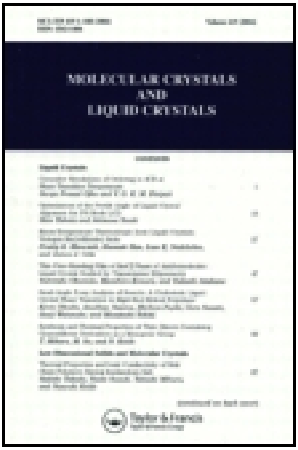

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Spectral Hole Burning in the Single-Molecule and Few-Molecule Limit: Terrylene in p-Terphenyl

Lothar Kador [a] & Andreas Müller [a]

[a] University of Bayreuth, Institute of Physics and “Bayreuther Institut für Makromolekülforschung (BIMF)”, D-95440, Bayreuth, Germany

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Spectral Hole Burning in the Single-Molecule and Few-Molecule Limit: Terrylene in *p*-Terphenyl

LOTHAR KADOR and ANDREAS MÜLLER
University of Bayreuth, Institute of Physics and "Bayreuther Institut für Makromolekülforschung (BIMF)", D-95440 Bayreuth, Germany

Persistent hole burning is possible in the inhomogeneous absorption bands X_1 and X_3 of the system terrylene in *p*-terphenyl. Whereas the holes are stable in X_1, they decay with a time constant of a few seconds in X_3. In crystals with very low dye concentration, shallow holes can be observed which consist of few (or even one single) molecular lines and can be distinctly narrower than twice the homogeneous linewidth. Monte Carlo simulations confirm the experimental findings.

Keywords: spectral hole burning; single-molecule spectroscopy; Monte Carlo simulations; terrylene; *p*-terphenyl

INTRODUCTION

Terrylene in *p*-terphenyl is one of the systems which are well suited for the optical spectroscopy of single dye molecules in solid matrices. Attractive features are its narrow homogeneous linewidth of about 40 MHz and the high achievable photon count rates up to 600,000 s^{-1}[1]. The optical absorption spectrum is characterized by four inhomogeneous zero-phonon bands (X_1, ..., X_4) at low temperatures which correspond to the electronic transition $|S_1\rangle \leftarrow |S_0\rangle$ and are caused by different local sites of the dopant molecule in the host crystal[1]. In two of the bands (X_2 and X_4) the molecular lines are stable, whereas in the other two they are subject to photobleaching. Recently it was shown that, starting from X_1, four new spectral positions can be optically populated and that optical switching of individual molecules between these positions is possible[2]. In crystals of slightly higher dye concentrations, the generation of spectral holes was observed in bands X_3[3] and X_1[4].

EXPERIMENTAL

Hole-burning spectra in crystals with very weak inhomogeneous absorption bands of terrylene were investigated with a fluorescence technique in an experimental set-up designed for single-molecule spectroscopy[3]. The measurements were performed at a temperature of 1.8 K. Growing the crystals was accomplished by co-sublimation of terrylene and *p*-terphenyl in evacuated glass cells at about 170° C.

RESULTS AND DISCUSSION

By the sublimation method, crystals of strongly different dye concentrations are obtained. Some of them contain virtually no terrylene molecules, whereas in others reasonably high absoption bands (with signal amplitudes of about five to ten times a single-molecule signal) are observed. For the hole-burning experiments, the crystals with the highest concentrations were selected.

Few-Molecule Hole Burning in Band X_1

Figure 1 shows a section of the fluorescence excitation spectrum near the maximum of the inhomogeneous X_1 band (upper curves). The statistical fine structure, *i. e.*, the static "noise" which is due to the statistical fluctuations of the number of molecular lines per homogeneous linewidth[5], is clearly visible. Between the two scans, the laser was held fixed at the center frequency position for 20 seconds with the same power which was used for recording the spectra. The decrease of the fluorescence signal around the burning position (plus a second spectral change at +0.42 GHz) is obvious. The lower trace is the difference spectrum which shows the changes more clearly. A Lorentz fit to the central feature (thick solid line) yields a spectral width (FWHM) of 32 ± 8 MHz which is in reasonable agreement with the single-molecule linewidth of 42 ± 4 MHz[1]. The width is distinctly narrower than twice the homogeneous linewidth which is the lower limit of the hole width when the inhomogeneous band and the hole spectrum are composed of a large number of lines[6]. Hence, we can conclude that the

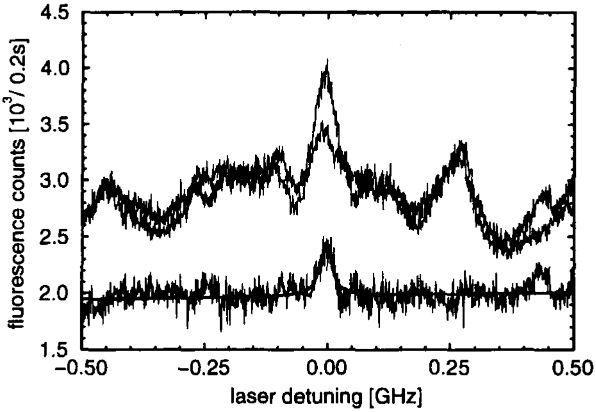

FIGURE 1 Spectral region in the inhomogeneous band X_I before and after laser irradiation for 20 s. The lower trace shows the difference spectrum together with a Lorentz fit to the central feature.

hole in Fig. 1 probably consists of only one single missing molecule.

In order to understand these narrow hole spectra and their saturation broadening behavior[6,7] more quantitatively, we performed Monte Carlo simulations. We built an inhomogeneous absorption band on the computer by adding up Lorentzian single-molecule lines with a Gaussian probability distribution. Afterwards, the hole-burning process was simulated by taking away molecules one by one, with the probability given by the amplitude of the respective molecular lines at the burning frequency. The results of three different runs are shown in Fig. 2. In each case, the ratio between Gaussian and Lorentzian width was 70 and the total number of molecules in the inhomogeneous band 1000. The broadening behavior of the three holes (and also the extrapolated width for zero hole area) is distinctly different. It cannot be described by a common master curve but rather depends on the local statistical fine structure around the burning frequency. If the fine structure has a maximum at this position, more molecules can be burned away before significant broadening occurs[8].

Dynamical Hole Burning in Band X_3

Spectral hole burning is also possible in band X_3[3], but the holes are not stable and cannot be observed in a usual scan of about one minute duration. Detecting the hole-burning process is possible, however, by irradiating the laser at a fixed frequency and observing the fluorescence intensity as a

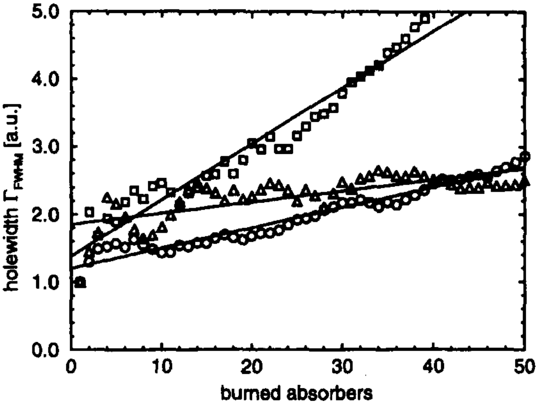

FIGURE 2 Computer simulations of the depletion broadening of hole spectra in the few-molecule limit. The symbols represent three different runs (with three different inhomogeneous bands). The hole width is plotted in units of the single-molecule linewidth.

function of time. This is shown in Fig. 3. During an initial period of

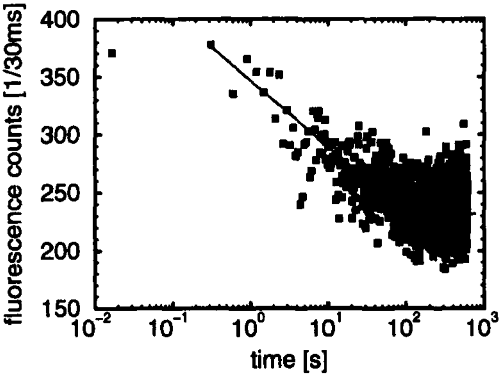

FIGURE 3 Fluorescence intensity during laser irradiation in band X_3 as a function of time.

about 50 seconds, the signal decreases and then reaches a constant level. The increasing amplitude of the noise is also an indication of the dynamical burning process: At any time, molecular lines are burned away while others keep returning to their original frequency positions. The corresponding signal fluctuations increase with increasing depth of the hole.

Reversible Photobleaching of Single-Molecule Lines

In some cases, also single-molecule lines show reversible photobleaching, as Fig. 4 demonstrates. The investigated spectral region is located close to the X_1 position and contains four strong single-molecule peaks. All of the scans were performed with the same laser intensity of about 20 W/cm^2 which is close to the saturation intensity of terrylene in *p*-terphenyl[1]. The two leftmost lines undergo distinct spectral changes during the scans. In particular the line at the center frequency exhibits dark intervals in which the fluorescence drops to the background level. These intervals are longer than one second in some cases which is much longer than the lifetimes of the triplet sublevels of 0.28 ms and 12 ms[9]. (The dwell time per data point was 90 ms.) Hence, we ascribe them to photoinduced spectral jumps and subsequent spontaneous back-reactions of the molecules ("reversible single-molecule hole burning"). The jumps were observed at all illumination intensities but the rate at which they occur turned out to increase with intensity. A similar effect had earlier been found on single perylene molecules in the semi-crystalline polymer polyethylene[10].

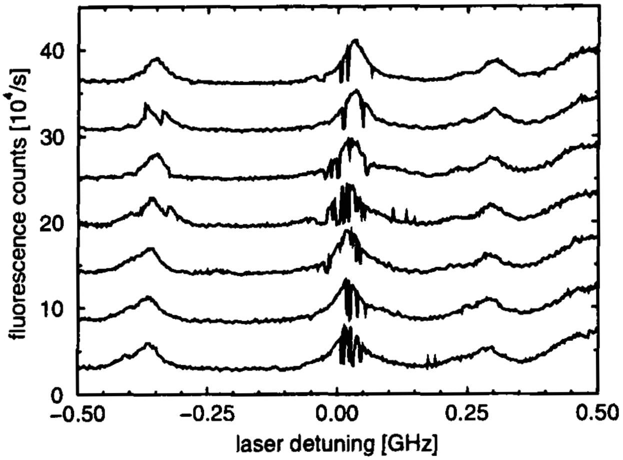

FIGURE 4 Repeated scans of four single-molecule lines in the vicinity of band X_1. The central line shows dark intervals.

CONCLUSIONS

It was demonstrated that various aspects of persistent spectral hole burning can be observed on the system terrylene in *p*-terphenyl in the limit of single and few molecules. In the inhomogeneous band X_1, permanent spectral changes were found which are most probably due to one single missing molecular line. In band X_3, the hole-burning process is reversible and a dynamical equilibrium between burned and spontaneously returning lines was observed. Finally, a similar process of burning and spontaneous back-reaction was also exhibited by some single molecules in the spectral vicinity of band X_1. Here the phototransformation gives rise to dark intervals in the fluorescence signal with durations up to more than one second.

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References

[1] S. Kummer, Th. Basché, and C. Bräuchle, *Chem. Phys. Lett.*, **229**, 309 (1994).

[2] F. Kulzer, S. Kummer, R. Matzke, C. Bräuchle, and Th. Basché, *Nature*, **387**, 688 (1997).

[3] A. Müller, W. Richter, and L. Kador, *Chem. Phys. Lett.*, **241**, 547 (1995).

[4] A. Müller, W. Richter, and L. Kador, *Mol. Cryst. Liq. Cryst.*, **283**, 185 (1996).

[5] T. P. Carter, M. Manavi, and W. E. Moerner, *J. Chem. Phys.*, **89**, 1768 (1988).

[6] S. Völker, R. M. Macfarlane, A. Z. Genack, H. P. Trommsdorff, and J. H. van der Waals, *J. Chem. Phys.*, **67**, 1759 (1977).

[7] L. Kador, G. Schulte, and D. Haarer, *J. Phys. Chem.*, **90**, 1264 (1986).

[8] A. Müller, W. Richter, and L. Kador, *Chem. Phys. Lett.* (submitted for publication).

[9] M. Vogel, A. Gruber, J. Wrachtrup, and C. v. Borczyskowski, *J. Phys. Chem.*, **99**, 14915 (1995).

[10] Th. Basché, W. P. Ambrose, and W. E. Moerner, *J. Opt. Soc. Am. B*, **9**, 829 (1992).