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Purely absorptive fifth-order three-dimensional electronic spectroscopy

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We demonstrate a method to measure a purely absorptive fifth-order three-dimensional (3D) electronic spectrum based on a pulse-shaper assisted pump-probe beam geometry setup. The 3D spectra are measured as a function of two independently controlled population times. With phase-cycling and data processing, purely absorptive 3D spectra of chlorophyll *a* are obtained. © 2012 Optical Society of America

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Third-order two-dimensional (2D) electronic and infrared (IR) spectroscopy has given us valuable insights on the dynamics of molecules [1,2]. Fifth-order three-dimensional (3D) spectroscopy in turn provides us with more information on the behavior of the molecules such as recovering three point frequency fluctuation correlation functions (3FFCFs) [3,4], measuring high lying excited states [5,6], and uncovering hidden couplings [7]. In 3D spectroscopy, the molecular system interacts with five pulses, as shown in Fig. 1(a). The emitted signal is a convolution of the fifth-order nonlinear response function of the molecular system and the interacting light fields. The fifth-order response functions can be expressed using double-sided Feynman diagrams (DSFDs) that show the possible coherence-transfer pathways [3]. The processes of interest are depicted in Fig. 1(b). The time periods t_1 , t_3 , and t_5 are known as the coherence time periods, while the time periods of t_2 and t_4 are termed the population time periods. Due to the complex nature of the experiments, there are only a few experimental demonstrations of fifth-order 3D spectroscopy up until now [5–7]. Zanni's work in the IR and Engel's work in the visible uses four pulses (including the local oscillator), 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 two and three to achieve five interactions is that the purely absorptive peaks cannot be obtained. In the work by Hamm [6], using a noncollinear phase-matching geometry, six pulses (including the local oscillator) are independently controlled using computer-controlled mechanical translational stages. All four processes described by the four DSFDs of Fig. 1(b) are measured and compiled to give a purely absorptive 3D IR vibrational spectrum.

We present here, to the best of our knowledge, the first 3D electronic spectroscopy (3DES) demonstration that measures a purely absorptive 3D peakshape. Furthermore, the 3D electronic absorptive spectra can be measured with controllable population times t_2 and t_4 . The experiment was performed in a pump-probe beam geometry. Phase cycling was then used to simultaneously measure the processes of Fig. 1. The data were subsequently compiled to retrieve the purely absorptive spectra.

In the partially collinear beam geometry [Fig. 1(a)], the four pump pulses are generated by an acousto-optic programmable dispersive filter (AOPDF) pulse shaper that varies the delays t_1 , t_2 , and t_3 and relative phases between the first three pulses and the fourth pulse, $\phi_{14} = \phi_1 - \phi_4$, $\phi_{24} = \phi_2 - \phi_4$ and $\phi_{34} = \phi_3 - \phi_4$. One advantage of using a pulse-shaping assisted setup is that very high interpulse phase stability is inherently achieved. This advantage has been routinely exploited in 2D spectroscopy [8–10], and avoids the need for active phase stabilization or a data-processing phasing step [6]. This interpulse phase stability is particularly desirable in the visible due to shorter wavelengths compared to the IR. The pump pulses provide the first four interactions with the system. The probe pulse, which provides the fifth interaction, then itself heterodyne detects the fifth-order signal that is emitted in the same direction. The frequency-resolved (ω_5 axis) heterodyne detected signal $\tilde{S}$ consists of the processes depicted in Fig. 1(b), as well as other processes. Each of these signals $\tilde{s}(\alpha, \beta, \gamma; t_1, t_3, \omega_5; t_2, t_4)$ are tagged with different phase signatures as shown in Eq. (1), due to them having pulse-phase-dependent interactions from different processes

$$\tilde{S}(\phi_{14}, \phi_{24}, \phi_{34}; t_1, t_3, \omega_5; t_2, t_4) \propto \sum_{\alpha\beta\gamma} \tilde{s}(\alpha, \beta, \gamma; t_1, t_3, \omega_5; t_2, t_4) \times \exp(+i\alpha\phi_{14} + i\beta\phi_{24} + i\gamma\phi_{34}), \quad (1)$$

Fig. 1. (Color online) (a) Pulse sequence for a fifth-order 3D spectroscopy experiment. (b) Double-sided Feynman diagrams of the processes necessary to obtain a purely absorptive 3D spectrum.

where α, β, γ represent the transition dipole operator interactions with the density matrix for the first, second, and third pulse interaction, respectively, and can be quantified by the number of arrows pointing to the right minus arrows pointing to the left in the DSFDs of Fig. 1(b). Phase-cycling enables the selection of specific terms from the summation in Eq. (1), while suppressing the undesirable terms [11,12].

The experimental setup is the same as that used to perform 2D electronic spectroscopy (2DES) in a previous paper and the schematic is presented in Fig. 2. Only the computer-controlled pulse-shaping routines and data-collection program were modified to change from 2DES into 3DES. We note that this setup allows us to independently control time delay t_2 using the AOPDF and t_4 using a computer-controlled mechanical delay stage. Pulses centered at 800 nm [0.85 mJ at 1 kHz, 40 fs full-width at half-maximum (FWHM) pulsewidth] from a regenerative amplifier (Legend Elite, Coherent) were used to pump a two-stage home-built optical parametric amplifier to generate near-IR light, which was then frequency doubled to give visible pump light centered at 665 nm, corresponding to the peak absorption wavelength of the Q_y absorption of the sample, chlorophyll a (Chl a) dissolved in methanol (peak optical density of 0.18, absorption maxima at 451 THz with a FWHM bandwidth of 14 THz). A fraction of the amplified fundamental was used to generate the white-light continuum probe beam with a sapphire window. The white-light continuum was chopped at 500 Hz to remove scattered light from the signal. A reference beam was used to normalize any intensity fluctuations in the probe beam. The AOPDF was used to compress the 665 nm pump light, to give a pulse duration FWHM of 50 fs (1.3 times transform limited). The pulse energy of the pump and probe were 350 and 180 nJ, respectively.

The pump light was modulated by the pulse shaper to give a four-pulse train with variable delays and phases needed to perform the presented phase-cycling scheme. Over both coherence period delays t_1 and t_3 , the data were collected in the rotating frame with the reference wavelength set at 715 nm ($\omega_{\text{ref}} = 420$ THz). The resultant detuning frequency $\Delta\omega_{10} = \omega_{10} - \omega_{\text{ref}}$ was 31 THz for the chromophore's peak absorption centered at $\omega_{10} = 451$ THz (665 nm). The delay for both t_1 and t_3 were increased with a step size of 5 fs, over a total delay of 150 fs, which is below the Nyquist limit of 15 fs.

A series of signals $\tilde{S}$ were measured with pulse phases cycled through ϕ_{14}, ϕ_{24} , and ϕ_{34} . In this present experiment for a quasi-two-level system such as the Q_y transition of Chl a , a $2 \times 2 \times 2 \times 1$ phase-cycling scheme was

Fig. 2. (Color online) Schematic of the setup for our 2D and 3D optical spectrometer.

used, where ϕ_{14}, ϕ_{24} , and ϕ_{34} were cycled through $\phi = 0$ and π . The details and theoretical explanation of the choice of $2 \times 2 \times 2 \times 1$ phase-cycling scheme and data management will be presented in a later paper. Here, only the relevant key points are presented. These signals $\tilde{S}$ are then linearly combined, as prescribed by the phase-cycling scheme selection process [12] to obtain a signal,

$$\begin{aligned} \tilde{S}'(t_1, t_3, \omega_5) = & XXXX - \bar{X}XXX - X\bar{X}XX + \bar{X}\bar{X}XX \\ & - XX\bar{X}X + \bar{X}X\bar{X}X + X\bar{X}\bar{X}X - \bar{X}\bar{X}\bar{X}X, \end{aligned} \quad (2)$$

where X and $\bar{X}$ denote pulses with phases 0 and π , respectively. The strings of letters denote the interpulse phase-dependent signals [for instance, $X\bar{X}\bar{X}X$ denotes $S(\phi_{14} = 0, \phi_{24} = \pi, \phi_{34} = \pi; \dots)$]. After Fourier transforming the phase-cycled signal $\tilde{S}'(t_1, t_3, \omega_5)$ with respect to both t_1 and t_3 , a 3D spectrum is obtained. The measured spectrum is dictated by the bandwidth of the interaction pulses. Shown in Fig. 3(a) is the real part of the measured 3D spectrum at $t_2 = 200$ fs and $t_4 = 400$ fs. The spectrum has four major features located at the separate quadrants on the plane of $\omega_5 = \omega_{10} = 451$ THz. The four features are labeled in Fig. 3(a). Feature I is centered at $(\omega_1 = \Delta\omega_{10}, \omega_3 = \Delta\omega_{10}, \omega_5 = \omega_{10})$ and contains the signal from R_1 and R_4^* . This is due to the aliasing of signals, where the $2 \times 2 \times 2 \times 1$ phase-cycling scheme cannot differentiate between signals from the two processes. Feature II is centered at $(-\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$ and contains signals from R_2 and R_3^* . Feature III is centered at

Fig. 3. (Color online) (a) Isosurfaces of a 3D spectrum obtained using a $2 \times 2 \times 2 \times 1$ phase-cycling scheme. Positive and negative amplitudes in red and blue, respectively (negative amplitudes enhanced by $\times 2$ for visibility). (b) 3D spectrum containing only purely absorptive peakshapes obtained after data processing of the spectrum in Fig. 3(a).

Fig. 4. (Color online) Isosurfaces of purely absorptive 3D spectrum of chlorophyll *a* Q_y transition at waiting times (a) $t_2 = 200$ fs and $t_4 = 400$ fs, (b) $t_2 = 500$ fs and $t_4 = 1500$ fs. 2D projections are depicted on the faces of the grid cube.

$(\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$ and contains signals from R_3 and R_2^* , and Feature IV, centered on $(-\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$, contains signals from R_4 and R_1^* . The peaks are situated at $\omega_{1,3} = \pm\Delta\omega_{10}$ due to the experiment being performed in the rotating frame, as explained earlier. R_1 , R_2 , R_3 , and R_4 contain both absorptive and dispersive features. In order to retrieve the purely absorptive signal, which should contain all four processes R_1 , R_2 , R_3 , and R_4 , we processed the data as follows: the mirror image of the 3D spectrum about the $\omega_1 = 0$ plane is taken and added to the original 3D spectrum (Using the mirror image about $\omega_3 = 0$ will achieve the same result.) The resultant real part of the summed spectrum, depicted in Fig. 3(b), will only have purely absorptive 3D peaks. The four peaks in Fig. 3(b) are exactly the same and only one of them suffices to be presented as a 3D purely absorptive spectrum. Therefore in Fig. 4(a), we depict, in detail, the peak from the $(+\omega_1, +\omega_3, +\omega_5)$ -octant of Fig. 3(b). Projections of the 3D peak to the 2D planes are also depicted in Fig. 4(a). The 2D projections can be, within approximation, viewed as 2D spectra [3]. Undergoing spectral diffusion, the peakshape of a 2D spectrum at increasing population time progresses from an elongation along the diagonal to become a more rounded feature [1,2]. This trend is clearly seen when comparing the 2D projections on the (ω_1, ω_3) , (ω_3, ω_5) , and (ω_1, ω_5) planes in Fig. 4(a), which can be interpreted as 2D spectra with population times of $t_2 = 200$ fs, $t_4 = 400$ fs, and $t_2 + t_4 = 600$ fs, respectively. We further

demonstrate that with this experimental setup, 3D electronic spectra can be measured with independently controllable population times t_2 and t_4 . Figure 4(b) depicts the purely absorptive 3D spectra at $t_2 = 500$ fs and $t_4 = 1500$ fs. The 2D projections are in general agreement with the spectral diffusion of Chl *a* measured in a separate work [13]. Third-order cascades [2] should not contribute significantly to the measured signal with the sample optical density and pulse energies used in our experiments [7].

In summary, we have performed the first example of a fifth-order 3DES with an absorptive peakshape and with independent control of the two population times. These capabilities will be important for studies measuring 3FFCFs. The $2 \times 2 \times 2 \times 1$ phase-cycling scheme and the data processing used is shown to be able to obtain the purely absorptive spectrum of a two-level system such as the Q_y transition of Chl *a*. It is possible to apply further data processing to obtain separate 3D spectra of R_1 , R_2 , R_3 , and R_4 processes. This, together with the full theoretical details and discussion of the phase-cycling schemes for 3D spectroscopy, will be presented in a later publication. This setup also has the advantage that no mechanical components need to be changed when switching from a 2D to a 3D spectrometer.

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