leegwater, J. A.; Mukamel, S. Exciton-scattering mechanism for enhanced nonlinear response of molecular nanostructures. *Phys. Rev. A: At., Mol., Opt. Phys.* **1992**, *46*, 452–464.

(33) Wu, Q.; Zhang, X.-C. Free-space electro-optics sampling of mid-infrared pulses. *Appl. Phys. Lett.* **1997**, *71*, 1285–1286.

(34) Bakker, H. J.; Cho, G. C.; Kurz, H.; Wu, Q.; Zhang, X.-C. Distortion of terahertz pulses in electro-optic sampling. *J. Opt. Soc. Am. B* **1998**, *15*, 1795–1801.

(35) van Bezouwen, L. S.; Caffarri, S.; Kale, R. S.; Kouřil, R.; Thunnissen, A.-M. W. H.; Oostergetel, G. T.; Boekema, E. J. Subunit and chlorophyll organization of the plant photosystem II supercomplex. *Nat. Plants* **201**7, *3*, 17080.