# Spectral Diffusion of Single Molecule Fluorescence: A Probe of Low-Frequency Localized Excitations in Disordered Crystals

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Spectral diffusion of the transition frequency of single pentacene molecules in *p*-terphenyl crystal was recently observed experimentally. In this Letter we propose a microscopic theoretical model to explain this phenomenon. Analysis of the experimental data with our model yields detailed microscopic information about the nature and spatial distribution of the localized excitations responsible for the observed spectral diffusion.

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Impurity spectroscopy provides a powerful means for elucidating the structure and dynamics of condensed phases. Recent experimental advances have made it possible, for the first time, to resolve the fluorescence of individual impurity molecules embedded in both molecular crystals and amorphous polymeric hosts [1–6]. A summary of the current state of single molecule spectroscopy is given in a recent review by Moerner and Basché [7]. The optical transition frequency of an impurity molecule depends sensitively on its local environment. Single molecule spectroscopy is therefore a uniquely sensitive probe of the local interactions and excitations in the solid state. An unexpected result from these experiments was the observation of spectral diffusion of individual molecule optical transitions [1,2,7]. That is, the absorption frequencies of some of the molecules change with time. Examples of single molecule spectral diffusion trajectories are shown in Fig. 1 (reproduced from Ref. [1]).

In this Letter we present a simple theoretical model with which to analyze single molecule spectral diffusion, specifically, the results for dilute pentacene in *p*-terphenyl crystal shown in Fig. 1. Our analysis yields detailed microscopic information about the nature of the localized excitations responsible for the observed spectral diffusion, their spatial distribution, and their coupling to the impurity molecule optical transition.

The structure of the *p*-terphenyl crystal has been extensively studied [8,9], and there are well-characterized intrinsic localized excitations that are thought to be responsible for the observed spectral diffusion [1]. *p*-terphenyl consists of three phenyl rings connected in a linear arrangement by single bonds. The two outer rings lie in the same plane and in its equilibrium configuration the central phenyl ring is twisted clockwise or anticlockwise relative to this plane [10]. In the low-temperature crystalline phase of *p*-terphenyl there is evidence that one orientation of the central ring is stabilized relative to the other, i.e., the central ring motion occurs in an asymmetric double well potential [11,12]. Recent electron paramagnetic resonance (EPR) experiments on pentacene in *p*-terphenyl have confirmed this picture [13]. We include only the two lowest-lying quantum states of this potential in our model.

In our analysis of the experiment we consider two specific models for these two-level systems (TLS). In the first model (denoted 3D), we associate an identical, independent TLS with each lattice site in the crystal (except the impurity's). To motivate our second model, we note that at low temperature the *p*-terphenyl crystal has domains of different central phenyl ring ordering, and that the central ring motion is expected to be particularly facile at the boundary between these domains [8]. In order to model this situation, we only associate TLSs with lattice sites in a plane at a given distance from the impurity molecule. We call this our 2D model.

The state of each TLS is described by a time-dependent occupation variable, $\xi_j(t)$, which is equal to 0 if TLS $j$ is in its ground state and is equal to 1 when the TLS is excited. The subscript $j$ runs over all lattice sites

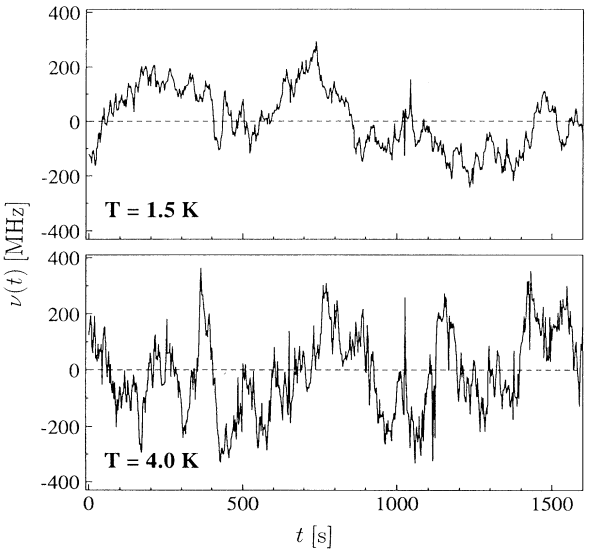


FIG. 1. Peak frequency of the fluorescence excitation spectrum of a single molecule of pentacene in *p*-terphenyl as a function of time. Zero detuning is at about 223 GHz to the red of the inhomogeneous band center (see Ref. [1] for details).

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for the 3D model and over all lattice sites in the plane for the 2D model. We assume that the peak frequency of the impurity (probe molecule), $\nu(t)$, depends linearly on the state of excitation of the TLSs, and we can therefore write

$$\nu(t)=\nu_0+\sum_j \xi_j(t)\nu_j . \quad (1)$$

$\nu_0$ is the transition frequency when all of the TLSs are in their ground states and $\nu_j$ is the perturbation of the probe molecule transition frequency when TLS $j$ is in its excited state. The dynamics of the TLSs are taken to be stochastic, with up and down transition rate constants $k_u$ and $k_d$, respectively. Furthermore, we assume that the TLSs are in thermal equilibrium at a temperature $T$. The transition rates are therefore related by detailed balance: $k_u/k_d=\exp(-\Delta E/kT)$, where $\Delta E$ is the energy splitting of the TLSs.

We now analyze the spectral diffusion trajectories shown in Fig. 1. The simplest way to characterize these trajectories is with the autocorrelation function of the frequency fluctuations: $C(t)\equiv\langle\nu(t)\nu(0)\rangle-\langle\nu\rangle^2$. Within our model this is given by [14]

$$C(t)=(p-p^2)M_2e^{-Kt}, \quad (2)$$

where $p$ is the probability that a TLS is excited,

$$p=\frac{\exp(-\Delta E/kT)}{1+\exp(-\Delta E/kT)}, \quad (3)$$

$K$ is the sum of the up and down rate constants ($K=k_u+k_d$), and $M_2=\sum_j \nu_j^2$. For our model the correlation function decays as a single exponential, with decay rate $K$ and initial value $(p-p^2)M_2$.

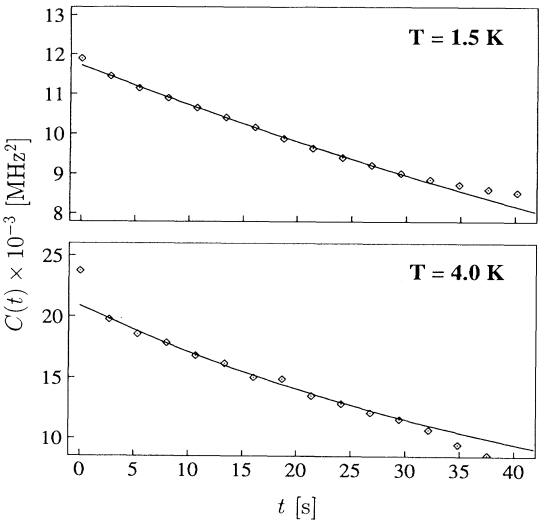


FIG. 2. Correlation function of frequency fluctuations as a function of time. The experimental results (◇) are calculated from the two time series shown in Fig. 1 and the solid lines are the least-squares best fits to a single exponential over the time range 1–30 s.

In Fig. 2 we show $C(t)$ calculated from the trajectories in Fig. 1, together with fits by Eq. (2). With the exception of the point at $t=0$, the experimental correlation function is well fit by a single exponential for times out to about 30 s. The short length of the experimental trajectories causes the correlation function to be noisy for times greater than about 30 s. Since we cannot estimate error bars for these points, we simply exclude them from the fit. The rapid drop of $C(t)$ at the shortest time must be due either to some as yet undetermined excitations that cause spectral diffusion on a time scale faster than the 3 s time resolution of the experiment or to experimental uncertainties such as laser jitter.

Using the fits to $C(t)$ shown in Fig. 2 we can determine the values of $M_2$, $\Delta E$ (and therefore $p$), and $K$ (and therefore $k_u$ and $k_d$). We find that $\Delta E/k=2.625$ K and $M_2=9.29\times10^4$ MHz$^2$. The results for $p$, $K$, $k_u$, and $k_d$ are summarized in Table I. One sees that the motion of the TLSs is extremely slow. At 1.5 K an individual TLS will make an up transition about once every 750 s. When the temperature is raised from 1.5 to 4.0 K the rate of flipping increases, and the total rate, $K$, approximately doubles over this temperature range. If the mechanism for the TLS transition is one-phonon-assisted tunneling, the total rate is given by $K(T)=A\coth(\Delta E/2kT)$ [15]. Using $\Delta E/k=2.625$ K the one-phonon-assisted mechanism predicts a ratio of $K(1.5)/K(4.0)\approx0.450$. Using the values of $K(T)$ given in Table I we find $K(1.5)/K(4.0)\approx0.455$. The temperature dependence of the TLS flipping rate is therefore consistent with a one-phonon-assisted tunneling mechanism, although more data at intermediate temperatures are needed to confirm this result.

The expression for $C(t)$ given in Eq. (2) was derived without reference to any model for the spatial distribution of TLSs or for the coupling of these TLSs to the probe molecule. As shown, the correlation function analysis does give us detailed information about the nature and dynamics of the individual TLSs but it does not differentiate between the 2D and 3D models. In order to extract this information, we must consider a more detailed characterization of the spectral diffusion trajectories. To this end, we have found it useful to analyze these trajectories in terms of their distribution of spectral jumps, $P(\Delta;t)$. This quantity is defined as the probability

TABLE I. Model parameters determined from the fit of the experimental correlation functions by Eq. (2).

| | $T=1.5$ K | $T=4.0$ K |
|---|---|---|
| $p$ | 0.148 | 0.342 |
| K ($s^{-1}$) | $8.98\times10^{-3}$ | $19.75\times10^{-3}$ |
| $k_d$ ($s^{-1}$) | $7.65\times10^{-3}$ | $13.00\times10^{-3}$ |
| $k_u$ ($s^{-1}$) | $1.33\times10^{-3}$ | $6.74\times10^{-3}$ |

that the transition frequency will change by an amount $\Delta$ in a time $t$, and in terms of our model can be written as [14]

$$P(\Delta;t)=\int_{-\infty}^{\infty}\frac{d\tau}{2\pi}e^{i\Delta\tau}\prod_j\{1+2(p-p^2)(1-e^{-Kt})[\cos(\nu_j\tau)-1]\}\,. \tag{4}$$

In order to calculate $P(\Delta;t)$ for our model we must specify the form of the coupling between the TLS excitations and the probe molecule transition frequency. For simplicity we assume a simple cubic lattice for the crystal structure, and take the coupling to be

$$\nu_j=\Lambda\frac{\psi(\Omega_j)}{(r_j/a)^3}\,. \tag{5}$$

$r_j$ is the distance from the probe molecule to TLS $j$, $a$ is the lattice spacing, $\psi(\Omega_j)$ is some function of the polar angles of the position of TLS $j$ with respect to the probe molecule, and $\Lambda$ is the coupling strength with units of frequency. The $1/r^3$ range dependence of this interaction follows from either electrostatic or elastic strain dipole-dipole interactions. In our analysis of the trajectories in Fig. 1 we found that the exact form of the angular dependence of the interaction is qualitatively unimportant. We will take $\psi(\Omega)=-3\cos\phi\sin\theta\cos\theta$, which is the $xz$ component of the strain tensor [16]. For our 2D model, we must also specify the perpendicular distance (taken to be in the $y$ direction) of the probe molecule from the TLS plane.

In Fig. 3 we show the distribution of spectral jumps at two representative times calculated from the lower-temperature trajectory shown in Fig. 1. In the upper panel we also show the results for our 3D and 2D models calculated by numerical integration of Eq. (4). For the 3D model there are no additional adjustable parameters in this calculation: $p$ and $K$ are given in Table I and $\Lambda$ is determined from the constraint that $\sum_j \nu_j^2=M_2$, which gives $\Lambda=232$ MHz. For the 2D model the distance of the probe molecule from the TLS plane, $h$ (in units of the lattice spacing), is an adjustable parameter, and we show results for $h=3$, 8, and 16, with corresponding values of $\Lambda=5060$, 36200, and 154000 MHz, respectively. From Fig. 3 we see that the 2D model with $h=8$ or 16 agrees well with the data, whereas the 2D model with $h=3$ and the 3D model are both qualitatively incorrect. We note from Eq. (5) that a TLS flip of a nearest neighbor host molecule would produce a transition frequency perturbation of the probe on the order of $\Lambda$. We might expect that this perturbation should be less than but on the order of the transition frequency difference for pentacenes in two similar but inequivalent substitutional sites. For the $O_1$ and $O_2$ sites this is about 4 $cm^{-1}$ or 120 GHz [2]. Therefore we conclude that the 2D model with $h=8$ is more reasonable than that with $h=16$. This estimate of the value of $\Lambda$ provides further evidence against the 2D model with $h=3$ and the 3D model. In the lower panel of Fig. 3 we show the distribution of spectral jumps at a later time, comparing experiment to the 2D model with $h=8$ (there are no further adjustable parameters), with satisfactory agreement. Although this model seems consistent with the available data, and we therefore put it forth as an explanation of the observed spectral diffusion, we of course cannot rule out other (as yet unspecified) mechanisms. We can say, however, that a model of coupling to one or two TLSs, as has been invoked to describe single molecule spectral diffusions in glasses [6], cannot be operative here, since the experimental trajectories show a very large number of possible frequencies.

In summary, we have shown that our simple theoretical model of a pentacene chromophore interacting with the central ring orientational degrees of freedom of many $p$-terphenyl host molecules can account for the observed spectral diffusion. In our model, the interactions are dipolar and the flipping of the phenyl rings occurs in a plane (presumably a wall between domains of different orientational order) that is about 8 lattice sites away from the chromophore. The two lowest quantum states of the asymmetric orientational potential are split by an energy on the order of a few degrees K, and the rate of flip-

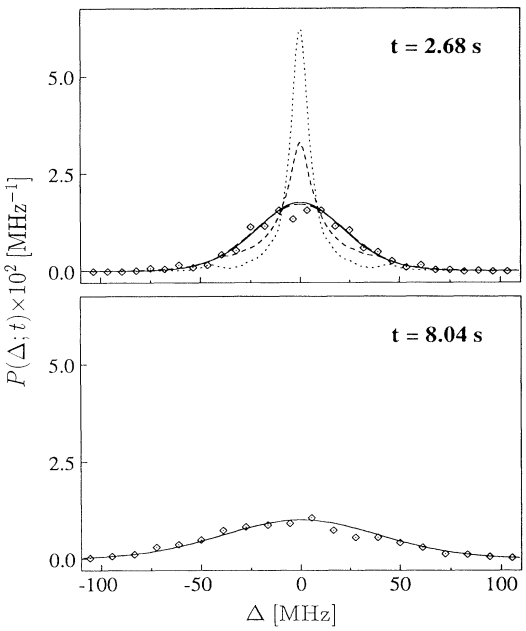


FIG. 3. Distribution of spectral jumps, $P(\Delta;t)$, as a function of jump distance, $\Delta$. The experimental results ($\diamond$) are calculated from the 1.5 trajectory (shown in Fig. 1) at two different times. For $t=2.68$ s the dotted line is the theoretical calculation for the 3D model. The remaining three lines are for the 2D model with $h=3$ (short dashed), $h=8$ (solid), and $h=16$ (long dashed). For $t=8.04$ s the solid line is the 2D model with $h=8$.

ping is very slow (on the order of $10^{-2}$ $s^{-1}$). The flipping mechanism appears to be one-phonon-assisted tunneling. This work shows that these remarkable single molecule spectral diffusion experiments, when coupled with a microscopic theoretical model, can provide detailed information about the nature of low-frequency excitations in disordered crystals.

The details of the theoretical analysis of the stochastic model as well as a full analysis of the experimental trajectories will be presented elsewhere [14]. Although our model was developed for an impurity molecule embedded in a crystalline host, it can be extended in a straightforward manner to allow for a dilute, spatially random distribution of TLS excitations. Therefore our model could be used to analyze single molecule spectral diffusion in noncrystalline hosts [6,17]. Information from these experiments should help in our understanding of the nature of localized low-frequency excitations in amorphous materials [18].

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[1] W. P. Ambrose, T. Basché, and W. E. Moerner, J. Chem. Phys. **95**, 7150 (1991).
[2] M. Orrit and J. Bernard, Phys. Rev. Lett. **65**, 2716 (1990).
[3] T. Basché and W. E. Moerner, Nature (London) **355**, 335 (1992).
[4] M. Orrit, J. Bernard, and A. Zumbrusch, Chem. Phys. Lett. **196**, 595 (1992).
[5] U. P. Wild, F. Guttler, M. Pirotta, and A. Renn, Chem. Phys. Lett. **193**, 451 (1992).
[6] A. Zumbrusch *et al.*, Phys. Rev. Lett. **70**, 3584 (1993).
[7] W. E. Moerner and T. Basché, Angew. Chemie. Int. Ed. Engl. **32**, 457 (1993).
[8] J. L. Baudour, Y. Delugeard, and H. Cailleau, Acta Crystallogr. B **32**, 150 (1976).
[9] J. L. Baudour, Acta Crystallogr. B **47**, 935 (1991).
[10] O. E. Polansky, Monatsch. Chem. **94**, 22 (1963).
[11] S. Ramdas and J. M. Thomas, J. Chem. Soc. Faraday II **72**, 1251 (1976).
[12] H. M. Reitveld, E. N. Maslen, and C. J. B. Clews, Acta Crystallogr. B **26**, 693 (1970).
[13] J.-L. Ong, D. Sloop, and T.-S. Lin, J. Phys. Chem. **96**, 4762 (1992).
[14] P. D. Reilly and J. L. Skinner (to be published).
[15] W. A. Phillips, in *Amorphous Solids and the Liquid State,* edited by N. H. March, R. A. Street, and M. Tosi (Plenum, New York, 1985).
[16] G. Davies, J. Phys. D **4**, 1340 (1971).
[17] P. Tchénio, A. B. Myers, and W. E. Moerner, J. Luminesc. (to be published).
[18] A. Heuer and R. Silbey, Phys. Rev. Lett. **70**, 3911 (1993).