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# The low-temperature dynamics of rhodamine 640 in polyvinylalcohol

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## INTRODUCTION

The unique low temperature optical dynamics of amorphous systems have been given considerable attention due to the influence of tunneling two level systems (TLSs).<sup>1,2</sup> TLS models are commonly used to explain the behavior of glasses at low temperature.<sup>1,3,4</sup> Recently, chemical and physical perturbations of amorphous matrices have been utilized as a means of investigating the physical nature and distribution of tunneling two level systems (TLS).<sup>5,6</sup> The low temperature linewidth of a chromophore doped in a glass is predicted to go as a  $T^\alpha$  (below 4 K),<sup>7</sup> where the exponent  $\alpha$  can be related to either the TLS density of states<sup>8</sup> or the distribution of TLS asymmetry parameters.<sup>9</sup> A variety of experimental and theoretical determinations of  $\alpha$  yield a value near 4/3.<sup>1,2,7-15</sup>

The present study was motivated by a recent paper discussing the affect of polymer cross linking on the value of  $a$  for Rh640 in a PVA host polymer.<sup>5</sup> Nakanishi *et al.* used incoherent photon echo measurements to obtain optical dephasing times for both Rh640 and Nile blue chromophores doped into a series of crosslinked polyvinylalcohol polymers over the temperature range 10–30 K. The observed changes in optical dephasing associated with cross linking of the host polymer was attributed to changes in TLS dynamics (i.e., a change in the exponent  $\alpha$ ). Intrigued by this result, we have investigated the optical dephasing of Rh640 in PVA at much lower temperatures in order to further evaluate the relative importance of TLS and electron–phonon contributions to the electronic linewidth over the temperature range 1.1–30 K.

## EXPERIMENT

The laser and detection systems have been described previously.<sup>6,16</sup> In brief, we generated 30 ps pulses of a 4  $\text{cm}^{-1}$  bandwidth at 5875 Å. These pulses are attenuated to about 0.1  $\mu\text{J}$ . The echo pulses are put through an iris and monochromator and detected by a photomultiplier with lock-in amplifier. To counteract the effects of persistent hole burning we employ a method described previously.<sup>16</sup> However, the refresh wavelength used was 580 nm instead of 532 nm. Using the transient grating method<sup>17</sup> we obtained a fluorescence lifetime value of 2 ns ( $T_1$ ).

## RESULTS AND DISCUSSION

The low temperature data of this study (solid squares), as well as the higher temperature data of Nakanishi *et al.*<sup>5</sup> (open circles), are shown in Fig. 1 in which both an Arrhenius and a log–log plot of the data are shown.

Based on hole-burning phonon side-band measurements on Rh640 doped PVA, Nakanishi *et al.* concluded that electron phonon coupling was not a significant factor in deter-

mining the electronic dephasing rate in the 10–30 K temperature range. However, the low temperature results of the present study indicate that thermally activated electron–phonon coupling appears to be dominant in the 10–30 K temperature region. In fact, deviations from a simple low

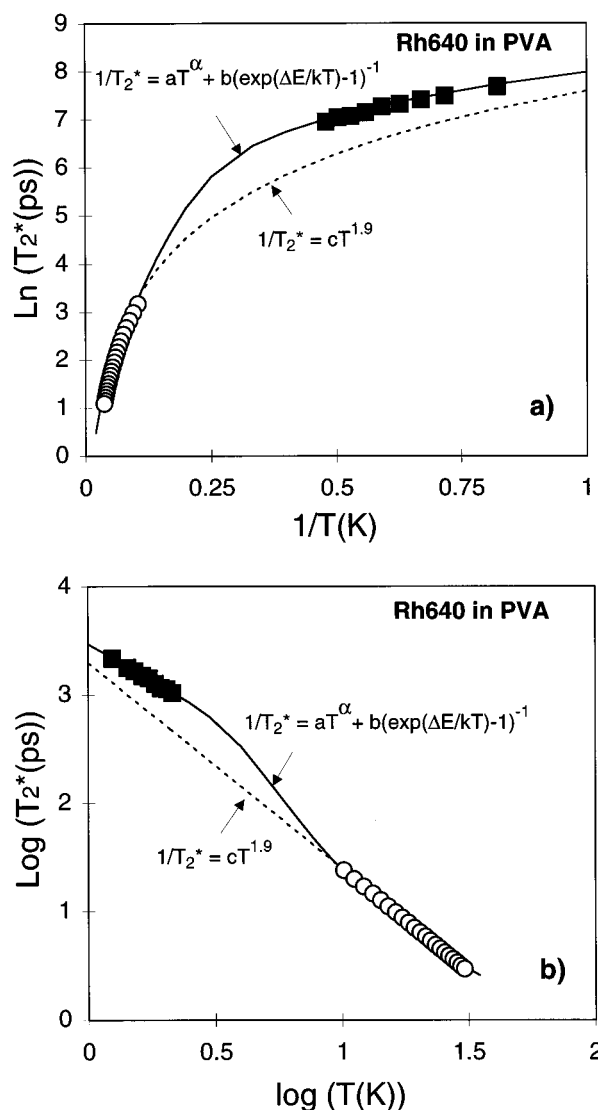


FIG. 1. (a) Arrhenius plot of the rhodamine 640 in polyvinylalcohol system. The open circles are the data reported in Ref. 5 and the solid squares are the lower temperature data from the present study. The dashed curve is the power law fit  $T^{1.9}$ , reported in Ref. 5, and the solid curve is a fit to Eq. (1) with  $\alpha=4/3$ ,  $a=(2915 \text{ ps})^{-1}$ ,  $b=(2.9 \text{ ps})^{-1}$ , and  $\Delta E=16.7 \text{ cm}^{-1}$ . (b) A log–log plot of the  $T_2^*$  data is also shown to better illustrate both the  $T^{4/3}$  power law dependence of the low temperature dephasing rate and the inability of the previously reported  $T^{1.9}$  power law (dashed line) (Ref. 5) to fit the low temperature data.

temperature power law dependence are evident at temperatures above about 4 K, as seen in Fig. 1(b).

The dashed line in Fig. 1 represents the equation  $1/T_2^* = c \cdot T^{1.9}$  used by Nakanishi *et al.*<sup>5</sup> to fit their data obtained in the temperature range 10–30 K. Although this equation does a good job of fitting the high temperature data, it clearly does not fit the lower temperature data of the present study. This is significant since TLS contributions to the linewidth is expected to be most dominant at lower temperatures. Thus at temperatures above 10 K, one clearly must be careful about attributing changes in optical dephasing to changes in TLS dynamics. Specifically, the changes in optical dephasing induced by cross linking of the PVA host reported in Ref. 5 appear to have a considerable contribution from an activated phonon process.

The solid curve in Fig. 1 represents a fit to Eq. (18),

$$1/T_2^* = aT^\alpha + b(\exp(\Delta E/kT) - 1)^{-1}, \quad (1)$$

where  $\alpha=4/3$ ,  $a=(2910 \text{ ps})^{-1}$ ,  $b=(2.9 \text{ ps})^{-1}$ , and  $\Delta E=16.7 \text{ cm}^{-1}$ . This equation includes a contribution from both TLS dynamics and electron phonon coupling.<sup>18,19</sup> This equation has been previously utilized to describe the temperature dependent optical dephasing in doped polymer systems.<sup>11</sup> As previously discussed, the power law exponent  $\alpha$  can be related to the TLS density of states, whereas  $\Delta E$  represents a bulk phonon energy of the host lattice.<sup>11</sup> Clearly the TLS power law temperature dependence will dominate at low temperature and electron phonon coupling is expected to contribute to the dephasing at higher temperatures as the phonon occupation number increases.

The bulk phonon energy ( $\Delta E=16.7 \text{ cm}^{-1}$ ) obtained by fitting Eq. (1) to the data yields a value similar to the  $15 \text{ cm}^{-1}$  value reported for Rh640 doped PMMA.<sup>11</sup> In addition, the power law temperature exponent for the tunneling two level systems is found to be  $\alpha \sim 4/3$ , similar to that reported for a variety of organic glasses and polymer hosts.<sup>1,2,7,10,12</sup> The temperature exponent value of about 2 reported by Nakanishi *et al.*<sup>5</sup> appears to include contributions from thermally activated electron–phonon contributions, and thus should not be attributed to TLS dynamics. Since Eq. (1) models electron–phonon coupling to only a single mode of energy  $\Delta E$ , the involvement of several phonon modes of different energy may explain any slight deviation of Eq. (1) from the data of Nakanishi *et al.* at temperatures above 25 K.

The low temperature results of the present study indicate that electron–phonon coupling is the dominant dephasing mechanism for Rh640 in PVA above 10 K. Thus the decreased optical dephasing rates induced by cross linking the PVA matrix at higher temperatures (i.e., 10–30 K)<sup>5</sup> are attributed to changes in the bulk phonon spectrum. Specifically, if Eq. (1) is applied to the cross-linked PVA data of Nakanishi *et al.*, one obtains reasonable fits to their data if the phonon energy increases with cross linking (i.e., 16.7

$\text{cm}^{-1}$  for the uncross-linked host versus  $22 \text{ cm}^{-1}$  for maximum cross linking). An increase in the frequency of intermolecular phonons is reasonable, given the increased intermolecular bonding associated with cross linking of the matrix. Furthermore, by constraining themselves to the TLS model, Nakanishi *et al.* attributed the decreased optical dephasing rate of Rh640 in cross-linked PVA to void space located near the cross linker. Although void spaces have been suggested as a physical model for TLS,<sup>20</sup> a recent high pressure study of the optical dephasing of Rh640 in PMMA has shown that optical dephasing can be insensitive to compression of sample void space.<sup>6</sup>

## CONCLUSIONS

The low temperature dephasing results for Rh640 in PVA are fit by a model including contributions from TLS dynamics and electron–phonon coupling. The results indicate that electron–phonon contributions for Rh640 doped PVA are significant above 5 K and that TLS models alone are not sufficient to describe the optical dynamics at higher temperatures. This is particularly important for studies which attempt to use chemical or physical modification of the matrix to investigate the nature of TLS. Thus recently reported changes in optical dephasing induced by cross linking the PVA host matrix at higher temperatures (i.e., 10–30 K) are attributed to changes in the distribution of bulk phonon energies, versus changes in the TLS dynamics.<sup>5</sup>

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