Two-photon spectroscopy using picosecond light continua

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Two-photon absorption is measured using two picosecond pulses: a monochromatic pulse and a pulse with broad frequency spectrum. Single pulses of high peak intensity were applied to crystalline samples without damage. Introducing a time delay of several picoseconds between the two pulses, possible two-step processes can be elucidated. As an example, two-photon absorption in CdS was investigated over an energy range from 2.4 to 3.5 eV.

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During the past decade a large number of papers has been published on two-photon spectroscopy in solids.[1] Considerable amount of work was done with a Q-switched laser in conjunction with flashlamps of broad spectral range. There are disadvantages in using these "long" light pulses for two-photon spectroscopy: The input peak intensities of the laser pulses are limited by surface and bulk damage of the crystal. With long pulses two-step absorption processes via impurity states cannot be distinguished from two-photon processes via virtual states.

In this letter we wish to discuss a new technique for two-photon spectroscopy. An intense monochromatic picosecond light pulse induces nonlinear absorption of a weak broad-band picosecond continuum in the sample. This method has several advantages: (i) Very high peak intensities can be applied to the sample without material damage. As a result, strong two-photon interaction is achieved. It is possible to measure small two-photon cross sections with good accuracy. (ii) Two-photon absorption spectra can be measured over a wide spectral range with one picosecond laser pulse (after proper calibration of the system). (iii) Using a pulse delay of several picoseconds between the two light pulses, it is possible to distinguish between two-step absorption and two-photon absorption. (iv) Polarization measurements can be carried out with two pulse systems.

Our investigations were made with a mode-locked Nd-glass laser system.[2] A single picosecond light pulse was selected from the early part of the pulse train and was amplified to an energy of 3 mJ. ($\Delta t_L \simeq 6$ ps FWHM, $\Delta\tilde{\nu}_L \simeq 3$ cm^{-1} FWHM). A second pulse of picosecond duration and broad frequency spectrum was generated by parametric four-photon interaction of the laser pulse in liquid water.[3] The spectral range extended from the ultraviolet to the infrared. This picosecond continuum is emitted in the forward direction with a small divergence angle; it is polarized parallel to the laser light. The input peak intensity of the laser pulse at the water cell was approximately 1.5×10^{11} W/cm^2. At this intensity range the parametric light generation is in the saturation range where the spectral distribution of the continuum is rather flat.[4]

Two experimental arrangements were used in our investigations. In Fig. 1(a), a single picosecond laser pulse passes first through a water cell of 2-cm length generating the second pulse with broad continuous spectrum. Both light pulses are then imaged onto sample S. The intensity of the input laser pulse is monitored by a technique using a saturable absorber.[5] The incoming and the transmitted spectral intensity distribution of the parametrically generated pulse is registered with the help of two optical multichannel analyzers consisting each of a 0.3-m Ebert polychromator, a vidicon, and a data-recording system. The laser pulse and the pulse with broad spectrum have the same polarization. Care has to be taken to minimize the pulse delay introduced by group velocity dispersion of the optical components.

In order to distinguish between two-photon absorption and two-step absorption, we used the experimental setup of Fig. 1(b). The laser pulse is divided into two beams by a 50% mirror M. One beam generates the parametric light in the water cell; this laser pulse is subsequently filtered out. The other beam is focused into the sample together with the parametric light. An optical delay line DL allows variation of the time interval between the continuum pulse and the laser pulse. With this system the nonlinear absorption of the continuum can be studied on a picosecond time scale. Two-photon absorption occurs only when the two pulses over-

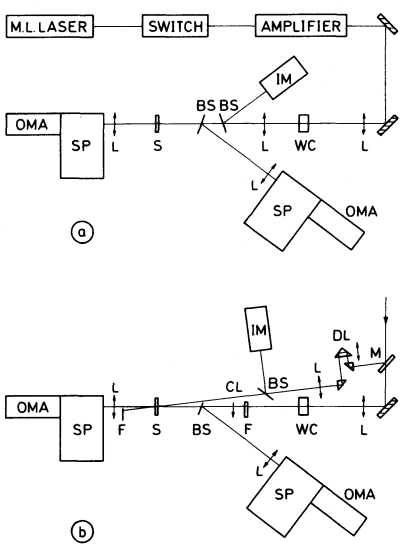

FIG. 1. Experimental setup for picosecond two-photon spectroscopy. (a) Laser pulse and continuum travel together. (b) Variable delay between laser pulse and parametric continuum. L lens; WC water cell; BS, beam splitter; S, sample; SP, spectrograph; OMA, optical multichannel analyzer; IM, intensity measurement with saturable absorber; F, stop filter for laser light; CL, cut lens; M, half-reflecting mirror; DL, optical delay system.

lap in time, while two-step absorption persists until the population of the intermediate real states relaxes to lower-lying states.

The two-photon absorption of the picosecond spectra $I(\omega)$ in the presence of the intense laser pulses I_L is given by

$$\frac{\partial I(\omega, r, t', z)}{\partial z} = -\alpha^{(2)}(\omega) I_L[r, t' + K(n_{gC} - n_{gL})z/c, z]\, I(\omega, r, t', z). \quad (1)$$

$\alpha^{(2)}$ (cm/W) is the two-photon absorption coefficient where $\alpha^{(2)} = N\sigma^{(2)}/\hbar\omega_L$; N is the number of molecules per unit volume, and $\sigma^{(2)}$ is the two-photon absorption cross section in $\mathrm{cm}^4\,\mathrm{s}$. The abbreviation $t' = t - n_{gC}z/c$ is used. $n_{gi} = n_i - \lambda_i\, dn_i/d\lambda$ $(i = C, L)$ are the refractive indices corrected for group dispersion. The constant K takes into account the initial pulse delay between laser L and continuum C at the entrance to the sample $z = 0$. Since the intensity of the continuum is much smaller than I_L, the laser pulse is practically unchanged in intensity. The intensity of the transmitted continuum $I(\omega, r, t', l)$ is obtained by integration of Eq. (1):

$$I(\omega, r, t', l) = I(\omega, r, t', 0) \exp[-\alpha^{(2)}(\omega) \times \int_0^l I_L(r, t' + K + (n_{gC} - n_{gL})z/c, z)\, dz]. \quad (2)$$

In our experiments the energy transmission of the continuum, T_E, i.e., the ratio of transmitted energy to input energy, is measured as a function of frequency. For radial symmetric light pulses the energy transmission is given by $T_E = \int_0^\infty 2\pi r \int_{-\infty}^{\infty} I(\omega, r, t', l)dt'dr / [\int_0^\infty 2\pi r \times \int_{-\infty}^{\infty} I(\omega, r, t', 0)\, dt'dr]$. In our calculations we assume Gaussian light pulses $I(\omega, r, t', 0) = I_0(\omega) \exp(-r^2/r_C^2 - t'^2/t_C^2)$ and $I_L(r, t' + K + (n_{gC} - n_{GL})z/c, z) = I_{0L} \exp[-r^2/r_L^2 - (t' + K + (n_{gC} - n_{gL})z/c)^2/t_L^2]$. With the substitution $\rho = r/r_C$ and $\tau = t'/t_C$, the following expression for the energy transmission is obtained:

$$T_E(\omega, l) = (4/\sqrt{\pi}) \int_0^\infty \rho \exp(-\rho^2) \int_0^\infty \exp(-\tau^2 - \alpha^{(2)}(\omega) I_{0L} \times \exp[-(\rho r_C/r_L)^2] \int_0^l \exp\{-[\tau t_C + K + (n_{gC} - n_{gL})z/c]^2/t_L^2\} dz)\, d\tau\, d\rho. \quad (3)$$

Linear losses are not included in Eqs. (1)–(3) since the transmission of the continuum in the presence of the strong laser pulse is compared to the transmission without the strong pulse.

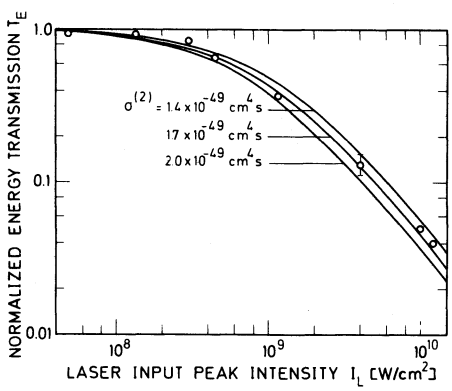

FIG. 2. Energy transmission of picosecond spectrum at $\lambda_C = 6000$ Å ($\Delta\lambda_C \simeq 16$ Å FWHM) vs laser pulse intensity. Both waves are polarized perpendicular to the c axis of the crystal. Curves are calculated, points are experimental data for 0.31-cm CdS.

Our technique of picosecond two-photon spectroscopy was tested by studying the frequency dependence of the two-photon absorption cross section of CdS single crystals at room temperature[1,6-9] (hexagonal; dark resistance $> 10^7\ \Omega$cm).

In a first measurement the transmission properties of CdS for monochromatic laser pulses were investigated. It was found that up to $I_L \simeq 10^{10}$ W/cm^2 no nonlinear absorption of laser light ($\lambda = 1.06\ \mu$m) occurs in CdS samples of thickness 0.1 and 0.31 cm. Nonlinear absorption was observed at higher input intensities.[10] The two-photon absorption measurements reported in this paper were carried out at laser intensities below 10^{10} W/cm^2. In the following measurements the experimental arrangement of Fig. 1(a) was used.

The energy transmission of the picosecond spectrum at $\lambda_C = 6000$ Å ($\Delta\lambda \simeq 16$ Å FWHM, $h\nu_L + h\nu_C = 3.24$ eV) is shown as a function of the input laser intensity ($\lambda = 1.06\ \mu$m) in Fig. 2. The optical axis of the crystal was oriented perpendicular to the propagation and polarization directions of the laser light and the continuum. In this experiment the two optical multichannel analyzers were replaced by photomultipliers. We note in Fig. 2 the strongly reduced transmission (~4%) in the presence of the laser pulse of 10^{10} W/cm^2. The various parameters entering Eq. (2) were determined experimentally. The length of the sample was 0.31 cm, the ratio of the beam radii was found to be $r_C/r_L = 0.67$. The pulse durations were measured with a picosecond streak camera (time resolution $\simeq 3$ ps); the obtained values were $t_C/t_L \simeq 0.8$ and $\Delta t_L \simeq 6$ ps. The pulse delay K of the continuum with respect to the laser pulse was calculated for the optical components to be smaller than

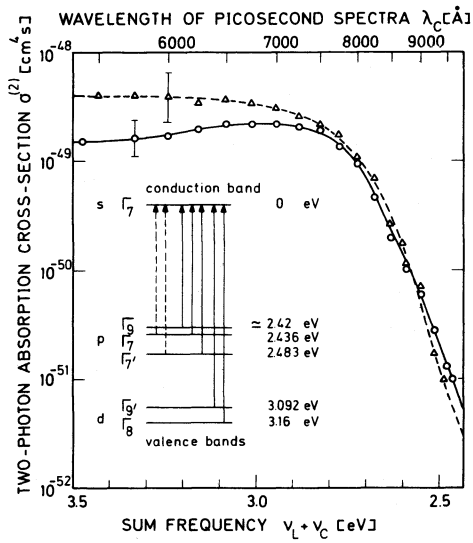

FIG. 3. Frequency dependence of two-photon absorption cross-section of CdS. Solid curve: $E \perp c$; dashed curve: $E \parallel c$. Curves are calculated from the measured energy transmission [Eq. (2)]. Inset: energy levels of CdS at the Γ point; electric-dipole-allowed two-photon transitions for $E \perp c$ (solid arrows) and $E \parallel c$ (dashed arrows).

1 ps. The n_{gL} and n_{gC} values were determined from dispersion data of the refractive indices. With these data the curves were calculated in Fig. 2. From our experimental points we deduce a nonlinear absorption cross section $\sigma^{(2)} = (1.7 \pm 0.3) \times 10^{-49}$ cm^4 s [$\alpha^{(2)} = (18 \pm 3)$ cm/GW; $N = 2 \times 10^{22}$ cm^{-3}].

The frequency dependence of the two-photon absorption cross section of CdS is presented in Fig. 3 for two cases: laser light and continuum parallel and perpendicular to the optical axis of the crystal. The nonlinear transmission of the picosecond spectrum through CdS samples of 0.1- and 0.31-cm thickness was measured. The two-photon absorption cross sections were determined by introducing the experimental energy transmission into Eq. (2). Within the investigated spectral range from 10 000 to 18 000 cm^{-1} (2.4 eV $< h\nu_L + h\nu_C <$ 3.50 eV) the two-photon absorption cross section changes by approximately 3 orders of magnitude from 2×10^{-49} to 5×10^{-52} cm^4 s. We note that values of $\sigma^{(2)}$ between 2×10^{-49} and 5×10^{-50} cm^4 s have been reported in previous publications.

The spectra for laser light parallel or perpendicular to the optical axis c are clearly different. For $E \perp c$ the spectrum shows a small maximum around $h\nu_L + h\nu_C \simeq 3$ eV; and in addition we find a tail of the spectrum which extends to lower energies than for $E \| c$. These findings are tentatively explained as follows: The inset of Fig. 3 presents the energy levels of CdS at the Γ point[8,9,11-13]; two-photon transitions allowed by selection rules for $E \| c$ (dashed arrows) and for $E \perp c$ (solid arrows) are indicated. It appears that there are more transitions for $E \perp c$. The observed maximum around 3 eV might be due to excitation from the d-like valence bands to the s-like conduction band[9] and the low-energy tail might result from excitations from the very top of the valence band to the conduction band.[8,9] More work is needed to ascertain these points.

A final remark should be made concerning possible two-step absorption processes. Using the experimental system depicted in Fig. 1(b), we measured the energy transmission of the continuum pulse. No absorption was detected at a delay time of 50 ps between the parametric light pulse and the laser pulse. This result suggests that two-step absorption processes can be neglected in our experiments.

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