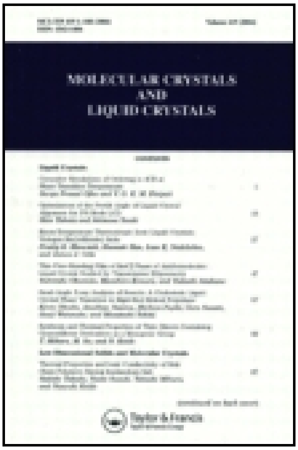

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Single Molecule Spectroscopy and Spectral Hole-Burning

Hermann Bach [a], Thomas Irngartinger [a], Alois Renn [a] & Urs P. Wild [a]

[a] Physical Chemistry Laboratory, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092, Zurich, Switzerland

Version of record first published: 04 Oct 2006.

To cite this article: Hermann Bach, Thomas Irngartinger, Alois Renn & Urs P. Wild (1996): Single Molecule Spectroscopy and Spectral Hole-Burning, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 291:1, 89-95

To link to this article: http://dx.doi.org/10.1080/10587259608042735

Mol. Cryst. Liq. Cryst., 1996, Vol. 291, pp. 89–95
Reprints available directly from the publisher
Photocopying permitted by license only

SINGLE MOLECULE SPECTROSCOPY AND SPECTRAL HOLE-BURNING

HERMANN BACH, THOMAS IRNGARTINGER, ALOIS RENN, AND
URS P. WILD*
Physical Chemistry Laboratory, Swiss Federal Institute of Technology,
ETH Zentrum, CH-8092, Zürich, Switzerland

Abstract Spectral hole-burning in the Shpol'skii system terrylene in n-octane has been investigated on the single molecule level. Fluorescence microscopy provides a link between the two methods of spectral hole-burning and single molecule spectroscopy. Information about many different individual molecules can be obtained simultaneously under identical experimental conditions allowing the determination of statistical properties. From a single frequency scan after spectral hole-burning, the ground state population function and an average hole-width, as well as the single molecule linewidth distribution of 700 molecules have been determined.

INTRODUCTION

Spectral hole-burning and single molecule spectroscopy of impurity centers in the solid state are sensitive spectroscopic techniques to probe guest-host interactions[1,2]. While the parameters obtained in a hole-burning experiment are average values reflecting the behavior of an ensemble of probe molecules, single molecule spectroscopy gives access to the individual properties of these molecules. It is fascinating to derive the parameters observed in a hole-burning experiment from experiments on single molecules. An easily accessible parameter in hole-burning is the hole-width and in single molecule spectroscopy is the individual linewidth. For terrylene in different polymeric and crystalline matrices, hole-width and single molecule linewidth distributions have been measured under different experimental conditions[3]. In order to compare the average values and the distributions of parameters it is advantageous to determine the parameters of many individual molecules simultaneously in a single experiment.

In this paper we report on an observation of spectral hole-burning in the Shpol'skii system terrylene in n-octane on the single molecule level. By means of fluorescence microscopy, many molecules were studied in parallel. From a single frequency scan after spectral hole-burning, the ground state population function and an average hole-width, as well as the single molecule linewidth distribution were obtained. N-octane was chosen as a matrix because a reasonable photophysical hole-burning efficiency was anticipated due to a geometrical misfit of terrylene in the n-octane lattice[4].

EXPERIMENTAL

Sample Preparation

A ~$2*10^{-7}$ M solution was prepared by dissolving terrylene (purchased from Dr. Schmidt, Institute for PAH research, Germany) in n-octane (Fluka, puriss). A small droplet of the solution was placed between two cover glasses to form a thin film. The sample was mounted on a holder at the working distance of a microscope objective and then inserted in a precooled cryostat to form a polycrystalline Shpol'skii system. All experiments were performed at 1.8 K.

Optical Setup

A single mode dye laser with Rhodamine-6G was used as an excitation source. The fluorescence light from a sample area (approximately 200 μm x 200 μm) was collected with a microscope objective (Newport type M-60 x / NA = 0.85) and imaged on a two-dimensional detector (video camera Hamamatsu C2400-25 and image intensifier). The laser light was rejected by a holographic notch filter (Kaiser HNPF-572-1.5) and two cut-off filters (Schott RG-610). The video frames obtained with a repetition rate of 25 Hz were processed with a real time processor (Datacube Maxvideo 10) and stored on a computer for subsequent analysis. More details on single molecule microscopy can be found elsewhere[5,6,7].

Experiment

The spectral hole-burning experiment was performed as follows: first, a spectral hole was burned by irradiating the sample with fixed laser frequency (λ=571.978 nm / I ~ 0.2 W/ cm^2) for 217.5 seconds. 50 fluorescence images formed by integrating over 16 video frames in real time (0.64 seconds integration time) in intervals of 4.35 seconds were recorded during the hole-burning process. Subsequently, a 2 GHz frequency scan in 10 MHz steps with the same laser power was performed. At every frequency position a fluorescence image was recorded with the parameters specified above resulting in a total

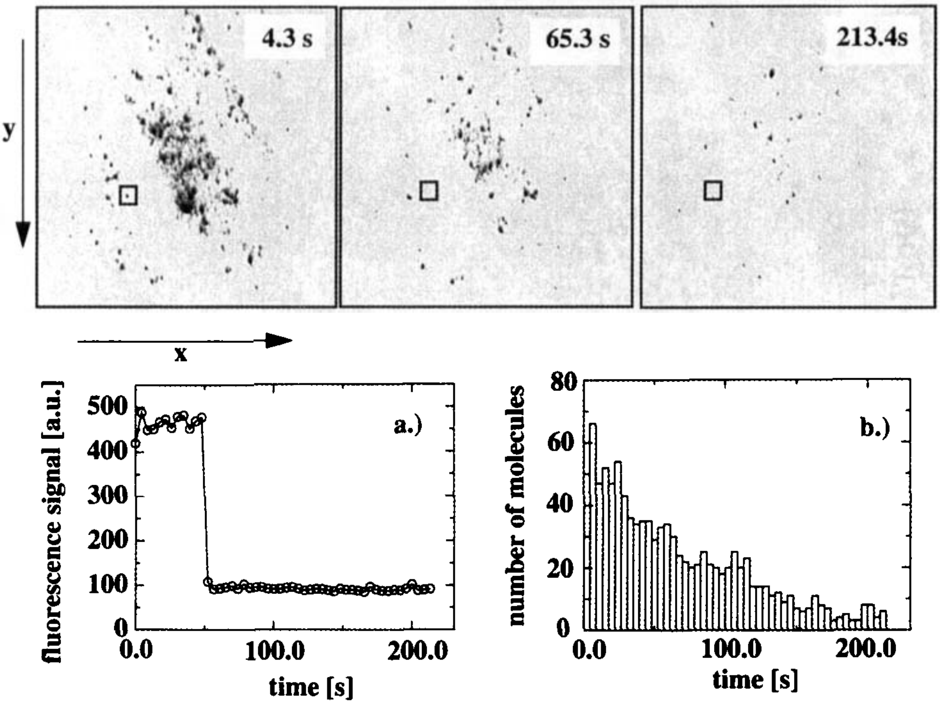

FIGURE 1 Upper images: Fluorescence images of a sample area (approximately 200 μm x 200 μm) recorded with fixed laser frequency (λ=571.978 nm / I ~ 0.2 W/ cm^2) during the spectral hole-burning process at 1.8 K. a.) Fluorescence signal of a single molecule obtained by integrating a 2 x 2 pixel area sketched in the images. b.) Histogram of the number of molecules per image.

recording time for the 200 images of 14.5 minutes. The laser was probing the sample during the integration period of 0.64 seconds for each image to reduce the effect of hole-burning during read out. The result of both experiments are 3D-data cubes with two spatial coordinates and a time or a frequency dimension, respectively.

RESULTS AND DISCUSSION

Holeburning Kinetics

The upper part of Figure 1 shows fluorescence images recorded during the hole-burning process with fixed laser frequency. The number of molecules visible in the images decreases with irradiation time. Figure 1 a.) shows the signal from a single molecule obtained by integrating over a 2 x 2 pixel area sketched in the upper images. The molecule is in resonance for about 50 seconds and then disappears suddenly. Not all the mole-

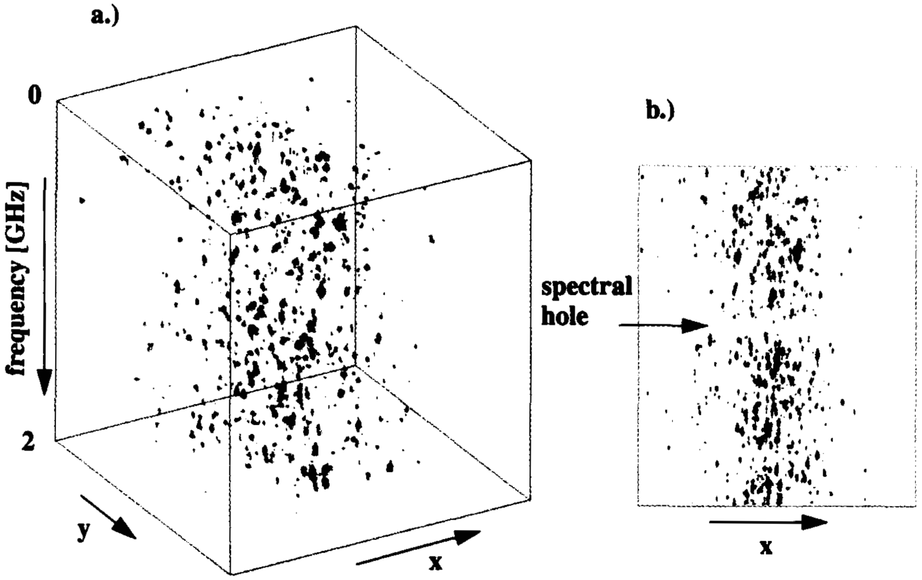

FIGURE 2 3D data cube obtained by recording 200 fluorescence images in 10 MHz steps after the spectral hole-burning at the center frequency. The fluorescence signals from single molecules are represented by dark spots b.) Projection of the data cube on the x, z plane. The spectral hole is marked with an arrow.

cules behave like the one shown in Figure 1 a.). Some disappear permanently, some molecules reappear and very few molecules not visible in the beginning jump into resonance during the progress of the experiment. These spectral dynamics account for the fluctuations in the sum of molecules per image as shown in Figure 1 b.).

Holewidth and single molecule linewidths

Figure 2 a.) shows a three dimensional representation of the 2 GHz frequency scan performed after the hole-burning experiment. The x and y axes are the spatial coordinates, and the z axis represents the frequency axis. The fluorescence signals from the individual molecules are represented by dark spots. This data cube was obtained by combining the information from 200 fluorescence images recorded in 10 MHz steps. Figure 2 b.) shows a projection of the data cube on the x, z plane. The spectral hole burned in the first experiment - indicated by a reduced density of single molecules in the central frequency range - is marked with an arrow. The analysis of the fluorescence signals from approximately 3000 molecules contained in the 3D data cube allows the simultaneous determination of

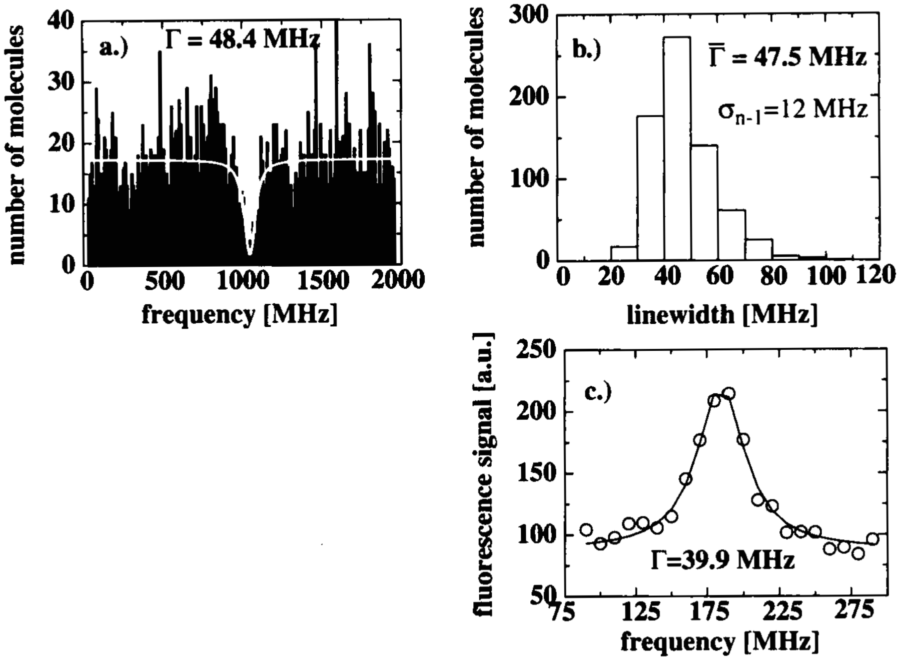

FIGURE 3 a.) Number of molecules versus frequency as derived from the 3D data cube shown in Figure 2. Each molecule is only counted once at its maximum intensity. The white solid line represents a fit of equation (1) to the data. b.) distribution of single molecule linewidths. c.) lineshape of a single molecule with Lorentian fit.

the distribution of single molecule linewidths and the spectral hole-width.

Figure 3. a.) shows the number of molecules versus frequency - the ground state population function $N^{\tau}(\nu)$ - after burning for τ=220s. Each molecule in the data cube is counted once at its maximum intensity. In spectral hole-burning, the ground state population function $N^{\tau}(\nu)$ for molecules that undergo hole-burning by absorption through its zero phonon line positioned at frequency ν after burning at ν_L for a time τ is described by[1]:

$$N^{\tau}(\nu) = N(\nu)_0 \cdot \exp\left(\frac{-(\Gamma/2)\cdot\tau\cdot k}{(\nu_L-\nu)^2+(\Gamma/2)^2}\right) \qquad (1)$$

where Γ is the single molecule homogeneous linewidth (FWHM) and k contains the laser intensity, the absorption cross section and the hole-burning yield. From a nonlinear least squares fit of equation (1) to the data we obtain a linewidth of Γ=48 MHz which is slightly higher then the lifetime limited value of 42 MHz[8].

This value is an average value since the linewidths of single molecules are actually distributed. Figure 3 b.) shows the linewidth histogram for those 700 out of the detected 3000 molecules where the linewidth determination by a Lorentzian fit was possible. Figure 3 c.) shows a single molecule lineshape with a Lorentzian fit. Some of the observed molecules jumped out of resonance during the scan or could not be resolved as single molecules. An asymmetry of the distribution with a tail to longer linewidth and a low power cut off at about 35 MHz is visible which is in good agreement with the linewidth distribution in different matrices reported so far[3]. The few molecules at 25 MHz are attributed to an inaccuracy of the single molecule linewidth determination, caused by the 10 MHz resolution of the experiment. From the histogram, an average linewidth of 47 MHz with a standard deviation of 12 MHz was calculated, which agrees well with the hole-width of 48 MHz obtained from the fit to the ground state population function. Both, the hole-width and the single molecule linewidth can be affected by broadening mechanisms. Fluence broadening of the hole can be neglected here because the ground state population function obtained in the experiment is described for all fluences by equation (1). At the excitation intensity of approximately 0.2 W/cm^2 used in this experiment no power broadening of terrylene molecules is expected[8]. An additional experiment with laser power three times higher showed no significant change of the linewidth histogram.

CONCLUSIONS

We investigated photophysical spectral hole-burning of terrylene in n-octane on the single molecule level. The photobleaching of many molecules in parallel was monitored. From a single frequency scan performed after hole-burning, the ground state population function, the average hole-width, and the single molecule linewidth distribution were obtained. The hole-width agreed well with the average linewidth calculated from the histogram of the single molecule linewidth distribution.

In further investigations, fluorescence microscopy will be applied to study photophysical hole-burning in even more detail. With improved time resolution (shorter integration and storage times) it should be possible to perform frequency scans before and during hole-burning and it might be possible to observe other distributions, e.g a distribution of burning rates, from such experiments.

ACKNOWLEDGMENT

We thank Markus Traber for writing the real time data acquisition routines and Jürg Keller for help with data analysis and visualization. This work was supported in part by the Swiss National Science Foundation, and by ETH-Zürich.

REFERENCES

1. J. Friedrich and D. Haarer, Angew. Chem. Int. Ed. Engl., 23, 113, (1984)
2. W.E. Moerner and Th. Basché, Angew. Chem. Int. Ed. Engl., 32, 457, (1993); M. Orrit, J. Bernard, and R.I. Personov, J. Chem. Phys., 79, 10256, (1993), W.E. Moerner, Science, 265, 46, (1994); L. Kador, Phys. Stat. Sol. (b), 189, 11, (1995), U.P. Wild, Nova Acta Leopoldina NF72, 294, 237, (1996)
3. B. Kozankiewicz, J. Bernard, and M. Orrit, J. Chem. Phys., 101, 9377 (1994)
4. K. Palewska, J. Lipinski, J. Sworakowski, J. Sepiol, H. Gygax, E.C. Meister, and U.P. Wild, J. Phys. Chem., 99, 16835, (1995)
5. J. Jasny, J. Sepiol, T. Irngartinger, M. Traber, A. Renn, and U. P. Wild, Rev. Sci. Instrum., 67(4), 1425, (1996)
6. M. Croci, T. Irngartinger, A. Renn, and U. P. Wild, Experimental Technique of Physics, 41(2), 249, (1995)
7. M. Croci, H.J. Müschenborn, and U.P. Wild in Optical Probing of Single Molecules, edited by T. Basché, W.E. Moerner, M. Orrit and U.P. Wild, to be published
8. W.E. Moerner, T. Plakhotnik, T. Irngartinger, M. Croci, V. Palm, and U. P. Wild, J. Phys. Chem., 98, 7382, (1995)