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Fifth-Order Three-Dimensional Electronic Spectroscopy Using a Pump-Probe Configuration

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We present the theoretical details and experimental demonstration of fifth-order three-dimensional (3D) electronic spectroscopy using a pump-probe beam geometry. This is achieved using a pulse shaper and appropriate phase cycling schemes. We show how 8-step and 27-step phase cycling schemes can measure purely absorptive 3D spectra as well as 3D spectra for the individual fifth-order processes that contribute to the purely absorptive spectrum. 3D spectra as a function of two separate controllable waiting time periods can be obtained. The peakshapes and positions of the peaks in the experimental measurement correspond well to theory.

Keywords: Ultrafast multidimensional spectroscopy, electronic spectroscopy, pulse shaping, phase cycling

I. Introduction

The extension of the by now well-established two-dimensional (2D) third-order optical spectroscopies¹⁻⁶ to three-dimensional (3D) fifth-order optical spectroscopies⁷⁻⁹, brings several

new observables to the spectroscopist inaccessible in lower order spectroscopies. This includes the ability to reach higher vibronic states to better characterize the anharmonicity of the investigated systems.^{7,10-12} 3D spectroscopy also allows higher spectral resolution and de-clutters congested spectra, by introducing a third frequency axis.¹² In 3D electronic spectroscopy, one can retrieve hidden couplings that were previously obscured in a congested 2D electronic spectrum.⁸ 2D electronic spectroscopy has been applied to studying energy transfers between excitonic states in light-harvesting complexes.¹³ These processes are highly complicated and consist of multiple steps. 2D electronic spectroscopy can only directly observe single step energy transfers and indirectly infer multiple step energy transfer.¹⁴ 3D electronic spectroscopy has the potential to provide direct measurements of multiple step energy transfer between these multi-level electronic systems. A recent topic of debate is the validity of commonly made assumptions, such as linear response theory, Gaussian statistics and Markovian processes. As shown, 3D spectroscopies can help answer these questions by studying the three-point correlation function.^{15,16} Recent work on liquid water unequivocally showed its heterogeneous structural relaxation dynamics.⁹ From these examples alone it is clear that fifth-order 3D spectroscopy will be of benefit for the optical spectroscopist and the extension to higher dimensions is expected to become even more pertinent with further advances in ultrafast laser technologies.

Figure 1(a) shows the fundamental idea of fifth-order 3D optical spectroscopy. The three coherence time periods t_1 , t_3 and t_5 are Fourier transformed to measure the instantaneous frequencies ω_1 , ω_3 and ω_5 , respectively, at waiting times t_2 and t_4 . Third-order 3D optical experiments have also been performed recently¹⁷⁻¹⁹ where an extra frequency dimension can be obtained from a conventional third-order 2D optical spectroscopy experiment by Fourier transforming over the waiting time period. Unlike third-order 3D spectroscopy, which arises

from three interactions with the light field, fifth-order 3D spectroscopy requires five interactions with the incoming light field. Fifth-order 3D spectroscopy in its conventional phase-matching implementation requires in its most general case six individual pulses (including a local oscillator pulse).⁷ The intricate optical setup hampers the applicability of 3D spectroscopy, even more so than 2D spectroscopy.

Figure 1. (a) Schematic setup for fifth-order 3D optical spectroscopy in a pump-probe geometry. The coherences times t_1 , t_3 , the waiting time t_2 as well as the phases ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 are set by a pulse shaping apparatus, while the second waiting time t_4 is introduced by a delay stage. (b) Double-sided Feynman diagrams (DSFD) for fifth-order 3D spectroscopy on a two level system in a pump-probe geometry contributing to the desired three-dimensional spectrum with populations during the waiting times. The resulting k_{signal} vector as well as the acquired phase

ϕ_{signal} and phase signatures are denoted. (c) A brief selection of the multitude of DSDFs for undesired processes that can be eliminated by phase cycling. From left to right these are pump-probe processes where the first pulse interacts twice, the second pulse interacts twice or both pulses interact twice. Lower order processes such as shown on the far right need to be discriminated as well. Their acquired phase and phase signature are denoted where applicable.

A limited form of fifth-order 3D spectroscopy can be performed using only four pulses (including the local oscillator) as shown in Zanni's work in the infrared¹² and Engel's work in the visible⁸, where multiple interactions are made by the second and third pulses, to measure the fifth-order signal. This necessarily means that there is no control over the population times t_2 and t_4 , which will always be equal to zero. The other limitations of using two interactions each for pulses one and three in Zanni's work or pulses two and three in Engel's work to achieve five interactions is that purely absorptive peaks cannot be obtained. A full form of fifth-order 3D spectroscopy with control over the population times was performed in the IR using a non-collinear phase-matching geometry with six pulses (including the local oscillator) independently controlled using computer-controlled mechanical translational stages.⁷ With the advent of 2D spectroscopy performed in a pulse shaper assisted pump-probe configuration, the experimental technique is simplified.²⁰⁻²⁴ One further major advantage of such a pulse shaper assisted set-up is that it allows the immediate extension to three dimensions and higher orders without the need of altering the optical setup. Recently, our group demonstrated a method to obtain purely absorptive fifth-order 3D electronic spectra based on a pulse shaper assisted pump-probe beam geometry setup.²⁵ In our 3D spectroscopy performed using a pump-probe configuration, the first four 'pump' pulses are provided collinearly by a pulse shaper, followed by subsequent interaction by a non-collinear probe pulse. In principal, the advantages of 2D spectroscopy in a pump-probe

geometry apply to 3D spectroscopy as well, such as intrinsic phasing of various contributions to the overall response function and data collection in the rotating frame, which allows under-sampling.^{22,23,26,27} However, just like in the two-dimensional case,^{23,27-30} to obtain three-dimensional spectra devoid of peak ambiguities and interferences from other spurious signals, phase cycling is essential. With phase cycling, the desired multi-dimensional signals can be retrieved by the weighted summation of data collected from using different inter-pulse phases. Phase cycling can be easily implemented using a pulse shaper by systematically changing the relative inter-pulse phases, which is cycled over 2π radians in a number of equally spaced steps.^{27,28} Recent works have shown that with the proper understanding of phase cycling theory and phase cycling scheme selection, two-dimensional spectra of desired Liouville pathways, such as rephasing and non-rephasing diagrams can be obtained.²¹⁻²³ In this article, the concept of phase cycling is extended to apply to the various implementations of 3D optical spectroscopy in the pump-probe beam geometry. The next section describes a general theoretical framework to choose appropriate phase cycling procedures needed to obtain fifth-order 3D spectra. Section III presents the experimental procedures for phase cycling in 3D spectroscopy, while in section IV we report our results that are obtained from various phase cycling schemes. Section V outlines the possibility of cascaded third-order signals in the 3D spectrum from a pump-probe geometry setup. The publication summarizes with a brief conclusion in section VI.

II. Theory

In the framework of diagrammatic time dependent perturbation theory, three-dimensional optical spectroscopy is a fifth-order nonlinear optical experiment where the system interacts five times with the incident light fields. Specifically, in the pump-probe beam geometry the pump

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2
3 pulse light field interacts four times, while the fifth interaction is provided by the probe pulse.
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5 Phase matching conditions result in the induced fifth-order sample polarization creating a signal
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7 light field that is emitted collinearly with the probe pulse, so that it is self-heterodyne detected
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9 and thus rendering an external local oscillator unnecessary. Since six light fields participate in
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11 the light-matter interaction it is also referred to as a six-wave mixing process (SWM).
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15 A general scheme of a pump-probe geometry 3D optical experiment is shown in Fig. 1(a). The
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17 required phase-locked four pulse pump train can be readily provided by a pulse shaping
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19 apparatus,³¹ with individually controllable coherence times t_1 , and t_3 , and waiting time t_2 . Due to
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21 the limited temporal window of pulse shapers there is a constraint on the achievable waiting time
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23 t_2 , but this constraint may not be crucial in many cases. For instance, Hamm showed that to study
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25 the three-point frequency fluctuation correlation functions, waiting times up to 3 ps are
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27 sufficient.¹⁵ Such time delays pose no problem to current pulse shaping technology. All four
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29 pump pulses are incident along the wave vector $\mathbf{k}_{pump}$ and have the individual phases ϕ_1 , ϕ_2 , ϕ_3 ,
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31 and ϕ_4 , respectively. The probe pulse is delayed by a second waiting time t_4 from the last pump
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33 pulse interaction via a translation stage and is incident onto the sample in the $\mathbf{k}_{probe}$ direction.
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37 The signal is emitted with the time delay t_5 . Phase matching conditions make sure that the
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39 desired signal field is emitted along the direction of the probe pulse $\mathbf{k}_{probe} = \mathbf{k}_{signal}$, so that the
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41 probe pulse intrinsically acts as a local oscillator to self-heterodyne the signal field. We do not
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43 take into consideration the phase relationship between the pump and probe pulses, as they
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45 interact non-collinearly.¹⁵ In section II(A), we will discuss the phase cycling schemes for such
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47 four pump pulse experiments.
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54 As there has been growing interest to use the rephasing and nonrephasing spectra to observe
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56 energy transfers within light-harvesting complexes in 2D spectroscopy,^{14,32,33} several groups
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have previously proposed ways to retrieve signals from the rephasing and nonrephasing processes in a pump-probe beam geometry setup.^{21,23} Similarly, we can independently retrieve signals from the four different pathways that contribute to the pure absorptive 3D spectrum in a pump-probe beam geometry setup, which we will discuss in section II(B).

A. Purely absorptive 3D spectra using four pump pulses in a pump-probe geometry

The pulse train incident on the sample in a 3D pump-probe experiment in a pump-probe geometry can be expressed in the time domain as:

$$\begin{aligned}
 E(t) = & E_1(t+t_4+t_3+t_2+t_1)\exp(-i\omega_L t + i\phi_1 + i\Delta\omega_{ref}t_1 + i\mathbf{k}_{pump}r) \\
 & + E_2(t+t_4+t_3+t_2)\exp(-i\omega_L t + i\phi_2 + i\Delta\omega_{ref}t_2 + i\mathbf{k}_{pump}r) \\
 & + E_3(t+t_4+t_3)\exp(-i\omega_L t + i\phi_3 + i\Delta\omega_{ref}t_3 + i\mathbf{k}_{pump}r) \\
 & + E_4(t+t_4)\exp(-i\omega_L t + i\phi_4 + i\mathbf{k}_{pump}r) \\
 & + E_5(t)\exp(-i\omega_L t + i\mathbf{k}_{probe}r) + c.c.
 \end{aligned} \tag{1}$$

where E_1 to E_5 denote the individual pulse envelopes and ω_L is the pulse center frequency, while $\Delta\omega_{ref}$ is the difference between the pulse center frequency ω_L and a reference frequency ω_{ref} set by the pulse shaper. In a ‘rotating frame’, $\Delta\omega_{ref} = \omega_L - \omega_{ref} = 0$.^{22,23} The macroscopic signal field $S(t_1, t_2, t_3, t_4, t_5)$ is a convolution of the fifth-order nonlinear response function $R^{(5)}(t_1, t_2, t_3, t_4, t_5)$, which contains all relevant information about the system under investigation, and the interacting light fields:

$$\begin{aligned}
 S(t_1, t_2, t_3, t_4, t_5) = & \int \int \int \int \int dt_5 dt_4 dt_3 dt_2 dt_1 R^{(5)}(t_1, t_2, t_3, t_4, t_5) E(\mathbf{k}, t-t_5) E(\mathbf{k}, t-t_5-t_4) \\
 & \times E(\mathbf{k}, t-t_5-t_4-t_3) E(\mathbf{k}, t-t_5-t_4-t_3-t_2) E(\mathbf{k}, t-t_5-t_4-t_3-t_2-t_1)
 \end{aligned} \tag{2}$$

In the semi-impulsive limit, i.e. when the pulses envelopes are considered as δ -functions while still retaining their carrier frequencies, phases and wave vectors, the emitted light field is directly proportional to the response function.⁶

The fifth-order nonlinear response function $R^{(5)}(t_1, t_2, t_3, t_4, t_5)$ consists of various coherence transfer pathways which can be illustrated using double sided Feynman diagrams (DSFDs). In this paper, we restrict the discussion to a two level system, but the extensions to multiple level systems and systems coupled to other degrees of freedom can be made. Representative DSFDs of various fifth-order nonlinear optical processes in the pump-probe geometry for a two-level system are depicted in Fig. 1(b) using the notation by Hamm.¹⁵ (For each of the processes $R^{(5)}$ that is portrayed in Fig. 1(b), there are additional DSFDs which are in the excited state population during the waiting time periods. These DSFDs are not depicted here). We restrict ourselves to diagrams in the observed $k_{\text{signal}} = k_{\text{probe}}$ direction, as well as DSFDs that exhibit only populations during the last waiting times. When using a phase-locked pump pulse train, as delivered by pulse shapers, the emitted signal acquires a phase signature $\phi_{\text{signal}} = \alpha\phi_1 + \beta\phi_2 + \gamma\phi_3 + \delta\phi_4$, where α is the number of first pump pulse arrows pointing to the right minus first pump pulse arrows pointing to the left of the DSFDs. Arrows pointing towards the DSFDs represent absorption, while arrows pointing away represent emission. β , γ , and δ can be calculated accordingly for the second, third and fourth pulse interaction. Practically, we denote the phase signatures in terms of relative phases $\phi_{14} = \phi_1 - \phi_4$, $\phi_{24} = \phi_2 - \phi_4$ and $\phi_{34} = \phi_3 - \phi_4$, since only the inter-pulse phase relationships matter. In this notation the overall acquired phase signature of the signal is $\phi_{\text{signal}} = \alpha\phi_{14} + \beta\phi_{24} + \gamma\phi_{34}$. As can be seen δ is in fact not necessary to denote a particular coherence transfer pathway. This stems from the fact that in a pump-probe geometry the system necessarily needs to end in a population state for the second waiting time t_4 , which constraints the values of α , β , γ , and δ to be:

$$\alpha + \beta + \gamma + \delta = 0 \quad (3)$$

If we furthermore restrict the problem to fifth and lower order processes while ignoring higher order terms, only up to four interactions from the four pump pulses need to be considered. This results in a second condition:

$$|\alpha| + |\beta| + |\gamma| + |\delta| \leq 4 \quad (4)$$

The signals from the four diagrams in Fig. 1(b) in the semi-impulsive limit from Eq. (2), gives:

$$\begin{aligned} R_1^{(5)}(t_1, t_2, t_3, t_4, t_5) &\propto \Theta(t_1)\Theta(t_3)\Theta(t_5)\exp(-i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3)\exp(-i\omega_{10}t_5)F_1(t_1, t_2, t_3, t_4, t_5) \\ R_2^{(5)}(t_1, t_2, t_3, t_4, t_5) &\propto \Theta(t_1)\Theta(t_3)\Theta(t_5)\exp(+i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3)\exp(-i\omega_{10}t_5)F_2(t_1, t_2, t_3, t_4, t_5) \\ R_3^{(5)}(t_1, t_2, t_3, t_4, t_5) &\propto \Theta(t_1)\Theta(t_3)\Theta(t_5)\exp(-i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3)\exp(-i\omega_{10}t_5)F_3(t_1, t_2, t_3, t_4, t_5) \\ R_4^{(5)}(t_1, t_2, t_3, t_4, t_5) &\propto \Theta(t_1)\Theta(t_3)\Theta(t_5)\exp(+i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3)\exp(-i\omega_{10}t_5)F_4(t_1, t_2, t_3, t_4, t_5) \end{aligned} \quad (5)$$

where ω_{10} is the resonance frequency of the two-level system, and $\Delta\omega_{10} = \omega_{10} - \omega_{ref}$ is the resonance frequency detuned from the reference frequency ω_{ref} . Over t_1 and t_3 , the data is collected over a rotating frame at ω_{ref} frequency.^{22,23} $\Theta(t)$ is a Heaviside step function. F_1 to F_4 are functions that account for dephasing and population relaxation dynamics,³⁴ and therefore determine the peak shapes. Each coherence transfer pathway contains valuable information, but for purely absorptive spectra which exhibit the highest possible frequency resolution, the overall response function needs to have contributions from all individual response functions $R_1^{(5)}$ to $R_4^{(5)}$.¹⁵ A characteristic of using a pump-probe geometry is that all coherence transfer pathways $R_1^{(5)}$ to $R_4^{(5)}$ will automatically emit in the same direction $\mathbf{k}_{signal} = \mathbf{k}_{probe}$, which is beneficial for the collection of purely absorptive spectra. However, there is also a multitude of other processes emitted in the $\mathbf{k}_{signal} = \mathbf{k}_{probe}$ direction, of which a few examples are depicted in Fig. 1(c). They consist of coherence transfer pathways of fifth-order processes, where certain light fields interact more than once with the system, as well as other lower order processes ($|\alpha| + |\beta| + |\gamma| + |\delta| \leq 2$). Although such processes will not be discriminated by the phase matching condition, they are distinguishable

from the desired coherence transfer pathways by their phase signature. The sum of the multitude of undesired processes is denoted with P . One purpose of phase cycling is to get rid of such unwanted signal contributions. In summary, for fixed waiting times t_2 and t_4 the following expression results for the overall phase dependent signal:

$$S(t_1, t_3, t_5) \propto R_1^{(5)}(t_1, t_3, t_5) \exp(+i\phi_{14} - i\phi_{24} + i\phi_{34}) + R_2^{(5)}(t_1, t_3, t_5) \exp(-i\phi_{14} + i\phi_{24} + i\phi_{34}) \\ + R_3^{(5)}(t_1, t_3, t_5) \exp(+i\phi_{14} - i\phi_{24} - i\phi_{34}) + R_4^{(5)}(t_1, t_3, t_5) \exp(-i\phi_{14} + i\phi_{24} - i\phi_{34}) + \dots \quad (6)$$

Experimentally, the first two coherence times t_1 and t_3 are typically collected in the time domain, while the third coherence time t_5 is acquired in the frequency domain by spectrally resolving the signal in a spectrometer, which mathematically is a Fourier transform about the t_5 axis (FT_{t_5}). For brevity, we will henceforth drop the waiting time variables t_2 and t_4 in our equations. Subsequent self-heterodyned detection of the signal field with a square-law detector is mathematically equivalent to selecting the real part of the product of the signal field and the intrinsic local oscillator field. In the semi-impulsive limit the detected frequency resolved signal $\tilde{S}$ can be expressed, using $S(t_1, t_3, t_5)$ of Eq. (6), as:

$$\tilde{S}(\phi_{14}, \phi_{24}, \phi_{34}; t_1, t_3, \omega_5) \propto \Re[\text{FT}_{t_5}\{S(t_1, t_3, t_5)\}] \\ \equiv \sum_{\alpha, \beta, \gamma} \tilde{s}(\alpha, \beta, \gamma; t_1, t_3, \omega_5) \exp(+i\alpha\phi_{14} + i\beta\phi_{24} + i\gamma\phi_{34}) \quad (7)$$

The summation in the last line of Eq. (7) groups all terms according to their phase signature α , β , and γ . Amongst all possible terms, those of interest are:

$$\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5) \propto \Theta(t_1)\Theta(t_3) \exp(-i\Delta\omega_{10}t_1) \exp(-i\Delta\omega_{10}t_3) \\ \times \left[\tilde{F}_1(t_1, t_3, \omega_5 - \omega_{10}) + \tilde{F}_4^*(t_1, t_3, \omega_5 - \omega_{10}) \right] \quad (8)$$

$$\tilde{s}_{2+3}^*(\alpha=-1, \beta=1, \gamma=1; t_1, t_3, \omega_5) \propto \Theta(t_1)\Theta(t_3) \exp(+i\Delta\omega_{10}t_1) \exp(-i\Delta\omega_{10}t_3) \\ \times \left[\tilde{F}_2(t_1, t_3, \omega_5 - \omega_{10}) + \tilde{F}_3^*(t_1, t_3, \omega_5 - \omega_{10}) \right] \quad (9)$$

$$\begin{aligned} \tilde{s}_{3+2^*}(\alpha=1, \beta=-1, \gamma=-1; t_1, t_3, \omega_5) &\propto \Theta(t_1)\Theta(t_3)\exp(-i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3) \\ &\times \left[\tilde{F}_3(t_1, t_3, \omega_5 - \omega_{10}) + \tilde{F}_2^*(t_1, t_3, \omega_5 - \omega_{10}) \right] \end{aligned} \quad (10)$$

$$\begin{aligned} \tilde{s}_{4+1^*}(\alpha=-1, \beta=1, \gamma=-1; t_1, t_3, \omega_5) &\propto \Theta(t_1)\Theta(t_3)\exp(+i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3) \\ &\times \left[\tilde{F}_4(t_1, t_3, \omega_5 - \omega_{10}) + \tilde{F}_1^*(t_1, t_3, \omega_5 - \omega_{10}) \right] \end{aligned} \quad (11)$$

where $\tilde{F}_i(t_1, t_3, \omega_5 - \omega_{10}) = \text{FT}_5 \{ F_i(t_1, t_3, t_5) \exp(-i\omega_{10}t_5) \}$. The asterisk denotes the complex conjugate.

Either one of the pair of Eq. (8) and (9) or Eq. (10) and (11) contains all the relevant terms shown in Eq. (5) to obtain the pure absorptive peaks in a 3D spectrum. We shall discuss here the choice of an appropriate phase cycling scheme to measure selectively Eqs. (8) and (9) from the summation series of Eq. (7).

Mathematically, to extract a specific signal $\tilde{s}(\alpha, \beta, \gamma; t_1, t_3, \omega_5)$ with phase signature $\exp(+i\alpha\phi_{14} + i\beta\phi_{24} + i\gamma\phi_{34})$ a three-dimensional Fourier transform of $\tilde{S}(\alpha, \beta, \gamma; t_1, t_3, \omega_5)$ over the interpulse phase-space needs to be performed:

$$\begin{aligned} \tilde{s}(\alpha, \beta, \gamma; t_1, t_3, \omega_5) &= \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} d\phi_{14} d\phi_{24} d\phi_{34} \tilde{S}(\alpha, \beta, \gamma; t_1, t_3, \omega_5) \\ &\times \exp(-i\alpha\phi_{14}) \exp(-i\beta\phi_{24}) \exp(-i\gamma\phi_{34}) \end{aligned} \quad (12)$$

In our approach, we experimentally sample the phase-spaces in discrete steps and Eq. (12) can be written as a discrete Fourier transform:

$$\begin{aligned} \tilde{s}^{L \times M \times N \times 1}(\alpha, \beta, \gamma; t_1, t_3, \omega_5) &= \frac{1}{LMN} \sum_{l=0}^{L-1} \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \tilde{S}(l\Delta\phi_{14}, m\Delta\phi_{24}, n\Delta\phi_{34}; t_1, t_3, \omega_5) \\ &\times \exp(-il\alpha\Delta\phi_{14}) \exp(-im\beta\Delta\phi_{24}) \exp(-in\gamma\Delta\phi_{34}) \\ &\equiv \frac{1}{LMN} \sum_{l=0}^{L-1} \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \tilde{S}(l\Delta\phi_{14}, m\Delta\phi_{24}, n\Delta\phi_{34}; t_1, t_3, \omega_5) \\ &\times W_L^{l\alpha} W_M^{m\beta} W_N^{n\gamma} \end{aligned} \quad (13)$$

where $\phi_{14} = l\Delta\phi_{14}$, $\phi_{24} = m\Delta\phi_{24}$, and $\phi_{34} = n\Delta\phi_{34}$, L is the number of sample points in the ϕ_{14} -phase space, M is the number of sample points in the ϕ_{24} -phase space, and N is the number of sample points in the ϕ_{34} -phase space. $W_L^{l\alpha}$, $W_M^{m\beta}$, and $W_N^{n\gamma}$ are the respective summation weights.

Experimentally, this means a series of experiments need to be conducted with different interpulse phases ϕ_{14} , ϕ_{24} , and ϕ_{34} , and the resultant series of phase dependent signals added according to the weights $W_L^{l\alpha}$, $W_M^{m\beta}$, and $W_N^{n\gamma}$. For a $L \times M \times N \times 1$ phase cycling scheme, it is desirable to keep L , M , and N minimal as this determines the total number of measurements that need to be performed. In principle, it does not matter which one of the four pulses we should reference the pulse phases to. Therefore the resultant signals from a $L \times M \times N \times 1$ phase cycling experiment and a $1 \times L \times M \times N$ experiment are the same, the latter being if we reference the interpulse phases to the first pulse. In this article, we have referenced it to the last pulse as it is simpler to set up experimentally.

Phase cycling is a technique that is analagous to theoretical methods developed by research groups to extract relevant terms from a nonperturbative calculation of nonlinear optical signals.³⁵⁻³⁷

A related technique to phase cycling can be found in phase modulated 2D fluorescence spectroscopy and related experiments.³⁸⁻⁴⁰ In this technique, instead of phase cycling through the laser pulses with discrete phase steps, phases are introduced in a continuously fashion and the desired signal with its corresponding phase modulation signature can be obtained using a lock-in detector.

The general conditions of Eq. (3) and (4) allow 55 coherence transfer pathways (See Supporting Information) to evolve without phase cycling. The phase cycling scheme discussed in this article is similar in nature to the phase cycling schemes of 2D collinear optical spectroscopy discussed in an earlier article.²⁹ In the 2D collinear optical spectroscopy discussed in Ref. 27, four interactions with the four collinear pulses leads to a population state which is then detected. After the consideration of aliasing, both rephasing and nonrephasing spectra can be obtained

using a $1 \times 3 \times 3 \times 3$ phase cycling scheme. In this present article, the first four interactions with the four pump pulses lead to a population which is then probed by the fifth interaction. The conditions denoted in Eqs. (3) and (4) are therefore the same as that presented in Ref. 27 with a four pulse train. Likewise a full 27 steps $1 \times 3 \times 3 \times 3$ (or a $3 \times 3 \times 3 \times 1$) phase cycling scheme can be performed and the appropriate linear combination of the signals provided by Eq. (13) can then be applied to extract the signals $\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5)$ and $\tilde{s}_{2+3}^*(\alpha=-1, \beta=1, \gamma=1; t_1, t_3, \omega_5)$ (Eq. (8) and (9), respectively) (The $3 \times 3 \times 3 \times 1$ phase cycling scheme to select $\tilde{s}(\alpha, \beta, \gamma; t_1, t_3, \omega_5)$ is listed in full details in the Supporting Information).

Upon obtaining the signal of Eq. (8) and (9) using the $3 \times 3 \times 3 \times 1$ phase cycling scheme where the first three pulses are each cycled over phases ϕ_{14} , ϕ_{24} , and $\phi_{34} = 0, 2\pi/3$ and $4\pi/3$, we explain here how the data can then be processed to obtain pure absorptive peaks. We make the following simplification that $F_1(t_1, t_3, t_5) = F_2(t_1, t_3, t_5) = F_3(t_1, t_3, t_5) = F_4(t_1, t_3, t_5) = F(t_1, t_3, t_5)$ are real functions and $F(t_1, t_3, t_5) = F(t_1, t_3)F(t_5) = F(t_1)F(t_3)F(t_5)$. These assumptions are only made for brevity to illustrate in a clearer fashion how pure absorptive peak shapes are obtained. More general expressions may be written if required. We can express the Fourier transform of $F(t_j)$ about any coherence time axis t_j , where $j = 1, 3$ or 5 , as $\text{FT}_j \{ \Theta(t_j) F(t_j) \exp(-i\omega_0 t_j) \} = A(\omega_j - \omega_{10}) + iD(\omega_j - \omega_{10})$, where $A(\omega_j - \omega_{10})$ and $D(\omega_j - \omega_{10})$ are the absorptive and dispersive terms, respectively. Fourier transformations of Eq. (8) about t_1 and t_3 and taking the real part of the signal only then results in a 3D spectrum:

$$\begin{aligned}
\tilde{s}_{1+4}^{3 \times 3 \times 3 \times 1}(\alpha=1, \beta=-1, \gamma=1; \omega_1, \omega_3, \omega_5) &= \Re \left\{ \text{FT}_{1,3} \left\{ \tilde{s}_{1+4}(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5) \right\} \right\} \\
&= \Re \left\{ \text{FT}_{1,3} \left\{ F(t_1) F(t_3) \exp(-i\Delta\omega_0 t_1 - i\Delta\omega_0 t_3) A(\omega_5 - \omega_{10}) \right\} \right\} \\
&= \Re \left\{ \left[\begin{array}{c} A(\omega_1 - \Delta\omega_{10}) + iD(\omega_1 - \Delta\omega_{10}) \\ A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \end{array} \right] A(\omega_5 - \omega_{10}) \right\} \quad (14) \\
&= A(\omega_1 - \Delta\omega_{10}) A(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10}) \\
&\quad - D(\omega_1 - \Delta\omega_{10}) D(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10})
\end{aligned}$$

From this expression we can see that the spectrum will be centered at $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$. Also, it is apparent that the spectrum still contains dispersive contributions along ω_1 and ω_3 . Similarly, the 3D spectrum resulting from $\tilde{s}_{2+3}(\alpha=-1, \beta=1, \gamma=1; t_1, t_3, \omega_5)$ of Eq. (9) becomes:

$$\begin{aligned}
\tilde{s}_{2+3}^{3 \times 3 \times 3 \times 1}(\alpha=-1, \beta=1, \gamma=1; \omega_1, \omega_3, \omega_5) &= \Re \left\{ \text{FT}_{1,3} \left\{ \tilde{s}_{2+3}(\alpha=-1, \beta=1, \gamma=1; t_1, t_3, \omega_5) \right\} \right\} \\
&= \Re \left\{ \text{FT}_{1,3} \left\{ F(t_1) F(t_3) \exp(i\Delta\omega_0 t_1 - i\Delta\omega_0 t_3) A_5(\omega_5 - \omega_{10}) \right\} \right\} \\
&= \Re \left\{ \left[\begin{array}{c} A(\omega_1 + \Delta\omega_{10}) + iD(\omega_1 + \Delta\omega_{10}) \\ A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \end{array} \right] A(\omega_5 - \omega_{10}) \right\} \quad (15) \\
&= A(\omega_1 + \Delta\omega_{10}) A(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10}) \\
&\quad - D(\omega_1 + \Delta\omega_{10}) D(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10})
\end{aligned}$$

We note that the signal now is centered at $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$. The peaks arising from Eq. (14) and (15) lie in different quadrants of the $\omega_5 = \omega_{10}$ plane in a 3D Cartesian coordinate system. Upon reflecting Eq. (15) about the $\omega_1 = 0$ plane, we obtain the mirrored spectrum:

$$\begin{aligned}
\tilde{s}_{2+3}^{3 \times 3 \times 3 \times 1, M(\omega_1)}(\alpha=-1, \beta=1, \gamma=1; \omega_1, \omega_3, \omega_5) &= A(\omega_1 - \Delta\omega_{10}) A(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10}) \\
&\quad + D(\omega_1 - \Delta\omega_{10}) D(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10}) \quad (16)
\end{aligned}$$

Eq. (14) and (16) can then be summed up to cancel out the remaining dispersive features by obeying the assumption made earlier leading to only the purely absorptive spectrum:

$$\begin{aligned}
\tilde{s}_{1+2+3+4}^{3 \times 3 \times 3 \times 1}(\omega_1, \omega_3, \omega_5) &= \tilde{s}_{1+4}(\alpha=1, \beta=-1, \gamma=1; \omega_1, \omega_3, \omega_5) + \tilde{s}_{2+3}^{M(\omega_1)}(\alpha=-1, \beta=1, \gamma=1; \omega_1, \omega_3, \omega_5) \quad (17) \\
&= A(\omega_1 - \Delta\omega_{10}) A(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10})
\end{aligned}$$

We will now discuss the application of a $2 \times 2 \times 2 \times 1$ phase cycling scheme. In a $2 \times 2 \times 2 \times 1$ phase cycling scheme, the first three pulses are each cycled over phases ϕ_{14} , ϕ_{24} , and $\phi_{34} = 0$ and π . A two step phase cycle cannot discriminate between summation weightings $\exp(i\phi)$ and $\exp(-i\phi)$ due to aliasing.²⁹ Therefore, by applying a $2 \times 2 \times 2 \times 1$ phase cycling scheme and using Eq. (7) to select the signal $\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5)$ of Eq. (8) with phase signature $\exp(+i\phi_{14} - i\phi_{24} + i\phi_{34})$, we will not be able to exclude signals from signals $\tilde{s}_{2+3}^*(\alpha=-1, \beta=1, \gamma=1; t_1, t_3, \omega_5)$, $\tilde{s}_{3+2}^*(\alpha=1, \beta=-1, \gamma=-1; t_1, t_3, \omega_5)$ and $\tilde{s}_{4+1}^*(\alpha=-1, \beta=1, \gamma=-1; t_1, t_3, \omega_5)$ of Eq. (9), (10) and (11), with phase signatures $\exp(-i\phi_{14} + i\phi_{24} + i\phi_{34})$, $\exp(+i\phi_{14} - i\phi_{24} - i\phi_{34})$ and $\exp(-i\phi_{14} + i\phi_{24} - i\phi_{34})$, respectively. Fourier transformations about t_1 and t_3 of this $2 \times 2 \times 2 \times 1$ phase cycled signal that consist of the sum of Eq. (8) to (11), followed by taking the real part will give:

$$\begin{aligned}
 \tilde{s}^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_3, \omega_5) &= \Re \left\{ \text{FT}_{1,3} \left\{ \begin{aligned} &\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5) \\ &+\tilde{s}_{2+3}^*(\alpha=-1, \beta=1, \gamma=1; t_1, t_3, \omega_5) \\ &+\tilde{s}_{3+2}^*(\alpha=1, \beta=-1, \gamma=-1; t_1, t_3, \omega_5) \\ &+\tilde{s}_{4+1}^*(\alpha=-1, \beta=1, \gamma=-1; t_1, t_3, \omega_5) \end{aligned} \right\} \right\} \\
 &= \Re \left\{ \text{FT}_{1,3} \left\{ \begin{aligned} &F(t_1)F(t_3)\exp(-i\Delta\omega_{01}t_1 - i\Delta\omega_{01}t_3)A(\omega_5 - \omega_{10}) \\ &+F(t_1)F(t_3)\exp(+i\Delta\omega_{01}t_1 - i\Delta\omega_{01}t_3)A(\omega_5 - \omega_{10}) \\ &+F(t_1)F(t_3)\exp(-i\Delta\omega_{01}t_1 + i\Delta\omega_{01}t_3)A(\omega_5 - \omega_{10}) \\ &+F(t_1)F(t_3)\exp(+i\Delta\omega_{01}t_1 + i\Delta\omega_{01}t_3)A(\omega_5 - \omega_{10}) \end{aligned} \right\} \right\} \\
 &= \Re \left\{ \begin{aligned} &\left[A(\omega_1 - \Delta\omega_{10}) + iD(\omega_1 - \Delta\omega_{10}) \right] \left[A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \right] A(\omega_5 - \omega_{10}) \\ &+ \left[A(\omega_1 + \Delta\omega_{10}) + iD(\omega_1 + \Delta\omega_{10}) \right] \left[A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \right] A(\omega_5 - \omega_{10}) \\ &+ \left[A(\omega_1 - \Delta\omega_{10}) + iD(\omega_1 - \Delta\omega_{10}) \right] \left[A(\omega_3 + \Delta\omega_{10}) + iD(\omega_3 + \Delta\omega_{10}) \right] A(\omega_5 - \omega_{10}) \\ &+ \left[A(\omega_1 + \Delta\omega_{10}) + iD(\omega_1 + \Delta\omega_{10}) \right] \left[A(\omega_3 + \Delta\omega_{10}) + iD(\omega_3 + \Delta\omega_{10}) \right] A(\omega_5 - \omega_{10}) \end{aligned} \right\} \\
 &= A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) - D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
 &\quad + A(\omega_1 + \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) - D(\omega_1 + \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
 &\quad + A(\omega_1 - \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) - D(\omega_1 - \Delta\omega_{10})D(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
 &\quad + A(\omega_1 + \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) - D(\omega_1 + \Delta\omega_{10})D(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \quad (18)
 \end{aligned}$$

This resultant 3D spectrum will have four peaks, each at the four different quadrants of the

$$\omega_5 = \omega_{10} \quad \text{plane,} \quad (\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10}), \quad (\omega_1, \omega_3, \omega_5) = (-\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10}),$$

$(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$, and $(\omega_1, \omega_3, \omega_5) = (-\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$, respectively. Upon reflecting Eq. (18) about the $\omega_1 = 0$ plane, we have:

$$\begin{aligned} \tilde{s}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_1, \omega_3, \omega_5) = & A(\omega_1 + \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) + D(\omega_1 + \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\ & + A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) + D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \quad (19) \\ & + A(\omega_1 + \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) + D(\omega_1 + \Delta\omega_{10})D(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\ & + A(\omega_1 - \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) + D(\omega_1 - \Delta\omega_{10})D(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \end{aligned}$$

And adding the spectrum (Eq. (18)) to its mirror image (Eq. (19)), yields a 3D spectrum that contains peaks that are purely absorptive:

$$\begin{aligned} \tilde{s}_{1+2+3+4}^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_3, \omega_5) = & A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) + A(\omega_1 + \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \quad (20) \\ & + A(\omega_1 - \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) + A(\omega_1 + \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \end{aligned}$$

The four purely absorptive peaks of the 3D spectrum are identical and separated by $2\Delta\omega_{10}$. In practice, $\Delta\omega_{10}$ can be experimentally manipulated with the pulse shaper so that the four identical peaks are well separated. It is therefore sufficient to show only one quadrant of the 3D spectrum. We should note here that reflecting Eq. (18) about the $\omega_3 = 0$ plane and the subsequent adding of the spectra will give the same outcome. We have recently demonstrated the measurement of this purely absorptive 3D spectrum.²⁵ For samples with a congested or broad spectrum with a bandwidth on the order of $2\Delta\omega_{10}$, the aliased signals will overlap in a $2 \times 2 \times 2 \times 1$ phase cycling scheme. To overcome this problem of aliasing, we have to either increase $\Delta\omega_{10}$ by changing ω_{ref} to a further displaced frequency, or we can choose a $3 \times 3 \times 3 \times 1$ phase cycling scheme. In a multileveled or coupled system, a $2 \times 2 \times 2 \times 1$ phase cycling scheme is insufficient to remove undesired signals such as two-quantum absorption signals from $\tilde{s}_{2Q1}(\alpha = 1, \beta = 1, \gamma = -1; \omega_1, \omega_3, \omega_5)$ and $\tilde{s}_{2Q2}(\alpha = -1, \beta = -1, \gamma = 1; \omega_1, \omega_3, \omega_5)$, which will appear at $(\omega_1, \omega_3, \omega_5) = (-2\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$ and $(\omega_1, \omega_3, \omega_5) = (2\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$, respectively. This necessitates a $3 \times 3 \times 3 \times 1$ phase cycling scheme to select the desired signal. However, if there are no peaks appearing in a $3 \times 3 \times 3 \times 1$ phase cycling

scheme when choosing $\tilde{s}(\alpha=1, \beta=1, \gamma=-1)$ and $\tilde{s}(\alpha=-1, \beta=-1, \gamma=1)$, we can assume that both the undesired pathways do not contribute significantly to the overall signal, and a $2 \times 2 \times 2 \times 1$ phase cycling scheme can be used.

B. Separating signals R_1 , R_2 , R_3 and R_4 in phase cycled 3D spectrum

The signals $\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5)$, $\tilde{s}_{2+3}^*(\alpha=-1, \beta=1, \gamma=1; t_1, t_3, \omega_5)$, $\tilde{s}_{3+2}^*(\alpha=1, \beta=-1, \gamma=-1; t_1, t_3, \omega_5)$ and $\tilde{s}_{4+1}^*(\alpha=-1, \beta=1, \gamma=-1; t_1, t_3, \omega_5)$ of Eq. (8–11) each contains two terms from Eq. (5). In order to selectively measure only one single term R_1 , R_2 , R_3 or R_4 from Eq. (5), the collected signals of Eq. (7) need to be mathematically treated before phase cycling schemes are applied. This procedure is similar to what is done to separate the rephasing and non-rephasing signal from a purely absorptive 2D spectrum by subjecting the data to the causality condition.^{21,23} The signal $\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5)$ shown in Eq. (8) is part of the total signal of Eq. (7) and contains R_1 and R_4 components. Using $\tilde{s}_{1+4}^*$ as an example, the procedures to impose causality to achieve the resultant signal will be demonstrated. The first step is to inverse Fourier Transform about ω_5 , and Eq. (8) will become:

$$\begin{aligned} \tilde{s}_{1+4}^C(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, t_5) = & \Theta(t_1)\Theta(t_3)\Theta(t_5)F_1(t_1, t_3, t_5)\exp(-i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3) \\ & + \Theta(t_1)\Theta(t_3)\Theta(-t_5)F_4^*(t_1, t_3, -t_5)\exp(-i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3) \end{aligned} \quad (21)$$

By imposing causality, any signal that arrives before $t = 0$ fs is discarded and hence terms containing $\Theta(-t)$ are removed from Eq. (21). We note that the R_4 term will be removed from Eq. (21). The remaining signal is back Fourier transformed with respect to t_5 to give:

$$\tilde{s}_1^C(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5) \propto \Theta(t_1)\Theta(t_3)\exp(-i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3)\tilde{F}_1(t_1, t_3, \omega_5 - \omega_{10}) \quad (22)$$

This process of imposing causality is applied on the experimentally collected signal of Eq. (7) and the resultant processed signal will be denoted as $\tilde{S}^C(\phi_{14}, \phi_{24}, \phi_{34}; t_1, t_3, \omega_5)$. Analogous to Eq. (22), the terms Eq. (9–11) that are also present in the Eq. (7), upon imposing causality will become, respectively:

$$\tilde{s}_2^C(\alpha = -1, \beta = 1, \gamma = 1; t_1, t_3, \omega_5) \propto \Theta(t_1)\Theta(t_3) \exp(+i\Delta\omega_{10}t_1) \exp(-i\Delta\omega_{10}t_3) \tilde{F}_2(t_1, t_3, \omega_5 - \omega_{10}) \quad (23)$$

$$\tilde{s}_3^C(\alpha = 1, \beta = -1, \gamma = -1; t_1, t_3, \omega_5) \propto \Theta(t_1)\Theta(t_3) \exp(-i\Delta\omega_{10}t_1) \exp(+i\Delta\omega_{10}t_3) \tilde{F}_3(t_1, t_3, \omega_5 - \omega_{10}) \quad (24)$$

$$\tilde{s}_4^C(\alpha = -1, \beta = 1, \gamma = -1; t_1, t_3, \omega_5) \propto \Theta(t_1)\Theta(t_3) \exp(+i\Delta\omega_{10}t_1) \exp(+i\Delta\omega_{10}t_3) \tilde{F}_4(t_1, t_3, \omega_5 - \omega_{10}) \quad (25)$$

Now, using the $3 \times 3 \times 3 \times 1$ phase cycling scheme to extract $\tilde{s}_1^C(\alpha = 1, \beta = -1, \gamma = 1; t_1, t_3, \omega_5)$ of Eq. (22) from the causality imposed signal $\tilde{S}^C(\phi_{14}, \phi_{24}, \phi_{34}; t_1, t_3, \omega_5)$ followed by Fourier transformation about t_1 and t_3 , will give $\tilde{F}_1(\omega_1 - \Delta\omega_{10}, \omega_3 - \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4)$ which is the 3D Fourier transform of the $R_1^{(5)}$ process as described in Eq. (5). Similarly, the $3 \times 3 \times 3 \times 1$ phase cycling scheme can extract $\tilde{s}_2^C(\alpha = -1, \beta = 1, \gamma = 1; \omega_1, \omega_3, \omega_5)$, $\tilde{s}_3^C(\alpha = 1, \beta = -1, \gamma = -1; \omega_1, \omega_3, \omega_5)$ and $\tilde{s}_4^C(\alpha = -1, \beta = 1, \gamma = -1; \omega_1, \omega_3, \omega_5)$ terms of Eq. (23), (24) and (25), respectively from $\tilde{S}^C(\phi_{14}, \phi_{24}, \phi_{34}; t_1, t_3, \omega_5)$ to give $\tilde{F}_2(\omega_1 + \Delta\omega_{10}, \omega_3 - \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4)$, $\tilde{F}_3(\omega_1 - \Delta\omega_{10}, \omega_3 + \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4)$ and $\tilde{F}_4(\omega_1 + \Delta\omega_{10}, \omega_3 + \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4)$.

When one uses the $2 \times 2 \times 2 \times 1$ phase cycling scheme to attempt to recover $\tilde{s}_1^C(\alpha = 1, \beta = -1, \gamma = 1; t_1, t_3, \omega_5)$, as explained in the previous section, one cannot distinguish between signals with phase terms with phase signatures $\exp(+i\phi_{14} - i\phi_{24} + i\phi_{34})$, $\exp(-i\phi_{14} + i\phi_{24} + i\phi_{34})$, $\exp(+i\phi_{14} - i\phi_{24} - i\phi_{34})$ and $\exp(-i\phi_{14} + i\phi_{24} - i\phi_{34})$. The resultant signal when similarly Fourier transformed about t_1 and t_3 , gives:

$$\tilde{S}^{C, 2 \times 2 \times 2 \times 1}(\omega_1, \omega_3, \omega_5) = \tilde{F}_1(\omega_1 - \Delta\omega_{10}, \omega_3 - \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4) + \tilde{F}_2(\omega_1 + \Delta\omega_{10}, \omega_3 - \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4) + \tilde{F}_3(\omega_1 - \Delta\omega_{10}, \omega_3 + \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4) + \tilde{F}_4(\omega_1 + \Delta\omega_{10}, \omega_3 + \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4) \quad (26)$$

where the signals for $\tilde{s}_1^{C,2 \times 2 \times 2 \times 1}(\alpha=1, \beta=-1, \gamma=1; \omega_1, \omega_3, \omega_5)$, $\tilde{s}_2^{C,2 \times 2 \times 2 \times 1}(\alpha=-1, \beta=1, \gamma=1; \omega_1, \omega_3, \omega_5)$, $\tilde{s}_3^{C,2 \times 2 \times 2 \times 1}(\alpha=1, \beta=-1, \gamma=-1; \omega_1, \omega_3, \omega_5)$ and $\tilde{s}_4^{C,2 \times 2 \times 2 \times 1}(\alpha=-1, \beta=1, \gamma=-1; \omega_1, \omega_3, \omega_5)$ are all retrieved in a single 3D spectrum. Each of the four processes will be in a different quadrant on the $\omega_5 = \omega_{10}$ plane. The real part of the summation of the four causality imposed signals upon proper mirror imaging will yield a purely absorptive signal.

III. Experiment

The experimental setup has been described in detail elsewhere.^{23,25} Briefly, a 1 kHz titanium sapphire regenerative amplifier pumps a home-built optical parametric amplifier (OPA) to generate pulses centered at 665 nm, with a bandwidth of 16 nm, as shown in Fig. 2.

Figure 2. A linear absorption spectrum of chlorophyll *a* in methanol (black) with the excitation pulse spectrum of the OPA (red) coinciding with the Q_y transition.

The pulses were compressed by an acousto-optic programmable dispersive filter (AOPDF) (Dazzler) to a duration of 50 fs. The 3D experimental setup was based on a pump-probe beam geometry, where the first four pump pulses interacted collinearly, while the last interaction from the probe pulse interacted at a small crossing angle. In the experiment, a four pulse train (12 nJ

per pulse) was created by the AOPDF with variable delays t_1 , t_2 and t_3 between pulses 1 and 2, pulses 2 and 3, and pulses 3 and 4, respectively. A whitelight continuum was created from a sapphire window to form pulse 5. The waiting time t_4 was the delay between pulse 4 and 5, and was set by a mechanical translation stage. We note that as the whitelight continuum probe is chirped, different frequency in the whitelight continuum will have a different delay t_4 , which may lead to distortion in the spectra.⁴¹ This problem can be overcome with post-data chirp-correction by characterization of the chirp and adjusting the delay of the corresponding wavelength accordingly.⁴² Delays t_1 and t_3 were coherence times, while t_2 and t_4 were population times. The fifth-order signal is emitted in the same direction as pulse 5, and was heterodyne-detected by pulse 5 and frequency-resolved by a spectrometer (PIXIS 100B) to form the emission axis ω_5 . Chlorophyll *a* (Chl *a*) was dissolved in methanol and placed in a 1 mm sapphire cell, and the linear absorption spectrum is shown in Fig. 2. An optical density of 0.2 is measured for the sample at 665 nm. It is known that distortions in multidimensional spectrum features can be due to sample thickness and the non collinear phase matching beam geometry used in most multidimensional spectroscopic setup.⁴³⁻⁴⁵ We believe that a pump probe configuration such as ours where four out of five interacting pulses are interacting collinearly will have less spectral distortions compared to a fully non collinear phase matching beam geometry. In our 3D spectrum, the distortion due to sample thickness is expected to be present and can be reduced by reducing the sample thickness.

To obtain a 3D spectrum, both coherence times t_1 and t_3 were scanned from 0 fs to 140 fs in 10 fs time steps. The population times t_2 and t_4 were kept fixed. The reference wavelength of the pulse shaper was set to 715 nm, such that the Nyquist limit was 15 fs for both t_1 and t_3 axis, and the difference between the peak absorption of the sample and the reference wavelength was $\Delta\omega_{10}$

= 31 THz. To perform phase cycling, for every step taken for the coherence time, the relative phases of the first three pulses, ϕ_1 , ϕ_2 and ϕ_3 were varied with respect to ϕ_4 . For $2 \times 2 \times 2 \times 1$ phase cycling scheme, the phases were cycled between $\phi_j = 0$ and π , while for $3 \times 3 \times 3 \times 1$ phase cycling scheme, the phases were cycled with $\phi_j = 0, 2\pi/3$ and $4\pi/3$, where $j=1,2,3$ for both schemes. Scattered light from the pump beam is removed by subtracting the signal with and without the probe beam using a 500 Hz chopper. To ensure that the pulse train was created accurately, power measurements were made to ensure comparability when phases of the pulses were cycled. A $2 \times 2 \times 2 \times 1$ or $3 \times 3 \times 3 \times 1$ phase cycling scheme is performed on the emitted fifth-order signal by systematic weighted summation as described in Eq. (13). The phase cycled data was then zero-padded up to 85 data points and Fourier transformed with respect to t_1 and t_3 to give a 3D spectrum with signals $\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1)$ and $\tilde{s}_{3+2}^*(\alpha=1, \beta=-1, \gamma=-1)$ without any undesired peaks as shown in Eq. (14) and (15). The addition of the mirror image of the spectrum to itself yielded the purely absorptive 3D spectrum. To retrieve signals $\tilde{s}_1(\alpha=1, \beta=-1, \gamma=1)$, $\tilde{s}_2(\alpha=-1, \beta=1, \gamma=1)$, $\tilde{s}_3(\alpha=1, \beta=-1, \gamma=-1)$ and $\tilde{s}_4(\alpha=-1, \beta=1, \gamma=-1)$, we modified the phase cycling data treatment by imposing causality to the collected data as described in Eqs. (21) and (22).^{21,23}

IV. Results

Without phase cycling, or with insufficient phase cycling, the detected spectrum would be contaminated with spurious peaks due to undesired processes (lower order signals, pump-probe signals etc.) as denoted by P in Eq. (6) and due to aliasing caused by undersampling of the discrete Fourier transform denoted in Eq. (13). In the following we will discuss the 3D spectra that are obtained when we apply different phase cycling scheme to choose the term

$\tilde{s}(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5)$ from the signal of Eq. (7). In Fig. 3, we present various phase cycling schemes that are insufficient to select the desired signal.

Figure 3. Isosurfaces of 3D spectra from insufficient phase cycling steps that results in unwanted signals. (a) Signals from a $1 \times 1 \times 1$ phase cycling scheme. The first-order signal at $(\omega_1, \omega_3, \omega_5) = (0, 0, \omega_{10})$ dominates the spectrum and is ~ 2500 times more intense than the fifth-order signal (Fig. 4). (b) A $2 \times 2 \times 1$ phase cycling scheme results in the unwanted third-order signals at $(\omega_1, \omega_3, \omega_5) = (\pm \Delta\omega_{10}, 0, \omega_{10})$, which is ~ 10 times more intense than the fifth-order signal (Fig. 4).

In Fig. 3(a), the spectrum depicted is measured without any phase cycling, or in the language of phase cycling, a $1 \times 1 \times 1$ phase cycling scheme. The isosurfaces in Fig. 3(a) are drawn at intensity ~ 2500 times of the desired fifth-order signals (signals presented in Fig. 4 onwards). It is dominated by a peak from a first-order linear signal of negative amplitude at position $(\omega_1, \omega_3, \omega_5) = (0, 0, \omega_{10})$. This signal arises from zero interactions with the first four pulses and one interaction from the fifth ‘probe’ pulse. Third-order and fifth-order signals are also present, but are less intense than the first-order signal and hence they do not show up in the spectrum. The desired fifth-order signals at $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$ remains unobserved under these intense

first-order contributions. In Fig. 3(b), the $2 \times 2 \times 1$ phase cycling scheme removes the first-order signal but is unable to remove the third-order signals at $(\omega_1, \omega_3, \omega_5) = (\pm \Delta \omega_{10}, 0, \omega_{10})$. This arises from the insufficient phase cycling of the third pulse. The signals that have no interaction with the third and fourth pulses are not eliminated. The third-order signals observed at $(\omega_1, \omega_3, \omega_5) = (\pm \Delta \omega_{10}, 0, \omega_{10})$ arises after an interaction each with the first and second pulse followed by an interaction with the fifth ‘probe’ pulse. The isosurfaces in Fig. 3(b) are drawn at intensity ~ 10 times of the isosurfaces in Fig. 4(a). Figure 4 depicts the isosurfaces of the 3D spectrum obtained from a $2 \times 2 \times 2 \times 1$ phase cycling scheme, shown in Eq. (18), at $(t_2, t_4) = (400 \text{ fs}, 300 \text{ fs})$. Using this phase cycling scheme, all the first- and third-order signals are eliminated, and only fifth-order signals remain. In Fig. 4(a), the 3D spectrum has four peaks labeled as I, II, III and IV and they are located in the separate quadrants on the plane of $\omega_5 = \omega_{10} = 451 \text{ THz}$ at $(\omega_1, \omega_3, \omega_5) = (\Delta \omega_{10}, \Delta \omega_{10}, \omega_{10})$, $(\omega_1, \omega_3, \omega_5) = (-\Delta \omega_{10}, \Delta \omega_{10}, \omega_{10})$, $(\omega_1, \omega_3, \omega_5) = (\Delta \omega_{10}, -\Delta \omega_{10}, \omega_{10})$, and $(\omega_1, \omega_3, \omega_5) = (-\Delta \omega_{10}, -\Delta \omega_{10}, \omega_{10})$, respectively.

Figure 4. Isosurfaces of 3D spectra from a $2 \times 2 \times 2 \times 1$ phase cycling scheme with $t_2 = 400 \text{ fs}$ and $t_4 = 300 \text{ fs}$. Only the peaks from fifth order processes remain. (a) Peaks I, II, III and IV represent signals $\tilde{s}_{1+4}^*$, $\tilde{s}_{2+3}^*$, $\tilde{s}_{3+2}^*$ and $\tilde{s}_{4+1}^*$, respectively. (b) A magnified view of peak I with 2D projections depicted on grid plane. The 2D projection, I_{13} is ‘phase-twisted’, while I_{35} and I_{15}

have purely absorptive peakshapes. (c) A magnified view of peak II, with the mirror image taken across $\omega_1 = 0$ to display the signal in a quadrant with all-positive frequency axis. The 2D projection Π_{13} is phase-twisted, while Π_{35} and Π_{15} have purely absorptive peakshapes.

As mentioned in the earlier section II(A) with Eq. (18), the peaks II, III and IV arise from aliasing. One major concern of aliasing is the possibility of overlapped aliased signals. Here, the reference signal was chosen to ensure that the peaks I, II, III and IV are well separated in the 3D spectrum by $2\Delta\omega_0 = 62$ THz so that there are no ambiguities in peak assignment. An enlarged 3D spectrum of peak I from Fig. 4(a) is depicted in Fig. 4(b). Figure 4(c) depicts an enlarged 3D spectrum of peak II after a mirror image of it is taken about the $\omega_1=0$ axis. We will explain in a later section on why the mirror image is obtained. The 2D projections of these peaks are also presented on the walls of the grid and labeled. To show that the peaks in the 3D spectrum are indeed the fifth-order signals as expected, we provide here the analysis to the positions and features of the observed 3D peaks. Since 3D peaks are difficult to visualize on a piece of paper, we use 2D projections of the 3D peaks for analysis.

Peak I (Fig. 4(a)) and the mirror imaged peak II (Fig. 4(b)) can be described in terms of the absorptive and dispersive components extracted from the first term of Eq. (18) and the second term of Eq. (19), respectively, and they are expressed as:

$$\tilde{s}_I^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_3, \omega_5) \propto A(\omega_1 - \Delta\omega_0)A(\omega_3 - \Delta\omega_0)A(\omega_5 - \omega_{10}) - D(\omega_1 - \Delta\omega_0)D(\omega_3 - \Delta\omega_0)A(\omega_5 - \omega_{10}) \quad (27)$$

$$\tilde{s}_{II}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_1, \omega_3, \omega_5) \propto A(\omega_1 - \Delta\omega_0)A(\omega_3 - \Delta\omega_0)A(\omega_5 - \omega_{10}) + D(\omega_1 - \Delta\omega_0)D(\omega_3 - \Delta\omega_0)A(\omega_5 - \omega_{10}) \quad (28)$$

The features of the projections can be simulated by integrating the above functions over the appropriate axis. The 2D projection onto the (ω_1, ω_3) axis that corresponds to the 2D projections

I_{13} and II_{13} from Fig. 4(b) and 4(c), respectively is achieved by integrating Eq. (27) and (28), respectively, over ω_5 . Since the absorptive and dispersion components are symmetric and anti-symmetric, respectively, the results are:

$$\tilde{s}_{I_{13}}^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_3) \propto A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10}) - D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10}) \quad (29)$$

$$\tilde{s}_{II_{13}}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_1, \omega_3) \propto A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10}) + D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10}) \quad (30)$$

These peaks on the 2D projection will appear with distinctive ‘phase-twisted’ shapes, where the peak broadens outwards along the diagonal (or anti-diagonal) axis and hence appears twisted.^{6,46}

These ‘phase-twisted’ shapes are due to dispersive contributions $D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})$ in Eq. (29) and (30) and have a bigger footprint on spectra compared to purely absorptive peaks (described by for example Eq. (31) to (34)). The peaks corresponding to Eq. (29) and (30) correspond to the rephasing and non-rephasing peaks, respectively, from 2D spectroscopy.^{2,6,46} In Fig. 5(a) and (b), the 2D projections I_{13} and II_{13} from Fig. 4(b) and 4(c) are depicted, respectively. The phase-twisted feature can be seen in the peaks. In the previous section, it is theoretically shown that peak I contains signal from the R_1 and R_4 processes (Eq. (8)) while peak II contains signals from the R_2 and R_3 processes (Eq. (9)).

Figure 5. Comparing the 2D projections I_{13} and II_{13} from Fig. 4 with simulated 2D projections. The phase-twisted feature is evident in both experimental and simulated results. As the simulation did not consider finite bandwidth of the interacting pulses, the resultant linewidth in the experimental projections are smaller as compared to the simulated spectra. (a) 2D projection I_{13} . (b) 2D projection II_{13} . (c) Simulated 2D projection I_{13} . (d) Simulated 2D projection II_{13} .

To show that the experimental 3D spectra is consistent with the derivations, the response functions R_1 , R_2 , R_3 and R_4 ¹⁵ were calculated and the corresponding 3D spectra and 2D projections were generated. The two-point frequency fluctuation correlation function of Chl *a* in methanol was obtained from experiment.⁴⁷ These simulated 2D projections are presented in Fig.

5(c) and 5(d). The simulation did not take into consideration the finite temporal pulsewidth of the interacting pulses, and hence the simulated 2D projections are broader than the experimental 2D projections which were obtained using a pulsewidth of ~60 fs. However, phase twisted features from both simulation and experiment are clearly consistent.

We now discuss the other 2D projections I_{15} , I_{35} , II_{15} and II_{35} . Integrating over ω_3 for Eq. (29) and (30), the resultant signals are:

$$\tilde{s}_{I_{15}}^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_5) \propto A(\omega_1 - \Delta\omega_{10})A(\omega_5 - \Delta\omega_{10}) \quad (31)$$

$$\tilde{s}_{II_{15}}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_1, \omega_5) \propto A(\omega_1 - \Delta\omega_{10})A(\omega_5 - \Delta\omega_{10}) \quad (32)$$

By integrating over ω_1 for Eq. (29) and (30), we have:

$$\tilde{s}_{I_{35}}^{2 \times 2 \times 2 \times 1}(\omega_3, \omega_5) \propto A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \Delta\omega_{10}) \quad (33)$$

$$\tilde{s}_{II_{35}}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_3, \omega_5) \propto A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \Delta\omega_{10}) \quad (34)$$

All these 2D projections have purely absorptive peakshapes and should look similar. In Fig. 6, the 2D projections I_{15} , I_{35} , II_{15} and II_{35} from Fig. 4(a) and (b) are presented.

Figure 6. Comparing 2D projections from Fig. 4 with experimental 2D spectra. All the 2D projections show similar purely absorptive peakshapes as those obtained in 2D spectra. (a) 2D

projection, I_{35} . (b) 2D projection, II_{35} . (c) 2D spectrum at $T_w=300$ fs. (d) 2D projection of I_{15} . (e) 2D projection of II_{15} . (f) 2D spectrum at $T_w=700$ fs.

As can be seen, the shapes are absorptive and similar, in contrast to the peakshapes in Fig. 5(a) and (b). In Fig. 6(c) and (f), the experimental purely absorptive 2D spectra of chlorophyll *a* at $T_w = 400$ fs and $T_w = 700$ fs are depicted as an example to show that the I_{15} , I_{35} , II_{15} and II_{35} are indeed purely absorptive lineshapes, in contrast to the phase-twisted features of I_{13} and II_{13} of Fig. 5(c) and 5(d).

As mentioned in section II(A), the 3D spectrum from a $2 \times 2 \times 2 \times 1$ phase cycling scheme can be manipulated to produce a purely absorptive 3D spectrum. This has been demonstrated in our earlier paper.²⁵ In Fig. 7(a), the purely absorptive 3D spectrum is obtained by the summation of Fig. 4(a) and its mirror image about $\omega_3 = 0$.

Figure 7. (a) Purely absorptive peaks obtained from a $2 \times 2 \times 2 \times 1$ phase cycling scheme by summing up Fig. 4(a) and its mirror image taken across $\omega_1 = 0$. (b) A magnified view of the peak in the $(+\omega_1, +\omega_3, +\omega_5)$ -octant, with the respective 2D projections at the grid plane.

This summed 3D spectrum contains four purely absorptive peaks described in Eq. (20) that are mirror imaged replicas of each other. In Fig. 7(b), we present the peak from the $(+\omega_1, +\omega_3, +\omega_5)$ - octant, together with the 2D projections on the grid wall that shows purely absorptive features.

In Fig. 8(a), the 3D spectra obtained from a $3 \times 3 \times 3 \times 1$ phase cycling scheme that chooses the signal $\tilde{s}_{1+4}^{3 \times 3 \times 3 \times 1} (\alpha = 1, \beta = -1, \gamma = 1)$ is depicted.

Figure 8. Isosurfaces of 3D spectra from a $3 \times 3 \times 3 \times 1$ phase cycling schemes. (a) The signal is the same as peak I of Fig. 4(a) and represents $\tilde{s}_{1+4}^*$. (b) A close up view of (a), with the respective 2D projections on the grid plane. (c) The signal is the same as peak II of Fig. 4(a) and represents $\tilde{s}_{2+3}^*$. (d) A magnified spectrum of (c) mirror imaged across $\omega_1 = 0$ onto the positive axis quadrant, and the corresponding 2D projections. (e) A purely absorptive peak obtained from the summation of (a) and the mirror image of (b) across $\omega_1 = 0$. (f) A magnified view of (e). The 2D projections show purely absorptive peakshapes on all three grid planes of the cube.

The peak is centered at $(\omega_1, \omega_3, \omega_5) = (+\Delta\omega_{10}, +\Delta\omega_{10}, \omega_{10})$, as predicted in Eq. (14), and is the same as peak I in Fig. 4(a). Comparing Fig. 8(a) with Fig. 4(a), one can also see that the $3 \times 3 \times 3 \times 1$ phase cycling scheme is able to selectively choose the terms $\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1)$ without the signals $\tilde{s}_{2+3}^*(\alpha=-1, \beta=-1, \gamma=1)$, $\tilde{s}_{3+2}^*(\alpha=1, \beta=-1, \gamma=-1)$ or $\tilde{s}_{4+1}^*(\alpha=-1, \beta=1, \gamma=-1)$ that arises from aliasing. Figure 8(b) depicts an enlarged spectrum from Fig. 8(a), and the 2D projections at the face of the grid cube are comparable to that of Fig. 4(b). Using the same $3 \times 3 \times 3 \times 1 = 27$ data set but in a different linear combination, the signal $\tilde{s}_{2+3}^{3 \times 3 \times 3 \times 1}(\alpha=1, \beta=-1, \gamma=-1)$ can then be chosen and the 3D spectrum is depicted in Fig. 8(c). The peak is located at $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$ as predicted in Eq. (15). In Fig. 8(d), the magnified view of Fig. 8(c) is presented in the positive frequency octant by taking the mirror image about the $\omega_1 = 0$ axis. The 2D projections can be compared to Fig. 4(c) and is shown to be similar. From these examples, the validity of the phase cycling schemes for 3D optical spectroscopy is shown experimentally. Upon summing both signals from Figs. 8(a) and the mirror image of Fig. 8(c) about the $\omega_1 = 0$ plane, as prescribed by Eq. (17), we obtain, in Fig. 8(e), a purely absorptive signal that is similar to the peak from the $(+\omega_1, +\omega_3, +\omega_5)$ -octant in Fig. 7(a). In Fig. 8(f), the close up view of Fig. 8(e) and 2D projections are similar to Fig. 7(b).

To retrieve the signals from individual coherence pathways R_1 , R_2 , R_3 and R_4 in Fig. 1, causality is imposed before applying phase cycling scheme as described in section II(B). Figure 9 depicts the 3D spectrum that is obtained from a causality imposed $2 \times 2 \times 2 \times 1$ phase cycling scheme, which is described in Eq. (26). Figure 9(a) contains the isosurfaces of four peaks I^c, II^c, III^c and IV^c which represents the processes R_1 , R_2 , R_3 and R_4 , respectively.

Figure 9. (a) 3D spectra of a causality imposed $2 \times 2 \times 2 \times 1$ phase cycling scheme. Magnified views and 2D projections of (b) I^c , (c) II^c , (d) III^c and (e) IV^c . All magnified spectra of II^c , III^c , and IV^c are mirror imaged onto the positive quadrant. The 2D projections all show phase-twisted features. (f) By summing up Figs. (b–e), a purely absorptive spectrum is obtained.

We compare Fig. 9(a) with Fig. 4(a). In Fig. 4(a), peaks I and IV are similar as they contain both processes R_1 and R_4 while peaks II and III are similar as they contain both processes R_2 and R_3 . Whereas in Fig. 9(a), the imposing of causalities have separated all the processes and they each occupy a separate quadrant. A close up view of peaks I^c , II^c , III^c , and IV^c is depicted in Figs. 9(b–e), respectively, where mirror images of the figures are taken about $\omega_1 = 0$ and/or $\omega_3 = 0$ planes for when applicable so that the peaks will appear in the positive frequency octant $(+\omega_1, +\omega_3, +\omega_5)$. For consistency, Fig. 9(f) shows a purely absorptive peak that is obtained by the sum of Figs. 9(b–e). As expected, it can be seen to be similar to Figs. 7(b) and 8(f).

For a causality imposed $3 \times 3 \times 3 \times 1$ phase cycling scheme, the signals for $\tilde{s}_1^{C,3 \times 3 \times 3 \times 1}(\alpha=1, \beta=-1, \gamma=1)$, $\tilde{s}_2^{C,3 \times 3 \times 3 \times 1}(\alpha=-1, \beta=1, \gamma=1)$, $\tilde{s}_3^{C,3 \times 3 \times 3 \times 1}(\alpha=1, \beta=-1, \gamma=-1)$, and $\tilde{s}_4^{C,3 \times 3 \times 3 \times 1}(\alpha=-1, \beta=1, \gamma=-1)$ are shown in Fig. 10(a-d), respectively, and they are located at the same positions as the retrieved signals from a causality imposed $2 \times 2 \times 2 \times 1$ phase cycling scheme of Fig. 9(a).

Figure 10. (a-d) Isosurfaces of 3D spectra from a $3 \times 3 \times 3 \times 1$ phase cycling scheme with causality imposed. The positions of the signals are the same as those in causality imposed $2 \times 2 \times 2 \times 1$ phase cycling scheme. (e-h) Magnified view of the respective peaks and their 2D projections. All the 2D projections have phase-twisted features.

The enlarged 3D spectra and the 2D projections of the respective signals are shown in Figs. 10(e-h). It can be observed that the phase-twisted features look comparable to Figs. 9(b-e), according to Eqs. (22–25). By summing $\tilde{s}_1^{C,3 \times 3 \times 3 \times 1}(\alpha=1, \beta=-1, \gamma=1)$, $\tilde{s}_2^{C,3 \times 3 \times 3 \times 1}(\alpha=-1, \beta=1, \gamma=1)$, $\tilde{s}_3^{C,3 \times 3 \times 3 \times 1}(\alpha=1, \beta=-1, \gamma=-1)$, and $\tilde{s}_4^{C,3 \times 3 \times 3 \times 1}(\alpha=-1, \beta=1, \gamma=-1)$, as shown in Eq. (17), we will obtain the purely absorptive peak as shown in Fig. 8(f).

Figure 11 shows the 2D projections of the 3D spectrum for the R_1 process shown in Fig. 10(a).

Figure 11. 2D projections of Fig. 10(e) in a causality imposed $3 \times 3 \times 3 \times 1$ phase cycling scheme are shown. The projections (a) I^c_{13} , (b) I^c_{35} , and (c) I^c_{15} all show phase-twisted features that is akin to a non-rephasing peakshape in 2D spectrum.

Here, the theoretical derivation for R_1 is presented as an example to predict the peakshape of the signal and compare it with the experimental result. With the simplification that was used in section II(A) that $F(t_1, t_3, t_5) = F(t_1, t_3)F(t_5) = F(t_1)F(t_3)F(t_5)$ and that $\text{FT}_j \{ \Theta(t_j)F(t_j) \exp(-i\omega_{10}t_j) \} = A(\omega_j - \omega_{10}) + iD(\omega_j - \omega_{10})$, we obtain from Eq. (23), after Fourier transform, the real part of the 3D spectrum that is due to the R_1 process which can be expressed as:

$$\begin{aligned} \tilde{s}_1^{C, 3 \times 3 \times 3 \times 1}(\alpha = 1, \beta = -1, \gamma = 1; \omega_1, \omega_3, \omega_5) &\propto \Re e \left\{ \begin{aligned} &\left[A(\omega_1 - \Delta\omega_{10}) + iD(\omega_1 - \Delta\omega_{10}) \right] \\ &\times \left[A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \right] \\ &\times \left[A(\omega_5 - \omega_{10}) + iD(\omega_5 - \omega_{10}) \right] \end{aligned} \right\} \\ &= A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\ &\quad - D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\ &\quad - D(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})D(\omega_5 - \omega_{10}) \\ &\quad - A(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})D(\omega_5 - \omega_{10}) \end{aligned} \quad (35)$$

In order to obtain the 2D projections onto (ω_1, ω_3) , (ω_3, ω_5) and (ω_1, ω_5) planes, Eq. (35) is integrated over ω_5 , ω_1 and ω_3 , respectively. The three resultant expressions are:

$$\tilde{s}_{I_{13}}^{C,3 \times 3 \times 3 \times 1}(\omega_1, \omega_3) = A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10}) - D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10}) \quad (36)$$

$$\tilde{s}_{I_{35}}^{C,3 \times 3 \times 3 \times 1}(\omega_3, \omega_5) = A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) - D(\omega_3 - \Delta\omega_{10})D(\omega_5 - \omega_{10}) \quad (37)$$

$$\tilde{s}_{I_{15}}^{C,3 \times 3 \times 3 \times 1}(\omega_1, \omega_5) = A(\omega_1 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) - D(\omega_1 - \Delta\omega_{10})D(\omega_5 - \omega_{10}) \quad (38)$$

All three expressions are similar with phase-twisted features and it proves that the experimental data obtained for R_1 shown in Fig. 10(a) is consistent with the theoretical derivation. By working out the equations it can be shown that all 2D projections for $\tilde{s}_{II}^{C,3 \times 3 \times 3 \times 1}$, $\tilde{s}_{III}^{C,3 \times 3 \times 3 \times 1}$, and $\tilde{s}_{IV}^{C,3 \times 3 \times 3 \times 1}$ are phase-twisted as well, which is in good agreement with Figs. 10(e–h), and the case is also true for 3D spectrum from a causality implemented $2 \times 2 \times 2 \times 1$ phase cycling scheme as shown in Figs. 9(b–e).

V. Cascading third-order contributions to the fifth-order signal

In higher-order nonlinear spectroscopy, there might be undesired third-order cascades that appear in the same phase-matched direction as the desired fifth-order signal, whilst having the same intensity dependence. This is evident in fifth-order Raman spectroscopy, where the experiments were contaminated with third-order signals.^{48–50} It is therefore important to determine the contributions of third-order cascades to the fifth-order signals. Third-order cascades occur when the third-order polarization response created by three pulse interactions is reabsorbed by the sample to produce a second third-order polarization response after interactions with the remaining two pulses. Sequential and parallel cascades are two types of third-order cascades that can result in an overall fifth-order signal.^{7,51} The contribution of the third-order cascades is dependent on the optical density of the sample and phase-matching geometry. A way to verify the contribution of cascaded third-order signals is by measuring the signal intensity with varying concentration. A fifth-order signal scales linearly with increasing concentration, while

third-order cascades scale quadratically with concentration.⁵¹ In Fig. 12, the peak signal intensity of the 3D spectra show a linear dependence on concentration, demonstrating that the majority of the signal from the experimental conditions presented here is from fifth-order process rather than cascades.

Figure 12. The maximum intensity of the measured pure absorptive signal is plotted against the optical density of sample with various concentrations. A best fit line (dashed) is drawn. The heterodyned fifth-order signal should scale linearly with concentration c , while cascaded third-order signals should be linear with c^2 . This shows that cascaded third-order signal do not contribute significantly to the 3D spectra.

Using a simple calculation,^{9,10} together with the consideration of sample absorption, the cascading signal contributes $\sim 10\%$ of the total signal at the optical density of 0.2. With optically thinner samples, the percentage contribution of cascades is further reduced.

VI. Concluding Remarks

We have presented the theoretical framework on how to obtain fifth order 3D electronic spectroscopy using a pulse shaper assisted pump probe beam geometry. The use of the pulse shaper allows phase cycling to be performed that is able to selectively measure fifth order signal

We discuss how purely absorptive 3D spectra as well as 3D spectra of processes from various coherence pathways processes can be obtained using phase cycling and data treatment. In the most general case this requires a 27-step phase cycling scheme, but an 8-step phase cycling scheme may be adequate for a two level system if the rotating frame reference frequency is chosen to be sufficiently far away from the resonance frequencies. There is only a small contribution of cascading third-order contribution to the fifth-order signals in this pump-probe geometry setup as deduced by the linear relationship between the absorption intensity and sample concentration. The current demonstration is performed on a quasi-two level system. We are currently working on understanding the applications of the phase cycling schemes and its restrictions for multilevel systems. In principle, the phase cycling scheme selection procedure demonstrated here in 3DES as well as in 2DES²³ can be applied to other nonlinear optical processes including extensions to even higher dimensional optical spectroscopy. It is hoped that this present article can spur further theoretical and numerical studies of fifth-order 3D spectroscopy and associated fifth-order optical processes^{15,52,53} to complement the advancement in experimental technique.

Supporting Information Available: Details on the all possible coherence pathways allowed in a pump-probe geometry, and the expression of the $3 \times 3 \times 3 \times 1$ phase cycling scheme are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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References

- (1) Jonas, D. M. Two-Dimensional Femtosecond Spectroscopy. *Annu. Rev. Phys. Chem.* **2003**, *54*, 425-463.
- (2) Khalil, M.; Demirdöven, N.; Tokmakoff, A. Coherent 2D IR Spectroscopy: Molecular Structure and Dynamics in Solution. *J. Phys. Chem. A* **2003**, *107*, 5258-5279.
- (3) Hochstrasser, R. M. Two-Dimensional Spectroscopy at Infrared and Optical Frequencies. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 14190-14196.
- (4) Cho, M. Coherent Two-Dimensional Optical Spectroscopy. *Chem. Rev.* **2008**, *108*, 1331-1418.
- (5) Mukamel, S.; Tanimura, Y.; Hamm, P. Coherent Multidimensional Optical Spectroscopy. *Acc. Chem. Res.* **2009**, *42*, 1207-1209.
- (6) Hamm, P.; Zanni, M. T. *Concepts and Methods of 2D Infrared Spectroscopy*; Cambridge University Press: New York, 2011.
- (7) Garrett-Roe, S.; Hamm, P. Purely Absorptive Three-Dimensional Infrared Spectroscopy. *J. Chem. Phys.* **2009**, *130*, 164510.
- (8) Fidler, A. F.; Harel, E.; Engel, G. S. Dissecting Hidden Couplings Using Fifth-Order Three-Dimensional Electronic Spectroscopy. *J. Phys. Chem. Lett.* **2010**, *1*, 2876-2880.
- (9) Garrett-Roe, S.; Perakis, F.; Rao, F.; Hamm, P. Three-Dimensional Infrared Spectroscopy of Isotope-Substituted Liquid Water Reveals Heterogeneous Dynamics. *J. Phys. Chem. B* **2011**, *115*, 6976-6984.
- (10) Ding, F.; Fulmer, E. C.; Zanni, M. T. Heterodyned Fifth-Order Two-Dimensional IR Spectroscopy: Third-Quantum States and Polarization Selectivity. *J. Chem. Phys.* **2005**, *123*, 094502.

- (11) Fulmer, E. C.; Ding, F.; Mukherjee, P.; Zanni, M. T. Vibrational Dynamics of Ions in Glass from Fifth-Order Two-Dimensional Infrared Spectroscopy. *Phys. Rev. Lett.* **2005**, *94*, 067402.
- (12) Ding, F.; Zanni, M. T. Heterodyned 3D IR Spectroscopy. *Chem. Phys.* **2007**, *341*, 95-105.
- (13) Schlau-Cohen, G. S.; Ishizaki, A.; Fleming, G. R. Two-Dimensional Electronic Spectroscopy and Photosynthesis: Fundamentals and Applications to Photosynthetic Light-Harvesting. *Chem. Phys.* **2011**, *386*, 1-22.
- (14) Schlau-Cohen, G. S.; Calhoun, T. R.; Ginsberg, N. S.; Read, E. L.; Ballottari, M.; Bassi, R.; Van Grondelle, R.; Fleming, G. R. Pathways of Energy Flow in LHCII from Two-Dimensional Electronic Spectroscopy. *J. Phys. Chem. B* **2009**, *113*, 15352-15363.
- (15) Hamm, P. Three-Dimensional-Ir Spectroscopy: Beyond the Two-Point Frequency Fluctuation Correlation Function. *J. Chem. Phys.* **2006**, *124*, 124506.
- (16) Garrett-Roe, S.; Hamm, P. What Can We Learn from Three-Dimensional Infrared Spectroscopy? *Acc. Chem. Res.* **2009**, *42*, 1412-1422.
- (17) Turner, D. B.; Stone, K. W.; Gundogdu, K.; Nelson, K. A. Three-Dimensional Electronic Spectroscopy of Excitons in Gaas Quantum Wells. *J. Chem. Phys.* **2009**, *131*, 144510.
- (18) Davis, J. A.; Hall, C. R.; Dao, L. V.; Nugent, K. A.; Quiney, H. M.; Tan, H. H.; Jagadish, C. Three-Dimensional Electronic Spectroscopy of Excitons in Asymmetric Double Quantum Wells. *The Journal of Chemical Physics* **2011**, *135*, 044510.
- (19) Li, H.; Bristow, A. D.; Siemens, M. E.; Moody, G.; Cundiff, S. T. Unraveling Quantum Pathways Using Optical 3D Fourier-Transform Spectroscopy. *Nat. Commun.* **2013**, *4*, 1390.
- (20) DeFlores, L. P.; Nicodemus, R. A.; Tokmakoff, A. Two-Dimensional Fourier Transform Spectroscopy in the Pump-Probe Geometry. *Opt. Lett.* **2007**, *32*, 2966-2968.
- (21) Myers, J. A.; Lewis, K. L. M.; Tekavec, P. F.; Ogilvie, J. P. Two-Color Two-Dimensional Fourier Transform Electronic Spectroscopy with a Pulse-Shaper. *Opt. Express* **2008**, *16*, 17420-17428.
- (22) Shim, S. H.; Zanni, M. T. How to Turn Your Pump-Probe Instrument into a Multidimensional Spectrometer: 2D IR and Vis Spectroscopies Via Pulse Shaping. *Phys. Chem. Chem. Phys.* **2009**, *11*, 748-761.
- (23) Zhang, Z.; Wells, K. L.; Hyland, E. W. J.; Tan, H.-S. Phase-Cycling Schemes for Pump-Probe Beam Geometry Two-Dimensional Electronic Spectroscopy. *Chem. Phys. Lett.* **2012**, *550*, 156-161.
- (24) Kumar, S. K. K.; Tamimi, A.; Fayer, M. D. Dynamics in the Interior of AOT Lamellae Investigated with Two-Dimensional Infrared Spectroscopy. *J. Am. Chem. Soc.* **2013**, *135*, 5118-5126.
- (25) Zhang, Z.; Wells, K. L.; Tan, H. S. Purely Absorptive Fifth-Order Three-Dimensional Electronic Spectroscopy. *Opt. Lett.* **2012**, *37*, 5058-5060.
- (26) Albrecht, A. W.; Hybl, J. D.; Gallagher Faeder, S. M.; Jonas, D. M. Experimental Distinction between Phase Shifts and Time Delays: Implications for Femtosecond Spectroscopy and Coherent Control of Chemical Reactions. *J. Chem. Phys.* **1999**, *111*, 10934-10956.
- (27) Keusters, D.; Tan, H. S.; Warren, W. S. Role of Pulse Phase and Direction in Two-Dimensional Optical Spectroscopy. *J. Phys. Chem. A* **1999**, *103*, 10369-10380.
- (28) Tian, P.; Keusters, D.; Suzuki, Y.; Warren, W. S. Femtosecond Phase-Coherent Two-Dimensional Spectroscopy. *Science* **2003**, *300*, 1553-1555.

- (29) Tan, H.-S. Theory and Phase-Cycling Scheme Selection Principles of Collinear Phase Coherent Multi-Dimensional Optical Spectroscopy. *J. Chem. Phys.* **2008**, *129*, 124501.
- (30) Yan, S.; Tan, H. S. Phase Cycling Schemes for Two-Dimensional Optical Spectroscopy with a Pump-Probe Beam Geometry. *Chem. Phys.* **2009**, *360*, 110-115.
- (31) Monmayrant, A.; Weber, S.; Chatel, B. A Newcomer's Guide to Ultrashort Pulse Shaping and Characterization. *J. Phys. B: At. Mol. Opt. Phys.* **2010**, *43*.
- (32) Schlau-Cohen, G. S.; Ishizaki, A.; Calhoun, T. R.; Ginsberg, N. S.; Ballottari, M.; Bassi, R.; Fleming, G. R. Elucidation of the Timescales and Origins of Quantum Electronic Coherence in Lhcii. *Nature Chemistry* **2012**, *4*, 389-395.
- (33) Wong, C. Y.; Alvey, R. M.; Turner, D. B.; Wilk, K. E.; Bryant, D. A.; Curmi, P. M. G.; Silbey, R. J.; Scholes, G. D. Electronic Coherence Lineshapes Reveal Hidden Excitonic Correlations in Photosynthetic Light Harvesting. *Nature Chemistry* **2012**, *4*, 396-404.
- (34) Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: New York, 1995.
- (35) Seidner, L.; Stock, G.; Domcke, W. Nonperturbative Approach to Femtosecond Spectroscopy: General Theory and Application to Multidimensional Nonadiabatic Photoisomerization Processes. *J. Chem. Phys.* **1995**, *103*, 3998-4011.
- (36) Kato, T.; Tanimura, Y. Multi-Dimensional Vibrational Spectroscopy Measured from Different Phase-Matching Conditions. *Chemical Physics Letters* **2001**, *341*, 329-337.
- (37) Gelin, M. F.; Egorova, D.; Domcke, W. Efficient Calculation of Time- and Frequency-Resolved Four-Wave-Mixing Signals. *Acc. Chem. Res.* **2009**, *42*, 1290-1298.
- (38) Cina, J. A. Wave-Packet Interferometry and Molecular State Reconstruction: Spectroscopic Adventures on the Left-Hand Side of the Schrödinger Equation. *Annu. Rev. Phys. Chem.* **2008**, *59*, 319-342.
- (39) Lott, G. A.; Perdomo-Ortiz, A.; Utterback, J. K.; Widom, J. R.; Aspuru-Guzik, A.; Marcus, A. H. Conformation of Self-Assembled Porphyrin Dimers in Liposome Vesicles by Phase-Modulation 2D Fluorescence Spectroscopy. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 16521-16526.
- (40) Perdomo-Ortiz, A.; Widom, J. R.; Lott, G. A.; Aspuru-Guzik, A.; Marcus, A. H. Conformation and Electronic Population Transfer in Membrane-Supported Self-Assembled Porphyrin Dimers by 2D Fluorescence Spectroscopy. *J. Phys. Chem. B* **2012**, *116*, 10757-10770.
- (41) Tekavec, P. F.; Myers, J. A.; Lewis, K. L. M.; Ogilvie, J. P. Two-Dimensional Electronic Spectroscopy with a Continuum Probe. *Opt. Lett.* **2009**, *34*, 1390-1392.
- (42) Tekavec, P. A.; Lewis, K. L. M.; Fuller, F. D.; Myers, J. A.; Ogilvie, J. P. Toward Broad Bandwidth 2-D Electronic Spectroscopy: Correction of Chirp from a Continuum Probe. *IEEE Journal on Selected Topics in Quantum Electronics* **2012**, *18*, 210-217.
- (43) Keusters, D.; Warren, W. S. Effect of Pulse Propagation on the Two-Dimensional Photon Echo Spectrum of Multilevel Systems. *J. Chem. Phys.* **2003**, *119*, 4478-4489.
- (44) Keusters, D.; Warren, W. S. Propagation Effects on the Peak Profile in Two-Dimensional Optical Photon Echo Spectroscopy. *Chem. Phys. Lett.* **2004**, *383*, 21-24.
- (45) Yetzbacher, M. K.; Belabas, N.; Kitney, K. A.; Jonas, D. M. Propagation, Beam Geometry, and Detection Distortions of Peak Shapes in Two-Dimensional Fourier Transform Spectra. *J. Chem. Phys.* **2007**, *126*, 044511.
- (46) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford University Press: New York, 1987.

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- Figure 1: A 3D plot of the signal intensity as a function of the probe frequency ω_p and the signal frequency ω_s . The plot shows two distinct peaks, one at low frequencies and one at high frequencies, indicating a non-linear response. A red line with a wavy signal is overlaid on the plot. A green arrow points from the plot to a table of the signal and probe frequencies, and an orange arrow points from the table back to the plot.

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