Excitonic Optical Stark Redshift: The Biexciton Signature

D. Hulin and M. Joffre
Laboratoire d'Optique Appliquée, Ecole Nationale Superieure de Techniques Avancées (ENSTA)-Ecole Polytechnique, Batterie de l'Yvette, 91120 Palaiseau, France
and Groupe de Physique des Solides, Université Paris VII, 2 Place Jussieu Paris 5, France
(Received 21 May 1990)

We report the observation of an exciton redshift with a below-gap laser beam, linked to the presence of a bound two-pair state in CuCl. This change in the shift direction for the optical Stark effect in semiconductors relies upon the predominant creation of virtual biexcitons, as shown by the polarization selection rules. Our experiment demonstrates the importance of the biexciton in the description of the optical Stark effect.

PACS numbers: 78.47.+p, 71.35.+z

The initial demonstration of the optical Stark effect in semiconductors[1-3] has triggered a wealth of theoretical and experimental works. This process corresponds to a coupling of the material energy levels with a below-gap light beam. Its major characteristic is that the light is not absorbed, implying no real creation of particles in the semiconductor and insuring therefore an ultrafast response time.[4] Such attractive features explain the great amount of effort devoted to this problem, and, in particular, the large number of theoretical investigations.[5-14] Experimentally, the effect has been evidenced as a *blueshift* of the exciton absorption line observed during a laser pulse whose photon energy is slightly smaller than the absorption edge.[1] In this paper we report the observation of an exciton *redshift* when pumping just below the band gap. This new result has been obtained in CuCl in which the excitonic molecule is stable with an appreciable binding energy.

Different theoretical approaches have pointed out the importance, for the complete description of the optical Stark effect, of the Coulomb interaction and particularly of the biexciton (two excitons bound by Coulomb and exchange interaction).[7,14] Combescot and Combescot have developed a theory which takes into account all two-pair states (electron-hole=one pair), *bound* and *unbound*. They predict that the excitonic blueshift will become a redshift if the molecular biexciton is stable. This should occur when the pump photon energy is tuned just *below* the biexciton resonance, more precisely below $\hbar\omega_r=\hbar(\omega_b-\omega_x)$, $\hbar\omega_b$ being the biexciton energy and $\hbar\omega_x$ the lowest exciton energy. This energy resonance is determined by the fact that the biexcitonic state can be reached through the simultaneous absorption of one pump photon at $\hbar\omega_r$ and one probe photon at $\hbar\omega_x$, the wavelength of observation. While the first Hartree-Fock treatment[5] did not take into account such biexcitonic effects, Balslev and Hanamura have recently published[14] an extended theory in this framework. They predict, however, an exciton redshift when now the pump is tuned *above* $\hbar\omega_r$. For pumping below $\hbar\omega_r$, they find a pronounced enhancement of the Stark blueshift. This prediction is in clear contradiction with the theory of Combescot and Combescot. A strong experimental effort was therefore justified to discriminate between these conflicting theories.

We have performed pump and probe experiments in CuCl at $T=20$ K in the femtosecond regime. Starting from the output of a passively mode-locked dye laser amplified by a seeded 20-Hz Nd-doped yttrium aluminum garnet (Nd-YAlG) laser, we produce a wavelength continuum from which we select a spectral line around 780 nm through an interferential filter. After three stages of amplification in ir dye cells pumped by the Nd-YAlG laser, the energy per pulse is raised to a level up to 50 μJ with a duration of 500 fs. Then the pump is frequency doubled using a 3-mm-thick phase-matched LAP crystal (L-arginine phosphate monohydrate) with a quantum yield of approximately 20%. The resulting pulse now has a wavelength around 390 nm with a tunability obtained by tilting the ir interferential filter and adjusting the phase-matching angle in the frequency doubler. The CuCl sample is a thin film (50-nm thickness) deposited on fused silica. The probe pulse is obtained from the UV part of the wavelength continuum and its duration is of the order of 100 fs. The probe polarization is selected after the sample.

Figure 1 shows the exciton absorption spectrum together with the pump profile. The absorption line at 385.5 nm (3.217 eV) corresponds to the lowest exciton built with the Γ_7 valence band whereas the line around 377 nm (3.289 eV) corresponds to the Γ_8 valence band; in the following, only the lowest exciton, called X_1, will be considered. Our critical energy value $\hbar\omega_r$ corresponds to the biexciton luminescence measured at 389.1 nm (3.189 eV), since the luminescence is a transition from the excitonic molecule towards the excitonic state with an energy equal to $\hbar(\omega_b-\omega_x)$.

Figure 2 exhibits the exciton absorption line for different delays between the pump and the probe. The pump photon energy is set just below $\hbar\omega_r$ and pump and probe beams have parallel polarizations. It is clear in this figure that the exciton absorption shifts towards

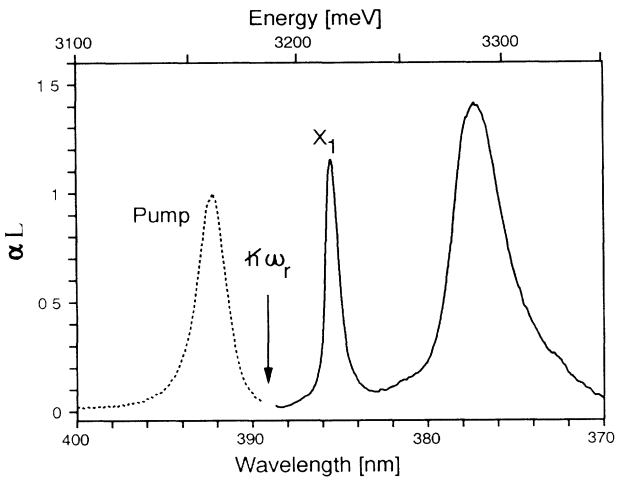

FIG. 1. Absorption spectrum of the CuCl sample held at 20 K (solid line). The dotted line shows a pump spectrum. The arrow indicates the position of the biexciton resonance $\hbar\omega_r$, as measured from the biexciton luminescence spectrum.

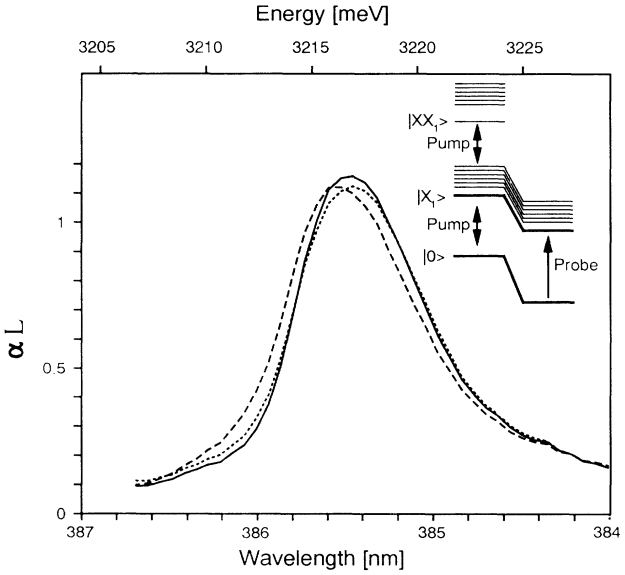

FIG. 2. Absorption spectra of the CuCl sample excited by a pump tuned at 3.162 eV, and recorded for different pump-probe delays: −2 ps (solid line), 0 ps (dashed line), and +2 ps (dotted line). The pump and probe polarizations are parallel. Inset: The semiconductor levels as coupled by the light.

lower energies (redshift) during the excitation (dashed line) associated with a small reduction of the absorption strength. This bleaching is also observed after the excitation has left the medium, when the absorption line has recovered its initial spectral position. This last experimental feature has already been seen in similar experiments and attributed to the presence of free electron-hole pairs created through a two-pump-photon absorption process.[15,16] Because of the asymmetric shape of the excitonic absorption, this makes differential spectra not so obvious to use.

We have reproduced the above experiment for different photon energies of the pump pulse, for a pump spectral position located either *below* the biexcitonic resonance $\hbar\omega_r$ or *between* $\hbar\omega_r$ and the exciton $\hbar\omega_x$. Figure 3 shows the observed shifts as a function of the delay between pump and probe.

First, let us discuss the results obtained for parallel polarizations (solid lines) corresponding to the case already seen in Fig. 2. The noticeable feature in Fig. 3 is the change of the shift direction from red to blue when the pump photon energy is increased above $\hbar\omega_r$. This opposite shift direction on each side of the biexciton resonance is only true during the pump pulse, as expected. At longer delays, whatever the pump wavelength is, there is a small permanent blueshift which may originate in a sample heating, following absorption through a two-photon process.[17]

We have performed the same experiments for perpendicularly polarized beams (dashed lines). We always observe a blueshift, decreasing like the inverse of the detuning with respect to the exciton. In this case, there is no special feature when crossing the biexciton resonance. Note the smaller signal for perpendicular polarizations than for the parallel configuration (due to pump scatter-

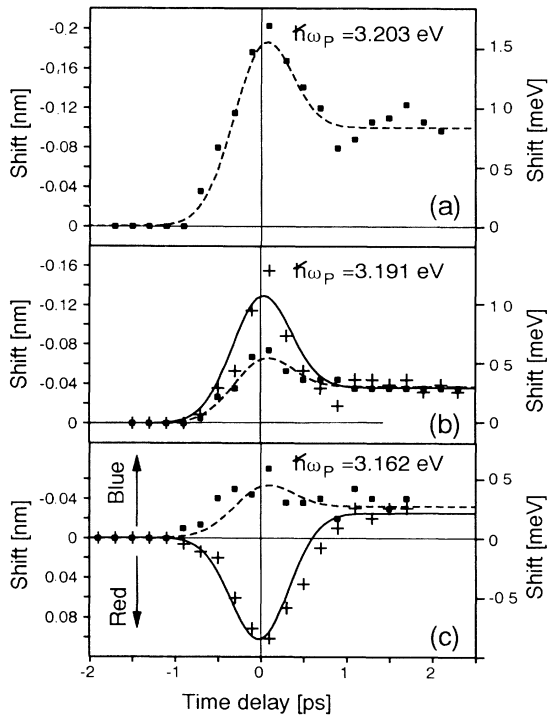

FIG. 3. Magnitude of the exciton shift as a function of pump-probe time delay for different pump photon energies and for relative pump-probe polarizations either parallel (crosses) or perpendicular (squares). Solid and dashed lines are theoretical shapes obtained from a linear combination of the pump intensity and the pump pulse energy. They are plotted here mainly as a guide for the eye.

ing it has not been possible to do such a comparison at 3.203 eV).

The experimental results are well explained in the theoretical framework developed by Combescot and Combescot. As shown in the inset of Fig. 2 the excitonic level which is under observation is coupled by the pump light to the ground state (vacuum) and to *all* two-pair states. Similarly, the vacuum level is coupled to *all* one-pair states. The probe beam is absorbed at the energy of the transition between the perturbed vacuum level and the perturbed exciton energy level. Following Ref. 7, the shift of the absorption line can be written in a perturbative approach:

$$\delta E \propto \left\{ \frac{|\langle 0|U|X_1\rangle|^2}{\omega_{X_1}-\omega_p} - \sum_n \frac{|\langle XX_n|U^\dagger|X_1\rangle|^2}{\omega_{XX_n}-\omega_{X_1}-\omega_p} \right\} + \left\{ \sum_i \frac{|\langle X_i|U^\dagger|0\rangle|^2}{\omega_{X_i}-\omega_p} \right\}, \quad (1)$$

where $|0\rangle$, $|X_i\rangle$, and $|XX_n\rangle$ are the vacuum, one-pair, and two-pair states, and U and $U^\dagger$ are the operators corresponding to the creation or destruction of one e-h pair by light. $|X_1\rangle$ is the exciton seen by the probe. This equation allows us to explain the blueshift usually observed for a below-gap pump beam. The result becomes quite different when a situation can be achieved where one of the coupling becomes resonant. This happens when one of the denominators in (1) goes towards zero, i.e., when the pump photon energy is nearing one of the possible optical transitions. This occurs, for example, at $\hbar\omega_p \sim \hbar\omega_r$, the energy for which the pump photon can promote the exciton $|X_1\rangle$ to the biexciton state $|XX_1\rangle$. If damping is ignored, the resonant term diverges when coming close to the resonance and its contribution dominates all the other nonresonant terms. It can then be easily seen from Eq. (1) that for $\hbar\omega_p < \hbar\omega_r$, the Stark shift is a redshift and that for $\hbar\omega_p > \hbar\omega_r$, it becomes a blueshift as predicted in Ref. 7 and as observed in our experiments.

The above considerations explain well why a redshift can be observed when pumping below the excitonic resonance. They do not justify the fact that this happens only for parallel polarized pump and probe beams. For a complete description, the numerator of the resonant term has also to be taken into account. The lowest (Γ_1) biexcitonic state in CuCl being symmetrical,[18] this implies well-defined selection rules for the light polarization. We first consider the creation of a biexciton.[19,20] For linear polarizations, a test beam polarized parallel to the pump beam will be absorbed by a two-photon absorption process (one from the probe, one from the pump) while it remains unabsorbed when being polarized perpendicularly.[21] Similar conclusions can be drawn for the optical Stark effect since the same optical transition matrix elements appear in Eq. (1). These matrix elements are not associated anymore to the absorption of light leading to the creation of real biexciton, but to the creation of virtual biexciton. Therefore, the same selection rules apply and the resonance which leads to the observation of a redshift will be significant only for parallel polarizations of the two beams and not for perpendicular polarizations. This has been predicted in Refs. 8 and 10 and is indeed what is observed in our experiments for $\hbar\omega_p < \hbar\omega_r$ as shown in Fig. 3.

For a pump photon energy above the biexciton resonance we now observe a blueshift for both polarizations. It can be noted that in this last case the origins of the blueshift are different but lead to the same experimental result. However, since the biexciton resonance acts only for parallel polarizations, the magnitude of the corresponding shift is larger than for perpendicular polarizations, where only the exciton level, which is not very close, has to be considered. This situation is also true for the signals obtained below the biexcitonic resonance.

A redshift due to the optical Stark effect (OSE) in condensed matter has already been reported in Cu_2O (Ref. 3) and in polydiacetylene.[22] In both cases, this has been described through a coupled three-level system. In polydiacetylene, while the experimental features are dominated by the stimulated inverse Raman scattering, the analysis of the "phonon-mediated OSE" also relies on three distinct levels: the ground state, the exciton, and the energy level shifted by one phonon energy. Our case is quite different, although there is a formal analogy. Here, the third level is not an extra level but corresponds to twice the first transition, namely, the exciton. It is only because two excitons are bound with an appreciable binding energy that we can experimentally separate this contribution.

In summary, we have observed for the first time an excitonic optical Stark redshift due to the influence of a biexciton. The experimental results are in agreement with the theory of Combescot and Combescot who predicted the occurrence of the redshift just below the biexcitonic resonance. In this case, the light-induced repulsion between the exciton and the biexciton levels overcomes all other contributions leading to the usual blueshift. We have verified that crossing this resonance changes the observed direction of the exciton shift. We have also shown that this redshift can only be seen for parallel-beam polarizations. Since the selection rules well known for the creation of real biexciton are also valid in our case, this points out the pertinence of the *virtual* biexciton physical picture. This demonstrates the importance of bound two-pair states in the complete description of the states coupled by the optical Stark effect.

We thank M. Combescot for suggesting to us this experiment and for many fruitful discussions. We are grateful to A. Migus for many helpful advices and to J. Paye for his invaluable contribution. The CuCl sample

has been elaborated at the Groupe d'Optique Nonlinéaire et d'Optoélectronique of Strasbourg and we thank J. L. Loison for giving it to us. We are grateful to E. Hanamura for making his manuscript available prior to publication. The LAP crystal has been kindly provided to us by Quartz et Silice. Laboratoire d'Optique Appliquée is laboratoire associé au CNRS Unité de Recherche Associée No. 1406. Groupe de Physique des Solides is laboratoire associé au CNRS Unité de Recherche Associée No. 17.

Note added.— During the reviewing process we have learned that E. Hanamura has obtained new theoretical results now in agreement with our experimental findings.

[1]A. Mysyrowicz, D. Hulin, A. Antonetti, A. Migus, W. T. Masselink, and H. Morkoç, Phys. Rev. Lett. **56**, 2748 (1986).

[2]A. Von Lehmen, D. S. Chemla, J. E. Zucker, and J. P. Heritage, Opt. Lett. **11**, 609 (1986).

[3]D. Fröhlich, A. Nöthe, and K. Reimann, Phys. Rev. Lett. **55**, 1335 (1985).

[4]M. Joffre, D. Hulin, J. P. Foing, J. P. Chambaret, A. Migus, and A. Antonetti, IEEE J. Quantum Electron. **25**, 2505 (1989).

[5]S. Schmitt-Rink and D. S. Chemla, Phys. Rev. Lett. **57**, 2752 (1986).

[6]S. Schmitt-Rink, D. S. Chemla, and H. Haug, Phys. Rev. B **37**, 941 (1988).

[7]M. Combescot and R. Combescot, Phys. Rev. Lett. **61**, 117 (1988).

[8]M. Combescot, Solid State Commun. **68**, 471 (1988).

[9]M. Combescot and R. Combescot, Phys. Rev. B **40**, 3788 (1989).

[10]M. Combescot, Phys. Rev. B **41**, 3517 (1990).

[11]R. Zimmermann and M. Hartmann, Phys. Status Solidi (b) **150**, 379 (1988).

[12]W. Schäfer, K. H. Schuldt, and R. Binder, Phys. Status Solidi (b) **150**, 407 (1988).

[13]I. Balslev, R. Zimmermann, and A. Stahl, Phys. Rev. B **40**, 4095 (1989).

[14]I. Balslev and E. Hanamura, Solid State Commun. **72**, 843 (1989).

[15]M. Joffre, D. Hulin, and A. Antonetti, J. Phys. (Paris), Colloq. **48**, C5-537 (1987).

[16]W. Knox, D. S. Chemla, D. A. B. Miller, J. B. Stark, and S. Schmitt-Rink, Phys. Rev. Lett. **62**, 1189 (1989).

[17]The permanent signal is more important for pumping at 3.203 eV, just below the exciton absorption line since a small overlap between the laser line and the exciton line occurs then.

[18]See, for instance, A. Goldmann, Phys. Status Solidi **81**, 1 (1977).

[19]G. M. Gale and A. Mysyrowicz, Phys. Rev. Lett. **32**, 727 (1974).

[20]N. Nagasawa, T. Mita, and M. Ueta, J. Phys. Soc. Jpn. **41**, 929 (1976).

[21]R. Levy, B. Hönerlage, and J. B. Grun, in *Optical Nonlinearities and Instabilities in Semiconductors,* edited by H. Haug (Academic, New York, 1988), and references therein.

[22]G. J. Blanchard, J. P. Heritage, A. C. Von Lehmen, M. K. Kelly, G. L. Baker, and S. Etemad, Phys. Rev. Lett. **63**, 887 (1989).