Raman Quantum Beats of Interacting Excitons

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Quantum beats involving the light hole (*lh*) and heavy hole (*hh*) excitons in GaAs are observed using homodyne detection of the transient four-wave mixing response. Unlike the beats of earlier studies, these beats are detected in a geometry for which the effect would be forbidden in the absence of exciton interactions and arise from coherence induced between the *lh* and *hh* excitons. The beats demonstrate the existence of the Raman coherence due to interaction, and the decay of the coherence shows the correlation of exciton dephasing rates to be relatively unaffected by the interaction. [S0031-9007(97)05064-3]

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Coherent nonradiative superpositions of electronic states produce novel and important nonlinear optical effects in atomic systems, such as dark states [1,2], population trapping [3,4], lasing without inversion [5–8], electromagnetically induced transparency [9,10], and quantum beats in absorption [11,12] and luminescence [13]. In the latter case, quantum beats have been an important spectroscopic tool, for example, in the determination of hyperfine and Zeeman splittings [14]. But, until recently, nonradiative coherences in semiconductors have remained comparatively unexplored, in part because rapid scattering severely limits coherence lifetimes. Using nonlinear coherent transient techniques, several groups have found important signatures of nonradiative semiconductor coherences in four-wave mixing (FWM) [15,16], the direct observation of the biexcitonic two-photon coherence in GaAs quantum wells [17], and in the recent report of quantum beats in the continuum [18].

In this work, we use homodyne-detected transient FWM to observe quantum beats arising from the Raman-like coherence between the *hh* and *lh* excitons. Unlike previously observed dipole quantum beats in self-diffracted FWM experiments, quantum beats in the homodyne geometry arise from the nonradiative coherence induced between the *lh* and *hh* excitons and are forbidden in the absence of *lh*-*hh* exciton interaction. Detection of the Raman coherence between *lh* and *hh* exciton states provides essential insight into the complex dynamics of excited direct-gap semiconductors, and measurements of the decay of this coherence provide new understanding of correlations between *hh*- and *lh*-exciton dephasing. Furthermore, the existence of this coherence is essential to the eventual observation of the recently predicted dark states of excitons in GaAs [19].

To facilitate understanding of the experimental results, we consider a simple physical model based on the exciton energy level diagram at zone center shown in Fig. 1(a). This two-electron picture follows a generalization of the four-level model first considered for this kind of problem [20,21] and later extended to more complex problems [22,23]. A more rigorous approach could be developed following the approach taken in Ref. [24], where the impact of these interactions on the coherent nonlinear optical response and heavy-hole–light-hole beating was first identified. The model shows the ground state of the system, two single-exciton states corresponding to the *lh* exciton and the *hh* exciton, and a two-exciton state, for which both a *lh* and *hh* exciton are created. In the absence of Coulomb interactions between excitons, the energy of the noninteracting two-exciton state $|\psi_{\mathrm{NI}}\rangle$ is $E_{2-\mathrm{ex}}^{\mathrm{NI}} = \hbar(\omega_{lh} + \omega_{hh})$ and the decay of this state are determined by the decays of the individual exciton states. In the presence of a *lh*-*hh* exciton interaction, the two-exciton state becomes $|\psi_{\mathrm{I}}\rangle$ and is characterized by energy $E_{2-\mathrm{ex}}^{\mathrm{I}} = \hbar(\omega_{lh} + \omega_{hh}) + E_{\mathrm{I}}$, where the interaction energy could, in principle, be positive for scattering states, or negative for a bound state, as in Fig. 1(a).

The nonradiative Raman coherence, described by the pure-state density matrix element $\rho_{lh\text{-}hh} = \langle lh|\Psi\rangle\langle\Psi|hh\rangle$,

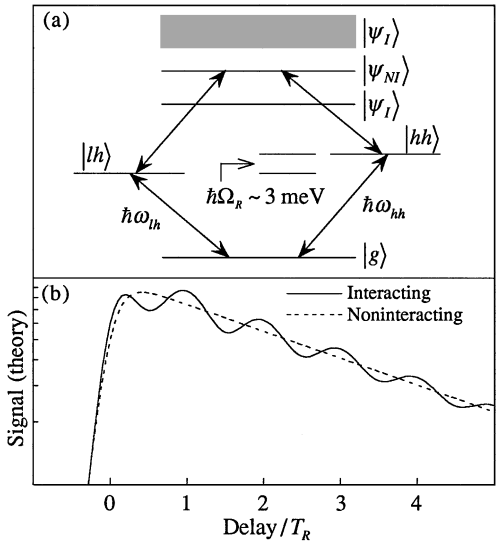

FIG. 1. The *lh*–*hh* interaction produces bound or scattering states $|\psi_{\mathrm{I}}\rangle$ (a) and produces Raman quantum beats [(b): solid], which would be absent for noninteracting excitons [(b): dashed]. Energy differences have been greatly exaggerated for clarity. The Raman period and frequency are related by $T_R\Omega_R = 2\pi$.

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is induced by dipole coupling of the ground state to the *lh* and *hh* excitons and gives rise to a polarization (at third order in the applied optical field) determined by $\langle lh|\Psi\rangle\langle\Psi|hh\rangle\langle hh|\hat{\mu}|g\rangle + \langle g|\hat{\mu}|lh\rangle\langle lh|\Psi\rangle\langle\Psi|hh\rangle$. However, in the absence of *lh*-*hh* exciton interaction, this term is canceled completely by destructive interference with a corresponding term coupled to the two-exciton state: $\langle lh|\Psi\rangle\langle\Psi|hh\rangle\langle hh|\hat{\mu}|\psi_{\mathrm{NI}}\rangle + \langle\psi_{\mathrm{NI}}|\hat{\mu}|lh\rangle\langle lh|\Psi\rangle\langle\Psi|hh\rangle$. This interference survives in the reduced density matrix, which includes decay.

In the presence of Coulomb coupling, optical coupling of the $|hh\rangle$ or $|lh\rangle$ states to the $|\psi_{\mathrm{I}}\rangle$ state differs considerably from the coupling to the $|\psi_{\mathrm{NI}}\rangle$ state: The energy shift leads to a decrease in effective excitation strength since the optical frequency is no longer exactly resonant; the change in the wave function leads to a change in the oscillator strength, and the dephasing rates and decay rates may also be different. Hence, cancellation of the $\langle lh|\Psi\rangle\langle\Psi|hh\rangle\langle hh|\hat{\mu}|\psi_{\mathrm{I}}\rangle + \langle\psi_{\mathrm{I}}|\hat{\mu}|lh\rangle\langle lh|\Psi\rangle\langle\Psi|hh\rangle$ term in the polarization is incomplete, and a net contribution of the Raman coherence persists in the polarization.

Figure 1(b) illustrates the prediction of a third-order perturbation theory for both interacting and noninteracting excitons in homodyne-detected FWM in the differential transmission experiment described below for collinearly polarized fields. In the presence of *lh*-*hh* exciton interaction, beats are observed (solid curve). The envelope of the beats decays with the Raman correlation time, and is superimposed on a slowly varying saturation response which decays with the recombination time. In the absence of *lh*-*hh* interaction, quantum beats are absent (dashed curve). In the limit that optical coupling to the two-exciton state (either $|\psi_{\mathrm{I}}\rangle$ or $|\psi_{\mathrm{NI}}\rangle$) is neglected, the analysis developed by Schmitt-Rink *et al.* [25] is recovered, if the simple model of Fig. 1 is augmented with the appropriate selection rules. The polarization dependence is not paramount to our consideration of the Raman coherence; for simplicity, we consider only the case of collinear field polarizations. Reference [25] has already addressed the polarization dependence of quantum beats in self-diffracted FWM experiments, and the theoretical distinction between dipole quantum beats in self-diffracted FWM and Raman quantum beats in the differential transmission (DT) geometry is also evident in their theory. But it is also clear that self-diffracted FWM experiments are sensitive to the temporal evolution of only the dipole coherence [26–29] and not the Raman coherence [30]. Like dipole quantum beats, Raman quantum beats evolve with the characteristic period $T_R = 2\pi/\Omega_R$, where $\hbar\Omega_R$ is the *lh*-*hh* splitting. However, the decay of the Raman coherence reveals dynamics different from dipole quantum beats. In particular, Raman coherence is sensitive to correlations between the *lh* and *hh* exciton dephasing processes.

Since the Raman coherence is established following excitation of both the *lh* and the *hh* excitons, the temporal evolution of this coherence can be observed only after their simultaneous excitation. Two different experimental methods are readily identified for this measurement: homodyne-detected FWM, which detects Raman beats through sensitivity to optical phase; and three-pulse direct-detected FWM, which employs spectrally narrow optical pulses to avoid dipole quantum beats and measures the Raman coherence without producing beats.

Measurements were performed at 5 K on several 2000-Å samples of MBE-grown high-quality bulk GaAs to probe the Raman coherence. The thin-film samples were bonded to a sapphire plate (*c*-axis normal), and the substrates were removed. Strain arising from the thermal mismatch of the GaAs to the sapphire was discussed in detail in [31] and induced a small *lh*-*hh* splitting ($\leq$3 meV), as shown in the inset of Fig. 2. Independent measurements demonstrated that the narrow lines seen in absorption are homogeneously broadened at 5 K and that there is no detectable Stokes shift in the luminescence. The excitation levels considered were sufficient (10^{15}–10^{16} cm^{-3}) to eliminate polariton effects [32].

The geometry for homodyne-detected FWM is identical to a simple pump-and-probe experiment for DT and so also includes contributions due to changes in absorption, which have been shown to be dominated by excitation-induced dephasing (EID) at these excitation levels [33]. The second, probing pulse induces a third-order polarization after the excitation of the first, pumping pulse. For collinearly polarized pulses, the induced polarization has the same field polarization. The induced polarization

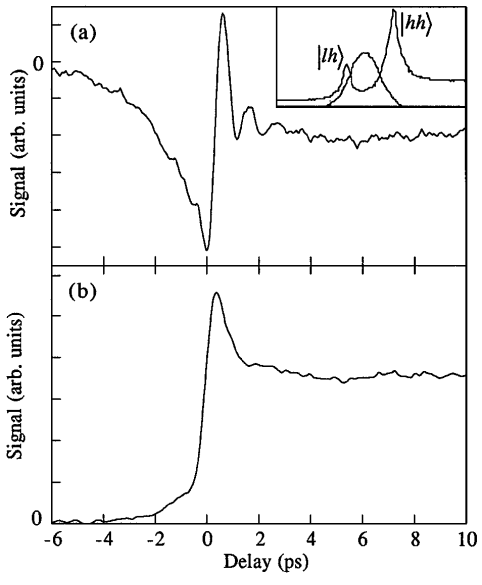

FIG. 2. (a) Raman coherence oscillations appear in homodyne-detected FWM for the tuning shown in the inset. The pulse bandwidth is 2 meV, and the total excitation density is 9×10^{15} cm^{-3}. (b) For a slightly different tuning, the beats are suppressed. [The overall sign of the DT response changes from (a) to (b), reflecting the sign change in EID as the laser is tuned closer to the *lh* exciton resonance.]

radiates a field copropagating with the probe pulse, and these two fields are detected by homodyne mixing in the square-law detector, which for this experiment is a photodiode. Hence, this experiment is sensitive to phase differences between the signal and pump fields and reveals the coherent evolution of the Raman coherence as a function of the delay between the pump and probe pulses. Phase-sensitive measurements have been made in the past in various geometries to extract important information about dynamics [17,18,34,35]. The calculation leading to the behavior in Fig. 1(b) shows the homodyne approach to be *inherently* immune to dipole quantum beats and, hence, particularly advantageous for isolating the Raman coherence.

Figure 2 shows data obtained using 1.5-ps pulses (bandwidth $\sim$2 meV) collinearly polarized. The inset shows the laser tuning, relative to the spectral positions of the *lh* and *hh* exciton features. We note that the overall signal goes negative, indicating an increase in absorption, consistent with effects of EID in the wings of the line and showing, as expected, that EID dominates the saturation at these excitation levels [33,36,37]. This effect decays slowly with the excitation relaxation time ($\sim$1 ns). More important, however, is the well defined oscillation superimposed on this signal in the photocurrent as a function of delay between the excitation and probe pulses. The observed beats clearly agree qualitatively with the prediction in Fig. 1 and reveal the temporal evolution of the Raman coherence. The oscillation period corresponds to the *lh*-*hh* energy splitting of the sample. The decay of the oscillation represents the scattering of the Raman coherence, distinct from the overall signal decay which corresponds to the recombination time. A non-pulse-width-limited Raman coherence time of approximately 2 ps is deconvolved from the data. Tuning the laser slightly, relative to the exciton resonances, provides a means to modulate the strength of the two interfering terms in the polarization. With the appropriate tuning, it is possible to suppress the beats completely, as seen in Fig. 2(b). We note, for completeness, that the simple model does not include effects of EID and local fields. These details determine the overall sign of the DT response and the origin of the negative delay signals and are not essential to the physics of this discussion. Similarly, the strong feature near zero delay in Figs. 2(a) and 2(b) is the coherent transient well known in DT studies [38].

We note that a spectrally nondegenerate three-beam direct-detected FWM experiment was also performed, but this approach requires the use of longer pulses to suppress ordinary dipole quantum beats. For 4-ps pulses, the observed decays were pulse width limited, as expected from the data in Fig. 2. In general, however, this approach is a more powerful spectroscopic approach because there are no background terms in the nonlinear response.

Direct observation of the temporal evolution of the Raman coherence affords an opportunity to examine correlated dynamical processes affecting the nonradiative coherence. A comprehensive microscopic model of dephasing is not available for semiconductors, but qualitative physical insight can be gained from a simple model admitting a variable degree of correlation between the scattering processes responsible for dephasing the *lh* and *hh* excitons. An illustrative model might assume that excitons are subject to normal distributions of weak (i.e., strictly elastic) Markovian scattering events, responsible for dephasing the macroscopic dipole coherences. The Raman dephasing rate under this simplifying approximation becomes

$$\gamma_{lh,hh} = \gamma_{lh,g} + \gamma_{hh,g} - 2R\sqrt{\gamma_{lh,g}\gamma_{hh,g}},$$

where the correlation R between the dipole dephasings depends on the underlying dynamics and represents the "similarity" of collisions affecting the dipole coherences, and $\gamma_{i,j}$ represents the dephasing rate between distinct states $|i\rangle$ and $|j\rangle$. Recombination is comparatively slow ($\sim$1 ns) and adds only a small correction of order 1%. If the scattering processes are uncorrelated ($R = 0$), the Raman coherence is rather short lived. Anticorrelation ($0 > R \geq -1$) would produce even faster decays. But if the dipole coherence times are comparable, as for GaAs, a long-lived Raman coherence is possible for positive correlations [39]. The observed Raman coherence time of approximately 2 ps is consistent within experimental uncertainty with uncorrelated dipole coherence scattering processes and independent measurements of the exciton dephasing rates. But at exciton densities exceeding 10^{15} cm^{-3}, for which the mean separation is comparable to the Bohr radius of the *hh* exciton, exciton-exciton scattering contributes significantly to the total dephasing rate. In this limit, correlations between collisions might be anticipated, as the binary collision approximation becomes less accurate with increasing density. Indeed, under these conditions, evidence suggesting failure of the binary collision approximation has been reported by Wang and co-workers in bulk GaAs [33] and in quantum wells [33,40], which would suggest a nonzero correlation R. Beyond this, a more detailed analysis must consider the effects of *hh* exciton coupling to the *lh* exciton continuum, which leads to complex Fano-like line shapes analogous to those observed in quantum wells [41,42].

We have made the critical distinction between Raman quantum beats and dipole quantum beats and have presented experimental results specifically probing Raman dynamics. The clear observation of Raman quantum beats in Fig. 2 establishes the existence of a *lh*-*hh* exciton interaction and provides a vital conceptual link between nonradiative coherences in GaAs and similar coherences long known to be important in atomic nonlinear optics. These studies support the possibility of observing semiconductor analogs of the atomic optical phenomena summarized above. In addition, the dipole dephasing processes which

affect the Raman dephasing were found to be essentially uncorrelated on the basis of a simple model, even at densities for which the binary collision approximation should fail. This surprising result may be explained by more sophisticated treatments of dephasing, possibly allowing exciton-exciton interactions to preserve the Raman phase in the presence of strong dipole dephasing, and remains under investigation.

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[1] E. Arimondo and G. Orriols, Nuovo Cimento Lett. **17**, 333–338 (1976).
[2] R. M. Whitley and C. R. Stroud, Jr., Phys. Rev. A **14**, 1498 (1976).
[3] D. P. Hodgkinson and J. S. Briggs, Opt. Commun. **22**, 45 (1977).
[4] H. R. Gray, R. M. Whitley, and C. R. Stroud, Jr., Opt. Lett. **3**, 218 (1978).
[5] O. A. Kocharovskaya and Y. I. Khanin, Zh. Eksp. Teor. Fiz. **90**, 1610 (1986) [Sov. Phys. JETP **63**, 945–950 (1986)].
[6] S. E. Harris, Phys. Rev. Lett. **62**, 1033 (1989).
[7] M. O. Scully, S. Y. Zhu, and A. Gavrielides, Phys. Rev. Lett. **62**, 2813 (1989).
[8] M. O. Scully, Quantum Opt. **6**, 203–215 (1994).
[9] K. J. Boller, A. Imamoglu, and S. E. Harris, Phys. Rev. Lett. **66**, 2593 (1991).
[10] J. E. Field, K. H. Hahn, and S. E. Harris, Phys. Rev. Lett. **67**, 3062 (1991).
[11] T. W. Ducas, M. G. Littman, and M. L. Zimmerman, Phys. Rev. Lett. **35**, 1752–1754 (1975).
[12] R. Zygan-Maus and H. H. Wolter, Phys. Lett. **64A**, 351–353 (1978).
[13] S. Haroche, in *High-Resolution Laser Spectroscopy*, edited by K. Shimoda, Topics in Applied Physics Vol. 13 (Springer-Verlag, Berlin, 1976).
[14] S. Haroche, M. Gross, and M. P. Silverman, Phys. Rev. Lett. **33**, 1063–1066 (1974).
[15] B. F. Feuerbacher, J. Kuhl, and K. Ploog, Phys. Rev. B **43**, 2439–2441 (1991).
[16] H. Wang *et al.*, Solid State Commun. **91**, 869–874 (1994).
[17] K. B. Ferrio and D. G. Steel, Phys. Rev. B **54**, 5231–5234 (1996).
[18] M. Joschko *et al.*, Phys. Rev. Lett. **78**, 737 (1997).
[19] M. Lindberg and R. Binder, Phys. Rev. Lett. **75**, 1403–1406 (1995).
[20] G. Finkelstein *et al.*, Phys. Rev. B **47**, 12 964 (1993).
[21] M. Koch *et al.*, Phys. Rev. B **48**, 11 480–11 483 (1993).
[22] K. Bott *et al.*, Phys. Rev. B **48**, 17 418–17 426 (1993).
[23] S. T. Cundiff *et al.*, Phys. Rev. Lett. **77**, 1107–1110 (1996).
[24] P. Kner, S. Bar-Ad, M. V. Marquezini, D. S. Chemla, and W. Schäfer, Phys. Rev. Lett. **78**, 1319 (1997).
[25] S. Schmitt-Rink *et al.*, Phys. Rev. B **46**, 10 460–10 463 (1992).
[26] E. O. Göbel *et al.*, Phys. Rev. Lett. **64**, 1801 (1990).
[27] K. Leo *et al.*, Appl. Phys. Lett. **57**, 19–21 (1990).
[28] K. Leo *et al.*, Phys. Rev. B **42**, 11 359–11 361 (1990).
[29] K. Leo *et al.*, Mod. Phys. Lett. B **5**, 87–93 (1991).
[30] The contributions of the Raman coherence to DT and self-diffracted FWM differ significantly. In FWM, a Raman coherence is generated jointly by $E_1E_2^*$, and E_2 immediately scatters again from this coherence, to produce a signal in the direction $2k_2 - k_1$. As a function of delay between the two fields, the signal reveals only decay of the dipole coherences created by E_1 and nothing about the evolution of the Raman coherence. In contrast, the DT geometry selects the Raman coherence produced by the simultaneous action of E_1 on both exciton transitions, given by $E_1E_1^*$. The signal is again given by the scattering of E_2 from the Raman coherence, but in the direction k_2, and the delay between E_1 and E_2 allows a measurement of the evolution of the Raman coherence.
[31] M. Jiang *et al.*, Phys. Rev. B **48**, 15 476 (1993).
[32] A. C. Schaefer and D. G. Steel, Phys. Rev. Lett. **79**, 4870 (1997).
[33] H. Wang *et al.*, Phys. Rev. Lett. **71**, 1261–1264 (1993).
[34] J.-Y. Bigot *et al.*, Phys. Rev. Lett. **70**, 3307–3310 (1993).
[35] D. S. Chemla *et al.*, Phys. Rev. B **50**, 8439–8453 (1994).
[36] H. Wang *et al.*, Phys. Rev. A **49**, 1551–1554 (1994).
[37] Y. Z. Hu *et al.*, Phys. Rev. B **49**, 14 382–14 386 (1994).
[38] S. L. Palfrey and T. F. Heinz, J. Opt. Soc. Am. B **2**, 674–678 (1985).
[39] The choice of dephasing rates in Ref. [24] corresponds to a strongly correlated system, with $R = 0.5$.
[40] H. Wang, J. Shah, and T. C. Damen, Phys. Rev. Lett. **74**, 3065 (1995).
[41] D. A. Broido *et al.*, Phys. Rev. B,Rapid Commun. **37**, 2725–2728 (1988).
[42] A. Honold *et al.*, Phys. Rev. B **45**, 6010–6014 (1992).