

Single-molecule probing of incommensurate biphenyl

M. Pärs*, V. Palm, and J. Kikas

Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

E-mail: jaak.kikas@ut.ee

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Our data on the distribution of purely-electronic linewidths of terylene single molecules in incommensurate biphenyl crystals are compared with the data of other groups for different low-temperature organic solid hosts and with results of numerical simulations. The first two moments of the distributions measured within a narrow temperature interval have been used to calculate a single dimensionless parameter characterizing each of the respective hosts — the variation coefficient. It appears that different amorphous hosts have similar values of this coefficient, but the value obtained for the incommensurate crystal of biphenyl is significantly different. One can conclude that the remarkable single-molecule line broadening in biphenyl at 1.8 K cannot be solely explained by the interaction with two-level systems, which is considered to cause the broadening in amorphous hosts.

PACS: 78.55.Kz Solid organic materials;
61.44.Fw Incommensurate crystals;
42.62.Fi Laser spectroscopy;
33.70.Jg Line and band widths, shapes, and shifts.

Keywords: single-molecule spectroscopy, single-molecule linewidth distribution, two-level systems, incommensurate biphenyl, terylene.

Introduction

According to the model of two-level systems (TLS) [1,2], specific localized excitations (TLSs) with broad distributions of parameters are present in amorphous solids. Although their microscopic nature is mostly unknown, TLSs affect many properties of glasses at liquid helium temperatures. Being strongly localized, each TLS can affect only a small number of nearby impurity molecules, which allows to study TLSs using the technique of single-molecule spectroscopy (SMS) [3]: an individual dopant molecule can provide direct information about the parameters of excitations in its local environment. Single-molecule (SM) spectral jumps, considered as signatures of tunneling TLS transitions, have been in addition to glasses registered in some low-temperature crystals as well [3].

Among other properties, TLSs are also held responsible for the anomalous spectral broadening of purely-electronic impurity lines in low-temperature glasses as compared to crystals. SMS allows to study this effect on the level of individual SM linewidths and their distributions in different matrices — such investigations have been performed

for several amorphous systems [4–6]. Experimentally obtained linewidth distributions for temperatures below 2 K are quite well described by the theory based on the standard tunneling TLS model of low-temperature glasses and on the stochastic sudden jump model for the TLS dynamics [7]. Even better fit for the low-linewidth region could be probably achieved by taking into account the obtained later more accurate experimental data on terylene fluorescence lifetimes in different hosts [15]. It seems that this rather phenomenological model, developed mainly for bulk (specific heat) or ensemble-averaged measurements, works well on microscopic level too.

In addition to amorphous matrices, an anomalous broadening of impurity lines has also been observed in low-temperature biphenyl (BP) [8]. BP is an interesting host matrix for SMS experiments due to an incommensurate modulation existing in its crystals at temperatures below 40 K (at normal pressure) [9], which leads to a broad distribution of local environmental conditions for individual impurity molecules. So far only two types of chromophore molecules, perylene [10] and terylene [8,11,12], have been used in SMS studies as dopants to BP.

* Present address: Experimental Physics IV, Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth, 95440 Bayreuth, Germany.

It is still little known about the specific excitations of the BP low-temperature incommensurate phase [9] and on their interaction with single impurity molecules. These excitations can play their role in the anomalous SM line broadening reported [8]. On the other hand, reported observations of SM spectral jumps [8,10–12] indicate the presence of TLSs in BP low-temperature crystals. An interesting question arises: can the low-temperature SM line broadening in BP be well described by the same TLS model [7] that works for several amorphous solids? In this paper we will try to answer this question.

Looking for an answer we analyzed our experimental data reported earlier on distribution of terylene SM linewidths in BP at $T=1.8$ K [8,11] in comparison with similar data reported for different amorphous hosts [4,5,13]. Our analysis is based on finding the first two moments of the linewidth distributions. Such an approach should not be confused with the one used in Ref. 14, where moments of *individual* SM lines were calculated.

Theoretical considerations

In order to compare different hosts characterized by varying strength of TLS–SM interaction, a statistical parameter independent on this variation should be useful. It must be calculable for any experimentally obtained SM linewidth distribution. We introduce such parameter, which we will call *the variation coefficient* C_γ , on the basis of the first two moments of a linewidth distribution — the first moment μ_1 , which is calculated about the lifetime-limited linewidth value and equals to the mean value of the linewidth broadening, and the second central moment $\mu_2 = \sigma_2^2$, where σ_2 is the standard deviation.

Any SM linewidth distribution can be characterized by a dimensionless *variation coefficient*

$$C_\gamma = \frac{\sqrt{\mu_2}}{\mu_1}, \quad (1)$$

which is independent on the coupling constant determining the strength of SM–matrix interaction. The latter can be treated as a scaling parameter for our SM linewidth distribution. It is easy to understand that any change of the coupling constant would result in changes of the mean value and of the standard deviation of the distribution, but the ratio C_γ of these two values would remain unchanged.

Let us now analyze the linewidth distribution in the frame of the TLS model [7], where the SM line broadening is caused by the interaction with many TLSs. Tunneling transitions between the two states of a TLS cause shifts of the SM transition frequency. Thus, the transition frequency at any time t is given by

$$\omega(t) = \omega_0 + \sum_i \zeta_i(t) f_i, \quad (2)$$

where $\zeta_i(t)$ equals 0 or 1, indicating whether the i th TLS is in its ground or excited state, and

$$f_i = 2\pi\alpha \frac{A_i \varepsilon_i}{E_i r_i^3}. \quad (3)$$

Here α is the TLS–chromophore coupling constant; $A_i, E_i, \varepsilon_i, r_i$ are the asymmetry, energy splitting, orientation parameter, and distance relative to the chromophore of the i th TLS, respectively. In the standard model, α is assumed to be constant for all TLS–SM pairs, whereas A_i, E_i, ε_i , and r_i are statistically distributed. According to Eq. (2), the distribution of f resembles the distribution of SM linewidths. When we calculate the mean value and the standard deviation, α can be treated as a coefficient, which rescales the SM linewidth distribution. Therefore C_γ is independent of the coupling constant α . Going through the similar discussions, it is easy to show that C_γ is also independent of the concentration ρ of TLSs as long as we assume the uniform distribution of their spatial locations. Different TLS concentrations in different host-guest systems would act similarly to renormalization of α .

Finally we consider the distributions of parameters A_i, E_i , and ε_i . According to the theory [7], these parameters are intrinsic for TLSs. In the simplest model their distributions are assumed to be similar for different hosts and yield no statistical differences. We conclude that the discussed parameters can be considered as scaling constants and do not affect the value of C_γ . However, the statistical uncertainty due to a small amount of experimental data would lead to the variation of C_γ values calculated for different sets of data.

Results and discussion

The SM linewidth distribution we experimentally obtained for terylene in BP single crystals at $T = 1.8$ K [8]

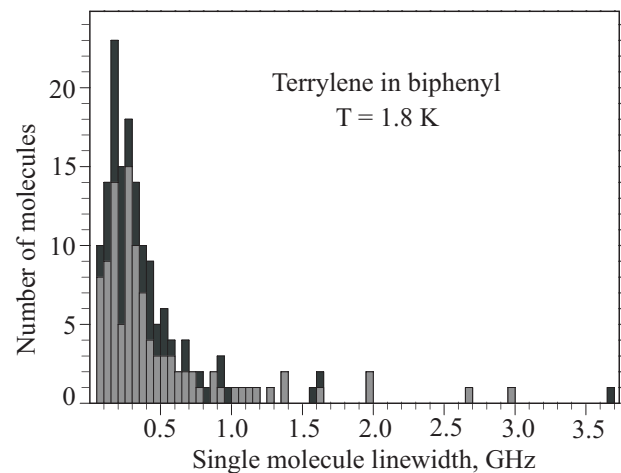


Fig. 1. Distribution of SM linewidths (FWHM) for 160 terylene molecules in BP at $T = 1.8$ K. Gray bars — data for 103 stable SM lines observed in BP single crystals; black bars — additional data for 57 stable lines found in a polycrystalline matrix [8,11].

Table 1. The values of moments of SM linewidth distributions, calculated for terrylene in different hosts and from numerical simulations: μ_1 — the mean value (obtained by calculating the first moment for the SM linewidth distribution and then subtracting the corresponding lifetime-limited linewidth value, which is taken from Ref. 15 for experimental distributions or is assumed to equal 42 MHz for all simulations [7]); $\sigma = \sqrt{\mu_2}$ — the standard deviation; C_γ — the variation coefficient

Host	μ_1 , GHz	$\sigma = \sqrt{\mu_2}$, GHz	$C_\gamma = \frac{\sqrt{\mu_2}}{\mu_1}$	T, K	Number of SMs	Ref.
Polystyrene (PS)	1.87	0.74	0.396	1.7	121	5
<i>Simulation for PS</i>	1.924	0.77	0.4	1.7	2000	7
Polymethylmethacrylate (PMMA)	1.03	0.45	0.437	1.7	68	5
<i>Simulation for PMMA</i>	1.05	0.48	0.457	1.7	2000	7
Polyvinylbutyral (PVB)	0.646	0.38	0.588	1.7	211	5
<i>Simulation for PVB</i>	0.642	0.267	0.416	1.7	2000	7
Polyethylene (PE)	0.082	0.055	0.671	1.8	176	4
<i>Simulation for PE</i>	0.075	0.05	0.664	1.8	2000	7
PE*	0.066	0.033	0.5	1.83	75	13
Biphenyl (BP) [#]	0.431	0.517	1.2	1.8	103	8

*Data for the sandwich PE sample [13].

[#]Although the exact value of the lifetime-limited linewidth for terrylene in BP is still unknown, we estimate it as 0.035 GHz, which is an approximate value for different hosts according to Ref. 15. We note that due to a relatively large value of μ_1 in BP, the calculated value of C_γ is quite insensitive to small variations of the lifetime-limited linewidth.

appeared to be quite similar to that we earlier found for terrylene in polycrystalline BP [11]. The histogram of the cumulative distribution is shown in Fig. 1 [8]. The calculated parameters of μ_1 , σ , and C_γ for this distribution along with those for analogous distributions reported for terrylene in different amorphous hosts [4,5,13] and with values calculated from the results of numerical simulations [7] are presented in Table 1.

The first three amorphous polymeric hosts in the table (PS, PMMA, PVB) exhibit large mean linewidth values (μ_1) and also high standard deviations. The mean linewidth values are much smaller for PE hosts, which are considered to be semicrystalline. The value of $\mu_1 = 0.431$ GHz for BP stands between the amorphous polymeric matrices (PS, PMMA, PVB) and the semicrystalline one (PE). The distribution of linewidths for BP is relatively broad: the standard deviation σ is comparable to those for the amorphous hosts, while the mean linewidth is about twice narrower.

It is remarkable that the calculated values of C_γ are quite similar for the three amorphous polymeric hosts, nearly fitting the region of $\pm 20\%$ around the value of ~ 0.5 (see Table 1); even adding the results for the semicrystalline PE does not change this accord much worse. Taking into account our analyses in the previous chapter and the conclusions made in Ref. 7, one can assume that this similarity of C_γ indicates the prevailing role of the TLS–SM interaction mechanism [7] in the SM line broadening for these systems at temperatures around 1.8 K. It is not surprising that the moments calculated from the

results of numerical simulation based on the TLS model match the experimental data pretty well. On the other hand, the notably different C_γ value for BP indicates a significant role of matrix-specific SM line broadening mechanisms in this incommensurate crystal.

Conclusion

The variation coefficient C_γ , for SM linewidth distribution has been calculated for terrylene dopant in several low-temperature organic solids. It is argued, that within the frame the TLS model [7] its value depends on the basic assumptions of the model only and *not* on the host-dependent TLS–SM interaction parameters. C_γ is found to have similar values for different amorphous hosts, but for BP crystals C_γ exceeds these values more than twice. We conclude that in a low-temperature matrix of BP the line broadening of terrylene molecules cannot be well described by the same TLS model [7], which works quite well for several amorphous solids. The remarkable SM line broadening in BP at 1.8 K [8] is at least partially caused by other dephasing processes acting in this crystal, tentatively related to the specific dynamics of incommensurate systems.

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