Single Pentacene Molecules Detected by Fluorescence Excitation in a p-Terphenyl Crystal

M. Orrit and J. Bernard

Centre de Physique Moléculaire Optique et Herztienne, Centre National de la Recherche Scientific et Université de Bordeaux I,
351, Cours de la Libération, F-33405 Talence CEDEX, France

Experiments clearly prove that narrow peaks in the fluorescence excitation spectrum of a pentacene-doped p-terphenyl crystal stem from single molecules. This claim is supported by the distribution, width, and height of the peaks, as well as by the correlation of the emitted light and the sudden drops and surges of the emission of certain peaks. We attribute these to the hole burning of a single molecule. These results show the feasibility of the optical study of a single molecule and its local environment.

Nondestructive optical detection of single absorbing centers such as molecules in a solid would provide new prospects for both fundamental science and applications. A molecule could serve in a microphysics experiment as a truly local probe addressable by the "macroscopic" light field. Single-molecule detection (SMD), the ultimate limit in chemical analysis, might be of interest in designing ultrasensitive sensors. More fundamentally, the spectroscopy of a single molecule, free from the usual averaging over many sites, would provide direct access to the distributions of microscopic parameters. Recent observation of single atoms[1] or atomic ions[2] in beams or electromagnetic traps has revealed several phenomena, such as quantum jumps, that are concealed on averaging over many individuals. This fascinating physics could be generalized to big molecules in a solid.

Cooling and trapping single molecules in a solid are not problems, in contrast to the case of confined ions. However, other difficulties arise from the complexity of the system, e.g., the shift of molecular resonances by the host's dynamics and the detection of the weak signal against the host background. Here, we use fluorescence excitation; i.e., we monitor the emitted intensity as a function of the excitation frequency. This very sensitive method can be used to study hole burning in samples with a low optical density.[3]

Let us try to optimize ideally a host-guest system for SMD by fluorescence excitation.

(i) In order to increase the interaction with light, the absorption cross section σ must be large; i.e., the homogeneous width γ_h of the transition must be small. For strong transitions, the radiative width of the zero-phonon transition may be comparable to γ_h and σ can take values of the order of 0.1 μm^2. For S_0-S_1 zero-phonon transitions of organic molecules in crystals,[4] the lifetime-limited width is usually reached at liquid-helium temperatures.

(ii) As the overall photon detection efficiencies are rather low (10^{-2}–10^{-3}), each molecule must be able to emit as many photons as possible before its resonance frequency shifts irreversibly. This rules out many photosensitive molecules and amorphous matrices showing hole burning.[5,6]

(iii) The rate at which emitted photons are detected must be higher than the dark count of the detector. As the intensity is usually limited by the bottleneck of the metastable triplet state T_1, the maximum average rate of absorption $(q_T \tau_T)^{-1}$ must be large enough (q_T is the intersystem crossing yield from S_1 and τ_T the triplet lifetime).

Recently, Moerner and Kador[7,8] demonstrated the first optical SMD in the far wings of the absorption spectrum of pentacene (Pc) in a *para*-terphenyl (p-TP) crystal. Our experiments bear on the same system, using fluorescence excitation instead of doubly modulated absorption. The pentacene–p-terphenyl (Pc–p-TP) system has been extensively studied by several authors.[9-11] The O_1 and O_2 sites of this system answer ideally the three above requirements.

The optical setup was basically the one we used for hole burning.[3] Our excitation source, a single-mode ring dye laser (Coherent Radiation CR-699, instant resolution 0.5 MHz) was intensity stabilized by an electro-optic modulator (Conoptics, Lass II). The samples were prepared from zone-refined p-TP (250 passes). Pc (Aldrich) was used without further purification because of the low concentration needed. A Bridgman crystal was grown from the melt at 10^{-6} mol/(mol Pc), from which samples could be cleaved. However, the concentration in the crystal was not known accurately as some Pc was rejected during growth. The same crystal served to prepare a powder load for sublimation. A dramatic decrease in the Pc concentration occurred on sublimation. SMD was achieved with two different ways of selectively exciting a small part of the crystal. In the first one, the crystal sat at the focus of a plano-convex lens (focal length 12 mm) inside the cryostat. The exciting light could be focused onto the crystal by adjusting the convergence of the incoming beam. The waist diameter was estimated to be about 5 μm. The focal point could be moved by slightly changing the angles of incidence on the lens. In the second method, the crystal was optically contacted to the end of a single-mode optical fiber either directly for sublimation flakes or using an index-adapting

oil for cleaved crystals. Thus, no adjustment was needed, since the waist was determined by the fiber core (about 4 μm in diameter), but it was impossible to vary the point under study. The excitation flux could be varied by means of neutral filters in the range 10–1000 mW cm^{-2}.

Fluorescence from the tiny excited volume was collected by a small parabolic mirror (25 mm diameter, N.A. 1, custom-made by Soptel) inside the cryostat and focused outside the cryostat on the photomultiplier (RCA 31034 A02). The laser light was filtered out by a Schott RG630 red-pass glass. The autocorrelation function of the intensity was recorded on a home-made correlator, devised for light-scattering measurements.

Figure 1, curve A, shows the broad excitation spectrum of the O_1 and O_2 sites of Pc in a melt-grown p-TP crystal at 1.8 K. The nearly Gaussian bands result from the superposition of a large number of the much narrower homogeneous lines of single molecules. The resonance frequency of each molecule is determined by the crystal defects in its surroundings. This is illustrated in Fig. 1, curve B, by the excitation spectrum of a sublimation-grown flake. The O_1 and O_2 bands are much
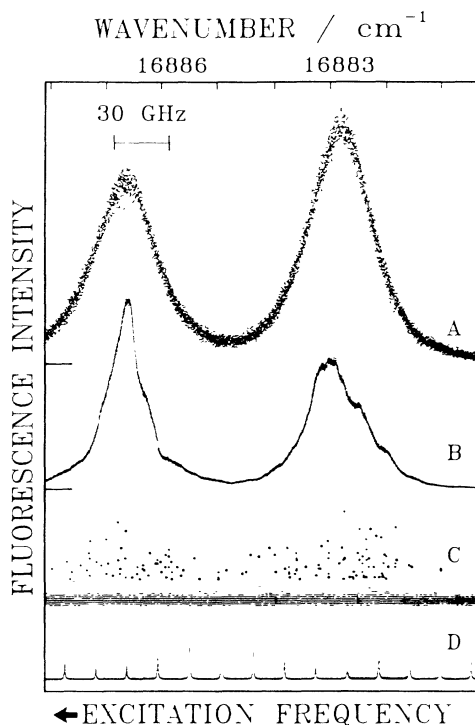

FIG. 1. O_1,O_2 region of the fluorescence excitation spectra of pentacene in different p-terphenyl crystals. Curve A, thick melt-grown crystal showing the Gaussian inhomogeneous bands. B, sublimation flake presenting narrower bands and substructure presumably due to cooling-induced defects. C, spectrum of a very small volume of a sublimation flake. The dots are the narrow excitation peaks of individual molecules. D, calibration spectrum of an etalon.

narrower in this spectrum and exhibit a clear structure. Sublimation flakes are known to be structurally much neater than melt-grown crystals. Therefore, special defects such as dislocations likely to appear on cooling can give rise to substructure in the spectrum.

If we reduce the number of absorbing centers in the laser beam, the absorption or excitation spectrum will display the statistical fluctuations of the number of molecules absorbing at a given frequency. This statistical fine structure was first described by Moerner and co-workers[12,13] in a Pc-p-TP sample. We could observe this effect in fluorescence excitation spectra of either a few tens of thousands of μm^3 of a sublimation flake excited with a broad beam or a few hundreds of μm^3 of a melt-grown crystal with focused excitation. By further reducing the number of molecules in the excited volume, either one or no molecule will absorb at a given frequency. The spectrum is then a set of sharp lines distributed irregularly across the inhomogeneous profile, each corresponding to an individual molecule. We claim that the excitation spectrum of Fig. 1, curve C, is an example of this, i.e., that most of the isolated but reproducible dots are the absorption lines of single Pc molecules. We note that the spectrum presents the expected irregular distribution. Hereafter, we examine several arguments strengthening our assertion.

The expanded frequency scale of Fig. 2 shows that most of the dots resolve into well-shaped (approximately Lorentzian) peaks. The widths of the peaks range from 10 to 15 MHz. The excitation flux was about 25 mW cm^{-2}, i.e., below the saturation flux 71 mW cm^{-2},[8] and
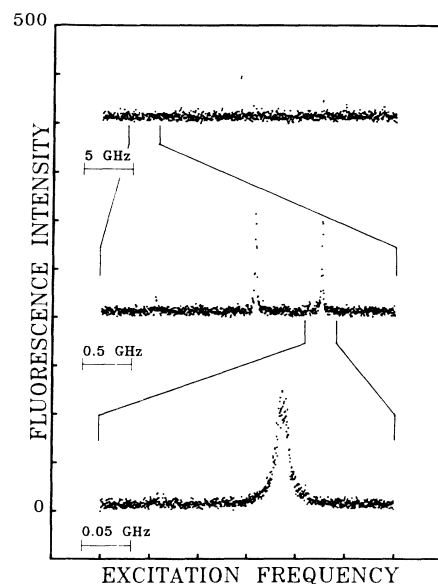

FIG. 2. Shape of a single molecule's excitation peak at different frequency scales. The bottom spectrum is approximately Lorentzian with FWHM about 12 MHz. The vertical scale is in counts/channel.

we checked that no much narrower structure could be measured with lower fluxes. Although the residual drift of our laser hinders an accurate determination of the width, the measured values were always larger than the expected 8 MHz measured on a short time scale from photon echoes by de Vries and Wiersma.[9] This deviation could arise from slow motion in the crystal (spectral diffusion) leading to line broadening on long time scales. However, as this hypothesis is at variance with width measurements by autocorrelation of the statistical fine structure,[13] more work is needed to establish the peaks' width. The narrow range of peak widths and their small values are strong arguments in favor of single molecules because even very weak perturbations (like isotopic substitutions) in one molecule's neighborhood could remove an accidental degeneracy.

The next useful parameter is the peak height. Study of the peak heights as a function of excitation intensity reveals a clear saturation[14] in the range of 100 mW cm^{-2} as expected.[8] However, an accurate determination of the absolute intensity is difficult with our setup. At high powers, the emission rate is fixed by the intersystem crossing yield q_T from S_1 and the triplet lifetime τ_T. The published values $q_T = 0.005$ and $\tau_T = 45$ μs (Ref. 9) give an average emission rate of about 5×10^6 photons/s molecule. We estimate our overall detection yield to be a few tenths of a percent, so that the measured signal (5000 counts s^{-1}) is consistent with that from a single molecule.

At high excitation flux, the molecule spends an average time τ_T "shelved" in the triplet state T_1, between emission sequences when it carries out excitation-emission cycles between S_0 and S_1. Therefore, the emission is interrupted by "dark periods"; i.e., photons are emitted in "bunches." Such an effect can only be observed when looking at a single quantum system (or at very few of them), because random overlapping of several such signals quickly blurs bunches and dark

periods. Therefore, photon bunching (and antibunching at much shorter times, out of reach of our equipment) is a true signature of a single molecule's fluorescence. Figure 3 presents the measured autocorrelation function of the emission at the maximum of one of the peaks. The exponential decay directly shows bunching at short times. The contrast also demonstrates the high degree of bunching, thereby confirming our assignment of the peak to a single molecule.

We also studied the temperature dependence of a few peaks. For most molecules we observed a broadening which increased markedly above 4 K. In an isolated case, we first saw broadening from 2.5 to 3 K, then narrowing, followed by renewed broadening above 4 K. This behavior could be an example of motional narrowing in the optical domain. It also demonstrates the advantage of individual-molecule spectroscopy for singling out anomalous cases that would otherwise disappear on averaging.

While scanning the excitation across certain peaks, we observed the sudden disappearance of the fluorescence signal. Most often the emission resumed after an interruption lasting a few seconds. Figure 4 shows an instance of this behavior, where both spectra were taken successively on the same resonance peak. This phenomenon is rather difficult to rationalize if one assumes that one peak involves several molecules, but it can be understood very simply by assuming transient "hole burning" of a single molecule. Since it depends on the particular molecule studied, we assume that this hole burning has a
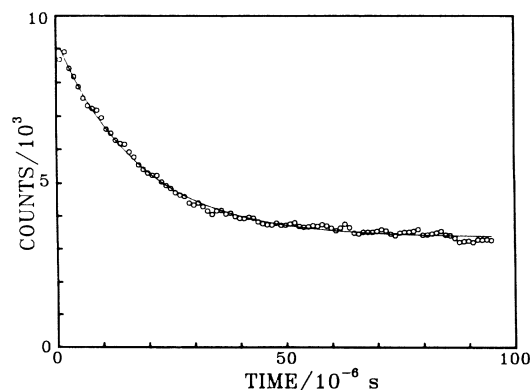
FIG. 3. Time-domain autocorrelation function of the intensity emitted by a single molecule in the saturated regime. The exponential decay shows photon bunching at short times, due to shelving in the metastable triplet state.
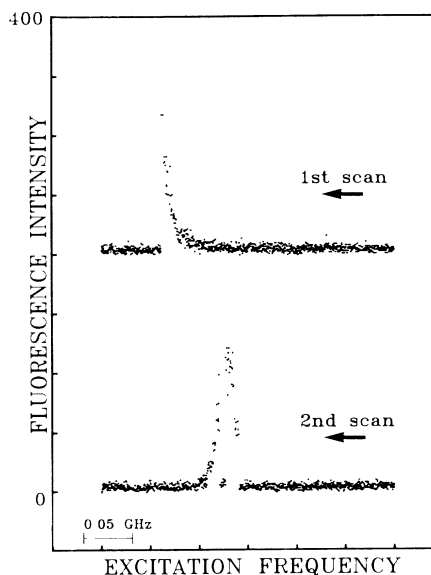
FIG. 4. Two successive scans of the excitation spectrum of a single molecule suggesting a photophysical hole-burning process. The sudden intensity falls and surges might arise from the flip-flops of a two-level system in the neighborhood of the molecule. The time per channel was 0.08 s and a scan lasted about 1 min. The vertical scale is in counts/channel.

photophysical origin; i.e., the resonance frequency of the molecule shifts according to an optically induced change of its environment. Kador, Horne, and Moerner[8] suggested a flip of one of the phenyl rings of the host to explain their observation of transient hole burning. If this is true, we have observed quantum jumps of a particular two-level system in a solid, using the Pc molecule as a probe. This result is obviously of great significance for the low-temperature dynamics of the condensed phase.

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