

Spectral Dynamics of Individual Molecules in Glasses and Crystals

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I. Introduction

The electronic energy levels of a chromophore in a solid, 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 solids, especially at very low temperatures. Consider first a typical absorption experiment in which a very large number (on the order of 10^{15}) of chromophores are illuminated. Crystals and 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 1 cm^{-1} in crystals, and 200 cm^{-1} in glasses.

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 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 photophysical¹) 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).^{2–4} 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

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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.^{6–10}

One can also perform a line shape experiment repeatedly on a single molecule. Since the molecule's average frequency will in general change from scan to scan because of spectral dynamics, so will the peak frequency of the excitation spectrum. A plot of the peak frequency as a function of time has been called a "spectral diffusion trajectory". Note that the term spectral diffusion is not meant to imply that the time-dependent probability distribution of a chromophore's frequency obeys a diffusion equation; in general it does not. Spectral diffusion trajectories have been measured for single molecules in both crystals and glasses.^{9–14} Spectral diffusion trajectories for a large number of molecules would again give information about the distribution of spectral dynamical behaviors. In summary, then, SMS line shape studies, which measure relatively short-time (shorter than the scan time) spectral dynamics, and spectral diffusion trajectory studies, which measure relatively long-time (longer than the scan time) spectral dynamics, can provide a wealth of complementary information about atomic motions in solids.

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).^{15–18} 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 are changed, resulting in spectral dynamics.

The main purpose of this Account 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 solids. The organization of the paper is as follows. In section II we describe

the theoretical model and a few key results. In section III we present some calculations on the distribution of SMS line widths of chromophores in glasses, and compare the distribution to that from experiments on terrylene in polystyrene. In section IV we describe the analysis of some spectral diffusion trajectory experiments on pentacene in *p*-terphenyl. In section V we conclude.

II. Theoretical Model and Results

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

$$\nu(t) = \bar{\nu} + \sum_j \xi_j(t) \nu_j \quad (1)$$

where $\nu(t)$ is the fluctuating transition frequency of the chromophore, $\bar{\nu}$ is its value when all of the TLSs are in their ground states, $\xi_j(t)$ is the fluctuating occupation variable for the j th 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 first 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^{19,20}

$$I(\nu) = \text{Re}\{(1/\pi) \int_0^\infty dx e^{i(\nu-\bar{\nu})x} e^{-x/4\pi T_1} \prod_j^F g_j(x)\} \quad (2)$$

where

$$g_j(x) = e^{-(a_j + ip_j)x} [\cosh(A_j x) + (a_j/A_j) \sinh(A_j x)] \quad (3)$$

$$A_j = \frac{1}{2\pi} \left(\frac{K_j^2}{4} - \pi^2 \nu_j^2 - i(2p_j - 1)\pi \nu_j K_j \right)^{1/2} \quad (4)$$

$$a_j = \frac{1}{2\pi} \left[\frac{K_j}{2} - i(2p_j - 1)\pi \nu_j \right] \quad (5)$$

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 TLS, times an exponential damping factor due to the excited state lifetime.

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Next let us consider the spectral diffusion trajectories. One way to characterize such a trajectory is by the correlation function $C(t) = \langle \nu(t) \nu(0) \rangle - \langle \nu \rangle^2$, where the angular brackets denote an average over the stochastic processes. One can show that²⁰⁻²²

$$C(t) = \sum_j^S p_j (1 - p_j) \nu_j^2 e^{-K_j t} \quad (6)$$

where the superscript S on the sum indicates that only those (slow) TLS with $K_j < 1/\tau$ are included. A more detailed characterization involves the distribution of spectral jumps, $P(\Delta; t)$, which is the probability density that the transition frequency will change by an amount Δ in time t . This is given by²⁰⁻²³

$$P(\Delta; t) = (1/\pi) \int_0^\infty dx \cos(\Delta x) \prod_j^S [1 + 2p_j(1 - p_j)(1 - e^{-K_j t})(\cos(\nu_j x) - 1)] \quad (7)$$

Finally, one can simply determine the distribution of frequencies visited during the trajectory, which is given by^{20,22-24}

$$P(\nu) = \text{Re}\{(1/\pi) \int_0^\infty dx e^{i(\nu - \bar{\nu})x} \prod_j^S [1 + p_j(e^{-i\nu_j x} - 1)]\} \quad (8)$$

III. Distribution of Single-Molecule Line Widths in Glasses

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 model²⁵⁻³⁰ (but also see refs 31 and 32). We have argued above that SMS experiments have the potential for obtaining more information than these ensemble 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

$$p = e^{-E/kT} / (1 + e^{-E/kT}) \quad (9)$$

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

$$K = CEJ^2 \coth(E/2kT) \quad (10)$$

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

$$E = (A^2 + J^2)^{1/2} \quad (11)$$

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 $P(A, J)$. In the usual TLS model

$$P(A, J) = \begin{cases} \frac{1 + \mu}{A_{\max}^{1+\mu} \ln(J_{\max}/J_{\min})} \frac{A^\mu}{J}, & 0 \leq A \leq A_{\max}, J_{\min} \leq J \leq J_{\max} \\ 0, & \text{otherwise} \end{cases} \quad (12)$$

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.^{33,34} 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.²⁵ The perturbation from a single TLS is given by

$$\nu = f \frac{A}{E} \frac{\alpha}{r^3} \quad (13)$$

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 terylene 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.³⁵) The full widths at half-maximum (fwhm) of the line shapes for 121 individual terylene 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 kelvin, distance in units of nanometers, and time in units of seconds. Thus, for example, for polystyrene $C = 3.9 \times 10^8 \text{ K}^{-3} \text{ s}^{-1}$.³⁶ The density of

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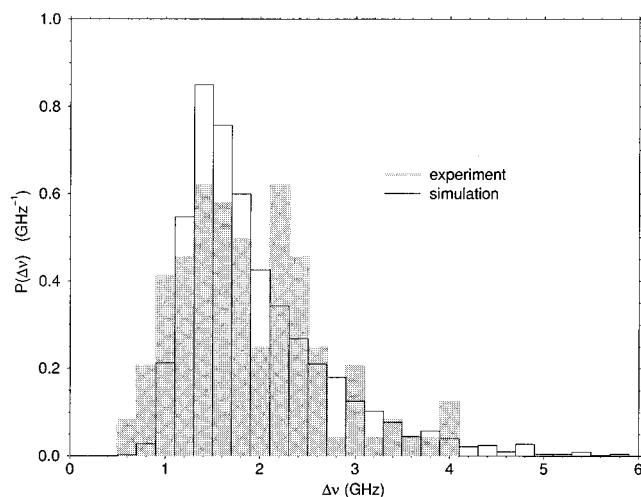


Figure 1. Histograms showing the experimental (from ref 8) and simulated line width distributions, $P(\Delta\nu)$, for individual molecules of terrylene in polystyrene.

TLs with $0.5 \text{ K} \leq E \leq 1.5 \text{ K}$ for polystyrene is³⁷ $3 \times 10^{-4} \text{ nm}^{-3}$. Taking $A_{\text{max}} = J_{\text{max}} = 17 \text{ K}$, we determine the total TLS density ρ from eq 12; we find that $\rho = 1.15 \times 10^{-2} \text{ nm}^{-3}$. J_{min} is determined by setting $K_{\text{min}} \equiv 2kTC J_{\text{min}}^2$ to be 10^{-4} s^{-1} , so that the slowest possible TLS relaxation time (10^4 s) is much longer than τ . This gives $J_{\text{min}} = 2.8 \times 10^{-7} \text{ K}$. The excited state lifetime of terrylene is $T_1 = 3.8 \text{ ns}$.¹³ 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 TLSs using Monte Carlo sampling. We then use eq 2 to calculate the exact line shape for each configuration. For each line shape the fwhm, $\Delta\nu$, 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 $\alpha = 3.75 \times 10^{11} \text{ nm}^3/\text{s}$. The comparison between the theoretical and experimental histograms is shown in Figure 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 analysis³⁵ 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. Also, there seems to be a systematic discrepancy at low widths. This may suggest that the standard model may need to be modified in order to capture the new information provided by SMS.

IV. Single-Molecule Spectral Diffusion Trajectories in Crystals

Spectral diffusion trajectories of individual molecules have been measured for chromophores in both glasses and crystals. Because of the large amount of

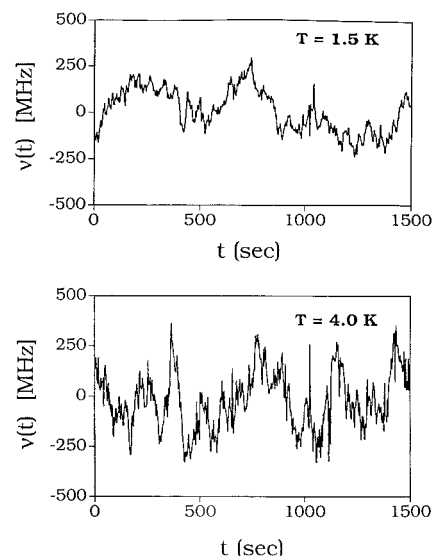


Figure 2. Peak frequency of the fluorescence excitation spectrum of a single molecule of pentacene in *p*-terphenyl as a function of time. From ref 12. Reprinted with permission from ref 22. Copyright 1995 American Institute of Physics.

disorder in glasses, as in the case of single-molecule line widths, meaningful results can only be obtained from analyzing a large number of trajectories, for the same system, at the same temperature. At present such data are not available. However, for crystals, there is substantially less disorder, and it is possible to obtain meaningful results from studies of fewer molecules. Below we discuss the analysis of a pair of trajectories at two different temperatures for one single molecule of pentacene in crystalline *p*-terphenyl.¹² The trajectories are shown in Figure 2. It is seen that the chromophore's transition frequency visits many different values during the course of the trajectory, and that both the amplitude and rate of the fluctuations increase as the temperature is increased.

Our physical picture of the situation is as follows.²² The low-temperature phase of *p*-terphenyl crystal is known to have two crystallographically distinct degenerate ground states, corresponding to different orientational ordering of the central phenyl rings.³⁸ A real crystal will therefore have domains of these two ground states, separated by domain walls. In each of the domains the potential curve for reorientation of a single central phenyl ring is very asymmetric, and at the temperature of the experiment reorientation does not occur. However, at a perfect domain wall this potential is symmetric, thus allowing for the possibility of central phenyl ring flips. The left and right states of this symmetric potential correspond to the two zeroth-order states of the TLS. The rate of TLS flipping is expected to be very slow since this process involves tunneling of the massive phenyl ring through a substantial barrier. Pentacene substitutes into *p*-terphenyl in well-defined sites, and chromophores that happen to be near a domain wall sense a large number of flipping TLSs and therefore show spectral diffusion behavior.

As discussed above, the simplest characterization of a spectral diffusion trajectory involves the transition frequency correlation function $C(t)$ from eq 6. The experimental results from the trajectories in Figure 2 can both be fit²² with an exponentially decaying $C(t)$,

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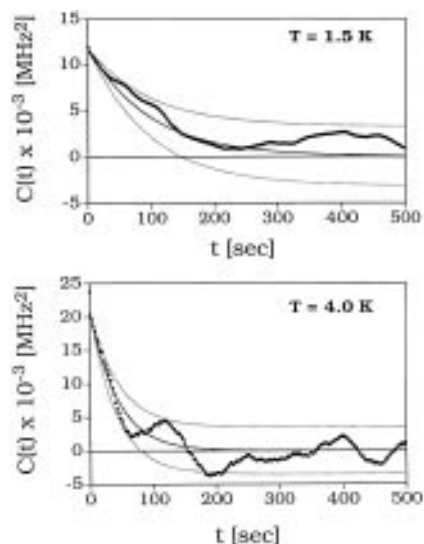


Figure 3. Experimental (solid circles) and theoretical (solid line) frequency correlation functions as a function of time for the trajectories shown in Figure 2. The dashed lines show expected one standard deviation error estimates. Reprinted with permission from ref 22. Copyright 1995 American Institute of Physics.

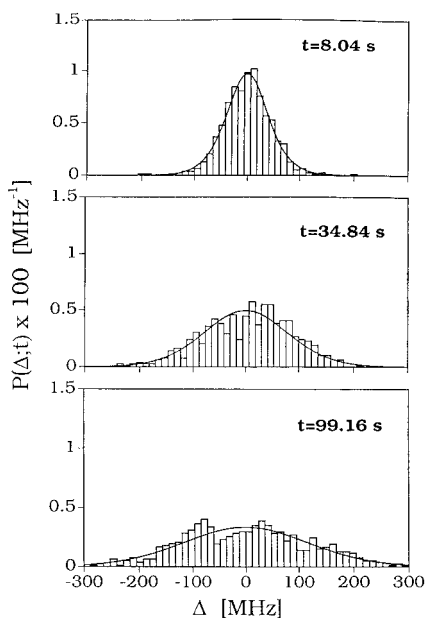


Figure 4. Experimental (bar graph) and theoretical (solid line) distribution of spectral jumps as a function of the frequency jump, Δ , for various times, t , for the trajectory shown in Figure 2 at 1.5 K. Reprinted with permission from ref 22. Copyright 1995 American Institute of Physics.

as shown in Figure 3. This suggests that all of the TLSs might have the same decay rate K . If we also assume that each TLS has the same energy splitting, analysis²² of the temperature dependence of $C(t)$ shows that $E = 2.64$ K, which is very small but nonzero. The origin of this energy splitting is not precisely understood. Possibilities include anything that breaks the symmetry of a perfect planar domain wall, including thermal fluctuations of the interface, the presence of other defects, or indeed, the chromophore itself. The coupling constant α was previously determined from the analysis²² of a second pentacene molecule; we found that $\alpha \approx 4 \times 10^9$ nm³/s. From this value we were able to determine that the chromophore analyzed above is about 4 nm from the domain wall. From eq

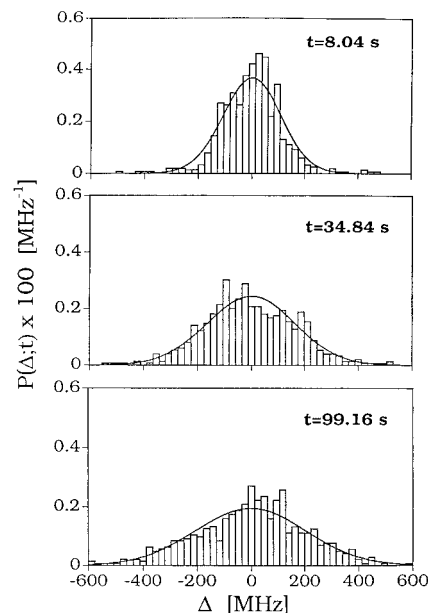


Figure 5. Same as Figure 4 but for the trajectory from Figure 2 at 4.0 K. Reprinted with permission from ref 22. Copyright 1995 American Institute of Physics.

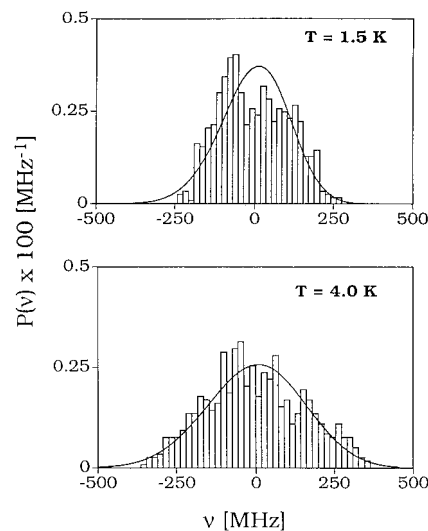


Figure 6. Experimental (bar graph) and theoretical (solid line) frequency distributions for the two trajectories in Figure 2. Reprinted with permission from ref 22. Copyright 1995 American Institute of Physics.

10 for the phonon-assisted tunneling flip rate (and in the absence of information for *p*-terphenyl, using the value of C for polystyrene), we can determine that $J = 2.5 \times 10^{-6}$ K, in very rough agreement with a WKB estimate of 8.3×10^{-5} K.²²

One can go further by analyzing $P(\Delta;t)$, the time-dependent frequency jump distribution. The comparison²² between theory and experiment for the two trajectories, using no further adjustable parameters, is shown in Figures 4 and 5. The comparison of the frequency distributions $P(v)$ is shown in Figure 6. (In the actual analysis of the data the expressions for $P(\Delta;t)$ and $P(v)$ in eqs 7 and 8 were modified to include the effect of additional experimental noise.²²) The good agreement between theory and experiment provides what seems to be compelling confirmation of the above physical picture. More experimental studies on more molecules, for longer times, and over a wide range of temperatures, would help determine the

mechanisms of TLS flipping, and would also provide further overall evidence to support (or refute) our picture.

V. Conclusions

In this Account we have endeavored to show that, from the spectral dynamics of individual molecules, as measured by line shapes and by spectral diffusion trajectories, 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 correlations³⁹) on the same system.

We have shown that, from the seminal spectral diffusion trajectory experiments on pentacene in *p*-terphenyl crystal,^{11,12} one can obtain detailed microscopic information about one single molecule. If our model is correct, it allows a microscopic identification of a particularly well-defined set of two-level systems. The parameters (energy splitting and the tunneling matrix element) of these two-level systems are typical of those found in glasses. Detailed study of the temperature dependence of spectral diffusion trajectories for many different pentacene molecules in *p*-terphenyl crystals may shed light on the precise mechanism of phonon-assisted tunneling in this system, which in turn may help us understand the glass experiments.

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