ADVANCED MATERIALS

Research News

Dye-Doped Polymer Films: From Supramolecular Photochemistry to the Molecular Computer

By Urs P. Wild,* Alexander Rebane, and Alois Renn

1. Introduction

Dye-doped polymers are new materials with exciting optical properties. At low temperatures the lowest electronic absorption bands of the dyes are strongly inhomogeneously broadened. Being sensitive to millions of different colors these materials allow for fascinating experiments in the field of optics. Applications in the frequency-domain range from high-density data storage[1] to holographic image storage.[2, 3] The new concept of "molecular computing"[4] is based on the spectroscopic properties of the dye-doped polymer film. The material allows for information storage as well as parallel processing of the recorded information. Complementary to the experiments performed in the frequency space, time domain applications have also been realized.

2. Supramolecular Photochemistry

In a low-temperature matrix, such as a frozen liquid or a polymer host, many of the traditional photochromic processes are sterically hindered in the rigid environment. There are, however, new "photochromic" processes to be observed at cryogenic temperatures which can be described through the concept of "supramolecular photochemistry". Placing a dye molecule in an amorphous material, for example, a polymer host, results in a specific molecular environment for each dye molecule. At high temperatures (300 K) averaging of the environment due to host dynamics or solvent relaxation leads to broad absorption bands. At very low temperatures (2 K), the host dynamics are frozen out and the wide spread in different microenvironments is reflected by inhomogeneously broadened bands.

The invention of tunable lasers led to new spectroscopic techniques based on energy selection, such as fluorescence line narrowing and spectral hole-burning.[1, 5] The resolution is now limited by the homogeneous linewidth and an improvement of experimental resolution by four to six orders of magnitude can be achieved. From a different perspective, such spectrally broad absorption structures consist of millions of different sets of absorbers selectively addressable by their transition energy into a million channels.

3. Frequency Domain Applications

Optical recording media are of growing interest and optical discs with storage densities of the order of 10^8 bit/cm^2 are already commercially available. In such storage media, data bits are either encoded as "real" holes or small domains of μm size with different magnetic properties. Lasers are used for recording and readout of the data and the minimum spot size, determining the storage density, is limited by the diffraction properties of the laser radiation. In order to further increase this storage capacity, shorter wavelengths have to be used or a different storage technology has to be applied. It would be easy to increase the storage density if we could use different colors for encoding bits. This can be easily done by means of spectral hole-burning. At very low temperatures the 10^6 different molecular subsets distinguishable "by color" within an inhomogeneously broadened band provide an additional dimension for the data storage. Thus, in every spot of the photochromic storage material we can store a large number of bits encoded as spectral holes in the frequency (color) space.[1]

Combining spectral hole burning and holography[6] is an alternative approach facilitating parallel recording and data access. Thousands of images have been stored within a single piece of polymer film, the storage capacity being still much larger.[7] In a typical set-up for holographic image storage[2] the beam of a tunable single mode dye laser is split into reference and object beams and a hologram is formed by exposing the sample to the interference pattern of the two beams. Images of size 50 × 50 mm are generated in the object beam through a liquid crystal TV and they are focused on the photocathode of a video camera. For retrieval, the sample is illuminated by the reference beam and the addressing of the individual images is performed by adjusting the corresponding parameter, "frequency" to the values used during recording. The image information is recorded with the camera

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and simultaneously, the integrated diffraction efficiency can be monitored by a photomultiplier.

The storage scheme reported here is a 3-dimensional one, using two spatial dimensions and the frequency (color). In Figure 1 a the integrated diffraction efficiency of ten images stored at different laser frequencies in a range of a single wavenumber (0.03 nm) is plotted as a function of the read-out frequency. Each of the peaks corresponds to a retrieved image. The signals have a spectral width of approximately 0.8 GHz and show a clear separation of the different images on the frequency axis. An electric field applied to the sample represents an alternative storage dimension,[8] or, in combination with the frequency, can be used to further increase the storage capacity.[9] The storage of 100 holograms in the same wavelength range, 1 cm^{-1}, as shown in Figure 1 b has been demonstrated. Being a 4-dimensional storage scheme, this experiment illustrates the increase of storage capacity by a factor of 10 when the electric field is used in addition to the frequency.[10] Typical images corresponding to the individual peaks and the spatial information recorded with the video camera are shown in Figure 2. Making use of the three-dimensional properties of holography even a five dimensional storage device is feasible (three spatial dimensions, frequency and electric field). Principally, it would be possible to include even an additional dimension: the angle of the reference and the object beam with respect to the sample. However, every dimension reduces the number of molecules per unit volume in this multidimensional space. Thus, the number of molecules and thus the signal to noise ratio finally becomes the limiting quantity.

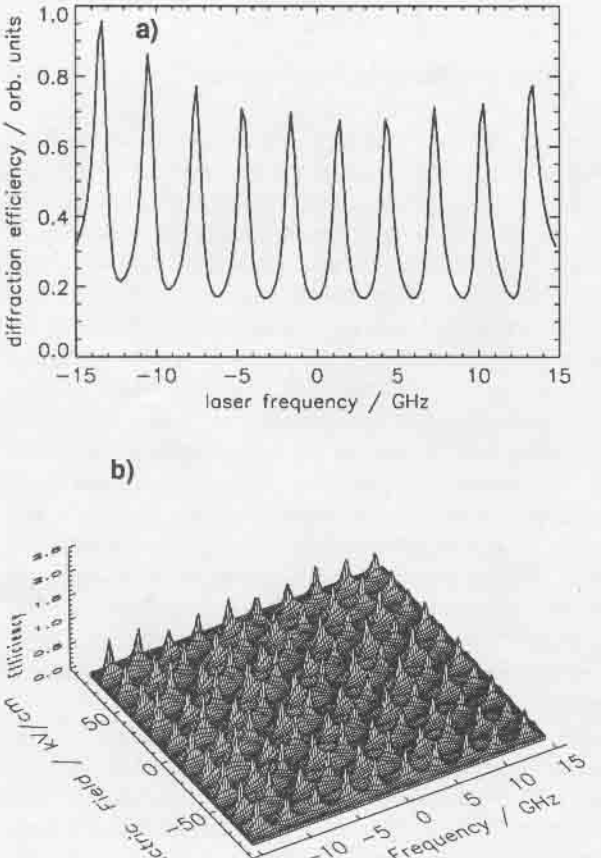

Fig. 1. Storage of 10 images within a wavenumber (30 GHz). The integrated diffraction efficiency is is plotted as a function of the laser frequency. Each of the peaks corresponds to a stored image.

Fig. 2. Images demonstrating the resolution and grey scale capabilities of the recording medium.

The frequency–electric field plane allows pairs of holograms to be stored in different arrangements, they can be burned either with a small frequency separation at the same field strength or at slightly different field strengths at the same burning frequency as shown in Figure 3. A molecular system showing a splitting of a spectral hole when an electric field is applied to the sample was used. The position of the maxima of the Stark components is indicated by the dashed lines. The images were recorded at different positions of the electric field, E_1 and E_2, at the laser frequency, ν. A horizontal bar was stored at the position (ν, E_1) and a vertical bar at (ν, E_2). The burning coordinates are drawn as filled circles. Both of the images can be reconstructed individually by adjusting the correct experimental parameters used during recording. The superposition of the images can be reconstructed at the frequency, ν' or ν'', and the electric field, $(E_1 + E_2)/2$. The results of the image superposition are plotted for a phase difference 0 and π. Constructive interference (phase 0) leads to an increase of the image intensity when the images overlap, the images are "added". Destructive interference (phase difference π) results in a "subtraction" of the images.[4, 11] Logical operations corresponding to "AND" or "XOR" functions can be derived when appropriate discrimination is applied. Whereas electronic processing of data is based on the properties of electrons in an electric field, the molecular processor introduced here relies on sprectroscopic properties—the behavior of molecular energy levels in an electric field. The storage device by itself becomes a parallel information processor—a molecular computer.

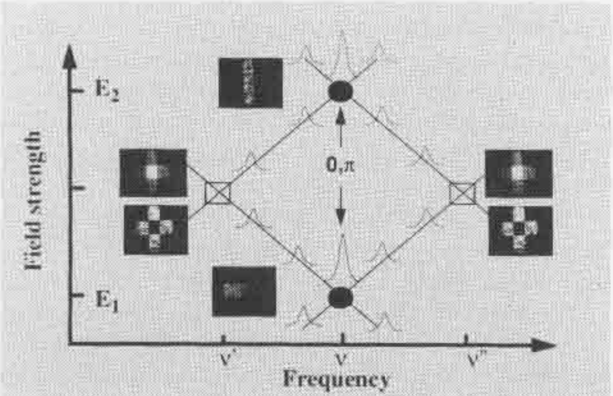

Fig. 3. Two images have been stored holographically in a plane defined by the laser frequency and the electric field at different values of the electric field (E_1, E_2). The recording parameters are indicated by circles. Due to the Stark splitting of the spectral holes the holograms are made to overlap in the regions indicated by the squares. The reconstructed images show the result of the superposition: constructive interference, when a phase difference of zero was adjusted, and destructive interference when a phase difference of π was chosen during the initial recording of the holograms.

4. Time Domain Applications

Time domain coherent optical responses of materials which are characterized by broad absorption bands actually comprising a quasi-continuous distribution of very narrow spectral lines (zero-phonon lines) can be approximated by the behavior of an ensemble of very ligthly damped harmonic resonators with each resonator tuned to a slighly different optical resonance frequency. In response to an impulse force, for example an ultrashort laser pulse applied upon a persistent spectral hole burning (PSHB) sample, each individual resonator starts to oscillate at its own resoncance frequency (zero-phonon transition frequency) with an initial amplitude given by the coupling strength between the external force and the resonator.

The oscillation amplitude decay constant, T_2, is given in our case by the electronic excitation dephasing time which is proportional to the inverse value of the homogeneous zero-phonon line width. The response of the whole ensemble of resonators, on the time scale of T_2 (for typical polymeric PSHB systems at 2 K $T_2 \sim 1-10$ ns), is a coherent superposition of the response amplitudes of the individual resonators. If we assume that the coupling for all the resonators is constant, then the total coherent response decays within a time which is much shorter than T_2 because the oscillations constituting the total response cover a broad interval of frequencies and interfere mutually destructively which makes the overall reaction to drop off to zero very fast. Ultimately, in the limit of a δ-like excitation pulse, the decay of the total response of an ensemble of zero-phonon lines is given by the inverse value of the inhomogeneous bandwidth which for polymeric systems is of the order of 10^{-13} s.[12]

On the other hand, if the coupling strengths within our resonator model could be varied from one frequency to another, there will be no complete destructive interference between the oscillations at different frequencies and the total response could stay "ringing" after the excitation for a time which is comparable to T_2. Specifically, if in the frequency domain the coupling strength parameter is modulated according to a periodic function, then a delayed "echo" response will occur.

In this context, persistent spectral hole burning can be viewed as a process which in effect allows the frequency dependent coupling strengths between the material and the external optical excitation to be altered in an almost arbitrary way (via decreasing the concentration of the resonant absorbers). The time-dependent response amplitude is given within the model of the harmonic oscillators by Fourier-transform of the function which describes the frequency dependence of the coupling strengths of the resonators. Similarly, the time domain response of PSHB material (i.e., the linear coherent optical recall induced by a low intensity ultrashort laser pulse) which contains a burned-in spectral absorption profile is given by the frequency domain distribution of the concentration of zero-phonon absorbers.

Coherent optical responses formed by means of tailoring of the spectral absorption profiles of PSHB media have several potential applications in holography and in coherent processing. Low-temperature polymers doped with organic dye molecules have been used for holographic storage and reproduction of pico- and subpicosecond signals, time- and space domain conjugation, correlation and associative recollection of ultrafast images, and also for storage of double-exposure picosecond time resolution holographic interferograms.[13]

An experimental example of the holographic recording of a picosecond time domain signal by using a polyvinylbutyral film doped with chlorin molecules at the temperature of 1 K is presented in Figures 4a–c. In the experiment[14] a train of

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picosecond data pulses (object beam) was produced when the output of a synchronously pumped picosecond dye laser was passed through a Fabry–Perot etalon. Every pulse at the input of the etalon (see Figs. 4a, b) produces a train of equally spaced pulses with intervals of 380 ps given by the separation betwen the mirrors of the etalon. The exponential decay of the data pulse train was determined by the reflectivity coefficient of the etalon mirrors.

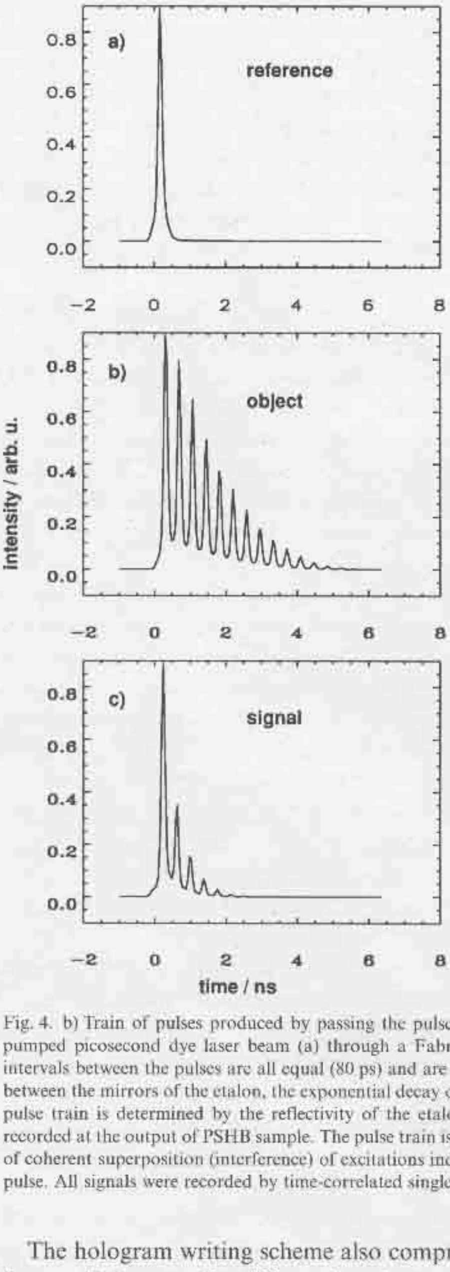

Fig. 4. b) Train of pulses produced by passing the pulse of a synchronously pumped picosecond dye laser beam (a) through a Fabry–Perot etalon. The intervals between the pulses are all equal (80 ps) and are given by the spacing between the mirrors of the etalon, the exponential decay of the envelope of the pulse train is determined by the reflectivity of the etalon mirrors. c) Signal recorded at the output of PSHB sample. The pulse train is produced as a result of coherent superposition (interference) of excitations induced by the probing pulse. All signals were recorded by time-correlated single-photon counting.

The hologram writing scheme also comprised a reference beam which was split off from the picosecond laser output and was directed at the storage sample at an angle of 5° with respect to the propagation direction of the signal beam. The reference beam pulses were adjusted to arrive some tens of picoseconds before the object beam data pulse train. To record the hologram the sample was illuminated with both the object and the reference beam for about 30 seconds with an average exposure of 20 mJ/cm^2. Afterwards, the object beam was blocked and only the attenuated reference beam was applied to illuminate the hologram. The picosecond signals were detected by using a time correlated single photon counting system with a time resolution of about 40 ps. The actual duration of the laser pulses was about 3 ps.

Figure 4c shows the temporal profile of the signal which was diffracted by the hologram in the object beam direction. Excellent reproduction of the temporal profile of the data pulse train (within the time resolution of the recording system) was observed. Note that the faster decay of the recalled pulse train as compared to the original object pulse train was due to the limited value of the dephasing time T_2 which, in the present experiment, was about 1 ns. The "echo" signals were recalled over more than one characteristic dephasing time which indicates a good time domain reproduction capability of the holograms stored in the dye-doped polymeric film.

Finally, we want to point out that recently[15] hole burning in a dye-doped polymeric system has been applied in an experiment on optical implementation of neural networks. The advantage of using hole burning optical recording materials in neural computing schemes is that it provides a possibility to combine the spatial domain parallel optical processing with the parallel access to the information stored in the frequency- and time dimensions. Hole burning gives, in addition to the spatial coordinates, extra degrees of freedom of the frequency and of the time coordinate which can be utilized for parallel processing of optical signals on an ultrafast time scale.

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