S. Völker
R. M. Macfarlane

Photochemical Hole Burning in Free-Base Porphyrin and Chlorin in n-Alkane Matrices

In inhomogeneously broadened lines, selective photochemistry with narrow band lasers leads to photochemical hole burning. We describe this phenomenon with particular reference to free-base porphyrin (H_2P) and chlorin molecules in n-alkane matrices at low temperatures. It is shown that hole burning, which is permanent at low temperatures, can be used to study homogeneous optical dephasing processes as a function of temperature, to measure fast vibronic relaxation, and to assign complex vibronic spectra. Some of the parameters that are important to the potential use of photochemical hole burning for information storage in inhomogeneously broadened lines are measured and discussed.

Introduction

The systems of concern to us here are those in which photochemically active molecules are present as dilute *guests* in a solid *host* matrix at low temperatures. In such systems the 0-0 electronic absorption lines, as well as many of the vibronic lines, are inhomogeneously broadened because of the slightly different environments in which the molecules sit; see Fig. 1(a). In n-alkane Shpol'skii matrices [1] this inhomogeneous width is usually a few cm^{-1}; in organic glasses such as alcohol or ether-isopentane-alcohol (EPA), or in polymer films such as polystyrene, we typically find widths of hundreds of cm^{-1}.

Irradiation into these inhomogeneously broadened lines with a narrow band laser of width Γ_ℓ and frequency ω_0 can induce resonant molecules to undergo a photochemical transformation such that they absorb at a different frequency. [*Editor's note:* The symbol $\Delta\omega$ is used for bandwidths in other papers in this issue.] This creates a hole in the original absorption band at ω_0; see Fig. 1(b).

If the laser width is negligible, the hole width is determined by the homogeneous relaxation of the photoactive molecules. Because the optical transition energy depends on the crystalline environment in a complicated way, the laser is not selecting molecules in a specific environment, but a set of molecules in different environments, all absorbing at ω_0. For this reason the photoproduct band ("antihole") will, in general, be broader than the hole. That is, the same relationship between transition energy and environmental parameters does not hold for the photoproduct; see Fig. 1(b). A sharp antihole would require unusual conditions, *i.e.*, that the photoproduct have the same functional dependence of the transition energy on the environment as do the original molecules. This has not yet been observed. In Fig. 1(b) the photoproduct absorption line A_2 has a width that is less than the inhomogeneous width of A_1 but greater than the hole width; thus, no sharp antihole exists in this case.

Photochemistry that is induced by the laser may be irreversible (*e.g.*, the photofragmentation of dimethyl tetrazine in durene [2, 3]), or it may be reversible in the sense that irradiation into the photoproduct fills the hole and reconstitutes the original line (*e.g.*, phototautomerism in free-base porphyrins [4, 5]).

The observation of photochemical hole burning requires that photochemistry occur upon excitation into inhomogeneously broadened bands. These are normally found in the case of zero-phonon lines, usually the electronic origin (0-0 transition) [6, 7], although sharp vibronic lines can also be inhomogeneously broadened. Single-photon photochemistry can occur directly from

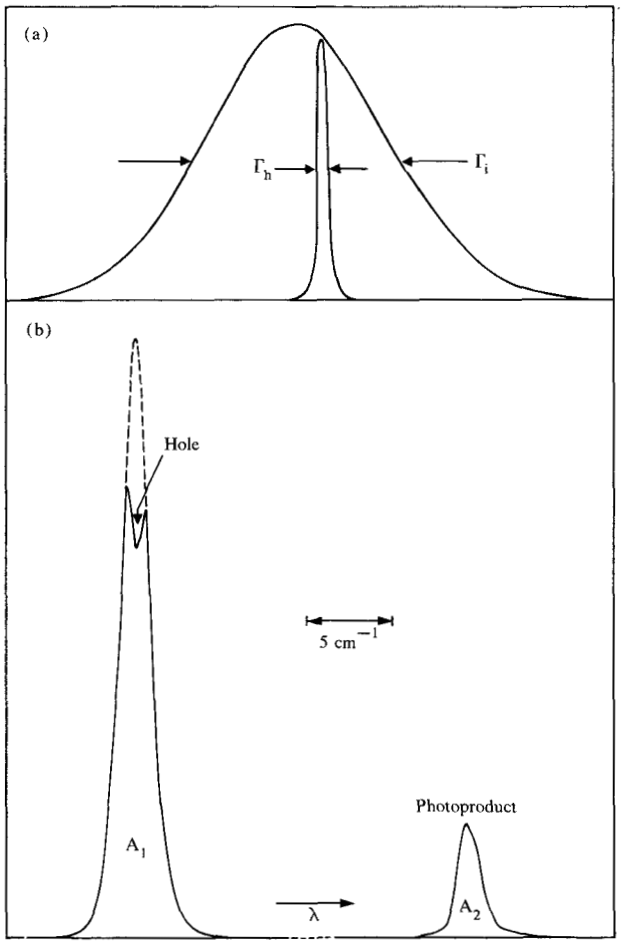

Figure 1 (a) Schematic diagram of an inhomogeneously broadened line of width Γ_i, which is the envelope of individual electronic transitions of homogeneous width Γ_h. (b) Illustration of a laser-induced photochemical hole burned in the 0-0 A_1 line of free-base porphyrin (H_2P) in n-octane at 2 K. Here, the photoproduct absorption line A_2 is somewhat broadened by the scanning laser.

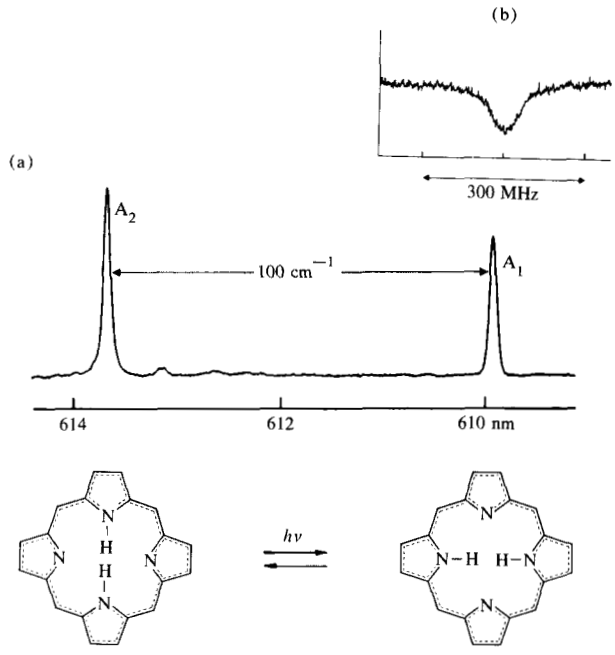

Figure 2 (a) Excitation spectrum of the 0-0 lines of the $S_1 \leftarrow S_0$ transition of H_2P in n-hexane showing the frequency difference ($\approx$100 cm^{-1}) between the two illustrated tautomeric forms (1, 2) in a single type of site. Irradiation into the line A_1 transforms it into A_2 and *vice versa*. (b) A hole burned in line A_1 at 4.2 K with a laser of width $\approx$2 MHz.

the level excited, or from any below it. However, in many cases more energy than that of the 0-0 transition is required to induce photochemistry. The variety of molecules accessible to study can therefore be significantly increased by using a two-photon, two-step process in which the first photon provides the selectivity and the second, the extra energy [3].

Photochemical hole burning (PHB) was first observed in 1974 by Gorokhovskii *et al.* [6] and by Kharlamov *et al.* [7]. They used fixed frequency lasers with accidental coincidences with inhomogeneously broadened molecular absorptions. Subsequent work [2, 5, 8–17] has frequently involved the use of tunable dye lasers that permit the study of selective photochemistry in a wide range of molecules and hosts. Questions that may be answered by using photochemical hole burning include the following:

- What is the mechanism for photochemistry following excitation in the 0-0 line?
- In what way does the photochemistry depend on the nature of the molecular environment?
- Can holes be burned in the photoproduct bands?
- Do selectively produced photoproducts exhibit narrow absorption lines (*i.e.*, do sharp antiholes exist)?
- What limits the width of the photochemical holes and how does this width depend on temperature and the host material?
- Can hole burning be observed in excited vibronic states?
- How are the holes affected by the application of external magnetic and electric fields?

In the following sections we describe work that answers some of these questions.

In addition to providing a wealth of spectroscopic information on photochemically active molecules, PHB has a potentially dramatic practical application. Since the width of a hole is often only 10^{-3} to 10^{-4} of the inhomogeneous linewidth Γ_i, many holes can be burned in a line; this provides a frequency dimension for optical information storage [18].

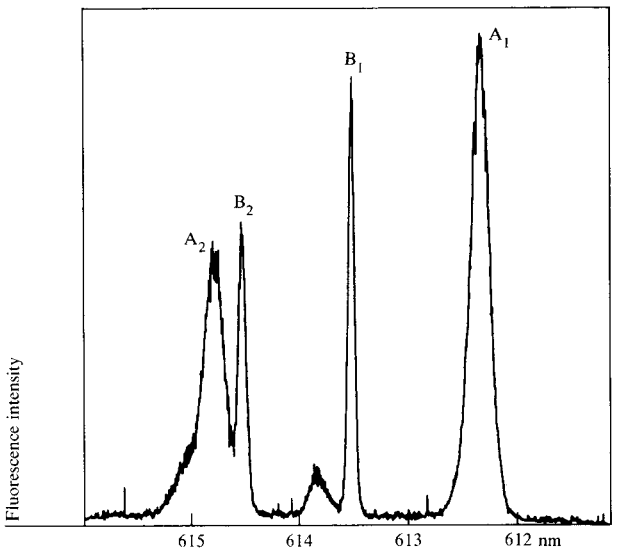

Figure 3 Fluorescence spectrum of the 0-0 lines of the $S_1 \rightarrow S_0$ transition of H_2P in n-octane showing lines for tautomers 1 and 2 of the stable A site and for tautomers 1 and 2 of the metastable B site.

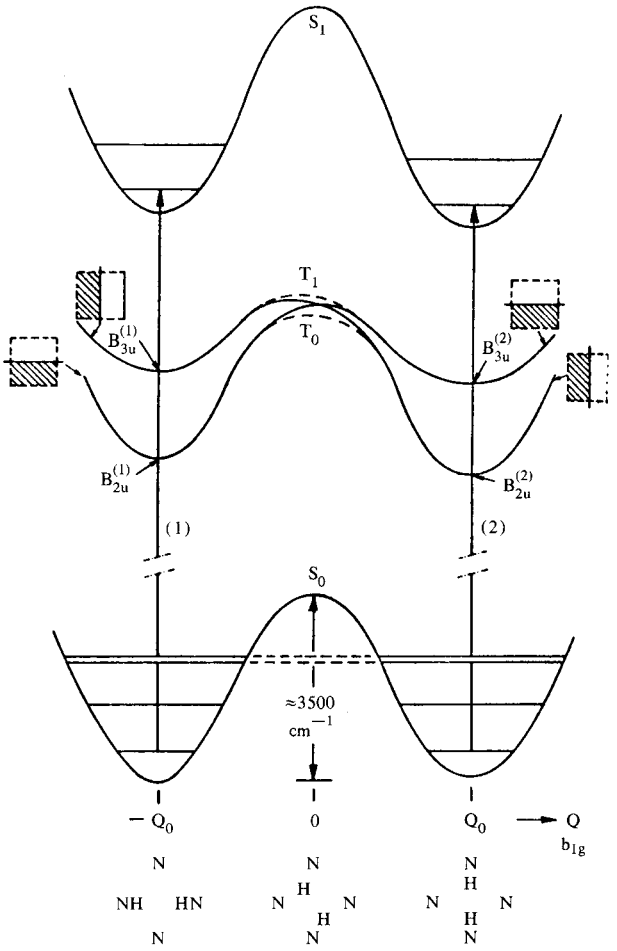

Figure 4 Schematic diagrams of the energies of the two lowest singlet (S_0, S_1) and triplet (T_0, T_1) states in H_2P as functions of the nuclear coordinate Q, illustrating the mechanism for phototautomerism.

Spectroscopic properties of free-base porphyrin (H_2P) in n-alkane Shpol'skii matrices

Porphyrin is a cyclic tetrapyrrole which, in its metallo and derivatized forms, is a central component in such important biological molecules as chlorophyll, cytochrome, and hemoglobin. In the free-base (metal-free) form, there are in the inner part of the molecule two protons hydrogen-bonded to opposite nitrogen atoms (see Fig. 2). From nuclear magnetic resonance (nmr) measurements in liquid solutions at room temperature [19, 20], it is known that the protons undergo a tautomerism between the pairs of opposite nitrogens. This motion ceases at low temperatures. When a diluted solution ($\approx 10^{-6}$ molar) of porphyrin in an n-alkane is frozen into a Shpol'skii matrix, the solute molecules are predominantly oriented in a few specific sites [5, 8, 21, 22]. Electron spin resonance (esr) experiments show that in each of these sites the porphyrin molecule can occur in two orientations or tautomeric forms, having the N—H · · · H—N directions at right angles [21]. The spectrum of H_2P in n-hexane shows a single site and two absorption lines for the $S_1 \leftarrow S_0$ transition corresponding to the two tautomers; see Fig. 2(a). These can be reversibly transformed by irradiation in the 0-0 line of either one.

Different n-alkane hosts have a different crystal field interaction with the two tautomers in each site, as well as with the different sites present [22, 23]. In n-alkanes such as heptane, octane, nonane, decane, and dodecane, the situation is more complicated than in hexane because of the presence of multiple sites (A, B, · · ·) with different geometries. We have observed that in each of these sites pairs of tautomers occur, and again they can be reversibly phototransformed into each other. As an example, Fig. 3 shows a spectrum of H_2P in a quickly frozen polycrystalline sample of n-octane, in which the metastable B site is present (tautomers B_1 and B_2) [5, 8] in addition to the stable A site (tautomers A_1 and A_2).

Photochemical hole burning in H_2P was first observed in n-octane [5] and studied later at high resolution [8, 14]. These holes are permanent at low temperatures due to the large energy barrier between the two tautomeric forms. The absorption spectra and holes were detected by measuring the excitation spectrum, *i.e.*, by scanning a probe laser through the absorption and monitoring the fluorescence signal with $\lambda \geq 630$ nm. The laser power density

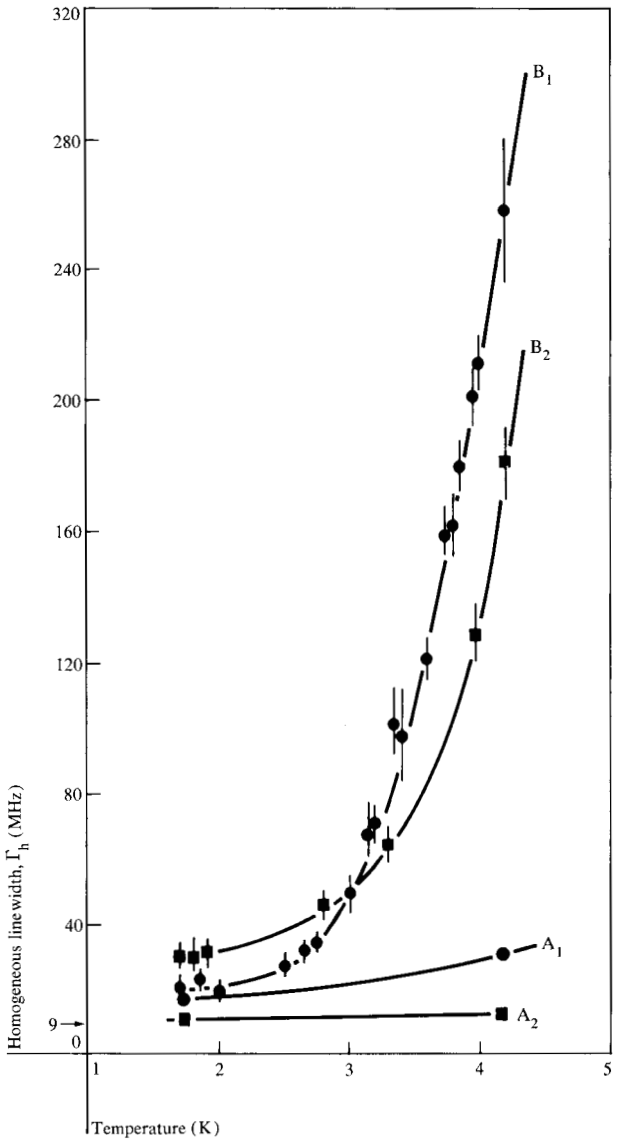

Figure 5 Temperature dependence of the 0-0 homogeneous linewidth of H_2P for two crystallographic sites (A, B) in n-octane measured using PHB. The limiting width at 0 K $[2\pi\Gamma(0)]_A^{-1}$ approaches that determined by the 17-ns decay time (*i.e.*, 9 MHz).

used for hole burning is typically $\approx 100\ \mu W/cm^2$ for a one-second burn time; for probing, it is about 10^{-4} of this. The laser bandwidth Γ_ℓ is ≈ 2 MHz. Figure 2(b) shows a hole burned under these conditions. In the case of a shallow hole and $\Gamma_\ell << \Gamma_h$, the hole has a width of $2\Gamma_h$.

In H_2P the quantum yield for photochemistry is very small (<1%) [5, 24], so the molecules must be optically pumped many times to burn a hole [8]. The proposed mechanism for phototautomerism [5] is illustrated in Fig. 4, which shows potential energy curves for the two lowest triplet (T_0, T_1) and singlet (S_0, S_1) states of H_2P as a function of the nuclear coordinate Q that describes the rotation of the two inner protons. Experiments have shown that crossing from one potential well to the other does not take place in S_1 [5] or in the lowest triplet T_0 [24], but probably does occur during intersystem crossing $S_1 \rightarrow T_0$ because of vibronic mixing of the T_1 and T_0 potential curves [5]. This allows the molecule to cross from $-Q_0$ to Q_0 with a small but finite probability. The nmr measurements [20] show that the barrier for proton rotation in the ground state of tetraphenylporphyrin is $\approx 3500\ cm^{-1}$. The barrier in H_2P is expected to be comparable, so that each tautomer is stable at liquid helium temperatures in the absence of light.

Temperature dependence of hole widths

As we have seen, the photochemical hole width is determined by homogeneous relaxation processes. At the lowest temperatures the population decay time (T_1) is ultimately the factor limiting the hole width. For H_2P the singlet decay time is 17 ns, and this gives a limiting hole width ($2\Gamma_h$) of 19 MHz. As the temperature increases, thermally induced dephasing processes rapidly broaden the holes. By 77 K, Γ_h is often 50 to 100 GHz, so that unless the molecules are in very inhomogeneous environments, hole burning no longer occurs [8].

The temperature dependence of the hole width gives insight into the nature of the dephasing processes, information that is otherwise difficult to obtain in inhomogeneously broadened systems. Figure 5 shows the results of such measurements on H_2P molecules in two of the sites in n-octane [8, 14]. For the A site, little broadening occurs below 5 K, whereas Γ_h for the B site increases strongly with temperature. The activation energies for the increase in these hole widths give characteristic mode frequencies of $15\ cm^{-1}$ for the B site and $30\ cm^{-1}$ for the A site [14]. These are interpreted as low-frequency librational modes of the H_2P molecule in the n-octane lattice [8, 14]. In the A site, two n-octane molecules are replaced by one H_2P molecule, whereas in the B site, three n-octane molecules are replaced [22, 25]. The resulting force constant changes are responsible for the different mode frequencies. Computer calculations [25] of the site energies and molecular dynamics support this picture.

In addition to line broadening, it is possible to measure thermal line shifts by hole burning since the long-lived holes provide a frequency reference. Figure 6 shows the result of measurements of this kind for the B_1 line of H_2P in n-octane. Here, holes are simultaneously burned in two samples at 1.6 K (curves 1 and 2). One sample then has its temperature increased to 3.9 K (curve 3), while the other stores the frequency at which the holes were burned (curve 4), and both holes are rescanned simultaneously.

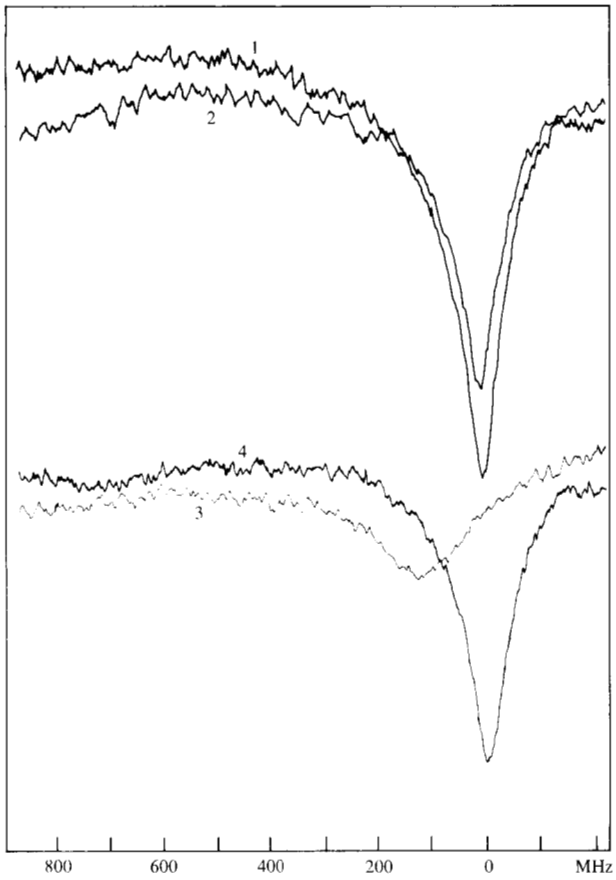

Figure 6 Temperature dependence of the frequency shift of holes in the B_1 line of H_2P in n-octane. Holes are burned at the same frequency in two samples in separate cryostats at 1.6 K (curves 1 and 2). The sample in one cryostat then has its temperature raised to 3.9 K (curve 3) and the shift (and broadening) of the hole relative to that in the reference sample at 1.6 K (curve 4) is shown.

The reference sample is very stable because the temperature of the liquid helium bath can be accurately controlled. This eliminates errors associated with drifts of external interferometers, which would otherwise be needed to record the frequency at which holes were burned. The results of the width Γ_h and shift $\delta\nu$ measurements can be summarized as follows. Below $\approx$40 K it was found [14] that the temperature dependence of Γ_h and $\delta\nu$ for the B_1 and B_2 lines could be described by $\exp(-E/kT)$ with the same value of $E = 15 \pm 3$ cm^{-1}. A model that predicts this behavior is the exchange model discussed by Schmidt *et al.* [26] and by Harris [27]. Here, the width and shift are due to a coupling of the electronic oscillators of frequency ω_0 to a low-frequency vibrational mode localized at the H_2P impurity. This mode has an energy E in the ground electronic state and $E + \Delta$ in the excited state. When the temperature is raised, the electronic oscillators make short stochastic jumps to the frequency $\omega_0 + \Delta$ by the absorption and subsequent re-emission of a phonon. A

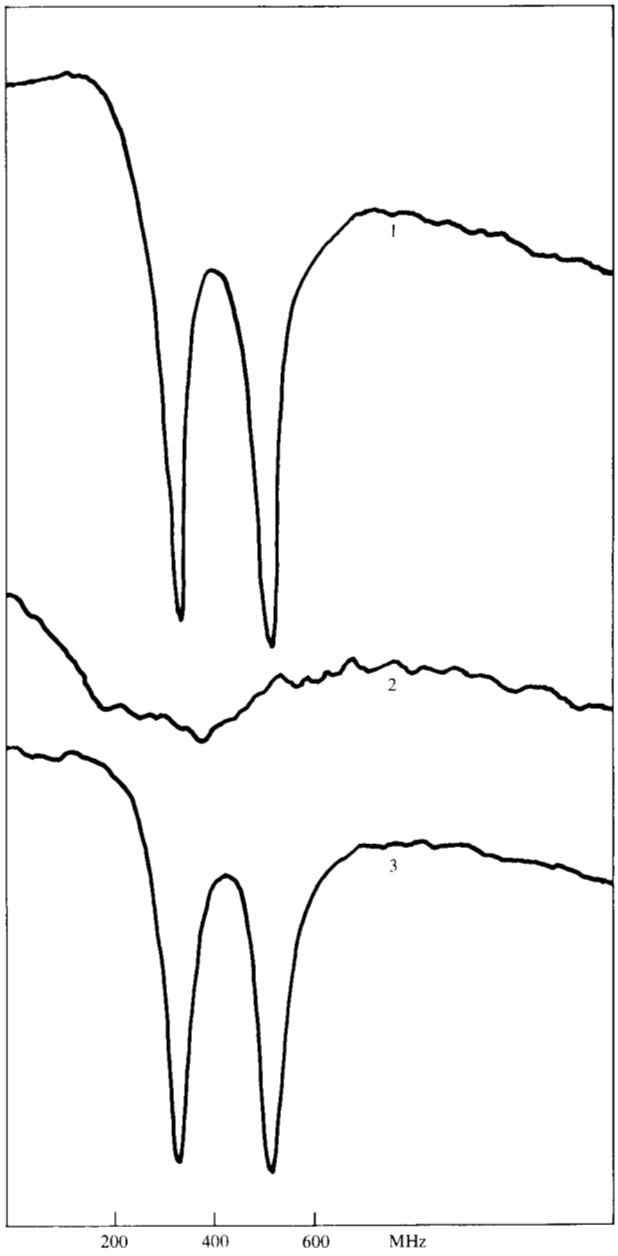

Figure 7 An example of thermal cycling of two adjacent holes. Two holes burned 180 MHz apart at 1.6 K in line B_1 of H_2P in n-octane (curve 1); heated to 4.2 K (curve 2); and on recooling to 1.6 K (curve 3).

combination of frequency shift and width information enables the parameters of this model (Δ and the lifetime of the local mode state τ) to be separately determined; see Eqs. (1) and (2) of Ref. [14]. We find for B_1, $\Delta_1/2\pi = 35$ GHz and $\tau_1 \approx 3$ ps; for B_2, $\Delta_2/2\pi \approx 25$ GHz and $\tau_2 \approx 3$ ps [14].

Figure 7 shows an example of the thermal cycling of two adjacent B_1 holes, in this case 180 MHz apart and

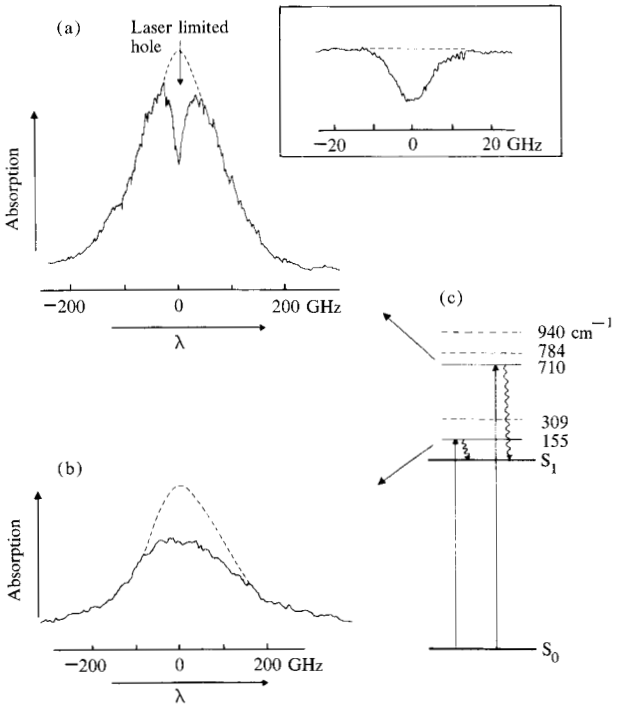

Figure 8 Examples of photochemical holes burned in vibronic lines of the $S_1 \leftarrow S_0$ transition of H_2P in n-octane at 4.2 K. (a) 10-GHz holes in the 710-cm^{-1} vibronic line of A_1; Γ_h = 5 GHz. (b) The 155-cm^{-1} vibronic line is essentially homogeneously broadened (Γ_h = 82 GHz) due to very rapid relaxation (≈2 ps) to the electronic origin S_1 and hole burning is not observed. (c) A level diagram showing the S_0 and S_1 electronic levels and some of the vibronic levels below 1000 cm^{-1}.

burned at 1.6 K (curve 1). When the temperature was increased to 4.2 K the holes coalesced and shifted (curve 2), but they were recovered upon cooling to 1.6 K (curve 3). When the temperature was increased to ≈30 K the holes were not recovered, indicating that at these higher temperatures irreversible molecular rotation or thermal tautomerism occurs. We have observed that at $T \approx 80$ K the B_2 molecules converted completely into B_1 molecules in a few minutes in the dark. This was measured by burning away the B_1 line at 50 K and observing its intensity increase in the dark. Simultaneously, the intensity of the B_2 line decreased until it disappeared. At even higher temperatures ($T \approx 150$ K) molecules transformed from the B site into the A site. In the A site at $T \approx 190$ K molecules were distributed equally over both tautomers A_1 and A_2. These experiments show that in H_2P major thermal motions (site interconversion and thermal tautomerism) occur at temperatures $T > 60$ K.

Hole burning in vibronic lines

So far we have been discussing hole burning in the electronic origin. We now consider vibronic lines, which are due to transitions where both electronic and vibrational excitation occurs. In this case it is expected that the hole width will be limited by vibrational relaxation rates to the electronic origin S_1. These rates can be very fast (≈ps) and difficult to measure in the time domain. Recent hole burning measurements on single vibronic lines [2, 8, 10, 12, 16, 17, 28] confirm that these levels relax much faster than the electronic origins. In some of these cases [2, 8, 16] no holes were observed because the inhomogeneous width Γ_i was less than or approximately equal to the homogeneous width Γ_h.

Two examples of vibronic hole burning in H_2P/n-octane at 4.2 K [28] are shown in Fig. 8. In one case, that of the vibronic line 710 cm^{-1} above the 0-0 origin [Fig. 8(a)], a 10-GHz-wide hole was observed (see insert). This width corresponds to a 32-ps relaxation time. On the other hand, the 155-cm^{-1} vibronic line [Fig. 8(b)] is essentially homogeneously broadened so that hole burning is not observed and its relaxation time is estimated to be ≈2 ps. An interesting result we have found from a systematic measurement of hole burning in a number of vibronic lines [17, 28] of the A site is that there is no simple correlation between vibronic relaxation and the energy or the symmetry species of the vibration involved. We have also found that relaxation times vary strongly (by a factor of ≥40) for the different vibronic lines. It is still not clear whether these large differences are due to intramolecular effects characteristic of H_2P or whether they result from coupling of H_2P to the lattice.

Selective photochemistry also provides a useful aid to excited-state vibrational assignments. This can be seen from the example shown in Fig. 9 for H_2P in n-hexane at 4.2 K. Figure 9(a) shows an excitation spectrum in the region of ≈1000 cm^{-1} above S_1. Both tautomeric forms of H_2P (1, 2) are present. Figure 9(b) shows the result of burning away the A_2 origin. This transforms molecules from tautomer 2 to tautomer 1, so that only the latter now absorb light. Figure 9(c) shows the reverse case. In complicated cases with several sites and often overlapping vibronic lines, selective burning can be a very useful technique.

Free-base chlorin

Chlorin is a derivative of H_2P in which a double bond on one pyrrole ring is reduced [19], giving the molecule an intrinsic asymmetry (Fig. 10). Because of this, the tautomers in chlorin are chemically inequivalent and absorb at very different frequencies (tautomer splitting $\Delta_2 - \Delta_1 \approx$ 1500 cm^{-1}) [29]; see Fig. 10(b). This is in contrast to the case of H_2P where, as we have seen, the tautomer splitting of ≲100 cm^{-1} comes about because of the crystalline environment; see Fig. 10(a). In addition we find that one

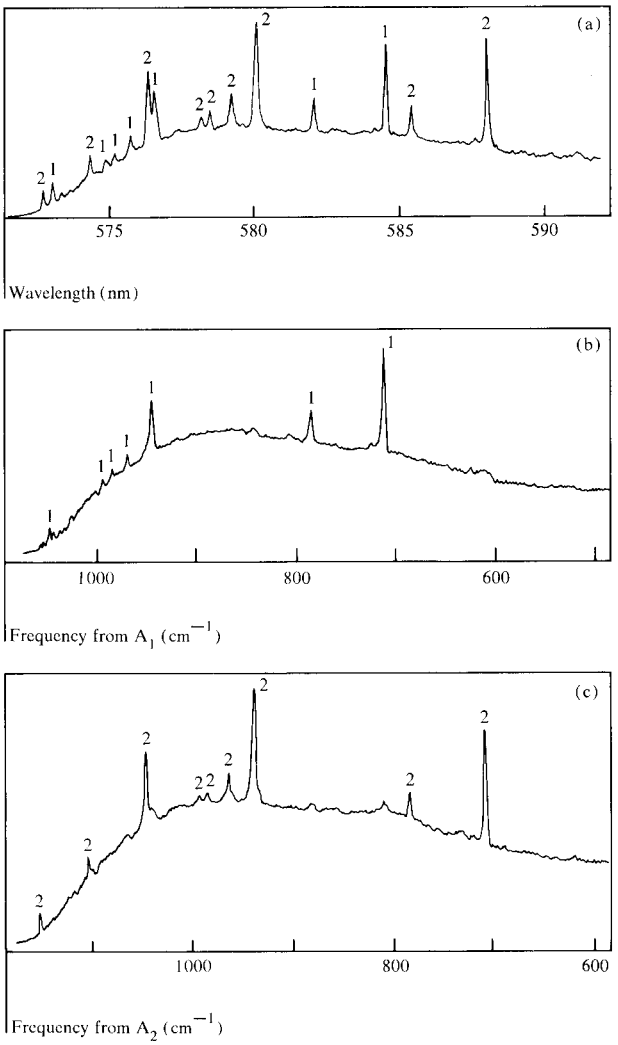

Figure 9 Vibrational assignment using selective photochemistry. (a) Excitation spectrum of H_2P in n-hexane in the region $\approx$1000 cm^{-1} above the $S_1 \leftarrow S_0$ origin at 4.2 K. (b) Vibronic excitation spectrum following selective burning of the A_2 origin. (c) Vibronic excitation spectrum following selective burning of the A_1 origin.

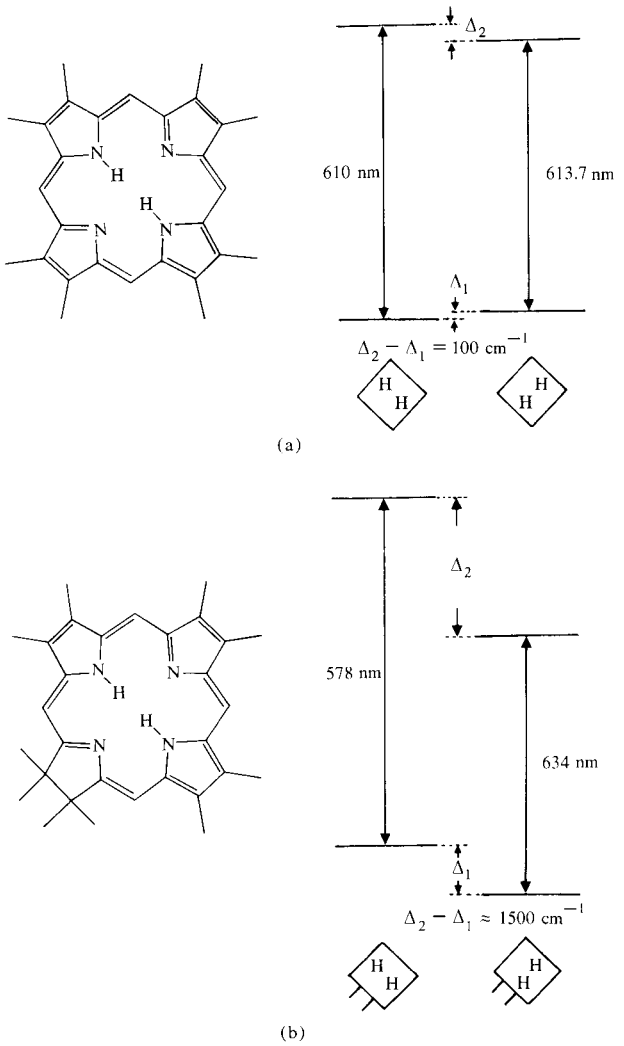

Figure 10 Molecular structure, and diagram of tautomer splittings for (a) H_2P and (b) chlorin.

tautomeric form is now preferred energetically over the other [19, 29]. For example, for chlorin in n-hexane, four electronic 0-0 absorption lines are observed around 634 nm [Fig. 11(a)], which are probably associated with four orientations ($\alpha, \beta, \gamma, \delta$) of the chlorin molecule in the most stable tautomeric form (1). The other tautomer of chlorin (2) can be produced by photoexcitation, and each of the four lines 1_α, 1_β, 1_γ, and 1_δ of Fig. 11(a) can be transformed into the other tautomer, which is found to absorb around 578 nm. This is shown for line 1_β (chlorin orientation β) in Fig. 11(b). Irradiating the photoproduct (line 2_β) restores the original stable tautomer (1_β). The photochemical hole burning rate for the less stable (*i.e.*, higher-energy) tautomer is three orders of magnitude faster than for the stable one, whose rate is comparable to that of H_2P. One reason for this difference in rates is suggested by the following observation. When line 2_α (574.2 nm) was excited, fluorescence emission was seen from line 1_α with approximately 6% efficiency. Thus the $S_1(2) \rightarrow S_1(1)$ transformation in chlorin is an additional path to that found in H_2P where the photochemistry occurs only through intersystem crossing to the triplet state. Energetically, the reverse process $S_1(2) \leftarrow S_1(1)$ cannot occur and the mechanism for the interconversion from the stable form to the photoproduct is probably the same as in H_2P. Narrow holes ($\approx$40 MHz) were burned in both the stable tautomer 1_α and the higher-energy photoproduct 2_α; see Fig. 11(c). The width of these holes is consistent with the fluorescence lifetime of chlorin ($\approx$8 ns), which is half that of H_2P.

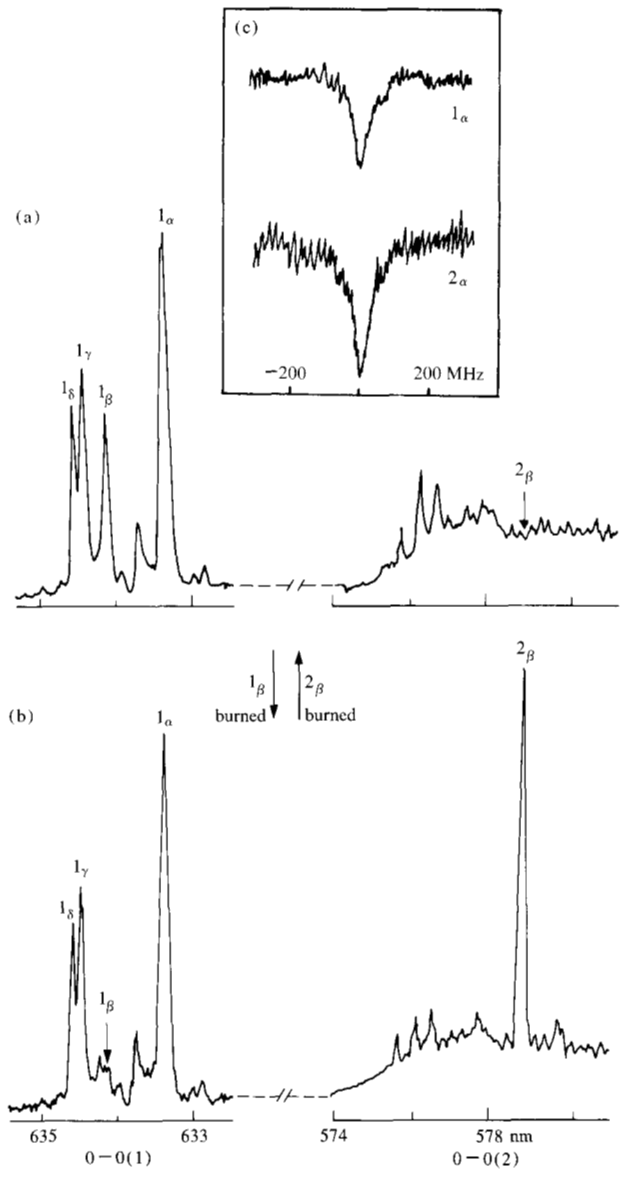

Figure 11 Phototransformation of chlorin in n-hexane at 4.2 K. (a) The original predominantly four-line pattern (1_α, 1_β, 1_γ, 1_δ) due to four orientations of the stable tautomer of the chlorin molecule in its plane. (b) Spectrum following irradiation in line 1_β, showing production of the less stable tautomeric product 2_β. The arrows indicate that burning 1_β produces 2_β and *vice versa*. (c) Narrow holes burned in the lines 1_α and 2_α.

Information storage

It has been suggested [18] that PHB can be used to store information in the frequency domain. The crucial parameter here is $N \approx \Gamma_i/\Gamma_h$, which is the number of frequency holes that can be burned at a single spatial spot. For H_2P in n-octane at 2 K, $N \gtrsim 10^3$ and at 77 K, $N \approx 1$. This underlines the advantage of very low temperatures for achieving high storage densities with this scheme. Limited temperature cycling apparently does not destroy the information stored in holes (see Fig. 7). One approach to higher-temperature operation is to increase Γ_i such that $\Gamma_i >> \Gamma_h$. We have incorporated H_2P in an alcohol glass, and found Γ_i to be ≈ 200 cm^{-1}, compared to ≈ 2 cm^{-1} in polycrystalline n-alkanes. Similar large values for Γ_i have been observed for other photochemically active species incorporated into glassy or polymeric matrices [7, 11-13, 15]. In order to ascertain the potential for achieving higher values of N in this way, further experiments are necessary to determine the limiting values of Γ_h and the way in which Γ_h depends on temperature in such systems.

Conclusion

Although photochemical hole burning is relatively new, it shows considerable promise as a spectroscopic tool and for information storage. As tunable lasers become available with reliable and convenient operation in the blue and uv spectral regions, the number of molecules that can be studied with this technique should rise significantly from the few examples known. We have shown that PHB is a very useful technique for studying homogeneous dephasing and frequency shifts, vibronic relaxation, and spectral assignments. Its range of usefulness will continue to grow with the capabilities of lasers.

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At the time this work was performed, S. Völker was employed at the IBM Research Division laboratory, 5600 Cottle Road, San Jose, California 95193; she is currently located at the Center for the Study of Excited States of Molecules, Huygens Laboratory, Leiden, Netherlands. R. M. Macfarlane is located at the IBM San Jose Research laboratory.