Isolating quantum coherence using coherent multi-dimensional spectroscopy with spectrally shaped pulses

Jonathan O Tollerud, Christopher R Hall and Jeffrey A Davis*

Centre for Quantum and Optical Science, and ARC Centre for Coherent X-Ray Science
Swinburne University of Technology, Hawthorn, 3122 Victoria, Australia

*JDavis@swin.edu.au

Abstract: We demonstrate how spectral shaping in coherent multidimensional spectroscopy can isolate specific signal pathways and directly access quantitative details. By selectively exciting pathways involving a coherent superposition of exciton states we are able to identify, isolate and analyse weak coherent coupling between spatially separated excitons in an asymmetric double quantum well. Analysis of the isolated signal elucidates details of the coherent interactions between the spatially separated excitons. With a dynamic range exceeding 10^4 in electric field amplitude, this approach facilitates quantitative comparisons of different signal pathways and a comprehensive description of the electronic states and their interactions.

OCIS codes: (300.0300) Spectroscopy; (300.6300) Spectroscopy, Fourier transforms; (300.6530) Spectroscopy, ultrafast; (320.5540) Pulse shaping; (300.6470) Spectroscopy, semiconductors.

References and links

1. P. Hamm and M. Zanni, *Concepts and Methods of 2D Infrared Spectroscopy* (Cambridge University Press, 2011).
2. H. Oschkinat, C. Griesinger, P. J. Kraulis, O. W. Sorensen, R. R. Ernst, A. M. Gronenborn, and G. M. Clore, "3-dimensional nmr-spectroscopy of a protein in solution," Nature **332**, 374–376 (1988).
3. G. S. Engel, T. R. Calhoun, E. L. Read, T. K. Ahn, T. Mancal, Y. C. Cheng, R. E. Blankenship, and G. R. Fleming, "Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems," Nature **446**, 782–786 (2007).
4. E. Collini, C. Y. Wong, K. E. Wilk, P. M. G. Curmi, P. Brumer, and G. D. Scholes, "Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature," Nature **463**, 644–649 (2010).
5. E. Collini and G. D. Scholes, "Coherent intrachain energy migration in a conjugated polymer at room temperature," Science **323**, 369–373 (2009).
6. J. Kasprzak, B. Patton, V. Savona, and W. Langbein, "Coherent coupling between distant excitons revealed by two-dimensional nonlinear hyperspectral imaging," Nature Photon. **5**, 57–63 (2011).
7. M. A. Nielsen and I. L. Chuang, *Quantum Information and Quantum Computation* (Cambridge University Press, 2000).
8. M. Mohseni, P. Rebentrost, S. Lloyd, and A. Aspuru-Guzik, "Environment-assisted quantum walks in photosynthetic energy transfer," J. Chem. Phys. **129**, 174106 (2008).
9. T. Brixner, J. Stenger, H. M. Vaswani, M. Cho, R. E. Blankenship, and G. R. Fleming, "Two-dimensional spectroscopy of electronic couplings in photosynthesis," Nature **434**, 625–628 (2005).
10. X. Q. Li, T. H. Zhang, C. N. Borca, and S. T. Cundiff, "Many-body interactions in semiconductors probed by optical two-dimensional fourier transform spectroscopy," Phys. Rev. Lett. **96**, 057406 (2006).
11. D. B. Turner, R. Dinshaw, K.-K. Lee, M. S. Belsley, K. E. Wilk, P. M. G. Curmi, and G. D. Scholes, "Quantitative investigations of quantum coherence for a light-harvesting protein at conditions simulating photosynthesis," Phys. Chem. Chem. Phys. **14**, 4857–4874 (2012).
12. P. F. Tekavec, G. A. Lott, and A. H. Marcus, "Fluorescence-detected two-dimensional electronic coherence spectroscopy by acousto-optic phase modulation," J. of Chem. Phys. **127**, 214307 (2007).

13. D. B. Turner, K. W. Stone, K. Gundogdu, and Keith A. Nelson, "Three-dimensional electronic spectroscopy of excitons in GaAs quantum wells" J. Chem. Phys. **131**, 144510 (2009).
14. J. A. Davis, C. R. Hall, L. V. Dao, K. A. Nugent, H. M. Quiney, H. H. Tan, and C. Jagadish, "Three-dimensional electronic spectroscopy of excitons in asymmetric double quantum wells," J. of Chem. Phys. **135**,044510 (2011).
15. C. R. Hall, J. O. Tollerud, H. M. Quiney, and J. A. Davis, "Three-dimensional electronic spectroscopy of excitons in asymmetric double quantum wells," New J. Phys. **15**, 045028 (2013).
16. H. Li, A. D. Bristow, M. E. Siemens, G. Moody, and S. T. Cundiff, "Unraveling quantum pathways using optical 3D Fourier-transform spectroscopy," Nat. Commun. **4**, 1390 (2013).
17. D. B. Turner, K. W. Stone, K. Gundogdu, and K. A. Nelson, "Invited article: The coherent optical laser beam recombination technique (colbert) spectrometer: Coherent multidimensional spectroscopy made easier," Rev. Sci. Instrum. **82**, 081301 (2011).
18. E. Read, G. Engel, T. Calhoun, T. Mancal, T. Ahn, R. E. Blankenship, and G. R. Fleming, "Cross-peak-specific two-dimensional electronic spectroscopy," Proc. Natl. Acad. Sci. U.S.A. **104**, 14203–14208 (2007).
19. T. Zhang, I. Kuznetsova, T. Meier, X. Li, R. P. Mirin, P. Thomas,and Steven T. Cundiff, "Polarization-dependent optical 2D Fourier transform spectroscopy of semiconductors" Proc. Natl. Acad. Sci. U.S.A. **104**, 14227-14232 (2007).
20. D. B. Turner and K. A. Nelson, "Coherent measurements of high-order electronic correlations in quantum wells," Nature **466**, 1089–1092 (2010).
21. P. Wen and K. Nelson, "Selective enhancements in 2D fourier transform optical spectroscopy with tailored pulse shapes" J. Phys. Chem. A **117**, 6380–6387 (2013).
22. G. H. Richards, K. E. Wilk, P. M. G. Curmi, H. M. Quiney, and J. A. Davis, "Coherent vibronic coupling in light-harvesting complexes from photosynthetic marine algae," J. Phys. Chem. Lett. **3**, 272–277 (2012).
23. J. M. Womick, S. A. Miller, and A. M. Moran, "Toward the origin of exciton electronic structure in phycobiliproteins," J. Chem. Phys. **133**, 024507 (2010).
24. H. Lee, Y. C. Cheng, and G. R. Fleming, "Coherence dynamics in photosynthesis: Protein protection of excitonic coherence," Science **316**, 1462–1465 (2007).
25. G. H. Richards, K. E. Wilk, P. M. G. Curmi, and J. A. Davis, "Disentangling electronic and vibrational coherence in the phycocyanin-645 light harvesting complex," J. Phys. Chem. Lett. **5**, 43–49 (2013).
26. J. Wright, "Multiresonant coherent multidimensional spectroscopy," Annu. Rev. Phys. Chem. **62**, 209–230 (2011).
27. B. Deveaud, A. Chomette, F. Clerot, P. Auvray, A. Regreny, R. Ferreira, and G. Bastard, "Subpicosecond luminescence study of tunneling and relaxation in coupled quantum wells," Phys. Rev. B **42**, 7021 (1990).
28. K. Leo, J. Shah, E. O. Gobel, T. C. Damen, S. Schmitt-Rink, W. Schafer, and K. Kohler, "Coherent oscillations of a wave packet in a semiconductor double-quantum-well structure," Phys. Rev. Lett. **66**, 201 (1991).
29. A. Perdomo, L. Vogt, A. Najmaie, and A. Aspuru-Guzik, "Engineering directed excitonic energy transfer," Appl. Phys. Lett. **96**, 093114 (2010).
30. J. Faist, F. Capasso1, D. L. Sivco1, C. Sirtori1, A. L. Hutchinson1, and A. Y. Cho1, "Quantum cascade laser," Science **264**, 553–556 (1994).
31. G. Nardin, G. Moody, R. Singh, T. M. Autry, H. Li, F. Morier-Genoud, and S. T. Cundiff, "Coherent excitonic coupling in an asymmetric double ingaas quantum well arises from many body effects," Phys. Rev. Lett. **112**, 046402 (2014).
32. J. C. Vaughan, T. Hornung, T. Feurer, and K. A. Nelson, "Diffraction-based femtosecond pulse shaping with a two-dimensional spatial light modulator," Opt. Lett. **30**, 323–325 (2005).
33. L. Yang, T. Zhang, A. D. Bristow, S. T. Cundiff and S. Mukamel, "Isolating excitonic Raman coherence in semiconductors using two-dimensional correlation spectroscopy," J. Chem. Phys **129**, 234711 (2008).
34. M. Koch, R. Hellmann, S. T. Cundiff, J. Feldmann, E. O. Gobel, D. R. Yakovlev, A. Waag, and G. Landwehr, "Excitonic quantum beats in CdTe/CdMnTe quantum wells," Sol. State Commun. **88**, 515 (1993).
35. S. T Cundiff "Effects of correlation between inhomogeneously broadened transitions on quantum beats in transient four-wave mixing," Phys. Rev. A **49** 3114-3118 (1994).
36. J. O. Tollerud, C. R. Hall, and J. A. Davis, "Peak-shape analysis of isolated peaks in 3d coherent multidimensional spectroscopy," *In Preparation* .
37. D. B. Turner, P. Wen, D. H. Arias, K. A. Nelson, H. Li, G. Moody, M. E. Siemens, and S. T. Cundiff, "Persistent exciton-type many-body interactions in GaAs quantum wells measured using two-dimensional optical spectroscopy," Phys. Rev. B **85**, 201303 (2012).
38. J. Yuen-Zhou, J. J. Krich, M. Mohseni, and A. Aspuru-Guzik, "Quantum state and process tomography of energy transfer systems via ultrafast spectroscopy," Proc. Natl. Acad. Sci. U.S.A. **108**, 17615–17620 (2011).
39. J. Yuen-Zhou, D. H. Arias, D. M. Eisele, C. P. Steiner, J. J. Krich, M. Bawendi, K. A. Nelson, and A. Aspuru-Guzik, "Coherent exciton dynamics in supramolecular light-harvesting nanotubes revealed by ultrafast quantum process tomography," arXiv:1308.4566 (2013).

1. Introduction

Coherent multi-dimensional spectroscopy (CMDS) for electronic transitions, much like equivalent techniques in infra-red (IR)[1] and nuclear magnetic resonance (NMR) spectroscopy, utilises multiple pulses that excite and probe the sample during different time periods to quantify excited state dynamics and interactions between states. In multi-dimensional NMR, this type of information facilitates complete structure determination of complex molecules, such as proteins[2]. CMDS for electronic transitions, being technically more challenging, is over 30 years of development behind multi-dimensional NMR and some way from being able to achieve an equivalent level of detail. Nonetheless, third order CMDS experiments have been used to explore energy transfer and relaxation dynamics and more recently to identify coherent coupling between excited states in light-harvesting complexes[3, 4], conjugated polymers [5] and well-separated semiconductor nanostructures[6].

In these experiments three phase-locked pulses generate a signal with phase and amplitude that is measured by a heterodyne detection scheme and is proportional to the third order susceptibility of the sample. Varying the delays between pulses results in three time periods (t_1, t_2, t_3) and three corresponding frequency domains ($\omega_1, \omega_2, \omega_3$), as described in Section II. To analyse these data, 2D spectra that correlate the absorption energy ($\hbar\omega_1$) and the emission energy ($\hbar\omega_3$) for different values of the t_2 are typically presented.

Coherent coupling between spatially separated systems has long been explored as a necessary requirement for quantum information and cryptography[7]. Recent discoveries suggest such phenomena appear in a much wider range of processes, including light-harvesting in photosynthesis[3, 4, 8]. These discoveries have been facilitated by developments in CMDS for electronic transitions. [9, 10, 11, 12]. Coherent coupling can be identified in such experiments in the form of a coherent superposition of states, which leads to peaks in 2D spectra with phase that oscillates as a function of t_2. Alternatively, Fourier transforming the data with respect to t_2 shifts these features along $\hbar\omega_2$ by an amount equal to the energy difference between the coupled states[13, 14, 15, 16, 17]. In simple systems these coherence pathways can thus be separated from other signal pathways that involve population relaxation, energy transfer, ground state bleach and excited state absorption. In complex systems, however (e.g. light-harvesting complexes from photosynthetic organisms) numerous states and spectral broadening lead to overlapping peaks that can be difficult or even impossible to identify and/or separate. Additionally, for systems where many-body effects are important (e.g. semiconductor nanostructures) excitation of transitions at one energy can alter the signal detected despite playing no direct role in its generation[10], which can further complicate the interpretation.

The origin of these limitations is the same broad spectral bandwidth that makes 2D spectroscopy so useful. On the one hand, the ability to explore multiple pathways simultaneously can speed-up data acquisition and the analysis of 2D peak shapes can provide more information than is otherwise accessible. On the other hand, if the many different pathways cannot be separated these advantages are lost. Several important and useful approaches to separate different pathways in broadband experiments have been established, [18, 19, 20, 11, 21] yet there often remain contributions that cannot be isolated, which can lead to difficulties and uncertainty in the analysis. In such cases a CMDS experiment that can further select specific pathways would prove useful.

Two-colour four-wave experiments that selectively excite and probe specific coherence pathways have recently shown some advantages over broadband CMDS[22, 23, 24, 25]. Similarly, Wright *et al.*[26] have developed 'Multiresonant Coherent Multidimensional Spectroscopy', which varies the wavelength of relatively narrow-band pulses to identify coherence pathways. What has been lacking, however, is the phase stability between pulses that allows coherent multi-dimensional spectra to be obtained, and with it the ability to analyse peak-shapes and

fully correlate the relative contributions from different pathways.

We have combined the selectivity achieved in these multi-wavelength approaches with the phase stability required for CMDS, allowing us to perform both broadband and pathway-selective experiments that can be quantitatively compared. We utilise this pathway-selective CMDS (PS-CMDS) experiment to reveal and explore coherent coupling between excitons localised to semiconductor quantum wells (QWs) separated by a 6 nm barrier, as depicted in Fig. 1. The different widths of the two QWs lead to different transition energies and the possibility of downhill energy and/or charge transfer between wells [27, 28, 29]. This type of system has been explored extensively for potential device applications [30] and as a tunable template to explore fundamental energy transfer processes[15, 31]. When the barrier between wells is low and/or narrow substantial coupling between the wells leads to hybridised wavefunctions and a significant role for coherent quantum effects in energy and charge transfer. For high, wide barriers, where the electron and hole wavefunctions are localised to single QWs separated by large distances, there is no coupling between excitons. In the intermediate regime, where excitons are well-localised to a single well but close enough that dipole interactions can induce coupling, the role and nature of quantum coupling between wells is less clear. We utilise the PS-CMDS technique described here to provide insight into these fundamental coherent interactions.

2. Materials and methods

The asymmetric double quantum well sample used in this study consists of two GaAs QWs 5.7 nm and 8 nm wide separated by a 6 nm wide $Al_{0.35}Ga_{0.65}As$ barrier, as shown in Fig. 1. This sample was grown by Metal-Organic Chemical Vapour Deposition (MOCVD) and throughout the experiments was cooled to 20K in a closed-cycle circulating cryostat.

Fig. 1. (a) The asymmetric double quantum well structure shows layers of GaAs 5.7 nm and 8 nm thick (the QWs) separated by a 6 nm layer of $Al_{0.35}Ga_{0.65}As$ (the barrier). The profile of the potential perpendicular to the layers is shown in (b), with four bright transitions between electron and hole states localised to each well, as indicated and labelled. (c) Calculated wavefunctions for electrons and holes in the ADQW

In order to determine the extent of localisation, the wavefunctions of both electrons and holes were calculated by solving the one dimensional Schrödinger equation for the relevant potential profile[15]. The calculated wavefunctions are shown in Fig. 1(c). Based on these wavefunctions we determine the probability of finding electrons and holes in each well by splitting the wavefunctions at the center of the barrier and integrating the square of the wavefunction on either side. These probabilities are shown in Table 1 and indicate that each of the wavefunctions are well-localised to one of the QWs.

Table 1. Calculated probability of finding the electrons or holes in each well.

Wavefunction	Wide Well	Narrow Well
WW_E	99.86%	0.14%
NW_E	0.3%	99.7%
WW_{HH}	99.9999%	0.0001%
WW_{LH}	99.8%	0.2%
NW_{HH}	0.0006%	99.9994%
NW_{LH}	1.4%	98.6%

The experiments reported here utilise a CMDS apparatus based on a pulse shaper that is used to delay and compress each of the beams and independently shape their spectral amplitudes.

This approach to performing CMDS with a pulse shaper was pioneered by Nelson *et al.* [17] and has the advantage of being intrinsically phase-stable since all pulses are incident on the same optics. We extend this approach to facilitate spectral shaping and the selective excitation of coherence pathways. The precise and known phase relation between the different spectral components, inherent in the initial femtosecond pulses, then allows the generation of 2D and 3D spectra that includes only the selected pathway/s.

We utilised a Titanium:Sapphire oscillator to produce transform limited $\sim$45 fs pulses centered at 785 nm (as confirmed by FROG and X-FROG) at a repetition rate of 97 MHz. The CMDS experimental apparatus utilised two spatial light modulators (Boulder Nonlinear 512 nematic SLM) in an arrangement similar to Turner et al. [17]. The first SLM is used as a Fourier beam shaper to split the incident beam into four beams in a boxcars geometry (three for exciting the third order polarization in the sample and one local oscillator (LO) which overlaps with the signal for heterodyne detection). These are relayed through a 4F imaging system to a pulse shaper based on the second SLM. Each beam is spectrally dispersed horizontally and separated from the other beams vertically on the SLM. A spectral phase is applied to each beam independently to compensate for any chirp and apply the specified delay (a linear phase gradient in frequency corresponds to a shift in the time domain). With the signal detected in the direction given by $-k_1+k_2+k_3$, where k_i is the wavevector of pulse i, the delay between pulse-1 and -2 is labelled t_1, the delay between pulse-2 and -3 is labelled t_2 and the time between the third pulse and the signal is labelled t_3.

In addition to the temporal pulse shaping, a vertical grating is applied to the SLM to diffract the beams down. This allows the time delayed beams to be separated from any replica pulses and picked off from the incident beams. Varying the depth of the vertical grating also facilitates amplitude control of each beam[32]. This spectrally resolved amplitude control then enables spectral shaping.

The delayed beams are then imaged to the sample, where they overlap and excite a third order polarization that radiates in momentum conserving directions. At the sample position each of the three excitation beams have average power of ≤ 2.8 mW and are focussed to a $150\mu m$ diameter spot. The incident photon density is $6.7\times10^{11}\mathrm{cm}^{-2}$ per pulse, which will lead to a coherent response primarily in the $\chi^{(3)}$ regime[31]. The four-wave mixing signal detected is collinear with the local oscillator and focussed into a spectrometer where spectral interferometry allows the amplitude and phase of the signal to be determined. An eight-step phase cycling procedure is used to minimise noise and scatter from the excitation beams and maximise the signal. Further details of the experimental configuration and operation can be found in the Supplemental Material.

To generate a 3D spectrum the delay t_1 was scanned in 10 fs steps from 0 to 2000 fs for fixed values of the delay t_2, which was varied in 15 fs steps from 0 to 900 fs. For all of the data presented here co-linearly polarized pulses were used and only the absolute value rephasing contribution (pulse-1 arriving first)are shown. A rotating frame of reference was used, with the carrier frequency set to 795 nm. This ensures that the phase at 795 nm does not change as the delays are varied and reduces the sampling requirements for complete determination of the electric fields. From the spectral interferograms the amplitude and phase are determined and the data Fourier transformed with respect to t_1 and t_2.

In the coherence pathway specific experiment, spectral amplitude shaping was used to tailor the excitation spectrum of the first two pulses so that they were centred on different transitions with very little spectral overlap. The spectral amplitude masks used are shown in Fig. 2(a) and were chosen to give spectral amplitudes that were close to Gaussian as shown in Fig. 2(b). The flat spectral phase leads to transform limited pulses and the approximately Gaussian spectra ensure good temporal profiles, as shown in Fig. 2(c). The average powers of these pulses are then

Fig. 2. (a) The amplitude masks applied to the SLM and (b) the broadband spectrum (green) and resultant spectra of the two shaped pulses (red and blue) together with the spectrum from the QW sample. (c) Temporal profile of narrowed and un-narrowed spectra as calculated by a Fourier transform of spectra in (b) assuming a flat spectral phase. Plots are normalized and offset for clarity.

reduced to 1.0 mW and 0.3 mW for the first two pulses, respectively. For the third excitation beam and the local oscillator the full laser spectrum was used. This pulse scheme drives only processes that involve coherent superpositions between states excited by the first two pulses (except where pulse-3 is overlapped with the other two pulses).

A major benefit of this experimental setup is flexibility. The pulse sequence utilised here is one of many possible combinations which can be designed to excite any given pathway. The excitation spectra can also be tailored to match the temporal and spectral requirements of the sample. The intrinsic ability to perform a series of such pathway-selective CMDS experiments, alongside broadband CMDS, with no changes to the optical setup allows quantitative comparisons that can facilitate precise and detailed understanding of interactions in complex systems.

3. Results and analysis

3.1. Broadband CMDS

Broadband CMDS was performed with the full spectral bandwidth shown in Fig. 2(a) for each pulse. The absolute value spectra for the rephasing contribution only are shown in Fig. 3. The 2D spectrum at $t_2 = 0$ in Fig 3(a) shows contributions from pathways involving each of the four excitons indicated by the horizontal and vertical lines and identified in Fig. 1(b). This 2D spectrum is dominated by the NW_{hh} diagonal peak due to a combination of the laser spectrum and the oscillator strength of this transition. Cross-peaks corresponding to heavy-hole - light-hole interactions in the same well are present both above and below the diagonal for each well. Below diagonal cross-peaks indicating interactions between the NW_{hh} exciton and both wide well excitons are also present. These cross peaks may combine contributions from both population (e.g. population relaxation, energy transfer, ground state bleach or excited state absorption) and coherence pathways, making it difficult to ascribe their origin from such a 2D spectrum.

The 3D spectrum separates these contributions as shown in Fig. 3(b). As discussed above, the presence of cross-peaks that are shifted along $\hbar\omega_2$ in the 3D spectrum by amounts equal to the energy differences between the coupled exciton states is indicative of coherent coupling. In Fig. 3(b) the majority of the signal is at $\hbar\omega_2 = 0$ and therefore due to population pathways. Coherences involving heavy-hole and light-hole excitons localised to the same well are the next strongest contributions, indicative of the expected strong coupling between these. Two further peaks corresponding to coherences involving the NW_{hh} exciton and the two WW excitons can also be resolved. These inter-well cross-peaks are, however, almost three orders of magnitude weaker than the strongest peaks and as a result sit on top of a large noisy background. Previous work has identified this type of coherence signal by examining different types of 2D spectra correlating ω_2 and either ω_1 or ω_3[33]. In the present case it is not possible to identify these coherence peaks in the projections and it is only because they can be isolated in the full 3D spectrum that they can be identified. Furthermore, the 3D spectrum allows the peaks to be isolated and 3D peak shapes to be analysed, as described in section 3.3. In the projections, however, different pathways can contribute and overlap, limiting the ability to fully analyse the peak shapes. This is particularly the case for projections onto the (ω_1, ω_3) plane where the coherence signal is typically swamped by competing signal pathways, making the significant information that can be extracted from the coherence peak shape in this projection inaccessible.

Fig. 3. Experimental results from broadband CMDS experiments. (a) shows the 2D spectrum at $t_2 = 0$ with a logarithmic color scaling. The dashed lines provide a guide to indicate the energy for each of the 4 bright transitions. (b) the 3D spectrum is represented as a series of isosurfaces, with the projections in each direction. The isosurfaces shown are plotted only for certain regions to minimise the complexity of the spectrum and highlight specific peaks. The full isosurfaces at each level are shown in Supplementary Information. The strongest peaks occur at $\hbar\omega_2 = 0$, indicating population pathways, while peaks away from this plane represent coherent superpositions. The inter-well coherence peaks are shown in more detail in (c) where the 3D spectrum and projections confirm the location and origin of these peaks.

Fig. 4. The pulse sequence and states excited in the coherence specific experiment are shown in (b), with the resultant 2D spectrum at $t_2 = 300$ fs in (a) showing only the four inter-well cross-peaks. The 3D spectrum (c) confirms that these peaks arise entirely from inter-well coherence pathways. The separation of the four peaks in three dimensions and enhanced signal to noise allows further quantitative and peak shape analysis.

Figure 3(c) shows the inter-well coherence peaks in isolation but due to the poor signal to noise little analysis beyond identifying their presence is possible. In contrast, the intra-well coherences, which are much stronger and well above the noise, demonstrate peak shapes that are elongated in the diagonal direction, indicating correlated inhomogeneous broadening, as will be discussed in Section 3.3.

3.2. Coherence specific PS-CMDS

To further examine the inter-well coherence peaks the pathways that lead to these signals were selectively excited using the pulse sequence shown in Fig. 4(b). With the first pulse resonant only with NW excitons and the second resonant only with WW excitons, all population and single well coherence pathways should be excluded.

A 2D spectrum using this pulse sequence is shown in Fig. 4(a). By comparison to the broadband 2D spectrum (Fig. 3(a)) it can be seen that all single well processes are suppressed and the only signal is in the region of the inter-well cross peaks. There are four inter-well peaks present, the two identified in Fig. 3 and two additional peaks at (NW_{lh},WW_{hh}) and (NW_{lh},WW_{lh}). The 3D spectrum in Fig. 4(c) shows each of the peaks to be well-resolved and confirms that these four peaks are all due to inter-well coherent superpositions. This is in stark contrast to the 3D spectrum in Fig. 3 where only two coherences are identified from noisy peaks that are not well separated from other signal pathways and background noise. The absence of signal at $\hbar\omega_2 = 0$ further confirms that the coherent superposition pathways are indeed being excited in isolation.

Selectively exciting the coherence pathways has not only identified two additional coherent signals (and hence inter-well coupling between two additional pairs of excitons), but also enhanced the signal to noise. This allows further detailed analysis of the shape, location and magnitude of each peak, as discussed in the following sections.

In these experiments the noise level varies as a function of ω_3 and is proportional to the total signal at each $\hbar\omega_3$ value. This is because the different peaks emitting at the same energy are not separately measured, but are separated by Fourier transforms. Slight variations in the spectral interferrograms between different steps of the phase cycling, likely caused by vibrations of the cryostat, is the major noise source. This noise is then amplified at $\hbar\omega_3$ values with strong signal. In the PS-CMDS results there are no strong diagonal peaks to add noise to the cross peaks, leading to the much cleaner signal observed.

Fig. 5. $\hbar\omega_1$ vs $\hbar\omega_3$ peakshapes for selected peaks from the broadband (a), (b) and pathway selective (c) - (f) 3D spectra. (a) and (b) are normalized individually, (c)-(f) are all normalized to the highest point of the (NW_{hh}, WW_{hh}) peak in the PS spectrum.

3.3. Peak shape analysis

Peak shape analysis of 2D peaks has become one of the strengths of CMDS. Such analysis can be used to separate homogeneous and inhomogeneous broadening, reveal correlated and uncorrelated inhomogeneous broadening or spectral diffusion and to identify contributions from different many-body effects. The ability to separate different quantum pathways, as described here, allows broader application of these analysis tools. Extension to 3D peak shape analysis, as we will show, adds further utility.

Figure 5 shows 2D spectra obtained by selecting specific peaks in the 3D spectrum and integrating the peak along ω_2. These spectra correlate $\hbar\omega_1$ and $\hbar\omega_3$ in much the same way as standard 2D spectroscopy, allowing many of the same peak shape analysis tools to be applied.

The spectrum for the NW_{hh} diagonal peak centred at $\omega_2 = 0$ is shown in Fig. 5(a). The analysis of this is exactly as for standard 2D spectra: this peak is elongated along the diagonal, indicative of inhomogeneous broadening, allowing the homogeneous linewidth of 1.7 ± 0.2 meV to be measured in the presence of an inhomogeneous linewidth of 4.7 ± 0.2 meV.

In Fig. 5(b) the (NW_{lh}, NW_{hh}) intra-well coherence peak is isolated and similarly broadened along the diagonal. Simulations presented previously for such coherence peaks have demonstrated that correlated broadening will result in peaks elongated along the diagonal, while uncorrelated broadening results in peaks with no diagonal elongation[15]. The major source of broadening in these wells is local fluctuations in the width of the wells, and since hh and lh excitons in the same well will experience the same fluctuations, the broadening is expected to be correlated[14], as indicated by the diagonal peak-shape. Closer inspection of this peak reveals that the major axis of the ellipse is not perfectly along the diagonal direction, but slightly tilted towards the horizontal. This suggests that the inhomogeneous broadening is greater along $\hbar\omega_1$, corresponding to the NW_{lh} exciton, than along $\hbar\omega_3$, corresponding to the NW_{hh} exciton. This is consistent with the inhomogeneous linewidths measured for the two diagonal peaks, and consistent with the origin of inhomogeneous broadening in this MOCVD grown sample being fluctuations in the well width, which will affect light-holes more than heavy-holes, as can be seen in Fig. 1(c). This differing dependence on well width is well-known [34, 35], but the 3D spectrum and 2D projections provide a clearer separation of the different effects than other techniques. Specifically, the imperfect correlation of the inhomogeneous broadening due to the different dependence on well width for the heavyhole and light-hole excitons is clear and immediately apparent.

In contrast, the inter-well cross peaks from the PS-CMDS experiment represented in Fig. 5(c)-5(f) show no apparent elongation along the diagonal, indicating uncorrelated inhomogeneous broadening. The fluctuations in well width that are responsible for the majority of inhomogeneous broadening are not expected to be correlated across the different wells and so for excitons localised in different wells uncorrelated broadening is expected. This observation confirms that these excitons are indeed localised to different wells and coherent coupling between them is not due to wavefunction hybridisation and spatial overlap.

Further analysis on the 3D peak shape and projections onto each 2D plane and 1D axis can reveal further details, some of which can be identified in Fig. 6. These show the complete 1D, 2D and 3D peakshapes for the (NW_{hh}, WW_{hh}) inter-well coherence peak and the (NW_{lh}, NW_{hh}) intra-well coherence peak, from the pathway selective and broadband CMDS data, respectively. The 2D (ii)-(iv) and 1D (v)-(vii) peak shapes are obtained by integrating windowed 3D peaks

(i) in one or two of the frequency dimensions. Each of the 1D peaks is fit well by a Gaussian function, plotted as the solid blue line in Fig. 6 (v)-(vii). The details of these fits including the centre, full width at half maximum (FWHM) and amplitude for each peak are compiled in Table 2.

Fig. 6. (i) 3D , (ii)-(iv) 2D and (v)-(vii) 1D peakshapes from the PS-CMDS 3D spectrum for the (a) (NW_{hh}, WW_{hh}) and (b) (NW_{lh}, NW_{hh}) coherence peaks. The solid blue lines in (v)-(vii) are Gaussian fits.

Table 2. Tabulated data taken from peak shape fits and peak heights. Uncertainties in the peak width and center are estimated by fitting the data using a range of different reasonable selections of data. Amplitude uncertainties are estimated based on the strength of background signal near the peak. Corrected amplitude uncertainties also include a contribution from the uncertainty of the excitation spectra used for the spectral correction.

		FWHM (meV)			Centre (eV)			Relative Amplitude (x100)	
		ω_1	ω_2	ω_3	ω_1 ±0.5 meV	ω_2 ±0.5 meV	ω_3 ±0.5 meV	Uncorrected	Corrected
CMDS	WW_{hh}	8.3 ± 0.9	7.1 ± 1.7	7.2 ± 0.4	1.568	0.000	1.570	1.4 ± 0.1	14 ± 3
	WW_{lh}	7.4 ± 1.7	5.7 ± 1.4	7.1 ± 0.4	1.586	0.000	1.587	1.5 ± 0.5	4 ± 1
	NW_{hh}	4.5 ± 0.2	5.8 ± 1.1	4.9 ± 0.2	1.608	0.000	1.609	100 ± 10	100 ± 11
	NW_{lh}	10.4 ± 5.4	6.3 ± 1.3	8.6 ± 0.7	1.634	0.000	1.635	0.4 ± 0.1	1.2 ± 0.4
	(NW_{lh}, NW_{hh})	7.7 ± 1.7	7.1 ± 0.9	6.1 ± 1.1	1.634	-0.026	1.609	1.1 ± 0.4	6 ± 2
	(NW_{hh}, WW_{hh})	10.1 ± 1.3	22.6 ± 1.4	7.1 ± 1.4	1.608	-0.041	1.570	0.2 ± 0.1	0.7 ± 0.3
	(NW_{hh}, WW_{lh})	9.4 ± 2.1	10.4 ± 2.0	10.3 ± 2.3	1.608	-0.020	1.588	0.2 ± 0.1	0.3 ± 0.1
PS-CMDS	(NW_{hh}, WW_{hh})	9.0 ± 0.3	17.7 ± 0.2	7.5 ± 0.3	1.607	-0.037	1.568	0.04 ± 0.01	1.2 ± 0.3
	(NW_{hh}, WW_{lh})	9.2 ± 0.3	17.3 ± 0.1	6.3 ± 0.5	1.607	-0.024	1.583	0.03 ± 0.01	0.8 ± 0.3
	(NW_{lh}, WW_{lh})	11.6 ± 0.4	20.1 ± 0.6	6.4 ± 0.5	1.632	-0.050	1.584	0.02 ± 0.01	0.2 ± 0.1
	(NW_{lh}, WW_{hh})	11.6 ± 0.6	17.9 ± 0.4	6.8 ± 0.4	1.632	-0.065	1.568	0.03 ± 0.01	0.3 ± 0.2

For population peaks on the diagonal the $\hbar\omega_1$ and $\hbar\omega_3$ peak widths should be equal. For coherence cross-peaks, the $\hbar\omega_3$ linewidths should match the linewidths of the diagonal peaks at the corresponding emission energy. Similarly, the linewidth along $\hbar\omega_1$ for coherence peaks should match the linewidth of the diagonal peaks at that absorption energy.

The width of peaks in $\hbar\omega_2$ will depend greatly on the nature of the transitions and the broadening mechanisms involved. For example, population peaks would be expected to have widths inversely proportional to the excited state lifetimes. Coherence peaks where inhomogeneous broadening is correlated would be expected to have a width less than or equal to the larger homogeneous linewidth of the states involved. Whereas coherence peaks where the inhomogeneous broadening is uncorrelated would be expected to have width in $\hbar\omega_2$ that is determined by the convolution of the two inhomogeneous distributions of the states involved.

The peak widths in Table 2 match the expected relative values within the measurement error. The $\hbar\omega_1$ and $\hbar\omega_3$ peak widths are roughly equal for all the diagonal population peaks and coherence peaks have $\hbar\omega_1$ and $\hbar\omega_3$ widths that match the widths of the diagonal peaks for the corresponding absorption or emission energy.

The $\hbar\omega_2$ widths also behave roughly as expected. The diagonal peaks in the broadband CMDS experiment all have $\hbar\omega_2$ linewidths that are less than or equal to the respective $\hbar\omega_1$ and $\hbar\omega_3$ widths as predicted for population peaks. For the intra-well (NW_{lh}, NW_{hh}) coupling peak, the $\hbar\omega_1$, $\hbar\omega_2$, and $\hbar\omega_3$ widths are all comparable, which is expected for correlated inhomogeneous broadening. The broadband CMDS intra-well $\hbar\omega_2$ widths are larger than the homogeneous linewidths of the individual transitions, but all are approximately at the $\hbar\omega_2$ resolution

limit based on the scan parameters used. On the other hand, the inter-well coupling peaks in both the broadband CMDS and PS-CMDS spectra have $\hbar\omega_2$ linewidths that are approximately the sum of $\hbar\omega_1$ and $\hbar\omega_3$, which is consistent with uncorrelated inhomogeneous broadening.

Further analysis of the 2D projections which correlate $\hbar\omega_2$ with $\hbar\omega_1$ and $\hbar\omega_3$ can add further insight into these types of interactions as detailed in [36]. Similarly, further analysis of the real part of the data and the corresponding 3D peak profiles contains additional information on many-body effects and the interactions between wells[10, 36, 37]. This detailed analysis is beyond the scope of this manuscript and the tools for understanding these features in isolated 3D spectra will be the subject of future work.

3.4. Quantitative comparisons

In addition to analysis of peak shapes and quantitative analyses of peak widths and locations, comparisons of peak amplitudes can provide important details. One of the significant advantages of our approach is that there is no change to the experimental setup between CMDS and PS-CMDS experiments and they can be conducted in immediate succession. This allows quantitative comparisons of signal strengths and hence the relative contribution of the different signal pathways. With these details it should be possible to determine precisely all transition dipole moments and the coupling strengths between each of the spatially separated excitons.

One factor that needs to be taken into account is that each of the transitions is excited by a different spectral intensity, which will vary in the different configurations. The simplest approach to take this into account is to scale the measured signal by the spectral amplitude of each pulse at the energy of each interaction. For example, the centre of the (NW_{hh}, WW_{hh}) coherence peak will be scaled by the spectral amplitudes of the first pulse at the NW_{hh} energy, the second pulse at the WW_{hh} energy, the third pulse at the NW_{hh} energy and the local oscillator at the WW_{hh} energy. These corrections have been made for each of the diagonal peaks in the broadband CMDS experiments and the inter-well coherence peaks in both the broadband and PS-CMDS experiments with the resultant values shown in the final column of Table 2. For the two inter-well coherence peaks that are present in both the experiments the corrected amplitudes agree within the experimental uncertainties, supporting the validity of this approach.

Finally, we note that the absolute (uncorrected) strength of the weakest peak in the PS-CMDS spectrum is nearly four orders of magnitude below the strongest peak in the broadband CMDS experiment. This dynamic range and an ability to quantitatively compare different signal pathways over this range will greatly enhance the versatility and applicability of the technique and enable determination of the dipole moments and coupling strengths. This represents an important step towards quantum state and process and tomography on these systems, extending recent demonstrations of quantum state and process tomography in simple systems[38, 16, 39].

4. Discussion

Recent work by Nardin *et al.* identified coupling between excitons predominantly localised to different InGaAs QWs and identified that the coupling was mediated by many body effects[31]. In that case they were unable to resolve the coherent superpositions ('zero-quantum coherence') that are explored here, but rather use the two-quantum coherence signal to identify and analyse the coherent interactions. These complementary approaches, which both identify coherent coupling between excitons, provide access to different details that help to understand the coherent interactions between the spatially separated excitons. One particular advantage of the approach described here, however, is the potential to identify very weak coupling. Indeed the system studied here consists of excitons that are very weakly coupled and spatially very well-separated.

In the present experiments co-linearly polarised pulses were used, meaning all resonant tran-

sitions were excited by each pulse. To gain an even deeper understanding of the mechanisms responsible for the coherent coupling, experiments with different combinations of circularly polarised pulses will be able to identify selection rules for the coupling and the role of angular momentum in determining the coupling strengths.

In the ADQW system studied here it is possible to sufficiently narrow the pulses to selectively excite the different transitions while maintaining sufficiently short pulse durations to provide the temporal resolution required. This may not be the case in all systems. For example, where the spectral separation between states is small, it becomes difficult to completely isolate a given pathway. It does, however, remain possible to significantly enhance the pathway of interest relative to competing pathways. Hence, it becomes a balance between maintaining sufficiently short pulses to access the relevant dynamics, while selectively enhancing the specific pathway of interest. However, even where transitions are separated by as little as a few meV some advantage can still be gained by utilising this PS-CMDS approach.

5. Conclusions

We have devised a pathway specific CMDS experiment that combines many of the benefits of CMDS with an ability to selectively excite specific quantum pathways. We utilise these capabilities to unambiguously reveal coherent coupling between excitons localised to quantum wells separated by 6 nm. With our experimental approach we are able to achieve a dynamic range of 4 orders of magnitude in amplitude, which corresponds to 8 orders of magnitude in intensity. With this dynamic range we are able to identify coherent superpositions of spatially separated excitons, some of which have not previously been seen. Furthermore because we are able to isolate these coherence peaks we are able to perform peak shape analysis and quantitative comparisons that are not possible with the equivalent data from broadband CMDS. In analysing the peak shapes we identify several new tools to help understand the interactions between different electronic states.

This ability to isolate and analyse coherences, and indeed any specific signal pathway, can provide significant insight into the interactions and dynamics in a range of complex systems. In photosynthetic light harvesting complexes, for example, this type of approach has the potential to resolve important questions regarding the nature and role of quantum effects in efficient energy transfer.

Acknowledgments

The authors would like to thank Prof C. Jagadish and Prof H.H. Tan at the Australian National University and The National Fabrication Facility for the quantum well sample. This work was supported by the Australian Research Council (FT120100587).