Three-Photon Spectroscopy of Exciton Polaritons in Alkali Halides

F. Beerwerth and D. Fröhlich

Institut für Physik, Universität Dortmund, 4600 Dortmund 50, Federal Republic of Germany

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Three-photon spectroscopy is introduced as a useful tool for the investigation of electronic transitions in solids. This technique is used to study resonances on the upper polariton branch, and even on the longitudinal exciton. This is the first such application for a system with inversion symmetry. The polariton structure of the lowest exciton in KI is analyzed with use of different wave-vector configurations. The fit of the experimental data yields a longitudinal-transverse splitting of 110 meV. For the more complicated exciton structure of CsI, a correspondingly complicated polariton structure is expected. For CsI, results are presented only for one wave-vector configuration.

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Excitonic transitions were first observed in alkali halides. More than fifty years ago Hilsch und Pohl[1] were able to resolve narrow resonances in the one-photon absorption spectra in the near ultraviolet. These measurements were extended to low temperatures and to shorter wavelengths by several authors. For literature and details, see Teegarden and Baldini.[2]

The first two-photon spectroscopy experiments were also reported in alkali halides. Hopfield, Worlock, and Park[3] measured the two-photon spectra of KI and CsI. Using an improved experimental setup, Fröhlich and Staginnus[4] were able to extend these measurements to other alkali halides and to do detailed polarization analyses. Though the two-photon spectra did not show any sharp structures, they were quite useful, since they allowed a new assignment of the band gap in the alkali bromides. Mahan[5] was able to explain the two-photon absorption, including the detailed polarization dependence, with a two-band model.

In this Letter we report the first three-photon spectra of excitonic transitions. Again the alkali halides are chosen to introduce now three-photon spectroscopy (TPS) as a powerful technique for the investigation of excitons and polarizations. Three-photon transitions in solids have been reported by other authors. We refer to a recent publication by Brost, Bräunlich, and Kelly[6] and to papers by Catalano *et al.*[7] In these experiments a fixed-frequency laser was used to induce multiphoton transitions to states in the continuum. Very recently three-photon measurements in gas-phase benzene were reported,[8] where a tunable dye laser was used. In our experiments we use two lasers, a high-power dye laser and a fixed-frequency laser, whose polarizations and propagation directions in the crystal can be varied. This technique enables, for the first time, detection of resonances on the upper polariton branch and the longitudinal exciton in crystals with inversion symmetry.

All dipole transitions which are allowed in one-photon absorption are also allowed for three-photon transitions. Despite this fact, the one- and three-photon spectra look quite different. In three-photon spectroscopy one has additional degrees of freedom. By changing the relative directions of the three-photon beams, one can tune the total k vector (within certain limits) independently of the total energy. We use this k-space spectroscopy to measure resonances on the upper polariton branch [transverse polariton (TP)], and even on the longitudinal exciton (LE), which cannot be excited in one-photon absorption. For the excitation of the longitudinal exciton it is necessary to choose a geometry for the k vectors which allows large components of all the polarization vectors along the total k vector. This can be understood by considering a two-band model[5] in third-order perturbation theory, where the intermediate states are S and P excitons of the Γ_8^- valence band and the Γ_6^+ conduction band. The final states are the upper polariton (twofold degenerate) and the longitudinal exciton of the $1S$ exciton resonance.

For our measurements we used ultrapure single crystals of KI, RbI, and CsI with sizes ranging from 2 to 10 mm. The CsI had to be cut and polished, whereas the other crystals were cleaved before being mounted in a helium cryostat. As a light source we used a frequency-doubled Nd-doped yttrium-aluminum-garnet laser (Quanta Ray DCR-2A) to pump a tunable dye laser (Lambda Physik FL 2002). For the first measurements three photons from the dye laser (605–640 nm) were used to induce the three-photon absorption. For the detailed measurement of the k-dependent resonances it was much more favorable to use one photon of the pump laser (532 nm) and two photons from the tunable dye-laser beam (665–695 nm); the latter was split into two beams before being focused on the sample. Using different geometrical configurations for the three laser beams, we were able to excite resonances between $\frac{1}{3}k_{\max}$ and $k_{\max}$. In the $k_{\max}$ configuration all laser beams are parallel. The spectral resolution of our laser system was better than 50 μeV. The maximum light intensity of the dye laser was about 200 MW/cm^2, whereas the fixed-frequency laser was kept below 50 MW/cm^2 in order to suppress three-photon transitions of this laser alone to continu-

um states.

Three-photon absorption was detected via the luminescence of the self-trapped exciton.[9] In alkali halides the dominant intrinsic decay channels of electronic excitations are luminescence bands of the self-trapped exciton. We measured the excitation spectrum of luminescence lines around 300 nm (KI, 300 nm; RbI, 315 nm; CsI, 290 nm). The luminescence pulses have a short decay time (about 10 ns). They could be well separated from the exciting laser pulses by a monochromator and appropriate filters. The luminescence signals were properly normalized to the intensities of the different laser beams. The signals showed the expected intensity dependence corresponding to a three-photon process. The electronic pulses from the photomultiplier were averaged over twenty shots by an on-line computer, which also controlled the wavelength setting of the dye laser and the polarizing optics (half-wave plates) for the different laser beams.

In Fig. 1 we present some experimental results for KI and CsI. The spectra for RbI look similar to the KI data except for a shift of about 90 meV to lower energies. For comparison we have indicated the one-photon spectra of Teegarden and Baldini.[2] For KI we selected resonances for two different k configurations. The low-energy resonance (curve A) is the first observation of the longitudinal exciton. Curve B represents the resonance for the maximum k vector on the upper polariton branch. In CsI we show the experimental results for only one k configuration (all k vectors parallel). As expected from the one-photon data we now get resonances on three polariton branches corresponding to the three exciton transitions. Upon tuning of the total k vector, these resonances shift according to the dispersion of their polariton branches.

In Fig. 2 we plot the energies of the measured bands for KI in the familiar polariton diagram. The dots and triangles represent the resonance on the upper polariton and longitudinal exciton branches, respectively. The arrows indicate the resonances A and B which are shown in Fig. 1. The total k vector is easily calculated for the different k configurations, with the use of tabulated refractive indices for the laser energies. The magnitude of k is calculated from $|\mathbf{k}| = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3|$ with $k_i = n_i \omega_i c^{-1}$. n_i and ω_i are the refractive index and frequency of the corresponding laser beam. The solid lines for the transverse polariton (TP) and the

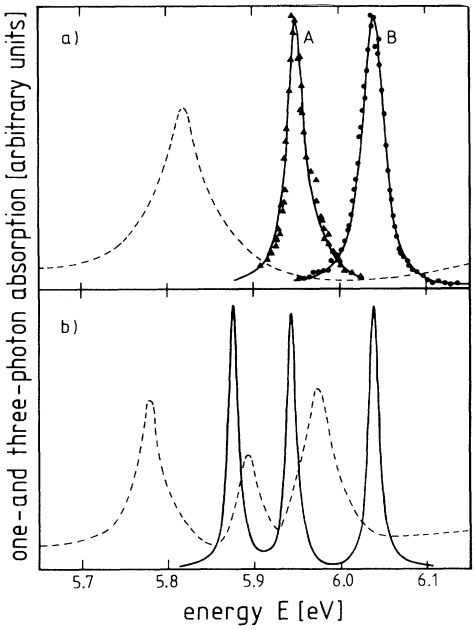

FIG. 1. Three-photon spectra at 4.5 K of the first exciton structure in (a) KI and (b) CsI. One-photon data at 10 K (dashed lines) are taken from Ref. 2. (a) Triangles show experimental results for a resonance on the longitudinal exciton; dots for a resonance on the upper polariton branch. The corresponding solid lines (curves A and B) are a fit of the experimental results by Lorentzian lines. Their k configurations are marked by arrows in Fig. 2. (b) Full line represents a fit to experimental results of the polariton structure in the k_{max} configuration.

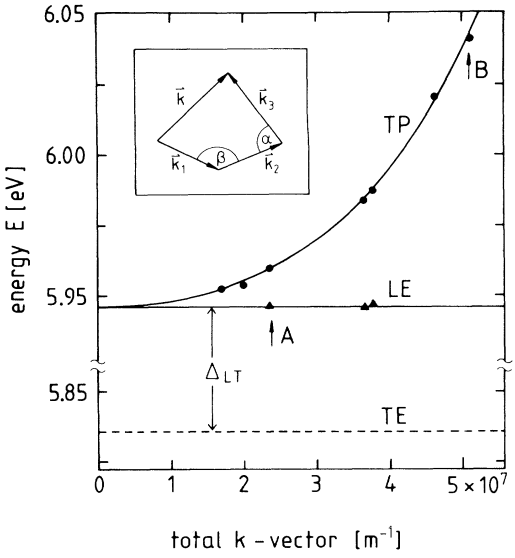

FIG. 2. Energy of the upper polariton and the longitudinal exciton of KI as function of total k vector. Triangles and dots represent experimental results for the longitudinal exciton and the upper polariton branch, respectively. Solid and dashed lines are a fit of the experimental results by a two-oscillator model for the upper polariton branch (TP), the longitudinal exciton (LE), and the transverse exciton (TE). Arrows mark resonances A and B shown in Fig. 1. Inset: Wave-vector–combination diagram for TPS. For resonance A, $\alpha = 50.2°$, $\beta = 180°$; for resonance B, $\alpha = \beta = 180°$. $\mathbf{k}_1$, $\mathbf{k}_2$, wave vectors of the dye-laser beams; $\mathbf{k}_3$, wave vector of the pump-laser beam.

longitudinal exciton (LE) and the dashed line for the transverse exciton (TE) represent least-squares fits of our experimental results and refractive-index values in the visible by a simple two-oscillator dispersion formula,[10]

$$\frac{\hbar^2c^2k^2}{E^2}=\epsilon_b\frac{E_{1L}^2-E^2}{E_{1T}^2-E^2}\frac{E_{2L}^2-E^2}{E_{2T}^2-E^2}.$$

E_{1L},E_{2L} and E_{1T},E_{2T} represent the fit parameters for the longitudinal excitons and the transverse excitons of the two oscillators, respectively. ϵ_b is a background dielectric constant due to still higher resonances. We have neglected the damping and spatial dispersion, which are expected to have little influence in the region of our experimental results. For the detailed analysis of one-photon data, however, they have to be taken into account. We get the following values for the KI fit parameters: $E_{1T}=5.836$ eV, $E_{1L}=5.946$ eV, $E_{2T}=6.64$ eV, $E_{2L}=7.73$ eV, and $\epsilon_b=1.91$. The last three parameters cannot be compared to experimental values, since they describe the contribution of all higher oscillators to the dielectric function without details taken into account. From our fit we get a longitudinal-transverse splitting of $\Delta_{LT}=110$ meV. Our value agrees quite well with the value $\Delta_{LT}=120$ meV obtained from a line-shape analysis of one-photon reflection data.[11] As expected from the oscillator strength of the one-photon absorption line, Δ_{LT} is much larger than, e.g., for the first exciton of CuCl[12] (5.4 meV) or GaAs[13] (0.08 meV). An equivalent analysis of the experimental data in CsI is more complicated, because one has to consider three closely spaced exciton states and their interactions.

For crystals with inversion symmetry, we believe that TPS is the only method as yet demonstrated to measure resonances on the upper polariton branch, and even on the longitudinal exciton. The method is specially suited for such high-gap materials as alkali halides, because lasers with photon energies of about one third of the exciton energy are used. Our measurements should be extended to other alkali halides. It should even be possible to measure the polariton structure of the first exciton in LiF at about 13 eV,[14] provided that a suitable luminescence band of the self-trapped exciton can be found. Of special interest are the higher exciton bands of alkali iodides, including NaI. As discussed in detail by Kunz[15] and lately by Onaka and Iwamoto[16] there are still questions open on the assignment of the Γ_6^- valence band in KI and RbI. A detailed polarization analysis of three-photon data should help to clarify this point.

It is of great interest to study the temperature dependence of the linewidths of the transverse polariton and of the longitudinal exciton in TPS. This spectroscopic method is specially suited, since the spectra are taken in bulk material; in contrast, for one-photon transmission measurements, evaporated films must be used. As seen in Fig. 1 for KI the width of our resonance lines is almost a factor of 3 smaller than the one-photon width. This fact cannot be explained by the temperature difference. Strain and surface effects are probably the reason for the larger linewidths of the one-photon data.

Another challenging task certainly is to investigate the pure triplet states which might be detectable by TPS with magnetic field. A detailed analysis, which must take into account the degeneracy of the valence band, would then yield reliable data for the exchange splitting and g values.

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