Single-Photon Spectroscopy of a Single Molecule

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(Received 6 November 2011; published 27 February 2012)

Efficient interaction of light and matter at the ultimate limit of single photons and single emitters is of great interest from a fundamental point of view and for emerging applications in quantum engineering. However, the difficulty of generating single-photon streams with specific wavelengths, bandwidths, and power as well as the weak interaction probability of a single photon with an optical emitter pose a formidable challenge toward this goal. Here, we demonstrate a general approach based on the creation of single photons from a single emitter and their use for performing spectroscopy on a second emitter situated at a distance. While this first proof of principle realization uses organic molecules as emitters, the scheme is readily extendable to quantum dots and color centers. Our work ushers in a new line of experiments that provide access to the coherent and nonlinear couplings of few emitters and few propagating photons.

DOI: 10.1103/PhysRevLett.108.093601 PACS numbers: 42.50.−p, 33.90.+h

Interaction of a propagating photon with an atom or molecule has been a cornerstone of quantum physics [1] and plays an elementary role in any optical phenomenon, but its discussions have been limited to gedanken experiments. By the end of the past century, a number of techniques were devised for experimental studies of single material particles such as ions, atoms, molecules, and quantum dots, and generation of single-photon streams came of age. In the wake of these developments, theoretical works have shown that single photons can be directly and perfectly absorbed or reflected by single emitters without the need for microresonators [2–6]. These proposals lay the groundwork for optical signal processing at the nanometer scale, where a quantum emitter can be used as the smallest elementary medium for achieving optical nonlinearity, and act as transistor, phase shifter, or memory at the single-photon level [7–10]. Some of the concepts have been recently examined in the laboratory using laser beams [11–15]; however, investigations at the single-photon level have been elusive because of the lack of suitable single-photon sources as well as the difficulty in achieving a very efficient emitter-photon interfacing. Here, we demonstrate a versatile strategy based on the creation of single photons from a single emitter and their use for performing coherent spectroscopy on a second emitter situated at a distance.

A single quantum emitter can generate up to one photon per spontaneous emission cycle, corresponding to a radiated power of 0.03–3 nW if one assumes a typical fluorescence lifetime of the order of 0.1–10 ns for dipole-allowed transitions. Although recent reports have shown that a very large fraction of this fluorescence can be collected [16], losses in the detection path commonly limit the usable power of single-photon sources to less than picowatt. Detection of this weak light on top of residual background fluorescence and detector noise was, in fact, the central challenge of single-molecule spectroscopy, which was surmounted in the 1990s [17]. Considering that in these experiments one usually relies on lasers with milliwatt or higher power, excitation and detection of one emitter with single photons generated by another might appear as a daunting experimental task. To achieve this, one has to both collect the photons from the ''source'' particle and funnel them to the ''target'' particle very efficiently. Furthermore, the frequency of the single-photon source should be tunable with respect to that of the target transition if one is to perform spectroscopy.

Three conceptual points have made it possible for us to reach these goals. First, the extinction cross section of a single two-level emitter is given by $\sigma = \frac{3\lambda^2}{2\pi}\frac{\gamma_0}{\gamma_{\mathrm{hom}}}$, where λ, γ_0, and γ_{hom} are the wavelength, natural linewidth, and homogeneous width of the transition at hand, respectively [18]. Second, if $\gamma_{\mathrm{hom}} \approx \gamma_0$ can be met for an emitter, its cross section reduces to about $\lambda^2/2$, which is comparable to the area of a beam focused with high numerical aperture (NA). Finally, the ultimate limit on the signal-to-noise ratio in extinction spectroscopy is set by the intensity shot noise of the excitation beam [19]. Therefore, deciphering an extinction signal of about 1% within 1 s would require a tightly focusable excitation beam with a photon flux larger than 10^4 per second. This can be obtained from a single emitter if high-NA collection optics is used.

In our current experiment we used the organic dye molecule dibenzanthanthrene (DBATT) embedded in organic matrix tetradecane at $T = 1.4$ K. Under these conditions, the photons emitted on the narrow zero-phonon

lines (00 ZPLs) between the lowest vibrational levels ($v = 0$) of the electronic ground and excited states [see Fig. 1(a)] have a coherence length that reaches several meters and is only limited by the spontaneous emission rate of the excited state (i.e., $\gamma_0 \approx \gamma_{\mathrm{hom}}$). As a result, the 00 ZPL cross section falls short of the optimal value of $3\lambda^2/2\pi$ only by 2–3 times caused by fluorescence to the $v \neq 0$ levels and the phonon wings [12,17].

Figure 1(b) shows the schematics of our experimental arrangement, where two different samples were mounted in separate cryogenic confocal microscopes. In each sample, the inhomogeneous distribution of the sharp 00 ZPL frequencies ensures that individual DBATT molecules can be excited selectively by tuning the frequency of a narrow-band light source around a wavelength of $\lambda = 589$ nm. Commonly, the redshifted fluorescence of the $v = 0$ level in the excited state to the $v \neq 0$ levels of the ground state is recorded [15]. However, recent developments have shown that single molecules can also be detected via coherent extinction spectroscopy [12]. Figure 2(a) displays an example of a 9.3% attenuation dip obtained when the frequency of a laser beam was scanned across the 00 ZPL resonance of a molecule with a FWHM of 20 MHz. In what follows, we will use this molecule as the target molecule.

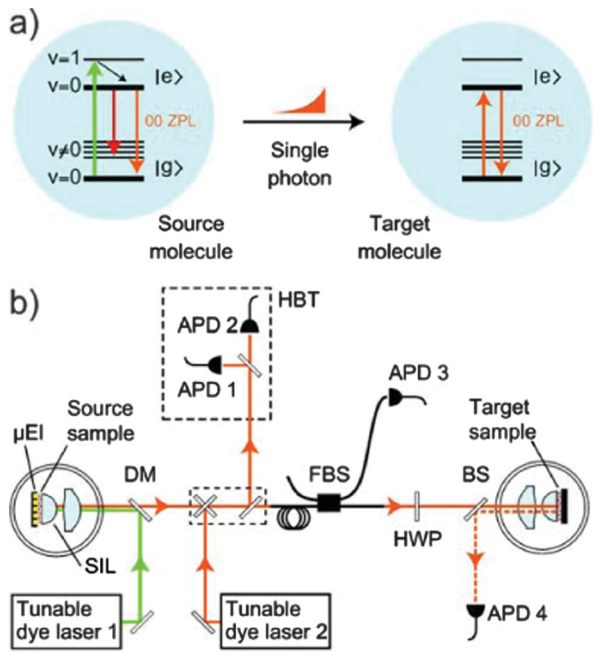

FIG. 1 (color). (a) Schematic view of the free-space connection between two molecules via a single photon. (b) Experimental setup. Two cryogenic microscopes house the source and target samples. μEl, microelectrodes; SIL, solid-immersion lens; DM, dichroic mirror; HBT, Hanbury Brown–Twiss correlator; FBS, polarization-maintaining single-mode fiber-coupled beam splitter; HWP, half-wave plate; BS, 50:50 beam splitter; APD, avalanche photodiode. A bandpass filter at 589 nm is not shown.

To produce photons that matched the 00 ZPL frequency of the target molecule (ω_t), we recorded excitation spectra from the source sample within a few GHz of ω_t. Once a suitable source molecule was found and characterized, it was excited via the 01 transition between the $v = 0$ and $v = 1$ levels of its ground and excited electronic states, respectively [see Fig. 1(a)]. A rapid radiationless decay of the $v = 1$ level in the excited state populates its $v = 0$ level, which then decays radiatively. By using suitable spectral filters, we isolated the narrow-band spontaneous emission on the 00 ZPL from the Stokes-shifted fluorescence to $v \neq 0$ levels. A Hanbury Brown–Twiss correlation measurement on this emission is presented in Fig. 2(b) and shows a clear reduction of the normalized second-order autocorrelation function $g^{(2)}(\tau = 0)$ below 0.5, verifying its single-photon character [18]. We emphasize that although the generated photons do not follow a triggered train, the resulting stream consists of individual photon pulses separated in time.

The schematics of our experimental setup is shown in Fig. 1(b). In both the source and target microscopes, we used a combination of aspherical and solid-immersion lenses for achieving a high NA in collection and excitation [12]. Two continuous-wave tunable dye lasers were employed for addressing the 00 and 01 transitions of DBATT, which are typically separated in wavelength by about 9 nm. Avalanche photodiodes (APD) were used as detectors in various stations. A polarization-maintaining single-mode optical fiber was used to facilitate the alignment of the optical axes of the two microscopes and to ensure a good spatial mode quality. An integrated beam splitter with variable transmission allowed us to probe the light in the fiber. In this work, we examined the extinction of the incident beam on APD4 after it was reflected from a gold mirror deposited on the back of the target sample [20]. This arrangement can be regarded as a folded transmission experiment.

In order to perform spectroscopy on the target molecule with the photon stream generated by the source molecule,

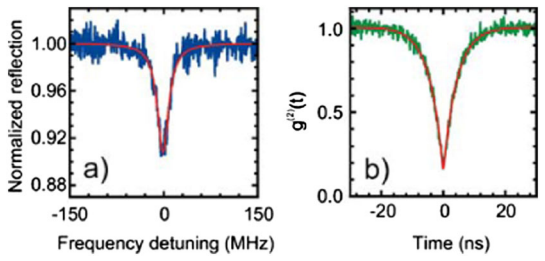

FIG. 2 (color online). (a) The intensity of a laser beam reflected by the target sample as a function of laser frequency detuning. The solid red line represents a Lorentzian fit with FWHM of 20 MHz and amplitude of 9.3%. (b) Intensity autocorrelation of the light emitted by the source molecule. The solid red line represents a fit to a double-sided exponential with a time constant of 4.2 ns.

we tuned the 00 ZPL frequency of the latter via Stark effect by applying a voltage to the interdigitated microelectrodes deposited on its substrate. Finally, we aligned the polarization of the single-photon stream with the transition dipole moment of the target molecule using a half-wave plate; we did not correct for a residual ellipticity of up to 10% acquired in the optical path.

The symbols in Fig. 3 present the intensity of the single-photon stream on APD4 as its frequency (ω_s) was scanned through ω_t. We find an attenuation of about 3% and a FWHM of about 60 MHz, in contrast to a dip of 9.3% and FWHM of about 20 MHz obtained in the extinction spectrum of the same molecule recorded under laser excitation [see Fig. 2(a)]. The difference between the two spectra stems from the fact that the linewidth of our dye laser is about 1 MHz, while the single photons generated via a spontaneous emission have a minimum linewidth of 20 MHz. In our case, the experimentally measured rise time of 4.2 ns in $g^{(2)}$ [see Fig. 2(b)] reveals that the single-photon source has been broadened to 38 MHz. This can be explained by the high depopulation rate of the ground state in the 01 pump process. We also note a slight shift of the center frequency, which we attribute to a delay in the data acquisition process when the Stark voltage was incremented. At this point, it is worth emphasizing that it should also be possible to detect the target molecule via fluorescence if the collection efficiency is sufficiently high and the detector dark counts are low enough [19].

Extinction of a light beam by a sample can be described by considering the addition of the incident and scattered fields [12,21]. To this end, the spectrum in Fig. 3 provides a direct signature of the interference between the two probability amplitudes for a single photon traversing the target molecule and scattering from it. To elucidate this process, we have theoretically considered the incidence of a photon wave packet at central frequency ω_s and spectral width γ_s onto a two-level system with transition frequency $\omega_t = \omega_s$ and a natural linewidth $\gamma_t = \gamma_s$ [22,23]. As indicated in Fig. 4(a), we took an exponentially rising temporal pulse to emulate the propagation of a photon that is spontaneously emitted by the source molecule with a $1/e$ time of $\tau_s = 1/2\pi\gamma_s$ [5,24]. The curves in Figs. 4(b) and 4(c) display snapshots of the wave packet evolution at times $t = 2\tau_s$ and $8\tau_s$ after the first encounter of the photon and the target molecule. The reflected components of the photon wave packet (red curves) display oscillations that signify its interference with the incoming part. The frequency spectrum of the reflected photon is plotted in Fig. 4(d) and can be associated with the steady-state resonance fluorescence (emission) spectrum of the target molecule in the backward half-space. This spectrum is narrower than that of the incident pulse (black curve) because it results from a temporal convolution of the latter with the exponential response of the molecule during the excitation process, yielding a scattered pulse that is stretched in time.

The theoretical model we have used [22,23] assumes a perfect coupling between the incident light and the emitter, leading to the perfect reflection of a monochromatic and resonant photon [4] (see also the Supplemental Material [25]). However, if the incident photon has a finite spectral width, as considered above in the condition $\gamma_s = \gamma_t$, some light is leaked to the transmitted channel. The blue curve in Figs. 4(b) and 4(c) shows the evolution of the

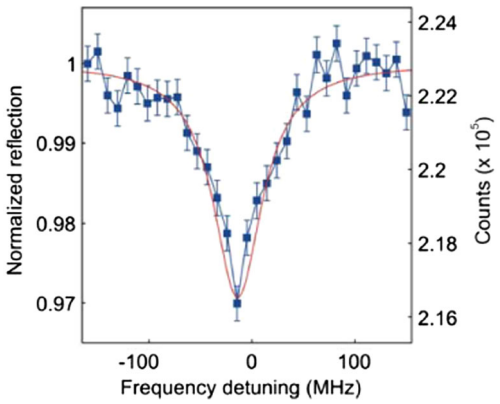

FIG. 3 (color online). Reflection of the single photons emitted by the source molecule from the target molecule as a function of frequency detuning between their 00 ZPLs. The right-hand axis shows the total number of detected counts in 143 s after subtracting 2×10^4 dark counts per pixel. The left-hand axis displays the normalized intensity of the single-photon stream. The solid curve represents the theoretical calculation (see text for details).

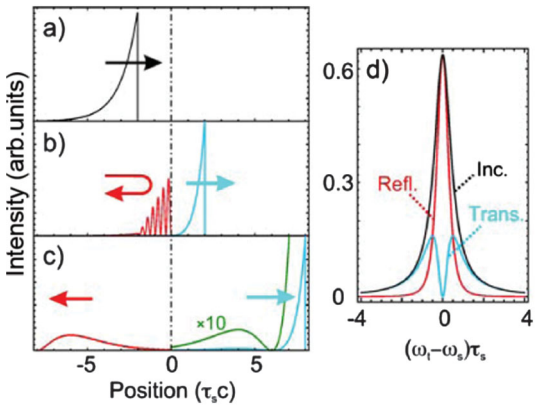

FIG. 4 (color). (a)–(c) The electric field intensity distribution of a photon as a function of the position z in units of $\tau_s c$. (a) The incident pulse before encountering the emitter. (b) The red and blue curves show the wave packet intensities in the backward and forward half-spaces at $2\tau_s$ after the first encounter. To visualize the standing-wave pattern, we have assumed a small transition frequency $\omega_s = 10/\tau_s$. (c) Same as in (b) but at time $8\tau_s$. The green curve displays a tenfold zoom of the blue curve. (d) The black, red, and blue profiles plot the frequency spectra associated with the incident, reflected, and transmitted photon pulses at long times $t \gg \tau_s$, respectively.

transmitted photon at two different times, and the green curve in Fig. 4(c) displays a tenfold zoom of the latter. We find that the transmitted component is fractionated in an approximately exponential pulse that is narrower than the incident one, followed by a flatter envelope. The frequency spectrum corresponding to this temporal behavior is a double-peaked profile that goes to zero on resonance as depicted by the blue curve in Fig. 4(d). It can also be obtained from the subtraction of the incident and reflected spectra. The direct experimental observation of the spectra of the reflected and transmitted channels requires a very strong interaction between the incoming photon and the emitter to ensure a substantial effect of the molecular scattering on top of the incident background field. Future improvements, as discussed below, should make such measurements possible. Furthermore, triggered generation of single photons via pulsed excitation can provide access to the temporal profiles of the reflected and transmitted photons as discussed in Fig. 4(c).

In order to reconstruct the extinction spectra obtained in our measurements, we took into account the experimentally measured parameters. First, we used $\tau_s = \tau_t = 8$ ns as deduced from the measured FWHM of 20 MHz for the 00 ZPL transition [see Fig. 2(a)]. To consider the spectral broadening of the single photons to a width of 38 MHz mentioned earlier, we introduced an uncertainty of 18 MHz in ω_s. Next, we repeated the calculations for different frequency detunings $(\omega_t - \omega_s)$ and plotted the areas under the emission spectra for each case. We then accounted for the experimental extinction efficiency of our system by equating the area under the spectra of Figs. 2(a) and 3. These considerations yielded a Lorentzian extinction spectrum with a FWHM of 58 MHz and amplitude of 2.9% (see also the Supplemental Material [25]), which, as displayed by the red curve in Fig. 3, provides an excellent agreement with the experimental spectrum.

In the past few years, clever efforts have been undertaken for exploring the interaction between single photons and single emitters. For example, single photons generated by a trapped ion were redirected back toward the ion upon reflection from a mirror [26]. Also, correlated photons generated in a down-conversion process have been used to record heralded absorption by a single ion [27]. The experiment described here represents the first demonstration of the direct coupling between two distant quantum emitters via a propagating stream of single photons. While the majority of studies on single quantum emitters rely on the detection of incoherent fluorescence, we have investigated the *coherent* scattering of a single photon by a single molecule. This approach sets the stage for achieving strong coherent coupling of two or more emitters separated by much smaller than the coherence length of the photon so that its back and forth scattering from the emitters can couple them in a fashion similar to dipole-dipole coupling [28,29]. To enter this regime, we envision replacing free-space lens coupling by near-field coupling via a nanoguide [9,30,31], which can serve as a bus for connecting many molecules or other quantum emitters within distances of tens or hundreds of micrometers on a chip.

The experimental scheme described here can be made more efficient by improving the spatial and spectral aspects of photon-emitter interfacing. Here, a modest inhibition of the spontaneous emission of the source molecule, e.g., via plasmonic nanoantennas [32], would render the spectral bandwidth of the single photons narrower than the target transition. Furthermore, one can engineer the radiation pattern of the source by an optical antenna and reach near-unity efficiency in collecting its emitted photons [16]. By reciprocity, such an antenna would also allow nearly perfect mode matching to the radiation pattern of the target molecule and therefore ideal coupling [4]. Implementation of these measures would ensure that a bright stream of photons interacts with the target emitter with very high probability. To this end, the strategy presented here provides an enabling platform for making sub-shot-noise measurements [33,34] and for accessing optical nonlinear effects at the few-photon level [7,8,10] when coupling an emitter to two or more triggered photons that arrive at the same time. In closing, we emphasize that our methodology is also applicable to other solid-state emitters and opens the door to a simple far-field optical connection among hybrid systems consisting of quantum dots, color centers, atoms, or ions.

We acknowledge the financial support from the Swiss National Science Foundation, ETH Zurich, and the Max Planck Society. Y. L. A. R. acknowledges support from the ETH fellowship program. We also thank I. Gerhardt, G. Wrigge, J. Hwang, and M. Pototschnig for their contributions to the very early stages of this project.

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