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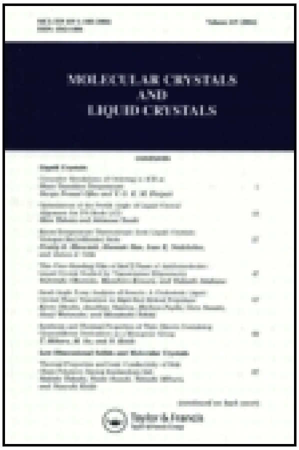

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Optical Detection of Single Molecules in Solids

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OPTICAL DETECTION OF SINGLE MOLECULES IN SOLIDS.

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Abstract We present results on optical detection of individual dye molecules diluted at low concentration in crystals and in polymers. There is now no doubt about the feasibility of such experiments which can easily allow the study of local environments. This paper is devoted to our contribution from the beginning to this spectroscopy domain in which several papers have recently appeared. We also report results about Stark effect on single molecule in a solid. In this particular case we choose to apply an electric field on a non–centrosymmetric molecule in a disordered system.

INTRODUCTION

The detection of a single molecule emission in a solid solution is the ultimate limit of chemical analysis. Dye molecules in matrices show at room temperature, bands 10^4 to 10^5 times broader than lines in gases. These broad bands are due to microscopic disorder (inhomogeneous broadening) and to time evolution of the transition frequency (homogeneous broadening). At liquid helium temperature although thermal fluctuations disappear we always observe inhomogeneous broadening. This broadening is the superposition of the homogeneous bands of each molecule. In order to measure the real homogeneous width, one can use photon echoes or hole burning techniques. If we suppose a very small number of molecules, we can expect to resolve directly homogeneous lines. This is illustrated on figure 1, where calculated absorption for different concentrations is plotted. Moerner's group[1,2] by doubly modulated absorption observed the fine statistical structure and then first showed the feasibility of the optical study of single molecules. In order to increase the signal over noise ratio we use the fluorescence excitation[3-4] of the same system. This technique allowed us to obtain very clearly single molecule lines on a low background.

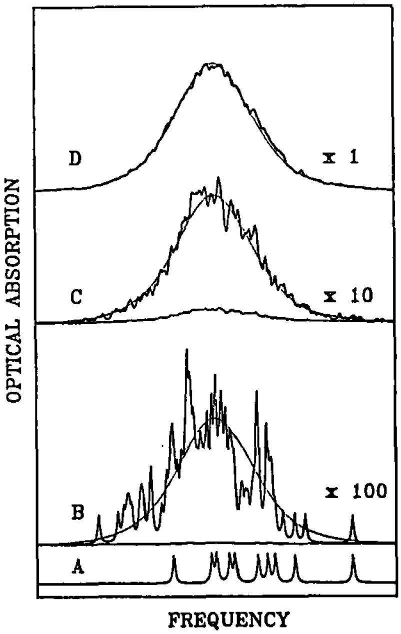

FIGURE 1 Simulation of inhomogeneous absorption of a doped sample. (D=10000, C=1000, B=100, A=10 molecules). In case A, each molecule gives rise to a Lorentzian resonance.

Then it is now possible to measure the homogeneous widths of such molecules. By measuring the correlation function of the emitted intensity it is possible to obtain informations about photon bunching due to inter-system crossing. Many papers[5-7] report about Stark effect in disordered systems via hole burning. Due to breaking of symmetry by microscopic forces of molecules in a matrix, in disordered systems we always found linear effect[8-11]. Here we choose to use the technique of single molecule spectroscopy, to measure the Stark effect on the molecule of terrylene diluted in polyethylene.

EXPERIMENTAL.

Sample

Till now, all our experiments were done on para-terphenyl doped with pentacene at very low concentration. Small flakes (a few microns thick) are prepared by sublimation at about 200°C under Ar atmosphere. This method allows to obtain typically concentrations around 10^{-9} mole/mole. As previously described[4], our samples are optically contacted at the end of an optical fiber, the core of which is

4 µm in diameter. In these conditions the excited volume is approximately 200 μm^3 in which one hundred of dopant molecules are present.

Set up

In order to avoid frequency drifts (at long time) the set up described in ref (4) has been changed. A stabilization on a frequency-stabilized HeNe laser has been added. With this set up we can scan 200 MHz with less than 1 MHz frequency jitter, see Ref (12).

RESULTS AND DISCUSSION

Excitation fluorescence of two samples of different thickness are plotted on figure 2.

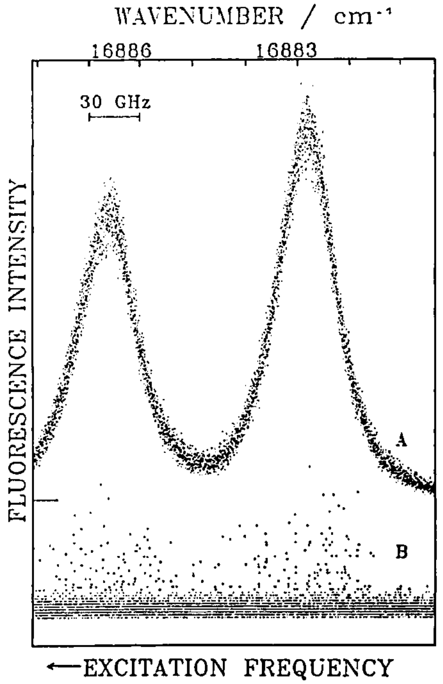

FIGURE 2 Fluorescence excitation spectra of a macroscopic sample (A, a few mm^3) and a microscopic sample (B, a few μm^3). The dots above background are reproducible signals from single pentacene molecules.

Curve A shows the broad excitation spectrum of sites O_1 and O of pentacene in a melt grown crystal of paraterphenyl. The two quasi Gaussian bands result from the superposition of the resonance frequency of each molecule determined by the crystal defects in its surrounding. In such a crystal (a few mm^3), the number of excited molecules is important (to be compared to spectrum D figure 1). If this number is reduced, by decreasing concentration and excited volume, the dopant molecules can be excited individually. This is shown in spectrum B of figure 2 (to be compared with spectrum A of figure 1). Above a very low background, we see well reproducible dots irregularly distributed across the two inhomogeneous bands O_1 and O_2, each one being the absorption line of one particular molecule. By reducing the frequency scale, these dots resolve into well-shaped Lorentzian peaks (see figure 3).

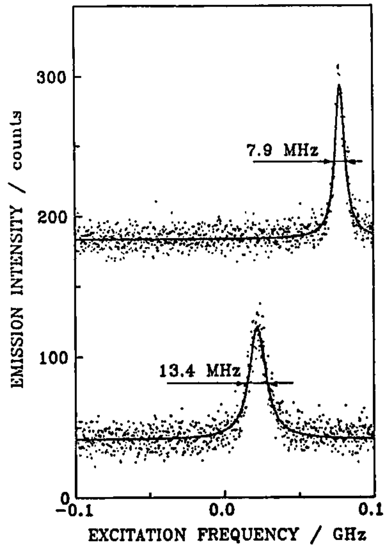

FIGURE 3 Example of single molecule excitation peaks recorded with the same very low exciting intensity (no power broadening). The lower spectrum shows spectral diffusion.

Most of the measured linewidths are around 8 MHz, in good agreement with photon echoes measurement of De Vries and Wiersma[13] and with results of Moerner and co-workers[14-15] . However, in some cases we obtain much wider lines up to 20 MHz (lower spectrum figure 3). Due to the resolution of our set-up, better than 1 MHz, we can exclude broadening due to laser drift. This is certainely due to spectral diffusion during recording. This has been confirmed by Moerner and co-workers[15-16] who followed spectrally diffusing molecules. In some few cases we observe sudden jumps between two well-defined positions. If this can be rather surprising in a crystalline system this is more understandable in a disordered system like a polymer. In polyethylene Moerner and Basché[17] observed single perylene molecules spectrally diffusing and more recently we made similar observations in polyethylene doped with terrylene. Large photo-induced frequency jumps are observed. After a few seconds or minutes the resonance frequency comes back to its first value. An other particular behavior of molecules can be shown by studying lines at different temperatures. This has been done in the case of pentacene in para-terphenyl and is shown in figure 4.

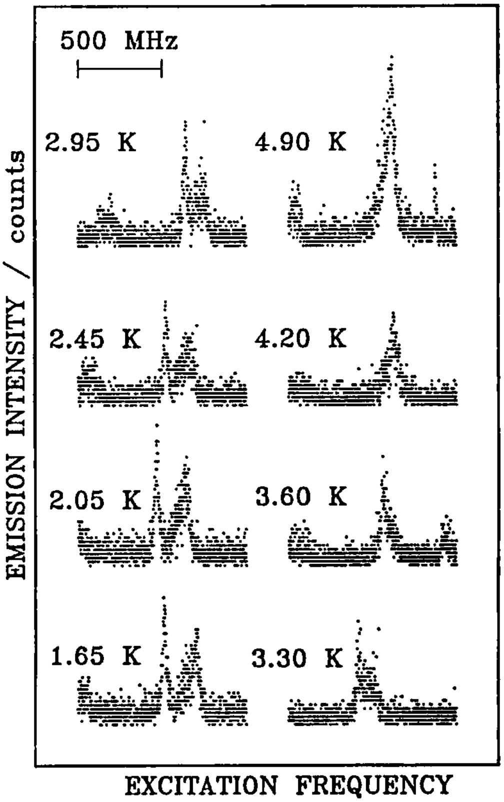

FIGURE 4 Temperature dependence of a small section of the excitation spectrum.

As the temperature increases, the two lines separated by about 100 MHz at 1.65 K draw closer and finally merge together for temperatures above 3.3 K. The reversibility and reproducibility of this behavior excludes the presence of two different molecules. We think in this case that the two lines originate from the same molecules in two possible environments (two-level system). When temperature increases the two well-potential could evolve and finally fuse into a single-well potential. We can also be in presence of motional narrowing. When the molecule is excited with high flux, emission occurs by sequences separated by dark periods where the molecule stays in the triplet state. It is evident that photon bunching and antibunching is a true signature of the emission of a single molecule's fluorescence[18]. In the case of pentacene as dopant of para-terphenyl, we measured the correlation function for increasing intensities. Figure 5 presents these functions with the excitation of the corresponding line for four increasing intensities. As described in ref (12) the decay can be fitted by a single exponential.

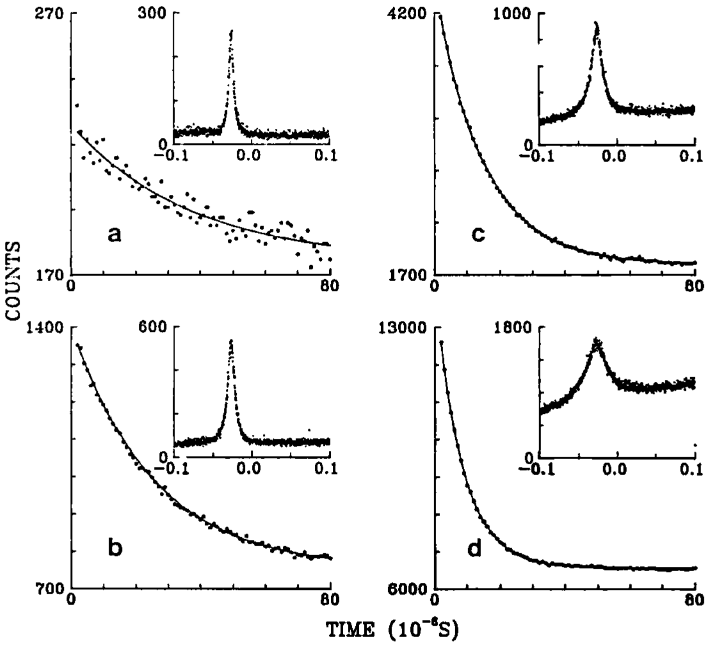

FIGURE 5 Auto-correlation function of intensity of fluorescence for increasing intensities. The decay, well-fitted by a single exponential, shortens when intensity increases.

As expected when increasing the power of excitation, the bunches get shorter (the correlation decreases faster), while due to saturation, the excitation spectra broaden. The molecule being in its ground state just after emitting a photon, a new excitation must occur before it can emit a second photon (antibunching). In these conditions at very short times there appears a hole in the correlation function. The first evidence of this phenomenon has been made by Kimble and colleagues[18]. Unfortunately with our setup we cannot observe this antibunching. Recently Moerner and Basché[19] could observe this effect. Their measurements allow them to determine a Rabi frequency in good agreement with fitted values.

Stark effect

Most of our experimental data and results on the Stark–effect are reported in (20).

In figure 6 are drawn experimental results obtained on different molecules with relatively low electric field.

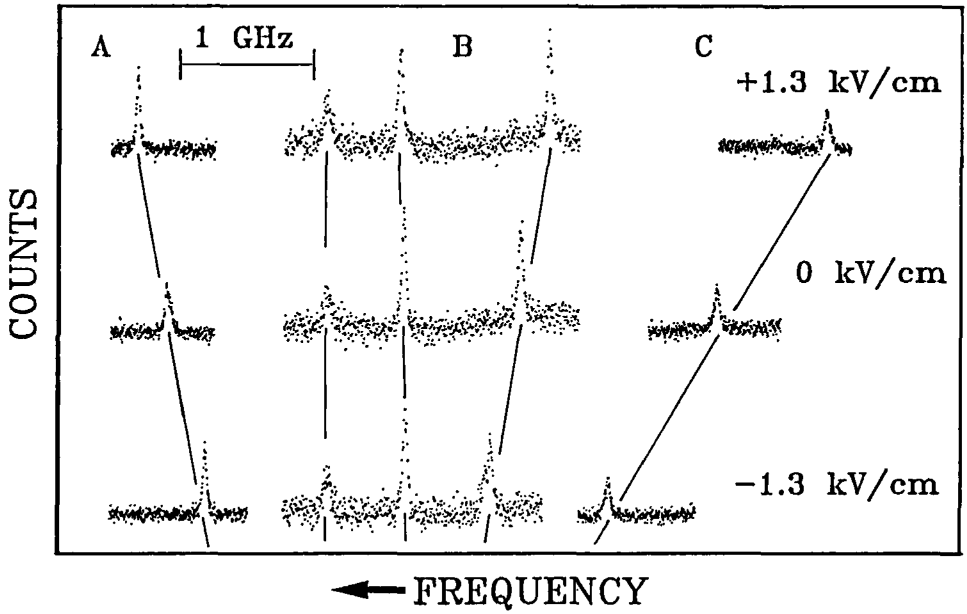

FIGURE 6 Experimental lines of single terrylene molecules in polyethylene in different spectral regions without and with opposite electric fields, showing the difference in sign and magnitude of the observed shifts.

The lines shift by different amounts and signs. This indicates clearly different orientations of molecules and their surroundings. We made measurements on 60 different molecules and calculated dipole moments assuming the uniformity of electric field (see ref(20) for description of the cell used). The average value of $\Delta\mu$ is about 1 D, may be due to the large size of the molecule. For a few molecules we calculate very high dipole moments, up to 4 D, which could indicate some anisotropy of the matrix.

CONCLUSION

The detection of single molecules diluted in cristalline and now in polymer hosts provides important informations (impossible to obtain by classical methods) about the detected molecule and its surrounding. We show that in polymer and even in cristalline matrices, we can observe spontaneous and photoinduced spectral diffusion. The rates of molecular dynamic processes can be obtained directly by looking at the correlation properties of photons emitted by a single molecule. We showed also interesting results on detection of single molecules in polymer matrices opening a field of investigations in new systems.

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