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## OPTICAL DEPHASING IN ORGANIC GLASSES BETWEEN 0.3 AND 20 K. A HOLE-BURNING STUDY OF RESORUFIN AND FREE-BASE PORPHIN

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Spectral holes have been burnt in the  $S_1 \leftarrow S_0$  0-0 transition of resorufin in polymethylmethacrylate (PMMA) and glycerol, and of free-base porphin ( $H_2P$ ) in PMMA and polyethylene (PE). The holewidths follow a  $T^{1.3}$  dependence over almost two orders of magnitude in temperature and extrapolate to the fluorescence lifetime-limited value of each guest when  $T \rightarrow 0$ . The discrepancy between the holewidths of resorufin in glycerol presented here and those reported in the literature are attributed to burning fluences. Photon-echo and hole-burning results are compared. Optical dephasing data are interpreted in terms of low-frequency localized phonon modes and are critically discussed.

### 1. Introduction

A wide variety of amorphous organic systems have shown a  $T^{1.3 \pm 0.1}$  temperature dependence of the homogeneous linewidth,  $\Gamma_{\text{hom}}$ , but the temperature range over which such behaviour was observed is relatively small, in many cases only between 1.2 and 4.2 K [1-8]. For some systems in which the temperature was extended down to 0.3 K [9-13], the same power law was found. Only a few hole-burning data above 4.2 K, however, have been reported that show this  $T$  dependence: free-base porphin ( $H_2P$ ) in a glycerol:ethanol (10:1) host up to 20 K [1], chlorophyll-a and -b in polystyrene up to 8.8 K [14] and tetracene in diphenyl- [15,16] and dimethyl-anthracene up to  $\approx 11$  K [16]. Whereas accumulated photon echoes on pentacene in polymethylmethacrylate (PMMA) between 1.5 and 12 K [17] reveal the same power law, two-pulse photon-echo and hole-burning data for resorufin in ethanol [8] and glycerol [18] measured up to 11.4 and 25.5 K, respectively, showed deviations from the  $T^{1.3 \pm 0.1}$  dependence of  $\Gamma_{\text{hom}}$  for temperatures above 4.2 K.

In order to check the conditions of validity of this power law, we have performed a hole-burning study of the  $S_1 \leftarrow S_0$  0-0 transition of various organic molecules in amorphous hosts over an extended tem-

perature range, between  $\approx 0.3$  and  $\approx 20$  K. The systems were resorufin in PMMA and glycerol, and  $H_2P$  in PMMA and polyethylene (PE). As will be shown, the results yield a  $T^{1.3}$  dependence over the entire temperature range investigated. This seems to confirm the "universality" of the power law of  $\Gamma_{\text{hom}}$  for organic molecules in amorphous environments at low temperatures, at least for linewidths determined by means of hole-burning techniques. From the dependence of the holewidth on the laser burning power and burning time for resorufin in glycerol, we were able to understand the source of the discrepancy between the holewidths presented here and those recently reported in the literature [18] for the same system.

A second aim of this study is to compare the results of hole-burning and photon-echo experiments. In principle, these techniques may yield different physical information because they measure on different time scales, and glasses - as is well known - have a broad range of relaxation rates. In fact, it has been claimed that optical linewidths of resorufin in ethanol [8] and glycerol [18] were different when measured with hole burning (time scale of minutes) as compared to two-pulse photon echoes (picosecond time scale), from which it was concluded that holewidths may not reflect the homogeneous line-

widths, but rather give information on slow relaxation (spectral diffusion) processes in glasses. We have compared the temperature dependence of our hole-burning data of resorufin in glycerol with the photon-echo data of ref. [18] and, as will be discussed (fig. 4), have reached a different conclusion to that of Fayer and co-workers [18].

Finally, we have tried to fit Jackson and Silbey's model for optical dephasing [19] to our experimental results between 0.3 and 20 K. In this model it is assumed that localized phonon modes, in addition to two-level systems (TLS) of the glass, are responsible for the optical dephasing. The activation energies which result from the fits to our data of resorufin in glycerol are much smaller than those reported for the same system in ref. [18]. The results obtained for the four amorphous systems studied here are discussed and compared with previously reported systems. Although localized phonon modes in glasses are assumed to exist, no experimental evidence has been found for them so far.

## 2. Experimental

Two samples of resorufin (Janssen Chimica) in glycerol were prepared with optical densities (OD) at 580 nm of 0.2 and 0.6, respectively. Samples of resorufin and free-base porphyrin ( $H_2P$ ) in PMMA with optical densities of 0.4 at 578 nm and  $6 \times 10^{-3}$  at 610 nm, respectively, were prepared by mixing solutions of the guest molecules in ethanol with PMMA dissolved in dichloromethane. After pumping in an oven at 60°C for three days, transparent films of PMMA were obtained with a thickness of 100  $\mu m$  for resorufin and 190  $\mu m$  for  $H_2P$ . Free-base porphyrin in PE (Wacker, high density  $\rho = 0.955$  g/ml) at  $c \approx 10^{-4} - 10^{-5}$  mol/l was prepared by adding a solution of  $H_2P$  in MTHF to molten PE. This mixture was kept above the melting point of PE (135°C) until the MTHF had evaporated. The sample was subsequently cooled down to room temperature in about 1 h.

Holes were burnt with a single-frequency dye laser (Coherent, model CR 599-21, amplitude stabilized to <0.5% by an EO modulator, with rhodamine 6G, scan range 30 GHz, frequency jitter  $\leq 2$  MHz). In order to burn holes of relative depth  $D \approx 2-3\%$ , dif-

Table 1  
Laser burning fluences,  $Pt$  ( $\mu J/cm^2$ ), used for various organic amorphous systems at different temperatures

Sample	$T$ (K)	$Pt$ ( $\mu J/cm^2$ )
resorufin/glycerol	0.4	0.8
	1.2	1.8
	12.6	140
	21.9	350
resorufin/PMMA	0.4	0.8
	1.2	1.8
	11.1	87
$H_2P$ /PMMA	0.35	28
	1.2	67
	11.2	1260
	13.4	3100
$H_2P$ /PE	0.3	2.8
	1.2	7.0
	10	70
	16.8	350

ferent burning fluences,  $Pt$  ( $P$ : laser power,  $t$ : burning time) were used. These  $Pt$  values increase with temperature and depend on the sample (see table 1). The laser was focused on an area of  $\approx 5$  mm<sup>2</sup>, and its power controlled with a variable beam attenuator (NRC, model M 928-B) and neutral density filters. The holes were probed by fluorescence excitation, that is the laser was scanned, attenuated by a factor of 5-100, over the spectral region of the hole and the fluorescence was detected (at  $\lambda > 610$  nm for resorufin, and at  $\lambda > 645$  nm for  $H_2P$ ) with a cooled photomultiplier (EMI, model 9658 R). The holes burnt in resorufin in glycerol were probed simultaneously by means of the fluorescence signal and the transmission signal through the sample (the latter was detected with a photodiode, EG&G, model HUV 4000). The holewidths of resorufin in glycerol, at a given temperature, were independent of the cooling rate of the sample. This is in contrast to the results of resorufin in ethanol, for which we found two solid phases that yielded very different holewidths [13].

The homogeneous linewidth,  $\Gamma_{\text{hom}}$ , was determined from the relation  $\Gamma_{\text{hom}} = \frac{1}{2}\Gamma_{\text{hole}} - \Gamma_{\text{g}}$ , where  $\Gamma_{\text{hole}}$  is the measured holewidth extrapolated to the lowest burning fluences,  $Pt$ , and  $\Gamma_{\text{g}}$  is the frequency jitter of the laser ( $\Gamma_{\text{g}} \leq 2$  MHz).

Between 1.2 and 4.2 K a conventional bath cryostat was used in which the temperature, varied by

means of the vapour pressure, was measured both by this pressure and by a calibrated carbon resistor with an accuracy of  $\pm 0.01$  K. For temperatures below 1.2 K, a  $^3\text{He}$ -glass insert was placed inside the  $^4\text{He}$ -bath cryostat [20]. After pumping the  $^4\text{He}$  bath to 1.2 K,  $^3\text{He}$  was condensed into the inner cryostat, where it could be kept liquid for  $\approx 3$ –5 h. By reducing the vapour pressure, temperatures down to 0.3 K were reached. The temperature was measured by a calibrated carbon resistor (Matsushita 100  $\Omega$ ,  $\frac{1}{8}$  W) placed in contact with the sample and, simultaneously, via the vapour pressure. The accuracy in the temperature determination was estimated to vary between  $\pm 0.01$  and  $\pm 0.02$  K [3,10,11,13,20].

Between 4.2 and 22 K a gas flow cryostat (Leybold-Heraeus) was used in which the temperature of the gas flow was stabilized by an electronic unit. The latter measures the resistance of a thermistor and controls the electric current through a heater [21]. In this cryostat the temperature is measured close to the sample (but not in direct contact with it) by a calibrated carbon resistor, via a Wheatstone bridge. The accuracy of the temperature given by the resistor is  $\approx \pm 0.01$ – $0.02$  K below 15 K and  $\approx 0.05$  K above it.

### 3. Results and discussion

In fig. 1 a log-log plot  $\Gamma_{\text{hom}} - \Gamma_0$  versus temperature between  $\approx 0.3$  and  $\approx 20$  K is given for the four systems.  $\Gamma_0 = (2\pi T_1)^{-1}$  is the fluorescence lifetime-limited value of the respective guest molecule when  $T \rightarrow 0$ . Holes were burnt in these samples in the red wing of their 0–0 absorption band at about 591 and 588 nm for resorufin in PMMA and glycerol, respectively, and at 610 and 615 nm for H<sub>2</sub>P in PMMA and PE, respectively. All four curves follow the same power law,  $\Gamma_{\text{hom}} - \Gamma_0 \propto T^{1.30 \pm 0.05}$ , over the entire temperature range, independent of the hole-burning mechanism (intramolecular for H<sub>2</sub>P, and intermolecular between guest and host for resorufin). These results confirm and extend the validity of the  $T^{1.3}$  dependence of  $\Gamma_{\text{hom}}$  previously observed by us in organic glassy systems in a more restricted temperature range [22]. This general power law seems to be valid over at least two orders of magnitude in temperature.

Fig. 2 is a plot of the homogeneous linewidth,  $\Gamma_{\text{hom}}$ ,

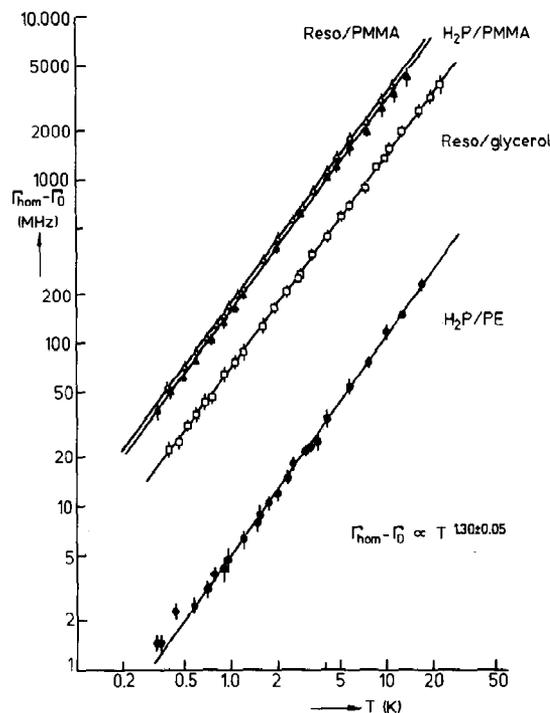


Fig. 1. log-log plot of  $\Gamma_{\text{hom}} - \Gamma_0$  versus temperature  $T$ , for resorufin in PMMA (open triangles), H<sub>2</sub>P in PMMA (closed triangles), resorufin in glycerol (open squares) and H<sub>2</sub>P in PE (closed circles).  $\Gamma_0 = (2\pi T_1)^{-1}$  is the fluorescence lifetime-limited value of each guest molecule. Note that the data follow a  $T^{1.3}$  power law between  $\approx 0.3$  and  $\approx 20$  K.

as a function of temperature for resorufin in PMMA [10], glycerol (from fig. 1) and PE [10], and for H<sub>2</sub>P in PMMA (from fig. 1) and PE [11]. Note that the three curves of resorufin and both curves of H<sub>2</sub>P extrapolate smoothly with a  $T^{1.3}$  dependence to a value  $\Gamma_{\text{hom}} = \Gamma_0 = (2\pi T_1)^{-1}$  when  $T \rightarrow 0$ , where  $T_1$  is the fluorescence lifetime of each guest:  $\Gamma_0 \approx 10$  MHz for H<sub>2</sub>P [23] and  $\Gamma_0 \approx 20$  MHz for resorufin [10]. It should be noted that the values of  $\Gamma_{\text{hom}}$  at 0.4 K obtained by us for resorufin in glycerol ( $\approx 42$  MHz) and PE ( $\approx 34$  MHz) are already markedly smaller than the extrapolation value (for  $T \rightarrow 0$ ) used in ref. [18]],  $\Gamma_0 = 46.8$  MHz, which was based on a fluorescence decay time of 3.4 ns.

The dependence of the holewidth,  $\frac{1}{2}\Gamma_{\text{hole}}$ , on the burning time for resorufin in glycerol at  $T = 1.2$  K is shown in fig. 3a for two different burning powers. The holes burnt at higher power ( $2.2 \mu\text{W}/\text{cm}^2$ ) were probed simultaneously by means of the fluorescence

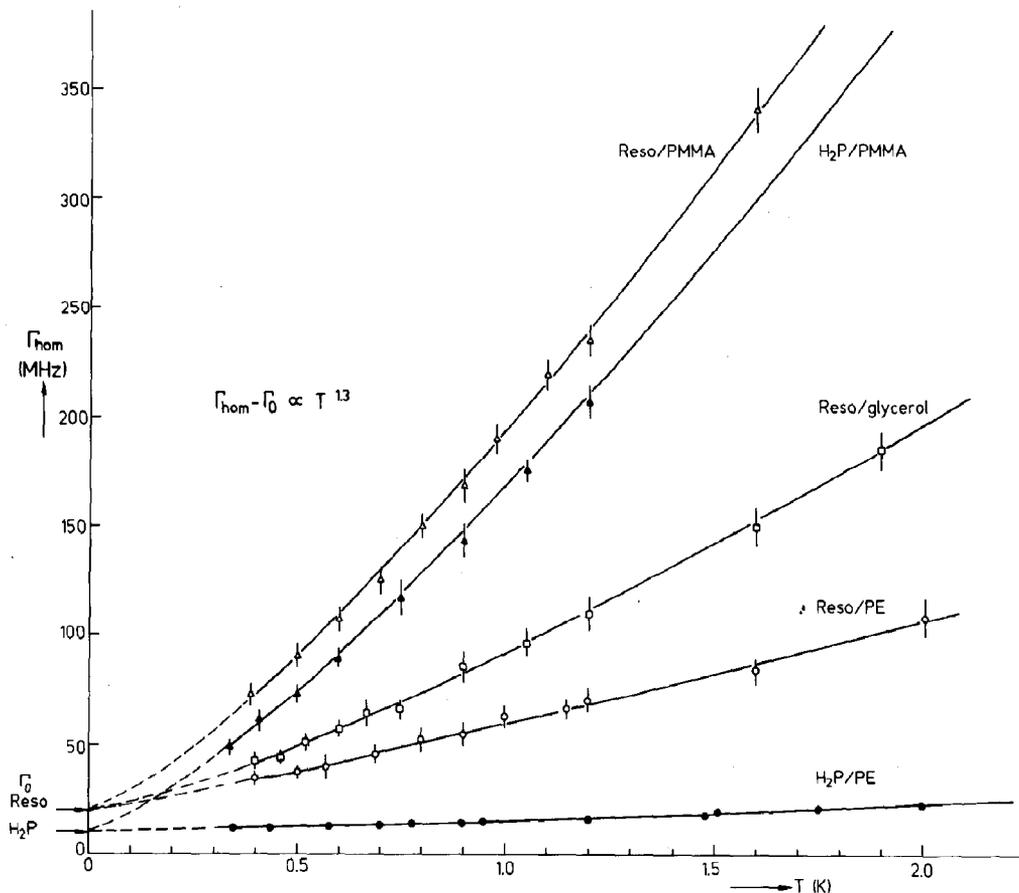


Fig. 2. Temperature dependence of  $\Gamma_{\text{hom}}$  of the 0-0 transition of resorufin in PMMA (open triangles), H<sub>2</sub>P in PMMA (closed triangles), resorufin in glycerol (open squares), resorufin in PE (open circles) and H<sub>2</sub>P in PE (closed circles) between  $\approx 0.3$  and  $\leq 2$  K. Note that the values of  $\Gamma_{\text{hom}}$  smoothly extrapolate to the fluorescence lifetime-limited value of each guest molecule,  $\Gamma_0 = (2\pi T_1)^{-1}$ , when  $T \rightarrow 0$ , with  $\Gamma_{\text{hom}} = \Gamma_0 + cT^{1.3}$ .

(at 90° from the excitation direction, open triangles) and the transmission through the sample (closed triangles). Holes burnt at lower power ( $0.38 \mu\text{W}/\text{cm}^2$ ) were detected in fluorescence only (open circles). Note that all curves extrapolate to the same value  $\frac{1}{2}\Gamma_{\text{hole}} = \Gamma_{\text{hom}} \approx 105 \pm 10$  MHz when  $t \rightarrow 0$ , but the two upper curves reach this value with a much steeper slope. A similar effect has previously been established for a non-photochemical hole-burning (NPHB) system, pentacene in PMMA [6]. Two conclusions can be drawn from these results: first, the true value of  $\Gamma_{\text{hom}}$  at a given temperature is only reached at very low laser fluences; second, for a given laser burning power (above a specific value), holes detected in transmission through the sample are

broader than holes detected in fluorescence. They only coincide at very short burning times (for resorufin in glycerol this occurs at  $t < 2$  s for  $P = 2.2 \mu\text{W}/\text{cm}^2$ ). The curves in fig. 3a were traced with a  $(Pt)^{0.23}$  dependence, as discussed below.

The data of fig. 3a, together with some additional values of  $\frac{1}{2}\Gamma_{\text{hole}}$ , were replotted in the form of  $\log \frac{1}{2}\Gamma_{\text{hole}}$  versus  $\log Pt$  in fig. 3b. The results fall on two straight lines (upper one for holes detected in transmission, lower one for holes probed in fluorescence), which can be represented by  $\frac{1}{2}\Gamma_{\text{hole}} = c(Pt)^{0.23 \pm 0.01}$  over more than three orders of magnitude, from  $Pt \geq 3 \mu\text{J}/\text{cm}^2$  up to  $13 \text{ mJ}/\text{cm}^2$ . The same dependence on  $Pt$  has been found by us for pentacene in PMMA [6] and other organic glasses

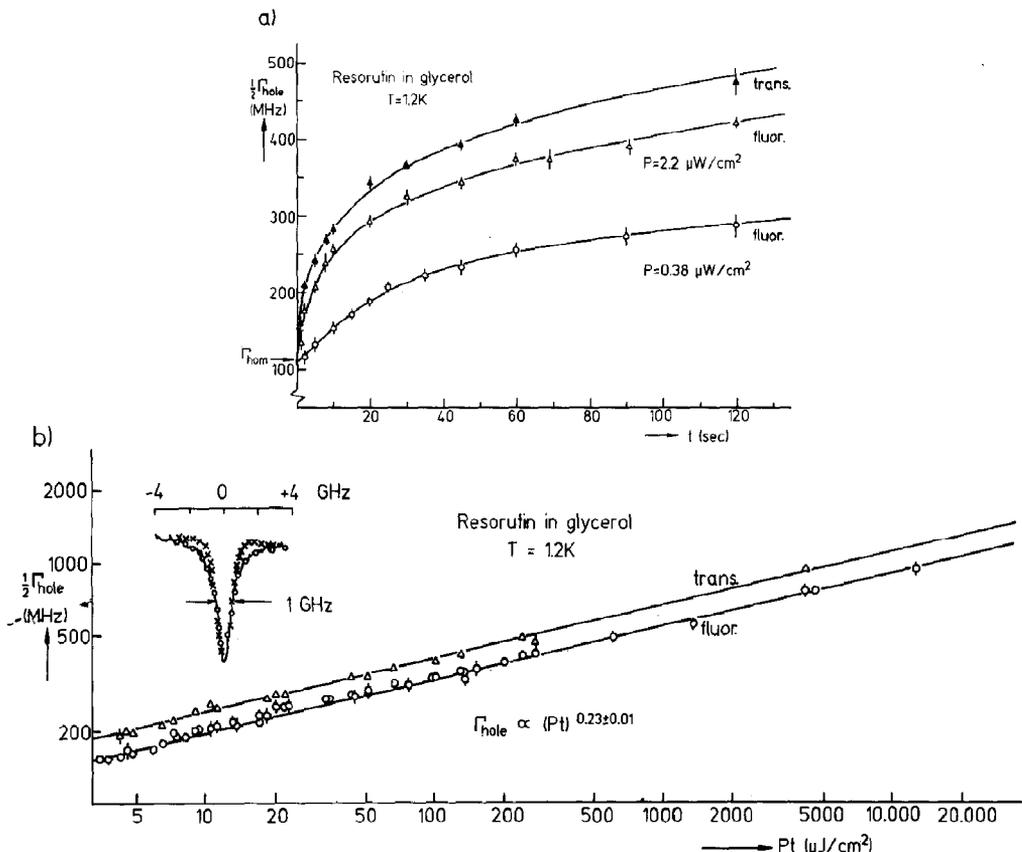


Fig. 3. (a)  $\frac{1}{2}\Gamma_{\text{hole}}$  as a function of burning time  $t$  for resorufin in glycerol at 1.2 K, for two burning powers. At  $P=2.2 \mu\text{W}/\text{cm}^2$  the holes were probed simultaneously via the fluorescence excitation signal and the transmission signal through the sample. At  $P=0.38 \mu\text{W}/\text{cm}^2$  holes were observed in fluorescence only. For  $t \rightarrow 0$   $\frac{1}{2}\Gamma_{\text{hole}} = \Gamma_{\text{hom}} \approx 105 \pm 10$  MHz. (b) log-log plot of  $\frac{1}{2}\Gamma_{\text{hole}}$  versus burning fluence,  $Pt$ , for resorufin in glycerol at 1.2 K. Holes were probed in transmission through the sample (upper curve) and fluorescence excitation (lower curve). The data follow  $\frac{1}{2}\Gamma_{\text{hole}} = c(Pt)^{0.23 \pm 0.01}$  over at least three orders of magnitude in  $Pt$  ( $Pt \geq 3 \mu\text{J}/\text{cm}^2$ ). Insert: Hole burnt with  $Pt = 600 \mu\text{J}/\text{cm}^2$  at 1.2 K.  $\frac{1}{2}\Gamma_{\text{hole}} = 500$  MHz. Note that the hole shape is Lorentzian (circles). For comparison, a Gaussian curve (crosses) has also been drawn.

[24]. It differs from simple saturation broadening, which is proportional to the square root of the power [25,26]. We have observed that for  $Pt < 3 \mu\text{J}/\text{cm}^2$ , the resorufin in glycerol data probed by fluorescence excitation at 1.2 K follow a linear dependence on  $Pt$ ,  $\frac{1}{2}\Gamma_{\text{hole}} = \Gamma_{\text{hom}} + aPt$ , with  $a = (1.0 \pm 0.1) \times 10^4$  when  $\frac{1}{2}\Gamma_{\text{hole}}$  and  $\Gamma_{\text{hom}}$  are given in GHz, and  $Pt$  in  $\text{J}/\text{cm}^2$ .

It should be noted that the absolute values of  $Pt$  needed to burn the 0-0 transition of resorufin in glycerol and PMMA at 1.2 K are  $\approx 10^4$  times smaller than those needed for pentacene in PMMA, a system in which non-photochemical hole burning (NPHB) occurs [6,17]. Because the optical densities and the holewidths of these three samples are similar

( $\text{OD} \approx 0.4-0.9$ , and  $\frac{1}{2}\Gamma_{\text{hole}} \approx 110-500$  MHz), we conclude that the hole-burning efficiency of resorufin is orders of magnitude larger than that of pentacene in PMMA. This suggests that photochemical hole-burning (PHB), known to have much larger hole-burning efficiencies than NPHB, is the mechanism that takes place in the ionic dye resorufin [10]. We should also remark that the ratio of  $Pt$  values used for  $\text{H}_2\text{P}$  and resorufin in PMMA to obtain the values of  $\Gamma_{\text{hom}}$  is of the same order of magnitude as the ratio of OD values of these two samples. Since  $\text{H}_2\text{P}$  undergoes PHB [27], these observations further support the idea of a PHB mechanism occurring in resorufin. It has previously been observed that the

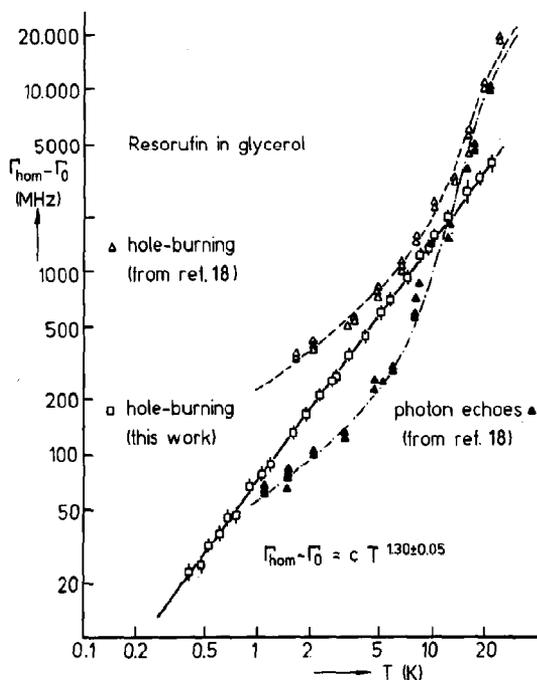


Fig. 4.  $\log(\Gamma_{\text{hom}} - \Gamma_0)$  versus  $\log T$  between  $\approx 0.3$  and  $\approx 25$  K for resorufin in glycerol. In order to compare our hole-burning results (open squares) with those taken from ref. [18] (hole burning, open triangles; photon echo, closed triangles), all data were plotted with  $\Gamma_0 = 20$  MHz. Note that our holewidths follow  $\Gamma_{\text{hom}} - \Gamma_0 = cT^{1.3}$  from 0.4 to at least 22 K.

photoproduct of this ionic dye absorbs at  $\approx 50$ – $400$   $\text{cm}^{-1}$  higher energy than the original molecule, the frequency being dependent on the polarity of the host [10]. From these results it was concluded that the photochemistry is due to an excited-state charge redistribution, and that an *intermolecular PHB* mechanism is responsible for the holes in resorufin.

The insert of fig. 3b shows a hole burnt in the 0–0 transition of resorufin in glycerol at 1.2 K with  $Pt = 600$   $\mu\text{J}/\text{cm}^2$  at 1.2 K. Although the holewidth ( $\frac{1}{2}\Gamma_{\text{hole}} = 500$  MHz) is about five times larger than  $\Gamma_{\text{hom}}$ , the hole shape is Lorentzian, as previously observed for other organic amorphous systems [15].

In fig. 4 we have plotted  $\log(\Gamma_{\text{hom}} - \Gamma_0)$  versus  $\log T$  for our hole-burning experiments on resorufin in glycerol between 0.3 and 20 K, together with the results of recent hole-burning and photon-echo experiments by Fayer and co-workers on the same system [18]. In order to compare their data to ours, we have taken the values of  $\Gamma_{\text{hom}}$  of ref. [18] and sub-

tacted  $\Gamma_0 = 20$  MHz [10]. The middle curve (open squares) represents our hole-burning data, which follow a  $T^{1.3}$  dependence between 0.4 and 22 K (see fig. 1). In contrast, the linewidths derived from both photon echoes and hole burning between  $\approx 1.5$  and  $\approx 25$  K show a strong deviation from this power law [18].

When first looking at the hole-burning data in fig. 4, we noticed that the results of ref. [18] are a factor of about three larger than ours for  $T \lesssim 2$  K and for  $T > 20$  K. This discrepancy is to be attributed to a difference in burning fluences (see fig. 3b): the value of  $\frac{1}{2}\Gamma_{\text{hole}} \approx 360$  MHz at 1.7 K for holes probed in transmission [18] was obtained with a burning fluence about ten times larger than that used by us at the same temperature for holes probed in fluorescence. For instance, for  $Pt = 18$   $\mu\text{J}/\text{cm}^2$ , the fluence used in ref. [18], a holewidth  $\frac{1}{2}\Gamma_{\text{hole}} \approx 280$  MHz at 1.2 K is obtained on the upper curve of fig. 3b. This value is of the same order as that obtained by extrapolating the hole-burning data of ref. [18] to 1.2 K. A similar argument explains the difference between holewidths observed at high temperature: for holes burnt at 25.5 K a fluence of 6.0  $\text{mJ}/\text{cm}^2$  was used [18], against our value of 350  $\mu\text{J}/\text{cm}^2$  at 22 K. Thus, in order to obtain reliable holewidths with the same physical meaning, the lowest possible burning fluences at each temperature should be used.

We will now compare the values of  $\Gamma_{\text{hom}} - \Gamma_0$  derived from our hole-burning data for resorufin in glycerol with those derived from photon-echo data [18]. Note in fig. 4 that the values found with the two techniques are very similar at 1.1 K and between 10 and 12 K, but they deviate at other temperatures; the photon-echo linewidths increase much faster than  $T^{1.3}$  above  $\approx 5$  K. Whether this difference has a physical meaning or is caused by some experimental artefact, we cannot say. In a photostable crystalline sample of good optical quality the photon-echo technique is an elegant way to determine the value of  $\Gamma_{\text{hom}}$ . It is much more difficult, however, to do this kind of experiment on a picosecond time scale on the present type of sample. In this case one has to correct the data for simultaneous burning by the laser pulses. Furthermore, the pulse powers that have to be used may be so high that the local thermal equilibrium around a guest molecule is disturbed due to the low thermal conductivity of the glassy host.

The authors of ref. [18] suggested that the extra broadening of their hole-burning (HB) data with respect to the photon-echo data,  $\Gamma_{SD} = \Gamma_{HB} - \Gamma_{ph.echo}$ , results from spectral diffusion (SD). That is, they assume that slow relaxation processes occur in the glass on a time scale much longer than that determined by the picosecond photon-echo experiment, but much shorter than that of conventional hole-burning experiments (of the order of  $10^2$  s) [18]. For the systems studied in refs. [8,18] the temperature dependence of this extra hole-broadening process was claimed to follow a power law with an exponent close to 1, the latter being dependent on the system. For the case of resorufin in glycerol it was concluded that  $\Gamma_{HB} - \Gamma_{ph.echo} = \Gamma_{SD} = T^{0.8 \pm 0.1}$  [18]. It is obvious from fig. 4 that the difference between our hole-burning results and those from the photon-echo work does not obey such a power law. In fact, the data cross each other at  $T \approx 12$  K and probably at  $T < 1.1$  K. No photon echoes, however, have been reported for such low temperatures. We conclude from these experiments that the temperature dependence of spectral diffusion processes, if defined as the difference between holewidths and photon-echo linewidths [18], cannot be described by a  $T^\alpha$  function.

Preliminary transient hole-burning experiments on  $H_2P$  in PE between 1.2 and 4.2 K performed on a time scale of milliseconds [28] have yielded results identical to those obtained in a conventional way on a time scale of minutes [5,11]. Furthermore, at 1.2 K no broadening of holes probed in fluorescence excitation was observed as a function of time after burning, not even many hours after they had been burnt. These results suggest that spectral diffusion does not take place over a time span of seven orders of magnitude (from  $10^{-3}$  to  $10^4$  s), at least for the system  $H_2P$  in PE. Long-time relaxation processes (on a time scale of hours) have also been studied in pentacene in PMMA [6] and resorufin in glycerol [29]. The results have again shown that holes probed in fluorescence do *not* broaden as a function of time after burning. Thus, spectral diffusion does *not* take place for these two systems on a time scale between a few seconds and  $10^4$  s.

Let us assume then that our hole-burning data *do* reflect the homogeneous linewidth for the four samples studied (see fig. 1). We have tried to fit the ex-

perimental values with a theoretical model [19], as recently done for resorufin in ethanol [13] and previously for various other organic amorphous systems [11]. Jackson and Silbey's model [19] was applied in either of the two following approximations:

(a) with a single activation energy  $E$ ,

$$\Gamma_{\text{hom}} - \Gamma_0 = aT + b \frac{\exp(-E/kT)}{1 - \exp(-E/kT)} \quad (1)$$

and (b) with a Gaussian distribution of activation energies,

$$\Gamma_{\text{hom}} - \Gamma_0 = aT + \sum_i b_i \frac{\exp(-E_i/kT)}{1 - \exp(-E_i/kT)}, \quad (2)$$

where  $b_i$  represents the weighting factor of a Gaussian distribution with central frequency  $E_0$  and total width at half height  $\Delta E$  (see ref. [11]).

The first term in eqs. (1) and (2) represents the contribution to the dephasing of two-level systems (TLS) of the glass, and the second term is attributed to low-frequency localized modes, like librational motions of the guest molecule in the host. We have assumed that at very low temperatures (between  $T \approx 0.3$  and 0.6 K) only the first term in eqs. (1) and (2) plays a role. Thus we can estimate the values of  $a$  at these temperatures for the four samples, see table 2. The librational frequencies  $E$  and  $E_0$  and the distribution value  $\Delta E$  were obtained from the best fits of eqs. (1) and (2) to the data between  $\approx 0.4$  K and up to various temperatures: 4.2 and  $\approx 12$  K for all samples,  $\approx 17$  K for  $H_2P$  in PE, and  $\approx 22$  K for resorufin in glycerol. The fits are rather good, since the  $\chi^2$  values, defined as

$$\chi^2 = \frac{1}{N} \sum_i (\Gamma_{\text{fit},i} - \Gamma_{\text{meas},i})^2 / \Gamma_{\text{fit},i}^2$$

are small ( $\chi^2 \leq 3\%$  for fits to eq. (1) and  $\leq 1\%$  for eq. (2)). The  $\pm$  values given with  $E$  on table 2 were calculated with the higher and lower limits of the  $a$  values.

Note that the values of  $E$  and  $E_0$  obtained over a temperature range from  $\approx 0.4$  to 4.2 K all lie between  $\approx 2.0$  and  $\approx 2.5$   $\text{cm}^{-1}$ , as previously observed for similar organic amorphous systems [11]. However, the  $E$  and  $E_0$  values increase at higher temperatures. This effect is more pronounced when a single librational frequency is assumed to be respon-

Table 2

Activation energies,  $E$ ,  $E_0$ , width of energy distribution,  $\Delta E$ , and coupling parameter  $a$ , calculated from fits of eqs. (1) and (2) to the experimental data (see fig. 1).  $\delta$  represents the hole-phonon-sidehole spectral distance

System	Eq. (1)		Eq. (2)		
	$a$ (MHz/K)	$E$ (cm <sup>-1</sup> )	$E_0$ (cm <sup>-1</sup> )	$\Delta E$ (cm <sup>-1</sup> )	$\delta$ (cm <sup>-1</sup> )
resorufin/PMMA					
0.39-4.2 K		2.5 ± 0.2	2.0	0.2	
0.39-11.1 K	145 ± 5	2.7 ± 0.1	2.5	0.2	16.7 ± 0.9
H <sub>2</sub> P/PMMA					
0.34-4.2 K		2.2 ± 0.2	2.0	0.2	
0.34-13.5 K	130 ± 5	3.1 ± 0.2	2.3	0.2	18.9 ± 1.0
resorufin/glycerol					
0.40-4.2 K		2.2 ± 0.2	1.9	0.2	
0.40-12.6 K	60 ± 2	5.0 ± 0.2	2.8	0.3	26.3 ± 0.8
0.40-21.9 K		5.9 ± 0.2	4.0	0.3	
H <sub>2</sub> P/PE					
0.33-4.2 K		2.4 ± 0.2	2.1	0.2	
0.33-12.9 K	4.1 ± 0.2	4.3 ± 0.2	2.3	0.2	17.6 ± 0.6
0.33-16.8 K		5.9 ± 0.3	2.9	0.3	

sible for the dephasing (eq. (1)). For example, for resorufin in glycerol  $E$  increases from 2.2 to  $\approx 6$  cm<sup>-1</sup> when the temperature range is extended from 4.2 to 22 K. A similar result is obtained for H<sub>2</sub>P in PE. In the case of a Gaussian distribution of localized modes (eq. (2)), a much smaller increase in the value of  $E_0$  is found (e.g. for resorufin in glycerol,  $E_0 \approx 2$  cm<sup>-1</sup> between 0.4 and 4.2 K and  $E_0 \approx 4$  cm<sup>-1</sup> between 0.4 and 22 K).

From site-selection spectra and hole-burning experiments there is no evidence, however, for localized modes with the activation energies calculated above. Neither does a direct correlation seem to exist between  $E$  values and  $\delta$  values, where  $\delta$  is the spectral distance between a hole and its phonon sidehole (see last column of table 2). These results make one wonder whether an interpretation of optical dephasing in glasses in terms of a single librational frequency, or even a Gaussian distribution of frequencies, is physically meaningful.

It should be noted that the  $E$  value of 5.9 cm<sup>-1</sup> obtained by us for resorufin in glycerol is much smaller than the value of 31 cm<sup>-1</sup> reported in ref. [18], both obtained from fits of eq. (1) to the experimental data. Even when using a different first term, namely  $cT^\alpha$  with  $\alpha = 1.2$ , as done by Fayer et al., we find  $E = 6.0 \pm 0.2$  cm<sup>-1</sup>, which is very similar

to the result obtained by us with  $\alpha = 1$ , but six times smaller than the value of ref. [18].

A final comment should be made concerning the identification of librational modes in the spectra. It was claimed for resorufin in glycerol that a phonon sidehole was observed at a frequency distance  $\delta$  from the original hole close to that of the librational frequency of 37 cm<sup>-1</sup> obtained from a fit to the photon-echo data [18]. However, the value of  $\delta \approx 26$  cm<sup>-1</sup> found by us in the spectrum by means of hole burning (see table 2) can neither be identified with the activation energy reported in ref. [18] nor, as noted above, with our values of  $E$  and  $E_0$ .

#### 4. Conclusions

The hole-burning results presented here for four organic amorphous systems measured between  $\approx 0.3$  and  $\approx 20$  K have shown that  $\Gamma_{\text{hom}} - \Gamma_0 \propto T^{1.3}$  over the entire temperature range. For the system resorufin in glycerol at 1.2 K the holewidths are a factor of  $\approx 3$  smaller than those reported in the literature [18]. An explanation for this discrepancy has been given in terms of burning fluences used in the different experiments. The data were fitted with a theoretical model for optical dephasing [19] from which

activation energie  $E < 6 \text{ cm}^{-1}$  for all four systems resulted. The values of  $E$  and  $E_0$  for resorufin in glycerol,  $E = 5.9 \pm 0.2 \text{ cm}^{-1}$  when fitted with eq. (1) and  $E_0 = 4.0 \pm 0.3 \text{ cm}^{-1}$  when fitted with eq. (2), are between five and nine times smaller than those of ref. [18]. The difference between our hole-burning data and the photon-echo data [18] does not follow a power law dependence on temperature, and cannot be interpreted in terms of spectral diffusion in the way suggested [18].

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