Two-Photon Spectroscopy of Odd-Parity States

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Magnetic-dipole two-photon absorption (MD-TPA) is introduced as a new spectroscopic technique for the study of odd-parity states. Contrary to the classical electric-dipole two-photon absorption (ED-TPA), where only spin-allowed even-parity transitions can be excited, MD-TPA allows us to excite spin-forbidden odd-parity states. This new technique is therefore very well suited to study paraexcitons in semiconductors and insulators. As examples MD-TPA measurements of RbI, NaI, and NaBr are presented.

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Two-photon absorption (TPA) was first treated theoretically more than sixty years ago by Göppert-Mayer [1] using second-order perturbation theory. With respect to selection rules two-photon processes can be interpreted as two successive one-photon transitions. From Laporte's rule which states that one-photon dipole transitions are only allowed between states of *different* parity, one immediately derives that two-photon transitions are allowed only between states of the *same* parity. About thirty years ago Hopfield and Worlock [2] were the first to do two-photon spectroscopy on excitons. In agreement with the above-mentioned selection rule they found that in alkali halides two-photon transitions are indeed allowed to even-parity P excitons but strictly forbidden to odd-parity S excitons.

In order to excite odd-parity states by nonlinear spectroscopy one has to step onto three-photon spectroscopy (TPS) as was again demonstrated in alkali halides [3]. By the use of different three-photon techniques one can observe the polariton dispersion and the longitudinal exciton with high accuracy [4].

In this Letter we introduce a new spectroscopic technique, which allows us to excite odd-parity states by two-photon absorption. Contrary to classical two-photon absorption where both photons induce *electric*-dipole transitions (ED-TPA), we consider two-photon processes where one of the photons induces a *magnetic*-dipole transition and the other an electric-dipole transition. In the following we will briefly outline the theoretical background of magnetic-dipole two-photon absorption (MD-TPA).

As in the case of ED-TPA [5] one can derive the two-photon transition probability $W_{g\to f}$ for MD-TPA from second-order perturbation theory:

$$W_{g\to f} \propto \left|\sum_i \left(\frac{\langle f|(\widehat{MD})_2|i\rangle\langle i|(\widehat{ED})_1|g\rangle}{E_i - E_g - \hbar\omega_1} + \frac{\langle f|(\widehat{MD})_1|i\rangle\langle i|(\widehat{ED})_2|g\rangle}{E_i - E_g - \hbar\omega_2}\right)\right|^2 \times \delta(E_f - E_g - \hbar(\omega_1+\omega_2)), \quad (1)$$

where E_g and E_f refer to the energy of the ground and final states, respectively. As intermediate states $|i\rangle$ (energy E_i) one has to consider all states which are allowed for electric-dipole transitions from the ground state $|g\rangle$. $(\widehat{ED})_\nu$ and $(\widehat{MD})_\nu$ refer to the electric- and magnetic-dipole operator, respectively. $\nu = 1, 2$ labels the incoming photons with energies $\hbar\omega_\nu$ and polarization directions $\mathbf{e}_\nu$. In Eq. (1) we have assumed that the first transition $(g \to i)$ is of electric-dipole type, which is expected to be the case for many solids, where the lowest energy transitions (e.g., $1S$ excitons) are dipole allowed.

As first shown by Inoue and Toyozawa [5], the two-photon polarization selection rules can be derived from group theory for all 32 point groups. For the derivation of these selection rules one has to know the symmetry properties of the transition operators [5]. As an example we will now discuss the selection rules for the cubic point group O_h. In O_h the electric-dipole operator $(\widehat{ED})_\nu$ transforms like a polar vector (irreducible representation Γ_4^-). The polarization vector $\mathbf{e}_\nu$ (direction of electric field) determines the components of the threefold representation Γ_4^- with respect to the crystalline axes. From a Γ_1^+ ground state, transitions to even-parity states of Γ_1^+, Γ_3^+, Γ_4^+, and Γ_5^+ symmetry are thus allowed for classical ED-TPA (direct product $\Gamma_4^- \otimes \Gamma_4^-$ [6]). The magnetic-dipole operator $(\widehat{MD})_\nu$, however, transforms like an axial vector (angular or spin momentum [7]). In O_h the magnetic-dipole operator therefore transforms like the threefold irreducible representation Γ_4^+ [6]. The polarization vector $\mathbf{b}_\nu$ (direction of magnetic field) determines the components of Γ_4^+. For the electromagnetic field we get $\mathbf{b}_\nu = (\mathbf{k}_0 \times \mathbf{e}_\nu)$, where $\mathbf{k}_0$ is the unit wave vector. From a Γ_1^+ ground state, transitions to odd-parity states of Γ_1^-, Γ_3^-, Γ_4^-, and Γ_5^- symmetry are thus allowed for MD-TPA (direct product $\Gamma_4^- \otimes \Gamma_4^+$ [6]). The detailed polarization selection rules are for O_h the same as tabulated in Ref. [5]. If only one laser beam is used in the experiment, the $\Gamma_1^+ \to \Gamma_1^-$ transition vanishes because the electric and magnetic field are perpendicular, and the $\Gamma_1^+ \to \Gamma_4^-$ transition gives no contribution since both photons have the same energy (antisymmetric transition [5,8]); accordingly only transitions to Γ_3^- and Γ_5^- states are observable in a one-beam experiment.

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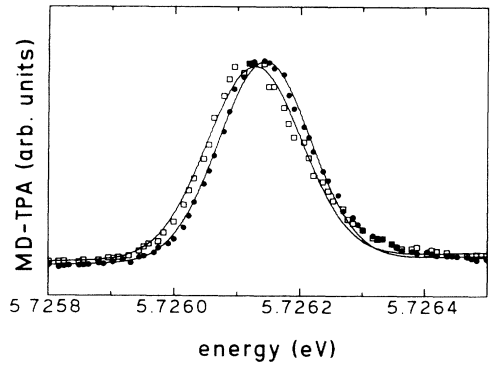

FIG. 1. Magnetic-dipole two-photon absorption (MD-TPA) of $1S$ paraexcitons in RbI. Open squares correspond to the polarization $\mathbf{e} = (100)$; closed circles correspond to the polarization $\mathbf{e} = \frac{1}{\sqrt{2}}(110)$. The solid lines are Lorentzian fits to the data.

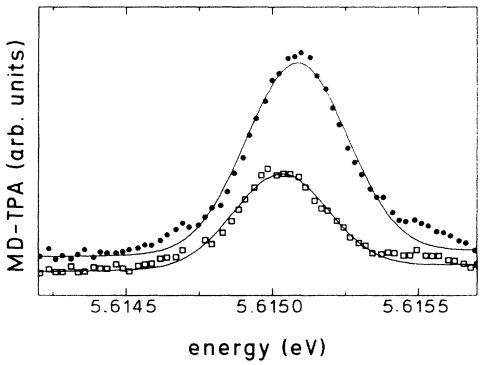

FIG. 2. MD-TPA of $1S$ paraexcitons in NaI. Open squares correspond to the polarization $\mathbf{e} = (100)$; closed circles correspond to the polarization $\mathbf{e} = \frac{1}{\sqrt{2}}(110)$. The solid lines are Lorentzian fits to the data.

We will now show that two-photon absorption via a magnetic-dipole transition is specially suited for the study of paraexcitons in semiconductors and insulators. In most cubic semiconductors and insulators (III-V, II-VI, I-VII) the uppermost valence band is derived from a $j = 3/2$ atomic state ($p_{3/2}$ state), which transforms in the cubic group O_h like Γ_8^- [6]. With a lowest conduction band of Γ_6^+ symmetry ($s_{1/2}$ state) the lowest S excitons are of Γ_3^-, Γ_4^-, and Γ_5^- symmetry (direct product $\Gamma_8^- \otimes \Gamma_6^+$). One can easily derive from the tables of Koster *et al.* [6] that Γ_4^- excitons are orthoexcitons (singlet-triplet mixed states) which are dipole allowed. The Γ_3^- and Γ_5^- excitons are paraexcitons (pure triplet states) and thus strictly spin forbidden for electric-dipole transitions. With the new technique of MD-TPA it is possible to excite paraexcitons since a magnetic-dipole transition is allowed between orthoexcitons and paraexcitons. From Eq. (1) one expects that the dipole-allowed S excitons (orthoexcitons) serve as intermediate states $|i\rangle$ for a magnetic-dipole transition to the final states $\langle f|$ (paraexcitons). By proper selection of the polarizations of the incoming laser beams one should then be able to determine the splitting ϵ_{ex} between the Γ_3^- and Γ_5^- paraexcitons, which is caused by anisotropic exchange interaction [9].

For a first application of this new spectroscopic method we have measured paraexcitons in three alkali halides (RbI, NaI, NaBr). The measurements were done on cleaved samples at 1.5 K. The two-photon signal was monitored via the σ or π luminescence of self-trapped excitons [10]. For further details of the experimental setup we refer to previous publications on two- and three-photon experiments [4,11]. As discussed before the polarization selection rules are the same as for classical two-photon processes, except for the fact that now odd-parity states are excited. Since we report on a one-beam experiment, there is only the orientation of the polarization vector $\mathbf{e}$ and the wave vector $\mathbf{k}$ with respect to the crystalline axes of relevance. The second vector $\mathbf{b}$ is then given by $\mathbf{b} = \mathbf{k}_0 \times \mathbf{e}$. From the tables of Koster *et al.* [6] one easily finds for $\mathbf{k}_0 = (001)$ that a transition to a Γ_5^- state is induced for $\mathbf{e} = (100)$ and to a Γ_3^- state for $\mathbf{e} = \frac{1}{\sqrt{2}}(110)$. In order to resolve the very small splitting of the paraexcitons due to the anisotropic exchange interaction both polarization configurations were measured in one run.

Paraexcitons in RbI had been measured by three-photon spectroscopy in high magnetic fields up to 7 T [4,11]. In good agreement with the previous results we get for the paraexciton energy $E_p = 5.7261 \pm 0.0001$ eV, which leads to an analytic exchange interaction [12] $\Delta_{ex} = \frac{3}{2}(E_T - E_p) = 33 \pm 2$ meV. $E_T = 5.748 \pm 0.001$ eV is the energy of the transverse exciton [11]. By extrapolating the three-photon data to zero field the authors [4] were able to give an estimate for the anisotropic exchange splitting $\epsilon_{ex} = 150 \pm 50$ μeV. As can be seen from Fig. 1 the splitting between Γ_3^- and Γ_5^- is clearly resolved although the splitting is much smaller than the previous estimate. We are now able to derive directly an accurate value for ϵ_{ex}. From the analysis of the spectra we get $\epsilon_{ex} = 16 \pm 4$ μeV.

In NaI and NaBr paraexcitons are reported for the first time (Figs. 2 and 3). From our data of NaI we derive for the paraexciton energy $E_p = 5.6150 \pm 0.0001$ eV, which leads to an analytic exchange interaction $\Delta_{ex} = 17 \pm 5$ meV. The large error of Δ_{ex} is due to the uncertainty of the transverse energy $E_T = 5.626 \pm 0.003$ eV, which is gained from three-photon spectroscopy. For the anisotropic exchange splitting we derive $\epsilon_{ex} = 50 \pm 10$ μeV. From our data of NaBr we get for the paraexciton energy $E_p(\Gamma_5^-) = 6.7082 \pm 0.0001$ eV and for the exchange interaction $\Delta_{ex} = 40 \pm 8$ meV. The large uncertainty of Δ_{ex} is again due to the uncertainty of $E_T = 6.735 \pm 0.005$ eV. From Fig. 3 we derive for the anisotropic exchange splitting $\epsilon_{ex} = 260 \pm 10$ μeV. It is

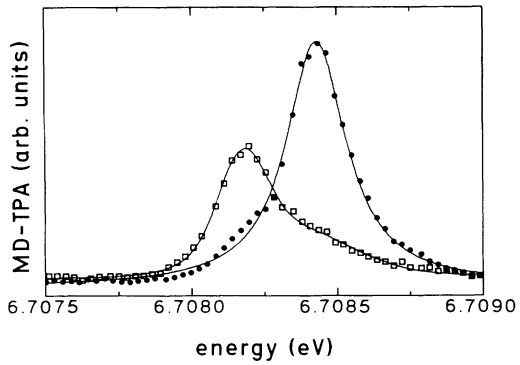

FIG. 3. MD-TPA of $1S$ paraexcitons in NaBr. Open squares correspond to the polarization $\mathbf{e} = (100)$; closed circles correspond to the polarization $\mathbf{e} = \frac{1}{\sqrt{2}}(110)$. The solid lines are Lorentzian fits to the data.

interesting to note that ϵ_{ex} is much larger in NaBr than in NaI and RbI.

The experimental determination of the exchange interaction in alkali bromides is a long-lasting problem. Onodera and Toyozawa [12] derived a formula which allows one to calculate the exchange interaction Δ_{ex} from the ratio of the oscillator strengths for the transitions from the $p_{3/2}$ and $p_{1/2}$ valence bands to the conduction band. From the analysis of absorption spectra of thin films obtained by Eby *et al.* [13] they got $\Delta_{ex} = 370$ meV for NaBr. Later Miyata [14] used the same formula [12] to derive a value for the exchange interaction. From a detailed analysis of reflection spectra of bulk crystals he got $\Delta_{ex} = 91.4$ meV, which is still larger than our value. We want to emphasize that our value for Δ_{ex} is directly gained from an energy separation between E_T and E_p, whereas Miyata had to do a Kramers-Kronig analysis in order to derive the oscillator strengths from reflection spectra.

In conclusion, we want to stress again that this new spectroscopic method is specially suited for the study of spin-forbidden odd-parity states like paraexcitons without application of an external perturbation. The investigation of these states is of principal interest, since important material parameters like isotropic and anisotropic exchange splitting, g values, and deformation potentials can be determined with high accuracy. As pointed out in Ref. [15], measurements on paraexcitons offer a direct access to these material parameters, since polariton effects are of no relevance. In addition, they cannot be observed directly in one-photon experiments and are therefore not known in many materials. Because of the high resolution it should now even be possible to resolve warping effects. This new method is not limited to insulators like alkali halides, but should also be applicable to semiconductors and organic materials. Detailed measurements in external fields (magnetic field, uniaxial stress, and hydrostatic pressure) can be performed more easily, since the paraexcitons are now two-photon allowed.

With the use of two laser beams with different photon energies Γ_1^- and Γ_4^- states can be excited besides the Γ_3^- and Γ_5^- states (O_h symmetry). With linearly and circularly polarized light a unique identification of excited states of different symmetry should be possible.

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