Chemical Physics

Photochemical hole burning of phthalocyanine in polymer glasses: Thermal cycling and spectral diffusion

G. Schulte, W. Grond, D. Haarer, and R. Silbey

A

Citation: J. Chem. Phys. **88**, 679 (1988); doi: 10.1063/1.454195 View online: http://dx.doi.org/10.1063/1.454195 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v88/i2 Published by the American Institute of Physics.

Additional information on J. Chem. Phys.

Journal Homepage: http://jcp.aip.org/ Journal Information: http://jcp.aip.org/about/about_the_journal Top downloads: http://jcp.aip.org/features/most_downloaded Information for Authors: http://jcp.aip.org/authors



Photochemical hole burning of phthalocyanine in polymer glasses: Thermal cycling and spectral diffusion

G. Schulte, W. Grond, and D. Haarer

Physikalisches Institut der Universität Bayreuth and BIMF, D-8580 Bayreuth, West Germany

R. Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 3 April 1987; accepted 5 October 1987)

In this paper we report an analysis of hole burning line shapes yielding both reversible and irreversible contributions to the linewidth which are due to spectral diffusion. These terms show a linear T dependence and can, through cycling experiments, be investigated in the temperature range of 0.5 < T < 25 K. The range 1 < T < 25 K is particularly interesting because, under normal conditions, Debye contributions and local mode contributions overwhelm the small spectral diffusion terms at these temperatures. Comparison between optical data and specific heat data supports our model of spectral diffusion.

I. INTRODUCTION

Over the last few years, many studies of hole burning in optical transitions in molecules embedded in glassy materials at low temperature have been done. The widths of the hole have been empirically found to vary with temperature as T^{α} , where α lies between 1 and 2.¹⁻²⁰ A large amount of theoretical work has been done attempting to explain this behavior, all of which suggests the involvement of low frequency two level systems (TLS), which had previously been invoked in order to explain the anomalous low temperature (T < 1 K) specific heat and thermal conductivity data.^{21,22} Depending on various theoretical assumptions about the coupling of the optical center to the TLS, different values of α have been found theoretically. Some authors suggest that the linewidth is due to phonon-TLS scattering dominated by electrostatic coupling^{19,23-30} and some suggest it is due to elastic (strain induced) spectral diffusion.³¹⁻³⁵ Finally, others^{36,37} have suggested that librational (local) modes are responsible for the dephasing and linewidths.

Recently, Walsh et al.³⁸ have performed photon echo experiments in conjunction with nonphotochemical hole burning experiments and have raised the question whether hole burning experiments do, in fact, yield the homogeneous linewidth. Since a hole burning experiment takes place on a time scale of seconds or longer, processes which are static on the time scale of a photon echo experiment may contribute to the hole width and can be seen in the thermal cycling experiments presented here. The spectral diffusion is due to the flipping of two level systems (TLS) found in glasses. Some of these TLS have flip rates (relaxation times) fast compared to the lifetime of the excited state and will thus contribute to the homogeneous linewidth (or dephasing time). Other TLS will have flip rates slow compared to this lifetime and may therefore contribute to the holewidth but not to the dephasing time.³⁹ Thus, a comparison among experiments which probe different time scales will yield important information about the distribution of relaxation times. These authors³⁸ have also reiterated the notion that more than one mechanism may be operative in the homogeneous dephasing of impurity molecules in amorphous matrices.

In addition to the work on optical hole burning and photon echoes, there have been efforts to understand the specific heat of these amorphous materials at low T. Above 1 K, the specific heats of the polymer hosts we study can only be explained with the Debye theory with the additional contribution of low frequency local modes.³⁹⁻⁴¹ Below 1 K, these specific heats are explained by a TLS contribution (linear in T) augmented to a T^3 contribution^{42,43}; however, it has been noted that the coefficient of the T^3 is larger than the Debye coefficient in general, suggesting that other modes may also play a role.

In the present work, we study the hole burning linewidths in two types of experiments. One is a straightforward measurement of the linewidth of the hole as a function of temperature. The second is a thermal cycling experiment which allows us to find the contribution of spectral diffusion processes to the linewidth. We find from this combination of experiments that spectral diffusion gives a contribution linear in temperature, and that the holewidth can be understood completely as a sum of this spectral diffusion term and a term from the local phonon modes. Thus, both the specific heat data and the optical hole burning data can be understood as a sum of TLS and vibrational contributions as long as local modes are included consistently.

The paper is laid out as follows. In Sec. II, the experimental result for the hole widths as a function of T is presented and analyzed in terms of two contributions, one due to the local phonon terms and one due to spectral diffusion. The analysis of the thermal cycling experiments shows that the irreversible line broadening in those experiments is due to the same spectral diffusion effects that cause the line broadening in the simple hole burning experiment. In Sec. III, the theoretical fits for the holewidths and for the specific heats are shown to be consistent with one another. In Sec. IV, we conclude with a discussion of these results.

II. EXPERIMENTAL RESULTS

The general background for photochemical hole burning is well described in recent review articles,^{44–46} where it is

J. Chem. Phys. 88 (2), 15 January 1988

0021-9606/88/020679-08\$02.10

shown that this technique is a promising tool for studying optical relaxation processes in glasses. In the present article, we focus on the interconnections among linewidths as determined by photochemical hole burning, specific heat measurements, and irreversible processes in glasses. In this section we present data on these three for the system free base phthalocyanine amorphous phases of the polymers polystyrene (PS), polymethylmethacrylate (PMMA), and polyethylene (PE) as hosts. In Sec. II A below, we present hole burning linewidths as a function of temperature from 0.5 to 25 K, a substantially wider range than measured previously.⁴⁶ The holewidths were measured via optical absorption spectroscopy using a stabilized dye laser in a low intensity scanning mode (typically 1-10 nW/cm²). The holes were burnt with the same laser at a fixed frequency and with typical laser powers of $1 \,\mu$ W/cm². In Sec. II B we present thermal cycling measurements, preliminary results of which were also presented in Refs. 46 and 17. In the present paper we present a much more complete set of measurements of this phenomenon. By this technique, we probe irreversible processes occurring in the polymer glass.

A. Total hole linewidth as a function of temperature

When a photochemical hole is burned in the H_2Pc absorption line at different temperatures, we find that the holewidth as a function of temperature can be fit as a sum of two terms:

$$\Gamma(T) = \Gamma_1(T) + \Gamma_2(T), \tag{1}$$

where

$$\Gamma_1(T) = K_{\rm SD} \cdot T \tag{2}$$

and

$$\Gamma_2(T) = K_{\text{LP}} \sum_{i=1}^{N_l} \bar{n}(\omega_i) [\bar{n}(\omega_i) + 1] \cdot \omega_i, \qquad (3)$$

with $n(\omega) = e^{-\beta\omega}(1 - e^{-\beta\omega})^{-1}$. These forms follow from our theoretical analysis, presented in Sec. III; however, a simple explanation can be presented here. The term $\Gamma_1(T)$ comes from spectral diffusion processes which take place due to two level system (TLS) flips. That is, TLS flips cause a small change in the excitation energy of the chromophore and since these flips are random and due to the thermal fluctuations in the sample, this leads to a linewidth depending on temperature. The linear dependence comes from using the standard low temperature model, assuming that the density of TLS states is constant at low energy.^{21,22} Although this is a question of current debate, at the present time this is still the simplest assumption (i.e., with the smallest number of adjustable parameters).

Since hole burning is a "slow" experiment in which the photochemical changes are accumulated over a time τ_c of order seconds to minutes, all pseudospin (TLS) flips occurring in a time $t < \tau_c$ will contribute to the linewidth. The linewidth will also contain contributions from processes occurring on a time scale $t < T_1$ ($\ll \tau_c$) which are usually called homogeneous line broadening processes. Only a careful comparison between photon echo experiments³⁸ with hole burning experiments will allow a final discrimination be-

tween homogeneous and inhomogeneous contributions. When the photon echo experiments yield dephasing times corresponding to considerably smaller homogeneous linewidths than seen in hole burning, the slow process discussed in this paper will dominate the holewidth. At the present time, there is not enough experimental data to give a definitive answer to what the relative magnitudes of the fast (homogeneous) and the slow (inhomogeneous) contributions to the holewidth.

The term $\Gamma_2(T)$ comes from assuming that the dominant dephasing process due to phonons is a Raman process associated with low frequency local modes.⁴⁷ Dephasing of optical transitions in *crystals* at low *T* is often dominated by Raman processes [which yield a T^7 dependence for acoustic modes and a temperature dependence as given in Eq. (3) for low frequency Einstein-like optical modes].⁴⁴ We assume the same is true in glasses. Recent arguments by Meissner *et al.*⁴⁸ suggest that local librational modes play an important role in the thermodynamics and dynamics of certain orientational glasses as well. In Sec. III, the precise form of $\Gamma_2(T)$ is discussed in full.

Note that we have assumed that N_i different local modes contribute to $\Gamma_2(T)$. In addition to the frequencies of these modes, we have two other parameters, K_{SD} and K_{LP} , which brings the total number of parameters to $\hat{N}_i + 2$. However, the frequencies of the local modes can be found from an analysis of the specific heat data⁴⁹ of Reese. These frequencies are given in Table I. We use these frequencies to fit $\Gamma_2(T)$ except for one change: in the case of PMMA, we changed the lowest frequency mode from 5 to 2 cm⁻¹. This makes almost no difference to the fit of the specific heat since this mode has such a small density⁴⁹; however, it allows us to fit the linewidth data quite well. Thus we have finally, at most, three adjustable parameters in the linewidth fit: K_{LP} , K_{SD} , and one ω_i in PMMA.

In addition to local modes of the host, there can be contributions from local modes of the guest embedded in the host, e.g., librational modes. In the interest of keeping the number of adjustable parameters small, we have not included this contribution; note however that the form of Γ_2 will not change if these are included.

Figure 1(a) shows the fit for the holewidths as a function of T for PE. This is the most reliable fit since the linear part ($K_{SD}T$) and the local mode part can be fit almost independently from one another. Note that below 3 K the spectral diffusion part of $\Gamma(T)$ dominates. Figure 1(b) shows

TABLE I. Cycling experiments.

Total linewidth measurements						
H ₂ Pc in:	PE	РММА	PS			
$K_{\rm irr}\left(10^{-3}\frac{\rm cm^{-1}}{\rm K}\right)$	0.8 ± 0.3	8.5 ± 1	21 ± 0.5			
$K_{\rm SD}\left(10^{-3}\frac{\rm cm^{-1}}{\rm K}\right)$	0.7	4.5	10			
$K_{\rm LP}(10^{-2})$	1.38	0.54	1.66			
$\omega_1(\mathrm{cm}^{-1})$	16	2(5)	3.5			
$\omega_2(\mathrm{cm}^{-1})$	•••	12	9			

J. Chem. Phys., Vol. 88, No. 2, 15 January 1988



FIG. 1. Fit of total holewidth as a function of burn temperature with spectral diffusion (Γ_{SD}) and local phonon (Γ_{Ip}) contributions. (a) H₂Pc in PE; (b) H₂Pc in PMMA; and (c) H₂Pc in PS.

the fit for PMMA; here $\Gamma_{SD}(T)$ dominates below 1 K. Finally, Fig. 1(c) shows the data for PS which are not as complete as the other two (since it spans only a decade in T); however, the fit is still reasonably good.

We give the constants K_{LP} and K_{SD} for the three systems in Table I. Note that although K_{LP} shows little variation for the three, K_{SD} varies by a factor of 15. In Sec. II B, we discuss an irreversible part of the linewidth revealed by thermal cycling¹⁷ and find a similar variation as a function of the host polymer.

B. Irreversible linewidth effects; cycling experiments

If we burn a photochemical hole at T_1 and then warm up the sample to T_2 , the linewidth of the hole increases. If we now return the sample to T_1 , we find that the linewidth is still larger than it was originally (see Fig. 2). The irreversible broadening phenomenon occurs during the *first* experimental cycle. A second cycle with the same temperature limits does not lead to additional line broadening, suggesting that the *observed* spectral diffusion processes follow the temperature change closely. This increase must be due to irreversible processes which occur in the thermal cycling process. We note a *remarkable* finding^{17,46}: the increase in the linewidth $\Delta\Gamma_{IRR}$ at T_1 due to a cycle to T_2 and back is given by

$$\Delta \Gamma_{\rm IRR} = \mathbf{K}_{\rm IRR} \left(T_2 - T_1 \right)$$

with K_{IRR} independent of T_1 and T_2 for a given system. This is illustrated in Figs. 3(a), 3(b), and 3(c) for temperature T_1 between 4 and 25 K for the three systems (PS, PE, and PMMA). The slopes of these plots give K_{IRR} which are listed in Table I along with the standard deviation. The largest scatter in the experimental data is in the case of PE; this is due to the small value of $\Delta\Gamma_{IRR}$ which are on the order of 10^{-3} cm⁻¹.

To understand the meaning of the $\Delta\Gamma_{IRR}$ values, one has to recollect the origin of the hole burning linewidth. Hole burning can be looked upon as a "tandem two photon" experiment. The first photon performs the photochemistry, leading to a change in the site distribution of the involved photoactive molecules. The second photon monitors the linewidth of the site population via absorption or emission spectroscopy (usually at lower light intensity in order to prevent further photochemistry). The total hole linewidth is therefore given by a convolution of a site population function $\delta N^{\tau}(\omega')$ and a linewidth function $g(\omega - \omega')$ (see, e.g., Ref. 46).



FIG. 2. Schematic description of thermal cycling hole burning experiment. Γ is holewidth, $\Delta\Gamma_{irr}$ is the increase in holewidth for a temperature excursion of ΔT .



FIG. 3. Irreversible part of linewidth increase for (a) H_2Pc in polystyrene; (b) H_2Pc in PMMA; and (c) H_2Pc in polyethylene.

$$L^{\tau}(\omega) = \int_{-\infty}^{\infty} \delta N^{\tau}(\omega) g(\omega - \omega') \, d\omega'. \tag{4}$$

 δN^{τ} is the change in the inhomogeneous line profile $N(\omega)$ due to the hole burning process; τ labels the state of the photochemical reaction, as controlled by the irradiation time τ . $g(\omega - \omega')$ is usually the "homogenous" line shape of the investigated transition, as given by the pertinent ("longitudinal" and "transverse") relaxation times. The term homogeneous is written in quotation marks because $g(\omega - \omega')$ also contains contributions to the linewidths which are due to spectral diffusion. It has been pointed out that $\delta N^{\tau}(\omega')$ behaves like a "photochemical fingerprint" in the frequency domain, which monitors slow matrix changes which occur after the initial photochemistry. It has therefore been also referred to as the "site memory function."^{17,46} If, for instance, after laser photochemistry a tunneling process of some kind changes the local site energies, δN^{τ} will change accordingly.

To a first approximation δN^{τ} monitors slow relaxation processes leading to changes in the site energy. If spectral diffusion does occur to a measurable extent, the real linewidth can change as a function of time driven by time dependent changes of $\delta N^{\tau,17}$ The line shapes which can be expected after a temperature-induced spectral diffusion has occurred have been analyzed in previous papers^{39,50,51}; it was concluded that if the δN^{τ} changes are governed by a diffusion process, a Gaussian linewidth contribution would be expected, yielding a total line shape with a Voigt profile.

Let us now discuss how we can understand the irreversible changes in linewidth as have been measured by thermal cycling for various polymers. If a linewidth does not return to its original value after a temperature cycle, it means, as one can see by inspecting Eq. (4), that δN^{τ} has changed irreversibly. $g(\omega - \omega')$ is a reversible function and does, to a very good approximation, not depend on the sample history. This can be verified experimentally: if one burns a new hole very near the original hole after the temperature cycle, it will have the line shape of the original hole before the cycle and, thus, have a line shape different from the "cycled hole." This can be taken as direct evidence for the fact that $\delta N^{\tau}(\omega')$ has a "memory" as far as the sample history is concerned and $g(\omega - \omega')$ does not.

In order to understand the structure of the $\delta N^{\tau}(\omega')$, one has to introduce the concept of spectral diffusion. Let us therefore assume that the form of $\delta N^{\tau}(\omega')$ is given by two different contributions: the dynamical line shape $g(\omega')$ and a contribution which is due to spectral diffusion, i.e., to an uncertainty in the site energies which develops within the time interval τ_a of the experiment ($\tau_a < 5 \text{ min}$). The contribution of $g(\omega')$ is due to the burning of molecules whose optical line shape overlaps the laser frequency.⁴⁶ The uncertainty in site energy could be due to the fact that certain tunneling states of the guest-host system are, at the temperature of the experiment, in thermal equilibrium, thus leading to adiabatic changes of the involved transition frequencies within the inhomogeneous band. By adiabatic changes we mean changes which are in general slower than the typical dynamical scattering times (i.e., the longitudinal and transverse relaxation times). With this assumption the line shape function $\delta N^{\tau}(\omega')$ of Eq. (4) can be written as

$$\delta N^{\tau}(\omega') = A(\tau) \int_{-\infty}^{+\infty} g(\omega'') S(\omega' - \omega'') \, d\omega'', \quad (5)$$

where $A(\tau)$ is a parameter which describes the photochemical progression of the hole burning event (for details see Ref. 46) and $S(\omega - \omega')$ is a normalized function describing the uncertainty in the site distribution due to the adiabatic changes of the tunneling systems coupling to the optical transition. Now we assume that the number of sites which contribute to the spectral diffusion process is a function of temperature and, therefore, the kernel of the above convolution integral S is a function of temperature. At higher temperatures more tunneling centers will be in thermal equilibrium and, hence, the inhomogeneous contributions in Eq. (5) will increase. Therefore, Eq. (5) will not only depend on the temperature T through the temperature dependence of $g(\omega'')$ (as given by the temperature dependence of the pertinent relaxation times), but it will also depend on the temperature excursion ΔT and therefore we have to rewrite Eq. (5) as follows:

$$\delta N^{\tau}(\omega',T,\Delta T) = A(\tau) \int_{-\infty}^{+\infty} g(\omega'',T) \\ \times S\{\omega'-\omega'',T,\Delta T\} \, d\omega''. \tag{6}$$

Having derived Eq. (6), we can now describe our experiments in a more quantitative fashion. The photochemical hole is given by a convolution of $\delta N^{\tau}(\omega',T,\Delta T)$ with the homogeneous dynamic linewidth $g(\omega - \omega')$ as described in Eq. (4). If we neglect, for the moment, all irreversible spectral diffusion processes, then $S(\omega' - \omega'')$ can be replaced by a δ function and Eq. (4) yields an autocorrelation integral of $g(\omega)$ with itself and, thus the total linewidth is twice the homogeneous linewidth [if we assume a Lorentzian line shape for $g(\omega)^{46}$]. If one now allows spectral diffusion to occur, the holewidth is a more complex quantity and, hence, the easiest experiment is a difference experiment. One burns a photochemical hole at a temperature T, then makes a thermal cycle from T to $T + \Delta T$ and returns to the original temperature (as shown in Fig. 1). With zero spectral diffusion one should return to the original linewidth and line shape. With nonzero spectral diffusion the difference in linewidth is solely due to the function $S(\omega' - \omega'', T, \Delta T)$ since all other parameters do not depend on ΔT , but solely on T (which is kept constant by our method of returning to the original temperature). If we perform our temperature cycle on a time scale between 20 and 60 min, the time scale of our experiment does not enter into the experimental results.

From our experimental data (Fig. 3), we come to the conclusion that $S\{\omega' - \omega'', T, \Delta T\}$ varies in a linear fashion with ΔT and can be described with one proportionality constant in the temperature regime 4 < T < 25 K *independent of the burning temperature.* For simplicity we have assumed a Lorentzian line shape for S so that the linewidths are additive.

If we denote the change in the width of S by ΔS , we can summarize our experimental results as follows [see also Figs. 3(a), 3(b), and 3(c)]:

$$\Delta S(\Delta T) = \Delta \Gamma_{\rm IRR} = K_{\rm IRR} \Delta T. \tag{7}$$

Note, as emphasized before, the above expression does not depend on the burn temperature. The constant K_{IRR} is the parameter determining the slope of the temperature induced irreversible spectral diffusion as measured experimentally. It varies from PE to PMMA to PS by about a factor of 26 (see Table I). Before going into a tentative interpretation of the origin of $\Delta S(\Delta T)$ we would like to comment on the understanding of the line shape of photochemical holes from our viewpoint. Equation (6) assumes that the site memory function $\delta N^{\tau}(\omega', T, \Delta T)$ has a dynamic part $g(\omega'', T)$ which reflects the relaxation times as well as the reversible spectral diffusion processes. It also has an "inhomogeneous" part which is given by an adiabatic dynamical site redistribution. In an experiment in which a hole is burnt and measured at each temperature this inhomogeneous contribution to the linewidth does not show up experimentally. It only shows up in $T - \Delta T$ experiments in which thermal cycles are performed. If we take our data for PS, where the largest linewidth contribution is observed, we see from Figs. 4(a) and 4(b), which shows the cycling curve for 4 and 10 K, respectively, that the *reversible* linewidth contributions of $g(\omega^{"}, T)$ are in fact generally larger than the irreversible contributions. However, the latter do contribute to the total linewidth in a measurable fashion, and are therefore present at all temperatures. This is particularly important for low temperatures.

III. THEORY

A. Total linewidth

As we pointed out above, the total linewidth in the absence of thermal cycling is written as^{52}

$$\Gamma = \Gamma_{\rm SD} + \Gamma_{\rm LP},\tag{8}$$



FIG. 4. Hole burning of H₂Pc in polystyrene: (a) Burn temperature = 4 K. Full circles are total holewidth as a function of T. Open circles are irreversible part of width ($\Gamma_{irr}\Delta T$) from cycling (b). Same as (a) for a burn temperature of 10 K.

J. Chem. Phys., Vol. 88, No. 2, 15 January 1988

where Γ_{SD} is the term due to the TLS and which we suggest, following Black and Halperin^{53,54} and Huber *et al.*,³⁴ is due to spectral diffusion via TLS flips. This model leads to a low temperature width which is linear in T (i.e., $\Gamma_{SD} = K_{SD}T$), based on the standard model that the density of TLS states is constant at low T. We assume that the apparent $T^{1.3}$ found in many organic hosts⁵² is due to a combination of mechanisms, as we have outlined here, and which has been seen in recent photon echo experiments.³⁸

The phonon contribution to the linewidth Γ_{ph} is made up of two terms: The well-known one from acoustic phonon interaction which at low T varies as T^7 and can be neglected, and another term from *local phonon* interactions, which we label Γ_{LP} . Assuming as usual that the interaction term in the Hamiltonian is quadratic in local phonon variables, the optical transition is dephased by creation of one local phonon and destruction of another.

The contribution of each band of local modes to the pure dephasing of the optical transition depends on the frequency of that mode ω_i and the coupling constant g_i (i.e., the coefficient of the quadratic phonon term of the Hamiltonian). In the usual second order perturbation theory calculation, the contribution to the width due to one narrow *band* of local modes will then be proportional to

$$N_i g_i^2 \bar{n}(\omega_i) \left[\bar{n}(\omega_i) + 1 \right], \tag{9}$$

where N_i is the number of modes of ω_i in this band, and $\bar{n}(\omega)$ is the Bose distribution function. The contribution due to all local modes will then be

$$\sum_{i}^{N_{i}} N_{i} g_{i}^{2} \overline{n}(\omega_{i}) [\overline{n}(\omega_{i}) + 1], \qquad (10)$$

where \hat{N}_i is the number of local phonon bands. The factor $N_i g_i^2$ has the dimension of energy, but is otherwise unknown. We therefore assume it to be of the form

$$N_i g_i^2 = k_i \omega_i, \tag{11}$$

where k_i is now a *dimensionless* parameter. Thus, we have finally

$$\Gamma_{\rm LP} = \sum_{i=1}^{N_l} k_i \omega_i \bar{n}(\omega_i) [\bar{n}(\omega_i) + 1].$$
(12)

For simplicity, since we consider at most two such bands in any host and to keep the number of parameters small, we take $k_i = K_{ip}$, for all *i*, to find

$$\Gamma_{\rm LP} = K_{lp} \sum_{i} \omega_i \bar{n}(\omega_i) [\bar{n}(\omega_i) + 1], \qquad (13)$$

in agreement with Eq. (3). Thus we find, at low T, the total linewidth is given by

$$\Gamma = K_{\rm SD} T + K_{lp} \sum_{i} \omega_i \left(\frac{e^{-\beta \omega_i}}{(1 - e^{-\beta \omega_i})^2} \right).$$
(14)

As pointed out above, this formula can be used to fit the experimental measured linewidths. The local mode frequencies are taken from those used to fit the specific heat from 1 < T < 20,³⁹⁻⁴¹ and since for T above ~10 K, the local phonon contribution dominates the linewidth, the linewidth and specific heat data are *consistent* in the sense that the same local mode parameters have been used to fit both sets of data.

B. Excess linewidth due to thermal cycling

Consider a hole burned at a temperature T_1 . As we saw above, the width of this hole has a contribution from local phonon modes and a contribution from spectral diffusion. These spectral diffusion processes take place on a time scale long compared to the relaxation times, but short compared to the experimentally relevant times of burning and measuring. We now construct an argument to find the maximum increase in linewidth due to thermal cycling based on these ideas. Denote the spectral diffusion width at T_1 by Γ_1 and the spectral diffusion width of a hole burned at T_2 by Γ_2 . That is, at T_1 molecules can undergo changes in transition frequency on the order of Γ_1 , and, similarly, at T_2 molecules undergo changes on the order Γ_2 . When a hole is burned at T_1 , a set of molecules is marked; this set spans a transition frequency range of Γ_1 . For estimating the maximum frequency span, the only consideration on the full range of frequencies at T_2 for all the marked molecules, is that this range must also contain the range of possible frequencies at T_1 (see Fig. 5). Thus, the maximum range of frequencies at T_2 due to spectral diffusion alone is $2\Gamma_2 - \Gamma_1$. When the sample is returned to T_1 , each molecule has a spectral diffusion range of Γ_1 ; however, some molecules will have been frozen into frequencies spanning the range $2\Gamma_2 - \Gamma_1$ and thus the maximum



FIG. 5. Maximum (a) and minimum (b) linewidth as given by spectral diffusion. Γ_1 is the frequency spread at T_2 (see the text).

increase in linewidth due to thermal cycling is $2(\Gamma_2 - \Gamma_1)$ (Fig. 5).

This argument is based on the most asymmetric possible spectral diffusion as illustrated by the rectangular distributions exhibited in Fig. 5(a). If we take the least asymmetric possible spectral diffusion distributions [see Fig. 5(b)], the increase in the linewidth due to thermal cycling is $\Gamma_2 - \Gamma_1$.

Therefore, we expect the irreversible linewidth increase on cycling from T_1 to T_2 will obey the following inequality:

$$2[\Gamma_{\rm SD}(T_2) - \Gamma_{\rm SD}(T_1)] \ge \Delta \Gamma_{\rm IRR} \ge \Gamma_{\rm SD}(T_2) - \Gamma_{\rm SD}(T_1),$$
(15)

or since Γ_{SD} and $\Delta\Gamma_{IRR}$ are both found experimentally to be linear in T:

$$2K_{\rm SD} \geqslant K_{\rm IRR} \geqslant K_{\rm SD}.$$
 (16)

IV. CONCLUSIONS AND OUTLOOK

We have now arrived at a model in which both the specific heat data above 1 K, the hole burning experiments and the thermal cycling experiments, are consistently described. That is, the local phonon modes which contribute to the specific heat⁴⁹ are used to interpret the phonon broadening of the observed optical linewidths. The TLS, which are thought to be responsible for the term in the specific heat which is linear in temperature, are invoked to explain the linear dependencies of the linewidths via a spectral diffusion mechanism has been shown to contribute to both the straightforward hole burning linewidths as well as the irreversible linewidth changes as measured by thermal cycling experiments. Spectral diffusion in our model is caused by TLS flips; those which are fast compared to the lifetime will contribute to the dephasing time, while those which are slow will not. Both sets will contribute to the holewidth and this contribution is linear in T, according to the standard model.⁵⁴ Thermal cycling experiments will allow irreversible holewidth increases because the range of frequency shifts via spectral diffusion is linear in temperature. Although our theoretical model for the latter experiments is only semiquantitative, it predicts that the linear coefficient of the irreversible linewidth changes is within a factor of 2 equal to the linear coefficient of the holewidth as measured by conventional optical hole burning spectroscopy. This prediction is borne out nicely by our measurements as shown in Table I.

In addition to this, we expect that, since the TLS which are responsible for the spectral diffusion part of the linewidth are also involved in the specific heat, the linear coefficient in specific heats⁵⁵ (C_{TLS} below 1 K) ought to scale *approximately* with our optically determined linear coefficients K_{SD} and K_{IRR} . This approximate correlation is exhibited in Table II. Note that the trend from PE through PMMA to PS is the same for C_{TLS} and K_{SD} and K_{IRR} , respectively, although the numerical values do not scale exactly. Since the specific heat data refer to temperatures below 1 K, whereas the major part of the optical data is taken well above 1 K, we regard the trends as significant. It should be emphasized, in addition, that the present thermal cycling experiments are a simple and direct way to examine the lin-

TABLE II. Specific heat and linewidth parameters.

	PE	РММА	PS	
$C_{\text{TLS}}\left(\frac{\text{erg}}{\text{cm}^3 \text{ K}^2}\right)$	9.94	41	50.5	Stephens ^a Finlayson <i>et al.</i> ^b
$K_{\rm irr}\left(10^{-3}\frac{\rm cm^{-1}}{\rm K}\right)$	0.8	8.5	21	This paper see also Table I
$K_{\rm SD}\left(10^{-3}\frac{\rm cm^{-1}}{\rm K}\right)$	0.7	4.5	10	This paper see also Table I
$C_2\left(\frac{\mathrm{erg}}{\mathrm{cm}^3 \mathrm{K}^4}\right)$	143	250	435	Stephens ^a Finlayson <i>et al.</i> ^b
$C_D\left(\frac{\mathrm{erg}}{\mathrm{cm}^3\mathrm{K}^4}\right)$	129	155	242	Computed in the Debye approximation from acoustic data

* Reference 41.

^bReference 42.

ear TLS contributions above 1 K which occur on a slow time scale.

More experiments are needed. Both thermal and optical measurements on a variety of systems are necessary to see whether this model can be made more quantitative and to see whether the optically determined parameters can be correlated with macroscopic thermodynamic materials properties.

ACKNOWLEDGMENTS

We would like to thank Th. Sesselmann for discussions concerning local phonons. R.S. acknowledges support from the NSF for partial support of this work.

- ¹A. A. Gorokhovskii, J. V. Kikas, V. V. Pal'm, and L. A. Rabane, Sov. Phys. Solid State 23, 602 (1981).
- ²J. M. Hayes, R. P. Stout, and G. J. Small, J. Chem. Phys. **74**, 4266 (1981).
- ³E. Cuellar and G. Castro, Chem. Phys. **54**, 217 (1981).
- ⁴L. A. Rebane, A. A. Gorokhovskii, and J. V. Kikas, Appl. Phys. B **29**, 235 (1982).
- ⁵J. Friedrich, H. Wolfrum, and D. Haarer, J. Chem. Phys. 77, 2309 (1982).
- ⁶H. P. H. Thijssen, A. I. Dicker, and S. Völker, Chem. Phys. Lett. **92**, 7 (1982).
- ⁷H. P. H. Thijssen, R. van den Berg, and S. Völker, Chem. Phys. Lett. **97**, 295 (1983).
- ⁸H. P. H. Thijssen, S. Völker, M. Schmidt, and H. Port, Chem. Phys. Lett. **94**, 537 (1983).
- ⁹H. P. H. Thijssen, R. E. van den Berg, and S. Völker, Chem. Phys. Lett. 103, 23 (1983).
- ¹⁰H. P. H. Thijssen and S. Völker, Chem. Phys. Lett. 120, 496 (1985).
- ¹¹H. P. H. Thijssen, R. van den Berg, and S. Völker, Chem. Phys. Lett. **120**, 503 (1983).
- ¹²R. M. Macfarlane and R. M. Shelby, Opt. Commun. 45, 46 (1983).
- ¹³T. P. Carter, B. I. Fearey, J. M. Hayes, and G. J. Small, Chem. Phys. Lett. **102**, 272 (1983).
- ¹⁴F. A. Burkhalter, G. M. Suter, U. P. Wild, V. P. Samoilenko, N. V. Rasumova, and R. I. Personov, Chem. Phys. Lett. **94**, 483 (1983).
- ¹⁵R. Jankowiak and H. Bässler, Chem. Phys. Lett. 95, 310 (1983).
- ¹⁶R. Jankowiak and H. Bässler, Chem. Phys. Lett. 101, 274 (1983).
- ¹⁷A. Guiterrez, G. Castro, G. Schulte, and D. Haarer, in *Organic Molecular Aggregates*, edited by P. Reineker, H. Haken, and H. C. Wolf (Springer, Berlin, 1983).
- ¹⁸T. Tani, H. Namikawa, K. Arai, and A. Makishima, J. Appl. Phys. 58, 3559 (1985).
- ¹⁹L. W. Molenkamp and D. A. Wiersma, J. Chem. Phys. 83, 1 (1985).
- ²⁰T. P. Carter and G. J. Small, Chem. Phys. Lett. 120, 178 (1985).

²¹P. W. Anderson, B. J. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972).

- ²²W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).
- ²³S. K. Lyo and R. Orbach, Phys. Rev. B 22, 4223 (1980).
- ²⁴S. K. Lyo, Phys. Rev. Lett. 48, 688 (1982).
- ²⁵H. Morawitz and P. Reineker, Solid State Commun. 42, 609 (1982).
- ²⁶P. Reineker and H. Morawitz, Chem. Phys. Lett. 86, 359 (1982).
- ²⁷S. K. Lyo, in *Electronic Excitations and Interaction Processes in Organic Molecular Aggregates*, edited by P. Reineker, H. Haken, and H. C. Wolf, Springer Series in Solid State Sciences (Springer, Berlin, 1983), Vol. 49, p. 215.
- ²⁸S. K. Lyo and R. Orbach, Phys. Rev. B 29, 2300 (1984).
- ²⁹P. Reineker, H. Morawitz, and K. Kassner, Phys. Rev. B 29, 4546 (1984).
 ³⁰P. Reineker, K. Kassner, and H. Morawitz, in *Photoreaktive Festkorper*,
- edited by H. Sixl (Wahl, Karlsruhe, 1984).
- ³¹T. L. Reinecke, Solid State Commun. 32, 1103 (1979).
- ³²D. L. Huber, J. Non-Cryst. Solids 51, 241 (1982).
- ³³S. Hunklinger and M. Schmidt, Z. Phys. B 54, 93 (1984).
- ³⁴D. L. Huber, M. M. Broer, and B. Golding, Phys. Rev. Lett. **52**, 2281 (1984).
- ³⁵M. M. Broer and B. Golding, J. Lumin. **31**, 733 (1984).
- ³⁶B. Jackson and R. Silbey, Chem. Phys. Lett. 99, 331 (1983).
- ³⁷R. Jankowiak, H. Bässler, and R. Silbey, Chem. Phys. Lett. **125**, 139 (1986).
- ³⁸C. A. Walsh, M. Berg, L. R. Narasimhan, and M. D. Fayer, J. Chem. Phys. 86, 77 (1987); Chem. Phys. Lett. 130, 6 (1986).
- ³⁹W. Breinl, J. Friedrich, and D. Haarer, J. Chem. Phys. **81**, 3915 (1984).
 ⁴⁰C. L. Choy, R. G. Hunt, and G. L. Salinger, J. Chem. Phys. **52**, 3629 (1970).
- ⁴¹(a) J. E. Tucker and W. Reese, J. Chem. Phys. 46, 1388 (1967); (b) W.

- Reese, J. Macromol. Sci. Chem. A 3, 1257 (1969).
- ⁴²R. B. Stephens, Phys. Rev. B 13, 852 (1976).
- ⁴³D. M. Finlayson and P. J. Mason, J. Phys. C 18, 1777 (1985).
- ⁴⁴G. J. Small, in Spectroscopy and Excitation Dynamics of Condensed Molecular Systems, edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983).
- ⁴⁵L. A. Rebane, A. H. Gorokhovskii, and J. V. Kikas, Appl. Phys. B 29, 235 (1982).
- ⁴⁶J. Friedrich and D. Haarer, Angew. Chem. 23, 113 (1984).
- ⁴⁷See, for example, D. B. Fitchen, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968).
- ⁴⁸M. Meissner, W. Knaak, J. P. Sethna, K. S. Chow, J. J. DeYoreo, and R. O. Pohl, Phys. Rev. B **32**, 6091 (1985).
- ⁴⁹W. Reese, J. Macromol. Sci. Chem. A 3, 1257 (1968).
- ⁵⁰J. Friedrich, D. Haarer, and R. Silbey, Chem. Phys. Lett. 95, 119 (1983).
 ⁵¹W. Breinl, J. Friedrich, and D. Haarer, Chem. Phys. Lett. 106, 487
- (1984).
- ⁵²For a recent review, see K. Kassner and R. Silbey, J. Lumin. 36, 283 (1987).
- ⁵³J. L. Black, Phys. Rev. B 17, 2740 (1978).
- ⁵⁴J. L. Black and B. I. Halperin, Phys. Rev. B 16, 2879 (1977).
- ⁵⁵The specific heat of glasses below 1 K is often represented as $C_1T^{\alpha} + C_2T^3$ (see Refs. 41 and 42 where $\alpha \simeq 1$) where C_2 is a fitting parameter not equal to the value given by the Debye theory (C_D) . This discrepancy has been discussed by Varma *et al.* (Ref. 56) where it is shown that alternative fits to the data are possible. It is clear from our discussion that the local phonon modes will also make a small contribution to the specific heat below 1 K.
- ⁵⁶C. M. Varma, R. C. Dynes, and J. R. Banavar, J. Phys. C 15, L1221 (1982).