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PHOTOCHROMISM: NON-LINEAR PICOSECOND KINETICS AND 3D COMPUTER MEMORY

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Abstract Spectroscopic and kinetic studies have made it possible to observe and assign all of the transient species and determine the formation and decay rates of some photochromic spiropyrans and naphthacenequinones. The non linear properties of these materials were utilized to design and operate a 3D optical memory system.

INTRODUCTION

As the need for more computational power is increased and the demand for high speed input and retrieval of information grows processors have become more effective and able to manipulate vast amounts of input data.[1] Continuing advances in silicon technology have improved computer technology to such high levels that memory capacity and I/O speed are the limiting factors for a gigabit/microsecond or nanosecond system. It is becoming therefore rather safe to predict that the component which may limit the practical limits of high speed computing is the memory. Because of the huge data storage requirements, the need for the parallel execution of tasks and necessity of a compact, very high capacity low cost memory is becoming mandatory.

It is not surprising, therefore, that a large concerted effort is being exerted to find means to store large amounts of data in small volumes. That such memories must also be able to operate with unusually large bandwidths and parallel access capabilities cannot be overemphasized. A possible means for a memory device which has the potential of providing all of these properties is a three dimensional storage system versus the two dimensional disks of today. Research efforts which may lead to 3D storage include persistent hole burning[2], phase holograms[3] and two photon processes, especially using organic materials.[4-8] In this paper we will present our research efforts in 3D storage by means of two photon absorption in photochromic spiropyrans and naphthacenequinones.

PERFORMING 3 DIMENSIONAL OPERATIONS

The theoretical bases for two-photon processes were established in the early 1930's.[9] It was shown that the probability for two-photon absorption may be expressed as a function of three parameters: line profile, transition probability for all possible two-photon processes and light intensity. For the purposes of this discussion the first two terms are not overly influential, however the third term shows that the transition probability is directly related to the square of the intensity. It will therefore be advantageous to utilize lasers emitting high intensity light, namely picosecond and subpicosecond pulses.

The experimental system used for the 3D-Memory and time resolved experiments has been described previously.[8] An active-passive Nd/YAG mode-locked picosecond laser emitting 30 ps pulses at a repetition rate of 20 Hz was the source of the intense laser light utilized for 3D writing and reading information by a two photon process. Wavelength tunability was achieved by using electrooptic crystals such as KDP and BBO, a dye laser, or utilizing the stimulated Raman generated in a cell of hydrogen, methane or other gases.

For the two photon experiments presented in this report the photon energy of each beam was smaller than the energy gap between the ground state S_o and the first allowed electronic level S_1, therefore such a beam of light propagates though the medium without observable absorption, Figure 1.

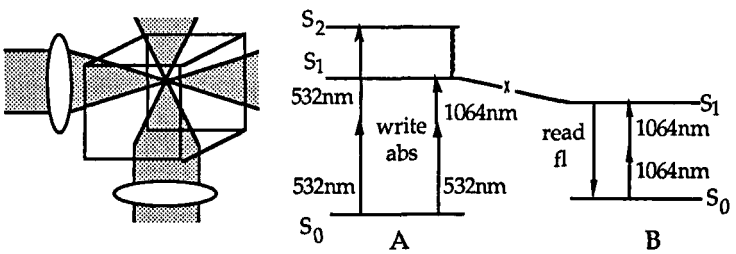


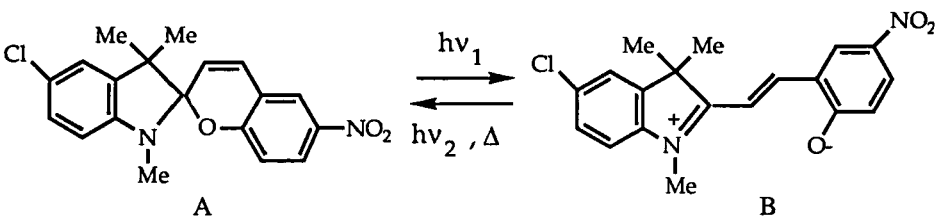
FIGURE 1 Writing and reading processes by two-photon absorption.

When two such beams are made to intersect at a point within the memory volume their effective energy is equal to the sum of the two photon energies $E_1 + E_2$ therefore absorption will occur if the $E_{S_1} - E_{S_0}$ energy gap is equal to or smaller than $E_1 + E_2$. At the point where the two beams interact, the absorption induces a physical and/or a chemical change in the absorbing molecule which distinguishes this 3D area from any other part of the memory volume which has not been excited. These two molecular

structures, i.e. the original and the one created by the two photon absorption, are subsequently utilized as the "write" and "read" forms of a 3D optical storage memory. For a successful completion of this type of writing and reading, the light beams which perform either function must also be capable of propagating through the medium and be absorbed only at preselected points within the memory volume where the two beams intersect, in time and space without any noticeable effect on other areas of the memory volume in which information may be written or not.

PHOTOCHROMIC SYSTEMS

Currently, information is stored in the form of binary code. The two states of the binary code, zero, 0 and one, 1, may be thought of as the photo-chemical changes which lead to two distinct structures of the particular molecular species used as the storage medium. Such an example is provided by the changes in molecular structure occurring in photochromic materials such as spiropyrans.[10] Spiropyran has two distinct forms: the original, stable, colorless form which is converted to the colored merocyanine form after excitation with UV light:



A B

These two forms which posses distinctly different structures and completely different absorption and emission spectra, Figure 2, become the "zero" and "one" in the binary computer format. Specifically the original form is designated as "zero" and the merocyanine form as "one". The procedure used to "read" the information written within the volume of the memory is similar to the "write" cycle except that the "read" form absorbs at longer wavelengths than the "write" form hence one or both laser beam wavelengths must also be longer than the ones used for writing. After the written molecule is excited by two photon absorption the molecule emits fluorescence with a lifetime of 5 ns and its spectrum is located at longer wavelength than the absorption of both the "write" and "read" forms, Figure 2. This fluorescence is detected by a photodiode or Charge Coupled Device (CCD) and is processed as 1 in the binary code.

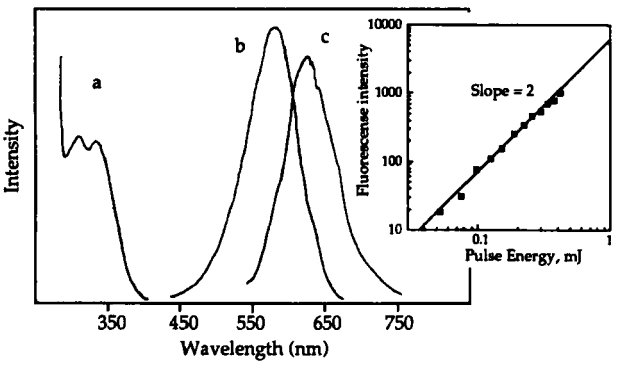


FIGURE 2 Absorption spectra of colorless (a), colored (b), and fluorescence of colored form (c) of spiropyran.

The proper selection of materials which provide widely separated spectra are extremely important because they assure that only the molecules that have been written will absorb this radiation and consequently induce fluorescence to be emitted only from that part of the written memory that is being read. The fluorescence emitted by the written form of SP is shown in Figure 2. That the process indeed proceeds by two photon absorption is verified by the slope of ~2 obtained from a log plot of the fluorescence intensity vs. laser energy (see insert). On the other hand, if the molecule has not been "written", fluorescence will not be observed because the "read" two-photon energy is not sufficient to populate the closed form of the original, unwritten, molecule, as shown in the energy level diagram of Figure 1 and in addition because form does not fluoresce.

The speed of the write process depends on the reaction kinetics of the molecule used. In the case of spiropyrans it is determined by the transformation of the closed spiro form to the open merocyanine. Picosecond transient absorption spectra of 6'-OCH_3-indolino-benzospiropyran in toluene reveal (Figure. 3) that right after excitation with a 25 ps, 355 nm laser pulse intermediates with absorption maxima in the region of 500-650 nm and 350-450 nm were formed. The absorption intensity of the long wavelength band continued to increase during the first 100 ps, and after that the spectrum remains unaltered for 15 ns.

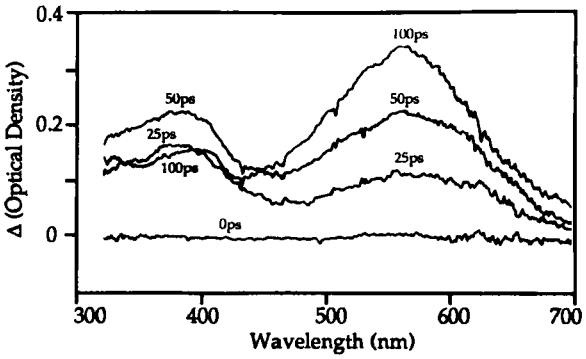


FIGURE 3 Transient absorption spectra of 6'-OCH_3-indolino-benzospiropyran in toluene solution.

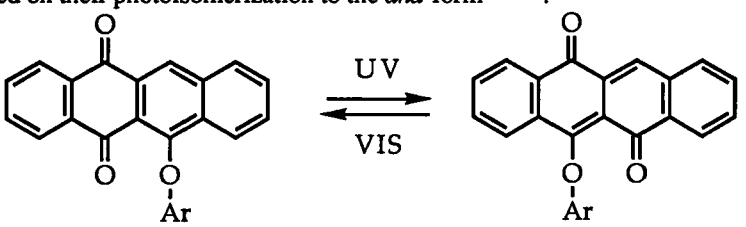
The short wavelength maximum also rises from 0 to 50 ps (practically during in the pulse duration) and after that drops down, at ~100 ps, to stable value. There is also a time associated red shift in short wavelength maximum from 380 nm at 25 ps, to 405 nm at 100 ps. Also a decrease in the ratio of the short wavelength maximum intensity to the long wavelength.

The spectra observed and kinetics derived from the experimental data can be explained by appearance of a cis-cisoid isomer[11] which is characterized by a transient absorption band with a maximum at ~380 nm. This transient isomer is formed immediately after excitation. After 100 ps it is completely transformed into the stable merocyanine isomer B which shows absorption maxima at 405 and 570 nm. From these data we may conclude that for photochromic spiropyrans the time required for the write process is approximately 100 ps. This is not for a single bit but rather for the simultaneous writing of several pages with Mbt content each.

In the case where written information has to be stored for long periods of time, the materials used for information storage should have both their "write" and "read" forms stable at room temperature. Usually the open forms of spiropyrans undergo reversible cyclization at room temperature and this process limits the long term storage application of these materials. The rate constant of the thermal reversibility strongly depends on the chemical structure of the molecule, solvent or polymer host. In most cases the hard polymer matrix extends the lifetime of the colored form compared to the liquid solution. The lifetime of the open form of 5-Cl-6'-NO_2-indolino-benzospiropyran was found to be ~ 10 sec in toluene solution while it was extended to about 10 hrs in a

matrix of polyhydroxyethyl methacrylate. It is also possible to stabilize the open form by decreasing the temperature because the cyclization process has an activation energy barrier of about 20 kcal/mol. We were able to store the written information spots for several months without any changes when the sample was kept at dry ice temperatures.

Other photochromic materials which have been studied in our laboratories and show promise for use as 3D Memory devices are naphthacenequinones which also exhibit coloration if excited by UV light. The photochemical mechanism and spectroscopy of photochromic naphthacenequinones has been studied much less than the spiropyrans. The synthesis[12,13] and luminescence spectra[14,15] of only a few photochromic naphthacenequinones have been published. Otherwise there is very little information regarding this interesting class of photoactive materials. It has been proposed however, that the photochromism of the photoactive naphthacenequinones is based on their photoisomerization to the *ana*-form[12-16]:



λ max ~ 380 nm ~ 480 nm

A B

A feature which distinguishes the naphthacenequinones from the spiropyrans is the absence of the back thermal reaction which is responsible for the instability of the colored form of the spiropyrans. This feature, namely the stability of both photochromic forms suggests that photochromic naphthacenequinones may be suitable for use as materials for optical devices and possibly to store, indefinitely, information in 3D optical memory devices.

The back reaction can be initiated photochemically by irradiation of the colored form at 420-520 nm. When the naphthacenequinones were exposed to extended irradiation, several hours, it was observed that they decompose to irreversible products. The rate of decomposition was found to be much faster in i-PrOH than in toluene solutions .

Solutions in toluene and in i-PrOH were irradiated with 355 nm 25 ps pulses. The time resolved absorption spectra, obtained in the 300-600 nm region, following excitation with a 355 nm pulse are shown in Figure 4a and b. The absorption band

located at ~ 380 nm decays with a fast rate during the first 75 ps, while the red-shifted secondary absorption band (λ_{max} ~ 500 nm) grows simultaneously with the same rate, as can be seen in Figure 4a.

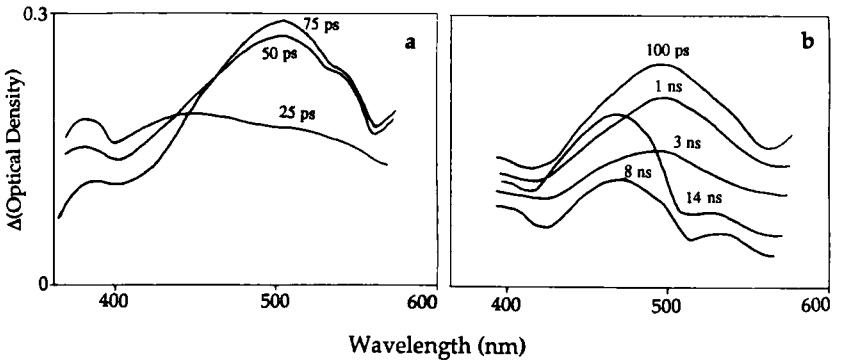


FIGURE 4 Transient absorption spectra of naphthacenequinone in toluene solution.

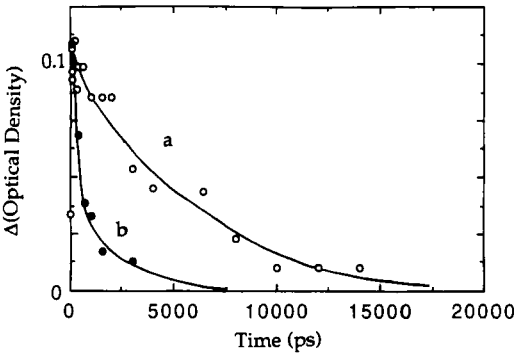


FIGURE 5 Naphthacenequinone transient kinetics (λ_{max} =500nm) (a) in toluene and (b) in i-PrOH solutions.

Figure 4b shows the change in the transient absorption spectrum at various time intervals between 0.1 and 14 ns.

When a solution of naphthacenequinone in i-PrOH was irradiated with 355 nm pulses, we observed that the decay rate of the secondary absorption band, λ_{max} ~ 500 nm, became much faster in comparison to the rate in toluene. These data are shown in Figure 5.

On the basis of our kinetic, time resolved specroscopic data and the information available in the literature, we have assigned the time constants we have measured to

specific processes and the transient spectra to specific intermediate species. These assignments allow us to propose a possible mechanism for the photochemical reactions leading to the formation of the *ana*-form of the naphthacenequinones studied.

The absorption spectrum of transient species which is characterized by an absorption band with a λ_{max} ~ 500 nm, coincides with that of the triplet-triplet absorption of the non-photochromic 5,12-naphthacene-quinone [13] in the same solvent. It is quite reasonable therefore to assume that the transient with λ_{max} ~ 500 nm is the triplet state of A, i.e. the initial quinoid form. This triplet state is capable of abstracting a hydrogen atom from i-PrOH because the decay of this triplet is accelerated in i-PrOH. The decay of the 380 nm band corresponds to the population decay of singlet, $(A)S_1$ to the triplet, $(A)T_1$ (λ_{max} =500 nm) which proceeds with a lifetime of 8.3×10^{-11} s and actually represents the intersystem crossing rate in A. The triplet state of A decays to the triplet state of the B form, $(B)T_1$, (λ_{max}=400 nm and 460 nm), with a lifetime of 8.3×10^{-9} s. The B form triplet decays into the final product B with a lifetime of 6.3×10^{-6} s.

Based on our kinetic data the most probable mechanism for the formation of the photochromic product, induced by the 355 nm excitation of naphthacenequinones may be represented as follows:

$$\begin{array}{lccccccc} & & & k_1=1.2\times10^{10} & & k_2=1.8\times10^{8} & & k_3=1.6\times10^{5} \\ A + h\nu & \longrightarrow & A(S_1) & \rightsquigarrow & A(T_1) & \rightsquigarrow & B(T_1) & \rightsquigarrow B \\ \lambda_{max} = & & 380\ nm & & 500\ nm & & 400, 460\ nm & 490\ nm \end{array}$$

It seems reasonable therefore, to suggest that the photoisomerization reaction of photochromic naphthacenequinones is an adiabatic photoreaction proceeding via the triplet state. Examples of similar types of adiabatic photoreactions for 1-(acyloxy)anthraquinones and for photoenolization have been reported previously.[17-20] The existence of triplet ketone intermediates suggests that H-atom abstraction could compete efficiently with the photochromic reactions.

CONCLUSION

We have presented a brief description of our studies on the spectroscopy, kinetics and systems for use in two photon 3D memory devices. The data shows that it is possible to write and read information in a 3D format.

It is evident however that much more research and in depth studies must be performed in order to understand the molecular characteristics of these materials, their non-linear properties and the parameters which influence the stability of the "write" and "read" forms before a practical device may be constructed. In addition, the background noise during the reading and writing processes and many optical and engineering requirements still need to be addressed. There are many difficulties encountered when one attempts to construct even a prototype 3D optical system. Our studies indicate that photochromic materials are promising candidates for utilization in 3D optical storage memory devices. We believe that continuing research on 3D memory devices will be eventually successful in providing the materials and systems with the required properties for a practical 3D memory.

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