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Two-dimensional fluorescence-detected coherent spectroscopy with absolute phasing by confocal imaging of a dynamic grating and 27-step phase-cycling

Arijit K. De,1,2,a) Daniele Monahan,2 Jahan M. Dawlaty,2,b) and Graham R. Fleming1,2,c)  
1Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94702, USA  
2Department of Chemistry, University of California at Berkeley, Berkeley, California 94702, USA  
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We present a novel experimental scheme for two-dimensional fluorescence-detected coherent spectroscopy (2D-FDCS) using a non-collinear beam geometry with the aid of “confocal imaging” of dynamic (population) grating and 27-step phase-cycling to extract the signal. This arrangement obviates the need for distinct experimental designs for previously developed transmission detected non-collinear two-dimensional coherent spectroscopy (2D-CS) and collinear 2D-FDCS. We also describe a novel method for absolute phasing of the 2D spectrum. We apply this method to record 2D spectra of a fluorescent dye in solution at room temperature and observe “spectral diffusion.”  

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I. INTRODUCTION

Two-dimensional coherent spectroscopy (2D-CS) at optical frequencies1–7 is a third order nonlinear optical spectroscopy8 that has enabled us recording time-resolved correlation spectra between absorption and emission frequencies. Analogous to two-dimensional nuclear magnetic resonance (2D-NMR) spectroscopy,2 2D-CS disentangles population and coherence dynamics, but with unprecedented time resolution compared with 2D-NMR; while the diagonal features of a 2D spectrum reveals ultrafast dephasing (and energy relaxation) dynamics, the cross peaks elucidates ultrafast dynamics of coupling (and energy transfer) between excited states.6–8 Over a decade, 2D-CS has evolved as a powerful tool to explore various aspects of ultrafast dynamics in condensed phase, from studying solvation dynamics to probing coupling in multi-chromophore molecular aggregates/complexes (e.g., probing coherent coupling9 and long-lived quantum beats11–13 within photosynthetic pigment-protein complexes). In 2DCS, interaction of a bulk sample with three optical fields from three non-collinear phase-stable pulses generates a time-dependent macroscopic third-order ($\chi^{(3)}$) polarization which emits a signal field in a background-free direction by virtue of momentum conservation of optical fields; this is known as phase-matching. The phase-stability at optical frequencies is maintained by a variety of techniques, e.g., (i) interferometer with (i) passive phase-locking using diffractive optics,2–4 (ii) active phase-locking using feedback electronics,14 and (iii) inherently phase-stabilized geometry15 and (2) (phase-only) pulse-shaping.16,17

However, in a bulk sample ultrafast (coherent) dynamics is often obscured by inhomogeneous dephasing due to averaging over a large ensemble of molecules or molecular complexes.17 Thus one of the remaining challenges in this field is to enhance the sensitivity of 2D-CS to small ensemble of molecules, ideally to single molecule (or molecular complex) level.18,19 Note that despite the pioneering work by van Hulst and co-workers,20–22 2D-CS of isolated single molecules has not been demonstrated yet. Although detection of isolated (immobilized) single molecules by absorption was demonstrated both at low temperature23 and quite recently at room temperature,24–26 the sensitivity is greatly enhanced by fluorescence detection27 which has been a standard tool for single molecule spectroscopy.28 Phase-matching, being a macroscopic phenomenon, does not apply in a small ensemble of molecules.8 This necessitates the extension of 2D-CS to two-dimensional fluorescence-detected coherent spectroscopy (2D-FDCS), pioneered by Warren and co-workers,28–31 In 2D-FDCS (incoherent) fluorescence is recorded as a function of time delay between four collinear pulses. Specific third-order ($\chi^{(3)}$) signal is retrieved either by cycling through different relative phase-combinations among phase-stable pulses known as phase-cycling29–31 or by synchronous detection with respect to a reference phase-modulation in an otherwise phase-unstable interferometric set-up as developed by Marcus and co-workers.32 The implementation of 2D-FDCS hinges on generation of collinear train of pulses with controllable delay and phase which requires instrumentation different from that in 2D-CS with non-collinear beam geometry; this is either met by spectral phase and amplitude shaping of a laser pulse with a pulse-shaper29–31 or using beam-splitters and delay-stages with Mach–Zehnder interferometers.32

In this paper, we demonstrate 2D-FDCS of a fluorescent dye in solution at room temperature using conventional non-collinear beam geometry employed for phase matching in 2D-CS; we discuss how to isolate the pathway-specific signal with a combination of confocal imaging of dynamic
(population) grating and 27-step phase-cycling; this allows us to use a single set-up to alternate between the two detection methods avoiding the need of having multiple experimental arrangements. We also present a new method for absolute phasing of the 2D spectrum. We compare and contrast the working principles of CS and FDCS, considering first the linear (1D) and then nonlinear (2D) cases, providing a unified approach.

II. THEORETICAL DISCUSSION

A. Linear (1D) FDCS

Since the first demonstration of linear FDCS with phase-locked pulses,33-35 also known as “phase-locked spontaneous light emission” (PLSLE),36 it has been implemented in numerous applications, e.g., control of photo-ionization37 and photo-fragmentation,38 quantum state holography and reconstruction,39-41 interference of vibrational wave-packets in isolated single-molecules,41 fluorophore discrimination,42 etc. For a two-level system, a comparison of the double-sided Feynman diagrams for linear absorption with that for linear FDCS is shown in Figure 1. A wave-packet interferometry (WPI) description was formulated34,35,40,43 for the interference between two (vibrational) wave-packets upon impulsive electronic excitation.

B. Nonlinear 2D-FDCS

Nonlinear 2D-FDCS29-32 has been implemented to probe conformation of fluorescent dye aggregates,44,45 spatially mapping nanoscale coherence.46 For a two-level system, a comparison of the double-sided Feynman diagrams for 2D-CS with that for 2D-FDCS is shown in Figure 2.

In 2D-FDCS four collinear phase-stable pulses modulate the excited state population which is proportional to the fluorescence intensity. The diagonal element of the density matrix may be written as

\[
\rho_{ii}^{(3+1)}(t) = \int \int dt_4 dt_3 dt_2 dt_1 Q^{(3+1)}(t_4, t_3, t_2, t_1) E(t - t_4) \times E(t - t_4 - t_3) E(t - t_4 - t_3 - t_2) \times E(t - t_4 - t_3 - t_2 - t_1),
\]

(1)

where \(Q^{(3+1)}\) is the correlation function which contains all possible pathways. For the rephasing pathway it may be written as (with \(\omega_{ge} = 0\))

\[
Q^{(3+1)}(t_1, t_2, t_3, t_4) \propto |\mu_{ge}|^4 e^{-i\omega_{et}t_1} e^{-i\omega_{et}t_2} e^{-i\omega_{et}t_3} e^{-i\omega_{et}t_4},
\]

(2)

where phenomenological decay constants are included to account for pure dephasing (\(\Gamma_k\)) and population relaxation (\(\Gamma_p\)). The signal phase for the rephasing \(Q^{(3+1)}\) pathway (for collinear geometry) in Figure 2 is

\[
e^{-i\phi_0} e^{i(\phi_2 + \phi_3 - \phi_1)} = e^{-i(\omega_0(t_1) - k\tau_1)} e^{i(\omega_0(t_2) - k\tau_2)}
\]

\[
\times \rho_{ii}^{(3+1)}(t_4) e^{-i(\omega_0(t_3) - k\tau_3)} e^{-i(\omega_0(t_4) - k\tau_4)} = e^{i(\omega_0(t_2) - \tau_1)}.
\]

(3)

Here \(\omega_0\) is the carrier frequency of the driving field and k’s are the wave-vectors. Unlike 2D-CS where only one coherence time (\(\tau_1\)) is scanned (Figure 2), in 2D-FDCS both coherence times (\(\tau_1\) and \(\tau_2\)) are scanned for a given waiting time (T) and for each \(\tau_1, \tau_2\) combination phase-cycling is performed to isolate the rephasing or non-rephasing signal with phase \(\pm(\phi_1 - \phi_2 + \phi_3 - \phi_4)\) or \(\pm(\phi_1 + \phi_2 + \phi_3 + \phi_4)\). Fourier transform of the time-domain two-dimensional
fluorescence interferogram along both \( \tau_1 \) and \( \tau_2 \) axes generates the 2D spectrum. An equivalent explanation based on nonlinear WPI was formulated when the interference between a third-order WP and a first-order WP is considered.\(^{38,49}\)

Note that (1) Since the observable is the excited state population, the role of the last pulse is just to convert the third-order coherence into a population; so this is still equivalent to a third order or \( \chi^{(3)} \) process and we denote it as \( \chi^{(3+1)} \) process to distinguish it from other fourth order or \( \chi^{(4)} \) processes. (2) Although the final population has a time dependence (Eq. (2)), we do not measure this time dependence of the excited state population; i.e., we measure the time-integrated or steady-state fluorescence instead of fluorescence life-time. (3) Any experiment probing excited state population, e.g., photoemission electron microscopy,\(^{46}\) works in the same spirit as 2D-FDCS.

### III. EXPERIMENTAL IMPLEMENTATION

Figure 3 shows a schematic of the experimental set-up. The expanded beam from a Ti:sapphire regenerative amplifier (RegA 9000, Coherent), producing nearly transform-limited pulses (~55 fs FWHM) at 250 kHz centered on 800 nm, was guided to a phase-only pulse-shaper, originally designed by Nelson and co-workers\(^{17,50}\) and described in Ref. \(^{51}\). Briefly, the 4f zero-dispersion pulse-shaper utilizes a liquid crystal on silicon spatial light modulator (LCOS-SLM) with rectangular array of 792 \( \times \) 600 pixels (X10468, Hamamatsu) kept in the Fourier plane where the spectral components of the laser pulse were horizontally spread. Only the first-order vertically diffracted beam from the LCOS-SLM was used for the experiment to remove the higher order satellite pulses. To generate different output beams/pulses from a single expanded input beam/pulse, the vertical array of 600 pixels was divided into several domains; within a given domain, application of a linear spectral phase with a partially rotating frame across the horizontal array of 792 pixels resulted in translation of the corresponding pulse in time. Thus the shaper can manipulate time delay and phase of each pulse. An additional spatial mask was placed at the output to generate a circular beam shape from the input rectangular beam. Note that, instead of the boxcar geometry usually employed for 2D photon-echo set-up, we chose the output beams vertically aligned for horizontal polarization (explained in Sec. IV A).

3,3’-Diethylthiatricarbocyanine iodide (DTTCI) dye was purchased from Exciton and used without further purification; a solution of the dye in 1:1 ethanol:ethylene-glycol mixture was percolated through a 1 mm path-length flow-cell (Starna) via a peristaltic pump to avoid photo-bleaching; in addition, we used a mechanical chopper running at 500 Hz as “bunched-pulse excitation” was shown to reduce photo-bleaching as well as photo-thermal effects.\(^{52,53}\) The optical density of the sample was <0.3 at 800 nm. The output beams from the pulse-shaper were focused on the sample using a long focal length lens (\( f = 100 \) cm). The forward scattered fluorescence (“trans-fluorescence”) was collected with a 0.5 NA aspheric lens (\( f_1 = 4 \) cm) and the collimated fluorescence beam was imaged, with another lens (\( f_2 = 20 \) cm), on the conjugate focal plane where a collapsible iris (or a pinhole, either with 500 \( \mu \)m diameter) was kept for confocal detection. Thus, the optical interference pattern of the shallow-focusing non-collinear beams at the sample was imaged at the confocal plane with \( \times 5 \) magnification (since \( f_2/f_1 = 5 \) ) and the iris (or pinhole) spatially selected a small portion of the interference fringe (Figure 4), thereby enabling us to probe a small sample volume without spatio-temporal averaging (explained later in Sec. IV A). To block the excitation beam, a beam-stop was kept at the Fourier plane of the fluorescence collection optics so that the beam-stop does not impart any shadow on the image other than a small reduction of the fluorescence intensity. A long-pass emission filter (OD > 6.0 for \( \leq 825 \) nm, custom-made, CVI-MellesGriot) was used before sending the fluorescence to a photo-multiplier (H7422P-50, Hamamatsu) with photon counting modules (C9744 and C8855-01, Hamamatsu). We used cage-structures for mechanical stability of the confocal system and light-tight lens tubing before the PMT for background rejection and enhanced sensitivity. All optical and opto-mechanical components were purchased from Thorlabs. The SLM and the PMT were interfaced with a personal computer where data acquisition was performed by LabView programming while for data processing and plotting we used Matlab programming.

Note that (1) Here we used a phase-only pulse-shaper to maintain phase-stability and perform phase-cycling, but the same can be met with any phase-stable non-collinear set-up where phase-cycling can be performed by delaying pulses by a fraction of the wavelength, e.g., by tilting a Brewster window.\(^{54}\) (2) Instead of shallow focusing with vertical spatial mask, tighter focusing with boxcar mask can also be employed as long as the fluorescence interferogram is perfectly imaged and signal from only one single period of the interferogram is recorded.
IV. RESULTS AND DISCUSSION

A. Confocal imaging of transient grating

We see from Eq. (3) that for perfectly collinear pulses, the relative phase varies only temporally (depends only on $\tau$’s) but does not vary spatially (does not depend on $r$) and as $\tau$’s are scanned a 2D temporal fluorescence interferogram is resulted. This is precisely the reason for using collinear pulses in linear33–35 and nonlinear29–32 FDCS experiments.

If two pulses interfere non-collinearly at the sample, for a given time delay between them the relative phase changes periodically across the sample as 

$$e^{i\Delta \phi_{12}} \propto e^{i(k_1-k_2)r}.$$  

(4)

Considering the projection of this interference pattern across the beam propagation (say, x-axis), the condition for having fringe maxima is given by

$$(k_1 - k_2) \cdot x = 2k \sin \theta = \frac{4\pi \chi}{\lambda} \sin \theta \equiv 2\pi n,$$  

(5)

where $\lambda$ is the wavelength, $\theta$ is the angle with respect to the normal of incidence, $n$ is an integer, and we have assumed $|k_1| = |k_2| = k$. Thus the spatial period of the interference pattern is

$$d = \frac{\lambda}{2 \sin \theta}.$$  

(6)

Thus the relative phase of two pulses varies temporally as well as spatially (depends on both $\tau$ and $r$). This spatial phase variation periodically produces modulation of the population in ground and excited states across the sample, resulting in a dynamic population grating.35–37 In fact, phase matching in 2D-CS (or “transient-grating pump-probe” spectroscopy) may be viewed as a scattering of the third pulse from this population grating encrypted by the first two pulses where the crossing-angle between pulses controls the phase-matching bandwidth;58, 59 this is why non-collinear pulses are used in regular 2D-CS. However, due to this very spatio-temporal coupling, only the spatial locations of crests and troughs change when $\tau$ is scanned and the total fluorescence intensity (spatially integrated over the population grating) does not change. Thus, no fluorescence modulation results while scanning $\tau$; in other words, the dynamic population grating washes away the temporal fluorescence interferogram.

In our experiment, the shallow focusing (approaching the collinear limit with crossing angle $\sim$0.1 degree) results in visibly six interference lobes which were magnified and imaged at the conjugate focal plane. The fringe-spacing (for the magnified image) for two outer beams (1 and 4) was slightly above 0.5 mm (measured with the CCD camera); an iris of 0.5 mm diameter selects only a single period of this pattern allowing us to probe only a portion of the excitation volume and to avoid spatial averaging. For two-pulse interferogram, this is depicted in Figure 5 where we recorded the two-pulse fluorescence interferogram while gradually opening the iris; the interferogram loses resolution because of spatial averaging. Note that the spatial interferogram along the beam propagation direction is negligible for a small angle focusing; also confocal detection naturally takes care of axial resolution. We deliberately used a vertical mask (instead of a boxcar mask) so that the polarizations of different beams remain parallel at

FIG. 5. The effect of confocal iris diameter on two-pulse fluorescence (from DTTCI in ethanol/ethylene-glycol mixture) interferogram; the oscillations wash out (due to spatial averaging over dynamic grating) as the diameter is increased from 0.5 mm (red) through 1.5 mm (green) to 2.5 mm (blue). One pulse was delayed with partially rotating frame centered on 975 nm in combination with 2-step phase-cycling.
the focus resulting in a simple and easily tractable four beam interference pattern.

**B. Absolute phasing of the 2D spectrum**

Since the 2D spectrum is sensitive to the temporal phase of the signal, temporal phase distortions must be corrected. In 2D-CS this is usually done by comparing the projection of the 2D spectra on the emission axis with pump-probe spectra, known as projection slice theorem. Since the signal phase is proportional to the relative of relative phases (Eq. (3)), i.e., between 1 and 2 ($\varphi_2 - \varphi_1$) and 3 and 4 ($\varphi_4 - \varphi_3$), one may directly measure the relative phases by recording the temporal interferogram (field autocorrelation) with a pinhole or by imaging the spatio-temporal interferogram at the focal plane with a camera. In a similar spirit, we set the phasing by adjusting the oscillation phase in the fluorescence interferogram (fluorescence-detected field autocorrelation); this is shown in Figure 6 where the each interference fringe is maximized at zero coherence time and superimposed. Thus no further phase adjustment is required.

**C. Pathway selection by phase-cycling**

In phase-cycling with a sequence of $n$ pulses, the phase of $i$th pulse ($\varphi_i$) is varied from 0 by increment of $2\pi/n_i$ (i.e., $\varphi_1 = 0, 2\pi/n_1, 2\pi/n_1, 3\pi/2n_1, \ldots$, $(m_i - 1)\pi/2n_i$) and this is done for all but one pulse (i.e., for $n - 1$ pulses). All possible permutations among $\varphi_i$’s are considered to get a set of phase configurations for a fixed inter-pulse delay; i.e., the total number of configuration would be $M = m_1 \times m_2 \times m_3 \times \ldots \times m_{(n-1)}$ and we denote it as $\text{M-step phase-cycling}$.

For a given phase configuration, the signal phase corresponding a specific dynamical pathway (that we wish to isolate) is calculated and the measured total signal (which has contribution from all pathways) is multiplied by a coefficient equal to the complex conjugate of the specific signal phase; thus the contribution of a specific pathway gets a weight of unity while that of any other unwanted pathway gets a different weight since it has a phase different from the specific signal phase. This is repeated for every phase combination in the set and the signal contributions (i.e., total signal multiplied by the coefficient) are summed over to get a processed signal; thus the contribution of a specific pathway gets a weight equal to the number of phase combinations in the set while that of any other pathway is minimized. The values of $m_i$’s are increased to get a new set of phase configurations and the process is repeated until the signal contributed from every other unwanted pathway gets a zero weight.

### 1. Linear FDCS

To illustrate, let us first consider phase-cycling in linear ($\chi^{(1+1)}$) FDCS. Here $n = 2$ and to begin with we may start with $m_1 = 2$ & $m_2 = 1$; i.e., the phase of the 1st pulse ($\varphi_1$) gets the value 0 and $\pi$ while the phase of 2nd pulse ($\varphi_2$) is set 0. Thus we get a set with two phase configurations corresponding to this $2 \times 1 = 2$-step phase-cycling. We now examine the signal phase ($\varphi_1 - \varphi_2$) corresponding to these two different phase configurations and multiply it with the coefficient. The unwanted signal is contributed by absorption by the first (or second) pulse alone as well as the pump-probe signal (the contribution from scatter is neglected in fluorescence detection), neither of which depends on the relative phase. Thus we record the processed signal as

$$S_{\text{processed}} = (+1) \times S_{\text{total}}^{\varphi_1=0, \varphi_2=0} + (-1) \times S_{\text{total}}^{\varphi_1=\pi, \varphi_2=0}$$

(7)

In our experiment, we varied the center of the rotating frame and compared the Fourier transform of the signal, as shown in Figure 7. The time steps were chosen so as to maintain identical sampling rate (nearly five times the Nyquist condition, i.e., about 11 data points per oscillation period).

### 2. Nonlinear (2D) FDCS

For 2D ($\chi^{(3+1)}$) FDCS $n = 4$ and as before we first implemented a phase-cycle corresponding to $m_1 = m_2 = m_3 = 2$ and $m_4 = 1$, i.e., a $2 \times 2 \times 2 \times 1 = 8$-step phase-cycle. It may be seen that with a 8-step phase cycle we can isolate all $\chi^{(3+1)}$ order pathways where each of the four pulses has perturbed the system only once; however, 8-step phase-cycling cannot separate between rephasing and non-rephasing pathways for which a higher step phase-cycling is required. The signal was processed as

$$S_{\text{processed}} = (+1) \times S_{\text{total}}^{\varphi_1=0, \varphi_2=0, \varphi_3=0, \varphi_4=0} + (-1) \times S_{\text{total}}^{\varphi_1=\pi, \varphi_2=0, \varphi_3=0, \varphi_4=0} + \cdots$$

$$+ (+1) \times S_{\text{total}}^{\varphi_1=\pi, \varphi_2=\pi, \varphi_3=0, \varphi_4=0} + (-1) \times S_{\text{total}}^{\varphi_1=\pi, \varphi_2=\pi, \varphi_3=\pi, \varphi_4=0}$$

(8)
FIG. 7. Linear FDCS: fluorescence (from DTTCI in ethanol/ethylene-glycol mixture) interferogram (top) and real part of the Fourier transform (bottom) when
the center of the reference frame was varied as (left to right): lab-frame, partially rotating-frame centered on 975 nm, 900 nm, and 850 nm, and complete
rotating-frame.

The spectra without phase-cycling and with 8-step phase-cycling are shown in Figure 8; only a zero frequency noise spectrum is recorded without phase-cycling (Figure 8(a)) while 2D spectrum is retrieved with 8-step phase-cycling (Figure 8(b)).

A $3 \times 3 \times 3 \times 1 = 27$-step phase-cycling ($m_1 = m_2 = m_3 = 3$, $m_4 = 1$) can isolate rephasing and non-rephasing pathways. To isolate the rephasing pathway, we processed the signal as

$$S_{\text{processed}} = (+1) \cdot S_{\text{total}}^{\phi_1=0, \phi_2=0, \phi_3=0, \phi_4=0} + (-0.5 + 0.866i) \cdot S_{\text{total}}^{\phi_1=4\pi/3, \phi_2=4\pi/3, \phi_3=2\pi/3, \phi_4=0} + \cdots + (0.5 + 0.866i) \cdot S_{\text{total}}^{\phi_1=4\pi/3, \phi_2=4\pi/3, \phi_3=4\pi/3, \phi_4=0}$$

(9)

In Figure 8, absolute 2D spectra with 27-step phase-cycling are shown; note that the rephasing (Figure 8(c)) and the non-rephasing spectra (Figure 8(d)) appear in different quadrants as expected.

As shown by Warren and co-workers,$^{29–31}$ with a $4 \times 1 \times 4 = 16$-step ($m_1 = m_3 = 4$, $m_2 = 1$) phase-cycling only the $(2 + 1)$-pulse photon-echo (equivalent to 2-pulse photon-echo in 2D-CS) signal ($T = 0$) can be isolated for which a simpler

FIG. 8. Absolute 2D spectrum (at $T = 0$ fs) of DTTCI in ethanol/ethylene-glycol mixture recorded (a) without phase-cycle, (b) with 8-step phase-cycling, and
(c) and (d) with 27-step phase-cycling isolating rephasing (c) and non-rephasing (d) spectra; data were collected with a partially rotating-frame centered on
975 nm and are presented without adjusting the frequency shift after FFT.
FIG. 9. Real, imaginary and absolute parts of the 2D rephasing, non-rephasing and relaxation spectra (at $T = 0$ fs) of DTTCl in ethanol/ethylene-glycol mixture; data were collected with a partially rotating-frame centered on 850 nm with 27-step phase-cycling.

To record the 2D spectrum for a particular waiting time within a reasonable experimental time window, we changed the rotating frame center to 850 nm. The 2D rephasing, non-rephasing, and relaxation or total correlation (i.e., rephasing plus non-rephasing) spectra at zero waiting time are shown in Figure 9. We also collected 2D relaxation spectra at waiting times; as evident from Figure 10, the diagonal elongation observed at early waiting time decays at later times as a result of “spectral diffusion.” This demonstrates that a 27-step phase-cycling is necessary to isolate specific signal pathways (i.e., rephasing vs non-rephasing pathways) as a function of waiting-time. Note that similar 27-step phase-cycling with four collinear pulses (followed by a fifth pulse in a non-collinear pump-probe geometry) have recently been implemented in a fifth-order 3D-CS experiment.

V. CONCLUSIONS AND FUTURE DIRECTION

To conclude, we have described a new method for implementing 2D-FDCS using the standard experimental design for 2D-CS with a non-collinear beam geometry, thus eliminating the requirement of having different types of experimental geometries and allowing facile interchange between the two methods. We have also demonstrated a novel way of absolute phasing of the 2D spectra by superimposing the two-pulse fluorescence interferograms. A comparative discussion on the machinery of linear and nonlinear (2D) CS and FDCS has been presented.

2D-FDCS is advantageous over 2D-CS where phase-matching is difficult, e.g., in a scattering medium (e.g., membrane extract) or in a small ensemble of molecules. An immediate application of the present method would be imaging the entire pattern of the dynamic grating (e.g., with a CCD camera) to perform space-resolved 2D spectroscopy. Extending the present technique with enhanced sensitivity to a smaller...
number of molecules in the probe volume will be of special interest to explore the microscopic detail of ultrafast coherent dynamics involving coupled chromophores.

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