Instantaneous Frequency Dynamics of Coherent Wave Mixing in Semiconductor Quantum Wells

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(Received 23 February 1993)

Using a combination of interferometric-correlation and time-resolved intensity measurement techniques, we characterize the phase and amplitude of the coherent emission of semiconductor quantum wells resonantly excited by ultrashort optical pulses. We demonstrate that exciton-exciton interaction produces nonlinear phase shifts of the instantaneous frequency relative to the incident laser.

PACS numbers: 71.35.+z, 42.65.−k, 71.45.Gm, 78.47.+p

Ultrashort-pulse optical spectroscopy has proved to be a valuable technique for investigating the dynamics of a wealth of mechanisms in solids, including scattering of elementary electronic excitations with vibrations and other quasiparticles [1]. Up to now investigation of dephasing dynamics in semiconductors, metals, and molecular materials has been restricted to measuring the amplitude decay of the field radiated by induced polarizations [2]. The full description of an electromagnetic field requires the knowledge of both its amplitude and its phase. The information contained in the phase is trivial only in the case of very simple systems, such as ideal independent two-level systems or harmonic oscillators. For almost all realistic condensed matter systems, the phase of the field contains important information on the mechanisms, Coulomb correlation, and quantum statistics that govern the establishment and decay of the polarization of the medium. In this Letter we present the first experimental investigation of the instantaneous frequency of the coherent emission of semiconductor quantum wells resonantly excited by ultrashort optical pulses. We show that exciton-exciton interaction, mediated by Coulomb interaction and by Pauli exclusion, manifests itself by nonlinear phase shifts of the instantaneous frequency of the emitted signal relative to the laser which excites the sample.

We have investigated the amplitude and phase of the coherent emission by four-wave mixing (FWM). In these experiments, two ultrashort laser pulses propagating in the directions k_1 and k_2, and incident on the sample at time t and $t-\Delta t$, respectively, generate a nonlinear polarization $P_{\mathrm{NL}}(t,\Delta t)$ that emits a coherent signal $S(t,\Delta t)$ in the direction $k_s=2k_2-k_1$. Recently time-integrated [3,4] and time-resolved measurements [5,6] have shown that the temporal profiles of the intensities $|S(t,\Delta t)|^2$ and $|S(\Delta t)|^2=\int dt|S(t,\Delta t)|^2$ exhibit significant departures from that which independent atomiclike systems would emit. In semicondutors, two mechanisms contribute to the nonlinearity that generate $P_{\mathrm{NL}}(t,\Delta t)$. The first is due to Pauli exclusion and is present in all material systems. This contribution is essentially instantaneous. The second originates from many-body Coulomb correlation among the extended and delocalized excitons. Through this Coulomb-mediated exciton-exciton interaction, coherent excitonic polarization waves can interact with one another [4]. Light emission through polarization-wave coupling is not instantaneous for it takes time to build up in the sample. The nonlinearity governing this coupling bears a striking resemblance to the Ginzburg-Landau mechanism which, near the superconducting transition, drives the Cooper pairs toward a coherent state [7]. The difference in dynamics between the two mechanisms is at the origin of the unusual features of the FWM intensity temporal profiles recently observed. Clearly these distinct dynamics should also influence the *phase* of the FWM signal, as is evident from direct inspection of the equations describing this process [8]. This remark has motivated the investigations we report here.

The simultaneous characterization of the amplitude $A(r,t)$ and phase $\phi(r,t)$ of an optical field is a difficult experimental task. Time-resolved interferometric autocorrelation and cross correlations are powerful techniques to characterize $A(r,t)$ and $\phi(r,t)$. They remain, however, difficult to use as spectroscopic tools in the case of a very weak signal, for practical and fundamental reasons. Indeed, in the absence of other information, one should measure the autocorrelation to all orders to completely specify the absolute phase. To circumvent these difficulties we have used the combination of measurements of five quantities, each of which gives complementary information on $A(r,t)$ and $\phi(r,t)$. These are the power spectrum $|S(\omega,\Delta t)|^2$; the first-order interferometric autocorrelation $C_{\mathrm{auto}}(\tau,\Delta t)=\int dt|S(t,\Delta t)+S(t-\tau,\Delta t)|^2$; the first-order interferometric cross correlation with the laser $C_{\mathrm{cross}}(\tau,\Delta t)=\int dt|L(t)+S(t-\tau,\Delta t)|^2$; the time-resolved signal intensity $|S(t,\Delta t)|^2$; and the time-integrated signal intensity $|S(\Delta t)|^2$. Although in theory $|S(\omega,\Delta t)|^2$ and $C_{\mathrm{auto}}(\tau,\Delta t)$ are a pair of Fourier conjugates, in practice they are measured over a limited window of frequency ω or time τ. Therefore, the information provided by the *experimental* $|S(\omega,\Delta t)|^2$ is good for frequencies ω close to ω_L and poor for short-τ behavior. Conversely, the experimental $C_{\mathrm{auto}}(\tau,\Delta t)$ is good for short-τ behavior and poor for frequencies ω close to ω_L.

The optical pulses were derived from a Ti:sapphire laser. The laser was precisely characterized by first-order and second-order interferometric autocorrelations and power-spectrum measurements. It delivers extremely stable, tunable, chirp-free, transform-limited pulses with

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a Gaussian profile, $L(t)$, and a duration of approximately 100 fs. The sample investigated was a 50-period 95-Å-GaAs/45-Å-$Ga_{0.7}Al_{0.3}As$ multiple quantum well structure. The GaAs substrate was removed by chemical etching and the sample was antireflection coated on both sides and glued on a sapphire holder. During the experiment, it was kept at room temperature so that the exciton resonances were homogenized by collision with thermal phonons [5]. The sample absorption spectrum shows the usual resonances for the heavy-hole ($\Omega_{hh} \sim 1.467$ eV) and light-hole ($\Omega_{lh} \sim 1.482$ eV) excitons, followed by a flat continuum. $C_{auto}(\tau,\Delta t)$ was obtained by analyzing the FWM signal in a Michelson interferometer. For measuring $C_{cross}(\tau,\Delta t)$, the whole FWM setup was put inside a Mach-Zender interferometer. $|S(\omega,\Delta t)|^2$ was measured with a spectrometer and an optical multichannel analyzer. Finally, as described in Ref. [5], for each time delay Δt, the FWM signal intensity $|S(t,\Delta t)|^2$ could be time resolved by sum-frequency generation with a laser pulse in a transparent nonlinear crystal. The FWM signal intensity could also be integrated by a slow detector to give $|S(\Delta t)|^2$. Measurements were taken as functions of time delay Δt, laser intensity, and central frequency ω_L. As explained below, using the laser as a reference, we performed differential measurements in order to eliminate any phase distortion introduced by optical elements other than the sample. In addition, extreme care was given to the selection of optical and mechanical components, especially the stepper motors, to ensure the reproducibility and reliability required for obtaining high quality interferometric data. The resolution of our measurements is such that one optical fringe (2.8 fs) is covered by 21 steps of a high precision stepper motor, giving an accuracy in the location of the fringe extrema of ~ 0.14 fs.

FWM power spectra $|S(\omega,\Delta t=0)|^2$ and laser spectra are shown in Fig. 1 for two densities when the laser is tuned slightly below [Figs. 1(a) and 1(b), $\omega_L < \Omega_{hh}$] and slightly above [Figs. 1(c) and 1(d), $\omega_L > \Omega_{hh}$] the heavy-hole exciton. At very low exciton densities, $N_x \sim 3 \times 10^9$ cm^{-2}, the FWM power spectra essentially reproduce the line shape of the exciton resonances within the laser spectra. The line shape is asymmetric: When $\omega_L < \Omega_{hh}$ it exhibits only one resonance, whereas two unequal resonances are present when $\omega_L > \Omega_{hh}$. As the exciton density is increased, the FWM power spectrum evolves toward that of the laser and becomes almost indistinguishable from it at the highest density shown in the figure, $N_x \sim 3 \times 10^{11}$ cm^{-2}. The low-density line shapes suggest, by Fourier transformation, dynamic nonlinear shifts of the FWM frequency during a single pulse. The FWM intensity temporal profiles are very similar to those reported in Ref. [5]. They are well behaved with a smooth rising edge and a nonexponential but smooth trailing edge.

Since the autocorrelation does not determine the phase of the FWM signal directly, we have analyzed the interferometric data in the following way. For each delay Δt,

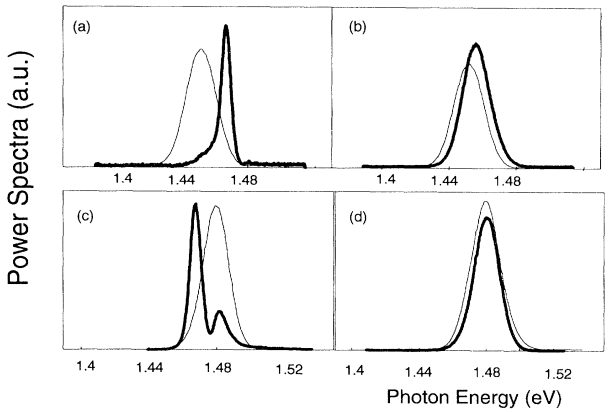

FIG. 1. Power spectra of the four-wave-mixing signal (thick lines) and laser spectra (thin lines) for two exciton densities, $N_x \sim 3 \times 10^9$ and $N_x \sim 3 \times 10^{11}$ cm^{-2}, when the laser is tuned slightly below the heavy-hole exciton [(a) and (b)] and slightly above the heavy-hole exciton [(c) and (d)].

we have first measured the dynamic fringe spacing, i.e., the number of interferometric fringes during the interferometer delay τ for the FWM signal, $F_{FWM}(\tau)$, and for the laser pulse (passing through the same experimental setup and the sapphire holder but missing the sample itself), $F_L(\tau)$. The differential fringe spacing defined as $\Delta F(\tau) = F_L(\tau) - F_{FWM}(\tau)$, could then be precisely extracted from the data. For precise calibration, the Ti:sapphire laser was operated cw, thus providing a reference frequency which was later used to analyze the laser $C_{auto}(\tau)$ when operated mode locked. The $\Delta F(\tau)$ *sign* was determined by measuring the cross correlation with the laser $C_{cross}(\tau)$. When the phase is constant or varies linearly versus t, $\Delta F(\tau)$ corresponds exactly to the phase difference between the laser and the signal. In the most

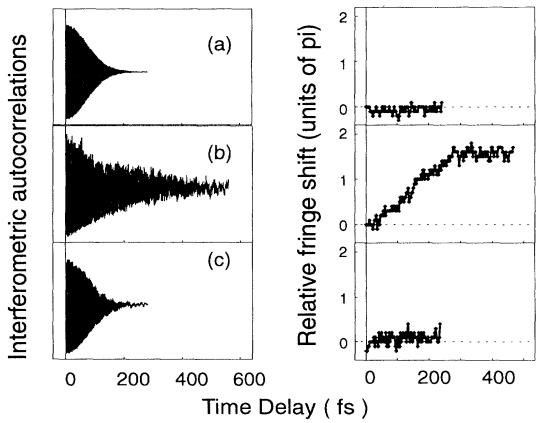

FIG. 2. Interferometric autocorrelation, $C_{auto}(\tau)$, and differential fringe spacing, $\Delta F(\tau)$, for (a) the laser, (b) the low-density, and (c) the high-density FWM signal, when the laser is tuned slightly below the heavy-hole exciton ($\omega_L < \Omega_{hh}$). The conditions where (b) and (c) were obtained correspond to the power spectra (a) and (b), respectively, of Fig. 1.

general case and in the absence of other information there is no simple mathematical relationship between $\Delta F(\tau)$ and the phase difference. In our experiments, however, we determine the power spectrum and we know that the FWM signal has a smooth and well-behaved temporal profile. We have checked numerically on numerous examples that in this case $\Delta F(\tau)$ reproduces quite faithfully the phase difference with the reference.

Figure 2 shows the $\Delta t = 0$ $C_{\text{auto}}(\tau)$ and $\Delta F(\tau)$ for (a) the laser (passing through the optical elements and calibrated to the reference frequency of the laser operated cw), (b) the low-density FWM signal, and (c) the high-density FWM signal in the case $\omega_L < \Omega_{\text{hh}}$. Figure 3 shows the same quantities when $\omega_L > \Omega_{\text{hh}}$. In both cases the high-density FWM $C_{\text{auto}}(\tau)$ envelopes are of the order of that of the laser and $\Delta F(\tau)$ indicates that the FWM instantaneous frequency presents no significant difference from that of the laser. Conversely, the low-density FWM $C_{\text{auto}}(\tau)$ envelopes are much longer than those of the laser and, more importantly, $\Delta F(\tau)$ shows significant nonlinear frequency shifts.

For $\omega_L < \Omega_{\text{hh}}$, the low-density $\Delta F(\tau)$ starts with a positive linear variation. The slope corresponds well to the difference in frequencies between the laser and the principal peak seen in the FWM power spectrum of Fig. 1(a). Then for $300 < \tau < 450$ fs, the $\Delta F(\tau)$ slope vanishes indicating that during the pulse the instantaneous frequency shifts toward that of the laser. These nonlinear phase dynamics are consistent with the power spectra of Figs. 1(a) and 1(b). In particular the power spectrum of Fig. 1(a), besides a main peak at the hh-exciton frequency, exhibits an asymmetric low-frequency tail extending well into the laser spectra.

For $\omega_L > \Omega_{\text{hh}}$, again the high-density $\Delta F(\tau)$ has a zero slope showing that the FWM frequency is essentially that of the laser. Conversely, the low-density $\Delta F(\tau)$ exhibits a negative variation with a curvature. This indicates that, in this case, the FWM frequency is dominated by a component below the laser central frequency. The dynamics of the instantaneous frequency, however, are complicated and do not correspond to a linear chirp. Again this is consistent with the power spectrum of Fig. 1(c), which shows strong but unequal contributions from both excitons. In order to further explore this case we have adjusted the excitation frequency ($\omega_L \sim \Omega_{\text{lh}}$) and intensity to obtain hh-exciton and lh-exciton contributions of roughly the same weight in the FWM power spectrum; see Fig. 4(a). In this case, $C_{\text{auto}}(\tau)$ presented in Fig. 4(b) clearly shows several interference patterns. In order to establish that the observed effect corresponds to the quantum beats of homogeneous system and not to polarization interferences from independent systems, we have applied the method of Ref. [9]. We verified that the asymmetric features seen in the interferometric cross correlation for various time delays, $C_{\text{cross}}(\tau,\Delta t)$, vary as Δt and not as $2\Delta t$. Quantum beats between hh and lh excitons have been observed recently as modulation of the decay of

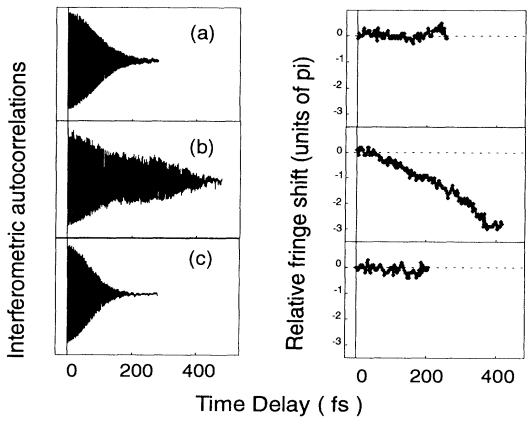

FIG. 3. Interferometric autocorrelation, $C_{\text{auto}}(\tau)$, and differential fringe spacing, $\Delta F(\tau)$, for (a) the laser, (b) the low-density, and (c) the high-density FWM signal, when the laser is tuned slightly above the heavy-hole exciton ($\omega_L > \Omega_{\text{hh}}$). The conditions where (b) and (c) were obtained correspond to the power spectra (c) and (d), respectively, of Fig. 1.

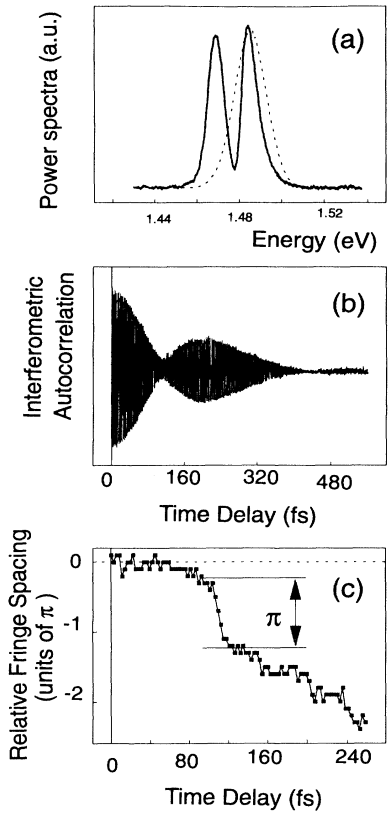

FIG. 4. (a) Power spectrum, (b) interferometric autocorrelation, and (c) differential fringe spacing of the FWM signal when the laser is tuned to give contributions of the hh and lh excitons of approximately the same weight.

FWM signal intensity [10,11]. The new information provided by the interferometric techniques is shown in Fig. 4(c) where $\Delta F(\tau)$ is depicted. It starts with a zero slope showing that the FWM frequency is the same as that of the laser, $\omega_L \sim \Omega_{\rm lh}$, and then it exhibits a negative curvature showing a change toward a lower frequency. Around $\tau \sim 120$ fs, $\Delta F(\tau)$ experiences a sudden phase shift of π before resuming its negative variation. This phase shift occurs over an interval of only ten optical fringes; its position corresponds to the first node of beat in $C_{\rm auto}(\tau)$ and is in excellent agreement with the separation of the two peaks of the FWM power spectrum of Fig. 4(a).

To the best of our knowledge there is, at present, no theory able to give a description of nonlinear phase shifts occurring in FWM within a single ultrashort pulse with an accuracy comparable to that of our experimental data. The case of single-resonance excitation can be understood qualitatively in terms of a model based on the one-resonance restriction of the two-band semiconductor Bloch equations [4,7]. The analytical solution in the case of optical fields with δ-function envelopes [Eq. (2) of Ref. [7]] gives the FWM signal a nonlinear phase which starts with a slope proportional to the ratio between the Coulomb and Pauli nonlinearities, and saturates to a value which depends on the relaxation times. The corresponding power spectrum is reminiscent of Fig. 1(a): It has a dominant peak at the exciton and an asymmetric low-frequency tail. Numerical calculations of $\Delta F(\tau)$ based on this crude model reproduced qualitatively the trends of Fig. 2(b) [12]. The case of two-resonance excitation requires two valence bands in the semiconductor Bloch equations. In this case one finds two families (hh and lh) of excitons, each one possessing "internal" Coulomb and Pauli nonlinearities. Furthermore, they are coupled by these two mechanisms as well. The Pauli coupling originates from the fact that the two families of excitons share the same conduction band. The Coulomb coupling originates from the inter-valence-band transitions, which provide an additional transition mechanism between the conduction band and either one of the valence bands [12]. This model implies that the inter-valence-band transitions can be driven by excitation near the fundamental gap and emit in the far infrared, in agreement with the recent observation of coherent THz emission by quantum wells [13].

In conclusion, we have performed the first experimental investigation of the instantaneous frequency of the coherent emission of semiconductor quantum wells resonantly excited by ultrashort optical pulses. We have observed nonlinear phase shifts of the instantaneous frequency of the emitted signal relative to the laser which excites the sample. We explain these phase variations in terms of the interplay between two nonlinearities: Coulomb-mediated exciton-exciton and Pauli exclusion.

Finally, we wish to stress that the experimental method presented in this Letter is quite general. It can be applied to a number of condensed matter systems and should provide new information on the dynamics of their interaction with electromagnetic fields.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

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