

HOLE BURNING ON PORPHYRIN CENTERS IN LANGMUIR-BLODGETT FILMS

J. BERNARD, M. ORRIT

Centre de Physique Moléculaire Optique et Hertzienne. CNRS et Université de Bordeaux I, 33405 Talence, France

R.I. PERSONOV and A.D. SAMOILENKO

Institute of Spectroscopy of the USSR Academy of Sciences, 142092 Moscow Region, Troitsk, USSR

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Spectral holes were burnt in the excitation spectra of porphyrin centers imbedded in a multilayer assembly of poly-heptylcyanoacrylate Langmuir-Blodgett films. We found a strong dependence of the hole width on the burning wavelength and attributed it to energy transfer to lower energy centers in our concentrated sample. The temperature dependence of the hole width was measured between 1.7 and 10 K for two wavelengths and found steeper than in glasses but weaker than in most crystals. The holes were shallower and broader in a monolayer sample.

1. Introduction

Since the first observation of persistent hole burning in inhomogeneously broadened spectral bands fifteen years ago [1,2], this method has been used for different photophysical and photochemical investigations of solids: optical homogeneous linewidth and excited-state dephasing, host-guest interactions, external field effects, etc. (see, for example, ref. [3], and references therein). Almost all papers dealt with conventional bulk solid solutions of both crystalline and amorphous types. However, it should also be interesting to apply high-resolution hole-burning spectroscopy to the investigation of thin and ultrathin molecular layer systems like Langmuir-Blodgett films (LBF).

The advantage of LBF is that they are a good basis for the creation of molecular ensembles with a predetermined architecture including superlattices and quasi-two-dimensional (2D) systems [4-7]. On the one hand, this opens up new possibilities for a detailed investigation of various intermolecular couplings. On the other hand, LBF are very promising for molecular electronics and engineering. In recent years a large number of potential applications for the optical properties of LBF have been put forward, ranging from non-linear devices to chemical sensors

[6-8]. However, the structure and dynamics of these complex molecular systems are still poorly known and new methods of investigating LBF may be of interest. Fluorescence line-narrowing and the decrease of its intensity during laser irradiation for perylene in Cd-arachidate LBF have been obtained by Bogner et al. [9]. They noted a possibility to observe a hole in the spectrum of this system, but the hole itself was not recorded. In the latest paper [10] of two of us the first direct observation of holes and the results of the homogeneous linewidth measurements for an ionic dye in LBF (resorufin adsorbed on an ammonium salt monolayer) have been reported. In the present paper, we give our results on high-resolution hole-burning spectroscopy performed on new systems: tetraazaporphin and its complex with Mg in polymerized heptylcyanoacrylate LBF. In particular, we have measured a "homogeneous" linewidth and its temperature dependence between 1.7 and 10 K and compared them to similar data for crystals, glasses and polymers.

2. Experimental

2.1. Materials

As a matrix we used heptyl- α -cyanoacrylate ($\text{H}_2\text{C}=\text{C}(\text{CN})\text{COOC}_7\text{H}_{15}$, hereafter referred to as HCA) obtained via the technique described in ref. [11]. As an active impurity we used a substituted derivative of free-base tetraazaporphin (TAP). The structural formula of TAP is given in figs. 3 and 4. We also used the magnesium complex (Mg-TAP) of a compound similar to TAP, without the phenoxy substituent.

The LBF samples were obtained by the standard technique [4,12]: they were prepared on the surface of bidistilled water at $t=20^\circ\text{C}$, polymerized and transferred onto glass slides. The glass surface, after plasma-chemical treatment, acquired a hydrophobic character in a solution of dimethyldichlorosilane. TAP was introduced into the HCA solution in chloroform ($c=1\text{ mM}$) in such quantity that its concentration in the HCA film was 1 mol%. The solution was spread on the water surface and the monolayer compressed. The surface pressure-area isotherms were measured and indicated a collapse of the film at 23 mN/m. The optimal transfer pressure at 20°C was 20 mN/m where the area per monomer was 15 \AA^2 . The monolayer polymerizes spontaneously at the air-water interface. The polymerized layer was then transferred onto glass with a transfer coefficient close to unity. By successive Y-type transfers, we obtained multilayer assemblies on both sides of the glass substrate. The thickness of a bilayer, according to the X-ray analysis data, was 20.1 \AA .

To obtain monolayer film samples, the surface of thin glass slides was subjected to a plasma-chemical treatment for cleaning and acquired hydrophilic properties. When working on monolayers, we used a stacking of 15 plates, the total number of monolayers being 30.

2.2. Hole-burning measurements

For the hole-burning experiments we used the fluorescence excitation method and the same apparatus as in ref. [10]. We burned holes using a tunable single-mode dye laser (Coherent Radiation CR-699) with bandwidth 0.5 MHz, which was pumped by an

argon ion laser (Coherent Innova 90 6W). The dye we used was a mixture of rhodamine 6G and sulforhodamine. The burning light flux ranged from 6 to $600\text{ }\mu\text{W}/\text{cm}^2$ according to temperature, and the burning times ranges from a few seconds to a few minutes. The intensity used for recording was 10 to 100 times lower than for burning. The light intensity was regulated by means of a commercial electrooptic system (Conoptics, Lass2). The sample was held in a helium flow cryostat allowing temperatures down to 1.7 K by pumping on the liquid helium. The emission was detected through a 665 nm red-pass Schott filter by a RCA C31034A photomultiplier tube operated in the photon counting mode. Counts were acquired and scans accumulated by a multichannel analyzer (Tracor Northern TN-7200) and further processed on a microcomputer.

Depth and width of the holes were determined by fitting a Lorentz curve to the experimental points. To determine the intrinsic hole width, we made in each case a series of measurements at different irradiation powers and various exposures. First, we selected a low enough irradiation power so that power broadening was practically absent. Then this power was used for burning a series of holes at various exposures. The hole width was determined by extrapolating the logarithm of the hole width versus the depth to zero depth (see fig. 5). A theoretical justification for such a procedure will be given in a forthcoming paper [13].

3. Results and discussion

3.1. Hole burning on the multilayer of the free base porphyrin

Fig. 1 shows the long-wavelength bands in the integral fluorescence excitation spectra of TAP ($\lambda_{\text{max}}=625\text{ nm}$) in a multilayer LBF. These bands have a width of about 300 cm^{-1} . Holes with relative depth up to 20% can be burnt in the long-wavelength part of these bands. We observed that the longer the burning wavelength, the deeper the hole was at constant fluence. We easily explain this fact if the Debye-Waller factor is less than unity, so that narrow zero-phonon lines (ZPL) make a considerable contribution to the absorption band only in its long-

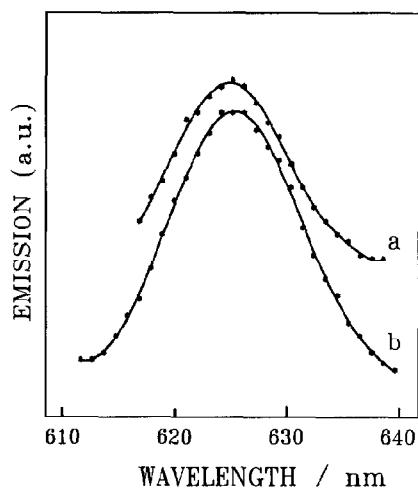


Fig. 1. Longwave part of the integral fluorescence excitation spectra of TAP in a single HCA monolayer (a) and of TAP in a multilayer assembly (150 layers) of HCA (b). The background in the monolayer spectrum arises from glass backing emission. These spectra were recorded at 6 K.

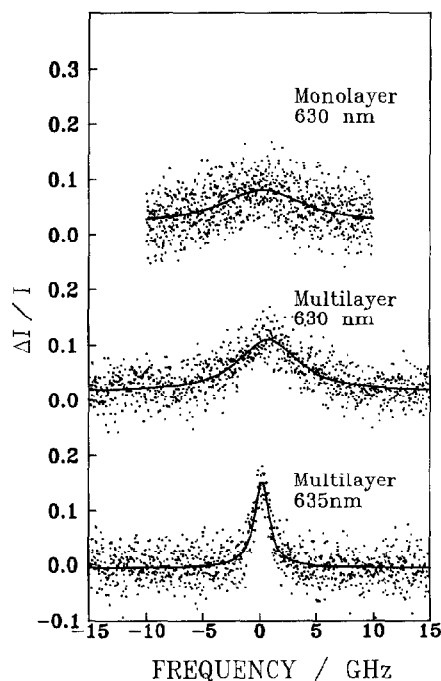


Fig. 2. Example of holes burnt in the TAP absorption band in the multilayer LBF (at 635 nm and at 630 nm) and in the monolayer (at 630 nm) at 1.85 K for comparable burning energy. Note the broadening of the shortwave hole in multi- and mono-layer.

wavelength part. Therefore, the main hole measurements were made in the region from 630 to 635 nm for TAP.

We think that the burning mechanism in TAP is connected to the reorientation of the two inner hydrogen atoms in the centre of the porphyrin ring, which is an easy process for many free-base porphyrins [14,15].

Fig. 2 shows two holes burnt at $\lambda_1=630$ nm and $\lambda_2=635$ nm in the absorption band of TAP in multilayer LBF at $T=1.85$ K. The difference in width between the two holes is striking. For a better comparison, we extrapolated to zero depth several series of holes burnt at different wavelengths between 628 and 638 nm. The results are shown in fig. 3. We note the large change in extrapolated width between 628 and 632 nm, while it remains approximately con-

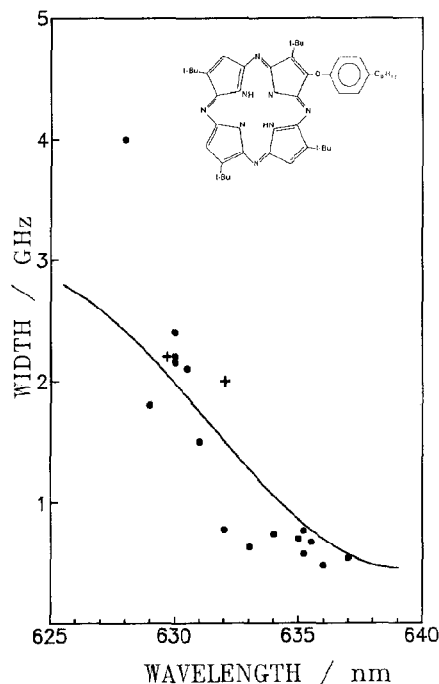


Fig. 3. Dependence of the intrinsic hole width at 1.85 K (extrapolated at zero depth) on the burning wavelength measured on the multilayer sample (discs) and on monolayers (crosses). The solid line shows the excitation profile in this region. Note the strong increase of the multilayer hole width as the hole moves towards the center of the band. Among the different interpretations proposed in the text, we retain fast energy transfer to lower energy centers to provisionally explain this effect. The monolayer hole width at 632 nm is much larger than in the multilayer.

stant, around 0.5 GHz, beyond 633 nm. Neglecting spectral diffusion on the experiment's time scale, this value corresponds to a homogeneous width $\Gamma_{ZPL} = \frac{1}{2}\Gamma_{\text{hole}} \approx 0.008 \text{ cm}^{-1}$. This width is approximately 4 times smaller than in resorufin at the same temperature [10], although the widths measured at 10 K in both systems do not differ by a factor larger than 2. The measurements in our sample show an increase in hole width when going to the blue, up to more than 3 GHz at 628 nm. This observation might be attributed to several causes, like:

- (i) the presence of different impurity centers (with correlation between excitation energy and dephasing),
- (ii) the existence of higher excited vibronic states of the guest molecule,
- (iii) the possibility of energy transfer from short-wavelength to long-wavelength centers. A similar dependence of a homogeneous ZPL width within an inhomogeneously broadened profile was observed in some inorganic systems via fluorescence line narrowing and photon echoes [16,17].

Since in diluted organic solutions Γ_{ZPL} is usually independent of the wavelength, we are inclined to suppose that in our somewhat concentrated sample (the average distance between centers within one monolayer is about 50 Å and thus about 35 Å in the multilayer assembly) energy transfer is responsible for the observed wavelength dependence. However, a concentration dependence study would be necessary to reach a final conclusion.

3.2. Temperature dependence of the hole width

The spectral hole burning of conventional bulk solutions has proved to be a very sensitive method for studying impurity-matrix interactions and dynamics (see ref. [3, chs. 3, 5], and references therein). It was shown that in most crystals, the homogeneous ZPL width Γ_{ZPL} is exponentially activated with increasing temperature. This behaviour is usually attributed to coupling of the electronic oscillator of the impurity to a local libration mode. In organic amorphous matrices (glasses and polymers) the temperature dependence of the homogeneous width at low temperatures is much weaker than in crystals and is connected to coupling between optical transitions and low-frequency modes (two-level tunneling systems,

TLS) existing in these systems. In many cases at $T \leq 20 \text{ K}$ this dependence is of the power law type $\Gamma_{ZPL} = \Gamma_0 + aT^\alpha$ with $\alpha \approx 1.3$. As shown by Thijssen and Völker [18] in semicrystalline polymers (between 0.3 and 4.2 K) the T dependence exponent is clearly larger than 1.3. For instance, for dimethyl-s-tetrazine in polyethylene between 1.2 and 4.2 K the exponent ranges from 1.6 to 3.0 depending upon the degree of matrix crystallinity. This means that there is an immediate relation between the matrix structure and the temperature dependence of the hole width.

In view of the abovementioned relation between structure and hole width, it was interesting to perform temperature measurements of the LBF spectral holes. Fig. 4 presents the temperature dependence of

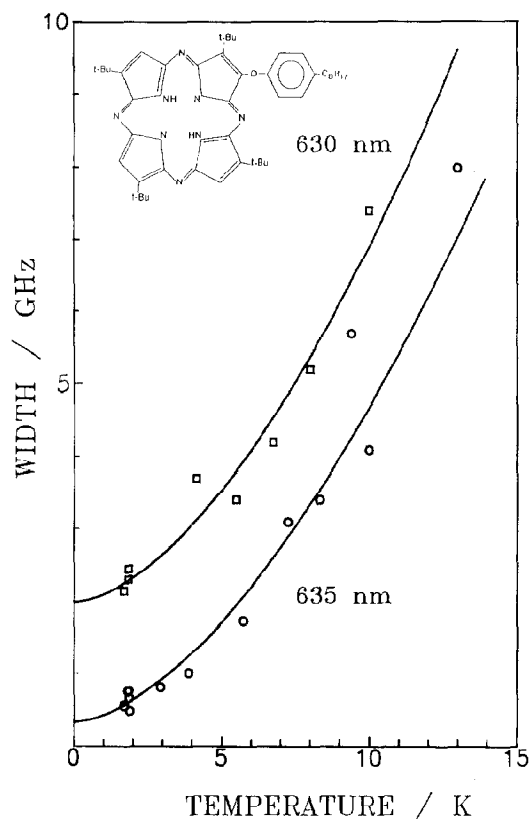


Fig. 4. Dependence on temperature of the "intrinsic" hole width determined as shown in fig. 4. The measurements were made at 635 nm (circles) and 630 nm (squares). The solid lines are power law fits given in the text. We note the parallel behaviour of both curves and the large residual width of the short-wavelength holes.

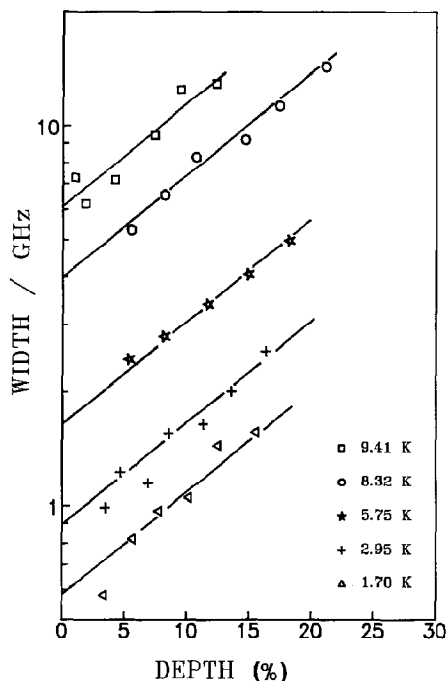


Fig. 5. Examples of logarithmic width–depth plots of series of holes burnt at constant power and increasing fluence, here at 635 nm for various temperatures. The straight lines extrapolating to zero depth have the same slope, assumed to depend only on wavelength. The “intrinsic” width is the extrapolated value.

the intrinsic hole width as determined using the extrapolation procedure illustrated in fig. 5. A crude power-law fitting gives the following dependence for the two wavelengths 635 and 630 nm:

$$\Gamma_{\text{hole}}/\text{GHz} = 0.35 + 0.10 T^{1.62 \pm 0.2}$$

at 635 nm,

$$\Gamma_{\text{hole}}/\text{GHz} = 2.0 + 0.11 T^{1.67 \pm 0.4}$$

at 630 nm.

The exponents are similar to those obtained for resorufin in monolayers [10] and somewhat larger than for bulk glasses. According to ref. [18], this can be connected with a semi-crystalline structure of our LBF. However, it should be noted that, according to the theory of Osad'ko [19], such low temperature dependences could be observed even in well-ordered systems, if at least one TLS interacts with the impurity. The residual width at 635 nm is much larger

than the natural width of the excited state, but a smaller value could still be compatible with our data. The exponent should then be smaller than 1.6 or, alternatively, a composed temperature dependence with an activated term could be used. This is in contrast with the case of resorufin [10], where the low-temperature points extrapolated unambiguously to about 2 GHz at $T=0$. As discussed above, we provisionally attribute the large residual width at 630 nm to energy transfer towards lower-lying impurities.

3.3. Hole burning on TAP in the monolayer of HCA

The excitation spectrum of TAP in the HCA monolayer is presented in fig. 1 and compared to that of the multilayer. While the shape and maximum of both spectra are identical, we note a strong background emission of the monolayer sample. We attribute this background to the glass of the 15 backing slides (a similar emission was observed using uncoated glass). The background emission makes it much more difficult to detect shallow holes in the longwave part of the band. Therefore, most of our data were obtained at waves shorter than 632 nm, where the multilayer holes are rather broad.

Two series of holes were measured at low temperature for the wavelengths 630 and 632 nm. The holes were as a rule broader and shallower for the same fluence than in multilayers, so that the extrapolation and a quantitative comparison are difficult. Nevertheless, we included these two points in fig. 3 to compare with the multilayer dependence on wavelength: while the extrapolated widths are comparable at 630 nm, the monolayer holes are much broader at 632 nm, where the multilayer width decreases. At still longer waves the monolayer holes were very shallow. Although the width was always larger than in the multilayer sample, our data are not reliable enough to extrapolate to zero depth.

3.4. Hole burning in the magnesium complex of TAP

The maximum of the excitation spectrum of Mg-TAP lies around 594 nm. Holes can be burnt in the region from 593 to 608 nm. To burn a hole of the required depth in Mg-TAP, we needed much more

irradiation energy than with TAP. The fluence needed to burn a hole about 5% deep in Mg-TAP was about 50 times larger than in TAP. The molecular burning mechanism is less evident in Mg-TAP than in TAP, and we assume it to be photophysical in origin. A photophysical hole burning process usually has a much lower quantum yield than a photochemical one [20].

Due to the low burning yield, only shallow holes could be recorded and evaluated. Thus, the extrapolation to zero depth was difficult and our results were not reliable enough to draw a temperature or wavelength dependence. Nevertheless, the hole widths obtained in the multilayer assembly were in the range 1–2 GHz at 1.9 K and thus similar to those of the free-base TAP multilayer. In contrast to these, the holes burnt in monolayers of Mg-TAP in HCA were always very broad, even at the lowest temperature and in the red part of the spectrum. In this system the monolayer spectral holes are several times broader than the multilayer ones. The origin of this difference is not yet clear, and more work is needed to compare holes in similar mono- and multilayers.

In conclusion, we wish to stress the fundamental interest of LB films as matrices for hole-burning spectroscopy. Although the results of the present work (together with those of ref. [10]) have a preliminary character, we expect this method soon to be generalized to many similar LBF systems. The comparison of the hole width in various matrices should help to determine the molecular motions involved in dephasing and spectral diffusion at low temperatures. As to the possible applications of the hole-burning method, in particular to frequency domain optical storage [21], LBF present a well-defined molecular thickness and a well-defined molecular orientation, both interesting for electric field scanning of the holes [22]. However, LBF are subject to the limitations of other molecular systems [21] so that the discovery of a photon-gated burning mechanism in these systems is highly desirable.

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References

- [1] B.M. Kharlamov, R.I. Personov and L.A. Bykovskaya, *Opt. Commun.* 12 (1974) 191.
- [2] A.A. Gorokhovskii, R. Kaarli and L.A. Rebane, *JETP Letters* 20 (1974) 216.
- [3] W.E. Moerner, ed., *Persistent spectral hole-burning: science and applications* (Springer, Berlin, 1988).
- [4] H. Kuhn, D. Möbius and H. Bücher, in: *Physical methods of chemistry*, Vol. 1, part IIIB, eds. A. Weissberger and B. Rossiter (Wiley, New York, 1972).
- [5] H. Kuhn, *Thin Solid Films* 99 (1983) 1.
- [6] D. Möbius, ed., *Langmuir-Blodgett Films*, *Thin Solid Films* 159 (1, 2) (1988); 160 (1, 2) (1988).
- [7] L.M. Blinov, *Usp. Fiz. Nauk.* 155 (1988) 443.
- [8] J.D. Swalen, *Thin Solid Films* 160 (1988) 197; G.H. Kim, T.M. Kotton and R.A. Uphaus, *Thin Solid Films* 160 (1988) 389.
- [9] U. Bogner, G. Röska and F. Graf, *Thin Solid Films* 99 (1983) 257.
- [10] M. Orrit, J. Bernard and D. Möbius, *Chem. Phys. Letters* 156 (1989) 233.
- [11] V.V. Korshak, A.M. Polyakova, K.A. Mager and V.N. Semyancev, *Bull. Izobretenii* No. 41 (1979).
- [12] K.B. Blodgett and I. Langmuir, *Phys. Rev.* 51 (1937) 964; G.G. Roberts, *Advan. Phys.* 34 (1985) 475.
- [13] H. Talon, M. Orrit and J. Bernard, to be published.
- [14] K.N. Solov'ev, I.E. Zalesski, U.N. Kotlo and S.F. Shkirman, *JETP Letters* 17 (1973) 332.
- [15] S. Völker and R.M. Macfarlane, *J. Chem. Phys.* 73 (1980) 4476.
- [16] P. Avouris, A. Campion and M.A. El-Sayed, *J. Chem. Phys.* 67 (1977) 3397; *SPIE* 113 (1977) 57.
- [17] R.M. Shelby and R.M. Macfarlane, *Phys. Rev. Letters* 45 (1980) 1098.
- [18] H.P.H. Thijssen and S. Völker, *J. Chem. Phys.* 85 (1986) 785.
- [19] I.S. Osad'ko, *Zh. Eksp. Teor. Fiz.* 90 (1986) 1453.
- [20] G.J. Small, in: *Spectroscopy and excitation dynamics of condensed molecular systems*, eds. V.M. Agranovich and R.M. Hochstrasser (North-Holland, Amsterdam, 1983).
- [21] W.E. Moerner, W. Lenth and G.C. Bjorklund, in: *Persistent spectral hole-burning: science and applications*, ed. W.E. Moerner (Springer, Berlin, 1988).
- [22] U.P. Wild, S.E. Bucher and F.A. Burkhalter, *Appl. Opt.* 24 (1985) 1526.