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The possibility of obtaining information about solids on a truly microscopic scale has stimulated several recent advances in the optical detection and spectroscopy of single impurity centers in solids. For the system composed of pentacene impurity molecules in the crystal p-terphenyl, absorption and fluorescence excitation studies at liquid helium temperatures have led to direct observations of the lifetime-limited homogeneous linewidth of a single pentacene molecule as well as the surprising observation of spontaneous spectral diffusion in a crystal. Spectral diffusion, or changes in the resonance frequency of an impurity molecule with time as a result of structural relaxation processes (two-level system (TLS) transitions) is generally expected in amorphous hosts. Using perylene impurity molecules in poly(ethylene), we have observed the optical spectra of single molecules in a polymeric host for the first time. At 1.5K, individual perylene molecules show the expected spectral diffusion; moreover, we observe light-induced changes in resonance frequency, i.e., persistent spectral hole-burning, which allows one to envision optical storage on the single-molecule level.

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T. Basche, and W. E. Moerner

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IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, California 95120-6099

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Th. Basché and W. E. Moerner

IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, California 95120-6099

ABSTRACT:

The possibility of obtaining information about solids on a truly microscopic scale has stimulated several recent advances in the optical detection and spectroscopy of single impurity centers in solids. For the system composed of pentacene impurity molecules in the crystal p-terphenyl, absorption and fluorescence excitation studies at liquid helium temperatures have led to direct observations of the lifetime-limited homogeneous linewidth of a single pentacene molecule as well as the surprising observation of spontaneous spectral diffusion in a crystal. Spectral diffusion, or changes in the resonance frequency of an impurity molecule with time as a result of structural relaxation processes (two-level system (TLS) transitions) is generally expected in amorphous hosts. Using perylene impurity molecules in poly(ethylene), we have observed the optical spectra of single molecules in a polymeric host for the first time. At 1.5K, individual perylene molecules show the expected spectral diffusion; moreover, we observe light-induced changes in resonance frequency, i.e., persistent spectral hole-burning, which allows one to envision optical storage on the single-molecule level.

The possibility of obtaining information about solids on a truly microscopic scale has stimulated several recent advances in the optical detection and spectroscopy of single impurity centers in solids. For the system composed of pentacene impurity molecules in the crystal p-terphenyl, absorption [1] and fluorescence excitation [2] studies at liquid helium temperatures have led to direct observations of the lifetime-limited homogeneous linewidth of a single pentacene molecule [3] as well as the surprising observation of spontaneous spectral diffusion in a crystal [4]. Spectral diffusion, or changes in the resonance frequency of an impurity molecule with time as a result of structural relaxation processes (two-level system (TLS) transitions [5]) is generally expected in amorphous hosts. Using perylene impurity molecules in poly(ethylene), we have observed the optical spectra of single molecules in a polymeric host for the first time. At 1.5K, individual perylene molecules show the expected spectral diffusion; moreover, we observe light-induced changes in resonance frequency, i.e., persistent spectral hole-burning [6], which allows one to envision optical storage on the single-molecule level.

Samples were prepared by predissolving zone-refined perylene in acetone; mixing with low-density poly(ethylene) (PE) powder ($\leq$ 25 % crystallinity), drying at 50 C for 30 min under high vacuum, pressing films at 140-150 C between glass slides, and quenching to 77 K for 1 min. The resulting 10-20 μm thick samples had excellent optical clarity (low scattering), little or no aggregate formation as tested by low-resolution optical absorption, and perylene/PE mass ratios of 9.5×10^{-7}. The samples were mounted in a low-temperature optical cryostat at the joint focus of a lens providing the excitation beam and a parabolic mirror collecting the emitted fluorescence as described in detail elsewhere [7]. The tunable excitation laser ($\simeq$ 2-3 MHz linewidth) generated 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). The emitted fluorescence was long-pass filtered with a low-fluorescence filter to reject Rayleigh scattered radiation. Fluorescence excitation spectra were obtained by scanning the dye laser and recording the red-shifted fluorescence with a GaAs phototube and a photon counter.

By tuning the laser to the long-wavelength side of the inhomogeneous line, isolated single-molecule spectra are easily observed, as in trace (a) of Figure 1. Moreover, even with low laser probing intensity, a variety of linewidths are observed at 1.5 K, as shown in traces (a)-(f). 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 24.9 MHz[8]. The different linewidths occur without correlation with position relative to the center of the inhomogeneous line and without correlation with the probing intensity. In fact, trace (a) of Figure 1 was recorded with the highest probing power of 9 nW (in a $\simeq 5$ μm diameter laser focal spot). It appears 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[9], this contribution to the width is generally assumed to be the same for all molecules. 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].

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 [10-12]. 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[13]. 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.

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 2 shows an example of persistent spectral hole-burning for a single perylene molecule in PE. This molecule was deliberately chosen to have little spontaneous spectral jumping from one resonance frequency to another. 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 $\pm$ 1.25 GHz as a result of the light-induced change. The exact location of the new resonance frequency is unknown at present; however, by analogy with previous nonphotochemical hole-burning studies on large ensembles of molecules[14], the shift may be expected to be up to 100 cm^{-1}. 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. (We note that other single molecules were observed to burn irreversibly, that is, after burning the molecules did not return to the original wavelength during observation times of up to 20 min. However, the behaviour reported in Fig. 2 was more common.)

To provide more evidence that the hole-burning process shown in Fig. 2 is laser-driven and not very slow coincidental spectral diffusion, studies of the kinetics of the process were performed. Figure 3 (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. Additional studies [15] 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. In Fig. 3 (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. 3(d)).

The generally accepted model for nonphotochemical hole-burning of impurity molecules in amorphous hosts [16, 17] 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. 2 is surprising, since it suggests that coupling to exactly one nearby TLS

is involved in the hole-burning process. If this is true, the single impurity molecule may in the future serve as a direct probe of a single TLS.

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 altering or ignoring each single molecule absorption. 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. This concept, while highly speculative at the present time, provides several advantages and disadvantages. Among the advantages are the extreme areal density (up to perhaps 10^{14} bits/cm^2) and the greatly increased signal from each molecule resulting from the use of sub-diffraction-limited beams (the SNR scales approximately as $\sqrt{\sigma P/A}$, where σ is the peak absorption cross section, P is the laser power, and A is the beam area). Some disadvantages are the required low temperatures, stochastically variable burning times, and variable frequency locations of the individual bits from laser spot to laser spot. Nevertheless, 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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*To whom correspondence should be sent.

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Figure Legends

Figure 1. 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.

Figure 2. 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.

Figure 3. 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.
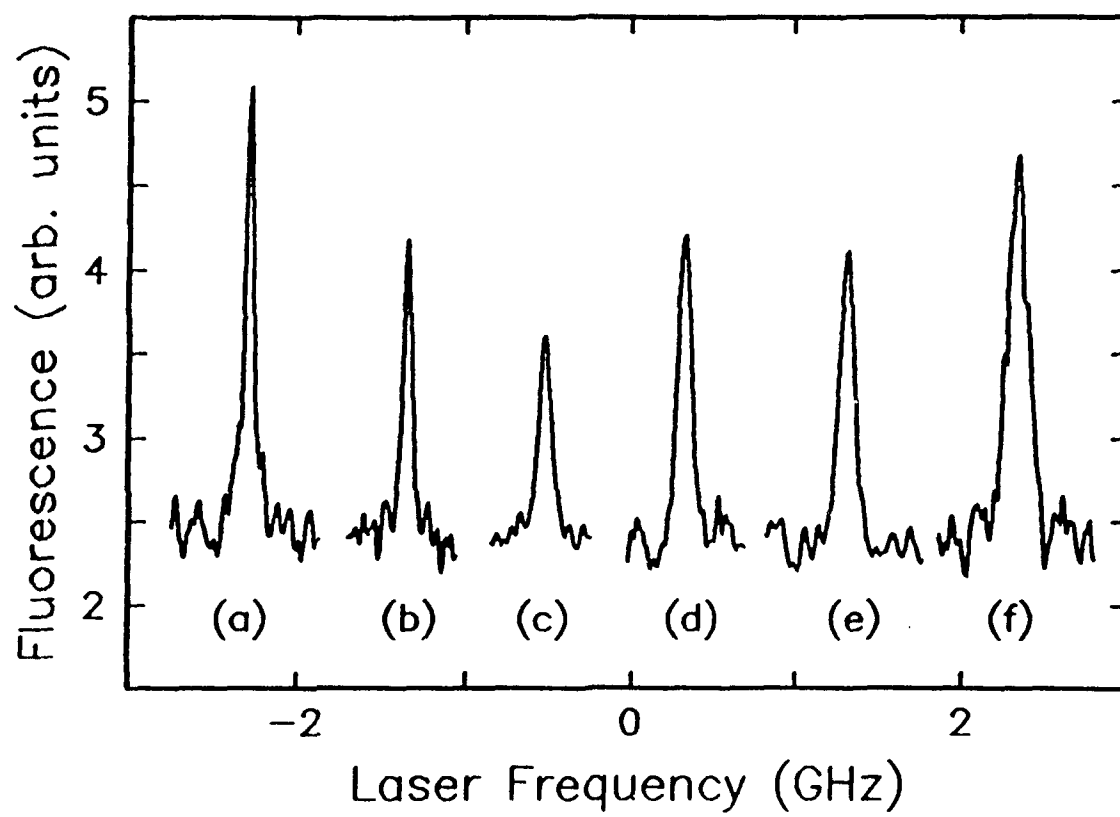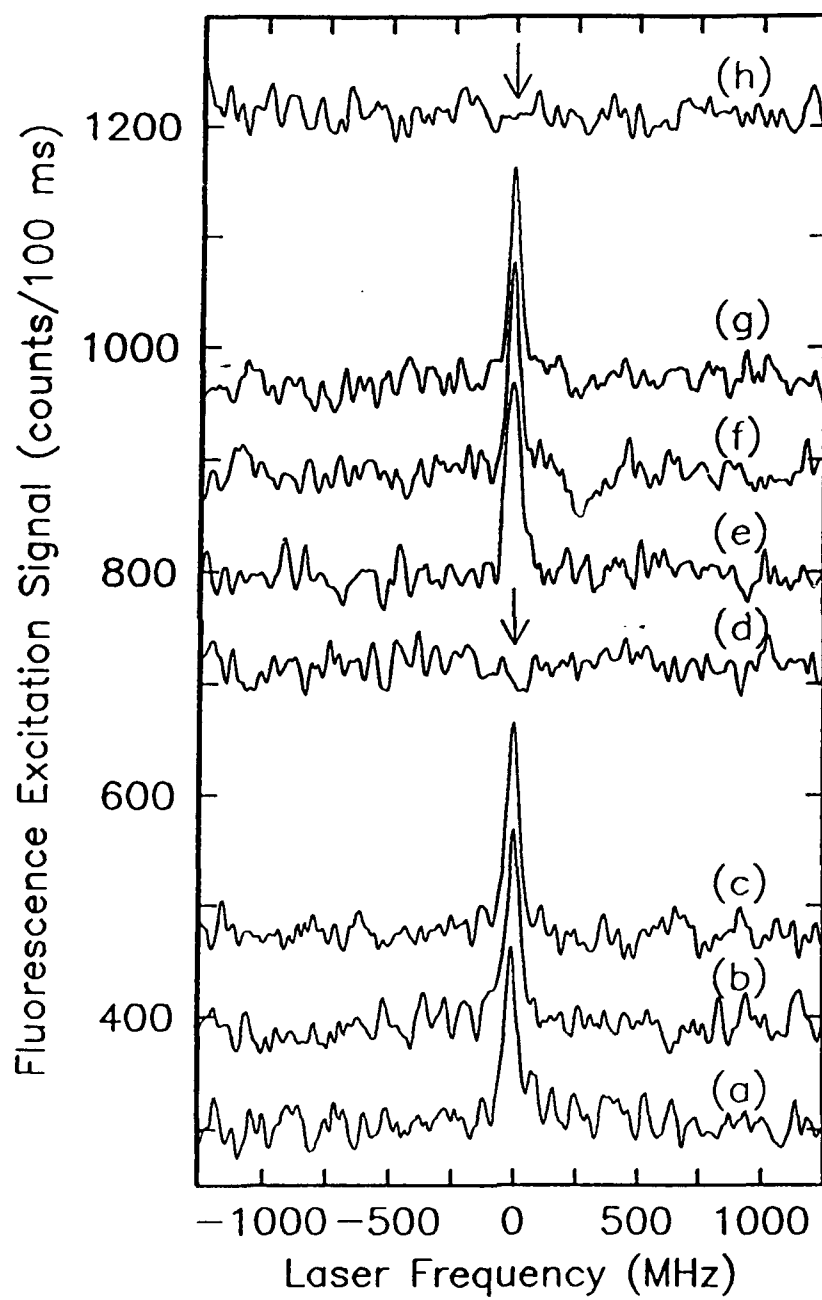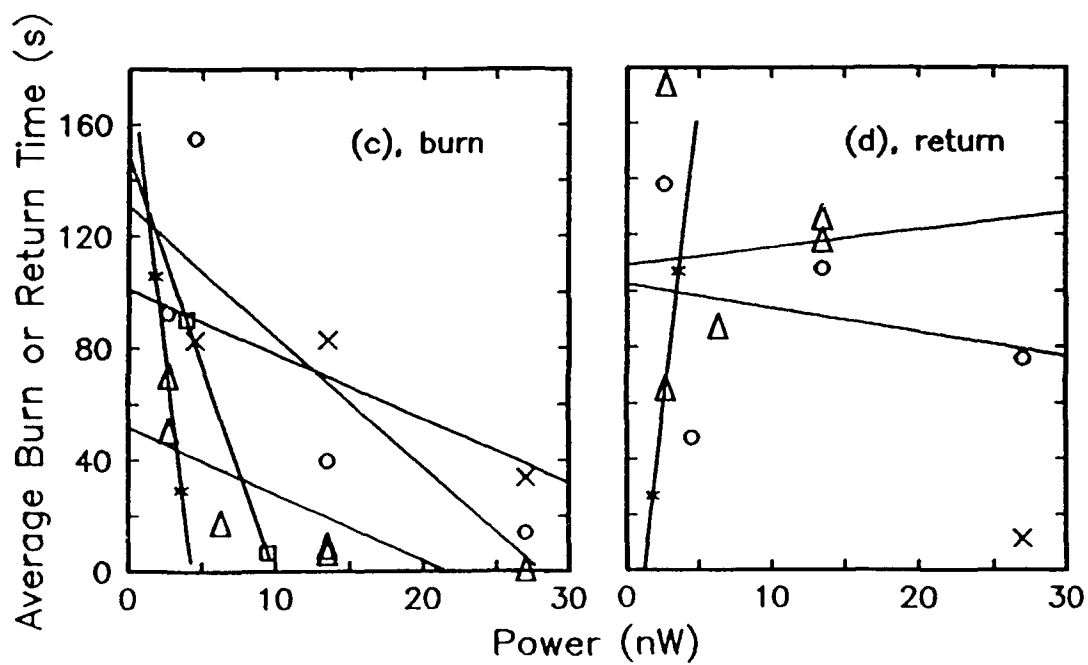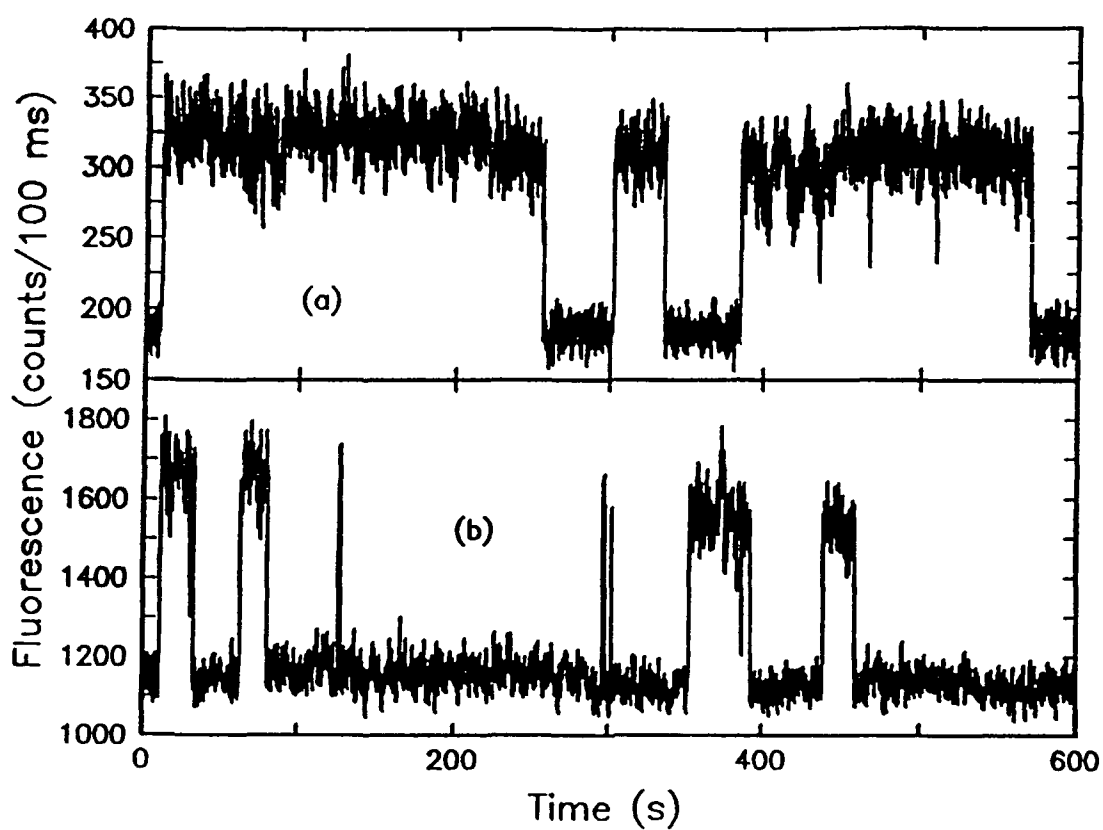
Figure 1

Figure 2

Figure 3

1. Office of Naval Research (2)
   Chemistry Division, Code 1113
   800 N. Quincy Street
   Arlington, VA 22217-5000

2. Defense Technical Information Center (2)
   Building 5, Cameron Station
   Alexandria, VA 22314

3. Commanding Officer
   Naval Weapons Support Center
   Attn: Dr. Bernard E. Douda
   Crane, Indiana 47522-5050

4. Dr. Richard W. Drisko
   Naval Civil Engineering Laboratory
   Code L52
   Port Hueneme, CA   93043

5. David Taylor Research Center
   Dr. Eugene C. Fischer
   Annapolis, MD 21402-5067

6. Dr. James Murday
   Chemistry Division, Code 6100
   Naval Research Laboratory
   Washington, D. C. 20375-5000

7. Dr. Robert Green, Director
   Chemistry Division (Code 385)
   Naval Weapons Center
   China Lake, CA 93555-6001

8. Chief of Naval Research
   Special Assistant for Marine Corps Matters
   Code 00MC
   800 North Quincy Street
   Arlington, VA 22217-5000

9. Dr. Bernadette Eichinger
   Naval Ship Systems Engineering Station
   Code 053
   Philadelphia Naval Base
   Philadelphia, PA 19112

10. Dr. Sachio Yamamoto
    Naval Ocean Systems Center
    Code 52
    San Diego, CA 92152-5000

11. Dr. Harold H. Singerman
    David Taylor Research Center
    Attn: Code 283
    Annapolis, MD 21402-5067