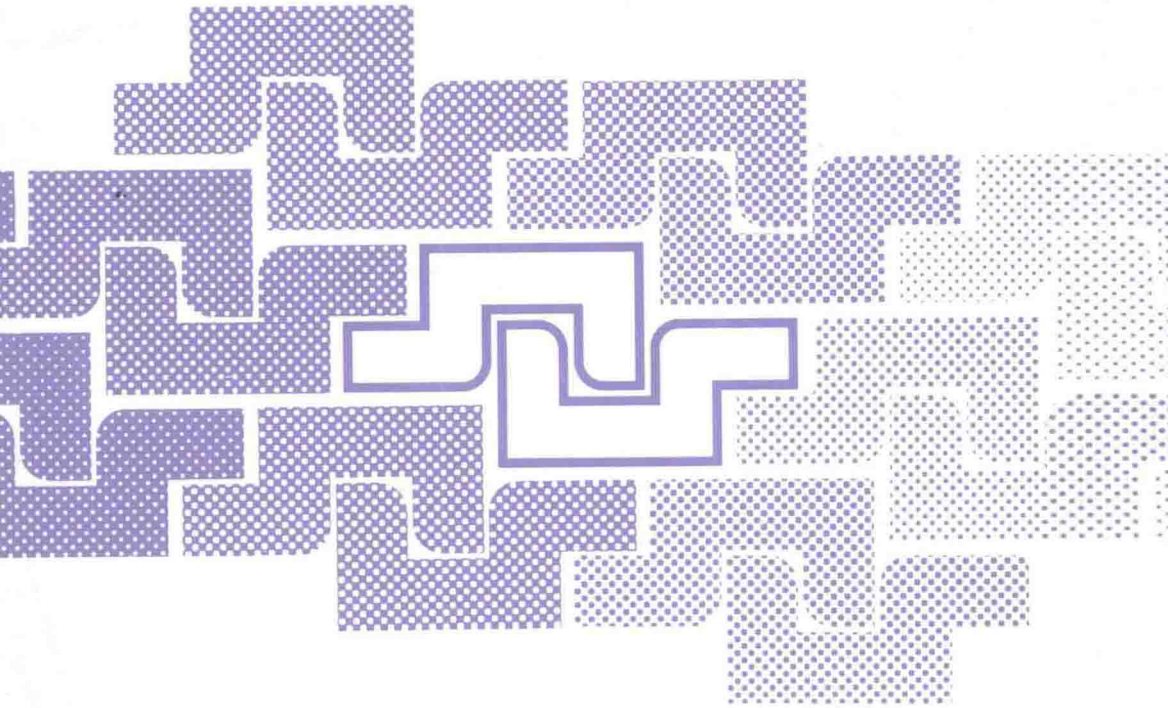

Multiphoton and Light Driven Multielectron Processes in Organics: New Phenomena, Materials and Applications

Edited by

François Kajzar and M. Vladimir Agranovich

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PREFACE

The book contains the proceedings of the NATO Advanced Research Workshop "Multiphoton and Light Driven Multielectron Processes. New Phenomena, Materials and Applications", held in the Royal Westminster hotel in Menton (France), August 26 - 31, 1999. The workshop consisted of plenary lectures, given by leading specialist in this field, shorter oral contributions , poster sessions and working groups meetings.

The contributions assembled in this volume give the present state of art and deal with the latest developments and discoveries with photoactive organic materials in view of their applications in photonic devices. Up to now the optical or electronic devices operate with atoms and molecules almost exclusively at fundamental states. With increasing high technology demand, new phenomena and new applications are envisaged involving the use of atoms and molecules at excited states. Written by leading specialists in the corresponding research fields the different, original, contributions address several actual and pertinent problems such as molecular design and synthesis of highly light sensitive molecules and phenomena connected with electron - photon interaction in organic molecules. In particular the topics treated are: nonlinear beam propagation, photorefractivity, multiphoton excitations and absorption, charge photogeneration and mobility, photo - and electroluminescence, photochromism and electrochromism, organic synthesis, material engineering and processing. Such device applications as optical power limiters, optical data storage, light emitting diodes, optical signal processing are described. The present proceedings are addressed not only to people active in this research field, but also to newcomers, graduate and postgraduate students in photonics science and technology. Three working groups were also organized on the subjects which were center of presentations and debates:
(i) multiphoton absorption : science and applications
(ii) organic electroluminescence
(iii) photochromism
The results of discussions are enclosed in this proceedings too as working group reports.

The organizers of this workshop are highly indebted to its main sponsor the NATO Scientific Affairs Division for a generous financial support. Thanks are also due to the other workshop sponsors: Service de Physique Electronique of Commissariat à l'Energie Atomique - LETI, France, Ministère de l'Education Nationale, de la Recherche et de la Technologie, France, Direction Général de l'Armement (DGA) and City of Menton. They would like also to thank the management of the Hotel Royal Westminster for the collaboration and very good working conditions offered to the participants of this workshop.

Thanks are also due to the members of the scientific committee: Prof. Paras N. Prasad and Prof. Carlo Taliani for useful suggestions and help in putting this workshop altogether. Special thanks are due to Dr. Malgorzata Helwig for the help in secretarial tasks and Dr. Pierre-Alain Chollet for his assistance in the organization of this meeting.

The workshop is dedicated to the memory of Dr. Bruce Reinhardt who played a key role in the organization of this meeting and who sadly passed away this spring. He was known not only as an excellent polymer chemist and scientist but also as a valuable friend and colleague. Dr. Reinhardt will be missed very much.

Saclay, December 1999

Vladimir M. Agranovich
François Kajzar
(workshop co-directors)

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NONLINEAR MATERIALS AND PROCESSES FOR ELECTRONIC DEVICES AND 3D OPTICAL STORAGE MEMORY APPLICATIONS

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1. Introduction

Many commercial and military applications generate enormous amounts of data which must be stored and be available for rapid parallel access and very fast processing. The major component which is expected to modulate the practical limits of high speed computing, will most probably be the memory. In addition 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 a practical necessity. However, at the present time, CD-ROMs and DVDs and even some of the most advanced optical storage systems, such as the 4.5 GB DVD, are not sufficient to fulfill some of the stringent demands imposed today by multimedia, medical and other applications. This method utilizes the inhomogeniously broadened zero phonon band as the storing medium. Storage media, including magnetic disk, electronic RAM and optical disks are fundamentally limited by their two-dimensional nature. The data capacity is proportional to the storage area divided by the minimum bit size. Three dimensional optical storage surmounts this limitation by extending the storage into the third dimension. They offer, therefore, an attractive possibility for highly parallel access, large storage capacity and high bandwidth memory. To circumvent this deficiency we have developed a high density fast read-out 3D optical storage memory system[1-4]. Our method relies on the non-linear absorption of two photons which causes changes in the structure and spectra of organic molecules.

Three-dimensional memories (3DM), because they extend the storage into the third dimension, make possible the achievement of higher capacities and shorter access times. Storing and retrieving, all of the data of a complete page composed of several megabits, simultaneously in contrast to the single bit access, dramatically increases the usable data rate. In addition, parallel-access optical memories are to a large extent compatible with the next generation of ultra-fast parallel hybrid, opto-electronic, computers which rely on optical interconnections and electronic processing. However, it is doubtful that a single 3D memory system may posses the optimum requirements for high speed computing, therefore tradeoffs between high storage density, access time and data transfer rates need be made. Holographic methods constitute another means for storing data in 3D.[5-7]

F. Kajzar and M.V. Agranovich (eds.), Multiphoton and Light Driven Multielectron Processes in Organics: New Phenomena, Materials and Applications, 1–19.

For optical memories, the density of stored information is dependent upon the reciprocal of the wavelength raised to the power of the dimension used to store information. For example, the information density which can be stored in a one-dimensional space, i.e.. tape, is proportionally 1/_ This relationship also suggests that the information storage density is much higher for UV rather than IR light. For a two dimensional memory, the maximum theoretical storage density for a 2D storage device which uses light at 200 nm is 2.5 x 10^9 bits/cm^2 . In the case of a 3D storage memory which utilizes the same wavelength of light, the maximum density which can be stored per cm^3 is 1.2 x 10^{14} bits/cm^3. This represents an increase of 10^5 bits/cm^3.

The two states of the binary code, 0 and 1, are formed by the photochemical changes which lead to two distinct structures of the molecular species used as the storage medium. The stored information is read by illuminating the written bits with either one photon of the energy necessary to induce fluorescence, or by intersecting two optical beams at that point. The energy of each photon is less than the energy gap between the ground and first allowed excited state, the sum of the energies of the two excited states is, however, larger than the energy needed to excite the molecule. In the case of the photochromic organic materials to be described[8], the information is stored in the form of binary code. The non-linear, i.e. two photon virtual absorption, makes possible the storage of data inside the volume of the 3D device and in fact enables the selection of any arbitrary location within the device volume to where data is to be written. By this means, two-photon 3-D memory devices with over 100 2D planes, within an 8 mm cube, have been stored, at a distance of a few microns between planes.

These optical storage memory devices have the capability of the parallel access needed to accommodate the demands of today's technologies. We expect that by this means it will be possible to construct an optical memory system which may provide a data capacity of 1 Gbit/cm^3 with a 10 ns-1 ms access.

2. Two-photon Processes

The theoretical bases for two-photon processes were established in the early 1930's[9]. It was shown that the probability for a two-photon transition may be expressed as a function of three parameters: line profile, transition probability fit for all possible two-photon processes (see Fig. 1 for a schematic representation of four such processes), and light intensity. These factors are related to P_{if} by:

$$P_{if} \cong \frac{\gamma_{if}}{\left[w_{if} - w_1 - w_2 - \bar{\nu} \bullet \left(\bar{K}_1 + \bar{K}_2 \right) \right]^2 + \left(\gamma_{if/2} \right)^2} \bullet \left| \sum_k \frac{\bar{R}_{ik} \bullet \bar{e}_1 \bullet \bar{R}_{kf} \bullet \bar{e}_2}{\left(w_{ki} - w_1 - \bar{K}_1 \bullet \bar{\nu} \right)} + \frac{\bar{R}_{ik} \bullet \bar{e}_2 \bullet \bar{R}_{kf} \bullet \bar{e}_1}{\left(w_{ki} - w_2 - \bar{K}_2 \bullet \bar{\nu} \right)} \right|^2 \bullet I_1 I_2 \qquad (1)$$

According to this postulate, two photon transitions may also allow for the population of molecular levels which are forbidden for one-photon processes such as g→g and u→u in contrast to the g→u and u→g transitions which are allowed for one-photon processes. In practice, however, when one is concerned with large molecules in condensed media, the

density of the states is very large, the levels broadened by collisions and the laser line bandwidth large enough to accommodate many levels. Therefore, there is little, if any, difference in the energy between the levels observed experimentally by one or two photon transitions in the large molecular entities used under the experimental conditions of the experiments presented here. The above expression is composed of three factors: the first factor describes the spectral profile of a two-photon transition. It corresponds to a single-photon transition at a center frequency $\omega_{if} = \omega_1 + \omega_2 + \underline{v}(\underline{k}_1 + \underline{k}_2)$ with a homogeneous width γ_{if}. If both light waves are parallel, the Doppler width which is proportional to $|\underline{k}_1 + \underline{k}_2|$ becomes maximum. For $\underline{k}_1 = \underline{k}_2$ the Doppler broadening vanishes and we obtain a pure Lorentzian line. The second factor describes the transition probability for the two-photon transition. This is the sum of products of matrix elements $R_{ik}R_{kf}$ for transitions between the initial state i and intermediate molecular levels k and between these levels k and the final state f. The sum extends over all molecular levels. Often a "virtual level" is introduced to describe the two-photon transition by a symbolic two-step transition $E_i \rightarrow E_v \rightarrow E_f$. Since the two possibilities

a) $E_i + \hbar\omega_1 \rightarrow E_v \;,\; E_v + \hbar\omega_2 \rightarrow E_f$ (first term) **(2)**

b) $E_i + \hbar\omega_2 \rightarrow E_v \;,\; E_v + \hbar\omega_1 \rightarrow E_f$ (second term) **(3)**

lead to the same observable result, the excitation of the real level E_f, the total transition probability for $E_i \rightarrow E_f$ is equal to the square of the sum of both probability amplitudes.

The frequencies of ω_1 and ω_2 can be selected in such a way that the virtual level is close to a real molecular state. This greatly enhances the transition probability and it is therefore generally advantageous to populate the final level E_f by means of two different energy photons with $\omega_1 + \omega_2 = (E_f - E_i)/\hbar$ rather than by two equal photons. The third factor shows that the transition probability depends upon the product of the intensities I_1, I_2. In the case where the photons are of the same wavelength, then the transition probability depends upon I^2. It will therefore be advantageous to utilize lasers emitting high intensity light such as picosecond and subpicosecond pulses. For practical use there is a trade off between very short pulses with very high intensity, i.e. femtosecond pulses, but small photon flux and wider pulses, i.e. picosecond pulses, and large number of photons per pulse. Also the damage cause by high intensities is a factor when selecting a laser pulse for optical devises. Organic materials are, in general, damages at lower power densities than inorganic materials.

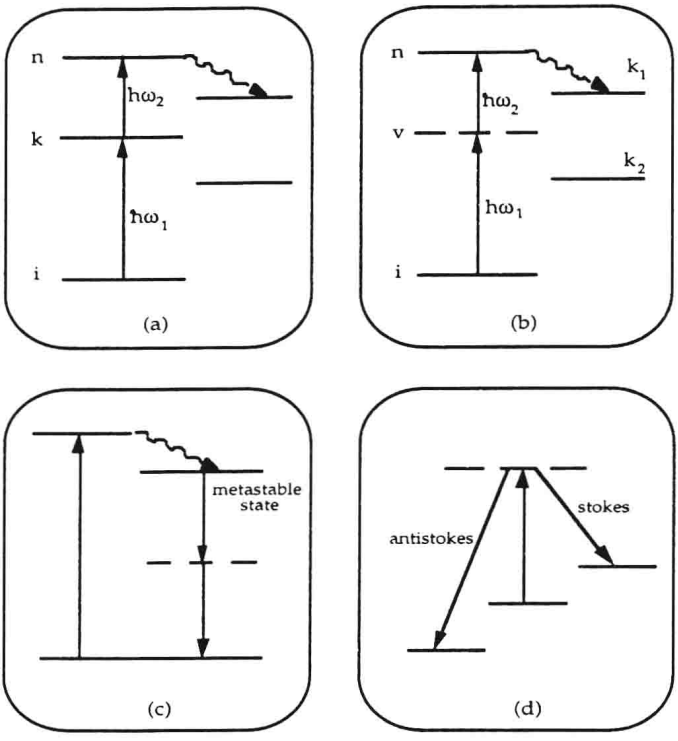


Figure 1. Two photon processes

Four possible processes which may operate by means of two photon excitation are shown in Fig. 1. The first corresponds to a stepwise or sequential two photon absorption process (Fig. 1a) in which each photon absorption is allowed (i.e., two allowed one- photon sequential processes). Even though the final state reached by the two photons may be the same as by the simultaneous absorption of two photons via a virtual level (Fig. 4b) the effect towards a volume memory is overwhelmingly different. In the case of the sequential two photon process, the first photon absorption takes place on a real level - by definition - by a molecule, or atom, which has an allowed state at that energy. It will therefore be absorbed by the first such molecule or atom on its path which is usually located on the surface. Subsequently, if sufficient photon intensity is available, several possibilities exist: a) the photons from the same pulse may be absorbed by the same molecule inducing a transition to higher electronic states; b) populate an additional molecule further, inside the volume; c) after energy decay, populate a metastable level such as a triplet. The second photon will encounter the same fate, namely it will be absorbed preferentially by the molecules first encountered in its path which are the molecules at or near the surface, then with decreasing intensity, this beam will propagate and be absorbed by molecules further inside the volume. This second sequential beam may be delayed by a time interval equal to or slightly longer than the time required by the first excited state to decay to a low lying

metastable level. If the wavelength of this second beam is adjusted to be longer (smaller in energy) than the energy gap between the ground state and the first allowed state, (wavelength of the first beam) then the second light beam will populate only upper electronic states of the excited metastable level. This is an interesting and important scientific aspect of nonlinear spectroscopy and photophysics, however, it does not result in a true 3D volume memory. This is because, as we mentioned above, there is no means possible by which light can interact preferentially with molecules located inside a volume without interacting first with at least equal efficiency with molecules residing on the surface.

The second scheme for two photon absorption (Fig.1b) makes it possible to excite preferentially, molecules inside a volume in preference to the surface. This may be achieved because the wavelength of each beam is longer, has less energy than the energy gap between the ground state and first allowed electronic level. However, if two beams are used the energy sum of the two laser photons must be equal to or larger than the energy gap of the transition. It is also important to note that there is no real level at the wavelength of either beam, therefore neither beam can be absorbed alone by a one photon mechanism. When two such photons collide within the volume, absorption occurs only within the volume and size defined by the width of the pulses. This is in sharp contrast to the sequential two photon process, fig.1, where the first step involves the absorption of a single photon by a real spectroscopic level and hence is not capable of preferential volume storage. The principal difference in the two cases as far as their suitability for 3D volume memory is concerned, is that the virtual case avails itself to writing and reading in any place within the 3D volume while the sequential excitation is restricted in writing and reading first at the surface. The other two processes shown in Fig. 4 show the possibility of two photon emission, (Fig. 1c) after single photon excitation and the Raman effect (Fig. 1d). Neither of these last two cases are relevant to the topic under discussion and will not be discussed further. We must note at this point that the same physics holds for all two photon transitions regardless of the sequence by which they take place let it be either via sequential steps between real levels or via virtual state interaction. In the case presented here we utilized two-photon process, the photon energy of each beam was smaller than the energy gap between the ground state S_0 and the first allowed electronic level S_1, therefore such a beam of light propagates though the medium without observable 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 which will distinguish this microvolume 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 maybe written or not.

3. Two Photon 3D Storage Method

Three dimensional storage memory, using two photon excitation, was first proposed by Parthenopoulos and Rentzepis in 1989[11] and Hunter, Esener, Dvornikov and Rentzepis(12) in 1991. This data storage approach has been under development at UCI ,UCSD and Call/Recall Inc. since 1989. Other research groups which have made significant contribution to this field include P.Prassad[12] and R. Birge[12]. The goal of these efforts is the development of a monolithic terabit capacity 3D storage memory devise. Call/Recall Inc. developed and built a prototype consisting of over 100 planes with 100Mgb/2D plane. The physical process at the heart of the 3DM is a molecular change caused by a two photon optical absorption, as shown in Fig. 2. A molecule in the ground (unwritten) state is excited to a higher energy state by simultaneous absorption of two distinct photons, one red (1064 nm) and one green (532 nm), or two green photons The energy required to reach the excited state is greater than either photon alone can provide, but when two photons interact simultaneously, at a preselected point within the volume, they are absorbed resulting in a bond dissociation. The molecular geometry (structure) is changed into a new, written, molecule with an entirely different absorption spectrum., as shown in Fig. 2. The written molecule, in this example, absorbs two 1064 nm photons, or one green photon and fluoresces in the red region, ~ 700 nm. Accessing of the stored information is achieved, either by the detection of the written' bit fluorescence, absorption, index of refraction or any other property which is preeminent, and can be detected, in either the written or the original form of the molecule

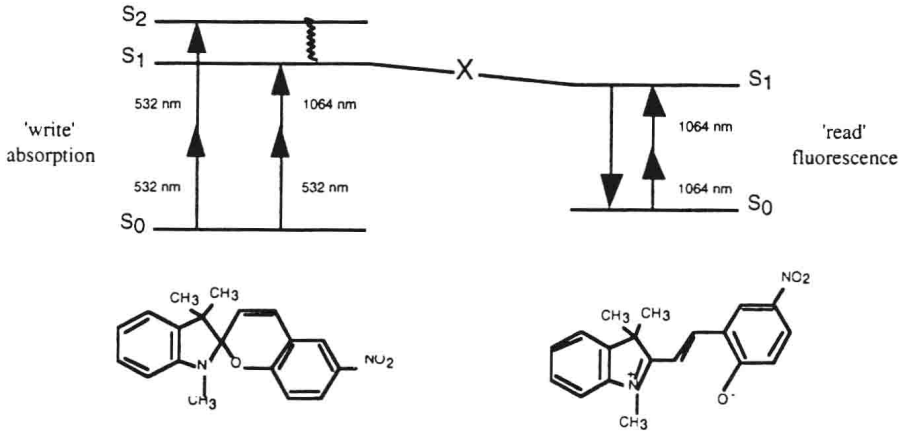


Figure 2. Two photon write (left) and readout (right) processes.

The basic importance of the two photon writing is its unique ability to select and write or read a single bit anywhere within a three-dimensional volume by simply intersecting two optical beams at that point. The capacity of such a bit-oriented volume memory is fundamentally limited only by the memory volume divided by the optical spatial resolution.

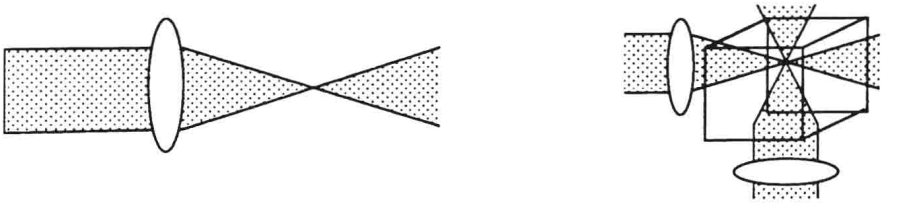


Figure 3. Paths for two photon absorption: : a) confocal: b, c) counter propagating and orthogonal

4. Materials

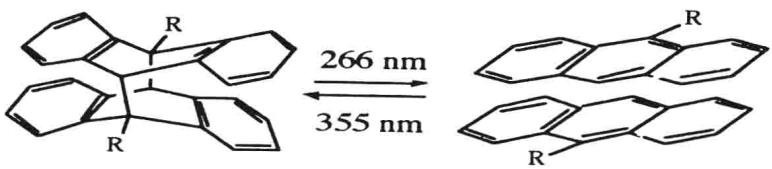
Organic photochromic materials have been dispersed in transparent polymer matrices and glasses to form a homogenious, monolythic, block or disk, which upon excitation with two photons allow for storing and accessing information in 3D format. In the case where the organic materials are used for storing information, the two states of the binary code, 0 and 1, are formed by the photochemical changes, which lead to two distinct structures of the molecular species used as the storage medium. Such an example, which is the first ever used in 3D memories, is provided by the changes in molecular structure occurring in photochromic materials such as spirobenzopyrans after the simultaneous absorption of two photons. The two molecular structures, i.e. the original and the one created by the two photon absorption, become in practice the "write" and "read" forms of a 3D optical storage memory.

The procedure used to access the information written within the volume of the memory is similar to the "store" process except that the "reading" form absorbs at longer wavelengths than the "write" form. Under these conditions reading is achieved by the use of longer wavelengths than writing, therefore no writing takes place while reading. After the written molecule is excited it emits fluorescence. The fluorescence spectrum is located at longer wavelengths than the absorption of both the write and read forms. The emission was detected by a photodiode or Charge Coupled Device (CCD) and processed as 1 in the binary code. The proper selection of materials which provide widely separated spectra is extremely important because it assures that only one of the two forms, usually designated as the "written" form, emit light and only from the area of the written memory that is being excited. The spirobenzospirans, although demonstrated very convincintly the two photon 3D method for storage, display and microscopy they were found to be unsuitable for use in practical storage devices because they do not meet some of the strigent requirements imposed. The major one is thermal stability. Similar difficulties have been found for the vast majority of organic compounds synthesized and proposed by several investigators. High two photon absorption crosssection is, undoubdetly, a very desired property, yet several of the molecules proposed as excellent choices for 3D two photon application, because of their very high two photon absorption, we found them to be inadequate because of their poor laser power stability or low read/write fatigue and poor fluorescence quantum yield. In addition many of the very high two photon cross section have weak absorption in the one photon wavelength. Even a very weak one photon absorption is sufficient to overshadow a very high two photon cross section.

There is a large number of materials, that change their molecular structure and spectroscopic properties after illumination with light and have relatively high two photon crosssection. However, to be suitable for use in the 3D memory devices the materials should possess certain characteristics, which strongly limit the number of possible candidates:

1) High two-photon absorption cross-section to perform efficient writing of information.
2) The photochemical reaction should have a high conversion yield.
3) One of the forms should emit fluorescence with high quantum yield.
4) Both write and read forms of the material must be stable between- 55 C and + 55 C.
5) High fatigue resistance to perform more than 10^6 write-read-erase cycles.
6) Wide absorption and emission spectra separation to minimize the crosstalk between thewritten Bits.
7) Capability for non-destructible readout process.
8) Withstand high laser power.

We have found a number of materials which may be used with some success for optical storage and access of information and which satisfy a large fraction if not all of the mendatory characteristics. One type of molecular photochromism, which may be used in 3D memory devices, is light induced dimer - monomer transformation[14]. The process of reversible photodimerization and photodissociation of polycyclic aromatic hydrocarbons, such as anthracene and its derivatives, may be used for developing photochromic materials for optical memory,and other electronic devices:



The dissociation of the dimer results in the regeneration of a conjugated double bond system and consequently a red shift of the absorption band of the dimer. The monomer has its long wavelength absorption band in the 300-400 nm region, while the dimer is blue shifted and has practically no absorption at wavelengths longer than 300 nm. The monomer was found to emit with a fluorescence quantum efficiency of approximately 30%, while the dimers are practically void of any fluorescence. The fluorescence spectrum of anthracene dispersed in PMMA is between 380-450 nm. One advantage of the dimer-monomer based 3D storage systems is that both dimer and monomer forms are highly stable at room temperature, unlike the spiropyrans, where the written state reverts spontaneously, within a few hours at room temperature, into the unwritten state and consequently the information previously stored is erased. In addition, the high absorption cross-section and high quantum efficiency of fluorescence suggest that this molecular system is very suitable for utilization in 3D memory optical devices.

A new memory material was designed by us lately for 3D-memory ROM devices, where the information is written once, stored indefinitely, but may be retrieved for very large number of times. It is composed of an organic dye whose structure is drastically different in acidic media than exhibits in basic host media. In addition while the basic form