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2017

Do, T. N., Gelin, M. F., & Tan, H.-S. (2017). Simplified expressions that incorporate finite pulse effects into coherent two-dimensional optical spectra. *The Journal of Chemical Physics*, 147(14), 144103-.

<https://hdl.handle.net/10356/86876>

<https://doi.org/10.1063/1.4985888>

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Simplified expressions that incorporate finite pulse effects into coherent two-dimensional optical spectra

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(Received 30 May 2017; accepted 18 September 2017; published online 10 October 2017)

We derive general expressions that incorporate finite pulse envelope effects into a coherent two-dimensional optical spectroscopy (2DOS) technique. These expressions are simpler and less computationally intensive than the conventional triple integral calculations needed to simulate 2DOS spectra. The simplified expressions involving multiplications of arbitrary pulse spectra with 2D spectral response function are shown to be exactly equal to the conventional triple integral calculations of 2DOS spectra if the 2D spectral response functions do not vary with population time. With minor modifications, they are also accurate for 2D spectral response functions with quantum beats and exponential decay during population time. These conditions cover a broad range of experimental 2DOS spectra. For certain analytically defined pulse spectra, we also derived expressions of 2D spectra for arbitrary population time dependent 2DOS spectral response functions. Having simpler and more efficient methods to calculate experimentally relevant 2DOS spectra with finite pulse effect considered will be important in the simulation and understanding of the complex systems routinely being studied by using 2DOS. *Published by AIP Publishing.* <https://doi.org/10.1063/1.4985888>

I. INTRODUCTION

Two-dimensional coherent optical spectroscopy (2DOS) has been employed as a powerful tool to investigate various physical, chemical, and biological systems.^{1–3} 2DOS has been applied over a broad electromagnetic spectrum extending from IR, visible to UV regime. This includes experiments designed to probe the vibrational levels of chemical compounds or solvation dynamics using 2D IR spectroscopy,^{4–7} 2D and 3D electronic spectroscopy to study electronic excitation and energy transfer in photosynthesis apparatus,^{8–11} and UV 2D spectroscopy to observe electron transfer processes in proteins.¹²

The third order non-linear optical response function formalism based on time dependent perturbation theory in the system-field interactions is usually used to formulate 2DOS spectra.^{13,14} In this formalism, the third order response functions $R^{(3)}(t_3, t_2, t_1)$ corresponding to the stimulated photon echo and anti-echo (rephasing and non-rephasing) signals of the material of interest are probed by multiple optical pulses. These response functions correlate single quantum coherences over t_1 with single quantum coherences over t_3 with population time (or waiting time) t_2 as a parameter. A typical 2DOS experiment seeks to measure the 2D spectral response function $R^{(3)}(\omega_3, t_2, \omega_1)$. This function is the Fourier transforms over t_1 and t_3 of the time-domain response function $R^{(3)}(t_3, t_2, t_1)$. However, due to the finite durations of the interacting pulses, the measured 2DOS spectrum is a non-trivial

convolution of the 2D spectral response function $R^{(3)}(\omega_3, t_2, \omega_1)$ with the interacting finite pulses. Nonetheless, it is still a common practice to simulate the 2DOS spectra in the semi-impulsive limit, where the pulses are assumed to be infinitely short. In this limit, the 2DOS spectrum is assumed to be the 2D spectral response function $R^{(3)}(\omega_3, t_2, \omega_1)$. This approximation simplifies derivations and reduces the computational costs for simulation. This approximation is valid if the system dynamics time scales are much longer than the pulse durations. However, for many recent applications of 2DOS, this is not always the case. For example, the energy relaxation pathways in Fenna-Matthews-Olson (FMO) complex of green sulfur bacteria *C. tepidum* were resolved with lifetimes from 500 fs to 1000 fs using 50 fs duration laser pulses.¹⁵ The coherent quantum beat in the above system was also observed by using 40 fs duration pulses revealing the beating frequency 250 cm⁻¹ corresponding to 133 fs period.¹⁶ In other studies on nanomaterials, the electronic coupling in GaAs double quantum wells was investigated. The observed dynamics was faster than the 150 fs pulse duration and could not be resolved.¹⁷ In those studies, the pulse durations cannot be considered impulsive when compared to the recovered dynamics.

There have been studies with calculations, both numerically^{18–22} and analytically,^{23–25} that take into consideration the finite duration of the laser pulses on the 2DOS spectra. These works provide better understanding of the bandwidth^{18,19} and pulse chirp²⁰ effects on the 2DOS spectra. The so-called nonperturbative methods of the calculation of 2DOS spectra take into account specific pulse shapes and finite pulse durations automatically.^{26–28} The standard approach to incorporate the finite pulse effect is to perform the convolution of the

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interacting pulses and the response functions.^{18–20} However, due to the need to numerically evaluate a triple integral, these approaches are computationally intensive. Another approach is to obtain expressions in the frequency domain which converts the convolutions into simple multiplications and thereby cutting down on the computational costs.^{23,29,30} More recently, there have been analytical expressions developed for specific types of response functions interacting with pulses of certain analytical forms: Perlík *et al.* and Smallwood *et al.* developed analytical expressions for 2DOS spectra simulated for Bloch model 3rd order response functions using Lorentzian²⁴ and Gaussian excitation pulses,²⁵ respectively.

In this paper, we derive general expressions for 2DOS spectra that take into account finite bandwidth effects for arbitrary pulse envelope functions. These general expressions aim to reduce the amount of numerical integration necessary to calculate the 2DOS spectra. It can then be shown that for certain common types of response functions, these expressions are exact or near-exact. This result is important for many 2DOS experiments that measure response functions that are represented in this study. A more detailed description of this motivation is provided in Sec. II. The section is then followed by the theory section providing the derivation of the expressions. The sections that follow explore some applications with simulations and discussions.

II. MOTIVATION

In the non-linear optical response function formalism based on time dependent perturbation theory, the observed signal derives from the polarization $P^{(n)}(t)$ which is generated by the interaction between the excitation pulses and the material response function.^{13,14} It can be expressed as

$$P^{(n)}(t) \propto \int_{-\infty}^t d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \dots \int_{-\infty}^{\tau_2} d\tau_1 \times R^{(n)}(t - \tau_n, \tau_n - \tau_{n-1}, \dots, \tau_2 - \tau_1) \times E(\tau_n) E(\tau_{n-1}) \dots E(\tau_1), \quad (1)$$

where $R^{(n)}(t_n, t_{n-1}, \dots, t_1)$ is the n th-order response function of the material of interest. $E(\tau_i)$ are the electric fields interacting with the material at specific time moment τ_i to generate the polarization. Typically, in a 2DOS experiment, there may be some different processes with different corresponding properties. Hence, the $R^{(n)}(t_n, t_{n-1}, \dots, t_1)$ term can be a sum of various n th-order response functions.

In linear spectroscopy where $n = 1$, the first order polarization $P^{(1)}(t)$ is a convolution between the first order response function and the optical field,

$$P^{(1)}(t) \propto \int_{-\infty}^t d\tau_1 R^{(1)}(t - \tau_1) \times E(\tau_1). \quad (2)$$

Upon Fourier transform along t , the polarization expression $P^{(1)}(t)$ gives the frequency expression

$$S(\omega_t) \equiv \int_{-\infty}^{+\infty} dt P^{(1)}(t) e^{i\omega_t t} = \tilde{E}(\omega_t) R^{(1)}(\omega_t). \quad (3)$$

In this convenient form, the absorption spectrum is simply a multiplication of the frequency domain linear response and the optical pulse spectrum. The convolution in Eq. (2) can be avoided. Equation (3) is a statement of the convolution theorem where the Fourier transform of the convolution of two functions is equal to the multiplication of the individual Fourier transform of the two functions.

For the third order response function used in 2DOS where $n = 3$, Eq. (1) becomes

$$P^{(3)}(t, T, \tau) \propto \int_{-\infty}^t d\tau_3 \int_{-\infty}^{\tau_3} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 R^{(3)}(t - \tau_3, \tau_3 - \tau_2, \tau_2 - \tau_1) \times E(\tau_3) E(\tau_2) E(\tau_1). \quad (4)$$

In a typical 2DOS measurement, the sample is usually excited by a three-pulse train as depicted in Fig. 1. The optical field used for such experiments typically consists of three pulses expressed as

$$E(t) = E_1(t + T + \tau) + E_2(t + T) + E_3(t) \\ = \mathcal{E}_1(t + T + \tau) e^{-i\omega_L(t+T+\tau)} + \mathcal{E}_2(t + T) e^{-i\omega_L(t+T)} \\ + \mathcal{E}_3(t) e^{-i\omega_L t}, \quad (5)$$

where τ and T are the time delays from the first to the second and from the second to the third pulse. $\mathcal{E}_i(t)$ are the envelopes of the i th pulses and ω_L is the laser frequency. In this article, we use $\mathcal{E}_i(t)$ to denote the pulse envelope and $E_i(t)$ to denote the optical pulse field that includes the pulse envelope and carrier wave. $\tilde{\mathcal{E}}_i(\omega)$ and $\tilde{E}_i(\omega)$ are the Fourier transform of $\mathcal{E}_i(t)$ and $E_i(t)$, respectively.

Typically, in order to obtain the 3rd order polarization, the triple integral in Eq. (4) needs to be calculated. However, with Eq. (3) as an example, it is therefore attractive to seek analogous expressions for higher orders that consist of multiplications of the response function in the frequency domain and the interacting pulse spectra. In the case of third order, it is possible to derive and show that the triple Fourier transform of the third order polarization signal yields^{23,25,29,30}

$$S(\omega_t, \omega_T, \omega_\tau) \equiv \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dt dT d\tau P^{(3)}(t, T, \tau) e^{i\omega_t t} e^{i\omega_T T} e^{i\omega_\tau \tau} \\ \sim \tilde{\mathcal{E}}_1(\omega_\tau) \tilde{\mathcal{E}}_2(\omega_T - \omega_\tau) \tilde{\mathcal{E}}_3(\omega_t - \omega_T) \\ \times R^{(3)}(\omega_t, \omega_T, \omega_\tau), \quad (6)$$

FIG. 1. The three-pulse train illustration with the average of response function centered at T and weighted by the pulse envelopes.

where $R^{(3)}(\omega_3, \omega_2, \omega_1)$ is the triple Fourier transform of the response function $R^{(3)}(t_3, t_2, t_1)$ along all three time domains. (We include a more detailed expression in the [supplementary material](#), Sec. I.) Analogous to Eq. (3), Eq. (6) can be viewed as a statement of the convolution theorem. This kind of expression is very useful as the finite pulse effect can be taken into consideration from a direct multiplication of the interacting pulse spectra and the frequency domain expression of the response function. Equations like Eq. (6) have been derived by Belabas and Jonas for applications in analyzing pulse propagation effects in 2DOS.^{29,30} Schweigert and Mukamel derived general expressions which extended applications to higher dimensional optical spectroscopies²³ of which Eq. (6) can be considered a special case.

However, 2D photon echo experiments are usually presented as 2D spectra of frequency axes ω_t and ω_τ with the population time T as a parameter. The standard approach to acquire a 2DOS spectrum with finite pulse effect is to obtain the 3rd order polarization by performing the triple integral in Eq. (4) followed by Fourier transformations over τ and t . We shall henceforth label this as the standard triple integration (STI) approach. As the STI approach is computationally intensive, and with Eq. (6) as a motivation, it is natural to seek such expressions for the 2DOS signal function,

$$S(\omega_t, T, \omega_\tau) \equiv \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d\tau P(t, T, \tau) e^{i\omega_t t} e^{i\omega_\tau \tau} \approx \tilde{E}_1(\omega_\tau) \tilde{E}_2(\omega_\tau) \tilde{E}_3(\omega_t) R^{(3)}(\omega_t, T, \omega_\tau), \quad (7)$$

where analogous to Eq. (6), we have the spectra of the three interacting optical fields multiplied by the 2D spectral response function $R^{(3)}(\omega_3, \omega_2, \omega_1)$ which is the Fourier transform of the third order response function along t_3 and t_1 domains. It is known that for the case where there is no longer any correlation between the excitation and detection frequencies, the 2D spectral response function is simply the product of the linear absorption spectra along both frequency dimensions, and Eq. (7) is valid.¹⁹ This typically is the case for long population time t_2 , for systems undergoing spectral diffusion. One major purpose of this article is to determine the general conditions under which the expression of Eq. (7) is valid.

In Sec. III, we present the derivation of expressions that will allow us to answer our questions better. We will then show that for the cases where 2D spectral response functions are not t_2 -dependent, the expression is exact for waiting times significantly longer than the pulse width. For t_2 -dependent 2D response functions, generally, we can only approximate the expressions. However, for two cases as shown

below, the t_2 -oscillating and t_2 -exponentially decaying 2D response functions, simplified expressions related to Eq. (7) are exact.

III. THEORY

In this section, we present the derivation of the simplified expressions for the 2DOS signal function $S(\omega_t, T, \omega_\tau)$. Equation (4) is evaluated with the pulse train expressed in Eq. (5). The first interaction comes from the first pulse presented in Eq. (4) as the first integral along τ_1 . Similarly, the second and the third integrals denote the second and the third interactions between the sample and the second and the third pulses, respectively.

The kind of pulse trains in Eq. (5) describes a train consisting of replica pulses that can be created by translational delay stages and are representative of pulses used in the phase matching non-collinear beam geometry, sometimes known as the Boxcar geometry. Substituting the electric field in Eq. (1) and assigning $E_i(\tau_i)$ to be the i th interaction, we have

$$P^{(3)}(t, T, \tau) \propto \int_{-\infty}^t d\tau_3 \mathcal{E}_3^{(\eta_3)}(\tau_3) e^{-i\eta_3 \omega_L \tau_3} \times \int_{-\infty}^{\tau_3} d\tau_2 \mathcal{E}_2^{(\eta_2)}(\tau_2 + T) e^{-i\eta_2 \omega_L (\tau_2 + T)} \times \int_{-\infty}^{\tau_2} d\tau_1 \mathcal{E}_1^{(\eta_1)}(\tau_1 + T + \tau) e^{-i\eta_1 \omega_L (\tau_1 + T + \tau)} \times R^{(3)}(t - \tau_3, \tau_3 - \tau_2, \tau_2 - \tau_1). \quad (8)$$

Here, the response function is either of the rephasing $R_R^{(3)}$ or non-rephasing $R_{NR}^{(3)}$ processes which is associated with the different sets of interaction indices η_i , respectively,

$$R_R^{(3)} \text{ with } [\eta_1, \eta_2, \eta_3] = [-1, +1, +1], \\ R_{NR}^{(3)} \text{ with } [\eta_1, \eta_2, \eta_3] = [+1, -1, +1]. \quad (9)$$

We use the notation of Smallwood *et al.* for the interaction indices η_i dictating whether an electric field ($\eta_i = 1$) interaction or a complex conjugated field ($\eta_i = -1$) interaction is being considered,²⁵

$$\mathcal{E}_i^{(\eta_i)}(\tau_i) e^{-i\eta_i \omega_L \tau_i} = \begin{cases} \mathcal{E}_i(\tau_i) e^{-i\omega_L \tau_i} & (\eta_i = +1) \\ \mathcal{E}_i^*(\tau_i) e^{+i\omega_L \tau_i} & (\eta_i = -1) \end{cases}.$$

We can substitute the upper bound of the integrals with infinity by adding the Heaviside step functions $\Theta(t)$ to satisfy the time order of the pulse sequence,

$$P^{(3)}(t, T, \tau) \propto \int_{-\infty}^{+\infty} d\tau_3 \mathcal{E}_3^{(\eta_3)}(\tau_3) e^{-i\eta_3 \omega_L \tau_3} \Theta(t - \tau_3) \int_{-\infty}^{+\infty} d\tau_2 \mathcal{E}_2^{(\eta_2)}(\tau_2 + T) e^{-i\eta_2 \omega_L (\tau_2 + T)} \Theta(\tau_3 - \tau_2) \times \int_{-\infty}^{+\infty} d\tau_1 \mathcal{E}_1^{(\eta_1)}(\tau_1 + T + \tau) e^{-i\eta_1 \omega_L (\tau_1 + T + \tau)} \Theta(\tau_2 - \tau_1) R^{(3)}(t - \tau_3, \tau_3 - \tau_2, \tau_2 - \tau_1). \quad (10)$$

The emitted signal that is proportional to the polarization is then resolved in a spectrometer which effectively carries out a Fourier transform along t . The first coherence time τ is scanned and Fourier transformed to produce the 2DOS signal function. As indicated in Eq. (7), we shall define the 2DOS signal function $S(\omega_t, T, \omega_\tau)$ as the Fourier transform result over t and τ domains of the polarization $P^{(3)}(t, T, \tau)$,

$$S(\omega_t, T, \omega_\tau) = \int_{-\infty}^{+\infty} d\tau e^{i\omega_\tau \tau} \int_{-\infty}^{+\infty} dt e^{i\omega_t t} P^{(3)}(t, T, \tau). \quad (11)$$

We notice that in Eq. (10), τ containing terms only appear in the first integral. We assume that all considered functions are well-behaved and satisfy the conditions for integration interchangeability.^{31,32} We can interchange the integration sequence and Eq. (11) becomes

$$\begin{aligned} S(\omega_t, T, \omega_\tau) \propto & \int_{-\infty}^{+\infty} dt e^{i\omega_t t} \int_{-\infty}^{+\infty} d\tau_3 \mathcal{E}_3^{(\eta_3)}(\tau_3) e^{-i\eta_3 \omega_L \tau_3} \Theta(t - \tau_3) \int_{-\infty}^{+\infty} d\tau_2 \mathcal{E}_2^{(\eta_2)}(\tau_2 + T) e^{-i\eta_2 \omega_L (\tau_2 + T)} \Theta(\tau_3 - \tau_2) \\ & \times \int_{-\infty}^{+\infty} d\tau_1 R^{(3)}(t - \tau_3, \tau_3 - \tau_2, \tau_2 - \tau_1) \Theta(\tau_2 - \tau_1) \int_{-\infty}^{+\infty} d\tau e^{i\omega_\tau \tau} \mathcal{E}_1^{(\eta_1)}(\tau_1 + T + \tau) e^{-i\eta_1 \omega_L (\tau_1 + T + \tau)}. \end{aligned} \quad (12)$$

After the operation of the two Fourier transformations, the obtained 2DOS signal function becomes

$$\begin{aligned} S(\omega_t, T, \omega_\tau) \propto & \tilde{\mathcal{E}}_1^{(\eta_1)}[\eta_1(\omega_\tau - \eta_1 \omega_L)] \int_{-\infty}^{+\infty} d\tau_3 \mathcal{E}_3^{(\eta_3)}(\tau_3) e^{-i\eta_3 \omega_L \tau_3} e^{i\omega_t \tau_3} \\ & \times \int_{-\infty}^{+\infty} d\tau_2 \mathcal{E}_2^{(\eta_2)}(\tau_2 + T) e^{-i\eta_2 \omega_L (\tau_2 + T)} e^{-i\omega_\tau (\tau_2 + T)} \Theta(\tau_3 - \tau_2) \times R(\omega_t, \tau_3 - \tau_2, \omega_\tau). \end{aligned} \quad (13)$$

We note that Eq. (13) is still equivalent to Eq. (11). The first thing to notice is that in this case, the first interaction pulse is now recast as a pulse spectrum. The triple integral has been reduced to a double integral multiplied by a pulse spectrum. Mathematically, the Heaviside function $\Theta(\tau_3 - \tau_2)$ in Eq. (13) ensures time-ordered interactions, i.e., the third pulse will always interact after the second pulse. The Heaviside function is important in cases where the second and the third pulses overlap in time. However, for cases in which the second and the third pulses do not overlap, i.e., in the case that the waiting time delay T is significantly larger than the pulse durations of the two last pulses, the time ordering is ensured even without the Heaviside function. In most experimental conditions, 2D spectra are presented only for T larger than the pulse widths. This is due to the fact that when pulses two and three overlap, there are inadvertently coherent artifacts that distort the 2D spectra and are usually not taken into consideration.^{8,33–35} Therefore, for such cases, we can drop the Heaviside function to obtain

$$\begin{aligned} S(\omega_t, T, \omega_\tau) \propto & \tilde{\mathcal{E}}_1^{(\eta_1)}[\eta_1(\omega_\tau - \eta_1 \omega_L)] \\ & \times \int_{-\infty}^{+\infty} d\tau_3 \mathcal{E}_3^{(\eta_3)}(\tau_3) e^{-i\eta_3 \omega_L \tau_3} e^{i\omega_t \tau_3} \\ & \times \int_{-\infty}^{+\infty} d\tau_2 \mathcal{E}_2^{(\eta_2)}(\tau_2 + T) e^{-i\eta_2 \omega_L (\tau_2 + T)} e^{-i\omega_\tau (\tau_2 + T)} \\ & \times R(\omega_t, \tau_3 - \tau_2, \omega_\tau). \end{aligned} \quad (14)$$

From Eq. (14), a clear physical interpretation can be discerned for the remaining two integrals. It is the average of the 2D spec-

tral response function centered at T , weighted by the pulse envelopes of the second and the third pulses as shown in Fig. 1.

In Secs. III A–III C, we consider further simplification of Eq. (14) under certain conditions.

A. t_2 -independent response functions and slowly varying response functions

We consider here for the case that the 2D spectral response function of the investigated system is t_2 -independent. In this case, the 2D spectral response function $R(\omega_t, t_2, \omega_\tau) = R(\omega_t, \omega_\tau)$ and can be taken out of the integrals in Eq. (14) to give

$$\begin{aligned} S(\omega_t, T, \omega_\tau) = & R(\omega_t, \omega_\tau) \tilde{\mathcal{E}}_1^{(\eta_1)}[\eta_1(\omega_\tau - \eta_1 \omega_L)] \\ & \times \int_{-\infty}^{+\infty} d\tau_3 \mathcal{E}_3^{(\eta_3)}(\tau_3) e^{-i\eta_3 \omega_L \tau_3} e^{i\omega_t \tau_3} \\ & \times \int_{-\infty}^{+\infty} d\tau_2 \mathcal{E}_2^{(\eta_2)}(\tau_2 + T) e^{-i\eta_2 \omega_L (\tau_2 + T)} e^{-i\omega_\tau (\tau_2 + T)}. \end{aligned} \quad (15)$$

The two remaining integrals can be easily evaluated as

$$\begin{aligned} & \int_{-\infty}^{+\infty} d\tau_2 \mathcal{E}_2^{(\eta_2)}(\tau_2 + T) e^{-i\eta_2 \omega_L (\tau_2 + T)} e^{-i\omega_\tau (\tau_2 + T)} \\ & = \tilde{\mathcal{E}}_2^{(\eta_2)}[-\eta_2(\omega_\tau + \eta_2 \omega_L)], \end{aligned} \quad (16)$$

$$\int_{-\infty}^{+\infty} d\tau_3 \mathcal{E}_3^{(\eta_3)}(\tau_3) e^{-i\eta_3 \omega_L \tau_3} e^{i\omega_t \tau_3} = \tilde{\mathcal{E}}_3^{(\eta_3)}[\eta_3(\omega_t - \eta_3 \omega_L)]. \quad (17)$$

Finally, the 2DOS signal function can be expressed as

$$S(\omega_t, \omega_\tau) = R(\omega_t, \omega_\tau) \tilde{\mathcal{E}}_1^{(\eta_1)} [\eta_1 (\omega_\tau - \eta_1 \omega_L)] \\ \times \tilde{\mathcal{E}}_2^{(\eta_2)} [-\eta_2 (\omega_\tau + \eta_2 \omega_L)] \tilde{\mathcal{E}}_3^{(\eta_3)} [\eta_3 (\omega_t - \eta_3 \omega_L)]. \quad (18)$$

For cases that the 2D spectral response function varies with a time scale that is slow compared to the pulse width, we can make the approximation that the response function does not vary so much over the last two pulse widths between the two integration time points $\tau_3 - \tau_2$ (see Fig. 1) and assume that the response function bears the value at T , i.e., $R(\omega_t, \tau_3 - \tau_2, \omega_\tau) \approx R(\omega_t, T, \omega_\tau)$ in Eq. (14), the resultant 2D spectra can be approximated as

$$S(\omega_t, T, \omega_\tau) \approx R(\omega_t, T, \omega_\tau) \tilde{\mathcal{E}}_1^{(\eta_1)} [\eta_1 (\omega_\tau - \eta_1 \omega_L)] \\ \times \tilde{\mathcal{E}}_2^{(\eta_2)} [-\eta_2 (\omega_\tau + \eta_2 \omega_L)] \\ \times \tilde{\mathcal{E}}_3^{(\eta_3)} [\eta_3 (\omega_t - \eta_3 \omega_L)]. \quad (19)$$

The result presented here physically means that the 2D spectrum obtained using the pulse train expressed in Eq. (5) can be approximated as the 2D spectral response function of the system in the spectral domain multiplied by the spectra of three excitation laser pulses. An expression similar to Eq. (19) has been stated previously.³⁶ The 2DOS of transitions that undergo spectral diffusion can also be described by Eq. (19) at sufficiently large waiting time, T , when the transitions are no longer correlated between the excitation frequencies ω_τ and detection frequencies ω_t .¹⁹

We now take a closer look at Eq. (18) for the two cases of non-rephasing and rephasing processes with the corresponding η_i value sets [Eq. (9)]. The non-rephasing (anti-echo) and rephasing (echo) 2DOS signal functions, from Eq. (18), are, respectively,

$$S_{NR}(\omega_t, \omega_\tau) = R_{NR}(\omega_t, \omega_\tau) \tilde{\mathcal{E}}_1(\omega_\tau - \omega_L) \\ \times \tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L) \tilde{\mathcal{E}}_3(\omega_t - \omega_L), \quad (20) \\ S_R(\omega_t, \omega_\tau) = R_R(\omega_t, \omega_\tau) \tilde{\mathcal{E}}_1^*(-\omega_\tau - \omega_L) \\ \times \tilde{\mathcal{E}}_2(-\omega_\tau - \omega_L) \tilde{\mathcal{E}}_3(\omega_t - \omega_L).$$

In the actual experimental practice of 2DOS, the signals are usually heterodyne detected using a local oscillator pulse. With this taken into consideration, the final measured 2DOS spectrum $\mathbb{S}(\omega_t, T, \omega_\tau)$ becomes (Appendix)

$$\mathbb{S}(\omega_t, T, \omega_\tau) = S(\omega_t, T, \omega_\tau) \tilde{E}_{LO}^*(\omega_t) \\ + S^*(\omega_t, T, -\omega_\tau) \tilde{E}_{LO}(\omega_t). \quad (21)$$

For 2DOS performed in the phase matching non-collinear beam geometry, where the non-rephasing and rephasing signals are acquired separately, the measured 2DOS spectra for the non-rephasing and rephasing processes are, respectively,

$$\mathbb{S}_{NR}(\omega_t, \omega_\tau) = R_{NR}(\omega_t, \omega_\tau) \tilde{\mathcal{E}}_1(\omega_\tau - \omega_L) \tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L) \\ \times \tilde{\mathcal{E}}_3(\omega_t - \omega_L) \tilde{E}_{LO}^*(\omega_t), \quad (22) \\ \mathbb{S}_R(\omega_t, \omega_\tau) = R_R^*(\omega_t, -\omega_\tau) \tilde{\mathcal{E}}_1(\omega_\tau - \omega_L) \tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L) \\ \times \tilde{\mathcal{E}}_3^*(\omega_t - \omega_L) \tilde{E}_{LO}(\omega_t).$$

We have only included the measured 2DOS spectra in the positive quadrant $(\omega_t, \omega_\tau) = (+, +)$, as is usually presented.

For 2DOS that is performed in the pump-probe geometry, the local oscillator is the “probe” pulse that is the same pulse as the third interacting pulse, i.e., $\tilde{E}_{LO}(\omega_t) = \tilde{\mathcal{E}}_3(\omega_t - \omega_L)$. The signal measured in the pump-probe geometry is in purely absorptive form, as both rephasing and non-rephasing signals are measured simultaneously.^{37–40} The measured 2D spectrum will be

$$\mathbb{S}_{abs}(\omega_t, T, \omega_\tau) = R_{NR}(\omega_t, \omega_\tau) \tilde{\mathcal{E}}_1(\omega_\tau - \omega_L) \tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L) \\ \times \tilde{\mathcal{E}}_3(\omega_t - \omega_L) \tilde{\mathcal{E}}_3^*(\omega_t - \omega_L) + R_R^*(\omega_t, -\omega_\tau) \\ \times \tilde{\mathcal{E}}_1(\omega_\tau - \omega_L) \tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L) \tilde{\mathcal{E}}_3^*(\omega_t - \omega_L) \\ \times \tilde{\mathcal{E}}_3(\omega_t - \omega_L). \quad (23)$$

In most cases, only the real part of Eq. (23) is presented.

B. Response functions with t_2 -dependent oscillation or exponential decay

As presented in Eq. (19), if the 2D spectral response function is t_2 -dependent, the multiplication expression is an approximation. However, for some cases of t_2 -dependent 2D spectral response functions, we can also derive exact expressions. Let us assume that the 2D spectral response function takes the form of

$$R(\omega_3, t_2, \omega_1) \equiv R(\omega_3, \omega_1) \times e^{-i\Xi t_2}, \quad (24)$$

where $\Xi = \Omega - i\gamma$ is a complex number with two real valued coefficients Ω and γ . The above expression can describe the oscillation in the peaks' amplitude and shape, which is one aspect of the 2DOS spectra for vibrational wave packet motion³⁶ and quantum coherent beatings^{41,42} ($\Xi = \Omega$ being the corresponding frequency) or the influence of vibrational relaxation during the population time ($\Xi = -i\gamma$, γ being the corresponding rate)⁴³ and linear combination of these expressions describes fairly general response function in the sum-over-state representation. The expressions of Eq. (24) can be substituted into the response function in Eq. (14). After simplification, the expression for 2DOS signal becomes

$$S(\omega_t, T, \omega_\tau) = R(\omega_t, \omega_\tau) e^{-i\Xi T} \tilde{\mathcal{E}}_1^{(\eta_1)} [\eta_1 (\omega_\tau - \eta_1 \omega_L)] \int_{-\infty}^{+\infty} d\tau_3 \mathcal{E}_3^{(\eta_3)}(\tau_3) e^{-i\eta_3 \omega_L \tau_3} e^{i\omega_t \tau_3} e^{-i\Xi \tau_3} \\ \times \int_{-\infty}^{+\infty} d\tau_2 \mathcal{E}_2^{(\eta_2)}(\tau_2 + T) e^{-i\eta_2 \omega_L (\tau_2 + T)} e^{-i\omega_\tau (\tau_2 + T)} e^{i\Xi (\tau_2 + T)}. \quad (25)$$

The subsequent integration then gives

$$S(\omega_t, T, \omega_\tau) = R(\omega_t, \omega_\tau) e^{-i\Xi T} \tilde{\mathcal{E}}_1^{(\eta_1)} [\eta_1 (\omega_\tau - \eta_1 \omega_L)] \\ \times \tilde{\mathcal{E}}_2^{(\eta_2)} [-\eta_2 (\omega_\tau + \eta_2 \omega_L - \Xi)] \\ \times \tilde{\mathcal{E}}_3^{(\eta_3)} [\eta_3 (\omega_t - \eta_3 \omega_L - \Xi)]. \quad (26)$$

This expression is similar to Eq. (18) except for the fact that the second and the third pulse spectra are “shifted” from its original spectrum by Ξ .

Let us first consider the case where the Ξ term is purely real, i.e., $\Xi = \Omega$. This represents a 2D spectral response function whose amplitude oscillates with t_2 . From Eq. (26), the resultant expressions for the 2DOS signal become

$$S(\omega_t, T, \omega_\tau) = R(\omega_t, \omega_\tau) e^{-i\Omega T} \tilde{\mathcal{E}}_1^{(\eta_1)} [\eta_1 (\omega_\tau - \eta_1 \omega_L)] \\ \times \tilde{\mathcal{E}}_2^{(\eta_2)} [-\eta_2 (\omega_\tau + \eta_2 \omega_L - \Omega)] \\ \times \tilde{\mathcal{E}}_3^{(\eta_3)} [\eta_3 (\omega_t - \eta_3 \omega_L - \Omega)]. \quad (27)$$

The expression in Eq. (27) shows that the 2D spectra consist of the 2D spectral response function oscillating during T multiplied with the first pulse spectrum. The second and the third pulse spectra that are multiplied onto the 2D spectral response function are shifted by oscillating frequency Ω . More detailed analysis will be conducted in Sec. IV.

We now consider the case where the Ξ term contains only an imaginary value, i.e., $\Xi = -i\gamma$. In this case, the t_2 -dependence is described as an exponential decay representing, for example, population transfer dynamics. Substituting $\Xi = -i\gamma$ into Eq. (26), we have the expression for the 2DOS signal function as

$$S(\omega_t, T, \omega_\tau) = R(\omega_t, \omega_\tau) e^{-\gamma T} \tilde{\mathcal{E}}_1^{(\eta_1)} [\eta_1 (\omega_\tau - \eta_1 \omega_L)] \\ \times \tilde{\mathcal{E}}_2^{(\eta_2)} [-\eta_2 (\omega_\tau + \eta_2 \omega_L + i\gamma)] \\ \times \tilde{\mathcal{E}}_3^{(\eta_3)} [\eta_3 (\omega_t - \eta_3 \omega_L + i\gamma)]. \quad (28)$$

Similar to the previous case, the expression for the 2DOS signal function is the product of the 2D spectral response function and the three excitation pulses. However, the second and the third pulse spectra contain an imaginary frequency $i\gamma$. More detailed interpretation will be presented in Sec. IV.

C. Cases with arbitrary 2D spectral response function and analytical pulse spectra

In some cases, it may be sufficient to use an analytical function to represent the pulse spectra. For example, Gaussian functions are regularly used to represent ultrashort laser pulses. The 2D spectra of an arbitrary t_2 -dependent response function can be generated taking into account the finite pulse effect. We can reduce the two integrals needed in Eq. (14) to one integral. Equation (14) can be expressed after changing the time variables $\tau_3 - \tau_2 = t_2$ to give

$$S(\omega_t, T, \omega_\tau) \propto \tilde{\mathcal{E}}_1^{(\eta_1)} [\eta_1 (\omega_\tau - \eta_1 \omega_L)] \int_0^{+\infty} dt_2 \mathcal{E}_3^{(\eta_3)} (\tau_2 + t_2) e^{-i\eta_3 \omega_L (\tau_2 + t_2)} e^{i\omega_t (\tau_2 + t_2)} \\ \times \int_{-\infty}^{+\infty} d\tau_2 \mathcal{E}_2^{(\eta_2)} (\tau_2 + T) e^{-i\eta_2 \omega_L (\tau_2 + T)} e^{-i\omega_\tau (\tau_2 + T)} R(\omega_t, t_2, \omega_\tau), \quad (29)$$

where the integral over τ_2 no longer involves the response function. By making the substitution $\tau_2 + t_2 = x - \xi$, $\xi = (T - t_2)/2$, we then obtain

$$S(\omega_t, T, \omega_\tau) \propto \tilde{\mathcal{E}}_1^{(\eta_1)} [\eta_1 (\omega_\tau - \eta_1 \omega_L)] \\ \times \int_0^{+\infty} dt_2 \Phi(\Omega_+, \xi) e^{-i\xi \Omega_-} R(\omega_t, t_2, \omega_\tau), \quad (30)$$

where

$$\Omega_+ = \eta_3 \omega_L - \omega_t + \eta_2 \omega_L + \omega_\tau,$$

$$\Omega_- = -\eta_3 \omega_L + \omega_t + \eta_2 \omega_L + \omega_\tau.$$

The quantity

$$\Phi(\Omega_+, \xi) = \int_{-\infty}^{+\infty} dx \mathcal{E}_2^{(\eta_2)} (x + \xi) \mathcal{E}_3^{(\eta_3)} (x - \xi) e^{-ix\Omega_+} \quad (31)$$

is known as the Wigner spectrogram.^{44,45} It can be easily evaluated analytically for certain functions. For example, for pulses

represented by a Gaussian function, $\mathcal{E}_i^{(\eta_i)}(t) = e^{-\Gamma^2 t^2}$, one obtains

$$\Phi(\Omega_+, \xi) \propto e^{-2\Gamma^2 \xi^2} e^{-\Omega_+^2 / (8\Gamma^2)}. \quad (32)$$

Equation (32) can then be substituted into Eq. (30), where only one integration needs to be performed. In the event if the pulses are short on the time scale of the population dynamics, $\Phi(\Omega_+, \xi)$ is sharply peaked around $\xi = 0$, one can write

$$S(\omega_t, T, \omega_\tau) \approx R(\omega_t, T, \omega_\tau) \tilde{\mathcal{E}}_1^{(\eta_1)} [\eta_1 (\omega_\tau - \eta_1 \omega_L)] \\ \times 2 \int_{-\infty}^{+\infty} d\xi \Phi(\Omega_+, \xi) e^{-i\xi \Omega_-}. \quad (33)$$

Equation (33) is equivalent to Eq. (19). The approximation made in the deduction of Eq. (33) from Eq. (30) is similar to the so-called doorway-window approximation, which is frequently used for the description of femtosecond signals induced by temporally well-separated pulses.⁴⁶

IV. APPLICATIONS AND SIMULATIONS

A. t_2 -independent response functions

A common example of a t_2 -independent 2D spectral response function is a system with linear spectrum that contains homogeneous and inhomogeneous linewidths. This is typically termed a Voigt's profile which is a convolution between a Lorentzian profile for the homogeneous broadening and a Gaussian profile for the inhomogeneous distribution. In such cases, the response functions for rephasing and non-rephasing processes can be expressed as

$$R_{NR}(t_3, t_2, t_1) = -\left(\frac{i}{\hbar}\right)^3 \mu^4 \Theta(t_3) \Theta(t_2) \Theta(t_1) \times e^{-i\omega_0(t_3+t_1)} e^{-\Gamma(t_3+t_1)} e^{-\Delta_0^2(t_3-t_1)^2}, \quad (34)$$

$$R_R(t_3, t_2, t_1) = -\left(\frac{i}{\hbar}\right)^3 \mu^4 \Theta(t_3) \Theta(t_2) \Theta(t_1) \times e^{-i\omega_0(t_3-t_1)} e^{-\Gamma(t_3+t_1)} e^{-\Delta_0^2(t_3-t_1)^2}.$$

To affirm that Eq. (18) is indeed the analytical equivalent of Eq. (11) for t_2 -independent 2D spectral response functions, we perform calculations of the 2DOS spectra that are generated using the STI approach and using Eq. (22). For simplicity, in the subsequent simulations, the center frequency of the response function is set as $\omega_0 = 0$. We investigate an ensemble of two-level systems having a homogeneous linewidth Γ of 0.2 eV and an inhomogeneous linewidth Δ_0 of 0.2 eV. Although the pulse spectra can be of arbitrary functions, for simplicity, we assume all three excitation pulses used are transform-limited Gaussian pulses with a full width

half maximum (FWHM) duration of 20 fs. We calculate the spectrum at population time $T = 100$ fs. The local oscillator in this simulation is the same as the last excitation laser pulse.

In Fig. 2(a), the spectrum depicts the real part of the non-rephasing 2DOS spectrum measured by impulsive pulses (δ pulses). It is therefore simply the 2D spectral response function which is obtained by the Fourier transform over t_3 and t_1 of the $R_{NR}(t_3, t_2, t_1)$ shown in Eq. (34). Figure 2(b) is obtained using the simplified expression in Eq. (22). The multiplication scheme is illustrated in the figure. The spectrum of the first pulse $\tilde{\mathcal{E}}_1(\omega_\tau - \omega_L)$ and the complex conjugated spectrum of the second pulse $\tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L)$ are multiplied along the ω_τ domain. Both of them are centered at ω_L . The last pulse spectrum $\tilde{\mathcal{E}}_3(\omega_t - \omega_L)$ and the local oscillator spectrum $\tilde{E}_{LO}^*(\omega_t) = \tilde{\mathcal{E}}_3^*(\omega_t - \omega_L)$ are multiplied along the ω_t dimension. Figure 2(c) presents the real part of 2DOS spectrum calculated using the STI approach. It can be seen that Figs. 2(b) and 2(c) are virtually identical. The only difference is the numerical background noise that comes from finite numerical integrations of the triple integral in Fig. 2(c).

Comparing Figs. 2(b) and 2(c) with Fig. 2(a), we clearly see that the main difference is that the finite bandwidth of laser pulses serves as a window and limits the accessible spectral range. This effect narrows the measured 2DOS spectra compared to the “ideal” 2D spectral response function.

As a further test, we also consider cases when the pump pulse spectra are asymmetric. As is expected, the 2DOS spectra calculated from both our expressions and using the STI approach are virtually identical (supplementary material, Sec. II).

FIG. 2. Simulation results for the 2D spectra of an ensemble of two-level systems. Figure 2(a) is the non-rephasing (anti-echo) response function, i.e., 2D spectrum in the impulsive regime. Figure 2(b) is the 2D spectrum obtained from the multiplication of Fig. 2(a) with suitable pulse spectra as presented. Figure 2(c) is the 2D spectrum obtained by calculating the triple integral in Eq. (8). All spectra are normalized to the maxima.

We note that although we perform the simulation to verify the validity of our expressions on this relatively simple system, our expressions in Eqs. (22) and (23) are applicable for arbitrary 2D spectral response functions that are t_2 -independent. Examples of systems with t_2 -independent 2D spectral response functions include the Fano model which is typically used to describe photoionization of atoms and photodissociation of molecules.⁴⁷

B. Quantum beat response functions

We now take a look at 2DOS spectra with response functions whose amplitude oscillates with t_2 . We have shown that the 2DOS signal function behaves according to Eq. (27) if we include finite pulse effects. This can come in the form of quantum beats generated by the coherence between different excited states during the population time. One typical system with such quantum beats is a system of atomic electronic levels with one ground state connected with many excited states. If the excitation laser spectrum is broad enough to cover two or more excited states, the quantum beat coherence can be created and the signal exhibits beatings during population time. One example of such a system is a three-level system having two excited states with slightly different resonant frequencies connected through a shared ground state as shown in Fig. 3. Quantum beats have also featured prominently in the discussions on efficient energy transfer dynamics in photosynthetic light harvesting systems.¹⁶ Cheng and Fleming proposed a model to study the interplay between rephasing and non-rephasing contributions into the quantum beat signal in 2D spectra.⁴¹ Ishizaki and Fleming examined the decay of quantum beat with two models and determined the observed decay is the ensemble dephasing.⁴² The beating peaks are different for rephasing and non-rephasing signals. The beating signals only appear in non-rephasing diagonal peaks and rephasing crosspeaks as presented by Khalil *et al.*⁴⁸ For a comprehensive simulation of 2DOS spectrum of this three-level system, all accessible double-sided Feynman diagrams should be enumerated and treated separately, i.e., the beating and non-beating processes have different finite pulse effects. The resultant 2DOS spectrum is the sum of all individually treated processes. In the scope of this paper, we present simulation of one specific non-rephasing diagonal beating peak and interpret the finite pulse effects. The corresponding double-sided Feynman diagram of the mentioned non-rephasing process is shown in Fig. 3.

For a non-rephasing process, the expression for the heterodyne detected 2DOS spectrum in Eq. (27) becomes

FIG. 3. (Left) Double-sided Feynman diagram of the interested non-rephasing beating process. (Right) Energy level diagram of the investigated three-level system.

$$\begin{aligned} \mathbb{S}_{NR}(\omega_t, T, \omega_\tau) &= R_{NR}(\omega_t, \omega_\tau) e^{-i\Omega T} \tilde{\mathcal{E}}_1(\omega_\tau - \omega_L) \\ &\times \tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L - \Omega) \tilde{\mathcal{E}}_3(\omega_t - \omega_L - \Omega) \\ &\times \tilde{E}_{LO}^*(\omega_t). \end{aligned} \quad (35)$$

When a 2DOS spectrum is presented, only the real part of Eq. (35) is usually taken. This gives rise to the oscillation of the 2DOS spectrum's peak amplitude and shape. In this simulation, we consider the same parameters as in Sec. IV A with both homogeneous and inhomogeneous linewidths of 0.2 eV. Three transform-limited Gaussian laser pulses have the same FWHM duration of 20 fs and are resonant with the transition $|0\rangle \rightarrow |1\rangle$. We let the local oscillator be the same as the third laser pulse, i.e., $\tilde{E}_{LO}^*(\omega_t) = \tilde{\mathcal{E}}_3^*(\omega_t - \omega_L)$. The energy difference between the $|1\rangle$ and $|1'\rangle$ states is set to 0.1 eV and yields the beating frequency $\Omega = 0.1$ eV which corresponds to a beating period of around 41.36 fs. This peak lies on the diagonal and its amplitude oscillates with population time.

Figure 4 is presented in a similar fashion as Fig. 2. It shows the simulated 2DOS spectra for the investigated non-rephasing process depicted in Fig. 3. Figure 4(a) is the real part of the 2DOS spectrum obtained with impulsive pulses (real valued 2D spectral response function). In this example, we have calculated the 2DOS spectra when the population time $T = 82.72$ fs was chosen to be twice as the beating period to keep the 2D spectral response function real valued (for ease of portrayal in the figure). The multiplication scheme according to Eq. (35) between Fig. 4(a) and the four pulse spectra leads to Fig. 4(b). Figure 4(c) shows the 2DOS spectrum calculated using the STI approach. The similarity between the two spectra of Figs. 4(b) and 4(c) shows the validity of our derivation. For comparison, Fig. 4(d) depicts the 2DOS spectrum calculated via Eq. (22). It is clear that the simple expressions of Eq. (22) are not adequate for this case. From Eq. (35) and Fig. 4, we can see that the first two pulse spectra $\tilde{\mathcal{E}}_1(\omega_\tau - \omega_L)$ and $\tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L - \Omega)$ are not centered at the same frequency. The second pulse spectrum has an apparent shift by Ω along the ω_τ dimension relative to the first pulse spectrum. In the ω_t dimension, the third pulse spectrum $\tilde{\mathcal{E}}_3(\omega_t - \omega_L - \Omega)$ also has an apparent shift of Ω from the local oscillator $\tilde{\mathcal{E}}_3^*(\omega_t - \omega_L)$. These frequency shifts cause an asymmetric distortion of the 2D peakshape. The 2D peak is more elongated towards the higher frequency. We perform further simulations for different population times T . They similarly show the validity of our expression [Eq. (35)]. They also show the trend of the asymmetric distortion of the 2D peakshapes compared with the spectra generated with the simple expressions of Eq. (22) (supplementary material, Sec. III).

The shift in the frequency for the second and third pulses in Eq. (35) may seem puzzling initially, as all the excitation pulses have the same central frequencies. A more physical interpretation of this shift can be made if we view it as a shift in the resonance frequency rather than a shift in the pulse center frequency. This can be seen from the double-sided Feynman diagram (Fig. 3), where the second and third interactions are the $|0\rangle$ to $|1'\rangle$ transitions which are shifted from the $|0\rangle$ to $|1\rangle$ transition (which is set as 0 frequency) by Ω . This interpretation is also in line with the expectation that

FIG. 4. Simulation results for 2D spectra of non-rephasing beating peak. Population time $T = 82.72$ fs was chosen to be twice as the beating period to keep the 2D spectral response function real valued (for ease of presentation in the figure). Figure 4(a) is the non-rephasing response function in the spectral domain. Figure 4(b) is the result of multiplication of Fig. 4(a) with the appropriate pulse spectra as depicted. Figure 4(c) is the calculated 2DOS spectrum using the STI approach. Figure 4(d) is obtained by a simple expression of Eq. (22) and presented for comparison.

with a bigger separation between states $|1\rangle$ and $|1'\rangle$, the intensity of resultant peaks will decrease with the separation of the first and the second pulse spectra, and one of the third and local oscillator pulse spectra. As Ω becomes large compared with the pulse spectral widths, the pulse spectra will cease to cover simultaneously both the $|0\rangle \rightarrow |1\rangle$ and $|0\rangle \rightarrow |1'\rangle$ transitions.

C. Exponential decay response functions

We now discuss the expressions that describe 2DOS peaks whose amplitudes decay exponentially with t_2 . Examples of such features are commonly observed in 2DOS spectra.

2DOS is routinely deployed to measure the excitonic energy transfer (EET) dynamics of light harvesting complexes.^{8,9,11} In such experiments, the amplitudes of the various peaks in the 2DOS spectrum reveal the strength of coupling and transfer rates between different coupled excitonic states. The change of the peak amplitude is typically modeled with exponential decays, and the response functions of the systems will include forms resembling Eq. (24), with imaginary $\Xi = -i\gamma$, where γ is the decay rate constant. The resultant 2D spectral function is described in Eq. (28). Here we simulate the measured purely absorptive 2DOS spectrum that is typically used in studies of EET processes,

$$\begin{aligned} \mathbb{S}_{abs}(\omega_t, T, \omega_\tau) = & R_{NR}(\omega_t, \omega_\tau) e^{-\gamma T} \tilde{\mathcal{E}}_1(\omega_\tau - \omega_L) \tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L + i\gamma) \tilde{\mathcal{E}}_3(\omega_t - \omega_L + i\gamma) \tilde{E}_{LO}^*(\omega_t) \\ & + R_R^*(\omega_t, -\omega_\tau) e^{-\gamma T} \tilde{\mathcal{E}}_1(\omega_\tau - \omega_L) \tilde{\mathcal{E}}_2^*(\omega_\tau - \omega_L - i\gamma) \tilde{\mathcal{E}}_3^*(\omega_t - \omega_L + i\gamma) \tilde{E}_{LO}(\omega_t). \end{aligned} \quad (36)$$

In this simulation, we consider the same parameters as in Sec. IV A with both homogeneous and inhomogeneous linewidths of 0.2 eV. Three laser pulses having a duration of 20 fs are used to excite the system resonantly. The population time T of 100 fs is significantly larger than the pulse durations. We consider two cases here. In the first case, the decay time is of the similar order as the pulse temporal width and the second case for the decay time scale is much longer than the pulse duration. In the first case, we assume a decay rate $\gamma = 0.1$ eV (corresponding to a lifetime of 40 fs) in the 2D spectral response

function. Figure 5 illustrates the resultant purely absorptive 2DOS spectra.

Figure 5 is presented in a similar fashion to Fig. 2. Figure 5(a) presents the real part of the purely absorptive 2DOS spectrum obtained with impulsive pulses. Figure 5(b) presents the real part of the purely absorptive 2DOS spectrum as calculated from Eq. (36), while Fig. 5(c) presents the real part of the 2DOS spectrum as calculated using the STI approach. It is clear that apart from noise from the numerical calculations, the spectra are identical. Figure 5(d) presents the real part of

FIG. 5. Simulation results of purely absorptive 2D spectra for the population transfer response function. Figure 5(a) is the purely absorptive 2D spectrum obtained using semi-impulsive pulses. Figure 5(b) is obtained using Eq. (36) with the multiplication scheme presented. Figure 5(c) is calculated using the STI approach. Figure 5(d) is the purely absorptive 2DOS spectrum without population decay calculated using Eq. (23) and shown for comparison purpose. All 2D spectra are normalized to the maxima.

the 2DOS calculated from applying the simple expression of Eq. (23). The obvious difference is that the simple expression of Eq. (23) results in a narrower peakshape than the actual peakshape. This can be understood by looking at the expression of Eq. (25). The two integrals that give rise to the pulse spectra with imaginary frequency shift can be viewed as Fourier transforms over the pulse envelope multiplied by the exponential decay $e^{-\gamma T}$. The resultant convolution introduces complex valued pulse spectra which upon the application of Eq. (36) mixes the dispersive part of the 2D spectral response function with the purely absorptive portions to give a “broadened” 2D peakshape [Fig. 5(b)] compared to Fig. 5(d). In the case above,

the decaying lifetime is in a similar order as the pulse durations, and the effects of the finite pulse width are apparent. We now consider the case where the population transfer lifetime is long compared to the pulse widths. In this case, we let the lifetime be 400 fs ($\gamma = 1/400 \text{ fs}^{-1}$) and the results are shown in Fig. 6.

The scheme of Fig. 6 follows that of Fig. 5. Figure 6(a) presents the real part of the purely absorptive 2DOS spectrum obtained with impulsive pulses. Figure 6(b) presents the real part of the 2DOS spectrum as calculated from Eq. (36), while Fig. 6(c) presents the real part of the 2DOS spectrum as calculated using the STI approach for comparison. Figure 6(d)

FIG. 6. Simulation results for slow decaying response function. All notations are the same as Fig. 5.

presents the real part of the 2DOS spectrum calculated from applying Eq. (23). In this case, Fig. 6(d) is similar to the spectra in Figs. 6(b) and 6(c).

Therefore, by comparing the simulations in Figs. 5 and 6, we can conclude that the finite pulse effect is significant and apparent in the regime where the population decay time scale is of the same order as the pulse durations. If the decay rate is slow compared to the excitation pulse duration, the approximation of Eq. (19) applies.

V. CONCLUSION

In this paper, we derive simplified expressions for 2DOS spectra that incorporate effects of finite pulse durations with arbitrary excitation pulse spectral profile. Compared to the standard triple integral approach, the simplified expressions are computationally less intensive. The expressions can be reduced to one integral for arbitrary t_2 -dependent 2D spectral response functions with analytical Gaussian shaped excitation pulses. For certain cases, the expressions can be reduced to the simple product of the 2D spectral response function $R(\omega_3, T, \omega_1)$ with arbitrary excitation pulse spectra. These cases include t_2 -independent 2D spectral response functions, quantum beat systems, and population evolving dynamics. For 2D spectral response functions that vary slowly with t_2 , the expression of Eq. (19) is a good approximation. We performed simulations to verify that the simplified expressions are indeed equivalent to the standard triple integral approach. We note that although in our simulations we used Gaussian pulse spectra, the expressions are applicable for arbitrary pulse spectra, as is the case for a realistic experiment. There are recent studies that consider analytical expressions for 2D spectra that incorporate pulse shapes of known functional forms.^{24,25} In the expressions we develop here, the pulse spectra can be arbitrary functions or simply the experimental pulse spectra that can be easily measured in an experiment. Our current work therefore is complementary to and a generalization of these previous studies.

The results of the presented work should be useful for the 2DOS community. With efficient procedures to simulate the 2DOS spectra and the resulting knowledge of how the finite pulse duration can alter 2DOS spectra, this opens up the possibility of recovering the original 2D spectral response functions of the material of interest by the deconvolution of the experimental 2DOS spectra. Trial 2D spectral response functions can be multiplied with the measured spectra of the pulses used, according to the appropriate expressions derived in this article, to generate numerical 2DOS spectra which can then be compared with the experimentally measured 2DOS spectra. An optimal search loop can then be formulated to arrive at a “best fit” 2D spectral response function.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for further simulations of (I) the detailed expressions for Eq. (6), (II) 2DOS spectra with asymmetric pulse spectra, and (III) 2DOS spectra of response functions with quantum beat at various population time T .

ACKNOWLEDGMENTS

The work is supported by grants from the Singapore Ministry of Education Academic Research Fund (Tier 2 MOE2015-T2-1-039) and the Singaporean-German S&T Cooperation Researcher Mobility Scheme (No. SGP-PROG2-018). H.-S.T. would like to acknowledge M. D. Fayer for posing the question phrased in Eq. (7) twelve years ago. That question eventually led to the subject of this article.

APPENDIX: HETERODYNE DETECTION

In a typical 2DOS experiment, after three interactions with the excitation laser pulses, the generated third order polarization results in an electric field emitting along the phase matching direction,

$$S(t, T, \tau) \propto -iP^{(3)}(t, T, \tau). \quad (\text{A1})$$

To retrieve the phase and time dependence of this emitted field $S(t, T, \tau)$, we need to perform a heterodyne detection using a local oscillator which is either an extra pulse in a BOXCAR geometry or the probe pulse in a pump-probe geometry. The local oscillator and emitted signal are detected in the frequency domain in a spectrometer using a square-law detector. Hence, the detected signal at the spectrometer is expressed as

$$\begin{aligned} & \left| \int_{-\infty}^{+\infty} dt e^{i\omega_t t} [S(t, T, \tau) + E_{LO}(t)] \right|^2 \\ &= |\tilde{E}_{LO}(\omega_t)|^2 + 2\Re[S(\omega_t, T, \tau) \tilde{E}_{LO}^*(\omega_t)] + |S(\omega_t, T, \tau)|^2. \end{aligned} \quad (\text{A2})$$

The last term of Eq. (A2) $|S(\omega_t, T, \tau)|^2$ is the intensity spectrum of the emitted field which is negligible compared to the other terms and is typically dropped. The first term $|\tilde{E}_{LO}(\omega_t)|^2$ is the intensity spectrum of the local oscillator. The heterodyne detected spectrum $\mathbb{S}(\omega_t, T, \tau)$ is the second term of Eq. (A2),

$$\begin{aligned} \mathbb{S}(\omega_t, T, \tau) &= 2\Re[S(\omega_t, T, \tau) \tilde{E}_{LO}^*(\omega_t)] \\ &= S(\omega_t, T, \tau) \tilde{E}_{LO}^*(\omega_t) + S^*(\omega_t, T, \tau) \tilde{E}_{LO}(\omega_t). \end{aligned} \quad (\text{A3})$$

To obtain the 2DOS spectrum $\mathbb{S}(\omega_t, T, \omega_\tau)$, discrete Fourier transformation is performed along τ ,

$$\begin{aligned} \mathbb{S}(\omega_t, T, \omega_\tau) &= \int_{-\infty}^{+\infty} d\tau e^{i\omega_\tau \tau} [S(\omega_t, T, \tau) \tilde{E}_{LO}^*(\omega_t) \\ &\quad + S^*(\omega_t, T, \tau) \tilde{E}_{LO}(\omega_t)] \\ &= S(\omega_t, T, \omega_\tau) \tilde{E}_{LO}^*(\omega_t) \\ &\quad + S^*(\omega_t, T, -\omega_\tau) \tilde{E}_{LO}(\omega_t). \end{aligned} \quad (\text{A4})$$

According to Eq. (A4), the heterodyne detected 2DOS spectrum consists of two terms. The first term $S(\omega_t, T, \omega_\tau) \tilde{E}_{LO}^*(\omega_t)$ is the conventional term with rephasing (echo) signal appearing at the $(\omega_t, \omega_\tau) = (+, -)$ quadrant and non-rephasing (anti-echo) signal at the $(\omega_t, \omega_\tau) = (+, +)$ quadrant. The

second term $S^*(\omega_t, T, -\omega_\tau) \tilde{E}_{LO}(\omega_t)$ is the complex conjugation and mirror image of the first term over the $\omega_\tau = 0$ axis.

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