

THEORETICAL DESCRIPTION OF PHOTOCHEMICAL HOLE BURNING IN SOFT GLASSES

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The temperature dependence of the photochemical hole widths of molecules in soft glasses (T^α , $\alpha \approx 1.3-1.5$) is explained by a combination of two dephasing mechanisms. The narrow distribution of two-level systems in such glasses gives rise to one contribution, and the dephasing of localized librational modes by long-wavelength phonons provides a second contribution. We show that in the range $T < 25$ K, the theoretical temperature dependence agrees with the experiment.

Recently, there have been several articles devoted to the anomalous low-temperature impurity linewidths in glasses, as studied by hole burning and fluorescence line-narrowing techniques [1-12]. The behavior is anomalous in that both the magnitude and temperature dependence differ significantly from that observed in similar crystalline hosts. The two-level system (TLS) model of Anderson et al. [1], and Phillips [2] has been successful in interpreting some of the experiments, but much of the data remain unexplained. We demonstrate here how some of these findings can be simply explained in terms of a combination of the TLS model and other dephasing mechanisms known to exist in such systems.

The TLS model, used to describe various glass properties, has been explained in detail elsewhere [1-5], and need only be outlined here. A double-well potential is used to describe two metastable configurations of a host atom or atoms near the impurity. The coupling of the impurity states to these moving atoms is responsible for the line broadening, Γ_{TLS} , which is set equal to the phonon-assisted transfer rate between the eigenstates of the TLS. We find, using first-order perturbation theory and a local linear phonon interaction [3-5] (for the tunnel states in thermal equilibrium),

$$\Gamma_{\text{TLS}} \propto (\Delta^2 E / \omega_D^3) \text{csch}(E/kT),$$

where $E = (\epsilon^2 + \Delta^2)^{1/2}$, 2ϵ is the energy asymmetry of the wells, Δ is the overlap energy between the wells

($|\Delta/\epsilon| \ll 1$) and ω_D is the Debye frequency. To calculate the experimentally observed width, we must average over the glass parameters ϵ and Δ . For kT larger than the width of the distribution of E , which based on other hole-burning experiments has been estimated to be $\approx 1 \text{ cm}^{-1}$ in H-bonding organic glasses [3], Γ_{TLS} should be linear in the temperature. Friedrich et al. [12], who perform temperature-cycling-hole-burning experiments to measure the extent of the irreversible hole-broadening processes which occur for DAQ in such glasses reach a similar conclusion concerning this width. (It should be pointed out that Lyo [13], in a modification of the above TLS model, has shown that a homogeneous width linear in the temperature results at low temperatures for a dipolar TLS-impurity interaction.) This linear behavior is confirmed by the work of Small and co-workers [3], and Cuellar and Castro [6], for non-photochemical hole-burning experiments in soft glasses. (In hard inorganic glasses, on the other hand, the width of this distribution is estimated to be $\approx 100 \text{ cm}^{-1}$ [1,2]. Therefore, in the latter systems at low temperatures, we should observe a T^2 dependence, assuming the distribution of E values is reasonably constant. This is confirmed by a number of authors who report T^α dependencies, with $\alpha \approx 2$: $\alpha = 1.8 \pm 0.2$ [7], 2.1 ± 0.1 [8], and 1.9 ± 0.2 [9] for Eu^{3+} and Pr^{3+} in various *hard* glasses.)

A few photochemical hole-burning experiments, however, remain anomalous in that they report ap-

parent T^α dependencies with $\alpha = 1.3 \pm 0.1$ [10], $\alpha = 1.5 \pm 0.3$ [11], and $\alpha = 2.0$ [12] for $kT > 1$ cm⁻¹ in soft H-bonding glasses. There have been various attempts at explaining non-integer power law dependencies. One method is to assume the distribution of TLS splittings has the form $f(E) \propto E^n$ and a width E_{\max} . Then, for $kT \ll E_{\max}$, $\Gamma_{\text{TLS}} \propto T^{2+n}$. This assumption has no firm basis and would not be valid in our soft glass system in any case, where $kT > E_{\max}$.

Another argument is that between the high- and low-temperature asymptotic regions, an α between 1 and 2 results. However, in this case α would vary much more than it does over the experimental range (usually 2–20 K). Also, Reineker and Morawitz [5] have shown that the T dependence depends sensitively upon the various glass parameters in this region. A survey of the literature [3,6,10–12], however, reveals that for a given impurity α is essentially independent of the glass used (as long as they are all soft or all hard), while for a given glass, α changes from impurity to impurity. This indicates a mechanism which is strongly dependent upon properties of the impurity.

In photochemical hole-burning experiments of porphyrin in crystalline alkanes, where the TLS processes do not occur, Völker et al. successfully explained their data by the dephasing of low-lying librational modes of the molecule in the crystal [14, 15]. There is good reason to believe that such processes will be important in the glassy matrix, and in this letter, we suggest that both of these dephasing mechanisms are important and, taken together, successfully explain the temperature dependence. We focus our attention on the experimental work of Völker et al. who report $\alpha \approx 1.3 \pm 0.1$ for porphyrins in soft glasses, but our methods also explain the data of Rebane et al. [11] ($\alpha \approx 1.5 \pm 0.3$). The exchange model for the photochemical hole width in crystals involves a librational mode localized on the impurity. For this model [16],

$$\Gamma_{\text{lib}} = \pi^{-1} [\delta^2 \tau / (1 + \delta^2 \tau^2)] \exp(-\Omega/kT),$$

where Ω is the librational frequency, δ is the change in this frequency upon optical excitation of the impurity, and for one-phonon relaxation of the libration,

$$\tau^{-1} = 2\pi g^2(\Omega) \rho(\Omega) [n(\Omega) + 1].$$

In the above, $\rho(\Omega)$ and $n(\Omega)$ are the density of states and thermal population of acoustic modes at the librational frequency, and $g(\Omega)$ is the coupling of these modes to the libration.

In the crystalline *n*-octane environment, where a porphyrin is confined in a fairly tight fit, it was found that $\Omega = 30$ and 15 cm⁻¹ (two types of sites), and $\delta\tau \lesssim 1$ (intermediate exchange). For a more loosely fitting cage in an *n*-decane crystal, $\Omega = 7$ cm⁻¹, and $\delta\tau = 37$ (slow exchange). This is similar to what we expect in a glass, where the impurity is not forced into a tight interstitial position. Therefore, assuming $\delta\tau > 1$,

$$\Gamma_{\text{lib}} = 2g^2(\Omega) \rho(\Omega) n(\Omega).$$

For long-wavelength acoustic modes, we might expect to see crystal-like behavior as is evidenced by the ω^2 density of states observed for acoustic modes in glasses at low frequencies. We therefore take $\rho(\Omega) = A\Omega^2$ and assume a deformation potential coupling $g^2(\Omega) = g^2\Omega$.

In a glass there will be a distribution of these librations. Assuming the cage sizes and configurations to be random, we write the distribution of Ω as a gaussian, centered at ω_0 , of width σ . We now have

$$\Gamma_{\text{lib}} = \frac{2A\langle g^2 \rangle}{\sigma\pi^{1/2}} \frac{2}{\text{erf}[(\omega_D - \omega_0)/\sigma] + \text{erf}(\omega_0/\sigma)} \times \int_0^{\omega_D} \exp[-(\omega - \omega_0)^2/\sigma^2] \frac{\omega^3}{\exp(\omega/kT) - 1} d\omega,$$

where ω_D is the Debye frequency and $\langle g^2 \rangle$ is some average coupling. This can be integrated to find

$$\Gamma_{\text{lib}} = \frac{2A\langle g^2 \rangle \sigma^3}{1 + \text{erf}(\omega_0/\sigma)} \frac{\exp(-\omega_0^2/\sigma^2)}{\sigma^2} \times \sum_{n=1}^{\infty} [\pi^{-1/2}(1 + z_n^2) - (\frac{3}{2} + z_n^2) \times z_n \exp(z_n^2)(1 - \text{erf} z_n)],$$

where $z_n = \sigma n / 2kT - \omega_0/\sigma$. We have set $\omega_D = \infty$ which is valid at the low temperatures of the experiment (1.2–20 K). Note that at low T , $\Gamma_{\text{lib}} \propto T^4$ at high T , $\Gamma_{\text{lib}} \propto T$.

We extract the value for $A\langle g^2 \rangle$ from the slow-exchange data of porphyrin in *n*-decane crystals, where it is observed that $A\langle g^2 \rangle \approx 3.3 \text{ MHz}/(\text{cm}^{-1})^3$. For $kT \leq 2 \text{ cm}^{-1}$, Γ_{lib} is essentially zero, so the dephasing should be equal to $\Gamma_{\text{TLS}} = aT$, and we therefore define a by equating Γ_{TLS} to the experimentally observed dephasing Γ_{ex} ($= cT^{1.3}$ where c depends on the glass) at $T = 2$ or 3 K .

In fig. 1a, we plot the calculated widths, $\gamma = \Gamma_{\text{lib}} + \Gamma_{\text{TLS}}$ versus temperature for various ω_0 (7, 9, 13,

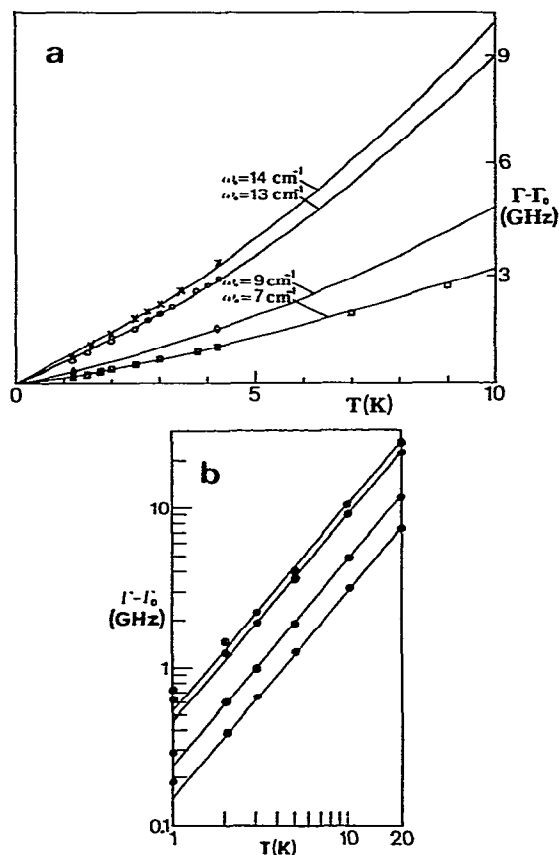


Fig. 1. (a) $\Gamma - \Gamma_0$ versus T for various librational frequencies ($\omega_0 = 7, 9, 13, 14 \text{ cm}^{-1}$). The experimental data are in glycerol (squares), glycol (diamonds), ethanol (circles) and MTHF (crosses) glasses [10]. (b) The points are computed values of $\Gamma - \Gamma_0$ versus T from (a) on a log-log plot for same ω_0 as in the various curves in (a). The lines have slope 1.3, showing that Γ varies as $T^{1.3}$ for $2 < T < 20 \text{ K}$. For $T < 2$, the experimental error limits would still allow an apparent exponent of 1.3.

14 cm^{-1}) and $\sigma = \frac{1}{2} \omega_0$. Also in fig. 1a, we compare these with the experimental width, Γ_{ex} , in glycerol (squares), glycol (diamonds), ethanol (circles) and MTHF (crosses). The agreement between theory and experiment is excellent throughout. When the theoretical calculations are plotted versus T on a log-log plot (see fig. 1b), an apparent $T^{1.3}$ appears. At the lowest temperatures, a smaller exponent is predicted in the present model, but it should be noted that for $T \lesssim 2 \text{ K}$, Γ_{TLS} no longer varies as T but as $T^{1+\epsilon}$, $\epsilon > 0$ [4,5]. Varying σ between 0 and ω_0 changes the result very little for $T < 20 \text{ K}$, but does make some difference for higher T . Γ is a bit more sensitive to ω_0 and $A\langle g^2 \rangle$. For the ethanol glass, for example, where we chose $\omega_0 = 13 \text{ cm}^{-1}$, we can vary ω_0 between 7 and 22 cm^{-1} , keeping the other variables constant, and still fit the data to within experimental error in α , the exponent of the temperature. For the same system with $\omega_0 = 13 \text{ cm}^{-1}$, we can vary $A\langle g^2 \rangle$ between 1.3 and $5.8 \text{ MHz}/(\text{cm}^{-1})^3$ and also stay within the error. A larger ω_0 or coupling leads to a larger α .

To recap, we should see a combination of TLS dephasing and crystal-like phonon mechanisms contributing to the homogeneous width of impurity transitions in glasses. Since most dephasing mechanisms fall off quickly as $T \rightarrow 0$ (compared to T or T^2), we usually see only Γ_{TLS} at low T as in the non-photochemical hole-burning experiments [3]. When coupling to the TLSs is small, or when there are crystal-like processes involving low enough frequency modes, as for porphyrins, we will see both processes. For porphyrins, a set of librations of reasonable width, with ω_0 and the coupling ($A\langle g^2 \rangle$) roughly equal to that in similar crystals, fits the data to within experimental error. At higher temperatures ($kT > \omega_0 + \sigma$) we would expect to see a \propto linear T dependence. As $T \rightarrow 0$, the hole width should go to twice the inverse fluorescence time as T^2 .

Rebane et al. [11] report a $T^{1.5}$ dependence between 1.8 and 4.2 K for a phthalocyanine derivative in H-bonding soft glasses. Since this system is nearly identical to that studied by Völker et al., we would expect the above theory to apply. The accuracy of the exponent is questionable, due to the narrow temperature range, but a larger ω_0 and/or larger coupling ($A\langle g^2 \rangle$) than for porphyrins could easily give an apparent $\alpha = 1.5$. It has recently been pointed out to

the authors that a calculation in the same spirit has been made by Stout [17] to explain the dephasing of rare-earth ions in hard glasses using a combination of the TLS interaction with a Raman process.

A few questions remain unanswered. Friedrich et al. [12] for instance report a T^2 dependence for DAQ in soft glasses, where we might expect a linear form. This could possibly be explained by the above methods, but may be due to an entirely unique mechanism. Their experiments revealed that impurity rearrangements, resulting in hole filling and broadening were also occurring. However, these extra broadening processes were accounted for in a recent paper [18] which shows that the data points to a homogeneous width increasing quadratically with temperature. Also, theory predicts that as $T \rightarrow 0$, the homogeneous width should approach the inverse fluorescence lifetime. This is observed by Völker et al. [10] and appears to be the case in the data of Rebane et al. [11]. However, many authors suggest that their $T = 0$ widths are much larger. This may be due to an improper extrapolation from linear data to temperatures below 2 K, where Γ_{TLS} should begin to go as T^2 . Finally, it should be mentioned that the effects of laser heating, if present, are not known.

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