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## Multiple Photochemical Hole Burning in Organic Glasses and Polymers: Spectroscopy and Storage Aspects

*A scheme for optical information storage using photochemical hole burning (PHB) in amorphous systems is evaluated. Limits imposed by the nature of PHB in polymers and glasses and its dependence on temperature are discussed. It is demonstrated that optical information storage can be multiplexed by a factor of  $10^3$  using the frequency dimension and PHB.*

### Introduction

The rapid development of lasers in the visible and near-ir spectral range has rekindled interest in optical storage schemes. If such schemes were carried to the diffraction limit of visible or near-ir light, one would be able to store  $10^8$  bits/cm<sup>2</sup> in a two-dimensional configuration and about  $10^{12}$  bits/cm<sup>3</sup> in a holographic configuration (without utilizing the frequency domain, as discussed here). Since holographic methods are quite complex in their technical implementation [1], they are not discussed in this article. It should be mentioned, however, that due to material inhomogeneities the achievable holographic storage density to date is about two orders of magnitude below the diffraction limit of  $10^{12}$  bits/cm<sup>3</sup> [2, 3].

This paper focuses on a novel approach utilizing the frequency domain as an additional storage dimension [4, 5]. This additional dimension converts a two-dimensional  $x$ - $y$  memory into a three-dimensional  $x$ - $y$ - $\nu$  scheme and a holographic memory into a four-dimensional  $x$ - $y$ - $z$ - $\nu$  scheme. In our paper, we show that this "frequency multiplexing" can, in principle, be performed via photochemical hole burning (PHB) and that about  $10^3$  bits can be stored in the frequency domain, if one is prepared to store the bits at temperatures below 20 K. The very attractive aspect of the hole-burning scheme is the high storage density, which allows one to store in a scheme of two spatial dimensions  $x$ ,  $y$  and one frequency dimension  $\nu$  about  $10^{11}$  bits/cm<sup>2</sup>. Whether such low-temperature schemes will be attractive from a technological viewpoint depends mainly on the availability of suitable optical

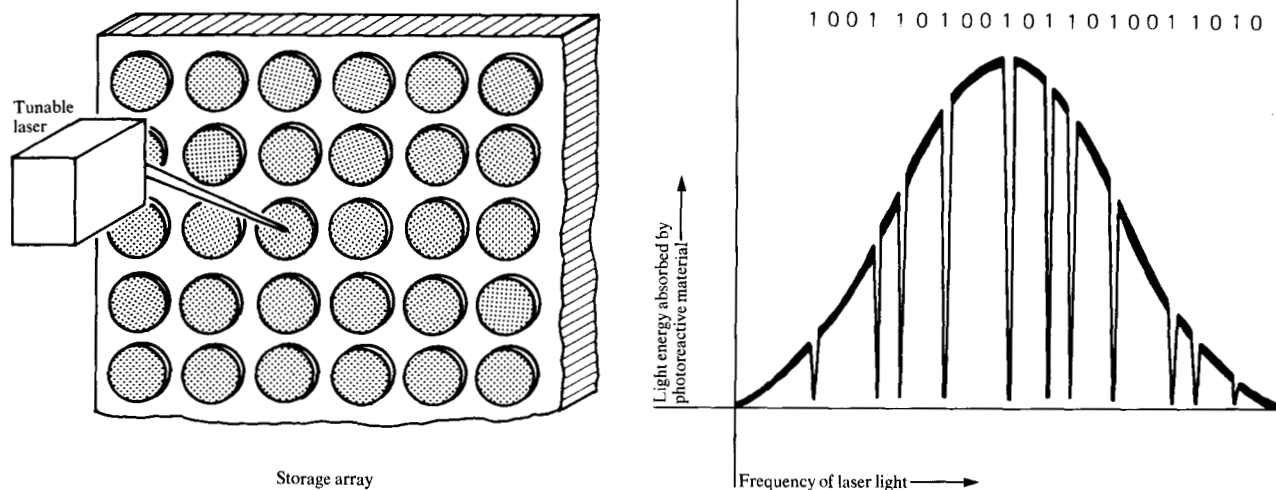
storage materials and on the development of efficient schemes to scan the frequency domain [6]. This article presents novel information on some aspects of optical storage materials and optical linewidths. These aspects need to be clarified before further technical progress can be predicted. In addition, we discuss utilization of amorphous storage materials, such as low-temperature glasses and polymers.

### The basic concept of a PHB memory

The simplest description of a PHB memory can be given for the case of two spatial dimensions and one frequency dimension. Figure 1 shows a tunable laser which is designed to address an  $x$ - $y$  array of bits, where each bit is on the order of  $1 \mu\text{m}^2$ . If one does not consider the tunability of the laser, the scheme corresponds exactly to a conventional two-dimensional optical store. The main additional requirement for a PHB memory is the tunability of the laser. Instead of simply having a spatial  $x$ - $y$  pattern of black and white dots, representing the optical bits, one adds a second tier of information storage by addressing bits within each spot in a multicolor frequency scheme. This is symbolically depicted in the right-hand section of Fig. 1. The figure shows that the laser can be tuned to  $n$  different frequency or color channels,  $\nu_n$  (in this case  $n = 22$ ), throughout the absorption envelope of the photoactive substrate. At each of these channels, the  $x$ - $y$  substrate can be transparent or opaque.

A similar frequency-selective scheme was first proposed by A. Szabo for excited atomic or ionic states in an optical

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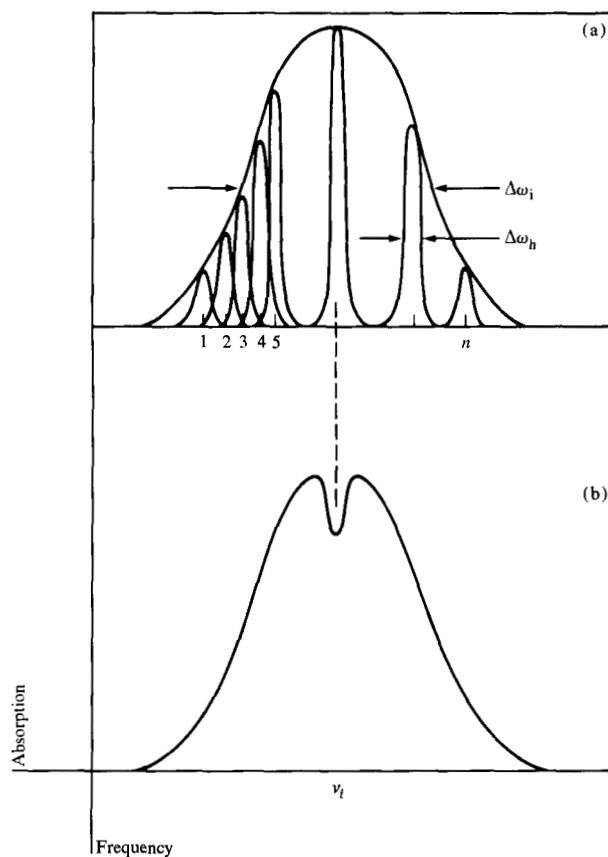
**Figure 1** Schematic description of a three-dimensional  $x$ - $y$ - $\nu$  storage scheme. The left-hand side shows the typical  $x$ - $y$  configuration with the circles representing spatial data bits. The right-hand side shows a schematic representation of a "bit pattern" in the frequency dimension that could be inscribed within each spatial bit.

substrate [7]. Szabo's hole-burning memory was based on relatively short-lived excited states and thus represented a volatile optical memory which had to be refreshed within the lifetime of the excited states. In the following, experimental data are presented which show that laser photochemistry can, at low temperatures, provide as many as  $10^3$  frequency channels. Furthermore, the data bits in the frequency domain are nonvolatile at low temperatures since they are based on photochemical processes with negligible thermal reversibility at these temperatures. We show that the basic limitations of photochemical holes are given by the properties of the photoreactive molecules and of the substrates. These are discussed along with the experimental data.

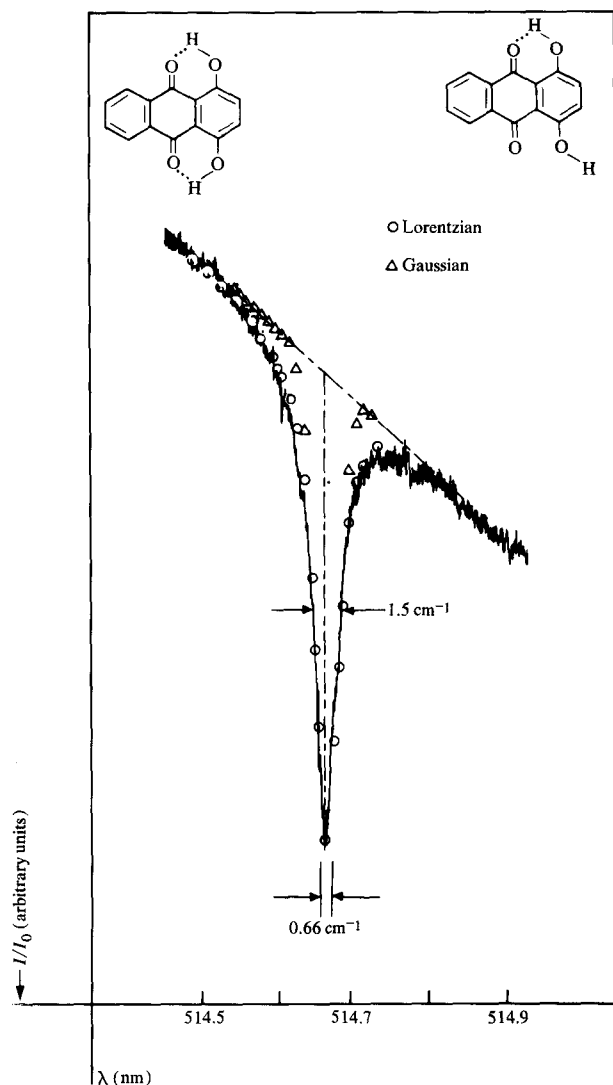
● *General features of narrow-band photochemistry*

If an ensemble of many ( $\geq 10^{17}/\text{cm}^3$ ) photoreactive molecules is dissolved in a solid "transparent" (*i.e.*, optically inert) matrix, the optical transition frequencies of the various molecules are distributed over a broad range due to the different environments of the guest molecules in the host matrix. In a single host crystal, the frequency range of this distribution, the so-called *inhomogeneous linewidth*, will be on the order of  $1 \text{ cm}^{-1}$  (which in the visible 500-nm range corresponds to a linewidth of 0.025 nm) [8]. This linewidth, or more appropriately this bandwidth, is due to inhomogeneities and strain effects within the crystal. In contrast to crystalline hosts, amorphous materials such as glasses or polymers have a much broader inhomogeneous bandwidth, on the order of 100 to 1000  $\text{cm}^{-1}$  due to the greater microscopic inhomogeneity of the disordered materials.

The upper part of Fig. 2 schematically shows such an inhomogeneous bandwidth. It is made up of the sum of the



**Figure 2** (a) Symbolic representation of an inhomogeneous absorption line as a superposition of  $n$  distinguishable sites of the width  $\Delta\omega_n$ . (b) Line profile during optical saturation or after photochemical reaction with light of frequency  $\nu_l$ , showing burned hole.



**Figure 3** Photochemical hole in the first singlet absorption of quinizarin in a 3:1 mixture of EtOH and MeOH (2 K), produced by 15-min irradiation with an Ar<sup>+</sup> laser (3 mW). The bandpass of the spectrometer was 0.66 cm<sup>-1</sup>.

various "local resonances" or sites for different subsets of molecules 1 through  $n$ . PHB is defined as the optical bleaching due to frequency-selective photochemistry, which involves only a specific subset of photoreactive molecules without affecting the other molecules in the matrix. The different subsets can be addressed by changing the laser wavelength. Such frequency-selective photochemical experiments were first performed by two Russian groups [9, 10] whose narrow-band laser photochemistry experiments resulted in narrow dips or holes in the absorption spectrum of the photoreactive substance. It can be shown that narrow holes can be created if the considered optical transition fulfills the zero-phonon requirement which has been discussed in a previous publication [11].

The gain in information storage density, *i.e.*, the frequency multiplexing factor, is given by the ratio of the total inhomogeneous linewidth  $\Delta\omega_i$  divided by the width  $\Delta\omega_h$  of the zero-phonon hole, which is twice the homogeneous linewidth (see Ref. [12]). We define this quantity as the I/H ratio. For many systems,  $\Delta\omega_h$  can be over a factor of 1000 narrower than the inhomogeneous linewidth  $\Delta\omega_i$ , which results in a corresponding I/H ratio of 1000. Typical values for  $\Delta\omega_h$  in crystalline materials are on the order of 10<sup>-3</sup> cm<sup>-1</sup> (at  $T \rightarrow 0$ ) [12]. In disordered materials, the corresponding homogeneous holewidths are quite different [9, 13]; these are discussed in the following section.

• *Narrow-band photochemistry in organic glasses and polymers*

*The homogeneous linewidth  $\Delta\omega_h$ .* The simplest PHB scheme consists of an electronic ground state, an electronic excited state, and an appropriate state of the photoproduct. This is sufficient to account for the main feature of a PHB spectrum. In this scheme laser irradiation at the frequency  $\nu_1$  leads to a photochemical hole, whose width, according to the Heisenberg uncertainty principle, is given by optical relaxation processes [14] which take place during the time of excitation:

$$\frac{\Delta\omega_h}{2} = \frac{1}{2T_1} + \frac{1}{T_2} \quad (1)$$

In Eq. (1)  $T_1$  is a scattering process that does not conserve energy, *e.g.*, radiative lifetime, fluorescence, phosphorescence, or radiationless transition to a lower-lying state. It is often called *spin-lattice* relaxation time because of analogies between spin-1/2 systems and two-level systems [15].  $T_2$  is an energy-conserving process in which the original phase relation between the absorbing species and the exciting laser is destroyed by scattering into states of equal energy, whose wave functions have a different phase factor. For this reason,  $T_2$  processes are often referred to as *dephasing* processes. In the spin language,  $T_2$  processes can be spin flips in which two energetically degenerate spins flip simultaneously (one up, one down), maintaining the total energy of the system but changing the phase of the spin-wave functions.

Figure 3 shows an example of a photochemical hole which was produced in an alcohol glass doped with the molecule quinizarin [16(a)]. The photochemistry is believed to be due to a light-induced proton transfer process, which occurs at 2 K with relatively high quantum yield [16(b)]. The proton transfer seems to be due to the cleavage of an intramolecular hydrogen bond and the formation of an intermolecular hydrogen bond, as indicated in the figure. The experimentally observed width of the hole is 1.5 cm<sup>-1</sup>, which is very large compared to holewidths produced in crystalline matrices. This large linewidth is believed to be due to fast  $T_2$

relaxation processes. In this case, the laser linewidth is negligible on the scale of the figure.

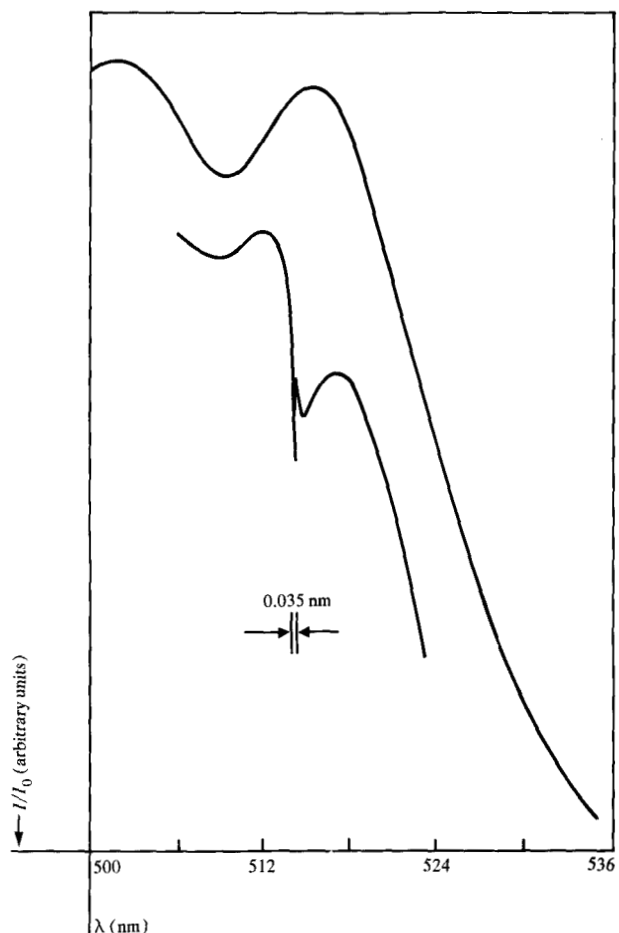
The origin of these fast relaxation processes is still not fully understood, but it is most likely related to the tunneling processes in glasses [17]. These can occur even at very low temperatures because the tunneling barrier heights in glasses can be quite low [18, 19]. Typical  $T_2$  dephasing times can be as short as 1 to 10 ps. In other matrices, the dephasing processes are slower, depending on the "hardness" of the glass and on its microscopic structure (see below).

**Broadband "phonon holes"** Figure 4 shows a photochemical hole in quinizarin in an alcohol glass. The sharp hole at the laser frequency (514.5 nm) is accompanied by a quite broad hole at longer wavelengths. This broadband hole can be several tens of wavenumbers wide ( $\approx 10$  nm) and hence may mask the narrow-band features of PHB. It was shown that the broad side-holes are due to low-energy phonon excitations of the matrix [13, 20]. These lattice excitations can be looked upon as frequency modulations of the well-defined, narrow electronic transitions. Since the broad phonon holes are not useful for information storage, they serve only to distort the absorption spectrum and complicate the recording of the zero-phonon holes.

There are three ways to achieve narrow-band "phonon-less" PHB spectra:

- Select matrix-molecule combinations for which phonon effects are small and can therefore be neglected. Examples of this kind of photoreactive system are presented in the second part of this article.
- Suppress phonon effects by choosing an appropriate photochemical cycle. The latter is briefly described in the following discussion.
- Work with materials, such as the aggregate color centers, that have large enough Stokes shifts to put the phonon sidebands entirely outside of the zero-phonon line.

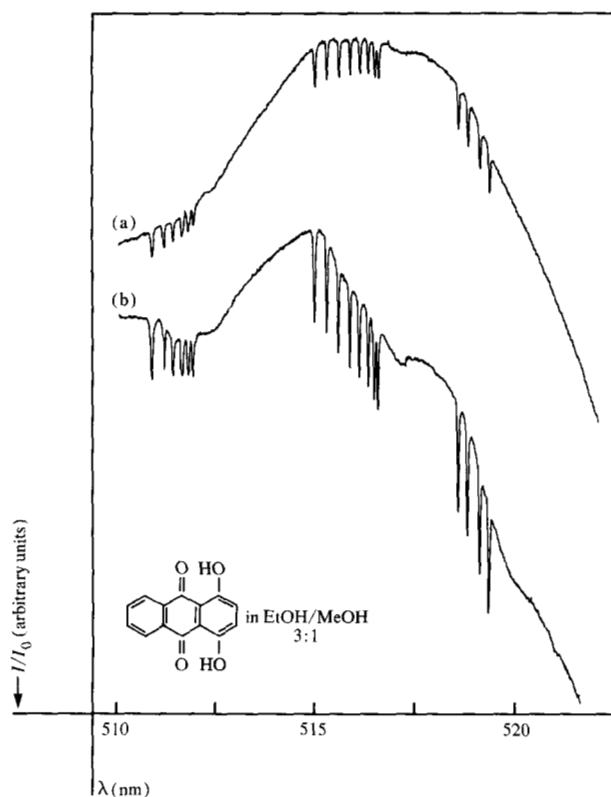
Figure 5(a) shows a series of narrow photochemical holes of quinizarin in an alcohol glass, at 2 K. In contrast to Fig. 4, the holes do not exhibit broadband phonon satellites; therefore, Fig. 5(a) is a good example for multiple hole burning from an applications point of view. About 500 holes can easily be burned in the inhomogeneous optical linewidth. The elimination of phonon effects was performed photochemically. It was shown recently [21] that narrow-band and broadband photochemistries have different wavelength dependencies. Therefore, the phonon wing which shows up as a broad hole in Fig. 4 and as broad indentations in Fig. 5(b) can be eliminated by "white-light" irradiation. This irradiation fills the broad phonon holes without totally eliminating the narrow zero-phonon holes. This is especially useful if only a few bits, well separated from one another, are



**Figure 4** Photochemical hole burning in quinizarin/alcohol showing the sharp zero-phonon hole and the broad phonon wing at longer wavelength characteristic of amorphous systems.

stored in the frequency domain. The nature of this quite complex photochemical process is due to the properties of the organic glass, *i.e.*, to the existence of photochemical barriers of various heights caused by interactions of the glass structure.

Without dwelling on the details of the complex photochemical scheme [21], we point out that multiple hole burning in amorphous organic glasses is possible and allows for multiplexing factors on the order of  $10^3$ . Whether photochemical systems of the above kind can be used for information storage depends mainly on the achievable photochemical quantum yields, on an improvement of the usable temperature range, and on the development of practical lasers capable of being scanned over the entire inhomogeneous line. So far, the achievable quantum yields for quinizarin are  $\leq 10^{-3}$  and the temperature range is  $2 \text{ K} \leq T \leq 10 \text{ K}$ .



**Figure 5** (a) Multiple PHB demonstrating the smoothing effect of white-light irradiation after PHB, and (b) spectrum before broadband irradiation.

### Some limits of information storage using photochemical hole burning: phthalocyanine in polymer matrices

The phenomenon of PHB itself is a rather recent discovery and consequently studies have been principally limited to the realm of physics rather than technology. Nevertheless, some notion of material requirements is available. Preferred materials should be nontoxic solids of high optical quality which can be used as thin films and which can withstand repeated cycling from room temperature down to at least 4.2 K. The photochemistry which leads to spectroscopic hole burning should be sufficiently efficient to permit rapid inscription of spectroscopic information, preferably within a few nanoseconds per hole, yet it should not be so efficient that significant further photobleaching occurs when the information is read with a weaker monitoring light source. The stability or lifetime of the photochemical hole is of the utmost importance. Once burned, the holes must persist for sufficiently long periods of time to allow for storage and subsequent retrieval of the information. Photochemical reversibility so that information can be photochemically erased at each two-dimensional spot is also a desirable

property. The physical properties of polymers make them attractive host materials for PHB [22]. In the remainder of this article, we discuss the use of free-base phthalocyanine,  $H_2Pc$ , in polymer matrices as a promising model material for information storage by PHB [23].

$H_2Pc$  was first found to produce permanent optical hole burning by Russian investigators in 1974 [10]. These early studies, however, were limited to  $H_2Pc$  in crystalline and polycrystalline environments (n-alkane matrices at 4.2 K) and focused principally on the evaluation of the homogeneous spectroscopic holewidth. Although previous work did not demonstrate the nature of the photochemical mechanism operating in the hole-burning process, it was believed to involve phototautomerization of the central protons, as has been demonstrated to occur in free-base porphyrin [24]. We have recently compiled substantial evidence which supports this type of photochemical tautomerization as the major transformation leading to hole burning in  $H_2Pc$  [25].

Figure 6 shows the schematic structure of  $H_2Pc$  and a model of the proposed mechanism. Because of the distortion caused by the central protons,  $H_2Pc$  is expected to have approximate rectangular,  $D_{2h}$ , symmetry [26]. The proposed tautomerization involves a concerted transfer of the central protons from opposite nitrogens to the two adjacent ones. Clearly, in the absence of an environment the tautomers are equivalent and therefore of identical energies. However, in condensed media at low temperatures, the presence of unique frozen site environments is expected to impose slight but significant steric and possibly dipolar interactions which become different if the tautomer changes with respect to the solvent cage molecules. The effect of the environment and the consequences of tautomerization are schematically depicted at the bottom of Fig. 6. In this model the  $H_2Pc$  tautomers are represented by rectangles distinguished only by the position of the central protons, which are aligned opposite each other on one axis. The wavy lines represent the static solvent cage molecules. Phototautomerization results in a transfer of the protons to a perpendicular axis, which also causes the orientation of the  $D_{2h}$  geometry of the molecule to change on that axis. Thus, tautomers 1 and 2 in Fig. 6 are identical, but they experience different environmental interactions (crystal fields) due to their perpendicular alignments in similar solvent cage environments. Consequently, the electronic transitions of one of the tautomers in one particular site will be of lower energy relative to the same electronic transitions of the other tautomer in a similar site. Our results are analogous to those found for free-base porphyrins [12, 24]. In studies of  $H_2Pc$  in polycrystalline p-terphenyl, we were able to identify photoreversible species which we assign to the tautomers. The largest energy difference between the two tautomers was found to be rather small at only  $125\text{ cm}^{-1}$  [25]. In this article, we are concerned with

$H_2Pc$  in amorphous media where the width of the inhomogeneously broadened 0-0 absorption band is about  $340\text{ cm}^{-1}$ . It is not possible to distinguish the different tautomers easily in such amorphous systems due to the overshadowing effect of inhomogeneous broadening, which causes overlapping in the absorptions of the two tautomers in the ensemble of sites. As a result, application possibilities are minimally affected, since photochemical holes and their overlapping photo-product represent only a very small number of molecules transformed relative to all the molecules in the inhomogeneously broadened band.

Usually, the narrowest holes (and therefore the highest density of information) are apt to be obtained by irradiating at the electronic 0-0 transition [11]. As mentioned earlier, information storage using hole burning is limited by the I/H ratio. Two important factors which greatly influence the I/H ratio are the temperature of the system and the nature of the 0-0 transition. The latter can find remedy in a well-chosen photoactive chromophore such as  $H_2Pc$ , which upon Franck-Condon excitation will lead to the nearly pure electronic excited state [11]. The effect of temperatures, however, is a more complicated problem because it affects the chromophore as well as its environment. The influence of temperature changes is greatest on the homogeneous widths with only small consequences on the inhomogeneous widths. Figure 7, for example, shows the inhomogeneously broadened absorption spectrum of phthalocyanine in poly(methyl methacrylate) (PMMA) at room temperature and at 4.2 K. The lack of temperature influence on an inhomogeneous width is particularly noted for samples that are solids at room temperature, since a large amount of the disorder in these systems is already trapped by the rigid environment even at room temperature.

$H_2Pc$  is also an attractive system for PHB studies because of its unusually high extinction coefficient. Literature values report a molar extinction coefficient at the maximum of the 0-0 transition of  $1.37 \times 10^5\text{ moles}^{-1}\text{-liter}^{-1}$  at room temperature in 1-chloronaphthalene [27]. This property helps to overcome the only major handicap of  $H_2Pc$ , which is its very low solubility in common solvents at room temperature. From a pragmatic viewpoint, the large extinction coefficient is attractive because it enhances the apparent hole burning efficiency and also because it allows the use of dilute solutions ( $\leq 10^{-6}$  moles per liter) or the use of thin films. Partially due to the large extinction coefficient, the rate of PHB for  $H_2Pc/PMMA$  is about an order of magnitude or more faster than for other systems such as porphyrins in PMMA [25], quinizarin in alcohol matrices [14, 15], and some metal complexes of phthalocyanine in alcohol matrices [28], all irradiated with similar light doses at their optimum wavelengths. This is in spite of an unfavorable quantum yield for  $H_2Pc$ .

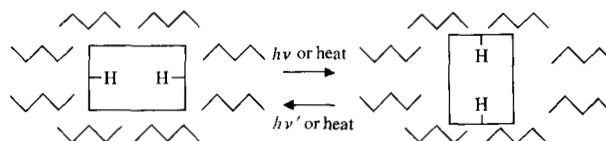
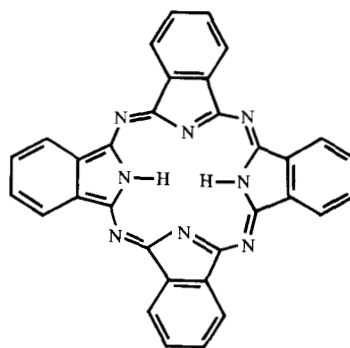


Figure 6 Free-base phthalocyanine ( $H_2Pc$ ) and a schematic representation of the proposed tautomerization of the central protons.

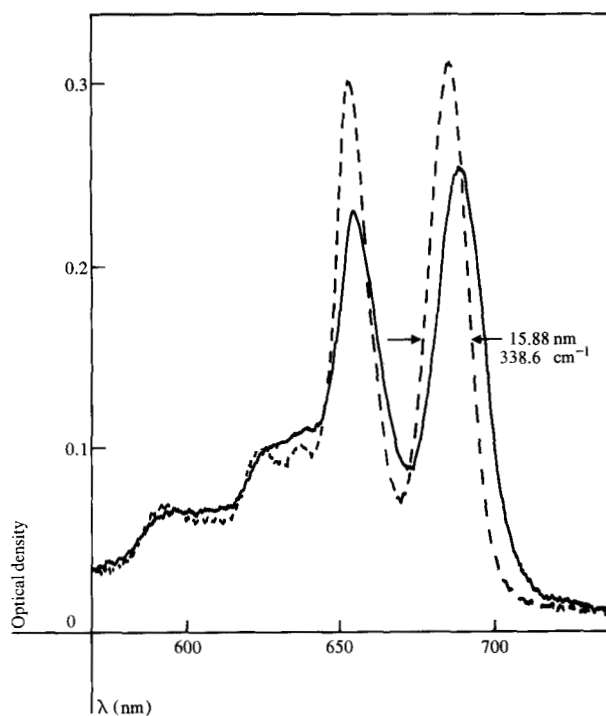
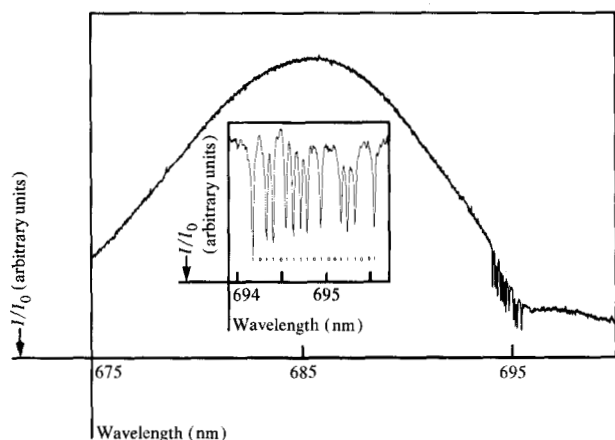


Figure 7 Absorption spectrum of  $H_2Pc$  in PMMA at room temperature (—) and at 4.2 K (---).

Figure 8 demonstrates PHB at the inhomogeneous 0-0 absorption band of  $H_2Pc$  in PMMA at 4.2 K. Figure 8 also puts spectral characteristics of the hole-burning process in



**Figure 8** Multiple PHB in the inhomogeneous 0-0 absorption band of  $H_2Pc/PMMA$  at 4.2 K. The inset shows the twelve-hole spectrum displayed as an expanded-difference spectrum, demonstrating a good signal-to-noise ratio and low background absorption. Labeling with ones and zeros illustrates a possible 19-bit PHB memory scheme.

perspective. The spectrum shows twelve holes burned as little as  $0.075 \text{ nm}$  apart. The homogeneous holewidth is  $0.34 \pm 0.05 \text{ cm}^{-1}$  ( $0.017 \text{ nm}$ ) at 4.2 K in this PMMA sample. Since the inhomogeneous full width at half maximum of the 0-0 band of  $H_2Pc$  in PMMA is  $340 \text{ cm}^{-1}$ , the I/H ratio is about  $10^3$ . This represents an approximate upper limit to the number of holes that can be burned in the entire inhomogeneous band of this system, assuming a spectroscopic pitch equal to twice the homogeneous width. The same twelve-hole spectrum is shown in Fig. 8 (inset) as a difference spectrum, after electronically expanding and recording it. Since the most important feature in PHB optical memories is the spectroscopic holes, it is useful to emphasize these over the background absorption of the vast remainder of the inhomogeneously broadened band (Fig. 8). This can easily be done by measuring difference spectra. In Fig. 8 (inset), the relative absorption spectrum was digitally recorded before and after PHB, and the difference between the two spectra was electronically determined with a computer. In this case, a small correction to compensate for the weak phonon wing of the holes was also included. The result is a rather level hole-burning spectrum unencumbered by irrelevant background absorption. Although this technique in its present stage is far too slow for application purposes, it demonstrates what can be done to obtain high-resolution hole-burning spectra with a reasonably large signal-to-noise ratio. The holes and "spaces" have been labeled with ones and zeros to illustrate a possible scheme for coding the information. The holes in this example are homogeneous and represent the intrinsic spectroscopic limit of the system. A somewhat different example of a hole-burning difference spectrum is

shown in Fig. 9. In this case, the relative absorptions before and after PHB were measured and electronically subtracted with an optical multichannel analyzer (OMA, Princeton Applied Research) coupled to a 0.85-m Spex spectrometer. The widths of the holes shown are limited by the bandwidth of the laser emission. Relative absorption spectra for calculating Fig. 9 were measured using a continuous broadband monitoring light source which passed through the sample and the monochromator and then impinged on the two-dimensional detector array of the OMA target. Instead of a continuous light source, however, the monitoring beam can easily be an appropriately timed broadband flash source, such as a nanosecond spatially coherent broadband laser pulse, which would reduce reading of all the spectral information in one spatial region to the nanosecond time regime. Techniques using detection systems such as the OMA are particularly intriguing because they eliminate the need for dynamic frequency scanning and, therefore, present a possible technology for multiplexing the optical reading of the information which would consequently increase the speed of accessing and transcribing the optically stored information. In implementing such techniques, however, measuring difference spectra would likely be too cumbersome. Therefore, if time limitations are to be minimized, one should measure the hole-burning spectrum without further manipulation. This requires that there be no distortions, such as deep phonon wings in the PHB spectrum, so that holes may be easily distinguishable from the remainder of the broad inhomogeneous absorption band. The 30-bit hole-burning spectrum in Fig. 9 covers over 6 nm or about 20% of the entire 0-0 absorption band without major curvatures or spectroscopic distortions. Thus, it seems possible to monitor most of the inhomogeneously broadened absorption band by the difference technique or by a direct absorption measurement without encountering overwhelming phonon wing effects, especially at low hole-burning depths. Other techniques, such as frequency modulation [6] and polarization spectroscopy [29], have also been successfully used to measure PHB, particularly in crystalline systems.

Apart from the basic limits originating from the I/H ratio, there are, for practical purposes, other limiting factors such as the achievable laser scanning rates, the rates for PHB, and the effect of temperature. With regard to hole-burning rates, the use of high-power lasers may be limited by bottlenecks in the photochemical mechanism when the reaction occurs via long-lived excited states or intermediate species. This is particularly important for low-quantum-yield systems, where saturation of absorption leads to only a few photochemical transformations.

### The effects of temperature on PHB memories

From a technological point of view, it is very important to understand the limits imposed by temperature effects on



hole-burning memories. The effect of temperature on the minimum width of the hole and its lifetime will ultimately determine whether PHB memories are limited to liquid helium temperatures ( $\leq 4.2$  K) or whether they can be practically implemented at temperatures above 4.2 K, and most importantly, whether they can be implemented at temperatures above the boiling point of liquid nitrogen (77 K).

Assuming a system whose excited-state lifetime is temperature-independent, there remain at least three different temperature-dependent phenomena which influence the nature and existence of a photochemical hole burned in a photochromic amorphous system. These are electron-phonon coupling, thermally assisted changes in the guest-host configurations, and thermally activated reverse chemistry. Electron-phonon coupling, the most fundamental of these phenomena, is an effect resulting from the interaction between the impurity chromophore (*i.e.*, the solute) and its environment, in particular, its local environment in amorphous systems. There has been some theoretical work developed to describe aspects of this phenomenon, as well as calculation intended to predict the effect of electron-phonon coupling on the shape of a photochemical hole as a function of temperature [19, 20]. A discussion of these theories is not within the intended scope of this work; however, it is useful to describe this phenomenon qualitatively. The extent of influence that temperature has on electron-phonon coupling and consequently on a homogeneous photochemically burned hole depends on three factors. First, it depends on the number of phonon states available, which is expected to be large in amorphous environments. Second, it depends on the strength of the interactions between the chromophore and its environments. Third, it depends on the nature of the transition, where weakly coupled transitions leading to relatively undistorted excited states are the least affected by phonons [17, 19].

The principal consequence of electron-phonon coupling is to increase the uncertainty of precisely exciting a pure electronic transition by increasing the probability of phonon-state participation in the excitation process. Experimentally, this means that it is not usually possible to burn the narrowest holes at elevated temperatures due to increased  $T_2$  processes arising from thermal population of phonon states [see Eq. (1)]. It also means that narrow holes which are burned at very low temperatures must appear broadened at elevated temperatures, because they also are probed by measuring the same type of electronic transitions subject to the same temperature-dependent processes. The phenomenon is demonstrated in Fig. 10(a) for a photochemically burned hole in  $H_2Pc/PMMA$  at 4.2 K with a laser of  $0.08\text{-cm}^{-1}$  bandwidth. The holewidth at 4.2 K is equal to  $0.34\text{ cm}^{-1}$ . When the same system is warmed to 10 and 15 K,

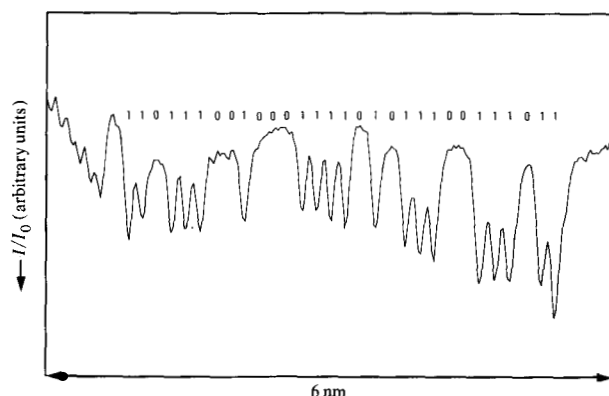


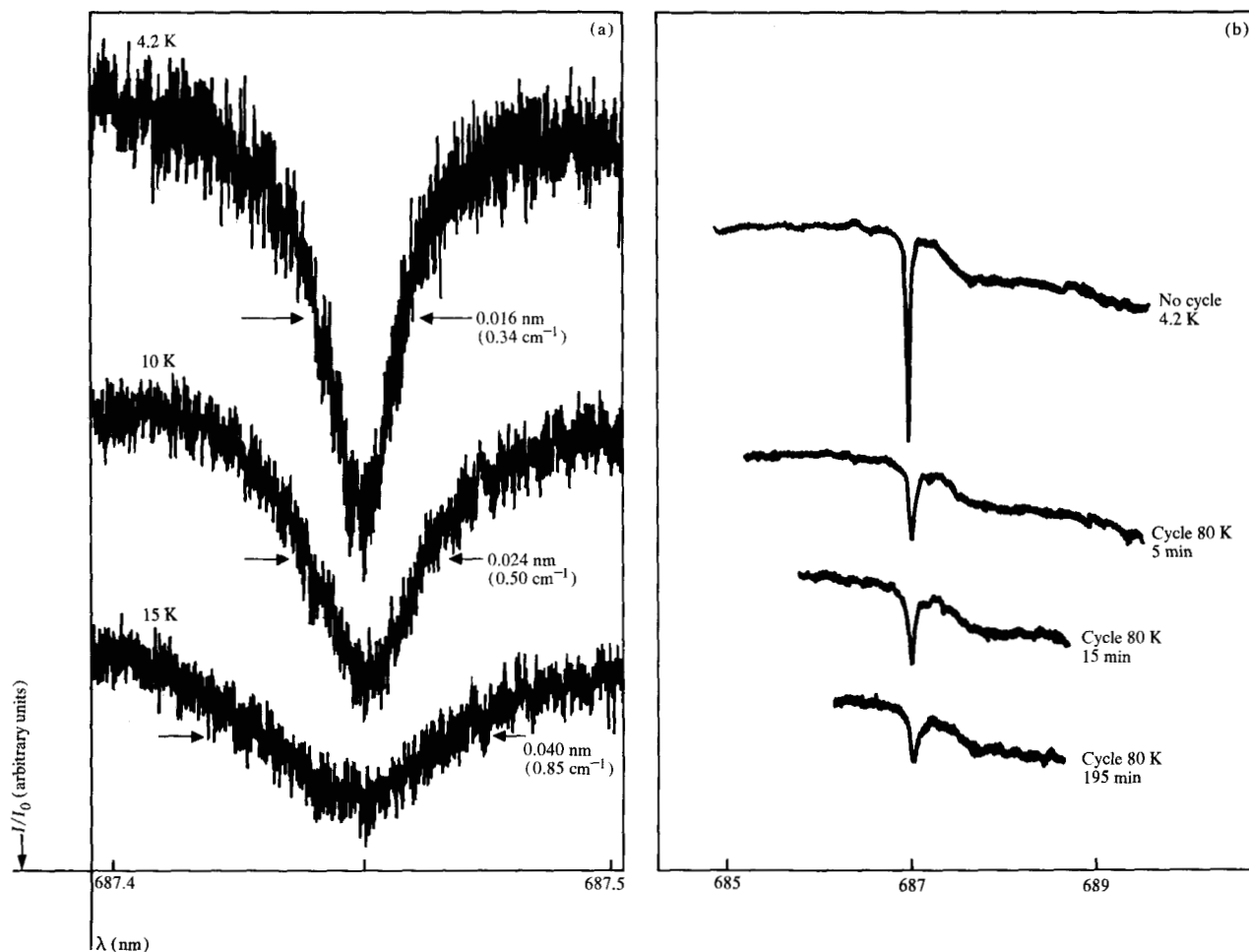
Figure 9 Multiple PHB in  $H_2Pc/PMMA$  at 4.2 K recorded as a difference spectrum with an optical multichannel analyzer. Presence and absence of holes designated by ones and zeros, respectively.

the holewidth increases to about  $0.50$  and  $0.85\text{ cm}^{-1}$ , respectively. If the system is recooled to 4.2 K and all thermal motion is again reduced, the original photochemically burned hole is totally recovered, still with a  $0.34\text{-cm}^{-1}$  holewidth.

Empirically, it has generally been found that at temperatures above 10 K the homogeneous linewidth usually increases as a function of the temperature squared [18, 19]. With regard to hole-burning memories, the fundamental limit imposed by electron-phonon coupling is one of reducing the  $I/H$  ratio (by increasing the homogeneous width) and also reducing the hole depth as temperatures increase. We recall that the inhomogeneous width is relatively temperature-independent. For the case of  $H_2Pc/PMMA$ , the holewidth at 50 K becomes so broad and its depth so shallow that it is difficult to measure. We find the holewidth at this temperature to be about  $6.5\text{ cm}^{-1}$ , which gives an  $I/H$  ratio of 52. Similar or worse limits are usually observed for other amorphous hole-burning systems. Consequently, PHB memories using only one inhomogeneously broadened system are not likely to be easily implemented in amorphous organic media above 77 K.

The effect of temperature on electron-phonon coupling as already described serves principally to broaden an absorption line by increasing the uncertainty of the excitation process. One can burn narrow holes in a photochromic memory system at low temperatures where uncertainties are minimized, but when the temperature of the system is raised, the holes appear broadened. The spectroscopic information, however, can often be fully recovered by recoiling the system to the temperature at which the holes were originally burned. Even though reading and writing the narrowest hole





**Figure 10** (a) The effect of temperature on the homogeneous width of a photochemical hole, burned in  $H_2Pc/PMMA$  at 4.2 K. Note that the ordinate is offset for each spectrum. (b) The effect of temperature cycling to 80 K on a photochemical hole burned in  $H_2Pc/PMMA$  at 4.2 K. Note that the ordinate is offset for each spectrum. All spectra were recorded at 4.2 K.

for maximum information density appears restricted to the lower temperatures, the nondestructive temperature-cycling phenomenon presents the possibility of storing the same high information density inscribed at low temperatures but archivially maintained at elevated temperatures.

The limits at which temperature cycling of photochemical holes is nondestructive in amorphous media depend on a second type of temperature-dependent phenomenon. Unlike electron-phonon coupling, it is totally a ground-state phenomenon. Nevertheless, it too depends on the nature of the chromophore and its environment and on their mutual interactions. Figure 10(b) shows the effect of cycling a photochemical hole in  $H_2Pc/PMMA$  from 4.2 to 80 K for 5 min and back to 4.2 K, then cycling the same hole from 4.2 to 80 K for 10 min more and back, and finally cycling the hole to 80 K for 195 min before recooling to 4.2 K. In all

cases, the hole is measured at 4.2 K. Temperature-cycling the system to 80 K results in about a 50% loss of the integrated area of the hole while the apparent width of the hole at 4.2 K is increased to about  $2\text{ cm}^{-1}$ . The process seems to be one of filling the hole rather than broadening it. Most importantly, the hole filling occurs principally in the initial 5-min cycle, and allowing the system to further equilibrate at 80 K for 15 min and then for 180 min has only a small added effect [Fig. 10(b)]. We concluded that only a selected number of low-energy sites are thermalized at 80 K while the others remain stable at this temperature. For temperature cycles to as high as 50 K, on the other hand, there is only a slight permanent effect on the depth and width of the holes (about a 10% loss in area). It seems possible, therefore, to store high-density hole-burning information for a considerable period of time at this temperature using  $H_2Pc/PMMA$ .

We find the temperature-dependent cycling to be strongly dependent on the host material. For example, when a 50% copolymer of methyl methacrylate and styrene is used as the host matrix, about half of the photochemical hole is lost (filled) during a 4.2- to 50-K cycle while less than 10% is lost when pure PMMA is the host. The temperature-dependent hole filling becomes much worse when the host for H<sub>2</sub>Pc is a glass composed of 2-methyltetrahydrofuran and 10% by volume 1-chloronaphthalene. In this case, the hole can be cycled only to 10 K before substantial hole deterioration begins to occur. In view of the site instabilities that we observe for organic glasses where partial hole deterioration occurs even at 10 K compared to the relatively stable polymer systems, mobility of the solvent environment or parts thereof relative to the chromophore (or vice versa) may play a major role in the hole-destruction process. If the analysis is accurate, one would predict that polymer-bound photochromic systems or photochromic molecules embedded in highly crosslinked polymers would likely yield photochemical holes with exceptional thermal durability. This hypothesis, however, has yet to be tested.

If holes burned in the H<sub>2</sub>Pc/PMMA system are elevated to approximately 100 K, they are totally destroyed and do not reappear even if the system is recooled to 4.2 K. This loss may be due to a third temperature-dependent phenomenon characteristic of many photochromic systems, namely reversible thermal chemistry. In this case, thermal tautomerization of the central protons is likely to occur at elevated temperatures. Unfortunately, we cannot say how important thermal tautomerization is for H<sub>2</sub>Pc/PMMA at 100 K, since an activation energy for the process is not known.

Another possible cause for the permanent destruction of holes at 100 K in this system may be related to the temperature-selective site deteriorations already discussed. From studies of the temperature-dependent phosphorescence of several chromophores in PMMA matrices, it has been reported that certain rather sharp deteriorations of phosphorescence beginning at specific temperature ranges are due to the onset of particular motions within the PMMA matrix [30]. At about 150 K and below, for example, they attribute the reduction of phosphorescence to the rotation of the ester methyl groups of the PMMA. The possibility that PHB deterioration at about 100 K is due to the specific rotation of these methyl groups in PMMA is important because it would represent the first example where the thermal influence on a photochemical hole could be attributed to one known specific process. It would also provide hope for using spectroscopic hole burning to study the dynamics of specific thermal processes such as conformational changes.

## Summary

We have described some processes which limit frequency multiplexing of optical storage by PHB in amorphous systems. The approximate spectroscopic limit for information density stored by PHB in any one system is equal to the ratio of the inhomogeneous holewidth to the homogeneous holewidth, the I/H ratio, at the temperatures where the holes are burned. Although the inhomogeneous width is relatively temperature-insensitive, the influence of temperature on the homogeneous width is usually strong and has a profound influence on the limiting I/H ratio. The effect of temperature on phonon-state population and on electron-phonon coupling fundamentally limits writing and reading of the narrowest photochemical holes to the lowest temperatures possible, usually less than 20 K. These effects make it impractical to write or read holes at 77 K or above for the systems studied here. High-density storage of information seems obtainable at 77 K with H<sub>2</sub>Pc/PMMA, as long as the PHB information is written and read at the lower temperatures. Limits imposed by the broad phonon wing accompanying PHB in amorphous systems can be reduced in quinizarin/alcohol systems by irradiating with broadband light subsequent to PHB. At 4.2 K, we demonstrate the feasibility of burning up to 1000 photochemical holes in one system. Carried to the diffraction limit for visible and near-ir light, this documents the possibility of a 10<sup>11</sup>-bit/cm<sup>2</sup> memory using a three-dimensional x-y-ν scheme, where ν is the added frequency dimension implemented by PHB.

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