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Author
Ha, T.

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Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials Sciences Division

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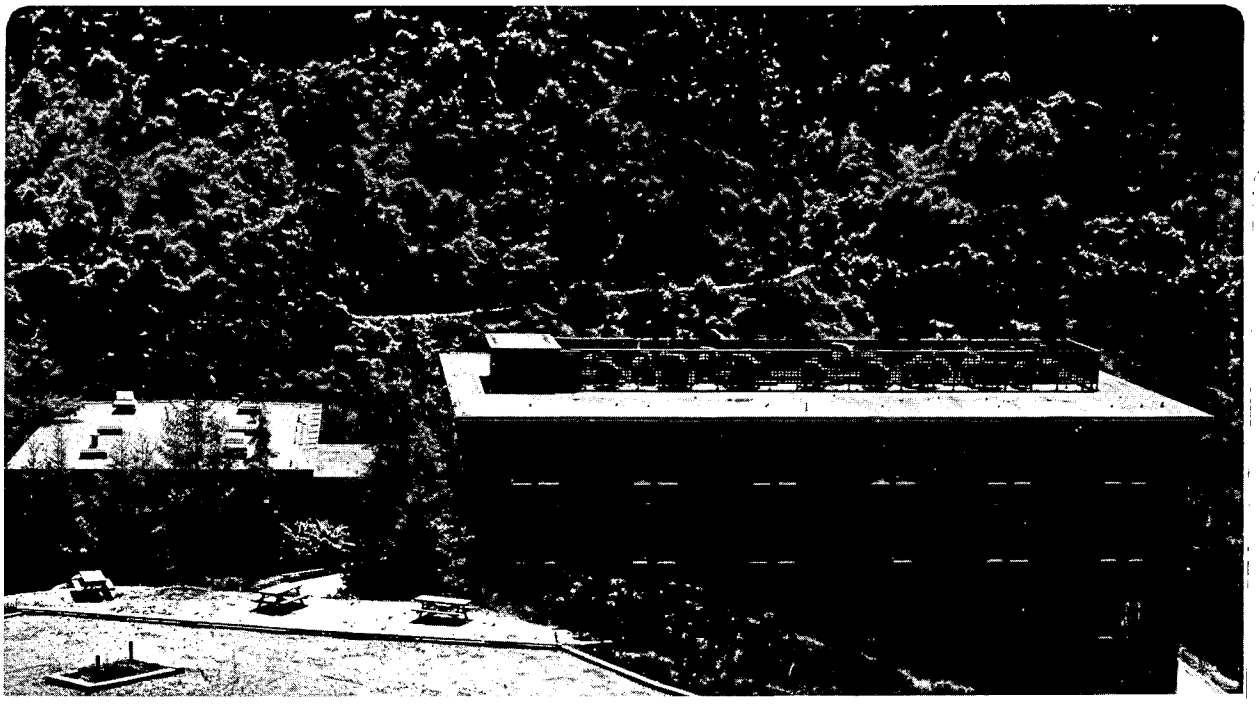

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T. Ha, Th. Enderle, D. F. Ogletree, P.R. Selvin, S. Weiss, and D.S. Chemla

Molecular Design Institute
Materials Sciences Division
Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720

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P.R. Selvin, S. Weiss and D.S. Chemla

Molecular Design Institute, Materials Sciences Division

Lawrence Berkeley National Laboratory

1 Cyclotron Road, Berkeley, CA 94720

TEL: 510-486-5202

FAX: 510-486-5530

e-mail: sweiss@ux5.lbl.gov

Abstract:

Fluctuations in the room temperature emission rate from single dye molecules which are excited with the near field scanning optical microscope reveal long (~ seconds) and short (~ milliseconds) lived dark states.

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T. Ha, Th. Enderle, D.F. Ogletree,
P.R. Selvin, S. Weiss and D.S. Chemla

Molecular Design Institute, Materials Sciences Division
Lawrence Berkeley National Laboratory
1 Cyclotron Road, Berkeley, CA 94720
TEL: 510-486-5202
FAX: 510-486-5530
e-mail: sweiss@ux5.lbl.gov

Summary:

We monitored the fluorescence emission rate of single dye molecules on dry surface with the near field scanning optical microscope (NSOM) [1]. A Texas Red fluorophore was covalently attached to a short strand of a DNA molecule and bound to an amino-propyl-silanized glass coverslip [2]. After imaging, the NSOM probe was stationed over a single molecule and its emission rate was recorded as function of time until its photodestruction. Counts were integrated for 5 - 20 ms and typical count rates were 5 - 30 kHz. A typical emission time trace is shown in Fig. 1.

In addition to the irreversible photodestruction event at 26s, reversible jumps to background level around 4s and 9s are noticeable. These long lived dark states last few seconds. The two curves are polarization resolved emission time traces recorded simultaneously with circular polarization excitation. As can be seen, the jumps to the background level are correlated on both channels, eliminating sudden rotation as the explanation. Spectral diffusion which explains similar jumps at low temperatures [3] is unlikely for our case, since the absorption spectrum at room temperature is very broad. Similar data, taken from many molecules, reveal transitions to dark states which last from 50ms to 5s. The origin of these transitions is yet to be understood.

The noise in the "on" state does not follow Poisson statistic. With improved time resolution (5ms vs. 20ms), the fluctuations in emission rate get bigger, suggesting transitions to short lived dark states (few ms).

Fig. 2a contrasts a molecule with shot noise limited emission (no transition to dark states) with molecules which are very "noisy" (Fig. 2b and 2c). Fig. 2a represents the typical emission from many molecules. It also suggests that systematic noise such as mechanical drift, vibration and laser coupling fluctuation are minimal at the relevant time scale. In some cases, however, large fluctuations are observed (Fig. 2b and 2c). In particular, Fig. 2c displays almost digital signal fluctuations.

To check the hypothesis of dark states, we modeled the molecular emission with Poissonic distribution of photon arrival at the "on" state, with $1/t_2$ transition probability to a dark state and with t_1 dark state lifetime. Noise distribution histograms were generated from simulated data and compared to histograms obtained from the measurements. In this way t_1 and t_2 could be extracted with better than 0.5ms accuracy. The traces in Fig. 2b and 2c resulted in t_1 = .075 (± 0.25) ms, t_2 = 1.75 (± 0.5) ms and t_1 = 2.0 (± 0.5) ms, t_2 = 2.0 (± 0.5) respectively. We found that t_1 ranges from below 0.5ms to 2ms and t_2 from 1.5ms to 2ms. Assuming 5% collection efficiency of fluorescence photons, we estimate that the transfer efficiency to the dark state is about 0.1%. Both the lifetime of dark state (< 2ms) and the transfer efficiency (or transfer rate of ~μs) are consistent with triplet state lifetime and intersystem crossing rate of dye molecules. Recently, similar quantum jumps to a triplet state were observed from single terrylene molecules in *p*-terphenyl at cryogenic temperatures where triplet state lifetime is the same for every molecule [4]. The distribution in t_1 and t_2 in our measurements, is probably a manifestation of different local environments and surface interactions.

References:

[1] E. Betzig and J.K. Trautman, Science, **257**, 189 (1992).

[2] T. Ha, Th. Enderle, D.F. Ogletree, D.S. Chemla, P.R. Selvin, and S. Weiss, to be published.

[3] W.E.Moerner, Science,**265**,46(1994)

[4] Th.Basche,S.Kummer and C.Brauchle, Nature, **373**,132 (1995).

Figure captions:

Figure1: Simultanously acquired time traces of single molecular emission at two orthogonal polarizations. Integration time is 20ms.

Figure2: Time traces of single molecular emission from three different molecules. The mean value and the standard deviation of the "on" portion of the signal are given.

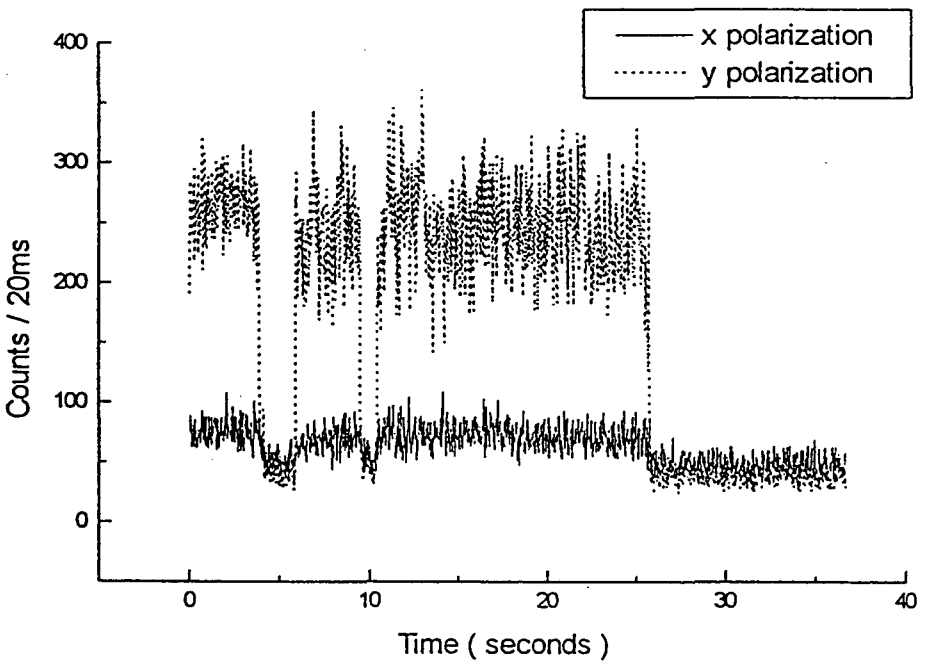
x polarization
y polarization
Counts / 20ms
400
300
200
100
0
0
10
20
30
40
Time (seconds)

Fig. 1, Ha et.al.

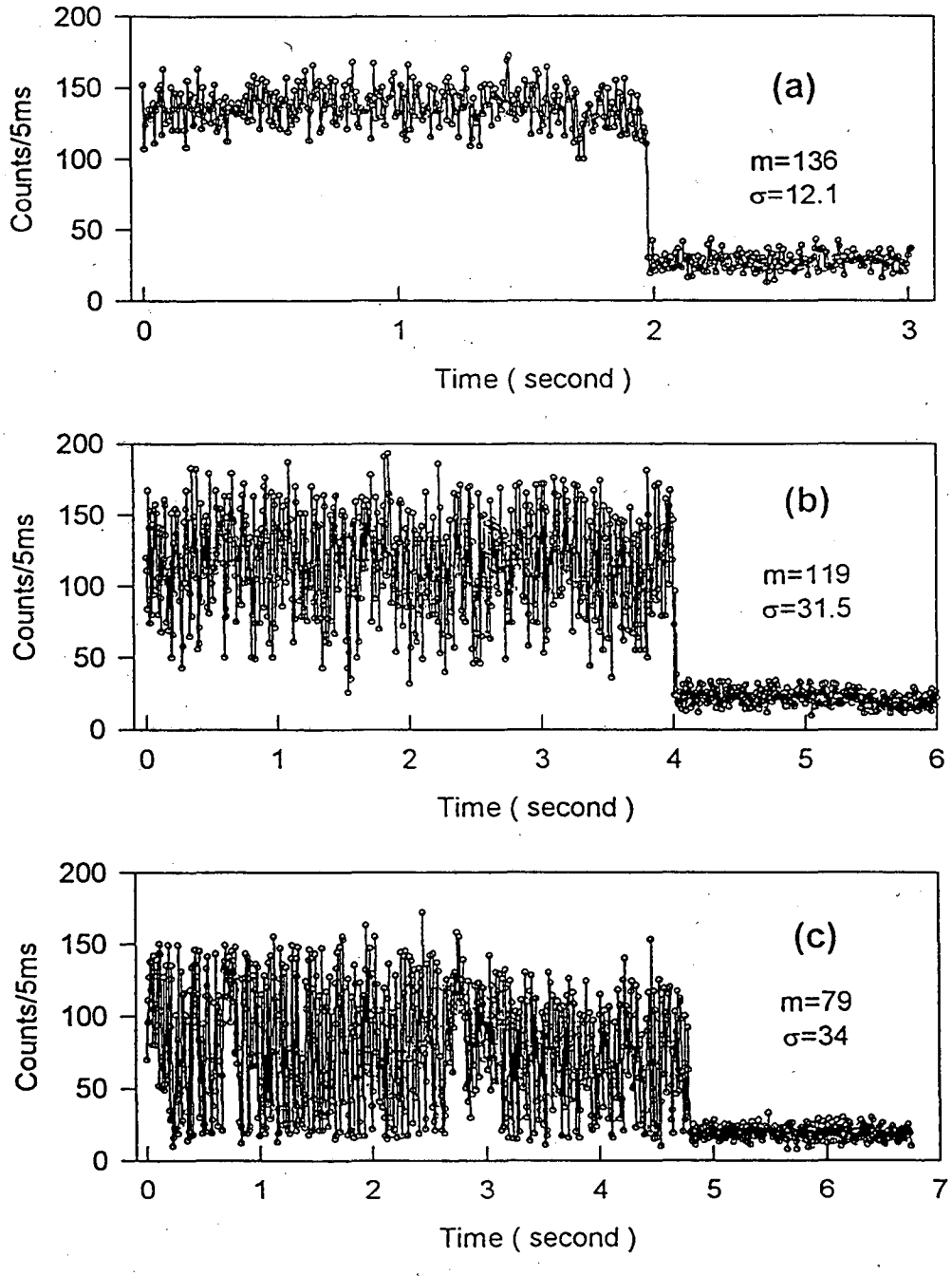

Fig. 2, Ha et.al.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720