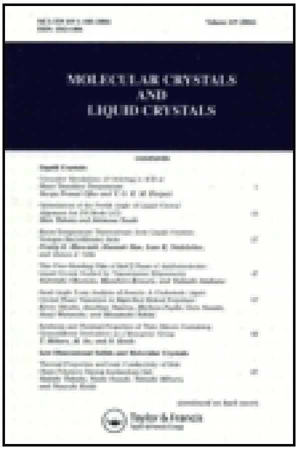

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OPTICAL SPECTROSCOPY OF SINGLE PENTACENE MOLECULES IN A NAPHTHALENE CRYSTAL

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Abstract Dilute mixed molecular crystals of pentacene in naphthalene were prepared by cosublimation of the two compounds. Single pentacene molecules could be detected in the thin platelets by fluorescence excitation spectroscopy. By analyzing the exponential decay of the fluorescence intensity autocorrelation function for a single molecule in the microsecond time regime we could determine the population (k_{23}) and depopulation (k_{31}) rate of the metastable triplet state. The increase of the population rate k_{23} by a factor of ~ 4 when compared to pentacene in p-terphenyl is responsible for the weaker fluorescence signals of single pentacene molecules in naphthalene crystals.

INTRODUCTION

Detection and spectroscopy of single molecules at low temperatures was first demonstrated in the single crystalline system pentacene in p-terphenyl (PC/PTP).[1] The extension of single molecule spectroscopy (SMS) to other systems was one major goal in the last years. Amorphous, semicrystalline and crystalline systems have been investigated by now (see some recent reviews[2,3]). Although the low probability for frequency jumps of molecules in a crystalline environment is a great advantage in many experiments, studies in single crystalline matrices were so far restricted to p-terphenyl doped with either pentacene[1] or terrylene[4] .

In this paper we report on the investigation of single pentacene molecules in naphthalene crystals (PC/NA) by fluorescence excitation and correlation spectroscopy. Like PC/PTP, PC/NA is well known from bulk experiments.[5-9] Low hole burning efficiency and the photophysical parameters[7,8] suggest that PC/NA is a suitable system for SMS. By means of the fluorescence intensity autocorrelation function, the intersystem crossing (ISC) parameters, i.e. the population and depopulation rates of the triplet state, were determined. The results permit to compare the influence of different crystalline matrices, NA and PTP, on a certain dye molecule, PC, and its photophysical behaviour.

EXPERIMENTAL

Single crystals of pentacene (Aldrich) in naphthalene (zone-refined) were grown by sublimation from a mixture (c = 10^{-3} mole/mole) of the two compounds in a N_2-atmosphere (p = 900 mbar) at 170°C. The thin platelets could be stored in a saturated naphthalene atmosphere at -18°C for several weeks.

As the experimental setup for SMS can be found in great detail in literature[10], we restrict ourselves to a brief summary: The crystals were glued between two LiF plates and placed at the joint focus of a lens and a parabolic mirror inside a liquid helium cryostat operating at 1.4 K. Fluorescence excitation spectra were recorded by scanning a R6G single frequency ring dye laser over the molecular resonance line and detecting the fluorescence light after long-pass filtering with a photomultiplier and photon counting electronics. The fluorescence intensity autocorrelation function was recorded with the laser frequency held fixed at the molecule's resonance frequency and feeding the photomultiplier pulses into a digital logarithmic correlator.

RESULTS AND DISCUSSION

NA possesses a monoclinic crystal structure with two equivalent molecules in the unit cell. Due to its size, PC replaces not one, but two translationally equivalent NA molecules.[8] This is possible with very small disturbance to the local host molecular packing

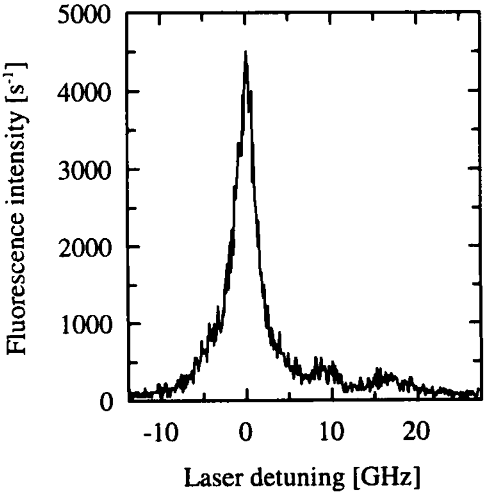

FIGURE 1 Fluorescence excitation spectrum of the inhomogeneously broadened absorption line of PC/NA at 1.4 K. (0 ≡ 602.847 nm).

and with very little unoccupied volume[6]. In contrast to PTP with its four inequivalent crystalline sites PC/NA gives rise to only one electronic origin in absorption and emission at $\lambda = 602.8$ nm.[5]

In some of the crystals investigated we found very narrow inhomogeneously broadened lines (see Fig. 1, $\Gamma_{inhom} = 3.2$ GHz), a typical result for high quality sublimation crystals mounted without excessive strain. The inhomogeneous line in Fig. 1 peaks at $\lambda_{max} = 602.847$ nm (vacuum wavelength). At the blue side of the inhomogeneous line a satellite structure arises due to ^{13}C-substitutional isomers of PC as was also observed for PC/PTP crystals recently[11]. The relative frequency distances to the all-^{12}C-isomer are consistent with PC/PTP. This is reasonable as the matrix effect that shifts the resonance frequency of PC/NA to longer wavelength as compared to PC/PTP is expected to be similar for the different substitutional isomers.

Fig. 2 shows two fluorescence excitation spectra of single PC molecules together with Lorentzian fits, one obtained in a NA crystal, the other in a PTP crystal. Both molecules were recorded in the red wings of the corresponding inhomogeneous distributions and were excited with approximately the same intensity. The excitation line of the PC

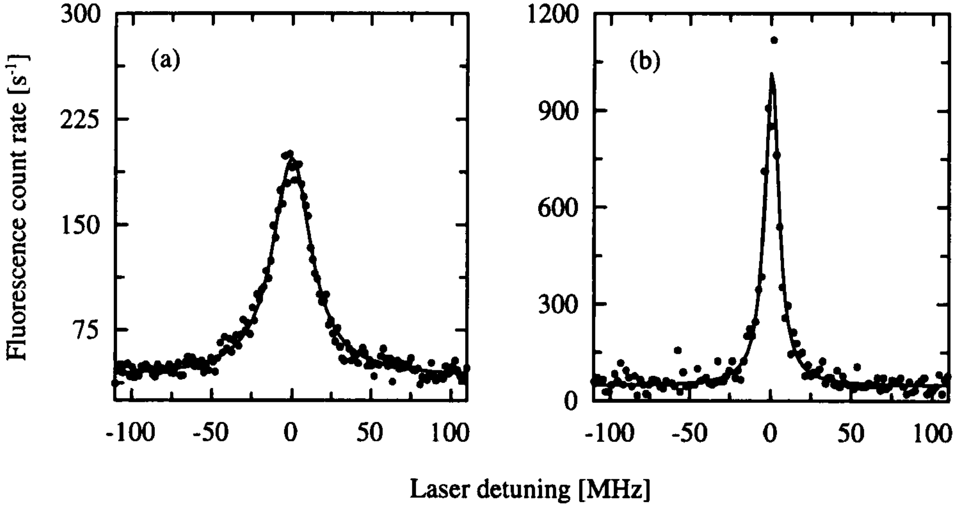

FIGURE 2 Fluorescence excitation spectra of single PC molecules in (a) NA and (b) PTP at 1.4 K. (a) 0 ≡ 602.899 nm, excitation intensity I = 2.5 mW/cm^2, linewidth (FWHM) $\Delta\nu = 29.1$ MHz, average of 16 scans; (b) 0 ≡ 592.373 nm, I = 2.9 mW/cm^2, $\Delta\nu = 11.5$ MHz, single scan; note the different scale at the ordinate!

molecule in the NA crystal is noticeably broader and shows a clearly lower peak photocount rate than the line of PC/PTP despite the fact that the fluorescence detection efficiency was similar in both experiments. As the fluorescence lifetime and thus the lifetime-limited linewidth is almost equal for PC/NA (τ_f = 19.5 ns)[7] and PC/PTP (τ_f = 21.7 ns)[12] the clear differences in the linewidth and the photocount rate have to be caused by saturation starting at lower intensities in PC/NA. This significant different behaviour of the same molecular species in two different matrices can be explained by matrix induced changes in the photophysical dynamics of PC.

Due to intersystem crossing, i.e. a transition from the singlet to the triplet state, fluorescence photons of a single molecule are not emitted continuously but in bunches. In their theoretical description of photon bunching Bernard et al.[13] showed that ISC leads to a decay of the fluorescence intensity autocorrelation function on a time scale determined by the population and depopulation rates of the triplet state. The decay of the normalized intensity autocorrelation function due to ISC is given by a single exponential when only one of the triplet sublevels is taken into account:[13]

$$g^2(\tau) = 1 + C * \exp(-\lambda\tau) \tag{1}$$

Fig. 3(a) shows the decay of $g^2(\tau)$ for PC/NA. As for PC/PTP[11], the decay of $g^2(\tau)$ at a given intensity is well approximated by a single exponential with rate parameter λ. λ depends on the intensity and the ISC rates k_{23} and k_{31} according to the following equation:[13]

$$\lambda = k_{31} + k_{31}\frac{I}{I_S}\left(1 + \frac{2k_{31}}{k_{23}}\frac{I}{I_S}\right)^{-1} \tag{2}$$

Fitting Eq. 2 to the rate parameters λ (see Fig. 3(b)) extracted from the autocorrelation function at different intensities with Eq. 1 yields a population rate $k_{23} = 1.2 \times 10^6$ s^{-1} of the triplet state. The value of k_{31} could not be determined by Eq. 2 with sufficient accuracy but by considering the intensity dependent contrast of the autocorrelation function. For high intensities the contrast of the autocorrelation function is given by $C = k_{23}/2k_{31}$.[13] Inserting k_{23} and the true contrast of 21.4 (the measured contrast corrected by the straylight contribution to the signal[13]) this yields $k_{31} = 2.8 \times 10^4$ s^{-1}. From photon echo[7] and electron spin-echo[8] measurements on large ensembles approximate values for k_{23}[7] and accurate values for k_{31}[8] for the different sublevels are known. The population rate of one of the sublevels (T_x) is at least higher by a factor of ten compared to the other levels, and it is vastly the dynamics of that level which we observe with high contrast in the single molecule correlation measurement. The value determined for k_{31}

(2.8×10^4 s^{-1}) lies by a factor of ≈ 2 within the result of the spin-echo measurement[8] while the value for k_{23} (1.2×10^6 s^{-1}) deviates much more from the estimate (9×10^6 s^{-1}) calculated from data in Ref. 7. It is well known from earlier investigations that the ISC rates may vary appreciably from molecule to molecule.[11,13] We possibly have picked the molecules with the lowest values of k_{23} because those give rise to the strongest fluorescence signals.

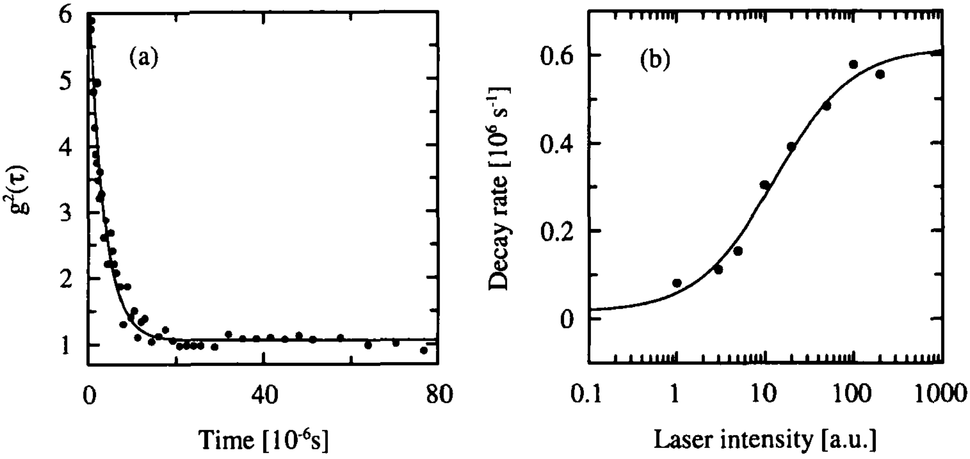

FIGURE 3 (a) Normalized intensity autocorrelation function of the fluorescence emission of a single PC molecule in NA at an relative laser intensity of 10. The drawn line is a fit of Eq. 1 to the decay of the correlation function, yielding $\lambda = 0.3 \times 10^6$ s^{-1}. (b) Plot of λ versus logarithmic laser intensity together with a fit of Eq. 2 to the experimental data.

The higher value of k_{23} in PC/NA compared to PC/PTP ($k_{23} \approx 0.3 \times 10^6$ s^{-1})[11] leads to saturation of the optical transition already at relatively low exciting intensities where the number of emitted fluorescence photons approximately equals or is less than the background level. Fluorescence excitation spectra are thus more noisy than in PC/PTP. The contrast of the correlation function, however, can be much higher in PC/NA because at saturating intensities it is given by the ratio of k_{23} and k_{31} (s. above).

Finally the question arises by which mechanism the different orders of magnitude for k_{23} in PC/NA and PC/PTP, respectively, can be explained. Most probably the red shift of the singlet transition in PC/NA (λ = 602.85 nm) as compared to PC/PTP (λ = 592.32 nm) changes the relative location of S_1 with respect to a higher lying triplet state T_n providing a more efficient route for coupling states of different multiplicity.[9]

CONCLUSIONS

We have presented fluorescence excitation spectra of single pentacene molecules in a naphthalene single crystal. In this system the nonradiative decay channel into the triplet state competes more efficiently with the fluorescence decay compared to PC/PTP yielding signals with lower signal-to-noise ratio. The special combination of the population and depopulation rates, however, still allows to measure the fluorescence correlation function with high contrast and to deduce those rates.

Further investigations of this system could give some insight in the mechanisms leading to spectral diffusion in crystalline matrices. Spectral diffusion of some PC molecules in PTP is explained by flipping of the central phenyl ring of PTP molecules located at domain boundaries.[14] In naphthalene crystals, where this degree of freedom does not exist, spectral diffusion of the guest molecules may not be observed. So far, the small number of molecules investigated in this study did not show any frequency jumps but more experiments are needed.

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