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by

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OBSERVATION OF SPECTRAL DIFFUSION IN CRYSTALS USING SINGLE
IMPURITY MOLECULES

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Early measurements of the optical absorption spectrum of a single impurity molecule in a
solid at low temperatures[1], while intriguing, nevertheless produced insufficient signal-to-noise
ratio (S/N) for the observation of new physical effects. Recent advances in high-efficiency
fluorescence excitation spectroscopy[2] with ultrathin sublimed crystals have removed this
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work[3]. However, for class II molecules which are only found far out in the wings of the
inhomogeneous line, the center frequency spontaneously jumps from one value to several
other possible values on a time scale ranging from seconds to minutes, independent of laser
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Early measurements of the optical absorption spectrum of a single impurity molecule in a solid at low temperatures[1], while intriguing, nevertheless *produced insufficient signal-to-noise ratio (S/N)* for the observation of new physical effects. Recent advances in high-efficiency fluorescence excitation spectroscopy[2] with ultrathin sublimed crystals have removed this obstacle. For the case of pentacene impurities in crystals of *p*-terphenyl, we observe two radically different behaviors. For class I guest molecules, the center frequency does not change with time and the low-power linewidth at 1.5 K is in agreement with previous work[3]. However, for class II molecules which are only found far out in the wings of the inhomogeneous line, the center frequency spontaneously jumps from one value to several other possible values on a time scale ranging from seconds to minutes, independent of laser power. This surprising effect is analogous to spectral diffusion processes that play a crucial role in the physics of the amorphous state[4,5]: here, the single-molecule technique allows the spectral changes to be followed in real time.

In our fluorescence excitation technique, a tunable dye laser (1 MHz linewidth) was used to excite the 0-0 electronic transition of pentacene substitutional impurities in the *p*-terphenyl crystal. As the excitation wavelength was varied, the emitted fluorescence that passed through a long pass filter was measured with a photon counter. While such methods are capable of measuring the extremely small absorptions from single ions in traps[6], in a single-molecule experiment in a solid the scattered light from the sample and other components must be reduced to very low levels. This was achieved by limiting the excited volume with 1-10 μm thick sublimed single crystal samples and laser focal diameters of 5 μm full width at half-maximum (FWHM). Following Orrit et al.[2], the Stokes-shifted fluorescence was collected with high efficiency using 0.98 numerical aperture optics.

The crystals were cooled to 1.5 K where the homogeneous linewidth of individual pentacene defects for the O_1 site[7] ($\gamma \simeq 7.5$ MHz[3]) is much less than the inhomogeneous line

width ($\Gamma_1 \simeq$ 2-42 GHz, depending upon strain in the crystal). This well-known inhomogeneous broadening effect[9] occurs for all zero-phonon transitions of defects in solids at low temperatures[10]. The inhomogeneous line profile represents the center frequency distribution of the pentacene guests produced by random strain and electric fields present in the crystal. For single-molecule spectra, the laser may be tuned far into the wings of the inhomogeneous line where the number of defects per homogeneous width is less than one; i.e., where non-overlapping individual pentacene defects may be found. For most measurements, the pentacene concentration was approximately 6.6×10^{-8} moles/mole, and $\Gamma_1 \simeq$ 6 GHz. To record single-molecule spectra we used laser wavelengths $\simeq$0.2 nm from the inhomogeneous line center for the O_1 0-0 site origin at 592.321 nm [7].

Fig 1. shows excitation spectra taken at a series of laser focal spot positions. The three largest peaks isolated in both position and frequency are single pentacene defects of class I. The width of the peaks along the position axis (FWHM = 5 μm) is a direct measure of the intensity profile of the focused laser beam in the crystal. The width of the peaks in frequency varies from 8 to 13 MHz as the laser intensity at the defect varies with position. This broadening is due to saturation of the defect optical transition. Using three-level saturation expressions [11], the saturation intensity of these defects is estimated to be 1.8 $\pm$ 0.8 mW/cm^2, which is a factor of 40 lower than the 70 mW/cm^2 value one would calculate from pentacene photophysical parameters including intersystem crossing[12]. Apparently (and not surprisingly), the local pentacene environment this far out in the wings of the line produces alterations in the intersystem crossing rates. In addition to the class I peaks, there are smaller features in Fig. 1 that do not follow a definite trend with position suggesting a time dependence from scan to scan.

Fig. 2 shows a typical time sequence of excitation spectra obtained at a fixed laser spot position. The spectra contain three time-independent class I peaks, which form stable ridges

along the time axis near -130, -70, and +10 MHz. In the 0 to 150 MHz region is a single class II defect whose frequency varies from one scan to the next. Indeed, this same molecule can appear several times in the same 2 min laser scan, or almost not at all. Notice that in the same $\simeq 50~\mu m^3$ volume of crystal and at nearly the same frequency there are both class I defects as well as spectrally migrating class II defects.

If the laser frequency in Fig. 2 is fixed at any detuning from 0 to +100 MHz, the collected fluorescence turns on and off discontinuously like a random telegraph [13] or quantum jump [14] signal. However, the absence of fluorescence only means that the defect is not absorbing at the laser frequency. To follow the resonance frequency directly, we scanned more rapidly and sacrificed S/N in order to measure the spectral position of the defect once each second. Fig. 3 (upper part) shows how the resonance frequency of a spectrally jumping class II defect evolves with time. A computer locates the peak in each scan and records this resonance frequency as a function of time as a trend in the lower part of Fig. 3. The optical transition energy appears to have a preferred set of values and performs spectral jumps between these values that are discontinuous on the 1 sec time scale of the measurement.

Using several samples from the same sublimation run, a variety of class II defects have been observed that have two or more preferred frequencies spaced by 20 to 60 MHz with mean times between jumps of 1 to 420 seconds. Moreover, the occurrence of class II behavior is quite common in the wings of the inhomogeneous line (to the red as well as to the blue). By observing 133 single molecules at several positions to the red of O_I, the fraction of class II increases from 13% at 592.365 nm to 40% at 592.550 nm. On the other hand, using a thin, strain-free, lightly doped sample with concentration 5×10^{-9} moles/mole and $\Gamma_I = 2$ GHz, single molecules could be observed 0.006 nm from line center and only class I behavior was found. We conclude that class II behavior is related to the improbable, highly strained local environments that occur far out in the wings of the inhomogeneous line.

The mean time between spectral jumps varies no more than 20% for laser intensities from 3.3 to 65 mW/cm². Therefore, the spontaneous spectral jumps do not appear to be photo-induced changes such as that which occurs when a persistent spectral hole is formed near the center of the inhomogeneous band[15]. By analogy to glasses, we call the spectral jumping effect spectral diffusion, because the absorbing molecule appears to be coupled to an ensemble of diagonal (energy-changing) perturbations that shift the resonance frequency in a stochastic manner. On the other hand, class I defects have not been observed to jump with the laser frequency fixed at the resonance frequency for periods up to 10 min, or by scanning and detecting the resonance at regular intervals up to 55 min. Thus we identify class I defects as isolated pentacene molecules that have stable surroundings.

Measurements of the temperature dependence and the power broadening behavior for class I and class II molecules show that both the saturation intensity and dephasing rates differ from center to center and from class to class. However, all centers appear to have the same lifetime-limited $\gamma \simeq 7.8 \pm 0.2$ MHz, in agreement with coherent transient data[3]. By comparison with the measured properties of dimers of pentacene in p-terphenyl[8], we find no strong evidence that either class of defect represents dimers. Individual defects at nearly the same frequency far in the wings of the inhomogeneous line each have unique spectral jumping behavior, which suggests different nearby host configurations. We are thus led to propose that class II defects are located in regions of the crystal where a variety of local structural configurations are energetically accessible at low temperatures. These local configurations may be modeled by an ensemble of two-level systems (TLS) in analogy with the glass case[5]. The TLS undergo phonon-assisted tunnelling [16] and the pentacene resonance shifts with changes in the quantum numbers describing the nearby host crystal configuration. One possible source for the TLS would be tipping of the central phenyl ring of p-terphenyl among various allowed orientations made available by disorder in the crystal structure[17]. The future proof of this model requires detailed temperature dependent measurements of the jump rate

for a single center over a wide range of temperature in hope of observing the characteristic coth($E/2k_BT$) dependence, where E is the energy splitting in an asymmetric TLS model and k_B is Boltzmann's constant.

With the ability to measure individual defect spectra at 1 sec intervals with reasonable S/N, we find that single pentacene molecules far from the center of the inhomogeneous line in crystals of p-terphenyl exhibit spontaneous spectral jumps at liquid-helium temperatures. Since the spectral jump rates and sizes are different for different defects, direct observation of this spectral diffusion effect would not be possible in any spectroscopy that averages over many defects. Direct measurement of the behavior of individual guest molecules in a glass would lead to a clearer understanding of the origins of amorphous solid dynamics[4, 18] than is available from ensemble-averaged measurements. Much more intriguing is the fact that spectral jumping has been first directly measured in a crystal where such an effect is not expected.

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Figure Legends

Figure 1. Single pentacene defect fluorescence excitation spectral landscape in a crystal of p-terphenyl. 0 MHz detuning $\equiv$ 592.544 nm, T = 1.5 K, laser power = 1.5 nW, 2 min. per spectrum.

Figure 2. Single defect fluorescence excitation spectra time dependence. Upper half: wire plot of individual spectra, lower half: contour plot of same data, 2 min. per spectrum, laser power = 1.5 nW, and 0 MHz detuning $\equiv$ 592.539 nm. The appearance of class I at negative detunings and class II at positive detunings has no significance.

Figure 3. Spectral jumps in the resonance frequency of a class II single pentacene defect. Upper half: individual 1 sec. spectra, lower half: time dependence of center frequency, 0 MHz detuning $\equiv$ 592.546 nm.
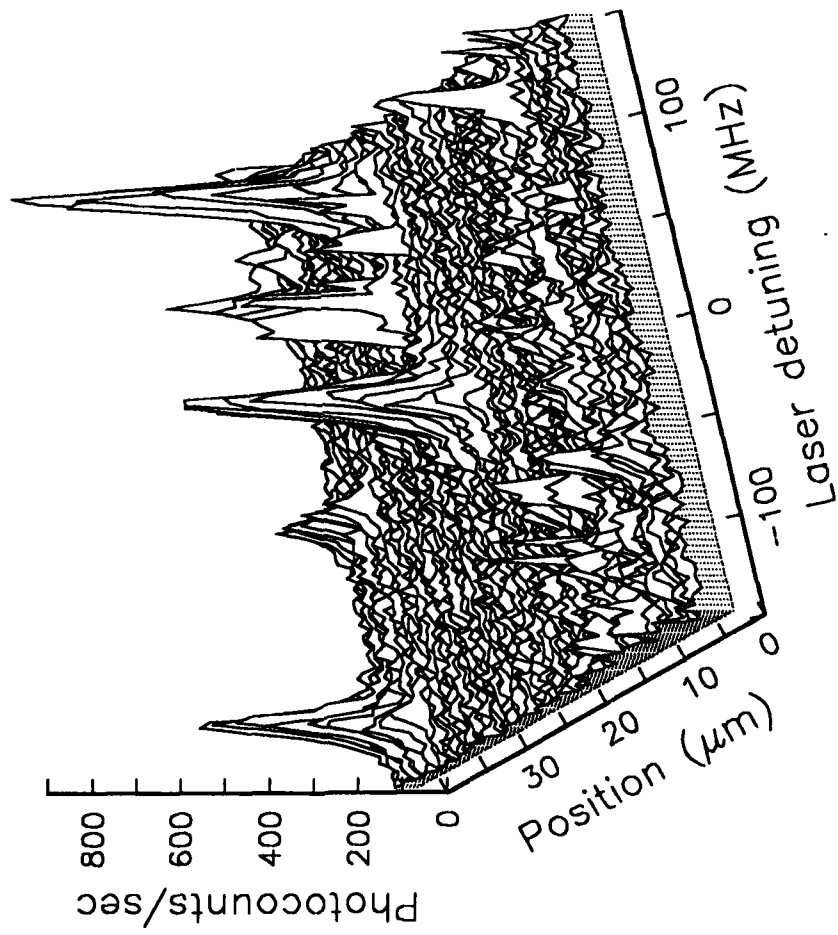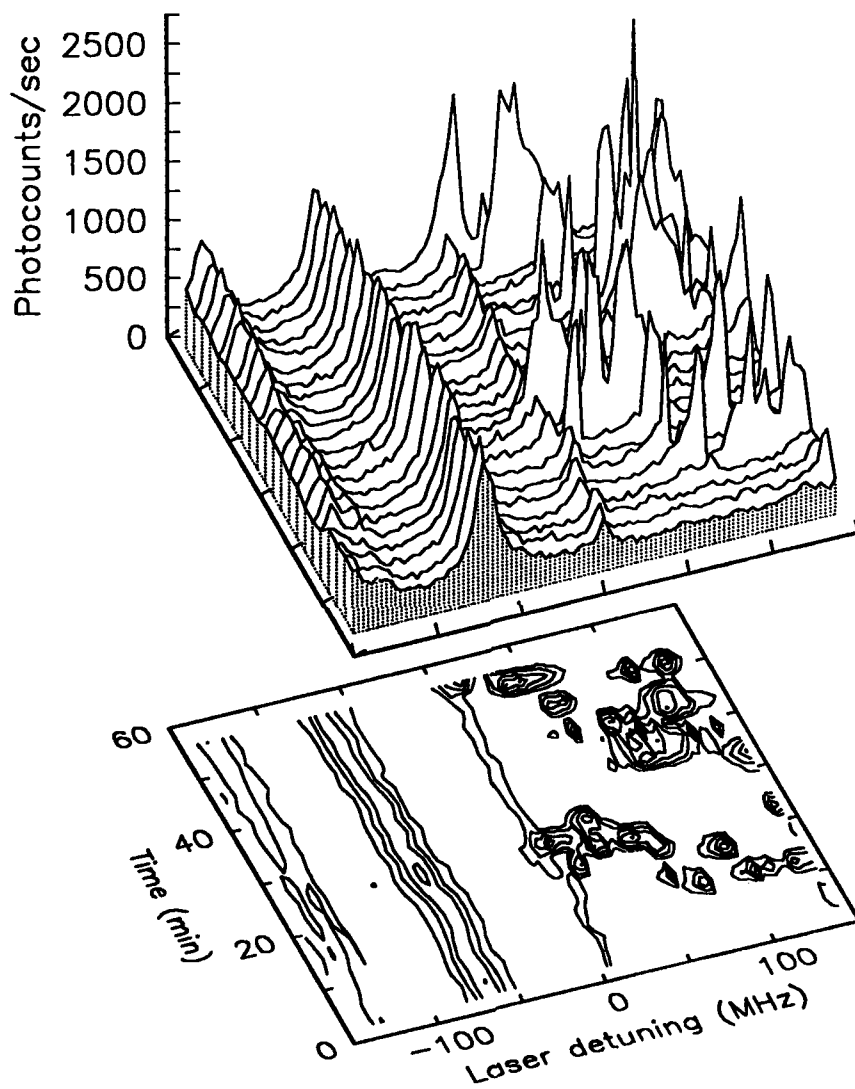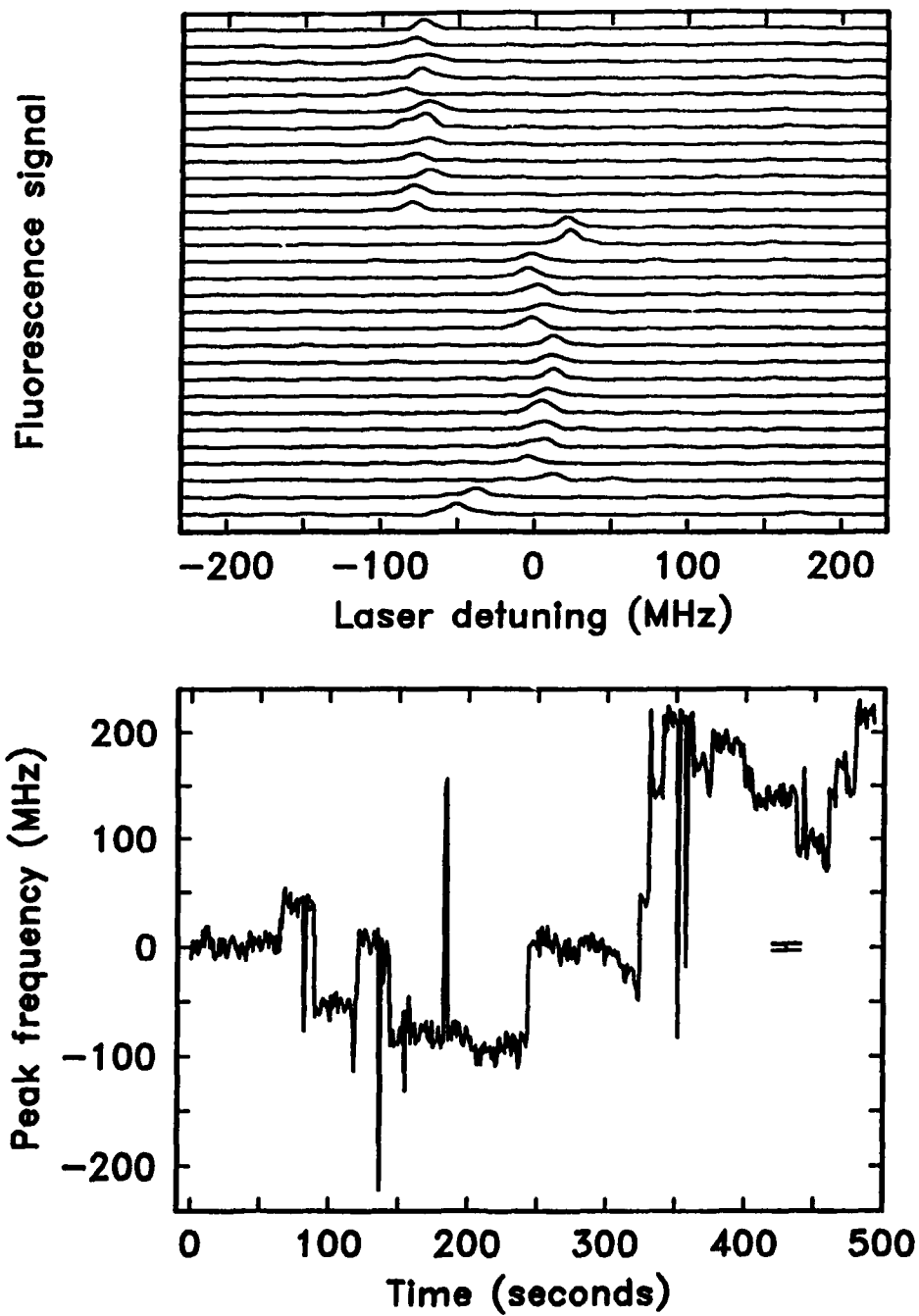
Figure 1

Figure 2

Figure 3

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