

Two-photon absorption into excited states of excitonic molecules and their inelastic scattering in ZnP_2

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Excited states of excitonic molecules have been observed by the direct method of giant two-photon absorption in a monoclinic ZnP_2 single crystal. Their origin and comparison with theoretical expectations are discussed. Photoluminescence of thermalized and nonthermalized “cold” excitonic molecules was studied under resonant two-photon excitation into their ground and excited states. An alternative mechanism of inelastic scattering of excitonic molecules is suggested.

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I. INTRODUCTION

Since the theoretical prediction of excitonic molecules by Lampert¹ and Moskalenko² and a number of their observations in many semiconductors, the problem of rotational and vibrational excited states of excitonic molecules has received considerable attention. This problem was first studied theoretically some time ago,³⁻⁵ but since then only a few experiments with evidence of observation of the excited states of biexciton were reported.^{6,7} This fact is understandable by taking account of the typical small binding energies of excitonic molecules in most semiconductors and of the expected large values for vibrational quantum and rotational constants due to small effective masses of biexcitons compared with the hydrogen molecule. Only for semiconductors with the heaviest holes (i.e., with the smallest ratio of effective masses of electrons and holes $\sigma = m_e^*/m_h^*$) can we expect that vibrational and rotational states of biexciton will be bound. The results of simple theoretical calculations based on the generalized Morse potential³ give numerical estimates. The first, second, and third vibrational excited state exist for $\sigma \leq 0.1$, $\sigma \leq 0.03$, and $\sigma \leq 0.015$, respectively. For the first three rotational excited states, the maximal values of σ should correspond to 0.12, 0.06, and 0.04, respectively. That is why the number of potential semiconductors for observation of the excited states of excitonic molecules is very limited. First, copper halides with well-known high binding energies of biexcitons should be considered. Some new features were found in the two-photon absorption spectrum of CuCl ,⁶ but later they were interpreted as due to exchange splitting of the ground state.⁸ Only one paper⁷ contains reliable data on the observation of some rotational and vibrational excited states in CuBr , showing new features in excitation and hyper-Raman cross-section spectra.

There are also observations of electronic excited states of

excitonic molecules.⁹⁻¹¹ Because of higher energies compared to rotational and vibrational excited states and the difference in symmetry they are not as difficult to resolve. Unlike these studies, in the present paper we focus on rotational and vibrational excited states of biexcitons. We looked for these states in a rather new, but very promising for exciton spectroscopy studies, semiconductor: monoclinic zinc diphosphide $\beta\text{-ZnP}_2$.

Several years ago an excitonic molecule with high binding energy was found in $\beta\text{-ZnP}_2$ in photoluminescence¹² and hyper-Raman scattering spectra.¹³ The unique properties of this crystal allowed us to observe the inverse hydrogenlike series of two-electron transitions¹² and a different type of two-photon radiative transitions.¹⁴ We therefore expect to observe excited states of excitonic molecule in $\beta\text{-ZnP}_2$. Such an investigation may be interesting not only as a problem by itself, but may be important for understanding the properties of the recently found dielectric biexcitonic liquid.¹⁵

Among many possible methods of excitonic molecule observations such as luminescence, hyper-Raman scattering, excitation, and two-photon absorption spectroscopy, we may have little chance to see luminescence of the excited states of excitonic molecules because of the short expected lifetimes of excited states and broadness of M bands. Hyper-Raman spectroscopy is sensitive to the fine structure and dispersion of the final state excitonic polariton so that the results sometimes are difficult to interpret. Excitation spectra tend to be complicated by hyper-Raman lines and phonon-assisted transitions. That is why we consider giant two-photon absorption to be the most direct and reliable method for the search of excited states of excitonic molecule. Moreover, this method is expected to provide the best resolution that is necessary to look for weakly bound excited states. Because of possible small absorption coefficients for the transitions into excited states of molecule we used a high spectral density picosecond laser.

II. SAMPLE PREPARATION AND EXPERIMENT

Zinc diphosphide was synthesized from phosphorus and zinc of 99.999% purity in quartz ampoules evacuated to $p = 2 \times 10^{-5}$ mm Hg in specially designed twelve-zone tubiform furnaces. Such furnaces are easy to set and maintain the temperature gradient along ampoule axis. For a total amount of 15 g of reagents (with phosphorus exceeding 2% from its stoichiometric quantity) it took about 100 h for complete synthesis at 1000 and 480 °C in zinc and phosphorus zones, respectively. The obtained product was refined two times by resublimation and then the amount of 5–6 g was used for crystal growth. In the ampoules of 18 mm diameter and 160 mm length at a temperature of 960 °C in the sublimation zone and 940 °C in growth zone it took about 100–150 h for complete mass transport with transport speed determined mainly by the feed surface area. Crystals were euhedral with the largest faces (100), (110) and also $(\bar{1}01)$, (102). The distance between (100) and $(\bar{1}00)$ was 1 to 6 mm. We would like to emphasize the high optical quality of the samples without cavities and cracks, which are often present in β -ZnP₂ crystals. For absorption measurements we used as-grown crystals or thinner plates prepared by means of mechanical polishing with subsequent etching in a Br₂:C₂H₅OH solution necessary to remove damaged surface layer.

A Ti:sapphire picosecond 3950B Tsunami laser with a repetition rate of 76 MHz and average power 600 mW was used as a source of incident radiation. The beam was focused on the crystal immersed in superfluid helium. High thermal conductivity of superfluid helium and duration of the laser pulse less than 2 ps prevented damage of the crystal surface. A picosecond laser provided us with good balance of spectral resolution and power density. The estimated power density at the focal point was up to 30 MW/cm². The incident intensity was changed by neutral-density filters. The simplest way to observe the difference in transmittance at different intensities is to move one of neutral-density filters from the incident beam to the transmitted beam. If no nonlinear absorption exists, the spectra must be identical. And they were actually identical for all the wavelengths except the area corresponding to the half-energy of biexciton. A Hamamatsu streak camera C5680 was used for time-resolved measurements.

III. GIANT TWO-PHOTON ABSORPTION

To distinguish two-photon absorption into biexcitons from strong exciton absorption and bound excitons usually existing even in high quality crystals, we performed measurements at different intensities of laser beam. Examples of the dependence of the optical density on incident intensity are presented in Fig. 1. For wavelengths shorter than 796 nm and longer than 797.5 nm the optical density is constant within experimental error. And it is clearly seen from Fig. 1 that the absorption increases at wavelength 797.1 nm which corresponds to the half-energy of the biexciton. The dependence of the optical density is not linear but tends to saturation because two-photon absorption is very strong and causes

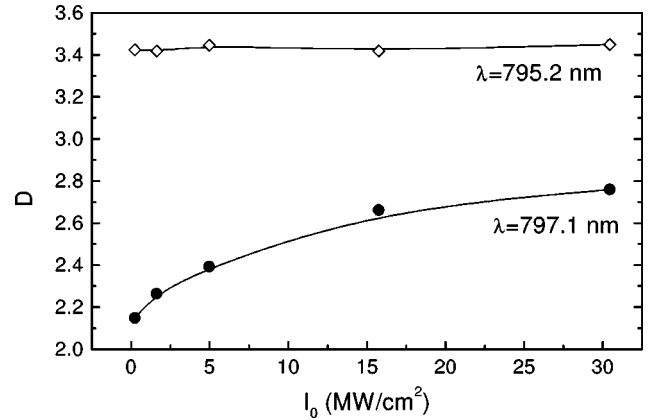


FIG. 1. Dependence of optical density on incident intensity at two different wavelengths. $T = 2$ K.

a nearly full absorption of part of the laser line (examples of transmitted spectra and a more detailed explanation will be presented later in this section). From such dependences we determined the intensity range, where the nonlinearity is clear enough and absorption is not too strong to have good spectral resolution. To obtain resolution better than the half-width of laser line, which was about 0.5 nm in our experiments, we measured spectra of transmitted pulses at two different incident intensities (Fig. 2). Dips corresponding to two-photon absorption are seen on the wings of laser line (the dip on the right wing is not so clear but the change of the contour of the transmitted line compared to the incident one is easy to notice). A number of such spectra at two different intensities were measured over the entire spectral area from the exciton line to biexciton luminescence band. Then the spectrum at low intensity is divided by that at high intensity and the results are summarized in Fig. 3.

It should be noted that the obtained absorption band does not correspond directly to the energy spectrum of the state transitions that cause absorption. For example, even in the case of a narrow final energy state E_M we will obtain a broad band formed by pairs of photons with the energies symmetri-

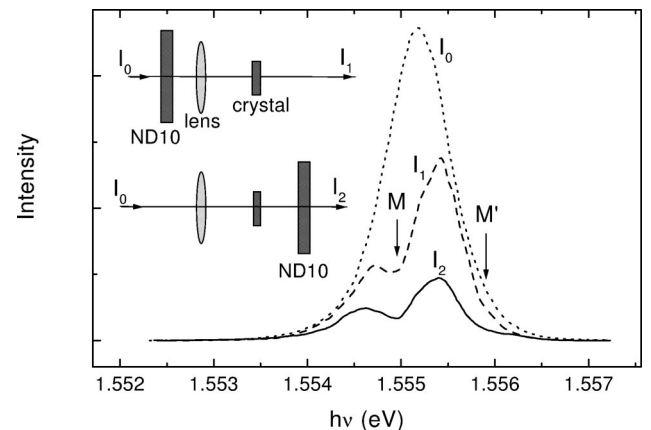


FIG. 2. Spectra of laser pulse transmitted through the β -ZnP₂ crystal at low (1.0 MW/cm², dashed line) and high (8.4 MW/cm², solid line) incident intensity. The dotted line represents the arbitrary normalized spectrum of incident laser pulse.

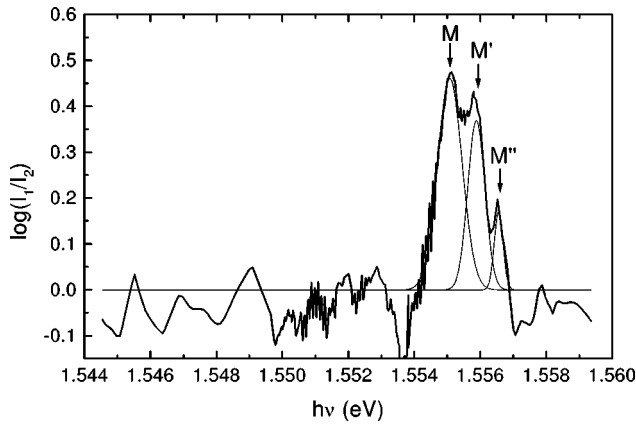


FIG. 3. Nonlinear absorption in the β -ZnP₂ crystal.

cal relative to energy position $E_M/2$: $\hbar\omega_1 + \hbar\omega_2 = E_M$. It becomes narrower at the wing of laser line, because only one photon largely contributes to the two-photon absorption and the other photon density becomes very weak, and it becomes broader at the center of the laser line when the two-photon absorption is stronger.

According to group-theoretical calculations two-photon absorption into biexcitons is allowed both in $\mathbf{E}\parallel\mathbf{c}$ and $\mathbf{E}\perp\mathbf{c}$ polarizations. But latter is much weaker because of the forbidden exciton transition in this polarization. The one-photon resonance with the exciton state is one of enhancement factors leading to giant oscillator strength. And in $\mathbf{E}\perp\mathbf{c}$ polarization only the transition into the $B_{n=1}$ exciton state, interpreted in Ref. 16 as a triplet exciton, is allowed but its oscillator strength is several orders of magnitude smaller than the $1S$ exciton in $\mathbf{E}\parallel\mathbf{c}$. Thus we could observe two-photon absorption at $\mathbf{E}\perp\mathbf{c}$ only in very thick samples (3 mm and more). But in this case the second excited state of molecule is difficult to resolve because its energy is too close to B -exciton energy. That is why in this paper we present the results for $\mathbf{E}\parallel\mathbf{c}$ in a thin sample ($d=50\ \mu\text{m}$) (Fig. 3). Three two-photon absorption lines at 1.5551, 1.5559, and 1.5565 eV designated by M , M' , and M'' are well resolved. The energy of line M agrees well with that of the symmetry point of inverse hydrogenlike series and excitonic series [797.3 nm, i.e., 1.5546 eV (Ref. 12)] and with half-energy of excitonic molecule (1.5551 eV) obtained from hyper-Raman cross-section spectra.¹³ Thus it should be interpreted as two-photon absorption into an excitonic molecule. Lines M' and M'' are less intense and appear on the high-energy side of line M . We tentatively interpret them as two-photon absorption into excited states of excitonic molecules lying 1.52 and 2.9 meV above the ground state.

To compare with theoretical predictions for the binding energy of rotational and vibrational excited states the ratio of effective masses $\sigma = m_e^*/m_h^*$ is necessary. The latest data on effective masses in β -ZnP₂ are presented in Ref. 17: $m_e^{*a} = 0.7$, $m_h^{*a} = 1.1$, $m_e^{*c} = 0.18$, $m_h^{*c} = 0.2$, $m_e^{*b} = 1.1$, $m_h^{*b} = 1.4$. It gives the ratio $\sigma^a = 0.64$, $\sigma^c = 0.9$, $\sigma^b = 0.79$. According to theoretical calculations^{3,18} for such σ values the binding energy of the ground state of excitonic molecule must be about 1.4 meV. Experimentally obtained binding

energies are 5 meV, 10.4 meV (Ref. 13), and 14.9 meV (Ref. 12). Different values were reported not due to experimental errors but because of the uncertainty in which an exciton state should be used for the calculation of the binding energy of biexcitons (experimentally obtained half-energies of biexciton differ less than 0.5 meV). We consider 10.4 meV to be the most correct value if the binding energy is measured from the $1S$ allowed exciton. Its discrepancy with the effective masses obtained in Ref. 17 has no explanation at the moment. That is why for estimates of binding energies of excited states we will proceed from the experimental value of the binding energy of the ground state.

From the theoretical calculations³ we can expect for biexcitons in the β -ZnP₂ crystal rotational excited states with energies 1.64, 4.36, and 7.07 meV above the ground state and one vibrational excited state with energy 6.79 meV. Energies of the first and second states are in reasonable agreement with the positions of the M' and M'' lines. The discrepancy in the energy value is understandable because the strong anisotropy of effective masses in β -ZnP₂ was not considered in Ref. 3. Transition into the third rotational excited state is forbidden by selection rules, and the vibrational excited state is probably not observed because of the high absorption of the sample at that energy.

IV. LUMINESCENCE UNDER RESONANT TWO-PHOTON EXCITATION

Finding well-resolved excited states of biexcitons in the β -ZnP₂ crystal provides an opportunity to study their participation in resonant two-photon excitation of biexciton luminescence. We have studied changes in photoluminescence spectra under two-photon excitation with different wavelengths in the spectral area of the transitions into ground and excited states of biexcitons at an excitation power density of 15 MW/cm². Such a power density was found to be high enough for strong two-photon absorption. Luminescence spectra are presented in Fig. 4 together with profiles of excitation laser lines for each spectrum. Positions of two-photon resonances with ground (M) and excited (M' , M'') states of excitonic molecules are indicated by dashed lines. First it should be noted that biexciton luminescence is efficiently excited only when the laser line is in resonance with its ground state or any of the excited states. In the case of excitation into the ground state (spectra c , d , e , f , in Fig. 4) the luminescence spectrum consists of a narrow line at 1.550 eV (C line) and a broad asymmetric band tailing to the low-energy side (T band). This narrow line corresponds to the luminescence of resonantly excited molecules with very small momentum (see schematic in Fig. 5), so-called ‘‘cold’’ molecules observed in CuCl crystal.¹⁹ The broad band is a result of optical transitions between ‘‘thermalized’’ excitonic molecules spread wide along the dispersion curve and underlying excitonic states (Fig. 5). It should be noted that the stationary temperature of the biexciton gas is usually higher than the lattice temperature and depends on excitation conditions. The narrow line at 1.5476 eV is present in the spectrum at nonresonant excitation, and it was observed also in the absorption spectrum. This line belongs likely to some

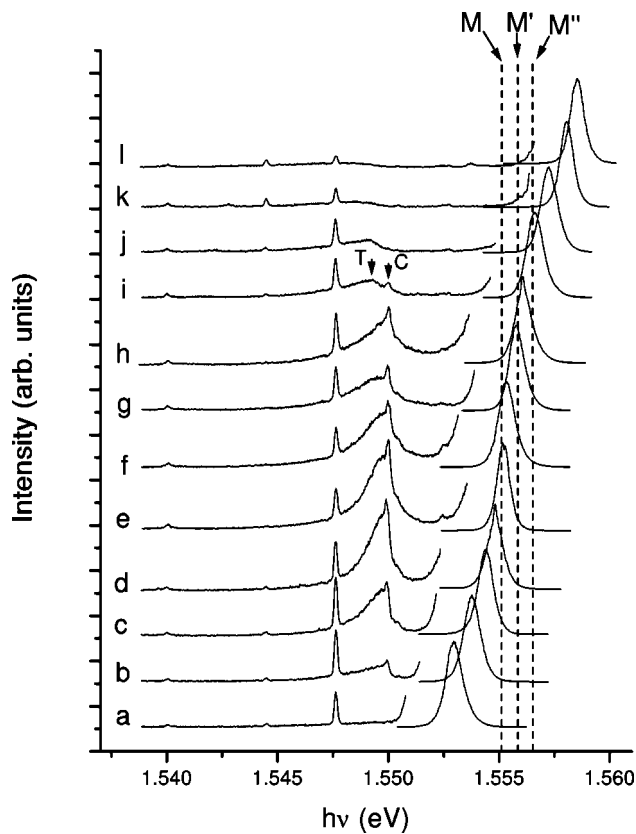


FIG. 4. Luminescence of the β -ZnP₂ crystal under resonant two-photon excitation. At the right side of each spectrum the excitation laser line is presented. Dashed lines mark the positions of two-photon resonances with ground and excited states of excitonic molecules.

bound excitons, a number of which is present in the luminescence spectrum of any β -ZnP₂ crystal.^{12,13,20} If the laser line is shifted to the high-energy side from the M -resonance energy we expect disappearance of the sharp line of “cold” biexcitons, an increase of the effective temperature of thermalized biexcitons, and maybe luminescence from excited states of biexcitons. Unfortunately, we have not observed any reliable luminescence from the excited states of excitonic molecules, perhaps because of very short lifetimes of such excited states due to their fast relaxation into the ground state. In the spectra obtained under excitation with energy higher than the M -resonance energy, the band of thermalized biexcitons broadens and changes its shape, reflecting the elevated temperature of biexcitons. Assuming a Maxwell-Boltzmann distribution of biexcitons and fitting their luminescence band, we estimated the effective temperature as 6.6, 9, and 12 K, for spectra d , g , and i (Fig. 4), correspondingly.

A surprising fact is that the narrow line of “cold” biexcitons appears even under excitation into the first excited state, as seen in curves g , h , i of Fig. 4. Its relative intensity is smaller and the half-width is slightly larger than that in the case of ground state excitation (curves b to f). Such nonthermalized “cold” biexciton luminescence under off-resonance excitation indicates existence of a different relaxation process between excited and ground states of biexcitons. Such

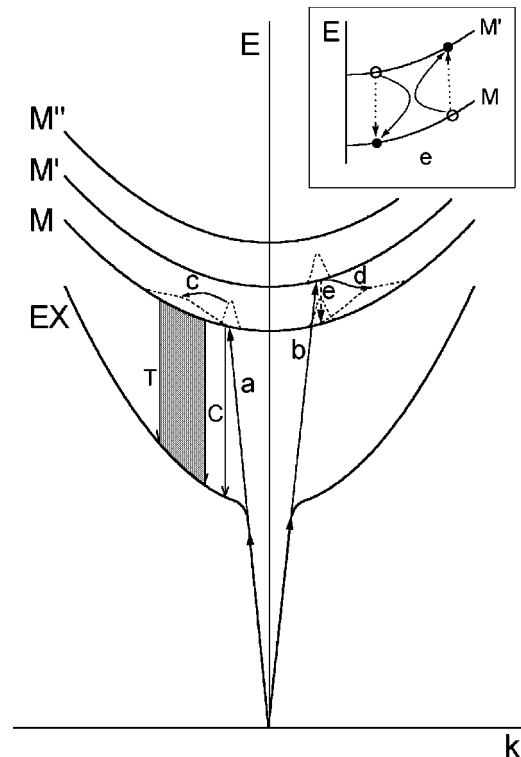


FIG. 5. Schematic diagram of the two-photon excitation of excitonic molecules, their relaxation, and luminescence. Dashed lines show the population of different states. Arrows indicate excitation, relaxation, and recombination processes in biexciton system: a , two-photon absorption into ground state; b , two-photon absorption into excited state; c , thermalization; d , relaxation from the excited state into the ground state; e , suggested mechanism of resonant transfer of excitation energy in intermolecular collisions; C , radiative recombination of “cold” biexcitons; T , radiative recombination of thermalized biexcitons.

relaxation must be rather fast and is not accompanied with significant broadening of the biexciton momentum distribution. Supposition that it could be a direct optical transition from the excited to ground state of the molecule, should be rejected because of the very low rate of such low frequency transitions. Any process involving phonons will inevitably broaden momentum distribution. As a possible explanation we can suggest some inelastic scattering process of a “cold” molecule in the excited state and a thermalized molecule in the ground state. Resonant exchange of excitation energy takes place, and as a result we have a “cold” molecule in the ground state and a thermalized molecule in the excited state (Fig. 5, inset). Of course there are other relaxation processes from the excited state (Fig. 5, d); they give thermalized molecules in the ground state. It should be noted that no “cold” biexciton luminescence was observed under excitation into the second excited state M'' (curve j , Fig. 4). This fact is in agreement with its assignment to the second rotational excited state $l=2$. The suggested excitation energy exchange in intermolecular collisions perhaps takes place due to the overlapping of wave functions of the excited state and the ground state when they are disturbed in the scattering process. Such

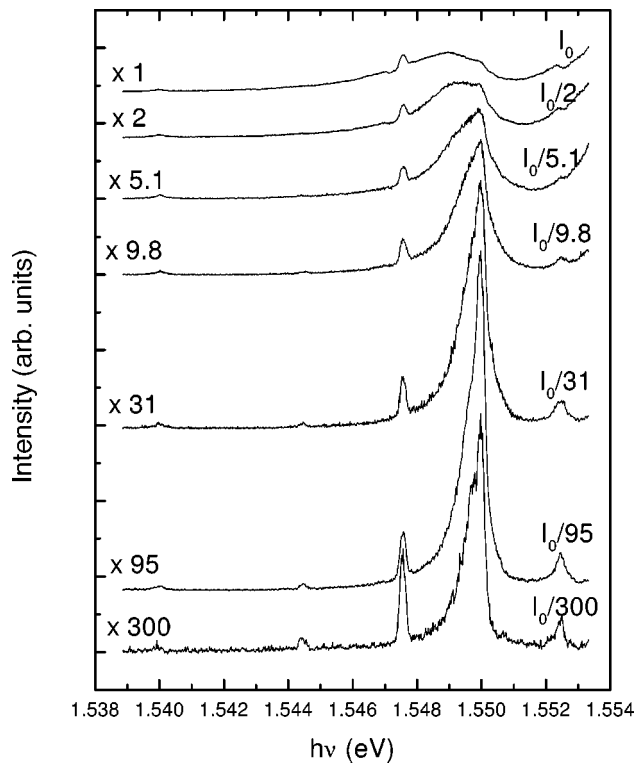


FIG. 6. Resonant luminescence of the β -ZnP₂ crystal under excitation into the molecular ground state with different power densities.

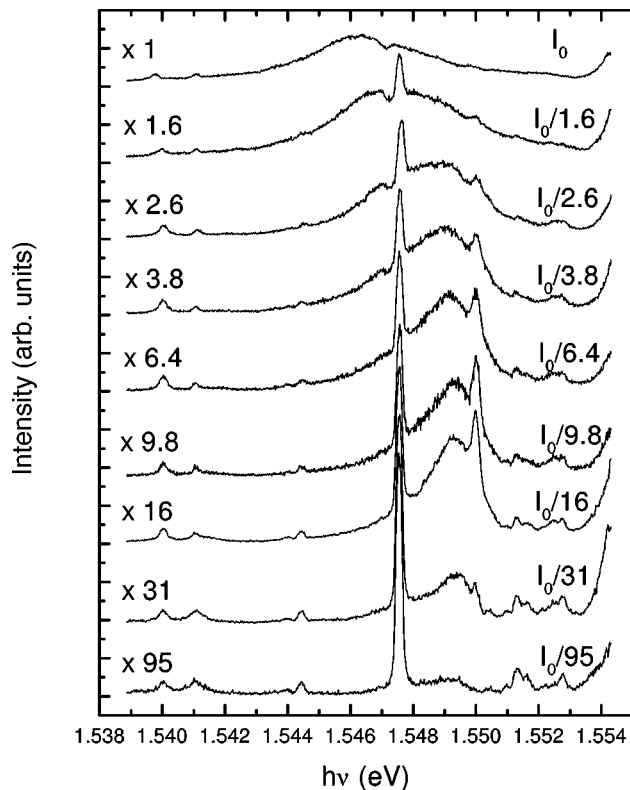


FIG. 7. Resonant luminescence of the β -ZnP₂ crystal under excitation into the molecular excited state with different power densities.

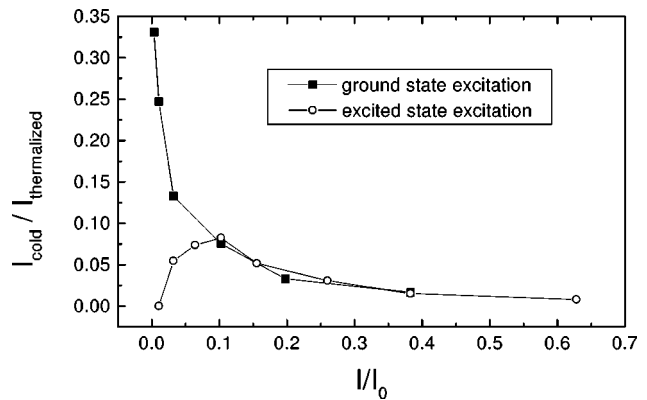


FIG. 8. Dependence of the ratio of intensities of “cold” and thermalized biexcitons bands on excitation intensity. Solid squares, excitation into the ground state; open circles, excitation into the first excited state.

overlapping for the second rotational excited state must be much smaller.

To check the validity of such a supposition we have studied the dependence of the luminescence spectrum on the excitation intensity in the cases of excitation into molecule ground state and the excited state. Results are presented in Fig. 6 and Fig. 7 correspondingly.

Under ground state excitation (Fig. 6) the relative intensity of the luminescence of “cold” molecules decreases with increasing excitation perhaps due to faster thermalization caused by frequent intermolecular scattering. The broad emission band of thermalized molecules changes its shape, broadens, and shifts the maximum energy to the low-energy side. This indicates an increment of their stationary temperature, which is considerably higher than the lattice temperature as was pointed out earlier in this section.

Under excitation into the molecular excited state (Fig. 7) the narrow *C* line is not seen in the lowest intensity spectrum. It appears and then becomes stronger with increasing excitation intensity. After reaching the maximum its intensity gradually decreases, similar to the case of ground state excitation. The difference in behavior of the “cold” biexciton line is clearer in Fig. 8, which presents the ratio of its intensity to the area of thermalized biexciton band obtained

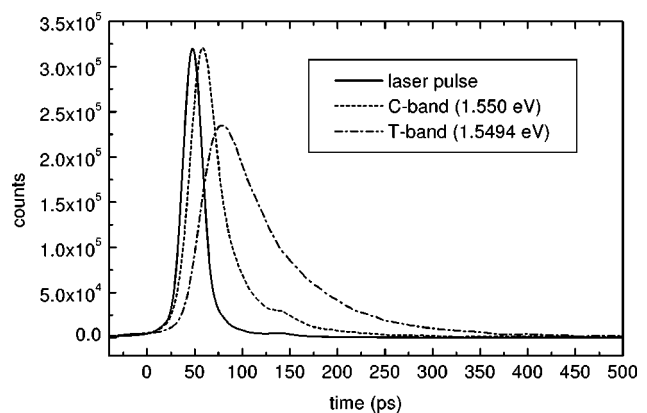


FIG. 9. Decay curves for the luminescence bands of “cold” and thermalized molecules. Solid line, instrument response function.

TABLE I. Time profiles of luminescence bands of excitonic molecules.

Excitation	C band (“cold” molecules)		T band (thermalized molecules)	
	Rise time (ps)	Decay time (ps)	Rise time (ps)	Decay time (ps)
1.555 eV (ground state)	<5	40	27	50
1.556 eV (excited state)	<5	27	12	63

from a multippeak analysis of the spectrum. The observed rapid increase of the “cold” molecule band at low excitation into excited state fully supports the above mechanism of resonant excitation energy exchange in intermolecular collisions, because its probability is proportional to the density of the thermalized exciton molecules in the ground state.

V. TIME-RESOLVED MEASUREMENTS

We have also measured time profiles of the mentioned bands using a streak camera. Examples of the obtained decay curves are presented in Fig. 9. The decay curves of all bands can be fitted well with a single exponent. But for the *T* band another exponent is necessary to describe the observed band rise. The results are summarized in Table I. From the measurements repeated several times and at different spectral positions within one band we estimate experimental errors as ± 5 ps. From the table we can see that *C*-line luminescence of “cold” molecules has shorter decay time than the *T* band. This is in agreement with its nonequilibrium nature. Thermalization of initially excited “cold” molecules gives rise to the *T* band, which is why the rise time for latter roughly corresponds to decay time for the *C* line. The decay time of the *T* band is about 50 ps and it should be considered as a lifetime of excitonic molecules in the β -ZnP₂ crystal. It is determined mostly by radiative recombination and Auger recombination. Unfortunately we do not know of any data on the Auger recombination rate in β -ZnP₂, and we cannot obtain the pure radiative recombination rate.

In the case of the 1.556 eV excitation into molecular excited state *M'* the decay time of “cold” biexcitons is shorter, perhaps due to the higher average temperature of biexcitonic system. We could not determine the rise time of this band. A probable explanation is the rather high excitation intensity in these experiments, which was necessary in order to have enough signal for time-resolved measurements. At such high excitation intensity the intermolecular scattering is too frequent to observe relaxation from the excited state. The main difference between the cases of excitations into the ground state and into the excited state is the shorter rise time in the latter case. It agrees well with the fast relaxation from excited state and higher effective temperature of biexcitonic system in this case.

VI. CONCLUSIONS

Two excited states of excitonic molecules have been observed in a β -ZnP₂ crystal by the direct method of giant two-photon absorption. They have energies 1.52 meV and 2.9 meV above the ground state and are interpreted as the first and the second rotational excited states. A comprehensive study of biexciton luminescence under resonant two-photon excitation into ground and excited states has led us to suggest an alternative mechanism of resonant transfer of excitation energy in intermolecular collisions. We have also determined in the β -ZnP₂ crystal the lifetime of excitonic molecules as 50 ps. Their thermalization time is several times shorter and depends on excitation conditions.

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