

## Direct Measurement of the Photon Statistics of a Triggered Single Photon Source

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We studied intensity fluctuations of a single photon source relying on the pulsed excitation of the fluorescence of a single molecule at room temperature. We directly measured the Mandel parameter  $Q(T)$  over 4 orders of magnitude of observation time scale  $T$  by recording every photocount. On time scale of a few excitation periods, sub-Poissonian statistics is clearly observed and the probability of two-photon events is 10 times smaller than Poissonian pulses. On longer times, blinking in the fluorescence, due to the molecular triplet state, produces an excess of noise.

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Over the past few years, there has been a growing interest for generating a regular stream of single photons on demand. This was mainly motivated by applications in the field of quantum cryptography [1]. An ideal single photon source (SPS) should therefore produce light pulses containing exactly one photon per pulse, triggered with a repetition period  $\tau_{\text{rep}}$ , and delivered at the place of interest with 100% efficiency. For any given measurement time  $T$ , this source would emit exactly  $N = T/\tau_{\text{rep}}$  photons, so that the standard deviation  $\Delta N \equiv \sqrt{\langle N^2 \rangle_T - \langle N \rangle_T^2} = 0$  ( $\langle \rangle_T$  has to be understood as a mean value over a set of measurements lasting  $T$ ). Such a source would then be virtually free of intensity fluctuations, therefore corresponding to perfect intensity squeezing [2].

A first category of SPS's already realized is that of sources operating at cryogenic temperature. They rely on optically [3–6] or electrically [7] pumped semiconductor nanostructures or on the fluorescence of a two level system coherently prepared in its excited state [8]. A one-atom micromaser has also been used to prepare arbitrary photon number states on demand [9]. However, the collection efficiency of photons is barely higher than a few  $10^{-3}$  in these experiments. Because of this very strong attenuation, the intensity statistics are very close to a Poisson law at the place where the stream of photons is available. Another route is to realize SPS's at room temperature. In this case higher collection efficiency (around 5%) is achieved. The existing room-temperature SPS's rely on the pulse saturated emission of a single four-levels emitter [10,11]. When the pulse repetition period  $\tau_{\text{rep}}$  is much longer than the dipole radiative lifetime  $\tau_{\text{rad}}$ , such a single emitter can only emit one photon at a time. This temporal control of the dipole excitation allows, therefore, to easily produce individual photons on demand [12–14].

Our experimental realization of the room-temperature SPS relies on the pulsed saturation of a single molecule embedded in a thin polymer film [15]. The samples are made of cyanine dye DiIC<sub>18</sub>(3) molecules dispersed at a concentration of about one molecule per  $10 \mu\text{m}^2$  into a 30 nm thick polymethylmetacrylate (PMMA) layer, spin

coated over a microscope cover plate. The fluorescence from the single molecule is excited and collected by the standard technique of scanning confocal optical microscopy [16]. The molecules are nonresonantly excited at 532 nm, with femtosecond pulses generated by a Ti:sapphire laser and frequency doubled by single pass propagation into a LiIO<sub>3</sub> crystal. The repetition rate, initially at 82 MHz, is divided by a pulse picker. The energy per pulse  $E_p$  is adjustable by an electro-optic modulator. The pulse duration is about  $\tau_p \approx 100$  fs. The excitation light is reflected by the dichroic mirror of an inverted microscope, and then focused by an oil-immersion objective ( $\times 60$ , NA = 1.4), to form a spot of  $\approx 1 \mu\text{m}^2$  surface area. The fluorescence light from the sample, spectrally centered on 570 nm (50 nm FWHM), is collected by the same objective and then focused into a  $30 \mu\text{m}$  diameter pinhole. After recollimation, a holographic notch filter removes the residual pump light. A standard Hanbury Brown and Twiss (HBT) setup is then used to split the beam and detect single photons on two identical avalanche photodiodes. Glass filters are placed onto each arm to suppress parasitic cross talk [17] between the two photodiodes.

In order to identify rapidly single molecule emission, we first measure the interphoton time histogram by the standard start-stop technique with a time-to-amplitude converter [8]. When a single emitter is addressed, there is virtually no event registered at  $\tau = 0$ , since a single photon cannot be simultaneously detected on both sides of a beam splitter [18]. The histogram shows a peak pattern at the pulse repetition period  $\tau_{\text{rep}}$ . As explained in Ref. [8], the peaks' areas allow one to infer the probabilities  $P_S(n)$  for the source ( $S$ ), of giving  $n = 0, 1, 2$  photocounts per excitation pulse, where two photon counts are due to deviation from the ideal SPS. Nevertheless, this technique can hardly be used to extract the intensity fluctuations on time scale longer than a single pulse. We have therefore chosen to record each photodetection event with a two-channel time interval analyzer computer board (GuideTech, Model GT653). Since each detection channel has a dead time of 250 ns, the excitation repetition rate was chosen to be 2 MHz.

In a typical experiment, we first raster scan the sample at low excitation energy per pulse (0.5 pJ). When a single molecule is located, we apply the excitation energy ramp  $E_p(t)$  shown in the inset of Fig. 1, and simultaneously record the fluorescence counts on a 1 ms integration time. Figure 1 displays the fluorescence counting rate  $R$  vs  $E_p$ . The large intensity fluctuations are due to triplet state excursion of the molecule (see Fig. 2). If this state is not taken into account, the molecular energy levels can be modeled by a two-level system assuming a very fast nonradiative relaxation between the two higher and lower energy states. The excited state population  $\sigma$  at the time  $\tau_p$  after the pulse arrival is then

$$\sigma = \frac{E_p/E_{\text{sat}}}{(1 + E_p/E_{\text{sat}})} (1 - e^{-(\tau_p/\tau_{\text{rad}})[1+(E_p/E_{\text{sat}})])}. \quad (1)$$

The data  $R(E_p)$  are fitted by the function  $R = R_0 \times \sigma$  in a two-step procedure. After a first fit of the raw data, the points below this fit by more than 1 standard deviation, which are attributed to triplet state excursion, are removed. The fit of the remaining set of data yields  $R_0 = 160 \times 10^3$  counts/s and  $E_{\text{sat}} = 5.6 \times 10^{-5}$  pJ.

In order to optimize the number of emitted photons and avoid rapid photobleaching, we set  $E_p^{\text{max}}$  to 5.6 pJ. Such a value would correspond to  $\sigma = 97\%$ , for the molecule studied in Fig. 1. During the constant maximum pumping energy period of the excitation ramp,  $10^4$  detection events are typically recorded before photobleaching. Because of the high stability of the period of the pulsed laser, this set of times can be synchronized on an excitation time base. We then build the table of the number of photocounts,  $n_i = 0, 1, 2$ , for each excitation pulse  $i$ . Photons which are delayed by more than  $10 \times \tau_{\text{rad}}$  are considered to come from the dark counts of the two photodiodes, and are therefore rejected.

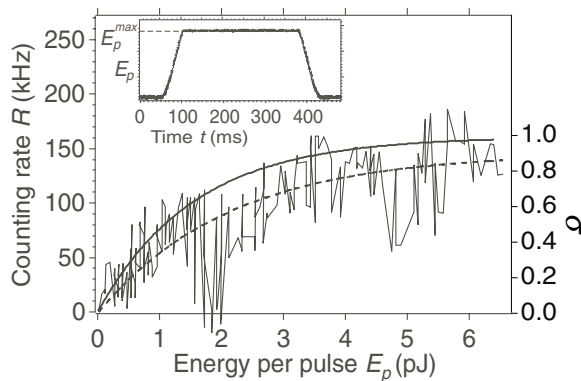


FIG. 1. Photon counting rate  $R$  vs energy per pulse, for a single molecule. The inset shows the excitation ramp  $E_p(t)$ , with  $E_p^{\text{max}} = 13$  pJ in this case. The record of the saturation curve was limited by the photobleaching of the dye. The dashed curve is a fit of the raw data according to Eq. (1), and the solid line is a fit after correction of triplet state excursion. The right scale shows the excited state population  $\sigma$ .

The data considered hereafter corresponds to a molecular source which survived during 319 769 periods (about 160 ms) yielding 14 928 recorded photons including 14 896 single photon events, 16 two-photon events. We deduced  $P_S(1) = 0.0466$  and  $P_S(2) = 5.0 \times 10^{-5}$  and a mean number of detected photon per pulse  $\bar{n}_S = 0.0467$  (see Table I). The real source is considered as the superposition of an attenuated ideal SPS with an overall quantum efficiency  $\eta$ , and a coherent source simulating the background, which adds a mean number of detected photons per pulse  $\gamma$ . From the measured values of  $P_S(1)$  and  $P_S(2)$ , we infer  $\eta \approx 0.0445$  and  $\gamma \approx 2.2 \times 10^{-3}$ . This leads to a signal-to-background ratio of about 20.

We also compared experimentally our SPS to a reference source ( $R$ ) made of attenuated pump laser pulses with approximately the same mean number of detected photons per pulse. Quantitative tests of this reference source and of the detection setup are, however, necessary. For a coherent source ( $C$ ) containing a mean number  $\alpha$  of photons per pulse [19], the photon number probability is  $P(n) = \frac{\alpha^n}{n!} e^{-\alpha}$ , from which one can infer the counting probability  $P_C(n)$ . Particular care has to be taken to the fact that, because the dead time is longer than the pulse duration, each detector cannot detect more than one photon per pulse. One readily has  $P_C(0) = P(0) = e^{-\alpha}$ .  $P_C(1)$  results either from pulses containing exactly one photon or from pulses containing more than one photon all falling on the same detector. These two contributions yield  $P_C(1) = 2e^{-\alpha/2}(1 - e^{-\alpha/2})$ . Similarly, one gets  $P_C(2) = (1 - e^{-\alpha/2})^2$ , and the mean number of detected photons per pulse  $\bar{n}_C = 2(1 - e^{-\alpha/2})$ . For the reference source, we measured  $\bar{n}_R = 0.0462$ ,  $P_R(1) = 0.0452$ ,  $P_R(2) = 50 \times 10^{-5}$ , whereas one predicts for  $\bar{n}_C = \bar{n}_R$ ,  $P_C(1) = 0.0451$  and  $P_C(2) = 53 \times 10^{-5}$ . The measured values are in good agreement with the predictions, which proves that the faint Ti:sapphire pulses make a good calibration

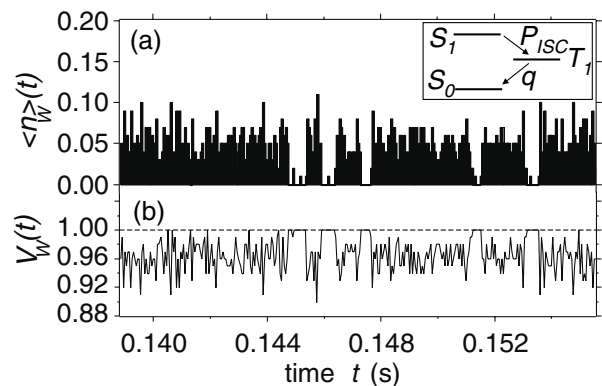


FIG. 2. (a) Mean number  $\langle n \rangle_w$  of photons detected in successive samples of the data of constant size  $W = 100$  cycles (bin period of  $50 \mu\text{s}$ ). (b) Corresponding time trace of the normalized variance  $V_w$  showing reduction of noise ( $V_w < 1$ ) during the emission period of the molecule. The inset of (a) displays the molecular level diagram.

TABLE I. Photocount probabilities  $P_X(n)$ ,  $n = 1, 2$ , of our SPS ( $X = S$ ), of an experimental reference source and a theoretical coherent source, the photocount statistics of which are affected by the detection setup.  $\bar{n}_X$  are the mean number of detected photons per pulse and  $V$  are the normalized variances. Negative values of  $V$  for the coherent and reference sources are due to a dead time effect.

$X$	$P_X(1)$	$P_X(2)$	$\bar{n}_X$	$V - 1$
$S$	0.0466	$5.0 \times 10^{-5}$	0.0467	-0.0445
$R$	0.0452	$50 \times 10^{-5}$	0.0462	-0.0244
$C$	0.0451	$53 \times 10^{-5}$	0.0462	-0.0231 <sup>a</sup>

<sup>a</sup>Calculated from  $P_C(n)$ .

source for Poisson statistics. We then infer the ratio  $P_S(2)/P_R(2) = 0.10$ , which tells that the number of two-photon pulses in our SPS, is 10 times smaller than in the reference Poissonian source.

In a first attempt to estimate the fluorescence intensity fluctuations per pulse, we considered samples of the data made of  $W$  excitation cycles. We introduced a normalized variance  $V_W$  defined, on the sample, by  $V_W \equiv \langle (\Delta n)^2 \rangle_w / \langle n \rangle_w$ , with  $\langle (\Delta n)^2 \rangle_w \equiv \sum_{i=1}^W (n_i - \langle n \rangle_w)^2 / W$ , where  $n_i$  is the number of detected photons for the pulse  $i$  and  $\langle n \rangle_w$  is the mean number of detected photons per pulse in the sample considered. In the very few samples for which  $\langle n \rangle_w = 0$ ,  $V_W$  is not defined and is set to 1. For a Poisson distribution of photocounts,  $V_W = 1$ , whereas  $V_W < 1$  for sub-Poissonian distribution.

In order to follow the time evolution of intensity fluctuations, we then extract from the set of  $\{n_i\}$  all the successive samples of photocount measurements of size  $W = 100$ , separated by a single pulse period. Figure 2(a) displays the mean number of detected photons per pulse vs time. We clearly see random intermittency in the fluorescence of the molecule, due to the presence of a dark triplet state  $T_1$  in the molecular energy levels diagram [see inset of Fig. 2(a)]. At each excitation cycle the molecule has a small probability to jump into this nonfluorescent state, where it stays for a time much longer than the repetition period. Figure 2(b) shows, in parallel, the time trace  $V_W(t)$  of the normalized variance. During an emission period,  $V_W$  stays below 1, and the statistics of the number of the detected photons per pulse is sub-Poissonian. On the other hand, when the molecule stops to emit, the background light yields  $V_W \approx 1$ . If we now consider the whole set of data, our measurements yield a single value for the variance  $V = 0.9555$ . In this intensity fluctuation analysis at the level of a single pulse, this value of  $V$  is also directly related to the Mandel parameter [20]  $Q \equiv \langle (\Delta n)^2 \rangle / \langle n \rangle - 1$  by  $Q = V - 1 = -0.0445$ . Let us point out that, due to the photodetection dead time, the triggered reference source also yields a sub-Poissonian counting statistic. More precisely, for the coherent source giving about the same mean number  $\bar{n}_C$  of photons per pulse than our SPS, one predicts

a value  $Q = -\bar{n}_C/2 = -0.0231$ . This value, confirmed by our measurements on the reference source (see Table I), is obtained in the case where the dead time of each detection channel is much longer than the duration of the pulse. Nevertheless, the fluctuations of the number of detected photons per pulse coming out of our SPS show a clear departure from the reference coherent source. Albeit still limited by the quantum efficiency  $\eta$ , this direct measurement of  $|Q|$  is larger by more than 1 order of magnitude compared to previous experiments [21–23]. In those experiments  $Q$  was inferred from the second order correlation function  $g^{(2)}(\tau)$ . The later can be identified to a normalized interphoton time histogram within some approximations. Our measurement of  $Q$  at the single pulse time scale is related to this histogram by  $Q = \bar{n}(h_0/2 - 1)$ , where  $h_0$  is the area of the peak at  $\tau = 0$  normalized to a coherent source [5], and where the  $1/2$  factor accounts for the photodetection dead time.

The measurement of the variance  $V$  of the detected photon number per pulse is, however, insufficient to characterize the noise properties of our SPS. Whereas such a characterization is usually inferred from the record of noise power spectra, photocount measurements such as ours are performed in the time domain. We therefore introduce as a new variable, the number  $N(T) = \sum_{i=1}^k n_i$ , of the detected photons during any period of observation  $T = k\tau_{\text{rep}}$ . The analysis of the fluctuations of the variable  $n_i$  can be generalized to the variable  $N(T)$ , by using the time dependent Mandel parameter [21]  $Q(T) \equiv \langle (\Delta N)^2 \rangle_T / \langle N \rangle_T - 1$ . We can also define a Mandel parameter  $Q_s(T)$  for the number of photons emitted by the source in the same period of time  $T$ . In the case of an ideal SPS, we have  $Q = \eta \times Q_s$  [24]. For such a source,  $Q_s = -1$ , and therefore  $Q(T) = -\eta$ , for any value of  $T$ .

Figure 3 shows that we did observe sub-Poissonian intensity fluctuations on time scales from  $T = 1 \times \tau_{\text{rep}}$  to  $T = 8 \times \tau_{\text{rep}}$ , with the minimum value  $Q(\tau_{\text{rep}}) = -0.0445$  achieved on a single pulse time scale, as explained above. When we consider the number of detected photons on time scales larger than  $10^{-5}$  s, the intensity fluctuations exhibit a super-Poissonian behavior [ $Q(T) > 0$ ] as shown in the inset of Fig. 3. This is a direct consequence of the leak in the dark triplet state, which induces correlation between consecutive pulses and photon bunching [25]. We developed a simple model to account for the intermittency of the SPS emission. In this model, the molecule is either available for fluorescence and is said to be in an “on” state, or it is in its triplet “off” state and does not fluoresce. Let us note  $p$ , the probability per unit of time to make an on  $\rightarrow$  off transition, and  $q = 1/\tau_T$ , the probability to make the reverse off  $\rightarrow$  on transition, where  $\tau_T$  is the lifetime of the triplet state. Note that  $p\tau_{\text{rep}} = \mathcal{P}_{\text{ISC}}$  is the intersystem crossing probability per excitation pulse. From measured values at the single molecule level with DiIC<sub>18</sub>(3) cyanine dye [26],  $p\tau_{\text{rep}} \approx 10^{-4} \ll 1$  and  $q\tau_{\text{rep}} \approx 2.5 \times 10^{-3} \ll 1$ . In this limiting case, the Mandel parameter of the source is

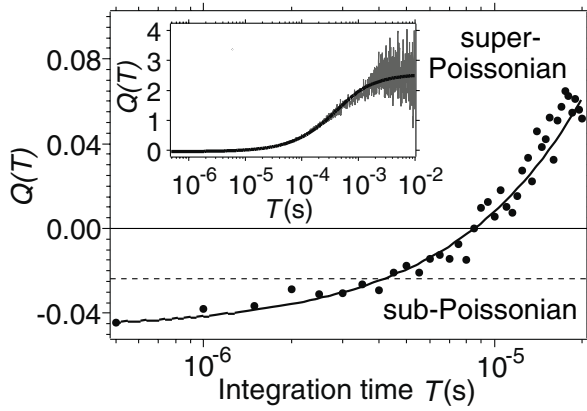


FIG. 3. Direct measurements of Mandel parameter  $Q(T)$  over short recording time  $T$ . The dashed line shows  $Q(T)$  for the equivalent coherent source (C). The inset shows  $Q(T)$  for a longer time of observation. The solid curve is a fit to the data by a model accounting for intermittency in the SPS emission.

$$Q_s(k\tau_{\text{rep}}) = \frac{2\mathcal{P}_{\text{ISC}}}{\beta^2} \left[ 1 - \frac{1}{k\beta} [1 - (1 - \beta)^k] \right] - 1, \quad (2)$$

where  $\beta \equiv (p + q)\tau_{\text{rep}} = \mathcal{P}_{\text{ISC}} + \tau_{\text{rep}}/\tau_T$ . The Mandel parameter of the detected photon counts is then  $Q(T) = \eta \times Q_s(T)$ . As shown in Fig. 3, our data for  $Q(T)$  are well fitted over more than 4 orders of magnitude, by Eq. (2) with  $\eta = 0.0445$  (measured) and the free parameters  $p$  and  $q$ . The fit yields  $p\tau_{\text{rep}} \approx 1.3 \times 10^{-4}$  and  $\tau_T \approx 250 \mu\text{s}$ , in good agreement with Ref. [26].

As presented in this Letter, the set of time tagged photo-counts allows one to make a direct time domain fluctuation analysis. From this, one can deduce all moments of the photon statistics in order to measure any type of characteristic function such as  $g^{(2)}(\tau)$  and  $Q$ . This analysis can be straightforwardly applied to characterize SPS in the prospect of applications to quantum cryptography. It is also complementary to fluorescent correlation spectroscopy technique for investigating photochemical properties at the single molecule level.

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