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by

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Physics

OPTICAL SPECTRA AND KINETICS OF SINGLE IMPURITY MOLECULES IN A POLYMER: SPECTRAL DIFFUSION AND PERSISTENT SPECTRAL HOLE-BURNING

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ABSTRACT:

Using high-efficiency fluorescence excitation techniques, optical spectra of single impurity molecules of perylene in a poly(ethylene) matrix can be obtained at 1.5 K. Analysis of such spectra show a variety of spectral diffusion effects, including fast (< 2 s) resonance frequency changes on the 1-100 MHz scale which lead to a range of apparent linewidths, as well as discontinuous jumps in the resonance frequency of 10-1000 MHz on a longer time scale. In addition, light-induced changes in resonance frequency of a single molecule (persistent spectral hole-burning) have been conclusively observed by showing that the burning time decreases with increasing laser power. Surprisingly, hole-burned single molecules often spontaneously return to the original frequency in 1-100 s. Measurements of the burning time for a large number of hole-burning events for the same single molecule yield an exponential burn time distribution, which is the first direct measurement to our knowledge of the stochastic kinetics of a single molecule. Analysis of the signal-to-noise function appropriate to these experiments gives the conditions under which other systems may allow single-molecule detection: strong absorption, high fluorescence yield, weak bottlenecks in the optical pumping process, and low hole-burning quantum efficiency.

A. INTRODUCTION

Recent successes in the optical detection and spectroscopy of single impurity molecules in solids (single molecule detection or SMD) by both absorption [1] and fluorescence excitation methods [2, 3] have opened up a new area of optical spectroscopy of solids where truly unique single environments and quantum effects can be studied in detail. In the pentacene in *p*-terphenyl system, the surprising observation of spectral diffusion of a single impurity in a crystal[4] proves that novel physical effects can be observed.

Until very recently, the reports of SMD have concentrated on the crystalline system of pentacene in *p*-terphenyl. Owing to the complex physical effects characteristic of the amorphous state[5], it is important to extend SMD experiments to amorphous hosts such as glasses or polymers. When impurity molecules are doped into amorphous materials, an important physical effect is expected: persistent spectral hole-burning (PSHB)[6]. When the impurity molecule has no specific photochemistry, nonphotochemical hole-burning due to transitions of the low-energy excitations characteristic of amorphous hosts can occur[7].

Recently, the first SMD and PSHB of impurity molecules in a polymer were reported[8] for the system composed of perylene molecules in poly(ethylene) (PE). This paper describes additional details and physical studies that have been performed on this system. After summarizing the samples and apparatus in Section B, a discussion of the signal-to-noise considerations for SMD is presented in Section C. An example of a material with excessive PSHB, pentacene in benzoic acid, is described briefly. The advantages of the perylene in PE system become evident immediately when statistical fine structure is observed, and specific results on spectral diffusion and PSHB for perylene in PE are described in Section D. The paper concludes with a description of the statistical determination of the PSHB kinetic distribution for an individual single molecule, the first such measurement of the kinetics of a single quantum system to our knowledge.

B. EXPERIMENTAL

Samples were prepared from zone-refined perylene and low density poly(ethylene) (PE, Microthene FN 500-00; Quantum Chemical Corp.; crystallinity ≤ 25 %). In the first step of the sample preparation the perylene was dissolved in acetone and the solution was mixed with the polymer. The coated powder was then dried under high vacuum at ≃50 C to evaporate the solvent. Finally, the polymer films were prepared by pressing a certain amount of the material between glass slides at 140 - 150 C and quenching to 77 K for 1 min. This procedure results in films with very good optical quality (low light scattering), the thickness of which was typically 10 to 20 μm. As seen qualitatively from the fluorescence emission at room temperature using high concentration samples, this technique produces a fairly homogeneous distribution of the absorbers in the host polymer. Low resolution optical absorption spectroscopy revealed that little or no aggregate formation occurred during sample preparation. The mass ratio of the perylene/PE films used in this study was between 5.8×10^{-5} and 9.5×10^{-7}. For the experiments on pentacene in benzoic acid crystals, thin doped crystals were prepared from sublimed pentacene and high-purity benzoic acid (Aldrich; 99+ %) by melting a mixture of the two solids, cooling it down slowly, and cutting out small pieces with a sapphire plate.

The experimental setup for our fluorescence excitation experiments is described in detail elsewhere[9], therefore only the differences from the earlier apparatus will be specified here. The tunable excitation laser light (≃ 2-3 MHz linewidth) was generated by a standing-wave single-frequency Stilbene 420 dye laser pumped by the all-lines uv output of an Ar^+ laser. This excitation light was tuned to wavelengths near the center and to the red of the inhomogeneous line of the perylene (0-0) $S_1 \leftarrow S_0$ transition in PE (442-450 nm). Before entering the cryostat, the beam was spatially filtered with a 50 cm piece of single-mode polarization-preserving optical fiber (York HB450). The emitted fluorescence collected by the parabolic mirror was long-pass filtered to remove Rayleigh scattered radiation with a low fluorescence filter (Schott KV500).

C. SIGNAL-TO-NOISE CONSIDERATIONS FOR SINGLE-MOLECULE DETECTION

The attainable signal-to-noise ratio (SNR) for single molecule detection in a solid using fluorescence excitation spectroscopy can be approximated by the following equation:

$$\frac{S_1}{(\text{noise})_{\text{rms}}} = \frac{D\phi_f\sigma P_0\tau/Ah\nu}{\left[\dfrac{D\phi_f\sigma P_0\tau}{Ah\nu} + C_bP_0\tau + N_d\tau\right]^{1/2}}, \tag{1}$$

where S_1 is the peak fluorescence signal from one molecule, ϕ_f is the fluorescence quantum yield, σ is the peak absorption cross section on resonance, P_0 is the laser power, τ is the integration time (counting interval), $A \simeq (5\mu m)^2$ is the laser beam area in the sample, $h\nu$ is the photon energy, N_d is the dark count rate, and C_b is the background count rate per Watt of excitation power. The factor $D = \eta_Q F_p F_f F_1$ describes the overall efficiency for the detection of emitted photons, where η_Q is the GaAs PMT quantum efficiency, F_p is the fraction of the total emission solid angle collected by the paraboloid, F_f is the fraction of emitted fluorescence which passes through the long pass filter, and F_1 is the total transmission of the windows and collection optics. The three terms in the denominator of Eq. 1 represent shot noise contributions from the emitted fluorescence, background, and dark signals, respectively.

According to Eq. 1 there are several important criteria that have to be fulfilled to generate optimum SNR, once the collection efficiency D is maximized. First, the peak absorption cross section σ and the fluorescence quantum yield ϕ_f of the impurity in the matrix should be as high as possible. The area of the laser spot at the sample plane should be as small as possible which requires tight focussing of the probing laser beam. The power P_0 cannot be increased arbitrarily because saturation causes the peak absorption cross section to drop according to [10]

$$\sigma \rightarrow \sigma(I) = \frac{\sigma_0}{1 + I/I_S} \tag{2}$$

where I is the laser intensity and I_S is the saturation intensity. To maximize I_S for organic molecules, a weak triplet bottleneck, which means low triplet quantum yield and short triplet lifetime, is favorable. Expressions for I_S are given in Ref. 11.

In single-molecule studies in solids, a crucial physical effect not included in Eq.1 has to be taken into account. Persistent spectral hole-burning (PSHB), which can be observed for certain impurities in crystals and which is a more or less general phenomenon in amorphous hosts[6], can cause the single impurity to change its absorption frequency before it emits enough photons to be detected above the noise level. The detrimental influence of PSHB for single-molecule spectroscopy can be demonstrated by a specific example. We choose the well-studied system of pentacene impurities in a benzoic acid (BZA) crystal in which the PSHB quantum yield was reported[12]. to be 2×10^{-6}. Fig. 1 shows fluorescence excitation spectra near the center of the (0,0) zero-phonon absorption line at 588.329 nm where the average number of molecules per homogeneous width is much larger than 1 ($\overline{N}_H \gg 1$). The traces show a number of wiggles and bumps the rms amplitude of which are higher than the rms noise level. These features are the well-known statistical fine structure (SFS) which is a static phenomenon caused by statistical number density fluctuations of the number of absorbers per homogeneous width. This effect was first observed in the pentacene in p-terphenyl system[13].

However, in contrast to pentacene/p terphenyl, in the BZA host the rms amplitude of the signal is only slightly above the noise level and the two successive traces shown in Fig.1 are only weakly correlated. Additionally, as seen in Fig.1, the average signal level has clearly dropped for the second trace. These effects are due to hole-burning which eventually prevents the detection of single molecules far out in the wings of the inhomogeneous line where $\overline{N}_H \leq 1$. Attempts to lower the probing power to reduce PSHB result in a loss in SNR as described by Eq. 1.

The negative result for SMD detection in pentacene/BZA is in agreement with the predictions of our SNR simulations for SMD in pentacene/p-terphenyl. We find, both experimentally and using Eq. 1, that the optimum SNR (30 in 1 Hz) is reached in pentacene/p-terphenyl when the number of excitations is $\simeq 2 \times 10^5$. As the photophysical parameters of pentacene/BZA are similar and the experimental setup is essentially the same, a similar number of excitations is needed to produce sufficient SNR for pentacene in BZA. However, in the BZA matrix the hole-burning quantum efficiency is 2.0×10^{-6} which means that after $\simeq 5 \times 10^5$ excitations, single pentacene molecules will change their absorption frequency (i.e., burn) on the average. Therefore - at least with our current experimental conditions - it is not possible to reliably detect single pentacene molecules in the BZA matrix, and systems with lower hole-burning quantum yield are required for convenient detection.

As is well-known, PSHB can occur in doped amorphous matrices via photochemical or nonphotochemical processes. Nonphotochemical hole-burning systems, especially aromatic hydrocarbons in non-hydrogen-bonding matrices, have in general lower hole-burning quantum efficiencies than photochemical systems, which makes them more appropriate for SMD investigations. Besides a low burning efficiency, it is favorable to have a system where the homogeneous linewidth Γ_{hom} is as narrow as possible because this has a direct influence on the peak absorption cross section of the impurity (for fixed oscillator strength, σ_0 drops as Γ_{hom} increases). From PSHB studies [14, 15] it is known that the quasi-homogeneous linewidths measured in doped poly(ethylene) films are some of the narrowest obtained in glassy or polymeric matrices. Following the above reasoning pentacene in poly(ethylene) (PE) should be an ideal candidate. However, due to the oxidative instability of pentacene and the poor solubility of this guest, it was not possible to prepare well-defined samples.

We therefore chose perylene/PE to be the system investigated. Perylene is a highly stable aromatic hydrocarbon and the burning efficiency in a PE matrix is expected to be low. The peak cross section for this system is $\sigma_0 = 3.2 \times 10^{-11}\mathrm{cm}^2$, using $T_2 = 2T_1 = 2 \times 6.4\mathrm{ns}$ [16] and an oscillator strength $f = 0.034$. This value of f uses an overall oscillator strength of 0.44 [17] corrected to include only the (0,0) contribution and the zero-phonon contribution as described by the Debye-Waller factor[18]. The values for σ_0 and $\phi_f(0.98)$ [19] are even more favorable than for pentacene which compensates for the inconvenient dye-laser wavelength range required to excite the lowest electronic transition.

D. RESULTS AND DISCUSSION

Figure 2 shows a fluorescence excitation spectrum of a sample with perylene/PE mass ratio of 5.8×10^{-5} at $\lambda = 447.160$ nm. Since this is a region where $\overline{N}_H \gg 1$, SFS is expected. As is quite obvious from Fig.2 the two traces shown are highly correlated over the investigated 8 GHz scan range and the average signal level does not drop for the second trace. However, the correlation is not as excellent as for pentacene/p-terphenyl[20], and the differences between the two traces suggest that spectral diffusion and/or spectral hole-burning are taking place during recording of the spectra. As this work is mainly concerned with the detection and spectroscopy of individual single molecules in a polymeric host, the SFS spectra will not be discussed in detail. Nevertheless, it is important to point out that reproducible, static SFS is an extremely valuable precursor for SMD, because it shows that the experimental conditions have been reached where the discreteness of individual molecular contributions to the overall absorption can be resolved.

By tuning the laser further to the long-wavelength side of the inhomogeneous line ($\overline{N}_H < 1$) single molecule spectra are easily observed. Although this is true for both concentrations investigated, the data shown and discussed below were all collected with low concentration samples (perylene/PE mass ratio: 9.5×10^{-7}).

In Figure 3, fluorescence excitation spectra of various single perylene molecules in the PE host at 1.5 K are displayed. The spectra of the individual absorbers were taken in the wavelength range between 447.875 and 450.152 nm. The different signal amplitudes occur for several reasons. (i) the power levels used for recording the spectra are different, (ii) some of the molecules shown may be not exactly in the center of the Gaussian laser intensity profile, and (iii) the polarization orientation of the incoming laser beam is not always optimized with regard to the orientation of the transition dipole moment of the individual absorbers. The slight differences of the experimental conditions are, however, not related to the essential phenomenon presented in Fig. 3: a variety of linewidths are observed at 1.5 K. The observed linewidths range from 52 ± 2 MHz in trace (a) to 142 ± 5 MHz in trace (f), and all these values are larger than the lifetime-limited width of 29.4 MHz[16]. The different linewidths occur without correlation with position relative to the center of the inhomogeneous line and - as stated above - without correlation with the probing intensity. In fact, trace (a) with the smallest width was recorded with the highest probing power of 9 nW and was also optimized with regard to focusing and polarization orientation. A likely explanation for this is that spectral diffusion on the 1-100 MHz scale is occurring during the $\simeq$ 2 s required to measure the lineshape. In addition, there may be a pure homogeneous dephasing (nondiagonal) contribution to the width at this temperature due to fast TLS transitions of the polymer host present at 1.5 K. According to the standard models[21], this contribution to the width is generally assumed to be the same for all molecules.

Recently, it was shown by a comparison of photon-echo and hole-burning linewidth measurements [22] - experiments which operate on very different time-scales - and by measuring the evolution of hole shapes in time [23] that spectral diffusion is a common feature in amorphous hosts. Therefore, such effects would not be unexpected in our single-molecule experiments. However, in the previous studies, spectral diffusion manifested itself in the time evolution of spectral holes which were burnt into a large ensemble of molecules. In contrast, in the single molecule regime we measured different linewidths for different molecules in a fixed time window (2 s). If one would measure the holewidth in a PSHB experiment with many molecules several times at a fixed time after burning, the hole width would always be the same, representing the ensemble average of spectral diffusion. The unique feature of the SMD experiment is that it enables us to reveal experimentally that a variety of local environments is characterized by a variety of spectral diffusion contributions to the linewidth.

In addition to the range of linewidths, we also observe slower spectral diffusion which appears as discontinuous jumps in resonance frequency on the scale of several hundred MHz between or during the 25 s laser scans in a fashion similar to the previous work on pentacene in *p* terphenyl[4]. One example of discontinuous jumping for a single perylene molecule in PE is shown in Figure 4. Here, after each 2.68 s laser scan the peak frequency of the molecule's absorption was located by a digital waveform recorder and the actual resonance frequency was plotted as a function of time to yield the displayed trend. During recording of the ~ 210 s trend the investigated molecule disappeared twice from the detection window (4.8 GHz) (see arrows in Fig. 4). After 210 s the molecule vanished irreversibly, at least for the time range of the experiment out to 450 s. This may have occurred as a result of spectral diffusion over a wider range than given by the actual detection frequency range or due to PSHB of the chromophore itself.

The spectral diffusion process in amorphous solids is thought to be caused by phonon-assisted tunnelling among the states of the TLS's which are characteristic of the amorphous state[24-26]. Both diagonal perturbations which shift the energy of the optical transition of the impurity and off-diagonal perturbations shifting the phase of the excited state are expected[27]. Due to the individual, unique nature of the observed spectral jumps for our single molecules, a detailed analysis of the spectral diffusion must be the subject of a future study, as the present work is focused on the truly novel light-driven process for single molecules, persistent spectral hole-burning.

The eventual disappearance of the molecule in Fig. 4 out of the detection range could have been due to PSHB. While in this particular case PSHB is only a speculative suggestion, the remainder of this paper will conclusively demonstrate the first PSHB experiments on the single molecule level by providing unambiguous evidence for a truly light-driven process. Usually, persistent spectral hole-burning (PSHB) in solids refers to optical modification of an inhomogeneous line where the number of centers in resonance is much greater than one. When light absorption induces photochemical changes in the excited centers or photophysical (nonphotochemical) alterations in the nearby host, a narrow spectral "hole" or dip can develop in the absorption spectrum because the altered centers no longer absorb at the laser wavelength. (By definition, "persistent" requires that the alteration persists longer than any excited state lifetime, and in practice, hole lifetimes from seconds to many years have been demonstrated.) In the single molecule regime, however, only the isolated homogeneous absorption profile of a single center is present. When photochemical or photophysical changes occur as a result of optical excitation, the resonance frequency of the single molecule may move far away from the laser scan range, that is, the absorption line appears to vanish.

Figure 5 serves as an example of the two types of experiments we performed in our PSHB studies on single molecules of perylene in PE. Fig. 5(a) shows a frequency scan at 1.5 K over a frequency range of 4 GHz. In this frequency interval two single molecules were observed. For all burning experiments we deliberately chose molecules which had little spontaneous spectral jumping from one resonance frequency to another. This is true for the molecule at the frequency position of $\simeq$2 GHz. Figure 5(b,c) shows time scans with a fixed laser frequency. In trace 5(b) the laser was tuned into resonance within the first 10 s at a power level of 3.8 nW. For the remaining 90 s of this time scan the fluorescence signal stays at a constant level indicating that no burning occurred under these experimental conditions. In trace 5(c) the power level was raised to 9.5 nW and sim9 s after the laser was tuned into resonance with the molecular absorption line the fluorescence signal suddenly dropped suggesting hole-burning. A frequency scan (Fig. 5(d)) recorded after the completion of the time scan shows (arrow) that the resonance frequency shifted by more than ± 2 GHz as result of the light-induced change. Fig. 5(d) also indicates that the second molecule in this trace, which serves as a frequency marker, is still present and spectrally diffusing.

In Figure 6 we provide evidence that single-molecule hole-burning is a controllable process which in principle allows modification of the transition frequency of any arbitrary chosen molecule in the polymer host. For this purpose we recorded spectra in a region where four different molecules were present in the frequency scan range. The first ten traces counting from the bottom in Figure 6 were taken during 29 min using a scanning power level of 4.7 nW. Besides spectral diffusion over a small frequency range - most clearly seen for the molecule at + 2.14 GHz and less so for the molecule at +0.5 GHz - the spectra show reproducible frequency positions for all molecules. After trace 10 the laser was deliberately brought into resonance with the molecule residing at 0.5 GHz. The laser frequency was then held constant at the scanning power level of 4.7 nW until the fluorescence signal dropped after ≃28 s indicating hole-burning. Trace 11 of Fig.6 was taken after the hole-burning event demonstrating that the molecule selected for hole-burning actually changed its resonance frequency and that the other molecules which serve as frequency markers did not change their absorption frequency. The remaining traces of Fig.6 (12 - 15) were taken in the next 15 min. , and within this time the burnt molecule did not reappear anywhere within the scan range.

As was seen in Figs. 5 and 6, the light-induced change we attribute to PSHB shifted the resonance frequency of the corresponding molecules at least by $\simeq \pm$ 2 GHz. The exact location of the new resonance frequency, however, is unknown at present. By analogy with previous nonphotochemical hole-burning studies on large ensembles of molecules[28], the shift may be expected to be up to 100 cm^{-1}.

The single-molecule hole-burning demonstrated in Figs.5 and 6 was irreversible, which means in the present context, that the molecules did not return to their original wavelength during observation times of up to 20 min. Actually, at low power levels, the return of the single molecule to the burning frequency is the more often observed feature. An example of this behavior is shown in Figure 7. Before the traces shown in the figure, the molecule was scanned 5 times and no significant changes were observed. Traces (a), (b), and (c) show three additional scans of the molecule. After trace (c), the laser was tuned into resonance with the molecule using the scanning power of 9 nW; within 30 s the size of the emitted fluorescence suddenly dropped to the background level indicating hole-burning. Trace (d) was then acquired, which shows that the resonance frequency shifted by more than ± 1.25 GHz as a result of the light-induced change. A further scan some minutes later (trace (e)) showed that the molecule surprisingly returned to the original wavelength within 10 MHz. Further scans (traces (f) and (g)) revealed no further changes in resonance frequency. After trace (g), the laser was again tuned into resonance until the fluorescence dropped; a final scan (trace (h)) showed that the molecule was again absent from the range of the laser scan.

The fact that one and the same molecule can be burnt several times provides a convenient means to study the power dependence and the kinetics of the hole-burning process. To illustrate, Figure 8 (a,b) shows time scans with a fixed laser frequency. In trace (a) the laser was tuned into resonance with the molecule in the first 10 s at a power level of 4.5 nW. The eventual abrupt drop of the fluorescence signal at 260 s is the hole-burning event; the return of the emitted fluorescence indicates that the molecule has returned to its original frequency, only to be burned again, and so on. In trace (b) of the figure, the laser power level was increased to 27 nW; now the time in resonance, although stochastic, is clearly shorter. This indicates that the average rate of PSHB for this perylene impurity in PE increases with laser power, providing unambiguous evidence that the spectral changes are indeed light-driven. Additional studies on a variety of single molecules at a variety of laser power levels over many thousands of seconds of observation yield a confirmation of this power dependence. For example, in Fig. 8 (c) the average burn times for several single molecules as obtained from time scans like traces (a) and (b) are plotted *versus* the laser power used. Even though the actual burn times are stochastic, the average burn time for all centers investigated decreases with increasing laser power. In contrast, and as expected, there is no correlation between the average return times and the laser power (Fig. 8(d)). This power dependence together with the other results presented above provides clear evidence that the hole-burning process is laser-driven and not very slow coincidental spectral diffusion.

The results in Fig. 8 (a,b) show that the burn time for a single molecule at a given power level is not fixed, but rather is stochastically distributed. To obtain insight into which form of distribution function can be used to characterize the random variable "burn-time", it is necessary to measure a large number of burning events. To this end, we measured 54 burning events on the same single molecule of perylene in PE. Since this number of samples of the distribution represents only a small random sample we therefore constructed a histogram of the data which is shown in Figure 9. The real time axis was divided into discrete time intervals with a width of 3 s; the ordinate gives the number of events per time interval (frequency). Also plotted in Fig.9 is the result of a single exponential fit to the data. It appears that the histogram of the random sample of burn times can be reasonably approximated by an exponential distribution function with rate parameter $0.18s^{-1}$.

For large ensembles of molecules the first order kinetics of many (photo)-chemical reactions and of the radioactive decay process are well-known examples of exponential distributions. Neglecting dispersion, in addition the hole-growth kinetics in a conventional hole-burning experiment involving many molecules is expected to be represented by an exponential distribution[29]. To our knowledge, all previous kinetic studies in the broader chemical context or in hole-burning experiments have measured the ensemble-averaged kinetics for an assembly of identical molecules. In the single-molecule regime we deal with the time averaged properties of one quantum system which by the ergodic theorem should be equivalent to the ensemble average. The data reported in Fig. 9 are a first step toward confirmation of the ergodicity of the PSHB process. Further investigations at a variety of power levels and at many positions within the inhomogeneous line will be necessary to reach a thorough understanding of the physical processes involved in the stochastic distribution of the burn times of a single molecule.

Finally, it seems appropriate to compare our results of spectral diffusion and spectral hole-burning of single perylene molecules in a poly(ethylene) host with existing models concerning these processes. The generally accepted model for nonphotochemical hole-burning of impurity molecules in amorphous hosts [7, 29] involves transitions among TLS's near the impurity as a result of the optical excitation, while spontaneous (phonon-assisted) transitions of TLS's far from the impurity affect the dephasing or optical linewidth. Since a transition of a TLS near the impurity should produce a large change in the local strain field, the resulting shift in the optical resonance frequency should be large, while frequency shifts from distant TLS's produce small frequency shifts. Our data provide direct evidence for the following general picture of a *hierarchy* of TLS's surrounding the impurity. The TLS's far away produce fast shifts that are small in magnitude; the closer TLS's produce larger shifts which are more infrequent; and TLS's very close to the impurity are effectively locked until

PSHB occurs. After the PSHB event, the return of the optically excited center to exactly the same wavelength in Fig. 7 is surprising, since it suggests that coupling to exactly one dominant nearby TLS is involved in the hole-burning process, rather than a succession of TLS configurations.

E. CONCLUSION

This paper has described the detection and spectroscopy of single perylene impurity molecules in a poly(ethylene) host using highly efficient fluorescence excitation techniques. In addition to providing the first single-center spectra in any polymeric or amorphous material, the perylene/PE system provides the first conclusive example of a solid host-guest combination where spectral hole-burning of single molecules could be observed

In the first part of the paper it was shown that for pentacene in benzoic acid single molecule detection single-molecule detection could not be performed with our current experimental setup due to excessive spectral hole-burning. In general, for given experimental conditions, the (average) hole-burning quantum efficiency of the investigated system must lie considerably below the inverse of the number of absorption events required to produce good detection SNR, and this critical parameter has to be determined for each specific host-guest combination. The requirement of low hole-burning quantum efficiency is fulfilled for perylene/PE; in addition the favorable photophysical parameters for this system make it an ideal candidate for SMD.

As expected in a polymeric host the single-molecule data revealed spectral diffusion processes occurring over a wide frequency range. Varying linewidths measured for different single perylene molecules during the same detection time window where interpreted as resulting from spectral diffusion on a 1 - 100 MHz frequency scale. Spectral diffusion over a frequency range of several 100 MHz appeared as discontinuous jumps in frequency space reminiscent of similar observations in doped crystals. By tuning the laser into resonance with arbitrarily chosen impurities and holding it at a fixed frequency, changes in the resonance frequency of single absorbers (persistent spectral hole-burning) could be induced in a controllable manner. We observed molecules which burnt irreversibly during measurement times of up to 20 min as well as molecules which returned to the burning frequency on a 1 - 100 s time scale. The possibility of burning one and the same molecule several times allowed measurement of the power dependence and kinetics of the hole-burning process for a single center. The observed power dependence unambiguously demonstrated that our observations indeed represent spectral hole-burning of single molecules and not slow coincidental spectral diffusion. By observing a large number of burning events, we were able to perform to our knowledge the first kinetic measurements on a single quantum system, which yielded an exponential distribution for the random variable "burn-time".

The ability to optically modify the absorption of single impurity centers in a solid leads naturally to the possibility of optical storage at the single-molecule level. One can imagine a very thin layer of a material with a very broad inhomogeneous line so that single molecules are isolated and spread over a large range of frequency space. The resonance frequencies constitute the addresses of all the bits to be encoded in a single focal volume. A binary sequence of "1"'s and "0"'s can be produced by hole-burning or ignoring each single molecule absorption, respectively. Of course, to achieve areal density higher than current PSHB schemes, a method of producing optical beams much smaller than the diffraction limit must be utilized. While this concept is highly speculative at the present time, the single-molecule persistent spectral hole-burning reported here not only provides a unique window into the photophysics and low-temperature dynamics of the amorphous state, but it also allows such novel optical storage schemes to be contemplated.

Acknowledgement

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Figure Captions

Figure 1. Fluorescence excitation spectra of pentacene in benzoic acid at λ = 588.329 nm where $\overline{N}_H \gg 1$ (P = 180 pW, T = 1.5 K). Each trace is a average of 16 scans over a 920 MHz frequency range. As the rms signal amplitude (large bar at upper left part of the figure) higher than the rms noise level (small bar at upper left part of the figure) the narrow features (bumps) can be regarded as a weak signature of statistical fine structure (SFS).

Figure 2. Fluorescence excitation spectra of perylene in poly(ethylene) (PE) at λ = 477.160 nm where $\overline{N}_H \gg 1$ (P = 4.5 nW, T = 1.5 K). Each trace is a average of 64 scans over a 8 GHz frequency range. The correlation between the two traces is very high which proves the narrow, reproducible features to be a clear signature of statistical fine structure. (Note that in contrast to all upcoming figures, here the perylene/PE mass ratio was 5.8×10^{-5}.)

Figure 3. Fluorescence excitation spectra of various single molecules of perylene in PE at 1.5 K. The excitation wavelengths and power levels, respectively, are (a) 448.438 nm, 9 nW; (b) 448.021 nm, 9 nW; (c) 450.152 nm, 4.7 nW; (d) 448.020 nm, 5 nW; (e) 447.875 nm, 4.5 nW; (f) 448.452 nm, 9 nW. Photon count interval = 100 ms, detection bandwidth = 10 Hz. The different signal amplitudes occur due to the different power levels and due to the fact that some molecules may not be exactly in the center of the laser spot. (After Ref. 8)

Figure 4. Spectral jumps in the resonance frequency of a single perylene molecule in a PE host (T = 1.5 K, λ = 446.740 nm). The peak frequency of consecutive 2.68 s laser scans over a range of 4.8 GHz was determined by a program and plotted against time to generate a trend of the peak (resonance) frequency. At the two positions marked with an arrow the molecule disappeared from the detection range and after 210 s it vanished for the rest of the observation time to 400 s.

Figure 5. Frequency scans (a,d) and time scans at fixed laser frequency (b,c) to demonstrate persistent spectral hole-burning of a single perylene defect at T = 1.5 K. To perform the time scan experiments shown in (b,c) the laser was tuned into resonance with the molecule marked with an arrow in trace (a). The laser power level was 3.8 nW in (b) and 9.5 nW in (c), respectively. The abrupt drop of the fluorescence signal in (c) indicates the hole-burning event, which is confirmed by the frequency scan (d).

Figure 6. Persistent spectral hole-burning of a single perylene molecule arbitrarily chosen out of four molecules in a 4.6 GHz scan range (T = 1.5 K, 0 GHz detuning = 448.019 nm). The burning event for the molecule residing at 0.5 GHz was executed after the tenth trace counting from the bottom or in terms of time 29 min after the first trace shown.

Figure 7. Persistent spectral hole-burning of a single perylene molecule in PE at 1.5 K. The content of scans (a)-(h) is described in the text. 0 MHz detuning = 448.021 nm, laser power for scanning and burning = 9 nW, detection bandwidth = 10 Hz, and scan time = 25 s. (After Ref. 8)

Figure 8. Illustration of the power dependence of the hole-burning process. (a) Time scan at a fixed laser wavelength of 448.159 nm with 4.5 nW laser power. (b) Time scan at the same wavelength with 27 nW laser power. (c) Average burn times *vs* laser power, with each point derived from 2-8 burning events. The different symbols represent five different single molecules, and the lines are simple linear fits to the data for each molecule to guide the eye only. (d) Average return times *vs* laser power for four of the single molecules shown in (c). Again, the lines are simple linear fits to guide the eye. The number of data points at the highest power is limited because irreversible PSHB was more common in this case. (After Ref. 8)

Figure 9. Histogram of a random sample of 54 burning events measured for one single perylene molecule using a power level of 4.5 nW (T = 1.5 K, λ = 448.156 nm). The real

time axis is divided into discrete time intervals with a width of 3 s; the ordinate gives the number of events per time interval (frequency). The drawn line is the result of an exponential fit to the data. As the fitted ordinate values lie at the center of each bin, the actual histogram was shifted to the left by 1.5 s for clarity. The single event at 30 s was not included in the fit.

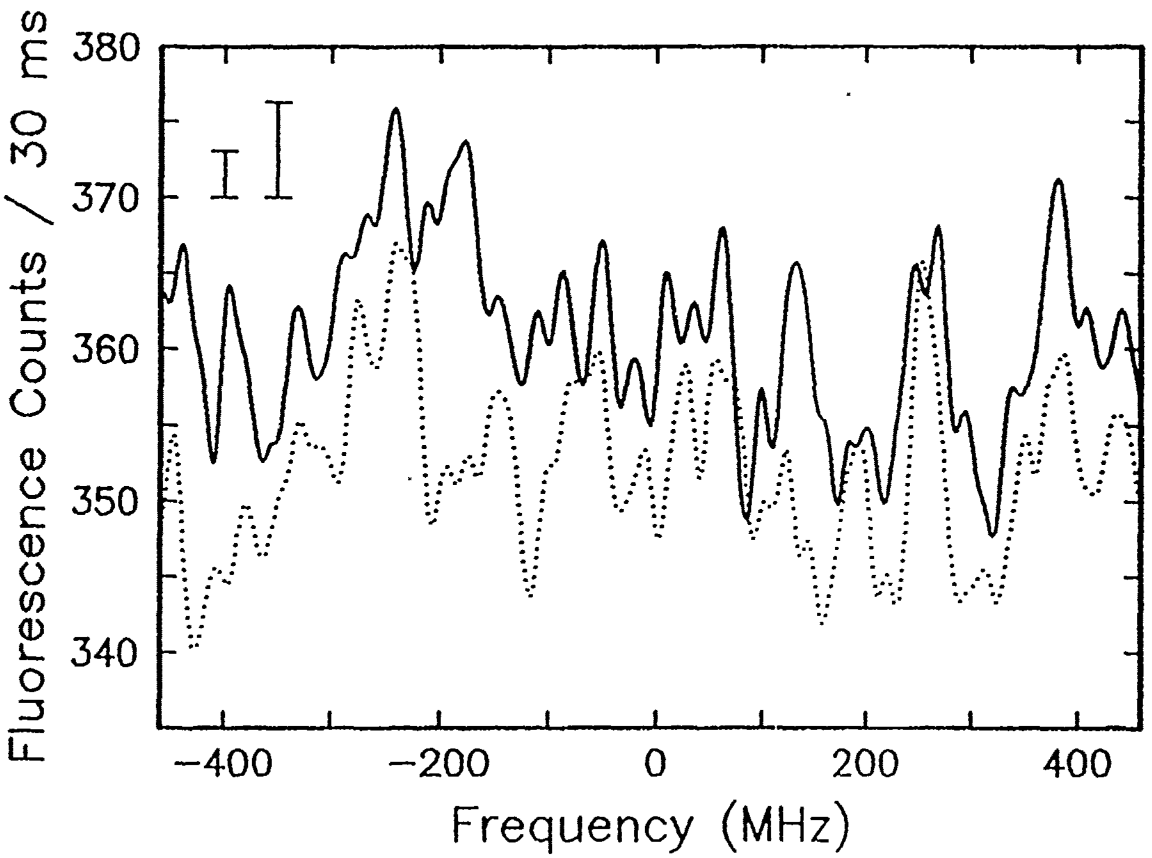
Fluorescence Counts / 30 ms
380
370
360
350
340
−400
−200
0
200
400
Frequency (MHz)

Figure 1

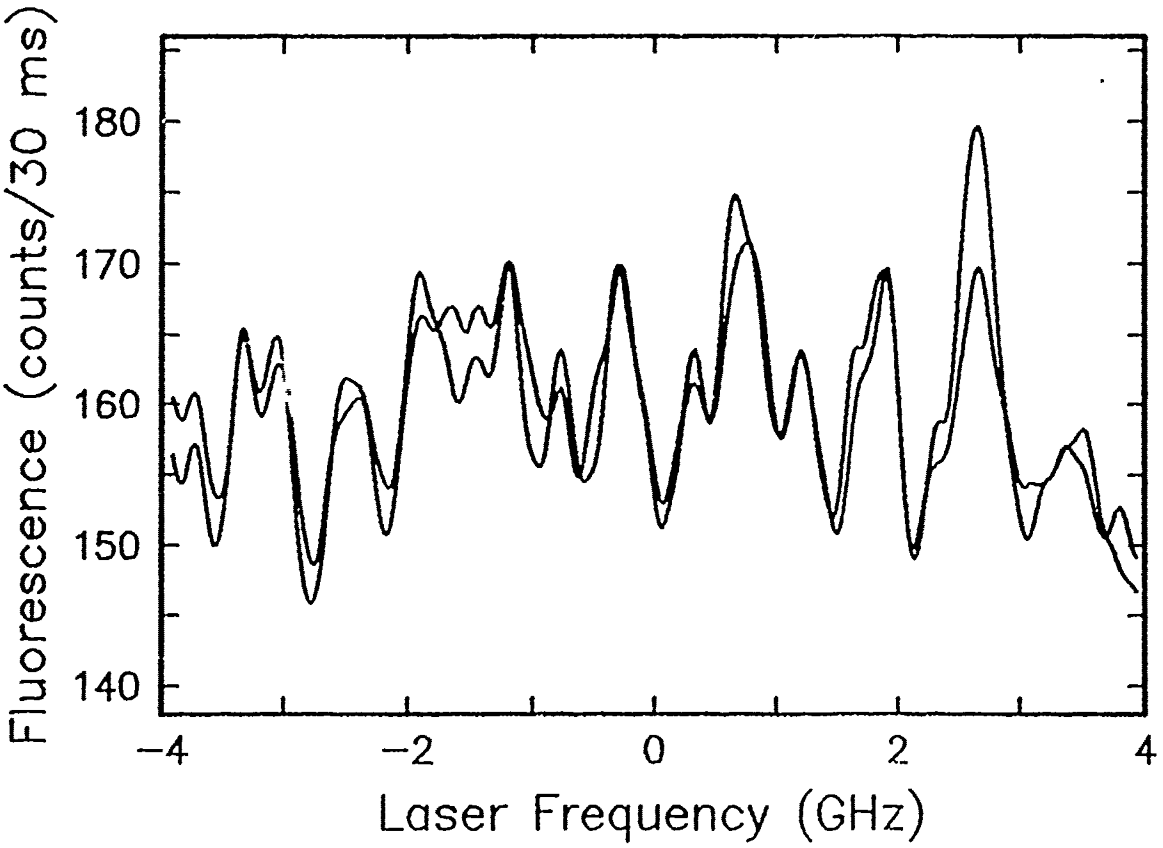
Fluorescence (counts/30 ms)
180
170
160
150
140
−4
−2
0
2
4
Laser Frequency (GHz)

Figure 2

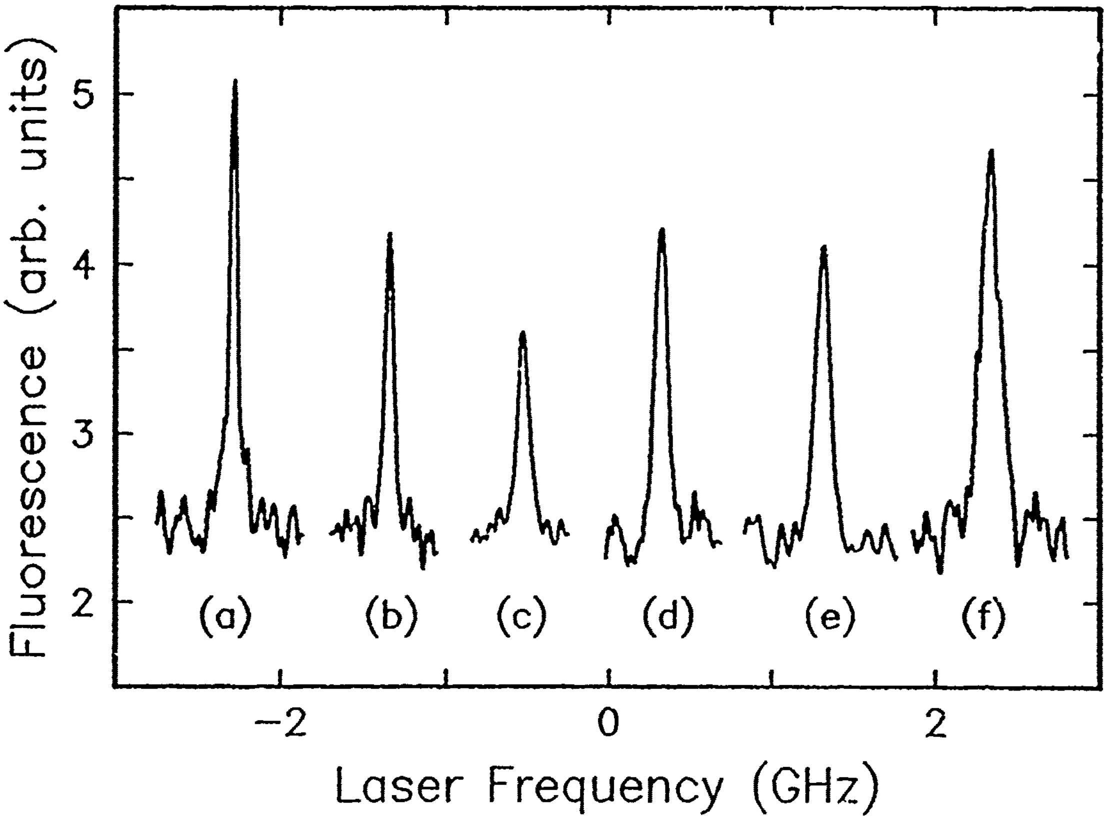
Fluorescence (arb. units)
2
3
4
5
(a)
(b)
(c)
(d)
(e)
(f)
−2
0
2
Laser Frequency (GHz)

Figure 3

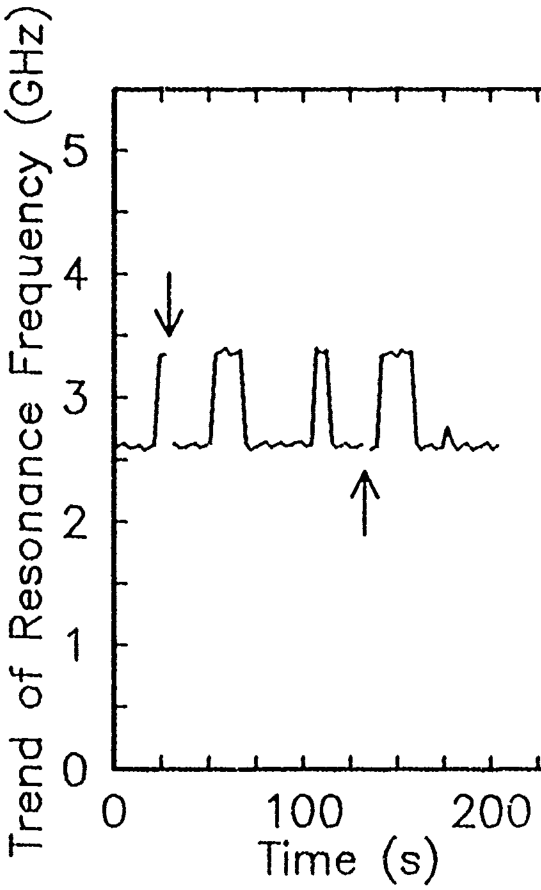

Figure 4

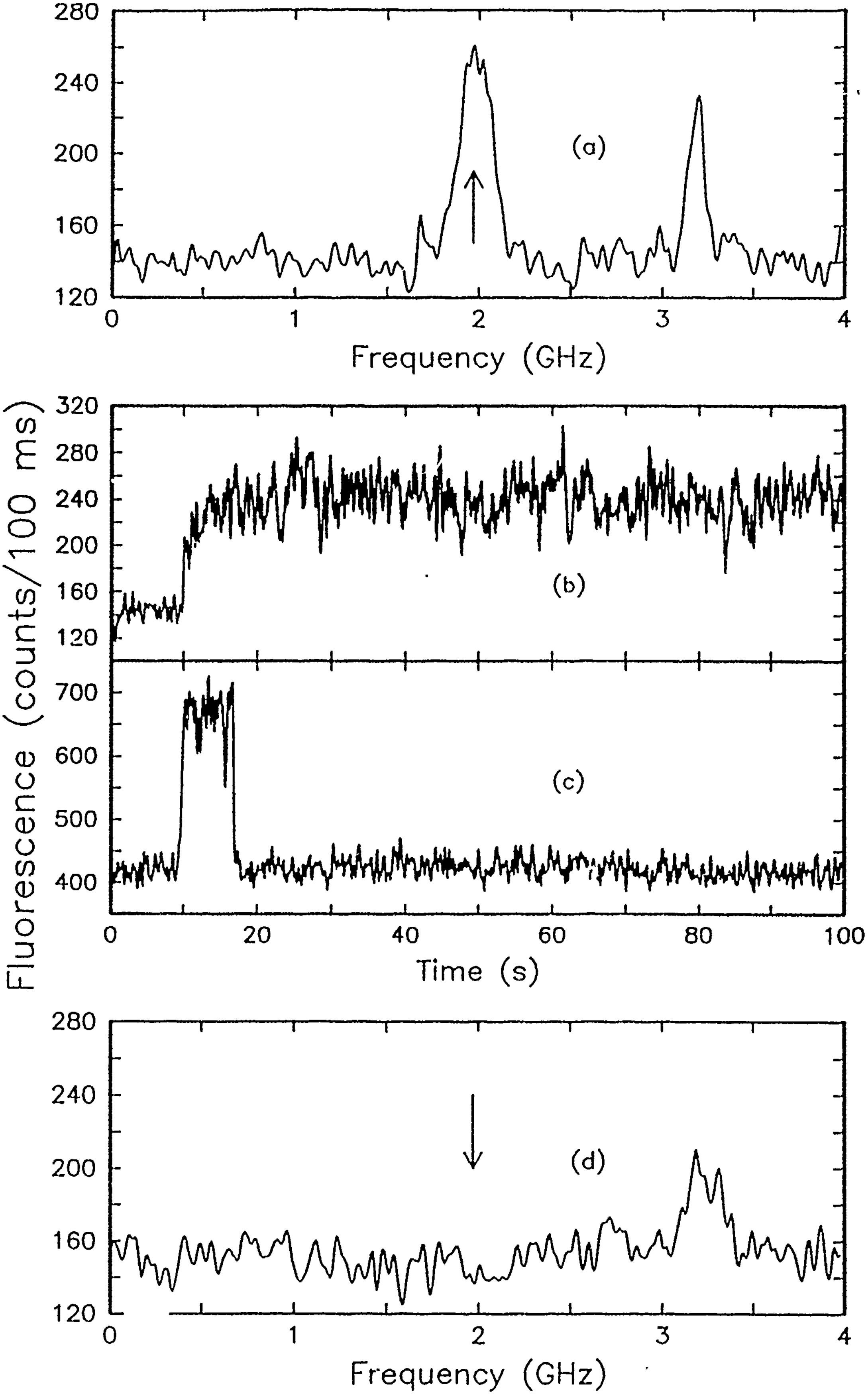
Fluorescence (counts/100 ms)
(a)
280
240
200
160
120
0
1
2
3
4
Frequency (GHz)
(b)
320
280
240
200
160
120
(c)
700
600
500
400
0
20
40
60
80
100
Time (s)
(d)
280
240
200
160
120
0
1
2
3
4
Frequency (GHz)

Figure 5

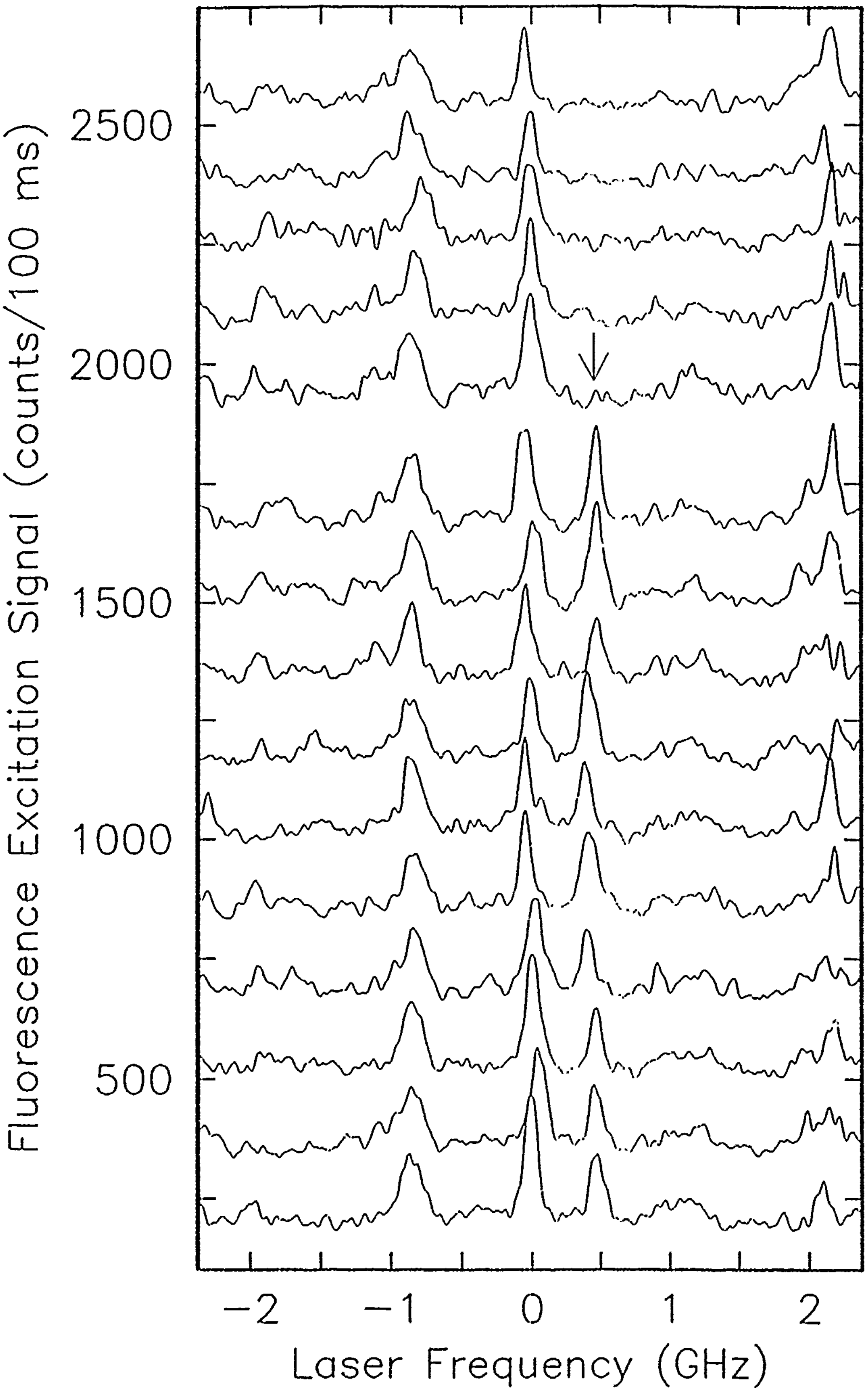
Fluorescence Excitation Signal (counts/100 ms)
2500
2000
1500
1000
500
−2
−1
0
1
2
Laser Frequency (GHz)

Figure 6

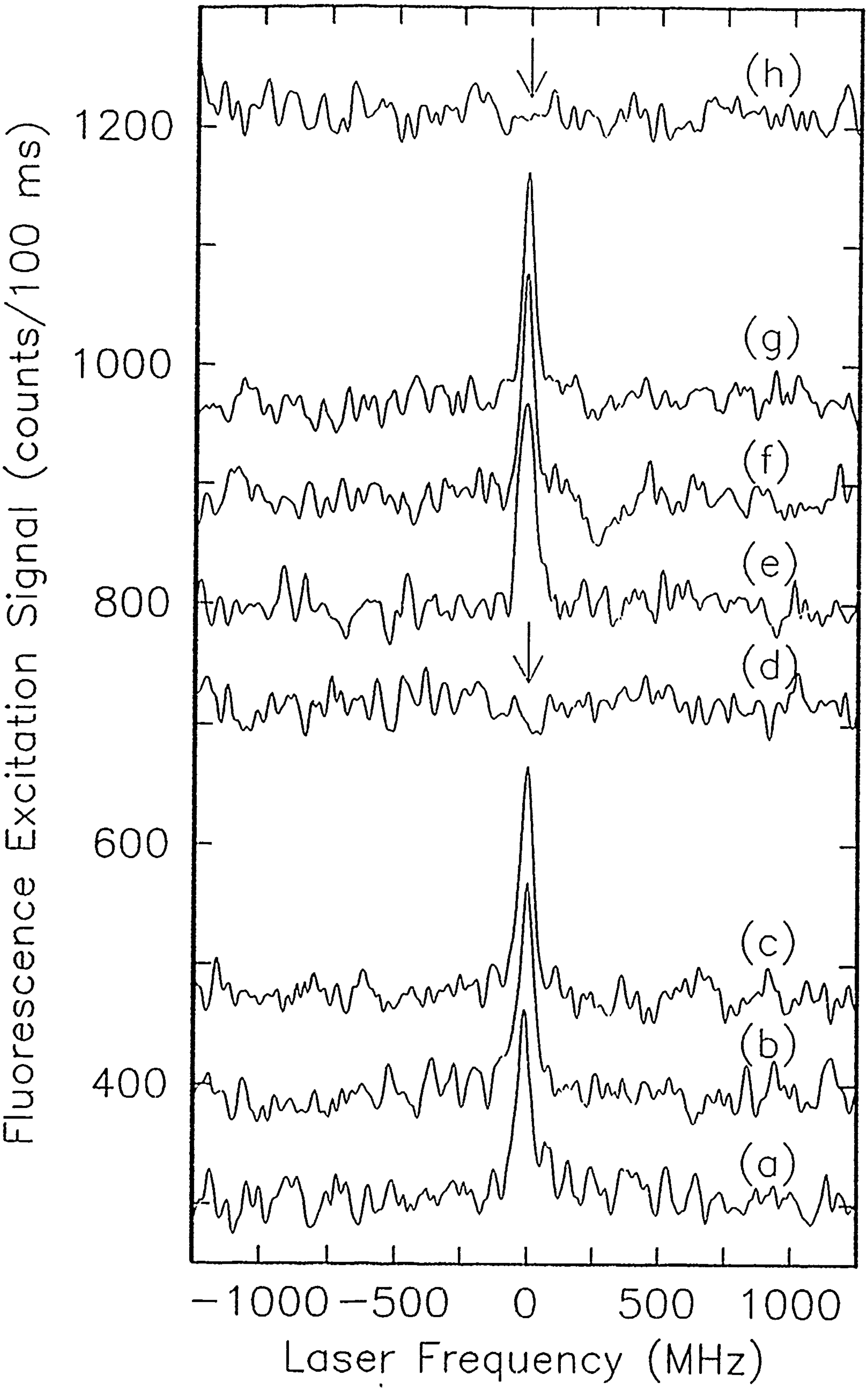
Fluorescence Excitation Signal (counts/100 ms)
1200
1000
800
600
400
(h)
(g)
(f)
(e)
(d)
(c)
(b)
(a)
−1000
−500
0
500
1000
Laser Frequency (MHz)

Figure 7

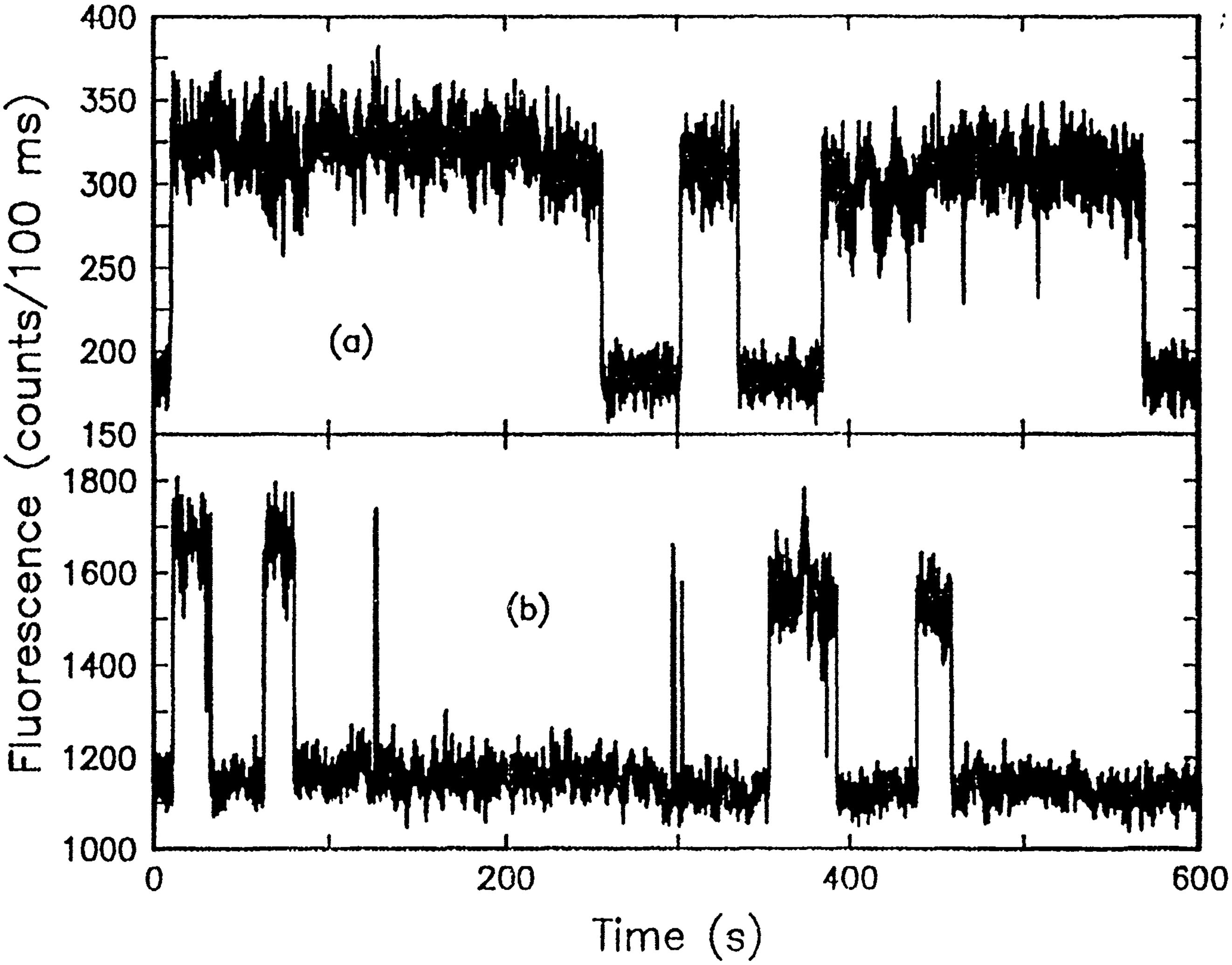
400
350
300
250
200
150
(a)
1800
1600
1400
1200
1000
(b)
Fluorescence (counts/100 ms)
0
200
400
600
Time (s)

Figure 8 a,b

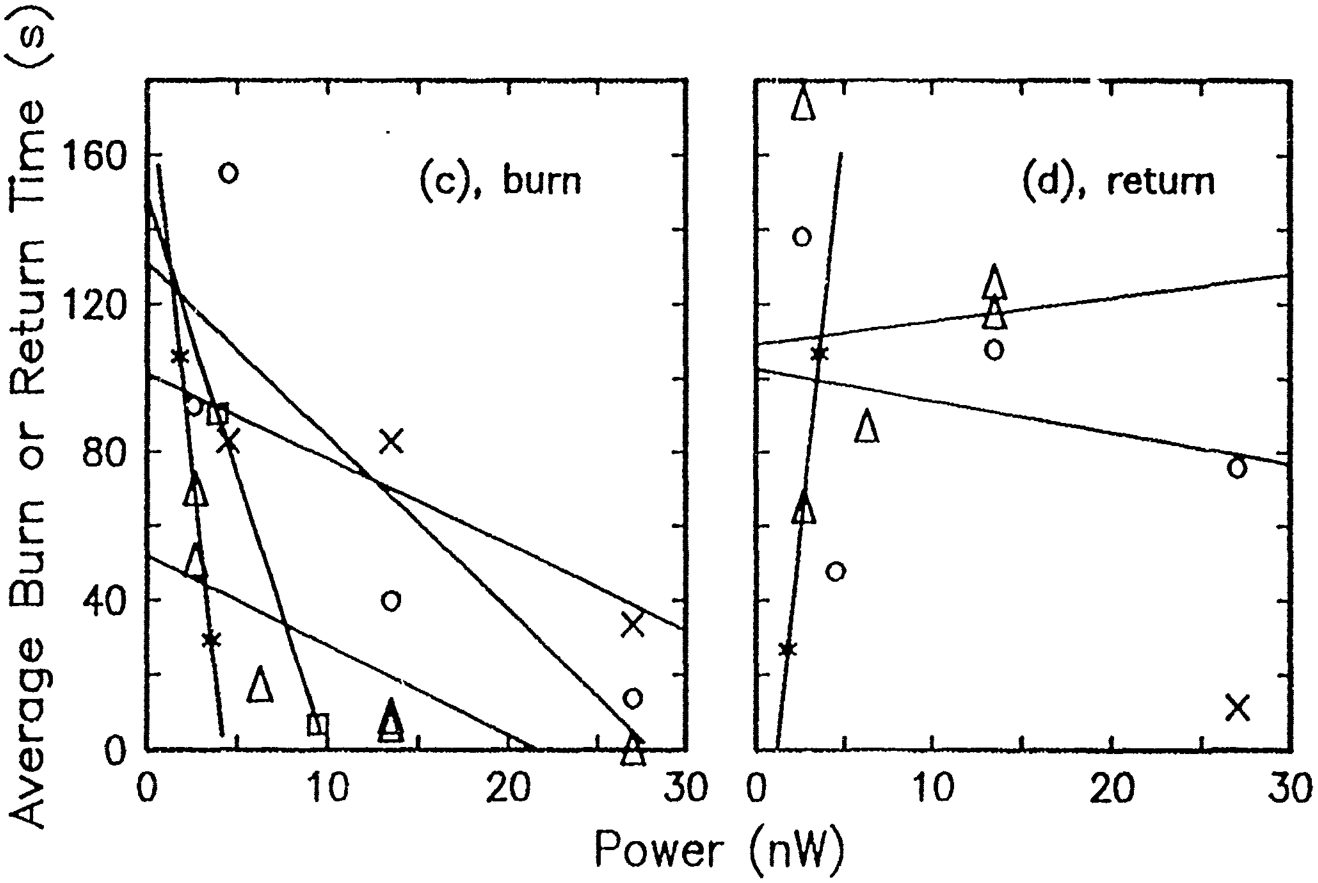
Average Burn or Return Time (s)
0
40
80
120
160
(c), burn
(d), return
0
10
20
30
0
10
20
30
Power (nW)

Figure 8 c,d

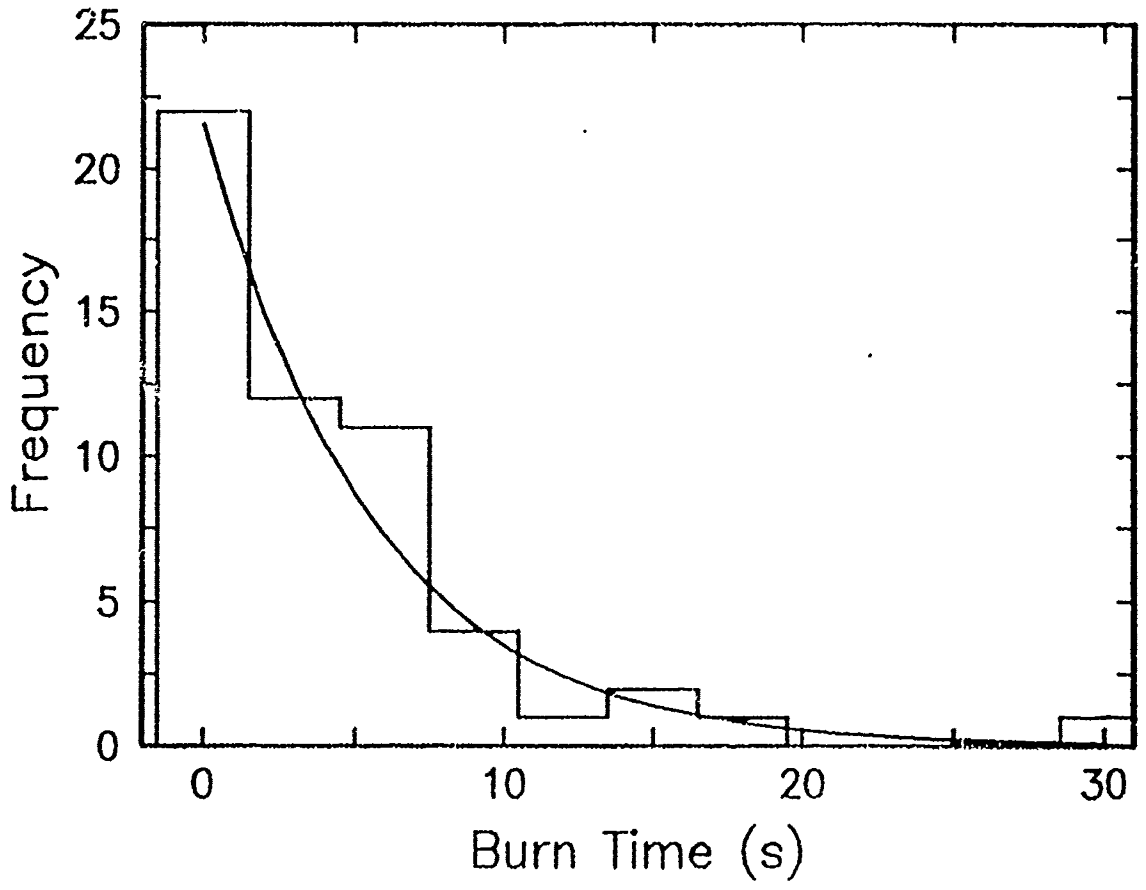

Figure 9

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