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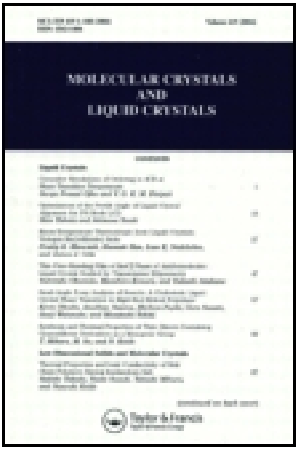

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ON THE DISTRIBUTION OF SINGLE MOLECULE LINE WIDTHS IN LOW-TEMPERATURE GLASSES

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Abstract We discuss a theoretical model for describing the spectral dynamics (fluctuating transition frequency) of individual chromophores in solids. We show that analysis, with this model, of line width distributions resulting from experiments on many individual chromophores in glasses may provide a discriminating test of the "two-level system" model of glasses.

INTRODUCTION

The electronic energy levels of a chromophore in a glass, and hence the chromophore's transition frequencies, are very sensitive to the chromophore's local environment. In principle, then, the optical spectroscopy of dilute chromophores can play an important role in elucidating the structure and dynamics of glasses. Consider first a typical absorption experiment in which a very large number (on the order of 10^{15}) of chromophores are illuminated. Glasses are both characterized by structural disorder that is essentially static on the time scale of an absorption experiment. This means that each chromophore finds itself in a different local environment, and has a different transition frequency. The measured absorption cross-section superposes the absorption line shapes of the large number of individual chromophores. Therefore, even if the line shape of a single molecule is quite narrow, because of the structural disorder and the large number of chromophores, the observed line shape is typically broad and structureless. This "inhomogeneous broadening" is usually on the order of 200 cm^{-1}.

Because the atoms in a solid are constantly in thermal motion, the local environment of an individual chromophore also fluctuates in time, and therefore so does its transition frequency. Indeed, these transition frequency fluctuations, which we will call "spectral dynamics," make a contribution to the line shape of an individual chromophore. Because in a typical absorption experiment one cannot observe line shapes of the individual molecules, this potential information about the dynamics of the solid is unobtainable. In recent years, however, several techniques have been invented that circumvent inhomogeneous broadening, and therefore do

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furnish information about spectral dynamics. For example, in the photochemical hole-burning technique,[1] the sample is irradiated with a narrow-band laser, exciting only those chromophores in resonance with the laser. Once in a great while, one of the chromophores will react photochemically, such that the photoproduct absorbs in some other frequency region. When the sample is subsequently scanned with a weak laser, some fraction of those molecules originally excited will be absent, producing a "hole" in the inhomogeneous absorption band. The hole shape is not obscured by inhomogeneous broadening, since it results from a set of chromophores all of which had the same frequency, and therefore the hole shape can reflect the spectral dynamics of the chromophores.

The great power of photochemical (or photophysical[1]) hole burning comes from the fact that only a subset of the ensemble of chromophores are involved in the experiment. By extrapolation, one might imagine that the most detailed and informative study of spectral dynamics could be obtained from experiments on individual chromophores. This new and exciting field of science has been called single molecule spectroscopy (SMS).[2, 3, 4] By studying many individual molecules one can measure the distribution of spectral dynamical behaviors. This distribution necessarily contains more information than can be obtained by experiments that average over many chromophores, even those with extreme frequency selectivity such as hole burning. In practice, however, certain technical limitations of SMS restrict the time scale over which the spectral dynamics of individual chromophores can be measured. So in the end, we believe that SMS and hole burning (for example) will prove to be complementarily useful techniques.

SMS line shapes are usually measured by fluorescence excitation techniques:[5] the probability that a molecule absorbs a photon is determined by collecting the resulting fluorescence. A line shape is constructed only after many absorption and emission cycles at many laser frequencies have been performed. At the simplest level, spectral dynamics affects the line shape of an individual molecule because over the course of the experiment the molecule has sampled a distribution of frequencies. This brings up one interesting wrinkle of SMS: in general, the line shape depends on how long you measure it! This is because as you wait longer and longer the molecule will sample more and more frequencies. For a fixed measuring time, each individual chromophore will have a different line shape, because each chromophore has statistically different spectral dynamics, again as a result of their different environments. By studying the distribution of single molecule line shapes, one can obtain detailed information about the distribution of spectral dynamical behaviors. Such distributions have been measured for a number of different chromophore/glass systems.[6, 7, 8, 9, 10]

It is thought that the types of atomic motions that are responsible for the spectral dynamics described above result from the flipping of "two-level systems" (TLSs).[11, 12, 13, 14] Each of these objects, which were originally invoked to explain the anomalous heat capacity of glasses, arises from a double-well feature in the potential energy surface along some collective coordinate of atomic displacements. The "two levels" refer to the two lowest energy eigenstates of the double-well potential. Flipping between these two states is thought to occur by phonon-assisted tunneling. Each chromophore has a large number of TLSs in its local environment, and if a TLS flips, the chromophore's environment and hence its transition frequency is changed, resulting in spectral dynamics.

The main purpose of this paper is to describe a theoretical model of spectral dynamics arising from the TLS mechanism, and to show how analysis of experimental data with this model can lead to information about dynamics in glasses. The organization of the paper is as follows. In Section II we describe the theoretical model and present the single molecule line-shape formula derived from it. In Section III we present some calculations on the distribution of SMS line widths of chromophores in glasses, and compare to experiments on terrylene in polystyrene. In Section IV we conclude.

THE SINGLE MOLECULE LINE SHAPE FORMULA

The basic theoretical model involves a single chromophore interacting with a number of noninteracting TLSs. As described above, the transition frequency of the chromophore depends upon the instantaneous configurations of the TLS. Thus we write

$$\nu(t) = \bar{\nu} + \sum_j \xi_j(t)\nu_j,$$

where $\nu(t)$ is the fluctuating transition frequency of the chromophore, $\bar{\nu}$ is its value when all of the TLS are in their ground states, $\xi_j(t)$ is the fluctuating occupation variable for the jth TLS, whose values are 0 or 1 for the ground and excited TLS states respectively, and ν_j is the perturbation that TLS j makes (when excited) to the chromophore's transition frequency. For TLS j $\xi_j(t)$ is a stochastic variable whose time-dependent probability distributions obey first-order rate equations. Thus the statistical properties of $\xi_j(t)$ are completely determined by K_j, the relaxation rate, which is the sum of the upward and downward transition rates, and p_j, which is the equilibrium probability of finding the TLS in its excited state.

Let us focus on the SMS line shape. As described above, if the time it takes to measure the line shape is τ, then the line shape is clearly only sensitive to dynamics on a time scale faster than τ. Within the TLS model, this means that only TLSs with relaxation times shorter than τ can contribute to the spectrum. To a good approximation one can write the line shape as[15, 16]

$$I(\nu) = Re\{\frac{1}{\pi}\int_0^\infty dx e^{i(\nu-\bar{\nu})x} e^{-x/4\pi T_1} \prod_j^F g_j(x)\},$$

where

$$g_j(x) = e^{-(a_j + ip_j\nu_j)x}[\cosh(A_j x) + \frac{a_j}{A_j}\sinh(A_j x)],$$

$$A_j = \frac{1}{2\pi}\sqrt{\frac{K_j^2}{4} - \pi^2\nu_j^2 - i(2p_j - 1)\pi\nu_j K_j},$$

$$a_j = \frac{1}{2\pi}[\frac{K_j}{2} - i(2p_j - 1)\pi\nu_j],$$

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and T_1 is the excited state lifetime. The superscript F on the product indicates that only those (fast) TLS with $K_j > 1/\tau$ are included. Thus we see that the line shape for an individual molecule is the Fourier transform of a product of factors, one for each effective TLS, times an exponential damping factor due to the excited state lifetime.

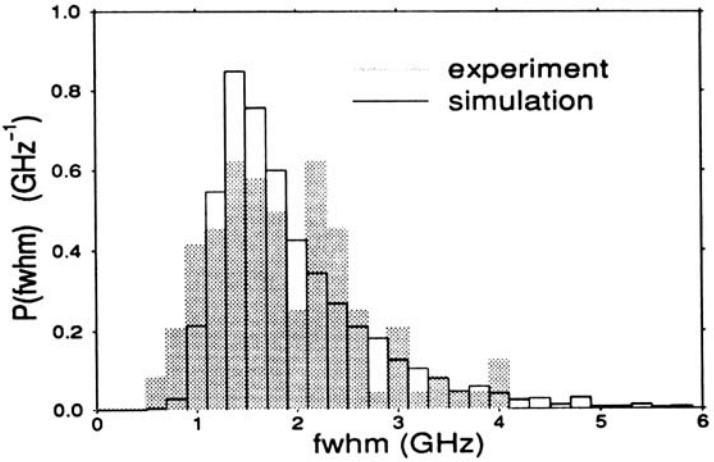

Figure 1: Histograms showing the experimental (from Ref. 8) and simlulated line width distributions, $P(\Delta\nu)$, for individual molecules of terrylene in polystyrene.

THE LINE WIDTH DISTRIBUTION

Line shapes of individual chromophores have been studied for a number of chromophore/glass systems. A simple way to characterize the distribution of line shapes is by a distribution of line widths. As discussed above, the distribution of line widths arises because each individual chromophore has a unique TLS environment. Two- and three-pulse echo and hole-burning experiments have all been analyzed with a more or less standard TLS model[17, 18, 19, 20, 21, 22] (but also see references [23, 24]). We have argued above that SMS experiments have the potential for obtaining more information than these ensemble averaged experiments. Thus our goal here is to analyze the SMS experiments with the same TLS model, in the hopes that they can provide a discriminating test of the model.

We begin by describing the standard TLS model. The dynamics of each TLS involves two parameters: K, the relaxation rate constant, and p, the probability that the TLS is excited. p is determined through the energy splitting E between the TLS eigenstates by the Boltzmann factor

$$p = e^{-E/kT}/(1 + e^{-E/kT}).$$

Relaxation is assumed to be dominated by one-phonon-assisted tunneling, and hence K takes the form

$$K = CEJ^2 \coth(E/2kT),$$

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where C is a TLS-phonon coupling constant and J is the tunneling matrix element between the two zeroth-order states localized in each well of the potential. E depends on J and A, the energy asymmetry between the localized states, by

$$E = \sqrt{A^2 + J^2}.$$

Because the glass is disordered each TLS has a unique pair of A and J, and the ensemble of TLSs is therefore described by the distribution function $P(A, J)$. Within the standard TLS model this distribution function is given by:

$$P(A, J) = \begin{cases} \frac{1+\mu}{A_{max}^{1+\mu}\ln(J_{max}/J_{min})}\frac{A^{\mu}}{J}, & 0 \leq A \leq A_{max},\ J_{min} \leq J \leq J_{max} \\ 0, & \text{otherwise} \end{cases},$$

where μ is a positive constant. As long as the cutoffs A_{max} and J_{max} are chosen to be much larger than kT, the results are insensitive to their values. It is typically found that the hole width of chromophores in glasses goes like T^{γ}, where γ is around 1.3.[25, 26] From the standard TLS model one can show that $\gamma = 1 + \mu$; therefore we take $\mu = 1/3$.

The TLSs are assumed to be randomly distributed in space. The perturbation of the chromophore's transition frequency results from dipolar interactions with the TLSs.[17] The perturbation from a single TLS is given by

$$\nu = f\frac{A}{E}\frac{\alpha}{r^3},$$

where α is the TLS-chromophore coupling constant, r is the distance between the chromophore and the TLS, and f is a dimensionless angular factor, which, for simplicity, we will take to be a random variable that has values ±1 with equal probability.

Our first effort to analyze SMS line width data involves the system terrylene in polystyrene,[8] primarily because many of the parameters described above are known. (A more complete report of the analysis of this and other systems will be submitted shortly.[27]) The full widths at half maximum (FWHM) of the line shapes for 121 individual terrylene molecules were measured at 1.7 K,[8] and the amount of time it took to measure each line shape was $\tau = 120$ s. In what follows we will measure energy and temperature in units of K (Kelvins), distance in units of nm, and time in units of s. The value of the phonon-TLS coupling constant is known for polystyrene: $C = 3.9 \times 10^8$ K^{-3}s^{-1}.[28] Also known is the density of TLSs with 0.5 K $\leq E \leq$ 1.5K for polystyrene is[29] 3×10^{-4} nm^{-3}. Taking $A_{max} = J_{max} = 17$ K, we determine the total TLS density ρ from Eq. (1); we find that $\rho = 1.15 \times 10^{-2}$ nm^{-3}. J_{min} is determined by setting $K_{min} \equiv 2kTCJ_{min}^2$ to be 10^{-4} s^{-1}, so that the slowest possible TLS relaxation time (10^4 s) is much longer than τ. This gives $J_{min} = 2.8 \times 10^{-7}$ K. The excited state lifetime of terrylene is $T_1 = 3.8$ ns.[30] Thus, the only unknown parameter is α, the TLS-chromophore coupling constant.

To compare the TLS model to SMS experiments, we generate representative configurations of a single chromophore surrounded by many TLSs using Monte Carlo sampling. We then use Eq. (1) to calculate the exact line shape for each configuration. It should be emphasized that these line shapes are in general not Lorentzian or of any other simple functional form. For each line shape the FWHM,

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$\Delta\nu$, is determined numerically, and a histogram of the line widths is obtained for a large number of chromophores. The theoretical histogram is compared to the experimental one in a least-squares sense, and the entire procedure is repeated for different values of α. The value of α that gave the best fit is $\alpha = 3.75 \times 10^{11}$ nm^3/s. The comparison between the theoretical and experimental histograms is shown in Fig. 1; it is seen that the agreement is only qualitative. However, it is important to point out that the theoretical histogram has 2000 chromophores, while the experimental one has only 121, and therefore the latter has much more statistical noise. Nonetheless, further analysis[27] shows that it is rather unlikely that the deviation between experiment and simulation arises solely from the small number of chromophores sampled in the experiment. The simulated distribution is distinctly narrower than the experimental one and a clear difference between to two is seen at low widths. Similar discrepancies are systematically repeated in other systems as well [27]. Provided that the experimental results are quantitatively reliable, these observations may suggest that the standard TLS model may need to be modified in order to capture the new information provided by SMS.

CONCLUSIONS

In this paper we have endeavored to show that from the spectral dynamics of individual molecules, as measured by line shapes, one can obtain interesting and useful information about atomic motions in solids. In particular, we believe that the measurement and analysis of line width distributions for chromophores in glasses will answer questions about the correctness of the standard tunneling model of glasses, and may eventually help us understand the microscopic origin of "two-level systems." To realize this goal it will be necessary to have experimental data for a large number of chromophores (at least several hundred), at several different temperatures, and on several different systems (preferably those for which parameters for the undoped glass are available). It would also be most helpful if one could obtain data from complementary spectroscopies (two-pulse echo, three-pulse echo, hole burning, single molecule line shapes, spectral diffusion trajectories, and fluorescence intensity correlations[31]) on the same system.

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