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Lévy Statistics for Random Single-Molecule Line Shapes in a Glass

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We demonstrate that the statistical behavior of random line shapes of single tetra-tert-butylterrylene chromophores embedded in an amorphous polyisobutylene matrix at $T = 2$ K is described by Lévy statistics as predicted theoretically by Barkai, Silbey, and Zumofen [Phys. Rev. Lett. **84**, 5339 (2000)]. This behavior is a manifestation of the long-range interaction between two-level systems in the glass and the single molecule. A universal amplitude ratio is investigated, which shows that the standard tunneling model assumptions are compatible with the experimental data.

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Experimental advances [1] have made it possible to measure the fluorescence of a single molecule (SM) embedded in a glass. Because each individual molecule is in a unique static and dynamic environment, the fluorescence of chemically identical SMs varies from molecule to molecule. In this way the molecules serve as local reporters on the dynamics and statics of the host glass. SM experiments have been performed both in low-temperature glasses [2–6] and recently close to the glass transition temperature [7]. For low-temperature glasses the fundamental question is this: Is the standard tunneling model valid for glasses? Related questions are how to analyze the complex line shape behaviors of SMs in glasses, and what do their random behaviors teach us on the SM-glass system.

The standard tunneling model [8] was suggested in the early seventies to explain universal features of glasses; for example, many glasses show a heat capacity which is nearly linear in temperature. At the center of this phenomenological model is the concept of the two-level system (TLS). It is assumed that at cryogenic temperatures excitations in glassy materials are two-level tunneling systems whose energies and tunneling matrix elements are randomly distributed. More recently, Geva and Skinner [9] modeled behaviors of SMs in glasses based on the standard tunneling model. Orrit and coworkers [2,3] used the fluorescence of single terrylene molecules in the polymer polyethylene to obtain the first *direct* experimental proof that two-level systems actually exist in an amorphous material. More recent experiments [4] revealed behaviors not compatible with the standard model for 21 out of 70 molecules; e.g., a molecule coupled to a three-level system [10]. We note that a fundamental first-principle understanding of TLSs is still missing, although numerical simulations of Heuer and Silbey [11] give some evidence on the microscopic nature of a few of these entities, while Lubchenko and Wolynes [12] relate the TLSs to motions of domain walls in the glass.

There are many open questions concerning the standard model. For example, are the TLSs uniformly distributed in space, or do they preferentially appear at boundaries of clusters of atoms/molecules, as suggested in [13]? Another open question is the nature of the interaction between the TLSs and the SM; e.g., is it dipolar as suggested in [9]? A method to obtain this important information using SM spectroscopy was suggested in [14] (see details below).

A theoretical investigation of the distribution of random line shapes of SMs in glass was carried out in [14,15] based on the standard model approach [9]. Interestingly, the theoretical results obtained in [14] showed that the problem of random line shapes of SMs in glasses is related to Lévy statistics; thus, the generalized central limit theorem [16] applies to this problem. This connection to Lévy statistics is a manifestation of long-range interactions between the TLSs in the glass and the SM (see details below). We note that Lévy statistics is known to describe several other long-range interaction models in diverse fields such as turbulence [17] and random magnetic systems [18]. Stoneham's theory [19] of inhomogeneous line broadening in crystals with defects is based on long-range forces, and it can be interpreted in terms of Lévy statistics [15].

In this Letter we analyze the statistical properties of random line shapes in a glass and compare it to the theoretical predictions in [14]. In Fig. 1 we show eight lines of single tetra-tert-butylterrylene chromophores embedded in an amorphous polyisobutylene matrix at $T = 2$ K. For experimental details, see [20]. The lines are typically multipeaked similar to the numerical predictions in [9]. Each line is different from any other line, since each individual SM is in a unique environment. The multipeaked behavior of the line shapes in Fig. 1 can be qualitatively explained using standard model arguments. If a SM is coupled to a single slow flipping TLS embedded in its vicinity, we expect that when the TLS flips from its up state to its down state or vice versa, the SM absorption frequency will shift. In this case, the line shape of the SM is a doublet. It follows that the frequency of a SM coupled to N such independent two-level systems will

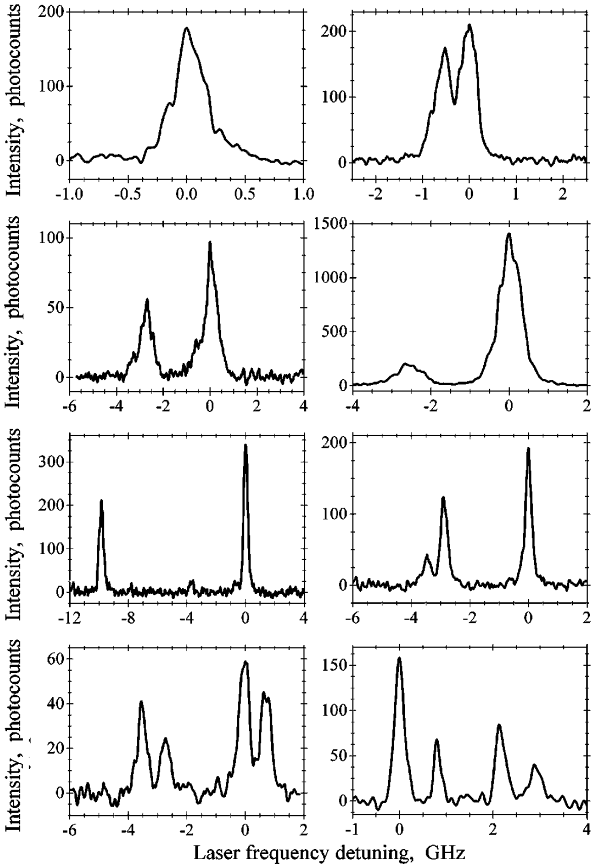

FIG. 1. Line shapes of single tetra-tert-butylterrylene chromophores embedded in an amorphous polyisobutylene matrix at $T = 2$ K. Note the doublet and quartet features of some of the line shapes due to strong coupling to one or two TLSs. One of the molecules has three peaks, indicating the possibility that this molecule is coupled to a three-level system. This *rare* type of behavior is not consistent with the standard tunneling model. Another possibility is that measurement time was not long enough in this case.

jump between 2^N states. Hence, as shown in Fig. 1, the single molecule's line shape will be composed of 2^N peaks. The width of these peaks depends on the dynamics of TLSs situated far from the molecule, fast dephasing processes, and the lifetime of the electronic transition [9,14,21,22].

To obtain the lines in Fig. 1, we used the spectral trail technique introduced by Moerner and co-workers [23], following the spectral activity of the molecule during a scan time which in our experiments was fixed to be 120 sec. Following the jump history of the SM enables us to identify the peaks in Fig. 1 as originating from a SM. Without using this method it is practically impossible to say if the lines in Fig. 1 are due to contributions from several SMs or originate from a SM.

Random multipeaked lines as shown in Fig. 1 are a novel feature of SM spectroscopy, not observed in ensemble averaging techniques. To obtain information on the SM-glass system, we investigate the distribution of the line shapes of SMs in a glass. Mathematically, we are dealing with the question of the distribution function of a function [i.e., the line $I(\omega_L)$ is a function of laser frequency]. Recently, Refs. [14,15] suggested to characterize the line shape of each molecule by its cumulants $\kappa_1, \kappa_2, \kappa_3, \ldots$. Thus, each line is characterized by an infinite set of cumulants, which are random variables that vary from one molecule to the other, thus reflecting the disordered nature of the glass. The distribution functions $P(\kappa_1), P(\kappa_2), P(\kappa_3), \ldots$ completely characterize the statistical properties of the line shapes of SMs in a glass. The cumulants are obtained from the moments of the line shape [24], $m_n = \int \omega_L^n I(\omega_L) d\omega_L$, according to the well-known relations $\kappa_1 = m_1$, $\kappa_2 = m_2 - (m_1)^2$, etc. From 244 SM spectra, we obtained the histograms of the first two cumulants, $P(\kappa_1), P(\kappa_2)$, which yield important information on the glass-SM system. We consider here the distribution of the cumulants and not the distribution of the moments, since the cumulants were predicted to be described by Lévy statistics [14].

To better understand the meaning of our data analysis and the relationship to Lévy statistics, it is useful to recall five main assumptions of the model used in [9,14]. (i) The absorption frequency of the SM follows a stochastic trajectory described by $\omega(t) = \omega_0 + \sum_{n=1}^{N} \xi_n(t)\nu_n(r)$, where ω_0 is the bare frequency of the molecule. $\xi_n(t)$ are random functions of time which follow a two-state process, $\xi_n(t) = 1$ when the nth TLS is in the up state or $\xi_n(t) = 0$ when it is in the down state. Thus, the flips of the TLSs induce spectral diffusion. The flipping rate between the up and down states is determined by a rate R which varies from TLS to TLS [the distribution of jumping rates of TLSs in a glass spans many orders of magnitude from nanoseconds to (at least) days]. (ii) The SM frequency shifts are $\nu_n = 2\pi\alpha\Psi(\Omega)(A/E)[1/(r_n)^3]$. The most important ingredient of the theory is the long-range interaction between the TLS and SM, $\nu \propto 1/r^3$, reflecting the assumption of dipolar interaction. This long-range type of interaction is the first important ingredient in the relationship between SM spectroscopy in glasses and Lévy statistics. Other parameters controlling the frequency shifts are α, the SM-TLS coupling constant; $E = \sqrt{A^2 + J^2}$, the energy splitting of the TLS; $\Psi(\Omega)$, a dimensionless function of order unity describing the orientation of the TLS and SM; and finally, the random parameters of the TLS: A (asymmetry parameter) and J (tunneling matrix element). (iii) The TLSs are uniformly distributed in space and are noninteracting. This assumption is the second important condition for Lévy statistics to be valid. (iv) The standard tunneling model is valid; this model determines the distribution of parameters describing ν_n and R_n as well as the density of TLSs. Note, however, that the Lévy statistics and results in [14] are not limited to this model. (v) The stochastic Kubo–Anderson theory of line shapes is applicable, implying weak laser fields. Under these conditions, the following two limiting behaviors were found [14].

The first case corresponds to the fast-modulation limit $\nu_n \ll R_n$ for all TLSs in the vicinity of the molecule. In this case, also called motional narrowing limit, the lines of individual molecules are Lorentzian in shape. Then the lines are characterized by two parameters only, e.g., the width at half maximum and the center location. The distributions of these two parameters are Lévy stable laws [14]. From Fig. 1 it is clear that the fast-modulation limit does not describe our experimental results.

The second case corresponds to the slow-modulation limit. If $R_n \ll \nu_n$ for all the TLSs in the vicinity of the molecule, the *shape* of the line is random and typically multipeaked [14]. In this slow-modulation limit the distributions of line shape cumulants, $P(\kappa_1)$, $P(\kappa_2)$, $P(\kappa_3)$, etc., are all Lévy stable. Specifically, the probability density function of the first cumulant κ_1 is given by the symmetrical Lévy density, $P(\kappa_1) = l_{1,0}(\kappa_1)$, namely, the Lorentzian

$$P(\kappa_1) = \frac{1}{\pi}\frac{z_1}{\kappa_1^2 + z_1^2}, \qquad (1)$$

where z_1 is a scaling parameter which can be calculated from the theory in [14]. In Fig. 2 we show that our experimental results are compatible with the theoretical prediction. We also fitted our results to a Gaussian probability density (not shown) and found that the distribution of the first cumulant is definitely not Gaussian.

We note that the reference frequency, determining the laser detuning in Fig. 1, was chosen on the maximum intensity of the spectrum of the SM $\omega_{\max}$, while the theoretical reference frequency in [14] was the bare frequency of the molecule ω_0. Using numerical simulation based on the approach in [9], we observed that also when the reference frequency is chosen as $\omega_{\max}$ distribution of first cumulant is well fitted by a Lorentzian, in agreement with the experimental results in Fig. 2. The value of z_1 in the two approaches slightly differs, as we discuss below. We now discuss the distribution of the second cumulant (i.e., the variance), which is not sensitive to definition of the reference frequency.

The distribution of the second cumulant κ_2 is given by the one-sided Lévy stable law, $P(\kappa_2) = l_{1/2,1}(\kappa_2)$, namely, Smirnov's one-sided probability density

$$P(\kappa_2) = \frac{1}{(z_{1/2})^2}\frac{2}{\sqrt{\pi}}\left(\frac{2\kappa_2}{z_{1/2}^2}\right)^{-3/2}\exp\left(-\frac{z_{1/2}^2}{2\kappa_2}\right), \qquad (2)$$

where the scaling parameter $z_{1/2}$ was derived in [14]. As shown in Fig. 3, the experimental data for the distribution of κ_2 are compatible with the theoretical prediction; the long tail of the Lévy stable law is visible. Yet, data of a larger number of molecules is needed to improve the statistical fluctuations. The analysis of a larger number of molecules will also enable us to compare theory and experiments for the higher-order cumulants κ_3, κ_4, etc.

As mentioned, the Lévy behavior is due to the long-range dipolar interaction of a SM with many TLSs, hence the Gauss or Lévy central limit theorem arguments are expected to hold. The Lévy central limit theorem applies since averaged frequency shifts diverge; $\langle \nu \rangle \propto \int_0^\infty r^{d-1}/r^3 dr = \infty$, where $d = 3$ is the dimensionality of the problem (for mathematical details, see [14]). Hence, the Lévy behavior obtained for the distributions $P(\kappa_1)$ and $P(\kappa_2)$ is used to test the assumptions of dipolar interactions and uniform-distribution of the TLSs in space. The information about the random distribution of the parameters of the glass, i.e., A and J, are contained in the values of $z_{1/2}$ and z_1, which we now discuss.

There are two distinct types of parameters describing the SM-glass system: those describing the bath of TLSs and the coupling constant α which depends on the properties of the SM probe. An important unsolved problem is how to extract information from SM experiments which is sensitive only to the statistical properties of the TLSs and is not affected by α [5]. The scaling parameters z_1 and $z_{1/2}$ depend on α; the magnitude of these two parameters depends also on the precise modeling of the

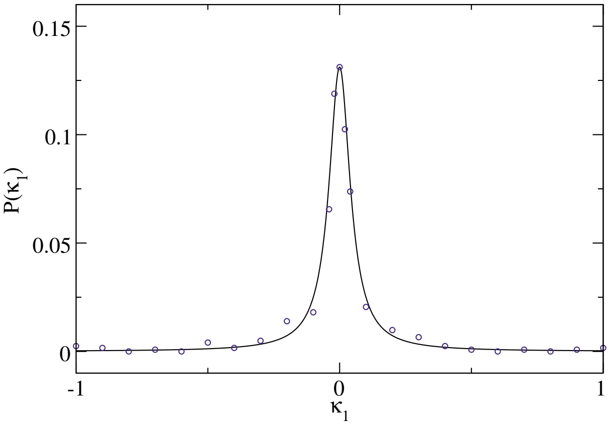

FIG. 2 (color online). Probability density of the first cumulant κ_1 (units are GHz). The dots are experimental results; the curve is a one-parameter fit to a Lorentzian.

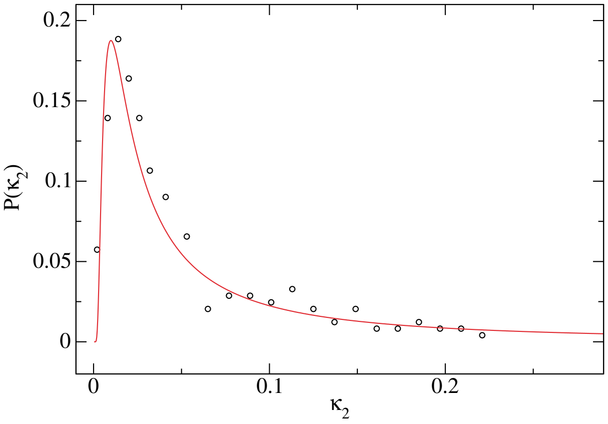

FIG. 3 (color online). Probability density of the second cumulant κ_2 (units GHz^2). The dots are experimental results; the curve is a one-parameter fit to Smirnov's probability density.

orientation function $\Psi(\Omega)$ [14]. Thus, z_1 and $z_{1/2}$ are not universal functions, in the sense that they depend on properties of the SM under investigation and not on the properties of the glassy state (which are supposed to be universal, according to the standard tunneling model). In fact, Donley *et al.* [5] suggested that the coupling constant α itself should be a random variable. This may seem to limit our ability to investigate low-temperature glasses with SM spectroscopy. If the statistical analysis of line shapes depends on an additional unknown distribution function of the coupling constant (besides the standard distributions of the glass parameters), fitting of data to the theory becomes rather arbitrary.

However, based on Eq. (9) in [14] one can show that the ratio $z_{1/2}/z_1$ depends only on the statistical properties of the glass and not on the distribution of the coupling constant α. More precisely,

$$\frac{z_{1/2}}{z_1} = \frac{1}{\sqrt{2\pi}} \frac{\langle \frac{A}{E} \operatorname{sech}(\frac{E}{2k_bT}) \rangle_{AJ}}{\langle \frac{A}{E} \frac{1}{1+\exp(E/k_bT)} \rangle_{AJ}}, \tag{3}$$

where the averaging is performed over the TLS parameters A and J [14]. Since Eq. (3) is independent of the exact distribution of α, it is a useful tool for describing the behavior of glasses. To derive Eq. (3) we assumed that the random variable α is independent of the glass parameters A and J.

From our fits we find $z_{1/2} = 0.175$ GHz and $z_1 = 0.0485$ GHz, which yields $z_{1/2}/z_1 = 3.6$. The theoretical prediction based on Eq. (3) yields $z_{1/2}/z_1 = 2.4$. The deviation between theory and experiment is now explained. As mentioned, the theoretical prediction is based on the assumption that the bare frequency of the molecule ω_0 is the reference frequency for measurement. Using numerical simulations [9] with the parameter set relevant for our experiment (details will be published), we find that the ratio of z_1 when ω_0 is the reference frequency and z_1 when $\omega_{\max}$ is the reference frequency is $z_1^{\omega_0}/z_1^{\omega_{\max}} = 1.6$. Varying the value of α in our simulations, in the interval $10\ \mathrm{GHz\,nm}^3 < \alpha < 40\ \mathrm{GHz\,nm}^3$ we observed that the ratio $z_1^{\omega_0}/z_1^{\omega_{\max}}$ does not depend on α. As expected, $z_1^{\omega_0} > z_1^{\omega_{\max}}$ since the value of κ_1 becomes smaller (in a statistical sense) if we assign the origin to the maximum of the spectrum. Using the correction factor $z_1^{\omega_0}/z_1^{\omega_{\max}} = 1.6$, we find that the theory yields $z_{1/2}/z_1 = 3.8$. Taking into account that the standard tunneling model does not address the chemical composition of the disordered system or the chemical and geometric details of the SM under investigation, we believe that the theoretical result is in surprisingly reasonable agreement with experiment. Measurements of the ratio $z_{1/2}/z_1$ for other types of SMs and glasses and for a wider range of control parameters (i.e., temperature and scan time) will show whether SM data are compatible with the universal predictions of the standard model.

To summarize, SM spectroscopy is an excellent method to investigate disordered systems by removing the ensemble averaging found in other techniques. We have shown that our experimental results are compatible with Lévy statistics and with standard tunneling model predictions. In particular, the following two assumptions are reasonable: (i) The two-level systems are uniformly distributed in space. (ii) The frequency shifts are caused by dipolar interactions $\nu \propto 1/r^3$. We introduced the universal ratio $z_{1/2}/z_1$, which is sensitive to details of the standard model, but not to the coupling of the SM to the TLSs in the glass (i.e., not to α). The comparison between the theoretical and the experimental value of this ratio can be used to test the validity of the standard model predictions.

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