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Three-dimensional electronic spectroscopy of excitons in asymmetric double quantum wells

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We demonstrate three-dimensional (3D) electronic spectroscopy of excitons in a double quantum well system using a three-dimensional phase retrieval algorithm to obtain the phase information that is lost in the measurement of intensities. By extending the analysis of two-dimensional spectroscopy to three dimensions, contributions from different quantum mechanical pathways can be further separated allowing greater insight into the mechanisms responsible for the observed peaks. By examining different slices of the complete three-dimensional spectrum, not only can the relative amplitudes be determined, but the peak shapes can also be analysed to reveal further details of the interactions with the environment and inhomogeneous broadening. We apply this technique to study the coupling between two coupled quantum wells, 5.7 nm and 8 nm wide, separated by a 4 nm barrier. Coupling between the heavy-hole excitons of each well results in a circular cross-peak indicating no correlation of the inhomogeneous broadening. An additional cross-peak is isolated in the 3D spectrum which is elongated in the diagonal direction indicating correlated inhomogeneous broadening. This is attributed to coupling of the excitons involving the two delocalised light-hole states and the electron state localised on the wide well. The attribution of this peak and the analysis of the peak shapes is supported by numerical simulations of the electron and hole wavefunctions and the three-dimensional spectrum based on a density matrix approach. An additional benefit of extending the phase retrieval algorithm from two to three dimensions is that it becomes substantially more reliable and less susceptible to noise as a result of the more extensive use of *a priori* information.

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I. INTRODUCTION

Over the past decade, two-dimensional (2D) electronic spectroscopy has become an increasingly useful tool for elucidating the ultrafast dynamics of complex condensed matter systems. The great advantage of 2D spectroscopy is that it can isolate different quantum mechanical pathways and reveal in more detail the mechanisms of energy transfer and relaxation.¹ In complex samples, however, there are often multiple pathways that can generate overlapping peaks in the 2D spectrum. Much work has been devoted to devising additional means to separate the signals from such pathways. Plotting the contributions from the rephasing and non-rephasing pulse orderings separately can isolate and distinguish between some different pathways.^{2,3} Polarisation control can be used to enhance or cancel specific pathways based on the orientational factors.^{3,4} Each of these advances enhances the analysis of 2D spectra, yet there remain cases where overlapping peaks prevent unambiguous analysis of the data.

One of the most significant applications of 2D electronic spectroscopy has been the ability to identify long-lived coherences in biological systems.^{5–8} In each reported case, the identification of the coherence has been based on the observation of oscillations of specific diagonal or cross-peaks in the 2D spectra as a function of waiting time. This evidence is convincing and further analysis has provided significant insight into the architecture of complex photosynthetic processes.^{7,8} A clear and detailed characterisation of the properties and origin of these long-lived coherences has, however, proven to be elusive. For example, there has been speculation that the reason why these long-lived coherences exist is because of the correlated nature of the interactions with the environment,^{5,6,8} but the evidence remains inconclusive.

Multidimensional spectroscopy, of which 2D spectroscopy is one example, is typically based on a three-pulse transient four-wave mixing experiment (TFWM), though higher-order experiments are also possible and have recently been reported.^{9–11} The corollary of employing three pulses is that there are three relevant time domains within which to describe the interactions: τ , the delay between the first two pulses; T , the delay between the second and third pulses, and t , the delay between the third pulse and the signal emission. A

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2D Fourier transform with respect to τ and t is typically performed to generate traditional 2D spectra as a function of the conjugate frequency variables, ω_τ and ω_t . Recent work has reported on the ability to resolve different pathways by the extension of 2D optical spectroscopy to three-dimensional (3D) spectroscopy.^{9,11,12} This is achieved by performing an additional Fourier transform with respect to T to give the data as a function of ω_τ , ω_t , and ω_T . In these reports the complete 3D spectrum is projected onto each pair of axes and shown as 2D spectra representing correlations in different temporal domains. In this manner, peaks proceeding via Raman-like coherences and are separated along the ω_T axis and correlated to either ω_τ or ω_t . In this work, we show through simulation and experiment that careful analysis of the complete 3D spectrum can reveal much more information. For example, by plotting 2D slices for different values of ω_T , peaks arising from coherence pathways can be isolated and analysed in the manner of traditional 2D spectra, allowing insight into the mechanisms of inhomogeneous broadening and interactions with the environment and the identification of any correlation of these across different transitions.

The application of this approach is demonstrated for a GaAs/AlGaAs asymmetric double quantum well (QW). 2D spectroscopy has previously revealed much detail of many-body effects in semiconductor QWs,^{9,10,13–16} including double QWs.¹⁷ Yang *et al.*¹² were also able to reveal the Raman-like coherence between heavy-hole and light-hole excitons by projecting the four-wave mixing (FWM) data onto the (ω_τ, ω_t) plane. Asymmetric double quantum wells have been studied for over a decade, for a range of potential applications and as a template to study fundamental quantum mechanical interactions, such as tunnelling and coherent coupling between spatially separated oscillators.^{18–20} For the experiments reported here, the barrier separating the two QWs was 4 nm wide. This limits the probability of tunnelling, as shown by calculations, but the separation is small enough that other Coulomb mediated coupling mechanisms, such as dipole-dipole coupling, remain possible. The widths of the two wells were chosen so that the energy separation between the two heavy hole exciton transitions was 45 meV. By acquiring 3D spectra we are able to observe the Raman-like coherence between the two heavy-hole excitons of the two QWs. In Sec. IV, we show how careful analysis of these data allows us to discern whether the inhomogeneous broadening of the two coupled transition is strongly correlated. Furthermore, we are able to use such analysis to identify an unexpected cross-peak that only becomes evident in the 3D spectrum.

In order to generate the experimental 3D spectra we measured the spectrally resolved intensity from three-pulse TFWM experiments. To recover the phase we extended the 2D phase retrieval approach developed by Davis *et al.*^{21–23} to include the evolution in T , making it a 3D phase retrieval problem. The details of this approach and the significant advantages gained are discussed in Sec. II.

II. OBTAINING 3D SPECTRA

Transient four-wave mixing experiments are performed using an 80 MHz repetition rate titanium-sapphire oscillator

FIG. 1. Some of the possible pathways for a simple three-level system are depicted. The top row shows pathways with the rephasing pulse ordering, the second row shows non-rephasing, and the bottom row shows the double coherence pulse ordering. The first two columns show population pathways leading to diagonal peaks, where b could replace a to give the other diagonal peak. The next two depict pathways leading to cross-peaks as a result of population relaxation. The final two represent the coherence pathways, with the rephasing pathways generating cross-peaks and the non-rephasing pathways generating diagonal peaks, all of which oscillate in T at the frequency matching the energy difference.

with near transform-limited pulses of 60 fs duration. For the purpose of this discussion the signal detected is the one emitted in the phase matched direction $\vec{k}_4 = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$, where $\vec{k}_1$, $\vec{k}_2$, and $\vec{k}_3$ are the wave vectors of the three incident pulses. The emitted signal is spectrally resolved and the delays τ and T varied to give the signal intensity $I(\tau, T, \omega_t)$. Multi-dimensional spectroscopy in all its forms relies on the Fourier transform relationship between time and frequency. In the present case, results from the three-pulse transient four-wave mixing experiments are analysed as a function of three temporal variables and the three corresponding frequency variables. To obtain the 3D spectrum from the measured intensity, $I(\tau, T, \omega_t) = |E(\tau, T, \omega_t)|^2$, a two-dimensional Fourier transformation of the electric field, $E(\tau, T, \omega_t)$, with respect to τ and T is required for each value of ω_t . In order to perform these Fourier transforms, however, the phase evolution typically lost in the intensity measurements is required. This phase information can be determined by heterodyne detection and interferometry, as is the case in traditional 2D spectroscopy realisations, where phase stability is only required between pairs of pulses.^{1,24}

In extending the analysis to 3D, phase stability is also required over the waiting time, T , meaning phase stability is required between all four pulses. During the waiting time, however, the phase does not evolve at optical frequencies, as is the case for τ and t , but depends instead on the pathway. For population pathways, as represented by the pathways in Fig. 1(i-iv, vii-x), it will be constant. For coherence pathways, such as those represented by pathways v, vi, xi, and xii in Fig. 1, it will oscillate at the frequency of the excited (or ground) state coherence. For double quantum coherence pathways, as depicted by Fig. 1(xiii, xiv), the phase will oscillate at frequencies twice the optical frequency. In double quantum coherence experiments the stability requirements over T are more stringent than for the other delays. This type of experiment has recently been realised by

several groups.^{10,16,25,26} In the first two cases, however, the stability requirements are relaxed due to the slow phase oscillations. This level of stability could easily be achieved in the most 2D spectroscopy experiments and in the discussions of this article we focus on these population and coherence pathways. Whilst the stability requirements are relaxed, care still needs to be taken that the experimental conditions do not change between temporal points at different values of T . Given that the complete scans at different values of T can often take several days, this becomes more difficult. Harel *et al.* recently demonstrated the acquisition of a complete 2D spectrum in a single shot,²⁷ which overcomes the time constraint. It does, however, acquire each time point from a different position on the sample which may lead to phase jumps if the sample is not homogeneous. To overcome such problems, we take an alternative approach and recover the complete phase information from intensity measurements using the phase retrieval procedure described below. In this case the measurements are insensitive to phase fluctuations and phase stability between pulses is not necessary. This type of algorithm could also be used to complement more common interferometric techniques by optimising the phase of each 2D spectrum acquired at different values of T to obtain a fully consistent dataset.

The approach utilised here draws on phase retrieval techniques that have been used for signal processing in a broad range of science and engineering applications for over 40 years.^{28–32} The utilisation of these techniques in 2D spectroscopy has been reported previously,^{21,22} and we follow a similar approach in extending the problem to three dimensions. In this case the measurements are insensitive to phase fluctuations and phase stability between pulses is not necessary.

Like all phase retrieval approaches, intensity information in one Fourier domain, $|E(\tau, T, \omega_t)|$ in this case, and some other *a priori* information in the conjugate Fourier domain are required. In the 2D case, the additional information is in the form of support constraints which specify where there may be signal and more particularly where there must be no signal. These constraints are typically defined based on the laser pulse properties, and the measured decoherence times, emission spectrum, and linear absorption spectrum of the sample under investigation. For the 3D case, we extended this process to include the evolution in the dual variables T and ω_T . We then define the support in the (τ, T, t) and $(\omega_\tau, \omega_T, \omega_t)$ domains. The support along the τ, t, ω_τ , and ω_t axes are determined in the same manner as for the 2D case. The support along T is defined by knowledge of the evolution in T based on causality and the measured lifetime. Along the ω_T axis the support is based on the maximum energy differences between the red and blue edges of the laser spectrum and/or the linear absorption spectrum of the sample under investigation. In all cases, it is essential that the constraints accurately represent the physics of the sample and do not unreasonably eliminate possible solutions. For example, many-body effects in some systems can lead to signals at negative delays where they might otherwise not be expected. In order to accommodate such effects it is imperative that the support constraints are defined such that

FIG. 2. The actual 3D spectrum directly from the simulated data is compared to the equivalent spectrum from the data recovered using the 3D phase retrieval algorithm. The red and yellow surfaces represent isosurfaces of the same amplitude (enhanced online) [URL: <http://dx.doi.org/10.1063/1.3613679.1>].

this type of negative delay signal is not ruled out where it may provide a feasible solution.

The accuracy of this 3D phase retrieval process was verified by comparison to simulated data in much the same way as was done for the 2D case.^{21,22} The 3D data obtained directly from the simulation is compared to the output of the phase retrieval algorithm, which uses the intensity as a function of τ , T , and ω_t from the simulation as pseudo experimental data. The complete 3D spectra are shown in Fig. 2, where the same peaks are present in the same location with the same peak shape and the same amplitude. Any variations or uncertainties in the phase would generate peaks away from $\omega_\tau = 0$ that would not necessarily match the correct 3D spectrum. This is clearly not the case here, confirming that the 3D phase retrieval algorithm has successfully recovered the phase information and the 3D spectrum. Fine details of the spectrum can more easily be resolved by examining 2D slices. The 2D spectrum for each waiting time is shown in the form of a movie in the supplementary material. This series of comparisons shows some slight differences between the actual and recovered data, but these are only very minor and inconsequential for any subsequent analysis.

By extending the phase retrieval problem to three dimensions it becomes much more tightly constrained due to the additional intensity data and the support constraints in ω_T . Specifically, the improvement compared to the 2D case comes from the definite relationship between each 2D slice. This is realised by the support constraints applied in ω_T and T , and the requirement that the phase of the signal evolves smoothly as a function of T . As a result, the phase retrieval procedure becomes significantly more reliable and reproducible and less susceptible to the effects of noise in the data. A comparison of the results from the 2D and 3D phase retrieval algorithms is depicted in Fig. 3, which shows the recovered 2D spectra for a waiting time of 230 fs. The intensity data from the simulation was normalised to the maximum of $I(\tau, T = 230 \text{ fs}, \omega_t)$ and noise was added with a normal distribution centred at 0 and standard deviation (σ) that was varied. In the case of $\sigma = 0.1$, both the 2D and 3D algorithms are able to accurately recover the 2D spectrum. As the noise level is increased, however, the quality of the recovery obtained from the 2D algorithm begins to decrease rapidly whereas the 3D algorithm continues to accurately

FIG. 3. Comparison of the 2D spectrum recovered by the 2D and 3D phase retrieval for a waiting time of 230 fs and different amounts of noise. The pseudo experimental data was normalised to the maximum at a waiting time of 230 fs. A random normal distribution of noise was added with standard deviation as listed on the right. For values greater than 0.5, the 2D algorithm fails to converge whilst the 3D algorithm continues to converge up to 1.0. The panel in the bottom left shows the spectrum at $\tau = 0$ and $T = 230$ fs, with a standard deviation of 1.0 for the noise distribution, for the pseudo experimental data (thin blue line), and recovered data (thick red line).

recover 2D spectrum. When the noise level exceeds 0.5 the 2D algorithm does not converge and no recovery is obtained. At this level of noise the 3D algorithm continues to accurately recover the 2D spectrum and it is not until the standard deviation of the noise distribution is greater than one that it fails to converge. The quality of the recovered spectrum from the 3D algorithm begins to diminish above $\sigma = 0.6$ but all of the main features of the data can still be observed up to $\sigma = 1.0$. To give an indication of the level of noise with $\sigma = 1.0$ the spectrum at $\tau = 0$, $T = 230$ fs for the pseudo experimental data is shown at the bottom of Fig. 3. The recovered spectrum from this point is also plotted and clearly demonstrates the extent of the noise on this the strongest part of the signal at $T = 230$ fs, and the ability of the phase retrieval algorithm to pick out the signal from the noise.

The lifetimes of the excitons probed in the experiments discussed here are typically of the order of hundreds of picoseconds. To obtain sufficient data over the entire range of T would consume enormous amounts of experimental time.

Such an approach is unnecessary, because, beyond a certain point, the response functions are known to decay exponentially. We therefore use this information in the phase retrieval and only acquire data out to the point where the evolution of the signal is purely exponential. The measured decay rate is then used in the phase retrieval algorithm to determine the complete evolution of the signal and allow the Fourier transforms to proceed without any edges. In general, the decay of the signal need not be exponential, but so long as its evolution can be described by a simple mathematical relation this approach can be used.

III. NUMERICAL SIMULATIONS

A. Simulating the 3D experiment

In order to identify the basic properties and characteristic behaviours of 3D spectroscopy, we report here some results from numerical simulations. The simulation is based on solving the Liouville formulation of the Schrödinger equation ($i\hbar\dot{\rho} = [H, \rho]$) for the time-evolution of the density matrix, $\rho(t)$, for a V-type three-level system, as described in detail previously.³³ This approach intrinsically includes all possible pathways, in contrast to the response function approach which is limited to the pathways specifically incorporated and so can be unrepresentative of real data if any pathways are left out.

Inhomogeneous broadening was incorporated by integrating over the inhomogeneous distribution of transition energies. The distributions for the two excited states can be correlated, so that the energy difference between them remains constant or uncorrelated, so that the energy difference varies randomly. In order to clarify the effects of correlated/uncorrelated inhomogeneous broadening, many-body effects were explicitly left out of these simulations.

For the discussions presented below the two electronic transition energies were 1.38 eV and 1.42 eV, with the laser pulse centred between them at 1.40 eV with a transform limited pulse duration of 50 fs. Correlated or uncorrelated inhomogeneous broadening was included with a FWHM of 10 meV for a Gaussian distribution. Decoherence times for the two electronic transitions were set to 300 fs and the lifetimes of the two excited states set to 600 fs. The decoherence time of the excited state coherence ($2|3\rangle$) was set to 300 fs.

Previous work analysing coherence beats in 2D spectra^{34,35} revealed that in the rephasing spectra the cross-peaks will beat as a function of T at a frequency corresponding to the energy difference between the two coupled states. For the non-rephasing pulse ordering, however, the cross-peaks do not oscillate and the diagonal peaks do. The same behaviour is reproduced in the simulations described here. We are, however, able to take this analysis a step further. The plots in Fig. 4(a) show the real part of the 2D rephasing spectrum with correlated inhomogeneous broadening for different values of T . Not only can the magnitude of the cross-peaks be seen to oscillate, but their line shape also oscillates, corresponding to phase oscillations. In Fig. 4(b), the cross section at $\omega_\tau = 1.42$ eV is plotted as a function of T and clearly depicts the phase oscillations of the cross-peak at $\omega_l = 1.38$ eV. This type of line shape modulation was

FIG. 4. (a) The real part of the simulated 2D spectrum for the rephasing pulse ordering only is shown for waiting times 30 fs, 70 fs, 110 fs, and 150 fs. The evolution of the two cross-peaks reveals the line shape oscillations corresponding to the changing phase as the coherences evolve. The cross section at $\omega_\tau = 1.42$ eV is shown in (b) as a function of waiting time, T , and clearly depicts the phase oscillations. oscillations (enhanced online) [URL: <http://dx.doi.org/10.1063/1.3613679.2>].

observed in simulations previously,^{36,37} and attributed to vibrational coupling. The results presented here show that this need not be the case and that line shape oscillations can be seen, and should be expected, for any pair of coupled transitions evolving as $\exp(\pm i\omega_{23}T)$. Though it is not discussed explicitly, similar behaviour can be identified in the simulations of Cheng and Fleming.³⁵ A corollary of the beating in T is that peaks are expected at $\omega_T \neq 0$. If just the amplitudes were beating without the phase evolution, one would expect to find symmetric peaks either side of $\omega_T = 0$. This, however, is not the case and peaks are present only at $\omega_T = \omega_{23}$ or $-\omega_{23}$, depending, respectively, on whether they arise from pathways involving the $|2\rangle|3\rangle$ or $|3\rangle|2\rangle$ coherence.

Fourier transforming $E(\omega_\tau, T, \omega_t)$ with respect to T generates the 3D spectrum,³⁸ slices of which are shown in Fig. 5(a) for $\omega_T = -\omega_{23} (= -0.04$ eV), $\omega_T = 0$, and $\omega_T = \omega_{23} (= 0.04$ eV). At $\omega_T = 0$, the inhomogeneous line shapes are apparent with all peaks elongated along the diagonal and the two diagonal peaks more intense than the two cross-peaks. At $\omega_T = -\omega_{23} = -0.04$ eV the peak at $(\omega_\tau, \omega_t) = (\omega_{13}, \omega_{12}) = (1.42$ eV, 1.38 eV) is enhanced with respect to the other peaks, and corresponds to the pathways proceeding via the $|2\rangle|3\rangle$ coherence. In the case in which $\omega_T = \omega_{23} = 0.04$ eV, the peak at $(\omega_{12}, \omega_{13}) = (1.38$ eV, 1.42 eV) is enhanced, corresponding to the pathways proceeding via the $|3\rangle|2\rangle$ coherence. The pathways shown in Fig. 1 suggest that these coherences should also generate signals on the diagonal at 1.42 eV for $\omega_T = -\omega_{23} = -0.04$ eV and 1.38 eV for $\omega_T = \omega_{23} = 0.04$ eV. This is indeed the case for homogeneous broadening, as shown in the supplementary material, but is reduced for inhomogeneous broadening. The incorpora-

FIG. 5. Slices of the 3D simulated spectrum are shown for $\omega_T = -\omega_{23}, 0, \omega_{23}$ with correlated, (a), and uncorrelated, (b), inhomogeneous broadening. (The full 3D images are available in the supplementary material (Ref. 38)). The peaks at $\omega_T \neq 0$ arise purely from the coherence pathways. The changes to the cross-peaks in the slices for $\omega_T \neq 0$ reveal whether the inhomogeneous broadening across the two transitions is correlated or uncorrelated. In (b), the colour scales of the spectra at $\omega_T = \pm 0.04$ are scaled by a factor of 10 to make the peaks visible.

tion of correlated inhomogeneous broadening leaves ω_{23} constant across the ensemble. As a result, the evolution in the period T is identical for each component in the ensemble and rephasing still occurs for the coherence pathways that appear on the cross-peaks. Those that appear on the diagonals, however, only arise from the non-rephasing pulse ordering and so the destructive interference caused by the inhomogeneous broadening in the periods τ and t is permanent and the signal strength is reduced.

The same slices are plotted in Fig. 5(b) for uncorrelated inhomogeneous broadening. In this case the cross-peaks are weaker and much closer to the magnitude of the diagonal coherence peaks. To make the peaks visible the colour scales of the spectra at $\omega_T = \pm 0.04$ eV are scaled by a factor of 10. In this case only the population pathways that appear on the diagonals are able to rephase. The coherence pathways that were able to rephase in the case of correlated inhomogeneous broadening are no longer able to because the evolution over the period T is different for each component of the ensemble, or in other words, ω_{23} is inhomogeneously broadened which in a third order experiment cannot be reversed. This discussion of whether different pathways can be rephased or not depending on whether the inhomogeneous broadening is correlated or not should be equally evident in analysis of peak shapes.³⁹ In systems much more complex than a pair of well separated two-level systems it can become extremely difficult to draw any firm conclusions regarding peak shapes due to the overlap of different pathways. Previous work has looked at how peak shapes change as a function of waiting time to examine the dynamics of the interactions with the environment.³⁹ By looking at the slices of the 3D spectrum we are able to isolate coherence pathways and analyse the peak shapes in detail, without worrying about overlapping contributions from different pathways. Consider the cross-peaks at $(\omega_\tau, \omega_t) = (\omega_{13}, \omega_{12}) = (1.42$ eV, 1.38 eV) for $\omega_T = -\omega_{23} = -0.04$ eV and at $(\omega_\tau, \omega_t) = (\omega_{12}, \omega_{13}) = (1.38$ eV, 1.42 eV) for $\omega_T = \omega_{23} = 0.04$ eV. Correlated

FIG. 6. The potential well profile for the asymmetric double QW sample under investigation is shown together with the calculated wavefunctions for the two lowest states of the electron, heavy hole and light hole.

inhomogeneous broadening of these cross-peaks, which proceed via the coherence pathways, cause elongation in the diagonal direction, much like the diagonal peaks. In the case of uncorrelated inhomogeneous broadening, however, these peaks are round, with widths approximately equal to the inhomogeneous linewidths. Consequently, correlated and uncorrelated inhomogeneous broadening can be distinguished by the shape of the coherence cross-peaks.

The separation of the coherence pathways in this manner clearly provides great advantages over previously reported means of identifying the presence of such pathways by allowing line shapes for different pathways to be analysed in isolation. As well as static inhomogeneous broadening this technique should be able to resolve whether transient bath interactions are correlated or not and provide evidence for or against the suggestion that correlated bath interactions allow the long-lived coherences observed in photosynthetic systems.^{5-8,40}

B. Asymmetric double QWs

The sample investigated here is a GaAs/AlGaAs double quantum well with 5.7 nm and 8 nm wide GaAs QWs separated by a 4 nm AlGaAs barrier. In order to understand the dynamics observed, we have calculated the first two electron and hole energies and wavefunctions by solving the Schrödinger equation for the one-dimensional potential profiles shown in Fig. 6. To solve the Schrödinger equation we used the Numerov's method to propagate the wavefunction and the shooting method with bisection to determine the eigenenergies. The effective masses were assumed to be constant across the sample at $0.067 m_e$, $0.51 m_e$ and $0.082 m_e$ (where m_e is the free electron mass) for the electron (E), heavy-hole (HH) and light-hole (LH), respectively. The band gap of GaAs and AlGaAs were 1.51 eV and 1.93 eV, respectively, with an offset ratio of 67:33.

The calculated wavefunctions are shown in Fig. 6. For each of the HH, LH, and E states, the two lowest wavefunctions are localised predominantly on either the wide well or

TABLE I. The calculated transition energy and wavefunction overlap integral are reported for each of the six most probable transitions in the asymmetric double quantum well described by Fig. 6.

Transition	Transition energy (eV)	Integrated overlap
$EE_w HH_w$	1.575	0.981
$EE_w LH_w$	1.599	0.992
$EE_n HH_n$	1.604	0.102
$EE_n HH_n$	1.610	0.970
$EE_w LH_n$	1.617	0.101
$EE_n LH_n$	1.646	0.990

the narrow well. This leads to the four direct transitions being the most probable, as determined by the wavefunction overlap. The transition energy for each of these and the integrated wavefunction overlap is shown in Table I. Closer examination of the wavefunctions reveals that the electron and light-hole wavefunctions are not entirely localised, but have a finite probability of tunnelling to the other well. This leads to the finite transition probabilities for the spatially “indirect” transitions and the two most probable of these are also included in Table I.

IV. EXPERIMENTAL RESULTS AND ANALYSIS

Transient four-wave mixing experiments were performed on the double QW sample as described in Sec. II, with the laser spectrum centred at 778 nm and with bandwidth sufficient to excite both HH transitions resonantly. The three incident beams were co-linearly polarised and focused to a $100 \mu\text{m}$ spot with photon densities of 10^{12} cm^{-2} and a sample temperature of 20 K. The spectrally resolved intensity as a function of τ for $T = 0$ is plotted alongside the corresponding 2D spectrum in Fig. 7. In both cases there are three peaks present at emission energies of 1.57 eV, 1.59 eV, and 1.614 eV. These are assigned to the HH exciton localised predominantly on the wide well (HHw), the LH exciton localised predominantly to the wide well (LHw), and the HH exciton localised on the narrow well (HHn), respectively. From the spectrally resolved FWM data in Fig. 7(a) it can be seen that the signal from the two lowest energy excitons, which are the HH and LH excitons localised on the wide well, decays very rapidly and within the pulse duration. This is also reflected in the 2D spectrum where the diagonal peaks corresponding to these transitions are elongated along the ω_t direction. This broadening and shortening of the decoherence time is far greater than expected from the inhomogeneous linewidth, which is taken as the spectral width along the ω_t direction. This type of behavior has been observed previously⁴¹⁻⁴³ and is attributed to the strong coupling of the exciton states to the unbound free-carriers that are also excited by the broad laser spectrum. In the previous work⁴⁴ broad but spectrally distinct peaks representing the scattering of these free-carrier states into the exciton states were seen in the 2D spectra. The broad peak is observed in Fig. 7(b), but it cannot be spectrally isolated because the width of both the continuum and exciton peaks is too great. This increased broadening

FIG. 7. (a) The spectrally resolved FWM intensity at $T = 0$ reveals three-peaks which are attributed as labeled and also discussed in the text. (b) The corresponding 2D spectrum at $T = 0$ reveals the same three emission peaks on the diagonal and at least one cross-peak at the emission energy of 1.614 eV. (c) The cross section at $\omega_l = 1.614$ eV for the real part of the 3D spectrum is plotted as a function of ω_τ and T , revealing oscillations in the lineshape of the cross-peak.

compared to Ref. 44 is due to the higher temperature, 20 K compared to 4 K, and because the lower quality of the metalorganic chemical vapour deposition grown samples in the current study leads to greater inhomogeneous broadening. These increased broadening processes are also responsible for hiding any clear evidence of biexcitons in this system.

The signal from the HH exciton localised on the narrow well is not strongly coupled to the free carriers in the wide well, and the free-carrier states in the narrow well are not excited. As a result, a long-lived signal is observed in Fig. 7(a) and the corresponding peak on the diagonal in Fig. 7(b) is elongated along the diagonal, as expected for an inhomogeneously broadened transition. In addition to this long-lived signal, some beating as a function of τ is present. The period of beating corresponds to the energy difference between the two HH excitons, and leads to a cross-peak in the 2D spectrum at $(\omega_\tau, \omega_l) = (1.570, 1.614)$. In general, this cross-peak could be due to coherent coupling between the two transitions, or to a population transfer from the HH exciton in the wide well to the one in the narrow well. In this case, it is more likely to be coherent coupling because population transfer to a higher energy state is likely to take a finite time and with a waiting time of $T = 0$, the negligible population transfer is expected. As the waiting time was varied, oscillations of the phase of this cross-peak were revealed, as shown in Fig. 7(c) where the cross section at $\omega_l = 1.614$ eV is plotted

FIG. 8. The solution to the 3D phase retrieval problem is plotted as a function of the three spectral dimensions, ω_τ , ω_l , and ω_r . The red and yellow isosurfaces represent the data with constant amplitudes (enhanced online). [URL: <http://dx.doi.org/10.1063/1.3613679.3>].

as a function of ω_τ and T for the real part of the 3D spectrum. The behavior depicted in this figure is qualitatively the same as that shown for the simulations in Fig. 4(b), revealing oscillations in the lineshape of the cross-peak and suggesting the presence of a Raman-like coherence. In addition to this clear cross-peak at (1.57, 1.614) there is clearly some signal between it and the diagonal peak at (1.614, 1.614), though a specific cross-peak cannot be isolated. These uncertain analyses are significantly clarified by the 3D spectrum shown in Fig. 8.

From the three-dimensional plot of the 3D spectrum shown in Fig. 8 revealed immediately that there are two peaks away from $\omega_T = 0$ corresponding to coherence pathways. These peaks are centred at $\omega_T = 0.046$ eV and $\omega_T = 0.023$ eV, respectively, and the slices of the 3D spectrum at these values are shown in Fig. 9. The strongest features of the 3D spectrum are at $\omega_T = 0$ eV and correspond to the diagonal peaks for each exciton and the cross-peaks discussed above. There is a narrow signal along the (ω_τ, ω_l) diagonal which is strongest at $\omega_T = 0$ but extends along the ω_T axis. This is due to laser scatter and is concentrated on the (ω_τ, ω_l) diagonal by the phase retrieval process and stretched along ω_T

FIG. 9. Slices of the 3D spectrum depicted in Fig. 8 are shown for $\omega_T = 0.046$ eV and $\omega_T = 0.023$ eV, revealing the enhancement of different cross-peaks.

because it is random and fluctuates as a function of T without a definite frequency.

The 2D slice at $\omega_T = 0.046$ eV reveals an enhancement of the $(\omega_{HHw}, \omega_{HHn})$ cross-peak originating from the coherence pathway shown in Fig. 1(v). The energy difference between the two HH excitons matches the value of ω_T confirming the origin of this peak. The coherent coupling of these two HH exciton transitions is expected, given the close proximity of the QWs. On the basis of the calculations presented in Sec. III B, it is expected that the two heavy hole excitons are spatially separate and, therefore, do not share any ground or excited state. The next most likely coupling mechanism to give Raman-like coherences, given the relatively close proximity, is dipole-dipole coupling, though other mechanisms are also possible. Further investigations of the coupling mechanism and the dependence on barrier width is discussed elsewhere along with a more detailed analysis of the many-body physics within these QW samples.⁴⁵ A closer examination of the cross-peak in Fig. 9(a) reveals a round peak-shape indicating uncorrelated inhomogeneous broadening. The sources of inhomogeneous broadening are likely to be monolayer fluctuations in the well width or defects and impurities in the QWs. Since each of these are local effects and the two HH excitons are predominantly localised in separate wells, it is expected that the inhomogeneous broadening should be uncorrelated, as revealed in the 3D spectrum.

As discussed in Sec. III, the pathways in Fig. 1 suggest that a peak on the diagonal at $(\omega_{HHn}, \omega_{HHn}) = (1.614, 1.614)$ should also be present in the slice at $\omega_T = 0.046$ eV. In Fig. 9(a), it is clear that there is indeed a signal on the diagonal at $(\omega_{HHn}, \omega_{HHn}) = (1.614, 1.614)$, although, this diagonal signal is rather broad along the ω_T axis (as seen in Fig. 8) and a separate peak cannot be isolated.

The 2D slice at $\omega_T = 0.023$ eV reveals a cross-peak at $(1.59, 1.614)$, closely matching the LHw and HHn exciton transition energies, respectively. The energy difference between ω_τ and ω_t for this cross-peak again matches the value of ω_T , confirming that this peak arises from a coherence pathway as shown in Fig. 1(v). Coupling between these two excitons is not expected to be as strong as the coupling between the two HH excitons, but is still possible. A closer look at the shape of this cross-peak, however, reveals that it is elongated in the diagonal direction indicating correlated inhomogeneous broadening. The inhomogeneous broadening in the two QWs was shown to be uncorrelated by the unambiguous peak attributed to the HHn-HHw coupling. This peak at $(1.59, 1.614)$ must not, therefore, be due to coupling between the wide well LH exciton and narrow well HH exciton.

Closer examination of the calculated wavefunctions in Fig. 6 and the values in Table I reveals that the two next most likely transitions are within 7 meV of the narrow well HH exciton transition. The transition between the wide well heavy hole and the narrow well electron is unlikely to be strongly coupled with the LHw exciton and the inhomogeneous broadening would still be uncorrelated, because the electron states are predominantly localised to different wells. The transition between the narrow well light hole and the wide well electron, which is calculated to be 7 meV higher in energy than the narrow well HH exciton, is a more likely candi-

date. Firstly, the fact that this transition shares the same electron state as the wide well LH exciton and both involve LH states makes strong coupling more likely. Secondly, inhomogeneous broadening of the electron states is expected to be stronger than for the hole states because monolayer fluctuations and impurities will have a greater effect on the energy for the lighter electrons in the deeper conduction band. As a result, the shared electron state will contribute correlated inhomogeneous broadening which will dominate the uncorrelated broadening of the hole states. Finally, closer examination of the data in Fig. 9 reveals that both the diagonal and the coherence cross-peak in the slice at $\omega_T = 0.023$ eV extend to higher values of ω_t than the peaks in the slice at $\omega_T = 0.046$ eV. The coherence cross-peak at $(\omega_\tau, \omega_T, \omega_t) = (1.59, 0.023, 1.614)$ is therefore attributed to absorption by the LH exciton localised to the wide well, a coherence between this exciton and the indirect exciton involving the electron in the wide well and the light hole from the narrow well, followed by emission from the indirect exciton state.

V. DISCUSSION AND CONCLUSION

Using 3D spectroscopy, we are able to reveal the Raman-like coherence between HH excitons localised to separate QWs. Further analysis of the 3D spectrum shows the inhomogeneous broadening of the two HH excitons is not correlated, as predicted based on the sources of inhomogeneous broadening. An additional coherence cross-peak was also isolated from the 3D spectrum, and the slice at $\omega_T = -0.023$ eV showed the inhomogeneous broadening of the two coupled states to be correlated. On this basis, the cross-peak was attributed to a coherence between the LH exciton localised to the wide well and the indirect exciton involving the wide well electron and the narrow well HH.

It has proven possible to gain these insights by isolating different pathways using 3D spectroscopy and the analysis tools described here. The subsequent ability to resolve details of the nature and origin of inhomogeneous broadening and interactions with the environment, as shown here, opens the door to many possibilities; including determining the extent to which long-lived coherences observed in photosynthetic light-harvesting complexes is due to correlated vibrational motion. Further insights may also be gained by subsequent analysis. For example, the relative contributions of different pathways could be quantified now that they have been separated; population or coherence dynamics could be isolated by removing other contributions and performing an inverse Fourier transform to obtain the evolution of each component in isolation.

The extension of the phase retrieval algorithm for FWM intensity measurements from two to three dimensions has been described. This extension has been shown to be extremely advantageous, both in terms of the additional information made available and the quality of the phase retrieval and its susceptibility to noise. The application of this approach was able to reveal otherwise unobservable behavior and properties of the semiconductor sample, which are supported by theoretical analyses. Such phase retrieval approaches may also be used as a correlative technique

for interferometric multidimensional spectroscopy, and particularly for extending traditional techniques to 3D.

The applicability of the phase retrieval approach to two-colour experiments also presents previously unexplored possibilities. For example, it was shown in the data in Fig. 7 and Refs. 41–43 that the broadband excitation resulted in excitation of the unbound electron and hole states which changed the properties of the sample. In order to understand fully the dynamics and mechanism of complex condensed matter systems, it is therefore imperative that different pathways and transitions be isolated to remove such effects. The phase retrieval approach described here, together with a two-colour experiment, presents one possible means of achieving this goal.

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