Hyper-Raman Gain due to Excitons Coherently Driven with Femtosecond Pulses

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(Received 19 February 1997)

We report the observation of optical gain in the transparency region of gallium arsenide highly excited by femtosecond pulses just below the excitonic resonance. We find a very good agreement of the pump-probe spectra with a model based on the fifth-order development of the time-dependent density operator. [S0031-9007(97)04540-7]

PACS numbers: 71.35.Cc

Excitons in direct-gap semiconductors have been shown to exhibit a behavior similar to atoms when coherently driven by an oscillating electric field. One such example is the optical Stark effect (OSE) [1,2] which occurs when the semiconductor is excited by a strong pump field whose frequency is slightly detuned from the optical transition, so that no actual absorption takes place. The OSE produces a spectral shift of the optical transition which, in the perturbative regime, is proportional to the light intensity and inversely proportional to the detuning. Another effect occurring in a coherently driven system is an optical gain [3] that has, to date, been observed only in atoms [4,5]. This gain can be ascribed to a hyper-Raman process (see inset of Fig. 1). In a two-level system, it involves a transition from the ground to the excited state with the annihilation of two pump photons. This process results in the amplification of probe photons at frequency $\omega_{\text{gain}} = 2\omega_p - \omega_0$, where ω_p and ω_0 are the pump and transition frequencies, respectively.

In this Letter, we report the observation of this *stimulated* hyper-Raman emission in a semiconductor. A related process has been observed in Copper halides as a *spontaneous* hyper-Raman emission [6], dominated by the biexciton contribution [7]. The observation of the stimulated emission should allow a more quantitative study than in spontaneous emission experiments and may allow a comparison between semiconductors and atomic systems.

We first consider the case of the two-level system consisting of the states $|g\rangle$ and $|e\rangle$, designating the ground and excited states, respectively. The hyper-Raman gain can be interpreted in the dressed-atom picture as a probe-stimulated transition from the state $|g, N\rangle$ to the state $|e, N-2\rangle$, N being the number of photons in the pump electromagnetic field. Although this transition is forbidden in the absence of light-matter coupling, it becomes slightly allowed due to the mixing between $|g, N\rangle$ and $|e, N-1\rangle$ and between $|e, N-2\rangle$ and $|g, N-1\rangle$. At lowest order in perturbation theory, we find that the mixing amplitude is proportional to $\sqrt{N}/\Delta\omega$ (where $\Delta\omega$ is the detuning $\omega_0 - \omega_p$). This amount is almost identical for both couples of levels when N is large (classical limit), so that the transition matrix element between $|g, N\rangle$ and $|e, N-2\rangle$ is proportional to $N/\Delta\omega^2$. Squaring this quantity, we obtain a gain amplitude proportional to $N^2/\Delta\omega^4$. This perturbative result is in agreement with the low-intensity development of the exact calculation [4]. At lowest order in pump intensity, the hyper-Raman gain in a two-level system is therefore proportional to the square of the pump intensity and inversely proportional to the fourth power of the detuning. An important implication of this dramatic dependence with pump detuning is that pump-probe experiments aiming at measuring the hyper-Raman gain must be performed with very small $\Delta\omega$. Note that the mixing between nearby states in the dressed-atom ladder is also responsible for the OSE, so that the gain coefficient g can be conveniently expressed using only the detuning and the optical Stark shift $\delta\omega$:

$$gL = \frac{\delta\omega^2}{4\Delta\omega^2}\,\alpha L\,, \tag{1}$$

where α is the excitonic absorption coefficient and L the sample thickness.

To address the hyper-Raman gain in semiconductors, we use the dressed-exciton picture [8]. As in a two-level

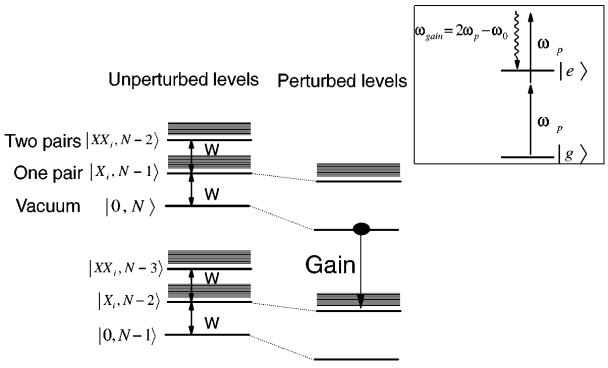

FIG. 1. Ladder of levels in the dressed-exciton formalism. The right part of the figure shows the levels perturbed by the light-matter coupling W. The thick lines show the first correlated electron-hole states and the thin lines correspond to higher-energy states. The inset describes the gain process for a two-level system.

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system, the advantage of such a formalism is that the Hamiltonian is time independent. The dressed-exciton level diagram is shown in Fig. 1, appearing significantly more complex than its two-level counterpart. Indeed, the electronic ground state $|0, N\rangle$ is coupled not only to the $1s$ exciton state but to all one-pair states $|X_i, N-1\rangle$, including both bound and unbound correlated electron-hole pairs. Furthermore, these states are themselves coupled to two-pair states $|XX_i, N-2\rangle$, including, for example, biexcitons and interacting exciton pairs [8]. The $1s$ exciton (X_1) gain amplitude can be expressed using second-order perturbation theory:

$$g \propto |\langle\psi_0|W_t|\psi_1\rangle|^2 \propto \left| \frac{\langle 0|W|X_1\rangle\sqrt{N}}{(\omega_{X_i} - \omega_p)} \sum_i \frac{\langle 0|W|X_i\rangle\sqrt{N}}{(-\omega_{X_i} + \omega_p)} \langle X_i|W_t|0\rangle + \sum_{i,j} \frac{\langle 0|W|X_i\rangle\langle X_i|W|XX_j\rangle N}{(\omega_{X_i} - \omega_p)(-\omega_{XX_j} + 2\omega_p)} \langle XX_j|W_t|X_1\rangle \right|^2, \quad (2)$$

where ψ_0 and ψ_1 are the perturbed wave functions of the initial and final states as shown separated by the one-side arrow in Fig. 1. W_t is the coupling to the classical probe field and W is the pump-semiconductor coupling. Note that Eq. (2) is written in the classical limit of the pump field ($N \approx N - 2$). The only purpose of the quantum-optics formalism is to remove the time dependence in the pump Hamiltonian. Therefore, this is equivalent to a classical analysis in the rotating frame [9]. As in the case of the optical Stark shift, Eq. (2) includes matrix elements involving correlated two-pair states, such as biexcitons, whose wave functions are not known exactly. Although a similar difficulty was encountered in the case of the OSE, it was then possible to perform a large-detuning development of the exact expression [8]. However, these developments are valid only for detunings much larger than the exciton Rydberg energy [10]. Therefore, any such attempt [11] cannot be used in the context of hyper-Raman gain experiments which, in contrast, must be performed for very small detunings. Small-detuning developments for the gain or for the OSE are still unsolved theoretical problems and would be most interesting for a comparison with experimental results.

To demonstrate the hyper-Raman gain, we performed a femtosecond pump-probe experiment in a bulk GaAs sample (thickness $d = 0.65\ \mu$m) held at 20 K. The optical transition involved is the excitonic resonance of GaAs. We use a cavity-dumped self-mode-locked titanium:sapphire oscillator delivering 30 fs pulses at 400 kHz repetition rate [12,13]. The energy per dumped pulse is about 30 nJ, an order of magnitude larger than what is delivered by a conventional oscillator. This facilitates the observation, in a spectrally resolved experiment, of the gain process which is proportional to the square of the pump intensity. The pump spectrum is tuned as close as possible to the excitonic absorption peak as shown in Fig. 2, to satisfy the small-detuning condition exposed above. This is achieved by selecting a narrow pump spectrum by use of a 1.2-nm interference filter, corresponding to a duration of 1 ps. The maximum intensity used in the experiments is 150 MW cm^{-2}. The probe pulse is about 30-fs long and spectrally encompasses the gain and excitonic absorption regions. The pump and probe beams have parallel, linear polarizations.

The differential absorption spectra are shown in Fig. 2 for several delay times between the pump and probe pulses. The differential shape observed around the excitonic absorption is the signature of the optical Stark blue shift of the exciton. This strong-signal regime corresponds to a shift of about 2 meV. Using this value of the shift, together with Eq. (1), we can then compute the gain, with no need for a measurement, often inaccurate, of the pump intensity. Taking into account a detuning of 10 meV, we obtain an expected differential gain signal of roughly 2×10^{-2}. The amplitude of the differential absorption signal actually measured is 4×10^{-3} (i.e., a gain coefficient of about 65 cm^{-1}). This discrepancy comes in part from the fact that the cw theory of Eq. (1) neglects all dynamical aspects which will lead to a broadening of the gain spectrum, and hence to a decrease of its peak value. The effect of a time-dependent excitation will be discussed in more detail in the last part of this Letter. As theoretically expected, the gain is indeed observed in Fig. 2 to appear at frequency $2\omega_p - \omega_0'$, where the OSE-shifted excitonic resonance ω_0' is taken into account. Furthermore, this signal occurs only during the pump pulse, in agreement with the expected instantaneous response time. We also varied the detuning while keeping the pump intensity constant. The results are shown in Fig. 3. When the pump detuning is increased by a certain amount, the gain shifts by twice that amount so that the law $\omega_{\text{gain}} = 2\omega_p - \omega_0'$ is respected. These

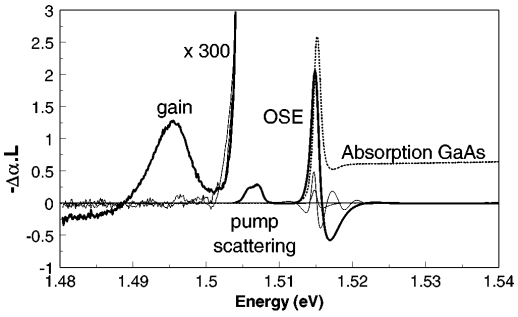

FIG. 2. Experimental differential absorption spectra obtained in a bulk GaAs sample. The thick solid line shows the signal measured when the pump and probe pulses are simultaneous, while the two thin-line curves correspond to time delays of -1.5 ps and 1.5 ps. The dotted line shows the linear absorption spectrum of the exciton line. The pump spectrum can also be seen through some pump scattering present in the signal. The low-energy part of the spectra where the gain signal appears has been magnified by a factor of 300 in order to be seen on the same vertical scale as the optical Stark effect signal.

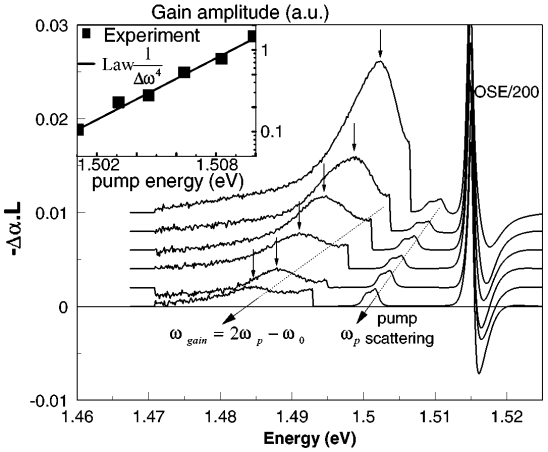

FIG. 3. Experimental differential absorption spectra obtained for several values of pump detuning. The solid vertical arrows show the positions of the gain signal. The spectra are vertically shifted for clarity and reduced by a factor 200 on their high-energy side in order to visualize on the same vertical scale the gain and OSE signals. The inset shows the gain surface amplitude as a function of the pump position.

measurements confirm our interpretation of the signal in terms of hyper-Raman gain [14]. Valuable information is obtained by measuring the gain amplitude as a function of the pump detuning which is plotted in the inset of Fig. 3. We find a good agreement with the law for a two-level system, that is a gain amplitude varying as $1/\Delta\omega^4$. However, the accuracy of the experiment is such that we cannot exclude a deviation from this law which would result from many-body effects [Eq. (2)] specific to the semiconductor.

In order to obtain information about the *dynamical aspect* of the experiment as well as estimate the importance of coherence effects, we developed a simulation based on the Bloch equations for two-level systems. Following the work of Brito-Cruz *et al.* [15], we calculate differential absorption spectra by developing the density operator with respect to the optical field. The third-order term (order one in the probe and two in the pump electric field) leads to effects such as absorption saturation and optical Stark effect. These $\chi^{(3)}$ terms correspond to a differential absorption signal proportional to the pump intensity. In contrast, the hyper-Raman gain we have observed, proportional to the square of the pump intensity, is a $\chi^{(5)}$ process. This required as to push the development of the density operator up to the fifth order, one in the probe and four in the pump electric field. Such fifth-order development has already been performed in the case of three-pulse spectroscopy [16] but not, to our knowledge, for spectrally resolved pump-probe experiments. We included in the simulation the actual pump temporal profile and the absolute time delays measured using Fourier-transform spectral interferometry [17]. Figure 4 shows a comparison of calculated and experimental spectra for several delays. The noise appearing in the calculated spectra is due to the introduction of the experimentally measured pump and probe

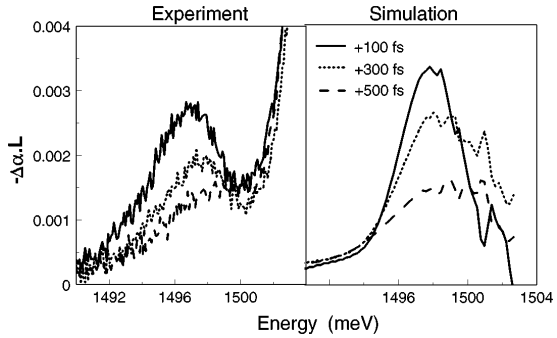

FIG. 4. Comparison of calculated and experimental differential absorption spectra for identical time delays.

pulses in the model. The calculated spectral shape and evolution with time delay are in very good agreement with the experiment. Further studies based on these simulations allowed us to assess the contributions from artifacts such as coherence effects [18] and cross-phase modulation [19,20], showing that they play no significant role in our experiments. We also confirm that the gain follows the squared pump temporal profile.

In summary, we have observed a new coherent optical process in semiconductors. We demonstrated the occurrence of the hyper-Raman gain in gallium arsenide with a femtosecond pump-probe experiment. The results are in good agreement with a two-level system model. At this stage, it is not possible to claim that the minor observed discrepancies are due to the difference between the excitonic transition and a two-level system. In fact, the dependence of the gain amplitude on detuning that can be extracted from Eq. (2) is a complicated theoretical problem that has yet to be solved. It would also be interesting to do experiments in guided-wave structures where the gain could reach a value of 5 after propagation through 200 μm.

We are grateful to R. Planel and V. Thierry-Mieg (Laboratoire de Microstructures et de Microélectronique, Bagneux, France) for providing us with the high-quality GaAs sample. We would like to thank A. Alexandrou and A. Migus for many fruitful discussions. We also thank J. White for his contribution in the early stage of this work.

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