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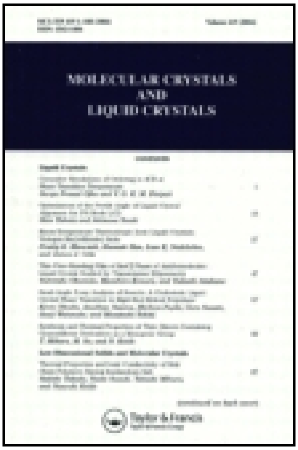

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Single-Molecule Spectroscopy and Persistent Hole Burning of Terrylene in p-Terphenyl: External-Field Effects

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Version of record first published: 04 Oct 2006.

To cite this article: Lothar Kador , Andreas Müller & Wolfgang Richter (1996): Single-Molecule Spectroscopy and Persistent Hole Burning of Terrylene in p-Terphenyl: External-Field Effects, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 291:1, 23-29

To link to this article: http://dx.doi.org/10.1080/10587259608042726

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Mol. Cryst. Liq. Cryst., 1996, Vol. 291, pp. 23–29
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SINGLE-MOLECULE SPECTROSCOPY AND PERSISTENT HOLE BURNING OF TERRYLENE IN *p*-TERPHENYL: EXTERNAL-FIELD EFFECTS

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Abstract Fluorescence excitation spectra of single terrylene molecules in *p*-terphenyl crystals were investigated at low temperatures. The line shifts due to hydrostatic pressure and external electric fields were measured, with the electric field strength oriented either parallel or perpendicular to the $\underline{k}$ vector of the laser light. A linear Stark effect was found for most molecules, indicating local environments of low symmetry. In sites X_1 and X_3 (and XY, a photoproduct state), spectral hole burning was observed. Whereas the holes are stable in sites X_1 and XY, they decay with a time constant of some minutes in X_3. Pressure experiments were performed on the stable hole spectra in sites X_1 and XY. In weakly doped samples, holes composed of very few molecular lines were generated with halfwidths distinctly narrower than twice the homogeneous linewidth.

INTRODUCTION

The optical spectroscopy of single dopant molecules in solids at low temperatures has made tremendous progress since its first demonstration.[1,2] Whereas in conventional site-selective spectroscopic techniques such as fluorescence line narrowing or persistent hole burning the signal still arises from a large number of molecules with only the inhomogeneous broadening eliminated, single-molecule spectroscopy is the only method which is not affected by any kind of ensemble average. Hence, with this techique it was proved that not only the magnitude of the solvent shift but also a number of other spectroscopic properties such as the (quasi-)homogeneous linewidth,[3,4] the spectral-diffusion behavior,[3,5] or the stability with respect to phototransformations[4] can be very different among the dopant molecules in a sample. For further details, the reader is referred to recent review articles.[6–8]

An important application of single-molecule spectroscopy has been the investigation of truly local external-field effects. The line shift due to hydrostatic pressure was studied for the dye molecules pentacene[9] and terrylene[10,11] in *p*-terphenyl crystals, and Stark effect measurements were performed on pentacene in *p*-terphenyl[12] and on terrylene in the partly amorphous polymer polyethylene.[13,14] A linear red shift with increasing pressure was found in all experiments, corresponding to an increase of the solvent shift upon compression of the matrix. The Stark shift, on the other hand, is linear in the polymeric system terrylene in polyethylene[13,14] and quadratic in the mixed crystalline system pentacene in *p*-terphenyl.[12] The presence of matrix-induced dipole moments shows that the local molecular environment must have a low symmetry in the polymer.

In the present study, the system terrylene in *p*-terphenyl was investigated. The line shifts due to hydrostatic pressure and static electric fields were measured. In addition, hole-burning experiments in the "few-molecule limit" were performed in which the hole width can be narrower than twice the homogeneous linewidth.

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EXPERIMENTAL

The principles of our experimental set-up were described previously.[10,11] Briefly, the light of a tunable single-mode dye laser Coherent CR 599-21 was focused onto the sample with a $f = 10$ mm lens inside the cryostat. The red-shifted fluorescence was collected either with an elliptical or a parabolic mirror. Hydrostatic pressure was applied by means of a pressure cell which contained both the focusing lens and the collecting mirror and which was connected to a helium gas cylinder. For the Stark effect studies, two different geometries were used. The electric field was applied to the sample either by means of two copper electrodes or by ITO coatings on two LiF plates between which the sample was placed. In the first case, the electric field strength $\underline{E}_{ext}$ was oriented perpendicular and in the second case parallel to the $\underline{k}$ vector of the laser light. Thin single crystals with a thickness of about 10 μm were grown by co-sublimation of *p*-terphenyl and terrylene at a temperature around 175°C.

RESULTS AND DISCUSSION

Pressure Experiments

The long-wavelength optical absorption spectrum of terrylene in *p*-terphenyl consists of four inhomogeneous bands, X_1 – X_4, corresponding to the presence of four inequivalent *p*-terphenyl molecules per elementary cell in the low-temperature phase.[15,16] In addition, a fifth band, XY, can be generated by laser irradiation into band X_1; it is located between X_1 and X_2. Single-molecule lines could be detected in the vicinity of all of these sites. Some crystals were so dilute that the bands consisted only of an accumulation of isolated single-molecule lines. The pressure shift of the lines was measured up to pressure values of about 10.5 bar. For all molecules, the pressure shift was linear and reversible with shift parameters between -0.92 and -1.55 MHz/hPa. This variation reflects the different microscopic environments (and, hence, the different local compressibilities) of the matrix around the dopant molecules; it corresponds to the pressure broadening of hole-burning spectra. The

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average shift parameter of -1.24 ± 0.32 MHz/hPa is somewhat larger than for pentacene in the same matrix (-0.9 ± 0.1 MHz/hPa[9]); this is assumed to be due, at least in part, to the higher polarizability of the larger terrylene molecule. Also the fact that terrylene fits less well into the crystalline matrix and, in contrast to pentacene, probably replaces more than one *p*-terphenyl molecule, may contribute to the difference.

Stable spectral holes could be burnt in sites X_1 and XY (see below). Upon pressure increase, also the hole spectra exhibited a linear shift towards lower frequencies. Whereas in band XY the shift parameter was within the range of that of the single-molecule lines, it was distinctly smaller in band X_1, namely, -0.71 ± 0.1 MHz/hPa. Figure 1 shows a portion of the blue side of band X_1 with two deep holes and one particularly strong single-molecule signal in between. The larger pressure shift of the single-molecule line as compared to the hole spectra is obvious. The microscopic origin of this difference is not clear at present.

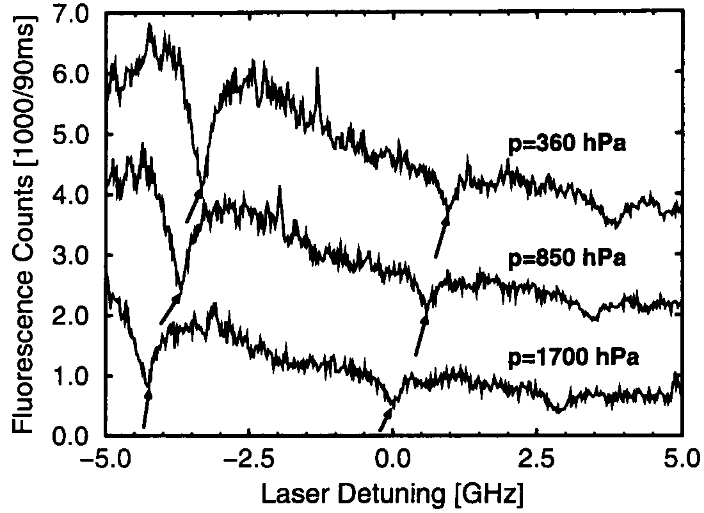

FIGURE 1 High-energy side of band X_1 in a crystal with a relatively high concentration of terrylene. The spectrum contains two deep holes (marked by arrows) and was recorded at three different pressure values. The center frequency corresponds to a wavelength of 580.38 nm.

Stark Effect Experiments

The line shift of single terrylene molecules due to an external electric field was investigated up to field strengths of 5 kV/cm. In contrast to the pressure experiments, the behavior of the molecules was not uniform in this case. Part of the lines exhibited a clear linear Stark effect whereas others did not shift at all within the range of our field strengths. A typical example of experimental data is shown in Figure 2. One of the three strong single-molecule lines shifts linearly with field strength, whereas the two others do not. At higher field strength values, these "static" molecules would probably show a second-order Stark effect, as is expected

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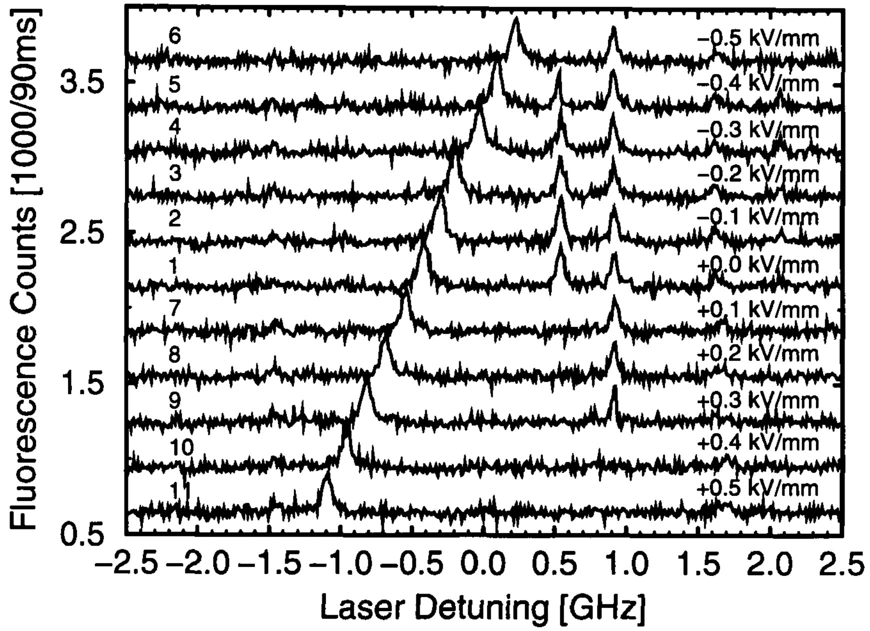

FIGURE 2 Spectrum with three single terrylene molecules, recorded at different values of the external electric field strength ($\underline{E}_{ext} \parallel \underline{k}$) as indicated on the right-hand side. Two of the molecules were burnt during the scans whose temporal order is given by the numbers on the left-hand side. The center frequency corresponds to a wavelength of 580.41 nm.

for centrosymmetric molecules in a well-ordered nonpolar matrix and was observed for pentacene in *p*-terphenyl.[12] The fact that part of the terrylene molecules exhibit permanent electric dipole moments is another indication that they have less well-ordered local environments.

For some of the molecules, the Stark shift data are plotted in Figure 3. Both positive and negative slopes with various different magnitudes were found. This is similar to the behavior of terrylene in the partly amorphous polymer polyethylene.[13,14] In the crystalline matrix *p*-terphenyl, however, only a limited number of stable configurations of the dopant molecule are expected to exist, which should correspond to discrete Stark shift values. Measurements on a larger number of molecules are necessary to clarify this point. By performing molecular-orbital calculations[17] it will perhaps even be possible to identify these configurations from the Stark effect data.

From the linear Stark effect, the effective matrix-induced dipole moment difference $\Delta\mu_{ind}$ of the dye molecules between excited and ground state can be calculated according to

$$\Delta\mu_{ind} = \frac{h}{\kappa}\left|\frac{\Delta\nu_E}{E_{ext}}\right|, \tag{1}$$

where h is Planck's constant, $\Delta\nu_E/E_{ext}$ the experimental Stark shift, and κ denotes

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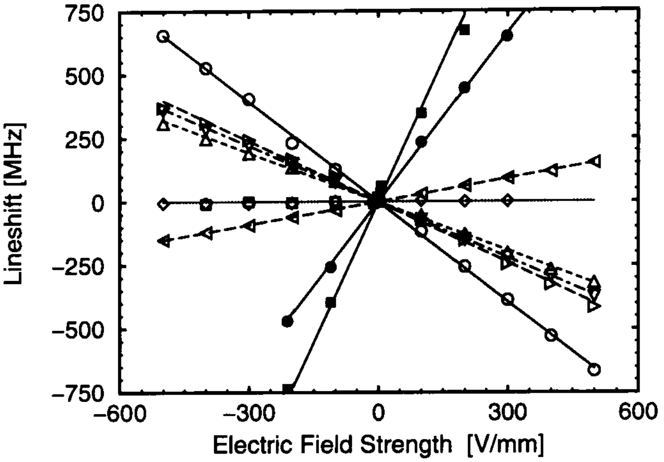

FIGURE 3 Line shift as a function of the external electric field strength for several single molecules (filled symbols, $\underline{E}_{ext} \parallel \underline{k}$; open symbols, $\underline{E}_{ext} \perp \underline{k}$).

the local Lorentz field correction factor. The latter is approximately equal to 1.75 in p-terphenyl.[18] From our data we obtain maximum values of $\Delta\mu_{ind} = 0.76 \pm 0.09$ D for the case $\underline{E}_{ext} \parallel \underline{k}$ and $\Delta\mu_{ind} = 0.16 \pm 0.03$ D for $\underline{E}_{ext} \perp \underline{k}$. This difference is reasonable, since the long axis of the terrylene molecule (with the highest polarizability) is oriented almost perpendicular to the crystal plane and, hence, parallel to the $\underline{k}$ vector. In a polyethylene matrix, on the other hand, $\Delta\mu_{ind}$ values as high as 2.3 D were measured.[14]

Single-Molecule Hole Burning

In the inhomogeneous bands X_2 and X_4, the single-molecule lines are stable and no persistent hole burning is possible. In sites X_1 and X_3 (and also in the photoproduct state XY), however, phototransformations can occur. Examples of deep hole spectra in band X_1 are shown in Figure 1. These spectra are affected by power broadening and photochemical depletion and, hence, are much broader than twice the single-molecule (homogeneous) linewidth which is the lower limit of the hole width in the case that the inhomogeneous band and the hole spectrum are composed of many molecular lines.[19] In very dilute samples and under the conditions of low burning doses, on the other hand, this "thermodynamic limit" does not apply and it should be possible to burn holes which are narrower. The distribution function of the burnt molecular lines is then no longer a smooth Lorentzian but it consists of only a few discrete lines, or, in the ultimate limit, of one single line which has been removed from the ensemble. Figure 4 demonstrates that this limit can be achieved in experiment. The upper two traces show a portion of the X_1 band with statistical fine structure. Between the scans, the sample was illuminated with the laser tuned to the center frequency for 20 seconds. The difference spectrum as given by the lower trace contains a Lorentzian peak at the burning frequency whose width of 30 ± 8 MHz is close to the single-molecule linewidth (40.6 ± 3.1 MHz[15]) within the error limits. Hence, it is probably due to the photobleaching of one single dye

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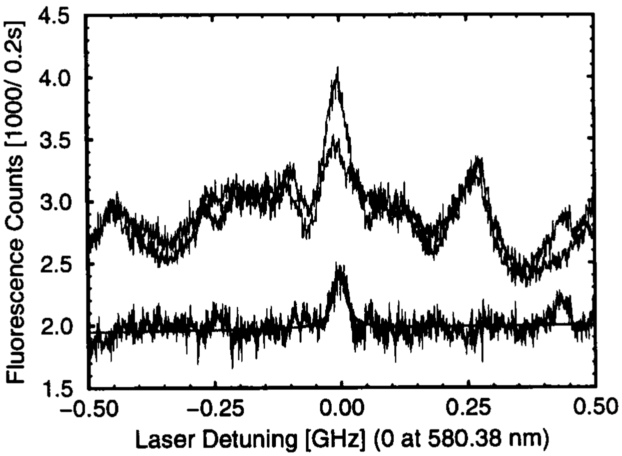

FIGURE 4 "Single-molecule hole burning" in band X_1 of a crystal with very low terrylene concentration. The center frequency corresponds to a wavelength of 580.38 nm. For details see text.

molecule. "Single-molecule" or "few-molecule hole burning" of this kind was also found in Monte Carlo simulations.[20]

Persistent hole burning is also possible in bands X_3 and XY. In X_3, however,[10] the holes are not stable but decay with a time constant of a few minutes.[20]

SUMMARY

We investigated the shift of single-molecule lines due to hydrostatic pressure and external electric fields in the system terrylene in *p*-terphenyl. In addition, the pressure shift of persistent hole-burning spectra in the bands X_1 and XY was measured. All the lines exhibited a linear and reversible red shift upon pressure increase with the shift parameter of the holes in band X_1 being distinctly smaller than that of the single-molecule lines. Part of the molecules showed a linear Stark effect whereas others did not shift up to field strength values of 5 kV/cm within our experimental accuracy. This leads to the conclusion that stable configurations of the terrylene molecule with different local symmetries must be present in the *p*-terphenyl crystal. Stable spectral holes could be burnt in bands X_1 and XY. In the case of weakly doped samples and with low irradiation doses, the hole spectra are composed of very few molecular lines. Hence, the distribution function of the photobleached molecules is not a smooth Lorentzian in this case but it consists of a few (or even one single) delta functions.

ACKNOWLEDGMENTS

The authors would like to thank D. Haarer, B. E. Kohler, and J. L. Skinner for many

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helpful discussions. Financial support of the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Emil-Warburg-Stiftung, Bayreuth, is gratefully acknowledged.

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