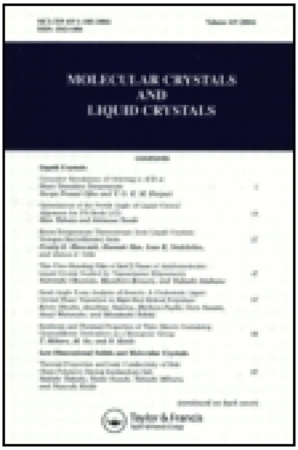

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Single Molecule and Shpolskii Spectroscopy of Terrylene in a Series of N-Alkanes

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SINGLE MOLECULE AND SHPOLSKII SPECTROSCOPY OF TERRYLENE IN A SERIES OF N-ALKANES

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Abstract We present a study of terrylene in a series of *n*-alkane matrices with increasing chain length, namely dodecane, tetradecane and hexadecane. Shpolskii absorption spectra provide the macroscopic characterization of the samples, such as site multiplicity, inhomogeneous line widths and positions. Based on this characterization the distributions of single molecule homogeneous line widths were measured in the maxima and in the wings of the inhomogeneous lines. The results indicate that in case of dodecane matrix the line broadening is caused by optical dephasing due to interaction with pseudolocal phonon modes. Exponential profile of temperature dependence of the line width gives the phonon energy of 23 cm^{-1}. In cases of tetradecane and hexadecane matrices there is additional broadening present which we interpret as spectral diffusion. Further, we present a new method for collecting the single molecule fluorescence using a selfoc micro lens.

INTRODUCTION

Single molecule spectroscopy (SMS)[1,2] has become one of the most advanced methods in the study of solid state matter on microscopic level (for a recent review see e.g. ref.3). Compared to other site-selective spectroscopic techniques such as hole burning it represents qualitative progress in the sense that it removes statistical averaging over a large number of molecules with degenerate optical transition frequency. SMS enables to study the optical properties of individual dye molecules and thus obtain wealth of information about local interactions on nanometer scales. An example is a distribution of single molecule homogeneous line widths. It has been measured for terrylene embedded in a number of crystalline and amorphous hosts[4-7] and mostly argued to be due to spectral diffusion. On the other hand, incoherent photon echo experiments performed on terrylene in polyethylene[8] showed that line broadening was dominated by fast dephasing and the contribution of spectral diffusion was negligible. This discrepancy stems from the long time resolution of SMS experiment which averages all dynamical processes shorter than seconds.

In the present paper we address this question. We measured Shpolskii absorption spectra of terrylene in a series of n-alkanes with different chain lengths. Based on the macroscopic characterization we measured distributions of single molecule line widths in selected regions within the inhomogeneous lines. Further information on molecular dynamics is obtained from the temperature dependence of the homogeneous line width. From the experimental point of view we introduce a new method for collecting the single molecule fluorescence using a selfoc lens and compare its signal-to-noise ratio and light collecting efficiency with a microscope objective.

EXPERIMENTAL

Terrylene (PAH Research Inst.) was dissolved in dodecane, tetradecane and hexadecane (Aldrich) to the final concentrations of 1.6 - 3.1 x 10^{-7} mol/l. Fluorescence of the samples was collected using two experimental configurations.

1. Microscope objective configuration[9,10]: a small amount of the sample solution was pressed between a 5 μm pinhole (Melles-Griot) and 2 micro cover glasses (0.12-0.17 mm thick), and placed at the focus of a microscope objective (magnification 20x, N.A. 0.40, working distance 1.5 mm).

2. Selfoc lens configuration: one side of a SELFOC Micro Lens (Nippon Sheet Glass type W20S25-063N; pitch 0.25, N.A. 0.46) is coated by sputtering with a 0.5 μm tungsten coating. The center of the coating is etched by a focused Au^{2+} ion beam to form a spot of approximately 4 μm in diameter. The spot was covered with a tiny amount of the sample solution and the whole selfoc lens is pressed and fixed against a micro cover glass (0.12 - 0.17 mm thick). Details can be found elsewhere[11].

In both configurations the samples were mounted in an optical bath cryostat (Torisha) working at 1.7 K. The fluorescence excitation spectra were measured by scanning a single mode dye laser (Coherent 699-29, Rhodamin 6G, jitter < 4 MHz). The laser output light was focused on the sample after passing an amplitude stabilizer and an interference filter. The sample fluorescence was focused into a parallel beam and detected with a cooled photomultiplier (Hammamatsu R943-02). The excitation light was separated from the fluorescence by three RG 610 Schott filters. The signal was processed in a Stanford SR400 photon counter.

Shpolskii spectra were measured by scanning a 1.5 m double-pass monochromator (Jobin Yvon THR 1500). The sample solutions of the above concentrations were loaded in 5 mm thick quartz optical cells and placed in a continuous flow cryostat (Oxford 1204) at 4.2 K.

RESULTS AND DISCUSSION

Collection of single molecule fluorescence with a selfoc lens

Fluorescence excitation spectrum of terrylene in hexadecane measured with the selfoc lens is shown in Figure 1. Within the 10 GHz scan range the spectrum exhibits one strong single molecule line with a Lorentzian lineshape. The signal-to-noise ratio (S/N) of 8.5 was obtained with the exciting laser intensity of 82 mW/cm^2. To obtain comparable S/N with the microscope objective we typically needed 4-5 times higher excitation intensity. This indicates considerably higher light collecting efficiency of the selfoc lens. The main reason for the higher efficiency is that the number of optical surfaces is reduced from 8 in case of the microscope objective (plus sample substrate), to just 2 in case of the selfoc lens. Apart from reflection losses the optical surfaces which are in contact with liquid helium are exposed to contamination during the cooling cycles. Other reasons include slightly higher N.A. of the selfoc lens (0.46 compared to 0.40) and complete elimination of any relative vibrations between the sample and light collective element. To add evidence that the observed line comes from the terrylene single molecule we measured its saturation behavior (the result is not shown). The behavior

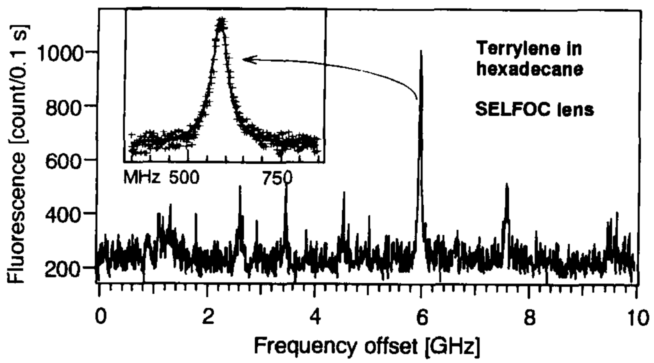

FIGURE 1
Single molecule fluorescence excitation spectrum at 1.7 K. The inset shows detailed scan of the most intense line together with its Lorentzian fit.

itself and the obtained saturation parameters agree reasonably with those reported by others[12,13] as well as with those obtained by us with the microscope objective. The obtained zero power line width limit is 45 MHz, the saturated fluorescence count rate is 30000 count/s and the saturation laser power is 380 mW/cm^2.

Shpolskii absorption spectra

Absorption spectrum at 4.2 K of terrylene in dodecane in the region of 0-0 electronic transitions is shown in Figure 2. There are five principle sites appearing between 550 and 575 nm (labeled A-C). Similar site pattern is a common feature in all solvents studied. The respective site maxima vary by less than 0.4 nm in different solvents. In analogy with perylene in *n*-heptane[14] and other organic dyes in *n*-alkane crystals[15,16] we assume that in site A one terrylene replaces two *n*-alkane molecules. Its longer axis is oriented along the alkane chain axis and its plane is nearly perpendicular to the crystal growth axis (that is, almost inplane with the alkane chains). Our further study is confined to the A site; Figure 3 shows its detailed spectra in all three solvents. In dodecane the line has a near perfect Gaussian profile with a width of 0.26 nm. In tetradecane the central Gaussian line is accompanied with a few minor sites. In hexadecane the minor sites seem to grow up to form a complex non-Gaussian line with a width of 0.54 nm.

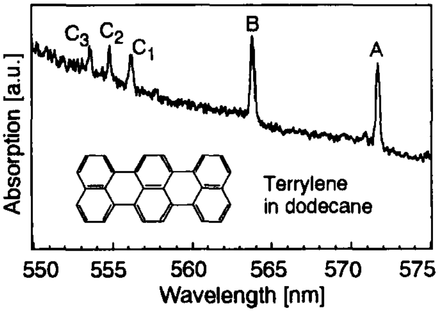

FIGURE 2 Shpolskii absorption spectrum at 4.2 K in the region of 0-0 transitions

Distributions of single molecule line widths

The distributions of single molecule homogeneous line widths were measured at the peaks and at the wings (or minor sites) of the inhomogeneous absorption lines, as indicated in Figure 3 by horizontal bars. The results for the three solvents are shown in Figure 4. The single molecule lines were scanned with 2 MHz resolution with the laser power well below the power broadening limit (determined from power dependencies of the line widths). Each line was fitted with Lorentzian line function and the obtained fit parameter was used as line width in the statistics. Spectrally jumping, weak or irregular shaped lines were excluded from the analyses; typically 2-3 molecules in 10 GHz scan could be used. Each histogram in Figure 4 is a result of several experimental days using different samples preparations. The line width distributions obtained around the maxima of the inhomogeneous lines (a,c,e in Figure 4) are centered at the 50 MHz interval. Those obtained at minor sites (d) or wings (b) have their centers shifted to the 60 MHz interval. It means that most of the molecular lines are broader than the fluorescence life-time limited value (estimated[12] to be 42 MHz).

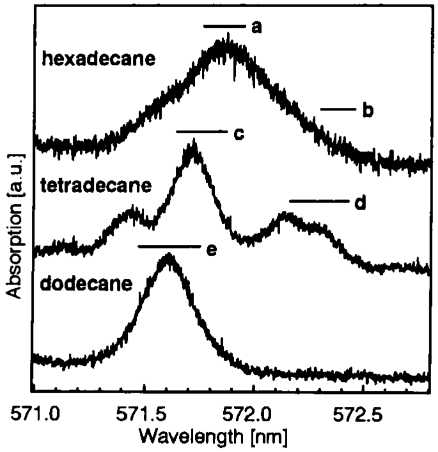

FIGURE 3 Detailed absorption spectra of site A at 4.2 K. Horizontal bars indicate regions where line width distributions were measured.

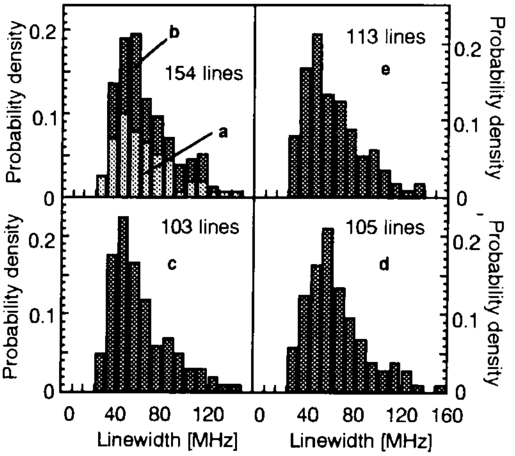

FIGURE 4 Histograms of single molecule line width distributions measured at 1.7 K. Letters a-e correspond to FIGURE 3.

To get more information about the line broadening mechanisms we measured temperature dependencies of the line widths. The results for dodecane (near the maximum of the inhomogeneous band, full dots) and for hexadecane (at the wing of the band, open squares) are shown in Figure 5. In spite of rather large scattering of the experimental points we managed to fit the results for dodecane with an exponential:

$$\Gamma(T) = \Gamma(0) + a.\exp(-h\omega_0/k_BT)$$

where $\Gamma(T)$ is the line width, a a constant, k_B the Boltzman constant and ω_0 an energy parameter. The fit gives the ω_0 value of 23 cm^{-1}. Unfortunately, the terrylene molecule in hexadecane was burned out of resonance below 3 K making it impossible to reasonably fit the data. Exponential temperature dependence is characteristic for organic molecules in crystalline matrices[17]. Thus, the temperature behavior of terrylene in dodecane is determined by the crystal properties of the matrix. This is because dodecane forms an almost perfect Shpolskii matrix as reflected by the absorption spectra. The dodecane chain length (1.40 nm; extrapolated from ref.15,18) matches well the terrylene longer axis (1.15 nm; deduced from perylene crystal structure[19]). The observed line broadening is most likely caused by optical dephasing involving pseudo-local phonon mode of the frequency 23 cm^{-1}. Similar conclusion has been reached for terrylene in another good Shpolskii matrix of *p*-terphenyl[20].

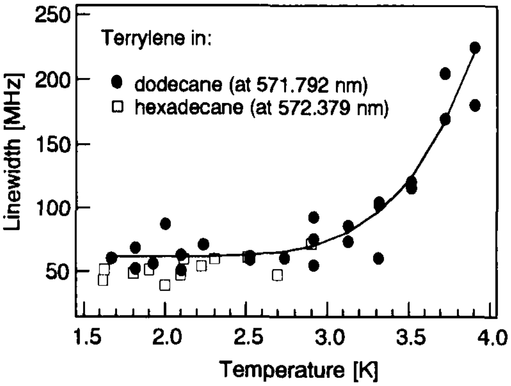

FIGURE 5 Temperature dependence of single molecule line width. Solid line is exponential fit for full dots (see text).

The situation is different for tetradecane and hexadecane. Here the alkane chain is considerably longer (almost twice in case of hexadecane) than the terrylene longer axis (tetradecane length 1.66 nm, hexadecane length 1.91 nm). This gives the terrylene wider choice of positions along the alkane crystal cage where it can be frozen. The positions in the center of the cage most resemble the situation of dodecane. We assume that these positions correspond to the center of the inhomogeneous band (in case of hexadecane) or to the main Gaussian band (in case of tetradecane) where also the single molecule line broadening is similar to dodecane. On the other hand, at the extreme positions on the edge of the cage the terrylene molecules leave large parts of the crystal cage empty. These empty parts provide space for possible conformational changes of the matrix. Such changes would affect the transition frequency of terrylene (e.g. giving rise to minor sites or larger inhomogeneous width), and, at the same time, may lead to spectral diffusion causing additional single molecule line broadening.

We note that similar effect was observed long ago in hole burning of chlorin in *n*-alkanes[21]. In hexane the holes were stable. In octane, and increasingly in decane they recovered even at dark pointing to increasing thermal instabilities of matrices with longer alkane chains.

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