## VERIFICATION OF THE IMPORTANCE OF LIBRATIONAL MODES FOR OPTICAL DEPHASING IN ORGANIC GLASSES

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Line-narrowed fluorescence spectra as well as photophysical hole-burning spectra provide evidence for a discrete low-energy libration coupling to the  $S_1$  state of tetracene in amorphous 9,10-diphenylanthracene and 2,3-dimethylanthracene matrices. The temperature dependence of the hole widths is in accord with the Jackson–Silbey theory of libration and TLS-induced dephasing.

#### 1. Introduction

There is consensus in the literature that the temperature dependence of the width  $\Gamma$  of photochemical or non-photochemical holes burnt into the inhomogeneous absorption profile of a guest molecule doped into an organic glass obeys a  $T^{\alpha}$  dependence with  $\alpha$ varying between 1.0 and 2.0 [1-3]. For free base porphine incorporated in various matrices such as aliphatic alcohols, polyethylene and MTHF, Thijssen et al. [4] found  $\alpha = 1.3 \pm 0.1$ . In some cases a crossover to a linear law was observed below 1 K. There have been several attempts to explain this behavior and it now appears that quite different models yield essentially the same result. It is therefore difficult to decide among those models on the basis of a  $\Gamma(T)$ measurement alone, and it may be that a mechanism valid in one system is invalid for other systems.

Based on the spectroscopic detection of low-energy phonons that couple to the  $S_1$  state of tetracene incorporated in random aromatic matrices we demon-

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strate in this Letter that the Jackson-Silbey (JS) [5] theory is able to explain  $\Gamma(T)$  in these systems consistently. The JS model assumes two independent mechanisms active in dephasing an excited guest: (i) coupling of the guest to two-level systems (TLS) of the glass which in turn couple to the phonons of the system and (ii) coupling to a low-energy librational mode localized on the guest and interacting with acoustic phonons of the glass. While the first mechanism predicts a linear T dependence for low T, according to either the Lyo [6] or Huber et al. [7] model (with dipole-dipole coupling and constant density of TLS states), the second term produced a faster rising contribution to  $\Gamma(T)$  leading to an apparent  $T^{1.3}$  law. Detection of librations of sufficiently low energy to be excited in the relevant T range is, therefore, crucial for any decision regarding applicability of this model.

#### 2. Experimental

Non-photochemical hole burning (NPHB) experiments were carried out with approximately 2000 Å thick amorphous 2,3-dimethylanthracene (DMA) and

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9,10-diphenylanthracene (DPA) layers doped with typically  $5 \times 10^{-5}$  M/M tetracene (TC). Layers were prepared by depositing the seeded vapor onto a glass substrate at a rate between 50 and 100 Å s<sup>-1</sup>. The substrate was kept in thermal contact with a temperature-controlled cold stage (Cryo-tip, model WMX-1) attached to the cold finger of a He flow cryostat. During sample fabrication the substrate temperature was kept at 2.5 K or 4.2 K. Holes were burnt at 491 nm into the inhomogeneous origin band of TC utilizing two different N2-pumped pulsed dye laser systems, the spectral resolutions and time averaged intensities being  $0.1 \text{ cm}^{-1}/2.6 \text{ mW cm}^{-2}$  and 0.025 $cm^{-1}/1$  mW  $cm^{-2}$ , respectively. Holes were read in the fluorescence excitation mode at 1% input intensity. Fluorescence spectra were recorded with a Jobin-Yvon U-1000 double monochromator with 1  $cm^{-1}$  resolution.

#### 3. Results

In the short-burning-time limit non-photochemical hole profiles burnt into the origin band of TC doped into DMA and DPA consist of a zero phonon (zp) hole, several  $cm^{-1}$  wide (fwhm), and well-resolved real- and pseudo-phonon structures covering an energy range of about 100  $\text{cm}^{-1}$  on both sides of zp hole [8]. Fig. 1 portrays only the central section of the hole spectrum. In both systems a low-lying mode is clearly resolved. If one assumes a Lorentzian profile for the zp hole, symmetric phonon side bands of approximately Gaussian shape are obtained, the band width being about twice the zp hole width. Since the phonon bands overlap with the wings of the zp hole, the assumption of a Lorentzian profile for the zp hole is not unambiguous. Moreover, antiholes produced in course of the burn process may somewhat alter the base line which is required to recover the hole spectrum. We nevertheless choose the Lorentzian instead of a Gaussian profile since (i) the latter would yield asymmetric phonon bands and no obvious reason for asymmetry appears to exist and (ii) we do not find evidence for inhomogeneous broadening of the zp holes. In any case the crucial point is the detection of the low-energy phonons as well as the determination of their energy, and not the exact form of the zp hole profile.



Fig. 1. Holes burnt into the  $S_1 \leftarrow S_0$  transition of tetracene doped into amorphous 9,10-diphenylanthracene (DPA) and 2,3-dimethylanthracene (DMA) matrices. The DPA : TC spectrum is the difference between fluorescence excitation spectra before and after burning. Full circles are Lorentzian profiles, dashed curves represent real- and pseudo-phonon wings.

It has been reported previously that the hole burning efficiency in the systems under study is strongly dependent on the position within the inhomogeneous absorption where burning is done [9]. This has been explained in terms of a manifold of different site structures only one of which is subject to photostimulated persistent site relaxation. It appears noteworthy that in DMA : TC systems the phonon energy turned out to be, within experimental accuracy (±1 cm<sup>-1</sup>), independent of the excitation energy  $\widetilde{\nu}_{ex}$  within the active site profile. This concurs with the previous observation [10] that TC molecules residing in different sites provided by a p-terphenyl matrix copie to the same librational mode (8.5  $\text{cm}^{-1}$ ). However, absolute zp widths were found to decrease by a factor of up to 2 upon lowering  $\tilde{\nu}_{ex}$ .

Low-lying phonons are also identified in the linenarrowed fluorescence spectrum of the dopant. Fig. 2 shows the resonantly excited fluorescence spectrum of DMA: TC in the vicinity of the 1387 cm<sup>-1</sup> vibronic mode. The 6.8 cm<sup>-1</sup> phonon is virtually identical with the phonon mode inferred from NPHB spectra.

In summary, the above experiments establish that



Fig. 2. Section of the resonant fluorescence spectrum of tetracene in DMA.

a low-lying phonon mode, attributable to a molecular libration, couples to TC in a variety of organic matrices. The librational energy  $\tilde{\nu}_1$  is matrix-sensitive and amounts to 7 cm<sup>-1</sup> in DMA : TC, 8.5 cm<sup>-1</sup> in terphenyl : TC, 11 cm<sup>-1</sup> in DPA : TC. The phonon band width (fwhm) is of order 5 cm<sup>-1</sup>. Assuming that the homogeneous width is the same as that of the zp hole we are left with an inhomogeneous contribution to the width characterized by a relative standard deviation  $\sigma/\tilde{\nu}_1 \leq 0.3$ .

In fig. 3 we plot the temperature dependence of the homogeneous width  $\Gamma_{zp}(T)$  (fwhm) of the zp hole calculated according to the relation  $\Gamma_{ex}(T_b, T)$ 



Fig. 3. Temperature dependence of the width of the zero phonon holes in DPA : TC and DMA : TC. Data points are experimental, full curves are theoretical.

=  $\Gamma_{zp}(T_b) + \Gamma_{zp}(T)$  where  $\Gamma_{zp}(T_b) = \frac{1}{2}\Gamma_{ex}(T = T_b)$ ;  $\Gamma_{ex}$  denotes the width of the zp hole,  $T_b$  and T are burn and read temperatures, respectively. Since in our experiment integrated hole areas did not decrease noticeably at  $T \leq 10$  K we believe that the error introduced by ignoring thermal hole refilling is small. The observation that  $\Gamma_{ex}$  decreases if burning is done at 4.2 K and the sample is subsequently cooled to lower T suggests that the hole widths are largely homogeneous and not caused by sample heating or efficient spectral diffusion during the burn process [11]. We therefore claim that  $\Gamma_{zp}(T)$  is of essentially homogeneous origin. It represents the convolution of the homogeneous linewidth of those molecules which by accident are energetically degenerate although sitting in different environments as evidenced by the dispersion of the burning rate [12]. Since different subsets of molecules are sampled upon scanning the laser across the inhomogeneous site band,  $\Gamma_{zp}(T)$  cannot be a well-defined property of the system, but will in general depend on  $\tilde{\nu}_{ex}$  as well as on the sample manufacturing process.

#### 4. Discussion

Since the phonon sideband has a small inhomogeneous broadening, a simple way to describe the temperature dependence of the hole width, is to assume that the optical transition of the guest is dephased both by coupling to the TLS and to a localized low energy libration of energy  $\tilde{\nu}_1$ . The dephasing due to the TLS will be linear in temperature at low  $T[6]^{\ddagger}$  while the contribution to the width due to the librational mode will be activated:

$$\Gamma(T) = aT + b \exp(-\nu_1/kT). \tag{1}$$

Using  $\tilde{\nu}_1 = 7 \text{ cm}^{-1}$  for DMA : TC and  $\tilde{\nu}_1 = 11 \text{ cm}^{-1}$  for DPA : TC, the experimental data can be fit with the parameters  $a = 0.48 \text{ cm}^{-1}/\text{K}$ ,  $b = 6.1 \text{ cm}^{-1}$  (DMA : TC) and  $a = 0.55 \text{ cm}^{-1}/\text{K}$ ,  $b = 21.5 \text{ cm}^{-1}$  (DPA : TC). In fig. 3 we have plotted  $\Gamma(T)$  versus T with these parameters; the agreement with the experimental data is good.

<sup>&</sup>lt;sup>‡</sup> Note that while the original Lyo-Orbach theory of hole widths [13] had  $\Gamma \approx T^2$  at low T, the latter theory has  $\Gamma \approx T$  at low T; it is the latter theory we adopt.

The parameter b can be determined in a simple one-phonon creation process of relaxing the librational mode. Using the acoustic phonons in the Debye model with dimensionless coupling constant  $\lambda$  [11], we find  $b = \lambda^2 \omega^3$ . Assuming that  $\lambda$  is about the same in DMA and DPA, we predict that b(DPA)/b(DMA)= 3.9. The values used in our fit have a ratio 3.5, again in good agreement with the simple model. The fact that the fit yields almost equal values of a in both cases suggests that the TLS-guest coupling is similar in both glasses.

Note that if the librational mode frequency is rather large, then the model reduces to a TLS dephasing only, which would predict a linear temperature dependence. An example of this may be the system studied by Carter et al. [14] who report such a dependence on T of  $\Gamma(T)$  for cresyl violet in a polyvinylalcohol matrix. The absolute value of  $\Gamma$  is a factor of 2 smaller in this case than found in the present study, and the pseudo-phonon wing appears at 32 cm<sup>-1</sup>. These data can be explained by eq. (1) for parameters  $a \approx 0.2$  cm<sup>-1</sup>/K and b < 50 cm<sup>-1</sup>. The latter suggests a value of  $\lambda$  about 1/3 of that found here.

The success of this two-mechanism model in describing  $\Gamma(T)$  in non-photochemical hole burning systems suggests that the librational modes in these systems may be important for the low-temperature dynamics of these optical transitions, just as they are important in molecular crystals [15]. Other explanations for the  $T^{\alpha}$  behavior have been put forward [16,17]; all rest on the TLS dephasing alone and assume, no matter which mechanism is invoked, that the density of TLS modes at low temperature varies as  $\alpha - 1$ . Except in the case of silica [18], there is no evidence for this, and even in that case, other explanations for the apparent behavior of the specific heat have been put forward [19].

One caveat should be stated: whenever in this paper, the word libration was used, it could be replaced by the phrase local optical mode. That is to say, the theory goes through for such modes in the same way as presented here, and the experiment cannot distinguish between the two possibilities. We use librations because it is a physically reasonable idea.

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