Evidence for Intervalence Band Coherences in Semiconductor Quantum Wells via Coherently Coupled Optical Stark Shifts

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We report the experimental observation of coherently coupled heavy-hole–light-hole Stark shifts, i.e., light-hole exciton shifts under heavy-hole exciton pumping conditions, in InGaAs quantum wells. The theoretical analysis of the data is based on a full many-body approach (dynamics-controlled truncation formalism) in the third-order nonlinear optical regime. It is shown that the Stark shift data can be interpreted as strong evidence of suitably defined nonradiative intervalence band coherences in a semiconductor quantum well. Hence, the observations establish a semiconductor analog of Raman coherences in three-level atoms.

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The optical Stark shift in semiconductors [1–3] is an important transient nonlinearity which helps to understand fundamental ultrafast microscopic processes. Studies of similarities and differences between optical Stark shifts in atomic two-level systems and those observed in semiconductors led to the understanding of semiconductor-specific many-body effects such as biexcitons [4] and Coulomb memory effects [5].

While the *two-level* analogies of Stark shifts in semiconductors have been successfully exploited, the question of what one can learn from a comparison of coherent atomic *three-level* effects with optical Stark shifts in semiconductors using the coherent coupling between heavy-hole (hh) and light-hole (lh) excitons has not been widely addressed so far. In atomic three-level systems, nonradiative or Raman coherences [indicated schematically as dotted arrow in Fig. 1(a)] are the foundation of important nonlinear optical effects such as electromagnetically induced transparency and lasing without inversion (see, e.g., [6,7]). Clearly, it is desirable and of general importance to establish analogies between those important atomic three-level effects and their semiconductor counterparts (e.g., [8] and references therein). In bulk semiconductors, observations of Raman quantum beats have been reported [9], but an unambiguous experimental proof of nonradiative intervalence band coherences in semiconductor quantum wells has, to our knowledge, not been given so far.

In this paper, we present our experimental observations of the coherently coupled optical Stark effect [which is schematically shown in Figs. 1(a)–1(c)] on hh and lh exciton resonances and show that these data provide direct evidence for the existence of an appropriately defined hh-lh Raman coherence in semiconductor quantum wells. Our theoretical analysis is based on a full many-body theory within the third-order nonlinear optical regime.

We first discuss the situation under consideration in the language of a three-level system. We consider only the case in which the pump light [thick arrow in Fig. 1(a)] couples levels $|1\rangle$ and $|2\rangle$. The corresponding dressed states are schematically shown in Fig. 1(b) (for simplicity, the sketch shows the case of zero detuning). Level $|3\rangle$ does not exhibit dressed state splitting since the pump light does not affect it. Probing the 1-2 transition, one sees the ordinary two-level Stark shift [short thin arrow in Fig. 1(b)], whereas probing the 1-3 transition corresponds to what we call the coherently coupled Stark shift.

An observation of the coherently coupled Stark shift provides direct evidence for the existence of the Raman coherence involving levels $|2\rangle$ and $|3\rangle$. This can easily be seen in a theory for the density matrix ρ_{ij} where the Raman coherence is ρ_{32}. The equation governing the 1-3 transition is $i\hbar\dot{\rho}_{31} = (\varepsilon_3 - \varepsilon_1)\rho_{31} - H_{31}(\rho_{33} - \rho_{11}) - \rho_{32}H_{21}$, where the level energies ε_i correspond to the

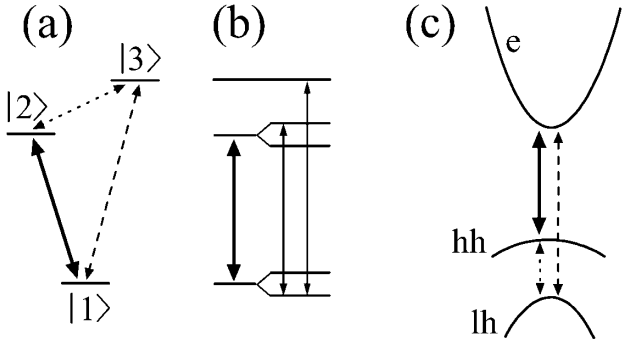

FIG. 1. (a) Energy levels of a three-level V system. The optical pump (probe) transition is indicated as thick (dashed) arrow, the nonradiative transition as dotted arrow. (b) Corresponding dressed states diagram (simplified). The Stark-shifted transitions are indicated as thin arrows. (c) Analogous semiconductor band structure with conduction band (e), heavy-hole (hh), and light-hole (lh) bands.

diagonal matrix elements of the Hamiltonian, H_{ii}. The dipole coupling gives rise to the two off-diagonal matrix elements H_{21} and H_{31}, while $H_{32} = 0$. Within first order of the light-coupling H_{31}, the inversion $\rho_{33} - \rho_{11}$ remains -1, and the 1-3 energy shift due to the strong light-coupling H_{21} follows from the term involving the Raman coherence, $\rho_{32}H_{21}$. Without Raman coherence no coupled Stark shift can be observed while with Raman coherence the 1-3 transition energy shift turns out to be half the ordinary 1-2 Stark shift as indicated in Fig. 1(b).

As already mentioned, the semiconductor quantum well analog to the three-level system is the (twofold degenerate) three-band system consisting of a conduction band, and hh and lh valence bands [see Fig. 1(c)]. While in the band picture the analogy holds for each in-plane momentum state k, the Coulomb interaction prevents the analogy from being completely accurate. In this paper, we assume the linear optical response as well as the Stark shift to be dominated by $1s$-hh and $1s$-lh excitons. But even within this simplified picture, the three-level vs semiconductor analogy is not strict. Exciton-scattering and biexcitonic contributions to the Stark shift have no counterparts in three-level systems, but as long as those processes do not dominate the Stark shift, an approximate analogy is possible and defining an excitonic Raman coherence (excitonic intervalence band coherence) is appropriate.

Our experimental sample contains ten $In_{0.04}Ga_{0.96}As$ quantum wells of 8 nm thickness. Its absorption spectrum, Fig. 2(a), is dominated by sharp hh and lh exciton resonances that are well separated. We measure the transient absorption changes at both resonances after excitation below the hh exciton transition. Since the splitting between hh and lh resonances is even larger than the pump-to-hh-exciton detuning, the pump light exclusively couples to the hh exciton transition. This possibility distinguishes our experiment from earlier Stark effect measurements where a small hh-lh splitting leads to direct pumping of hh and lh excitons as well as coupling to all six bands in the two twofold degenerate three-band systems [10]. In our configuration, we effectively reduce the two degenerate three-band systems to a single three-band system by driving a single hh transition with a circularly polarized pump pulse and probing the coherently coupled lh transition with the opposite circular polarization.

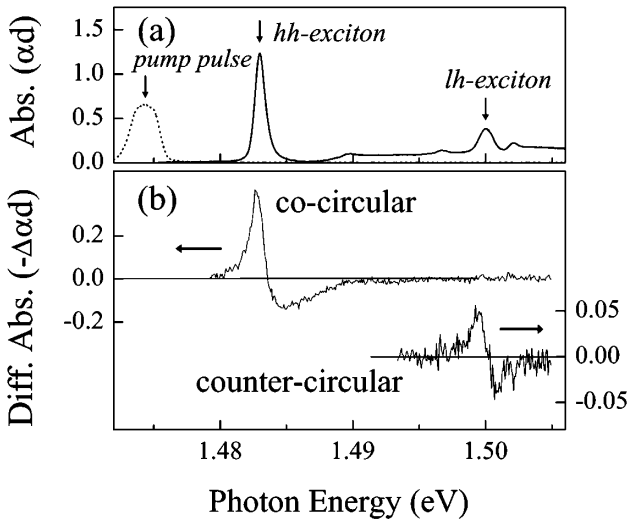

FIG. 2. (a) Absorption spectrum of the InGaAs QW at $T = 4$ K (solid line) and the pump pulse spectrum (dotted line). (b) Differential absorption spectra ($-\Delta\alpha d = -\alpha_{\text{with pump}}d + \alpha_{\text{without pump}}d$) measured at maximum temporal pump-probe overlap with co- and countercircularly polarized pump (intensity = 21 MW/cm^2) and probe pulses, respectively.

The weak, broadband probe pulses are generated by focusing amplified Ti:sapphire laser pulses of about 100 fs duration on a sapphire crystal. Using the same amplified pulses and an optical parametric amplifier we generate tunable pump pulses and pass them through a pulse shaper. This spectrally narrows them to a 2.2 meV bandwidth [see Fig. 2(a)] and stretches them to 1.2 ps duration. The spectral pump pulse maximum is varied between 3.5 and 10.6 meV below the hh exciton absorption maximum. For most measurements, we apply 2.4 nJ pump pulses focused to a 240 μm diameter spot at the sample for a peak intensity of 3.7 MW/cm^2, while for larger pump-to-hh-exciton detunings we also performed measurements at 21 MW/cm^2.

Figure 2(b) shows two differential absorption spectra. The pump pulse in this case has an intensity of 21 MW/cm^2 and is detuned 8.8 meV below the linear hh exciton resonance, but the general features observed here are common to all of our measurements. For cocircularly polarized pulses, and in agreement with earlier Stark effect experiments [1–3], we find a pronounced decrease in absorption below and at the original (undressed) hh exciton resonance and an increase in absorption at the high-energy side. This corresponds to a blueshift of the hh exciton resonance that is accompanied by exciton bleaching. Within our accuracy we do not observe any nonlinear response at the lh exciton resonance indicating negligible direct coupling between the pump field and the lh exciton. For the same pumping conditions but with an oppositely circularly polarized probe pulse, a definite blueshift appears at the lh exciton resonance [11].

The transient character of the nonlinear response is revealed by observing the differential absorption as a function of temporal pump-probe delay. Figure 3(a) shows the delay dependence of the hh exciton shift for cocircular polarization, while Fig. 3(b) shows that of the lh exciton shift for countercircular polarization. The pumping conditions are the same as in Fig. 2(b). The shifted exciton energies are obtained by calculating the first-moment expectation values (= frequency integral of absorption times frequency) of the measured nonlinear hh and lh exciton absorption lines (linear absorption + absorption change) within 7 meV windows around the respective absorption peaks. Both hh and lh exciton shifts closely follow the driving pump field indicating the absence of incoherent nonlinear effects.

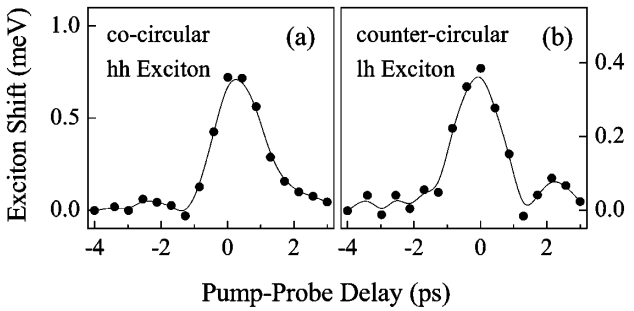

FIG. 3. Dynamics of the shift of the hh (a) and lh (b) exciton resonance for the conditions of Fig. 2(b).

Figure 4(a) shows the shifts of the central energies of the coherently coupled hh and lh exciton resonances at zero time delay for various pump-to-hh-exciton detunings. Within the range of our data, the coupled dynamic Stark shifts are always blueshifts with the lh exciton shift being similar but always smaller than the hh exciton shift. Since the Stark shifts decrease with increasing detuning [2], we also show data for higher pump intensity at larger detunings (open symbols) utilizing the approximately linear increase of the shifts with pump intensity [2] to obtain a better signal to noise ratio.

Our theoretical analysis of the nonlinear response is based on a third-order expansion of the dynamics-controlled truncation formalism [12]. Within that theory, the third-order optical polarization induced by the pump and/or probe light is determined by phase-space filling (PSF), Hartree-Fock (HF), and two-exciton-correlation (including biexciton) contributions. The momentum-dependent interband polarization coupling the conduction band s (where $s = \pm 1/2$ denotes the spin) with valence band j (where $j = \pm 3/2$ in the case of hh's and $j = \pm 1/2$ for lh's) is given, in terms of electron (a) and hole (b) annihilation operators, by $P_{sj}(\vec{k}) = \langle b_{j,-\vec{k}} a_{s,\vec{k}} \rangle$. The nonlinear contributions determining $P_{sj}(\vec{k})$ contain electron (hole) distribution functions $f_{ss}(\vec{k}) = \langle a^{\dagger}_{s,\vec{k}} a_{s,\vec{k}} \rangle$ ($f_{jj}(\vec{k}) = \langle b^{\dagger}_{j,\vec{k}} b_{j,\vec{k}} \rangle$), intervalence band coherence functions $f_{j\neq j'}(\vec{k}) = \langle b^{\dagger}_{j',\vec{k}} b_{j,\vec{k}} \rangle$ (with $j \neq j'$), and two-exciton correlation functions $B_{sjs'j'}(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4,) = \langle b_{j',-\vec{k}_4} a_{s',\vec{k}_3} b_{j,-\vec{k}_2} a_{s,\vec{k}_1} \rangle - \langle b_{j',-\vec{k}_4} a_{s',\vec{k}_3} \rangle \langle b_{j,-\vec{k}_2} a_{s,\vec{k}_1} \rangle + \langle b_{j',-\vec{k}_4} a_{s,\vec{k}_1} \rangle \langle b_{j,-\vec{k}_2} a_{s',\vec{k}_3} \rangle$. As mentioned above, the appearance of $B_{sjs'j'}$ makes it impossible to formulate a strict analogy between atomic three-level systems and semiconductor quantum wells, even if one restricts oneself to the lowest-order nonlinear optical regime. However, $f_{j\neq j'}$ represents a direct generalization of the atomic Raman coherence ρ_{32}. If, therefore, the contribution of $B_{sjs'j'}$ to the optical Stark shift is negligible with respect to that of the distribution and Raman coherence functions f, the analogy is well defined, and it is meaningful to study the role of $f_{j\neq j'}$ on the measured Stark shift.

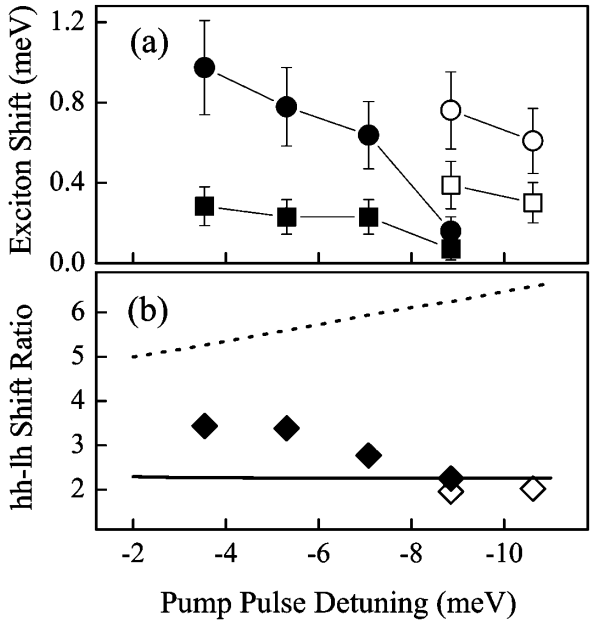

FIG. 4. (a) Measured Stark shifts of the hh (dots) and lh (squares) exciton for co- and countercircular pump-probe polarization, respectively, at zero pump-probe delay as a function of detuning between pump pulse and hh exciton energy. (b) Ratio between the Stark shift of the hh exciton and the coherently coupled lh exciton Stark shift. Solid and dotted lines show the theoretical results with and without intervalence band coherences, respectively. In (a) and (b), solid (open) symbols correspond to 3.7 (21) MW/cm^2 pump pulses.

Within the third-order regime, the f's factorize, $f_{jj'}(\vec{k}) = \sum_s P^{(1)}_{sj}(\vec{k}) P^{(1)*}_{sj'}(\vec{k})$ (for all j, j') where the $P^{(1)}$'s are first-order polarizations [a similar relation holds for $f_{ss'}(\vec{k})$]. Assuming that the polarization is dominated by $1s$ excitons, the k dependence is given by $P_{sj}(\vec{k}) = P_{sj} \phi^{(j)}_{1s}(\vec{k})$ where, for $j = \pm 3/2 (\pm 1/2)$, $\phi^{(j)}_{1s}$ is the hh (lh) exciton wave function. The resulting equation of motion for the total polarization P has the following general structure ($\hbar = 1$):

$$i\dot{P}_{sj} = (\varepsilon_j - i\gamma) P_{sj} + \mathcal{L}_1(\Omega P^{(1)} P^{(1)*}) + \mathcal{L}_2(P^{(1)} P^{(1)} P^{(1)*}) - \Omega_{sj} \phi^{j}_{1s}(0), \quad (1)$$

where ε_j is the energy of the $1s$ exciton involving band j, γ is the dephasing rate, Ω is the Rabi frequency, $\phi^{j}_{1s}(0)$ is the exciton wave function in configuration space taken at the origin, and the $\mathcal{L}$'s are linear operators that contain all of the above-listed nonlinear effects. To obtain the Stark shift, we solve the time-dependent equations for $P^{(1)}(t)$ and $P(t)$ and numerically Fourier transform the resulting total polarization to obtain the frequency-resolved nonlinear susceptibility and nonlinear absorption spectrum. We then proceed exactly as in the case of the experimental definition of the shift discussed above.

In addition to the numerical results, which will be discussed below, it is instructive to look at the following analytical calculation of the shift $\Delta\varepsilon_j$. This method is not a strict third-order analysis, but yields results that are in good quantitative agreement with our purely numerical third-order result if all contributions are taken into account. For the case without intervalence band coherence it agrees

only qualitatively with the numerical results, mainly because of correlation-induced line asymmetries, which are not accounted for in $\Delta\varepsilon_j$. To obtain $\Delta\varepsilon_j$, we replace the first-order P's by total P's in Eq. (1), assume time-independent light fields with frequencies ω_p and ω_t for the pump and probe field, respectively, and linearize Eq. (1) with respect to the probe field. This way, $\Delta\varepsilon_j$ corresponds to the terms multiplying the probe polarization $P_{sj}^{(t)}$. With hh pumping we obtain the lh exciton shift $\Delta\varepsilon_{-1/2}$ and hh exciton shift $\Delta\varepsilon_{3/2}$,

$$\Delta\varepsilon_j = \mathrm{Re}\big(|\Omega_{1/2,3/2}|^2\{-x_j L_{3/2}^* A^{j,3/2,j} + x_j |L_{3/2}|^2 [V^{\mathrm{HF}(j,3/2)} + 2G^{j,3/2;+}(\bar{\omega})]\} + |L_{1/2}\Omega_{-1/2,1/2}|^2 [G^{j,1/2;+}(\bar{\omega}) + G^{j,1/2;-}(\bar{\omega})]\big). \quad (2)$$

Here $L_j = \phi_{1s}^j(0)/(\omega_p - \varepsilon_j + i\gamma)$, $x_j = 1 + \delta_{3/2,j}$, and $\bar{\omega} = \omega_p + \omega_t$. $A^{jj'j''}$ is the exciton wave function integral associated with excitonic PSF, V^{HF} is the HF matrix element, and $G^{jj';\lambda}$ is the two-exciton correlation function in the singlet ($\lambda = -$) and triplet ($\lambda = +$) channels [13,14]. The PSF and part of the HF term result from the intervalence band coherence. If the hh and lh masses were equal, the matrix elements A and V^{HF} would be the same for $j = -1/2$ and $3/2$, which yields the previously mentioned factor of 2 between the hh and lh Stark shifts as far as only PSF and HF contributions are concerned. The same is true for the first correlation term, whereas the second and third correlation terms alone would yield equal shifts (i.e., no factor of 2). Concerning the relative importance of PSF and HF, at large detunings ($\omega_p - \varepsilon_{3/2}$) the PSF term dominates the shift. For the parameter regime relevant in our study, we find that, as long as the intervalence band coherences are not removed, the PSF and HF terms are generally larger than the correlation terms, and that, regardless of the presence of the intervalence band coherences, the calculated shifts are essentially the same with and without correlation terms.

In Fig. 4(b) we show theoretical results obtained from numerical solutions of the $\chi^{(3)}$ equations [according to [13], i.e., not from Eq. (2)] with and without intervalence band coherences for the polarization conditions of the experiment. When the intervalence band coherences are included (solid line), the hh-lh shift ratio is, as expected, roughly 2, because the lh shift is much larger when the coherences are included. Deviations from an exact factor of 2 come from the hh and lh mass differences and, especially at small detunings, from (still small) correlation contributions. In the large detuning limit the ratio behaves essentially like a three-level system, i.e., it is two (infinity) for the case with (without) Raman coherences. Therefore, the large detuning limit is the proper place to look for the Raman coherence [15]. Clearly, the experimental observations (diamonds) can be understood only if the Raman coherence is present, because the observed hh-lh shift ratio is close to the ideal value of 2 at large detunings.

In summary, a full many-body analysis of lh exciton Stark shifts with hh exciton pumping, especially for large pump detuning, can be understood only if nonradiative intervalence band coherences are present and important. These lh-hh coherences are semiconductor analogs of Raman coherences in three-level atoms, currently of considerable interest.

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[15] The observed hh-lh shift ratio increases at small detunings, whereas the theoretical result is roughly constant for the detunings shown here. We believe that a theory beyond $\chi^{(3)}$ would be needed to reproduce the observed detuning dependence, but a quantitative verification of this hypothesis is currently beyond our numerical means.
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