Stable single molecules for quantum optics and all-optical switches

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CHAPTER 2

Spectral diffusion of a single molecule

The aim of this chapter is to get a deeper understanding of the physical origin of the spectral diffusion that single molecules in many solid materials have shown over the years. We use single dibenzoterrylene (DBT) molecules as a fluorescent nano-probe to extract information about the local dynamics of a single crystal of 2, 3-dimethylanthracene (2, 3-DMA). Single-molecule fluorescence excitation spectroscopy and fluorescence correlation measurements allow us to identify that the methyl groups combined with the static “dipolar disorder” present in the 2, 3-DMA may be the physical reason for such observations. Line broadening, spectral diffusion and/or frequency jumps are expected whenever the activation energies for librational degrees of freedom (acoustic phonons) or local low-frequency modes (LFM’s) are active in the host at the experimental conditions (1.5 K). The presence of the methyl groups together with dipolar disorder of the host must be avoided when looking for new single molecule ‘host-guest” systems with lifetime-limited linewidths and high spectral stability.

The content of this chapter is published.
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2.1.Introduction

Since the first optical detection of a single molecule at cryogenic temperature by absorption and fluorescence[1,2], single-molecule spectroscopy (SMS) has become a powerful tool for investigating structure and dynamics of condensed matter. The biggest advantage of SMS is to investigate the properties of heterogeneous systems without any ensemble averaging[3]. The properties of a single molecule depend not only on its chemical structure but also on its specific local environment. Single molecules can be thus used as probes to study the local environments at nanometer scales.

Dibenzoterrylene (DBT) was found to be a good fluorophore for SMS[4,5]. The important advantages of the DBT molecule are its photo-stability as well as its absorption in the near infrared range[6,7]. Single DBT molecules have been studied in crystal matrixes in which they are located in well-defined insertion sites with associated orientations. Lifetime-limited linewidths and a narrow inhomogeneous distribution of the zero-phonon lines (ZPLs) at low temperature were observed in these matrixes[5,7,8]. However, the molecules in the different insertion sites presented different properties, such as saturation intensity, temperature dependence and linewidth[9].

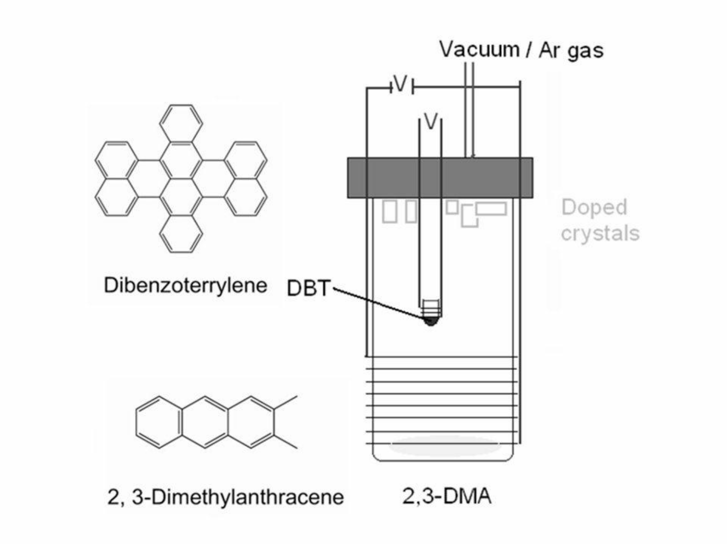
In glasses, the distribution of molecular properties is generally much broader than in crystals. The glassy disorder creates specific defects which are known as two-level systems (TLS's). These TLS's can assume two different quasi-degenerate conformations, and switch from one to the other by phonon-assisted processes. Although the TLS model was already proposed approximately 40 years ago[10,11], SMS experiments provided the first experimental evidence of the TLS's as individual entities. Single molecules thus have been used to investigate the TLS's in disordered glass matrices[12-17].

Recently, single molecules have been studied in crystals with dipolar disorder. In such crystals, the position of the host molecules at the nodes of a lattice is conserved, but each of the non-symmetric molecules can assume one of two possible orientations. The three dipolar-disordered crystals used so far have been 1,2-dichlorobenzene (1,2-DCB)[18], 2,3-dimethylnaphthalene (2,3-DMN)[19-21], and 2,3-dimethylanthracene (2,3-DMA)[22]. For terrylene in 1, 2-DCB, stable lines with lifetime-limited linewidths were observed[18]. For 2, 3-DMA and 2, 3-DMN, the two methyl groups substituted on the 2, 3 positions of the anthracene or naphthalene molecules make them non-centrosymmetric. The crystal structure of 2, 3-DMA (2, 3-DMN) resembles that of the anthracene (naphthalene) crystal, with fairly sharp Bragg reflections arising from positional order[23-25]. However, optical experiments have revealed that guest molecules doped into these crystals display active dynamics and broad inhomogeneous distributions[19,20,22,26]. Despite these earlier works at low temperature which were limited by the laser resolution (about 30 GHz), no high-resolution, low-temperature spectroscopy has been attempted yet on these systems.

In this chapter, we study single DBT molecules in 2, 3-DMA crystal at cryogenic temperatures with high spectral resolution (2 MHz). We discuss our findings on static disorder and dynamic disorder of the single molecule lines and discuss the consequences for the crystal's structure and dynamics.

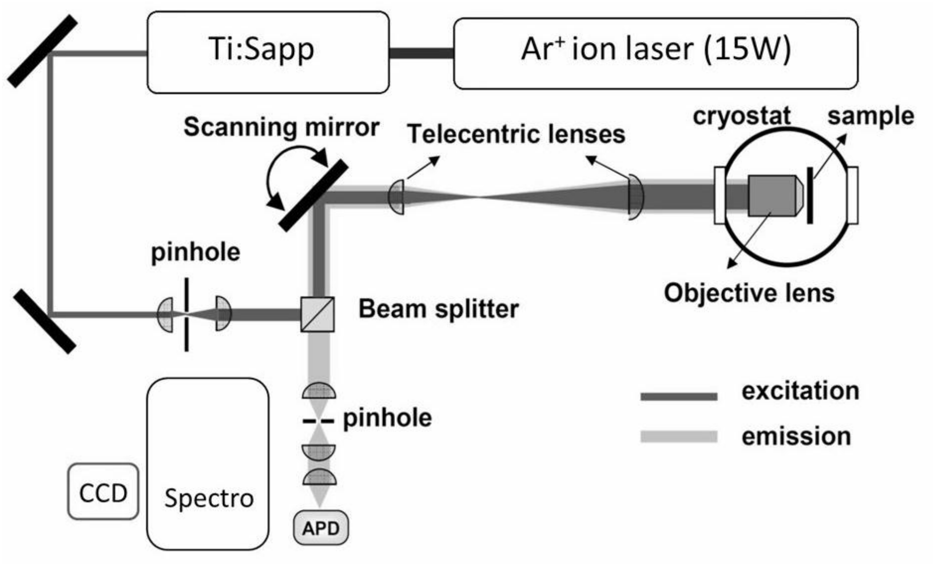
2.2.Experimental

Single crystals of 2, 3-DMA (zone-refined before use) as host, doped with DBT were grown by co-sublimation in a home-built device in Warsaw under a 150 mbar argon atmosphere (scheme 1). Briefly, the 2, 3-DMA powder was heated (higher than its sublimation point ≈200°C) by applying a voltage (V) through a metallic wire that surrounds the outer glass container. Another wire around the small container where the DBT was placed was heated independently with a second voltage. The doped crystals grow in the surface of the upper stopper as thin flakes. For single-molecule experiments, the sample was then cooled down to 1.25 K in a helium cryostat (Janis). For temperature-dependent experiments, the sample was set in the sample chamber and the temperature was controlled by the helium flow over the sample at very low pressure (below 10 mbar).



Scheme 2.1: *Glass chamber for co-sublimation of host-guest crystals for SMS. Big amount of host (23, DMA) is placed on the bottom and heated at T > sublimation. The impurity (DBT) has to be keep at very low concentration respect to the host. The vacuum reduces the vapor pressure of the molecular crystal helping sublimation. Ar or N gas keep the atmospheric pressure at desired value (150mbar) and remove impurities.*

A single-frequency Ti:Sapphire laser (Coherent 899-21) pumped by an Argon ion laser (Coherent Sabre 150) provided the excitation light at 780 nm (Scheme 2.2). A fast scanning mirror (Newport FSM-300-01) allowed us to scan the sample over about 75 × 75 μm^2. The fluorescence was collected by an objective mounted inside the cryostat (60×, NA=0.85, Edmund Optics) and detected by an avalanche photodiode (SPCM-AQR-16, Perkin-Elmer) after proper spectral and spatial filtering. In case that it is required a flip mirror in the detection path can send the fluorescence signal into a spectrograph (Princeton Instruments, i500) mounted with a CCD detector. From the fluorescence intensity traces, autocorrelation functions were obtained with a data acquisition card (TimeHarp 200, Pico Quant) and its associated software.



Scheme 2.2: *Optical set-up used to perform single molecule experiments inside the cryostat. The maximum conversion efficiency of TiSapp is 20 % at optimal conditions operating in single frequency. Long pass filters with cut in 810 nm were used for detect the red shifted photons, from the excitation light at 785nm.*

2.3.Results

2.3.1. Saturation intensity

We measured the fluorescence intensity and the spectral linewidth of several single DBT molecules in 2, 3-DMA as functions of the excitation intensity. The most striking observation is the large width of the molecular lines of about 1 GHz, as the insert of Figure 2.1 shows. In addition, the fluorescence (circles) becomes saturated for high excitation powers. This trend was fitted with the standard saturation expression given by Equation 5 and 6 in the introduction of this thesis.

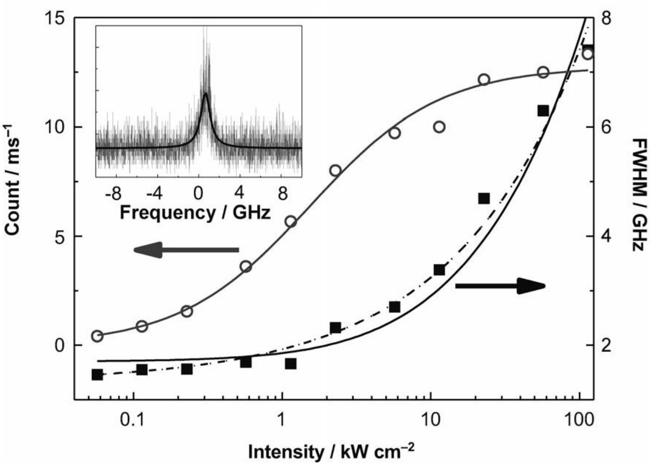


Figure 2.1: *Fluorescence intensity (○) and linewidth (■) of a single DBT molecule in 2, 3-DMA crystal versus excitation intensity. The solid lines are fits with equation (5) and (6) in introduction, for the linewidth and intensity, respectively. The dashed line is fitted considering the spectral diffusion effect. Insert: excitation spectrum of a single molecule showing FWHM =1 GHz and the solid line is a Lorentz fit.*

The linewidth (squares) shows a similar trend as seen for DBT in anthracene and was thus fitted by the corresponding expressions presented in introduction of this thesis. The obtained saturation intensity for the measured DBT molecule in 2,3-DMA (1.4 kW/cm^2) was about 1000 times higher than that of DBT in anthracene (~1 W/cm^2).[7] To understand the origin of this difference, we simulated the line broadening by saturation for two different cases, through dephasing (solid line) and through spectral diffusion (dash-dotted line), and both shown together with the results of Fig 2.1.

Both spectral diffusion (SD) and dephasing can broaden the linewidth of the molecules. Because the linewidth is larger, a larger intensity is required to achieve the same relative broadening effect. Therefore, the saturation intensity will be increased in both cases, but to different extents. Plakhotnik has proposed to separate the dephasing and the spectral diffusion effects by fitting the saturation curve of the linewidth with the ratio of dephasing to spectral diffusion as a fit parameter[27]. However, without prior information about the natural linewidth and the transition dipole moment, it was difficult to identify these two contributions reliably. So now, we intend to show that, by using prior information about the lifetime-limited linewidth of DBT in anthracene, the difference between the contributions of spectral diffusion and dephasing can be obvious.

2.3.1.1 Line broadening by dephasing only

For a single molecule line without spectral diffusion and without pure dephasing (e.g., DBT in anthracene), the linewidth γ_0 is determined by the coherence lifetime T_2, related to the population lifetime T_1, itself including radiative k_r and non-radiative k_{nr} components:

$$\gamma_0 = \frac{1}{T_2} = \frac{1}{2T_1}, \qquad \frac{1}{T_1} = k_r + k_{nr}.$$

For the DBT molecule in the main site, the lifetime-limited linewidth (FWHM) was reported to be 32 MHz. Thus the saturation curve of the linewidth $\gamma(I)$ should follow the equation:

$$\gamma(I) = \gamma_0\sqrt{1+\frac{I}{I_s}}\text{, with } \gamma_0 = \pi \times 32\ \text{MHz}\text{, and } I_s = 1.0\ \text{W/cm}^2,$$

where I is the excitation intensity and I_s is the saturation intensity. This dependence is shown as a dashed line in Fig.2.2.

For DBT in 2,3-DMA, the molecular lines are much broader than 32 MHz. If this broadening is due to pure dephasing only, and assuming that the radiative and non-radiative rates, and the transition dipole moment of DBT remain the same as in anthracene, the linewidth γ_D will be given by:

$$\gamma_D = \frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2'}, \quad \text{where} \quad \frac{1}{T_2'} \quad \text{represents the pure dephasing rate.}$$

The saturation intensity can be deduced from the saturation parameter s by:

$$s = \frac{I}{I_s'} = \Omega^2 T_1 T_2 ,$$

the Rabi frequency , Ω , is related to the light electric field and transition dipole moment

by, $$\Omega = \frac{\left|\vec{\mu}_{eg} \cdot \vec{E}_0\right|}{\hbar}$$

The new saturation intensity with dephasing, I_s' is related to the previous one by:

$$I_s' = \frac{2\,T_1}{T_2} I_s .$$

The measured linewidth of DBT in 2,3-DMA is ~ 1 GHz. Thus, the new saturation intensity is about 30 kW/cm^2, and the saturated linewidth should follow the equation:

$$\gamma_D(I) = \gamma_D \sqrt{1 + \frac{I}{I_s'}}$$

plotted as a dotted line in Figure 2.2.

2.3.1.1. Line broadening by spectral diffusion only

If the measured linewidth is only broadened by spectral diffusion, the line shape should be the convolution of the (possibly saturated) excitation line of the molecule with the probability distribution of the spectral jumping. To perform the calculation, we assume this probability distribution to be Lorentzian, centered on ω_0 and with FWHM 2Δ . The probability density of presence of the molecular line at frequency ϖ is thus:

$$L_\Delta(\varpi, \omega_0) = \frac{1}{\pi} \frac{\Delta}{(\varpi - \omega_0)^2 + \Delta^2} .$$

The excited state population for laser excitation at ω and for resonance frequency at ϖ is:

$$p_e(\omega,\varpi)=\frac{\gamma_0^{\,2}}{2}\frac{s}{(\omega-\varpi)^2+\gamma_0^{\,2}(1+s)},$$

s being the corresponding saturation parameter. Thus, the molecular lineshape will be the convolution product of these two profiles:

$$p_e(I)=p_e(\omega,\varpi)\otimes L_\Delta(\varpi,\omega_0)=\frac{\gamma_0 s}{4\pi^2\sqrt{1+s}}\frac{\Delta+\gamma_0\sqrt{1+s}}{(\omega-\omega_0)^2+(\Delta+\gamma_0\sqrt{1+s})^2},$$

which is also a Lorentzian with linewidth $\gamma_{SD}(I)=\Delta+\gamma_0\sqrt{1+s}$.

In our case, for DBT in 2,3-DMA with a linewidth of 1 GHz, Δ= 0.97 GHz, γ_0 and I_s keeping their values as in anthracene. The saturation curve is then given by the solid line in Figure 2.2. which compares very well to the experimental data.

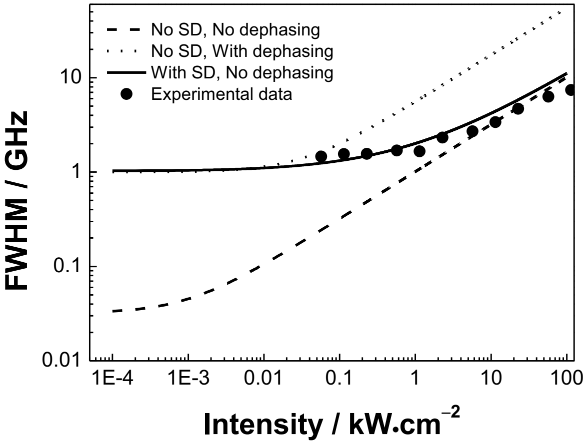


Figure 2.2. *Linewidth broadening versus excitation intensity for three different situations: natural linewidth without pure dephasing and without spectral diffusion (dashed line); pure dephasing without spectral diffusion (dotted line); spectral diffusion without pure dephasing (solid line). The dots are experimental data for DBT in 2,3-DMA.*

From these results we see that spectral diffusion leads to a much higher saturation intensity than pure dephasing. This is a strong indication that the large linewidth of single

DBT molecules in 2, 3-DMA is due to spectral diffusion. Thus, when the intensity was lower than 1 kW/cm^2 the linewidths reported hereafter were mainly determined by spectral diffusion. Saturation broadening becomes significant at excitation intensities higher than 1 kW/cm^2.

2.3.2. Linewidth distribution

We measured the excitation spectra of 34 single DBT molecules in 2, 3-DMA around 780 nm. The full-widths at half maximum (FWHM) values were deduced from Lorentzian fits, as shown in the insert of Figure 2.1. To get enough signal-to-noise ratio but avoid saturation, we used an excitation intensity of 1 kW/cm^2 for all linewidth measurements.

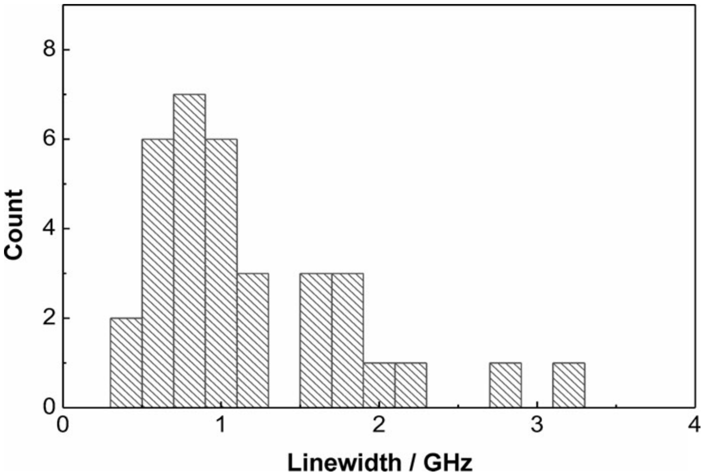


Figure 2.3: *Histogram of the linewidths of 34 DBT molecules (excitation wavelength 780 nm). An excitation intensity of 1 kW/cm^2 was used to get good signal-to-noise ratios and avoid saturation.*

The molecules were measured at 1.25 K and the histogram of their FWHMs is shown in Figure 2.3. The linewidths are widely distributed from 0.4 to 3.2 GHz with a maximum around 0.8 GHz. This average linewidth is much broader (~30 times) than the

ZPL of DBT in an anthracene crystal[7]. Saturation at our excitation intensity (1 kW/cm^2) cannot be significant in these measurements, because the reported saturation intensity (1.4 kW/cm^2) was the lowest one from all the measured molecules. Indeed, no molecules with linewidths less than 0.4 GHz was ever observed, even at very low intensities.

2.3.3. *Temperature dependences of the linewidth and shift*

We measured the temperature dependences of the linewidth and of the central frequency of some single DBT molecules in 2, 3-DMA in the range of 1.5–12 K, as shown in Figure 2.4. The linewidth increases with temperature (Figure 2.4 a) according to the Arrhenius law, in agreement to what has been reported for other molecules in crystals and polymer matrices[6,28,29]:

$$\gamma(T) = \gamma(0) + Ae\left(-\frac{E_a}{kT}\right)$$

Here, $\gamma(0)$ is the linewidth at zero temperature, k is the Boltzmann constant, E_a is the activation energy, and A is a constant depending on the electron–phonon coupling. Most of the molecules we measured could be fitted by using the Arrhenius equation shown above (see examples in Figure 2.4.a). The obtained activation temperatures for DBT/2,3-DMA (ranging from 20 to 26 K) are quite similar to those for DBT/anthracene[6] and for terrylenediimide (TDI)/hexadecane (HD)[29]. Vainer et al.[30] proposed a more accurate expression, including both TLSs and phonon contributions. However, the dynamic range and the accuracy of our measurements do not allow us to fit more than two parameters reliably.

The spectral shift was also observed as a function of temperature. To exclude pressure effects, we kept the sample in vacuum at constant pressure. The shifts present

different variations from molecule to molecule (see Figure 2.4.b), an observation that has previously been reported for TDI/HD by Mais et al.[29] Some lines shifted to the blue, others to the red. Again, most of the curves can be fitted with an Arrhenius equation:

$$\Delta\nu(T) = B \bullet e\left(-\frac{E_a}{kT}\right)$$

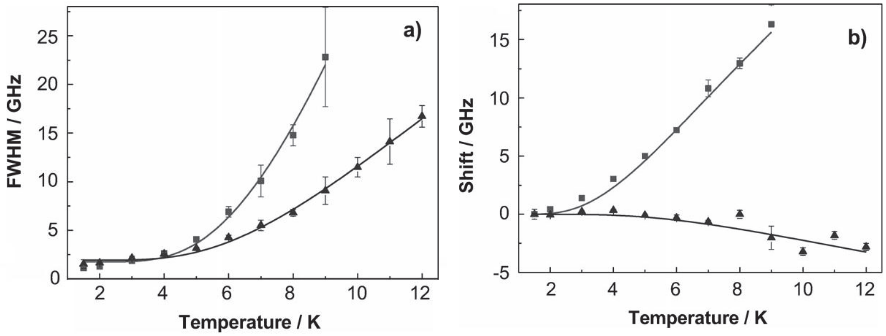


Figure 2.4: *Temperature dependence of the linewidths (a) and frequency shifts (b) of two typical single DBT molecules in 2,3-DMA. The solid lines are the fitted curves using Arrhenius equations for the linewidths and shifts, respectively.* ■ *and*▲, *correspond to two different molecules.*

The fitted activation temperature for the resonant shift varies from 10 K to 30 K from molecule to molecule but remains comparable with reported values[6,29]. The mechanism of the spectral shift is not completely clear, but there are at least two possible contributions to its temperature dependence. Firstly, the thermal expansion of the crystal changes the solvent shift, thereby shifting the optical line, and secondly, based on the second-order perturbation theory, the broadening of the optical transition by coupling to phonons and vibrations is associated to shifts of the ground and excited states, causing a shift of the optical transition.

2.3.4. Qualitative observations of spectral diffusion

DBT molecular lines were found to be very unstable in 2,3-DMA compared to anthracene. Sudden intensity jumps, known as blinking of DBT, were assigned to spectral jumping due to the coupling with surrounding TLSs, as discussed above. Both the spectral-jump sizes and rates are quite different from molecule to molecule. Some of the molecules showed spectral jumping between two different frequencies, attributable to coupling to one TLS. Some other molecules that jump between four frequencies, as shown in the examples of Figure 2.5.a & 2.5.b, appear to be coupled to two independent TLSs. More complicated cases of molecules showing noisy traces might arise from coupling to a large number of TLSs (Figure 2.5.c), or from more complex dynamics.

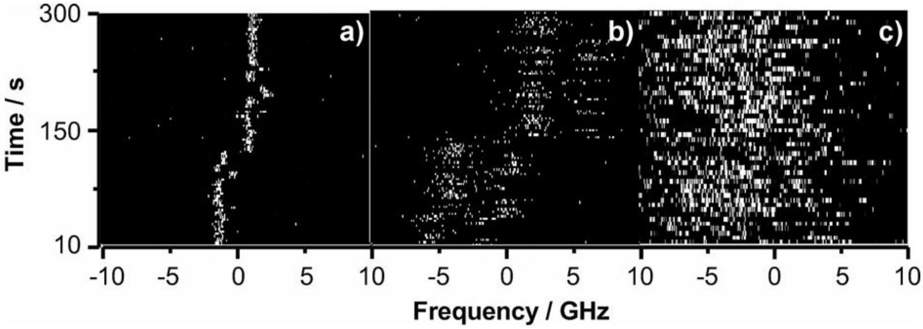


Figure 2.5: *Frequency scan over 20 GHz of single DBT molecules a) with slow spectral jumping, b) with fast spectral diffusions between four levels, and c) with very fast jumps between many different levels.*

2.3.5. Fluorescence correlation studies

To analyze the dynamics of the spectral jumps of DBT molecules in 2,3-DMA, we measured the autocorrelation functions of the fluorescence intensity for times ranging from 10 µs to 10 s. Figure 2.6.a shows the autocorrelation functions of three example molecules. As was the case for polymers,[13,31] the correlation functions can show mono, bi- or multi-exponential decays attributable to molecules coupled to one, two or more TLSs (Figure 2.6.a).

Figure 2.6.b shows a histogram of the correlation times (in ms) measured on 36 molecules at 1.25 K with an excitation intensity of 1 kW/cm^2. A significant fraction (~50%) of the molecules studied show a well-defined exponential component with a correlation decay rate of around 400 s^{-1}. The time distribution is quite broad with a clear maximum around 2.5 ms. For the few molecules which show multi-exponential decays, all components have been included in the histogram. Our traces were too short to measure reliably times longer than 1 s. The slight excess of rates around 2 s^{-1} may be due to a statistical fluctuation.

We cannot completely exclude the possibility that the component with the correlation time of 2.5 ms is due to the triplet state of DBT. However, observing the correlation due to intersystem crossing would be very difficult with an intersystem crossing-quantum yield of 10^{-7} and a lifetime of 40 µs, as reported for DBT in anthracene[7]. We do not expect the quantum yield and the lifetime of the triplet state to change much upon substitution with two methyl groups.

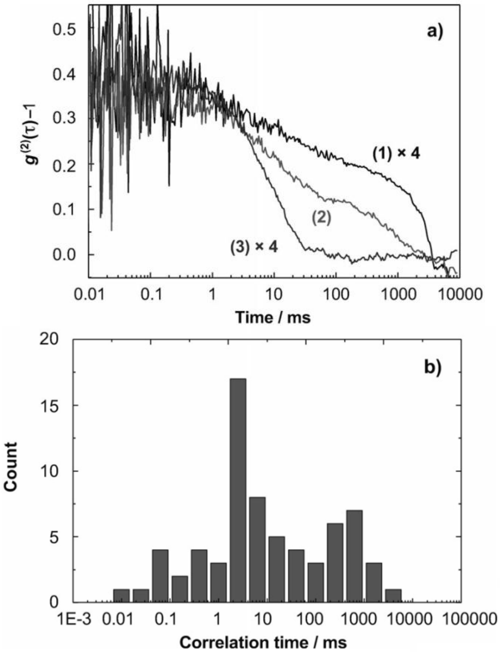


Figure 2.6: *a) Auto-correlation functions of three DBT molecules in 2,3-DMA crystals showing a multi-exponential (1), a bi-exponential (2) and mono-exponential (3) components. b) Histogram of the correlation times measured on 36 DBT molecules. All the measurements were done at 1.25 K with an excitation intensity of 1 kW/cm^2.*

2.3.6. Excitation intensity dependence of the correlations

Measuring the excitation intensity dependence of the spectral jumps was not easy for DBT/2,3-DMA due to the instability of the dye. The molecules often jumped during the measurement to a new frequency outside our scanning range (20 GHz), especially when the excitation intensity was high. Nevertheless, we successfully investigated the excitation intensity dependence for two molecules. Both of them showed bi-exponential decays (see Figure 2.7.a for one example). The two components showed different dependences on the excitation intensity. The fast component (rate~400 s^{-1}) did not seem to have any significant intensity dependence within the range from 0.5 to 200 kW/cm^2

(squares, Figure 2.7.b). The slow component (rate <20 s^{-1}) became faster with increasing excitation intensity, indicating a photo-induced spectral jumping (circles, in Figure 2.7.b).

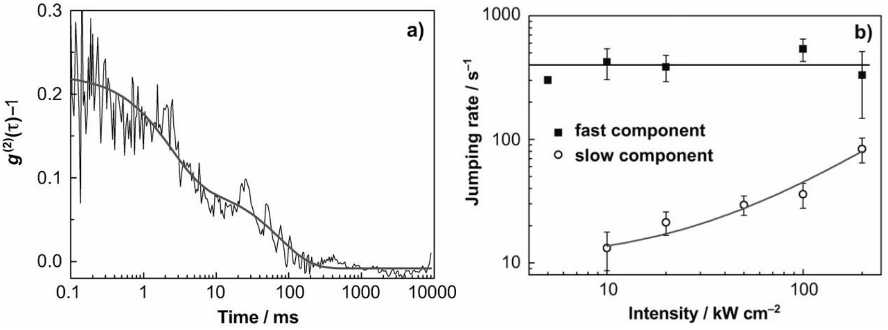


Figure 2.7: a) Correlation function of a single DBT molecule in 2,3-DMA and b) excitation intensity dependence of the fast (■) and slow (○) components. The rates were obtained by bi-exponential fitting of the correlation function. The solid lines are linear fits of the data points with a linear dependence on the intensity, $r = r_0 + aI$.

2.3.7. Temperature dependence of the correlations

We also tried to investigate the temperature dependence of the spectral jumping for several molecules within the range of 1.5–12 K. We discuss the dependence of the fast component from two representative molecules. Molecule 1 (■ in Figure 2.8) shows an increase in the jumping rate with increasing temperature up to 400 s^{-1} above 5 K, whereas molecule 2 (○ in Figure 2.8) shows a rather constant jumping rate with increasing temperature. The slower correlation component, which was observed for a few molecules, did not show any clear temperature dependence.

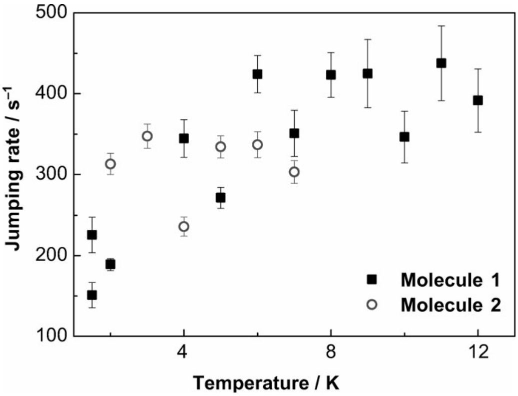


***Figure 2.8:** Jumping rate of the fast component of two DBT molecules in the temperature range 1.5–12 K.*

2.4.Discussion

2.4.1. Heterogeneity

Our results present a large heterogeneity of linewidths (distributed between 0.4 and 3.2 GHz), saturation excitation intensities, spectral jumping (jump sizes and rates), and shifting behaviors. The broad distribution of ZPLs in the inhomogeneous absorption band (350 cm^{-1} wide) has also been reported earlier[22]. Such heterogeneity is generally observed for single molecules embedded in polymer matrices[32] and in another dipolar disordered crystal, 1,2-DCB[18]. Herein, the 2, 3-DMA molecules form an ordered crystal lattice. However, the non-symmetric molecules are randomly oriented, giving rise to dipolar disorder. Based on the crystal structure from DBT in anthracene[6], we assume that, here too, one DBT molecule replaces three host 2,3-DMA molecules. Moreover, we suppose that the insertion site corresponds to the main site of DBT in anthracene. Therefore, the local environment of a DBT molecule in the crystal plane should consist of ten 2,3-DMA molecules. With two different orientations for each of them, and considering the C2 symmetry of the system, there are 512 spectroscopic possibilities for degenerated local environments. Taking into account the orientations of host molecules in the nearby planes, these multiple insertion sites lead to a broad quasi-continuum of spectroscopic sites. The heterogeneity of spectral properties we observed is consistent with the static disorder produced by the environment.

2.4.2. *Spectral diffusion*

The broad linewidth and the high saturation intensity of DBT in 2,3-DMA was the most striking and surprising observation. We safely attributed it to spectral diffusion based on saturation (Figure 2.1), time traces (Figure 2.4), and correlation studies (Figure 2.5). Generally, in crystalline matrices, single molecules are very stable. Well known examples are terrylene in naphthalene or DBT in anthracene, which show stable lines and lifetime-limited linewidths[7]. Although spectral jumping of single molecules has been observed for terrylene or pentacene in *p*-terphenyl, this crystal is a special case because of its ferro-elastic transition. Moreover, the linewidth of guest molecules remains lifetime-limited in most cases[33-35].

The spectral diffusion of DBT in 2, 3-DMA resembles that of terrylene and tetra-ter-butylterrylene (TBT) molecules in polyethylene and other polymers[13,14,31,36,37]. In many cases, the spectral diffusion of a single molecule can be described in terms of its coupling to nearby TLS's. When a TLS which is coupled to the molecule flips, the excitation spectrum jumps between two different frequencies. The jump size and rate depend on physical parameters, such as distance from the molecule, relative orientation, and temperature. For each molecule, the spectral diffusion pattern depends on the density and location of the TLS's.

2.4.3. Model for spectral diffusion

In previous literature, spectral diffusion was observed in systems with structural disorder[13,14,31,36,37] or in crystals with domain walls and other defects[27,33]. Spectral diffusion might thus appear as a general consequence of disorder. However, Gorshelev et al. recently reported stable and lifetime-limited terrylene lines in 1, 2-DCB, even though this crystal presents dipolar disorder[18]. This result is understandable because the orientations of the host molecules, albeit disordered, are fixed at low temperature and cannot give rise to flipping dynamics. Therefore, our observation of a very active spectral diffusion in another crystal with dipolar disorder is surprising. We propose that the main difference between these two dipolar crystals arises from the chemical structure of the host molecules, which includes two methyl groups in the case of 2,3-DMA but not for 1,2-DCB.

The methyl groups in 2,3-DMA present additional degrees of freedom due to the rotational flexibility around the C-CH_3 single bond, which is absent in rigid molecules like anthracene and 1,2-DCB. One of the possible dynamical processes is rotational tunneling of the methyl groups. However, rotational tunneling processes are usually very slow because of spin selection rules. Moreover, their effect on the electronic transition would be very weak if they were not directly substituted on the guest molecule[38]. Another motion able to produce spectral diffusion at low temperature would be a two-level system involving a limited rotation of the CH_3 group within its libration potential well. These reorientations can become possible due to the free space in the lattice caused by dipolar disorder.

In other words, the spectral diffusion would arise from the coexistence within the same structure of strong and weak links, which is known to give rise to complex potential energy landscapes and to additional dynamics[39]. Unexpected spectral dynamics of TBT in toluene (which also has a methyl group) has also been reported by Naumov et al[40]. By analyzing the isotope effect, they proposed that the motion of the methyl group is mainly of librational character and probably gives rise to low-frequency vibration modes. Interestingly, the presence of methyl groups in a crystal does not appear to cause systematically additional dynamics, as was shown in the case of durene (tetramethylbenzene) [41,42]. No evidence for low-temperature dynamics was found from neutron scattering or from calculations in that work. Based on our observations and on the previous ideas, we propose that the spectral diffusion found in the dipolar-disordered crystal 2, 3-DMA originates from a combination of structural disorder of the matrix and of subtle rearrangements of the methyl groups. A systematic experiment was performed to support this conclusion, and is presented in Chapter 3.

2.5.Conclusion

We studied single DBT molecules embedded in a dipolar-disordered crystal, 2,3-DMA. We found broad linewidths, high saturation excitation intensities, as well as spectral instability. Spectral jumping was also observed and investigated further varying the excitation intensity and the temperature. The spectral diffusion and dynamic disorder in this system are believed to arise from a combination of static disorder with a slight reorientation of the methyl groups of the host 2,3-DMA molecules.

Acknowledgement

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