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Experimental evidence for Lévy statistics in single-molecule spectroscopy in a low-temperature glass—manifestation of long-range interactions

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Abstract

We demonstrate that the statistical behavior of the random line shapes of single tetra-tert-butylterrylene chromophores embedded in an amorphous polyisobutylene matrix at $T = 2$ K is described by Lévy statistics. Recently, Barkai et al., suggested to characterize random line shapes of single molecules in glasses by their cumulants $\kappa_1, \kappa_2, \kappa_3$, etc. Using Geva–Skinner model for single-molecule spectroscopy in low-temperature glasses, which is based on the standard tunneling model, the theory predicts that probability densities $P(\kappa_1)$, $P(\kappa_2)$, etc., are Lévy stable laws provided that the glass dynamics is described by a slow modulation limit. Analyzing our experimental data we show that the distributions of the first two cumulants are indeed compatible with Lévy statistics; thus, the generalized central limit theorem is applicable to this system. The emergence of Lévy stable laws in this system is due to long-range interactions between two-level systems and the single molecule. The widths of the distribution functions $P(\kappa_1)$ and $P(\kappa_2)$ are non-universal in the sense that they depend on the coupling of the molecule to the host glass. We investigate a universal amplitude ratio (i.e., ratio of widths) which shows that our results are in agreement with the assumptions of the standard tunneling model of low-temperature glasses. We briefly discuss other long-range interacting systems and models, for which Lévy statistics plays an important role.

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1. Introduction: single-molecule spectroscopy in glasses

Experimental advances [1–4] have made it possible, to measure the fluorescence of a single

molecule (SM) embedded in polymer glasses. Because each individual molecule is located 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. The problem of ensemble averaging, found in usual

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condensed-phase spectroscopy and in other macroscopic measurements, is totally removed (e.g. Ref. [5] and references therein). SM experiments are performed both on low-temperature glasses [6–15], and recently close to the glass transition temperature [16,17]. For low-temperature glasses, the fundamental question is: is the standard tunneling model for glasses valid? Related questions are how to analyze the complex line shape behaviors of SMs in glasses, and what their random behaviors teach us on the SM–glass system.

The phenomenological standard tunneling model [18,19] was suggested in the early 1970s 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 model is the concept of the two-level system (TLS). It is assumed that at temperatures below 2–3 K, low-energy excitations of glassy materials are two-level tunneling systems whose asymmetries and tunneling matrix elements are randomly distributed. To a first approximation, it is assumed that these TLSs are interacting with phonons but not with each other [20]. The main ansatz is that the complicated free-energy landscape of the glass can be replaced by independent double-well potentials. A fundamental first-principle understanding of the TLSs is still missing, although numerical simulations [21] give some evidence on the microscopic nature of a few of these entities while Ref. [22] relates the TLSs to motions of domain walls in the glass.

Geva and Skinner [23] modeled the behaviors of SMs in a low-temperature glass, based on the standard tunneling model. Their numerical work predicted correctly that the line shape of a single molecule in a low-temperature glass: (i) varies from molecule to molecule and (ii) is typically multi-peaked (see examples below). A theoretical investigation of the distribution of random line shapes of SMs in glass was carried out in Refs. [24,25]. Interestingly, the theoretical results obtained in Ref. [24] showed that the problem of random line shapes in glasses is related to Lévy statistics; thus the generalized central limit theorem [26] applies to this problem (see details below). As we discuss in Section 5, several other long-range interacting systems and models are described

by Lévy statistics. Thus the relation between Lévy statistics and long-range forces is not limited to the system under investigation. The specific goal of this paper is to analyze experimental data of random SM line shapes and to compare it with the theory in Refs. [24,25]. We also investigate a certain universal amplitude ratio, which can be used to test the assumptions of the standard tunneling model. A brief summary of part of our results appeared in Ref. [27].

Previously, Orrit et al. used the fluorescence of single terrylene molecules in the polymer polyethylene, and gave the first *direct* experimental proof that TLSs actually exist in a disordered solid [6,7]. If an SM is coupled to a single TLS, we expect that when the TLS flips from its up state to its down state or vice versa, the SM absorption frequency will shift. Briefly, the SM's absorption frequency jumps at random times between two states ω_+ and ω_- . In this case the line shape of the molecule is a doublet. In Fig. 1 we show the behavior of such a molecule based on a simple simulation [28]. It follows that the frequency of an

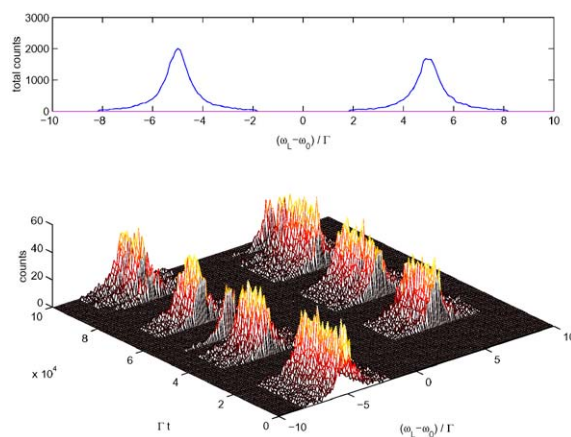


Fig. 1. The spectral trail (lower panel) and the line shape (upper panel) of a model SM coupled to a slowly flipping single TLS. The three-dimensional plot shows the photon count number versus time and laser detuning frequency. Each flip of the TLS results in a shift of the absorption frequency. The upper panel yields the line shape of the molecule which is the total count number versus laser detuning frequency $\omega_L - \omega_0$. Γ is the radiative rate, ω_L is the laser frequency, and ω_0 is the bare absorption frequency of the molecule. For further details see Ref. [29].

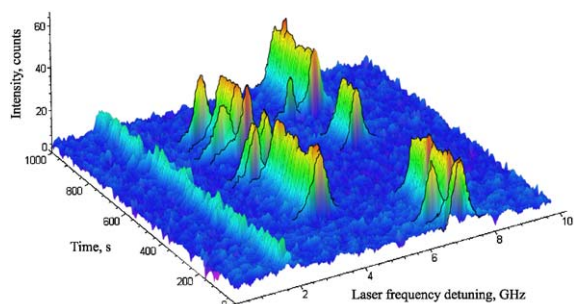


Fig. 2. The spectral trail of a single tetra-tert-butylterrylene chromophore embedded in an amorphous polyisobutylene matrix, at $T = 2$ K. This individual molecule is strongly coupled to two slowly flipping TLSs. The straight and weak spectral line on the left is the spectral line of a second molecule which does not show spectral activity on the time scale of the experiment.

SM coupled to N slowly flipping¹ independent TLSs will jump between 2^N states. For example, in Fig. 2 we show a spectral trail of a single tetra-tert-butylterrylene chromophore embedded in an amorphous polyisobutylene matrix. This SM is coupled strongly to two TLSs, hence the absorption frequency jumps between four states. At the same time the molecule is also coupled to distant TLSs which control the line broadening of each peak. Under certain conditions [28–30] (see footnote 1) the frequency jumps, known as spectral diffusion, can be observed in experiment. In the experiments of Orrit's group [8], behaviors not compatible with the standard tunneling model were observed, for 21 out of 70 molecules; e.g., a molecule coupled to a three-level system or molecules coupled to *interacting* TLSs. In our experiments, the relative number of spectral trails, which are not consistent with the standard TLS model, was a few percent. Thus majority of individual molecules exhibit behaviors which confirm the standard model predictions. We note that spectral jumps are observed in many other

SM fluorescence experiments and are not limited to glasses [31,32].

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 Ref. [33]. Another open question is the nature of the interaction between the TLSs and the SM, is it dipolar as suggested in Ref. [23,67]. Here we investigate these topics, based on a method suggested in Refs. [24,25].

This paper is organized as follows: In Section 2 random line shapes for SMs in a glass are presented, and the method of the data analysis is presented. In Section 3 we give a detailed description of the physical assumptions used to describe the low-temperature glass, emphasizing the assumptions that lead to emergence of Lévy stable law. In Section 4 we compare our experimental result with theory and investigate the new universal amplitude ratio. In Section 5 Lévy statistics in other long-range interacting systems is presented, mostly for cases where this relation was overlooked.

2. Random line shapes and their cumulants

To a first approximation, we note that the line shape of an SM *not interacting with the TLSs in the glass* is Lorentzian. The width of this line would be determined by the lifetime of the electronic transition under investigation. This situation is radically changed when the molecule interacts with its environment. As mentioned, the line shape of an SM in a low-temperature glass is usually multi-peaked and looks random and complex. This is due to the coupling of the SM to the random distribution of active TLSs in the glass. Measured line shapes (i.e., fluorescence excitation signals) are shown in Fig. 3. The figure illustrates that line shapes of individual single molecules differ from one another, i.e., the lines do not self-average. The doublet and quartet features of some of the line shapes in Fig. 3 are due to strong coupling to one or two TLSs. Such lines yield direct evidence for the existence of TLSs in glasses in a way similar to

¹More precisely, if $1/\tau < R < \Gamma < \nu$, where τ is the measurement time, R is the frequency jump rate, Γ the fluorescence rate, and ν is the frequency shift due to a flipping TLS, one can use the spectral-trail technique to follow directly the dynamics of a TLS. If these conditions do not hold, a more detailed analysis of photon counting statistics can in principle yield the dynamics of the TLS [29].

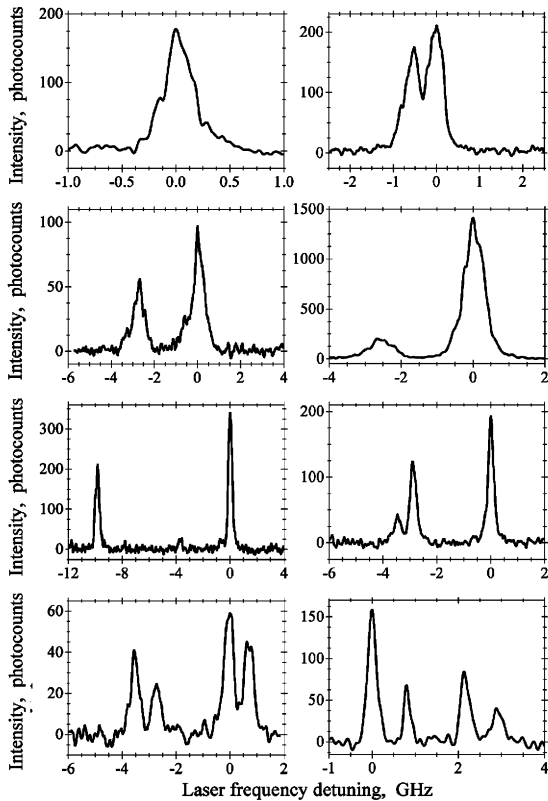


Fig. 3. Line shapes of single tetra-tert-butylterrylene chromophores embedded in an amorphous polyisobutylene matrix. Note the doublet and quartet features of some of the line shapes due to strong coupling to one or two TLSs. One of the molecules has three peaks, indicating the possibly that this molecule is coupled to a three-level system. This *rare* type of behavior is not consistent with the standard tunneling model. Another possibility is that the measurement time was not long enough in this case and that in a longer measurement the molecule would be seen jumping between four states. Note that the analysis of the spectral trail histories allows us to distinguish between these possibilities. Following this line, we note that due to the non-ergodicity of the glass, increasing the measurement time might reveal different line shapes; thus the statistical properties of the line shapes in a glass generally depend on the time scale of the measurement.

the observations made in Ref. [8]. Geva and Skinner [23] have numerically generated line shapes of single molecules in glasses, predicting line shapes which are multi-peaked and random, similar to what we observe in Fig. 3.

To obtain the lines in Fig. 3 we used the spectral trail technique introduced by Moerner and

co-workers [34] (see examples in Figs. 1 and 2). Following the spectral activity of the molecule during a fixed scan time, which was 120 s, enables us to identify the peaks in Fig. 3 as originating from an SM. Without using this approach it is difficult to say if the lines in Fig. 3 are due to contributions from several SMs or originate from one SM.

Random multi-peaked lines as shown in Fig. 3 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 of a function [i.e., the line $I(\omega_L)$ is a function of the laser frequency]. Recently, Barkai et al. [24,25] suggested to characterize the line shape of each molecule by its cumulants $\kappa_1, \kappa_2, \dots$. Thus each line is characterized by an infinite set of cumulants, these being random variables which vary from one molecule to the other, thus reflecting the disordered nature of the glass. The distributions of $P(\kappa_1)$, $P(\kappa_2)$, etc. completely characterize the statistical properties of the line shapes of SMs in a glass. As we show below, these distribution functions yield important information on the SM–glass system and can be used to check the validity of the standard model.

The cumulants are obtained from the moments² of the normalized line shape,

$$m_n = \int_0^\infty \omega^n I(\omega) d\omega, \quad (1)$$

according to the well-known relations

$$\kappa_1 = m_1, \quad \kappa_2 = m_2 - (m_1)^2 \quad (2)$$

and higher order cumulants are given in Ref. [35]. The normalization condition we use is $m_0 = 1$. We consider here the cumulants, not the moments, since the cumulants are predicted to be distributed according to Lévy statistics, which, as we show below, yields useful information on the glass.

²We assume here that moments of the line shape are finite. Since the spectral-trail technique is limited to a certain frequency interval, moments are finite, in principle they may be sensitive to the frequency interval scanned in the experiment. See Ref. [24].

Experimental data on line shape moments were previously presented in Refs. [36,37].

The approach we use here is based on the analysis of the distribution of line shape cumulants; it is different from a second approach used in other studies [7,13,23]. Previously, the line was characterized by its width at half-maximum, and the distribution of the random line shapes was described by the distribution of line widths. Clearly such a method does not capture the multi-peaked behavior of the SM lines shown in Fig. 3.³ For line shapes of SMs in glasses, the width at half-maximum is in many cases not uniquely defined, as can be easily seen from Fig. 3.

3. Lévy statistics due to long-range TLS–SM interaction

To better understand the meaning of our data analysis and its relationship to Lévy statistics, it is useful to recall the main assumptions of the theory [23–25] (see Appendix A for more details):

(i) The absorption frequency of the molecule follows a stochastic trajectory described by

$$\omega(t) = \omega_0 + \sum_{n=1}^N \xi_n(t) v_n(r), \quad (3)$$

where ω_0 is the bare frequency of the molecule. $\xi_n(t)$ are random functions of time which follow a two-state process, $\xi_n(t) = 1$ or $\xi_n(t) = 0$ depending on the state of the n th TLS. The flipping rate between these two states is determined by R_n given in Appendix A, Eq. (A.2).

(ii) The SM frequency shifts are

$$v_n = 2\pi\alpha\Psi(\Omega)f(A, J)\frac{1}{(r_n)^\delta}, \quad (4)$$

where α is a coupling constant. $\Psi(\Omega)$ is a dimensionless function of order unity, Ω is the

vector of angles determined by the orientation of the TLS and SM, $f(A, J)$ is a dimensionless function of the random internal degrees of freedom of the TLS, A (asymmetry parameter) and J (tunneling matrix element), and δ is the interaction exponent. For dipolar interactions $\delta = 3$, hence the standard approach is [23]

$$v_n = 2\pi\alpha\Psi(\Omega)\frac{A}{E}\frac{1}{(r_n)^3}, \quad (5)$$

where $E = \sqrt{A^2 + J^2}$ is the energy splitting of the TLS. As we discuss below, the long-range type of interaction is an important ingredient in the relationship between SM spectroscopy in glasses and Lévy statistics.

(iii) The TLSs are uniformly distributed in space and are non-interacting. This is the second important condition for Lévy statistics to be valid.

(iv) The standard tunneling model is valid; this model determines the distribution of the parameters describing v_n and R_n as well as the density of TLSs (see Appendix A for details). Note, however, that Lévy statistics and results in Ref. [24] are not limited to this model.

(v) The stochastic Kubo–Anderson theory [38,39] of line shapes is valid, implying, among other things, weak laser fields. We also neglect time-dependent fluctuations in the number of photon counts from individual molecules [28–30,40]. Under these conditions the following two limiting behaviors were found.

The first case corresponds to the slow-modulation limit. Then if $R_n \ll v_n$ for TLSs in the vicinity of the molecule, the *shape* of the line is random and typically multi-peaked [24]. For 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 , Eqs. (2) and (5), is given by the symmetrical Lévy density, $P(\kappa_1) = l_{\gamma_1,0}(\kappa_1)$ where the Lévy exponent is

$$\gamma_1 = \frac{d}{\delta}, \quad (6)$$

provided that $0 < \gamma_1 < 2$. Here d is the dimensionality of the problem. The distribution of the second cumulant κ_2 , Eq. (A.6), is given by the

³In the early days of SM spectroscopy, it was difficult to determine if a multi-peaked line shape is the line shape of an SM, or the line shape of several molecules, each one being single-peaked. Thus, in some of the early experiments, multi-peaked line shapes were rejected from statistical analysis and only single-peaked lines (which were fitted to a Lorentzian) were considered.

one-sided Lévy stable law, $P(\kappa_2) = l_{\gamma_2,1}(\kappa_2)$,

$$\gamma_2 = \frac{d}{2\delta}, \quad (7)$$

provided that $0 < \gamma_2 < 1$. Details on higher-order cumulants are given in Ref. [24]. From Eqs. (6) and (7) we see that the Lévy exponents depend only on the dimensionality of the problem and on the exponent δ describing the power law interaction between the TLSs and the SM. The distribution of parameters describing the TLSs in the glass control the width of $P(\kappa_2)$, $P(\kappa_1)$, as will be discussed below. We note that numerical simulations [24,41], for a parameter set modeling terrylene in polystyrene, indicate that the slow-modulation limit is valid at least for $T = 1$ K.

The second case corresponds to the fast-modulation limit $v_n \ll R_n$ for all TLSs in the vicinity of the molecule. In this limit, 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 the latter two parameters are Lévy stable laws [24]. From Fig. 3 it is clear that the fast modulation limit does not describe our experimental results (i.e., the lines are not simple Lorentzians).

Let us briefly discuss the importance of Lévy stable distributions, which are generalizations of the Gaussian distribution [26]. Consider the sum of independent identically distributed random variables, $X = \sum_{i=1}^N x_i$. According to the Gaussian central limit theorem, the distribution of $X/N^{1/2}$, in the limit $N \rightarrow \infty$, is Gaussian, provided that the variance of x_i is finite. Lévy and Khintchine have generalized the central limit theorem to the case when the variance of x_i is infinite, i.e., when the probability density of x_i falls off as a slow power law. In this case the sum X , when scaled properly, converges to a distribution which is called Lévy stable distribution (see examples below). The importance of Lévy statistics in modeling physical and chemical systems is discussed in Refs. [42–46] and references therein.

The relationship between Lévy statistics and the SM–glass system can be rationalized as follows (for mathematical details see Ref. [24]).

(i) The SM is interacting with an infinite number of TLSs, hence $N \rightarrow \infty$.

(ii) The TLSs are non-interacting corresponding to the summation of independent random variables.

(iii) Since $v \propto 1/r^\delta$ and since the distribution of TLSs is uniform in space, large fluctuations of the frequency shifts occur. For $\delta = 3$ and $d = 3$, TLSs in the vicinity of the SM will cause large frequency shifts, while those in the background will cause small shifts. The large frequency shifts result in a diverging variance $\omega(t)$, which leads to the breakdown of the Gaussian central limit theorem in this problem and to the emergence of Lévy stable laws. While the theory is generally valid even when δ is large, Lévy statistics of this type may be observed only for systems with long-range interactions, for example, dipolar or Coulomb interactions. As δ becomes large, Lévy statistics becomes sensitive to finite-size corrections e.g., if the molecule has a typical size of a few nanometers [25,47].

4. Experiment versus theory

4.1. Lévy statistics

We have analyzed 244 single tetra-tert-butylterylene molecules in the amorphous polymer polyisobutylene at $T = 2$ K. The scan time for each individual molecule was 120 s. Using the spectral trail technique, we obtained line shapes of SM as shown in Fig. 3. The moments of the line shape are obtained using Eq. (1), from which we obtain the corresponding cumulants according to Eq. (2). As mentioned, we discuss the cumulants rather than the moments, since the cumulants are predicted to behave according to Lévy stable laws. For a detailed description of the experimental setup and the measurement procedure see Ref. [48].

Assuming $\delta = 3$ and $d = 3$, $P(\kappa_1)$ is a Lorentzian according to Eq. (6),

$$P(\kappa_1) = \frac{1}{\pi} \frac{z_1}{\kappa_1^2 + z_1^2}, \quad (8)$$

where z_1 is a scaling parameter which can be calculated based on the theory in Ref. [24]. As is well known, the Lorentzian density belongs to the

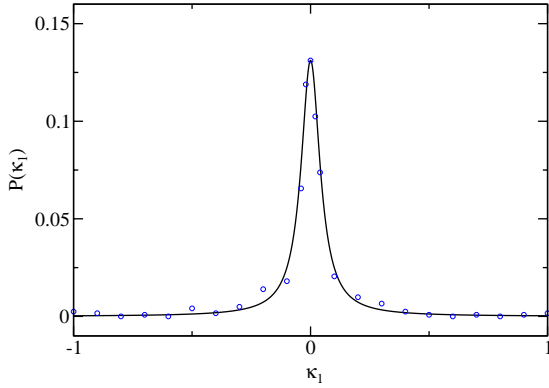


Fig. 4. Probability density of the first cumulant κ_1 (in GHz). The dots are experimental results and the curve is a one-parameter fit to a Lorentzian.

more general family of Lévy stable probability densities [26]. In Fig. 4 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 concluded that the distribution of the first cumulant is definitely not Gaussian.

We note that the reference frequency, determining the laser detuning in Fig. 3, was chosen at the maximum intensity of the spectrum of the SM (ω_{\max}), whereas the theoretical reference frequency in Ref. [24] was the bare frequency of the molecule ω_0 . As shown in Fig. 5, using numerical simulations based on the approach in Ref. [23] (with parameters given in Table 1) we observe that also when the reference frequency is chosen as ω_{\max} , the distribution of first cumulant is well fitted by a Lorentzian. These numerical results are in agreement with the experimental results in Fig. 4. From Fig. 5 we see that the value of z_1 in the two approaches differs, we address this issue in further detail below.

Note that in our simulations we included a minimum distance between the SM and TLS r_{\min} . We also used a uniform distribution of coupling constants α . These features are not included in the theory developed in Ref. [24]. The simulations are compatible with a Lévy distribution for $P(\kappa_1)$, thus a main conclusion in Ref. [24] is not changed when these additional details are included in the model.

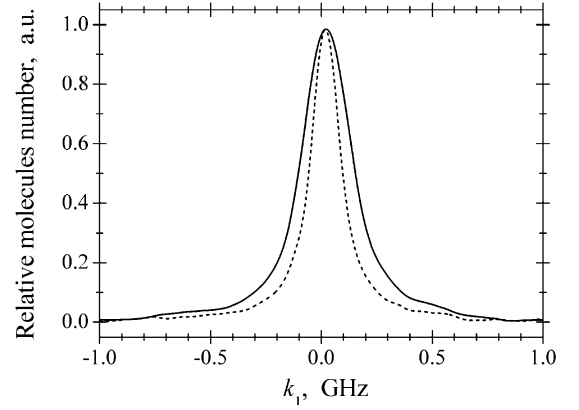


Fig. 5. Histograms of the first cumulant as obtained from numerical simulations of the Geva-Skinner model for two different values of the reference frequency. The solid (dashed) line represents the case where the reference frequency of each line is ω_0 (ω_{\max}). The figure illustrates that: (i) The shape of distribution function $P(\kappa_1)$ is not sensitive to the definition of the reference frequency, and (ii) the width of $P(\kappa_1)$ (i.e., z_1) depends on the choice of reference frequency.

Table 1

	Description	Value
T	Temperature	2 K
A_{\max}	Maximal asymmetry	20 K
J_{\min}	Minimal tunneling element	2.5×10^{-7} K
J_{\max}	Maximal tunneling element	20 K
r_{\max}	Maximal radial distance	35 nm
r_{\min}	Minimal radial distance	2 nm
ρ	TLS density	$1.15 \times 10^{-2} \text{ nm}^{-3}$
$\bar{\alpha}$	Average SM-TLS coupling	$27.5 \text{ nm}^3 \text{ GHz}$
$\Delta\alpha$	Standard deviation of α	$18 \text{ nm}^3 \text{ GHz}$
ck^3	TLS-phonon coupling	$1.16 \times 10^9 \text{ K}^{-3} \text{ Hz}$
T_1	Lifetime of transition	2.8 ns

We now discuss the distribution of the second cumulant (i.e., the variance) which is independent of definition of the reference frequency. According to Eq. (7), and assuming $d = \delta = 3$, Smirnov's one-sided probability density is

$$P(\kappa_2) = \frac{1}{(z_{1/2})^2} \frac{2}{\sqrt{\pi}} \left(\frac{2\kappa_2}{z_{1/2}^2} \right)^{-3/2} \exp\left(-\frac{z_{1/2}^2}{2\kappa_2}\right), \quad (9)$$

where the scaling parameter $z_{1/2}$ was derived in Ref. [24]. As shown in Fig. 6, the experimental data are compatible with the theoretical

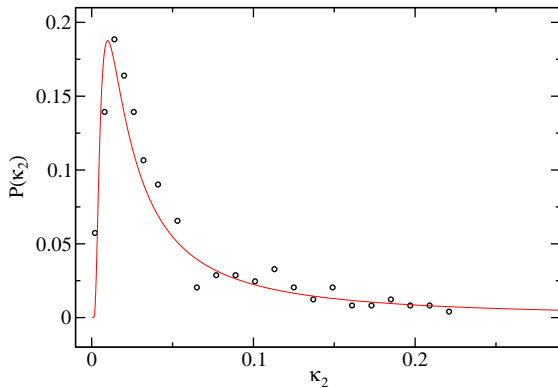


Fig. 6. Probability density of the second cumulant κ_2 (in GHz^2). The dots are experimental results and the curve is a one-parameter fit to Smirnov's probability density ($z_{1/2}$ is the fitting parameter). The bin length was 0.012 GHz.

prediction; the long tail of the Lévy stable law is visible. However, the measurement 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 experiment for the higher-order cumulants κ_3 , κ_4 , etc.

The physical meaning of the distributions $P(\kappa_1)$ and $P(\kappa_2)$ is now discussed. $P(\kappa_1)$ is a measure for the asymmetry of the lines. For symmetric lines, e.g. Lorentzian or Gaussian, $\kappa_1 = 0$ (i.e., when reference frequency is the maximum of intensity). Thus Lévy distribution of κ_1 indicates the strong asymmetry of the lines. κ_2 is a measure of the frequency spread of each line. Hence the fact that we find Lévy distribution of κ_2 indicated a very broad distribution of the spread of individual lines (i.e., the average of κ_2 is infinite).

4.2. Universal amplitude ratio

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 [see Eq. (5)]. 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 [10,12,13]. The scaling parameters z_1 and $z_{1/2}$ depend on α and the

magnitude of these two parameters depends also on the precise modeling of the orientation function $\Psi(\Omega)$. Thus z_1 and $z_{1/2}$ are not universal functions, in the sense that they depend on the 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. suggested that the coupling constant α itself should be a random variable [13] (and see [37] for related work). At first this may seem to limit our ability to investigate low-temperature glasses with SM spectroscopy. If statistical analysis of line shapes depends on an additional unknown distribution function of coupling constants (besides the standard distributions of glass parameters) comparing data and theory becomes rather arbitrary.

However, based on Eq. (9) in Ref. [24] and using Eq. (5), 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,

$$\frac{z_{1/2}}{z_1} = \frac{1}{\sqrt{2\pi}} \frac{\langle \frac{A}{E} \text{Sech}(\frac{E}{2k_b T}) \rangle_{AJ}}{\langle \frac{A}{E} \frac{1}{1+\exp(E/k_b T)} \rangle_{AJ}}, \quad (10)$$

where the averaging is performed over the random matrix elements of the TLSs in the glass. Since only TLSs flipping on the time scale of the experiment contribute to the line shape of the SM, the average in Eq. (10) depends also on the measurement time [24]. Since Eq. (10) is independent of the exact distribution of α , it is a useful tool for describing the behavior of glasses. To derive Eq. (10), we assume that: (i) the mean value of the coupling constant α is finite, (ii) $\delta = d = 3$ (generalizations for other cases are straightforward), and (iii) the distribution of α is independent of other TLS parameters A and J . Note that Eq. (10) does not depend explicitly on the density of TLSs.

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. (10), yields $z_{1/2}/z_1 = 2.4$. The deviation between theory and experiment is now addressed. As mentioned above the theoretical prediction is based on the assumption that the bare frequency of the molecule ω_0 is the reference frequency for the measurement.

Using numerical simulations based on the procedure developed in Ref. [23] with the parameter set relevant for our experiment we find that the ratio of z_1 when ω_0 is the reference frequency and z_1 when ω_{\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 $10 \text{ GHz nm}^3 < \alpha < 40 \text{ GHz nm}^3$ 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 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 the experiment. Measurements of the ratio $z_{1/2}/z_1$ for other types of SMs and glasses and for a wider range of parameters (i.e., temperature and scan time) will show whether SM data are compatible with the universal predictions of the standard model.

5. Lévy statistics in other long-range interacting systems

The relationship between Lévy stable laws and long-range interacting systems is not limited to SM spectroscopy in glasses. It is found in other systems and models, but in many cases this relation was over-looked. One example is the well-known Klauder and Anderson [49] approach for the description of spin echoes. Briefly, Klauder and Anderson [49] consider spin A interacting with spin B which are situated on a lattice (i.e., an *ordered* dynamical spin system). The interaction between spin A and spin B is dipolar, where a flip of spin B causes a spectral jump for spin A (the dynamics of spin A is the observable). Klauder and Anderson found a Lorentzian Green function for spectral diffusion of the individual spin A. The work of Zumofen and Klafter [50] showed that for other power law interactions, one gets a Lévy Green function for the spectral diffusion. Hence the Klauder–Anderson result is a manifestation of

Lévy stable laws [25]. Interestingly, Kharlamov and Zumofen [51] have recently reported on Lévy-type spectral diffusion in hole-burning experiments in glasses.

Stoneham's [52] inhomogeneous line shape theory, describing ensemble-averaged line shapes in a static *disordered* medium, is based on long-range interacting models. It can be shown to be described by Lévy statistics, namely, the ensemble-averaged inhomogeneous spectra found by Stoneham are all Lévy stable laws [25]. An example for a Lévy inhomogeneous line is the Holtsmark function, which was recently observed in anomalous line shapes of a localized vibrational mode in InP [53].

SM spectroscopy in glasses, considered here, combines both dynamical and spatial disorder and in this way is different from the models considered previously [49,52]. Finally, we note that Lévy statistics has also applications in other long-range interacting models [54], including gravitational systems [55,56], plasma models [57], hydrodynamic systems [58,59], and spin precession in models of disordered magnetic fields [60].

6. Summary

SM spectroscopy is an excellent method to probe 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 the theory developed in Ref. [24]. This implies that the following assumptions are reasonable: (i) The TLSs are uniformly distributed in space, (ii) the frequency shifts are caused by dipolar interactions $\nu \propto 1/r^3$. The fact that we find Lorentzian and Smirnov densities, for $P(\kappa_1)$ and $P(\kappa_2)$, respectively, is related to the dimension of the system $d = 3$ and the exponent $\delta = 3$ in the distance dependence of the interaction potential. We introduced the 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 experimental value of this ratio can be used to test the validity of the standard model predictions.

The relationship between long-range interacting systems and Lévy statistics is far reaching and not limited to the system under investigation. Furthermore, the relationship between Lévy statistics and SM spectroscopy is not limited to SMs in low-temperature glasses. Very recently, Jung et al. [61] clarified the connections between Lévy statistics and the blinking behavior of single quantum dots [62–65].

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Appendix A

Following Ref. [23], we assume an SM to be coupled to independent nonidentical TLSs at distance \mathbf{r} in three-dimensional space. Each TLS is characterized by its asymmetry A and tunneling matrix element J . The density of the TLSs is ρ . The energy splitting of the TLS is $E = \sqrt{A^2 + J^2}$. The probability of finding a TLS in its upper energy state is given by

$$p = \frac{1}{1 + \exp[E/(k_b T)]}. \quad (\text{A.1})$$

The transitions between the two states are described by the transition rates R_u and R_d related to each other by detailed balance and $R = R_u + R_d$. The coupling of the TLSs to phonons yields, for single-phonon excitation,

$$R = cJ^2 E \coth[E/(2k_b T)], \quad (\text{A.2})$$

where c is the TLS–phonon coupling constant. According to the standard tunneling model, the distributions of A and J are $P(J)P(A) = N^{-1}A^\mu J^{-1}$ and $J_{\min} < J < J_{\max}$ and $A_{\min} < A < A_{\max}$, where N is a normalization constant and the values $\mu = 0$ or $\frac{1}{3}$ are considered in the literature. We note that our results in this paper are not very sensitive to the choice $\mu = \frac{1}{3}$ or 0. The exponent μ is related to the exponent describing the heat capacity of the glass, $C(T) \propto T^{1+\mu}$.

According to linear-response theory, the line shape of the SM is given by the complex Laplace transform of a relaxation function

$$I_{\text{SM}}(\omega) = \frac{1}{\pi} \text{Re} \left[\int_0^\infty dt e^{i\omega t} \prod_{n=1}^{N_{\text{act}}} \Phi_n(t) \right], \quad (\text{A.3})$$

provided that the natural lifetime of the SM excited state is sufficiently long. N_{act} are the TLS which are flipping on the time scale τ of the experiment, i.e., $1/R < \tau$. The subscript n in Eq. (A.3) denotes the n th TLS in the system. The relaxation function of a single TLS was evaluated in Ref. [66] based on methods developed in Ref. [38],

$$\Phi(t) = e^{-(\Xi + ipv)t} \left[\cosh(Bt) + \frac{\Xi}{B} \sinh(Bt) \right], \quad (\text{A.4})$$

with $B = [R^2/4 - v^2/4 - i(p - 1/2)vR]^{1/2}$, $\Xi = R/2 - i(p - \frac{1}{2})v$. The line shape given in Eq. (A.3) is clearly a random function of the random variables describing the glass. Its first two cumulants

$$\kappa_1 = \omega_0 + \sum_n p_n v_n \quad (\text{A.5})$$

and

$$\kappa_2 = \sum_n p_n (1 - p_n) v_n^2 \quad (\text{A.6})$$

are random variables. Using Eqs. (5), (A.1) and (A.5),

$$\begin{aligned} \kappa_1 = \omega_0 + 2\pi \sum_n \alpha_n \Psi(\Omega_n) \frac{A_n}{E_n} \frac{1}{(r_n)^3} \\ \times \frac{1}{1 + \exp[E_n/(k_b T)]}. \end{aligned} \quad (\text{A.7})$$

References

- [1] W.E. Moerner, L. Kador, Phys. Rev. Lett. 62 (1989) 2535.
- [2] W.E. Moerner, M. Orrit, Science 283 (1999) 1670.
- [3] P. Tamarat, A. Maali, B. Lounis, M. Orrit, J. Phys. Chem. A 104 (2000) 1.
- [4] W.E. Moerner, J. Phys. Chem. B 106 (2002) 910.
- [5] Y. Jung, E. Barkai, R.J. Silbey, J. Chem. Phys. 117 (2002) 1.
- [6] A. Zumbusch, L. Fleury, R. Brown, J. Bernard, M. Orrit, Phys. Rev. Lett. 70 (1993) 3584.
- [7] L. Fleury, A. Zumbusch, M. Orrit, R. Brown, J. Bernard, J. Lumin. 56 (1993) 15.

- [8] A.M. Boiron, P. Tamarat, B. Lounis, R. Brown, M. Orrit, *Chem. Phys.* 247 (1999) 119.
- [9] J. Tittel, et al., *J. Lumin.* 64 (1995) 1.
- [10] Yu.G. Vainer, T.V. Plakhotnik, R.I. Personov, *Chem. Phys.* 209 (1996) 101.
- [11] L. Kador, *J. Phys. Chem.* 102 (1998) 9745.
- [12] S.J. Zilker, et al., *J. Chem. Phys.* 109 (1998) 6780.
- [13] E.A. Donley, H. Bach, U.P. Wild, T. Plakhotnik, *J. Phys. Chem. A* 103 (1999) 2282.
- [14] E.A. Donley, T. Plakhotnik, *J. Chem. Phys.* 114 (2001) 9993.
- [15] E.A. Donley, T. Plakhotnik, *J. Chem. Phys.* 113 (2000) 9294.
- [16] L.A. Deschenes, D.A. Vanden Bout, *Science* 292 (2001) 255.
- [17] L.A. Deschenes, D.A. Vanden Bout, *J. Phys. Chem. B* 105 (2001) 11978.
- [18] P.W. Anderson, B.I. Halperin, C.M. Varma, *Philos. Mag.* 25 (1971) 1.
- [19] W.A. Philips, *J. Low Temp. Phys.* 7 (1972) 351.
- [20] F.L.H. Brown, R.J. Silbey, *J. Chem. Phys.* 108 (1998) 7434.
- [21] A. Heuer, R. Silbey, *Phys. Rev. Lett.* 70 (1993) 3911.
- [22] V. Lubchenko, P.G. Wolynes, *Phys. Rev. Lett.* 87 (2001) 195901.
- [23] E. Geva, J.L. Skinner, *J. Phys. Chem. B* 101 (1997) 8920.
- [24] E. Barkai, R. Silbey, G. Zumofen, *Phys. Rev. Lett.* 84 (2001) 5339.
- [25] E. Barkai, R. Silbey, G. Zumofen, *J. Chem. Phys.* 113 (2001) 5853.
- [26] W. Feller, *An Introduction to Probability Theory and its Applications*, Vol. 2, Wiley, New York, 1970.
- [27] E. Barkai, A.V. Naumov, Yu.G. Vainer, M. Bauer, L. Kador, *Phys. Rev. Lett.* 91 (2003) 075502.
- [28] Y. Jung, E. Barkai, R. Silbey, *Adv. Chem. Phys.* 123 (2002) 199.
- [29] E. Barkai, Y. Jung, B. Silbey, *Phys. Rev. Lett.* 87 (2001) 207403.
- [30] Y. Zheng, F.L.H. Brown, *Phys. Rev. Lett.* 90 (2003) 238305.
- [31] W.P. Ambrose, W.E. Moerner, *Nature* 349 (1991) 225.
- [32] W.P. Ambrose, T. Basche, W.E. Moerner, *J. Chem. Phys.* 95 (1991) 7150.
- [33] J.C. Philips, *Phys. Rev. B* 24 (1981) 1744.
- [34] W.E. Moerner, T. Plakhotnik, T. Irngartinger, M. Croci, V. Palm, U.P. Wild, *J. Chem. Phys.* 98 (1994) 7382.
- [35] G.H. Weiss, *Aspects and Applications of the Random Walk*, North-Holland, Amsterdam, New York, Oxford, 1994.
- [36] A.V. Naumov, Y.G. Vainer, M. Bauer, S. Zilker, L. Kador, *Phys. Rev. B* 63 (2001) 212302.
- [37] A.V. Naumov, et al., *J. Chem. Phys.* 116 (2002) 8132.
- [38] P.W. Anderson, *J. Phys. Soc. Japan* 9 (1954) 316; R. Kubo, *J. Phys. Soc. Japan* 6 (1994) 935.
- [39] R. Kubo, *Adv. Chem. Phys.* 15 (1969) 101.
- [40] T. Plakhotnik, *J. Lumin.* 83 (1999) 221.
- [41] W. Pfluegl, F.L.H. Brown, R.J. Silbey, *J. Chem. Phys.* 108 (1998) 6876.
- [42] J.P. Bouchaud, A. Georges, *Phys. Rep.* 195 (1990) 127.
- [43] J. Klafter, M.F. Shlesinger, G. Zumofen, *Phys. Today* 49 (2) (1996) 33.
- [44] L. Kador, *Phys. Rev. E* 60 (1999) 1441.
- [45] R. Metzler, J. Klafter, *Phys. Rep.* 339 (2000) 1.
- [46] E. Barkai, *Phys. Rev. E* 63 (2001) 046118.
- [47] A.V. Naumov, Y.G. Vainer, *J. Lumin.* 98 (2002) 63.
- [48] Yu.G. Vainer, A.V. Naumov, M. Bauer, L. Kador, *Opt. Spectrosc.* 94 (2003) 864.
- [49] J.R. Klauder, P.W. Anderson, *Phys. Rev.* 125 (1962) 912.
- [50] G. Zumofen, J. Klafter, *Chem. Phys. Lett.* 219 (1994) 303.
- [51] B.M. Kharlamov, G. Zumofen, *J. Chem. Phys.* 116 (2002) 5107.
- [52] A.M. Stoneham, *Rev. Mod. Phys.* 41 (1969) 82.
- [53] R.S. Leigh, M.J.L. Sangster, R.C. Newman, *Phys. Rev. B* 60 (1999) 10845.
- [54] T. Dauxois, S. Ruffo, E. Arimondo, M. Wilkens (Eds.), *Dynamics and Thermodynamics of Systems with Long Range Interactions*, Lecture Notes in Physics, Springer, Berlin, 2002.
- [55] P.H. Chavanis, *Statistical mechanics of two-dimensional vortices and stellar systems*, in: T. Dauxois, S. Ruffo, E. Arimondo, M. Wilkens (Eds.), *Dynamics and Thermodynamics of Systems with Long Range Interactions*, Lecture Notes in Physics, Springer, Berlin, 2002.
- [56] L. Pietronero, et al., *J. Phys.: Condens. Matter* 14 (2002) 2141.
- [57] J. Puetra, C. Cerededa, *Astrophys. Space Sci.* 256 (1998) 349.
- [58] I.A. Min, I. Mezik, A. Leonard, *Phys. Fluids* 8 (1996) 1169.
- [59] B.N. Kuvshinov, T.J. Schep, *Phys. Rev. Lett.* 84 (2000) 650.
- [60] P. Maass, F. Scheffler, *Physica A* 314 (2002) 200.
- [61] Y. Jung, E. Barkai, R.J. Silbey, *Chem. Phys.* 284 (2002) 181.
- [62] M. Kuno, D.P. Fromm, H.F. Hamann, A. Gallagher, D.J. Nesbitt, *J. Chem. Phys.* 112 (2000) 3117.
- [63] K.T. Shimizu, R.G. Neuhauser, C.A. Leatherdale, S.A. Empedocles, W.K. Woo, M.G. Bawendi, *Phys. Rev. B* 63 (2001) 205316.
- [64] G. Messin, J.P. Hermier, E. Giacobino, P. Desbiolles, M. Dahan, *Opt. Lett.* 26 (2001) 1891.
- [65] X. Brokmann, et al., *Phys. Rev. Lett.* 90 (2003) 120601.
- [66] P.D. Reilly, J.L. Skinner, *J. Chem. Phys.* 101 (2) (1994) 959.
- [67] T.L. Reinecke, *Solid State Commun.* 32 (1979) 1103.