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May 1980

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Photochemical and Non-photochemical Hole Burning in Dimethyl-s-tetrazine in a Polyvinyl Carbazole Film

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ABSTRACT

Hole burning as well as fluorescence line narrowing experiments have been performed on the system dimethyl-s-tetrazine in polyvinyl carbazole films at low temperatures. The first singlet electronic absorption bands are typical (300 cm^{-1} wide) of inhomogeneously broadened bands of guest molecules in amorphous organic hosts. Evidence is presented for both photochemical and non-photochemical hole burning. The narrowest holes observed were Lorentzian, had a width of 0.44 cm^{-1} at 1.8 K, and are believed to be of non-photochemical origin. A model which envisions the guest molecules to occupy different sites in the polymer host with a distribution of energy barriers between sites is used to describe these observations. The fast (20 psec) relaxation time implied by the 0.44 cm^{-1} Lorentzian linewidth is interpreted as indicative of the rate of site interconversion in the excited state.

I. INTRODUCTION

Photochemical hole burning[1,2] (PHB) and fluorescence line narrowing[3] (FLN) are relatively new and powerful laser spectroscopic techniques for obtaining high resolution features of spectra of large organic molecules under conditions where ordinary absorption and emission measurements yield broad inhomogeneous bands, even at low temperatures. Both techniques can be considered as variants of optical site selection spectroscopy,[4] and depend on the ability of narrow band laser excitation to selectively excite only those molecules which, by virtue of their local environments, are in resonance with the laser frequency.

FLN experiments in mixed crystals have yielded spectra of very high resolution, where linewidths limited only by excited state lifetimes have been observed. For example, Marchetti *et al.*[5] found the underlying homogeneous linewidth of the 3 cm^{-1} wide (inhomogeneous) vibronic transition of pentacene in paraterphenyl to be 0.034 cm^{-1}, and these authors concluded that the vibrational relaxation in this state was 0.2 nsec or longer. Similarly, deVries and Wiersma[6,7] found the 0-0 transition of dimethyl-s-tetrazine in a durene crystal at 5875 Å to be 7.3 GHz (0.24 cm^{-1}) wide. PHB experiments on this line gave a homogeneous linewidth of 24±5 MHz (8.0×10^{-4} cm^{-1}), completely determined by the 6 nsec lifetime.[8] The same authors[7] also burned a 0.7 GHz (0.023 cm^{-1}) hole in the origin of the lowest $S_1 + S_0$ transition of a s-tetrazine in a benzene cystal. From this width, a homogeneous linewidth of 350 MHz (0.012 cm^{-1}) and a fluorescence lifetime of 455 psec were obtained.

When similar molecules are prepared in organic glasses or polymers, the linewidths obtained by optical site selection spectroscopy are in the range 0.1 - 10 cm^{-1}, several orders of magnitude larger than those obtained in mixed crystals.[1-3,9-12] For example, Kharlamov *et al.*[1] and Abram *et al.*[10] measured the linewidth of a (non-photochemical hole burned in the absorption spectrum of

perylene in an ethanol glass. From the width of the hole (0.7 cm^{-1}), Kharlamov and co-workers estimated the homogeneous width of the 0-0 transition as 0.45 cm^{-1}. This width, although small in comparison with the inhomogeneously broadened absorption band of the alcohol solution ($\sim$200 cm^{-1}), exceeds the natural width by two or three orders of magnitude[1]. A theoretical framework describing photochemical and photophysical hole burning experiments on molecular mixed crystals appeared recently[13].

We are interested in understanding the limitations on the linewidth of organic molecules in amorphous hosts as determined by photochemcial hole burning experiments. We present here studies on dimethyl-s-tetrazine (DMST) in a polyvinyl carbazole (PVK) film. DMST has been extensively studied in mixed crystals,[6,8,14,15] and polyvinyl carbazole is a convenient aromatic readily available in high purity form and easy to prepare in optically clear films.

PHB experiments on organic molecules dispersed in films have been reported by Marchetti et al.,[11] and also by Graf et al.[16] The latter reported spectrometer limited, $\sim$1 cm^{-1} wide holes in the spectrum of a hydroxy quinone in polymethyl methacrylate. The former studied the ionic dye resorufin, also in a polymethyl methacrylate thin film. The width of the hole burned in this line was $\sim$0.2 cm^{-1}, from which a homogeneous linewidth of $\sim$0.1 cm^{-1} was determined for the 0-0 transition. No explanation was offered for this width.

II. EXPERIMENTAL

Dimethyl-s-tetrazine was synthesized by the method of Skorianetz and Kovats,[17] and was purified by sublimation. Polyvinyl carbazole, molecular weight 9 x 10^5, was obtained from BASF (Luvican, M170) and purified by repeated precipitation.[18] The monomer concentration in the polymer was less than 1 ppm. The DMST and PVK were both dissolved in tetrahydrofuran (THF) and mixed thoroughly before casting. A few drops of the solution were placed inside a teflon ring on a glass plate, and the THF was allowed to evaporate slowly overnight. In this manner, optically clear films could be obtained routinely. Typically, the films were 300-400μ

thick and ∿0.3% DMST in PVK by weight. Visible spectra of the films were recorded at room temperature, and from the known molar extinction coefficient in solution (525 ℓ/mole - cm at λ_{max} = 5500 Å)[15], we estimate the concentration of DMST to be ∿0.03 moles/ℓ.

The films were mounted in a liquid helium dewar (Andonian Associates, Inc.) and the temperature was measured with a calibrated silicon diode (Lake Shore Cyrotronics). The spectra were recorded using a Jobin-Yvon THR 1500 monochromator (dispersion at 6000 Å = 0.95 Å/mm), an EMI 6256B photomultiplier tube, and either a Hewlett-Packard 7561A log amplifier (for absorption measurements) or a Keithley 416 picoammeter (for fluorescence measurements).

Hole burning was performed with either a Molectron N_2-pumped pulsed dye laser (DL-200 dye laser and UV 1000 pulsed N_2-laser, coumarin 153 dye, laser linewidth ∿0.6 cm^{-1}), or a Coherent model 599-05 dye laser (using Rhodamine 110 dye) pumped by a CR 15 argon ion laser (dye laser linewidth <300 MHz ≈ 0.01 cm^{-1}).

A 500W tungsten lamp was used to record the absorption spectrum of DMST in PVK following laser irradiation and hole burning. The output of the broad band lamp was filtered through an H_2O cell and one or more Corning glass or narrow band-pass filters.

III. RESULTS AND DISCUSSION

A. Absorption and Emission Spectra

The absorption spectrum of DMST in PVK at low temperature is shown in Fig. 1a, and is qualitatively similar to the spectrum of DMST in hexane at room temperature[14]. The 0-0 and first vibronic bands lie at 5670 and 5500 Å respectively, shifted to shorter wavelengths relative to the room temperature solution spectrum. The bands remain broad down to 1.8 K, typically about 300 cm^{-1} wide. When the sample was irradiated with a narrow band laser source, a fluorescence spectrum such as that shown in Fig. 1b is obtained. In Fig. 1b, the DMST is excited with a cw

dye laser (laser linewidth <0.01 cm^{-1}) at 5500 Å, near the top of the first vibronic band. The 0-0 band consists now of a sharp line (5 cm^{-1} FWHM) and a broad (180 cm^{-1}) phonon wing, similar to the fluorescence spectra of organic molecules in glasses. Vibronic emission lines also appear, although these features are dominated by the phonon wings. A high resolution spectrum of the 1-0 zero phonon emission line shows that this line is 9 cm^{-1} in width, almost twice as broad as the zero phonon line in the origin band. The relative intensity of the zero phonon lines to the phonon wings is indicative of strong electron-phonon coupling[3] in this polymer film.

Laser irradiation at various other wavelengths along the first excited vibronic band shifts the fluorescence spectrum, but leaves it otherwise unchanged. Particularly, the difference between the laser wavelength and the wavelegth of the 0-0 transition remains unchanged at 517 cm^{-1}, in agreement with other spectroscopic measurements of the vibrational spacings of the ground state of DMST[15]. Furthermore, this shows that the broad nature of the bands of the absorption spectrum of DMST in PVK is due to an essentially continuous distribution of sites which can be probed by narrow band laser excitation.

B. Hole Burning Experiments

1. Photochemical hole burning

If the absorption spectrum is scanned following excitation with the pulsed dye laser, holes appear in the absorption at wavelengths coincident with the laser frequency, and also at higher energies corresponding to quanta of vibrational energy. The hole spectrum shown in Fig. 2 was obtained by irradiating DMST in PVK at 5672 Å using the pulsed dye laser. In the broad absorption bands there is a sharp hole corresponding to the zero phonon lines observed in fluorescence, plus a broad hole similar to the phonon side band, and shifted

9-12 cm^{-1} to lower energies. Both holes appear in the 0-0 band as well as in the vibronic bands. The sharp hole in the first vibronic band is 518 cm^{-1} from the coincident sharp hole in the origin, completely analogous to the situation observed in fluorescence. The appearance of narrow zero phonon holes accompanied by broad side band holes lying lower in energy has been observed previously [11, 12], and can be attributed to a loss of absorbers due to zero phonon excitation at the laser frequency, and a loss of absorbers at lower energies due to phonon side band excitation.

At 10K, the width of the zero phonon holes in the origin and in the first vibronic bands are 1.8 and 5.0 cm^{-1} respectively (pulsed dye laser linewidth = 0.6 cm^{-1}, λ_{laser} = 5672 Å). As the irradiation time is increased, these holes deepen considerably and broaden slightly, as shown in Fig. 2. The hole depth, in optical density units, is not a linear function of irradiation time, indicating that saturation effects become important. The saturation depth, however, is considerable: after 9 min irradiation time the optical density of the origin band at the laser frequency decreased by over 40%. If the sample is warmed up to liquid nitrogen temperature and cooled down again, the original absorption spectrum (before irradiation) is not recovered. This is exemplified by the dotted spectrum in Fig. 2, and is taken as evidence that an irreversible photochemical process is taking place. The photochemistry of DMST is well documented[14, 19, 20] and apparently proceeds by a biphotonic mechanism through the formation of metastable intermediates.

The widths of the zero phonon holes obtained upon irradiation with the pulsed dye laser were found to be two to three times larger than the laser linewidths. For example, at 10K, hole widths ranging from 1.8 to 2.3 cm^{-1} were obtained with the pulsed dye laser whose laser widths ranged from 0.6 to 0.9 cm^{-1}. Even at 1.8K, the narrowest holes obtained with the laser were 1.8 cm^{-1} in width. We attribute this width to local heating of the sample (see below). Figure 3a

shows a typical record of the hole burned at the top of the origin band following 2 min irradiation at 8K. The shape of the hole is approximately Gaussian.

The temperature dependence of these photochemical holes is shown in Fig. 4. A deep hole was burned in the 0-0 band of DMST in PVK by irradiation with the pulsed dye laser (λ = 5668 Å, linewidth = 0.9 cm^{-1}). The sample was irradiated for 45 min at a temperature of 8K. A zero phonon hole of width $\Delta\nu$ = 2.3 cm^{-1} and a broad hole of width 72 cm^{-1} were obtained. The sample was then warmed up slowly, and the zero phonon hole became shallower and broader. At 22K, the zero phonon hole was about 10 cm^{-1} in width, and the phonon side band hole had also increased to $\sim$100 cm^{-1}. If the temperature was then dropped to 7K, the narrow hole deepened and sharpened, as shown in Fig. 4, while the broad hole became narrower also, $\Delta\nu$ $\sim$84 cm^{-1}. Even when the temperature was increased to 55K and the narrow hole (but not the broad hole) had completely vanished, cooling down to 7K recovered the narrow hole, although it was shallower and broader ($\Delta\nu$ $\sim$16 cm^{-1}) that the original hole obtained at 8K. The broad hole reached a width of 150 cm^{-1} at 55K.

The ability to recover the holes after warming the sample up to 55K is in marked contrast with the non-photochemical hole burning experiments of Hayes and Small[12, 21]. This temperature dependence further supports our interpretation that these holes obtained with the pulsed dye laser are photochemical rather than photophysical in origin. Thermal heating introduces a homogeneous broadening which masks the hole at T > 20 K. Complete site interconversion, which would result in replenshing the sites depleted by hole burning (and a non-reappearance of the hole upon re-cooling) does not occur until the sample temperature approaches 77K.

2. Non-photochemical Hole Burning

Considerably narrower holes were obtained when the sample was irradiated with a single frequency cw dye laser. The laser linewidth was measured with a Fabry-Perot interferometer to be about 1.7 x 10^{-3} cm^{-1} (50 MHz), but the effective linewidth was determined by the laser jitter of about 0.01 cm^{-1} (300 MHz). At 1.8K, the width of the hole obtained with the cw laser was 0.44 ± 0.03 cm^{-1}.

This hole is Lorentzian, as shown in Fig. 4b. To insure that local heating was not contributing to the width of the hole, the laser intensity was attenuated using neutral density filters and the hole width was monitored as a function of laser intensity at the sample. At a cw laser power of ~40 mW, the hole width was 1.5 times larger than that at lower powers P~10 mW. Further attenuation of the laser did not result in narrower holes. We conclude that local heating of the sample is not a problem at laser power of 10 mW or less. All of these holes obtained with the cw dye laser were shallow (<10%), but the saturation depth was not measured.

A second possible contribution to the observed hole width is spectral diffusion, which would manifest itself as a dependence of hole width on sample concentration. This effect was tested by irradiating a sample at the top of the 0-0 band (5671 Å) and on the side (5622 Å), where a four fold decrease in optical density was measured. Within experimental error, no difference was observed in the widths of the holes at these two wavelengths. As a further confirmation that spectral diffusion was not a problem with the films used, a sample with a concentration of 0.34 moles/ℓ (3.4% DMST in PVK by weight), ten times more concentrated than the samples indicated above was prepared. Holes whose widths were the same as in the less concentrated sample were obtained all along the top of the origin band.

Various observations are presented below which argue for the non-photochemical nature of these narrow holes: temperature dependence, intensity dependence, hole width, and time dependence. Furthermore, a picture emerges which is completely analogous to the mechanism presented by Hayes and Small[12, 21] to explain their non-photochemical hole burning experiments in organic glass.

The width of these holes depends on the temperature of the sample at the time of irradiation. For example, at 1.8K, 3.2K, and 7.0K, the measured hole widths are 0.44 ± 0.03 cm^{-1}, 0.68 ±0.03 cm^{-1}, and 0.91 ± 0.06 cm^{-1} respectively.

The cw laser powers were comparable in all three cases (∿8 mW), the holes burned were shallow (<10%), and the uncertainties given are indicative of the scatter found by irradiating different samples (c∿3 x 10^{-2} moles/ℓ) on different days. It is clear, however, that the hole width does not vary linearly with the temperature of the sample during irradiation. On the other hand, once a hole is obtained by irradiating at low temperature, the width of this hole increases linearly with increasing temperture in the same temperature range. At ∿12K, the hole had essentially disappeared, and was not recovered by cooling the sample back to 1.8 K. This behavior is analogous to that observed by Hayes and Small[12, 21], and is quite different from that observed for photochemical holes obtained with the more intense pulsed dye laser (see above) where the hole was recovered after warming the sample to temperatures well above 20K.

We investigated the intensity dependence of the hole burning in order to determine if the photoprocess was photochemical or photophysical in nature. The photochemical dissociation of DMST at low temperatures is believed to be biphotonic[14, 19, 20], as indicated by a quadratic dependence of photodissociation on exciting light intensity. A sample of DMST in PVK was held at 1.8K and irradiated at various wavelengths in the range 5652 to 5688 Å. The laser intensity was varied using neutral density filters, and was measured at the sample. Since spectral diffusion is not a factor in the experiments described here (see above), no correction was made for holes burned at slightly different wavelengths near the top of the 0-0 absorption band. Care was taken to make all measurements at approximately the same time after irradiation ended in order to correct for the lack of persistence of the holes (see below).

If we let A(I) be the area (in relative optical density units) of the hole burned at laser intensity I, then we define the photoprocess efficiency P of the laser light at intensity I as

$$P = \frac{A(I)}{t}$$

where t is the duration of irradiation time at intensity I. A normalized plot of P versus I is shown in Fig. 5. In contrast to the observations on DMST in molecular crystals where an I^2 dependence was observed[14, 19, 20] the intensity dependence we observe here is sub-linear. Non-photochemical hole burning is known to saturate very easily[12] and can result in a sub-linear intensity dependence. A rough estimate of the quantum yeild ϕ for this photoprocess was made from the measured areas under the origin band before and after 1 min. irradiation with the cw dye laser. The small value obtained, $\phi \approx 10^{-4}$, lends additional support for the non-photochemical nature of these holes.

From the measured hole width $\Delta\nu$=0.44±0.03 cm^{-1}, a homogeneous linewidth Γ_h=0.27±0.14 cm^{-1} can be calculated using the expression $\Delta\nu/2 \leq \Gamma_h \leq \Delta\nu/\sqrt{2}$ from Kharlamov et. al.[1] In all of these experiments, care was taken to insure that the holes were shallow (<10%). This homogeneous linewidth is of the same order of magnitude as that observed by Marchetti and co-workers[11] for the ionic dye resorufin in a polymethyl methacrylate film. Such broad Lorentzians have been observed in other systems involving amorphous hosts[21, 22]. The homogeneous linewidth implies a relaxation time of DMST in a PVK film of $(2\pi c\Gamma_h)^{-1}$= 20 psec, three orders of magnitude faster than the 6 nsec excited singlet state lifetime of DMST in the gas phase.[8] The very fast relaxation time implied by the observed hole widths of organic molecules in polymer films suggest that the amorphous host provides for an effective relaxation pathway which is not available if the same molecule is located in a fixed crystalline host.

One of the most interesting results obtained in these experiments on hole burning on DMST in PVK films was the observation that these holes are not persistent. Typcially, the depth of a zero phonon hole obtained at the top of the 0-0 band (T = 1.8K, irradiation time 0.3 - 2 min) decreased by 20% over a period of about 15 min after irradiation was started, and had further decreased to half of the original depth 1.5 hours after irradiation began. Over the same period of time and at constant temperature, the hole

width did not change. We found that the hole depth h could be related to the time t (t = 0 is the time at which irradiation starts) by an expression of the form $h = at^b$, where a and b are constants which can be determined from a least squares analysis. Figure 6 shows a typical plot of ln h versus ln t, from which a and b were found to be a = 6.2 and b = -0.25[23] The DMST in PVK film (c = 0.03 moles/ℓ) was held at 1.8K during the entire experiment, and the shallow (less than 10%) hole was burned at the top of the origin band with the cw dye laser (λ = 5668 Å). The room lights were kept off during the experiment and the tungsten lamp used to record the hole spectra was filtered through an H_2O cell and either Corning glass filter (C.S. Numbers 4-96 and 3-68) or a Baird-Atomic band-pass filter (central λ = 5621 Å, T_{max} = 54%, bandwidth at 10%T_{max} = 76 Å). The W lamp was on only during the 3-4 min required to make each scan. To make sure that heating of the sample by the W lamp was not contributing to the disappearance of the hole with time, measurements were carried out in which the lamp was left on during the entire experiment, 1-2 hrs, and no difference was apparent.

We believe that the hole burning process described above resulting from irradiation of DMST in PVK with the cw dye laser is non-photochemical. The narrow hole widths, permanent disappearance of the holes upon warming to T $\sim$12K, and the sub-linear intensity dependence and low quantum yield are consistent with a non-photochemical process. All of these observations can be explained with a model analogous to that presented by Hayes and Small[12, 21], that envisions the molecules to occupy many different energy sites with a distribution of energy barriers between sites. The energy barriers between sites are considered to be higher in the ground state than in the excited state. Thus, when a molecule is excited from one potential well in the ground state (corresponding to one site) into the excited state, it can readily convert into another site either by tunneling or by thermal activation due to the low energy barrier between

sites. The molecule can then relax to the ground state of this other site, and only slowly convert back to the original site because of the higher energy barriers between sites in the ground state. In this model, the width of the Lorentzian hole observed is determined by the rate of site rearrangement in the excited state, or 20 psec. Using the Arrhenius rate equation, $k = Ae^{-\Delta E/kT}$, assuming a frequency factor of 10^{12}, this rate requires an energy barrier of $\sim 4\ cm^{-1}$.

Hayes and Small used "hole-filling" experiments[12] to indicate that the holes they observed were of non-photochemical origin. Such experiments could not be conducted here because of the natural filling of the holes with time. Using the Arrhenius rate equation and the same frequency factor, the 1.5 hrs. needed for the hole depth to decrease by 50% requires an energy barrier of $\sim 50\ cm^{-1}$. The softness of the PVK film, even at 2K, allows for the ground state DMST molecules to interconvert from site to site, which results in a gradual filling of the hole formed by laser irradiation.

The disappearance of the holes with time is indicative of the softness of the lattice cage around the guest molecules in this system. This may result from the relative compactness of the DMST molecule compared to the PVK ring. The rate of hole filling may be related to a diffusion process as DMST molecules that are in thermal equilibrium move to different thermodynamic configurations. Experiments similar to the ones presented here, when performed on larger and more elongated molecules than DMST, may help clarify this mechanism.

IV. Summary and Conclusions

Evidence is presented for both photochemical and non-photochemical hole burning in DMST in PVK films. When the films are irradiated with the pulsed dye laser, narrow laser limited holes appear at the laser frequency and also at higher energies corresponding to quanta of vibrational energy. These narrow holes are accompanied by broad holes shifted to lower energies, due to

molecules in different sites absorbing the laser light into their phonon side bands. Saturation effects are observed, although the saturation depths are large (>40%). The most direct evidence that these holes are photochemical is provided by the overall decrease in intensity of the absorption bands following warm-up to 77K.

Considerably narrower holes were obtained when the sample was irradiated with a single frequency cw dye laser. These holes were Lorentzian and had a width of 0.44 ± 0.03 cm^{-1}. Upon warming to T ≈ 12K, the holes disappear, and cannot be recovered by cooling. Furthermore, the holes gradually disappear with time (in the dark), indicative of the softness of the lattice in this system. These observations, coupled with a sub-linear intensity dependence for the photoprocess and an estimated 10^{-4} quantum yield suggest that these holes are of non-photochemical origin. A model described by Hayes and Small[12, 21] which envisions the DMST molecules to occupy different sites in the polymer host with a distribution of energy barriers between sites is used to describe these results. The fast (20 psec) relaxation time implied by the 0.44 cm^{-1} Lorentzian linewidth is interpreted as indicative of the rate of site interconversion in the excited state.

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23. Both a power curve $h = at^b$ and a logarithmic curve $h = a' + b'\ln t$ could be fit to the observed time dependence of hole depth. The reproducibility of these results is indicated by the uncertainties obtained for six different measurements: for $h = at^b$, $a = 6.40 \pm 0.31$, $b = -0.22 \pm 0.05$, $r^2 = 0.90 \pm 0.03$; for $h = a' + b'\ln t$, $a' = 5.81 \pm 0.47$, $b = 0.79 \pm 0.07$, $r^2 = 0.91 \pm 0.03$.

FIGURE CAPTIONS

Figure 1. (a) Absorption spectrum of dimethyl-s-tetrazine in a polyvinyl carbazole film. T = 10K. Concentration: 0.3% DMST by weight, or 0.03 moles/ℓ.
(b) Laser induced fluorescence spectrum of DMST in PVK (c = 0.03 moles/ℓ); T = 1.8K, λ_{laser} = 5500 Å. The laser linewidth is <0.01 cm^{-1}.

Figure 2. Absorption spectrum of DMST in PVK (0.05 moles/ℓ) at 10K. The sample was irradiated for 3 min and for 9 min at 5672 Å. Zero phonon holes accompanied by phonon side band holes appear in the 0-0 and the vibronic bands. The dotted line represents the absorption spectrum of the same irradiated sample after warm-up to 77K followed by cooling back to 10K.

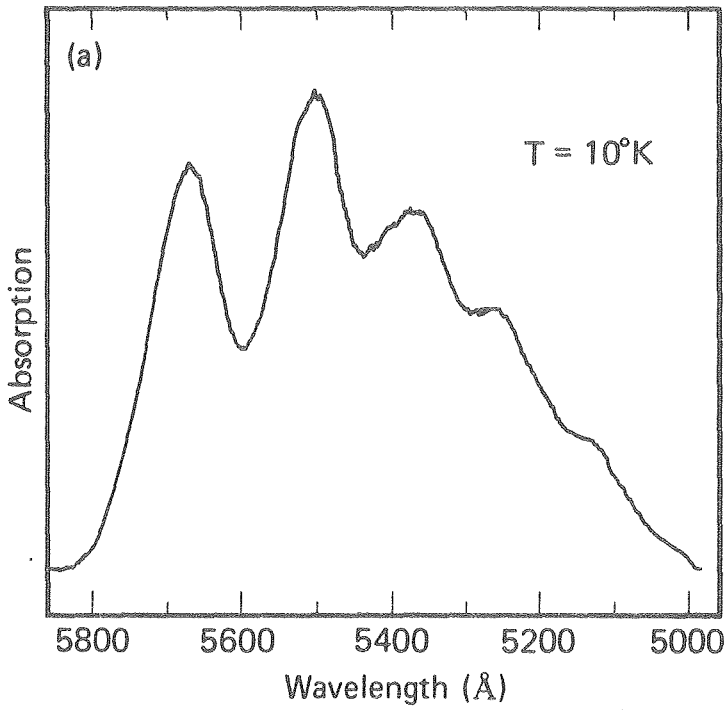
Figure 3. (a) Hole burned at the top of the 0-0 band of DMST in PVK (0.03 moles/ℓ); T = 8K, 2 min irradiation time. Pulsed dye laser linewidth: 0.84 cm^{-1}.
(b) Hole burned at λ = 5661.4 Å with a cw dye laser. Laser linewidth less than 0.01 cm^{-1}. T = 1.8K, 20 sec irradiation time.

Figure 4. Temperature dependence of the width of the hole obtained in the 0-0 absorption band of DMST in PVK (c$\sim$0.03 moles/ℓ).

Figure 5. The intensity dependence of the photoprocess efficiency. Both the the laser intensity I and the photoprocess efficiency P = A(I)/t (see text) are normalized. Sample: 3.4% DMST in PVK by weight, T = 1.8K.

Figure 6. Power curve fit of hole depth h versus time t after irradiation began. T = 1.8K, 2 min irradiation at 5668.4 Å, c = 0.03 moles/ℓ. A least squares fit to the expression lnh = lna + blnt gives a = 6.2, b = -0.25. The coefficient of correlation is r^2 = 0.94.

FIG 1


(a)
T = 10°K
Absorption
5800
5600
5400
5200
5000
Wavelength (Å)

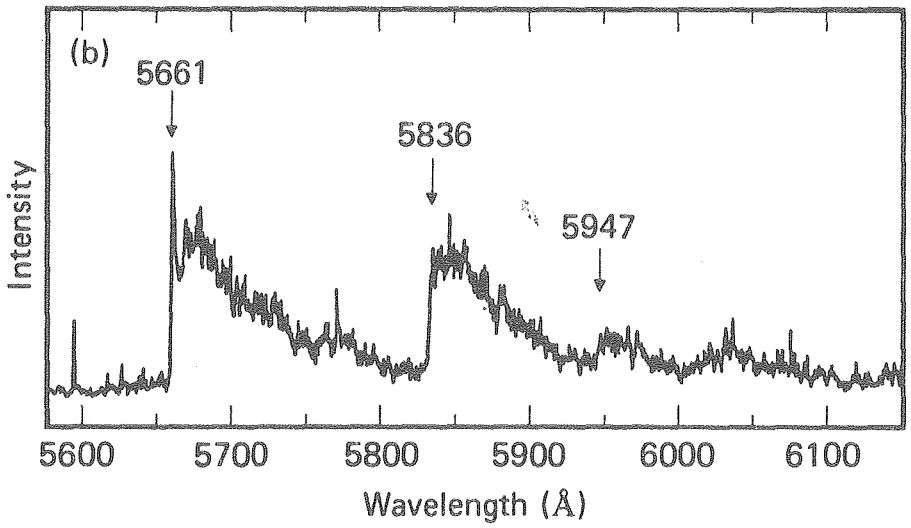

(b)
5661
5836
5947
Intensity
5600
5700
5800
5900
6000
6100
Wavelength (Å)

FIG 2

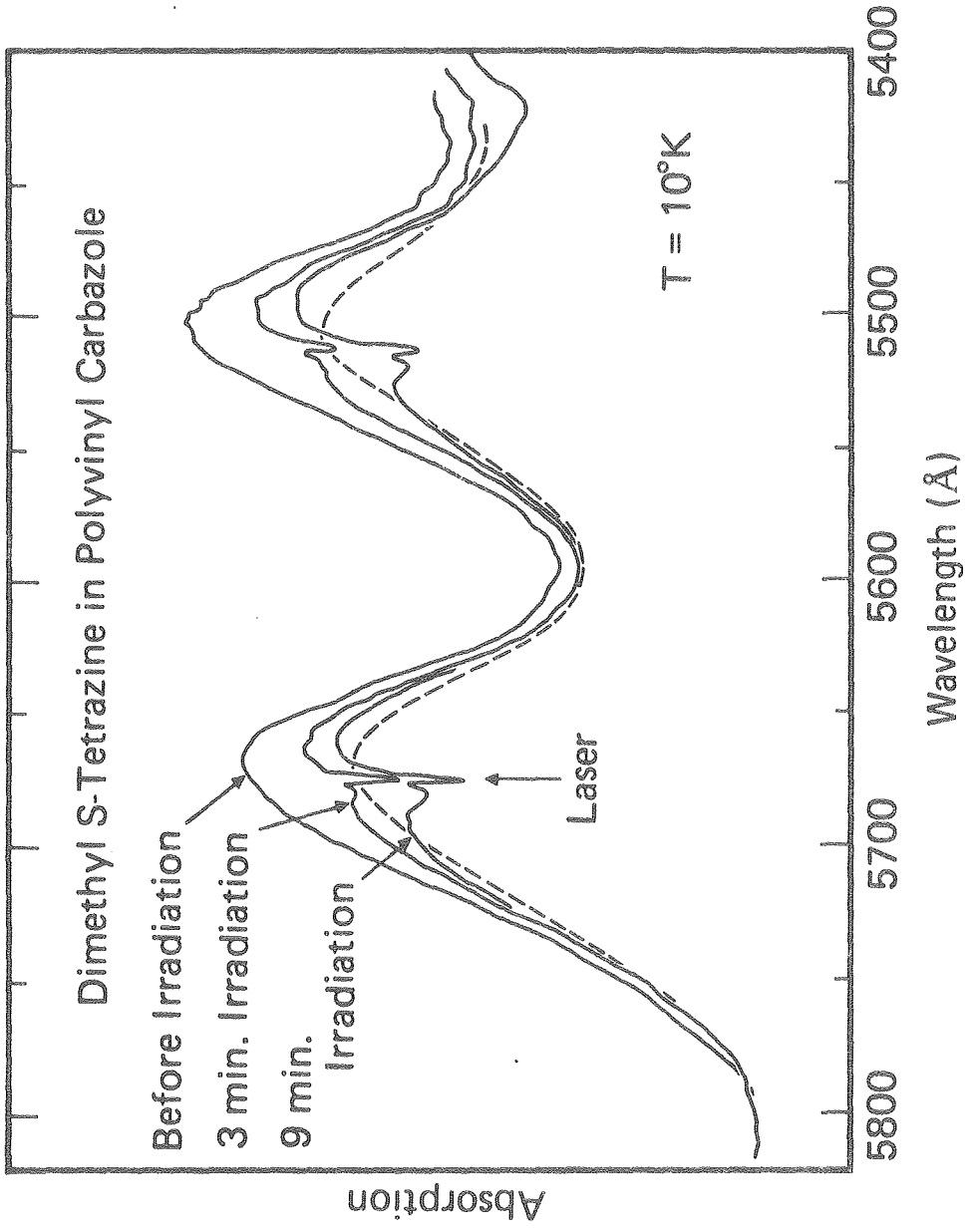

Dimethyl S-Tetrazine in Polyvinyl Carbazole
Before Irradiation
3 min. Irradiation
9 min. Irradiation
Laser
T = 10°K
Absorption
5800
5700
5600
5500
5400
Wavelength (Å)

FIG 3

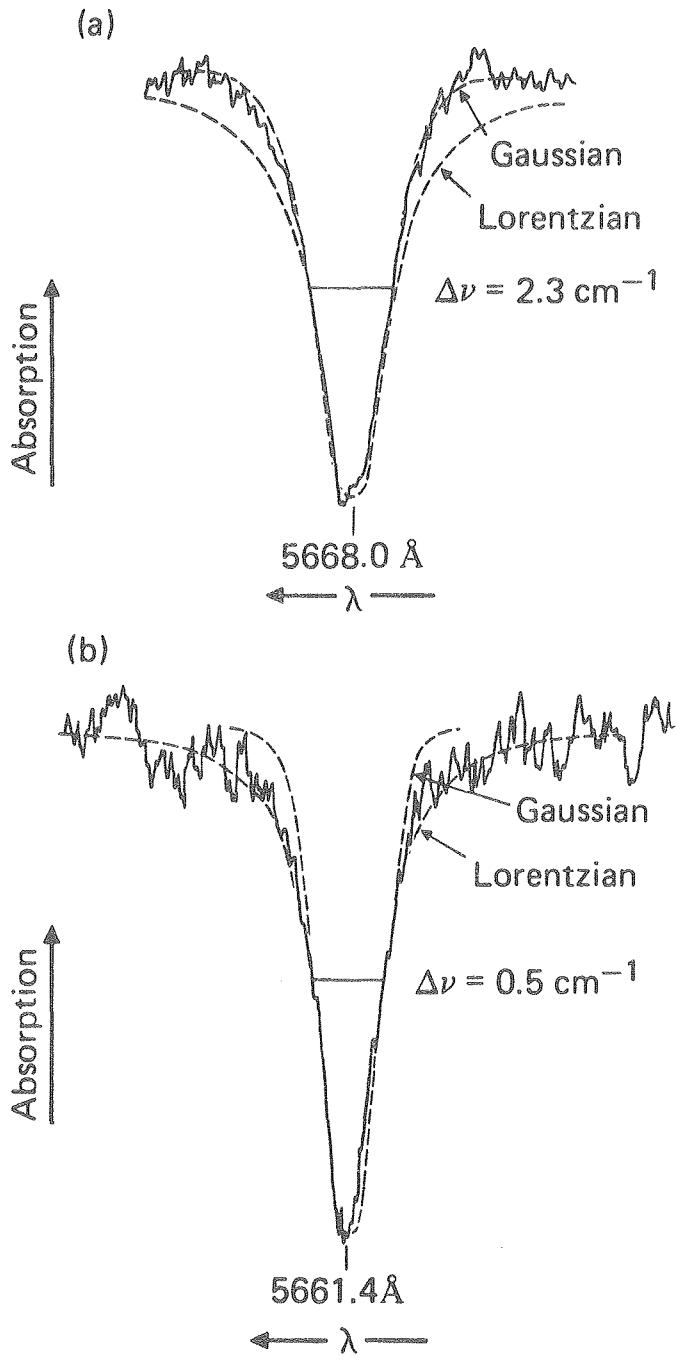

(a)
Gaussian
Lorentzian
$\Delta\nu$ = 2.3 cm^{-1}
Absorption
5668.0 Å
λ
(b)
Gaussian
Lorentzian
$\Delta\nu$ = 0.5 cm^{-1}
Absorption
5661.4Å
λ

FIG 4

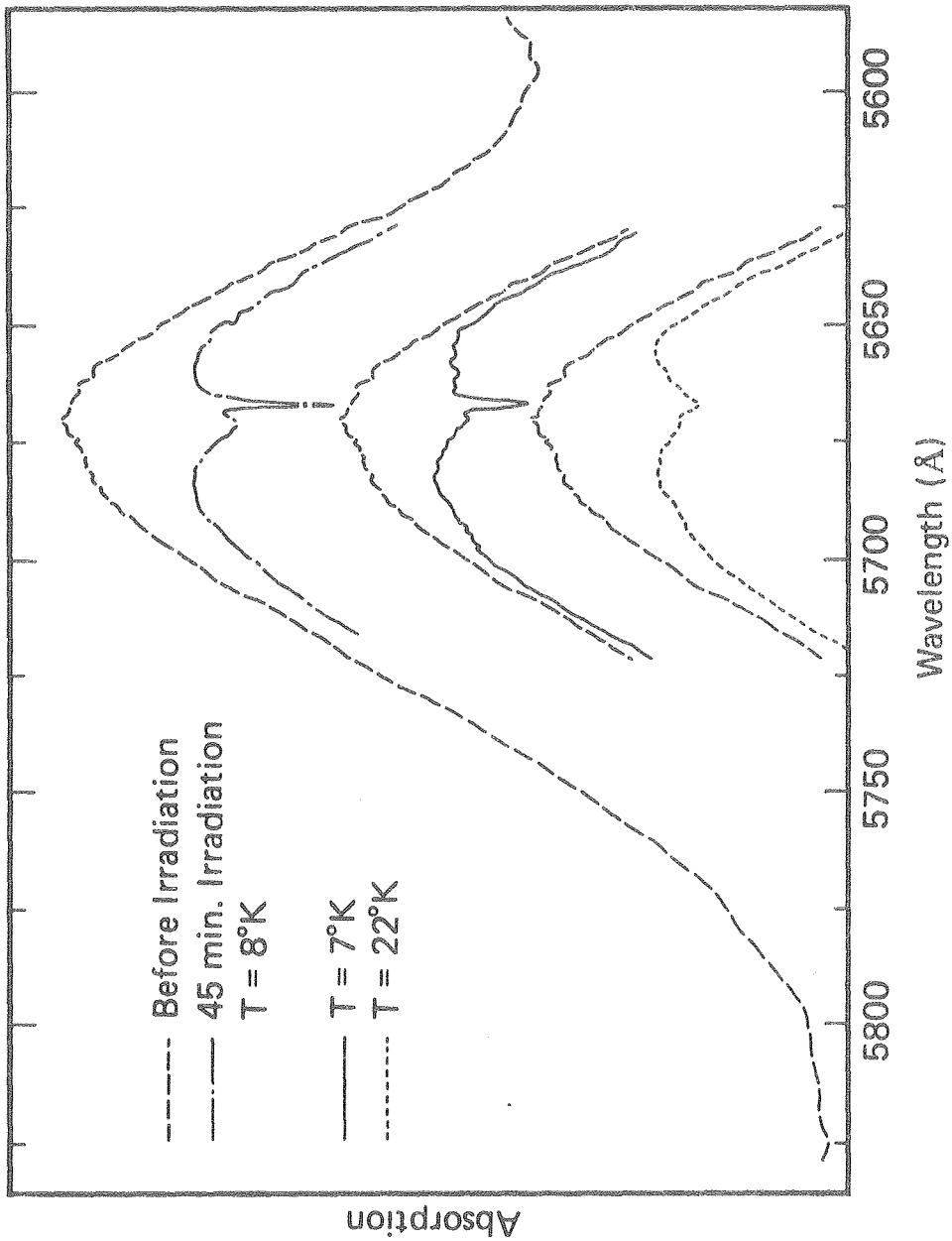

Absorption
Wavelength (Å)
5800
5750
5700
5650
5600
Before Irradiation
45 min. Irradiation
T = 8°K
T = 7°K
T = 22°K

FIG 5

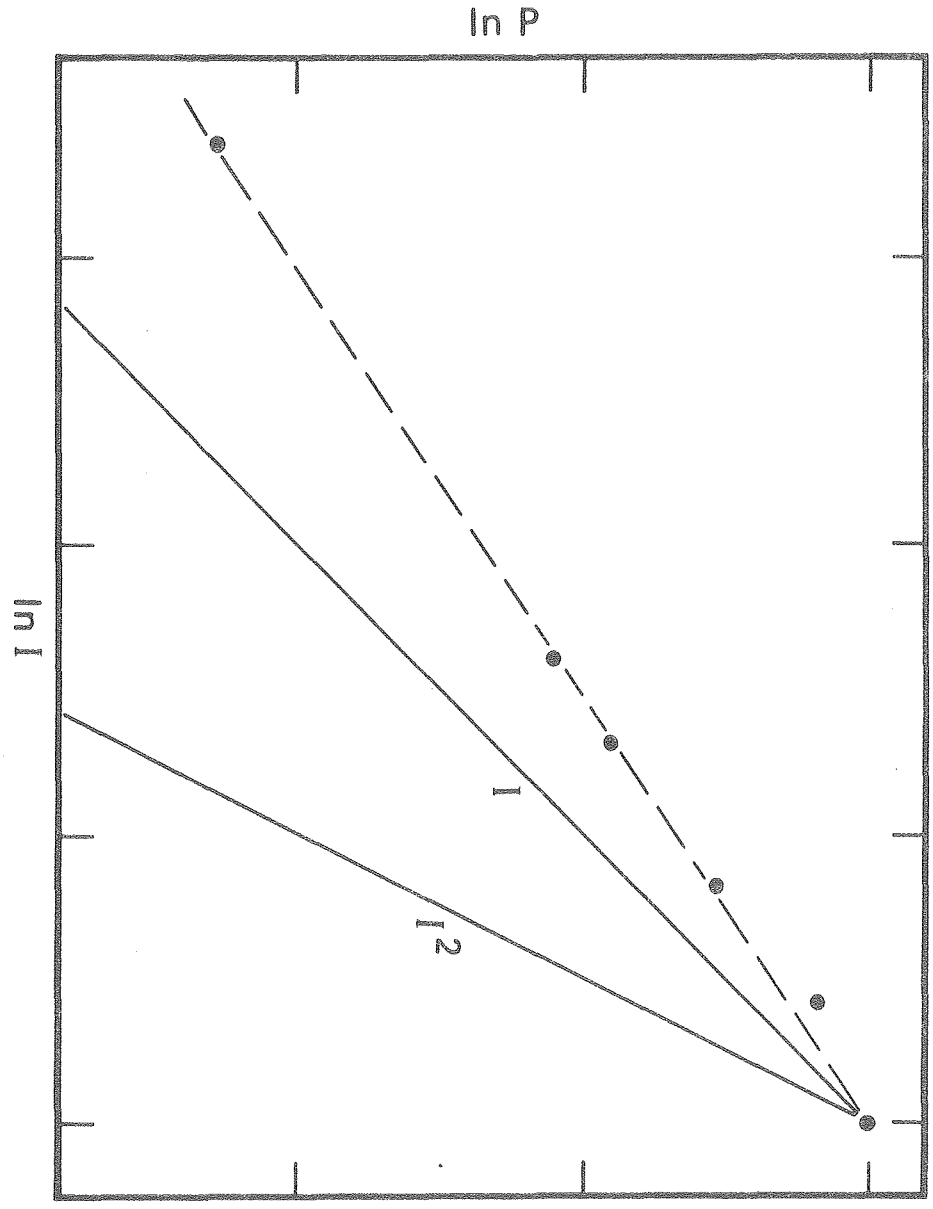
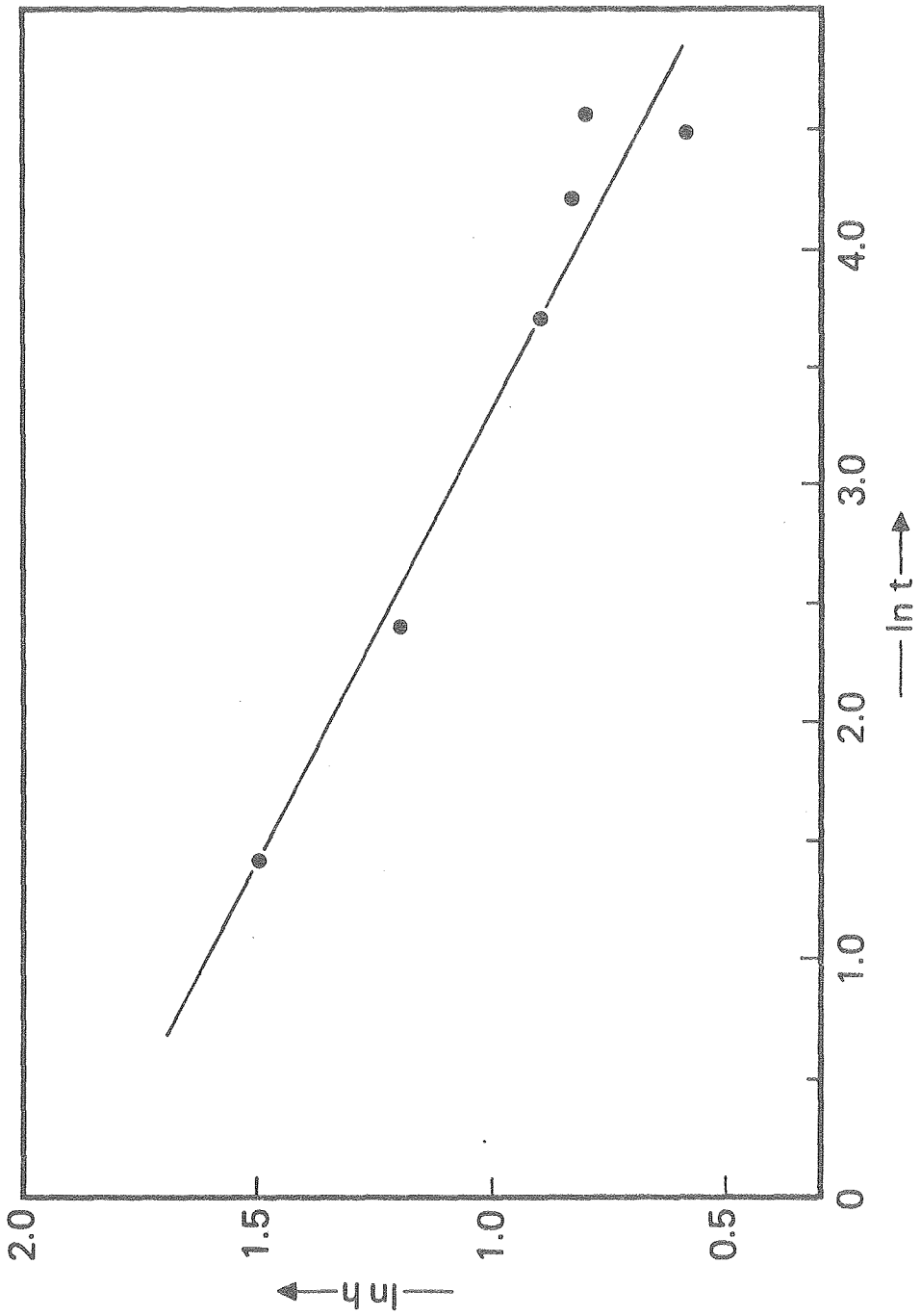



FIG 6