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Optical two-dimensional Fourier transform spectroscopy of semiconductors

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Abstract

Two-dimensional Fourier transform spectra of optical excitations in semiconductor quantum wells are obtained. Coupling between heavy-hole excitons, light-hole excitons and unbound electron–hole-pairs results in off-diagonal features. A qualitative analysis of these features reveals the dominance of many-body interactions.

Many-body interactions in solids are a topic of long-standing and continuing interest. Optical excitations in direct-gap semiconductors are a convenient system for the study of many-body interactions [1]. The primary tool for these studies has been transient-four-wave-mixing (TFWM) using ultrashort (~100 fs duration) laser pulses, which has also proven to be powerful for studying molecular dynamics [2]. The strong similarities between coherent optical excitation of resonant systems (including TFWM) and nuclear magnetic resonance (NMR) has meant the NMR concepts and language are often used in optics. This similarity means that NMR advances suggest improvements to optical spectroscopy. Indeed, the concepts of multi-dimensional NMR spectroscopy [3] have recently been adapted to the infrared and optical regimes to study vibrational [4] and electronic [5,6] excitations in molecules [7]. Here, we implement optical two-dimensional Fourier transform spectroscopy to study coupling among excitonic states in semiconductors. Although they are not dominant, the understanding of many-body interactions obtained in these studies will also impact studies of molecular systems.

Significant progress has been made in understanding how many-body interactions are manifest in the TFWM signal from exciton resonances in semiconductors. Early experiments [8,9] were interpreted in terms of a two-level model [10]. The observation of signals for 'negative' time delay in a two-pulse experiment [11] indicated that such a simple picture was insufficient. Negative delay signals have also been observed in experiments on molecular iodine [12] and atomic potassium [13]. Time-resolving the emitted signal provided further evidence for the inadequacy of a simple two level system description [14,15]. A phenomenological description of these observations was obtained by adding biexcitonic effects [16], the local field correction (LFC) [17], excitation induced dephasing (EID) [18] or excitation induced shift (EIS) [19] to the two-level model. A fundamental theoretical description also reproduces these observations, although correlation terms beyond Hartree–Fock must be included [20]. Coupling between optically induced excitations was also addressed, starting with beats in the TFWM signal due to excitons localized by well-width fluctuations [21]. To determine if the beats were due to electromagnetic or quantum interference, time-resolved TFWM [22] and spectrally-resolved TFWM [23] were used. Interference between the exciton resonance and unbound electron–hole continuum states was also observed [24]. The fact that the exciton and continuum states

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are coupled by many-body interactions was discovered using partially-non-degenerate TFWM [25] and in three-pulse TFWM [26,27]. These results explained the earlier observation that the TFWM signal from the exciton decays anomalously fast when the excitation spectrum overlapped continuum states [28].

A single two-dimensional Fourier transform spectrum (2DFTS) exemplifies virtually the entire body of work on TFWM spectroscopy of excitons in semiconductors. Furthermore, significant insight can be obtained directly from qualitative descriptions of two-dimensional spectra and detailed calculations are not required, although we provide phenomenological calculations to support our conclusions. In this Letter, we concentrate on the issues of coupling between excitonic resonances, particularly the heavy-hole and light-hole excitons in quantum wells, and coupling between continuum states (unbound electron–hole pairs) and excitons. The power of Fourier-transform spectroscopy to address these issues does not come from use of a Fourier transform per se, but rather it comes from the fact that the *phase* of the TFWM signal is coherently tracked as a function of the *phase-delay* between the first two excitation pulses. Consequently, it is significantly more powerful than previous experiments that characterized the emitted TFWM signal without considering how its phase dependence on the delay between input pulses [29]. A closer analogy to 2DFTS is a variation on partially-non-degenerate TFWM, known as coherent excitation spectroscopy, which was developed and used to examine the question of coupling between disorder localized excitons [30].

To understand why coherent tracking of the signal phase is so powerful, consider the TFWM signal that is emitted from a transition with angular frequency ω_{ik} due to excitation of a transition ω_{ij} by the first pulse. If the first pulse is the conjugated field, this signal field can be written

$$S(\tau,t) = \mu_{ij}^2\mu_{ik}^2 e^{i(\omega_{ik}t-\omega_{ij}\tau)}D(\tau,T,t), \quad (1)$$

where t is time with respect to the last pulse, τ is delay between the first two pulses, T is delay between second and third pulses in a three-pulse experiment ($T=0$ in a two-pulse experiment), μ_{ij} and μ_{ik} are the dipole moments of the respective transitions and we have lumped all of the decay dynamics plus any evolution between second and third pulses into $D(\tau,T,t)$. Eq. (1) shows that phase evolution between the first two pulses results in a constant overall phase in the emitted field. Thus, by coherently tracking the phase of the signal as we vary the delay between the excitation pulses with sub-cycle precision, we can determine the frequency of the absorbing transition simultaneously with that of the emitting transition. Taking the two-dimensional Fourier transform of the resulting time-domain data provides a convenient display of the results. Two level systems ($\omega_{ij}=\omega_{ik}$) will result in peaks on the diagonal, whereas a three-level system will also have peaks off the diagonal. Thus, a 2DFTS immediately determines if two resonances observed in a one-dimensional spectrum (e.g., absorption or luminescence) arise from two uncoupled transitions (2 two-level systems) or from coupled transitions (1 three-level system). A 2DFTS can also easily distinguish between a three-level system consisting of a ground state and two singly excited states (a 'V' system) and a three-level system consisting of a ground state, one singly excited state and a doubly excited state (a 'ladder' system). Interactions between 2 two-level systems can be described as a four-level system (one ground state, two singly excited states and one doubly excited state where the doubly excited state is energetically shifted from being the sum of the energies of the singly excited states due to the interactions) [16], which can also be identified in a phase resolved 2DFTS [31]. This capability to distinguish between these level schemes is not surprising as non-Fourier Transform two dimensional techniques [22,23] are able to make this determination. However, from the two-dimensional Fourier transform spectrum, we are also able to immediately determine that the coupling is dominated by many-body interactions, i.e., it cannot be described as a simple three-level system, and coupling to a continuum is simultaneously evident.

Coherently tracking the phase of the signal field as a function of the time delay between the excitation pulses, while maintaining sub-cycle precision of the delay, is experimentally challenging. We implement this in a three-pulse excitation geometry (see Fig. 1) using two actively stabilized interferometers. The phase information of the signal is obtained by spectral interferometry with a reference pulse [5,32]. The reference pulse phase is actively stabilized to that of the third excitation pulse. The delay between the first two excitation pulses is monitored with interference fringes from a helium–neon laser beam that is coaligned with the femtosecond pulses through the delay stages. A feedback loop locks the delay between the excitation pulses with RMS fluctuation of less than 1/100 optical cycles during acquisition of the spectral interferograms. The delay is then incremented by disabling the feedback loop and moving a delay stage while monitoring the interference fringes [33]. We designate the frequency corresponding the Fourier transform with respect to $\tau(t)$ as $\omega_\tau(\omega_t)$, referred to as absorption and emission frequencies, respectively. For the data shown here, the signal is detected in the direction $\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ where $\mathbf{k}_i$ is the wavevector of incident pulse i and i designates time ordering. This is known as a rephasing time-ordering as it results in a photon echo from an inhomogeneously broadened medium. For data presented here, there is no delay between $\mathbf{k}_2$ and $\mathbf{k}_3$. The delay τ between $\mathbf{k}_1$ and $\mathbf{k}_2$ is defined to increase as $\mathbf{k}_1$ arrives earlier. For all experimental data and theoretical results presented here, $\tau > 0$.

Using this actively stabilized apparatus, we have obtained a two-dimensional Fourier transform spectrum of the optical excitations in a GaAs multiple quantum well. The sample consists of 10 periods of a 10 nm GaAs well and 10 nm Al-GaAs barrier and is held at 8 K in an optical cryostat. Due to confinement, the heavy-hole and light-

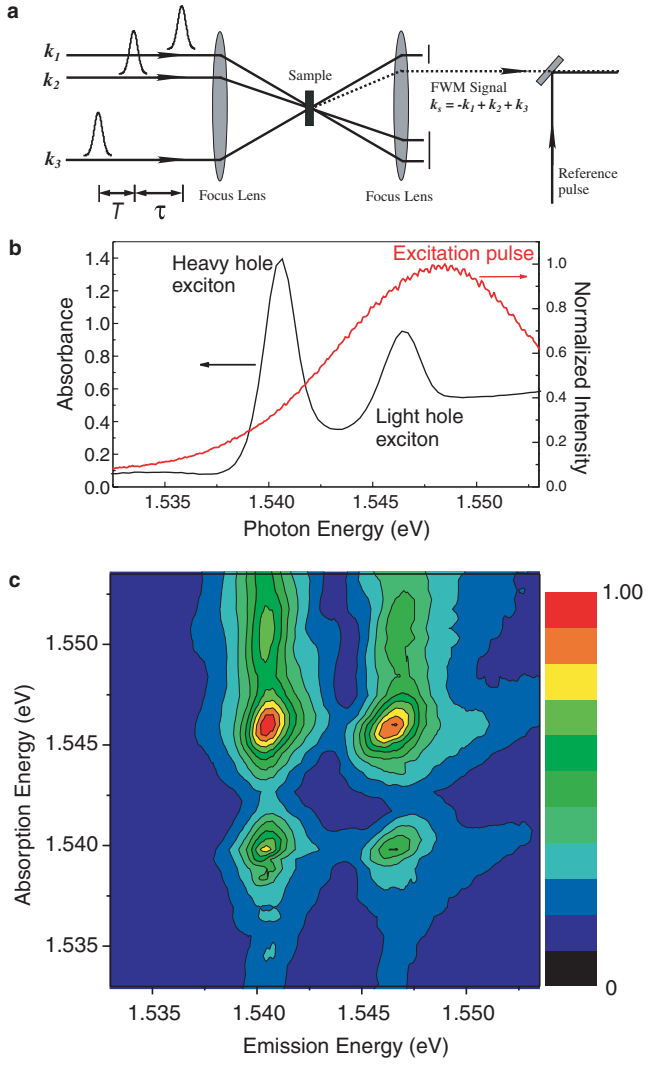

Fig. 1. (a) Schematic of the experimental configuration. (b) Linear absorption spectrum of the sample and spectrum of the excitation pulses. (c) Normalized magnitude of the two-dimensional Fourier-transform spectrum.

hole valence bands are energetically split by approximately 6 meV, resulting in two corresponding exciton resonances. Coincidentally, the exciton binding energy is also approximately 6 meV, which results in the light-hole exciton being degenerate with the edge of the heavy-hole continuum states. The linear absorption spectrum, shown in Fig. 1b gives a heavy-hole linewidth of about 1.5 meV, which is due in part to inhomogeneous broadening from well width fluctuations. At the excitation densities used in these experiments of $\sim 10^{10}$ excitons/well/cm^2, the homogeneous linewidth is $\sim$0.8 meV. The incident laser pulses are approximately 100 fs in duration. They are tuned above the light-hole exciton in order to compensate for the oscillator strengths and get comparable excitation density of heavy-hole excitons, light-hole excitons and unbound electron–hole pairs.

The magnitude of the 2DFTS is shown in Fig. 1c. Several features are apparent, including diagonal peaks corresponding to the heavy-hole and light-hole excitons, off-diagonal peaks corresponding to absorption by the light-hole exciton but emission by the heavy-hole exciton and vice-versa and a vertical stripe at the heavy-hole emission energy due to absorption by continuum states. Two features are qualitatively striking and due to the strong many-body interactions. The first is that the off-diagonal peak is the strongest and that the off-diagonal peaks are unequal in strength. The second is that the continuum shows up as a vertical stripe at the heavy-hole exciton emission energy. We will separately discuss each of these.

The relative strengths of the diagonal and off-diagonal peaks can be estimated from Eq. (1) for a three-level system. The diagonal peaks should have amplitudes of μ_{ij}^4 and μ_{ik}^4 while the off-diagonal peaks should be equal in strength with amplitude $\mu_{ij}^2\mu_{ik}^2$. If $\mu_{ij} > \mu_{ik}$ then $\mu_{ij}^4 > \mu_{ij}^2\mu_{ik}^2 > \mu_{ik}^4$ and we see that the off-diagonal peaks should never be stronger than the diagonal peaks. This analysis ignores weighting due the finite bandwidth and tuning of the excitation pulses, which can be taken into account by weighting the dipole moments, and does not change the conclusion. We have also done numerical simulations of the optical Bloch equations for a three-level system where the levels represent the ground state, excitation of a heavy-hole exciton and excitation of a light-hole exciton with a tuning consistent with the experimental results presented above. The calculations use a spatial Fourier expansion of the incident fields and the density matrix elements [34]. The calculated linear absorption spectrum and spectrum of the incident pulses are shown in Fig. 2a. The resulting 2DFTS is shown in Fig. 2b, confirming the simple analysis of the peak strengths.

The dominance of one off-diagonal peak, and asymmetry between the two off-diagonal peaks can be explained by including many-body effects. Specifically, this occurs if the signal is dominated by EID or EIS and there is an asymmetry in how each resonance is affected by them [35]. To verify this, we show in Fig. 2c a calculation where we have included EID that only effects the lower energy resonance, clearly this calculation more closely matches the experimental results. The goal of these phenomenological calculations is simply to demonstrate that many-body effects can explain our experimental results, not to make a detailed theoretical simulation. The latter is better done with a full semiconductor theory, however, to the best of our knowledge, such full calculations of 2DFTS of semiconductors have not been performed yet. Note that the relative strength of the peaks in the 2DFTS provides a quantitative test of the theory that cannot be obtained from any technique used previously.

The other striking feature in the experimental data are the vertical 'ridges' for ω_t equal to the heavy-hole exciton or light-hole exciton energy. These ridges are due to the excitation of continuum states. A simple model of the continuum states treats them as a set of inhomogeneously broadened two level systems. This results in not a vertical feature, but rather a diagonal feature, as shown in Fig. 3b

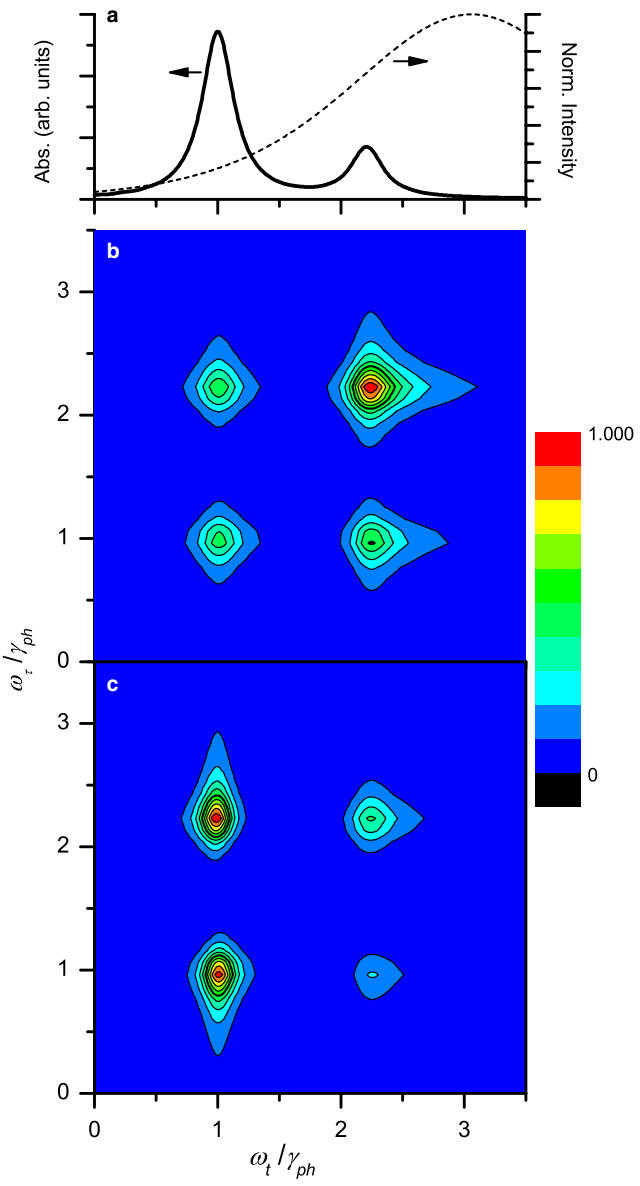

Fig. 2. Simulations for a three-level system, (a) calculated linear absorption spectrum and spectrum of excitation pulses, two-dimensional magnitude spectra calculated (b) neglecting and (c) including EID, which results in the off-diagonal peak being strongest. Frequencies are normalized to the dephasing rate γ_{ph} and in a rotating frame chosen such that the lower resonance has a frequency of 1. Magnitudes of spectra are normalized separately.

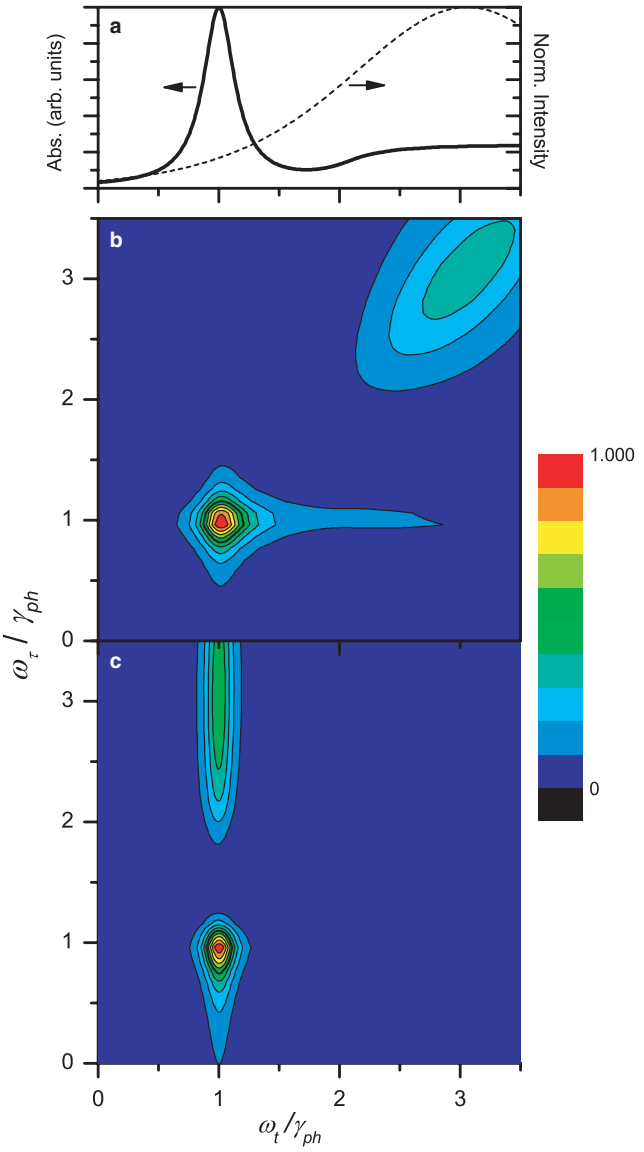

Fig. 3. Simulations for a single resonance plus a continuum modelled by 20 equally distributed resonances, (a) calculated linear absorption spectrum and spectrum of excitation pulses, two-dimensional magnitude spectra calculated (b) neglecting and (c) including EID.

where we have included a single strong resonance to model the exciton and a set of 20 weaker resonances with higher dephasing rates to model the continuum states. As shown in Fig. 3c, we can obtain a 2DFTS that is quantitatively similar to the experiment by including EID that only effects the strong resonance. Since the simulation only includes a single strong resonance (modelling the heavy-hole exciton), only a single vertical ridge appears, whereas in the experiment two vertical ridges appear, one associated with the heavy-hole exciton and the other with the light-hole exciton.

These results show that optical two-dimensional Fourier-transform spectroscopy is a powerful tool for observing many-body interactions among optical excitations in semiconductors. The results clearly show which states are coupled and gives insight into how the coupling modifies the coherent optical response. Furthermore, the results provide quantitative results against which a full many-body theory can be tested. These results do not give insight into the microscopic nature of the many-body interactions. The real and the imaginary parts do provide information on the microscopic origins of the interactions [36]. However, the separation into the real and imaginary parts, as opposed to the magnitude shown herein, is experimentally challenging. This can be done by comparing projections of the two-dimensional spectra to other experiments, such as spectrally resolved transient absorption [5].

Acknowledgments

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References

[1] D.S. Chemla, J. Shah, Nature 411 (6837) (2001) 549.
[2] S. Mukamel, Principles of Nonlinear Optical Spectroscopy, Oxford University Press, Oxford, 1995.
[3] R.R. Ernst, G. Bodenhausen, A. Wokaun, Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Oxford University Press, Oxford, 1987.
[4] O. Golonzka, M. Khalil, N. Demirdoven, A. Tokmakoff, Phys. Rev. Lett. 86 (10) (2001) 2154.
[5] J.D. Hybl, A.A. Ferro, D.M. Jonas, J. Chem. Phys. 115 (14) (2001) 6606.
[6] T. Brixner, J. Stenger, H.M. Vaswani, M. Cho, R.E. Blankenship, G.R. Fleming, Nature 434 (2005) 625.
[7] D.M. Jonas, Annu. Rev. Phys. Chem. 54 (2003) 425.
[8] L. Schultheis, A. Honold, J. Kuhl, K. Köhler, C.W. Tu, Phys. Rev. B 34 (12) (1986) 9027.
[9] L. Schultheis, J. Kuhl, A. Honold, C.W. Tu, Phys. Rev. Lett. 57 (1986) 1797.
[10] T. Yajima, Y. Taira, J. Phys. Soc. Jpn. 47 (5) (1979) 1620.
[11] K. Leo, M. Wegener, J. Shah, D.S. Chemla, E.O. Göbel, T.C. Damen, S. Schmitt-Rink, W. Schäfer, Phys. Rev. Lett. 65 (11) (1990) 1340.
[12] V.V. Lozovoy, I. Pastirk, M.G. Comstock, M. Dantus, Chem. Phys. 266 (2001) 205.
[13] S.T. Cundiif, Laser Phys. 12 (8) (2002) 1073.
[14] D.-S. Kim, J. Shah, T.C. Damen, W. Schäfer, F. Jahnke, S. Schmitt-Rink, K. Khler, Phys. Rev. Lett. 69 (18) (1992) 2725.
[15] S. Weiss, M.-A. Mycek, J.-Y. Bigot, S. Schmitt-Rink, D.S. Chemla, Phys. Rev. Lett. 69 (18) (1992) 2685.
[16] K. Bott, O. Heller, D. Bennhardt, S.T. Cundiff, P. Thomas, E.J. Mayer, G.O. Smith, R. Eccleston, J. Kuhl, K. Ploog, Phys. Rev. B 48 (23) (1993) 17418.
[17] M. Wegener, D.S. Chemla, S. Schmitt-Rink, W. Schäfer, Phys. Rev. A 42 (1990) 5675.
[18] H. Wang, K. Ferrio, D.G. Steel, Y.Z. Hu, R. Binder, S.W. Koch, Phys. Rev. Lett. 71 (8) (1993) 1261.
[19] J.M. Shacklette, S.T. Cundiff, Phys. Rev. B 66 (04) (2002) 045309.
[20] H. Haug, S.W. Koch, Quantum Theory of the Optical and Electronic Properties of Semiconductors, second edn., World Scientific, Singapore, 1993.
[21] E.O. Göbel, K. Leo, T.C. Damen, J. Shah, S. Schmitt-Rink, W. Schäfer, J.F. Mller, K. Khler, Phys. Rev. Lett. 64 (1990) 1801.
[22] M. Koch, J. Feldmann, G. von Plessen, E.O. Göbel, P. Thomas, K. Köhler, Phys. Rev. Lett. 69 (25) (1992) 3631.
[23] V. Lyssenko, J. Erland, I. Balslev, K.-H. Pantke, B.S. Razbirin, J.M. Hvam, Phys. Rev. B 48 (8) (1993) 5720.
[24] J. Feldmann, T. Meier, G. von Plessen, M. Koch, E.O. Göbel, P. Thomas, G. Bacher, C. Hartmann, H. Schweizer, W. Schäfer, H. Nickel, Phys. Rev. Lett. 70 (20) (1993) 3027.
[25] S.T. Cundiif, M. Koch, W.H. Knox, J. Shah, W. Stolz, Phys. Rev. Lett. 77 (6) (1996) 1107.
[26] M.U. Wehner, D. Steinbach, M. Wegener, Phys. Rev. B 54 (8) (1996) R5211.
[27] D. Birkedal, V.G. Lyssenko, J.M. Hvam, K. El Sayed, Phys. Rev. B 54 (20) (1996) 14250.
[28] D.-S. Kim, J. Shah, J.E. Cunningham, T.C. Damen, W. Schäfer, M. Hartmann, S. Schmitt-Rink, Phys. Rev. Lett. 68 (7) (1992) 1006.
[29] J.-Y. Bigot, M.-A. Mycek, S. Weiss, R.G. Ulbrich, D.S. Chemla, Phys. Rev. Lett. 70 (21) (1993) 3307.
[30] A. Euteneuer, E. Finger, M. Hofmann, W. Stolz, T. Meier, P. Thomas, S.W. Koch, W.W. Rühle, R. Hey, K. Ploog, Phys. Rev. Lett. 83 (10) (1999) 2073.
[31] M. Zanni, N.-H. Ge, Y.S. Kim, R.M. Hochstrasser, Proc. Natl. Acad. Sci. USA 98 (2001) 11265.
[32] L. Lepetit, G. Cheriaux, M. Joffre, J. Opt. Soc. Am. B 12 (12) (1995) 2467.
[33] T. Zhang, X. Li, C.N. Borca, S.T. Cundiff, Opt. Express 13 (19) (2005) 7432.
[34] J.M. Shacklette, S.T. Cundiff, J. Opt. Soc. Am. B 20 (4) (2003) 764.
[35] We note that incoherent relaxation from the upper excited state to the lower one can also result in asymmetric off-diagonal peaks, however only for finite delay between second and third pulses, so it cannot explain our observations.
[36] X. Li, T. Zhang, C.N. Borca, S.T. Cundiff (submitted for publication).