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PICO- AND FEMTOSECOND PHOTON ECHOES IN DOPED LOW-TEMPERATURE ORGANIC POLYMERS AND APPLICATIONS IN TIME–SPACE OPTICAL DATA PROCESSING

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The phenomenon of burning of persistent photochemical holes in inhomogeneously broadened spectra of molecular impurities allows doped low-temperature organic polymers to be used as a recording medium of spectrally selective holograms. Ultimate temporal resolution of time domain holographic storage, Fourier-related to the inhomogeneous band width of the storage media was investigated by using femtosecond pulses generated by a colliding pulse mode locked dye laser. Recall of photochemically accumulated stimulated photon echo (PASPE) with pulse duration shorter than 100 fs was demonstrated in polystyrene doped with protoporphyrine at 1.8 K. Experiments presenting evidence of spectral diffusion in low temperature polystyrene as probed by PASPE and two-pulse photon echo are also reported.

1. Introduction

The low temperature homogeneous absorption spectrum of an impurity introduced into solid matrices has characteristic structures comprising very narrow and high peak intensity purely electronic lines (PEL) which are accompanied by much broader and less intense phonon sidebands [1]. This description holds not only for impurity ions in crystals but also for large organic molecules in different solid matrices e.g. polycrystals, glasses and organic polymers [1,2].

In real solids the impurity PEL spectra is usually smeared by very large inhomogeneous broadening (in organic polymers $\delta_{IB} \sim 10^2$–10^3 (cm^{-1}) and to study these sharp spectral features (in organic polymers at liquid He temperatures they are typically $\delta_{PEL} \sim 10^{-2}$–$10^{-4}$ cm^{-1}) special spectroscopic methods such as photoburning of persistent spectral holes (PHB) [3] and photon echoes [4,5] have to be used (for spectroscopic applications of PHB and photon echoes see review papers [2,6–10] and [11,12]).

Actually, an inhomogeneously broadened band of purely electronic transitions is a quasicontinuum of well defined and spectrally narrow (high Q-factor) optical resonances and presents a number of possibilities for practical applications. It is important that this high spectral selectivity can be achieved even in very small volumes of the material at least as far as there are enough impurity molecules to average out the statistical fluctuations [13].

One of the most promising applications is the frequency selective optical memory [14,15], particularly in the presence of PHB which provides the permanent storage of the data [15]. The high spectral selectivity of the media allows the data bits to be assigned not only to different spatial locations but also to different frequencies which can increase the storage density up to 10^{12} bits per cm^2. Additional possibilities arise from photon-gated hole-burning materials [16] as well as from external electric field effects [17].

A time-domain holographic approach to frequency selective data storage has been suggested [18,19]. In this case all the data bits assigned to a given spatial location are written in parallel by a temporally modulated laser pulse. The time-domain optical storage has been explored with micro- and nanosecond timescale photon echo experiments carried out in gaseous media [20] and impurity crystals [21]. PHB-active low-temperature organic polymers provide several additional possibilities such as ultrahigh temporal resolution as well as permanent storage of the data [18,22–25].

The purpose of the present paper is to survey the experimental results on recording and playback of ultrashort time-domain signals by making use of the phenomena of PHB and photon echoes in low-temperature doped organic polymers. In §2 we describe the photochemically accumulated stimulated photon echo (PASPE) and summarize the experimental results obtained in the picosecond domain. In §3 we discuss the possibility of achieving the ultimate temporal resolution and present experimental results on the storage and recall of femtosecond signals of duration less than 100 fs. In §4 experiments on probing spectral diffusion in an organic polymer by picosecond two-pulse photon echoes and

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photochemically accumulated echoes are discussed. Finally we consider some practical applications of PASPE-based data storage and processing.

2. Photochemically accumulated stimulated photon echo (PASPE) and picosecond time- and space domain holography

In ref. [18] we demonstrated experimentally that time-domain storage can be carried out in spectrally selective PHB media by sequence of pairs of coherent picosecond pulses, with the spectral width two orders of magnitude larger than the homogeneous hole width (0.05 cm^{-1}). As the duration of each of the applied burning pulses is less than the impurity-molecule phase relaxation time T_2, the complex shape of the resulting hole corresponds to the Fourier spectrum of the pulse pair, i.e. the width of the hole envelope is the reciprocal of the pulse width, whereas the fine spectral structure (containing up to 100 peaks) of the hole originating from the interference of the burning pulses is determined by the interval between the pulses (fig. 1).

We have also shown [22,23] that passing a single arbitrarily weak probe picosecond pulse through the sample with such a broad structured spectral hole in its inhomogeneous absorption spectrum will result in a delayed echo pulse that reproduces the burn-in-pulse shape (directly or temporally reversed). These delayed pulses were interpreted as the temporal response of the sample acting as a linear filter with a burned-in persistent ground state population grating. In terms of time-domain coherent phenomena, the physical nature

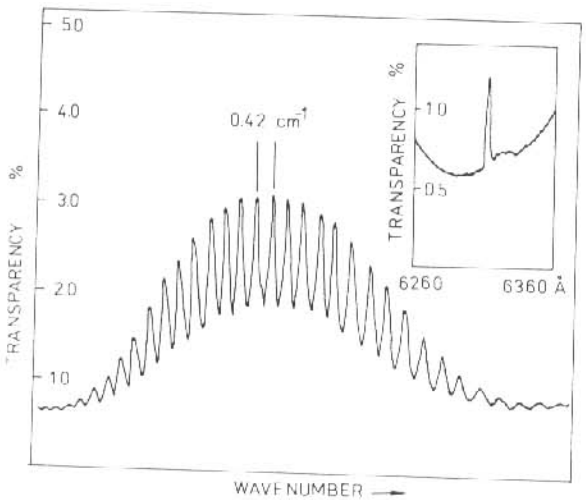

Fig. 1. Transparency spectrum measured after PHB exposure to the sequence of picosecond pulses. Insert – burned-in photochemical hole and its pseudophonon sideband (1 Å resolution), main-frame fine structure of the hole (0.075 cm^{-1} resolution).

of these coherent optical responses lies in the free-induction decay under weak excitation. The observed phenomenon was called a photochemically accumulated stimulated phonon echo (PASPE) because it is most closely related to the accumulated three-pulse stimulated photon echo [26]. However, PASPE displays several special features. First, whereas the conventional three-pulse stimulated echo can be recalled only within the relaxation time limits of light-induced transient frequency-domain population gratings, the lifetime of PASPE is determined by the very long lifetime (at least several hours, maybe years) of PHB photoproducts, and so the time available to recall the echo is practically unlimited. This allows the spectral gratings in PASPE to be accumulated with high contrast by repeating the excitation pulses many times which results in very high relative intensity echo signals. Second, because of the accumulation effect (it is not the intensity of the photoburning light but its dose that counts!), PASPE can be performed well even under modest excitation conditions. In a first approximation, a simple theory based on a linear dielectric susceptibility approach has been established [27]. Third, since only weak readout pulses are required, the replica of the signal, once it is stored, can be recalled from the sample many times before distortion appear.

As a result the spectrally selective PHB media may be considered as a special kind of light-sensitive material for information storage. The time-domain storage can, in this context, be described in terms of optical holography rather than in terms of nonlinear optics. Taking this simple approach we have performed model experiments demonstrating time-domain holographic storage and time reversal of complicated picosecond signals along with the storage and wavefront conjugation of holographic spatial images [25].

3. Storage and recall of femtosecond signals

In the previous experiments the temporal resolution of the time-domain storage has been limited by the duration of the laser pulses to about 2–3 ps. In principle, if one considers the reciprocal value of the inhomogeneous bandwidth of typical presently available polymeric PHB systems, a temporal resolution of about 0.1 ps should be feasible. Such a time resolution would permit optical data processing at rates up to 10^{12}–10^{13} bits per second and increase, simultaneously, the length of the optical code. This simple up-scaling is based, however, on the unproven assumptions that: (1) the hole-burning efficiency is almost constant across the total extension of the absorption band (some previous work has been done along these lines [28]); and that (2) nonlinear interactions between the different frequency components in the PHB medium are negligible.

To study these fundamental questions, experiments in Professor J. Kuhl's laboratory were performed in Stuttgart [29] using a colliding pulse mode-locked (CPM) dye ring laser which generated almost band-width limited pulses as short as 45 fs with a spectral band-width of 250 cm^{-1} at a repetition rate of 110 MHz. The CPM laser comprised a standard 4-prism configuration for intracavity dispersion compensation and delivered 60 mW average power for each of the two output beams. The pulse duration was adjusted to about 70 fs and the laser wavelength was tuned to 621 nm in order to achieve optimum overlap of the laser spectrum with the PHB absorption band of the samples. For the recording of holograms, samples were used which were similar to those of the earlier picosecond work and which consisted of 0.7 mm thick polystyrene plates doped with molecules of octaethyporphine (OEP) or protoporphyrine (PrP) at a concentration of 10^{-3}–10^{-4} mol/l. The maximum of the PHB active impurity absorption at low temperature ($T = 1.8$ K) occurred at 619 and 622 nm for the OEP-doped and PrP-doped sample, respectively. The FWHM of the absorption band amounts to 130 cm^{-1} for both types of samples.

The experimental arrangement was similar to that used in standard picosecond work and is described elsewhere [29]. Writing the hologram required an exposure level of 100 mJ/cm^2, corresponding to an exposure time of about 100 s for the CPM laser pulse energy of the order of 100 pJ or roughly 10^{10} writing pulse sequences.

The temporal analysis of the recalled signals was accomplished by measuring the cross-correlation profile using noncollinear sum frequency generation in a 0.7 mm-thick $LiIO_3$ crystal with an additional reference beam, split off from the CPM laser output.

Fig. 2 depicts cross-correlation traces corresponding to the PASPE signal recalled from a hologram in a PrP-doped sample with delays of 30 and 400 ps between

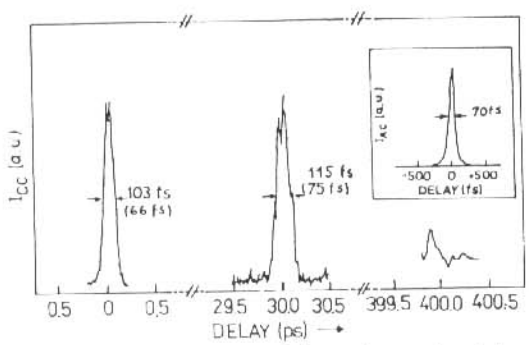

Fig. 2. Cross-correlation traces of the read-out pulses (at zero delay) and recalled pulses (at 30 and 400 ps delays) with a short reference pulse. The insert shows the autocorrelation trace of the reference pulse.

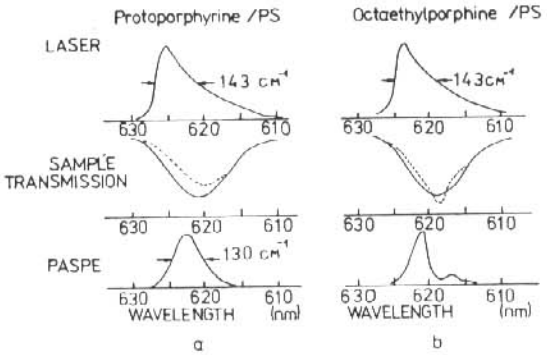

Fig. 3. Spectra of the laser pulse, PHB sample transmission, and the recalled PASPE signal. (a) PrP-doped sample; (b) OEP-doped sample.

the signal and reference pulses. The curve at zero time represents the cross correlation with the reading pulse. Compared to the original signal the images reproduced by PASPE exhibited about a 10–20% broadening. Assuming a $sech^2$ pulse shape, we obtained, after deconvolution, 75 fs duration for the PASPE signal, instead of the 66 fs observed for the original. Fig. 3(a) shows the spectra of the PASPE signal and the original together with the transmission of the sample. The maximum of the PASPE spectrum coincides with the absorption maximum and its width is equal to the 130 cm^{-1} width of the impurity absorption band. This width is roughly 10% narrower than the width of the original laser pulses and is in accordance with the broadening observed in the time domain. In fig. 3(b) the same spectra is presented but obtained with an OEP-doped sample. In this case the PASPE spectrum was distorted due to the formation of PHB photoproduct of OEP-molecules which absorbed light in the same spectral region. As a result of these spectral distortions the temporal shape of the PASPE signal was also distorted and broadened to about 200 fs.

These experiments indicate that efficient hole burning can be achieved over a broad inhomogeneous absorption band (at least in the PrP-doped system) and that no essential intermixing of spectral components takes place. The present experiment also achieves the ultimate temporal resolution, less than 100 fs, provided by the present storage media. Composite samples containing several overlapping absorption bands may be suggested as a way to further increase the temporal resolution.

The potential of PASPE for storing the detailed temporal structure of a femtosecond pulse is depicted in fig. 4. To produce a femtosecond pulsetrain, a 0.25 mm-thick solid quartz plate etalon was inserted into the input signal beam. This PASPE signal was obtained from a OEP-doped sample. The cross correlation shown

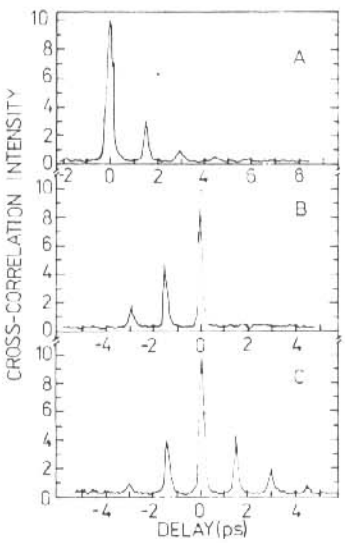

Fig. 4. Cross-correlation traces of the pulse trains, recalled from the burned-in PASPE holograms: (A) recorded with a leading reference pulse; (B) recorded with a trailing reference pulse; (C) recorded with a trailing reference pulse and read-out with a pulse train.

in fig. 4(a) proves the excellent reproduction of the temporal profile of the initial signal pulsetrain. Insertion of the etalon in the beam of leading pulses, i.e. reversing the delay between the signal and reference pulses during the burn-in exposure, allowed the temporally reversed replicas of the original signal to be recalled (fig. 4(b)). This last result provides also a possibility for time-domain correlation analysis of femtosecond optical signals previously demonstrated on nanosecond [30] and picosecond [31] timescales.

In conclusion, these experiments have demonstrated the potential of the PHB-based holographic techniques for time- and space-domain storage and the processing of optical data on femtosecond timescales.

4. Investigation of optical dephasing via two pulse photon echo and PASPE

Two pulse photon echoes (2PPE) yield information about optical dephasing (phase relaxation time T_2) during the short excited state lifetime (for organic molecules the energy relaxation time is typically $T_1 \sim 10^{-8}$ s). The study of homogeneous linewidths via PHB, and hence also via PASPE, gives basically the same information but averaged over a long interval (seconds) needed for the burning (accumulating) and detection of spectral holes.

The question of the correspondence between the homogeneous dephasing times obtained by these two different techniques has been discussed by several authors [12,32]. The concept of spectral diffusion [33] implies that the structural changes occurring during the slow PHB procedure should broaden the photochemical hole [34] and shorten the calculated value of T_2 as compared to the 'true' value obtained via 2PPE.

In [35] experimental results on 2PPE and PASPE measured under identical conditions for the system octaethylporphine in polystyrene matrix were reported. Actually PASPE provides the same data as PHB but through a photon-echo-type time-domain measurement [22]. In this experiment, performed in Professor Haarer's laboratory in Bayreuth, the ratio of the intensity decays of two different signals, 2PPE and PASPE, was directly obtained, eliminating possible systematic errors due to different experimental conditions in conventional PHB and photon echo experiments.

First experimental results obtained at 1.9 K showed that both echoes had a different decay behavior: whereas 2PPE decayed with a time constant of 1300 ps, the PASPE decayed with a shorter time constant of 600 ps. This difference in temporal behavior of both signals can be tentatively attributed to spectral diffusion and is in qualitative agreement with recent experiments on temperature cycling of photochemical holes [36].

In the same experiment it was also observed that 2PPE signals were capable of reproducing the spatial structure of the picosecond excitation pulses and that the repetition of the two pulse excitation (about 10 times) was enough to accumulate a high contrast permanent hologram. For the details of the experiments see ref. [35]).

5. Conclusions

In conclusion we present a list of experiments demonstrating further possible uses of PASPE and holographic time- and space-domain data storage:

(1) PHB filters and filter-holograms can be used to compensate time- and space-domain phase and amplitude distortions of ultrashort signals. Recovery of temporal profiles of picosecond signals distorted due to group velocity dispersion has been demonstrated [37].

(2) Associative optical memories [38] offer several useful features such as highly parallel data storage and address-ability of the data due to its content. PHB can supply an associative memory with a new (spectral) dimension which can be used as an extra parameter to discriminate between different portions of data as well as to increase the parallelism of the storage and readout processes. Experiments have been performed to model an associative recall scheme by picosecond time- and space-domain holograms [39].

(3) Recall and phase conjugation of arbitrarily polarised picosecond time–space signals has been demonstrated [40].

(4) Storage of multiple time–space images on a single PHB hologram plate provides a means for the interferometric analysis of ultrashort optical signals in the spatial and frequency domains [41]. Experiments have been carried out demonstrating the feasibility of holographic time–space interferometry on the picosecond timescale [42].

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