

# From supramolecular photochemistry to the molecular computer

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*A molecule and its noncovalently bonded solvent shell can be termed "supermolecule". It is assumed that its ground-state hypersurface consists of many shallow local minima which have approximately the same energy and correspond to different arrangements of the solvent shell. At cryogenic temperatures each supermolecule sits in one of the different minima. Supermolecules might show different physical properties, specifically a spread in their absorption frequencies. This property forms the basis for spectral hole-burning, a special type of photochemistry. Spectral hole-burning not only allows high resolution spectroscopy of matrix isolated organic molecules, it also opens a wide field of technical applications, especially with respect to frequency selective information storage. Recently more than 2000 images were stored in a single polymer film at different frequencies of the visible spectrum. More general this type of wavelength-selective photochemistry allows the storage of all the properties associated with an optical wave field, such as frequency, polarization, direction of propagation, intensity, and, in conjunction with holographic methods, also the phase. One might say that supermolecular photochemistry freezes in all the properties of light.*

*It is often claimed that the top end of the current generation of electronic computers will be replaced by optical computers having fast parallel computing capacities. A further development might be a molecular computer. The properties of light are transferred to photochemical changes in the material and the stored patterns can then be operated on by logical operations at will. The interaction of the molecular energy levels with an external electric field provides dynamical responses. A functional model of a molecular processor which is based on spectral hole-burning and on the spectroscopic properties of a dye doped polymer film is described here. Hole-burning materials can be used for image recording as well as for parallel processing of stored information.*

## 1. IMAGE STORAGE BY SPECTRAL HOLE-BURNING

A monochromic image can be considered as a two-dimensional distribution of a single dye. It is sufficient to know the concentration of the dye at let's say  $512 \times 512 = 0.25 \times 10^6$  grid points with an accuracy of about 8 bits (a resolution of 256 "gray" scales). Such a picture gives an image of good quality on a TV screen. The resolution of a standard 24 x 36 mm black and white film is still larger and reaches about  $10 \times 10^6$  picture elements or pixels. In a generalized fashion we can consider any two dimensional recording of a specific physical property as an image. We can talk of "charge" images, of "index of refraction" images or images defined by any other property.

In order to increase the information density which can be recorded in a single two-dimensional array, more than one "image" can be stored in the same recording material. A color film is the prototype of such a device. A color picture consists of a two-dimensional support which contains three different dyes with absorption maxima at 470 nm, 560 nm, and 660 nm. Three corresponds to the number of different color-sensitive receptors of the human eye. With the three fundamental colors all the existing colors in the visible range can be satisfactorily displayed. The eye lacks, however, the property of spectral resolution.

Clearly, a color film is a light-sensitive device, matched to the properties of the eye, displaying simultaneously three images in the basic colors. The information content with respect to a single color image is increased by a factor of three, nevertheless, the true spectral properties of the original are not faithfully reproduced. From the standpoint of spectroscopy there is no magic in the number three and one could envision a "super color-film" with more than three colors working on the same principles. Such a film provides much higher information storage density and would also allow the "spectral" properties of the origi-

nal scene to be stored in a faithful way. It is known that the trichromatic color vision system of the human eye is surpassed by some animals having a four or five color vision system. It has even been reported that the Manta Shrimp has as many as 10 spectral classes of photoreceptors.

To design a "super color-film" which can store 10 different images at a set of 10 distinct frequencies appears, from the standpoint of a chemist, straightforward. A possible concept of such a film is shown in fig 1. The chemist would be left with the problem of designing dyes which have absorption maxima clearly separated and comparable photochemical and photophysical properties. She/he would probably use a single chromophore, differently substituted, giving slightly different absorption maxima. For non visual purposes it would not be necessary that the range of absorption spans the whole visible absorption spectrum. In a first step, our focus is directed toward the property of high density information storage and for a faithful representation of the spectral properties of the original scene, the relationship between the original and the recorded image could be given by a suitable wavelength transformation. As far as we know, no "super color-film" has ever been designed according to these concepts.

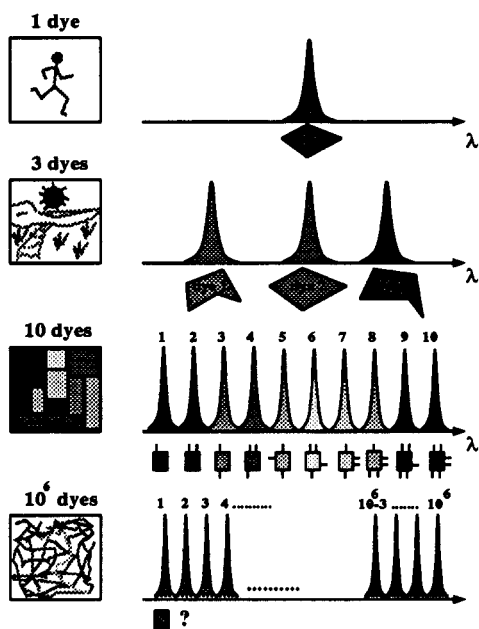


Fig. 1. Absorption spectra of dyes. *The number of dyes with a sharp absorption spectrum determine the number of images which can be stored in a single sheet of polymer. It is a challenge to try to "synthesize"  $10^6$  dyes which absorb at slightly different wavelengths and have similar photochemical and photophysical properties.*

Let us now ask if it is - at least in principle - possible to design a "super color-film" which has the potential to record chemically a million different images in the same frame. At first such an idea seems outrageous. From the standpoint of chemical synthesis it seems simply impossible to synthesize a set of a million compounds which absorb almost monochromatically at closely spaced positions in a given spectral range. To ask in addition for similar photochemical and photophysical properties seems almost absurd.

Indeed, we will show below that it is pretty simple to produce a system which has the potential of the "million color film" but one is almost hesitant to use the term "synthesis" for the simple two-step procedure necessary to realize such a system.

## 2. MOLECULAR AND SUPRAMOLECULAR PHOTOCHEMISTRY

The photochemical reaction which is used in the present work is a simple one and is shown in fig 2. In free base porphyrins the light induced proton transfer is a well known photoreaction. For the nonsymmetric molecule chlorin, initially absorbing at 635 nm, the absorption of the  $S_1 \leftarrow S_0$  of the phototautomer is shifted to 580 nm. This photoreaction is well protected and takes place independently of the molecular environment. No significant sterically hindrance is observed even at very low temperatures.

In low temperature media one has also to consider the solvent shell around the chromophore. Let us start with a molecular dynamics calculation of a "supermolecule" which is formed from the molecule chlorin as chromophore being surrounded by a set of water molecules which simulate the solvent shell. Molecular dynamics allows the study of the motion of the whole "supermolecule". The amount of energy put into the system determines its temperature. The calculation starts with a random arrangement of the solvent shell and the high temperature motion is followed for a given time interval. Then the amount of energy is reduced and a cooling process is initiated. The results of two such calculations are shown in fig 3. Every single calculation leads to a different microenvironment! The "solvent" molecules can be arranged

in many different ways around the chromophore. The energy surface of such a system consists of a flat envelope with a rough surface, a potential which can be compared to an "orange peel". The surface will contain an enormous number of local minima which are only very slightly different. Each of the minima can be associated at low temperature with a stable "supermolecule" if the potential barriers can not be crossed with the available thermal energy. Each of these "supermolecules" will be different and will have a specific geometry. Naturally, many properties of these supermolecules will be slightly different. Each supermolecule will have an individual shape, and what will be of greatest interest here, the interaction of each electronic state of the unperturbed chlorin with the "solvent" shell will be a very specific and individual one. The

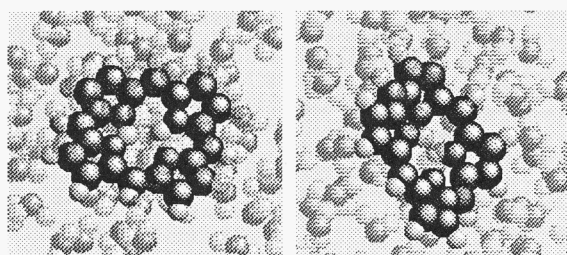
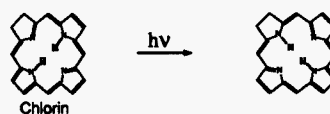


Fig 3. Two different supermolecules with a chlorin chromophore. *The solvent shell is shown as being transparent.*

#### Molecular Photochemistry



#### Supramolecular Photochemistry

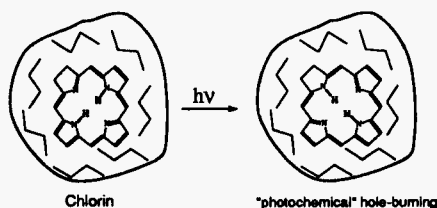


Fig 2. Molecular and supramolecular photochemistry.

number of possible supermolecules is almost infinitely large and an accidental realization of two identical molecules can be practically excluded. If we want to study a specific property, such as for instance the transition energy  $S_1 \leftarrow S_0$ , we have to classify the supermolecules according to this specific property. In order to determine the maximum number of classes which can be distinguished by looking at a single property we have to discuss the range this property can span and the resolution with which this property can be determined.

Very recently spectroscopic investigations of single molecules in solids have become feasible. Individual molecules of pentacene in a crystalline p-terphenyl host have been studied and the Stark effect on spectral lines arising from single molecules was investigated. In fig 4 the Stark shifts measured at a field strength of 29 kV/cm are shown for four individual supermolecules, A, B, C and D. Linear and quadratic contributions to the energy shifts were observed which varied from supermolecule to supermolecule [1] reflecting the spread of microenvironments even in a almost perfect molecular crystal.

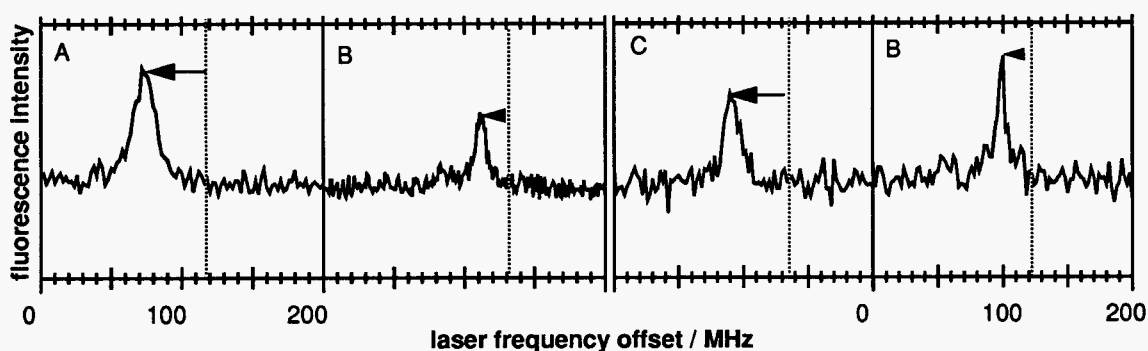


Fig 4. Single molecule spectroscopy. *Stark shifts at 29 kV/cm observed by excitation spectroscopy of single pentacene p-terphenyl supermolecules. The zero electric field strength positions of the lines are indicated by the dotted lines and the energy shifts by the arrows. Clearly visible are the different energy shifts for the different "supermolecules" A, B, C and D.*

### 3. INHOMOGENEOUS AND HOMOGENEOUS LINEWIDTH

The basic concepts of high resolution spectroscopy of a typical organic dye molecule in a host matrix are schematically shown in fig 5. Only the sharp features such as the zero-phonon lines are drawn. The effects of the much broader phonon-wings will not be considered here. The width of the vibrationless  $S_1 \leftarrow S_0$  transition is typically  $500 \text{ cm}^{-1}$  or in frequency units  $15'000 \text{ GHz}$ . All the individual supermolecules absorb within this energy range which is also called the inhomogeneous line width. The absorption profile of an individual supermolecule is, however, much smaller and its minimum width is fundamentally determined by the uncertainty principle. For a fluorescence lifetime of about  $10 \text{ ns}$  a value of  $0.0005 \text{ cm}^{-1}$  or  $15 \text{ MHz}$  is expected to be the lowest value. This width of an individual molecule is called the homogeneous width. Thus, ratios of the inhomogeneous/homogeneous width of up to  $10^6$  can result.

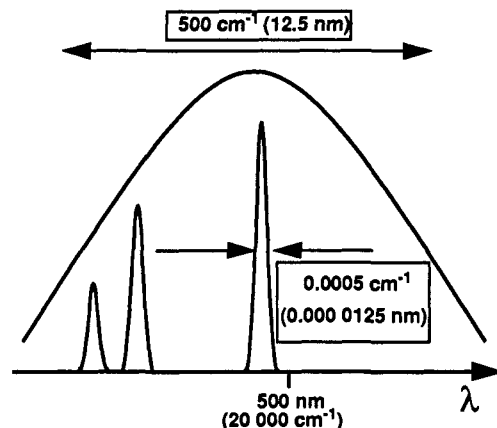


Fig 5. Inhomogeneous and homogeneous line broadening.

How do we synthesize such a multitude of distinguishable supermolecules? We simply follow the ideas outlined in the molecular dynamics calculation. First we dissolve the guest dye in a solvent or in a polymer matrix as a mono-disperse system. The guest molecule and a sufficiently sized solvent shell can be considered as a supermolecule. Upon cooling this solution to a few Kelvin each dye center will thus create such a unique supermolecule.

Modern techniques, such as fluorescence line narrowing and spectral hole-burning [2], allow one to measure the inhomogeneous and homogeneous bandwidth. Let us follow the synthesis of the supermolecules by total luminescence spectroscopy. In such spectra the emission intensity of

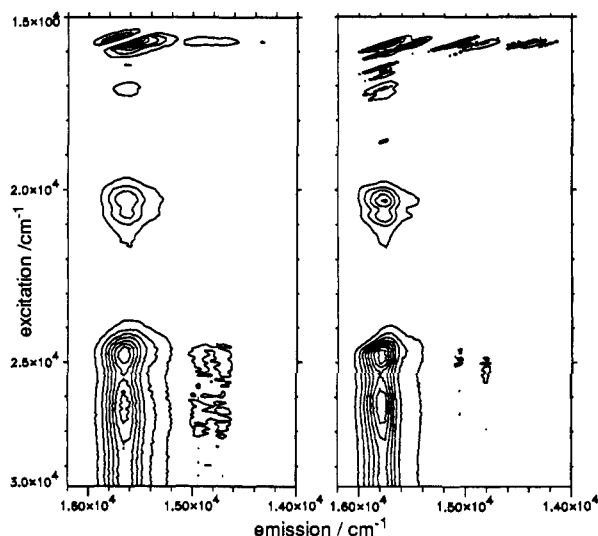


Fig 6. Total luminescence spectroscopy. *Excitation-emission spectra of chlorin in ethanol at room temperature and at 12 K.*

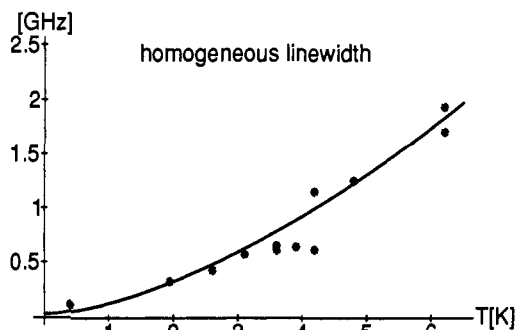


Fig 7. Temperature dependence of the homogeneous linewidth of chlorin in a polyvinylbutyral film.

a sample is recorded as a function of both the excitation and emission wavelength. In fig 6 the room and low temperature spectra of chlorin in ethanol are compared. At room temperature the total luminescence spectrum is characteristic of a pure compound. The shape of the emission spectra are almost independent of the excitation energy. At low temperature the pattern in the total luminescence spectrum changes dramatically within the range of the  $S_1 \leftarrow S_0$  transition. The spectrum contains fine structure and many features which lie in a diagonal direction. Such a spectrum is not expected for a single pure compound, consisting of molecules with identical properties. It can, however, easily be un-

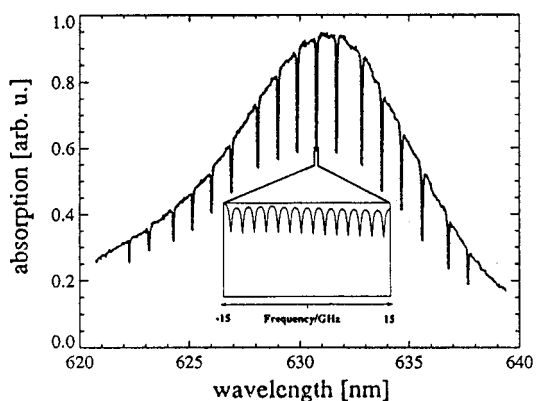


Fig 8. Spectral hole-burning. Holes burnt into the inhomogeneously broadened band are shown as recorded with "low" and "high" wavelength resolution techniques.

derstood in terms of a superposition of a set of total luminescence spectra of a large number of supermolecules. The inhomogeneous bandwidth, which depends on the interaction between the dye and its solvent surrounding, is almost independent of temperature, whereas the homogeneous bandwidth is extremely sensitive to the temperature. In fig 7 the homogeneous linewidth is shown as a function of temperature for chlorin in a polyvinylbutyral film [3]. Indeed, the expected ratio of about  $10^6$  is reached as the limit of 0 K is approached. The ratio is about 20 times smaller at a temperature of 1.8 K where experiments can be easily performed. Still, the multiplexing factor of  $20 \times 10^3$  is large! An example of wavelength selective photochemistry is shown in fig 8. The top spectrum shows obviously sharp holes burnt into the  $S_1 \leftarrow S_0$  absorption band of chlorin in a polyvinylbutyral film in the spectral range of 622-644 nm and using an UV-spectrometer for recording. Modern laser

techniques allow even much higher spectral resolution. In the inset a wavelength scan is shown which is expanded by a factor of more than 200 and which still allows 14 well resolved spectral holes to be recorded. Even though the basic feasibility of the wavelength-multiplexed optical storage by spectral hole-burning has been impressively demonstrated, there are still a series of problems to be solved before any technical applications can be attempted. To name a few:

First: The limiting resolution is only achieved at extremely low temperatures which are not easily reached. One has probably to compromise with a lower storage density at somewhat higher temperatures [4].

Second: The recording and read-out of the information occurs at the same wavelength. Each read-out leads to a partial erasing of the stored information. Systems which allow photon-gated hole-burning with two-photon chemistry might help to achieve almost unlimited read-out. The development of suitable photochemical systems is a challenge to photochemists.

Third: The recording time is determined by the molecular properties - triplet relaxation rates, photochemical quantum yields - leading to a recording time of the order of several seconds for a single frame. Increasing the writing power to the level where power broadening sets in might be the solution in conjunction with the design of appropriate supermolecules.

To summarize, from the standpoint of chemistry our original problem has been solved: Supermolecules can easily be "synthesized" and they absorb at a large number of spectrally distinguishable positions with a unique photochemical reaction. Supramolecular photochemistry is a useful concept and applications to wavelength-multiplexed image storage have already been performed. Even if it is somewhat inconvenient to work at low temperatures, this - we think - is a small price one has to pay for the synthesis of a million compounds!

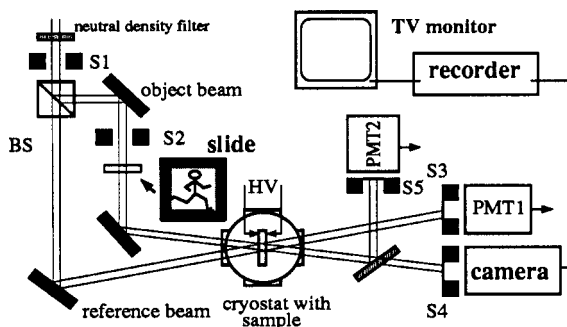


Fig 9. Experimental setup for holographic image storage. Recording of images is performed with object and reference beams. For reconstruction of the images the object beam is blocked and the individual images are addressed by adjusting the corresponding parameters "frequency" and "electric field".

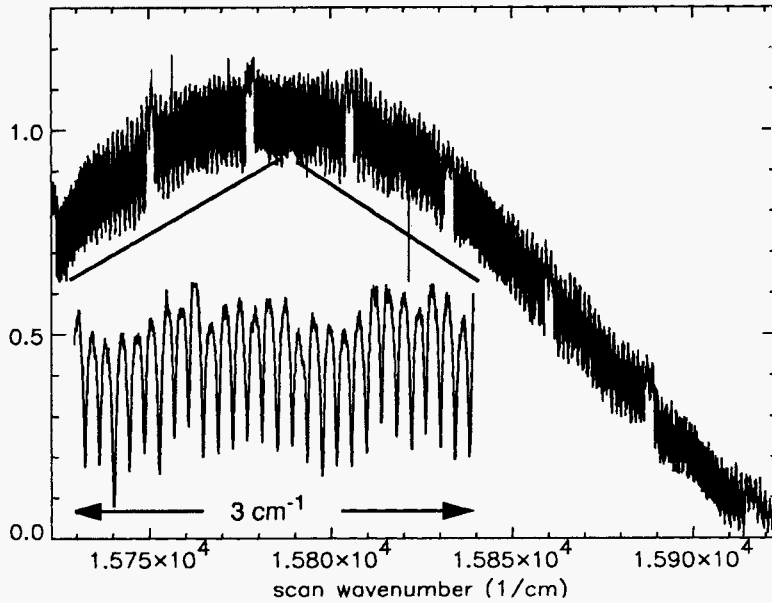


Fig 10. Holographic image storage. 2100 images are stored in a range of 7 nm. Each peak corresponds to an image.

#### 4. HOLOGRAPHIC IMAGE STORAGE

Combining spectral holeburning and holography [5] has led to frequency and electric field selective image storage [6,7,8] allowing the storage of thousands of images within a single piece of polymer film. In fig. 9 an experimental set-up for holographic image storage is shown. The beam of a tunable single mode dye laser is split into reference and object beams and the sample is exposed to the interference pattern of the two beams. Slides of 50x50 mm can be inserted into the object beam. The images are focussed on the photocathode of a video camera. During exposure ( $500\mu\text{J}/\text{cm}^2$ ) the detection system is protected by shutters ( $S_3, S_5$ ). For retrieval of the images the object shutter is closed and the image information is recorded with the camera. The integrated diffraction efficiency and the transmitted signal are monitored by the photomultipliers PM2 and PM1, respectively. The addressing of the individual images is performed by adjusting the corresponding parameters, "frequency" and "electric field", to the values used during recording. In fig. 10 the transmission spectrum of 2100 spectral holes stored at different laser frequencies is plotted as a function of the read-out frequency and gives a demonstration of the storage capacity of a dye doped polymer film at very low temperatures. Actually, each of the peaks corresponds to a stored image. The signals have a spectral width of approximately 0.8 GHz and the insert shows the clear separation of the different images on the frequency axis. A video movie consisting of 2100 images was stored in the polymer film corresponding to a sequence of 80 s duration. Five typical frames corresponding to individual holograms are shown in fig 11.

The electric field applied to the sample represents a further storage dimension and storage capacity can be increased even more [9].



Fig 11. Holographic Image storage. Five of the 2100 images stored in a single sheet of chlorin in polyvinylbutyral. It takes more than 80 sec to display the full sequence at the speed of a video movie.

## 5. LOCAL OPERATIONS WITH IMAGES

Pairs of holograms can be stored in the frequency - electric field plane in different arrangements. They can be burnt either with a small frequency separation at the same field strength or at slightly different field strengths at the same burning frequency. The separation of the burning coordinates is chosen such that the hole contours overlap within an accessible frequency and electric field range. The maxima of the Stark components are indicated as dashed lines and the burning coordinates are drawn as filled circles. At the burning coordinates the stored images can be reconstructed separately, however, at the regions where the dashed lines intersect, marked by squares, the phase properties of the holograms become

very important. In fig 12 the result of image superposition is shown. The images were recorded at different positions of the electric field,  $E_1$  and  $E_2$ , at the laser frequency,  $\nu$ . A horizontal bar was stored at the position  $(\nu, E_1)$  and a vertical bar at  $(\nu, E_2)$ . Both of the images can be reconstructed individually by ad-

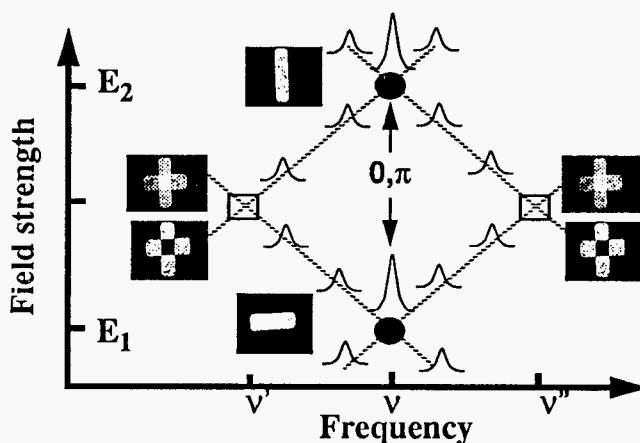


Fig 12. Logical operation with images. Two images have been stored holographically at different values of the electric field ( $E_1$ ,  $E_2$ ) in a plane defined by the laser frequency and the electric field. The recording positions are indicated by circles. Due to the Stark splitting of the spectral holes the holograms are made to overlap at the regions indicated by the squares. The reconstructed images show the result of the superposition: constructive interference, when a phase difference of zero was used and destructive interference with a phase difference  $\pi$ .

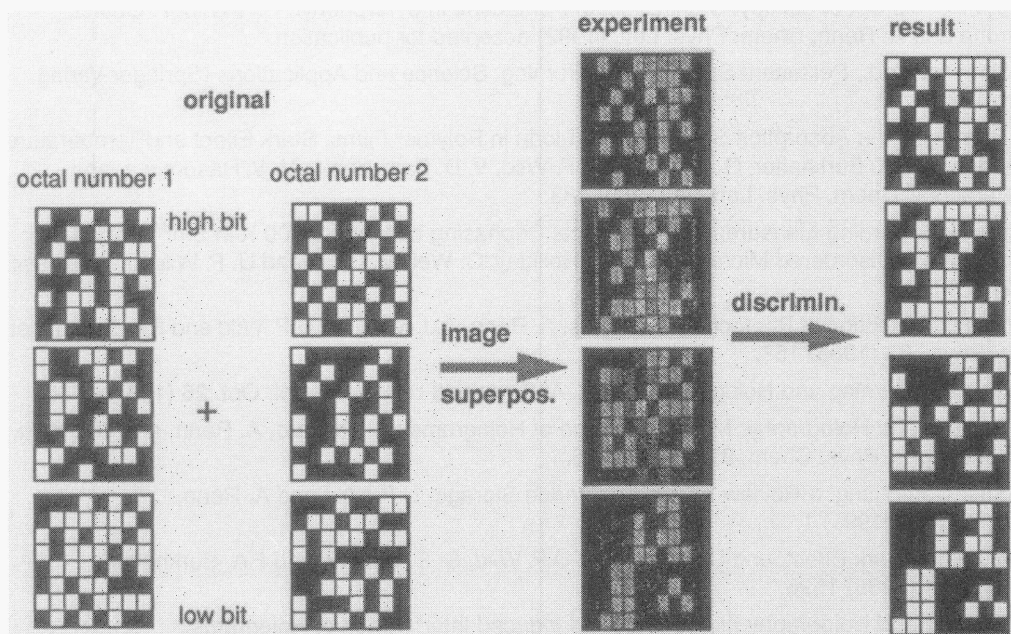


Fig 13 Parallel addition by means of spectral hole burning. Two arrays of octal numbers have been stored and subsequently processed using a sequence of "AND" and "XOR" operations.

justing the correct experimental parameters used during recording. The superposition of the images can be reconstructed at the frequency,  $\nu_1$  or  $\nu_2$ , and the electric field,  $(E_1+E_2)/2$ . The results of the image superposition are plotted for a phase difference 0 and  $\pi$ . Constructive interference (phase 0) leads to an increase of the image intensity when the images overlap, the images are added. Destructive interference (phase difference  $\pi$ ) results in a subtraction of the images [10,11]. Logical operations corresponding to "AND" or "XOR" functions can be derived when appropriate discrimination is applied. In fig 13 a parallel addition using the AND as well as the XOR operations is shown. Each of the 8x8 patterns represents one bit of an array of 64 octal numbers, each encoded by a specific position within the grids. Bright areas symbolize a digital "1", dark areas correspond to "0". The patterns have been transferred to the object beam by means of a liquid crystal display light modulator and were stored in the hole burning material as holograms. The superposition of two images has been performed in the material and the results have been obtained by appropriate thresholding subsequent to the read-out.

Whereas electronic processing of data is based on the properties of electrons in an electric field, the molecular processor introduced here relies on spectroscopic properties of molecules - the behavior of molecular energy levels in an electric field. The molecular system by itself becomes a parallel information processor - a molecular computer. Still being far away even of a prototype the basic properties of a molecular computer have been demonstrated.

We can summarize:

- a large amount of information can be stored in hole burning materials;
- holographic techniques are very helpful, allow parallel data storage and retrieval, provide the coherent properties for processing of the stored information;
- based on the energy shifts in an electric field logical operations can be performed in the material directly;
- the basic device consists of a photosensitive polymer cooled down to a few K. Such sheet of polymers can be easily produced and are by far the cheapest part of the apparatus;
- no moving parts are involved and nanostructures are directly produced by the holographic method.

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