Time–domain chirally–sensitive three–pulse coherent probes of vibrational excitons in proteins

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Abstract

The third order optical response of bosonic excitons is calculated using the Green’s function solution of the Nonlinear Exciton Equations (NEE) which establish a quasiparticle-scattering mechanism for optical nonlinearities. Both time ordered and non ordered forms of the response function which represent time and frequency domain techniques, respectively, are derived. New components of the response tensor are predicted for isotropic ensembles of periodic chiral structures to first order in the optical wavevector. The nonlocal nonlinear response function is calculated in momentum space, where the finite exciton-exciton interaction length greatly reduces the computational effort. Applications are made to coupled anharmonic vibrations in the amide I infrared band of peptides. Chirally–sensitive and non sensitive signals for α helices and antiparallel β sheets are compared.
I. INTRODUCTION

Calculating the nonlinear optical response of large molecules using conventional sum-over-states expressions is a challenging task since the number of states accessible by multiple quantum excitations increases rapidly with system size [1, 2]. For example, the Frenkel exciton model for $\mathcal{M}$ coupled three level systems has $\mathcal{M}$ one-exciton states and $\mathcal{M} \times (\mathcal{M} + 1)/2$ two-exciton states. Diagonalizing the two-exciton hamiltonian is the bottleneck in numerical simulations. The Nonlinear Exciton Equations (NEE) [3, 4, 5] offer an alternative exact method for computing the exact nonlinear optical response of systems whose Hamiltonian conserve the number of excitons. The NEE establish an exciton scattering mechanism and provide a practical algorithm for computing the third order optical response, totally avoiding the calculation of two-exciton states. The NEE were first developed by Spano and Mukamel [6, 7, 8] and applied for four-wave mixing of coupled two-level [3, 9, 10] and three-level [1, 5, 11, 12] molecules. The local-field-approximation was generalized by adding two-exciton variables which properly account for double quantum resonances. Additional dynamical variables have subsequently been added, allowing to describe population transport via the Redfield equation for the reduced exciton density matrix [13, 14]. The NEE were further extended to particles with arbitrary commutation relations, and to Wannier excitons in semiconductors [4, 13, 16]. We have recently studied the frequency-domain third order susceptibility of isotropic exciton systems and calculated the leading terms of its tensor elements going beyond the dipole approximation [17]. In this paper we apply these results to the time domain response function in a collinear field configuration, which leads to the strongest signals.

The NEE provide a unified treatment of vibrational and electronic excitons. The Frenkel excitons corresponding to electronic excitations are Paulions whose non-Boson operator statistics results in nonlinear hard-core repulsive interactions between excitons. The NEE were originally derived using a Bosonization procedure [6, 7, 8, 13, 18, 19, 20] whereby the Pauli exciton operators are replaced by Boson operators and a repulsive potential is added to the hamiltonian. This results in a soft-core boson model with a finite anharmonicity $\Delta$; the original hard-core boson hamiltonian is recovered by setting $\Delta \to \infty$.

This article focuses on vibrational excitons which are intrinsically bosons [11, 12, 17] and the finite anharmonicities serve as the source of nonlinearities. Third order impulsive optical techniques performed with linearly polarized light (figure 1) are commonly used to probe ultrafast processes in isotropic systems. The corresponding nonlinear response function $S^{(3)}_{\nu_4\nu_3\nu_2\nu_1}$ is a fourth rank tensor [21] which relates the third order polarization, $P^{(3)}(r, t)$, at position $r$ and time $t$ to the optical field $E(r', t')$; $\nu_i = x, y, z$ are the polarization components of the $i$’th laser pulse in the lab frame. In general the response function has $3^4$ tensor elements. For isotropic systems in the dipole approximation, only those elements with $\delta_{\nu_4\nu_3}\delta_{\nu_2\nu_1}$, $\delta_{\nu_4\nu_2}\delta_{\nu_3\nu_1}$, and $\delta_{\nu_4\nu_1}\delta_{\nu_3\nu_2}$ (e.g. xxxx, and zzyy) survive rotational averaging, and three linearly-independent elements xxyy, xyxy and xyyx, are necessary to describe the response for an arbitrary pulse polarization configuration [22, 23]. However, other elements with an odd number of repeating indices (such as xxyy, zzxy), which vanish in this approximation due to isotropic symmetry, appear when the dipole approximation is relaxed. We have recently shown that these elements are chirally-sensitive i.e appear only in chiral molecules (“handed” systems which are distinct from their mirror images [23, 24]), and vanish in racemates, equal mixtures of molecules with opposite sense of chirality.
The dipole approximation implies that the optical electric field is uniform across the molecule, thus, its phase factor \(\exp(i\mathbf{k}\mathbf{r})\), where \(\mathbf{k}\) is the wavevector, does not affect the response and can be set to zero. However, the wavevector does play an important role in the spectroscopy of chiral molecules, where the variation of the phase induces new tensor components of the response function to first order in the wavevector, which vanish in the dipole approximation. The various tensor elements can be probed directly using different time-domain techniques which control the sequences of optical interactions.

The difference in absorption of left- and right-handed circularly polarized light \(^{23, 25, 26, 27}\) known as circular Dichroism (CD) is the simplest example of a wavevector–induced signal and is related to the \(S^{(1)}_{xy}\) elements of the linear response tensor (when the field propagates along \(z\)). The technique is sensitive to molecular structure and is extensively used for protein structure determination both in the UV (180 - 220 nm \(n - \pi^*\) and \(\pi - \pi^*\) transitions) and the IR (1000 - 3500 cm\(^{-1}\) which covers most of the amide vibrational bands) \(^{28, 29, 30, 31, 32}\). Pattern-recognition and decomposition algorithms are used to distinguish between \(\alpha\)-helical and \(\beta\)-sheet formations using electronic \(^{33, 34, 35}\) and vibrational CD \(^{36}\).

Polypeptides often have almost translationally-invariant secondary structures (helices, sheets, strands) which form periodic arrays of localized vibrations. Analyzing secondary structure motifs, thus, provides specific information which can be used for studying globular proteins with different secondary structures. Periodicity can be used to greatly reduce the computational effort, as is the case for electronic excitations in molecular crystals and semiconductor superlattices \(^{16, 37, 38, 39, 40, 41, 42}\). Due to different translational properties of one-exciton and two-exciton states in the Frenkel exciton model, multi-exciton resonances cannot be generally calculated analytically even for infinite periodic systems. The NEE only require the one-exciton states, and yield closed expressions for infinite periodic systems, where translational symmetry helps reduce the problem size even further. Relaxing the dipole approximation using the NEE, is straightforward. The CD spectra of molecular aggregates modelled as collections of coupled electric dipoles were calculated to first order in wavevectors \(^{43}\). This model has been applied to biological light harvesting antennae and cylindrical aggregates \(^{44, 45}\). By extending this procedure to the nonlinear response we obtain the complete set of tensor elements for the response function of infinite periodic systems.

In section II we present the time-domain expressions for the third order optical response. The hamiltonian and the NEE for vibrational excitons are given in section III and the third order response function is derived in section IV. Two techniques for probing one-exciton and two-exciton resonances are discussed in section V. The two-dimensional infrared frequency correlation signals of two typical structural motifs of polypeptides: the one-dimensional \(\alpha\) helix and the two-dimensional antiparallel \(\beta\) sheet (figure 1) in the amide I region (1550 - 1750 cm\(^{-1}\)) are compared. The results are discussed in section VI. The linear absorption is calculated in appendix A. Rotational averages for isotropic systems are given in appendix B. The nonlinear signals are calculated in appendices C (four-wave mixing in various phase matching directions) and D (pump-probe). The frequency domain signal is given in appendix E and the exciton scattering matrix for an infinite periodic system is presented in appendix F.
II. TIME–DOMAIN OPTICAL RESPONSE OF EXCITONS

The optical response of molecules is determined by the induced polarization, which serves as the source in the Maxwell equations for the generated signal field. The response functions $S_{\nu_{n+1}\nu_n...\nu_1}^{(n)}$ are system property-tensors which allow to calculate the induced polarization for an arbitrary incoming pulse configuration $(1)$:

$$P_{\nu_{n+1}}^{(n)}(x_{n+1}) = \sum_{\nu_{n},...\nu_1} \int dx_{n}...\int dx_{1} S_{\nu_{n+1}\nu_n...\nu_1}^{(n)}(x_{n+1},x_{n}...x_{1})E_{\nu_{n}}(x_{n})...E_{\nu_1}(x_{1}).$$

Here $E$ is the optical electric field vector and $\nu = x, y, z$ denote its Cartesian components in the lab frame; $x = (r, t)$ is the space-time vector and $\int dx \equiv \int dr \int dt$, where the $r$ integration runs over the molecular volume, while the $t$ integration is from $-\infty$ to $+\infty$. $x$ represent the times and coordinates of the interaction with the optical pulses.

Using causality $S^{(n)}$ vanishes unless $t_1 \ldots t_n$ precede $t_{n+1}$ for all $n$. We focus on time-domain experiments where the interaction sequence is controlled by short optical pulses and the time-ordered response function is finite for $t_{n+1} > t_n > ... > t_2 > t_1$ and vanish otherwise as shown in figure $2a$. Alternatively we can require that the response function to be symmetric with respect to permutation of $\nu_j x_j$, $j = 1, 2, 3$. This non-time-ordered response function, which is useful for frequency domain techniques is given in appendix $E$.

The linear polarization is given by:

$$P_{\nu_2}^{(1)}(x_2) = \sum_{\nu_1} \int dx_{1} S_{\nu_2\nu_1}^{(1)}(x_2, x_1)E_{\nu_1}(x_1),$$

where $S_{\nu_2\nu_1}(x_2, x_1)$ is the nonlocal linear response function. $S^{(1)}$ is responsible for linear absorption (local response; see appendix $A$ and CD (non local response). Four wave mixing (4WM) signals are described by the third order polarization

$$P_{\nu_4}^{(3)}(x_4) = \sum_{\nu_3\nu_2\nu_1} \int dx_3 \int dx_2 \int dx_1 S_{\nu_4\nu_3\nu_2\nu_1}^{(3)}(x_4, x_3, x_2, x_1)E_{\nu_3}(x_3)E_{\nu_2}(x_2)E_{\nu_1}(x_1).$$

We assume three short well-separated incoming pulses:

$$E_{\nu}(x) = \frac{1}{2} \sum_{s=1}^{3} \tilde{E}_{\nu}^{(s)}(t - t_s) \exp(i k_s r - i \omega_s (t - t_s) + i \phi_s) + c.c.,$$

where $\tilde{E}_{\nu}^{(s)}(t - t_s)$ is the (real) envelope of pulse $s$ centered at $t_s$, with wavevector $k_s$, carrier frequency $\omega_s$ and phase $\phi_s$. When the pulses are much shorter than the relevant molecular timescale, $\tilde{E}_{\nu}(t - t_s)$ in eq. (2) can be approximated as $E_{\nu}^{(s)}(t - t_s)$. Since the pulses are longer than the optical periods we must then invoke the rotating wave approximation - RWA and only retain $S^{(3)}$ terms resonant with optical fields which fall within the pulse bandwidth $\tilde{\omega}_s$ [46]. In this approximation the field amplitude in the frequency domain is taken to have a rectangular shape centered at $\omega_s$ with width $\tilde{\omega}_s$. We next assume that the pulses are temporally well separated and ordered, i. e. the first pulse $\tilde{E}^{(1)}$ interacts at $t_1$, followed by $\tilde{E}^{(2)}$ at $t_2$ and the last pulse is $\tilde{E}^{(3)}$ at $t_3$. The third order polarization is then given by

$$P_{\nu_4}^{(3)}(x_4) = \exp(\pm i \phi_3 \pm i \phi_2 \pm i \phi_1)$$
signal wavevectors $\mathbf{k}$ space-time Fourier transform $F(\mathbf{k}, \omega) = \int dt \int d\mathbf{r} \exp(i\omega t + i\mathbf{k}\mathbf{r}) F(\mathbf{r}, t)$.

When the system is initially at equilibrium, the response function is time translationally invariant and only depends on the positive time intervals $T_s \equiv t_{s+1} - t_s$ (see figure 2). Space translational invariance for isotropic systems implies $\mathbf{k}_4 = \mp \mathbf{k}_3 \mp \mathbf{k}_2 \mp \mathbf{k}_1$. We thus denote $\mathbf{P}^{(3)}_{\nu_4}(-\mathbf{k}_4, t_4) \equiv \mathbf{P}^{(3)}_{\nu_4}(T_3, T_2, T_1)$ with $\mathbf{k}_S \equiv -\mathbf{k}_4$. There are four independent signal wavevectors $\mathbf{k}_S$: $\mathbf{k}_I = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$, $\mathbf{k}_{II} = +\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$, $\mathbf{k}_{III} = +\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$ and $\mathbf{k}_{IV} = +\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$.

### III. THE NEE FOR VIBRATIONAL EXCITONS

The amide vibrations of polypeptides can be modeled as $N$ coupled anharmonic vibrational modes localized at the peptide bonds and described by the exciton Hamiltonian:

$$
\hat{H} = \sum_m \varepsilon_m \hat{B}_m^\dagger \hat{B}_m + \sum_{m \neq n} J_{m,n} \hat{B}_m^\dagger \hat{B}_n 
+ \sum_{mn,m'n'} U_{mn,m'n'} \hat{B}_m^\dagger \hat{B}_n^\dagger \hat{B}_{m'} \hat{B}_{n'} - \int d\mathbf{r} \hat{\mathbf{P}}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}, \tau).
$$

The creation, $\hat{B}_m^\dagger$, and annihilation, $\hat{B}_m$, operators for mode $m$ satisfy the boson $[\hat{B}_m, \hat{B}_m^\dagger] = \delta_{mn}$ commutation relations. The first two terms represent the free-boson harmonic hamiltonian where $\varepsilon_m$ is the frequency of mode $m$, and the quadratic intermode coupling, $J_{m,n}$, is calculated in the Heitler-London approximation where off resonant $\hat{B}_m^\dagger \hat{B}_n^\dagger$ and $\hat{B}_m \hat{B}_n$ terms are neglected. The third term represents a quartic anharmonicity. We assume a pairwise anharmonic interaction, $U_{mn,m'n'} = \frac{\Delta_{mn}}{4}(\delta_{mn} \delta_{n'n'} + \delta_{m'n} \delta_{nm'})$, where $\Delta_{mn}$ is the on-site anharmonicity of the overtone band and $\Delta_{nm}$ is the intermode anharmonicity of the combination band. These anharmonicities constitute the exciton-exciton scattering potential. For $\Delta = 0$ the hamiltonian describes free bosons, which is a linear system whose nonlinear response vanishes identically [1]. The fourth term in the hamiltonian represents the interaction with the optical field $\mathbf{E}(\mathbf{r}, t)$, where

$$
\hat{\mathbf{P}}(\mathbf{r}) = \sum_m \delta(\mathbf{r} - \mathbf{r}_m) \mathbf{\mu}_m (\hat{B}_m^\dagger + \hat{B}_m)
$$

is the polarization operator and $\mathbf{\mu}_m$ is the transition dipole moment of mode $m$ located at $\mathbf{r}_m$; a vector with components $(\mathbf{\mu}^x_m, \mathbf{\mu}^y_m, \mathbf{\mu}^z_m)$.

The expectation value of the polarization operator which describes the vibrational response to the optical field will be calculated by solving the NEE [3, 4, 7]. This hierarchy of equations of motion for exciton variables may be exactly truncated order by order in the field since the molecular hamiltonian conserves the number of excitons, and the optical field creates or annihiilates one exciton at a time. When pure-dephasing is neglected, the only required variables for the third order response are $B_m = \langle \hat{B}_m \rangle$ (one-exciton) and $Y_{mn} = \langle \hat{B}_m \hat{B}_n \rangle$ (two-exciton) and the NEE read [3, 4]:

$$
-i \frac{\partial B_m}{\partial \tau} + \sum_n h_{m,n} B_n = \tilde{\mu}_m(\tau) - \sum_{l'm'n'} V_{m'l'n'} B_{l'} Y_{m'n'},
$$

where $\tilde{\mu}_m(\tau)$ and $\mathbf{k}_m$ now coincide with the central pulse times and wavevectors and we have applied the space-time Fourier transform $F(\mathbf{k}, \omega) = \int dt \int d\mathbf{r} \exp(i\omega t + i\mathbf{k}\mathbf{r}) F(\mathbf{r}, t)$.
\[-i \frac{\partial Y_{mn}}{\partial \tau} + \sum_{m' n'} (h^{(Y)}_{mn, m'n'} + V_{mn, m'n'}) Y_{m'n'} = \tilde{\mu}_m(\tau) B_n + \tilde{\mu}_n(\tau) B_m. \]  

(9)

Here $h_{m,n} = \delta_{m,n}\varepsilon_m + J_{m,n}(1 - \delta_{m,n})$ is an effective one-exciton hamiltonian, $h^{(Y)}_{mn, m'n'} = \delta_{m',m}\varepsilon_{n'} + \delta_{n,n'}\varepsilon_{m'}$ is a free-two-exciton hamiltonian, $V_{mn, m'n'} = U_{mn, m'n'} + U_{nm, m'n'} = \frac{\Delta_{m,n}}{2}(\delta_{m,n}\delta_{m'n'} + \delta_{m'n}\delta_{m,n'})$ is the anharmonicity matrix and $\tilde{\mu}_m(\tau) = \mu_m \cdot E(r_m, \tau)$ (for the actual times we use $\tau$ instead of $t$ which were defined as time-ordered).

The polarization is given by the expectation value of eq. (7):

\[ P(r, \tau) = \sum_m \delta(r - r_m) \mu_m B_m(\tau) + \text{c.c.} \]  

(10)

The nonlinearities in these equations originate from the anharmonicity: as indicated earlier, for $V = 0$ eq. (8) is linear, and the nonlinear response vanishes (the two-exciton variable can be exactly factorized as $Y_{mn} = B_mB_n$ in eq. (9)).

The evolution of a single-exciton created by an impulsive excitation, $B_m^{(1)}(\tau)$, is described by the one-exciton Green’s function $G(\tau)$:

\[ B_m^{(1)}(\tau) = \sum_{m'} G_{m,m'}(\tau) B_m^{(1)}(0), \]  

(11)

which satisfies the equation:

\[ \frac{dG_{m,n}(\tau)}{d\tau} + i \sum_{n'} h_{m,n'} G_{n',n}(\tau) = \delta(\tau). \]  

(12)

This equation can be solved using the one-exciton eigenenergies, $e_\xi$, and eigenvectors, $\psi_\xi_m$:

\[ \sum_n h_{m,n} \psi_\xi_n = e_\xi \psi_\xi_m. \]  

(13)

We then get

\[ G_{m,n}(\tau) = \sum_\xi \psi_\xi_m I_\xi(\tau) \psi_\xi_n, \]  

(14)

where

\[ I_\xi(\tau) = \theta(\tau) \exp(-i e_\xi \tau - \gamma_\xi \tau), \]  

(15)

$\gamma_\xi$ is a dephasing rate of the $\xi$ exciton state, and the Heavyside step function ($\theta(\tau) = 0$ for $\tau < 0$ and $\theta(\tau) = 1$ for $\tau \geq 0$) guarantees causality.

Similarly we define the two-exciton Green’s function $G^Y$:

\[ Y_{mn}(\tau) = \sum_{m' n'} G^Y_{mn, m'n'}(\tau) Y_{m'n'}(0), \]  

(16)

whose equation of motion:

\[ \frac{dG^Y_{mn, m'n'}(\tau)}{dt} + i \sum_{m'' n''} (h^{(Y)}_{mn, m''n''} + V_{mn, m''n''}) G^Y_{m'n'', m'n'} = \delta(\tau). \]  

(17)
\( G^V \) is connected to the zero-order noninteracting \((V = 0)\) two-exciton Green’s function \( G \) by the Bethe-Salpeter equation

\[
G^V(\tau) = G(\tau) + \int_0^\tau d\tau' \int_0^{\tau'} d\tau_1 G(\tau - \tau') \Gamma(\tau' - \tau_1) G(\tau_1),
\]

which defines the two exciton scattering matrix \( \Gamma \). Both the two-exciton Green’s function and the scattering matrix are tetradic matrices; like \( G(\tau) \), the scattering matrix is causal as well. \( G \) can be factorized into a product of one-exciton Green’s functions,

\[
G_{mn,m'n'}(\tau) = G_{m,m'}(\tau) G_{n,n'}(\tau).
\]

The frequency domain scattering matrix \( \Gamma(\omega) \) obtained by the Fourier transform, \( \Gamma(\omega) = \int dt \exp(i\omega t) \Gamma(t) \), is calculated in appendix F:

\[
\Gamma(\omega) = -iV(1 + iG(\omega)V)^{-1}.
\]

where

\[
G_{mn,m'n'}(\omega) = \sum_{\xi\xi'} \psi_{\xi m}(\omega) \psi_{\xi'n'}(\omega) \psi_{\xi m'}(\omega) \psi_{\xi'n'}(\omega),
\]

with

\[
\mathcal{I}_{\xi\xi'}(\omega) = \frac{i}{\omega - E_\xi - E_{\xi'} + i(\gamma_\xi + \gamma_{\xi'})}.
\]

Calculating the scattering matrix requires the inversion of the matrix \( D = 1 + iG(\omega)V \) whose matrix elements:

\[
D_{mn,ij}(\omega) = \delta_{mi} \delta_{nj} + i \sum_{m'n'} G_{mn,m'n'}(\omega) V_{m'n',ij}.
\]

The required numerical effort can be reduced considerably for periodic systems and when the short range nature of anharmonicities is taken into account.

IV. THE NONLINEAR OPTICAL RESPONSE: GREEN’S FUNCTION SOLUTION OF THE NEE

The nonlinear response is calculated by an order-by-order expansion of the NEE variables in the field using the exciton Green’s functions, where the optical field and the lower order variables serve as the sources. Setting \( B_m = B_m^{(1)} + B_m^{(2)} + B_m^{(3)} + \ldots \) and \( Y_{mn} = Y_{mn}^{(1)} + Y_{mn}^{(2)} + Y_{mn}^{(3)} + \ldots \) we get to third order:

\[
B_{n_4}^{(3)}(\tau_4) = \sum_{n_1 n_2 n_3 n'_1 n'_2 n'_3} \mathcal{I}_{n_1 n_2 n_3} \mathcal{I}_{n'_1 n'_2 n'_3} \sum_{\tau_2 - \tau_1} \Gamma_{n_1 n'_1, n_2 n'_2, n_3 n'_3} (\tau'' - \tau')
\]

\[
\times G_{n_4,n'_4} (\tau_4 - \tau') G_{n_3,n'_3} (\tau'' - \tau_3) G_{n'_2,n_2} (\tau' - \tau_2) G_{n'_1,n_1} (\tau' - \tau_1)
\]

\[
\times \mu_{n_3}(\tau_3) \mu_{n_2}(\tau_2) \mu_{n_1}(\tau_1),
\]
The $\tau'$ and $\tau''$ variables denote the times of the first and the last exciton-exciton interaction respectively, as shown in figure 2a. The third order polarization is finally obtained from eqs. 10 and 24:

$$\mathbf{P}_{\nu_4}^{(3)}(r_4, r_1) = 2i \int dr_3 \int dr_2 \int dr_1 \int_{-\infty}^{\infty} d\tau_3 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_1$$

$$\sum_{n_4 \neq n_2 \neq n_1} \langle \mathbf{M}_{n_4 n_3 n_2 n_1}^{\nu_4 \nu_3 \nu_2 \nu_1}(r_4, r_3, r_2, r_1) \rangle$$

$$\times \int_{-\infty}^{\infty} d\tau'' \int_{-\infty}^{\infty} d\tau' \sum_{n_4' \neq n_3' \neq n_1'} \theta(\tau_2 - \tau_1) \Gamma_{n_4' n_3' n_2 n_1'}(\tau'' - \tau')$$

$$\times G_{n_4, n_4'}(\tau_4 - \tau'')G_{n_3', n_3}(\tau'' - \tau_3)G_{n_2, n_2'}(\tau'' - \tau_2)G_{n_1', n_1}(\tau'' - \tau_1)$$

$$\times E_{\nu_4}(r_3 \tau_3)E_{\nu_3}(r_2 \tau_2)E_{\nu_1}(r_1 \tau_1) + c.c.,$$

(24)

where

$$\mathbf{M}_{n_4 n_3 n_2 n_1}^{\nu_4 \nu_3 \nu_2 \nu_1}(r_4, r_3, r_2, r_1) = \delta(r_4 - r_{n_4}) \delta(r_3 - r_{n_3}) \delta(r_2 - r_{n_2}) \delta(r_1 - r_{n_1})$$

$$\times \mu_{\nu_4}^{\nu_1} \mu_{\nu_3}^{\nu_2} \mu_{\nu_2}^{\nu_1},$$

(25)

"c.c" is the complex conjugate and $\langle \ldots \rangle$ denotes rotational averaging (appendix 3). It is important to note that unlike $t_1$, $t_2$ and $t_3$, the integration variables $\tau_1$, $\tau_2$ and $\tau_3$ do not have any particular time ordering.

Since the Green’s functions are retarded (i. e. they vanish for negative time arguments) only three sequences of interaction times contribute to eq. 24: i) $\tau_3 > \tau_1 > \tau_3$, ii) $\tau_2 > \tau_3 > \tau_1$, iii) $\tau_3 > \tau_2 > \tau_1$. In each case we switch to a different set of time-ordered variables: i) $t_4 = \tau_4$, $t_3 = \tau_2$, $t_2 = \tau_1$, $t_1 = \tau_3$, ii) $t_4 = \tau_4$, $t_3 = \tau_2$, $t_2 = \tau_3$, $t_1 = \tau_1$, iii) $t_4 = \tau_4$, $t_3 = \tau_2$, $t_2 = \tau_3$, $t_1 = \tau_1$ (figure 2b). Eq. 3 together with eq. 24 then result in the following three contributions to the response function:

$$S_{\nu_4 \ldots \nu_1}^{(3)}(x_4, \ldots, x_1) = S_{\nu_4 \ldots \nu_1}^{(I)}(x_4, \ldots, x_1)$$

$$+ S_{\nu_4 \ldots \nu_1}^{(II)}(x_4, \ldots, x_1)$$

$$+ S_{\nu_4 \ldots \nu_1}^{(III)}(x_4, \ldots, x_1) + c.c.$$  

(26)

Each term now corresponds to one particular interaction sequence ($S^{(I)}$ is obtained from (i), $S^{(II)}$ – from (ii) and $S^{(III)}$ – from (iii)). These are given by:

$$S_{\nu_4 \ldots \nu_1}^{(I)}(x_4, \ldots, x_1) = 2i \sum_{n_4 \ldots n_1} \langle \mathbf{M}_{n_4 n_3 n_2 n_1}^{\nu_4 \nu_3 \nu_2 \nu_1}(r_4, r_3, r_2, r_1) \rangle$$

$$\times \int_{0}^{t_{43}} d\tau'' \int_{0}^{t_{\nu_4 \nu_5 \nu_2 \nu_1}} d\tau' \sum_{n_4' \neq n_3' \neq n_2'} \Gamma_{n_4' n_3' n_2' n_1'}(\tau'' - \tau')$$

$$\times G_{n_4 n_4'}(\tau_4 - \tau'')G_{n_3' n_3}(t_{43} - \tau''\nu_5)G_{n_2' n_2}(t_{42} - \tau'' \nu_1)G_{n_1' n_1}(t_{41} - \tau'),$$

(27)

$$S_{\nu_4 \ldots \nu_1}^{(II)}(x_4, \ldots, x_1) = 2i \sum_{n_4 \ldots n_1} \langle \mathbf{M}_{n_4 n_3 n_2 n_1}^{\nu_4 \nu_3 \nu_2 \nu_1}(r_4, r_3, r_2, r_1) \rangle$$

$$\times \int_{0}^{t_{43}} d\tau'' \int_{0}^{t_{\nu_4 \nu_5 \nu_2 \nu_1}} d\tau' \sum_{n_4' \neq n_3' \neq n_2'} \Gamma_{n_4' n_3' n_2' n_1'}(\tau'' - \tau')$$

$$\times G_{n_4 n_4'}(\tau_4 - \tau'')G_{n_3' n_3}(t_{43} - \tau'' \nu_5)G_{n_2' n_2}(t_{42} - \tau'' \nu_1)G_{n_1' n_1}(t_{41} - \tau''),$$

(28)
Here $\tau_s'$ denotes the time interval between the polarization detection and first exciton scattering event, while $\tau_s''$ denotes the interval between the detection and the last exciton scattering event, as shown in figure 2b. Using these time-ordered expressions we can switch to new variables representing the time intervals between interactions $t_{ij} = t_i - t_j$ with $i > j$: $t_{43} = T_3$, $t_{42} = T_3 + T_2$, $t_{41} = T_3 + T_2 + T_1$. Thus, all terms in the response function only depend on these three positive time intervals. So far, the three terms in the response function merely represent different time orderings in the integrations, however, we will shortly see that they represent distinct optical signals.

The time intervals in eqs. (27-29) and their relations to the actual interaction times are depicted in figure 2. The response can be interpreted using figure 2c: Let us consider the interval between the detection and the last exciton scattering event, as shown in figure 2a. Using these time-intervals $s$ and $s'$, with $s' > s$, we use the RWA and express the nonlinear polarization for the signal wavevectors $\nu_1, \nu_2, \nu_3$ and $\nu_4$ where all pulses are resonant with the one-exciton manifold, we select the resonances in the response functions (eqs. (27)-(29)) to the wavevectors and times of the optical pulses. Assuming that the carrier frequencies of all pulses are resonant with the one-exciton manifold, we select the resonances in the response functions using the RWA and express the nonlinear polarization for the signal wavevectors $\nu_1, \nu_2, \nu_3$ and $\nu_4$. To find out the wavevector dependence we transform eqs. (27-29) to momentum space using $F(k) = \int dr F(r) \exp(ikr)$. Then:

$$P^{\nu_4}_{\nu_1}(T_3, T_2, T_1) = \frac{1}{23} \exp(+i\phi_3 + i\phi_2 - i\phi_1)$$

$$\times \sum\sum S^k_{\nu_1 \nu_2 \nu_3 \nu_4} (T_3, T_2, T_1) E^{(3)}_{\nu_3} E^{(2)}_{\nu_2} E^{(1)}_{\nu_1},$$

(30)

$$P^{\nu_4}_{\nu_1}(T_3, T_2, T_1) = \frac{1}{23} \exp(+i\phi_3 - i\phi_2 + i\phi_1)$$

$$\times \sum\sum S^{k}_{\nu_1 \nu_2 \nu_3 \nu_4} (T_3, T_2, T_1) E^{(3)}_{\nu_3} E^{(2)}_{\nu_2} E^{(1)}_{\nu_1},$$

(31)

$$P^{\nu_4}_{\nu_1}(T_3, T_2, T_1) = \frac{1}{23} \exp(-i\phi_3 + i\phi_2 + i\phi_1)$$

$$\times \sum\sum S^{k}_{\nu_1 \nu_2 \nu_3 \nu_4} (T_3, T_2, T_1) E^{(3)}_{\nu_3} E^{(2)}_{\nu_2} E^{(1)}_{\nu_1},$$

(32)

where we have denoted

$$S^k_{\nu_1 \nu_2 \nu_3 \nu_4} (T_3, T_2, T_1) \equiv S^{(I)}_{\nu_1 \nu_2 \nu_3 \nu_4} ((k_1 - k_2 - k_3)t_4, k_2 t_3, k_2 t_2, -k_1 t_1),$$

(33)
\[ S^{(II)}_{\nu_1\nu_2\nu_2\nu_1}(T_3, T_2, T_1) \equiv \langle \{ \epsilon_l - k_1 - k_3 \} t_4, k_3 t_3, -k_2 t_2, k_1 t_1 \rangle. \]  \hfill (34)

\[ S^{(III)}_{\nu_1\nu_3\nu_2\nu_1}(T_3, T_2, T_1) \equiv \langle \{ \epsilon_l - k_2 - k_1 \} t_4, -k_3 t_3, k_2 t_2, k_1 t_1 \rangle. \]  \hfill (35)

We, thus, find that the response function \( S^{(I)} \) generates the \( k_I \) signal, \( S^{(II)} \) generates \( k_{II} \) and \( S^{(III)} \) generates \( k_{III} \).

The fourth possible signal \( P_{k IV} \) vanishes for the present model since it has no transition dipole connecting the three-exciton states with the ground state. The three terms in eqs. (27) - (29) were obtained by a simple bookkeeping of time variables. The RWA has connected these terms with the impulsive signals in eqs. (34)-(36). Each of the three signals is thus given by a single term.

Equations (27) - (29) are used in appendix C to calculate the signals in the eigenstate basis. The frequency domain scattering matrix (see appendix F) allows to simplify response functions in eqs. (C6)-(C8). The three signals are given by eqs. (C10), (C11) and (C14). The sequential pump-probe spectrum is calculated in appendix D.

By transforming all time variables to the frequency domain, \( S(\Omega_3, \Omega_2, \Omega_1) = \int_0^\infty dT_3 \int_0^\infty dT_2 \int_0^\infty dT_1 S(T_3, T_2, T_1) \exp(i\Omega_3 T_3 + i\Omega_2 T_2 + i\Omega_1 T_1) \), (see appendix C) equations (36) - (38) give:

\[ S^{(I)}_{\nu_1\nu_2\nu_2\nu_1}(\Omega_3, \Omega_2, \Omega_1) = 2i \sum_{\xi_4} \langle d^{\nu_4}_1(k_1 - k_2 - k_3) d^{\nu_3*}_2(-k_3) d^{\nu_2*}_2(-k_2) d^{\nu_1*}_1(-k_1) \rangle \times I^{(N)}_{\xi_4\xi_2}(\Omega_2) I^{(I)}_{\xi_3}(\Omega_3) \Gamma_{\xi_4\xi_2\xi_3\xi_4} \langle \Omega_3 + \epsilon_{\xi_1} + i\gamma_{\xi_1}, \xi_4 \rangle, \]  \hfill (36)

\[ S^{(II)}_{\nu_1\nu_3\nu_2\nu_1}(\Omega_3, \Omega_2, \Omega_1) = 2i \sum_{\xi_4} \langle d^{\nu_3}_1(k_2 - k_3 - k_1) d^{\nu_2*}_2(-k_3) d^{\nu_2*}_2(-k_2) d^{\nu_1*}_1(-k_1) \rangle \times I^{(N)}_{\xi_2\xi_1}(\Omega_2) I^{(I)}_{\xi_3}(\Omega_3) \Gamma_{\xi_4\xi_2\xi_3\xi_4} \langle \Omega_3 + \epsilon_{\xi_2} + i\gamma_{\xi_2}, \xi_1 \rangle, \]  \hfill (37)

\[ S^{(III)}_{\nu_1\nu_2\nu_3\nu_1}(\Omega_3, \Omega_2, \Omega_1) = 2i \sum_{\xi_4} \langle d^{\nu_4}_1(k_3 - k_2 - k_1) d^{\nu_3*}_3(-k_3) d^{\nu_2*}_2(-k_2) d^{\nu_1*}_1(-k_1) \rangle \times I^{(I)}_{\xi_1}(\Omega_1) I^{(I)}_{\xi_2}(\Omega_3) I^{(I)}_{\xi_3}(\Omega_2 - \Omega_3) \Gamma_{\xi_4\xi_3\xi_2\xi_4} \langle \Omega_2 \rangle \langle \Omega_3 + \epsilon_{\xi_2} + i\gamma_{\xi_2}, \xi_1 \rangle, \]  \hfill (38)

where we have defined the exciton transition dipole for state \( \xi_3 \)

\[ d^{\nu}_\xi(k) = \sum_m e^{ikr_m} \mu^{\nu}_m \psi^{m}_{\xi_m} \]  \hfill (39)

and

\[ I^{(N)}_{\xi_2\xi_1}(\Omega) = \frac{i}{\Omega + \epsilon_{\xi_2} - \epsilon_{\xi_1} + i(\gamma_{\xi_2} + \gamma_{\xi_1})}. \]  \hfill (40)

The application of the Green’s functions expressions for periodic infinite systems is straightforward [17]: the summations over one-exciton eigenstates are replaced by summations over different Davydov exciton bands at zero momentum. The scattering matrix of infinite systems which involves all possible momenta of different Davydov bands is given in appendix D.
V. APPLICATION TO THE AMIDE I BAND OF PEPTIDES

We have applied the present theory to the amide I vibrations of two ideal structural motifs of polypeptides: \(\alpha\) helices (one dimensional) with 18 amide residues in the unit cell and antiparallel \(\beta\) sheets (two dimensional) with 4 residues per unit cell. The structural and coupling parameters were reported earlier \[17, 47\]. The anharmonicity \(\Delta_{mn}\) is local (\(\Delta = -16 \text{ cm}^{-1}\) for \(m = n\) and zero otherwise) and the same dephasing rate, \(\gamma_\xi = 3 \text{ cm}^{-1}\) was assumed for all excitons. We used 100 cells in each dimension to calculate the scattering matrix with periodic boundary conditions (eq. (F2)).

The linear absorption of both motifs presented in figure 3 shows two absorption peaks for the \(\alpha\) helix and the \(\beta\) sheet. For the \(\alpha\) helix the longitudinal transition – along the helix axis gives a peak at 1642 cm\(^{-1}\), and transverse – in the plane perpendicular to the helical axis gives a weaker peak at 1661 cm\(^{-1}\) \[47\]. For the \(\beta\) sheet the main peak at 1632 cm\(^{-1}\) is horizontal (parallel to the sheet surface). The other weak peak at 1700 cm\(^{-1}\) consists of two transitions \[47\]: vertical (perpendicular to the sheet surface transition) at 1707 cm\(^{-1}\) and horizontal at 1699 cm\(^{-1}\).

Signals were calculated for a collinear field configuration where, \(k_1, k_2\) and \(k_3\), propagate along \(z\). We further assume all fields to have the same carrier frequency so that \(|k_j| = \omega_s/c\) for all \(k_j\) \((j = 1, 2, 3)\) where \(c\) is the speed of light. The absolute magnitudes of the \(S^{k_I}_{\nu_4,\nu_3,\nu_2,\nu_1}(\Omega_3, T_2 = 0, \Omega_1)\) and \(S^{k_III}_{\nu_4,\nu_3,\nu_2,\nu_1}(\Omega_3, \Omega_2, T_1 = 0)\) signals were computed using eqs. (C11) and (C17). These are one-sided Fourier transforms of the time domain \(k_I\) and \(k_{III}\) signals.

The \(S^{k_I}_{\nu_4,\nu_3,\nu_2,\nu_1}\) signals for the \(\alpha\) helix are shown in the left column in figure 4. The \(xxxx\) component is finite in the dipole approximation and shows one major peak associated with the longitudinal transition \[47\] and a much weaker 20 cm\(^{-1}\) blue shifted transverse transition. The crosspeaks between these two peaks are symmetric with respect to the diagonal and have roughly the same amplitudes. This signal resembles our previous calculation of large (90 residue) helices \[47\], which could be treated as infinite helices with small edge defects.

This \(xxxx\) pattern is changed in the chirally-sensitive \(xxxy\) component. The diagonal peaks are suppressed. This can be explained by noting that the distance between sites enters the signal amplitude: diagonal peaks have no such distance factor since they originate from interactions with the same mode. The crosspeaks are induced by interactions of different modes and depend on their distance. Thus, in the chiral signal the crosspeaks are amplified compared to the diagonal peaks. Additionally, the crosspeak pattern is asymmetric since one of the crosspeaks (below the diagonal) dominates. The other, above the diagonal, crosspeak is much weaker. The remaining two chiral components \(xxyx\) and \(xyxx\) also suppress the diagonal peaks, while show two crosspeaks.

The antiparallel \(\beta\) sheet signals displayed in the right column in figure 4 show a similar pattern, however only one horizontal diagonal peak (as shown in \[47\]) is visible in \(xxxx\) with very weak crosspeaks shifted to much higher frequencies compared to the diagonal. Since there are four sites per unit cell, we generally expect four optical transitions (Davydov components). This could result in four diagonal peaks and six crosspeaks in both sides of the diagonal if all transitions are correlated. However, \(xxxx\) is dominated by a single strong horizontal transition. Similar to the helix, this peak structure changes in the chiral component, \(xxxy\), which shows much stronger crosspeaks than the diagonal peaks. The strongest crosspeak is well separated from the strongest \(xxxx\) peak. Like the helix, the \(xxyx\) and \(xyxx\) configurations are both similar and show crosspeaks above and below the diagonal.
We next turn to the $k_{III}$ technique. $S_{k_{III}x_{y_{1}y_{2}y_{3}y_{4}}}$ shows two-exciton resonances along $\omega_2$ (double quantum coherence); the resonances along $\omega_3$ originate both from one- to two-exciton resonances ($e$ to $f$ in figure 1) and from one-exciton to ground state resonances (0 to $e$). The $xxxx$ component for the $\alpha$ helix presented in figure 5 shows one major peak and a weaker peak originating from the same two-exciton resonance. The main peak of the chiral components $xxyy$, $xyyx$, $xyxy$ is shifted compared to $xxxx$, indicating that different two-exciton resonances make the strongest contribution to the signal. The $xxyy$ and $xyyx$ signals are very similar and show two strong peaks unlike $xyxx$ which only shows one major peak. The $xxxx$ component of the $\beta$ sheet displayed in figure 5 has a similar structure to the $\alpha$ helix. The chiral $xxyy$ component shows two peaks at higher two-exciton resonance comparing to $xxxx$. $xyyx$, is very similar. $xyxx$ shows one major peak at $\omega_3 = 1700 \text{ cm}^{-1}$.

VI. DISCUSSION

In the electric dipole approximation, the linear absorption of isotropic systems is related to the diagonal tensor elements of the linear susceptibility \[17, 43\]. Nonlinear signals calculated within this approximation then provide a limited window onto the optical responses of isotropic ensembles through three independent chirally-non-sensitive tensor components of the third order response function: $xxyy$, $xyyx$, $xyxy$. The signal propagation direction is determined by phase-matching. Going beyond the dipole approximation, we found three additional components for a collinear laser configuration: $xxyy$, $xyyx$, $xyxy$. Noncollinear configurations (which can also satisfy phase matching) lead to six nonzero elements (the three additional components are: $(z)xyzx$, $(z)zxzy$ and $(z)xzyz$, where the first index $(z)$ denotes the wavevector, and the other four are polarization components). These are chirally-sensitive and show a different pattern in the correlation plots, which reflects the polarization properties of optical transitions. For example, from figures 4 and 5 we see that the strongest peaks originate from correlations between perpendicular transitions: longitudinal - transverse in the $\alpha$ helix and horizontal - vertical in the $\beta$ sheet (see figure 1).

The differences between the chiral components can be deduced by following the interaction and evolution sequences: in $S^{k_{I}}$, $\Omega_1$ corresponds to the free evolution after the first interaction. Subsequently two simultaneous interactions take place. Therefore $xxyy$ and $xyxy$ reflect a similar excitation pattern: there is one interaction first, followed by two interactions with the perpendicular polarization. $xxyy$ is qualitatively different: the first interaction is followed by two interactions with parallel polarizations. This is why, $xxyy$ and $xyxy$ show a different peak pattern. For $S^{k_{III}}$ there are two simultaneous interactions first, followed by one interaction. Thus, $xxyy$ and $xyxy$ give very similar signals since in both cases the first two interactions are with perpendicular fields. The $xyxx$ component is qualitatively different since the first two interactions are with parallel fields.

The signal further carries information regarding the redistribution of excitonic amplitudes between states with different polarization properties. For instance, $S^{k_{III}}_{xyxx}$ originates from exciton amplitude transfer between a state with $x$ polarization to a state with $y$ polarization during $T_2$. $S^{k_{III}}_{xxyy}$ is qualitatively different since the evolution during $T_2$ corresponds to $x$ polarized exciton amplitude transfer to another $x$ exciton. $S^{k_{I}}_{xxyy}$ again originates from exciton amplitude transfer during $T_1$ between states with perpendicular ($y \rightarrow x$) polarizations; $xyxx$ does not require such exciton evolution.
In the present work we only included homogeneous line broadening caused by fast frequency fluctuations. Slow fluctuations result in inhomogeneous broadening which should affect the 2D lineshapes. The ideal peak patterns predicted for periodic structures can be used for structure decomposition and parameter determination of real structures. Dynamical information on exciton evolution can be obtained by varying $T_2$ in $S^{ki}(\Omega_3,T_2,\Omega_1)$. Population transport may be incorporated using the theory developed in [13, 21], but this goes beyond the scope of this paper.

We next compare the exciton scattering mechanism offered by the NEE with the more conventional picture of transitions among eigenstates, as described by double-sided Feynman diagrams. The relation between the two for $k_I$, $k_{II}$ and $k_{III}$ is shown in figure 6. For $k_I$ the exciton coherence during $T_1$ in both pictures is represented by the same Green’s function. However, during $T_3$ the Feynman diagrams show two independent coherence evolutions, only one of them involves the two-exciton states. The scattering representation is more complex: during $T_3$ the evolution consists of scattering + two free evolutions. This is natural in the molecular basis set where the exciton pathways can be followed in real space: the short range exciton scattering is then followed by free evolution as the excitons separate.

The role of the distance parameter is much less obvious in the eigenstate picture. $k_{II}$ is similar, except the density matrix evolution during the first and the last intervals has the same frequency sign. In $k_{III}$ two excitons are created by the initial excitation. Thus the scattering can occur at any time. In the sum over states representation this is given as independent evolutions of two-exciton coherences during $T_1$. Both representations of the response are equivalent as long as pure dephasing is neglected. The NEE and the corresponding response become more complicated by pure dephasing which induces incoherent population transport and requires additional dynamic variables [4, 13, 21].

The response function in eq. 3 is not required to be time ordered, thus, we can define it to be symmetric with respect to permutation of different time arguments. This choice is useful for overlapping optical pulses and frequency domain response, where time ordering of interactions is not enforced. Frequency domain signals can be expressed using the third order susceptibility given in terms of the exciton scattering matrix as shown in appendix E. The susceptibility is then directly related to non time ordered response function. Expressions for $k_I$, $k_{II}$ and $k_{III}$ can be derived using the RWA.

Our theory may be applied to other periodic (infinite) as well as to non periodic (finite) systems. Periodicity and cyclic boundary conditions result in exciton band structure where only zero momenta exciton states are active. This applies as long as the optical wavevector is small compared with the exciton momentum. Exciton-exciton interactions are the source of anharmonicities and are described using quasi-particle scattering. This description may also be applied to semiconductors and quantum superlattices [16, 40, 42, 50]. When the exciton coherence size becomes comparable to the optical wavelength the theory needs to be extended to include polariton effects [14].

VII. ACKNOWLEDGEMENTS

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Appendix A: LINEAR ABSORPTION OF EXCITONS

In this appendix we connect the linear absorption with the response function. The linear response function and the linear polarization were defined by eq. (2). The linear absorption can be calculated using the linear susceptibility \( \chi^{(1)} \) \[17\]. The linear response, especially for vibrations, is often measured in the time domain using ultrashort laser pulses: Fourier transform of the time dependent induced polarization (free induction decay) gives the Fourier Transform Infrared (FTIR) spectrum.

We assume a single excitation pulse with envelope \( \hat{E}_\nu^{(0)}(t - t_0) \) centered at \( t_0 \) with the carrier frequency \( \omega_0 \) and wavevector \( k_0 \):

\[
E_\nu(x) = \frac{1}{2} \delta_{\nu \omega_0} \hat{E}_\nu^{(0)}(t - t_0) \exp(i k_0 r - i \omega_0(t - t_0)) + c.c., \tag{A1}
\]

The linear response function of the excitonic system is given in terms of the one-exciton Green’s functions \[17\]:

\[
S^{(1)}_{\nu \nu'}(\mathbf{x}_2, \mathbf{x}_1) = i \sum_\xi \langle \hat{d}_\xi^2 (k_2) \hat{d}_\xi^{*2} (-k_1) \rangle I_\xi (t_2 - t_1) + c.c. \tag{A2}
\]

Within the dipole approximation rotational averaging (eq. (A2)) gives \( \langle \hat{d}_\xi^2 (k_2) \hat{d}_\xi^{*2} (-k_1) \rangle \approx \frac{1}{4} \delta_{\nu \nu'} |\xi|_0^2 \) \[17\]. Substituting eqs. (A1) and (A2) into eq. (2) and using assumptions for the field given in section II we can integrate \( \int d\mathbf{x}_1 \) which leads to:

\[
P_{\nu_0} (k_2 t_2) = \frac{i}{6} E_{\nu_0}^{(0)} \sum_\xi |\xi|_0^2 \delta(k_2 + k_0) I_\xi (t_2 - t_1) - \delta(k_2 - k_0) I_\xi (t_2 - t_1), \tag{A3}
\]

where \( \delta(k) \) accounts for the translational invariance of an isotropic system. This expression shows that \( P_{\nu_0} (k_2 t_2) \) only depends on the delay \( T_1 = t_2 - t_1 \) and can, thus, be denoted \( P_{\nu_0} (k_2, T_1) \). The first term in eq. (A3) in real space is proportional to \( e^{i k_2 r} \) and, thus, describes forward propagation of the induced polarization.

The absorption spectrum is defined as the imaginary part of Fourier transform of the linear polarization with respect to \( T_1 \): \( \sigma_A(\omega) = \text{Im} \int_0^\infty dT_1 \exp(i \omega T_1) P_{\nu_0} (k_2, T_1) \), while the real part of this integral describes dispersive lineshapes. By eliminating the prefactor \( 1/6 \)\( E_{\nu_0}^{(0)} \delta(k_2 + k_0) \) and keeping only terms resonant to the positive frequency we obtain:

\[
\sigma_A(\omega) = \sum_\xi \frac{\gamma_\xi |\xi|_0^2}{(\omega - \varepsilon_\xi)^2 + \gamma_\xi^2}. \tag{A4}
\]

The CD spectrum must be calculated by going beyond the dipole approximation \[17\].

Appendix B: THE RESPONSE OF ISOPTROPIC ENSEMBLES

Optical fields, wavevectors, and space coordinates are defined in the lab frame, while the transition dipoles and their position vectors are given in the molecular frame. The rotational averaging in eqs. (C3) and (C5), \( \langle \cdots \rangle \), needs to be performed over the relative orientation of the two frames in order to calculate the response functions for isotropic (randomly oriented) ensembles of molecules \[22\] \[23\]:
The dipole of eq. (39) can be expanded to first order. This leads to

\[
\psi_{\xi} \left[ \sum_{n_4 n_3 n_2 n_1} \psi_{\xi n_4} \psi_{\xi n_3} \psi d_{\xi_1 n_1}^* \right] \times \left( e^{i k_4 r_{n_4} + i k_3 r_{n_3} + i k_2 r_{n_2} + i k_1 r_{n_1}} \mu_{n_4}^\mu \mu_{n_3}^\nu \mu_{n_2}^\rho \mu_{n_1}^\lambda \right),
\]

(B1)

In the phase-matching directions the microscopic response functions only depend on the relative positions of molecules and are independent on the origin of the coordinate system. Since the coordinates \( r_m \) vary only within one molecule, for molecules smaller than the wavelength of light we have \( kr_m \ll 1 \), and the exponential function in the transition dipole of eq. (39) can be expanded to first order. This leads to

\[
\left\langle e^{i k_4 r_{n_4} + i k_3 r_{n_3} + i k_2 r_{n_2} + i k_1 r_{n_1}} \mu_{n_4}^\mu \mu_{n_3}^\nu \mu_{n_2}^\rho \mu_{n_1}^\lambda \rightangle 
\approx \left\langle \mu_{n_4}^\mu \mu_{n_3}^\nu \mu_{n_2}^\rho \mu_{n_1}^\lambda \right\rangle
\]

\[
+ i \sum_{\kappa} k_1^\lambda (r_{n_4} \mu_{n_4}^\mu \mu_{n_3}^\nu \mu_{n_2}^\rho \mu_{n_1}^\lambda)
\]

\[
+ i \sum_{\kappa} k_2^\lambda (r_{n_3} \mu_{n_4}^\mu \mu_{n_3}^\nu \mu_{n_2}^\rho \mu_{n_1}^\lambda)
\]

\[
+ i \sum_{\kappa} k_3^\lambda (r_{n_2} \mu_{n_4}^\mu \mu_{n_3}^\nu \mu_{n_2}^\rho \mu_{n_1}^\lambda)
\]

\[
+ i \sum_{\kappa} k_4^\lambda (r_{n_1} \mu_{n_4}^\mu \mu_{n_3}^\nu \mu_{n_2}^\rho \mu_{n_1}^\lambda).
\]

(B2)

In the exciton basis, eqs. (B1) and (B2) give

\[
\left\langle d_{\xi_4}^\mu (k_4) d_{\xi_3}^\nu (k_3) d_{\xi_2}^\rho (k_2) d_{\xi_1}^\lambda (k_1) \right\rangle
\]

\[
= \left\langle d_{\xi_4}^\mu d_{\xi_3}^\nu d_{\xi_2}^\rho d_{\xi_1}^\lambda \right\rangle
\]

\[
+ i \sum_{\kappa} k_1^\lambda \left( d_{\xi_4}^\mu d_{\xi_3}^\nu d_{\xi_2}^\rho d_{\xi_1}^\lambda \right)
\]

\[
+ i \sum_{\kappa} k_2^\lambda \left( d_{\xi_4}^\mu d_{\xi_3}^\nu d_{\xi_2}^\rho d_{\xi_1}^\lambda \right)
\]

\[
+ i \sum_{\kappa} k_3^\lambda \left( d_{\xi_4}^\mu d_{\xi_3}^\nu d_{\xi_2}^\rho d_{\xi_1}^\lambda \right)
\]

\[
+ i \sum_{\kappa} k_4^\lambda \left( d_{\xi_4}^\mu d_{\xi_3}^\nu d_{\xi_2}^\rho d_{\xi_1}^\lambda \right),
\]

(B3)

where we have used the fact that \( \psi_{\xi,m} \) are real and have defined the transition dipole vector for zero momentum exciton state

\[
d_{\xi}^\mu \equiv d_{\xi}^\mu (k = 0) = \sum_{m} \mu_{m}^\mu \psi_{\xi,m},
\]

(B4)

and the tensor

\[
\tilde{d}_{\xi}^{\mu,\nu} = \sum_{m} r_{m}^\mu \mu_{m}^\nu \psi_{\xi,m}.
\]

(B5)

Eq. (B3) requires fourth and fifth rank rotational averagings. The first term in this equation corresponds to the dipole approximation. The remaining terms which contain the wavevector and a coordinate, represent a first order correction to that approximation. These terms do not depend on the origin of the molecular frame provided \( k_4 + k_3 + k_2 + k_1 = 0 \) (i.e. the signal wavevector \( k_4 = -k_4 \)), which is the phase matching condition.
Rotational averaging can be performed using the transformation between the lab and molecular frames \[23\]:

\[
\langle a_{s}^{\nu} \ldots a_{1}^{\nu} \rangle \equiv \langle (e^{\nu} \cdot a_{s})(e^{\nu} \cdot a_{1}) \rangle = \sum_{\alpha_{s} \ldots \alpha_{1}} T_{\nu_{s} \ldots \nu_{1}, \alpha_{s} \ldots \alpha_{1}}^{(s)} a_{s}^{\alpha_{s}} \ldots a_{1}^{\alpha_{1}},
\]

where \( T_{\nu_{s} \ldots \nu_{1}, \alpha_{s} \ldots \alpha_{1}}^{(s)} \) is the average of transformation tensor where \( l_{\nu\alpha} \) is the cosine of the angle between laboratory frame axis \( \nu = x, y, z \) and molecular frame axis \( \alpha = x, y, z \). The necessary averages of ranks four and five transformation tensors, which are universal quantities independent of system geometry are given in table \[??\].

Using table \[??\], we obtain for the rotational averages of the transition dipoles:

\[
\langle d_{\xi_{4}}^{\nu_{4}} d_{\xi_{3}}^{\nu_{3}} d_{\xi_{2}}^{\nu_{2}} d_{\xi_{1}}^{\nu_{1}} \rangle = \sum_{\alpha_{4} \alpha_{3} \alpha_{2} \alpha_{1}} T_{\nu_{4} \nu_{3} \nu_{2} \nu_{1}, \alpha_{4} \alpha_{3} \alpha_{2} \alpha_{1}}^{(4)} d_{\xi_{4}}^{\nu_{4} \alpha_{4}} d_{\xi_{3}}^{\nu_{3} \alpha_{3}} d_{\xi_{2}}^{\nu_{2} \alpha_{2}} d_{\xi_{1}}^{\nu_{1} \alpha_{1}}
\]

\[
\langle \tilde{d}_{\xi_{4}}^{\nu_{4}, \nu_{4}} d_{\xi_{3}}^{\nu_{3} \alpha_{3}} d_{\xi_{2}}^{\nu_{2} \alpha_{2}} d_{\xi_{1}}^{\nu_{1} \alpha_{1}} \rangle = \sum_{\alpha_{4} \ldots \alpha_{1}} T_{\nu_{4} \nu_{3} \nu_{2} \nu_{1}, \alpha_{4} \alpha_{3} \alpha_{2} \alpha_{1}}^{(5)} d_{\xi_{4}}^{\nu_{4} \alpha_{4}} d_{\xi_{3}}^{\nu_{3} \alpha_{3}} d_{\xi_{2}}^{\nu_{2} \alpha_{2}} d_{\xi_{1}}^{\nu_{1} \alpha_{1}}.
\]

The remaining averages can be simply obtained by permutation of indices.

**Appendix C: TIME-DOMAIN FWM SIGNALS**

The response functions (eqs. \[??\] - \[??\]) can be readily calculated using the single exciton basis (eq. \[??\]) where the number of terms in the response function is considerably reduced. We define:

\[
J_{\xi_{4}\xi_{3}\xi_{2}\xi_{1}}(\tau_{3}, \tau_{2}, \tau_{1}) = \int_{0}^{\tau_{2}} d\tau_{s}^{''} \int_{0}^{\tau_{2}} d\tau_{s}^{'} \Gamma_{\xi_{4}\xi_{3}\xi_{2}\xi_{1}}(\tau_{s}^{''} - \tau_{s}^{'})
\times I_{\xi_{4}}(\tau_{s}') I_{\xi_{3}}(\tau_{3} - \tau_{s}') I_{\xi_{2}}(\tau_{2} - \tau_{s}''') I_{\xi_{1}}(\tau_{1} - \tau_{s}'')
\]

with the eigenstate basis scattering matrix:

\[
\Gamma_{\xi_{4}\xi_{3}\xi_{2}\xi_{1}}(\tau) = \sum_{m_{4} \ldots m_{1}} \psi_{\xi_{4}m_{4}}^{*} \psi_{\xi_{3}m_{3}}^{*} \Gamma_{m_{4}m_{3}m_{2}m_{1}}(\tau) \psi_{\xi_{2}m_{2}} \psi_{\xi_{1}m_{1}}.
\]

By transforming the coordinates to momentum space, we obtain from eqs. \[??\] - \[??\]:

\[
S_{\nu_{4} \ldots \nu_{1}}^{(I)}(\tilde{x}_{4}, \ldots, \tilde{x}_{1}) = 2i \sum_{\xi_{4} \ldots \xi_{1}} \langle d_{\xi_{4}}^{*}(k_{4}) d_{\xi_{3}}^{*}(k_{3}) d_{\xi_{2}}^{*}(k_{2}) d_{\xi_{1}}^{*}(k_{1}) \rangle J_{\xi_{4}\xi_{3}\xi_{2}\xi_{1}}(t_{41}, t_{43}, t_{42}),
\]

\[
S_{\nu_{4} \ldots \nu_{1}}^{(II)}(\tilde{x}_{4}, \ldots, \tilde{x}_{1}) = 2i \sum_{\xi_{4} \ldots \xi_{1}} \langle d_{\xi_{4}}^{*}(k_{4}) d_{\xi_{3}}^{*}(k_{3}) d_{\xi_{2}}^{*}(k_{2}) d_{\xi_{1}}^{*}(k_{1}) \rangle J_{\xi_{4}\xi_{3}\xi_{2}\xi_{1}}(t_{42}, t_{43}, t_{41}),
\]

\[
S_{\nu_{4} \ldots \nu_{1}}^{(III)}(\tilde{x}_{4}, \ldots, \tilde{x}_{1}) = 2i \sum_{\xi_{4} \ldots \xi_{1}} \langle d_{\xi_{4}}^{*}(k_{4}) d_{\xi_{3}}^{*}(k_{3}) d_{\xi_{2}}^{*}(k_{2}) d_{\xi_{1}}^{*}(k_{1}) \rangle J_{\xi_{4}\xi_{3}\xi_{2}\xi_{1}}(t_{43}, t_{42}, t_{41}).
\]
The wavevector-dependence enters through the transition dipoles. These expressions need to be rotationally averaged for isotropic ensembles, as described in appendix B.

Equations (C3) - (C5) can be conveniently expressed in terms of the frequency domain scattering matrix (eqs. (14) and (15)). These expressions then involve triple integrals (two with respect to time and one with respect to the scattering matrix frequency). However, the integration limits in eq. (C4) are controlled by multiple $\theta(t)$ functions coming from the Green’s functions. Taking these into account and using the frequency domain scattering matrix (eq. (19)), the integrals over the exponential functions can be considerably simplified. The integration limits $(-\infty, \tau_2)$ for $\tau_3''$ and $(0, \tau_3)$ for $\tau_3'$ always hold for $S^I$, $S^{II}$ and $S^{III}$ in eqs. (C3)-(C5). However, for $S^I$ (eq. (C3)) and $S^{II}$ (eq. (C4)) (but not for eq. (C5)) other integration limits $(0, \tau_2)$ for $\tau_3'$ can also be used. These considerations allow to calculate time integrals:

\[
S^{(I)}_{\nu_4, \cdots \nu_1}(\bar{x}_4, \ldots, \bar{x}_1) = 2 \sum_{\xi_4 \cdots \xi_1} \langle d_{\xi_4}^{\nu_4}(k_4)d_{\xi_3}^{\nu_3*}(-k_3)d_{\xi_2}^{\nu_2*}(-k_2)d_{\xi_1}^{\nu_1}(k_1) \rangle \\
\times I_{\xi_1}(t_{21})I_{\xi_4}(t_{32}) I_{\xi_2}(t_{32}) \int \frac{d\omega}{2\pi} \frac{\Gamma_{\xi_4\xi_1\xi_3\xi_2}(\omega) I_{\xi_4}(t_{43}) - e^{-i\omega t_{43}} I_{\xi_4}(t_{43})}{\omega - E_{\xi_4} - E_{\xi_1} + i(\gamma_{\xi_4} - \gamma_{\xi_1})} \tag{C6}
\]

\[
S^{(II)}_{\nu_4, \cdots \nu_1}(\bar{x}_4, \ldots, \bar{x}_1) = 2 \sum_{\xi_4 \cdots \xi_1} \langle d_{\xi_4}^{\nu_4}(k_4)d_{\xi_3}^{\nu_3*}(-k_3)d_{\xi_2}^{\nu_2*}(k_2)d_{\xi_1}^{\nu_1*}(-k_1) \rangle \\
\times I_{\xi_1}(t_{21})I_{\xi_4}(t_{32}) I_{\xi_2}(t_{32}) \int \frac{d\omega}{2\pi} \frac{\Gamma_{\xi_4\xi_1\xi_3\xi_2}(\omega) I_{\xi_4}(t_{43}) - e^{-i\omega t_{43}} I_{\xi_4}(t_{43})}{\omega - E_{\xi_4} - E_{\xi_1} + i(\gamma_{\xi_4} - \gamma_{\xi_1})} \tag{C7}
\]

\[
S^{(III)}_{\nu_4, \cdots \nu_1}(\bar{x}_4, \ldots, \bar{x}_1) = 2 \sum_{\xi_4 \cdots \xi_1} \langle d_{\xi_4}^{\nu_4}(k_4)d_{\xi_3}^{\nu_3*}(k_3)d_{\xi_2}^{\nu_2*}(-k_2)d_{\xi_1}^{\nu_1*}(-k_1) \rangle \\
\times I_{\xi_1}(t_{21}) \int \frac{d\omega}{2\pi} \frac{\Gamma_{\xi_4\xi_3\xi_2\xi_1}(\omega) I_{\xi_3}(t_{32}) - e^{-i\omega t_{32}} I_{\xi_3}(t_{32})}{\omega - E_{\xi_3} - E_{\xi_1} + i(\gamma_{\xi_3} - \gamma_{\xi_1})} \tag{C8}
\]

Equations (C6) - (C8) constitute our most general expressions for the time domain nonlocal third order responses in momentum space. The wavevectors and times in these expressions correspond to the interaction events with the fields. All three response functions depend only on time delays between different interactions.

We next turn to on the three signals defined by eqs. (80) - (82). The polarization evolution is commonly transformed to the frequency-domain where the signal spectra are displayed. The technique $k_1$ is known as photon echo. According to the Feynman diagrams (figure 6) the system is transferred to a coherence after the first interaction. The second interaction leaves the system either in a population or in a coherence between two excitonic states. We hold the second delay time, $T_2$ (often referred to as population or waiting time) fixed. Then the population and coherence evolution can be probed. The third interaction creates coherences either between the ground and one-exciton states or between one- and two-exciton states. To display the signal we perform a double Fourier transform with respect to the first and third time delays: $T_1 \rightarrow \Omega_1$ and $T_3 \rightarrow \Omega_3$ in eqs. (80) - (82). The signal also depends on the directions of optical wavevectors. Thus, the Fourier transform of eq. (80) can be performed analytically since the Green’s functions given by eq. (16) are simple exponential functions. We finally obtain

\[
P^{k_1}_{\nu_4}(\Omega_3, T_2, \Omega_1) = \frac{1}{2} \exp(+i\phi_3 + i\phi_2 - i\phi_1) \sum_{\nu_3,\nu_2,\nu_1} S^{k_1}_{\nu_4,\nu_3,\nu_2,\nu_1}(\Omega_3, T_2, \Omega_1) E^{(3)}_{\nu_3} E^{(2)}_{\nu_2} E^{(1)}_{\nu_1}. \tag{C9}
\]
In terms of the scattering matrix and the one-exciton Green’s functions, eq. (C10) gives:

\[
S^{k_i}_{\nu_1,\nu_2,\nu_3,\nu_4,\nu_5}(\Omega_3, T_2, \Omega_1) = 2i \sum_{\xi_1, \ldots, \xi_5} \langle d^{\nu_5}_{\xi_5}(k_1 - k_2 - k_3) d^{\nu_3*}_{\xi_3}(-k_3) d^{\nu_2*}_{\xi_2}(-k_2) d^{\nu_1*}_{\xi_1}(-k_1) \rangle \times I^{\nu_5}_{\xi_5}(T_2) I^{\nu_3}_{\xi_3}(T_2) I^{\nu_2}_{\xi_2}(\Omega_1) I^{\nu_3}_{\xi_3}(\Omega_2) \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \Gamma_{\xi_4,\xi_5,\xi_6}(\omega) I^{\nu_4}_\xi(\omega + \Omega_1).
\]

(C10)

The frequency integration can be calculated analytically as follows. We note that \( \Gamma(\omega) I(\omega) \sim i(\omega - 2\bar{E} + 2i\gamma)^{-1} \) is a two-exciton Green’s function with poles in negative imaginary half-plane (bars indicate averages), while \( I^{\nu_5}_{\xi_5}(\omega - \Omega_3) = -i(\omega - \Omega_3 - E_{\xi_5} - i\gamma_{\xi_5})^{-1} \) has one pole in positive imaginary half-plane: \( \omega_p = \Omega_3 + E_{\xi_5} + i\gamma_{\xi_5} \). In this case we can use the Cauchy integral formula by adding integration contour at the positive imaginary half-plane. Then

\[
S^{k_i}_{\nu_1,\nu_2,\nu_3,\nu_4,\nu_5}(\Omega_3, T_2, \Omega_1) = 2i \sum_{\xi_1, \ldots, \xi_5} \langle d^{\nu_5}_{\xi_5}(k_1 - k_2 - k_3) d^{\nu_3*}_{\xi_3}(-k_3) d^{\nu_2*}_{\xi_2}(-k_2) d^{\nu_1*}_{\xi_1}(-k_1) \rangle \times I^{\nu_5}_{\xi_5}(T_2) I^{\nu_3}_{\xi_3}(T_2) I^{\nu_2}_{\xi_2}(\Omega_1) I^{\nu_3}_{\xi_3}(\Omega_2) \Gamma_{\xi_4,\xi_5,\xi_6}(\Omega_3 + E_{\xi_5} + i\gamma_{\xi_5}) I^{\nu_4}_\xi(\Omega_3 + E_{\xi_5} + i\gamma_{\xi_5}).
\]

(C11)

Similar to \( k_f \), \( k_{II} \) (which does not show an echo) can be defined with the same Fourier transform and the same time delays:

\[
P^{k_{II}}(\Omega_3, T_2, \Omega_1) = \frac{1}{2^3} \exp(+i\phi_3 - i\phi_2 + i\phi_1) \sum_{\nu_1,\nu_2,\nu_3,\nu_4,\nu_5} S^{k_{II}}_{\nu_1,\nu_2,\nu_3,\nu_4,\nu_5}(\Omega_3, T_2, \Omega_1) E^{(3)}_{\nu_3} E^{(2)}_{\nu_2} E^{(1)}_{\nu_1}.
\]

(C12)

In terms of the scattering matrix and the Green’s functions we get from eq. (C11):

\[
S^{k_{II}}_{\nu_1,\nu_2,\nu_3,\nu_4,\nu_5}(\Omega_3, T_2, \Omega_1) = 2i \sum_{\xi_1, \ldots, \xi_5} \langle d^{\nu_5}_{\xi_5}(k_1 - k_2 - k_3) d^{\nu_3*}_{\xi_3}(-k_3) d^{\nu_2*}_{\xi_2}(-k_2) d^{\nu_1*}_{\xi_1}(-k_1) \rangle \times I^{\nu_5}_{\xi_5}(T_2) I^{\nu_3}_{\xi_3}(T_2) I^{\nu_2}_{\xi_2}(\Omega_1) I^{\nu_3}_{\xi_3}(\Omega_2) \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \Gamma_{\xi_4,\xi_5,\xi_6}(\omega) I^{\nu_4}_\xi(\omega + \Omega_1).
\]

(C13)

and after integration over frequency

\[
S^{k_{II}}_{\nu_1,\nu_2,\nu_3,\nu_4,\nu_5}(\Omega_3, T_2, \Omega_1) = 2i \sum_{\xi_1, \ldots, \xi_5} \langle d^{\nu_5}_{\xi_5}(k_1 - k_2 - k_3) d^{\nu_3*}_{\xi_3}(-k_3) d^{\nu_2*}_{\xi_2}(-k_2) d^{\nu_1*}_{\xi_1}(-k_1) \rangle \times I^{\nu_5}_{\xi_5}(T_2) I^{\nu_3}_{\xi_3}(T_2) I^{\nu_2}_{\xi_2}(\Omega_1) I^{\nu_3}_{\xi_3}(\Omega_2) \Gamma_{\xi_4,\xi_5,\xi_6}(\Omega_3 + E_{\xi_5} + i\gamma_{\xi_5}) I^{\nu_4}_\xi(\Omega_3 + E_{\xi_5} + i\gamma_{\xi_5}).
\]

(C14)

This expression is very similar to \( k_f \).

For \( k_{III} \), two interactions with the delay \( T_1 \) create two-exciton coherence with \( k_1 + k_2 \). By performing the Fourier transforms with respect to the second and third time delays: \( T_2 \to \Omega_2 \) and \( T_3 \to \Omega_3 \) we can observe the two-exciton coherence along \( \Omega_2 \) and mixed, 0-to-one and one-to-two, coherences along \( \Omega_3 \):

\[
P^{k_{III}}(\Omega_3, \Omega_2, T_1) = \frac{1}{2^3} \exp(-i\phi_3 + i\phi_2 + i\phi_1) \sum_{\nu_1,\nu_2,\nu_3,\nu_4,\nu_5} S^{k_{III}}_{\nu_1,\nu_2,\nu_3,\nu_4,\nu_5}(\Omega_3, \Omega_2, T_1) E^{(3)}_{\nu_3} E^{(2)}_{\nu_2} E^{(1)}_{\nu_1},
\]

which is obtained from eq. (C13) as

\[
S^{k_{III}}_{\nu_1,\nu_2,\nu_3,\nu_4,\nu_5}(\Omega_3, \Omega_2, T_1) = 2i \sum_{\xi_1, \ldots, \xi_5} \langle d^{\nu_5}_{\xi_5}(k_3 - k_2 - k_1) d^{\nu_3*}_{\xi_3}(-k_3) d^{\nu_2*}_{\xi_2}(-k_2) d^{\nu_1*}_{\xi_1}(-k_1) \rangle \times I^{\nu_5}_{\xi_5}(T_1) I^{\nu_3}_{\xi_3}(\Omega_3) \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \Gamma_{\xi_4,\xi_5,\xi_6}(\omega) I^{\nu_4}_\xi(\omega + \Omega_3) \theta(\Omega_2 - \omega).
\]

(C16)
The function $\theta(\omega) = i(\omega + i\gamma')^{-1}$ is taken in the limit $\gamma_\xi > \gamma' > 0$. Analytic integration over frequency involves more terms. Again, $\Gamma(\omega)\mathcal{I}(\omega) \sim i(\omega - 2\bar{e} + 2i\gamma)^{-1}$ is a two-exciton Green’s function with poles in the negative imaginary half-plane, while $I^*_\xi(\omega - \Omega_3) = -i(\omega - \Omega_3 - \epsilon_\xi - i\gamma_\xi)^{-1}$ has one pole in positive imaginary half-plane: $\omega_p = \Omega_3 + \epsilon_\xi + i\gamma_\xi$, $\theta(\Omega_2 - \omega) = -i(\omega - \Omega_2 - i\gamma')^{-1}$ has another pole with positive imaginary part: $\omega_{pp} = \Omega_2 + i\gamma'$.

In this case Cauchy results integrate into two terms and

$$S^{kk}_{\nu\nu,\nu_2=\nu_1}(\Omega_3,\Omega_2, T_1) = 2i \sum_{\xi_4 \cdots \xi_1} \langle d^e_{\xi_4}(k_3 - k_2 - k_1) d^{\nu}_{\xi_2}(-k_3) d^{\nu_{\Omega_2}}(-k_2) d^{\nu_{\Omega_2}}(-k_1) \rangle \times I_{\xi_4}(T_1) I_{\xi_4}(\Omega_3) I^*_{\xi_4}(\Omega_2 - \Omega_3)[\Gamma_{\xi_4\xi_3\xi_2\xi_1}(\Omega_2) I_{\xi_2\xi_1}(\Omega_2) - \Gamma_{\xi_4\xi_3\xi_2\xi_1}(\Omega_3 + \epsilon_\xi + i\gamma_\xi)], \quad (C17)$$

where we have used $\gamma_\xi > \gamma'$.

### Appendix D: THE SEQUENTIAL PUMP-PROBE SIGNAL

Sequential pump-probe is an incoherent two-pulse FWM technique commonly used for monitoring excited state dynamics. The pump and the probe pulses are assumed well-separated and characterized by their carrier frequencies $\omega_{pu}$ for pump and $\omega_{pr}$ for probe, and their delay $\tau_{pp}$. We ignore population transport and assume that the delay between pump and probe shorter than the population evolution time. In addition, we assume that the pulse bandwidths are much narrower than the exciton bandwidth (which always holds for electronic spectroscopy).

There are two interactions with the pump pulse ($k_1 = \pm k_{pu}$, $k_2 = \mp k_{pu}$, where $k_{pu}$ is the pump pulse wavevector) and one with the probe ($k_3 = \pm k_{pr}$, where $k_{pr}$ is the probe wavevector). We assume that the pump has various polarization components with phases $\phi'_{pu}$ in eq. (4), which can describe e.g. circular polarization of pump. The probe can also have all polarization components with phases $\phi'_{pr}$. The pump-probe experiment measures change of absorption of probe with respect to its linear absorption. The absorption of the optical field is given by (51):

$$\sigma_A = \int dx [\frac{\partial P_{\nu}(x)}{\partial t}] E_{\nu}(x)], \quad (D1)$$

where $P_{\nu}(x)$ is a third order induced polarization and $E_{\nu}(x)$ is a probe field when considering pump-probe experiment.

Using the response function (eq. (3)) we obtain for the pump-probe signal:

$$\sigma_{pp}(\omega_{pr}, \tau_{pp}, \omega_{pu}) = \frac{1}{16} \sum_{\nu_4 \nu_2 \nu_1} \int dt_4 \int dt_3 \int dt_2 \int dt_1 \int \frac{\partial S^{(3)}_{\nu_4 \nu_2 \nu_1}}{\partial t} \times \exp[i\omega_{pp}(t_4 - t_3) - i\omega_{pu}(t_2 - t_1) + i(-\phi'_{pr} + \phi_{pr} + \phi'_{pu} - \phi_{pu})]$$

$$+ \frac{\partial S^{(3)}_{\nu_4 \nu_2 \nu_1}}{\partial t_4} \times \exp[i\omega_{pp}(t_4 - t_3) + i\omega_{pu}(t_2 - t_1) + i(-\phi'_{pr} + \phi_{pr} + \phi'_{pu} + \phi_{pu})]$$

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\[ \chi_{\nu_4,\nu_3,\nu_2,\nu_1}(-k_4, -\omega_4; k_3, \omega_3, k_2, \omega_2, k_1, \omega_1) = 2\pi i \delta(\omega_4 - \omega_3 - \omega_2 - \omega_1) \]

\[ \times \frac{1}{3} \sum_{\text{perm}_{s_3}} \sum_{\xi_4, \xi_3, \xi_2, \xi_1} \left( d^{\nu_4}_{\xi_4}(k_4) d^{\nu_3}_{\xi_3}(-k_3) d^{\nu_2*}_{\xi_2}(k_2) d^{\nu_1*}_{\xi_1}(k_1) \right) \]

\[ \times I_{\xi_4, \xi_3, \xi_2, \xi_1}(\omega_2 + \omega_1) I_{\xi_4}(\omega_4) I_{\xi_3}^*(\omega_3) I_{\xi_2}(\omega_2) I_{\xi_1}(\omega_1) + \text{c.c}'. \]
where $\sum_{\text{perm}_3}$ denotes a sum over the three permutations: $(\nu_1 k_3 \omega_3, \nu_2 k_2 \omega_2, \nu_1 k_1 \omega_1)$, $(\nu_2 k_2 \omega_2, \nu_3 k_3 \omega_3, \nu_1 k_1 \omega_1)$ and $(\nu_1 k_1 \omega_1, \nu_2 k_2 \omega_2, \nu_3 k_3 \omega_3)$ (the expression is already symmetric to the permutation of $\nu_1 k_1 \omega_1$ and $\nu_2 k_2 \omega_2$).

We consider CW laser fields characterized by their amplitude $E^{(s)}_\nu$, wavevector $k_s$ and optical frequency $\omega_s$:

$$E^{(s)}_\nu(k, \omega) = \frac{(2\pi)^4}{2} e^{i\omega t} \chi(k, \omega) \delta(\omega - \omega_s) + c.c.'$$  \hspace{1cm} (E4)

We consider the signal in the direction $-k_1 - k_2 + k_3$:

$$P^{(3)}_{\nu_4} (-k_1 - k_2 + k_3, \omega_1 + \omega_2 - \omega_3) = \frac{1}{2^3} \sum_{\nu_2 \nu_3 \nu_1} e^{-i\omega_3} e^{i\omega_2} e^{i\omega_1} E^{(3)}_{\nu_3} E^{(2)}_{\nu_2} E^{(1)}_{\nu_1} \chi^{(3)}_{\nu_4, \nu_3 \nu_2 \nu_1} (k_1 + k_2 - k_3, -\omega_1 - \omega_2 + \omega_3; k_3, -\omega_3, -k_2 \omega_2, -k_1 \omega_1).$$  \hspace{1cm} (E5)

In the RWA this gives

$$\chi^{(3)}_{\nu_4, \nu_3 \nu_2 \nu_1} (k_1 + k_2 - k_3, -\omega_1 - \omega_2 + \omega_3; k_3, -\omega_3, -k_2 \omega_2, -k_1 \omega_1) = 2\pi i \frac{1}{3} \sum_{\xi_4 \xi_3 \xi_2 \xi_1} (d^{\xi_4}_{\xi_1} (-k_1 - k_2 + k_3) d^{\xi_3}_{\xi_1} (-k_3) d^{\xi_2}_{\xi_1} (-k_2) d^{\xi_1}_{\xi_1} (-k_1)) \chi_{\xi_4 \xi_3 \xi_2 \xi_1} (\omega_2 + \omega_1) I_{\xi_4} (\omega_1 + \omega_2 - \omega_3) I_{\xi_2} (\omega_3) I_{\xi_1} (\omega_1) + c.c.'.$$  \hspace{1cm} (E6)

This is a three dimensional signal of optical frequencies. Two dimensional sections at $\omega_3 = \omega_1$ of that signal can be used [17].

**Appendix F: THE EXCITON SCATTERING MATRIX FOR PERIODIC STRUCTURES**

In this appendix we calculate the time domain scattering matrix (eq. (21)) for periodic systems, which can be easily extended to non periodic finite systems. Using eq. (19) we calculate the scattering matrix in the frequency domain, which is directly used in appendix C. The time domain scattering matrix is then given by the Fourier transform:

$$\Gamma_{\xi_4 \xi_3 \xi_2 \xi_1} (t) = \int d\omega \exp(-i\omega t) \Gamma_{\xi_4 \xi_3 \xi_2 \xi_1} (\omega).$$  \hspace{1cm} (F1)

An infinite system is constructed by replicating a unit cell where all vibrational or electronic modes are fixed at particular sites inside each cell in some crystal lattice. We will assume a cubic lattice of dimensionality $D$ with a finite number $N^D$ cells. To guarantee translational invariance we use cyclic boundary conditions. Each mode is represented by a pair of indices, $Rm$, where $R$ is a position vector of the cell and $m$ is the index of the site within the unit cell; the position of the $m$-th site inside the molecule is given by the vector $R + \rho_m$ where $R$ is the origin of the unit cell and $\rho_m$ is the displacement from that origin. We denote the number of sites in the cell by $M$ and the lattice constant $a$. Since the system is translationally invariant, the intermode coupling $J_{Rm, R'n} = J_{m,n} (R' - R)$ now depends on the distance between cells $R' - R$ and on the site indices of each cell, $m$ and $n$. When $R' = R$, $J_{m,n}(0)$ describes the coupling of modes inside the cell. $J_{m,n} (R' - R)$ with $R' \neq R$ defines inter-cell couplings. Similar to this coupling the intermode anharmonicity $\Delta J_{Rm, R'n} = \Delta m,n (R' - R)$ now depends on the distance between cells and on the site indices of each cell. We note that $\Delta m,m (R' - R)$ with $R' \neq R$ defines anharmonicity of the combination band, where two excitations are localized on different sites.
The one-exciton eigenstates $\xi$ of a periodic system are characterized by two quantum numbers: the Davydov band index $\lambda$ is related to different sites in the unit cell, and the exciton momentum (Bloch wavevector) $q$. For molecular systems much smaller than the optical wavelength only zero momentum, $q = 0$, exciton states contribute to nonlinear optical response. The infinite size only enters into the scattering matrix, where excitons with different momenta can be involved in the exciton scattering process.

The equations for the optical response (C10) – (C16) can be equivalently used for periodic structures with cyclic boundary conditions provided the eigenstates $\xi$ are replaced with the periodic system eigenstates $\lambda$ at momentum $q = 0$. The scattering matrix is then considerably simplified:

$$\bar{\Gamma}_{\lambda\lambda\lambda_1}(\omega) = \sum_{m_1} \bar{\psi}_{\lambda m_1} \bar{\gamma}_{\lambda m_1} \sum_{l_s < r' < l_c} \bar{\Gamma}_{r'' m_1 m_2}(\omega) \bar{\psi}_{\lambda m_2} \bar{\psi}_{\lambda m_1}, \quad (F2)$$

where $\bar{\Gamma}_{r_1, m_1; r_2, m_2}(\omega)$ is the mixed space scattering matrix (taken at zero momentum). This scattering matrix is given by [17]:

$$\bar{\Gamma}_{r_1, m_1; r_2, m_2}(\omega) = -i \Delta_{mn}(r_1) \langle \bar{D}(\omega) \rangle_{r_1, m_1; r_2, m_2}^{-1}, \quad (F3)$$

and the matrix

$$\bar{D}_{r_1, m_1; r_2, m_2}(\omega) = \delta_{r_1, r_2} \delta_{m_1, m_2} \delta_{n_1, n_2} + i \bar{C}_{r_1, m_1; r_2, m_2}(\omega) \Delta_{m n}(r_2), \quad (F4)$$

where the mixed space two-exciton Green’s function

$$\bar{G}_{r_1, m_1; r_2, m_2}(\omega) = \frac{1}{V} \sum_{q} e^{-i q (r_2 - r_1)} g_{m_1 m_2}(q, -q, \omega), \quad (F5)$$

involves the sum over two-exciton Green’s function of one unit cell with different momenta:

$$g_{m_1 m_2}(q, -q, \omega) = \sum_{\lambda \lambda'} \bar{\psi}_{\lambda m_1}(q) \bar{\psi}_{\lambda m_2}(q) \bar{\varphi}_{\lambda m_1}(q) \bar{\varphi}_{\lambda m_2}(q). \quad (F6)$$

We have adopted the following notation. $\bar{\psi}_{\lambda m}$ is a zero momentum wavefunction of exciton band $\lambda$ obtained from

$$\sum_{m'} J_{m,m'}(q = 0) \bar{\psi}_{\lambda m'} = e_{\lambda} \bar{\psi}_{\lambda m}, \quad (F6)$$

where $J_{m,m'}(q = 0) = \sum_{r} J_{m,m'}(r)$ and $e_{\lambda}$ is the eigenenergy of this state. The prime in the sums denotes the summation either over sites within one cell or over different Davydov bands at zero momentum, while the sum over $r$ is a sum over cells including $r = 0$ within the scattering length $l_c$ defined by $\Delta_{mn}(r > l_c) = 0$. All site indices $m$ run within one cell, while $\sum_{q}$ is the sum over momenta. For infinite systems this sum becomes an integral over all exciton bands.

The scattering matrix calculation (eq. (C11)) is the same for the finite non-periodic system except that $r$ and $q$ are set to 0 in eqs. (F2) – (F6), site indices $m$ and $n$ then correspond to different modes in the entire system and the exciton band indices $\lambda$ are changed into exciton states $\xi$. 

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Figure Captions

Figure 1. (top) Time domain third order experiments: three short laser pulses with wavevectors $k_1$, $k_2$ and $k_3$ generate a nonlinear polarization with wavevector $k_S$. (bottom left) Structures of the peptide backbone in $\alpha$ helix and antiparallel $\beta$ sheet structures: green - C atoms, blue - N atoms, red - O atoms. C=O responsible for amide I mode (1600-1700 cm$^{-1}$) are emphasized. (bottom right) Energy level scheme of excitonic system with one ground state, a manifold of one-exciton states ($e$) and a manifold with two-exciton states ($f$).

Figure 2. a) Time variables used in calculating the excitonic response. Red peaks indicate laser pulses, blue area corresponds to the exciton-exciton scattering process. $t_1$, $t_2$ and $t_3$ are the first, second and third interactions with laser pulses. $t_4$ is the signal generation time. $t_{i+1,i} = t_{i+1} - t_i$ are the delay times (always positive) between two interactions. $\tau^{"}_s$ and $\tau'_s$ are the delay times of the exciton scattering. b) Transformation from the non ordered time variables $\tau_1$, $\tau_2$ and $\tau_3$ to ordered times $t_1$, $t_2$ and $t_3$ in eqs. (24-26) which defines the three different scattering pathways. c) Three scattering pathways: $k_I = -k_1 + k_2 + k_3$ involves scattering of the excitons created by $k_2$ and $k_3$, $k_{II} = k_1 - k_2 + k_3$ involves scattering of the excitons created by $k_1$ and $k_3$, and $k_{III} = k_1 + k_2 - k_3$ involves scattering of the excitons created by $k_1$ and $k_2$.

Figure 3. Linear absorption of the $\alpha$ helix (top) and the antiparallel $\beta$ sheet (bottom).

Figure 4. Absolute value of $S_{\nu_4 \nu_3 \nu_2 \nu_1}^k(\Omega_3, T_2 = 0, \Omega_1)$ signal of the $\alpha$ helix and antiparallel $\beta$ sheet (eq. (C10)). Shown are one nonchiral, $xxxx$, and three chiral, $xxxy$, $xxyx$, $xyxx$, components as indicated. Blue crosses mark the crosspeaks of $xxxx$.

Figure 5. Absolute value of the $S_{\nu_4 \nu_3 \nu_2 \nu_1}^{k_{III}}(\Omega_3, \Omega_2, T_1 = 0)$ signal of the $\alpha$ helix and antiparallel $\beta$ sheet (eq. (C16)). Shown are one nonchiral, $xxxx$, and three chiral, $xxxy$, $xxyx$, $xyxx$, components, as indicated.

Figure 6. Comparison of the exciton-scattering and the transition-among-eigenstates pictures of the three signals $S^k_1(\Omega_3, T_2, \Omega_1)$, $S^{k_{II}}_1(\Omega_3, T_2, \Omega_1)$ and $S^{k_{III}}_1(\Omega_3, \Omega_2, T_1)$. $\Omega_1$, $\Omega_2$ and $\Omega_3$ are the Fourier transform variables conjugate to $T_1$, $T_2$ and $T_3$. Red dots represent the interaction of the system with the field, blue dots mark the exciton scattering space.
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