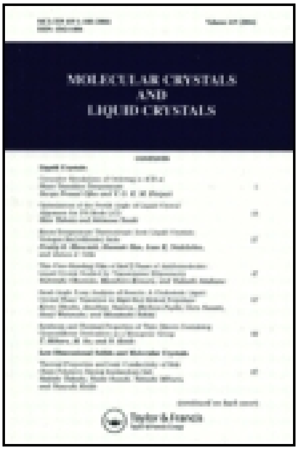

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# Pressure Effects on Single Molecules of Terrylene in p-Terphenyl

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# PRESSURE EFFECTS ON SINGLE MOLECULES OF TERRYLENE IN *p*-TERPHENYL

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Abstract Fluorescence excitation spectra of single molecules and persistent holes of terrylene in *p*-terphenyl crystals were investigated under hydrostatic pressure up to 10510 hPa. Single-molecule lines could be observed around all four inhomogeneous bands $X_1$ to $X_4$. They showed a linear and reversible pressure shift between −0.92 MHz/hPa and −1.55 MHz/hPa with no clear differences between the inhomogeneous bands. The relative fluctuations of the pressure shift parameter between different molecules are larger than for pentacene in *p*-terphenyl which indicates a less well-ordered local environment of the dopant molecules. Persistent hole-burning was possible in the bands $X_1$ and $X_3$ of the same samples in which single-molecule lines were observed. The pressure shift of the hole spectra (which are close to the band center) is smaller than the shift of the single-molecule lines (in the wings of the band). Hence, the molecules seem to feel different local compressibilities.

## INTRODUCTION

The optical spectroscopy of single organic dye molecules in crystalline or amorphous solids at low temperatures has meanwhile almost become a standard technique.[1,2] The two most important advantages of this method are its extreme increase in optical resolution as compared to conventional absorption or fluorescence spectroscopy and its ability to investigate really local phenomena of the dopant molecules. Both of these features have their origin in the total absence of inhomogeneous-broadening or ensemble-averaging effects. A third point is that very small doping concentrations are sufficient so that also dye molecules with low solubility in the matrix material can be investigated.

One of the applications of single-molecule spectroscopy has been the local investigation of the effects of external perturbations. Stark effect experiments were performed on the crystalline system pentacene in *p*-terphenyl[3] and on terrylene in partly amorphous polyethylene.[4] Although both dye molecules are centrosymmetric, only pentacene in *p*-terphenyl exhibits a quadratic Stark effect, whereas for terrylene in polyethylene the observed frequency shift is linear with the corresponding matrix-induced dipole moment difference between excited and ground state varying from molecule to molecule with respect to both magnitude and sign. This behavior has its origin in the low local symmetry of the disordered matrix environment. Pressure-tuning experiments have only been reported for pentacene in *p*-terphenyl so far.[5] A linear and reversible red shift of the lines with increasing pressure was found whose magnitude varied between −0.74 and −1.0 MHz/hPa. This variation was ascribed to local perturbations or defects of the crystal lattice.

Single-molecule lines were also observed for terrylene in *p*-terphenyl single crystals.[6,7] This system has the remarkable property that the light intensity for saturating the optical transition is very high (around 20 W/cm$^2$), which is due to an extremely low triplet quantum yield on the order of $10^{-5}$.[6] Similar to pentacene in the same matrix, there are four zero-phonon lines of the electronic $|S_1\rangle \leftarrow |S_0\rangle$ transition which probably correspond to four sites of the dye molecule in the crystal lattice.

We investigated the pressure shift of single terrylene molecules in *p*-terphenyl crystals in all four inhomogeneous bands. Furthermore, deep persistent spectral holes could be burned in two of the bands ($X_1$ and $X_3$) and their pressure shift was compared to that of the single-molecule lines. Spectral hole-burning and the observation of single-molecule lines were performed on the same samples for the first time.

## EXPERIMENTAL

Single crystals of *p*-terphenyl very weakly doped with terrylene were grown by co-sublimation as described elsewhere.[8] The measurements were conducted at 1.8 K in a custom-built $^4$He bath cryostat containing a hydrostatic-pressure cell. For pressurizing the sample, the cell was connected to a helium gas cylinder. The optical experiments were performed with a tunable single-mode dye laser Coherent CR 599-21 whose radiation was focused on the sample with a small $f$ = 10 mm lens inside the cryostat. The fluorescence from the sample was collected with an elliptical mirror and the red-shifted fluorescence was separated from the laser light by means of a red-pass filter Schott RG610 and detected with a photomultiplier Hamamatsu R928. The integration time per data point was usually 90 ms.

## RESULTS AND DISCUSSION

### Single-Molecule Lines

The four inhomogeneous bands $X_1$ to $X_4$ of the lowest-energy electronic transition $|S_1\rangle \leftarrow |S_0\rangle$ of terrylene in *p*-terphenyl are not of simple Gaussian shape, but the blue wings of the bands $X_1$ and $X_2$ decay more slowly than the corresponding red wings and the bands $X_3$ and $X_4$ possess distinct side maxima on the blue side. These features were tentatively ascribed to microsites of the dopant molecule in the host crystal.[8] Single-molecule lines could be recorded in the vicinity of all four bands with good signal-to-noise ratio. Upon pressure increase, the lines exhibit a linear and reversible red shift. An example is shown in Fig. 1. The line of the molecule was located at the red edge of band $X_2$ at a wavelength of 578.82 nm and showed a pressure shift of $-1.48$ MHz/hPa. During the 10th scan, it disappeared irreversibly, probably due to photobleaching. The slight variation of the signal amplitude is not a real effect but was probably caused by a slow motion of the laser focus on the sample in the course of the experiment.

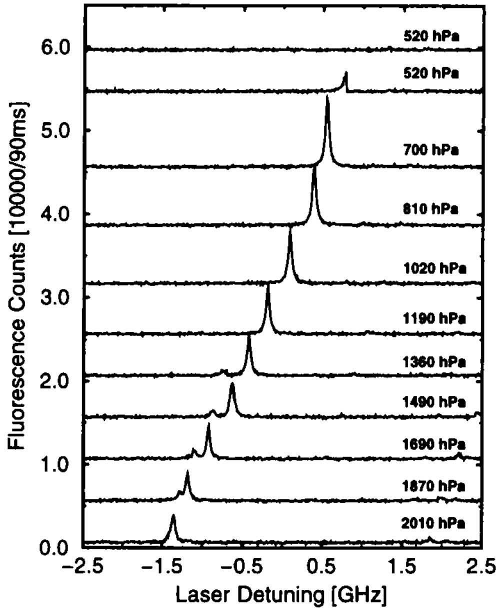

FIGURE 1 Fluorescence excitation signal of a single terrylene molecule at different pressure values as indicated on the right-hand side.

A total of 43 molecules were investigated. Their pressure shift parameters varied between $-0.92$ and $-1.55$ MHz/hPa. No clear differences between the inhomogeneous bands could be found. The relative variation of the shift parameter (*i. e.*, the difference between the highest and the lowest value, divided by the average) amounts to 51% which is distinctly larger than for pentacene in the same matrix (31%).[5] This points into the same direction as the above-mentioned indication of the microsites, namely, that the larger terrylene molecule has a less well-ordered local environment in the host crystal than the pentacene molecule. Pentacene is known to replace exactly one *p*-terphenyl molecule, whereas terrylene, due to its size, requires more space. Hence, one can expect that terrylene is less tightly bound or is located in a larger free volume which may give rise to structural instabilities of the surrounding crystal lattice.

From the average pressure shift parameter of terrylene ($\Delta\nu_p/\Delta p = -1.24$ MHz /hPa) and the local compressibility of the *p*-terphenyl crystal ($\kappa_{\text{loc}} = 0.086 \pm$

0.009 $\text{GPa}^{-1}$) which was determined from the pressure shift of single pentacene dopant molecules,[5] we can estimate the vacuum absorption wavelength of terrylene to be located at $\lambda_{\text{vac}} = 508 \pm 11$ nm. This value is calculated using the simple empirical formula

$$\frac{\Delta\nu_p}{\Delta p} = 2\kappa_{\text{loc}}(\nu - \nu_{\text{vac}}) \tag{1}$$

which was originally derived for the pressure shift of hole-burning spectra in polymers.[9] The position of the absorption line in vacuum has not been measured so far.

## Spectral Hole-Burning

Persistent hole-burning and single-molecule spectroscopy were often considered to be largely incompatible with each other because of the conflicting requirements with respect to the photostability of the dye molecules. Nevertheless, it was recently demonstrated[10] that molecules of greatly different photostability can be found in the same dye–matrix systems so that both experiments were feasible. Hole-burning and single-molecule spectrocopy were performed on samples of very different thickness and, hence, very different optical density, however.

In the system terrylene in *p*-terphenyl, spectral hole-burning and single-molecule spectroscopy can be performed on the same sample.[8] Thus, it is possible to record hole spectra and single-molecule lines next to each other in the same spectral region as Fig. 2 shows. The upper trace contains the fluorescence excitation spectrum in the vicinity of the inhomogeneous $X_1$ band at an absolute pressure of 1410 hPa. The molecular lines constituting the band differ strongly in intensity which may be due, at least in part, to different photostabilities. The three dips

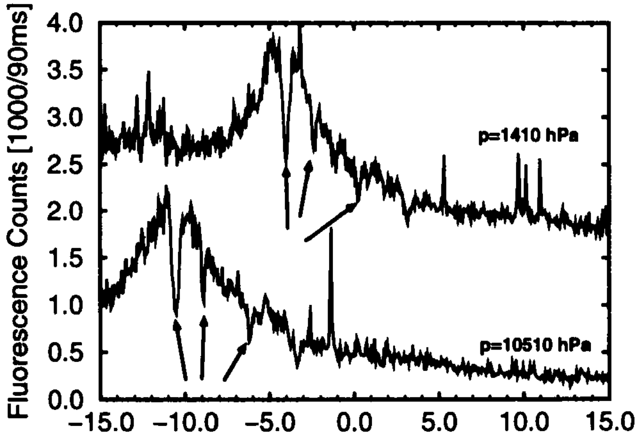

FIGURE 2 Spectral region around the $X_1$ band with three spectral holes (marked by the arrows) and several strong single-molecule lines. The upper trace was recorded at a pressure of 1410 hPa and the lower trace at 10510 hPa.

in the band marked by arrows are spectral holes which were burned with a light intensity of roughly 1000 W/cm$^2$ and burning times of 5 minutes each. The deep and broad hole in the center is especially remarkable because its depth is about two thirds of the height of the band. The width (120 MHz) is roughly three times larger than the widths of typical single-molecule lines due to power broadening and photochemical saturation.

Upon increase of the pressure to 10510 hPa, the spectrum shifts to lower frequencies [lower trace in Fig. 2]. The pressure shift of the three holes is almost equal and amounts to $-0.71 \pm 0.02$ MHz/hPa. This value is distinctly lower than the red shift of the single-molecule lines (see Fig. 3). Since only three holes were investigated, a detailed interpretation is difficult at present. The most striking difference between the single-molecule lines and the molecular lines constituting the hole spectra is that the latter are located much closer to the maximum of the inhomogeneous band and, hence, much closer to an "equilibrium" absorption frequency. Thus, it appears that molecules in a strongly disturbed or strained environment (whose absorption lines are farther away from a band maximum) feel a different local matrix compressibility. Single-molecule lines located both to the red and to the blue of the inhomogeneous bands experience a stronger pressure shift than the hole spectra.

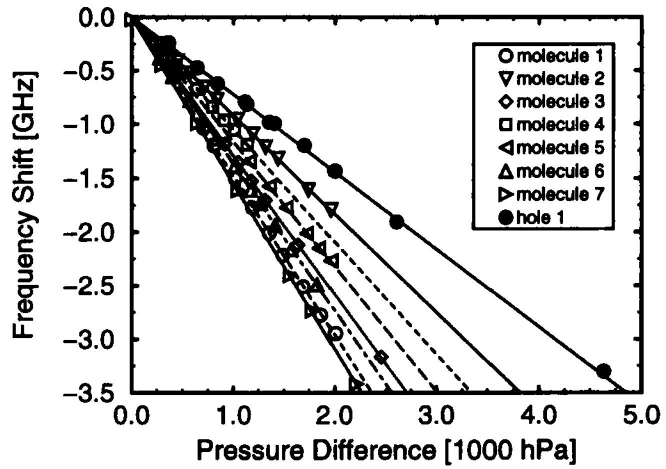

FIGURE 3 Pressure shift of seven different single-molecule lines (empty symbols) and of one of the hole spectra shown in Fig. 2 (full circles). The single-molecule data encompass the whole variation of the shift parameters of all the 43 molecules investigated.

## SUMMARY AND CONCLUSIONS

The pressure shift of single-molecule lines of terrylene in a *p*-terphenyl crystal was investigated. All molecules showed a linear and reversible red shift upon pressure increase with the shift parameter varying between −0.92 and −1.55 MHz/hPa. The relative variation of the shift parameter is larger than for pentacene in the same matrix by a factor of about 1.6, which indicates a less well-ordered local environment of the terrylene molecules.

Persistent spectral holes could be burned in two of the four inhomogeneous bands ($X_1$ and $X_3$) of the dye molecule. Holes as deep as two thirds of the height of the band could be generated in very thin samples which at the same time showed strong single-molecule signals. Hence, the terrylene molecules in the host crystal have greatly different stabilities with respect to phototransformations. The pressure shift of the three hole spectra investigated is smaller than the shift of the single-molecule lines. This indicates that molecules absorbing close to the band center and farther out in the wings seem to feel different local matrix compressibilities. Further studies are necessary to elucidate the microscopic origin of this effect.

## ACKNOWLEDGMENT

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