Polarization dependence of semiconductor exciton and biexciton contributions to phase-resolved optical two-dimensional Fourier-transform spectra

Alan D. Bristow,¹ Denis Karaiskaj,¹ Xingcan Dai,¹ Richard. P. Mirin,² and Steven T. Cundiff¹,*

¹JILA, University of Colorado & National Institute of Standards and Technology, Boulder CO 80309-0440

²National Institute of Standards and Technology, Boulder CO 80305

(Dated: December 15, 2008)

Abstract

We study the coherent light-matter interactions of GaAs quantum wells associated with excitons, biexcitons and many-body effects. For most polarization configurations, excitonic features dominate the phase-resolved two-dimensional Fourier-transform (2DFT) spectra and have dispersive lineshapes, indicating the presence of many-body interactions. For cross-linear excitation, excitonic features become weak and absorptive due to the strong suppression of many-body effects; a result that can not be directly determined in transient four-wave mixing experiments. The biexcitonic features do not weaken for cross-polarized excitation and thus are more important.

PACS numbers: 78.47.Fg, 78.47.nj, 78.67.De
Coherent excitation of semiconductor quantum wells (QWs) produces electron-hole pairs, which can bind together through the Coulomb interaction to form excitons. The excitation dynamics of these systems have been extensively studied with ultrafast spectroscopic techniques, such as transient four-wave mixing (TFWM), where it was found that the coherent response itself is modified by the excitation due to many-body effects. For a recent review with extensive references see, for example, Ref. [1].

The coherent response of the system is strongly dependent on the excitation conditions and on material properties, such as inhomogeneous broadening due to well-width fluctuations. Effects that play a role in the light-matter interactions include the excitons themselves, many-body interactions and the formation of bound exciton “molecules,” or biexcitons. This interplay of effects has been explored though intensity- and polarization-dependent TFWM studies. The latter have produced surprising effects, such as changes in the dephasing time,[2,3,4,5] phase shift of the quantum beats (QBs)[4,6] and changes in the temporal profile of the emission.[2,4,7] Some experiments have characterized the Stokes parameters of the emission with detailed polarimetry.[8,9] Explanations of these results vary and include inhomogeneity,[2,4] or exciton-exciton interactions,[7,10] such as exciton-exciton exchange,[4,9] excitation-induced dephasing (EID),[8,11,12,13] local-field corrections,[8,12] and excitation-induced shift (EIS).[14] Many authors have attributed the polarization dependence to biexcitons and their subsequent interactions.[3,5,15,16,17,18,19]

TFWM measurements have not provided a completely satisfactory explanation of the polarization-dependent coherent response. Additional information was gained by recording the time evolution of the emission.[2,20] However, great enhancements are obtained by explicitly tracking the evolving phase of the TFWM signal along two time axes and then performing a two-dimensional Fourier transform. Application of two-dimensional Fourier-transform (2DFT) spectroscopy to semiconductor excitons has separated population from coupling contributions,[21,22,23] confirmed EID and EIS,[24] and shown that agreement with theory requires the inclusion of terms beyond Hartree-Fock.[25]

In this paper, 2DFT spectroscopy is used to separate and isolate the competing excitonic, biexcitonic and many-body processes, which are strongly polarization dependent. Exploiting the selection rules definitively demonstrates the suppression of either many-body or biexcitonic effects in the coherent response. Clear indication of the associated contributions are observed in the 2DFT spectra, whereas they had only previously been inferred in TFWM
experiments. Through a quantitative comparison of the magnitude of 2DFT data and the
lineshape in the phase-resolved spectra, the dominance of many-body interactions are ob-
served for most excitation conditions. The suppression of many-body interactions lead to
comparable exciton and biexciton contribution, where the latter is expected to be respon-
sible for the faster dephasing rates in cross-polarized TFWM experiments. Moreover, the
strength of the coupling features in 2DFT spectra can be directly related to the QBs in the
one-dimensional nonlinear data.

A schematic diagram of the experimental setup is shown in Fig. 1. Experiments are
performed in the box geometry with a mode-locked Ti:sapphire laser as the source. Pulses
are $\sim 200$ fs and centered around 800 nm. Pulses are split into four identical copies within a
stabilized set of cascaded, phase-stabilized and folded interferometers. The TFWM signal
is heterodyne detected with a phase-stabilized reference pulse that is routed around the
sample. Signal and reference are collinearly recombined and recorded using spectral interfer-
ometry. In this geometry there are three time periods, $\tau$ between the first and second
pulse, $T$ between the second and third pulse and $t$ between the third pulse and the TFWM
emission. $S_f(\omega_\tau,T,\omega_t)$ 2DFT spectra are the Fourier transform projections of the first and
third time periods $\tau$ and $t$, measured with the phase-matching condition $k_s = -k_A + k_B + k_C$.
These spectra are known as “rephasing” because dephasing due inhomogeneous broadening
is cancelled, which results in a photon echo.

2DFT experiments require sub-cycle phase-tracking and stabilization. However, experi-
mentally introduced phase shifts mix the real and imaginary parts of the complex spectrum in
the as-measured data. Correcting these shifts, i.e. determining the global phase of the 2DFT
spectrum, has previously been done through comparison to the spectrally resolved transient
absorption in an auxiliary measurement. Consequently, phase-resolved cross-polarization
spectra have not been previously acquired as there is not a corresponding configuration for
the spectrally resolved transient absorption. In this experimental apparatus the global phase
is determined by a new all-optical technique, this method combines in situ spatial interfer-
ence patterns between the pump beams at the sample and various spectral interferometry
measurements. The former are measured in pairs at the replica focus shown in Fig. 1. These
phases can be related to the signal phase through spectral interferometry measurements be-
 tween (1) the signal and reference (Ref) pulses, and (2) the reference and tracer (Tr) pulses,
where the tracer is also interfered at the replica focus.
A GaAs multiple-QW sample is epitaxially grown with four periods and $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ barriers; both wells and barriers are 10 nm thick. The substrate was removed for transmission measurements that are performed at approximately 7 K. The linear absorbance spectrum is shown in Fig. 2(a). Two peaks are observed corresponding to the heavy-hole $X_{hh}$ and light-hole $X_{lh}$ excitons, which are separated by approximately 8 meV due to the confinement in the QW. The excitonic level scheme is shown in the top right corner of Fig. 2(a). The selection rules in a circular basis are shown in the diagram, and allow for pure ($B_{hh}$ and $B_{lh}$), as well as mixed ($B_m$) biexcitons.

Figure 2(b) shows the three-pulse time-integrated TFWM signal of the four period QW sample, where $T$ is set to 200 fs, the excitation density is $\sim 8 \times 10^9 \text{ cm}^{-2}$ per layer and the laser is tuned between the excitons; see red dashed line in Fig. 2(a). The spectrally and temporally integrated signal has a cubic dependence on the incident power at this excitation density. Transients are shown for co-linear (XXXX), co-circular ($\sigma^+ \sigma^+ \sigma^+ \sigma^+$), cross-linear (XYYX) and cross-circular ($\sigma^- \sigma^- \sigma^+ \sigma^+$) polarized excitation in the $\chi^{(3)}$ nonlinear regime. This notation corresponds to the polarization state of the three pump pulses ($A$, $B$ and $C$) and the emission, from left to right. In each case the transient is normalized to the maximum of the XXXX polarized data (at $\tau = 0$ fs). QBs at the frequency of the splitting between $X_{hh}$ and $X_{lh}$ are observed in each case and the dephasing rates are similar except for XYYX polarization. This configuration gives a much weaker signal, a more rapid dephasing and QBs that are out of phase with the other transients due to the circular selection rules. The significance of these transients is more apparent when examining the 2DFT spectra.

The amplitude and real part of the rephasing 2DFT spectra are shown in Fig. 3 for the various co- and cross-polarized configurations. Real spectra for both co-polarized excitations have been demonstrated previously, but not for cross-polarized excitation, where only
magnitude spectra have been presented. The excitation density, laser tuning and time $T$ are
the same as those used in the TFWM data. The emission frequency is used to determine the
arithmetic sign of the frequencies, thus the frequencies on the vertical axis are negative as
the first pulse is conjugated. All spectra are normalized to the strongest peak, namely the
$X_{hh}$ peak in the amplitude spectrum for XXXX configuration. Because the signal amplitudes
vary for the different polarization configurations, each spectrum has an individual scale on its
colorbar. To aid the quantitative comparison amplitude change dots are added to the XXXX
polarized colorbar (adjacent the top left panel of Fig. 3): the four dots represent the relative
strength of the $X_{hh}$ peak for XXXX (black dot), $\sigma^+ \sigma^+ \sigma^+ \sigma^+$ (blue dot), $\sigma^- \sigma^- \sigma^+ \sigma^+$ (red dot)
and XYYX (green dot) polarizations, respectively from top to bottom. In general the 2DFT
spectra show similar contributions, which are labelled in the amplitude spectrum for XXXX

![Diagram](image)

**FIG. 2:** (Color online) (a) The linear absorption (solid black line) and excitation laser (red dotted
line) spectra. Inset shows the level scheme for the heavy- and light-hole excitons ($X$) and biexcitons
($B$) in GaAs quantum wells. (b) Time-integrated four-wave mixing data for various excitation
polarizations.
polarization (top left panel). These features include two diagonal features for the exciton populations \((X_{hh} \text{ and } X_{lh})\); two off-diagonal coupling peaks of various strengths \((X_{hh-lh} \text{ and } X_{lh-hh})\); in some cases axial peaks corresponding to biexciton states (most prominently \(B_{hh}\)); and vertical stripes at higher \(-\Omega \tau\) energies related to continuum absorption. Diagonal elongation of the peaks is a sign of inhomogeneity and is present for all polarizations.

The first (top) row of Fig. 3 shows a 2DFT spectrum for co-linear polarized excitation, where the dominant peak is the \(X_{hh}\); for this laser tuning the difference in the oscillator strengths of the excitons is apparent. A weak axial \(B_{hh}\) peak is observed to be about 10% of the \(X_{hh}\), displaced towards the \(\Omega \tau\) axis. The real part of the spectrum shows dispersive lineshapes resulting from EIS many-body interactions. Additionally, the \(B_{hh}\) feature is a negative dip sitting on the shoulder of the \(X_{hh}\). This negative dip occurs because the polarization associated with the \(|X\rangle \text{ to } |B\rangle\) transition has the opposite sign to those for the \(|g\rangle \text{ to } |X\rangle\) transition. Overall, the surprising strength of the exciton populations (and of course the lineshapes) can only be attributed to many-body interactions and exceed the strengths expected from perturbative calculations based on the excitonic level scheme.

The second row of Fig. 3 shows a 2DFT spectrum for co-circular polarized excitation, where the strength of the \(X_{hh}\) peak and its dispersive lineshape indicate the continued dominance of many-body interactions. This spectrum is generally weaker than for XXXX excitation (approximately 75%), because some quantum pathways that contribute to the exciton features are switched off. For this polarization pure biexcitons are also forbidden and the \(B_{hh}\) feature is absent from the spectrum. Mixed biexcitons features are allowed and expected as axial peaks adjacent to the hh-lh and lh-hh cross peaks. The lack of a biexcitonic features suggest that they are weaker than the single-species contributions. Additionally, the hh-lh exciton coupling peak strengths are more asymmetric for co-circular excitation, which is consistent with the reduced QBs in the co-circular TFWM data in Fig. 2(b). Indeed the cross-peaks in this polarization configuration are purely due to many-body coupling. Modelling this spectrum theoretical has been addressed previously, where it was found that experiments can only be reproduced by including Coulomb correlations beyond the Hartree-Fock approximation.

The third row of Fig. 3 shows a cross-linear polarized 2DFT spectrum, which can only be phase resolved due to the new all-optical method. The overall strength of the spectrum is significantly weaker than the others presented (approximately 13% that of XXXX excita-
tion), and the real part exhibits an absorptive lineshape for the $X_{hh}$ feature. This indicates that many-body interactions are strongly suppressed for this polarization, although they still contribute sufficiently to cause a dispersive lineshape for the real part of the diagonal $X_{lh}$ feature. Many-body effects are suppressed for cross-polarized excitation because there is no spatial modulation of the net population and the excitation-induced scattering processes are spin independent. Thus the strengths of the $X_{hh}$ and $B_{hh}$ peaks are comparable and the spectrum is fairly well described by the perturbative pathways determined from the level scheme. The dominant features are $X_{hh}$, $X_{lh}$, $B_{hh}$ and possibly $B_{lh}$ population peaks. The

---

**FIG. 3:** (color online) Amplitude and real-part 2DFT spectra for various polarizations are shown in the left and right panels respectively. Each spectrum has its own colorbar and the amplitude of the $X_{hh}$ is marked on the top left colorbar for the various polarizations. Vertically the rows correspond to $XXXX$, $\sigma^+\sigma^+\sigma^+\sigma^+$, $XYYX$ and $\sigma^-\sigma^-\sigma^+\sigma^+$ polarized excitation. All spectra are taken at a delay between the second and third pulses of $T = 200$ fs.
same number of perturbative pathways contribute to this spectrum as for XXXX polarized excitation, therefore many-body interactions are indeed a dominating factor in the strength of the coherent signal for the other polarization configurations. Additionally, the minute off-diagonal coupling peaks in this cross-linear polarization spectrum is consistent with the negligible QBs observed in the TFWM data of Fig. 2(b). As for XXXX polarized excitation, the $B_{hh}$ feature is a negative dip in the real part of the spectrum.

The fourth row of Fig. 3 shows the 2DFT spectra for cross-circular polarized excitation. The $X_{hh}$ peak is about 63\% of its strength for co-linear excitation, and the real part of the spectrum shows dispersive lineshapes. Therefore, many-body interactions are once again dominant. This spectrum also has the largest hh-lh coupling peaks, which coincides with the cleanest QBs in the TFWM data. For this configuration the $B_{hh}$ is once again visible and almost unchanged in strength, suggesting that biexcitons experience less many-body effects. We attribute the slight weakening of $X_{hh}$ peak compared to co-circular polarized excitation to transfer of spectral weight to the $B_{hh}$.

The 2DFT spectra clearly elucidate the transients behavior of Fig. 2(b). Relative strengths for the four polarization configurations match well between the TFWM and 2DFT data. In addition, the strength of the oscillations in the transients coincides with the strength of the off-diagonal coupling peaks in the spectra. This indicates that in all cases the oscillations are QBs and not polarization beats. Additionally the very weak, fast decaying transient for cross-polarized excitation corresponds to a significantly weak 2DFT spectrum with suppressed many-body interactions. The fast dephasing rate in cross-polarized excitation is related to the comparable strengths of the exciton and biexciton contribution.

In summary, we have shown a set of phase-resolved 2DFT spectra for co- and cross-polarized excitation conditions, of which the latter were previously unattainable. For cross-linear polarized excitation, the many-body contributions to the hh excitonic resonance are suppressed, which is evident from the change in the lineshape. The suppression of the exciton means that the biexciton is relatively more important. This conclusion had been inferred from extensive TFWM studies, however it is unambiguous in our 2DFT spectra.

This work was supported by the National Science Foundation and the Chemical Sciences, Geosciences, and Biosciences Division Office of Basic Energy Sciences, U.S. Department of...
Energy.

---

* Electronic address: cundiffs@jila.colorado.edu

1 S. T. Cundiff, Opt. Express 16, 4639 (2008).
2 S. T. Cundiff, H. Wang and D. G. Steel, Phys. Rev. B 46, R7248 (1992).
3 H. H. Yaffe, Y. Prior, J. P. Haribison and L. T. Florez, J. Opt. Soc. Am. B 10, 578 (1993).
4 D. Bennhardt, P. Thomas, R. Eccleston, E. J. Mayer and J. Kuhl, Phys. Rev. B 47, 13485 (1993).
5 T. Saiki, M. Kuwata-Gonokami, T. Matsusue and H. Sakaki, Phys. Rev. B 49, 7817 (1994).
6 S. Schmitt-Rink, D. Bennhardt, V. Heuckeroth, P. Thomas, P. Haring, G. Maidorn, H. Bakker, K. Leo, D.-S. Kim, J. Shah, K. Köhler, Phys. Rev. B 46, 10460 (1992).
7 D.-S. Kim, J. Shah, T. C. Damen, W. Schäfer, F. Jahnke, S. Schmitt-Rink and K. Köhler, Phys. Rev. Lett. 69, 2725 (1992).
8 S. Patkar, A. E. Paul, W. Sha, J. A. Bolger and A. L. Smirl, Phys. Rev. B 51, 10789 (1995).
9 D. Robart, T. Amand, X. Marie, M. Brousseau, J. Barrau and G. Bacquet, J. Opt. Soc. Am. B 13, 1000 (1996).
10 K. Bott, O. Heller, D. Bennhardt, S. T. Cundiff, P. Thomas, E. J. Mayer, G. O. Smith, R. Eccleston, J. Kuhl and K. Ploog, Phys. Rev. B 48, 17418 (1993).
11 H. Wang, K. Ferrio, D. G. Steel, Y. Z. Hu, R. Binder, S. W. Koch, Phys. Rev. Lett. 71, 1261 (1993).
12 Y. Z. Hu, R. Binder, S. W. Koch, S. T. Cundiff, H. Wang and D. G. Steel, Phys. Rev. B 49, 14382 (1994).
13 A. L. Smirl, M. J. Stevens, X. Chen and O. Buccafusca, Phys. Rev. B 60, 8267 (1999).
14 J. M. Shacklette and S. T. Cundiff, Phys. Rev. B 66, 045309 (2002).
15 E. J. Mayer, G. O. Smith, V. Heuckeroth, J. Kuhl, K. Bott, A. Schulze, T. Meier, D. Bennhardt, S. W. Koch, P. Thomas, R. Hey and K. Ploog, Phys. Rev. B 50, 14730 (1994).
16 W. Schäfer, D. S. Kim, J. Shah, T. C. Damen, J. E. Cunningham, K. W. Goossen, L. N. Pfeiffer and K. Köhler, Phys. Rev. B 53, 16429 (1996).
17 S. Adachi, T. Miyashita, S. Takeyama, Y. Takagi, A. Tackeuchi and M. Nakayama, Phys. Rev. B 55, 1654 (1997).
18 H. Nickolaus and F. Henneberger, Phys. Rev. B 57, 8774 (1998).
19 W. Langbein and J. M. Hvam, Phys. Rev. B 61, 1692 (2000).
20 H. Schneider and K. Ploog, Phys. Rev. B 49, 17050 (1994).
21 T. Zhang, C. N. Borca, X. Li and S. T. Cundiff, Opt. Express 13, 7432 (2005).
22 C. N. Borca, T. Zhang, X. Li and S. T. Cundiff, Chem. Phys. Lett. 416, 311 (2005).
23 W. Langbein and B. Patton, J. Phys.: Condens. Matter 19, 295203 (2007).
24 X. Li, T. Zhang, C. N. Borca, S. T. Cundiff, Phys. Rev. Lett. 96, 057406 (2006).
25 T. Zhang, I. Kuznetsova, T. Meier, X. Li, R. P. Mirin, P. Thomas and S. T. Cundiff, Proc. Natl. Soc. USA, 104, 14227 (2007).
26 A. D. Bristow, D. Karaiskaj, X. Dai, T. Zhang, C. F. Carlsson, K. R. Hagan, R. Jimenez and S. T. Cundiff, to be published.
27 D. M. Jonas, Annu. Rev. Phys. Chem. 54, 425 (2003).
28 A. D. Bristow, D. Karaiskaj, X. Dai and S. T. Cundiff, Opt. Express 16, 18017 (2008).
29 L. Yang, I. V. Schweigert, S. T. Cundiff and S. Mukamel, Phys. Rev. B 75, 125302 (2007).
30 I. Kuznetsova, P. Thomas, T. Meier, T. Zhang, X. Li, R. P. Mirin and S. T. Cundiff, Sol. State Comm. 142, 154 (2007).