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 $T^\alpha$, where $\alpha$ 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 $\alpha$ have been found theoretically. Some authors suggest that the linewidth is due to phonon-TLS scattering dominated by electrostatic coupling23-30 and some suggest it is due to elastic (strain induced) spectral diffusion.31-35 Finally, others36,37 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 $T^3$ contribution42,43; 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
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.\(^4\) The holewidths were measured via optical absorption spectroscopy using a stabilized dye laser in a low intensity scanning mode (typically 1–10 nW/cm\(^2\)). The holes were burnt with the same laser at a fixed frequency and with typical laser powers of 1 \(\mu\)W/cm\(^2\). 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 \(\text{H}_2\text{Pc}\) absorption line at different temperatures, we find that the holewidth as a function of temperature can be fit as a sum of two terms:

\[
\Gamma (T) = \Gamma_1(T) + \Gamma_2(T),
\]

where

\[
\Gamma_1(T) = K_{SD} \cdot T
\]

and

\[
\Gamma_2(T) = K_{LP} \cdot \sum_{i=1}^{N_i} \frac{\tilde{n}(\omega_i)}{[\tilde{n}(\omega_i) + 1]} \cdot \omega_i,
\]

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 \(\tau_c\) 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 experiments\(^28\) with hole burning experiments will allow a final discrimination between 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.\(^43\) Dephasing of optical transitions in crystals at low \(T\) is often dominated by Raman processes which yield a \(T^2\) 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 Meisssner 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 \(N_i + 2\). However, the frequencies of the local modes can be found from an analysis of the specific heat data\(^49\) 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 density\(^49\); 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 \(\omega_i\) 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 \(\Gamma_2\) 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.**

<table>
<thead>
<tr>
<th>Total linewidth measurements</th>
<th>PE</th>
<th>PMMA</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_0) ((10^{-3} \text{ cm}^{-1}))</td>
<td>0.8 ± 0.3</td>
<td>8.5 ± 1</td>
<td>21 ± 0.5</td>
</tr>
<tr>
<td>(K_{SD}) ((10^{-3} \text{ cm}^{-1}))</td>
<td>0.7</td>
<td>4.5</td>
<td>10</td>
</tr>
<tr>
<td>(K_{LP}) ((10^{-3} \text{ cm}^{-1}))</td>
<td>1.38</td>
<td>0.54</td>
<td>1.66</td>
</tr>
<tr>
<td>(\omega_i) ((\text{cm}^{-1}))</td>
<td>16</td>
<td>2(5)</td>
<td>3.5</td>
</tr>
<tr>
<td>(\omega_j) ((\text{cm}^{-1}))</td>
<td>...</td>
<td>12</td>
<td>9</td>
</tr>
</tbody>
</table>
the fit for PMMA; here $\Gamma_{\text{SD}}(T)$ 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 $K_{\text{LP}}$ and $K_{\text{SD}}$ for the three systems in Table I. Note that although $K_{\text{LP}}$ shows little variation for the three, $K_{\text{SD}}$ varies by a factor of 15. In Sec. II B, we discuss an irreversible part of the linewidth revealed by thermal cycling\textsuperscript{17} 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\textsuperscript{17,46}: the increase in the linewidth $\Delta \Gamma_{\text{IRR}}$ at $T_1$ due to a cycle to $T_2$ and back is given by

$$\Delta \Gamma_{\text{IRR}} = K_{\text{IRR}}(T_2 - T_1)$$

with $K_{\text{IRR}}$ 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 $K_{\text{IRR}}$ 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 $\Delta \Gamma_{\text{IRR}}$, which are on the order of $10^{-3}$ cm$^{-1}$.

To understand the meaning of the $\Delta \Gamma_{\text{IRR}}$ 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 $\delta N' (\omega')$ and a linewidth function $g(\omega - \omega')$ (see, e.g., Ref. 46).
FIG. 3. Irreversible part of linewidth increase for (a) H$_2$Pc in polystyrene; (b) H$_2$Pc in PMMA; and (c) H$_2$Pc in polyethylene.

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

\( \delta N^\tau \) is the change in the inhomogeneous line profile \( N(\omega) \) due to the hole burning process; \( \tau \) labels the state of the photochemical reaction, as controlled by the irradiation time \( \tau \). \( g(\omega - \omega') \) is usually the "homogeneous" 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." If, for instance, after laser photochemistry a tunneling process of some kind changes the local site energies, \( \delta N^\tau \) will change accordingly.

To a first approximation \( \delta N^\tau \) 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 \( \delta N^\tau \). The line shapes which can be expected after a temperature-induced spectral diffusion has occurred have been analyzed in previous papers; it was concluded that if the \( \delta N^\tau \) 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 \( \delta N^\tau \) 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 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 \( \tau \) of the experiment (\( \tau < 5 \) min). The contribution of \( g(\omega') \) is due to the burning of molecules whose optical line shape overlaps the laser frequency. 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

\[ \delta N^\tau(\omega') = A(\tau) \int_{-\infty}^{\infty} g(\omega'')S(\omega' - \omega'') \, d\omega'', \]  
(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 convolu-
tion 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 $\Delta T$ and therefore we have to rewrite Eq. (5) as follows:

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

Having derived Eq. (6), we can now describe our experiments in a more quantitative fashion. The photochemical hole is given by a convolution of $\delta N(\omega', T, \Delta T)$ 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 $\delta$ 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 $g(\omega)$]66]. 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 $\Delta T$, 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 $\Delta T$ 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 $\Delta S$, we can summarize our experimental results as follows [see also Figs. 3(a), 3(b), and 3(c)]:

$$
\Delta S(\Delta T) = \Delta S_{\text{IRR}} = K_{\text{IRR}} \Delta T.
$$

Note, as emphasized before, the above expression does not depend on the burn temperature. The constant $K_{\text{IRR}}$ 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 $\delta N(\omega', T, \Delta T)$ 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

$$
\Gamma = \Gamma_{\text{SD}} + \Gamma_{\text{LP}} + \Gamma_{\text{IRR}}.
$$

FIG. 4. Hole burning of H$_2$Pc in polystyrene: (a) Burn temperature $T_B = 4$ K. Full circles are total holewidth as a function of $T$. Open circles are irreversible part of width ($\Gamma_{\text{IRR}} \Delta T$) from cycling (b). Same as (a) for a burn temperature of 10 K.

Downloaded 21 Oct 2012 to 18.111.99.30. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions
where $\Gamma_{SD}$ is the term due to the TLS and which we suggest, following Black and Halperin\textsuperscript{33,34} and Huber et al.,\textsuperscript{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 $T^{1.5}$ found in many organic hosts\textsuperscript{32} is due to a combination of mechanisms, as we have outlined here, and which has been seen in recent photon echo experiments.\textsuperscript{38}

The phonon contribution to the linewidth $\Gamma_{\rho\phi}$ is made up of two terms: The well-known one from acoustic phonon interaction which at low $T$ varies as $T^{\gamma}$ and can be neglected, and another term from local phonon interactions, which we label $\Gamma_{LP}$. 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 $\omega_i$, 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

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

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

$$\bar{\Gamma}_{LP} = \sum_i N_i g_i^2 \bar{n}(\omega_i) \left[ \bar{n}(\omega_i) + 1 \right], \quad (10)$$

where $N_i$ 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

$$N_i g_i^2 = k_i \omega_i, \quad (11)$$

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

$$\Gamma_{LP} = \sum_i k_i \omega_i \bar{n}(\omega_i) \left[ \bar{n}(\omega_i) + 1 \right]. \quad (12)$$

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

$$\Gamma_{LP} = K_{ip} \sum_i \omega_i \bar{n}(\omega_i) \left[ \bar{n}(\omega_i) + 1 \right], \quad (13)$$

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

$$\Gamma = K_{SD} T + K_{ip} \sum_i \omega_i \left( \frac{e^{-\beta \omega_i}}{(1 - e^{-\beta \omega_i})^2} \right). \quad (14)$$

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 $1 < T < 20,$\textsuperscript{39-41} and since for $T$ above $\sim 10$ 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.
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:

\[
2[\Gamma_{SD}(T_2) - \Gamma_{SD}(T_1)] > \Delta \Gamma_{IRR} > \Gamma_{SD}(T_2) - \Gamma_{SD}(T_1),
\]

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

\[
2\Gamma_{SD} > \Gamma_{IRR} > \Gamma_{SD}.
\]

### 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 heat 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.\(^{44}\) 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 semi-quantitative, 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 heats \(\left(C_{TLS} \text{ below 1 K}\right)\) ought to scale approximately with our optically determined linear coefficients \(\Gamma_{SD}\) and \(\Gamma_{IRR}\). 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 \(\Gamma_{SD}\) and \(\Gamma_{IRR}\), 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 line-
686

Schulte et al.: Photochemical hole burning

39 For a recent review, see K. Kassner and R. Silbey, J. Lumin. 36, 283 (1987).
42 The specific heat of glasses below 1 K is often represented as \( C_1 T^\alpha + C_2 T^3 \) (see Refs. 41 and 42 where \( \alpha = 1 \)) 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.