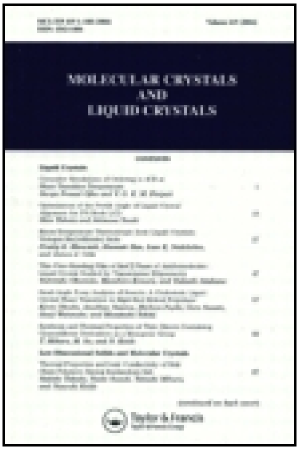

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Hole-Burning Memories: A Frequency Selective Mesoscopic Approach to Molecular Storage

Dietrich Haarer [a]

[a] Physics Institute, University of Bayreuth and BIMF, P.O.Box 101251, 8580, Bayreuth, Germany

Version of record first published: 05 Dec 2006.

To cite this article: Dietrich Haarer (1993): Hole-Burning Memories: A Frequency Selective Mesoscopic Approach to Molecular Storage, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 236:1, 1-12

To link to this article: http://dx.doi.org/10.1080/10587259308055202

Mol. Cryst. Liq. Cryst. 1993, Vol. 236, pp. 1–12
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

HOLE-BURNING MEMORIES: A FREQUENCY SELECTIVE MESOSCOPIC APPROACH TO MOLECULAR STORAGE

DIETRICH HAARER
Physics Institute, University of Bayreuth and BIMF, P.O.Box 101251, 8580 Bayreuth, Germany

Abstract Due to the long wavelength of visible light, most straight forward optical methods, like absorption or emission spectroscopy, are not well suited for spectroscopy on a 'molecular level'. The hole-burning method is a selective spectroscopy scheme based on energy selection. This method yields, at low temperatures, very high spectral resolution and, hence, can be used to investigate molecular environments and molecular potentials. With the simultaneous application of external fields the hole-burning technique is a true two-dimensional spectroscopy method. Hole-burning can also be used for enhancing the schemes of presently used optical memories by many orders of magnitude. In this context new developments based on the use of semiconductor laser diodes are reported. The question of the requirement of low temperatures is also critically reviewed and, finally, a comparison between mesoscopic storage schemes and molecular schemes is given.

I. INTRODUCTION

In biological systems the use of macromolecular units has proven to be a powerful scheme for performing the most vital biological processes. It is known, for instance, that the storage of information in the human brain is achieved by the synapses of the cortical tissues and it is also known, that one human neuron receives up to 40.000 synapses[1]. With these figures one can roughley estimate the capacity of the human brain as being equivalent to about 10^{15} bits even though this figure has to be taken as a very crude approximation since the details of the synaptic storage and its functionality in terms of a limited gray-scale are not known yet. Still, the above figure is so impressive that it is obvious that most 'technical' storage devices are orders of magnitude smaller in storage capacity and less efficient in energy utilization (see for instance[2]) as compared to the biological 'molecular devices'.

In biological systems the information is typically stored and tranferred in aqueous and ionic environments. These environments are not well suited for technical schemes; here electrical and optical systems are the most elegant solutions. For the 'photonic' approach, which may be the most promising future approach, there is one basic limitation, namely the wavelength of the visible light. This is symbolically sketched in Figure 1. which shows that a volume of λ^3 typically accommodates about

10^8 molecules which cannot be selectively addressed by light. This problem also leads to the limit of all optical storage schemes of close to 10^8 bits/cm^2 (visible light). A way around this limit may be achieved with means of near-field techniques and tunneling techniques which will not be addressed in this article.

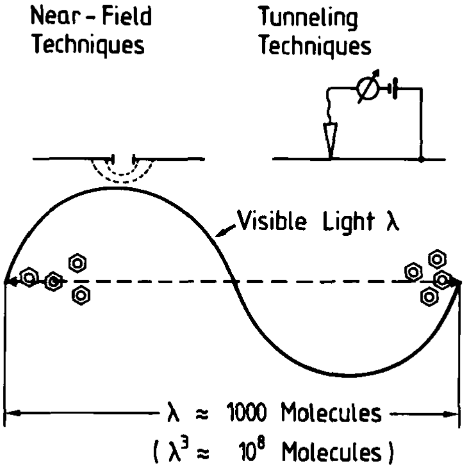

FIGURE 1 Schematic view of the wavelength limitation of optically addressed molecular systems as compared to near-field techniques and tunneling techniques

It has been shown that the hole-burning technique is very suitable for removing some of the limitations which are inherently given by the long optical wavelength of visible light which, in a straight forward optical experiment, always yields averages over at least 10^8 molecules (namely λ^3) by frequency multiplexing. Here the wavelength is still large, but can be varied over a small range and, thus, one can select in a volume of λ^3 a number of molecular sub-groups, the latter being determined by the multiplexing factor F as given by

$$F = \frac{\Delta\omega_i}{\Delta\omega_h} \tag{1}$$

Here the inhomogeneous linewidth $\Delta\omega_i$ is dependent on the matrix and is, in amorphous media, on the order of 10^2 cm^{-1}. For achieving a large selectivity a large F-factor and, hence, a large $\Delta\omega_i$ is desirable (Figure 2). The homogeneous width $\Delta\omega_h$ is given by the pertinent relaxation processes of the optical transitions involved. These transitions are typically the lowest electronic transitions of the dye molecules which are incorporated into the host matrix as dopants to carry the 'molecular information'. $\Delta\omega_h$ obeys the following simple relation:

$$\Delta\omega_h = \frac{1}{2T_1} + \frac{1}{T_2^*} \tag{2}$$

where T_1 is the lifetime of the excited state and T_2^* is the dephasing time of the excited state. This dephasing time is strongly temperature dependent and the actual numbers for $\Delta\omega_h$ vary from 10^{-3} cm^{-1} at ultralow temperatures[3] to about 10 cm^{-1} at about 100 K[4] (for details see for instance [5]).

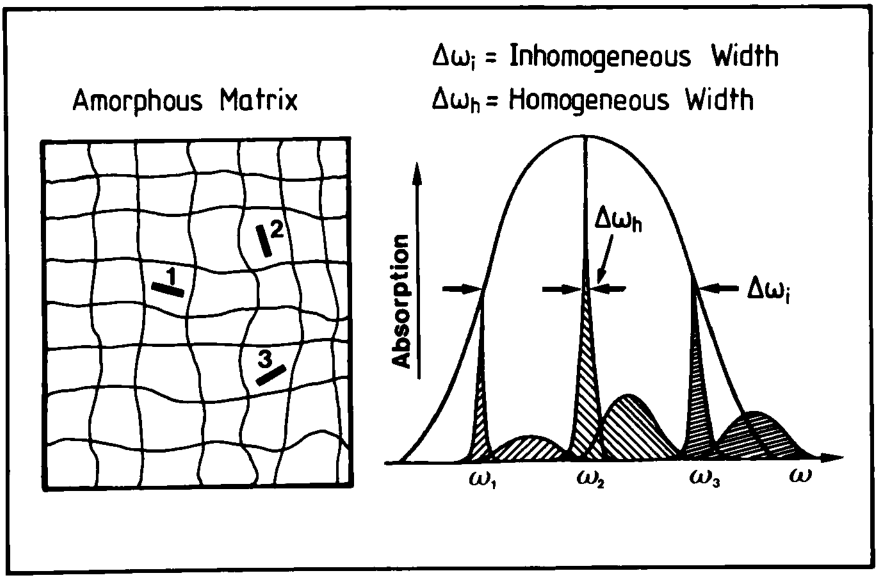

FIGURE 2 Absorption spectra of three different chromophores in an amorphous matrix. The transition energies ω_1 through ω_3 mark the zero-phonon transitions of the lowest electronic states in the different matrix environments. $\Delta\omega_h$ is the width of the 'molecular' transitions; $\Delta\omega_i$ is the width of the total inhomogeneous band of the molecular ensemble.

The strong dependence of $\Delta\omega_h$ on temperature (variation of about 4 decades between 0.01 and 100 K). gives rise to a large variation of the multiplexing factor F with temperature. This also limits the storage capacity of various memory applica-tions as will be shown in the following.

II. PHOTOCHEMICAL OPTICAL SWITCHES BASED ON PROTON TRANSFER: SPECTROSCOPIC ASPECTS

The most prevalent dye molecules showing reversible photochemical reactions are molecules involving light-induced proton transfer reactions. Such reactions can involve either external hydrogen bonds (Fig. 3a) or they can involve the inner protons of porphins or phthalocyanines. In the first class of molecules the photoreaction is the formation of an intermolecular hydrogen bond starting with a lower lying intramolecular hydrogen bond; in the second class of molecules (Fig. 3b) a tautomeric reaction of the inner protons is involved[6]. It is obvious that the photo-induced reactions involving the external hydrogen bonds are true photochemical reactions, in which the product and educt states are well separated[7]. In case of the tautomeric reactions the two states would, in vacuum, be degenerate; however, they become inequivalent in a polymeric medium through the preferential direction of the one-dimensional polymer chains as is symbolically depicted in Fig. 3 (see reference [8] und references therein).

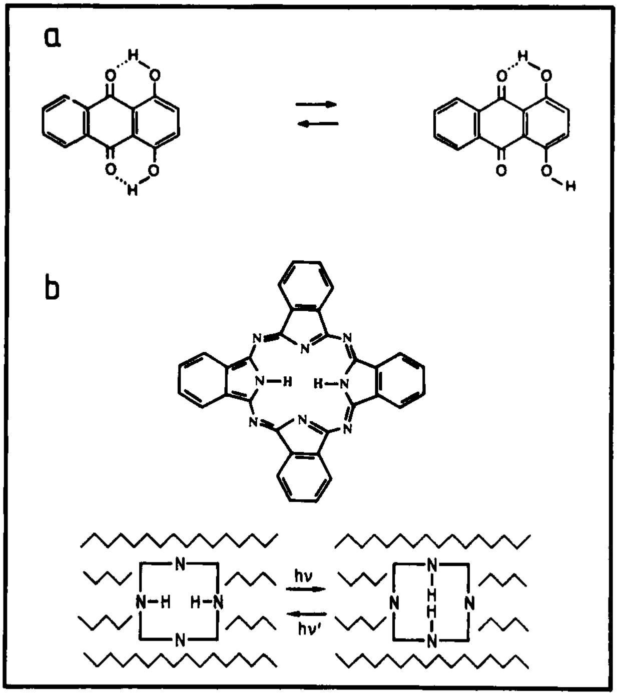

FIGURE 3: Photochemical mechanism of external (3a) and internal proton transfer reactions (3b; see text).

Proton transfer reactions are well suited for reversible photo-induced reactions, since the degree of reversibility is very high and may not be a limiting factor in possible storage applications. For these systems the main limitation is the temperature limit. This limit has been well investigated for phthalocyanines and it is on the order of 100 K i.e. up to a temperature of 100 K the involved photochemical tautomeric mechanism can be considered as stable[9].

More serious for memory applications is the temperature dependence of the involved molecular linewidths. Here the multiplexing factor decreases very steeply as the values for $\Delta\omega_h$ increase (equ. 1). As has been pointed out, the increase in linewidth is mostly given by the decrease of the effective dephasing time T_2^* (equ. 2). Here an empirical algebraic dependence of $\Delta\omega_h$ seems to explain the experimental situation for the tautomeric proton transfer systems quite well. As an example we show the homogeneous linewidth of phthalocyanine (free base), as measured in two polymer matrices and one inorganic glass matrix (Vycor). Here the following algebraic law seems to hold for temperatures up to about 100 K

$$\Delta\omega_h \sim T^{\alpha} \tag{3}$$

with $1 < \alpha < 2$. The physics behind the above temperature behavior is rather involved (see reference 5). It involves tunneling states at temperatures < 10 K and it may involve other low lying modes at intermediate temperatures.

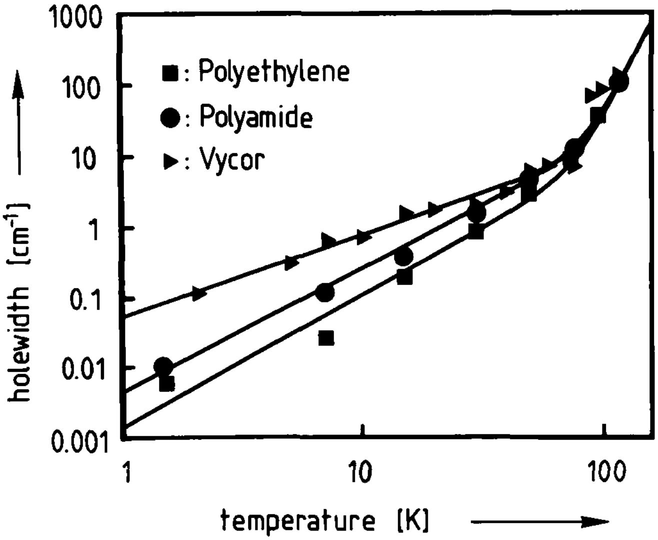

FIGURE 4 Temperature dependence of the homogeneous linewidths of phthalocyanine (free base) in various materials in a double logarithmic plot (see text).

Figure 4 shows that, with the hole-burning materials which are best known from our present view, the temperature of 100 K seems to be a limitation in both, the stability of the photoproduct and the linewidth, since the multiplexing factor i.e. the gain in storage density as well as the spectroscopic gain is only on the order of 10 if one approaches the high temperature limit of 100 K.

Possible means to improve this situation would be the search for new materials with narrower homogeneous linewidths at temperatures > 100 K or the search for materials with very large inhomogeneous bandwidths. The first objective may be reached by also looking into inorganic materials, doped with rare earth ions[10]. In these materials the well-shielded transitions of the rare earth ions tend of have narrower homogeneous linewidths, yet, they also tend to show rather narrow inhomogeneous linewidths due to the same shielding phenomen.

The objective of larger inhomogeneous linewidths can, in principle, be solved with organic materials (polymer blends etc.), yet, no systematic studies have been performed thus far.

At the time being two main developements can be observed.

a) The utilization of the narrow-band features of the low temperature spectra for obtaining information on molecular environments and molecular fields.

b) Experiments in the infrared spectral range to take advantage of cheap, narrow-band semiconductor laser diodes.

Figure 5 shows as an example for ultrahigh resolution a sequence of narrow-band holes at a temperature of 50 mK in the system phthalocyanine (H_2Pc) in PMMA (polymethylmethacrylate). The linewidth is about 2 x 10^{-3} cm^{-1} i.e. the multiplexing factor is on the order of 10^5.

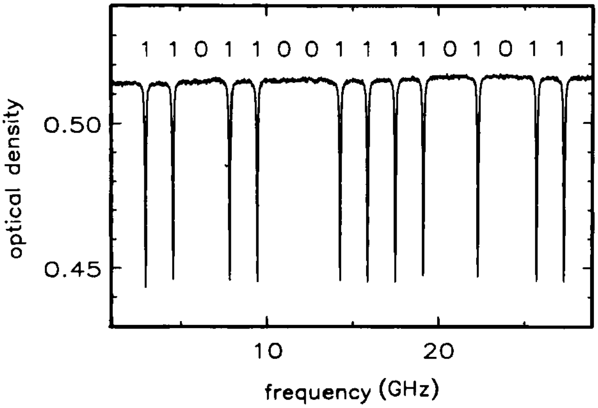

FIGURE 5 Sequence of holes labelled as a bit pattern at ultralow temperatures (50 mK; see text, reference[3]).

It is rather obvious that the high resolution conditions which can be obtained for the low temperature hole-burning systems can yield important information on molecular environments and on molecular local fields, if combined with strain fields (Fig. 6) or electric fields (Fig. 7).

Figure 6 shows the red-shift of the lowest electronic transition of H_2Pc in PE (polyethylene). The applied pressures are only on the order of one atmosphere. It can be shown that these data can be interpreted in terms of local compressibilities and local molecular environments and potentials[11,12] (and references therein).

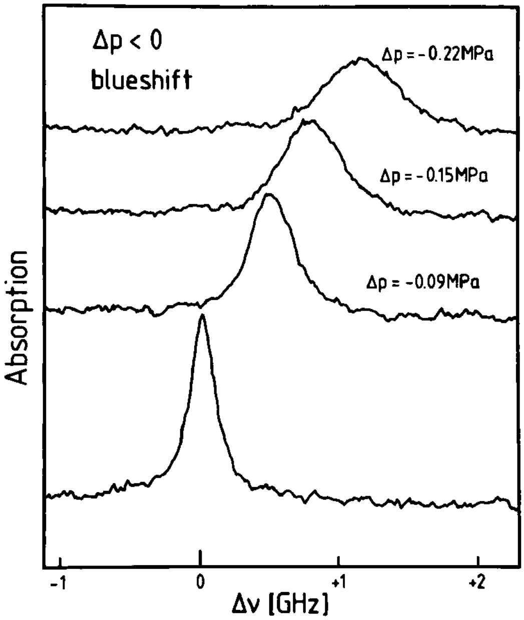

FIGURE 6 Shift and broadening of a photochemical hole with applied pressure in the system H_2Pc in PE. Note, that the involved pressures are only on the order of one atmosphere.

For molecules with inherent dipole moments one can also apply electric fields and perform Stark-spectroscopy to obtain information on molecular dipole changes $\Delta\mu$ between ground-and excited state and on the magnitude of the involved internal molecular fields. A typical example is given for the dye molecule chlorin in the polymer PVB (polyvinylbutyral) (Fig. 7). Due to the fact that the molecules are randomly oriented, the spectrum broadens symmetrically to lower and higher fields.

A detailed evaluation of the electrical splittings and shifts yields both, internal matrix-fields[13] and intenal induced dipoles[14].

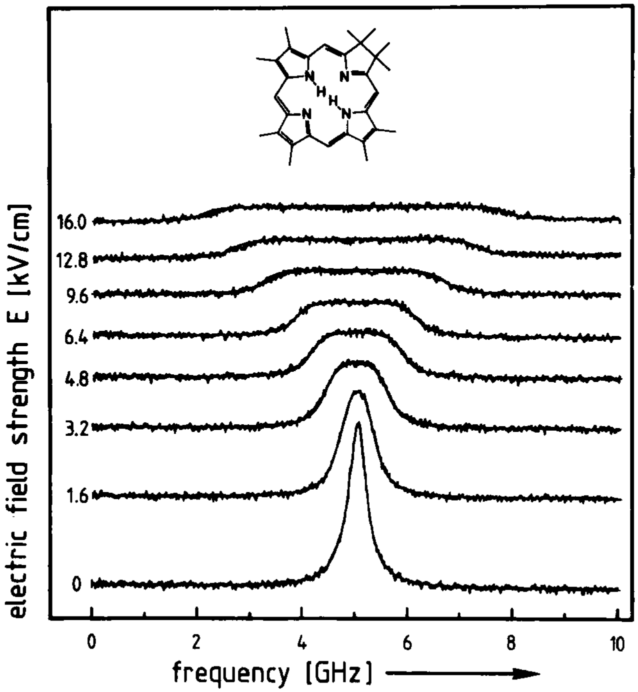

FIGURE 7 Hole-Broadening in an external electric field. The molecule is chlorin (see insert); the matrix is PVB (see text;[15]).

It is interesting to note that amorphous media tend to have very large internal dipole fields on the order of > 10^6 V/cm which are due to local disorder.

III. STEPS TOWARDS TECHNICAL IMPLEMENTATIONS OF HOLE BURNING MEMORIES

IIIa) Visible Wavelength Lasers

It can readily be shown that the hole-burning scheme is well suited for high resolution imaging. If one uses a laser beam manipulator (Fig. 8), one can write freqeuncy-selective patterns on a photosensitive hole-burning material with a 1 μ-resolution. The various patterns (for instance Fig. 9) can be spaced at 2 K in the frequency domain with a spacing of about about 0.2 cm^{-1}. The patterns can, after the writing process has been finished, be read with a commercial CCD-camera with very good signal-to-noise ratio.

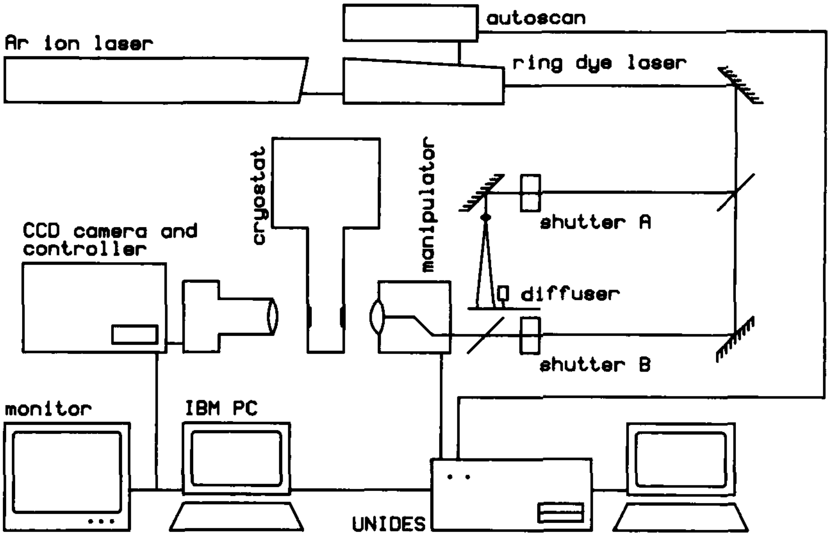

FIGURE 8 Laser hole-burning scheme for achieving spatial resolution. During the writing process the shutter A is closed and the shutter B is open; during the reading process the reverse setting is used. Here a diffuser illuminates the sample evenly and the information is read with a CCD-camera.

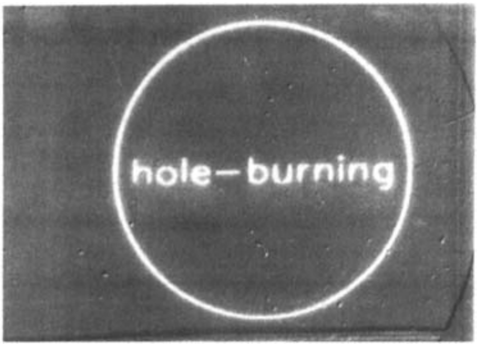

FIGURE 9 The figure shows a hole-burning pattern (resolution 6 μ) as written by the above beam manipulator. At the present time we have the imaging lens positioned outside the cryostat, which limits our resolution to about 6 μ. In principle, the resolution can be in the 1 μ-regime. The frequency spacing between different writing patterns can, at 2 K, be as small as 0,2 cm^{-1}.

There is presently no doubt that the imaging quality of hole-burning materials is sufficient for data storage. This has also been proven in the group of U. Wild et al. These authors have implemented a scanning scheme which is based on the Stark-effect (see for instance reference [16]). The presently used writing energies are on the order of a few nJ/bit. Compared to the presently used 'thermo-optical' storage schemes this figure is rather small. For photonic materials with higher quantum yields the above figure could be reduced by up to three orders of magnitude however, with the present figures of comparitively low quantum yield materials (10^{-3} to 10^{-4}) the scheme has the advantage that multiple reading is no problem with more than 1000 reading processes without major image degradation.

IIIb) IR-Semiconductor Laser Diodes

With the advent of inexpensive diode laser in the infrared spectral range one has to devise light sensitible chromophore systems which are sensitive in the near IR. The most straight forward alternative to the phthalocyanine molecule is a naphthalocyanine molecule whose absorption pattern peaks around 785 nm. The absorption of this chromophore is shown in Fig. 10 together with the absorption of the H_2Pc-molecule.

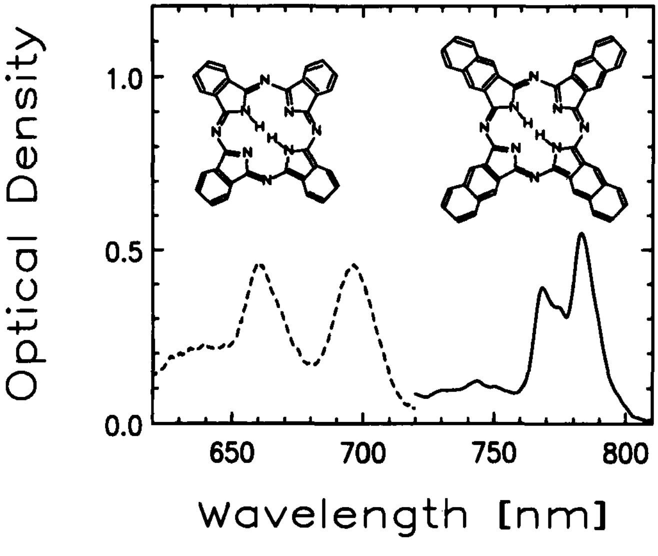

FIGURE 10 Absorption spectra of two different phthalocyanine dyes (see text).

The feasibility test of the IR systems can easily be made by using the multi-mode pattern of an IR-laser diode as light source and imaging the laser modes of the diode onto the inhomogeneous band of an appropriate dye-polymer material. Such a straight forward experiment has been performed with a naphthalocyanine doped polyethylene matrix. The mode pattern is displayed in Fig. 11. It shows the individual laser modes and a sub-structure of the modes which was due to a frequency jitter of the available laser diode.

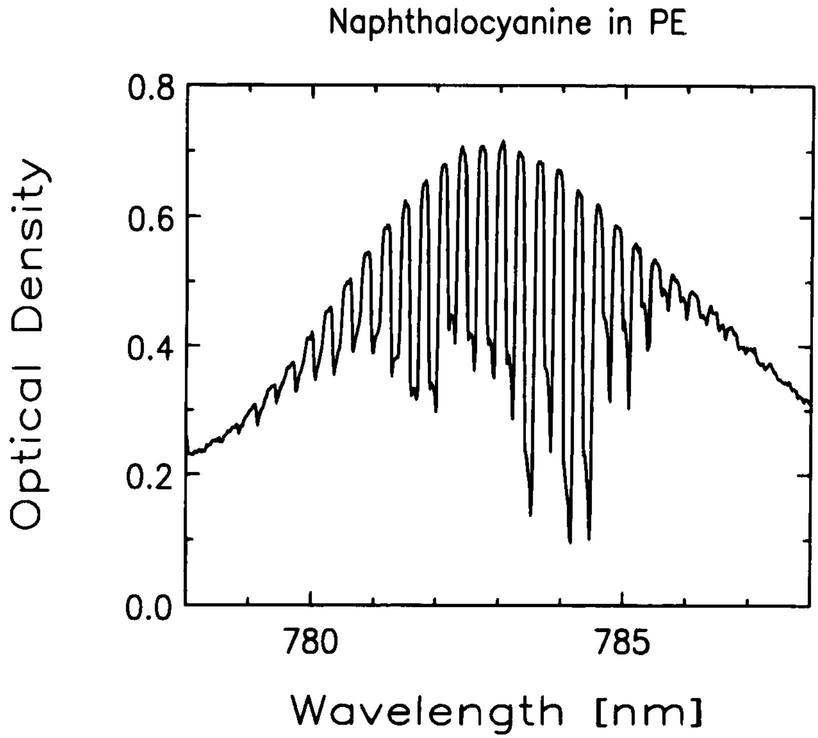

FIGURE 11 Mode pattern of diode laser (see text).

For more quantitative experiments with single mode lasers we have to optimize our present current - and temperature-scanning equipment.

IV. OUTLOOK

There is no doubt that hole-burning is very suitable for gaining molecular information in amorphous host-guest systems. It also has the potential for high density storage schemes in which molecular sub-ensembles are used to store information. With conservative figures one still needs about 10^3 molecules/bit for our present memory prototypes. This means that we do not have a true molecular scheme but a more mesoscopic system, exceeding the presently used technical systems by about a factor up to 10^4.

Whether or not true molecular systems will be feasible in the foreseeable future will strongly depend on the improvement of the involved photon light sources and photon detection schemes. In both areas there has been considerable progress in the past few years

ACKNOWLEDGEMENT

This work was supported by the BMFT (Bundesministerium für Forschung und Technologie). We thank the Fonds der Chemischen Industrie for support. We also thank Prof. E. Vogel and Prof. D. Wöhrle for providing the dye materials and Dr. I. Renge for preparing the thin film samples.

REFERENCES

1. M. Abeles in Cortionics p. 56 ff Cambridge University Press, (1991)
2. D. Haarer, Angewandte Chemie Int. Ed. Advanced Materials 28, 1544, (1989)
3. K.P. Müller and D. Haarer, Phys.Rev.Lett. 66, 2344 (1991)
4. R. Ao, S. Jahn, L. Kümmerl, R. Weiner and D. Haarer, Jpn.J.Appl.Phys. 31, 693 (1992)
5. W.E. Moerner 'Persistant Spectral Hole Burning, Science and Spplications'; Topics in Current Physics 44, Springer (1988)
6. J. Friedrich and D. Haarer, Angew. Chemie Int. Ed. 23, 113 (1984)
7. F. Graf, H.K. Hong, A. Nazzal and Haarer, Chem.Phys.Lett. 59, 217 (1978)
8. S. Völker, Annu.Rev.Phys. Chem. 40, 499 (1989)
9. L. Kümmerl, M. Scherl and D. Haarer to be published
10. R. Jaaniso and H. Bill, Europhys. Lett 16, 569 (1991)
11. B.B. Laird and J.L. Skinner, J.Chem.Phys. 90, 3274 (1989)
12. S. Reul, W. Richter and D. Haarer, Chem.Phys.Lett 180, 1 (1991)
13. L. Kador, S. Jahn, D. Haarer and R. Silbey, Phys.Rev. B 41, 12215 (1990)
14. R.B. Altmann, I. Renge, L. Kador and D. Haarer, J.Chem. Phys. in print
15. L. Kador, D. Haarer and R. Personov, J.ChemPhys. 86, 5300 (1987)
16. U.P. Wild and A. Renn, J.Mol.Electronics 7, 1 (1991)