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**PHOTON ANTIBUNCHING IN THE FLUORESCENCE OF A SINGLE DYE MOLECULE  
TRAPPED IN A SOLID**

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**ABSTRACT:** The correlation between fluorescence photons emitted by an optically pumped single molecule of pentacene in a p-terphenyl host has been investigated at short times. The correlation function shows photon antibunching, an unique feature of nonclassical radiation field, which decreases if two molecules rather than one are pumped at the same time. The peculiarities of the correlation function for a three-level molecule are discussed and the theoretical description outlined.

The nonclassical phenomenon of photon antibunching was first observed in the resonance fluorescence of sodium atoms in a low-density atomic beam<sup>1</sup>. In this purely quantum-mechanical effect, the correlation between successive photons emitted by a single atom decreases near  $t = 0$ , in marked contrast to the case for coherent light (where the correlation is independent of the time separation between photons) and for thermal (Gaussian) light, which shows an increase in correlation (bunching) near  $t = 0$ . Subsequently, advances in the ability to store single atomic ions in a radio-frequency trap by photon-recoil cooling allowed observation of antibunching and sub-Poissonian statistics for a single trapped  $Mg^+$  ion<sup>2</sup>. Indeed, single-ion cooling and trapping has proven to be a powerful way to investigate the fundamental interactions of matter and radiation in a variety of fascinating experiments such as quantum jumps, quantum collapse and revival, and many others<sup>3-5</sup>.

The extension of these studies to single molecules has failed so far, because all molecules - even diatomic species - possess several internal degrees of freedom as well as rotational modes which prevent laser cooling. Recently, it was demonstrated that single molecules can be conveniently detected by absorption<sup>7</sup> and fluorescence excitation<sup>8</sup> spectroscopy when the molecules are doped as impurities in a solid and the samples cooled to liquid helium temperatures. In this case, the solid acts as a "trap" for the single molecules which maintains the molecule effectively at rest, and in many cases, rotation of the impurity molecule is quenched. In addition, recoil effects are usually small (less than the optical linewidth), since a zero-phonon optical transition in a solid may be viewed as the optical analog of the Mößbauer line<sup>9,10</sup>.

Most single-molecule experiments in solids to date have focused on the interaction of the impurity with the host dynamics. Using the fluorescence excitation technique, certain individual pentacene impurity molecules in a p-terphenyl crystal<sup>11</sup> were observed to spectrally diffuse, i.e. their absorption spectrum changed spontaneously due to local configurational transitions of the host; Similar effects were observed<sup>12</sup> for perylene in amorphous polyethylene; in addition, changes in the resonance frequency of single perylene impurities could be induced by laser irradiation (persistent spectral hole-burning). In this paper, we

demonstrate that a single pentacene molecule in a p-terphenyl crystal emits fluorescence photons with uniquely quantum-mechanical correlations, that is, the emitted photons show antibunching in a fashion similar to that for single atom resonance fluorescence.

As was predicted by Carmichael and Walls<sup>13</sup>, the statistical properties of the fluorescence light emitted by a single atom should exhibit photon antibunching. This effect becomes experimentally evident by measuring the second order correlation function (intensity correlation)  $g^{(2)}(t)$  which goes to zero for  $t \rightarrow 0$ . The phenomenon of antibunching is a true signature of a quantum field; however, the effect can be nicely rationalized with the following simple picture. In the correlation measurement the joint probability for the arrival of a photon at time  $t = 0$  and the arrival of a photon at  $t > 0$  is recorded. After emission of a photon at  $t = 0$  the quantum system is prepared in its ground state since it just emitted a photon. The probability of emitting a second photon at  $t = 0$  is zero because the molecule cannot emit from the ground state. On the average a time of half a Rabi period has to elapse to have a finite probability for the molecule to be in the excited state and emit a second photon.

In the single molecule antibunching reported here we pump the lowest zero-phonon purely electronic transition and detect the (long-wavelength) vibronically shifted fluorescence from the excited singlet state  $S_1$  rather than the resonance fluorescence as in single ion experiments. The lifetimes of the vibrational states where the emission terminates, however, are on a much shorter timescale (ps) than the relevant timescale, the fluorescence lifetime, and therefore the antibunching phenomenon is not significantly affected. Because of this, the multiatom pentacene in p-terphenyl system reduces to an effective three-level system (3LS).

In many two-photon correlation experiments, the number of all pairs of detected photons separated by time  $\tau$  ( $\tau$ -pairs) is accumulated over some long period, i.e., the full correlation function is measured. Here, the distribution of consecutive pairs only,  $N(\tau)$ , is measured in a start-stop experiment. Under the experimental conditions (low counting rates and short separation times) these two quantities are indistinguishable<sup>14</sup>. Under stationary conditions

the number  $C(\tau)$  of  $\tau$ -pairs per (unit time)<sup>2</sup> is equal to the number of detected photons per unit time  $\langle I_f \rangle$  and to the joint probability per unit time  $p(t + \tau | t)$  of detecting a photon at time  $t + \tau$  once a photon has been detected at time  $t$ <sup>15</sup>, i. e.  $C(\tau) = \langle I_f \rangle p(t + \tau | t)$ . The time evolution of  $p(t + \tau | t)$  must now be related to the single molecule's dynamics. The molecule is modelled as a 3LS along the same lines as deVries et al.<sup>16</sup> (Fig.1 inset). Incoherent transitions such as intersystem crossing (ISC) between  $S_1$  and  $T_1$ ,  $T_1$  and  $S_0$ , and such as spontaneous emission and internal conversion between  $S_1$  and  $S_0$  are accounted for by population transfer rates shown. The coherent transitions between  $S_0$  and  $S_1$  induced by the laser field are described in a semi-classical way by optical Bloch equations for the density matrix  $\rho$  of the 3LS. The calculation of the correlation function differs from previous treatments of atomic 3LS<sup>17</sup> in the arrangement of the levels and in the treatment of dephasing. The experimental values of the photophysical parameters were taken from Ref. 16.

Since the observation of the first photon has prepared the molecule in the ground state, the joint probability  $p(t + \tau | t)$  is proportional to the probability of occupation of  $S_1$  at time  $\tau$ ,  $\rho_{22}(\tau)$ :  $p(t + \tau | t) = \eta k_{21}^R \rho_{22}(\tau)$ , where  $\eta$  is the overall detection yield (number of photoelectrons per fluorescence photon),  $k_{21}^R = \phi_F(k_{21} + k_{23})$ , and  $\phi_F$  is the fluorescence quantum yield. Due to excitation by the laser,  $p(t + \tau | t)$  is a growing function of  $\tau$ , starting from zero at  $\tau = 0$  and approaching  $\eta k_{21}^R / 2$  for  $\tau$  large compared to the fluorescence lifetime and small compared to the triplet lifetime.

By analytically solving the Laplace transform of the Bloch equations (Eqs. 13-17 of Ref. 16) the correlation function is obtained as a sum of complex exponentials:

$$C(\tau) = \frac{1}{2} \eta k_{21}^R \langle I_f \rangle \Omega^2 \left\{ \frac{k_{31} \Gamma_2}{\lambda_1 \lambda_2 \lambda_3 \lambda_4} + \sum_{\substack{i=1 \\ i \neq j \neq k \neq l}}^4 \frac{(\lambda_i + k_{31})(\lambda_i + \Gamma_2)}{\lambda_i(\lambda_i - \lambda_j)(\lambda_i - \lambda_k)(\lambda_i - \lambda_l)} e^{\lambda_i \tau} \right\} \quad (1)$$

where  $\Omega$  is the on resonance Rabi frequency ( $\Omega = |\vec{\mu}_{12}\vec{E}|/\hbar$ ,  $\vec{\mu}_{12}$  is the transition dipole moment of 0.7 Debye and  $\vec{E}$  is the laser field),  $\Gamma_2 = (k_{21} + k_{23})/2$  is the dephasing rate (no pure dephasing) and the  $\lambda_i$  are the roots of the fourth degree equation:

$s^4 + a s^3 + b s^2 + c s + d = 0$  with:

$$\begin{aligned}
 a &= 2\Gamma_2 + k_{21} + k_{23} + k_{31} \\
 b &= k_{31}(k_{21} + k_{23}) + 2\Gamma_2(k_{21} + k_{23} + k_{31}) \\
 &\quad + \Gamma_2^2 + \delta_L^2 + \Omega^2 \\
 c &= 2\Gamma_2 k_{31}(k_{21} + k_{23}) + (k_{21} + k_{23} + k_{31}) \\
 &\quad \times (\Gamma_2^2 + \delta_L^2) + \Omega^2(\Gamma_2 + k_{31} + k_{23}/2) \\
 d &= k_{31}(k_{21} + k_{23})(\Gamma_2^2 + \delta_L^2) \\
 &\quad + \Omega^2\Gamma_2(k_{31} + k_{23}/2)
 \end{aligned} \tag{2}$$

with  $\delta_L$  the detuning. Plots of the correlation function are shown in Fig.1 (a-c). The decrease of  $C(\tau)$  for long times due to photon bunching is a specific feature of the 3LS, i.e., due to shelving of the molecule in the dark triplet state, bursts of emission are separated by dark intervals. Photon bunching has been previously observed in the single molecule case on  $\mu$ s timescales<sup>8</sup>, where it appears as an exponential decay of the correlation function. On the ns timescale of the experiments presented here, antibunching gives rise to a correlation dip around  $t = 0$ , and for high Rabi frequencies damped oscillations appear.

Crystal platelets of pentacene in p-terphenyl (conc.  $\approx 10^{-6} - 10^{-9}$  mole/mole) were mounted in a low temperature optical cryostat ( 1.5 K ) at the joint focus of a lens providing the excitation beam and a N.A. = 0.98 parabolic mirror collecting the emitted fluorescence, as described in detail elsewhere<sup>18</sup>. The excitation source was a tunable, standing wave Rhodamine 6G dye laser generating linewidths of  $\approx 2 - 3$  MHz in order to pump the 592.32 nm  $O_1$  site inhomogeneous line distribution of the  $S_1 \leftarrow S_0$  electronic transition of pentacene. The laser polarization was parallel to the transition dipole of the pentacene molecules. Isolated single molecule excitation spectra were observed easily by tuning the laser to the long wavelength side of  $O_1$  (typically at  $\approx 593.4$  nm). The red-shifted fluorescence

transmitted through a long-pass filter was detected with a GaAs phototube and photon counting electronics with a total efficiency of  $\eta = 0.011$ . Besides the single molecule fluorescence there is a second contribution to the total signal which appears as a frequency-independent background and which is attributed to Raman scattered radiation from the  $\approx 10^{12}$  p-terphenyl matrix molecules.

In order to achieve reasonable photon count rates, most of the correlation measurements were done at power levels where the fluorescence emission rate is already in the saturated regime. As the background increases approximately linearly in the spectrum and quadratically in the correlation function with the laser power, the signal-to-background ratio decreases leading to a diminished contrast of the antibunching with increasing power levels. To accurately determine the laser spot size, the laser beam was translated spatially across the face of the crystal to measure the spatial width of a single molecule excitation peak. This is a direct replica of the Gaussian intensity profile (typically  $\approx 5\mu\text{m}$  full-width at half-maximum) of the laser beam in the crystal, as probed with the fluorescence emitted by the molecule.

To measure the number distribution of consecutive pairs, the laser is tuned to the center frequency of the single molecule absorption line and the fluorescence is divided by a beam-splitter and focused onto two GaAs photomultipliers. The output pulses of the phototubes are converted into fast NIM pulses by two amplifier/discriminator units. These NIM pulses activate the Start and Stop inputs of a time-to-pulse height converter (Ortec 457) where the time delay between the two pulses is converted into a voltage. A fixed delay in the stop channel was used to measure the correlation function for negative times. The voltage pulses from the time-to-pulse height converter are stored in a pulse-height analyzer.

Figure 2 shows  $N(\tau)$  for different levels of pumping intensity (Rabi frequency). The antibunching in the correlation function (which is proportional to  $N(\tau)$ ) is clearly evident at short times ( $t \rightarrow 0$ ). As described above, with increasing power the background due to accidental pair correlations increases, leading to an increasing deviation of  $N(\tau)$  from zero.



The solid lines in Fig. 2 show the results of numerical fits of Eq. (1) to the experimental data using two parameters,  $\Omega$  and the signal at 300 ns, after subtraction of the accidental pair correlations. The fit to trace (a) is insensitive to the laser intensity and in this case the risetime is approximately given by the lifetime of  $S_1$ , 25 ns<sup>19</sup>. The Rabi frequencies obtained from the fits to traces (b) and (c) are in good agreement with those calculated from our intensity measurements including the proper local field correction<sup>20</sup>. At the highest power level (Fig. 3 (c)) the correlation function shows - besides the antibunching - the expected Rabi oscillations which are damped out during the excited state lifetime.

It is interesting to investigate the situation when two molecules are optically pumped at the same time. In this case the contrast of the antibunching in the correlation function is expected to be drastically reduced since the two molecules emit photons independently. The fluorescence excitation profiles of one and two molecules, the latter being so close in frequency space that their absorption lines overlap, are shown in Fig.3 (a) and (b), respectively. In Fig.3 (b) the absorption linewidth is clearly broader and the overall lineshape is not a single Lorentzian. The "two molecule" fluorescence is approximately a factor of 2 stronger than the "one molecule" fluorescence. The signal-to-background ratio, however, is very similar in both cases due to a larger background in the "two-molecule" spectrum (which was taken from a different sample); therefore the experimentally measured correlations can be compared directly. Measured values for  $N(\tau)$  (normalized) for the one and two-molecule cases, respectively, are given in Figs. 3 (c,d). A comparison between (c) and (d) reveals the expected decrease of the antibunching signal by a factor of  $\simeq 0.5$  when two molecules are excited simultaneously.

These results demonstrate that single molecule spectroscopy in solids can be used to investigate truly quantum-mechanical effects for multi-atom molecules with zero-phonon optical transitions. Here the experimental data are not affected by transit time or secular motion effects as are the beam or ion-trapping methods. However, background signals and intersystem crossing into the triplet state do limit the single-molecule antibunching signal and must be controlled in each specific case. As long as the lowest electronic transition of the

molecule is pumped, the presence of vibrational levels in the ground state and the detection of non-resonant fluorescence does not prevent the observation of photon antibunching. Future improvements in collection efficiency may allow direct detection of individual quantum jumps due to intersystem crossing.

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14. The distribution of consecutive pairs can be easily deduced from the correlation function. The relation between the Laplace transforms of  $C(\tau)$  and the distribution of consecutive pairs  $N(\tau)$  is:  $N(s) = C(s) / (1 + C(s))$ . See for example, S. Reynaud, *Ann. Phys. Fr.* (1983), p. 351.
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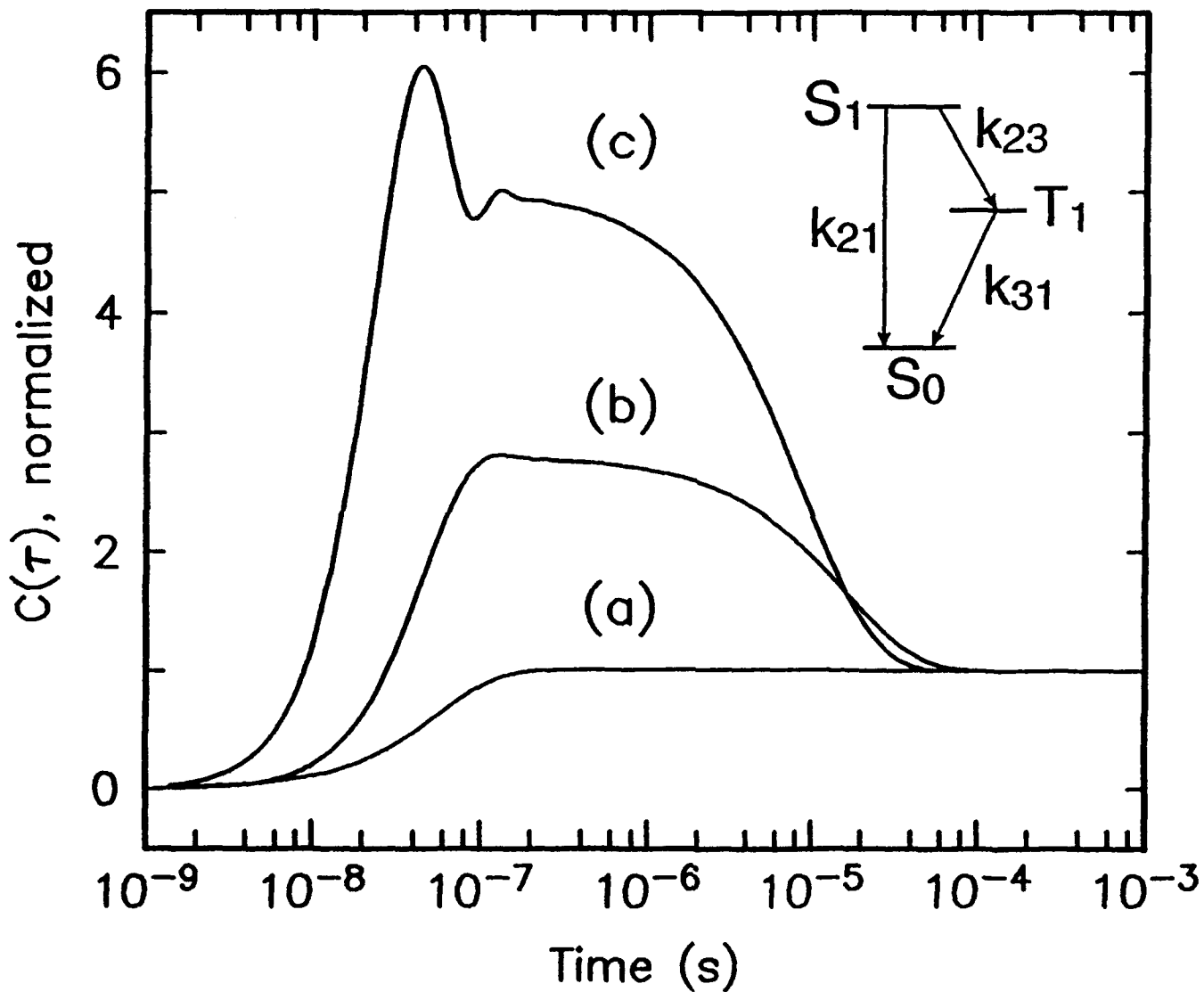


FIG. 1. (inset) The three level scheme for pentacene used in the calculation.  $S_0$ : singlet ground state;  $S_1$ : first excited singlet state;  $T_1$ : first excited triplet state. The  $k$ 's are the incoherent transition rates between the levels. The plots are simulations of the correlation function for different Rabi-frequencies  $\Omega$ : (a) 3 MHz; (b) 25.5 MHz; (c) 71.3 MHz.

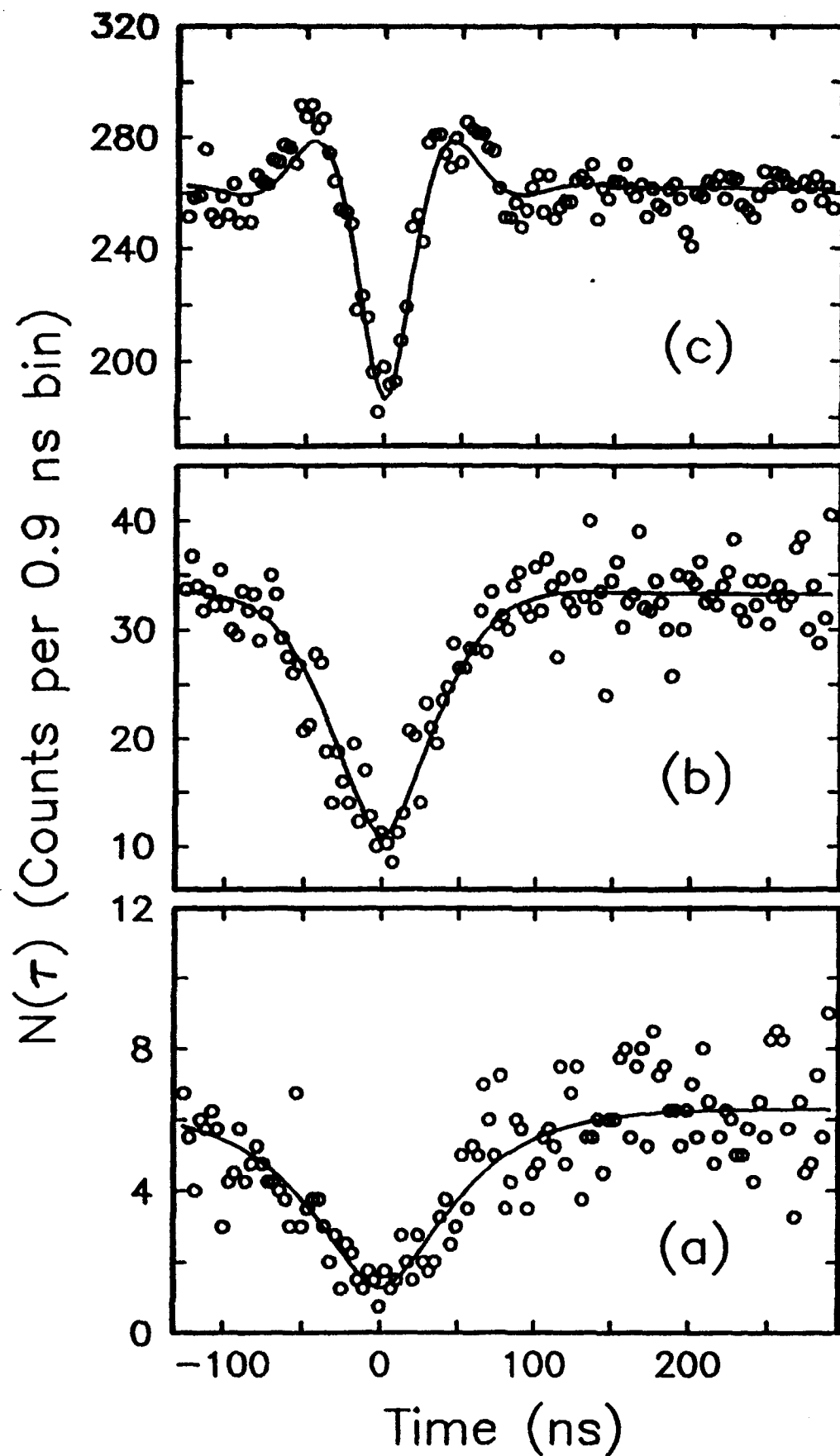


FIG. 2.  $N(\tau)$  for a single pentacene molecule ( $\lambda_{exc} \approx 593.4 \text{ nm}$ ). The antibunching is clearly seen for  $t \rightarrow 0$ . Rabi-frequencies  $\Omega$ : (a) 11.2 MHz; (b) 26.2 MHz; (c) 68.9 MHz. For example, case (b) involved  $3.6 \times 10^3$  start-stop events over a time period of 1 hr. The solid lines are fits to the data with  $\Omega =$  (a) 1-10 MHz, (b) 25.5 MHz, and (c) 71.3 MHz.

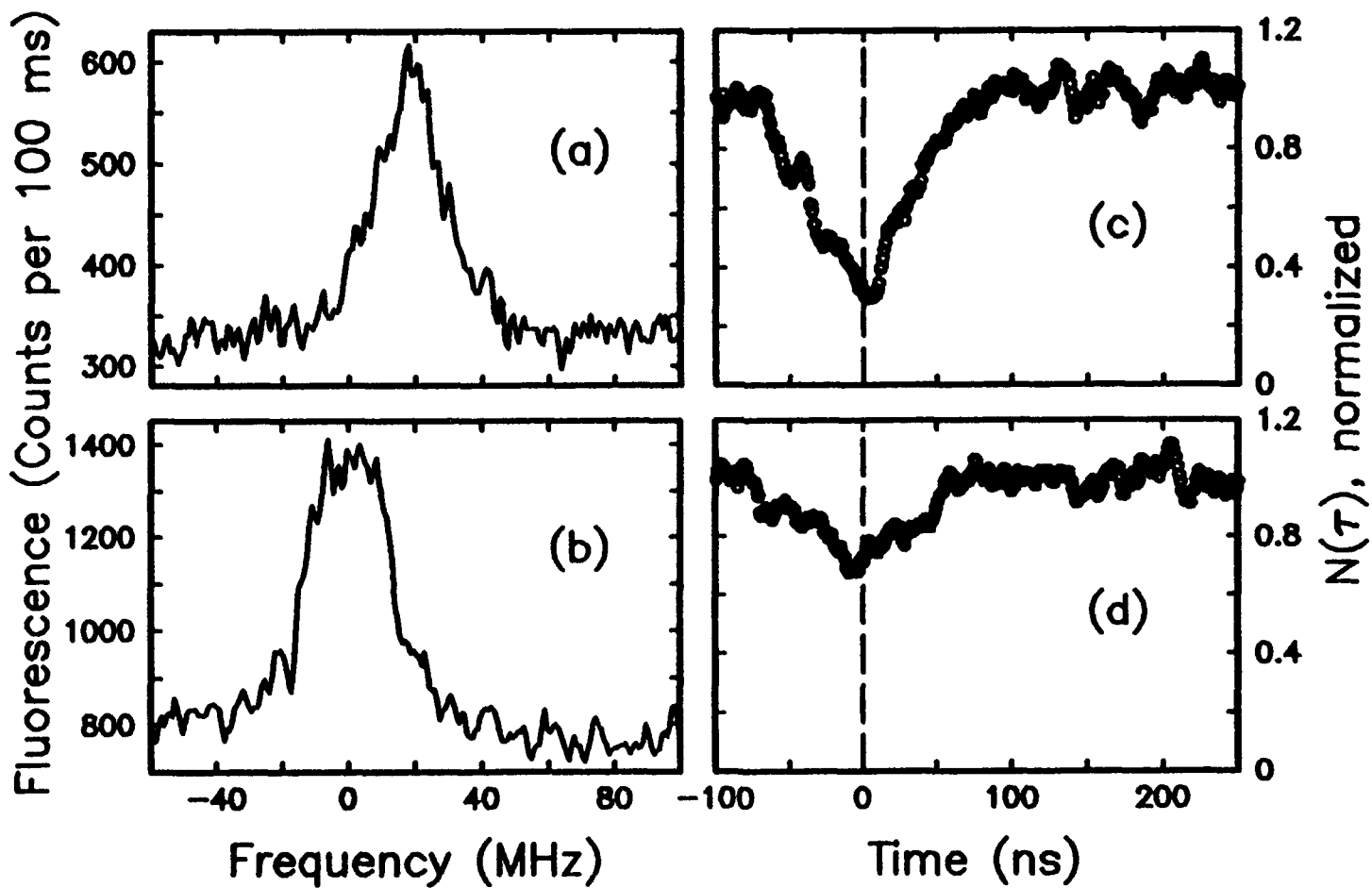


FIG. 3. Fluorescence excitation spectra near 593.4 nm with  $\Omega = 26.2\text{MHz}$  of one (a) and two (b) single pentacene molecules. (c) and (d) show  $N(\tau)$  for cases (a) and (b), respectively, normalized to the values of  $N(\tau)$  at long times.

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