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ARTICLE TYPE
www. rsc.org/xxxxxx | XXXXXXXX

Optical three dimensional coherent spectroscopy

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Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

Optical multdimensional coherent spectroscopy has recently been the subject of significant activity. While two-dimensional spectroscopy is most common, it is possible to extend the method into three dimensions. This perspective reviews the different approaches to three-dimensional spectroscopy and the systems that have been studied with it. The advantages of adding an additional dimension are discussed and compared to the resulting experimental challenges.

1 Introduction

Over the last two decades, there has been significant effort in the development of multidimensional coherent spectroscopy in the optical spectral region.[1] While most of the effort has been directed towards two-dimensional (2D) methods, it is also possible to produce three-dimensional spectra. Because 3D coherent spectroscopy is technically more demanding, there have naturally been fewer 3D results. However, the published results so far do show that there are compelling reasons to add a third dimension.

In this perspective, I will briefly introduce the concepts of multidimensional spectroscopy and discuss several experimental realizations. I will then introduce the various approaches to extending the methods into a third dimension and the types of spectra that are obtained. This introduction will provide the basis for a brief review of the key 3D spectroscopy results. Finally, I will discuss and compare these results, in the context of the following question: “Is 3D coherent spectroscopy worth the effort?”

The basic idea of multidimensional spectroscopy was originally developed in nuclear magnetic resonance (NMR),[2] where it is typically known as “multidimensional Fourier transform spectroscopy,” a term also used in the optical domain. However, the fact that a Fourier transform is used does not really define the method. Rather, the essential distinguishing feature is that the spectrum measures the coherent response of the sample. In contrast, it is also possible to produce an incoherent two-dimensional optical spectrum by, for example, measuring emission (fluorescence or luminescence) spectra as function of the exciting laser’s wavelength.

Although multidimensional spectra are typically plotted as function of multiple frequencies, the experiments are usually performed using ultrashort optical pulses (thus the need to perform Fourier transforms), similar to NMR where radio frequency pulses are used. As a consequence, the concepts and methods used for optical multidimensional coherent spectroscopy are based on those developed for ultrafast spectroscopy.

The idea of optical 2D coherent spectroscopy was proposed in 1993 by Tanimura and Mukamel using a Raman excitation sequence to probe molecular vibrations.[3] Early experimental efforts to use Raman excitation were found to suffer from contamination by cascades.[4,5] This difficulty lead to development of 2D infrared spectroscopy for probing molecular vibrations.[6–8] To probe electronic transitions, shorter wavelengths are needed, usually in the near-IR or visible parts of the spectrum.[9] At these wavelengths, maintaining sufficient phase stability is more challenging than in the IR. A variety of approaches have been developed, including the use of diffractive optics,[10,11] pulse shapers,[12] active stabilization[13] and common path geometries[14].

Typically 2D coherent spectroscopy has used the third order nonlinear optical response, i.e., the signal is radiated by an induced polarization that is proportional to the cube of the incident electric field, $P = \chi^{(3)}E^3$. Higher order terms, e.g., fifth-order terms involving $\chi^{(5)}$, are typically unwanted and distort the measured spectra. In contrast, 3D spectra are often based on the fifth order response, but can also use the third order response. Indeed, since these two types of 3D spectroscopy are fundamentally different, it is useful to classify 3D spectra by the order of nonlinearity that they use.

There is now a large body of work on 2D coherent spectroscopy, all of which cannot possibly be mentioned here. A few highlights include the measurement of vibrational anharmonicities,[7] observing the formation and dissociation of molecular complexes,[15] probing the dynamics of the hydrogen bond network in liquid water,[16] probing many-body interactions in semiconductors[17,18] and monitoring energy transfer in light harvesting centers[19,20].

There has been much less work on 3D spectroscopy than

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on 2D spectroscopy. The first demonstration of 3D spectroscopy used an IR fifth-order response[21] in a 5 beam apparatus to reveal heterogeneous structural relaxation dynamics in liquid water.[22] 3D electronic spectroscopy has also been demonstrated using the fifth-order response.[23] However 3D electronic spectroscopy has tended to focus more on the third order response,[24] where it has been used to extract more information about the excitonic basis of light harvesting materials[25] and fully determine the Hamiltionian of an atomic vapor.[26] Adding a third dimension is also very useful for multidimensional spectroscopy based on phase retrieval.[27]

The use of 3D coherent spectroscopy is motivated by a number of advantages it provides compared to 2D coherent spectroscopy. Some of these are improvements of capabilities already present in 2D coherent spectroscopy, such as disentangling congested spectra, and some are completely new capabilities, such as measuring populations of multiply excited states, that cannot be realized in 2D coherent spectroscopy. The advantages are discussed in more depth in section 4.

It is worthwhile to briefly address what is meant by "3D coherent spectroscopy". In principle a "3D spectrum" is simply one that is a function of three variables. The same is true in 2D, however a 2D coherent spectrum is clearly different, and contains more information, than a 2D incoherent spectrum that is simply a series of power spectra as function of excitation wavelength. Furthermore, simply taking a series of one dimensional power spectra and measuring them as a function of an additional time variable, and possibly taking a Fourier transform, is different than a 2D coherent spectrum. The key difference is that a 2D coherent spectrum is produced by measuring the 1D *complex* spectra, which means that they contain phase information. The same is true for constructing 3D spectra, they are produced by taking a series of complex 2D spectra as function of a third time delay, and then taking a Fourier transform. Clearly the distinction is whether the lower dimensional spectra are power spectra of complex spectra, i.e., including phase information. By using complex spectra, it is possible to track the phase evolution of any terms that oscillate during the third time delay, and thus determine their frequency(s) including the signs. If power spectra are used, all that can be determined are the absolute values of any frequency differences, which provides much less separation between peaks. In addition, the use of complex spectra means that the phases of the signal are obtained, which can contain very useful information. Furthermore, the use of a "prepulse" that incoherently prepares the system, followed by the measurement of a 2D coherent spectrum, does not fall within the definition of a 3D coherent spectrum.

2 Basic concept of multidimensional spectroscopy

Multdimensional coherent spectroscopy (MDCS) can be seen as an enhancement of related one-dimensional coherent spectroscopies. In the case of optics, it is natural to think of it as an enhancement to transient four-wave-mixing (TFWM).[†] The nonlinear interaction that produces the signal is the same in MDCS and TFWM (see Fig. 1). In a traditional TFWM experiment, the intensity of the nonlinear signal is recorded as function of the delay between the incident pulses.

The key enhancements in MDCS is that the phase of the signal is recorded, and the dependence of the phase on the delay(s) between the excitation pulses determined. The phase evolution is then correlated by taking a multidimensional Fourier transform. This step helps analyze and visualize the data, but is not essentail in of itself. Different types of spectra can be generated based on the time ordering of the pulses and the times/delays that are scanned and Fourier transformed.

An important point is that the phase of the signal depends on the phase(s) accumulated during the time delays between the excitation pulses. Thus, the measurement of the signal must record not just its internal phase evolution, but the actual phase with respect to an appropriate reference (typically the final pulse of the excitation sequence). Moreover, if the signal is to be properly decomposed into real and imaginary parts, all the relevant input phases must be accurately determined, and corrections must be made for any phase shifts of the reference.

There are two experimental enhancements, compared to TFWM spectroscopy, that must be made to enable the implementation of coherent spectroscopy. The first enhancement is the measurement of the field, not just the intensity, of the emitted nonlinear signal. Since all detectors at optical frequencies measure the intensity of the light, this requires the use of a heterodyne method where the signal is interfered with a local oscillator pulse. In ultrafast optics, the most prevalent technique is spectral interferometry,[28] where the spectral interferogram is measured. The complex spectrum of the signal pulse can easily be extracted by straightforward data processing.

The second enhancement is the use of phase stable delays between the excitation pulses. This requirement actually has two aspects. First, the time delay between the pulses must be stable to a fraction of a wavelength while the interferogram is recorded, otherwise the fringes would wash out. Secondly, the steps must be equally spaced and accurate to a fraction of a wavelength. This requirement is partly based on the use of fast Fourier transform (FFT) algorithms that require equally

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[†] The term "photon echo" is often used as a synonym for "transient four-wave-mixing". The signal in a transient four-wave-mixing experiment is a photon echo for a specific time ordering and for an inhomogeneously broadened system, thus photon echo spectroscopy is correctly a subset of transient four-wave-mixing spectroscopy, although the distinction is often ignored.

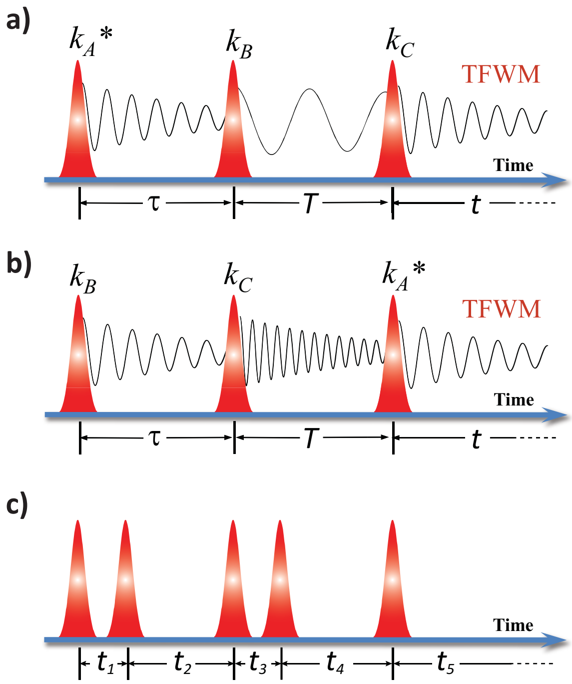

Fig. 1 Pulse sequences used in multidimensional coherent spectroscopy. (a) & (b) are used to produce third-order spectra. In (a) the conjugated pulse arrives first to produce a S_I spectrum that is analogous to a photon echo. In (b) the conjugated pulse arrives last to produce a S_{III} spectrum that proves double-quantum coherences during time T. To produce a 3D spectrum all three time delays, τ, T and t are scanned. The pulse sequence used for fifth-order spectra is shown in (c). If only three pulses are used, it is equivalent to setting two of the delays to zero. To produce a 3D spectrum, 3 of the 5 delays are scanned.

spaced steps. But it is also more than just that. If the steps have on average the right size, but a randomly varying about the correct average, it will effectively add noise. In addition, if there is a slight inaccuracy in the steps, then the effective phase of the excitation pulses will drift and the decomposition into real and imaginary parts will be incorrect.

There are a number of experimental approaches to overcoming these challenges. In the next section, the experimental approaches that have been used for producing 3D spectra will be briefly reviewed. Note that this is not meant to be a comprehensive review of experimental methods used for 2D coherent spectroscopy, but rather is focused on those that have been used to produce 3D spectra.

The most common pulse sequences for producing multidimensional spectra are shown in Fig. 1. As mentioned above, there are two distinct types of 3D spectra, those produced using the third order response and those using the fifth order response. For spectra that use the third-order response, only three pulses are needed, and the delays are typically labeled τ for the delay between the first and second pulses, T for the delay between the second and third pulses and the time after the third pulse, during the signal, is labeled t. This labeling is use in Fig. 1 (a) & (b), which shows pulse sequence for (a) a "rephasing" spectrum and (b) a "double quantum" spectrum. These are often designated as S_I and S_{III}, respectively. The corresponding frequencies are ω_x where $x = \tau, T, t$. For spectra that use the fifth-order response, the use of different symbols becomes cumbersome, so the delays are typically labeled by simply using t_i, where i is the number of the first pulse in the pair. This labeling is shown in Fig. 1. Note that this convention is usually used for fifth-order spectra, even if only three pulses are used because all 5 times need to be tracked in the calculations. The frequency associated with time t_i is typically designated as ω_i.

2.1 Experimental Approaches

The difficulty of achieving the require stepping stability and accuracy, of course, depends on the wavelengths being used. In the IR the demands are significantly easier to meet, whereas at visible wavelengths it is much more challenging.

In the IR the passive stability of a well designed apparatus is usually sufficient to generate 2D spectra. However, the much longer times need to acquire 3D spectra create difficulties due to slow drifts in path lengths due, for example, to thermal effects. Thus 3DIR spectroscopy often require some type of stabilization or correction. The correction can be achieved by retaking certain spectra and measuring the phase difference between the signals.[29] Alternatively, an continuous wave (CW) auxiliary laser can be used to monitor and lock the path lengths.[30]

In the near-IR and visible, the greater challenges have been met in a number of ways. As in the infrared, it is possible to use a CW laser auxiliary laser and actively stabilize the delays using servo feed back.[13,30,31] Another approach is to use diffractive optics and common paths for beam pairs.[10,11] In this approach, the delays between the phase related beams are generated using glass wedges, which has a very limited range. In addition, the delay between the pairs of beams is unstabilized.

It is also possible to use pulse shapers to generate the required pulse sequences. This can be implemented using a 2D spatial light modulator in a diffractive mode to generate beams in the box geometry.[32] This approach produces beam with all delays phase locked, however the delay range produced by pulse shaping is typically limited to a few tens of picoseconds. Another approach is to use a pump-probe geometry where the pump is a pulse pair produced by a pulse shaper.[33] This is probably one of the easiest ways to produce 2D spectra, but does have the limitation on delay range and the fact that the delay between the pump pulses and probe are not locked.

Finally, an interesting approach is to not phase stabilize or correct at all, but rather to use a phase retrieval algorithm to correct the phases of the as-measured spectra.[34] Phase retrieval in optics is best known for its use in frequency resolved optical gating, a method for determining the electric field of ultrashort pulses.[35]

3 Three-dimensional spectroscopy

Only a limited number of 3D spectroscopy results have been reported in the literature. They will be reviewed in this section, virtually in their entirety. The results will be classified by the wavelength regime (IR or visible) and the order of nonlinearity (third order or fifth order). Some reports have been focused primarily on demonstrating 3D techniques, although many of the more recent ones are moving beyond technique development and focusing on the unique information that can be obtained from 3D spectra.

3.1 Fifth-order 3D infrared spectroscopy

Extending multidimensional spectroscopy into a third dimension was discussed theoretically for infrared and/or Raman excitation of molecular vibrations by Park and Cho[36]. Their results showed that three-mode coupling constants could be measured using 3D vibrational spectroscopy, while they are not accessible using 2D spectroscopy. This work was later generalized to properly describe the effect of bath degrees of freedom[37]. Further theoretical investigations by Hamm considered 3D spectra that are generated from a fifth order nonlinear response[38]. The motivation of this study was to provide information about solvation effects beyond a linear response theory. Such non-Gaussian effects require the measurement of the three-point frequency fluctuation correlation function, which is inaccessible in third order measurements. In addition, fifth-order spectroscopy can access $v = 2$ to $v = 3$ vibrational transitions, which are also not accessible in third-order experiments.

Some of the first 3D infrared measurements were published by Ding and Zanni[21]. This paper reported 3DIR of spectra carbonyl vibrations in 3 different model systems, $\mathrm{W(CO)}_6$ in hexane, azide in an ionic glass and an iridium dicarbonyl in a mixture of hexane and cholorform. These systems were chosen because the properties and dynamics of their carbonyl vibrations were well known. This work used the fifth-order response in a two-quantum three-pulse sequence. The fifth-order response was isolated by phase matching. The results for azide in glass are reproduced in Fig. 2. The elongation is due to inhomogeneous broadening from interactions with the ions in the glasseous solvent. These results extended earlier work using fifth-order 2DIR spectroscopy to study the same system[39] and helped set the foundations for interpreting 3DIR spectra.

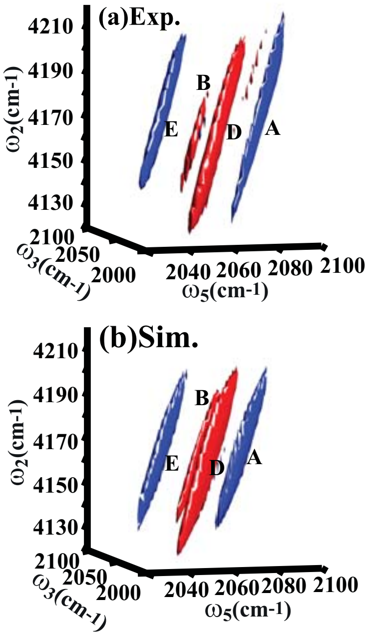

Fig. 2 Experimental real fifth-order 3D IR spectrum of azide in glass generate using a 3 pulse excitation sequence. [adapted from ref[21], with permission of the authors].

One drawback of using only 3 pulses to generate a fifth-order signal is that a purely absorptive spectrum, as was demonstrated in 2DIR spectroscopy[40], cannot be generated. This difficulty was overcome by Garrett-Roe and Hamm using a 5-beam apparatus[41,42]. Their measurements of CO_2 in water agreed well with simulations. This work established a basis for studying isotope substituted liquid water using 3D spectroscopy.[22] These measurements revealed heterogeneous structural relaxation dynamics. The heterogeneity was attributed to subensembles of water molecules that did not interconvert on the half-picosecond timescale of the measurements.

Another advantage of a fifth-order signal is that it can produce population in the doubly excited states, whereas a third-order signal can only create a coherence between the singly and doubly excited states. This ability was used to study the vibrational dynamics of the OD stretch mode in ice.[43] Fifth-order 3DIR spectra, an example is shown in Fig. 3, were acquired using a 5 pulse excitation sequence as function of the waiting time between the 4th and 5th pulses. By plotting decay of peak volumes, the decay of the populations of the vibrationally excited states could be measured and compared with simulations. The results suggest that the second excited state lives for such a short time that the concept of a second excited state of the OD vibration becomes essentially meaningless as the mode is strongly mixed with lattice degrees of freedom.

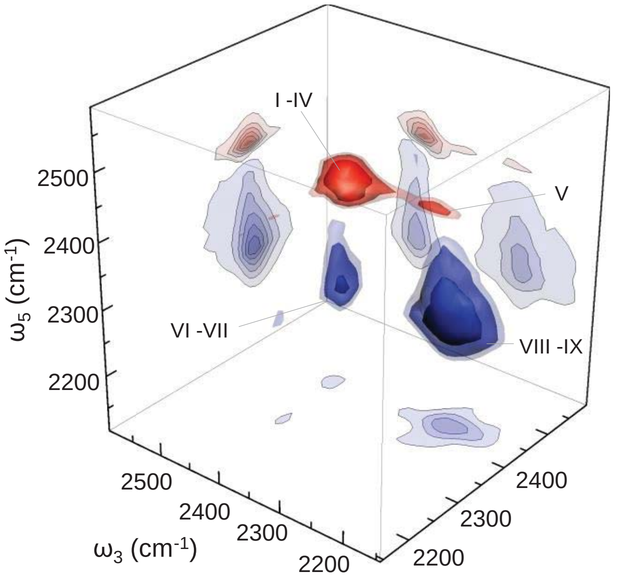

Fig. 3 Experimental 3D IR coherent spectrum of the OD stretch of isotope diluted ice at populations times of $t_2 = t_4 = 100$ fs.[adapted from ref[43], with permission of the authors]

Very recently, a new implementation of fifth-order 3DIR spectroscopy has been demonstrated[44]. This approach uses a dual pulse shaper that generates a pair of pump beams and each pump beam is a pair of pulses. The effect of the pump pulses on a probe beam is measured and used to construct a 3D spectrum, as was done earlier for 2D spectroscopy[33].

3.2 Fifth-order 3D electronic spectroscopy

Visible or near-IR light must be used to access electronic transitions, rather than the vibrational transitions excited by infrared light. Performing multidimensional coherent spectroscopy in the near-IR or visible regime is more challenging than in the infrared because of the difficulty in maintaining the phase stability between the excitation pulses. This difficulty is greatly increased when performing 3D spectroscopy. Not only is the acquisition time longer, thus phase stability must be maintained that much longer, but in addition phase stability is typically required for all time delays, whereas for 2D spectroscopy it is typically only needed between two pairs of pulses.

One demonstration of 3D spectroscopy in the visible regime used a fifth order response from a 3-pulse sequence.[23] The geometry and pulse sequence was similar to that used in the IR by Ding and Zanni,[21] however, it used a single-shot method to acquire underlying one-dimensional spectra.[45] Using this method, a 3D spectrum, as shown in Fig. 4, could be acquired in 8 minutes, which greatly reduced the issues of long term phase drift. The initial measurements were made on IR144 dye dissolved in methanol. The 3D spectrum revealed a vibronic cross-peak that was fully resolved. This peak cannot be observed in 2D spectra because it is masked by the diagonal peak. Simulations based on a cumulant expansion truncated at second order reproduced the basic features in the 3D spectrum. Since fifth-order spectroscopies are sensitive to three-point frequency correlations, truncating the cumulant expansion at second order is typically insufficient, however it is exact if the system displays Gaussian statistics. While the simulations displayed similar overall structure to the experiment, the spectral locations did not match. The disagreement between experiment and simulation were attributed to not having included the proper vibrational modes or incorrect coupling strengths.

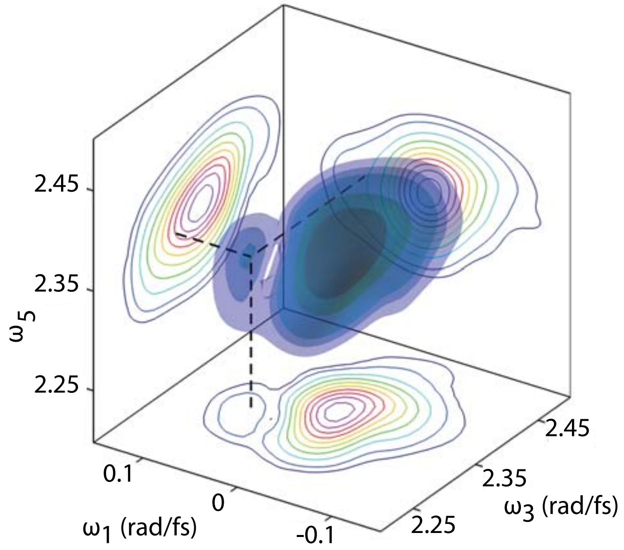

Fig. 4 Experimental fifth-order electronic 3D spectrum of IR144 produced using 3 excitation pulses. The dashed lines indicate a vibronic cross peak that is hiden in a 2D spectrum. The ω_1 axis is detected in a rotating frame. [adapted from ref[23], with permission of the authors]

Purely absorptive fifth-order electronic 3D spectroscopy was demonstrated using a 5-pulse sequence.[46] This approach uses a pump-probe geometry as was first demonstrated for 2D spectroscopy[33]. In 2D spectroscopy, the pump is a two-pulse sequence and the appropriate terms are separated by the Fourier transform. To perform the fifth-order experiment the pump consisted of a 4 pulse sequence, again generated by a pulse shaper. The method was demonstrated on cholorophyll *a* dissolved in methanol.

3.3 Third-order 3D Electronic Spectroscopy

The previous two sections have desribed 3D spectroscopy based on the fifth-order nonlinear response, whereas 2D spectroscopy is usually based on the third-order response. It is natural to increase the order of the nonlinearity when increasing the dimensionality of the spectroscopy. In the most common pulse sequence used to generate a 2D spectrum, known as a rephasing spectrum (often designated as S_I), the two frequency dimensions correspond to times in which the system is in a coherent superposition state between two levels connected by a dipole-allowed transition. During the third time, known as the "waiting" time or "mixing" time, the system is usually described as being in a population state, which does not oscillate. Thus to have a third frequency dimension that corresponds to the system being in a dipole-allowed superposition state, the fifth-order nonlinear response must be used.

However, the description of the system being in a population state during the waiting time, T, is strictly only correct for a two-level system. If the system is has two excited states, then it can be in a coherent superposition of those two states, which will oscillate, during T. These coherences can be observed by scanning T and displaying an alternate 2D spectrum.[47] But they will also result in a 3D spectrum that has peaks at finite ω_T. In addition, by using a different pulse ordering known as S_{III} because the conjugated pulse arrives third, it is possible to put the system in a "two-quantum coherence" during the time T,[48–50] which will also generate peaks in third order 3D spectra.

Third-order 3D electronic spectroscopy was demonstrated on excitonic resonances in GaAs quantum wells.[24] This measurement used a diffractive pulse-shaper to generate four phase locked pulses (3 for exciation, one as local oscillator).[12] Both S_I and S_{III} spectra were generated. Projections of the 3D spectra were used to show that individual quantum pathways could be isolated, even though they are not isolated in standard 2D spectra. A similar setup has recently been used to study asymmetric double GaAs quantum wells[51]. In addition to using 3D spectra, this work also selects specific pathways by tailoring the spectra of the exciting pulses. The pathway-select spectra reveal coherent interactions between the spatially separated excitons.

Adding a third dimension proved to be quite useful for multidimensional spectroscopy based on phase retrieval.[27] Phase retrieval methods, first demonstrated in two-dimensions,[34] do not rely on phase stabilization of the pulse sequence, but rather utilize phase retrieval algorithms, similar to those used in ultrashort pulse measurement method such as frequency resolved optical gating,[35] to correct the as-measured phases. Extending this to a third dimension actually improves the method because it eliminates some ambiguities. An example of a 3D spectrum produced by solving the phase retrieval problem is shown in Fig. 5 for a GaAs double quantum well sample, which display a very rich 2D spectrum.[52] Extending the spectrum into a third dimension helps to isolate the various contributions and give greater insight into the mechanisms responsible for the various peaks. More recently, these studies have been to extended to examine the correlation of the inhomogeneous broadening, which is due to fluctuations of the well widths.[53] The 3D spectra show that the broadening is uncorrelated for excitons localized in different wells, whereas it is correlated for the heavy-hole and light-hole excitons localized in the same well.

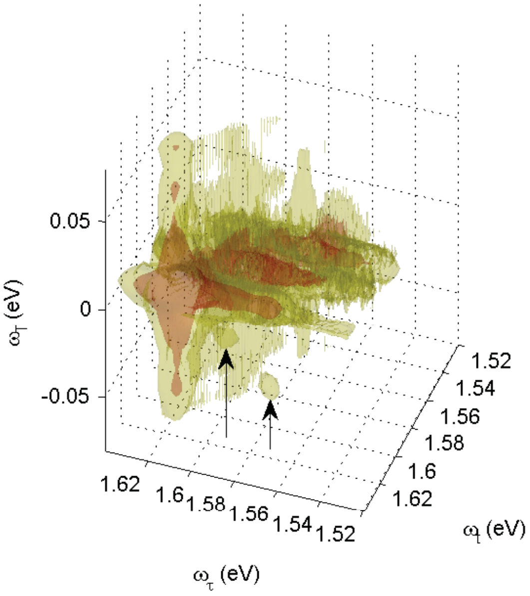

Fig. 5 Experimental 3D electronic spectrum produced by solving the phase retrieval problem. The sample is double GaAs quantum well. [adapted from ref[27], with permission of the authors]

Two-dimensional electronic spectroscopy of light harvesting centers provided evidence for the involvement of quantum coherence.[19,20] These results have provoked significant discussion. The evidence was based on monitoring the evolution of peaks in the 2D spectrum as a function of waiting time T, which suggest that a 3D spectrum could provide further insight. Third-order 3D electronic spectroscopy was performed on the Fenna-Matthews-Olson complex by Hayes and Engel.[25] The 3D spectra helped resolve the different excitonic transitions, which are strongly overlapping in 1D and 2D spectra. Analysis of planes of constant ω_T in the 3D spectra improved the determination of the excitonic transition energies. This improved information was used to calculate the Hamiltonian in a site basis.

The idea of using a 3D spectrum to determine the parameters of the Hamiltonian was taken further by Li *et al.*[26] This work showed that by using a 3D spectrum generated by the third order response (see Fig. 6), it was possible to isolate spectral "peaks" that corresponded to a single quantum pathway. By analyzing such a peak, it is possible to determine all of the parameters of the Hamiltonian that are relevant for the third order response. These parameters include the transition frequencies, dipole moments and relaxation rates, including both the dephasing rate and population rate. This ability was demonstrated on a potassium vapor, which is a simple 3-level system. For a system that has a manifold of doubly excited states, the population decay of the doubly excited states cannot be determined, nor can any information about higher lying states. However, a full third order susceptibility can be determined. The ability to determine the Hamiltonian could be enabling for coherent control, where it is essential for deterministic control and greatly improves the efficiency of optimal control schemes.

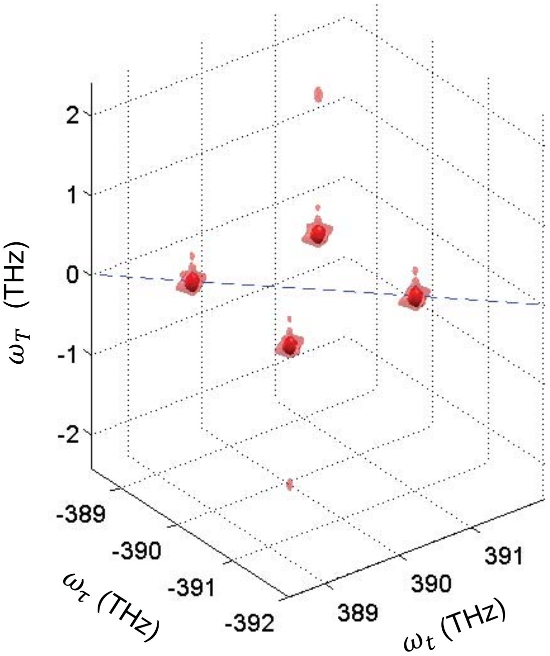

Fig. 6 Experimental rephasing 3DFT spectrum of a potassium vapor obtained with the conjugated pulse arriving first, corresponding the S_I 2D coherent spectrum. [adapted from ref[26], with permission of the authors].

3.4 3D Coherent Frequency Domain Spectroscopy

An alternative approach to multidimensional coherent spectroscopy has been pioneered by Wright.[54,55] In this approach, the two-dimensional spectrum is produced by tuning two narrow band lasers. A third laser, with a fixed frequency, produces a signal, which can be at a very different wavelength than the tunable lasers. In the first demonstration of producing a 2D spectrum using this method, the tunable lasers were in the infrared and excited vibrations, whereas the third laser was 532 nm, thereby producing a visible signal.[55] The spectra demonstrated the spectral selectivity of this approach, its sensitivity to the interactions causing mode coupling and ability to spectrally resolve isotopic mixtures.

This method has recently been extended to produce 3D spectra.[56] To produce 3D spectra, the third laser is broadband and a spectrometer is used to measure the signal spectrum. The three dimensions are then the frequencies of the first two lasers and the signal frequency. The goal of this demonstration was to examine gas phase Br_2 with high resolution. The one-dimensional spectrum is very dense and congested. By spreading it out in a higher dimensional space, it is easier to identify and assign the spectral lines.

4 Discussion

Whenever a new measurement method is introduced that seems more complex and demanding than existing methods, it is natural the wonder whether or not the extra effort if merited. This question certainly arose when 2D coherent spectroscopy was getting started. At this point it seem that for 2D spectroscopy, the answer is clearly "yes". It is natural for this discussion to occur for 3D spectroscopy as well, and it has already begun.[42] In the case of NMR, 3D, and even 4D, Fourier transform spectra have proven very useful for studying larger proteins.[57]

As optical 3D spectroscopy is still in its early stages, it is difficult foretell how this question will play out. Studying the examples given above, it is interesting to note that they mostly all demonstrate a distinct or unique advantage to 3D spectroscopy, which indicates that the use of the technique is still in an early "exploratory" phase where its strengths and weaknesses are still being identified. The examples discussed in section 3 demonstrate that 3D spectroscopy has the following capabilities:

- disentangling peaks congested spectra,
- revealing hidden peaks,
- observing higher-order correlatons and non-Gaussian statistics,
- measuring populations of multiply-excited states,
- completely determining the Hamiltonian,
- enabling phase retrieval.

The first two of these can also be attributed to 2D coherent spectroscopy when compared to 1D or 2D incoherent spectroscopies. Thus they are not really "new" for 3D spectroscopy, but rather a further enhancement of the capabilities of 2D spectroscopy. This enhancement will be more important with increasing complexity of the system being studied, which will happen gradually as multidimensional spectroscopy becomes more widespread.

The ability of 3D spectroscopy to probe higher-order correlations and non-Gaussian statistics may seem esoteric. However, these do represent qualitative progress over 2D spectroscopy that is enabled by going to a spectrum with a higher dimensionality. While Gaussian statistics are often used because they are mathematically tractable, the truth is most interesting systems actually have non-Gaussian statistics, it has just been hard to adequately characterize them. Thus, the improved characterization provided by 3D spectroscopy may be impetus needed to push our understanding to the next level.

Multiply-excited states can become populated for strong driving fields. Understanding their dynamics is important in some circumstances, and it cannot be done with a simple 2D measurement. However, these populations can be accessed by simply pre-exciting the sample and then taking a 2D spectrum, which may be simpler approach than 3D spectroscopy.

Completely determining the Hamiltonian of a system, or determining part of it, can be very useful, but is rarely an end in of itself. It could serve as auxiliary measurement in support of a goal such as coherent control. It can also be help provide a complete description of complex systems, such as in light harvesting, that are intrinsically interesting and thus worth the effort.

Finally, the significant improvement in solving the phase retrieval problem for a 3D spectrum, as compared to a 2D spectrum, suggest that it is a better choice. The question here will be whether the simplification of the experiment enable by phase retrieval will prove to outweigh the increase in data processing complexity. In addition, it remains to be seen if phase retrieval can be applied to more complex systems.

5 Conclusions

The first experiments demonstrating optical 3D coherent spectroscopy were performed about 6 years ago. [21] Since then, additional optical 3D spectroscopy experiments have been performed, although the number remains relatively small. These experiments have demonstrated some of the unique capabilities of 3D spectroscopy, however it remains to be seen if these capabilities will warrant the extra technical effort required to perform 3D spectroscopy.

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