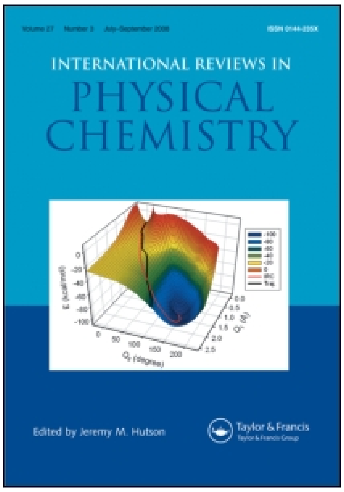

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Non-photochemical hole burning—versatility and theoretical status

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A summary of the mechanism for burning of non-photochemical holes in amorphous solids is presented. The universality of the technique and applications to vibrational spectroscopy and to studies of biologically significant molecules are reviewed and illustrated with examples of previously unpublished data. In addition, the various theories of optical dephasing in amorphous solids are summarized.

1. Introduction

A non-photochemical mechanism for the production of holes in the inhomogeneously broadened absorption spectra of impurity molecules in organic glasses, originally observed by Kharlomov *et al.* (1974, 1975), was first proposed by Hayes and Small (1978 a, b). According to this mechanism, illustrated schematically in figure 1, two conditions are necessary for non-photochemical hole burning (NPHB): (*a*) the presence of a distribution of nearly isoenergetic configurations of solvent molecules and (*b*) a coupling between the impurity and solvent such that electronic excitation of the impurity induces an orders-of-magnitude increase in the rate of interconversion of these configurations. The existence of such a distribution of low-energy excitations had previously been proposed (Anderson *et al.* 1972, Phillips 1972) to explain anomalies in the low-temperature, ($T \lesssim 1$ K) specific heat and ultrasonic attenuation of glasses and

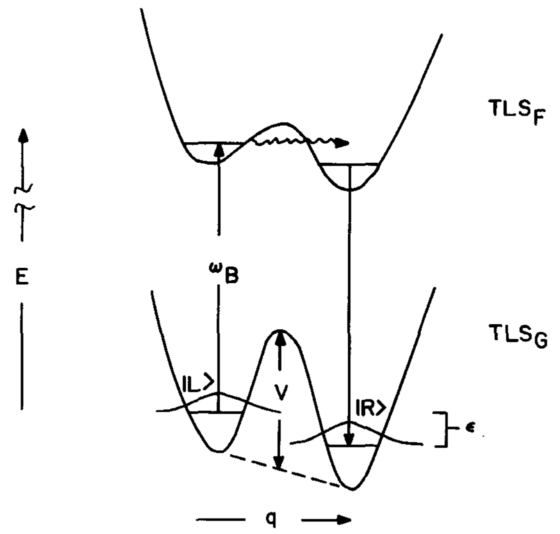

Figure 1. Potential energy diagrams for a two-level system coupling to an impurity in its ground (TLS$_G$) and excited electronic state (TLS$_F$). TLSs are characterized by a distribution of barrier heights, V, zero-point energies, E, and well separations. There may also be a variety of different TLS coordinates, q.

has since been used in numerous theories proposed to explain a variety of experiments which measure the dephasing of electronic excitation and energy transport in glasses. This distribution of configurations is commonly referred to as the two-level system (TLS) model and TLSs are generally accepted as being a universal property of the amorphous state. For a full discussion of the NPHB mechanism and review of the theories of dephasing in glasses available through 1982 the reader is referred to the paper by Small (1983). In this paper we will focus on our more recent applications of NPHB as well as present a discussion of progress in the understanding of dephasing in glasses.

2. Experimental

Experimental and procedural methods used have been described previously (Carter *et al.* 1983 and references therein). However, for completeness, a brief summary of the experimental techniques shall be given. Holes were probed at low temperature in a Janis variable temperature helium cryostat by one of three methods: (1) by absorption via a home-built high-resolution, low-noise double-beam spectrometer (typically $\lesssim 0{\cdot}05$ Å), obtained by using a JY HR-1500 monochromator (resolving power $\sim 2{\cdot}5 \times 10^5$) and lock-in amplifiers, (2) by transmission using the same monochromator as above, or (3) by photoexcitation, i.e., monitoring the total fluorescence while scanning a dye laser, thereby reproducing the absorption spectrum. Holes were burned by any of a plethora of lasers; a pulsed Quantel or Quanta-Ray Nd–YAG pumped dye laser, a pulsed Chromatix CMX-4 laser, a cw Control or Coherent argon ion laser, a cw Coherent ring dye laser or a cw Spectra-Physics helium–neon laser. The choice of burn laser generally depended upon availability, spectral range and limiting linewidth of the laser (1·5 to 0·002 cm^{-1}) for each particular system of interest. Samples consisted of some impurity molecule or ion doped into a host. The dopants used were always of high purity and when necessary were purified by zone refining, recrystallization or vacuum sublimation. Impurity concentrations were typically adjusted so that an optical density of $\sim 0{\cdot}5$ was obtained yielding concentrations ranging from 10^{-5} to 1·5 M. Due to the high diversity of host materials (see table 1), a variety of cooling rates, from less than a minute to many hours for the touchiest glasses, were required to cool the samples to liquid helium temperatures. To minimize thermal gradients, soft glasses were enclosed by a copper cylinder and the polymers were firmly attached to copper plates. Temperatures were accurately measured with a silicon diode sensor.

3. Results and discussion

3.1. *Universality of NPHB*

Given the universal nature of TLS in amorphous solids one might expect, based on the proposed mechanism (Hayes and Small 1978 a, b) that NPHB would be a universal phenomenon, i.e. independent of the particular natures of the impurity or the matrix, requiring only that the matrix be amorphous. Over the past few years, a large variety of systems have been surveyed for their propensity toward hole burning. Table 1 is a partial summary of those survey experiments. The table consists mainly of results obtained by the present authors but also contains other published reports in which a non-photochemical nature can be ascribed to the holes. The table indicates, for the systems listed, if hole burning has been observed and, if it has, the hole-burning facility. We hasten to add that the indicated facilities are meant to serve only as a rough guide. They are based on the time and burn flux required to burn a hole corresponding to an optical density change of ~10 per cent. The hole-burning facility is not necessarily correlated with the hole-burning quantum efficiency.

From the table, it can be seen that there are systems in which hole burning has not been observed. This can be understood within the mechanism depicted in figure 1, in the following way. NPHB requires a change of the potential energy surface for the TLS to be induced by electronic excitation of the impurity. Furthermore, the effect of this change must be to increase the interconversion rate between TLS wells from a time-scale of hours to a time-scale on the order of the lifetime of the excited state (i.e., $\sim 10^{-8}$ s). The magnitude of the electron–TLS coupling which induces this change will vary both with the nature of the impurity and with the nature of the TLS modes, i.e. with the particular atomic displacement coordinate, q. For most glasses identification of the TLS modes has not been made. For example, NPHB experiments on tetracene show that hole burning is more facile in hydrogen-bonding glasses suggesting that the TLS responsible for hole burning may be hydroxyl groups. Indeed, it has been shown that the efficiency of hole production is dependent upon deuteration whereas dephasing is not (Fearey *et al.* 1983 b). In summary, for systems where hole burning has not been observed, it might be inferred that the electron–TLS coupling is not strong enough to induce the substantial TLS interconversion rate in the excited state required for NPHB. However, another possibility is that TLS interconversion in the ground state is too rapid to permit the observation of a hole on the time-scale of the experiment. Thus, one cannot say that hole burning is impossible in such a system, but only that under the conditions used it was not observed.

3.2. *Vibrational spectroscopy*

In view of the diversity of materials which can form low-temperature amorphous solids, the existence of systems in which hole-burning facility is so low as to be unobservable on a reasonable time-scale does not limit potential applications of NPHB. One area of application is in vibrational spectroscopy of large molecules and especially biologically important species (*vide infra*). For such molecules NPHB spectroscopy can yield high-resolution vibrational spectra. The presence of polar substituents on such molecules, which often leads to additional inhomogeneous broadening through either charge transfer interactions or a strong electron–phonon coupling, can be utilized to ensure that the electron–TLS coupling will lead to hole formation. For example, in figure 2 is shown a portion of the absorption spectrum of cresyl violet perchlorate in polyvinyl alcohol (PVA). The individual vibronic bands are all inhomogeneously broadened with widths greater than the vibronic splittings (i.e., $\Gamma_{\text{inhom}} \gtrsim 500\,\text{cm}^{-1}$). Thus prior to hole burning the spectrum consists of a single, unstructured absorption with a width on the order of $1000\,\text{cm}^{-1}$. As shown in the figure, the underlying vibronic structure can be revealed by the use of hole burning. In this particular case a hole was burnt at frequency ω_B, on the high-energy side of the broad absorption. The satellite holes appearing at lower energy correspond to the fundamental vibrations of the molecule, as well as combinations and overtones of the fundamentals. In general, the sample may be burnt anywhere in the broad absorption and vibronic holes will appear at both higher and lower energy. It should be pointed out that whether or not the resolution shown in figure 2 is obtainable is dependent upon the linear electron–phonon coupling between the molecule and the matrix as well as other factors. When this coupling is strong, the hole (and the satellite holes) will be accompanied by a phonon sideband hole. The relative intensities of phonon and phonon-less sideband holes is determined by the Debye–Waller factor for the

Table 1. Summary of NPHB systems examined.

	← Hydrogen bonding							→ ← Non-hydrogen bonding						→
	← Organic glasses				→ ← Polymers					→ ← Organic glasses			→
	methanol/ethanol	glycerol/dimethylsulphoxide/dimethylformamide	ethanol/methyltetrahydrofuran	glycerol/ethanol/water	ethyl ether/ethanol/water	polyacrylic acid	polyvinyl alcohol	polymethylmethacrylate	polyvinylcarbazole	polystyrene	decalin	pentane/methylpentane/methylcyclopentane	amorphous anthracene	silicate glass
Aromatic hydrocarbons														
naphthalene	*													
anthracene	*													
tetracene	**	**			**			no	no	no	no	no	no	**†
pentacene								*‡		no				
phenanthrene	**													
pyrene		**												
perylene	**§													
azulene			*											
phenylazaazulene				*										

Organic dyes									
rhodamine 560					**				
rhodamine 640				***	***	**	no	no	
cresyl violet	***	***		***	***		*		
nile blue				***	***				
oxazine 720				***	***				
oxazine 725				***	***				
oxazine 750				*					
DCM								no	
Rare-earth ions									
Pr^{+3}					**				*¶
Nd^{+3}					**				*¶
Biomolecules									
chlorophyll a			*‖					***	
chlorophyll b			*‖					***	

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* Hole-burning facility is weak.
** Hole-burning is moderately facile.
*** Hole-burning is facile.
† Jankowiak and Bässler (1983)—also observed NPHB for tetracene in amorphous substituted anthracenes.
‡ Mollenkamp and Wiersma (1985).
§ Kharlamov *et al.* (1974, 1975)—solvent was glassy ethanol.
¶ MacFarlane and Shelby (1983).
‖ Avarmaa *et al.* (1981).

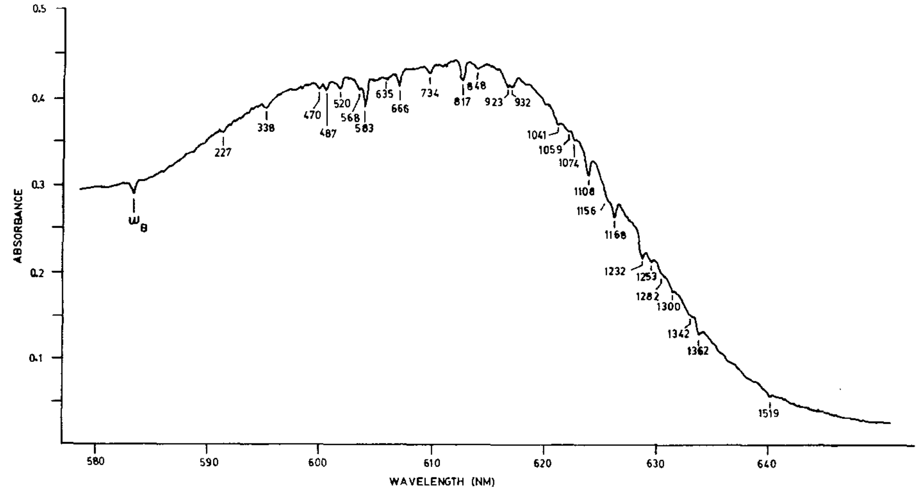

Figure 2. Hole burning of cresyl violet perchlorate in PVOH. The sample was burned for 1 min at 5830 Å. Laser flux ~100 mW/cm^2, $T=4{\cdot}2$ K.

transition. When the Debye–Waller factor is small, the phonon sideband holes will be intense and may limit the resolution of vibronic bands.

A somewhat unusual example of phonon sideband holes is shown in figure 3. For these systems, oxazine 725 perchlorate in PVA and in polyacrylic acid (PAA), well resolved phonon sideband holes symmetrically displaced at $\pm 45\,\mathrm{cm}^{-1}$ relative to the burn frequency are observed. The observation of both lower and higher-energy phonon sideband holes is explained by considering that the broad absorption consists of a distribution of homogeneously broadened absorptions consisting of a phononless line and a higher-energy phonon band. Thus at the burn frequency, those molecules which absorb in their phononless line will produce a zero phonon hole and a higher-energy phonon hole. For other sites, which absorb at the burn frequency through their phonon side bands, a hole due to zero-phonon absorption will occur at lower energy. In many cases, only the lower-energy phonon hole is observed due to a large Debye–Waller factor.

One final comment on figures 2 and 3 is, that both of these systems, ionic dyes in hydrogen bonding polymers, are representative of a class of systems in which NPHB is very efficient. Measurable holes can be produced in these systems with exposure times of a few seconds and laser fluxes of ~1–25 mW/cm^2 (Fearey *et al.* 1983 a).

3.3. *NPHB of biomolecules*

As described above, the availability of a diverse selection of solvents which form amorphous solids provides matrices for the study of a variety of classes of molecules. As a prelude to the study of excitonic effects in self-aggregates (dimers) of chlorophylls, NPHB of chlorophyll monomers has recently been studied (Carter and Small 1985). This work is somehat akin to photochemical hole-burning studies on free-base porphin derivatives (see e.g., Thijssen *et al.* 1983). In those studies a hole is produced via phototautomerization of the porphin ring protons. In chlorophyll, however, the ring protons are replaced by a Mg(II) ion, blocking the photochemical mechanism. Hole burning of

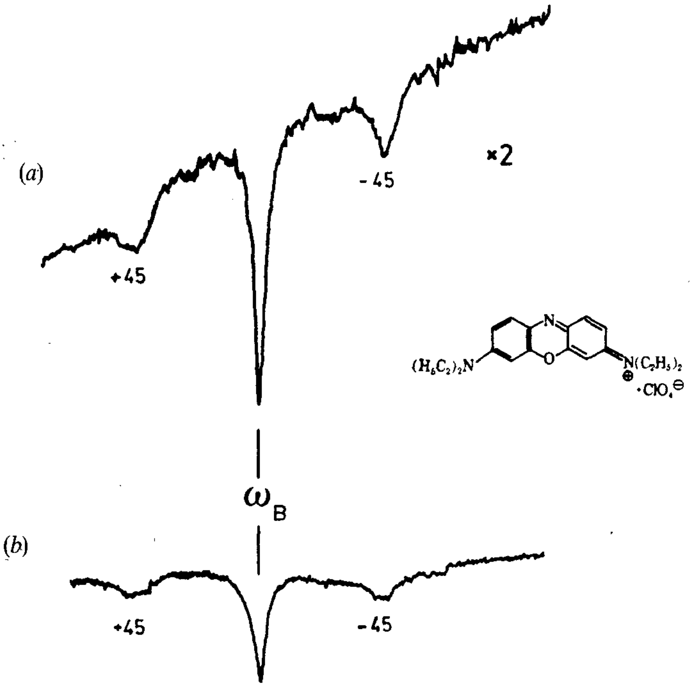

Figure 3. Hole burning of oxazine 725 perchlorate in (*a*) polyvinyl alcohol, (*b*) polyacrylic acid. Both holes were burnt at 6328 Å with a flux of ~25 mW/cm^2, with $T=5$ K. Spectrum (*a*) was burnt for 2 min; (*b*) for 12 min.

chlorophyll in ether has previously been observed and attributed to a non-photochemical process (Avarmaa *et al.* 1981). In the present work NPHB was observed for both chlorophyll a and chlorophyll b in a polystyrene film.

Figure 4 shows holes burnt in the spectra of chlorophyll b, and also illustrates laser-induced hole filling of the initial hole by subsequent burns at wavelengths away from the initial burn wavelength. Burn 1 at 15441·6 cm^{-1} represents a change in optical density (Δ_{OD}) of 10 per cent produced by a 1-minute burn with a laser power density of ~5 mW/cm^2. The width of the hole is 0·16 cm^{-1}. Shifting the burn frequency to lower energy and with a similar exposure a second hole is produced with depth and width similar to the initial hole. The burning of this hole results in a decrease of the intensity of the initial hole by ~13 per cent. A third burn at higher energy again produces a hole with Δ_{OD} ~10 per cent, and width ~0·16 cm^{-1} and fills both lower-energy holes. Hole 1 is now reduced by 33 per cent of its initial depth and hole 2 by 31 per cent. This hole filling as well as thermal annealing data (Carter and Small 1985) are indicative of the non-photochemical nature of the holes (Hayes and Small 1978 a).

Hole burning in the chlorophylls was extremely facile, i.e. relatively deep holes are produced with short exposure times and low power density. The holes produced, although somewhat broader than those observed in photochemical hole burning, are still narrow enough so that splitting which might occur (e.g. for dimeric species) can be resolved. Thus NPHB is a promising method of studying photophysics of biologically significant molecules.

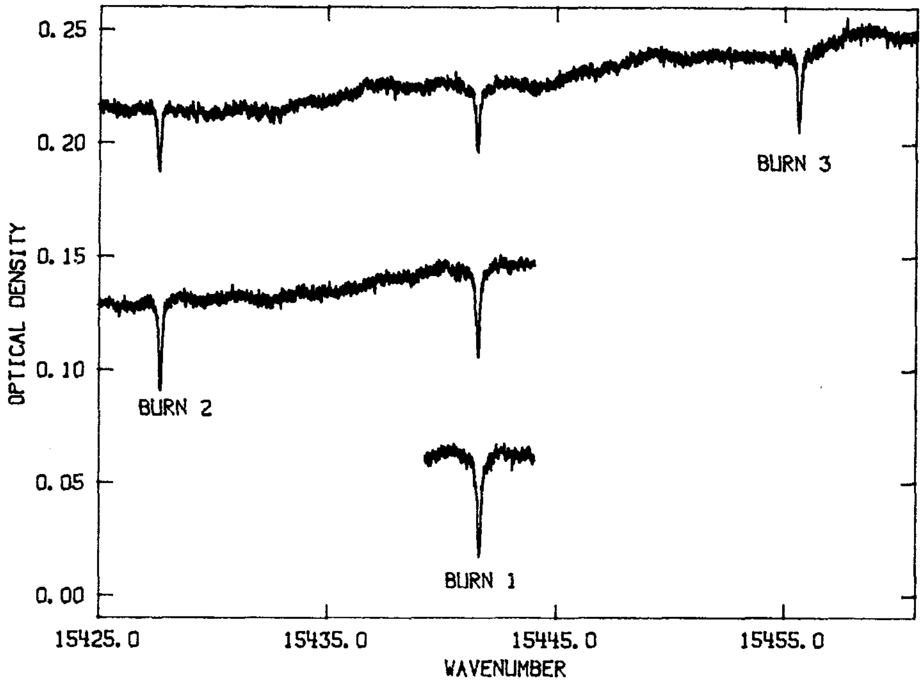

Figure 4. Hole burning of chlorophyll b in polystyrene. Holes were burnt for 1 min at 6476 Å with a flux of $\sim 5\,\mathrm{mW/cm^2}$, $T = 1{\cdot}9\,\mathrm{K}$.

3.4. *Optical dephasing in amorphous solids*

A general feature of homogeneous optical linewidths in both organic and inorganic glasses and in polymers at low temperature is that they are one to two orders of magnitude greater than those observed in crystalline solids. This difference, as well as differences in the thermal variation of linewidths between crystalline and amorphous solids, has been probed not only by NPHB but also by photochemical hole burning, fluorescence line narrowing and photon echoes. The variety of systems and techniques which are involved has prompted a number of theories which attempt to explain these large differences in dephasing times. In table 2, we have listed the various theories which have been proposed.

The starting point for all the theories is that the dephasing anomaly is primarily due to the glass TLSs which are coupled to the impurity. Additionally one must consider the vibrational modes of the solid (phonons). The coupling of the phonons to the TLS and/or to the impurity can be included in the system hamiltonian. In table 2 we have described which of the possible coupling modes are included in the various theoretical models. Having developed a model, it is then possible to obtain a solution for the optical lineshape assuming fixed values for the system coordinates. However, the TLSs have a broad distribution of energy asymmetries, barrier heights, and tunnelling frequencies. This in turn causes differences in the strengths of the TLS–impurity and TLS–phonon couplings. Thus it is necessary to average the lineshape function over the various distributions.

Table 2. Theories of optical dephasing in glasses.

Reference	Model used	Temperature dependence
Reinecke (1979)	Spectral diffusion due to strain-mediated coupling of impurity to TLS	T ($n(E)=\text{const}$)
Lyo and Orbach (1980)	Off-diagonal electrostatic coupling of TLS and impurity with diagonal phonon modulation	$T \longrightarrow T^2$ as $T \longrightarrow 0$ ($n(E)=\text{const}$)
Hayes *et al.* (1980, 1981)	Coupling of impurity to subset of TLS with maximum PAT rates	$T \longrightarrow T^2$ as $T \longrightarrow 0$
Morawitz and Reineker (1982)	Coupling of impurity to TLS and to low-lying optical and librational modes	T (except at very low T)
Reineker and Morawitz (1982)	Coupling of TLS to impurity and to phonons	T (except at very low T)
Lyo (1982, 1983)	Diagonal coupling of TLS and impurity with phonon modulation of TLS	$T^{4+\mu-9/s}$ ($V \propto \frac{1}{r^s}; n \propto E^{\mu}$)
Jackson and Silbey (1983)	Addition of dephasing due to local libration to model of Hayes *et al.*	$T^{1\cdot 3}$
Lyo and Orbach (1984)	Considered role of fractons in place of phonons in previous theory of Lyo	$T^{1+\bar{d}/4}$ ($N_{\mathrm{fr}} \propto E^{\bar{d}-1}$)
Reineker *et al.* (1984)	Coupling of TLS to impurity and to phonons	T (except at very low T)
Huber *et al.* (1984)	Spectral diffusion due to diagonal interaction between impurity and TLS	$T^{1+\mu}$ ($n \propto E^{\mu}$)
Molenkamp and Wiersma (1985)	Dipolar coupling of impurity and TLS	T^{1+a} ($n \propto E^{a}$)

It is in the details of taking this average that the major differences between the theories arise. It is beyond the scope of this paper to delve into the intricacies of the various averaging procedures. Rather we will restrict ourselves to a few general comments. In most of the theories, following the model of Anderson *et al.* (1972) and of Phillips (1972) the averaging assumes that the TLS density of states is constant. In some of the more recent theories this condition is relaxed so that the density of states is considered to vary slowly with the energy, i.e. $n(E) \propto E^{\mu}$, $\mu < 1$. The exceptions to this general trend are Hayes *et al.* (1981) who argue that the dephasing is dominated on average by one type of TLS with a dephasing frequency in a maximum range or interval. The distribution function for these particular TLSs may then be sharply peaked although the entire TLS distribution will still obey the near-constant density-of-states relationship.

Finally, let us remark that a fully satisfactory theory remains to be developed. Those theories which purport to explain all the observed experimental data tend to do so at the expense of being predictive, i.e. the parameters required to reconcile theory and experiment are themselves not available but must be inferred from the experiment.

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