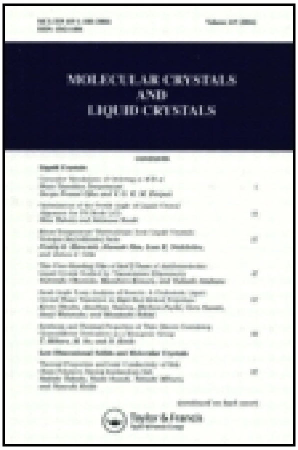

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Single Molecule Spectroscopy: Terrylene in the Polymorphic Matrix Benzophenone

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SINGLE MOLECULE SPECTROSCOPY: TERRYLENE IN THE POLYMORPHIC MATRIX BENZOPHENONE

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Abstract We report a new matrix for single molecule spectroscopy: terrylene doped into benzophenone. The peculiarity of this matrix consists of its polymorphism. Single terrylene molecules were detected in the polycrystalline phase of the benzophenone host. In the glassy phase of the matrix, single molecules were not resolved. An upper limit for the homogeneous width of the terrylene molecules in the glassy phase was obtained from hole-burning experiments. Total luminescence spectra in both amorphous and crystalline phase of bulk samples were measured.

INTRODUCTION

Single molecule spectroscopy (SMS) in the solid state was developed in the system pentacene in p-terphenyl[1,2], and most of the new experiments have been tested in this "classical" system. To fully exploit the possibilities offered by the spectroscopy of a single impurity and to bring this technique to the status of a spectroscopic tool, which hole-burning became, it is needed to extend its applications to a larger number of interesting systems. The host systems accessible nowadays for SMS extend from crystalline hosts (p-terphenyl, anthracene[3]) to Shpol'skii systems[4] (n-hexadecane[5,3], n-nonane[6]) to amorphous polymer systems (polyethylene[7], polyisobutylene[8], polyvinylbutyral[3], polymethylmethacrylate[3], polystyrene[3]), but no glassy or atomic (noble gases) matrices have yet been used. The chromophores applied were pentacene, perylene[7], terrylene[9], tetra-tert-butylterrylene[8], whereby terrylene, because of its favorable photophysical properties, was doped into most of the listed matrices.

The use of benzophenone as a matrix for single molecule spectroscopy was triggered by the possibility to have the same guest impurity in two structurally different (ordered and amorphous), but chemically equivalent phases of one and the same host.

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The polymorphic benzophenone can easily produce a (poly)crystalline or a glassy matrix depending on the cooling conditions. This property has been successfully exploited in hole-burning studies using chlorin as impurity by Kikas et al.[10]. The temperature dependence of the hole-width in the two different phases showed the typical behavior expected for a glass, and for a crystalline matrix, respectively. In order to fit the data for the crystalline matrix they assumed scattering to a local phonon with a frequency of 36 cm^{-1} to be responsible for the observed behavior. For the glass sample they used a power law and added the interaction to a local phonon with a frequency of 18 cm^{-1} to explain the deviation from the power law for higher temperature.

EXPERIMENTAL

Sample Preparation

The melting point of benzophenone is at 47–49° C. It has the tendency to remain in the liquid phase below is melting temperature (supercooling), down to the liquid-glass transition around 200 K. Crystallization can be started anywhere from the supercooled liquid using a seed (small crystal). The glass is produced by simply quenching the supercooled liquid in liquid nitrogen. Benzophenone crystallizes in a rhombic structure with $a = 1.026$ nm, $b = 1.209$ nm and $c = 0.788$ nm. Other less stable structures are also possible. For comparison the long axis of terrylene is estimated to be 1.34 nm.

A ~ 2 10^{-7} mol l^{-1} (calculated from the optical density[5]) solution was prepared by dissolving a tiny speck of solid terrylene at 60° C in liquid benzophenone. A drop (< 1 μl) of the solution is sucked in by capillary action between a microscope coverslit and a LiF disk, forming a thin film. Crystallization can be initialized in situ by touching one edge of the coverslit with a seed. To produce the glass, the liquid film is quenched in the precooled cryostat (Janis SVT). The sample is then placed at the joint focus of a small lens, for focusing the excitation light, and of a paraboloidal mirror, collecting the emitted fluorescence[5,11].

Optical setup

A single mode ring dye laser with Rhodamine 6G was used as excitation source. An external actively locked cavity is used to monitor the laser frequency. To separate the excitation light from the fluorescence, red cutoff filters were used (RG 610). More details of the experimental setup are reported elsewhere[5,11].

Total Luminescence Spectra

The luminescence intensity is measured as a function of both the excitation and emission wavelength using two high resolution monochromators and a Xe-excitation lamp. All the spectra were recorded at 8 K using a concentration of ~ 10^{-6} mol l^{-1}. The result is plotted in a two-dimensional contour plot in the emission-excitation plane. More detail on this technique and a detailed description of the apparatus can be found in the literature[4,12].

RESULTS AND DISCUSSION

Total Luminescence Spectra (TLS)

Figure 1 shows the TLS-spectra of terrylene doped in crystalline (grown at low temperature)(a) and amorphous (b) benzophenone. Above the main diagonal, where the excitation energy is smaller than the emission energy, no signal is observed at these temperatures. Although the main diagonal is cut off, it is possible to see part of the bands lying on it. They correspond to different sites. The spectrum of the ordered phase show a main site located at 17530 cm^{-1} and a weaker one at 17788 cm^{-1}. A broad signal is superimposed to the sites, stemming probably from molecules not located in a proper site or located in the amorphous phase. The weaker site at higher energy was absent in a sample crystallized at room temperature. The vibronic levels in emission and excitation spectra are related, within experimental error, by a mirror symmetry. Therefore the vibronic bands are located on a line parallel to the main diagonal. Furthermore, assuming that the vibronic levels do not depend strongly on the specific site, a second site should give exactly the same vibronic pattern but shifted along the same diagonal. The horizontal, respectively, vertical wings, correspond to phonon sidebands in emission, and respectively, in excitation. As discussed later there are two phonon bands.

The vibrational levels of terrylene are located 246, 495, 544, 577, 740, 785, 823 (±5) cm^{-1} above the ground and the excited state. This spectrum can be compared with the systematic study of n-alkanes doped with terrylene reported by Palewska et. al.[4]. In those systems two main sites are present, the one at higher energy is broader and weaker. As expected from the large difference in sizes, benzophenone is not such a good matrix for terrylene, compared to the n-alkanes reported[4], if one considers spectral resolution. The glassy matrix (b) exhibits a broad structureless band, whose center is shifted to lower energy as compared to the crystal.

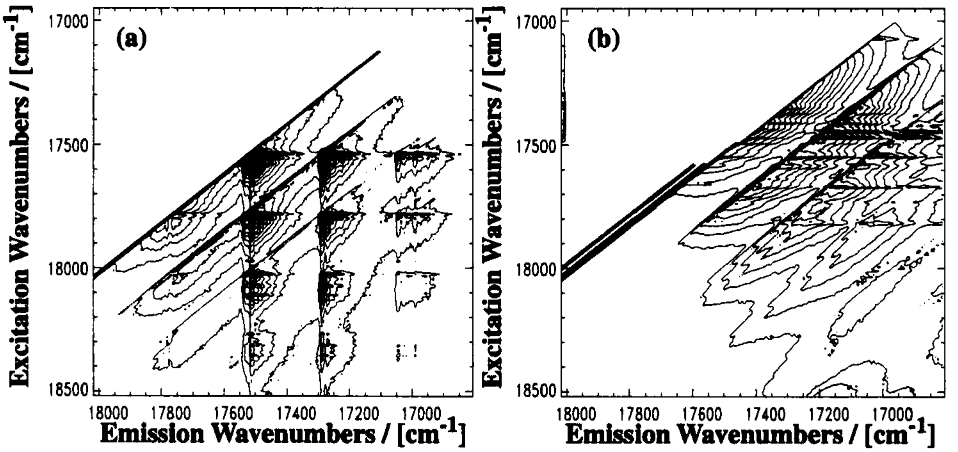

FIGURE 1 Total luminescence spectra of two different samples of terrylene doped benzophenone drawn as contour plots. (a) Crystal (b) Glassy sample.

Single Molecules

The upper part of Figure 2 shows the inhomogeneous, low resolution (20 GHz) excitation spectra of terrylene doped into benzophenone, for a crystalline (black trace), respectively a glassy (grey trace) sample at 1.9 K. In the crystalline sample one strong site origin is observed near 570.7 nm (the weak site is outside the tuning of the used laser dye), accompanied by two side-bands shifted by 18 cm^{-1}, respectively 38 cm^{-1} towards higher energy. These two local modes seem to correspond to the two local modes mentioned in the introduction, one for the crystal and one for the glass. The inhomogeneous spectrum of the glass consists of a broad structureless band centered around 575.1 nm having a FWHM of approximately 10 nm, compared to 0.17 nm for the main site in the crystalline phase.

The lower spectra (a)-(h) in the figure show frequency scans 10 GHz wide recorded with single molecules resolution at the corresponding positions labeled in the inhomogeneous spectrum. Starting from the blue side of the spectrum the density of single molecules is low, even close to the center of a side-band (spectrum (c)) indicating that these are not sites. Spectrum (d) recorded near the center of the main band shows a pronounced statistical fine structure, a second scan has been shifted upward to show its reproducibility. Moving to the lower energy side, single impurity lines can be resolved ((e)-(f)) and are still present, in lower number, far out in spectrum (h). Some of the observed molecules are not stable in frequency and photobleach, others exhibit a reversible jumping behavior.

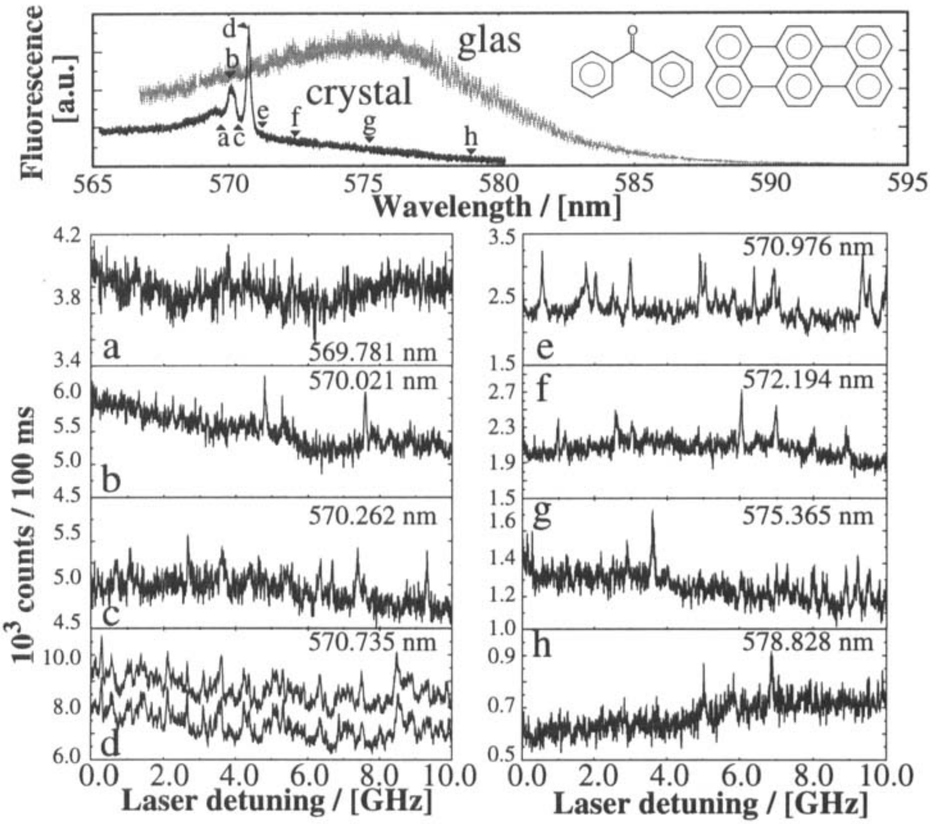

FIGURE 2 Upper spectra: low resolution inhomogeneous spectra of a crystalline (black trace) respectively a glassy (grey trace) sample, recorded at 2 K. (a)-(h) single molecule spectra of terrylene in crystalline benzophenone at different wavelengths as indicated in the upper inhomogeneous spectrum by the markers.

Figure 3 illustrates the saturation behavior of a stable terrylene molecule. The full width at half maximum and the peak emission rate of the Lorentian single molecule resonance are plotted as a function of the excitation power. The black lines show least square fits using the standard equations given in the figure. The obtained homogeneous width is 60 MHz, which is larger than the lifetime limited value of 42 MHz[5]. The obtained saturation intensity and the maximum emission rate (see figure 3) have not been corrected for the geometrical orientation of the terrylene molecules[13]. However, compared with terrylene in hexadecane, a higher saturation intensity is expected, because of the lowering of the absorption cross-section in the benzophenone system, caused by the phonon wings.

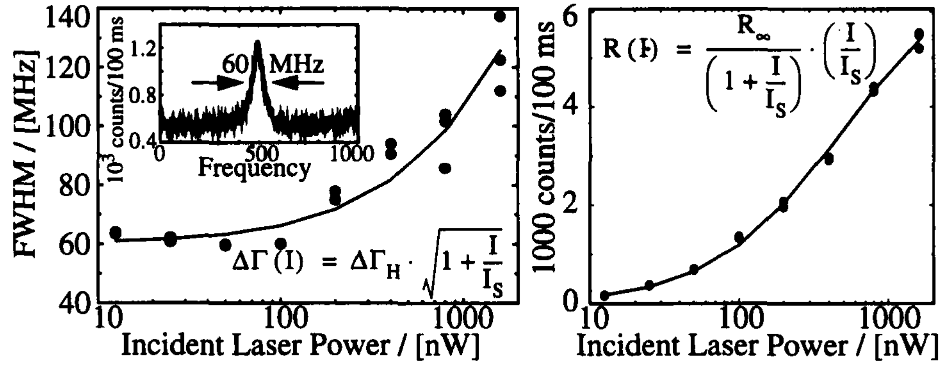

FIGURE 3 Saturation behavior for a stable molecule located at 571.016 nm. FWHM (left) and peak rate (right) of a single molecule as a function of the excitation intensity. The inset shows the low power lineshape and a Lorentian fit (white thin line). The solid curves in both figures represent a nonlinear fit using the given equation with $I_S = 1.7\ \mathrm{W} \cdot \mathrm{cm}^{-2}$, $\Delta\Gamma_H = 60$ MHz and $R_\infty = 7 \cdot 10^4$ cps.

From hole-burning experiments performed in the glass, the expected low power width for a single molecule was found to be around 900 MHz, a factor of 15 larger than in the crystal. If we assume a reduction of peak intensity by the same factor (neglecting changes in the Debye-Waller factor and hole-burning efficiency) it becomes difficult to detect a molecule. A further reduction of the temperature below 0.5 K, using an ^{3}He-cryostat, should make possible the detection of a single molecule in the glassy phase.

REFERENCES

1. W. E. Moerner and L. Kador, Phys. Rev. Lett., 62, 2535 (1989).
2. M. Orrit and J. Bernard, Phys. Rev. Lett., 65, 2716 (1990).
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. Meister, U. P. Wild, accepted for publication in J. Phys. Chem..
5. W. E. Moerner, T. Plakhotnik, T. Irngartinger, M. Croci, V. Palm and U. P. Wild, J. Phys. Chem., 98, 7382 (1994).
6. M. Pirotta, A. Renn, Martinus H. V. Werts and U. P. Wild in preparation.
7. Th. Basché and W. E. Moerner, Nature, 355, 335 (1992).
8. R. Kettner, J. Tittel, Th. Basché and C. Bräuchle, J. Phys. Chem., 98, 6671 (1994).
9. M. Orrit, J. Bernard and A. Zumbusch, Chem. Phys. Lett., 196, 595 (1992).
10. J. Kikas, P. Schellenberg and J. Friederich, Chem. Phys. Lett., 207, 143 (1993).
11. M. Croci, V. Palm, T. Irngartinger, W. E. Moerner. and Urs P. Wild, in preparation.
12. A. J. Kallir, G. W. Suter, S. E. Bucher, E. Meister, M. Lüönd and U. P. Wild, Acta Phys. Polon., A71, 755, (1987).
13. T. Plakhotnik, W. E. Moerner, V. Palm and U. P. Wild, Opt. Commun., 114, 83 (1995).