

# **Two-Dimensional Electronic Spectroscopy: A Review**

by

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## LIST OF ACRONYMS

- 2DES: Two Dimensional Electronic Spectroscopy
- TG: Transient Grating
- TA: Transient Absorption
- 3PEPS: Three Pulse Photon Echo Peak Shift
- PE: Photon echo
- 2PE: Two pulse photon echo
- 3PE: Three pulse photon echo
- DO: Diffractive Optic
- LO: Local Oscillator
- ESA: Excited State Absorption
- FR-TG: Frequency Resolved Transient Grating
- FWM: Four Wave Mixing
- SLM: Spatial Light Modulator
- CARS: Coherent Anti-Stokes Raman Spectroscopy
- 2DNMR: Two Dimensional Nuclear Magnetic Resonance
- 2DIR: Two Dimensional Infrared
- L: Lens
- M: Mirror
- SM: Spherical Mirror
- BS: Beam splitter
- T: Tracer
- R: Reference
- MC: Monochromator
- Det: Detector
- RGA: Regenerative Amplifier
- NOPA: Noncollinear Optical Parametric Amplifier
- FROG: Frequency resolved optical gating

## 1. INTRODUCTION

**1.1. Why 2DES?.** Optical spectroscopy is a valuable tool in chemistry and physics that uses light to investigate matter. Through light matter interactions it is possible to observe the energy levels and dynamics of a system [1]. Understanding structural and dynamic information of molecules and their interactions with their environment is especially valuable [2]. Two dimensional electronic spectroscopy (2DES) is an ultrafast, nonlinear optical spectroscopy that is used to observe dynamics through the generation of correlation maps [3–6].

Steady state spectroscopy techniques include absorption and fluorescence spectroscopy. While the broadened lines in these measurements imply dynamics, it can be impossible to tease out the different contributions to this broadening and understand the specific dynamical processes that cause them. There could be many states with different linewidths, or a few states with strong coupling between the states and the surrounding bath; both could indistinguishably contribute to 1D condensed phase spectra [7]. We need techniques to time resolve the dynamics; many such techniques involve multiple light matter interactions and are classified under nonlinear spectroscopy. The lowest order nonlinear technique applicable for a centrosymmetric sample in the electric dipole approximation is third order because second order signal lost due to inversion symmetry [8].

There are a number of other third order, or four wave mixing (FWM), experiments available. Some of these third order measurements include Transient Absorption (TA), sometimes referred to as pump probe, Transient Grating (TG) [9, 10], and Three Pulse Photon Echo Peak Shift (3PEPS). Before 2DES, 3PEPS was a popular technique for measuring “correlation functions” to obtain dynamic information. 3PEPS is capable of separating the timescales of processes contributing to the nonlinear signal. For an ideal 2-level system with a large inhomogeneous broadening [11]. However, for any multi-level system with coupling 3PEPS is limited and cannot unambiguously separate components of the signal.

The response function formalism is frequently used to model nonlinear optical signals and to identify contributing processes. The response function approach uses correlation functions representing the nonlinear material response. Correlation functions contain all



the information about dynamical processes and are at the heart of the response function formalism. 3PEPS, in particular sought to measure this correlation function directly. This technique can be readily extended to generate a 2D spectra, where excitation and emission signal frequencies are correlated, allowing further separation of signal components. By careful control of time delays between pulses, the detection of a photon echo as a function of the first time delay with a fixed time delay and Fourier transforming the “stacked” spectra along the first time delay produces the ‘rephasing’ 2DES spectra [6]. Rephasing 2DES is discussed in more detail in section 1.2.

2DES can be seen as an extension of other third order measurements, including TG. Accessing the same third order nonlinear optical signal, both 2DES and TG measure the same dynamics but the ability to resolve contributions to TG is limited.

Figure 1 provides hints as to why we would want to make 2DES measurements over some of the more common third order techniques, such as TA or TG. The figure has four subplots that contain examples of what the data for 2DES might look like as well as TG spectroscopy and frequency resolved transient grating (FR-TG) spectroscopy. Each type of third order spectroscopy measures information in the nonlinear response but the information available is often limited by the type of measurement and how the signal is detected.

In Figure 1(d), the TG data is shown with respect to a time delay which is called  $t_2$  or T (see Figure 2) where integrating detection techniques have already hidden contributions to the signal. The TG and pump probe signal can be frequency resolved with a spectrometer and CCD. As seen in Figure 1(c) the signal in the FR-TG showing multiple frequency components. The different frequency components contributing to the TG signal decay at different rates, which is hidden in the integrated TG signal. Figure 1(c) is made up of the slices shown in (b) with respect to the same time delay  $t_2$ . This slice of FR-TG data can be obtained by integrating across the frequency axis. A new 2D plot is generated for each set  $t_2$  time delay, whereas the two frequency axis come from the first and third delays. The time corresponding to each  $t_2$  2DES plot is the same time axis for frequency resolved (Figure

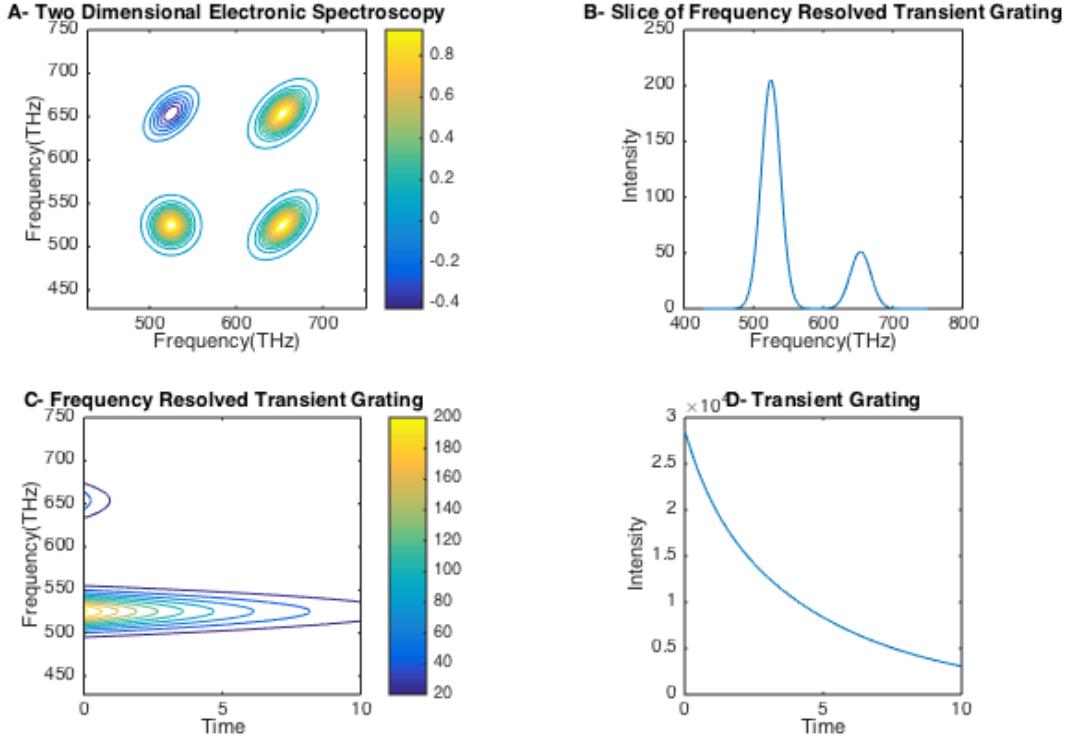


FIGURE 1. Representation of data from (a) a 2DES surface at a particular time  $t_2$ , (b) one slice through frequency resolved transient grating (FR-TG) surface for a given time (the same time as (a)), (c) Stacked together collection of FR-TG slices with increasing time  $t_2$  and (d) TG. Each 2D plot is made for one value of time  $t_2$  (see Figure 2). This time  $t_2$  corresponds to the same time axis in (c) and (d). This would similarly apply to a TA/2DES comparison as TG and PP are very similar.

1(c)) and one dimensional TG measurements (Figure 1(d)). Each 2D plot contributes to one point on the one dimensional TG decay shown in Figure 1(d).

2DES measurements are information rich and while you can determine TG from 2DES, there is not enough information contained in TG to unambiguously reveal all of the individual contributions to the 2DES signal. Cross peaks that appear in 2DES can have a large impact on the third order signal. Negative peaks caused by excited state absorption (ESA) can cancel each others contribution to the integrated signal [12]. In Figure 1(a) (and in Figure 7) the negative ESA peak is the top left peak and this is why the 2nd peak is smaller in Figure 1(b) and (c).

**1.2. Technical Aspects.** Three excitation fields are needed to generate a third order non-linear signal in four wave mixing (FWM) experiments, such as 2DES. Other examples of third order experiments are TA, Photon Echo (PE), and TG spectroscopy. While most of these techniques seem disparate, all of these measurements probe the third order nonlinear response. There are a number of specific technical requirements for a 2DES experiment. These requirements include the creation and management of time delays between independent and often degenerate pulses, management of pulse phase stability, and phase matching conditions. Some of these apply also to other related spectroscopic techniques.

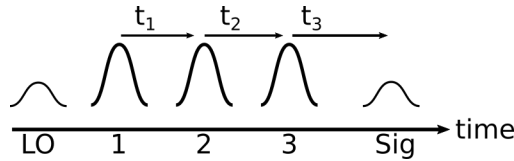


FIGURE 2. Pulses for 2DES and corresponding time delays.

In 2DES, there are two experimentally controlled time delays, shown in Figure 2 as  $t_1$  and  $t_2$ . It is in the scanning of time delay  $t_1$  that the excitation axis of our 2DES plots can be generated. In pump probe and TG experiments,  $t_1$  is set to zero and the fields are time coincident with each other, and the signal is integrated during the last interval  $t_3$ . In photon echo experiments,  $t_1$  and  $t_2$  are scanned. 3PEPS experiments have a controllable  $t_1$  variable and the associated photon echo delay. In 2DES,  $t_1$  and  $t_3$  are Fourier transformed and become the two frequency axes.

While third order measurements require three excitation fields or pulses, it is usually required for there to be another non-interacting field present. While signal amplitude measurements can be made, heterodyne detection is required in order to determine the signal field phase through interference with the fourth reference field, sometimes called the local oscillator (LO). Heterodyning is the interference of two sets of frequencies and is used to characterize the unknown components of a signal using a known reference. Here the LO is known and the modulus square of the sum is measured, so that the signal frequency can be characterized.

The LO passes through the system with the same wavevector as the generated signal field. In references [13, 14] the beam that acts as the LO is sometimes referred to as the tracer beam (though the term tracer beam does not always refer to the LO). The LO provides a signal to noise advantage as well as making it possible to separate the real and imaginary signal components by making the signal phase determinable. The LO also creates the interferogram on the CCD during detection. The reason why we are able to predict the wavevector of our signal, and therefore know the direction of the LO, is due to conservation of momentum requirements. The wavevector of a given wave describes the spatial direction as well as frequency. The generation of nonlinear signals relies on both conservation of momentum and conservation of energy. The phase matching condition is a statement of conservation of momentum and dictates that the nonlinear signal is scattered into the  $k_s = -k_1 + k_2 + k_3$  direction, the 4th corner in the BOXCARS geometry. Here, three excitation fields occupy three corners of a square and signal is emitted into the remaining fourth corner. BOXCARS geometry also has the benefit of allowing a background-free measurement. BOXCARS stems from its use as a phase matching geometry in Coherent Anti-stokes Raman Spectroscopy (CARS) [15, 16]. There are other possible wavevector combinations that can be used, including pump probe geometry.

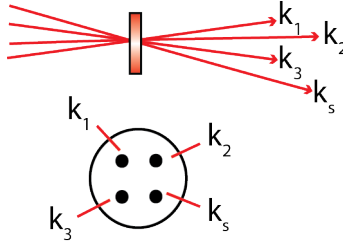


FIGURE 3. BOXCARS geometry.

Pump probe geometry 2DES (see Figure 4) has some extra complexity to it due to its partially collinear nature. As with one dimensional pump probe measurements,  $k_1$  and  $k_2$  are equal, with the first two pump excitation fields being spatially coincident but separated in time. Because  $k_1 = k_2$  in pump probe geometry 2D,  $k_s = -k_1 + k_2 + k_3 = -k_1 + k_1 + k_3 = k_3$  where  $k_1$  is the pump wavevector and  $k_3$  is the probe wavevector. In this way, the signal field

is generated in the direction of the probe pulse. Replacing  $k_2$  with  $k_1$  for both rephasing and non rephasing signal directions results in the same signal direction. Pump probe geometry always measures both the rephasing and non-rephasing signal contributions at the same time and they can't be separated.

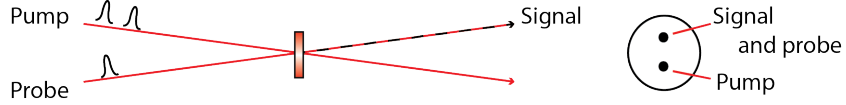


FIGURE 4. Pump probe geometry.

Mukamel's text [8] more fully discusses the phase matching conditions required for non-linear spectroscopy. Working from Maxwell's wave equation, the electric field of the signal generated by the mixed waves can be determined. The equation for the nonlinear electric field signal is

$$(1) \quad E_s(l, t) = \frac{2\pi i}{n(\omega_s)} \frac{\omega_s}{c} l P_s(t) \text{sinc}(\Delta k l / 2) \exp(i\Delta k l / 2)$$

$$(2) \quad \text{sinc}(x) = \frac{\sin(x)}{x}$$

where  $E_s$  is the signal field,  $\omega_s$  is the signal frequency,  $n$  is the refractive index,  $c$  is the speed of light,  $l$  is the length of the sample,  $P_s$  is the polarization of the medium contributing to the generation of the electric field, and  $\Delta k = k_s - k'_s$ .  $k_s$  is the wavevector signal determined by a vector sum of the waves entering the sample.  $k'_s$  is the wavevector determined by dispersion conditions in the sample defined by the relationship between wavevector and frequency. Ideally when  $k_s$  and  $k'_s$  are the same,  $\Delta k$  is zero, but usually they are slightly different and  $\Delta k$  is no longer negligible. The sinc function in the equation then provides insight into the strength of the signal generated by relating the signal to  $\Delta k$  and the length of the sample. The phase matching conditions determine the origin of the signal scattered into a particular direction. In a 2DES experiment one signal direction may contain both the rephasing and nonrephasing components of the measurement.

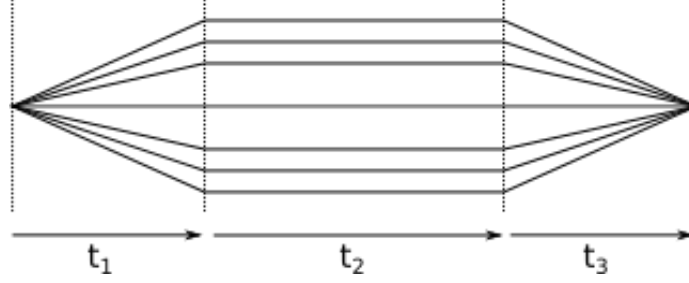


FIGURE 5. Image of lens analogy used to explain phase evolution and the generation of a photon echo.

The concept of rephasing and nonrephasing signals in a photon echo (PE) or 2DES experiment can be confusing. The lens analogy (see Figure 5) is useful to visualize the rephasing process associated with the photon echo signal. The horizontal axis represents time. The first three vertical lines represent the three pulse interactions. During  $t_1$ , coherent superposition state dephases. To put it in terms of Figure 5, if instead of looking collimated, there is still divergence in the rays, the third “lens” or pulse cannot refocus the beam to a single point. As a result, the PE signal will be more stretched in time as the so-called rays come to focus at different times. The lines in Figure 5 are representative of phase.

The first pulse that interacts with the sample generates a coherence between electronic states which evolves during  $t_1$ . After the first time interval  $t_1$ , the second laser pulse converts coherent superposition into a population. While in a population there is no evolution of phase. The coherent superposition can become either an excited or ground population, see Figure 5 and 6. The third light matter interaction forms a coherence again. During this coherence, further phase evolution occurs. The coherent oscillation generates signal; for the rephasing pathways a photon echo is generated; for the nonrephasing pathways a free induction decay occurs. The corresponding Feynman diagrams are shown in Figure 6.

The rephasing pathway generates a photon echo signal. Early PE measurements using two pulse photon echo (2PE), three-pulse photon echo (3PE), and 2DES detected rephasing signal field matter interactions. When the first field initiates a coherence, phase starts to accumulate. Although the second field converts the coherence into a population, there can be “evolution” of phase (spectral diffusion). The rephasing process initiated by the third

field matter interaction causes the phase “fanned out” during the first interval to reverse and cause a signal to peak at a  $t_3$  that equals  $t_1$ .

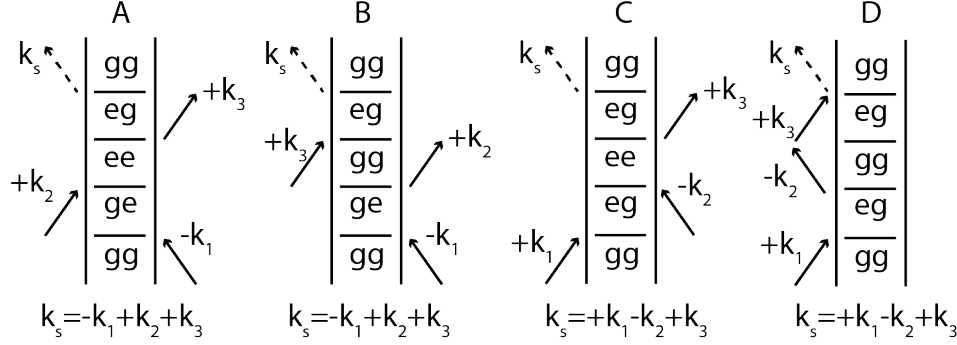


FIGURE 6. (a) Rephasing pathway through the excited state. (b) Rephasing pathway through the ground state. (c) Nonrephasing pathway through the excited state. (d) Nonrephasing pathway through the ground state.

Feynman diagrams are representative of complex path integrals that can be used to describe the time evolution of the density matrix [8]. While the integrals can be very complex, when the rules are followed, Feynman diagrams help us to visualize and interpret the results. Feynman diagrams are tools that we can use to understand the contribution of different pathways that contribute to the signal.

It is important for both the rephasing and nonrephasing signal contributions to be obtained. Both signal contributions are needed to remove phase twisting from the signal and make it possible to distinguish the real and imaginary signals. There may be different information contained in the rephasing and nonrephasing spectra. Schlau-Cohen *et al.* use the nonrephasing spectra for energy transfer dynamics [17]. The rephasing data makes up the positive time half of the data while the nonrephasing makes up the negative time portion. The time delay between pulses 1 and 2,  $t_1$ , is scanned and eventually the two pulses overlap such that pulse 2 is now the first light matter interaction and pulse 1 is the second. This overlap occurs at  $t=0$  and that change marks the cross from rephasing to nonrephasing. A mathematical consequence of having both portions is that the Fourier transform process maintains phase information between the real absorptive and imaginary refractive components.

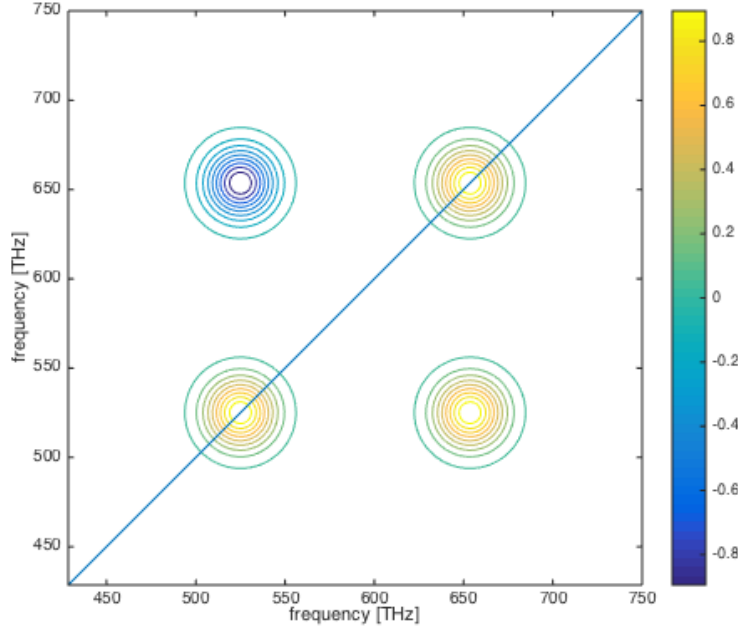


FIGURE 7. 2DES surface at a time  $t_2$  (sometimes referred to as  $T$ ) between the second and third pulses showing peaks. Both diagonal and cross peaks are present.

**1.3. Correlation Map.** The 2DES spectrum makes up a correlation map with two frequency axes. The two frequency axes are often called excitation and emission frequency axes. These frequency axes are formed as a Fourier transform of accurately controlled time delays between the pulses that make up the light matter interactions. Two dimensional plots are useful because they allow for the clear resolution of the shapes and positions of peaks. In a 2DES experiment, the peak position contains information about energy levels and coupling of these levels. The peak shapes and sizes contain information about dynamics. Two main types of peaks are of interest to us, those that fall on the diagonal and those that do not (referred to as cross peaks).

The correlation map provides many features of interest for 2D spectroscopy. Peak location is one of these key features as well as the presence of diagonal and cross peaks [12]. In Figure 7 the diagonal is indicated by the solid diagonal running across the figure. When the signal emission frequency is the same as excitation frequency, peaks appear on the diagonal. Cross peaks arise from an interaction or coupling of states such that the excitation and emission



frequencies are not the same. Cross peaks that appear below the diagonal may be due to an energy transfer process where energy initially absorbed into a higher lying state is transferred to a lower energy state and subsequently emitted. The negative cross peak above the diagonal is caused by excited state absorption. Positive or negative peaks may also arise from other interactions such as strong electronic-vibrational coupling.

Figure 7 has only round peaks as an example, but these diagonal and cross peaks have shapes which are usually affected by different broadening processes as seen in Figure 8. Peak shape is discussed in great detail by Hybl *et al.* [18]. The elongation of the peak along the diagonal indicates the “memory” of the system under interrogation. The diagonal elongation is caused by longer timescale or inhomogeneous broadening while the anti-diagonal is associated with shorter timescale or homogeneous broadening. As time progresses, the system relaxes through interaction with the bath or surroundings, changing the peak shape. The effect is that the peak becomes more round. One can visualize that a system “frozen” in a glass environment might keep the diagonally elongated peak shape much longer than a system in a constantly fluctuating bath or solvent.

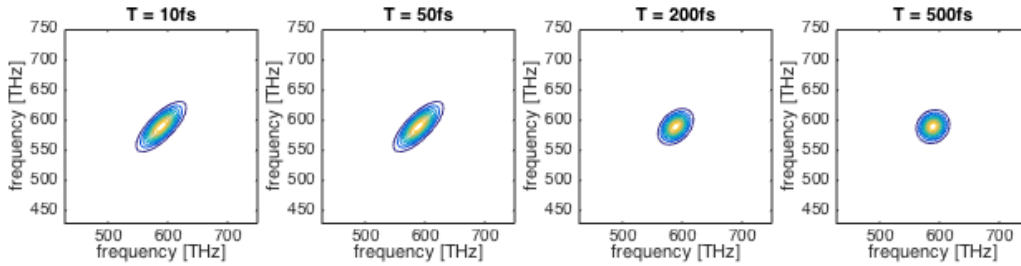


FIGURE 8. 2D spectra as a function of increasing  $t_2$ . As the second time delay is increased the peak becomes less elongated and more symmetric. The changing lineshape can give us information about the relaxation dynamics of the system.

There are other types of processes that can be followed with changes in time  $t_2$ . Time  $t_2$  is the time between pulses two and three when the system is in a population and population relaxation may occur. There can be oscillations or quantum beats present with waiting time

( $t_2$ ) as shown by the Fleming group in the Fenna-Mathews-Olson (FMO) complex [19]. New peaks may appear with a larger  $t_2$  due to an energy transfer process.

**1.4. Historical Context.** Two dimensional nuclear magnetic resonance (2DNMR) helped to shape the development of optical 2D spectroscopy measurements. First proposed in 1971 by Jean Jeener and experimentally demonstrated by Ernst in 1976, correlation spectroscopy (COSY) was the first implementation of 2DNMR [20]. 2DNMR can unravel couplings between hydrogens and are invaluable when it comes to determining molecular structure [21]. Much of the usefulness in 2DNMR comes from an interpretation of its cross peaks (those peaks which occur where the two frequencies are not equal). Like with 2DNMR, extending the optical third order measurements to a second frequency axis aids with interpretation of congested spectra. Where as NMR relies on nuclear spin transitions, two dimensional infrared (2DIR) uses vibrational transitions and 2DES uses electronic transitions to get new structural and dynamic information.

Work was done by Warren and Zewail in 1981 to bring NMR techniques to the optical regime using acoustic-optic modulation [22]. Though 2DES measurements would not be demonstrated until the late 1990's [13], it was already realized that an optical analog of 2DNMR would be incredibly useful. Complexities with the creation of phase stable pulses and with fully characterizing the electric field made it very challenging to successfully achieve electronic 2D spectroscopy.

In an effort to bring NMR techniques into the optical, Lepetit and Joffre made important advances in spectral interferometry when they applied nonlinear NMR techniques to optics to measure the second-order nonlinear susceptibility of a material [23]. As spectral interferometry is a key component to 2DES and especially the interferometric 2DES in Section 2, these advances were especially valuable to the field.

2DIR spectroscopy is another similar 2D Fourier transform spectroscopy measurement with important advances that could be applied to 2DES [5, 24, 25]. Similar techniques to 2DES are used in 2DIR spectroscopy, though transitioning a technique between the two measurements involves solving some considerable technical challenges. Shorter wavelengths,

as those in 2DES, have stricter technical requirements, such as with phase stability. Rather than obtaining information about electronic states, 2DIR can be used to observe vibrational energy and couplings [26].

In 1999, the use of diffractive optics was shown for heterodyne detection in TG by the Miller group [27]. The method provided benefits in pulse front tilt, and pulse phase stability. As 2DES measurements are extensions of TG and TA measurements, this demonstration of the use of diffractive optics suggested its application in 2DES. Building on the previous work done in 2DNMR, 2DIR and other nonlinear electronic techniques, 2DES was first realized at the end of the 1990s by the Jonas group (see section 2) [13].

**1.5. Methods.** A number of different methods are used to tackle some key challenges faced by the field of 2DES [4]. Meeting phase matching conditions, accurate control of time delay, phase stability, measurement of both the rephasing and nonrephasing signals, and phasing the spectra are some of the items of concern. The methods described in this report follow the progression of 2DES since its first demonstration by the Jonas group in 1998 [13]. Active phase stabilization and interferometric measurements make this initial experiment successful. The subsequent demonstration of the diffractive optic based 2DES was a natural progression that eliminated the need for the active phase stabilization. Phasing the data in both of the previous methods can be problematic, requiring the need for separate real pump probe measurements as reference to determine the phase of the data. An answer to this dilemma was pump probe geometry 2DES which allowed for simultaneous measurement of pump probe and 2D data together.

Phase stability is managed differently in each of the following sections that describe different iterations of 2DES. Section 2 discusses the interferometric 2DES experiment where phase stability between pulses is managed through interference. Passive stabilization methods are employed in the diffractive optic based experiment shown in Section 3. The pump probe geometry 2D experiment in Section 4 maintains phase stable pulses through accurate pulse shaping methods in its partially collinear geometry.

The time delays are also managed differently by the different experiments. Translation delay lines are used in the interferometric experiment. Glass wedge pairs are used in the diffractive optic 2D experiment. The nature of the pump probe geometry 2D experiment is that the pulse shaper is used also for the time delay between pulses one and two, but a delay line with mirrors, similar to Section 2 is used to control time  $t_2$ .

## 2. INTERFEROMETRIC 2DES

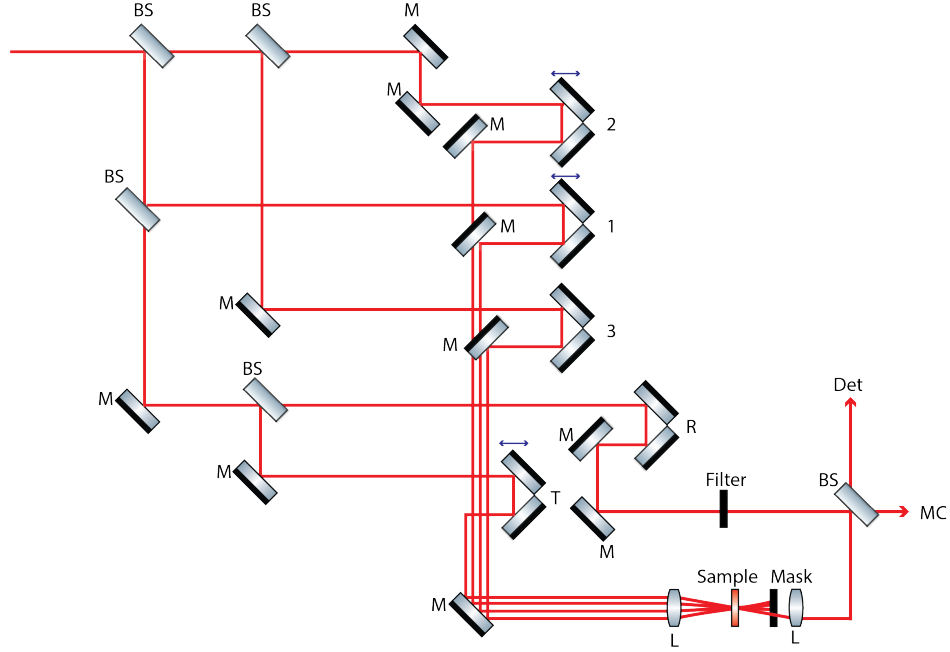


FIGURE 9. Layout of an interferometric 2DES setup. BS: Beam Splitter. M: Mirror. L: Lens. R: Reference. T: Tracer. MC: Monochromator. Det: Detector. Arrow indicates translation. Figure drawn using many components from the ComponentLibrary by Alexander Franzen.

**2.1. Experimental Design.** One of the first experimental designs demonstrating 2DES was shown by the Jonas group in 1998 [13]. Frequency resolved optical gating (FROG) and a five beam interferometer make up a large part of the experiment. Approximately 800 nm, 30 fs pulses are generated from a mode-locked Ti:sapphire laser. The beam is separated into five using a series of beam splitters: the three beams needed for the three light matter interactions required to generate a third order nonlinear signal, a beam to act as a LO to take advantage of heterodyne detection, and a fifth reference beam. Each arm of the interferometer incorporates a delay line. The change in distance for each beam directly changes the amount of time a pulse needs to travel to the sample. Precision in control of the delay lines is essential for accurate control of the time between pulses. The time delays in this experiment are scanned interferometrically. Fourier transform of the time axis generated

by the scanning of the pulses with relationship to each other gives the second frequency axis mentioned above.

The design also requires management of pulse dispersion, which is managed by allowing the pulses to pass through prism pairs before entering the first beam splitter of the five beam interferometer. These prism pairs are not shown in the diagram. Three 50-50 beam splitters are used to divide the entering beam into the three required pulses for the light matter interactions as well as a fourth beam that will then be further split to make the tracer and reference arms of the interferometric measurement. Additional fused silica compensating blocks are required to ensure that each pulse passes through the same amount of material. Two main things alter ultrafast pulses as they pass through a material. Dispersion causes pulses to spread in time, which is why the pulses are first compressed with the prism pairs. Secondly, adding material to the optical path length of greater index of refraction increases the path length and changes the amount of time a pulse will take to get to the sample. It is important that all of the beams experience the same amount of dispersion and have the same path length, which can be achieved by using the compensating blocks. These are commonly found in interferometers.

Each arm of the interferometer has a delay line. Three of these delay lines have active translation throughout the experiment and those are indicated in the diagram with the arrows. Pulses one and two as well as the tracer have translation in their delay lines. The translation in the delay lines allows for accurate timing between pulses that is needed to generate the time information for the measurement. After the delay lines, the beams are then directed into a lens with a BOXCAR arrangement to be focused into the sample. The timing for the pulses to interact with the sample is critical. It is also necessary that the pulses are spatially overlapped in the sample. The sample must be very thin, with path lengths usually around 100-200  $\mu\text{m}$ . The lens focusses each pulse into sample and the signal is emitted in the same direction as the tracer. A mask is used to block all the beams except the signal and tracer. The beam needs to be collimated again using another lens. Once the

beam containing the tracer and the signal is collimated the beam is directed into the final beam splitter where it will interfere with the reference path.

Signal leaves the beam splitter and either goes to the monochromator or the photodiode detector. Mixing of the signal with the tracer allows for heterodyned detection methods to be applied. The tracer here is often called the LO and may be referred to as such in other sections. One of the benefits of using heterodyne detection is a valuable drop in the signal to noise ratio. Interference with the reference beam provides information on the reference beam phase which is removed. The removal of the reference phase allows for the use of a neutral density filter to maximize the signal to noise ratio benefits of the heterodyne detection. The monochromator collects the interference pattern between the reference and the combined tracer-signal beams. Fringe spacing in the interferogram produced tells us the amount of delay between pulses.  $t_{delay} = 2\pi/\Delta\omega$  where  $\Delta\omega$  is the fringe spacing.

Projection slice theorem uses 1D PP or TG data to determine the signal phase in a 2DES plot [3, 28]. The theorem relates the 1D projection of the 2D spectrum to a 1D slice through the 2D spectrum. When properly phased, the projection of the 2D spectrum onto the frequency axis and the FR-TG data, each at the same time  $t_2$ , are equivalent. The projection slice theorem can help to phase the 2D spectrum by rotating the PP/TG signal phase until it matches the the projection from the 2D spectrum, providing the overall signal phase. Knowing the overall signal phase allows for the absorptive, real component and the refractive, imaginary component to be separated from each other.

### 3. DIFFRACTIVE OPTIC 2DES

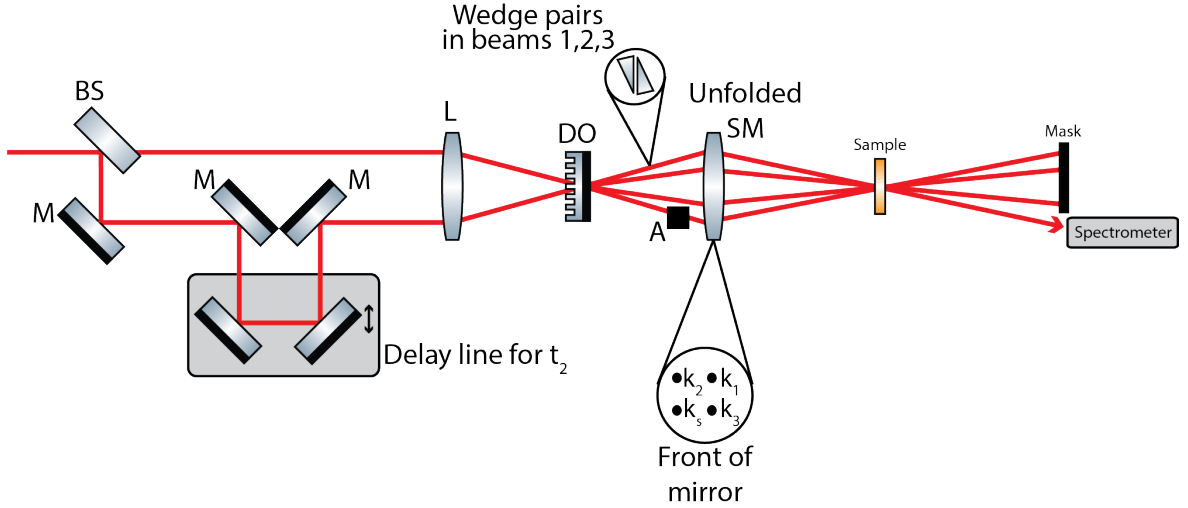


FIGURE 10. Layout of Diffraction Optic 2DES. SM: Spherical Mirror. A: Attenuator. Figure drawn using many components from the ComponentLibrary by Alexander Franzen.

**3.1. Experimental Design.** While the previously discussed 2DES measurement (Section 2) uses interferometry to actively control the phase stability between pulses, another design based on a diffractive optic takes advantage of inherent passive phase stability. There are some variations in the field with the diffractive optic 2DES experiment in the different research groups. The Fleming group demonstrated use of glass wedges for time delay [29]. The Miller group makes use of rotating slides for the time delays [27, 30]. This same basic diffractive optic design has also been used successfully for other experiments including TG spectroscopy [10]. Similar passive phase stability has been shown with beam splitters rather than diffractive optics by Selig *et al* [31].

As with other 2DES methods, the diffractive optic technique makes use of pulses from a Ti:sapphire laser with a regenerative amplifier and usually an apparatus to adjust the central wavelength and spectral width such as a noncollinear optical parametric amplifier (NOPA).



Though it is worth noting that these are commonly used sources for reliable ultrafast pulses, the Ti:sapphire regenerative amplifier is not the only source available to use for 2DES.

In the diffractive optic 2DES experiment the beam is separated by a beam splitter into two separate beams. One of the two beams has a translation delay line placed in it. It is with this delay line that time  $t_2$  is set as it will allow for the larger translations needed for the longer time delay between pulses two and three. The two beams are then focused into a diffractive optic (DO) to generate the two pulse pairs (pulses 1 and 2 then 3 and LO) in place of the previously used series of beamsplitters [32]. The LO here is used for heterodyne detection purposes. The four beams are then reflected from a spherical mirror that focusses the light fields onto the sample. From the DO to the mirror, the beams are arranged in the BOXCAR geometry due to the nature of generating the pulse pairs in the DO.

There are a few more things that happen before the light pulses can interact with the sample. Path length increases due to a change in the refractive index necessitates that each pulse travel through the same amount of material. In this method, the experiment uses the increased path length to its advantage to create the needed time delays. Glass wedges are placed in the paths of pulses one and two [29]. The wedges can be very precisely moved back and forth so that the amount of glass that the pulses pass through changes, increasing or decreasing the path length and changing the amount of time that it takes for a pulse to get from the spherical mirror to the sample. To prevent the beam from moving due to refraction at the wedges, identical pairs of wedges are used and arranged such that they have opposing directions. The third beam will also pass through a fixed (no translation) wedge pair to compensate for dispersion effects. Calibration of the wedge pairs can be done by placing a second DO in the sample position and measuring the resulting interference pattern.

As with the reference beam in the previous section, the LO here is also attenuated with the neutral density filter to be used for heterodyne detection. The LO pulse is also offset in time from the other pulses, generally arriving first to prevent contamination of the signal with other types of signal [29]. Heterodyned mixing of the signal with the LO provides information about the signal phase.

In all of the 2DES techniques it is necessary to be able to completely characterize the pulses. FROG, second harmonic generation FROG (SHG-FROG), and TG-FROG are sometimes used to do this. There is a detailed book available discussing FROG as well as other pulse measurement techniques [33]. FROG techniques allow for measurement of the pulse amplitude and phase, allowing complete characterization of the field. FROG is a frequency resolved autocorrelation type measurement, with the pulse gated with itself. An algorithm is required to achieve the phase. SHG-FROG mixes the pulse with itself in a crystal to generate the second harmonic which is measured. TG-FROG is commonly used for measuring pulses used for 2DES due to its improved sensitivity and bandwidth [34]. TG-FROG uses three beams in a BOXCAR geometry with the signal generated in the usual 4th corner of the box.

## 4. PUMP-PROBE GEOMETRY 2DES



FIGURE 11. Layout of pump probe geometry.

Pump probe geometry 2DES uses the same geometry as the standard pump probe (TA) measurement. There are a number of advantages and disadvantages to attempting to complete this type of experiment. As with other techniques pump probe 2D requires three light matter interactions from three separate pulses. When first looking at the diagram, it might appear that there are no longer three pulses in this experiment, but we know that three incoming pulses with controllable time delays are a fundamental requirement for 2DES. For pump probe geometry 2DES, the required time delays are generated by the pulse shapers. The pulse shaping methods are required due to the collinear nature of the first two pulses.

**4.1. Advantages and Disadvantages of Pump Probe Geometry.** Pump probe geometry is one of the more technically challenging experimental types of 2DES but there are some strong advantages to this design. One of the difficulties in all 2DES measurements lies in phasing the spectra. For both the interferometric 2DES and the DO 2DES design, a separate pump probe measurement of the sample is taken and projection slice theorem is applied to phase the 2D spectra. It can be challenging to get accurate pump probe data with similar signal to noise as the 2D data. One of the main reasons why pump probe geometry 2DES was actively pursued was the ability to collect the pump probe signal at the same time as the 2DES data. This simultaneous collection allows for an accurate pump probe data for phasing the 2DES spectra. While this is one of the major advantage of pump probe geometry 2DES, it can also be another aspect of the experiment that makes it challenging. Both the 2DES data and the pump probe data have the same phase matching signal directions and the signals are mixed. It is essential that the two signals are separated from each

other. Schemes have been developed to remove the background from pump probe geometry 2DES [35].

One big challenge for pump probe geometry 2DES is the difficulty in creating the time delay,  $t_1$ . The collinear geometry of the first two pulses makes it impossible to apply some of the techniques previously discussed in this report. Using a delay line as with the interferometric experiment or the glass wedges as in the diffractive optic experiment would not create the required time delay. For this reason pulse shaping in the Fourier domain is required to create the required phase stable pulses with a reliable time delay.

Another aspect of the pump probe geometry 2DES measurement that is different from the rest of the techniques discussed here is the concurrent measurement of the rephasing and non-rephasing signals. Both signals are measured along the direction of the “probe” pulse,  $k_3$ . In Figure 12 the probe-signal beam is shown by the black and red dashed line leaving the sample. This means that, for this experiment, the 2DES spectra is real. The real contribution of 2DES spectra is the absorptive component where as the imaginary contribution of the 2DES is the refractive component. The inability to separate the nonrephasing signal from the rephasing signal can be either advantageous or problematic depending on the application. This means that the signal is not plagued by phase twisting that arises from measuring the two components separately. However, it also means that the signal components associated with only the rephasing or the nonrephasing parts cannot be resolved.

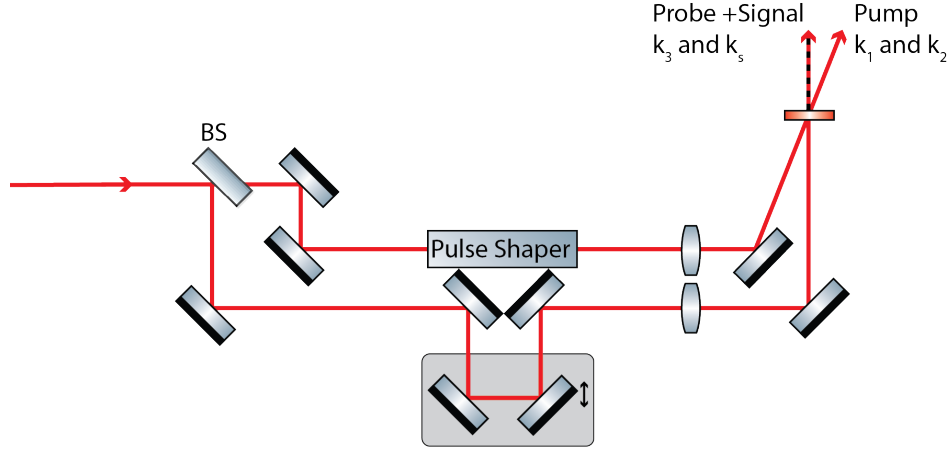


FIGURE 12. Layout of pump probe geometry 2DES setup.

**4.2. Experimental Design.** Pump probe geometry 2DES is a partially collinear geometry 2D measurement requiring the two pump pulses to be generated along the same beam path with a controllable time delay. Pulses in pump probe geometry 2DES are often generated using Ti:Sapphire laser in conjunction with a NOPA. The NOPA is used to generate broad-band pulses in the desired frequency range. This being said, pump probe geometry can also be applied to 2DIR spectroscopy and is not only available for 2DES [24].

Pump probe geometry 2DES starts with a beam splitter to split the beam into two arms. The probe arm contains a delay line which controls time  $t_2$ . For this geometry the  $t_2$  time delay is the time between the “pump” pulses and the “probe” pulse.

The second arm of the experiment from the beam splitter is sent through a pulse shaper. The Fastlite Dazzler is a commonly used pulse shaper for many groups working with pump probe geometry 2D. The Dazzler is an example of an acousto-optic programmable dispersive filter, originally demonstrated by Pierre Tournois [37]. The coupling of optical and acoustic waves in a birefringent crystal is used in this device. The filtering of the optical pulses are done in the Fourier domain, which can be accessed through a 4f optical line with two lenses [38], taking advantage of the Fourier transforming properties of a lens (see Figure 13). Figure 14 shows an example of how the time delay can be generated in the Fourier domain.

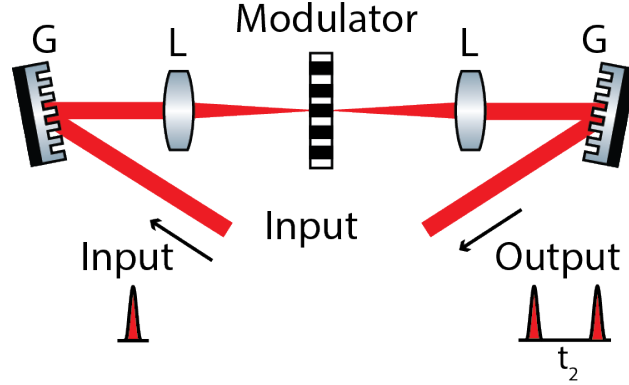


FIGURE 13. Basic elements for pulse shaping through the Fourier domain with a modulator. [36]

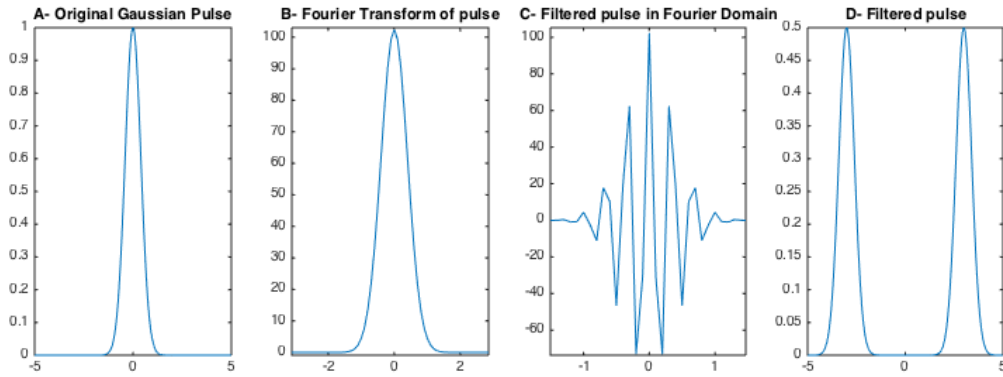


FIGURE 14. Filtering an optical pulse in the Fourier domain allows for pulse shaping and the creation of a controllable delay. (a) A single Gaussian pulse in time. (b) The pulse from (a) in the frequency domain, after Fourier transform. Accessed in the  $4f$  line via a lens. (c) The frequency domain pulse is modulated with a single frequency wave. (d) A Fourier transform back into the time domain results in two pulses with a time delay based on the filter frequency.

**4.3. Pulse Shaping.** The Dazzler is only one of many available pulse shaping methods. Each method has advantages and disadvantages concerning speed, resolution, accuracy, and bandwidth. A review of methods for optical pulse shaping has been published [36]. Some of the pulse shaping methods include various spatial light modulator and acousto-optic modulator schemes. The technique of using pulse shaping to manipulate ultrafast optical pulses is not limited to ultrafast spectroscopy.

4.3.1. *Acousto-Optic Modulator*. The Warren group first showed that coherent pulse trains could be generated using acousto-optic modulation in 1981 for the use of making an optical analog to 2DNMR [22]. They also showed in 2003 that this method can be used to generate three pulses with controllable time delays to successfully demonstrate 2D optical spectroscopy [39]. This acoustic-optical modulation affect can also be used to create the two spatially coincident pump pulses for pump-probe geometry 2DES.

4.3.2. *Spatial Light Modulator (SLM)*. Another method that can be used for the pulse shaper is SLM technology [38, 40, 41]. The use of an SLM pulse shaper with pump probe geometry has been demonstrated in 2DIR spectroscopy [42]. While the SLM has been applied to 2DES [43, 44], it's potential use as a programmable pulse shaper has not been used with optical pump probe geometry 2DES measurements. SLM technology uses a liquid crystal display (LCD) with an applied phase mask. In the SLM based 2DES, linear phase would be applied in the Fourier domain to generate a time delay. Pixel size and the total number of pixels and size of the array have a large impact on resolution and maximum amount of time delay that can be applied.

4.4. **Variations of Pump Probe Geometry 2DES**. Some experiments have been performed which have made variations to pump probe geometry 2DES experiment. Some of the changes are to eliminate some of the disadvantages facing this method, while others are made to expand upon the information available. Ogilvie and Fleming groups are making much of the advances in the field to expand the usefulness of pump probe geometry 2DES. The Ogilvie group changed the wavelength of the probe from the pump pulses to take two color pump probe geometry 2D measurements [45]. Oliver *et. al.* was able to use pump probe geometry to link 2DES and 2DIR spectroscopy for the first time in 2014 by using IR probe pulses [46]. The purpose of such an experiment was to observe coupling between electronic and vibrational dynamics. Another variation made by the Ogilvie group involved the use of a white light probe [47].

## 5. CONCLUSION

There are a number of advantages and disadvantages associated with each experimental 2DES technique described in this report (see Table 5). Each new method was developed to solve a problem not yet solved, and for this reason new techniques will continue to evolve. For the interferometric 2DES it was the first successful demonstration that 2DES was possible in a time where it was thought it could not be done. The technical rigor involved with active phase stabilization can be incredibly valuable. The diffractive optic 2DES removed some of the technical challenge of the extra interference measurements needed for phase by handing phase stability passively. The DO, while often used does have it's limits. And like with the interferometric 2DES, phasing the 2D spectra is difficult and less precise. Pump probe geometry 2DES simultaneous measurement of real pump probe spectra allows for more accurate phasing of the data. Accompanying this method are limits in the time delay generation by pulse shaping methods. The advantages and the disadvantages of each method must be carefully considered before one is chosen for a measurement. Table 5 summarizes some of these advantages and disadvantages.

|                          | Advantages                                                                                                                                                  | Disadvantages                                                                                                                                                                                                 |
|--------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Interferometric 2DES     | <ul style="list-style-type: none"> <li>- First successful 2DES demonstration</li> <li>- Pulse phase stability actively controlled for all pulses</li> </ul> | <ul style="list-style-type: none"> <li>- Technically challenging</li> <li>- Difficulty in accurately phasing the 2D spectra</li> </ul>                                                                        |
| Diffractive Optic 2DES   | <ul style="list-style-type: none"> <li>- Passive phase stabilization</li> <li>- Removes need for extra interferometer</li> </ul>                            | <ul style="list-style-type: none"> <li>- Unknown phase factor between pulse pairs</li> <li>- Difficulty in accurately phasing the 2D spectra</li> </ul>                                                       |
| Pump probe geometry 2DES | <ul style="list-style-type: none"> <li>- Accuracy in phasing 2D spectra with real pump probe data</li> </ul>                                                | <ul style="list-style-type: none"> <li>- Difficult to generate time delays</li> <li>- Limits to extent of delay that can be generated</li> <li>- Inseparable rephasing and nonrephasing components</li> </ul> |



**5.1. Brief Comment on Other Techniques.** The 2D spectroscopy experiments discussed above are not all encompassing. There are other methods that are worth mentioning here for completeness. There are requirements that each 2DES measurement must fulfill, and while it may not always be immediately apparent, each of these experiments meets those technical requirements. Both the methods contained in Sections 2, 3, and 4 and those discussed here each apply different methods to meet these requirements: that there exists independently controllable time delays between a minimum of three pulses, that there are phase matching requirements.

**5.1.1. GRAPES.** Gradient-assisted photon-echo spectroscopy (GRAPES) is a single shot approach developed to formulate a means to measure 2DES spectra with a single measurement, rather than by a series of scans through time delays,  $t_1$  and  $t_2$ . The GRAPES experiment was demonstrated by Harel *et al.* in the Engel group [48]. This measurement uses controllable pulse front tilt to generate time delays. Pulse front tilt distributes different spectral components of a pulse with time and this distribution of times is the delay.

**5.1.2. Phase modulation.** Phase modulation has also been used as a method to achieve 2DES spectroscopy [49]. It is a complex technique using acousto-optic modulators and Mach-Zhander interferometers.

**5.2. Closing Remarks.** 2DES encompasses a number of multidimensional spectroscopic techniques, including those discussed in this report. By expanding 1D spectra into the second frequency axis, unprecedented insight is being gained in many areas of spectroscopic importance. Energy levels and couplings, especially those that suffer from averaging effects in one dimensional or linear spectroscopy, are clearer and more information is accessible to allow for better interpretation. Dynamic processes, timescales of system-bath interactions, and previously ambiguous multiple contributions to a signal are areas where 2DES excels.

Interferometric 2DES, a challenging technique that was a natural extension of 3PEPS, was the result of an accumulation of a number of technological advances. Reliable generation of accurate ultrafast pulses, advances in pulse and field characterization techniques,

and a concurrent growth in the analogous 2DNMR field were some of these advances. As interferometric 2DES was a natural progression from 3PEPS, so was DO 2DES from interferometric 2DES. The passive phase stabilization from DO generated pulse pairs can be seen as an improvement to the technical challenges of maintaining active interferometric phase stabilization. Not without its own share of advantages and disadvantages, DO 2DES is very prevalent in the field. Pump probe geometry 2DES is another natural extension of another useful technique, TA. It has demonstrated some advantages over BOXCAR geometry 2DES in terms of phase twisting and phasing the 2D spectrum.

Each technical challenge with the already demonstrated techniques serves as inspiration for new ways to solve these problems and more accurately probe ultrafast dynamical processes. While 2DES techniques are maturing and a wealth of new information is being gained, new 2DES designs are being created that will push forward the boundaries of this experiment.

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