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# POLARIZATION AND PROPAGATION EFFECTS IN ACTIVE NON LINEAR SPECTROSCOPY OF SOLIDS : FEATURES OF THE MULTIPLE RESONANCES ON EXCITONS AND EXCITONIC MOLECULES

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We present and discuss experimental results on forward, energy degenerate, optical mixing in CuCl and CdS. The efficiency of the process is huge around the biexcitonic two photon resonance. The propagation effects are shown to be crucial for a proper interpretation of the data. Higher order scatterings appear to be due to cascade processes rather than to direct mixing.

Multiphoton spectroscopy in semiconductors around electronic resonances is of very great interest and can provide features of the states hardly suspected or nearly unobservable otherwise. In particular, the study of excitons and biexcitons has benefited from salient and specific advantages of those methods ; they are briefly reviewed and referenced in [1] . We have presented in [2] a method of active non linear spectroscopy :

Two laser beams, with the same energy $\hbar\omega$ and with the wave vectors $k_p$ and $k_t$ (p= pump beam ; t = test beam) combine in a semiconductor. A signal with energy $\hbar\omega$ and wave vector $k^{(n)} = nk_p - n'k_t$ ($|n-n'|=1$) is generated through successive coherent scatterings in that forward degenerate mixing. The process is very efficient when $2\hbar\omega$ is around $W_{x2}$ the formation energy of the $\Gamma_1$ biexciton in CuCl or CdS. Actually, incident intensities of $2MWcm^{-2}$ (800W/(200μm)$^2$ ) were enough to allow the observation of scatterings up to the fifth order, corresponding to the mixing of ten photons .
in regions of fairly high absorption. Since the most probable intermediate state is an exciton ($Z_3^\Gamma$ in CuCl and $A_1$ or $B_1$ in CdS), that is mostly due to the very great value of the exciton-biexciton oscillator strength [3] . A study of the lowest order scattering (four wave mixing, n=2, n'=1) has been reported for CuCl in [4] and for CdS in [5] . Those studies have shown the necessity of considering the autoionizing character of biexcitons and have quantitatively accounted for it. We focus here on the propagation effects and the discussion of higher order scatterings.

Propagation and polarization effects are very important in CdS ; as shown in [6] , proper polarizations of the impinging beams select the symmetries of the intermediate levels involved in the phenomenon, so that either $A_1$ or $B_1$ exciton is excited. Then one can derive from the experimental data many parameters of the exciton-biexciton system including the $A_1$-$\Gamma_1$ oscillator strengths. A very careful analysis is needed for that purpose. Figure (1) shows the result of a computation, which fits very nicely to the set of experimental data. Those curves stress, in particular, that it would be definitely wrong to locate the biexciton resonance at twice the energy of the peak of the signal.

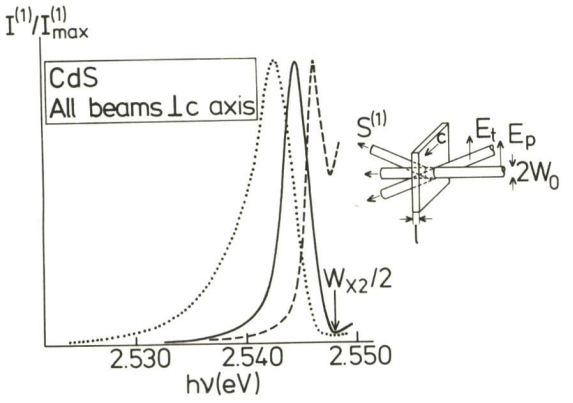


Fig.(1) Normalized line shapes for the first order scattering in CdS at low temperature for different experimental conditions and small $I_t/I_p$, corresponding to the hyperparametric approximation
--- $\ell$ = 10 μm, $I_t^{(\omega)}$ = 0.1 kW
—— $\ell$ = 10 μm, $I_t^{(\omega)}$ = 1.0 kW
... $\ell$ =100 μm, $I_t^{(\omega)}$ = 1.0 kW
laser beam waist = 200 μm

The case of CuCl is simpler in that respect since the position of the resonance can be estimated from inspection of the data. However, and as shown in Fig.(2), that is only true in the hyperparametric limit, in which the incident intensities $I_t$ and $I_p$ verify $I_t/I_p \ll 1$. The exact analytical solutions which have been derived in that

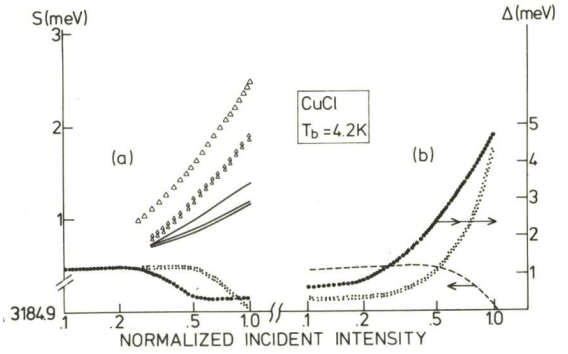


Fig.(2) Propagation effects in the first and second order scattering spectra in CuCl, as a function of the normalized incident intensity ; in all cases $I_t/I_p$ = 0.3 ; the maximum value of the total intensity is 2.5 MW.cm
(a) :.... position of the low energy maximum of the first order scattering
—— position of the dip
ΔΔΔ position of the high energy maximum
The corresponding symbols for the second order scattering are :::: , ═══ and ΔΔΔ respectively
(b) : Total linewidth of the first order (...) and second order (:::) scatterings and energetic position of the ratio $\rho = I^{(2)}(\hbar\omega)/I^{(1)}(\hbar\omega)$

case [7] show that the minimum of the first order scattering spectrum is, whatever $I_p^{(\omega)}$, at $\hbar\omega$ = Wx2/2. That is no more true as long as $I_t/I_p > 0.2$ and the minimum of the curves undergoes a blue shift while the two maxima shift in opposite directions. The second order scattering spectra are shown in Fig.(3) for different incident intensities. We could keep a remarkably good signal-noise ratio with incident powers as low as $I_p$ = 80 W and $I_t \simeq$ 3 W (spot size ≃ 200 μm). The deformation of the curves and their spectacular narrowing is again solely due to propagation effects and their dependence on the incident intensities is very complicated. The low intensity limit of the linewidth is around our laser linewidth in the case of Fig.(3) and equal to it in the hyperparametric limit. The crucial problem here is the distinction between direct and cascade processes.

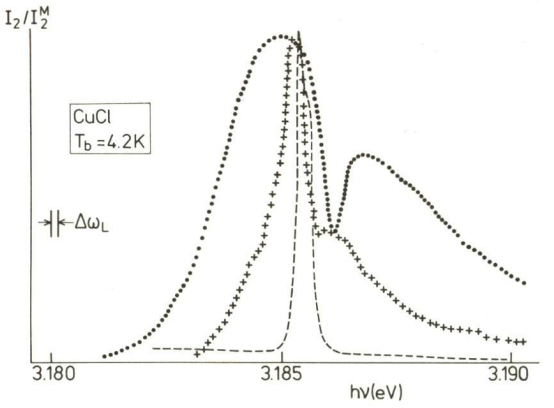


Fig.(3) Normalized second order scattering spectrum in CuCl ; in all cases the ratio $I_t^{(o)}/I_p^{(o)}=1/3$. ----- $I_p^{(o)}$= 0.8 kW ; +++ $I_p^{(o)}$= 0.4 kW ; ····· $I_p^{(o)}$= 0.08 kW The laser linewidth is $\Delta\omega_L$ ; the sample temperature can be estimated around 25 K Sample thickness : 200 μm

Figure (4) shows the corresponding vectorial diagrams.

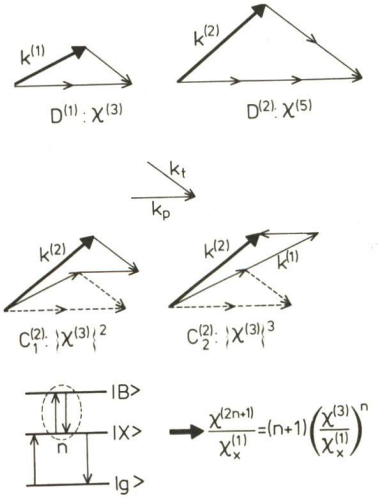


Fig.(4) Upper part : Vectorial diagrams for the direct processes : 1st order (left) and 2nd order (right). Middle : The two types of cascade in second order scattering : in "cascade 1" (left) the inhomogeneous term in Maxwell equations ("gain") is $\propto\chi^{(3)}E^{(1)}E_p E_t^*$ and in "cascade 2" the elementary process leading to the same state is proportional to $\chi^{(3)}(E^{(1)})^2 E_p^*$ Lower part : relation between higher order nonlinearities and excitonic linear susceptibility $(\chi_{ex}^{(1)} = N|\mu_{eg}|^2(\hbar\Omega_{eg}-\hbar\omega)^{-1} \simeq 1.51)$ in the hypothesis that a 2n+1 photon process involves n "boomerang" transition exciton-biexciton.

Accordingly to the formula in that figure and under very simplifying assumptions (neglecting all propagation effects) one derives that the signal would be proportional to $(I_p^{(o)})^3\,(I_t^{(o)})^2$ in all cases, and proportional to $|\chi^{(5)}|^2$ for direct processes and $|\chi^{(3)}|^4$ or $|\chi^{(3)}|^6$ for both types of cascade. As shown by Compaan et al. [8] and ourselves [2] , for sufficiently thick samples, or for sufficiently large effective interaction lengths, the cascade processes should dominate. Moreover $I^{(n+1)}/I^{(n)}$ associated with the electronic diagram of Fig.(4) should be constant for the direct processes or for the cascade 1 processes but proportional to $I_p^{(o)}I_t^{(o)}$, in the case of cascade 2 processes. While that constancy has been checked, one can not rule out at this stage any of the three above processes. Our attempts to evidence a triexciton or to favor direct processes by working whith very thin samples (0,9 μm) were unsuccessful. On the other hand, we could derive in the hyperparametric approximation and analytical solution to the complete propagation problem, involving the contribution of direct and cascade processes with their interferences. The only unknown parameter is $a = \chi^{(5)}E_p^2(o)/\chi^{(3)}$; this computation, which moderates somewhat the

conclusions of [9] will be detailed elsewhere ; however, it seems to confirm already what was inferred from the above qualitative arguments namely the neat dominance of cascade processes over direct ones in our experimental conditions.

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