Moments distributions of single dye molecule spectra in a low-temperature polymer: Analysis of system ergodicity

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Abstract. This article demonstrates the principal advantages of the technique for analysis of the long-term spectral evolution of single molecules (SM) in the study of the microscopic nature of the dynamic processes in low-temperature polymers. We performed the detailed analysis of the spectral trail of single tetra-tert-butylterrylene (TBT) molecule in an amorphous polyisobutylene matrix, measured over 5 hours at T = 7K. It has been shown that the slow temporal dynamics is in qualitative agreement with the standard model of two-level systems and stochastic sudden-jump model. At the same time the distributions of the first four moments (cumulants) of the spectra of the selected SM measured at different time points were found not consistent with the standard theory prediction. It was considered as evidence that in a given time interval the system is not ergodic

1. Introduction

One of the most significant areas of modern science and technology is the study of the properties of solid-state materials and structures composed of complex molecular systems (glasses, polymers and other). A significant amount of new information about the internal dynamics of solids can be obtained from the laser selective optical electronic-vibrational spectra of impurity centers (molecules, ions) embedded as spectral probes into a medium (matrix) transparent in the selected spectral range. The laser selective spectroscopy of impurity centers in solids is especially informative at cryogenic temperatures, when zero-phonon lines (ZPL) are reachable for observation (see [1] and references therein).

The possibilities of the methods of selective laser spectroscopy (persistent spectral hole burning and laser fluorescence line narrowing) are significantly limited because they provide data averaged over a large ensemble of impurity centers. The method of Single-molecule spectroscopy (SMS) completely eliminates this drawback. Single-molecule spectroscopy (SM), embedded as a spectral probe into a solid matrix, is a powerful tool for obtaining information about low-temperature dynamic processes in the local environment of these molecules [2]. In particular, SMS allows one to directly investigate the interaction of the electron transition impurity center with elementary excitations of a matrix of tunnel type - tunneling two-level systems (TLSs), (see [1-3] and references there).

In the present work we performed the analysis of the long-term temporal dynamics of the spectrum of a single chromophore molecules in the polymer matrix at cryogenic temperature, in order to clarify the applicability of the basic assumption of theories describing the spectral dynamics of such systems.

2. Evolution of spectra over time

As is well know from numerous studies, the low temperature (below several kelvins) dynamics of disordered solids is determined by the dynamics of specific low-energy elementary excitations - tunneling two-level systems (TLS)[4, 5]. Each (TLS) corresponds to the tunnel transitions of groups of atoms of a matrix between the two localized potential minima separated by a potential barrier. The interaction of the electronic transition of impurity chromophore molecules with active TLSs leads to spectral jumps of zero-phonon line (ZPL) of impurity chromophore molecule. As a result, the SM spectra changes during the time [3].

One of the most convenient and informative ways to observe the SM spectral evolution over a period of time is the method of multiple repeating detections of fluorescence excitation spectra within a selected spectral range [6]. The measurement of the SM spectra by recording their spectral trails has an important advantage; namely, it allows one to relatively, simply, and reliably identify the spectral lines and attribute them to individual molecules for further study [3, 7].

As a result of interaction of SM with an ensemble of TLSs spectra of different molecules have individual random shape and may consist of several peaks and stochastically alter with time (figure 1.b). In this case the description of the impurity system using only one parameter for the width of the SM spectral line is obviously not enough. To characterize and to explore the properties of impurity system, it was necessary to develop new approaches that adequately reflect the complex shapes of the spectra of single dye molecules.

To solve the above mentioned problem in the early 2000th it was suggested to describe the SM spectra within concepts of cumulants [8] and moments [9] of complex distributions. Moments and cumulants of various orders reflect the different peculiarities of complex (in general - multilines) SM spectral bands. In the case of a discrete distribution (in our case, the spectrum of single molecules), the first four central moments are expressed as follows:

$$M_1 = \frac{1}{\sum_i I_i} \sum_i I_i \omega_i, \quad M_p = \frac{1}{\sum_i I_i} \sum_i I_i (\omega_i - M_1)^p \quad \text{p=2, 3, 4,} \tag{1}$$

where I_i is the signal amplitude of the data point of frequency ω_i.

In some cases, the description of complex distributions the concept of cumulants is more convenient, which are related to the central moments as follows:

$$k_1 = M_1, \quad k_2 = M_2 - M_1^2. \tag{2}$$

As it has been shown in several studies, distribution of SM spectra cumulants, calculated on the basis of the standard TLS model and the stochastic model of sudden jumps [10], is described by the Levy statistics [9]. In this case the distribution of the first two cumulants of the spectra of single molecules P(k1), P(k2) [9] are of the form:

$$P(k_1) \sim \frac{z_1}{k_1^1 + z_1^2} \text{ (Lorentz function)}, \quad P(k_2) \sim \frac{z_{1/2}}{(k_2)^{3/2}} \exp(-\frac{z_{1/2}^2}{2k_2}) \text{ (Smirnov function),} \tag{3}$$

where z_1 and $z_{1/2}$ coefficients are determined by the parameters of the impurity molecules and two-level systems. The very interesting property of this statistical description is that the ratio of parameters $z_1/z_{1/2}$ depends only on the general nature of dye-doped system (type of the dye-TLS interaction, isotropy and ergodicity of the system etc.).

In [11] it was shown that the distribution of the first and second cumulants of the spectra of 244 single molecules of tetra- tert -butylterrylene (TBT) in polyisobutylene (PIB) (420000) measured at T = 2 K, are satisfactorily described by the expressions (3), that is Levy statistics used to describe the measured spectra [8]. Moreover the value $z_1/z_{1/2}$ was obtained, which corresponds to the dipole-dipole type of interaction between SM and TLS, as well as a uniform spatial TLS distribution.
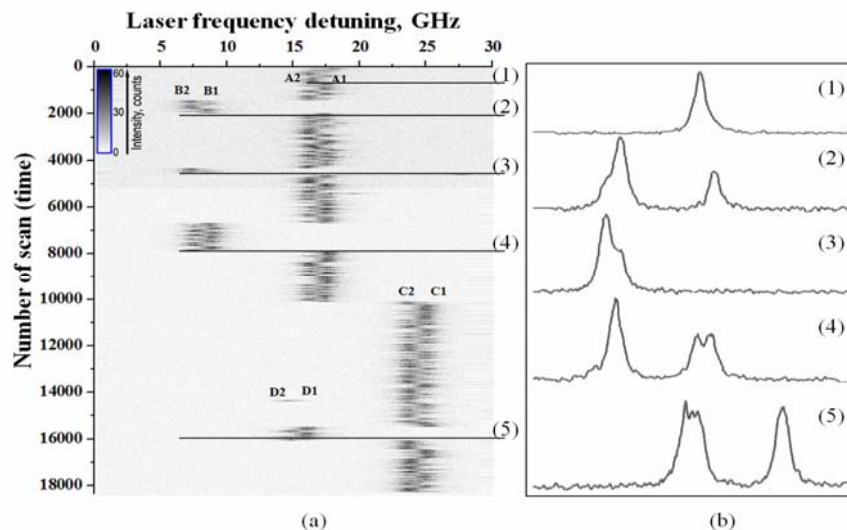
3. Approximation theory: the replacement of averages and the ergodic hypothesis

All the theories which describe the spectral characteristics of dye-doped disordered solid systems (e.g. for calculation of the photon-echo decay curves, shapes of spectral holes or spectra of single molecules), have quite complex mathematical apparatus which includes numerous averaging over various parameters. As result, in order to obtain analytical formulas different simplifications are applied based on some assumption about nature of system under study. For example, the in the theory of photon echo in low-temperature impurity glasses the correlation function $\Phi_{3\Phi\Theta}(\tau,t_w)$ is defined as follows [8]:

$$\Phi_{3\Phi\Theta}(\tau,t_w) = \exp\left\{-i\left[\int_0^\tau dt\omega(t) - \int_{t_w+\tau}^{t_w+2\tau} dt\omega(t)\right]\right\}_{stochastic,\varepsilon,A,J,config}$$

(4)

Here, the angle brackets indicate averaging over all the two-level systems jumps histories (the so-called stochastic averaging, or averaging over the phase trajectories), over the TLS parameters and over the positions of the TLS (configuration averaging).

It should be noted that one of the essential conditions for the derivation of the analytical formulas was the validity of the ergodic hypothesis [12], namely, that the stochastic averaging over all phase trajectories can be replaced by averaging over time. Moreover, while analytically deriving the respective working formulas the integration sequence on various parameters was often changed [13]. In this context, the question remains how these approximations are valid. To date, the direct experimental data that shed light on this issue are lacking. The experiment provides only indirect information. Here we propose a method for studying this issue, which is to analyze the statistical regularities in the spectrum of the same single molecule which spectral dynamics were observed during a long time.
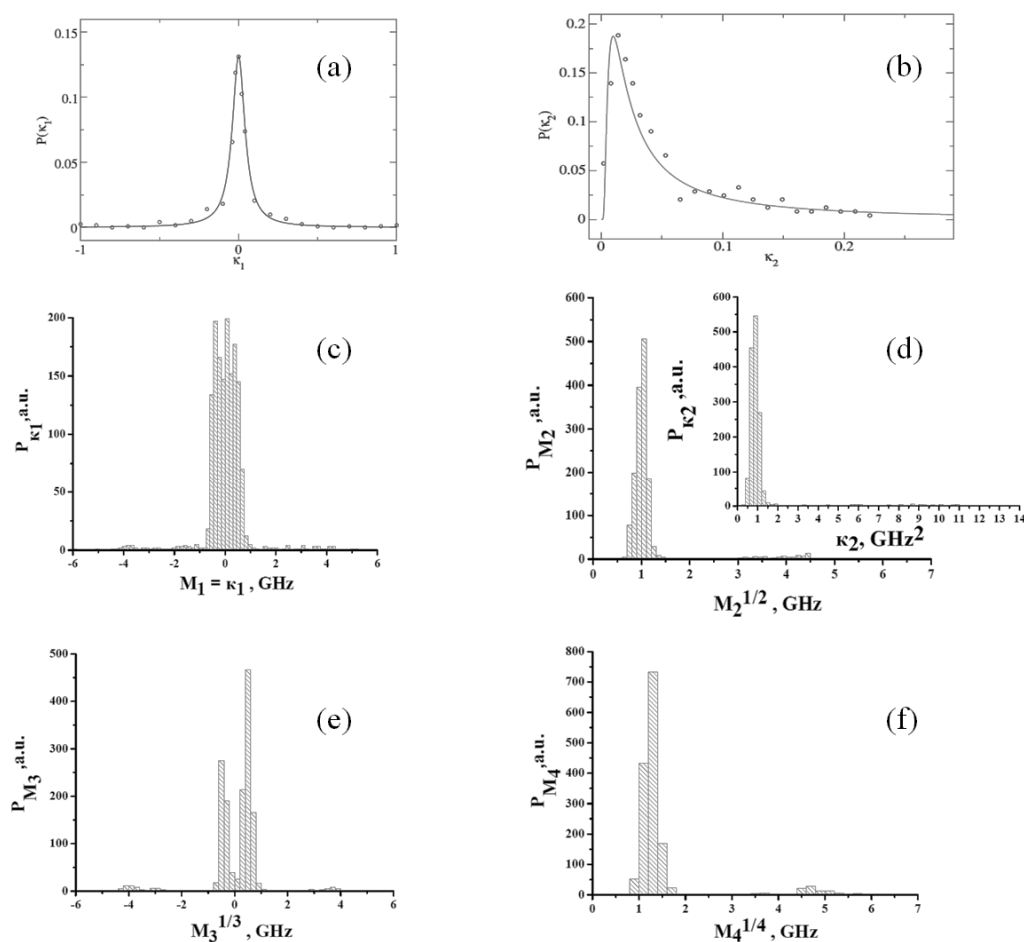

Figure 1. (a) Spectral trail of a single TBT molecule in PIB at T = 7 K. (b) Examples of spectra of the selected single TBT molecule as measured at different time points (shown by horizontal lines on (a)) with the selected integration time (120 seconds – 10 scans)

The spectral trail of the single molecule of tetra-tert-butylterrylene (TBT) in the thin (~0.5 μm) film of polyisobutylene (PIB) was measured over a long time (about 5 hours). Repeated measurement of the fluorescence excitation spectrum of the selected molecules was performed at T=7 K. Each scan

was performed by a discrete tuning of the laser frequency in the 30 GHz range, number of frequency positions (steps) in scan was 500; exposition time per frequency point was 20 ms. Time for laser tuning back to the initial laser frequency was 2 seconds. By this way, 1536 scans were obtained (which corresponds to 18432 seconds). Two-dimensional plot of the measured spectral trail is shown in figure 1a.

As it is clearly resolved on the figure 1a. the ZPL of the selected TBT SM experiences correlated jumps between 8 spectral positions. It means that in the nearest environment of the analyzed chromophore there are three independent active TLS (we will call them as "strong" TLSs) which parameters are so specific that they cause ZPL jumps in frequency scale markedly out of ZPL width. First "strong" TLSs causes ZPL jumps like A1→A2, B1→B2, C1→C2; D1→D2. Transitions in the second "strong" TLS lead to the repeated ZPL jumps like A→B, C→D. Finally, third "strong" TLS excites the jump like A→C.

Of course, in the local environment of the observed impurity molecule there is a big number of active TLS, but most of them are either very slow, i.e. perform jumps extremely rarely and we cannot observe their dynamics in the spectrum of the SM during the selected period of time, or they are too far and lead to "small" (in frequency scale) jumps, which contribute to the overall broadening and shift of the spectral line.

Figure 2. (a, b) Distribution of the 1st and 2nd cumulant spectra of single molecules, for an ensemble of 244 of TBT in PIB at $T = 2$K, approximated by a Lorentzian and Smirnov functions, respectively [11]. (c-f) Histograms of distributions of selected spectra of a single molecule of TBT in PIB at T = 7K, measured in different time points during the observation for about 5 hours.

In general, the data looks consistent with a model of the TLS. However, it is of interest to see how the system behaves over time and also make an attempt to analyze the applicability of the ergodic hypothesis in this case. Is our measurement time enough to verify its validity? For this we found the distribution of first four moments of the SM spectra measured in a different time points. Whole spectral trail was divided into sequential segments of 120 s. For each segment the integrated SM spectrum was found (see figure 1b). After that for each spectrum the first four moments (cumulants) of SM spectra were obtained using a special computer program. In addition width of a spectrum was defined by the approximation of a SM spectrum with Lorentz's function. In this way, a set of 1525 values or the width and the first four moments of SM spectra was found and the corresponding histograms were plotted (figure 2c-f).

Analysis of the distribution of points and comparison with the distributions obtained for the ensemble of single molecules in the same system TBT/PIB [11] leads to the following conclusions:

- The distributions of the first and second cumulants of spectra measured at different time points during the observation of the spectrum for 5 hours differ from the functions of the Lorentz and Smirnov (Eq. 3), respectively. This indicates that the Levy statistics is not applicable to describe the dynamics of the selected emitter in the realized time scale.

- There are some separate "tails" in the distributions of the second, third and fourth moments, which are associated with a strong splitting of the spectrum under the influence of a particular "strong" TLSs.

Based on above results, we can conclude that in a selected time interval (about 5 hours), the system is not ergodic. This fact must be taken into account in the theoretical analysis of the results in the field of spectroscopy of the impurity center, during the configuration and temporal averaging in the derivation of formulas describing the spectrum, a spectral hole shape, the photon-echo decay curves, etc.

Acknowledgments

References

[1] Naumov A V 2013 *Phys. Usp.* **56** 605
[2] Orrit M, Moerner W E 2011 *Physics and Chemistry at Low Temperatures* vol 1 (Singapore: Pan Stanford Publishing) pp 381-417
[3] Naumov A V, Vainer Y G 2009 *Phys. Usp.* **52** 298
[4] Anderson P W, Halperin, B I, Varma C M 1972 *Phil. Mag.* **25** 1
[5] Philips W A 1972 *J. Low. Temp. Phys.* **7** 351
[6] Ambrose W P, Moerner W E 1991 *Nature.* **349** 225
[7] Vainer Y G, Naumov A V, Bauer M, Kador L 2003 *Opt. Spectr.* **94** 864
[8] Naumov A V, Vainer Y G, Bauer M, Zilker S, Kador L 2001 *Phys Rev B.* **63** 212302
[9] Barkai E, Silbey R, Zumofen G 2000 *Phys. Rev. Lett.* **84** 5339
[10] Klauder J R, Anderson P W1962 *Phys. Rev.* **125** 912
[11] Barkai E, Naumov A V, Vainer Y G, Bauer M, Kador L 2003 *Phys. Rev. Lett.* **91** 075502
[12] Geva E, Skinner J L 1997 *J. Chem. Phys.* **107** 7630
[13] Sinai Ya G 1963 *Soviet Math. Dokl.* **4** 1818
[14] Vainer Y G, Naumov A V, Kador L 2008 *Phys Rev B.* **77** 224202